

## Supplementary Information

### **Synthesis of a Phthalocyanine and Porphyrin 2D Covalent Organic Framework**

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### Section A. Materials and methods:

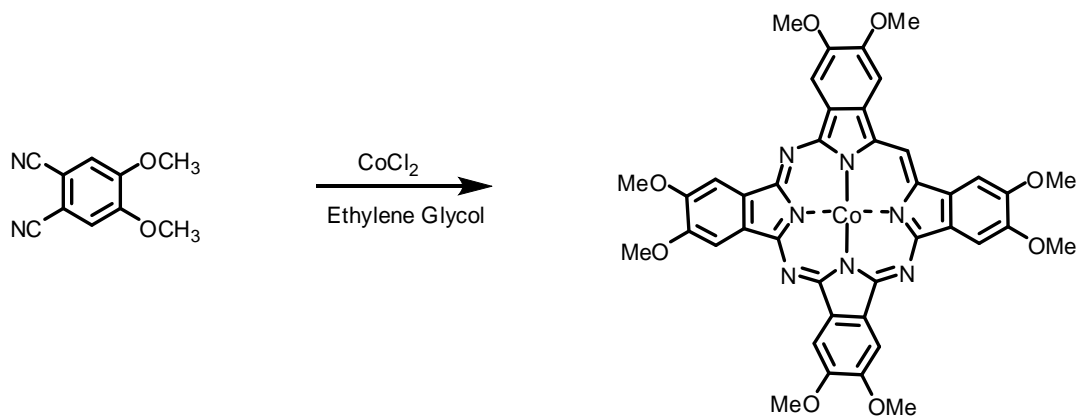
Co octahydroxy phthalocyanine<sup>1,2</sup> and 5, 15-bis[(dihydroxyboryl)phenyl]-21*H*,23*H*-porphine<sup>3,4</sup> was prepared according to literature procedures. All chemicals and solvents were purchased from Sigma-Aldrich except dibromoveratrole (Alfa Aesar). Fourier transform Infrared (FT-IR) spectra were recorded on a Perkin-Elmer Spectrum one infrared spectrometer (ATR). <sup>1</sup>H NMR spectra were recorded on JEOL 600MHz spectrometer, where chemical shifts ( $\delta$  in ppm) were determined with a residual proton of the solvent as standard. Matrix-assisted laser desorption ionization time-of-flight mass (MALDI-TOF MS) spectra were recorded on Bruker benchtop microflex model using matrix trihydroxyanthracene. Field-emission scanning electron microscopy (FE-SEM) was performed on a Hitachi S-4800 fitted with an EDAX energy-dispersive spectrometry system by adhering sample on a sampling platform. Powder X-ray diffraction (PXRD) data were recorded on a Bruker DiscoverD8 model diffractometer by depositing powder on plastic substrate, from  $2\theta = 1^\circ$  up to  $30^\circ$  with  $0.05^\circ$  increment. In order to determine pore textural properties including the specific Brunauer–Emmet–Teller (BET) surface area, pore volume and pore size distribution, nitrogen adsorption and desorption isotherm on CoPc-PorDBA COF sample at 77 K were measured in an ASAP-2020 adsorption apparatus (Micromeritics). The as-synthesized samples were degassed in situ at  $150^\circ\text{C}$  with a heating rate of  $3^\circ\text{C}/\text{min}$  under a vacuum (0.0001 mmHg) for 12 h before nitrogen adsorption measurements in order to ensure the micro-channels in the structure were guest-free. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas by using the non-local density functional theory (NLDFT) model, the pore volume was derived from the sorption curve. Thermogravimetric analysis from  $30$ - $700^\circ\text{C}$  was carried out on a Mettler-Toledo thermogravimetric analyzer in an  $\text{N}_2$  atmosphere using a  $3^\circ\text{C}/\text{min}$  ramp time.

