Electronic Supplementary Material (ESI) for Chemical Science.

Controlled Growth of Imine-Linked Covalent Organic Framework Nanoparticles

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Supplementary Information

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A. Materials and Instrumentation

Materials. Reagents were purchased in reagent grade from commercial suppliers and used without further purification, unless otherwise described. Anhydrous MeCN was obtained from a solvent purification system (JC Meyer System) with alumina-based drying columns. 1,3,5-Tris(4-aminophenyl)benzene (TAPB) and scandium triflate were purchased from TCI. Terephthaldehyde (PDA) was purchased from Sigma Aldrich. 4,4'-Biphenyldicarbaldehyde (BDA) was purchased from TCI.

Instrumentation.

Dynamic Light Scattering

Dynamic light scattering (DLS) samples were prepared by diluting COF colloid samples in MeCN to create a two-volume percent colloid solution. A Malvern Zetasizer with a 633 nm He-Ne 5mW laser was used to collect the data at room temperature with 10 mm pathlength quartz cuvette. The data was analyzed using the Zetasizer software.

X-Ray Diffraction

Powder X-ray diffraction patterns were collected with a STOE-STADI MP powder diffractometer in transmission geometry with CuKα1 radiation. Samples are mounted in a rotating holder secured between acetate foils. The instrument uses an asymmetric curved germanium monochromator and silicone strip detector and line focused Cu X-ray tube.

Small-angle and wide-angle X ray scattering (SAXS / WAXS) were collected at sectors 5-ID-D and 12-ID-D of the Advanced Photon Source at Argonne National Lab. A beam energy 13.3 keV was used at 5-ID-D and 12.0 keV was used at 12-ID-D. Each pattern was obtained by collecting ten one second frames on a Pilatus 2D detector and then averaged and radially integrated using software available at APS. Borosilicate capillaries that are 1.5 mm in diameter and a wall thickness of 0.01 mm were purchased from Charles Supper.

Modeling and Structural Refinement

Materials Studio Version 4.2 was used to construct COF structures initially with a primitive hexagonal unit cell and a P6 space group. The geometry was optimized using the Forcite software package with parameters from the Universal Force Field. The Reflex software package was used to carry out the Pawley refinement on the geometrically optimized structure. The patterns were subjected to refinement with the pseudo-Voigt profile function until RWP value reaches convergence. The refined unit cell was used to calculate the XRD patterns and compared with the experimentally obtained patterns.

Scanning Electron Microscopy

COF colloid samples were drop casted onto a silicon wafer substrate and the solvent was allowed to evaporate at room temperature. The silicon wafer was attached to flat aluminum sample holder and COF colloids were coated with 9 nm of Osmium and imaged with a SEM Hitachi SU8030

Transmission Electron Microscopy

Samples were drop cast onto a formvar grid, and the solvent was allowed to evaporate at room temperature. Samples were then loaded onto a single tilt TEM holder. TEM images were taken using a JEOL ARM300F GrandARM TEM equipped with a Gatan OneView-IS camera with an acceleration voltage of 300 kV and an emission current of 15 μA.

Atomic Force Microscopy

Samples were diluted and drop casted on silicon wafer. Micrographs were taken on the Bruker Dimension FastScan Atomic Force Microscope using tapping mode.

FT-IR

Infrared spectra were collected on a Nicolet iS10 FT-IR spectrometer with a ZnSe ATR attachment.

Gas Adsorption

Gas adsorption isotherms were collected with a Micromeritics ASAP 2420 accelerated surface area and porosity analyzer. The mass of an activated sample was determined by the difference between the mass of the sample and an analysis tube after degassing procedure and the mass of an empty and dried analysis tube. An analysis tube includes a filler rod and a Transeal cap. The degassing procedure consists of heating the sample to 40 °C at a rate of 1 °C/min, then pumping under vacuum at 40 °C for 20 minutes, then heating to 100 °C at a rate of 1 °C/min and pumping under vacuum at 100 °C for 5 hours. Gas adsorption measurements was performed using UHP grade N_2. Surface area parameters were determined by using BET adsorption models and pore width distributions were determined using DFT models available within the instrument software.

Syringe Pump

Syringe pumps used for monomer addition are KD Scientific Model 100.

Critical Point Dryer

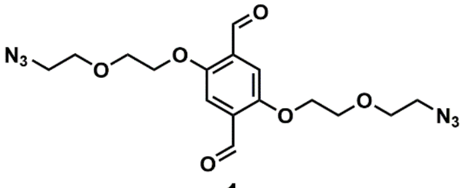
Supercritical point drying was performed with an automated critical point dryer Leica EM CPD 300. Prior to drying process, all samples were loaded into tea bags (ETS Drawstring Tea Filters sold by English Tea Store on Amazon.com) and subjected to Soxhlet extraction with methanol. The drying chamber was first cooled to 15 °C and then filled with liquid CO_2 with speed “slow” and delay time to be “120s”. The chamber subsequently undergoes 45 exchange cycles with speed of “5”. Finally, the chamber was heated to 40 °C with a speed of “medium” and the pressure was let out at a rate of “slow 50%”.

Sonication

Branson 3510 ultrasonic cleaner with a power output of 100W and a frequency of 42 kHz was used for sonication.

B. Experimental Protocols

Functionalized PDA Monomer



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PDA functionalized with azide-terminated diethylene glycol chains was synthesized from a reported procedure.[1]

Synthesis of TAPB – PDA COF Colloidal Seeds with 0.16 equiv of $Sc(OTf)_3$

TAPB (0.424 mmol, 149 mg) and PDA (0.634 mmol, 85.0 mg) were added to MeCN (100 mL) and the solution was sonicated briefly to dissolve the monomers. Scandium triflate (0.203 mmol, 100 mg) was subsequently added and sonicated for 10 seconds to dissolve and disperse the catalyst. The reaction mixture was left at room temperature and reacted for 20 hours before further manipulation.

