Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information for

Subphthalocyanine-Based Porous Organic Polymers

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A. Materials

Unless stated otherwise all reagents were purchased from commercial sources and used without further purification. Dioxane, mesitylene, 3-pentanone, and acetonitrile were distilled over CaH_2.

B. Instrumentation and Methods

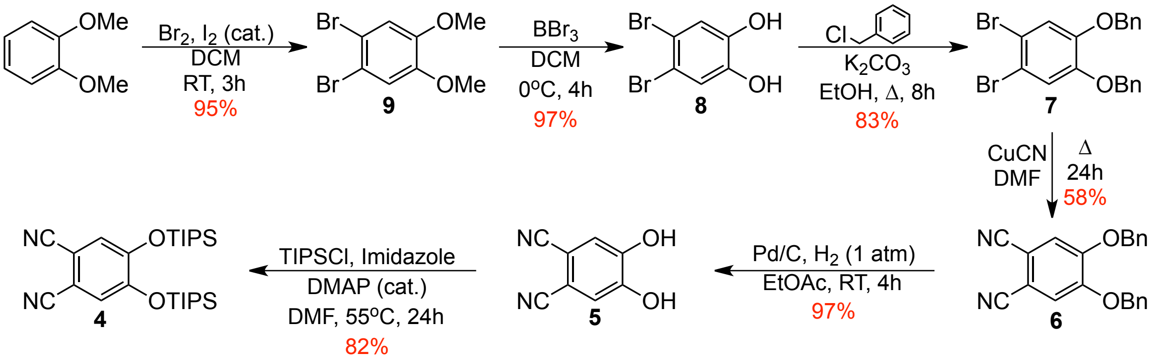
Infrared spectra were recorded on a Thermo Scientific Nicolet iS5 with an iD7 diamond ATR attachment and are uncorrected.

UV-Vis absorbance spectra were recorded on a Cary 5000 UV-Vis/NIR spectrophotometer using an internal DRA with stock powder cell holder to record the % reflectance spectra. Emission spectra were recorded on a Cary Eclipse Fluorescence spectrophotometer equipped with a xenon flash lamp.

Surface area measurements were conducted on a Micromeritics ASAP 2020 Surface Area and Porosity Analyzer using ca. 15 mg samples. Nitrogen isotherms were generated by incremental exposure to ultra high purity nitrogen up to ca. 1 atm in a liquid nitrogen (77 K) bath. Surface parameters were determined using BET adsorption models in the instrument software. Pore size distributions were determined using the non-local density functional theory (NLDFT) model (cylinder pore, N_2-cylindrical pores-oxide surface with high regularization) in the instrument software (Micromeritics ASAP 2020 V4.02).

^{1}H NMR spectra were recorded in deuterated solvents on a Bruker Avance DPX 400 (400 MHz). Chemical shits are reported in parts per million (ppm, δ) using the solvent as the internal standard. ^{13}C NMR spectra were recorded on a Bruker Avance DPX 400 (100 MHz) using the solvent as an internal standard.

C. Synthetic Methods

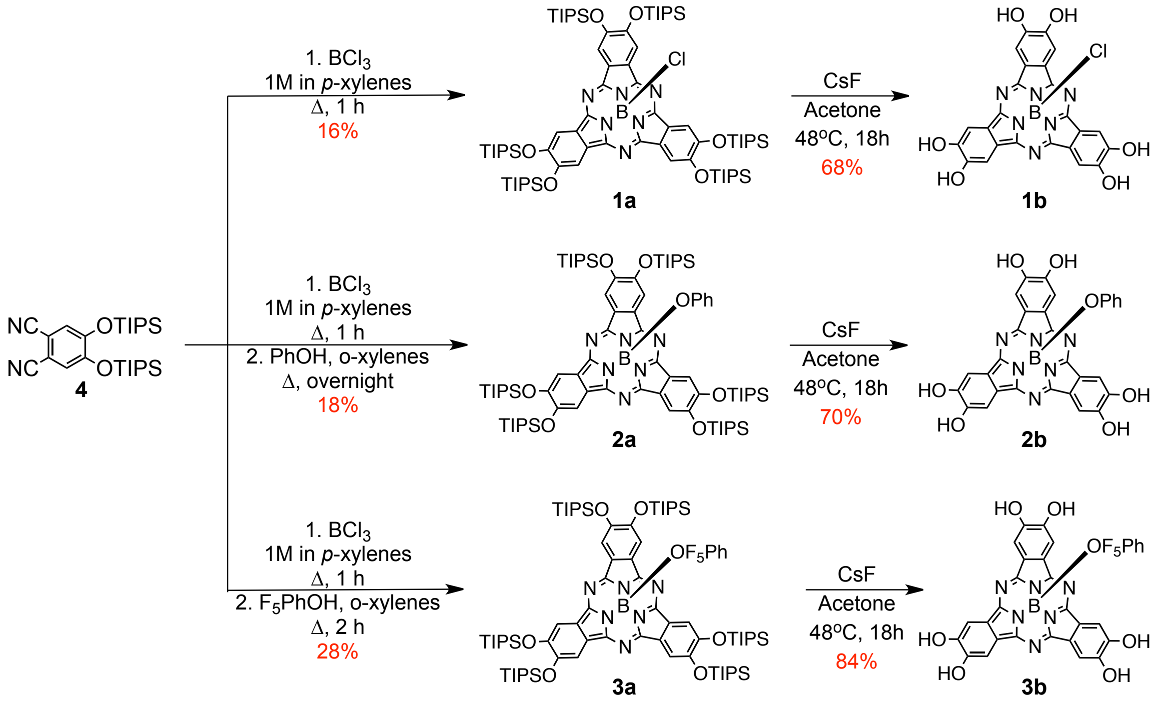


Scheme 1. Synthesis of 4,5-bis(triisopropylsilyloxy)phthalonitrile (**4**)

Compounds 5-9 have been synthesized previously by Torres et al.[1]

Synthesis of 4,5-bis(triisopropylsilyloxy)phthalonitrile (**4**)

To a dry flask was added **5** (1.5 g, 9.36 mmol), imidazole (3.8 g, 56.2 mmol, 6 eq), DMAP (0.034 g, 0.28 mmol, 0.03 eq), and TIPSCl (8 mL, 7.22 g, 37.44 mmol, 4 eq). The mixture was degassed with N_2 while dry DMF (30 mL, 0.3 M)added via syringe. The mixture was further degassed with N_2 before submerging in a 55˚C oil bath. The mixture was allowed to react for 24 h under N_2. After cooling, the mixture was quenched by pouring into saturated NH_4Cl solution. Product was extracted into ether, dried over Na_2SO_4 and reduced on the rotovap to a yellow oil. Overnight the oil yields needle shaped crystals, which were swamped with MeOH and cooled in the fridge before filtering, washing with additional MeOH. Product isolated in 82% yield as white needly solids. ^1H NMR (400 MHz $CDCl_3$) $\delta = 7.10$ (s, 2H), 1.31 (m, 6H), 1.11 (d, 36H) ^{13}C NMR (100 MHz $CDCl_3$) $\delta = 151.72$, 123.77, 115.78, 108.29, 17.76, 13.04. HRMS (ESI-MS) *m/z* calculated for $C_{26}H_{44}N_2O_2Si_2$ $[M+Na]^+$, 495.2834 Found 495.2835. IR (FT-IR, ATR): 2946, 2867, 2229, 1513, 1342 cm^{-1}. Melting point: 159-160 ˚C.



Scheme 2. Synthesis of hexahydroxy-SubPcs

Synthesis of **1a**

To a dry 2 neck flask was added **4** (0.5 g, 1.05 mmol) and the flask was fitted with reflux condenser and septa. The apparatus was degassed with N_2. BCl_3 (1.05 mL, 1.05 mmol, 1M solution in p-xylenes) was added to the solids at room temperature under 1 ATM N_2. The mixture was submerged in a 150˚C oil bath and allowed to react for 1 h. After cooling, solvents were removed via hivac. Product was extracted from the crude solids by grinding in a mortar and pestle, then washing with hexanes. The red filtrate was reduced on the rotovap. Product was separated by column chromatography (alumina, 1:1 hexanes:acetone) and further crashed out from hot DCM with acetonitrile. Solids filtered to yield the desired product in 16% yield as dark purple solids. ^{1}H NMR (400 MHz $CDCl_3$) δ = 8.16 (s, 6H), 1.51 (m, 18H), 1.19 (t, 108H) ^{13}C NMR (100 MHz $CDCl_3$) δ = 151.14, 149.97, 125.04, 110.86, 17.99, 13.26. HRMS (ICR MALDI) *m/z* calculated for $C_{78}H_{132}BClN_6O_6Si_6$ $[M]^+$ 1462.82 Found 1463.86. IR (FT-IR, ATR): 2938, 2862, 1457, 1145 cm^{-1}. Melting point: 271 ˚C

Synthesis of **1b**

CsF (0.429 g, 2.83 mmol, 18 eq) was added to a dried flask and held under N_2. Solutions of **1a** (0.23 g, 0.157 mmol) were created in acetone (~0.007 M), then added to the CsF via syringe. The mixture was degassed with N_2 briefly before heating in a 40˚C oil bath overnight (~16 h). The mixture was further cooled in an ice bath before quenching with TFA (20 eq) and diluting with water. Volatile solvents removed via rotovap and solids were isolated via filtration, washing with water, DCM and hot hexanes. Product isolated in 68% yield as plum-colored solids. ^{1}H NMR (400 MHz D_6 acetone) δ = 9.03 (s, 6H), 8.13, (s, 6 H) ^{13}C NMR (100 MHz D_6-acetone) δ = 149.94, 149.18, 124.17, 106.71. HRMS (ESI-MS) *m/z* calculated for $C_{24}H_{12}BN_6O_6$ $[M\text{-}Cl]^+$ 491.09 Found 491.09. IR (FT-IR, ATR): 3053, 1469, 1128, 1043 cm^{-1}. Melting point: 266 ˚C (decomposed without melting)

Synthesis of **2a**

To a dry 3 neck flask was added **4** (0.5 g, 1.05 mmol), one neck fitted with an addition funnel, one with reflux condenser, and the third a septa. The addition funnel was loaded with phenol (0.98 g 10.5 mmol, 10 eq), and o-xylenes (10 mL, 1.05 M). The apparatus was capped and degassed with N_2. BCl_3 (1.05 mL, 1.05 mmol, 1M solution in p-xylenes) was added to the solids at room temperature under 1 ATM N_2. The mixture was submerged in a 150˚C oil bath and allowed to react for 1 h before the phenol solution was added slowly to the hot mixture. The mixture was further heated while shielded from light overnight (~16h). After cooling, high boiling solvents were removed on rotovap and the dark residue was further dried on hivac. Product extracted from the crude solids by grinding in a mortar and pestle, then washing with hexanes. The red filtrate was reduced on rotovap, and the resulting residue was crashed out from minimal hot DCM with rt MeCN. The suspension was cooled in the fridge several hours before filtering to isolate solids. Product was isolated in 18% yield as a reddish-pink solid. ^{1}H NMR (400 MHz $CDCl_3$) δ = 8.09 (s, 6H), 6.77 (t, 2H), 6.58 (t, 1H) 5.42 (d, 2H) 1.49 (m, 18H) 6.58 (t, 108H) ^{13}C NMR (100 MHz $CDCl_3$) δ =152.30, 150.67, 149.11, 127.74, 124.01, 119.62, 117.66, 109.74, 16.98, 12.24. MS (MALDI) *m/z* calculated for $C_{84}H_{137}BN_6O_7Si_6$ $[M]^+$, 1522.35 Found 1522.11. IR (FT-IR, ATR): 2944, 2866, 1463, 1146 cm^{-1}. Melting point: 271 ˚C (decomposed without melting)

Synthesis of **2b**

To a dry flask was added CsF (0.52 g, 3.43 mmol, 18 eq). The flask was capped and degassed with N_2. Solutions of **2a** (0.29 g, 0.19 mmol) in 5:1 acetone: hexanes (~0.007 M) were added to the flask via syringe under degassing conditions. The mixture was heated to 45˚C under 1 ATM N_2 and allowed to react in the dark overnight (~16h). After cooling, low boiling solvents were removed via rotovap. The mixture was further diluted with water, and a few drops of 1M HCl were added to protonate. The mixture was filtered to isolate solids, which were further washed with water, DCM, and hot hexanes. Product was isolated in 70% yield as plum-colored solids. ^{1}H NMR (400 MHz D_6-acetone) δ = 9.09 (s, 6H), 8.16 (s, 6H), 6.74 (t, 2H), 6.56 (t, 2H), 5.33 (d, 2H) ^{13}C NMR (100 MHz D_6-acetone) δ = 153.58, 150.67, 148.46, 128.58, 125.02, 120.64, 118.97, 106.30. MS (MALDI) *m/z* calculated for $C_{30}H_{17}BN_6O_7$ $[M]^+$, 584.30 Found 584.14. IR (FT-IR, ATR): 3196, 2946, 1474, 1143 cm^{-1}. Melting point: 254 ˚C (decomposed without melting)

Synthesis of **3a**

To a dry 3 neck flask was added **4** (0.5 g, 1.05 mmol), one neck fitted with an addition funnel, one with reflux condenser, and the third a septa. The addition funnel was loaded with pentafluorophenol (1.93 g, 10.5 mmol, 10 eq) and o-xylenes (10 mL, 1.05 M). The apparatus was capped and degassed with N_2. BCl_3 (1M solution in p-xylenes) was added to the solids at room temperature under 1 atm N_2. The mixture was submerged in a 150˚C oil bath and allowed to react for 1 h before the phenol solution was added slowly to the hot mixture. The mixture was further heated while shielded from light 2h. After cooling, high boiling solvents were removed on rotovap and the dark residue was further dried on hivac. Product extracted from the crude solids by grinding in a mortar and pestle, then washing with hexanes. The red filtrate was reduced on rotovap, and the resulting residue was crashed out from minimal hot DCM with rt MeCN. The suspension was cooled in the fridge several hours before filtering to isolate solids. Product was isolated in 28% yield as dark colored solids. ^{1}H NMR (400 MHz $CDCl_3$) δ = 8.10 (s, 6H), 1.49 (m, 18H), 1.17 (m, 108H) ^{13}C NMR (100 MHz $CDCl_3$) δ = 151.28, 150.39, 124.96, 110.73, 17.99, 13.22. MS (MALDI) *m/z* calculated for $C_{84}H_{132}BF_5N_6O_7Si_6$ $[M]^+$, 1612.30 Found 1611.05. IR (FT-IR, ATR): 2945, 2868, 1467, 1149 cm^{-1}. Melting point: 284 ˚C (decomposed without melting)

