Development of Synthetic Processes and Characterization of BsubPcs with High Crystal Densities for Application in Organic Photovoltaic Devices

by

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A thesis submitted in conformity with the requirements for the degree of Master of Applied Science
Chemical Engineering and Applied Chemistry
University of Toronto

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Abstract

The original goal of this thesis was to develop process chemistry to yield boron subphthalocyanine (BsubPc) derivatives which were previously difficult to access. Retrospectively, it was found that these compounds show extremely high density crystal packing in comparison to other known BsubPcs, and thus this also became a focus of the thesis. A process to synthesize and purify fluoro-BsubPc was developed. This led to a detailed comparison of the physical and chemical properties of the three halo-BsubPcs in order to answer the question of which halo-BsubPc is appropriate for different purposes. Through this work, the previously unpublished crystal structure of the oxygen bridged dimer, µ-oxo-BsubPc, was found. A process was subsequently developed for the practical synthesis of µ-oxo-BsubPc for use in vacuum deposition and a number of µ-oxo-BsubPc crystal polymorphs were found and analyzed. The properties of this group of compounds are discussed in the context of other known BsubPcs.
Acknowledgments

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Chapter 1

1 Introduction

1.1 Organic Solar Cells and Organic Electronics

Organic solar cells (OSC) offer the potential for low cost, large scale manufacture of flexible, lightweight solar photovoltaic (PV) panels. The materials used are abundant and the cells can be manufactured in efficient, low-energy intensive processes, eliminating two major problems of traditional silicon based PV cells.

Another major advantage OSCs have over silicon is the ability to use organic chemistry to design and optimize component materials to fit the desired purpose, such as the ability to match the absorption band of a material to the solar spectrum, just as plants do. Currently a challenge is to find a molecule that absorbs light strongly in the most intense region of the solar spectrum whilst maintaining good electronic properties. One promising such molecule is boron subphthalocyanine (BsubPc), a $14\pi$ electron macrocycle with three N-fused diiminoisindole units.

Design of new organic solar cell devices requires a good understanding of what factors affect device performance, and how these can be used to select appropriate materials for each role in a device. The two major criteria to consider in selecting a material are performance – the matching of photophysical and electronic characteristics to desired purpose; and process – the ease, cost and reliability of the fabrication of devices or synthesis of active materials. The ultimate purpose of materials research in this field is to both create functional organic electronic compounds and to describe all properties relevant to their performance against the aforementioned criteria, to enable fabricators of organic solar cells to select the best suited material for their purpose.

1.1.1 Device Architectures

The simplest possible organic solar cell (OSC) structure consists of a single material in an active layer sandwiched between two electrodes. The active layer absorbs sunlight and generates charge carriers. Holes travel to the cathode, and electrons to the anode. While in inorganic solar cells holes and electrons are generated in the bulk of the material, the defining characteristic of
OSC is that an absorbed photon generates a hole and an electron tightly bound to one another in an exciton, which can only dissociate at an interface (in this case, the electrodes). Since power conversion is limited by the number of excitons that reach an interface before recombining, it is advantageous to have an interface in the bulk of the active layer to provide a location where charge carriers can be separated.\(^{(1)}\) This is achieved in one of two major designs, each using a donor and acceptor material. The first involves a planar interface, shown in Figure 1.1a, in which the two are deposited in sequential layers. The second is a bulk heterojunction, shown in Figure 1.1b, which has a bicontinuous blend of the donor and acceptor phases. This aims to maximise interfacial surface area (where dissociation can occur) whilst providing a continuous path for charge carrier transport to the electrodes.

![Figure 1.1. Graphic representation of two OSC device structures, showing exciton diffusion towards, and charge carrier dissociation at, donor-acceptor interface.](image)

Either the acceptor or the donor (or both) can act as the active layer absorbing photons and generating excitons, which must diffuse to the interface before recombining to contribute to device current. The acceptor transports holes and the donor transports electrons away from the interface. Exciton diffusion length is small, on the order of 10nm, but an active layer thickness of ca. 0.2µm is required for efficient photon absorption.\(^{(2)}\) The bulk heterojunction structure resolves these two competing length scales and represents the most promising device structure for application, while planar heterojunction devices remain the most convenient structure with which to study material fundamentals.\(^{(2)}\) Various adaptations of these two structures have been fabricated to compensate for their limitations. For example, tandem organic cells use multiple
acceptor-donor pairs stacked one above the other so that the combination of materials absorbs a wider section of the solar spectrum and therefore uses a higher proportion of the incident photons. Ordered bulk heterojunction structures offer the same advantages of high interfacial area as bulk heterojunctions, but with the benefits of ordered planar heterojunctions such as avoiding cul-de-sac or bottleneck creation, excellent reproducibility and the ability to geometrically optimize and control morphology.

1.1.2 Organic Electronic Material Properties

Many properties of a material play a key role in determining its performance in an OSC, including absorption coefficient, band gap, highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels, photoluminescent quantum efficiency, solid state arrangement and charge carrier mobility. This can be illustrated by following the conversion process from sunlight to the flow of charges out of the electrodes. The initial step in this chain is absorption of incident light – the absorption spectrum of a material determines which photons from the solar spectrum can be absorbed, and the extinction coefficient describes how many. Analogous to inorganic semiconductors, the band gap in organic semiconductors is the energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) (equivalent to semiconductors’ valence and conduction bands, respectively). Only photons with equal or greater energy as the material’s band gap can be absorbed and lead to generation of an exciton. The excess energy over the band gap in higher energy photons is dissipated as thermal losses, representing a fundamental efficiency limit.

The following step is exciton creation and diffusion, and these excitons must reach a donor-acceptor interface before recombination to contribute to power conversion. The fluorescence behavior of a material can offer insight into its energy transfer processes. The fluorescence spectrum defines the colour of light emitted by the compound and so is clearly relevant to selection of materials for application in organic light emitting diodes (OLEDs), a device which at a basic level is equivalent to an OPV in reverse. However, fluorescence can also represent an efficient energy transfer pathway within the material, contributing to exciton diffusion in OSCs. When energy from an absorbed photon is re-emitted by a molecule at a different (longer) wavelength, this can then be absorbed by a molecule elsewhere in the film, representing a long-distance energy transfer mechanism. The efficiency of this energy transfer process can be
quantified by the fluorescent or photoluminescent quantum efficiency. The Stokes’ shift is another useful parameter indicating the increase in wavelength from the absorption to the emission peak (representing energy lost in the conversion).

At the interface where charge separation occurs, the maximum open circuit voltage, $V_{oc}$, of a cell is related to the offset of the donor HOMO and acceptor LUMO, and energy level matching is key to achieving good device performance. Additionally, it is thought that the degree or absence of similarities in solid state arrangement or packing of the materials plays a significant role in interface effects such as charge recombination. Once charges are separated they must be transported to the electrodes. The range of charge carrier mobility in organic semiconductors is extremely broad ($10^{-6} – 10^{0} \text{ cm}^{2} \text{ V}^{-1} \text{ s}^{-1}$) but even the highest organic mobilities are typically many orders of magnitude below those of inorganic semiconductors ($10^{2} – 10^{3} \text{ cm}^{2} \text{ V}^{-1} \text{ s}^{-1}$), and hence charge carrier mobility is of major importance in material selection and design in OSCs. Charge carrier mobility is strongly related to the solid state arrangement of a material. Highly ordered crystals with short intermolecular distances, $\pi$-stacking interactions and overlap of orbitals have been found to lead to higher mobilities. Analysis of the crystal structure becomes a source for both predicting what compounds have the potential for high mobility and are of further interest, and, in combination with mobility measurements, for elucidating the relationship between form and function to help guide future research.

1.1.3 Device Fabrication

There are two main approaches to make thin film OSC devices: one is solution processing and the second is vacuum deposition. In solution processing methods the active materials are dissolved in a solvent which is subsequently removed, leaving behind the solid materials in the designed format. These include coating techniques, such as spincoating, and printing techniques, such as screen printing and inkjet printing. Polymer materials are typically solution-processed, and a great deal of research exists on optimization of physical properties and process conditions to obtain desired film morphologies and structures. The low solubility of small molecules typically renders solution processing impractical, so derivatives with increased solubility are of interest to explore the potential of this technique and show great promise. Vacuum sublimation is often preferred for small molecules because it is a powerful research tool – the process is controlled, repeatable and well understood. Vacuum deposition is carried out inside a chamber at low pressure with the desired component material held in a crucible and heated to
sublimation temperature. The OSC substrate is cooled to slightly below this temperature, so the sublimed material deposits in a thin film on the surface. This is repeated for a series of compounds, creating a structure with multiple layers. This technique has also been adapted to fabricate bulk heterojunction architectures. Both methods are compatible with high-throughput, low cost roll-to-roll manufacturing techniques.

1.2 Boron Subphthalocyanine (BsubPc)

Chloro-boronsubphthalocyanine (Cl-BsubPc) was first synthesized in 1972 and its crystal structure determined in 1974. Cl-BsubPc still represents the prototypical derivative of the broader class of boron subphthalocyanines (BsubPcs). BsubPcs are comprised of a 14 π electron macrocyclic ring consisting of three N-fused diiminoisoindole units around a tetracoordinated boron atom core. The subPc ligand coordinates in three positions, while the chloride (in Cl-BsubPc) occupies the fourth position (referred to as the axial position, Figure 1.2). BsubPc has C3v symmetry, with three distinct ring systems: a 6 membered carbon ring (R6), a 6 membered heteroatom ring (R6h), and a 5 membered ring (R5).

The axial chloride is labile on reaction with phenols and water. The unique non-planar bowl-shape of all BsubPc derivatives confers interesting properties compared to their higher analogs, the so-called normal phthalocyanine (which has four diiminoisoindole units). Both are members of the porphyrinoid family, the building blocks of photosynthetic systems, and absorb light with high extinction coefficients (ε > 50,000 L mol⁻¹ cm⁻¹) in the ultraviolet and visible portions of the electromagnetic spectrum. The maximum absorption of BsubPcs falls close to maximum solar irradiance, making it an attractive molecule for application in organic solar photovoltaics. The absorption of Cl-BsubPc is shown superimposed on solar irradiance in Figure 1.3. All known BsubPcs have a very similar absorption maximum with the exception of...
the oxygen-bridged dimer, $\mu$-oxo BsubPc, which is blue-shifted by approximately 30nm. As can be seen in Figure 1.3, the absorption of $\mu$-oxo BsubPc falls even closer to the solar maximum.

Figure 1.3. Standard AM 1.5 extraterrestrial, direct normal and global total solar spectral irradiance,\(^{(20)}\) plotted with the normalized absorption of Cl-BsubPc and $\mu$-oxo BsubPc.

Recently, research targeting organic electronic devices has triggered renewed interest in BsubPcs as functional organic molecules.\(^{(23)}\)–\(^{(24)}\),\(^{(26)}\)–\(^{(49)}\) As organic electronic materials, BsubPcs have been successfully incorporated into organic photovoltaic cells (OPVs)\(^{(29)}\),\(^{(30)}\) where the energy levels of the frontier molecular orbitals of BsubPc are a better match than normal phthalocyanine with commonly used OPV materials such as C\(_{60}\), resulting in better device performance\(^{(31)}\). They also have applications in other areas of organic electronics, such as organic light emitting diodes (OLEDs)\(^{(32)}\)–\(^{(37)}\) and field effect transistors.\(^{(38)}\) Crucially, BsubPcs are stable under typical process conditions\(^{(39)}\). BsubPcs are also very functionalizable: it has been found that different axial groups can vary BsubPc’s solubility\(^{(27)}\),\(^{(40)}\),\(^{(41)}\) and alter its solid state arrangement\(^{(42)}\) without changing the inherent electronic and physical properties.\(^{(34)}\),\(^{(43)}\)–\(^{(45)}\). Changes at the molecule’s peripheral positions can change the electronic characteristics such as electron accepting or donating behavior.\(^{(46)}\) These two ‘handles’ have been used to obtain BsubPc derivatives with an extensive range of physical, chemical and electronic properties.\(^{(23)}\)\(^{(33)}\)\(^{(43)}\)\(^{(47)}\)

1.2.1 Solid State Arrangement of BsubPcs

Analysis of the crystal structure of an organic electronic compound can provide information on the existence, direction and distance of intermolecular interactions. Examining the motif formed
by these interactions in three dimensions can identify whether pathways exist for charge transport throughout the material. For example, planar aromatic molecules, or units within a molecule, form cofacial π-stacking due to the interaction of π-orbitals on adjacent molecules, providing a pathway for intermolecular charge transport.\(^\text{(6)}\) However, the non-planar molecular shape of BsubPc introduces complex intermolecular packing arrangements and motifs in three dimensions (3D).

In order to describe common BsubPc packing motifs, the BsubPc ‘bowl’ is differentiated from the attached axial ‘ligand’, and the two faces of the bowl are described as ‘convex’ (outward facing, attached to axial ligand) and ‘concave’ (inward facing). A 2010 review of BsubPc crystal structures contained in the Cambridge Crystallographic Database identified two types of packing motifs.\(^\text{(34)}\) The first, observed in perhydrogenated BsubPcs, is characterized by bowl-bowl interactions between adjacent BsubPc molecules (concave-concave or convex-convex). The second, in perfluorinated BsubPc derivatives, instead exhibits bowl-to-ligand interactions (concave-ligand). Bowl-bowl interactions typically result in intermolecular dimer pairs isolated from one another in 3D, whereas bowl-ligand interactions create one dimensional (1D) chains or columns of BsubPcs.

A subsequent review of the literature in 2011 confirmed that all observed BsubPc crystal structures belong to one of these two categories, but identified another possible motif formed by concave-concave interactions.\(^\text{(50)}\) In this motif each BsubPc interacts with the bowls of two adjacent BsubPc molecules, one on either side (ie bowl\(_a\)-bowl\(_b\), bowl\(_a\)-bowl\(_c\)), which creates a 1D ribbon of adjacent interacting BsubPcs. The para-halo-phenoxy-BsubPcs investigated within this study exhibited the typical concave-concave dimer motif, however a second, kinetically-favoured polymorph of 4-BrPhO-BsubPc was also identified which exhibits a new form of crystal packing directed by π-Br interactions. In this structure, Br–concave interactions between adjacent molecules create 1D chains as in the common ligand-bowl motif, and additionally convex-convex interactions are present between adjacent chains providing interactions in a second dimension.

Recently, it was found that phthalimido-BsubPc (Phth-BsubPc) forms a novel variant of these typical crystal packing motifs more similar to those found in molecular dyads of BsubPc with conjugated axial ligands.\(^\text{(32)}\) In this case, the same concave-concave interactions forming the base of the dimer motif are present. However, the axial ligands also form π–π interactions with
one another, thus linking the dimers together and forming 1D chains of extended $\pi$ stacking in a bowl-to-bowl, ligand-to-ligand arrangement (ie Phth-BsubPc…BsubPc-Phth…Phth-BsubPc).

The paper also found that Cl$_4$Phth-BsubPc crystals exhibit ligand–bowl interactions resulting in the typical aforementioned 1D columns, but in this case HOMO and LUMO electron density is found on the axial group as well as the BsubPc and thus this motif also implies orbital overlap.

1.2.2 The Halo-BsubPcs

The vast majority of the BsubPc research described above uses Cl-BsubPc as a starting material, whereby a substitution reaction is carried out to replace the labile chloride with another molecular fragment and thereby obtain the desired compound.$^{(28)}$ It has been claimed that Cl-BsubPc is the most practical halo-BsubPc, representing a middle ground of ease of synthesis, stability and availability.$^{(48)}$ However, up until now there has been no comprehensive comparison between the other halogen derivatives (F-BsubPc and Br-BsubPc). Swapping of the axial halogen may provide for the simplest of ‘handles’ to tailor the physical properties without introducing atom expensive substituents. A systematic description of the halo-BsubPcs and quantification of the similarities and differences amongst them would thus be beneficial to subsequent research efforts, to guide selection of compounds and synthetic pathways according to the desired application or chemical derivative.

An optimized synthesis of Cl-BsubPc is available in the literature$^{(49)}$ and has proven reliable and consistent.$^{(34)}$ A process to synthesize Br-BsubPc with reasonable yield and high purity has been previously developed in this research group.$^{(51)}$ However, no comparable synthesis method exists for F-BsubPc. There are several reasons why F-BsubPc is a compound of interest. Fluorine is the most electronegative element and fluorine bonds are typically extremely stable, leading to the expectation that F-BsubPc may be less reactive than Cl- or Br-BsubPc and less likely to undergo hydrolysis or other degradation. Long term stability under a variety of conditions is essential for practical application of a material in devices. Fluorine substituents reduce the sublimation temperature of BsubPcs, as well as increasing the solubility. Both of these would be beneficial in the context of device fabrication, reducing energy requirements for vacuum deposition and making solution processing possible respectively. The crystal structures of Cl- and Br-BsubPc have higher densities of light-absorbing chromophores than any other BsubPc for which the crystal structure has been determined. This is due to the small size of the axial substituent – similar packing distances are observed as the solid state arrangement of other
BsubPcs, but the halogen atoms do not act as ‘spacers’ which spread out the BsubPc moieties as bulkier axial substituents do. Since fluorine has an even smaller atomic radius than chlorine and bromine, it is expected this trend of high crystal density would continue with F-BsubPc. It is not yet known precisely how high density of chromophores in the crystal translates into properties and performance of a thin film in a device, such as a potential increase in charge carrier mobility. Representing the high extreme of the density spectrum, the halo-BsubPcs are a useful class of compounds through which to study this relationship. With potentially the highest density within this group and thus of any currently known BsubPc crystal, the solid state arrangement of F-BsubPc is of great interest in this context.

Two methods of synthesizing F-BsubPc have been reported in the literature. The first, reported by Potz et al.,\(^{(24)}\) employs a similar approach to that used in the synthesis of Cl- and Br-BsubPc by combining a boron trihalide with phthalonitrile. High-boiling quinoline was used as the solvent and heated to reflux (237 °C). After cooling, bronze-coloured crystals were filtered off and purified by vacuum sublimation. A mass yield was not provided. The second method was reported by Rodríguez-Morgade et al.\(^{(48)}\) and employed a different reaction mechanism. Previously synthesized Cl-BsubPc was used as the starting reagent for a halide exchange reaction with 25 molar equivalents of boron trifluoride. Following the reaction, the solvent was removed by rotary evaporation and the crude products separated on silica gel. A 17% yield of F-BsubPc was realized, which is poor in comparison to the synthesis of Cl-BsubPc (60-70\(^{\%}\)\(^{(34)}\)) and Br-BsubPc (71\(^{\%}\)\(^{(51)}\)). The authors qualitatively observed that the B-F bond was more stable to hydrolysis than B-Cl and B-Br due to the absence of HO-BsubPc as a reaction byproduct, and this was reinforced by mass spectrometry results which showed [M]\(^{\circ}\) as the main peak rather than [M-F]\(^{\circ}\). This confirms that the characteristics of F-BsubPc are distinct from Br-BsubPc and Cl-BsubPc in at least this respect, which is of importance in the selection of stable compounds for use as organic electronic materials.

1.2.3 \(\mu\)-oxo BsubPc

Despite the first description of Cl-BsubPc dating to 1972\(^{(1)}\) and the recent renewed interest in BsubPc molecules, literature references and the associated preparatory methods for the oxygen bridged boron subphthalocyanine dimer (\(\mu\)-oxo-(BsubPc)\(_2\)) or \(\mu\)-oxo BsubPc, Figure 1.4) are scarce. First described in a review, \(\mu\)-oxo-(BsubPc)\(_2\) was obtained (in a 10 mg/7.6\(^{\%}\) yield) by reacting Cl-BsubPc with NaOH in refluxing xylene in the presence of dicyclohexano-18-crown-
6. Since then a single US patent application outlines several other methods for the direct synthesis of \( \mu \)-oxo-(BsubPc)\(_2\). Thereafter, \( \mu \)-oxo-(BsubPc)\(_2\) has been observed as a byproduct of other chemical processes and reactions. It can easily be identified within a chemical mixture or as an isolated byproduct based on its unique spectroscopic properties. The novelty of \( \mu \)-oxo-(BsubPc)\(_2\) compared to other BsubPc derivatives is in its spectroscopic behaviour. Differences are seen in both the \(^1\)H NMR spectrum as well as the optical absorption spectrum where the intensities of the Q and D bands are changed relative to one another and relative to normal BsubPc derivatives. As depicted above in Figure 1.3, its absorption spectrum matches maximum solar irradiance even more closely than Cl-BsubPc and the family of non dimerized BsubPcs.

Figure 1.4. (a) Molecular structure of \( \mu \)-oxo BsubPc; and (b) view of \( \mu \)-oxo BsubPc in 3-dimensions, with shading showing regions above and below the plane of the page.

However, due to its significant molecular size it may be presumed that \( \mu \)-oxo BsubPc is not mobile under sublimation conditions, which is a major barrier to incorporating it into OSC devices by vacuum deposition, the most common technique used for BsubPcs. Equally, its solubility is assumed to be extremely low, since dimerization of a dye reduces solubility and the solubility of BsubPcs is already limited. This eliminates the possibility of device fabrication by solution processing. Therefore, despite its unique and attractive spectroscopic properties, these presumed physical properties would prohibit its use as a functional material in a device due to the extreme difficulty of fabrication. However, early in this thesis research, single crystals of \( \mu \)-oxo BsubPc were discovered following train sublimation of Br-BsubPc. The crystals were hemi-hydrated, and the solid state arrangement was unlike any previously seen BsubPc motif with an extremely high crystal density, exceeding even the density in halo-BsubPcs. Added to its shifted absorption spectrum, this makes \( \mu \)-oxo BsubPc an ideal candidate material for OSC application. Additionally, its formation under sublimation conditions suggested that even if
traditional vacuum deposition was not possible, a novel methodology could be developed. Subsequently, it was established that μ-oxo BsubPc is both mobile under typical sublimation conditions and that it is highly soluble, indicating that in fact it is versatile in the context of device fabrication. Therefore, there is a strong motivation to develop a process that enables the synthesis of μ-oxo BsubPc in sufficient quantities and at sufficient purity to enable the study of its properties as a functional organic electronic layer within devices.

1.2.4 BsubPc Chemistry Toolkit

In the pursuit of new process chemistries for BsubPc synthesis, a number of tools are available which have been developed through accumulated experience of BsubPc chemistry. Synthesis of BsubPc compounds typically begins with the cyclotrimerization of a phthalonitrile with a boron trihalide. Hydrogenated phthalonitrile results in the BsubPc with no peripheral substitution, or a phthalonitrile with appropriate substituent groups (perfluorinated or tert butylated, for example) can be used to generate the corresponding peripherally substituted BsubPc. If the halo-BsubPc is not the desired product, this is typically followed by a substitution reaction to replace the halogen with a desired axial group. For some chemistries, this can be done by adding the axial ligand in excess and running the reaction at elevated temperature, such as in the synthesis of phenoxyalted BsubPcs. Recently, new chemistry has been developed that uses Lewis acids as catalysts for BsubPc axial substitution reactions. This has enabled chemistry that was previously thought inaccessible, such as the synthesis of the \( p \)-thiocresol, aniline and N-methylaniline substituted BsubPcs. It also enables reactions to proceed under milder conditions – phenoxylation can even proceed at room temperature under these conditions in 6-8h, whereas without AlCl\(_3\) a temperature of 111 °C is required for conversion in 16h.

Reaction progress is typically monitored by high-performance liquid chromatography (HPLC). HPLC is also used to analyse the solid products of reactions and separation steps. This laboratory uses a reversed phase column and the mobile phase is acetonitrile (ACN). A detector measures the ultraviolet and visible (UV-vis) light absorption of the eluent which generates 3D data, collecting a 2D absorption spectrum for each point in time reflecting the composition of the mobile phase. A 2D plot against time of the total integrated absorption (across all wavelengths; MAXPlot channel) reveals peaks for all sample components that absorb UV-vis light, including non-BsubPc small molecules and solvents. Plotting the absorption at just one wavelength (\( x \) nm channel) is often more meaningful, isolating only the compounds that absorb at that wavelength.
The characteristic absorption of BsubPcs means that channels between 500 and 600 nm typically detect only the BsubPc components in the sample. Since the molar extinction coefficients of BsubPcs are similar to one another, the percent area of each peak is approximately equivalent to their relative molar quantities. HPLC samples must be prepared in the same solvent as the mobile phase, so the low solubility of BsubPc in ACN is a limitation. Dimethylformamide (DMF) is a better solvent for BsubPcs, so an alternative method using an 80%:20% mix of ACN:DMF (80/20 method) was developed in our laboratory which increases the solubility of BsubPcs in the sample. However, this method cannot separate BsubPcs as effectively. HPLC also cannot detect other insoluble compounds, or compounds that do not absorb UV-vis light.

The low solubility of BsubPcs also affects what separation techniques can be used following a reaction to recover the desired product. The two most common techniques are Soxhlet extraction and Kauffman column chromatography\(^{(34),(57)}\). Both utilize the evaporation/condensation cycle of a continuously refluxing solvent so that the crude product is exposed to a continuous supply of fresh solvent, with each cycle incrementally dissolving more product without requiring prohibitively large volumes of solvent. A Soxhlet extraction is useful if the desired compound is somewhat soluble in a solvent while undesired components of the mixture are insoluble (or vice versa). A cellulose thimble containing the solids is gradually filled with condensing solvent after the flask below is heated to boiling. Once a critical liquid level is reached, the liquid drains through a siphon arm into the flask below which collects the extracted compounds. The solvent continues to evaporate from the refluxing flask, and the cycle is repeated in the apparatus as shown in Figure 1.5a. This allows an infinite number of extractions using a small defined quantity of recycled solvent. Since BsubPcs strongly absorb visible light, extractions of BsubPc can be stopped when the solvent extract is clear. In Kauffman chromatography, a column containing an adsorbent (silica or alumina) is suspended inside an outer tube, as is depicted in Figure 1.5b. Solvent is boiled in a flask underneath and fills the outer chamber. The inner column has two openings near the top to allow vaporized solvent to enter, which then condenses and drips down into the column. The solvent initially wets the solid adsorbent from the top down, and once the column is full the solvent elutes from the bottom of the column and drips into the flask below.
Finally, train sublimation is often used to obtain single crystals of BsubPc and can also be used as a separation technique. BsubPc is placed in a crucible in the heating zone of a sublimation tube. A cold finger at the opposite end of the tube creates a temperature gradient. A pump puts the tube under vacuum, and the temperature is slowly increased to 220 °C and held for an hour. At this temperature, small molecule impurities sublime out of the crucible and travel down the tube. The temperature is then incrementally increased until a faint pink film is observed, indicating the sublimation of BsubPc. If crystals are the intended product, this temperature is held constant for an hour to encourage formation of seed crystals. The temperature is incrementally increased by a further ca. 100 °C to achieve a reasonable rate of sublimation, and this temperature is held for 2 – 6 hours to allow full sublimation of BsubPc from the boat. The compounds form bands on the sublimation tube at different distances from the crucible according to their sublimation point due to the temperature gradient – small molecule impurities are found at the far end of the tube, and BsubPc compounds with lower sublimation points are found further from the heating zone than BsubPcs with high sublimation points. The apparatus set up and resulting BsubPc deposition profile are shown in Figure 1.5c. However, the differences between BsubPcs are not typically sufficient for them to form discrete bands. As a separation technique, it is most useful for removal of small molecules (or very large molecules which remain in the crucible) and for preparation of BsubPc samples of sufficient purity for vacuum deposition.
1.3 Thesis Statement

The goals of research into organic electronic materials as described in the introduction are twofold: synthesis of novel and high-performing compounds, and characterization of these compounds to enable selection of the most appropriate material for a given purpose. This is especially important given the breadth of applications of organic electronic materials, with several types of devices and multiple components within each device architecture each fulfilling a specific purpose. The current state of research into halo-BsubPc and \( \mu \)-oxo BsubPc compounds is incomplete in each of these key elements. Two of the three halo-BsubPcs can be and are regularly synthesized, while synthesis of F-BsubPc remains challenging. In addition, data that fully characterizes the suitability of all three for application as organic electronic materials or as chemical precursors in the synthesis of other materials is lacking. While spectroscopic properties of \( \mu \)-oxo BsubPc have been identified and appear to be promising for application in OSCs, few other properties are known and no practical synthesis process exists.

Therefore, the aim of this thesis is to further develop the state of knowledge in these two areas to fill the identified gaps. A process to synthesize F-BsubPc with reasonable yield and purity will be developed. Once this has been achieved, all three halo-BsubPcs will be fully characterized. Several properties relevant to their chemistry and processability will be assessed, such as solubility, melting and sublimation temperatures, and reactivity. Other properties to be investigated relate to their performance as organic electronic materials: solid state arrangement, photophysics, including absorption and fluorescence emission spectra, photoluminescent quantum efficiency, and electrochemistry, including cyclic voltammetry.\(^{(34)}\) In order to provide a route to study \( \mu \)-oxo BsubPc as a functional organic material in devices, a directed synthesis process will be developed. The goal is to enable characterization of the material in terms of its device performance, and thus the process development will be guided by criteria including the ability to meet yield and purity needs of these characterization methods. HO-BsubPc is a precursor and the closest monomeric structural analogue of \( \mu \)-oxo BsubPc. As with the halo-BsubPcs, its synthesis is known but a gap exists in the study of its relevant properties. Therefore, selected properties of both the pure, isolated \( \mu \)-oxo BsubPc and HO-BsubPc will be explored and assessed in comparison to one another and other known BsubPcs. The outcome of these studies will fill current gaps in the information needed to assess suitability of these materials for use in OSCs, and will provide the means to access these materials by developing appropriate synthetic processes.
Chapter 2

This Chapter is adapted from a manuscript of which I am first author, which has been published in the *Journal of Chemical & Engineering Data*. Its contents address the goals outlined in the thesis statement concerning halo-BsubPcs.

