

Pore Surface Engineering in Porous, Chemically Stable Covalent Organic Frameworks for Water Adsorption

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(Supporting Information)

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Section S1: General Remarks

The 1,3,5-Triformylphloroglucinol was prepared from Phloroglucinol using literature procedure (J. H. Chong, M. Sauer, B. O. Patrick, M. MacLachlan, *J. Org. Lett.* **2003**, 5, 3823). All other reagents and solvents were commercially available and used as received. Powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku SmartLab X-ray diffractometer in reflection mode using CuK α radiation ($\lambda = 1.54 \text{ \AA}$). The 2θ range from 3° to 40° was scanned with a scan rate of 3° min^{-1} . Fourier transform infrared (FT-IR) spectra were taken on a Bruker Optics ALPHA-E spectrometer with a universal Zn-Se ATR (attenuated total reflection) accessory in the $600\text{-}4000 \text{ cm}^{-1}$ region or using a Diamond ATR (Golden Gate). Thermogravimetric analyses (TGA) were carried out on a TG50 analyzer (Mettler-Toledo) or a SDT Q600 TG-DTA analyzer under N $_2$ atmosphere at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ within a temperature range of $30\text{-}800 \text{ }^\circ\text{C}$. SEM images were obtained with a Zeiss DSM 950 scanning electron microscope and FEI, QUANTA 200 3D Scanning Electron Microscope with tungsten filament as electron source operated at 10 kV and and in FEI Nova NanoSEM 650 Scanning Electron Microscope. The samples were sputtered with Au (nano-sized film) prior to imaging by a SCD 040 Balzers Union. TEM images were recorded using FEI Tecnai G2 F20 X-TWIN TEM at an accelerating voltage of 200 kV. The TEM Samples were prepared by dropcasting the sample from isopropanol on copper grids TEM Window (TED PELLA, INC. 200 mesh). Imaging was done at room temperature and ambient environment. All gas adsorption experiments (up to 1 bar) were performed on a Quantachrome Quadrasorb automatic volumetric instrument.

Section S2: Procedures for COF Synthesis

Synthesis of COFs [TpPa-1, TpPa-2, TpBD, TpPa-NO $_2$, TpPa-F $_4$, TpBD-(NO $_2$) $_2$, TpBD-Me $_2$, TpBD-(OMe) $_2$]

In the typical synthesis, a Pyrex tube (o.d. \times i.d. = $10 \times 8 \text{ mm}^2$ and length 18 cm) is charged with 1,3,5-triformylphloroglucinol (**Tp**) (0.3 mmol), corresponding diamine {[*p*-phenylenediamine (**Pa-1**), 2,5-dimethyl-*p*-phenylenediamine (**Pa-2**), Benzidine (**BD**), 2-nitro-1,4-phenelynediamine (**Pa-NO $_2$**), 2,3,5,6-tetrafluoro-1,4-phenylenediamine (**Pa-F $_4$**), 3,3'-dinitrobenzidine [**BD-(NO $_2$) $_2$**], o-tolidine (**BD-Me $_2$**), and o-dianisidine [**BD-(OMe) $_2$**]} (0.45 mmol), 1.5 mL of mesitylene, 1.5 mL of 1,4-dioxane, 0.5 mL of 6 M aqueous acetic acid. This mixture was sonicated for 10 minutes in order to get a homogeneous dispersion. The tube was then flash frozen at 77 K (liquid N $_2$ bath) and degassed by three freeze-pump-thaw cycles. The tube was sealed off and then heated at $120 \text{ }^\circ\text{C}$ for 3 days. A colored [TpPa-1 (red), TpPa-2 (dark red), TpBD (yellow), TpPa-NO $_2$ (wine red), TpPa-F $_4$ (orange), TpBD-(NO $_2$) $_2$ (wine red), TpBD-Me $_2$ (orange) and TpBD-(OMe) $_2$ (yellowish orange)] precipitate was collected by filtration and washed with dimethylacetamide (DMAc) and acetone thrice. The powder

collected was then solvent exchanged with acetone 5-6 times and dried at 150 °C under vacuum for 12 hours to get corresponding COFs in ~80 % isolated yield.