Synthesis of **3b**

To a dry flask was added CsF (0.339 g, 2.23 mmol, 18 eq). The flask was capped and degassed with N_2. Solutions of **3a** (0.2 g, 0.124 mmol) in 5:1 acetone: hexanes (~0.007 M) were added to the flask via syringe under degassing conditions. The mixture was heated to 45˚C under 1 atm N_2 and allowed to react in the dark overnight (~16h). After cooling, low boiling solvents were removed via rotovap. The mixture was further diluted with water, and a few drops of 1M HCl were added to protonate. The mixture was filtered to isolate solids, which were further washed with water, DCM, and hot hexanes. Product was isolated in 84% yield as plum-colored solids. ^{1}H NMR (400 MHz D_6-acetone) δ = 9.08 (br s, 6H), 8.08 (s, 6H) ^{13}C NMR (100 MHz D_6-DMSO) δ = 169.85, 151.33, 150.19, 149.81, 125.19. 124.25, 109.82, 106.88. MS (MALDI) *m/z* calculated for $C_{30}H_{12}BF_5N_6O_7$ $[M]^+$, 674.26 Found 674.07. IR (FT-IR, ATR): 3028, 1463, 1275, 1133, 986 cm^{-1}. Melting point: 239 ˚C (Decomposed without melting)

SubPc POP Synthesis (**SubPc-POP 1, 2**)

To a dry ampule was added **1b**, **2b**, or **3b** (0.03 mmol) and BDBA (0.05 mmol, 1.5 eq). Solvent mixture (0.05 M) was added, and the mixture was sonicated for 1 minute. Mixture was freeze-pump-thawed for 3 cycles before ampule was sealed under vacuum. The sealed ampule was placed in a closed oven for 3 d. POP powder was isolated by filtration. Powder was suspended in dry acetonitrile to remove residual monomers over a period of 2 days, periodically changing out the acetonitrile. Powder was dried on high vacuum ~8 h then degassed 12 h at 75 °C on the porosity analyzer. SubPc-POP 1: 17 mg, 67% yield. SubPc-POP-2: 17.4 mg, 58% yield.

Table S1. Summary of SubPc-POP reaction screening conditions.

R_{ax}=	Eq SubPc	Eq BDBA	Solvents	Time	Temp	Porosity
Cl	1	1.5	2:1 Diox:Mes	72 h	105 °C	Nonporous
	1	1.5	1:1 Diox:Mes	72 h	105 °C	Nonporous
OPh (POP-1)	1	1.5	1:1 Diox:Mes	72 h	105 °C	231 m^2/g
	1	1.5	1:2 Diox:Mes	72 h	120 °C	123 m^2/g
	1	1.5	1:2 Diox:Mes	72 h	95 °C	160 m^2/g
	1	1.5	1:1 Diox:Mes	72 h	120 °C	103 m^2/g
OF_5Ph (POP-2)	1	1.5	1:1 Pent:Mes	72 h	105 °C	66 m^2/g
	1	1.5	1:2 Pent:Mes	72 h	105 °C	93 m^2/g
	1	1.5	1:1 Pent:Mes	72 h	105 °C	24 m^2/g

