

Electronic Supplementary Information

Facile synthesis of azo-linked porous organic frameworks via reductive homocoupling for selective CO₂ capture

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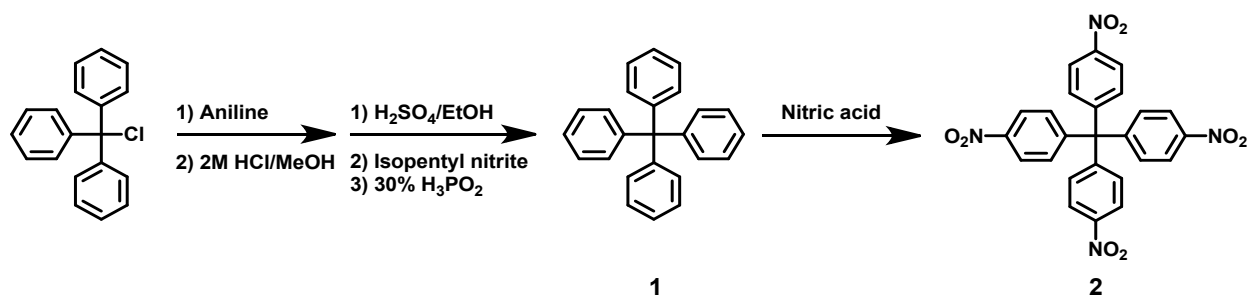
1. Materials and measurements

Trityl chloride (97%), aniline (99.5%), isopentyl nitrite (96%), 50% hypophosphorous acid solution, fuming nitric acid (99.5%) and tetrahydrofuran (THF, 99%) were obtained from Sigma-Aldrich. Tetraphenylethylene (98%), Sodium hydroxide (pellet, 98%), zinc powder (99.9%) and *N,N*-dimethylformamide (DMF, 99.9%) were purchased from Alfa Aesar. Acetic acid (glacial), concentrated hydrochloric acid and concentrated sulfuric acid were obtained from Fisher Scientific. Ethanol (200 proof) was purchased from Decon Lab. All chemicals were used without purification unless otherwise noted.

Solution NMR was performed on either a Bruker FT-NMR spectrometer (400 MHz) or a Bruker FT-NMR spectrometer (300 MHz). Solid-state CP/MAS ¹³C NMR spectra were collected on a Bruker Avance III three-channel spectrometer. Infrared spectroscopy was performed on a Nicolet Avatar 360 FT-IR. UV-Vis absorption spectra were obtained on an Aligent Cary 300 facility with DRA-CA-30I solid-state sample holder. Thermogravimetric Analysis (TGA) was performed on a Perkin Elmer STA 6000 Thermogravimetric Analyzer, heated from 30 °C to 1000 °C at a rate of 10 °C/minute under N₂ atmosphere. X-ray diffraction patterns were acquired from 3 to 80° by a Rigaku Multiflex Diffractometer.

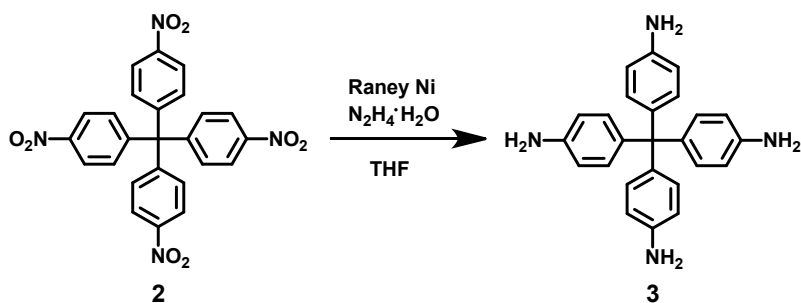
Gas adsorption isotherms were collected using a Micromeritics ASAP 2020-accelerated surface area and porosimetry analyser after the samples had been degassed at 150 °C for 8 h under vacuum. Before the every adsorption measurement, the samples were degassed further at 150 °C for 5 h.

2. General Synthetic Routes

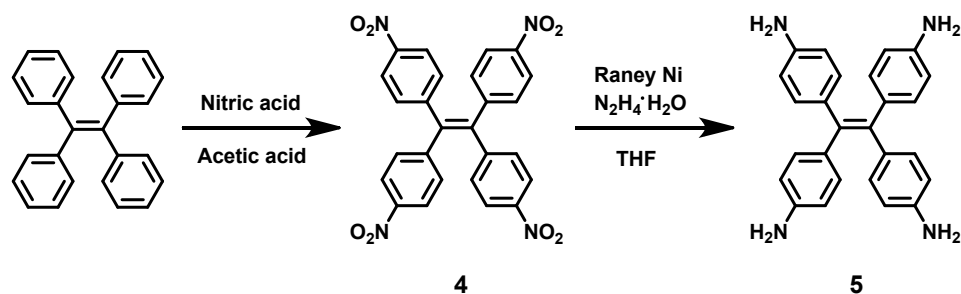


Synthesis of tetraphenylmethane (1). Prepared by a known procedure.¹ : Trityl chloride (15 g, 53.8 mmol) was mixed with aniline (13.7 g, 147.1 mmol) in a round bottom flask charged with argon. The mixture was slowly heated to 200 °C for 5 minutes and cooled to room temperature. The obtained solid was crushed into small pieces and heated with 100 ml of 2M HCl and 90 ml of methanol at 100 °C for 2 hours. After filtration, the gray solid was washed with 100 ml water and 100 ml methanol and dried under vacuum. The dried gray solid was suspended in 120 ml of ethanol and 16.5 ml concentrated sulfuric acid and cooled to -10 °C. After 12 ml of isopentyl nitrite was slowly added, the mixture was stirred for another 1 hour. 40 ml of 30 % hypophosphorous acid was slowly added at -10 °C and the mixture was heated to 50 °C for 2 hours. An olive colored solid was obtained after filtration, followed by washing with ethanol and 1,4-dioxane to get tetraphenylmethane as a light yellow solid in 80% yield. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.17 -7.06 (m, 20H, Ar-H).

Synthesis of tetrakis(4-nitrophenyl)methane (TNPM, 2). Prepared by a known procedure.¹ 13 ml of fuming nitric acid was added in a round bottom flask and cooled to -10 °C. Tetraphenylmethane (5 g, 15.6 mmol) was added to the pre-cooled fuming nitric acid in small portions under vigorous stirring. After addition, 6 ml of acetic anhydride and 8 ml of glacial acetic acid were added drop-wise and the mixture was stirred for about 15 minutes. Then, 16 ml glacial acetic acid was added to dilute the mixture. After filtration, the yellow solid was washed with plenty of water to get light yellow product in 40% yield. ¹H NMR (300 MHz, DMSO) δ (ppm): 8.51 (d, *J* = 8.7 Hz, 8H, Ar-H), 7.85 (d, *J* = 8.7 Hz, 8H, Ar-H).

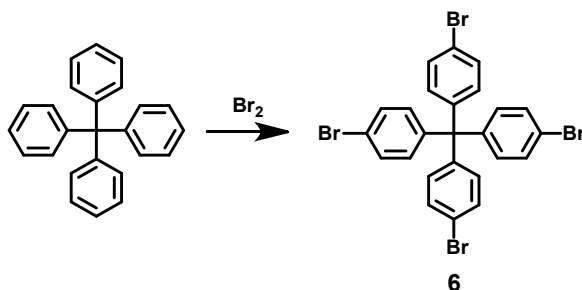


Synthesis of tetrakis(4-aminophenyl)methane (TAPM, 3). Prepared by a known procedure.¹ Tetrakis(4-nitrophenyl)methane (500 mg, 1 mmol) was dissolved in 10 ml THF. Raney nickel (~2 g) and hydrazine monohydrate (670 mg, 13.4 mmol) were added to the solution carefully and the reaction mixture was heated to reflux for 2 hours. After the reaction mixture was cooled to room temperature, the nickel was filtered off and the solvent was evaporated under reduced pressure to get off-white solid in 86 % yield. ¹H NMR (300 MHz, DMSO) δ (ppm): 6.67 (d, *J* = 8.9 Hz, 8H, Ar-H), 6.38 (d, *J* = 8.9 Hz, 8H, Ar-H), 4.83 (s, 8H, Ar-NH₂)

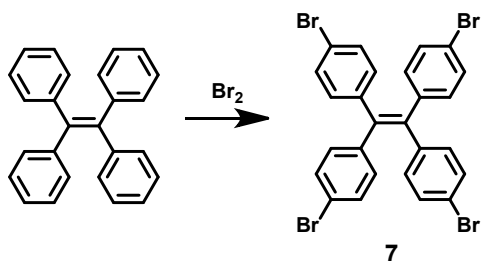


Synthesis of 1,1,2,2-tetrakis(4-nitrophenyl)ethene (TNPE, 4). Prepared by a known procedure.² A mixture of 30 ml of acetic acid and 30 ml fuming nitric acid was cooled to 0 °C by ice bath and 1,1,2,2-tetraphenylethene (3g, 9 mmol) was added in small portions. After addition, the ice bath was removed and the mixture was stirred at room temperature for 3 hours. The resulting brown solution was poured into 300 g ice water to get light yellow precipitation. The precipitation was filtered off and recrystallize from 1,4-dioxane to get light yellow crystal in 50% yield. ¹H NMR (300 MHz, DMSO) δ (ppm): 8.10 (d, *J* = 8.7 Hz, 8H, Ar-H), 7.36 (d, *J* = 8.7 Hz, 8H, Ar-H).

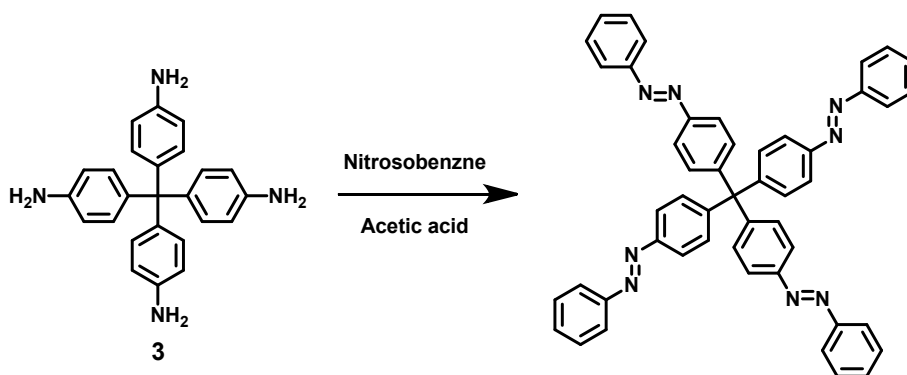
Synthesis of 1,1,2,2-tetrakis(4-aminophenyl)ethene (TAPE, 5). Synthetic method was adapted from the preparation of TAPM. 1,1,2,2-tetrakis(4-nitrophenyl)ethene (525 mg, 1 mmol) was dissolved in 10 ml THF. Raney nickle (~2 g) and hydrazine monohydrate (670 mg, 13.4 mmol) were added to the solution carefully and the reaction mixture was heated to reflux for 2 hours. After the reaction mixture was cooled to room temperature, the nickle was filtered off and the solvent was evaporated under reduced pressure to get light yellow solid in 84 % yield. ¹H NMR (300 MHz, DMSO) δ (ppm): 6.57 (d, *J* = 8.7 Hz, 8H, Ar-H), 6.25 (d, *J* = 8.7 Hz, 8H, Ar-H), 4.84 (s, 8H, Ar-NH₂)



Synthesis of tetrakis(4-bromophenyl)methane (TBPM, 6). Prepared by a known procedure.³ Bromine (16 ml, 49.75 g, 312.5 mmol) was loaded in a round-bottom flask. Under vigorous stirring, tetraphenylmethane (5 g, 15.6 mmol) was added to the flask in small portions in five minutes at room temperature. After the completion of the addition, the mixture was stirred for another 20 minutes at room temperature and was cooled to -78 °C by acetone-dry ice bath. After 40 ml of ethanol was slowly added, the cooling bath was removed and the mixture was stirred overnight. The precipitate was collected by filtration and washed with aqueous sodium hydrogensulfite solution, water and ethanol. The solid was dry in vacuo and the product was obtained as a light yellow solid in 80 % yield. ¹H NMR (300 MHz, CDCl₃) δ (ppm): 7.41 (d, *J* = 8.7 Hz, 8H, Ar-H), 7.02 (d, *J* = 8.7 Hz, 8H, Ar-H).

