# Pseudohalides of Boron Subphthalocyanine

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Ⓢ Supporting Information

**ABSTRACT:** The synthesis and study of a series of pseudohalides of boron subphthalocyanine (BsubPc) are reported. Each pseudohalide has been compared to the more common chloride and bromide of BsubPc, and we have found that most react slower under standard phenoxylation and hydrolysis conditions. Three pseudohalides (TsO-BsubPc, MsO-BsubPc, and BsO-BsubPc) do not hydrolyze at all even after prolonged periods of time in the presence of water. Single crystals of TsO-, MsO-, and ClsO-BsubPc were obtained, and their structures were unambiguously determined.
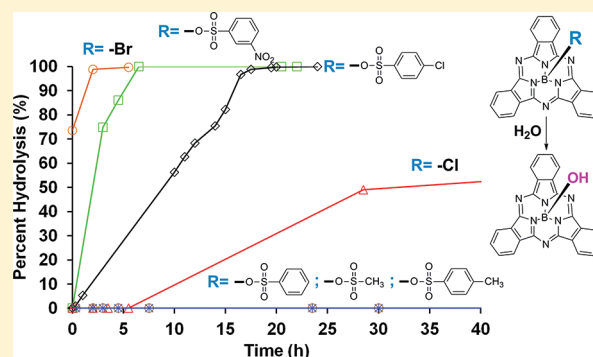
Boron subphthalocyanine (BsubPc, Scheme 1) is a unique, ring-reduced member of the common phthalocyanine family of compounds. Its aromatic, three-membered heterocyclic ring is nonplanar and bowl-shaped. BsubPcs typically have a maximum absorption in the visible region of the electromagnetic spectrum around 565 nm. There has been recent interest in incorporating BsubPc derivatives into organic electronic devices, particularly into organic light-emitting diodes[1] and organic photovoltaics.[2] Common BsubPc derivatives in use contain an axial halogen (commonly chloride) or those in which the halogen has been displaced by a nucleophile (most commonly oxygen-based such as phenol). The latter are of particular interest, as we have previously shown that variations in the axial phenoxy fragment can provide new solid-state arrangements.[3−5] The most commonly used precursor to phenoxylated BsubPcs is Cl-BsubPc.[6,7] We have noticed that the conversion from Cl-BsubPc to phenoxylated derivatives can be exceedingly slow;[3] others have shown that alkynyl derivatives produced through reaction of a Grignard reagent with Cl-BsubPc react with some speed.[2e,8] While the synthesis of Br-BsubPc is known,[9,10] it is difficult to produce with high purity, and we have noticed that it is hydrolytically sensitive, which may contribute to the limited literature surrounding its use as a precursor compound.[11]