Synthesis of Tp-Azo

In the typical synthesis, a Pyrex tube (o.d. × i.d. = 10 × 8 mm² and length 18 cm) is charged with 1,3,5-triformylphloroglucinol (**Tp**) (0.3 mmol), 4,4'-azodianiline [**Azo**] (0.45 mmol), 3 mL of DMAc and 3 mL of o-dichlorobenzene. This mixture was sonicated for 10 minutes in order to get a homogeneous dispersion. The tube was then flash frozen at 77 K (liquid N₂ bath) and degassed by three freeze-pump-thaw cycles. The tube was sealed off and then heated at 120 °C for 3 days. A dark red coloured precipitate was collected by filtration and washed with DMAc thrice. The powder collected was then solvent exchanged with acetone 5-6 times and dried at 150 °C under vacuum for 12 hours to get corresponding COFs in ~75 % isolated yield.

Synthesis of DhaTab (S. Kandambeth, *et al.*, *Nature Commun.*, 2015, **6**, Article No. 6786)

A pyrex tube (o.d. × i.d. = 12 × 10 mm² and length 18 cm) is charged with 2,5-dihydroxyterephthalaldehyde (**Dha**) (21.6 mg 0.13 mmol) and 1,3,5-tris(4-aminophenyl)benzene (**Tab**) (30.2 mg 0.09 mmol), 1.7 mL of mesitylene, 0.3 mL of dioxane, 0.2 mL of 8 M aqueous acetic acid. This mixture was sonicated for 10 minutes in order to get a homogenous dispersion. The tube was then flash frozen at 77 K (liquid N₂ bath) and degassed by three freeze-pump-thaw cycles. The tube was sealed off and then heated at 120 °C for 3 days. A yellowish orange colored precipitate formed was collected by filtration and washed with DMAc, water and then ethanol. The powder collected was then solvent exchanged with ethanol 3 times and then dried at 150 °C under vacuum for 24 hours to give a yellowish orange colored powder in ~80% isolated yield.

Synthesis of 2,3-DhaTph

The synthesis of **2,3-DhaTph** was carried out by utilizing the same protocol with a mixture of 2,3-dihydroxyterephthalaldehyde (**2,3-Dha**) (26.6 mg, 0.16 mmol) and tetra(*p*-amino-phenyl)porphyrin (**Tph**) (54 mg, 0.08 mmol) in presence of 6 M acetic acid (0.6 mL) using 1,2-dichlorobenzene (*o*-DCB) (1 mL) and dimethyl acetamide (DMAc) (3 mL). This mixture was sonicated for 20 minutes in order to get a homogenous dispersion. The tube was then flash frozen at 77 K (liquid N₂ bath) and degassed by three freeze-pump-thaw cycles. The tube was sealed off and then heated at 120 °C for 72 hours. After the reaction the COF powders are filtered out, washed with ethanol and dried under vacuum at 150 °C for 12 hours to give purple colored powder in 80 % (56 mg) isolated yield based on **Tph**.

Synthesis of 2,5-DhaTph

The synthesis of **2,5-DhaTph** was carried out by utilizing the same protocol as described above for **2,3-DhaTph** with only difference is that here a mixture of 2,5-dihydroxyterephthalaldehyde (**2,5-Dha**) (13.3 mg, 0.08 mmol) and tetra(*p*-aminophenyl) porphyrin (**Tph**) (27.0 mg, 0.04 mmol) was taken in

presence of 6 M acetic acid (0.2 mL) using dichlorobenzene, ethanol (1:1) as solvent combination (2 mL). After the reaction the COF powders are filtered out, washed with ethanol and dried under vacuum at 150 °C for 12 hours to give purple colored powder in 79 % (28 mg) isolated yield based on **Tph**.