D. FT-IR Spectra

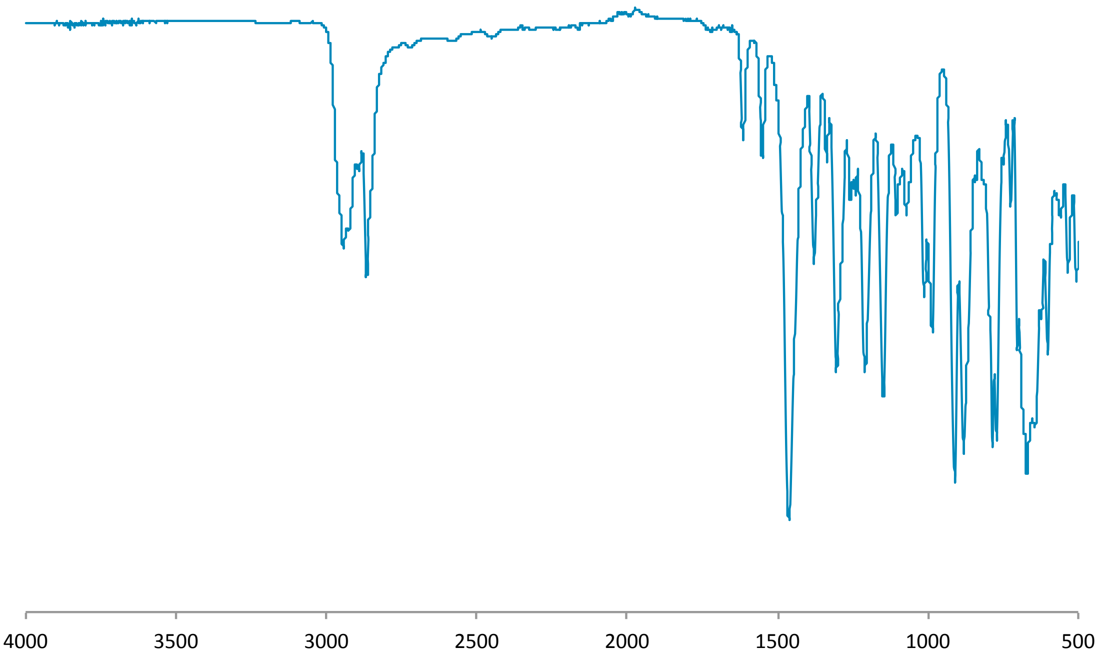


Figure S1. FT-IR spectrum of **1a**

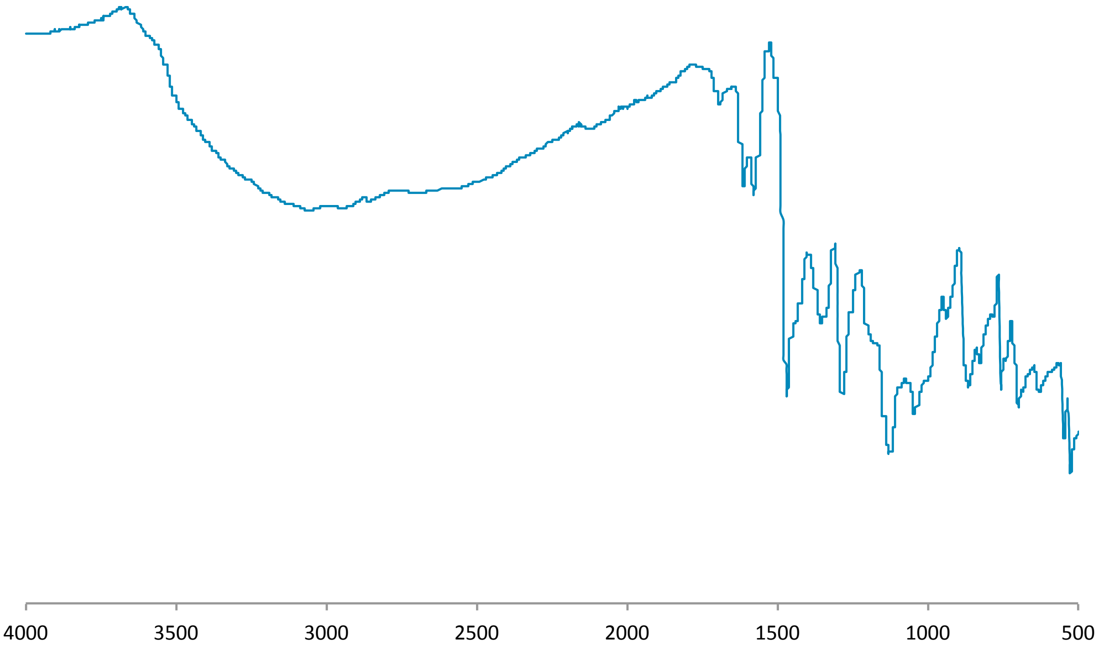


Figure S2. FT-IR spectrum of **1b**

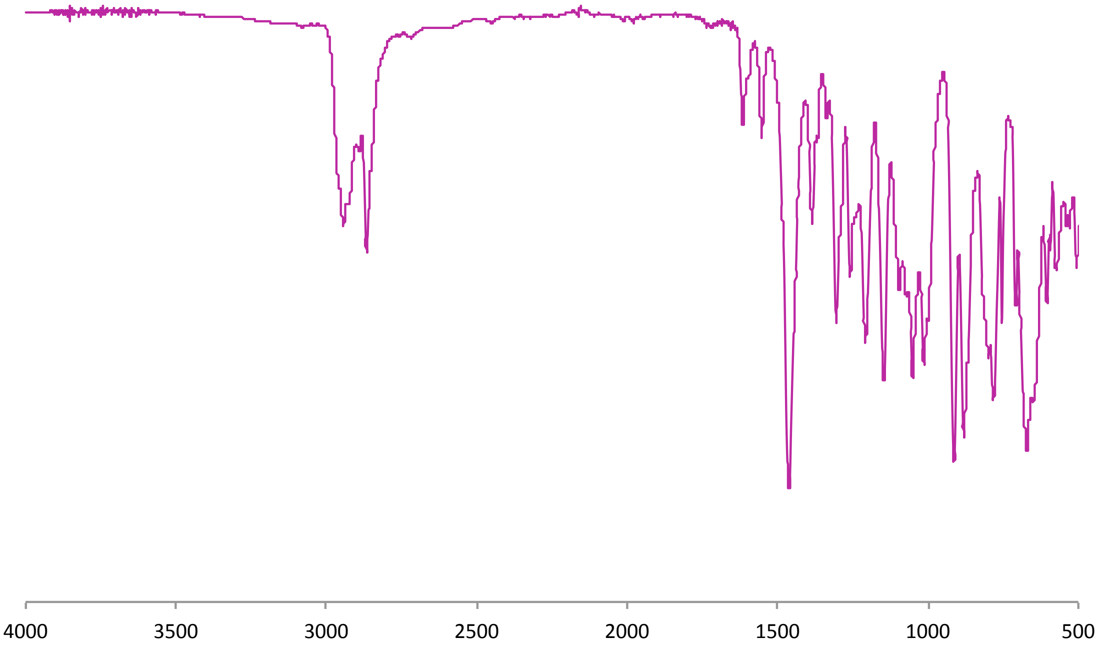


Figure S3. FT-IR spectrum of **2a**

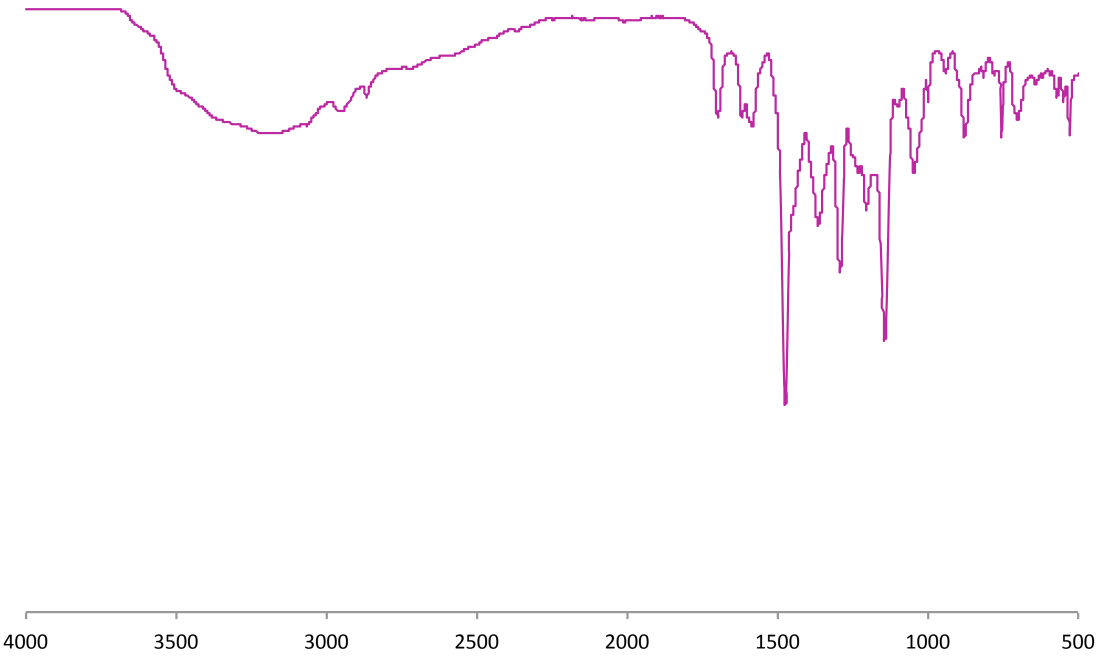


Figure S4. FT-IR spectrum of **2b**

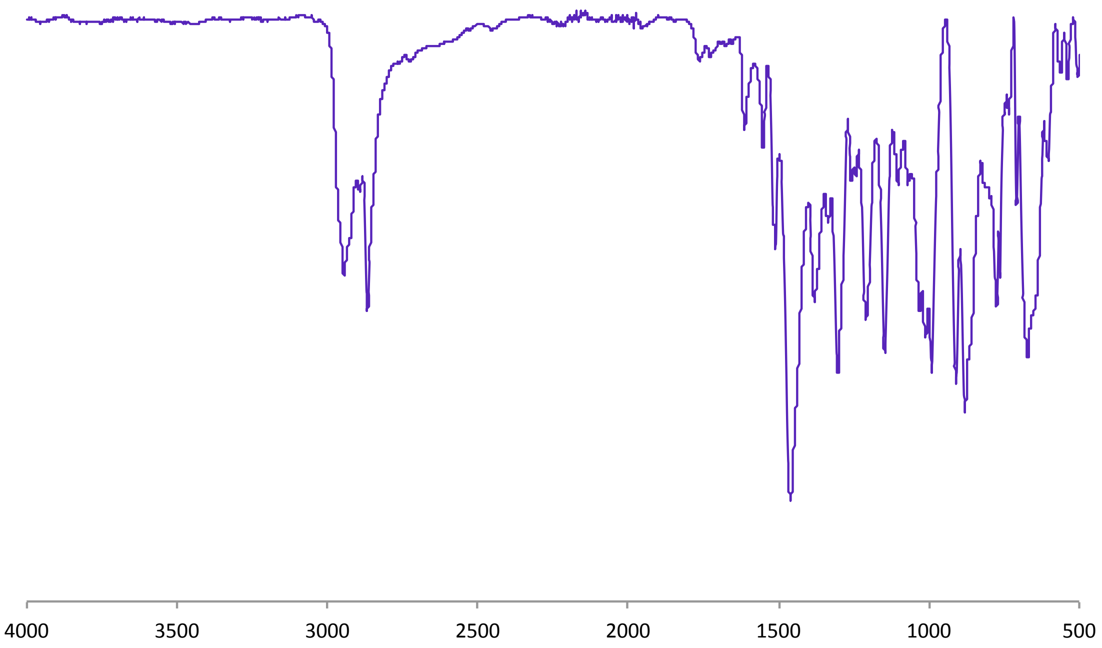


Figure S5. FT-IR spectrum of **3a**

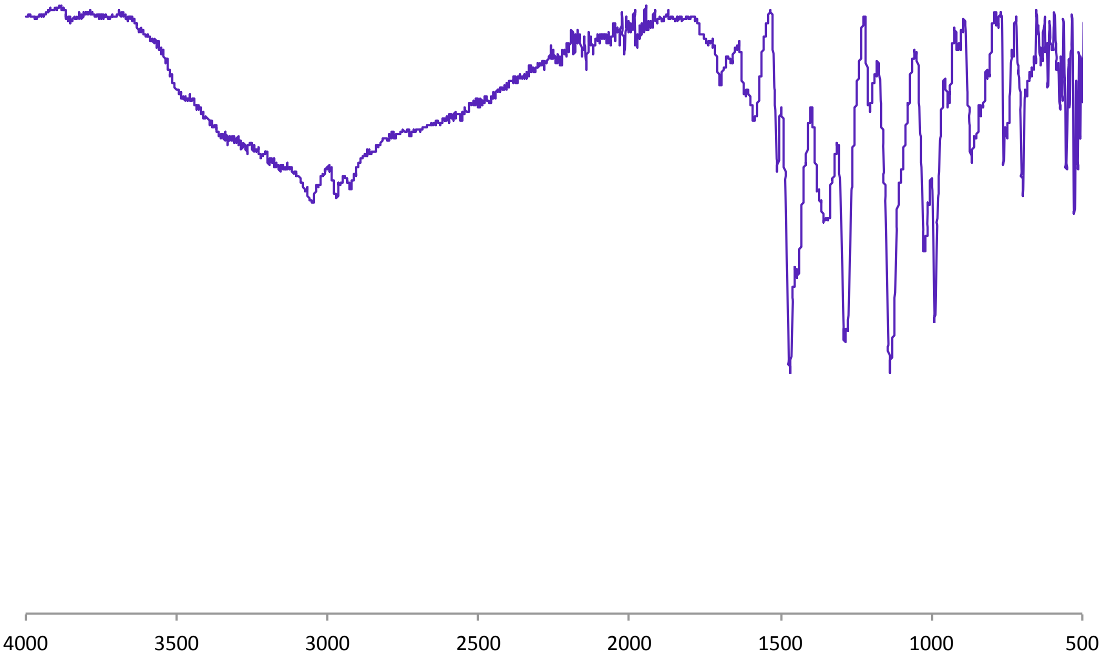


Figure S6. FT-IR spectrum of **3b**

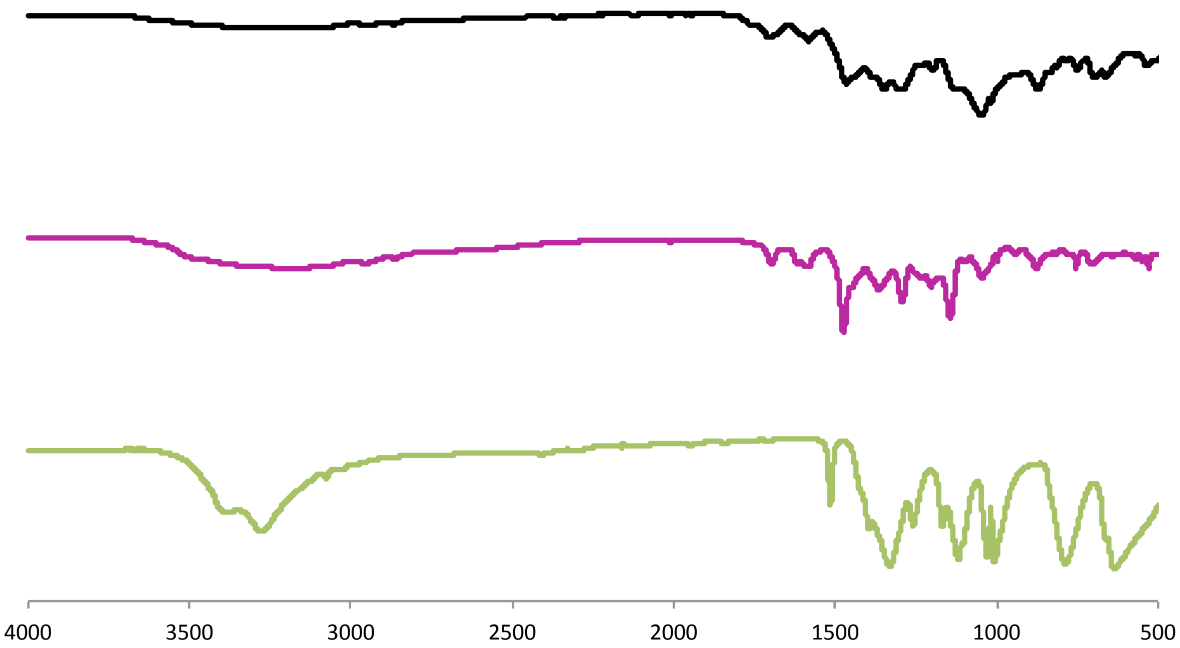


Figure S7. Stacked FT-IR spectra of SubPc-POP 1 (black, top), hexahydroxy OPh-SubPc (**2b**) (pink, middle), and BDBA (green, bottom).

Resonance	Assignment
1465 cm^{-1}	C=N
1347 cm^{-1}	B-O (boronate ester)
1046 cm^{-1}	B-O (axial ligand)

Table S2. Resonances and assignments for SubPc-POP 1

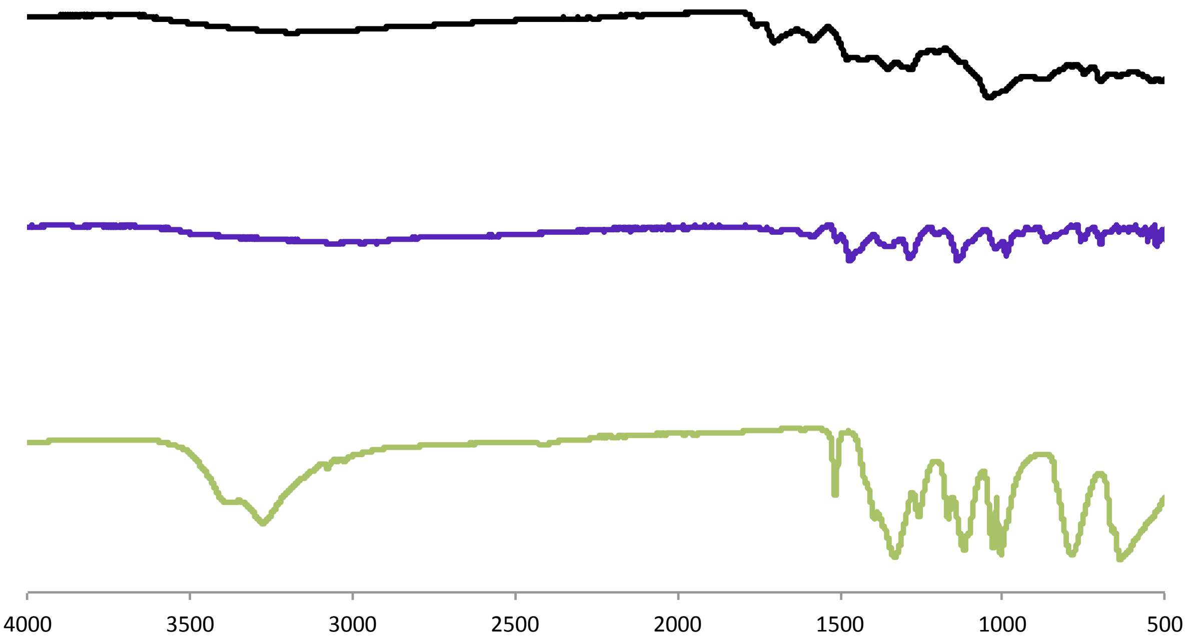


Figure S8. Stacked FT-IR spectra of SubPc-POP 2 (black, top), hexahydroxy F_5OPh-SubPc (**3b)** (purple, middle), and BDBA (green, bottom).

Resonance	Assignment
1468 cm^{-1}	C=N
1352 cm^{-1}	B-O (boronate ester)
1039 cm^{-1}	B-O (axial ligand)

