[Supplementary Information to accompany]

Accessing functionalized porous aromatic frameworks (PAFs) through a de novo approach

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I. General information. ¹H and ¹³C NMR spectra were recorded on a Bruker Avance 500 MHz (499.4 MHz for ¹H, 125.8 MHz for ¹³C) spectrometer (Bruker Biospin Corp., Billerica, MA, USA). ¹H NMR data are reported as follows: chemical shift (multiplicity (bs = broad singlet, s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), coupling constant and integration). ¹H and ¹³C chemical shifts are reported in ppm downfield from tetramethylsilane (TMS, δ scale) using the residual solvent resonances as internal standards.

¹H-¹³C cross-polarization, magic angle spinning (CP MAS) nuclear magnetic resonance spectra were recorded on a Varian VNMRS 400 MHz (400 MHz for ¹H, 100. MHz for ¹³C) spectrometer (Varian, Inc., Palo Alto, CA, USA) 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 with a Teflon spacer. The spinning rate was at 8 or 10 kHz. ¹³C 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, USA) with a line broadening of 20 Hz.

Fourier-transformed infrared (FTIR) spectroscopy was performed on a Thermo Nicolet Nexus 879 FTIR spectrometer (Thermo Scientific, Waltham, MA, USA) using a smart diffuse reflectance accessory. Frequencies are

given in reciprocal centimeters (cm⁻¹). The FTIR spectra were analyzed using EZ Omnic software (Thermo Scientific, Waltham, MA, USA). Thermogravimetric analysis (TGA) data were obtained with a Mettler-Toledo TGA/DSC1 Star thermal analyzer (Mettler-Toledo, Columbus, OH, USA) with a heating rate of 5 °C min⁻¹ under nitrogen flow. Elemental analyses were carried out by Micro Analysis Inc. (Wilmington, DE, USA)

All N₂ adsorption and desorption measurements were performed on a Micromeritics Tristar 3020 system (Micromeretics, Norcross, GA) and measured at 77 K. Between 40-100 mg of samples were employed in each measurement and the data were analyzed using the ASAP 2020 software (Micromeretics, Norcross, GA). Before measurements, samples were degassed for 12 h at 150 °C under high vacuum (< 10^{-4} bar). The specific surface areas for N₂ 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 density functional theory (DFT) in the range of $5.0 \times 10^{-5} < P/P_0 > 0.95$. The pore size distributions obtained were calculated using the slit-pore NLDFT model.

 CO_2 adsorption measurements (< 1 bar) were performed using an Autosorb 1-MP instrument (Quantachrome Instruments, Boynton Beach, FL). Low-pressure CO_2 adsorption isotherms were measured at 273, 283, and 293 K; the temperature was held constant using an automated cooling system. CO_2 isotherms were fit using non-linear least-squares fitting to either a single-site or dual-site Langmuir equation (Eqs. S1 and S2, respectively):

$$N = \frac{N_m BP}{1 + BP}$$
(S1)

$$N = \frac{N_{m1}B_1P}{1+B_1P} + \frac{N_{m2}B_2P}{1+B_2P}$$
(S2)

where *P* is the pressure, *N* is the coverage of adsorbate, $N_{\rm m}$ is the saturation coverage of the adsorbate and *B* is the Langmuir parameter. $N_{\rm m1}$, $N_{\rm m2}$, B_1 , and B_2 indicate two separate saturation coverage regimes and Langmuir parameters. Pressures at constant coverage (*N*) were either explicitly calculated by solving equation S1 or numerically approximated in Mathematica (Wolfram Research, Champaign, IL, USA). The Clausius-Clapeyron equation (Eq. S3) was employed to calculate the isosteric heat of adsorption ($Q_{\rm sl}$).

$$\ln(P)_N = \frac{Q_{st}}{RT} + C \tag{S3}$$

where *P* is the pressure, *N* is the amount adsorbed, *T* is the temperature in ${}^{\circ}$ K, *R* is the universal gas constant, and *C* is a constant.

