Altering the Crystal Packing of Boronsubphthalocyanine Derivatives through Molecular Engineering

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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2013

Abstract

There are currently three known crystal packing motifs of boronsubphthalocyanine derivatives. Each motif is associated with a particular class of BsubPc derivatives, and none are ideal for organic electronic applications according to the criteria we defined for evaluation: having a continuous pathway for charge-carrier conduction in the solid-state, resistance to hydrolysis, good electrochemical and optical properties, and possession of a robust crystal form. In this thesis, we present five methods for altering the crystal packing structure of phenoxy-BsubPc derivatives in order to meet the above four criteria. We find that neither addition of steric bulk to the axial derivative nor changing the symmetry of the compounds is sufficient for creating a new crystal packing motif. We do find that reducing the symmetry of the axial group does increase the solubility greatly, however. We identify a new motif for BsubPc crystals that occurs when the intermolecular interactions between the axial phenoxy segment and the BsubPc ligand are increased. We present two methods for achieving this new motif, one is through addition of a $\pi$-Br interaction and the other is through creation of a strong $\pi$-acid/$\pi$-base stacking by making the axial phenoxy more $\pi$-electron rich. Unfortunately, the $p$-bromophenoxy-BsubPc forms this new motif as a kinetic product, isolation of which is unreliable. Attaching a naphthol fragment axially to the BsubPc creates a stable version of this new motif. We also synthesized a
new class of BsubPc pseudohalides based on sulfonate derivatives. Of the derivatives in this
ew class, we found that mesylate-BsubPc forms into a crystal packing structure that possesses
a one-dimensional pathway for charge carrier mobility, but is still resistant to hydrolysis under
the conditions tested. Overall, we show four compounds that meet the criteria for further study
as organic electronic materials: $p$-methoxyphenoxy-BsubPc, $\alpha$-naphthoxy-BsubPc, $\beta$-
naphthoxy-BsubPc, and mesylate-BsubPc.
Acknowledgments

First and foremost, I must thank my wife Lindsey for her unending support and her understanding of the strange stresses that occur in the last few months of graduation. I also need to thank my family, parents, Bubbie, and grandma, for even though they probably did not understand most of what I was saying, were happy to listen to me explain my research.

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I would also like to thank Dr. Graham Morse, my frequent co-author and first graduate from our group for his help developing the BsubPc purification methods, and also for demonstrating that it is possible to graduate. A heartfelt thank you goes out to Bender Lab Classic and Neo-Bender Lab (Brett Kamino, Emma Brisson, Jessica Virdo, Graham Morse, Eli Bultz, Jenn Sauks, Jason D’Souza, Jeffrey Castrucci, Jeremy Dang, Mabel Fulford, Ahmed Abdelrahman, Mike Gretton, Ivan Gong, Bridget Mills, Deepak Prakhya, Yazan Kawar, Alina Makukhina, Nina Varlamova, Mona Khatibi, Benoit Lessard), first for being the most active lab in the building, and second while it was distracting you all made the time in grad school pass way too quickly. Specifically, I should thank Brett Kamino, the heart of the lab, for teaching me to always play from the hips.
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<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>BsubPc</td>
<td>Boronsubphthalocyanine</td>
</tr>
<tr>
<td>OPV</td>
<td>Organic photovoltaic</td>
</tr>
<tr>
<td>( V_{oc} )</td>
<td>Open circuit voltage</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>( \text{nm} )</td>
<td>Nanometre ((10^{-9} \text{ m}))</td>
</tr>
<tr>
<td>Cl-BsubPc</td>
<td>Chloro-boronsubphthalocyanine</td>
</tr>
<tr>
<td>Br-BsubPc</td>
<td>Bromo-boronsubphthalocyanine</td>
</tr>
<tr>
<td>F(_{12})BsubPc</td>
<td>Dodecafluoroboronsubphthalocyanine</td>
</tr>
<tr>
<td>OEM</td>
<td>Organic electronic material</td>
</tr>
<tr>
<td>OLED</td>
<td>Organic light emitting diode</td>
</tr>
<tr>
<td>H(_{12})BsubPcs</td>
<td>Boronsubphthalocyanine</td>
</tr>
<tr>
<td>CSD</td>
<td>Cambridge Structural Database</td>
</tr>
<tr>
<td>BCl(_{3})</td>
<td>Boron trichloride</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>TMS</td>
<td>Tetramethyl silane</td>
</tr>
<tr>
<td>UV-Vis</td>
<td>Ultraviolet-visible ((\text{absorption spectroscopy}))</td>
</tr>
<tr>
<td>HPLC</td>
<td>High performance liquid chromatography</td>
</tr>
<tr>
<td>ACN</td>
<td>Acetonitrile</td>
</tr>
<tr>
<td>CDC(_{3})</td>
<td>Deuterated chloroform</td>
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<tr>
<td>CHCl(_{3})</td>
<td>Chloroform</td>
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<tr>
<td>nPc</td>
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<td>PhO-BsubPc</td>
<td>Generic phenoxy-boronsubphthalocyanine</td>
</tr>
<tr>
<td>MHz</td>
<td>Megahertz</td>
</tr>
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<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>GC</td>
<td>Gas chromatography</td>
</tr>
<tr>
<td>CLFR</td>
<td>Crystal-liquid fugacity ratio</td>
</tr>
<tr>
<td>( \Delta S_m )</td>
<td>Change in entropy upon melting</td>
</tr>
<tr>
<td>( T_m )</td>
<td>Melting temperature</td>
</tr>
<tr>
<td>( \sigma )</td>
<td>Rotational symmetry number</td>
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<td>( \tau )</td>
<td>Molecular flexibility number</td>
</tr>
<tr>
<td>( n_{SP3} )</td>
<td>Number of SP3-hybridized carbons in the molecule</td>
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<tr>
<td>( n_{SP2} )</td>
<td>Number of SP2-hybridized carbons in the molecule</td>
</tr>
<tr>
<td>( n_{\text{ring}} )</td>
<td>Number of ring systems in the molecule</td>
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<tr>
<td>TfO-BsubPc</td>
<td>Trifluoromethylsulfonate-boronsubphthalocyanine</td>
</tr>
<tr>
<td>TsO-BsubPc</td>
<td>4-Methylbenzenesulfonate-boronsubphthalocyanine</td>
</tr>
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<td>Methylsulfonate-boronsubphthalocyanine</td>
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<td>Symbol</td>
<td>Description</td>
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<tr>
<td>ClsO-BsubPc</td>
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<td>3-Nitrobenzenesulfonate-boronsubphthalocyanine</td>
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<tr>
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<td>millilitre</td>
</tr>
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<td>PDA</td>
<td>Photodiode Array</td>
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<tr>
<td>DMSO</td>
<td>Dimethyl sulfoxide</td>
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<tr>
<td>Cg</td>
<td>Centre of gravity (of an aromatic ring)</td>
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Chapter 1
Motivation, Thesis, and Scope

1 Motivation, Thesis, and Scope

1.1 Motivation of the Project

1.1.1 Boronsubphthalocyanine

1.1.1.1 Structure and Properties

Boronsubphthalocyanine (BsubPc) was first reported in 1972 [1] and was chosen as the molecule of interest for this project because it has been shown to have optical and electrical properties suitable for organic electronic devices. Unlike many other organic chromophores, the maximum wavelength of light absorption of BsubPc is around 565 nm. This wavelength is fairly close to the maximal wavelength of light emission from the sun, as shown in Fig 1.1, making BsubPc a good candidate for organic photovoltaic devices (OPVs), and has in fact been incorporated into many devices already. [2] Even these preliminary OPVs with BsubPc as an active layer demonstrate relatively high typical power conversion efficiencies of 1 to 3% for unoptimized devices using a new material. An interesting feature of all of the OPVs of BsubPc is that they in general display a particularly high open circuit voltage (V_{oc}) of over 1.0 V, likely due to their HOMO and LUMO energies, a property that has been desirable in photovoltaics since their inception. The emission wavelength of BsubPc is around 575 nm, and has been shown to have a narrow emission band with a full width half maximum of only 30 nm. Furthermore, it has been shown to be a successful material for orange organic light emitting diodes (OLEDs) with high fluorescence quantum efficiency. [3]

Another factor in the choice to study BsubPc crystals was its unique structure and potential for relatively facile attachment of substituent groups. The BsubPc ligand consists of three isoindoline units templated around a central boron atom. These isoindoles are connected through imino nitrogens, giving BsubPc an aromatic \pi-system of 14 \pi-electrons. Boron is the only known element to template the formation of this three-membered construct, with all other elements under the same conditions leading to the four-membered analogue phthalocyanine likely due to the smaller size of the boron atom. However, the cyclization of the subPc ligand...
Figure 1.1: Spectral irradiance spectra of solar radiation above Earth’s atmosphere (ASTM G173) (gray) and at sea level (from ASTM E490) (black), shown overlaid with the solution phase absorption spectrum of phenoxy-BsubPc (pink).

around boron leads to a non-planar shape of the molecule, as shown in Fig 1.2a. In this formation, boron makes two covalent bonds and one dative bond with the three isoindoline nitrogens, leaving one additional bond perpendicular to the plane of the subPc ligand. This is known as the axial position on boron, and is the most common site on BsubPc for derivatization reactions.

Nomenclature related to the BsubPc molecule can be found in Fig 1.2b. As mentioned above, the boron bond perpendicular to the BsubPc ligand is known as the axial bond. The atoms on the outside of the isoindole units are known as the peripheral substituents, of those the two that face towards the spaces between the isoindole units are known as the bay positions, while the
outermost atoms are in the exterior position. The nitrogen atoms that link the isoindole units together are known as the imine nitrogens. Since the BsubPc ligand is cone-shaped, it is convenient to refer to the underside of the cone as the concave face of the BsubPc, while the outside of the cone is called the convex face.

1.1.1.2 Synthesis

The BsubPc molecule is synthesized according to the reaction shown in Scheme 1.1. Phthalonitrile is mixed with a boron-containing Lewis acid and heated to induce cyclization.[4-6] Most commonly, boron trichloride (BCl$_3$) is used as the boron source, which results in a chlorine atom in the axial position. [4,6] However, more recently an efficient synthetic method using boron tribromide (BBr$_3$) as the Lewis acid has been gaining acceptance, which leaves a bromine atom in the axial position. [5] There has also been a similar synthesis reported which uses triphenylboron as the source, which leaves a phenyl group axially attached to the boron atom. [7]

Another variable in the synthesis is the choice of phthalonitrile. Many phthalonitrile derivatives have been shown to be reactive to this cyclization reaction, including tetrafluorophthalonitrile, [8-14] 4-$t$-butylphthalonitrile, [15] 4-nitrophthalonitrile, [6,16] 4-iodophthalonitrile, [6,17] the
Scheme 1.1: Typical synthesis scheme of X-BsubPc, where X is either Cl or Br, and R₁ and R₂ are peripheral substitutions on the resulting boronsubphthalocyanine.

sulfur containing 4,5-bis(octylsulfonyl)phthalonitrile and 4,5-bis(octylthio)phthalonitrile, [6,18] the π-extended derivatives naphthalonitrile [19,20] and a pyrene derivative, [13] and even more exotic derivatives such as a difunctional phthalonitrile that can result in BsubPc dimers, [9] and very recently a class of larger phthalonitriles with a pair of phenyl or naphthyl units connected through in the 3,4 and 5,6 positions via diether linkages. [21] While changing the phthalonitrile derivative allows peripheral changes in the BsubPc derivative, the method for BsubPc synthesis remains largely unchanged.

1.1.1.3 Common Reactions

As discussed above, derivatization of the BsubPc molecule can be achieved in the axial or peripheral positions. Peripheral substitution is rare, and requires a particular BsubPc derivative synthesized from a phthalonitrile derivative. An example from the literature is cross-coupling performed on iodo-substituted BsubPc. [22-23] Axial derivatization is more common and can be performed on Cl-BsubPc or Br-BsubPc with various peripheral substituent groups. Nucleophiles that have been used for substitution include oxygen, nitrogen, sulfur, and carbon-based groups. A general scheme for the axial substitution can be found in Scheme 2.2. For various classes of nucleophiles and halo-BsubPcs, the reaction conditions differ due to the different reactivities of the reagents. Cl-BsubPc can in general be reacted directly with oxygen nucleophiles such as phenols, [6,8] whereas nitrogen-based nucleophiles require an activator such as a triflate intermediate [14] or carbon-based nucleophiles such as alkynes can be attached.
by using Grignard chemistry. [24] Br-BsubPc has a much higher reactivity than Cl-BsubPc and so can undergo all the same reactions as Cl-BsubPc, but there is evidence that some nitrogen-based nucleophiles can be reacted directly with Br-BsubPc. Both Cl-BsubPc and Br-BsubPc can undergo hydrolysis with water to form OH-BsubPc. [5]

1.1.2 Crystals in Organic Electronics

The role that crystalline phases play in organic electronics is being viewed more seriously as a potential area of large enhancement to the charge carrier mobilities of the active layers in devices. Due to the fact that most compounds used in organic electronics are rigid and planar, as they are small aromatic molecules, there are two common crystalline motifs among these materials. The first is known as the herringbone motif, which consists of offset-stacked aromatic molecules forming columns. These columns are then set at angles to each other, stabilized by edge-on-face $\pi$-stacking interactions. A schematic of this system is shown in Fig. 1.3a. The second motif also consists of offset stacked molecules, however the edge-on-face $\pi$-stacking is removed and all molecules now sit in parallel planes. Two submotifs of this are seen in organic electronic compounds: One where the molecules $\pi$-stack with more than one neighbour in a brick-work fashion, and one where the molecules lie on a single columnar axis forming lamellae. Schematics of these two motifs are shown in Fig 1.3b and c, respectively.

Those studying the crystalline phases of organic electronic materials have shown that the crystal structure of a compound can affect the charge carrier mobility. [26-29] Furthermore, there has been shown to be a large increase in charge carrier mobilities of single crystals of traditional OEMs over the same material in the amorphous phase. [30] In order to facilitate this, studies have been undertaken in order to ensure that flat planar molecules crystallize into closely packed $\pi$-stacked motifs. Anthony et al. have demonstrated this with TIPS-pentacene derivatives, showing that closer molecular spacing increases the charge carrier mobility. [29]

1.1.3 Crystals of Boronsubphthalocyanine

Unlike most OEMs, however, BsubPc is not a planar molecule. This means that it cannot align in the traditional $\pi$-stacked or herringbone motifs normally associated with small molecule OEM crystals and therefore empirically-known methods of increasing device performance may not apply. Despite the many studies of organic electronic devices incorporating BsubPc, there is relatively little in the literature on BsubPc derivatives in the solid state. Some of the BsubPc
derivatives discussed above have had crystal structures published in literature. The following section describes the crystal structures of these BsubPc compounds. For all of the published structures, there are three main motifs seen: 1) head-to-tail concave-concave chains, 2) stacks perpendicular to the BsubPc plane, and 3) head-to-head concave-concave dimers. Schematics of these three motifs are shown in Figure 1.4. In the first, one of the isoindoline unit overlaps in a π-stacking interaction with one of the imine nitrogens of the neighbouring BsubPc ligands.
Figure 1.4: Common crystal packing motifs of BsubPcs. a) Head-to-tail, which is commonly a concave-concave overlap forming 1-D chains, b) the stacked motif, and c) head-to-head concave-concave dimer motif. In these images both the hydrogen atoms and double bonds have been omitted for clarity. Adapted from [11].

This repeats with the next BsubPc and creates a chain of BsubPc ligands overlapping on their concave faces. The second motif is characterized by the specific interaction of the axial substituent with the concave side of the neighbouring BsubPc ligand, in which said neighbor is located “above” in a position perpendicular from the plane of the BsubPc itself. In that way, stacks of BsubPc molecules are created. Generally there is no or little specific interaction between stacks in this motif. The third motif, and also seen as the most common for axially substituted BsubPcs, is one in which isoindoline units of neighbouring BsubPcs overlap in a centrosymmetric π-stacking interaction, creating pairs or dimers of BsubPc molecules.

1.1.3.1 Halogen Derivatives

The halogen derivatives are the most basic BsubPc derivatives. Of these, the crystal structures of Cl-BsubPc, [31] Br-BsubPc, [32] and F-Bsubpc [32] are known. The main crystal structure motif of these compounds is the head-to-tail chains. Other than these one-dimensional chains, there are no specific close interactions. All three of these structures are very similar, and only differ in their intermolecular spacing due to the atomic size difference of their axial halogens. They all belong to the orthorhombic space group Pnma, which consists of three orthogonal screw axes perpendicular to three mirror planes.
1.1.3.2 Hydroxy Derivative

The hydrolyzed form of BsubPc, OH-BsubPc, forms a non-solvated crystal of space group C2/c. Although the hydroxyl substituent is not so different in size from the halogens discussed above, the crystal packing motif seen in this structure is not head-to-tail chains but the head-to-head concave-concave dimer motif.

1.1.3.3 Peripherally Halogenated Derivatives

The BsubPc crystals reported in literature that possess peripheral substitution are all peripherally halogenated. More specifically, because there is an effect on energy levels that is desirable for organic electronic materials, the derivatives possess peripheral perfluorination. In this group, there are Br-F_{12}BsubPc, [10] Cl-F_{12}BsubPc, [currently unpublished] and phenoxy-F_{12}BsubPc [8] which are all in the P2\textsubscript{1}/c space group, and F-F_{12}BsubPc [12] and pentafluorophenoxy-F_{12}BsubPc [33] which are in the P2\textsubscript{1}2\textsubscript{1}2\textsubscript{1} space group. All of the crystal structures in this group are of the stacked motif. The halogen-F_{12}BsubPcs show halogen-boron distances less than the sum of the van der Waals radii. The two phenoxy-derivatives in this section show π-stacking between the phenoxy ring and the concave face of the next BsubPc in the stack.

1.1.3.4 Oxygen-Nucleophile Derivatives

Most derivatives of BsubPc are from axial substitution with an oxygen-based nucleophile. In fact, most of the nucleophiles here are either aryl or alkyl alcohols. In this group there are crystals of pentafluorophenoxy-BsubPc, [11] 3-hydroxypyridine-BsubPc, [34] 3-hydroxypyridine-BsubPc with the pyridinyl nitrogen linked to a Ru-centred tetraphenyltetracarbaporphyrin, [34] 4-hydroxypyridine-BsubPc, [34] tert-butoxy-BsubPc, [5,14] ethoxy-BsubPc, [35] methoxy-BsubPc, [36] t-butyl-dimethyl-siloxy-BsubPc, [36] and two oligothiophene-derivatives linked through phenoxy units: 4-tetrathieno-phenoxy-BsubPc and 4-dithieno-phenoxy-BsubPc. [37] While these derivatives crystallize into a few different centrosymmetric space groups, they all possess their clearest interaction as forming into head-to-head dimers. That is, despite their varying character, from short chain alkyl alcohols to oligothiophene derivatives, the main crystal packing feature is the π-π stacking of the concave faces of the BsubPc ligands. Only two oxygen derivatives do not show this motif in their crystal structures: one polymorph of methoxy-BsubPc, [38] which crystallizes in the Pnma space group.
and shows the motif of head-to-tail chains like the halogen-$\text{B}_{\text{subPc}}$, and 2-allylphenoxy-$\text{B}_{\text{subPc}}$, [37] which crystallizes into the common $P2_1/c$ space group, but shows a unique slip-stacked motif of alternating concave-convex $\pi$-stacking to create columns of molecules purely by the $\text{B}_{\text{subPc}}$ ligands themselves. Interestingly, the allyl group shows disorder within the crystal, implying it is not involved in intermolecular interactions that might stabilize the structure.

1.1.3.5 Nitrogen-Nucleophile Derivatives

There are currently no nitrogen derivatives that have been crystallized without being a solvate structure, however there is current effort in synthesizing more of these derivatives. There are two published crystal structures of nitrogen-based nucleophile derivatives of $\text{B}_{\text{subPc}}$: one is diphenylamine-$\text{B}_{\text{subPc}}$ and the other is phenothiazine-$\text{B}_{\text{subPc}}$. [14] While these will be included in the section about solvates below, they deserved special note as non-oxygen-based nucleophile derivatives of $\text{B}_{\text{subPc}}$ are an area of study that is receiving much attention in our group.

1.1.3.6 Carbon-Nucleophile Derivatives

Carbon-based nucleophile derivatives of $\text{B}_{\text{subPc}}$ have been the product of using triphenylboron as the boron source in the cyclization reaction to form phenyl-$\text{B}_{\text{subPc}}$ [5,7,36] or the product of a Grignard reaction to supplant the chlorine atom of Cl-$\text{B}_{\text{subPc}}$ with an alkyne derivative as in the case of 4-methylphenyl-ethynyl-$\text{B}_{\text{subPc}}$. [24] For phenyl-$\text{B}_{\text{subPc}}$ there have been three reported structures, but all have the same Pbca space group and all fit in the head-to-head dimer motif. The alkyne derivative, on the other hand, while having a C2/c space group does not fit easily into one of the three usual $\text{B}_{\text{subPc}}$ crystal motifs. Its major interaction is similar to the head-to-tail chain of the halogen-$\text{B}_{\text{subPc}}$ derivatives, except that its interaction is between the convex faces of the isoindole unit and the imino nitrogen rather than the concave faces. Because it is so similar, it will be categorized as a head-to-tail chain.

1.1.3.7 Solvates and hydrates

A variety of solvents in many different proportions form solvates with $\text{B}_{\text{subPc}}$ derivatives in the solid state. The most common found in the structures are dichloromethane, [9,39] chloroform, [13,14,40,41] toluene, [42] and water. [5,14,38,41] That these solvents are found in the most examples of structures likely does not reflect a preference of $\text{B}_{\text{subPc}}$ to interact with them, but
rather the preference of the researcher in using these solvents for performing crystallization. Of all of the solvates, 15 of them are oxygen nucleophile derivatives, including two different solvate structures of acetoxy-BsubPc, [5] bisphenolF-BsubPc, [33] two different structures for phenoxy-\textit{F}_8BsubPc with one isoindole replaced with a dicyano-di-\textit{t}-butylpyrene unit, [13] 4-(dimethyl-bis(2-(4-methoxyphenyl)ethenyl)-B,B-difluoro-N,N'-dipyrroloidine)-phenoxy-BsubPc, [39] 4-(tetramethyl-B,B-difluoro-N,N'-dipyrroloidine)-phenol, [39] axially phenoxy substituted BsubPc derivative with 2 \textit{p}-\textit{t}-butylphenoxy units on each of two of the isoindoles and a chloropyrene unit replacing the third isoindoline, [42] the 3- and 4-hydroxybyrididine-BsubPc derivatives N-linked to a Zn-(tetraphenyl)-tetracarbaporphyrin, [34] trifluoroacetate-BsubPc, [14] 4-hydroxyphenoxy-BsubPc, [14] a hydrate of hydroxy-BsubPc, [38] a dimeric BsubPc linked axially through 1,1'-binaphth-2,2'-dioxy, [40] and a \textit{µ}-oxo dimer of BsubPc. [43] All of these structures show the concave-concave head-to-head dimer motif, except for the \textit{µ}-oxo dimer which shows convex-convex \textit{π}-stacking as the main interaction.

There are also two BsubPc derivatives with nitrogen-based substituents, as mentioned above. [14] Both of them also demonstrate the typical dimer motif. A crystal structure has been published for one additional derivative with a carbon-based substituent: 4-(N,N-dibutyl)-aminophenyl-ethynyl-BsubPc. [24] This structure shows a head-to-tail chain motif. There are also three perfluorinated Cl-BsubPc derivatives: one has two isoindoline units perfluorinated and the third is a non-fluorinated naphthalene group, [20] and the other two are the syn- and anti- of a related peripherally linked BsubPc dimer, which is perfluorinated except for the linkage isoindole which is \textit{π}-extended to link the two BsubPc units together. [9] All three of these structures fit in with the stacked motif that perhalogenated-BsubPcs adopt. The last structure reported has no substituent on the boron and is in fact a solvate with hexabromopentamethyldodecaborate. [43] This particularly unique BsubPc structure does not fit in to any of the three common crystal packing motifs.

\subsection{1.1.3.8 Subporphines}

Just as the phthalocyanines are related to the porphyrins, the subphthalocyanines have their counterpart in the subporphyrins, triazasubporphyrins, and tribenzosubporphyrins. [44] The subporphyrins are less bowl-shaped than the subphthalocyanines, a difference which makes comparison of their crystals structures less useful; however, there are some similarities, and therefore a brief summary of their crystal structures is illuminating. Axially, all of the
compounds in the crystal structures are axially derivatized with short chain oxygen-based nucleophiles such as methoxy, trifluoroacetoxy, hydroxy, or isopropanoxy, and have various peripheral substituents. [41] Despite their structural differences, of the 4 structures reported without peripheral derivatization, 3 crystallize into the head-to-tail dimeric motif common to \textbf{BsubPcs}: isopropanoxy-tribenzosubporphyrin, [38] trifluoroacetoxy-tribenzosubporphyrin, [38] and a hydrate of hydroxy-tribenzosubporphyrin. [38] Due to their structural differences with the \textbf{BsubPcs}, the remaining structures do not fit into any of the three above-defined motifs, nor do they form their own consistent submotif.

1.1.3.9 Summary of crystal structures

All of the crystal structures, a summary of their main substituent groups, crystal packing motifs, and space groups are summarized in Table 1.1. One can note that the distribution of space groups of the true \textbf{BsubPc} crystals mirrors the typical distribution of organic crystals in general, with nearly half of all structures in the P2\textsubscript{1}/c group. Noticeably absent from this list is P2\textsubscript{1}, one of the top five most common space groups of organic crystals. It also becomes clear that the most common motif for non-peripherally halogenated \textbf{BsubPcs} is that of the head-to-head dimer formation, with 16 out of 22 structures showing this structure. For the peripherally halogenated structures, however, the stacked motif dominates.

It has been suggested that those space groups containing a two-fold rotation element are more preferred by concave molecules, since this allows close-packing and self-complementarity. However, the inversion centre element is also favoured for the same reason. [45] That the most common space groups for \textbf{BsubPc} crystals, P1 \textbar, P2\textsubscript{1}/c and Pnma, contain these elements is then not surprising, and that the less-concave subporphines crystallize into more varied space groups likely reflects this trend. One other factor to consider in the crystallization is that crystals are more likely to form into close-packed structures that are neutral in their intermolecular vectors. [45] The inversion element produces this effect inherently. However, for derivatives where the symmetry of the molecule is higher, such as the halo-\textbf{BsubPcs}, it is more likely that additional symmetry elements can exist in the crystal, such as glide elements or more complex screw axes. Perhaps it is because of the higher-symmetry of the halo-\textbf{BsubPcs} that they avoid the P1 space group and crystallize into Pnma and a different non-dimer crystal packing motif. Furthermore, if there are specific interactions in the structure that can dominate the crystal packing motif, then certain symmetry relationships between molecules can be designed into the crystal. For instance
Table 1.1: Summary of BsubPc crystal packing motif and space group.

<table>
<thead>
<tr>
<th>Compound group</th>
<th>Crystal Packing Motif</th>
<th>Space Group</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Head-to-tail chains (Halo-BsubPc Motif)</td>
<td>P1</td>
<td>3</td>
</tr>
<tr>
<td>Halo-BsubPc</td>
<td>3</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>Stacks (Phenoxy-(F_{12})BsubPc Motif)</td>
<td>P2/c</td>
<td>1</td>
</tr>
<tr>
<td>Hydroxy-BsubPc</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Head-to-head dimers (Phenoxy-BsubPc motif)</td>
<td>P2(_{12}2_1)</td>
<td>5</td>
</tr>
<tr>
<td>Peripherally Halogenated BsubPc</td>
<td>5</td>
<td>1</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>Other</td>
<td>P2(_{12}2_1)</td>
<td>3</td>
</tr>
<tr>
<td>Oxygen Nucleophile</td>
<td>1</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Nitrogen Nucleophile</td>
<td>1</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Carbon Nucleophile</td>
<td>1</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td><strong>BsubPc Total</strong></td>
<td>5</td>
<td>12</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>Solvate</td>
<td>P2(_{12}2_1)</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>1</td>
<td>12</td>
</tr>
<tr>
<td>Related compounds</td>
<td>1</td>
<td>2</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>Subtotal</td>
<td>C2/c</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>11</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>Pbca</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>3</td>
<td>60</td>
</tr>
</tbody>
</table>
if a strong interaction between two of the peripheral edges of the isoindoline units of the BsubPc ligand existed, then likely in the crystal the BsubPc ligand would line up in a plane. If this interaction were directional, then perhaps the dimer phase could be avoided. Or, if a strong interaction could be designed that causes the concave side of the BsubPc to be occupied with one of the axial substituents, then likely there would be no room for the concave-concave dimer motif to exist. Also, it would be expected that if the symmetry of the new interaction allowed alignment along a mirror plane in the molecule then this element would be seen in the structure.

1.1.4 Outlook

The frequency of BsubPc crystals that fall into the dimer motif is around 60% of the currently published structures. Of the rest, the stacked motif can be achieved by peripherally halogenating the BsubPc ligand, and the halo-BsubPcs, with no further substitution on the boron, account for three of the head-to-tail motif structures. Without those structures, the frequency of peripherally hydrogenated and axially substituted BsubPcs in the dimer motif rises to more than 80% of reported structures. Figure 1.5 shows examples of each of these types of molecules in their respective motifs.

As mentioned earlier, a crystal packing motif that possesses a continuous pathway for charge carrier conduction is desirable for a material designed for use in organic electronics applications. Of the three classes of BsubPc derivatives that fall into the three motifs discussed above, both the head-to-tail motif of the halo-BsubPcs and the stacked motif of the peripherally halogenated BsubPcs possess a one- or two-dimensional pathway for charge carrier conduction. The dimer motif of the H12BsubPcs does not. It would seem desirable, then, to use the halo-BsubPcs or the peripherally halogenated BsubPcs as OEMs in devices. However, there are more criteria for materials than just solid-state motif. The halo-BsubPcs, for example, are not ideal candidates since they are susceptible to hydrolysis. The peripherally halogenated BsubPcs have been shown in some reports to possess irreversible first oxidations and reductions, [11] which is also not a desirable characteristic of an organic electronic material, since the lifetime of an effective material will be shortened through irreversible redox processes. On the other hand, there are also reports that demonstrate reversibility of the first redox events for F12BsubPc materials. [17] For these reasons, a valid goal would be to use the materials that have both good electrochemical
Figure 1.5: a) Crystal structure of Br-BsubPc in the halo-BsubPc head-to-tail motif, b) the crystal structure of phenoxy-F\textsubscript{12}BsubPc showing the stacked motif, and c) phenoxy-BsubPc crystal structure in the dimer motif.

properties and are not susceptible to hydrolysis, namely the H\textsubscript{12}BsubPcs. However, as discussed above this class of molecules predominantly forms into the dimer motif, which does not have a pathway for charge carrier conduction.