In order to expand the number of BsubPc precursors, we have been interested in the synthesis and study of the pseudohalides of BsubPc. The aim for our study was to determine if there was a pseudohalide of BsubPc that could be easily isolated and was more reactive than Cl-BsubPc but less reactive (and thus more hydrolytically stable) than Br-BsubPc. The result would be a precursor that could be produced in significant quantities and used over time without concerns of hydrolysis on storage. Whi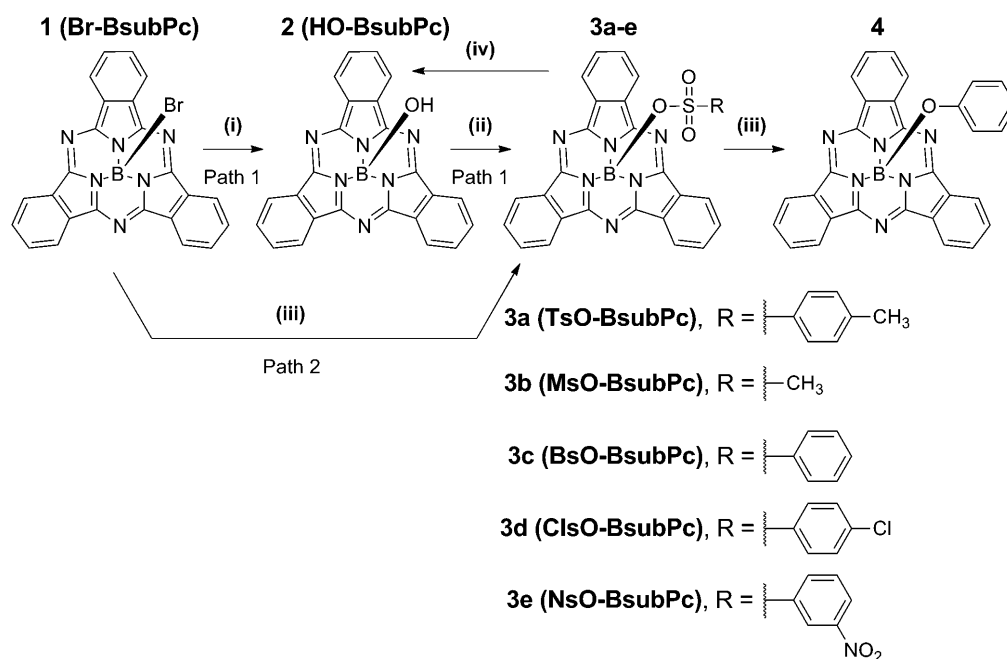le pseudohalides have long been used as leaving groups in basic chemistry, modern uses for pseudohalides (such as mesylates and tosylates) include their use as leaving groups in Heck and Suzuki cross-coupling reactions.[12] Concurrent with our study, Guilleme et al. published a method for the generation of triflate-BsubPc (TfO-BsubPc). This intermediate was generated in situ using silver triflate or trimethylsilyl triflate to effect the abstraction of chloride from Cl-BsubPc and form TfO-BsubPc.[13] They further showed that TfO-BsubPc could react at a high rate with oxygen, nitrogen, and carbon-based nucleophiles in order to produce new BsubPc derivatives. TfO-BsubPc could not be isolated because of its high reactivity with water.

In this note, we report the synthesis and isolation of a series of five sulfonic-acid-based pseudohalides of BsubPc. Their structures were unambiguously confirmed using either spectroscopic or crystallographic methods or both. We compare the rates of reaction of the pseudohalides under phenoxylation and hydrolysis conditions and compare them to Cl-BsubPc and Br-BsubPc. We draw a conclusion on their suitability to replace Cl-BsubPc and Br-BsubPc as standard precursor compounds. We also compared the electrochemical and optical properties of the pseudohalides using cyclic voltammetry, absorption spectroscopy, and fluorescence spectroscopy against Cl-BsubPc, should someone consider them as replacements for Cl-BsubPc in organic electronic devices.

Typically, the synthesis of sulfonic-acid-based pseudohalides involves the reaction of the corresponding sulfonic acid chloride (R—S(═O)$_2$Cl) or anhydride (R—S(═O)$_2$—O—S(═O)$_2$—R) with a hydroxy group. While this approach was the most obvious first method to obtain a pseudohalide BsubPc

**Scheme 1. Synthesis of Pseudohalides of BsubPc (3a–e) via Two Different Pathways[a]**



3a (TsO-BsubPc), R = —⟨benzene⟩—CH₃

3b (MsO-BsubPc), R = —CH₃

3c (BsO-BsubPc), R = —⟨benzene⟩

3d (ClsO-BsubPc), R = —⟨benzene⟩—Cl

3e (NsO-BsubPc), R = —⟨benzene⟩—NO₂

[a]Conditions: (i) water, pyridine, reflux. (ii) R—S(=O)₂O—S(=O)₂—R, pyridine, toluene, reflux. (iii) (py⁺)(R—S(=O)₂O⁻), toluene, reflux and subsequent phenoxylation to phenoxy-BsubPc **4**. ((iii) path 2: phenol, chlorobenzene, 100 °C.) and hydrolysis back to HO-BsubPc **2**. (iv) DMSO, pyridine, water, 60 °C.