All vapor sorption isotherms were performed at 25 °C on a VTI MB-300G Gravimetric Analyzer (VTI Corp., Hialeah, FL, USA). All samples (between 4-10 mg) were degassed at 120 °C under high vacuum (< 10^{-3} bar) for 120 min or until weight equilibration (< 0.0010 wt% change over 5 min). Data was logged at 2 min intervals or every 0.200 wt% change while samples were allowed to equilibrate for ~45 min for each step or < 0.0010 wt% change over 5 min.

II. Materials and synthetic protocols. All air- or water-sensitive reactions were carried out under nitrogen using oven-dried glassware. All flash-chromatography was carried out using silica gel (MP silitech 60-200 mesh).

Analytical thin layer chromatography (TLC) was performed using glass-backed silica gel 60 F_{254} plates (Merck EMD-571507). Visualization of the TLC results was achieved by observation under UV light (254 nm).

All the gases used for the adsorption/desorption were ultra high purity grade 5 and were obtained from Airgas Specialty Gases (Chicago, IL). Tetrahydrofuran and dichloromethane (Fisher Scientific) were dried over neutral alumina in a Dow-Grubbs solvent system^{S1} installed by Glass Contours (now SG Water, Nashua, NH, USA). All other reagents were purchased from the Aldrich Chemical Company (Milwaukee, WI, USA) and used without further purification, unless otherwise noted. Deuterated solvents were purchased from Cambridge Isotope Laboratories (Andover, MA, USA) and used without further purification. PSM reactions were performed using 20 mL microwave vials (Biotage, LLC, Charlotte, NC, USA). Deionized (DI) water was provided as part of the laboratory facility at Northwestern University.

III. Preparation of tetrakis(4-bromophenyl)methane monomers



(3-Methylphenyl)triphenylmethane (1). Compound 1 was synthesized following a modified literature procedure.^{S2} Into a 250 mL round-bottom flask equipped with a water-cooled reflux condenser and a magnetic stir bar were added trityl chloride (9.2 g, 32.9 mmol) and *o*-toluidine (9.4 mL, 88.8 mmol). This mixture was stirred at reflux (200 °C) for 0.5 h with use of a 250 mL round-bottom aluminum block (Radleys Heat-OnTM Synthesis Blocks, Radleys Discovery Technologies, Essex, UK). The resulting purple slurry reaction mixture was allowed to cool to room temperature when it solidified. This solid was grounded with a spatula and the resulting powder was combined with a mixture of 2M HCl and MeOH (25 mL : 60 mL) mixture. The reflux condenser was reattached and the mixture was then heated at 80 °C for 0.5 h. After cooling to room temperature, the reaction mixture was filtered and washed with DI H₂O (125 mL) to afford a light purple solid, which was briefly air-dried on a Büchner funnel.

Into a 250 mL round-bottom flask equipped with a magnetic stir bar were combined the crude 3-methyl-4-aminotetraphenylmethane salt, EtOH (65 mL), and concentrated H₂SO₄ (10 mL, 96 wt%). The resulting mixture was then cooled down to -15 °C (ethylene glycol, CO₂ bath). Isoamyl nitrite (7.5 mL, 55.8 mmol) was then added slowly over a 10 min period and the resulting mixture was stirred at -15 °C for 1 h. Aqueous 50% hypophosphoric acid (15 mL) was then added to the reaction mixture at -15 °C and the resulting mixture was warmed up to room temperature before being stirred at 50 °C for 2 h. The resultant precipitate was collected by suction filtration and washed with DI H₂O (100 mL) and EtOH (100 mL). The tan brown crude product (8.8 g, 26.3 mmol, 80%) was used without any further purification in the next step. ¹H NMR (499.4 MHz, CDCl₃, Fig. S1): δ 2.29 (s, 3H, CH₃), 7.02 (s, 1H, Ar-*H*), 7.04 (s, 1H, Ar-*H*), 7.06 (s, 1H, Ar-*H*), 7.16 (t, 1H, Ar-*H*), 7.19 to 7.28 (m, 12H, Ar-*H*). {¹H}¹³C NMR (125.8 MHz, CDCl₃, Fig. S2): δ 21.7, 64.9, 125.8, 126.6, 127.2, 127.4, 128.4, 131.1, 131.7, 136.8, 146.6, 146.7.



