Observations regarding the crystal structures of non-halogenated phenoxyboronsubphthalocyanines having *para* substituents on the phenoxy group†

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We report the synthesis and systematic description of a series of five *para*-substituted phenoxy-**BsubPcs** including their characterization in the crystal state. The nature of the substituents on the phenoxy molecular fragment was chosen so as to vary both the size and electronegativity: specifically with increasingly bulky *para*-alkyl groups from hydrogen to *tert*-octyl and a single electronegative substitute (F). Examination of the arrangement of the phenoxy-**BsubPcs** within single crystals allows us to place each into one of the two categories. The first, which contains all but one of the derivatives, has a repeating motif which is made up of dimers of the **BsubPc** molecular fragments. The second, containing only the derivative possessing the large *tert*-octyl substituent, is characterized by the formation of ribbons instead of dimers of the **BsubPc** fragment. Regardless of motif the arrangement of the **BsubPc** molecular fragments was found to be convace–concave.

Introduction

Chloro boron subphthalocyanine (Cl-**BsubPc**), first synthesized in 1972,[1] is a non-planar, aromatic metal–organic hybrid molecule consisting of a heterocyclic organic moiety comprising three repeating isoindoline units the sum of which ligates a B(III) atom. A chlorine atom in the axial position completes the Cl-**BsubPc** structure. The related phthalocyanines (Pcs) have four repeating isoindoline units and have been shown to coordinate to a large variety of metals across the periodic table.[2] The smaller **subPc** ligand is only known to chelate boron and in doing so stresses the ligand into its unique non-planar C_{3v} symmetric bowl shape (**1**, Fig. 1a). As a result of its shape and the lone ability of boron to chelate its formation, Cl-**BsubPc** has been described as an anomalous member of the broader phthalocyanine (Pc) family. While Pcs possess absorption maxima at wavelengths greater than 700 nm, Cl-**BsubPc** has a blue shifted maximum absorption wavelength of 560 nm.[3] The reduced conjugation length and bowl shape of Cl-**BsubPc** provide it with unique optoelectronic properties compared with the broader Pc class of compounds and researchers have studied it for applications in non-linear optics,[4] organic light emitting diodes (OLEDs),[5] organic field effect transistors (OTFTs),[6] and solar cells.[7] Recently our group has become similarly interested in the solid-state application of **BsubPc** and more specifically its phenoxy derivatives. One can assume that the nature of both the **BsubPc** moiety and the phenoxy substituent will play a role in its solid state intermolecular arrangement. While the chemistry to produce phenoxy-**BsubPc** derivatives is known[8] we were unable to locate a comprehensive study of the intermolecular arrangement of phenoxy-**BsubPcs** in the solid state. Nor are there any crystal structures deposited in the CCD of non-halogenated phenoxy-**BsubPcs**. However a report detailing the arrangement in the solid state of a series of alkoxy-**BsubPc** derivatives does not appear in the literature.[9]

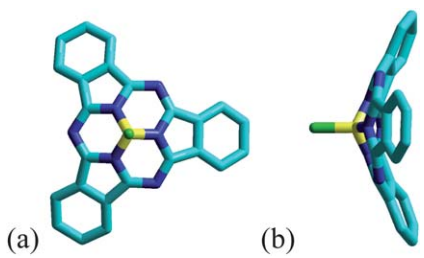

Fig. 1 Illustration of Cl-**BsubPc** (**1**) reproduced from single crystal X-ray diffraction data:[1b] (a) top view and (b) side view (cyan—carbon; blue—nitrogen; green—chlorine and yellow—boron).

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

Results and discussion

Cl-**BsubPc** (**1**, Scheme 1) was required as a starting material for our study; however, no commercial source of sufficiently high purity could be identified. Therefore, we synthesized Cl-**BsubPc**