(path i in Scheme 1), it was unclear whether the hydroxyl group of HO-BsubPc would react as a "normal" hydroxyl group. After synthesizing hydroxy-BsubPc (HO-BsubPc) using the method of Potz,[10] it was mixed with *p*-toluene sulfonic acid chloride (TsCl) in toluene with pyridine and heated to reflux. Surprisingly, we observed complete transformation of HO-BsubPc to Cl-BsubPc (confirmed by HPLC retention time to a genuine standard). We hypothesized that the liberated chloride anion reacted with TsO-BsubPc produced in situ to form Cl-BsubPc. The same result was obtained if the reaction was conducted in chlorobenzene. Next, we tried to use the sulfonic acid anhydride in place of the chloride. Following the same procedure, conversion to TsO-BsubPc (**3a**, Scheme 1) was observed without the formation of Cl-BsubPc (Scheme 1, path i). The product was purified by simple removal of the reaction solvent under vacuum followed by rinsing with methanol until pure. This route was also successful in producing MsO-BsubPc (**3b**, Scheme 1). In these two cases, the purity and composition of the final compounds was confirmed using chromatography, spectroscopy (including HRMS), and crystallography (Figures S23–S25, Supporting Information). Single crystals were grown through vapor diffusion of heptane into a benzene solution of TsO-BsubPc and of pentane into a dichloromethane solution of MsO-BsubPc. In the case of MsO-BsubPc, two different crystal types were obtained: rhomboids and needles (Figure S27, Supporting Information). Although both are solvates, the rhomboid structure contains two MsO-BsubPc molecules and one dichloromethane molecule in the asymmetric unit (Figure S24), whereas the needle solvate incorporated disordered solvent into its structure (which has been removed from the atomic displacement plot shown in Figure S25, Supporting Information). A more detailed discussion of the solid state arrangement of these derivatives is given in the Supporting Information accompanying this article.

Given our observation that chloride could displace/exchange with tosylate in the presence of pyridine, we began to consider whether halides and pseudohalides could be interchanged by treatment of a common precursor (Br-BsubPc) with a pyridinium salt of the respective pseudohalide ((py⁺)(R—S(=O)₂—O⁻)). Indeed, we found this to be the case (Scheme 1, path ii). Briefly, Br-BsubPc was dissolved in toluene, and 2.2 equiv of the pyridinium salt of the pseudohalide was added. Under stirring and a positive pressure of argon, the solution was heated to reflux until complete conversion was observed by HPLC analysis (<8 h). The solvent was then removed under vacuum, and the solid was rinsed with methanol until pure. This method proved successful to use the pyridinium salts of *p*-toluene, methane, benzene, *p*-chlorobenzene, and *m*-nitrobenzene sulfonic acid to produce TsO-BsubPc, MsO-BsubPc, BsO-BsubPc, ClsO-BsubPc, and NsO-BsubPc, respectively (compounds **3a–e**, Scheme 1). Where the pyridinium salt was not commercially available, we made it beforehand by neutralization of the corresponding acid with pyridine. In each case, the composition and purity of the final compounds was confirmed using a combination of spectroscopy, and in the case of ClsO-BsubPc, crystallography. Synthetic path ii negates the need to hydrolyze Br-BsubPc to HO-BsubPc and to produce the sulfonic acid anhydride while providing yields upward of 90% in all cases. We also attempted the synthesis of TfO-BsubPc using this method, starting with pyridinium triflate and Br-BsubPc. Similar to the observations of Guilleme et al.,[13] we were unable to isolate the TfO-BsubPc product, presumably because of its high sensitivity to water; we saw rapid conversion into a mixture of HO-BsubPc and μ-oxo(BsubPc)₂ (the μ-oxo dimer is easily identified based on its unique UV–vis spectrum[14]) by HPLC analysis (in each case confirmed against a genuine sample).

Next, we performed a series of experiments to compare the conversion over time of each pseudohalide to phenoxy-BsubPc

and to HO-BsubPc. The phenoxylation reaction was performed under conditions that we have previously established (5 equiv phenol, chlorobenzene), albeit at slightly reduced temperature (100 °C) to facilitate long reaction times without loss of solvent.[3] For hydrolysis, each pseudohalide BsubPc was heated at 60 °C in a mixture of pyridine, water, and DMSO. The conversion to product was monitored by HPLC (retention times compared against know standards), and the conversion percentage was calculated as a function of time (as the integrated area of the product peak divided by the sum of the area of the starting material and product peaks in a 2d chromatogram extracted from a PDA 3d chromatogram at 560 nm).

