Supporting Information

Colloidal Three-Dimensional Covalent Organic Frameworks and Their Application as Porous Liquids

Rachel E. Mow,[ab] Andrew S. Lipton,[c] Sarah Shulda,[b] E. Ashley Gaulding,[b] Thomas Gennett,*[ab] and Wade A. Braunecker*[ab]

Contents

* Co-corresponding authors
[a] *Department of Chemistry, Colorado School of Mines, Golden, CO 80401, United States. Fax: 303-273 3629; Tel: 303-273 3610*
[b] *National Renewable Energy Laboratory, Golden, CO 80401, United States. Tel: 303-275-3000*
[c] *Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, Washington 99354, United States*

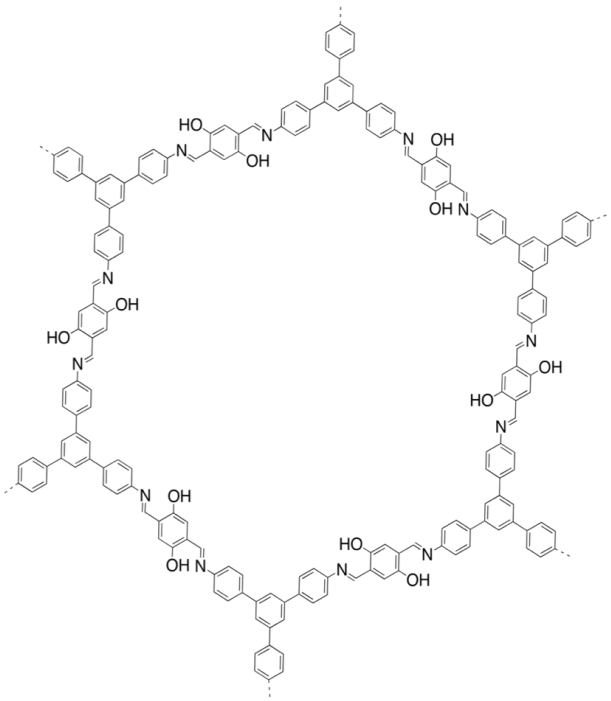


Fig. S1 Structure of 2D COF with 37Å pores

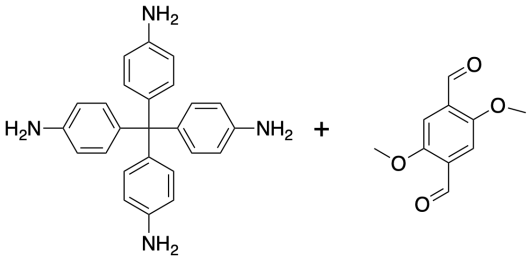
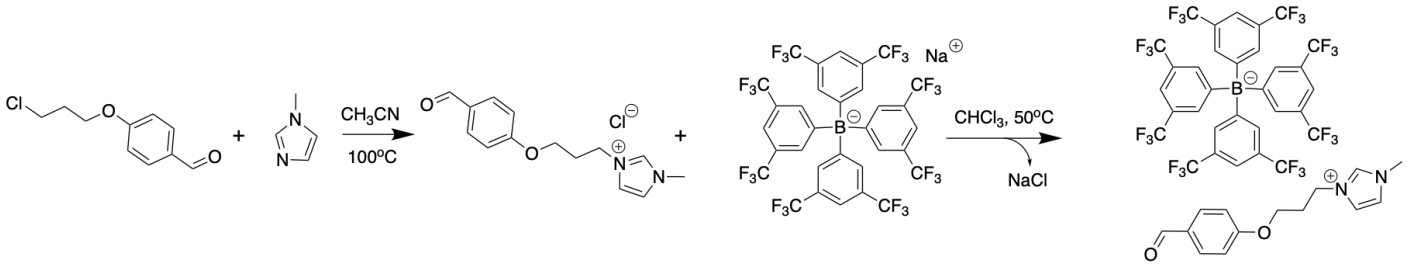


Fig. S2 Monomers for the methoxy-functionalized COF



Scheme S1 Synthesis of 3-(3-(4-formylphenoxy propyl)-1-methyl-1H-imidazol-3-ium BAr^F

Summary of Colloidal Synthetic Conditions and Surface Areas

Table S1 Summary of the synthetic conditions for COF-300 colloids – each reaction was done with 4.4 mM tetrakis(4-aminophenyl)methane in dry acetonitrile for 72 hours

Catalyst	Temperature	Surface Area
$Sc(OTF)_3$	RT	193 m^2/g
$Sc(OTf)_3$	90°C	377 m^2/g
$Sc(OTf)_3$	120°C	black precipitate
CF_3CO_2H	RT	34 m^2/g
CF_3CO_2H	90°C	313 m^2/g
CF_3CO_2H	**120°C**	**600 m^2/g**

