Supplementary Information

Synthesis of a Phthalocyanine 2D Covalent Organic Framework

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Section A. Materials and methods:

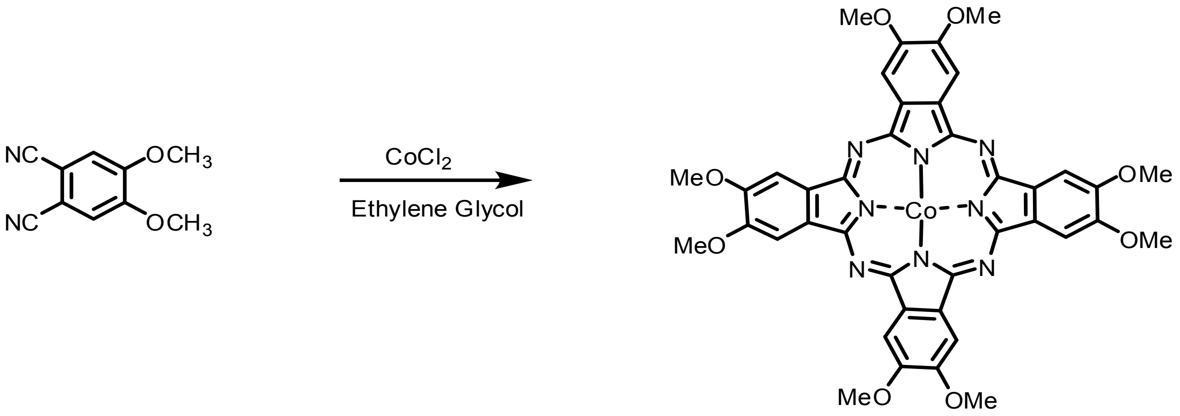
All chemicals and solvents were purchased from Sigma-Aldrich except dibromoveratrole (Alfa Aesar). Co octahydroxy phthalocyanine [1,2] was prepared according to literature procedures.

^{1}H NMR spectra were recorded on JEOL 600MHz spectrometer, where chemical shifts (δ in ppm) were determined with a residual proton of the solvent as standard. Fourier transform Infrared (FT-IR) spectra were recorded on a Perkin-Elmer Spectrum one infrared spectrometer (ATR). 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. Transmission electron microscopy (TEM) images were obtained on a Hitachi H-9500 model. Samples were prepared by drop-casting an acetone suspension of CoPc-BPDA COF onto a copper grid. Powder X-ray diffraction (PXRD) data were recorded on a Bruker DiscoverD8 model diffractometer by depositing powder on plastic substrate, from $2\theta = 1°$ up to 30° with 0.05° 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-BPDA COF sample at 77 K were measured in an ASAP-2020 adsorption apparatus (Micromeritics). The as-synthesized samples were degassed in situ at 165 °C with a heating rate of 3°C /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 30-900 °C was carried out on a Mettler-Toledo thermogravimetric analyzer in an N_2 atmosphere using a 3 °C/min ramp time.

Section B. Synthetic Procedure:

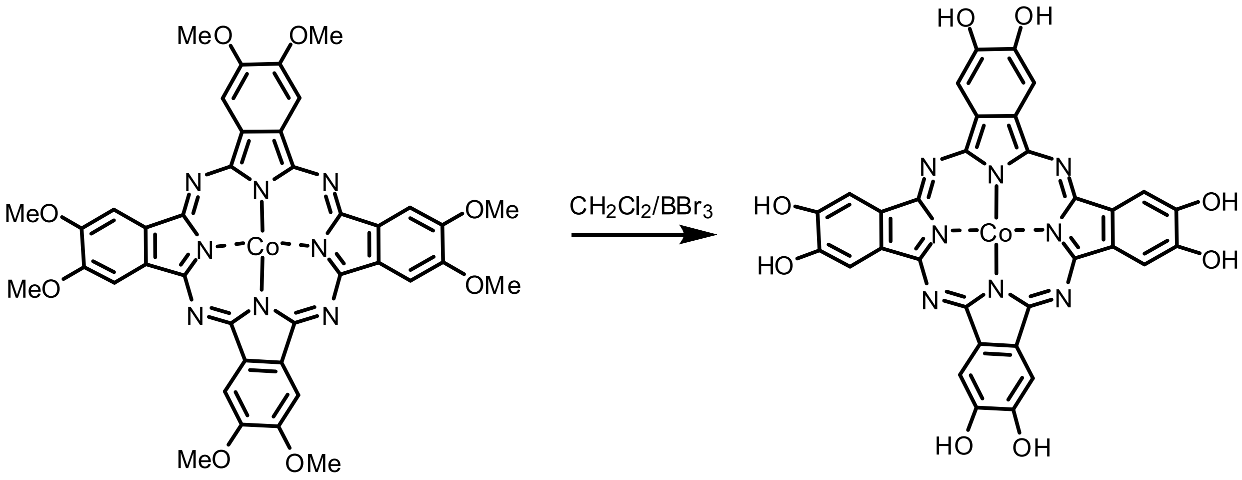
Synthesis of 2,3,9,10,16,17,23,24-Octamethoxyphthalocyaninato)cobalt(II) $(MeO)_8PcCo$