I performed all data analysis with the exception of photostability which was done by Damish Jaidka in collaboration with Professor Bender. I conducted the experimental work with the following exceptions which were contributed by my co-authors. Andrew Paton obtained solution-grown crystals of Br-BsubPc. Graham Morse performed sublimation of Cl-BsubPc. Emma Brisson developed the synthesis of Br-BsubPc. Alan Lough collected all XRD data and provided crystal structure determinations. Professor Bender supervised the research and subsequent publication, and provided guidance on choice of analysis techniques and throughout the development of a synthesis process to access F-BsubPc.

2 Crystal Structures, Reaction Rates and Selected Physical Properties of Halo-Boronsubphthalocyanines (Halo = Fluoride, Chloride and Bromide).

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ABSTRACT: The physical properties, including the solid state arrangement, photophysics, solubility and electrochemical behavior of a series of halo-B\textsubscript{sub}Pcs (halo = F, Cl, Br) have been measured. We have found that across the series all are relatively similar in most regards. Exceptions include that F-B\textsubscript{sub}Pc can be 5-25x more soluble than Cl-B\textsubscript{sub}Pc in common organic solvents. F-B\textsubscript{sub}Pc was also found to be hydrolytically stable under the conditions tested whereas Cl-B\textsubscript{sub}Pc and Br-B\textsubscript{sub}Pc readily hydrolyzed to form HO-B\textsubscript{sub}Pc. The relative rates of reaction for the series of halo-B\textsubscript{sub}Pcs under standard phenoxylation conditions have also been measured. It was found that F-B\textsubscript{sub}Pc does not undergo phenoxylation whereas Br-B\textsubscript{sub}Pc showed a markedly higher reaction rate relative to Cl-B\textsubscript{sub}Pc. Based on this data some assumptions can be made as to the suitability of either F-B\textsubscript{sub}Pc or Br-B\textsubscript{sub}Pc to be used in place of the more common Cl-B\textsubscript{sub}Pc. The data indicates that F-B\textsubscript{sub}Pc is a potential replacement for Cl-B\textsubscript{sub}Pc in organic electronic materials whereas Br-B\textsubscript{sub}Pc might be more suitable as a chemical intermediate. Comments on the synthetic methods used to produce each halo-B\textsubscript{sub}Pc are also made.
2.1 Introduction

This paper aims to compile data for F- and Br-BsubPc and to compare that data to the more common Cl-BsubPc. Combined, this data can assist in developing efficient process chemistry for BsubPc derivatives, balancing stability and reactivity as needed. This paper also presents the data necessary to evaluate suitability of the halo-BsubPcs for application in organic electronic applications, including HOMO and LUMO energy levels and photoluminescence quantum efficiency ($\phi$), and enable informed comparison and choice amongst them. We have also obtained single crystal x-ray determined structures for F- and Br-BsubPc and verified the 1974 x-ray determined structure of Cl-BsubPc.\(^{(22)}\) We are thus also able to compare the solid state arrangement of each to Cl-BsubPc.

2.2 Experimental

2.2.1 Methods and Materials.

All solvents were purchased from Caledon Laboratories Ltd and used as received unless stated otherwise. Anhydrous toluene for spectroscopy was obtained from Caledon Laboratories Ltd and purified and stored in a Pure Solv\textsuperscript{TM} solvent purification system prior to use. The boron trihalides were obtained from Sigma Aldrich Canada. All nuclear magnetic resonance (NMR) spectra were acquired on a Bruker 400 MHz system in deuterated chloroform (CDCl\textsubscript{3}) purchased from Cambridge Isotope Laboratories which was used as received. All \textsuperscript{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 25 with a 10.00 mm path length for solution phase samples. Photoluminescence spectra were collected using a Perkin-Elmer LS 55. Differential pulse and cyclic voltammetry was conducted with a Bioanalytical Systems C3 electrochemical workstation. The working electrode was a 1mm platinum disk, the counter electrode was a platinum wire, and the reference electrode was Ag/AgCl in a saturated salt solution. All electrochemistry was done in spec-grade dichloromethane (DCM) with decamethylferrocene as an internal reference. The solvent was purged with Argon at room temperature prior to use. 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 $\times$ 100 mm SunFire\textsuperscript{TM} C\textsubscript{18} 3.5 $\mu$m column. HPLC grade acetonitrile and DMF were eluted at 0.6 mL/min during operation at a composition of 80:20,
respectively. Mass spectrometry was performed on a JEOL AccuTOF-DART mass spectrometer with a DART-ion source (no solvent required). Soxhlet extractions were performed using Whatman® single thickness cellulose extraction thimbles (33 × 118 mm, 25 × 80 mm). The apparatus used and method followed for train sublimation has previously been disclosed. Carbon-hydrogen-nitrogen elemental analysis was performed using a Perkin-Elmer 2400 Series II CHNS Analyzer. Melting points were measured with a Stuart SMP3 melting point apparatus.

2.2.2 Molar extinction coefficients

Molar extinction coefficients were determined using a standard method as follows: a solution with known concentration was prepared in 250 mL of toluene in a volumetric flask, and left to stir overnight to ensure complete dissolution. This solution was then sampled and serially diluted until its absorbance fell within the linear range of the spectrometer. The final absorption spectra and the known diluted concentration were used to calculate the extinction coefficient at the $\lambda_{\text{max}}$.

2.2.3 Solubility analysis

Solubility analysis was performed using a standard procedure as follows: The respective BsubPc was added to a solvent until a precipitate was visible after being left to stir overnight (to ensure the solution was saturated). The solution was then left to settle with the stirring turned off, and subsequently centrifuged at 4500 rpm for 5 minutes to separate any remaining fine precipitate. The saturated solution was then sampled, passed through a GS-Tek PTFE 13mm 0.22µm syringe filter, and serially diluted until the absorbance fell within the linear range of the spectrometer. The absorption spectrum was recorded, and the extinction coefficients combined with the number and size of dilutions was used to calculate the original concentration of the saturated solution.

2.2.4 Chloro-boronsubphthalocyanine (Cl-BsubPc, 1a, Scheme 2.1).

Synthesized as previously reported.\textsuperscript{(27)(49)}

2.2.5 Bromo-boronsubphthalocyanine (Br-BsubPc, 1b, Scheme 2.1).

Br-BsubPc was synthesized by modifying the procedure of Potz et al.\textsuperscript{(24)} as follows: In a 100 mL three-neck round bottomed flask, equipped with a magnetic stir-bar, a gas inlet, a condenser, and two rubber sleeve stoppers, phthalonitrile (4.0 g, 0.0312 mol) was dissolved in a 3:1 mixture of
toluene:bromobenzene (50 mL). The vessel was kept under an inert atmosphere of argon and a syringe and needle were used to slowly add boron tribromide (0.96 mL, 0.010 mol) to the solution. The mixture changed color to a deep brown almost immediately, as the temperature slowly increased from room temperature to approximately 37 °C. The mixture was left overnight under inert atmosphere with a stirring rate of about 500 rpm. The next day, the magnetic stirring was turned off and after waiting one hour, the solution was gravity filtered through a cone shaped filter. The filter cake was immediately rinsed with approximately 250 mL of methanol. Yield: 3.37 g (71%). HPLC $R_t$: 2.35 min (>99.9%, MAXplot); UV-Vis: 565 nm; $^1$H NMR (400 MHz, CDCl$_3$, Me$_4$Si) 7.97-7.99 (m, 6H), 8.92-8.94 (m, 6H); HRMS (DART) calcd. for C$_{24}$H$_{12}$BBrN$_6$ ([M]+): m/z 475.0478, found 475.0469. Anal. Calcd for C$_{24}$H$_{12}$BBrN$_6$: C, 60.67; H, 2.55; N, 17.69. Found: C, 59.34; H, 2.75; N, 16.05.

2.2.6 3,4-Dimethylphenoxy-boronsubphthalocyanine (DMPh-BsubPc, 2, Scheme 2.1).

Synthesized as previously reported.$^{(41)}$

2.2.7 Fluoro-boronsubphthalocyanine (F-BsubPc, 1c, Scheme 2.1).

F-BsubPc was synthesized by adapting the method of Rodríguez-Morgade et al.$^{(48)}$ Toluene (45 mL) was added to Br-BsubPc (3.32 g, 7.00 x 10$^{-3}$ mol) in a 250 mL three-neck round bottom flask fitted with a condenser and stir-bar. Boron trifluoride diethyl etherate (Et$_2$O•BF$_3$, 22.5 mL, 25 molar equiv.) was added dropwise. A positive pressure of argon was maintained throughout the experiment. The reaction progress was monitored by HPLC. The mixture was heated at reflux (111 °C) for 12 hours at which point Br-BsubPc was no longer detectable and the reaction was cooled to room temperature. Pyridine (22.5 mL) was added dropwise to quench the reaction until the dark blue color returned to a characteristic BsubPc color of dark pink/magenta. The flask was placed in an ice bath for one hour, and the precipitate subsequently isolated by vacuum filtration. The filter cake was rinsed with methanol followed by ether to give a bronzy solid. The solid was then placed in a vacuum oven overnight (40 °C, 10 mmHg). Yield: 1.89 g (64%). HPLC $R_t$: 2.23 min (>99.9%, MAXplot); UV-Vis: 562 nm; $^1$H NMR (400 MHz, CDCl$_3$, Me$_4$Si) 7.93-7.96 (m, 6H), 8.88-8.90 (m, 6H); HRMS (DART) calcd. for C$_{24}$H$_{12}$BFN$_6$ ([M]+): m/z 415.1279, found 415.1280. Anal. Calcd for C$_{24}$H$_{12}$BFN$_6$: C, 69.59; H, 2.92; N, 20.29. Found: C, 69.54; H, 3.15; N, 20.15.
2.2.8  Fluoro-boronsubphthalocyanine (Alternative method, see Scheme 2.1).

Toluene (1 mL) was added to DMPh-BsubPc (0.080 g, 0.155 mmol) in a 4 dram vial fitted with a condenser and stir-bar. Boron trifluoride diethyl etherate (Et₂O•BF₃, 0.5 mL, 25 molar equiv.) was added dropwise. A positive pressure of argon was maintained throughout the experiment. The reaction progress was monitored by HPLC. The mixture was heated at reflux (111 °C) for 3 hours. Pyridine (0.5 mL) was added dropwise to quench the reaction until the dark blue color returned to a characteristic BsubPc color of dark pink/magenta. 0.05M NaOH solution saturated in NaCl (2 mL) was added to the reaction mixture and stirred. The organic phase was retained and then filtered to obtain the product as a precipitate. The solid was then placed in a vacuum oven overnight (40 °C, 10 mmHg). Yield: 0.052 g (81%). HPLC Rₜ: 2.23 min (98%, MAXplot).

2.2.9  Phenoxylation of Halo-BsubPcs.

The halo-BsubPc (0.075 g) was dissolved in chlorobenzene (10 mL) and phenol (5 molar equiv.) was then added. The reaction mixture was continuously stirred and heated to 100 °C under argon gas. At periodic time intervals, samples were extracted and analyzed by HPLC to determine percentage conversion. These conditions were maintained until no further change was detectable. It was assumed that the extinction coefficients of the BsubPc compounds were approximately equivalent, and thus percent conversion from reactant (halo-BsubPc) to product (phenoxy-BsubPc) versus time was determined by the percentage of the total area of the integrated product and reactant peaks extracted at 560 nm by HPLC.

2.2.10 Hydrolysis of Halo-BsubPcs to HO-BsubPc.

The halo-BsubPc (0.100 g) was dissolved in DMSO (12.0 mL) and pyridine (0.4 mL) and stirred in a closed container for a few minutes. Distilled water (0.8 mL) was then added and the reaction mixture was continuously stirred and heated to 60 °C under normal ambient atmosphere. These conditions were maintained until no further change was detectable. Samples were taken and the percentage conversion determined in the same manner as above.
2.3 Results and Discussion

2.3.1 Synthesis

The synthesis of Cl-BsubPc (Scheme 2.1) is well documented and has been carried out with typical yields between 60 and 70% in our laboratory. The procedure we commonly use is a modification of the method of Zyskowski and Kennedy. In brief, boron trichloride as a solution in heptanes is added to phthalonitrile dissolved in 1,2-dichlorobenzene and heated at reflux with distillation of the heptanes. Thereafter, soxhlet extraction is capable of purifying Cl-BsubPc to levels of >98% purity.

In our hands, the synthesis of Br-BsubPc as described by Potz et al. was found to be successful after some adaptations. The process is similar to that used for Cl-BsubPc in that it starts by dissolving phthalonitrile in solvent and adding a boron trihalide (in this case neat BBr₃, Scheme 2.1). However, unlike the case for the synthesis of Cl-BsubPc, this reaction occurred entirely at room temperature presumably due to the increased reactivity of BBr₃ over BCl₃. A small exotherm was also observed (+12-15 °C) which did not require any special means to control. The reaction was left overnight at room temperature so as to complete. If bromobenzene was used exclusively as the solvent (as reported by Potz) we saw the formation of impurities which could be confirmed to be BsubPcs based on their UV-Vis absorption spectrum but could not be unambiguously identified. We hypothesized that they were BsubPcs which had been partially brominated around the periphery. Thus we moved to the use of a mixture of toluene and bromobenzene (3:1 vol:vol) with the idea that the toluene would be a sacrificial reactant for bromination. Using the mixed solvent system allowed for the production of exclusively Br-BsubPc. Immediately washing the filter cake with methanol, prior to the cake drying or cracking, is critical to the success of the procedure. As a side note, we found that Br-BsubPc was not stable under sublimation conditions in our apparatus. It formed small quantities of the oxygen-bridged BsubPc dimer, µ-oxo-(BsubPc)₂ (which can easily be identified by its distinctive UV-Vis spectrum) and thus sublimation cannot be used as a purification step.
Scheme 2.1. Synthesis of X-BsubPc, where X = Br, Cl or F. Conditions: (i) For X = Cl: BCl$_3$ (in heptanes), 1,2-dichlorobenzene, reflux, 1.5 hours; For X = Br: BBr$_3$, bromobenzene, toluene, r.t., overnight. (ii) Et$_2$O•BF$_3$, toluene, reflux, 12 hours. (iii) 3,4-Dimethylphenol, toluene, reflux, 24 hours. (iv) Et$_2$O•BF$_3$, toluene, reflux, 3 hours.

The synthesis of F-BsubPc has also been previously reported by both Potz et al. (24) and Rodríguez-Morgade et al. (48) In our laboratory the method of Potz et al. (24) proved challenging, giving overall yields which were extremely low (<1%). The process is analogous to that of Cl-BsubPc and Br-BsubPc: the cyclotrimerization of phthalonitrile around and facilitated by a boron trihalide. In this process, quinoline is used as the solvent for both its high boiling point and (unique to this process) because it forms a Lewis adduct with BF$_3$ thereby keeping it in solution. In our hands, a lengthy workup was necessary to separate the desired F-BsubPc product from both the quinoline and other deeply colored (black) intractable by-product(s). The unidentified black by-product(s) were produced in significant quantities; over ten times the mass of isolated F-BsubPc. It was therefore decided that this process was impractical. The method of Rodríguez-Morgade et al. (48) involves the reaction of pre-formed Cl-BsubPc with a large excess of BF$_3$•Et$_2$O producing F-BsubPc in a halogen/halide exchange reaction (Scheme 2.1). We therefore attempted the synthesis of F-BsubPc on a small scale starting from both Br-BsubPc and Cl-BsubPc. We found that while Br-BsubPc reached full conversion within 5.5h, when the Cl-BsubPc reaction was stopped after 28h it still had not reached completion. The reaction using Br-BsubPc as a starting material at reflux in toluene was selected, given the simplicity of the synthesis route and speed to reach full conversion.

Surprisingly, we also found that 3,4-dimethylphenoxy-BsubPc (DMPh-BsubPc) converted to F-BsubPc on treatment with BF$_3$•Et$_2$O (Scheme 2.1). Interestingly, this method using DMPh-BsubPc reached full conversion faster than the Br-BsubPc in small-scale tests. However, by comparison the conversion and subsequent isolation and purification of F-BsubPc derived from Br-BsubPc as a starting material was relatively facile, whereas the DMPh-BsubPc route is atom
inefficient and requires an additional synthesis step and thus it is deemed impractical to choose as an optimal process to produce F-BsubPc.

2.3.2 Physical Characterization

2.3.2.1 Sublimation and Melting Point.

The melting point of each halo-BsubPc was measured and all were found to be over 300 °C, the maximum range of the instrument used. Indicative sublimation temperatures measured in train sublimation apparatus\(^{(34)}\), corresponding to the recorded temperature at which a visible film forms on the tube, were 240 °C for F-BsubPc, 275 °C for Cl-BsubPc and 340 °C for Br-BsubPc. For Br-BsubPc, please note as stated above that on sublimation small quantities of \(\mu\)-oxo-(BsubPc)\(_2\) are produced. These are not equal to the true sublimation temperatures as the apparatus is not calibrated to the internal sample temperature, but rather the temperature is taken on the outside of the tube at the position of the crucible. However, they serve as a useful relative measure amongst the materials studied. It can therefore be noted that sublimation temperature increases down the group from F-BsubPc to Br-BsubPc.

2.3.2.2 Crystal Structure Analysis.

Following synthesis, the three materials were train sublimed with the goal of obtaining single crystals suitable for x-ray diffraction. The solid state arrangement of these materials is highly relevant in the context of their performance in an organic electronic device, in which the materials would be vapor deposited as thin solid films (solid state). Single crystals of Cl-BsubPc were obtained and diffraction confirmed that these crystals match the original 1974 report\(^{(22)}\). Single crystals of F-BsubPc were also obtained by train sublimation, and its solid state arrangement is reported here for the first time. However, Br-BsubPc was not thermally stable at its sublimation temperature and no crystals could be obtained from train sublimation. Instead, single crystals of Br-BsubPc were grown by slow vapor diffusion crystallization of heptane (poor solvent) into benzene (good solvent). A selection of relevant crystallographic and geometric data is presented in Table 2.1. The crystal system and space group of all three compounds was found to be identical, and the unit cell lengths, although they increase slightly down the group from F- to Br-BsubPc, are very similar. The geometric distances included in the lower portion of the table are intended to facilitate comparison of the crystal structures. The length of the boron-halogen (B-X) bond and the bowl depth together quantitatively describe the shape of each
individual BsubPc molecule. The bowl depth was calculated by measuring the distance between
the boron and a plane defined by the 6 outermost carbons (those furthest from the central boron,
two on each “R6” ring). All other distance values describe the smallest distance between the two
stated components that can be found in the crystal structure. Distances less than 4 angstroms (≤
4 Å) indicate a significant intermolecular interaction. In order to describe the type of
overlapping seen in the solid state arrangements, the different ring systems have been labeled as
depicted in Figure 2.1.

![Diagram](image)

**Figure 2.1.** (a) Cl-BsubPc with peripheral and axial positions identified and annotated to highlight ring
systems R5, R6 and R6h. (b) Top view of Cl-BsubPc in 3-dimensions. (c) Side view of Cl-BsubPc in 3-
dimensions.\(^{(22)}\)

This distinguishes between possible types of π-stacking and other interactions between adjacent
molecules: for example, the outer carbon ring (R6) of two BsubPc molecules may interact with
one another and effectively direct the boron centers away from one another; however,
interactions with a 5 membered ring (R5) or the central heterogeneous 6 membered ring (R6h)
indicate close interactions with larger proportions of the molecule. Two views of the crystal
structure and packing of each compound are shown in Figure 2.2. These images visually
illustrate the equivalence of the crystal structures of all three halo-BsubPcs.
Table 2.1. Selected crystallographic and geometrical parameters for Br-BsubPc (1a), Cl-BsubPc (1b) and F-BsubPc (1c).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Br-BsubPc (1a)</th>
<th>Cl-BsubPc (1b)</th>
<th>F-BsubPc (1c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical formula</td>
<td>C₂₄H₁₂BBN₆</td>
<td>C₂₄H₁₂BCN₆</td>
<td>C₂₄H₁₂BFN₆</td>
</tr>
<tr>
<td>Formula Mass</td>
<td>475.12</td>
<td>430.65</td>
<td>414.21</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Orthorhombic</td>
<td>Orthorhombic</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>a/Å</td>
<td>12.0161(4)</td>
<td>12.123(5)</td>
<td>12.1108(3)</td>
</tr>
<tr>
<td>b/Å</td>
<td>15.0606(5)</td>
<td>14.824(7)</td>
<td>14.3211(3)</td>
</tr>
<tr>
<td>c/Å</td>
<td>10.4064(5)</td>
<td>10.378(4)</td>
<td>10.3258(3)</td>
</tr>
<tr>
<td>α/°</td>
<td>90.00</td>
<td>90.00</td>
<td>90.00</td>
</tr>
<tr>
<td>β/°</td>
<td>90.00</td>
<td>90.00</td>
<td>90.00</td>
</tr>
<tr>
<td>γ/°</td>
<td>90.00</td>
<td>90.00</td>
<td>90.00</td>
</tr>
<tr>
<td>Unit cell volume/Å³</td>
<td>1883.24(13)</td>
<td>1865.04</td>
<td>1790.91(8)</td>
</tr>
<tr>
<td>Temperature/K</td>
<td>150(1)</td>
<td>150(1)</td>
<td>150(1)</td>
</tr>
<tr>
<td>Space group</td>
<td>Pnma</td>
<td>Pnma</td>
<td>Pnma</td>
</tr>
<tr>
<td>No. of formula units per unit cell, Z</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>No. of reflections measured</td>
<td>15914</td>
<td>26018</td>
<td></td>
</tr>
<tr>
<td>No. of independent reflections</td>
<td>2242</td>
<td>1295</td>
<td>2131</td>
</tr>
<tr>
<td>R_int</td>
<td>0.1300</td>
<td>0.0512</td>
<td></td>
</tr>
<tr>
<td>Final R₁ values (I &gt; 2σ(I))</td>
<td>0.0559</td>
<td>0.0382</td>
<td></td>
</tr>
<tr>
<td>Final wR(F²) values (I &gt; 2σ(I))</td>
<td>0.0994</td>
<td>0.0896</td>
<td></td>
</tr>
<tr>
<td>Final R₁ values (all data)</td>
<td>0.1142</td>
<td>0.0507</td>
<td></td>
</tr>
<tr>
<td>Final wR(F²) values (all data)</td>
<td>0.1191</td>
<td>0.0985</td>
<td></td>
</tr>
<tr>
<td>Goodness of fit on F²</td>
<td>1.032</td>
<td>1.043</td>
<td></td>
</tr>
<tr>
<td>B-X bond length (Å)</td>
<td>2.051(6)</td>
<td>1.8636(7)</td>
<td>1.395(2)</td>
</tr>
<tr>
<td>B-B distance (Å)</td>
<td>8.74(1)</td>
<td>7.24(4)</td>
<td>7.232(3)</td>
</tr>
<tr>
<td>Bowl depth (Å)</td>
<td>2.46(1)</td>
<td>2.47(2)</td>
<td>2.48(6)</td>
</tr>
<tr>
<td>R6-R6 centroid distance (Å)</td>
<td>3.704(2)</td>
<td>3.708(9)</td>
<td>3.7524(8)</td>
</tr>
<tr>
<td>R5-R5 centroid distance (Å)</td>
<td>4.761(3)</td>
<td>4.733(8)</td>
<td>4.59(1)</td>
</tr>
<tr>
<td>R6-R5 centroid distance (Å)</td>
<td>3.672(3)</td>
<td>3.654(5)</td>
<td>3.5835(8)</td>
</tr>
<tr>
<td>R6-R6h centroid distance (Å)</td>
<td>4.16(8)</td>
<td>4.20(4)</td>
<td>4.11(3)</td>
</tr>
</tbody>
</table>
Figure 2.2. Crystal structure/solid state arrangement of (a) Br-BsubPc (b) Cl-BsubPc and (c) F-BsubPc. Ellipsoids shown at 35% probability level. Hydrogens have been omitted for clarity.

2.3.2.3 Spectroscopy Analysis.

Given that halo-BsubPcs are of interest as optical functional materials, it is necessary to quantify both their absorbance and photoluminescence properties. Figure 2.3 illustrates the absorbance and photoluminescence spectra of each of F-BsubPc, Cl-BsubPc and Br-BsubPc in toluene solution. The maximum absorbance in the strongest absorption band of Cl-BsubPc occurs at a $\lambda_{\text{max}} = 565$ nm. The peak absorption of Br-BsubPc is almost identical at 566 nm, and the maximum absorption of F-BsubPc is slightly blue-shifted with a $\lambda_{\text{max}} = 562$ nm. The photoluminescence (PL) spectra were collected by excitation at the $\lambda_{\text{max}}$ of absorption of each compound. The peak emission wavelength of Cl-BsubPc occurs at a $\lambda_{\text{max}}$ of 571 nm, the $\lambda_{\text{max}}$ of Br-BsubPc is very slightly red-shifted at 572 nm and the $\lambda_{\text{max}}$ of F-BsubPc is slightly blue-shifted at 568 nm. Cl-BsubPc was found to have a very small Stokes shift of 6 nm, similar to what has
been previously observed.\(^{(58)(59)}\) The Stokes shifts shown by both F-BsubPc and Br-BsubPc are identical at 6 nm (Table 2.2).

![Absorption and photoluminescence spectra](image)

**Figure 2.3.** Absorption (blue) and photoluminescence (red) of (a) F-BsubPc, (b) Cl-BsubPc and (c) Br-BsubPc.

**Table 2.2.** Photophysical and Electronic Properties of Br-BsubPc (1a), Cl-BsubPc (1b) and F-BsubPc (1c).

<table>
<thead>
<tr>
<th></th>
<th>(\lambda_{\text{max,abs}}) (nm)</th>
<th>(\lambda_{\text{max,PL}}) (nm)</th>
<th>(\Phi_{\text{PL}})</th>
<th>(E_{\text{ox}}) (mV)</th>
<th>HOMO (eV)</th>
<th>(E_{\text{g,opt}}) (eV)</th>
<th>LUMO (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-BsubPc</td>
<td>562</td>
<td>568</td>
<td>0.51</td>
<td>532(^{\text{P}})</td>
<td>5.3(^{\text{P}})</td>
<td>2.1</td>
<td>3.2(^{\text{P}})</td>
</tr>
<tr>
<td>Cl-BsubPc</td>
<td>565</td>
<td>571</td>
<td>0.73</td>
<td>584(^{\text{P}})</td>
<td>5.4(^{\text{P}})</td>
<td>2.1</td>
<td>3.3(^{\text{P}})</td>
</tr>
<tr>
<td>Br-BsubPc</td>
<td>566</td>
<td>572</td>
<td>0.10</td>
<td>632(^{\text{P}})</td>
<td>5.5(^{\text{P}})</td>
<td>2.1</td>
<td>3.4(^{\text{P}})</td>
</tr>
</tbody>
</table>

\(^{\text{P}}\) Peak oxidation potential by differential pulse voltammetry. \(^{\circ}\) Potential at onset of oxidation by differential pulse voltammetry.
2.3.2.4 Solubilities.

In order to measure solubilities, the extinction coefficient of each halo-BsubPc was first determined. This was done in triplicate for each halo-BsubPc compound. The extinction coefficients are recorded in Table 2.3.

Table 2.3. Molar Extinction Coefficients (ε) of Br-BsubPc (1a), Cl-BsubPc (1b) and F-BsubPc (1c) in toluene.

<table>
<thead>
<tr>
<th></th>
<th>ε, L mol⁻¹ cm⁻¹</th>
<th>±</th>
<th>at λmax, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br-BsubPc</td>
<td>8.37 x10⁴</td>
<td>0.243 x10⁴</td>
<td>566</td>
</tr>
<tr>
<td>Cl-BsubPc</td>
<td>8.86 x10⁴</td>
<td>0.142 x10⁴</td>
<td>565</td>
</tr>
<tr>
<td>F-BsubPc</td>
<td>8.76 x10⁴</td>
<td>0.446 x10⁴</td>
<td>562</td>
</tr>
</tbody>
</table>

Solubilities were measured in eight common solvents covering a range of chemical properties and polarity. The results are summarized in Table 2.4. The calculated error is equivalent to two times the standard deviation (±2σ). All solubilities were measured by forming saturated solutions of each compound in each of the chosen solvents at room temperature. The exception was the solubility of Cl-BsubPc as its solubility in all solvents except acetone, DMF and acetonitrile has been previously reported by our group,²⁷ but were calculated using an extinction coefficient measured in chloroform of 6.75 x10⁴ ± 1.39 x10⁴ L mol⁻¹ cm⁻¹. To enable comparison, the original absorption value was back-calculated using the reported chloroform extinction coefficient, and this absorption was then converted in the same way as all other solubilities using the measured extinction coefficient in toluene. The error associated with both the chloroform and toluene extinction coefficients was compounded. The solubility of each BsubPc was measured in triplicate. The error associated with the absorption measurements was compounded with the extinction coefficient’s error to calculate overall error associated with the solubility measurement. Both the molal (mol kg⁻¹ x 10⁻⁵) and mass fraction (in ppm) solubilities are reported in Table 2.4.
Table 2.4. Molal (MS, mol kg$^{-1}$ x 10$^{-5}$) and mass fraction (WS, parts per million by mass) solubility of compounds Br-BsubPc (1a), Cl-BsubPc (1b) and F-BsubPc (1c).

