

Supporting Information

General Considerations

Hexanes, EtOAc, THF and 1,4-dioxane, and HPLC grade acetonitrile and *N,N*-dimethylformamide solvents were purchased from Caledon Laboratory Ltd. (Caledon, ON, Canada); THF was dried and purified by passing through activated alumina and 1,4-dioxane was dried over 4Å molecular sieves. Mg turnings, I₂ and γ -butyrolactone were purchased from Sigma Aldrich (Mississauga, ON, Canada) and used as is. Bromo-2,4,6-trifluorobenzene was purchased from Oakwood Products Inc. (West Columbia, SC, USA) and used as is. Column chromatography was carried out on Silicycle silica 60 silica gel (particle size 40–63 μ m) (Quebec City, Quebec, Canada) and thin layer chromatography on silica gel 60 coated with F₂₅₄ nm. All NMR spectra were recorded in CDCl₃ (purchased from Cambridge Isotope Laboratories Inc. (Tewksbury, MA, USA) and used as is) on a Bruker Advance III 400 MHz spectrometer operating at 400 MHz (¹H), 128 MHz (¹¹B), and 100 MHz (¹³C) at 25 °C. Chemical shifts are reported in ppm relative to the residual solvent signal (¹H and ¹³C) and BF₃•OEt₂ (¹¹B, 0 ppm) standard. High-pressure liquid chromatography analyses were carried on a Waters 2695 separation module with a Waters 2998 photodiode array and a Waters Styragel HR 2 THF 4.6 \times 300 mm column. The mobile phase consisted of MeCN:DMF (4:1 v/v). UV-VIS spectra were obtained using a PerkinElmer Lambda 25 spectrophotometer operating in double-beam mode with a slit width of 1 nm. Fluorescence spectra were obtained using a PerkinElmer LS55 spectrophotometer. All reactions were carried out in a standard fumehood under ambient lighting conditions.

Br-BsubPc (**1**) was synthesized according to the literature procedure [1].

Syntheses

4-Bromobutoxy-BsubPc 2. Under an atmosphere of Ar, magnesium turnings (0.288 g, 12 mmol) and a crystal of I₂ were added to 15 mL of anhydrous THF. The slurry was stirred until complete dissolution of I₂ and 1-bromo-2,4,6-trifluorobenzene (1.18 mL, 10 mmol) was added dropwise and the mixture was stirred 1.5 h at room temperature. The solution was then transferred to a suspension of Br-BsubPc (2.447 g, 5.15 mmol) in 400 mL of anhydrous THF. The mixture was refluxed for four days and after being cooled to room temperature, volatiles were removed via rotovap. The crude material was purified by column chromatography over SiO₂ using hexanes:EtOAc (gradient from 3:1 to 1:1) as the eluent. The oily material was triturated MeOH and the solids were filtered and dried, affording **2** as a magenta solid (0.356 g, 0.76 mmol, 15%). ¹H-NMR (400 MHz, CDCl₃): δ = 8.85 (m, 6H), 7.90 (m, 6H), 2.90 (t, 2H, ³J_{HH} = 6.6 Hz), 1.67 (br, 1H), 1.48 (t, 2H, ³J_{HH} = 6.4 Hz), 1.07 (m, 2H), 0.64 (m, 2H). ¹³C{¹H}-NMR (100 MHz, CDCl₃): δ = 151.6, 131.1, 129.9, 122.2, 58.2, 33.5, 29.4, 28.9. ¹¹B{¹H}-NMR (128 MHz, CDCl₃): δ = -14.8 (s). HRMS (DART): [M + H]⁺ *m/z* calcd [¹²C₂₈¹H₂₁¹¹B⁷⁹Br¹⁴N₆¹⁶O]⁺ 547.10533; found, 547.10603.