(Octamethoxyphthalocyaninato)cobalt(II) was prepared using a literature procedure.[1,2] $(MeO)_8PcCo$ obtained as a green solid in 40% yield. MALDI-TOF MS for $C_{40}H_{32}N_8O_8Co$ (Calculated 811.17), found m/z = 811.87 $[M]^+$.



Synthesis of 2,3,9,10,16,17,23,24-Octahydroxyphthalocyaninato)cobalt(II) $(OH)_8PcCo$

(Octahydroxyphthalocyaninato) cobalt(II) was prepared using a literature procedure.[1,2] $(OH)_8PcCo$ obtained as a dark green solid in 67% yield. MALDI-TOF MS for $C_{32}H_{16}N_8O_8Co$ (Calculated 699.04), found m/z = 698.99 $[M]^+$.



CoPc-BPDA COF. 4, 4'-Biphenyldiboronic acid (BPDA, 14.51mg, 0.06 mmol) and $(OH)_8PcCo$ (21 mg, 0.03 mmol) were sonicated in a mixture of DMAC/*o*-dichlorobenzene (2/1 in vol.; 2 mL) in a glass vial, then the mixture was transferred into a glass ampoule. The ampoule was flash frozen in liquid N_2 bath and sealed off at the neck of the ampoule. The ampoule was placed in an oven at 120 °C for 74hrs. Then the mixture was filtered off, washed with anhydrous toluene and dried at 150 °C under vacuum for 12 h, to give a dark green powder in 80% isolation yield. Elemental analysis (%) calcd. for CoPc- BPDA COF $(C_{56}H_{24}B_4N_8O_8Co)_n$ Theory: C (64.74), H (2.33), N (10.78), found C (57.05), H (3.26), N (9.76) 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}B MAS NMR spectroscopy.