## Section B. Synthetic procedures

### Synthesis of 2,3,9,10,16,17,23,24-Octamethoxyphthalocyaninato)cobalt(II) (MeO)<sub>8</sub>PcCo

(Octamethoxyphthalocyaninato) cobalt (II) was prepared using a literature procedure.<sup>1,2</sup>

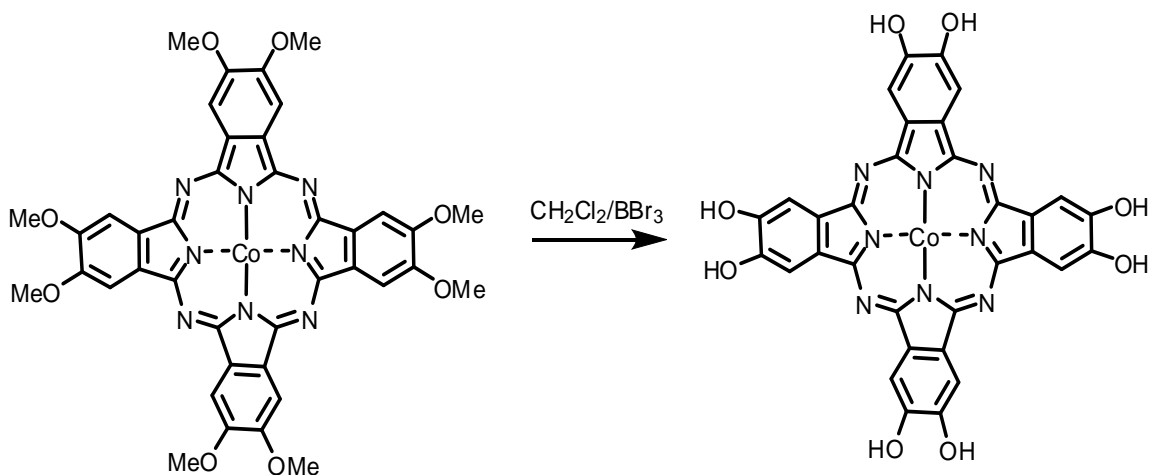
(MeO)<sub>8</sub>PcCo obtained as a green solid in 40% yield. MALDI-TOF MS for C<sub>40</sub>H<sub>32</sub>N<sub>8</sub>O<sub>8</sub>Co (Calculated 811.17), found  $m/z$  = 811.87 [M]<sup>+</sup>.



### Synthesis of 2,3,9,10,16,17,23,24-Octahydroxyphthalocyaninato)cobalt(II) (OH)<sub>8</sub>PcCo

(Octahydroxyphthalocyaninato) cobalt (II) was prepared using a literature procedure.<sup>1,2</sup>

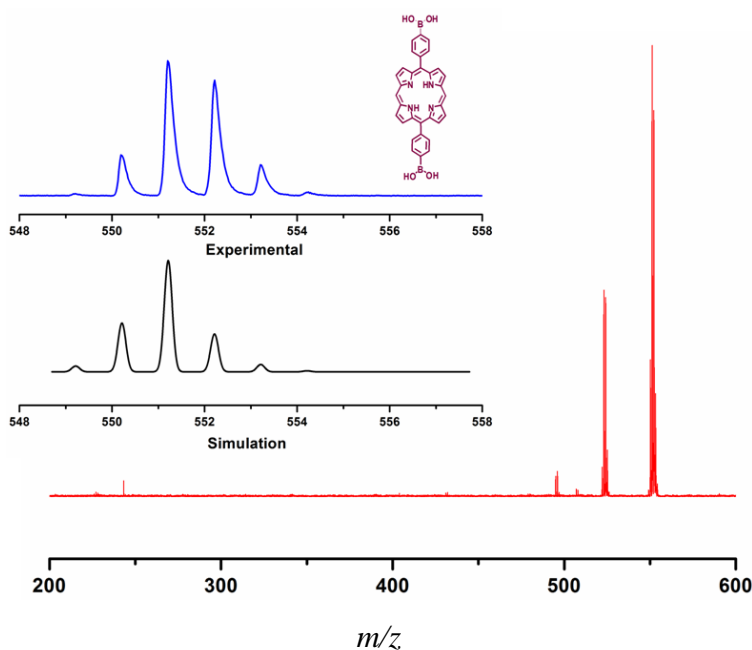
(OH)<sub>8</sub>Pc Co obtained as a dark green solid in 67% yield. MALDI-TOF MS for C<sub>32</sub>H<sub>16</sub>N<sub>8</sub>O<sub>8</sub>Co (Calculated 699.04), found  $m/z$  = 698.99 [M]<sup>+</sup>.