2-(2-Bromoethoxy)ethoxy-BsubPc 3. Under an atmosphere of Ar, Br-BsubPc (500 mg, 1.05 mmol) was suspended in 60 mL of dry 1,4-dioxane and the mixture was refluxed three days. Volatiles were removed *in vacuo* and the residue was purified via column chromatography over SiO₂ using hexanes:EtOAc 2:1 as the eluent, affording **3** as a magenta solid (0.161 g, 0.29 mmol, 27%). ¹H-NMR (400 MHz, CDCl₃): δ = 8.85 (m, 6H), 7.90 (m, 6H), 3.19 (t, 2H, ³J_{HH} = 6.4 Hz), 3.03 (t, 2H), 2.58 (t, 2H, ³J_{HH} = 4.9 Hz), 1.64 (t,

2H). $^{13}\text{C}\{^1\text{H}\}$ -NMR (100 MHz, CDCl_3): $\delta = 151.6, 131.1, 129.8, 122.2, 71.1, 70.8, 58.8, 30.0$. $^{11}\text{B}\{^1\text{H}\}$ -NMR (128 MHz, CDCl_3): $\delta = -14.7$ (s). HRMS (DART): m/z calcd [$^{12}\text{C}_{28}^1\text{H}_{21}^{11}\text{B}^{79}\text{Br}^{14}\text{N}_6^{16}\text{O}_2$] $^+$ 563.10024; found, 563.10017.

4-Bromobutanoyl-BSubPc **4**. Under an atmosphere of Ar, Br-BsubPc (500 mg, 1.05 mmol) was suspended in 60 mL of γ -butyrolactone and the mixture was refluxed 12 h. Volatiles were removed *in vacuo* and the residue was purified via column chromatography over SiO_2 using hexanes:EtOAc 3:1 as the eluent, affording **4** as a magenta solid (0.185 g, 0.33 mmol, 31%). ^1H -NMR (400 MHz, CDCl_3): $\delta = 8.88$ (m, 6H), 7.92 (m, 6H), 2.95 (m, 2H), 1.45 (m, 4H). $^{13}\text{C}\{^1\text{H}\}$ -NMR (100 MHz, CDCl_3): $\delta = 171.3, 151.7, 131.1, 130.0, 122.4, 32.8, 32.7, 27.1$. $^{11}\text{B}\{^1\text{H}\}$ -NMR (128 MHz, CDCl_3): $\delta = -15.2$ (s). HRMS (DART): $[\text{M} + \text{H}]^+$ m/z calcd [$^{12}\text{C}_{28}^1\text{H}_{19}^{11}\text{B}^{79}\text{Br}^{14}\text{N}_6^{16}\text{O}_2$] $^+$ 561.08459; found, 561.08300.

Absorption and Fluorescence Spectra

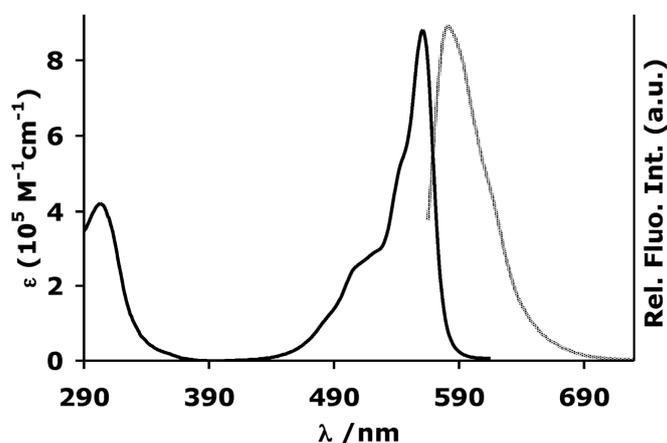


Figure S1. UV-vis (black) and photoluminescence (grey) spectra of **3** recorded in CH_2Cl_2 . The excitation monochromator was set at 561 nm.

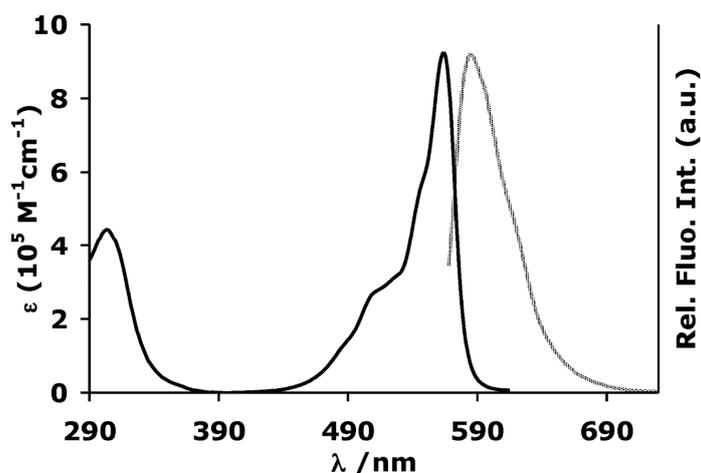


Figure S2. UV-vis (black) and photoluminescence (grey) spectra of **4** recorded in CH_2Cl_2 . The excitation monochromator was set at 564 nm.