Section S3: Powder X-ray Diffraction

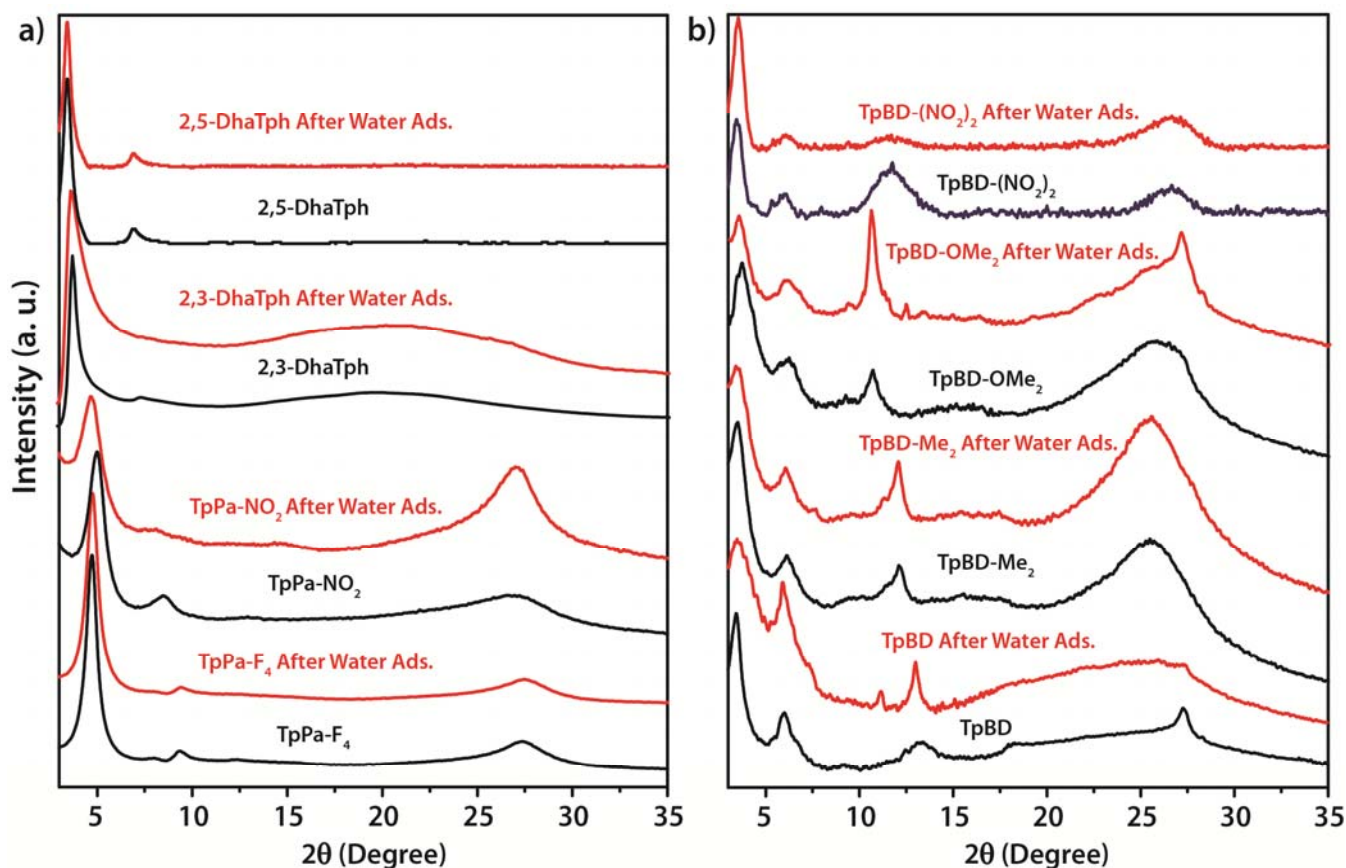


Figure S1. a) and b) Powder X-ray diffraction of COFs, as synthesized and after water adsorption experiment.