This discussion leads to a definition of materials and solid-state packing properties that will act as criteria for the evaluation of BsubPc crystals throughout this thesis. There are three criteria that we can use to define a material as having basic properties making it a candidate for incorporation into photovoltaic devices:

i) Electrochemical properties: at least one of either the first oxidation or first reduction event is reversible.

ii) Hydrolytic stability: the derivative does not hydrolyze during storage as detectible by HPLC.

iii) Pathway in structure: the crystal structure of the material possesses a one, two, or three dimensional pathway through the entire crystal, defined by specific interactions between neighbouring molecules in the pathway.

A comparison between the known derivatives and how they rate against these criteria is summarized in Table 1.2. It is important to point out that the halo-BsubPcs also possess poor electrochemistry (both first oxidation and reduction are irreversible), but since they have been
Table 1.2: A comparison of the three main BsubPc classes and their performance versus criteria for a desirable organic electronic material.

<table>
<thead>
<tr>
<th></th>
<th>Electrochemical Properties</th>
<th>Hydrolytic Stability</th>
<th>Pathway in Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Halo-BsubPc</td>
<td>~</td>
<td>x</td>
<td>✓</td>
</tr>
<tr>
<td>Phenoxy-F_{12}BsubPc</td>
<td>x</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Phenoxy-BsubPc</td>
<td>✓</td>
<td>✓</td>
<td>x</td>
</tr>
</tbody>
</table>

successfully incorporated into devices they are defined as neither good nor bad in this respect, but we believe that if even one of the first redox events were reversible there would be improvement in performance. The use of the ‘~’ symbol and yellow colour in Table 1.2 reflects this definition.

1.2 Thesis

One would expect that there should be a way to alter the crystal packing of BsubPc ligand in a predictable fashion, while still maintaining the good optical, electrical, and photostability properties desirable in BsubPc. Since intermolecular forces stabilize crystal structures, the addition of more or stronger forces within the crystal structure could cause the solid-state arrangement to pack in a predictable way. In this thesis I explore this idea by creating intermolecular forces in the crystal through addition of substituent groups on the BsubPc. In order to maintain the optical and electrochemical properties of BsubPc, axial substitutions are favoured over peripheral substitutions. This thesis examines BsubPc crystal structures with forces added to the compounds through:

- Non-interacting alkyl bulk,
- Change in symmetry,
- Specific halogen-containing interactions,
- \(\pi\)-acid/\(\pi\)-base interactions, and
- Addition of sulfonate groups.
1.3 Scope

This thesis describes the study of BsubPc derivatives in the solid state. First the introduction provides the background material on organic crystals and the available literature on the crystal structures of BsubPc. The content of this thesis is based mainly on papers already published in literature, and this will be elucidated prior to each manuscript. A primer on intermolecular interactions, crystal symmetry, and organic crystal growth is provided in Appendix A.

In Chapter 2, the nature of the phenoxy-BsubPc crystallization is examined. I present a manuscript discussing the similarities in crystal packing structures between phenoxy-BsubPcs with alkyl substituents of varying lengths in the para position of the phenoxy. From this study it is determined that the aromatic π-electron stacking into dimers is the repeated common unit in the phenoxy-BsubPc crystal structure.

Once the para derivatives were formed, we wanted to study the effect of a change in symmetry on the crystal structure, which is covered in Chapter 3. Although not much difference was seen in crystal structure, the new derivatives were found to solvate more efficiently, and also the compounds possessed a surprisingly high solubility. We determined that merely by changing single methyl group on the phenoxy unit from the para position to the meta position, the solubility of the entire phenoxy-BsubPc molecule can be increased by two orders of magnitude.

Next, crystals are engineered to have different crystal packing motifs from the typical phenoxy-BsubPcs. I present two methods on specific interactions being used to alter the crystal packing structure from the isolated dimeric structure and create 1-D ribbons of BsubPc molecules. The first method, in Chapter 4, uses a boron-halogen interaction to show that only 4-bromophenoxy-BsubPc crystallizes into a 1-D ribbon motif, while the other halogens, which do not geometrically fit into the binding position, maintain their dimeric pattern. Unfortunately, we found that this desired bromophenoxy-BsubPc structure is in fact a kinetic polymorph that we could not recreate using typical crystallization methods. Methods for isolating kinetic polymorphs for future studies are outlined in this section as well. The other method uses high π-electron density substituent groups such as α- or β-naphthoxy to bind through π-stacking to the neighbouring BsubPc molecule, which is presented in Chapter 5. The cases of π-electron deficient substituents are also given, and show that there is in fact a stronger interaction between the π-basic substituents and the π-acidic BsubPc ligand.
Finally I present the development of new chemistry for BsubPc substitution in Chapter 6. By extending the known derivatives of BsubPc, it increases the potential for the use of this material in a variety of applications. Furthermore, the addition of new chemical groups to BsubPc creates the opportunity to design into the molecule different intermolecular interactions. The crystals of these sulfonate derivatives of BsubPc are presented and compared to each other and to the other precursor compounds, the halo-BsubPcs. The sulfonate group included in the derivatives leads to a variety of interesting solid-state arrangements. The chemical properties of these compounds are then discussed, and we study the reactivity, hydrolysis rates, and electrochemical properties of the new materials.

I wrap up this thesis with a comparison of all of the materials found in the various studies that have been identified as fitting the criteria discussed above. After this, possible extensions to this work are suggested in the form of future work.

1.4 References


Chapter 2
p-Alkylphenoxy-Substituted Boronsubphthalocyanines

In order to design crystal forms of BsubPc, the forces that control its solid-state packing must first be elucidated. Derivatives of phenoxy-BsubPc could contain substituent groups that provide additional intermolecular forces that would confound the isolation of forces from the basic phenoxy-BsubPc. For this reason, in this chapter we studied a series of five phenoxy-BsubPc derivatives substituted with alkyl groups of different sizes. The alkyl groups act as non-interacting ‘spacer’ molecules which still provides alteration of the crystal form while allowing the forces that act to stabilize the phenoxy-BsubPc in the crystal phase.

The content of the Chapter consists of a manuscript that was published in the journal Crystal Engineering Communications as a full paper. Of the work in the manuscript, Graham Morse assisted in the development of the purification methods for Cl-BsubPc and phenoxy-derivatized BsubPc, the diffraction and refinement of the crystal structures was performed by Alan Lough, and all other work was performed by Andrew Paton. The full reference is: Andrew S. Paton, Graham E. Morse, Alan J. Lough, and Timothy P. Bender. “Observations regarding the crystal structures of non-halogenated phenoxyboronsubphthalocyanines having para substituents on the phenoxy group.” CrystEngComm, 2010, 13: 914-919.

2 p-Alkylphenoxy-Substituted Boronsubphthalocyanines

2.1 Introduction

As discussed in Chapter 1, the unique geometric and optical properties of BsubPc have made it desirable for organic electronics applications. Recently our group has become similarly interested in the solid-state application of BsubPc and more specifically its phenoxy derivatives. One can assume that the nature of both the BsubPc moiety and the phenoxy substituent will play a role in its solid state intermolecular arrangement. While the chemistry to produce phenoxy-BsubPc derivatives is known [1] and the preparation of several phenoxy-BsubPc derivatives have been reported, [2] we were unable to locate a comprehensive study of the intermolecular arrangement of phenoxy-BsubPcs in the solid state, nor are there any crystal
structures deposited in the CSD of non-halogenated phenoxy-$\text{BsubPcs}$. This despite a report detailing the arrangement of a series of alkoxy-$\text{BsubPc}$ derivatives in the solid state. [2a-c]

In this chapter, we report the systematic study of a series of five non-halogenated phenoxy $\text{BsubPcs}$ all made by reaction of $\text{Cl-BsubPc}$ (1, Scheme 2.1) with a series of structurally similar phenols having a variety of substituents in the para-position. The substituents were chosen so as to vary in size and electronegativity and the single crystal structures of each of the phenoxy-$\text{BsubPcs}$ were determined.

2.2 Experimental

2.2.1 Materials

Phthalonitrile and 4-fluorophenol were purchased from TCI Company Ltd. (Portland, Oregon) and used as received. Boron trichloride ($\text{BCl}_3$) 1.0 M solution in heptane, phenol, p-cresol, 4-\textit{tert}-butylphenol and 4-\textit{tert}-octylphenol were obtained from Sigma Aldrich (Mississauga, Ontario, Canada) and used without further purification. Other common solvents, reagents and standard basic alumina (300 mesh) were purchased from Caledon Laboratories (Caledon, Ontario, Canada) and used as received.

2.2.2 Methods

X-ray diffraction results were analyzed using PLATON 40M-version 250809 [3] for bond angles and lengths, and crystal packing images were generated using Mercury version 2.2. [4] All crystal structures were collected using a Nonius KappaCCD diffractometer equipped with an Oxford Cryostream variable temperature apparatus. 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 $^1\text{H}$ NMR reference purchased from Cambridge Isotope Laboratories and used as received. All ultraviolet-visible (UV-Vis) spectroscopy was performed using PerkinElmer Lambda 25 in a PerkinElmer quartz cuvette with 10.00 mm path length.

The reaction progress was monitored using a Waters 2695 high pressure liquid chromatography (HPLC) separation module with a Waters 2998 photodiode array. A Waters 150 mm reverse phase Sunfire® C18 5μm column was used with HPLC grade acetonitrile (ACN, 1.2 mL/min isocratic) purchased from Caledon Laboratories as the eluent.
Chloroboronsubphthalocyanine (Cl-BsubPc, 1). Compound 1 was synthesized by adapting a previously published procedure. [5] Phthalonitrile (5.32 g, 0.0415 mol) was dissolved with stirring in 1,2-dichlorobenzene (220 mL) in a rounded bottomed flask fitted with a short path distillation column and placed, under a constant flow of argon gas towards the short path distillation column. To this solution BCl$_3$ (100 mL of 1.0 M solution (0.1 mol) in heptane) was added in a single portion. On gradual heating the heptane was distilled off. When distillation was complete the reaction heated at reflux for an additional 1.5 hours. After cooling, the solvent was removed by rotary evaporation. The resulting crude product was extracted with hot methanol in a Soxhlet extraction apparatus for 8 hours. The resulting golden-brown powder was then rinsed with diethyl ether and dried in the vacuum oven yielding compound 1 (3.76 g, 63%). Purity by HPLC (99.5%, maxplot). $\delta$H(400 MHz; CDCl$_3$; Me$_4$Si) 7.95-7.97 (6H, m), 8.90-8.92 (6H, m); $\lambda_{max}$(CHCl$_3$)/nm 564.

The phenoxy-BsubPc derivative was synthesized by a method adapted from Claessens et al.: [1]

Phenoxyboronsubphthalocyanine (2a) [2b]. Cl-BsubPc (1, 0.56 g, 0.0013 mol) was mixed with phenol (0.615 g, 0.0065 mol) in toluene (10 mL) in a cylindrical vessel fitted with a reflux condenser and argon inlet. The mixture was stirred and heated at reflux under a constant pressure of argon for 8 hours. Reaction was determined complete via HPLC by the absence of 1. The solvent was evaporated under rotary evaporation. The crude product 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. The dichloromethane was then removed under reduced pressure yielding a dark pink/magenta powder of compound 2a (0.609 g, 95%). $\delta$H(400 MHz; CDCl$_3$; Me$_4$Si) 5.37-5.41 (2H, d), 6.59-6.64 (1H, t), 6.72-6.78 (2H, t), 7.88-7.94 (6H, m), 8.83-8.88 (6H, m); $\lambda_{max}$(CHCl$_3$)/nm 563.

Similarly for other phenoxy-BsubPcs:

4-methylphenoxyboronsubphthalocyanine (2b). [2d]2b was synthesized as for 2a except p-cresol (4-methylphenol, 0.707 g, 0.0065 mol) was used in place of phenol, yielding compound 2b (0.605 g, 79%). $\delta$H(400 MHz; CDCl$_3$; Me$_3$Si) 2.01-2.03 (3H, s), 5.27-5.31 (2H, d), 6.51-6.55 (2H, d), 7.88-7.93 (6H, m), 8.82-8.88 (6H, m); $\lambda_{max}$(CHCl$_3$)/nm 563.
4-tert-butylenoxyboronsubphthalocyanine (2c). [2e] 2c was synthesized as for 2a except 4-tert-butyleno (0.977 g, 0.0065 mol) was used instead of phenol yielding compound 2c (0.571 g, 81%). δH(400 MHz; CDCl3; Me4Si) 1.07 (9H, s), 5.28-5.30 (2H, d), 6.73-6.75 (2H, d), 7.89-7.92 (6H, m), 8.84-8.86 (6H, m); λmax(CHCl3)/nm 563.

4-tert-octylenoxyboronsubphthalocyanine (2d). 2d was synthesized as for 2a except 4-tert-octyleno (1.34 g, 0.0065 mol) was used instead of phenol. In this case, before Kauffman column purification, the excess 4-tert-octyleno was removed by dissolving the product in toluene (300 mL) and extracting with 3.0 M KOH in distilled water (3 x 300 mL). Removal of the toluene and purification by Kauffman column as above yielding compound 2d (0.453 g, 58%). δH(400 MHz; CDCl3; Me4Si) 0.56-0.58 (9H, s), 1.11-1.14 (6H, s), 1.48-1.49 (2H, s), 5.29-5.32 (2H, d), 6.71-6.74 (2H, d), 7.87-7.92 (6H, m), 8.81-8.86 (6H, m); λmax(CHCl3)/nm 563.

4-fluorophenoyboronsubphthalocyanine (2e). 2e was synthesized as for 2a except of 4-fluorophenol (0.729 g, 0.0065 mol) was used instead of phenol, yielding compound 2e (0.486 g, 74%). δH(400 MHz; CDCl3; Me4Si) 5.32-5.35 (2H, m), 6.40-6.45 (2H, t), 7.91-7.93 (6H, m), 8.84-8.87 (6H, m); λmax(CHCl3)/nm 563.

Preparation of single crystals: All crystals used for x-ray diffraction were prepared through vapour diffusion using benzene as the solvent and heptane as the diffusing solvent. All samples (0.050 g) were dissolved in benzene (5 mL) and sealed in an air tight jar with heptane (150 mL). Single crystals of high quality suitable for x-ray diffraction were obtained within 1-2 weeks. All crystallographic information can be found in the supplementary information.

2.3 Results and Discussion

Cl-BsubPc (1, Scheme 3.1) was required as a starting material for our study, however no commercial source of sufficiently high purity could be identified. Therefore, we synthesized Cl-BsubPc in our own laboratory using a method adapted from Kennedy. [5] We found that the crude synthesis proceeded as described but a simple Soxhlet extraction with methanol after synthesis was sufficient to purify the resulting Cl-BsubPc past 99%. We have since repeated this procedure in excess of 15 times with consistent results.

Subsequently, a series of five phenoxy-derivatized BsubPc (2a-2e, Scheme 2.1) were synthesized from Cl-BsubPc (1) in a single additional step. In regards to compounds 2a-2e,
phenoxy substituents were targeted so as to vary the size and the electronegativity of the substituent in the para-position of the phenoxy moiety. Progressing from a hydrogen atom (2a) to a methyl (2b) to a tert-butyl (2c) allowed a large increase in the bulkiness of the substituent while keeping the orientation similar and the number of degrees of freedom the same, thus maintaining the rotational symmetry of the phenoxy group as a whole. Further increasing the size of the hydrocarbon substituent from tert-butyl (2c) to tert-octyl (2d) not only increases the number of hydrocarbon atoms and the associated bulk but also the number of degrees of freedom due to rotational variations inherent in the tert-octyl group - although this increase is minimized for the relatively large number of carbons (eight) due to the structure of the tert-octyl group. Variations in electronegativity of the substituent were also made, progressing from phenoxy (2a) to 4-fluorophenoxy (2e) while again maintaining symmetry. The use of the fluorine atom was deliberate due to its electronegativity and its similar atomic size to hydrogen.

Scheme 2.1: Synthesis of phenoxy-derivatized BsubPcs.
The method used to obtain the phenoxy derivatives is a robust, general method and was used for all five derivatives (2a-e). The method of Claessens et al. [1] was adapted as follows: Cl-BsubPc (1) was heated in toluene with 5 molar equivalents of the appropriate phenol derivative for between 8 and 72 hours (time varied for complete conversion as monitored by HPLC). After the synthesis was complete, the toluene was evaporated and the residual phenol was removed on standard basic alumina in a Kauffman column chromatography apparatus [5] using dichloromethane as the eluent. The excess phenol remained adsorbed to the alumina and the product eluted through the alumina with hot dichloromethane. On removal of the dichloromethane, product in excess of 99% purity was obtained in all cases. In the case of tert-octylphenol (compound 2d), in our first attempt the entire mass of residual phenol could not be adsorbed onto the alumina and an aqueous/organic workup was needed in order to remove the excess tert-octylphenol prior to Kauffman column chromatography. Compounds 2a, [2a]2b [2d] and 2c [2e] have been previously described in the literature with reported yields after purification of 18%, 79% and 58%, respectively. They have been obtained using a variety of synthetic and purification methods including crystallization, [2b] column chromatography [2d] and preparative thin layer chromatography. [2e] Using the combination of the synthetic method of Claessens [1] and Kauffman column chromatography [6] we have achieved yields of 95%, 79% and 81% for compounds 2a, 2b and 2c respectively all with purities exceeding 99%.

While in two of the three cases our yields are markedly higher we wish to highlight Kauffman column chromatography as a facile method to obtain high purity phenoxy-BsubPcs regardless of whether base extraction is performed first. See Scheme 2.2 for a scheme and description of Kauffman column chromatography.

We were able to form diffractable single crystals of compounds 2a-2e by slow diffusion crystallization using benzene (good solvent) and heptane (diffusing solvent). Attempts at classic crystallization were also successful in obtaining single crystals for compounds 2a-2c, as were crystallizations through simple solvent evaporation. In each case the equivalence of the crystal structure was confirmed by x-ray diffraction. The ability for these crystals to be grown under varying conditions shows the resilience of the crystal structures of 2a-2c and that the forces directing this crystallization are strong. Conversely, only diffusion crystallization was capable of producing high quality single crystals of compounds 2d-e.
Scheme 2.2: Kauffman column set up used for purification of derivatized subphthalocyanine. The column consists of two concentric cylinders mounted above a solvent reservoir and below a condenser and gas inlet. The sample is loaded onto the adsorbant by dissolving in solvent and pipetting onto the sand with the condenser removed. The solvent in the reservoir is heated under stirring and holes in the top of the small cylinder allow the vapours to rise and liquefy in the condenser. The solvent liquid then drips into the inner cylinder, eluting through the adsorbant and bringing the BsubPc product with it. The excess phenol from the reaction is remains on the adsorbant, and the product is collected in the solvent reservoir.
The single crystal structure of Cl-\textit{BsubPc} (1) is known and a reprocessed displacement ellipsoid plot is shown for reference in Figure 2.1A. [7] With reference to the unique bowl shaped structure of the \textit{subPc} ligand, we will denote the face of the \textit{BsubPc} containing the axial chlorine atom as the convex face and the opposite the concave face. In its crystal, Cl-\textit{BsubPc} molecules are oriented roughly in columns, with neighboring columns vertically interdigitating their isoindoline units causing the vertical stacking of molecules to be spaced apart (Figure 2.1B). Each \textit{BsubPc} molecule has two closest interactions with inverted \textit{BsubPc} molecules through their convex faces, as shown in Figure 2.1C.

The crystal structure of compound 2\textit{a} is shown in Figure 2.2A. This structure does not possess the vertical columns of \textit{BsubPc} molecules as seen in the structure of 1, but instead shows a lamellar structure made of alternating layers of interdigitated phenoxy and \textit{BsubPc} subunits. These layers are shown on a diagonal from top right to bottom left in Figure 2.2A. The \textit{BsubPc} molecules in the planes interact in dimers through $\pi-\pi$ stacking between the five-membered and six-membered rings on the bowl-shaped base to give a concave face to concave face intermolecular interaction at a distance of 3.76 Å. This interaction is shown in the overlap between the orange and green pair of molecules in Figure 2.2A'. The angle at which the phenol ring extends from the \textit{BsubPc} base allowed the favourable interactions of the $\pi$-electrons of the \textit{BsubPc} of one molecule with those on other molecules. These intermolecular aromatic interactions resulted in a crystal structure in which the phenoxy units interdigitated between

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**Figure 2.1:** Single crystal X-ray diffraction determined structure of compound 1. (A) Displacement ellipsoid plot of 1 (black – carbon; blue – nitrogen; green – chlorine; yellow – boron) (B) part of the crystal structure showing the stacked columns (hydrogen atoms are removed for clarity), and (C) a view parallel to the columns and approximately along the c-axis.
each other and the isoindoline units on the other BsubPc molecules. No angular variation of the phenoxy substituent was seen in the crystal structure.

It was found that the crystal structure of compound 2b was nearly identical to compound 2a (Figure 2.2B). Despite the additional methyl group of 2b, its crystal structure showed the same lamellar structure of planes consisting of interdigitating phenoxy units alternating with planes of BsubPc units associating through $\pi$-$\pi$ stacking on their concave surfaces at a distance of 3.60 Å, which is decreased from that of compound 2a. Additionally, the spacing of the molecules and their crystal packing density was nearly the same as measured for compound 2a.

The single crystal structure of compound 2c, however was different from 2a and 2b (Figure 2.2C). Although there was a similar packing motif to the previous derivatives, the spacing of the layers was significantly increased. The bulkiness of the tert-butyl in the para-position of the phenoxy substituent appears to push pairs of BsubPc units apart from other pairs of interacting BsubPc molecules, as can be seen in Figure 2.2C. The crystal structure possessed lamellae of pairs of BsubPc molecules separated by layers of 4-tert-butylphenoxy substituents. The lamella are more clearly defined in this structure than in either of the structures of compounds 2a or 2b, and the larger spacing of the layers of BsubPc pairs causes a lowered crystal density. The $\pi$-$\pi$ interaction between the molecules in the pairs remained between their concave faces, as shown in Figure 2.2C', but despite the lower crystal density the interaction distance was smaller, at 3.55 Å.

Compound 2d, which contains the bulky tert-octyl substituent, crystallized into a markedly different structure than the compounds 2a-2c. The tert-octyl hydrocarbon chain, which has a large number of carbons but a relatively low number of degrees of freedom (compared to n-octyl, for example), was sufficiently large to result in a disruption of the $\pi$-$\pi$ interactions which dominated the single crystal structure of compounds 2a, 2b and 2c. Similar to crystals of compounds 2a-2c, crystals of compound 2d had BsubPc molecules formed into a lamellar region made entirely of BsubPcs; however, unlike the other crystal structures these BsubPc planes were spaced much farther apart and entirely separated by a plane comprised of tert-octylphenoxy units and associated solvent molecules (benzene). These layers are shown in Figure 2.2D. The tert-octylphenol substituent has sterically disrupted the close packing of the BsubPc molecules to make a region into which solvent molecules could co-crystallize with the relatively ‘fatty’ tert-octyl group. The interaction between the 4-tert-octylphenol substituent
and benzene is through a weak C-H–π interaction from C[26] on the phenoxy moiety to the benzene π-electron density over a distance of 2.83 Å. This association also caused a rearrangement in the nature of the concave-concave interactions of the BsubPc molecules which are no longer arranged in pairs, but in head to toe lines or ribbons, as shown in Figures 2.2D′ and 2.2D″. The π–π intermolecular interactions that link the ribbon together in compound 2d are through the convex face of the BsubPc molecule at a distance of 3.69 Å, unlike compounds 2a-c which associate through their concave faces and over smaller distances.

Placement of a fluorine atom on the phenoxy substituent (compound 2e) allows for direct examination of placing a dipole on the phenoxy ring while not changing the overall substituent size. A single fluorine added to the substituent ring as in compound 2e caused very little change to the packing motif of the molecule. The x-ray determined structure of compound 2e (Figure 2.2E) was nearly indistinguishable from the analogous non-fluorinated structure (compound 2a) with the BsubPc units associating through the concave faces. To quantify the changes in crystal structure of all BsubPc derivatives in this study, certain inter- and intra-molecular features that were common to each structure were noted and measured. These included the distance between one BsubPc unit and its nearest neighbour in both the dimer concave-concave arrangement (d₁) and to next nearest BsubPc unit in another dimer (d₂), the angle of the phenoxy bond to the boron atom in the molecule (B-O-C angle) and the lengths of the boron-oxygen bond (B-O bond length) and oxygen-carbon bond (O-C bond length). These parameters are schematically represented in Figure 2.3 and a summary of the metrics is found in Table 2.1 and illustrated in Figure 2.4. Crystal density was also noted. Additionally, the nature of the closest intermolecular aromatic interaction was also noted and the ring centroid to ring centroid (Cg-Cg) distances of those interactions were measured.

What immediately stands out is that the distance between two BsubPc units in a dimer (for compounds 2a-c,e) or ribbon (for compound 2d) arrangement did not change along the series of compounds 2a-e and is in fact relatively unchanged even from the same distance in the crystal of Cl-BsubPc – at approximately 8.83 Å to 8.18 Å. This is supported by the ring centroid to ring centroid π-stacking distances between the pairs, which were fairly constant, from 3.55 Å to 3.69 Å, between the five compounds.

As the substituent in the para-position of the phenoxy group was increased in size from a hydrogen atom (2a) to a methyl group (2b), no change in molecular separation occurred, as
indicated by the B-B bond distance (d<sub>2</sub>) remaining constant at about 5.58 Å to 5.59 Å. A more significant increase to 8.61 Å was seen when the substituent was changed to a tert-butyl group in 2c, and the tert-octyl substituent group of 2d showed a d<sub>2</sub> distance of 12.01 Å, an increase of 2.15 times from 2a. We found a significant increase in the angle of the B-O-C bond with the increase of the size of the substituent (Table 2.1). As the bulkiness of the substituent group was raised (2a-2d), the bond connecting the phenoxy to the BsubPc, increasing in angle from 115° for 2a and 2b, to 119° for 2c and finally highly strained 129° for compound 2d. For reference, using a simply semi-empirical RM1 modeling, the B-O-C angle from a single isolated molecule of each of compounds 2a-e was calculated. The calculated angles ranged from 115° to 116° therefore placing the large increase to 129° for compound 2d in context. If the B-O-C bond angle distorts to such a great extent, this suggests that the driving force for crystallization of phenoxy-BsubPc is the formation of closely associated dimers or ribbons of the BsubPc moieties arranged in a concave-concave fashion even at the energetic expense of any bond angle distortions within the remainder of the molecule. Finally, the bond distances (d<sub>1</sub>, d<sub>2</sub>) and bond angles (B-O-C) were nearly identical and the space group was the same for compound 2e as for compound 2a indicating the presence of the electronegative fluorine had little effect on the crystal structure.

Although we have determined that the π-π interactions are the main force directing the crystallization of the presented phenoxy-BsubPcs in the solid state, we have identified possible C-H…π interactions. For compounds 2a, 2b, 2c and 2e, C-H…π interactions were found between the outermost carbons on the 6-membered ring involved in the π-π interactions in the close-packed pairs and the π-electrons in the 5-membered nitrogen-containing rings on the other molecule on the concave face. Similarly to the π-π stacking interactions, these are related through an inversion centre and thus are mirrored between the close-packed pair of BsubPc molecules, and range in distance from 2.71 Å in compound 2c to 2.85 Å in compound 2a. For compounds 2a, 2b, and 2e, an additional C-H…π interaction was identified between one of the outermost carbons in a 6-membered ring that is not involved in the π-stacking and the convex side of the π-electrons of the 6-membered ring involved in the π-stacking in an adjacent pair. This interaction potentially assists in the location of the pairs with respect to each other in the crystal structure, making the crystal density of 2a, 2b, and 2e higher than that of the other compounds. The distances of these interactions ranged from 2.82 Å for compound 2e to 2.94 Å for compound 2c. The crystal structure of compound 2d, has entirely different C-H…π
Figure 2.2: Views of the crystal structures of compounds (A) 2a, (B) 2b, (C) 2c, (D) 2d, and (E) 2e. A, B, C, D and E show four pairs of interacting molecules and their spatial relationship to each other. A’, B’, C’ and E’ show the molecules rotated 60° in the x-direction of their respective compounds to elucidate the overlap of the closest interacting rings in the pairs. D’ shows a 90° rotation in the y-direction from D to demonstrate the closest interacting lines of molecules in the crystal structure. D” is a 90° rotation in the x-direction from D’ to show the interacting line of molecules from the top. The green and orange molecules maintain their colouring through the rotations, and the colouring is intended to more clearly show the crystal structures.
Table 2.1: Selected metrics of the crystal structures of Cl-BsubPc (1) and phenoxy-BsubPcs (2a-e).

<table>
<thead>
<tr>
<th>#</th>
<th>B-B</th>
<th>B-B</th>
<th>B-O-C</th>
<th>B-O</th>
<th>O-C</th>
<th>Density</th>
<th>Cg-Cg</th>
<th>Cg-Cg</th>
<th>Space</th>
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<tr>
<td>2a</td>
<td>8.26</td>
<td>5.58</td>
<td>115.5(1)</td>
<td>1.443(2)</td>
<td>1.379(2)</td>
<td>1.422</td>
<td>conc/conc</td>
<td>3.674(1)</td>
<td>triclinic (P 1)</td>
</tr>
<tr>
<td>2b</td>
<td>8.39</td>
<td>5.59</td>
<td>115.6(1)</td>
<td>1.436(2)</td>
<td>1.386(2)</td>
<td>1.422</td>
<td>conc/conc</td>
<td>3.6045(9)</td>
<td>triclinic (P 1)</td>
</tr>
<tr>
<td>2c</td>
<td>8.78</td>
<td>8.61</td>
<td>118.9(2)</td>
<td>1.437(3)</td>
<td>1.387(2)</td>
<td>1.363</td>
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<td>3.548(1)</td>
<td>triclinic (P 1)</td>
</tr>
<tr>
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<td>129.1(2)</td>
<td>1.436(3)</td>
<td>1.368(2)</td>
<td>1.292</td>
<td>conv/conv</td>
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<td>1.383(2)</td>
<td>1.483</td>
<td>conc/conc</td>
<td>3.694(1)</td>
<td>triclinic (P 1)</td>
</tr>
</tbody>
</table>

*Conc – concave face; conv – convex face. *Ring centroid to ring centroid distance.