Fig. S1 The ¹H spectrum of (3-methylphenyl)triphenylmethane (1).



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(4-Bromo-3-methylphenyl)tris(4-bromophenyl)methane (2). Compound 2 was synthesized following a modified literature procedure.^{S3} A 150 mL 2-neck round-bottom flask equipped with a magnetic stir bar was charged with compound 1 (crude mass 3.0 g, 8.96 mmol). One neck of the flask was fitted with a rubber septum and the other one was then fitted with a side arm adapter that is connected to a section of Tygon tubing that extended to the back of the fume hood (for venting). Neat bromine (3.5 mL, 67.3 mmol) was slowly added dropwise through the septum via a syringe over a 5 min period before the resulting solution was allowed to stir at room temperature for 0.5 h. EtOH (60 mL) was then added to the reaction mixture and the reaction was allowed to stir for an additional 0.5 h. The resultant precipitate was collected by suction filtration and washed with a copious amount of EtOH (150 mL). The collected crude product was then combined with an equivolume mixture of EtOH:CHCl₃ (60 mL) in an 125 mL round-bottom flask and boiled at ~80 °C for 10 minutes. After cooling to room temperature, the solid was filtered, washed with a minimum amount of EtOH (10 mL) and dried under vacuum to afford **2** (2.9 g, 4.46 mmol, 50%) as an off white solid. ¹H NMR (499.4 MHz, CDCl₃, Fig. S3): δ 2.33 (s, 3H, CH₃), 6.83 (d, *J* = 8.5 Hz 1H, Ar-*H*), 7.01 (s, 1H, Ar-*H*), 7.04 (d, *J* = 8.7 Hz , 6H, trityl Ar-*H*), 7.41 (d, *J* = 8.7 Hz, 6H, trityl Ar-*H*), 7.43 (d. *J* = 8.5 Hz , 1H, Ar-*H*). {¹H} {¹³C NMR (125.8 MHz, CDCl₃, Fig S4): δ 23.31, 63.6, 120.7, 123.2, 129.8, 131.0, 131.8, 132.4, 132.9, 137.4, 144.5.



Fig. S3 The ¹H spectrum of (4-bromo-3-methylphenyl)tris(4-bromophenyl)methane (2).



Fig. S4 The ¹³C NMR spectrum of (4-bromo-3-methylphenyl)tris(4-bromophenyl)methane (2).



(4-Bromo-3-(bromomethyl)phenyl)tris(4-bromophenyl)methane (3). Compound 2 (1.0 g, 1.53 mmol) was dissolved with anhydrous CCl₄ (40 mL) in a 100 mL round bottom flask equipped with a magnetic stir bar and a rubber septum. This mixture was degassed with a stream of nitrogen for 10 minutes. *N*-bromosuccinimide (0.356 g, 1.99 mmol) and benzoyl peroxide (0.010 g, mmol) were then added under N₂, a water-cooled reflux condenser was attached to the flask, and the reaction mixture was refluxed under nitrogen overnight (16 h). In the morning, the reaction mixture was cooled to room temperature and filtered. The filtrate was concentrated to dryness under reduced pressure to give a pale yellow oil, which was triturated with EtOH (25 mL) to give an off-white powder that was filtered and washed with EtOH (50 mL). This crude material was then dissolved in CHCl₃ (20 mL), filtered to remove trace succinimide impurities, and concentrated to dryness under reduced pressure to give a pale yellow (1.10 g, 1.5 mmol, 98%). ¹H NMR (499.4 MHz, CDCl₃, Fig. S5): δ 4.42 (s, 2H, CH₂Br), 6.87 (dd, *J* = 8.6 Hz 1H, Ar-*H*), 6.94 (d, *J* = 8.9 Hz 6H, Ar-*H*), 7.16 (s, 1H), 7.34 (d, *J* = 8.4 Hz, 1H, Ar-*H*), 7.4 (d, *J* = 8.6 Hz, 1H, Ar-*H*). {¹H}¹³C NMR (125.8 MHz, CDCl₃, Fig. S6): δ 33.3, 63.6, 120.9, 122.7, 131.2, 132.3, 132.8, 133.3, 136.7, 140.1, 144.1, 145.5.