Figure 1a shows the conversion of the pseudohalides (**3a−e**) and halides (Cl-BsubPc and Br-BsubPc) to phenoxy-BsubPc (**4**,
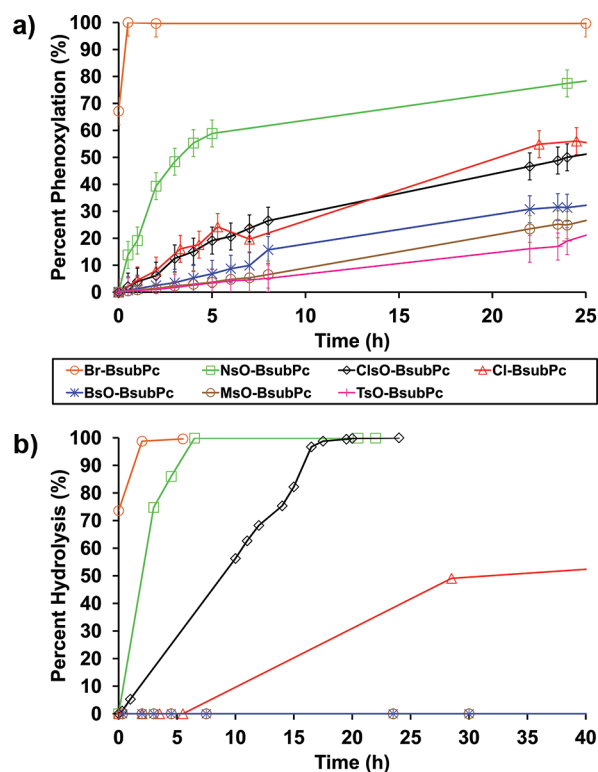


**Figure 1.** Reactions of Br-BsubPc, Cl-BsubPc, and the pseudohalides (**3a−e**) under (a) phenoxylation at 100 °C to give phenoxy-BsubPc (**4**) and (b) hydrolysis at 60 °C to give HO-BsubPc (**2**).

Scheme 1). The rate of reaction of Cl-BsubPc and Br-BsubPc (**1**) was as expected, with Br-BsubPc being the more reactive and achieving 100% conversion in about 1 h, whereas Cl-BsubPc reached 56% conversion in 24 h. In general, pseudohalides **3a−e** were slower to react than both of the halides with two exceptions. ClsO-BsubPc (**3d**) reacted at approximately the same rate as Cl-BsubPc and NsO-BsubPc (**3e**), which reacted faster, reaching ∼77% conversion after 24 h. Complete conversion of Cl-BsubPc took well in excess of 150 h, whereas it took approximately 140 h to achieve complete conversion of NsO-BsubPc (Figure S28, Supporting Information). We have noted some variability in the rate of conversion, and we have represented this as error bars on the conversion percentage. While we take precautions to minimize the loss of solvent over such prolonged reaction times, we cannot absolutely ensure a constant solvent volume, especially with

frequent sampling. It is perhaps then not surprising to see some variability, given the accepted mechanism for these substitution reactions is $S_N1$ in nature[11a] and thus highly dependent on concentration of the pseudohalide/halide of BsubPc. It should also be noted that we make no attempt to sequester the halo acid or sulfonic acid produced as a byproduct of these reactions,[15] The other pseudohalide derivatives ClsO-BsubPc (**3d**), BsO-BsubPc (**3c**), MsO-BsubPc (**3b**), and TsO-BsubPc (**3a**) achieved 50, 32, 25, and 17% conversion to phenoxy-BsubPc after 24 h, respectively. In each case, complete conversion could not be achieved in a reasonable amount of time. By best fitting a line through the initial data points of Figure 1a (for a magnified view, see Figure S28, Supporting Information) and examining the slope, we can quantify the relative reactivities for the series Br-BsubPc, NsO-BsubPc, ClsO-BsubPc, Cl-BsubPc, BsO-BsubPc, MsO-BsubPc, and TsO-BsubPc as follows: ∼200, 19, 4, 4, 1.2, 0.7, and 0.5% h$^{-1}$, respectively. We did not see any evidence of the formation of normal phthalocyanines by ring expansion under the conditions studied.