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Br-BsubPc</th>
<th>Cl-BsubPc</th>
<th>F-BsubPc</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MS$_{Br}$ ±</td>
<td>MS$_{Cl}$ ±</td>
<td>MS$_{F}$ ±</td>
</tr>
<tr>
<td>Acetone</td>
<td>4.18</td>
<td>3.60</td>
<td>17.8</td>
</tr>
<tr>
<td>Chloroform</td>
<td>157</td>
<td>8.9</td>
<td>205</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>42</td>
<td>28.7</td>
<td>220</td>
</tr>
<tr>
<td>Propyl-acetate</td>
<td>5</td>
<td>4.44</td>
<td>19.6</td>
</tr>
<tr>
<td>THF</td>
<td>26</td>
<td>19.6</td>
<td>137</td>
</tr>
<tr>
<td>Toluene</td>
<td>24</td>
<td>15.1</td>
<td>130</td>
</tr>
<tr>
<td>DMF</td>
<td>37</td>
<td>9.25</td>
<td>60.8</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>1.068</td>
<td>4.20</td>
<td>4.54</td>
</tr>
</tbody>
</table>

The solubility of F-BsubPc was generally higher than that of Cl-BsubPc and Br-BsubPc in every solvent tested, and the difference between F-BsubPc and Cl-BsubPc approaches one order of magnitude in most solvents except DMF. The ranges of error of the Br-BsubPc and Cl-BsubPc measurements overlap in acetone, propyl-acetate, THF and acetonitrile, leading to the conclusion that their solubilities are approximately equivalent. However, in each of the other solvents the solubility of Br-BsubPc is greater than that of Cl-BsubPc. The molal solubility (MS) of Br-BsubPc is close to that of Cl-BsubPc in chlorobenzene (MS$_{Br,Clbz}$ = 1.2 x MS$_{Cl,Clbz}$) and toluene (MS$_{Br,tol}$ = 1.6 x MS$_{Cl,tol}$) compared to the solubility of F-BsubPc (MS$_{F,Clbz}$ = 7.7 x MS$_{Cl,Clbz}$ and MS$_{F,tol}$ = 8.6 x MS$_{Cl,tol}$, respectively). Conversely, in DMF the solubility of Br-BsubPc approaches that of F-BsubPc and in chloroform the ranges of error for Br-BsubPc and F-BsubPc overlap and so their solubility is approximately equivalent. This can be seen more clearly in Figure 2.4, where the molal solubilities of Br-BsubPc and F-BsubPc are indexed to the solubility of Cl-BsubPc in each solvent (MS$_{Cl,any solvent}$ = 1). Nevertheless, in comparison to other BsubPc derivatives, the solubility of all three halo-BsubPcs are low – for example, the reported molal solubility of phenoxy-BsubPc$^{(27)}$ ranges from 391 to 895 mol kg$^{-1}$ x 10$^{-5}$ in this group of solvents, excluding DMF and acetonitrile, which exceeds the MS of Cl-BsubPc by one or more orders of magnitude (MS$_{Phenoxy}$ = 17.6 to 142 x MS$_{Cl}$) and also exceeds F-BsubPc in each solvent (MS$_{Phenoxy}$ = 1.9 to 32 x MS$_{F}$).
2.3.2.5 Photoluminescence Quantum Efficiency.

The photoluminescent quantum yield ($\Phi_{PL}$) of each halo-BsubPc was measured at room temperature in toluene. A dilute solution of the halo-BsubPc was prepared with a maximum absorbance below 0.08 A and its absorption spectrum was recorded. This sample was then excited at the wavelength corresponding to its maximum absorbance ($\lambda_{max,abs}$) and the photoluminescence spectrum was collected. This was done in triplicate for each of the three halo-BsubPc compounds as well as for the standard (phenoxy-dodecafluoro-boronsubphthalocyanine (F_{12}BsubPc)) which was repeated in every distinct session of data collection to control for any use-to-use drift in the fluorimeter. The quantum yield of F_{12}BsubPc has been previously reported as 0.40, and this value was used as the reference to calculate quantum yield of each the halo-BsubPcs. Both the F_{12}BsubPc and the halo-BsubPc values are involved in the calculation of quantum yield, and so the calculation was done on all 9 possible combinations (ie F_{12}BsubPc-a with X-BsubPc-a, X-BsubPc-b, X-BsubPc-c; F_{12}BsubPc-b with X-BsubPc-a, etc) and the average of these was taken as the quantum yield with an error of ±2σ.

The quantum yield was found to vary widely within the group. Cl-BsubPc was found to have a quantum yield far greater than the F_{12}BsubPc standard at 0.73 ± 0.04. The quantum yield of F-BsubPc, 0.51 ± 0.02, was found to be lower than that of Cl-BsubPc but is still greater than the F_{12}BsubPc reference. Finally, the quantum yield of Br-BsubPc was found to be far lower than
either compound as well as the reference, at 0.10 ± 0.01. The low quantum yield of Br-BsubPc may have implications for its usefulness as a functional organic electronic material.

2.3.2.6 Electrochemistry.

Cyclic and differential pulse voltammetry were conducted in dichloromethane to assess the electronic characteristics of the halo-BsubPcs and to estimate their HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) energy levels. Tetrabutylammonium perchlorate was used as the electrolyte, and oxidation/reduction potentials were corrected using an internal standard of decamethylferrocene. The half-wave reduction potential of decamethylferrocene has been previously established to be -0.012 V versus Ag/AgCl.\(^{60}\) Initially each sample was scanned over the range of +1.4 to -1.4 V at a scan rate of 100 mV s\(^{-1}\), followed by three cycles in the range -0.35 V to +1.4 V to focus on the oxidation event, since no consistent electrochemical events were found on the reduction side for any of the halo-BsubPcs. In each of the halo-BsubPcs, one irreversible oxidation peak was detected. The half-wave potential cannot be extracted from an irreversible peak in a cyclic voltammogram. Therefore, differential pulse voltammetry was performed on each sample in the range -0.35 V to +1.4 V. The peak potentials of oxidation, E\(_{\text{ox}}\) (mV), for F-BsubPc, Cl-BsubPc and Br-BsubPc are outlined in Table 2.2 (again against an Ag/AgCl electrode). The values compare favorably with previously reported values for the peak oxidation potential of Cl-BsubPc\(^{43}\) and Br-BsubPc\(^{61}\). The equation developed by D’Andrade et al.\(^{62}\) was used to estimate the HOMO energy level of each compound. This equation was developed for used with the half wave potentials of a compound, data which is not available for the halo-BsubPcs due to the irreversibility of their oxidatized states. Therefore, the calculation was carried out twice for each compound, once using the peak oxidation potential and a second time using the potential at the onset of the oxidation peak, since it is unknown which corresponds most accurately to the potential modeled by the equation. Using this approach it was possible to compare the results to one another. The optical band gap, E\(_{\text{g,op}}\), was calculated from the wavelength at the onset of the lowest energy absorption band of each compound and was found to be the same for each halo-BsubPc to two significant figures at 2.1 eV given the similarity of their absorption spectra. This was added to the HOMO to obtain a value for the LUMO energy level. The peak oxidation potential of Cl-BsubPc was found to correspond to a HOMO of 5.4 eV, while the HOMO corresponding to the onset of the oxidation event was 5.2 eV. For comparison, the HOMO of Cl-BsubPc in a solid thin film has been reported to be 5.6 eV\(^{63}\) and 5.7 eV.\(^{31}\) While part of this
difference is accounted for due to the lack of reversible oxidation behavior, it is also to be expected that electrochemical behavior of a compound in solution will not precisely match its behavior in the solid state. The data for all three halo-BsubPcs is summarized in Table 2.2, which shows that the HOMO, and thus LUMO, energy levels of the halo-BsubPcs increase slightly down the group from F- to Br- but are very similar to one another.

2.3.3 Reaction Rates

One challenge in working with halo-BsubPcs is that the boron-halogen (B-X) bond is hydrolytically unstable and can form hydroxy-BsubPc (HO-BsubPc) in the presence of water including atmospheric water. This has partially driven the study of phenoxy-BsubPcs which contain the more hydrolytically stable B-O bond. The hydrolytic stability of the bond is also expected to vary amongst the halo-BsubPcs and thus will indicate whether the halo-BsubPcs are suitable for use themselves as functional materials, rather than simply as chemical intermediates. Equally, the general chemical reactivity of the axial B-X bond drives ease and availability of axial substitution reactions such as the phenoxylation reaction. It is therefore also desirable to understand the reaction rates of a common chemical reaction of halo-BsubPc which will give an indication of the reactivity of the B-X bond and determines whether and how easily the halo-BsubPc can be used as a starting material in the synthesis of more complex BsubPc derivatives.

Following the conditions we have previously published and which are outlined in the experimental section of this paper, we subjected each halo-BsubPc to standard phenoxylation and hydrolysis conditions (Scheme 2.1). The results are shown in Figure 2.5a-b and clearly illustrate the trend of increasing reaction rates on progressing from Br-BsubPc to F-BsubPc. Both reactions with Br-BsubPc reached full conversion within a few hours. The reactions starting with Cl-BsubPc were much slower: it took approximately 6 days for the phenoxylation to reach completion, and the hydroxylation of Cl-BsubPc had reached ~66% conversion after 3 days. Most interestingly, F-BsubPc showed no conversion to either phenoxy-BsubPc or HO-BsubPc even after 124 hours (beyond 80 hours not shown on hydroxylation graph) indicating that it is chemically unreactive under the conditions tested. Given that the alternative synthesis method of F-BsubPc starting from DMPhO-BsubPc proceeds (i.e. fluoride can displace phenoxide) but F-BsubPc cannot be converted to phenoxy-BsubPc (under optimal phenoxylation conditions) a conclusion that the F-B bond of F-BsubPc is significantly more stable than the B-O bond of phenoxy-BsubPc can be reached. This likely indicates that F-BsubPc is not useful as a precursor
to other BsubPc compounds. However, the lack of detectable hydroxylation of F-BsubPc over
the same timeframe suggests that it is extremely hydrolytically stable and thus may be useful
where this is a desired quality, such as in an organic electronic device. At the other end of the
spectrum, the fast phenoxylation rate of Br-BsubPc illustrates its value as a reactive intermediate
in the synthesis of other BsubPc compounds. It has the potential to speed up and reduce the
energy needs of a synthesis process. Cl-BsubPc may well represent a good balance of the two
qualities of reactivity and stability, if the reaction of the B-Cl bond to form other desired
derivatives such as phenoxy-BsubPcs is, although slower than of B-Br, faster than the process of
hydrolysis of the B-Cl bond.

![Graph showing reaction rates of different BsubPc compounds](image)

**Figure 2.5.** Phenoxylation (a) and hydroxylation (b) rates of Br-BsubPc (◇) Cl-BsubPc (□) and F-
BsubPc (△).

### 2.3.4 Photostability

Finally, we measured the photostability of each of F-, Cl- and Br-BsubPc using our previously
published method. While this method is not standardized in that it only provides relative
photostability, it can be seen in Figure 2.6 that the photostability of all halo-BsubPcs are
approximately equal. Variations can be seen late in the experiment whereby F-BsubPc seems to
be less photostable than Cl-BsubPc and Br-BsubPc. We believe these variations might be a
result of the differential solubility of each halo-BsubPc in the polystyrene binder used for the
experiment. Based on the solubility data presented in Figure 2.4 we would expect F-BsubPc to
be more soluble in polystyrene (using toluene as an analogous solvent) than Br-BsubPc or Cl-
BsubPc. As such, F-BsubPc could be more molecularly dispersed than either Cl-BsubPc or Br-
BsubPc accounting for its moderately poorer photostability later in the experiment.
2.4 Conclusions

We have presented data which will allow individual research groups make a conclusion as to the suitability of halo-BsubPcs (halo = F, Cl, Br) as functional organic materials in organic electronic devices or as chemical precursors for other BsubPc derivatives. Based on our data we would conclude that F-BsubPc is a viable candidate for application in organic electronic materials. We make this conclusion based on its hydrolytic stability and similar physical properties (including its solid state arrangement, photophysics and electrochemical behavior) to the commonly used Cl-BsubPc. Additionally, F-BsubPc was found to be 5-25x more soluble in common organic solvents indicating its potential for incorporation into organic electronic devices using either vacuum deposition or solution deposition techniques. Conversely, while Br-BsubPc again has similar physical properties to the other halo-BsubPcs, we would conclude that due to the similarity of its solubility to Cl-BsubPc and its poorer hydrolytic stability (including under sublimation conditions and solution hydrolysis) it is not suitable for direct application in organic electronic devices. However, Br-BsubPc has been demonstrated to have an increased reaction rate over Cl-BsubPc under standard phenoxylation conditions and as such is a candidate as a chemical precursor to other BsubPc derivatives. This is in contrast to F-BsubPc which is entirely unreactive under standard phenoxylation conditions and therefore is not a candidate as a chemical precursor.

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Chapter 3

This Chapter is adapted from a manuscript of which I am first author, which has been published in the journal *Acta Crystallographica Section B: Structural Science*. The paper outlines the initial exploration of µ-oxo BsubPc chemistry, followed by an in depth analysis of its observed crystal structures. Although the process chemistry described herein is not believed to be efficient or effective as a route to synthesize pure µ-oxo BsubPc, it was sufficient to obtain preliminary results which characterize the solid state arrangement of the molecule. The analysis of these results suggest an organic electronic material of great promise and thus justify an extensive investigation into routes for directed µ-oxo BsubPc synthesis, which is described in Chapter 4 of this thesis.

I conducted all experimental work described within this manuscript. Alan Lough collected all XRD data and provided crystal structure determinations, and assisted in processing crystallographic data. Professor Bender supervised the research and subsequent publication, and provided guidance throughout the development of the µ-oxo synthesis process. All authors contributed to selection of structural analysis metrics, in addition to input from the reviewers.

3 The first report of the crystal structure of non-solvated \(\mu\)-oxo boron subphthalocyanine and the crystal structures of two solvated forms.

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Synopsis. The solvent and water free solid state arrangement of the oxygen bridged dimer of boron subphthalocyanine (\(\mu\)-oxo-(BsubPc)\(_2\)) has been determined from single crystals grown by sublimation. In the course of this study single crystals of the quarter-hydrate and dichlorobenzene solvate were also obtained. Comparison of the sublimate with these and the previously published toluene solvate show the sublimate is unique in a number of ways including in its solid state arrangement and its density.

Abstract. The first instance of the solvent free x-ray determined single crystal structure of the oxygen bridged boron subphthalocyanine dimer (\(\mu\)-oxo-(BsubPc)\(_2\), \(C_{48}H_{24}B_2N_{12}O\)) is reported. Single crystals obtained by train sublimation were found to have \(\mu\)-oxo-(BsubPc)\(_2\) organized into a C2/c space group. The crystal structure obtained by sublimation is of particular interest as it is highly symmetric and also of notably high density when compared to other BsubPc crystals. The acquisition of this crystal structure came about from the direct chemical synthesis of \(\mu\)-oxo-(BsubPc)\(_2\) followed by a workup which culminated in obtaining the single crystals by sublimation. Several methods for the direct chemical synthesis of \(\mu\)-oxo-(BsubPc)\(_2\) were also investigated each using dichlorobenzene as the solvent. On standing, these reaction mixtures produced a crystal of the dichlorobenzene solvate of \(\mu\)-oxo-(BsubPc)\(_2\) (\(\mu\)-oxo-(BsubPc)\(_2\)•2DCB). It is also reported that the conversion of bromo boronsubphthalocyanine (Br-BsubPc) to \(\mu\)-oxo-(BsubPc)\(_2\) happens on train sublimation which resulted in the acquisition of a partially hydrated crystal (\(\mu\)-oxo-(BsubPc)\(_2\)•0.25H\(_2\)O).
3.1 Introduction.

Herein we report that we have isolated three separate and unique single crystals of μ-oxo-(BsubPc)₂ including the first report of a solvent free single crystal structure determination of μ-oxo-(BsubPc)₂. Others include the partially hydrated and dichlorobenzene solvated crystals of μ-oxo-(BsubPc)₂. The solid state arrangement as well as the density of each m-oxo-(BsubPc)₂ crystal (polymorph) is distinctly different than what is seen for either Cl-BsubPc (22) or other derivatives of BsubPc. A summary of the common solid state arrangements of BsubPc derivatives can be found in Chapter 1 of this thesis. Concurrent with our investigation, the direct synthesis of μ-oxo-(BsubPc)₂ via self condensation of HO-BsubPc (4.5 g; 34% yield) was reported in the academic literature by Mori and Yamasaki (65) along with the x-ray determined structure of its toluene solvate μ-oxo-(BsubPc)₂•3toluene. This structure is included in the discussion.

3.2 Experimental and Methodology.

3.2.1 General Methods and Materials.

All solvents were purchased from Caledon Laboratories Ltd and used as received unless stated otherwise. Boron tribromide and phthalonitrile was obtained from Sigma Aldrich Canada. All nuclear magnetic resonance (NMR) spectra were acquired on a Bruker 400 MHz system in deuterated chloroform (CDCl₃) purchased from Cambridge Isotope Laboratories which was used as received. All 1H NMR spectra were referenced to an internal standard of 0.05% TMS. All ultraviolet-visible (UV-Vis) spectroscopy was performed using PerkinElmer Lambda 25 with a 10.00 mm path length for solution phase samples. 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 × 100 mm SunFireTM C18 3.5 μm column. HPLC grade acetonitrile and DMF were eluted at 0.6 mL/min during operation at a composition of 80:20, respectively. Mass spectrometry was performed on a JEOL AccuTOF-DART mass spectrometer with a DART-ion source (no solvent required).

3.2.2 Preparation.

3.2.2.1 Bromo(subphthalocyanato)boron(III) (Br-BsubPc).

Br-BsubPc was synthesized according to the procedure of Potz et al. (24) On train sublimation (32) diffractable crystals were obtained which were determined to be (H₂O)₀.₂₅•μ-oxo-(BsubPc)₂.
3.2.2.2 Hydroxy(subphthalocyanato)boron(III) (HO-BsubPc) (Method (i) Scheme 3.1).

Br-BsubPc (1.063 g, 0.0022 mol) was added to DMSO (120 mL), water (8 mL, 0.444 mol) and pyridine (4 mL, 0.0496 mol) in a 250 mL three necked round bottom flask. The mixture was heated to 60°C for 24 hours with stirring. After 24 hours, the heat was turned off and the mixture was added to 360mL of distilled water. This was allowed to stand overnight, and was filtered the next day to remove HO-BsubPc as a fine precipitate which was then placed in a vacuum oven overnight (40°C, 10 mmHg). Yield: 0.587 g (61.3%). HPLC R\(_T\): 1.790 min; UV-Vis: 557.4 nm; \(^1\)H NMR (400 MHz, CDCl\(_3\), Me\(_4\)Si) 8.77-8.83 (m, 6H), 7.85-7.91 (m, 6H), -1.13 (s, 1H).

3.2.2.3 \(\mu\)-oxo-bis[(subphthalocyanato)boron(III)] (\(\mu\)-oxo-(BsubPc)\(_2\)) (Method (ii) Scheme 3.1).

1,2-Dichlorobenzene (1.4 mL) was added to Br-BsubPc (0.200 g, 4.21 \times 10^{-4} mol) in a 4 Dram (15 mL) vial fitted with a condenser. One drop of water was added initially and the mixture was heated at reflux (181°C). The reaction progress was monitored by HPLC. A positive pressure of argon was maintained in the vessel throughout the experiment. Additional drops of water were added during the reaction such that the proportion of HO-BsubPc was approximately equal to that of Br-BsubPc by HPLC analysis. After 24 hours Br-BsubPc was no longer detectable by HPLC and the reaction was cooled to room temperature. On standing in the dark for a prolonged period of time, diffractable crystals were formed on the vial walls and on the stir bar. They were determined to be (DCB)\(_2\)• \(\mu\)-oxo-(BsubPc)\(_2\). No further workup was performed.

3.2.2.4 \(\mu\)-oxo-bis[(subphthalocyanato)boron(III)] (\(\mu\)-oxo-(BsubPc)\(_2\)) (Method (iii) Scheme 3.1).

Adapted from the method of Mori et al.:\(^{53}\) 1,2-Dichlorobenzene (1.5 mL) was added to HO-BsubPc (0.100 g, 2.43 \times 10^{-4} mol) and Br-BsubPc (0.115 g, 2.43 \times 10^{-4} mol) in a 4 Dram (15 mL) vial fitted with a condenser and heated at reflux (181°C). A positive pressure of argon was maintained in the vessel throughout the experiment. The reaction progress was monitored by HPLC. After 20 hours the reaction was cooled to room temperature. The solvent was removed by rotary evaporation, and the solid was then placed in a vacuum oven overnight to dry (40°C, 10 mmHg). (Yield: 0.298 g (>100 %); HPLC R\(_T\): 2.88 min (56.5%, at 545 nm)). The crude solid was then purified by Kauffman column using alumina as the stationary phase and dichloromethane as the mobile phase. A first fraction contained an unknown impurity (HPLC R\(_T\): 2.0 min) and the second fraction (stopped collection after 3 hours) was a mixture of the same
impurity (HPLC R_T: 2.0 min) and µ-oxo-(BsubPc)_2. The solvent of the second fraction was removed by rotary evaporation, and the solid was then placed in a vacuum oven overnight (40°C, 10 mmHg). (Yield: 0.090 g (46 %)). The solid (0.088 g) was train sublimed at 450°C. A pink film at the end of the tube first became visible at 350°C. Pure crystals were obtained/removed by gentle tapping of the glass tube (Yield: 0.031 g (15.8%)). These crystals were confirmed to be µ-oxo-(BsubPc)_2^ubl.

3.2.2.5 µ-oxo-bis[(subphthalocyanato)boron(III)] (µ-oxo-(BsubPc)_2) (Method (iii), larger scale, Scheme 3.1).

Method (iii) was subsequently scaled-up by a factor of 5 as follows: 1,2-Dichlorobenzene (1.5 mL) was added to HO-BsubPc (0.500 g, 1.21 × 10^{-3} mol) and Br-BsubPc (0.576 g, 1.21 × 10^{-3} mol) in a scintillation vial (20 mL) fitted with a condenser and heated at reflux (181°C) for 31 hours. A positive pressure of argon was maintained in the vessel throughout the experiment. It was observed that on cooling and if left stationary in the dark that visible crystals would form on the vial walls and on the stir bar as above. These crystals were determined to be (DCB)_2• µ-oxo-(BsubPc)_2. No further workup was performed.

Scheme 3.1. Synthesis of µ-oxo-(BsubPc)_2. Conditions: (i) Water, pyridine, DMSO, 60 °C. (ii) 1,2-Dichlorobenzene, water (trace), reflux. (iii) 1,2-Dichlorobenzene, reflux.

3.2.3 X-ray Diffraction and Depiction.

All crystal structures were collected using computer-controlled KappaCCD system and an Oxford Cryostream variable temperature apparatus. Additional details: Data collection: COLLECT;{66} cell refinement: DENZO-SMN;{67} data reduction: DENZO-SMN; program(s) used to solve structure: SIR92;{68} program used to refine structure: SHELXTL;{69} molecular
graphics, molecular visualization and parameter measurements: Mercury,\(^{(70)}\)–\(^{(72)}\) software used to prepare material for publication: SHELXTL;\(^{(69)}\) s.u. values on calculated parameters: OLEX2.\(^{(73)}\)

### 3.3 Results and Discussion.

This study was initiated when we attempted to train sublime\(^{(32)}\) bromo-boron subphthalocyanine (Br-BsubPc, 1, Scheme 3.1). Instead of acquiring high purity Br-BsubPc we found single crystals within the crucible. Diffraction of these crystals revealed that they were in fact partially hydrated \(\mu\)-oxo-(BsubPc)\(_2\) \(\mu\)-oxo-(BsubPc)\(_2\)•0.25H\(_2\)O, Figure 3.1a, Table 3.1). We presumed that these were formed by reaction of Br-BsubPc with the trace amounts of water present in the nitrogen gas used for train sublimation to produce HO-BsubPc followed by self-condensation to \(\mu\)-oxo-(BsubPc)\(_2\); the self-condensation of HO-BsubPc is known to occur in the solid state at high temperature.\(^{(24)}\) \(\mu\)-oxo-(BsubPc)\(_2\)•0.25H\(_2\)O crystallized in a P 1 \(\bar{1}\) space group (Figure 3.1a, Table 3.1, with a summary of all intermolecular interactions given in Table 3.2–Table 3.5). What is perhaps most interesting about the crystal structure is that water is present in the crystal lattice and hydrogen bonded to two \(\mu\)-oxo-(BsubPc)\(_2\) molecules through one of the imine nitrogens of the subPc heterocyclic triazaborinine ring (N3, N5, N...O distance of 2.95(1) Å and 3.04(1) Å respectively, Table 3.4, Figure 3.1c). The imine nitrogens have once before been shown to be capable of forming hydrogen bonds in the reported crystal structure of HO-BsubPc.\(^{(24)}\) Finally, the \(\mu\)-oxo-(BsubPc)\(_2\)•0.25H\(_2\)O crystal structure shows \(\pi\)–\(\pi\) and C-H...\(\pi\) interactions between the isoindoline fragments of neighbouring subPc heterocyclic rings at distances under 4 Å (Table 3.2 and Table 3.3). Notably, the isoindolines comprising N4, N10 and N12 (Figure 3.1b; see numbering Figure 3.1a) show \(\pi\)–\(\pi\) interactions with their nearest neighbours (symmetry operations (1-x, 1-y, -z), (-x, -y, -z) and (-x, -y, 1-z) respectively) in a concaved-to-concaved manner (for N4 and N12 at a distance of 3.8215(19) Å and 3.6806(17) Å) or a convex-to-convex manner (for N10 at a distance 3.5319(18) Å). This type of intermolecular association between isoindoline fragments is very common in the solid state arrangement of BsubPcs\(^{(50)}\) and we have previously compiled a survey of the known crystals of BsubPcs for reference.\(^{(32)}\)(\(^{(34)}\). These interactions typically result in a one dimensional ribbon motif, however in this case each BsubPc is covalently bound to another BsubPc and thus the ribbons are linked together resulting in a two dimensional motif.
We subsequently undertook a preliminary survey of synthetic methods to directly synthesize \( \mu \)-oxo-(BsubPc)\(_2\). Initially we focused on two possible synthetic routes. The first was the hydrolysis of Br-BsubPc and \textit{in situ} self condensation to \( \mu \)-oxo-(BsubPc)\(_2\) (route (ii) in Scheme 3.1) mimicking what had occurred on sublimation of Br-BsubPc. The second was the hydrolysis of Br-BsubPc to HO-BsubPc followed by reaction with equal molar quantities of Br-BsubPc to give \( \mu \)-oxo-(BsubPc)\(_2\) (route (iii) in Scheme 3.1). The latter method was outlined in a recent patent application.\(^{(53)}\) Br-BsubPc was chosen as a common precursor as we understood that its hydrolysis was much more facile than that of Cl-BsubPc.\(^{(64)}\)
The first synthetic method attempted to replicate the conditions which occurred in the train sublimation apparatus. We took Br-BsubPc, placed it in dichlorobenzene and added water to wet the solvent (no stoichiometric control, method (ii) in Scheme 3.1). On heating, indeed we observed the formation of \( \mu \text{-oxo-}(\text{BsubPc})_2 \) which can easily be detected using standard HPLC methods with UV-Vis spectroscopic detection (see Experimental section). At the end of the heating period the composition of the reaction mixture was 61% \( \mu \text{-oxo-}(\text{BsubPc})_2 \) and 39% other unidentified BsubPc derivatives (Table 3.6, identifiable as BsubPcs due to their absorption spectrum). We observed that on standing single crystals precipitated from the reaction mixture. Diffraction of these crystals revealed that they were the dichlorobenzene solvate of \( \mu \text{-oxo-}(\text{BsubPc})_2 \) (\( \mu \text{-oxo-}(\text{BsubPc})_2 \cdot 2\text{DCB}, \) Table 3.2a, Table 3.1, with a summary of all intermolecular interactions given in Table 3.2–Table 3.5). \( \mu \text{-oxo-}(\text{BsubPc})_2 \cdot 2\text{DCB} \) also crystallized in a P1 space group. Though DCB and toluene are both aromatic solvents, the DCB solvate is very different than what was observed for the toluene solvate \( \mu \text{-oxo-}(\text{BsubPc})_2 \cdot 3\text{toluene}. \) Most notably the DCB solvate has two solvent molecules incorporated into its crystal instead of three toluene molecules for the toluene solvate, and the molecular conformation in the two structures is different. There are also several halogen – \( \pi \) intermolecular interactions observed in the DCB structure due to the halogenated solvate molecules (Table 3.5). What is similar is that the solid state arrangement of \( \mu \text{-oxo-}(\text{BsubPc})_2 \cdot 0.25\text{H}_2\text{O} \) is dominated by the aforementioned \( \pi-\pi \) interactions (Table 3.2) between isoindoline fragments of neighbouring molecules (symmetry operation (-x, 1-y, 1-z), (-x, -y, -z), and (-x, -y, 2-z) for N2, N6 and N10 interaction, respectively). In this case interactions were noted between the concave-concave faces of neighbouring isoindoline fragments comprised of N2 and N10 (distance of 3.769(2) Å and 3.557(2) Å respectively) and between the convex faces of neighbouring isoindoline fragments comprised of N6 (distance of 3.472(2) Å). The same two dimensional motif is observed as in \( \mu \text{-oxo-}(\text{BsubPc})_2 \cdot 0.25\text{H}_2\text{O} \). Regarding the synthetic method for the production of \( \mu \text{-oxo-}(\text{BsubPc})_2 \), we found that it was not particularly clean, producing several unidentified BsubPc byproducts (Table 3.6). The removal of the by-products has proved challenging and we do not believe the described precipitation method is an efficient nor effective way to achieve a high yield of pure \( \mu \text{-oxo-}(\text{BsubPc})_2 \).
We then took equal molar amounts of HO-BsubPc and Br-BsubPc and heated them also in dichlorobenzene (method (iii) in Scheme 3.1). This method, alluded to in the patent application of Mori et al.,\(^{(53)}\) also produced \(\mu\)-oxo-(BsubPc)\(_2\) although again also coproduced significant amounts of by-products including the same unidentified BsubPc by-products albeit with a different compositional profile (Table 3.6). On sitting, crystallographically identical single crystals of the DCB solvate described above (\(\mu\)-oxo-(BsubPc)\(_2\)•2DCB) can be obtained. Subsequent Kauffman column chromatography\(^{(57)}\) of the crude mixture removed the small amount of the impurity with \(R_T\) 3.4 min, the remaining HO-BsubPc and the other unidentified BsubPc impurities (no Br-BsubPc was present). Surprisingly the remaining mixture of \(\mu\)-oxo-(BsubPc)\(_2\) and the impurity with \(R_T\) 2.0 min was able to be train sublimed allowing for the isolation of pure \(\mu\)-oxo-(BsubPc)\(_2\) (31 mg, 15.8 % overall yield). Crystals obtained from train sublimation were examined by x-ray diffraction and were shown to be exclusively \(\mu\)-oxo-(BsubPc)\(_2\) (\textit{not} solvated and \textit{not} hydrated, denoted \(\mu\)-oxo-(BsubPc)\(_2\)\textsubscript{subl} Figure 3.3a, Table 3.1) in a monoclinic C2/c space group. This is very different than either the hydrated or solvated (toluene or DCB) crystal structures described above in both its basic crystallographic parameters and also in its solid state arrangement.
Figure 3.3. (a) Thermal ellipsoid plot of \( \mu\text{-oxo-(BsubPc)}_2 \) (35\% probability level); (b) Populated unit cell of \( \mu\text{-oxo-(BsubPc)}_2 \) with nearest neighbour interactions. Members of the unit cell are illustrated in elemental colouring (carbon – gray; nitrogen – blue; oxygen – red; boron – pink). Centroids of isoindoline fragments interacting with nearest neighbours (containing N6) shown in magenta; centroids of closest intramolecular isoindoline fragments (containing N2, N4) shown in green; (c) Picture of the extended solid state arrangement of \( \mu\text{-oxo-(BsubPc)}_2 \) along the a- and c-crystallographic axis; (d) Picture of the extended solid state arrangement of \( \mu\text{-oxo-(BsubPc)}_2 \) along the a- and b-crystallographic axis. Hydrogens are omitted for clarity.