### Synthesis of 5, 15-bis(4-[1,3,2]-dioxaborinan-2-yl-phenyl)porphyrin:

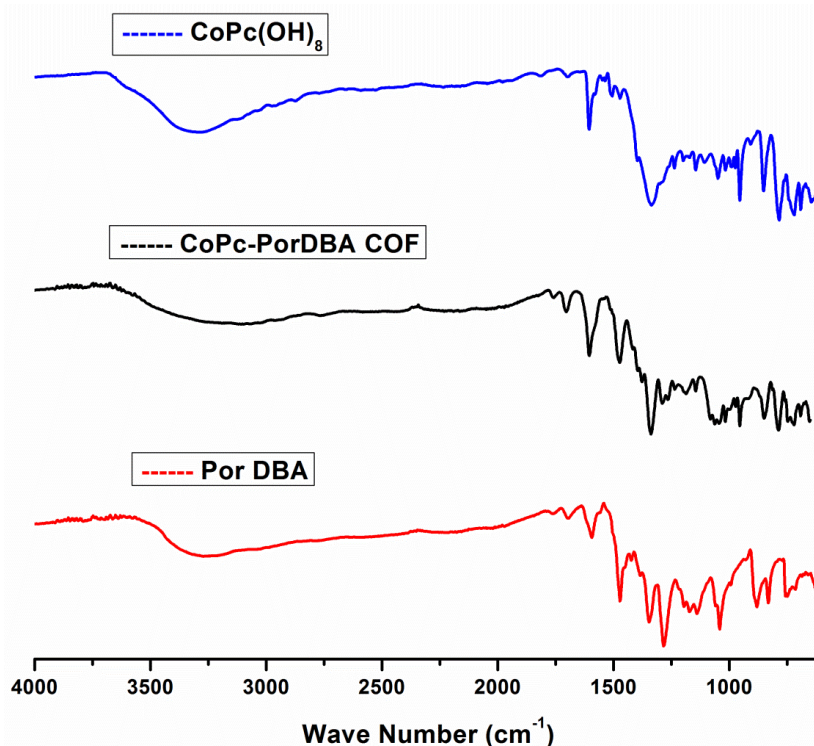
4-(1,3-dioxaborinan-2-yl)benzaldehyde (115 mg, 0.605 mmol), 2, 2'-dipyrrromethane (80 mg, 0.55 mmol) were dissolved in 100 mL of dry dichloromethane and then 50  $\mu$ l  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  was added to the mixture and then the mixture was stirred for 12hrs at room temperature. To this reaction mixture was added chloranil (560 mg, 0.605 mmol). After evaporation of the solvent, the crude mixture was chromatographed (silica gel,  $\text{CHCl}_3$ ) to produce 50 mg of 5,15-bis(4-[1,3,2]-dioxaborinan-2-yl-phenyl)porphyrin. Yield 30%.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ , 298K,  $\delta =$  ppm,  $J =$  Hz): 2.25 (m, 4H), 4.37 (m, 8H), 8.21 (d,  $J = 7.8$ , 4H), 8.28 (d,  $J = 7.8$ , 4H), 9.08 (d,  $J = 4.6$ , 4H), 9.40 (d,  $J = 4.6$ , 4H), 10.3 (s, 2H). MALDI TOF-MS (THA): calcd. (found) for  $[\text{M}+\text{H}]^+$ : 630.26 (631.46).

**Synthesis of 5, 15-bis[(dihydroxyboryl)phenyl]-21H,23H-porphine:** 5, 15-bis(4-[1,3,2]-dioxaborinan-2-yl-phenyl)porphyrin (100 mg) was dissolved in THF (100 mL), an aqueous solution of HCl (pH = 1.0, 100 mL) was added to the mixture. The mixture was stirred at r.t for 24 hrs. Dichloromethane (100 mL) was added to the mixture, and the organic layer was washed with aqueous saturated solution of  $\text{NaHCO}_3$  (200 mL) and water (200 mL), and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvents were removed under reduced pressure and then poured into hexanes (50 mL). The purple precipitate was collected by centrifugation, yield 60%.  $^1\text{H}$  NMR (600 MHz,  $\text{DMSO}-d_6$ , 298K,  $\delta =$  ppm,  $J =$  Hz): -3.31 (s, 2H, pyrrole-N-H) 8.38-8.43 (dd,  $J = 12.6$ , 8H), 9.04 (d,  $J = 3.88$ , 4H), 9.67 (d,  $J = 4.1$ , 4H), 10.67 (s, 2H), 13.31 (brs, 4H, B-OH). MALDI TOF-MS (THA): calcd. (found) for  $[\text{M}+\text{H}]^+$ : 550.19 (551.29).

