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A “click-based” porous organic polymers from tetrahedral building blocks

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S1. Materials and methods.

Unless otherwise stated, all chemicals and solvents were purchased from Aldrich Chemicals Co. (Milwaukee, WI) and used without further purification. Deionized water was provided by Northwestern University facility. Ethanol (absolute) was obtained from Pharmco and used as received. Deuterated solvents were purchased from Cambridge Isotope Laboratories (Andover, MA) and used as received. All the gases used for the adsorption/desorption were Ultra High Purity Grade 5 and were obtained from Airgas Specialty Gases (Chicago, IL).

^{1}H and ^{13}C NMR spectra were recorded on either a Varian INOVA 500 FT-NMR (499.6 MHz for ^{1}H, 125.6 MHz for ^{13}C) or a Bruker AVANCE 400 FT-NMR spectrometer (400.6 MHz for ^{1}H, 100.7 MHz for ^{13}C. ^{1}H NMR data are reported as follows: chemical shift [multiplicity (bs = broad singlet, s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet) integration, and peak assignments]. ^{1}H and ^{13}C chemical shifts are reported in ppm downfield from tetramethylsilane (TMS).

Fourier-transformed infrared (FTIR) spectroscopy was performed on a Thermo Nicolet Nexus 870 FTIR spectrometer (Thermo Scientific, Waltham, MA), using KBr pellets for all samples. Frequencies are given in reciprocal centimeters (cm^{-1}). The FTIR spectra were analyzed using EZ Omnic software (Thermo Scientific, Waltham, MA). TGA data were obtained with a Shimadzu TGA-50 thermal analyzer (Shimadzu Scientific Instruments, Columbia, MD) at a heating rate of 5 °C min^{-1} under nitrogen flow.

^{13}C cross-polarization, magic angle spinning (CPMAS) nuclear magnetic resonance spectra were recorded on a VNMRS 400 MHz spectrometer (Varian, Inc., Palo Alto, CA) (400 MHz for ^{1}H, 100.7 MHz for ^{13}C) equipped with a 5-mm HXY T3 PENCIL probe. The samples were packed into a standard 5-mm (external diameter) zirconia rotor with a volume of 160 μL and capped by a Teflon spacer. The spinning rate was at 10 kHz. Spectra were acquired using a ^{1}H-^{13}C CP contact time of 2 ms, acquisition time 20 ms, and a recycle delay of 5 s between scans. High-power, two-pulse phase-modulation (TPPM) ^{1}H decoupling was applied during data acquisition to ensure the sharper peaks. The number of scans used was 6028. ^{13}C NMR chemical shifts are reported in ppm downfield relative to tetramethylsilane (TMS) as zero ppm, calibrated using adamantane (38.3 ppm) as a secondary standard. All the spectra were acquired with neat powdered samples at room temperature. All the data were processed by VnmrJ software (Varian, Inc., Palo Alto, CA) with a line broadening of 20 Hz.

All H_2 and N_2 adsorption and desorption measurements were performed on a Micromeritics Tristar 2010 system (Micromeretics, Norcross, GA). Between 20-80 mg of samples were employed in each measurement and the data were analyzed using the ASAP 2020 software (Micromeretics, Norcross, GA). Before measurement, samples were degassed for 12 h at 110 °C under high vacuum (<10^{-4} mbar). N_2 adsorption and desorption isotherms were measured at 77 K. The specific surface areas for N_2 were calculated using the Brunauer-Emmet-Teller (BET) model in the range of $0.01 < P/P_0 < 0.1$. The pore size distributions were calculated from the adsorption-desorption isotherms by non-local density functional theory (NLDFT). CO_2 adsorption and desorption measurements were carried out on an Autosorb 1-MP instrument (Quantachrome Instrument, Boynton Beach, FL). The specific surface areas for CO_2 were calculated using the NLDFT slit-pore model for CO_2 at 273 K. The micropore volumes obtained were calculated using the Dubinin-Raduskevich model.

H_2 uptake measurements were performed at 77 and 87K. The collected data for each sample was fitted to virial equation 1:[S1]

$$\ln p = \ln v + \frac{1}{T}\sum_{i=0}^{m} a_i v^i + \sum_{i=0}^{n} b_i v^i \qquad (1)$$

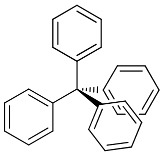
where p is the pressure in mmHg, v is the adsorbed amount in mmol g^{-1}, T is the temperature in K and a_i and b_i are adjustable parameters. The isosteric heat of H_2 adsorption, Q_{st}, was calculated according to the equation 2:

$$Q_{st} = -R\sum_{i=0}^{m} a_i v^i \qquad (2)$$

where R is the gas constant (8.314 J mol^{-1} K^{-1}).

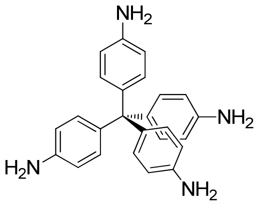
S2. Synthesis of starting materials and model compound.

Synthesis of tetraphenylmethane (1).