Table S3. Resonances and assignments for SubPc-POP 2

E. PXRD Profiles

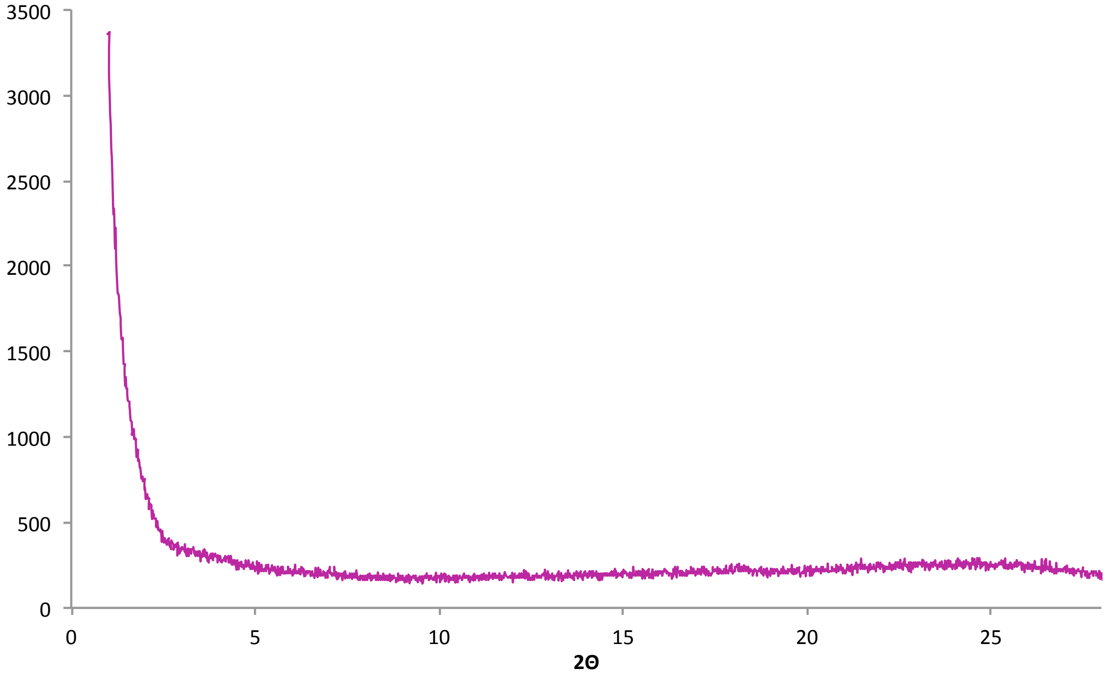


Figure S9. PXRD profile of SubPc-POP 1

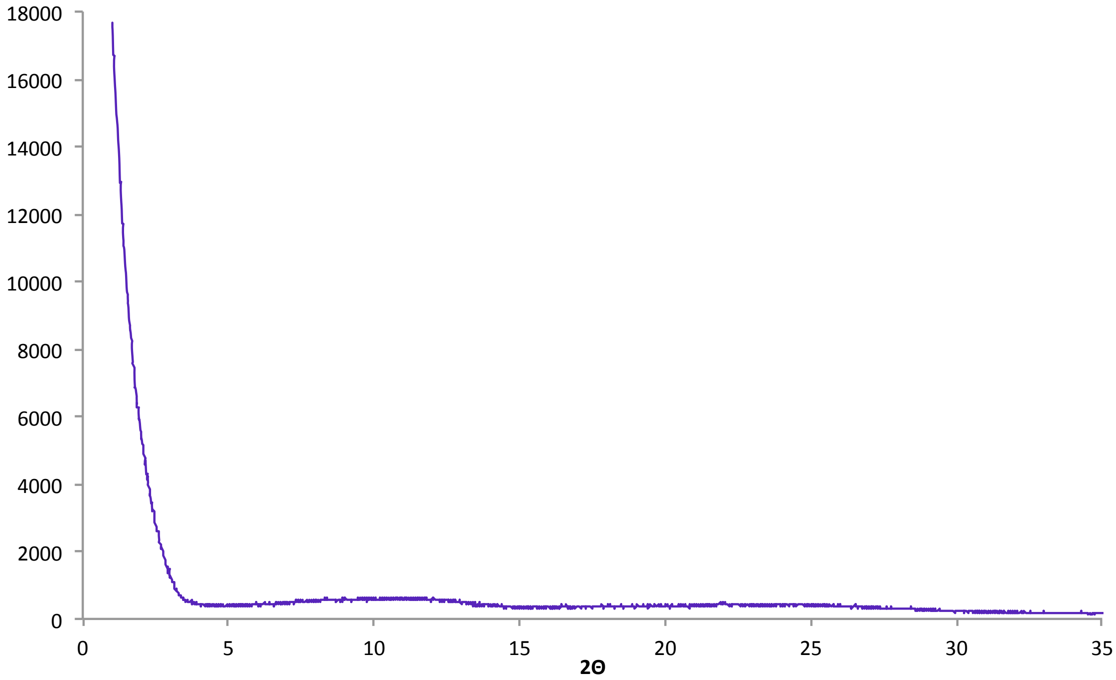


Figure S10. PXRD profile of SubPc-POP 2

F. Solid State NMR Spectra

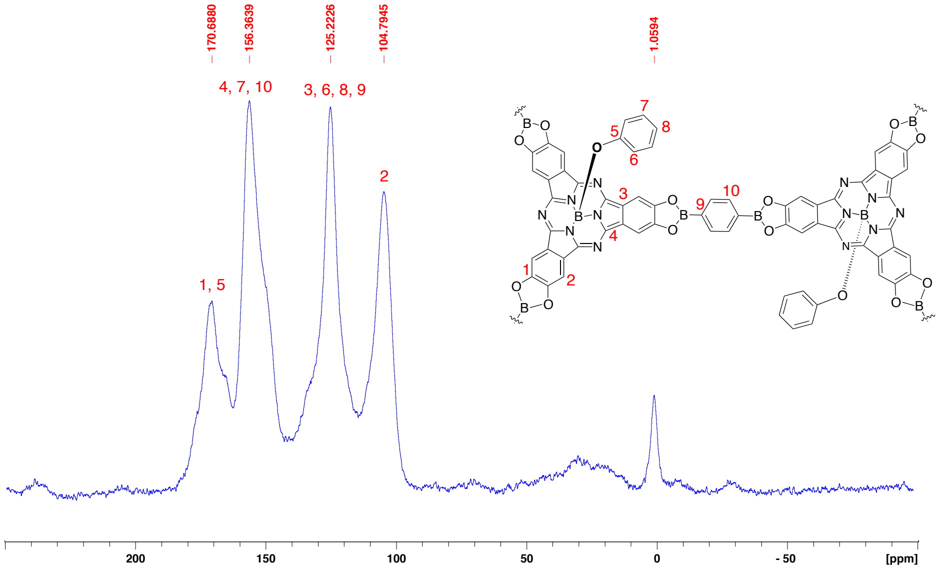


Figure S11. ^{13}C CP-MAS of SubPc-POP 1

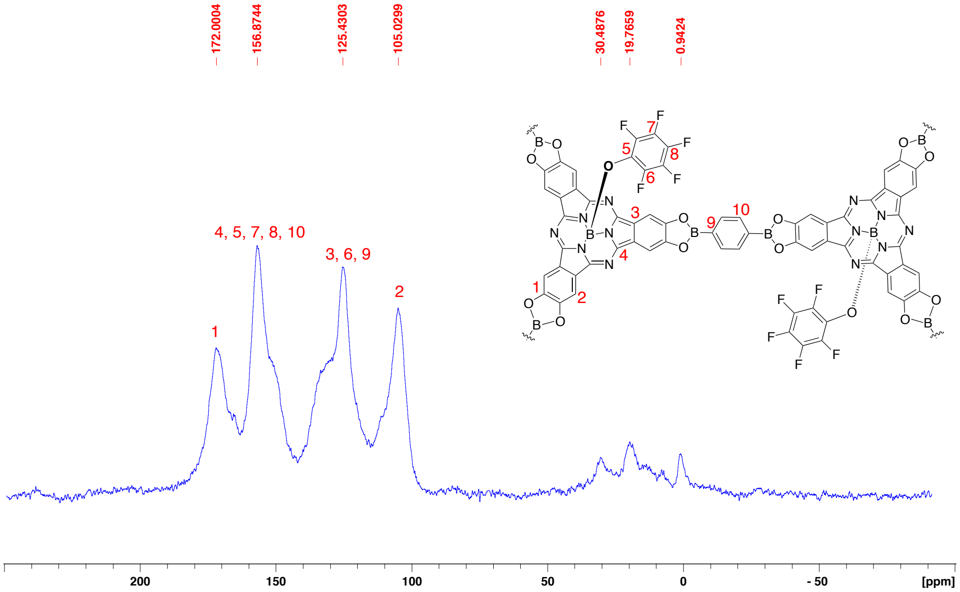


Figure S12. ^{13}C CP-MAS of SubPc-POP 2

G. TGA Profile

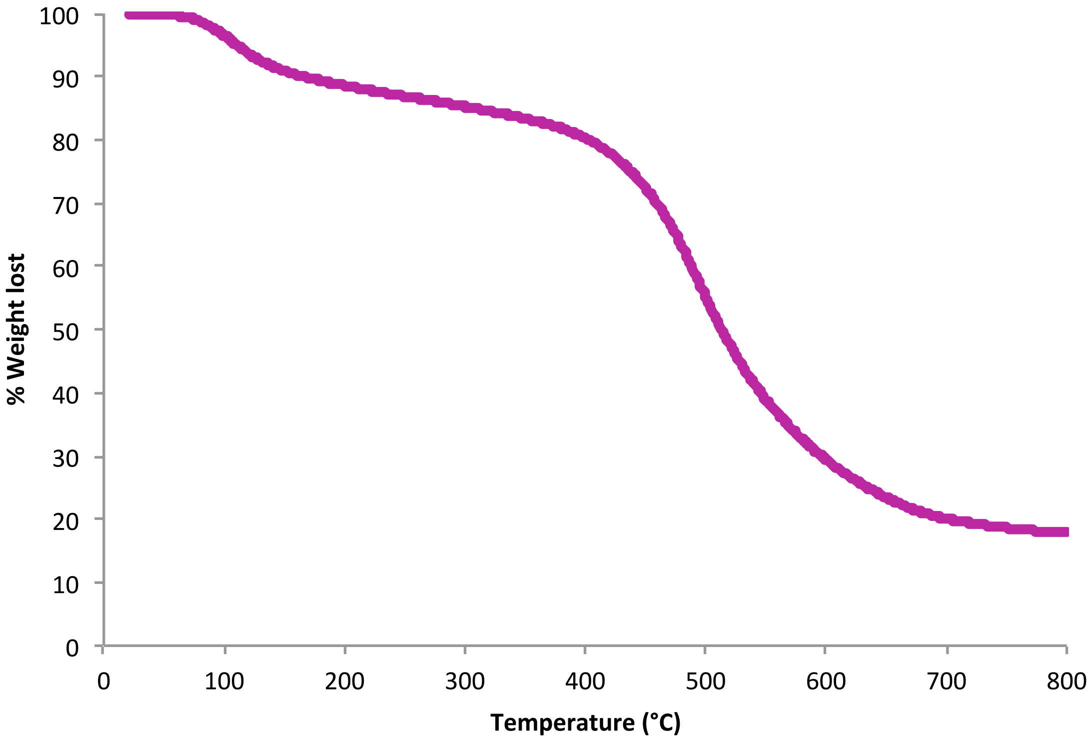


Figure S13. TGA profile of SubPc-POP 1

H. Surface Area Analysis

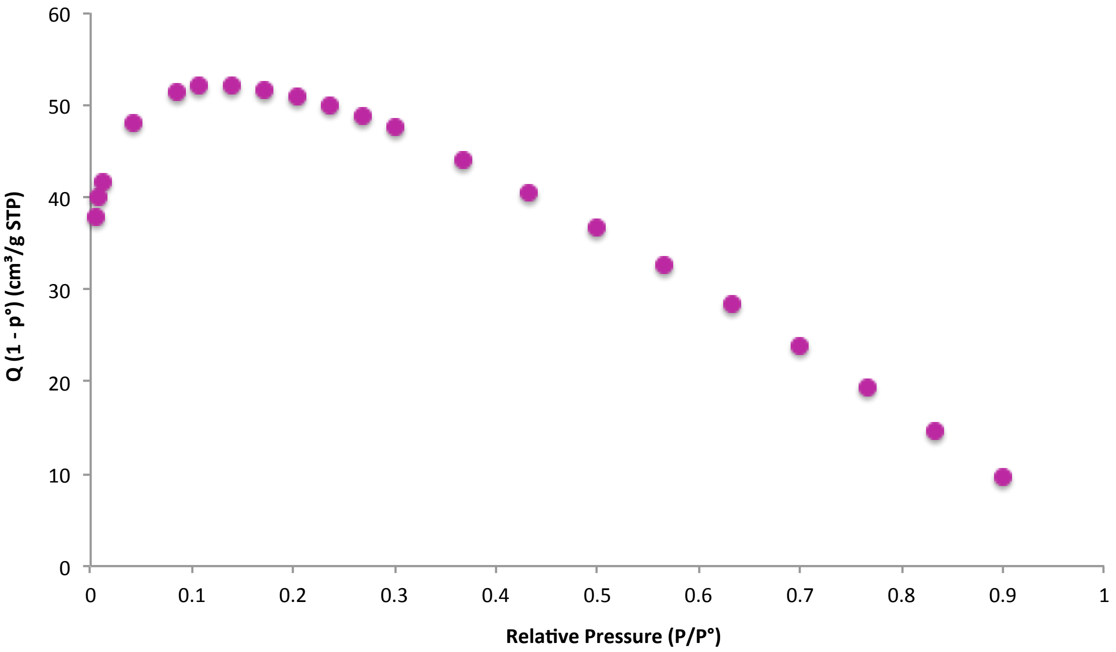


Figure S14. Roquerol BET analysis for SubPc-POP 1

Table 4. BET values derived from Roquerol BET analysis for SubPc-POP 1.

SubPc-POP 1			
(P/P°)	BET (m2/g)	Correlation Coefficient	C
0.005939-0.139089	231	0.9999	321.478
0.005939-0.106749	231	0.9998	320.559
0.005939-0.084445	229	0.9997	339.447

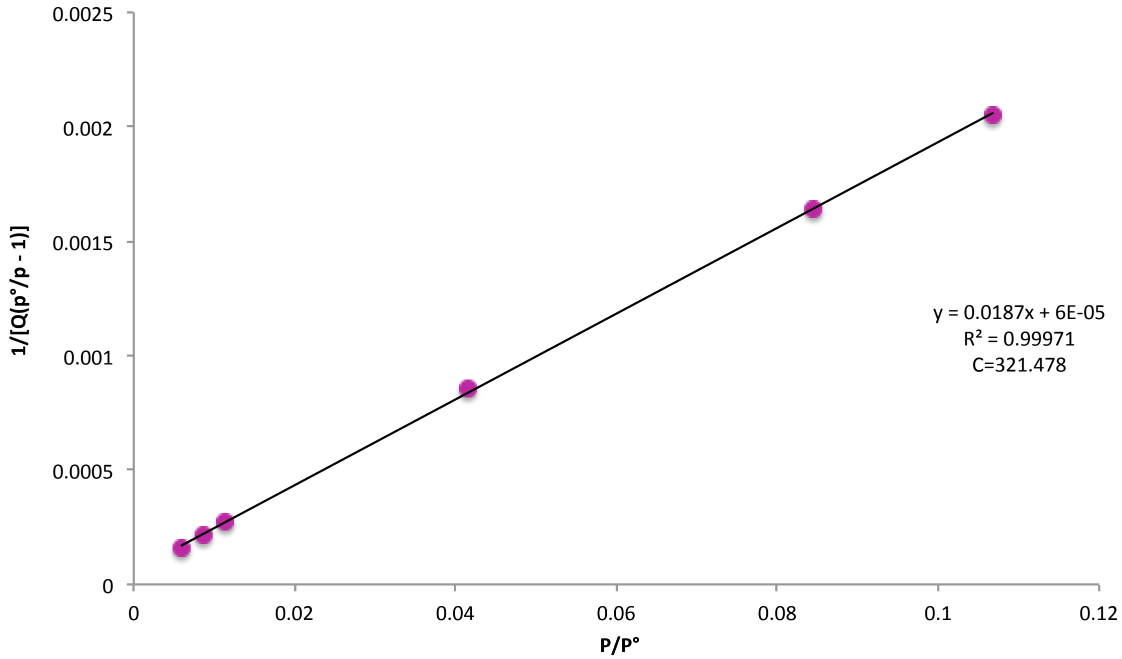


Figure S15. BET surface area plot for SubPc-POP 1

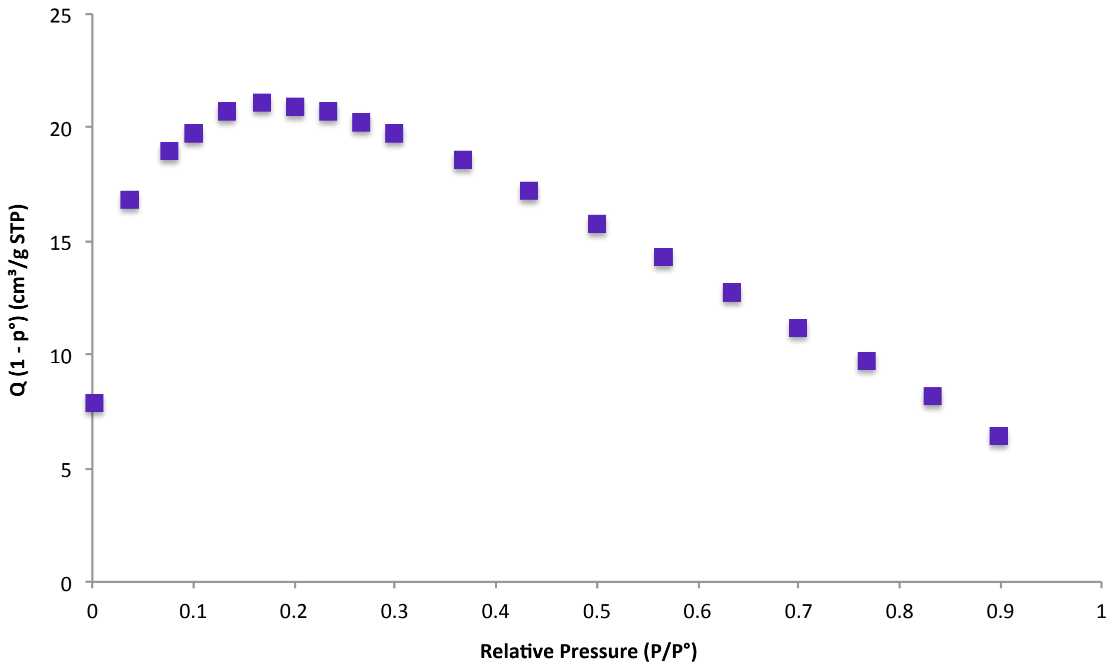


Figure S16. Roquerol BET analysis of SubPc-POP 2

Table 5. BET values derived from Roquerol BET analysis for SubPc-POP 2.