Fig. S5 The ¹H spectrum of (4-bromo-3-(bromomethyl)phenyl)tris(4-bromophenyl)methane (3).



Fig. S6 The ¹³C NMR spectrum of (4-bromo-3-(bromomethyl)phenyl)tris(4-bromophenyl)methane (3).

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(4-Bromo-3-(phthalimidomethyl)phenyl)tris(4-bromophenyl)methane (4). In a 250 mL round-bottom flask equipped with a magnetic stir bar a water-cooled reflux condenser were combined compound 3 (1.45 g, 1.48 mmol), potassium phthalimide (0.442 g, 2.38 mmol), and DMF (100 mL). The resulting mixture was then stirred at 100 °C under nitrogen for 16 h. DI H₂O (100 mL) was then added and the suspension was extracted with CH₂Cl₂ (250 mL). The combined organics were concentrated to dryness under reduced pressure and the crude product was purified by silica gel chromatography (hexanes/CH₂Cl₂ = 1:1 v/v) to give compound **4** as a white solid (1 g, 1.2 mmol, 63%). ¹H NMR (499.4 MHz, CDCl₃, Fig. S7): δ 4.80 (s, 2H, CH₂-phthalimide), 6.73 (bs, 1H, HCCCH₂), 6.78 (d, 6H, trityl-Ar-H), 7.17 (d, 6H, trityl-Ar-H), 7.39 (d, 1H), 7.75 (m, 4H, phthlamide-Ar-H). {¹H}¹³C NMR (125.8 MHz, CDCl₃, Fig. S8): δ 41.6, 63.4, 120.7, 123.4, 129.2, 130.8, 131.5, 131.7, 132.3, 134.2, 134.4, 144.0, 144.8, 167.6.



Fig. S7 The ¹H spectrum of (4-bromo-3-(phthalimidomethyl)phenyl)tris(4-bromophenyl)methane (4).



180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 (ppm)

Fig. S8 The ¹³C NMR spectrum for (4-bromo-(3-phthalimidomethyl)phenyl)tris(4-bromophenyl)methane (4).

IV. Preparation of functionalized PAF-1 derivatives



PAF-1. **PAF-1** was synthesized following a modified literature procedure.^{S4} Inside an inert atmosphere drybox, 2,2'-bipyridine (1.28 g, 8.18 mmol), bis(1,5-cyclooctadiene)nickel(0) ($[Ni(cod)_2]$; 2.25 g, 8.18 mmol), and 1,5-cyclooctadiene (cod; 1.05 mL, 8.32 mmol), and anhydrous DMF (120 mL) were combined into an 250 mL roundbottom flask. The flask was capped with a solid-addition tube containing tetrakis(4-bromophenyl)methane (1 g, 1.57 mmol). The closed reaction assembly was then taken outside of the drybox and placed into an 85 °C oil bath where the liquid portion of the assembly was allowed to stir for 2 h. Tetrakis(4-bromophenyl)methane was then added to the mixture from the solid-addition tube and the closed reaction assembly was allowed to stir at 85 °C overnight.

In the morning, the assembly was open, 6 M HCl (15 mL) was added to yield a suspension of flocculated solid, which was stirred for an additional 1 h. The solid was collected by filtration, washed with DMF, water, and acetone, and dried under vacuum at 150 °C to afford **PAF-1** as an off-white powder (0.5 g, 100%).