In situ TAPB-PDA COF Colloid Formation over Time

Separate stock solutions of TAPB (1.00 mL, 17.0 mM) and PDA (2.16 mL, 11.8 mM) in MeCN were prepared and combined accordingly to the specified volume. A solution of $Sc(OTf)_3$ (0.80 mL, 10.2 mM) in MeCN was added, and then the mixture was shaken to ensure efficient mixing, which we defined as t=0 for the experiment. Approximately 100 µL of the solution was added to a borosilicate capillary and SAXS/WAXS patterns were collected as the reaction proceeded without moving the capillary.

SAXS / WAXS Modeling

The small angle scattering (q < ~.09 1/Å) profiles collected at different time points showed the emergence of regular hump-like features, indicating the emergence of monodisperse shapes in solution. Fitting the humps using well documented analysis on the small angle scattering revealed sizes of the colloidal particles at each time point.[2] Intensity was related to size using the spherical form factor: $FF = \frac{(\sin(q*r) - q*r*\cos(q*r))^2}{(qr)^6}$. Additionally, dispersity was accounted for using the equation for normal distributions: $D = e^{-\left(\frac{r_O - r}{\sigma*\sqrt{2}}\right)^2}$, which was incorporated into the intensity equation via: $I(q) = \sum FF * \frac{D}{\sum D}$. Fits of the first zero of the form factor for sphere in the small angle scattering region (.001<q<.006) were employed to reveal sizes of nanoparticles. In the WAXS region, a Lorentzian function was used to model the (100) diffraction peaks with a signal to noise ratio greater than 2 to determine the full width at half max (FWHM) with respect to time. Particle size curve with respect to time was fitted with the equation size = $a_1 * e^{\frac{-t}{\tau_1}} + a_2 * e^{\frac{-t}{\tau_2}} + c$ and FWHM change with time was fitted with the equation FWHM = $b * e^{\frac{-t}{\tau_2}} + c$ to determine the time constant (τ_1, τ_2 and τ_3).

Isolation of Colloids as Powder for Surface Area

1 mL of brine solution was added to 20 mL of colloidal COF solution, and the vial was shaken by hand for 10 seconds. The coagulated COF colloids were collected in a tea bag and subjected to Soxhlet extraction with methanol for 24 hours.

Isolation of Colloids as Powder for WAXS Diffraction

4 mL of as synthesized colloid solution was centrifuged at 7800 rpm for 15 minutes. Solids that sediment at the bottom of the tube were pipetted into a borosilicate capillary along with some supernatant and packed tightly with a needle.

Addition of Monomers to Synthesized Seeds

TAPB (0.051 mmol, 17.9 mg) was dissolved in MeCN (6 mL) and a separate solution of PDA (0.076 mmol, 10.2 mg) and $Sc(OTf)_3$ (0.024 mmol 12.0 mg) in MeCN (6 mL) was prepared and each were loaded into separate syringes. The syringes were mounted on a syringe pump and the solutions were added to a solution of TAPB-PDA COF colloids (2 mL) at the rates noted. After increments of monomer equivalents were added, aliquots were taken for *ex situ* analysis.

The rates defined in the manuscript are equivalents of monomers per hour. Equivalents of monomers is the millimoles of monomers added in growth process divided by the millimoles of monomers used to make the initial starting seeds.

Synthesis of COF Colloid with Various Aldehyde Linkers with Optimized Catalyst Loading

Separate stock solutions of TAPB (1.00 mL, 14.8 mM) and 4,4′-biphenyldicarbaldehyde (0.57 mL, 38.9 mM) in MeCN were prepared and combined accordingly to the specified volume. A solution of $Sc(OTf)_3$ (1.91 mL, 3.74 mM, 0.16 equiv $Sc(OTf)_3$) in MeCN was added, and then the mixture was shaken to ensure efficient mixing. The combined reaction mixture was held at room temperature for 20 hours before further manipulation.

Separate stock solutions of TAPB (1.00 mL, 15.3 mM) and PDA derivative **1** (1.00 mL, 23.0 mM) in MeCN were prepared and combined accordingly to the specified volume. An additional 1.40 mL of blank MeCN was added and finally, a solution of $Sc(OTf)_3$ (0.20 mL, 9.09 mM, 0.04 equiv) in MeCN was added, and then the mixture was shaken to ensure efficient mixing. The combined reaction mixture was held at room temperature for 20 hours before further manipulation.

The equivalents of $Sc(OTf)_3$ are calculated with respect to amine functional groups.

C. Synthesis, Characterization and Formation of COF Colloids

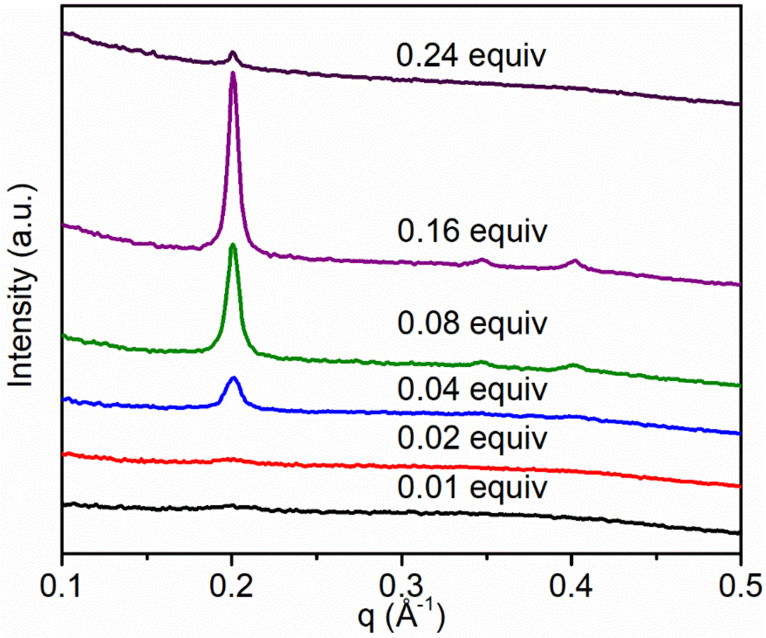

Figure S1. WAXS diffraction pattern of TAPB-PDA COF colloid prepared with varying equivalents of Sc(OTf)$_3$ with respect to each amine group of TAPB.

