Supporting Information

The Excited-State Intramolecular Proton Transfer Properties of Three Imine-Linked Two-Dimensional Porous Organic Polymers.

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A. Materials

All starting materials and reagents were obtained from commercial sources and used without further purification. Tetrahydrofuran (THF) was obtained from a solvent purification system (activated alumina columns) and used without further drying. All reactions were performed under nitrogen atmosphere, unless stated otherwise. Thin-layer chromatography (TLC) was conducted with SiliCycle glass backed 60 Å UV254 plates (0.25 mm) and visualized with UV lamps (254 nm). Flash chromatography was performed using normal phase Aldrich 40-63 μm 60 Å silica gel. ^{1}HNMR spectra were recorded in deuterated solvents on a Bruker Avance DPX 400 (400MHz). Chemical shifts are reported in parts per million (ppm, δ) using the solvent as internal standard.

B. Instrumentations and Methods

Infrared spectra were recorded on a Thermo Scientific Nicolet iS5 with a iD7 diamond ATR attachment and are uncorrected. UV-Vis/NIR absorbance spectroscopy was recorded on a Cary 5000 spectrophotometer using an internal DRA with stock powder cell holder to record % reflectance spectra. Emission spectra were recorded on a Cary Eclipse Fluorescence spectrophotometer equipped with a xenon flash lamp.

High-resolution solid-state ^{13}C NMR spectra were obtained at room temperature utilizing a Bruker DPX spectrometer operating at 75.5 MHz. The ^{13}C chemical shifts are reported with respect to adamantane (29.5 ppm) relative to the TMS at 0.00 ppm. The ^{13}C CP-MAS NMR spectra were collected using a two- channel probe in 4mm rotors spinning at 10 kHz. Data were collected by the routine cross polarization (CP-MAS) pulse sequence with a 2ms contact time. The proton decoupling field strength was constant at 100 kHz during the acquisition of the spectra, the relaxation delay was 2 sec, and 32k transients were collected. Data processing included 20 Hz line broadening.

Elemental analysis was performed by Galbraith Laboratories.

X-ray diffraction patterns were recorded on a Bruker D8 Powder X-Ray Diffractometer employing Cu K(α)1 line focused irradiation at 40 kV, 50 mA power and equipped with a Ge (111) monochromator. Samples were mounted on a zero background sample holder by dropping powders from a vial and then flattening them by firmly pressing the sample with a wide-blade spatula. No sample grinding was used prior to analysis. The holder was then placed on the mounting apparatus in the diffractometer. Data was collected after a 12 minute delay time using a 0.015 ° 2θ step scan from 1-34 ° with an exposure timer of 2-3 sec per step.

Scanning electron microscopy (SEM) was performed on a FEI Sirion XL-30-SEM. Materials were deposited onto a film of wet colloidal silver paint on an aluminum sample stub and dried in a vacuum oven at 40 °C. The samples were coated with iridium in a Leica EM ACE600 coater, using rotation, to a depth of approximately 10 nm. After coating the samples were imaged in the SEM with an accelerating voltage of 15 kV, without tilting, using both the secondary electron (SE) detector and the through lens detector (TLD).

Surface area measurements

Surface area measurements were conducted on a Micromeritics TriStar II 3020 Surface Area and Porosity Analyzer using ca. 20 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 non-local density functional theory (NLDFT) model (cylinder pore, N_2-cyclindrical pores-oxide surface with high regularization) in the instrument software (Micromeritics TriStar II 3020 Version 3.02).

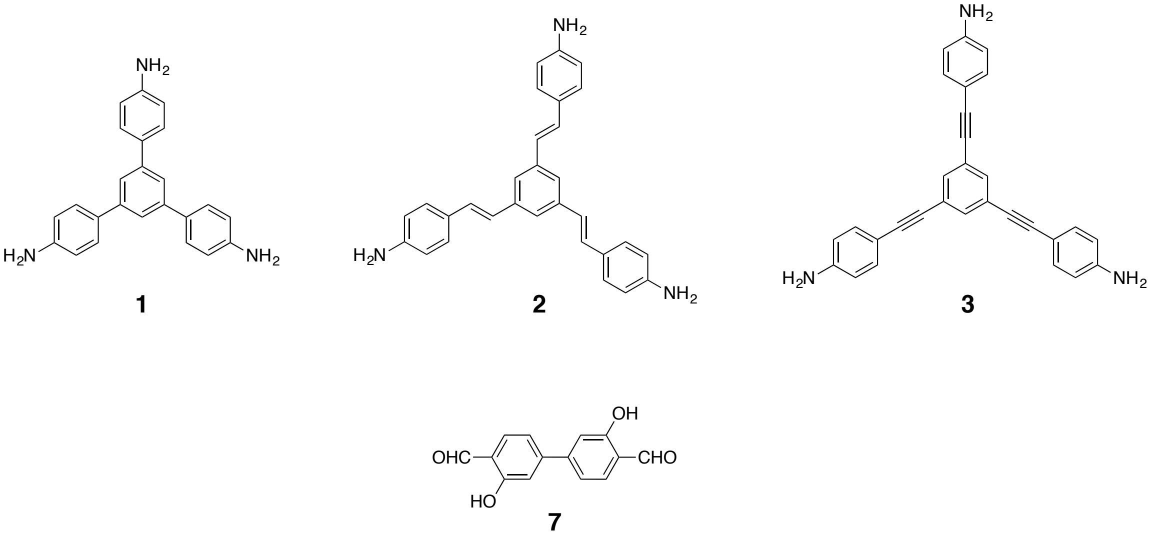
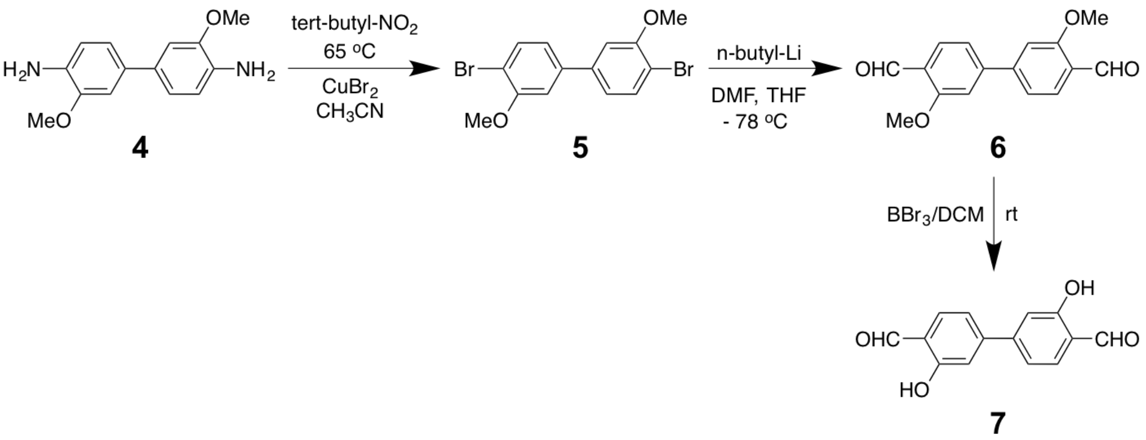


Figure S1. Structures of monomers **1-3** and **7**.

C. Synthetic Methods

Compounds 1-3: Compounds **1-3** were synthesized by following a known literature procedure.[1]



Scheme S1. Synthesis of 3,3'-dihydroxy-[1,1'-biphenyl]-4,4'-dicarbaldehyde (**7**).

4,4'-dibromo-3,3'-dimethoxy-1,1'-biphenyl (5): Compound **5** was prepared by the modification of a known literature procedure.[2] To a flame dried flask under nitrogen, $CuBr_2$ (0.84 g, 3.7251 mmol, 1.3 eq.), tert-butylnitrite (0.42 mL, 3.4384 mmol, 1.2 eq.), and 20 mL acetonitrile were charged. To the above suspension a solution of **4** (0.7 g, 2.8654 mmol) in acetonitrile (40 mL) was added in a dropwise manner over about 10 minutes. The reaction mixture was stirred at room temperature for 30 min and at 65 °C for 15 min. Then cooled to room temperature and distilled off the solvent completely and added 50 mL EtOAc. The EtOAc layer was washed twice with 30 mL D.I. water, dried with anhydrous sodium sulfate and evaporated the solvent completely. The crude solid was eluted through a silica gel column chromatography (mobile phase: hexanes/ethyl acetate) to obtain the pure product as a white solid (0.74 g, 1.9889 mmol, 70 % yield).