Section S4: FT-IR Analysis

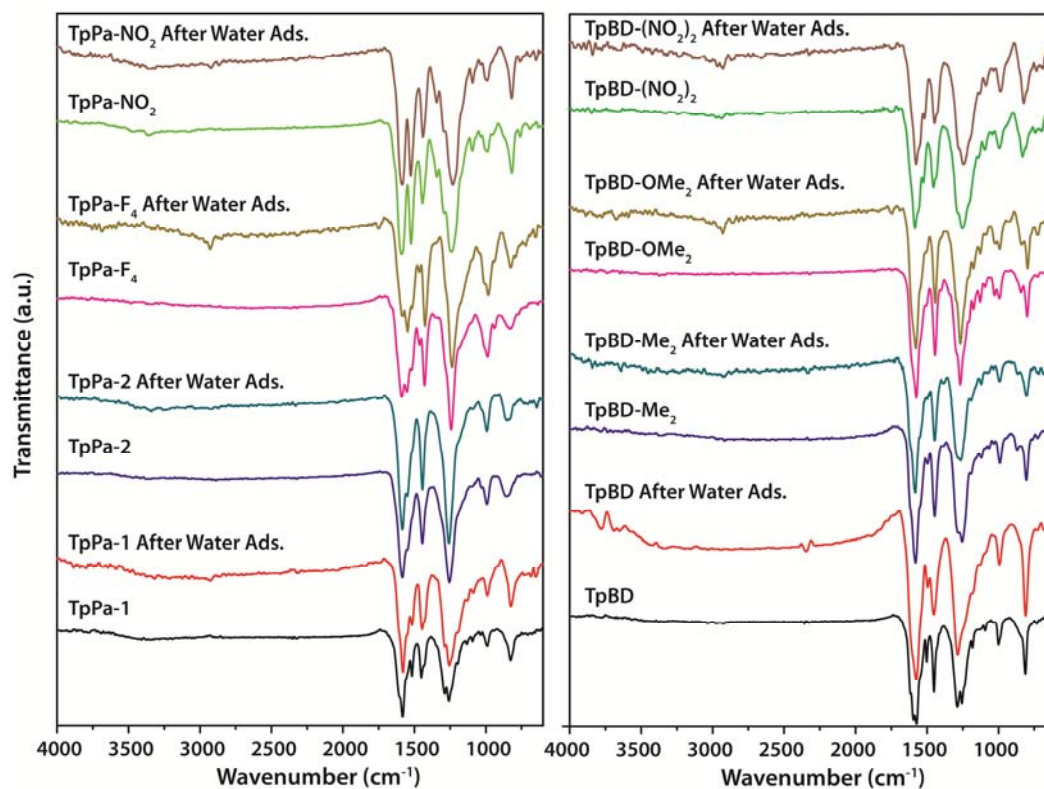


Figure S2. FT-IR of a) TpPa-series and b) TpBD-series COFs, as synthesized and after water adsorption.

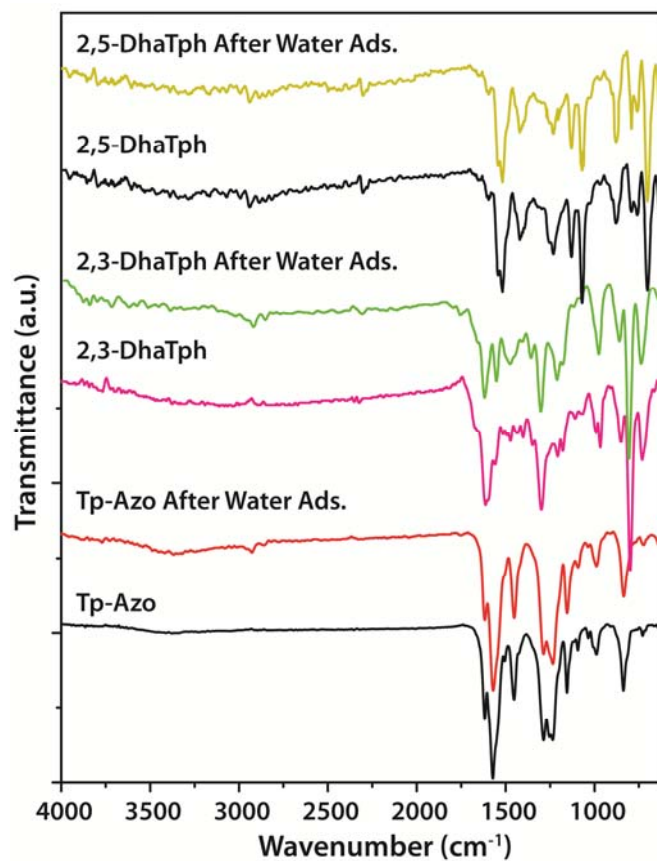


Figure S3. FT-IR of porphyrin-series COFs and Tp-Azo, as synthesized and after water adsorption.