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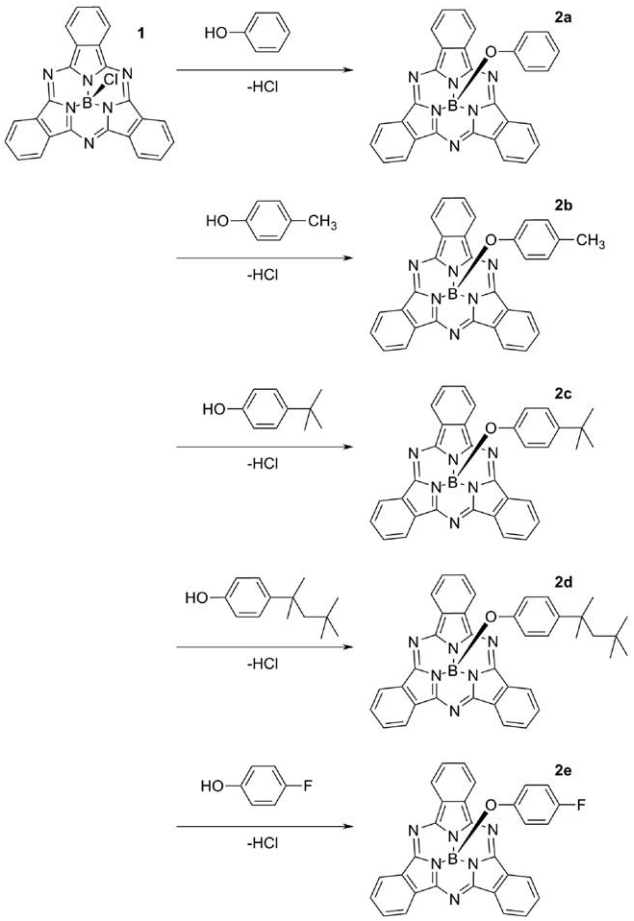
† Electronic supplementary information (ESI) available: Displacement ellipsoid plots, bond distances and selected interaction distances for compounds **2a–e**, as well as a schematic of the Kauffman chromatography column along with the instructions on its use. CCDC reference numbers 783165–783169. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0ce00599a



Scheme 1 Synthesis of phenoxy-**BsubPcs** used in this study.

in our own laboratory using a method adapted from Zyskowski and Kennedy.[10] We found that the crude synthesis proceeded as described but a simple Soxhlet extraction with methanol after synthesis was sufficient to purify the resulting Cl-**BsubPc** past 99%. We have since repeated this procedure in excess of 15 times with consistent results.

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

The method used to obtain the phenoxy derivatives is a robust, general method and was used for all five derivatives (**2a–e**). The method of Claessens *et al.*[8a] was adapted as follows: Cl-**BsubPc** (**1**) was heated in toluene with 5 molar equivalents of the appropriate phenol derivative for between 8 and 72 hours (time varied for complete conversion as monitored by HPLC). After the synthesis was complete, the toluene was evaporated and the residual phenol was removed on standard basic alumina in a Kauffman column chromatography apparatus[10] using dichloromethane as the eluent. The excess phenol remained adsorbed to the alumina and the product eluted through the alumina with hot dichloromethane. On removal of the dichloromethane, product in excess of 99% purity was obtained in all cases. In the case of *tert*-octylphenol (compound **2d**), in our first attempt the entire mass of residual phenol could not be adsorbed onto the alumina and an aqueous/organic workup was needed in order to remove the excess *tert*-octylphenol prior to Kauffman column chromatography. Compounds **2a**,[8a] **2b**[8b] and **2c**[8c] have been previously described in the literature with reported yields after purification of 18%, 79% and 58%. They have been obtained using a variety of synthetic and purification methods including crystallization,[8a] column chromatography[8b] and preparative thin layer chromatography.[8c] Using the combination of the synthetic method of Claessens *et al.*[8a] and Kauffman column chromatography[11] we have achieved yields of 95%, 79% and 81% for compounds **2a**, **2b** and **2c** respectively all with purities exceeding 99%. While in two of the three cases our yields are markedly higher, we wish to highlight Kauffman column chromatography as a facile method to obtain high purity phenoxy-**BsubPcs** regardless of whether base extraction is performed first.

We were able to form diffractable single crystals of compounds **2a–e** by slow diffusion crystallization using benzene (good solvent) and heptane (diffusing solvent). Classic crystallization was also successful in obtaining single crystals suitable for diffraction of compounds **2a–c**. We also obtained single crystals through simple solvent evaporation. In each case we confirmed the structure of the single crystals was equivalent by X-ray diffraction. However, we only report in detail the single crystals obtained by vapour diffusion as conversely, only diffusion crystallization was capable of producing high quality single crystals of compounds **2d** and **2e**. Depictions of the unit cell and a summary of structural parameters (lengths and angles) for single crystals of compounds **2a–e** formed through vapour diffusion are given in the ESI† accompanying this article.