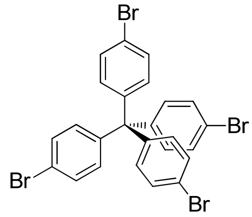
Compound **1** was synthesized following a previously reported procedure.[S2] ^{1}H NMR (400.6 MHz, $CDCl_3$): δ 7.25 (m, 5H, Ar-*H*). ^{13}C NMR (100.7 MHz, $CDCl_3$): δ 67.0 (*C*q), 125.7 (Ar-*C*Cq), 127.3 (Ar-C_{ortho}), 131,1 (Ar-C_{meta}), 146.7 (C_{para}).

Synthesis of tetrakis(4-aminophenyl)methane (2).



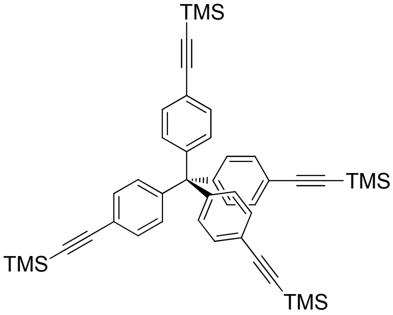
Compound **2** was synthesized following a previously reported procedure.[S3] ^{1}H NMR (400.6 MHz, DMSO-d_6): δ 4.80 (s, 8H, Ar-NH_2); 6.35 (d, 8H, Ar-H_{ortho}, J = 8.7 Hz), 6.65 (d, 8H, Ar-H_{para}, J = 8.7 Hz). ^{13}C NMR (100.7 MHz, DMSO-d_6): δ 64.2 (*Cq*) , 130.4 (Ar-C_{ortho}), 145.0 (Ar-*C*Cq), 149.9 (Ar-C_{para}), 122.7 (Ar-C_{meta}).

Synthesis of tetrakis(4-bromophenyl)methane (3).



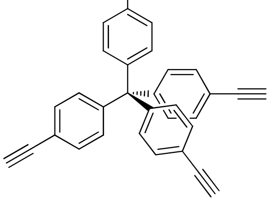
Compound **3** was synthesized following a modification of a previously reported procedure.[S4] A 150-mL round-bottom flask equipped with a magnetic stir bar and a water-cooled reflux condenser was charged with tetraphenylmethane (**1**, 5 g, 15.6 mmol). Neat bromine (6 mL, 117.1 mmol) was slowly added and the resulting solution was stirred for 20 minutes. The dark slurry was diluted with ethanol (100 mL) and further stirred for 30 minutes. The precipitate was then filtered and boiled in a mixture of ethanol:$CHCl_3$ (1:1 v/v, 200 mL) for 10 minutes. The solution was allowed to cool to room temperature and the precipitated solid was filtered and dried under dynamic vacuum to afford **3** as a white solid (6.6 g, > 66% yield). ^{1}H NMR (499.6 MHz, $CDCl_3$): δ 7.03 (d, 2H, Ar-H_{ortho}, J = 8.8 Hz); 7.40 (d, 8H, Ar-H_{para}, J = 8.8 Hz). ^{13}C NMR (125.6 MHz, $CDCl_3$): δ 63.8 (Ar-*Cq*) , 120.9 (Ar-*C*Cq), 131.2 (Ar-C_{ortho}), 132.6 (Ar-C_{meta}), 144.6 (Ar-C_{para}).

Synthesis of tetrakis(4-((trimethylsilyl)ethynyl)phenyl)methane (4).



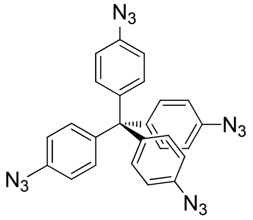
A 500-mL Schlenk flask equipped with a magnetic stir bar and a water-cooled reflux condenser was charged with tetrakis(4-bromophenyl)methane (**3**, 4 g, 6.3 mmol), triphenylphosphine (300 mg, 1.1 mmol), trimethylsilyl acetylene (12 mL, 84.3 mmol), and diisopropyl amine (50 mL). The resulting solution was cooled down to -78 °C in acetone/ dry ice bath and subjected to three cycles of brief vacuum-degas/N_2 back-fill with no stirring and kept under nitrogen before $Pd(PPh_3)_2Cl_2$ (400 mg, 0.56 mmol) and CuI (100 mg, 0.52 mmol) were added. The flask was then fitted to a water-cooled reflux condenser and stirred at 80 °C for 24 h, after which the reaction was allowed to cool to room temperature. Tetrahydrofuran (THF, 100 mL) was added and the resulting mixture was sonicated in a Bransonic laboratory sonicator for 5 min before being filtered. The collected precipitate was then redissolved in a minimum amount of CH_2Cl_2 and passed through a plug of silica using a mixture of hexanes:CH_2Cl_2 (1:1 v/v) as an eluent. The collected fraction was evaporated to dryness and the resulting solid was sonicated in ethanol (50 mL) for 5 min. The sonicated solution was then cooled in a laboratory freezer (-10 ºC) for 30 minutes to yield an off-white precipitate, which was filtered and dried (3 g, 67% yield). ^{1}H NMR (400.6 MHz, $CDCl_3$): δ 0.17 (s, 36H, Si-CH_3); 6.99 (d, 8H, Ar-H_{ortho}, J = 8.5 Hz), 7.26 (d, 8H, Ar-H_{meta}, J = 8.5 Hz). ^{13}C NMR (100.7 MHz, $CDCl_3$): δ 0.5 (Si-*C*H_3) , 63.5 (*C*q), 95.3 (C≡*C*-Si), 105.2 (*C*≡C-Si), 121.8 (Ar-C_{para}), 131.3 (Ar-C_{ortho}), 131.9 (Ar-C_{meta}), 146.5 (Ar-*C*Cq).