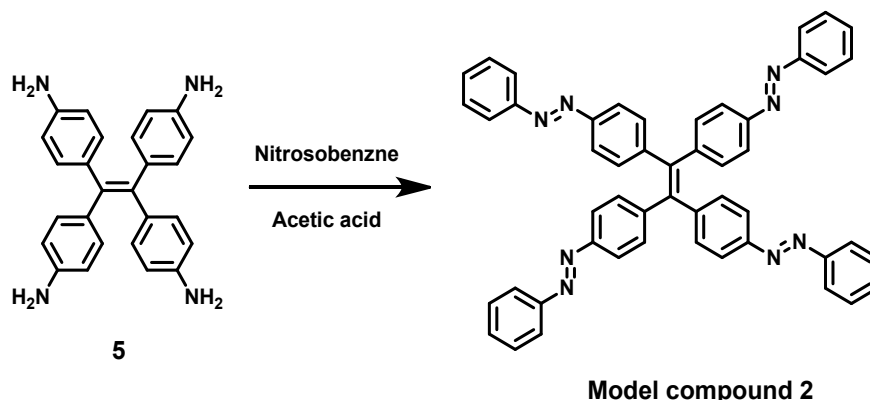


Synthesis of 1,1,2,2-tetrakis(4-bromophenyl)ethene (TBPE, 7). Prepared by a known procedure.⁴ Bromine (8 ml, 25 g, 156.3 mmol) was loaded in a round-bottom flask. Under vigorous stirring, tetraphenylethene (5 g, 15.6 mmol) was added to the flask in small portions in five minutes at room temperature. After the completion of the addition, the mixture was stirred for another 16 h at room temperature and was cooled to -78 °C by acetone-dry ice bath. After 40 ml of ethanol was slowly added, the cooling bath was removed and the mixture was stirred overnight. The precipitate was collected by filtration and washed with aqueous sodium hydrogensulfite solution, water and ethanol. After the solid was recrystallized from mixture of benzene and ethanol, the product was obtained as a white solid in 55 % yield. ¹H NMR (300 MHz, CDCl₃) δ (ppm): 7.28 (d, *J* = 8.4 Hz, 8H, Ar-H), 6.86 (d, *J* = 8.4 Hz, 8H, Ar-H)

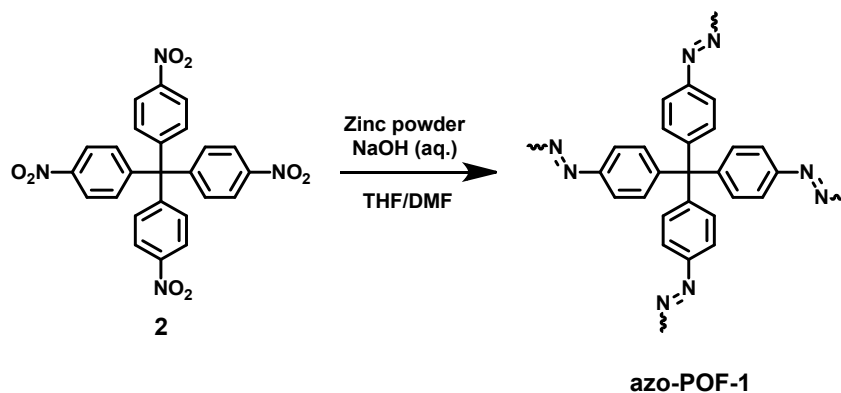


Model compound 1

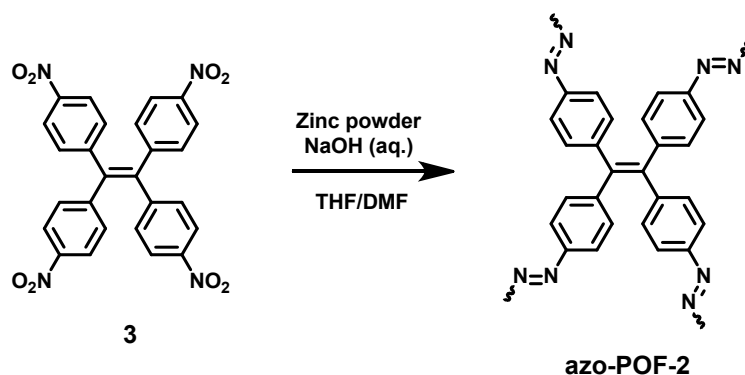
Synthesis of model compound 1: Tetrakis(4-aminophenyl)methane (200 mg, 0.53 mmol) and nitrosobenzene (340 mg, 3.18 mmol) were dissolved in 10ml of glacial acetic acid. The solution was heated at 80 °C for 18 hours and cooled to room temperature. The orange precipitate was filtered and washed with water and methanol to get orange solid in 49 % yield. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.94-7.88 (m, 16H, Ar-H), 7.56-7.52 (m, 20H, Ar-H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 152.7, 151.0, 148.7, 131.7, 131.1, 129.1, 122.9, 122.4, 65.3. Calc. MS: 736.3063, MALDI found [M+H]⁺: 737.3146.



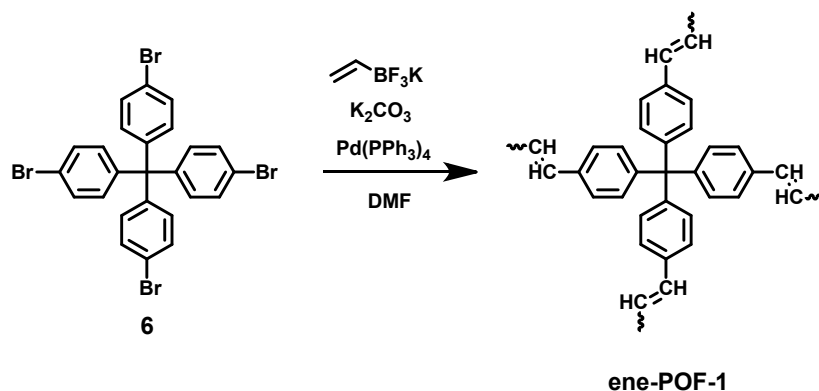
Synthesis of model compound 2: 1,1,2,2-tetrakis(4-aminophenyl)ethene (210 mg, 0.53 mmol) and nitrosobenzene (340 mg, 3.18 mmol) were dissolved in 10ml of glacial acetic acid. The solution was heated at 80 °C for 18 hours and cooled to room temperature. The orange precipitate was filtered and washed with water and methanol to get orange solid in 33 % yield. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.90 (d, *J* = 8.2 Hz, 8H, Ar-H), 7.77 (d, *J* = 8.4 Hz, 8H, Ar-H), 7.54-7.47 (m, 12H, Ar-H), 7.31 (d, *J* = 8.4 Hz, 8H, Ar-H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 152.7, 151.3, 145.8, 141.6, 132.3, 131.0, 129.1, 122.9, 122.7. Calc. MS: 748.3063, MALDI found [M+H]⁺: 749.3039.



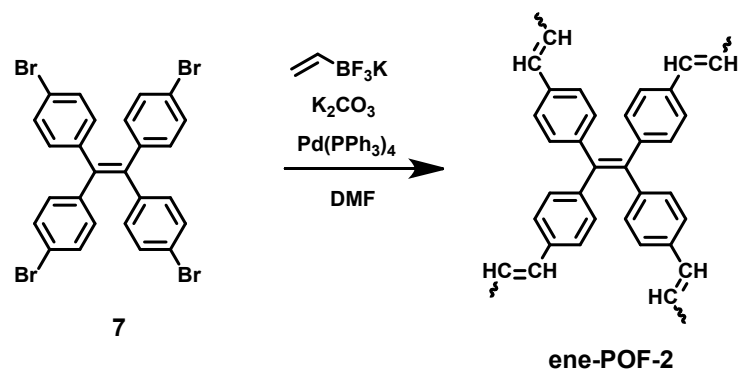
Synthesis of azo-POF-1: Tetrakis(4-nitrophenyl)methane (500 mg, 1 mmol) was dissolved in a mixture of 7 ml of THF and 8 ml of DMF. NaOH (640 mg, 16 mmol) in 1.5 ml de-ionized water and zinc powder (588 mg, 9 mmol) were added to the solution. The mixture was heated at 65 °C for 36 h and cooled to room temperature. The reaction mixture was poured into 100 ml 2M HCl and stirred for 1h. The yellow-orange solid was filtered off and washed with water, acetone and THF, followed by Soxhlet extraction from water (48 hours) and THF (48 hours). The yellow-orange solid was dried at 110 °C under vacuum for 8 hours to yield Azo-POF-1 in 78% yield. Anal. Calcd. For azo-POF-1: C, 80.63%; H, 4.33%; N, 15.04%. Found: C, 71.15%; H, 4.60%; N, 12.75%.



Synthesis of azo-POF-2: 1,1,2,2-tetrakis(4-nitrophenyl)ethene (525 mg, 1 mmol) was dissolved in a mixture of 7 ml of THF and 8 ml of DMF. NaOH (640 mg, 16 mmol) in 1.5 ml de-ionized water and zinc powder (588 mg, 9 mmol) were added to the solution. The mixture was heated at 65 °C for 36 h and cooled to room temperature. The reaction mixture was poured into 100 ml 2M HCl and stirred for 1h. The yellow-orange solid was filtered off and washed with water, acetone and THF, followed by Soxhlet extraction from water (48 hours) and THF (48 hours). The yellow-orange solid was dried at 110 °C under vacuum for 8 hours to yield azo-POF-2 in 92% yield. Anal. Calcd. For azo-POF-2: C, 81.23%; H, 4.20%; N, 14.57%. Found: C, 69.62 %; H, 4.20%; N, 12.16%.



Synthesis of ene-POF-1: Prepared by a known procedure.⁵ A two neck round bottom flask was charged with compound 6 (250 mg, 0.393 mmol), K₂CO₃ (651 mg, 4.72 mmol), potassium vinyltrifluoroborate (105 mg, 0.784 mmol) and 10 ml DMF. After the mixture was degassed with Ar for 30 minutes, Pd(PPh₃)₄ (30 mg, 0.026 mmol) was added. The mixture was stirred at 80 °C for 12 h and the temperature was raised to 120 °C. After kept at 120 °C for 60 h, the reaction was cooled to room temperature, and the solid was collected by filtration. The gray solid was washed with water, acetone and THF, followed by Soxhlet extraction from acetone for 24 h to obtain ene-POF-1 as a gray solid in quantitative yield.



Synthesis of ene-POF-2: Prepared by a known procedure.⁵ A two neck round bottom flask was charged with compound 7 (254 mg, 0.393 mmol), K_2CO_3 (651 mg, 4.72 mmol), potassium vinyltrifluoroborate (105 mg, 0.784 mmol) and 10 ml DMF. After the mixture was degassed with Ar for 30 minutes, $\text{Pd}(\text{PPh}_3)_4$ (30 mg, 0.026 mmol) was added. The mixture was stirred at 80 °C for 12 h and the temperature was raised to 120 °C. After kept at 120 °C for 60 h, the reaction was cooled to room temperature, and the solid was collected by filtration. The gray solid was washed with water, acetone and THF, followed by Soxhlet extraction from acetone for 24 h to obtain ene-POF-2 as a yellow solid in quantitative yield.

3. FT-IR spectra

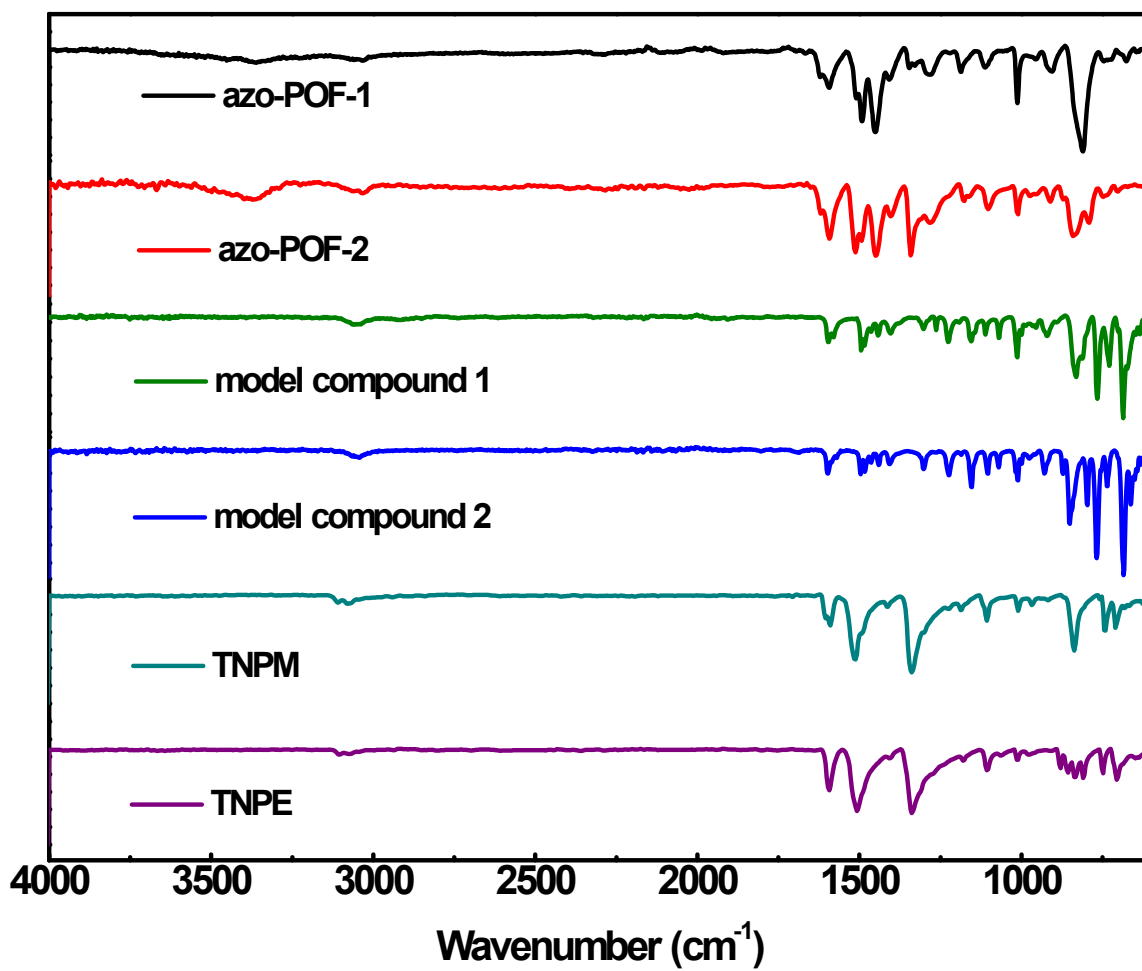


Figure S1. FT-IR spectra of azo-POFs, model compounds, and related starting materials.

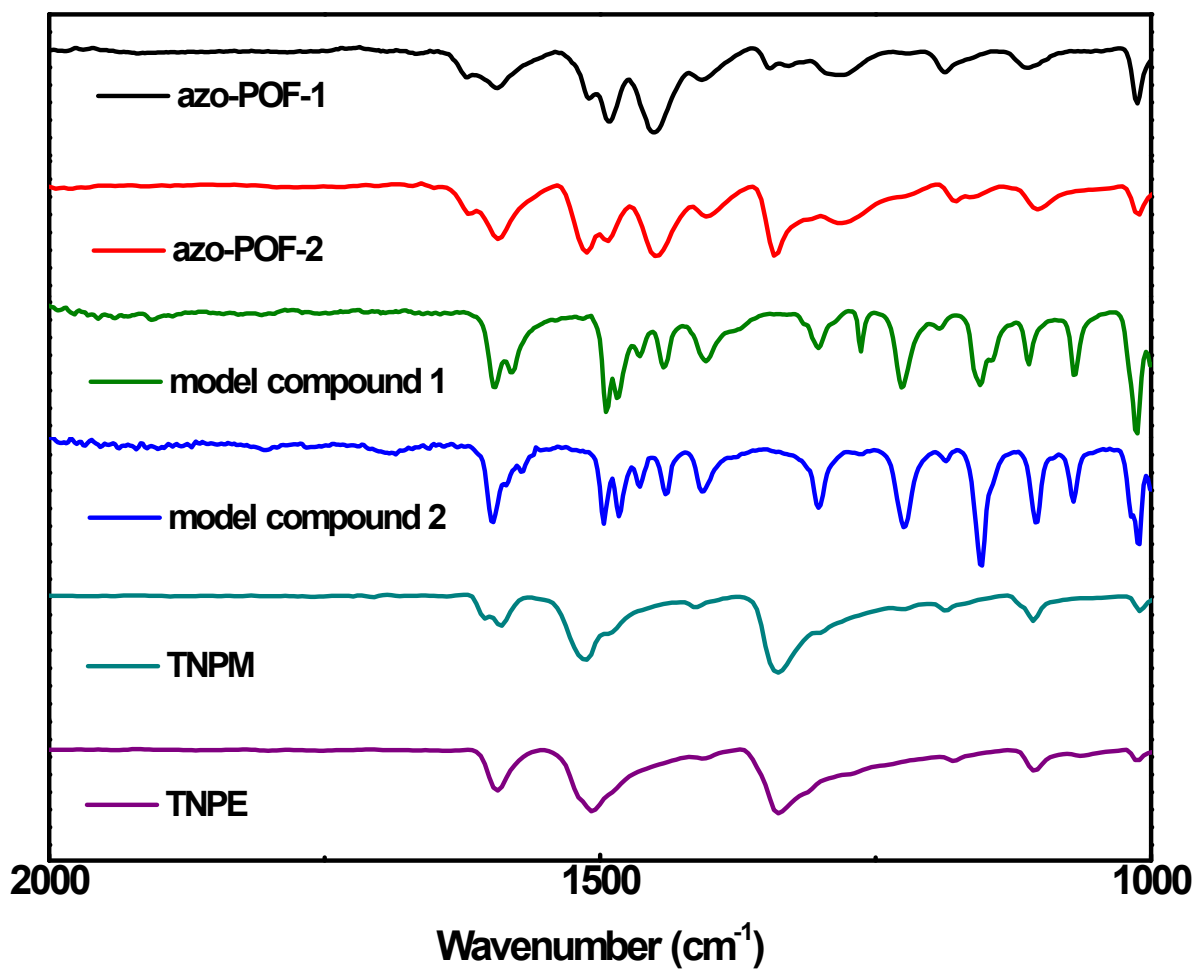


Figure S2. FT-IR spectra of azo-POFs, model compounds, and related starting materials (2000-1000 cm⁻¹).