Images of COF colloids and porous liquids

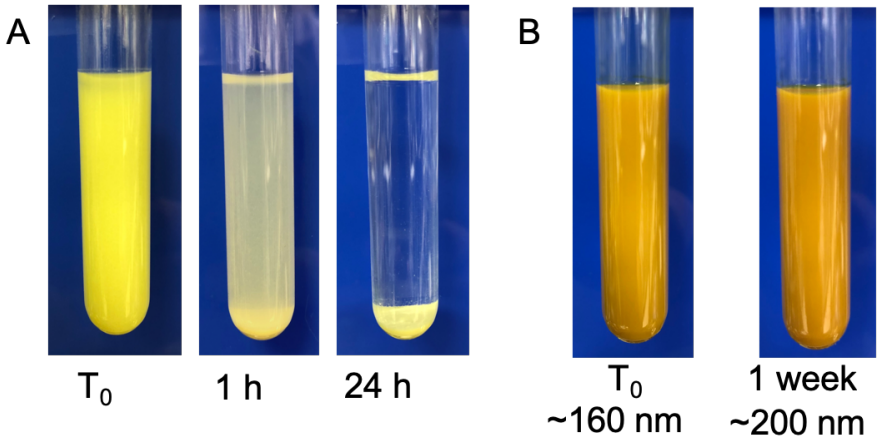


Fig. S3 a) Large particle COF-300 (purified, dried, resuspended in acetonitrile) rapidly settles with time, compared to b) colloidal COF-300, which is stable towards flocculation over many weeks. DLS suggests average particle sizes slowly increase over the course of one week from 160 to 200 nm.

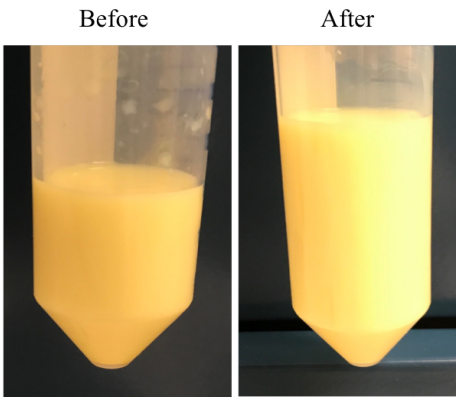


Fig. S4 Stable colloidal suspension of BAr^F functionalized COF in acetonitrile (left). Following centrifugation and vacuum to dryness, the functionalized material could be resuspended as a stable colloidal solution in acetonitrile (right).

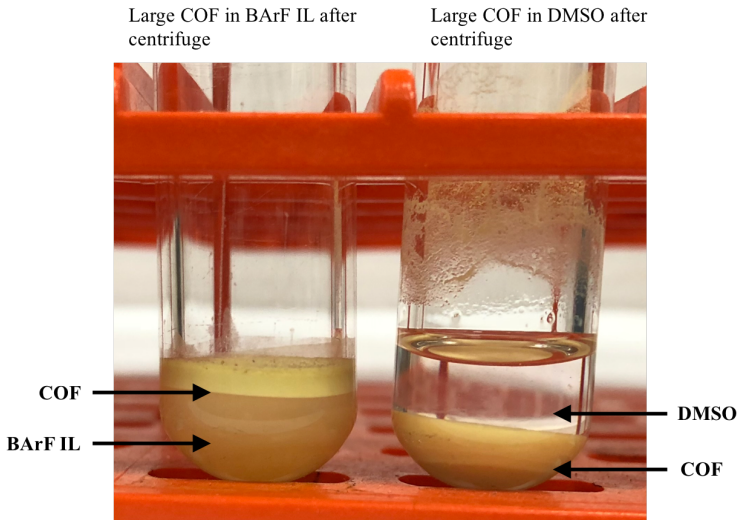


Fig. S5 Separation of large-particle COF-300 from BAr^F ionic liquid after 3 h of centrifugation at 6000 rpm (left) and 10 min of centrifugation in DMSO (right).

Fig. S6 10 wt.% porous liquid made from 200 nm COF-300 particles and BAr^F ionic liquid, showing no visible separation after centrifugation at 6000 rpm for 5 hours.