SubPc-POP 2			
(P/P°)	BET (m2/g)	Correlation coefficient	C
0.001086-0.200654	93	0.9988	136.591
0.001086-0.167247	93	0.9981	139.102
0.001086-0.133936	91	0.9977	170.091

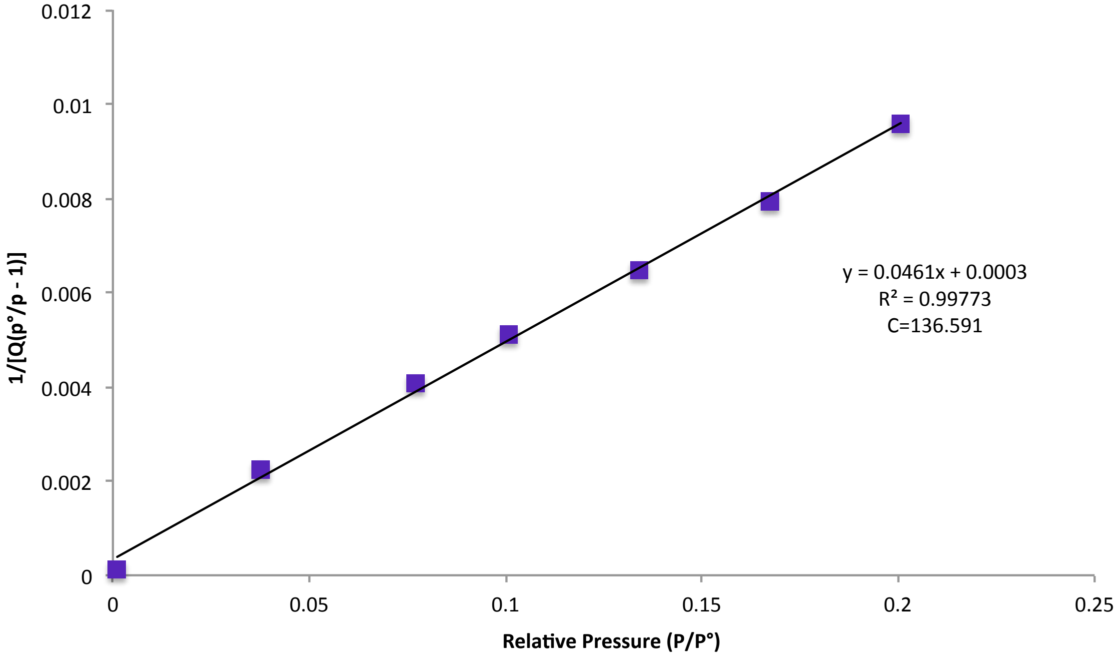


Figure S17. BET surface area plot for SubPc-POP 2

I. UV-Vis and Fluorescence

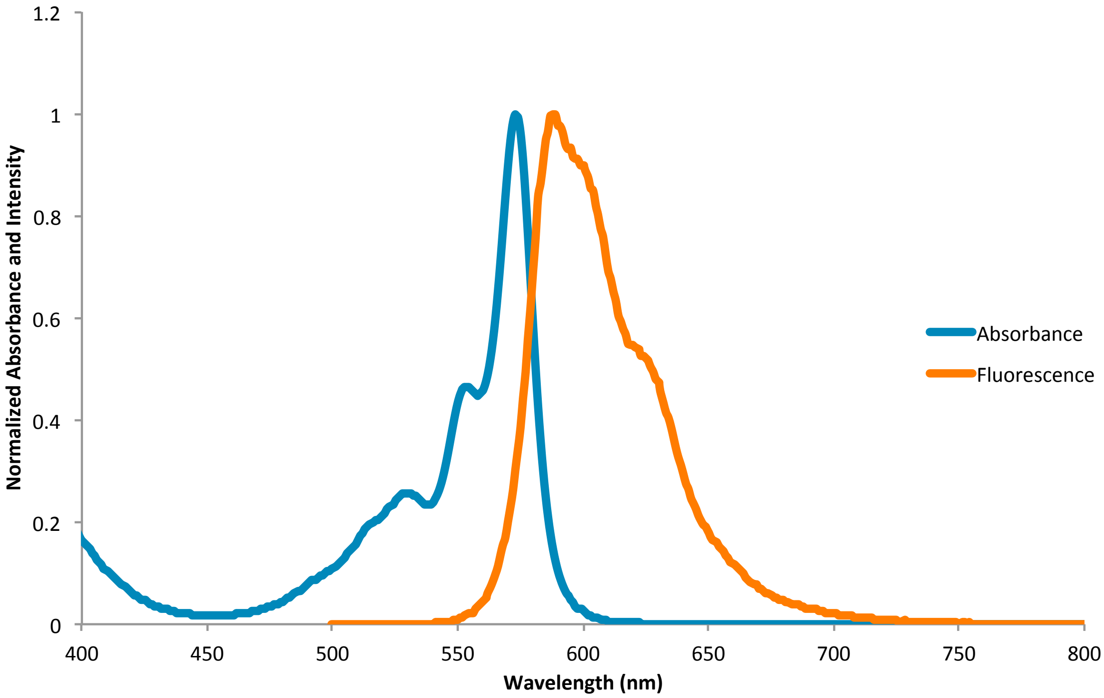


Figure S18. UV-Vis and fluorescence spectra of **1a** in toluene ($\lambda_{excitation}$=574 nm).

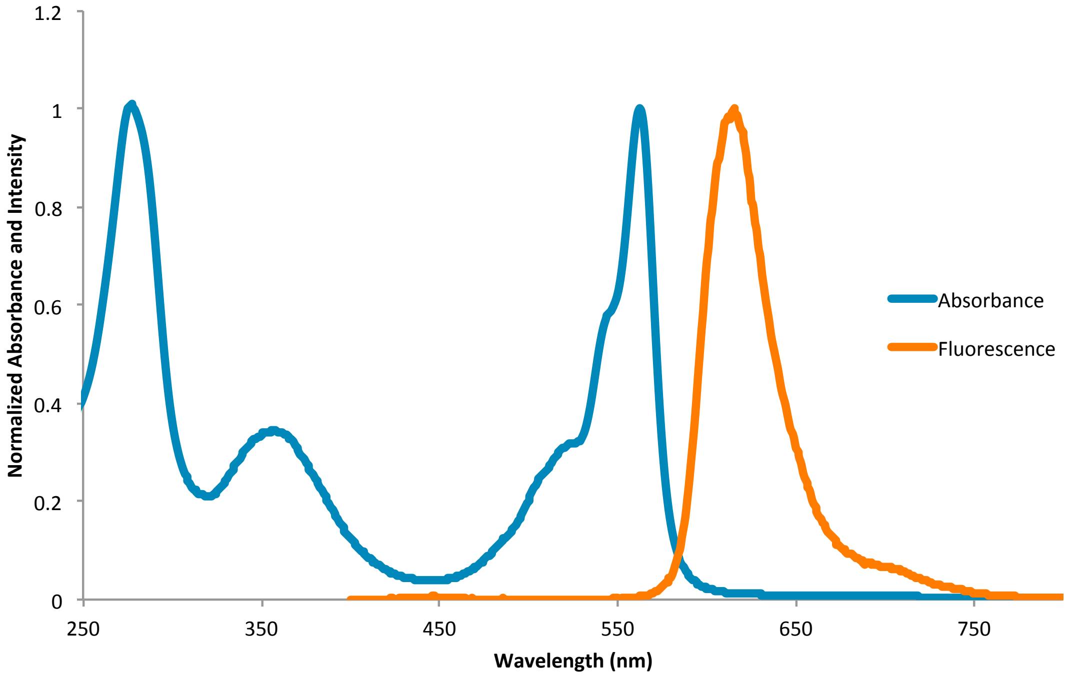


Figure S19. UV-Vis and fluorescence spectra of **1b** in acetone ($\lambda_{excitation}$= 564 nm)

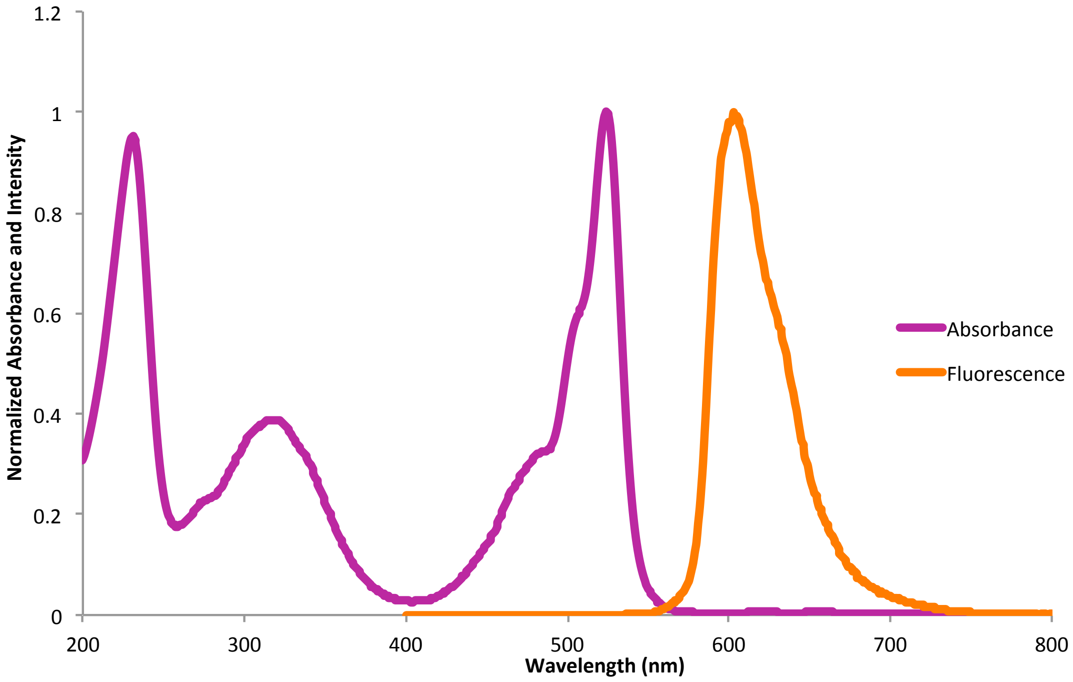


Figure S20. UV-Vis and fluorescence spectra of **2a** in toluene ($\lambda_{excitation}$=522 nm).

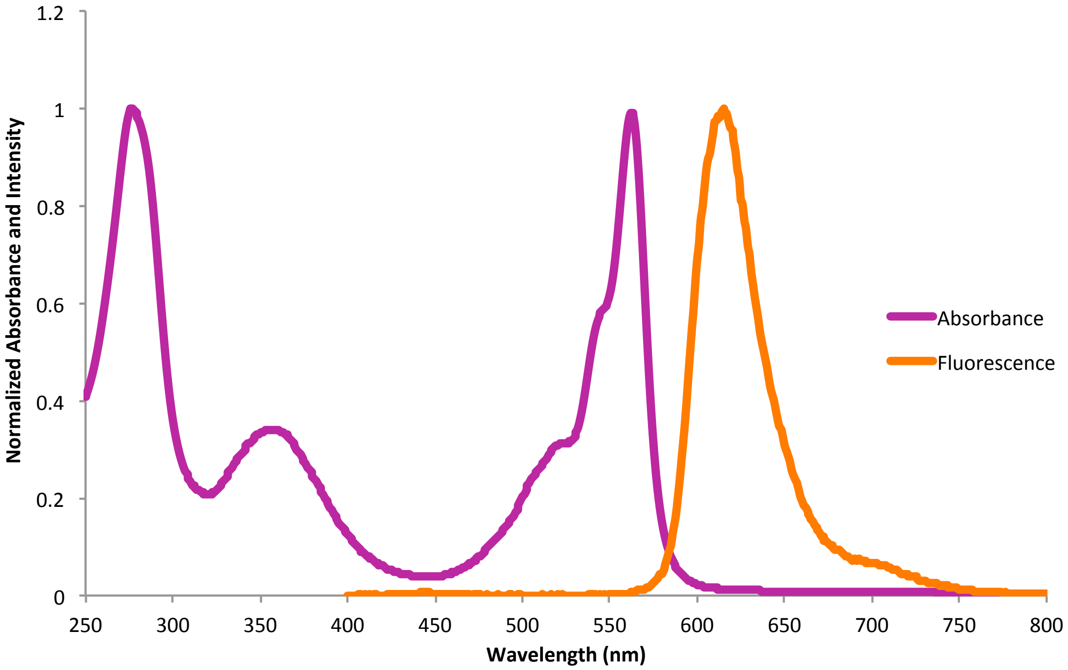


Figure S21. UV-Vis and fluorescence spectra of **2b** in acetone ($\lambda_{excitation}$= 561 nm)

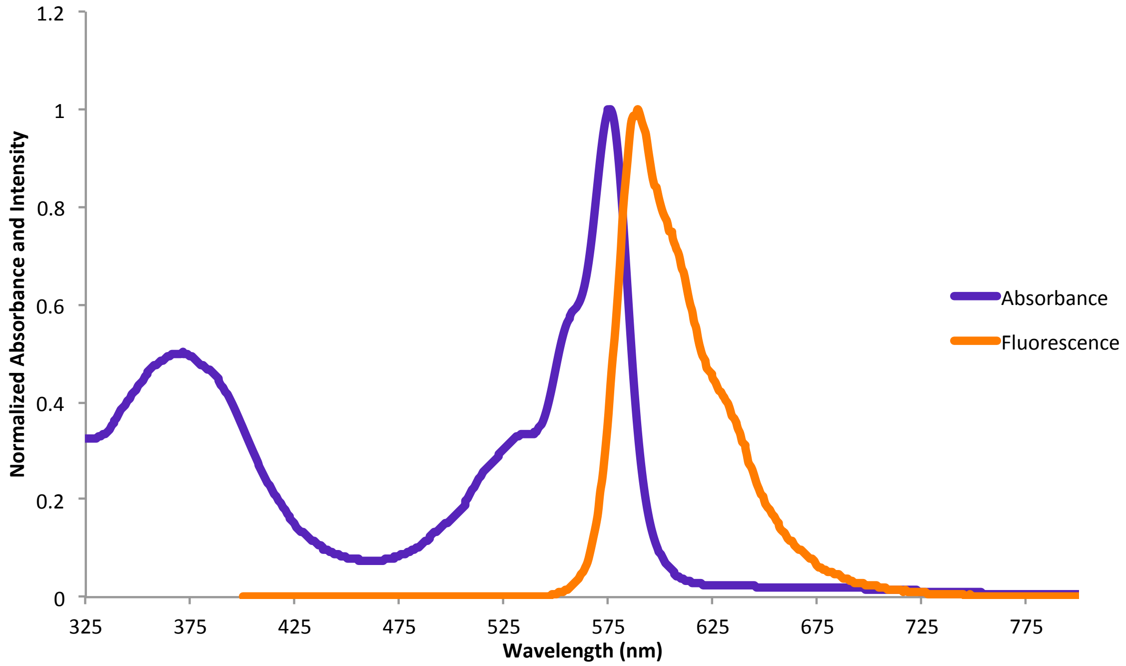


Figure S22. UV-Vis and fluorescence spectra of **3a** in toluene ($\lambda_{excitation}$=578 nm).