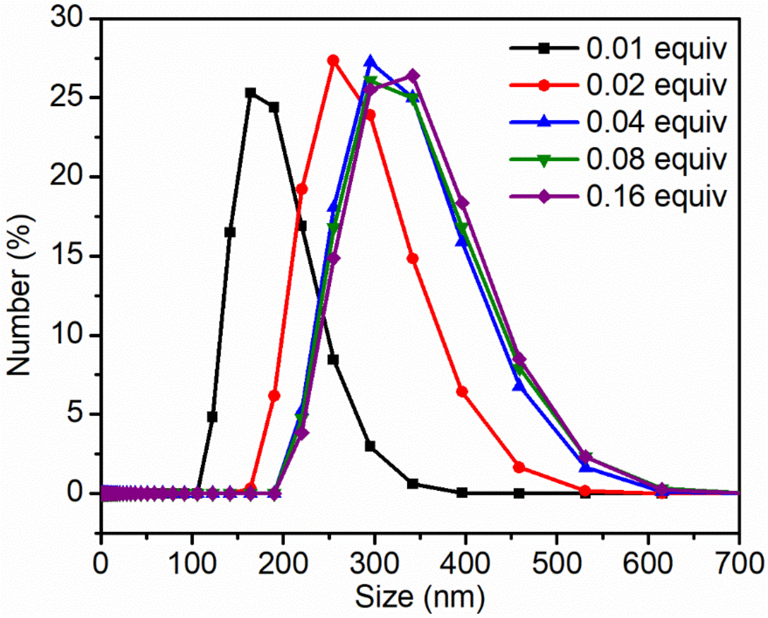

Figure S2. DLS number percentage distribution of TAPB-PDA COF colloid prepared with varying equivalents of Sc(OTf)$_3$ with respect to each amine group of TAPB.

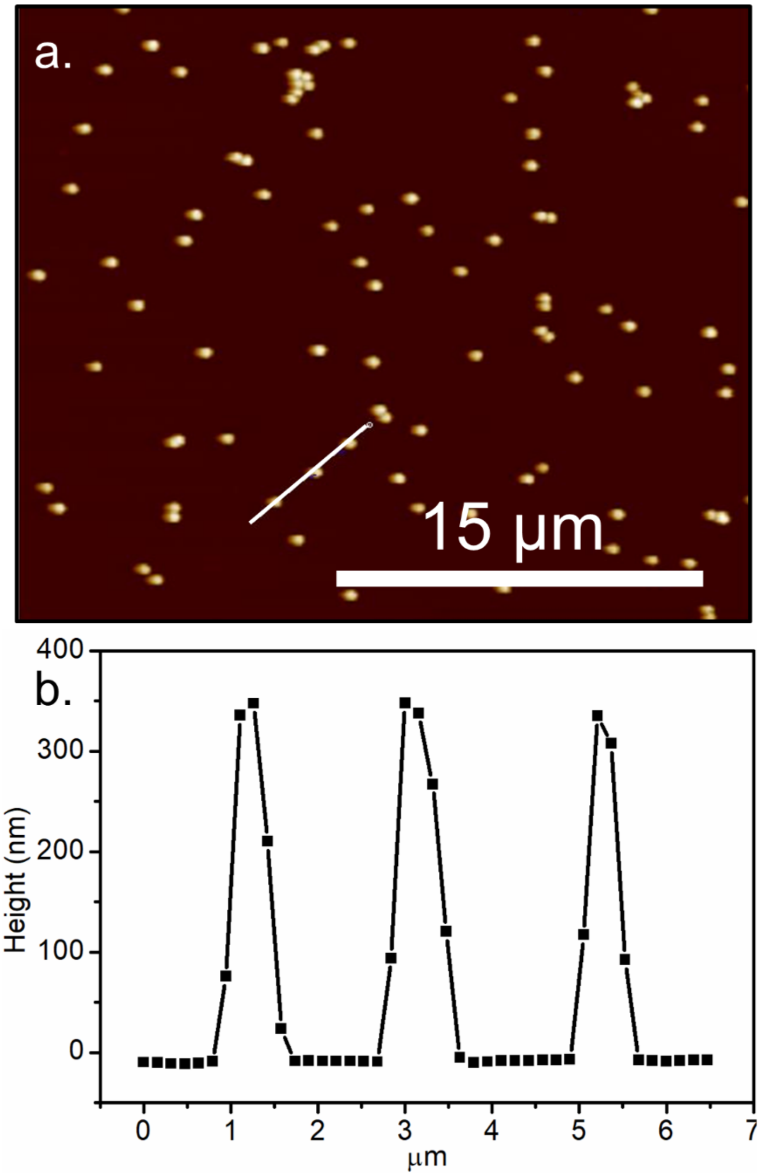

Figure S3. a) AFM of TAPB-PDA COF colloid prepared with 0.16 equivalent of Sc(OTf)$_3$ with respect to each amine group of TAPB. b) Height profile of three individual colloids taken under the white line.