The solid state arrangement of \( \mu\text{-oxo-(BsubPc)}_2 \) is still dominated by the existence of \( \pi-\pi \) interactions between isoindoline fragments within the unit cell at a distance of 3.575(3) Å (between isoindoline fragments containing N6 on neighbouring molecules with symmetry operation \( \frac{1}{2}-x, \frac{1}{2}-y, -z \); Figure 3.3b, Table 3.2). No convex-to-convex interaction is observed, and thus the motif of the non-solvated crystal is one dimensional in contrast to the two dimensional motif seen in both solvated structures. However, adding to the uniqueness of \( \mu\text{-oxo-(BsubPc)}_2 \), the two pairs of isoindoline rings containing N2 and N4 within a single isolated \( \mu\text{-oxo-(BsubPc)}_2 \) molecule eclipse one another at a marginal distance of 3.987(3) Å (Figure
This results in an orientation whereby each of the two subPc fragments of the molecule are equivalent by C₂ symmetry (the second generated from the first by the symmetry operation (1-x, y, ½-z)). The unique spectroscopic characteristics of μ-oxo-(BsubPc)₂ alluded to above are attributable to this close interaction between two subPc fragments within the μ-oxo-(BsubPc)₂ molecule and are not seen in the other crystal structures presented herein (nor in μ-oxo-(BsubPc)₂•3toluene).

The difference in the arrangement between each BsubPc fragment in μ-oxo-(BsubPc)₂ subl compared with the other solvated μ-oxo-(BsubPc)₂ crystal structures discussed herein can be quantified by considering a pair of torsion angles within μ-oxo-(BsubPc)₂ (Table 3.7). We will denote α and β for the BsubPc fragments containing B1 and B2 respectively. As outlined in Table 3.8, the B-O-B angle in each structure is relatively constant. Additionally, each BsubPc fragment retains the C₃ᵥ symmetry characteristic of BsubPcs. Therefore, the conformation of μ-oxo-(BsubPc)₂ can be treated as a two equivalent C₃ᵥ bent rotor molecule with two freely rotating C₃ᵥ units attached to a rigid B-O-B axis, analogous to dimethyl ether or acetone. With this model, the z-molecular axis passes through the central O bisecting the B-O-B angle, the y-molecular axis is aligned with the Bα...Bβ line and the x-molecular axis is perpendicular to the B-O-B plane (Figure 3.4(a)). The two BsubPc fragments are free to rotate around the fixed B-O bonds, and the torsion angle N-B-O-B describes the clockwise rotation of a pyrrole nitrogen, and corresponding isoindoline fragment, away from the B-O-B plane (Figure 3.4(a)). Any rotation of 120° of a BsubPc fragment yields an equivalent conformation due to its C₃ᵥ symmetry, so the torsion angle within ±60° fully describes the rotational position. The combination of this torsion from the α-BsubPc (ωₐ) and the β-BsubPc (ω₇) fully describes the conformation of the μ-oxo-(BsubPc)₂ molecule within the crystal. Additionally, the degree to which the α and β isoindoline lobes eclipse one another or are interdigitated can be described by the pseudo-torsion angle Nα-Bα...Bβ-Nβ, which is equivalent to the sum of ωₐ and ω₇ under the assumption of rigid C₃ᵥ BsubPc symmetry. The pseudo-torsion angle of a conformation in which the isoindoline lobes are fully eclipsed is 0° while the maximum offset between interdigitated isoindoline lobes corresponds to a pseudo-torsion angle of ±60° (‘eclipsed’ and ‘staggered’ conformation respectively).

The conformation of a two bent rotor molecule can adopt three possible ideal symmetries: Cₛ, C₂ and C₂ᵥ. These can be plotted on a scatterplot which comprises a map of all possible
Conformations of µ-oxo-(BSubPc)₂ \(^{(75)}\). Conformations at \((0°,0°)\) and at \((±60°,±60°)\) have C\(_{2v}\) symmetry. C\(_{s}\) symmetry is found at \((0°,0°)\), \((0°,±60°)\) and \((±60°,0°)\) with a mirror plane perpendicular to the x-molecular axis, and also at all points \((ω_β = -ω_α)\) with a mirror plane perpendicular to the y-molecular axis. The latter also corresponds to an eclipsed conformation since the sum of \(ω_α\) and \(ω_β\) is zero. C\(_2\) symmetry exists when \(ω_α\) and \(ω_β\) are equal, at all points \((ω_β = ω_α)\). In the staggered conformation the sum of \(ω_α\) and \(ω_β\) is \(±60°\), located on the plot at all points \((ω_β = 60-ω_α)\) and \((ω_β = -60-ω_α)\). These positions are all identified on a conformational map in Figure 3.4(b), where the torsion angles of the µ-oxo-(BSubPc)₂ structures are plotted.

![Figure 3.4(a) Selected torsion angles and coordinate system used to describe the conformation of µ-oxo-(BSubPc)₂ within the crystals. Red plane is defined by B\(_α\), O, B\(_β\) atoms. (b) Conformational map of µ-oxo-(BSubPc)₂ crystal structures. (■) - µ-oxo-(BSubPc)₂·0.25H₂O; (●) - µ-oxo-(BSubPc)₂·2DCB; (▲) - µ-oxo-(BSubPc)₂·3toluene\(^{(65)}\). This plot facilitates a comparison of the observed µ-oxo-(BSubPc)₂ conformations. The position of µ-oxo-(BSubPc)₂·0.25H₂O lies close to the line of C\(_2\) symmetry, with similar values of \(ω_α\) and \(ω_β\) (\(ω_α = 34.4(5)°\), \(ω_β = 43.4(5)°\), Table 3.7, Figure A1.1). Additionally, it lies in between but closer to a line of staggered than eclipsed conformation, and correspondingly its smallest pseudo-torsion angle is \(-40.0(3)°\) (Table 3.7) representing the offset between interdigitated isoindoline lobes (maximum possible offset is \(±60°\)). Conformationally this means that the lobe of the one isoindoline on the α-BSubPc is interdigitated in space between the other two isoindoline units on
the β-BsubPc. The toluene solvated structure does not fall close to any conformation with ideal symmetry. However, the μ-oxo-(BsubPc)$_2$•3toluene$^{(65)}$ and μ-oxo-(BsubPc)$_2$•0.25H$_2$O points appear to be on a line parallel to the ‘eclipsed’ conformational line, and indeed the smallest pseudo-torsion angle of the toluene solvated crystal structure is strikingly similar to that of the hydrate at -37.6(2)$^\circ$ (Table 3.7, Figure A1.2). Therefore, the offset of the α and β isoindoline lobes is equivalent in both of these structures. In comparison, the μ-oxo-(BsubPc)$_2$•2DCB conformation lies much closer to a ‘staggered’ line, and its smallest pseudo-torsion angle of 52.0(4)$^\circ$ (Table 3.7) approaches the maximum possible offset between the α and β isoindoline lobes (Figure A1.3). In this conformation, the BsubPc fragments are rotated to minimize the degree of overlap of the α and β isoindoline lobes when viewed down the y-molecular axis. The molecule as a whole does not lie near any point of ideal symmetry defined above. However, an approximate mirror plane (defined by the atoms N2, B1, B2 and N10) can be identified when viewed down the y-molecular axis which forms a dihedral angle of 18.2(4)$^\circ$ with the yz molecular plane (Figure A1.3b). The oxygen atom is situated at a perpendicular distance of 0.205(4) Å from this plane (Figure A1.3c). As the only structure that has a symmetry element in the crystal, μ-oxo-(BsubPc)$_2$subl lies on the line of C$_2$ symmetry by definition, but Figure 3.4(b) shows that it also lies very near a point of C$_{2v}$ symmetry, which is the highest possible symmetry for the μ-oxo-(BsubPc)$_2$ molecule. The approximate C$_{2v}$ symmetry of μ-oxo-(BsubPc)$_2$subl is confirmed by its $\omega_{\alpha,\beta} \sim \pm 60^\circ$, at -57.7(7)$^\circ$, and a smallest pseudo-torsion angle close to zero, at 5.8(4)$^\circ$ (Table 3.7, Figure A1.4a). In this conformation, the α- and β-BsubPcs are almost fully eclipsed, as seen when viewed along the molecular y-axis (Figure A1.4b), and two mirror planes are clearly identifiable when viewed down the molecular z-axis (Figure A1.4c). In total, the three structures reported here represent all possible symmetries of μ-oxo-(BsubPc)$_2$. Both possible extremes of mutual orientation of the α and β isoindoline lobes within the molecule were also observed; in μ-oxo-(BsubPc)$_2$subl the lobes are fully eclipsed, while in μ-oxo-(BsubPc)$_2$•2DCB they are oriented with maximum possible offset. In addition, a partially interdigitated orientation was seen in both μ-oxo-(BsubPc)$_2$•0.25H$_2$O and μ-oxo-(BsubPc)$_2$•3toluene. The observation of three mutual orientations of the α and β isoindoline lobes within the molecule (fully eclipsed, maximum offset and partially offset) suggests that degree of overlap of α and β isoindoline lobes is not the only or the major driver of molecular conformation. It is also interesting to note that the mutual orientation of isoindolines is equivalent in μ-oxo-(BsubPc)$_2$•0.25H$_2$O and μ-oxo-(BsubPc)$_2$•3toluene while the structures do not share other characteristics.
Figure 3.5. Selected geometrical measurements for $\mu$-oxo-(BsubPc)$_2$ crystal structures, showing (a) pyrrole plane depth (b) imine plane depths and (c) bowl depth, B-O-B bond angle and angle between $\alpha$- and $\beta$-BsubPc planes.

Other geometric parameters can be examined and compared. The BsubPc fragment includes three pyrrole nitrogens complexing the boron atom and three imine nitrogens (mentioned above). The boron is located above two planes, the first defined by the three pyrrole nitrogens and the second by the three imine nitrogens. The relative geometries of the BsubPc fragments in each of $\mu$-oxo-(BsubPc)$_2$$\cdot$0.25H$_2$O, $\mu$-oxo-(BsubPc)$_2$$\cdot$2DCB, $\mu$-oxo-(BsubPc)$_2$$_{\text{subl}}$ and $\mu$-oxo-(BsubPc)$_2$$\cdot$3toluene$^{(65)}$ can thus be described by two parameters: pyrrole plane depth, defined as the perpendicular distance from the boron atom to a plane defined by the three pyrrole nitrogens (N2|N4|N6 Figure 3.5a, Table 3.8); and imine plane depth, defined as the perpendicular distance from the boron atom to a plane defined by the three imine nitrogens (N1|N3|N5 Figure 3.5b, Table 3.8). The observed values of both parameters are very similar in the $\alpha$-BsubPc and $\beta$-BsubPc ligand of each crystal (within 0.013 Å of one another). The pyrrole plane depth varies from a minimum of 0.642(4) Å in the $\beta$-BsubPc of $\mu$-oxo-(BsubPc)$_2$$\cdot$0.25H$_2$O to a maximum of 0.653(6) Å in $\mu$-oxo-(BsubPc)$_2$$_{\text{subl}}$. Imine plane depth varies from 1.192 Å in the $\alpha$-BsubPc of $\mu$-oxo-(BsubPc)$_2$$\cdot$3toluene$^{(65)}$ to 1.238(6) Å in $\mu$-oxo-(BsubPc)$_2$$_{\text{subl}}$. Therefore, there is no significant difference in the BsubPc fragment for the four $\mu$-oxo-(BsubPc)$_2$ structures. If we calculate a plane comprising the outermost carbons of each isoindoline lobe
(C4\(\text{C5C12C13C20C21}\), Figure 3.5c) for each of the \(\alpha\)-BsubPc and \(\beta\)-BsubPc ligands we can look at two additional geometric parameters; the BsubPc bowl depth and the angle between the \(\alpha\) and \(\beta\) planes (Table 3.8) in each crystal. The bowl depth is defined as the perpendicular distance between the plane and the boron atom of the BsubPc. In the cases of \(\mu\)-oxo-(BsubPc)_2\(\cdot\)0.25H\(_2\)O and \(\mu\)-oxo-(BsubPc)_2\(\cdot\)2DCB the \(\alpha\) and \(\beta\) subPc ligands are not related by symmetry and bowl depths of 2.741(4) Å|2.738(4) Å and 2.641(4) Å|2.686(5) Å are seen (respectively). The observed bowl depths are common with the range which can be observed for other BsubPc derivatives. A similar comment can be made if you include \(\mu\)-oxo-(BsubPc)_2\(\cdot\)3toluene\(^{65}\) in the discussion.

If we then consider the angle between the \(\alpha\) and \(\beta\) planes, it varies widely from a high of 46.09(6)° for \(\mu\)-oxo-(BsubPc)_2\(\text{subl}\) to 29.17(3)° for \(\mu\)-oxo-(BsubPc)_2\(\cdot\)0.25H\(_2\)O and does not correlate to the measured B-O-B bond angles and any associated strain the B-O-B angles have from ideality (Table 3.8). Therefore we must conclude that \(\mu\)-oxo-(BsubPc)_2\(\text{subl}\) is not remarkable in these regards compared to other structures reported herein nor to the structure of \(\mu\)-oxo-(BsubPc)_2\(\cdot\)3toluene\(^{65}\).

The known crystal structure of the \(\mu\)-oxo-(BsubPc)_2 dication described by Kato \textit{et al}\(^{54}\) has been excluded from this discussion for two reasons. The first is that the crystal is highly solvated with a mixture of toluene and dichlorobenzene (the solvent present is also highly disordered) and more importantly contains two large carborane counterions per \(\mu\)-oxo-(BsubPc)_2 molecule. The presence of such large amounts of excess molecules in the crystal likely distorts the conformation of \(\mu\)-oxo-(BsubPc)_2. Secondly, Kato \textit{et al} notes the distortion of the BsubPc fragment (indicated by an elongated C-N bond) due to the formation of the dication by protonation thus tainting any geometric comparisons to the three crystal structure discussed herein.

However, what is perhaps most notable is that \(\mu\)-oxo-(BsubPc)_2 adopts a solid-state arrangement on sublimation which has extremely high density for a BsubPc derivative of any type (either the other \(\mu\)-oxo-(BsubPc)_2s reported herein or more generally). We have calculated the crystal density of \(\mu\)-oxo-(BsubPc)_2\(\text{subl}\) to be 1.45 Mg/m\(^3\) or converted to a molar basis 1.80 kmol/m\(^3\). Adjusting this number to represent the number of BsubPc chromophores present increases the value to 3.60 kmol/m\(^3\). By comparison the chromophore density of the remaining \(\mu\)-oxo-(BsubPc)_2s reported herein are 3.50 and 2.61 kmol/m\(^3\) for \(\mu\)-oxo-(BsubPc)_2\(\cdot\)0.25H\(_2\)O and \(\mu\)-oxo-
(BsubPc)₂•2DCB respectively and for comparison the chromophore density of µ-oxo-(BsubPc)₂•3toluene is 2.37 kmol/m³. If we compare more broadly across other sub-classes of BsubPc derivatives the halo-BsubPcs (which contain an axial halide ligand) range from 3.56 to 2.88 kmol/m³ and BsubPcs containing a variety of hydrocarbon substituents in the axial position range from ~3 to ~2 kmol/m³ (Table A1.1). The high density can be directly attributed to the lack of atomic mass associated with the chromophore (only ½ oxygen atom per chromophore) and the non-solvated nature of µ-oxo-(BsubPc)₂subl. The survey of crystal densities and the method for conversion to molar equivalent chromophore density is outlined in Appendix 1. It is this high chromophore density which makes the sublimed form of µ-oxo-(BsubPc)₂ attractive for further study in organic electronic devices and surrogates.²³,³⁴,⁷⁶

3.4 Conclusions.

In conclusion, the solvent and water free crystal structure of µ-oxo-(BsubPc)₂subl is reported. Unique to this structure compared to the partially hydrated or solvated structures is the spatial arrangement of the individual BsubPc molecular fragments. The arrangement noted for µ-oxo-(BsubPc)₂subl is consistent with the observed unique spectroscopic characteristics previously reported. Coupled with this, the solid state arrangement of µ-oxo-(BsubPc)₂subl is of high symmetry and has an unusually high density for a BsubPc derivative of any type thus making it attractive for further study as a functional material in organic electronic devices. Finally, while not the focus of this report, some comments are made, based on preliminary observations, regarding suitable preparatory methods of µ-oxo-(BsubPc)₂subl in dichlorobenzene solvent which may yield larger quantities of µ-oxo-(BsubPc)₂subl at higher crude and final purities.

Acknowledgements

We acknowledge the financial support from the National Sciences and Engineering Research Council (NSERC) for providing support in the form of a Discovery Grant (T.P.B.).
Table 3.1. Selected crystallographic experimental parameters and details for \(\mu\text{-oxo-(BsubPc)}\text{\textsubscript{2}}\cdot0.25\text{H}_{2}\text{O}, \mu\text{-oxo-(BsubPc)}\text{\textsubscript{2}}\cdot2\text{DCB}\) and \(\mu\text{-oxo-(BsubPc)}\text{\textsubscript{2}}^{\text{subl}}\). Details: Experiments were carried out with Mo K\(\alpha\) radiation using a Nonius KappaCCD diffractometer. Absorption was corrected for by multi-scan methods, multi-scan from symmetry-related measurements SORTAV.\(^{(77)}\) H-atom parameters were constrained.

<table>
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<th>(\mu\text{-oxo-(BsubPc)}\text{\textsubscript{2}}\cdot0.25\text{H}_{2}\text{O})</th>
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<th>(\mu\text{-oxo-(BsubPc)}\text{\textsubscript{2}}^{\text{subl}})</th>
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<td>(\text{C}<em>{48}\text{H}</em>{24}\text{B}<em>{2}\text{N}</em>{12}\text{O})</td>
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<tr>
<td>(M_r)</td>
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<td>Triclinic, (P\bar{1})</td>
<td>Monoclinic, (C_2/c)</td>
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<td>(a, b, c) (Å)</td>
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<td>25.6932 (18), 8.3375 (5), 20.8860 (16)</td>
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<td>2541.89 (12)</td>
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<td>0.34 × 0.16 × 0.08</td>
<td>0.20 × 0.10 × 0.10</td>
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</table>

**Data collection**

|                     |                                                 |                                                 |                 |
|---------------------|-------------------------------------------------|-------------------------------------------------|                 |
| \(T_{\text{min}}\), \(T_{\text{max}}\)    | 0.561, 0.653                                    | 0.808, 0.985                                    | 0.561, 1.007 |
| No. of measured, independent and observed \([I > 2\sigma(I)]\) reflections | 35416, 8597, 3742 | 26858, 11383, 6168 | 12572, 3233, 1908 |
| \(R_{\text{int}}\) | 0.113                                           | 0.076                                           | 0.138           |

**Refinement**

|                     |                                                 |                                                 |                 |
|---------------------|-------------------------------------------------|-------------------------------------------------|                 |
| \(R[F^2 > 2\sigma(F^2)], wR(F^2), S\) | 0.067, 0.214, 0.96 | 0.085, 0.217, 1.01 | 0.088, 0.229, 1.09 |
| No. of reflections  | 8597                                            | 11383                                           | 3233            |
| No. of parameters  | 578                                             | 738                                             | 285             |
| No. of restraints  | 0                                               | 48                                              | 0               |
| \(\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}\) (e Å\(^{-3}\)) | 0.29, −0.29 | 0.83, −0.49 | 0.47, −0.30 |

Computer programs: Collect;\(^{(66)}\) DENZO-SMN;\(^{(67)}\) DENZO-SMN, SIR92;\(^{(68)}\) SHELXL V6.1,\(^{(69)}\) PLATON;\(^{(78)}\)

Table 3.2 \(\pi\text{-}\pi\) interactions (Å\(^2\)).

<table>
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<th>Ring J</th>
<th>Cg(I)…Cg(J)</th>
<th>Dihedral angle</th>
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<td>4.71(16)</td>
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<td></td>
<td>C34-C39</td>
<td>C34-C39^u</td>
<td>3.650(2)</td>
<td>0</td>
</tr>
<tr>
<td>------------</td>
<td>----------</td>
<td>------------</td>
<td>----------</td>
<td>---------</td>
</tr>
<tr>
<td>µ-oxo-(BsubPc)_2•2DCB</td>
<td>N2/C1/C2/C7/C8</td>
<td>C2-C7^iv</td>
<td>3.769(2)</td>
<td>4.14(19)</td>
</tr>
<tr>
<td></td>
<td>N6/C17/C18/C23/C24</td>
<td>C18-C23^u</td>
<td>3.472(2)</td>
<td>2.1(2)</td>
</tr>
<tr>
<td></td>
<td>N10/C33/C34/C39/C40</td>
<td>C34-C39^v</td>
<td>3.557(2)</td>
<td>2.2(2)</td>
</tr>
<tr>
<td></td>
<td>C18-C23</td>
<td>C18-C23^u</td>
<td>3.813(2)</td>
<td>0</td>
</tr>
<tr>
<td>µ-oxo-(BsubPc)_2 subl</td>
<td>N6/C17/C18/C23/C24</td>
<td>C18-C23^v</td>
<td>3.575(3)</td>
<td>1.4(3)</td>
</tr>
<tr>
<td></td>
<td>C18-C23</td>
<td>C18-C23^v</td>
<td>3.818(3)</td>
<td>0</td>
</tr>
</tbody>
</table>

Symmetry codes: (i) 1-x,1-y,-z; (ii) -x,-y,-z; (iii) -x,-y,1-z; (iv) -x,-y,2-z; (v) 1-x,y,½-z; (vii) ½-x,½-y,-z

Table 3.3. C-H...π interactions (Å,°).

<table>
<thead>
<tr>
<th>X</th>
<th>H</th>
<th>Ring J</th>
<th>H...Cg(J)</th>
<th>X-H...Cg(J)</th>
<th>X...Cg(J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>µ-oxo-(BsubPc)_2•0.25H_2O</td>
<td>C12</td>
<td>H12</td>
<td>N6/C17/C18/C23/C24^i</td>
<td>2.87</td>
<td>105</td>
</tr>
<tr>
<td></td>
<td>C12</td>
<td>H12</td>
<td>C18-C23^i</td>
<td>2.99</td>
<td>134</td>
</tr>
<tr>
<td></td>
<td>C13</td>
<td>H13</td>
<td>N2/C1/C2/C7/C8^i</td>
<td>2.85</td>
<td>111</td>
</tr>
<tr>
<td></td>
<td>C30</td>
<td>H30</td>
<td>N4/C9/C10/C15/C16^vim</td>
<td>2.95</td>
<td>170</td>
</tr>
<tr>
<td></td>
<td>C30</td>
<td>H30</td>
<td>C10-C15^vim</td>
<td>2.68</td>
<td>131</td>
</tr>
<tr>
<td></td>
<td>C44</td>
<td>H44</td>
<td>N8/C25/C26/C31/C32^vim</td>
<td>2.73</td>
<td>118</td>
</tr>
<tr>
<td></td>
<td>C44</td>
<td>H44</td>
<td>C26-C31^vim</td>
<td>2.87</td>
<td>148</td>
</tr>
<tr>
<td></td>
<td>C45</td>
<td>H45</td>
<td>N10/C33/C34/C39/C40^vim</td>
<td>2.79</td>
<td>127</td>
</tr>
<tr>
<td>µ-oxo-(BsubPc)_2•2DCB</td>
<td>C4</td>
<td>H4</td>
<td>N4/C9/C10/C15/C16^iv</td>
<td>2.84</td>
<td>115</td>
</tr>
<tr>
<td></td>
<td>C5</td>
<td>H5</td>
<td>N6/C17/C18/C23/C24^iv</td>
<td>2.77</td>
<td>107</td>
</tr>
<tr>
<td></td>
<td>C5</td>
<td>H5</td>
<td>C18-C23^iv</td>
<td>2.98</td>
<td>138</td>
</tr>
<tr>
<td></td>
<td>C9s</td>
<td>H9s</td>
<td>C34-C39^iv</td>
<td>2.92</td>
<td>174</td>
</tr>
<tr>
<td></td>
<td>C36</td>
<td>H36</td>
<td>N12/C41/C42/C47/C48^v</td>
<td>2.72</td>
<td>121</td>
</tr>
<tr>
<td></td>
<td>C37</td>
<td>H37</td>
<td>N8/C25/C26/C31/C32^v</td>
<td>2.72</td>
<td>119</td>
</tr>
<tr>
<td>µ-oxo-(BsubPc)_2 subl</td>
<td>C20</td>
<td>H20</td>
<td>N2/C1/C2/C7/C8^vii</td>
<td>2.72</td>
<td>135</td>
</tr>
<tr>
<td></td>
<td>C21</td>
<td>H21</td>
<td>N4/C9/C10/C15/C16^vii</td>
<td>2.68</td>
<td>139</td>
</tr>
</tbody>
</table>

Symmetry codes: (i) 1-x,1-y,-z; (iii) -x,-y,1-z; (iv) -x,1-y,1-z; (v) -x,-y,2-z; (vii) 1-x,½-y,-z; (viii) 1-x,-y,z; (ix) x,1+y,z

Table 3.4. Hydrogen-bond geometry in µ-oxo-(BsubPc)_2•0.25H_2O (Å,°).

| D-H...A   | D-H H...A D...A D-H...A |
|-----------|-----------------------|-----------------|-----------------|
| O(1W)-H(1WA)...N5^ii | 0.84 | 2.20 | 3.038(13) | 179 |
| O(1W)-H(1WB)...N3 | 0.84 | 2.11 | 2.946(13) | 180 |

Symmetry codes: (i) 1-x,1-y,-z
Table 3.5. Y-X-π interactions in μ-oxo-(BsubPc)₂•2DCB (Å,°).

