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Supplementary Materials for

A self-assembling, biporous, metal-binding covalent organic framework and its application for gas separation

Veronica Spaulding,¹ Katarina Zosel,² Phuoc H. H. Duong,³ Katie D. Li-Oakey,³ Bruce A. Parkinson,^{1,4} Diego A. Gomez-Gualdron^{2*} and John O. Hoberg^{1*}

¹Department of Chemistry, University of Wyoming, Laramie, Wy 82071 USA

²Department of Chemical and Biological Engineering, Colorado School of Mines, Golden, CO 80401 USA

³Department of Chemical Engineering, University of Wyoming, Laramie, Wy 82071 USA

⁴ School of Energy Resources, University of Wyoming, Laramie, Wy 82071 USA

*Corresponding author: Email: <u>hoberg@uwyo.edu</u> (J.O.H.)

This PDF file includes:

Materials and Methods:

Figs. S1 to S21:

 Contents Materials and Methods Experimental details for the synthesis of monomers 1-7 Polymerization conditions for formation of COFs Characterization data for 1-2 Characterization data for 4-7 	Page # 3 3-7 8 9-10 11-14
COF characterization 1. TEM, Diffraction and FFT 2. Computational figures 3. BET analysis 4. ¹ H Solid State NMR	15-19 17-19 19 25
Membrane fabrication and separation testing NMR data for propane/H ₂ separation	26-27 28
References	29

Unless otherwise noted, all reagents were purchased from commercial sources and used as received. Syntheses were preformed using either a Monowave Pro or Monowave 300 microwave reactor. NMR data were collected on a Bruker Advance III 400 MHz NMR spectrometer at room temperature. Spectra were referenced to residual DMSO (2.50 ppm, ¹H) or water (4.80 ppm, ¹H). Chemical shifts are reported in δ values (ppm) relative to internal Me₄Si, and J values are reported in hertz (Hz). The following abbreviations are used to describe peaks: brs (broad singlet), m (multiplet).

Infrared spectra were collected on a Perkin Elmer Spectrum Two FT-IR spectrometer with an ATR attachment and TEM images were taken on a FEI Tecnai G2 F20 S-Twin. HRMS experiments were performed using a Voyager-DE PRO MALDI-TOF mass spectrometer.

The following precursors were synthesized as previously reported: hexaketocyclohexane-octahydrate (HKH),¹ 1,2-ditosylamidobenzene,² *1,2-Dinitro-4,5-ditosylamidobenzene*,² *3,6-dibromo-9,10-phenanthrenequinone*.³ Solvents were used as received. The below synthetic scheme illustrates the synthesis of monomer **4** used in COF formations.



1,2-Diamino-4,5-ditosylamidobenzene (1). The reported literature method² was modified as follows. A 500 mL flask was loaded with solid 1,2-dinitro-4,5-ditosylamidobenzene (4.35 g, 8.59 mmol) and sodium dithionite (10.95 g, 62.89 mmol). A 1:1:1: solution of H₂O:MeOH:CH₂Cl₂ (336 mL) was added

at room temperature and the solution was stirred at reflux for 50 minutes. The solution was cooled to RT and reduced in vacuo to give a bright yellow solid. The solid was filtered with the aid of water (~200 mL) and dried to give 3.79 g of **1** (99% yield). ¹H NMR (400 MHz, DMSO-D₆, 295K), δ 8.53 (s, 1H), 7.51 (d, J= 8 Hz, 2H), 7.32 (d, J=8 Hz, 2H), 6.14 (s, 1H), 4.49 (s, 2H), 2.36 (s, 3H).





Solid 1,2-diamino-4,5-ditosylamidobenzene **1** (1.076 g, 2.410 mmol), HKH (233 mg, 0.746 mmol) in acetic acid (175 mL) was refluxed for 48 hours. The resulting precipitate was filtered while hot and washed with hot glacial acetic acid (2x10 mL) then dried under vacuo to give **2** as a brown solid (701 mg, 67%). ¹H NMR (DMSO-d₆): δ 7.95 (s, 1H, ArH), 7.83 (d, J=8.3 Hz, 2H, Ts ArH), 7.40 (d, J=8.3 Hz, 2H, Ts ArH), 7.34 (brs, 1H, NH), 2.36 (s, 3H). IR: 3250, 1493, 1332, 1160, 1088 cm⁻¹. HRMS m/z: calcd for C₆₆H₅₅N₁₂O₁₂S₆ [(M + H)⁺] 1399.2308, found 1399.2030.

