Crystal Engineering of Boron Subphthalocyanine Derivatives Using Hydrogen and Halogen Bonding for Organic Photovoltaic Applications

by

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A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy
Department of Chemical Engineering and Applied Chemistry
University of Toronto

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Abstract

Boron subphthalocyanines (BsubPcs) are a class of aromatic bowl-shaped small molecules of interest for organic electronic applications such as organic solar cells. In solid state organic electronic devices, the orientation of the molecules and the spacing between them affect important material properties. In this thesis, the structure-property relationships between molecular structure, solid state arrangement and organic electronic device characteristics are explored for BsubPc derivatives.

Hydrogen bonds and halogen bonds are of particular interest in the field of crystal engineering, due to the strength and directionality of these intermolecular interactions. The ability of BsubPcs to form hydrogen and halogen bonds was systematically explored. BsubPc derivatives which display either halogen or hydrogen bonds in their solid state arrangement were incorporated into organic solar cell devices and their thin film properties were studied in order to investigate the relationship between solid state arrangement and material properties.
Dedication

This work is dedicated to my mother, Wendy Diane Virdo. She taught me, through example, nearly all that I know about perseverance and strength of will.

Mom, you did not get to see this completed, but I know you would have read it cover to cover.
Acknowledgments

I would like to begin by thanking my supervisor, Professor Tim Bender, for his guidance and enthusiasm over the years. I joined his research group as an undergraduate fourth year thesis student, and liked it so much that I decided to stay for a PhD. I’m still very happy with that decision.

Special thanks go to Alan Lough, the staff crystallographer in the Department of Chemistry. Alan has diffracted countless crystals for me over the years, and has provided me with beautifully refined crystal structures for my publications.

I thoroughly enjoyed my time spent as a graduate student, and that was due in no small part to the people in my research group. My colleagues in the Bender lab were a pleasure to work with. Aside from being a great set of people to brainstorm with, the working atmosphere was great and there was never a dull moment in the lab.

I would also like to thank Professor Tim Jones and his research group in the UK, for making me feel welcome during my time spent abroad and for teaching me the device fabrication side of OPV science.

Last but not least, I would like to thank my brother, Guytano, for extended discussions on statistical analysis. He has also been invaluable in helping me with life logistics issues over the past year, and was always available to have a glass of scotch with me during the rough times. I could not ask for a better sibling.
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# List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>length of the $a$-axis of a crystal unit cell</td>
</tr>
<tr>
<td>AFM</td>
<td>atomic force microscopy</td>
</tr>
<tr>
<td>$b$</td>
<td>length of the $b$-axis of a crystal unit cell</td>
</tr>
<tr>
<td>BHJ</td>
<td>bulk heterojunction</td>
</tr>
<tr>
<td>$c$</td>
<td>length of the $c$-axis of a crystal unit cell</td>
</tr>
<tr>
<td>CCDC</td>
<td>Cambridge Crystallographic Data Centre</td>
</tr>
<tr>
<td>Cg</td>
<td>centroid of an aromatic ring in a crystal structure</td>
</tr>
<tr>
<td>CV</td>
<td>cyclic voltammetry</td>
</tr>
<tr>
<td>$d_e$</td>
<td>external distance on a Hirshfeld surface</td>
</tr>
<tr>
<td>$d_i$</td>
<td>internal distance on a Hirshfeld surface</td>
</tr>
<tr>
<td>$d_{\text{norm}}$</td>
<td>normalized distance on a Hirshfeld surface</td>
</tr>
<tr>
<td>EQE</td>
<td>external quantum efficiency</td>
</tr>
<tr>
<td>FF</td>
<td>fill factor</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>GC</td>
<td>gas chromatography</td>
</tr>
<tr>
<td>GIXRD</td>
<td>grazing incidence x-ray diffraction</td>
</tr>
<tr>
<td>GPC</td>
<td>gel permeation chromatography</td>
</tr>
<tr>
<td>HOMO</td>
<td>highest occupied molecular orbital</td>
</tr>
<tr>
<td>HPLC</td>
<td>high pressure liquid chromatography</td>
</tr>
<tr>
<td>HS</td>
<td>Hirshfeld surface</td>
</tr>
<tr>
<td>$J_{\text{SC}}$</td>
<td>short circuit current density</td>
</tr>
<tr>
<td>LUMO</td>
<td>lowest unoccupied molecular orbital</td>
</tr>
</tbody>
</table>
$M_r$  molecular weight of a compound in a crystal

$N_i$  imine nitrogen

NMR  nuclear magnetic resonance

$N_p$  pyrrole nitrogen

OLED  organic light emitting diode

OPV  organic photovoltaic

OTFT  organic thin film transistor

PDI  polydispersity index

PHJ  planar heterojunction

PL  photoluminescence

QCM  quartz crystal microbalance

R[F2 > 2σ(F2)]  see R-factor

R-factor  residual factor (sometimes referred to as 'reliability factor') for crystal structures; a measure of the agreement between the crystallographic model and the experimental x-ray diffraction data

$R_{int}$  merging error of a crystal structure; a measure of the precision or reproducibility

SD  standard deviation

TLC  thin layer chromatography

UV-vis  ultraviolet-visible

$V$  volume, i.e. of a crystal unit cell

$V_{OC}$  open circuit voltage

XRD  x-ray diffraction

$Z$  the number of molecules in the unit cell of a crystal
1.1 The Motivation for Organic Photovoltaics

The sun is an abundant yet underutilized source of renewable energy. Sunlight delivers approximately 96,000 TW of energy to the earth’s surface, with approximately 28,000 TW of this energy falling on portions of the earth’s surface covered by land.\footnote{To put this into context, the global energy demand was 17.5 TW in 2010 and is estimated to reach 30 TW by 2050.} Collecting only a fraction of the energy available from sunlight could theoretically satisfy the global energy demand, yet solar energy currently accounts for less than 1% of the global energy supply (Figure 1.1). At present, solar cell technology remains prohibitively expensive for widespread use.\footnote{Photovoltaic (PV) technology is commonly categorized into three generations based on differences in materials and fabrication methods. The first generation is largely comprised of technologies which use silicon, an inorganic semiconductor material, in either monocrystalline or polycrystalline wafer form. The basis of the modern silicon solar cell, consisting of a bilayer between negatively doped and positively doped silicon, was engineered in 1954 by Chapin, Fuller and Pearson from Bell Laboratories. This technology was first commercialized in 1963, when Sharp Corporation of Japan began producing monocrystalline silicon modules. Crystalline silicon solar modules are by far the most mature form of PV technology and accounted for 90% of the PV market in 2014. However, the relatively high costs of these conventional solar...}
modules represent an ongoing obstacle to their widespread adoption. Due to the low absorption coefficient of silicon (approximately 50–100 cm$^{-1}$), these modules require fairly thick layers of crystalline silicon wafers, typically ranging from 150–180 μm.$^7$ The silicon purification and wafer fabrication processes contribute significantly to the cost of module production.$^8$ Crystalline silicon solar modules are made with rigid glass structures and installed by racking in metal frames, and therefore the transportation and installation costs for such modules are also significant.$^6$

Second generation PV technologies are based on thin films of inorganic semiconducting materials and accounted for approximately 10% of the PV market in 2014.$^6$ This generation includes amorphous silicon, cadmium telluride (CdTe), and copper indium gallium diselenide (CIGS). With film thicknesses on the order of a few microns, second generation PV technologies require significantly less material than wafer-based technologies and can be compatible with flexible substrates. They offer the advantages of lower production, transportation and installation costs, with the tradeoff of lower overall power conversion efficiency when compared to first generation technologies.$^6$ Additional challenges include susceptibility to light-induced degradation for amorphous silicon cells,$^9$ use of toxic elements (e.g., cadmium) and reliance on rare elements (e.g., tellurium and indium).

The third generation encompasses a range of emerging PV technologies that are currently in the research and development phase, including but not limited to perovskite-based solar cells, quantum dot solar cells, dye-sensitized solar cells and organic photovoltaic (OPV) devices. The rest of this discussion will focus on OPV technology; detailed overviews of various other third generation technologies can be found in the literature.$^6$ Since the initial discovery in 1906 that anthracene possesses photoconductive properties,$^{10}$ the field of organic electronics has expanded to include the study of a wide range of \( \pi \)-conjugated organic materials with semiconductor properties, including small molecules, oligomers and polymers.$^{11}$ The first bilayer OPV device was developed by Tang at Kodak in the 1980s.$^{12}$ OPV technology has been an ever-growing field of research ever since, with considerable research being undertaken in both academic and industrial settings.

OPV devices are attractive for a variety of reasons. The organic materials used in such devices tend to have high absorption coefficients on the order of \( 10^5 \) cm$^{-1}$, and therefore films as thin as
100 nm can potentially absorb most of the incident sunlight despite containing relatively small amounts of material. Thin film OPV devices are compatible with flexible substrates, allowing them to be integrated in a wider range of applications than silicon-wafer solar cells. OPV devices also have the potential to be manufactured using inexpensive, high-throughput fabrication technologies such as solution-processing or vacuum deposition approaches, and are a promising area of research for the eventual development of more affordable solar energy technology. Due to their light weight and mechanical flexibility, OPV devices can potentially offer cost savings beyond lowering the cost of individual devices through simplified installation and reduced transportation costs. These potential cost saving features may offset the lower overall device efficiencies generally exhibited by OPV devices. Organic materials are also intrinsically tunable; modifications made to the molecular structure can be used to alter the electronic and optical properties of an organic semiconductor, allowing materials to be tailored for specific applications.

Although there is considerable interest in eventually developing OPV technology as an inexpensive method of harnessing solar energy, this is generally considered to be a long-term goal requiring further progress in materials design and process engineering. In the short term, it is more likely that OPV technology will be successfully developed in response to niche applications requiring light weight, flexibility, and/or customization. Such applications may include passive charging technology for personal electronic devices or decorative, energy-producing architectural features with customizable colours. As an interesting and recent example, the German pavilion at the 2015 world exhibition in Milan (EXPO 2015) featured printed OPV modules incorporated into five large, stylized tree forms termed “Solar Trees.” Solar energy collected during the day was used to power light-emitting diodes (LEDs) at night, lighting the trees from below. The Solar Trees will be in place for a total of 7 months, from May 1 to October 31 2015.

At present, OPV technology is largely in the research and development phase. In order to fully exploit the advantages that OPV technology can offer, in either short-term or long-term timescales, there is an ongoing need to study the material properties of organic semiconductors in order to improve device performance characteristics.
1.2 Interest in Boron Subphthalocyanine (BsubPc) Derivatives

Subphthalocyanines (subPcs) are conjugated, non-planar aromatic moieties, consisting of three repeating diiminoisoindoline groups arranged in a unique C$_{3v}$ symmetric bowl shape. Boron is unique among the elements for its ability to template the formation of the subPc ligand, commonly through the reaction of its halides (Cl, Br) with phthalonitrile. This results in the formation of either chloro- or bromo-boron subphthalocyanine (Cl-BsubPc (1) or Br-BsubPc (2); Scheme 1.1). Since the first report of Cl-BsubPc in 1972,\textsuperscript{16} the synthetic chemistry of BsubPcs has been significantly expanded to yield a variety of derivatives.\textsuperscript{17} BsubPcs can be synthesized with a variety of substituents in either the axial or peripheral positions ($R_a$ and $R_p$, respectively; Figure 1.2). Axial substituents can consist of a range of nucleophiles, with phenoxy moieties perhaps being the most common, since the chemistry to produce phenoxy-BsubPc derivatives (4, Scheme 1.1) has been known for some time.\textsuperscript{17} The peripheral positions of BsubPc derivatives are typically perhydrogenated or perhalogenated, although derivatives containing various other symmetric and asymmetric peripheral moieties have also been successfully synthesized.\textsuperscript{18}

\textbf{Scheme 1.1:} General preparation of phenoxy-boron subphthalocyanine derivatives (4) from either chloro- or bromo-boron subphthalocyanine (1 or 2). Reagents and conditions: (i) chlorobenzene, reflux.

\textbf{Figure 1.2:} General BsubPc molecule, showing positions of axial ($R_a$) and peripheral ($R_p$) substitutions.
BsubPcs possess chemical and physical properties that make them attractive for various organic electronic applications, including organic light emitting diodes (OLEDs), organic photovoltaics (OPVs), organic field effect transistors (OTFTs), and non-linear optics. Figure 1.3 demonstrates the absorption profile of two BsubPc derivatives, the prototypical Cl-BsubPc and phenoxy-BsubPc (PhO-BsubPc), overlaid on the reference spectra of solar radiation. The peak absorption of BsubPc compounds corresponds to a region of the solar spectrum that has a high power density, and these compounds are therefore of particular interest for OPV technology.

![Figure 1.3: ASTM G173-03 reference spectra of solar radiation above Earth’s atmosphere (in grey) and at ground level (in black), overlaid with the solid state absorption spectra of chloro-BsubPc (Cl-BsubPc, in pink) and phenoxy-BsubPc (PhO-BsubPc, in blue).](image)

Substitution of the axial chloride atom in Cl-BsubPc with a phenoxy moiety causes the absorption spectrum to blueshift very slightly, by a few nanometers (Figure 1.3). Generally speaking, changing the axial substituent (R\textsubscript{a}) of a BsubPc derivative has an essentially negligible effect on the optical properties. Changes to R\textsubscript{a} also have minimal impact on the frontier molecular orbitals of interest in OPV material selection, namely the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO), as these orbitals are centered on the aromatic subPc ligand. In contrast, changes made to the peripheral substituents (R\textsubscript{p}) can significantly affect both the optical and electronic properties of BsubPc derivatives. This characteristic allows different properties of BsubPc derivatives to be tuned.
independently; Rₚ can be used to tune properties such as solubility and crystal structure without altering the optical or electronic properties.

Cl-BsubPc was the first BsubPc derivative to be incorporated into an OPV device, as reported by Mutolo et al. in 2006.²² In this pioneering work, Cl-BsubPc was used as an electron donor material (also referred to as a p-type and/or hole transport material) and paired with fullerene (C₆₀) as an electron acceptor (also referred to as an n-type or electron transport material). BsubPc derivatives were first investigated as electron acceptor materials for OPV devices by Gommons et al. in 2009.²³ In that study, two different perfluorinated (Rₚ=F, n=4, Figure 1.2) BsubPc derivatives were studied as electron acceptors and paired with Cl-BsubPc as an electron donor. BsubPc derivatives can therefore function as either electron donors or electron acceptors, depending on their peripheral substituents (Rₚ) and the materials they are paired with in devices. The Bender laboratory is actively investigating both functions in OPV applications.²⁴-²⁶
1.3 Crystal Engineering

Gautam Desiraju defined crystal engineering as “the understanding of intermolecular interactions in the context of crystal packing and the utilization of such understanding in design of new solids with desired physical and chemical properties.” The basic premise is that modifications made at the molecular level can be used to control the arrangement of molecules in the solid state by introducing or altering non-covalent, intermolecular interactions. Alterations to the solid state arrangement of a material, in turn, can be used to modify material properties of interest. This approach has been applied in the pharmaceutical industry for decades, and has more recently been adopted by other disciplines for the design of a wide range of functional materials.

Crystal engineering is also applicable to the field of organic electronics, wherein functional organic molecules are routinely utilized in the solid state and the arrangement of those molecules in relation to each other would be expected to influence properties such as charge transport. Methods of influencing, controlling and ultimately engineering the solid state arrangement of organic electronic materials are therefore of increasing interest.

In this context, pentacene derivatives represent a particularly well-known example of crystal engineering principles being applied to an organic electronic material. The relationship between the solid state arrangement of pentacene derivatives and their electronic properties has been extensively studied by the research group of John Anthony. The crystal structure of unsubstituted pentacene features molecules arranged in a herringbone pattern, whereas the inclusion of bulky sidegroups in 6,13-bis(triisopropylsilylethynyl)pentacene (commonly abbreviated to TIPS-pentacene) results in a crystal structure with adjacent molecule stacked in a columnar array. The distances between the planar aromatic regions of neighbouring pentacene molecules are significantly shorter in the columnar array, and this has been correlated to improved charge carrier mobility, both in single crystal samples and crystalline films. This general trend has also been observed in other semiconducting organic materials, with shorter intermolecular distances correlating to improved charge transport. In a 2011 review article on electron acceptors for OPV applications, Anthony emphasized the need for “developing structure-property relationships for transport and morphology that are as accurate and broadly applicable as the relationships already developed for tuning the absorption and electronic properties of..."
small molecules. Such studies, as applied to the BsubPc class of materials, are of particular interest to our research group.

According to the principles of crystal engineering, the crystal structure of a molecule can be altered by introducing functional groups which promote certain types of attractive, non-covalent interactions. Hydrogen bonding and halogen bonding are two such interactions (Figure 1.4). These interactions are somewhat similar, in that they both involve attractive, non-covalent interactions between electrophilic regions (also known as electron-poor regions, or Lewis acids) and nucleophilic regions (also known as electron-rich regions or Lewis bases).

![Figure 1.4: Schematic representation of hydrogen and halogen bonding interactions.](image)

A hydrogen bonding interaction has the general form D-H···A, where there is evidence of an attractive interaction between the hydrogen atom (H) and a hydrogen bond acceptor (A). The molecular fragment D-H is referred to as a hydrogen bond donor. The D-H bond is polarized, and the strength of the hydrogen bond (H···A) generally increases as the electronegativity of D increases. For example, OH groups are classified as very strong hydrogen bond donors, while CH groups are weak hydrogen bond donors. The D-H···A angle is usually linear, and tends to
approach $180^\circ$ as the strength of the hydrogen bond increases.\textsuperscript{36} Hydrogen bond strengths range from very weak (approximately 0.5 kcal/mol) to very strong (approximately 40 kcal/mol, which approaches the strength of covalent bonding).\textsuperscript{37}

A halogen bonding interaction has the general form R-X···A, where there is evidence of an attractive interaction between a halogen atom (X) and a halogen bond acceptor (A).\textsuperscript{38} A halogen bond forms as the result of a localized electrophilic region on the halogen atom, referred to as a $\sigma$-hole, which is centered on the R-X axis and positioned on the surface of the halogen atom farthest from R.\textsuperscript{39} This localized electrophilic region is demonstrated visually in Figure 1.5. The size of the $\sigma$-hole and the strength of the halogen bond (X···A) generally increase as the size of the halogen atom increases, with the tendency to form a halogen bond following the trend F << Cl < Br < I. This trend is the result of two factors. First, the size of the $\sigma$-hole increases as the polarizability of the halogen atom increases (F < Cl < Br < I). Second, aside from its poor polarizability, fluorine is also the most electronegative atom; for these reasons, fluorine does not tend to participate in halogen bonding interactions.\textsuperscript{40} Since the electrophilic region on a halogen atom (X) is much more localized than the electrophilic region on a hydrogen atom (H), halogen bonding interactions are particularly reliant on a linear geometry (R-X···A $\approx 180^\circ$) in order to be attractive. Halogen bond interaction strengths range from approximately nil to 5 kcal/mol.\textsuperscript{40}

For both interactions, the acceptor (A) is a molecular entity possessing at least one nucleophilic region. Common examples include atoms possessing a lone electron pair (typically nitrogen or oxygen), $\pi$ systems (double or triple bonds, or aromatic rings) and anions. The strength of both interactions (D···A and X···A) will tend to increase as the nucleophilic nature of A increases, with $\pi$ systems being one of the weakest acceptor groups.\textsuperscript{37}

Hydrogen and halogen bonds both represent good starting points for the investigation of intermolecular interactions in a class of materials. These are reasonably strong non-covalent interactions, and therefore they tend to be fairly robust and reliable. In other words, modifying a molecule to include functional groups capable of participating in either hydrogen or halogen bonding will have a reasonably good chance of producing hydrogen or halogen bonding in the crystal structure of that molecule.
1.4 Purpose and General Methodology

The main focus of the work carried out over the course of this thesis has been to test the following hypothesis statement:

Halogen and hydrogen bonds can be used to alter the solid state arrangement of BsubPc derivatives and that alteration can be correlated to organic photovoltaic (OPV) device performance.

The general areas of investigation related to this hypothesis are illustrated visually in Figure 1.6. As a starting point, the solid state arrangement of Cl-BsubPc, the most commonly used BsubPc derivative in organic electronic applications, is determined and described in detail in Chapter 2. In subsequent chapters, systematic modifications were made to the molecular structure of BsubPc molecules, specifically with the incorporation of functional groups that were capable of forming halogen or hydrogen bonds. Single crystals of the new BsubPc derivatives were obtained, and their crystal structures were analyzed in order to determine the intermolecular interactions present in the solid state. These studies (Chapters 3 and 4) were used as a basis to understand which molecular modifications resulted in the formation of halogen and hydrogen bonding interactions in the solid state, and to understand the influence of these interactions on the solid state arrangement of BsubPc derivatives. In Chapter 5, derivatives that were shown to display halogen and hydrogen bonding interactions in their crystal structure were incorporated into OPV devices in order to investigate the relationship between solid state arrangement and OPV device performance.

Figure 1.6: Visual representation of the goals of this thesis, which are to investigate the relationship between the molecular structure of a BsubPc derivative and its solid state arrangement, and the relationship between the solid state arrangement and device characteristics.
As a continuation of the investigation between molecular structure and solid state arrangement, hydrogen bonding interactions were explored as a method to produce co-crystals. These co-crystals contained two distinct molecular species within the same crystal structure: a BsubPc derivative and an additional molecule capable of participating in hydrogen bonds. This work is presented in Chapter 6.

Chapter 7 details the development of the first BsubPc-containing polymer material. It is reasonable that analogous structure-property relationships could be investigated for the relationships between BsubPc polymer molecular structure, solid state arrangement and device properties as ongoing areas of exploration in the Bender research group, and the work in Chapter 7 lays the groundwork for such studies to be carried out in the future.

Finally, Chapter 8 summarizes the results and significance of the work presented in this thesis. Recommendations for future work are included.
1.5 References


Chapter 2
Redetermination of the Crystal Structure of Chloro Boron Subphthalocyanine (Cl-BsubPc) Enabled by Slow Train Sublimation

I proposed this study after working extensively with the crystal structure analysis of BsubPcs bearing phenoxy moieties in the axial position.

Figure 2.1 puts the importance of this chapter into perspective. Cl-BsubPc was first synthesized in 1972\(^1\) and its crystal structure was first determined in 1974\(^2\) using a crystal grown using solvent methods and film-based X-ray diffraction technology. As discussed in Chapter 1, Cl-BsubPc was first used in an OPV device in 2006\(^3\). Since then, interest in BsubPcs for OPV applications has grown steadily. The vast majority of the publications concerning BsubPc derivatives in OPV devices (Figure 2.1) use Cl-BsubPc, likely due to its commercial availability. The crystal structure of Cl-BsubPc is therefore of widespread interest, and has been increasingly cited as interest in BsubPc derivatives for OPV applications has increased. At present, the published literature lacks an article containing a detailed explanation of the intermolecular interactions in Cl-BsubPc.

![Figure 2.1: History of Cl-BsubPc and the use of BsubPc derivatives in OPV devices.](image)

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\(^1\) First synthesized: 1972
\(^2\) Crystal structure first determined: 1974
\(^3\) First use in an OPV device: 2006
The work in this chapter has been submitted for publication and is currently out for review. The full reference is:

Jessica D. Virdo, Alan J. Lough, and Timothy P. Bender. “Redetermination of the crystal structure of chloro boron subphthalocyanine (Cl-BsubPc) enabled by slow train sublimation.” *Acta Crystallographica Section C: Structural Chemistry*. Submitted; manuscript reference no. fm3033.

AJL performed the crystal diffraction experiments and crystal structure refinements. TPB developed the design for the train sublimation system, which was constructed as a group project by several members of the Bender research group. The rest of the work in this chapter was performed by me, including synthesis and purification of Cl-BsubPc, development of the heating algorithm for single crystal growth, and analysis of the crystal structure. All text and images were created by me. The work was supervised by TPB. Note that the introduction section has been shortened from the original manuscript draft in order to remove redundant portions, such as an introduction to the BsubPc class of materials.
2.1 Introduction

Although over 100 boron subphthalocyanine (BsubPc) derivatives have been synthesized and the Cambridge Crystallographic Data Centre (CCDC) contains over 50 unique entries for BsubPc crystals,\(^4\) the prototypical chloro boron subphthalocyanine (Cl-BsubPc) derivative continues to be the most widely utilized BsubPc material for organic electronic devices.\(^5\) The crystal structure of Cl-BsubPc, originally obtained using solvent crystallization methods and reported by Kietaibl in 1974,\(^2\) is of widespread interest and has therefore been cited over 90 times since its publication, with the majority of those citations occurring in the last decade. Solntsev \textit{et al.} \(^6\) also published a crystal structure of Cl-BsubPc obtained by solution growth methods. We have confirmed it was equivalent to the 1974 structure,\(^2\) however with a higher R-factor (6.68\% vs. 6.4\%). The R-factor, which is sometimes referred to as the R-value, residual factor or reliability factor, is a measure of the residual experimentally-determined electron density that is not accounted for by the crystallographic model. In other words, the R-factor is a measure of how well the refined crystal structure predicts the observed data, with lower R-factors signifying better fits.

![Molecular structure of Cl-BsubPc](image)

**Figure 2.2:** Molecular structure of Cl-BsubPc (1).

Herein we report a redetermination of the Cl-BsubPc crystal structure using single crystals grown via train sublimation, a technique which approximates the vacuum deposition conditions commonly used in the fabrication of organic electronic devices. Diffraction data were collected over a range of temperatures in order to facilitate a comparison with the two previously published crystal structures of Cl-BsubPc. Although the structure of the crystals grown by train sublimation was found to be generally equivalent to the previously published Cl-BsubPc crystal structures obtained using solvent crystallization methods, there are some small but significant differences. The redetermined structure also has improved geometric precision and lower R-values, which enabled an in-depth discussion of the $\pi-\pi$ and halogen-$\pi$ intermolecular
interactions using Hirshfeld surface analysis. Additionally, we have included details on the construction and operation of a train sublimation apparatus which enabled the growth of large, high quality single crystals of Cl-BsubPc.
2.2 Experimental

2.2.1 Synthesis and Crystallization

Cl-BsubPc was synthesized and purified according to a previously described procedure.\textsuperscript{7}

The train sublimation apparatus is depicted in Figure 2.3. The sublimation chamber consists of a borosilicate glass tube measuring 60 cm in length and 2.9 cm in outer diameter, fitted with ground glass joints on either end: a 29/32 female joint on the gas inlet end and a 19/22 female joint on the gas outlet end. The sublimation chamber passes through a copper-nickel pipe (30 cm in length, 3.3 cm in outer diameter, McMaster-Carr). A hot temperature gradient zone was created by placing a high-temperature nozzle band heater (5 cm in length, 3.8 cm in inner diameter, McMaster-Carr) around the copper-nickel pipe at a distance of approximately 10 cm from the inlet end. The copper-nickel pipe and heating band were wrapped with extreme-temperature ceramic insulation material (McMaster-Carr). The temperature in the hot zone was regulated using a thermocouple placed at the center of the heating band and connected to a Digi-Sense temperature controller (model no. 89000-15, Cole-Parmer), with an operational range from room temperature to approximately 600 ℃.

At the gas outlet side of the sublimation tube, a cooling zone was created using an air condenser fitted with a 19/22 male ground glass joint (University of Toronto Glassblowing Shop). Tygon tubing was used to supply a flow of compressed air to the coolant side of the condenser. A rotary vane vacuum pump (model Edwards RV5, Kurt J. Lesker) was connected to the gas outlet side of the condenser using wire-reinforced PVC vacuum tubing.

At the other end of the apparatus, a flow of nitrogen was introduced using a nitrogen gas cylinder and regulator (not shown in Figure 2.3). The gas flow rate was adjusted using a needle valve, and the pressure was monitored using a 275 Series gauge tube (model KJL275196, Kurt J. Lesker). PVC vacuum tubing was used from the nitrogen tank to the pressure gauge and wire-reinforced PVC vacuum tubing was used from the pressure gauge to the inlet elbow. The nitrogen supply line was connected to the sublimation tube using a borosilicate glass elbow fit with a 29/32 male ground glass joint on one end. Tube-to-glass connectors were used as appropriate.

To operate the apparatus, material to be sublimed was placed into a specially constructed
Figure 2.3: Schematic of the train sublimation apparatus. For clarity, the insulation layer is not shown.

The boat was shaped as a hollowed-out half-cylinder (2.2 cm in outer diameter) measuring 5 cm in length and had a capacity up to approximately 2 g of material. The boat was lined with fresh aluminum foil before each use. The sublimation chamber was loaded with the boat and a total of four borosilicate glass tube inserts (each measuring 10 cm in length and 2.2 cm in outer diameter, supplied by the University of Toronto Glassblowing Shop) according to the placement guide in Figure 2.3, which places the boat in the hottest area of the heated zone. Vacuum grease was placed on the ground glass joint ends of the sublimation chamber before connecting it to the inlet elbow and air condenser. The compressed air feed to the air condenser was turned on. The vacuum pump was turned on and the apparatus was evacuated to an internal pressure of approximately 80-90 mTorr. The nitrogen gas flow was turned on and the needle valve was adjusted until the internal pressure was approximately 110-120 mTorr. The Digi-Sense temperature controller was then programmed with a heating algorithm consisting of a series of ramp and soak segments. After sublimation, crystals and purified material were scraped off the glass tube inserts.
For the Cl-BsubPc crystals reported in this work, the heating algorithm was as follows: the temperature was ramped to 150 °C over a period of 10 minutes and held at that temperature for 30 minutes, then ramped to 250 °C over 100 minutes and held there for 30 minutes, and finally ramped very slowly to 400 °C over 300 minutes. The apparatus was kept at 400 °C for 8 hours before being cooled to room temperature. From 500 mg of starting material, this technique produced 61 mg of high-quality single crystals of Cl-BsubPc suitable for X-ray diffraction.

2.2.2 Refinement

Two crystals obtained via train sublimation (Crystal 1 and Crystal 2) were selected for diffraction experiments at different temperatures (90 K, 123 K, 147 K and 295 K). Crystal data, data collection and structure refinement details are summarized in Table 2.1. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined independently with isotropic displacement parameters.

Table 2.1: Experimental details for (1). Data collected from two crystal samples at various temperatures.

<table>
<thead>
<tr>
<th>Crystal data</th>
<th>(1) – Crystal 1</th>
<th>(1) – Crystal 2</th>
<th>(1) – Crystal 2</th>
<th>(1) – Crystal 2</th>
<th>(1) – Crystal 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCDC no.</td>
<td>1052234</td>
<td>1414465</td>
<td>1414466</td>
<td>1414467</td>
<td>1414468</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>147</td>
<td>90</td>
<td>123</td>
<td>147</td>
<td>295</td>
</tr>
<tr>
<td>Chemical formula</td>
<td>C_{24}H_{12}BClN_{6}</td>
<td>C_{24}H_{12}BClN_{6}</td>
<td>C_{24}H_{12}BClN_{6}</td>
<td>C_{24}H_{12}BClN_{6}</td>
<td>C_{24}H_{12}BClN_{6}</td>
</tr>
<tr>
<td>M_r</td>
<td>430.66</td>
<td>430.66</td>
<td>430.66</td>
<td>430.66</td>
<td>430.66</td>
</tr>
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<td>Crystal system, space group</td>
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<td>Orthorhombic, Pnma</td>
<td>Orthorhombic, Pnma</td>
<td>Orthorhombic, Pnma</td>
<td>Orthorhombic, Pnma</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>1833.2 (5)</td>
<td>1822.6 (3)</td>
<td>1815.9 (4)</td>
<td>1825.3 (3)</td>
<td>1863.0 (2)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Molar density (kmol m⁻³)</td>
<td>3.6233(10)</td>
<td>3.6444(6)</td>
<td>3.6579(8)</td>
<td>3.6390(6)</td>
<td>3.5654(4)</td>
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<td>Radiation type</td>
<td>Mo Kα</td>
<td>Mo Kα</td>
<td>Mo Kα</td>
<td>Mo Kα</td>
<td>Mo Kα</td>
</tr>
<tr>
<td>Crystal size (mm)</td>
<td>0.36 × 0.19 × 0.18</td>
<td>0.19 × 0.15 × 0.08</td>
<td>0.19 × 0.15 × 0.08</td>
<td>0.19 × 0.15 × 0.08</td>
<td>0.19 × 0.15 × 0.08</td>
</tr>
</tbody>
</table>
Table 2.1 continued

<table>
<thead>
<tr>
<th>Data collection</th>
<th>Bruker Kappa APEX-DUO CCD diffractometer</th>
<th>Bruker Kappa APEX-DUO CCD diffractometer</th>
<th>Bruker Kappa APEX-DUO CCD diffractometer</th>
<th>Bruker Kappa APEX-DUO CCD diffractometer</th>
<th>Bruker Kappa APEX-DUO CCD diffractometer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diffractometer</td>
<td>Bruker Kappa APEX-DUO CCD diffractometer</td>
<td>Bruker Kappa APEX-DUO CCD diffractometer</td>
<td>Bruker Kappa APEX-DUO CCD diffractometer</td>
<td>Bruker Kappa APEX-DUO CCD diffractometer</td>
<td>Bruker Kappa APEX-DUO CCD diffractometer</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Multi-scan SADABS (Bruker, 2014)</td>
<td>Multi-scan SADABS (Bruker, 2014)</td>
<td>Multi-scan SADABS (Bruker, 2014)</td>
<td>Multi-scan SADABS (Bruker, 2014)</td>
<td>Multi-scan SADABS (Bruker, 2014)</td>
</tr>
<tr>
<td>No. of measured, independent and observed ([I &gt; 2\sigma(I)]) reflections</td>
<td>15856, 2189, 1997</td>
<td>20761, 2181, 1729</td>
<td>8774, 2170, 1541</td>
<td>12814, 2221, 1597</td>
<td>9199, 2187, 1581</td>
</tr>
<tr>
<td>(R_{int})</td>
<td>0.026</td>
<td>0.048</td>
<td>0.064</td>
<td>0.071</td>
<td>0.044</td>
</tr>
</tbody>
</table>

| Refinement | | | | | |
| \(R[F^2 > 2\sigma(F^2)]\) | 0.030 | 0.032 | 0.043 | 0.041 | 0.040 |
| No. of reflections | 2189 | 2181 | 2170 | 2221 | 2187 |
| No. of parameters | 175 | 175 | 175 | 175 | 175 |
| No. of restraints | 0 | 0 | 0 | 0 | 0 |
| H-atom treatment | All H-atom parameters refined | All H-atom parameters refined | All H-atom parameters refined | All H-atom parameters refined | All H-atom parameters refined |
| \(\Delta \rho_{max}, \Delta \rho_{min}\) (e Å\(^{-3}\)) | 0.36, −0.33 | 0.35, −0.39 | 0.29, −0.34 | 0.31, −0.33 | 0.29, −0.30 |

2.2.3 Molar density

Molar density (\(\rho_{mol}\), in kmol\(^{-3}\)) was calculated by dividing the number of molecules in a unit cell (\(Z\)) by the cell volume (\(V\)) and Avogadro’s number, and subsequently applying the appropriate unit conversions.

\[
\rho_{mol} = \left(\frac{Z}{6.022 \times 10^{23} \times V}\right) \times (10^{27})
\]

Equation 2.1
2.2.4 Hirshfeld Surface Analysis

Hirshfeld surfaces and molecular fingerprint plots were prepared using *Crystal-Explorer 3.1*.8
2.3 Results and Discussion

We are particularly interested in crystal structures obtained via sublimation, as opposed to solvent crystallization techniques, because sublimation most closely approximates the vacuum deposition conditions used in the fabrication of organic electronic devices. Additionally, crystals grown via sublimation should be free of residual solvent molecules. We have previously described the construction and operation of a different train sublimation apparatus that we used primarily to purify materials prior to utilizing them in vacuum deposition chambers, and which was occasionally used to obtain single crystals of some BsubPc derivatives suitable for x-ray diffraction. This apparatus had previously produced very small single crystals of Cl-BsubPc, which were of sufficient quality to only confirm the unit cell parameters of the original crystal structure reported in 1974. Due to the very small size of these crystals, we sought to improve upon our existing train sublimation system in order to more easily and reliably produce large, high-quality single crystals suitable for x-ray diffraction.

It should be noted that although the original train sublimation apparatus was reliably useful in purifying material for organic electronic device fabrication, several sublimation attempts were typically required to produce single crystals. Those crystals that were obtained were typically very small and not always suitable for x-ray diffraction. Heating profiles generally consist of a short amount of time at a relatively low temperature (≈150 °C) in order to remove small molecule contaminants such as water or solvent molecules. This is followed by a period with moderate temperature ramping until the material was observed to begin to deposit downstream of the boat, signifying nucleation. Following the nucleation period, a period with very slow temperature ramping is used to grow the crystals to a larger size. In our experience, large, high-quality single crystals were most reliably produced when the temperature within the sublimation chamber was slowly and steadily increased over a period of several hours in the last phase of the heating profile. Slow crystallization processes tend to produce larger, more ordered crystals with fewer defects, as the slower process allows condensing molecules time to build up on existing crystal seeds rather than spontaneously forming new nucleation sites. However, the temperature set point of the original train sublimation apparatus was controlled manually and it was therefore difficult in practice to slowly and steadily increase the temperature.
The new train sublimation apparatus, described in section 2.2.1, includes a Digi-Sense temperature controller that can be programmed with a heating algorithm consisting of a series of ramp (increasing temperature) and soak (consistent temperature) segments. The automatic temperature controller allowed for slow and steady ramping periods, easily enabling, for example, a ramp rate of 0.5 °C per minute over the course of several hours. The new train sublimation apparatus features several other design improvements. It can accommodate larger quantities of starting material due to the use of a reusable, sturdy aluminum boat. The use of several glass tube inserts facilitates extraction of the purified material and crystals, and facilitates clean-up of the sublimation apparatus. By incorporating an automatic temperature controller, a reusable aluminum boat and a sturdily constructed support frame, it was also designed to minimize run-to-run variations in operating procedures and thereby improve reproducibility of results.

Using a slow ramping rate, as described in the Experimental section, we have been able to use the new sublimation system to reproducibly obtain relatively large, high-quality single crystals of BsubPc derivatives. The sublimation crystals obtained for Cl-BsubPc measure up to approximately 0.8 mm in their longest dimension (Figure 2.4).

**Figure 2.4:** Crystals of Cl-BsubPc grown via slow train sublimation. For scale, gradations shown are mm markings on a ruler.

An initial diffraction experiment with data collected at 147 K yielded a structure for Cl-BsubPc with a very low R-value of 3.0% and very good precision on the geometric parameters (Fig. 2.4 and Crystal 1, Table 2.1). Although the structure of crystals grown by sublimation was found to be generally equivalent to the two earlier structures obtained by solution growth methods, there are some small but significant differences in the unit cell parameters and resulting unit cell volume and molar density (Table 2.1, Table 2.2). We expect the molar density to be of particular interest in the field of organic electronics, as the number of molecules present in a thin film of a
given thickness directly affects the number of photons that can be absorbed by the film and, by extension, the amount of current that can be generated by the solar cell. In order to investigate the differences in unit cell parameters, a second sublimation crystal was selected for a series of diffraction experiments at different temperatures, including the two temperatures used for previous studies of Cl-BsubPc.

![Molecular structure and atom labeling of (1), demonstrated with data obtained from Crystal 1 at 147 K. All atoms are rendered at the 50% probability level, meaning that the size of each drawn ellipsoid corresponds to a volume in which there is a 50% probability of finding the electron density of the atom.](image)

**Figure 2.5:** Molecular structure and atom labeling of (1), demonstrated with data obtained from Crystal 1 at 147 K. All atoms are rendered at the 50% probability level, meaning that the size of each drawn ellipsoid corresponds to a volume in which there is a 50% probability of finding the electron density of the atom.

**Table 2.2:** Diffraction experimental details from previously published structures of Cl-BsubPc (1).

<table>
<thead>
<tr>
<th></th>
<th>Kietaibl (1974) (^2)</th>
<th>Solntsev et al. (2012) (^6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (K)</td>
<td>~ 295 (room temperature)</td>
<td>123</td>
</tr>
<tr>
<td>(a, b, c) (Å)</td>
<td>12.123 (5), 14.824 (7), 10.378 (4)</td>
<td>12.1224 (2), 14.8449 (10), 10.3283 (1)</td>
</tr>
<tr>
<td>(V) (Å(^3))</td>
<td>1865.0 (14)</td>
<td>1858.64 (13)</td>
</tr>
<tr>
<td>Molar density (kmol m(^{-3}))</td>
<td>3.5616(27)</td>
<td>3.5737(2)</td>
</tr>
</tbody>
</table>

Unit cell parameters for data collected at 147 K from Crystal 1 and Crystal 2 show slight differences, indicating a small amount of variability among crystals grown in the same batch.
Figure 2.6: Comparison of unit cell parameters for Cl-BsubPc at different temperatures, including diffraction experiments from this work in blue, from Kietaiibl (1974) in red and from Solntsev et al. (2012) in green. Shaded regions correspond to 3 standard deviations ($\pm 3\sigma$).

Figure 2.7: Comparison of intramolecular parameters for Cl-BsubPc at different temperatures, including diffraction experiments from this work in blue, from Kietaiibl (1974) in red and from Solntsev et al. (2012) in green. Bowl depth (b) is defined as the distance from the central boron atom to the plane formed by the six outermost carbon atoms. Shaded regions correspond to 3 standard deviations ($\pm 3\sigma$).
The lengths of the unit cell axes are denoted $a$, $b$ and $c$. For room temperature diffraction experiments, there is good agreement between the volume and molar density measured from sublimation crystals and the data reported by Kietaibl, although there are some small differences in the values obtained for $a$ and $b$ (Figure 2.6). The unit cell parameters ($a$, $b$, $c$) and cell volumes obtained in this work at colder temperatures (90 K, 123 K and 147 K) are all smaller than the values reported by Solntsev et al. for data collected at 123 K. Overall, this suggests that the sublimation crystals obtained in this work and the solution-grown crystals reported by Kietaibl are of equivalent molar density, while the solution-grown crystals reported by Solntsev et al. are slightly less dense. Intramolecular metrics such as the B–Cl bond length and the BsubPc bowl depth (defined as the distance from the central boron atom to a plane passing through the six outermost carbon atoms) are very consistent across the five structures reported in this study and the two previously reported structures (Figure 2.7). The small differences in unit cell parameters and density between crystals in the same batch, and the slightly larger differences between crystals grown by different methods, are therefore the result of differences in intermolecular distances.

As Cl-BsubPc is an organic semiconducting material, the intermolecular interactions in the solid state arrangement are of paramount importance and interest, particularly with regards to the aromatic $\pi$-system and its component diiminoisoindoline fragments. In order to facilitate the discussion of the intermolecular interactions in BsubPc crystal structures, some terminology to describe different molecular fragments has been previously established. First, due to the distinctive bowl-shape of the BsubPc molecule, the subPc ligand can be referred to as having both a “concave” side and a “convex” side. Second, due to the arrangement of diiminoisoindoline units in the subPc ligand, the three 6-membered carbon rings protruding farthest from the boron center can be referred to as “heads,” and the three 6-membered heterocyclic rings encompassing the boron center can be referred to as “tails.” These terms, which describe the diiminoisoindoline units, are particularly useful in describing close $\pi-\pi$ interactions between adjacent molecules.

As illustrated in Figure 2.8a, close intermolecular contacts involving the diiminoisoindoline units are prominent throughout the crystal structure of Cl-BsubPc. Each BsubPc molecule is closely associated with two adjacent molecules through convex-convex head-to-head $\pi-\pi$ interactions, forming one-dimensional ribbons parallel to the $b$ axis. Additionally, close concave-concave
Figure 2.8: Illustration of the molecular packing arrangement within the redetermined crystal structure of Cl-BsubPc. (a) Molecule fragments participating in convex-convex head-to-head distances are shown in blue, and fragments participating in concave-concave head-to-tail distances are shown in orange. (b) Halogen-π interaction shown in green, convex-convex interactions shown in blue, and close C5-C9 distance shown as a black dashed line. Colours: carbon = grey; nitrogen = light purple; boron = pink; chlorine = green. Hydrogen atoms omitted for clarity. Ellipsoids shown at 50% probability level.

head-to-tail motif forms one-dimensional ribbons parallel to the a axis. The non-planar nature of the BsubPc molecule translates into the formation of non-planar ribbon motifs, and the two intersecting ribbon motifs therefore form an overall three-dimensional network of BsubPc molecules with close distances between their aromatic subPc ligands. Although close intermolecular distances involving the diiminoisoindoline units of Cl-BsubPc have been tabulated previously \cite{11} with reference to the original structure,\cite{2} these distances were not demonstrated visually and the overall packing motifs present in the crystal structure were not
discussed in terms of ribbons or networks. Furthermore, the lower R-factor of the redetermined structure allows a more precise discussion of the geometry of these interactions (Table 2.3).

The possible role of the chlorine atom in influencing the crystal structure of Cl-BsubPc has not been explored or discussed previously. Analysis of the crystal structure reveals that there is a relatively short distance (approximately 3.5–3.6 Å) between the chlorine atom and the convex side of an adjacent diiminoisoindoline head fragment (Figure 2.8b, Table 2.3). Additionally, there is a short distance between two carbon atoms (C5···C9 \( \approx 3.33 \) Å for Crystal 2 at 90 K.