PAF-1-CH₃. Inside an inert atmosphere drybox, 2,2'-bipyridine (1.28 g, 8.18 mmol), bis(1,5-cyclooctadiene)nickel(0) ([Ni(cod)₂]; 2.25 g, 8.18 mmol), and 1,5-cyclooctadiene (cod; 1.05 mL, 8.32 mmol), and anhydrous DMF (120 mL) were combined into an 250 mL round-bottom flask. The flask was capped with a solid-addition tube containing (4-bromo-3-methylphenyl)tris(4-bromophenyl)methane (2) (1 g, 1.53 mmol). The closed reaction assembly was then taken outside of the drybox and placed into an 85 °C oil bath where the liquid portion of the assembly was allowed to stir for 2 h. (4-Bromo-3-methylphenyl)tris(4-bromophenyl)methane was then added to the mixture from the solid-addition tube and the closed reaction assembly was allowed to stir at 85 °C overnight.

In the morning, the assembly was open, 6 M HCl (15 mL) was added to yield a suspension of flocculated solid, which was stirred for an additional 1 h. The solid was collected by filtration, washed with DMF, water, and acetone, and dried under vacuum at 150 °C to afford **PAF-1-CH**₃ as an off-white powder (0.5 g, 98%).



PAF-1-CH₂OH. Inside an inert atmosphere drybox, 2,2'-bipyridine (0.64 g, 4.1 mmol), bis(1,5-cyclooctadiene)nickel(0) ([Ni(cod)₂]; 1.125 g, 4.1 mmol), and 1,5-cyclooctadiene (cod; 0.53 mL , 4.3mmol), and anhydrous DMF (120 mL) were combined into an 250 mL round-bottom flask. The flask was capped with a solid-addition tube containing (4-bromo-3-(bromomethyl)phenyl)tris(4-bromophenyl)methane (**3**) (0.57 g, 0.79 mmol). The closed reaction assembly was then taken outside of the drybox and placed into an 85 °C oil bath where the liquid portion of the assembly was allowed to stir for 2 h. (4-Bromo-3-(bromomethyl)phenyl)tris(4-bromophenyl)methane was then added to the mixture from the solid-addition tube and the closed reaction assembly was allowed to stir at 85 °C overnight.

In the morning, the assembly was open, 6 M HCl (15 mL) was added to yield a suspension of flocculated solid, which was stirred for an additional 1 h. The solid was collected by filtration, washed with DMF, water, and acetone, and dried under vacuum at 150 °C to afford **PAF-1-CH₂OH** as an off-white powder (0.27 g, 84%).



PAF-1-CH₂-phthalimide. Inside an inert atmosphere drybox, 2,2'-bipyridine (0.64 g, 4.1 mmol), bis(1,5-cyclooctadiene)nickel(0) ([Ni(cod)₂]; 1.125 g, 4.1 mmol), and 1,5-cyclooctadiene (cod; 0.53 mL , 4.3mmol), and anhydrous DMF (120 mL) were combined into an 250 mL round-bottom flask. The flask was capped with a solid-addition tube containing (4-Bromo-3-(phthalimidomethyl)phenyl)tris(4-bromophenyl)methane (**4**) (0.63 g, 0.79 mmol). The closed reaction assembly was then taken outside of the drybox and placed into an 85 °C oil bath where the liquid portion of the assembly was allowed to stir for 2 h. (4-Bromo-3-(phthalimidomethyl)phenyl)tris(4-bromophenyl)methane was then added to the mixture from the solid-addition tube and the closed reaction assembly was allowed to stir at 85 °C overnight.

In the morning, the assembly was open, 6 M HCl (15 mL) was added to yield a suspension of flocculated solid, which was stirred for an additional 1 h. The solid was collected by filtration, washed with DMF, water, and acetone, and dried under vacuum at 150 °C to afford **PAF-1-CH₂OH** as an off-white powder (0.31 g, 83%).



