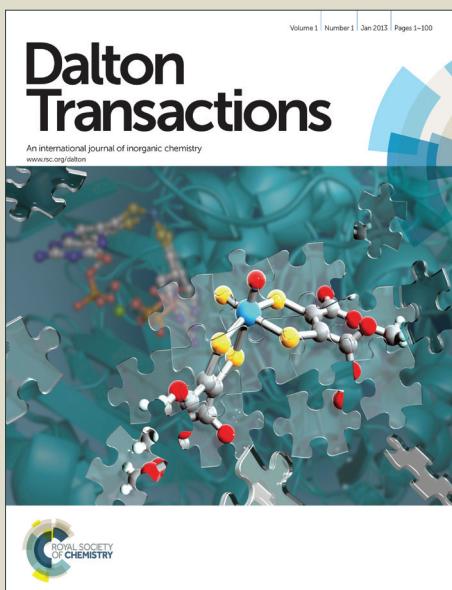


Dalton Transactions

Accepted Manuscript



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Process for the synthesis of symmetric and unsymmetric oxygen bridged dimers of boron subphthalocyanines (μ -oxo-(BsubPc)₂s)

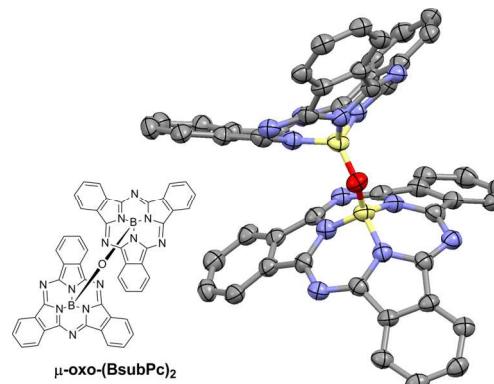
Jeremy D. Dang,^{a,||} Mabel V. Fulford,^{a,||} Brett A. Kamino,^a Andrew S. Paton,^a and Timothy P. Bender^{*a,b,c}*Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX*

DOI: 10.1039/b000000x

A process for the gram scale synthesis of the oxygen bridged dimer of boron subphthalocyanine, μ -oxo-(BsubPc)₂, has been developed. During the development it was found that a wide range of reaction pathways under diverse conditions lead to μ -oxo-(BsubPc)₂ formation. However, obtaining μ -oxo-(BsubPc)₂ as the main reaction product in appreciable yields and its subsequent isolation was extremely challenging. The best balance of purity, yield and conversion was achieved with a time controlled reaction of an equimolar reaction of HO-BsubPc with Br-BsubPc in the presence of K₃PO₄. The purification involved sequentially Soxhlet extraction, Kauffman column chromatography and train sublimation. We have repeated the process and yields ranged from 27 to 30 % of pure, doubly-sublimed μ -oxo-(BsubPc)₂. This process also enabled the synthesis of unsymmetric μ -oxo-(BsubPc)₂s by reaction of HO-BsubPc with Br-F₁₂BsubPc, Cl-Cl₆BsubPc and Cl-Cl₁₂BsubPc. After synthesis the solution-state properties of the unsymmetric μ -oxo-(BsubPc)₂s were investigated, and compared to the symmetric μ -oxo-(BsubPc)₂ and more broadly to other BsubPcs. The electronic properties of the μ -oxo-(BsubPc)₂s were found to be similar to other peripherally hydrogenated BsubPcs, however, their photophysical properties differ greatly from all other known BsubPcs.

Boron subphthalocyanine (BsubPc) is the sole known lower analogue of phthalocyanines, a family of common pigments. Like the phthalocyanines, BsubPcs have high extinction coefficients ($\epsilon > 50,000 \text{ L mol}^{-1} \text{ cm}^{-1}$)¹ and also are of interest as functional organic electronic materials. However, in comparison to the planar four-membered heterocyclic ring of phthalocyanines, the three covalently bound diiminoisoindole units of BsubPc form a non-planar bowl shape which results in unique electro- and photo-physical properties. The non-planar molecular shape of BsubPc introduces complex intermolecular packing arrangements and motifs in three dimensions, which may have implications for charge transport when applied as an organic electronic material.² Cl-BsubPc was first discovered by Meller & Ossko in 1972³ and its structure confirmed in 1974.⁴ The recent body of research into the use of BsubPc(s) as a functional material remains predominantly focused on Cl-BsubPc. Cl-BsubPc has been applied and studied in organic electronic devices, including solar cells (OSCs), light emitting diodes (OLEDs) and field effect transistors (OFETs).⁵ However, BsubPc is highly substitutable, both at the axial position and around the periphery.⁶ More recently, a number of substituted BsubPcs have been reported and characterized, including halides,⁶ pseudohalides,⁷ phenols,⁸⁻¹² bisphenols,¹³ alcohols^{14,15} and phthalimides¹⁶.

Although frequently observed as a byproduct of BsubPc reactions¹⁶⁻¹⁹ and known to have unique spectroscopic properties amongst the BsubPcs,²⁰ there are very few reports concerning the synthesis or study of the oxygen bridged dimer, μ -oxo-(BsubPc)₂ (Figure 1). In 1996, Geyer *et al.* reported a synthetic method with

Fig. 1 2-D and 3-D molecular structure of μ -oxo-(BsubPc)₂.

a 10 mg (7.6 %) yield starting from Cl-BsubPc and using NaOH as an oxygen source, dicyclohexano-18-crown-6 refluxing as a phase transfer catalyst and xylenes as the reaction solvent. The reaction pathway presumably involves the reaction of Cl-BsubPc with hydroxide ('OH) to yield HO-BsubPc *in situ*. HO-BsubPc either then self-condenses or reacts with another molecule of Cl-BsubPc yielding μ -oxo-(BsubPc)₂. This small sample of 10 mg was enough to measure the characteristic absorption spectrum of μ -oxo-(BsubPc)₂.²⁰ In 1999, Kobayashi *et al.* described the synthesis of μ -oxo-(*t*-butyl-BsubPc)₂ and also described its absorption spectrum. The synthetic procedure involved the self-condensation of HO-*t*-butyl-BsubPc in nitrobenzene with some molecular sieves present and yielded 8.8 mg (4.7 %).²¹ No other

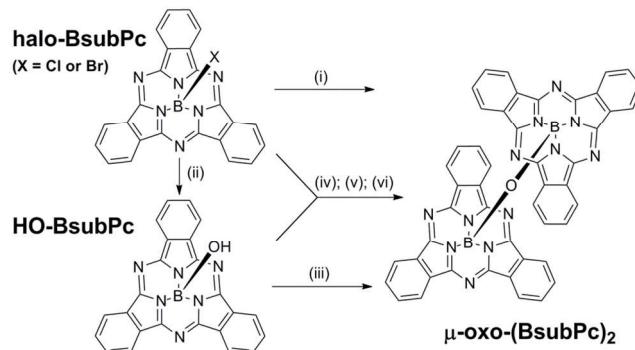
synthesis was reported until a 2008 US patent application by Yamasaki, Mori, and Furuya which outlined two reaction pathways. The first is the self-condensation of HO-BsubPc to afford the desired compound and water as a by-product. The second involves the reaction of a HO-BsubPc derivative with a halo-BsubPc derivative to produce a peripherally-substituted μ -oxo-(BsubPc)₂ and a halo-acid as a byproduct. Each example was performed at a reasonable scale claiming to yield between 0.65 – 4.5 g of material.²² More recently and coincident with our interest in μ -oxo-(BsubPc)₂, Yamasaki & Mori²³ published the material found in their patent application. Using the self-condensation reaction pathway, they reported the synthesis of μ -oxo-(BsubPc)₂ in 34 % yield and four peripherally substituted μ -oxo-(BsubPc)₂ compounds in yields that ranges from 2.3 % to 28.4 %.