Figure 2.3: Schematic representation of the compared quantities of the single crystal x-ray determined structures of compounds shown in Scheme 2.1.
interactions from the other crystals in this series. It possesses one between a carbon on the phenoxy substituent and the π-electrons on the incorporated benzene molecule, as described above. Also identified were possible C-H⋯π interactions between a carbon on the end of the tert-octyl chain and both the phenoxy π-electrons and those on the convex side of the 5-membered ring closest to the phenoxy unit on the BsubPc itself. These interactions are at a distance of 2.83 Å and 2.77 Å, respectively.

Despite the identification of these CH⋯π interactions, we believe that the π-π stacking described above between two BsubPc units is the primary driving force behind the crystallization of the present series of compounds. This is not the case for the crystallization of all aromatic compounds [8] and in fact the CH-π interaction has been noted as a possible explanation and main driving force for the formation of the common ‘herringbone’ structure of planar organic semiconductors. [9]
2.4 Conclusions

We synthesized, purified, and obtained single crystals of a series of five phenoxy-\textbf{BsubPc} derivatives. We have analyzed the single crystals by x-ray diffraction and made observations on the similarities and differences in their crystal structures. We have noted that the driving force for crystallization of these molecules is the formation of dimers or ribbons of \textbf{BsubPc} moieties within the crystal structure arranged by π-electron interactions between their respective concave faces. The determination that this is the driving force is supported by the bond angle distortions seen in each molecule which preserve the dimer or ribbon formation (in the crystal structure of compound \textbf{2d} for example). We have also noted that the bulkiness of the phenoxy substituent, while having no effect on the formation of these dimers, does affect the overall crystal packing. The density decreased and the spacing between the dimers or ribbons increased significantly with bulkier substituent groups. We hope the understanding of the solid state structure of phenoxy-\textbf{BsubPc} derivatives will enhance the understanding of the molecular level structure of these compounds as they are applied in optical and electronic devices. This study illustrates that the differences in the crystal structures are not obvious from the relatively small differences between the molecular compositions of phenoxy-\textbf{BsubPc} derivatives.

The compounds crystallized in this study fit mainly in the dimer motif. The only structure that does not is that of t-octylphenoxy-BsubPc. That structure, however, is a solvate, and therefore the structure will not be reliably formed in all crystallizations attempts. If we compare the compounds with the original criteria, we find that they match up, expectedly, with the generalized phenoxy-BsubPc in the dimer motif as outlined in Chapter 1. This is summarized in Table 1.2. The phenoxy-BsubPcs are known to have good electrochemical and optical characteristics, but the dimer motif, which all of the structures in this Chapter display, is not a target structure in this Thesis.

2.5 References


Chapter 3
The Effect of Symmetry on Phenoxy-BsubPc Crystallization

The basic symmetry of the BsubPc ligand is changed when it is substituted with a phenoxy substituent. The effect that this symmetry difference has on the crystal packing of BsubPcs has not been studied. However, one would expect that a less-symmetric compound would crystallize less easily, since additional rotations could be necessary for the molecule to adopt the orientation for the crystal. Having done a study on para-substituted phenoxy derivatives in Chapter 3, a further reduction in the symmetry of the phenoxy group and its effect on crystal packing was the next step in this direction. However, we found that these less-symmetric compounds crystallize easily into large, high-quality crystals, with a structure similar to their more symmetric analogues, which were discussed previously. We did find that in addition to the ability to crystallize, these compounds possessed a surprisingly high solubility with only an incremental change in molecular weight, which is a desirable characteristic in an organic electronic material.

The text in the Chapter was published as a full paper in Industrial and Engineering Chemistry Research. In it Alan Lough performed the diffraction and refinement of the crystal structures, and all other work was performed by Andrew Paton. The full reference is: Andrew S. Paton, Alan J. Lough, and Timothy P. Bender. “One Well-Placed Methyl Group Increases the Solubility of Phenoxy Boronsubphthalocyanine Two Orders of Magnitude.” Industrial & Engineering Chemistry Research, 2012, 51: 18. 6290-6296.

3 The Effect of Symmetry on Phenoxy-BsubPc Crystallization

3.1 Introduction

Aside from the highly soluble t-octylphenoxyBsubPc derivative mentioned in Chapter 2, most BsubPc derivatives are relatively insoluble in common organic solvents. [1] Solution-based fabrication techniques are often cited as necessary for organic electronic materials to achieve cost-effectiveness over their inorganic counterparts. [2-3] The insolubility observed for BsubPc derivatives could therefore be a barrier to their application where solution-based deposition techniques are desirable.
A common method for increasing the solubility of normal phthalocyanines (nPcs) has been to use 3-t-butylphthalonitrile as a precursor material. The placement of t-butyl substituents peripherally on the nPc ring results in the formation of multiple constitutional isomers differing in the relative orientation of the t-butyl groups around the nPc structure. The formation of isomers combined with the size of the t-butyl group contributes to increasing the solubility. This method has also been used to form soluble derivatives of BsubPcs [4] and similar methods have been used to create water-soluble BsubPcs by using a phthalonitrile with ionically charged groups. [5-6]

Beyond cases related to nPcs and BsubPcs another common method for solubilizing small molecules for solution processing (without the formation of structural isomers) utilizes the incorporation of long-chain and/or branched alkyl substituents into the molecular structure to increase association with particular solvents or to physically inhibit aggregation in the solid state. [7-10] Similarly others have used 2-allylphenoxy-BsubPc as a soluble derivative amenable to solution processing. [11] Recently, we have shown that this approach can be used to acquire very soluble PhO-BsubPc† derivatives. Our approach utilized the incorporation of the 3-pentadecylphenoxy molecular fragment into a variety of positions of the PhO-BsubPc molecule. [12] When the 3-pentadecylphenoxy fragment is placed in either the axial or peripheral position of the BsubPc moiety the resulting derivatives were very soluble in common organic solvents. This included the derivative made by the simple reaction of Cl-BsubPc with 3-pentadecylphenol.

Given the solubility of this simple derivative and the considerable size of the pentadecyl chain, we were interested to know the smallest possible hydrocarbon chain which could be placed in the 3-position of the phenoxy molecular fragment of a PhO-BsubPc and still impart high solubility to the derivative. Stated another way, we were interested to understand the most mass-efficient way to impart high solubility to a PhO-BsubPc derivative. While this should have no effect on the molar extinction coefficient (ε), high mass efficiency would have the net result of improving the specific absorptivity (absorption per unit mass, a value more commonly used in the colorant industry). We started with a methyl group and found the resulting derivative 3-methylphenoxy-BsubPc (compound 2a, Scheme 3.1) to be surprisingly soluble in common organic solvents. For example in chloroform it was ~31 times more soluble than its counterpart with the methyl group in the 4-position (Table 3.1). In this article we suggest one
factor in why we believe there is such a dramatic difference in solubility between these two
\textbf{B}_{\text{sub}} \text{Pc} \text{ derivatives}. The consideration of the symmetry of each molecular fragment of the
\text{PhO-} \text{B}_{\text{sub}} \text{Pc}s is an important factor.

\section*{3.2 Experimental}

\subsection*{3.2.1 Materials}

3,4-Dimethylphenol was purchased from TCI America (Portland, Oregon). Toluene, dichloromethane, chloroform, acetone, chlorobenzene, THF, KOH (pellets) and standard basic alumina were all purchased from Caledon Laboratories (Caledon, Ontario). Propyl acetate, 3-methylphenol, and \textit{n}-propanol were purchased from Sigma-Aldrich. All materials were used as received.

\subsection*{3.2.2 General Methods}

All nuclear magnetic resonance (NMR) spectra were acquired on a Bruker 400 MHz system in deuterated chloroform (CDCl$_3$) purchased from Cambridge Isotope Laboratories which was used as received. All $^1$H NMR spectra were referenced to an internal standard of 0.05\% TMS. All crystal structures were collected using computer-controlled KappaCCD system and an Oxford Cryostream variable temperature apparatus. All ultraviolet-visible (UV-Vis) spectroscopy was performed using PerkinElmer Lambda 1050 with a 10 mm path length in a quartz cuvette. High pressure liquid chromatography (HPLC) analysis was conducted using a Waters 2695 separation module with a Waters 2998 photodiode array and a Waters 4.6 mm x 100 mm SunFireTM C18 3.5 \textmu m column. HPLC grade acetonitrile and DMF were eluted at 0.6 mL/min during operation at a constant composition of 80:20, respectively. 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 data were collected on a Nonius Kappa-CCD diffractometer using monochromated Mo-K\textalpha radiation and were measured using a combination of $\phi$ scans and $\omega$ scans with $\kappa$ offsets, to fill the Ewald sphere. The data were processed using the Denzo-SMN package. [13] Absorption corrections were carried out using SORTAV. [14] The structure was solved and refined using SHELXTL V6.1 [15] for full-matrix least-squares refinement that was based on $F^2$. All H atoms were included in calculated positions and allowed to refine in riding-motion approximation with $U_{\text{iso}}$ tied to the carrier atom. X-
ray diffraction results were analyzed using PLATON 40M[16] for bond angles and lengths, and crystal packing images were generated using Mercury version 3.0. [17]

3.2.3 Methods

3-Methylphenoxyboronsubphthalocyanine (2a). Cl-BsubPc (0.673 g, 0.00156 mol) was mixed with 3-methylphenol (0.878 g, 0.00812 mol) in toluene (10 mL) in a cylindrical vessel fitted with a reflux condenser and argon inlet. The mixture was stirred and heated at reflux under argon until reaction was determined complete via HPLC analysis (approximately 72 hours). The excess 3-methylphenol was removed by dissolving the product in toluene (300 mL) and extracting with 3.0 M KOH in distilled water (3 x 300 mL). The aqueous phase was discarded and the solvent was removed under rotary evaporation. The crude product was purified on a Kauffman column using standard basic alumina (300 mesh) as the adsorbent and dichloromethane as the eluent. The product eluted from the Kauffman column while the excess phenol remained adsorbed. The dichloromethane was then removed under reduced pressure yielding a dark pink/magenta powder with gold sheen. Yield 0.656 g (0.00131 mol, 84.6 %). Tm = 280 °C; 1H NMR 400 MHz (CDCl3 ref to TMS): δ = 1.94 (s, 3H), 5.13 (dd, 1H), 5.25 (s, 1H), 6.42 (d, 1H), 6.63 (t, 1H), 7.87-7.92 (m, 6H), 8.82-8.87 (m, 6H); UV-vis (CHCl3) λmax = 563 nm; HRMS (EI) Calcd. for [C31H19BN6O] ([M]+): m/z 502.1712, found 502.1713.

3,4-Dimethylphenoxyboronsubphthalocyanine (2b). Cl-BsubPc (0.493 g, 0.00114 mol) was mixed with 3,4-dimethylphenol (0.723 g, 0.00592 mol) in toluene (10 mL). The reaction and purification proceeded as for 2a, except that reflux was maintained for 100 hours. Yield 0.290 g (0.000562 mol, 49.1 %). Tm = 280°C; 1H NMR 400 MHz (CDCl3 ref to TMS): δ = 1.83 (s, 3H), 1.92 (s, 3H), 5.09 (d, 1H), 5.24 (s, 1H), 6.48 (d, 1H), 7.85-7.89 (m, 6H), 8.81-8.85 (m, 6H); UV-vis (CHCl3) λmax = 563 nm; HRMS (EI) Calcd. for [C32H21BN6O] ([M]+): m/z 516.1868, found 516.1870.

3.3 Results and Discussion

In accordance with our statements above and with the goal of minimizing molecular weight, we initially targeted the smallest phenol derivative containing a hydrocarbon in the 3-position for reaction with Cl-BsubPc. On reaction of Cl-BsubPc with 3-methylphenol (m-cresol) we formed 3-methylphenoxy-BsubPc (compound 2a, Scheme 3.1) using previously established procedures. [1, 18-19] We also synthesized 3,4-dimethylphenoxy-BsubPc (compound 2b) as a
Scheme 3.1: Synthesis of BsubPc derivatives (2a-b) from Cl-BsubPc (1). Conditions: (i) 5 equiv, toluene, reflux, -HCl.

point of comparison (by reaction of Cl-BsubPc with 3,4-dimethylphenol). After the reaction was complete, the excess phenol was partitioned into aqueous base. Upon removal of the organic phase the residue was purified via Kauffman column chromatography which on evaporation of the eluting solvent resulted in a powder with a gold luster. Identity, purity, and spectroscopic characteristics were established using standard techniques.

The solubilities of compounds 2a and 2b were measured, using our previously published method [1] in which small amounts of the compounds were added to a variety of solvents until undissolved material remained after stirring at room temperature for 24 h. The results of the solubility measurements are summarized in Table 3.1. According to the definitions for dye and pigment we have previously proposed, a solubility of at least 3 mg/mL was chosen to represent a soluble derivative of BsubPc. [1] Both compounds 2a and 2b were found to exceed the threshold to be classified as a dye for five of the seven solvents measured. Chloroform, chlorobenzene, propyl acetate, tetrahydrofuran (THF), and toluene dissolved > 3 mg/mL of both compounds. Solubilities below this limit were found for acetone and n-propanol, two of the more polar solvents in the series. Solubilities of compounds 2a-b in chloroform were found to be 103 mg/mL for compound 2a and 90 mg/mL for compound 2b. For comparison, the solubilities of phenoxy-BsubPc and 4-methylphenoxy-BsubPc in chloroform were previously found to be 2.9 and 3.2 mg/mL respectively; ~30 times less soluble despite only differing by the presence or location of a single methyl group. [1]
Table 3.1. Solubilities of PhO-BsubPcs 2a-b and reference compounds.

<table>
<thead>
<tr>
<th></th>
<th>Acetone</th>
<th>Chloroform</th>
<th>Chlorobenzene</th>
<th>n-Propanol</th>
<th>Propyl acetate</th>
<th>THF</th>
<th>Toluene</th>
</tr>
</thead>
<tbody>
<tr>
<td>R₁=H, R₂=CH₃ [1]</td>
<td>309</td>
<td>1500</td>
<td>597</td>
<td>2920</td>
<td>559</td>
<td>2730</td>
<td>20.9</td>
</tr>
<tr>
<td></td>
<td>51.3</td>
<td>260</td>
<td>648</td>
<td>3260</td>
<td>554</td>
<td>2780</td>
<td>4.23</td>
</tr>
<tr>
<td>R₁=CH₃, R₂=H</td>
<td>500</td>
<td>2500</td>
<td>20600</td>
<td>103000</td>
<td>&gt;597</td>
<td>&gt;3000</td>
<td>24.5</td>
</tr>
<tr>
<td>(2a)</td>
<td>309</td>
<td>1600</td>
<td>17300</td>
<td>90000</td>
<td>&gt;581</td>
<td>&gt;3000</td>
<td>23.3</td>
</tr>
<tr>
<td>R₁=R₂=CH₃</td>
<td>309</td>
<td>1600</td>
<td>17300</td>
<td>90000</td>
<td>&gt;581</td>
<td>&gt;3000</td>
<td>23.3</td>
</tr>
<tr>
<td>(2b)</td>
<td>309</td>
<td>1600</td>
<td>17300</td>
<td>90000</td>
<td>&gt;581</td>
<td>&gt;3000</td>
<td>23.3</td>
</tr>
</tbody>
</table>

αMS = molar solubility in mol/l × 10⁻⁵

βSS = specific solubility in mg/l

In an effort to explain the dramatic solubility difference we obtained single crystals of compounds 2a and 2b by two different vapor diffusion methods. Single crystals obtained from benzene/heptane (good solvent/diffusing solvent, respectively) were found to contain a benzene solvate (Figure 3.1) whereas crystallizations from acetone/heptane formed solvent-free single crystals (Figure 3.2) for both 2a and 2b. Crystallographic details are provided in the electronic supporting information. The benzene solvates of compounds 2a and 2b (Figure 3.1) are in contrast to crystals of phenoxy-BsubPc and 4-methylphenoxy-BsubPc which when grown from the same solvent system do not form solvated crystals. That 2a and 2b form a solvate with benzene under these conditions may be construed as evidence of their tendency to associate with aromatic solvents, leading to their high solubility. However, such a direct conclusion would be ill advised as we have observed benzene solvation for other phenoxy-BsubPc derivatives. [19] Furthermore, it is not easily used as a design criterion for obtaining future soluble BsubPc derivatives.
Each benzene solvate showed a similar solid-state arrangement. However, the distance between one $\text{BsubPc}$ unit and its nearest neighbor (the $d_1$ distance defined as the boron-boron distance between two nearest neighbouring molecules [19]) is increased to 12.26 Å for $2b$ compared with 11.32 Å for $2a$ due to two benzene molecules associated within the concave sides of the $\text{BsubPc}$ fragment, in between the $\text{BsubPc}$ molecules forming the crystal packing dimer. The benzene solvent molecule was refined as disordered over two sets of sites with equal occupancy. It is also interesting to note that despite the potential for variation in the orientation of the 3-methylphenoxy and 3,4-dimethylphenoxy groups (solid-state rotational isomerism), there is no observed disorder in the position of the methyl groups as exemplified in the solid state arrangement of the solvated crystal of $2a$ (Figure 3.1a). The methyl group of the 3-methylphenoxy fragment alternates facing ‘left’ and ‘right’ in neighboring molecules along the crystallographic axis. Disorder within the solid would lead to higher solubility, however since none is observed we can rule this out as a reason for our observation regarding the high solubility of $2a$ and $2b$.

Comparison of the solvent-free crystal structures of $2a$, $2b$, phenoxy-$\text{BsubPc}$ and 4-methylphenoxy-$\text{BsubPc}$ again highlights the similarities between this selection of compounds. Each structure shows the same close packed pairs of molecules (dimers), which we have previously noted as a common packing motif for phenoxyalted$\text{BsubPc}$s,including phenoxy-$\text{BsubPc}$ and 4-methylphenoxy-$\text{BsubPc}$. [19] According to the metrics we have previously established, [19] a direct quantitative comparison of this packing structure shows that the spacing of the molecules in all of the solvent-free crystal structures varies only slightly (Table 3.2). The molecules making up the close packed pairs are the same distance apart (as indicated by the B-B $d_1$ and C$_g$ to C$_g$ distances) in each arrangement, with the boron-boron ($d_1$) distance between the closest molecules in different pairs ranging between 5.576(3)Å and 7.011(4) Å for phenoxy-$\text{BsubPc}$ and compound $2a$, respectively. Accompanying this change is an increase in the B-O-C angle and a corresponding small decrease in the crystal density (~1.36 g/cm$^3$ for $2a$ and $2b$ versus ~1.42 g/cm$^3$ for the reference compounds). This comparison is summarized in Table 3.2. Due to the similarities between the solvent-free crystal structures of compounds $2a$ and $2b$ and the reference compounds, we must conclude that it is not the solid-state arrangement that leads to the noted increase in solubility for each compound.
Figure 3.1: Single crystal x-ray diffraction determined solid state arrangements. (a) Compound 2a grown from benzene/heptane with incorporated benzene: (i) front and (ii) a perspective approximately 45° from the front. (b) Compound 2b grown from benzene/heptane with incorporated benzene: (i) front and (ii) a perspective approximately 45° from the front. Coloured for clarity as follows: BsubPc carbons – grey; benzene carbons – black; phenoxy molecular fragments – alternating orange and magenta; boron – yellow; oxygen – red.
Figure 3.2: Single crystal x-ray diffraction determined solid-state arrangements. (a) Compound 2a grown from acetone/heptane with no incorporated solvent: (i) front and (ii) side. (b) Compound 2b grown from acetone/heptane with no incorporated solvent: (i) front and (ii) side. Associated dimer pairs of BsubPcs are shown in cyan, yellow or magenta for clarity.

Ruling out crystal packing structure and solid-state disorder as causes for the high solubility of 2a and 2b, the only difference between these structures and phenoxy-BsubPc and 4-
methylphenoxy-\textit{BsubPc} is that \textit{2a} and \textit{2b} have a \textit{meta}-positioned methyl group on the phenoxy substituent. This difference means that phenoxy-\textit{BsubPc} and 4-methylphenoxy-\textit{BsubPc} possess C$_{1V}$ symmetry and while the molecular weights, molecular shapes and solid state arrangement of the compounds are essentially the same, the presence of the \textit{meta} methyl group removes the vertical reflection plane, giving compounds \textit{2a} and \textit{2b} a reduced symmetry of C$_1$. We must then conclude that it is the loss of the vertical reflection plane, or in other words the presence of rotational isomerism in the phenoxy molecular fragment that results in the large increase in solubility. While this is not seen in the respective solid state arrangement it is surely present in solution. This conclusion may seem intuitive as it is well known that molecular symmetry has an effect on both the melting temperature and solubility of organic crystals. [20-21] Over the past two decades, empirical formulas have been developed based on thermodynamic arguments which allow reasonably accurate estimations of the ideal solubility from knowledge of just the molecular structure and the melting temperature of a small molecule organic compound. [21-25] It would be of interest to see if these empirical frameworks can be used to support our observations and move from the realm of intuition to prediction.

According to Yalkowsky and Wu, [22] to estimate the ideal solubility, or crystal-liquid fugacity ratio (CLFR), the equation

\[
\log(\text{CLFR}) = -\left(\Delta S_m/5700\right)(T_m(°C) - 25) \quad (3.1)
\]

can be used, where $T_m$ is the melting point (°C) and $\Delta S_m$ is the entropy of melting (J·mol$^{-1}$·K$^{-1}$) given by

\[
\Delta S_m = 50 - (19.1)\log(\sigma) + 7.4\tau \quad (3.2)
\]

where $\sigma$ is the molecular rotational symmetry number and $\tau$ is the molecular flexibility number. The value of $\sigma$ is defined as the number of ways the molecule can be superimposed on itself.
Table 3.2: Selected measurements extracted from the solid state arrangement of BsubPc derivatives 2a and 2b within single crystals.

<table>
<thead>
<tr>
<th>Crystal Structure</th>
<th>B-B distance $d_1$ (Å)</th>
<th>B-B distance $d_2$ (Å)</th>
<th>B-O-C Angle (°)</th>
<th>B-O bond length (Å)</th>
<th>O-C bond length (Å)</th>
<th>Crystal Density (g/cm$^3$)</th>
<th>Cg-Cg interaction (CI)$^{a,b}$</th>
<th>Cg-Cg distance (Å)</th>
<th>Space group</th>
</tr>
</thead>
<tbody>
<tr>
<td>R$_1$=R$_2$=H [1,19]</td>
<td>8.256(3)</td>
<td>5.576(3)</td>
<td>115.5(1)</td>
<td>1.443(2)</td>
<td>1.379(2)</td>
<td>1.422</td>
<td>conc/conc</td>
<td>3.674(1)</td>
<td>triclinic (P$ar{1}$)</td>
</tr>
<tr>
<td>R$_1$=H, R$_2$=CH$_3$ [1,19]</td>
<td>8.388(2)</td>
<td>5.586(2)</td>
<td>115.6(1)</td>
<td>1.436(2)</td>
<td>1.386(2)</td>
<td>1.422</td>
<td>conc/conc</td>
<td>3.6045(9)</td>
<td>triclinic (P$ar{1}$)</td>
</tr>
<tr>
<td>R$_1$=CH$_3$, R$_2$=H (2a)</td>
<td>8.685(3)</td>
<td>7.011(4)</td>
<td>120.3(2)</td>
<td>1.450(3)</td>
<td>1.381(3)</td>
<td>1.365</td>
<td>conc/conc</td>
<td>3.596(2)</td>
<td>monoclinic (P2$_1$/n)</td>
</tr>
<tr>
<td>R$_1$=CH$_3$, R$_2$=H (2a) benzene solvate</td>
<td>12.256(4)</td>
<td>8.842(4)</td>
<td>125.4(2)</td>
<td>1.445(3)</td>
<td>1.373(3)</td>
<td>1.337</td>
<td>conv/conv</td>
<td>3.592(2)</td>
<td>monoclinic (P2$_1$/c)</td>
</tr>
<tr>
<td>R$_1$=R$_2$=CH$_3$ (2b)</td>
<td>8.415(4)</td>
<td>6.965(4)</td>
<td>121.1(2)</td>
<td>1.440(3)</td>
<td>1.384(3)</td>
<td>1.352</td>
<td>conc/conc</td>
<td>3.614(1)</td>
<td>triclinic (P$ar{1}$)</td>
</tr>
<tr>
<td>R$_1$=R$_2$=CH$_3$ (2b) benzene solvate</td>
<td>12.106(5)</td>
<td>8.785(6)</td>
<td>122.8(3)</td>
<td>1.457(4)</td>
<td>1.377(4)</td>
<td>1.329</td>
<td>conv/conv</td>
<td>3.664(2)</td>
<td>monoclinic (P2$_1$/c)</td>
</tr>
</tbody>
</table>

$^a$ Orientation of the closest aromatic ring to ring centre of gravity separation as calculated by PLATON [16]

$^b$conc = BsubPc concave face; conv = BsubPc convex face.

through rigid rotation, and conceptually is proportional to the probability that a molecule will be properly oriented for incorporation in a crystal or solid. [17] The flexibility number $\tau$ is defined as

$$\tau = n_{SP3} + 0.5n_{SP2} + 0.5n_{RING} - 1$$ (3.3)

where $n_{SP3}$ and $n_{SP2}$ are the number of non-ring, non-terminal sp$^3$ and sp$^2$ atoms in the molecule (respectively) and $n_{RING}$ is the number of fused ring systems present. [22] It is a representation of the probability that any flexible part of a molecule will be in the correct orientation for incorporation into a crystal or solid. The application of the above variables and equations has been shown to provide accurate estimates of CLFR based on comparisons to measured entropies of melting for organic molecules. [22] Common ranges for log(CLFR) are -0.1 to -4.0. If we consider the entire molecule (2a-b or one of the reference compounds) and following the
definitions of \( \sigma \) and \( \tau \), the closely related derivatives all possess a \( \sigma \) of 1. Consideration of the \textit{BsubPc} molecular fragment as a single fused ring system and the phenoxy as another each separated by a single sp\(^3\) oxygen atom yields a \( \tau \) of 1 for each derivative. It then follows that application of Eq 3.3 and Eq 3.2 will yield the same value for \( \Delta S_m \). Thus the only difference would come about from their difference in \( T_m \) and the application of Eq 4.1 using the melting point of 4-methylphenoxy-\textit{BsubPc} (307 °C). Considering only the difference in \( T_m \) yields values for log(CLFR) of -2.56 and -2.80 for compound 2a (3-methylphenoxy-\textit{BsubPc}; \( T_m = 280^\circ \text{C} \)) and 4-methylphenoxy-\textit{BsubPc}, respectively. Considering the same but instead treating the \textit{BsubPc} fragment as 7 fused rings yields values for log(CLFR) of -3.39 and -3.75 respectively. These values are in the correct order of magnitude but their difference is small and thus cannot adequately explain the large differences in solubilities we have observed.

Although not the intention of Yalkowsky \textit{et al.}, who considers a molecule as a whole, if we consider the general phenoxy-\textit{BsubPc} molecule as a two-component system (two molecular fragments) connected by a rigid rotor at the B-O-C bond this may allow for a comparison of the molecules by the symmetry of their substituent groups. Since the B-O-C bond allows the rotation of the phenoxy group, the orientation of that group can be in any direction with respect to the \textit{BsubPc} and this is the same for both 2a and 4-methyl-phenoxy-\textit{BsubPc}. Because of this rotation, discussion of the symmetry of the molecule is the same whether or not the molecules are treated as a whole or in parts. It is simpler, however, to treat the \textit{BsubPc} and phenoxy molecular fragments as separate moieties, which eliminates the common \textit{BsubPc} unit from the discussion. The lack of variation in the B-O-C angle for these and similar structures implies that this bond does not possess a great deal of flexibility unless deformed by other factors in the solid state. [14] Thus, the linkage to the phenoxy moiety is more of a rigid rotor than a point of flexibility in the molecule and it can also be eliminated from the discussion. Therefore taking the B-O-C bond as rigid (\( n_{SP3} = 0 \)) and considering only one fused ring system (\( n_{RING} = 1 \)) yields a \( \tau = 0.5 \). The reflection plane of the 4-methyl-phenoxy fragment sets \( \sigma = 2 \), whereas \( \sigma = 1 \) for the 3-methyl-phenoxy fragment. This gives a different value for \( \Delta S_m \) in Eq 3.1 and after consideration of the difference in \( T_m \) yields a log(CLFR) of -2.40 and -2.34 for compound 2a (3-methylphenoxy-\textit{BsubPc}) and 4-methylphenoxy-\textit{BsubPc}, respectively. Again, only a small difference which cannot help to explain the large difference in observed solubility.
In a discussion which is complementary to that of Yalkowsky et al., Pinal considers the case of two isomers of identical chemical constituents that differ only in their symmetry. [24] Since the chemical constituents of the two isomers are identical, flexibility is removed from the argument as it assumed each isomer is equally flexible. The author uses the similarity of the two molecules to compare their ideal solubilities with respect to their symmetry numbers. Because their symmetries differ, they will have different melting points, with that of compound 1 ($T_{m,1}$) being lower than compound 2 ($T_{m,2}$), but they will have similar thermodynamic properties otherwise due to their similarity in structure. The ideal solubility is related to melting point, enthalpy and entropy of melting, symmetry number, and difference in heat capacity in the solid and liquid. Taking the difference between the ideal solubility expressions of the two isomers and simplifying provides an equation relating the ratio of the ideal solubilities (CLFR) at 298 K to their symmetry numbers ($\sigma$) and the melting point of the more symmetric compound ($T_{m,2}$):

\[
\ln(\text{CLFR}_1/\text{CLFR}_2) = (2T_{m,2}(K) - 298)/298 \times \ln(\sigma_2/\sigma_1)
\]  

(3.4)

The melting point of the less symmetric compound ($T_{m,1}$) was eliminated from Eq 3.4 during its derivation. By considering only the phenoxy molecular fragment (refer to discussion above) and substituting the symmetry numbers $\sigma_2 = 2$ and $\sigma_1 = 1$ (for 4-methyl-phenoxy and 3-methyl-phenoxy respectively) and $T_{m,2}$ of 4-methylphenoxy-$\text{BsubPc}$ into Eq 3.4 gives a CLFR$_1$/CLFR$_2$ ratio of 7.32; meaning compound 2a (3-methylphenoxy-$\text{BsubPc}$) is predicted to have a solubility greater than that of 4-methylphenoxy-$\text{BsubPc}$ by a factor of ~7: a value which is more in line with the observed solubility difference. The application of this conceptual framework to a class of molecules such as phenoxy-$\text{BsubPc}$ is untested and not considered by Pinal, but we can conclude that it better describes our observations. Unfortunately, it lacks a method of prediction as it is based on the measured $T_m$ of a known compound. It would also fail to describe the difference in solubility between 2a (3-methylphenoxy-$\text{BsubPc}$) and our previously reported 3-pentadecylphenoxy-$\text{BsubPc}$. Perhaps more importantly it would also predict the same factor of 7 for a solubility difference between 4-methylphenoxy-$\text{BsubPc}$ and 3-pentadecylphenoxy-$\text{BsubPc}$. While the use of the framework of Pinal allows us to move beyond intuition, we have determined that it does not fully describe the $\text{BsubPc}$ system. Likely this is
due to the large size of the BsubPc molecules, but it is beyond the scope of this work to develop similar empirical formulae for similar-sized molecules.