2,3,8,9,14,15-Hexatosyl-5,6,11,12,17,18-hexaazatrinaphthlene-triphenanthenequinone (4).



To a round-bottom flask equipped with side-arm was added **2** (319 mg, 0.227 mmol), 3,6dibromo-9,10-phenanthrenequinone **3** (278 mg, 0.752 mmol), palladium acetate (27.0 mg, 0.120 mmol, 15 mol% relevant to the dibromo ligand), potassium acetate (156 mg, 1.59 mmol), and 2dicyclohexylphosphino-2,6-dimethoxybiphenyl (59 mg, 0.14 mmol, 20 mol %). The vessel was purged with argon, dimethyl acetamide (DMA) (30 mL) was added and the mixture was brought to reflux for 10 days. Deionized water was added (30 mL) and the resulting precipitate was vacuum filtered. The solid was Soxhlet extracted with water (250 mL), and 1:1 acetone/ethanol (250 mL) at intervals of 10-12 hours for each solvent. The solid was dried in vacuo overnight to produce a shiny black solid (450 mg, 98%), which was insoluble in deuterated solvents. IR: 3300-3000 br, 1700, 1595, 1400, 1217, 1153, 1086 cm⁻¹. HRMS m/z: calcd for C₁₀₈H₆₇N₁₂O₁₈S₆ [(M + H)⁺] 2011.3025, found 2011.1084. 2,3,8,9,14,15-Hexatosyl-5,6,11,12,17,18-hexaazatrinaphthlene-triphenanthenequinone-tricylcoiridium(III)trichloride (5).



Under an air atmosphere, **4** (232.0 mg, 0.112 mmol), IrCl₃ (130.0 mg, 0.404 mmol) and a 1:3 solution of DMA/ethoxy ethanol (12 mL) were microwaved at 145 °C for 30 minutes (x2). The resulting black solid was vacuum filtered, washed with hot water (2x10 mL), propionitrile (2x10 mL), acetone (2x10 mL), and dried overnight under vacuo (281.0 mg, 93%). HRMS m/z: calcd for C₁₀₈H₆₁N₁₂O₁₈S₆Ir₃Cl₃ [(M + H)⁺] 2689.0504, found 2689.0476.

2,3,8,9,14,15-Hexatosyl-5,6,11,12,17,18-hexaazatrinaphthlene-triphenanthenequinone-tricylcoplatinum(II) (**6**).



Under an air atmosphere, **4** (141 mg, 0.068 mmol), PtCl₂ (65.0 mg, 0.245 mmol) and a 1:3 solution of DMA/ethoxy ethanol (12 mL) were microwaved at 145 °C for 1 h. The resulting black solid was vacuum filtered, washed with hot water (2x10 mL), propionitrile (2x10 mL), acetone (2x10 mL), and dried overnight

under vacuo (174 mg, 98%). HRMS m/z: calcd for $C_{108}H_{61}N_{12}O_{18}S_6Pt_3$ [(M + H)⁺] 2590.1495, found 2590.3855.

2,3,8,9,14,15-Hexatosyl-5,6,11,12,17,18-hexaazatrinaphthlene-triphenanthenequinone-tricylconickel(II) trihydrate (**7**).



Under an argon atmosphere, **4** (186 mg, 0.092 mmol) and NiCl₂·6H₂O (0.083 g, 0.305 mmol) was added to a 2:3 solution of DMA:ethoxy ethanol (20 mL). The mixture was microwaved at 140 °C for 90 min. The resulting black solid was sequentially vacuum filtered, washed with acetone and hot water (2x10 mL), then Soxhlet with water (12h) and EtOH (3h). After drying overnight under vacuo 190 mg of a black solid was isolated (92%). HRMS m/z: calcd for C₁₀₈H₆₆N₁₂O₂₁S₆Ni₃ [(M + H)⁺] 2233.09282, found 2232.9233.

Polymerization reactions

DPCOF. Solid **4** (286 mg, 0.138 mmol), 1-methylnaphthalene (10mL) and 1M HCl (3 mL) were added to a glass G30 microwave reactor vessel and microwaved at 200 °C for 3 h. The precipitate was vacuum filtered and purified by Soxhlet extraction approximately 10-12 h per solvent (water, ethanol, and acetone) then dried under vacuo to give **DPCOF** as a black solid (220 mg, 91%).