**Table 2.3:** Selected molecular and intermolecular metrics for Cl-BsubPc (1) at different temperatures.

<table>
<thead>
<tr>
<th></th>
<th>90 K (^a)</th>
<th>123 K (^b)</th>
<th>123 K (^c)</th>
<th>147 K (^a)</th>
<th>147 K (^b)</th>
<th>295 K (^a)</th>
<th>295 K (^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>B-Cl /Å</strong></td>
<td>1.881(2)</td>
<td>1.874(3)</td>
<td>1.890(6)</td>
<td>1.879(2)</td>
<td>1.879(3)</td>
<td>1.880(3)</td>
<td>1.863(7)</td>
</tr>
<tr>
<td><strong>Bowl depth /Å</strong></td>
<td>2.450(2)</td>
<td>2.450(3)</td>
<td>2.454(6)</td>
<td>2.4587(19)</td>
<td>2.451(3)</td>
<td>2.457(3)</td>
<td>2.472(9)</td>
</tr>
<tr>
<td><strong>Convex-convex:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cg(I)···Cg(J)</td>
<td>3.5988(10)</td>
<td>3.5989(13)</td>
<td>3.629(2)</td>
<td>3.6127(9)</td>
<td>3.6065(11)</td>
<td>3.6495(11)</td>
<td>3.6545(17)</td>
</tr>
<tr>
<td><strong>Concave-concave:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cg(K)···Cg(L)</td>
<td>4.1282(10)</td>
<td>4.1291(13)</td>
<td>4.178(2)</td>
<td>4.1494(10)</td>
<td>4.1368(12)</td>
<td>4.1959(12)</td>
<td>4.2043(17)</td>
</tr>
<tr>
<td><strong>Halogen-π:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Cl···Cg(L)</td>
<td>3.5167(9)</td>
<td>3.5218(11)</td>
<td>3.567(2)</td>
<td>3.5404(9)</td>
<td>3.5316(10)</td>
<td>3.6012(10)</td>
<td>3.5986(17)</td>
</tr>
<tr>
<td>B-Cl···Cg(L)</td>
<td>169.99(8)</td>
<td>170.09(12)</td>
<td>169.7(2)</td>
<td>170.18(6)</td>
<td>170.02(12)</td>
<td>170.58(12)</td>
<td>170.0(5)</td>
</tr>
</tbody>
</table>

\(^a\) Data from this work. Centroid definitions: Cg(I)=Cg(1)=N2-C1-C2-C7-C8; Cg(J)=Cg(6)=C2-C3-C4-C5-C6-C7; Cg(K)=Cg(3)=B1-N2-C1-N1-C1a-N2a; Cg(L)=Cg(7)=C10-C11-C12-C12a-C11a-C10a. Atoms labeled according to Figure 2.5.

\(^b\) Data from Solntsev et al. (2012). Centroid definitions: Cg(I)=N1-C1-C2-C3-C4; Cg(J)=C2-C3-C8-C7-C6-C5; Cg(K)=B1-N1a-C4a-N4a-C9a-N2; Cg(L)=C10-C11-C12-C12a-C11a-C10a.

\(^c\) Data from Kietaiibl (1974). Centroid definitions: Cg(I)=N2-C1-C5-C10-C11; Cg(J)=C5-C6-C7-C8-C9-C10; Cg(K)=B1-N2-C1-N1-C1a-N2a; Cg(L)=C2-C3-C4-C4a-C3a-C2a.
Figure 2.8b) which does not appear to be the result of $\pi-\pi$ or CH-$\pi$ interactions. The surrounding geometry was investigated with consideration of the recently developed definition of a halogen bond, which is: a net attractive interaction of the form $A\cdots X\cdots Y$, where $X$ is a halogen atom with an electrophilic region and $A$ is a halogen bond acceptor moiety with a nucleophilic region.\textsuperscript{12}

Several observations suggest that the chlorine atom (Cl1) does participate in a halogen-$\pi$ interaction. First, we have previously computed the electrostatic potential surface for a series of BsubPc derivatives using the 6-31G* basis set with the B3LYP DFT method,\textsuperscript{13} which shows that there is a moderately electron-rich region in the center of each of the six-membered diiminoisoindoline head fragments that could act as a halogen bond acceptor site. Second, although the Cl$\cdots$Cg (halogen$\cdots$centroid) distance of approximately 3.53 Å (Crystal 2 at 90 K) is slightly greater than the sum of the van der Waals radii for a chlorine atom and a carbon ring (3.45 Å),\textsuperscript{14} there is structural evidence for the presence of a halogen bonding interaction. Comparison of the Cl-BsubPc crystal structure with the structures for F-BsubPc and Br-BsubPc,\textsuperscript{11} which are isostructural, reveals that the X$\cdots$Cg distance decreases as the halogen atom (X) is changed from F (F$\cdots$Cg $\approx$ 4.09 Å) to Cl (Cl$\cdots$Cg $\approx$ 3.53 Å) to Br (Br$\cdots$Cg $\approx$ 3.47 Å), while the B-X$\cdots$Cg angle is consistently 170°. The X$\cdots$Cg distance decreases in the order Br$\cdots$Cg < Cl$\cdots$Cg < F$\cdots$Cg, despite an increase in the atomic radius of the halogen atom involved (Br > Cl > F), implying a stronger intermolecular interaction. This is consistent with the usual trends regarding the ability and tendency of halogen atoms to participate in halogen bonds, specifically: F < Cl < Br < I.\textsuperscript{12} Finally, the close C5$\cdots$C9 distance can be explained by a combination of $\pi-\pi$ interactions and the presence of a B-Cl$\cdots$halogen bond (Figure 2.8b). The halogen-$\pi$ interactions form an additional ribbon motif running parallel to the $a$ axis.

Table 2.3 includes intermolecular interaction metrics for crystal data collected at several temperatures, and this information is also presented visually in Figure 2.9. Intermolecular distances increase as the crystal temperature increases, while the B-X$\cdots$Cg angle in the halogen-$\pi$ interaction remains consistent. For room temperature data, there is good agreement between the metrics determined in this work and those extracted from the structure originally reported by Kietaiibl (1974),\textsuperscript{2} although the metrics presented in this work are significantly more precise. Intermolecular distances extracted from the structure reported by Solntsev et al.\textsuperscript{6} are longer than
those determined in this work, which is in keeping with the previously discussed differences in molar density.

Figure 2.9: Comparison of intermolecular parameters for Cl-BsubPc at different temperatures, including diffraction experiments from this work in blue, from Kietabl (1974)\(^2\) in red and from Solntsev et al. (2012)\(^6\) in green. Shaded regions correspond to 3 standard deviations (± 3\(\sigma\)).

In contrast to the previously reported crystal structures for Cl-BsubPc \(^2,6\), all hydrogen atoms in this work were refined independently. This allows the crystal structure of Cl-BsubPc to be examined using Hirshfeld surface (HS) analysis, which requires a well-characterized crystal structure with all hydrogen atoms located accurately.\(^15\) To date, there have not been any reports featuring HS analysis on crystal structures of BsubPc derivatives. The crystal structure of Cl-BsubPc is a prime candidate for this method of analysis, as it is the prototypical BsubPc derivative and it remains the most widely used BsubPc material in the field of organic electronics.

HS analysis was recently developed\(^15\) as a computational tool to visually examine all of the close intermolecular contacts in a crystal structure. The concept of a HS surface developed from attempts to define the space occupied by a molecule in a crystal structure in order to partition the
Figure 2.10: Hirshfeld surface of Cl-BsubPc (Crystal 2 at 90 K) mapped with (a) $d_{\text{norm}}$ and (b) shape index. The ‘top’ view corresponds to the view along the $c$ axis, with atoms in the same orientation as the labels in Fig. 3. Red spots on the $d_{\text{norm}}$ surface indicate contacts at distances closer than the sum of the corresponding van der Waals radii, namely: H3-H1, H3a-H12a, C5-C9 and C5a-C9a. Complementary regions on the shape index surface are circled and marked for (1) the convex-convex $\pi$-$\pi$ interaction, (2) the halogen-$\pi$ interaction and (3) the concave-concave $\pi$-$\pi$ interaction.

crystal electron density into molecular fragments. The HS of a molecule in a crystal structure is calculated based on a molecular weight-function, $w(r)$, that includes summation terms for the spherically-averaged atomic electron density of atoms in the molecule of interest (known as the promolecule) and analogous summation terms for atoms in the crystal structure (the procystal). The HS surface is the three-dimensional surface defined by $w(r) \geq 0.5$, i.e., the
surface where the promolecule’s contribution to the procystal electron density exceeds the contribution from all other molecules in the crystal. Details related to the calculation of the HS can be found in the literature.\textsuperscript{15,17-18} Interestingly, molecular volumes defined by such surfaces interlock in a manner analogous to molecular Lego or three-dimensional puzzle pieces, which aids in visualizing the packing arrangement of molecules in a crystal. In the HS figures below, the shape of the HS surface is defined by the weighting function described above, while the colour is defined by different properties (i.e., shape index, \(d_{\text{norm}}\) or normalized distance, etc.) mapped onto the HS.

The HS of Crystal 2 at 90 K is mapped with \(d_{\text{norm}}\) and shape index in Figure 2.10. On the \(d_{\text{norm}}\) map (Figure 2.10a), regions are shaded red (for contacts at distances shorter than the sum of the van der Waals radii) through white to blue (for contacts at distances longer than the sum of the van der Waals radii). Two close contacts (and their symmetry equivalents) are readily identified on this map: the aforementioned C5–C9 contact, and H3–H12 at a distance of 2.35(2) Å. The H3–H12 contact is just slightly shorter than the sum of the van der Waals radii, and is consequently marked by a very small red dot on the surface. This contact does not appear to be directly related to the intermolecular \(\pi-\pi\) interactions.

The shape index (Figure 2.10b) is based on the two local principal curvatures of the HS, with concave regions shaded in red and convex regions shaded in blue. Regions of the surface which differ only in the sign of the shape index will have the same patterning with opposite colouring (i.e., a matched blue/red pair), and such complementary regions can be used to visually identify areas where two molecular surfaces touch.\textsuperscript{15} The convex-convex \(\pi-\pi\) interaction appears as a matched triangle pattern (marker 1, Figure 2.10b). Matched triangle patterns, or ‘bowties’, on the shape index surface are diagnostic of close C–C interplanar contacts in \(\pi-\pi\) stacking interactions.\textsuperscript{18} Complementary shape index patterns for the halogen-\(\pi\) interaction and the concave-concave \(\pi-\pi\) interaction are demonstrated in Figure 2.10b, at markers 2 and 3 respectively.

Fingerprint plots combining \(d_e\) (\(d_{\text{external}}, \) or the distance from the HS to the nearest nucleus outside the HS) and \(d_i\) (\(d_{\text{internal}}, \) or the distance from the HS to the nearest nucleus inside the HS) are shown in Figure 2.11. Points on the fingerprint plot are coloured according to the frequency
Figure 2.11: Summary of the closest contacts in Cl-BsubPc (Crystal 2 at 90 K), demonstrated with (a-h) two-dimensional fingerprint plots and (i) the percentage contribution of each interaction type to the Hirshfeld surface.

with which the corresponding \((d_l, d_e)\) pair occurs on the HS, from blue (low frequency) through green to red (high frequency). Fingerprint plots also allow for the extraction of quantitative information regarding the percentage contribution of each contact type to the total HS, and this data is presented in Figure 2.11i. The close C⋯C contacts from the convex-convex \(\pi-\pi\) stacking appear as a small red region near the centre of the fingerprint plot (Figure 2.11b), which is typical of planar \(\pi-\pi\) stacking arrangements involving aromatic carbon rings. The concave-concave \(\pi-\pi\) interaction mainly involves close C⋯N contacts, and corresponds to the section of
the fingerprint plot highlighted in Figure 2.11c. The C⋯Cl contacts, which correspond to the halogen-π interaction, also appear near the center diagonal of the fingerprint plot (Figure 2.11d). The remainder of the fingerprint plot consists of contacts involving at least one hydrogen atom (Figure 2.11e-h). Contacts involving hydrogen account for approximately 81% of the HS (Figure 2.11i), which is not unexpected, since the hydrogen atoms are situated on the periphery of the molecule and therefore in relative proximity to neighbouring molecules. Despite involving comparatively localized portions of the molecule, the convex-convex π-π interactions, concave-concave π-π interactions, and halogen-π interactions make significant contributions to the HS (Figure 2.11i).
2.4 Conclusions

Large single crystals of Cl-BsubPc were obtained using an improved train sublimation apparatus designed to enable slow temperature ramping and to minimize run-to-run variations in operating conditions. The structure of crystals obtained via train sublimation is of particular interest in the field of organic electronics, and we have confirmed that the structure of Cl-BsubPc crystals grown via sublimation is equivalent to the structure obtained via previously reported solution crystallization methods. Diffraction data were collected using two crystal samples and four temperatures, revealing that there is some variability in the density of crystals grown in the same batch and crystals grown using different methods. The crystal structure features both π-π and halogen-π interactions, and a total of three distinct ribbon motifs. The improved geometric precision of the redetermined structure enabled the use of Hirshfeld surface analysis, providing improved visualization and quantification of the intermolecular interactions present within the crystal structure. The in-depth analysis of these interactions is expected to be of interest to the organic electronics community, where Cl-BsubPc is routinely applied in devices.
2.5 References


Chapter 3
Halogenated Phenoxy-Boron Subphthalocyanines

The work in the first part of this chapter was published as a full length article in *CrystEngComm*. The full reference is:


YHK performed the initial synthesis and crystallization of two compounds: pentachlorophenoxy-BsubPc and pentabromophenoxy-BsubPc, using chloro boron subphthalocyanine as a starting material. AJL performed the crystal diffraction experiments and crystal structure refinements. I performed all of the other work, including synthesis and crystallization of the remaining eight compounds, additional synthesis of pentachlorophenoxy-BsubPc and pentabromophenoxy-BsubPc using bromo boron subphthalocyanine as a starting material, and analysis of all of the crystal structures. I also wrote all of the text and created all of the figures. The work was supervised by TPB. Note that the introduction section has been shortened from the original article in order to remove redundant portions, such as an introduction to the boron subphthalocyanine (BsubPc) class of materials. Some of the information originally contained in the electronic supplementary information (ESI) has been moved to the main body of text.

The work in the second part of this chapter is currently in preparation and will be submitted as a manuscript shortly. The full reference is:


TM performed the crystal diffraction experiments and crystal structure refinements. I performed all of the other work, including synthesis, crystallization, crystal analysis, writing and figure creation. The work was supervised by TPB. Note that the introduction section has been shortened from the original manuscript draft in order to remove redundant portions.
3.1 Halogen Bonds Can Direct the Solid State Arrangement of Phenoxy-Boron Subphthalocyanines

3.1.1 Introduction

Previous work published by members of the Bender research group highlighted that perhydrogenated phenoxy-BsubPc derivatives (R= H, n=12, Figure 3.1) commonly adopt one of two motifs. The first is a dimer motif characterized by concave-concave π-π interactions between pairs of adjacent BsubPc molecules (Figure 3.2a). This motif is typical of para-substituted phenoxy-BsubPc derivatives, and has also been observed in tert-butoxy-BsubPc and ethoxy-BsubPc. The second common motif consists of one-dimensional ribbons, wherein each BsubPc molecule participates in concave-concave π-π interactions with two neighbouring molecules, forming a continuous ribbon of subPc ligands associated through π-π interactions (Figure 3.2b). The concave-concave π-π ribbon motif has been observed in tert-octylphenoxy BsubPc, and is similar to the arrangement observed for an alkylphenyl-substituted BsubPc and at least one alkoxy-BsubPc. In contrast, peripherally perfluorinated BsubPc derivatives (F12BsubPcs, R=F, n=12, Figure 3.1) typically adopt motifs dominated by interactions between the axial substituent of one molecule and the subPc ligand of a neighbouring molecule. In the case of phenoxy-F12BsubPc and p-methylphenoxy-F12BsubPc, phenoxy-to-concave-face π-stacking interactions direct the crystal motif into one-dimensional columns (Figure 3.3a). Similar one-dimensional column arrangements have also been observed for the axially halogenated F12BsubPc derivatives: Cl-F12BsubPc, Br-F12BsubPc, and F-F12BsubPc (Figure 3.3b).

![Figure 3.1: General structure of boron subphthalocyanine (BsubPc) showing axial (X) and peripheral (R) positions for substitution. N_i and N_p refer to imine and pyrrole nitrogen atoms, respectively.](image-url)
Figure 3.2: Common solid state packing arrangements for perhydrogenated BsubPc derivatives: (a) concave-concave $\pi$-$\pi$ dimer motif, demonstrated with phenoxy-BsubPc and (b) concave-concave $\pi$-$\pi$ ribbon motif, demonstrated with in tert-octylphenoxy-BsubPc. Colours: carbon = grey; nitrogen = light purple; boron = light pink; oxygen = red. $\pi$-$\pi$ interactions shown in cyan. Hydrogens omitted for clarity. Redrawn from reference 1.

Figure 3.3: Common solid state packing arrangements for perfluorinated BsubPc derivatives, as demonstrated with (a) $p$-methylphenoxy-$\text{F}_{12}$BsubPc and (b) Br-$\text{F}_{12}$BsubPc. Colours: carbon = grey; nitrogen = light purple; boron = light pink; bromine = yellow; fluorine = magenta. Hydrogens omitted for clarity. (a) Redrawn from reference 8. (b) Redrawn from reference 10.
We have previously reported the formation of a unique ribbon motif in the solid state arrangement of \textit{para}-bromophenoxy-BsubPc ($p$-BrPhO-BsubPc), in which one-dimensional ribbons are directed through $\pi$-Br interactions.\textsuperscript{2} In notable contrast to typical perhydrogenated BsubPc packing motifs, this arrangement displays significant interaction between the subPc ligand and an axial substituent. While we have shown this is likely a kinetically-favoured packing arrangement, it nonetheless suggests the potential to use halogen-directed interactions with the subPc ligand in order to direct the solid state packing arrangement of BsubPc derivatives.

In this paper, we report the synthesis and crystal structure analysis of a series of twelve halo-substituted phenoxy-BsubPc derivatives. The series includes the full set of \textit{meta}-halogenated-phenoxy-BsubPcs, the full set of \textit{ortho}-halogenated-phenoxy-BsubPcs, and two penta-halogenated-phenoxy-BsubPcs, namely pentabromophenoxy-BsubPc ($\text{Br}_5\text{PhO-BsubPc}$) and pentachlorophenoxy-BsubPc ($\text{Cl}_5\text{PhO-BsubPc}$). Crystal structure analysis across this series reveals distinctly new solid state packing motifs, which are directed by $\pi$-$\pi$ interactions and halogen bonding. The halogen bonding occurs between the halogen atoms and the imine nitrogens ($N_i$, Figure 3.1) of the subPc ligand. It is known that these imine nitrogen atoms are available for hydrogen bonding, as demonstrated in the solid state packing arrangement of hydroxy-BsubPc (HO-BsubPc).\textsuperscript{3} The new motifs presented in this paper are noteworthy exceptions to the typical BsubPc solid state packing arrangements and represent the first report of halogen bonding observed for BsubPc derivatives.
3.1.2 Experimental

3.1.2.1 Materials

*meta*-Bromophenol was purchased from TCI Company Ltd. (Portland, Oregon). *meta*-Fluorophenol, *meta*-chlorophenol, *meta*-iodophenol, *ortho*-fluorophenol, *ortho*-chlorophenol, *ortho*-bromophenol, *ortho*-iodophenol, pentachlorophenol and pentabromophenol were purchased from Sigma Aldrich (Mississauga, Ontario, Canada). All reagents were used as received. Other common solvents, reagents and standard basic alumina (300 mesh) were purchased from Caledon Laboratories (Caledon, Ontario, Canada) and used as received. Cl-BsubPc was synthesized according to a previously described procedure° and Br-BsubPc was synthesized according to a procedure previously described by Potz.°

3.1.2.2 Methods

The reaction progress and purity analysis was performed using a Waters 2695 high pressure liquid chromatography (HPLC) separation module with a Waters 2998 photodiode array and a Waters 4.6 mm x 100 mm SunFire C_{18} 3.5 μm column. HPLC grade acetonitrile and dimethylformamide was eluted with an isocratic flow of 80/20 acetonitrile/dimethylformamide at 0.6 mL/min during operation.

All nuclear magnetic resonance (NMR) spectra were acquired on a Varian Mercury 400 MHz system in deuterated chloroform with 0.05% (v/v) tetramethylsilane (TMS) as a ¹H NMR reference purchased from Cambridge Isotope Laboratories and used as received. Mass spectrometry was performed on a Waters GC time-of-flight mass spectrometer with an electron ionization probe and accurate mass determination.

X-ray diffraction results were analyzed using PLATON 40M-version 300311 for bond angles and lengths, and crystal packing images were generated using Mercury version 2.4. All data sets were collected using a Nonius KappaCCD diffractometer equipped with an Oxford Cryostream variable temperature apparatus, with the exception of the data set for *m*-IPhO-Bsubc, which was collected using a Bruker APEX-II CCD equipped with an Oxford Cryostream variable temperature apparatus. Hydrogen positions were calculated.
Molecular modeling was performed with HyperChem for Windows OS version 8.0, using a modified set of RM1 parameter files that have been previously published. The crystal state heat of formation (ΔH_{f,cry}) values were obtained by isolating a single molecule from the appropriate crystallographic information file and performing a single-point calculation using the RM1 semi-empirical method. The single molecule used in the previous calculation was then optimized by using the MM+ molecular mechanics forcefield and then further refined using the RM1 semi-empirical method in order to obtain the corresponding optimized state heat of formation value (ΔH_{f,opt}). Geometric optimization was performed using the Polak-Ribiere conjugated gradient method with a 0.02 kcal/Å mol root-mean-squared convergence limit.

3.1.2.3 Synthesis

meta-Fluorophenoxy-boron subphthalocyanine (m-FPhO-BsubPc, 2a).

Cl-BsubPc (1, 1.001 g, 0.0023 mol) was mixed with meta-fluorophenol (0.781 g, 0.0070 mol) in chlorobenzene (22 mL) in a round-bottom flask fitted with a reflux condenser and argon inlet. The mixture was stirred and heated at reflux under a constant pressure of argon for 20 to 40 hours. The reaction was monitored via HPLC and determined to be complete by the non-detection of 1. The crude product was isolated by removing the solvent under rotary evaporation. Preliminary purification was achieved by dissolving the crude product in toluene (700 mL) and vigorously stirring the toluene mixture with 3.0 M KOH solution in distilled water (300 mL) overnight. Using this purification method, residual unreacted phenol is dissolved in the aqueous phase. The toluene phase was isolated and the solvent was removed under rotary evaporation. The product was further purified on a Kauffman column using standard basic alumina (300 mesh) as the adsorbent and dichloromethane as the eluent. The product elutes from the Kauffman column while the excess phenol remains adsorbed, as previously described. The dichloromethane was then removed under rotary evaporation yielding a dark pink/magenta powder. Compound 2a (yield 1.030 g, 88%). Purity by HPLC (> 99%, max plot). HPLC λ_{max} (nm) = 561.0, R_{T} (min) = 2.26; δ_{H} (400 MHz; CDCl₃; Me₄Si) 5.11-5.14 (1H, m), 5.14-5.18 (1H, m), 6.29-6.35 (1H, m), 6.66-6.72 (1H, m), 7.88-7.92 (6H, m), 8.83-8.87 (6H, m); HRMS (EI) Calcd. for [C₃₀H₁₆BF₆N₆O] ([M]⁺): m/z 506.1463, found 506.1470.
**meta-Chlorophenoxy-boron subphthalocyanine** (*m*-ClPhO-BsubPc, 2b).

2b was synthesized as for 2a except *meta*-chlorophenol (0.896 g, 0.0070 mol) was used in place of *meta*-fluorophenol, yielding compound 2b (1.013 g, 83%). Purity by HPLC (> 99%, max plot). HPLC $\lambda_{\text{max}}$ (nm) = 561.0, $R_T$ (min) = 2.55; $\delta_H$ (400 MHz; CDCl$_3$; Me$_4$Si) 5.18-5.21 (1H, m), 5.46-5.47 (1H, t), 6.57-6.60 (1H, m), 6.65-6.69 (1H, t), 7.87-7.92 (6H, m), 8.83-8.88 (6H, m); HRMS (EI) Calcd. for [C$_{30}$H$_{16}$BClN$_6$O] ([M]+): m/z 522.1167, found 522.1168.

**meta-Bromophenoxy-boron subphthalocyanine** (*m*-BrPhO-BsubPc, 2c).

2c was synthesized as for 2a except *meta*-bromophenol (1.206 g, 0.0070 mol) was used in place of *meta*-fluorophenol, yielding compound 2c (1.159 g, 88%). Purity by HPLC (> 99%, max plot). HPLC $\lambda_{\text{max}}$ (nm) = 561.0, $R_T$ (min) = 2.63; $\delta_H$ (400 MHz; CDCl$_3$; Me$_4$Si) 5.23-5.26 (1H, m), 5.64-5.65 (1H, t), 6.60-6.64 (1H, t), 6.74-6.77 (1H, m), 7.89-7.94 (6H, m), 8.84-8.89 (6H, m); HRMS (EI) Calcd. for [C$_{30}$H$_{16}$BBrN$_6$O] ([M]+): m/z 566.0662, found 566.0668.

**meta-Iodophenoxy-boron subphthalocyanine** (*m*-IPhO-BsubPc, 2d).

2d was synthesized as for 2a except *meta*-iodophenol (1.206 g, 0.0070 mol) was used in place of *meta*-fluorophenol, yielding compound 2d (1.173 g, 82%). Purity by HPLC (> 99%, max plot). HPLC $\lambda_{\text{max}}$ (nm) = 561.0, $R_T$ (min) = 2.71; $\delta_H$ (400 MHz; CDCl$_3$; Me$_4$Si) 5.26-5.29 (1H, m), 5.83-5.84 (1H, t), 6.46-6.50 (1H, t), 6.94-6.96 (1H, m), 7.90-7.95 (6H, m), 8.85-8.90 (6H, m); HRMS (EI) Calcd. for [C$_{30}$H$_{16}$BIN$_6$O] ([M]+): m/z 614.0523, found 614.0533.

**ortho-Fluorophenoxy-boron subphthalocyanine** (*o*-FPhO-BsubPc, 4a).

In a manner similar to the synthesis of 2a, Br-BsubPc (3, 1.200 g, 0.0025 mol) was mixed with *ortho*-fluorophenol (0.849 g, 0.0076 mol) in chlorobenzene (26 mL) and heated at reflux under a constant pressure of argon. The reaction was monitored via HPLC and determined to be complete by the non-detection of 3. The crude product was isolated and purified as described in the synthesis of 2a, yielding compound 4a (0.857 g, 67%). Purity by HPLC (> 99%, max plot). HPLC $\lambda_{\text{max}}$ (nm) = 561.0, $R_T$ (min) = 2.07; $\delta_H$ (400 MHz; CDCl$_3$; Me$_4$Si) 5.40-5.45 (1H, t), 6.50-6.60 (3H, m), 7.89-7.94 (6H, m), 8.83-8.89 (6H, m); HRMS (EI) Calcd. for [C$_{30}$H$_{16}$BFN$_6$O] ([M]+): m/z 506.1463, found 506.1458.
**ortho-Chlorophenoxy-boron subphthalocyanine** (o-ClPhO-BsubPc, 4b).

4b was synthesized as for 4a except *ortho*-chlorophenol (0.974 g, 0.0076 mol) was used in place of *ortho*-fluorophenol, yielding compound 4b (1.002 g, 76%). Purity by HPLC (> 99%, max plot). HPLC $\lambda_{\text{max}}$ (nm) = 561.0, R_T (min) = 2.21; $\delta_H$ (400 MHz; CDCl$_3$; Me$_4$Si) 5.32-5.36 (1H, m), 6.57-6.62 (1H, m), 6.65-6.71 (1H, m), 6.81-6.84 (1H, m), 7.90-7.95 (6H, m), 8.84-8.89 (6H, m); HRMS (EI) Calcd. for [C$_{30}$H$_{16}$BClN$_6$O] ([M]+): m/z 522.1167, found 522.1172.

**ortho-Bromophenoxy-boron subphthalocyanine** (o-BrPhO-BsubPc, 4c).

4c was synthesized as for 4a except *ortho*-bromophenol (1.311 g, 0.0076 mol) was used in place of *ortho*-fluorophenol, yielding compound 4c (0.764 g, 53%). Purity by HPLC (> 99%, max plot). HPLC $\lambda_{\text{max}}$ (nm) = 562.2, R_T (min) = 2.25; $\delta_H$ (400 MHz; CDCl$_3$; Me$_4$Si) 5.29-5.32 (1H, m), 6.50-6.55 (1H, m), 6.69-6.75 (1H, m), 6.98-7.01 (1H, m), 7.89-7.95 (6H, m), 8.83-8.89 (6H, m); HRMS (EI) Calcd. for [C$_{30}$H$_{16}$BBrN$_6$O] ([M]+): m/z 566.0662, found 566.0667.

**ortho-Iodophenoxy-boron subphthalocyanine** (o-IPhO-BsubPc, 4d).

4d was synthesized as for 4a except *ortho*-iodophenol (1.667 g, 0.0076 mol) was used in place of *ortho*-fluorophenol, yielding compound 4d (0.945 g, 61%). Purity by HPLC (> 99%, max plot). HPLC $\lambda_{\text{max}}$ (nm) = 562.2, R_T (min) = 2.29; $\delta_H$ (400 MHz; CDCl$_3$; Me$_4$Si) 5.19-5.22 (1H, m), 6.36-6.41 (1H, m), 6.72-6.78 (1H, m), 7.22-7.25 (1H, m), 7.89-7.95 (6H, m), 8.84-8.90 (6H, m); HRMS (EI) Calcd. for [C$_{30}$H$_{16}$BIN$_6$O] ([M]+): m/z 614.0523, found 614.0529.

**Pentachlorophenoxy-boron subphthalocyanine** (Cl$_5$PhO-BsubPc, 4e).

4e was synthesized as for 4a except pentachlorophenol (2.018 g, 0.0076 mol) was used in place of *ortho*-fluorophenol, yielding compound 4e (1.075 g, 64%). Purity by HPLC (> 99%, max plot). HPLC $\lambda_{\text{max}}$ (nm) = 564.7, R_T (min) = 4.51; $\delta_H$ (400 MHz; CDCl$_3$; Me$_4$Si) 7.92-7.97 (6H, m), 8.86-8.90 (6H, m); HRMS (EI) Calcd. for [C$_{30}$H$_{12}$BCl$_5$N$_6$O] ([M]+): m/z 657.9608, found 657.9626.
Pentabromophenoxy-boron subphthalocyanine (Br₅PhO-BsubPc, 4f).

4f was synthesized as for 4a except pentabromophenol (3.702 g, 0.0076 mol) was used in place of ortho-fluorophenol, yielding compound 4f (0.803 g, 39%). Purity by HPLC (97.6%, max plot, with the remainder being pentabromophenol). HPLC $\lambda_{\text{max}}$ (nm) = 565.9, RT (min) = 3.902; $\delta_H$ (400 MHz; CDCl₃; Me₄Si) 7.94-7.96 (6H, m), 8.87-8.89 (6H, m); HRMS (EI) Calcd. for [C₃₀H₁₂BBr₅N₆O] ([M]+): m/z 877.7082, found 877.7088.

3.1.2.4 Preparation of Single Crystals

Slow diffusion crystallization was performed using two solvent systems. In the first solvent system, benzene was used as the good solvent and heptane was used as the diffusing solvent. In the second solvent system, dichloromethane was used as the good solvent and pentane was used as the diffusing solvent. Samples of 2a-d and 4a-d were prepared by dissolving the appropriate phenoxy-BsubPc compound (0.040 g) in a good solvent (8 mL of benzene or dichloromethane). Due to the lower solubility of 4e and 4f, samples of these compounds were prepared by dissolving the appropriate phenoxy-BsubPc compound (0.025 g) in a good solvent (10 mL of benzene or dichloromethane). The sample solution was then transferred to a 20-mL vial. The opening of the vial was covered with aluminum foil, and the foil was punctured with small holes. The vial was sealed in a larger airtight container with the appropriate diffusing solvent (150 mL of heptane or pentane). Single crystals of high quality suitable for X-ray diffraction were obtained within 1-2 weeks.

Schematics and instructions for use for the train sublimation apparatus have been previously disclosed.¹⁴ Briefly, samples to be crystallized were placed in a small boat constructed of aluminum foil and inserted into the hot zone of the sublimation chamber. The chamber was evacuated and the internal temperature of the hot zone was increased to 120 °C for 10 minutes, then to 180 °C for 10 minutes, and then to 220 °C for approximately 1 hour in order to remove small molecule contaminants. Next, the nitrogen flow was set with the needle valve creating an internal pressure of 1x10⁻¹ Torr. With the cooling water circulating, the internal temperature of the hot zone was slowly incremented at a rate of 10 °C/10 minutes until the material began to sublime (between 300 °C and 340 °C). The temperature was maintained at the sublimation point for 1 hour in order to seed crystals. The temperature was then increased at a rate of 3°C/10
minutes until the temperature was 100 °C past the sublimation point and held at that temperature for 2 hours before being cooled to room temperature. Finally, the crystals produced from the sublimation process were scraped from the sublimation tube and analyzed.
3.1.3 Results and Discussion

3.1.3.1 Synthesis

Scheme 3.1: Synthesis of meta-halogenated-phenoxy-BsubPcs (2a-d), ortho-halogenated-phenoxy-BsubPcs (4a-d), and penta-halogenated-phenoxy-BsubPcs (4e-f). Conditions: (i) 3 molar equivalents, chlorobenzene, reflux; (ii) 3 molar equivalents, chlorobenzene, reflux.

The meta-halogenated-phenoxy-BsubPcs (2a-d), ortho-halogenated-phenoxy-BsubPcs (4a-d) and penta-halophenoxy-BsubPcs (2e and 2f) were synthesized based on an adaptation of two previously published procedures. Briefly, either chloro-BsubPc (Cl-BsubPc, 1) or bromo-BsubPc (Br-BsubPc, 3) was reacted with 3 molar equivalents of the appropriate phenol at reflux in chlorobenzene. The reaction progress was monitored via HPLC and determined to be complete by the non-detection of 1 or 3, as appropriate. Preliminary purification was accomplished by a two-phase extraction, wherein the crude product was dissolved in toluene and excess phenol was extracted with an aqueous solution of potassium hydroxide. Final purification was achieved using Kauffman column chromatography, wherein standard basic alumina was used as the adsorbent and dichloromethane was used as the eluent. The solvent extraction step
was typically able to remove nearly 100% of the excess phenol, as determined by HPLC. Any residual phenol was successfully removed using Kauffman column chromatography.

In previous studies, we have utilized Cl-BsubPc (1) exclusively to synthesize BsubPc derivatives. The halo-substituted phenoxy-BsubPc derivatives (2a-d, 4a-f) are accessible using either Cl-BsubPc or Br-BsubPc as the starting material. However, we have observed that Br-BsubPc is significantly more reactive than Cl-BsubPc, allowing for shorter reaction times and the use of fewer molar equivalents of phenol. This proved particularly advantageous for the penta-halogenated-phenoxy-BsubPcs; the synthesis of 4f required reaction times upwards of 50 hours when using Cl-BsubPc and 5 molar equivalents of phenol, but was complete within 24 hours when using Br-BsubPc and 3 molar equivalents of phenol.

3.1.3.2 Single Crystal Structure Determination

Slow diffusion crystallization using benzene as a good solvent and heptane as a diffusing solvent yielded diffractable single crystals of compounds 2b-d and 4a-f. To explore the sensitivity of the solid state packing arrangement to the choice of solvent system, slow diffusion crystallization was repeated using dichloromethane (DCM) as a good solvent and pentane as a diffusing solvent. This solvent system yielded diffractable single crystals of 2c-d and 4d-f. Finally, good quality, diffractable single crystals of 2b-2d were obtained by train sublimation using a previously published procedure. In all cases, the x-ray determined structure confirmed the molecular structure of compounds 2b-d and 4a-f. Selected crystallographic results are presented in Table 3.1. Attempts to obtain diffractable crystals of m-FPhO-BsubPc (2a) using any of these methods were unsuccessful; however, a single crystal obtained via slow train sublimation was successfully obtained after this work was published. The crystal structure of m-FPhO-BsubPc is discussed in the second half of this chapter.

Regarding the series of meta-halogenated-phenoxy-BsubPcs (2a-d, Scheme 3.1), the extended solid state arrangements obtained for m-ClPhO-BsubPc (2b), m-BrPhO-BsubPc (2c) and m-IPhO-BsubPc (2d) are isostructural; these three share the same space group, the same number of molecules per unit cell, and very similar unit cell parameters. The solid state arrangements for 2b and 2c were robust and independent of the crystallization method used, whereas the unsolvated arrangement for 2d was only obtained via train sublimation. During the refinement of the 2d solvate structure, electron density peaks were located that were believed to be highly disordered.
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<td>Final R_{f} values (I &gt; 2σ(I))</td>
<td>0.0865</td>
<td>0.0914</td>
<td>0.0479</td>
<td>0.0624</td>
<td>0.0656</td>
<td>0.0439</td>
</tr>
</tbody>
</table>
solvent molecules (benzene/heptane). Attempts made to model the solvent molecules were not successful. The SQUEEZE option in PLATON 40-M\(^{16}\) indicated that there was a large solvent cavity (496 e/Å\(^3\)). In the final cycles of refinement, this contribution of 149 electrons to the electron density was removed from the observed data. Similar treatments of disordered solvent molecules have been reported elsewhere.\(^{17-20}\) The same 2d solvate structure was obtained using the DCM/pentane solvent system.

The solid state arrangements obtained for the ortho-halogenated-phenoxy-BsubPc series (4a-d, Scheme 3.1) show a greater dependence on the identity of the halogen atom. The arrangement of o-FPhO-BsubPc (4a) is in a P-1 space group, while the arrangement of o-ClPhO-BsubPc (4b) is in a P2\(_1\)/n space group. There are two molecules in the asymmetric unit of 4b, resulting in a unit cell which contains 8 molecules despite having a P2\(_1\)/n space group. The two molecules have slight geometric differences, which in reflected in differences in the intra- and intermolecular metrics summarized in Table 3.2. The arrangements obtained for o-BrPhO-BsubPc (4c) and o-IPhO-BsubPc (4d) are isostructural, and both contain disorder in the phenoxy moiety, resulting in relatively disordered crystal structures. In both cases, the phenoxy moiety can adopt one of two positions, where the two positions are roughly related through a translation operation which shifts the phenoxy atoms by approximately 0.4 to 0.7 Å. The atoms of the o-BrPhO group were refined as disordered over two sets of sites with refined occupancies in a ratio of 0.570(10):0.430(10). The atoms of the o-IPhO group were refined as disordered over two sets of sites with refined occupancies in a ratio of 0.568(10):0.432(10).

The unsolvated arrangements of Cl\(_5\)PhO-BsubPc (4e) and Br\(_5\)PhO-BsubPc (4f) are isostructural. The crystal studied for the structural determination of unsolvated 4f was a non-merohedral twin with the ratio of refined components being 0.275(3):0.725(3).

### 3.1.3.3 Distortion of the Molecular Conformation of BsubPc

In order to facilitate discussion of BsubPc crystal structures, we begin our analysis at the molecular level. We have previously established a number of inter- and intramolecular metrics for the description of the BsubPc and phenoxy molecular fragments of phenoxy-BsubPcs,\(^1\) which are summarized in Table 3.2 and illustrated in Figure 3.4. Molecular strains and distortions within BsubPc molecules can be quantified with the intramolecular metrics: the length of the boron-oxygen bond (B-O bond length), the length of the oxygen-carbon bond (O-C bond length),
the angle of the phenoxy moiety relative to the BsubPc ligand (the B-O-C angle), and bowl depth. We define bowl depth as the distance from the boron atom to a plane passing through the six outer carbon atoms of the bowl-shaped BsubPc ligand (Figure 3.4a). The values for B-O bond length, O-C bond length, and bowl depth are fairly constant and similar to what we have observed in the solid state arrangements of other phenoxy-BsubPcs.\textsuperscript{1-2}

**Figure 3.4:** Depiction of inter- and intra-molecular metrics using \( m \)-ClPhO-BsubPc as an illustrative example. (a) Illustrating the bowl depth metric. The yellow plane passes through the six outermost carbon atoms of the bowl-shaped subPc ligand. The bowl depth is the distance between the boron atom and the plane, shown here as a black dotted line. (b) Illustrating the B-O-C angle and Cg-Cg distance for a concave-concave \( \pi-\pi \) interaction. Colours: carbon = grey; nitrogen = light blue; oxygen = red; boron = pink; chlorine = green. Hydrogen omitted for clarity.

In contrast, the B-O-C angle varies considerably across the series of crystals studied. The preferred B-O-C angle for a single isolated phenoxy-BsubPc molecule, determined using a simple semi-empirical RM1 model, is typically between 115° and 116°, and similar values have been observed in the solid state.\textsuperscript{1} Within this study, however, only three structures have B-O-C angles of approximately 115 – 116°: \( o \)-FPhO-BsubPc, \( o \)-ClPhO-BsubPc, and solvated \( Br_3 \)PhO-BsubPc (Table 3.2). Three \textit{meta}-halogenated crystal structures (\( m \)-ClPhO-BsubPc, \( m \)-BrPhO-BsubPc and unsolvated \( m \)-IPhO-BsubPc), two \textit{ortho}-halogenated crystal structures (\( o \)-BrPhO-BsubPc and solvated \( o \)-IPhO-BsubPc) and two penta-halogenated crystal structures (\( Cl_5 \)PhO-
BsubPc and unsolvated Br₅PhO-BsubPc) display larger B-O-C angles of approximately 118 – 122°. Finally, one meta-halogenated crystal structure (solvated m-IPhO-BsubPc) and one ortho-halogenated crystal structure (unsolvated o-IPhO-BsubPc) display very large B-O-C angles of approximately 128°.

Table 3.2: Selected BsubPc intra- and intermolecular metrics.

<table>
<thead>
<tr>
<th>Motif</th>
<th>B-O bond length/Å</th>
<th>O-C bond length/Å</th>
<th>B-O-C angle/°</th>
<th>Bowl depth /Å</th>
<th>Cg-Cg distance/Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>2b</td>
<td>m-ClPhO-BsubPc</td>
<td>1.441(5)</td>
<td>1.384(3)</td>
<td>119.7(2)</td>
<td>3.745(2)</td>
</tr>
<tr>
<td>2c</td>
<td>m-BrPhO-BsubPc</td>
<td>1.443(5)</td>
<td>1.379(3)</td>
<td>119.6(2)</td>
<td>3.769(2)</td>
</tr>
<tr>
<td>2d</td>
<td>m-IPhO-BsubPc</td>
<td>1.441(1)</td>
<td>1.377(7)</td>
<td>120.0(5)</td>
<td>3.782(4)</td>
</tr>
<tr>
<td>2d</td>
<td>m-IPhO-BsubPc solvate</td>
<td>1.442(4)</td>
<td>1.361(3)</td>
<td>127.9(2)</td>
<td>3.7027(14)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.7475(15)</td>
</tr>
<tr>
<td>4a</td>
<td>o-FPhO-BsubPc</td>
<td>1.451(4)</td>
<td>1.382(3)</td>
<td>116.9(2)</td>
<td>3.6814(18)</td>
</tr>
<tr>
<td>4b</td>
<td>o-ClPhO-BsubPc</td>
<td>1.451(4)</td>
<td>1.381(4)</td>
<td>116.3(2)</td>
<td>3.6887(19)</td>
</tr>
<tr>
<td></td>
<td>o-ClPhO-BsubPc</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4c</td>
<td>o-BrPhO-BsubPc</td>
<td>1.441(1)</td>
<td>1.414(8)</td>
<td>122.2(6)</td>
<td>3.774(4)</td>
</tr>
<tr>
<td>4d</td>
<td>o-IPhO-BsubPc</td>
<td>1.441(1)</td>
<td>1.38(1)</td>
<td>127.9(8)</td>
<td>3.780(6)</td>
</tr>
<tr>
<td></td>
<td>o-IPhO-BsubPc solvate</td>
<td>1.442(5)</td>
<td>1.361(5)</td>
<td>118.4(3)</td>
<td>3.881(2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.426(2)</td>
</tr>
<tr>
<td>4e</td>
<td>Cl₅PhO-BsubPc</td>
<td>1.462(5)</td>
<td>1.362(5)</td>
<td>121.1(3)</td>
<td>3.558(2)</td>
</tr>
<tr>
<td>4f</td>
<td>Br₅PhO-BsubPc</td>
<td>1.48(1)</td>
<td>1.36(1)</td>
<td>121.7(8)</td>
<td>3.489(7)</td>
</tr>
<tr>
<td></td>
<td>Br₅PhO-BsubPc solvate</td>
<td>1.469(6)</td>
<td>1.365(5)</td>
<td>115.5(3)</td>
<td>3.505(3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.476(2)</td>
</tr>
</tbody>
</table>

a,b o-ClPhO-BsubPc contains two molecules (‘A’ and ‘B’) within an asymmetric unit; metrics are provided for both molecules, denoted ‘a’ and ‘b’ respectively.

c Refers to distances between two molecules interacting through convex-convex π-π interactions.

d Refers to distances between two molecules interacting through concave-concave π-π interactions.

e Refers to distances between two molecules interacting through phenoxy-concave π-π interactions.

3.1.3.4 Halogen-Nitrogen Interactions

The significant distortion of the B-O-C angle observed in most of these crystals suggests that there is a significant enthalpically favourable interaction present, which has formed at the enthalpic expense of the preferred B-O-C angle. Examination of the crystals beyond the single molecule shows that nearly all of the crystals studied display halogen bonds. These bonds are
indicated by significant halogen-nitrogen interactions (Figure 3.5), which are easily detected by calculating the distance between the halogen (X) and nitrogen atoms and showing that this distance is less than the sum of their respective van der Waals radii. For the compounds/crystals containing halogen bonds, the X⋯N distance is compared to the sum of the van der Waals radii in Table 3.3. The reduction in distance (Δd) is the sum of the van der Waals radii minus the X⋯N distance, with a positive value indicating that the two atoms are closer together than the sum of their van der Waals radii. The carbon-halogen⋯nitrogen angle (C-X⋯N angle) has also been calculated, as halogen bonds tend to be highly directional with nearly linear C-X⋯N angles. Three structures (o-FPhO-BsubPc, o-BrPhO-BsubPc and unsolvated o-IPhO-BsubPc) have been excluded from Table 3.3 because they did not display halogen bonds. This is unsurprising in the case of o-FPhO-BsubPc, as fluorine is not typically known to participate in halogen bonding. The crystal structures of o-BrPhO-BsubPc and o-IPhO-BsubPc show some evidence of halogen-halogen interactions; however, the relatively high disorder in these structures precludes a meaningful analysis of the halogen-halogen interactions.

**Figure 3.5:** A close-up example of halogen bonding, demonstrated using a 50% ellipsoid plot of m-BrPhO-BsubPc. The halogen bonds, shown as black dotted lines, occur between the halogen atom of one molecule and the imine nitrogen (N_i) of a neighbouring molecule. Colours: carbon = grey; nitrogen = light blue; oxygen = red; boron = pink; bromine = yellow. Hydrogen omitted for clarity.

Across the series of meta-halogenated-phenoxy-BsubPcs (2b-d), the X⋯N distance is consistently less than the sum of the van der Waals radii (X=Cl, Br, I), and the C-X⋯N angle is fairly constant at approximately 169 – 170°. Additionally, there appears to be a trend when comparing the observed X⋯N distance with the sum of the van der Waals radii. As the meta-halogen substituent is changed across the series from Cl to Br to I, Δd (Table 3.3) increases in magnitude, indicating that there is an increasingly greater reduction in the X⋯N distance as
Table 3.3: Halogen bond geometry.