3.4 Conclusions

In conclusion, we have observed a large solubility difference between 3-methylphenoxy-BsubPc and 3,4-dimethylphenoxy-BsubPc each containing a methyl group in the 3-position relative to their counterparts that do not. The result is a soluble BsubPc derivative which is also highly mass efficient (or has a high specific absorptivity) relative to other BsubPc derivatives. The single methyl group in this case increases the molar mass of the derivative by less than 3%. This simple addition of a methyl group in a particular position is in contrast to the more common method of solubilization of organic compounds which involves the addition of large ‘fatty’ hydrocarbon chains such as pentadecyl which results in considerable molar mass increase of the molecule. While that approach does result in soluble BsubPc, it is markedly less mass efficient than the presented method. We have attempted to find a justification which could lead to rational design criteria for further soluble BsubPc derivatives. After consideration of two empirical frameworks, we found the framework of Pinal [24] to best fit our observed solubility increase but only after consideration of the phenoxy-BsubPc molecule as two individual molecular fragments. Overall, treatment of these large molecules as two smaller pieces produced a better estimation of their relative solubilities than treatment of the BsubPc molecules as a whole. We also hope that the identification of these highly-soluble BsubPc derivatives will lead to the wider utilization of BsubPc derivatives in applications where high solubility for solution-based deposition techniques is desirable. Determining the quality of BsubPc films produced by solution deposition and whether this symmetry-induced solubility can be used a general method for increasing solubility in other OEMs are two areas of further work that would be worthwhile follow-up studies based on this effect.

While the property of high solubility is desirable in solution-processing of thin films, the application of these particular materials to the criteria outlined in Chapter 1 is not as promising. The optical and electrochemical properties of these materials are presumed similar to the other phenoxy-BsubPcs discussed earlier (See Table 1.2), since there is little variation between phenoxy derivatives. The crystal packing structures of these compounds, when not solvated, are the typical dimer motif that is not the target of this thesis. However, their high solubility would
make them interesting for further study in other applications in comparing solution-cast films against sublimation-cast films in organic electronic devices.

3.5 References

† - we will use the acronym PhO-\textbf{BsubPc} to denote a generic phenoxyalted \textbf{BsubPc}. We will use the name phenoxy-\textbf{BsubPc} to denote the specific derivative made from Cl-\textbf{BsubPc} and phenol.


Chapter 4

\textit{p}-Halophenoxy-Substituted Boronsubphthalocyanines

In Chapter 2, a phenoxy-\textit{BsubPc} derivative with a para-positioned fluorine atom was shown to not alter the crystal structure from its non-halogenated counterpart; the strength of halogen bonding is known to increase down the periodic table. For this reason, the remainder of the \textit{para}-halophenoxy-\textit{BsubPc} derivatives were synthesized and crystallized. The crystal structures of all of the \textit{para}-halophenoxy-\textit{BsubPcs} possessed the isolated dimer motif of typical phenoxy-BsubPcs, but a polymorph of \textit{p}-bromophenoxy-\textit{BsubPc} was identified that instead was in a 1-D ribbon arrangement, named as the \textit{α}-polymorph. We proposed that this structure was allowed by a balance between the halogen-\textit{π} and halogen-boron interactions and the geometry and size of the bromine atom located within the underside of the bowl of the \textit{BsubPc}. We suggest that this is the reason the bromo derivative is the only compound in the series that forms this arrangement.

The following manuscript was recently published as a communication in \textit{Crystal Engineering Communications}. The crystal diffraction and structure refinement was performed by Alan Lough, and all other work was performed by Andrew Paton. The complete reference is: A. S. Paton, A. J. Lough, T. P. Bender. “A role for \textit{π}-Br interactions in the solid-state molecular packing of para-halo-phenoxy-boronsubphthalocyanines.” \textit{CrystEngComm}, 2011, 13: 11, 3653-3656.

4 \textit{p}-Halophenoxy-substituted boronsubphthalocyanines

4.1 Introduction

Regarding common solid state molecular packing of \textit{BsubPcs}, we have recently highlighted that typical motifs for crystals of phenoxy-substituted boron subphthalocyanines (phenoxy-\textit{BsubPcs}) are the formation of dimers or ribbons associated through their concave faces. [1] Others have shown that \textit{tert}-butoxy-\textit{BsubPc} and ethoxy-\textit{BsubPc} also form the dimer motif. [2-3] Even one of the few crystal structures of the related alkoxy-tribenzosubporphyrins arranges into a similar concave-face to concave-face dimer motif. [4] Two polymorphs of methoxy-\textit{BsubPc} have been found, one of which possesses the dimeric motif and the other arranges into a ribbon motif associated through the concave faces, not unlike the ribbon structure observed in some phenoxy-
Peripheral perfluorination of the $\text{BsubPc}$ ligand on the other hand results in a wholly different motif for the crystal structures of phenoxy-$\text{F}_{12}\text{BsubPc}$ and 4-methylphenoxy-$\text{F}_{12}\text{BsubPc}$. This packing structure consists of phenoxy-to-concave-face $\pi$-stacking that forms distinctive 1-dimensional columns of molecules aligned roughly perpendicular to the plane of the $\text{BsubPc}$ ligand – distinctly different from their corresponding perhydrogenated analogues. In summation, there are two commonly observed motifs for $\text{BsubPc}$ in the crystalline state: dimeric or ribbon motifs arranged concave-concave common to perhydrogenated derivatives and 1-dimensional columns common to perfluorinated derivatives.

Recently, the importance of intermolecular halogen (X) interactions in influencing crystal packing has been recognized. In particular, C-X---$\pi$, C-H---X, and X---X interactions have been shown to be important in influencing crystal structures. It has been shown that there are particular orientations through which these interactions occur, and that the average distances for intermolecular C-X---$\pi$ interactions are 3.224±0.025, 3.525±0.007, 3.625±0.009, and 3.698±0.013 Å for X=F, Cl, Br, and I, respectively. Specifically, C-Br---$\pi$ and C-I---$\pi$ intermolecular interactions have been shown to mediate a tris-(halophenoxy)triazine and trihalobenzene guest-host inclusion complex, with the trihalobenzene molecule held in channels created by three triazine derivatives. These C-X...$\pi$ (X=Br, I) interactions, with the X in the para position, has been shown to be the driving force of crystallization of trihalo-trityl alcohols. Also, a groups of C-X---$\pi$ (X=Br, I) intermolecular interactions working in concert have been shown to construct a building block for a series of staircase inclusion compounds and crystalline networks of tetraarylethylene halobenzoyl esters. The C-X...$\pi$, C-H---X and X---X (X = F, Cl, Br, I) interactions have also been shown to affect the crystal packing structure and solid-state molecular structure of (2,2’-bipyridine-N,N)-dibromo-cis-bis[1,1-diphenylhydrazido]-molybdenum(VI) derivatives, tris-haloarenes, and 5,5’-bisdiazo-dipyrmethanes.

There are three reported crystal structures that suggest halogen-boron or halogen-$\pi$ interactions may influence the crystallization of $\text{BsubPc}$ derivatives: Cl-$\text{F}_{12}\text{BsubPc}$, Br-$\text{F}_{12}\text{BsubPc}$, and F-$\text{F}_{12}\text{BsubPc}$. Each is arranged in a concave to convex arrangement having halogen-boron distances of 3.671, 3.720, and 3.092 Å, respectively, which are all below the sum of their respective B---X van der Waals radii. However, it is difficult to determine whether this arrangement is formed under the thermodynamic direction of a halogen-boron interaction, a
halogen-\(\pi\) interaction or rather the preferred crystallization motif of perfluorinated \(\text{BsubPc}\) based solely on geometric considerations. Additionally, these halo-\(\text{BsubPc}\) derivatives do not offer an opportunity for synthetic variation and thus they also do not allow for the examination of the potential use of the possible halogen-boron interactions to engineer crystals.

It would be of interest to see whether boron-halogen interactions could be used to crystal engineer \(\text{BsubPcs}\) bearing synthetically variable halogenated fragments preferably resulting in arrangements within the crystal not previously seen. Furthermore it would be of interest to see evidence to the affirmative or to the contrary of the role of direct halogen-boron or halogen-\(\pi\) interactions. Given our recent experience with phenoxy-\(\text{BsubPc}\), [1] the incorporation of halogens onto a phenoxy moiety would allow us to study the effect of halogenation as well as have multiple reference structures for comparison. Furthermore, if the carbon spacer is a phenoxy unit or higher aryloxy unit, specific angular (\textit{meta-} and \textit{para-}) and distal options are possible for future studies. In our previous study we synthesized and characterized 4-fluorophenoxy-boronsubphthalocyanine (FPhO-\(\text{BsubPc}\), compound \(2a\), Scheme 4.1). [1] For this derivative there was no evidence of halogen-boron interactions and the derivative crystallized into an arrangement nearly identical to phenoxy-\(\text{BsubPc}\) itself.

4.2 Experimental

4.2.1 Materials

4-Fluorophenol was purchased from TCI Company Ltd. (Portland, Oregon). 4-Chlorophenol, 4-bromophenol, and 4-iodophenol were obtained 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. C1-\(\text{BsubPc}\) was synthesized according to a previously described procedure. [16]

4.2.2 Methods

X-ray diffraction results were analyzed using PLATON 40M-version 250809 [17] for bond angles and lengths, and crystal packing images were generated using Mercury version 2.2. [18] All data sets were collected using a Nonius KappaCCD diffractometer equipped with an Oxford Cryostream variable temperature apparatus. Hydrogen positions were calculated.
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 $^1$H NMR reference purchased from Cambridge Isotope Laboratories and used as received. All ultraviolet-visible (UV-Vis) spectroscopy was performed using PerkinElmer Lambda 25 in a PerkinElmer quartz cuvette with 10.00 mm path length.

The progress of reactions was monitored using a Waters 2695 high pressure liquid chromatography (HPLC) separation module with a Waters 2998 photodiode array. A Waters 150 mm reverse phase Sunfire® C18 5μm column was used with HPLC grade acetonitrile (ACN, 1.2 mL/min isocratic) purchased from Caledon Laboratories as the eluent.

Molecular level computer modeling was performed at the density functional theory level using the 6-31G* basis set with the B3LYP method in the SPARTAN ’06 V102 software package, except for that of IPhO-$\text{BsubPc}$, which was performed using the 6-311G* basis set.

Crystal level computer modeling was performed as follows: the crystallographic information files (.cif) were imported into Materials Studio version 5.0 (Accelrys Inc.) [19]. The aromatic pattern of the $\text{BsubPc}$ ligand was recreated in the visualization window. Next, using the DMol$^3$ module [20-21] the electrostatic potential (ESP) surface was calculated at DFT level (fine quality) employing the PW91 functional and DNP basis set. The ESP surface was imported and applied to the crystal lattice, and the Forcite module was used to calculate the crystal lattice energies of the experimental structures at the molecular mechanics (MM) level. The DREIDING forcefield[22] with Ewald summations for the van der Waal and electrostatic intermolecular interactions was chosen since not only does it natively support all of the atom types within the molecules, but it also has been shown to provide an accurate calculation for the energy ranking of crystal structures.[23] Subsequently, the Forcite module was used to perform a MM single point energy calculation on the structure.

4.2.3 Synthesis

4-Fluorophenoxyboronsubphthalocyanine ($\text{FPhO-BsubPc}$, 2a, previously reported in Chapter 2 [1]).

4-Chlorophenoxyboronsubphthalocyanine ($\text{ClPhO-BsubPc}$, 2b).
Cl-BsubPc (1, 0.601 g, 0.0014 mol) was mixed with 4-chlorophenol (0.896 g, 0.0069 mol) in toluene (10 mL) in a cylindrical vessel fitted with a reflux condenser and argon inlet. The mixture was stirred and heated at reflux under a constant pressure of argon for 20 hours. Reaction was determined complete via HPLC by the absence of 1. The solvent was removed under rotary evaporation. The crude product was purified first by dissolving the product in toluene (300 mL) and extracting with 3.0 M KOH solution in distilled water (3 x 300 mL). After removal of the toluene, the product was then 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. The dichloromethane was then removed under reduced pressure yielding a dark pink/magenta powder. Compound 2b (yield 0.228 g, 31 %). δH(400 MHz; CDCl₃; Me₄Si) 5.32 (2H, d), 6.70 (2H, d), 7.91-7.93 (6H, m), 8.85-8.87 (6H, m); λ_max(CHCl₃)/nm 563. HRMS (EI) Calcd. for [C₃₀H₁₆BN₆OCl] ([M]+): m/z 522.1167, found 522.1180.

4-bromophenoxyboronsubphthalocyanine (BrPhO-BsubPc, 2c). 2c was synthesized as for 2b except 4-bromophenol (1.205 g, 0.0069 mol) was used in place of 4-fluorophenol, yielding compound 2b (0.468 g, 59 %). δH(400 MHz; CDCl₃; Me₄Si) 5.27 (2H, d), 6.84 (2H, d), 7.91-7.93 (6H, m), 8.85-8.87 (6H, m); λ_max(CHCl₃)/nm 563. HRMS (EI) Calcd. for [C₃₀H₁₆BN₆OBr] ([M]+): m/z 566.0662, found 566.0668.

4-iodophenoxyboronsubphthalocyanine (IPhO-BsubPc, 2d). 2d was synthesized as for 2b except 4-iodophenol (1.531 g, 0.0069 mol) was used in place of 4-fluorophenol, yielding compound 2d (0.540 g, 74 %). δH(400 MHz; CDCl₃; Me₄Si) 5.18 (2H, d), 7.01 (2H, d), 7.90-7.92 (6H, m), 8.85-8.87 (6H, m); λ_max(CHCl₃)/nm 563. HRMS (EI) Calcd. for [C₃₀H₁₆BN₆OI] ([M]+): m/z 614.0523, found 614.0530.

4.3 Results and Discussion

In this communication, we wish to report the synthesis, crystallization and characterization of the three additional para-halogenated-phenoxy-BsubPcs. The syntheses were carried out according to a procedure outlined previously (Scheme 4.1). [1] Briefly, Cl-BsubPc (1) was reacted with the appropriate para-halophenol at reflux in toluene. Purification was carried out via Kauffman column chromatography on standard basic alumina as the adsorbant and dichloromethane as the eluent yielding compounds 2b-d. Finally, all crystallizations were
performed via vapour diffusion with benzene as the solvent and heptane as the anti-solvent. For compound 2c a further vapour diffusion crystallization was also performed using dichloromethane as the solvent and pentane as the anti-solvent. In all cases, within one to two weeks, high quality single crystals suitable for x-ray diffraction were grown.

The molecular arrangements within the crystal (extended beyond the unit cell) for 4-chlorophenoxy- (ClPhO-) and 4-iodophenoxy- (IPhO-) BsubPc are illustrated in Figure 4.1b and Figure 4.1e (compounds 2b and 2d) respectively. The arrangement of the previously reported FPhO-BsubPc is redrawn in Figure 4.1a for comparison. As was the case for the solid state molecular packing of FPhO-BsubPc (and other para-phenoxy-BsubPcs), [1] ClPhO-BsubPc and IPhO-BsubPc orient themselves into distinct dimers; however, each is distinctly different in its arrangement of the dimers relative to one another. Despite the larger size of the iodine atom, IPhO-BsubPc arranges into a nearly identical crystal structure as FPhO-BsubPc as can been seen by a comparison of Figure 4.1a and 4.1d. In the case of ClPhO-BsubPc, while it does arrange into discernable dimers, the arrangement of dimers relative to one another is markedly different than in the case of FPhO-BsubPc and IPhO-BsubPc.

In contrast, when grown from benzene/heptane the crystal structure of BrPhO-BsubPc (Figure 4.1c) does not show the association of pairs of BsubPc molecular fragments into dimers; rather, it is arranged into 1-D ribbons of BsubPc molecules. The bromine of one molecule is located nearly in the centre of the concave-side of the neighboring molecule beneath the boron atom (Figure 4.1c). A closer examination of the geometry (Figure 4.2) shows the separation between

![Scheme 4.1: Synthesis of para-halophenoxy-BsubPcs (2a-d) from Cl-BsubPc (1). Conditions: (i) 5 equiv., toluene, reflux, -HCl.](image-url)

Scheme 4.1: Synthesis of para-halophenoxy-BsubPcs (2a-d) from Cl-BsubPc (1).
Conditions: (i) 5 equiv., toluene, reflux, -HCl.
Figure 4.1: Illustration of the molecular packing arrangement within the single crystal (extended beyond the unit cell) of (a) FPhO-BsubPc, (b) ClPhO-BsubPc, (c) α-BrPhO-BsubPc, (d) β-BrPhO-BsubPc and (e) IPhO-BsubPc. Colours: carbon – grey; nitrogen – blue; boron – light brown; fluorine – violet; chlorine – green; bromine – yellow; iodine – dark brown. Hydrogens omitted for clarity. (* - redrawn from [1]).
Figure 4.2: Illustration of the area of the bromine atom and the boron of its nearest neighbor in α-BrPhO-BsubPc.

Figure 4.3: Electrostatic potential 3D mapped isosurface plot of BrPhO-BsubPc generated using the 6-31G* basis set with the B3LYP DFT method. Areas of electron deficiency are coloured blue, areas of electron excess are coloured red.
Figure 4.4: Electrostatic potential 3D mapped isosurface plot of FPhO-BsubPc (2a) generated using the 6-31G* basis set with the B3LYP DFT method. Areas of electron deficiency are coloured blue areas of electron excess are coloured red.

Figure 4.5: Electrostatic potential 3D mapped isosurface plot of ClPhO-BsubPc (2b) generated using the 6-31G* basis set with the B3LYP DFT method. Areas of electron deficiency are coloured blue areas of electron excess are coloured red.
the bromine and the boron in the neighboring molecule is 3.850 Å, which is equal to the sum of the van der Waals radii. [15] There is also a measurable C-Br---π interaction at a distance of 3.380 Å between the bromine and the centroid (Cg) of the concave-side of the five-membered π-ring consisting of C9-C10-C15-C16-N3 of the BsubPc (see numbering Figure 4.3). Additionally, between the rows of molecules there is a convex-side to convex-side π-π interaction between two BsubPc molecular fragments at a distance of 3.716 Å (Figure 4.1c). An examination of the bond angles of this molecule (in particular the B1-O1- C25 angle) reveals no bond angle strain is present. Unlike other cases of phenoxy-BsubPcs where the phenoxy molecular fragment is positioned between lobes of the BsubPc ligand, in this case it is positioned over a lobe (above N5-C24-C23-C18-C17). This form of BrPhO-BsubPc will hereafter be referred to as α-BrPhO-BsubPc.‡ Single crystals of BrPhO-BsubPc were also obtained from dichloromethane/pentane diffusion crystallization. In this case a second polymorph was found wherein the solid-state arrangement is again dominated by the formation of discernable dimers and for which the overall arrangement is identical to that obtained for
IPhO-BsubPc (Figure 4.1d). This form of BrPhO-BsubPc will hereafter be referred to as β-BrPhO-BsubPc.\textsuperscript{4} Using a commercial software package (Materials Studio version 5.0, Accelrys Inc. [19]), we calculated the energy difference between \(\alpha\)-BrPhO-BsubPc and \(\beta\)-BrPhO-BsubPc to be \(-4.35\) kcal/mol, with \(\beta\)-BrPhO-BsubPc being lower in energy. This analysis was performed by using the experimentally-determined crystal structures of both polymorphs and performing single-point energy calculations with the DMol\textsuperscript{3} and Forcite packages on the extended crystal structure. The software packages then provide an estimate of the energy inherent in each structure, allowing comparison of electrostatic and dispersion terms as well as the total energy. Through this, we found that the \(\beta\) polymorph was only slightly lower in energy, thus indicating that the \(\alpha\)-BrPhO-BsubPc might be kinetically favoured whereas \(\beta\)-BrPhO-BsubPc might be thermodynamically favoured.

In an effort to explain the uniqueness of \(\alpha\)-BrPhO-BsubPc and what structural features might be influencing its formation, we computed the electrostatic potential surface for each of BrPhO-BsubPc, FPhO-BsubPc, and ClPhO-BsubPc using the 6-31G* basis set with the B3LYP DFT method (as implemented in the commercial software package Spartan ‘06) and IPhO-BsubPc using instead the 6-311G* basis set: the results of which are illustrated in Figures 4.3, 4.4, 4.5, and 4.6, respectively. According to these calculations, considering first BrPhO-BsubPc, a region of relative electron deficiency is present in the \(\pi\)-system at the boron atom on the underside of the molecule, while a moderate yet noticeable electron surplus is present around the circumference of the bromine atom (Figure 4.3). If we consider the spatial arrangement of these two areas of electron deficiency and surplus within the crystal structure they are oriented in such a way and at a suitable distance (Br-B, 3.850 Å and Br-\(\pi\), 3.380 Å, as mentioned above) to constitute an electrostatic interaction between the bromine atom and the \(\pi\)-system of the BsubPc molecular fragment. However, the same electrostatic distribution can also be found in the remaining derivatives (see Figures 4.4, 4.5 and 4.6 for FPhO-BsubPc, ClPhO-BsubPc and IPhO-BsubPc, respectively). Clearly, it is not simply the electrostatic interaction which is motivating the formation of the unique solid-state molecular packing of \(\alpha\)-BrPhO-BsubPc.

Examination and comparison of Figures 4.3, 4.4, 4.5, and 4.6 also shows the expected increase in size of the halogen on moving from fluorine to iodine. We are therefore left with the following explanation in an attempt to describe the uniqueness of \(\alpha\)-BrPhO-BsubPc: The intermolecular interactions between the halogen and the \(\pi\)-system also depend on the steric
the system; it is not only the electrostatic interaction between the $\text{BsubPc}$ molecular fragment and the halogen atom but rather the unique combination of the electrostatics of the molecule, the size of the bromine atom, and the size of the underside of the bowl of the $\text{BsubPc}$ ligand which leads to the formation of this new molecular packing arrangement. While this new packing motif does place the phenoxy fragment over a lobe of the $\text{BsubPc}$ ligand, it can be formed without placing strain on the bond angles within the $\text{BrPhO-BsubPc}$ molecule.

4.4 Isolating a Kinetically-Favoured Polymorph

The isolation of kinetically-favoured crystal structures is not a trivial task. There are so many variables that can affect the resulting polymorph that even isolating a particular thermodynamically favoured structure can be a difficult task. Additionally, there have been reports of well-known crystallization procedures suddenly producing a different polymorph than was formed during the previous decades. This is known as a “disappearing polymorph,” and while not a common occurrence, it is a well-known possibility in crystal engineering circles. It is believed that this effect is caused by an uncounted variable in the original procedure that has suddenly changed, such as an impurity in the compound at undetectable levels, or a slight change in concentration, humidity, or temperature. This effect is certainly not seen as a ‘mystical’ occurrence, but it does highlight the sensitivity of some crystallizations to something as seemingly trivial as batch to batch variations of one of the starting materials used in the synthesis of the desired compound.

In the manuscript above we determined that a desirable polymorph of $p$-bromophenoxy-$\text{BsubPc}$ ($\alpha$), which has $P2_1$ symmetry is in fact a kinetically-favoured polymorph. Further attempts after the first discovery resulted in the growth of the $\beta$ polymorph of $P1$ symmetry in every situation of a polymorph search. This search included the determination of structure from multiple syntheses of the purified material through powder x-ray diffraction studies (PXRD). The following section will outline the approaches taken to attempt to recreate the original $\alpha$ polymorph of the compound.

4.4.1 Polymorph Search

Since there are a multitude of variables affecting crystallization, we narrowed down the polymorph search to the ones that typically are known to greatly affect crystallization conditions. These are temperature, speed of crystallization, solvent system, and type of
Table 4.1: Polymorph search conditions. All conditions gave the $\beta$ polymorph.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temperature Study</th>
<th>Speed of crystallization</th>
<th>Size of solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>fluorophenoxy-B_{sub}Pc</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>acetone</td>
<td>Classic</td>
<td>Vapour Diffusion</td>
<td>Vapour diffusion</td>
</tr>
<tr>
<td>propyl acetate</td>
<td>Microwave</td>
<td>Liquid Layering</td>
<td></td>
</tr>
<tr>
<td>cyclohexane</td>
<td></td>
<td>Evaporation</td>
<td></td>
</tr>
<tr>
<td>dichlorobenzene</td>
<td>DCM/cyclopentane</td>
<td></td>
<td></td>
</tr>
<tr>
<td>benzene/heptane</td>
<td>acetone/cyclohexane</td>
<td></td>
<td></td>
</tr>
<tr>
<td>chloro benzene</td>
<td>DCN/naphthalene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>nonane</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>benzene/heptane</td>
<td>THF</td>
<td></td>
<td></td>
</tr>
<tr>
<td>chloro benzene</td>
<td>propyl acetate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>benzene</td>
<td>dichlorobenzene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EGDM</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E acetone</td>
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<td></td>
<td></td>
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<tr>
<td>pro pyl acetate</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cyclohexane</td>
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</tbody>
</table>

crystallization. The array of crystallizations is listed in Table 4.1. The crystallization systems studied were selected to test the different variables affecting crystallization. In all cases the $\beta$ form was produced. The original crystallization which gave the $\alpha$ form of the compound was a room temperature vapour diffusion crystallization using benzene as the solvent and heptane as the anti-solvent. This was done at a concentration of 25 mg in 7 mL of benzene, with 150 mL of heptane in the outer chamber to diffuse in.

4.4.2 Raman Spectroscopy

Next we theorized that since the $\alpha$ polymorph was kinetically favoured, perhaps we could isolate it directly after the final step of purification after the reaction, which is removal of the solvent through rotary evaporation. Rotary evaporation (rotovap) quickly removes solvent at an elevated temperature under vacuum. This provides a relatively fast method of drying a sample, which, when the sample crystallizes, is a rapidly performed crystallization. For this reason, we wanted to examine the crystals that appear directly out of the rotovap. Unfortunately the small size of these quickly grown crystals was a detriment to the process, since single crystal x-ray diffraction (SC-XRD) could not be used on crystals that small.

First, we attempted to use Raman spectroscopy to identify the crystal structure. One of the limitations of using Raman spectroscopy to identify polymorph is that one must have genuine samples of the known polymorphs to compare against. This comparison is done by identifying a region of the Raman spectrum that possesses easily discernible peaks that completely appear, disappear, or change between the different polymorphs. This region is then known as a
fingerprint region for that compound. Once the fingerprint region has been established it is straightforward to scan a crystal or powder of a sample and identify the polymorph using the absorption peaks in the fingerprint region of the spectrum.

Unfortunately, we only had a genuine sample of the $\beta$ polymorph for determining the Raman spectrum. Thus we could not establish a fingerprint region for the spectrum, and therefore we were unable to use this method for identifying polymorphs.

4.4.3 Powder X-Ray Diffraction

Upon discussion with Dr. Petrov of the X-ray Diffraction Laboratory at University of Toronto, we discovered that we could perform PXRD studies on material directly out of the rotovap after

![Figure 4.7: Comparison of a simulated powder x-ray diffraction spectrum with two experimental spectra (R1 and R2).](image)
purification. By finding the PXRD spectrum of the compound, and comparing with the theoretically generated PXRD spectra of the two known polymorphs of \( p \)-bromophenoxy-BsubPc, we could use Rietveld refinement methods in order to determine the symmetry, unit cell parameters, and crystal packing structure of the compound in the powder.

We synthesized two additional batches of \( p \)-bromophenoxy-BsubPc for this purpose, named here as \textbf{R1} and \textbf{R2}. An overlay of the theoretically generated PXRD spectrum of the \( \beta \) polymorph and the two PXRD spectra gathered for samples R1 and R2 is shown in Figure 4.7. The fit between the simulated and real spectra was a good fit, within error, proving that even the powder samples that were rapidly crystallized were the \( \beta \) polymorph.

### 4.5 Conclusions

In summation, we have observed a new crystal packing motif for \textbf{BsubPcs}. This different packing structure occurs only in the case of BrPhO-BsubPc and not for the other para-halophenoxy-BsubPcs presented in this study. Given the similar electrostatic distributions for all compounds in this study, we must conclude the unique motif observed (\( \alpha \)-BrPhO-BsubPc) is a result of the combination of the electrostatics and the particular size of the bromine atom giving a favourable \( \pi \)-Br interaction that directs its solid-state packing. Based on computer aided modeling, indications are that this new form is a kinetically favoured polymorph, which could not be reliably isolated.