PAF-1-CH₂NH₂. Into a 20 mL microwave vial (Biotage) were combined **PAF-1-CH₂-phthalimide** (0.1 g, 0.21 mmol), hydrazine monohydrate (1 mL, 20.6 mmol), and EtOH (9 mL). The vial was crimp-capped and refluxed at 85 °C for 48 h using an oil bath. The PAF was collected by filtration, washed with DMSO, DMF, and EtOH (50 mL each), and dried under vacuum to afford an off-white powder that was then Soxhlet extracted with EtOH for 16 h. Yield = 40 mg (55% initial mass recovered, unoptimized) after drying under vacuum.

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PAF-1-CH₂N=CMe₂. Into a 20 mL microwave vial (Biotage) were combined **PAF-1-CH₂-phthalimide** (0.1 g, 0.21 mmol), hydrazine monohydrate (1 mL, 20.6 mmol), and EtOH (9 mL). The vial was crimp-capped and refluxed at 85 °C for 48 h using an oil bath. The PAF was collected by filtration, washed with EtOH, DMF, CH₂Cl₂, and acetone (50 mL each), and dried under vacuum to afford an off-white powder that was then Soxhlet extracted with acetone for 16 h. Yield = 40 mg (49% initial mass recovered, unoptimized) after drying under vacuum.

V. Solid-state ¹H-¹³C CP-MAS NMR spectra of functionalized PAF-1 derivatives



Fig. S9 The solid-state ¹H-¹³C CP-MAS NMR spectrum of PAF-1-CH₃ recorded at a MAS rate of 10 kHz.



Fig. S10 The solid-state ¹H-¹³C CP-MAS NMR spectrum of PAF-1-CH₂OH recorded at a MAS rate of 8 kHz.



Fig. S11 The solid-state ¹H-¹³C CP-MAS NMR spectrum of **PAF-1-CH₂-phthalimide** recorded at a MAS rate of 10 kHz.



Fig. S12 The solid-state ¹H-¹³C CP-MAS NMR spectrum of PAF-1-CH₂NH₂ recorded at a MAS rate of 10 kHz.



Fig. S13 The solid-state ¹H-¹³C CP-MAS NMR spectrum of **PAF-1-CH₂N=CMe₂** recorded at a MAS rate of 10 kHz.

VI. N2 isotherms of PAF-1 derivatives



Fig. S14 The N₂ isotherms of PAF-1 derivatives recorded at 77 K. Closed symbols = adsorption; open symbols = desorption.



VII. FTIR spectra of PAF-1 derivatives

Fig. S15 The FTIR spectra of PAF-1 derivatives.

VIII. TGA profiles of PAF-1 derivatives



Fig. S16 The TGA profiles of the PAF-1 derivatives measured under N_2 .

IX. Elemenal analysis data for PAF-1 derivatives

Table S1. Elemental analysis data for PAF-1 derivatives.

Sample Identification	% C	% H	% N	%0	% Br
PAF-1-CH ₂ OH	90.48	5.50	0.48	2.16	0.3
Calculated	90.13	5.24		4.63	
PAF-1-CH ₃	90.89	5.59	0.20		
Calculated	94.49	5.50			
PAF-1-CH ₂ -phthalimide	84.24	4.66	2.84	6.73	
Calculated	85.86	4.45	2.94	6.72	-
PAF-1-CH2NH2	82.31	5.69	3.83		
Calculated	90.38	5.55	4.05		-
PAF-1-CH ₂ N=CMe ₂	85.86	5.71	3.80		
Calculated	90.34	6.02	3.63		

X. Pore size distribution of PAF-1 derivatives



Fig. S17 The pore size distribution plots for PAF-1 and derivatives according to DFT analysis.

XI. EtOH, toluene, and H₂O isotherms for PAF-1 and PAF-1-CH₂OH.



Fig. S18 The EtOH adsorption isotherms of PAF-1 and PAF-1-CH₂OH recorded at 298 K.



Fig. S19 The toluene adsorption isotherms of PAF-1 and PAF-1-CH₂OH recorded at 298 K.



Fig. S20 The H₂O adsorption isotherms of PAF-1 and PAF-1-CH₂OH recorded at 298 K.