In order to shape the discussion of the crystal structures of compounds **2a–e**, we wish to outline some terminology and will use the single crystal structure of Cl-**BsubPc** (**1**, illustrated in Fig. 1) as a reference point.[1b] With regard to the unique bowl shaped structure of the **BsubPc** molecular fragment, we will denote the face of the **BsubPc** containing the axial chlorine atom as the convex face and the opposite the concave face, consistent with previously established terminology.[9a]

On examination of the organization within the single crystal of compounds **2a–e** we have found that this series of compounds can be subdivided into two categories. The first, represented by compounds **2a–c** and **2e**, have a consistent motif present within their crystal structures which consists of two **BsubPc** molecular

fragments associated in a dimeric concaved-to-concaved orientation. This motif is illustrated in Fig. 2 for compound **2a** where the associated pair is illustrated in orange (the same illustrations for compounds **2b**, **2c** and **2e** appear in the ESI† accompanying this article, Fig. S7†). The presence of this dimer motif within the single crystal is independent of both the steric bulk of the substituent on the phenoxy group (as indicated by examination and comparison of compounds **2a–c**) as well as the electronegativity of the substituent (as indicated by examination and comparison of compound **2a** *versus* **2e**). Also illustrated in Fig. 2 is the spatial relationship between each dimer unit. In each case the phenoxy molecular fragment of one molecule is in close proximity to the convex face of a neighbouring **BsubPc**. The spatial arrangement of the phenoxy fragment with companion phenoxy **BsubPc** fragments does change on increasing steric bulk of the substituent for compounds **2a–c**. This qualitative observation will be quantified below. This tendency to form dimeric pairs of **BsubPc** molecular fragments is not seen in other **BsubPc** derivatives. For example phenoxy-perfluorinated-**BsubPc**,[12a] halo-perfluorinated-**BsubPc**,[12b,c] and some alkoxy-**BsubPcs**[12d,e] tend to arrange in a similar concave–convex motif.

Phenoxy-**BsubPc 2d** contains the sizable *tert*-octyl substituent, which has a large number of carbons but a relatively low number of degrees of freedom (compared to *n*-octyl, for example) and is the sole occupant of the second category. Compound **2d** crystallized into a distinctly different arrangement than did compounds **2a–c** and **2e**. The **BsubPc** fragments are no longer associated in discrete pairs, but rather are arranged in one dimensional ribbons. Each ribbon consists of one **BsubPc** fragment associating with two additional **BsubPc** fragments in a concave–concave–concave arrangement, illustrated in Fig. 3. These one dimensional ribbons are further arranged within a second dimension and form a plane permeating throughout the crystal. This plane of **BsubPc** fragments is entirely separated by another plane comprising the *tert*-octylphenoxy fragments and associated solvent molecules (benzene). The solvent molecules are not present in discrete locations within the crystal, rather disordered through this plane and there are *tert*-octylphenoxy fragments inserted into the plane from each side. There is also observed disorder amongst the *tert*-octyl substituents themselves. This arrangement is very similar to the one which has been observed for an alkylphenyl substituted **BsubPc** although in this case there was no inclusion of solvent or disorder present.[13a] It can also be found in at least one alkoxy-**BsubPc**.[13b]

In order to attempt to quantify the changes in crystal structure of all **BsubPc** derivatives in this study, certain inter- and intra-

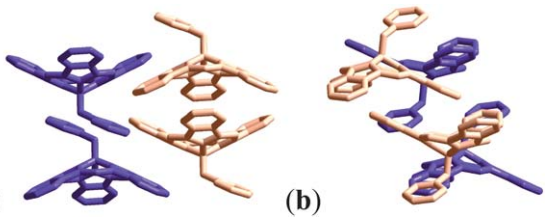


Fig. 2 Illustrations of the extended crystal structure of exemplary compound **2a**: (a) 'front' view and (b) 'side' view (rotated 90° from front view). **BsubPc** dimers shown in orange and neighbouring **BsubPc** shown in violet. Hydrogens are omitted for clarity.