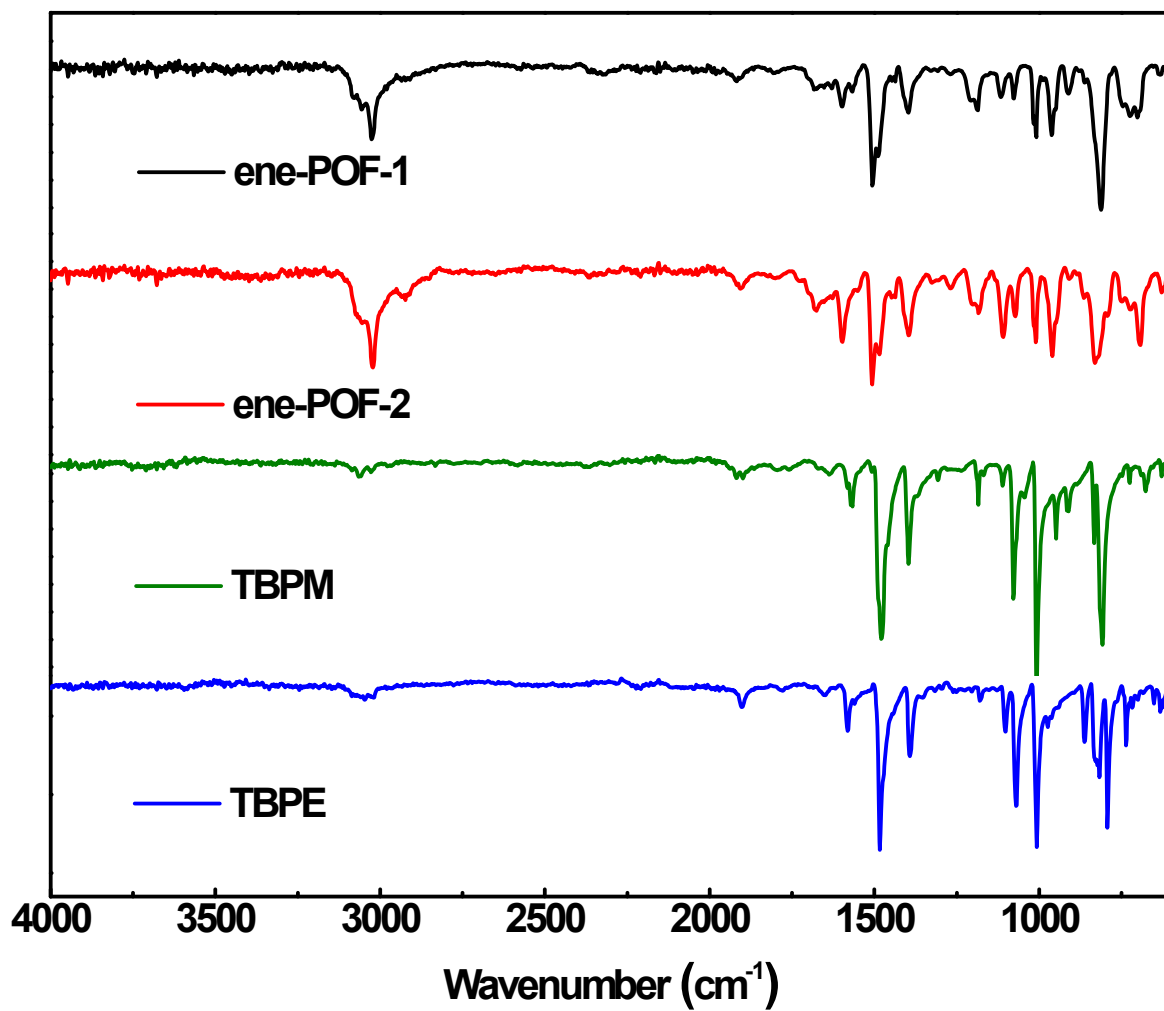


Figure S3. FT-IR spectra of ene-POFs and related starting materials.

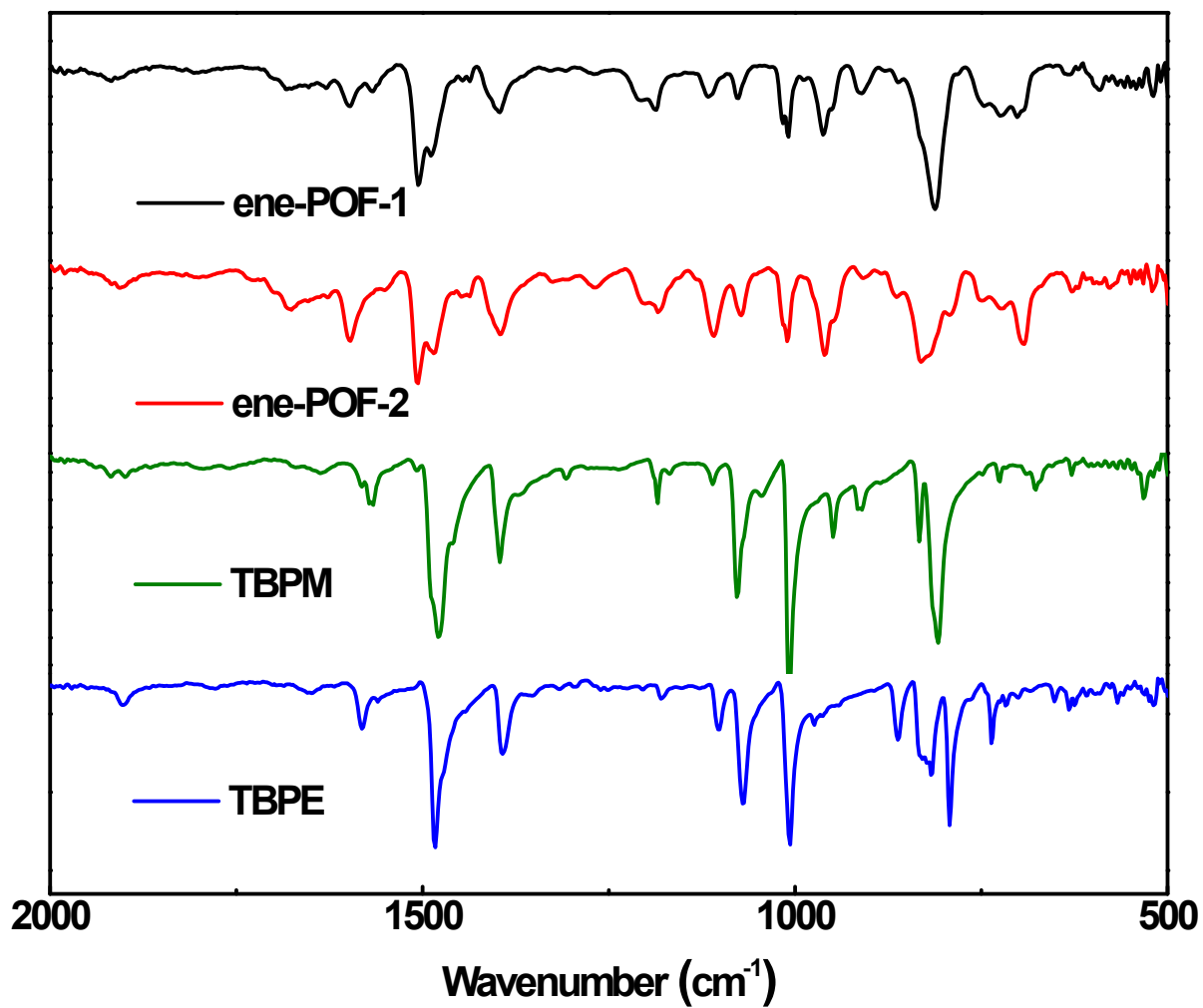


Figure S4. FT-IR spectra of ene-POFs and related starting materials (2000-500 cm⁻¹).

4. ^{13}C NMR spectra

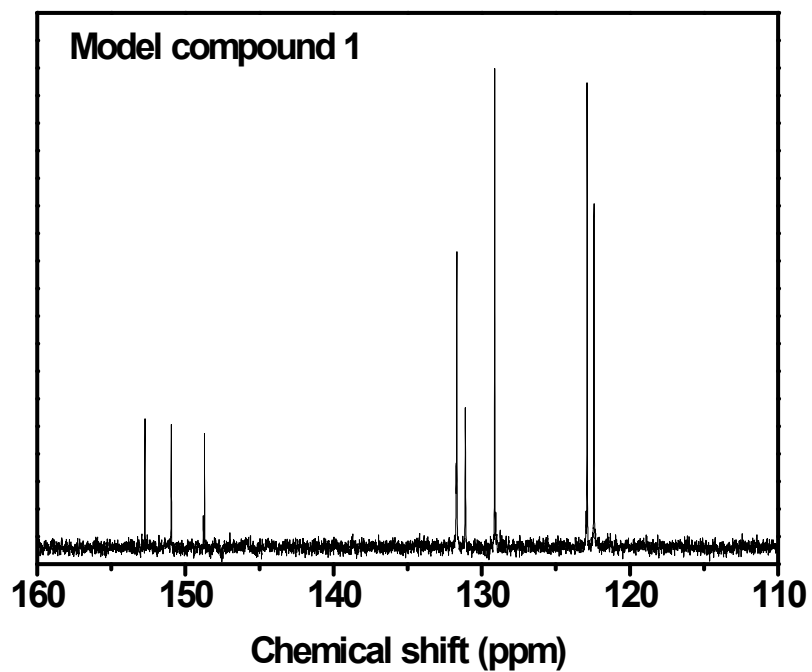
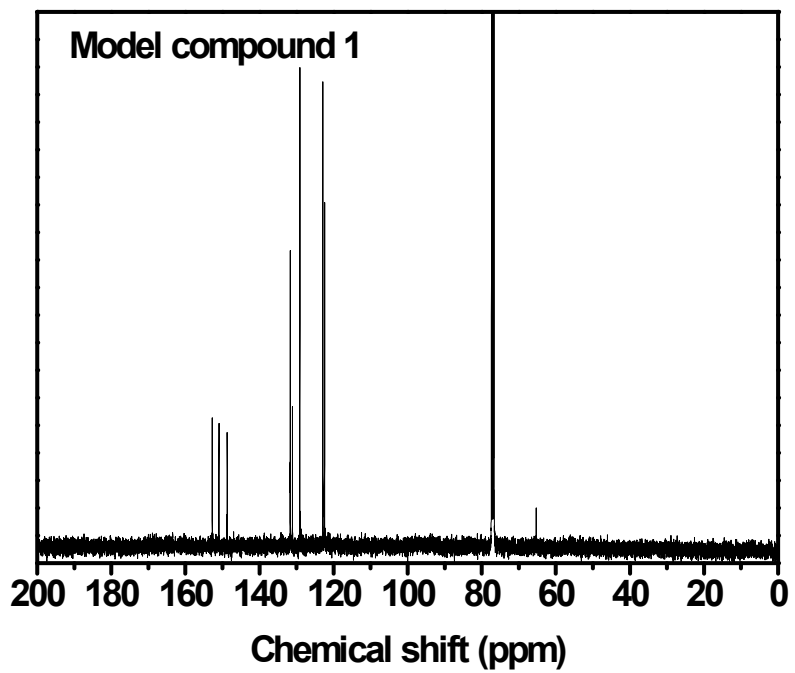


Figure S5. ^{13}C NMR spectra of model compound 1.