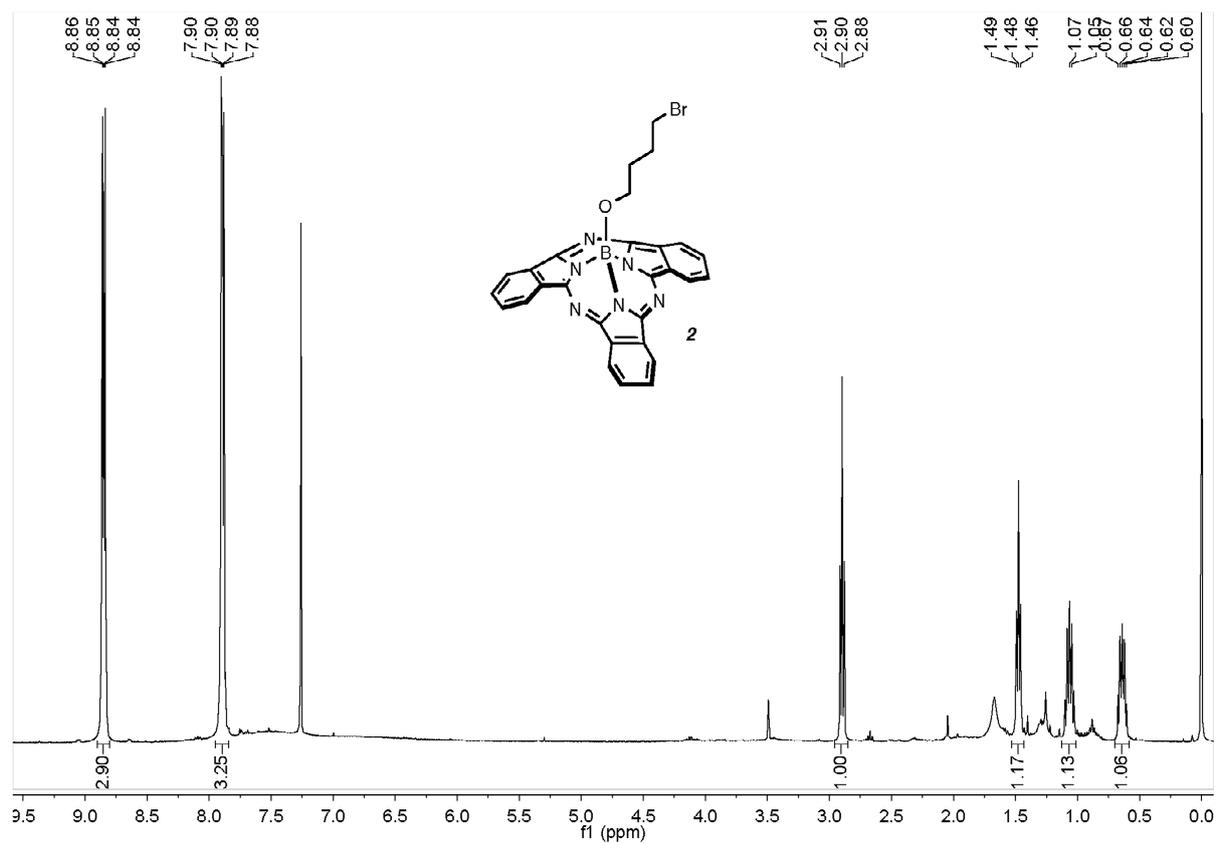


Figure S3. ¹H-NMR spectrum of compound 2.