IrNCOF. Solid **5** (102 mg, 0.038 mmol), 1-methylnaphthalene (10mL) and conc. HCl (6 drops) were added to a glass G30 microwave reaction vessel and microwaved at 185 °C for 12 min. followed by 200 °C for 2 h. The precipitate was vacuum filtered, purified by Soxhlet extraction approximately 10-12 hours per solvent (water, ethanol, and acetone) and dried under vacuo (93 mg, 91%).

PtNCOF. Solid **6** (152 mg, 0.056 mmol), 1-methylnaphthalene (10mL) and conc. HCl (6 drops) were added to a glass G30 microwave reaction vessel and microwaved at 200 °C for 3.5 h. The precipitate was vacuum filtered, purified by Soxhlet extraction over approximately 10-12 hours per solvent (water, ethanol, and acetone) and dried under vacuo (130 mg, 98%).

NiCOF. Solid **7** (107 mg, 0.049 mmol) was added to a glass G30 microwave reactor vessel with 1methylnaphthalene (10mL) and 1M HCl (5 mL). The solution was microwaved at 200 °C for 3 hours. The precipitate was vacuum filtered and purified by Soxhlet (water, ethanol, and acetone) then dried under vacuo (55 mg, 60%).





Figure S1: ¹H NMR of **1** in DMSO-d6. Residual acetone is present at 2.1 along with H₂O at 3.4 ppm.



Figure S2: A - ¹H NMR of **2** in DMSO-d6. Residual H₂O is present at 3.4 ppm. Broad NH peak is at 7.4ppm (underneath Ts Ar doublet). **B** – IR of **2**.



Figure S3: MALDI data for monomer **4**. HRMS m/z: calcd for $C_{108}H_{67}N_{12}O_{18}S_6$ [(M + H)⁺] 2011.3025, found 2011.1084.



Figure S4: IR of monomer 4.

AB Sciex TOF/TOF™ Series Explorer™ 72170

TOF/TOF™ Reflector Spec #1 MC=>AdvBC(22,0.5,0.1)=>BC=>RSM10000[BP = 1585.4, 107]



S5: MALDI data for monomer **5**. HRMS m/z: calcd for $C_{108}H_{61}N_{12}O_{18}S_6Ir_3CI_3$ [(M + H)⁺] 2689.0504, found 2689.0476.

AB Sciex TOF/TOF™ Series Explorer™ 72170

TOF/TOF™ Reflector Spec #1 MC=>AdvBC(32,0.5,0.1)=>BC=>RSM5000=>NR(2.00)=>TR[BP = 2593.5, 33]



Figure S6: MALDI data for monomer **6**. HRMS m/z: calcd for C₁₀₈H₆₁N₁₂O₁₈S₆Pt₃ [(M + H)⁺] 2590.1495, found 2590.3855.

AB Sciex TOF/TOF[™] Series Explorer[™] 72170

TOF/TOF™ Reflector Spec #1 MC=>AdvBC(32,0.5,0.1)=>NF0.7[BP = 1273.5, 1005]



Figure S7: MALDI data for monomer **7**. HRMS m/z: calcd for $C_{108}H_{66}N_{12}O_{21}S_6Ni_3$ [(M + H)⁺] 2233.09282, found 2232.9233.





Figure S8: A: space filling model. B: Theoretical FFT of **MCOF**. C: experimental diffraction. D: Diffractions of **DPCOF** with measurements.



Figure S9. Overlay of smaller MM-optimized **DPCOF** sheets over larger ones. a) Overlap of the monomer model over the 4-monomer sheet. b) Overlap of the 4-monomer sheet over the 13-monomer sheet.



Figure S10. A. Comparison of simulated PXRD pattern for preliminary constructed model for **DPCOF** and experimental one. Labels in peaks in simulated pattern correspond to the panel illustrating the planes associated with the reflection. A) Two simulated PXRDs are shown as absorptions, small relative to peak *iv* were seen in the $6 - 9 2\theta$ range and only clearly visible when less intense peaks existed to be compared to on the relative intensity axis. **B.** Miller planes corresponding to the PXRD reflections *i*) (210) plane, 20 = 5.7° *ii*) (200) plane, $2\theta = 6.59^{\circ}$, *iii*) (310) plane, $2\theta = 8.72^{\circ}$ *iv*) (001) plane, $2\theta = 18.08^{\circ}$



Figure S11. Subsections around the monomer (left) and pore B (right) optimized with B3LYP (black), M06L (blue), and ω B97XD functionals. All calculations done with the 6-31g* basis set. Notice that all functional yield similar rippling on the structures.