Section S5: SEM Images

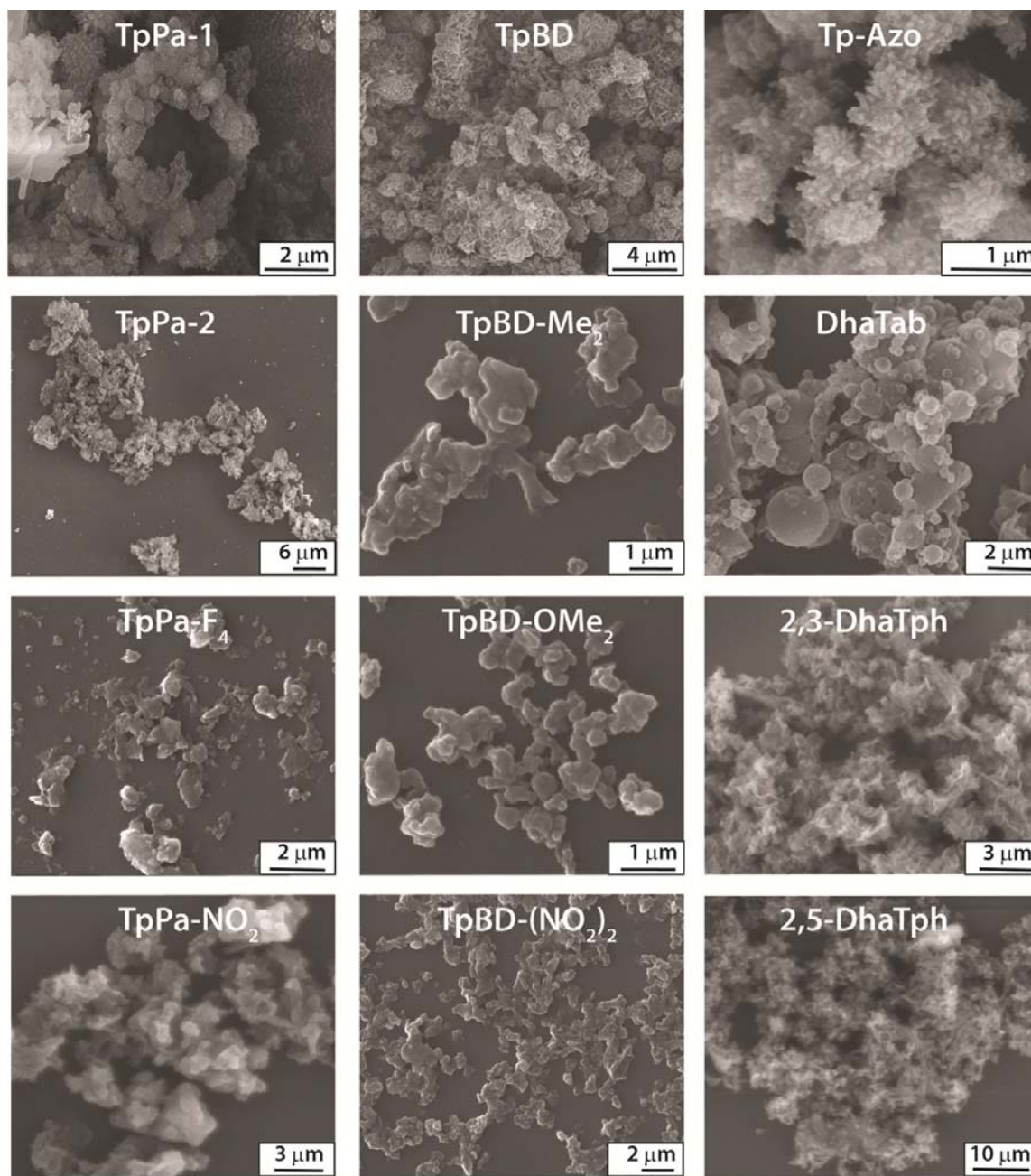


Figure S4. SEM images of all COFs under study.