Synthesis of tetrakis(4-ethynylphenyl)methane (5).



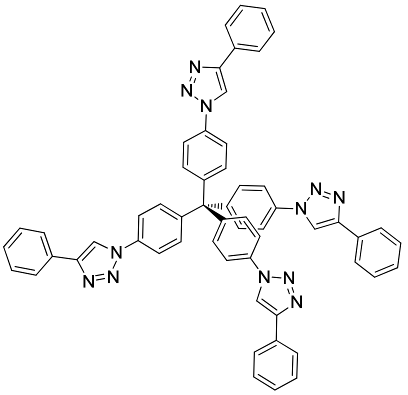
A 500-mL round-bottom flask equipped with a magnetic stir bar and a water-cooled reflux condenser was charged with tetrakis(4-((trimethylsilyl)ethynyl)phenyl)methane (**4**, 2.8 g, 4.0 mmol) and $CHCl_3$ (30 mL). To this solution was added a saturated solution of KOH in methanol (150 mL) and the combined mixture was refluxed for 4 h. After cooling to room temperature, the reaction mixture was concentrated to dryness using a rotary evaporator. The resulting solid was washed using a mixture of CH_2Cl_2:water (1:1 v/v, 500 mL) and the organic fraction was separated, dried over magnesium sulfate, and concentrated to 50 mL using a rotary evaporator. This solutions was then passed through a plug of silica using CH_2Cl_2 as an eluent. The collected organic was concentrated to dryness to afford **5** as an off-white solid (1.55 g, 93% yield). ^1H NMR (400.6 MHz, $CDCl_3$): δ 3.0 (s, 4H, C≡C*H*); 7.06 (d, 8H, Ar-H_{ortho}, J = 8.5 Hz), 7.32 (d, 8H, Ar-H_{meta}, J = 8.5 Hz). ^{13}C NMR (100.7 MHz, $CDCl_3$): δ 64.8 (*Cq*) , 78.3 (C≡*C*H), 83.1 (*C*≡CH), 120.9 (Ar-*C*Cq), 131.4 (Ar-C_{ortho}), 132.3 (Ar-C_{meta}), 146.8 (Ar-*C*Cq).

Synthesis of tetrakis(4-azidophenyl)methane (6).



Tetrakis(4-aminophenyl)methane (**1**, 2 g, 5.2 mmol) was dissolved in 2 N aqueous HCl (100 mL) in a 1-L round-bottom flask and cooled down to 0 °C. A solution of $NaNO_2$ (1.6g, 23.3 mmol) in H_2O (10 mL) was then added drop-wise into the cooled reaction flask with vigorous stirring. The reaction mixture was kept at 0 °C for 30 minutes before being neutralized with $CaCO_3$. To this mixture was then added a solution of NaN_3 (1.8g, 27.7 mmol) in H_2O (10 mL) at 0 °C. The resulting mixture was allowed to stir at 0 °C for an additional 20 min and then filtered. The collected solid was washed with excess H_2O and dried under dynamic vacuum to afford **6** as an off-white solid (2 g, 79% yield). ^1H NMR (400.6 MHz, $CDCl_3$): δ 6.86 (d, 8H, Ar-H_{meta}, J = 8.8 Hz); 7.06 (d, 8H, Ar-H_{ortho}, J = 8.8 Hz). ^{13}C NMR (100.7 MHz, $CDCl_3$): δ 63.8 (*Cq*) , 119.0 (Ar-C_{ortho}), 132.6 (Ar-C_{meta}), 138.8 (C_{para}), 143.5 (Ar-*C*Cq).

Synthesis of (tetrakis(4-(4-phenyl-1H-1,2,3-triazol-1-yl)phenyl)methane (7):



Tetrakis(4-azidophenyl)methane (**6**, 200 mg, 0.4 mmol) and dimethylformamide (DMF, 25 mL) were combined in a 50-mL round-bottom flask equipped with a magnetic stir bar and a water-cooled reflux condenser. Then $CuSO_4{\cdot}5H_2O$ (119.8 mg, 0.48 mmol, 0.3 equiv per azide functional group), sodium ascorbate (221.9 mg, 1.12 mmol, 0.7 equiv per azide functional group), and phenylacetylene (0.9 mL, 8 mmol) were added subsequently. The reaction mixture was refluxed at 90 ^oC for 48 h before being stopped. The reaction mixture was filtered through a fine fritted funnel and the collected solid precipitate was washed with excess water, methanol, and dichloromethane. This solid was then dried under dynamic vacuum to afford **7** as a yellow solid (355 mg, >99% yield). ^1H NMR (499.6 MHz, DMSO-d_6): δ 7.39 (t, 4H, Ar-H_{para}, J = 7.5 Hz); 7.51 (t, 8H, Ar-H_{meta}, J = 7.5 Hz), 7.64 (d, 8H, Ar_{ortho}(N)-*H*, J = 8.8 Hz), 7.96 (d, 8H, Ar-H_{ortho}, J = 7.5 Hz), 8.02 (d, 8H, Ar_{meta}(N)-*H*, J = 8.8 Hz), 9.33 (s, 4H, triazole-*H*). ^{13}C NMR (125.6 MHz, DMSO-d_6): δ 63.9 (C_q) , 119.6 (triazole, *C*H), 120.1 (Ar(N)-C_{meta}), 125.3 (Ar-C_{ortho}), 126.3 (Ar-C_{para}), 129.0 (Ar-C_{meta}), 130.2 (Ar-*C*C_q), 131.7 (Ar(N)-C_{ortho}), 134.8 (Ar(N)-C_q), 146.0 (Ar-C_q), 147.3 (triazole-C_q).