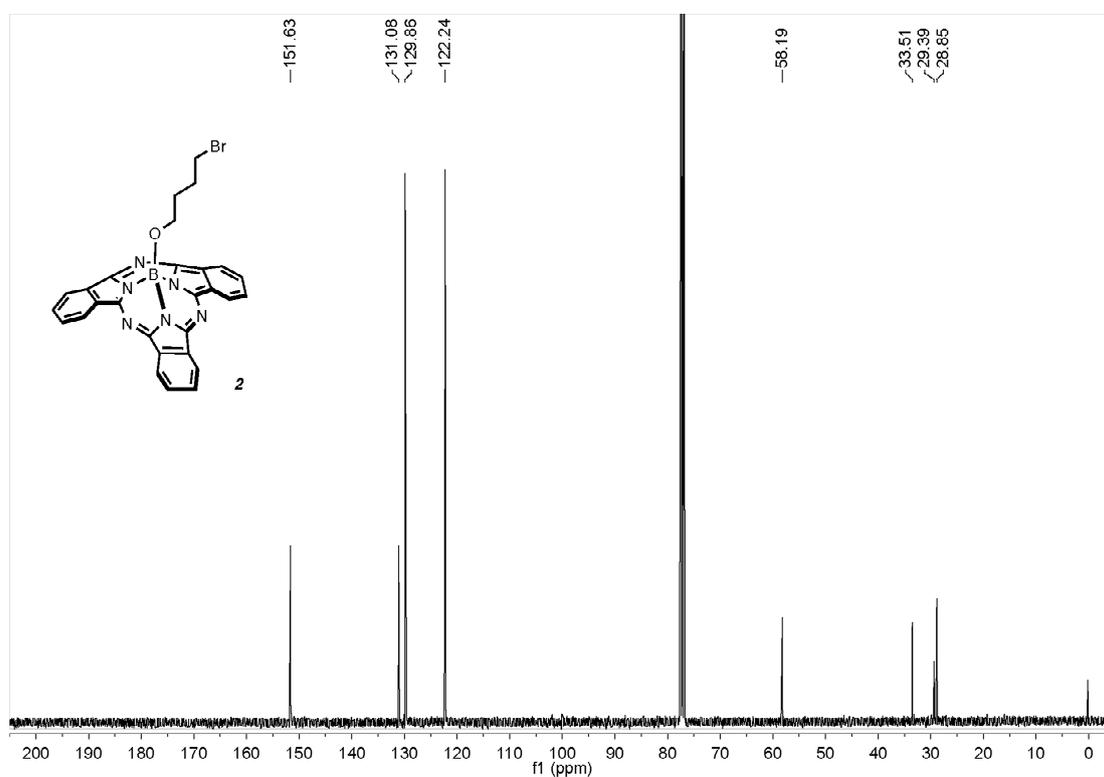
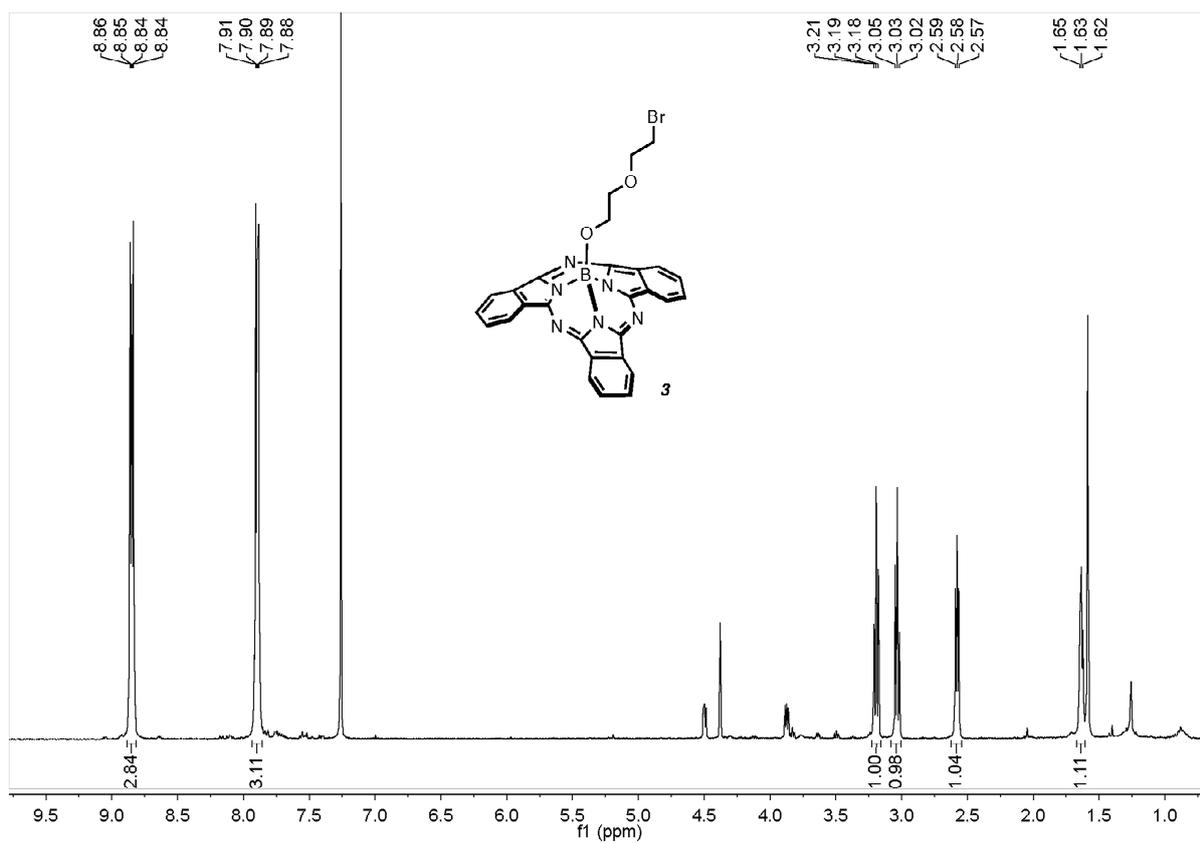