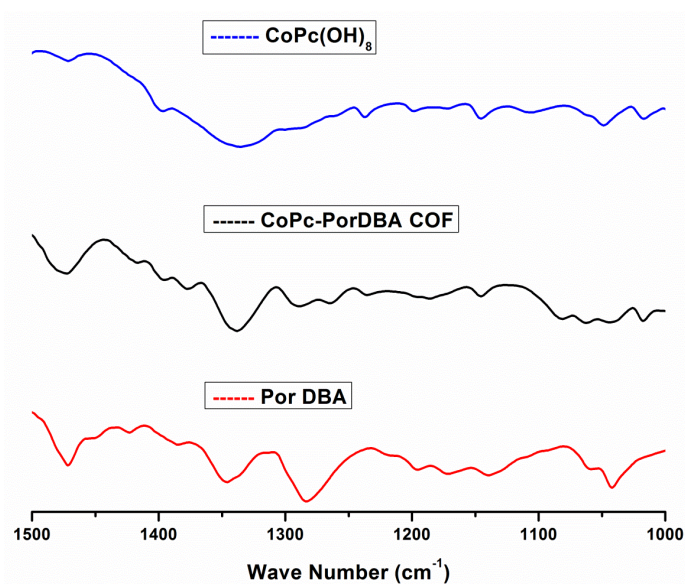


**CoPc-PorDBA COF.** 5, 15 porphyrin diboronic acid (PorDBA, 33mg, 0.06 mmol) and  $(\text{OH})_8\text{Pc Co}$  (21 mg, 0.03 mmol) were sonicated in a mixture of DMAC/*o*-dichlorobenzene (2/1 in vol.; 3 mL) in a glass ampoule and then ampoule was flash frozen in liquid  $\text{N}_2$  bath and sealed off at the neck of the ampoule under high vacuum. The ampoule was placed in an oven at  $120^\circ\text{C}$  for 74hrs. Then the mixture was filtered off, washed with anhydrous toluene and dried at  $100^\circ\text{C}$  under vacuum for 12 h, to give a dark green powder in 65% isolation yield and was totally insoluble in common organic solvents (such as DCM, THF, DMF, DMSO, etc.). Elemental analysis (%) calcd. for CoPc-PorDBA COF  $(\text{C}_{96}\text{H}_{48}\text{B}_4\text{N}_{16}\text{O}_8\text{Co})_n$  Theory: C (69.64), H (2.92), B (2.61), N (13.54), O (7.73) found C (63.95), H (3.02), N (14.12) respectively. Elemental analysis of boronate COFs generally give lowered carbon values from the formation of non-combustible boron carbide byproducts. The presence of boron was confirmed by a  $^{11}\text{B}$  MAS NMR spectroscopy.