In comparing the hydrolysis rates of the pseudohalide BsubPcs, the compounds that were more reactive during phenoxylation were also more susceptible to hydrolysis. As shown in Figure 1b, Br-BsubPc converted to HO-BsubPc after a period of only 2 h, while Cl-BsubPc took >40 h. NsO-BsubPc showed the highest hydrolysis rate of the pseudohalides, becoming fully hydrolyzed after only 7 h. The next most reactive pseudohalide (ClsO-BsubPc) showed faster hydrolysis than Cl-BsubPc (100% converted to HO-BsubPc after 24 h), even though under phenoxylation conditions it had a nearly identical rate to Cl-BsubPc. The other three pseudohalides, BsO-BsubPc, MsO-BsubPc, and TsO-BsubPc showed no hydrolysis under the conditions tested. By examining the initial slope of the data in Figure 1b, we can also quantify the relative hydrolysis rate for the series Br-BsubPc, NsO-BsubPc, ClsO-BsubPc, Cl-BsubPc, BsO-BsubPc, MsO-BsubPc, and TsO-BsubPc as follows: ∼50, 18, 5.6, 1.7, 0, 0, and 0% h$^{-1}$, respectively.

We can then examine whether we have achieved our goal of having a precursor BsubPc, which is more reactive than Cl-BsubPc while possessing better hydrolytic stability than Br-BsubPc. NsO-BsubPc fits the criteria with a rate of phenoxylation that is 4−5 times that of Cl-BsubPc while simultaneously having a hydrolysis rate that is approximately half that of Br-BsubPc. However, and perhaps more interesting, we have obtained several pseudohalides that do not hydrolyze even on prolonged contact with water. Given that Cl-BsubPc has been applied in organic electronic derivatives, it would be of interest to compare the basic photophysical and electronic properties of the hydrolytically stable pseudohalides (and for that matter, all the pseudohalides) to that of Cl-BsubPc, as the application of a hydrolytically stable alternative to Cl-BsubPc in an organic electronic device may be desirable.[1,2]

Cyclic voltammetry was first used to examine the electrochemical properties of the pseudohalides (dichloromethane solution; tetrabutylammonium perchlorate electrolyte; decamethylferrocene as an internal reference[16]). In general, the pseudohalide BsubPcs possessed irreversible oxidation and reduction events, and thus, we are only able to comment on their respective peak potentials which ranged from a low of 1.237 V for ClsO-BsubPc to a high of 1.316 V for MsO-BsubPc (Table S22, Supporting Information). The reduction peak potentials ranged from a low of −0.975 V for ClsO-BsubPc to a

high of −1.051 V for MsO-BsubPc. For comparison, Cl-BsubPc shows a reduction peak potential in a similar range of −1.050 V, while the oxidation peak potential is much lower at 0.981 V, and each oxidation and reduction events are also irreversible (Table S22, Supporting Information).

The fluorescence quantum efficiencies ($\phi_{PL}$) of the pseudohalide BsubPcs were measured using a standard procedure.[1b,17] The $\phi_{PL}$ of Cl-BsubPc and Br-BsubPc were also measured for comparison (Table S22, Supporting Information). It was found that the $\phi_{PL}$ of all of the pseudohalides were all approximately 0.4: the highest was 0.42 (TsO-BsubPc), and the lowest was 0.36 (NsO-BsubPc). We also found that the $\phi_{PL}$ of Br-BsubPc was low at 0.18 and that the $\phi_{PL}$ of Cl-BsubPc was rather high at 0.77. Thus, the pseudohalides had neither an unusually low nor an unusually high $\phi_{PL}$.

In summary, a series of sulfonic-acid-based pseudohalide BsubPcs were synthesized and characterized. A comparison has been made between their rates of reaction (phenoxylation and hydrolysis) relative to the reference compounds Cl-BsubPc and Br-BsubPc. On the basis of their relative conversions, we have identified one pseudohalide, NsO-BsubPc, to be both more reactive than Cl-BsubPc and more hydrolytically stable than Br-BsubPc; however, its rate of reaction falls off considerably at high conversion, thus potentially limiting its usefulness. Three of the other pseudohalides TsO-BsubPc, MsO-BsubPc, and BsO-BsubPc were shown to have very good hydrolytic stability (we did not observe hydrolysis under the conditions studied). Their resistance to hydrolysis while maintaining a electrochemical and photophysical properties typical of BsubPcs suggests that the hydrolytically stable pseudohalides might be suitable for application and study in organic electronic devices. We have also highlighted in the Supporting Information accompanying this article the solid state arrangements of TsO-BsubPc and ClsO-BsubPc, which showed enhanced $\pi$-stacking compared to Cl-BsubPc, an attractive feature for an organic electronic material.