<table>
<thead>
<tr>
<th>Motif</th>
<th>C-X⋯N</th>
<th>X⋯N distance/Å</th>
<th>Sum of van der Waals radii/Å</th>
<th>Reduction in distance (Δd), as compared to sum of van der Waals radii/Å</th>
<th>C-X⋯N angle/°</th>
</tr>
</thead>
<tbody>
<tr>
<td>2b m-ClPhO-BsubPc</td>
<td>C27-Cl1⋯N2</td>
<td>3.134(2)</td>
<td>3.30</td>
<td>0.17</td>
<td>169.3(1)</td>
</tr>
<tr>
<td>2c m-BrPhO-BsubPc</td>
<td>C27-Br1⋯N2</td>
<td>3.107(2)</td>
<td>3.40</td>
<td>0.29</td>
<td>169.7(1)</td>
</tr>
<tr>
<td>2d m-IPhO-BsubPc</td>
<td>C27-I1⋯N6</td>
<td>3.211(4)</td>
<td>3.53</td>
<td>0.32</td>
<td>169.3(2)</td>
</tr>
<tr>
<td>2d m-IPhO-BsubPc solvate</td>
<td>C27-I1⋯N4</td>
<td>3.246(2)</td>
<td>3.53</td>
<td>0.28</td>
<td>169.66(8)</td>
</tr>
<tr>
<td>4b o-ClPhO-BsubPc</td>
<td>C26A-C11A⋯N5B</td>
<td>3.092(2)</td>
<td>3.30</td>
<td>0.21</td>
<td>158.1(1)</td>
</tr>
<tr>
<td>4d o-IPhO-BsubPc solvate</td>
<td>C26-I1⋯N1</td>
<td>3.256(3)</td>
<td>3.53</td>
<td>0.27</td>
<td>166.5(1)</td>
</tr>
<tr>
<td>4e Cl₃PhO-BsubPc</td>
<td>C28-Cl3⋯N4</td>
<td>2.968(3)</td>
<td>3.30</td>
<td>0.33</td>
<td>171.4(2)</td>
</tr>
<tr>
<td></td>
<td>C30-Cl5⋯N6</td>
<td>3.415(2)</td>
<td>3.30</td>
<td>-0.12</td>
<td>156.6(1)</td>
</tr>
<tr>
<td>4f Br₃PhO-BsubPc</td>
<td>C26-Br1⋯N2</td>
<td>3.301(7)</td>
<td>3.40</td>
<td>0.10</td>
<td>159.1(4)</td>
</tr>
<tr>
<td></td>
<td>C28-Br3⋯N4</td>
<td>2.92(1)</td>
<td>3.40</td>
<td>0.48</td>
<td>169.3(4)</td>
</tr>
<tr>
<td>Br₃PhO-BsubPc solvate</td>
<td>C27-Br2⋯N6</td>
<td>2.934(4)</td>
<td>3.40</td>
<td>0.47</td>
<td>171.5(1)</td>
</tr>
<tr>
<td></td>
<td>C29-Br4⋯N2</td>
<td>3.158(4)</td>
<td>3.40</td>
<td>0.24</td>
<td>174.8(1)</td>
</tr>
</tbody>
</table>

Compared to the sum of the van der Waals radii. While the observed trend in reduction of \(X⋯N\) distances alone is not sufficient to conclude a relative ranking of halogen bond strengths, it is known that the ability of halogen atoms to participate in halogen bonding tends to increase in the order \(Cl < Br < I\).\(^{23}\) Based on the increase in the reduction of the sum of the van der Waals radii across the series \(Cl < Br < I\) and the approximately linear \(C-X⋯N\) angle of 169 – 170°, we can conclude that indeed these are halogen bonds, their presence providing the enthalpic counterbalance to the distortion of the above-mentioned B-O-C bond angle.

Two of the crystal structures within the ortho-halogenated-phenoxy-BsubPcs series also demonstrate halogen bonding, namely \(o-ClPhO-BsubPc (4b)\) and solvated \(o-IPhO-BsubPc (4d)\). Once again, as the halogen substituent is changed from \(Cl\) to \(I\) (Table 3.3), there is an increasingly greater reduction in the \(X⋯N\) distance. The \(C-X⋯N\) angle also increases.
significantly, from approximately 158° for o-ClPhO-BsubPc to approximately 166° for solvated o-IPhO-BsubPc.

Interestingly, the introduction of additional bromine atoms on the phenoxy moiety, as in compound 2f, results in two significant bromine-nitrogen interactions in each of the observed arrangements. In the solvated Br₅PhO-BsubPc crystal structure, the bromines in both meta positions participate in halogen bonds, albeit asymmetrically, with Br₂ having a very short X···N distance of 2.93 Å and Br₄ having a somewhat longer X···N distance of 3.16 Å. Both Br₂ and Br₄ display very nearly linear C-X···N angles of approximately 172° and 175° respectively. These interactions will be further discussed in the next section, which includes figures and detailed discussions of the crystal packing motifs.

In the unsolvated Br₅PhO-BsubPc crystal structure, the bromine in the para position and one of the bromines in an ortho position participate in halogen bonding. Again, the two bromines participate to different degrees, with the para bromine having a very short X···N distance of approximately 2.92 Å and the ortho bromine having a X···N distance of approximately 3.30 Å. In this case, the Br₃ para bromine has a fairly linear C-X···N angle of approximately 169°, and the Br₁ ortho bromine has a significantly smaller angle of approximately 159°. Although the Br₁···N₂ distance (3.30) is less than the sum of the van der Waals radii (3.40), the small C-X···N angle suggests that this bromine-nitrogen interaction is not as strong as the Br₃···N₄ interaction. The second ortho bromine (Br₅) has a close Br-Br contact with a Br₅ atom from a neighbouring molecule, occurring at a distance of 3.4573(17) Å. This contact occurs through a crystallographic inversion centre, and consequently the two associated C-Br···Br angles are identical (θ₁=θ₂=145.4(3)°) (see Figure 3.6). Based on the symmetrical geometry, this can be classified as a type-I (i.e., van der Waals type) halogen-halogen contact,²⁴-²⁵ which likely results as a consequence of close packing.

In contrast to Br₅PhO-BsubPc (2f), the crystal structure found for Cl₅PhO-BsubPc (2e) displays one strong halogen-nitrogen interaction and one halogen-nitrogen interaction of borderline significance. The X···N distance of the chlorine in the para position, Cl₃, is very short at approximately 2.97 Å and the C-X···N angle is very nearly linear at approximately 171°. One of the chlorines in an ortho position, Cl₅, has a X···N interaction distance of 3.42 Å, which is
greater than the sum of the van der Waals radii (3.30 Å). The C-X···N angle is also relatively small at approximately 157°. Thus, although the crystal packing arrangement of Cl₅PhO-BsubPc would appear to facilitate two halogen bonds, only one chlorine-nitrogen interaction is actually significant enough to be considered a halogen bond. It is worth noting that there are no close Cl-Cl contacts in this structure, despite the presence of close Br-Br contacts in the isostructural Br₅PhO-BsubPc arrangement. We therefore believe that the absence of short Cl-Cl contacts further suggests that the Br₅-Br₅ contacts in unsolvated Br₅PhO-BsubPc arise mainly from close packing, and not from significant halogen-halogen interactions.

Figure 3.6: Illustration of the molecular packing arrangement within the single crystal (extended beyond the unit cell) of Br₅PhO-BsubPc (compound 4f), showing the close Br-Br contact as a black dotted line. The Br(5)-Br(5) distance is 3.4573(17) Å. Crystallographic inversion centres are shown as orange spheres. Colours: carbon = grey; nitrogen = light blue; oxygen = red; boron = pink; bromine = yellow. Hydrogens are omitted for clarity.

Lastly, as a result of halogen bonding between a halogen atom and a nitrogen atom, one might expect there to be some stretching of the covalent carbon-halogen bond. We compared the length of the carbon-halogen (C-X) bonds observed for compounds 2b-d and 4a-f with the C-X bond lengths observed for para-substituted halo-phenoxy-BsubPcs (Table 3.4).² The para-substituted analogues do not exhibit halogen bonding, and are therefore reasonable estimates for the preferred C-X bond lengths in phenoxy-BsubPcs.
Table 3.4: Halogen-carbon covalent bond distances.

<table>
<thead>
<tr>
<th>Motif</th>
<th>C-X</th>
<th>C-X distance observed/Å</th>
<th>C-X distance expected/Å</th>
<th>Δ Bond length/Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>2b m-ClPhO-BsubPc</td>
<td>C27-C11</td>
<td>1.731(3)</td>
<td>1.739(2)</td>
<td>-0.008(5)</td>
</tr>
<tr>
<td>2c m-BrPhO-BsubPc</td>
<td>C27-Br1</td>
<td>1.899(3)</td>
<td>1.893(3)</td>
<td>0.006(6)</td>
</tr>
<tr>
<td>2d m-IPhO-BsubPc</td>
<td>C27-I1</td>
<td>2.114(7)</td>
<td>2.094(3)</td>
<td>0.02(1)</td>
</tr>
<tr>
<td>m-IPhO-BsubPc solvate</td>
<td>C27-I1</td>
<td>2.105(2)</td>
<td>2.094(3)</td>
<td>0.011(5)</td>
</tr>
<tr>
<td>4a o-FPhO-BsubPc</td>
<td>C26-F1</td>
<td>1.344(3)</td>
<td>1.363(2)</td>
<td>-0.019(5)</td>
</tr>
<tr>
<td>4b o-ClPhO-BsubPc</td>
<td>C26A-ClA</td>
<td>1.729(3)</td>
<td>1.739(2)</td>
<td>-0.010(5)</td>
</tr>
<tr>
<td></td>
<td>C26B-C1B</td>
<td>1.738(3)</td>
<td>1.739(2)</td>
<td>-0.001(5)</td>
</tr>
<tr>
<td>4c o-BrPhO-BsubPc</td>
<td>C26-Br1</td>
<td>1.811(7)</td>
<td>1.893(3)</td>
<td>-0.082(10)</td>
</tr>
<tr>
<td>4d o-IPhO-BsubPc</td>
<td>C26-I1</td>
<td>2.05(1)</td>
<td>2.094(3)</td>
<td>-0.04(1)</td>
</tr>
<tr>
<td>o-IPhO-BsubPc solvate</td>
<td>C26-I1</td>
<td>2.089(4)</td>
<td>2.094(3)</td>
<td>-0.005(7)</td>
</tr>
<tr>
<td>4e Cl2PhO-BsubPc</td>
<td>C26-C11</td>
<td>1.726(3)</td>
<td>1.739(2)</td>
<td>-0.013(5)</td>
</tr>
<tr>
<td></td>
<td>C27-Cl2</td>
<td>1.723(4)</td>
<td>1.739(2)</td>
<td>-0.016(6)</td>
</tr>
<tr>
<td></td>
<td>C28-Cl3</td>
<td>1.718(5)</td>
<td>1.739(2)</td>
<td>-0.021(7)</td>
</tr>
<tr>
<td></td>
<td>C29-Cl4</td>
<td>1.725(4)</td>
<td>1.739(2)</td>
<td>-0.014(6)</td>
</tr>
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<td></td>
<td>C30-Cl5</td>
<td>1.719(4)</td>
<td>1.739(2)</td>
<td>-0.020(6)</td>
</tr>
<tr>
<td>4f Br3PhO-BsubPc</td>
<td>C26-Br1</td>
<td>1.871(1)</td>
<td>1.893(3)</td>
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<tr>
<td></td>
<td>C27-Br2</td>
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<td>1.893(3)</td>
<td>0.01(1)</td>
</tr>
<tr>
<td></td>
<td>C28-Br3</td>
<td>1.88(1)</td>
<td>1.893(3)</td>
<td>-0.01(1)</td>
</tr>
<tr>
<td></td>
<td>C29-Br4</td>
<td>1.89(1)</td>
<td>1.893(3)</td>
<td>0.00(1)</td>
</tr>
<tr>
<td></td>
<td>C30-Br5</td>
<td>1.90(1)</td>
<td>1.893(3)</td>
<td>0.01(1)</td>
</tr>
<tr>
<td>Br3PhO-BsubPc solvate</td>
<td>C26-Br1</td>
<td>1.890(4)</td>
<td>1.893(3)</td>
<td>-0.003(7)</td>
</tr>
<tr>
<td></td>
<td>C27-Br2</td>
<td>1.887(4)</td>
<td>1.893(3)</td>
<td>-0.006(7)</td>
</tr>
<tr>
<td></td>
<td>C28-Br3</td>
<td>1.899(4)</td>
<td>1.893(3)</td>
<td>0.006(7)</td>
</tr>
<tr>
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a These C-X distances correspond to halogens which are not participating in halogen-nitrogen interactions.

b C-X bond lengths observed for para-substituted halo-phenoxy-BsubPcs, which do not exhibit halogen bonding.

For many of the C-X bonds listed in Table 3.4, the change in bond length is too minor to be considered significant (-0.01 Å < Δ bond length < 0.01 Å). This category includes the motifs m-ClPhO-BsubPc, m-BrPhO-BsubPc, o-ClPhO-BsubPc, solvated o-IPhO-BsubPc, all of the C-X bonds in solvated Br3PhO-BsubPc and all but one of the C-X bonds in unsolvated Br3PhO-BsubPc. Notable exceptions are the C-X bonds for both solvated and unsolvated m-IPhO-BsubPc, which are involved in halogen bonding and which display significant bond stretching of approximately 0.01 Å and 0.02 Å, respectively. The remaining C-X bonds, some of which participate in halogen bonding, display mild to significant bond compression (Δ bond length < -
In sum, the presence of a halogen bond, as determined by a significantly short X···N distance and a nearly linear C-X···N angle, has been observed to occur alongside both C-X bond stretching and C-X bond compression. With regards to the crystal structures for compounds 2b-d and 4a-f, there does not appear to be a significant correlation between halogen bonding and distortions in the C-X bond.

### 3.1.3.5 Solid State Packing Arrangements

The presence of halogen bonding between adjacent halo-substituted phenoxy-BsubPcs results in solid state arrangements that are markedly different from any previously published phenoxy-BsubPc packing arrangements. In addition to halogen bonds, these new solid state arrangements also demonstrate π-π interactions, which can occur between two neighbouring concave surfaces (concave-concave), between two neighbouring convex surfaces (convex-convex), and between a phenoxy moiety and an adjacent concave surface (phenoxy-concave). These π-π interactions can be described by the intermolecular metric of Cg-Cg (ring centroid to ring centroid) distance (Table 3.2). Many of these π-π interactions are supported by weak CH-π interactions.

Beginning with the meta-halogenated-phenoxy-BsubPcs 2b-d, the packing motif observed for m-ClPhO-BsubPc, m-BrPhO-BsubPc, and unsolvated m-IPhO-BsubPc is illustrated in Figure 3.7. The halogen atom of one BsubPc molecule interacts with the nitrogen atom of an adjacent BsubPc molecule, forming continuous one-dimensional ribbons throughout the crystal structure. Each subPc ligand is also associated with an adjacent subPc ligand through concave-concave π-π interactions. As a result of the π-π interactions, each one-dimensional ribbon is associated with two neighbouring ribbons, forming a two-dimensional sheet of interacting molecules.

The second meta-halo-substituted phenoxy-BsubPc motif, observed for solvated m-IPhO-BsubPc, is illustrated in Figure 3.8. In this case, rather than forming one-dimensional ribbons, the iodine-nitrogen interactions form dimers. The iodine atom and one nitrogen atom of each BsubPc molecule interact with the same adjacent BsubPc molecule, forming a structure resembling a small loop (Figure 3.8a). Each subPc ligand participates in one concave-concave π-π interaction with an adjacent subPc ligand, effectively stacking the dimers formed by halogen bonds into column-like structures (Figure 3.8c). Each subPc ligand also participates in two convex-convex π-π interactions (Figure 3.8b), forming continuous rows of interacting molecules.
**Figure 3.7:** Illustration of the molecular packing arrangement within the single crystal (extended beyond the unit cell) of \( m \)-ClPhO-BsubPc. The centroids of rings participating in concave-concave \( \pi \)-\( \pi \) interactions are shown in cyan, and the \( \pi \)-\( \pi \) interactions are shown as cyan dotted lines. Halogen-nitrogen interactions are shown as black dotted lines. Colours: carbon = grey; nitrogen = light blue; oxygen = red; boron = pink; chlorine = green. Hydrogen omitted for clarity.

The end result is a three-dimensional network of closely associated molecules. A view along the c axis of this motif (Figure 3.8d) reveals a substantial amount of void space. This crystal structure consistently contained residual solvent, regardless of whether the crystals were obtained using the benzene/heptane solvent system or the dichloromethane/pentane solvent system. The X-ray diffraction results were analyzed using PLATON 40-M,\(^{16}\) and the unit cell was determined to contain approximately 5536 Å\(^3\) (17.9%) solvent-accessible void space.

Of the five packing arrangements observed for ortho-halogenated-phenoxy-BsubPcs, only two demonstrated halogen-nitrogen interactions: o-ClPhO-BsubPc (4b, Figure 3.9) and solvated o-IPhO-BsubPc (4d, Figure 3.10). Interestingly, both of these motifs also display \( \pi \)-\( \pi \) interactions between the phenoxy moiety and the concave side of an adjacent subPc ligand; this interaction is typically seen in perfluorinated BsubPc derivatives, and its presence in perhydrogenated derivatives is noteworthy. In the case of both the perfluorinated BsubPc derivatives and the crystal structure of 4b, this arrangement is likely the result of an enthalpically favourable interaction between an electron-poor aromatic fragment (i.e., the o-ClPhO fragment or pentafluorinated phenoxy fragment) and an electron-rich fragment (i.e., the subPc ligand). A closer examination of the solid state arrangement for o-ClPhO-BsubPc (4b) reveals that the two molecules (‘A’ and ‘B’) within the asymmetric unit have slightly different conformations and
Figure 3.8: Illustration of the molecular packing arrangement within the single crystal (extended beyond the unit cell) of solvated \( m \)-IPhO-BsubPc. The centroids of rings participating in concave-concave \( \pi-\pi \) interactions are shown in cyan, and the centroids of rings participating in convex-convex \( \pi-\pi \) interactions are shown in purple. Halogen-nitrogen interactions are shown as black dotted lines. (a) Dimers formed by I-N interactions. (b) Side view 1, showing convex-convex \( \pi-\pi \) interactions. (c) Side view 2, showing I-N and convex-convex \( \pi-\pi \) interactions. (d) View along the c axis, showing where side views 1 and 2 are located. Colours: carbon = grey; nitrogen = light blue; oxygen = red; boron = pink; iodine = brown. Solvent molecules removed using SQUEEZE option in Platon. Hydrogen omitted for clarity.
Figure 3.9: Illustration of the molecular packing arrangement within the single crystal (extended beyond the unit cell) of \( o\text{-ClPhO-BsubPc} \). The centroids of rings participating in phenoxy-concave \( \pi-\pi \) interactions are shown in cyan, and the \( \pi-\pi \) interactions are shown as cyan dotted lines. Halogen-nitrogen interactions are shown as black dotted lines. Colours: carbon = grey; nitrogen = light blue; oxygen = red; boron = pink; chlorine = green. Gold colouring denotes an example of Molecule A and blue denotes an example of Molecule B. Hydrogen omitted for clarity.

also participate in interactions differently. The phenoxy-concave \( \pi-\pi \) interaction occurs at a distance of approximately 3.68 Å between adjacent ‘A’ molecules and at a distance of approximately 3.69 Å between adjacent ‘B’ molecules. These phenoxy-concave \( \pi-\pi \) interactions form columns of associated molecules. A column of ‘A’ molecules is then associated with a column of ‘B’ molecules through a halogen bond between the chlorine atom of molecule ‘A’ and a nitrogen atom of molecule ‘B’, effectively forming a double column of associated molecules. The chlorine atom of molecule ‘B’ does not interact with any nitrogen atoms.

In contrast, all of the halogen atoms in the solid state arrangement of solvated \( o\text{-IPhO-BsubPc} \) (4d, Figure 3.10) are involved in halogen bonds; these I-N interactions form dimers, similar to what was observed for solvated \( m\text{-IPhO-BsubPc} \) (Figure 3.8a). As was the case for \( o\text{-ClPhO-BsubPc} \) (4b, Figure 3.9), the phenoxy-concave \( \pi-\pi \) interactions form columns of associated molecules, and the adjacent columns are associated through halogen-nitrogen bonds. Each subPc
ligand also participates in convex-convex $\pi$-$\pi$ interactions, resulting in a three-dimensional network of closely associated BsubPc molecules.

**Figure 3.10:** Illustration of the molecular packing arrangement within the single crystal (extended beyond the unit cell) of solvated $o$-IPhO-BsubPc. The centroids of rings participating in phenoxy-concave $\pi$-$\pi$ interactions are shown in cyan, and the centroids of rings participating in convex-convex $\pi$-$\pi$ interactions are shown in purple. Halogen-nitrogen interactions are shown as black dotted lines. Colours: carbon = grey; nitrogen = light blue; oxygen = red; boron = pink; iodine = brown. Hydrogen omitted for clarity.

The ability of the two iodo derivatives, $m$-IPhO-BsubPc (2d) and $o$-IPhO-BsubPc (4d), to participate in dimeric halogen bond arrangements appears to be unique, since the halogen bonds formed by the chloro and bromo derivatives were solely catemeric (ribbon-like) in arrangement. We do not have a definite explanation for this behaviour, but we speculate that there may be two contributing factors. First, the iodine-nitrogen interactions, which are typically stronger than other halogen-nitrogen interactions, may be able to provide a sufficiently strong enthalpic interaction to allow the formation of a dimeric motif. Second, the larger size of the iodine atom
may more readily enable the geometry required for a dimeric motif, as compared to the smaller chlorine and bromine atoms. Aside from these speculations, it is worth noting that we have only observed the dimer iodo motif in solvated crystals, whereas the unsolvated crystals display halogen-nitrogen bonds in a catemeric arrangement. This suggests that the catemeric arrangement is preferred for all three derivatives (chloro, bromo and iodo) in their unsolvated forms.

Moving on to the penta-halogenated-phenoxy-BsubPcs, the solvated and unsolvated arrangements of Br$_5$PhO-BsubPc are illustrated in Figure 3.11 and Figure 3.12 respectively. In solvated Br$_5$PhO-BsubPc, each bromine in a meta position interacts with a nitrogen atom of an adjacent BsubPc molecule. Each BsubPc molecule participates in a total of four Br-N interactions with four different neighbours (twice as a donor and twice as an acceptor), forming a two-dimensional sheet of interacting molecules (Figure 3.11a). Each subPc ligand also participates in one concave-concave π-π interaction and one convex-convex π-π interaction. In this manner, each sheet is associated with both neighbouring sheets, forming a three-dimensional network of interacting BsubPc molecules.

In unsolvated Br$_5$PhO-BsubPc, each BsubPc molecule again participates in a total of four Br-N interactions. In contrast to the motif for solvated Br$_5$PhO-BsubPc, however, each BsubPc molecule only interacts with two neighbouring molecules via Br-N interactions, instead of interacting with four neighbouring molecules. The end result is an arrangement which resembles a one-dimensional ribbon rather than a sheet (Figure 3.12a). Similar to the ribbon motif previously described for m-ClPhO-BsubPc, m-BrPhO-BsubPc, and unsolvated m-IPhO-BsubPc (Figure 3.7), each subPc ligand also participates in one π-π interaction with a subPc ligand from a neighbouring ribbon. As a result, each one-dimensional ribbon is associated with two neighbouring ribbons, forming a two-dimensional sheet of interacting molecules.

Finally, the motif of Cl$_5$PhO-BsubPc is isostructural with the motif observed for unsolvated Br$_5$PhO-BsubPc, and is therefore equivalent to the arrangement in Figure 3.12). It should be restated, however, that the Cl-N interactions with a distance of 3.42 Å do not, strictly speaking, meet the criteria for a halogen bond if only distance criteria are considered. However, the linear geometry of the interaction suggests that this is a weak halogen bonding interaction. In terms of
Figure 3.11: Illustration of the molecular packing arrangement within the single crystal (extended beyond the unit cell) of solvated Br$_5$PhO-BsubPc. The centroids of rings participating in concave-concave π-π interactions are shown in cyan, the centroids of rings participating in convex-convex π-π interactions are shown in purple. Halogen-nitrogen interactions are shown as black dotted lines. Colours: carbon = grey; nitrogen = light blue; oxygen = red; boron = pink; bromine = yellow. Hydrogen omitted for clarity.

Figure 3.12: Illustration of the molecular packing arrangement within the single crystal (extended beyond the unit cell) of unsolvated Br$_5$PhO-BsubPc. The centroids of rings participating in concave-concave π-π interactions are shown in cyan, and the π-π interactions are shown as cyan dotted lines. Halogen-nitrogen interactions are shown as black dotted lines. (a) Ribbon formed by halogen-nitrogen interactions. (b) Two adjacent ribbons associated through π-π interactions. Colours: carbon = grey; nitrogen = light blue; oxygen = red; boron = pink; bromine = yellow. Hydrogen omitted for clarity.

halogen bonding, this observation suggests that this particular packing motif is primarily directed by the interaction between the para halogen of one molecule and an imine nitrogen atom of an adjacent molecule. The interaction of the ortho halogen of one molecule and an imine nitrogen atom of an adjacent molecule plays a secondary, supportive role.
3.1.3.6 Approximate Strength of Halogen-Nitrogen Interactions

As mentioned earlier in this discussion, we have previously reported the synthesis of the full set of \textit{para}-halogenated-phenoxy-\textsubscript{Pcs}, and solved their single crystal structures under conditions identical to those which are described in this paper for the \textit{meta}-halogenated-phenoxy-\textsubscript{Pcs}.\textsuperscript{2} In their solid state packing arrangements, both the \textit{para}-halogenated and \textit{meta}-halogenated derivatives display comparable concave-concave $\pi-\pi$ interactions. However, only the \textit{meta}-halogenated derivatives display halogen bonds, and these halogen bonds coupled with the associated B-O-C angle distortions represent the single most significant difference between the two series of derivatives. This provides a unique opportunity to use computational methods to explore the strength of the halogen bonds in the crystals studied herein.

Our approach uses computational methods to calculate and compare the heat of formation of \textit{meta}-halogenated-phenoxy-\textsubscript{Pcs} (2b-d) with their isomeric \textit{para}-halogenated counterparts, both in the crystal state and as geometry-optimized molecules (as single isolated molecules in the gas phase). The heat of formation calculated for a given molecule is dependent on the geometric conformation of that molecule, which in turn is dependent on the molecule’s environment. Naturally, an isolated molecule with an optimized geometry has relatively few geometric constraints and therefore has a low heat of formation. In contrast, the conformation of a molecule within a crystal lattice is constrained and distorted by the presence of enthalpic interactions with neighbouring molecules; these molecular distortions result in an increase in the heat of formation, which in turn is indicative of the intermolecular forces present within the crystal environment. In this study comparing the isomeric \textit{meta}- and \textit{para}-halogenated-phenoxy-\textsubscript{Pcs}, the only significant difference in solid state intermolecular forces between the two series is the presence of halogen bonding in the \textit{meta}-halogenated series. It follows that differences in molecular conformation between analogous molecules are also mainly attributable to the presence of halogen bonding. Furthermore, quantitative differences in heat of formation between the two isomeric series should provide a reasonable indication as to the strength of halogen bonding within the \textit{meta}-halogenated series.

It must be emphasized that our assertion is that the use of this technique, and the associated comparison, is limited to the case of isomers with similar solid state arrangements, where the solid state arrangements differ by only one type of significant intermolecular interaction. This
allows significant differences between the two solid state arrangements to be attributed to a single type of intermolecular interaction. Thus, this technique cannot be used to estimate the strength of halogen bonding in the packing arrangements for solvated $m$-IPhO-$B_{sub}$Pc, the ortho-halogenated-phenoxy-$B_{sub}$Pcs or the penta-halogenated-phenoxy-$B_{sub}$Pcs. Likewise, of the two reported polymorphs for $para$-bromophenoxy-$B_{sub}$Pc, $^{2}$the $\beta$-$p$-BrPhO-$B_{sub}$Pc polymorph was used for this study. The only significant intermolecular interactions within the packing arrangement of $\beta$-$p$-BrPhO-$B_{sub}$Pc are concave-concave $\pi$-$\pi$ interactions and it is isostructural with the packing arrangements found for $p$-ClPhO-$B_{sub}$Pc and $p$-IPhO-$B_{sub}$Pc, making it a suitable point of comparison.

The results of this study are presented graphically in Figure 3.13. Two heat of formation values were computed for each molecule using HyperChem for Windows OS version 8.0. The first value, hereafter referred to as $\Delta H_{f,cry}$, was obtained by isolating a single molecule from the appropriate solid state packing arrangement and performing a single-point calculation using a modified RM1 semi-empirical method which we have previously described.$^{13}$ This value represents the heat of formation of a single molecule as it exists in the crystal lattice. Next, the geometry of the isolated molecule extracted from the single crystal determination was optimized using the MM+ molecular mechanics force field, and then further refined using the aforementioned modified RM1 semi-empirical method.$^{13}$ The heat of formation obtained after geometry optimization is hereafter referred to as $\Delta H_{f,opt}$, and represents the heat of formation of a single isolated molecule in a geometry-optimized state. The crystal state ($\Delta H_{f,cry}$) and optimized state ($\Delta H_{f,opt}$) heat of formation values are represented by circles and diamonds, respectively, in Figure 3.13.

For each pair of analogous isomeric molecules, the $\Delta H_{f,opt}$ values are nearly identical (103-104 kcal/mol for $p$- and $m$-ClPhO-$B_{sub}$Pc, 116 kcal/mol for $\beta$-$p$- and $m$-BrPhO-$B_{sub}$Pc, and 129 kcal/mol for $p$- and $\beta$-$m$-IPhO-$B_{sub}$Pc). Optimized intramolecular metrics (bowl depth, B-O bond length, O-C bond length and B-O-C angle) for each pair of analogous molecules were also found to be nearly identical. These observations support the basis of our approach, i.e. that differences in molecular conformation and heat of formation are due to the presence of intermolecular interactions.
Figure 3.13: Crystal state and optimized state heat of formation values calculated for meta-halo-substituted phenoxy-BsubPcs (2b-d) and their para-halo-substituted counterparts.

The difference between $\Delta H_{f,cry}$ and $\Delta H_{f,opt}$ is denoted D1 and represented by the bars in Figure 3.13. In all cases, the $\Delta H_{f,cry}$ values are considerably higher than the $\Delta H_{f,opt}$ values. This is to be expected, as the process of crystallization introduces enthalpic interactions which distort the geometry of the molecule. Thus, D1 provides a rough indication of the strength of the sum of intermolecular interactions associated with crystallization.

The difference between the D1 value for a meta-halogenated-phenoxy-BsubPc and the D1 value for its para-halogenated-counterpart is denoted D2. The D2 values are all positive; in other words, the D1 values for the meta-halogenated-phenoxy-BsubPcs are consistently higher than the D1 values of their para-halogenated counterparts. For the para-halogenated series, which is directed by intermolecular concave-concave $\pi$-$\pi$ interactions, D1 is attributable to concave-concave $\pi$-$\pi$ interactions. For the meta-halogenated series, D1 is attributable to both the concave-concave $\pi$-$\pi$ interactions and the halogen-nitrogen interactions. In this context, D2 represents the contribution of halogen-nitrogen interactions and thereby provides a rough indication of the strength of the halogen-nitrogen interactions in compounds 2b-d.

Using this technique, the strength of the halogen-nitrogen interactions for $m$-ClPhO-BsubPc (2b) and $m$-BrPhO-BsubPc (2c) are essentially equal, as these compounds have D2 values of approximately 0.8 and 0.5 kcal/mol, respectively. The strength of the iodine-nitrogen interactions
for 2d is considerably higher, with $m$-IPhO-BsubPc having a D2 value of approximately 3.9 kcal/mol. Despite the approximate method used to calculate the strength of halogen-nitrogen interactions, these values are within the typical range reported for halogen bonding (i.e., from nil to 5 kcal/mol).\textsuperscript{22-23, 26}

In summary, based on our observations here and elsewhere,\textsuperscript{1-2} $\pi-\pi$ interactions are extremely common in the solid state arrangements of BsubPcs. Significant distortions of the preferred B-O-C angle are relatively rare, and they occur here alongside close halogen-nitrogen interactions. Further, our computational modeling results indicate that the observed molecular distortions, particularly of the B-O-C angle, require the presence of an enthalpic interaction to offset the energy associated with the B-O-C distortion that is approximately equivalent to a halogen-nitrogen bond. These results suggest that these solid state arrangements are primarily driven by the presence of halogen-nitrogen interactions, with the $\pi-\pi$ interactions playing a supportive role.
3.1.4 Conclusions

Ten previously unreported halogenated phenoxy-BsubPc derivatives have been synthesized and characterized. Using single crystal x-ray diffraction, a total of twelve solid state arrangements were obtained for nine of these derivatives. Of these twelve solid state arrangements, nine displayed halogen bonding, including all four meta-halogenated-phenoxy-BsubPc crystals ($m$-ClPhO-BsubPc, $m$-BrPhO-BsubPc, solvated and unsolvated $m$-IPhO-BsubPc), two of the ortho-halogenated phenoxy-BsubPc crystals ($o$-ClPhO-BsubPc and solvated $o$-IPhO-BsubPc) and all three penta-halogenated-phenoxy-BsubPc crystals ($Cl_5$PhO-BsubPc, solvated and unsolvated $Br_5$PhO-BsubPc). The presence of halogen bonds within these solid state arrangements was proven by $X\cdots N$ ($X=Cl, Br, I$) bond lengths measured to be significantly shorter than the sum of the respective van der Waal radii, as well as nearly-linear C-$X\cdots N$ angles.

The identity of the halogen atom is known to be an important factor in the formation of halogen bonds. We have, unsurprisingly, observed halogen bonds only in cases where the halogen was chlorine, bromine or iodine. In addition, the results of our computational modeling indicate that within the meta-halogenated-BsubPcs, iodine forms the strongest halogen-nitrogen interaction, followed by bromine and chlorine each with approximately equal strength. Lastly, within the penta-halogenated-BsubPcs, we observed that the solid state arrangement of unsolvated $Br_5$PhO-BsubPc contained two bromines involved in significant halogen-nitrogen interactions, whereas the isostructural solid state arrangement of $Cl_5$PhO-BsubPc contained one chlorine involved in a significant interaction and one chlorine involved in an interaction of borderline significance. This would suggest that bromine participates in halogen bonds more readily than chlorine. Thus, we have generally observed that the tendency of a halogen atom to participate in a halogen bond increases in the order $Cl < Br < I$. These observations are consistent with the current understanding of the relationship between the halogen atom identity and halogen bonding.

Interestingly, we have observed that the position of the halogen atom on the phenoxy moiety also plays a vital role in facilitating the occurrence of halogen bonds within phenoxy-BsubPcs. The meta-halogenated-BsubPc series consistently demonstrated halogen bonding, suggesting that a halogen atom ($X = Cl, Br, I$) situated in a meta position will promote halogen bonding irrespective of the halogen atom identity or the crystallization method. The ortho-halogenated series demonstrated halogen bonding only in two solid state arrangements ($o$-ClPhO-BsubPc and
solvated o-IPhO-BsubPc), indicating that the formation of a halogen bond involving the ortho position is sensitive to both the identity of the halogen atom and the crystallization method. In contrast, the previously published para-halogenated series\(^2\) did not show any evidence of halogen bonds, and therefore a single halogen atom situated in the para position does not appear to facilitate halogen bonding. Even so, halogen bonds involving the para position were observed in the solid state arrangements of penta-halogenated-phenoxy-BsubPcs, which suggests that increasing the number of halogen atoms on the phenoxy moiety favours the formation of halogen bonds.

In summation, we have demonstrated the ability of halogen bonds to direct the solid state arrangement of phenoxy-BsubPcs into a variety of new packing motifs. These findings represent the first reported instance of halogen bonding in BsubPcs. We have also explored the effect of halogen atom identity and position on influencing the formation and strength of halogen bonds within these new solid state arrangements. We expect these observations will lead to a greater understanding of the methods available for influencing and ultimately engineering the solid state arrangement of BsubPcs.
3.2 Meta-Fluorophenoxy-Boron Subphthalocyanine: Crystal Structure Effects of Fluorine as a Hydrogen Bond Acceptor

3.2.1 Introduction

As a result of their promising optical and electronic properties, BsubPc derivatives are of increasing interest in organic electronic device applications. As discussed in Chapter 1, these derivatives are of particular interest as electron donor and electron acceptor materials in organic photovoltaics (OPVs). BsubPcs are typically utilized in the solid state in such applications, providing motivation to study and understand the intermolecular interactions that influence the solid state packing arrangements of BsubPc molecules. To date, we have conducted studies on the influence of halogen bonding, hydrogen bonding and interactions between π-acid and π-basic moieties on the solid state arrangements of BsubPc molecules.

This chapter discusses the crystal structure analysis of meta-fluorophenoxy-BsubPc (m-FPhO-BsubPc, 1). This derivative was synthesized and purified as part of a larger study of the effects of halogen bonding in BsubPc derivatives, but at the time we were unsuccessful in obtaining a single crystal suitable for x-ray diffraction. The crystal structure of (1) reported here was determined using twinned crystals obtained by train sublimation, the same technique used in our previous report concerning halogen bonding. The crystal structure of (1) is markedly different from that of any previously published BsubPc derivatives, and features a combination of π-π interactions, CH-π interactions, and weak CH-F hydrogen bonds. In contrast to other meta-halogenated-phenoxy-BsubPc derivatives, the crystal structure of (1) does not contain any halogen bonds.

Figure 3.14: Molecular structure of m-FPhO-BsubPc (1).
3.2.2 Experimental

3.2.2.1 Synthesis and Crystallization

Synthesis, purification and characterization details for \textit{m-}FPhO-BsubPc have been previously reported in the first half of this chapter,\cite{29} and crystals suitable for x-ray diffraction were obtained via slow train sublimation according to a published procedure.\cite{14}

3.2.2.2 Refinement

Crystal data, data collection and structure refinement details are provided in Table 3.5. After structure solution, as the R-factor did not decrease below 17\% with all of the non-hydrogen atoms refined with anisotropic displacement parameters, pseudo merohedral twinning was suspected and confirmed by the TWINROTMAT routine in PLATON.\cite{16} Pseudo merohedral twinning occurs when a lattice row or a lattice plane of the crystal approximately corresponds to an element of symmetry. This can occur, as in this case, for a monoclinic crystal (defined as a crystal with only two of the three unit cell angles equal to 90\(^\circ\), i.e., \(\alpha = \gamma = 90\(^\circ\)\) and \(\beta \neq 90\(^\circ\)\)) where the oblique angle is nonetheless very close to 90\(^\circ\) (i.e., \(\beta \approx 90\(^\circ\)\)). The resulting crystal lattice is pseudo-orthorhombic and thus contains two pseudo twofold axes and two pseudo mirror planes. The resultant approximate symmetry tends to produce twinned crystals. Application of the twin law 1 0 0 0 -1 0 0 0 -1 using a TWIN/BASF set of instructions reduced the R-factor by roughly 4\%. Ultimately, a slightly better result was obtained by refining the structure using the HKLF5 reflections file with 17326 overlaps from both domains generated with PLATON.\cite{16} The refined ratio of major versus minor components is 79.38(15):20.62(15). The fluorine atom F3 was found statistically disordered over two sites with occupancy factor refined at 0.626(7) and 0.374(7). All H atoms were placed in geometrically idealized positions with \(U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C)\).
### Table 3.5: Experimental details

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| Refinement |  |
| No. of reflections | 17386 |
| No. of parameters | 1416 |
| No. of restraints | 0 |
| H-atom treatment | H-atom parameters constrained |
| $\Delta \rho_{max}$, $\Delta \rho_{min}$ (e Å$^{-3}$) | 1.53, −0.65 |
3.2.3 Results and Discussion

The title compound, \textit{m-FPhO-BsubPc} (1), crystallized in the $P2_1/c$ space group and contains four independent molecules within the asymmetric unit cell, resulting in a total of 16 molecules within the full unit cell. The unit cell is monoclinic and the beta angle is almost exactly 90° (Table 3.5); this situation often produces severely twinned crystals, as was the case for this derivative. The R-factor was reduced from approximately 17\% to 11.6\% once the twin law was introduced and the twin component fractions were refined. Displacement ellipsoid plots of the four independent molecules are provided in Figure 3.15.

\textbf{Figure 3.15:} Displacement ellipsoid plot drawn at the 30\% probability level, showing atom labeling for the four independent molecules within the asymmetric unit cell of \textit{m-FPhO-BsubPc}. Hydrogen atoms have been omitted for clarity.
Prior to describing the intermolecular interactions present within the crystal structure of (1), it is useful to introduce some common terminology for describing intermolecular π-π interactions between adjacent BsubPc molecular fragments. The subPc ligand consists of a total of 9 rings. Typically, the three 6-membered carbon rings furthest from the boron centre are referred to as “heads,” while the three 6-membered heterocyclic rings surrounding the boron centre are referred to as “tails.” Additionally, due to the distinctive bowl shape of the subPc ligand, the intermolecular interactions can be described as involving either the convex or concave side of the bowl.

On a molecular level, (1) is similar to two sets of phenoxy-BsubPc derivatives: those containing a different halogen atom in the meta position, i.e. meta-chlorophenoxy-BsubPc (m-ClPhO-BsubPc), meta-bromophenoxy-BsubPc (m-BrPhO-BsubPc), and meta-iodophenoxy-BsubPc (m-IPhO-BsubPc); and those containing a single fluorine atom in a different position, i.e. ortho-fluorophenoxy-BsuPc (o-FPhO-BsuPc) and para-fluorophenoxy-BsuPc (p-FPhO-BsuPc). The single crystal structures of the three other meta-halogenated BsubPc derivatives are isostructural and crystallize in the $P2_1/n$ space group with $Z=4$. The packing arrangement of these derivatives, demonstrated with $m$-ClPhO-BsubPc in Figure 3.16, features halogen-nitrogen bonds that form a 1-dimensional ribbon motif. Neighbouring ribbons are stacked on top of each other through concave-concave head-to-head π-π interactions. In contrast to the $m$-ClPhO-BsubPc, $m$-BrPhO-BsubPc and $m$-IPhO-BsubPc derivatives, we encountered considerable difficulty in attempting to obtain a good quality single crystal of $m$-FPhO-BsubPc. We hypothesized at the time that this might suggest the crystal structure of $m$-FPhO-BsubPc differed significantly from the other three meta-halogenated derivatives, and that it would likely lack of halogen-nitrogen interactions. We can now confirm that this hypothesis was correct, as there is no evidence of fluorine-nitrogen interactions within the crystal structure of (1).

The crystal structure of (1) also differs from that of the other fluorophenoxy-BsubPc derivatives, namely o-FPhO-BsubPc and p-FPhO-BsubPc. As demonstrated by the packing arrangements in Figure 3.17 and the unit cell parameters in Table 3.6, single crystal structures of the ortho and para analogues are isostructural to unsubstituted phenoxy-BsubPc (PhO-BsubPc) and crystallize in the P-1 space group. The packing arrangements of PhO-BsubPc, o-FPhO-BsubPc and p-FPhO-BsubPc are characterized by a dimer motif formed through concave-concave head-to-
head $\pi$-$\pi$ interactions between adjacent subPc ligands (Figure 3.17d), and a lack of significant intermolecular interactions involving the axial moiety of the BsubPc molecules.

Figure 3.16: The molecular packing arrangement of $m$-ClPhO-BsubPc, with halogen-nitrogen interactions depicted as black dashed lines and $\pi$-$\pi$ interactions shown as green dashed lines. Key: carbon = grey; nitrogen = light purple; oxygen = red; boron = light pink; chlorine = green. Non-interacting hydrogen atoms omitted for clarity. Redrawn from reference 29.

Figure 3.17: The molecular packing arrangements of (a) $o$-FPhO-BsubPc; (b) $p$-FPhO-BsubPc; and (c) PhO-BsubPc. (d) Concave-concave head-to-head $\pi$-$\pi$ interactions in PhO-BsubPc shown as green dashed lines. Key: carbon = grey; nitrogen = light purple; oxygen = red; boron = light pink; fluorine = magenta. Arrangement of $o$-FPhO-BsubPc redrawn from reference 29; arrangement of $p$-FPhO-BsubPc and PhO-BsubPc redrawn from reference 1.
**Table 3.6:** Unit cell parameters of PhO-BsubPc, o-FPhO-BsubPc and p-FPhO-BsubPc

<table>
<thead>
<tr>
<th></th>
<th>PhO-BsubPc¹</th>
<th>o-FPhO-BsubPc²⁹</th>
<th>p-FPhO-BsubPc¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCDC ref.</td>
<td>783165</td>
<td>906278</td>
<td>783169</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Triclinic</td>
<td>Triclinic</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P -1</td>
<td>P -1</td>
<td>P -1</td>
</tr>
<tr>
<td>a/Å</td>
<td>10.0492(5)</td>
<td>10.1276(3)</td>
<td>10.0420(3)</td>
</tr>
<tr>
<td>b/Å</td>
<td>10.7503(4)</td>
<td>10.8350(3)</td>
<td>10.7558(4)</td>
</tr>
<tr>
<td>c/Å</td>
<td>11.8342(5)</td>
<td>11.8593(4)</td>
<td>11.7366(4)</td>
</tr>
<tr>
<td>α/°</td>
<td>85.893(2)</td>
<td>86.4627(15)</td>
<td>85.8210(18)</td>
</tr>
<tr>
<td>β/°</td>
<td>77.4510(19)</td>
<td>77.0822(13)</td>
<td>77.1560(19)</td>
</tr>
<tr>
<td>γ/°</td>
<td>66.043(2)</td>
<td>64.9040(15)</td>
<td>66.5820(19)</td>
</tr>
</tbody>
</table>

The relative packing arrangement of the four independent molecules comprising the asymmetric unit cell of (1) is illustrated in Figure 3.18a. Although the single crystal structure lacks halogen-nitrogen interactions, it also differs significantly from the P-1 structure common to PhO-BsubPc, o-FPhO-BsubPc, and p-FPhO-BsubPc, which indicates that the inclusion of a fluorine atom in the meta position is influencing the structure. Analysis of the close intermolecular contacts in (1) reveals the presence of close π-π interactions (Table 3.7), CH-π interactions (Table 3.8) and CH-F hydrogen bonds (Table 3.9).