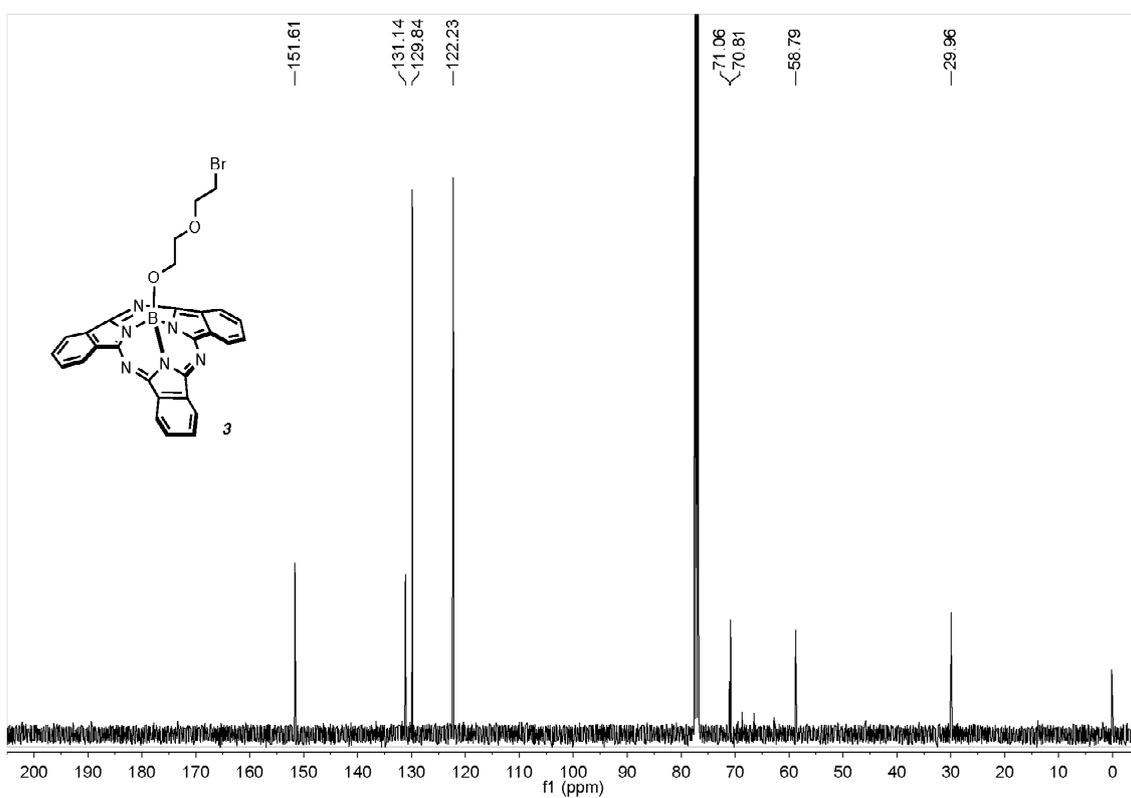