We have previously reported the non-solvated crystal structure of μ -oxo-(BsubPc)₂ along with two solvated crystals.²⁴ In that paper we detailed some preliminary work on the development of a process for the synthesis of μ -oxo-(BsubPc)₂; two methods for the directed synthesis of μ -oxo-(BsubPc)₂ were reported by our group, including some preliminary work-up procedures. It was also observed that μ -oxo-(BsubPc)₂ has a higher solubility than its precursor HO-BsubPc or any halo-BsubPc in a broad range of solvents, consistent with the findings of Yamasaki & Mori.²³ μ -Oxo-(BsubPc)₂ was also found to be mobile under sublimation conditions.²⁵ The solid state arrangement of the non-solvated μ -oxo-(BsubPc)₂ crystal and its solvates and hemi-hydrate were found to exhibit high symmetry, close intermolecular interactions and remarkably high crystal densities by comparison against other BsubPcs. These results provided us with the impetus for further investigation of effective synthetic routes for μ -oxo-(BsubPc)₂ including and beyond those that first resulted in the isolation of single crystals.²⁴

In this paper we complete our survey of the synthetic routes to μ -oxo-(BsubPc)₂ including those of Geyer *et al.*²⁰ and Yamasaki & Mori.²³ Our assessment of the various routes is that the reaction of equal molar amounts of HO-BsubPc and Br-BsubPc in 1,2-dichlorobenzene in the presence of K₃PO₄ is the most effective method to reliably and reproducibly produce μ -oxo-(BsubPc)₂ in reasonable quantities. We also adapted this synthetic methodology towards the synthesis of three unsymmetric μ -oxo-(BsubPc)₂ derivatives. Each unsymmetric derivative was assessed for its solution-state photo- and electro-physical properties.

Our first goal was to develop a practical synthetic method that yields reasonable quantities of doubly-train-sublimed μ -oxo-(BsubPc)₂. The criteria for practicability include the potential to carry out the reaction and subsequent work-up procedure using commonly available equipment in a research group involved in the synthesis of phthalocyanines or organic electronic materials. The criteria for reasonable quantity was defined as a quantity having sufficient purity after being “doubly-sublimed” to enable the characterization of μ -oxo-(BsubPc)₂ as an organic electronic material within a device fabricated by vacuum deposition.²⁵ “Doubly-sublimed” is a standard purity threshold applied by our laboratory prior to electrical characterization, and means that once a sample is obtained that is pure by common analytical means (*e.g.* HPLC, ¹H NMR) it must then be further purified by train sublimation²⁶ twice to ensure any trace impurities are removed. While atom and energy efficiency are typical priorities

in process chemistry development, the priority and selection of the ‘best’ process herein was focused on obtaining train-sublimed pure samples of μ -oxo-(BsubPc)₂ at ‘reasonable’ yields above other process chemistry considerations.



Scheme 1 Synthesis of μ -oxo-(BsubPc)₂. Reagents and conditions: (i) X = Cl, sodium hydroxide, dicyclohexano-18-crown-6, *p*-xylene, reflux; (ii) X = Br, water, pyridine, dimethyl sulfoxide, 60 °C; (iii) 1,2-dichlorobenzene, reflux; (iv) X = Br, 1,2-dichlorobenzene, water (trace), reflux; (v) X = Br, *p*-xylene (105 °C), nitrobenzene (200 °C), diphenyl ether (200 °C), or 1,2-dichlorobenzene (reflux); and (vi) X = Br, tripotassium phosphate, 1,2-dichlorobenzene, reflux.

We began our survey by attempting to replicate the first published synthetic method by Geyer *et al.*²⁰ (Scheme 1, conditions (i)). This reported method involved the reaction of Cl-BsubPc with NaOH in *p*-xylene in the presence of a phase transfer catalyst, dicyclohexano-18-crown-6, under high dilution conditions. In our hands this process yielded no μ -oxo-(BsubPc)₂ and in fact HPLC analysis showed that the starting Cl-BsubPc remained unreacted (Table S1, conditions 1.1). We then replaced Cl-BsubPc with Br-BsubPc which is known to be more reactive and still we observed no reaction (Table S1, condition 1.2). We then moved out of high dilution conditions by using $\frac{1}{4}$ the amount of *p*-xylene. In this case, the reaction did occur yielding 36 % of μ -oxo-(BsubPc)₂ and 64 % of an unknown BsubPc compound, which was neither Br-BsubPc or HO-BsubPc (Table S1, condition 1.3). Finally we reduced the molar equivalents of NaOH used in the reaction to 1.0 (relative to Br-BsubPc), which resulted in a final reaction composition of ~2 % μ -oxo-(BsubPc)₂, 15 % HO-BsubPc, 60 % Br-BsubPc and 23 % of an unknown BsubPc compound (Table S1, condition 1.4). None of these variations yielded more than 36 % μ -oxo-(BsubPc)₂ and therefore in our opinion none fit the criteria outlined above.

Turning our attention to the processes described by Yamasaki & Mori,²³ we began with the self-condensation of HO-BsubPc in 1,2-dichlorobenzene (Scheme 1, conditions (iii)). In our hands the result was a mixture of compounds as follows: 34.7 % of μ -oxo-(BsubPc)₂, 23.9 % of an unknown BsubPc compound with a HPLC retention time (r.t.) of 3.4 min, 35.4 % of HO-BsubPc and 6.1 % of additional unknown BsubPc compounds (Table S2, conditions 2.1). Despite our best attempts, including the workup procedure described by Yamasaki & Mori, we could not separate μ -oxo-(BsubPc)₂ from the other BsubPc compounds. Especially difficult was the removal of the unknown BsubPc compound with r.t. = 3.4 min.

In an attempt to generate HO-BsubPc *in situ* and promote its self-condensation we refluxed Br-BsubPc in 1,2-dichlorobenzene

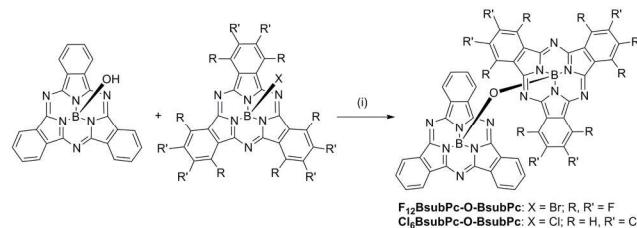
with the periodic addition of drops of water to keep the reaction ‘wet’ (Scheme 1, conditions (iv)). This process actually produced a final reaction mixture containing 61.0 % μ -oxo-(BsubPc)₂, however another unknown BsubPc with r.t. = 2.0 min was formed 5 (35.4 %). Small amounts of HO-BsubPc and other unknown BsubPcs were also present (2.2 % and 1.4 %, respectively, Table S2, conditions 2.2). However again, we could not separate μ -oxo-(BsubPc)₂ from the other components especially from the unknown BsubPc with r.t. = 2.0 min.

10 In the introduction of the patent application by Yamasaki, Mori, and Furuya,²² the inventors eluded to a method for the formation of μ -oxo-(BsubPc)₂ involving the reaction of HO-BsubPc with X-BsubPc (X = F, Cl, Br, I; albeit I-BsubPc is unknown and F-BsubPc is known to be non-reactive) in the 15 presence of a base in a variety of solvents. Bases mentioned include hydrides, hydroxides and carbonates. However specific examples were only given in the patent application for the hydride case. Given that BsubPcs are known to be sensitive to bases we initially tried the reaction of HO-BsubPc with Br-BsubPc without base (Scheme 1, conditions (v)). We selected the 20 solvents *p*-xylene, nitrobenzene, diphenyl ether and 1,2-dichlorobenzene (Table S3, conditions 3.1 – 3.6). In some cases we achieved conversions greater than 80 %, however the unknown BsubPc compound with r.t. = 2.0 min persisted and we 25 were unable to remove even small amounts (~10 %) of it from the crude products to give pure μ -oxo-(BsubPc)₂.