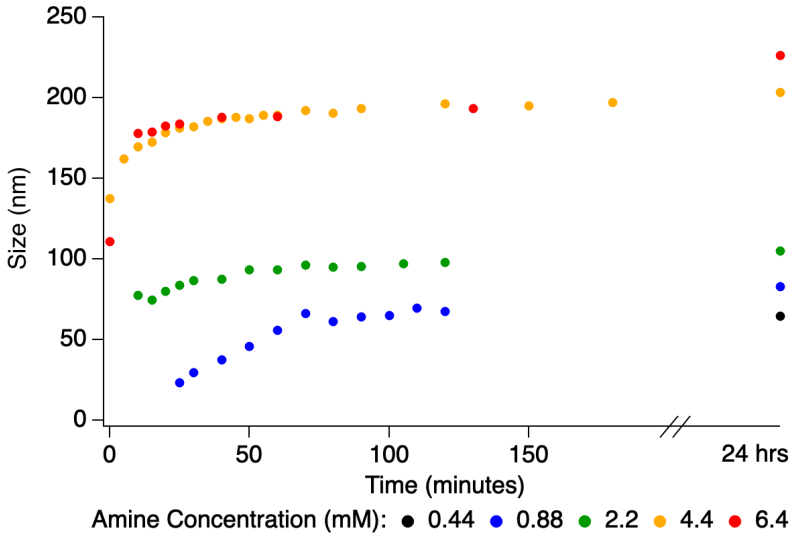


Fig. S7 Average particle size distribution of COF-300 colloids with time, as monitored by DLS. Reaction was done in acetonitrile with $Sc(OTf)_3$ at room temperature. The concentrations reported are the concentration of tetrakis(4-aminophenyl)methane in acetonitrile. Aliquots were taken from the reaction, diluted with acetonitrile, and immediately measured with DLS.

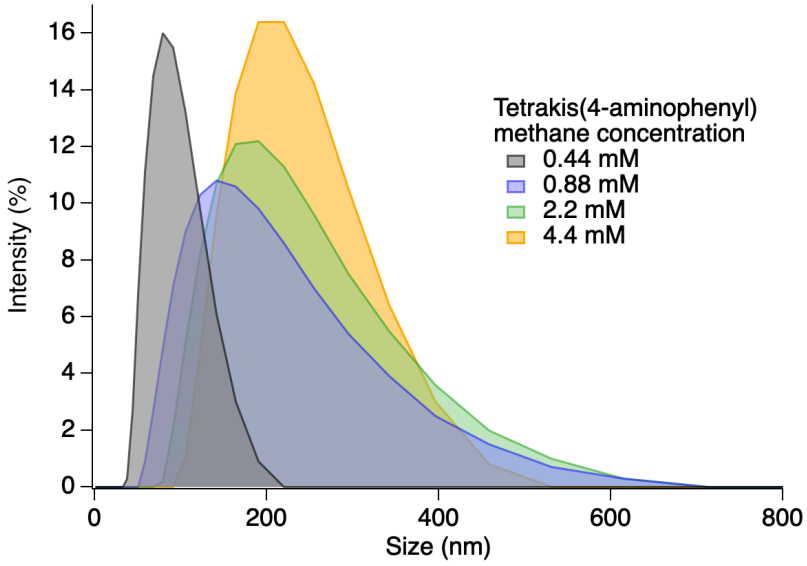


Fig. S8 Effect of dilution on particle size distribution for COF-300 syntheses at 120℃ in acetonitrile, catalyzed by trifluoroacetic acid.

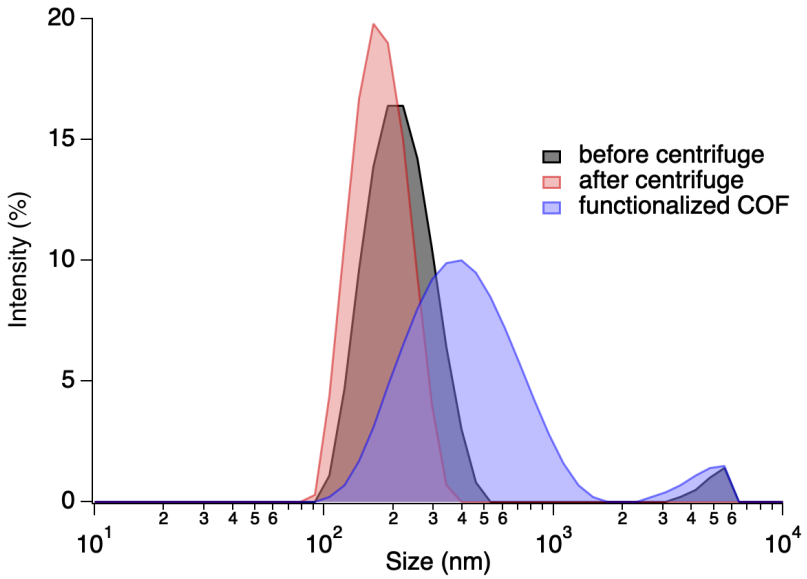


Fig. S9 Particle size distributions for COF-300 synthesized at 120 °C in acetonitrile with trifluoroacetic acid catalyst. The black trace shows the size distribution before the colloids were centrifuged and the red trace shows the size distribution after the colloids were centrifuged and resuspended in acetonitrile through ultrasonication, revealing no apparent irreversible aggregation occurs during centrifugation. The blue trace indicates the size distribution approximately doubles after functionalization with the BAr^F compound.