Figure S4. ¹³C-NMR spectrum of compound 2.

Figure S5. ¹H-NMR spectrum of compound 3.Figure S6. ¹³C NMR spectrum of compound 3.

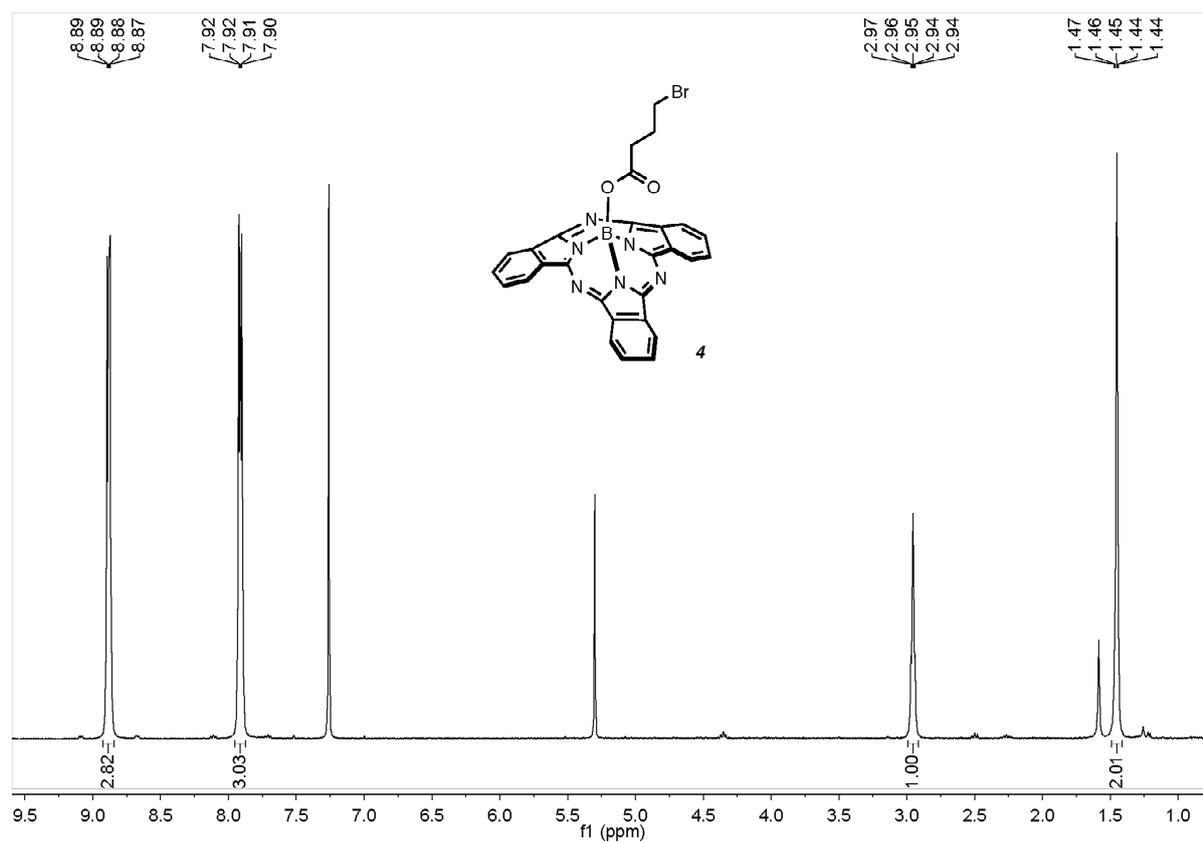


Figure S7. ¹H-NMR spectrum of compound 4.

Reference

1. Fulford, M.V.; Jaidka, D.; Paton, A.S.; Morse, G.E.; Brisson, E.R.L.; Lough, A.J.; Bender, T.P. Crystal structures, reaction rates, and selected physical properties of halo-boronsubphthalocyanines (halo = fluoride, chloride, and bromide). *J. Chem. Eng. Data* **2012**, *57*, 2756–2765.