3,3'-dimethoxy-[1,1'-biphenyl]-4,4'-dicarbaldehyde (6): Compound **6** was prepared by following a known literature procedure.[3]

3,3'-dihydroxy-[1,1'-biphenyl]-4,4'-dicarbaldehyde (7): Compound **7** was prepared by the modification of a known literature procedure.[3] To a flame dried flask under nitrogen, **6** (1.1 g, 4.0699 mmol) and 100 mL dichloromethane were charged. The solution was cooled to -78 °C. To the above solution 2 mL of BBr_3 was added in a drop wise manner over about 10 min. The solution was stirred at room temperature for 12 h. Then added 30 mL D.I. water to quench the excess BBr_3. Then distilled off the dichloromethane completely and added 60 mL EtOAc. The EtOAc layer was washed twice with 40 mL D.I. water, dried with anhydrous sodium sulfate and evaporated the solvent completely. The crude solid was eluted through a silica gel column chromatography (mobile phase: hexanes/ethyl acetate) to obtain the pure product as a pale yellow solid (0.53 g, 2.1880 mmol, 54 % yield).

General Solvothermal Conditions for POPs synthesis: Triamine and **7** monomers were combined in a 10.6 cm x 1.8 cm (L x W), 10 mL prescored ampule (Sigma-Z184985). Solvent and 6 M AcOH were then added and the suspension was sonicated for 5 minutes before freezing in a liquid nitrogen bath. The solution was then degassed using standard freeze-pump-thaw (3 cycles) procedures and sealed under vacuum (~150 mTorr), which subsequently reduces the ampule to 8.5 cm (L) upon sealing, and placed in the oven for 3 days. After the reaction is complete the POPs were allowed to cool to room temperature, filtered, washed with acetone, dichlorobenzene and THF and suspended in THF for 2 days. Then filtered, washed with THF and dried under high vacuum for 6 hours to remove most of the residual solvent before being activated on the Micromeritics TriStar II 3020 for further analysis.

TSA-POP 1: A mixture of **2** (21.5 mg, 0.05 mmol, 1 equiv.), **7** (18.2 mg, 0.075 mmol, 1.5 equiv.) and 0.2 mL 6M AcOH in dimethyacetamide (DMA)/toluene (0.5:1.5 mL) was sonicated in a 10 mL prescored glass ampule for 5 min. Note: Solid product crashed out during sonication. The suspension was then degassed via 3 freeze-pump-thaw cycles at 77 K before sealing under vacuum. After warming to room temperature the ampule was placed in a gravity convection oven at 120 ^{o}C for 72 hours. The ampule was then allowed to cool to room temperature and solids were filtered, washed with acetone, dichlorobenzene and THF and suspended in THF for 2 days. Then filtered, washed with THF and under high vacuum for 6 hours to remove most of the residual solvent to give a yellow solid (23.3 mg).

FT-IR (powder, ATR) 1612, 1582, 1504, 1353, 1189, 1168, 958, 908, 844, 804, 528 cm-1. Elemental Analysis for $(C_{102}H_{72}N_6O_6)_n$: Calculated: C (82.9%), H (4.9%), N (5.7%); Observed: C (80.6%), H (5.3%), N (5.4%).

Table S1. Screening conditions for TSA-POP 1:

2 (Vertex)	7 (Linker)	2:7 ratio	Solvent Conditions	6M ACOH	Surface Area (m^2/g)
0.05	0.075	1:1.5	2 mL Dioxane	0.1 mL	457
0.05	0.075	1:1.5	1.5 mL/1.5 mL Dioxane:Mesitylene	0.1 mL	112
0.05	0.075	1:1.5	2 mL/1 mL Dioxane:Mesitylene	0.1 mL	181
0.05	0.075	1:1.5	3 mL Dioxane	0.1 mL	223
0.05	0.075	1:1.5	2 mL Dioxane (90 ^{0}C)	0.3 mL	42
0.05	0.075	1:1.5	2 mL Dioxane	0.3 mL 9 M AcOH	123
0.05	0.075	1:1.5	2 mL THF (75 ^{o}C)	0.1 mL	186
0.05	0.075	1:1.5	0.25 mL DMA/0.75 mL Mesitylene	0.1 mL	361
0.05	0.075	1:1.5	0.25 mL DMA/0.75 mL 1,2-Diclorobenzene		304
0.05	0.075	1:1.5	0.5 mL DMA/1.5 mL Mesitylene	0.2 mL	510
0.05	**0.075**	**1:1.5**	**0.5 mL DMA/1.5 mL Toluene**	**0.2 mL**	**601**
0.05	0.075	1:1.5	0.5 mL DMA/1.5 mL 1,2-Diclorobenzene	0.2 mL	592
0.04	0.08	1:2	0.5 mL DMA/1.5 mL 1,2-Diclorobenzene	0.2 mL	478
0.04	0.07	1:1.75	0.5 mL DMA/1.5 mL 1,2-Diclorobenzene	0.2 mL	430
0.05	0.075	1:1.5	0.25 mL DMA/ 0.25 mL Dioxane/1.5 mL Toluene	0.2 mL	405
0.05	0.075	1:1.5	2 mL DMA	0.2 mL	452

TSA-POP 2: A mixture of **1** (17.6 mg, 0.05 mmol, 1 equiv.), **7** (18.2 mg, 0.075 mmol, 1.5 equiv.) and 0.2 mL 6M AcOH in dimethyacetamide (DMA)/mesitylene (0.5:1.5 mL) was sonicated in a 10 mL prescored glass ampule for 5 min. Note: Solid product crashed out during sonication. The suspension was then degassed via 3 freeze- pump-thaw cycles at 77 K before sealing under vacuum. After warming to room temperature the ampule was placed in a gravity convection oven at 120 ^{o}C for 72 hours. The ampule was then allowed to cool to room temperature and filtered, washed with acetone, dichlorobenzene and THF and suspended in THF for 2 days. Then filtered, washed with THF and dried under high vacuum for 6 hours to remove most of the residual solvent to give a yellow solid (17 mg).

FT-IR (powder, ATR) 1614, 1590, 1506, 1353, 1191, 1174, 908, 829, 799, 539 cm-1. Elemental Analysis for $(C_{90}H_{60}N_6O_6)_n$: Calculated: C (81.8%), H (4.6%), N (6.4%); Observed: C (51.7%), H (3.5%), N (3.9%).

Table S2. Screening conditions for TSA-POP 2:

1 (Vertex)	7 (Linker)	1:7 ratio	Solvent Conditions	6M ACOH	Surface Area (m^2/g)
0.04	0.08	1:2	0.5 mL DMA/1.5 mL Mesitylene	0.2 mL	287
0.04	0.08	1:2	0.25 mL DMA/1 mL Mesitylene	0.2 mL	363
0.04	0.08	1:2	0.5 mL DMA/1.5 mL Toluene	0.2 mL	320
0.04	0.08	1:2	0.5 mL DMA/1.5 mL 1,2-Diclorobenzene	0.2 mL	290
0.04	0.08	1:2	0.5 mL DMA/1.5 mL 1,2-Diclorobenzene	0.2 mL 9 M AcOH	257
0.05	0.075	1:1.5	0.5 mL DMA/1.5 mL Toluene	0.2 mL	133
0.05	**0.075**	**1:1.5**	**0.5 mL DMA/1.5 mL 1,2-Diclorobenzene**	**0.2 mL**	**427**
0.04	0.08	1:2	0.25 mL DMA/0.75 mL Mesitylene	0.1 mL	398
0.04	0.08	1:2	1 mL Dioxane/1mL Mesitylene	0.2 mL	275

TSA-POP 3: A mixture of **3** (21.2 mg, 0.05 mmol, 1 equiv.), **7** (18.2 mg, 0.075 mmol, 1.5 equiv.) and 0.2 mL 6M AcOH in dimethyacetamide (DMA)/1,2-dichlorobenzene (0.5:1.5 mL) was sonicated in a 10 mL prescored glass ampule for 5 min. Note: Solid product crashed out during sonication. The suspension was then degassed via 3 freeze-pump-thaw cycles at 77 K before sealing under vacuum. After warming to room temperature the ampule was placed in a gravity convection oven at 95 ^{o}C for 72 hours. The ampule was then allowed to cool to room temperature and filtered, washed with acetone, dichlorobenzene and THF and suspended in THF for 2 days. Then filtered, washed with THF and dried under high vacuum for 6 hours to remove most of the residual solvent to give a yellow solid (31.7 mg).