S3. Synthesis and isolation of POPs C1-D1.

General procedure for the synthesis of POPs C1-D1 (Table 1 and Table S1)

Tetrakis(4-azidophenyl)methane (**6**, 48.5 mg, 0.1 mmol) and DMF (10 mL, to make a 0.04 M solution of azide functional group, at 1:1 alkyne to azide functional group ratio) were added into a 50-mL flask equipped with a magnetic stir bar and a water-cooled reflux condenser. Then $CuSO_4 \cdot 5H_2O$ (10 mg, 0.04 mmol, 0.1 equiv per acetylene functional group), sodium ascorbate (see Table 1 for quantity) and tetrakis(4-ethynylphenyl)methane (**5**, 41.6 mg, 0.1 mmol) were added subsequently. The reaction mixture was then heated to100 ^{o}C (25 ^{o}C for POP **C1-D1**, Table S1, entry 6) for 24 h before being stopped. A yellow precipitate was observed after 15-30 min for the reaction at 100 ^{o}C and after 1 h for the reaction at 25 ^{o}C.

Workup procedure I for POPs C1-D1 (Table 1, entries 1b-5 and Table S1, entries 1b-6). After the reaction was stopped and cooled down to room temperature, the reaction mixture was filtered over coarse filter paper using a Büchner funnel and successively washed with water (2 × 50 mL), methanol (2 × 50 mL), and THF (2 × 50 mL). The resulting brown material was then stirred in water (10 mL) for 5 h at room temperature before being filtered through a Büchner funnel. The final product was yellow to brown in color. The yields ranged from 64-81 % (see table S1, entries 1b-6).

Workup procedure II for POP C1-D1 (Table 1, entry 1a). After the reaction was stopped and cooled down to room temperature, the reaction mixture was then filtered over a fine fritted funnel and successively washed with water (2 × 50 mL), methanol (2 × 50 mL), and THF (2 × 50 mL). The resulting brown material was then stirred in water (10 mL) for 5 h at room temperature before being filtered through a fine fritted funnel. The final product was yellow to brown in color. The yield was quantitative (>99%).

Soxhlet Extraction. A fine cellulose extraction thimble (12 × 50 mm) containing POP **C1-D1** obtained from the workup procedure was placed inside a soxhlet extractor. The soxhlet extractor was then fitted to a water-cooled reflux condenser and a 100-mL round-bottom flask containing water (60 mL). The water was then refluxed for 12 h. POP **C1-D1** obtained after the soxhlet extraction was washed with methanol (2 × 50 mL) and THF (2 × 50 mL). The final product was brown in color.

S4. Effect of extraction procedure, amount of sodium ascorbate used, and reaction temperature on the pore properties of POPs C1-D1.

Table S1. Effect of extraction procedure, amount of sodium ascorbate used, and reaction temperature on the pore properties of POPs **C1-D1**.

Entry*	Sodium ascorbate (mol %)	Specific surface area (m^2g^{-1})	Micropore volume (cm^3g^{-1})	Total pore volume (cm^3g^{-1})	Yield (%)
1a^{a,T1}	10	1440	0.56	0.76	>99
1b^{b,T1}	10	1360	0.53	0.74	67
2^{b,T1}	20	1320	0.51	0.73	62
3^{b,T1}	30	1260	0.49	0.67	64
4^{b,T1}	50	1140	0.44	0.64	81
5^{b,T1}	70	1090	0.42	0.52	77
6^{b,T2}	30	440	0.17	0.37	56

[*] All reactions were carried out in DMF using 10 mol% $CuSO_4 \cdot 5H_2O$ and at 0.04 M solution of azide functional group (1:1 alkyne to azide functional group ratio). [a] Obtained using workup procedure II. [b] Obtained using workup procedure I. [T1] Reactions were carried out at 100 °C. [T2] Reaction was carried out at 25 °C.

Table S2. Effect of Soxhlet extraction on the pore properties of POPs **C1**-**D1**.

Materials	Soxhlet extraction	Sodium ascorbate (mol %)	Specific surface area (m^2g^{-1})	Micropore volume (cm^3g^{-1})	Total pore volume (cm^3g^{-1})
Table S1, entry 3	before	30	1260	0.49	0.67
	after		1250	0.49	0.65
Table S1, entry 4	before	50	1140	0.44	0.64
	after		1150	0.45	0.65
Table S1, entry 5	before	70	1090	0.42	0.52
	after		1100	0.43	0.54

S5. Chemical stability of POPs C1-D1.

Procedure for testing the chemical stability of POP C1-D1 (Table 1, entries 1a and 1b)

Under acidic condition I. A 20-mL round-bottom flask equipped with a magnetic stir bar and a water-cooled reflux condenser was charged with POP **C1**-**D1** (30 mg, sample from Table 1, entry 1b) and 6 N aqueous HCl (10 mL). The mixture was heated to 80 °C and stirred for 24 h. The mixture was then filtered through a fine fritted funnel and the obtained solid was washed with excess water and methanol to obtain acid-treated POP **C1**-**D1** as a brown powder.