XII. CO₂ isosteric heat of adsorption (Q_{st}) of PAF-1-CH₂N=CMe₂, PAF-1-CH₂OH, and PAF-1-CH₂NH₂. In the evaluation of the CO₂ Q_{st} of PAF-1-CH₂OH, PAF-1-CH₂N=CMe₂, we employ the single-site Langmuir model, which assumes: (i) the surface of the adsorbent is uniform, (ii) adsorbed molecules do not interact, (iii) all adsorption occurs through the same mechanism, and (iv) a monolayer is formed. This model works well for these two materials as shown by the excellent fits of the adsorption data at 273, 283, and 293 K (Figs. S22 and S23).

However, because the CO₂ isotherms for PAF-1-CH₂NH₂ clearly indicates the presence of at least two different

adsorption sites (the amine group and the **PAF-1** framework, see Fig. 3 in the main text), we applied the dual-site Langmuir model to evaluate its CO₂ Q_{st} . This model results in excellent fits (e.g., $R^2 = 0.999$) of the adsorption data at 273, 283, and 293 K (Fig. S24) in comparison to the fits generated using the single-site Langmuir model (e.g., $R^2 = 0.98$). The application of the single- and dual-site Langmuir models to account for different sets of data has been reported by Long and coworkers^{S5} as well as Zhou and coworkers.^{S6}



Fig. S21 Plots of CO₂ isosteric heats of adsorption (Q_{st}) of PAF-1-CH₂OH, PAF-1-CH₂N=CMe₂ (calculated from the single-site Langmuir model) and PAF-1-CH₂NH₂ (calculated from the dual-site Langmuir model) recorded at 273, 283, and 293 K.



Fig. S22 Fitting and parameters for PAF-1-CH₂N=CMe₂ determined by the single-site Langmuir model.

S20



Fig. S23 Fitting and parameters for PAF-1-CH₂OH determined by the single-site Langmuir model.



Fig. S24 Fitting and parameters for PAF-1-CH₂NH₂ determined by the dual-site Langmuir model.

XIII. Densities of PAF-1 derivatives. According to Lowell *et al.*,^{S7} the *skeletal density* is the ratio of the mass to the volume occupied by the *framework* of the sample excluding the volume of any open pores while the *bulk density* is the ratio of the mass to the volume occupied by the *whole* sample, including all internal pore and interparticle void space (*pore volume*). Hence, the bulk density can be calculated if the measured skeletal density

and the total pore volume of each material are known (Eq. S4).

$$\rho_{\text{bulk}} = 1/[(1/\rho_{\text{skeletal}}) + V_{\text{total pore}}]$$
(S4)

From the data in Table S2, the NLDFT-derived bulk densities of **PAF-1-CH₃** and **PAF-1-CH₂OH**, as measured by helium pycnometry, are quite similar to that of the parent **PAF-1**, suggesting that their networks are also noncatenated as in **PAF-1**. In contrast, NLDFT-derived the bulk densities of **PAF-1-CH₂-phthalimide**, **PAF-1-CH₂NH₂**, and **PAF-1-CH₂N=CMe₂** are approximately twice that of **PAF-1**. While this may indicate catenation, an alternate interpretation is that the large phthalimide groups within **PAF-1-CH₂-phthalimide** may interact with each others during the polymerization and cause defects that generate non-uniform pores that are not accessible to either He or N₂. This would subsequently affect the volume and the density calculations as shown in Eq S4.