## ■ EXPERIMENTAL SECTION

**Materials and Methods.** Toluene, methanol, chlorobenzene, 1,2-dichlorobenzene, pyridine, HPLC-grade acetonitrile, triflic acid, 4-toluenesulfonic anhydride, 4-toluenesulfonyl chloride, pyridinium 4-toluenesulfonate, methylsulfonic anhydride, methylsulfonyl chloride, methylsulfonic acid, 4-chlorobenzenesulfonic acid, benzenesulfonic acid, and pyridinium 3-nitrobenzenesulfonate were purchased from normal suppliers and used as received. For general methods of phenoxylation and hydrolysis, please see the Supporting Information (ESI) accompanying this article. Cl-BsubPc,[3,7] Br-BsubPc,[10] and HO-BsubPc[10] were synthesized according to the reported procedures. Pyridinium trifluoromethylsulfonate was synthesized according to the reported procedure.[18] The remaining pyridinium salts were prepared as follows.

**Pyridinium Methylsulfonate.** A modification of a reported procedure:[19] Pyridine (2.95 g, 0.037 mol) was dissolved in toluene and slowly neutralized with methylsulfonic acid (3.58 g, 0.037 mol). The precipitate was filtered, and the resulting solid was dried under vacuum, leaving a white solid product, pyridinium methylsulfonate. Yield 6.20 g (95%): mp = 185−189 °C, lit. 185 °C.[19]

**Pyridinium Benzenesulfonate.** Benzenesulfonic acid (5.06 g, 0.032 mol) was dissolved in toluene and stirred until well mixed. Then pyridine was slowly added in high excess. After neutralization had occurred, the toluene and excess pyridine were removed through rotary evaporation, leaving the respective pyridinium salt as an off-white/tan powder, pyridinium benzenesulfonate. Indications are that this salt is hygroscopic, although in our study it was used before water absorption. Yield 7.2 g (95%): mp = 127−132 °C, lit. 125−130 °C.[20]

**Pyridinium 4-Chlorobenzenesulfonate.** Compound has been previously reported, but the report does not contain detailed characterization.[21] Similar to pyridinium benzenesulfonate, except 4-chlorobenzene sulfonic acid (5.05 g, 0.026 mol) was used. The result was a white powder, pyridinium 4-chlorobenzenesulfonate. Indications are that this salt is hygroscopic, although in our study it was used before water absorption. Yield 6.31 g (89%): mp = 137−139 °C; ^{1}H NMR (400 MHz, CDCl₃, Me₄Si) δ 7.32−7.35 (2H, m), 7.84−7.87 (2H, m), 8.00 (2H, t, J = 7.2 Hz), 8.46 (1H, tt, J = 7.9, 1.5 Hz), 9.02 (2H, dd, J = 6.5, 1.5 Hz); ^{13}C NMR (400 MHz, DMSO) δ 127.2, 127.5, 127.7, 133.0, 142.2, 146.4, 147.1.

**4-Toluenesulfonate-boronsubphthalocyanine (TsO-BsubPc, 3a).** *Path 1.* HO-BsubPc (0.071 g, 0.00017 mol) and 4-toluenesulfonic anhydride (0.300 g, 0.00092 mol) were dissolved in toluene (5 mL) and pyridine (3 mL). The mixture was stirred under argon and heated at reflux for 60 min. Reaction was determined complete via HPLC by the absence of HO-BsubPc. The solvent was removed using rotary evaporation, and the solid was rinsed with methanol until pure to give a pink powder, **TsO-BsubPc**. Yield 0.051 g (51%): ^{1}H NMR (400 MHz; CDCl₃; Me₄Si) δ 2.23 (3H, s), 6.83−6.89 (4H, m), 7.93−7.95 (6H, m), 8.84−8.86 (6H, m); ^{13}C NMR (400 MHz, CDCl₃, Me₄Si) δ 21.5, 96.9, 122.5, 126.2, 129.1, 130.2, 131.1, 143.1, 150.9; ^{11}B NMR (400 MHz; CDCl₃; BF₃·OEt₂) δ −15.19 (s); $\lambda_{abs,max}$(toluene) 566 nm; $\lambda_{PL,max}$(toluene) 573 nm; HRMS (EI) Calcd. for [C₃₁H₁₉BN₆O₃S] ([M]+) m/z 566.1332, found 566.1332.

