[Supplementary Information to accompany]

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


*Department of Chemistry and the Institute for Catalysis in Energy Processes, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208-3113, USA. Department of Chemical and Biological Engineering, Northwestern University, Evanston, IL 60208 (USA)*

**Table of Contents**

I. General information
II. Materials and synthetic protocols
III. Preparation of tetrakis(4-bromophenyl)methane monomers
IV. Preparation of functionalized PAF-1 derivatives
V. Solid-state $^1$H-$^{13}$C CP-MAS NMR spectra of functionalized PAF-1 derivatives
VI. $N_2$ isotherms of PAF-1 derivatives
VII. FTIR spectra of PAF-1 derivatives
VIII. TGA profiles of PAF-1 derivatives
IX. Elemental analysis data for PAF-1 derivatives
X. Pore size distribution of PAF-1 and derivatives
XI. EtOH, toluene, and $H_2O$ isotherms for PAF-1 and PAF-1-CH$_2$OH
XII. CO$_2$ isosteric heats of adsorption ($Q_{st}$) of PAF-1-CH$_2$N=CMe$_2$, PAF-1-CH$_2$OH, and PAF-1-CH$_2$NH$_2$
XIII. Densities of PAF-1 derivatives.
XIV. Authors contributions audit
XV. References

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

$^1$H-$^{13}$C cross-polarization, magic angle spinning (CP MAS) nuclear magnetic resonance spectra were recorded on a Varian VNMRS 400 MHz (400 MHz for $^1$H, 100. MHz for $^{13}$C) 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 $\mu$L and capped with a Teflon spacer. The spinning rate was at 8 or 10 kHz. $^{13}$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, 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 \(\text{N}_2\) adsorption and desorption measurements were performed on a Micromeritics Tristar 3020 system (Micromeritics, 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 (Micromeritics, Norcross, GA). Before measurements, samples were degassed for 12 h at 150 °C under high vacuum (< 10\(^{-4}\) bar). The specific surface areas for \(\text{N}_2\) 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 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.

\(\text{CO}_2\) adsorption measurements (< 1 bar) were performed using an Autosorb 1-MP instrument (Quantachrome Instruments, Boynton Beach, FL). Low-pressure \(\text{CO}_2\) adsorption isotherms were measured at 273, 283, and 293 K; the temperature was held constant using an automated cooling system. \(\text{CO}_2\) isotherms were fit using non-linear least-squares fitting to either a single-site or dual-site Langmuir equation (Eqs. S1 and S2, respectively):

\[
N = \frac{N_m B P}{1 + BP} \\
N = \frac{N_{m1} B_1 P}{1 + B_1 P} + \frac{N_{m2} B_2 P}{1 + B_2 P}
\]

where \(P\) is the pressure, \(N\) is the coverage of adsorbate, \(N_m\) is the saturation coverage of the adsorbate and \(B\) is the Langmuir parameter. \(N_{m1}, N_{m2}, B_1,\) 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 \((Q_{st})\).

\[
\ln(P)_N = \frac{Q_{st}}{RT} + C
\]

where \(P\) is the pressure, \(N\) is the amount adsorbed, \(T\) is the temperature in °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 F254 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 systemS1 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-On™ 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-amino-tetraphenylmethane 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 $^1$H spectrum of (3-methylphenyl)triphenylmethane (1).

**Fig. S2**  The $^{13}$C NMR spectrum of (3-methylphenyl)triphenylmethane (1).
(4-Bromo-3-methylphenyl)tris(4-bromophenyl)methane (2). Compound 2 was synthesized following a modified literature procedure.\textsuperscript{3} 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:CHCl\textsubscript{3} (60 mL) in an 125 mL round-bottom flask and boiled at ~80 ºC 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. \textsuperscript{1}H NMR (499.4 MHz, CDCl\textsubscript{3}, Fig. S3): δ 2.33 (s, 3H, CH\textsubscript{3}), 6.83 (d, \textit{J} = 8.5 Hz 1H, Ar-H), 7.01 (s, 1H, Ar-H), 7.04 (d, \textit{J} = 8.7 Hz , 6H, trityl Ar-H), 7.41 (d, \textit{J} = 8.7 Hz, 6H, trityl Ar-H), 7.43 (d, \textit{J} = 8.5 Hz ,1H, Ar-H). \textsuperscript{13}C NMR (125.8 MHz, CDCl\textsubscript{3}, 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.

\textbf{Fig. S3} The \textsuperscript{1}H 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 oil. This oil was triturated with EtOH (25 mL) to afford a precipitate, which was collected by filtration and dried under vacuum to afford 3 as an off-white powder (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). 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. S4   The ¹³C NMR spectrum of (4-bromo-3-methylphenyl)tris(4-bromophenyl)methane (2).
**Fig. S5** The $^1$H spectrum of (4-bromo-3-(bromomethyl)phenyl)tris(4-bromophenyl)methane (3).

**Fig. S6** The $^{13}$C NMR spectrum of (4-bromo-3-(bromomethyl)phenyl)tris(4-bromophenyl)methane (3).
(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%).