The close π-π contacts listed in Table 3.7 are all less than 4 Å. The shortest of these represents the concave-concave head-to-head interaction illustrated in Figure 3.18b, which is supported by a total of four CH-π interactions. This particular interaction motif is present in the vast majority of phenoxy-BsubPc crystal structures, including those demonstrated in Figure 3.16 and Figure 3.17. Despite the prevalence of this motif in phenoxy-BsubPc crystal structures, it is relatively scarce in the structure of (1), with only one of the four independent molecules adopting the concave-concave head-to-head arrangement.

Interestingly, many of the other π-π interactions listed in Table 3.7 are relatively rare in phenoxy-BsubPc crystal structures. Although convex-convex head-to-head π-π interactions have been shown for phenoxy-BsubPcs before, the geometry of the convex-convex head-to-head π-π interactions demonstrated in Figure 3.18c and 3.18d is somewhat unusual. In the previously published examples, the two arms of the diiminoisoindoline units involved in the interaction are arranged in a parallel manner, analogous to the π-π interaction demonstrated in Figure 3.18h. In
Figure 3.18:  (a) The asymmetric unit of (I). (b-h) The molecular packing arrangement of (1), with hydrogen bonds depicted as magenta dashed lines, close π-π contacts shown as green dashed lines, and close CH-π contacts shown as light blue dashed lines. Key: carbon = grey; nitrogen = light purple; oxygen = red; boron = light pink; fluorine = magenta; hydrogen = white. Ellipsoids drawn at the 20% probability level. Non-interacting hydrogen atoms omitted for clarity.
Table 3.7:  Selected Cg⋯Cg (π–π) interactions in (I) (Cg⋯Cg ≤ 4.0 Å)

<table>
<thead>
<tr>
<th>Figure</th>
<th>Residues</th>
<th>Cg(I)⋯Cg(J)</th>
<th>Cg⋯Cg (Å)</th>
<th>Alpha (°)a</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.18b</td>
<td>3 &amp; 3</td>
<td>Cg(22)⋯Cg(29)</td>
<td>3.625(2)</td>
<td>2.0(2)</td>
<td>Concave–concave head-to-head</td>
</tr>
<tr>
<td>3.18c</td>
<td>1 &amp; 2</td>
<td>Cg(19)⋯Cg(9)</td>
<td>3.755(2)</td>
<td>11.5(2)</td>
<td>Convex–convex head-to-head</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cg(19)⋯Cg(2)</td>
<td>3.853(2)</td>
<td>11.5(2)</td>
<td></td>
</tr>
<tr>
<td>3.18d</td>
<td>3 &amp; 4</td>
<td>Cg(40)⋯Cg(30)</td>
<td>3.722(2)</td>
<td>10.1(2)</td>
<td>Convex–convex head-to-head</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cg(40)⋯Cg(23)</td>
<td>3.778(2)</td>
<td>9.4(2)</td>
<td></td>
</tr>
<tr>
<td>3.18e</td>
<td>1 &amp; 4</td>
<td>Cg(10)⋯Cg(36)</td>
<td>3.915(2)</td>
<td>11.1(2)</td>
<td>Convex–concave head-to-tail</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cg(10)⋯Cg(33)</td>
<td>3.934(2)</td>
<td>16.6(2)</td>
<td></td>
</tr>
<tr>
<td>3.18f</td>
<td>2 &amp; 3</td>
<td>Cg(28)⋯Cg(12)</td>
<td>3.731(2)</td>
<td>14.4(2)</td>
<td>Convex–convex head-to-tail</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cg(28)⋯Cg(14)</td>
<td>3.802(2)</td>
<td>9.5(2)</td>
<td></td>
</tr>
<tr>
<td>3.18g</td>
<td>1 &amp; 2</td>
<td>Cg(8)⋯Cg(11)</td>
<td>3.757(3)</td>
<td>22.4(2)</td>
<td>Convex–concave head-to-head</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cg(1)⋯Cg(18)</td>
<td>3.845(3)</td>
<td>21.9(2)</td>
<td></td>
</tr>
<tr>
<td>3.18h</td>
<td>4 &amp; 4</td>
<td>Cg(32)⋯Cg(39)</td>
<td>3.853(3)</td>
<td>3.3(2)</td>
<td>Convex–convex head-to-head</td>
</tr>
</tbody>
</table>

a Alpha is the dihedral angle between planes I and J (°)

Table 3.8:  CH–π interaction geometry (H⋯Cg < 3.0 Å, C–H⋯Cg ≥ 130°)

<table>
<thead>
<tr>
<th>Figure</th>
<th>Residues</th>
<th>C(K)-H(L)⋯Cg(M)</th>
<th>H⋯Cg (Å)</th>
<th>C⋯Cg (Å)</th>
<th>C–H⋯Cg (°)</th>
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</thead>
<tbody>
<tr>
<td>3.18b</td>
<td>3, 3</td>
<td>C48-H48⋯Cg(23)</td>
<td>2.86</td>
<td>3.562(4)</td>
<td>132</td>
</tr>
<tr>
<td></td>
<td>3, 3</td>
<td>C49-H49⋯Cg(21)</td>
<td>2.94</td>
<td>3.779(5)</td>
<td>147</td>
</tr>
<tr>
<td>3.18e</td>
<td>1, 4</td>
<td>C115-H115⋯Cg(7)</td>
<td>2.49</td>
<td>3.419(4)</td>
<td>165</td>
</tr>
<tr>
<td>3.18f</td>
<td>2, 3</td>
<td>C17-H17⋯Cg(27)</td>
<td>2.52</td>
<td>3.441(4)</td>
<td>164</td>
</tr>
<tr>
<td>3.18g</td>
<td>3, 2</td>
<td>C55-H55⋯Cg(20)</td>
<td>2.78</td>
<td>3.707(5)</td>
<td>165</td>
</tr>
<tr>
<td>3.18h</td>
<td>1, 4</td>
<td>C77-H77⋯Cg(38)</td>
<td>2.82</td>
<td>3.735(5)</td>
<td>162</td>
</tr>
</tbody>
</table>

Figure 3.18c and 3.18d, the two arms are perpendicular, with the six-membered head of one arm roughly centred over the five- and six-membered rings of the other arm.

Figure 3.18e and 3.18f demonstrate the concave-convex head-to-tail π–π interactions. Although concave-concave head-to-tail interactions are pervasive in the crystal structures of the smaller halo-BsubPc derivatives,32–33 head-to-tail interactions are relatively rare in phenoxy-BsubPc crystal structures. The convex-concave interactions in halo-BsubPcs are typically centred, with the shortest contact distance occurring between the centroids of the six-membered carbon ring of one molecule (the head) and the six-membered heteroatom ring of the other molecule (the tail).
The interactions shown in Figure 3.18e and 3.18f are off-centre, with the six-membered head of one molecule roughly centred under the six-membered tail and a five-membered ring of the other molecule. This is likely due to an attractive effect from the CH-\pi interactions involving the phenoxy rings, namely \text{Cg}(7) in Figure 3.18e and \text{Cg}(27) in Figure 3.18f, which would shift the \pi-\pi interaction off-centre.

Finally, the close convex-concave head-to-tail \pi-\pi contact shown in Figure 3.18g is also unusual for a phenoxy-BsubPc crystal structure. In total, there are five distinct \pi-\pi stacking motifs present in (1), three of which are rare for phenoxy-BsubPcs. This single structure therefore showcases the surprisingly diverse range of \pi-\pi motifs that are possible in the solid state arrangement of BsubPc derivatives, in cases where the concave-concave interaction in Figure 3.18b is not pervasive in the structure. These unusual packing motifs likely result from the presence of weak hydrogen bonding interactions, which appear to have been sufficiently strong to disrupt the concave-concave interaction typically observed in phenoxy-BsubPc derivatives.

The hydrogen bonds demonstrated in Figure 3.18c-f represent the first example of fluorine atoms accepting hydrogen bonds in a BsubPc single crystal structure. All of these interactions have short H-\cdots-A distances ranging from approximately 2.4 to 2.8 Å, with many of the distances being less than approximately 2.5 Å (Table 3.9). The D-H-\cdots-A angles range from 133 to 163°. The C-F bond length (Table 3.10) also varies significantly across the four independent molecules of (1). This indicates that, rather than being solely determined by an optimized molecular geometry, the C-F bond length is instead influenced by the environment surrounding the fluorine atom, providing further evidence for the presence of hydrogen bonding involving the fluorine atoms.

The fluorine atoms F3 and Figure 3.18c and F2 in Figure 3.18d both participate in hydrogen bonds as bifurcated acceptors. The linear tendency of hydrogen bonds translates to a planar tendency for bifurcated hydrogen bonds.\textsuperscript{34} As such, in Figure 3.18c, the hydrogen atoms H25 and H80 lie close to a plane passing through C25, C80 and F3 with distances of approximately 0.43 and 0.39 Å respectively. In Figure 3.18d, the hydrogen atoms H58 and H99 are located approximately 0.38 and 0.40 Å, respectively, from a plane passing through C58, C99 and F2.

The fluorine atom in residue 1 is disordered, with two possible positions for the fluorine atom. The site occupancy factor of F3 is 0.626(7) and the site occupancy factor of F3B is 0.374(7).
Table 3.9: CH-F hydrogen bond geometry.

<table>
<thead>
<tr>
<th>Figure</th>
<th>Res(D), Res(A)</th>
<th>D-H···A</th>
<th>D-H (Å)</th>
<th>H···A (Å)</th>
<th>D···A (Å)</th>
<th>D-H···A (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4c</td>
<td>1, 1</td>
<td>C80-H80···F3</td>
<td>0.95</td>
<td>2.40</td>
<td>3.166(6)</td>
<td>138</td>
</tr>
<tr>
<td></td>
<td>2, 1</td>
<td>C25-H25···F3</td>
<td>0.95</td>
<td>2.54</td>
<td>3.337(6)</td>
<td>142</td>
</tr>
<tr>
<td>4d</td>
<td>4, 3</td>
<td>C99-H99···F2</td>
<td>0.95</td>
<td>2.49</td>
<td>3.310(5)</td>
<td>144</td>
</tr>
<tr>
<td></td>
<td>3, 3</td>
<td>C58-H58···F2</td>
<td>0.95</td>
<td>2.46</td>
<td>3.186(5)</td>
<td>133</td>
</tr>
<tr>
<td>4e</td>
<td>4, 1</td>
<td>C110-H110···F3B</td>
<td>0.95</td>
<td>2.76</td>
<td>3.677(8)</td>
<td>163</td>
</tr>
<tr>
<td></td>
<td>1, 4</td>
<td>C79-H79···F4</td>
<td>0.95</td>
<td>2.43</td>
<td>3.254(6)</td>
<td>145</td>
</tr>
<tr>
<td>4f</td>
<td>3, 2</td>
<td>C57-H57···F1</td>
<td>0.95</td>
<td>2.44</td>
<td>3.246(6)</td>
<td>143</td>
</tr>
</tbody>
</table>

Table 3.10: C-F bond lengths

<table>
<thead>
<tr>
<th>Residue</th>
<th>C-F</th>
<th>C-F bond length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C64-F3</td>
<td>1.311(6)</td>
</tr>
<tr>
<td></td>
<td>C62-F3B</td>
<td>1.238(8)</td>
</tr>
<tr>
<td>2</td>
<td>C2-F1</td>
<td>1.350(8)</td>
</tr>
<tr>
<td>3</td>
<td>C32-F2</td>
<td>1.359(5)</td>
</tr>
<tr>
<td>4</td>
<td>C92-F4</td>
<td>1.351(6)</td>
</tr>
</tbody>
</table>

Therefore, the fluorine atom has a greater tendency to occupy the F3 site and participate in a bifurcated hydrogen bond arrangement as shown in Figure 3.18c. However, the fluorine atom can also occupy site F3B, where there is a fairly short H···A contact of 3.677(8) Å (Figure 3.18e). Although this distance is slightly larger than the sum of the van der Waals radii, which is 2.67 Å for hydrogen and fluorine, the D-H···A angle is very nearly linear at 163°, and a nearly-linear D-H···A angle is generally considered to be a more reliable criterion than the H···A distance for the identification of a weak hydrogen bond. Since there is disorder in the fluorine position, it is likely that there is a weak attractive hydrogen bond involving the F3B site. There is no analogous disorder in the position of F2 in residue 3 (Figure 3.18d). Due to slight differences in the geometry of the interactions shown in Figure 3.18e and 3.18f, if the same sort of disorder were present for F2, the alternate site for F2 would be too far from the neighbouring BsubPc molecule to participate in a hydrogen bond.

The fluorine atoms F4 and F1 in Figure 3.18e and 3.18f each participate in a single hydrogen bond. Interestingly, the thermal ellipsoids for F4 and F1 are larger than the thermal ellipsoids for
F3 and F2. This suggests that there may be some mild variance in the positions of F4 and F1, which only participate in one hydrogen bond, whereas the sites of fluorine atoms participating in bifurcated hydrogen bonds are more precisely located.

The geometric parameters listed in Table 3.9 and Table 3.10, and the presence of planar bifurcated arrangements in Figure 3.18c and 3.18d, support the presence of CH⋯F hydrogen bonds in the single crystal structure of (I). Organic fluorine is a weak hydrogen bond acceptor and CH is a weak hydrogen bond donor. In single crystal structures, the interaction geometry of weak hydrogen bonding interactions can be distorted by stronger intermolecular interactions, and therefore it can be difficult to prove the presence of weak hydrogen bonds based solely on simple criteria such as the use of van der Waals radii. Since the single crystal structure of (I) varies significantly from the single crystal structures of o-FPhO-BsubPc and p-FPhO-BsubPc, we can conclude that the short CH⋯F interactions described in Figure 3.18c-3.18f and in Table 3.9 are sufficient to alter the molecular packing of (I) and can therefore be classified as hydrogen bonds.
3.2.4 Conclusions

The single crystal structure of (1) varies significantly from its closest molecular relatives. Due to a lack of halogen-nitrogen interactions, (1) does not crystallize in the \( P2_1/n \) space group common to the other meta-halogenated-phenoxy-BsubPc derivatives, which is directed by a halogen-bonded ribbon motif. The lack of halogen bonding interactions is unsurprising since fluorine does not typically participate in halogen bonding, as discussed in Chapter 1. Derivative (1) also does not crystallize in the \( P-1 \) space group adopted by the ortho- and para-fluorinated analogues and characterized by a pervasive concave-concave head-to-head \( \pi-\pi \) interaction. The unusual crystal structure of (1) can be attributed to the role of the meta fluorine atom as a hydrogen bond acceptor. Further evidence for the role of the fluorine atom as a hydrogen bond acceptor includes several geometric criteria, including variances in C-F bond length, fairly short H···F distances, fairly linear C-H···F angles, and planar bifurcated bond arrangements. The CH···F hydrogen bonds disrupt the concave-concave \( \pi-\pi \) interactions commonly observed in phenoxy-BsubPc derivatives, and the structure of (1) contains a diverse range of \( \pi-\pi \) interaction motifs that are typically not observed in phenoxy-BsubPcs.
3.3 References


Chapter 4

The Influence of Strong and Weak Hydrogen Bonds on the Solid State Arrangement of Hydroxy-Containing Boron Subphthalocyanines

The work in this chapter was published as a full length article in *CrystEngComm*. The full reference is:


LC and WSD developed the synthesis and purification procedures for the hydroxy-phenoxy-BsubPc derivatives (3a-3c). LC also performed UV-Vis measurements and prepared a single crystal sample of compound 3a. JDD prepared a single crystal of 3b solvated with water and a single crystal of 3c solvated with toluene. MVF synthesized hydroxy-BsubPc (2) and also obtained single crystals of 2 via train sublimation. All single crystal diffraction experiments and structure refinements were performed by AJL. I synthesized additional batches of compounds 3a-3c as required, performed train sublimation experiments on compounds 3a-3c, and prepared both a single crystal of 3b solvated with benzene and an unsolvated single crystal of 3c. I performed all crystal structure analysis in order to establish and discuss the presence and effects of hydrogen bonds. I also wrote all of the text and created all of the figures. The work performed by LC was supervised by WSD and the work performed by myself and JDD was supervised by TPB.

Note that the introduction section has been shortened from the original article in order to remove redundant portions, such as an introduction to the boron subphthalocyanine (BsubPc) class of materials. Some of the information originally contained in the electronic supplementary information (ESI) has been moved to the main body of text.
4.1 Introduction

We previously studied a series of halogenated phenoxy-BsubPcs, in which we demonstrated that the imine nitrogens (Ni, Figure 4.1) of BsubPcs can act as acceptors for halogen bonds.\(^1\) Due to the similarities between halogen bonding and hydrogen bonding, this observation suggested that the imine nitrogens of BsubPcs could also serve as reliable hydrogen bond acceptors. Two previously published crystal structures support this hypothesis. Potz et al. reported a structure for hydroxy-BsubPc (HO-BsubPc), in which there is a significant interaction between the hydroxy moiety and an imine nitrogen on the subPc ligand,\(^2\) and a similar interaction can be observed in a solvated structure for para-hydroxy-phenoxy-BsubPc (p-HOPhO-BsubPc) reported by Guilleme et al.\(^3\) In both cases, the geometries of these interactions were not discussed in detail in the publication, possibly due to the high R-factors of the structures (approximately 14% for HO-BsubPc and 13% for p-HOPhO-BsubPc).

**Figure 4.1:** Common terms used to identify portions of a BsubPc molecule, illustrated with a generic BsubPc molecule and with p-HOPhO-BsubPc.

Herein we report on the synthesis and characterization of a series of hydroxyl phenoxy BsubPc derivatives in which the axial position has been substituted by a hydroxyl containing phenoxy moiety. The occurrence of hydrogen bonding in these BsubPcs has been examined through crystal structure analysis of four hydroxyl containing BsubPcs, namely HO-BsubPc as well as para-, meta-, and ortho-hydroxy-phenoxy BsubPc (p-, m- and o-HOPhO-BsubPc). These derivatives were synthesized and crystallized in order to obtain high quality crystal structures via single-crystal x-ray diffraction. In order to discuss the geometry of the hydrogen crystal structures, only crystal structures with low R-factors (<7%) were considered. This criterion excludes a detailed discussion of the two previously reported structures for hydroxy-containing BsubPcs mentioned.
above,\textsuperscript{2-3} although we include herein a redetermined structure for HO-BsubPc with an improved R-factor of 3.9\%. Crystal structure analysis of these four derivatives reveals the presence of classical, strong hydrogen bonds (O-H\cdots N, O-H\cdots O) as well as weak (C-H\cdots O, C-H\cdots N) hydrogen bonds, both of which influence the solid state arrangement of hydroxy-containing BsubPcs.
4.2 Experimental

4.2.1 Materials

Catechol, resorcinol and hydroquinone were purchased from Sigma Aldrich (Mississauga, Ontario, Canada) and used as received. Other common solvents, reagents and silica gel were purchased from Caledon Laboratories (Caledon, Ontario, Canada) and used as received. HO-BsubPc (2) was synthesized according to a previously described procedure\(^4\) and Br-BsubPc (1) was synthesized according to a procedure previously described by Potz.\(^2\)

4.2.2 Methods

The reaction progress and purity analysis was performed using a Waters 2695 high pressure liquid chromatography (HPLC) separation module with a Waters 2998 photodiode array and a Waters 4.6 mm x 100 mm SunFire C\(_{18}\) 3.5 \(\mu\)m column. HPLC grade acetonitrile and N,N-dimethylformamide were eluted with an isocratic flow of 80/20 (volume/volume) acetonitrile/N,N-dimethylformamide at 0.6 mL/min during operation.

UV-visible spectra were recorded on a Hewlett-Packard 8453 diode-array spectrophotometer. All nuclear magnetic resonance (NMR) spectra were acquired on a Bruker 300 MHz Avance spectrometer equipped with a broadband probe. NMR samples were prepared in deuterated chloroform with 0.05\% (v/v) tetramethylsilane (TMS) as a 1H NMR reference purchased from Cambridge Isotope Laboratories and used as received. Mass spectra (FAB) were obtained at the Michigan State University Mass Spectrometry Facility.

X-ray diffraction results were analyzed using PLATON for MS-Windows (April 24 2013 version) for bond angles and lengths, and crystal packing images were generated using Mercury version 3.0. All data sets were collected using a Bruker Kappa APEX-DUO diffractometer, with the exception of the data set for \(o\)-HOPhO-BsubPc (3a), which was collected using a Nonius KappaCCD diffractometer. The positions of the hydrogen atoms in hydroxy groups were refined independently with isotropic displacement parameters. All other hydrogen atom positions were placed in calculated positions and refined in a riding-model approximation. In the structure for \(m\)-HOPhO-BsubPc ·2.5 C\(_6\)H\(_6\) (3b benzene solvate), one of the solvent molecules is disordered.
over a twofold rotational axis. A half occupancy full benzene molecule was modeled as a perfect hexagon with C-C bonds of 1.39 Å.

4.2.3 Synthesis

**ortho-Hydroxyphenoxy-boron subphthalocyanine** (*o*-*HO*Ph*O*-BsubPc, 3a).

*Method A – Preparation from solution:* Br-BsubPc (I, 0.45 g, 0.95 mmol) was mixed with catechol (1.15 g, 10.4 mmol) in chlorobenzene (15 mL) in a round-bottom flask fitted with a reflux condenser and argon inlet. The mixture was stirred and heated at reflux under a constant pressure of argon for 3 to 5 hours. The reaction was monitored via HPLC and determined to be complete by the non-detection of I. The crude product was isolated by removing the solvent under rotary evaporation. Preliminary purification was achieved by washing the crude product with a 1:1 water/methanol mixture followed by filtration; this process was repeated several times. The product was then adsorbed onto silica and columned in 1.5:1 ethyl acetate/n-hexane. The solvent was removed under rotary evaporation and the final product was dried under vacuum at 100 °C for 24 h, yielding compound 3a as a dark pink/magenta powder (0.11 g, 23%).

*Method B – Preparation from melt:* Br-BsubPc (I, 0.16 g, 0.34 mmol) and catechol (0.23 g, 2.1 mmol) were placed in a round-bottom flask and heated in a sand bath at 115 °C for 1.5 hours. The reaction was allowed to cool to room temperature. The crude product was repeatedly washed with a 1:1 water/methanol mixture and filtered. The product was then adsorbed onto silica and columned in 1.5:1 ethyl acetate/n-hexane. The solvent was removed under rotary evaporation and the final product was dried under vacuum at 100 °C for 24 h, yielding compound 3a as a dark pink/magenta powder (0.055 g, 32%).

Purity by HPLC (> 99%, max plot). HPLC λ_max (nm) = 556.3, R_T (min) = 1.81; UV-vis (CH₂Cl₂), λ_max = 563 nm (ε = 65,000 M⁻¹cm⁻¹), 520 (sh), 350 (sh), 305 (40,000), 267 (41,000); δ_H (400 300 MHz, CDCl₃) 4.67 (br, 1H), 5.05 (d, J = 8.8 Hz, 1H), 6.33 (t, J = 8.7 Hz, 1H), 6.41 (d, J = 8.8 Hz, 1H), 6.51 (t, J = 8.3 Hz, 1H), 7.92 (m, 6H), 8.84 (m, 6H); HRMS (FAB) M⁺ = 504.1517 (Calculated for C₃₀H₁₇BN₆O₂: 504.1511).
**meta-Hydroxyphenoxy-boron subphthalocyanine** *(m-HOPhO-BsubPc, 3b).*

*Method A – Preparation from solution:* 3b was synthesized as for 3a except resorcinol (1.15 g, 10.4 mmol) was used in place of catechol, yielding compound 3b (0.20 g, 42%).

*Method B – Preparation from melt:* 3b was synthesized as for 3a except resorcinol (0.23 g, 2.1 mmol) was used in place of catechol, yielding compound 3b (0.083 g, 49%).

Purity by HPLC (93%, max plot). HPLC $\lambda_{\text{max}}$ (nm) = 561.2, $R_T$ (min) = 1.82; UV-vis (CH$_2$Cl$_2$), $\lambda_{\text{max}}$ = 562 nm ($e$ = 68,000 M$^{-1}$cm$^{-1}$), 520 (sh), 306 (29,000), 273 (28,000); $\delta_H$ (400 300 MHz, CDCl$_3$) 4.99 (d, J = 8.9 Hz, 1H), 5.08 (s, 1H), 5.59 (br, 1H), 6.20 (d, J = 8.9 Hz, 1H), 6.64 (t, J = 8.9 Hz, 1H), 7.88 (m, 6H), 8.83 (m, 6H); HRMS (FAB) M+ = 504.1514 (Calculated for C$_{30}$H$_{17}$BN$_6$O$_2$: 504.1511).

**para-Hydroxyphenoxy-boron subphthalocyanine** *(p-HOPhO-BsubPc, 3c).*

*Method A – Preparation from solution:* 3c was synthesized as for 3a except hydroquinone (1.15 g, 10.4 mmol) was used in place of catechol, yielding compound 3c (0.19 g, 40%).

*Method B – Preparation from melt:* 3c was synthesized as for 3a except hydroquinone (0.23 g, 2.1 mmol) was used in place of catechol, yielding compound 3c (0.037 g, 22%).

Purity by HPLC (> 80%, max plot). HPLC $\lambda_{\text{max}}$ (nm) = 561.2, $R_T$ (min) = 1.81; UV-vis (CH$_2$Cl$_2$), $\lambda_{\text{max}}$ = 561 nm ($e$ = 81,000 M$^{-1}$cm$^{-1}$), 520 (sh), 311 (29,000); $\delta_H$ (400 300 MHz, CDCl$_3$) 5.30 (d, J = 8.7 Hz, 2H), 6.29 (d, J = 8.7, 2H), 7.90 (m, 6H), 8.84 (m, 6H); HRMS (FAB) M+ = 504.1524 (Calc’d for C$_{30}$H$_{17}$BN$_6$O$_2$: 504.1511).

**4.2.4 Preparation of Single Crystals**

Single crystals of HO-BsubPc (2) and p-HOPhO-BsubPc (3c) were obtained using train sublimation. Schematics and instructions for use for the train sublimation apparatus have been previously disclosed.$^5$ Briefly, samples to be crystallized were placed in a small boat constructed of aluminum foil and inserted into the hot zone of the sublimation chamber. The chamber was evacuated and the internal temperature of the hot zone was increased to 120 °C for 10 minutes, then to 180 °C for 10 minutes, and then to 220 °C for approximately 1 hour in order to remove
small molecule contaminants. Next, the nitrogen flow was set with the needle valve creating an internal pressure of $1 \times 10^{-1}$ Torr. With the cooling water circulating, the internal temperature of the hot zone was slowly incremented at a rate of 10 °C/10 minutes until the material began to sublime (between 300 °C and 340 °C). The temperature was maintained at the sublimation point for 1 hour in order to seed crystals. The temperature was then increased at a rate of 3°C/10 minutes until the temperature was 100 °C past the sublimation point and held at that temperature for 2 hours before being cooled to room temperature. Finally, the crystals produced from the sublimation process were scraped from the sublimation tube and analyzed.

Single crystals of $o$-HOPhO-BsubPc (3a), $m$-HOPhO-BsubPc · 0.69 CH$_2$Cl$_2$ · 0.31 H$_2$O (3b DCM/H$_2$O solvate) and $p$-HOPhO-BsubPc · C$_7$H$_8$ (3c toluene solvate) were obtained using slow evaporation. In a typical example, a solution was prepared by dissolving 5 mg of material in 15 mL of solvent. This solution was filtered, and approximately 2 mL were transferred to a 4-mL glass vial. In cases where ether or dichloromethane (DCM) were used as the solvent (for 3a and 3b respectively), the vial was tightly capped. In cases where a mixture of toluene and acetone was used as the solvent (for 3c), the vial was loosely capped. The vials were left to stand until high quality crystals were formed.

Single crystals of $m$-HOPhO-BsubPc · 2.5 C$_6$H$_6$ (3b benzene solvate) were obtained using solvent diffusion crystallization. A solution was prepared by dissolving 5 mg of 3b in 15 mL of benzene. This solution was filtered, and 0.5 mL of this solution was placed into the bottom of an NMR tube. Approximately 1 mL of heptane was carefully layered over the benzene solution in the NMR tube. The tube was capped and left to stand until high quality crystals were formed.
4.3 Results and Discussion

4.3.1 Synthesis and Characterization

Hydroxy-containing BsubPcs (2 and 3a-c) were synthesized according to Scheme 4.1. The synthesis of hydroxy-BsubPc (HO-BsubPc, 2) has been previously published. The syntheses of o-HOPhO-BsubPc (3a) and m-HOPhO-BsubPc (3b) have not been previously reported, but full preparation details are provided in the Experimental section. Briefly, bromo-BsubPc (Br-BsubPc, 1) was reacted with 11 molar equivalents of the appropriate dihydroxy benzene (catechol, resorcinol or hydroquinone) at reflux in chlorobenzene. The reaction progress was monitored by HPLC and determined to be complete by the non-detection of 1; this typically required less than 5 hours. The crude product contained small amounts of the corresponding 1:2 phenoxy:BsubPc dimer (typically 2-5%, as determined by HPLC) in addition to the desired 1:1 hydroxyl phenoxy BsubPc product. The unreacted dihydroxy benzene compounds are readily soluble in water, allowing preliminary purification to be accomplished by washing the crude product in a mixture of water and methanol (1:1). Final purification was achieved by column chromatography on silica, which facilitated removal of residual dihydroxy benzenes and the undesired BsubPc dimer products. Compounds 3a-c can also be prepared from a melt of the appropriate dihydroxy benzene.

Scheme 4.1: Synthesis of hydroxy-BsubPc (2) and hydroxy-phenoxy-BsubPcs (3a-3c). Conditions: (i) water, pyridine, dimethylsulfoxide, 60 °C; (ii) 11 molar equivalents, chlorobenzene, reflux.
BsubPcs show two intense transitions in their UV-vis spectra: a near UV band (the Soret band) and a visible absorption band (the Q-band). The Q and Soret bands of 1 are at $\lambda_{\text{max}} = 565\,\text{nm}$ ($\varepsilon = 90,000\,\text{M}^{-1}\text{cm}^{-1}$) and $305\,\text{nm}$ ($50,000\,\text{M}^{-1}\text{cm}^{-1}$), respectively. Higher energy transitions appear as shoulders on both of these peaks. Replacement of the axial bromide with other substituents has very little effect on the electronic spectrum of BsubPcs, as discussed in Chapter 1, and thus the diol-substituted BsubPcs (3a-c) display spectra that are virtually identical to the spectrum of the Br-BsubPc starting material 1.

### 4.3.2 Single Crystal Formation and Structure Determination

Selected crystallographic results for HO-BsubPc (2) and HO-PhO-BsubPcs (3a-c) are presented in Table 4.1. The positions of hydrogen atoms in hydroxy moieties were refined independently with isotropic displacement parameters.

A good quality, diffractable single crystal of HO-BsubPc (2) was obtained by train sublimation. The structure determined for the sublimed crystal is equivalent to the non-solvated HO-BsubPc structure previously reported by Potz et al., which was obtained using solvent crystallization methods. The redetermined structure from sublimation reported herein has an improved R-factor, enabling a more detailed analysis of intermolecular interactions within the structure.

A variety of crystallization methods and solvent systems were explored in order to obtain diffractable single crystals of the HOPhO-BsubPc compounds (3a-c). These included: slow evaporation from chloroform, dichloromethane (DCM), diethyl ether, toluene, and toluene/acetone (8:1); vapor diffusion with benzene/heptane and benzene/hexanes; solvent diffusion with benzene/heptane and DCM/hexanes; and train sublimation. Despite their structural similarity, no single technique was able to produce good quality single crystals for all three HOPhO-BsubPc compounds. This is reflected in the variety of crystallization methods listed in Table 4.1.

Compounds $m$-HOPhO-BsubPc (3b) and $p$-HOPhO-BsubPc (3c) tended to form solvated crystals. Indeed, a solvated form of 3c has been previously reported. The two solvates of $m$-HOPhO-BsubPc have the highest R-factors in Table 4.1. The solvate obtained from slow evaporation of DCM contains water within the crystal structure, indicating that the DCM was not
Table 4.1: X-Ray crystallographic data for compounds 2 and 3a-3c

<table>
<thead>
<tr>
<th>Compound reference</th>
<th>2 HO-BsubPc</th>
<th>3a o-HOPhO-BsubPc</th>
<th>3b m-HOPhO-BsubPc · DCM/H2O</th>
<th>3b m-HOPhO-BsubPc · benzene</th>
<th>3c p-HOPhO-BsubPc</th>
<th>3c p-HOPhO-BsubPc · toluene</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCDC ref.</td>
<td>949042</td>
<td>949043</td>
<td>949040</td>
<td>949038</td>
<td>949041</td>
<td>949039</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C24H13BN6O</td>
<td>C30H17BN6O2</td>
<td>C30H17BN6O2 · 0.69 CH2Cl2 · 0.31 H2O</td>
<td>C30H17BN6O2 · 2.5 C6H6</td>
<td>C30H17BN6O2</td>
<td>C30H17BN6O2 · C7H8</td>
</tr>
<tr>
<td>Crystallization method</td>
<td>Sublimation</td>
<td>Slow evaporation (diethyl ether)</td>
<td>Slow evaporation (DCM)</td>
<td>Solvent diffusion (benzene/heptane)</td>
<td>Sublimation</td>
<td>Slow evaporation (toluene/acetone)</td>
</tr>
<tr>
<td>Formula mass</td>
<td>412.21</td>
<td>504.31</td>
<td>568.33</td>
<td>699.58</td>
<td>504.31</td>
<td>596.44</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Triclinic</td>
<td>Monoclinic</td>
<td>Triclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>C 2/c</td>
<td>C 2/c</td>
<td>P -1</td>
<td>C 2/c</td>
<td>P -1</td>
<td>P 21/c</td>
</tr>
<tr>
<td>Temperature/K</td>
<td>147(2)</td>
<td>150(1)</td>
<td>150(1)</td>
<td>147(2)</td>
<td>147(2)</td>
<td>147(2)</td>
</tr>
<tr>
<td>a/Å</td>
<td>26.2251(13)</td>
<td>23.4583(4)</td>
<td>8.9397(5)</td>
<td>32.393(3)</td>
<td>9.8450(9)</td>
<td>16.2110(11)</td>
</tr>
<tr>
<td>c/Å</td>
<td>12.0258(6)</td>
<td>19.4923(5)</td>
<td>13.0121(7)</td>
<td>20.303(2)</td>
<td>12.2165(10)</td>
<td>20.4044(14)</td>
</tr>
<tr>
<td>α/°</td>
<td>90</td>
<td>90</td>
<td>105.828(3)</td>
<td>90</td>
<td>107.938(2)</td>
<td>107.938(2)</td>
</tr>
<tr>
<td>β/°</td>
<td>92.248(3)</td>
<td>120.188(1)</td>
<td>109.874(3)</td>
<td>96.286(2)</td>
<td>106.262(2)</td>
<td>110.991(4)</td>
</tr>
<tr>
<td>γ/°</td>
<td>90</td>
<td>90</td>
<td>99.661(3)</td>
<td>90</td>
<td>101.412(2)</td>
<td>101.412(2)</td>
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<tr>
<td>Unit cell volume/Å³</td>
<td>3710.2(3)</td>
<td>4639.60(16)</td>
<td>1299.93(13)</td>
<td>7086.7(12)</td>
<td>1169.37(18)</td>
<td>2928.8(3)</td>
</tr>
<tr>
<td>Z</td>
<td>8</td>
<td>8</td>
<td>2</td>
<td>8</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Density, Mg/m3</td>
<td>1.476</td>
<td>1.444</td>
<td>1.452</td>
<td>1.311</td>
<td>1.432</td>
<td>1.353</td>
</tr>
<tr>
<td>No. of reflections measured</td>
<td>11749</td>
<td>18756</td>
<td>14212</td>
<td>24445</td>
<td>17972</td>
<td>18659</td>
</tr>
<tr>
<td>No. of independent reflections</td>
<td>3179</td>
<td>4990</td>
<td>4276</td>
<td>8073</td>
<td>5363</td>
<td>5000</td>
</tr>
<tr>
<td>Final R1 values (I &gt; 2σ(I))</td>
<td>0.0387</td>
<td>0.0387</td>
<td>0.0674</td>
<td>0.0520</td>
<td>0.0388</td>
<td>0.0346</td>
</tr>
</tbody>
</table>
fully dry and resulting in mixed solvent sites. In the benzene solvate, one of the solvent molecules is disordered over a twofold rotational axis.

Train sublimation yielded single crystals of HO-BsubPc (2) and p-HOPhO-BsubPc (3c); however, despite numerous attempts, single crystals from sublimation could not be obtained for o-HOPhO-BsubPc (3a) or m-HOPhO-BsubPc (3b). In our experience, we expect BsubPc materials to either sublime upon heating under vacuum, or to decompose and form an ash-like dark powder. The sublimation behaviour of 3a and 3b was unusual: initially, small amounts (a few milligrams) of material would slowly sublime at relatively low temperatures (200 °C to 250 °C, at a pressure of approximately 1x10⁻¹ Torr). Upon further heating, the remaining material formed a dark-colored, highly bubbled residue. The dark colour suggests some form of decomposition, while the formation of a bubbled structure instead of a powdery char structure suggests the persistent presence of strong intermolecular interactions which interfered with sublimation.

In order for a material to be sublimed successfully, the individual molecules must be thermally stable up to the temperatures required for sublimation. Additionally, the intermolecular interactions should be small enough to allow molecules to be evaporated in a vacuum. In cases where there are strong intermolecular interactions, the thermal energy required to disrupt the intermolecular interactions may approach the energy required to decompose the molecule, and the material will tend to decompose rather than sublime. Strong intermolecular interactions can therefore hinder the ability of a material to undergo sublimation; this may explain the unusual sublimation behaviour observed for 3a and 3b. It has been observed, for example, that the sublimation ability of squarine derivatives can be improved by suppressing intermolecular hydrogen bonding interactions. Regardless of the underlying cause of this unusual bubbling behaviour, our observations indicate that 3a and 3b would not be suitable materials for vacuum deposition.

4.3.3 Distortion of the Molecular Conformation of BsubPc

We have previously studied a number of intra- and intermolecular phenoxy-BsubPc metrics, and have found the angle of the phenoxy moiety relative to the BsubPc ligand (the B-O-C angle, Figure 4.1) to be particularly sensitive to the presence of strong intermolecular interactions. The preferred B-O-C angle, as determined using a semi-empirical RM1 model, is typically 115-
116°. B-O-C angles within this range have been observed in the solid state arrangement of various phenoxy-BsubPcs, including many structures where the arrangements are primarily directed by π-π and CH-π interactions. In contrast, distorted B-O-C angles of up to approximately 128° have been observed in crystal structures with relatively strong halogen bonding. The B-O-C angles observed for the HOPhO-BsubPc derivatives (Table 4.2) range from mildly distorted (approximately 117° in solvated p-HOPhO-BsubPc) to significantly distorted (approximately 130° for m-HOPhO-BsubPc · DCM/H₂O). These distortions suggest the presence of strong intermolecular interactions, beyond the π-π and CH-π interactions typically seen in phenoxy-BsubPcs.

**Table 4.2:** BsubPc boron-oxygen-carbon angle and hydrogen bond geometry.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>2    HO-BsubPc</td>
<td>n/a</td>
<td>O1-H10···N2</td>
<td>0.87(2)</td>
<td>2.13(2)</td>
<td>3.0050(16)</td>
<td>177(2)</td>
</tr>
<tr>
<td>3a   o-HOPhO-BsubPc</td>
<td>120.0(1)</td>
<td>C11-H11A···O1</td>
<td>0.95</td>
<td>2.67</td>
<td>3.2699(18)</td>
<td>122</td>
</tr>
<tr>
<td>O2-H10···O1</td>
<td></td>
<td>C22-H22A···O1</td>
<td>0.95</td>
<td>2.37</td>
<td>2.7667(17)</td>
<td>105.9(18)</td>
</tr>
<tr>
<td>C3-H3A···O2</td>
<td></td>
<td></td>
<td>0.95</td>
<td>2.32</td>
<td>3.165(2)</td>
<td>148</td>
</tr>
<tr>
<td>3b   m-HOPhO-BsubPc · DCM/H₂O</td>
<td>129.5(3)</td>
<td>O2-H20···N2</td>
<td>0.87(7)</td>
<td>1.98(7)</td>
<td>2.817(6)</td>
<td>161(6)</td>
</tr>
<tr>
<td>C11-H11A···O2</td>
<td></td>
<td>C3-H3A···O1</td>
<td>0.95</td>
<td>2.70</td>
<td>3.323(6)</td>
<td>124</td>
</tr>
<tr>
<td>m-HOPhO-BsubPc · benzene</td>
<td>127.5(1)</td>
<td>O2-H20···N6</td>
<td>0.95(2)</td>
<td>1.95(2)</td>
<td>2.878(2)</td>
<td>167(2)</td>
</tr>
<tr>
<td>C3-H3A···O2</td>
<td></td>
<td></td>
<td>0.95</td>
<td>2.61</td>
<td>3.443(2)</td>
<td>147</td>
</tr>
<tr>
<td>3c   p-HOPhO-BsubPc</td>
<td>128.3(1)</td>
<td>O2-H20···N6</td>
<td>0.92(2)</td>
<td>1.94(2)</td>
<td>2.8537(17)</td>
<td>178.0(16)</td>
</tr>
<tr>
<td>C22-H22A···O2</td>
<td></td>
<td>C27-H27A···N4</td>
<td>0.95</td>
<td>2.55</td>
<td>3.493(2)</td>
<td>173</td>
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<tr>
<td>p-HOPhO-BsubPc · toluene</td>
<td>117.1(1)</td>
<td>O2-H10···N4</td>
<td>0.933(19)</td>
<td>1.868(19)</td>
<td>2.7993(14)</td>
<td>175.4(19)</td>
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<tr>
<td>C13-H13A···O1</td>
<td></td>
<td></td>
<td>0.95</td>
<td>2.44</td>
<td>3.2974(16)</td>
<td>150</td>
</tr>
</tbody>
</table>
4.3.4 Hydrogen Bonding

Closer inspection reveals that all six of the reported solid state arrangements contain both strong and weak hydrogen bonding (D-H⋯A) interactions, which are described geometrically in Table 4.2. These interactions are depicted in Figures 4.2 to 4.7, with classical strong hydrogen bonds (O-H⋯N and O-H⋯O) depicted as red dashed lines and weak hydrogen bonds (C-H⋯O and C-H⋯N) depicted as blue dashed lines. Since the positions of the hydrogen atoms in hydroxy moieties were refined independently, the presence of strong O-H⋯N and O-H⋯O hydrogen bonds are easily detected by examining the H⋯N and H⋯O distances (Table 4.2). These distances are all well below the sum of the applicable van der Waals radii, i.e. 2.75 Å for hydrogen and nitrogen and 2.72 Å for hydrogen and oxygen. Further, in most cases these strong bonds have nearly linear geometries, with D-H⋯A angles greater than 160° (Table 4.2). The O-H⋯N and O-H⋯O angles in o-HOPhO-BsubPc (3a) are smaller due to the presence of bifurcated hydrogen bonds, which will be discussed in greater detail below.

Although the positions of hydrogen atoms covalently bound to carbon atoms have not been independently refined, all six of the crystal structures reported herein include close C-H⋯O contacts with H⋯O distances ≤ approximately 2.7 Å (Table 4.2), prompting a closer look at these contacts. In all of these interactions the C⋯O distances are also fairly short (≤ approximately 3.3 Å).

Figure 4.2: The molecular packing arrangement of 2 (HO-BsubPc), with strong hydrogen bonds depicted as red dotted lines and weak hydrogen bonds depicted as blue dotted lines. The centroids of rings participating in convex-convex π-π interactions are shown in green. Key: carbon = grey; nitrogen = light purple; oxygen = red; boron = pink; hydrogen = white. For clarity, non-hydrogen atoms involved in hydrogen bonds shown as 50% ellipsoids; interacting hydrogen atoms shown as balls; non-interacting hydrogen atoms omitted.
**Figure 4.3:** Illustration of the molecular packing arrangement of 3a (o-HOPhO-BsubPc), with strong hydrogen bonds depicted as red dotted lines and weak hydrogen bonds depicted as blue dotted lines. Key: carbon = grey; nitrogen = light purple; oxygen = red; boron = pink; hydrogen = white. For clarity, non-hydrogen atoms involved in hydrogen bonds shown as 50% ellipsoids; interacting hydrogen atoms shown as balls; non-interacting hydrogen atoms omitted.

**Figure 4.4:** Illustration of the molecular packing arrangement of the 3b DCM/H$_2$O solvate (m-HOPhO-BsubPc · 0.69 CH$_2$Cl$_2$ · 0.31 H$_2$O), with strong hydrogen bonds depicted as red dotted lines and weak hydrogen bonds depicted as blue dotted lines. The centroids of rings participating in convex-convex π-π interactions are shown in green. Key: carbon = grey; nitrogen = light purple; oxygen = red; boron = pink; hydrogen = white. For clarity, non-hydrogen atoms involved in hydrogen bonds shown as 50% ellipsoids; interacting hydrogen atoms shown as balls; non-interacting hydrogen atoms omitted.
**Figure 4.5:** Illustration of the molecular packing arrangement of the 3b benzene solvate (m-HOPhO-BsubPc · 2.5 C₆H₆), with strong hydrogen bonds depicted as red dotted lines and weak hydrogen bonds depicted as blue dotted lines. Key: carbon = grey; nitrogen = light purple; oxygen = red; boron = pink; hydrogen = white. For clarity, non-hydrogen atoms involved in hydrogen bonds shown as 50% ellipsoids; interacting hydrogen atoms shown as balls; non-interacting hydrogen atoms omitted.

**Figure 4.6:** Illustration of the molecular packing arrangement of 3c (p-HOPhO-BsubPc), with strong hydrogen bonds depicted as red dotted lines and weak hydrogen bonds depicted as blue dotted lines. Key: carbon = grey; nitrogen = light purple; oxygen = red; boron = pink; hydrogen = white. For clarity, non-hydrogen atoms involved in hydrogen bonds shown as 50% ellipsoids; interacting hydrogen atoms shown as balls; non-interacting hydrogen atoms omitted.
Figure 4.7: Illustration of the molecular packing arrangement of the 3c solvate (p-HOPhO-BsubPc ·C7H8), with strong hydrogen bonds depicted as red dotted lines and weak hydrogen bonds depicted as blue dotted lines. Key: carbon = grey; nitrogen = light purple; oxygen = red; boron = pink; hydrogen = white. For clarity, non-hydrogen atoms involved in hydrogen bonds shown as 50% ellipsoids; interacting hydrogen atoms shown as balls; non-interacting hydrogen atoms omitted.