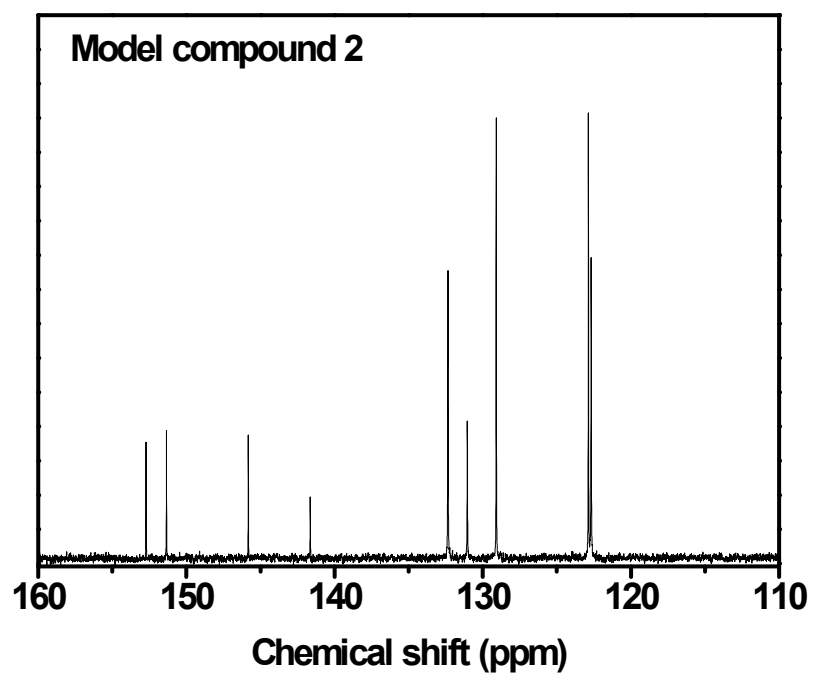
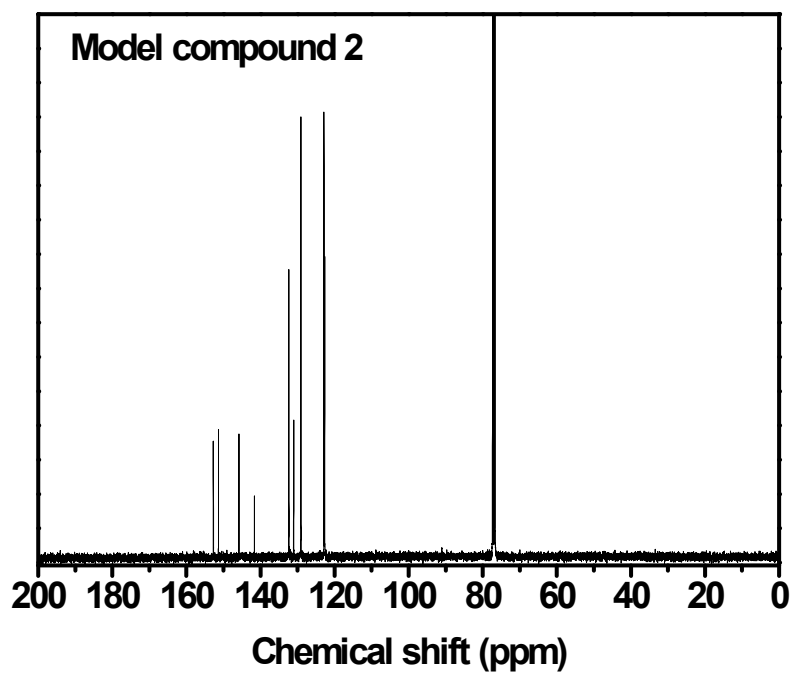


Figure S6. ¹³C NMR spectra of model compound 2.

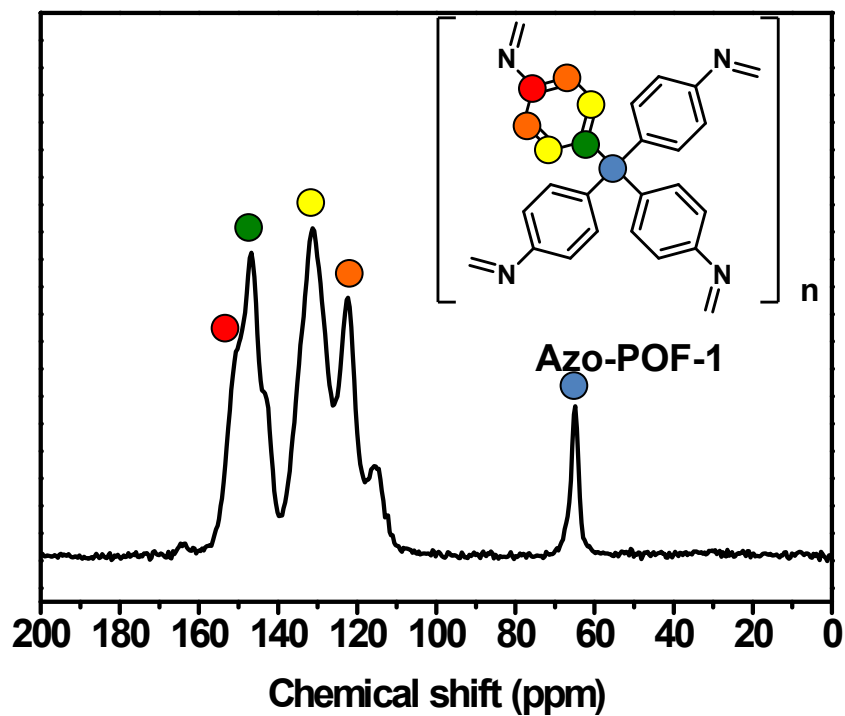


Figure S7. Solid-state ^{13}C CP-MAS NMR spectrum of azo-POF-1.

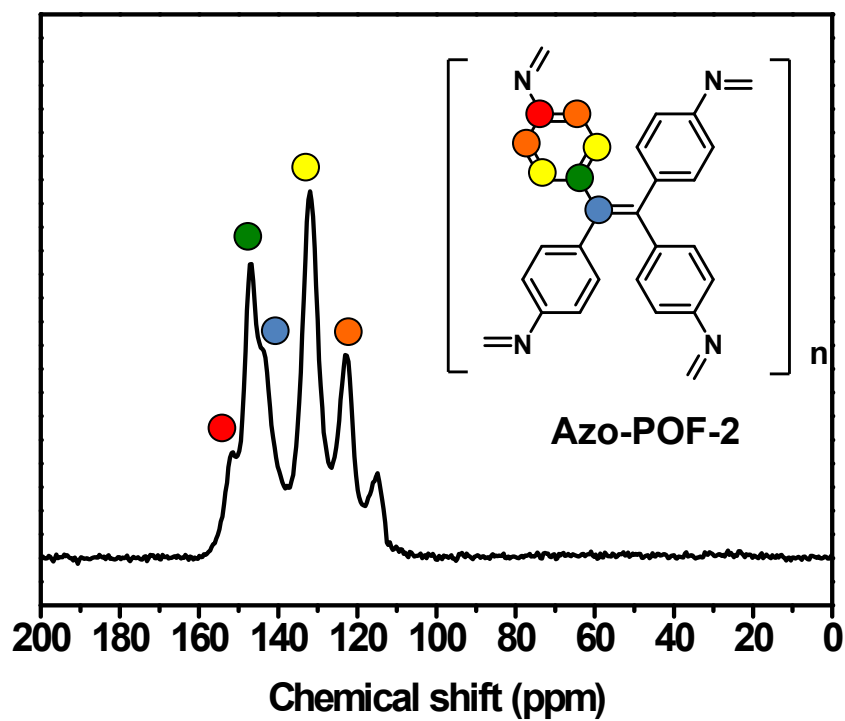


Figure S8. Solid-state ^{13}C CP-MAS NMR spectrum of azo-POF-2.

5. Powder X-ray diffraction

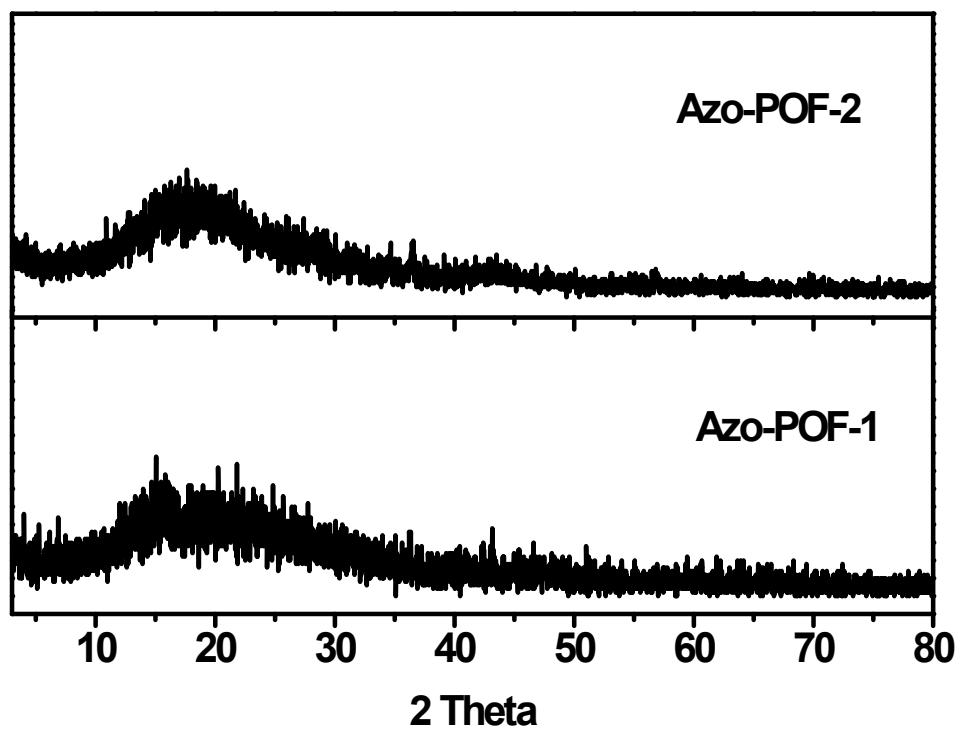


Figure S9. Powder X-ray diffraction patterns of azo-POFs

6. Thermal gravimetric analysis of azo-POFs

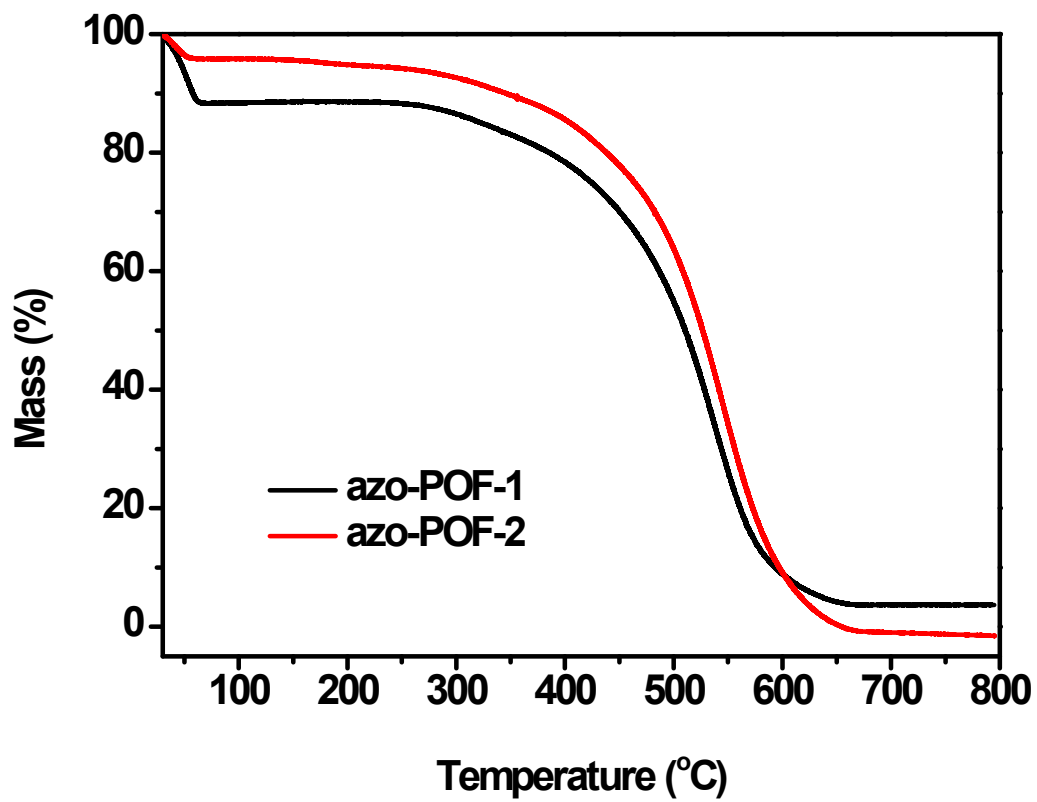


Figure S10. Thermal gravimetric analysis of azo-POFs

7. Additional gas adsorption data for azo-POFs and ene-POFs

Gas adsorption measurements were performed using an ASAP 2020 volumetric adsorption analyzer using high-purity grade (99.999%) gases. N₂ and gas adsorption isotherms were measured at 77 K using a liquid N₂ bath; CO₂ adsorption isotherms were measured at 273 K using an ice water bath and 291 K and 298 K using water bath. All samples were degassed at 150 °C for 5 h before gas measurements. Pore size distribution was calculated from N₂ isotherms using a spherical/cylindrical pore NLDFT adsorption branch model.

The isosteric heats of adsorption were calculated using a virial type thermal equation given below based on the adsorption at 273 K and 291 K:

$$\ln(P) = \ln(n) + \frac{1}{T} \sum_{i=0}^x a_i n^i + \sum_{i=0}^y b_i n^i$$

where the pressure (P) is expressed in mmHg, the amount absorbed (n) is expressed in mmol/g, and the temperature (T) is expressed in K. The virial coefficients a_i and b_i were fit by increasing the respective number of each (x and y) until a sufficient goodness of fit was reached. The values of the virial coefficients a_0 to a_x were then used to calculate the isosteric heat of adsorption (Q_{st}) based on the equation given below:

$$Q_{st} = -R \sum_{i=0}^x a_i n^i$$

Henry's law selectivities (S_H) were calculated by the ratio of Henry's law constants of CO₂ (H_C) and N₂ (H_N).

$$S_H = \frac{H_C}{H_N}$$

The Henry's law constants for CO₂ and N₂ were obtained by the slope of linear fitting of the initial data (pressure less than 0.1 bar) of the gas adsorption isotherms.

Ideal adsorbed solution theory (IAST) selectivities were calculated by fitting the single-site Langmuir model for N₂ isotherms as given below:

$$q = \frac{q_{sat} bP}{1 + bP}$$

and the dual-site Langmuir model for CO₂ isotherms as given below:

$$q = q_1 + q_2 = \frac{q_{sat,1} b_1 P}{1 + b_1 P} + \frac{q_{sat,2} b_2 P}{1 + b_2 P}$$

where the pressure (P) is expressed in mmHg, the saturation loading (q_{sat}) is expressed in mmol/g, the molar loading of adsorbate (q) is measured in mmol/g, and b is the fitted parameter for the isotherm. 1 and 2 refer to two different sites. The IAST selectivity factors (S_{IAST}) were then calculated using the following equation:

$$S_{IAST} = \frac{q_A / q_B}{P_A / P_B}$$

where q_A and q_B are the amount of amounts of A and B absorbed respectively, and P_A and P_B are the partial pressure of A and B respectively.