Section C. FT-IR spectral profiles

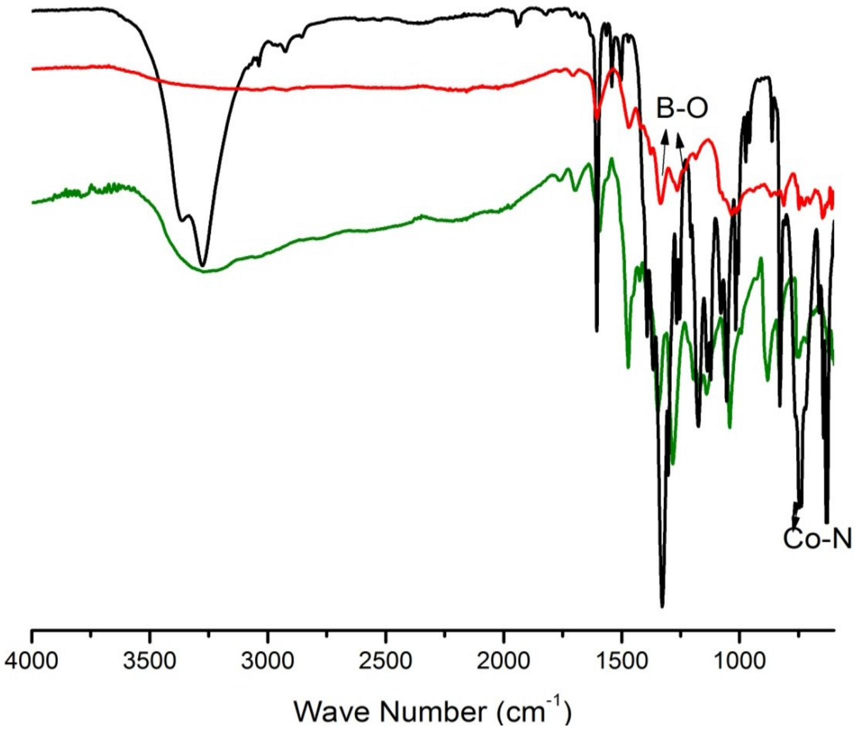


Figure S1. IR spectra of 4, 4'-Biphenyldiboronic acid (black curve), $(OH)_8PcCo$ (green curve) and CoPc-BPDA COF (red curve).

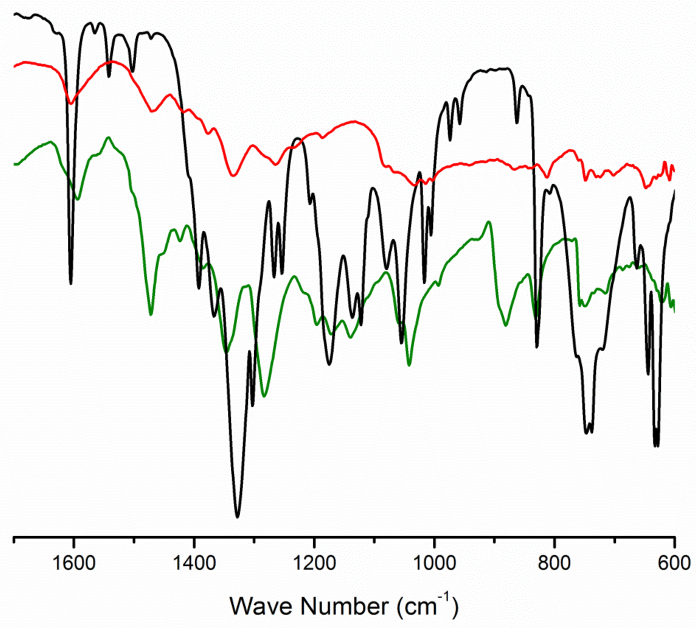


Figure S2. Expansion of 600-1700 cm^{-1} region of the above spectrum.