That the NLDFT-derived bulk densities of **PAF-1-CH₂NH₂** and **PAF-1-CH₂N=CMe₂** are quite similar to that of the **PAF-1-CH₂-phthalimide** starting material is quite intriguing. While this may be interpreted as a consequence of these materials being isostructural, the values obtained from do not make sense from molecular mass considerations. The post-synthesis removal of the phthalimide group from **PAF-1-CH₂-phthalimide** ($\rho_{bulk} = 0.78$ g mL⁻¹) should have result in a **PAF-1-CH₂NH₂** material with about 89% of the initial bulk density ($\rho_{bulk} = 0.69$ instead of 0.74 g mL⁻¹). In the same vein, **PAF-1-CH₂N=CMe₂** should have a density that is 93% of the density of **PAF-1-CH₂-phthalimide** ($\rho_{bulk} = 0.73$ instead of 0.78 g mL⁻¹). To reconcile these differences, which can be due to the aforementioned presence of non-uniform pores, we calculated the total micropore-only volumes for these materials using the Dubinin-Radushkevich (DR) equation at 77 K.^{S8} The resulting DR-derived bulk densities for **PAF-1-CH₂NH₂** and **PAF-1-CH₂N=CMe₂** are quite close to the values calculated from simple considerations of molecular mass changes upon PSM (Table S2, *cf.* the values of the last two entries in the last column with the values in the parentheses), suggesting that density changes for a series of related materials derived from PSM are better approximated by DR-derived bulk densities.

PAF derivatives	Total NLDFT-	Total DR-derived	$\rho_{\text{skeletal}} (\text{g mL}^{-1})^c$	NLDFT-	DR-derived				
	derived pore	pore volume		derived ρ_{bulk} (g	$\rho_{\text{bulk}} (\text{g mL}^{-1})^{e}$				
	volume $(\text{cm}^3 \text{ g}^{-1})^a$	$(\text{cm}^3 \text{g}^{-1})^b$		$mL^{-1})^{d}$					
PAF-1	2.23	1.82	1.425	0.34	0.40				
PAF-1-CH ₃	2.01	1.42	1.457	0.37	0.47				
PAF-1-CH ₂ OH	1.77	0.68	1.567	0.42	0.76				
PAF-1-CH ₂ -	0.58	0.35	1.445	0.78	0.95				
phthalimide									
PAF-1-CH ₂ NH ₂	0.74	0.55	1.618	$0.74 (0.69)^{f}$	$0.85(0.85)^{f}$				
PAF-1-	0.73	0.54	1.823	$0.78 (0.73)^{f}$	$0.91 (0.88)^{f}$				
CH-N-CMo.									

 Table S2.
 Densities of PAF-1 derivatives

^{*a*}Total NLDFT-derived pore volume from the N₂ adsorption profiles at $p/p_0 = 0.98$; data is averaged from at least two independent measurements. ^{*b*}Total pore volumes derived from the Dubinin-Radushkevich (DR) equation at 77 K, i.e., excluding any mesopore volumes.^{S5} ^{*c*}Derived from helium pycnometry. Data is averaged from ten measurements with standard deviations of less than 0.01. ^{*d*}The bulk densities calculated using the NLDFT-derived pore volumes. ^{*e*}The bulk densities calculated using the pore volumes derived from the DR equation. ^{*f*}Calculated from the corresponding ρ_{bulk} of **PAF-1-CH₂-phthalimide**, assuming an appropriate molecular mass changes upon PSM. Finally, we note that the NLDFT-derived bulk densities for **PAF-1-CH**₃ and **PAF-1-CH**₂**OH** are also different from their DR-derived bulk densities (Table S2), with the biggest difference in values observed for the latter materials. This suggests that similar to the case of **PAF-1-CH**₂**-phthalimide**, the OH groups in **PAF-1-CH**₂**OH** were also interacting with each other during the polymerization, thus influencing the shape of the pores and their uniformity. This is supported by both the drop in its total pore volume (both NLDFT- and DR-derived) compared to the **PAF-1-CH**₃ derivative, and the fact that its skeletal density is the highest of all the values reported in Table S2.

XIV. Author contributions audit. S.J.G., O.K.F., J.T.H., and S.T.N. conceived the experiments presented herein. S.J.G synthesized all compounds and carried out the characterization of all compounds. M.H.W performed the solvent adsorption experiments. J.E.M. performed the CO_2 isotherm fittings and Q_{st} calculations. Y.J.M. performed the densities determination. O.K.F., J.T.H., and S.T.N. supervised the project. S.J.G wrote the initial draft of the paper and received inputs and corrections from all co-authors. S.J.G. and S.T.N. finalized the manuscript.

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