### Section C. FT-IR spectral profiles

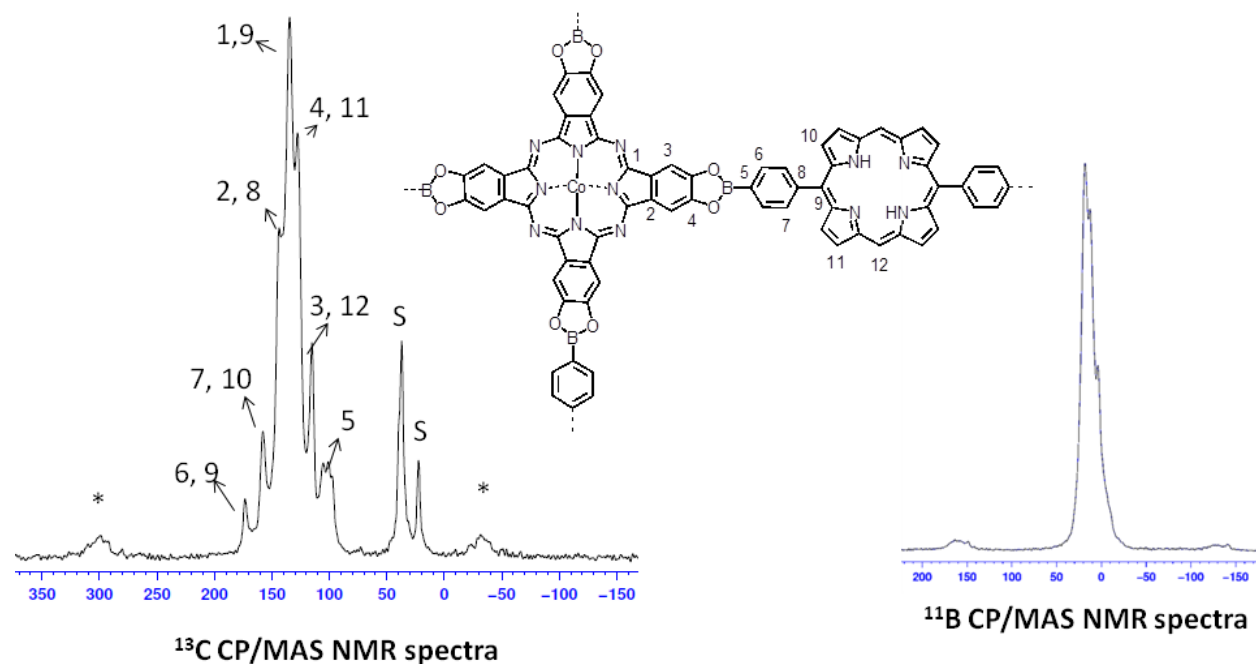


**Figure S1.** IR spectra of  $(\text{OH})_8\text{Pc Co}(\text{II})$  (blue),  $\text{CoPc-PorDBA COF}$  (black) and 5, 15 porphyrin diboronic acid (red).

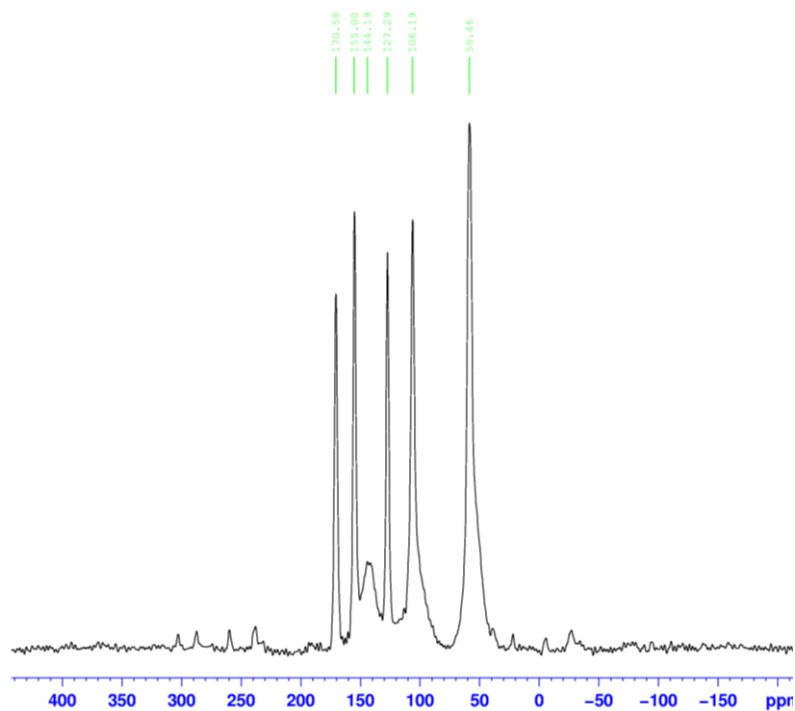


**Figure S2.** Expanded IR spectra of  $(\text{OH})_8\text{Pc Co(II)}$  (blue),  $\text{CoPc-PorDBA COF}$  (black) and 5, 15 porphyrin diboronic acid (red).