Section S6: TEM Images

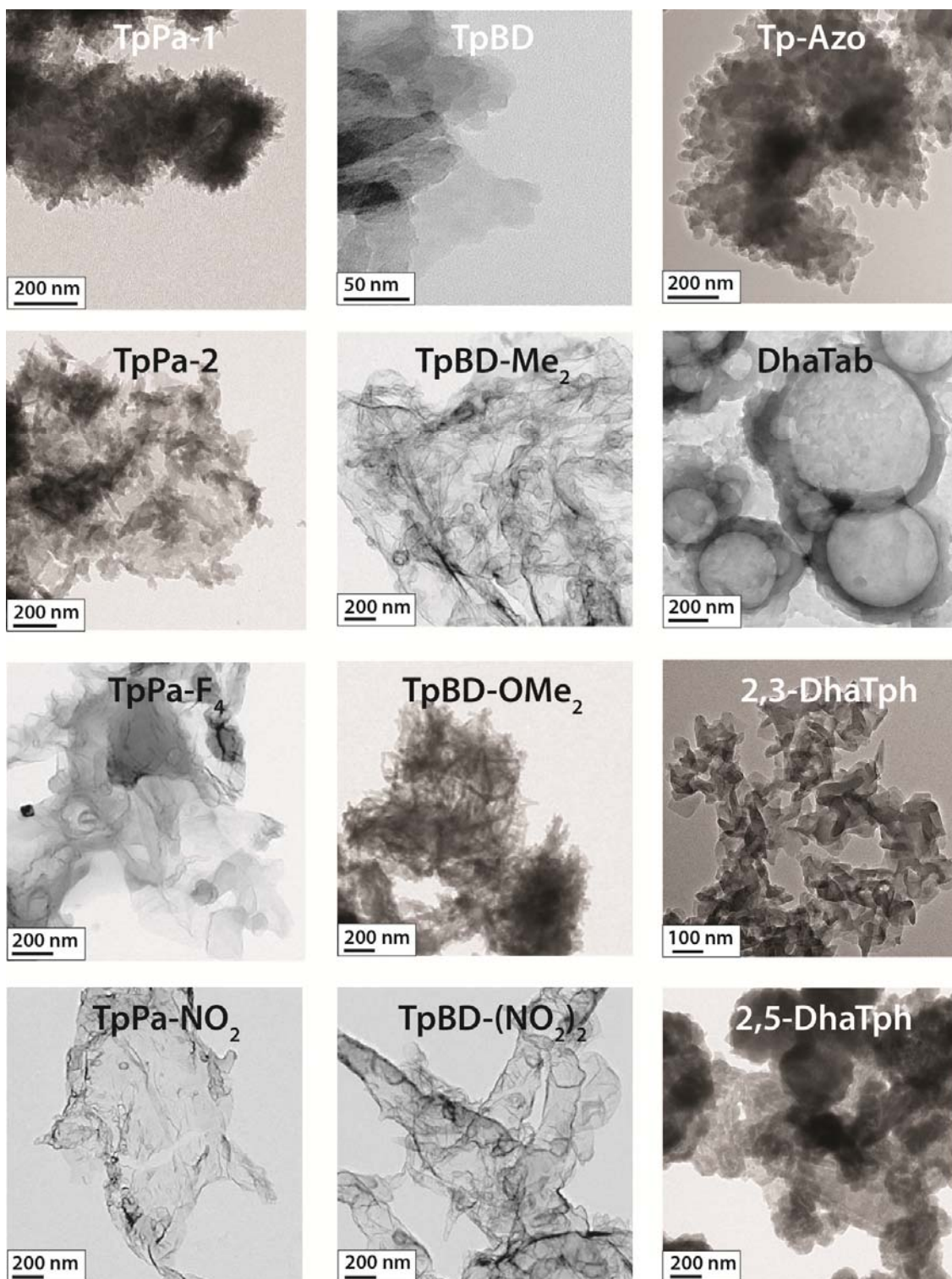


Figure S5. TEM images of all COFs under study.

Section S7: Water Adsorption Isotherms

Water adsorption experiments were performed on Quantachrome Autosorb-iQ-MP automatic volumetric instrument, up to $P/P_0 = 0.9$ at 298 K.