Under basic condition I. A 20-mL round-bottom flask equipped with a magnetic stir bar and a water-cooled reflux condenser was charged with POP **C1**-**D1** (30 mg, sample from Table 1, entry 1b) and 6 N aqueous NaOH (10 mL). The mixture was heated to 80 °C and stirred for 24 h. The mixture was then filtered through a fine fritted funnel and the obtained solid was washed with excess water and methanol to obtain base-treated POP **C1**-**D1** as a brown powder.

Under acidic condition II. A 20-mL round-bottom flask equipped with a magnetic stir bar and a water-cooled reflux condenser was charged with POP **C1**-**D1** (30 mg, sample from Table 1, entry 1a) and 6 N aqueous HCl (10 mL). The mixture was heated to 60 °C and stirred for 8 h. The mixture was then filtered through a fine fritted funnel and the obtained solid was washed with excess water and methanol to obtain acid-treated POP **C1**-**D1** as a brown powder.

Under basic condition II. A 20-mL round-bottom flask equipped with a magnetic stir bar and a water-cooled reflux condenser was charged with POP **C1**-**D1** (30 mg, sample from Table 1, entry 1a) and 6 N aqueous NaOH (10 mL). The mixture was heated to 60 °C and stirred for 8 h. The mixture was then filtered through a fine fritted funnel and the obtained solid was washed with excess water and methanol to obtain base-treated POP **C1**-**D1** as a brown powder.

Table S3. Pore properties analysis of POP**s C1**-**D1** (Table 1, entry 1b) tested under acidic and basic conditions.

Entry	POP **C1**-**D1**	Specific surface area (m^2g^{-1})	Micropore volume (cm^3g^{-1})	Total pore volume (cm^3g^{-1})
1	As-synthesized (Table 1, entry 1b)	1360	0.53	0.74
2	Treated with 6 N aqueous HCl at 80 °C for 24 h	1220	0.48	0.60
3	Treated with 6 N aqueous NaOH at 80 °C for 24 h	1190	0.46	0.57
4	As-synthesized (Table 1, entry 1a)	1440	0.56	0.76
5	Treated with 6 N aqueous HCl at 60 °C for 8 h	1430	0.56	0.74
6	Treated with 6 N aqueous NaOH at 60 °C for 8 h	1320	0.51	0.67

S6. N_2 adsorption-desorption isotherms of POPs C1-D1.

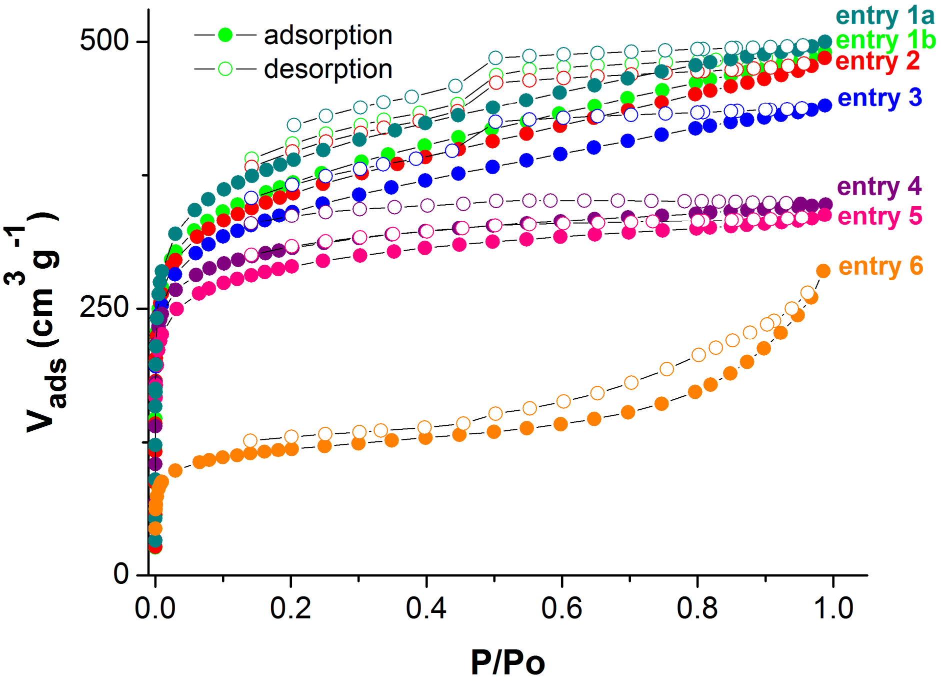


Figure S1. Nitrogen adsorption-desorption isotherms of POPs **C1-D1** (Table S1, entries 1a-6).