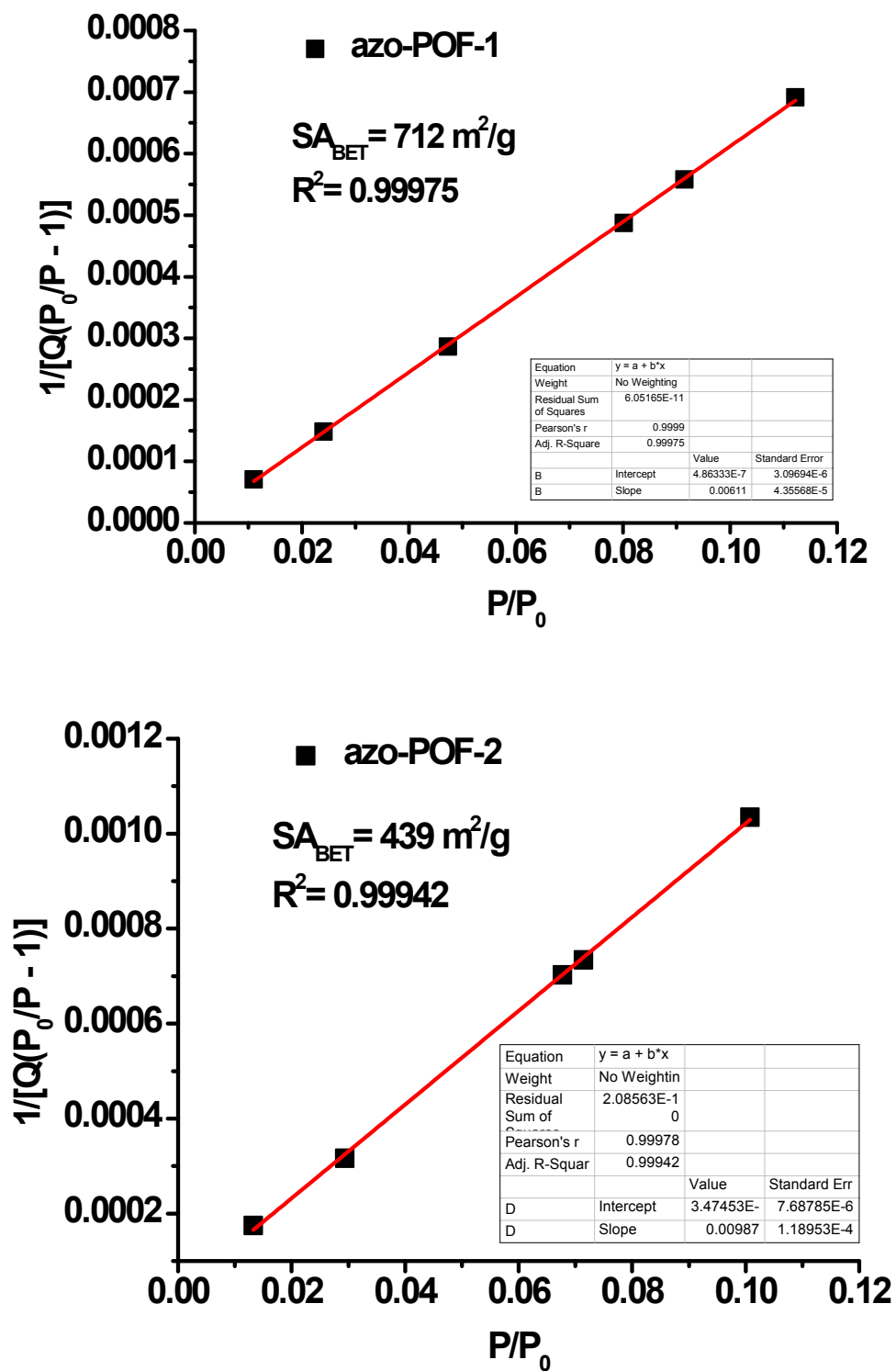


Figure S11. BET surface area plots of azo-POFs based on N₂ adsorption isotherms.

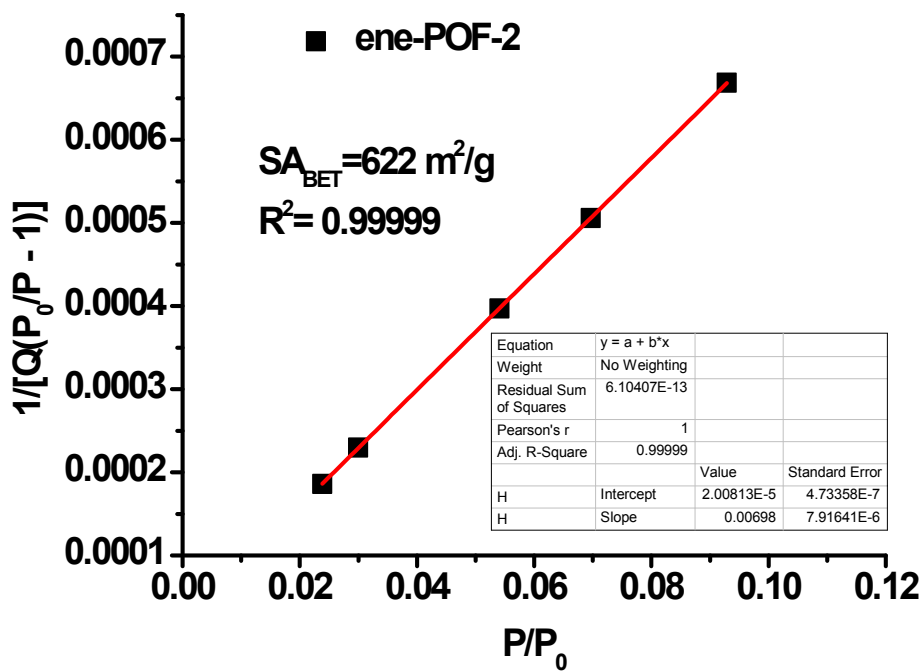
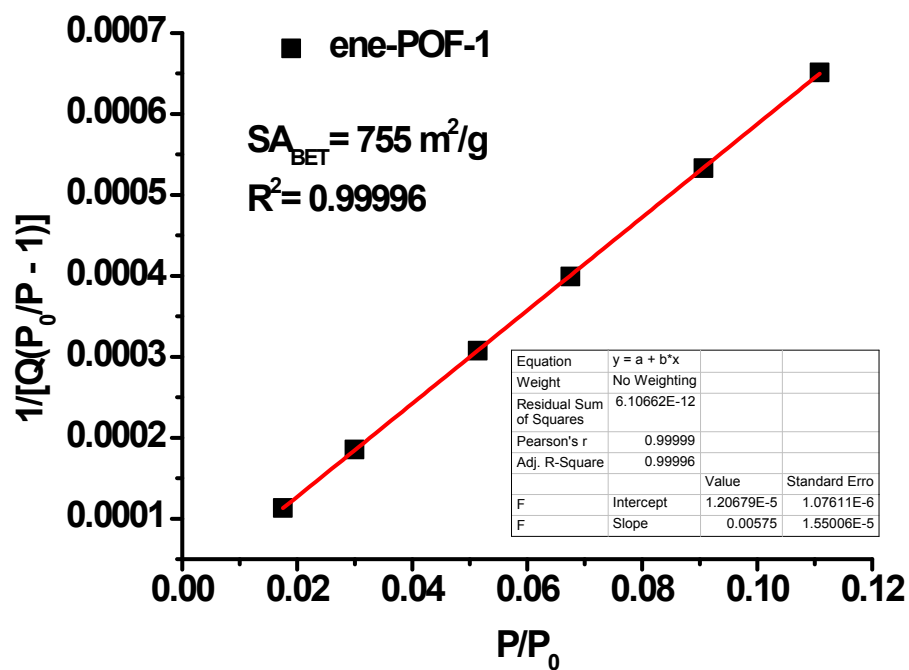


Figure S12. BET surface area plots of ene-POFs based on N₂ adsorption isotherms.

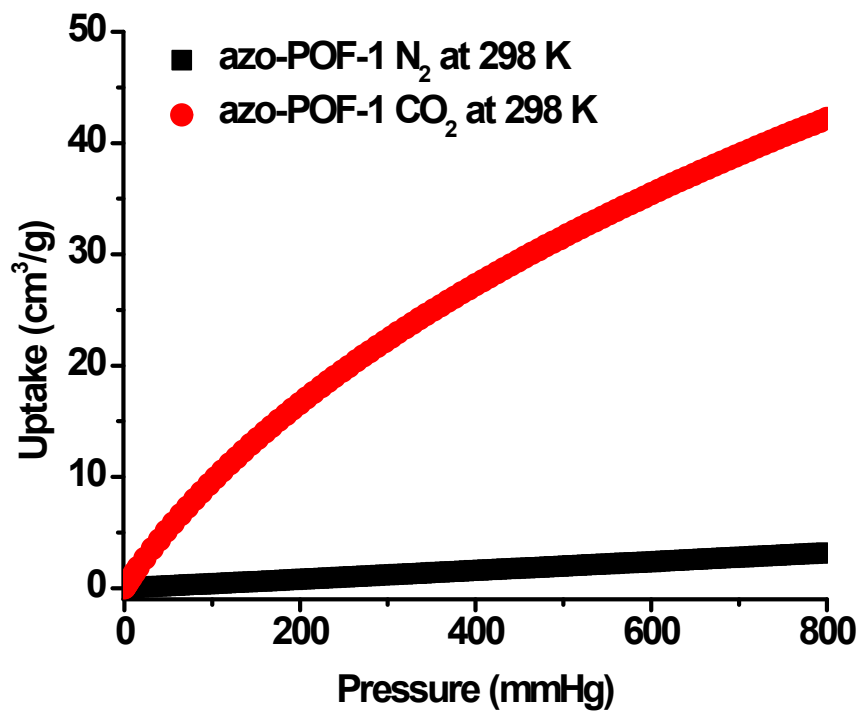
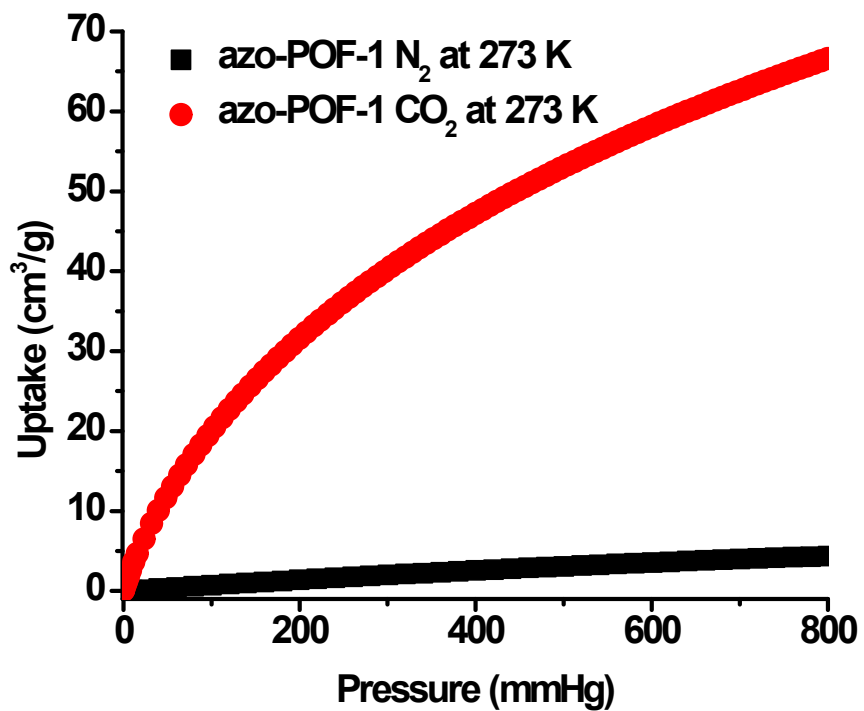


Figure S13. CO₂ and N₂ adsorption isotherms of azo-POF-1.

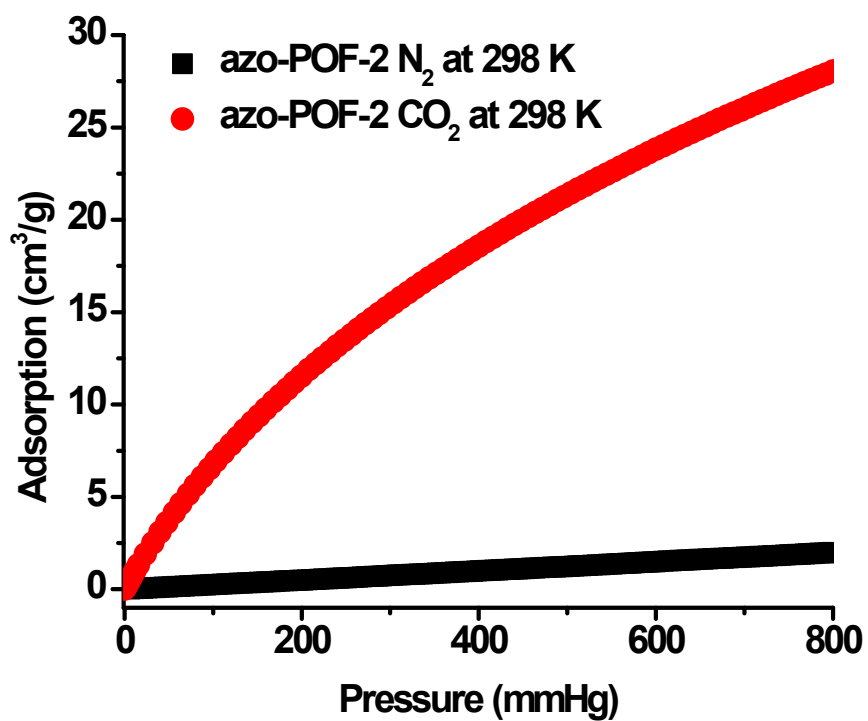
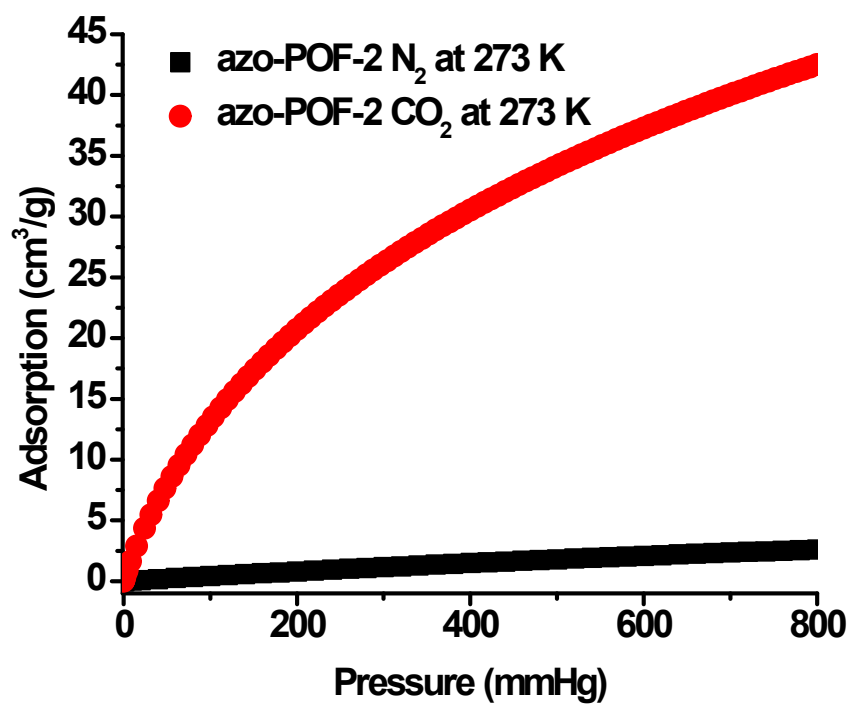


Figure S14. CO₂ and N₂ adsorption isotherms of azo-POF-2.