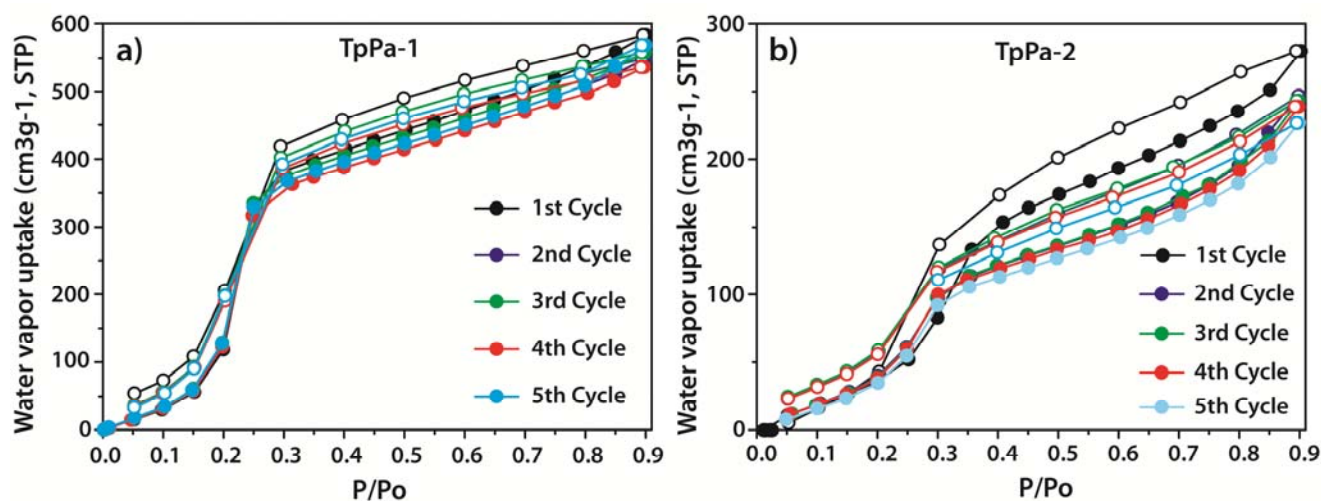


Figure S6. Water adsorption isotherms of TpPa-1 and TpPa-2 at different adsorption-desorption cycles.

Section S8: Thermogravimetric Analysis (TGA)

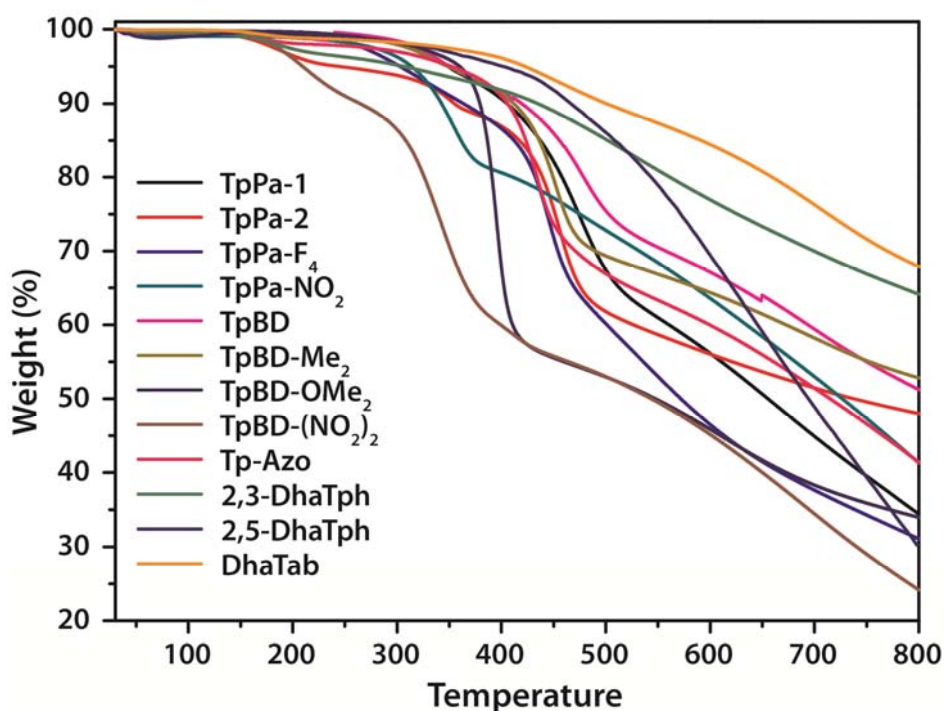


Figure S7. TGA profiles of all COFs measured under N₂ atmosphere.