After achieving relatively high conversions by the equimolar reaction of HO-BsubPc with Br-BsubPc, we then considered the addition of base to the process with the hypothesis that the 30 persistence of the produced haloacid might lead to the formation of the persistent BsubPc impurity with r.t. = 2.0 min. Regarding the suggested addition of base by Yamasaki, Mori, and Furuya²² we ruled out the use of hydrides for safety reasons. We felt the sensitivity of BsubPcs to bases negated the possibility of using 35 hydroxides. We also ruled out the use of carbonates or bicarbonates due to the production of carbon dioxide gas on reaction with acids which might/could lead to excessive bubbling of the reaction mixture. We therefore decided to explore the use of tripotassium phosphate (K_3PO_4) as a scavenger of HBr (Scheme 1, conditions (vi)). While not commonly referred to as a 40 base, K_3PO_4 does have the ability to react with acids for example: $HBr + K_3PO_4 \rightarrow KBr + HK_2PO_4$. Of course K_3PO_4 is not soluble in common organic solvents so under this scenario it will be the surface of the K_3PO_4 that would react with HBr. Therefore we 45 began by dispersing as much K_3PO_4 as possible in 1,2-dichlorobenzene (80 wt% K_3PO_4 , Table S4, conditions 4.1) and conversion to μ -oxo-(BsubPc)₂ was >96 % with trace amounts of HO-BsubPc remaining. However the absolute yield was low and was attributed to the excessively purple-colored solid filtered 50 from the reaction, which undoubtedly contained adsorbed/absorbed BsubPc compounds on its surface. We were unable to remove the adsorbed/absorbed BsubPc compounds from the surface of the solid. We then reduced the amount of K_3PO_4 and subsequently used dried K_3PO_4 and also found high 55 conversion (~97 % and ~100 % respectively, Table S4, conditions 4.2 and 4.3). Finally we tried using ‘wet’ K_3PO_4 to promote the hydrolysis of Br-BsubPc *in situ* to HO-BsubPc but found no conversion to μ -oxo-(BsubPc)₂ (Table S4, conditions

4.4). During these three reactions (conditions 4.1-4.3), we noted 60 qualitatively that although the conversion appeared to be >97 % the intensity of the color of the solution seemed to decrease with time indicating decomposition of the BsubPc chromophore. This was confirmed as only 8 % of μ -oxo-(BsubPc)₂ was isolated from reaction 4.2. We then repeated 4.3 and 4.4 except the reaction 65 progress was monitored as a function of time (Table S4, conditions 4.5 and 4.6). Samples were taken of approximately the same volume, diluted with approximately the same amount of eluent and injected into the HPLC. The intensity of the μ -oxo-(BsubPc)₂ peak was observed to decrease over time. Given the 70 lack of precise quantification the results are not provided, however it was found that a reaction time of 1 hour gave the best balance between conversion and isolated yield. Complete conversions were not achieved when the reaction was stopped after 1 hour, rather conversions of 67 % and 78 % were observed. 75 Oddly enough residual HO-BsubPc was detected, perhaps indicating our conditions were not absolutely anhydrous.

Throughout these trials a variety of purification strategies were attempted. For example, removal of the reaction solvent followed by a Soxhlet extraction with toluene was tried. The work-up steps 80 reported by Yamasaki *et al.*,²³ which involved dispersing the crude solid in *N,N*-dimethylformamide (DMF) followed by filtration and washing sequentially with DMF and water, were also tried. We also tried Kauffman column chromatography²⁶ using alumina as the adsorbent and toluene as the eluent. After 2 85 days of elution, a purple band likely corresponding to μ -oxo-(BsubPc)₂ was visible but did not elute out of the column. Kauffman column chromatography was repeated with dichloromethane (DCM) as the eluent and this turned out to be successful. We settled on a combination of a Soxhlet extraction 90 with toluene, followed by a Kauffman column with DCM and finally a train sublimation²⁶ at 450 °C (measured external temperature) to achieve a pure sample of μ -oxo-(BsubPc)₂ at high purity. Typical yields were 53-59 % after Kauffman column chromatography and 50 % following sublimation, resulting in an 95 overall yield of 27-30 %. A final optimized synthetic method is detailed in method 4.9 in the ESI (Table S4).



Scheme 2 Synthesis of $\text{F}_{12}\text{BsubPc-O-BsubPc}$, $\text{Cl}_6\text{BsubPc-O-BsubPc}$, and $\text{Cl}_{12}\text{BsubPc-O-BsubPc}$. Reagents and conditions: (i) tripotassium phosphate, 1,2-dichlorobenzene, reflux.

The feasibility and success of the K_3PO_4 -mediated bimolecular condensation reaction for the formation of μ -oxo-(BsubPc)₂ motivated us to adapt this methodology towards the synthesis of 105 unsymmetric μ -oxo-(BsubPc)₂ compounds, where the two BsubPc moieties are not identical. To the best of our knowledge, there is no precedent of an unsymmetric μ -oxo-(BsubPc)₂ compound in the literature. Using our K_3PO_4 -mediated procedure, we synthesized three unsymmetric μ -oxo-(BsubPc)₂

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

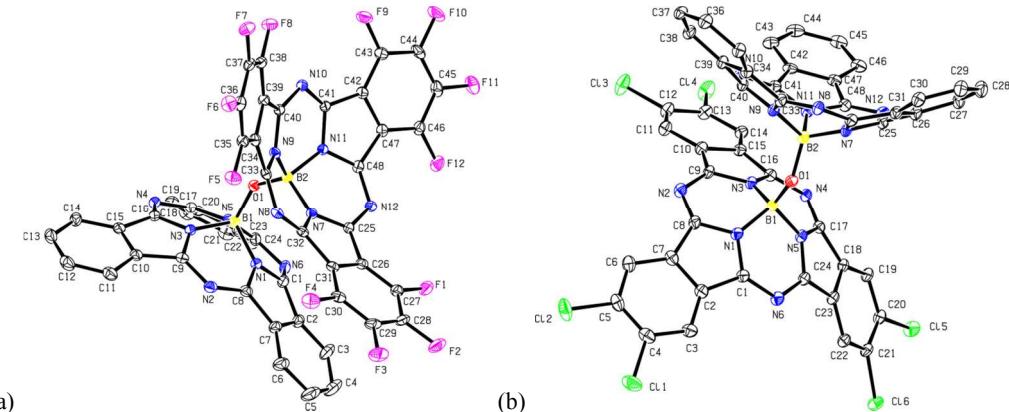


Fig. 2 Ellipsoid plot (50 % probability) showing the structure and atom numbering scheme of (a) $\text{F}_{12}\text{BsubPc-O-BsubPc} \bullet \text{C}_7\text{H}_{16}$ (CCDC deposition number: 1018494) and (b) $\text{Cl}_6\text{BsubPc-O-BsubPc}$ (CCDC deposition number: 1018458). Hydrogen atoms and solvent inclusions have been omitted for clarity. Colors: boron - yellow; nitrogen - blue; carbon - white; oxygen - red; fluorine - magenta; chlorine - green.