*Path 2.* Br-BsubPc (1.002 g, 0.00211 mol) and pyridinium p-toluenesulfonate (1.063 g, 0.00425 mol) were dissolved in toluene (50 mL) and heated under argon while stirring. The reaction was maintained at reflux until it was determined complete via HPLC (about 6 h). The solvent was removed using rotary evaporation, and the solid was rinsed with methanol until pure and dried in air to give a pink powder with a golden sheen, **TsO-BsubPc**. Yield 0.905 g (76%). Characterization equivalent to product obtained above using path 1.

**Methylsulfonate-boronsubphthalocyanine (MsO-BsubPc, 3b).** *Path 1.* HO-BsubPc (0.071 g, 0.00017 mol) and methylsulfonic anhydride (0.300 g, 0.00092 mol) were dissolved in toluene (5 mL) and pyridine (3 mL). The mixture was stirred under argon and heated at reflux for 60 min. Reaction was determined complete via HPLC by the absence of HO-BsubPc. The solvent was removed using rotary evaporation, and the solid was rinsed with methanol until pure to give a pink powder, **MsO-BsubPc**. Yield 0.051 g (51%): ^{1}H NMR (400 MHz; CDCl₃; Me₄Si) δ 1.91 (3H, s), 7.95−7.97 (6H, m), 8.90−8.92 (6H, m); ^{13}C NMR (400 MHz, CDCl₃, Me₄Si) δ 38.8, 122.7, 130.4, 131.2, 151.3; ^{11}B NMR (400 MHz; CDCl₃; BF₃·OEt₂) δ −15.00 (s); $\lambda_{abs,max}$(toluene) 566 nm; $\lambda_{PL,max}$(toluene) 572 nm; HRMS (EI) Calcd. for [C₂₅H₁₅BN₆O₃S] ([M]+) m/z 490.1031, found 490.1019.

*Path 2.* Br-BsubPc (1.115 g, 0.00235 mol) and pyridinium methylsulfonate (1.205 g, 0.00688 mol) were dissolved in toluene (50 mL) and heated under argon while stirring. The reaction was maintained at reflux until it was determined complete via HPLC (about 6 h). The solvent was removed under rotary evaporation, and the solid was rinsed with methanol until pure and dried in air to give a pink powder with a golden sheen, **MsO-BsubPc**. Yield 0.750 g (65%). Characterization equivalent to product obtained above using path 1.

**Benzenesulfonate-boronsubphthalocyanine (BsO-BsubPc, 3c).** Br-BsubPc (0.195 g, 0.00041 mol) and pyridinium methylsulfonate (0.244 g, 0.00103 mol) were dissolved in toluene (15 mL) and heated under argon while stirring. The reaction was maintained at reflux until it was determined complete via HPLC (about 6 h). The solvent was removed using rotary evaporation, and the solid was rinsed with methanol until pure and dried in air to give a pink powder with a golden sheen, **BsO-BsubPc**. Yield 0.126 g (56%): ^{1}H NMR (400 MHz; CDCl₃; Me₄Si) δ 6.96 (2H, d, J = 8.4 Hz), 7.09 (2H, t, J = 7.9 Hz), 7.28 (1H, t, J = 7.4 Hz), 7.93−7.95 (6H, m), 8.84−8.86 (6H, m); ^{13}C NMR (400 MHz, CDCl₃, Me₄Si) δ 122.5, 126.1, 128.5, 130.4,

131.1, 132.3, 151.0 (only 7 $^{13}$C resonances observed due to low solubility); $^{11}$B NMR (400 MHz; CDCl$_3$; BF$_3$·OEt$_2$) $\delta$ −15.13 (s); $\lambda_{abs,max}$(toluene) 566 nm; $\lambda_{PL,max}$(toluene) 573 nm; HRMS (EI) Calcd. for [C$_{30}$H$_{17}$BN$_6$O$_3$S] ([M]+) $m/z$ 552.1176, found 552.1177.