<table>
<thead>
<tr>
<th>Table 4.2: Evaluation of compounds of Chapter 4.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Electro-Chemical Properties</strong></td>
</tr>
<tr>
<td>Halo-BsubPc</td>
</tr>
<tr>
<td>Phenoxy-( F_{12} )BsubPc</td>
</tr>
<tr>
<td>Phenoxy-BsubPc</td>
</tr>
<tr>
<td>4-Br-phenoxy-BsubPc</td>
</tr>
</tbody>
</table>
The structure of $\alpha$-BrPhO-BsubPc displayed a new motif, and it must be compared against the criteria outlined in Chapter 1. This is summarized in Table 4.2. The new structure shows a two-dimensional pathway for charge carrier conduction. There is no evidence that its optical, electrochemical, or hydrolytic stability are different from any typical phenoxy-BsubPc, which means that they suit the criteria. However, this is a kinetic polymorph. The reliability of the particular crystal form must be taken into account in the criteria. Therefore, I suggest a new criterium, that of robustness of crystal structure, which this compound does not meet. If a reliable, robust method of crystallization of $\alpha$-BrPhO-BsubPc could be developed, then it would become a compound of interest for organic electronic materials.

4.6 References

‡ Crystal data for $\alpha$-BrPhO-BsubPc: C$_{30}$H$_{16}$BBrN$_6$O, $M =$ 567.21, monoclinic, $a =$ 15.7312(12) Å, $b =$ 10.2246(9) Å, $c =$ 16.4141(13) Å, $\alpha =$ 90.00°, $\beta =$ 113.281(5)°, $\gamma =$ 90.00°, $V =$ 2425.2(3) Å$^3$, $T =$ 150(1) K, 20 space group $P2_1/n$, $Z =$ 4, 14248 reflections measured, 5448 independent reflections ($R_{int}$ = 0.0961). The final $R_I$ values were 0.0638 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.1388 ($I > 2\sigma(I)$). The final $R_I$ values were 0.1368 (all data). The final $wR(F^2)$ values were 0.1690 (all data).

¶ Crystal data for $\beta$-BrPhO-BsubPc: C$_{30}$H$_{16}$BBrN$_6$O, $M =$ 567.21, triclinic, $a =$ 10.1389(4) Å, $b =$ 11.0056(4) Å, $c =$ 11.6749(5) Å, $\alpha =$ 86.929(2)°, $\beta =$ 78.811(2)°, $\gamma =$ 68.0100(19)°, $V =$ 1184.74(8) Å$^3$, $T =$ 150(1) K, space group $P1$, $Z =$ 2, 12718 reflections measured, 5379 independent reflections ($R_{int}$ = 0.0437). The final $R_I$ values were 0.0413 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.0906 ($I > 2\sigma(I)$). The final $R_I$ values were 0.0659 (all data). The final $wR(F^2)$ values were 0.1009 (all data).


Chapter 5
π-Basic Aryl-Substituted Boronsubphthalocyanines

The aromatic BsubPc ligand was shown in Chapter 1 to prefer crystallizing into π-stacked pairs of molecules. To alter this crystal packing motif, additional intermolecular interactions must be designed into the compound. Usually this is done by adding groups that will provide hydrogen-bonding, halogen-bonding, or other polar non-bonding interactions. However, since organic electronic materials conduct charge carriers through the π-electrons in their aromatic regions, addition of substituents meant only to control the crystal structure will only dilute the density of charge carrying aromatic units in the resulting crystal.

In this Chapter, we coupled the inherent π-electron deficiency of the BsubPc ligand with π-electron rich substituents such as methoxy-phenoxy and naphthoxy. This coupling provides a strong interaction between the electron-deficient π-acid and the electron-rich π-base, allowing a new interaction to guide the crystal structure while providing additional π-electrons that could enhance the charge carrier mobility.

The data in the following Chapter was not the sole work of the primary author. The crystal diffraction and structure refinement was performed by Alan Lough, and the syntheses of compounds 3a and 3b and the precursor Br-F_{12}BsubPc were performed by Graham Morse. All other work was performed by Andrew Paton. The crystal structures of 4-nitrophenoxy-BsubPc, 4-acetylphenoxy-BsubPc, and 4-cyanophenoxy-BsubPc have all been previously published in Acta Crystallographica Section E. Their references are: A. S. Paton, A. J. Lough and T. P. Bender, Acta Cryst., 2011, E67, o57; A. S. Paton, A. J. Lough and T. P. Bender, Acta Cryst., 2010, E66, o3246; and A. S. Paton, A. J. Lough and T. P. Bender, Acta Cryst., 2011, E67, o505, respectively.

5 π-Basic Aryl-Substituted Boronsubphthalocyanines

5.1 Introduction

The potential benefit from control of π-stacking has been established. As briefly mentioned in Chapter 1, there have been a number of studies correlating intermolecular π-stacking distance with charge carrier mobility. The pioneering work by Anthony and coworkers on silyl-derivatized pentacenes has shown that smaller intermolecular distances between carbon atoms in
the solid-state structure leads to increased mobility and better performance of organic electronic devices such as organic light emitting diodes (OLEDs) and organic photovoltaics (OPVs) [1-2]. Recently, a report was published on the charge carrier mobilities of a series of boronsubphthalocyanine (BsubPc) derivatives with varying number of fluorine atoms in their chemical structures. This study showed that the series had a consistent packing motif in the solid state, but variation in the distances between neighbouring molecules. These nearest neighbor molecular distances in the crystals varied with their mobilities in thin films. [3]. Additionally, organic photovoltaic devices have been fabricated with active layers consisting of mixtures of C$_{60}$ and BsubPc. It was shown that BsubPc forms crystallites in the devices that were linked with an increase in the device performance versus BsubPc in the amorphous form. [4] In fact, there are many reports of organic electronic materials that show that the crystal polymorph [5], the crystal orientation [6], and the quality of the crystal [6] used in devices all affect device performance.

It is known that the packing density of aromatic molecules has a great effect on the charge transport properties of a solid-state material [7]. However, crystal engineering of aromatic molecules usually involves the addition of non-$\pi$-electron-containing sidegroups in order to change the packing structure. The use of $\pi$-stacking to control the solid-state arrangement would be ideal, as one could then minimize the number of non-aromatic groups in the molecular structure in order to avoid dilution of the conducting $\pi$-electron-containing aromatic sections of organic molecules. There has been recent evidence that a combination of electron-rich and electron-deficient aromatic groups in molecules can be used to engineer $\pi$-stacked crystals with a hole mobility greater than 2 cm$^2$V$^{-1}$s$^{-1}$. [8] In the crystal structure in that study, the $\pi$-rich thiophene segments and $\pi$-deficient pyridinyl segments stack on top of each other, displaying an energetic preference for a $\pi$-electron donor-acceptor interaction. Another study has shown that co-crystallization of perylene diimides with chlorinated or fluorinated perylene diimides co-crystallize in a 1:1 ratio with alternating units of halogenated and non-halogenated molecules in $\pi$-stacked motifs. [9] In fact, the arene-perfluoroarene alternating co-crystal interaction is well known, with many studies in crystal engineering using it to co-crystallize specific solid-state structures. [8,10-11] That the halogenated molecules alternate with the non-halogenated units demonstrates a preference for a $\pi$-stacking interaction between the different molecules rather than between two of the same molecules. The halogens are classic electron withdrawing substituents, which makes the most favourable $\pi$-stacking interaction between a $\pi$-electron-
deficient compound and a π-electron-rich compound. In each of these situations, the electron-rich or electron-deficient aromatic rings are known as π-bases or π-acids, respectively, due to their ability to donate or accept π-electrons during π–π stacking interactions.

In our laboratory, we have been interested in boronsubphthalocyanine (BsubPc) as a material for organic electronics. BsubPc is known to be π-electron deficient. In this paper we demonstrate a method of crystal engineering of BsubPc derivatives using a π-acid/π-base π-stacking interaction. By attaching π-basic substituent groups axially on the boron atom, a π-stacking interaction is created in the solid-state that outcompetes the typical concave-face to concave-face π-stacking motif seen in many phenoxy-BsubPc crystal structures as shown in Chapters 1 and 2. We synthesized and crystallized six BsubPc compounds with π-basic substituents: 4-methoxy-phenoxy-BsubPc (2a), α-naphthoxy-BsubPc (2b), β-naphthoxy-BsubPc (2c), phenoxy-F_{12}BsubPc (3a), 4-methylphenoxy-F_{12}BsubPc (3b), and β-naphthoxy-F_{12}BsubPc (3c). To compare, we also synthesized and crystallized a set of compounds with π-acidic substituents: 4-nitrophenoxy-BsubPc (4a), 4-acetylphenoxy-BsubPc (4b), and 4-cyanophenoxy-BsubPc (4c).

5.2 Experimental

5.2.1 Syntheses

4-methoxy-phenoxy-boronsubphthlocyanine (2a): Cl-BsubPc (1, 0.601 g, 0.0014 mol) was mixed with 4-methoxyphenol (0.925 g, 0.0085 mol) in toluene (10 mL) in a cylindrical vessel fitted with a reflux condenser and argon inlet. The mixture was stirred and heated at reflux under a constant pressure of argon for 48 hours. Reaction was determined complete via HPLC by the absence of 1. The solvent was removed under rotary evaporation. The crude product was purified first by dissolving the product in toluene (300 mL) and extracting with 3.0 M KOH solution in distilled water (3 x 300 mL). Removal of the toluene, the product was then 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. The dichloromethane was then removed under reduced pressure yielding a dark pink/magenta powder. Yield 0.475 g (0.00092 mol, 66 %). \(^1\)H NMR 400 MHz (CDCl\(_3\) ref to TMS): \(\delta = 3.56\) (s, 3H), 5.31-5.36. (d, 2H), 6.28-6.30 (d, 2H), 7.89-7.93 (m, 6H), 8.83-8.87 (m, 6H); UV-vis (CHCl\(_3\)) \(\lambda_{max} = 562.6\) nm; HRMS (EI) Calcd. for \([C_{31}H_{19}BN_6O_2]\)
**Scheme 5.1:** Molecular structures of compounds studied in Chapter 5.


**α-naphthoxy-boronsubphthalocyanine (2b):** Cl-BsubPc (1, 0.442 g, 0.001 mol) was mixed with 1-naphthol (0.756 g, 0.005 mol) in toluene (10 mL) in a cylindrical vessel fitted with a reflux condenser and argon inlet. The mixture was stirred and heated at reflux under a constant pressure of argon for 72 hours. Reaction was determined complete via HPLC by the absence of 1. The solvent was removed under rotary evaporation. The crude product was purified first by dissolving the product in toluene (300 mL) and extracting with 3.0 M KOH solution in distilled water (3 x 300 mL). Removal of the toluene, the product was then 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. The dichloromethane was then removed under reduced pressure yielding a dark pink/magenta powder. Yield 0.498 g (0.00093 mol, 90.1 %). $^1$H NMR 400 MHz (CD$_2$Cl$_2$ (s, 5.320 ppm)) : $\delta$ = 5.19 (d, 1H), 6.68 (d, 1H), 6.87 (t, 1H), 7.02 (t, 1H), 7.13 (t, 1H), 7.15 (td, 1H), 7.46 (d, 1H), 7.90-7.95 (m, 6H), 8.80-8.85 (m, 6H); UV-vis (CHCl$_3$) $\lambda_{max}$ = 563.5 nm;
HRMS (EI) Calcd. for \([C_{34}H_{19}BN_6O]\) ([M]+): \(m/z\) 538.1713, found 538.1713; Anal. Calcd for: C, 75.85; H, 3.56; N, 15.61. Found: C, 75.02; H, 2.80; N, 14.57.

**β-naphthoxy-boronsubphthalocyanine** (2c): Cl-BsubPc (1, 0.815 g, 0.0019 mol) was mixed with 2-naphthol (0.595 g, 0.0041 mol) in toluene (10 mL) in a cylindrical vessel fitted with a reflux condenser and argon inlet. The mixture was stirred and heated at reflux under a constant pressure of argon for 24 hours. Reaction was determined complete via HPLC by the absence of 1. The solvent was removed under rotary evaporation. The crude product was purified first by dissolving the product in toluene (300 mL) and extracting with 3.0 M KOH solution in distilled water (3 x 300 mL). Removal of the toluene, the product was then 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. The dichloromethane was then removed under reduced pressure yielding a dark pink/magenta powder. Yield 0.537 g (0.0010 mol, 52.7 %). \(1^1H\) NMR 400 MHz (CDCl\(_3\) (s, 5.320 ppm)): \(\delta = 5.66\) (dd, 1H), 5.71 (d, 1H), 7.19 (dt, 1H), 7.24 (d, 1H), 7.25 (dt, 1H), 7.35 (d, 1H), 7.52 (d, 1H), 7.92-7.97 (m, 6H), 8.82-8.87 (m, 6H); UV-vis (CHCl\(_3\)) \(\lambda_{\text{max}} = 563.2\) nm; HRMS (EI) Calcd. for \([C_{34}H_{19}BN_6O]\) ([M]+): \(m/z\) 538.1713, found 538.1719; Anal. Calcd for: C, 75.85; H, 3.56; N, 15.61. Found: C, 75.54; H, 3.84; N, 14.57.

**Phenoxy-borondecadecafluorosubphthalocyanine** (3a). Synthesized by a published procedure. [3]

**4-Methylphenoxy-borondecadecafluorosubphthalocyanine** (3b). Adapted from [12]. A solution of 1.00 g (0.00145 mol) of Br-F\(_{12}\)BsubPc [19] in 5 mL of toluene was mixed with 0.78 g (0.00721 mol) of 4-methylphenol. The mixture was stirred and heated to reflux under argon for 8 hours. Reaction was determined complete via HPLC. The crude product was purified first by dissolving the product in toluene (300 mL) and extracting with 3.0 M KOH solution in distilled water (3 x 300 mL). The solvent was evaporated under vacuum and the product purified on a Kauffman column of alumina with dichloromethane as the eluent. The dichloromethane was then removed under reduced pressure leaving a dark pink powder (0.52 g, 0.00072 mol, 44 %). \(1^1H\) NMR 400 MHz (CDCl\(_3\) ref to TMS): \(\delta = 2.06\) (s, 3H), 5.25-5.27 (d, 2H), 6.57-6.59 (d, 2H); \(1^9F\) NMR 400 MHz (CDCl\(_3\) ref to (C\(_2\)H\(_5\))\(_2\)O·BF\(_3\)): \(\delta = 5.49\) (dt, 6F), 16.21 (dt, 6F); UV-vis (CHCl\(_3\)) \(\lambda_{\text{max}} = 570.2\) nm;
4-Nitrophenoxy-boronsubphthalocyanine (4a).Cl-BsubPc (0.510 g, 0.0012 mol) was mixed with 4-nitrophenol (0.567 g, 0.0041 mol) in toluene (10 ml) in a cylindrical vessel fitted with a reflux condenser and argon inlet. The mixture was stirred and heated at reflux under a constant pressure of argon for 17 h. Reaction was determined complete via HPLC by the absence of Cl-BsubPc. The solvent was evaporated under rotary evaporation. The crude product 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. The dichloromethane was then removed under reduced pressure yielding a dark pink/magenta powder of the product (0.223 g, 37%).

4-Acetylphenoxy-boronsubphthalocyanine (4b).Cl-BsubPc (0.510 g, 0.0012 mol) was mixed with 4-hydroxy-acetophenone (4-acetyl-phenol, 0.860 g, 0.0063 mol) in 1,2-dichlorobenzene (10 ml) in a cylindrical vessel fitted with a reflux condenser and argon inlet. The mixture was stirred and heated at reflux under a constant pressure of argon for 17 h. Reaction was determined complete via HPLC by the absence of Cl-BsubPc. The solvent was evaporated under rotary evaporation. The crude product 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. The dichloromethane was then removed under reduced pressure yielding a dark pink/magenta powder of the product (0.215 g, 34%).

4-Cyanophenoxyboronsubphthalocyanine (4c).Cl-BsubPc (0.510 g, 0.0012 mol) was mixed with 4-cyanophenol (0.714 g, 0.0060 mol) in toluene (10 ml) in a cylindrical vessel fitted with a reflux condenser and argon inlet. The mixture was stirred and heated at reflux under a constant pressure of argon for 17 h. Reaction was determined complete via HPLC by the absence of Cl-BsubPc. The solvent was evaporated under rotary evaporation. The crude product was purified on a Kauffman column using standard basic alumina (300 mesh) as the adsorbent and dichloromethane as the eluent. The product eluted from the Kauffman column while the excess phenol remained adsorbed. The dichloromethane was then removed under reduced pressure yielding a dark pink/magenta powder of the product (0.236 g, 40%).
5.3 Results and Discussion

Surveying the $\text{F}_{12}\text{BsubPc}$ and $\text{BsubPc}$ crystal structures published in the literature there are noticeable trends in the structures. In general, compounds with axial halogens (e.g. $\text{Cl-BsubPc}$ and $\text{Br-F}_{12}\text{BsubPc}$) crystallize into sparse columns perpendicular to the plane of the $\text{BsubPc}$ ligand, without intra-column molecular close-packing. [13-14] The notable exception to this is $\text{F-F}_{12}\text{BsubPc}$. [15] in which the columns intercalate. In comparison, the packing structures of phenoxy-derivatized $\text{F}_{12}\text{BsubPcs}$ show a tendency to associate into columns perpendicular to the plane of the $\text{F}_{12}\text{BsubPc}$ ligand with close-packing between adjacent columns. [16-17] Phenoxy-derivatized $\text{BsubPc}$ molecules, on the other hand, show an entirely different, but consistent, packing motif. These derivatives pack into dimers of molecules associated through intermolecular $\pi\cdots\pi$ stacking across an inversion centre. This concave-face to concave-face $\pi$-stacking interaction seems to be a commonality between nearly all of the phenoxy-derivatized $\text{BsubPcs}$. As a reference, the Cg to Cg $\pi\cdots\pi$ interaction distance of the crystal structure of phenoxy-$\text{BsubPc}$ is 3.6742(10) Å. [18]

The first set of compounds examined comprises 2a-2c, the single crystal x-ray diffraction-determined structures of which are shown in Figure 5.1. In addition to the typical molecular pairing seen in phenoxy-$\text{BsubPcs}$, the structure of compound 2a displays an extra $\pi\cdots\pi$ stacking interaction between the methoxy-phenoxy unit and the $\text{BsubPc}$ ligand in a neighbouring pair, at a distance of 3.5124(8) Å. The distance of the $\pi\cdots\pi$ interaction between the $\text{BsubPc}$ ligand dimers is 3.5512(9) Å in this structure, which is slightly shorter than in the standard phenoxy-$\text{BsubPc}$. In contrast, the structures of 2b and 2c do not resemble the typical phenoxy-$\text{BsubPc}$ crystal packing motif at all. These structures display one-dimensional ribbons of $\text{BsubPcs}$ parallel to the molecular plane. These ribbons show a close-packing distance of 3.876(2) and 3.807(6) Å in the N…$\pi$ interaction between the centroid of the outermost ring of the naphthoxy unit and the closest imine nitrogen in the next $\text{BsubPc}$ ligand in the crystal structures of 2b and 2c, respectively. Interestingly, there is disorder in the naphthoxy unit across the mirror plane of each row, but this disorder does not affect the region in which there is intermolecular close-contact between the naphthoxy and the neighbouring $\text{BsubPc}$ ligand. Furthermore, there is no disorder in the $\text{BsubPc}$ ligands themselves. This implies a strong intermolecular interaction between the naphthoxy and $\text{BsubPc}$. 
The second set of compounds examined contains the perfluorinated $\text{F}_{12}\text{BsubPcs}$, the single crystal x-ray diffraction-determined structures of compounds $3a$ and $3b$ are shown in Figure 5.2, and that of compound $3c$ in Figure 5.3. Since perfluorinated $\text{BsubPc}$ should be more $\pi$-electron-deficient than $\text{BsubPc}$, one might expect a greater effect from $\pi$-electron-rich substituents in this series over the $\text{BsubPc}$ series above. The structures of $3a$ and $3b$ have been previously published, the structure of $3a$ was confirmed in the current study by crystals grown under different conditions than in the original publication [17] and that of $3b$ was discovered by our group [19]. Both of the structures of $3a$ and $3b$ conform to the trends seen in other $\text{F}_{12}\text{BsubPc}$ crystal structures in literature. The phenoxy moieties are centred below one of the indole units on the concave side of the $\text{F}_{12}\text{BsubPc}$ and stabilized through a $\pi-\pi$ interaction with the 5-membered ring of the indole at distances of 3.6048(19) Å and 3.532 Å and through a slightly weaker interaction with the 6-membered ring of the indole at 3.7256(19) Å and 3.749 Å for $3a$ and $3b$, respectively. Increasing the number $\pi$-electrons in the axial group with a naphthoxy derivative as in compound $3c$ produced a similar stacked motif, but with important differences (Figure 5.3). The naphthoxy unit is centred on the concave side of an indole unit and interacts with the $\text{F}_{12}\text{BsubPc}$ through $\pi-\pi$ stacking at a distance of 3.603(2) Å; however, the same indole unit also interacts through its convex side with another naphthoxy group via $\pi$-electron stacking at a distance of 3.570(2) Å. This second interaction joins two neighbouring columns within the structure. There is also a convex face to solvent (benzene) $\pi-\pi$ stacking at 3.548(3) Å which joins adjacent columns. The additional naphthoxy to $\text{F}_{12}\text{BsubPc}$ interaction demonstrates the increased affinity that the $\pi$-electron-rich group has for the aromatic system of the $\text{F}_{12}\text{BsubPc}$ over the related single-ring phenoxy and methylphenoxy groups.
Figure 5.1: The single crystal x-ray diffraction determined structures of a) 2a, b) 2b, and c) 2c. Some whole molecules are coloured green, orange, or fuschia for clarity, while atomic colourings on the other molecules are C – gray, N – blue, B – yellow, O – red. Hydrogens are omitted for clarity.
Figure 5.2: The single crystal x-ray diffraction determined structures of a) 3a,[16] b) 3b. Some whole molecules are coloured green, orange, or fuschia for clarity, while atomic colourings on the other molecules are C – gray, N – blue, B – yellow, O – red, F-purple. Hydrogens are omitted for clarity.

Figure 5.3: The single crystal x-ray diffraction determined structure of 3c showing a) the unit cell, and b) a close-up of the π-stacking motif. Atomic colourings are C – gray, N – blue, B – yellow, O – red, F-purple. Hydrogens are omitted for clarity.
Figure 5.4: The single crystal x-ray diffraction determined structures of a) 4a and b) 4b. Atomic colourings are C – gray, N – blue, B – yellow, O – red. Hydrogens are omitted for clarity.
Figure 5.5: The single crystal x-ray diffraction determined structure of 4c, showing a) the ligand to ligand $\pi$-stacking in the unit cell, and b) the channel-like solvent solvent-accessible voids (in gold). Some molecules are coloured green or purple for clarity, and the atomic colouring on the other molecules are C – gray, N – blue, B – yellow, O – red. Hydrogens are omitted for clarity.
In addition to these \(\pi\)-basic substituent groups, a series of \(\text{BsubPc}\) derivatives with \(\pi\)-acidic substituent groups were synthesized and crystallized. The crystal structures of these compounds are shown in Figures 5.4 and 5.5. Since the BsubPc ligand is \(\pi\)-acidic, we would expect that there would be reduced interaction between it and a \(\pi\)-acidic substituent group. There are in fact no specific interactions between the substituent groups and the \(\text{BsubPc}\) ligands in any of the three structures. Additionally, these structures all show unusual geometries compared to other, typical phenoxy-\(\text{BsubPc}\)s. Compounds 4a and 4b exhibit larger than normal B-O-C bond angles of 124.56(14)° and 130.3(2)°, respectively, compared to 115.2(2)° for phenoxy-BsubPc. [18] They also show different torsion angle between the \(\text{BsubPc}\) ligand and the plane of the phenoxy group. Compound 4c also shows a larger B-O-C bond angle, of 128.89(11)°, and possesses the most different phenoxy to \(\text{BsubPc}\) torsion angle. Phenoxy-\(\text{BsubPc}\) has a B-O-C-C torsion angle of -91.0 (2)°, while 4a, 4b, and 4c have torsion angles of -44.7 (3)°, -22.0 (5)°, and -1.9 (3)°, respectively. This means that the phenoxy group of 4c is nearly perpendicular to the orientation of the regular phenoxy-\(\text{BsubPcs}\). Compound 4c also possesses large solvent-accessible voids that propagate through the unit cell. The channel-like solvent-accessible voids in which the disordered solvent resides extend along the \(c\) axis (see Figure 5.5b) and are bordered by the convex-faces of the BsubPc fragment and the cyanophenoxy units.

5.4 Conclusions

The addition of a \(\pi\)-basic substituent onto both \(\text{BsubPc}\) and \(\text{F}_{12}\text{BsubPc}\) produces increased \(\pi\)-stacking interactions at shorter distances over those with less \(\pi\)-basic substituents. These additional interactions produce variations in the crystal packing motifs of typical phenoxy-\(\text{BsubPcs}\) and phenoxy-\(\text{F}_{12}\text{BsubPcs}\), suggesting that an increase in the available \(\pi\)-electron density interacts favourably with any \(\text{BsubPc}\). It has been previously shown that \(\text{BsubPc}\) is \(\pi\)-electron deficient and thus a \(\pi\)-acid. For this reason, we believe that the increased \(\pi\)-electron stacking is due to a \(\pi\)-acid/\(\pi\)-base interaction between the \(\pi\)-basic axial derivatives naphthoxy and methoxyphenoxy and the \(\pi\)-acidic \(\text{BsubPc}\) and \(\text{F}_{12}\text{BsubPc}\). This conclusion is further supported by the decreased number of \(\pi\)-\(\pi\) interactions seen in the phenoxy-\(\text{BsubPc}\) derivatives having \(\pi\)-acidic phenols as the axial substituent.

This study provides evidence that \(\pi\)-acid/\(\pi\)-base interactions can successfully be used in the crystal engineering of \(\text{BsubPc}\) and other chromophores. The evaluation of naphthoxy-\(\text{BsubPc}\) and methoxyphenoxy-\(\text{BsubPc}\) in by the criteria outlined in Chapter 1 is summarized in Table
5.1. In fact, the three naphthoxy-\textit{BsubPc} derivatives pack in a one-dimensional ribbon structure which can provide improved electronic properties in the solid state. The naphthoxy-\textit{F}_{12}\textit{BsubPc} (3a), however, is a solvate and therefore discounted from the evaluation. For the other two, 2b and 2c, we have seen no indication that there is degradation over long-term storage due to hydrolysis, nor that the optical and electrochemical properties are different from that of normal

Table 5.1: Evaluation of Chapter 5 compounds.

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<tr>
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<th>Electro-Chemical Properties</th>
<th>Hydrolytic Stability</th>
<th>Pathway in Structure</th>
<th>Robust Crystal Form</th>
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<tr>
<td>Halo-\textit{BsubPc}</td>
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<td>x</td>
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<tr>
<td>\textit{Phenoxy-}F_{12}\textit{BsubPc}</td>
<td>x</td>
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<tr>
<td>\textit{Phenoxy-BsubPc}</td>
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<td>✓</td>
<td>x</td>
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<tr>
<td>4-MeO-\textit{phenoxy-BsubPc}</td>
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<td>✓</td>
<td>~</td>
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</tr>
<tr>
<td>\textit{Naphthoxy-BsubPc}</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
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</tbody>
</table>

\textit{Phenoxy-BsubPcs}. Furthermore, the after a large polymorph search on 2b, every crystallization attempt, including sublimation, produced the same crystal packing structure. For these reasons, these materials possess great potential for use as electronic materials. \textit{Methoxy-phenoxy-BsubPc}, 3a, on the other hand, has been less studied in our laboratory as a compound for use in organic electronics. It should have the same optical, electrochemical, and hydrolysis properties as any \textit{phenoxy-BsubPc}. Its crystal structure is somewhere in the middle between the new motif of the naphthoxy-\textit{BsubPcs} and the dimer motif. It does possess a pathway for charge carrier conduction in one-dimension, albeit in a zig-zag through the crystal. There is evidence that the inclusion of this compound in a follow up study to determine charge carrier mobilities would perhaps show that this material performs better than a \textit{phenoxy-BsubPc} in the dimer motif and is suggested as a follow-up study.

5.5 References


Chapter 6
Sulfonate Pseudohalide Boronsubphthalocyanines

The chemistry of BsubPc axial substitution has been limited to mainly hydroxyl-based nucleophiles. There have been few examples of nitrogen-based and alkynyl-based nucleophiles, but these require more complex chemistries and are a minority. Because of the finite number of hydroxyl-based nucleophiles available, an easy synthetic route to alternative nucleophilic substitutions is desirable to increase the variety of BsubPc derivatives.

This manuscript describes the synthesis of a series of sulfonate pseudohalide derivatives of BsubPc. A new synthetic route was developed which uses a pyridinium salt of the pseudohalide to displace the initial halide. This simple synthesis produced five sulfonate-BsubPcs, which were then crystallized. In addition to their crystal structures, the use of these new compounds as starting materials for derivatization was tested by a standardized phenoxylation and hydrolysis.

This Chapter consists of two manuscripts together. Section 6.4 is a paper that has been submitted to Acta Crystallographica Section C. Section 6.3 is the majority of a manuscript that was recently published as a note in the Journal of Organic Chemistry. Many of the phenoxylation and hydrolysis experiments were initially performed by David Castelino and repeated by Andrew Paton. Graham Morse provided six \(^{13}\)CNMR spectra and the interpretation. The crystal diffraction and structure refinement was performed by Alan Lough. All other work was performed by Andrew Paton. The complete reference for the published manuscript is: Andrew S. Paton, Graham E. Morse, David Castelino, Timothy P. Bender. “The Pseudohalides of Boronsubphthalocyanine” J. Org. Chem., 2012, 77: 5, 2531–2536.

6 Sulfonate Pseudohalide Boronsubphthalocyanines

6.1 Introduction

Most derivatives of BsubPc are substituted with phenoxy substituent groups. In order to expand the number of BsubPc crystal packing motifs, new nucleophiles to substitute onto the boron atom must be found. The sulfonic acids are generally used as pseudohalides in organic chemistry. This means that they possess good leaving group capabilities, similarly to the halogens. However, due to the size and polarity of the sulfonate group, it would be expected that the solid-state arrangement would be different than both the halogens and the phenoxy
derivatives. In this Section we report the crystal structures of five sulfonate pseudohalide-
BsubPcs and compare them. We also compare these to the published structures of halide
BsubPcs.