compounds - $\text{F}_{12}\text{BsubPc-O-BsubPc}$, $\text{Cl}_6\text{BsubPc-O-BsubPc}$, and $\text{Cl}_{12}\text{BsubPc-O-BsubPc}$ – in 36 %, 40 %, and 43 % yield, respectively. Each was made by reacting equimolar amounts of HO-BsubPc with Br- $\text{F}_{12}\text{BsubPc}$, Cl- Cl_6BsubPc , or Cl- $\text{Cl}_{12}\text{BsubPc}$, respectively, in the presence of K_3PO_4 in 1,2-dichlorobenzene at 180 °C (Scheme 2). The reaction progress was monitored by HPLC for the complete consumption of the starting BsubPc materials, which normally took between 17 and 19 hours. Unlike the μ -oxo-(BsubPc)₂ synthesis, the color intensity of each solution for the three reactions did not decrease over time; these reactions were not time-sensitive at least for the first 17–19 hours. It is worth noting that for all three reactions the halo-BsubPcs (Br- $\text{F}_{12}\text{BsubPc}$, Cl- Cl_6BsubPc , and Cl- $\text{Cl}_{12}\text{BsubPc}$) were fully consumed while residual amount of HO-BsubPc were present at the end of each reaction. Moreover, traces of μ -oxo-(BsubPc)₂ were detected via HPLC at the end of each reaction. Single crystals of $\text{F}_{12}\text{BsubPc-O-BsubPc}$ solvated with heptane (Figure 2a, CCDC deposition number: 1018494) and of $\text{Cl}_6\text{BsubPc-O-BsubPc}$ (Figure 2b, CCDC deposition number: 1018458) were successfully grown by vapor diffusion of heptane into a DCM solution and by slow evaporation from DCM solution, respectively. X-ray diffraction analysis confirmed the molecular structures of the two compounds (Figure 2).

UV-Vis absorption spectra of μ -oxo-(BsubPc)₂, $\text{F}_{12}\text{BsubPc-O-BsubPc}$, $\text{Cl}_6\text{BsubPc-O-BsubPc}$, and $\text{Cl}_{12}\text{BsubPc-O-BsubPc}$ were acquired in toluene solutions at room temperature (Figure 3). All compounds were purified sequentially by column chromatography and train sublimation prior to performing these measurements. As already reported, the photophysical properties of μ -oxo-(BsubPc)₂ is unique among BsubPcs.²⁰ For example, it has a λ_{max} of absorption ($\lambda_{\text{max}} = 533$ nm in toluene)²⁰ that is significantly blue-shifted by comparison against typical monomeric BsubPcs, which are generally above 560 nm (Table S5). Furthermore, its absorption spectrum is broader compared to typical monomeric BsubPcs and this is attributed to the π - π

interactions of the two BsubPc moieties of the μ -oxo-dimer (Figure S11a).²³ Like μ -oxo-(BsubPc)₂ but to a lesser degree, the three unsymmetric μ -oxo-(BsubPc)₂ compounds have λ_{max} values that are blue-shifted relative to monomeric BsubPcs; $\text{F}_{12}\text{BsubPc-O-BsubPc}$, $\text{Cl}_6\text{BsubPc-O-BsubPc}$, and $\text{Cl}_{12}\text{BsubPc-O-BsubPc}$ have a λ_{max} of absorption at 547, 541 and 558 nm, respectively (Table 1). In addition to sharing this blue-shifting feature with μ -oxo-(BsubPc)₂, the absorption spectra of the three unsymmetric μ -oxo-(BsubPc)₂ compounds are broader in comparison to monomeric BsubPcs (Figure S12a), indicating that these compounds also experience π - π interaction between the BsubPc macrocycles in a similar manner as μ -oxo-(BsubPc)₂.

The photoluminescence (PL) spectra of μ -oxo-(BsubPc)₂, $\text{F}_{12}\text{BsubPc-O-BsubPc}$, $\text{Cl}_6\text{BsubPc-O-BsubPc}$, and $\text{Cl}_{12}\text{BsubPc-O-BsubPc}$ were also acquired in toluene solutions at room temperature (Figure 3). Although the absorption properties of μ -oxo-(BsubPc)₂ is known, its fluorescence properties have not been explored. The PL spectrum of μ -oxo-(BsubPc)₂ at an excitation wavelength (λ_{ex}) of 532 nm showed a minor shoulder peak at 576 nm and a primary peak at 636 nm (Table 1). The latter emission peak is heavily red-shifted compared to the emission spectra of typical monomeric BsubPcs (568 to 572 nm for halo-BsubPcs⁶, Figure S11b), demonstrating once again its uniqueness among BsubPcs. Similarly to μ -oxo-(BsubPc)₂, the PL spectra of the three unsymmetric μ -oxo-(BsubPc)₂ compounds obtained at a λ_{ex} of 530 nm each showed two emission peaks (Figure 3, Figure S12b). $\text{F}_{12}\text{BsubPc-O-BsubPc}$ has a more intensive emission peak at 575 nm and a less intensive peak at 729 nm, $\text{Cl}_6\text{BsubPc-O-BsubPc}$ has a less intensive peak at 575 nm and a more intensive peak at 672 nm, while $\text{Cl}_{12}\text{BsubPc-O-BsubPc}$ has a less intensive peak at 585 nm and a more intensive peak at 739 nm (Table 1).

The presence of two emission peaks is uncharacteristic of BsubPcs in the solution state. This dual emission behavior, however, has previously been observed for pentafluorophenoxy-

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

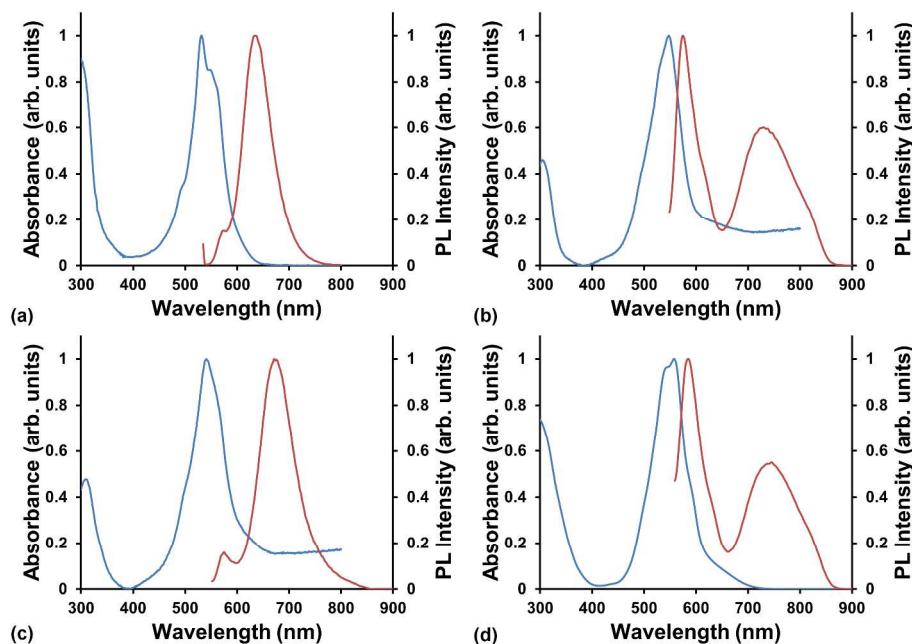


Fig. 3 Absorption (blue) and photoluminescence (red) spectra of (a) $\mu\text{-oxo-(BsubPc)}_2$, (b) $\text{F}_{12}\text{BsubPc-O-BsubPc}$, (c) $\text{Cl}_6\text{BsubPc-O-BsubPc}$, and (d) $\text{Cl}_{12}\text{BsubPc-O-BsubPc}$ in toluene solutions at room temperature.