X-Ray Diffraction

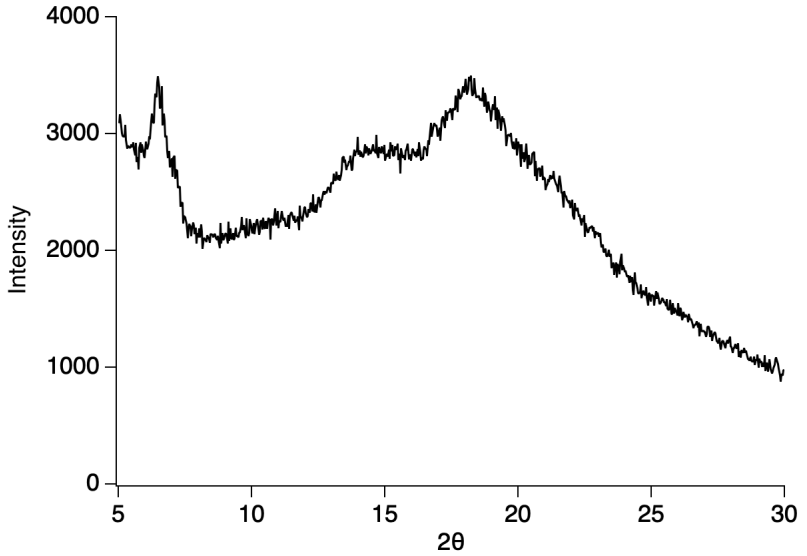


Fig. S10 XRD of colloidal COF-300.

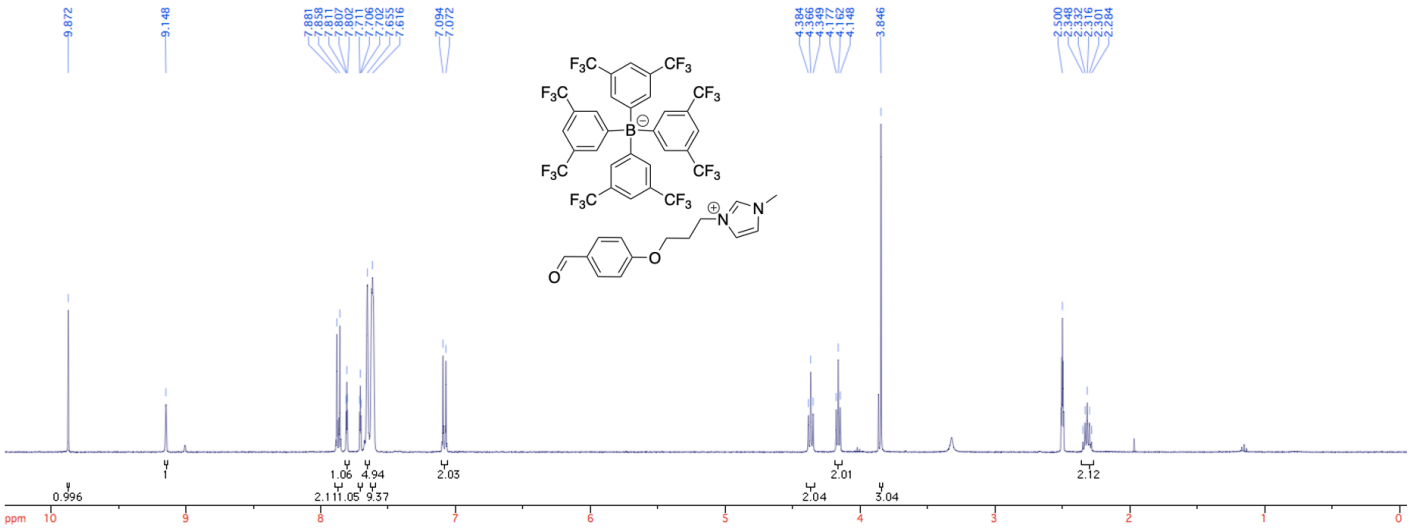


Fig. S11 ^{1}H NMR on 3-(3-(4-formylphenoxy)propyl)-1-methyl-1H-imidazol-3-ium BAr^{F}