Å) and the C-H···O angles tend to linearity (ranging from approximately 122° to approximately to 150°); these values are within the ranges typically associated with weak C-H···O hydrogen bonds. More importantly, many of these C-H···O interactions have a noticeable influence on the solid state arrangement of BsubPc molecules, providing structural evidence for the significance of these weak hydrogen bonds.

Four of the short C-H···O contacts (C3-H3A···O2 in o-HOPhO-BsubPc, C11-H11A···O2 in m-HOPhO-BsubPc·DCM/H2O, C3-H3A···O2 in m-HOPhO-BsubPc·benzene, and C22-H22A···O2 in p-HOPhO-BsubPc) involve the oxygen atom of the hydroxy moiety and share a common motif. In order to investigate the significance of this motif, the geometric arrangement surrounding the hydroxy moiety is illustrated in Figure 4.8. Here, the structure of p-HOPhO-BsubPc (3c) is used as an example, but analogous geometric parameters can be obtained for all six solid state arrangements, leading to the values in Table 4.3. The strong O-H···N hydrogen bond is shown as a red dotted line (Figure 4.8). The distances from the hydroxy oxygen atom to the two closest bay carbon atoms are denoted Oi···Ci and Oi···Ck, with the longer distance arbitrarily assigned as Oi···Ci. If the strong O-H···N interaction is the only interaction with a significant effect on the spatial relationship between the hydroxy and the imine nitrogen, we
Figure 4.8: Representative illustration of the metrics relating the position of the hydroxide oxygen (O₁) to the nearest bay carbon atoms (Cᵢ and Cⱼ) of a neighbouring BsubPc molecule, demonstrated using a 50% ellipsoid plot of p-HOPhO-BsubPc (3c). The strong O-H···N hydrogen bond is depicted as a red dotted line. Key: carbon = grey; nitrogen = light purple; oxygen = red; boron = pink; hydrogen = white. For clarity, non-hydrogen atoms involved in hydrogen bonds shown as 50% ellipsoids; interacting hydrogen atoms shown as balls; non-interacting hydrogen atoms omitted. Non-hydroxy hydrogen atoms omitted for clarity.

Table 4.3: Selected hydroxy intermolecular metrics.

<table>
<thead>
<tr>
<th>Motif</th>
<th>O₁···Cᵢ</th>
<th>O₁···Cⱼ (Å)</th>
<th>O₁···Cⱼ</th>
<th>O₁···Cⱼ / O₁···Cⱼ</th>
</tr>
</thead>
<tbody>
<tr>
<td>2  HO-BsubPc</td>
<td>O₁···C₁₁</td>
<td>3.789(2)</td>
<td>O₁···C₆</td>
<td>3.611(2)</td>
</tr>
<tr>
<td>3a o-HOPhO-BsubPc</td>
<td>O₂···C₂₂</td>
<td>4.094(2)</td>
<td>O₂···C₃</td>
<td>3.165(1)</td>
</tr>
<tr>
<td>3b m-HOPhO-BsubPc DCM/H₂O solvate</td>
<td>O₂···C₁₁</td>
<td>4.103(6)</td>
<td>O₂···C₁₁</td>
<td>3.287(5)</td>
</tr>
<tr>
<td>m-HOPhO-BsubPc benzene solvate</td>
<td>O₂···C₂₂</td>
<td>3.913(3)</td>
<td>O₂···C₃</td>
<td>3.443(2)</td>
</tr>
<tr>
<td>3c p-HOPhO-BsubPc</td>
<td>O₂···C₃</td>
<td>3.794(2)</td>
<td>O₂···C₂₂</td>
<td>3.507(2)</td>
</tr>
<tr>
<td>p-HOPhO-BsubPc toluene solvate</td>
<td>O₂···C₁₉</td>
<td>3.629(2)</td>
<td>O₂···C₁₄</td>
<td>3.589(2)</td>
</tr>
</tbody>
</table>

would expect the hydroxy moiety to lie approximately equidistant from the two closest bay carbon atoms, and therefore the ratio of O₁···Cᵢ / O₁···Cⱼ would be approximately equal to 1.

Conversely, if there is a C-H···O hydrogen bond between one of the bay hydrogen atoms and the oxygen atom of the hydroxy moiety, we would expect the hydroxy moiety to lie closer to the bay carbon atom participating in the hydrogen bond, and the ratio of O₁···Cᵢ / O₁···Cⱼ would be greater than 1.
Figure 4.9: Representative illustration of the metrics relating the position of the halogen atom (X; X = Cl, Br, I) to the nearest bay carbon atoms (Cj and Ck) of a neighbouring BsubPc molecule in mono-halogenated BsubPc derivatives. The X···N interaction is depicted as a red dotted line. Colours: carbon = grey; nitrogen = light purple; oxygen = red; boron = pink; halogen = orange. Hydrogen atoms omitted for clarity.

Table 4.4: Selected intermolecular metrics for mono-halogenated phenoxy-BsubPc derivatives.¹

<table>
<thead>
<tr>
<th>Motif</th>
<th>X···Cj</th>
<th>X···Cj (Å)</th>
<th>X···Ck (Å)</th>
<th>X···Cj / X···Ck</th>
</tr>
</thead>
<tbody>
<tr>
<td>m-ClPhO-BsubPc</td>
<td>Cl1···C6</td>
<td>4.028(3)</td>
<td>C11···C11</td>
<td>3.792(3)</td>
</tr>
<tr>
<td>m-BrPhO-BsubPc</td>
<td>Br1···C6</td>
<td>4.011(3)</td>
<td>Br1···C11</td>
<td>3.810(3)</td>
</tr>
<tr>
<td>m-IPhO-BsubPc</td>
<td>I1···C3</td>
<td>4.074(6)</td>
<td>I1···C22</td>
<td>3.921(6)</td>
</tr>
<tr>
<td>m-IPhO-BsubPc benzene solvate</td>
<td>I1···C14</td>
<td>4.089(2)</td>
<td>I1···C19</td>
<td>4.079(3)</td>
</tr>
<tr>
<td>o-ClPhO-BsubPc</td>
<td>Cl1A···C14B</td>
<td>3.891(3)</td>
<td>Cl1A···C19B</td>
<td>3.859(3)</td>
</tr>
<tr>
<td>o-IPhO-BsubPc benzene solvate</td>
<td>I1···C22</td>
<td>4.309(4)</td>
<td>I1···C3</td>
<td>4.107(5)</td>
</tr>
</tbody>
</table>

For comparison, analogous metrics have been calculated for mono-halogenated phenoxy-BsubPc derivatives that demonstrate halogen bonding (Figure 4.9 and Table 4.4). The ratio of X···Cj / X···Ck (X=Cl, Br, I) has a very narrow range, from approximately 1.00 to approximately 1.06, confirming that the spatial relationship between the halogen and imine nitrogen atoms is mainly determined by the halogen bond, and is not significantly influenced by other interactions in the solid state (i.e., π-π or CH-π interactions). In contrast, the ratio of O···Cj / O···Ck for hydroxy-containing BsubPcs ranges from approximately 1.01 to approximately 1.29 (Table 4.3), indicating that in at least some of these structures, there appears to be an attractive interaction.
between the hydroxy moiety and a bay hydrogen. Further, the four structures with large $O_i\cdots C_j$, $O_i\cdots C_k$ values (greater than approximately 1.08) are the same four structures with short contacts between the hydroxy oxygen and a bay hydrogen atom. Based on the observed distortion of the $O_i\cdots C_j$, $O_i\cdots C_k$ values in these structures, we can conclude that these four short C-H⋯O contacts are indeed weak yet significant hydrogen bonds, as evidenced by their influence on the solid state molecular arrangement. Further, the oxygen atom in the hydroxy moiety can, in some instances, simultaneously act as both a donor in O-H⋯N hydrogen bonds and an acceptor in C-H⋯O hydrogen bonds.

The oxygen atom in the hydroxy moiety of 2 (HO-BsubPc) also acts as both a hydrogen bond donor and an acceptor (Figure 4.2). Pairs of adjacent molecules form dimeric arrangements, related through two C-H⋯O contacts (with a H⋯O distance of approximately 2.7 Å) and two close convex-convex π-π contacts (approximately 3.61 Å). Evidence for the significance of the C-H⋯O contact arises from examining the geometry of the π-π contact. In other solid state arrangements where adjacent BsubPc molecules display convex-convex π-π interactions, the two diiminoisoindoline arms participating in the interaction are parallel, or very nearly parallel. That is, the two planes passing through the arms typically meet at very small angles, ranging from 0 to approximately 3°. In contrast, in the solid state arrangement of HO-BsubPc, the two planes passing through the diiminoisoindoline arms involved in a close convex-convex π-π contact meet at an angle of approximately 17° (Figure 4.10). The significant distortion of the typical geometry observed in BsubPc convex-convex π-π interactions suggests that the C-H⋯O interaction, while relatively weak, has significantly influenced the solid state arrangement of HO-BsubPc.

Inspection of the solid state arrangement of o-HOPhO-BsubPc (3a, Figure 4.3) reveals a dimeric hydrogen bond arrangement, with pairs of neighbouring BsubPc molecules associated through a network of strong and weak hydrogen bonds. In each dimer pair of molecules, there are two weak C3-H3A⋯O2 bonds involving the oxygen of the hydroxy moiety, as already discussed. The hydroxy H10 atom, which has been independently refined with isotropic displacement parameters, is close to both the phenoxy oxygen atom (H10⋯O1 = 2.4 Å) and an imine nitrogen atom (H10⋯N6 = 2.1 Å). Although the H10⋯O1 interaction is intramolecular, we believe this is a stabilizing hydrogen bond; if the contact was not stabilizing, we would expect the O-H⋯N
Figure 4.10: Geometry of close convex-convex π-π contacts in BsubPc derivatives. The centroids of rings participating in close convex-convex π-π contacts are shown in green, and distances between centroids are shown as green dashed lines. (a) Typical geometry, demonstrated with \( \alpha \)-FPhO-BsubPc,\(^1\) where the two diiminoisoindoline arms participating in the contact are parallel or nearly parallel (angle between the planes typically ranges from 0° to approximately 3°). \(^1\) (b) Geometry in HO-BsubPc (2), where the two planes formed by the diiminoisoindoline arms participating in the close contact are at an angle of approximately 17°.

Colours: carbon = grey; nitrogen = light purple; oxygen = red; boron = pink; hydrogen = white; fluorine = magenta. For clarity, non-hydroxy hydrogen atoms omitted.

angle to be more linear, as it is for the other HOPhO-BsubPc derivatives. Further, the geometry suggests that the H10 atom is participating in a hydrogen bond with a bifurcated donor arrangement, i.e. an arrangement wherein a single donor-hydrogen pair is simultaneously associated with two separate acceptors. The linear tendency of hydrogen bonds leads to a planar tendency in bifurcated hydrogen bonds,\(^1\) and indeed, the H10 atom lies very close (approximately 0.03 Å) to a plane passing through O2, N6 and O1 (Figure 4.11). Bifurcated arrangements also tend to have smaller D-H···A angles, which accounts for the fairly small angles observed with these two strong hydrogen bonds (O2-H10···N6 \( \cong 150° \) and O2-H10···O1 \( \cong 110° \)). Interestingly, there is a second bifurcated set of hydrogen bonds in the solid state arrangement of 3a: the phenoxy O1 atom acts as a bifurcated acceptor, participating in both the strong O2-H10···O1 interaction and the weak C22-H22A···O1 interaction. The distances between the H10 and H22A atoms and a plane passing through the heavy atoms O2, O1 and C22 are reasonably short at approximately 0.61 and 0.41 Å, respectively (Figure 4.11). The phenoxy
oxygen atom is therefore also capable of acting as a hydrogen bond acceptor in solid state arrangements of BsubPc molecules.

Figure 4.11: The molecular packing arrangement of \( o\text{-HO}_2\text{Ph}_2\text{O}\text{-BsubPc} \) (3a), demonstrating bifurcated hydrogen bonds. Strong hydrogen bonds are depicted as red dotted lines and weak hydrogen bonds are depicted as blue dotted lines. (a) Hydrogen atom H10 is in a bifurcated donor arrangement, and H10 is at a distance of approximately 0.03 Å to a plane passing through O2, N6 and O1. (b) Oxygen atom O1 is in a bifurcated acceptor arrangement. Hydrogen atoms H10 and H22A are at distances of approximately 0.61 Å and 0.41 Å, respectively, to a plane passing through O1, O2 and C22. Colours: carbon = grey; nitrogen = light purple; oxygen = red; boron = pink; hydrogen = white. For clarity, non-hydrogen atoms involved in hydrogen bonds shown as 50% ellipsoids; interacting hydrogen atoms shown as balls; non-interacting and non-hydroxy hydrogen atoms omitted.
There is some evidence that the phenoxy oxygen (O1) atom acts as a C-H···O hydrogen bond acceptor in two other solid state arrangements: \( m \)-HOPhO-BsubPc·DCM/H\text{\(2\)O (3b, Figure 4.4)} and \( p \)-HOPhO-BsubPc·C\text{\(7\)H\text{\(8\)}} (3c, Figure 4.7). Although the positions of the hydrogen atoms involved in these contacts have not been independently refined, the short C···O distances and large C-H···O angles suggest that these are weak hydrogen bonds. These weak C-H···O interactions do not appear to be associated with any noticeable distortions of the solid state arrangements, either with regards to the molecular conformation of BsubPc molecules or to the geometry of other intermolecular interactions such as \( \pi \)-\( \pi \) or CH–\( \pi \). Unlike the C-H···O bonds discussed above, these two C-H···O interactions do not benefit from cooperativity effects and are therefore expected to be weaker. It is therefore unsurprising that they do not seem to have a strong effect on the solid state arrangement of BsubPc molecules.

Lastly, in addition to the prominent O-H···N hydrogen bonds displayed in each of these solid state arrangements, a second imine nitrogen participates in a C-H···N hydrogen bond in unsolvated \( p \)-HOPhO-BsubPc (3c, Figure 4.6). The short C27···N4 distances and remarkably linear C27-H27A···N4 angle (Table 4.2) demonstrate that an imine atom in a BsubPc molecule can accept weak hydrogen bonds as well as strong hydrogen bonds.

### 4.3.5 Extra-Molecular Solid State Packing Arrangements

In addition to hydrogen bonding, these six solid state arrangements also contain \( \pi \)-\( \pi \) and CH-\( \pi \) interactions. In particular, solid state arrangements of perhydrogenated BsubPc molecules often demonstrate concave-concave \( \pi \)-\( \pi \) interactions, wherein there is a close association between the concave surfaces of two adjacent BsubPc bowls. Typically, this concave-concave interaction is further stabilized by a total of four CH-\( \pi \) interactions between the neighbouring bowls. BsubPc solid state arrangements also occasionally contain convex-convex \( \pi \)-\( \pi \) interactions, wherein there is a close association between the convex surfaces of two adjacent BsubPc bowls, but this is typically less common than concave-concave \( \pi \)-\( \pi \) interactions. Metrics for \( \pi \)-\( \pi \) and CH-\( \pi \) are provided in the Tables 4.5 and 4.6.

The solid state arrangement of HO-BsubPc (2) includes both concave-concave \( \pi \)-\( \pi \) interactions and close (distorted) convex-convex \( \pi \)-\( \pi \) contacts. These close contacts, together with the two hydrogen bonds, result in a three-dimensional network of closely associated molecules.
Table 4.5: Selected Cg…Cg (π-π) interactions.

<table>
<thead>
<tr>
<th>Motif</th>
<th>Cg(I)-Cg(J)</th>
<th>Cg-Cg (Å)</th>
<th>Alpha (°) a</th>
<th>π-π Interaction Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>HO-BsubPc</td>
<td>Cg(3)-Cg(9)</td>
<td>3.5042(9)</td>
<td>1.17(8)</td>
<td>concave-concave</td>
</tr>
<tr>
<td></td>
<td>Cg(2)-Cg(8)</td>
<td>3.6085(9)</td>
<td>17.63(8)</td>
<td>convex-convex</td>
</tr>
<tr>
<td>3a o-HOPhO-BsubPc</td>
<td>Cg(2)-Cg(8)</td>
<td>3.6934(9)</td>
<td>3.07(8)</td>
<td>concave-concave</td>
</tr>
<tr>
<td></td>
<td>Cg(7)-Cg(7)</td>
<td>3.6988(8)</td>
<td>12</td>
<td>convex-convex</td>
</tr>
<tr>
<td>3b m-HOPhO-BsubPc · DCM/H₂O</td>
<td>Cg(3)-Cg(9)</td>
<td>3.563(3)</td>
<td>2.02(2)</td>
<td>concave-concave</td>
</tr>
<tr>
<td></td>
<td>Cg(1)-Cg(7)</td>
<td>3.778(2)</td>
<td>2.62(2)</td>
<td>convex-convex</td>
</tr>
<tr>
<td>m-HOPhO-BsubPc · benzene</td>
<td>Cg(2)-Cg(8)</td>
<td>3.5443(12)</td>
<td>2.30(10)</td>
<td>convex-convex</td>
</tr>
<tr>
<td></td>
<td>Cg(9)-Cg(9)</td>
<td>3.5753(12)</td>
<td>0</td>
<td>convex-convex</td>
</tr>
<tr>
<td></td>
<td>Cg(1)-Cg(11)</td>
<td>3.9108(13)</td>
<td>23.72(11)</td>
<td>concave-solvent</td>
</tr>
<tr>
<td></td>
<td>Cg(2)-Cg(11)</td>
<td>4.0465(13)</td>
<td>29.73(11)</td>
<td>concave-solvent</td>
</tr>
<tr>
<td></td>
<td>Cg(3)-Cg(11)</td>
<td>3.9952(13)</td>
<td>25.98(11)</td>
<td>concave-solvent</td>
</tr>
<tr>
<td>3c p-HOPhO-BsubPc</td>
<td>Cg(7)-Cg(7)</td>
<td>3.9686(10)</td>
<td>0</td>
<td>convex-convex</td>
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<tr>
<td></td>
<td>Cg(3)-Cg(9)</td>
<td>3.9864(9)</td>
<td>4.15(7)</td>
<td>concave-concave</td>
</tr>
<tr>
<td>p-HOPhO-BsubPc · toluene</td>
<td>Cg(8)-Cg(8)</td>
<td>3.7303(9)</td>
<td>0</td>
<td>convex-convex</td>
</tr>
<tr>
<td></td>
<td>Cg(2)-Cg(26)</td>
<td>3.9980(10)</td>
<td>23.10(8)</td>
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<td>Cg(3)-Cg(26)</td>
<td>3.7919(10)</td>
<td>17.04(8)</td>
<td>concave-solvent</td>
</tr>
</tbody>
</table>

a Alpha is the dihedral angle between planes I and J (°)

Interestingly, there are a number of close intermolecular contacts that cannot be explained either through the previously mentioned hydrogen bonds or π-π interactions, but which seem to result from two weak CH-π interactions (Figure 4.12 and Table 4.7). Although the H···Cg (hydrogen···ring centroid) distances are relatively large (≈4.1 Å), the C-H···Cg angles are remarkably linear (>165°). This geometry is consistent with the classification of CH-π interactions as very weak hydrogen bonds, in which the interaction strength is not expected to fall off sharply with increased distance. We therefore consider these two weak interactions to be CH-π interactions, on the basis of their linear geometry and the presence of otherwise unexplained close intermolecular contacts. Since the structure for HO-BsubPc (2) obtained via sublimation is equivalent to the structure obtained via solvent crystallization methods and reported by Potz et al., the same molecular interactions are present within both structures.
Table 4.6:  Selected C-H…Cg (C-H-π) interactions.

<table>
<thead>
<tr>
<th>Motif</th>
<th>X-H(I)</th>
<th>Cg(J)</th>
<th>H..Cg (Å)</th>
<th>X-H..Cg (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 HO-BsubPc</td>
<td>C(11)-H(11A)</td>
<td>Cg(1)</td>
<td>2.99</td>
<td>101</td>
</tr>
<tr>
<td></td>
<td>C(20)-H(20A)</td>
<td>Cg(1)</td>
<td>2.99</td>
<td>135</td>
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<tr>
<td></td>
<td>C(21)-H(21A)</td>
<td>Cg(2)</td>
<td>2.85</td>
<td>135</td>
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<tr>
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<td>C(14)-H(14A)</td>
<td>Cg(7)</td>
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<td>C(19)-H(19A)</td>
<td>Cg(7)</td>
<td>4.13</td>
<td>170</td>
</tr>
<tr>
<td>3a o-HOPhO-BsubPc</td>
<td>C(4)-H(4A)</td>
<td>Cg(8)</td>
<td>2.96</td>
<td>144</td>
</tr>
<tr>
<td></td>
<td>C(6)-H(6A)</td>
<td>Cg(9)</td>
<td>2.92</td>
<td>143</td>
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<td></td>
<td>C(12)-H(12A)</td>
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<td>C(13)-H(13A)</td>
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<td>C(1S)-H(1SA)</td>
<td>Cg(10)</td>
<td>2.92</td>
<td>154</td>
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<tr>
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<td>C(5)-H(5A)</td>
<td>Cg(10)</td>
<td>2.76</td>
<td>168</td>
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<td>C(20)-H(20A)</td>
<td>Cg(1)</td>
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<td>C(21)-H(21A)</td>
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<td>C(28)-H(28A)</td>
<td>Cg(9)</td>
<td>2.89</td>
<td>166</td>
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<tr>
<td>m-HOPhO-BsubPc · benzene</td>
<td>C(8S)-H(8SA)</td>
<td>Cg(10)</td>
<td>2.93</td>
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<td>C(14)-H(14A)</td>
<td>Cg(13)</td>
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<td>C(21)-H(21A)</td>
<td>Cg(12)</td>
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<td>139</td>
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<tr>
<td>3c p-HOPhO-BsubPc</td>
<td>C(11)-H(11A)</td>
<td>Cg(10)</td>
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<td>164</td>
</tr>
<tr>
<td></td>
<td>C(20)-H(20A)</td>
<td>Cg(1)</td>
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<td>101</td>
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<td></td>
<td>C(21)-H(21A)</td>
<td>Cg(2)</td>
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<td>110</td>
</tr>
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<td>p-HOPhO-BsubPc · toluene</td>
<td>C(4S)-H(4SA)</td>
<td>Cg(1)</td>
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<td>119</td>
</tr>
</tbody>
</table>

Table 4.7:  Selected short intermolecular contacts for HO-BsubPc (2).

<table>
<thead>
<tr>
<th>Atom (I)</th>
<th>Atom (J)</th>
<th>d (I-J) (Å)</th>
<th>Sum vdw radii (Å)</th>
</tr>
</thead>
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<tr>
<td>H(5A)</td>
<td>H(14A)</td>
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<tr>
<td>H(4A)</td>
<td>H(19A)</td>
<td>2.23</td>
<td>2.4</td>
</tr>
<tr>
<td>C(3)</td>
<td>C(3)</td>
<td>3.326(2)</td>
<td>2.9</td>
</tr>
</tbody>
</table>
Figure 4.12: The molecular packing arrangement of HO-BsubPc (2), demonstrating two CH-π interactions that result in close contacts between neighbouring molecules (short contacts listed in Table 4.7, below). Concave-concave π-π interactions are shown in purple and summarized in Table 4.5. CH-π interactions are shown in cyan and summarized in Table 4.6. Short C3-C3 distances are shown as a gray dotted line. Colours: carbon = grey; nitrogen = light purple; oxygen = red; boron = pink; hydrogen = white. For clarity, non-interacting and non-hydroxy hydrogen atoms omitted.

In the solid state arrangement of o-HOPhO-BsubPc (3a), each BsubPc molecule is associated with a total of seven neighbouring BsubPc molecules, forming a three-dimensional network. One neighbour is associated through the hydrogen bond network previously discussed, one through concave-concave π-π interactions, and one through convex-convex π-π interactions. The remaining four neighbouring molecules are associated through CH-π interactions (Figure 4.13).

Despite the presence of solvent molecules in both solid state arrangements for m-HOPhO-BsubPc (3b), both structures consist of three-dimensional networks of associated BsubPc molecules. In the m-HOPhO-BsubPc-DCM/water solvate, each BsubPc molecule is associated with six adjacent BsubPc molecules: three via hydrogen bonds, one via concave-concave π-π interactions, one via convex-convex π-π interactions, and one via CH-π interactions (Figure 4.14). There is also some evidence of interactions with solvent molecules; however, the presence of mixed solvent molecules within the solvent sites precludes a meaningful geometric analysis of these interactions. In the m-HOPhO-BsubPc-benzene solvate, each BsubPc molecule is associated with three neighbouring BsubPc molecules: one via hydrogen bonding and two via convex-convex π-π interactions (Figure 4.15). There are numerous benzene-BsubPc interactions, which is unsurprising given the large portion of benzene molecules within this structure (Figure
**Figure 4.13:** The molecular packing arrangement of $o$-HOPhO-BsubPc (3a), demonstrating a central molecule (in gold) and intermolecular interactions with seven neighbouring molecules. The central molecule is associated with the blue molecule through a network of hydrogen bonds; with the green molecule through a convex-convex $\pi-\pi$ interaction; with the purple molecule through concave-concave $\pi-\pi$ interactions; and with the red molecules through CH-$\pi$ interactions. The result is a 3-dimensional network of closely associated molecules.

**Figure 4.14:** The molecular packing arrangement of $m$-HOPhO-BsubPc ·0.69 CH$_2$Cl$_2$ ·0.31 H$_2$O (3b DCM/H$_2$O solvate), demonstrating a central molecule (in gold) and intermolecular interactions with six neighbouring molecules. The central molecule is associated with the green molecule through convex-convex $\pi-\pi$ interactions; with the purple molecule through concave-concave $\pi-\pi$ interactions; with the blue molecules through hydrogen bonding; and with the red molecule through a CH-$\pi$ interaction.
Figure 4.15: The molecular packing arrangement of \( m\)-HOPhO-BsubPc \( \cdot \) 2.5 \( C_6H_6 \) (3b benzene solvate), demonstrating a three-dimensional network of closely associated molecules. A strong hydrogen bond (red dashed line) and a weak hydrogen bond (blue dashed line) form pairs of associated molecules. Each molecule is also associated with two neighbouring molecules through two separate convex-convex \( \pi \)-\( \pi \) interactions, shown in green and purple. For clarity, non-interacting and non-hydroxy hydrogen atoms omitted.

Figure 4.16: The molecular packing arrangement of \( m\)-HOPhO-BsubPc \( \cdot \) 2.5 \( C_6H_6 \) (3b benzene solvate), demonstrating BsubPc-benzene interactions. Metrics for the \( \pi \)-\( \pi \) interactions (Cg11-Cg1, Cg11-Cg2, Cg-11-Cg3) are provided in Table S4.5 and metrics for the CH-\( \pi \) interactions (C8S-H8SA···Cg10, C14-H14A···Cg13, C21-H21A···Cg12) are provided in Table 4.6. There are two possible locations for centroid Cg13, due to presence of disorder in the corresponding benzene molecule. For clarity, non-interacting and non-hydroxy hydrogen atoms omitted.
4.16). One benzene molecule is situated in the bowl of the BsubPc molecule, which correlates with the absence of concave-concave \( \pi-\pi \) interactions in this arrangement.

**Figure 4.17:** The molecular packing arrangement of \( p\text{-HOPhO-BsubPc (3c)} \), demonstrating a central molecule (in gold) and intermolecular interactions with five neighbouring molecules. The central molecule is associated with the two blue molecules through hydrogen bonding; with the green molecule through convex-convex \( \pi-\pi \) interactions; with the purple molecule through concave-concave \( \pi-\pi \) interactions; and with the red molecule through CH-\( \pi \) interactions. This results in a three-dimensional network of closely associated molecules.

In the unsolvated arrangement of \( p\text{-HOPhO-BsubPc (3c)} \), each BsubPc molecule interacts with five adjacent molecules: two via hydrogen bonding, one via concave-concave \( \pi-\pi \) interactions, one via convex-convex \( \pi-\pi \) interactions, and one via CH-\( \pi \) interactions. The result is a three-dimensional network of associated BsubPc molecules (Figure 4.17). In the solvated \( p\text{-HOPhO-BsubPc} \) arrangement, each BsubPc molecule is associated with three adjacent molecules: two through hydrogen bonding and one through convex-convex \( \pi-\pi \) interactions. The toluene molecule is situated in the bowl of the BsubPc molecule (Figure 4.18), and unsurprisingly, there are no concave-concave \( \pi-\pi \) interactions. Of the six structures reported herein, this solid state arrangement is the only one which does not consist of a three-dimensional network of associated BsubPc molecules. The hydrogen bonds and convex-convex \( \pi-\pi \) interactions form sheets of
associated molecules, but adjacent two-dimensional sheets are isolated from each other by toluene molecules (Figure 4.19).

**Figure 4.18:** The molecular packing arrangement of \( p\text{-HOPhO-BsubPc} \cdot C_7H_8 \) (3c toluene solvate), demonstrating interactions between the BsubPc molecule and the toluene solvent molecule: two \( \pi-\pi \) interactions (Cg26-Cg2, Cg26-Cg3) and one CH-\( \pi \) interaction. Colours: carbon = grey; nitrogen = light purple; oxygen = red; boron = pink; hydrogen = white. For clarity, non-interacting hydrogen atoms omitted.

**Figure 4.19:** The molecular packing arrangement of \( p\text{-HOPhO-BsubPc} \cdot C_7H_8 \) (3c toluene solvate). Each BsubPc molecule is associated with three neighbouring molecules: two through hydrogen bonding (red and blue dashed lines) and one through convex-convex \( \pi-\pi \) interactions. This results in a two-dimensional sheet of closely associated molecules. Adjacent sheets are separated by a layer of toluene solvent molecules, shown in light blue. Colours: carbon = grey; nitrogen = light purple; oxygen = red; boron = pink; hydrogen = white. For clarity, non-interacting and non-hydroxy hydrogen atoms omitted.
4.4 Conclusions

For the first time, the occurrence of hydrogen bonding in BsubPcs has been methodically examined by studying six solid state arrangements of hydroxy-containing BsubPc derivatives. The imine nitrogen atoms are robust hydrogen bond acceptors; they consistently accept hydrogen bonds from hydroxy moieties and can also accept weak hydrogen bonds from CH moieties. In all but one arrangement (solvated p-HOPhO-BsubPc), the oxygen of the hydroxy moiety functioned as both a hydrogen bond donor (for a strong OH⋯N bond) and a hydrogen bond acceptor (for a weak C-H⋯O bond). The resulting C-H⋯O bonds, while classified as weak interactions, have discernible effects on the solid state arrangement of BsubPc molecules. Specifically, C-H⋯O bonds involving the hydroxy oxygen atom were associated with pulling of the hydroxy group toward a bay carbon atom or distortion of a convex-convex π-π contact. The strength of these C-H⋯O bonds were likely enhanced by cooperativity effects, which are a well-documented phenomenon associated with hydrogen bonding.¹¹

The phenoxy oxygen atom can also function as a hydrogen bond acceptor (for a weak C-H⋯O bond), although this occurred less frequently (in three of five solid state arrangements containing a phenoxy group). Hydrogen bonds involving the phenoxy oxygen atom were not associated with significant effects on solid state packing arrangements. Additionally, with the exception of the solid state arrangement of o-HOPhO-BsubPc (3a), the phenoxy oxygen atom typically cannot benefit from cooperativity effects due to the molecular structure of the BsubPc compounds.

Remarkably, five of the six solid state arrangements consisted of three-dimensional networks of associated BsubPc molecules. This degree of connectivity is relatively rare for perhydrogenated BsubPc derivatives, and especially rare for unsolvated arrangements.¹ ³⁸⁻⁹ The three-dimensional networks reported herein combine hydrogen bonding with two separate π-π interactions: either one concave-concave and one convex-convex, or two convex-convex involving two distinct diiminoisoindoline arms. The concurrence of hydrogen bonding and two separate π-π interactions therefore result in unique solid state arrangements of BsubPc molecules.
4.5 References


Chapter 5
Phenoxy-Boron Subphthalocyanines as a Platform to Study the Effects of Halogen and Hydrogen Bonds in Organic Photovoltaics

The experimental work in this chapter was facilitated with a Michael Smith Foreign Study Supplement (MS-FSS), which enabled me to spend six months studying the performance of BsubPc derivatives in organic photovoltaic (OPV) devices with the research group of Professor Tim Jones at the University of Warwick (UK). At the time, our research group did not have access to OPV device fabrication and testing facilities at the University of Toronto.

The work in this chapter is currently being prepared for submission as a manuscript to the journal *Physical Chemistry Letters*. The author list will be: Jessica D. Virdo, David S. Josey, Thomas J. Howells, Tim S. Jones and Timothy P. Bender.

I synthesized and purified all phenoxy-BsubPc materials (derivatives 2-7) used in this study. Members of the Jones group trained me on the use of their laboratory’s equipment, including the device fabrication and testing facilities and the atomic force microscopy (AFM). TJH performed all UV-vis absorption measurements, fabricated and tested approximately half of the OPV devices, and performed AFM imaging for fresh films of *m*-FPhO-BsubPc and *p*-HOPhO-BsubPc. DSJ performed sample preparation of neat films of BsubPc derivatives for FTIR studies, while I carried out the FTIR measurements. I performed all other experimental work, including: the majority of the AFM imaging, dilute film preparation for FTIR sample analysis, and the remaining half of the device fabrication and testing. I also carried out all of the data analysis, wrote all of the text, and created all of the figures. This study was supervised by both TSJ and TPB.
5.1 Background on Organic Photovoltaic Devices

The field of organic photovoltaic (OPV) research is interdisciplinary in nature, with ongoing research in areas including but not limited to: organic small molecule design and synthesis, polymer design and synthesis, hybrid organic-inorganic materials chemistry, theoretical chemistry, materials engineering, electrical engineering, and physics. Rather than provide a comprehensive review on OPV technology, the purpose of this section is to provide a basic introduction to OPV device functioning and characteristics, such that a reader unfamiliar with the field will be equipped with enough background knowledge to understand the following discussion on OPV devices containing boron subphthalocyanine (BsubPc) derivatives. Further details on OPV device history and operating principles can be found in review articles in the published literature.1-2

OPV devices typically are based on one of two standard architectures, as shown in Figure 5.1: a planar heterojunction (PHJ) device or a bulk heterojunction (BHJ) device.3 In a PHJ device, the donor and acceptor materials are in two discrete layers with a single, well-defined interface. In contrast, the donor and acceptor materials are intermixed in BHJ devices. In either configuration, incident light is absorbed by the active layer(s) of the solar cell, which is comprised of two distinct materials: an electron donor and an electron acceptor (pink and blue, respectively, in Figure 5.1). Incident light can be absorbed by one or both of these materials, depending on the absorption properties of the materials selected for the OPV device.

For the purposes of this introduction, chloro boron subphthalocyanine (Cl-BsubPc) will be used as the electron donor material, fullerene C_{60} will be used as the electron acceptor material, and it will be assumed that a photon is absorbed by the Cl-BsubPc material. When an organic light-absorbing material such as Cl-BsubPc absorbs a photon, it generates an exciton, which is a short-lived, Coulombically-bound electron and hole pair. The electron and hole are denoted by the – and + symbols, respectively, in Figure 5.2. The electron and hole pair is too tightly bound to dissociate into free charge carriers (electrons and holes) in the bulk. In order to dissociate into free charge carriers, the exciton must diffuse to the donor-acceptor interface. At the interface, the offset between the frontier orbital energy levels of the donor and acceptor material facilitates the dissociation of the exciton into electrons and holes. The electron moves from the highest singly occupied molecular orbital (SOMO) of the donor material to the LUMO of the acceptor
Figure 5.1: Standard OPV device architectures: planar heterojunction (PHJ) and bulk heterojunction (BHJ).

Figure 5.2: Energy level diagram of a typical Cl-BsubPc / C\textsubscript{60} OPV device.

material. Free electrons and holes are collected at the cathode and anode, respectively, generating a current from the OPV device.

It is worth noting that exciton diffusion lengths in organic semiconductor materials are typically on the order of tens of nanometers, which imposes a strict upper limit on the thickness of the active layers in OPV devices. The requirement of thin layers for efficient exciton diffusion is in direct contrast to the ideal case for maximizing light absorption, where thicker layers would be beneficial in order to absorb more photons. This is why BsubPc are of interest and emerging top
performing materials, as they have molar extinction coefficients ($\varepsilon$) approaching 80,000. More detailed discussion regarding the physical processes occurring in OPV devices, as well as approaches to designing OPV materials and devices, can be found in the literature.\textsuperscript{1,3}

OPV device performance is characterized by measuring the current density $J$ (i.e., current per device area) as a function of applied voltage $V$. Figure 5.3 demonstrates a typical $J$-$V$ curve resulting from such a measurement. The response of the solar cell is measured under dark (dashed line) and illuminated (solid line) conditions. There are several important features to note on a $J$-$V$ curve. The y- and x-intercepts of an illuminated $J$-$V$ curve correspond, respectively, to the short-circuit current density $J_{SC}$ (when $V = 0$) and the open-circuit voltage $V_{OC}$ (when $J=0$). Since the power produced by a solar cell is equal to the product of current density and voltage, the power at both of these intercepts is zero. Even so, $J_{SC}$ and $V_{OC}$ are points of interest in an OPV because they represent the maximum current density and voltage that can be produced by an illuminated device.

![Figure 5.3: Typical current density-voltage ($J$-$V$) characteristics of an organic solar cell.](image)

The light blue shaded box in Figure 5.3 corresponds to $P_{\text{ideal}}$, which is the theoretical maximum power density of the OPV device based on the product of $J_{SC}$ and $V_{OC}$. The dark blue shaded box corresponds to $P_{\text{max}}$, which is the actual maximum power density measured for the device. The ratio between these two boxes is referred to as the fill factor (FF), a parameter which describes the ‘squareness’ of the $J$-$V$ curve:\textsuperscript{4}
Equation 5.1

\[ FF = \frac{P_{\text{max}}}{P_{\text{ideal}}} = \frac{P_{\text{max}}}{J_{\text{SC}}V_{\text{OC}}} \]

The efficiency, \( \eta_p \), of a solar cell is the percentage of input power from provided by a light source that is converted to output power at the maximum power point (\( P_{\text{max}} \)):

\[ \eta_p = \frac{P_{\text{max}}}{P_{\text{in}}} \times 100\% = \frac{FF J_{\text{SC}} V_{\text{OC}}}{P_{\text{in}}} \times 100\% \]

Equation 5.2

Based on equation 5.2, the efficiency of an OPV can be improved by increasing \( FF \), \( J_{\text{SC}} \) and/or \( V_{\text{OC}} \). The upper limit of the \( V_{\text{OC}} \) for a given pair of donor and acceptor materials is determined by the difference between the highest occupied molecular orbital (HOMO) of the donor material and the LUMO of the acceptor material.\(^5\) The origin of \( J_{\text{SC}} \) is more complicated, as it is affected by numerous processes within the OPV, including photon absorption and exciton formation, exciton diffusion and dissociation, and charge transport of holes and electrons to their respective electrodes.\(^4\) The shape of the \( J-V \) curve and the corresponding \( FF \) are also affected by several complex factors, including charge transport properties\(^7\)\(8\) and material resistances,\(^5\) and these topics are an ongoing area of research in the OPV field.

In addition to \( J-V \) measurements, OPV devices are typically characterized by measuring the external quantum efficiency (EQE). An EQE measurement provides the ratio of incident photons that are converted into current as a function of wavelength (\( \lambda \)).

\[ EQE (\lambda) = \frac{J(\lambda)}{q N(\lambda)} \]

Equation 5.3

In the above equation, \( J(\lambda) \) is the current generation density as a function of wavelength, \( q \) is the elementary charge (1.602 x 10\(^{-19}\) C) and \( N(\lambda) \) is the monochromatic incident photon flux density. The \( J_{\text{SC}} \) can be estimated from the EQE by multiplying the EQE measurement by the incident spectrum and integrating.
5.2 Introduction

Within the organic electronic field, there is growing interest in understanding the relationships between molecular structure, supramolecular structure, and device performance characteristics of photovoltaic active materials.\textsuperscript{9,10} The supramolecular structure of a material, including intermolecular orientation and spacing, can be modified by introducing or tuning non-covalent intermolecular interactions. Due to their conjugated nature, at a molecular level, many organic electronic materials feature prominent planar regions composed of rigid aromatic rings. As a result, aromatic $\pi-\pi$ interactions are pervasive in the solid state arrangements of organic electronic materials, and approaches to understanding and tuning these interactions have been studied in small molecules, oligomers and polymers.\textsuperscript{11,12}

Although relatively unexplored in organic electronic materials, hydrogen bonds and halogen bonds are potentially useful for the design of intermolecular arrangement, due to their relative strength and robustness as well as their directionality.\textsuperscript{13} To the best of our knowledge, halogen bonding materials have not been studied in either a BHJ or PHJ architecture, although halogen bonding interactions have been employed for surface passivation of organic-inorganic halide perovskite solar cells.\textsuperscript{14} Studies involving hydrogen bonds in organic electronic materials have only emerged within the last few years.\textsuperscript{15} The majority of these studies have focused on the effects of incorporating hydrogen bonds into bulk heterojunction (BHJ) solar cells, with mixed results. Hydrogen bonds can have beneficial\textsuperscript{16-20} or detrimental\textsuperscript{21-24} effects on the interpenetrative morphology of donor and acceptor materials in BHJ devices, with corresponding improvements or decreases in device performance. Hydrogen bonds have also been utilized to stabilize the morphology of BHJ devices, leading to improved device stability, particularly at elevated temperatures.\textsuperscript{25,26}

In planar heterojunction (PHJ) solar cells, unlike BHJ solar cells, morphological effects resulting from intermolecular interactions are isolated within a single layer and do not significantly increase or decrease the interfacial area between donor and acceptor materials. The PHJ architecture therefore allows the effects of intermolecular interactions on device performance to be studied with minimal impact on the overall morphology of the donor-acceptor interface. The use of hydrogen bonding materials in PHJ solar cells has thus far been limited to cases of electron donor materials based on indoline\textsuperscript{27} and isoindigo.\textsuperscript{28} Due to the nature of the molecules
used in these two studies, hydrogen bonding could not be incorporated into either the indoline or isoindigo derivatives without changing the optical and electronic properties of these materials. These studies were therefore unable to probe the effects of hydrogen bonding in an OPV device while maintaining consistency in other variables of interest (i.e., optical and electronic properties).

Within this context, boron subphthalocyanine (BsubPc) derivatives are an appropriate platform to study the effect of incorporating halogen bonds and hydrogen bonds in the active material of photovoltaic devices. BsubPcs are aromatic, bowl-shaped small molecules (Figure 5.4) which are of interest in organic electronic applications due to their useful optical and electronic properties. The imine nitrogen (N_i, Figure 5.4) of BsubPc derivatives has been previously demonstrated to be a reliable acceptor for both hydrogen-bonding and halogen-bonding interactions. BsubPcs can be readily substituted in the axial position (R_a, Figure 5.4) with phenoxy moieties capable of acting as halogen bond or hydrogen bond donors. Additionally, by introducing the bond donor in the axial position, intermolecular interactions can be introduced in BsubPc materials without significantly altering the optical or electronic properties, since properties such as the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of BsubPc derivatives are relatively insensitive to axial substitution.

This study includes device fabrication and characterization of 6 BsubPc derivatives which have not been previously used for organic photovoltaic devices (Figure 5.4): phenoxy-BsubPc (2), four meta-halogenated phenoxy-BsubPcs (3-6), and para-hydroxy phenoxy-BsubPc (6). Chloro boron subphthalocyanine (Cl-BsubPc, 1) is included for comparison as it is the most widely used BsubPc derivative in organic electronic applications. The crystal structure of 1 is composed of a network of concave-concave and convex-convex π-π interactions (Figure 5.4b). Despite having similar molecular structures, the phenoxy BsubPc compounds 2-7 represent a range of intermolecular interactions in the solid state, as revealed through x-ray diffraction studies of single crystals obtained via train sublimation. These seven derivatives can be grouped into five categories based on their crystal structure (Figure 5.4b-f). PhO-BsubPc (2) does not contain any donor groups for halogen or hydrogen bonds and the solid state arrangement is
Figure 5.4:  (a) Molecular structure of BsubPc compounds, denoting the location of the axial position (R_a) as well as pyrrole (N_p) and imine (N_i) nitrogens. Solid state arrangements of BsubPc compounds demonstrating (b) concave-concave (green dashed lines) and convex-convex (blue dashed lines) \( \pi-\pi \) interactions in Cl-BsubPc (1)\(^{33} \); (c) concave-concave (green dashed lines) \( \pi-\pi \) interactions in PhO-BsubPc (2)\(^{34} \); (d) C-H---F hydrogen bonds (orange dashed lines) in \( m\)-FPhO-BsubPc (3)\(^{35} \); (e) C-X---N halogen bonds (black dashed lines) in \( m\)-ClPhO-BsubPc, \( m\)-BrPhO-BsubPc, and \( m\)-IPhO-BsubPc (4-6) demonstrated using \( m\)-ClPhO-BsubPc\(^{31} \); and (f) O-H---N hydrogen bonds (red dashed lines) in \( p\)-HOPhO-BsubPc.\(^{30} \) Key: carbon = grey; nitrogen = light purple; oxygen = red; boron = light pink; fluorine = magenta; chlorine = green; hydrogen = white. For clarity, non-interacting hydrogen atoms are omitted.

composed of a dimer motif directed by concave-concave \( \pi-\pi \) interactions (Figure 5.4c).\(^{34} \) The \( m\)-FPhO-BsubPc (3) molecule adopts four different conformations in the crystal structure, with
each fluorine atom accepting one or two weak C-H···F hydrogen bonds (Figure 5.4d).\textsuperscript{35}

Compounds 4-6 have been shown to reliably demonstrate C-X···N (X=Cl, Br, I) halogen bonding interactions (Figure 5.4e),\textsuperscript{31} and the hydroxy moiety of 7 participates in strong O-H···N hydrogen bonds (Figure 5.4f).\textsuperscript{30} The ability to study the effects of intermolecular interactions without simultaneously introducing significant changes to other variables of interest (i.e., morphology, optical and electronic properties) is a distinct advantage of the BsubPc derivatives studied here.
5.3 Experimental

5.3.1 Materials

Indium tin oxide (ITO)-coated glass substrates (Thin Film Devices, 145 nm thick, R<sub>s</sub> < 15 Ω sq<sup>−1</sup>) were cleaned by the following process: sonication in a mixture of decon-90 and deionized water (30:70 decon: water) for 15 minutes, rinsing with deionized water, sonication in deionized water for 15 minutes, rinsing with isopropanol, sonication in isopropanol for 15 minutes, drying with a stream of dry nitrogen and finally treatment with UV-ozone (Novascan PSD-UVT) for 30 minutes to remove carbon residues. Fullerene C<sub>60</sub> (Nano-C Inc., 99.5%) and bathocuproine (BCP, Aldrich, 96%) were purified using thermal gradient sublimation before deposition. Chloro boron subphthalocyanine (Cl-BsubPc, Lumtec, sublimation-grade), molybdenum oxide (MoO<sub>x</sub>, Aldrich, 99.99%) and aluminum (Aldrich, 99.999%) were used as received. Other subphthalocyanine derivatives (PhO-BsubPc, m-FPhO-BsubPc, m-ClPhO-BsubPc, m-BrPhO-BsubPc, m-IPhO-BsubPc and p-HOPhO-BsubPc) were synthesized using bromo boron subphthalocyanine (Br-BsubPc) as a precursor according to previously published procedures<sup>30-31</sup> and purified using train sublimation<sup>36</sup> before deposition.