Section D. Solid-state ^{13}C CP-MAS NMR spectrum of CoPc-BPDA COF

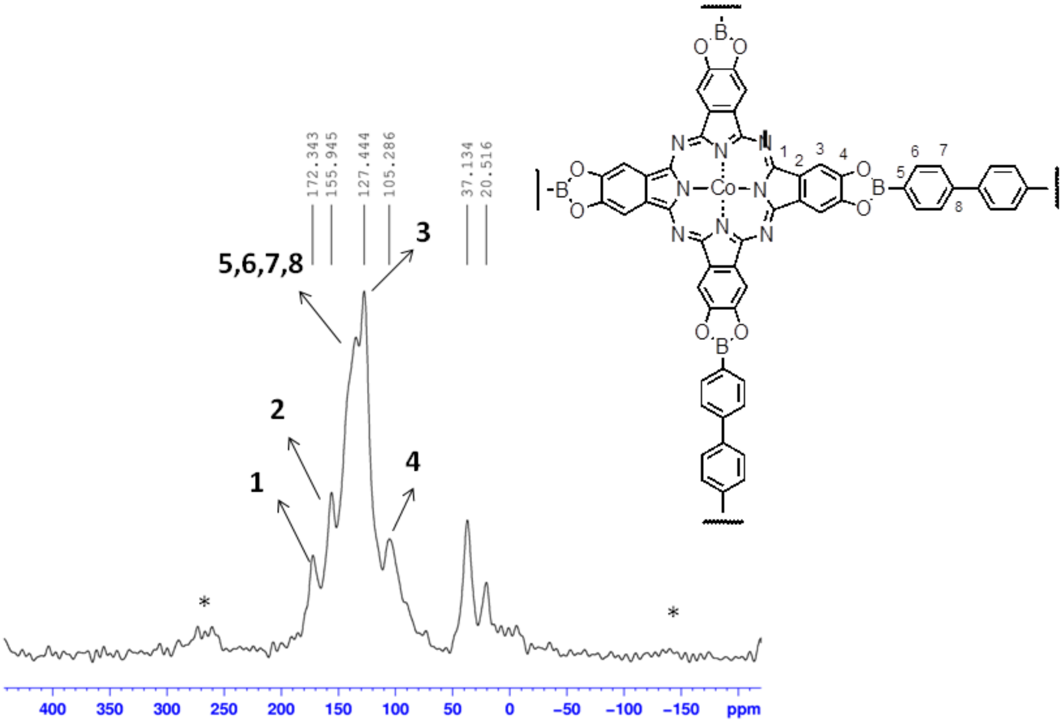


Figure S3. Solid state ^{13}C CP/MAS NMR spectra of CoPc-BPDA COF recorded at a MAS rate of 12.5 kHz. Signals with * are side bands.

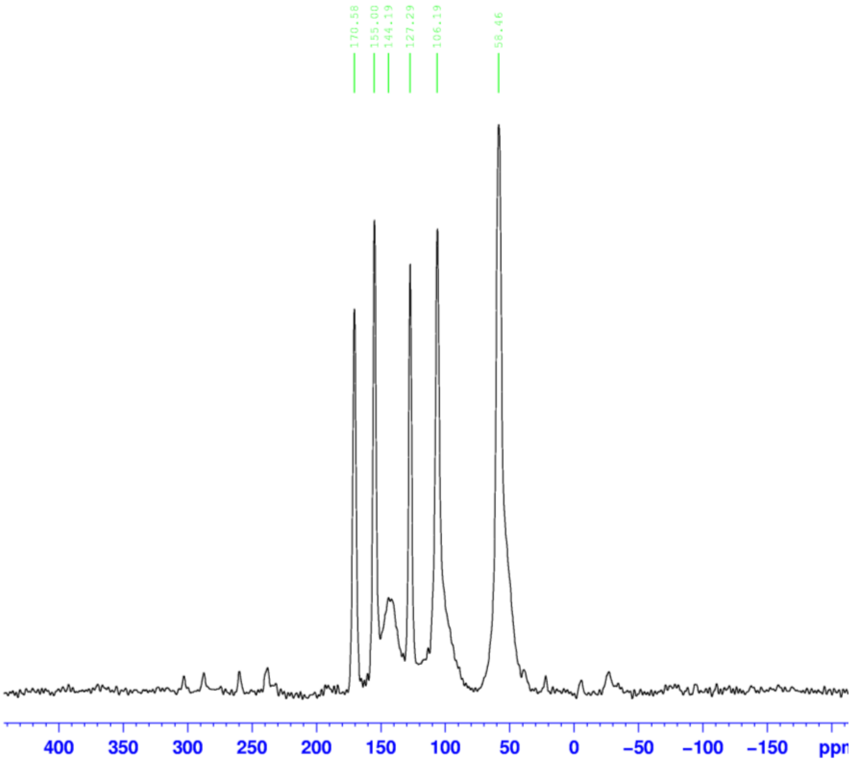


Figure S4. Solid state ^{13}C CP/MAS NMR spectra of CoPc $(OMe)_8$ recorded at a MAS rate of 12.5 kHz. Signals with * are side bands.