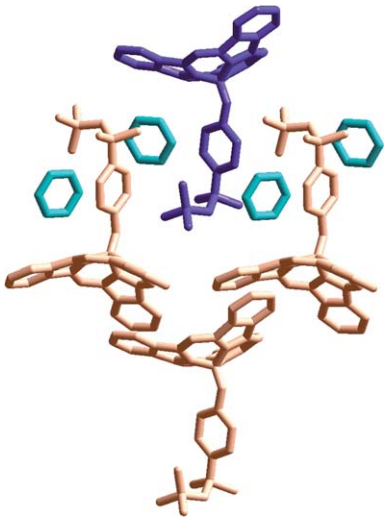


Fig. 3 Illustration of the extended crystal structure of compound **2d**. **BsubPc** ribbons shown in orange, an additional *tert*-octylphenoxy-**BsubPc** shown in violet and benzene shown in cyan. Hydrogens are omitted for clarity. Disorder of benzene and *tert*-octyl substituents are also omitted for clarity.

molecular features that were common to each structure were noted. They are schematically illustrated in Fig. 4. The noted values included the distance between one **BsubPc** unit and its nearest neighbour in both the dimer or ribbon concave–concave arrangement (d_1) and to next nearest **BsubPc** unit in another dimer or ribbon (d_2): so as to quantify the concave–concave association. For the same reason, the ring centroid to ring centroid (Cg–Cg) distances of the associated **BsubPc** fragments were also noted. Additionally, in order to quantify any bond angle strain or bond elongation between the **BsubPc** and phenoxy molecular fragments resulting from crystallization, we noted the angle of the phenoxy fragment relative to the **BsubPc** fragment (as indicated by the B–O–C angle) and the lengths of the boron–oxygen bond (B–O bond length) and oxygen–carbon bond (O–C bond length). The noted values are summarized in Table 1.

What immediately stands out is that the distance between two **BsubPc** units in a dimer (for compounds **2a–c** and **2e**) or ribbon (for compound **2d**) arrangement does not change along the series

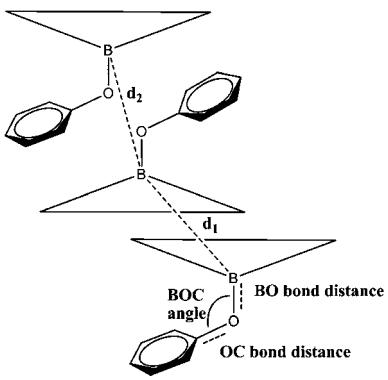


Fig. 4 Schematic representation of the compared quantities of the single crystal X-ray determined structures of compounds shown in Scheme 1.

Table 1 Selected metrics of the crystal structures of Cl-**BsubPc** (**1**) and phenoxy-**BsubPcs** (**2a–e**)

#	B–B distance, d_1/Å	B–B distance, d_2/Å	B–O–C angle/°	B–O bond length/Å	O–C bond length/Å	Cg–Cg distance/Å[a]	Space group
1[1b]	8.82	10.30	—	—	—	—	Orthorhombic (P_{nma})
2a	8.26	5.58	115.5(1)	1.443(2)	1.379(2)	3.674(1)	Triclinic ($P\bar{1}$)
2b	8.39	5.59	115.6(1)	1.436(2)	1.386(2)	3.6045(9)	Triclinic ($P\bar{1}$)
2c	8.78	8.61	118.9(2)	1.437(3)	1.387(2)	3.548(1)	Triclinic ($P\bar{1}$)
2d	8.83	12.01	129.1(2)	1.436(3)	1.368(2)	3.691(1)	Monoclinic ($P2_1/c$)
2e	8.18	5.55	115.2(2)	1.447(3)	1.383(2)	3.694(1)	Triclinic ($P\bar{1}$)

[a] Ring centroid to ring centroid distance.

of compounds **2a–e**—at approximately 8.83 Å to 8.18 Å. This is further supported by the ring centroid to ring centroid distances between the pairs of **BsubPc** fragments, which were fairly constant, from 3.55 Å to 3.69 Å.

As the substituent in the *para*-position of the phenoxy group was increased in size from a hydrogen atom (**2a**) to a methyl group (**2b**), no change in the separation between two dimers occurred, as indicated by the B–B bond distance (d_2) remaining constant at about 5.58 Å to 5.59 Å. A more significant increase to 8.61 Å was seen when the substituent was changed to a *tert*-butyl group in **2c**, and the *tert*-octyl substituent group of **2d** showed a d_2 distance of 12.01 Å, an increase of 2.15 times from **2a**. A significant increase in the angle of the B–O–C bond with the increase of the size of the substituent accompanied the increase in d_2 distance. As the bulkiness of the substituent group was raised (**2a–d**), the bond connecting the phenoxy to the **BsubPc**, increasing in angle from 115° for **2a** and **2b** to 119° for **2c** and finally 129° for compound **2d**. For reference, using a simple semi-empirical RM1 model, the B–O–C angle from a single isolated molecule of each of the compounds **2a–e** was calculated. The calculated angles ranged from 115° to 116° therefore placing the large increase to 129° for compound **2d** in context. The distortion of the B–O–C bond angle is not accompanied by a lengthening of the associated bond lengths (B–O or O–C). If the B–O–C bond angle distorts to such a great extent, this suggests that amongst this series of phenoxy-**BsubPcs** the formation of closely associated dimers or ribbons of **BsubPc** fragments arranged in a concave–concave fashion occurs even at the energetic expense of bond angle distortions present within the remainder of the molecule. Finally, the bond distances (d_1 and d_2) and bond angles (B–O–C) were nearly identical and the space group was the same for compound **2e** as for compound **2a** indicating the presence of an electronegative fluorine atom had little effect on the crystal structure.