D. Isolated Solid from COF Colloid Characterization

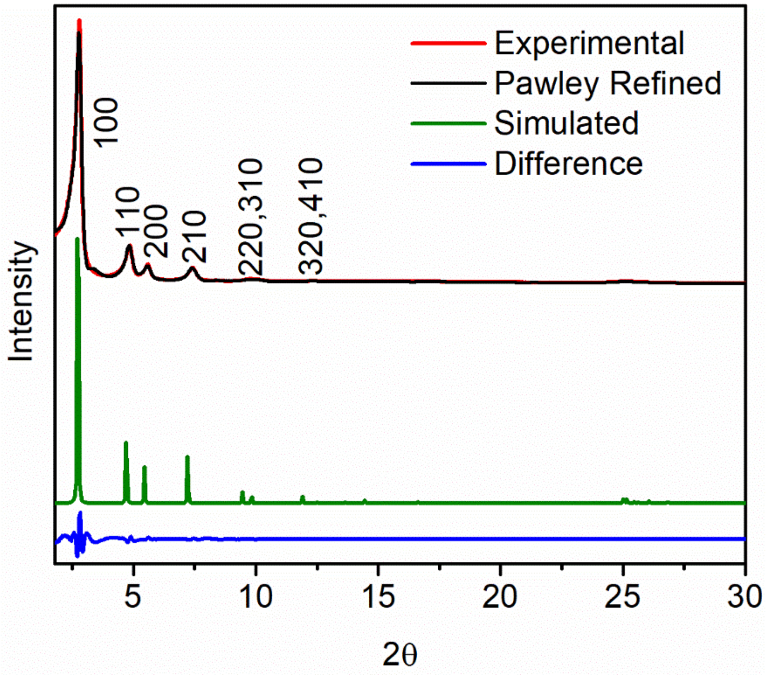

Figure S4. Experimental PXRD pattern for TAPB-PDA COF colloid isolated as bulk powder (Red) compared with the Pawley refined PXRD pattern (Black), the difference between the two patterns (Blue), and the simulated PXRD pattern (Green)

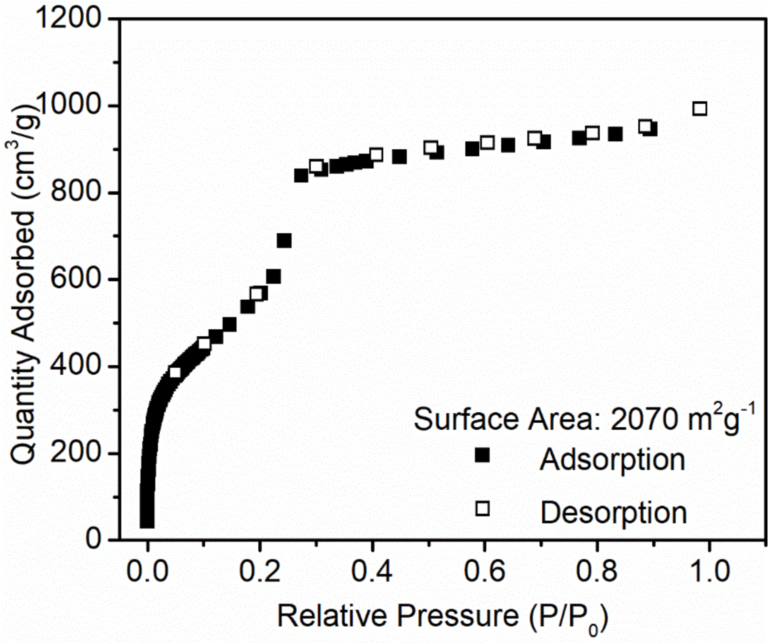

Figure S5. Nitrogen adsorption isotherm for TAPB-PDA COF colloid prepared with 0.16 equivalent of $Sc(OTf)_3$, purified with Soxhlet extraction and activated with supercritical CO_2.

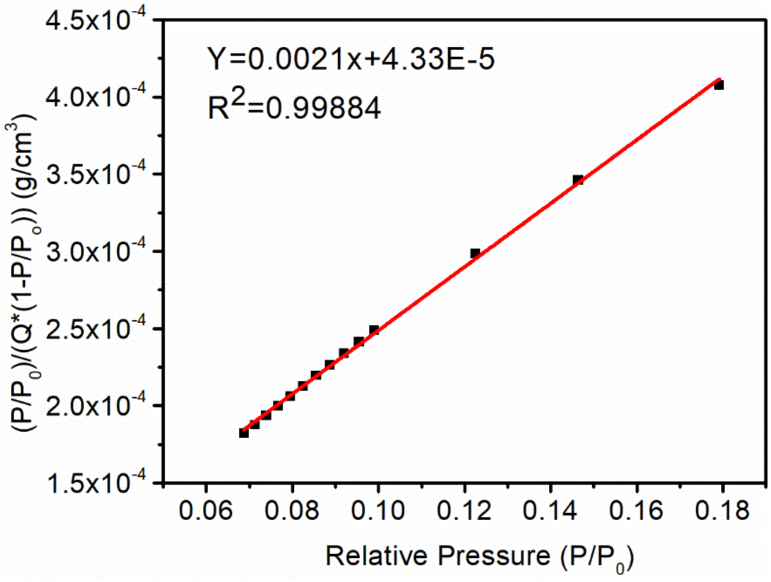

Figure S6. BET plot for TAPB-PDA COF colloid prepared with 0.16 equivalent of Sc(OTf)$_3$, purified with Soxhlet extraction and activated with supercritical CO$_2$.