³¹H NMR (499.4 MHz, CDCl₃, Fig. S7): \[ \delta 4.80 \text{ (s, 2H, } CH₂\text{-phthalimide)}, \delta 6.73 \text{ (bs, 1H, } HCCCH₂), \delta 6.78 \text{ (d, 6H, trityl-Ar-H)}, \delta 7.17 \text{ (d, 6H, trityl-Ar-H)}, \delta 7.39 \text{ (d, 1H), } 7.75 \text{ (m, 4H, phthlamide-Ar-H)}. \]

{³¹H}¹³C NMR (125.8 MHz, CDCl₃, Fig. S8): \[ \delta 41.6, 63.4, 120.7, 123.4, 129.2, 130.8, 131.5, 131.7, 132.3, 134.2, 134.4, 144.0, 144.8, 167.6. \]

Fig. S7  The ¹H spectrum of (4-bromo-3-(phthalimidomethyl)phenyl)tris(4-bromophenyl)methane (4).
**IV. Preparation of functionalized PAF-1 derivatives**

**PAF-1.**  PAF-1 was synthesized following a modified literature procedure. 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 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%).

---

**Fig. S8**  The ¹³C NMR spectrum for (4-bromo-(3-phthalimidomethyl)phenyl)tris(4-bromophenyl)methane (4).
**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 a 250 mL round-bottom flask. The flask was capped with a solid-addition tube containing (4-bromo-3-methylphenyl)tris(4-bromophenyl)methane \( \text{(2)} \) (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-CH₃ 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, 4.3 mmol), and anhydrous DMF (120 mL) were combined into a 250 mL round-bottom flask. The flask was capped with a solid-addition tube containing (4-bromo-3-(bromomethyl)phenyl)tris(4-bromophenyl)methane \( \text{(3)} \) (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, 4.3 mmol), and anhydrous DMF (120 mL) were combined into a 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 ºC 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 ºC 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 ºC to afford PAF-1-CH₂-OH as an off-white powder (0.31 g, 83%).

PAF-1-CH₂-NH₂. 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 ºC 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.
PAF-1-CH$_2$N=CMe$_2$. Into a 20 mL microwave vial (Biotage) were combined PAF-1-CH$_2$-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, CH$_2$Cl$_2$, 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 $^1$H-$^{13}$C CP-MAS NMR spectra of functionalized PAF-1 derivatives

Fig. S9  The solid-state $^1$H-$^{13}$C CP-MAS NMR spectrum of PAF-1-CH$_3$ recorded at a MAS rate of 10 kHz.
**Fig. S10**  The solid-state $^1$H-$^{13}$C CP-MAS NMR spectrum of PAF-1-CH$_2$OH recorded at a MAS rate of 8 kHz.

**Fig. S11**  The solid-state $^1$H-$^{13}$C CP-MAS NMR spectrum of PAF-1-CH$_2$-phthalimide recorded at a MAS rate of 10 kHz.
**Fig. S12** The solid-state $^1$H-$^{13}$C CP-MAS NMR spectrum of PAF-1-CH$_2$NH$_2$ recorded at a MAS rate of 10 kHz.

**Fig. S13** The solid-state $^1$H-$^{13}$C CP-MAS NMR spectrum of PAF-1-CH$_2$N=CMe$_2$ recorded at a MAS rate of 10 kHz.
VI. N₂ isotherms of PAF-1 derivatives

![N₂ isotherms of PAF-1 derivatives](image)

**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

![FTIR spectra of PAF-1 derivatives](image)

**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 N₂.

IX. Elemental analysis data for PAF-1 derivatives

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

<table>
<thead>
<tr>
<th>Sample Identification</th>
<th>% C</th>
<th>% H</th>
<th>% N</th>
<th>% O</th>
<th>% Br</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAF-1-CH₃OH</td>
<td>90.48</td>
<td>5.50</td>
<td>0.48</td>
<td>2.16</td>
<td>0.3</td>
</tr>
<tr>
<td>Calculated</td>
<td>90.13</td>
<td>5.24</td>
<td>–</td>
<td>4.63</td>
<td>–</td>
</tr>
<tr>
<td>PAF-1-CH₃</td>
<td>90.89</td>
<td>5.69</td>
<td>0.20</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Calculated</td>
<td>94.49</td>
<td>5.50</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>PAF-1-CH₂-phthalimide</td>
<td>84.24</td>
<td>4.66</td>
<td>2.84</td>
<td>6.73</td>
<td>–</td>
</tr>
<tr>
<td>Calculated</td>
<td>85.86</td>
<td>4.45</td>
<td>2.94</td>
<td>6.72</td>
<td>–</td>
</tr>
<tr>
<td>PAF-1-CH₂ NH₂</td>
<td>82.31</td>
<td>5.69</td>
<td>3.83</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Calculated</td>
<td>90.38</td>
<td>5.55</td>
<td>4.05</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>PAF-1-CH₂N=CM乙</td>
<td>85.86</td>
<td>5.71</td>
<td>3.80</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Calculated</td>
<td>90.34</td>
<td>6.02</td>
<td>3.63</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>
X. Pore size distribution of PAF-1 derivatives

![Fig. S17](image1.png)

**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](image2.png)

**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=CMc₂, PAF-1-CH₂OH, and PAF-1-CH₂NH₂. In the evaluation of the CO₂ Q_st of PAF-1-CH₂OH, PAF-1-CH₂N=CMc₂, 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 CO$_2$ $Q_{st}$. 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$^{55}$ as well as Zhou and coworkers.$^{56}$

**Fig. S21** Plots of CO$_2$ isosteric heats of adsorption ($Q_{st}$) of PAF-1-CH$_2$OH, PAF-1-CH$_2$N=CMe$_2$ (calculated from the single-site Langmuir model) and PAF-1-CH$_2$NH$_2$ (calculated from the dual-site Langmuir model) recorded at 273, 283, and 293 K.