<table>
<thead>
<tr>
<th>Y</th>
<th>X</th>
<th>Ring J</th>
<th>X..Cg(J)</th>
<th>Y-X..Cg(J)</th>
<th>Y..Cg(J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C8S</td>
<td>Cl4</td>
<td>C1S-C6S</td>
<td>3.979(3)</td>
<td>66.7(2)</td>
<td>3.655(6)</td>
</tr>
<tr>
<td>C2B</td>
<td>Cl2B</td>
<td>C7S-C12S</td>
<td>3.89(2)</td>
<td>79.8(17)</td>
<td>3.97(5)</td>
</tr>
<tr>
<td>C7A</td>
<td>Cl3A</td>
<td>C10-C15S</td>
<td>3.955(9)</td>
<td>106.5(10)</td>
<td>4.74(3)</td>
</tr>
</tbody>
</table>

Symmetry codes: (ix) x,1+y,z; (x) x,-1+y,z; (xi) 1-x,1-y,1-z

Table 3.6. Final compositions of reaction mixtures for various methods of synthesizing μ-oxo-(BsubPc)₂
(indicators refer to pathway in Scheme 3.1).

<table>
<thead>
<tr>
<th>Pathway</th>
<th>μ-oxo-(BsubPc)₂</th>
<th>unknown BsubPc-1</th>
<th>unknown BsubPc-2</th>
<th>HO-BsubPc</th>
<th>Other BsubPcs</th>
</tr>
</thead>
<tbody>
<tr>
<td>(ii)</td>
<td>61.0%</td>
<td>35.4%</td>
<td>Not observed</td>
<td>2.2%</td>
<td>1.4%</td>
</tr>
<tr>
<td>(iii)</td>
<td>56.7%</td>
<td>12.5%</td>
<td>1%</td>
<td>26.2%</td>
<td>3.6%</td>
</tr>
</tbody>
</table>

Table 3.7. Selected Torsion Angles (°) where Ωα is X-Bα-O-Bβ, Ωβ is Y-Bβ-O-Bα and Ω' is the pseudotorsion angle X'-Bα...Bβ-Y'.

<table>
<thead>
<tr>
<th></th>
<th>Ωα</th>
<th>X</th>
<th>Ωβ</th>
<th>Y</th>
<th>Ω'</th>
<th>X'</th>
<th>Y'</th>
</tr>
</thead>
<tbody>
<tr>
<td>μ-oxo-(BsubPc)₂•0.25H₂O</td>
<td>34.4(5)</td>
<td>N2</td>
<td>43.4(5)</td>
<td>N12</td>
<td>-40.0(3)</td>
<td>N2</td>
<td>N8</td>
</tr>
<tr>
<td>μ-oxo-(BsubPc)₂•2DCB</td>
<td>-18.9(5)</td>
<td>N2</td>
<td>-43.7(5)</td>
<td>N8</td>
<td>52.0(4)</td>
<td>N4</td>
<td>N8</td>
</tr>
<tr>
<td>μ-oxo-(BsubPc)₂ subl</td>
<td>-57.7(7)</td>
<td>N2(α)</td>
<td>-57.7(7)</td>
<td>N2(β)</td>
<td>5.8(4)</td>
<td>N4(α)</td>
<td>N2(β)</td>
</tr>
<tr>
<td>μ-oxo-(BsubPc)₂•3toluene(65)</td>
<td>21.5(3)</td>
<td>N1</td>
<td>58.9(3)</td>
<td>N11</td>
<td>-37.6(2)</td>
<td>N1</td>
<td>N7</td>
</tr>
</tbody>
</table>

Table 3.8. Selected geometrical measurements for μ-oxo-(BsubPc)₂ crystal structures (measurements are defined in Figure 3.5).

<table>
<thead>
<tr>
<th>μ-oxo-(BsubPc)₂</th>
<th>Pyrrole plane depth (Å)</th>
<th>Imine plane depth (Å)</th>
<th>Bowl depth (Å)</th>
<th>Angle between α and β planes (°)</th>
<th>B-O-B bond angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>μ-oxo-(BsubPc)₂•0.25H₂O</td>
<td>0.651(4)</td>
<td>0.642(4)</td>
<td>1.217(4)</td>
<td>1.204(4)</td>
<td>2.741(4)</td>
</tr>
<tr>
<td>μ-oxo-(BsubPc)₂•2DCB</td>
<td>0.654(4)</td>
<td>0.650(5)</td>
<td>1.211(4)</td>
<td>1.215(5)</td>
<td>2.641(4)</td>
</tr>
<tr>
<td>μ-oxo-(BsubPc)₂ subl</td>
<td>0.653(6)</td>
<td>0.653(6)</td>
<td>1.238(6)</td>
<td>1.238(6)</td>
<td>2.752(6)</td>
</tr>
<tr>
<td>μ-oxo-(BsubPc)₂•3toluene(65)</td>
<td>0.648</td>
<td>0.644</td>
<td>1.192</td>
<td>1.202</td>
<td>2.613</td>
</tr>
</tbody>
</table>
Chapter 4

4 Synthesis and Characterization of μ-oxo BsubPc

Following the discovery of crystals of μ-oxo BsubPc upon sublimation of Br-BsubPc and the unique properties of the crystal structure, the next step was to develop a method for the directed synthesis of this compound. This study was undertaken simultaneously with the discovery and analysis of the three crystal structures outlined in Chapter 3, and the results of its assessment of μ-oxo BsubPc’s solid state arrangement provided the impetus for further investigation of effective synthesis routes including and beyond those described in Chapter 3 that first resulted in the isolation of single crystals. Chapter 4 first describes the approach taken and provides a summary of investigated synthetic pathways, and subsequently defines a practical procedure for the synthesis and isolation of pure μ-oxo BsubPc. This is followed by an assessment of the pure compound’s solution-state material properties in comparison to those of HO-BsubPc, its monomeric precursor, and other previously studied BsubPcs.

4.1 Guiding Principles

The primary goal of this synthetic effort is to allow the characterization of μ-oxo BsubPc to determine whether and how it is of use for application in OSC devices. The criteria for practicability include the potential to carry out the reaction and subsequent work-up procedure, using commonly available equipment in BsubPc research groups, at a sufficiently high scale and in sufficient purity to enable the full characterization of its performance as an organic electronic material. In our research group this corresponds to 500mg of pure, double-sublimed μ-oxo BsubPc. “Double-sublimed” is a purity threshold, and means that once a sample is obtained that is pure by common means of detection (for example, HPLC) it must then be train sublimed twice to eradicate any trace impurities that may be present. Further criteria would be relevant for developing a process geared towards supporting widespread use or study of μ-oxo BsubPc in a variety of devices, however in the case of this material its device performance is currently unknown. Therefore, the priority is to obtain the pure 500mg above other considerations, after which the results of its characterization will lead to further synthesis goals. For example, while atom and energy efficiency are typical priorities in process chemistry development, in this case purity takes precedence over yield concerns. This is particularly relevant in the context of the
extreme conditions required for the $\mu$-oxo reaction to go to completion, which also favour the production of multiple unknown BsubPc species.

4.2 Survey of $\mu$-oxo BsubPc Synthesis Reactions

The most successful synthesis routes proceeded by the reaction pathways outlined in Chapter 3: an equimolar addition reaction of HO-BsubPc and Br-BsubPc; and a ‘1 pot’ synthesis from Br-BsubPc in the presence of water. Additionally, several methods found in the literature were attempted as reported and with adaptations, including the self-condensation of HO-BsubPc reported by Yamasaki et al.,$^{(65)}$ the Torres procedure$^{(52)}$ using NaOH and a crown ether, and the observation of Potz et al.$^{(24)}$ that $\mu$-oxo BsubPc is formed from HO-BsubPc under sublimation conditions. Following observed formation of $\mu$-oxo BsubPc by colleagues in this laboratory, Lewis acid chemistry was investigated. No method was as effective as the equimolar and ‘1 pot’ reactions carried out in 1,2-dichlorobenzene (DCB), and therefore these became the focus of study. It was hypothesized that the acidic HBr could be a cause of BsubPc impurity formation, which is supported by the lack of one particularly troublesome impurity in the self-condensation reaction (in which no HBr is produced). Two methods attempting to eliminate HBr were investigated. In one, Br-BsubPc is replaced by nosyl-BsubPc (NsO-BsubPc), chosen because the reactivity of this pseudohalide BsubPc falls between that of Br-BsubPc and Cl-BsubPc,$^{(64)}$ and the reaction produces the far weaker nosylic acid in the place of HBr. The second and final approach was to eliminate HBr from the reaction environment after its formation by precipitation as a salt by reaction with potassium phosphate ($K_3PO_4$), depicted in Scheme 4.1. The reaction of HO-BsubPc and a halo-BsubPc in the presence of a base is also included in the patent application of Mori et al.$^{(53)}$

Scheme 4.1. Removal of HBr in the presence of $K_3PO_4$ by formation of KBr

Table 4.1 shows the composition of BsubPcs in the final reaction mixture in each $\mu$-oxo synthesis reaction attempted. The table identifies several recurring impurities, which could not be identified by mass spectrometry (insufficient mass could be isolated to obtain useful results from other analytical techniques) and remain unknown. They are identifiable as BsubPcs by
their characteristic UV-vis absorption. The “3.4RT” impurity remained adsorbed at the baseline on basic alumina, along with Br-BsubPc and HO-BsubPc, and thus these three compounds could be effectively removed from the crude product by Kauffman chromatography. However, no efficient or reliable way of separating the “2.0RT” impurity from μ-oxo BsubPc was found.

**Table 4.1. Final composition of the reaction mixture in all investigated μ-oxo synthesis pathways (by HPLC, 545 nm channel).**

<table>
<thead>
<tr>
<th>Label</th>
<th>Description</th>
<th>HPLC % Area of: μ-oxo BsubPc</th>
<th>unknown at RT: 2.0min</th>
<th>unknown at RT: 3.4min</th>
<th>HO-BsubPc</th>
<th>Other BsubPcs</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>10mL p-xylene (~2wt%), 0.44mL pyridine, 115°C</td>
<td>1.3%</td>
<td>NA</td>
<td>37.2%</td>
<td>26.8%</td>
<td>34.8% (33.8% Br-BsubPc, 1.0% unkn)</td>
</tr>
<tr>
<td>1.2</td>
<td>10mL nitrobenzene (~2wt%), 200°C</td>
<td></td>
<td>Reaction degraded</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.3</td>
<td>10mL diphenylether (~2wt%), 200°C</td>
<td>55.9%</td>
<td>21.9%</td>
<td>0.0%</td>
<td>NA</td>
<td>21.7%</td>
</tr>
<tr>
<td>1.4</td>
<td>10wt% in diphenylether, 200°C</td>
<td>82.2%</td>
<td>15.3%</td>
<td>NA</td>
<td>0.7%</td>
<td>1.8%</td>
</tr>
<tr>
<td>1.5</td>
<td>Equimolar Br-BsubPc and HO-BsubPc in DCB</td>
<td>56.7%</td>
<td>12.5%</td>
<td>1.0%</td>
<td>26.2%</td>
<td>3.6%</td>
</tr>
<tr>
<td>1.6</td>
<td>Equimolar Br-BsubPc and HO-BsubPc in DCB (scaled up x5)</td>
<td>78.5%</td>
<td>10.2%</td>
<td>7.4%</td>
<td>0.8%</td>
<td>3.1%</td>
</tr>
<tr>
<td>2.1</td>
<td>Br/OH-F12BsubPc mix (30:70) in DCB (10wt%) with water</td>
<td>22.9%</td>
<td>7.8%</td>
<td>NA</td>
<td>61.4%</td>
<td>(N/A; Br-F12BsubPc overlaps with F12 m-oxo)</td>
</tr>
<tr>
<td>2.2</td>
<td>Repeat of 2.1 above</td>
<td>27.7%</td>
<td>29.9%</td>
<td>NA</td>
<td>37.0%</td>
<td>(N/A; Br-F12BsubPc overlaps with F12 m-oxo)</td>
</tr>
<tr>
<td>3.1</td>
<td>'1 pot' Br-BsubPc in DCB with water (10wt%)</td>
<td>61.0%</td>
<td>35.4%</td>
<td>NA</td>
<td>2.2%</td>
<td>1.40%</td>
</tr>
<tr>
<td>3.2</td>
<td>Self-condensation of HO-BsubPc in DCB (10wt%)</td>
<td>34.7%</td>
<td>NA</td>
<td>23.9%</td>
<td>35.4%</td>
<td>6.10%</td>
</tr>
<tr>
<td>4.1</td>
<td>Torres method using Br-BsubPc</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>100% (all Br-BsubPc)</td>
<td></td>
</tr>
<tr>
<td>4.2</td>
<td>Torres method using Br-BsubPc, with ¼ solvent</td>
<td>36.2%</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>63.8% (unknwn)</td>
</tr>
<tr>
<td></td>
<td>Description</td>
<td>1.7%</td>
<td>NA</td>
<td>NA</td>
<td>15.2%</td>
<td>83.2% (60.1% Br-Bspc; 23.1% unknown)</td>
</tr>
<tr>
<td>---</td>
<td>------------------------------------------------------------------------------</td>
<td>------</td>
<td>----------</td>
<td>----------</td>
<td>-------</td>
<td>-----------------------------------</td>
</tr>
<tr>
<td>5</td>
<td>Sublimation of HO-BsubPc</td>
<td>None</td>
<td>NA</td>
<td>NA</td>
<td>100.0%</td>
<td>NA</td>
</tr>
<tr>
<td>6.1</td>
<td>Lewis acid hydrates - AlCl₃</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>30.3%</td>
<td>69.7% (67.2% Br-BsubPc, 2.5% unknown)</td>
</tr>
<tr>
<td>6.2</td>
<td>Lewis acid hydrates - AlCl₃·6H₂O</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>37.3%</td>
<td>62.7% (61.9% Br-BsubPc, 0.8% unknown)</td>
</tr>
<tr>
<td>6.3</td>
<td>Lewis acid hydrates - FeCl₃·6H₂O</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>32.2%</td>
<td>67.9% (17.4% Br-BsubPc, 50.5% unknown)</td>
</tr>
<tr>
<td>6.4</td>
<td>Lewis acid hydrates - SnCl₄·5H₂O</td>
<td>8.0%</td>
<td>NA</td>
<td>2.9%</td>
<td>50.4%</td>
<td>38.7% (Br-BsubPc)</td>
</tr>
<tr>
<td>6.5</td>
<td>Lewis acid hydrates - AlCl₃·6H₂O + K₃PO₄</td>
<td>1.0%</td>
<td>NA</td>
<td>NA</td>
<td>72.6%</td>
<td>26.4% (2.5% Br-BsubPc, 23.9% single unknown)</td>
</tr>
<tr>
<td>6.6</td>
<td>Lewis acid non-hydrate - SnCl₄ + Br-BsubPc</td>
<td>4.3%</td>
<td>NA</td>
<td>8.7%</td>
<td>41.1%</td>
<td>45.9% (Br-BsubPc)</td>
</tr>
<tr>
<td>6.7</td>
<td>Lewis acid non-hydrate - SnCl₄ + HO-BsubPc</td>
<td>NA</td>
<td>NA</td>
<td>0.7%</td>
<td>93.7%</td>
<td>5.7% (unknown)</td>
</tr>
<tr>
<td>7.1</td>
<td>Equimolar nosyl-BsubPc and HO-BsubPc</td>
<td>38.3%</td>
<td>11.6%</td>
<td>0.3%</td>
<td>NA</td>
<td>49.9% (48.8% nosyl-Bspc, 1.1% unknown)</td>
</tr>
<tr>
<td>7.2</td>
<td>HO-BsubPc and 10mol% nosyl-Bspc</td>
<td>4.0%</td>
<td>18.2%</td>
<td>NA</td>
<td>77.8%</td>
<td>NA</td>
</tr>
<tr>
<td>8.1</td>
<td>Equimolar Br-BsubPc and HO-BsubPc in DCB with K₃PO₄ (0.8:1 solvent by mass)</td>
<td>97.6%</td>
<td>NA</td>
<td>NA</td>
<td>1.4%</td>
<td>1.0% (Br-BsubPc)</td>
</tr>
<tr>
<td>8.2</td>
<td>Equimolar Br-BsubPc and HO-BsubPc in DCB with K₃PO₄ (0.2:1 solvent by mass)</td>
<td>97.4%</td>
<td>NA</td>
<td>NA</td>
<td>2.6%</td>
<td>NA</td>
</tr>
<tr>
<td>8.3</td>
<td>Thoroughly dry repeat of 8.2</td>
<td>100.0%</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>8.4</td>
<td>'1 pot' Br-BsubPc in DCB with wet K₃PO₄ (0.2:1 solvent by mass)</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>100% (Br-BsubPc)</td>
</tr>
</tbody>
</table>
Appendix 2 describes the development of μ-oxo reaction pathways and separation techniques in full. The first sections describe work done towards developing an initial synthesis method that could produce pure μ-oxo BsubPc, albeit in low yields, which led to the study of crystal structures described in Chapter 3. The later sections describe subsequent work towards an improved synthesis process due to the conclusion from Chapter 3 that, although representing a significant challenge, development of a practical process for the synthesis of μ-oxo was indeed of high importance. As is evident in Table 4.1 above, the K$_3$PO$_4$ reactions demonstrated the most promise due to their ability to produce μ-oxo BsubPc with high conversion in some cases, but more importantly the production of μ-oxo BsubPc in the absence of the 2.0RT BsubPc impurity that cannot be separated.

### 4.3 Development of the K$_3$PO$_4$ μ-oxo BsubPc Synthesis Process

The first K$_3$PO$_4$ reaction appeared highly successful according to HPLC composition, showing close to 100% conversion with no other BsubPc impurities. However, upon Soxhlet extraction to remove the K$_3$PO$_4$ and precipitated salts it became clear that an interaction of BsubPc with K$_3$PO$_4$, which turned the removed solids a deep turquoise colour, resulted in a significant loss of total BsubPc mass. Therefore, the quantity of K$_3$PO$_4$ used was decreased to boost the mass yield whilst still suppressing impurity formation. However, although the mass remaining after Soxhlet extraction was improved, the mass of BsubPc remaining after train sublimation was found to be extremely low (8% overall mass yield) due to the presence of small-molecule BsubPc degradation products such as phthalimide. It was subsequently observed that the colour intensity of samples taken from the reaction decreased over time, indicating loss of BsubPcs from solution. Therefore, a graph was plotted of approximate relative μ-oxo BsubPc concentration over time, using the peak absorption value from HPLC data (rather than %area indicating BsubPc composition).
Figure 4.1. Profile of normalized maximum $\mu$-oxo BsubPc absorption over time in the (a) dry equimolar reaction and (b) wet '1 pot' reaction, in the presence of 20% $K_3PO_4$

Figure 4.1 (a and b) illustrate that the maximum quantity of $\mu$-oxo BsubPc is present in solution within the first hour, after which more is lost through degradation processes or removed from solution by $K_3PO_4$ than is produced by incremental conversion. The final synthesis procedure is outlined in Section 4.4 below. Three batches of this procedure are sufficient to provide 500mg of pure, double-sublimed $\mu$-oxo BsubPc.

4.4 Synthesis Procedure for $\mu$-oxo BsubPc

$\mu$-oxo BsubPc was synthesized by reacting equimolar quantities of OH-BsubPc and Br-BsubPc in the presence of a base, a reaction pathway which is included in the patent application of Mori, Furuya and Yamasaki.\(^{(53)}\) 1,2-Dichlorobenzene (6.9mL) was added to make up a 10wt% solution of HO-BsubPc (0.464 g, $1.13 \times 10^{-3}$ mol) and Br-BsubPc (0.535 g, $1.13 \times 10^{-3}$ mol) in a scintillation (20 mL) vial fitted with a condenser. A mass of potassium phosphate equivalent to 20% of the solvent’s mass ($K_3PO_4$; 1.801 g, $8.49 \times 10^{-3}$ mol), ground in a mortar and pestle and activated in an oven at 200°C, was added. Stirring and a positive pressure of argon were maintained throughout the experiment. The reaction progress was monitored by HPLC. The mixture was heated at reflux (181°C) for 1 hour, at which stage the reaction was cooled and immediately transferred to a Soxhlet thimble. A Soxhlet extraction in toluene was carried out for 2 days. The solvents were removed by rotary evaporation, and the solids were fully redissolved in dichloromethane (DCM). This was run through a Kauffman column of basic alumina prior to application of heat, and the eluent collected. The column was left to dry overnight, after which a fresh flask of DCM was placed under the column and reflux established. The Kauffman was run for 1 day. The solvent was removed by rotary evaporation, and the solids then placed in a vacuum oven overnight (40°C, 10 mmHg) (537mg, 59% overall mass yield; HPLC $R_T$: 2.8 min
The solids were train sublimed at a temperature of 450 °C (held for 5h45min, total heating time 10h15min), and single crystals as well as a band of µ-oxo BsubPc were collected (357mg, overall 39% mass yield; sublimation step yield 70%). Removed white crystals were found to be phthalimide (ca. 10mg), and bands containing small quantities of HO-BsubPc were also discarded (mass below collection limit). The µ-oxo BsubPc was train sublimed once again under the same conditions. The same resulting compounds were observed and the single crystals and µ-oxo BsubPc band were collected (sublimation step yield 58%).

Yield: 0.204 g (22.5%). HPLC R_T: 2.8 min (>99.9%, MAXPlot); ^1H NMR (400 MHz, CDCl3, Me_4Si) 7.77–7.79 (m, 12H), 8.61–8.63 (m, 12H). Anal. Calcd. for C_{48}H_{24}B_2N_12O: C, 71.49; H, 3.00; N, 20.84. Found (±0.3%): C, 71.04; H, 3.19; N, 20.82.

4.5 Characterization of µ-oxo BsubPc and HO-BsubPc

4.5.1 Spectroscopy and Photophysics Analysis

The absorbance and photoluminescence spectra of µ-oxo BsubPc and HO-BsubPc in toluene solution are shown in Figure 4.2. The photophysical properties of µ-oxo BsubPc, and of HO-BsubPc for comparison, were measured using the methods described in Chapter 2 with respect to the halo-BsubPcs. The results of the data analysis are tabulated in Table 4.2.

<table>
<thead>
<tr>
<th></th>
<th>(\lambda_{\text{max,abs}}) (nm)</th>
<th>(\lambda_{\text{max,PL}}) (nm)</th>
<th>(\Phi_{\text{PL}})</th>
<th>(\varepsilon) (L mol(^{-1}) cm(^{-1})) (^{a})</th>
</tr>
</thead>
<tbody>
<tr>
<td>HO-BsubPc</td>
<td>561</td>
<td>567</td>
<td>0.51</td>
<td>9.22 x10(^4)</td>
</tr>
<tr>
<td>µ-oxo BsubPc</td>
<td>532</td>
<td>636</td>
<td>0.02</td>
<td>9.11 x10(^4)</td>
</tr>
</tbody>
</table>

\(^{a}\) Molar extinction coefficient \(\varepsilon\) at \(\lambda_{\text{max,abs}}\)
It can be seen that the properties of HO-BsubPc are very similar to those of F-BsubPc: an absorption maximum, $\lambda_{\text{max,abs}}$, of 561 nm compared to 562 nm for F-BsubPc, a peak emission wavelength, $\lambda_{\text{max,PL}}$, of 567 nm compared to 568 nm, an equivalent Stokes shift of 6 nm and an equivalent photoluminescent quantum yield, $\Phi_{\text{PL}}$, of 0.51. However, the molar extinction coefficient of HO-BsubPc at its $\lambda_{\text{max,abs}}$, measured in toluene, was found to be higher than that of F-BsubPc, at $9.22 \times 10^4$ compared to $8.76 \times 10^4$ L mol$^{-1}$ cm$^{-1}$.

In contrast, the photophysical properties of µ-oxo BsubPc are unique amongst BsubPcs. As previously mentioned, the $\lambda_{\text{max,abs}}$ is known to be blue-shifted in comparison to typical BsubPcs, at 532 nm in toluene. The overlay of µ-oxo BsubPc’s absorption spectra with that of HO-BsubPc in Figure 4.3 illustrates the differences in the dimer’s absorption. Not only is the maximal absorption wavelength 30 nm lower, but the peak is broadened and its base extends to higher wavelengths than HO-BsubPc. The broadening of the absorption peak can be understood in the context of the greater geometry relaxations available in the dimer, across two large conjugated systems rather than just the one.$^9$

The photoluminescence of µ-oxo BsubPc has not been previously reported, and the observed fluorescence of µ-oxo BsubPc is again different than typically observed in BsubPcs. In contrast to its absorption, its emission is significantly red-shifted in comparison to its own absorption band and to emission of other BsubPcs; its $\lambda_{\text{max,PL}}$ is 636 nm, while HO-BsubPc’s 567 nm. This results in an extremely large Stokes shift of 104 nm compared to the characteristically low Stokes shifts of monomeric BsubPcs (6 nm in HO-BsubPc and all three halo-BsubPcs, 20-29 nm among fluorinated PhO-BsubPcs.$^{34}$) A significant broadening of the emission band is also observed, as depicted in Figure 4.3b. Additionally, the quantum efficiency of µ-oxo BsubPc is
more than an order of magnitude lower than that of HO-BsubPc at 0.02. The quantum yields of BsubPcs are not characteristic across the group, and have been found to vary widely.\(^{(43)}\) This low quantum yield may be related to the structure of μ-oxo BsubPc with two covalently-linked BsubPc units, so even in dilute solutions interactions between chromophores cannot be neglected and may result in self-quenching. It is not possible to determine whether or to what extent the invalidity of this assumption, which underlies the analysis of dilute solutions, contributes to the low observed quantum yield, and to what degree this low yield translates to the solid state which has implications for the efficiency of energy transfer mechanisms in exciton diffusion processes. Interestingly, an equivalent photoluminescence quantum yield of 0.02 has been observed in two thiophene-BsubPc dyads, one of which showed very good performance in an OPV device.\(^{(30)}\) The investigators attribute the low solution-state photoluminescence quantum yield to the “free rotor” effect of the bent ether bond, and find that this low anomaly in fluorescence behaviour compared to other compounds in the series is not observed near freezing at 77 K where rotation is suppressed (as it would be in the solid state). μ-oxo BsubPc is also characterized by a “free rotor” effect at the linking oxygen which is expected to rotate freely when in solution.

### 4.5.2 Electronic properties of μ-oxo BsubPc

The electrochemical and electronic properties of μ-oxo BsubPc in solution were also assessed, again using the methods described in Chapter 2, and are summarized in Table 4.3. As was the case with the halo-BsubPcs, one irreversible oxidation peak was detected and thus the calculation of estimated HOMO and LUMO levels was carried out with both the peak oxidation potential and the potential at the onset of oxidation. The oxidation potential, \(E_{\text{ox}}\), and HOMO and LUMO levels were consistent with those found for the halo-BsubPcs, continuing the downward trend to sit below F-BsubPc (peak oxidation estimates of HOMO levels of Br-BsubPc (5.5 eV) > Cl-BsubPc (5.4 eV) > F-BsubPc (5.3 eV) > μ-oxo BsubPc (5.1 eV)). Despite the 30 nm blue-shift of μ-oxo BsubPc’s absorption maximum, the broader absorption band results in an optical band gap, \(E_{\text{g, opt}}\), of 2.1 eV equivalent to the halo-BsubPcs to 2 significant figures. These values suggest that μ-oxo BsubPc would be a candidate material for application in a similar role as other peripherally hydrogenated monomeric BsubPcs in devices, the design of which is largely driven by energy level alignment. This also facilitates study of how the differences in μ-oxo BsubPc’s photophysical properties and solid state arrangement affect its performance in devices, as it allows for the control of some major variables such as device architecture.
Table 4.3. Electrochemical and electronic properties of \( \mu \)-oxo BsubPc

<table>
<thead>
<tr>
<th></th>
<th>( E_{ox} ) (mV)</th>
<th>HOMO (eV)</th>
<th>( E_{g,OPT} ) (eV)</th>
<th>LUMO (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \mu )-oxo BsubPc</td>
<td>376(^\circ)</td>
<td>5.1(^\circ)</td>
<td>2.1</td>
<td>3.1(^\circ)</td>
</tr>
<tr>
<td></td>
<td>298(^\circ)</td>
<td>5.0(^\circ)</td>
<td>3.0</td>
<td>3.0(^\circ)</td>
</tr>
</tbody>
</table>

\(^\circ\) Peak oxidation potential by differential pulse voltammetry. \(^\circ\) Potential at onset of oxidation by differential pulse voltammetry.