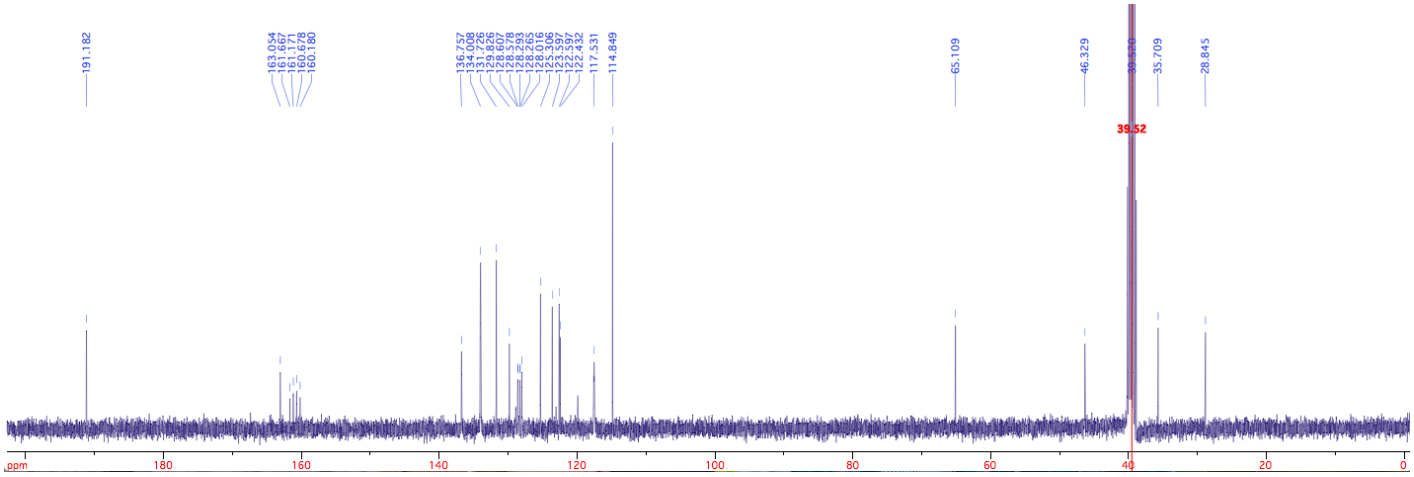


Fig. S12 ^{13}C NMR on 3-(3-(4-formylphenoxy)propyl)-1-methyl-1H-imidazol-3-ium BAr^{F}

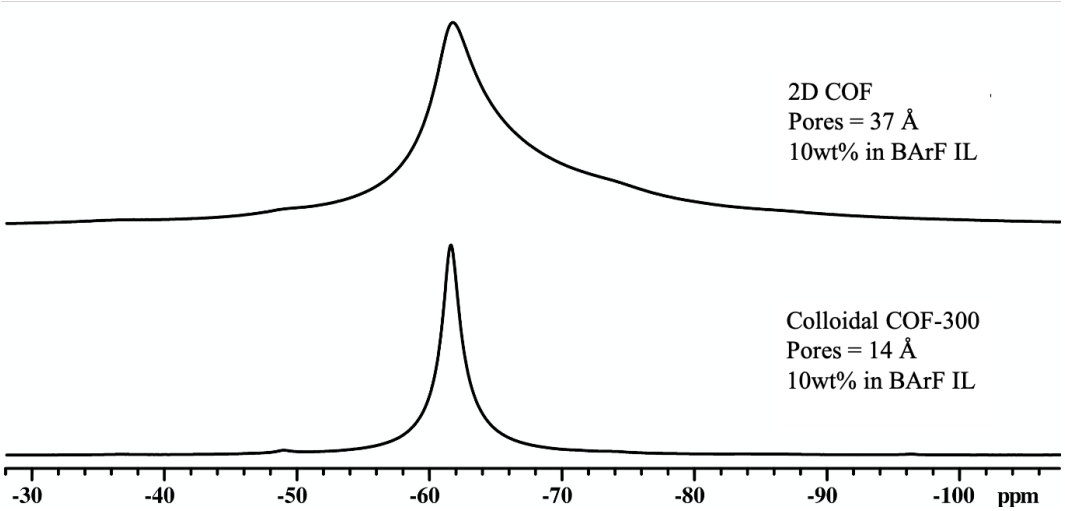


Fig. S13 ^{19}F MAS NMR spectra (799 MHz) acquired at 0 ℃ for 10 wt.% COF suspensions in BAr^F ionic liquid. The CF_3 resonances of the BAr^F anion are shown for the (top) 2D COF suspension with 37Å pores and (bottom) COF-300 with 14Å pores.

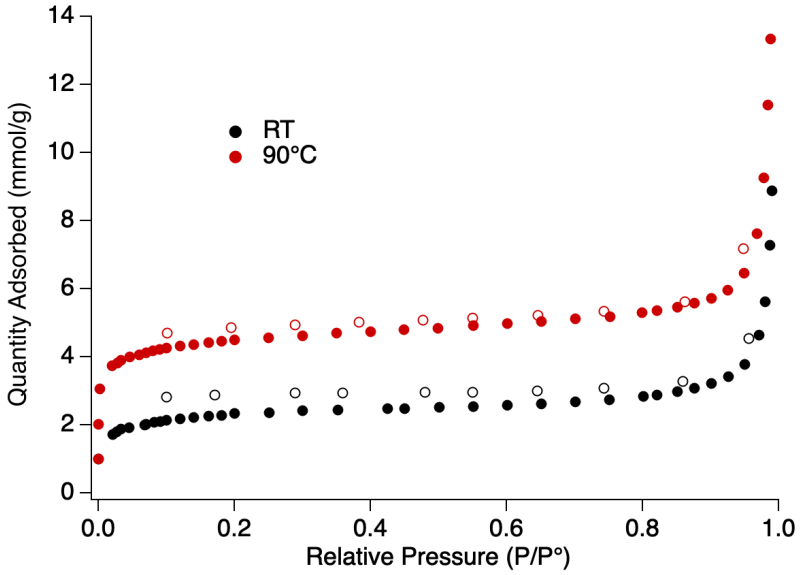


Fig. S14 Nitrogen isotherms of colloidal COF-300 synthesized at room temperature (black) and 90℃ (red) with $Sc(OTf)_3$. Filled circles represent adsorption and open circles represent desorption. Surface Areas: RT = 193 +/- 1 m^2/g and 90℃ = 377 +/- 4 m^2/g.