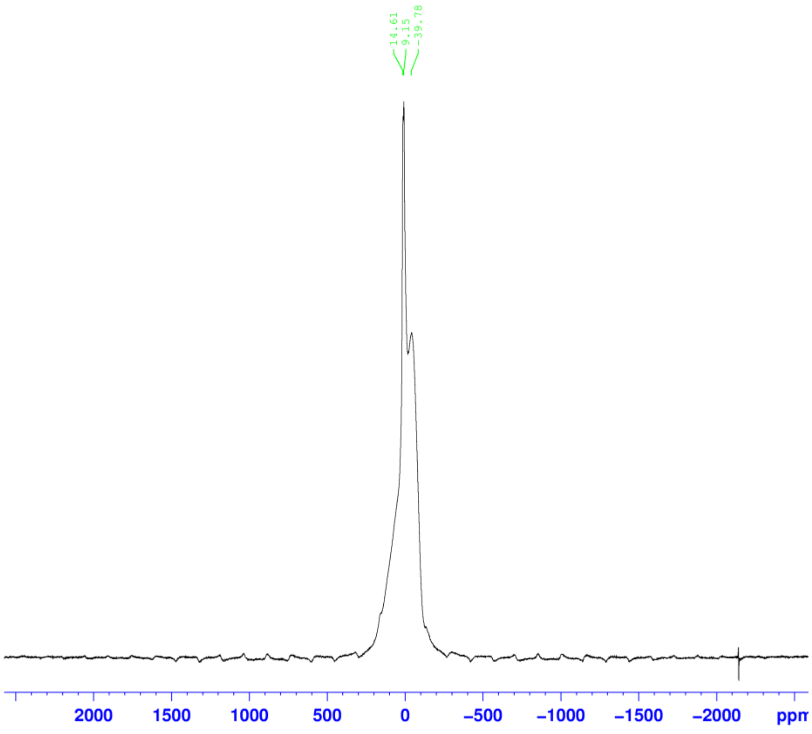


Figure S5. Solid state ^{11}B MAS NMR spectra of CoPc-BPDA COF recorded at a MAS rate of 14 kHz.

Section E. X-ray fluorescence spectroscopy

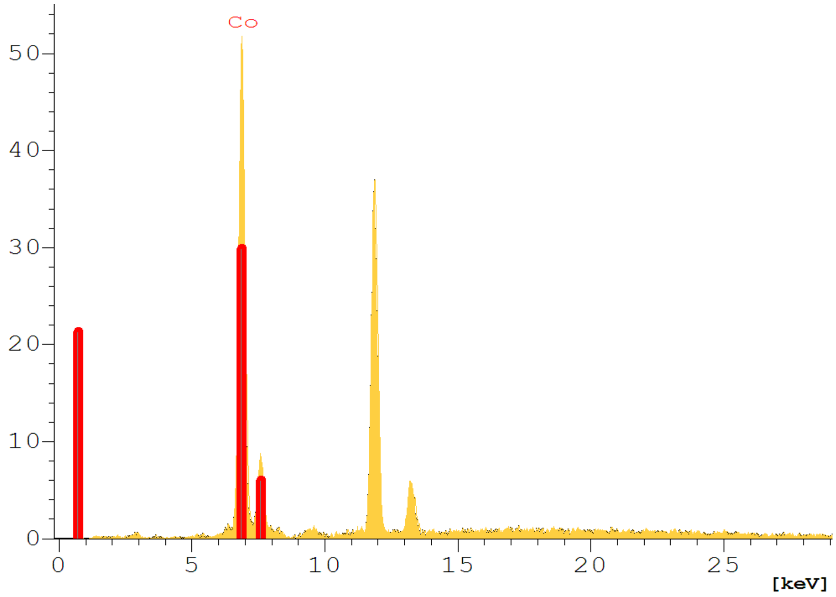
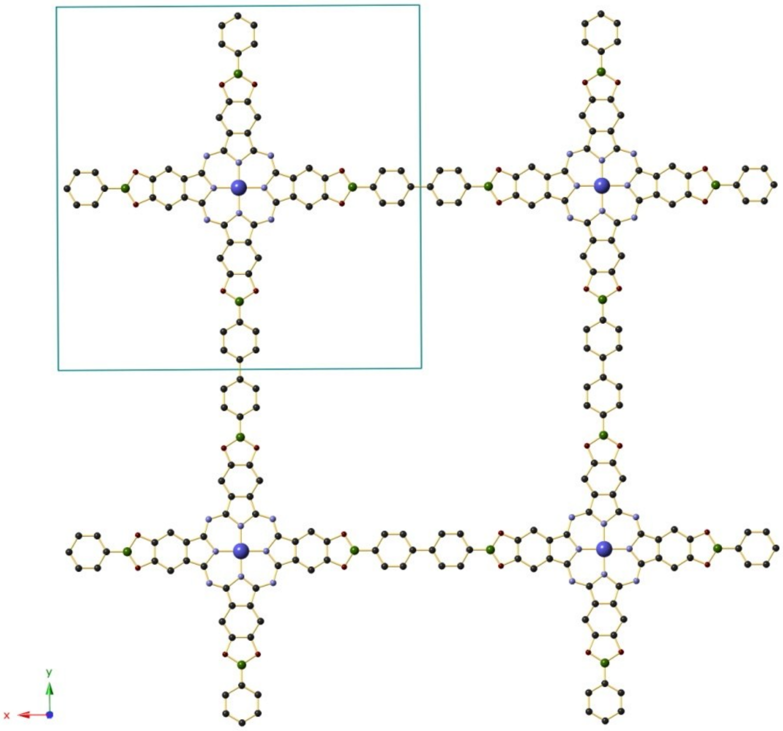