FT-IR (powder, ATR) 1612, 1560, 1541, 1350, 1187, 1169, 907, 835, 794, 543 cm-1. Elemental Analysis for $(C_{102}H_{60}N_6O_6)_n$: Calculated: C (83.6%), H (4.1%), N (5.7%); Observed: C (82.1%), H (7.7%), N (3.7%).

Table S3. Screening conditions for TSA-POP 3:

3 (Vertex)	7 (Linker)	3:7 ratio	Solvent Conditions	6M ACOH	Surface Area (m^2/g)
0.05	0.075	1:1.5	1 mL Dioxane	0.1 mL	22
0.05	0.075	1:1.5	0.25 mL DMA/0.75 mL 1,2-Diclorobenzene	0.1 mL 75 °C	32
0.05	0.075	1:1.5	0.5 mL DMA/ 1.5 mL Mesitylene	0.1 mL 95 °C	32
0.05	0.075	1:1.5	1 mL Dioxane / 1 mL Mesitylene	0.3 mL 9 M AcOH, 105 °C	33
0.05	0.075	1:1.5	0.5 mL DMA/ 1.5 mL Toluene	0.2 mL 105 °C	38
0.05	0.075	1:1.5	0.5 mL DMA/ 1.5 mL 1,2-Diclorobenzene	0.2 mL 105 °C (7 days)	94
0.05	0.075	1:1.5	0.5 mL DMA/ 1.5 mL Toluene	0.2 mL 105 °C (7 days)	123
0.05	0.075	1:1.5	0.5 mL DMA/ 1.5 mL 1,2-Diclorobenzene	0.2 mL 95 °C	112
0.05	0.075	1:1.5	0.3 mL DMA/ 1.7 mL 1,2-Diclorobenzene	0.2 mL 95 °C	Non porous
0.05	**0.075**	**1:1.5**	**0.5 mL DMA/ 1.5 mL 1,2-Diclorobenzene**	**0.2 mL** **95 °C**	**135**

D. TGA Analysis

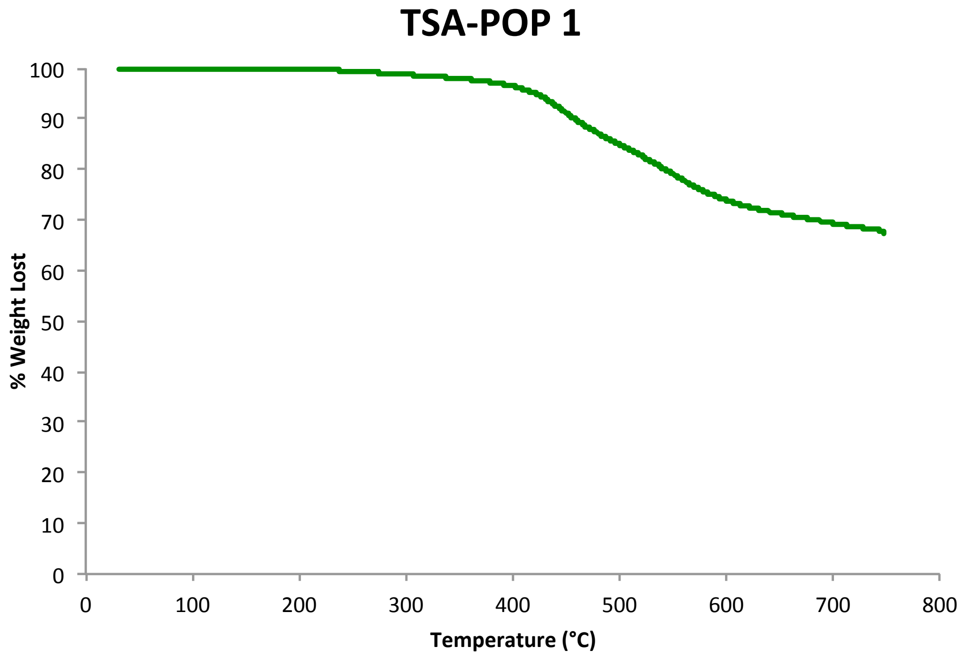


Figure S2. TGA plot for TSA-POP 1.

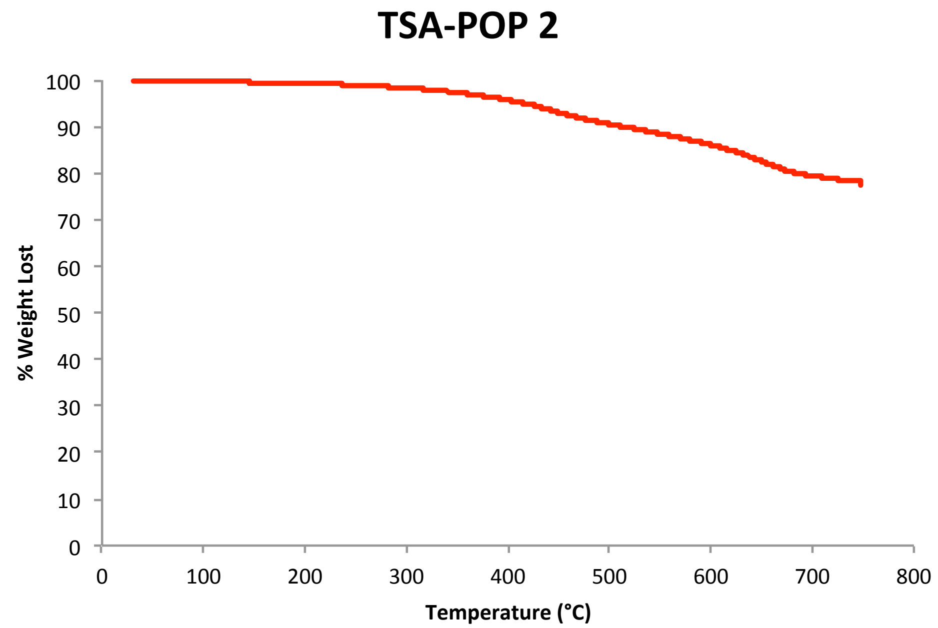


Figure S3. TGA plot for TSA-POP 2.

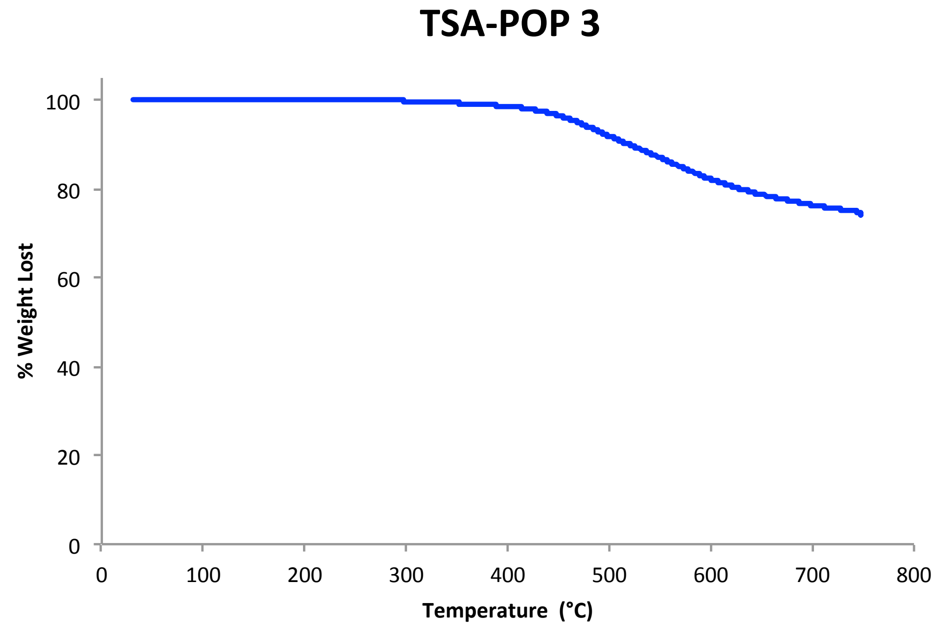


Figure S4. TGA plot for TSA-POP 3.