Section S9: N₂ Adsorption Study

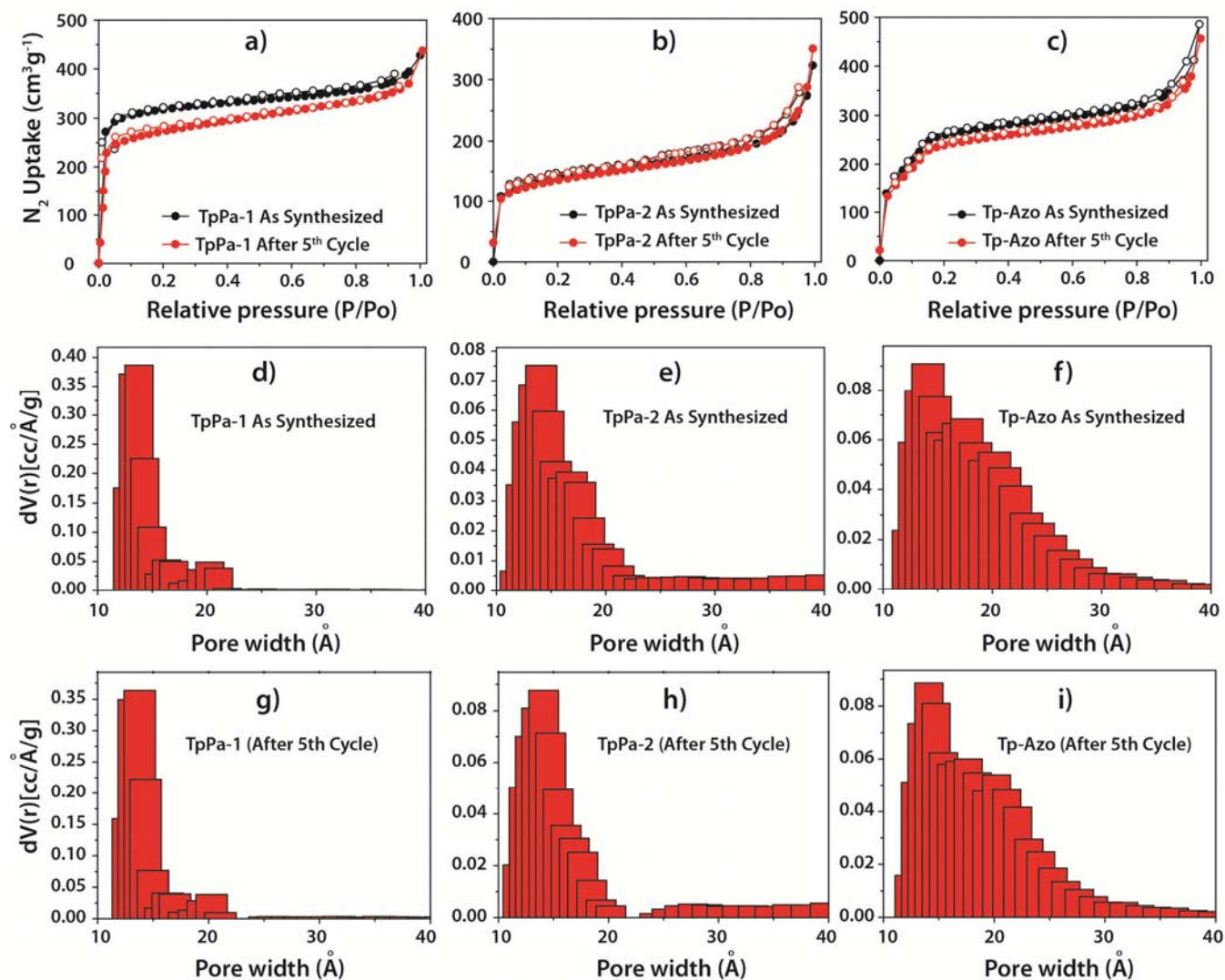


Figure S8. a), b) and c) N₂ adsorption isotherms of TpPa-1, TpPa-2 and Tp-Azo, before water adsorption (as synthesized) and after water adsorption (5th cycle); d), e), f), g), h) and i) pore size distribution of TpPa-1, TpPa-2 and Tp-Azo respectively before water adsorption (as synthesized) and after water adsorption (5th cycle).