Figure S6. Presence of Cobalt within the framework of CoPc-BPDA COF

Section F. Simulation and calculation of structure

Modeling of the CoPc-BPDA COF structure:



Simulation & Refinement of the CoPc-PorDBA COF

Geometry optimization and Pawley refinement of the CoPc-BPDA COF was carried out with Accelrys MS Modeling 4.3 using Reflex module. The unit cell dimensions were calculated from 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 R_{WP} and R_{P} values were 10.69% and 16.39%, 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 = 26.65 Å and c = 3.55 Å. Simulated PXRD patterns were calculated for an eclipsed arrangement of *P*4/*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	27.30	3.6235
Pawley refinement	26.65	3.55

	B	C	Co	N	O
C1	2	0.02713	0.5	0.5	0.25
B2	1	0.18692	0.5	0.5	0.25
N3	4	0.43026	0.5	0.5	0.25
C4	2	0.13009	0.5	0.5	0.25
C5	2	0.0533	0.45571	0.5	0.5
C6	2	0.10447	0.45571	0.5	0.5
C7	2	0.26281	0.47453	0.5	0.5
C8	2	0.30645	0.44741	0.5	0.5
C9	2	0.34987	0.47465	0.5	0.5
C10	2	0.39788	0.45912	0.5	0.5
O11	5	0.21603	0.45501	0.5	0.5
N12	4	0.41198	0.41198	0.5	0.25
Co13	3	0.5	0.5	0.5	0.0625