E. SEM Images

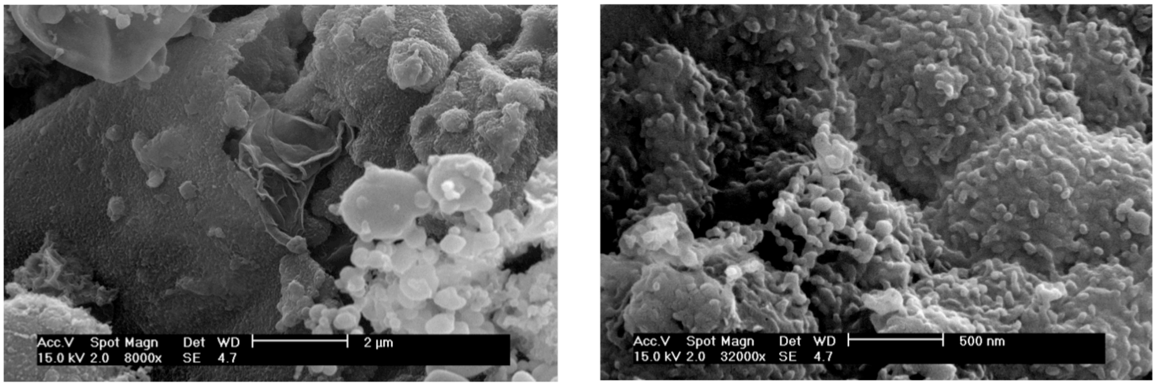


Figure S5. SEM images of TSA-POP 1.

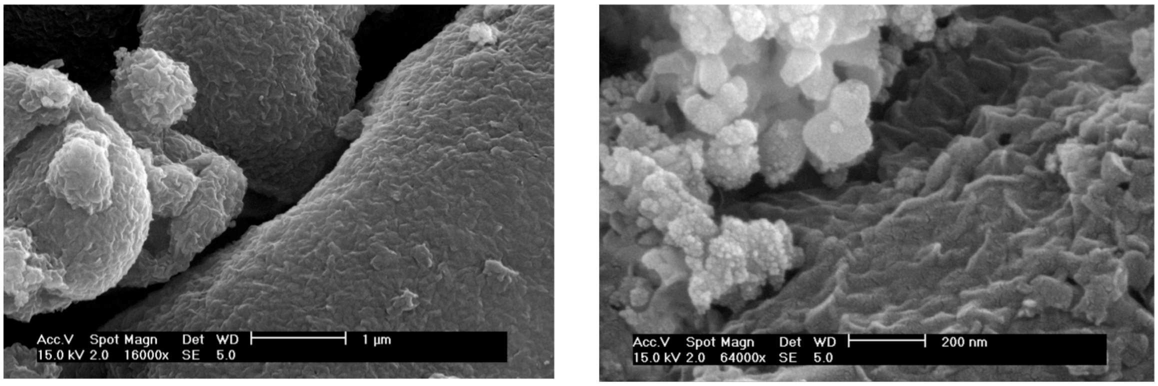


Figure S6. SEM images of TSA-POP 2.

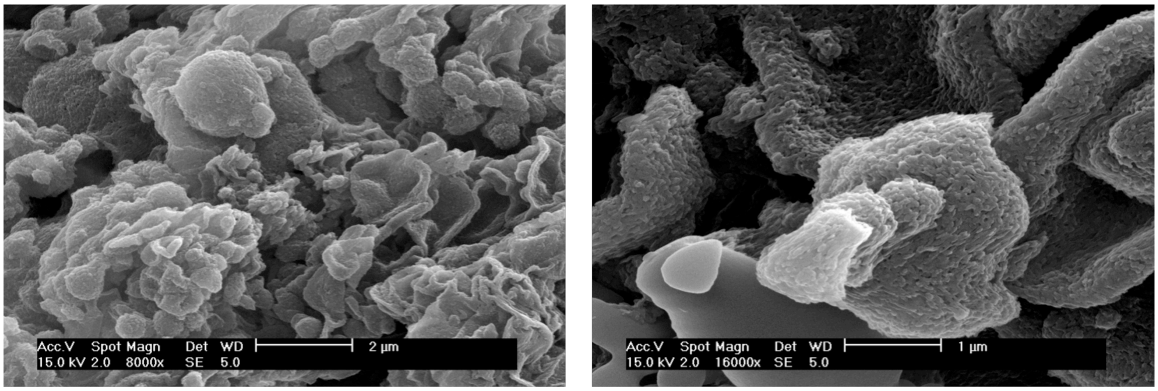


Figure S7. SEM images of TSA-POP 3.

F. FT-IR Spectra

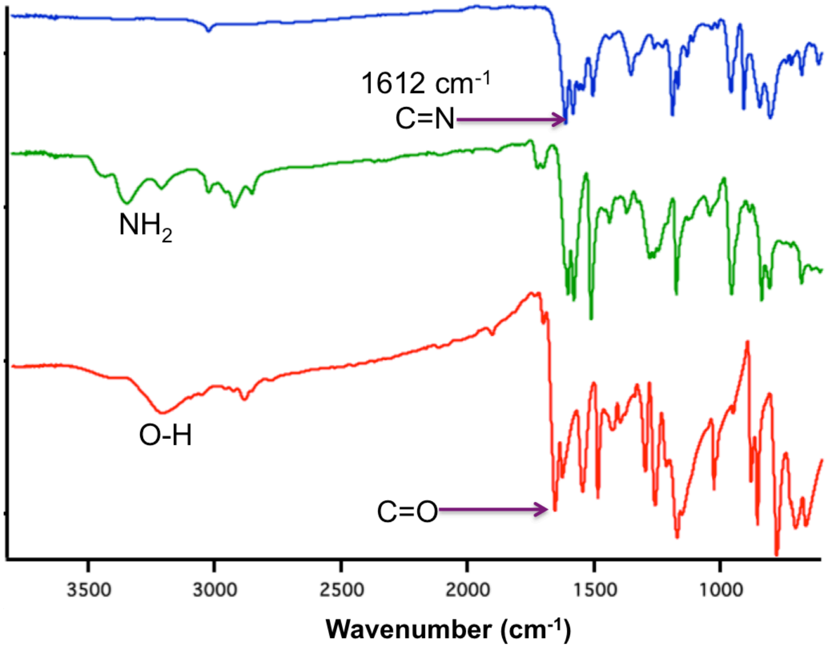


Figure S8. FT-IR of TSA-POP 1 (blue), **2** (green) and **7** (red).

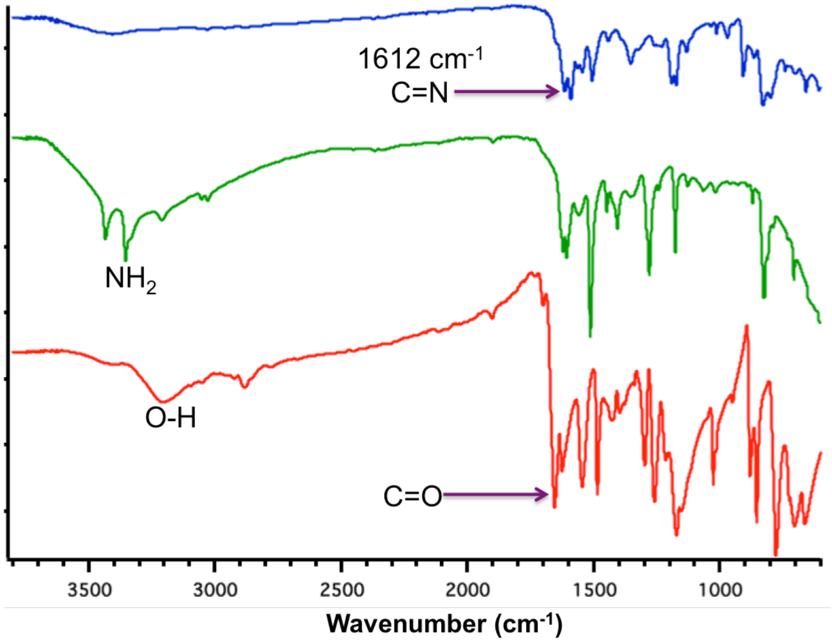


Figure S9. FT-IR of TSA-POP 2 (blue), **1** (green) and **7** (red).