**4-Chlorobenzenesulfonate-boronsubphthalocyanine (ClsO-BsubPc, 3d).** Br-BsubPc (0.209 g, 0.00044 mol) and pyridinium methylsulfonate (0.263 g, 0.00097 mol) were dissolved in toluene (15 mL) and heated under argon while stirring. The reaction was maintained at reflux until it was determined complete via HPLC (about 6 h). The solvent was removed using rotary evaporation, and the solid was rinsed with methanol until pure and dried in air to give a pink powder with a golden sheen, **ClsO-sBsubPc**. Yield 0.160 g (62%): $^1$H NMR (400 MHz; CDCl$_3$; Me$_4$Si) $\delta$ 6.89 (2H, d, $J$ = 8.8 Hz), 7.06 (2H, d, $J$ = 8.8 Hz), 7.94−7.96 (6H, m), 8.85−8.88 (6H, m); $^{13}$C NMR (400 MHz, CDCl$_3$, Me$_4$Si) $\delta$ 122.6, 127.6, 128.8, 130.5, 131.1, 136.8, 150.9; $^{11}$B NMR (400 MHz; CDCl$_3$; BF$_3$·OEt$_2$) $\delta$ −15.47 (s); $\lambda_{abs,max}$(toluene) 567 nm; $\lambda_{PL,max}$(toluene) 574 nm; HRMS (EI) Calcd. for [C$_{30}$H$_{16}$BN$_6$O$_3$SCl] ([M]+) $m/z$ 586.0786, found 586.0804.

**3-Nitrobenzenesulfonate-boronsubphthalocyanine (NsO-BsubPc, 3e).** Br-BsubPc (0.106 g, 0.00022 mol) and pyridinium methylsulfonate (0.160 g, 0.00057 mol) were dissolved in toluene (15 mL) and heated under argon while stirring. The reaction was maintained at reflux until it was determined complete via HPLC (about 6 h). The solvent was removed using rotary evaporation, and the solid was rinsed with methanol until pure and dried in air to give a pink powder with a golden sheen, **NsO-BsubPc**. Yield 0.088 g (66%): $^1$H NMR (400 MHz; CDCl$_3$; Me$_4$Si) $\delta$ 7.28 (1H, dt, $J$ = 8.0, 1.4 Hz), 7.38 (1H, t, $J$ = 8.0 Hz), 7.82 (1H, s), 7.95−7.97 (6H, m), 8.15−8.18 (1H, m), 8.85−8.87 (6H, m); $^{13}$C NMR (400 MHz, CDCl$_3$, Me$_4$Si) $\delta$ 122.7, 130.7, 150.9 (only 3 $^{13}$C resonances detectable due to low solubility); $^{11}$B NMR (400 MHz; CDCl$_3$; BF$_3$·OEt$_2$) $\delta$ −15.04 (s); $\lambda_{abs,max}$(toluene) 568 nm; $\lambda_{PL,max}$(toluene) 575 nm; HRMS (EI) Calcd. for [C$_{30}$H$_{16}$BN$_7$O$_5$S] ([M]+) $m/z$ 597.1027, found 597.1046.

**Phenoxylation of Various Boron Subphthalocyanines.** BsubPc precursor (0.075 g) was dissolved in chlorobenzene (10 mL), and the respective phenol (5 equiv) was then added. The reaction mixture was continuously stirred and heated to 100 °C under argon gas. The temperature was maintained for a period of 120 h, during which samples were extracted from the homogeneous reaction mixture at periodic time intervals. These samples were analyzed by HPLC in order to determine conversion percentage. The percent conversion from reactant (BsubPc) to product (phenoxy-BsubPc) versus time was determined from the HPLC data as the percentage of the integrated product peak of the total area of the integrated product and reactant peaks extracted at 560 nm.

**Hydrolysis of Various Boron Subphthalocyanines.** BsubPc precursor (0.1 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 heated to a temperature of 60 °C under normal atmosphere while stirring. The temperature was maintained for a period of 28 h, during which samples were taken and analyzed by HPLC as described above. The percent conversion from reactant (BsubPc) to hydrolysis product (HO-BsubPc) versus time was determined from the HPLC data similar to above.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

General procedures for phenoxylation and hydrolysis; $^1$H NMR spectra of all newly synthesized pyridinium salts and compounds **3a−3e**; cyclic voltammograms of compounds **3a−3e**; absorption and fluorescence spectra of compounds **3a−3e**; X-ray crystallographic data, thermal ellipsoid plots, and CIF files for all crystal structures; a discussion of crystal packing; and longer time-scale phenoxylation data. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**

The authors declare no competing financial interest.

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