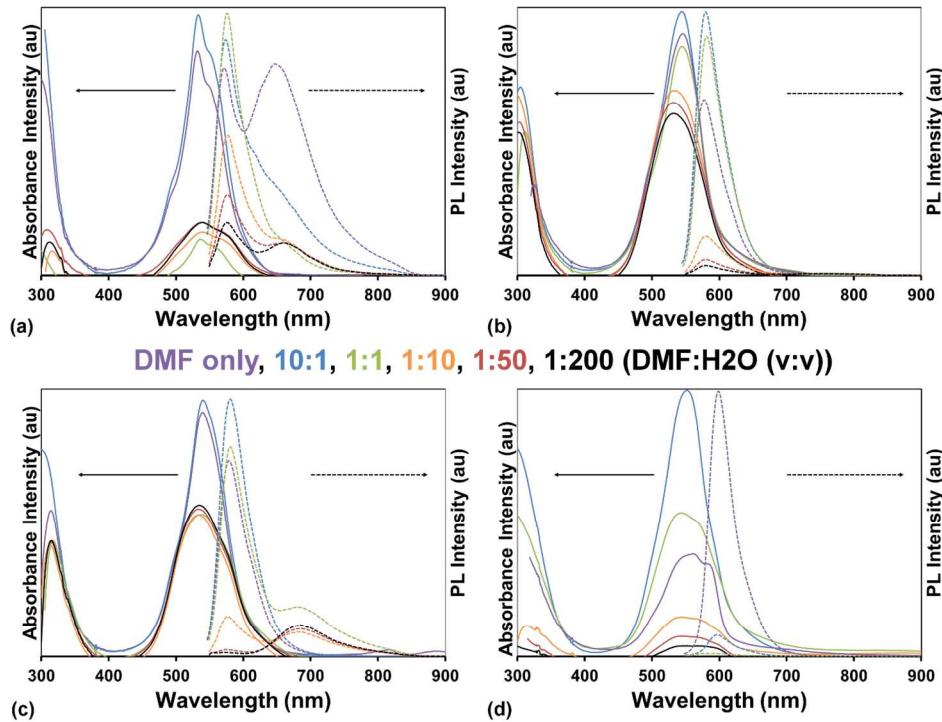


Fig. 4 UV-vis absorption (solid) and PL ($\lambda_{\text{exc}} = 530$ nm, dash) spectra (concentration = 2.30×10^{-6} M) of (a) $\mu\text{-oxo-(BsubPc)}_2$, (b) $\text{F}_{12}\text{BsubPc-O-BsubPc}$, (c) $\text{Cl}_6\text{BsubPc-O-BsubPc}$, and (d) $\text{Cl}_{12}\text{BsubPc-O-BsubPc}$ in DMF (violet), 10:1 (blue), 1:1 (green), 1:10 (orange), 1:50 (red), and 1:200 (black) DMF/H₂O (v/v).

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

BsubPc (F_5PhO -BsubPc) in solvent mixtures consisting of DMF (a good solvent) and water (a poor solvent) in a 1:128 v/v ratio or lower.²⁷ Under these conditions, a secondary emission peak at 706 nm emerges and its intensity increases relative to the primary emission peak at the 576-593 nm range as the ratio of DMF/H₂O decreases. This phenomenon is caused by molecular aggregation, an effect that becomes more pronounced with a higher concentration of water.²⁷ An aggregation effect and thus a secondary emission peak was not anticipated for the three unsymmetric μ -oxo-(BsubPc)₂ compounds considering that toluene, a normally good solvent for BsubPcs, is used to dissolve these compounds and also that the analyses were done under dilute conditions (solution-state absorbance < 0.05).

To examine whether the emission peak at the longer wavelength - 636, 729, 672, and 739 nm - for μ -oxo-(BsubPc)₂, F₁₂BsubPc-O-BsubPc, Cl₆BsubPc-O-BsubPc, and Cl₁₂BsubPc-O-BsubPc, respectively, was actually due to an aggregation effect, PL spectra (concentration = 2.30×10^{-6} M) were acquired in a series of DMF/H₂O mixtures ranging from pure DMF to 1:200 (v/v) DMF/H₂O (Figure 4). For μ -oxo-(BsubPc)₂ in pure DMF, two emission peaks at 572 and 647 nm of nearly equal intensities were observed. Strangely between 10:1 and 1:1 DMF/H₂O mixture, the shorter wavelength emission (574-576 nm) was only seen. The longer wavelength emission (661-662 nm) began to appear at 1:10 DMF/H₂O and intensified relative to the shorter wavelength emission as the ratio dropped towards 1:200 DMF/H₂O. For all three unsymmetric μ -oxo-(BsubPc)₂ in pure DMF, a single emission peak at the shorter wavelength was observed. The longer wavelength emission peak began to emerge at 1:10, 1:1, and 1:1 DMF/H₂O for F₁₂BsubPc-O-BsubPc, Cl₆BsubPc-O-BsubPc, and Cl₁₂BsubPc-O-BsubPc, respectively, and increased in intensity relative to the shorter wavelength emission peak as the DMF/H₂O ratio dropped towards 1:200. Moreover, the longer wavelength emission peak became the strongest/primary peak for both Cl₆BsubPc-O-BsubPc (at 1:50 DMF/H₂O and below) and Cl₁₂BsubPc-O-BsubPc (at 1:10 DMF/H₂O and below). It is also interesting to note that for only Cl₁₂BsubPc-O-BsubPc, a third emission peak (635-640 nm) was formed in DMF/H₂O ratio of 1:10 and below. Overall, these results/trends are consistent with those reported for F_5PhO -BsubPc²⁷ as mentioned earlier, suggesting that the PL emission at the longer wavelength - 636, 729, 672, and 739 nm for μ -oxo-(BsubPc)₂, F₁₂BsubPc-O-BsubPc, Cl₆BsubPc-O-BsubPc, and Cl₁₂BsubPc-O-BsubPc, respectively - in toluene solutions at room temperature is likely attributable to an aggregation-caused emission. An examination of the rate at which the longer wavelength emission peak increased relative to the shorter wavelength emission peak as the DMF/H₂O ratio approached 1:200, suggests that the order in the degree of aggregation is Cl₁₂BsubPc-O-BsubPc > Cl₆BsubPc-O-BsubPc > μ -oxo-(BsubPc)₂ > F₁₂BsubPc-O-BsubPc.

It is also very apparent from the PL spectra acquired from the

series of DMF/H₂O mixture that the emission intensities weakened with increasing volume fraction of H₂O (Figure 4). In addition to this, small shifts in the position of the PL spectra were generally observed with the exception of Cl₁₂BsubPc-O-BsubPc. A bathochromic shift of 4-5 nm and 2-3 nm were observed for μ -oxo-(BsubPc)₂ and F₁₂BsubPc-O-BsubPc, respectively, while a hypsochromic shift of 6-8 nm and 45-46 nm were observed for Cl₆BsubPc-O-BsubPc and Cl₁₂BsubPc-O-BsubPc, respectively, from pure DMF to 1:200 DMF/H₂O. Based on the observed light emission quenching effect and the shifts, although not very pronounced, in the PL spectra with increasing volume fraction of H₂O, the four compounds under study especially Cl₁₂BsubPc-O-BsubPc display solvatochromic fluorescence (*i.e.* solvent-dependent emission).