Section G: Thermogravimetric Analysis

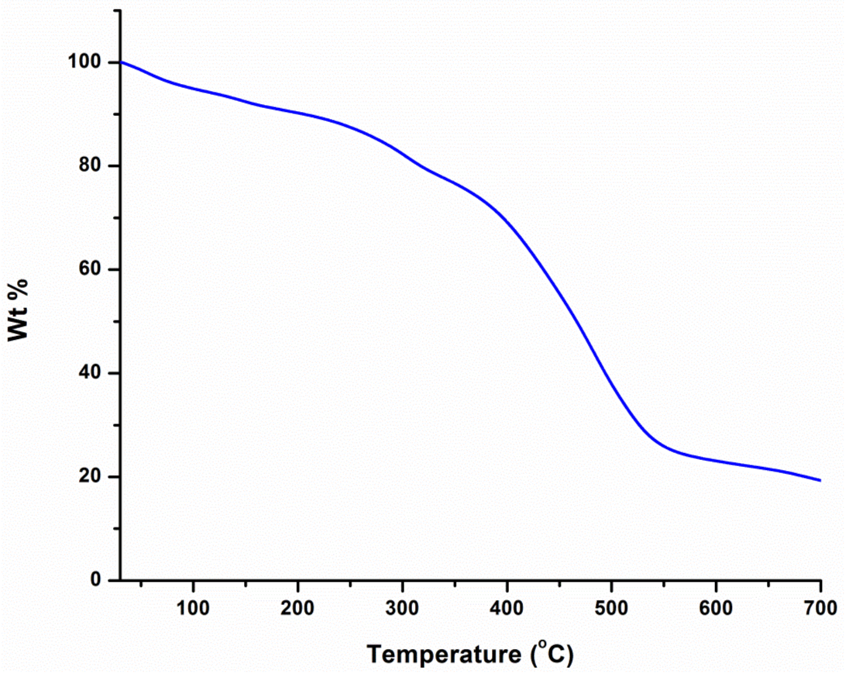
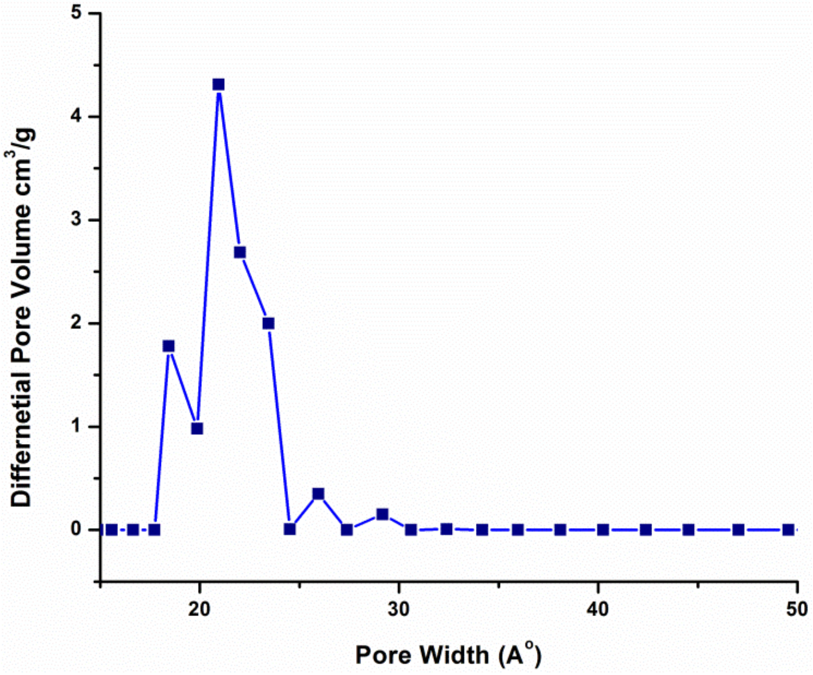


Figure S7. TGA of COF obtained up to 700°C using a linear 3 °C/min ramp method

Section H: Surface Area measurements



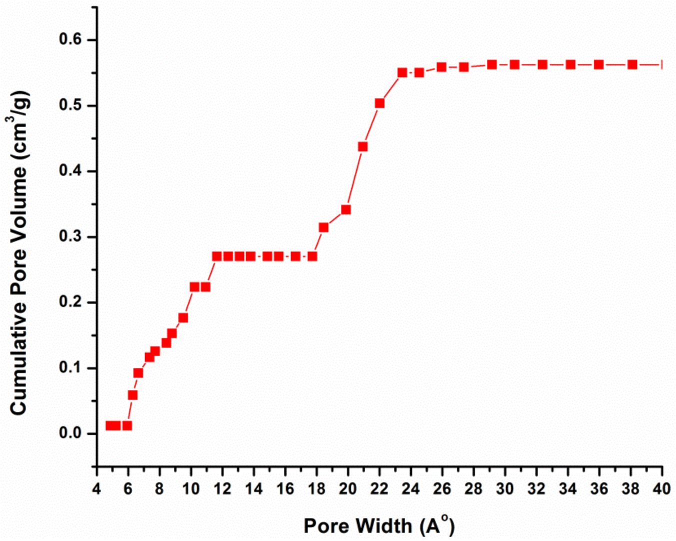


Figure S8. Differential (top) and cumulative (bottom) pore size distribution plot of CoPc-BPDA COF from the application of the NLDFT model to the N_2 isotherm.