Figure S12: Nitrogen Adsorption BET data obtained at 77K. Analysis were performed on neat DPCOF samples with no exfoliation or processing. Similar ranges have been reported, see "Urea-Linked Covalent Organic Frameworks" Zhao, C.; Diercks, C. S.; Zhu, C.; Hanikel, N.; Pei, X. and Yaghi, O. M. *J. Am. Chem. Soc.* **2018**, *140*, 16438.



Sample prep was performed via bath sonication overnight and dropcast on Cu/Carbon grid.

Figure S13: A) EDX of **IrCOF** with the expected Ir:Cl:N ratio. B) diffraction images with measurements, C and D) additional HRTEM images with layer spacing. E) enlargement of Figure 3b from manuscript.



Figure S14: HRTEM (A, C & D) and diffraction images (B & E) of PtCOF.



Figure S15: HRTEM (A and B) and diffraction images (C) of NiCOF.



Figure S16: SAD of **NiCOF** (A), which confirms the peak at 2 theta 17.5°. EDX (B) confirming Nickel incorporation.



Figure S17: PXRD (Top) and EDX (bottom) of PtCOF with Pt nanoparticles highlighted.



of all COFs.



Figure S19: PXRD of NiCOF.



Figure S20: ¹H CP-MAS solid state NMR for monomer **4** (bottom red), **DPCOF** (middle blue) and PtCOF (top green). Sidebands (*) are observed at ~26 and ~-5ppm. Hydrate signals are observed in all three at ~4ppm. NH resonance in **4** assigned at 7.4ppm (**#**).

Membrane fabrication and testing

DPCOF composite membranes were fabricated by low vacuum assisted filtration of an exfoliated **DPCOF** solution on a 20-nm pore size anodic aluminum oxide membrane support (AAO, Whatman). Briefly, 10 mg of DPCOF was dispersed in 20 mL of dimethylformamide (DMF) using a probe sonicator (Qsonica, 55W) for 1 h, followed by sonicating in a bath sonicator (Branson 2510) for 2 h. The dispersion was kept at room temperature overnight before transferring 18 mL of the supernatant onto AAO membrane for vacuum filtration. The **DPCOF** composite membranes were dried at 80 °C for 2 days under vacuum before the measurements.

Liquid filtration tests

All liquid filtration tests were performed at room temperature under a trans-membrane pressure of 10 bar with an effective membrane area of 4.9 cm². Deionized (DI) water, ethanol, or hexane were used as feeds. Membrane permeance (L m⁻² h⁻¹ bar⁻¹) was calculated by the following equation:

$$Liquid permeance = \frac{\Delta V}{\Delta t A_{eff} \Delta P}$$
(1)

where ΔV (L) is the volume of liquid that has permeated through the membrane in a predetermined time Δt (h), A_{eff} is the effective membrane surface area (m²), ΔP is the trans-membrane pressure (bar).

Gas permeation tests

Gas permeation of the **DPCOF** composite membrane was determined by a constant pressure/variable volume method. Pure gases of H₂, O₂, or N₂ were employed for the permeation tests. The membrane with an effective surface area of 4.9 cm² was tested under a transmembrane pressure of 5 psi (0.344 bar) at room temperature. The gas permeate flow rate was measure using a flowmeter. The gas permeance can be expressed in GPU unit or L m⁻² h⁻¹ bar⁻¹ (GPU, 1 GPU = 1 x 10⁻⁶ cm³ (STP)/cm² s cm Hg) is determined by the following equation:

Gas permeance

$$=\frac{Q}{A_{\rm eff}\Delta P}$$
(2)

where Q (L/h) is the gas permeate flow rate, A_{eff} is the effective membrane surface area (m²), ΔP is the trans-membrane pressure (bar).



Figure S21: Membrane cell used in gas studies. Flow meters are connected to the incoming and exhaust ports.



Figure S18: Separation studies of propane and H_2 . Top spectrum: ¹H NMR data for feed mixture with an 80:1 ratio of propane to H_2 (H_2 resonance at 4.65 ppm). Bottom spectrum: ¹H NMR data for outlet mixture with a 1:1 ratio of propane to H_2 (ratios obtained using integration of H_2 vs Me groups of propane). Gases were collected in NMR tubes loaded with CDCl₃. The membrane used in this study was different than that used for the study of pure propane and appeared to be damaged at an edge.

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