UV-Vis absorption spectra were also acquired in the same series of DMF/H₂O mixtures as used above to determine if the four compounds under study are also solvatochromic in absorption (Figure 4). There were generally small changes to the position of the spectra going from pure DMF to 1:200 DMF/H₂O. A bathochromic shift of 6-8 nm was observed for μ -oxo-(BsubPc)₂, while a hypsochromic shift of 13-14 nm and 4-6 nm were observed for F₁₂BsubPc-O-BsubPc and Cl₆BsubPc-O-BsubPc, respectively. For Cl₁₂BsubPc-O-BsubPc, a trend was not very clear as the spectra blue shifted initially before it red shifted. However, by just looking at the λ_{max} values in pure DMF (560 nm) and in 1:200 DMF/H₂O (552 nm), a general hypsochromic shift is observed. The absorbance intensities were also found to decrease with increasing volume fraction of H₂O. Given this observed effect combined with the shifts, although not very pronounced, in the absorption spectra with increasing volume fraction of H₂O, the four compounds under study are solvatochromic in absorption (*i.e.* solvent-dependent absorption).

It is interesting to note that in toluene the characteristics are different. For μ -oxo-(BsubPc)₂ and Cl₆BsubPc-O-BsubPc in toluene at room temperature the primary/strongest emission peak is actually the aggregate-induced emission peak at 636 and 672 nm, respectively (Figure 3). For F₁₂BsubPc-O-BsubPc and Cl₁₂BsubPc-O-BsubPc the primary emission peak is the one at 575 and 585 nm (shorter wavelength emission), respectively. This suggests that μ -oxo-(BsubPc)₂ and Cl₆BsubPc-O-BsubPc are more prone to aggregation compared to F₁₂BsubPc-O-BsubPc and Cl₁₂BsubPc-O-BsubPc. Since the intensity of the shorter wavelength emission peak is nearly the same for Cl₆BsubPc-O-BsubPc (~16 %) than μ -oxo-(BsubPc)₂ (~15 %), this suggests that both of these compounds aggregate to the same degree. Likewise, since the intensity of the longer wavelength emission peak is higher for F₁₂BsubPc-O-BsubPc (~60 %) than Cl₁₂BsubPc-O-BsubPc (~55 %), this suggests that F₁₂BsubPc-O-BsubPc aggregates slightly more than Cl₁₂BsubPc-O-BsubPc. Overall, the trend in the degree of aggregation observed here is μ -oxo-(BsubPc)₂ ~ Cl₆BsubPc-O-BsubPc > F₁₂BsubPc-O-BsubPc > Cl₁₂BsubPc-O-BsubPc. This contradicts the trend found from the

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

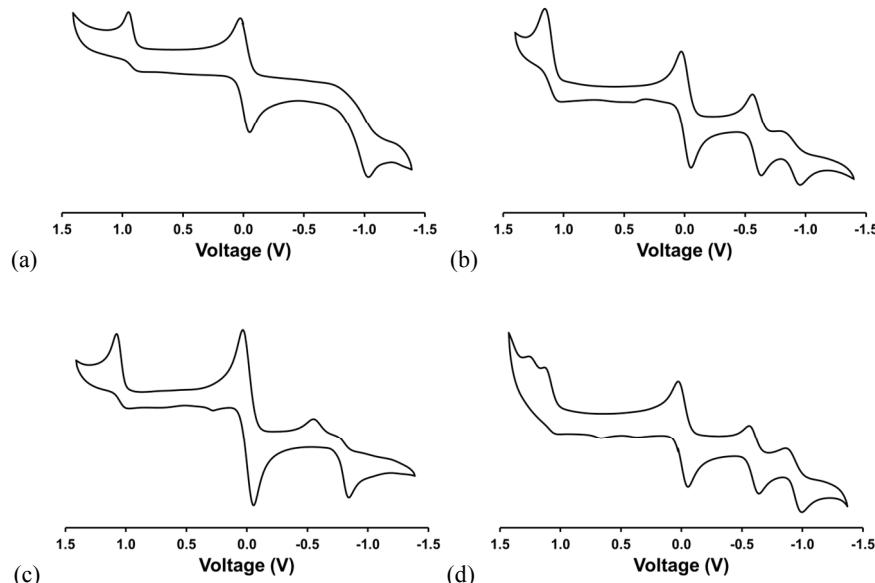


Fig. 5 Cyclic voltammograms of (a) μ -oxo-(BsubPc)₂, (b) F₁₂BsubPc-O-BsubPc, (c) Cl₆BsubPc-O-BsubPc, and (d) Cl₁₂BsubPc-O-BsubPc in DCM with 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte and decamethylferrocene as the internal reference ($E_{1/2,\text{red}} = -0.012$ V vs. Ag/AgCl) at room temperature.

5

DMF/H₂O-aggregation experiments (Cl₁₂BsubPc-O-BsubPc > Cl₆BsubPc-O-BsubPc > μ -oxo-(BsubPc)₂ > F₁₂BsubPc-O-BsubPc), signifying that solvent effects play a major factor in the aggregation of these BsubPc dimers.

10 As mentioned earlier, the PL emission spectrum of μ -oxo-(BsubPc)₂ is considerably red-shifted relative to its absorption spectrum, leading to a Stokes shift of 44 nm for the shorter wavelength emission and 104 nm for the longer wavelength emission (Table 1). This is not characteristic of monomeric 15 BsubPcs, which normally have small Stokes shifts (*e.g.* 6 nm for halo-BsubPcs⁶, 20-29 nm range for fluorinated PhO-BsubPcs²⁶). The large Stokes shift indicates that μ -oxo-(BsubPc)₂ undergoes significant geometric relaxation (*i.e.* nonradiative) following photoexcitation; the ground state structure is significantly 20 different from the excited state structure. For the unsymmetric μ -oxo-(BsubPc)₂ compounds, the smaller Stokes shift is in line with fluorinated phenoxy-BsubPcs (20-29 nm)²⁶ while the larger Stokes shift surpasses that of the μ -oxo-(BsubPc)₂ (Table 1). These large Stokes shifts signify that these unsymmetric μ -oxo- 25 (BsubPc)₂ compounds undergo even greater structural relaxation in the excited state compared to μ -oxo-(BsubPc)₂.

Fluorescence quantum yields (Φ) were measured for the four compounds under study and they were found to be in the range of 0.3-2.0 % relative to a standard of phenoxy-dodecafluoro-BsubPc 30 (PhO-F₁₂BsubPc, Table 1, Eq. S1). The very low values indicate that, despite the discussion above, these compounds are essentially non-emissive. These low Φ values are not characteristic of BsubPcs, which normally have much higher quantum yields ($\Phi > 40\%$).^{16,26,28} The low Φ are likely related to

35 the structure of the dimers, where the two BsubPc chromophores are in close proximity to one another. Therefore even under very dilute conditions (solution-state absorbance < 0.05), interactions between the two BsubPc chromophores cannot be neglected and may lead to self-quenching of the fluorescence.

40 The electrochemical properties of μ -oxo-(BsubPc)₂, F₁₂BsubPc-O-BsubPc, Cl₆BsubPc-O-BsubPc, and Cl₁₂BsubPc-O-BsubPc were analyzed via cyclic voltammetry in degassed DCM solution containing 0.1 M tetrabutylammonium perchlorate at room temperature (Figure 5, Table 1). All potentials were 45 corrected to the half-wave reduction potential ($E_{1/2,\text{red}}$) of decamethylferrocene, which was previously reported to be -0.012 V vs. Ag/AgCl.²⁹ All compounds underwent an irreversible oxidation while Cl₁₂BsubPc-O-BsubPc underwent a second irreversible oxidation. The irreversibility in the oxidation regime 50 is a property that is commonly observed for BsubPcs.^{26,28} Therefore since all oxidation peaks were irreversible, oxidation potentials (E_{ox}) were reported based on peak potentials as opposed to half-wave potentials. For the reduction regime, μ -oxo-(BsubPc)₂ was found to undergo a single irreversible reductive 55 process while the unsymmetric μ -oxo-(BsubPc)₂ compounds were found to undergo two reductive processes. Both reduction events were irreversible for Cl₆BsubPc-O-BsubPc and reversible for both F₁₂BsubPc-O-BsubPc and Cl₁₂BsubPc-O-BsubPc. Reduction potentials (E_{red}) were reported based on half-wave potentials for 60 reversible reduction peaks and on peak potentials for irreversible reduction peaks.