Conclusions

We synthesized, purified, and obtained single crystals of a series of five phenoxy-**BsubPc** derivatives. We have analyzed the single crystals by X-ray diffraction and made observations on the similarities and differences in their crystal structures. We have been able to classify each derivative into one of the two categories depending on the nature of its repeating motif: either the formation of dimers or ribbons of the **BsubPc** moieties within the crystal structure arranged between their respective concave faces. As the size of the substituent on the phenoxy ring is increased we have measured an associated B–O–C bond angle distortion within the molecule while preserving the dimer or ribbon motif (in the crystal structure of compound **2d** for example). The preferential formation of dimers of the **BsubPc** molecular fragment has not been previously observed in the crystal structure of either alkoxy-**BsubPcs**[12d,e] or perfluorinated-**BsubPc**[12a] derivatives, while the ribbon motif has been previously seen.[13a,b] We hope an enhanced understanding of the solid state structure of phenoxy-**BsubPc** derivatives will aid other research groups as these compounds are applied to (for example) optical and electronic devices.

Experimental

Materials

Phthalonitrile and 4-fluorophenol were purchased from TCI Company Ltd. (Portland, Oregon) and used as received. Boron trichloride (BCl_3) 1.0 M solution in heptane, phenol, *p*-cresol, 4-*tert*-butylphenol and 4-*tert*-octylphenol were obtained from Sigma Aldrich (Mississauga, Ontario, Canada) and used without further purification. Other common solvents, reagents and standard basic alumina (300 mesh) were purchased from Caledon Laboratories (Caledon, Ontario, Canada) and used as received.

Methods

X-Ray diffraction results were analyzed using PLATON 40M-version 250809[14] for bond angles and lengths, and crystal packing images were generated using Mercury version 2.2.[15] All crystal structures were collected using a Nonius KappaCCD diffractometer equipped with an Oxford Cryostream variable temperature apparatus. All nuclear magnetic resonance (NMR) spectra were acquired on a Varian Mercury 400 MHz system in deuterated chloroform with 0.05% (v/v) tetramethylsilane (TMS) as a ^{1}H NMR reference purchased from Cambridge Isotope Laboratories and used as received. All ultraviolet-visible (UV-Vis) spectroscopy was performed using PerkinElmer Lambda 25 in a PerkinElmer quartz cuvette with 10.00 mm path length.

The reaction progress was monitored using a Waters 2695 high pressure liquid chromatography (HPLC) separation module with a Waters 2998 photodiode array. A Waters 150 mm reverse phase Sunfire® C18 5 μm column was used with HPLC grade acetonitrile (ACN, 1.2 mL min^{-1} isocratic) purchased from Caledon Laboratories as the eluent.

Cl-**BsubPc**[10] and phenoxy-**BsubPc** derivatives **2a**,[9b] **2b**[9d] and **2c**[9e] have been previously described in the literature. In the case of the synthesis of compounds **2a–c** our synthetic methods are

higher yielding and we wish to highlight the use of Kauffman chromatography[11] as a facile and high yielding method for the purification of these compounds to >99% purity.

Chloro boron subphthalocyanine (Cl-BsubPc, 1). Compound **1** was synthesized by adapting a previously published procedure.[10] Phthalonitrile (5.32 g, 0.0415 mol) was dissolved with stirring in 1,2-dichlorobenzene (220 mL) in a round bottomed flask fitted with a short path distillation column and placed, under a constant flow of argon gas towards the short path distillation column. To this solution BCl_3 (100 mL of 1.0 M solution (0.1 mol) in heptane) was added in a single portion. On gradual heating the heptane was distilled off. When distillation was complete the reaction heated at reflux for an additional 1.5 hours. After cooling, the solvent was removed by rotary evaporation. The resulting crude product was extracted with hot methanol in a Soxhlet extraction apparatus for 8 hours. The resulting golden-brown powder was then rinsed with diethyl ether and dried in the vacuum oven yielding compound **1** (3.76 g, 63%). Purity by HPLC (99.5%, max plot). δ_H(400 MHz, $CDCl_3$, Me_4Si) 7.95–7.97 (6H, m), 8.90–8.92 (6H, m); λ_{max}($CHCl_3$)/nm 564.