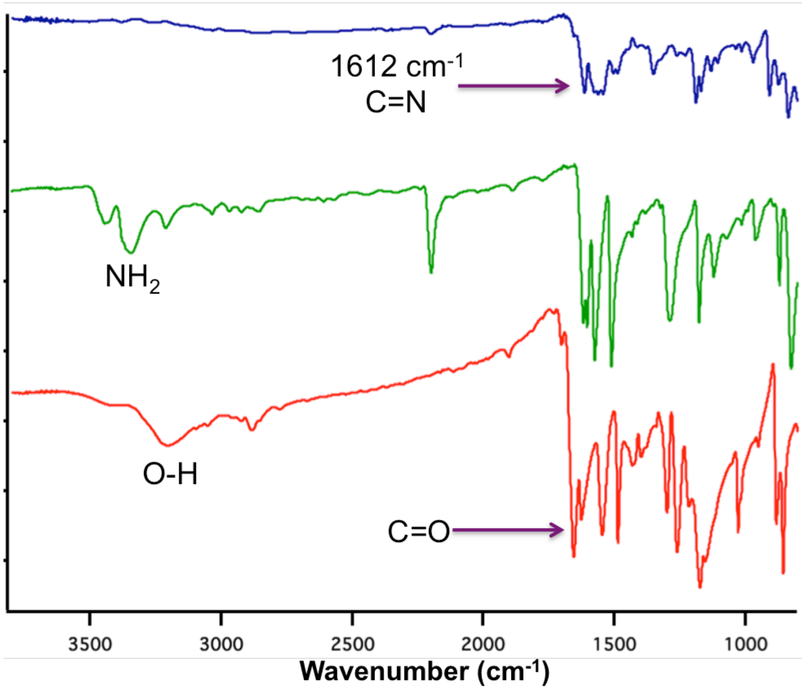


Figure S10. FT-IR of TSA-POP 3 (blue), **3** (green) and **7** (red).

G. Solid state ^{13}C NMR Spectra

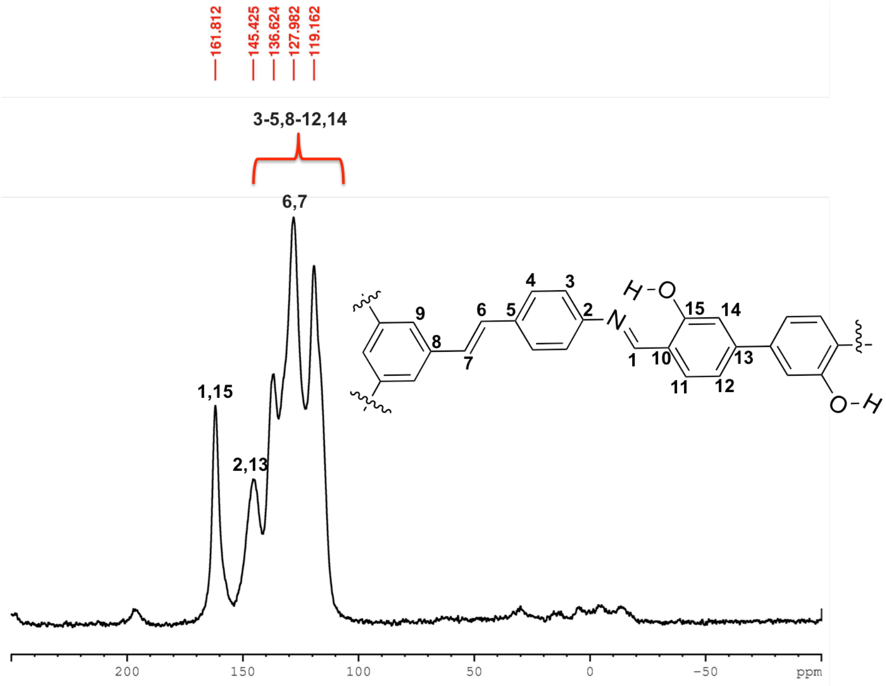


Figure S11. ^{13}C CP-MAS 75 MHz solid-state NMR spectrum of TSA-POP 1.

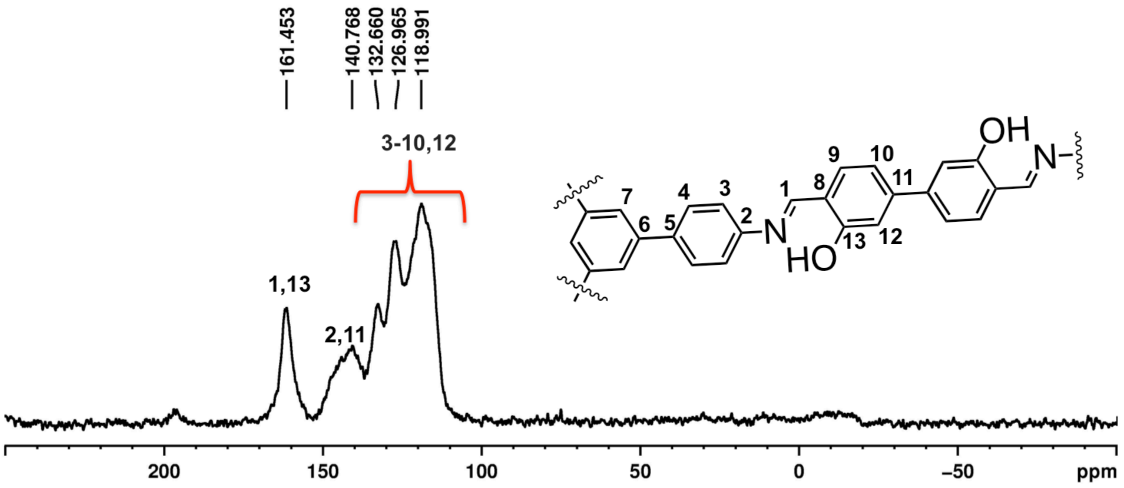


Figure S12. ^{13}C CP-MAS 75 MHz solid-state NMR spectrum of TSA-POP 2.

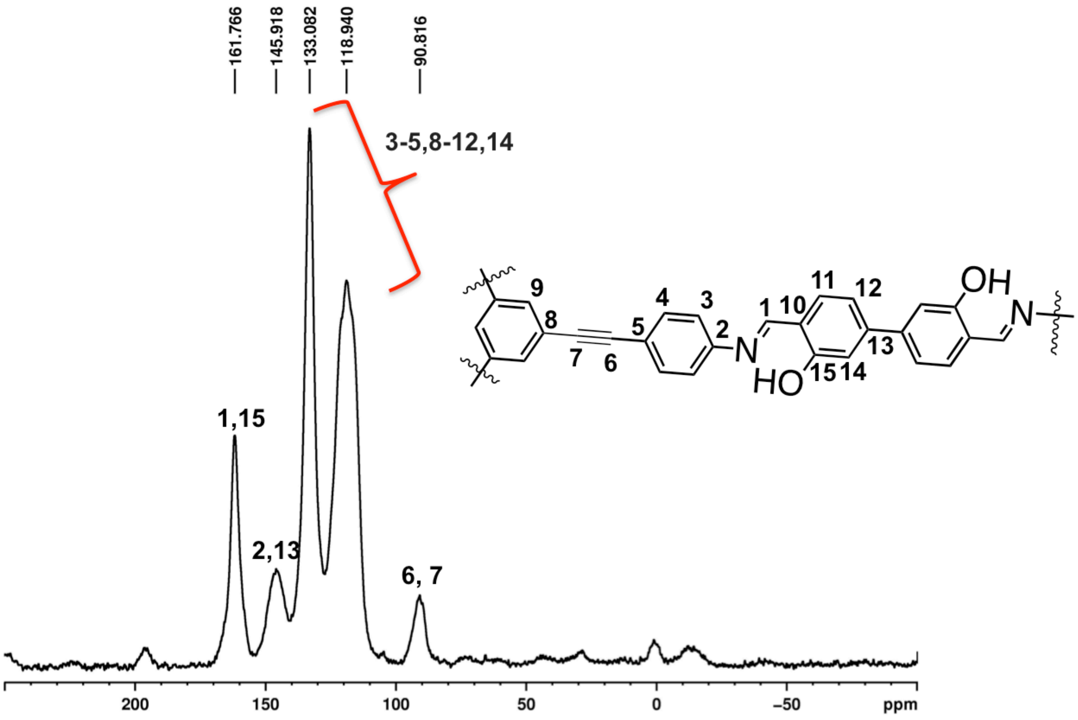


Figure S13. ^{13}C CP-MAS 75 MHz solid-state NMR spectrum of TSA-POP 3.