**Section D. Solid-state  $^{13}\text{C}$  and  $^{11}\text{B}$  CP MAS NMR spectrum of  $\text{CoPc-PorDBA COF}$**

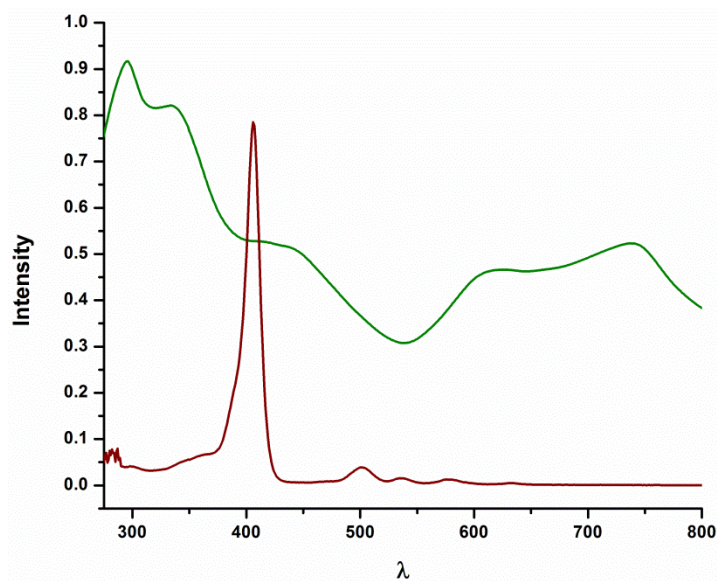


**Figure S3.** Solid state  $^{13}\text{C}$  CP/MAS NMR and  $^{11}\text{B}$  CP/MAS spectra of  $\text{CoPc-PorDBA COF}$  recorded at a MAS rate of 12.5 kHz. Signals with S and \* are residual solvent and side bands.

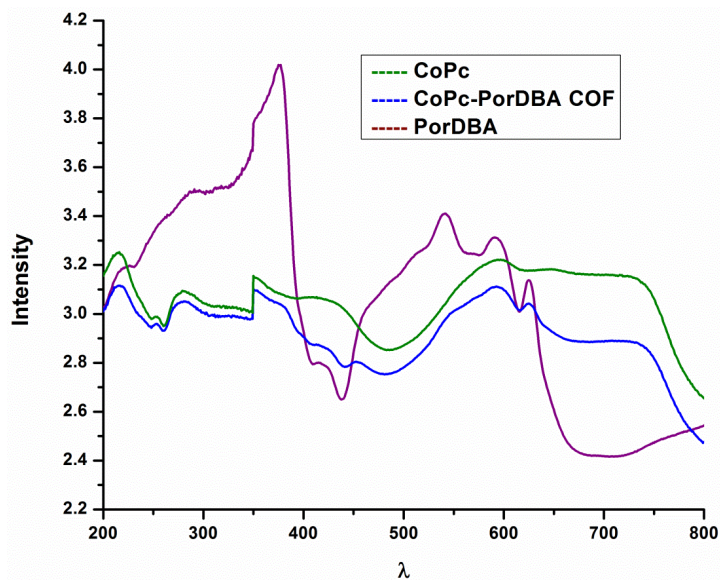


**Figure S4.** Solid state  $^{13}\text{C}$  CP/MAS NMR spectra of  $\text{CoPc}(\text{OMe})_8$  recorded at a MAS rate of 12.5 kHz.

### Section E: UV-Vis absorption spectra

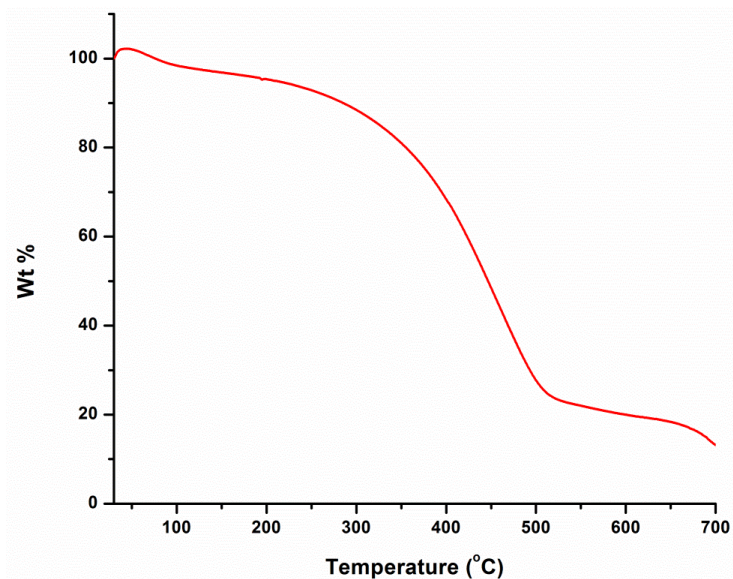


**Figure S5.** UV-Vis absorption spectra of  $\text{CoPc}$  (green curve) in dichloromethane and  $\text{PorDBA}$  (purple curve) in THF.