Next, we examine the leaving group capabilities of the pseudohalide BsubPcs, as well as their
chemical and optoelectronic properties. The aim for our study was to determine if there was a
pseudohalide of BsubPc which could be easily isolated, more reactive than Cl-BsubPc but less
reactive (and presumably more hydrolytically stable) than Br-BsubPc. We would therefore
obtain a precursor compound which could be produced in a significant quantity and used over
time while not being concerned with its hydrolytic stability upon storage. While pseudohalides
have long been used as leaving groups in traditional chemistry, modern uses for pseudohalides
such as mesylates and tosylates include their use as leaving groups in Heck and Suzuki cross-
coupling reactions [1]. Concurrent with our study, Guilleme et al. published a method for the
generation of triflate-BsubPc (TfO-BsubPc). They generated this intermediate in situ using
silver triflate or trimethylsilyl triflate as halophilic reagents which effected an extraction of the
chloride from Cl-BsubPc and formation of TfO-BsubPc. [2] They then further showed that
TfO-BsubPc could react at a high rate with oxygen, nitrogen, or carbon-based nucleophiles in
order to produce new BsubPc derivatives. TfO-BsubPc could not be isolated due to its high
reactivity with water.

In this Chapter, we report the synthesis and isolation of a series of five sulfonic acid based
pseudohalides of BsubPc. Their structures were unambiguously confirmed using spectroscopic
and crystallographic methods. We compare the rates of reaction of the pseudohalides under
phenoxylation and hydrolysis conditions and compare them to the conventional halides Cl-
BsubPc and Br-BsubPc thereby making a conclusion as to their suitability to replace Cl-
BsubPc and Br-BsubPc as standard precursor compounds. We also examined the
electrochemical and optical properties of these materials using cyclic voltammetry, absorption
spectroscopy, and fluorescence spectroscopy. We are therefore able to provide the basic
photophysical and electronic properties of the pseudohalides should someone consider them as
replacements for Cl-BsubPc in organic electronic devices.
6.2 Experimental

6.2.1 Materials
Toluene, methanol, chlorobenzene, 1,2-dichlorobenzene, pyridine, and HPLC-grade acetonitrile were purchased from Caledon Laboratories (Caledon, Ontario). Triflic acid, 4-toluenesulfonic anhydride, 4-toluenesulfanyl chloride, pyridinium 4-toluenesulfonate, methylsulfonic anhydride, methylsulfanyl chloride, methylsulfonic acid, 4-chlorobenzenesulfonic acid, benzenesulfonic acid, and pyridinium 3-nitrobenzenesulfonate were purchased from Sigma-Aldrich (Mississauga, Ontario, Canada). All materials were used as received.

6.2.2 Methods
The crystallization conditions are as follows: Crystals were grown through vapour diffusion of heptane into benzene for TsO-\textbf{BsubPc} and ClsO-\textbf{BsubPc}. Vapour diffusion of pentane into dichloromethane was used for MsO-\textbf{BsubPc} where two different crystal types were obtained in the same pot: rhomboids and needles. For NsO-\textbf{BsubPc}, evaporation of the solvent from a solution in benzene produced crystals suitable for diffraction over a period of a few days. Evaporation of the solvent from a solution in chloroform produced crystals of BsO-\textbf{BsubPc} overnight. For MsO-\textbf{BsubPc}, to produce the non-solvated structure sublimation was performed in a custom built trained sublimation apparatus, at a temperature of 285 °C and 80 mTorr of pressure. The same trained sublimation parameters were used to produce a crystal structure of TsO-\textbf{BsubPc} in the same form as the solution-grown crystal.

Data were collected on a Bruker Kappa APEX-DUO diffractometer using a Copper ImuS tube with multi-layer optics for NsO-\textbf{BsubPc} and MsO-\textbf{BsubPc} or monochromated (Triumph) Mo-K radiation for BsO-BsubPc and were measured using a combination of $\varphi$ scans and $\omega$ scans. The data were processed using APEX2 and SAINT. [3] Absorption corrections were carried out using SADABS. [3] The structure was solved and refined using SHELXTL [4] for full-matrix least-squares refinement that was based on $F^2$. All H atoms were included in calculated positions and allowed to refine in riding-motion approximation with U~iso~ tied to the carrier atom.
6.2.3 Syntheses

Pyridinium trifluoromethylsulfonate was synthesized according to the reported procedure. [5] 
Cl-BsubPc, [6-7] Br-BsubPc, [8] and HO-BsubPc [8] were synthesized according to the reported procedures. The remaining pyridinium salts were prepared as follows:

**Pyridinium methylsulfonate:** Pyridine (2.95 g, 0.37 mol) was dissolved in toluene and slowly neutralized with methylsulfonic acid (3.58 g, 0.37 mol). The precipitate was filtered and the resulting solid was dried under vacuum leaving a white solid product, pyridinium methylsulfonate. Yield 6.20 g (95 %). m.p. = 189 °C [9]; δH(400 MHz; DMSO-d₆) 2.43 (3H, s), 8.10 (2H, t), 8.63 (1H, t), 8.95 (2H, d).

**Pyridinium benzenesulfonate:** Benzenesulfonic acid (5.06 g, 0.032 mol) was dissolved in toluene and stirred until well mixed. Then pyridine was slowly added in excess. After neutralization had occurred, the toluene and excess pyridine were removed through rotary evaporation leaving the respective pyridinium salt as a off-white to tan, hygroscopic powder, Pyridiniumbenzenesulfonate. Yield: 7.2 g (95 %). m.p.: 133 °C [10]; δH(400 MHz; DMSO-d₆) 7.29-7.34 (3H, m), 7.62-7.64 (2H, m), 8.08 (2H, t), 8.61 (1H, t), 8.94 (2H, d).

**Pyridinium 4-chlorobenzenesulfonate:** Similar to pyridiniumbenzenesulfonate, 4-chlorobenzene sulfonic acid (5.05 g, 0.026 mol) was mixed with excess pyridine to form the pyridinium salt as a white, hygroscopic powder, pyridinium4-chlorobenzenesulfonate. Yield: 6.31 g (89 %). m.p. 139 °C; δH(400 MHz; CDCl₃; Me₄Si) 7.33 (2H, d), 7.86 (2H, d), 8.00 (2H, t), 8.46 (1H, t), 9.02 (2H, d). [9] Compound has been previously reported, but the report contains no characterization.

4-Toluenesulfonate-boronsubphthalocyanine (TsO-BsubPc, 3a)

**Path 1:** OH-BsubPc (0.071 g, 0.00017 mol) and 4-toluenesulfonic anhydride (0.300 g, 0.00092 mol) were dissolved in toluene (5 mL) and pyridine (3 mL). The mixture was stirred under argon and heated at reflux for 60 minutes. Reaction was determined complete via HPLC by the absence of OH-BsubPc. The solvent was removed under rotary evaporation and the solid was rinsed with methanol to give a pink powder, TsO-BsubPc. Yield 0.051 g (51 %). δH(400 MHz; CDCl₃; Me₄Si) 2.23 (3H, s), 6.83-6.89 (4H, m), 7.93-7.95 (6H, m), 8.84-8.86 (6H, m); δB¹¹(400
\[ \text{MHz; CDCl}_3; \text{BF}_3\cdot\text{OEt}_2 \] -14.93 (s); \[ \lambda_{\text{abs,max}}(\text{toluene})/\text{nm} 566; \lambda_{\text{PL,max}}(\text{toluene})/\text{nm} 573; \text{HRMS (EI) Calcd. for } [C_{31}H_{19}B_{6}N_{6}O_{3}S] ([M]+): m/z 566.1332, \text{ found 566.1332.} \]

**Path 2:** \( \text{Br-BsubPc} \) (1.002 g, 0.00211 mol) and pyridinium \( p \)-toluenesulfonate (1.063 g, 0.00425 mol) were dissolved in toluene (50 mL) and heated under argon while stirring. The reaction was maintained at reflux until it was determined complete via HPLC, about 6 hours. The solvent was removed under rotary evaporation and the solid was rinsed with methanol and dried in air to give a pink powder with a golden sheen, \( \text{TsO-BsubPc} \). Yield 0.905 g (76 %). Characterization as above.

**Methylsulfonate-boronsubphthalocyanine (MsO-BsubPc, 3b)**

**Path 1:** \( \text{OH-BsubPc} \) (0.071 g, 0.00017 mol) and methylsulfonic anhydride (0.300 g, 0.00092 mol) were dissolved in toluene (5 mL) and pyridine (3 mL). The mixture was stirred under argon and heated at reflux for 60 minutes. Reaction was determined complete via HPLC by the absence of \( \text{OH-BsubPc} \). The solvent was removed under rotary evaporation and the solid was rinsed with methanol to give a pink powder, \( \text{MsO-BsubPc} \). Yield 0.051 g (51 %). \[ \delta_{\text{H}}(400 \text{ MHz; CDCl}_3; \text{Me}_4\text{Si}) 1.91 (3H, s), 7.95-7.97 (6H, m), 8.90-8.92 (6H, m); \delta_{\text{B}}^{11}(400 \text{ MHz; CDCl}_3; \text{BF}_3\cdot\text{OEt}_2) -15.00 (s); \lambda_{\text{abs,max}}(\text{toluene})/\text{nm} 566; \lambda_{\text{PL,max}}(\text{toluene})/\text{nm} 572; \text{HRMS (EI) Calcd. for } [C_{25}H_{15}B_{6}N_{6}O_{3}S] ([M]+): m/z 490.1031, \text{ found 490.1019.} \]

**Path 2:** \( \text{Br-BsubPc} \) (1.115 g, 0.00235 mol) and pyridinium methylsulfonate (1.205 g, 0.00688 mol) were dissolved in toluene (50 mL) and heated under argon while stirring. The reaction was maintained at reflux until it was determined complete via HPLC, about 6 hours. The solvent was removed under rotary evaporation and the solid was rinsed with methanol and dried in air to give a pink powder with a golden sheen, \( \text{MsO-BsubPc} \). Yield 0.750 g (65 %). Characterization as above.

**Benzenesulfonate-boronsupphthalocyanine (BsO-BsubPc, 3c):** \( \text{Br-BsubPc} \) (0.195 g, 0.00041 mol) and pyridinium benzenesulfonate (0.244 g, 0.00103 mol) were dissolved in toluene (15 mL) and heated under argon while stirring. The reaction was maintained at reflux until it was determined complete via HPLC, about 6 hours. The solvent was removed under rotary evaporation and the solid was rinsed with methanol and dried in air to give a pink powder with a golden sheen, \( \text{BsO-BsubPc} \). Yield 0.126 g (56 %). \[ \delta_{\text{H}}(400 \text{ MHz; CDCl}_3; \text{Me}_4\text{Si}) 6.96 (2H, d), 7.09 (2H, t), 7.28 (1H, t), 7.93-7.95 (6H, m), 8.84-8.86 (6H, m); \lambda_{\text{abs,max}}(\text{toluene})/\text{nm} 566; \lambda_{\text{PL,max}}(\text{toluene})/\text{nm} 572; \text{HRMS (EI) Calcd. for } [C_{25}H_{15}B_{6}N_{6}O_{3}S] ([M]+): m/z 490.1031, \text{ found 490.1019.} \]
λ_{PL,max}(toluene)/nm 573; HRMS (EI) Calcd. for [C_{30}H_{17}BN_{6}O_{3}S] ([M]+): m/z 552.1176, found 552.1177.

4-Chlorobenzenesulfonate-boronsubphthalocyanine (ClSO-BsubPc, 3d): Br-BsubPc (0.209 g, 0.00044 mol) and pyridinium 4-chlorobenzenesulfonate (0.263 g, 0.00097 mol) were dissolved in toluene (15 mL) and heated under argon while stirring. The reaction was maintained at reflux until it was determined complete via HPLC, about 6 hours. The solvent was removed under rotary evaporation and the solid was rinsed with methanol and dried in air to give a pink powder with a golden sheen, ClSO-sBsubPc. Yield 0.160 g (62 %). δH(400 MHz; CDCl$_3$; Me$_4$Si) 6.89 (2H, d), 7.06 (2H, d), 7.94-7.96 (6H, m), 8.85-8.88 (6H, m); λ_{abs,max}(toluene)/nm 567; λ_{PL,max}(toluene)/nm 574; HRMS (EI) Calcd. for [C_{30}H_{16}BN_{6}O_{3}SCl] ([M]+): m/z 586.0786, found 586.0804.

3-Nitrobenzenesulfonate-boronsubphthalocyanine (NsO-BsubPc, 3e): Br-BsubPc (0.106 g, 0.00022 mol) and pyridinium 3-nitrobenzenesulfonate (0.160 g, 0.00057 mol) were dissolved in toluene (15 mL) and heated under argon while stirring. The reaction was maintained at reflux until it was determined complete via HPLC, about 6 hours. The solvent was removed under rotary evaporation and the solid was rinsed with methanol and dried in air to give a pink powder with a golden sheen, NsO-BsubPc. Yield 0.088 g (66 %). δH(400 MHz; CDCl$_3$; Me$_4$Si) 7.28 (1H, d), 7.38 (1H, t), 7.82 (1H, s), 7.95-7.97 (6H, m), 8.16 (1H, d), 8.85-8.87 (6H, m); λ_{abs,max}(toluene)/nm 568; λ_{PL,max}(toluene)/nm 575; HRMS (EI) Calcd. for [C_{30}H_{16}BN_{7}O_{5}S] ([M]+): m/z 597.1027, found 597.1046.

6.3 Results and Discussion of Chemical Properties

Typically the synthesis of sulfonic acid based pseudohalides involves the reaction of the corresponding sulfonic acid chloride (R-S(=O)Cl) or anhydride (R-S(=O)$_2$-O-S(=O)$_2$-R) with a hydroxy group. While this approach was the most obvious first attempt at creating a pseudohalide BsubPc (Path 1 in Scheme 6.1) it was unclear whether the hydroxyl group of HO-BsubPc would react as a ‘normal’ hydroxyl group. After synthesizing hydroxy-BsubPc (HO-BsubPc) using the method of Potz [8] the resulting powder was mixed with p-toluene sulfonic acid chloride (TsCl) in toluene with pyridine and heated to reflux. Surprisingly, we observed complete transformation of HO-BsubPc to Cl-BsubPc (confirmed by HPLC retention time to a genuine standard). We hypothesized that the liberated chloride anion reacted with TsO-BsubPc
Scheme 6.1: Synthesis of pseudohalides of BsubPc (3a-e) via two different pathways

(Conditions: (i) water, pyridine, reflux. (ii) R-S(=O)\(_2\)O-S(=O)\(_2\)-R, pyridine, toluene, reflux. (iii) (py\(^+\))(R-S(=O)\(_2\)O\(^-\)), toluene, reflux.) and subsequent phenoxylation to phenoxy-BsubPc (4, Conditions: (iii) phenol, chlorobenzene, 100 °C.) and hydrolysis back to HO-BsubPc (2, Conditions: (iv) DMSO, pyridine, water, 60 °C.).

produced in situ to form Cl-BsubPc. The same result was obtained if the reaction was conducted in chlorobenzene. Next we tried to use the sulfonic acid anhydride in place of the chloride. Following the same procedure, conversion to TsO-BsubPc (3a, Scheme 6.1) was observed without the formation of Cl-BsubPc (Scheme 6.1 Path 1). The products were purified by removal of reaction solvent under vacuum followed by rinsing with methanol until pure. This route was also successful in producing MsO-BsubPc (3b, Scheme 6.1). In these two cases the purity and composition of the final compound grown under the unds was confirmed using chromatography, spectroscopy (including HRMS) and crystallography (Figure 6.1a-c). Single crystals were grown through vapor diffusion of heptane into a benzene solution of TsO-BsubPc.
Figure 6.1: Atomic displacement plots of (a) TsO-BsubPc, (b) MsO-BsubPc (rhomboid), (c) MsO-BsubPc (needle) and (d) ClsO-BsubPc. Colors: grey – carbon, blue – nitrogen, pink – boron, red – oxygen, yellow – sulphur. Ellipsoids are shown at the 50% probability level.
and of pentane into a dichloromethane solution of MsO-BsubPc. In the case of MsO-BsubPc, two different crystal types were obtained: rhomboids and needles (Figure 6.2). Although both are solvates, the rhomboid structure contains two MsO-BsubPc molecules and one dichloromethane molecule in the asymmetric unit (Figure 6.1b) whereas the needle solvate incorporates disordered solvent into its structure (which has been removed from the atomic displacement plot shown in Figure 6.1c).

Given our observation that chloride could displace/exchange with tosylate in the presence of pyridine we began to consider whether halides and pseudohalides could be interchanged by treatment of a common precursor (Br-BsubPc) with a pyridinium salt of the respective pseudohalide ((py\(^+\))(R-S(=O)\(_2\)-O\(^-\))). Indeed we found this to be the case (Scheme 6.1 Path 2). Briefly, Br-BsubPc was dissolved in toluene and 2.2 equiv of the pyridinium salt of the pseudohalide was added. Under stirring and argon the solution was heated to reflux until complete conversion was observed by HPLC analysis (< 8 hours). The solvent was then removed under vacuum and the solid was rinsed with methanol until pure by HPLC, and
confirmed by NMR. This method proved successful using the pyridinium salts of \(p\)-toluene, methane, benzene, \(p\)-chlorobenzene and \(m\)-nitrobenzene sulfonic acid to produce \(\text{TsO-Br}_{\text{BsubPc}}\), \(\text{MsO-Br}_{\text{BsubPc}}\), \(\text{BsO-Br}_{\text{BsubPc}}\), \(\text{ClsO-Br}_{\text{BsubPc}}\) and \(\text{NsO-Br}_{\text{BsubPc}}\), respectively (compounds 3a-e, Scheme 6.1). Where the pyridinium salt was not commercially available we made it beforehand by neutralization of the corresponding acid with pyridine and isolating the corresponding powder. In each case the composition and purity of the final compounds was confirmed using a combination of spectroscopy and in the case of \(\text{ClsO-Br}_{\text{BsubPc}}\) crystallography. This synthetic pathway obviously negates the need to hydrolyze \(\text{Br-Br}_{\text{BsubPc}}\) to \(\text{HO-Br}_{\text{BsubPc}}\) and to produce the sulfonic acid anhydride while providing yields upwards of 90% in all cases.

Initially, we had also attempted the synthesis of \(\text{TfO-Br}_{\text{BsubPc}}\) using this method starting with pyridinium triflate and \(\text{Br-Br}_{\text{BsubPc}}\). Similar to the observations of Guilleme et al.,[2] we were unable to isolate the \(\text{TfO-Br}_{\text{BsubPc}}\) product presumably due to its high sensitivity to water as we also saw fast conversion into a mixture of \(\text{HO-Br}_{\text{BsubPc}}\) and \(\mu\)-oxo(\(\text{BsubPc}\))\(_2\) (the \(\mu\)-oxo dimer) by HPLC analysis, in each case confirmed against a genuine sample.

In order to test the viability of the pseudo derivatives to act as precursor materials we performed a series of experiments where we compared the conversion over time of each to phenoxy-\(\text{Br}_{\text{BsubPc}}\) (by reaction with phenol) and to \(\text{HO-Br}_{\text{BsubPc}}\) (by reaction with water in DMSO and pyridine). The phenoxylation reaction was performed under conditions we have previously published (5 equiv phenol, chlorobenzene) albeit at slightly reduced temperature to facilitate long reaction times. For hydrolysis each pseudohalide was heated at 60 °C in a mixture of pyridine, water, and DMSO. The conversion to product was monitored by HPLC, retention times compared against known and previously characterized standards and the conversion percentage was calculated as a function of time (as the integrated area of the product peak divided by the sum of the area of the starting material and product peaks all extracted from a PDA 3-d chromatogram at 560 nm).

Figure 6.3a shows the conversion of the pseudohalides (3a-e) and halides (\(\text{Cl-Br}_{\text{BsubPc}}\) and \(\text{Br-Br}_{\text{BsubPc}}\)) into phenoxy-\(\text{Br}_{\text{BsubPc}}\) (4, Scheme 6.1) at 100°C in chlorobenzene. The rate of reaction of \(\text{Cl-Br}_{\text{BsubPc}}\) and \(\text{Br-Br}_{\text{BsubPc}}\) (1) was as expected, with \(\text{Br-Br}_{\text{BsubPc}}\) being the more reactive and achieving 100% conversion in about 1 hour whereas \(\text{Cl-Br}_{\text{BsubPc}}\) reached 67% conversion in 24 hours. In general, pseudohalides 3a–e were slower to react than both of the halides with two exceptions. \(\text{ClsO-Br}_{\text{BsubPc}}\) (3d) reacted at approximately the same rate as \(\text{Cl-Br}_{\text{BsubPc}}\) and \(\text{NsO-}
BsubPc (3e), which reacted faster, reaching \( \sim 77\% \) conversion after 24 h. Complete conversion of Cl-BsubPc took well in excess of 150 h, whereas it took approximately 140 h to achieve complete conversion of NsO-BsubPc (Figure 6.4). We have noted some variability in the rate of conversion, and we have represented this as error bars on the conversion percentage. While we take precautions to minimize the loss of solvent over such prolonged reaction times, we cannot absolutely ensure a constant solvent volume, especially with frequent sampling. It is perhaps then not surprising to see some variability, given the accepted mechanism for these substitution reactions is S\(_{N1}\) in nature [11a] and thus highly dependent on concentration of the pseudohalide/halide of BsubPc. It should also be noted that we make no attempt to sequester the halo acid or sulfonic acid produced as a byproduct of these reactions, [15] The other pseudohalide derivatives ClsO-BsubPc (3d), BsO-BsubPc (3c), MsO-BsubPc (3b), and TsO-BsubPc (3a) achieved 50, 32, 25, and 17% conversion to phenoxyl-BsubPc after 24 h, respectively. In each case, complete conversion could not be achieved in a reasonable amount of time. By best fitting a line through the initial data points of Figure 6.3a (for a magnified view, see Figure B.23 in Appendix B) and examining the slope, we can quantify the relative reactivities for the series Br-BsubPc, NsO-BsubPc, ClsO-BsubPc, Cl-BsubPc, BsO-BsubPc, MsO-BsubPc, and TsO-BsubPc as follows: \(-200, 19, 4, 4, 1.2, 0.7, \) and \(0.5\% \text{ h}^{-1}\), respectively. We did not see any evidence of the formation of normal phthalocyanines by ring expansion under the conditions studied.

In comparing the hydrolysis rates of the pseudohalides under the reaction conditions tested, the compounds which were more reactive during phenoxylation were also more susceptible to hydrolysis. As shown in Figure 6.3b, Br-BsubPc converted to HO-BsubPc after a period of only 2 hours, while Cl-BsubPc took 24 hours. NsO-BsubPc showed the highest hydrolysis rate of the pseudohalides becoming fully hydrolyzed after only 7 hours. The next most reactive pseudohalide (ClsO-BsubPc) showed slower hydrolysis than Cl-BsubPc (52% converted to HO-BsubPc after the 40 hours of the experiment). The other three pseudohalides, BsO-BsubPc, MsO-BsubPc and TsO-BsubPc showed no hydrolysis under the conditions tested.

We can then examine whether we have achieved our stated goal of having a precursor material which is more reactive than Cl-BsubPc while possessing better hydrolytic stability than Br-BsubPc. NsO-BsubPc partially fits these criteria although as we highlight its reaction rate slows
Figure 6.3: Reactions of Br-BsubPc, Cl-BsubPc, and the pseudohalides (3a-e) under (a) phenoxylation at 100°C to give phenoxy-BsubPc (4) and (b) hydrolysis at 60°C to give HO-BsubPc (2).
Figure 6.4: Phenoxylation of Cl-BsubPc (red triangles) and NsO-BsubPc (green squares) over a long time scale.

compared to Cl-BsubPc at the latter stages of phenoxylation. Perhaps more interestingly, we have obtained several pseudohalides which do not hydrolyze even on prolonged contact with water. Given that Cl-BsubPc has been applied in organic electronic derivatives it would be of interest to compare the basic photophysical and electronic properties of the hydrolytically stable pseudohalides (for that matter all the pseudohalides) to that of Cl-BsubPc as the application of a hydrolytically stable alternative to Cl-BsubPc may be desirable.

Cyclic voltammetry was first used to examine the electrochemical properties of the pseudohalides. The measurements were performed in dichloromethane solution using tetrabutylammoniumperchlorate as the electrolyte and decamethylferrocene as an internal reference material [13]. In general, the pseudohalides possessed irreversible peaks for both the primary oxidation and reduction events and thus we are only able to comment on peak potentials of the respective electrochemical event. The oxidation peak potentials for these compounds ranged from 1.237 V for ClsO-BsubPc to the highest being 1.316 V for MsO-BsubPc (Table 6.1). The reduction peak potentials ranged from the lowest at -0.975 V for ClsO-BsubPc to the
Table 6.1: Photophysical and Electronic Properties of pseudohalides 3a-e compared to reference compounds Cl-BsubPc and Br-BsubPc.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( V_{\text{ox,peak}} ) (^a) (V)</th>
<th>( V_{\text{red,peak}} ) (^a) (V)</th>
<th>( \text{B}^{11} \text{NMR} ) (^b) (ppm)</th>
<th>( \lambda_{\text{max,abs}} ) (^c) (nm)</th>
<th>( \lambda_{\text{max,PL}} ) (^c) (nm)</th>
<th>( \phi_{\text{PL}} ) (^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl-BsubPc</td>
<td>0.981</td>
<td>-1.05</td>
<td></td>
<td>565</td>
<td>571</td>
<td>0.77</td>
</tr>
<tr>
<td>Br-BsubPc</td>
<td></td>
<td></td>
<td>-16.12</td>
<td>566</td>
<td>572</td>
<td>0.18</td>
</tr>
<tr>
<td>TsO-BsubPc (3a)</td>
<td>1.273</td>
<td>-1.044</td>
<td>-15.19</td>
<td>566</td>
<td>573</td>
<td>0.42</td>
</tr>
<tr>
<td>MsO-BsubPc (3b)</td>
<td>1.316</td>
<td>-1.051</td>
<td>-15.00</td>
<td>566</td>
<td>572</td>
<td>0.41</td>
</tr>
<tr>
<td>BsO-BsubPc (3c)</td>
<td>1.204</td>
<td>-0.988</td>
<td>-15.13</td>
<td>566</td>
<td>573</td>
<td>0.41</td>
</tr>
<tr>
<td>ClsO-BsubPc (3d)</td>
<td>1.237</td>
<td>-0.975</td>
<td>-15.47</td>
<td>567</td>
<td>574</td>
<td>0.41</td>
</tr>
<tr>
<td>NsO-BsubPc (3e)</td>
<td>1.232</td>
<td>-0.893</td>
<td>-15.04</td>
<td>568</td>
<td>575</td>
<td>0.36</td>
</tr>
</tbody>
</table>

\(^a\)Peak potential, in CH\(_2\)Cl\(_2\), vs. decamethylferrocene  
\(^b\)versus BF\(_3\)·OEt\(_2\) as standard  
\(^c\)Solution in toluene  
\(^d\)Fluorescence quantum yield in toluene, using phenoxy-F\(_{12}\)BsubPc with \( \phi_{\text{PL}} \) = 0.4 as standard \([14]\)  
\(^e\)Not available due to low solubility of compound in testing conditions

highest at -1.051 V for MsO-BsubPc. For comparison, Cl-BsubPc shows a reduction peak potential in a similar range of -1.050 V while the oxidation peak potential is much lower at 0.981 V. As with the pseudohalides, Cl-BsubPc also shows irreversible oxidation and reduction events.

The fluorescence quantum efficiencies (\( \phi_{\text{PL}} \)) of the pseudohalide-BsubPc derivatives in this paper were measured according to the standard procedure \([15]\) using phenoxy-F\(_{12}\)BsubPc as a standard reference compound \([14]\). The \( \phi_{\text{PL}} \) of Cl-BsubPc and Br-BsubPc were also measured as a comparison and the results are summarized in Table 6.1. It was found that the \( \phi_{\text{PL}} \) of all of the
pseudohalides were approximately 0.4. The highest was 0.42 (TsO-$\text{BsubPc}$) and the lowest was 0.36 (NsO-$\text{BsubPc}$). We also found that the $\phi_{PL}$ of Br-$\text{BsubPc}$ was low at 0.18 and that the $\phi_{PL}$ of Cl-$\text{BsubPc}$ was rather high at 0.77.

6.4 Results and Discussion of Crystal Structures

The first crystals to grow were that of chlosylate-$\text{BsubPc}$ (ClsO-$\text{BsubPc}$) and tosylate-$\text{BsubPc}$ (TsO-$\text{BsubPc}$), which were grown via vapour diffusion of heptane into a solution of the compound in benzene, and two different solvates of mesylate-$\text{BsubPc}$ (MsO-$\text{BsubPc}$), which were grown in one container by diffusing pentane into a solution of the compound in dichloromethane. The latter system of pentane/DCM was used, as crystals of MsO-$\text{BsubPc}$ could not be grown using the benzene/heptane system. These crystal structures can be grouped into two categories: ClsO-$\text{BsubPc}$ and TsO-$\text{BsubPc}$, which contain a benzenesulfonate group, and the two solvates of MsO-$\text{BsubPc}$ which have a methylsulfonate group. The former group crystallized into very similar crystal structures of P1 symmetry. The structure is characterized by a centrosymmetric $\pi$-stacking interaction between concave faces of the $\text{subPc}$ ligand at centroid-to-centroid (Cg-Cg) distances of 3.5229(12) Å and 3.521(2) Å for ClsO-$\text{BsubPc}$ and TsO-$\text{BsubPc}$, respectively. This interaction creates a pairing of molecules that is typically seen in phenoxy-$\text{BsubPc}$ derivatives. In these derivatives, however, the polarity of the benzenesulfonate group produces an additional centrosymmetric $\pi$-stacking interaction between the benzenesulfonate groups at Cg-Cg distances of 3.6813(13) Å and 3.701(2) Å for ClsO-$\text{BsubPc}$ and TsO-$\text{BsubPc}$, respectively. In contrast, the MsO-$\text{BsubPc}$ crystal structures are both solvates. One, which crystallized into a rhombus of space group Pna2$_1$, possesses two $\text{BsubPc}$ molecules and one molecule of dichloromethane in the asymmetric unit, the latter stabilized by a weak C-H...Cl interaction. Instead of the typical concave-concave centrosymmetric $\pi$-stacking that creates pairs of molecules, this crystal has a concave-concave head-to-tail $\pi$-stacking interaction creating a ribbon of $\text{BsubPc}$ ligands in the structure. The other, which crystallized into a needle shape of space group C2/c, has disordered solvent incorporated into the solvent accessible void. The structure is stabilized by three sets of $\pi$-stacking interactions: the typical concave-concave centrosymmetric stacking at a Cg-Cg of 3.7169(19) Å; a convex-convex interaction at a Cg-Cg of 3.6405(19) Å; and an unusual convex-convex head-to-tail interaction creating rows of $\text{BsubPc}$ ligands. Further, the sulfonate group in this structure is involved in several interactions, which include three C-H...O interactions and more interestingly a S-O...$\pi$
Figure 6.5: Crystal packing structures of a) ClsO-BsubPc, b) TsO-BsubPc, c) MsO-BsubPc (needle), and d) MsO-BsubPc (rhomboid).
interaction at a O...π distance of 3.630(3) Å. The displacement of ellipsoid plots of these crystals are given in Figure 6.1, and the crystal packing structures are shown in Figure 6.5.