H. Experimental PXRD

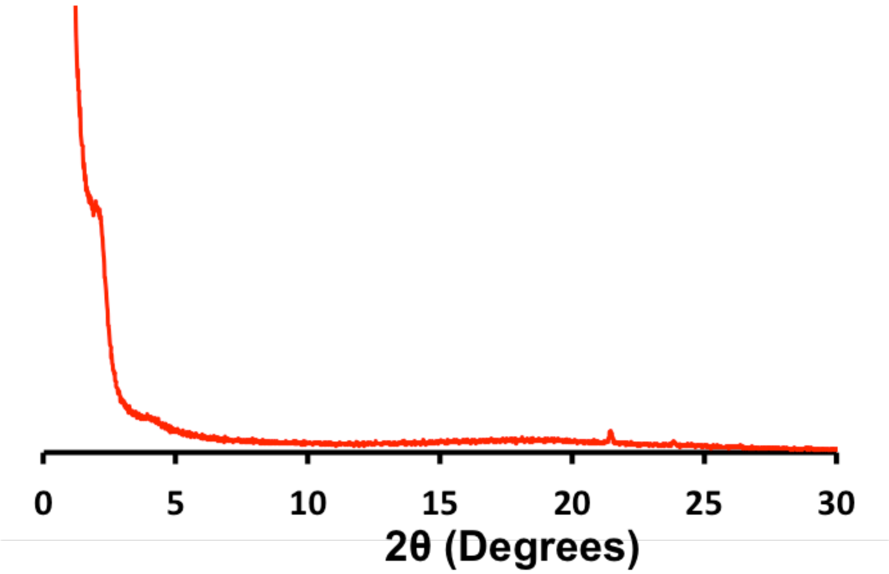


Figure S14. PXRD of TSA-POP 1.

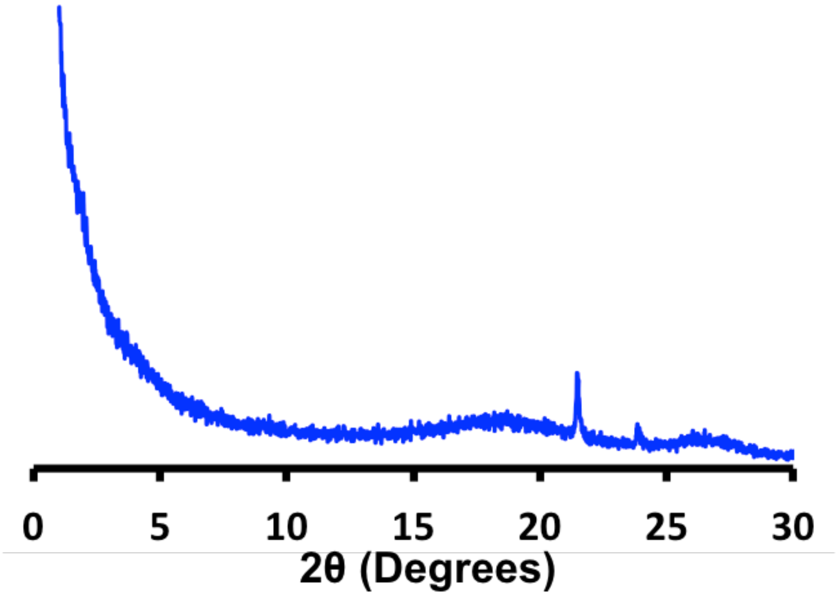


Figure S15. PXRD of TSA-POP 2.

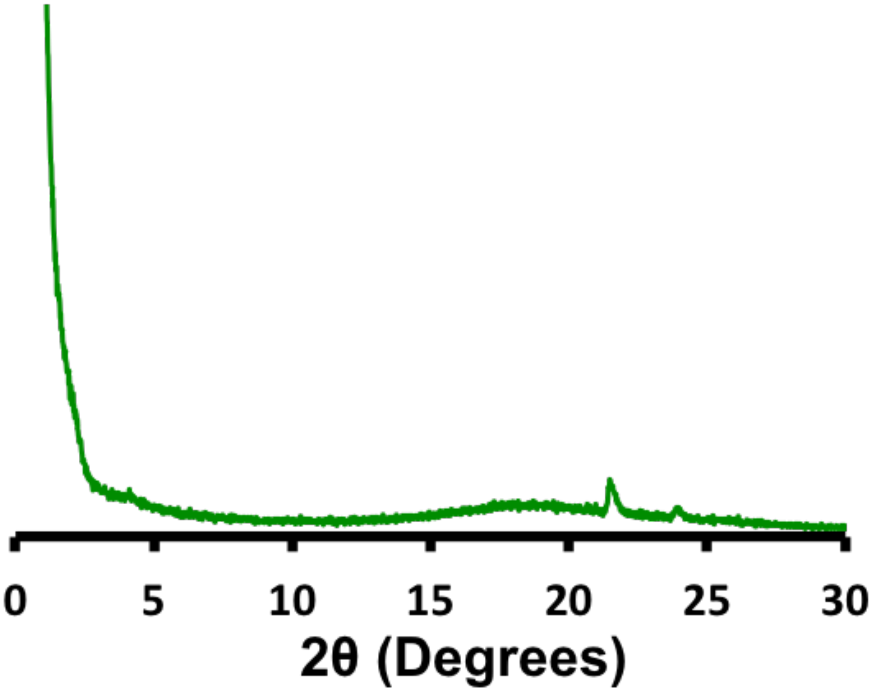


Figure S16. PXRD of TSA-POP 3.

I. UV-vis and Fluorescence Spectra

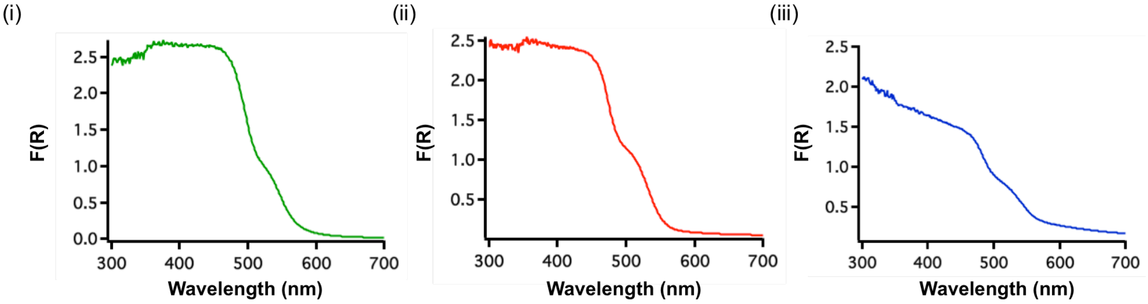


Figure S17. Diffuse reflectance spectra of (i) TSA-POP 1, (ii) TSA-POP 2 and (iii) TSA-POP 3.