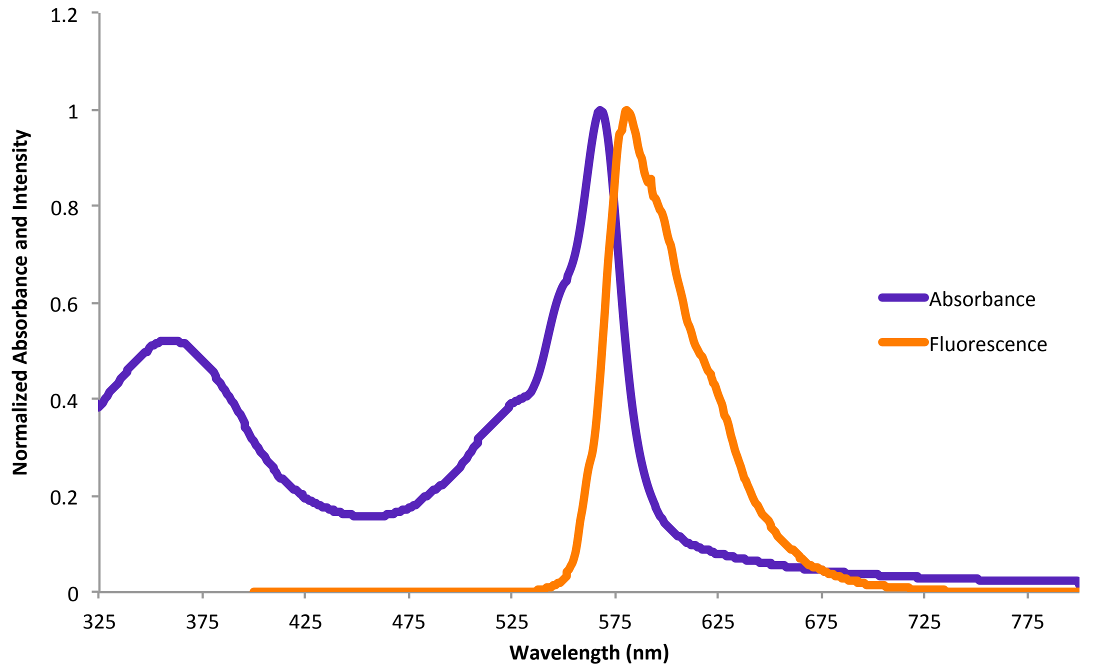


Figure S23. UV-Vis and fluorescence spectra of **3b** in acetone ($\lambda_{excitation}$= 570 nm)

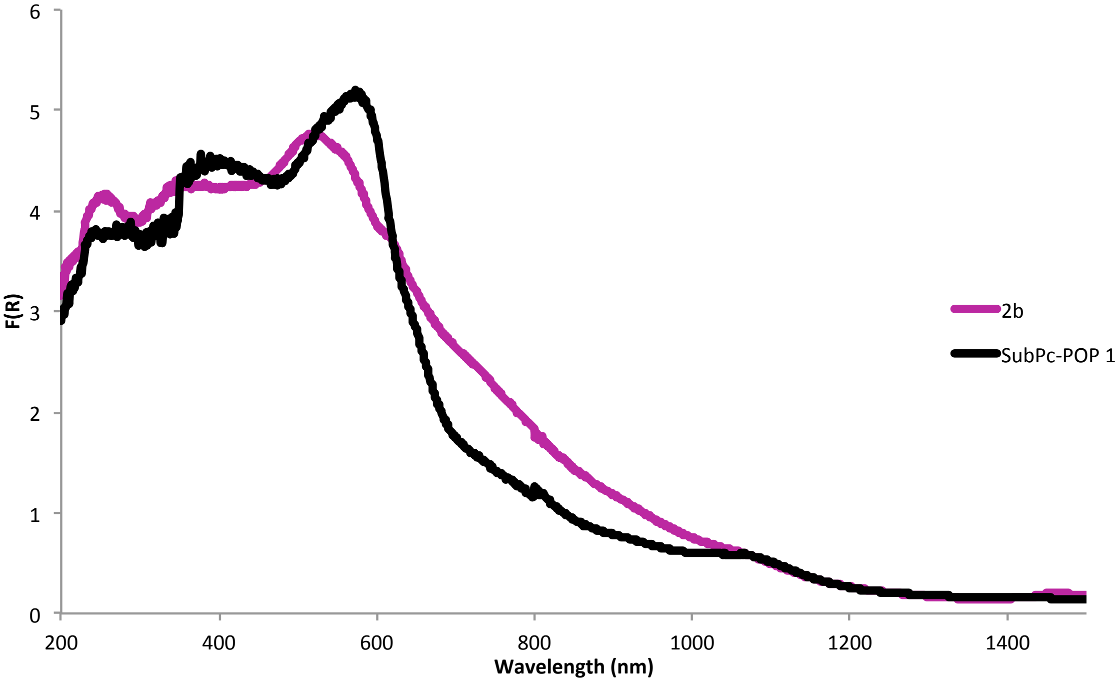


Figure S24. Kubelka-Munk function diffuse reflectance spectrum of **2b**, and SubPc-POP 1

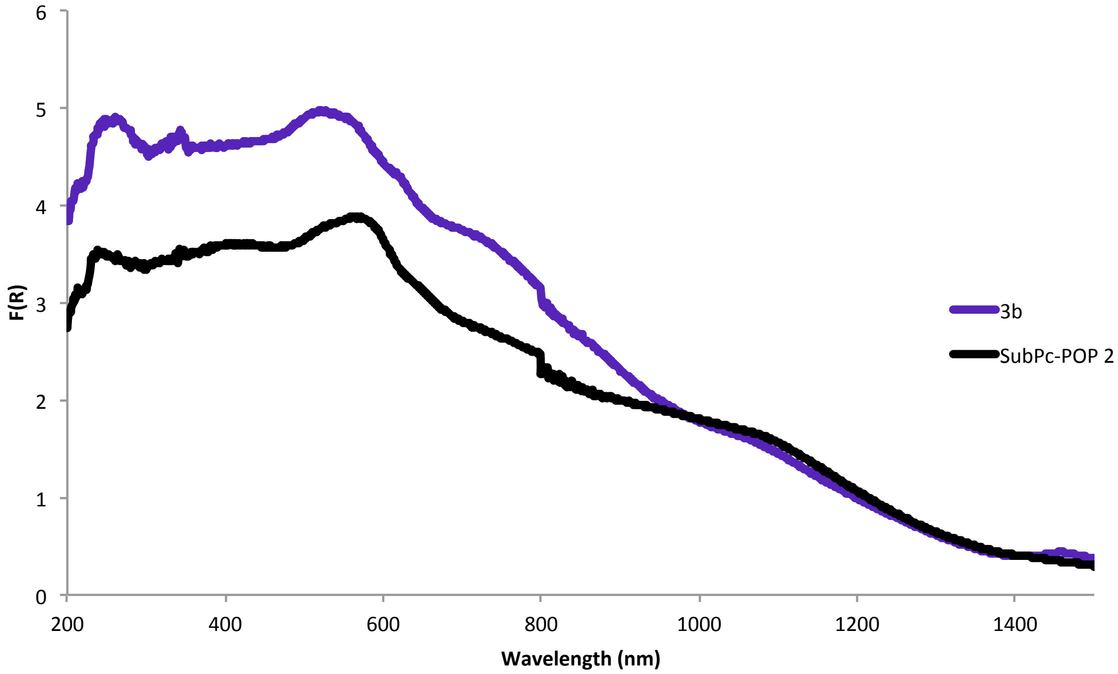


Figure S25. Kubelka-Munk function diffuse reflectance spectrum of **3b**, and SubPc-POP 2

J. SubPc-POP hydrolysis ^{1}H NMR

A small sample (~5 mg) of POP powder was hydrolyzed by addition of D_2O and the monomers were redissolved in deuterated acetone. Samples were sonicated briefly to help solubilize monomers. This technique is used to confirm the presence of both monomers in the polymer.