The first oxidation (E_{ox}^1) and reduction (E_{red}^1) potentials of μ -oxo-(BsubPc)₂ were found to be similar to both Cl-BsubPc and

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Table 1 Photophysical and electronic properties of μ -oxo-(BsubPc)₂, F₁₂BsubPc-O-BsubPc, Cl₆BsubPc-O-BsubPc, and Cl₁₂BsubPc-O-BsubPc.

Compound	$\lambda_{\text{max,abs}}^a$ (nm)	$\lambda_{\text{max,ems}}^a$ (nm)	$\Phi_{\text{PL}}^{a,b}$ (%)	Stokes Shift ^a (nm)	E_{ox}^{l} (E_{ox}^2) ^c (V)	$E_{\text{red}}^{\text{l}}$ (E_{red}^2) ^c (V)
μ -oxo-(BsubPc) ₂	532	576, 636	2.0	44, 104	+0.95 ^d	-1.03 ^d
F ₁₂ BsubPc-O-BsubPc	547	575, 729	0.3	28, 182	+1.15 ^d	-0.60 ^e (-0.89 ^e)
Cl ₆ BsubPc-O-BsubPc	541	575, 672	1.1	34, 131	+1.08 ^d	-0.55 ^d (-0.84 ^d)
Cl ₁₂ BsubPc-O-BsubPc	558	585, 745	1.9	27, 187	+1.13 ^d (+1.26 ^d)	-0.60 ^e (-0.93 ^e)
Cl-BsubPc	565 ^f	571 ^f	73 ^f	6 ^f	+1.04 ^g	-1.05 ^g
Br-BsubPc	566 ^f	572 ^f	10 ^f	6 ^f	+1.03 ^h	-1.06 ^h

^a In toluene solution. ^b Relative to a PhO-F₁₂BsubPc standard using an excitation wavelength of 533 nm for μ -oxo-(BsubPc)₂ and 530 nm for the three unsymmetric μ -oxo-(BsubPc)₂ compounds. ^c In degassed DCM solution relative to Ag/AgCl. ^d Peak potential. ^e Half-wave potential. ^f Data taken from Fulford *et al.*⁶ ^g Data taken from del Rey *et al.*³⁰ ^h Data taken from Kasuga *et al.*³¹

Br-BsubPc, but were found to differ from the unsymmetric μ -oxo-(BsubPc)₂ compounds (Table 1). When comparing the E_{ox}^{l} across the four compounds under study, μ -oxo-(BsubPc)₂ (+0.95 V) was the easiest to oxidize, followed by Cl₆BsubPc-O-BsubPc (+1.08 V), Cl₁₂BsubPc-O-BsubPc (+1.13 V), and lastly F₁₂BsubPc-O-BsubPc (+1.15 V). Based on this trend, peripheral halogenation on the μ -oxo-(BsubPc)₂ scaffold raises the E_{ox}^{l} (*i.e.* harder to oxidize); having chlorine or fluorine in place of the peripheral hydrogen increases the E_{ox}^{l} . From this trend, it also appears that the more peripheral halogens present, the higher the E_{ox}^{l} . When comparing the $E_{\text{red}}^{\text{l}}$ across the four compounds, Cl₆BsubPc-O-BsubPc (-0.55 V) was the easiest to reduce, followed by both Cl₁₂BsubPc-O-BsubPc and F₁₂BsubPc-O-BsubPc (-0.60 V), and lastly μ -oxo-(BsubPc)₂ (-1.03 V). Based on this result, a clear trend is not observed other than the fact that peripheral halogenation lowers the $E_{\text{red}}^{\text{l}}$ (*i.e.* easier to reduce); having chlorine or fluorine in place of the peripheral hydrogen decreases the $E_{\text{red}}^{\text{l}}$. Overall, peripheral halogenation on the μ -oxo-(BsubPc)₂ scaffold increases the E_{ox}^{l} and decreases the $E_{\text{red}}^{\text{l}}$ but its effect is more severe for the $E_{\text{red}}^{\text{l}}$. A similar effect was reported for the peripherally iodinated Cl-BsubPc (+1.13 V and -0.92 V), where it was found that its reduction potential was lower (*i.e.* less negative) and its oxidation potential was higher (*i.e.* more positive) relative to Cl-BsubPc (+1.04 V and -1.05 V).³⁰

Conclusions

In this paper we presented an optimized procedure for the synthesis and isolation of μ -oxo-(BsubPc)₂ in a sufficient yield and purity. It was discovered that, while μ -oxo-(BsubPc)₂ can be created through a broad range of reaction pathways and under diverse conditions, its formation as the major product 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 K₃PO₄ in 1,2-dichlorobenzene at 180 °C for 1 hour. Following the development of this methodology, we adapted it towards the synthesis of three unsymmetric μ -oxo-(BsubPc)₂ compounds -

F₁₂BsubPc-O-BsubPc, Cl₆BsubPc-O-BsubPc, and Cl₁₂BsubPc-O-BsubPc. UV-vis absorption and fluorescence spectroscopy revealed that the μ -oxo-(BsubPc)₂ and the three unsymmetric μ -oxo-(BsubPc)₂ compounds had absorption and fluorescence properties that differ greatly from typical monomeric BsubPcs. Moreover, very low fluorescence quantum yields were measured for the four compounds under study and these values are uncharacteristic of typical monomeric BsubPcs. A self-quenching effect between the BsubPc chromophores is likely occurring following photoexcitation as a result of the close proximity of the BsubPc moieties within the dimeric environment. The electrochemical properties of μ -oxo-(BsubPc)₂ were found to be similar to those of the halo-BsubPcs, while the unsymmetric μ -oxo-(BsubPc)₂ compounds were found to have higher oxidation potentials and much lower reduction potentials compared to μ -oxo-(BsubPc)₂.

Notes and references

⁶⁰ ^a Department of Chemical Engineering and Applied Chemistry, University of Toronto, 200 College St., Toronto, Ontario, Canada, M5S3E5

^b Department of Chemistry, University of Toronto, 80 St. George St., Toronto, Ontario, Canada, M5S3H6