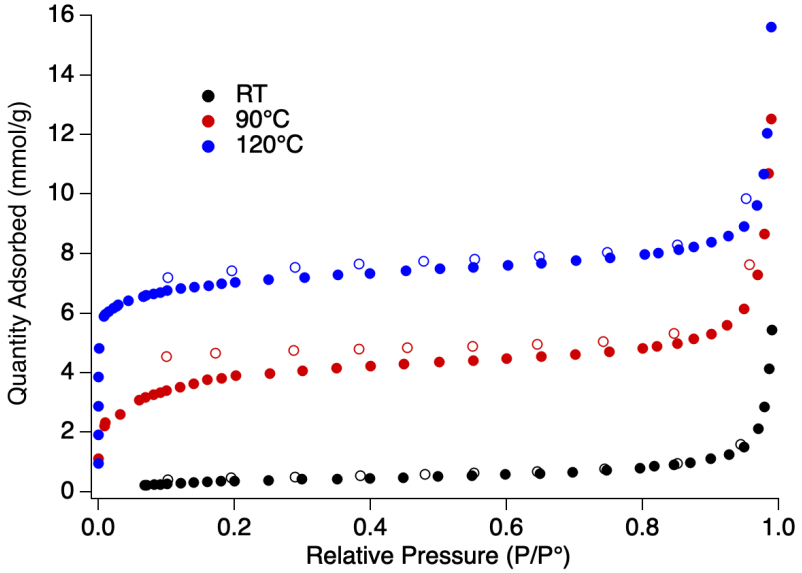


Fig. S15 Nitrogen isotherms of colloidal COF-300 synthesized at room temperature (black), 90℃ (red), and 120℃ (blue) with trifluoroacetic acid. Filled circles represent adsorption and open circles represent desorption. Surface Areas: RT = 33.8 +/- 0.7 m^2/g, 90℃ = 313 +/- 4 m^2/g, and 120℃ = 601.2 +/- 0.4 m^2/g.

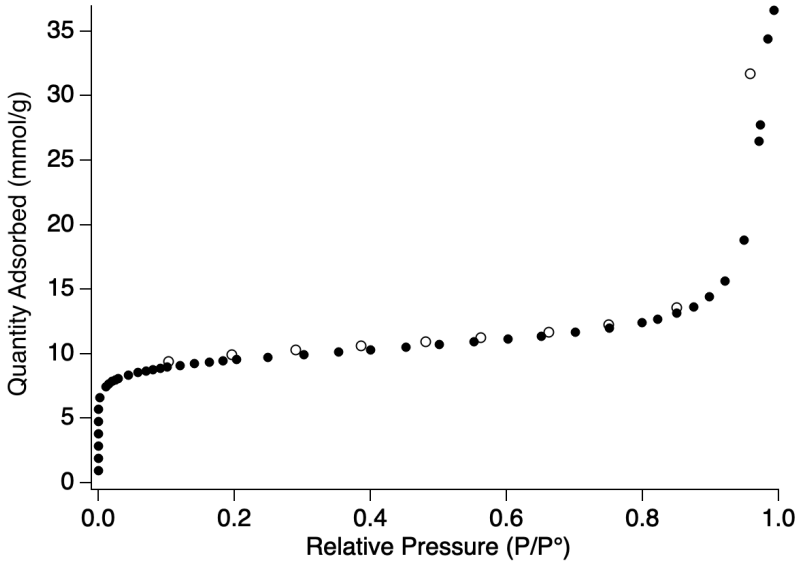


Fig. S16 Nitrogen isotherm of methoxy-functionalized COF synthesized at 120 °C with trifluoroacetic acid. Filled circles represent adsorption and open circles represent desorption. Surface Area = 783 +/- 8 m^2/g.