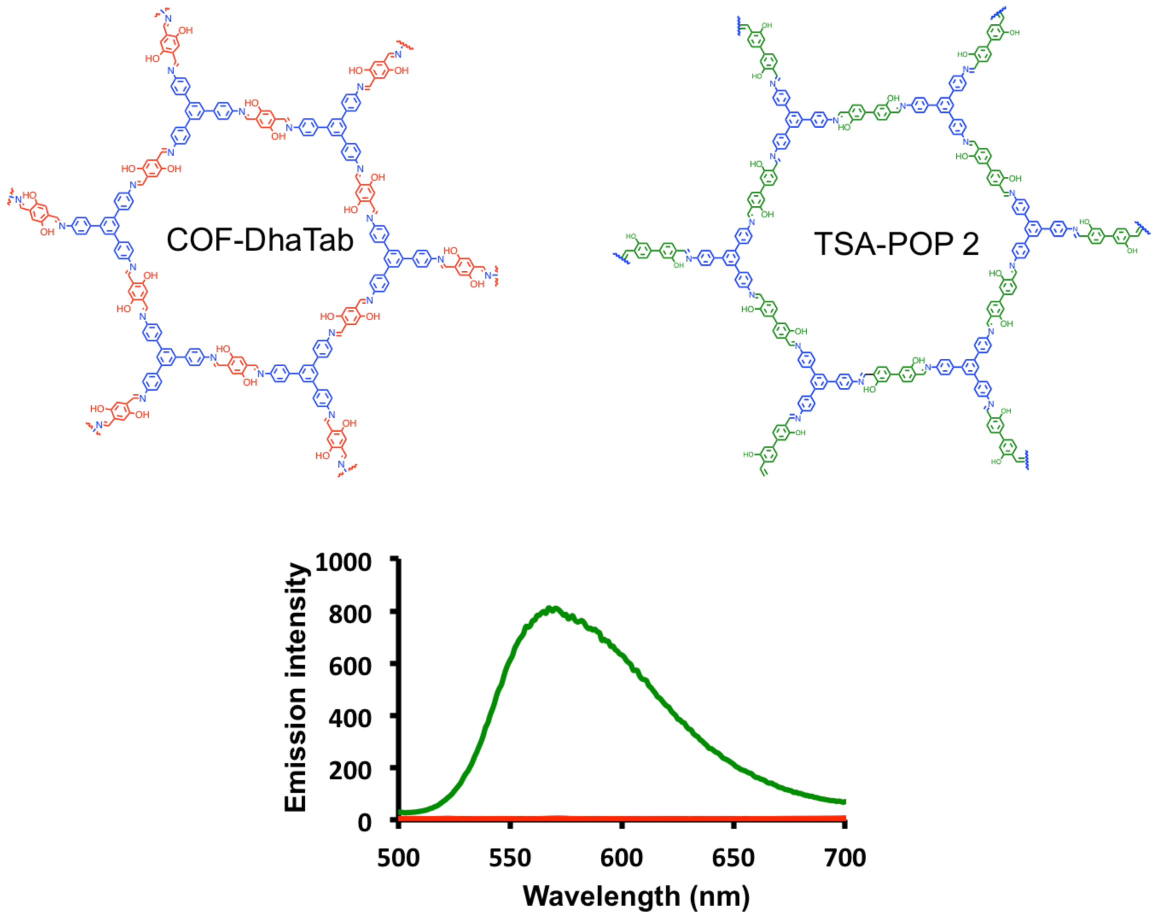


Figure S18. Solid-state emission spectra of COF-DhaTab (red) and TSA-POP 2 (green) (λ_{ex} = 360 nm). COF-DhaTab was synthesized by following a known literature procedure.[4]

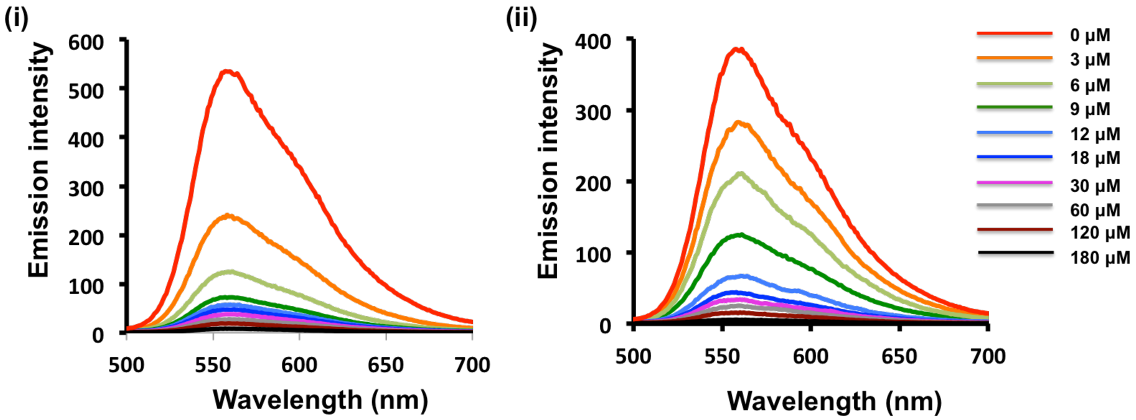


Figure S19. Quenching of emission upon the addition of (i) Cu^{2+} (30 mM in DMSO) and (ii) Pd^{2+} (30 mM in DMSO) to the suspensions of TSA-POP 1 in THF (λ_{ex} = 370 nm).

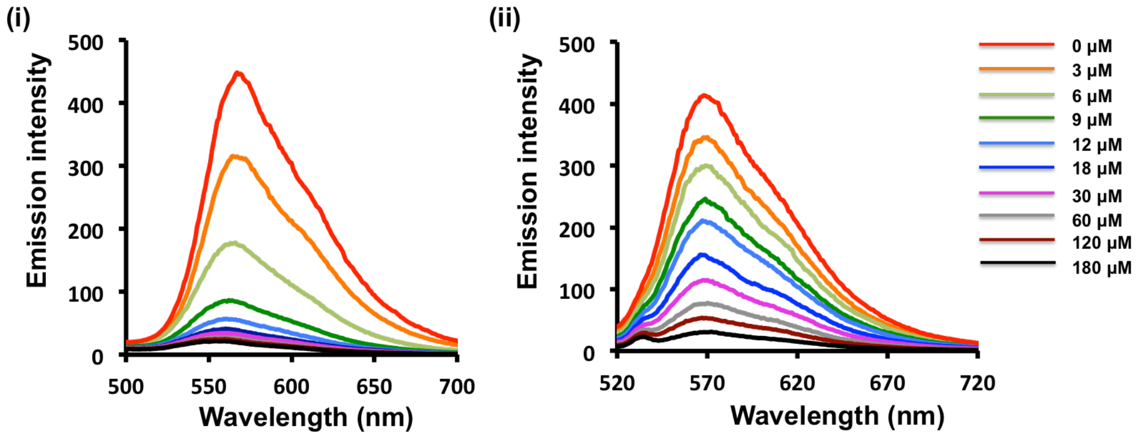


Figure S20. Quenching of emission upon the addition of (i) Cu^{2+} (30 mM in DMSO) and (ii) Pd^{2+} (30 mM in DMSO) to the suspensions of TSA-POP 2 in THF (λ_{ex} = 360 nm).

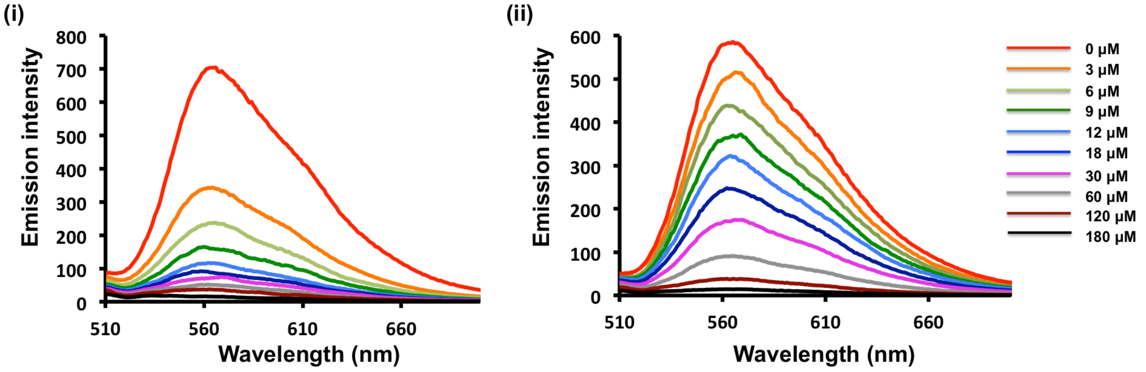


Figure S21. Quenching of emission upon the addition of (i) Cu^{2+} (30 mM in DMSO) and (ii) Pd^{2+} (30 mM in DMSO) to the suspensions of TSA-POP 3 in THF (λ_{ex} = 360 nm).