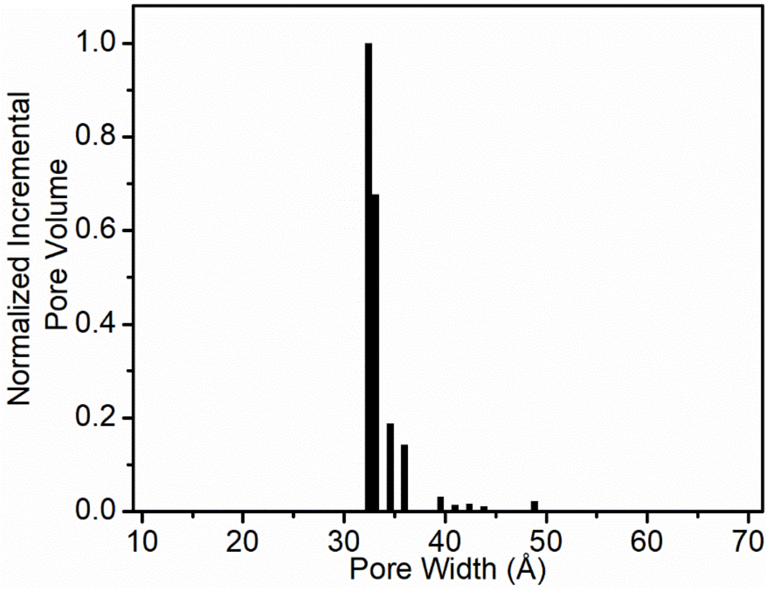

Figure S7. Pore width distribution for TAPB-PDA COF colloid prepared with 0.16 equivalent of Sc(OTf)$_3$, precipitated with saturated NaCl, purified with Soxhlet extraction and activated with supercritical CO$_2$.

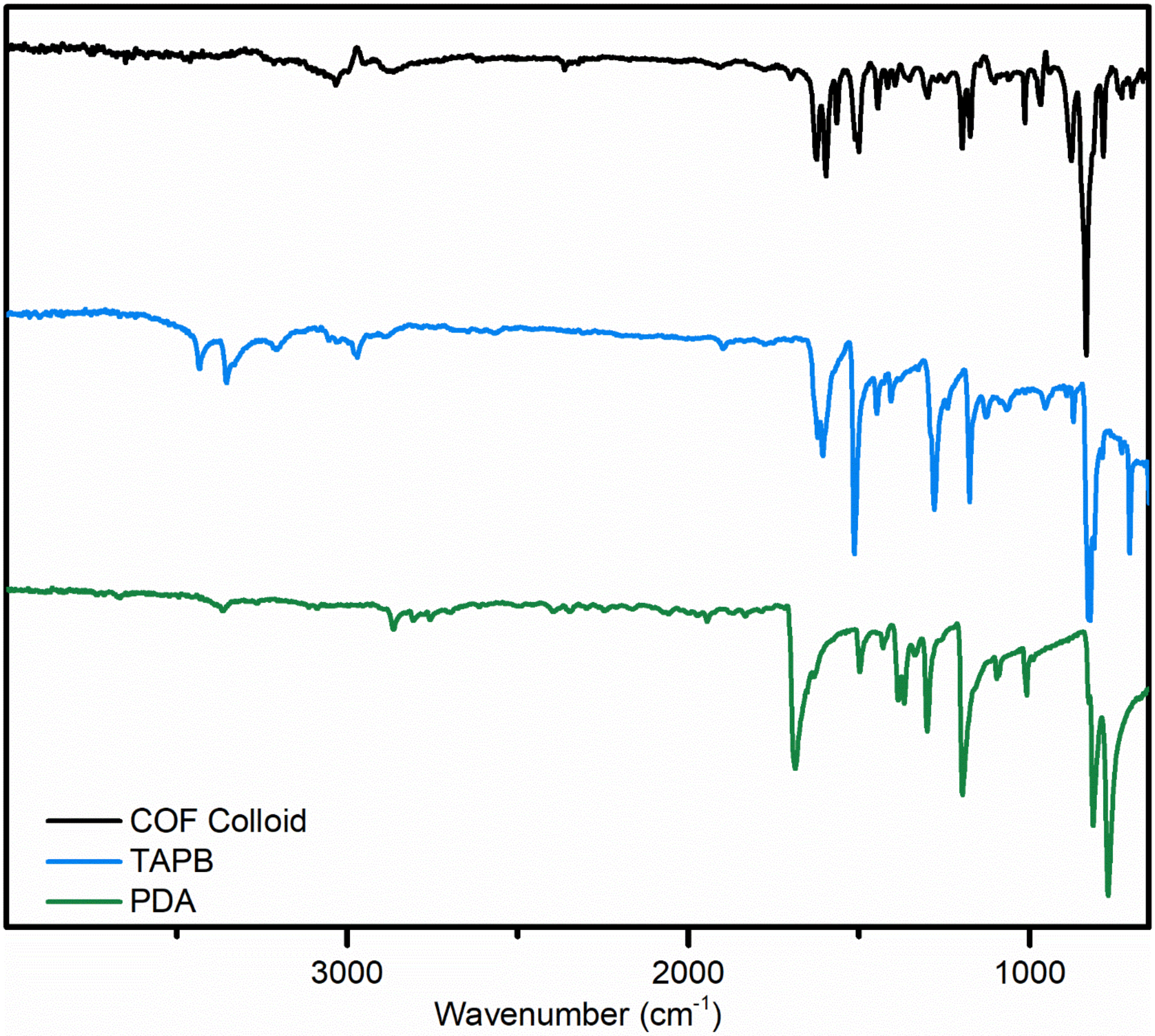

Figure S8. FTIR spectra for TAPB-PDA COF colloid prepared with 0.16 equivalent of Sc(OTf)$_3$, purified with Soxhlet extraction and activated with supercritical CO$_2$.