After the chemical properties study shown above was completed, four more crystal structures of these compounds were obtained. Sublimation of TsO-BsubPc produced crystals of the same structure as described above for that compound, showing its robustness. The second was a non-solvated structure of MsO-BsubPc, that was obtained by sublimation, and possessed space group P2₁/n with Z=2. The molecular structure is shown in Figure 6.6a and the packing structure shown in Figure 6.6b. This structure is stabilized by a concave-concave interaction between the Cg of the 6-membered ring C10/C11/C12/C13/C14/C15 and N6 at a distance of 3.793(7) Å. Interestingly, there are no π-stacking interactions shorter than 4.0 Å in the structure. There are two C-H...π interactions at H...π distances of 2.91 and 2.90 Å between C19/H19A and the ring C2/C3/C4/C5/C6/C7 and C22/H22A and the ring C10/C11/C12/C13/C14/C15, respectively. There are two C-H...O and one C-H...N hydrogen bonds in the structure as well, at H...A distances of 2.56, 2.56, and 2.49 Å, respectively, with the C-H...O interactions between the oxygen atoms of the sulfonate and the BsubPc ligand, and the C-H...N interaction between the mesylate methyl and an imine nitrogen.

Figure 6.6: a) The molecular structure of MsO-BsubPc with displacement ellipsoids drawn at the 30% probability level and b) the crystal packing structure with the main interactions displayed.
The other two structures obtained were that of NsO-\textbf{BsubPc} and BsO-\textbf{BsubPc}. Neither of the solvent systems described above that produced crystals of the other pseudohalides were successful in producing crystals of NsO-\textbf{BsubPc} or BsO-\textbf{BsubPc} of suitable quality for diffraction. For this reason, many crystallization attempts were undertaken for these two compounds, including the vapour diffusion in the two solvent systems above, liquid layering using the two same solvent systems, and evaporation from a variety of solvents, such as dichloromethane, toluene, chlorobenzene, benzene, and chloroform. Finally, evaporation from benzene produced crystals of NsO-\textbf{BsubPc}, and evaporation from chloroform produced crystals of BsO-\textbf{BsubPc} that were diffracted and described below.

![Figure 6.7: a) The molecular structure of NsO-BsubPc with displacement ellipsoids drawn at the 30% probability level, and b) the crystal packing structure with the main interactions displayed.](image)
3-Nitrobenzenesulfonate-boronsubphthalocyanine crystallized in space group $P2_1/c$ with $Z = 4$ and two molecules in the asymmetric unit. The displacement ellipsoid plot is shown in Figure 6.7a extended crystal packing structure is shown in Figure 6.7b. The subPc ligands overlap one of their isoindole units with a $\pi$-stacking interaction through their convex faces. The isoindole units overlap with a slight angle between them, with the closest $\pi$-stacking interaction between the N3/C9/C10/C15/C16 and C2/C3/C4/C5/C6/C7 rings at a centroid-to-centroid separation distance of 3.537(2) Å. It is also stabilized by two weak C-H...O hydrogen bonds between C5-H5A...O3 at an H...O distance of 2.56 Å and C28-H28A...O3 at an H...O distance of 2.32 Å. The crystal structure also contains an intermolecular S-O...$\pi$ interaction from the sulfonate group to a 5-membered ring (N1/C1/C2/C7/C8) on the concave side of neighbouring BsubPc ligand at an O...$\pi$ distance of 3.151(3) Å. This S-O...$\pi$ construct stabilizes with the sulfonate group positioned within the bowl of the adjacent subPc ligand, which forms a column of molecules approximately perpendicular to the plane of the subPc ligand.

Benzenesulfonate-boronsubphthalocyanine crystallized in space group $P1$ with $Z = 2$, and it possesses 30.0 Å$^3$ of solvent accessible void. The displacement ellipsoid plot is shown in Figure 6.8a extended crystal packing structure is shown in Figure 6.8b. The structure is stabilized by two pairs of
π-stacking interactions. The closer of the two pairs is between isoindoline units through their convex faces. The pair of π-stacking interactions are centrosymmetric, and have a centroid to centroid distance of 3.5170(10) Å. The other pair is between isoindoline units through their concave faces and is also centrosymmetric, but at a Cg-Cg distance of 3.7528(11) Å. The structure also contains three weak C-H...O hydrogen bonds, between C12-H12A...O2, C13-H13A...O2, and C26-H26A...O3, at H...O distances of 2.52, 2.57, and 2.43 Å, respectively. The last C-H...O bond is a pair of centrosymmetric interactions between the sulfonate oxygen O3 and a carbon in the phenyl ring of the benzenesulfonate group.

One would expect that BsO-BsubPc and NsO-BsubPc would crystallize in a similar motif to the TsO-BsubPc and ClsO-BsubPc, since those two are also benzenesulfonate derivatives. However, there are more differences than similarities. BsO-BsubPc does possess similar concave-concave π-stacking of the BsubPc ligands, but the centrosymmetric interaction between the benzenesulfonate groups is based around C-H...O hydrogen bonds and not π-stacking as it is for TsO-BsubPc and ClsO-BsubPc. We propose that this is likely due to the dipole produced in the para-derivatives of benzenesulfonate, which does not occur in the non-substituted benzenesulfonate itself. The centrosymmetric C-H...O interactions in BsO-BsubPc are evidently weaker than the π-stacking produced by the substituted benzenesulfonates. The NsO-BsubPc structure is even more different, with no concave-concave π-stacking and no interactions between benzenesulfonate units. What is present, however, is a S-O...π interaction from the sulfonate group to the neighbouring BsubPc unit. Both of these observations are likely from the strongly electron-withdrawing nature of the nitro group on the benzenesulfonate, which would make π-stacking less favourable and cause the sulfonate to be electron-deficient and therefore a better group to accept electrons in a weak hydrogen bond.

In terms of their chemical properties, the halo-BsubPc derivatives are the closest analogues to the sulfonate-BsubPc derivatives, which act as pseudohalides. The halo-BsubPcs form two crystal structure motifs, which depend on whether their peripheral substituents are hydrogen (H_{12}) or fluorine (F_{12}). The halo-H_{12}BsubPc motif displays two interactions that seem to stabilize the structure [16]. The first is concave-concave head-to-tail π-stacking interactions which form ribbons in one dimension. The second interaction is a centrosymmetric pair of convex-convex π-stacking of isoindoline units which links the ribbons of BsubPc molecules together. In contrast, the halo-F_{12}BubPc motif is characterized by columns of BsubPc
molecules oriented approximately perpendicular to the \textbf{BsubPc} molecular plane [17-18]. These columns are associated through the halogen atom on the boron, which sits directly under the next \textbf{BsubPc} and consistently displays an intermolecular boron to halogen distance that is shorter than the sum of the van der Waals radii. These motifs are consistent with peripherally-fused or hybrid \textbf{BsubPcs} as well. For example, fluorinated \textbf{BsubPc} dimers joined peripherally through one isoindole unit in both the \textit{cis} and \textit{trans} forms crystallize according to the \textbf{F}_{12}\textbf{BsubPc} motif. [18] The \textit{cis} form’s crystal structure shows columns of \textbf{BsubPcs} as the \textbf{F}_{12}\textbf{BsubPc} motif would predict, with the other \textbf{BsubPc} of the dimer protruding from the stack and alternating opposite directions with neighbouring molecules. These half-molecules that are not within the columns \textit{π}-stack with other half-molecules from other columns through their concave faces, linking the columns together. The \textit{trans} form follows the \textbf{F}_{12}\textbf{BsubPc} motif more closely, with both \textbf{BsubPc} parts of the dimer in neighbouring columns that face opposite directions. An example of a hybrid halo-\textbf{BsubPc} is an asymmetric \textbf{BsubPc} with two fluorinated isoindoles and one peripherally-hydrogenated \textit{π}-extended isoindole. [19] This structure shows examples of both motifs: the fluorinated sides stack into columns with the halogen in the bowl of the next \textbf{BsubPc} unit, while the naphthalene side of the molecule forms a convex-convex \textit{π}-stacking interaction with its closest neighbours.

Since the size and polarity of the sulfonate unit is different than the halogens in the same position on the halo-\textbf{BsubPcs}, we expected to see differences in the solid-state packing structures. However, there were important similarities in the structures. The TsO-\textbf{BsubPc}, ClsO-\textbf{BsubPc} and BsO-\textbf{BsubPc} structures demonstrate convex-convex \textit{π}-stacking as in the halo-\textbf{H}_{12}\textbf{BsubPc} motif. The MsO-\textbf{BsubPc} dichloromethane solvate shows concave-concave head-to-tail overlap as found in the halo-\textbf{H}_{12}\textbf{BsubPc} crystal structures. The NsO-\textbf{BsubPc} structure shows the most similarity to the halo-\textbf{F}_{12}\textbf{BsubPc}. It contains oriented stacks linked together by S-O...\textit{π} interactions, where the halo-\textbf{F}_{12}\textbf{BsubPcs} have oriented stacks connected by X...\textit{π} interactions. A difference between them is that the nitrobenzene group exists between the two neighbouring \textbf{BsubPc} ligands in the column, however the angle at which it is oriented to the \textbf{BsubPc} units, as well as its distance, precludes it from being involved in stabilizing \textit{π}-stacking interactions. This additional molecular fragment in the column caused the increase in the boron-boron (B-B) distance to 7.197(7) Å for NsO-\textbf{BsubPc} from, e.g., 5.471(5) Å for Br-\textbf{F}_{12}\textbf{BsubPc}. [20] This similarity between these structures is likely from the electron-withdrawing nature of the nitro group on the benzenesulfonate, which, coupled with the electron-deficient \textbf{BsubPc}
ligand prevents strong π-stacking interactions within the crystal that could outcompete even the weak S-O⋯π interactions that are present. The MsO-BsubPc dichloromethane solvate shows concave-concave head-to-tail overlap as found in the halo-H12BsubPc crystal structures. The non-solvated MsO-BsubPc structure shows even more similarity to that of the halo-BsubPcs. The concave-concave head-to-tail overlap that exists in the MsO-BsubPc structure at 3.793(7) Å is the same centroid to N interaction that is seen in the crystal structures of Cl-BsubPc [16] and Br-BsubPc, [21] at 3.701(1) Å and 3.689(7) Å, respectively.

6.5 Conclusions

A series of five sulfonic acid pseudohalides of BsubPc were synthesized, crystallized, and characterized. A comparison has been made between their relative rates of reaction (phenoxylation and hydrolysis) to the reference compounds Cl-BsubPc and Br-BsubPc. Based on their relative conversions, we have identified one pseudohalide, NsO-BsubPc, to be both more reactive than Cl-BsubPc and more hydrolytically stable than Br-BsubPc. Additionally, while possessing low reactivity, three of the other pseudohalides TsO-BsubPc, MsO-BsubPc, and BsO-BsubPc showed very good hydrolytic stability (we did not observe hydrolysis under the conditions studied). The relative quantum efficiencies were also examined, and the pseudohalides had a $\phi_{PL}$ around 0.4; a range common for BsubPc derivatives including ones that have previously been used in organic light emitting diodes.[15] Their resistance to hydrolysis while maintaining the fluorescence quantum efficiency typical of BsubPc derivatives suggests that these pseudohalides might be suitable for application and study in organic electronic devices. Examining the electrochemical characteristics of these derivatives, the pseudohalides generally showed that they have a higher oxidation potential than Cl-BsubPc, although both of the oxidation and reduction events are irreversible (as they are for Cl-BsubPc).

The crystal structures were compared to each other and to other derivatives of BsubPc. The lack of substituents on the benzene group of BsO-BsubPc likely caused the absence of the π-stacking interaction between the benzene units that appeared in the TsO-BsubPc and ClsO-BsubPc structures. Instead, weaker C-H⋯O interactions were seen between the benzenesulfonate groups. In the case of NsO-BsubPc the electron-withdrawing character of the nitro group caused a completely different packing structure which included no π-stacking between benzenesulfonate groups, and a S-O⋯π interaction to stabilize the columns of BsubPc molecules in the crystal. In fact, this NsO-BsubPc structure was most reminiscent of the halo-F12BsubPc crystal packing
motif. The non-solvated MsO-\text{BsubPc} structure obtained through sublimation possessed a head-to-tail concave-concave interaction between the \pi-system of one \text{BsubPc} and the imine nitrogen of another. This interaction is similar to that of Cl-\text{BsubPc} and Br-\text{BsubPc}, which is of special note since it has been shown that the electrochemical and optical properties of the MsO-\text{BsubPc} and the Cl-\text{BsubPc} are also quite similar, but MsO-\text{BsubPc} is much more resistant to hydrolysis. In solid-state applications where Cl-\text{BsubPc} is currently used, such as OPVs and OLEDs, we suggest that MsO-\text{BsubPc} would be an ideal substitute.

Evaluation of these compounds with respect to the criteria set out in Chapter 1 is next. The two compounds noted in this Chapter for their properties were MsO-\text{BsubPc} (non-solvated) for its hydrolytic stability, and NsO-\text{BsubPc} for its high reactivity. A summary of their evaluation is shown in Table 6.2. MsO-\text{BsubPc} possesses a good crystal packing motif, very similar to the halo-\text{BsubPc} motif. Its electrochemical properties have been shown to be also very similar to those of the halo-\text{BsubPcs}. However, its hydrolytic stability has been shown to be extremely good, unlike the halo-\text{BsubPcs}. A drawback of the material is that it tends to make solvates with organic solvents. If the crystallization is limited to sublimation, however, this should not pose an issue to the robustness of the crystal form. The NsO-\text{BsubPc} structure, on the other hand, is

<table>
<thead>
<tr>
<th>Table 6.2: Evaluation of Chapter 6 compounds.</th>
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<tbody>
<tr>
<td><strong>Electro-</strong></td>
</tr>
<tr>
<td><strong>Chemical</strong></td>
</tr>
<tr>
<td>Properties</td>
</tr>
<tr>
<td>Halo-\text{BsubPc}</td>
</tr>
<tr>
<td>Phenoxy-\text{F}_{12}\text{BsubPc}</td>
</tr>
<tr>
<td>Phenoxy-\text{BsubPc}</td>
</tr>
<tr>
<td>Tosylate-\text{BsubPc}</td>
</tr>
<tr>
<td>Chlosylate-\text{BsubPc}</td>
</tr>
<tr>
<td>Besylate-\text{BsubPc}</td>
</tr>
<tr>
<td>Nosylate-\text{BsubPc}</td>
</tr>
<tr>
<td>Mesylate-\text{BsubPc}</td>
</tr>
</tbody>
</table>
actually a solvate, is difficult to crystallize, and has been shown to have poor hydrolytic stability. While it does not meet the criteria for use in organic electronics, it is noted for its reactivity and may be useful in other applications.

6.6 References


9. Although the compound was used in literature, no characterization was reported. See: Enomoto, T., Iino, M., Matsuda, M., and Tokura, N. Bull. Chem. Soc. Japan, 1971, 44, 3140-3143.

10. The compound was reported in literature with only melting point as characterization, which our measurements matched. See: Field, L. J. Amer. Chem. Soc., 1952, 74, 394-398.


Chapter 7

Summary, Conclusions, and Future Work

7 Summary, Conclusions, and Future Work

7.1 Summary

The material in this thesis draws relationships between molecular structure of BsubPc and its architecture and stability in the solid state. As outlined in the introduction, the crystal structure of a material has a large effect on its electrical, optical, and photostability properties. BsubPc is uniquely suited for use in organic photovoltaics, therefore we wanted to study the relationship between molecular structure and solid-state packing arrangement.

In Chapter 2, a series of alkyl substituted phenoxy-BsubPc derivatives were synthesized and crystallized. A metric was created that compared the structures by their intermolecular spacing by boron to boron atomic distances, by the angle at which the phenoxy attaches to the boron atom, and certain interatomic distances. The structures were compared, and we identified a common π-stacking interaction between the concave faces of the BsubPc ligands. Despite the increasing size of the alkyl group, this concave-face to concave-face π-stacking in the crystal structure remained in the structure and at a consistent centroid-to-centroid (Cg-Cg) distance. This interaction directed the molecules of the compounds under study into isolated pairs in the solid state. Only the most bulky substituent, \( \tau \)-octyl, provided enough separation to the molecules to form a different structural motif, and this different form is in fact a benzene solvate. The main conclusion from this work was the existence and persistence of this dimeric form in the solid state, which we identified as potentially being undesirable from a charge carrier mobility perspective.

Next, in Chapter 3, we performed a study on the effect of symmetry on the crystal packing structure of BsubPc. We synthesized less-symmetric analogues to those developed in the previous Chapter, 3-methylphenoxy-BsubPc and 3,4-dimethylphenoxy-BsubPc. We found that the lower symmetry of these derivatives did not prevent them from crystallizing, but they consistently were more susceptible to solvate formation. We also identified that these derivatives were highly soluble. These have industrial advantages over the common solubilization technique of adding long alkyl chains since adding only a single methyl group
uses much less material per mole, making them less expensive to produce. The compounds were then both crystallizable and highly-soluble derivatives, a combination of properties that are traditionally incompatible.

In Chapter 4 we examined the effect of halogen-specific interactions on BsubPc crystals. We identified a kinetic polymorph of bromophenoxy-BsubPc that is stabilized through bromine to boron and bromine to π intermolecular interactions. This α-polymorph possesses a 1-D ribbon structure. As far as we know, this is the first example of true polymorphism in a BsubPc molecule; that is, two crystal structures of one compound, neither of which are solvates. It was also shown in the manuscript that α-p-bromophenoxy-BsubPc is a kinetic polymorph of slightly lower energy than β-p-bromophenoxy-BsubPc. Unfortunately, the former structure is of a more interesting and potentially useful crystal structure than the β form, which forms into the common dimeric motif. We were unable to isolate the α crystal structure following the publication, even with an extensive polymorph search.

Chapter 5 discusses the crystal structures of the compounds with increasing π-basicity of the substituent group. We found that the π-π stacking interactions in the crystal structures both increase in number and in strength with an increase in the π-basicity of the substituent. Specifically, for the series of peripherally hydrogenated BsubPcs, methoxyphenoxy-BsubPc shows an additional π-stacking interaction while the more π-basic naphthoxy-substituted BsubPcs show that the packing motif had been altered to give 1-D ribbons connected by π-stacking between the naphthoxy units and the neighbouring BsubPc ligand. The perfluorinated series displays a similar trend with increasing π-basicity. A series of BsubPc derivatives with π-acidic substituents were also synthesized and crystallized, and these showed no substituent to BsubPc specific interactions. We conclude that the π-acid/π-base interaction can be used to direct solid-state packing arrangements.

Lastly, in Chapter 6 a new series of BsubPc derivatives was explored. A series of five sulfonic acid pseudohalides of BsubPc were synthesized and crystallized. The crystal structures were compared, and they were not found to have consistent crystal packing motifs associated with the series. However, we demonstrated a new synthetic method for BsubPc substitution chemistry, and we identified interesting properties of some of the resulting compounds. 3-nitrobenzenesulfonate-BsubPc (NsO-BsubPc) was noted due to its reactivity to under phenoxylation conditions that exceeds that of the usual substitution starting material Cl-BsubPc.
This material has inspired further study as a material that may be useful for encouraging the reaction of BsubPc in polar solvents. Two other compounds of note were methylsulfonate-BsubPc (MsO-BsubPc) and p-toluenesulfonate-BsubPc (TsO-BsubPc). These were identified due to their resistance to hydrolysis. Under the hydrolysis conditions in the manuscript, these compounds displayed no conversion into the hydrolyzed HO-BsubPc after more than 100 hours.

7.2 Conclusions

The guidelines set out in Chapter 1 for evaluating the BsubPc derivatives synthesized and characterized in this thesis are that to be considered a possible organic electronic material the compound must have good optical and electrochemical properties, be hydrolytically stable, and possess a crystal structure in which there is a pathway for charge carrier conduction. Most of the compounds made in this Thesis, however, showed the typical phenoxy-BsubPc dimer motif, thus not being identified as potential materials for further study. However, that most of the compounds produced crystals in the dimer motif provides a suggestion for how common that structure actually is, and that is not an easy feat to choose the proper intermolecular interaction.

Figure 7.1: Summary of the selected crystal measurements of the compounds that crystallized into the dimer motif.
Table 7.1: Summary of the compounds of interest identified in the thesis, and a comparison with the criteria from Chapter 1.

<table>
<thead>
<tr>
<th>Electro-Chemical Properties</th>
<th>Hydrolytic Stability</th>
<th>Pathway in Structure</th>
<th>Robust Crystal Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>Halo-BsubPc</td>
<td>~</td>
<td>✗</td>
<td>✓</td>
</tr>
<tr>
<td>X₁₂BsubPc</td>
<td>✗</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>H₁₂BsubPc</td>
<td>✓</td>
<td>✓</td>
<td>✗</td>
</tr>
<tr>
<td>3-methyl-phenoxy-BsubPc</td>
<td>✓</td>
<td>✓</td>
<td>✗</td>
</tr>
<tr>
<td>4-Br-phenoxy-BsubPc</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>4-MeO-phenoxy-BsubPc</td>
<td>✓</td>
<td>✓</td>
<td>~</td>
</tr>
<tr>
<td>Naphthoxy-BsubPc</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Tosylate-Bsubc</td>
<td>~</td>
<td>✓</td>
<td>✗</td>
</tr>
<tr>
<td>Chlosylate-BsubPc</td>
<td>~</td>
<td>✗</td>
<td>✗</td>
</tr>
<tr>
<td>Besylate-BsubPc</td>
<td>~</td>
<td>✓</td>
<td>✗</td>
</tr>
<tr>
<td>Nosylate-BsubPc</td>
<td>~</td>
<td>✗</td>
<td>✗</td>
</tr>
<tr>
<td>Mesylate-BsubPc</td>
<td>~</td>
<td>✓</td>
<td>✓</td>
</tr>
</tbody>
</table>

in order to disrupt and outcompete that motif. A summary of the compounds that formed into the dimer is given in Figure 7.1. One will notice that the compounds all maintain a very similar boron-boron and π-stacking distances. Perhaps the most interesting of the compounds on this list are 4-t-butylphenoxy-BsubPc, 4-t-octylphenoxy-BsubPc, which has a much increased B-B distance \(d_2\) and B-O-C bond angle, and the set of 3-methylphenoxy-BsubPc, 3,4-dimethylphenoxy-BsubPc, and 4-methoxyphenoxy-BsubPc. The latter three compounds have a
B-B distance $d_2$ that is similar to that of the halo-phenoxy $\text{BsubPcs}$, while still crystallizing into the dimer motif. They also have increased B-O-C bond angles. It would seem that an increase in $d_2$ is associated with an increase in the B-O-C angle.

The compounds that did not form the dimer motif, however, tended to form into a motif that possessed a pathway for charge carrier conduction. In this Thesis a new motif of $\text{BsubPc}$ was discovered, in the crystals of $\alpha$-4-bromophenoxy-$\text{BsubPc}$, $\alpha$-naphthoxy-$\text{BsubPc}$, and $\beta$-naphthoxy-$\text{BsubPc}$. This form contains one-dimensional chains linked together through $\pi$-stacking between the substituent group (phenol or naphthol) and the concave face of the next $\text{BsubPc}$ ligand. Other compounds identified in the thesis are MsO-$\text{BsubPc}$, which follows the halo-$\text{BsubPc}$ motif but without the problem of hydrolytic instability and 4-methoxyphenoxy-$\text{BsubPc}$, which forms a motif that is in between the stacked motif and the dimer motif, as it possesses stacks of dimers linked through $\pi$-stacking between the methoxy-phenoxy substituent and the convex face of the neighbouring $\text{BsubPc}$ ligand. In Chapter 4, an additional criterium was added, that of robustness of crystal structure, which refers to reproducibility of the structure through crystallizations, particularly via sublimation. Of the preceding structures, the structure $\alpha$-4-bromophenoxy-$\text{BsubPc}$ is eliminated from the list of potential candidates by this new criterium due to its existence as a kinetic product with no reliable method of isolation. A summary of the comparison of these structures is given in Table 7.1.

The compounds that have been identified by this thesis as potential organic electronic materials are $\alpha$-naphthoxy-$\text{BsubPc}$, $\beta$-naphthoxy-$\text{BsubPc}$, MsO-$\text{BsubPc}$, and MeO-Phenoxy-$\text{BsubPc}$.

### 7.3 Future Work

The ability to be able to alter the crystal packing structure of boron subphthalocyanine as described in this thesis lays a framework upon which many future studies can be based. Some chapters provide the basis for short-term extensions and follow-up projects suitable for a summer student or undergraduate thesis, but the methodology as a whole inspires ideas for longer term areas of study that could be a Master’s or Ph.D.
7.3.1 Short term projects

7.3.1.1 Advantages of Symmetry-Induced Solubility

The work discussed in Chapter 3 identified two highly soluble derivatives of $\text{B}_{\text{subPc}}$, 3-methylphenoxy-$\text{B}_{\text{subPc}}$ and 3,4-dimethylphenoxy-$\text{B}_{\text{subPc}}$. These were found to be highly soluble derivatives, crystallizable, and sublimable. This combination of materials properties is not common in the literature for organic electronic materials, since normally solubility is given by the addition of large alkyl chains, causing a large increase in flexibility molecular weight.

The utility of the solubilization technique identified in Chapter 3 provides a student with the opportunity to study the differences between solution deposition of a film of $\text{B}_{\text{subPc}}$ and the vapour deposition of the same material. These films could be compared in terms of crystallinity, surface quality, charge carrier mobility, and even performance in devices. As far as I know this has not been studied before.

7.3.1.2 Halogen-Boron Effects

As outlined in Chapter 4, the Br-B and Br-$\pi$ interactions in $\text{B}_{\text{subPc}}$ can produce a polymorph with a modified crystal packing structure. These halogen-containing interactions of the para-phenoxy derivatives have already inspired a project looking at the meta- and ortho-phenoxy halogen derivatives of $\text{B}_{\text{subPc}}$, which has identified a new crystal packing motif stabilized by halogen to imine-nitrogen intermolecular interactions. [1] Although we did not have success in reliably isolating the kinetic polymorph of 4-bromophenoxy-$\text{B}_{\text{subPc}}$, there has been some success in literature of developing procedures for isolating kinetically-favoured crystal structures. A suitable project could be in the development of a robust technique for isolating this polymorph.

There are four methods in literature that could be used to isolate this elusive polymorph: crystallization in porous substrates [2], contact line crystallization [3], grinding to decrease particle size [4], and microfluidic crystallization with rapid cooling [5]. While this project depends on a variety of different techniques and collaborations, the utility of each technique could first be tested with a substance such as acetaminophen that is known to crystallize into multiple polymorphs. [6] The construction of an apparatus for microfluidic crystallization and a process for any of the above methods would be a long-term asset to the group, even if a robust and repeatable procedure for isolating this kinetic polymorph were not found.
7.3.2 Long term projects

As a whole, this thesis shows that through minor modifications of the BsubPc molecule changes to the overall crystal structure could be made. It also shows that some changes are more robust than others. For example, the π-acid/π-base interactions produced similar effects for a variety of different substituents, whereas the sulfonic acid derivatives show a variety of crystal structures with no apparent consistency between derivatives. The bromophenoxy-BsubPc derivative that crystallized into two separate polymorphs is an interesting case, as the apparent similarity in their energetics provides the opportunity for an in-depth study of minor variables on BsubPc crystallization. There are a few longer term studies that would be interesting extensions of this work.

7.3.2.1 Relationship between Crystalline Phase and Charge Carrier Mobility

A direct follow up to the work done in this thesis is to develop a relationship between crystal packing structure and charge carrier mobility. As discussed earlier in this thesis, it is known that charge carrier mobility depends on the polymorph of the material. [7] In this thesis we identified a number of different crystal packing structures, between which the basic molecular structure is fairly similar. Thin films of these materials would need to be laid down on a conductive surface and charge mobility measurements performed in order to determine which crystal motif has the highest charge carrier mobilities. In our lab, this first step has started recently. [8]

However, developing a crystal structure to property relationship is more complex than merely measuring mobilities. There also must be a reliable method for showing the crystallinity in the film. As discussed in Chapter 1, it is not just the crystallinity of the film that affects mobility, but also orientation of the crystal on the substrate and how many crystalline domains are in the film. [9] To determine these values a combination of analytical methods would be required. A method used on organic thin films that can determine the crystallinity of the film, the parameters of the crystal packing unit cell, and its orientation on the substrate is grazing incidence x-ray diffraction (GRIN-XRD). [10] However, this method requires a specialized x-ray source and is not available as an everyday technique at this University. A more accessible method of determining crystallinity and of differentiating between polymorphs is through Raman spectroscopy. [11] This technique however, requires a known crystalline sample for reference of each polymorph before it is useful. A third method that would be useful is atomic force
microscopy (AFM), which can provide a two-dimensional surface image of crystalline domains, [10] which would provide an estimate of the monocrystallinity of the thin films.