5.3.2 Methods

<sup>UV-vis.</sup> Solid state absorption spectra were obtained using thin film samples with thicknesses of approximately 100 nm deposited on quartz substrates and measured using the EQE instrumentation set-up described below. Samples were prepared using a Kurt J. Lesker Spectros vacuum evaporation system.

<sup>Atomic force microscopy (AFM). </sup>Thin film samples were prepared on ITO substrates using a Kurt J. Lesker Spectros vacuum evaporation system. Deposition rates of 1 Å/s were used for MoO<sub>x</sub> and BsubPc derivatives<sup>1-7</sup>. Images were obtained using an Asylum Research MFP-3D instrument in tapping mode. MFP-3D software (based on Igor Pro) was used for image reconstruction and analysis. Average values and standard deviations for R<sub>q</sub> (root mean square, RMS) roughness were obtained by averaging values from 4-5 images.

<sup>Fourier transform infrared (FTIR) spectroscopy. </sup>KBr substrates (Sigma Aldrich ZS27084) were removed from cardboard holders and sonicated in toluene for 90 seconds to remove residual
adhesive, then dried with nitrogen and cleaned by 5 minutes of atmospheric plasma treatment. Neat, evaporated thin film samples were prepared in a custom-built thermal evaporation system with a working pressure of approximately $1 \times 10^{-7}$ Torr. Deposition rates were monitored using quartz crystal microbalances (QCMs). BsubPc derivatives were deposited at a rate of 1 Å/s to a thickness of approximately 100 nm. Dilute thin film samples were prepared by making a solution consisting of 90 wt% toluene and 10 wt% dissolved components, with the dissolved components consisting of 1 mol% BsubPc derivative and 99 mol% decafluoro biphenyl. The dilute solution was then drop cast onto KBr substrates and left to dry in a vacuum oven at room temperature for 48 hours. FTIR measurements were obtained in ambient conditions using a Perkin Elmer Spectrum 100 instrument, with each measurement consisting of 5000 scans at a resolution of 0.5 cm$^{-1}$.

**Device fabrication.** OPV devices were fabricated using a Kurt J. Lesker Spectros vacuum evaporation system with a base pressure of approximately $4 \times 10^{-8}$ Torr. Materials were evaporated at the following deposition rates: 1 Å/s for MoO$_3$, BsubPc derivatives 1-7, and aluminum; 0.5 Å/s for C$_{60}$; and 0.1 Å/s for BCP. Deposition rates were monitored using quartz crystal microbalances (QCMs). Tooling factors to calibrate QCM measurements with layer thickness were obtained by creating step edges in thin film samples and measuring the thickness of the step edges with atomic force microscopy (AFM) in tapping mode. Aluminum electrodes with a thickness of 100 nm and an active pixel area of 0.16 cm$^2$ were deposited in situ by evaporation through a shadow mask. Silver conductive paint (RS Components Ltd.) was used to create contact points on the ITO and aluminum electrodes.

**Device characterization.** Current density-voltage (J-V) characteristics of OPV devices were measured using a Keithley 2400 sourcemeter. Simulated AM1.5 G solar illumination at 100 mW cm$^{-2}$ (1 sun) was provided by a Newport Oriel solar simulator (class AAA) and the light intensity was measured using a calibrated photodiode (PVM482, PV Measurements Inc.). External quantum efficiency (EQE) spectra were obtained using a Scientech SF150 xenon arc lamp light source equipped with a PTI monochromator. Monochromatic light was chopped at 510Hz, and the light intensity was monitored by a fixed Si reference photodiode (Newport 818-UV). A second identical photodiode was used to calibrate the signal at the sample location, then removed and replaced with the photovoltaic sample mount. For UV-vis absorption spectroscopy the second photodiode was left in place and the sample was mounted directly in front of the diode.
Signal detection was performed using a current-voltage amplifier (Femto DHPCA-100) and National Instruments DAQ (NI USB-4431); custom LabVIEW software performed the function of a multi-channel lock-in amplifier to monitor the fixed reference diode and sample simultaneously, controlling for variations in the light source intensity. The OPV device holder held the samples under a nitrogen atmosphere for the duration of J-V and EQE testing, while UV-vis absorption was measured in ambient conditions.
5.4 Results and Discussion

5.4.1 Synthesis and Crystal Structure

Phenoxy BsubPc derivatives 2-7 were synthesized according to previously published procedures\(^{30,31,34}\) and purified by train sublimation\(^{36}\) prior to incorporation into organic photovoltaic devices. Commercially available Cl-BsubPc (1) was selected as a reference material, as it has been used extensively in organic electronic device fabrication.\(^{29}\)

The intermolecular interactions present in the solid state arrangement of compounds 1-7 have been discussed in detail in previous chapters of this thesis. Briefly, three of the meta-halogenated compounds (4-6) demonstrate C-X···N halogen bonding interactions (X=Cl, Br, I), which increase in interaction strength according to the order Cl < Br < I.\(^{31}\) The hydroxy moiety of p-HOPhO-BsubPc (7) participates in strong, classical O-H···N hydrogen bonds,\(^{30}\) while m-FPhO-BsubPc (2) demonstrates weak C-H···F hydrogen bonds.\(^{35}\) The solid state arrangements of Cl-BsubPc (1)\(^{33}\) and PhO-BsubPc (2)\(^{34}\) are directed primarily through aromatic π-π interactions. It is noteworthy that all of these interactions have been observed through x-ray diffraction studies of single crystals obtained via train sublimation rather than solvent crystallization methods.

5.4.2 Thin Film Characterization

Solid state absorption measured from thin films of BsubPc derivatives 1-7 are presented in Figure 5.5. The UV-vis spectra of BsubPc derivatives display two characteristic absorption regions: a very prominent absorption band in the visible region, known as the Q-band, and a less intense absorption band in the near-UV region, known as the Soret band. The Q-band typically has a shoulder to the blue side of the band. For vacuum deposited films of Cl-BsubPc (1), the Q and Soret bands are located at \(\lambda_{\text{max}} = 581\) nm and \(\lambda_{\text{max}} = 304\) nm respectively. The onset of the Q-band absorption occurs at 640 nm, corresponding to an optical band gap (\(E_{g,\text{opt}}\)) of approximately 1.9 eV. Replacement of the axial chlorine atom in 1 with a phenoxy moiety results in slight changes to the UV-vis spectra, and the spectra of the different phenoxy-BsubPc derivatives (2-7) are generally equivalent. This is to be expected, as the optical and electronic properties of BsubPcs have been shown to be relatively insensitive to substitution in the axial position.\(^{32}\) Compared to Cl-BsubPc (1), the phenoxy derivatives (2-7) have slightly narrower Q
and Soret bands. The maximum absorption of the Q-band is slightly blueshifted to $\lambda_{\text{max}} = 576$ nm and the absorption onset also blueshifts to 620 nm ($E_{\text{g, opt}} \approx 2.0$ eV). These results indicate that there is a small change in the optoelectronic properties of BsubPc derivatives upon substitution of the axial chlorine atom in Cl-BsubPc (1) with the phenoxy moiety in PhO-BsubPc (2), whereas additional functional groups on the phenoxy moiety (in compounds 3-7) do not result in further changes.

**Figure 5.5:** Normalized solid state UV-vis absorbance spectra of BsubPc derivatives.

The thin film morphologies of derivatives 1-7 were investigated using atomic force microscopy (AFM). The film morphology of Cl-BsubPc (1) has been previously investigated using AFM for films deposited onto bare glass as well as several organic sublayers, with the morphological features being reported as either approximately spherical or elongated in shape. There have not been any previous AFM studies of the phenoxy derivatives 2-7.

Figure 5.6 includes a reference image of a bare glass/ITO substrate as well as images of thin layers of derivatives 2-7 deposited on glass/ITO substrates. The film thickness (20 nm) and deposition rates (1 Å/s) were selected to be representative of typical device fabrication conditions. All films were found to be fairly smooth and free of cracks. The morphological features for each derivative adopt a roughly spherical shape, with the feature size and corresponding root mean square (RMS) roughness varying depending on the derivative. The
Figure 5.6: AFM images of (a) a bare ITO substrate and (b)-(h) 20 nm films of BsubPc derivatives (1-7) deposited onto ITO. \( R_q \) values refer to the root mean square (RMS) roughness, with standard deviations denoted in brackets.

Figure 5.7: AFM images of (a) 5 nm of MoO\(_x\) on an ITO substrate and (b)-(e) films composed of ITO/ MoO\(_x\) (5 nm)/ BsubPc derivative 1 or 6 (20 nm). Images (b) and (c) represent freshly deposited film morphologies, whereas images (d) and (e) were obtained after the films were stored in a nitrogen atmosphere for 3-4 days. \( R_q \) values refer to the root mean square (RMS) roughness, with standard deviations denoted in brackets.
films formed by Cl-BsubPc (1), PhO-BsubPc (2), and the three derivatives capable of halogen bonding (m-ClPhO-BsubPc (4), m-BrPhO-BsubPc (5) and m-IPhO-BsubPc (6)) display features which are roughly the same size as the features observed on the bare ITO substrate. The films formed by derivatives 1, 4, 5 and 6 are slightly rougher than the underlying ITO layer, while the film formed by derivative 2 is slightly smoother. Interestingly, the films of the two materials which display hydrogen bonding in their crystal structure (m-FPhO-BsubPc (3) and p-HOPhO-BsubPc (7)) display features which are considerably smaller than the underlying ITO surface, and these two films are also significantly smoother, indicating that these materials tended to deposit in a manner which fills in the gaps of the underlying layer. At a molecular level, m-FPhO-BsubPc (3) is most similar to the other meta-halogenated phenoxy BsubPcs (4-7), yet the film morphology of 3 is considerably different. Based on the marked differences between the crystal structure of 3,35 which features hydrogen bonding, and the crystal structures of 4-7,31 which feature halogen bonding, this suggests that the crystal structure has more of an influence on film morphology than the molecular structure.

In order to investigate the sensitivity of the BsubPc film morphology to the underlying layer, films of Cl-BsubPc (1) and m-IPhO-BsubPc (6) were deposited onto 5 nm layers of molybdenum oxide (MoOx), which is a common hole extraction layer in OPV devices.42 A 5 nm layer of MoOx deposited onto ITO (Figure 5.7a) has features and roughness which are nearly identical to the underlying ITO surface (Figure 5.6a), and the 20 nm layers of 1 and 6 deposited over the MoOx (Figure 5.7) are very similar to 20 nm layers of these materials deposited directly onto ITO (Figure 5.6). The trends observed for films deposited onto ITO therefore appear to be transferable to films deposited onto a 5 nm layer of MoOx.

Finally, we wish to note that we have observed the film morphology of unprotected layers of BsubPc derivatives to be generally unstable in both ambient and nitrogen atmospheres. Figure 5.7d-e displays the morphology of films of 1 and 6 after aging for a few days in a nitrogen atmosphere provided by a glovebox. Both derivatives show a drastic change in morphology, with the previously round features being replaced with long, branch-like shapes. We have observed this morphological change with all seven BsubPc derivatives, both for films deposited directly onto ITO and films deposited onto a 5 nm MoOx underlayer. The branching habit of the features and the roughness of the aged films vary somewhat depending on the BsubPc derivative, as can be observed in Figure 5.7, with the aged film of 1 being rougher and having more branching.
points than the aged film of 6. This aging effect occurs faster if the samples are exposed to ambient atmosphere conditions, and may be a factor in some of the differences in film morphology found in the literature. The BsubPc films are stable enough in ambient conditions to enable fairly extensive AFM characterization; however, we caution that AFM measurements should be taken on freshly deposited films and that care should be taken to minimize unnecessary exposure to ambient conditions. Covering stored samples with foil to minimize exposure to light also appears to slow down the aging process.

Overall, the AFM analysis indicates that film morphology varies for different BsubPc derivatives, particularly with respect to feature size, film smoothness, and the feature shape of aged films. Of particular note are the differences in film morphology observed between \( m\)-FPhO-BsubPc (3) and the other meta-halogenated phenoxy-BsubPc derivatives (4-6) (Figure 5.6), which are molecularly very similar but which have distinctly different crystal structures. We sought to investigate the extent to which the crystal structures of BsubPc derivatives determined through single crystal x-ray diffraction (XRD) experiments were applicable to the arrangement of BsubPc molecules in thin films. However, investigating the arrangement of organic molecules in a thin film is not a trivial area of exploration, and is an ongoing area of research.

It is worth providing some background information on XRD techniques at this point. XRD experiments on single crystals are often employed to determine the arrangement of atoms and molecules within that crystal. In XRD experiments, the location of atoms in a sample is determined by measuring the scattering of x-rays as they interact with the electrons present in the sample.\(^{43}\) The signals detected through XRD techniques are effectively a map of electron density in space. As such, the locations of relatively heavy atoms, containing a large number of electrons, are easier to measure and determine than the locations of light atoms. Hydrogen, containing only one electron, is therefore the most difficult atom to detect using XRD techniques, and the locations of hydrogen atoms in a crystal structure are typically determined with the use of a fitting algorithm rather than from direct measurement of the electron. Organic compounds, including BsubPc derivatives, are by definition largely composed of hydrogen, carbon and other atoms from the second row of the periodic table. Boron, carbon, nitrogen, oxygen and hydrogen, which are the main elements present in BsubPc derivatives, are all considered to be ‘light’ atoms in the context of XRD experiments. BsubPc crystals are therefore
more difficult to diffract than inorganic or hybrid crystals containing heavier atoms such as metals.

Fortunately, BsubPc derivatives typically produce fairly large and high quality crystals with the crystallization techniques developed in our research group. Single crystals of BsubPc derivatives typically measure 0.1 to 0.3 mm in their smallest dimension, and aside from the occasional case involving twinning or some disorder which requires additional modeling during the refinement process, the single crystal sample is composed entirely of a repeating set of unit cells with uniform orientation. XRD experiments with single crystals of BsubPc derivatives are therefore a fairly routine procedure, and can be accomplished with the modern diffractometers readily available at many universities. In contrast, the thin films employed in OPV devices are typically only 10-40 nm thick, and consequently thin film samples are effectively 5 orders of magnitude smaller than the samples typically used in single crystal XRD experiments. To further complicate matters, thin films of organic materials do not form a single crystal with uniformly oriented unit cells. Even in cases where films of organic materials are highly crystalline, they are polycrystalline and therefore composed of different crystal grains with different orientations. We are therefore unable to use routine XRD techniques to characterize the crystallinity of thin films of BsubPc derivatives, due to the light nature of the atoms in the compounds, the very thin film thickness, and the polycrystalline nature of thin films.

Fourier transform infrared (FTIR) spectroscopy can be used to determine the presence of intermolecular interactions such as hydrogen bonding and halogen bonding, and was investigated as an alternative method of characterizing thin films of BsubPc materials. FTIR has been used extensively for the investigation of hydrogen bonds, including as a method to confirm the existence of hydrogen bonds in thin films of materials for BHJ OPV devices.\textsuperscript{16, 18, 25-26} Compared to hydrogen bonding, halogen bonding is a relatively recent area of research.\textsuperscript{44} To the best of our knowledge, there are no literature examples on the use of FTIR to investigate the presence of halogen bonding interactions in thin films of organic material, although there are solution state FTIR studies on this topic.\textsuperscript{45-46}

In order to investigate whether FTIR could be used to determine the presence of halogen bonding in BsubPc films, evaporated thin film samples of the three compounds that display halogen bonding in their crystal structure (\textit{m-ClPhO-BsubPc} (4), \textit{m-BrPhO-BsubPc} (5) and \textit{m-IPhO-BsubPc} (6)) were prepared. The FTIR spectra of these films were then compared to those of the corresponding single crystals in order to determine if any differences could be attributed to the presence of halogen bonding.

The FTIR spectra of the thin films of the three compounds were found to be similar to those of the single crystals, indicating that the presence of halogen bonding in the films was not significantly different from that in the single crystals. This suggests that FTIR spectroscopy is a viable technique for characterizing the presence of halogen bonding in thin films of organic materials, and could be used as a valuable tool in the development of new materials for OPV applications.
BsubPc (6)) were analyzed (Figure 5.8). The FTIR spectrum of PhO-BsubPc (2), which does not contain any moieties capable of halogen bonding, was included as a reference. A film thickness of 100 nm was selected as a reasonable compromise between two opposing selection criteria: although a thinner film (≈ 20 nm) would be more representative of the film thicknesses used in organic electronic devices, a thicker film was needed to obtain a reasonable signal on the FTIR instrument.

The bending vibrations of the carbon-halogen (C-X) covalent bonds are typically located in the following regions: 600-800 cm\(^{-1}\) for C-Cl, 500-750 cm\(^{-1}\) for C-Br, and 500-570 cm\(^{-1}\) for C-I.\(^{47}\) If the halogen atom in question is participating in a strong intermolecular interaction, such as a halogen bond, the signal from the C-X bond should shift and/or split. Unfortunately, the FTIR spectra measurements were particularly noisy in the region of interest (500-800 cm\(^{-1}\)), as can be seen by the dashed lines in Figure 5.8. The high frequency oscillations in the FTIR data appear to be a consistent problem when measuring thin and/or dilute films of material on KBr. The “data tune-up” feature in the Perkin Elmer Spectrum Express software can be used to remove some of the noise, resulting in the smoother, solid lines in Figure 5.8. Even after using the data tune-up feature, the remaining noise-to-signal ratio in the FTIR data precludes the use of this technique as a technique to identify which halogen atom is present in which material, as the four spectra are difficult to conclusively differentiate from each other. The shift in C-X bending vibration associated with different halogen atoms (i.e., C-Br vs. C-I) would be significantly greater than the shift associated with the same halogen atom in a different environment (i.e., C-Br with the Br participating in a halogen bond, vs. C-Br without halogen bonding). Since the FTIR technique is not sensitive enough to distinguish between different halogen atoms, we can conclude that it will not be sensitive enough to detect the presence of halogen bonding.

It is worth mentioning that halogen atoms covalently bound to aromatic carbon rings are generally considered to be difficult diagnostic tools in FTIR analysis. In aromatic halide moieties, the signals from C-H groups on the aromatic ring tend to overlap with the signals from the C-X bond.\(^{48}\) For this reason, alkyl halides are considered an easier diagnostic tool for determining the presence of halogen bonding via FTIR, and this likely explains why the literature examples with solution state FTIR experiments on halogen bonding compounds use alkyl halide compounds exclusively.\(^{45-46}\) Additionally, in alkyl halide compounds, the signals from C-H moieties adjacent to the C-X bond also demonstrate some shifting and/or splitting.
Figure 5.8: FTIR investigation of halogen bonding in BsubPc thin films: spectra of neat (100 nm) layers of BsubPc derivatives evaporated onto KBr, highlighting the range where C-X (X=Cl, Br, I) signals are expected.

Figure 5.9: FTIR investigation of hydrogen bonding in BsubPc films: spectra of neat (evaporated) and dilute (drop cast) films of BsubPc derivatives on KBr.
behavior upon formation of a halogen bond,\textsuperscript{45-46} providing additional regions of the spectrum (approximately 1255-1475 cm\textsuperscript{-1})\textsuperscript{47} which can be inspected for evidence of halogen bonds. Therefore, although FTIR was not useful for examining the presence of halogen bonding interactions for BsubPc compounds 4-6, it may still be a useful technique for investigating compounds where the halogen atom is not bound to an aromatic ring.

In the crystal structure of $p$-HOPhO-BsubPc (7), the hydroxy group participates in intermolecular hydrogen bonds.\textsuperscript{30} In order to investigate the occurrence of hydrogen bonding in films of $p$-HOPhO-BsubPc, two samples were prepared: a neat sample prepared by deposition of a 100 nm layer and a dilute sample prepared by drop casting a solution containing a small amount of $p$-HOPhO-BsubPc. The dilute solution consisted of 90 wt% toluene and 10 wt% dissolved components, with the dissolved components consisting of 1 mol\% $p$-HOPhO-BsubPc and 99 mol\% decafluoro biphenyl. The composition of the dilute solution was selected to ensure that the $p$-HOPhO-BsubPc molecules were too dispersed to participate in intermolecular hydrogen bonds. Decafluoro biphenyl was selected as a mixing component because it does not product FTIR signals in the regions of interest for this experiment, and is not expected to participate in intermolecular interactions with $p$-HOPhO-BsubPc.

Figure 5.9 presents the FTIR spectra obtained from neat and dilute thin films of $p$-HOPhO-BsubPc (7), as well as neat films of PhO-BsubPc and $m$-ClPhO-BsubPc for comparison. The spectrum obtained from a neat film of $p$-HOPhO-BsubPc shows a broad signal between 3100 and 3500 cm\textsuperscript{-1}, consistent with intermolecular hydrogen bonding.\textsuperscript{47,48} Similar signals in this region have been used in the literature to establish the presence of hydrogen bonding interactions in thin film materials for BHJ OPV devices.\textsuperscript{18,25} Notably, the neat film of $p$-HOPhO-BsubPc is the only sample to display a broad signals in the region associated with intermolecular hydrogen bonding. For reference, the O-H stretch associated with free hydroxy groups that do not participate in hydrogen bonding would appear as sharp signals around 3500-3700 cm\textsuperscript{-1}, and the O-H stretch associated with intramolecular hydrogen bonding would appear as sharp signals around 2500-3200 cm\textsuperscript{-1}.\textsuperscript{47} The dilute sample of $p$-HOPhO-BsubPc displays signals between 600 and 1600 cm\textsuperscript{-1} similar to the signals observed in other BsubPc derivatives, confirming the presence of $p$-HOPhO-BsubPc in quantities sufficient to provide a signal. The dilute sample does not display any signals associated with intermolecular hydrogen bonding, although it does contain prominent features in the 2700-3100 cm\textsuperscript{-1} range, consistent with –CH\textsubscript{3} signals from residual toluene.\textsuperscript{47} The
residual toluene was present in the film despite the use of a vacuum oven for 48 hours to dry the sample. Nonetheless, these results confirm that thin, evaporated films of \( p\)-HOPhO-BsubPc (7) do contain intermolecular hydrogen bonds.

### 5.4.3 Organic Photovoltaic (OPV) Device Characterization

OPV devices were fabricated using thermal evaporation according to the device architecture depicted in Figure 5.10. Since the focus of this study is on investigating the effects of intermolecular interactions on device performance, rather than attempting to create an optimal OPV device, we selected a standard device architecture which has been previously studied with the commonly utilized Cl-BsubPc (1) derivative.\(^{29,49}\) As an electron donor material, Cl-BsubPc has been shown to pair well with fullerene as an electron acceptor material.\(^{50}\) Since axial substitution of the Cl atom with a phenoxy moiety is not expected to change the electronic properties of the BsubPc molecule,\(^{32}\) and based on the similar solid state absorption of derivatives 1-7, it was expected that this device architecture would also function with the new derivatives 2-7. Molybdenum oxide (MoO\(_x\)) acts as a hole extraction layer,\(^{42}\) while bathocuproine (BCP) acts as an exciton blocking layer and also serves as a protective layer between the underlying organic C\(_{60}\) layer and the subsequent deposition of hot aluminum atoms.\(^{51}\)

![Figure 5.10: Schematic of the OPV device architecture.](imageURL)

Figure 5.11 demonstrates current density-voltage (J-V) curves measured in the dark (dashed lines) and under 1 sun illumination (solid lines) for the OPV devices, with the shaded regions of the illuminated curves corresponding to the 95\% confidence interval. Average device performance parameters and standard deviations are summarized in Table 5.1. In a single
Figure 5.11: J-V data under 1 sun illumination for BsubPc derivatives as electron donor materials. Shaded regions indicate 95% confidence intervals.

Table 5.1: OPV Device Characterization and Crystal Molar Density, with standard deviations in brackets.

<table>
<thead>
<tr>
<th>BsubPc derivative</th>
<th>$J_{SC}$/mA cm$^{-2}$</th>
<th>$J_{SC,EQE}$/mA cm$^{-2}$</th>
<th>$V_{OC}$/V</th>
<th>FF</th>
<th>$\eta_p$/%</th>
<th>$R_s$/Ω cm$^2$</th>
<th>$R_{SH}$/kΩ cm$^2$</th>
<th>No. of cells, batches</th>
<th>Density/kmol m$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl-BsubPc (1)</td>
<td>4.49 (0.25)</td>
<td>4.09 (0.29)</td>
<td>1.08 (0.01)</td>
<td>0.62 (0.02)</td>
<td>3.03 (0.21)</td>
<td>22.3 (7.3)</td>
<td>1.32 (0.15)</td>
<td>119, 9</td>
<td>3.63 $^{33}$</td>
</tr>
<tr>
<td>PhO-BsubPc (2)</td>
<td>4.38 (0.06)</td>
<td>4.08 (0.01)</td>
<td>1.00 (0.01)</td>
<td>0.62 (0.01)</td>
<td>2.74 (0.05)</td>
<td>28.9 (2.0)</td>
<td>1.60 (0.12)</td>
<td>12, 1</td>
<td>2.91 $^{34}$</td>
</tr>
<tr>
<td>m-FPhO-BsubPc (3)</td>
<td>4.28 (0.05)</td>
<td>3.96 (0.03)</td>
<td>1.04 (0.01)</td>
<td>0.59 (0.01)</td>
<td>2.63 (0.05)</td>
<td>61.2 (3.7)</td>
<td>1.24 (0.05)</td>
<td>28, 1</td>
<td>2.87 $^{35}$</td>
</tr>
<tr>
<td>m-CIPhO-BsubPc (4)</td>
<td>4.37 (0.16)</td>
<td>4.03 (0.05)</td>
<td>1.05 (0.01)</td>
<td>0.65 (0.01)</td>
<td>2.98 (0.09)</td>
<td>17.5 (1.8)</td>
<td>1.30 (0.09)</td>
<td>32, 2</td>
<td>2.81 $^{31}$</td>
</tr>
<tr>
<td>m-BrPhO-BsubPc (5)</td>
<td>4.04 (0.30)</td>
<td>3.83 (0.03)</td>
<td>1.05 (0.01)</td>
<td>0.64 (0.01)</td>
<td>2.73 (0.24)</td>
<td>23.0 (2.2)</td>
<td>1.41 (0.09)</td>
<td>27, 2</td>
<td>2.79 $^{31}$</td>
</tr>
<tr>
<td>m-IPhO-BsubPc (6)</td>
<td>3.89 (0.33)</td>
<td>3.69 (0.01)</td>
<td>1.05 (0.01)</td>
<td>0.62 (0.01)</td>
<td>2.52 (0.20)</td>
<td>26.1 (3.7)</td>
<td>1.40 (0.08)</td>
<td>27, 2</td>
<td>2.73 $^{31}$</td>
</tr>
<tr>
<td>p-HOPhO-BsubPc (7)</td>
<td>3.45 (0.07)</td>
<td>3.11 (0.05)</td>
<td>1.02 (0.01)</td>
<td>0.36 (0.01)</td>
<td>1.26 (0.04)</td>
<td>140 (20)</td>
<td>1.17 (0.05)</td>
<td>9, 1</td>
<td>2.84 $^{30}$</td>
</tr>
</tbody>
</table>
deposition, devices of a new derivative (one of 2-7) were fabricated alongside devices of Cl-BsubPc (1), with the Cl-BsubPc devices serving as an internal reference to verify that the device performances from that deposition were reasonable. The parameters of derivatives 2-7 (Table 5.1) represent average data from 1-2 batches, whereas the parameters for Cl-BsubPc represent average data across all batches. The standard deviation for Cl-BsubPc device parameters is generally significantly higher than the standard deviation for the other derivatives, indicating that device performance varies more greatly batch-to-batch than within-batch. Variations between batches are expected to be the result of minor variations in film thickness, as it is difficult to control layer growth accurately batch-to-batch.

The open circuit voltage ($V_{OC}$) of an OPV device is proportional to the difference between the HOMO of the donor material and the LUMO of the acceptor material. As it is mainly determined by material properties, the $V_{OC}$ is relatively insensitive to variations in film thickness and therefore consistent across various deposition batches, as reflected by the small standard deviation values for the $V_{OC}$ of every material in Table 5.1. The $V_{OC}$ of these devices varies slightly depending on the donor material, from approximately 1.0 V to 1.1 V. This narrow range of values is to be expected, since the same electron acceptor material ($C_{60}$) has been used in every device. In addition, the molecular structure of the donor materials in this study vary only in their axial substituents, and the energy levels of BsubPc derivatives are relatively insensitive to axial substitution. Unsubstituted Cl-BsubPc displays the highest $V_{OC}$, while substitution of the axial chlorine atom with a phenoxy moiety coincides with a slight decrease in $V_{OC}$. The meta-halogenated derivatives ($m$-FPhO-BsubPc (3), $m$-ClPhO-BsubPc (4), $m$-BrPhO-BsubPc (5) and $m$-IPhO-BsubPc (6)) display equivalent $V_{OC}$ values of approximately 1.04-1.05 V, while the PhO-BsubPc and $p$-HOPhO-BsubPc derivatives display the lowest $V_{OC}$ values of approximately 1.00-1.02 V (Figure 5.11).

The batch-to-batch variation for the short-circuit current ($J_{SC}$) is considerably higher than the batch-to-batch variation of either the $V_{OC}$ or the fill factor (FF), as demonstrated by the dataset for Cl-BsubPc (Table 5.1). The $J_{SC}$ of an organic solar cell is sensitive to film thickness, which can vary slightly between batches. The $J_{SC}$ also varies considerably across the materials included in this study. Derivatives 1-4 have similar have very similar $J_{SC}$ values ($J_{SC} \approx 4.3-4.5$ mA cm$^{-2}$), while the $J_{SC}$ values of derivatives 5-7 are substantially lower. For reference, the $J_{SC}$ as determined from the $J$-$V$ curves (Figure 5.11) and the $J_{SC}$ estimated from external quantum
efficiency experiments \( (J_{SC, EQE}) \) are both included in Table 5.1. The corresponding EQE traces are provided in Figure 5.12. The \( J_{SC, EQE} \) values are within 10% of the \( J_{SC} \) values obtained from the J-V data, and these differences are likely due to spectral mismatch between the solar simulator and AMG1.5. Both sets of \( J_{SC} \) data display similar trends.

Figure 5.12: External quantum efficiency (EQE) of devices with BsubPc derivatives as electron donor materials. Gray shaded region indicates the 95% confidence interval for Cl-BsubPc obtained from measurements of 17 cells. Other EQE traces represent average values for 2-3 cells.

The \( J_{SC} \) can be influenced by a number of factors, including: 1) the number of photons that are absorbed from a light source in order to form excitons; 2) the diffusion of excitons to the donor-acceptor interface; 3) the separation of excitons into electrons and holes; 4) the efficiency of charge transport to the electrodes; and 5) the efficiency of charge collection at the electrodes.\(^5\)

The influences of factors 3 and 5 are expected to be minimal, due to the similar optoelectronic and film formation properties of derivatives 1-7 and the use of a consistent architecture for all OPV devices.

With regards to the first factor, one potential cause of a drop in \( J_{SC} \) might be a change in molar density. As molar density decreases, there are fewer molecules in a layer of a given thickness, and fewer photons will be absorbed. The molar density of materials 1-7, as determined from their crystal structures, is included in Table 5.1. Although derivatives 1-4 have very similar \( J_{SC} \) values, they have a fairly large range of molar densities \((2.8 – 3.6 \text{ kmol m}^{-3})\). Derivatives 4-6 have
similar molar densities, yet replacing the meta-chlorine atom with a bromine atom or iodine atom corresponds to a substantial drop in $J_{SC}$. Overall, the molar densities of derivatives 1-7 can be divided into two main categories: the molar density of Cl-BsubPc (1) is the highest at approximately 3.6 kmol m$^{-3}$, while the molar densities of the phenoxy-BsubPc (2-7) derivatives are clustered around 2.8 kmol m$^{-3}$. The trends in molar density are in good agreement with preliminary ellipsometry measurements performed by Dr. Thomas Howells, which predict a drop in absorption of approximately 10% upon changing the axial chlorine atom in 1 to a phenoxy group in derivatives 2-7, with no significant difference in absorption between 2-7. Altogether, these results indicate that differences in molar density account for a drop in photon absorption between 1 and the phenoxy-BsubPc derivatives 2-7. However, differences in molar density and corresponding absorption do not fully account for the differences observed in $J_{SC}$ between derivatives 2-7. The substantial decreases in $J_{SC}$ for derivatives 5-7 are therefore most likely due to problems with exciton diffusion and/or charge transport in these materials.

Interestingly, as the meta-halogen atom is changed from Cl to Br to I in derivatives 4-6, there is a corresponding decrease in the $J_{SC}$ (Cl > Br > I, Table 5.1). As previously mentioned, these materials are capable of halogen bonding. Halogen bond strength increases based on the halogen atom acting as a donor, in the order Cl < Br < I. The lowest $J_{SC}$ was observed for $p$-HOPhO-BsubPc (7), a material which demonstrates strong O-H···N hydrogen bonds in its crystal structure and which also forms hydrogen bonds in thin films as demonstrated using FTIR. Although the crystal structure of $m$-FPhO-BsubPc (3) also includes hydrogen bonds, C-H···F hydrogen bonds are substantially weaker than O-H···N hydrogen bonds.$^{52}$ Taken together, these observations suggest that stronger intermolecular interactions (such as C-Br···N, C-I···N and O-H···N) decrease the $J_{SC}$ of OPV devices, likely by having a detrimental effect on exciton diffusion and/or charge transport.

In addition to noted differences in $J_{SC}$, the FF can also change substantially depending on the BsubPc derivative. The FF values for derivatives 1, 2, and 4-6 are very similar with a range of 0.62 to 0.65, and $J$-$V$ curves of these derivatives (Figure 5.11) correspondingly have very similar shapes. Despite molecular similarities between $m$-FPhO-BsubPc (3) and the other meta-halogenated phenoxy-BsubPcs (4-6), the $J$-$V$ curve of 3 has a distinctly different shape with a slight S-kink (Figure 5.11) and a lower FF (0.59). This observation provides further evidence
that despite molecular similarities, derivatives with different crystal structures will display different characteristics in organic electronic devices. The FF of \( p\text{-HOPhO-BsubPc} \) (7) is the lowest of all seven derivatives (0.36), due to a very pronounced S-kink. The standard Cl-BsubPc devices grown alongside the \( m\text{-FPhO-BsubPc} \) (3) and \( p\text{-HOPhO-BsubPc} \) (7) devices displayed typical device characteristics, confirming that the observed S-kinks are due to a material property related to 3 and 7 rather than a problem with the deposition. S-kinks in \( J-V \) curves may be caused by interface problems due to a mismatch in the energy levels of the materials involved,\(^7\) or may be indicative of charge transport problems, such as a mismatch in the charge carrier mobilities of the donor and acceptor layers.\(^8\) Since derivatives 1-7 have similar electronic properties, the S-kinks in 3 and 7 are therefore most likely related to a charge transport problem.

Aside from the presence or absence of S-kinks, the \( J-V \) curves of derivatives 2-7 also display more subtle differences in shape which can be investigated through the metrics of shunt resistance (\( R_{sh} \)) and series resistance (\( R_s \)). The \( R_{sh} \) and \( R_s \) values in Table 5.1 were estimated from the inverse of the slope of illuminated \( J-V \) curves around \( J_{SC} \) and \( V_{OC} \), respectively. The \( R_{sh} \) of a device accounts for leakage currents caused by recombination sites or device defects such as pinholes, while the \( R_s \) accounts for the resistance associated with the different organic layers and electrodes in the device, as well as contact resistance associated with layer interfaces.\(^5\) In order to have a high FF, the slope of the \( J-V \) curve around \( J_{SC} \) should be low, corresponding to a high \( R_{sh} \), and the slope around \( V_{OC} \) should be high, corresponding to a low \( R_s \). The slope of the \( J-V \) curve around \( J_{SC} \) is similar for all seven derivatives (Figure 5.11), and the \( R_{sh} \) values are therefore also fairly similar (Table 5.1). In contrast, the \( R_s \) values of \( m\text{-FPhO-BsubPc} \) (3) and \( p\text{-HOPhO-BsubPc} \) (7) are significantly higher than the other BsubPc derivatives, indicating that layers of these materials contribute to a higher resistance across the OPV device.

In terms of overall power conversion efficiency (\( \eta_p \), Table 5.1), \( m\text{-ClPhO-BsubPc} \) (4) and Cl-BsubPc (1) are very similar with average efficiencies of approximately 3%. The efficiencies of devices made with other materials are lower, due to: lower \( V_{OC} \) in the case of PhO-BsubPc (2); lower \( J_{SC} \) in the case of \( m\text{-BrPhO-BsubPc} \) (5) and \( m\text{-IPhO-BsubPc} \) (6); and the presence of S-kinks and low FF in the case of \( m\text{-FPhO-BsubPc} \) (3) and \( p\text{-HOPhO-BsubPc} \) (7).
5.5 Conclusions

An array of phenoxy-BsubPc materials featuring similar molecular structures yet distinctly different crystal structures was used to investigate the effect of halogen and hydrogen bonding intermolecular interactions on OPV device performance. Thin films of these materials were characterized using solid state UV-vis absorption and AFM imaging. Direct evidence of the presence of hydrogen bonding interactions in thin films of \( p \)-HOPhO-BsubPc (7) was detected using FTIR techniques. Further indirect evidence, such as notable differences in film morphology and J-V characteristics between \( m \)-FPhO-BsubPc (3) and the molecularly similar meta-halogenated derivative 4-6, suggest that crystal structure and intermolecular interactions play a significant role in determining the film and device characteristics of BsubPc derivatives.

Based on trends observed with relation to crystal structure and device performance characteristics, these results suggest that using materials which are incapable of forming strong halogen or hydrogen bonds (i.e., PhO-BsubPc (2)) or materials that can only for weak halogen bonds (i.e., \( m \)-ClPhO-BsubPc (4)) will not negatively affect FF or \( J_{SC} \). Stronger intermolecular interactions, and particularly the presence of strong, classical hydrogen bonds (i.e., \( p \)-HOPhO-BsubPc (7)), can negatively affect device performance by decreasing FF and/or \( J_{SC} \).
5.6 References


Chapter 6
Predicting the Structure of Co-Crystals Containing Boron Subphthalocyananes Using Symmetry and Compactness Parameters

The work in the second part of this chapter is currently in preparation and will be submitted as a manuscript shortly, to either *Crystal Growth & Design* or *CrystEngComm*. The full reference is:


AJL performed the crystal diffraction experiments and crystal structure refinements. I performed all of the other work, including synthesis, crystallization, crystal analysis, writing and figure creation. The work was supervised by TPB. Note that the introduction section has been shortened from the original manuscript draft in order to remove redundant portions. Parts of the electronic supplementary information (ESI) have also been moved to the main portion of the manuscript.
6.1 Introduction

The importance of relating organic electronic device performance characteristics, such as charge carrier mobility, to the solid state arrangement of the active materials has been emphasized in various studies over the past decade.\textsuperscript{1-7} In the case of BsubPc devices, our group has recently correlated the charge carrier mobility of three fluorinated phenoxy BsubPcs with intermolecular spacing differences.\textsuperscript{8} Since the solid state arrangement is reliant on molecular structure, it is vital to develop a thorough understanding of the methods available for crystal structure modification through chemical derivatization. To this end we have systematically studied the influence of hydrogen bonding,\textsuperscript{9} halogen bonding,\textsuperscript{10} and interactions between $\pi$-acid and $\pi$-basic molecular fragments\textsuperscript{11} on the solid state arrangements of BsubPc derivatives.

Co-crystallization, wherein two or more distinct molecular species of neutral charge self-assemble into a single crystal lattice, offers an additional method of crystal structure control. The permutations and combinations available with co-crystallization enable a much wider variation in solid state arrangements compared with crystals containing a single species. Co-crystal design, chemical component screening and preparation strategies are therefore of interest in a growing number of fields, including but not limited to pharmaceuticals,\textsuperscript{12} the control of solid state reactivity,\textsuperscript{13} and the design of ferroelectric,\textsuperscript{14} porous\textsuperscript{15} and energetic materials.\textsuperscript{16} To date, there are no reports of deliberate co-crystals containing BsubPc molecules, although the Cambridge Crystallographic Data Centre (CCDC) contains several examples of crystal structures incorporating solvent molecules.\textsuperscript{8,9,17}

The design of co-crystals, specifically the selection of two or more complementary molecules that may form a co-crystal, can be aided through considerations such as hydrogen bonding rules\textsuperscript{18} and supramolecular synthons.\textsuperscript{19} However, screening to determine whether or not the selected molecules will form co-crystals, in practice, largely relies on relatively time-consuming empirical methods such as hot stage microscopy,\textsuperscript{20} microfluidic approaches\textsuperscript{21} or high-throughput crystallization techniques.\textsuperscript{22} In contrast, computational co-crystal screening strategies, such as those involving lattice energy calculations,\textsuperscript{23} are comparatively quick and inexpensive with ever-improving success rates. Such methods can also be used to screen molecules that have not yet been synthesized and thereby guide the development of novel compounds for co-crystallization.
In this study, we have developed a method of screening potential pairs of molecules for a specific co-crystal motif using a combination of molecular dynamics and molecular mechanics geometry optimization. We have previously observed that the imine nitrogen atoms (Nᵢ, Figure 6.1) of BsubPcs are reliable hydrogen bond acceptors, and expected that the co-crystal motif illustrated in Figure 6.2 could be created using an appropriate hydrogen bond acceptor in the axial position of a BsubPc derivative. The three pyridyl-substituted BsubPcs (1a-1c) are likely to accept hydrogen bonds through an imine nitrogen atom on the subPc ligand and/or through the pyridine substituent. As bifunctional hydrogen bond donors, three commercially available dihydroxy benzenes (2a-2c) were considered, resulting in a total of 9 possible BsubPc-dihydroxy benzene combinations.

**Figure 6.1:** Structure of pyridyl-substituted BsubPcs (1a-1c) and dihydroxy benzenes (2a-2c). The locations of the imine and pyrrole nitrogens (Nᵢ and Nᵢ, respectively) are indicated on the subPc ligand.

**Figure 6.2:** Targeted co-crystal motif directed by O-H···N hydrogen bonds.
6.2 Experimental
6.2.1 Materials

Catechol, resorcinol and hydroquinone, as well as para-, meta-, and ortho-hydroxy pyridine were purchased from Sigma Aldrich (Mississauga, Ontario, Canada) and used as received. Other common solvents, reagents and silica gel were purchased from Caledon Laboratories (Caledon, Ontario, Canada) and used as received. Br-BsubPc (1) was synthesized according to a procedure previously described by Potz.24

6.2.2 Methods

The reaction progress and purity analysis was performed using a Waters 2695 high pressure liquid chromatography (HPLC) separation module with a Waters 2998 photodiode array and a Waters 4.6 mm x 100 mm SunFire C18 3.5 μm column. HPLC grade acetonitrile and N,N-dimethylformamide were eluted with an isocratic flow of 80/20 (volume/volume) acetonitrile/N,N-dimethylformamide at 0.6 mL/min during operation.

All nuclear magnetic resonance (NMR) spectra were acquired on a Varian Unity 500 MHz spectrometer equipped with a broadband probe. NMR samples were prepared in deuterated chloroform with 0.05% (v/v) tetramethylsilane (TMS) as a 1H NMR reference purchased from Cambridge Isotope Laboratories and used as received. High resolution mass spectrometry (HRMS) was performed on an AccuTOF mass spectrometer (JEOL USA Inc., Peabody, MA) with a DART-SVP ion source (Ionsense Inc., Saugus, MA) using He gas.