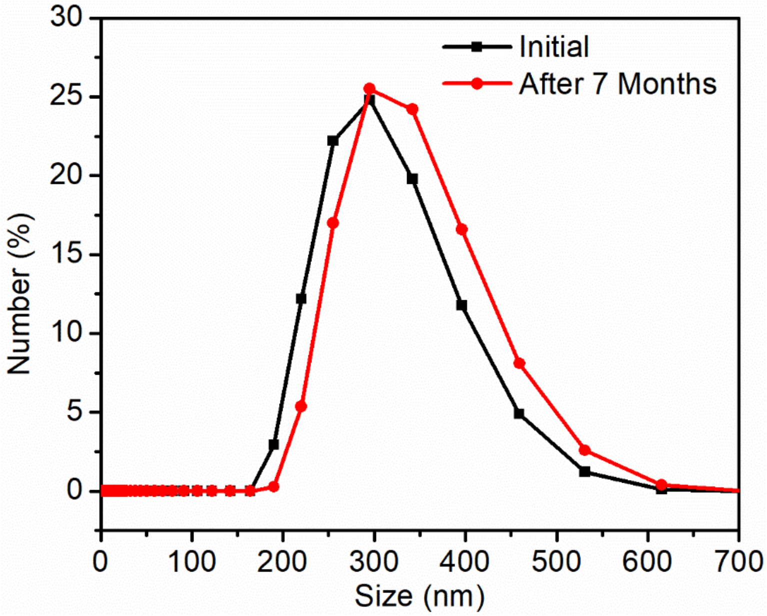

Figure S9. DLS number percentage distribution of TAPB-PDA colloids synthesized with 0.16 equivalents of $Sc(OTf)_3$ measured initially and after 7 months at room temperature.

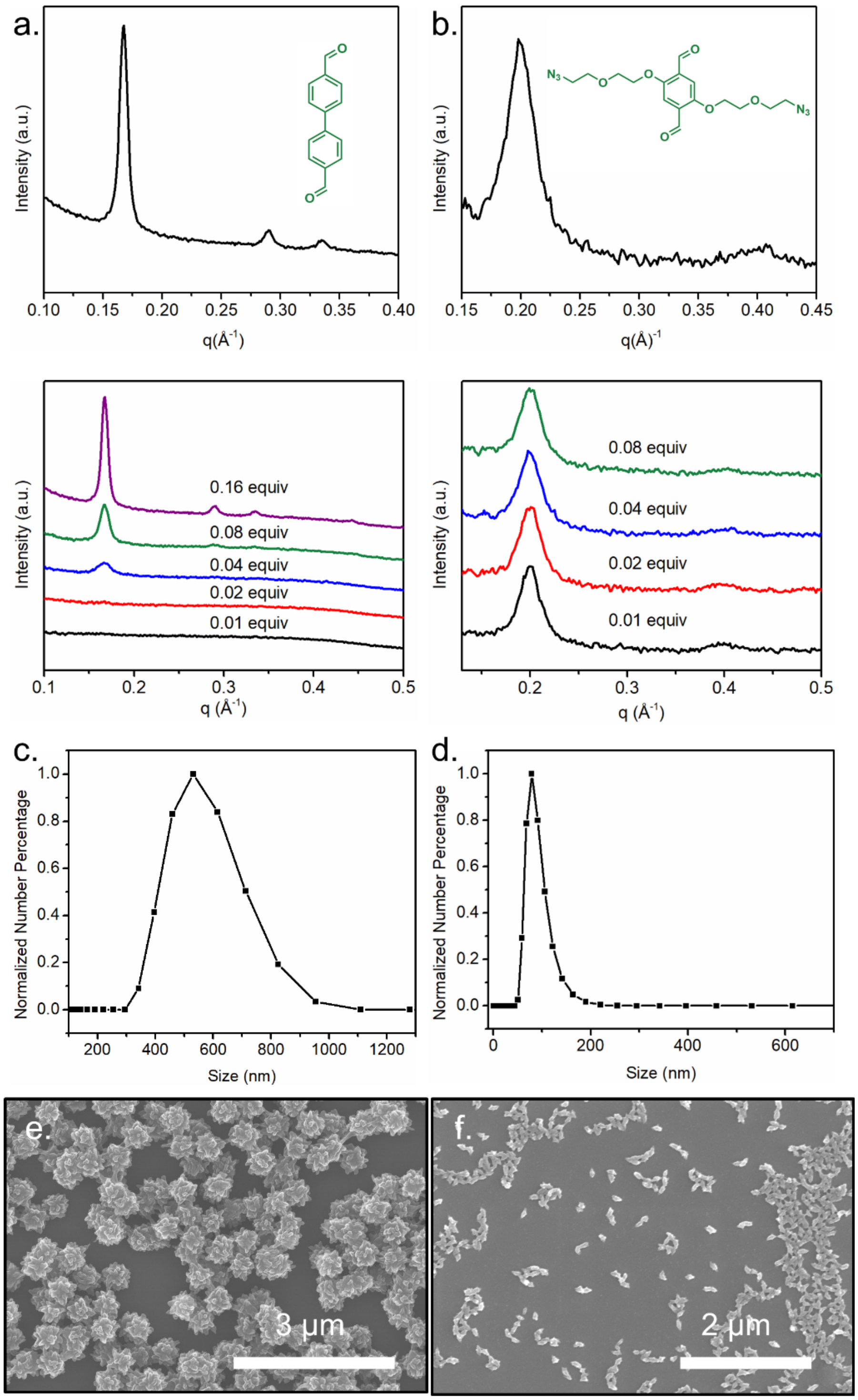

Figure S10. COF Colloid Monomer Modularity. a-b.) WAXS diffraction of COF colloid synthesized with BDA and PDA derivative **1** at the optimized catalyst loading c-d.) DLS number percentage distribution of COF colloid synthesized with BDA and PDA derivative **1** e-f.) SEM images of COF colloid synthesized with BDA and PDA derivative **1**.