The phenoxy-**BsubPc** derivative was synthesized by a method adapted from Claessens *et al.*[8]

Phenoxyboronsubphthalocyanine (2a)[9b]. Cl-**BsubPc** (**1**, 0.56 g, 0.0013 mol) was mixed with phenol (0.615 g, 0.0065 mol) in toluene (10 mL) in a cylindrical vessel fitted with a reflux condenser and argon inlet. The mixture was stirred and heated at reflux under a constant pressure of argon for 8 hours. Reaction was determined complete *via* HPLC by the absence of **1**. The solvent was evaporated under rotary evaporation. The crude product purified on a Kauffman column using standard basic alumina (300 mesh) as the adsorbent and dichloromethane as the eluent. The product elutes from the Kauffman column while the excess phenol remains adsorbed. The dichloromethane was then removed under reduced pressure yielding a dark pink/magenta powder of compound **2a** (0.609 g, 95%). δ_H(400 MHz, $CDCl_3$, Me_4Si) 5.37–5.41 (2H, d), 6.59–6.64 (1H, t), 6.72–6.78 (2H, t), 7.88–7.94 (6H, m), 8.83–8.88 (6H, m); λ_{max}($CHCl_3$)/nm 563.

Similarly for other phenoxy-**BsubPcs**:

4-Methylphenoxyboronsubphthalocyanine (2b)[9d]. Compound **2b** was synthesized as for **2a** except *p*-cresol (4-methylphenol, 0.707 g, 0.0065 mol) was used in place of phenol, yielding compound **2b** (0.605 g, 79%). δ_H(400 MHz, $CDCl_3$, Me_4Si) 2.01–2.03 (3H, s), 5.27–5.31 (2H, d), 6.51–6.55 (2H, d), 7.88–7.93 (6H, m), 8.82–8.88 (6H, m); λ_{max}($CHCl_3$)/nm 563.

4-*tert*-Butylphenoxyboronsubphthalocyanine (2c)[9e]. Compound **2c** was synthesized as for **2a** except 4-*tert*-butylphenol (0.977 g, 0.0065 mol) was used instead of phenol yielding compound **2c** (0.571 g, 81%). δ_H(400 MHz, $CDCl_3$, Me_4Si) 1.07 (9H, s), 5.28–5.30 (2H, d), 6.73–6.75 (2H, d), 7.89–7.92 (6H, m), 8.84–8.86 (6H, m); λ_{max}($CHCl_3$)/nm 563.

4-*tert*-Octylphenoxyboronsubphthalocyanine (2d). Compound **2d** was synthesized as for **2a** except 4-*tert*-octylphenol (1.34 g, 0.0065 mol) was used instead of phenol. In this case, before Kauffman column purification, the excess 4-*tert*-octylphenol was removed by dissolving the product in toluene (300 mL) and extracting with 3.0 M KOH in distilled water (3 × 300 mL). Removal of the toluene and purification by Kauffman column as above yielded compound **2d** (0.453 g, 58%). δ_H(400 MHz, $CDCl_3$, Me_4Si) 0.56–0.58 (9H, s), 1.11–1.14 (6H, s), 1.48–1.49 (2H, s), 5.29–5.32 (2H, d), 6.71–6.74 (2H, d), 7.87–7.92 (6H, m), 8.81–8.86 (6H, m); λ_{max}($CHCl_3$)/nm 563.

4-Fluorophenoxyboronsubphthalocyanine (2e). Compound **2e** was synthesized as for **2a** except 4-fluorophenol (0.729 g, 0.0065 mol) was used instead of phenol, yielding compound **2e** (0.486 g, 74%). δ_H(400 MHz, $CDCl_3$, Me_4Si) 5.32–5.35 (2H, m), 6.40–6.45 (2H, t), 7.91–7.93 (6H, m), 8.84–8.87 (6H, m); λ_{max}($CHCl_3$)/nm 563.

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

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