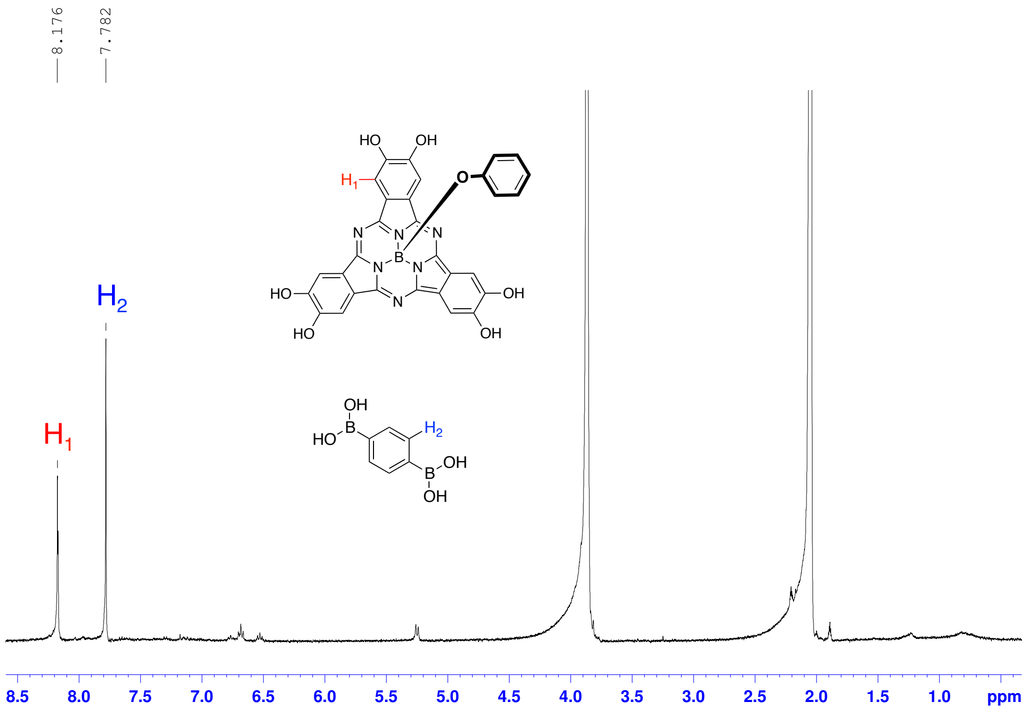


Figure S26. ^{1}H NMR spectrum of SubPc-POP 1 after hydrolysis

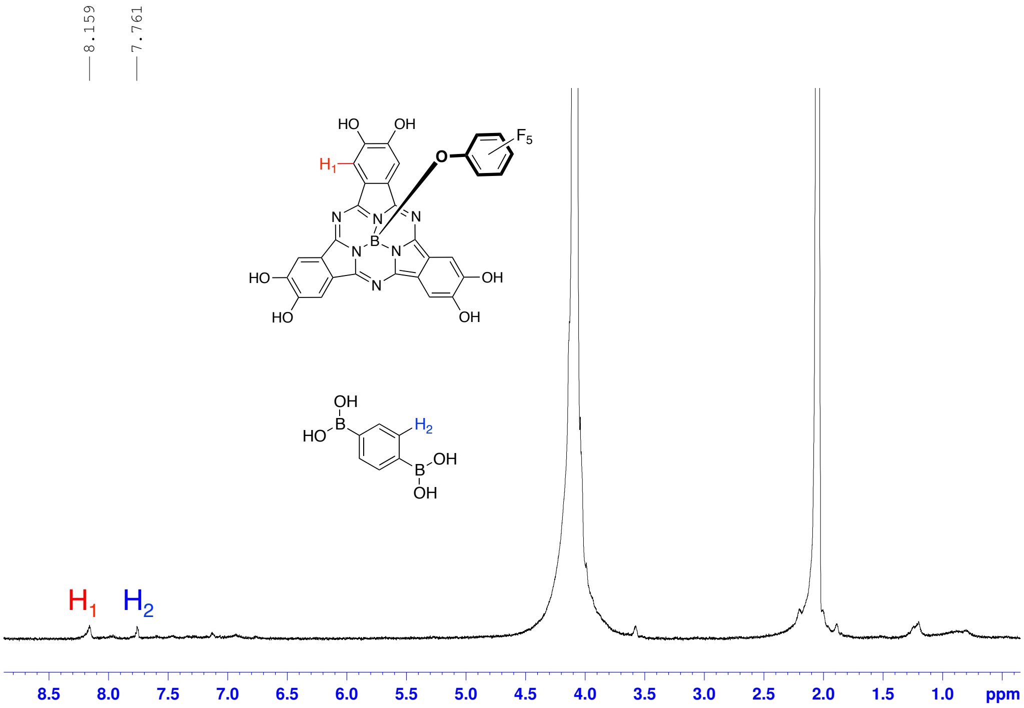


Figure S27. ^{1}H NMR spectrum of SubPc-POP 2 after hydrolysis

K. ^{1}H and ^{13}C NMR Spectra

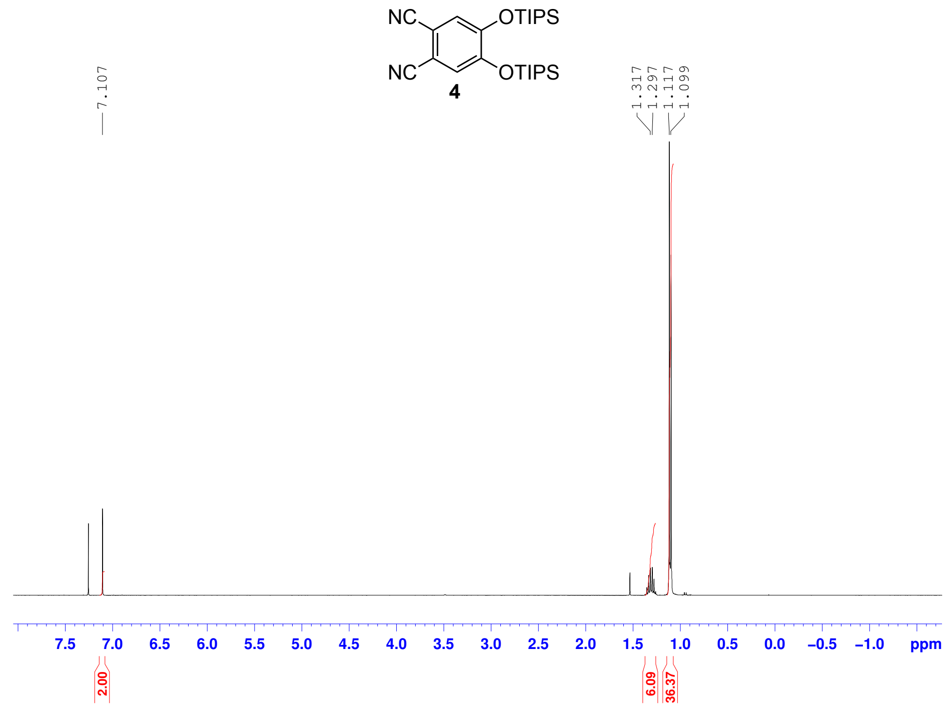


Figure S28. ^{1}H NMR spectrum of **4**

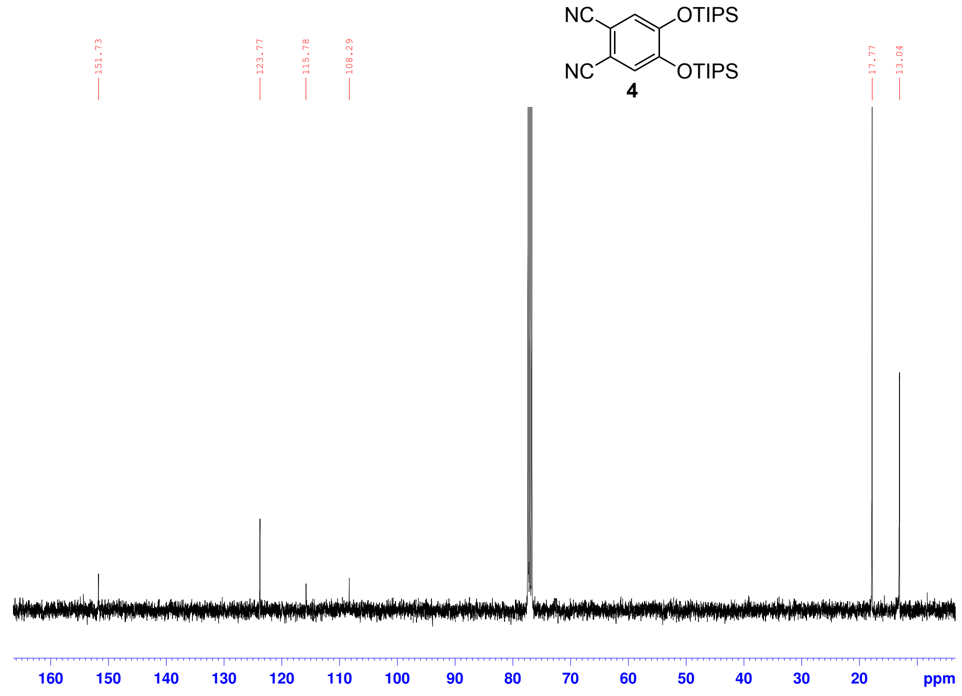


Figure S29. ^{13}C NMR spectrum of **4**

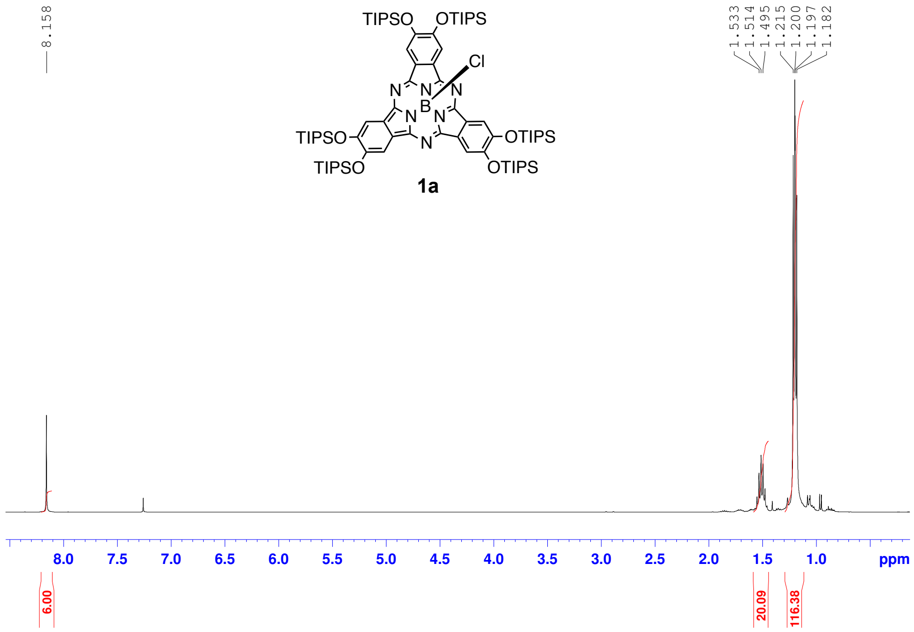


Figure S30. ^{1}H NMR spectrum of **1a**

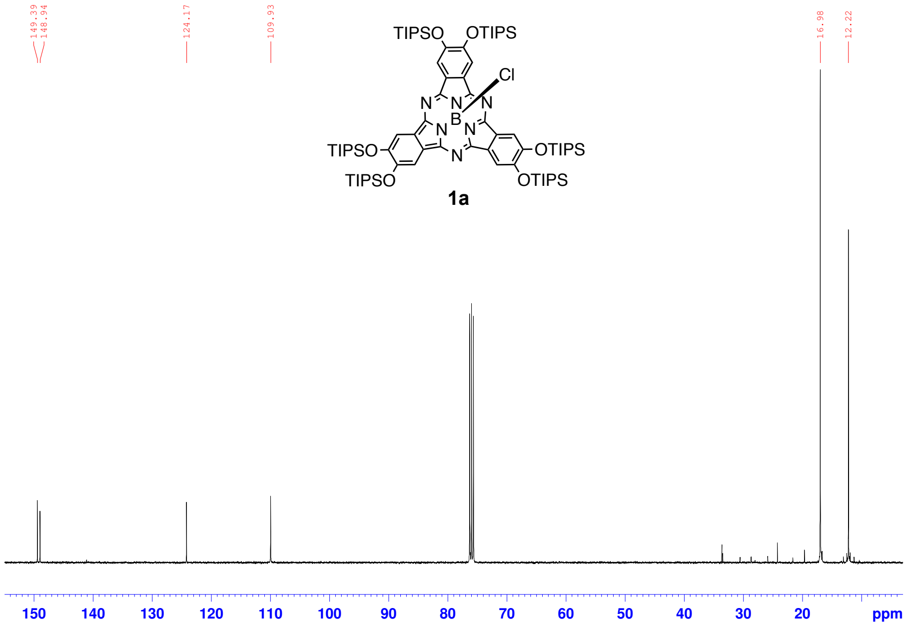


Figure S31. ^{13}C NMR spectrum of **1a**

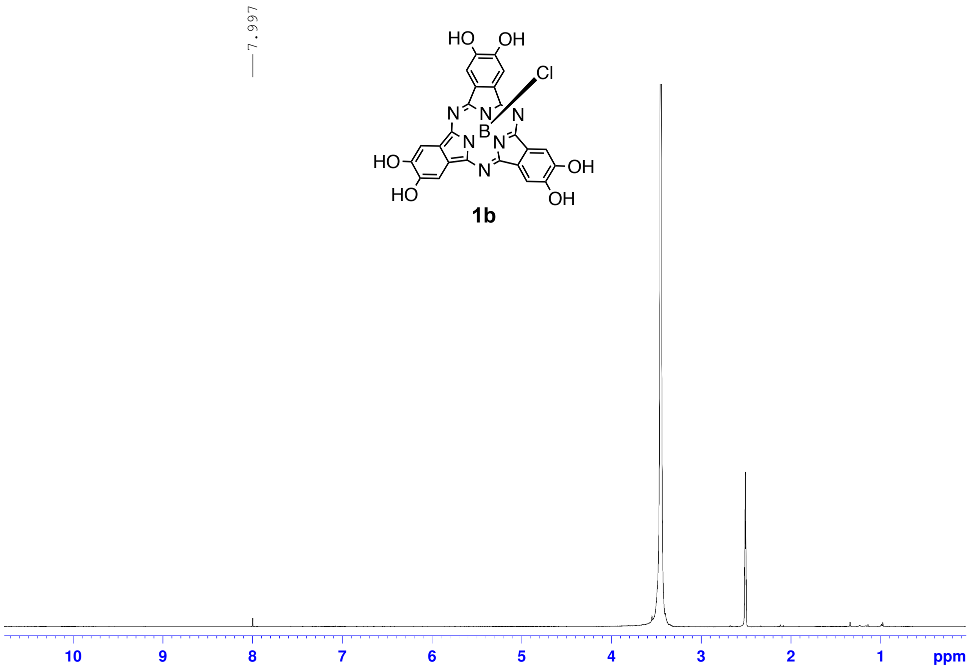


Figure S32. ^{1}H NMR spectrum of **1b**

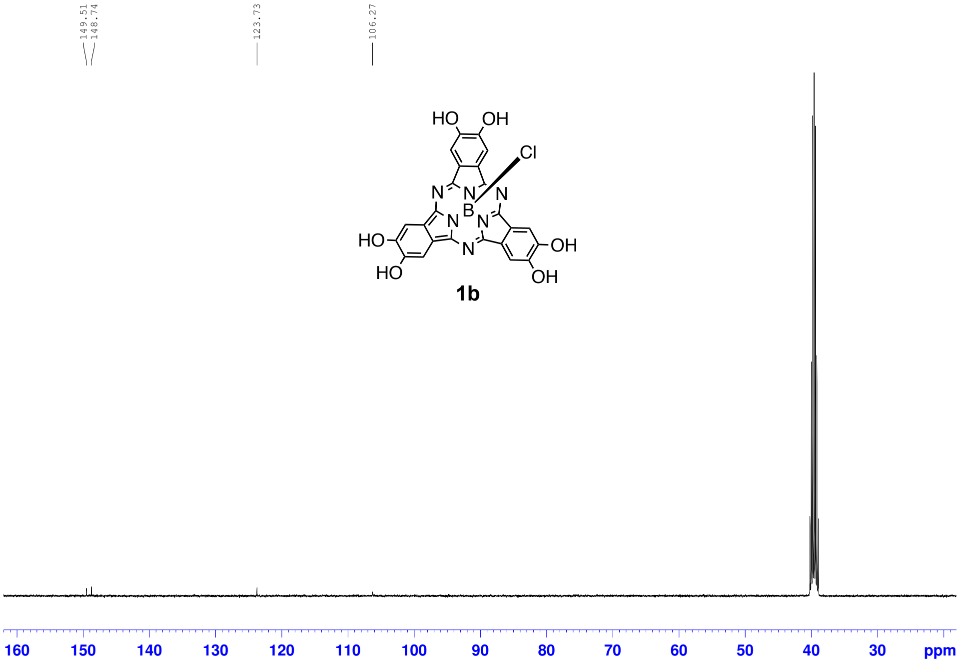


Figure S33. ^{13}C NMR spectrum of **1b**