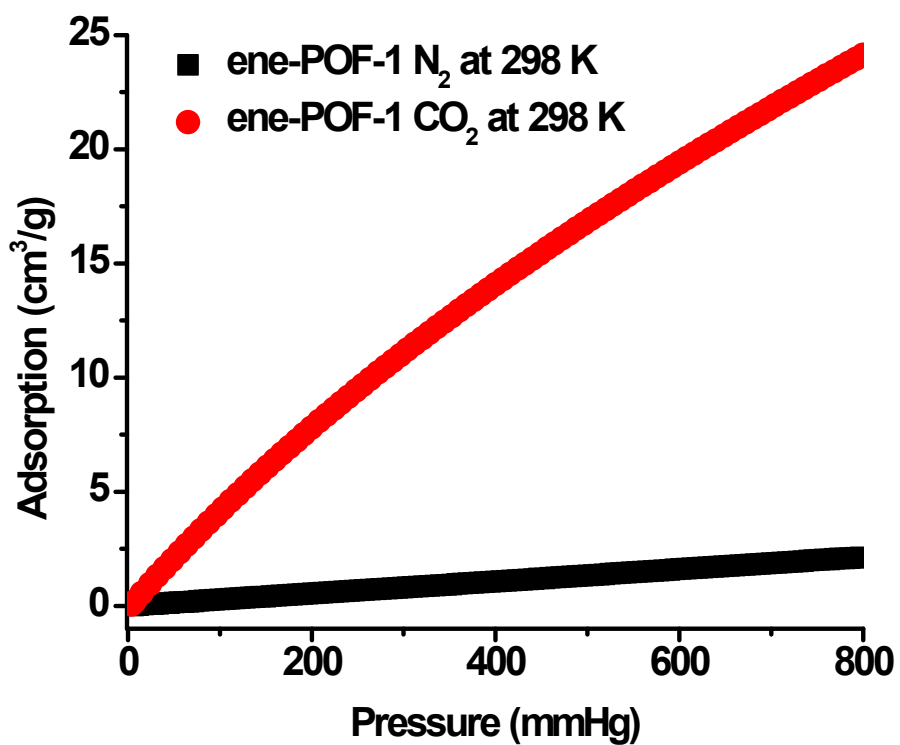
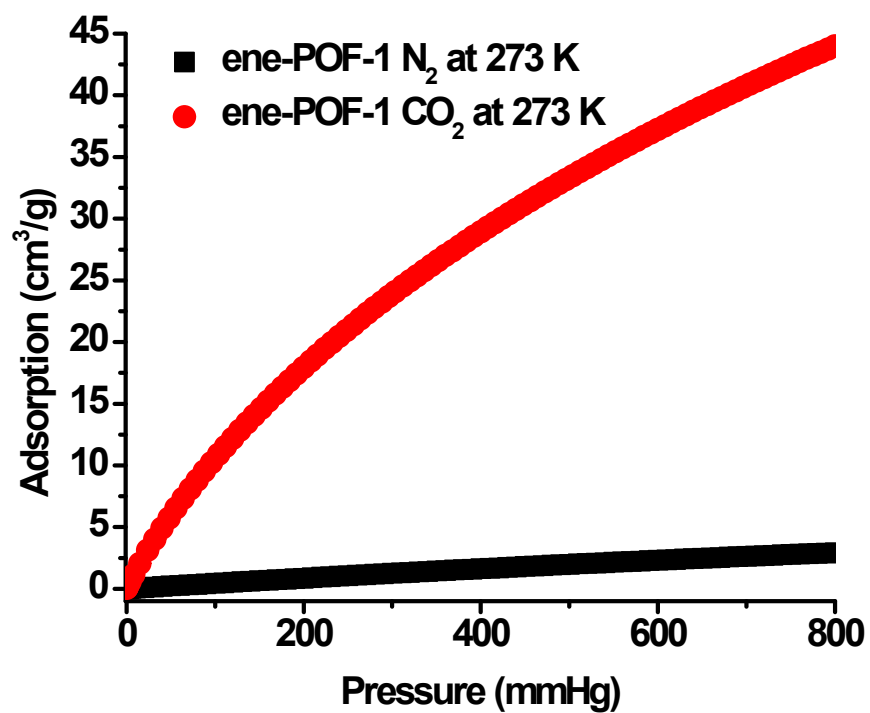


Figure S15. CO₂ and N₂ adsorption isotherms of ene-POF-1.

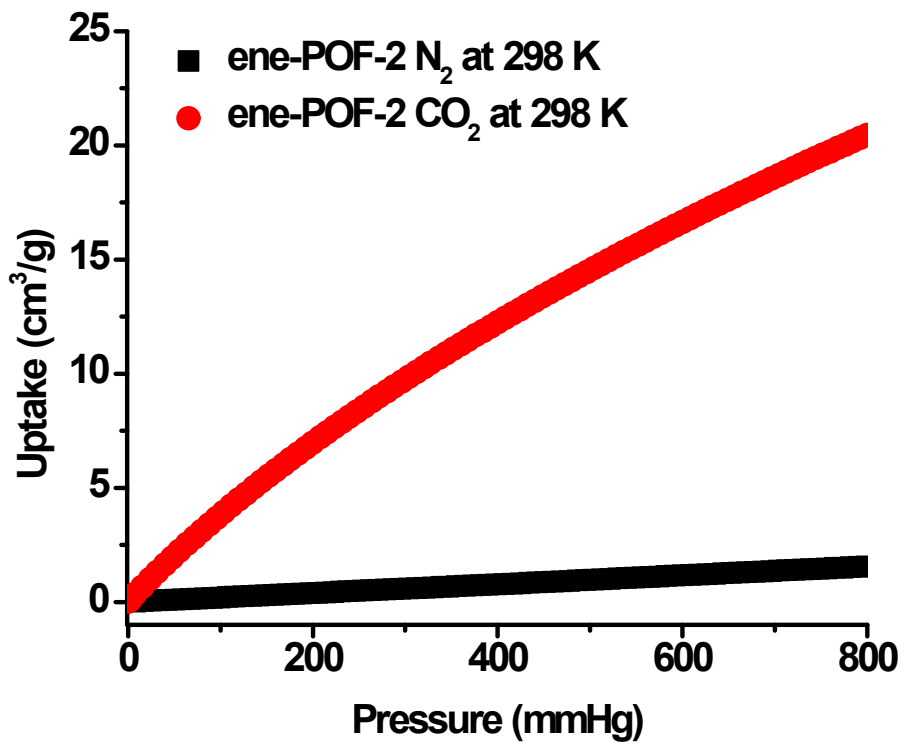
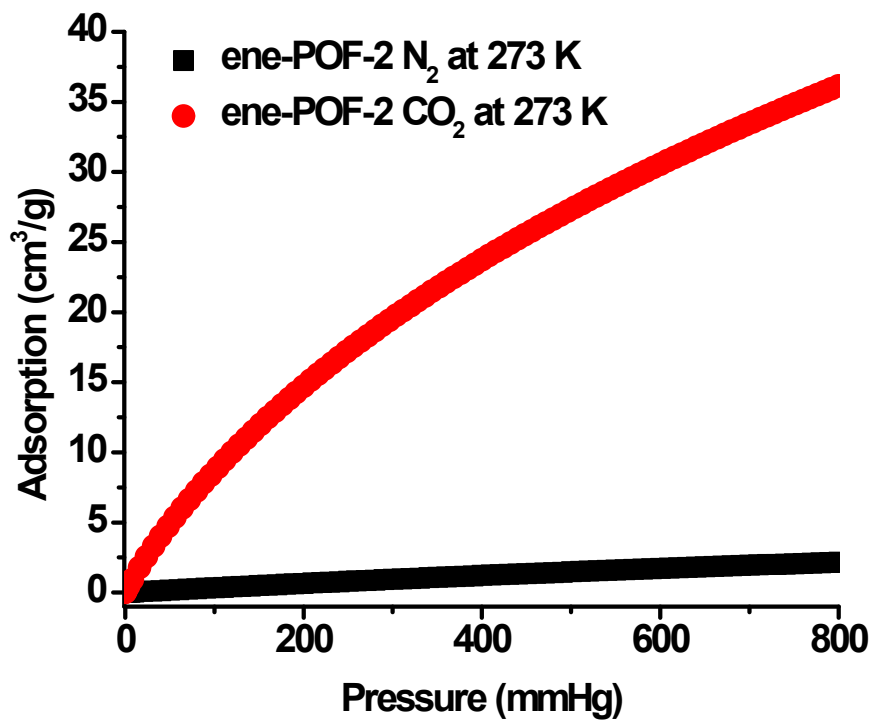


Figure S16. CO₂ and N₂ adsorption isotherms of ene-POF-2.

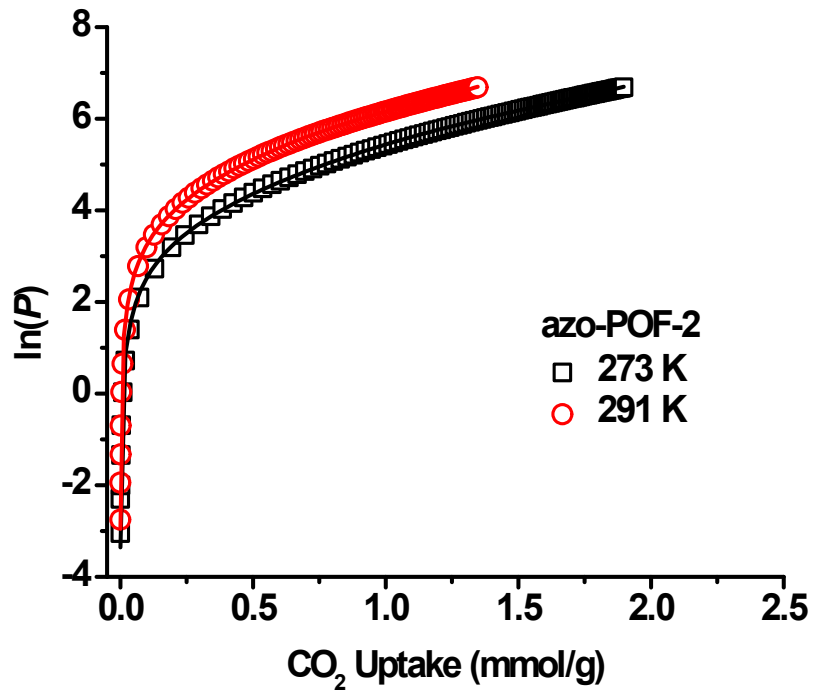
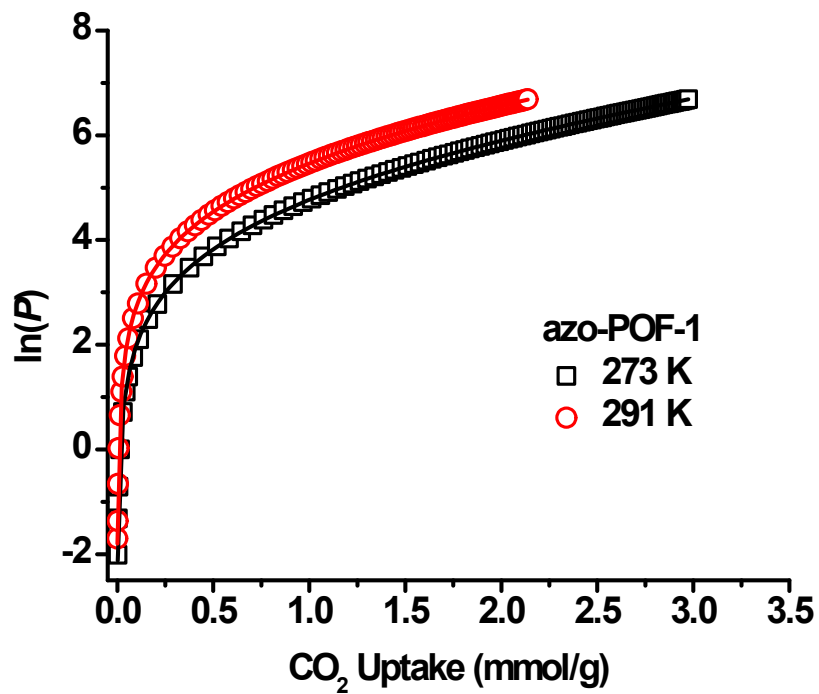