4.5.3 Solid state arrangement of HO-BsubPc

Based on previous observations of the thermal degradation of HO-BsubPc to form \( \mu \)-oxo BsubPc under sublimation conditions,\(^{(24)}\) train sublimation of HO-BsubPc at the maximum temperature of our laboratory’s apparatus (450 °C) was attempted as a synthesis route to \( \mu \)-oxo BsubPc (5, Appendix 2). However, although small crystals of \( \mu \)-oxo were found in the crucible, \( \mu \)-oxo BsubPc could only be detected at trace levels (below the HPLC integration limit) in some sublimed bands of HO-BsubPc and could not be detected at all in other locations. Instead, this experiment yielded the first known crystals of HO-BsubPc from sublimation, which matches the non-hydrated HO-BsubPc in the Cambridge Crystallographic Database\(^{(24)}\) (structure reference KAJGIL) obtained from solution methods. The re-determined structure from sublimation was much more precise than the original, with R=3.9% in comparison to ca. 15%, which is reflected in the standard uncertainties on bond angles and lengths. The solid state arrangement illustrates the same typical concave-to-concave \( \pi \ldots \pi \) stacking interaction common to many BsubPcs and seen in the \( \mu \)-oxo BsubPc crystal structures described in Chapter 3, which typically result in a 3D motif of isolated bowl-bowl pairs. Convex-to-convex interactions are also present, which associate adjacent bowl-bowl pairs with one another. However, as was the case with the \( \mu \)-oxo BsubPc crystals, an additional interaction makes the solid state arrangement of HO-BsubPc unique. In the \( \mu \)-oxo BsubPc structure, the covalent B–O–B bond links together sets of bowl-bowl interacting molecules to extend an additional dimension of interaction pathways. In HO-BsubPc, a hydrogen bond is present between the axial hydroxyl group and an imine nitrogen on an adjacent molecule (N2), an O–H \ldots N interaction, and this is what directs the HO-BsubPc molecules into 1-dimensional stacked, staggered columns. In Figure 4.4a, each nearest-neighbour interaction of one molecule (coloured orange) has been identified. “1” is the hydrogen bond to N2 from the –OH group of its neighbour below, and “2” is a hydrogen bond from its –OH group to the N2 of its neighbour above. “3” is a concave-concave interaction with an adjacent molecule, and “4” is a convex-convex interaction with its adjacent neighbor on the other
The resulting interaction pathways in the 3D structure are illustrated in Figure 4.4b. The staggered columns directed by hydrogen bonding alternate between an ‘up’ and ‘down’ orientation of the B–O bond. The two bowl-bowl interactions of each molecule combine to create a pathway across these columns, creating a concave-concave/convex-convex alternating chain. The resulting motif is a 2-dimensional network of interactions pathways, creating ‘sheets’ of molecules in the 3D material. An expanded set of data describing the HO-BsubPc crystal structure is provided in Appendix 3.

Figure 4.4. A view of the crystal packing in HO-BsubPc showing (a) labeled interactions of one molecule; and (b) one-dimensional packing motifs created by hydrogen bonding (green) and $\pi$-$\pi$ interactions (blue). Molecules illustrated in elemental colouring (carbon – gray; nitrogen – blue; oxygen – red; boron – pink). Hydrogen bonding (turquoise; red if second molecule not shown) and selected concave-concave (red dashed) and convex-convex (green dashed) $\pi$-$\pi$ interactions are shown. Hydrogens are omitted for clarity.

The chromophore density of this crystal is equivalent to that of the sublimed µ-oxo BsubPc and Cl-BsubPc crystals, placing it amongst the three densest known BsubPc crystal structures. The lack of thermal degradation to µ-oxo BsubPc under sublimation conditions was unexpected, especially at this high temperature. This suggests that it is possible to find conditions at which HO-BsubPc sublimes without thermal degradation and opens up the possibility of putting HO-BsubPc in devices by vapour deposition, something previously not thought possible. Given its highly dense crystal structure and multi-dimensional packing motif, this represents an exciting new avenue of research. Not only would the study of vacuum deposited HO-BsubPc contribute to the discussion on whether high chromophore density translates into materials with good device performance, but it also would be of interest in the context of studies on the impact of hydrogen bonding on electronic properties of organic materials.
4.6 Conclusion

This Chapter presents a procedure for the synthesis and separation of μ-oxo BsubPc in sufficient yields and purity to allow its study as a functional organic electronic material. It was discovered that, while μ-oxo BsubPc can be created through a broad range of reaction pathways and under diverse conditions, its synthesis as the main reaction product in appreciable yields and its subsequent isolation is extremely challenging. The best compromise between the competing goals of purity, yield and extent of conversion was found to be an equimolar addition reaction of HO-BsubPc and Br-BsubPc in the presence of K$_3$PO$_4$, for its suppression of BsubPc impurities, stopped after 1 hour before reaching full conversion, to limit K$_3$PO$_4$’s effect of degradation and removal of desired BsubPcs from solution. The products of this reaction can be purified using typical BsubPc process chemistry, including Soxhlet extraction, Kauffman column chromatography and train sublimation. The isolation of pure μ-oxo BsubPc also allowed study of some of its solution-state material properties. These were compared to HO-BsubPc, its precursor and closest monomeric equivalent, and in the context of the broader class of BsubPcs. The data suggest that the electronic properties of μ-oxo BsubPc do not differ substantially from other peripherally hydrogenated BsubPcs. However, its photophysical properties, including its well-known shift of $\lambda_{\text{max, abs}}$ and its newly described fluorescence behavior presented in this thesis, differ greatly from both HO-BsubPc and BsubPcs in general. It remains to be seen whether the low observed photoluminescence quantum efficiency translates into poor energy transfer properties in devices, or whether this result is a consequence of the “free rotor” effect of the two linked BsubPcs in solution. The assessment of this behavior in solid state devices will be key in determining its suitability as an active layer in OSCs. The combination of similar electronic properties and differing photophysical properties when compared to typical BsubPc molecules illustrates an opportunity to study the performance of μ-oxo BsubPc in direct comparison to typical BsubPcs in equivalent device structures and functional roles in organic electronic devices. It was also found that the photophysical properties of HO-BsubPc are consistent with commonly observed BsubPc properties, including the halo-BsubPcs. Additionally, similar to μ-oxo BsubPc, HO-BsubPc demonstrates highly dense crystal packing with potential 3-dimensional energy transfer pathways. Therefore, HO-BsubPc represents an interesting material to study as an organic electronic material for application in its own right, and, as the closest lower analogue of μ-oxo BsubPc, is also a good source of comparison for the properties of the dimer against a typical ‘monomeric’ equivalent.
Chapter 5

5 Conclusions

5.1 Conclusions

This thesis has presented research in two areas of BsubPc chemistry, halo-BsubPcs and μ-oxo BsubPc. In each of these, a new compound has been made accessible by development of a synthesis method and subsequent separation processes which address the challenges and limitations of the chemistry (F-BsubPc and μ-oxo BsubPc). Additionally, relevant properties of these, and the compounds in the category they belong to, have been measured and analysed in order to characterize their suitability for use as functional materials in OSCs, their usefulness as chemical precursors and their processability. Therefore, results have been obtained that meet the objectives in both of the dual thesis goals.

A method for the synthesis of F-BsubPc has been developed with 64% yield. A comprehensive study of the halo-BsubPcs (halo = F, Cl, Br) found that their solid state arrangement, spectroscopic and electronic properties were shared across the series, with the exception of photoluminescence quantum yield, and differences were observed in their physical characteristics, such as reactivity and solubility. Therefore, this research suggests that the halo-BsubPcs may be interchangeable in circumstances in which performance is governed by crystal packing, spectroscopic or electronic properties and thus a selection can be made according to the desired physical properties. For example, these results suggest that Br-BsubPc is a good choice as a chemical precursor to access a wider range of chemistries than with Cl-BsubPc.

Alternatively, for the purposes of robust device design, it would be valuable to study the properties of F-BsubPc in devices to assess whether it is an attractive material for the replacement of Cl-BsubPc

Initial study of μ-oxo BsubPc resulted in the observation of multiple crystal polymorphs of solvated and non-solvated μ-oxo BsubPc. Analysis of these crystals revealed that the density of chromophores in all μ-oxo BsubPc polymorphs is extremely high in comparison to previously observed BsubPc structures, and the highest is observed in the non-hydrated, non-solvated sublimed crystal. The crystals also exhibited intermolecular interactions in more than one dimension. This suggests the crystalline material could possess high charge carrier mobility. It
was also discovered that \( \mu \)-oxo BsubPc is mobile under vacuum sublimation conditions, and thus could be vapour deposited for incorporation into organic electronic devices.

Finally, a synthesis process was developed for \( \mu \)-oxo BsubPc which will allow study of its performance as a functional organic electronic material in the solid state. One main observation throughout the development process was that a number of synthetic pathways provide a route to \( \mu \)-oxo BsubPc. It was also noted that under the harsh conditions required for quantitative production of \( \mu \)-oxo BsubPc, formation of unknown BsubPc byproducts presents a significant challenge. The spectroscopic and photoluminescence properties of HO-BsubPc were found to be remarkably similar to those of F-BsubPc, while the properties of \( \mu \)-oxo BsubPc were unique. However, the electronic properties of \( \mu \)-oxo BsubPc are similar to those of other perhydrogenated BsubPcs. This result highlights an opportunity to study the performance of \( \mu \)-oxo BsubPc in direct comparison to a series of BsubPcs, using a common device architecture in which only the ‘BsubPc’ layer is modified. Additionally, the solid state arrangement of HO-BsubPc was found to have an equally high chromophore density as \( \mu \)-oxo BsubPc and the halo-BsubPcs. Intermolecular interactions in multiple dimensions were observed in the crystal structure of both \( \mu \)-oxo and HO-BsubPc.

### 5.2 Future Work

This research was focused on process chemistry and preliminary characterization methods. The next step in filling the remaining research gaps is study of these materials in the solid state and in devices to investigate how these solution-state and single-crystal properties translate into performance. Additionally, drawing on the findings of this thesis, three new research questions can be defined, each of which could direct a novel and exciting area of study.

1. How does chromophore density of crystal structures influence solid state electronic properties, such as charge carrier mobility? How important is this effect in comparison to the existence or lack of multi-dimensional intermolecular interaction pathways?

This thesis has described a number of crystal structures characterized by their high chromophore density. A study of their properties in solid state devices, in comparison to previously studied lower density compounds\(^{15}\), will enable development of structure-property relationships within the group to elucidate how this characteristic contributes to, or can be used to predict, behaviour of the compounds in devices. Additionally, while the halo-BsubPcs share the same relatively
typical packing motif, the crystals of both $\mu$-oxo BsubPc and HO-BsubPc were distinguished by their novel 3D packing arrangement and multi-dimensional interaction pathways. The similar chromophore densities within this group of crystals with different packing arrangements offers a further set of structure-property relationships that could be better understood by study of their solid state characteristics.

2. Is the $\mu$-oxo BsubPc process chemistry developed for the peripherally hydrogenated BsubPc extendable to other peripheral derivatives, for both homo- and hetero-dimers?

Preliminary investigation of a $\mu$-oxo F$_{12}$BsubPc reaction yielded promising results, showing production of the dimer in the presence of a similar number of impurities as the unsubstituted BsubPc although at a slower reaction rate. If the technique using $\text{K}_3\text{PO}_4$ and limiting reaction time can be successfully transferred to substituted BsubPcs, a number of derivatives could be synthesized by simple adaptations to the process described here. The equimolar addition reaction could potentially provide a route for the synthesis of asymmetrical dimers as well as new symmetrical derivatives. The reaction of one equivalent of HO-(a)BsubPc with one equivalent of Br-(b)BsubPc may result in an asymmetrical dimer. The (a) compound should be the derivative with slower kinetics than (b), to reduce the likelihood or ratio of Br-(a)BsubPc hydrolyzing to form HO-(a)BsubPc and reacting with the original Br-(a)BsubPc to form $\mu$-oxo-$[(a)\text{BsubPc}]_2$ instead of $\mu$-oxo-[$(a)\text{BsubPc}][(b)\text{BsubPc}]$. Based on the challenges of $\mu$-oxo BsubPc chemistry observed in this research, the main challenge of this approach may be separation of products if a mix of hetero- and homo-dimers is obtained. However, the resulting properties of these materials could exhibit highly interesting behavior, representing a novel dyad structure of two structurally similar BsubPcs.

3. Under what conditions can HO-BsubPc be sublimed without thermal degradation to $\mu$-oxo BsubPc, and can its synthesis be improved to facilitate its wider study?

The observation of the highly dense crystal structure of HO-BsubPc with multi-dimensional intermolecular interaction pathways, obtained under sublimation conditions without significant formation of $\mu$-oxo BsubPc, redefines HO-BsubPc as a compound of interest for application in OSCs. The implication that HO-BsubPc can be incorporated into devices by vacuum deposition means it can be studied alongside other BsubPc derivatives rather than requiring alternative solution-processing techniques. However, the range of conditions under which zero thermal degradation is observed must be confirmed before use in vacuum deposition apparatus to ensure
that the upper limits of the range can be avoided and no $\mu$-oxo BsubPc will be present in the resulting films. The synthesis of HO-BsubPc is a limiting step in the synthesis of $\mu$-oxo BsubPc, leading to investigation of the ‘1 pot’ mechanism in addition to the final equimolar pathway as it is a lengthy and somewhat troublesome process. Further optimization of the HO-BsubPc synthesis procedure would be beneficial if it becomes necessary to synthesize large quantities for its study in the solid state and in devices. This would also represent an improvement in the overall $\mu$-oxo BsubPc synthesis pathway.

Additional study in any of these three areas would further build on the base of knowledge developed in this thesis, contributing to the global research effort towards high performing materials for efficient and practical organic solar cells.
6 References


Appendix 1

Supplementary Information on the Crystal Structures of $\mu$-oxo-$(B_{sub}Pc)_2$

Figure A1. 1. Conformation of $\mu$-oxo-$(B_{sub}Pc)_2\cdot0.25H_2O$ showing (a) torsion angles $\omega_\alpha$ and $\omega_\beta$; (b) a view down the molecular $y$-axis.

Figure A1. 2. Conformation of $\mu$-oxo-$(B_{sub}Pc)_2\cdot3$toluene showing (a) torsion angles $\omega_\alpha$ and $\omega_\beta$; (b) a view down the molecular $y$-axis.
Figure A1.3. Conformation of $\mu$-oxo-(BsubPc)$_2$$^\text{subl}$ showing (a) torsion angles $\omega_{a}$ and $\omega_{b}$; (b) a view down the molecular $y$-axis; (c) perpendicular distance of oxygen from the approximate mirror plane N2-B1...B2-N10 (0.205(4) Å) and angle between the B1-O-B2 plane and the N2-B1...B2-N10 approximate mirror plane (18.2(4) °).

Figure A1.4. Conformation of $\mu$-oxo-(BsubPc)$_2$$^\text{subl}$ showing (a) torsion angles $\omega_{a}$ and $\omega_{b}$; (b) a view down the molecular $y$-axis; (c) a view down the molecular $z$-axis identifying two approximate mirror planes (the $xz$ molecular plane and the $yz$ molecular plane).
Table A1.16.1. Density Comparison of BsubPc Crystal Structures.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Reference</th>
<th>Unit Cell Volume, Å³</th>
<th>Z</th>
<th>Calculated Density</th>
<th>Calculated Chromophore Density †</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>kmol/m³</td>
<td>Mg/m³</td>
</tr>
<tr>
<td>(H₂O)₀.₂₅·µ-oxo-(BsubPc)₂</td>
<td>This work</td>
<td>1899.35</td>
<td>2</td>
<td>1.75</td>
<td>1.42</td>
</tr>
<tr>
<td>(DCB)₂·µ-oxo-(BsubPc)₂</td>
<td>This work</td>
<td>2541.89</td>
<td>2</td>
<td>1.31</td>
<td>1.44</td>
</tr>
<tr>
<td>µ-oxo-(BsubPc)₂subl</td>
<td>This work</td>
<td>3691.63</td>
<td>4</td>
<td>1.80</td>
<td>1.45</td>
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Phthalimido-BsubPc (sublimation)
\[ R_1 = \]

\[ R_2 = R_3 = H \]

Phthalimido-BsubPc (vapour diffusion)

\[ R_1 = \]

\[ R_2 = R_3 = H \]

\[
\begin{array}{cccccc}
\text{GOHDIR}^{(18)} & 1161.97 & 2 & 2.86 & 1.40 & 2.86 & 1.13
\end{array}
\]

\[
\begin{array}{cccccc}
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† Density of the BsubPc bowl-shaped unit (without the R₁ substituent, and where R₂ = R₃ = H).
A1. References.

Appendix 2

Development of a μ-oxo BsubPc Synthesis Process

This Appendix describes the development of a synthesis process for μ-oxo BsubPc in sufficient detail for the experiments to be reproduced. It also steps through the results seen in each attempted synthesis, and describes the decision-making process that led to each subsequent reaction and ultimately to the finalized synthesis process.

Appendix 2 - Table of Contents

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Samples were dissolved in ACN or DMF, depending on which HPLC method was to be used, and solvent choice was found to influence the analysis results. The solubility of Br-BsubPc is so low in comparison to both μ-oxo BsubPc and HO-BsubPc that dissolving samples in DMF was still insufficient to obtain a representative measure of Br-BsubPc content. For this reason, the size of the Br-BsubPc peak cannot be used as indicative of the actual concentration of Br-BsubPc in the reaction. The 80/20 HPLC method takes longer to run than ACN, and shows poorer separation between different peaks. Therefore, after it was determined that HO-BsubPc and μ-oxo BsubPc could fully dissolve in ACN at concentrations beyond the maximum absorption limit of HPLC, the analysis switched to using ACN method. However, analysis of a group of samples on both methods illustrated that the ACN method identifies higher levels of small molecule impurities than the 80/20 method, but the main discrepancy occurs when a solid is sampled. μ-oxo BsubPc exhibits a strong tendency to form crystals whenever solvent is removed from the system, and its subsequent rate of dissolution is slow. In these cases, it seems that DMF and the 80/20 method are necessary to get a representative (or more representative) concentration of μ-oxo BsubPc in the solution sample.
1 Initial Trial Reactions

Scheme A2.1. Potential reaction pathways to \( \mu \)-oxo BsubPc: (a) addition of HO-BsubPc and Br-BsubPc; (b) self-condensation of HO-BsubPc; (c) hydrolysis of Br-BsubPc to form HO-BsubPc (which may then participate in (a) or (b))

1.1 Equimolar HO- and Br-BsubPc in p-xylene with pyridine

The initial trial reaction conditions attempted to mirror elements from successful synthesis procedures of other BsubPcs. P-xylene has been shown to be the optimal solvent in Cl-BsubPc synthesis\(^{(1)}\) and therefore was selected here. As shown in Scheme A2.11a, the hypothesized reaction pathway of an equimolar addition of Br-BsubPc and HO-BsubPc produces HBr. Synthesis of HO-BsubPc also produces HBr (equivalent to Scheme A2.11c, under mild conditions). In the synthesis procedure of HO-BsubPc a small quantity of pyridine, a Lewis base, is used to interact with the free \( \text{H}^+ \) in solution to drive the reaction forwards. Therefore, pyridine was added here in the same molar ratio as is used in the HO-BsubPc synthesis method (22.5 mol equiv., 0.44mL). The reaction was done in 10mL p-xylene, equivalent to 2.4wt%, at 10 °C below the boiling point of pyridine (105 °C). The reaction was monitored by HPLC. Although it is known that Br-BsubPc and HO-BsubPc are initially present in equimolar quantities, within experimental error, the HPLC at \( t=0 \) shows 74% HO-BsubPc and 25% Br-BsubPc which illustrates the limitations of HPLC detection of Br-BsubPc. After 9h a trace of \( \mu \)-oxo is visible, but the peak does not grow for the remainder of the experiment. The sample at
t=22h instead has a new peak at 3.4 min retention time (RT) with a maximum absorption ($\lambda_{\text{max}}$) at 546 nm, which grew slowly until t=117h. At t=189.5h, the reaction was stopped and the composition of the final HPLC sample is shown in Table 4.1. The solvent was removed by rotary evaporation and dried overnight in a vacuum oven, and the composition of the collected solids remained similar with 28% HO-BsubPc, 39% Br-BsubPc and 31% unknown impurity with 3.4 min RT with no µ-oxo detected. This unknown compound will be henceforth referred to as “3.4RT”. Although the 3.4RT impurity was not the desired product, it is of interest due to its unique absorption spectra with a $\lambda_{\text{max}}$ between that of a typical BsubPc (560 nm) and the µ-oxo dimer (530 nm). It could not be separated from the other compounds by chromatography, and therefore mass spectrometry was performed on the crude product since the mass spectrometry profiles of the other compounds are known. However, the unknown 3.4RT compound could not be identified.

1.2 Equimolar HO- and Br-BsubPc at 200 °C in nitrobenzene; and
1.3 Equimolar HO- and Br-BsubPc at 200 °C in diphenylether

Following this reaction, two high boiling solvents were investigated since negligible conversion to µ-oxo BsubPc was observed at 105 °C. In these reactions, pyridine was not used and p-xylene was replaced by nitrobenzene (in 1.2) and by diphenyl ether (in 1.3) and run at 200 °C. All other quantities and conditions were the same. The 1.2 reaction in nitrobenzene appeared initially to produce µ-oxo BsubPc, but the reaction mixture degraded and had turned from magenta to a murky brown colour by t=22h. In the 1.3 diphenyl ether reaction, a µ-oxo peak was present from the t=2h sample onwards which grew over time. The unknown 3.4RT impurity was also present from the t=2h sample and remained at approximately 2% throughout the experiment. The reaction was stopped at t=31h, and the final composition is shown in Table 4.1. Upon retrospective review, the HPLCs indicate that there is another unknown impurity present at a retention time of 2.0 min with a maximum absorption at 567 nm, matching an unknown BsubPc produced in many subsequent reactions. This was not apparent at the time, as the solvent diphenyl ether has a large and broad peak at 1.9 min which overlaps and obscures the BsubPc impurity at 2.0 min. This unknown compound will henceforth be referred to as “2.0RT”.

1.4 Equimolar HO- and Br-BsubPc at 200 °C in diphenylether at 10wt%  
Since µ-oxo was successfully produced in diphenyl ether, the reaction was repeated but at an increased concentration of 10wt%. Two replicates were run in parallel. Both produced µ-oxo
BsubPc and both produced the 2.0RT impurity. In one replicate, 1.4a, the HPLC spectra are clean and the μ-oxo product (82%) outweighs the impurity (15%). However, in the other (1.4b), the HPLC shows multiple overlapping unknown BsubPc peaks and the 2.0RT impurity (42%) outweighs the μ-oxo BsubPc product (30%). The reason for the disparity is unknown. Both reactions were stopped after 15.5h since the concentration of μ-oxo no longer appeared to be increasing. The boiling point of diphenyl ether is too high to be removed by rotary evaporation, and the purpose of the duplicates was to enable two alternative work-ups to be investigated. Methanol was added to 1.4b but no precipitate could be obtained. Precipitate (123mg, 63% yield) was obtained from 1.4a after 200mL cyclohexane was added and left in an ice bath overnight, and the composition of the crude product was 3% HO-BsubPc, 9% 2.0RT impurity, 5% Br-BsubPc and 82% μ-oxo BsubPc. These results provided the first indication that μ-oxo is highly soluble in comparison to both the Br-BsubPc precursor and BsubPcs in general. Using 200mL solvent for precipitation is highly impractical given that the reaction volume is 1.8mL. Therefore, 1,2-dichlorobenzene (DCB) was selected as an alternative because it is the highest boiling solvent commonly used for BsubPc reactions that can be removed by rotary evaporation.

1.5 Equimolar HO- and Br-BsubPc at reflux in 1,2-dichlorobenzene at 10wt%

The reaction in DCB was also run at 10wt% and was heated to reflux (180 °C). It did produce μ-oxo BsubPc, which increased in concentration until the reaction was stopped at t=20h. However, the 2.0RT impurity was again somewhat obscured by the solvent peak but was clearly present, and the 3.4RT impurity was also produced. The final HPLC sample composition in Table 4.1 includes 57% μ-oxo BsubPc and quantities of both impurities and both starting reagents around 10%. Following thin layer chromatography (TLC) tests on both alumina and silica with a variety of solvents, a Kauffman column on alumina in dichloromethane (DCM) was selected as an appropriate separation method. Both Br-BsubPc and HO-BsubPc stayed at the baseline, while μ-oxo eluted with a retardation factor, $R_f$, of 0.7 and one unknown impurity eluted ahead of μ-oxo with $R_f = 0.9$. After the Kauffman column had been running for a few minutes and before the dark purple phase reached the bottom, the flask was removed and switched with fresh solvent. The solvent was removed by rotary evaporation from the first fraction and HPLC identified the fast-eluting impurity as the unknown 2.0RT compound. The mass yield was in the order of 1mg, so mass spectrometry was performed on the entirety of the sample. However, the compound could not be identified from the mass spectrometry results. The Kauffman column was stopped when the column ran clear, and the solvent was removed by rotary evaporation. Crystals which
formed on the sides of the flask were found to be pure \( \mu \)-oxo BsubPc, but the bulk of the solid was 18% 2.0RT impurity and 82% \( \mu \)-oxo BsubPc by HPLC. The sublimation temperature of \( \mu \)-oxo BsubPc was expected to be extremely high, and possibly outside the range of the lab’s sublimation apparatus. Therefore, the solids were train sublimed at 450 °C in the hopes of achieving separation – either to sublime the 2.0RT impurity and leave \( \mu \)-oxo in the crucible, or to sublime both compounds in separate bands due to different sublimation temperatures. \( \mu \)-oxo BsubPc did in fact sublime at this temperature and loose crystals of pure \( \mu \)-oxo BsubPc were obtained. The resulting crystal structure is described in Chapter 3, and is the first report of the non-solvated, non-hydrated \( \mu \)-oxo BsubPc structure (at the time of the experiment no \( \mu \)-oxo BsubPc crystal structure had been published, but Yamasaki and Mori\(^{(2)}\) subsequently reported a toluene solvate). The bands on the sides of the sublimation tube became more enriched in the 2.0RT impurity at increasing distance from the crucible, but even the bands closest to the crucible contained trace amounts of the impurity and thus the yield of pure \( \mu \)-oxo was limited to the mass contained in the single crystals. The details of this synthesis are contained in Chapter 3.

### 1.6 Scale up of equimolar HO- and Br-BsubPc at reflux in DCB at 10wt%

This reaction was also scaled up by a factor of 5, details of which are likewise in Chapter 3. As indicated in Chapter 1, Kauffman columns are typically used in the work-up of BsubPc reactions since the low solubility of BsubPcs means large volumes of solvent are required for them to fully elute. However, in this case both the \( \mu \)-oxo and the 2.0RT impurity elute although TLC on alumina shows that they have different retardation factors \( (R_f) \). Therefore, a standard alumina column was used to separate the products of the scaled up reaction with DCM as the mobile phase. The crude products were dry-loaded due to their low solubility. The 2.0RT impurity did elute ahead of \( \mu \)-oxo BsubPc, but there was a wide band of fractions that contained both the 2.0RT impurity and \( \mu \)-oxo BsubPc and the yield from fractions containing pure \( \mu \)-oxo BsubPc was low (27mg, 3% overall yield).

### 2 Initial Trial Reactions with Perfluorinated BsubPc

#### 2.1 and 2.2 ‘1 pot’ reaction from 25% HO- and 75% Br-\( \text{F}_{12}\)BsubPc

Simultaneously with this first reaction in DCB, an equivalent reaction \((2.1)\) was run attempting to produce the \( \mu \)-oxo dimer of \( \text{F}_{12}\)BsubPc, which has peripheral fluorination instead of hydrogenation of the BsubPc. At the time it was believed that the sublimation temperature of \( \mu \)-oxo BsubPc exceeded the upper limit of the laboratory’s train sublimation apparatus. Therefore,
the motivation for this reaction was to synthesize a $\mu$-oxo derivative with a suppressed sublimation temperature, which can typically be achieved by fluorination of BsubPcs. It was hypothesized that perfluorination of two BsubPc moieties in the dimer (total of 24 fluorine atoms) could result in a significant drop in sublimation temperature. A supply of Br-F$_{12}$BsubPc was available which had partially degraded over time to form HO-F$_{12}$BsubPc, creating a mix with approximately 75% Br-F$_{12}$BsubPc and 25% HO-F$_{12}$BsubPc. Therefore, a ‘1-pot’ synthesis was carried out, adding a drop of water to the reaction to facilitate the in-situ creation of HO-F$_{12}$BsubPc from Br-F$_{12}$BsubPc to reach an approximately equimolar level of Br- and HO-F$_{12}$BsubPc by HPLC. The same scale of 0.243 mmol was used, and the reaction was done at 10wt% in DCB at reflux. The solubility of F$_{12}$BsubPcs is higher than H$_{12}$BsubPcs, so the relative concentration of Br-F$_{12}$BsubPc could be measured by HPLC. However, it was found that Br-F$_{12}$BsubPc and $\mu$-oxo F$_{12}$BsubPc elute at the same retention time of 2.2 min. This makes it very challenging to track conversion, which appears as a shift over time in the UV-vis of the 2.2RT peak. An unknown impurity peak forms between the HO- and Br-/µ-oxo F$_{12}$BsubPc peaks at 1.9 min RT. It is possible that this is a perfluorinated analogue of the 2.0RT compound seen in reactions 1.4 – 1.6. If this is the case, it appears that the F$_{12}$BsubPc reaction occurs in a similar manner to equivalent the H$_{12}$BsubPc reaction of 1.5, but at a slower reaction rate (allowed to run for 192h) and a lower final conversion (23% $\mu$-oxo F$_{12}$BsubPc; seeTable 4.1). Very little change was seen in conversion after 48h, so it is possible that conversion was limited by the ratio of HO-to Br-F$_{12}$BsubPc (leaving excess HO-F$_{12}$BsubPc). The solvent was removed by rotary evaporation, and it was determined by TLC that a Kauffman column on alumina in DCM was also an effective method of separating the F$_{12}$ products. However, an experimental error caused the Kauffman to fail. The reaction was repeated (2.2), and the same compounds were observed by HPLC with a slightly higher conversion to $\mu$-oxo (28%) but in this case production of the 1.9 min RT compound was far greater (30% vs 9%) with the balance made up by a lower remaining amount of HO-F$_{12}$BsubPc (37% vs 61%). Interestingly, although exposed to the same conditions over the same period of time, the products of this reaction did not appear to form crystals upon sitting unlike the reactions 1.6 and 3.1 described in Chapter 3.