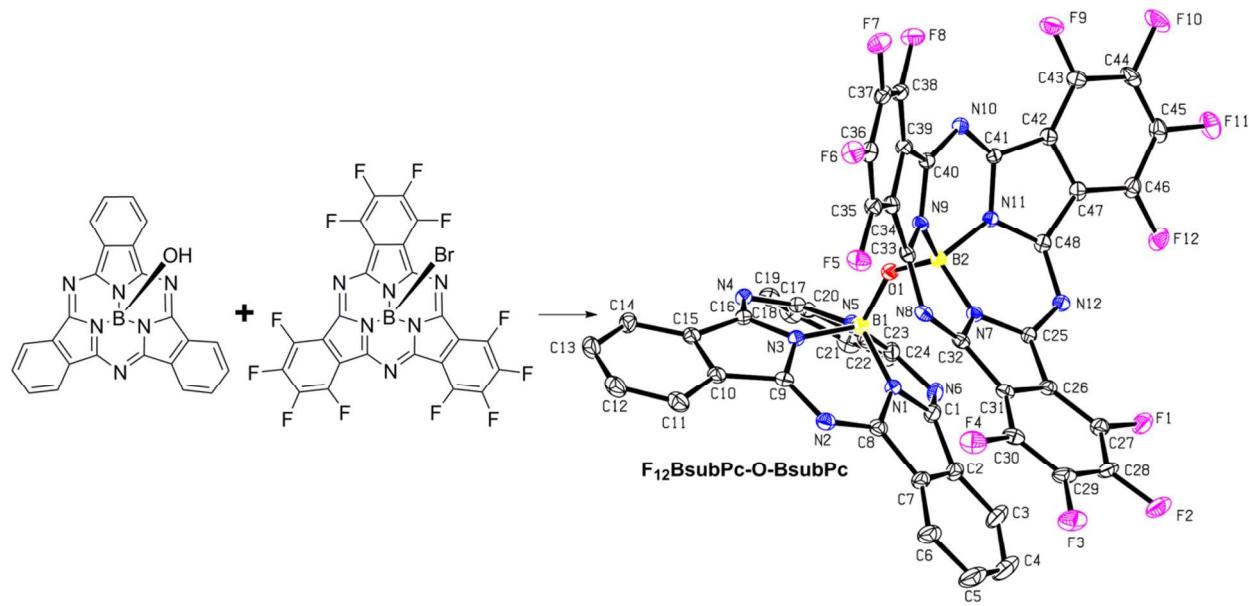
⁶⁵ ^c Department of Materials Science and Engineering, University of Toronto, 184 College St., Toronto, Ontario, Canada M5S3E4. E-mail: tim.bender@utoronto.ca

¹ These two authors contributed equally to the execution of the work described herein and to the preparation of the manuscript.

⁷⁰ [†] Electronic Supplementary Information (ESI) available: Complete experimental methods, synthetic procedures, NMR spectra, UV-vis absorption and photoluminescence plots, fluorescence quantum yields, and detailed crystallographic data. See DOI: 10.1039/b000000x/

- ⁷⁵ 1 G. E. Morse, A. S. Paton, A. Lough and T. P. Bender, *Dalton Trans.*, 2010, **39**, 3915–3922.
- 2 J. S. Castrucci, M. G. Helander, G. E. Morse, Z.-H. Lu, C. M. Yip and T. P. Bender, *Cryst. Growth & Des.*, 2012, **12**, 1095–1100.
- 3 A. Meller and A. Ossko, *Monatsh. Chem.*, 1972, **103**, 150–155.
- 80 4 H. Kietabl, *Monatsh. Chem.*, 1974, **105**, 405–418.
- 5 G. E. Morse and T. P. Bender, *ACS Appl. Mater. Interfaces*, 2012, **4**, 5055–5068.

- 6 M. V. Fulford, D. Jaidka, A. S. Paton, G. E. Morse, E. R. L. Brisson,
A. J. Lough and T. P. Bender, *J. Chem. Eng. Data*, 2012, **57**, 2756-
2765.
- 7 A. S. Paton, G. E. Morse, D. Castelino and T. P. Bender, *J. Org.
Chem.* 2012, **77**, 2531-2536.
- 8 G. E. Morse, M. G. Helander, J. Stanwick, J. M. Sauks, A. S. Paton,
Z.-H. Lu and T. P. Bender, *J. Phys. Chem. C*, 2011, **115**, 11709-
11718.
- 9 A. S. Paton, A. J. Lough and T. P. Bender, *CrystEngComm.*, 2011,
13, 3653-3656.
- 10 A. S. Paton, G. E. Morse, A. J. Lough and T. P. Bender,
CrystEngComm., 2011, **13**, 914-919.
- 11 D. González-Rodríguez, T. Torres, E. L. G. Denardin, D. Samios, V.
Stefani and D. S. Corrêa, *J. Organomet. Chem.* 2009, **694**, 1617-
1622.
- 12 D. González-Rodríguez, M. V. Martínez-Días, J. Abel, A. Perl, J.
Huskens, L. Echegoyen and T. Torres, *Org. Lett.*, 2010, **12**, 2970-
2973.
- 13 G. E. Morse, A. S. Paton, A. Lough and T. P. Bender, *Dalton Trans.*,
2010, **39**, 3915-3922.
- 14 N. Shibata, B. Das, E. Tokunaga, M. Shiro and N. Kobayashi, *Chem
Eur. J.*, 2010, **16**, 7554-7562.
- 15 H. Xu, E. A. Ermilov, B. Röder and D. K. P. Ng, *Phys. Chem. Chem.
Phys.*, 2010, **12**, 7366-7370.
- 16 G. E. Morse, J. S. Castrucci, M. G. Helander, Z.-H. Lu and T. P.
Bender, *ACS Appl. Mater. Interfaces*, 2011, **3**, 3538-3544.
- 17 R. Potz, M. Göldner, H. Hückstädt, U. Cornelissen, A. Tutass and H.
Homborg, *Z. Anorg. Allg. Chem.*, 2000, **626**, 588-596.
- 18 T. Kato, F. S. Tham, P. D. W. Boyd and C. A. Reed, *Hetero. Chem.*,
2006, **17**, 209-216.
- 19 J. Guilleme, D. González-Rodríguez and T. Torres, *Angew. Chem.,
Int. Ed.*, 2011, **50**, 3506-3509.
- 20 M. Geyer, F. Plenzig, J. Rauschnabel, M. Hanack, B. del Rey, A.
Sastre and T. Torres, *Synthesis*, 1996, **9**, 1139-1151.
- 21 N. Kobayashi, T. Ishizaki, K. Ishii and H. Konami, *J. Am. Chem.
Soc.*, 1999, **121**, 9096-9110.
- 22 T. Mori, F. Furuya and Y. Yamasaki, US Patent Application
2008/210128 A1.
- 23 Y. Yamasaki and T. Mori, *Bull. Chem. Soc. Jpn.*, 2011, **84**, 1208-
1214.
- 24 M. V. Fulford, A. J. Lough and T. P. Bender, *Acta Cryst. B*, 2012, **68**,
636-645.
- 25 J. S. Castrucci, J. D. Dang, B. A. Kamino, A. Campbell, D. Pitts, Z.-
H. Lu and T. P. Bender, *Vacuum*, 2014, **109**, 26-33.
- 26 G. E. Morse, M. G. Helander, J. F. Maka, Z.-H. Lu and T. P. Bender,
ACS Appl. Mater. Interfaces, 2010, **2**, 1934-1944.
- 27 M. G. Helander, G. E. Morse, J. Qiu, J. S. Castrucci, T. P. Bender
and Z.-H. Lu, *ACS Appl. Mater. Interfaces*, 2010, **2**, 3147-3152.
- 28 D. González-Rodríguez, T. Torres, D. M. Guldi, J. Rivera, M. Á.
Herranz and L. Echegoyen, *J. Am. Chem. Soc.*, 2004, **126**, 6301-
6313.
- 29 I. Noviandri, K. N. Brown, D. S. Fleming, P. T. Gulyas, P. A. Lay, A.
F. Masters and L. Phillips, *J. Phys. Chem. B*, 1999, **103**, 6713-6722.
- 30 B. del Rey, U. Keller, T. Torres, G. Rojo, F. Agulló-López, S.
Nonell, C. Martí, S. Brasselet, I. Ledoux and J. Zyss, *J. Am. Chem.
Soc.*, 1998, **120**, 12808-12817.
- 31 K. Kasuga, T. Idehara, M. Handa, Y. Ueda, T. Fujiwara and K. Isa,
Bull. Chem. Soc. Jpn., 1996, **69**, 2559-2563.



Unsymmetric oxygen bridged dimers of boron subphthalocyanines have been prepared for the first time.