In addition to just determining mobility and crystallinity, further studies can be performed, such as the performance of the various crystal packing structures along different crystal planes. The anisotropy of crystalline charge carrier mobilities is known, and some of the crystal packing motifs may provide better performance parallel to the substrate while others might perform better in a perpendicular direction.

7.3.2.2 Crystallization in an Electric Field

Surprisingly, the effects of electric fields on crystallization of small-molecule materials have been little studied. Electrocrystallization, [12] which depends on the electron transfer and deposition of a compound (mainly metals) to the surface of an electrode when a field is applied in a solution of the material has been known since the 1940s. There are many references to the alignment of organic dyes and liquid crystals [13]. There is also literature regarding the induced crystallization of inorganic semiconductors in an electric field during annealing. [14-15] In fact, recently the field of protein crystallization, prompted by the availability of equipment from electrophoresis, has found that nucleation and growth of protein crystals can be controlled by the use of electric fields. [16] There have been a few accounts of vinylidene fluoride-co-trifluoroethylene films grown under high electric fields that have been shown to grown with dipole moments normal to the substrate. [17-18] Other than a few studies on phthalocyanines grown under electric fields, such as chloro-aluminum phthalocyanine [19] and titanyl(IV)-phthalocyanine, [20] and the technique being reviewed in Forrest’s 1997 molecular beam epitaxy review, [21] there has not been any application of which we are aware to small molecules.

One would expect that in an electric field, polarizable molecules in solution would align with the electric field, and that this effect would be more pronounced for molecules with higher polarizabilities. In some liquid crystals this is a necessary phenomenon. One of the fundamental directors of crystallization is that molecules will crystallize into forms that provide zero or negligible electrostatic surface potentials and polarizabilities in the bulk. [13] However, for aromatic compounds and those with \( \pi \)-electrons the molecular polarizabilities can be relatively
high, [13] and in fact BsubPc itself, being a non-planar molecule as well as aromatic, should have a particularly high polarizability.

The derivatives developed in this thesis showed a variety of polarities in their axial substituents. Their electrostatic potential distribution also varied, for example the halo-phenols as discussed in Chapter 4. The polarizability of the molecule would change the effect of the applied electric field on the alignment of the molecules. Other than the polarity of the substituent, variables that could be tested are the solvent, voltage, and the shape of the electrode from a sharp tip to a planar, capacitor-like geometry. This method may be a way to end up with crystals that have a non-zero polarity, which could create an internal field that could enhance the charge separation in photovoltaic devices.

7.4 References


Appendix A

Background on Organic Crystals

In this chapter, I will give a brief outline of organic crystals and their terminology. I will then outline the major intermolecular interactions that will be discussed in subsequent chapters and provide background on the theory of crystallization processes. Much of the first few sections of this primer were written with reference to general reference books by Desiraju et al. [1,2]

Following this I will give a brief summary of the current uses of crystals in organic electronics and end with a review of the current literature on crystals of boron subphthalocyanine and other relevant molecules.

A Background on Organic Crystals

A.1 Organic Crystals

The growth of organic crystals is complex process, with many variables affecting the final structure. Despite this complexity, theories on the growth processes are well-developed for ideal cases. In this section, an introduction to crystal growth processes and methods is given, and definitions and specifics relating to the growth of organic crystals are discussed.

A.1.1 Crystal Growth

The growth of a crystal has two distinct stages: Nucleation and growth. Nucleation occurs when a certain number of molecules of the compound reach a state of where it is more favourable to be aggregated in the solid state than in the liquid or gas phase. In terms of free energy, nucleation is the formation of crystal nuclei to the point where the addition of molecules to the nucleus lowers the total Gibbs free energy of the system. During the nucleation phase, growth of nuclei raises the free energy of the system, and is this not favourable. Since the energy balance between the free energy of the more stable molecules in the bulk of the nucleus and the higher free energy of the molecules in the surface layer (interfacial energy) dictates the stability of the particle, smaller particles are energetically unstable, and they will tend to dissolve, regrow, and redissolve, thus preferentially forming the lowest energy conformations. Once a critical size of
the nucleus is reached, however, the addition of further molecules produces a decrease in the free energy of the system, due to there being a higher proportion of molecules in the lower energy bulk rather than on the surface of the nucleus. Growth, then, begins in the situation once the critical size for stable nuclei has been achieved. The nucleation step generally templates the growth phase, and therefore is the most important stage to control in order to produce a specific structure, although transformations from crystalline phase to crystalline phase can occur for meta-stable crystal structures.

A.1.1.1 Solution Crystal Growth

The most common type of crystal growth is from the solution phase, since it has been used for many years as a purification technique in organic chemistry under the moniker of recrystallization. In this type of crystallization, nucleation occurs in a state of supersaturation of the solution; i.e., in a non-equilibrium state where the amount of material dissolved is higher than normally possible for a specific solvent, temperature, and pressure. The nucleation phase, however, also has a kinetic aspect that depends on the concentration and degree of supersaturation. If these variables are higher, then the nucleation rate increases and the number of nuclei in the system increases. Furthermore, with faster nucleation rates it is more likely that crystal phases that are not the thermodynamically most favourable states will proceed to the growth stage.

There are many ways to access the metastable state of supersaturation, and therefore many types of solution-based crystal growth:

**Classic crystallization** uses the difference in solubility at different temperatures to induce this state. By reaching the saturation concentration at a high temperature and then cooling the solution to a point where the solubility of the material in the system is lower, nucleation is induced. The nucleation rate in this case can be controlled by the solvent choice, the temperature used to dissolve the compound, and the cooling rate of the solution.

**Solvent evaporation** produces nucleation conditions by allowing the evaporation of solvent until the concentration of the compound in the solvent is above the saturation concentration. This is the most straightforward of all crystallization techniques. Nucleation rate can be controlled by choice of solvent and by the surface area of the solution. Both of these factors
control the evaporation rate; by choosing a more volatile solvent and by choosing a larger area container that provides a large surface area the evaporation rate and therefore nucleation rate goes up.

**Liquid layering** uses a near-saturation solution in a good solvent, which is then carefully layered with a poor solvent (anti-solvent). Criteria for solvent choice are solubility difference and that the solvents are miscible. Nucleation is induced by the diffusion of the solvents across the interface, which produces a solubility of the compound in the solvent mixture that is lower than the concentration of the compound in the total volume of solvent added. For this reason, the amount of good solvent to anti-solvent used is usually about 1:4 or 1:5. Nucleation rate can be controlled by concentration of the original solution, relative volumes of the solvents, and surface area of diffusion. For slower rate of nucleation a lower original concentration, higher amount of good solvent, and narrow crystallization vessel (an old NMR tube is often used) are chosen.

**Vapour diffusion** is a technique that is similar to liquid layering, but involves the diffusion of solvent through the vapour phase rather than across a liquid-liquid interface. Generally, a solution of the compound in a good solvent is located inside a small container, which is then placed inside a larger container that holds a volume of a miscible anti-solvent. The outer container is sealed and the vapours diffuse between the two liquids phases to reach equilibrium. As the anti-solvent diffuses into the solution of the compound and the good solvent diffuses out to mix with the anti-solvent, the solubility of the compound in the solution decreases, leading to the nucleation condition of supersaturation. Often a loose, perforated cover is placed over the inner container to slow the rate of diffusion. A crystal is grown by this method in a period of days to weeks, but the slow time frame can produce very high quality, large-sized single crystals.

### A.1.1.2 Gas-phase Crystal Growth

Crystals can also be grown by sublimation, where the solid powder is turned directly into gas, and redeposited, slowly, in a crystalline phase. For this to occur, the liquid phase of the material must be avoided. This is done by heating the compound under low pressure conditions. In the setup used in this thesis, a glass tube was used as the sublimation container, with heat applied to the compound on one end. A cold finger condenser was located at the opposite end, and this created a heat gradient through the tube. A low flow of nitrogen gas was applied to promote
diffusion of vapour along the tube. As the gas-phase compound flowed through the tube, when it encountered a low enough temperature, the compound would return to the solid phase. Since this crystallization is performed at a temperature close to the minimum for sublimation to occur, the transition to gas-phase and back to the solid phase is slow. This slow deposition into the solid phase allows a crystalline solid to deposit within the tube. The advantage to this method is that impurities in the material of lower molecular weight and volatility will travel farther down the sublimation apparatus, separating from and purifying the material, which can lead to higher quality crystals.

A.2 Crystal Engineering

The field of crystal engineering is one of the newest branches of chemistry and applied chemistry. The term was first coined in the 1950s, but the field did not become a predictive science until nearly 40 years later. It was originally developed as a method for templating solid-phase chemical reactions, [3,4] but since that time, the potential of weak, non-covalent intermolecular interactions for affecting the growth of crystal structures and their resulting properties, taking the focus of solid phases away from covalent bonds only.

The current state of the field of crystal engineering has progressed from a purely observational science to one that is beginning to possess predictive and design-based theories. An accepted definition of the field is “the understanding of intermolecular interactions in the context of crystal packing and in the utilisation of such understanding in the design of new solids with desired physical and chemical properties.” [1,2] The intermolecular interactions that have become the basis of crystal engineering are the weak, non-covalent interactions mentioned above, which include, in approximate order from strongest to weakest: strong hydrogen bonds, halogen bonds, π-electron-containing interactions, and weak hydrogen bonds. It has been noted that certain combinations and geometric orientations of atoms commonly evoke specific non-covalent interactions in the solid state. As one would expect, by adding these commonly interacting groups to a molecule, one can “design in” interactions into the crystal packing arrangements of that molecule. In order to facilitate the language surrounding crystal engineering these common interactions became known as “synthons” [1,5], and have been likened to the intermolecular equivalent of covalent bonds for molecules. A classic example of a
Figure A.1: A typical synthon: The centrosymmetric hydrogen bonding of carboxylic acids.

A synthon is the carboxylic acid dimer, in which the carbonyl oxygen and the hydroxy oxygen and hydrogen form paired, centrosymmetric hydrogen bonds, as shown in Figure A.1.

These synthons, while allowing a certain amount of predictability of crystal structure in molecular design, still are highly dependent on the class and type of molecule being crystallized, as well as competition between different building blocks and interactions. For example, certain functional groups can act in multiple different synthons, [5] or some robust synthons can be overpowered by other, stronger interactions. [6] Because there are so many different forces affecting the crystallization process, reliable predictability across all compounds has not yet been achieved. But the experimental work in the field is also being complemented by in silico crystal structure prediction (CSP). There has been much work towards the ability for molecular modeling software to be able to predict the crystal structure given only the molecular structure of the compound. While there are a number of software packages designed to achieve reliable CSP [7], only during the two most recent blind tests conducted by the CCDC did a single group predict the correct structure for all of the target molecules. [8,9] These results show that software for predicting crystal structures is improving. They also point out that all of the molecules in the test that were predicted by most of the groups were small and relatively rigid, and larger or more flexible molecules were less predictable. One can infer that current in silico CSP of larger molecules such as boronsubphthalocyanine are not fully tested, nor reliable. They also show that developing in silico models is the best way to test and improve the current theories on the factors guiding crystallization. For this reason, while this type of modeling is beyond the scope of this thesis it is worth mentioning due to the importance to the field at large. It is these models that allow experimentalists in the field to refine their theories and aid in the design of molecular crystals.
A.3 Crystals, Co-crystals, and Solvates

When crystallization occurs, there is no guarantee that the desired compound will crystallize properly and form high-quality crystals, nor that the desired compound will crystallize on its own to form crystals with one constituent only. For the former, crystallizing compounds of very high purity and slowing the rate of nucleation and growth can assist. The latter, however, is a common problem and current research area in the field of crystallization.

When one successfully crystallizes a single compound and the resulting crystal unit cell contains only molecules of that compound, this is a true crystal. Often, however, the solvents in which the crystallization is performed interact with the compound and can incorporate itself into the structure. This is known as a solvate. Solvates can possess ordered solvent molecules at numbers commensurate with the numbers of molecules of the target compound, e.g., 1:1, 2:1, etc., but solvates can also be of disordered solvent, only loosely attached to the crystal lattice in solvent accessible voids within the crystal. A special case is that of water solvates, known as hydrates. The water molecules in hydrates are often stabilized by true hydrogen bonds, which are some of the strongest intermolecular interactions within crystals. For this reason, hydrates are some of the most common solvates observed in compounds that have sites available for hydrogen bonding. [1]

A recent branch of crystal engineering that is particularly popular in pharmaceuticals, is the process of co-crystallization. A co-crystal is a crystal where two or more compounds are intended to be crystallized together in commensurate numbers. Traditionally, co-crystals utilize hydrogen bond-based synthons, since in the pharmaceutical industry most drugs possess hydrogen bond donor or acceptor sites.

A.4 Polymorphism

One of the major difficulties in crystal engineering is the phenomenon of polymorphism, in which a single compound has the ability to crystallize into more than one crystalline phase. Since the goal of crystal engineering is to design the solid-state structure of a compound, the possibility that multiple structures can be grown from the same molecule makes the task even more difficult. In order to solve this problem, the crystal engineer must attempt to make strong intermolecular interactions that can only arrange in one possible way. However, despite efforts
to avoid polymorphic forms of compounds, periodically a new polymorph of a well-known compound will emerge. An interesting case is that of maleic acid, where the process of crystallization was changed slightly and after 124 years of producing one crystal form a new polymorph was found. [10]

Historically, the nomenclature surrounding polymorphism has been shrouded in confusion. Terms such as pseudo-polymorph, used for the description of a new solvate or hydrate of a known crystal, have fallen out of favour, and the word polymorph is now reserved for structures that have identical components. In this definition, two structures of a single component (true crystals) are polymorphs, but one true crystal structure and one solvate structure are not polymorphs. However, two solvates of the same compound may be considered polymorphic co-crystals.

A.5 Space Groups and Organic Crystals

Since crystals are by definition made up of repeating units, the mathematical and geometrical descriptions of crystals are generally described by symmetry operators acting on the smallest repeatable unit in the crystal. This smallest unit of the crystal that can be described purely by translations is known as the unit cell. Within the unit cell is a smaller group called the asymmetric unit which contains an example of each molecule in the crystal that cannot be related to each other through rotations and transformations, that is, of different geometrical parameters. For example, if there is a molecule with a flexible or rotationally active bond, and two molecules in the crystal have different bends in the flexible group or a different angle of rotation in the rotatable group, then one of each of these molecules would be within the asymmetric unit. The number of molecules in the unit cell is defined as $Z$, and the number of structurally distinct molecules in the crystal (i.e., within the asymmetric unit) is defined as $Z'$. [1]

The unit cell is a geometric construct that contains the asymmetric unit of the crystal structure, and can be repeated by translation operators only to reproduce the entire crystal. It is defined by the lengths $(a, b, c)$ of its axes and the angles $(\alpha, \beta, \gamma)$ between them. A schematic of a unit cell is shown in Figure A.2. The values of these parameters determine the shape of the unit cell and to which crystal system the structure belongs. The 7 crystal systems, from least symmetric to most symmetric are: Triclinic, monoclinic, orthorhombic, tetragonal, trigonal, hexagonal, and cubic.
The symmetry operators that are applied to the asymmetric unit to relate the spatial orientations of the molecules to each other then split these crystal systems into 230 unique space groups. For organic molecules, however, 76% of the structures reported in the CSD are members of only 5 of these space groups: P1, P2₁, C2/c, P2₁2₁2₁, and P2₁/c, which fall into only the three least symmetric space groups: triclinic, monoclinic, and orthorhombic. Kitaigordskii suggests that the reason these space groups are most frequently seen for organic molecules is that they are the ones that allow the closest packing within the structures. [11] This preference is likely due to distance dependence of intermolecular interactions and the balance between repulsive and attractive van der Waals forces. Additionally, it has been suggested that these space groups provide crystals with close-packed two-dimensional planes that provide stability when cleaved or growing.

Briefly, the symmetry elements associated with these five most common space groups describe the relationship between molecules in the unit cell. P1 is the least symmetric space group, comprising only one inversion element, which is a reflection of the asymmetric unit through a point. Figure A.3 shows an example of an inversion. P2₁ is the next least symmetric, displaying only a single screw symmetry element along one dimension. A screw element is a molecular rotation plus a translation, an example of which is shown in Figure A.3b. C2/c is also quite asymmetric, showing a glide element and an inversion. A glide symmetry element is a translation element and a reflection across a reflection plane, an example is shown in Figure A.3c. The second most symmetric of these five space groups is P2₁2₁2₁, which possesses screw elements along all three of the unit cell axes. Lastly, the most symmetric is P2₁/c, which comprises as many as 30% of all organic crystal structures in the CSD. It possesses a screw element along the c-axis as well as a glide element.

It has been suggested that the symmetry operators found in the most common space groups, i.e. inversion centres, screw axes, and glide axes, are most favourable due to close-packing arguments, [11] while others suggest that it could be due to minimization of electrostatic potentials. [13] It has also been suggested that the complementarity of many intermolecular interactions, such as hydrogen bonding or π-stacking, makes the close-packing due to inversion centres or screw axes able to engage a maximum number of these strong intermolecular interactions. [14-15]
Furthermore, these types of symmetry elements often result in paired dimers, rows, or planes within the crystal, which can produce pseudo-symmetrical groups that may have higher symmetry than the molecules themselves. [16] These more symmetrical groups will then be
more likely to crystallize into long-range patterns. It has also been found that if the molecular
symmetry allows, mirror planes will tend to fall through the centre of the molecules, creating
more opportunity for complementarity and higher symmetry in the crystal. [14]

A.6 Types of Intermolecular Interactions

As described earlier, the intermolecular interactions that can be designed into organic molecules
in order to control their structure in the solid state are weak when compared to covalent bonds.
In fact, covalent bonds have a strength upwards of 120 Kcal/mol, whereas the non-covalent
bonds discussed herein are ca. a factor a ten weaker, ranging from about 0.2-40 Kcal/mol. [17]
In addition, some of these interactions also have angular dependence, which can act as a director
of crystal structures as well.

A.6.1 Hydrogen-bonding

Hydrogen bonds (H-bonds) can be the strongest of the non-covalent interactions. While many
theoretical discussions of the nature of the H-bond exist, empirically it is accepted that the
strength of the H-bond is determined by the balance between the proton affinities (PA) and the
Pₐ of the groups involved. It is also accepted that the H-bond is mainly electrostatic in nature.
The H-bond interaction is essentially a sharing of the hydrogen atom between two
electronnegative atoms. It is written as D-H…A, where D is known as the H-bond donor and A is
known as the H-bond acceptor.

Because H-bonds are electrostatic in nature and the result of interactions between monopoles,
dipoles, and quadropoles with each other, the range over which they exert their influence
depends on the donor and acceptor atoms involved. For the strongest H-bonds, two strongly
polarized monopoles interacting provide a force that drops off with r⁻². When these become
dipoles or quadropoles (for the case of π-acceptors or donors) the force can then be shown to
drop off with a separation distance of r⁻⁵. Other combinations of monopoles, dipoles, and
quadropoles can provide forces that depend on a separation of r⁻³ or r⁻⁴. This is in contrast with
straight van der Waals dispersion forces, which weaken with a separation dependence of r⁻⁶. The
longer range of influence of H-bonds means that they are both discernable from pure dispersion,
and also that they can be useful, and are shown to be useful in both supramolecular chemistry
and biological applications. [17]
A.6.1.1 Strong H-Bonds

For strong hydrogen bonds, D and A are highly electronegative non-metals, such as N, O, or F. Because the positively charged H atom in the H-bond can act as a shield between the negatively charged D and A atoms, H-bonds in practice tend towards a linear geometry; that is, strong H-bonds in crystal structures have a D-H…A angle of close to 180°. In the solid state, there are other intermolecular interactions arranging crystal structures, and often these additional forces bend the hydrogen bonds away from the ideal 180° making the typical angle being between 130-180° with the median H-bond angle closer to 165°. Typical lengths of strong H-bonds are nearly always shorter than the sum of the van der Waals radii of the donor and acceptor atoms. A summary of these interactions is given in Table A.1. Strong H-bonds are usually those classified as possessing strength between 4-40 Kcal/mol, [17] however this varies depending on the interaction distance as well as the D-H…A angle, with closer and more linear H-bonds possessing higher strengths.

Table A.1: Summary of the properties of hydrogen bonds, ranging from very strong through to weak. Reproduced from [17].

<table>
<thead>
<tr>
<th></th>
<th>Very strong</th>
<th>Strong</th>
<th>Weak</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond energy (±kcal/mol)</td>
<td>15–40</td>
<td>4–15</td>
<td>&lt;4</td>
</tr>
<tr>
<td>Examples</td>
<td>[F⋯H⋯F]⁺</td>
<td>O−H⋯O=C</td>
<td>C−H⋯O</td>
</tr>
<tr>
<td></td>
<td>[N⋯H⋯N]⁺</td>
<td>N−H⋯O=C</td>
<td>O−H⋯π</td>
</tr>
<tr>
<td></td>
<td>P−OH⋯O=P</td>
<td>O−H⋯O−H</td>
<td>Os−H⋯O</td>
</tr>
<tr>
<td>IR ν, relative shift</td>
<td>&gt;25%</td>
<td>5–25%</td>
<td>&lt;5%</td>
</tr>
<tr>
<td>Bond lengths</td>
<td>H−A ≈ X−H</td>
<td>H⋯A &gt; X−H</td>
<td>H⋯A &gt;&gt; X−H</td>
</tr>
<tr>
<td>Lengthening of X−H (Å)</td>
<td>0.05–0.2</td>
<td>0.01–0.05</td>
<td>≤0.01</td>
</tr>
<tr>
<td>D(X⋯A) range (Å)</td>
<td>2.2–2.5</td>
<td>2.5–3.2</td>
<td>3.0–4.0</td>
</tr>
<tr>
<td>d(H⋯A) range (Å)</td>
<td>1.2–1.5</td>
<td>1.5–2.2</td>
<td>2.0–3.0</td>
</tr>
<tr>
<td>Bonds shorter than vdW</td>
<td>100%</td>
<td>Almost 100%</td>
<td>30–80%</td>
</tr>
<tr>
<td>θ(X−H⋯A) range (°)</td>
<td>175–180</td>
<td>130–180</td>
<td>90–180</td>
</tr>
<tr>
<td>kT (at room temperature)</td>
<td>&gt;25</td>
<td>7–25</td>
<td>&lt;7</td>
</tr>
<tr>
<td>Effect on crystal packing</td>
<td>Strong</td>
<td>Distinctive</td>
<td>Variable</td>
</tr>
<tr>
<td>Utility in crystal engineering</td>
<td>Unknown</td>
<td>Useful</td>
<td>Partly useful</td>
</tr>
<tr>
<td>Covalency</td>
<td>Pronounced</td>
<td>Weak</td>
<td>Vanishing</td>
</tr>
<tr>
<td>Electrostatics</td>
<td>Significant</td>
<td>Dominant</td>
<td>Moderate</td>
</tr>
</tbody>
</table>
A.6.1.2 Weak H-Bonds

Weak H-bonds, while similar in nature to their strong counterparts, have one of the D and A atoms less electronegative in nature. This causes a weakened polarity in the D-H or H…A interactions, decreasing the interaction strength of the entire unit. Typical examples of weak H-bonds include C-H…O, O-H…π, N-H…π, and the weakest example, C-H…π. The π-electrons refer to a carbon atom involved in a C=C or C≡C bond, with the latter triple bond providing a stronger interaction than the weaker double bond. These bonds possess strengths less than 4 kcal/mol. [17] Similar to the strong H-bonds, a linear preference is seen in these bonds, but since they are weaker in nature, the angle of interaction can be more easily perturbed. For this reason it is not uncommon to find these kinds of H-bonds forming interactions at D-H…A angles of between 90°-180°. [17] Table A.2 summarizes the observed and functional differences between the strong and weak H-bonds.

A.6.2 Halogen-bonding

It is known that halogen atoms can be involved in weak intermolecular interactions in a number of ways. These bonds are typically seen as interaction between two halogen atoms in a C-X…X-C motif. However, more recently this definition has been replaced by the more inclusive C-X…Y, where X is a halogen atom and Y is an electron rich atom acting as the halogen bond donor. In this definition Y can be any atom with lone pairs, such as X, O, or N, but it can also be the π-electrons of a carbon atom. Halogen-containing interactions are generally at interaction distances well below the sum of their van der Waals radii, on average π-electrons as a donor will form a halogen bond 0.3 Å less than the vdW radii, while n-type donors (e.g. N, O) will form interactions of distances 0.8 Å shorter. A range of interactions strengths are found for halogen bonds, but usually lie between 2 and 6 Kcal/mol. Similarly to the H-bonds, halogen bonds have an angular dependence, but for halogen bonds it is linear with respect to the symmetry of the π-electrons or lone pairs of the donor atom. [18]

A.6.3 Aromatic interactions

One of the most important types of intermolecular interactions for organic crystals that possess aromatic rings is π-electron containing interactions. The most well-known aromatic interaction is between two ring systems aligned in parallel planes with typical centroid to centroid (Cg-Cg)
distances of less than 4.0 Å. These interactions are commonly referred to as π-stacking or π-π interactions. While there has been discussion over the last few decades of the nature of these interactions, whether they are a specific aromatic-aromatic interaction or just a byproduct of close packing and electrostatics, [19] or whether they are mostly defined by the substituent groups on the aromatic rings, [20] it is now accepted that these interactions are important in a variety of situations both in crystal engineering [21-24] and nature [25]. It has also been shown that for aromatic systems larger than two single benzene rings, i.e. fused ring systems such as naphthalene, the π-stacking interaction increases in strength. [26]

Figure A.4: Electrostatic potential computer using Hartree-Fock and 6-31G* basis set of benzene. Red is low electrostatic potential and blue is high electrostatic potential. Adapted from [20].

Figure A.5: π-stacking configurations of benzene dimers. (a) Offset stack configuration, (b) face-to-face stacking, and (c) edge-on-face configuration. Adapted from [27].
The \( \pi \)-stacking interaction exists mainly due to the electrostatic potential surface of aromatic rings systems, which possess \( \pi \)-electrons situated above the atoms creating a relatively negative electrostatic charge directly above the atoms in the ring, and leave a relatively positive electrostatic potential in the centre of the ring. This is shown in Fig A.4. From this charge distribution there are three different \( \pi \)-stacking motifs possible, depending on the angle of interaction and the offset of the ring systems. [27] Of the three, the most common seen is the offset-stack, an example of which is shown in Fig. A.5a. In the offset stack, the two rings are on parallel planes, and the carbon atoms in the ring do not align but the Cg-Cg distance is between 3.4 Å and 4.0 Å. The second and least energetically favourable of the systems is the true stacking motif face-to-face stacking, in which the two ring systems lie on parallel planes, but the carbon atoms align perpendicularly to those planes. An example is shown in Fig. A.5b. The third possible interaction is two rings lying on non-parallel planes, with the edge of one aligned with the face of the other and is aptly called edge-on-face. While there is in silico evidence that for simple benzene dimers this conformation is energetically equal to the offset stack interaction, [27] this interaction is not a true \( \pi \)-stacking interaction and would now be considered a weak C-H...\( \pi \) H-bond as discussed above. A schematic of this is shown in Fig. A.5c.

A.7 References


Appendix B

Supplementary Characterization of Pseudohalide Compounds

In Chapter 6, sulfonate pseudohalide derivatives of boronsubphthalocyanines are synthesized and characterized. In this Appendix, further characterization not directly relevant to the discussion in Chapter 6 is presented.

B Characterization of Pseudohalide Compounds

B.1 Spectral Characterization

B.1.1 NMR Spectra

Figure B.1: ¹H NMR spectrum of pyridinium 4-chlorobenzenesulfonate.
Figure B.2: $^{13}$C NMR spectrum of pyridinium 4-chlorobenzenesulfonate.

Figure B.3: $^1$H NMR spectrum of compound 3a (TsO-BsubPc).
Figure B.4: $^{13}$C NMR spectrum of compound 3a (TsO-BsubPc).

Figure B.5: $^1$H NMR spectrum of compound 3b (MsO-BsubPc).
Figure B.6: $^{13}$C NMR spectrum of compound 3b (MsO-BsubPc).

Figure B.7: $^1$H NMR spectrum of compound 3c (BsO-BsubPc).
Figure B.8: $^{13}$C NMR spectrum of compound 3c (BsO-BsubPc).

Figure B.9: $^1$H NMR spectrum of compound 3d (ClSO-BsubPc).
Figure B.10: $^{13}$C NMR of compound 3d (ClsO-BsubPc).

Figure B.11: $^1$H NMR spectrum of compound 3e (NsO-BsubPc).
Figure B.12: $^{13}$C NMR spectrum of compound 3e (NsO-BsubPc).

B.1.2 Cyclic Voltammograms

All CV performed in dichloromethane solvent, with decamethylferrocene as the reference compound. The working electrode was a platinum disc electrode, and the reference electrode was Ag/AgCl. Reported in the following charts are the 2nd scans.

Figure B.13: Cyclic Voltammagram of compound 3a (TsO-BsubPc).
Figure B.14: Cyclic Voltammagram of compound 3b (MsO-B\textsubscript{sub}Pc).

Figure B.15: Cyclic Voltammagram of compound 3c (BsO-B\textsubscript{sub}Pc).
Figure B.16: Cyclic Voltammogram of compound 3d (ClsO-BsubPc).

Figure B.17: Cyclic Voltammogram of compound 3e (NsO-BsubPc).
B.1.3 Absorption and Fluorescence Spectra

Figure B.18: Normalized absorption and photoluminescence spectra of compound 3a (TsO-BsubPc) in toluene.

Figure B.19: Normalized absorption and photoluminescence spectra of compound 3b (MsO-BsubPc) in toluene.
Figure B.20: Normalized absorption and photoluminescence spectra of compound 3c (BsO-BsubPc) in toluene.

Figure B.21: Normalized absorption and photoluminescence spectra of compound 3d (ClsO-BsubPc) in toluene.
Figure B.22: Normalized absorption and photoluminescence spectra of compound 3e (NsO-BsubPc) in toluene.

B.2 Detailed Reaction Kinetics of Pseudohalide Compounds

Figure B.23: First 10 hours of reactions of Br-BsubPc, Cl-BsubPc, and the pseudohalides (3a-e) under (a) phenoxylation at 100 °C to give phenoxy-BsubPc.