These results imply that similar chemistry is shared by the perhydrogenated and perfluorinated $\mu$-oxo BsubPc reactions albeit at different reaction rates, which suggests that lessons learned with $\mu$-oxo BsubPc could be applied to the synthesis of $\mu$-oxo F$_{12}$BsubPc or other peripherally substituted BsubPcs. However, it is not possible to verify this without further experimentation,
which would be time consuming as each reaction is complicated by the fact that peripheral substitution affects absorption spectrum and retention time. Even if the same mechanism occurred, each reaction would generate a new set of unknown impurities that would be challenging to conclusively link to an 'equivalent' impurity in the original perhydrogenated reaction. Since it was now known that $\mu$-oxo BsubPc could be train sublimed in our apparatus, it was decided to focus on developing an appropriate process for $\mu$-oxo BsubPc. As $\mu$-oxo F$_{12}$BsubPc did not readily form single crystals, the reaction results provided no other motivation to continue this investigation. Since this investigation, $\mu$-oxo F$_{12}$BsubPc has been detected in the crucible following sublimation of Br-F$_{12}$BsubPc. There appear to be tiny crystals in the crucible with a similar appearance to when $\mu$-oxo BsubPc single crystals were isolated from sublimation of Br-BsubPc, but they were too small to collect so it cannot be confirmed that the $\mu$-oxo F$_{12}$BsubPc in the crucible is in the form of single crystals rather than as an unsublimed byproduct of the Br-F$_{12}$BsubPc synthesis process.

3 Other Reaction Mechanisms in Dichlorobenzene

3.1 ‘1 pot’ reaction with Br-BsubPc and water in DCB

Following the success of the ‘1 pot’ F$_{12}$BsubPc reaction, the principle was applied to the perhydrogenated $\mu$-oxo BsubPc reaction. A reaction with only Br-BsubPc as a starting product is advantageous because the synthesis of HO-BsubPc is long, troublesome and incurs yield loss. This is elaborated in section 9 of this Appendix. However, a ‘1 pot’ reaction pathway does exclude the possibility of synthesizing asymmetrical dimers. The first step of the reaction is the in-situ production of HO-BsubPc from Br-BsubPc and water, followed by the formation of $\mu$-oxo BsubPc in a second step. The reaction was carried out under the same conditions as 1.5 at 10wt% in DCB at reflux, and details are outlined in Chapter 3. HO-BsubPc, $\mu$-oxo BsubPc and a small quantity of the 2.0RT impurity were present from the first HPLC sample at $t=1$hr. The reaction was stopped after 24h, and the final HPLC indicated 61% $\mu$-oxo BsubPc accompanied by 35% 2.0RT impurity (see Table 4.1). DCB-solvated $\mu$-oxo BsubPc crystals were obtained from the reaction mixture upon sitting (see Chapter 3). This reaction illustrates that the ‘1 pot’ mechanism is indeed feasible, but there remains a need to separate or prohibit the formation of the 2.0RT impurity.
3.2 Self-condensation of HO-BsubPc in DCB

At this time, a paper was published by Yamasaki and Mori\(^2\) which reported synthesis of a number of µ-oxo dimers by self-condensation reaction of HO-BsubPc in addition to the toluene solvated µ-oxo BsubPc crystal structure discussed in Chapter 3. This had not been attempted in this lab so far, since HO-BsubPc is not a desirable starting reagent. Interestingly, the reported reaction was also done in DCB at reflux, although at a lower concentration. However, the reported experiments were done at vastly higher scale – a factor of 67 times the 0.243mmol scale used in this thesis. Details were not explicit, but the reported work-up procedure did not appear to be designed to remove impurities. Therefore, the self-condensation reaction was attempted.

Two equivalents of HO-BsubPc to match the standard 0.243mmol scale (200mg) were heated to reflux at 10wt% in DCB. A trace of µ-oxo BsubPc, the 3.4RT impurity and a new unknown impurity at 2.2min RT were visible after 2h. After 12h, it appeared that µ-oxo and the 3.4RT impurity were present at similar compositions of 11% and 14% respectively. The peaks of both µ-oxo and the 3.4RT impurity grew at a similar rate and very slowly as the reaction continued, and the reaction was stopped before full conversion after 5 days. The composition is listed in Table 4.1 with similar quantities of the starting HO-BsubPc, µ-oxo BsubPc and the 3.4RT impurity present as well as two new unknown impurities at 2.2min RT and 3.7min RT. The solvent was removed by rotary evaporation, and a Kauffman column with alumina and DCM successfully removed most of the remaining HO-BsubPc and some impurities. The first fraction was richer than the second in µ-oxo with 94% µ-oxo BsubPc and only 4% of the new unknown 3.7min RT impurity. It also contained the 2.0RT impurity (2%). The second fraction contained 87% µ-oxo and 13% of the new unknown 3.7min RT impurity, and traces of other impurities were present in amounts below the quantitative integration limit of the HPLC. After removing the solvent by rotary evaporation, the two fractions yielded a total 45mg of solids which equates to a 23% yield prior to sublimation and including impurities. Therefore, this is not an improvement on the equimolar reaction in DCB\(^1\) which had a yield of 46% prior to sublimation. The extremely slow rate of this reaction in comparison to the previous DCB reactions suggests that the equimolar and ‘1 pot’ reactions do proceed by mechanism (a) in Scheme A2.1, the addition of Br-BsubPc and HO-BsubPc to form µ-oxo BsubPc and HBr, rather than mechanism (c)+(b) in Scheme A2.1 in which Br-BsubPc is first converted to HO-BsubPc and µ-oxo BsubPc is formed by the self-condensation of two HO-BsubPc molecules. However, the slow rate, production of the unknown 3.4RT impurity as a byproduct in almost equal
quantities as the desired µ-oxo BsubPc product, and production of additional unknown impurities makes this reaction inefficient and impractical.

4 Reactions adapted from Literature – the Torres Procedure

4.1 Torres Procedure with Br-BsubPc

Since unknown impurities had not been eliminated thus far, the two other procedures for µ-oxo BsubPc from the literature were investigated, despite their low reported yields. The first was reported by the Torres group in 1996, with a 7.6% yield. In the Torres method, Cl-BsubPc (0.14g), dicyclohexano-18-crown-6 (0.28g) and NaOH (80mg) were refluxed for 24h in 200mL p-xylene. Due to its higher reactivity, Br-BsubPc was used in the place of Cl-BsubPc. The extremely dilute conditions made analysis of the reaction mixture by HPLC challenging. However, even after 48h a large sample concentrated by rotary evaporation of the solvent prior to injection contained no products other than the starting Br-BsubPc by HPLC.

4.2 Concentrated Torres Procedure with Br-BsubPc

The initial concentration of Br-BsubPc by mass in 4.1 (0.09wt%) is over 2 orders of magnitude lower than in the previous DCB reactions, and therefore another reaction based on the Torres procedure was run with a quarter of the original solvent volume (50mL p-xylene) (4.2). After 6h, HPLC results indicate 32% µ-oxo but the HPLC sample turned black after the addition of DMF and so the result may not be representative of the reaction mixture. At 24h, results show 36% µ-oxo BsubPc and 64% a new unknown BsubPc at a retention time of 2.6min but again the sample had turned black. In both cases, there were a multitude of peaks visible on the MAXPlot HPLC chromatogram, indicating that the sample contained many non-BsubPc compounds. When the heat was turned off after 24h the reaction mixture was a dark red colour, suggesting a
predominance of Br-BsubPc or other non-dimer BsubPcs (µ-oxo has a deep purple colour). However, after cooling the reaction mixture turned green. The reaction mixture was filtered and the UV-vis absorption was collected, which is displayed in Figure A2.1. The compound has an absorption maximum of 671nm, a red shift of approximately 100nm compared to typical BsubPcs. This unknown green compound was not investigated further.

4.3 Concentrated Torres Procedure with Br-BsubPc and Reduced NaOH

The Torres method was attempted once more with further modification. It was hypothesized that NaOH, a strong base, may negatively affect the reaction or promote generation of byproducts. Therefore the amount of NaOH was reduced from over 6 molar equivalents to 1 molar equivalent of Br-BsubPc. The molar ratio of NaOH (13mg) to dicyclohexano-18-crown-6 (45mg) was maintained. The reaction was again done in 50mL p-xylene rather than the original 200mL, and heated to reflux. It was established that NaOH interacts with DMF and has caused degradation of HPLC samples in the experience of lab colleagues, and therefore the HPLC was run using the pure acetonitrile (ACN) method to eliminate use of DMF. After the heat was turned off at t=24h, an equivalent volume of water was added to the reaction mixture as soon as sufficient cooling had occurred for a liquid-liquid extraction, intended to remove the NaOH and dicyclohexano-18-crown-6 from the organic BsubPc phase as soon as possible to prevent whatever processes produced a green compound upon cooling of the previous reaction. The organic phase did not turn green; however, the final samples contained just 1.7% µ-oxo BsubPc along with 15% HO-BsubPc, 60% Br-BsubPc, the starting material, and several other unidentified BsubPcs (see Table 4.1). It was therefore decided that the Torres method did not represent a better alternative to the earlier approaches to µ-oxo synthesis in DCB.

5 Reactions adapted from Literature – the Potz Procedure

The remaining method of synthesising of µ-oxo BsubPc found in the literature was published by Potz et al. in 2000(4). µ-oxo BsubPc was inadvertently created by attempting to sublime HO-BsubPc under vacuum at 300 °C, although it is not clear how much µ-oxo was found or whether and how it was separated from HO-BsubPc. Previous experiments in this research group have also indicated that HO-BsubPc thermally degrades to µ-oxo BsubPc(5). Therefore, HO-BsubPc was sublimed at the upper temperature limit of this lab’s train sublimation apparatus, 450 °C, in an attempt to replicate this result. If no other impurities were created this method would be an improvement even if the overall conversion from HO-BsubPc to µ-oxo BsubPc was low, since...
the separation of µ-oxo BsubPc from HO-BsubPc is facile. However, although small crystals of µ-oxo were found in the crucible, µ-oxo BsubPc could only be detected at trace levels (below the HPLC integration limit) in some sublimed bands of HO-BsubPc and could not be detected at all in other locations. This experiment also yielded the first known crystals of HO-BsubPc from sublimation, which are described in Chapter 4 with additional details in Appendix 3.

6 The Lewis Acid Mechanism

Following these unsuccessful attempts based on procedures from the literature, two new approaches were investigated. The first explored a phenomenon observed by colleagues in the Bender laboratory, using Lewis acids to catalyse the reaction. The second revisited the earlier reactions in DCB but attempted to eliminate the HBr byproduct, either by preventing its production or by removing the HBr from solution.

The motivation to explore using Lewis acids came from the recently developed AlCl$_3$ chemistry mentioned in Chapter 1. This set of experiments attempted to synthesize µ-oxo BsubPc by adapting the previously developed synthesis of PhO-BsubPc from Cl-BsubPc in the presence of a Lewis acid$^6$. Whilst undertaking a survey of the ability of a variety of Lewis acids to participate in this chemistry, a colleague observed that µ-oxo BsubPc and HO-BsubPc were present in samples taken before addition of the phenoxy nucleophile, particularly with the Lewis acid tin chloride. Although µ-oxo has been observed as a byproduct in very many reactions in this laboratory, in this case it appeared to be the main product and was one of only two (with HO-BsubPc) or three (with Cl-BsubPc) BsubPc compounds which are easily separable. Therefore, it was decided that this reaction mechanism should be investigated for the directed synthesis of µ-oxo BsubPc. The original reaction was done in a glovebox, with 100mg Cl-BsubPc and 1.5 molar equivalents of the Lewis acid stirring in 5mL chlorobenzene at 60 °C with no cooling. The tin chloride reaction in which a high quantity of µ-oxo BsubPc was observed was repeated but the results could not be replicated under these conditions in the glovebox. In order to create µ-oxo and HO-BsubPc water must be present, and the moisture level in the glovebox or a starting material or solvent may have been higher than usual when the reaction was first observed to take place. It is extremely difficult to control the level of water at such low quantities, and this could account for the variability in results.
6.1 to 6.5 Lewis Acid Hydrates

Lewis acid hydrates were chosen to provide water to the reaction, and allow a ‘1 pot’ synthesis route that avoids the necessity of synthesizing HO-BsubPc. These experiments were done outside the glovebox due to the use of water. Cl-BsubPc was replaced by Br-BsubPc. The synthesis of μ-oxo BsubPc is presumed to occur via the in-situ hydrolysis of Br-BsubPc to OH-BsubPc and the subsequent reaction of OH-BsubPc with Br-BsubPc or itself as in reaction 3.1. The scale was increased to match the 0.243mmol scale of previous μ-oxo reactions, and chlorobenzene (5.22mL) was added to Br-BsubPc (115mg, 2wt%) and a Lewis acid hydrate (1.5 equiv) in a scintillation (20 mL) vial with a screw cap. In one case a non-hydrated lewis acid, AlCl₃, was used for comparison (also 1.5 equiv). Also, an AlCl₃•6H₂O reaction was run with potassium phosphate (K₃PO₄, 4.64g, equivalent to 80% of the solvent mass), ground in a mortar and pestle and activated in an oven at 200°C, added to the initial reaction mixture to explore the effects of removing HBr from solution. Details and quantities for each reaction are in Table A2.

1. The mixture was stirred and heated at 60 °C for the duration of the reaction time (27 or 44.5 hours) and monitored by HPLC, following which the reaction was cooled to room temperature. These reactions showed varied final results, which are included in Table 4.1. The reaction conducted with FeCl₃ hexahydrate (7.3) appeared to facilitate some conversion of Br-BsubPc to HO-BsubPc, but degraded over time and the final samples had very low absorption, indicating low BsubPc content. Conversion from Br- to HO-BsubPc was observed in both the AlCl₃ (7.1) and the AlCl₃ hexahydrate (7.2) reactions, and was slightly higher in the latter. In both cases, approximately 20% HO-BsubPc was present after just 1 hour, and at 44.5 hours this had increased to 30% and 37% respectively. In some cases the HPLC samples indicated a decrease in HO-BsubPc concentration between consecutive samples rather than a steady gradual increase, suggesting inconsistency in the sample measurements which were possibly due to solubility limits of Br-BsubPc. In the reaction with AlCl₃ hexahydrate and K₃PO₄ (7.5), μ-oxo BsubPc could be detected after 5 hours but the peak was too small to be quantitatively integrated by the HPLC until 27h (at which point it was 1%). The μ-oxo content did not increase any further. However, even in the t=0 sample, taken just a few minutes after adding the reactants, a new BsubPc compound was observed which partially overlapped the HO-BsubPc peak with a retention time of 1.9 min and a maximum absorption of 562 nm. The partial overlap meant that the quantitative assessment of HO-BsubPc and the new BsubPc may not precisely correspond to their true ratio. The t=0 sample was found to be 62% HO-BsubPc, 34% the new BsubPc and just 4% Br-BsubPc. The composition of Br-BsubPc increased to 10% in the t=1h sample and
fluctuated between 5% and 15% for the remainder of the reaction, likely due to its low solubility resulting in unrepresentative samples. However, it is clear that the conversion to HO-BsubPc and the new BsubPc occurred very quickly. The composition did not appear to change significantly from the first sample until the final one at t=44.5h. It is hypothesized that the newly formed BsubPc was phosphate BsubPc, which has been known to form\(^{(7)}\), due to the presence of K\(_3\)PO\(_4\) and a Lewis acid catalyst. The remaining reaction, with SnCl\(_4\) pentahydrate (7.4), was the only reaction mixture to visibly turn to the colour of the blue reactive complex. Similar quantities of HO-BsubPc were formed in the initial few samples as in the other reactions. However, 1.9% µ-oxo BsubPc was present at t=3.5h, which slowly grew to 8% in the final sample.

### Table A2.1. Details of the Lewis acid and Lewis acid hydrate reactions.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Other Reagent(s)</th>
<th>Lewis Acid (Hydrate)</th>
<th>Reaction Time, h</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.1</td>
<td>Br-BsubPc</td>
<td>AlCl(_3)</td>
<td>0.049</td>
</tr>
<tr>
<td>7.2</td>
<td>Br-BsubPc</td>
<td>AlCl(_3)•6H(_2)O</td>
<td>0.088</td>
</tr>
<tr>
<td>7.3</td>
<td>Br-BsubPc</td>
<td>FeCl(_3)•6H(_2)O</td>
<td>0.098</td>
</tr>
<tr>
<td>7.4</td>
<td>Br-BsubPc</td>
<td>SnCl(_4)•5H(_2)O</td>
<td>0.128</td>
</tr>
<tr>
<td>7.5</td>
<td>Br-BsubPc, K(_3)PO(_4)</td>
<td>AlCl(_3)•6H(_2)O</td>
<td>0.088</td>
</tr>
<tr>
<td>7.6</td>
<td>Br-BsubPc, water</td>
<td>SnCl(_4)</td>
<td>0.05 mL</td>
</tr>
<tr>
<td>7.7</td>
<td>HO-BsubPc</td>
<td>SnCl(_4)</td>
<td>0.05 mL</td>
</tr>
</tbody>
</table>

**6.6 Tin Chloride with Br-BsubPc and water; and**

**6.7 Tin Chloride with HO-BsubPc**

The focus then turned to tin chloride due to its initial positive results. In the initial reaction, low and slow conversion of Br- to HO-BsubPc and of both to µ-oxo BsubPc was observed. It was hypothesized that the slow conversion despite presence of water could be due to the fact that the water was relatively strongly bound to the metal chloride as a hydrate, which also greatly decreases the lewis acidity of the metal chloride. Therefore, the next pair of reactions employed non-hydrated SnCl\(_4\) and efforts were made to control the water content so that the amount of available water was quantifiable and replicable. Two experiments were run in an attempt to elucidate the reaction mechanism. The first (6.6) started with Br-BsubPc, a ‘1 pot’ reaction similar to the initial reactions above, but water was added separately after the non-hydrated tin
chloride rather than in combination as a hydrate. The second experiment (6.7) started with HO-BsubPc and no water was added. If the ‘1-pot’ reaction proceeds by addition of Br- and HO-BsubPc, this second experiment would show no or far slower conversion to µ-oxo BsubPc. If instead the ‘1 pot’ reaction proceeds by self-condensation of HO-BsubPc, the second experiment would show faster conversion since the full theoretical yield of HO-BsubPc is provided at the start. In each, dry chlorobenzene (5.22mL) was added to 0.243mmol of Br-BsubPc (115mg) (6.6) or HO-BsubPc (100mg) (6.7) in a scintillation (20 mL) vial sealed with a septa and purged with a flow of Argon for 30 minutes. The vial was put under positive pressure of Argon and non-hydrated tin chloride (SnCl₄, 1.5 equiv, 0.05 mL) was added. To the reaction containing Br-BsubPc (6.6), water (2.5 equiv, 0.01 mL) was also added. The mixture was stirred and heated at 60°C and the reaction progress was monitored by HPLC for 5 days, following which the reaction was cooled to room temperature. Both vials quickly turned the deep blue colour of the reactive complex, but this did not translate into a fast reaction. In 6.6, Br-BsubPc slowly converted to HO-BsubPc until they were present in approximately equimolar proportions after 5 days. The unknown 3.4RT impurity was also slowly produced, reaching 9% after 5 days. The 6.7 reaction remained predominantly HO-BsubPc after 5 days, with traces of the 3.4RT compound (0.7%). Following the reaction, the flow of argon was removed and the vials were left sealed at room temperature without stirring and shielded from the light. The blue colour of the reactive complex was still not quenched several months later, even though the complex is quenched by air and the seal was imperfect enough for evaporation of solvent to take place. However, no crystals of the blue compound were found in the vials.

Since no µ-oxo BsubPc was formed in these reactions and promising results had been achieved through other approaches, the Lewis acid mechanism was pursued no further. Recent results from another colleague’s work have also yielded µ-oxo BsubPc from tin chloride reactions before addition of a ligand, in this case observed outside the glove. Although the reaction has no unknown byproducts, it does not produce a higher conversion of HO- to µ-oxo BsubPc than can be achieved by other approaches, and it remains challenging to replicate the results which seem to be sensitive to uncontrolled variables such as atmospheric humidity. The chemistry represents an interesting topic of study to gain understanding into BsubPc reaction mechanisms, but until it is better understood its seemingly temperamental nature makes it an impractical method for the synthesis of µ-oxo BsubPc.
7 Removing HBr – the Nosylate Reaction

The creation of μ-oxo by addition of Br- and HO-BsubPc also produces HBr, which is a strong acid and therefore could be a cause of the observed unknown BsubPc impurities. The greatly reduced production of the 2.0RT impurity by the self-condensation reaction suggests that the HBr byproduct of the addition reaction could be involved in creation of this impurity. Therefore, several methods were investigated that avoid production of HBr or remove it from solution.

These approaches revisited the reactions conducted in DCB, but addressed the formation of HBr in these reactions and its potential role in formation of unknown impurities. The first of two methods achieved this by replacing Br-BsubPc with nosyl-BsubPc (NsO-BsubPc). It is known that the rate of reaction of NsO-BsubPc is faster than that of Cl-BsubPc, but slower than Br-BsubPc\(^8\). The pseudo-halide leaving group results in the production of nosylic acid, a much weaker acid than HBr, as illustrated in Scheme A2. 2a.

![Scheme A2. 2. Formation of μ-oxo BsubPc using NsO-BsubPc in (a) an addition reaction; and (b) a catalytic role.](image)

7.1 Equimolar HO- and NsO-BsubPc in DCB

All other conditions were kept the same as the previous equimolar reaction in DCB with Br-BsubPc (1.5: 0.243mmol of both HO-BsubPc (100mg) and nosyl-BsubPc (145mg) were stirred and heated to reflux at 10wt% in dichlorobenzene (1.7mL) under argon with cooling, and the reaction was monitored by HPLC. The peaks of HO- and NsO-BsubPc overlap on the HPLC, with a retention time of 1.9 and 1.8 minutes respectively on a pure acetonitrile column, but can be distinguished by their maximum absorption wavelengths of 559 and 566nm respectively. A significant quantity of μ-oxo was produced after just 1 hour, accounting for 43% of the sample by HPLC, and the reaction was run for 24 hours. As the reaction progressed, the quantity of HO-
BsubPc decreased and the quantity of μ-oxo BsubPc and the 2.0RT impurity increased, while the peak size of NsO-BsubPc stayed the same (note that it is not possible to determine whether the HO-BsubPc was fully consumed, because a small peak would be obscured by the far larger overlapping NsO-BsubPc peak.) However, the NsO-BsubPc must be involved in the reaction since the rate of μ-oxo formation is fast in comparison to the HO-BsubPc self-condensation reaction 3.2 (which took 5 days to reach 35% conversion). This could be explained by a mechanism in which the NsO-BsubPc acts as a catalyst and is regenerated after formation of μ-oxo BsubPc when a second molecule of HO-BsubPc reacts with the nosylic acid byproduct, as is demonstrated in Scheme A2. 2b, which is a common mechanism of pseudo-halides in organic chemistry.

### 7.2 HO-BsubPc with 10mol% NsO-BsubPc in DCB

A second experiment was conducted to investigate whether this mechanism did occur. The quantity of HO-BsubPc and all other conditions remained the same but only 0.0243mmol of NsO-BsubPc (14.5mg) was added, equivalent to 10mol% of HO-BsubPc. If the proposed mechanism was valid, full conversion of HO-BsubPc should be observed with no consumption of the NsO-BsubPc. However, the reaction was extremely slow and μ-oxo BsubPc reached a maximum of 36% after 75h. Following this the μ-oxo BsubPc peak decreased as the 2.0RT impurity peak increased until the reaction was stopped at t=126h with 4% and 18% repectively. The remaining 78% peak was HO-BsubPc, and possibly included NsO-BsubPc. It was not possible to detect the NsO-BsubPc peak in most samples since it was equal or less than 10mol% of HO-BsubPc in this experiment and was fully obscured by the larger overlapping HO-BsubPc peak. This experiment did not confirm or conclusively disprove the proposed mechanism, but since the reaction did not produce high yields of μ-oxo BsubPc or avoid formation of unknown impurities this was not selected as an appropriate route for μ-oxo synthesis.

### 8 Removing HBr – the Potassium Phosphate Method

The remaining method to address the elimination of HBr focused on removing it from the reaction environment after it is generated. The Br⁻ anion can be precipitated out of solution as a salt by reaction of HBr with a base. However, if the acid-base reaction also produced water, this may interfere with the reaction kinetics and also with the ratio of Br-BsubPc to HO-BsubPc in the equimolar reaction. The base potassium phosphate (K₃PO₄) does not produce water upon reaction with HBr, and provides three potential reaction sites per molecule as illustrated in
Scheme A2.3. $\text{K}_3\text{PO}_4$ is hygroscopic and therefore it is dried in an oven at 200 °C before use. The pellets are ground in a mortar and pestle prior to drying to maximise the accessible surface area.

Scheme A2.3. Removal of HBr in the presence of $\text{K}_3\text{PO}_4$ by formation of KBr.

8.1 Equimolar HO- and Br-BsubPc in DCB with 80% $\text{K}_3\text{PO}_4$

The equimolar reaction (1.5) with 0.243mmol of HO-BsubPc and Br-BsubPc at 10wt% in DCB was repeated, but in this case dry $\text{K}_3\text{PO}_4$ powder was added to form a thick slurry (1.56g, equivalent to 80% of the solvent mass). This was stirred under argon and heated to reflux, and the reaction progress was monitored by HPLC. Samples were filtered before injection into the HPLC to remove $\text{K}_3\text{PO}_4$, KBr precipitate and any undissolved BsubPcs (in particular, Br-BsubPc). The first HPLC sample after 1h indicated 90% $\mu$-oxo BsubPc with the remainder HO-BsubPc. This slowly increased to 98% $\mu$-oxo BsubPc after 24h, with a small impurity of HO-BsubPc. The MAXPlot HPLC data indicated traces of a compound with the characteristic RT of 1.5min and $\lambda_{\text{max}}$ of 291nm of phthalimide, a known degradation product of BsubPcs, and traces of an unknown non-BsubPc impurity with a $\lambda_{\text{max}}$ at 305nm. The 2.0RT impurity was not seen in any HPLC sample throughout the reaction. A Soxhlet extraction was performed to remove the solid $\text{K}_3\text{PO}_4$ and salt precipitate. Toluene was chosen as the solvent, since the solubility of $\mu$-oxo BsubPc in toluene was reported to be a high 10g/L (2). The toluene was removed from the filtrate by rotary evaporation, and the solid was 89% $\mu$-oxo BsubPc and 11% HO-BsubPc by HPLC (the difference in composition compared to the reaction samples could be due to the inhomogeneous reaction samples, and the tendency of $\mu$-oxo to form crystals upon evaporation of solvent reducing its subsequent solubility). The dry mass of collected solids after being left in a vacuum oven overnight (40°C, 10 mmHg) was 0.06g, corresponding to a mass yield of 31%. The solids retained in the Soxhlet thimble were found to be a deep blue-turquoise colour, and were insoluble in a range of organic solvents. This indicates that a reaction or interaction is taking place between the $\text{K}_3\text{PO}_4$ and a BsubPc which gives colour to the insoluble solids, and is a contributing factor to the low yield. The mass yield of 31% is an improvement over the previous 16% yield, but was not pure $\mu$-oxo BsubPc. This crude product contained HO-BsubPc and thus required two further steps incurring mass losses, a Kauffman column and sublimation, to obtain
comparable pure sublimed μ-oxo BsubPc. The deep turquoise colour of the remaining K₃PO₄ was a visible source of mass loss, and therefore it was hypothesized that reducing the quantity of K₃PO₄ would increase the yield.