Figure S17. Virial fitting for CO_2 isotherms of azo-POFs

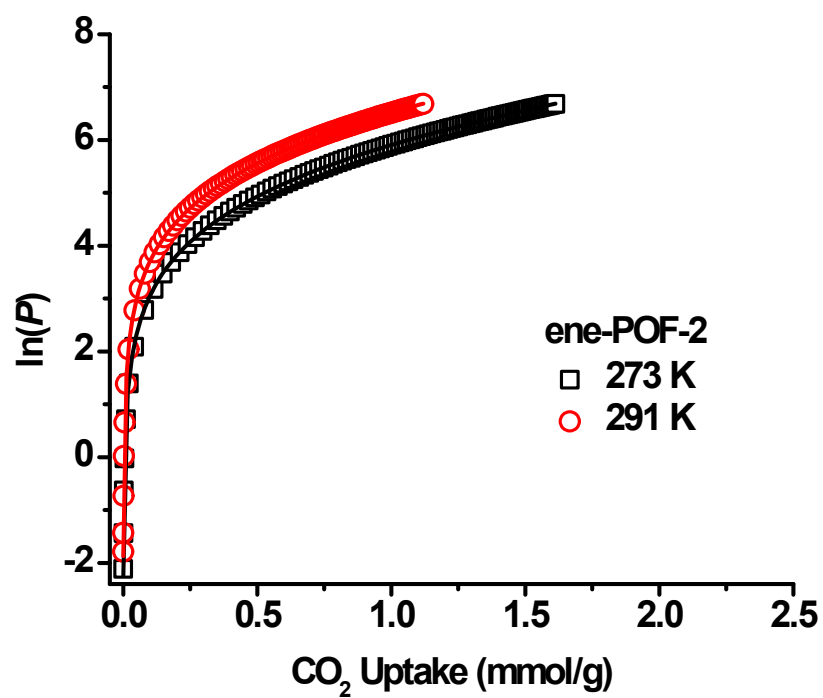
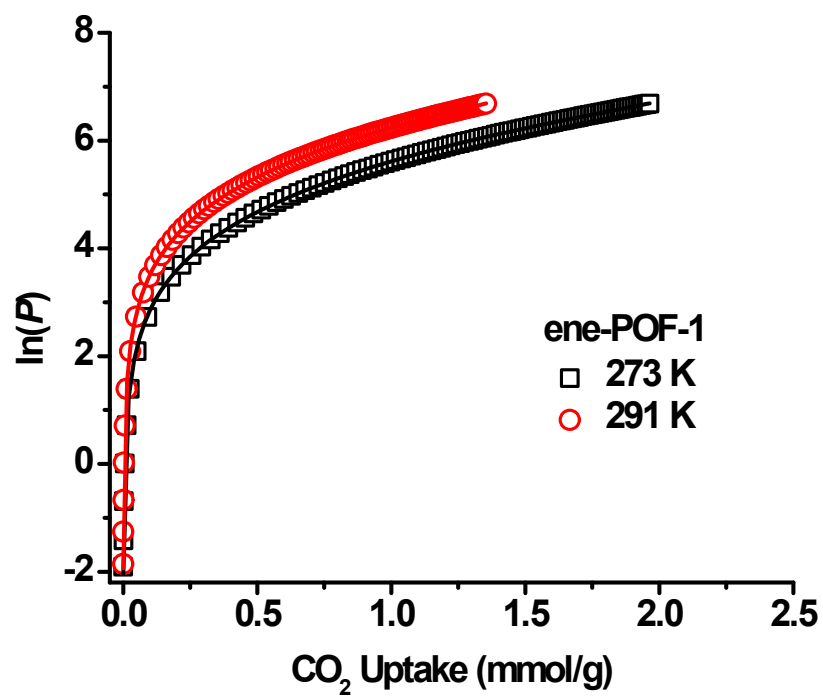


Figure S18. Virial fitting for CO_2 isotherms of ene-POFs

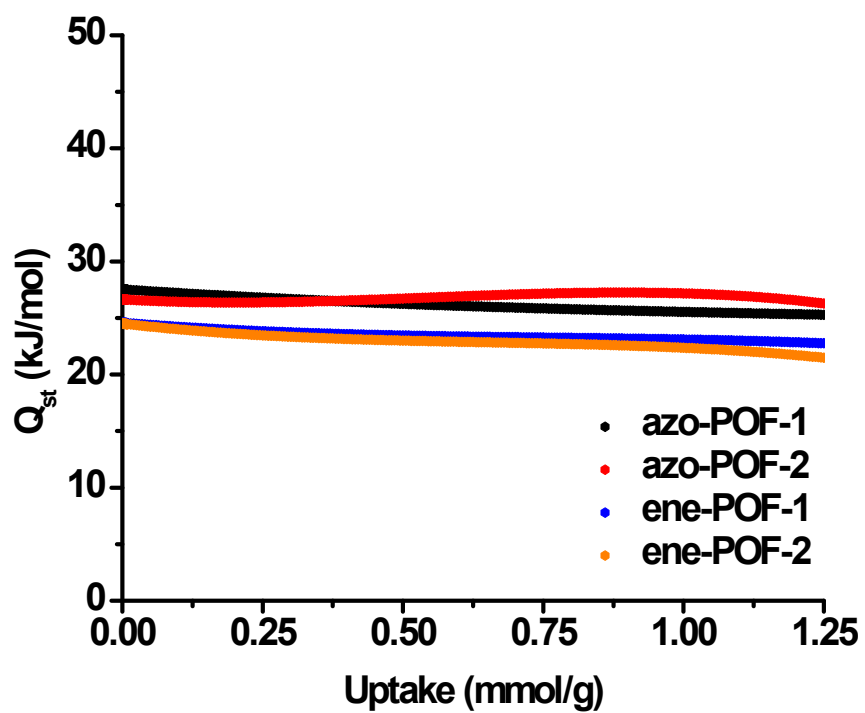


Figure S19. Isosteric heats of adsorption for CO₂.

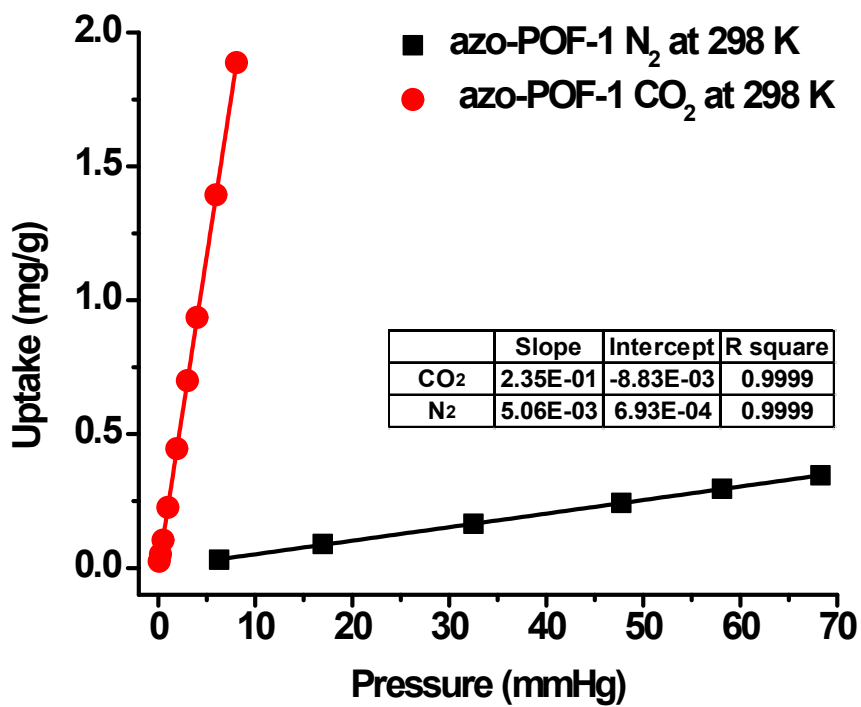
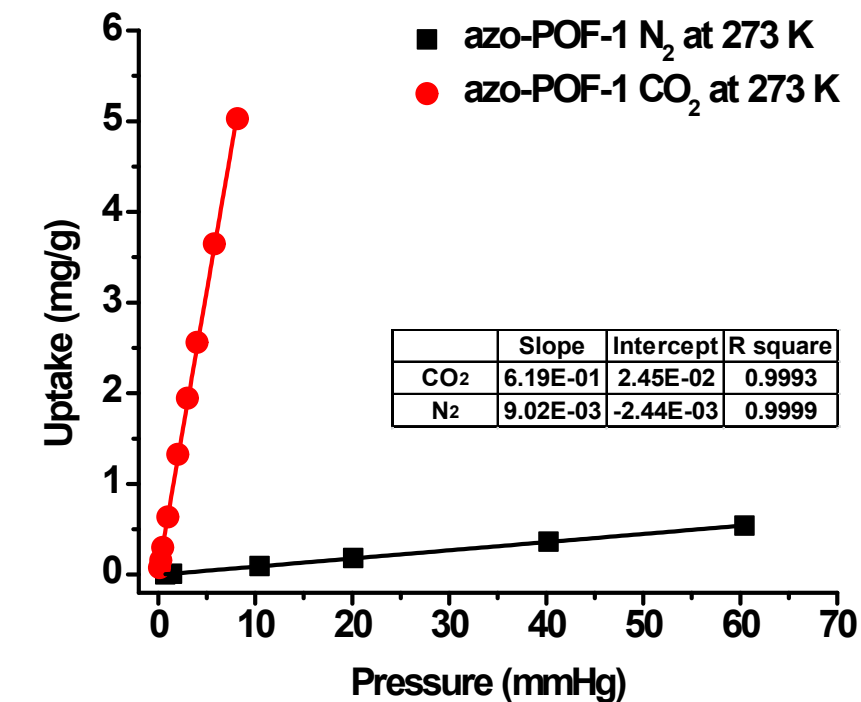


Figure S20. CO₂/N₂ initial slope selectivity studies for azo-POF-1.

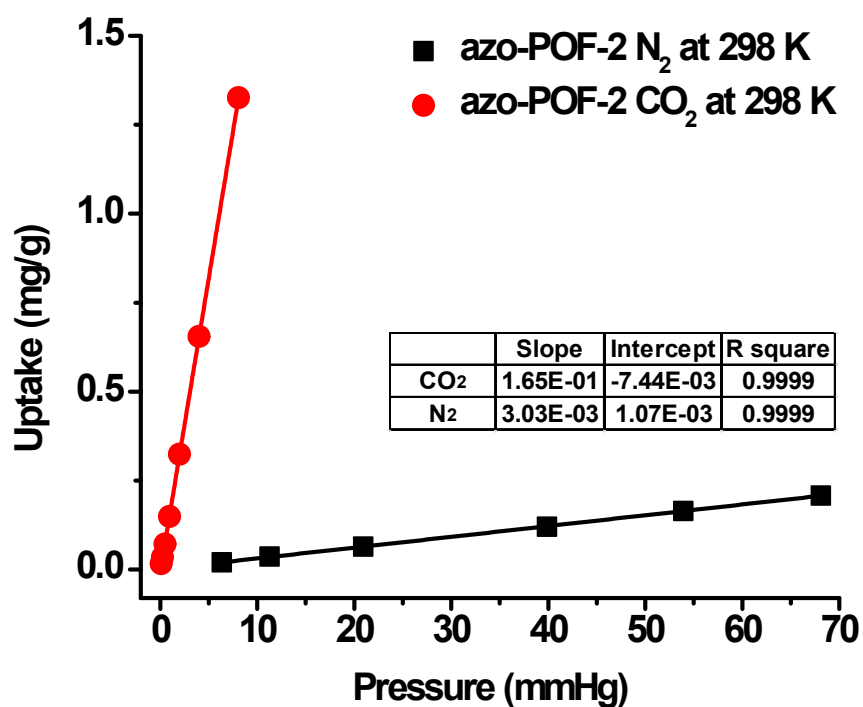
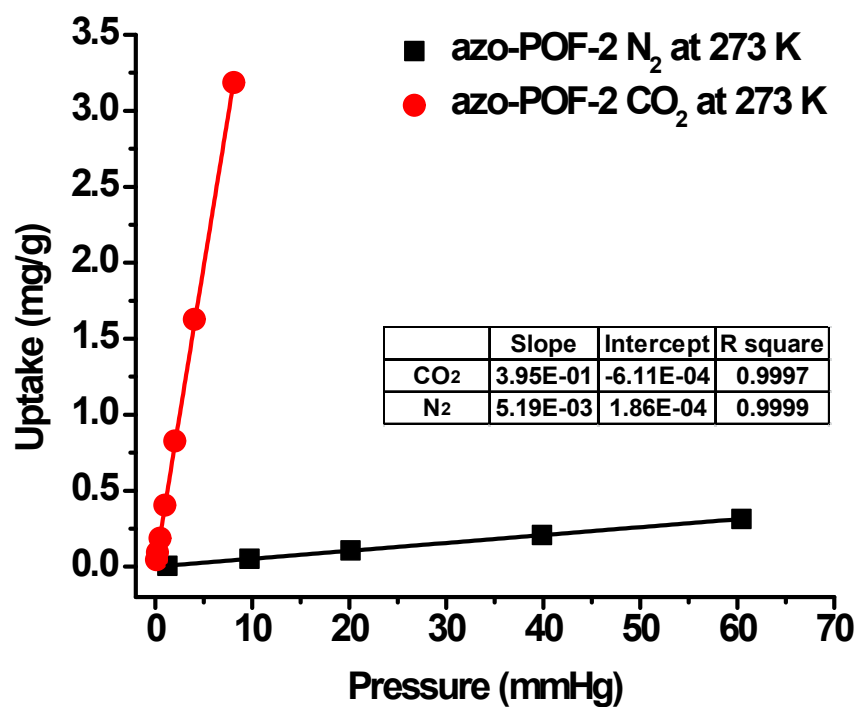


Figure S21. CO₂/N₂ initial slope selectivity studies for azo-POF-2.