**Fig. S22** Fitting and parameters for PAF-1-CH$_2$N=CMe$_2$ determined by the single-site Langmuir model.
Fig. S23  Fitting and parameters for PAF-1-CH$_2$OH determined by the single-site Langmuir model.

<table>
<thead>
<tr>
<th></th>
<th>$N_{m1}$</th>
<th>$B_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>273 K</td>
<td>11.82</td>
<td>0.3315</td>
</tr>
<tr>
<td>283 K</td>
<td>9.106</td>
<td>0.3180</td>
</tr>
<tr>
<td>293 K</td>
<td>9.491</td>
<td>0.2308</td>
</tr>
</tbody>
</table>

Fig. S24  Fitting and parameters for PAF-1-CH$_2$NH$_2$ determined by the dual-site Langmuir model.

<table>
<thead>
<tr>
<th></th>
<th>$N_{m1}$</th>
<th>$B_1$</th>
<th>$N_{m2}$</th>
<th>$B_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>273 K</td>
<td>8.893</td>
<td>0.7342</td>
<td>0.5721</td>
<td>173.6</td>
</tr>
<tr>
<td>283 K</td>
<td>8.433</td>
<td>0.6842</td>
<td>0.4775</td>
<td>76.67</td>
</tr>
<tr>
<td>293 K</td>
<td>8.183</td>
<td>0.4576</td>
<td>0.4404</td>
<td>33.74</td>
</tr>
</tbody>
</table>

XIII. Densities of PAF-1 derivatives. According to Lowell et al.,$^{57}$ 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).

\[ \rho_{\text{bulk}} = \frac{1}{\left(1/\rho_{\text{skeletal}} + V_{\text{total pore}}\right)} \]  

(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 non-catenated 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 (\(\rho_{\text{bulk}} = 0.78\) g mL\(^{-1}\)) should have result in a PAF-1-CH2NH2 material with about 89% of the initial bulk density (\(\rho_{\text{bulk}} = 0.69\) 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 (\(\rho_{\text{bulk}} = 0.73\) 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.\(^{58}\) 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.

<table>
<thead>
<tr>
<th>PAF derivatives</th>
<th>Total NLDFT-derived pore volume (cm(^3) g(^{-1}))(^a)</th>
<th>Total DR-derived pore volume (cm(^3) g(^{-1}))(^b)</th>
<th>(\rho_{\text{skeletal}}) (g mL(^{-1}))(^c)</th>
<th>NLDFT-derived (\rho_{\text{bulk}}) (g mL(^{-1}))(^d)</th>
<th>DR-derived (\rho_{\text{bulk}}) (g mL(^{-1}))(^e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAF-1</td>
<td>2.23</td>
<td>1.82</td>
<td>1.425</td>
<td>0.34</td>
<td>0.40</td>
</tr>
<tr>
<td>PAF-1-CH3</td>
<td>2.01</td>
<td>1.42</td>
<td>1.457</td>
<td>0.37</td>
<td>0.47</td>
</tr>
<tr>
<td>PAF-1-CH2OH</td>
<td>1.77</td>
<td>0.68</td>
<td>1.567</td>
<td>0.42</td>
<td>0.76</td>
</tr>
<tr>
<td>PAF-1-CH2-phthalimide</td>
<td>0.58</td>
<td>0.35</td>
<td>1.445</td>
<td>0.78</td>
<td>0.95</td>
</tr>
<tr>
<td>PAF-1-CH2NH2</td>
<td>0.74</td>
<td>0.55</td>
<td>1.618</td>
<td>0.74 (0.69)(^f)</td>
<td>0.85 (0.85)(^f)</td>
</tr>
<tr>
<td>PAF-1-CH2N=CMe2</td>
<td>0.73</td>
<td>0.54</td>
<td>1.823</td>
<td>0.78 (0.73)(^f)</td>
<td>0.91 (0.88)(^f)</td>
</tr>
</tbody>
</table>

\(^a\)Total NLDFT-derived pore volume from the N\(_2\) 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.\(^{55}\) \(^c\)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 \(\rho_{\text{bulk}}\) 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\textsubscript{3} and PAF-1-CH\textsubscript{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\textsubscript{2}-phthalimide, the OH groups in PAF-1-CH\textsubscript{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\textsubscript{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\textsubscript{2} isotherm fittings and $Q_s$ 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.

**XV. References**