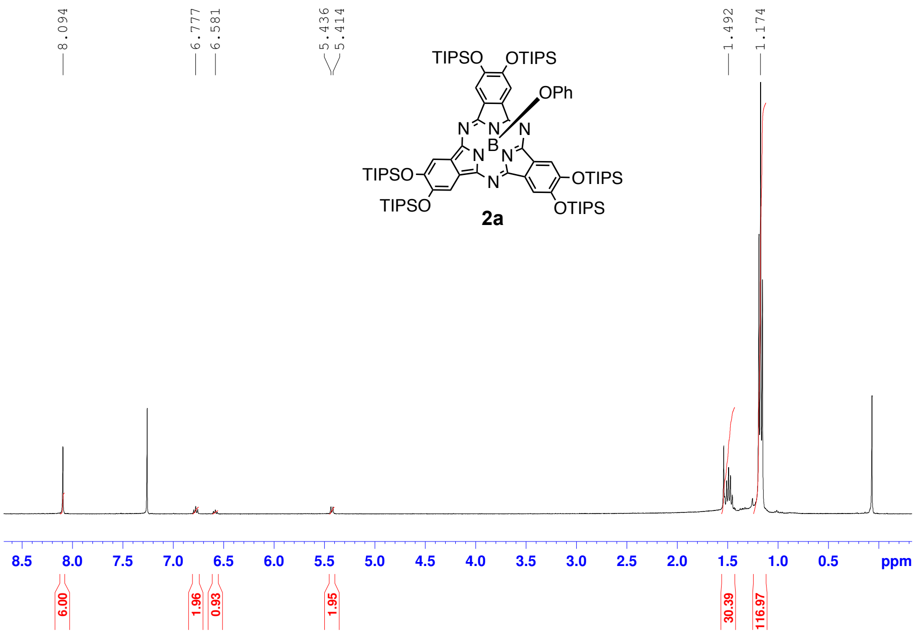


Figure S34. ^{1}H NMR spectrum of **2a**

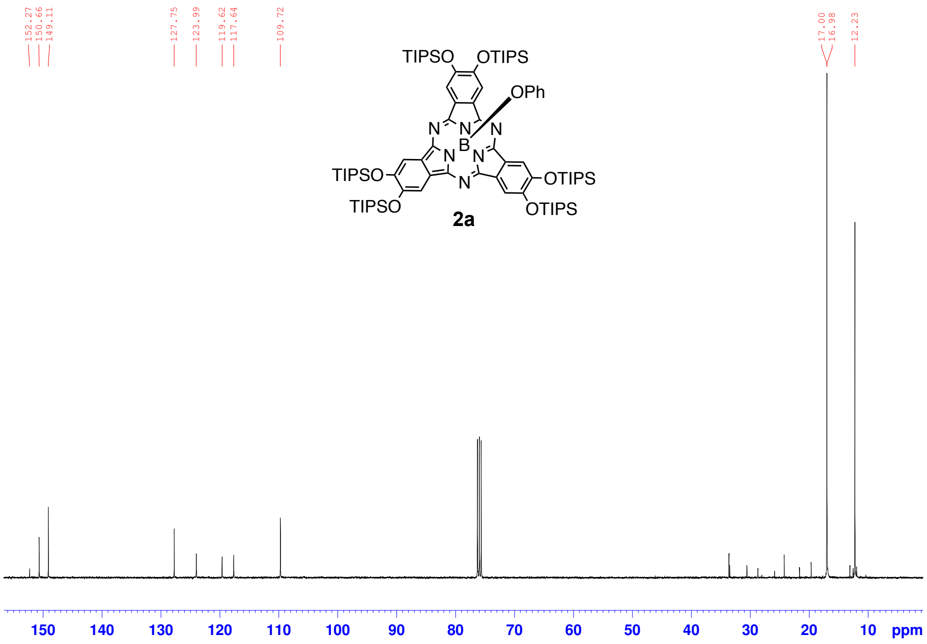


Figure S35. ^{13}C NMR spectrum of **2a**

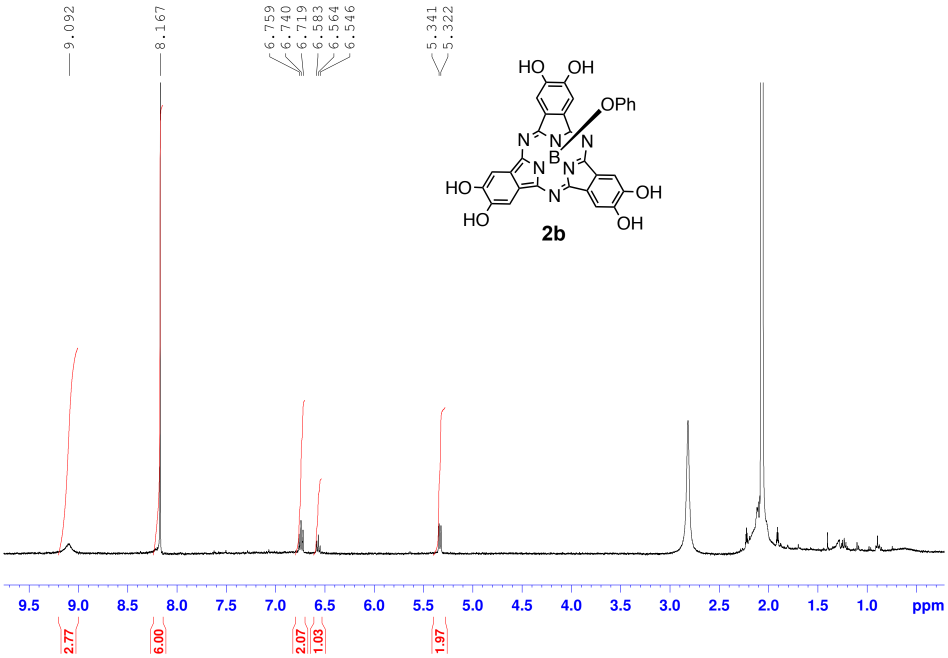


Figure S36. ^{1}H NMR spectrum of **2b**

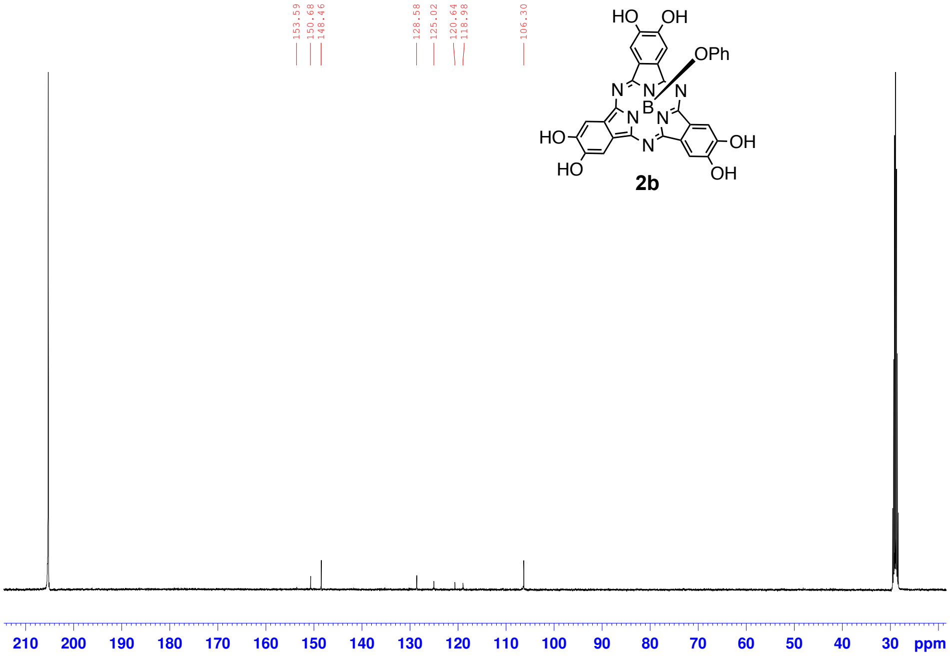


Figure S37. ^{13}C NMR spectrum of **2b**

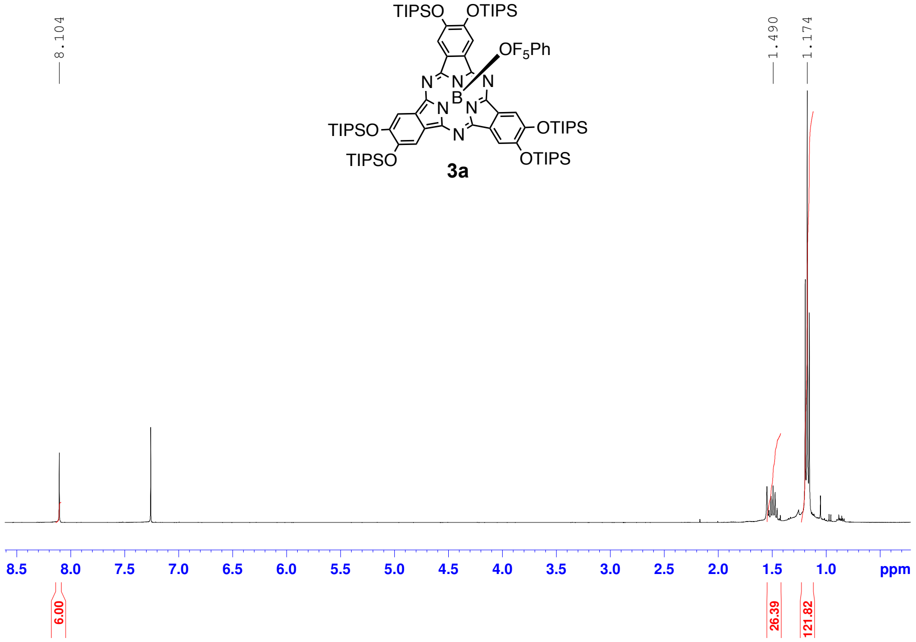


Figure S38. ^{1}H NMR spectrum of **3a**

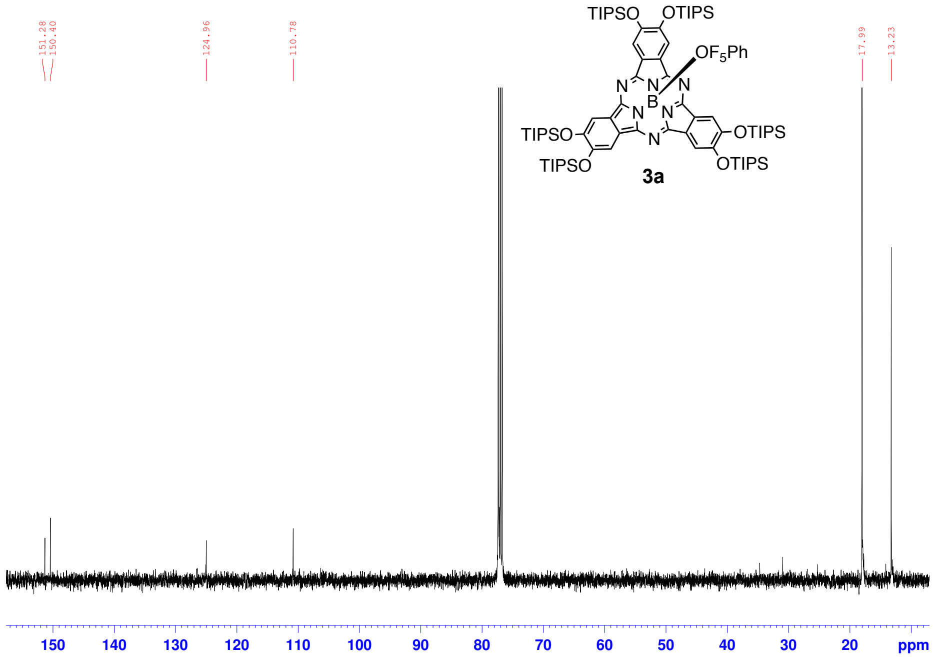


Figure S39. ^{13}C NMR spectrum of **3a**

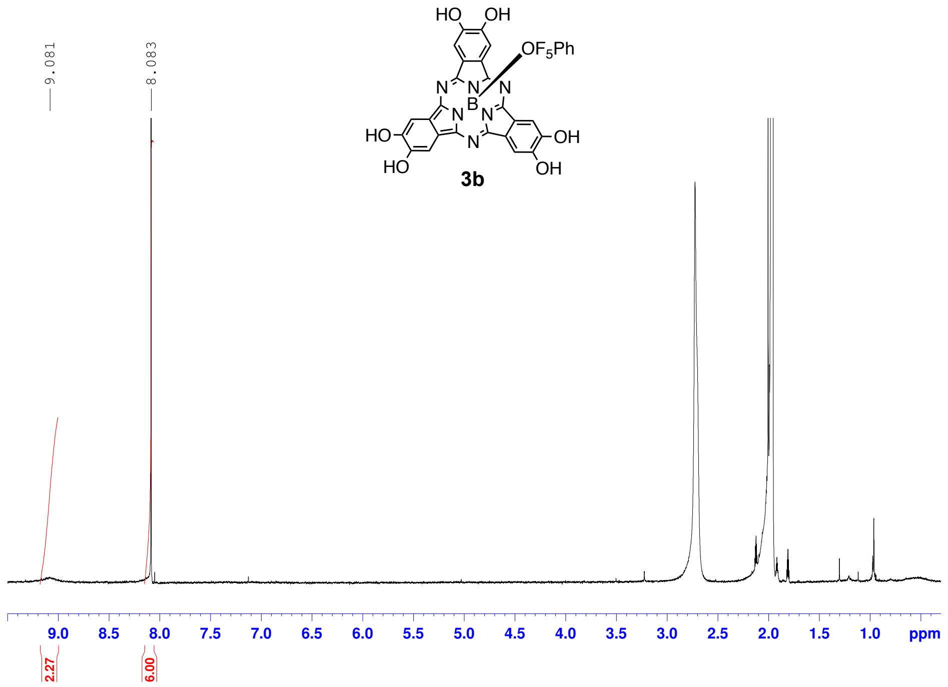


Figure S40. ^{1}H NMR spectrum of **3b**

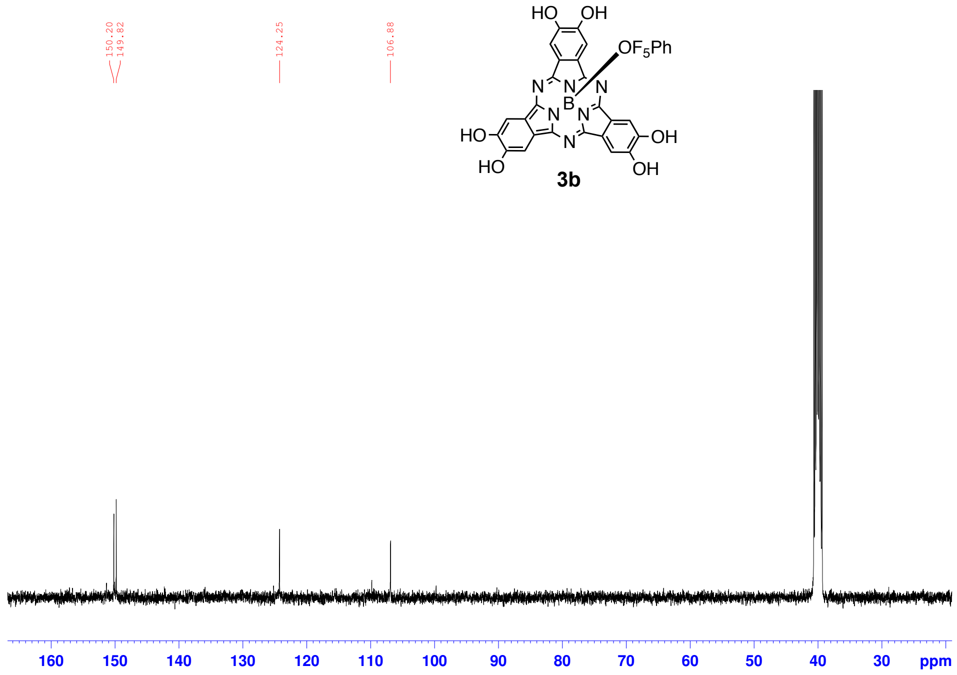


Figure S41. ^{13}C NMR spectrum of **3b**

Reference

(1) Quesada, E.; Esperanza, S.; Cabezo, B.; Torres, T. *Eur. J. Org. Chem.* **2000**, 2767–2775.