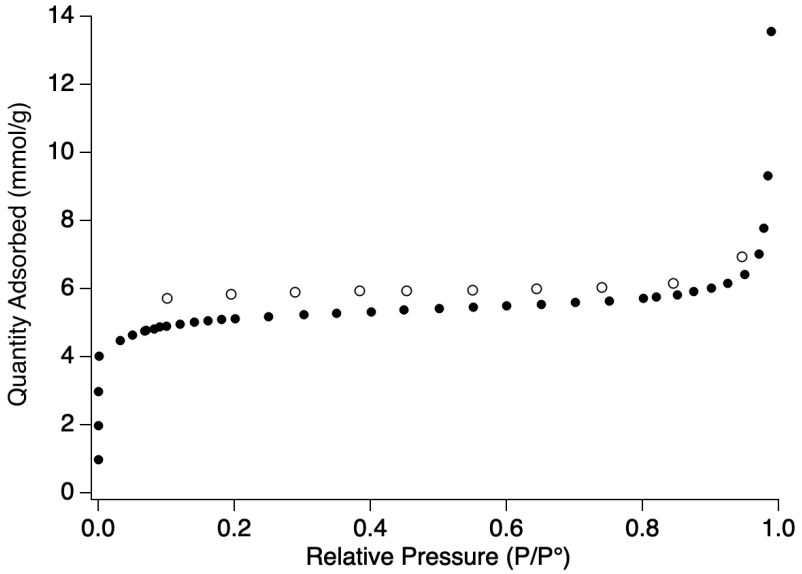


Fig. S17 Nitrogen isotherm for COF-300 functionalized with the BAr^F compound. Filled circles represent adsorption and open circles represent desorption. Surface Area = 433 +/- 3 m^2/g.

Pore Size Distributions

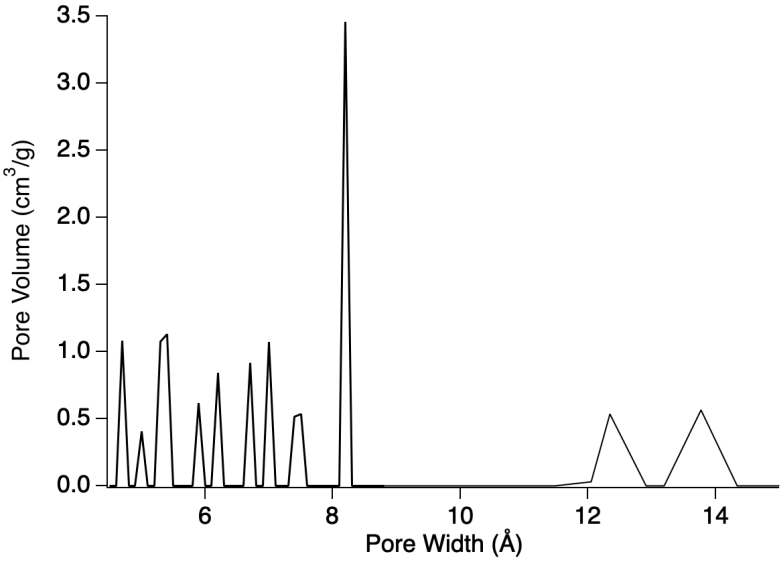


Fig. S18 Pore size distribution of colloidal COF-300. The pore volume below 9 Å was collected with CO_2, and above 9 Å was collected with nitrogen

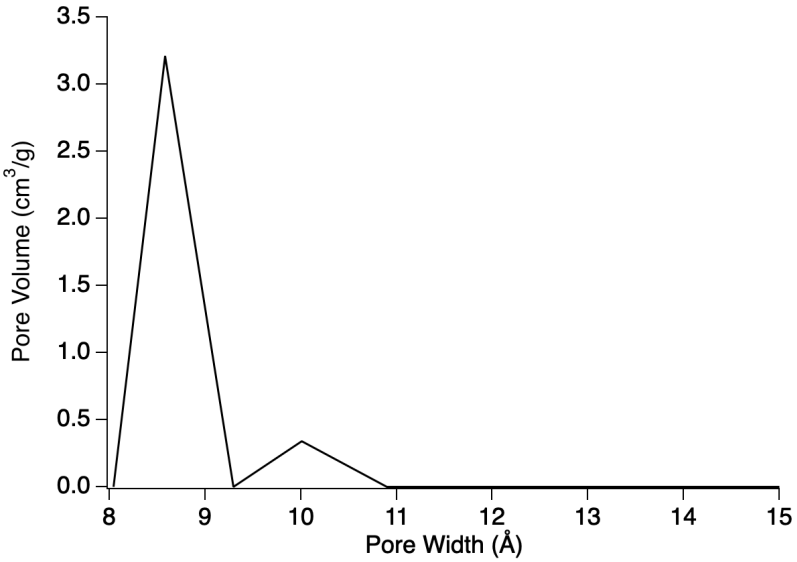


Fig. S19 Pore size distribution for COF-300 functionalized with BAr^F ionic liquid counter ion, collected with nitrogen adsorption