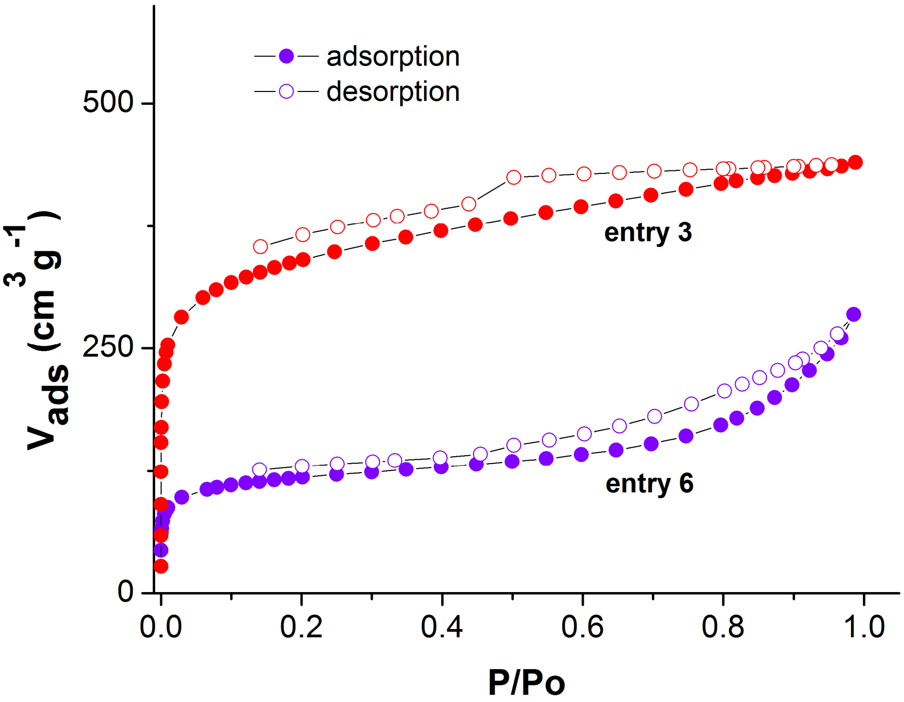


Figure S2. Nitrogen adsorption-desorption isotherms of POPs **C1-D1** (Table S1, entries 3 and 6).

S7. FTIR spectra of POPs C1-D1.

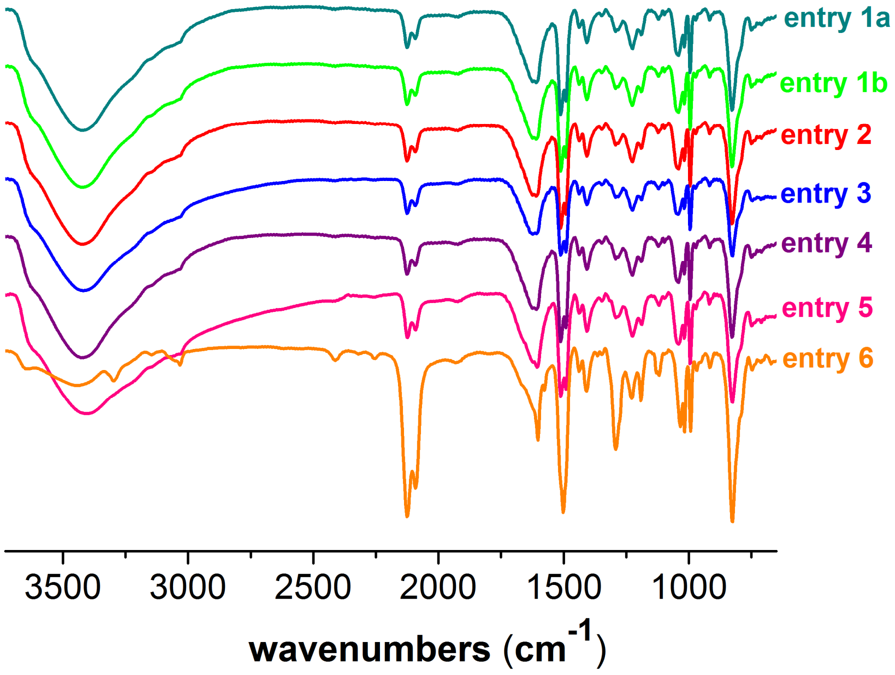


Figure S3. FTIR spectra of POPs **C1-D1** (Table S1, entries 1a-6).

S8. H_2 and CO_2 adsorption-desorption isotherms and isosteric heat of H_2 adsorption of POP C1-D1.