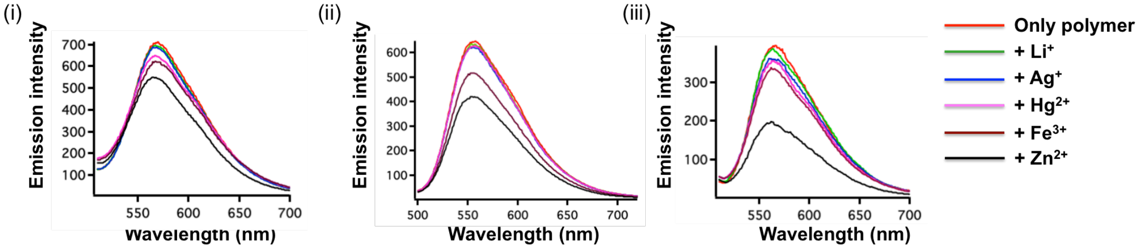


Figure S22. Addition of various metal ions (180 μM) to a suspension of (i) TSA-POP 1 (λ_{ex} = 370 nm), (ii) TSA-POP 2 (λ_{ex} = 360 nm), and (iii) TSA-POP 3 (λ_{ex} = 360 nm) in THF.

J. Surface Area Analysis

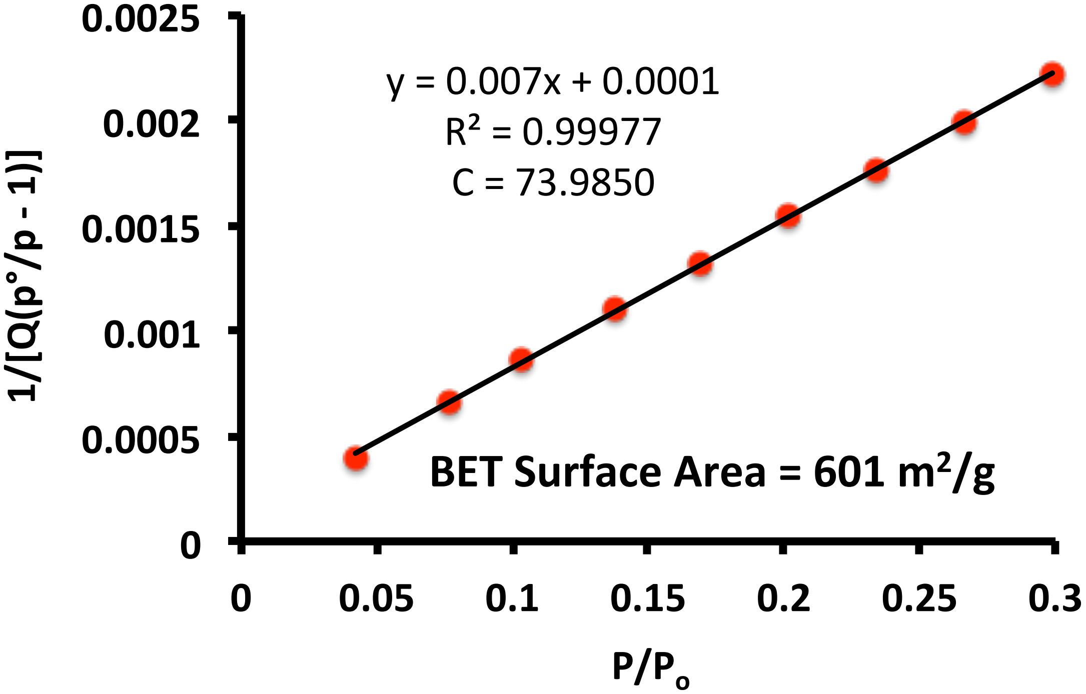


Figure S23. BET surface area plot for TSA-POP 1.

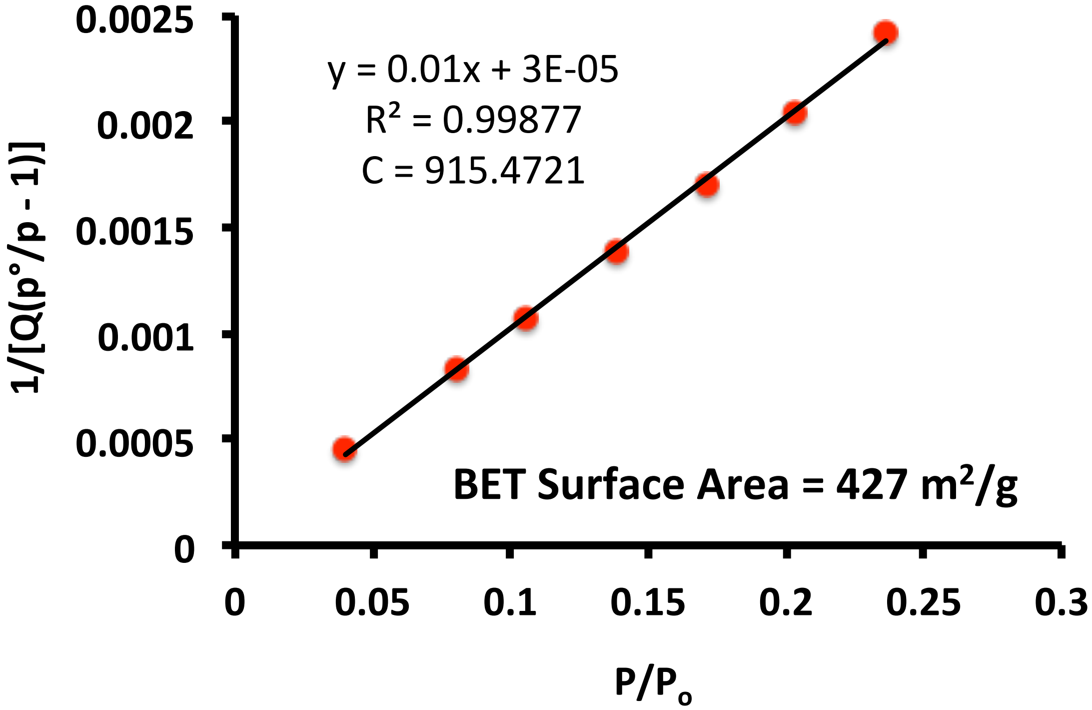


Figure S24. BET surface area plot for TSA-POP 2.

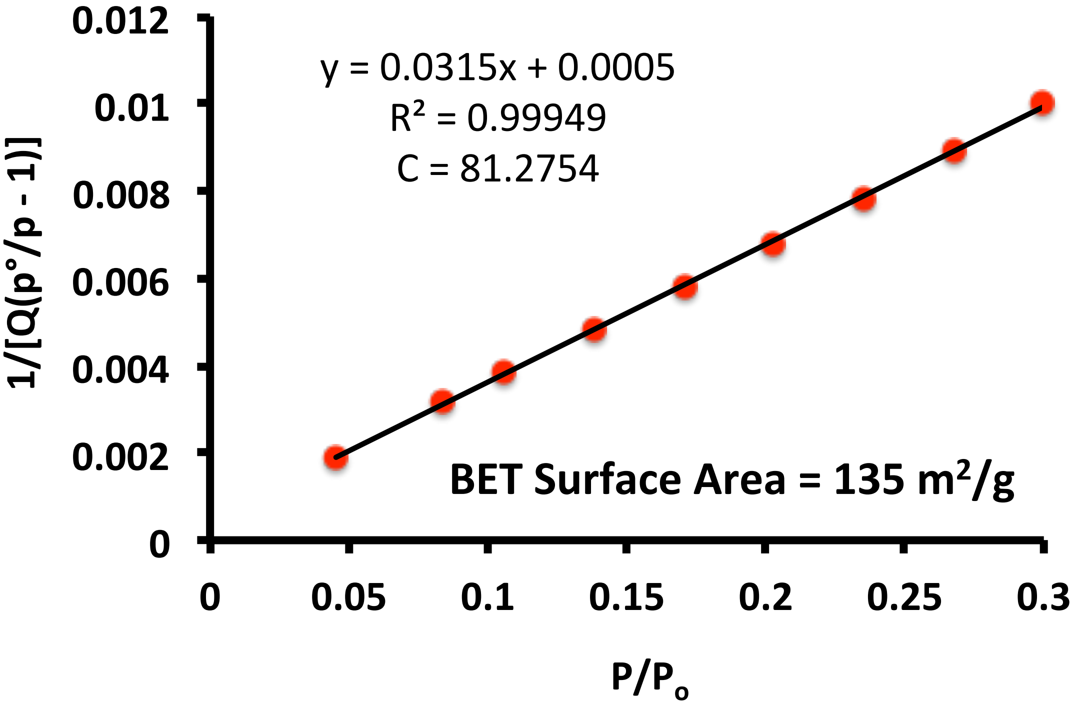


Figure S25. BET surface area plot for TSA-POP 3.

K. References

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