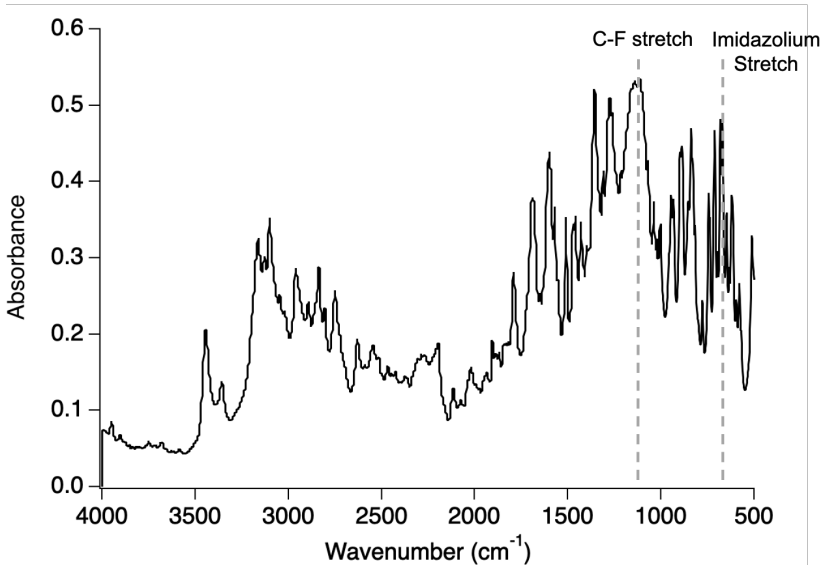


Fig. S20 DRIFTS showing 3-(3-(4-formylphenoxy)propyl)-1-methyl-1H-imidazol-3-ium

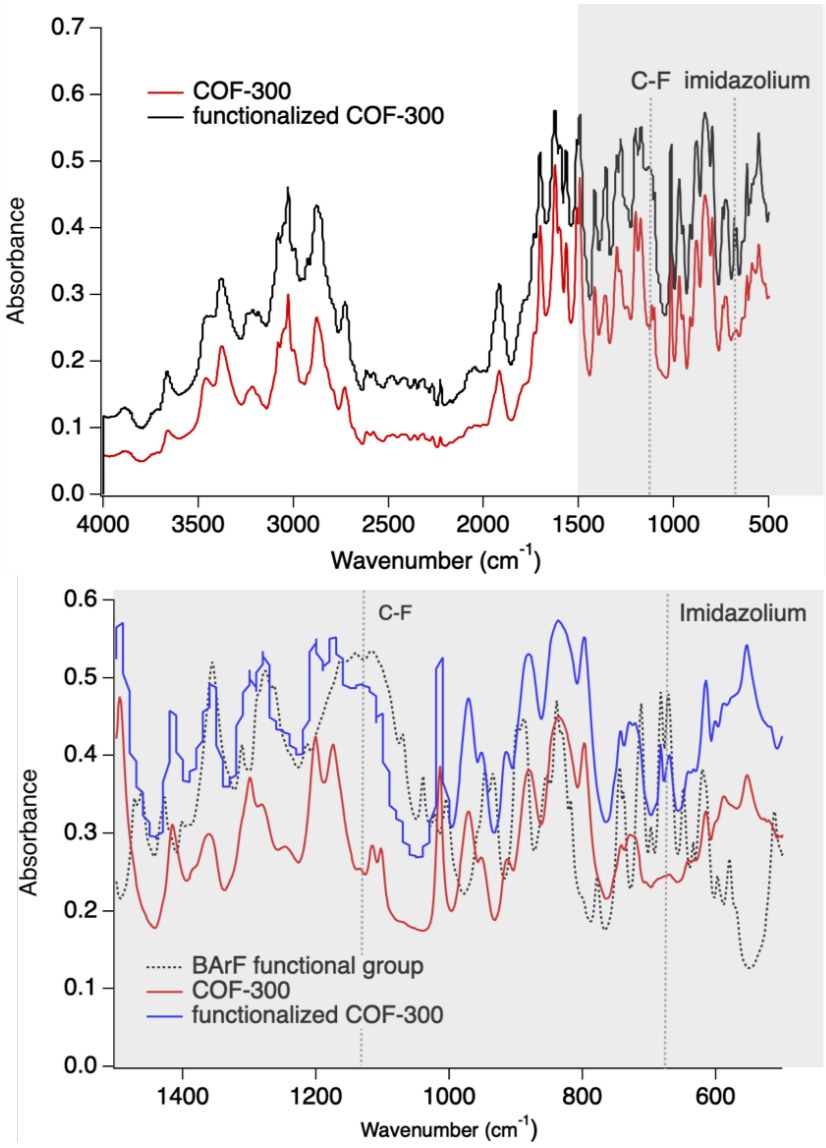


Fig. S21 DRIFTS showing (a) the full spectrum and (b) a portion of the spectrum for COF-300 with and without functionalization. The stretch at 1150 cm^{-1} represents C-F [1] and the stretch at 680 cm^{-1} represents the imidazolium, [2] which are components of the 3-(3-(4-formylphenoxy)propyl)-1-methyl-1H-imidazol-3-ium, not the COF itself. This data proves successful functionalization of the COF with the tethered BAr^F ionic liquid counter ion.

Notes and references

1 Libretexts, *Infrared Spectroscopy Absorption Table*, 2019, https://chem.libretexts.org/Bookshelves/Ancillary_Materials/Reference/Reference_Tables/Spectroscopic_Parameters/Infrared_Spectroscopy_Absorption_Table.

2 *1H-Imidazole, 1-methyl*, https://webbook.nist.gov/cgi/cbook.cgi?ID=C616477&Mask=80#IR-Spec.