X-ray diffraction results were analyzed using PLATON for MS-Windows (April 24 2013 version)25 for bond angles and lengths. Crystal packing images were generated using Mercury version 3.026 and POV-Ray version 3.6.27 All data sets were collected using a Bruker Kappa APEX-DUO diffractometer, with the exception of the data set for the 1:1 p-Py-BsubPc: resorcinol (1c:2b) co-crystal, which was collected using a Nonius KappaCCD diffractometer. The positions of the hydrogen atoms in hydroxy groups were refined independently with isotropic displacement parameters. All other hydrogen atom positions were placed in calculated positions and refined in a riding-model approximation.
Models for co-crystal screening were constructed in the HyperChem Professional 8.0\textsuperscript{28} molecular modeling environment using the MM+ force field. Two explicit hydrogen bonding interactions were introduced per BsubPc molecule: one between an imine nitrogen (N\textsubscript{i}) of the BsubPc bowl and a hydroxy moiety of the dihydroxy benzene molecule, and one between the BsubPc axial pyridyl group and the second hydroxy moiety of the dihydroxy benzene. Starting geometries were generated through molecular dynamics simulations performed in vacuo, with a heating period of 0.1 ps, a soak period of 10 ps at 573 K, and a cooling period of 20 ps. The geometries were then optimized using a modified RM1 semi-empirical method which we have previously described.\textsuperscript{29} Distance and angle metrics between atoms in the models (H⋯N, O⋯N, O-H⋯N and B-O-C) were measured using Mercury version 3.0.\textsuperscript{26}

### 6.2.3 Calculation of Radius of Gyration

For each model, the (x,y,z) coordinates of the atoms were extracted from HyperChem and used in the following equations. In a group of \( n \) atoms, the radius of gyration (\( R \))\textsuperscript{30} is defined as the square root of the weight average of \( r_i^2 \):

\[
R = \left( \frac{\sum_{i=1}^{n} m_i r_i^2}{\sum_{i=1}^{n} m_i} \right)^{1/2}
\]

where \( r_i \) is the distance from a given atom to the center of mass of the group of atoms:

\[
r_i = \sqrt{(x_i - x_{cm})^2 + (y_i - y_{cm})^2 + (z_i - z_{cm})^2}
\]

and the coordinates of the center of mass (\( x_{cm}, y_{cm}, z_{cm} \)) are given by:

\[
x_{cm} = \frac{\sum_{i=1}^{n} m_i x_i}{\sum_{i=1}^{n} m_i} \quad y_{cm} = \frac{\sum_{i=1}^{n} m_i y_i}{\sum_{i=1}^{n} m_i} \quad z_{cm} = \frac{\sum_{i=1}^{n} m_i z_i}{\sum_{i=1}^{n} m_i}
\]

### 6.2.4 Synthesis

**ortho-Pyridylenoxy-boron subphthalocyanine** (\( o-Py\)-BsubPc, 1a).

Bromo-boron subphthalocyanine (Br-BsubPc, 1 g, 2.1 mmol) was mixed with ortho-hydroxypyridine (0.4 g, 4.2 mmol) in chlorobenzene (33 mL) in a round-bottom flask fitted with
a reflux condenser and argon inlet. The reactants were heated to reflux and stirred under argon until HPLC analysis indicated 100% conversion. The reaction liquor was cooled and the solvent was removed by rotary evaporation. Purification was achieved by dissolving the crude product in toluene and vigorously stirring the toluene mixture with 0.15 M KOH solution in distilled water (200 mL) for thirty minutes. The toluene phase was isolated and the toluene was removed by rotary evaporation, yielding a dark pink/magenta powder. Compound 1a (yield 0.83 g, 81%). Purity by HPLC (>99%, max. plot). HPLC $\lambda_{\text{max}}$ (nm) = 562.4, $R_T$ (min) = 2.46; $\delta_H$ (400 MHz; CDCl$_3$; Me$_4$Si) 5.60-5.62 (1H, m), 6.39-6.42 (1H, m), 6.98-7.01 (1H, m), 7.74-7.76 (1H, m), 7.88-7.92 (6H, m), 8.87-8.90 (6H, m); HRMS (DART-TOF+) Calc’d. for [C$_{29}$H$_{16}$BN$_7$O] ([M+H]): m/z 490.15876, found 490.15842.

meta-Pyridylphenoxy-boron subphthalocyanine ($m$-Py-BsubPc, 1b).

1b was synthesized as for 1a except meta-hydroxypyridine was used in place of ortho-hydroxypyridine, yielding compound 1b (yield 0.79 g, 77%). Purity by HPLC (>99%, max. plot). HPLC $\lambda_{\text{max}}$ (nm) = 561.2, $R_T$ (min) = 2.04; $\delta_H$ (400 MHz; CDCl$_3$; Me$_4$Si) 5.68-5.71 (1H, m), 6.70-6.72 (1H, m), 6.82-6.83 (1H, d), 7.88-7.89 (1H, m), 7.90-7.94 (6H, m), 8.84-8.88 (6H, m); HRMS (DART-TOF+) Calc’d. for [C$_{29}$H$_{16}$BN$_7$O] ([M+H]): m/z 490.15876, found 490.15898.

para-Pyridylphenoxy-boron subphthalocyanine ($p$-Py-BsubPc, 1c).

1c was synthesized as for 1a except para-hydroxypyridine was used in place of ortho-hydroxypyridine, yielding compound 1c (yield 0.86 g, 84%). Purity by HPLC (>99%, max. plot). HPLC $\lambda_{\text{max}}$ (nm) = 562.4, $R_T$ (min) = 2.23; $\delta_H$ (400 MHz; CDCl$_3$; Me$_4$Si) 5.27-5.29 (2H, m), 7.92-7.96 (8H, m), 8.87-8.91 (6H, m); HRMS (DART-TOF+) Calc’d. for [C$_{29}$H$_{16}$BN$_7$O] ([M+H]): m/z 490.15876, found 490.15828.

6.2.5 Preparation of Single Crystals

The 1c:2b combination, identified as the most likely pair of molecules to form a co-crystal, was screened using vapor diffusion crystallization with a variety of solvent combinations, as listed in Table 6.1. The largest, highest-quality single crystals were obtained using 1.5 mg of pyridyl-substituted BsubPc per mL of acetone, with hexanes as the antisolvent and 2.2 moles of
resorcinol per mole of pyridyl-substituted BsubPc. These crystallization conditions were subsequently used in attempts to grow single crystals using the other 8 molecule pairs.

Samples solutions were prepared by dissolving the appropriate pyridyl-containing BsubPc derivative (20 mg, 0.041 mmol) and the appropriate dihydroxy benzene derivative (10 mg, 0.090 mmol) in acetone (13.5 mL). The sample solution was then filtered using a syringe microfilter and transferred to a 20-mL vial. The opening of the vial was covered with aluminum foil, and the foil was punctured with small holes. The vial was sealed in a larger airtight container with the appropriate diffusing solvent (150 mL of hexanes or heptane) and left undisturbed for 2-3 weeks.

Table 6.1: Crystallization conditions screened with p-Py-BsubPc:resorcinol (1c:2b)

<table>
<thead>
<tr>
<th>Variable</th>
<th>Conditions screened</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent</td>
<td>Acetone, Acetonitrile, Tetrahydrofuran</td>
</tr>
<tr>
<td>Antisolvent</td>
<td>Hexanes, Heptane</td>
</tr>
<tr>
<td>Concentration of p-Py-BsubPc (1c) in solvent (mg/mL)</td>
<td>1.5, 2.0, 2.5</td>
</tr>
<tr>
<td>Molar ratio of resorcinol (2b) to p-Py-BsubPc (1c)</td>
<td>1.1, 2.2</td>
</tr>
</tbody>
</table>
6.3 Results and Discussion

In order to screen these 9 combinations for their potential to form the targeted co-crystal motif, models of each combination were constructed in the HyperChem Professional 8.0 (Hypercube, Inc.) molecular modeling environment. Two explicit hydrogen bonding interactions were introduced per BsubPc molecule: one between an imine nitrogen (N_i) of the BsubPc bowl and a hydroxy moiety of the dihydroxy benzene molecule, and one between the BsubPc axial pyridyl group and the second hydroxy moiety of the dihydroxy benzene. To generate the starting geometries, molecular dynamics simulations were performed in vacuo. The geometries were then optimized using a modified RM1 semi-empirical method which we have previously described.\textsuperscript{29}

We evaluated each of the resulting 9 models (Figure 6.3) on the basis of typical hydrogen bonding metrics and the boron-oxygen-carbon (B-O-C) angle. Strong hydrogen bonds typically have hydrogen-acceptor (H⋯A) distances ranging from 1.5-2.2 Å, donor-acceptor (D⋯A) distances ranging from 2.5-3.2 Å, and donor-hydrogen-acceptor (D-H⋯A) angles ranging from 130-180°.\textsuperscript{31} The preferred B-O-C angle for a single isolated phenoxy-BsubPc molecule is approximately 115-116°,\textsuperscript{32} although angles of up to approximately 130° have been observed in single crystal structures containing particularly strong intermolecular interactions.\textsuperscript{9-10} Other than the 1a:2a model, which contains one very distorted hydrogen bond, all of the models contain reasonable hydrogen bonding metrics and B-O-C angles. The absolute values of these metrics do not differ substantially from model to model, and therefore the values alone do not seem to provide a clear method of evaluating or screening the models for their ability to produce co-crystals, aside from eliminating 1a:2a as a likely candidate.

The models were next evaluated by considering the fundamental properties of a crystal structure. Crystals are, by definition, composed of atoms or molecules in a condensed state, which are arranged according to a significant degree of symmetry. If the molecules of a molecular crystal are in a symmetric arrangement, then it follows that the intramolecular angles within the molecules and the intermolecular interactions between the molecules are also symmetric. The symmetry of the models can therefore be evaluated by calculating the standard deviation of the hydrogen bonding metrics and the B-O-C angles; these values are also provided in the graphs in Figure 6.3b-6.3c. Lower standard deviation values on these metrics correspond to models that are more symmetrical. In order to evaluate how condensed or compact the models are, the radius of
Figure 6.3: Modeled pairs of BsubPc-dihydroxy benzene molecules obtained from molecular dynamics and molecular mechanics geometry optimization simulations. (a) Radius of gyration (R) values are given below each model. The graphs summarize the modeled (b) H···N and O···N distances, and (c) the O-H···N and B-O-C angles.
gyration (R) was calculated for each model (calculation details provided in the Experimental section); these values are given in Figure 6.3a. If the models in Figure 6.3a are conceptualized as a collection of atoms, each of mass \( m_i \) and located a distance \( r_i \) from the center of mass of the model, then the R value is essentially a mass-averaged distance of an atom in the model relative to the center of mass of the model. Smaller R values correspond to more compact models. On the basis of symmetry (small standard deviation values in Figure 6.3b and 6.3c) and compactness (small R values in Figure 6.3a), the 1c:2b model was identified as the most likely candidate to form the targeted co-crystal motif.

In order to assess the accuracy of the computational model screening method, the 9 molecule pairs were used for solution phase co-crystal experiments (Table 6.2). Pyridyl-substituted BsubPcs (1a-1c) were synthesized by adapting a previously published procedure.\(^{32,33}\) Full synthesis and crystallization details are provided in the Experimental section. The positions of hydrogen atoms in hydroxy moieties were refined independently with isotropic displacement parameters. Three BsubPc:dihydroxy benzene combinations (1b:2a, 1c:2b and 1c:2c) yielded co-crystals. Despite numerous attempts, we were not able to obtain a single crystal from the 1c:2a combination. All combinations involving o-Py-BsubPc (1a) yielded single crystals of the parent compound (1a) rather than co-crystals. Likewise, the 1b:2b and 1b:2c combinations yielded single crystals of 1b. A solid state arrangement for m-Py-BsubPc (1b) has been previously published,\(^{34}\) and the structure we report here is equivalent. The synthesis and solid state arrangement of the ortho-substituted analogue (1a) are reported here for the first time. Despite crystallizing in different space groups, the intermolecular interactions in the solid state arrangements for 1a and 1b are similar: both contain weak C-H-\( \cdots \)N hydrogen bonds (Table 6.3), as well as \( \pi-\pi \) interactions between concave surfaces of adjacent subPc bowl fragments (Table 6.4) and several weak CH-\( \pi \) interactions (Table 6.5).

The crystal structure obtained for 1c:2b (1:1 p-Py-BsubPc: resorcinol), shown in Figure 6.4a, is strikingly similar to the arrangement predicted by computational modeling (Figure 6.3). A total of four strong O-H-\( \cdots \)N hydrogen bonds between two resorcinol molecules and two p-Py-BsubPc molecules direct the solid state arrangement into the targeted co-crystal motif. The O3-H30-\( \cdots \)N6 hydrogen bond is supported by a cooperative, weak C3-H3A-\( \cdots \)O3 hydrogen bond; we have previously observed similar supporting C-H-\( \cdots \)O hydrogen bonds in the solid state arrangements.
Table 6.2:  Selected crystallographic parameters.

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<th>Compound reference</th>
<th>1a</th>
<th>1b</th>
<th>1b: 2a</th>
<th>1c: 2b</th>
<th>1c: 2c</th>
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</thead>
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<tr>
<td></td>
<td>(o-Py-BsubPc)</td>
<td>(m-Py-BsubPc)</td>
<td>(1:1</td>
<td>(1:1</td>
<td>(2:1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>m-Py-BsubPc: catechol</td>
<td>p-Py-BsubPc: resorcinol</td>
<td>p-Py-BsubPc: hydroquinone</td>
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<tr>
<td>Empirical formula</td>
<td>C_{29}H_{16}BN_7O</td>
<td>C_{29}H_{16}BN_7O</td>
<td>C_{29}H_{16}BN_7O \cdot C_6H_6O_2</td>
<td>C_{29}H_{16}BN_7O \cdot C_6H_6O_2</td>
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<td>Formula mass</td>
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<td>489.30</td>
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<td>599.40</td>
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<td>triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P 2_1/n</td>
<td>P -1</td>
<td>P -1</td>
<td>P 2_1/n</td>
<td>P -1</td>
</tr>
<tr>
<td>Temperature/K</td>
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</tr>
<tr>
<td>a/Å</td>
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<td>10.0610(5)</td>
<td>8.6045(4)</td>
<td>15.333(4)</td>
<td>9.390(4)</td>
</tr>
<tr>
<td>b/Å</td>
<td>9.6111(12)</td>
<td>10.6973(6)</td>
<td>11.3342(6)</td>
<td>11.262(3)</td>
<td>11.807(7)</td>
</tr>
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<td>c/Å</td>
<td>16.998(2)</td>
<td>11.6977(6)</td>
<td>14.8480(8)</td>
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<td>95.731(3)</td>
<td>90</td>
<td>66.23(2)</td>
</tr>
<tr>
<td>β/°</td>
<td>112.947(3)</td>
<td>77.423(2)</td>
<td>99.123(3)</td>
<td>97.686(6)</td>
<td>69.401(17)</td>
</tr>
<tr>
<td>γ/°</td>
<td>90</td>
<td>65.203(2)</td>
<td>98.033(3)</td>
<td>90</td>
<td>77.85(2)</td>
</tr>
<tr>
<td>Unit cell volume/Å^3</td>
<td>2238.3(5)</td>
<td>1115.13(10)</td>
<td>1404.64(13)</td>
<td>2776.1(13)</td>
<td>1250.9(12)</td>
</tr>
<tr>
<td>No. of formula units per unit cell, Z</td>
<td>4</td>
<td>2</td>
<td>2</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>No. of reflections measured</td>
<td>39795</td>
<td>11626</td>
<td>13229</td>
<td>48564</td>
<td>18207</td>
</tr>
<tr>
<td>No. of independent reflections</td>
<td>5148</td>
<td>3740</td>
<td>4758</td>
<td>6401</td>
<td>5733</td>
</tr>
<tr>
<td>Final R_f values (I &gt; 2σ(I))</td>
<td>0.0383</td>
<td>0.0319</td>
<td>0.0327</td>
<td>0.0388</td>
<td>0.0385</td>
</tr>
<tr>
<td>Final wR(F^2) values (all data)</td>
<td>0.0963</td>
<td>0.0815</td>
<td>0.0831</td>
<td>0.0948</td>
<td>0.0997</td>
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### Table 6.3: BsubPc intramolecular metrics and hydrogen bond geometry

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</tr>
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<tbody>
<tr>
<td>1a</td>
<td>o-Py-BsubPc</td>
<td>121.44(11)</td>
<td>2.5445(17)</td>
<td>C13-H13A···N4</td>
<td>0.95</td>
<td>2.61</td>
<td>3.360(19)</td>
</tr>
<tr>
<td>1b</td>
<td>m-Py-BsubPc</td>
<td>115.52(9)</td>
<td>2.5479(14)</td>
<td>C14-H14A···N4</td>
<td>0.95</td>
<td>2.61</td>
<td>3.367(16)</td>
</tr>
<tr>
<td>1b:2a</td>
<td>m-Py-BsubPc: catechol (1:1)</td>
<td>116.73(10)</td>
<td>2.2091(15)</td>
<td>O2-H20···N1</td>
<td>0.87(2)</td>
<td>1.93(2)</td>
<td>2.7940(15)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>O3-H30···O2</td>
<td>0.87(2)</td>
<td>2.31(2)</td>
<td>2.7171(15)</td>
</tr>
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<td></td>
<td>O3-H30···N7</td>
<td>0.87(2)</td>
<td>1.93(2)</td>
<td>2.7528(17)</td>
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<td>C6-H6A···O1</td>
<td>0.95</td>
<td>2.53</td>
<td>3.3763(16)</td>
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<td>C21-H21A···O3</td>
<td>0.95</td>
<td>2.56</td>
<td>3.4388(18)</td>
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<td>1c:2b</td>
<td>p-Py-BsubPc: resorcinol (1:1)</td>
<td>119.15(11)</td>
<td>2.7244(16)</td>
<td>O2-H20···N7</td>
<td>0.98(2)</td>
<td>1.77(2)</td>
<td>2.7308(18)</td>
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<td></td>
<td>O3-H30···N6</td>
<td>0.94(2)</td>
<td>1.88(2)</td>
<td>2.7791(18)</td>
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<td></td>
<td>C3-H3A···O4</td>
<td>0.95</td>
<td>2.46</td>
<td>3.245(2)</td>
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<td>C20-H20A···O3</td>
<td>0.95</td>
<td>2.5</td>
<td>3.253(2)</td>
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<td>1c:2c</td>
<td>p-Py-BsubPc: hydroquinone (1:0.5)</td>
<td>127.99(12)</td>
<td>2.5898(16)</td>
<td>O2-H20···N7</td>
<td>0.95(3)</td>
<td>1.83(3)</td>
<td>2.741(3)</td>
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<td>C13-H13A···O2</td>
<td>0.95</td>
<td>2.44</td>
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### Table 6.4: Selected Cg···Cg (π-π) interactions

<table>
<thead>
<tr>
<th>Motif</th>
<th>Cg(I)-Cg(J)</th>
<th>Cg-Cg (Å)</th>
<th>Alpha (°) a</th>
<th>π-π Interaction Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>o-Py-BsubPc</td>
<td>Cg(3)-Cg(10)</td>
<td>3.5450(9)</td>
<td>4.08(7)</td>
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<tr>
<td>1b</td>
<td>m-Py-BsubPc</td>
<td>Cg(3)-Cg(10)</td>
<td>3.6876(7)</td>
<td>4.51(6)</td>
</tr>
<tr>
<td>1b:2a</td>
<td>m-Py-BsubPc: catechol (1:1)</td>
<td>Cg(8)-Cg(3)</td>
<td>4.1327(8)</td>
<td>30.92(7)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cg(8)-Cg(2)</td>
<td>4.1687(8)</td>
<td>39.17(7)</td>
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<tr>
<td></td>
<td></td>
<td>Cg(8)-Cg(1)</td>
<td>4.3089(8)</td>
<td>3.47(7)</td>
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<tr>
<td></td>
<td></td>
<td>Cg(2)-Cg(9)</td>
<td>4.6071(8)</td>
<td>1.06(7)</td>
</tr>
<tr>
<td>1c:2b</td>
<td>p-Py-BsubPc: resorcinol (1:1)</td>
<td>Cg(2)-Cg(9)</td>
<td>3.8652(13)</td>
<td>3.97(8)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cg(1)-Cg(7)</td>
<td>3.9211(13)</td>
<td>13.93(7)</td>
</tr>
<tr>
<td>1c:2c</td>
<td>p-Py-BsubPc: hydroquinone (1:0.5)</td>
<td>Cg(1)-Cg(8)</td>
<td>3.490(2)</td>
<td>0.37(7)</td>
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<td>Cg(3)-Cg(10)</td>
<td>3.633(2)</td>
<td>3.81(8)</td>
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* Alpha is the dihedral angle between planes I and J (°)
Table 6.5: Selected C-H…Cg (C-H-\(\pi\)) interactions

<table>
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<tr>
<th>Motif</th>
<th>X-H(I)</th>
<th>Cg(J)</th>
<th>H..Cg (Å)</th>
<th>X-H..Cg (°)</th>
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<tbody>
<tr>
<td>1a o-Py-BsubPc</td>
<td>C(12)-H(12A)</td>
<td>Cg(3)</td>
<td>2.75</td>
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<td>C(20)-H(20A)(^a)</td>
<td>Cg(1)(^a)</td>
<td>2.73</td>
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<td>C(21)-H(21A)(^a)</td>
<td>Cg(2)(^a)</td>
<td>2.82</td>
<td>114</td>
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<tr>
<td>1b m-Py-BsubPc</td>
<td>C(12)-H(12A)</td>
<td>Cg(10)</td>
<td>2.78</td>
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<td>C(20)-H(20A)(^a)</td>
<td>Cg(1)(^a)</td>
<td>2.85</td>
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<td>C(21)-H(21A)(^a)</td>
<td>Cg(2)(^a)</td>
<td>2.79</td>
<td>110</td>
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<tr>
<td>1b:2a m-Py-BsubPc: catechol (1:1)</td>
<td>C(20)-H(20A)</td>
<td>Cg(26)</td>
<td>2.91</td>
<td>150</td>
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<td>C(27)-H(27A)</td>
<td>Cg(26)</td>
<td>2.82</td>
<td>140</td>
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<td>1c:2b p-Py-BsubPc: resorcinol (1:1)</td>
<td>C(4)-H(4A)</td>
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<td>2.80</td>
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<td>C(6)-H(6A)</td>
<td>Cg(10)</td>
<td>2.65</td>
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<tr>
<td></td>
<td>C(12)-H(12A)(^a)</td>
<td>Cg(3)(^a)</td>
<td>2.92</td>
<td>106</td>
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<tr>
<td></td>
<td>C(12)-H(12A)(^a)</td>
<td>Cg(10)(^a)</td>
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<tr>
<td></td>
<td>C(13)-H(13A)(^a)</td>
<td>Cg(1)(^a)</td>
<td>2.88</td>
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<tr>
<td></td>
<td>C(28)-H(28A)</td>
<td>Cg(26)(^a)</td>
<td>2.98</td>
<td>118</td>
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<td>1c:2c p-Py-BsubPc: hydroquinone (1:0.5)</td>
<td>C(3)-H(3A)</td>
<td>Cg(7)</td>
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<td>C(20)-H(20A)(^a)</td>
<td>Cg(1)(^a)</td>
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<td></td>
<td>C(21)-H(21A)(^a)</td>
<td>Cg(2)(^a)</td>
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<tr>
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<td>C(30)-H(30)</td>
<td>Cg(7)</td>
<td>2.90</td>
<td>112</td>
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</table>

\(^a\)These interactions support the concave-concave \(\pi\)-\(\pi\) interactions listed in Table 6.4.

of hydroxy-containing BsubPcs.\(^9\) The \(O3\) atom acts as a bifurcated hydrogen bond acceptor by participating in the weak C20-H20A-\(O3\) hydrogen bond (Table 6.3, Figure 6.5). In addition to the described hydrogen bonds, the crystal structure of the 1c:2b co-crystal contains examples of \(\pi\)-\(\pi\) and CH-\(\pi\) interactions; details of these interactions are demonstrated in Figures 6.6 and 6.7. As a result of the \(\pi\)-\(\pi\) and CH-\(\pi\) interactions, the targeted co-crystal motif is incorporated into a larger three-dimensional network of molecules.

Although the co-crystal crystal structure obtained for 1b:2a (Figure 6.4b) also consists of a 1:1 ratio of pyridyl-substituted BsubPc:dihydroxy benzene molecules, this combination adopts a catemeric arrangement rather than the targeted tetrameric co-crystal motif. Each \(m\)-Py-BsubPc
Figure 6.4: The molecular packing arrangements of the (a) 1:1 \( p \)-Py-BsubPc: resorcinol (1c: 2b), (b) 1:1 \( m \)-Py-BsubPc: catechol (1b: 2a), and (c) 1:0.5 \( p \)-Py-BsubPc: hydroquinone (1c: 2c) co-crystals. Strong hydrogen bonds depicted as red dotted lines and weak hydrogen bonds depicted as blue dotted lines. Key: carbon = grey; nitrogen = light purple; oxygen = red; boron = pink; hydrogen = white. For clarity, non-hydrogen atoms involved in hydrogen bonds shown as 50% ellipsoids; interacting hydrogen atoms shown as balls; non-interacting hydrogen atoms omitted.
**Figure 6.5:** Bifurcated hydrogen bond in 1:1 *p*-Py-BsubPc: resorcinol (1c:2b) co-crystal. Oxygen atom O1 is in a bifurcated acceptor arrangement. Hydrogen atoms H3A and H20A are at distances of approximately 0.45 Å and 0.02 Å, respectively, to a plane passing through O3, C3 and C20; this planarity is typical of bifurcated hydrogen bonds.31 Strong hydrogen bonds are depicted as red dotted lines and weak hydrogen bonds are depicted as blue dotted lines. Colours: carbon = grey; nitrogen = light purple; oxygen = red; boron = pink; hydrogen = white. For clarity, non-hydrogen atoms involved in hydrogen bonds shown as 50% ellipsoids; interacting hydrogen atoms shown as balls; non-interacting and non-hydroxy hydrogen atoms omitted.

**Figure 6.6:** The molecular packing arrangement of the 1:1 *p*-Py-BsubPc: resorcinol (1c:2b) co-crystal, demonstrating two π-π interactions: a concave-concave π-π interaction (shown in green) and an interaction between the pyridyl axial group and the convex side of a bowl (shown in purple). The latter results in a close contact between two carbon atoms on neighbouring molecules (shown in grey: C27···C8 \( \equiv 3.10 \) Å). Colours: carbon = grey; nitrogen = light purple; oxygen = red; boron = pink; hydrogen = white. Hydrogen atoms omitted for clarity.
**Figure 6.7:** The molecular packing arrangement of the 1:1 *p*-Py-BsubPc: resorcinol (**1c:2b**) co-crystal, demonstrating CH-π interactions. Colours: carbon = grey; nitrogen = light purple; oxygen = red; boron = pink; hydrogen = white. For clarity, non-interacting and non-hydroxy hydrogen atoms omitted.

The molecule is associated with two different catechol molecules through strong O-H···N hydrogen bonds (Table 6.3). The H30 atom of the resorcinol molecule is in a bifurcated donor arrangement, as it is closely associated with both the N7 pyridyl atom in *m*-Py-BsubPc and the intramolecular O2 atom (Figure 6.4b and 6.8). Although the O3-H30···O2 hydrogen bond is intramolecular, the relatively small O3-H30···N7 and O3-H30···O2 angles (approximately 158° and 109°, respectively) are characteristic of bifurcated arrangements. This catemeric co-crystal motif is therefore primarily directed by three strong hydrogen bonds, although two weak C-H···O hydrogen bonds (Table 6.3, Figure 6.9) are also present. As discussed in Chapter 4, the phenoxy oxygen atom can sometimes act as an acceptor for weak C-H···O hydrogen bonds, though such interactions do not appear to have a very significant effect on the overall crystal structure. In addition to the hydrogen bonding interactions, each BsubPc molecule is associated with two neighbouring BsubPc molecules through one concave-concave π-π interaction and one convex-convex π-π interaction. These π-π interactions form a second ribbon-like motif (Figure 6.10, Table 6.4) within the crystal structure.
Figure 6.8: Bifurcated hydrogen bond in the 1:1 m-Py-BsubPc: catechol (1b:2a) co-crystal. Hydrogen atom H30 is in a bifurcated donor arrangement, and lies at a distance of approximately 0.06 Å to a plane passing through O3, N7 and O2; this planarity is typical of bifurcated hydrogen bonds. Strong hydrogen bonds are depicted as red dotted lines. Colours: carbon = grey; nitrogen = light purple; oxygen = red; boron = pink; hydrogen = white. For clarity, non-hydrogen atoms involved in hydrogen bonds shown as 50% ellipsoids; interacting hydrogen atoms shown as balls; non-interacting and non-hydroxy hydrogen atoms omitted.

Figure 6.9: Weak hydrogen bonds, shown as blue dashed lines, in the 1:1 m-Py-BsubPc: catechol (1b:2a) co-crystal. Colours: carbon = grey; nitrogen = light purple; oxygen = red; boron = pink; hydrogen = white. For clarity, non-hydrogen atoms involved in hydrogen bonds shown as 50% ellipsoids; interacting hydrogen atoms shown as balls; non-interacting and non-hydroxy hydrogen atoms omitted.
Figure 6.10: The molecular packing arrangement of the 1:1 \( m \)-Py-BsubPc: catechol (\( 1b:2a \)) co-crystal, demonstrating two \( \pi-\pi \) interactions: a concave-concave \( \pi-\pi \) interaction (shown in green) and a convex-convex \( \pi-\pi \) interaction (shown in purple). The latter results in a close contact between two carbon atoms on neighbouring molecules (shown in grey: C14⋯C16 \( \equiv 3.05 \, \text{Å} \)). Colours: carbon = grey; nitrogen = light purple; oxygen = red; boron = pink; hydrogen = white. Hydrogen atoms omitted for clarity.

It is worth noting that the geometry of the concave-concave \( \pi-\pi \) interaction in the \( 1b:2a \) co-crystal is somewhat unusual. In typical BsubPc solid state arrangements, the closest contacts of the concave-concave \( \pi-\pi \) interaction occur between two parallel or nearly-parallel diiminoisoindoline arms of adjacent molecules (Figure 6.6); this particular geometry could be termed a parallel concave-concave \( \pi-\pi \) interaction. In the \( 1b:2a \) co-crystal, the six-membered ring of one BsubPc molecule’s diiminoisoindoline arm is roughly centered in the bowl of an adjacent BsubPc molecule, resulting in three close contacts between that six-membered ring and the three five-membered rings of the adjacent molecule’s bowl (Figure 6.10). Interestingly, this deviation from the expected concave-concave \( \pi-\pi \) interaction geometry occurs alongside a noticeable distortion to the depth of the BsubPc bowl. The preferred bowl depth of a single isolated phenoxy-BsubPc molecule, determined using a simple semi-empirical RM1 model, is approximately 2.71 to 2.72 Å.\(^{11}\) The bowl of \( 1b \) in this solid state arrangement is significantly shallower with a bowl depth of approximately 2.21 Å (Table 6.3). Additionally, the parallel concave-concave \( \pi-\pi \) interaction is typically supported by close CH-\( \pi \) interactions occurring between the two adjacent bowls. The crystal structure of \( 1b:2a \) does contain two CH-\( \pi \)
Figure 6.11: The molecular packing arrangement of the 1:1 \( m \)-Py-BsubPc: catechol (1b:2a) co-crystal, demonstrating CH-\( \pi \) interactions. Colours: carbon = grey; nitrogen = light purple; oxygen = red; boron = pink; hydrogen = white.

Figure 6.12: The molecular packing arrangement of the 1:0.5 \( p \)-Py-BsubPc: hydroquinone (1c:2c) co-crystal, demonstrating two \( \pi-\pi \) interactions: a concave-concave \( \pi-\pi \) interaction (shown in green) and a convex-convex \( \pi-\pi \) interaction (shown in purple). Strong hydrogen bonds shown as red dashed lines. Colours: carbon = grey; nitrogen = light purple; oxygen = red; boron = pink; hydrogen = white. For clarity, non-hydrogen atoms involved in hydrogen bonds shown as 50% ellipsoids; interacting hydrogen atoms shown as balls; non-interacting and non-hydroxy hydrogen atoms omitted.
interactions between a BsubPc molecule and a resorcinol molecule (Figure 6.11), but there are no CH-π interactions associated with the concave-concave π-π interaction.

**Figure 6.13:** Strong and weak hydrogen bonds in the 1:0.5 p-Py-BsubPc: hydroquinone (1c:2c) co-crystal, shown as red and blue dashed lines respectively. Colours: carbon = grey; nitrogen = light purple; oxygen = red; boron = pink; hydrogen = white. For clarity, non-hydrogen atoms involved in hydrogen bonds shown as 50% ellipsoids; interacting hydrogen atoms shown as balls; non-interacting and non-hydroxy hydrogen atoms omitted.

In contrast to the two previously discussed co-crystals, the crystal structure of 1c:2c (Figure 6.4c) contains a 2:1 molar ratio of p-Py-BsubPc:hydroquinone. The hydroquinone molecules are located on inversion centers, and two strong O2-H20···N7 hydrogen bonds (Table 6.3) associate each hydroquinone molecule with two neighbouring pyridyl groups, forming a trimeric arrangement with inversion symmetry. Both concave-concave and convex-convex π-π interactions are present within the structure, forming ribbon-like arrangements of BsubPc molecules (Figure 6.12, Table 6.4). The ribbons formed by π-π interactions are bridged by hydroquinone molecules through hydrogen bonds, forming two-dimensional sheets of closely associated molecules (Figure 6.12). The O2 atom participates in a second hydrogen bond by accepting a weak C-H···O hydrogen bond from the bowl of an adjacent BsubPc molecule (Table 6.3, Figure 6.13); these weak hydrogen bonds extend the network of associated molecules into
three dimensions. Additionally, the axial pyridyl group of each BsubPc molecules participates in two CH-π interactions; further details are provided in Figure 6.14 and Table 6.5).

**Figure 6.14:** The molecular packing arrangement of the 1:0.5 p-Py-BsubPc: hydroquinone (1c:2c) co-crystal, demonstrating the strong O2-H20···N7 hydrogen bond (shown as red dashed lines) as well as two CH-π interactions (shown in cyan). The C30-H30···Cg(7) interaction occurs alongside a close contact between two carbon atoms on neighbouring molecules (shown in grey: C24···C30 ≈ 3.18 Å). Colours: carbon = grey; nitrogen = light purple; oxygen = red; boron = pink; hydrogen = white. For clarity, non-hydrogen atoms involved in hydrogen bonds shown as 50% ellipsoids; interacting hydrogen atoms shown as balls; non-interacting and non-hydroxy hydrogen atoms omitted.
6.4 Conclusions

To summarize, in this study we have developed a virtual method of screening potential pairs of molecules for a specific co-crystal motif using a combination of molecular dynamics and molecular mechanics. The models generated using this method can be quantitatively evaluated by considering two essential elements of a crystal solid state arrangement: (1) symmetry, as exemplified by small standard deviations for inter- and intramolecular metrics, and (2) compactness, as exemplified by small radius of gyration values. This rational approach has been successfully employed to screen nine molecule pairs and correctly identify the pair of molecules that were most likely to self-assemble in the targeted tetrameric co-crystal motif, ultimately producing the first reported co-crystals containing BsubPc derivatives.
6.5 References


Chapter 7
A Boron Subphthalocyanine Polymer: Poly(4-methylstyrene)-co-Poly(Phenoxy Boron Subphthalocyanine)

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JDD and I are both credited as first authors on this publication.

ASP conducted the experiments attempting to synthesize a BsubPc-containing monomer (Scheme 7.1). BHL conducted the experiments to determine that compound 1b was a radical scavenger. EB conducted initial experiments to develop the synthetic process for homopolymers 3 and 4 (Scheme 7.2). I determined that the target homopolymer 5 could not be synthesized from 3 or 4. I proposed using the “patterns of reactivity” method to select an appropriate comonomer in order to synthesize copolymers. I then developed synthesis and purification procedures for the copolymers 6a, 7a, 8a, 9a, 9b, 10a, 10b, 11a and 11b (Scheme 7.2). I also performed GC and GPC analysis confirming that the copolymers were approximately random and that BsubPc was incorporated into the final polymer. JDD performed additional copolymer synthesis as required, and characterized the copolymers via NMR. JDD also performed characterization with UV-vis, photoluminescence and fluorescence. JDD and I were equally responsible for creating the text and figures. The work was supervised by TPB.

Note that the introduction section has been shortened from the original article in order to remove redundant portions, such as an introduction to the boron subphthalocyanine (BsubPc) class of materials. Some of the information originally contained in the electronic supplementary information (ESI) has been moved to the main body of text.
7.1 Introduction

Despite the widespread use of both small molecules and polymer materials as functional components in organic electronics, all investigations focusing on BsubPc derivatives to date have been limited to the study of BsubPcs as small molecule species; there has yet to be a report on the synthesis and physical characterization of a BsubPc-containing polymer. In contrast, there are a number of reports on normal phthalocyanine (Pc) containing polymers, which differ in the location of the Pc fragments within the macromolecule: within the main chain,\(^\text{1-4}\) as a side chain (pendant),\(^\text{5-7}\) or as the main fragment making up a network polymer.\(^\text{8-12}\)

Many semiconducting polymers of interest in the field of organic electronics contain the functional conjugated component within the main chain of the polymer. Examples include poly(paraphenylene)s, poly(thiophene)s, poly(pyrrole)s, poly-(ethylene dioxythiophene)s, poly(fluorene)s, poly(carbazole)s, and various donor−acceptor copolymers.\(^\text{13}\) In each case, the polymer is produced by the polycondensation of two difunctional monomers or a single bifunctional monomer. We can surmise that the lack of precedent for a BsubPc-containing polymer is attributed to the practical improbability of producing a difunctional or bifunctional monomer of the \(\text{C}_{3\text{v}}\) symmetric BsubPc.

It has been stated that polymeric organic electronic materials benefit from cost-effective fabrication techniques including roll-to-roll solution coating\(^\text{14}\) and inkjet printing,\(^\text{15}\) and it is thus desirable to study a polymeric version of BsubPc for direct comparison with its small molecule analogues. Herein, we describe the synthesis of the first polymeric BsubPc, poly(4-methylstyrene)-co-poly(Phenoxy boron subphthalocyanine), which has been achieved using a postpolymerization transformation strategy. We emphasize the practical importance of this approach and outline the basic physical properties of the novel BsubPc-containing polymer(s).
7.2 Experimental

7.2.1 Materials

All ACS grade solvents, HPLC grade solvents, potassium hydroxide, sulfuric acid, and sodium bicarbonate were purchased from Caledon Laboratories (Caledon, Ontario, Canada) and used without further purification unless otherwise stated. 2,2,6,6-Tetramethyl-1-piperidinyloxy (TEMPO), 4-acetoxy styrene (4-AS), 4-methyl styrene (4-MS), benzoyl peroxide (BPO), and boron tribromide were purchased from Sigma-Aldrich Chemical Co. (Mississauga, Ontario, Canada) and used as received. Phththalonitrile was purchased from TCI America (Portland, OR) and used as received. Bromobenzene was purchased from Alfa Aesar (Ward Hill, MA) and used as received. Deuterated chloroform with 0.05% (v/v) tetramethylsilane (TMS) was purchased from Cambridge Isotope Laboratories (St. Leonard, Quebec, Canada) and used as received. Column chromatography was performed with Silica Gel P60 (mesh size 40–63 μm) obtained from Silicycle. Thin layer chromatography (TLC) was performed on aluminum plates coated with silica (pore size of 60 Å) and fluorescent indicator, obtained from Whatman Ltd., and visualized under UV (254 nm) light. Soxhlet extractions were performed using Whatman single thickness cellulose extraction thimbles (25 × 80 mm).

7.2.2 Methods

Nuclear magnetic resonance (NMR) spectra were recorded on a Varian Mercury spectrometer at 23 °C in deuterated chloroform, operating at 400 MHz for $^1$H NMR. Chemical shifts (δ) are reported in parts per million (ppm) relative to tetramethylsilane (0 ppm) for $^1$H NMR spectra. Coupling constants (J) are reported in hertz (Hz). Spin multiplicities are designated by the following abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad). Fourier transform infrared spectroscopy (FTIR) were performed on a PerkinElmer Spectrum 100 FT-IR spectrometer using pellets prepared with KBr. Ultraviolet–visible (UV/vis) absorption spectra were acquired on a PerkinElmer Lambda 25 UV/vis spectrometer using a PerkinElmer quartz cuvette with a 10 mm path length. Photoluminescence (PL) spectra were recorded on a PerkinElmer LS55 fluorescence spectrometer using a PerkinElmer quartz cuvette with a 10 mm path length. High-pressure liquid chromatography (HPLC) analysis was carried out on a Waters 2695 separation module with a Waters 2998 photodiode array and a Waters Styragel HR 2 THF 4.6 × 300 mm column. The mobile phase used was HPLC grade acetonitrile.
(80 vol %) and N,N-dimethylformamide (20 vol %). Gel permeation chromatography (GPC) analysis was conducted on a Waters 2695 separation module with a Waters 2998 photodiode array, a Waters 2414 refractive index detector, and two Waters Styragel 5 μm, HR 4E 7.8 × 300 mm column in series. The mobile phase used was HPLC grade THF, which was run at a flow rate of 1.2 mL/min. Gas chromatography (GC) was conducted on a PerkinElmer AutoSystem with a Rtx-35 (Fused Silica) column with dimensions of 15 m × 0.32 mm × 1.00 μm. Helium was used as the mobile phase, and a flame ionization detector was used for detection. Electrochemical measurements were carried out using a Bioanalytical Systems C3 electrochemical workstation. Spec-grade solvents were purged with argon gas at room temperature prior to their use. Three cycles from +1.6 to −1.6 V at a scan rate of 100 mV/s were measured for each sample. Tetrabutylammonium perchlorate (1 M) was used as the supporting electrolyte.

7.2.3 Synthesis

Bromo Boron Subphthalocyanine (Br-BsubPc, 1b)

1b was prepared according to a modified literature procedure. To an oven-dried three-neck round-bottom flask equipped with a condenser, an addition funnel, and a gas inlet was added phthalonitrile (42.3 g, 0.330 mol, 3.1 equiv), bromobenzene (136 mL), and toluene (362 mL) under argon. To the addition funnel was charged boron tribromide (10.0 mL, 26.5 g, 0.106 mol, 1 equiv), which was subsequently added to the reaction mixture dropwise. An immediate color change to a dark brown was observed, and the reaction was allowed to stir overnight. The following morning, the stirring was turned off, and the reaction was left undisturbed for 1 h. The reaction was gravity filtered, and the solid was immediately washed with methanol (250 mL) and dried in an oven to give 1b (23.1 g, 46%) as a brown solid. 1H NMR (400 MHz, CDCl3) δ 8.89−8.83 (m, 6H), 8.00−7.94 (m, 6H).

2:1 Poly(4-methylstyrene)-co-poly(4-acetoxy styrene) (9a)

A flame-dried three-neck round-bottom flask equipped with a condenser, an internal temperature probe, and a gas inlet was purged with nitrogen. Two pipettes were packed with inhibitor remover replacement packing for removing tert-butylcatechol. 4-AS (11.31 g, 70 mmol) was uninhibited by passing it through one pipette and introduced into the reaction flask. 4-MS (16.49
g, 140 mmol) was uninhibited by passing it through the second pipette and introduced into the reaction flask. To the reaction mixture was added TEMPO (0.024 g, 0.15 mmol), followed by BPO (0.025 g, 0.10 mmol). A small amount of 1,2-dichlorobenzene (1.2 mL) was added as an internal standard to monitor the consumption of the monomer via GC. The reaction was purged with nitrogen for 15 min and heated to 125 °C. The reaction progress was monitored by GC and GPC, and the reaction was stopped when the polymer had reached a desirable molecular weight (Mw ≥ 15 000–18 000 Da). The reaction was precipitated into methanol (1 L) and suction filtered to obtain 9a as a white solid (yield 16.2 g, 58%; Mw = 30 800; PDI = 1.85). ¹H NMR (400 MHz, CDCl₃) δ 7.05−6.17 (br d, 12H), 2.26 (br s, 9H), 1.78 (br s, 3H), 1.35 (br s, 6H).

**4:1 Poly(4-methylstyrene)-co-poly(4-acetoxy styrene) (9b)**

9b was obtained as a white solid (yield 53%; Mw = 25 200; PDI = 1.75) via the same procedure used for the synthesis of 9a. ¹H NMR (400 MHz, CDCl₃) δ 7.05−6.17 (br d, 20H), 2.26 (br s, 15H), 1.80 (br s, 5H), 1.35 (br s, 10H).

**2:1 Poly(4-methylstyrene)-co-poly(4-vinylphenol) (10a)**

To a round-bottom flask equipped with a condenser was added potassium hydroxide (1.12 g, 0.02 mol) and water (150 mL). To the solution was added 9a (2.00 g) and isopropanol (100 mL). The reaction mixture was heated to 75 °C for 12 h and analyzed by FTIR for the absence of the ester signal at 1768 cm⁻¹. The reaction was allowed to cool to room temperature, and the copolymer was precipitated out of solution by neutralizing the reaction mixture via a dropwise addition of 2 M HCl. The product was isolated by suction filtration and washed with water (3 × 50 mL), followed by hexane (3 × 50 mL). The crude product was purified by dissolving it in a minimum volume of THF with the assistance of a sonicator, precipitating it dropwise into ice cold stirring hexane (500 mL) via a cotton-plugged pipette, suction filtering the suspension, and washing the solids with water (3 × 50 mL) and hexane (3 × 50 mL) to obtain 10a (yield 1.58 g, 88%; Mw = 27 600; PDI = 2.29) as a beige solid. ¹H NMR (400 MHz, CDCl₃) δ: 7.10−6.20 (br d, 12H), 2.26 (br s, 6H), 1.86 (br s, 3H), 1.39 (br s, 6H).
4:1 Poly(4-methylstyrene)-co-poly(4-vinylphenol) (10b)

To a round-bottom flask equipped with a condenser was added 9b (2.50 g), toluene (60 mL), ethanol (20 mL), and concentrated sulfuric acid (5 drops). The reaction mixture was heated to 75 °C for 12 h and analyzed by FTIR for the absence of the ester signal at 1768 cm\(^{-1}\). The reaction was allowed to cool to room temperature where sodium bicarbonate (0.80 g) was added to the mixture and stirred for 4 h to neutralize the sulfuric acid. The reaction mixture was filtered to remove the base and the filtrate was concentrated under reduced pressure. The crude product was purified by dissolving it in a minimum volume of THF with the assistance of a sonicator, precipitating it dropwise into ice cold stirring hexane (600 mL) via a cotton-plugged pipette, suction filtering the suspension, and washing the solids with water (3 × 50 mL) and hexane (3 × 50 mL). The copolymer was reprecipitated a second time in hexane as described above and dried in a vacuum oven at 80 °C overnight to afford 10b (yield 3.20 g, 85%; \(M_W = 24 200; PDI = 1.88\)) as a white solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 7.12–6.11 (br d, 20H), 2.27 (br s, 12H), 1.85 (br s, 5H), 1.38 (br s, 10H).

2:1 Poly(4-methylstyrene)-co-poly(phenoxy boron subphthalocyanine) (11a)

An oven-dried three-neck round-bottom flask equipped with a condenser and a gas inlet was purged with argon for 15 min. To the reaction flask was added 10a (1.58 g) and anhydrous chlorobenzene (180 mL). The reaction was purged for 10 min before adding 1b (2.53 g, 5.33 mmol). The reaction mixture was heated to 120 °C under argon, and the reaction progress was monitored via GPC. When the ratio of BsubPc-containing copolymer and unreacted 1b had reached a steady value, the reaction was stopped and was allowed to cool to room temperature. The reaction mixture was concentrated under reduced pressure to a volume of \(\sim 30\) mL, precipitated dropwise into ice cold stirring methanol (1 L) via a cotton-plugged pipette, suction filtered, and washed with hexane (3 × 50 mL) and methanol (3 × 50 mL). The crude product was purified by adding it to a cellulose thimble and extracting with methanol in a Soxhlet extraction apparatus setup until the extract was clear. Three additional reprecipitations into ice cold methanol followed by a single reprecipitation into ice cold hexane was done as described above, and the solid was dried in a vacuum oven at 80 °C overnight to afford 11a (yield 1.85 g, 56%; \(M_W = 8 700; PDI = 5.65\)) as a dark purple solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 8.74 (br s, 6H),
7.69 (br s, 6H), 7.05–6.12 (br d, 8H), 5.72 (br s, 2H), 5.19 (br s, 2H), 2.21 (br s, 6H), 1.85 (br s, 3H), 1.29 (br s, 6H).