**Figure S6:** Solid-state absorption spectra CoPc-PorDBA COF (blue), CoPc (green) and PorDBA (purple) as powders using a praying mantis diffuse reflectance accessory. Small, jagged peaks around 340nm are due to instrument lamp shift.

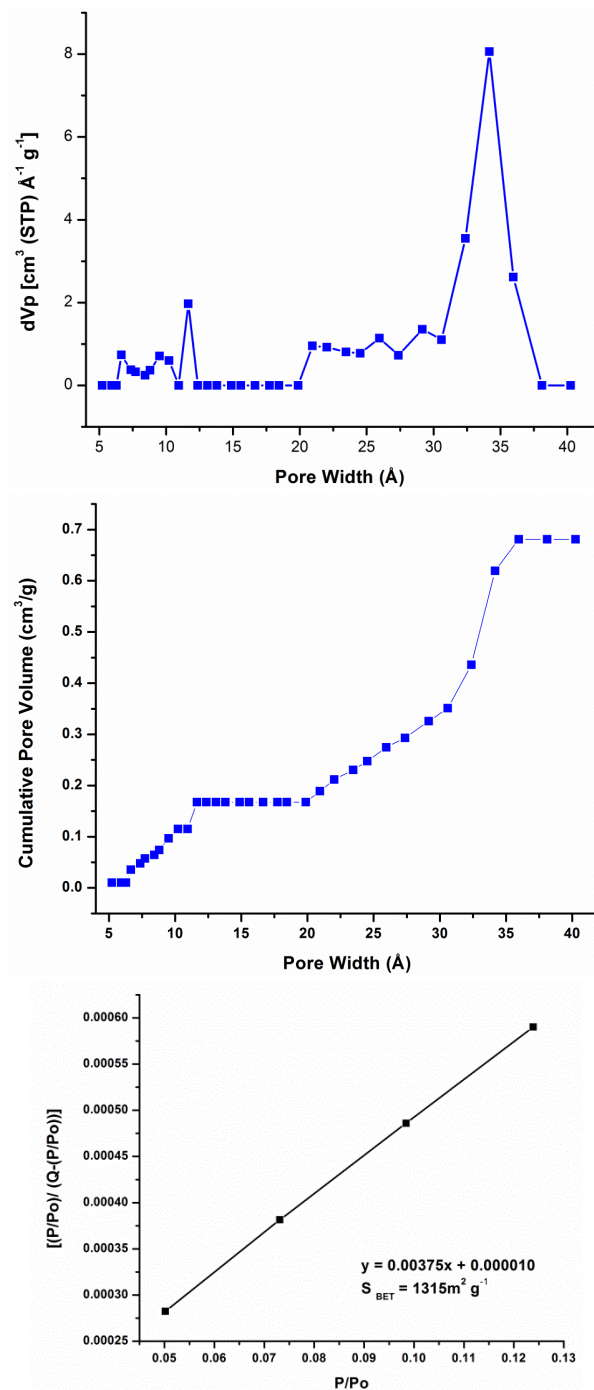
### Section F: Thermogravimetric Analysis



**Figure S7.** TGA of CoPc-PorDBA COF obtained up to 700 $^{\circ}\text{C}$  using a linear 3  $^{\circ}\text{C}/\text{min}$  ramp method.