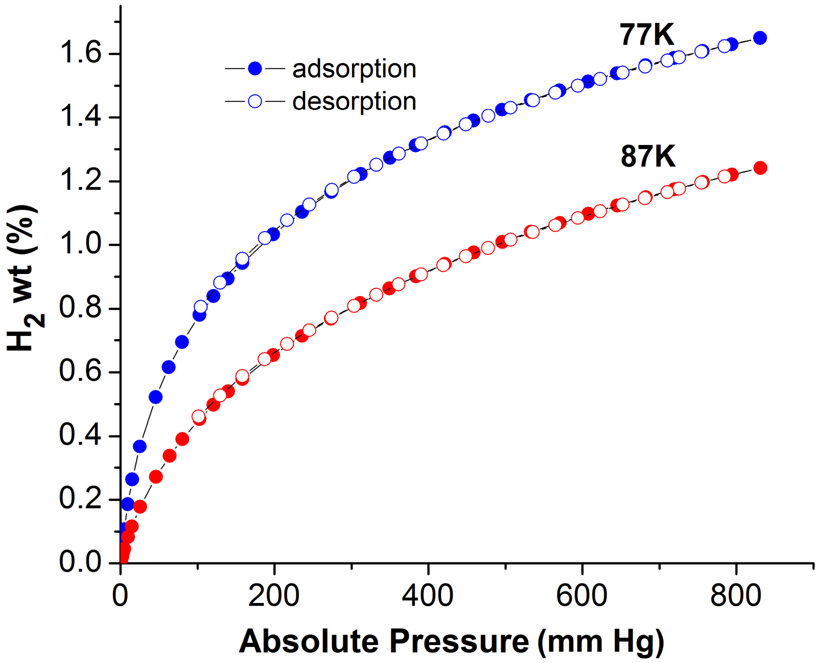
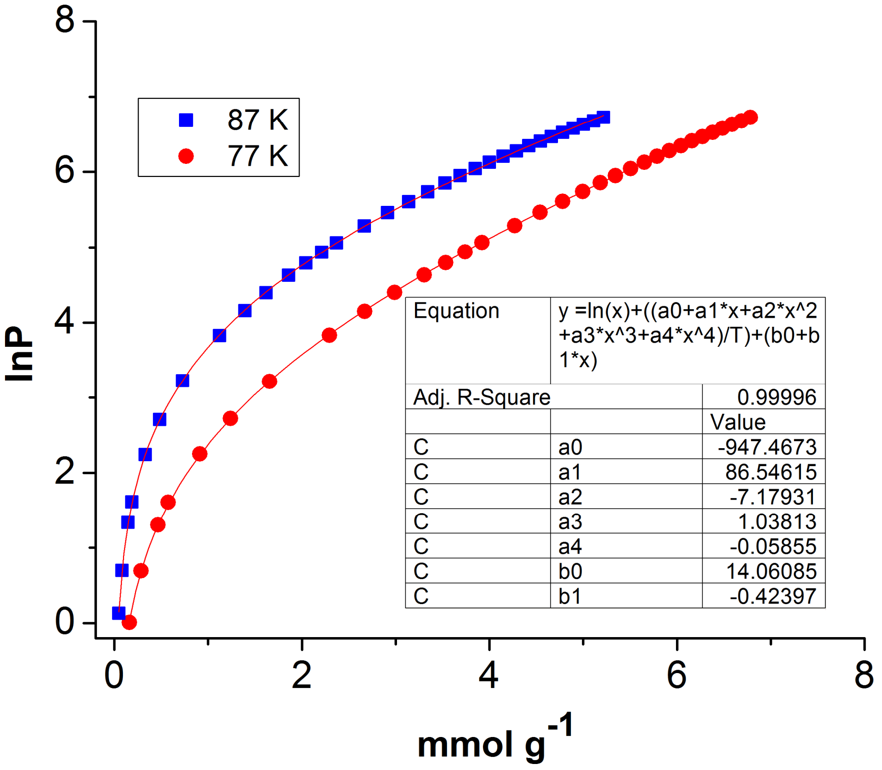


Figure S4. Hydrogen adsorption-desorption isotherms of POP **C1-D1** (Table 1, entry 1a) at 77 and 87 K.



Equation	y =ln(x)+((a0+a1*x+a2*x^2+a3*x^3+a4*x^4)/T)+(b0+b1*x)	
Adj. R-Square		0.99996
		Value
C	a0	-947.4673
C	a1	86.54615
C	a2	-7.17931
C	a3	1.03813
C	a4	-0.05855
C	b0	14.06085
C	b1	-0.42397

Figure S5. Fitting curves for hydrogen adsorption isotherms of POP **C1-D1** (Table 1, entry 1a) at 77 and 87 K.

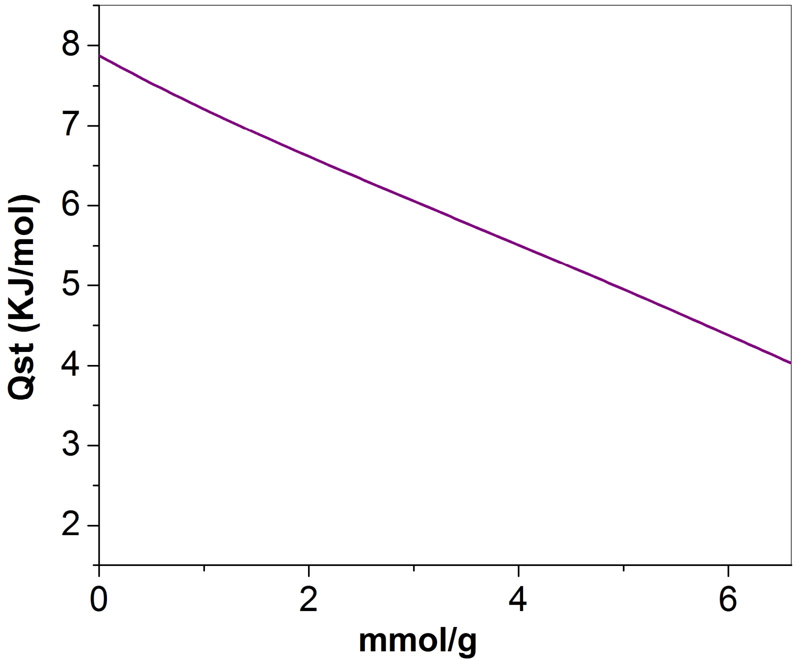


Figure S6. Isosteric heat of hydrogen adsorption of POP **C1-D1** (Table 1, entry 1a).