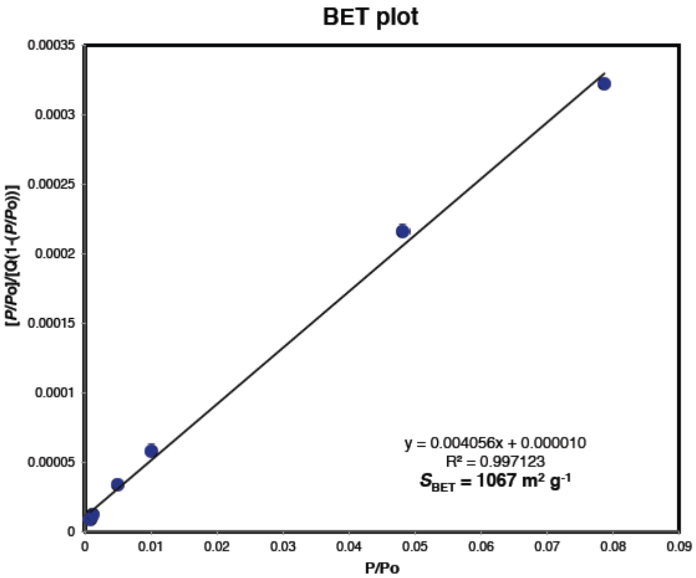


Figure S9. BET plot for CoPc-BPDA COF calculated from isotherm data.

Calculation of isosteric heat of adsorption

The adsorption enthalpy at zero coverage was calculated from Henry constant using the Van't Hoff equation as

$$\ln \mathrm{K} = -\frac{\Delta \mathrm{H}}{\mathrm{RT}} + \frac{\Delta \mathrm{S}}{\mathrm{R}}$$

K is Henry constant, T is temperature, plotting ln *K* v.s. 1000/T

Section I: Cryo Electron Microscope Images

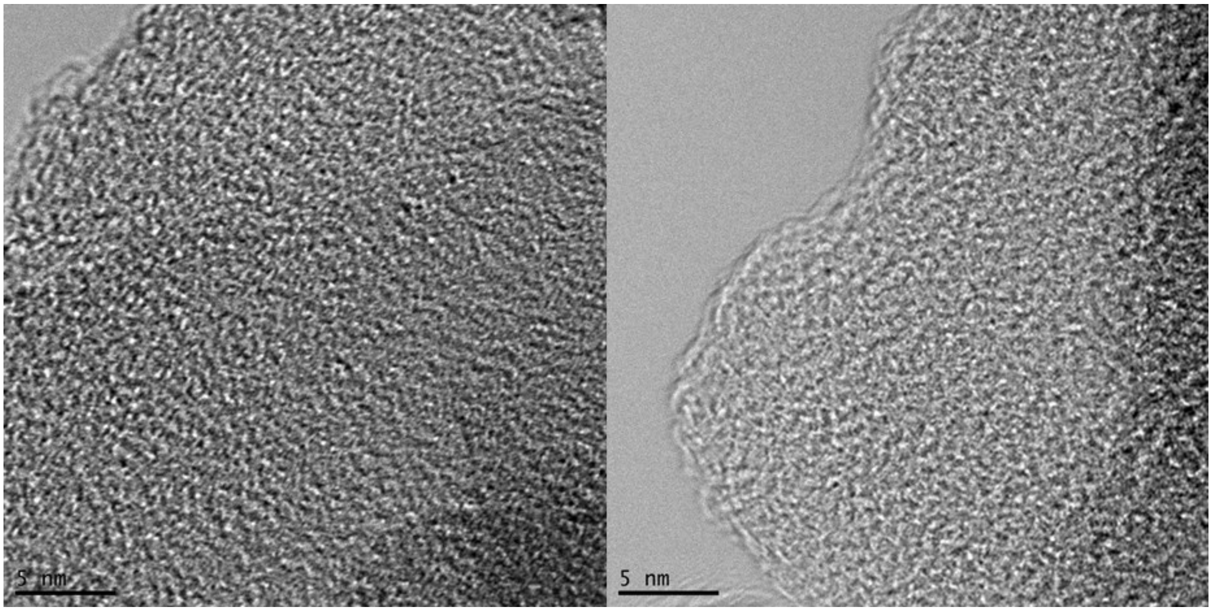


Figure S10. Cryo Electron Microscope Images of CoPc-BPDA COF.

Section J. Supporting reference

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