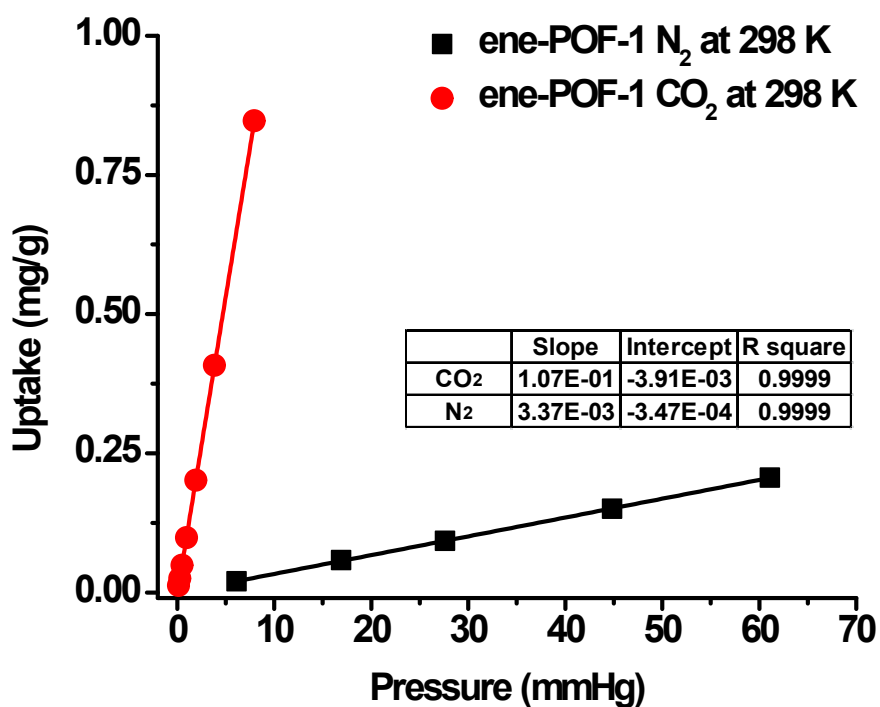
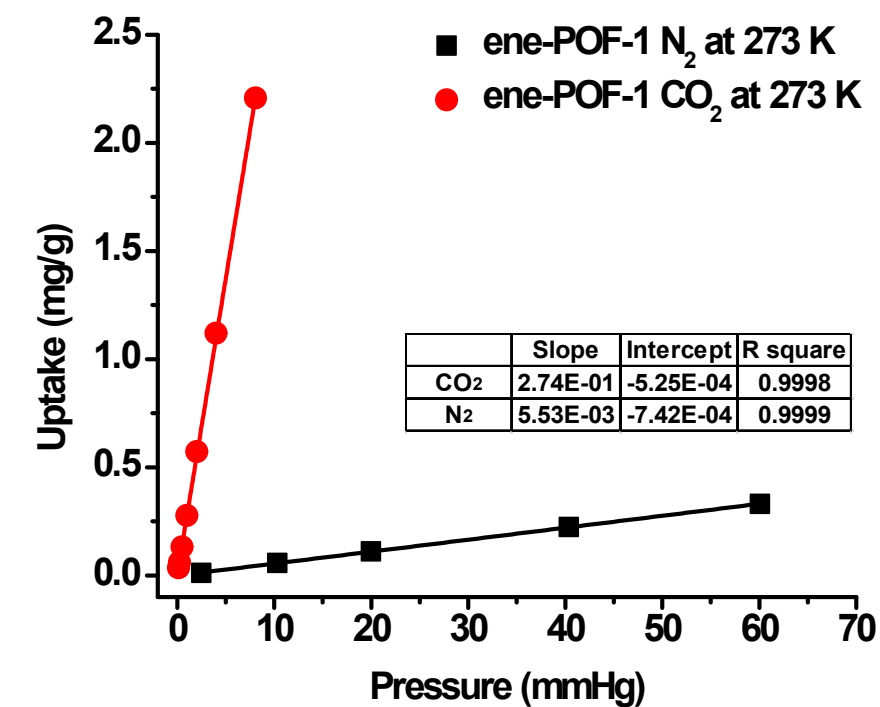


Figure S22. CO₂/N₂ initial slope selectivity studies for ene-POF-1.

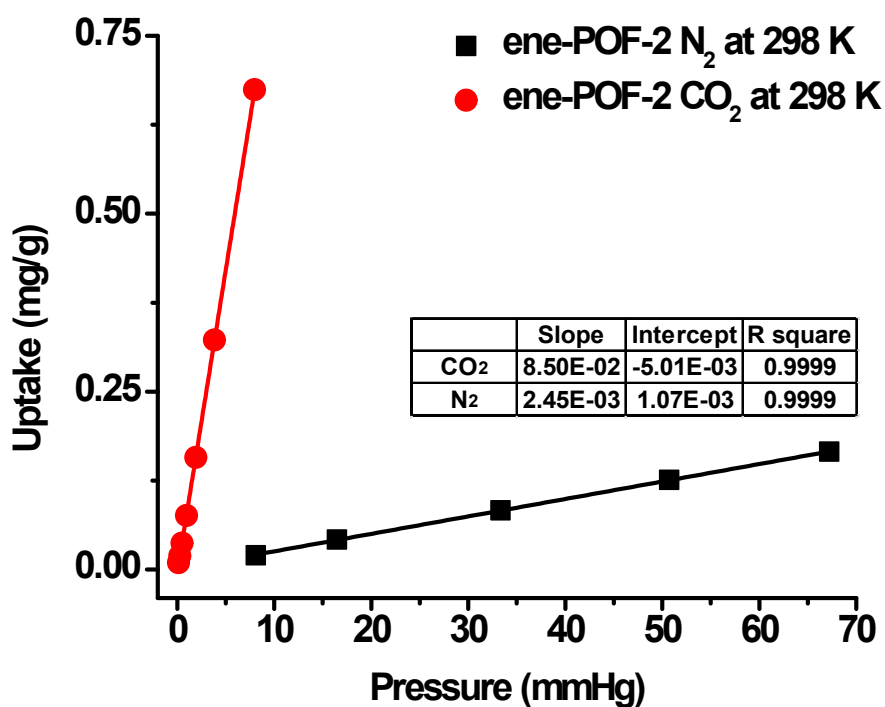
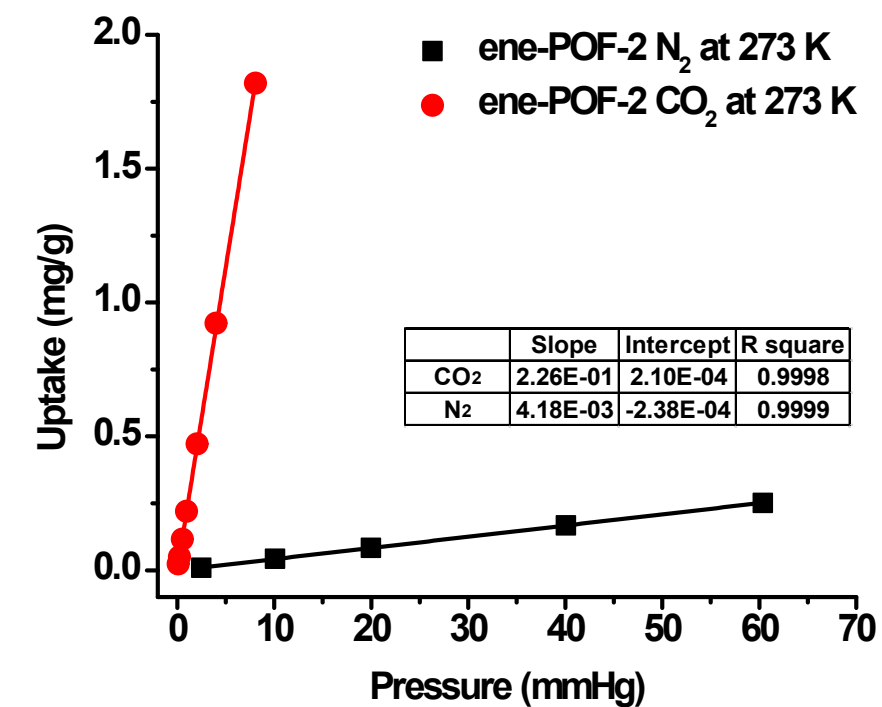


Figure S23. CO₂/N₂ initial slope selectivity studies for ene-POF-2.

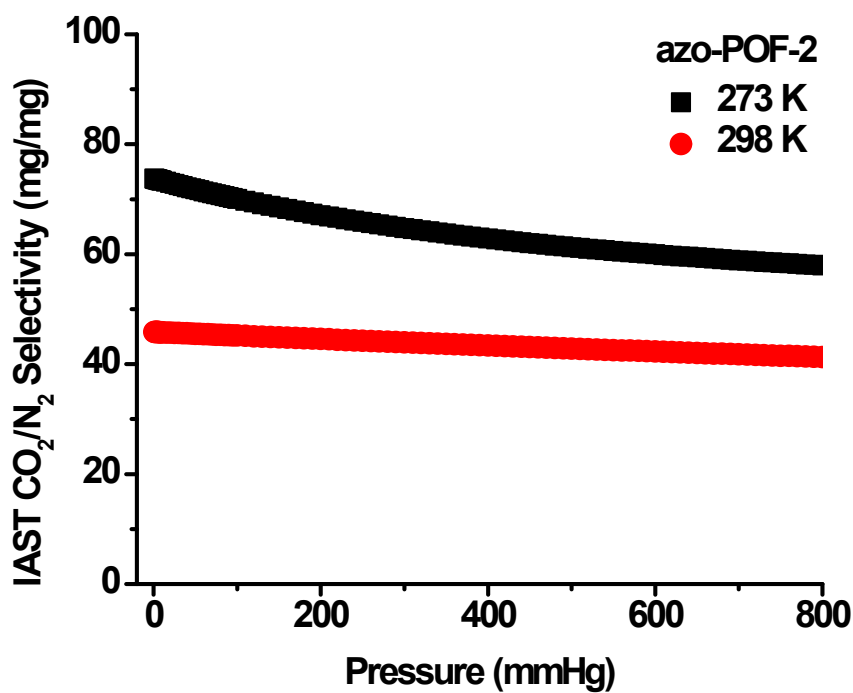
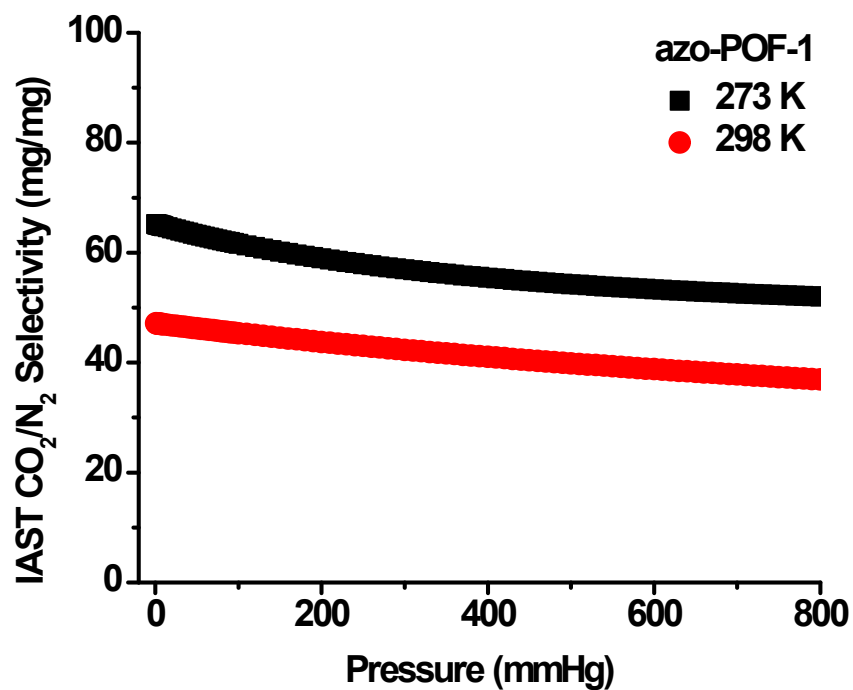


Figure S24. CO₂/N₂ IAST selectivity studies for azo-POFs for a molar ratio of 15:85.

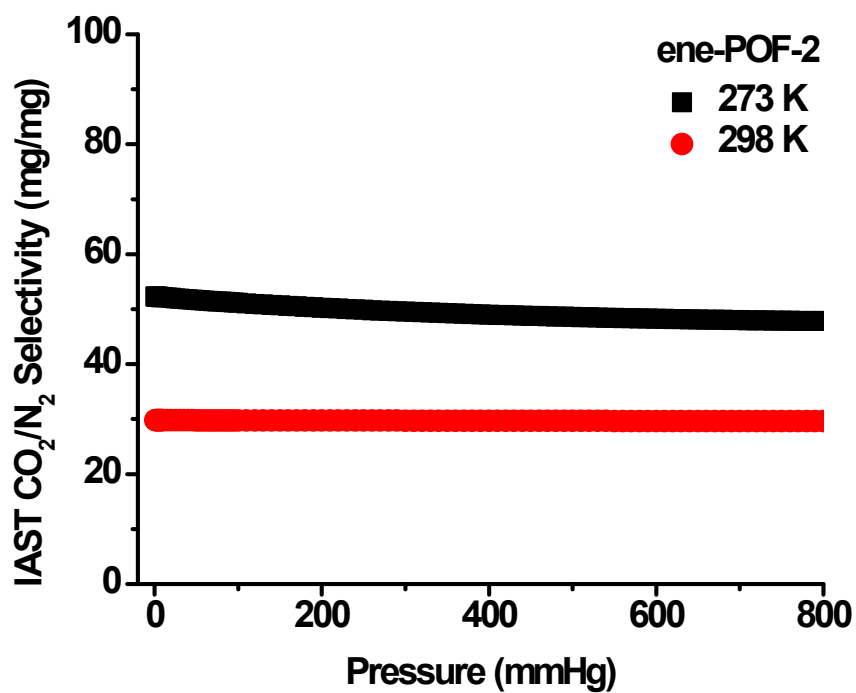
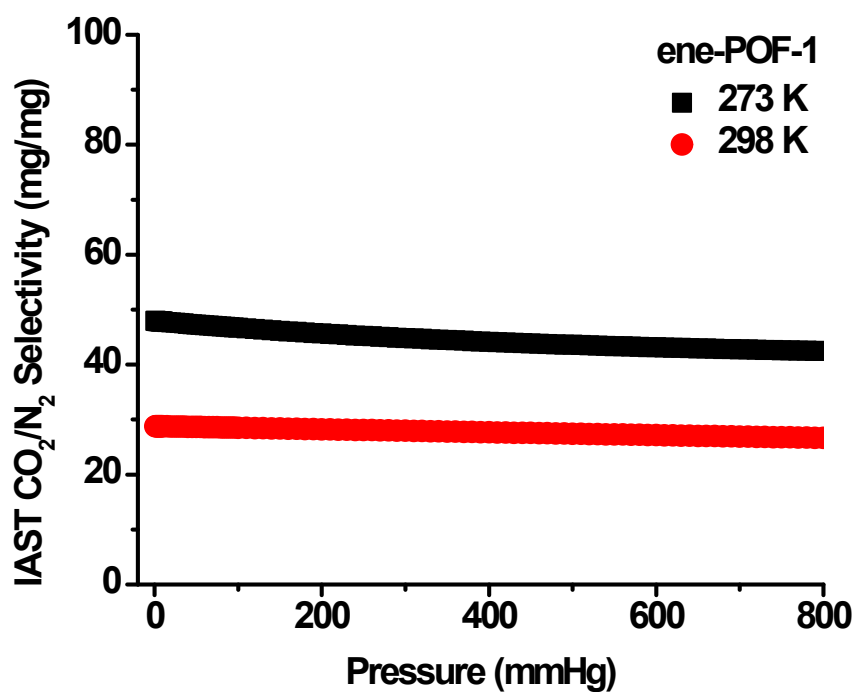


Figure S25. CO₂/N₂ IAST selectivity studies for ene-POFs for a molar ratio of 15:85.

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