4:1 Poly(4-methylstyrene)-co-poly(phenoxy boron subphthalocyanine) (11b)

An oven-dried three-neck round-bottom flask equipped with a condenser and a gas inlet was purged with argon for 15 min. To the reaction flask was added 10b (2.00 g) and anhydrous chlorobenzene (250 mL). The reaction was purged for 10 min before adding 1b (1.90 g, 4.00 mmol). The reaction mixture was heated to 120 °C under argon, and the reaction progress was monitored via GPC. When the ratio of BsubPc-containing copolymer and unreacted 1b had reached a steady value, the reaction was stopped and was allowed to cool to room temperature. The reaction mixture was concentrated under reduced pressure to a volume of ~30 mL, precipitated dropwise into ice cold stirring methanol (1 L) via a cotton-plugged pipette, suction filtered, and washed with hexane (3 × 50 mL) and methanol (3 × 50 mL). The crude product was purified by adding it to a cellulose thimble and extracting with methanol in a Soxhlet extraction apparatus setup until the extract was clear. Three additional reprecipitations into ice cold methanol followed by a single reprecipitation into ice cold hexane was done as described above, and the solid was dried in a vacuum oven at 80 °C overnight to afford 11b (yield 1.98 g, 60%; $M_w = 17600$; PDI = 8.34) as a bright purple solid. $^1$H NMR (400 MHz, CDCl$_3$) δ: 8.75 (br s, 6H), 7.71 (br s, 6H), 7.05–6.10 (br d, 16H), 5.73 (br s, 2H), 5.11 (br s, 2H), 2.23 (br s, 12H), 1.81 (br s, 5H), 1.33 (br s, 10H).
7.3 Results and Discussion

As mentioned above, incorporation of a BsubPc unit into a polymer main-chain by a polycondensation strategy would be synthetically challenging due to the C\textsuperscript{3v} symmetric nature of BsubPc. We therefore aimed to attach the BsubPc as a pendant group onto an inert polymer backbone. The obvious first step was the synthesis of a BsubPc molecule containing a vinyl functional group, which could then be polymerized using either conventional or reversible-deactivation radical polymerization (RDRP)\textsuperscript{17} methods (for example, nitroxide mediated polymerization (NMP)\textsuperscript{18}). This prepolymerization functionalization approach has been successfully employed for the synthesis of a range of monomers bearing functional pendants, including acrylate monomers bearing Disperse Red 1\textsuperscript{19-20} and various other azobenzene pendants,\textsuperscript{21} a vinylbenzene monomer bearing carbazole,\textsuperscript{22} and a p-cyanomethylstyrene modified with a number of benzaldehyde pendants.\textsuperscript{22}

In our case, we targeted a styrene-based polymer as styrene is well-known to not interfere with charge transport while other polymers and their associated dipoles might hinder charge transport by the so-called pinning effect (e.g., acrylates).\textsuperscript{23} It has been shown many times that chloro boron subphthalocyanine (Cl-BsubPc, 1a, Scheme 7.1) can be axially substituted with a phenol or its derivative in refluxing toluene, chlorobenzene, or other aromatic solvents.\textsuperscript{24-26} Thus, our first attempt to synthesize a monomer of BsubPc utilized 4-vinylphenol. Despite its structural simplicity, 4-vinylphenol is not commercially available and thus was obtained through the hydrolysis of 4-acetoxy styrene (4-AS) with aqueous potassium hydroxide at 0 °C and either stored in the refrigerator prior to use or used immediately after preparation.\textsuperscript{27} Reaction of 4-vinylphenol with 1a resulted in autopolymerization of the 4-vinylphenol at a temperature of 80 °C, which is lower than what would be required to facilitate the production of monomer 2a (Scheme 7.1). Similar observations were seen for the reaction of 1a with 2-methoxy-4-propenylphenol or isoeugenol in an attempt to make monomer 2b (Scheme 7.1).

From these experiments, it was apparent that lower temperatures were required for the phenoxylation of 1a to overcome the issue of premature autopolymerization. However, using low reaction temperatures will not permit phenoxylation of 1a to proceed. We thus turned to the use of the more reactive Br-BsubPc (1b, Scheme 7.1). Reaction of 1b with 4-vinylphenol in toluene...
Scheme 7.1: Attempted synthesis of BsubPc-containing styrenic monomers via prepolymerization functionalization approach. Reagents and conditions: (i) $X = \text{Cl}, R_1 = \text{H}, R_2 = \text{H}$, toluene, $80 \, ^\circ\C$, 24 h; (ii) $X = \text{Cl}, R_1 = \text{OCH}_3, R_2 = \text{CH}_3$, toluene, $80 \, ^\circ\C$, 24 h; (iii) $X = \text{Br}, R_1 = \text{H}, R_2 = \text{H}$, toluene, $40 \, ^\circ\C$, 48 h.

at $40 \, ^\circ\C$ formed several products that included a compound with a different HPLC retention time than $1b$ and a UV–vis absorption profile characteristic of a BsubPc derivative as well as a polymer (detected by GPC) with a molecular weight of $\sim 20\,000$ Da. Attempts to isolate pure compounds from this mixture via silica gel column chromatography were unsuccessful due to the elution of the side products and what seemed to be the result of further reaction promoted by the silica gel. We supposed that the polymer was likely formed by a polymerization catalyzed by HBr acid, a side product liberated from the phenoxylation of $1b$. In a second attempt, the experiment was repeated in the presence of pyridine so as to neutralize any HBr formed during the reaction. Premature polymerization was indeed inhibited and a compound with the same HPLC retention time and UV–vis absorption profile as the previous base-free experiment was formed. However, the compound could not be isolated even after successive purification via silica gel chromatography for what we assume are the same reasons outlined above.

Before additional effort was put into obtaining a BsubPc vinyl monomer we first wanted to determine whether or not the BsubPc group is a radical scavenger. Therefore, two 4-methylstyrene (4-MS) homopolymerizations were carried out under nitroxide-mediated polymerization (NMP) conditions, where one of the homopolymerizations was performed with the addition of 0.04 wt % $1b$ (as an additive, not as a monomer). Even with a minimal amount of
1b in the homopolymerization mixture a significant termination was observed. This termination therefore indicates that 1b and perhaps more generally BsubPcs are radical scavengers.

Because of the challenges associated with obtaining a styrenic monomer of BsubPc and its apparent ability to scavenge radicals, we turned to a postpolymerization functionalization approach (Scheme 7.2) whereby 1b would be reacted with a preformed polymer (prepolymer) to produce the final BsubPc-containing polymer/macromolecule. Using this approach we first tried to functionalize the prepolymer poly(4-vinylphenol) with BsubPc. Rather than using commercially available poly(4-vinylphenol), which has a very large polydispersity (~6), we synthesized poly(4-vinylphenol) in house using NMP. Specifically, we produced the homopolymer by homopolymerization of 4-AS using benzoyl peroxide (BPO) as the initiator and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) as the mediator at a BPO:TEMPO ratio of 1:1.5. Intermediate poly(4-AS) (3, Scheme 7.2) had the following characteristics: $M_w = 21,600$; $PDI = 1.32$. Subsequent hydrolysis of 3 to poly(4-vinylphenol) (4, Scheme 7.2) was accomplished using aqueous ammonium hydroxide in an approach analogous to that of Barclay et al. Subsequent reaction of 4 with 1a or 1b turned out to be problematic since polymer 4 was not soluble in aromatic solvents such as toluene or chlorobenzene, solvents commonly used for phenoxylation of halo-BsubPcs. Instead, a 1:1 (v/v) mixture of 1,2-dichlorobenzene and a polar aprotic solvent such as DMF or DMAc was needed to solubilize polymer 4. Addition of either 1a or 1b with heating under a positive pressure of argon caused some initial conversion/partial substitution to the desired BsubPc-containing polymer 5 (as could be seen in the GPC chromatogram that the polymer obtained the characteristic UV–vis absorption profile of a BsubPc derivative), but significant decomposition of the BsubPc chromophore occurred well before 50% substitution. The unidentified decomposition product(s) were green in color, and it was suspected that the decomposition was a result of the known disproportionation and ring expansion of BsubPc derivatives, although we could not isolate/purify the decomposition products for detailed characterization. We can, however, surmise that the decomposition is a result of the presence of the polar aprotic solvent or the combination of the aprotic solvent and the liberated HCl or HBr, as 1a is stable under refluxing dichlorobenzene for periods of time exceeding 100 h and 1b is stable in refluxing toluene for periods of at least 5 h. We also verified that decomposition of the BsubPc occurred regardless of the source or batch of prepolymer used including if the prepolymer is simply commercially available poly(4-
Scheme 7.2: Synthesis of BsubPc-containing copolymers via postpolymerization functionalization approach. Reagents and conditions: (i) aqueous ammonium hydroxide, isopropanol, reflux, 18 h; (ii) 1a (X = Cl)/1b (X = Br), 1:1 (v/v) N,N-dimethylacetamide:1,2-dichlorobenzene, reflux, 24 h; (iii) method 1 (6a): aqueous ammonium hydroxide, isopropanol, reflux, 70 h; method 2 (9a): aqueous potassium hydroxide, isopropanol, reflux, 12 h; method 3 (9a and 9b): sulfuric acid, toluene/ethanol, reflux, 12 h; (iv) method 1 (7a): 1b, toluene/chlorobenzene, reflux, 2 h; method 2 (10a and 10b): 1b, chlorobenzene, 120 °C, ∼24–48 h.

vinylphenol). We can thus eliminate the presence of nitroxide end-groups as another possible source of the decomposition. As a final confirmation of the effect of polar aprotic solvents, 1b was reacted with 5 equiv of phenol under standard conditions except using 1:1 (v/v) of toluene:DMAc. In this case decomposition of the BsubPc was also observed, definitely proving that it is the presence of the polar aprotic solvent possibly combined with the presence of the liberated HBr that causes the decomposition of the BsubPc chromophore.
Thereafter, we shifted our investigation to the use of copolymers as prepolymers rather than poly(4-vinylphenol) homopolymers. The aim was the inclusion of a selected comonomer that would produce a 4-AS-containing prepolymer, which upon hydrolysis would produce a phenol-containing prepolymer that was soluble in solvents such as toluene and/or chlorobenzene-solvents we knew would not promote the decomposition of the BsubPc chromophore.

For a given pair of a monomers (M₁ and M₂) undergoing free-radical copolymerization, the reactivity ratios ($r_{1,2}$ and $r_{2,1}$) are defined as:

$$r_{1,2} = \frac{k_{1,1}}{k_{1,2}} \quad \text{and} \quad r_{2,1} = \frac{k_{2,2}}{k_{2,1}}$$  \hspace{1cm} \text{Equation 7.1}

The first subscript identifies the monomer at the end of the propagating chain and the second subscript refers to the monomer added next to the chain. For a propagating chain with M₁ at the end, the reactivity ratio $r_{1,2}$ is the ratio of the propagation rate constants for the addition of M₁ (k₁₁ – i.e., homopolymerization) and addition of M₂ (k₁₂ – i.e., copolymerization). If both reactivity ratios equal unity, then there is no preferential monomer incorporation into the propagating chain (i.e., k₁₁ = k₁₂ and k₂₂ = k₂₁). In this case, the monomer sequence in the copolymer is entirely random and the copolymer composition is equal to the initial monomer feed composition at the beginning of the reaction. If both reactivity ratios are zero (i.e., k₁₁ = k₂₂ = 0), then the monomer sequence will be alternating, independent of the monomer feed composition at the beginning of the reaction. If both reactivity ratios are small, but not exactly zero, then the polymer sequence will not be entirely alternating but will have an alternating tendency.

As measured reactivity ratios were not widely available for 4-AS, we used the “patterns of reactivity” method to examine a variety of potential comonomers. This method uses eight experimentally-determined input parameters to predict the reactivity ratios for a given pair of monomers, as shown in the pair of equations:

$$\log r_{1,2} = \log r_{1,s} - u_2 \pi_1 - v_2$$  \hspace{1cm} \text{Equation 7.2}
$$\log r_{2,1} = \log r_{2,s} - u_1 \pi_2 - v_1$$
Here \( r_{1,s} \) and \( r_{2,s} \) are the experimentally-determined reactivity ratios of monomer 1 and monomer 2 copolymerized with styrene, respectively.

The polarity parameter, \( \pi_i \), for monomer i is calculated according to:

\[
\pi_i = 0.385 \log \left( \frac{r_{i,a}}{0.377 \ r_{i,s}} \right)
\]

Equation 7.3

Here \( r_{i,a} \) and \( r_{i,s} \) are the experimentally-determined reactivity ratios of monomer i with acrylonitrile and styrene, respectively. Acrylonitrile and styrene are used for this calculation because they represent extremes in the range of radical polarity, with styrene having a very low value (zero) and acrylonitrile having one of the highest values known (0.701).\(^{32}\)

Finally, values for \( u_i \) and \( v_i \) are obtained by referring to data for the separate copolymerizations of monomer i with the members of a ‘basic monomer set.’ The basic monomer set includes five monomers for which reliable data exists in the literature, namely: styrene, methyl methacrylate, methyl acrylate, methacrylonitrile and acrylonitrile. A plot is made of \([\log r_{B,i} - \log r_{B,s}]\) against \( \pi_B \). The subscript i refers to the monomer for which \( u \) and \( v \) values are to be determined; the subscript B refers to the members of the basic monomer set. The resulting plot yields a straight line, with the slope equal to \(-u_i\) and the intercept on the ordinate axis equal to \(-v_i\), in conformance with equation (7.2).

This method can be used to calculate values for \( u_i \) and \( v_i \) even if copolymerization data is not available for monomer i with all five members of the basic monomer set. In that case, the extent of the data available can be used, as long as it includes data for acrylonitrile and styrene to ensure that the model is valid over a range of radical polarities.

Parameter values (\( r_{i,s}, \pi_i, u_i, \) and \( v_i \)) for most monomers needed for this method were obtained from the Polymer Handbook\(^ {32}\) and used in the patterns of reactivity calculations (Table 7.1). In considering candidate monomers for copolymerization with 4-AS, several selection criteria were used: (1) The monomer, as stated above, should produce a copolymer with 4-vinylphenol that is soluble in solvents such as toluene, chlorobenzene, or dichlorobenzene. (2) The monomer should produce a polymer that is insoluble in methanol and/or hexanes to facilitate work-up via precipitation and Soxhlet extraction. (3) The monomer should not be an ester since hydrolysis is
necessary to transform the acetoxy groups of 4-AS to the hydroxyl group of 4-vinylphenol and such conditions would obviously also hydrolyze any other ester present.

**Table 7.1:** Candidate monomers. Monomer reactivity ratios were predicted using the Patterns of Reactivity method.

<table>
<thead>
<tr>
<th>Monomer 1</th>
<th>Structure</th>
<th>Monomer 2</th>
<th>Structure</th>
<th>$r_{1,2}$</th>
<th>$r_{2,1}$</th>
</tr>
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<tbody>
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<td><img src="image" alt="Structure" /></td>
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</tr>
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<td>Pyridine, 4-vinyl-</td>
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<td>0.05</td>
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<td></td>
</tr>
<tr>
<td>Tetrazole, 1-vinyl-</td>
<td><img src="image" alt="Structure" /></td>
<td>4.65</td>
<td>0.20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vinyl methyl ketone</td>
<td><img src="image" alt="Structure" /></td>
<td>0.31</td>
<td>0.42</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Experimentally determined values, for comparison: $r_{1,2}=0.40$ and $r_{2,1}=0.03$
Thus, on consideration, only one monomer fit these criteria and was selected for copolymerization with 4-AS:4-MS. The predicted reactivity ratios for 4-AS and 4-MS are closest to unity, and therefore this monomer pair is likely to produce a copolymer with a random tendency. Thus, we initially set an arbitrary target of $M_w = 40 \, 000$ for a 4-AS/4-MS copolymer. The arbitrary target was thought to be high enough to ensure good film-forming properties of the resulting polymer. Using NMP, 4-MS and 4-AS were copolymerized at a charged ratio of 2:1 (mol/mol, Scheme 4.2). This successfully yielded copolymer 6a with $M_w = 41 \, 000$ and PDI = 1.44. GC analysis confirmed an equal rate of consumption for 4-AS and 4-MS, thus verifying that 6a is a random copolymer. Hydrolysis of 6a to 7a was accomplished by suspending 6a in isopropanol and heating to a reflux with excess ammonia hydroxide. As hydrolysis proceeded, the copolymer became increasingly soluble eventually forming a clear and homogeneous solution. The overall reaction time was quite long requiring ~3 days for complete hydrolysis.

Next the reaction of 7a with 1b was explored. The desired reaction solvent was either toluene or chlorobenzene. Using either would only form a solution at 2–4 wt % of polymer 7a even at high temperatures. This was significantly more dilute than the typical phenoxylation reaction conditions used. Given the $S_N1$ nature of the reaction, the low concentration would severely limit the reaction rate, and thus the reaction of 7a with 1b was only attempted due to its known higher reaction rate. The reaction was monitored by GPC and after 90 min the reaction had stalled as indicated by the presence of unreacted and unchanging quantities of 1b. Removal of the mother liquor and isolation of the solubilized polymer showed that only ~5% of the polymer had stayed in solution. GPC analysis of the isolated polymer revealed that it did contain BsubPc (based on the characteristic UV–vis absorption spectrum) but had a $M_w$ of 20 000 Da. Thus, based on this observation, fractionation had occurred, and given the precipitation, a target $M_w$ of 40 000 was too high when limited to the use of toluene or chlorobenzene as solvents. The synthesis was repeated with a target $M_w$ of 15 000–18 000 in an attempt to ensure complete dissolution during the postpolymerization reaction process in either toluene or chlorobenzene.

Again, using NMP, 4-MS and 4-AS were copolymerized in a 2:1 (mol/mol) ratio this time with a targeted $M_w$ of 15 000–18 000. The evolution of molecular weight and polydispersity was observed over time (Figure 7.1). Monomer consumption was also measured over time using gas chromatography (GC) against an internal standard of 1,2-dichlorobenzene (Figure 7.2). In this case, 4-AS was consumed at a slightly higher but comparable rate to 4-MS, indicating
**Figure 7.1:** Molecular weight (Mw) and polydispersity index (PDI) over time for the low molecular weight copolymerization of 4-acetoxy styrene and 4-methyl styrene.

**Figure 7.2:** Percentage consumption of the 4-methyl styrene and 4-acetoxy styrene monomers over the course of the copolymerization. The slope of the lines indicates a consumption rate, which is also the rate at which the monomers were incorporated into the polymer product.
approximate equivalence in their reactivity and the production of a random copolymer. Noting that copolymer 9a still had somewhat low solubility in toluene and chlorobenzene, we also synthesized a 4-MS/4-AS copolymer in a 4:1 (mol/mol) ratio to produce 9b. In the synthesis of both 9a and 9b, the process produced copolymers with M\textsubscript{w} that varied from batch-to-batch and, in some cases, the target M\textsubscript{w} was overshot especially at slightly larger scale. Despite this, copolymer 9a (M\textsubscript{w} = 30 800, PDI = 1.85) and 9b (M\textsubscript{w} = 25 200, PDI = 1.75) were both carried forward to the subsequent deacetylation reaction.

Deacetylation was carried out via base hydrolysis of 9a to give 2:1 poly(4-methylstyrene)-co-poly(4-vinylphenol) (10a, M\textsubscript{w} = 27 600, PDI = 2.29) and via acid-catalyzed transesterification of 9b to give 4:1 poly(4-methylstyrene)-co-poly(4-vinylphenol) (10b, M\textsubscript{w} = 24 200, PDI = 1.88). Different reaction conditions were employed for the deacetylation reaction due to the poor solubility of 9b in aqueous basic solution. Copolymer 9a can also be converted to 10a using the same acid-catalyzed transesterification reaction used to deacetylate 9b. The deacetylated copolymers 10a and 10b were subsequently reacted with 1.2 equiv of 1b in chlorobenzene at 120 °C, and the reaction progress was monitored by GPC (Figure 7.3) until the ratio of BsubPc-containing copolymer (R\textsubscript{T} ∼ 13.0−13.2 min) and unreacted 1b (R\textsubscript{T} ∼ 16.7−17.0 min) had reached a steady value. Although the GPC retention time for the polymer peak did not shift with reaction progress, phenoxylation was known to occur based on a change in the UV−vis absorption profile for the polymer peak from that of a standard styrenic polymer to that which is characteristic of a BsubPc compound (Figure 7.4). Each of the 2:1 (11a, final M\textsubscript{w} = 8700, PDI = 5.65) and 4:1 (11b, final M\textsubscript{w} = 17 600, PDI = 8.34) poly(4-methylstyrene)-co-poly(phenoxo boron subphthalocyanine) were isolated and purified via precipitation and a Soxhlet extraction.

The GPC spectrum of 11a and 11b (Figure 7.4) both showed a tailing effect, signifying a potential solubility issue with these copolymers. As a consequence of this, high PDIs were obtained, which were assumed to be inaccurate based on the fact that the PDIs for 9a and 9b were significantly lower (<2). Furthermore, the reported M\textsubscript{w} of 11a and 11b were low compared to the M\textsubscript{w} of the prepolymers, again indicating a potential solubility issue resulting in a decreased hydrodynamic volume upon reaction with BsubPc.

The solubilities of 11a and 11b were confirmed to be generally poor in common organic solvents with 11b displaying a slightly better solubility than 11a. THF was found to be the best solvent
for dissolving these BsubPc-containing copolymers. However, for NMR purposes THF was not an ideal solvent since one of its residual peaks overlapped with one of the aliphatic peaks of the copolymers. Chloroform-d was chosen instead as it demonstrated the best compromise between solubility and minimal residual peak overlap with the sample.

Figure 7.3: GPC spectrum at 1.5 (top), 4.5 (middle), and 19 hours (bottom) for the reaction of 1b with 10a.

The UV−vis absorption spectra were acquired for 11a and 11b in toluene (Figure 7.5). Both polymers have a $\lambda_{\text{max}}$ of absorption at ~564 nm. This is similar to the $\lambda_{\text{max}}$ of absorption for small molecule phenoxy-BsubPc derivatives, which typically occurs over the range of 560–565 nm. A representative example spectrum of 3,4-dimethylphenoxy-BsubPc$$^{33}$$ is shown in Figure 7.4. When comparing the absorption spectra of polymers 11a and 11b, each are essentially identical (small differences in the UV); however, the respective long wavelength absorptions are slightly broadened when compared to the small molecule analogue, indicating that the BsubPc chromophores are partially associated in solution. Fluorescence emission spectra were also acquired for the polymers 11a and 11b (Figure 7.5) in nondeaerated toluene using a $\lambda_{\text{excitation}}$ of 564 nm. The fluorescence spectra are a mirror of the absorption spectra, indicating that this is fluorescence rather than phosphorescence; this is consistent with the fluorescent behaviour of
small-molecule phenoxy-BsubPc derivatives.\textsuperscript{34} The fluorescence spectra show that 11\textit{a} and 11\textit{b} have $\lambda_{\text{max}}$ of emission at 573 and 575 nm, respectively, which is again in the range typically observed for small molecule phenoxy-BsubPcs. The fluorescence quantum yields ($\phi$) for 11\textit{a} and 11\textit{b} were found to be relatively low at 0.12 and 0.06, respectively, relative to a standard of phenoxy-dodecafluoro- BsubPc (F\textsubscript{12}BsubPc). This is significantly lower than the $\sim$0.50 that is commonly observed for phenoxy-BsubPc derivatives.\textsuperscript{35}

![Figure 7.4: GPC chromatograms and extracted UV–vis absorption spectra (inset) of boron subphthalocyanine polymers 11\textit{a} (a) and 11\textit{b} (b).](image-url)

Cyclic voltammetry (CV) of 11\textit{a} and 11\textit{b} was carried out to determine the energy levels of the frontier orbitals (the HOMO and LUMO). Initial experiments using Ag/AgCl as the reference electrode, Pt disk as the working electrode, Pt wire as the counter electrode, and tetrabutylammonium perchlorate in either DCM or THF as the electrolyte did not show any reduction or oxidation process present for either 11\textit{a} or 11\textit{b}. It was suspected that the concentration of these copolymers in DCM or THF was too low to be detected due to their generally poor solubilities. To address this issue, the Pt disk was coated by drop-casting with a
solution of 11a or 11b onto the electrode, thus ensuring that their concentration at the working electrode was always high during the electrochemical study. Acetonitrile was used as the solvent as it does not solubilize the copolymers. However, once again, there was an absence of a reduction or oxidation process. To furthermore increase the amount of 11a or 11b at the working electrode, the low-surface-area Pt disk was substituted with a high-surface-area ITO-coated glass plate. Coating on the ITO plate was done via a drip-coat method, where the ITO plate was dipped into a THF solution of the copolymer and allowed to dry. Numerous CV studies using this setup were conducted, and the results were inconsistent. In most cases no current was observed across the entire voltage scanned. Thus, the basic electrochemical properties of the title polymer remain unknown.

**Figure 7.5:** Ultraviolet/visible absorption (blue) and fluorescence (red) spectra of 3,4-dimethylphenoxy boron subphthalocyanine and polymers 11a and 11b (as indicated).
7.4 Conclusions

After outlining why the synthesis of a BsubPc-containing monomer was not successful and perhaps pointless since BsubPc may be a radical scavenger, we demonstrated the synthesis of BsubPc-containing polymers for the first time by employing a postpolymerization functionalization approach. Two polymers were synthesized: a 2:1 (11a) and 4:1 (11b) poly(4-methylstyrene)-co-poly(phenoxy boron subphthalocyanine). The three-step process begins with the nitroxide mediated copolymerization of 4-MS and 4-AS in a 2:1 and 4:1 molar ratio to give the 2:1 (9a) and 4:1 (9b) poly(4-methylstyrene)-co-poly(4-acetoxy styrene), respectively. Following deacetylation, 9a and 9b were converted to their respective 2:1 (10a) and 4:1 (10b) poly(4-methylstyrene)-co-poly(4-vinylphenol), which was subsequently reacted with 1b via phenoxylation to afford the target 2:1 (11a) and 4:1 (11b) poly(4-methylstyrene)-co-poly(phenoxy boron subphthalocyanine). UV–vis absorption spectroscopy revealed that both 11a and 11b had similar absorption profiles as other BsubPc derivatives. Low fluorescence quantum yields of 0.12 and 0.06 were measured for 11a and 11b, respectively. Cyclic voltammograms of BsubPc-containing polymers 11a and 11b could not be obtained.
7.5 References


18. Grubbs, R. B. Polymer Reviews 2011, 51 (2), 104-137.
Chapter 8
Summary & Future Work

8.1 Summary

In summation, the work produced over the course of my PhD studies encompasses a total of seven first-author papers. Three of these have already been published, one is currently out for review, and the remaining three are scheduled to be completed and submitted within the next few months. I have analyzed and submitted over twenty crystal structures of BsubPc derivatives to the Cambridge Crystallographic Data Centre (CCDC), including the first reported co-crystals of BsubPc. I also synthesized the first BsubPc-containing polymer. The various conclusions related to each of these pieces of work have already been discussed in detail in the appropriate chapters.

Recalling my hypothesis statement from the introduction chapter:

Halogen and hydrogen bonds can be used to alter the solid state arrangement of BsubPc derivatives and that alteration can be correlated to organic photovoltaic (OPV) device performance.

With regards to the first half of that statement, I have confirmed that both halogen and hydrogen bonds can be used to alter the solid state arrangement of BsubPc derivatives. I have also shown that hydrogen bonds can be exploited to create deliberate co-crystals containing BsubPc.

For the second half, I have shown that different BsubPc derivatives, which adopt different solid state arrangements in their crystal structure, also display different device performance characteristics. There is some indication of a correlation between solid state arrangement and OPV performance. However, with the exception of the proof of hydrogen bonding in thin films of p-HOPhO-BsubPc, most of the current evidence correlating solid state arrangement in a crystal to arrangement in a thin film (and therefore arrangement in an OPV device) is circumstantial in nature. This is a challenging area of research, due to the limitations of the currently available technology for probing the organization of very thin films of organic material. While I have made progress in investigating this area, there is certainly a need for future research on the arrangement of BsubPc derivatives in thin films and devices.
8.2 Future Work

8.2.1 Crystal Structure Analysis Using Crystal Explorer

Crystal structure determination and structure analysis are ongoing areas of investigation in the Bender research group. This includes research on the crystal structures of boron subphthalocyanine derivatives, as described in this thesis, but also extends to other materials of interest in organic electronic devices, such as phthalocyanines. Up to this point, we have used a combination of the programs Mercury\(^2\) and Platon\(^3\) to analyze crystal structures and packing arrangements. However, based on conversations I have had with my colleagues, I know that these programs are not generally found to be intuitive or user-friendly. It can also be easy for users unfamiliar with crystal structures to miss important intermolecular interactions.

![Figure 8.1: Comparison of programs for crystal structure analysis, using Cl-BsubPc\(^4\) as an example case: a) the “short contact” view in Mercury,\(^2\) commonly used as a first step in analyzing crystal structures within the lab group; b) the Hirshfeld surface mapped with \(d_{\text{norm}}\) using Crystal Explorer; c) the Hirshfeld surface mapped with the shape index in Crystal Explorer,\(^5\) with complementary shape regions circled.](image)

I would recommend that members of the research group become familiar with Crystal Explorer,\(^5\) and I intend to put together a quick introductory guide to using this program before I leave the group. While using Crystal Explorer to analyze the crystal structure of chloro boron subphthalocyanine (Cl-BsubPc), I found the program to be very intuitive and useful for structure analysis. Figure 8.1 compares some features from the three programs. The “short contact” view in Mercury is useful for identifying close atoms next to the adjacent molecule, but many users
seem to find the graphics a little difficult to understand spatially. In contrast, the Hirshfeld surface calculation in Crystal Explorer effectively renders the molecules as three-dimensional puzzle pieces, which makes spatial interpretation of the structure more intuitive. The $d_{\text{norm}}$ parameter is useful for quickly identifying close contacts, as any points on the surface which coincide with atoms separated by a distance shorter than the sum of their van der Waals radii are displayed as red circles, and complementary red circles designating the two halves of an interaction will be the same diameter. The shape index surface is also useful for identifying regions on the molecule which ‘fit’ together, as complementary regions will have the same patterning but in different colours (blue and red). In particular, the shape index facilitates identifying $\pi-\pi$ interactions, as those are displayed with a diagnostic ‘bow-tie’ shape.\footnote{There is a caveat to using Crystal Explorer for structure analysis. The developers of the program have suggested that it should only be used for well-characterized crystal structures, and I would recommend that these guidelines be followed for any published work using Crystal Explorer. Generally, a ‘well-characterized’ structure would require the R-factor to be low (at least $<8\%$, but preferably $<5\%$) and for the hydrogen atoms to be independently refined. This should be possible with a fair percentage of the crystal structures obtained in our research group, although independent refinement of the hydrogen atoms will add some time to the refinement process. Realistically, there will be structures where the R-factors are not low enough to be classified as well-characterized, and there will be cases where the crystal structure is a minor component in a larger paper. In such cases, I think analysis using Crystal Explorer would still be beneficial as an aid to understanding the crystal structure, even if the analysis is not included in the final manuscript.}

8.2.2 Film Morphology Studies of BsubPc Derivatives Using AFM

The atomic force microscopy (AFM) studies of BsubPc derivatives in Chapter 5 revealed some morphological differences between thin films of different derivatives. Specifically, in freshly evaporated films, the feature size and film smoothness varied depending on the derivative. In aged films, the morphology changed drastically and also appeared to vary based on the derivative. These observations both warrant further study.

*Morphology of freshly evaporated films*. The cumulative research from the Bender group has produced an extensive library of BsubPc derivatives and crystal structures. In order to investigate
differences in film morphology based on crystal structure, a subset of derivatives which display distinctly different crystal structures could be selected. In addition to the derivatives capable of halogen or hydrogen bonding described in this thesis, other possible candidates for such a study might include: oxygen-bridged dimers, such as $\mu$-oxo-(BsubPc)$_2$ (1 in Figure 8.2); $\pi$-acid/$\pi$-base BsubPc derivatives, such as $\beta$-naphthoxy-BsubPc$^9$ (2 in Figure 8.2); and/or BsubPcs with peripheral fluorine atoms, such as F$_{12}$-Cl-BsubPc$^{10}$ (3 in Figure 8.2). These three groups of BsubPc have distinctly different crystal structures. To the best of my knowledge, there have been only limited AFM studies of perfluorinated BsubPc films,$^{10}$ and no AFM studies focusing on bridged dimers or $\pi$-acid/$\pi$-base derivatives. Studying the relationship between crystal structure and thin film morphology would be beneficial in improving our understanding of how BsubPc molecules are arranged in thin films.

![Figure 8.2: Suggested BsubPc derivatives](image)

**Figure 8.2:** Suggested BsubPc derivatives for as-deposited thin film morphology studies: $\mu$-oxo-(BsubPc)$_2$ (1), $\beta$-naphthoxy-BsubPc (2) and perfluorinated F$_{12}$-Cl-BsubPc (3).

**Morphology of aged films.** Based on observations in Chapter 5, bare thin films of BsubPc derivatives undergo an aging process which drastically changes their morphology from fairly smooth films with circular features to rougher films with elongated, branch-like features. This aging process appears to be sensitive to the environment around the sample, occurring at slower rates if the sample is stored in a dark, inert atmosphere. It would be beneficial to understand what environmental factors impact this aging process. Controlled experiments could be performed by preparing several thin films in the same deposition batch and then exposing them to different conditions. AFM analysis should be done at specific, regular time intervals. Exposure to light, oxygen and moisture could be controlled in order to determine which of these factors contribute to the aging process. It would be useful to select Cl-BsubPc as a starting point for this study, as it is the most widely used material in organic electronic devices.
In addition to experiments involving bare thin films of Cl-BsubPc, it would be beneficial to investigate whether this morphological change occurs when the Cl-BsubPc layer is capped with another layer, as it would be in a photovoltaic device. An additional layer would complicate the AFM analysis, but would be more applicable to understanding possible degradation mechanisms in BsubPc devices. Very thin layers (5-10 nm) of materials which are commonly used overtop BsubPc derivatives (such as fullerene C_{60}) could be investigated. The capping layer would need to be thick enough to cover the underlying Cl-BsubPc layer, but thin enough to allow for morphological changes in the layer below to affect the surface topography. Control experiments would need to be performed as well, for example to establish whether the capping layer itself undergoes an aging process.

Finally, since the aged morphologies of Cl-BsubPc and m-IPhO-BsubPc were found to be different in Chapter 5, this represents another possible area for future work. Thin films of other BsubPc derivatives, covering a range of crystal structures and intermolecular interactions, could be aged in a controlled manner and studied by AFM. If the observed trend continues, and materials which adopt different crystal structures are observed to also adopt different aged morphologies in thin films, this would provide further insight into the relationship between crystal structure and thin film structure.

8.2.3 Study of Aged BsubPc Films in OPV Devices

This study would be an extension of the AFM analysis performed in Chapter 5 and suggested in the previous section, Section 8.2.2. In Chapter 5, it was observed that aged films of BsubPc derivatives were significantly rougher than fresh films. The rougher morphologies of aged BsubPc films should be incorporated into OPV devices and studied. A rougher surface for the BsubPc layer would increase the surface area at the donor-acceptor interface, and would therefore increase the surface area available for exciton dissociation. This may be beneficial for OPV device performance. Additionally, the aged films are likely to be representative of the eventual equilibrium morphology of the films, and therefore their device performance characteristics are relevant to OPV device studies. Care must be taken to age the BsubPc film without allowing the film surface to become contaminated, and so the aging process will likely need to be carried out in a glove box environment.
8.2.4 Synthesis and Characterization of BsubPc Derivatives Containing Fluorinated Alkyl Halides in the Axial Position

The Fourier transform infrared (FTIR) studies performed on thin films of meta-halogenated phenoxy-BsubPc derivatives in Chapter 5 revealed that FTIR was not a useful technique for investigating the presence of intermolecular halogen bonds in these materials. However, as discussed in Chapter 5, halogen atoms covalently bound to aromatic carbon rings are difficult diagnostic tools in FTIR analysis, due to the tendency of the signals from the aromatic C-H groups to overlap with the signal from the aromatic C-X group (where X is a halogen atom).\textsuperscript{11} Conversely, alkyl halides are considered an easier diagnostic tool, and there are literature precedents for using FTIR to identify intermolecular halogen bonds involving fluorinated alkyl halides.\textsuperscript{12-13} In addition to the C-X signal (X=Cl, Br, I), the signals from C-F moieties adjacent to the C-X bond in alkyl halide compounds demonstrate some shifting and/or splitting effects upon formation of an intermolecular halogen bond,\textsuperscript{12-13} providing additional regions of the spectrum (approximately 1000-1400 cm\textsuperscript{-1})\textsuperscript{14} which can be inspected for evidence of halogen bonds.

![Figure 8.3: Proposed synthesis of alkyl halide BsubPc derivatives. Reagents and conditions: (i) PhenolMgBr, THF, reflux.\textsuperscript{15}](image)

On this basis, the synthesis and characterization of BsubPc derivatives bearing a fluorinated alkyl halide group in the axial position may be useful in investigating halogen bonding interactions in thin films using FTIR. Note that substitution in the axial position of the BsubPc base molecule is preferred to peripheral substitution; this is because substitution in the axial position will not affect the optical or electronic properties of the base molecule, whereas peripheral substitution will affect those properties. The Bender research group has developed a synthetic procedure for preparing bromoalkoxy-BsubPc derivatives from cyclic ethers (i.e. 5, Figure 8.3).\textsuperscript{15}
Following synthesis of suitable BsubPc derivatives, crystallization studies would need to be carried out in order to identify candidates which display halogen bonding in their crystal structures. Those derivatives which display halogen bonding in their crystal structures can then be studied in thin films using FTIR to determine whether they also form halogen bonds in thin films. Although this project would require a fair amount of work (synthesis, crystal growth and structure analysis, thin film preparation, FTIR characterization), it has the advantage that all of the required equipment is readily available to members of the Bender research group. Other methods of investigating intermolecular interactions and crystal structures in thin films, which will be discussed below, require more specialized equipment that we do not presently have access to.

BsubPc derivatives bearing fluorinated alkyl halide moieties may also show improved solubility and could be explored as solution-processed organic electronic materials.

8.2.5 Investigation of Halogen Bonding Interactions in Thin Films and Single Crystals Using X-Ray Photoelectron Spectroscopy (XPS)

XPS is a surface characterization technique available through collaboration with Professor Lu in the Department of Materials Science and Engineering at the University of Toronto. In XPS analysis, a sample material is irradiated with a beam of X-rays. The photoelectric effect causes absorption of the X-ray photons to eject electrons from the material. The kinetic energy and number of electrons escaping from the top 0 to 15 nm of the sample are measured, and the final XPS spectra is a plot of the number of electrons detected versus the electron binding energy.\(^{16}\) XPS can provide quantitative information about the elements present in a material, as well as qualitative information about chemical bonding and valence states. The surface sensitivity of XPS makes it a suitable technique for thin film analysis. Samples consisting of powders and crystals\(^{17}\) can also be analyzed; however, it is important for the samples to be prepared in a manner which ensures compatibility with ultra-high vacuum conditions.

In the literature, XPS studies have been performed to confirm the presence of hydrogen\(^{17-18}\) and halogen bonding interactions.\(^{19-21}\) The presence of these interactions results in some perturbation to the electron densities of the associated atoms, causing detectable shifts in electron binding energy. In the case of halogen bonding interactions, shifts of approximately 0.4 eV and 0.3 eV have been found for the N1s of nitrogen and the I3d doublet of iodine, respectively.\(^{19-20}\)
It should be possible to use XPS analysis on thin films and single crystals of BsubPc derivatives in order to detect the presence of halogen bonding interactions. Analysis of thin films and sublimation crystals of PhO-BsubPc would be a good starting point, as this derivative should not display halogen or hydrogen bonding interactions. The binding energy associated with the imine nitrogen atoms, in the absence of halogen and hydrogen bonding interactions, can therefore be determined. Subsequent analysis of thin films and sublimation crystals of the meta-halogenated BsubPc derivatives (m-FPhO-BsubPc, m-ClPhO-BsubPc, m-BrPhO-BsubPc and m-IPhO-BsubPc) should display a shift in the imine nitrogen binding energy for the chloro, bromo and iodo analogues if there is halogen bonding present. Additionally, if the halogen bonding present in the crystal samples is also present in thin films, then the binding energy of the imine nitrogen measured from thin film samples should be equivalent to those measured from crystals samples. Similar analysis can also be carried out to compare thin film and crystal samples of p-HOPhO-BsubPc, in order to test for the presence of hydrogen bonding.

8.2.6 Investigation of Intermolecular Interactions and Crystal Structure in Thin Films

As discussed in Chapter 5, investigating the arrangement of organic molecules in a thin film is not a trivial area of exploration. The film thicknesses relevant to organic electronic devices (<100 nm) contain very little material, and the light atoms common to organic materials (C, H, O, N, and in the case of BsubPcs, B) have low scattering cross sections and therefore do not provide strong diffraction signals in very small samples. Because of these factors, the diffractometers designed for typical university research, such as those available at the University of Toronto, are insufficient to study the structure of thin films of BsubPc derivatives. In order to fully investigate the structure of thin films of BsubPc materials, and to determine the extent to which observations relating to single crystal structures are applicable to thin films, collaboration with a synchrotron radiation facility will likely be necessary.

Synchrotron facilities offer a number of advantages for studying thin films of weakly diffracting materials. Such facilities typically combine several different electron accelerator types, and can produce electron beams of varying energy at intensities higher than those achievable in standard university diffraction facilities. A single facility will have several different beamlines, which include different experimental facilities and focus on different areas of research. Since
determining the structure of very thin films is effectively a surface science investigation, a beamline catered to surface science analysis would be ideal for studying thin films of BsubPcs materials. In particular, a technique such as grazing incidence x-ray diffraction (GIXRD), which is designed to be depth-dependent and capable of scanning a very shallow volume at the surface of a sample, coupled with a synchrotron electron beam would likely produce the signal strength and surface sensitivity necessary to characterize the structure of BsubPc films. Beamlines focusing on surface science will also typically have other useful equipment available for sample preparation and surface analysis, such as vacuum deposition equipment and atomic force microscopy instruments.

The Hard X-ray MicroAnalysis (HXMA) beamline at the Canadian Light Source synchrotron facility located in Saskatchewan appears to be a particularly promising beamline to collaborate with. Its facilities include GIXRD and this beamline has been used to characterize thin films of pentacene and tetracene ranging from approximately 1.2 to 15 monolayers in thickness.22

Unsurprisingly, time on synchrotron beamlines is typically in high demand. In order to secure beamline time, an experimental proposal must be submitted in the form of an application, and the applications are then reviewed and allotted a set amount of time on the beamline. Securing time for using a beamline and running the experiments would be a fairly intensive process, and would greatly benefit from a senior researcher familiar with crystallography and surface characterization techniques. This approach is likely to be very useful for investigating thin films of BsubPc materials.

The m-IPhO-BsubPc derivative would likely be a good candidate for initial GIXRD studies. It includes an iodine atom, which is fairly heavy and should provide a good scattering signal. Furthermore, if there are indeed halogen bonds in the thin film of this material, that should provide a driving force for the formation of polycrystalline films and facilitate characterization.

8.2.7 Extension of Co-Crystallization Study

Chapter 6 detailed the development of a simple simulation method to screen pairs of molecules for their potential to form a targeted, cyclic co-crystal motif. This approach was developed using pyridyl-substituted BsubPcs (6-8, Figure 8.4) as hydrogen bond acceptors and dihydroxy benzenes (12-14) as hydrogen bond donors.
The general applicability of this screening method could be investigated with further studies. Other molecules expected to be capable of accepting hydrogen bonds, such as cyano-substituted BsubPcs (9-11) could be screened with the same dihydroxy derivatives. The study could also be extended to screen for pairs of molecules capable of forming co-crystals via halogen bonding, using the same derivatives (6-11) as potential halogen bond acceptors and 1,4-diido-tetrafluorobenzene (15) as a potential halogen bond donor. Compound 15 is a good starting point for extending co-crystallization studies into halogen bonding, as iodine is known to be a strong halogen bond donor, and the adjacent fluorine atoms serve to strengthen its halogen bond forming abilities.\textsuperscript{23}

This stream of investigation would serve to establish the general applicability of the screening methodology developed in Chapter 6. In addition, these studies would provide additional insight into the co-crystal formation capabilities of BsubPc derivatives, which is a fairly unexplored area of investigation. Such co-crystal studies could eventually lead to design guidelines for co-crystallizing BsubPc with other materials of interest in organic electronic applications.

![Potential hydrogen-bond and halogen-bond acceptors](Image)

**Figure 8.4:** Proposed compounds for extended co-crystallization studies.
Chapter 7 described the synthesis of the first reported BsubPc-containing polymer (21, Figure 8.5). The pendant groups on the BsubPc polymer chain have three imine nitrogens which are potentially available for intermolecular interactions. BsubPc polymers are a very new area of research, and their ability to participate in intermolecular interactions is entirely unexplored.

The potential of such polymers to participate in halogen bonding could be explored using 1,4-diiodo-tetrafluorobenzene (20). Studies could be based solely on solution processing techniques, such as preparing films from a mixed solution of the polymer 21 and the halogen bond donor 20. Alternatively, a layer of 20 could be prepared as a templating layer using vacuum deposition techniques, followed by a subsequent layer of 21 prepared using solution processing techniques. In either approach, the morphology of the film should be compared with a solution-cast film of polymer 21 without the use of a halogen bond donor species, in order to discern morphological changes indicative of halogen interactions. This line of investigation would lead to the development of methods to control the morphology of BsubPc polymers, and the morphology of organic electronic materials is relevant to their performance in devices.

**Figure 8.5:** Possible intermolecular halogen bonding interactions between a BsubPc-containing polymer (16) and 1,4-diiodo-tetrafluorobenzene (15).
8.3 References


15. Bonnier, C.; Bender, T. *Molecules* **2015**, *Submitted, manuscript ID molecules-95896*.