E. Concentration Controlled Colloid Size Characterization

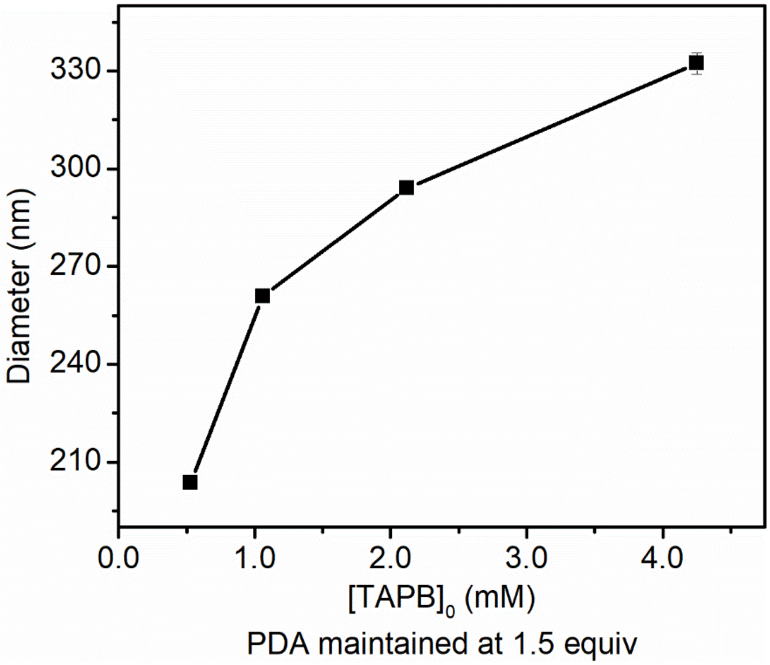

Figure S11. Average size dependence of TAPB-PDA COF colloid determined by DLS Z-average as a function of TAPB concentration

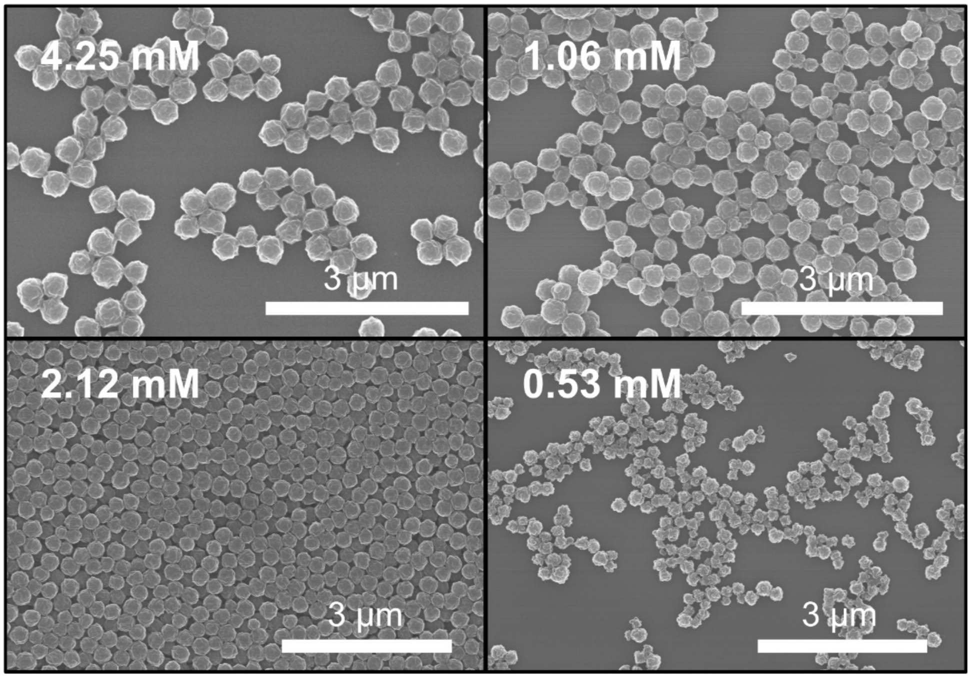

Figure S12. SEM of as synthesized TAPB-PDA COF colloid prepared with 0.16 equivalent of Sc(OTf)$_3$ at varying TAPB concentration. PDA concentration is held at 1.5 times TAPB concentration.

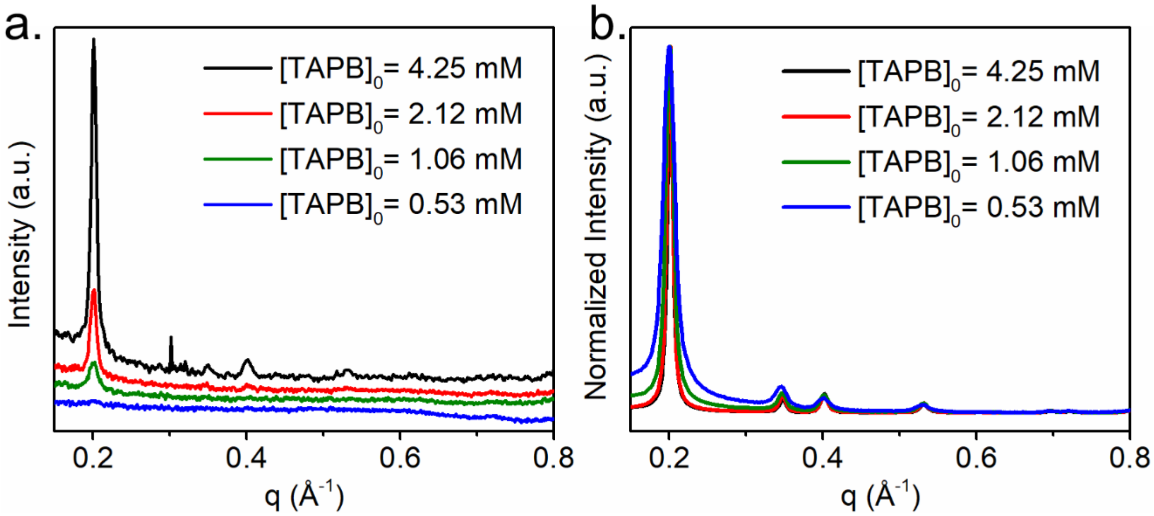

Figure S13. WAXS diffraction pattern of a) as synthesized colloids in solution b) solids obtained post centrifugation of TAPB-PDA COF colloid prepared with 0.16 equivalent of $Sc(OTf)_3$ at varying TAPB concentration. PDA concentration is held at 1.5 times TAPB concentration.