8.2 Equimolar HO- and Br-BsubPc in DCB with 20% K₃PO₄

Another equimolar DCB reaction was run, with a quarter of the mass of K₃PO₄ (0.388g, 20% of solvent mass). Traces of three unknown impurities were present in the sample from t=0.5h to t=3h, but they were apparently consumed as none were detected in later samples. The 3.4RT impurity was also produced, reaching a maximum of 9% by HPLC after 1.5h, but subsequently declined and was not detected beyond t=3h. The conversion of HO-BsubPc to μ-oxo BsubPc followed a similar profile over time as the first K₃PO₄ reaction. However, several non-BsubPc compounds were identified on the MAXPlot HPLC data including the two compounds seen in the first K₃PO₄ reaction. In this case, the mass yield was 66% following a Soxhlet extraction and was pure μ-oxo BsubPc by HPLC at 545nm. However, this sample was just 30% μ-oxo BsubPc at MAXPlot, with the possible phthalimide peak at 1.9RT reaching 22% and approximately 5 other unknown non-BsubPc compounds making up the remainder. Since the extinction coefficients of these compounds are not known, it is not possible to determine a concentration or composition profile from the MAXPlot data and the 30% area of μ-oxo BsubPc cannot be equated with a mass percentage. Train sublimation at a low temperature (220 °C) was used to remove the small molecule impurities visible on the MAXPlot HPLC results. The white solids that sublimed out of the crucible were confirmed to be phthalimide by HPLC and ¹H NMR. The mass of the solids in the crucible decreased by 30%, indicating the small molecule content of the original crude product was at least 30wt% (some non-BsubPcs may have remained in the crucible). The remaining 70mg in the crucible was subsequently train sublimed at 450 °C, and 16mg of pure μ-oxo BsubPc was collected from the sublimation tube, corresponding to an overall mass yield of 8%. 29mg of material remained in the crucible.

8.3 Dry equimolar HO- and Br-BsubPc in DCB with 20% K₃PO₄

The achievable mass yield of this process is severely reduced by degradation of BsubPc to form phthalimide and other unknown compounds. The reaction was repeated under dry conditions, in case water was contributing to degradation. Glassware was dried in an oven at 100 °C overnight, and the solvent was filtered through alumina before use. The K₃PO₄ was added immediately after being dried in the oven at 200 °C while still hot. The conversion of HO-BsubPc to m-oxo
BsubPc was similar, but no 3.4RT impurity was observed to form. Traces of one unknown BsubPc impurity were observed until t=4h but not beyond. After 24h only µ-oxo BsubPc could be detected on the 545nm channel but at an extremely low absorption. The MAXPlot data followed a similar profile to the previous reaction, and produced the same degradation products.

8.4 Wet ‘1 pot’ reaction with Br-BsubPc in DCB with 20% K₃PO₄

At the same time, a reaction using similar conditions but following the ‘1 pot’ mechanism was run. The hygroscopic nature of K₃PO₄ was put to use by exposing K₃PO₄ to the atmosphere before adding it to the reaction, which becomes the water source for in-situ conversion of Br-BsubPc to HO-BsubPc. The reaction quantities and conditions were identical to 3.1, but wet K₃PO₄ instead of a drop of water was added. A vial of K₃PO₄ was left exposed to atmosphere overnight, and the mass increased by 12%. The amount of wet K₃PO₄ (0.437g) equivalent to the quantity of dry K₃PO₄ (0.388g, 20% solvent mass) used in the previous 8.2 reaction was added. Two BsubPc impurities at 2.3RT and at 2.9RT reached a maximum of 4% and 7% respectively after 5h. µ-oxo BsubPc was formed very quickly, reaching 62% at 0.5h and plateauing at approximately 2/3rd conversion although this is lower than the previous equimolar reactions with K₃PO₄ (final µ-oxo content of 90 to 100%). In this case, only Br-BsubPc could be detected in the 545nm data after 24h which was present with an extremely low absorption signal. The same generation of non-BsubPc impurities was observed in the MAXPlot data.

Whilst monitoring the 8.3 and 8.4 reactions by HPLC, it was qualitatively observed that the colour intensity of the samples appeared to decrease over time and a higher concentration was required to make up an HPLC sample with appropriate absorption. By the second day, it was clear that substantial degradation of BsubPcs had taken place because the sample colours were extremely light, and the absorption of the maximum concentration HPLC samples at 545nm were at the limit of detection. Following this observation, the maximum absorption of µ-oxo BsubPc in each HPLC sample was converted to an equivalent absorption of the original reaction sample by factoring in the volume of solvent added to dilute the reaction samples. The reaction samples are taken by capillary action into a pipette, and therefore the volume removed from the reaction is assumed to be approximately constant. The results of this conversion for reaction 8.3 and 8.4 are shown in Figure A2. 2 (a) and (b) respectively. These both illustrate that, while the percent conversion may increase over time, the absolute concentration of µ-oxo BsubPc peaks within 1hr and subsequently declines. Therefore, the maximum quantity of µ-oxo BsubPc is present during
the first hour of reaction, after which more is lost through degradation processes or removed from solution by K₃PO₄ than is produced by incremental conversion. A substantial quantity of HO-BsubPc is still present at this time (28% and 32% in 8.3 and 8.4 respectively), but HO- and μ-oxo BsubPc can be separated and the yield cost of the separation process is less than the yield cost of allowing the reaction to go to completion in the presence of K₃PO₄. It also appears that almost double the quantity of μ-oxo BsubPc was produced by 0.5h and by 1h in the dry equimolar reaction 8.3 (0.6 – 1.0 equiv. AU) than in the wet ‘1 pot’ reaction 8.4 (0.3 – 0.6 equiv. AU). This could suggest that water does indeed play a role in BsubPc degradation, or that the reaction within this time frame is limited by Br-BsubPc and excess water leads to production of HO-BsubPc rather than μ-oxo BsubPc. However, other factors may influence the comparison between two different reaction conditions, such as if water affects the volume of liquid drawn into the capillary.

Figure A2. 2. Profile of normalized maximum μ-oxo BsubPc absorption over time in the (a) dry equimolar reaction 8.3 and (b) wet ‘1 pot’ reaction 8.4, in the presence of 20% K₃PO₄.

8.5 Dry equimolar HO- and Br-BsubPc in DCB with 20% K₃PO₄ for 1 hour; and
8.6 Wet ‘1 pot’ reaction with Br-BsubPc in DCB with 20% K₃PO₄ for 1 hour

Both reactions were repeated, but the heat was turned off after 1h and the reaction vessel cooled immediately. In the dry equimolar reaction (8.5), the composition at 0.5h and 1h matched the samples at those times of the previous dry equimolar reaction 8.3, with traces of the same two unknown BsubPc impurities. The composition by MAXPlot was also very similar, with the same unknown impurities. In the case of the wet ‘1 pot’ reaction (8.6), the same BsubPc impurities as in the previous wet ‘1 pot’ reaction 8.4 were observed but the ratio of μ-oxo to HO-BsubPc was higher (see Table 4.1). The MAXPlot data showed the same impurity profile as the previous reaction also. It was also noted that when weighing the K₃PO₄, the solid became gel-
like around the edges of the vial and spatula as it absorbed more water – therefore, the precise quantity of K$_3$PO$_4$ and water present may be different than in the previous reaction and is difficult to control. A Soxhlet extraction in toluene was performed on the crude products of both reactions. However, the DCB reaction solvent was not removed by rotary evaporation prior to transferring the products into the Soxhlet. This was due to the fact that the results of rotary evaporation on the reaction mixture of aggregated insoluble solids and precipitated B$\text{subPc}$, some of which appeared to form crystals upon rotary evaporation, were very messy and it was extremely challenging to manually remove the caked solids from the reaction vial or to re-disperse the solids in toluene for transfer into the Soxhlet thimble. It is undesirable to place large solid particles in a Soxhlet extraction as the surface area accessible to the extracting solvent is greatly reduced and may result in very poor yields by encapsulating the desired compounds within these solid particles.

Different subsequent workup procedures were performed on the products of each reaction. In the case of the wet ‘1 pot’ reaction (8.6), the composition prior to Soxhlet was 17% HO-B$\text{subPc}$, 4% of the 2.3RT impurity and 79% $\mu$-oxo B$\text{subPc}$. After the Soxhlet extraction the solvent was removed by rotary evaporation and dried in a vacuum oven overnight. The composition of the collected product (157mg, 80% mass yield) was 12% HO-B$\text{subPc}$, 5% 2.3RT impurity and 81% $\mu$-oxo B$\text{subPc}$, and traces (1%) of the 3.4RT impurity were present although none was detected earlier in the reaction. A set of samples run in both the ACN and 80/20 methods for comparison indicate that the “2.3RT” impurity in the ACN method is equivalent to the previously discussed 2.0RT compound (which refers to its retention time in the 80/20 method). The workup described by Yamasaki et al$^{(2)}$ following the self-condensation of HO-B$\text{subPc}$ involves dispersing the product in DMF, filtering it and washing the retained solids with DMF then water. This had not been previously attempted because DMF is typically a very good solvent for B$\text{subPc}$ and observations had indicated that DMF is also a good solvent of $\mu$-oxo B$\text{subPc}$, so it would be expected that the described method would simply dissolve all the solids. However, based on our experience of the HO-B$\text{subPc}$ self-condensation reaction, it seemed likely that the purpose of this work-up was to separate $\mu$-oxo B$\text{subPc}$ from remaining unreacted HO-B$\text{subPc}$ and other byproducts of that reaction. The composition of B$\text{subPcs}$ following the Soxhlet workup called for a method that could achieve this, and the yield and purity reported by Yamasaki et al$^{(2)}$ were high, so the method was followed and the quantities of solvent were scaled down to the 0.243mmol reaction scale. As expected, no solids were retained when the mixture was filtered
because the solids fully dissolved in DMF. However, when rinsed with water, a gold precipitate formed in the vial and, as further water was added, in the filtrate. The filtrate was collected and approximately 4 volume equivalents of water were added. This was filtered, and the collected solids were rinsed with more water. The dry solids (115mg, 59% yield) were found to be depleted in HO-BsubPc and the 3.4RT impurity, and enriched in µ-oxo BsubPc (8% vs 12%, 3% vs 5%, and 90% vs 81% respectively). If the HPLC composition is converted to a mass composition using extinction coefficients at 545nm and multiplied by the total mass (neglecting non-BsubPc contributions to mass), there was a net 20% mass loss of µ-oxo BsubPc (84wt% of 157mg before, 92wt% of 115mg after). However, the MAXPlot data indicates that this method also reduced the content of non-BsubPc impurities and phthalimide is no longer detectable, although multiple other impurities are still present. Therefore, a set of experiments were run to find whether there is a ratio of DMF and water that solubilizes HO-BsubPc without solubilizing µ-oxo BsubPc which could remove all HO-BsubPc from the reaction mixture without causing significant mass loss of µ-oxo BsubPc. A small quantity of HO-BsubPc (1-2mg) was added to a 2Dr vial, and 2mL solvent was added. The solvent was 0, 5, 10, 20 or 30% DMF by volume with water, and two trials of methanol, another known good solvent of HO-BsubPc, were also tried (5% and 10% by volume). Each vial was sonicated for 20 seconds, left to settle for 10 minutes, and then centrifuged for 3min at 6000 rpm to separate the solids. The 20vol% DMF vial looked slightly darker than the 100% water standard, but only the 30vol% DMF vial took on the characteristic pink-magenta colour of dissolved HO-BsubPc. This colour was extremely light, and a significant amount of undissolved solid can also been seen in the vial (see Figure A2.3). Therefore, very large volumes of solvent would be required to remove all the HO-BsubPc from the µ-oxo reaction and it is likely that at higher DMF concentrations µ-oxo would also be solubilized (no sufficiently large sample of pure µ-oxo BsubPc exists for testing). Therefore, it was decided that other methods should be investigated before pursuing this further.

Figure A2.3. Solubilization of HO-BsubPc in a mix of water and, from left to right, 10% and 5% methanol; 30%, 20%, 10%, 5% DMF; and pure water.
After the Soxhlet on the products of the dry 1hr equimolar reaction 8.5 a TLC in toluene of the retentate on alumina identified that µ-oxo eluted while HO-BsubPc stayed at the baseline. Therefore, alumina (40g) was added directly to the toluene retentate (approx. 100mL) and stirred. The liquid was decanted into a filter, and more toluene was added to the flask containing alumina and stirred. This was repeated several times (approx. 3 additional volume equivalents), and the alumina and liquid was poured into a filter and rinsed with toluene. However, the runoff was still very deeply coloured illustrating that a significant quantity of µ-oxo remained adsorbed on the alumina. It was therefore decided that a Kauffman column with alumina would be a more appropriate separation technique allowing use of a far larger volume of solvent to gradually elute µ-oxo from the column. After the alumina was rinsed, the solvent was removed from the filtrate by rotary evaporation and the solids dried in a vacuum oven overnight. The collected solid (42mg, 21% yield) was 100% µ-oxo BsubPc on the 545nm channel, and no phthalimide was detected on the MAXPlot channel although other impurities remained. A Kauffman was subsequently run on the retained alumina with adsorbed BsubPcs with a mobile phase of DCM, and yielded further solids(14mg) which were also pure µ-oxo BsubPc, resulting in a total 29% mass yield (56mg). Therefore, this method is preferable to dispersion in a DMF/water mix.

8.7 Scale-up of wet ‘1 pot’ reaction in DCB with 20% K₃PO₄ for 1 hour

The reaction was scaled up by a factor of 2.5 to a basis of 0.606 mmol, which corresponds to a theoretical yield of 489mg µ-oxo BsubPc. Since the wet ‘1 pot’ reaction had 59% mass yield after removal of all solids and apparent removal of phthalimide, and was 92% µ-oxo by HPLC despite a non-ideal separation process, this reaction was chosen for scale up because it eliminates the necessity to synthesize large quantities of HO-BsubPc. In this case, the K₃PO₄ (1.039g) was weighed and added to the reaction vessel while hot immediately after being dried in the oven at 200 °C so that it could be weighed as a powder. The vial was then left open inside a larger sealed vessel containing water and heated to 50 °C. It was removed, agitated and weighed periodically until the mass increase was consistent with the same degree of water saturation as was assumed in the previous reactions (15wt%, 154mg). Since it was not known whether the rate of the scaled-up reaction would be the same, the samples were analysed immediately after being collected and the reaction was turned off as soon as the total absorption level of µ-oxo BsubPc decreased. In this case, phthalimide (1%) was detected at t=0 and may be present in the Br-BsubPc starting material. The HPLC sample at 0.5h matched the 0.243mmol scale reactions. The sample at 1h showed a decrease in total µ-oxo absorption so the reaction was turned off and
cooled after 1.25h. The MAXPlot data at 1h and 1.25h showed a similar impurity profile as the 
t=1h sample of the smaller scale reaction, but impurities appeared to be present at lower levels. 
The only BsubPc impurity visible at 1h was the 2.3RT compound, but the ratio of $\mu$-oxo (70%) to 
HO-BsubPc (29%) was lower than the smaller scale reaction at 1h (78% to 18%). When the 
reaction was turned off at 1.25h, the content of HO-BsubPc, $\mu$-oxo BsubPc and the impurities 
matched the 0.243mmol reaction 1h sample. The total absorption of $\mu$-oxo also appeared to have 
increased. Upon taking all three samples, formation of white smoke and violent splashes of the 
reaction mixture up the sides of the vial and sampling pipette were observed. This could have 
led to variation in the sample volumes, and thus the total absorption levels would not be 
comparable. However, it appears that the kinetics are similar to the 0.243mmol reaction scale 
based on sample compositions and 1h appears to be the best time to end the reaction to avoid 
formation of additional impurities. A Soxhlet extraction in toluene was then run. Following this, 
the retained liquid was added directly into the top of a Kauffman column with alumina and 
collected at the bottom. Once all the liquid had been added to the column, the Kauffman was set 
up with condenser and inert gas and the heat turned on. However, due to the high heat required 
to establish reflux with high-boiling toluene, the resulting temperature at the bottom of the 
column caused the toluene to bump inside the column. A purple band was visible near the 
bottom of the column, but this had not eluted out after 2 days when the Kauffman was stopped. 
Yellow solids were visible near the top of the column after cooling, and the lack of depth of 
colour in the retained liquid indicated that very little BsubPc eluted out of the column, which 
suggests that degradation took place. After removing the solvent by rotary evaporation, just 1mg 
of solids were recovered. HPLC analysis indicated that $\mu$-oxo was still present (57%), as were 
the 2.3RT impurity (14%) and two other unknown BsubPc compounds (15 and 14%). Very high 
quantities of phthalimide and other non-BsubPc impurities (with peaks overlapping each other 
and the solvent peak, so %area could not be quantified) were present on the HPLC MAXPlot 
channel. Following this result, it was decided to remove the solvent by rotary evaporation after 
the Soxhlet extraction and run the Kauffman column using DCM as the mobile phase in the place 
of toluene, as DCM’s far lower boiling point (40 °C compared to 111 °C) reduces the likelihood 
of bumping in the Kauffman column and of thermal degradation. It also reduces the energy 
requirements of the process substantially, which is beneficial should the process need to be 
scaled up further. HO-BsubPc also stayed at the baseline on alumina TLC plates with DCM and 
$\mu$-oxo travelled further from the baseline than with toluene as the mobile phase.
8.8 Replicate of scaled-up wet ‘1 pot’ reaction in DCB with 20% K$_3$PO$_4$ for 1 hour

This reaction was repeated, with the heat stopped after 1h and a DCM instead of toluene Kauffman column. The ratio of μ-oxo to HO-BsubPc was similar to the final 1.25h sample in the previous run, but one fewer BsubPc impurity was observed (see Table 4.1). The MAXPlot profile was also very similar. Following the Soxhlet extraction, the composition was 12% HO-BsubPc, 4% 2.3RT compound, and 84% μ-oxo BsubPc. Since a large volume of solvent was required to fully dissolve the solids to transfer into the Kauffman column, it was run as a normal column until 250mL of liquid was collected and subsequently left to dry overnight before turning on the heat with fresh solvent underneath to decrease the likelihood of bumping inside the column. The Kauffman was run for 1 day. The DCM was removed by rotary evaporation and the collected solids (235mg, 48% mass yield) were 9% 2.3RT impurity and 91% μ-oxo BsubPc. Phthalimide was not detected but multiple other non-BsubPc impurities (cumulatively 29%) were present in the MAXPlot HPLC data. These solids were train sublimed following the same procedure as when the products of 1.5 were sublimed to obtain non-solvated single crystals. A wide band of BsubPc was observed on the sublimation tube walls, but no separation of distinct BsubPc bands was achieved. The collected yield of loose crystalline solids was 42mg, representing a 9% overall yield. Other collected bands were not pure μ-oxo BsubPc. This is not enough material to carry out further sublimation, and so it cannot meet purity requirements.

8.9 Scaled up dry equimolar HO- and Br-BsubPc in DCB with 20% K$_3$PO$_4$ for 1 hr

Following a reassessment of the reaction profiles and results of the K$_3$PO$_4$ reactions, it was identified that the 2.3RT, or 2.0RT, impurity had not been observed in the dry equimolar reactions (although traces of other BsubPc impurities are present). It is not initially present in significant quantities in the wet ‘1 pot’ reactions, but it is concentrated throughout the work-up as other impurities are removed. Therefore, the dry equimolar addition reaction was chosen to fully avoid the problem. This reaction is described in Chapter 4, as the final selected μ-oxo synthesis procedure.

The scale of this reaction was determined by the size of a batch of synthesized HO-BsubPc (0.464g), which corresponds to a scale-up factor of approximately 5, or a reaction scale of 1.13 mmol and a theoretical μ-oxo BsubPc yield of 908 mg. The HO-BsubPc and reaction vial had been dried and stored in a vacuum oven immediately prior to the reaction, and the K$_3$PO$_4$ was dried in an oven at 200 °C for several hours on this occasion, and therefore the only potential
source of water was the Br-BsubPc (0.535 g) which had been stored as usual. Since the K₃PO₄
(1.801 g) was used dry, all three compounds were in powder form when added and the vial could
be sealed and shaken to ensure good mixing of the three components, resulting in a uniformly
coloured dusky purple powder prior to adding solvent. This contrasts to the previous wet ‘1 pot’,
in which the wet K₃PO₄ became sticky and aggregated, and could explain why, when the reaction
was stopped and the contents transferred to a Soxhlet thimble, the reaction mixture resembled a
slurry with well-mixed evenly sized particles. This is stark comparison to the previously
observed mixtures of liquid with a variety of dark-coloured particles that resist dissolution and
dispersion, despite the use of sonication. The presence instead of a slurry meant this process step
was very straightforward. The Soxhlet was run for 2 days, followed by removal of the solvents
by rotary evaporation. The solids were redissolved in DCM, which was passed through the
Kauffman column and collected. The Kauffman was left to dry, and was then run for one day.
After the DCM was removed by rotary evaporation and the solids dried (537 mg, 59% mass
yield), they were train sublimed following a similar profile as that used to obtain single crystals
from 1.5. The sublimation temperature was maintained for an additional hour to ensure all
sublimable materials sublimed out of the boat, given that this was a scale-up of the 1.5 reaction.
The full sublimation procedure is given in Table A2.2.

Table A2. 2. µ-oxo train sublimation temperature profile.

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>Time at that temperature, min</th>
<th>Effective ramp rate, °C/min</th>
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<tr>
<td>120</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>180</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>220</td>
<td>60 (1h)</td>
<td></td>
</tr>
<tr>
<td>280</td>
<td>10</td>
<td>2</td>
</tr>
<tr>
<td>300</td>
<td>10</td>
<td>3</td>
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<td>330</td>
<td>10</td>
<td>2</td>
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<td>350</td>
<td>10</td>
<td>2</td>
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<td>370</td>
<td>20</td>
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<td>400</td>
<td>20</td>
<td>0.75</td>
</tr>
<tr>
<td>415</td>
<td>20</td>
<td>0.5</td>
</tr>
<tr>
<td>425</td>
<td>20</td>
<td>0.5</td>
</tr>
<tr>
<td>435</td>
<td>10</td>
<td>0.5</td>
</tr>
<tr>
<td>440</td>
<td>20</td>
<td>0.25</td>
</tr>
<tr>
<td>445</td>
<td>30</td>
<td>0.17</td>
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<tr>
<td>450</td>
<td>5h 45min</td>
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</table>

A total 357 mg (39% overall yield) of pure µ-oxo BsubPc was collected from the sublimation
tube, of which 232 mg were loose single crystals – some crystals were sufficiently large to be
seen by the naked eye. Bands containing traces of HO-BsubPc and another BsubPc impurity
were also identified, and discarded. White crystalline solids found on the cold finger were found to be phthalimides. The collected pure μ-oxo BsubPc was train sublimed following the same method a second time. A total of 204 mg of pure μ-oxo BsubPc was collected, of which 105 mg was loose crystalline μ-oxo BsubPc.

9 HO-BsubPc synthesis

This section does not describe a μ-oxo BsubPc synthesis reaction, but addresses a precursor step. As previously mentioned, the ‘1 pot’ reaction mechanism is attractive because it avoids the necessity of an additional, separate HO-BsubPc synthesis step. Because of the low solubility of Br-BsubPc, the current procedure can result in inconsistent yields. Although HPLC results indicate full conversion, the HPLC assesses the composition of the solution and cannot identify whether Br-BsubPc precipitate remains. This is only discovered when sampling the dry solid following the full work-up, which takes three to four days in addition to the 24h reaction time. This length of the process is due to the technique of precipitating the crystals in water and the subsequent necessity of removing residual water using a drying agent. Microwave chemistry was investigated as a possible way of speeding up the process and driving conversion. However, although initial results were highly promising, indicating 100% conversion of Br-BsubPc to HO-BsubPc within 4 minutes, when the work-up was complete unreacted Br-BsubPc was always found in the solid samples. This could not be eliminated by longer heating times or different heating rates. This is because the presence of Br-BsubPc cannot be detected in solution once a certain degree of conversion has taken place, and it appears as though Br-BsubPc has been consumed. It is not possible to tell when full conversion truly has been achieved. Additionally, the microwave experiments utilized the same system and reaction components as the original reaction, and thus the lengthy work-up procedures were not eliminated. Upon review of the synthesis procedures reported in literature and previously replicated by a Bender lab colleague, Emma Brisson, as well as of her own developed method, the Brisson procedure remained the best available alternative (5). A few adaptations were made based on her previous analysis of the method. The temperature was increased from 60 °C to 80 °C, and the reaction time increased from 24h to 28h, or until two successive HPLC samples run using the 80/20 method cannot detect any contribution from Br-BsubPc. To resolve the issue of Br-BsubPc remaining as a precipitate, a filtration step is added prior to precipitation of the filtrate in water to remove any compounds that were not in solution and therefore not visible in the HPLC samples.
A2. References


(2) Yamasaki, Y.; Mori, T. Bulletin of the Chemical Society of Japan 2011, 84, 1208–1214.


Appendix 3

Supplementary Information on the Crystal Structure of HO-BsubPc

Table A3. 1. Selected crystallographic and geometrical parameters for HO-BsubPc.

<table>
<thead>
<tr>
<th>Compound reference</th>
<th>d12198</th>
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<tbody>
<tr>
<td>Chemical formula</td>
<td>C_{24}H_{13}BN_{6}O</td>
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<tr>
<td>Formula Mass</td>
<td>412.21</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>a/Å</td>
<td>26.2251(13)</td>
</tr>
<tr>
<td>b/Å</td>
<td>11.7733(7)</td>
</tr>
<tr>
<td>c/Å</td>
<td>12.0258(6)</td>
</tr>
<tr>
<td>α/°</td>
<td>90.00</td>
</tr>
<tr>
<td>β/°</td>
<td>92.248(3)</td>
</tr>
<tr>
<td>γ/°</td>
<td>90.00</td>
</tr>
<tr>
<td>Unit cell volume/Å³</td>
<td>3710.2(3)</td>
</tr>
<tr>
<td>Temperature/K</td>
<td>147(2)</td>
</tr>
<tr>
<td>Space group</td>
<td>C2/c</td>
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<tr>
<td>No. of formula units per unit cell, Z</td>
<td>8</td>
</tr>
<tr>
<td>No. of reflections measured</td>
<td>11749</td>
</tr>
<tr>
<td>No. of independent reflections</td>
<td>3179</td>
</tr>
<tr>
<td>R_{int}</td>
<td>0.0325</td>
</tr>
<tr>
<td>Final R_{1} values (I &gt; 2σ(I))</td>
<td>0.0387</td>
</tr>
<tr>
<td>Final wR(F^2) values (I &gt; 2σ(I))</td>
<td>0.0961</td>
</tr>
<tr>
<td>Final R_{1} values (all data)</td>
<td>0.0440</td>
</tr>
<tr>
<td>Final wR(F^2) values (all data)</td>
<td>0.1003</td>
</tr>
<tr>
<td>Goodness of fit on F^2</td>
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<tr>
<td>B-X bond length (Å)</td>
<td>1.4126(19)</td>
</tr>
<tr>
<td>B-B distance (Å)</td>
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<td>Bowl depth (Å)</td>
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Table A3. 2. π-π interactions (Å,°).

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<tr>
<th>Ring I</th>
<th>Ring J</th>
<th>Cg(I)...Cg(J)</th>
<th>Dihedral angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>N3/C9/C10/C15/C16</td>
<td>C10–C15'</td>
<td>3.6085(9)</td>
<td>17.63(8)</td>
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<tr>
<td>N5/C17/C18/C23/C24</td>
<td>C2–C7''</td>
<td>3.9143(9)</td>
<td>25.19(8)</td>
</tr>
<tr>
<td>N5/C17/C18/C23/C24</td>
<td>C18–C23 iii</td>
<td>3.5042(9)</td>
<td>1.17(8)</td>
</tr>
<tr>
<td>C2–C7</td>
<td>C18–C23 ii</td>
<td>3.9749(9)</td>
<td>24.92(7)</td>
</tr>
<tr>
<td>C10–C15</td>
<td>C10–C15'</td>
<td>3.8062(9)</td>
<td>16</td>
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<tr>
<td>C18–C23</td>
<td>C18–C23 iii</td>
<td>3.7515(9)</td>
<td>0</td>
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Symmetry codes: (i) -x,y,3/2-z; (ii) x,-y,1/2+z; (iii) -1/2-x,1/2-y,2-z; (iv) x,-y,-1/2+z

Table A3. 3. C-H...π interactions (Å,°).

<table>
<thead>
<tr>
<th>X</th>
<th>H</th>
<th>Ring J</th>
<th>H...Cg(J)</th>
<th>X-H...Cg(J)</th>
<th>X...Cg(J)</th>
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<tr>
<td>C11</td>
<td>H11A</td>
<td>N1/C1/C2/C7/C8 i</td>
<td>2.99</td>
<td>101</td>
<td>3.2978(16)</td>
</tr>
<tr>
<td>C20</td>
<td>H20A</td>
<td>N1/C1/C2/C7/C8 ii</td>
<td>2.99</td>
<td>135</td>
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Symmetry codes: (i) x,-y,-1/2+z; (ii) -1/2-x,1/2-y,2-z

Table A3. 4. Hydrogen-bond geometry (Å,°).

<table>
<thead>
<tr>
<th>D-H...A</th>
<th>D-H</th>
<th>H...A</th>
<th>D...A</th>
<th>D-H...A</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(1)-H(1o)...N2</td>
<td>0.87(2)</td>
<td>2.13(2)</td>
<td>3.0050(16)</td>
<td>177(2)</td>
</tr>
</tbody>
</table>

Symmetry codes: (i) x,-y,1/2+z

Figure A3. 1. (a) Molecular structure of HO-BsubPc showing 30% displacement ellipsoids. Hydrogens are omitted for clarity. (b) Populated unit cell of HO-BsubPc and its hydrogen bonding (dashed line). Members of the unit cell are illustrated in elemental colouring (carbon – black; nitrogen – blue; oxygen – red; boron – green). Hydrogens are omitted for clarity.