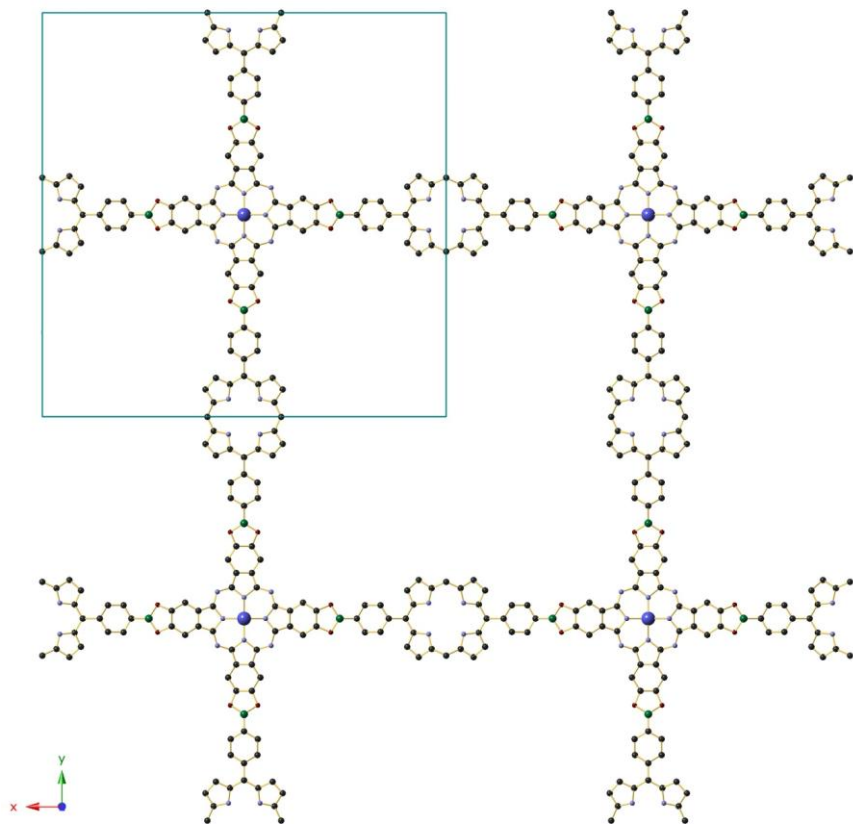
## Section G. Surface Area Measurements



**Figure S8.** Differential (top) and cumulative (bottom) pore size distribution plot of CoPc-PorDBA COF from the application of the NLDFT model to the N<sub>2</sub> isotherm. BET plot (below) for CoPc-PorDBA COF calculated from isotherm data.

## Section H. Simulation and calculation of structure

Modeling of the CoPc-PorDBA COF structure:



### Simulation & Refinement of the CoPc-PorDBA COF.

Geometry optimization and Pawley refinement of the CoPc-PorDBA COF was performed with Accelrys MS Modeling 4.3 using Reflex. The final tetragonal unit cell was calculated with the geometrical parameters from the optimized structure. Pawley refinement was performed to optimize the lattice parameters iteratively until the RWP value converges. After Pawley refinement the peak profile was refined using the Pseudo-Voigt peak shape function and whole profile fitting was done using Berrar - Baldinozzi function for asymmetry correction during the refinement processes. The final *RWP* and *RP* values were 10.26% and 15.68%, respectively. The unit cell parameters were first calculated and then refined from the experimentally observed peak positions, as a result we obtained cell parameters of  $a = b = 36.54 \text{ \AA}$  and  $c = 3.67 \text{ \AA}$ . Simulated

PXRD patterns were calculated for an eclipsed arrangement of  $P4/mmm$  space group, where all atoms in an each layer of the framework lay over one another.

Refined unit cell parameters and fractional atomic coordinates for CoPc-PorDBA COF.

CoPc-PorDBA COF	$a$ (Å)	$c$ (Å)
MS modeling	36.1427	3.6235
Pawley refinement	36.5499	3.6746

Atom name	x	y	z
C1	0.5	0.5	0.25
B2	0.5	0.5	0.25
N3	0.5	0.5	0.25
C4	0.5	0.5	0.25
C5	0.5	0.5	0.25
C6	0.46689	0.5	0.5
C7	0.46669	0.5	0.5
C8	0.48075	0.5	0.5
C9	0.46026	0.5	0.5
C10	0.48086	0.5	0.5
C11	0.46913	0.5	0.5
O12	0.46596	0.5	0.5
C13	0.53479	0.5	0.5
C14	0.56997	0.5	0.5
C15	0.59558	0.5	0.5
C16	0.57509	0.5	0.5
N17	0.53879	0.5	0.5
N18	0.43351	0.5	0.25
C19	0.5	0.5	0.0625
C20	0.59115	0.5	0.25

### Section I: Supporting References

- 1) J. Metz, O. Schneider, and M. Hanack, *Inorg. Chem.* **23**, 1065-1071 (1984).
- 2) X. Ding, X. Feng, A. Saeki, S. Seki, A. Nagai and D. Jiang, *Chem. Commun.*, 2012, **48**, 8952.
- 3) M. Ikeda, S. Shinkai, and A. Osuka., *Chem. Commun.*, 2000, 12, 1047-1048.
- 4) X. Feng, L. Chen, Y. Dong, and D. Jiang., *Chem. Commun.*, 2011, **47**, 1979–1981.