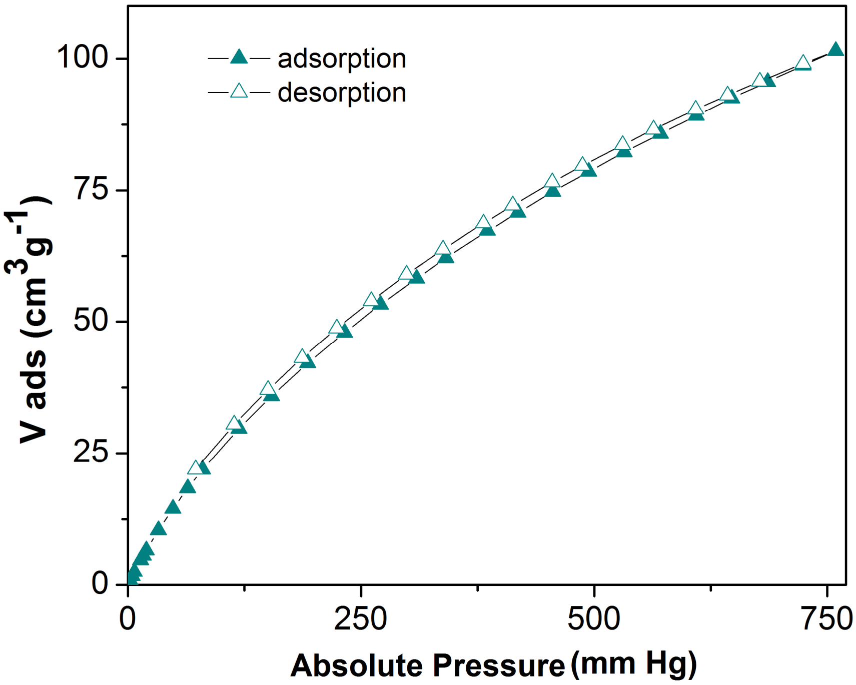


Figure S7. Carbon dioxide adsorption-desorption isotherm of POP **C1-D1** (Table 1, entry 1a) at 273 K.

S9. TGA profiles of POP C1-D1.

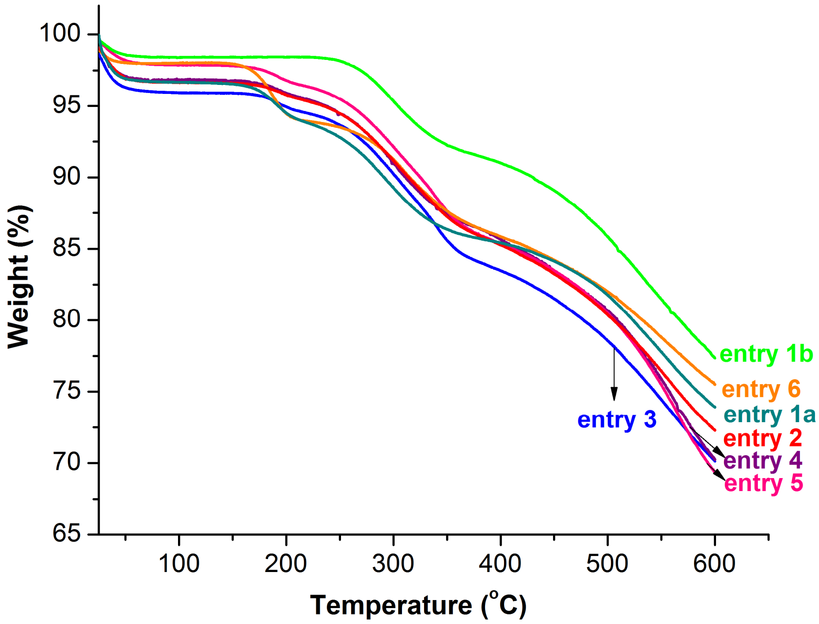


Figure S8. Thermal gravimetric analyses of POPs **C1-D1** (Table S1, entries 1a-6).

Author contributions audit. P.P., O.K.F. and S.T.N. conceived the experiments presented herein. A.M.S synthesized tetrakis(4-aminophenyl)methane, the precursor to one of the starting materials. The starting materials and model compound are prepared and characterized by O.K.F. P.P. carried out the synthesis, characterization, gas adsorption measurements and analysis of all the POPs. O.K.F., J.T.H., and S. T. N. supervised the project. P.P. wrote the initial draft of the paper. M.G.K, C.A.M, O.K.F., J.T.H., and S. T. N. finalized the manuscript.

References

S1. L. Czepirski and J. JagieŁŁo, *Chem. Eng. Sci.*, 1989, **44**, 797-801.
S2. P. Ganesan, X. Yang, J. Loos, T. J. Savenije, R. D. Abellon, H. Zuilhof and E. J. R. Sudhölter, *J. Am. Chem. Soc.*, 2005, **127**, 14530-14531.
S3. O. K. Farha, A. Spokoyny, B. Hauser, Y.-S. Bae, S. Brown, R. Q. Snurr, C. A. Mirkin and J. T. Hupp, *Chem. Mater.*, 2009, **21**, 3033-3035.
S4. M. Ng, D. Craig, J. Harper, L. van-Eijck and J. Stride, *Chem.–Eur. J.*, 2009, **15**, 6569-6572.