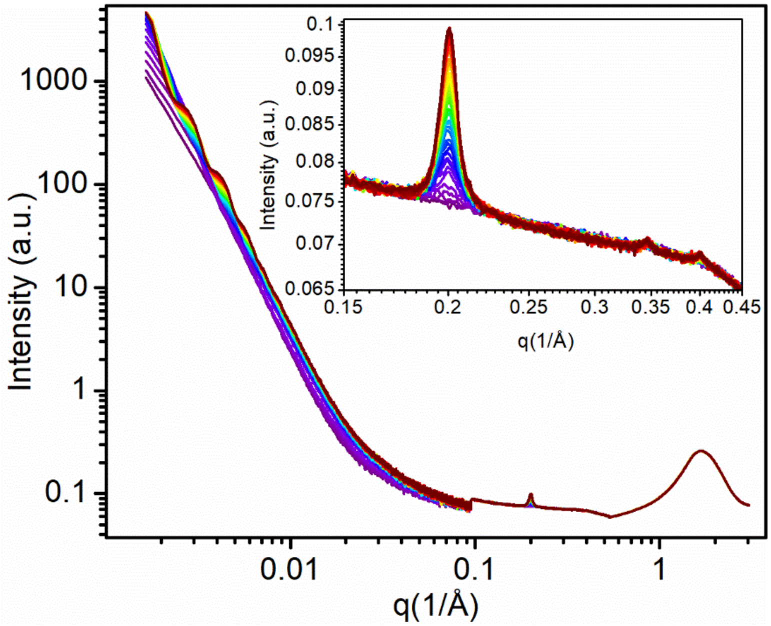

Figure S14. *In situ* SAXS and WAXS diffraction of TAPB-PDA COF formation over time. Inset: Expansion of the WAXS region of the diffraction pattern.

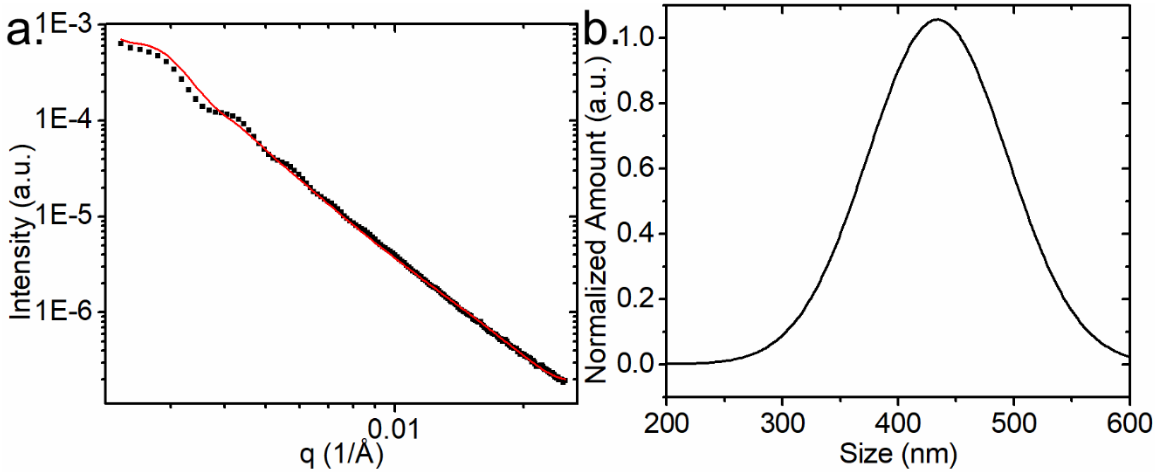

Figure S15. Representative fit of SAXS region and resulting size distribution with SSE of .95

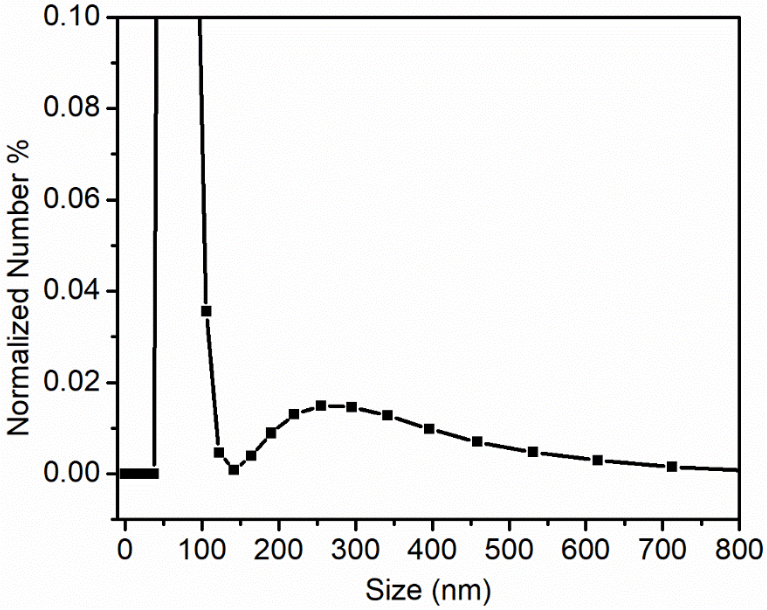

Figure S16. DLS normalized number percent distribution after 4 equivalents of monomers were added at a fast rate of 50 equiv h^{-1}.

F. References

1. W. Ji, L. Xiao, Y. Ling, C. Ching, M. Matsumoto, R. P. Bisbey, D. E. Helbling and W. R. Dichtel, *J. Am. Chem. Soc.*, 2018, **140**, 12677-12681.
2. M. Kotlarchyk and S. H. Chen, *J. Chem. Phys.*, 1983, **79**, 2461-2469.