

Supporting information

Fluorinated porous organic frameworks for improved CO₂ and CH₄ capture

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1. General experimental methods

Solution NMR spectroscopy

^1H , ^{13}C and ^{19}F solution NMR spectra were recorded at 400, 100 and 377 MHz, respectively, on a Bruker Avance 400 Spectrometer. In the following, ^1H data are reported as follows: chemical shifts (in ppm and referenced to internal TMS), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), and coupling constants (in Hz). ^{13}C data are reported as follow: chemical shifts (in ppm and referenced to internal TMS), multiplicity (s = singlet, d = doublet), coupling constants (in Hz) ^{19}F data are reported as follows: chemical shifts (in ppm and referenced to internal CFCl_3).

IR spectroscopy

IR spectra were acquired by ATR method by means of a Nicolet iS10 instrument over the range 4000-600 cm^{-1} . In the following, signal intensities are denoted as br = broad, vs = very strong, s = strong, m = medium, and w = weak.

Calorimetric Analysis

Differential Scanning Calorimetry (DSC) analyses were performed on a Mettler-Toledo StarE instrument from 0 to 450°C under an 80 ml/min flux of N_2 . Thermogravimetric Analyses (TGA) were performed on a Mettler-Toledo DSC/TGA 1 StarE System from 0 to 800 °C at a 10°C/min heating rate under a 50 ml/min flux of air.

Gas Adsorption Isotherms

N_2 adsorption/desorption isotherms were collected at liquid nitrogen temperature (77 K) and up to 1 bar of pressure by means of a Micromeritics ASAP 2020 HD analyzer. All samples were degassed by heating at 130°C for 5 hours under vacuum (approx. 10^{-3} mmHg) right before the analysis. Specific surface area values were calculated using the Brunauer, Emmett, and Teller (BET) model and the Langmuir model. Pore size distributions were calculated considering a slit pore geometry and the Non-Local Density Functional Theory (NLDFT). CO_2 adsorption/desorption isotherms were measured at 195 K up to 1 bar of pressure and at 273, 283, 298 K up to 10 bar using a Micromeritics ASAP 2050 analyzer. Samples were degassed at 130°C for 5 hours before each analysis.

Solid State NMR Spectroscopy

^{13}C solid-state NMR experiments were carried out with a Bruker Avance 300 instrument operating at a static field of 7.04 T equipped with high-power amplifiers (1 kW) and a 4 mm double resonance MAS probe. $^{13}\text{C}\{^1\text{H}\}$ ramped-amplitude cross polarization (CP) experiments were performed at a spinning speed of 12.5 kHz using a recycle delay of 5 s and a contact time of 2 ms. The 90° pulse for proton was 2.9 μs . Crystalline polyethylene was taken as an external reference at 32.8 ppm from TMS. Quantitative solid-state ^1H MAS NMR spectra (single-pulse excitation SPE) were performed with a Bruker Avance III 600 instrument operating at 14.1 T,

using a recycle delay of 20 s. A MAS Bruker probe head was used with 2.5 mm ZrO₂ rotors spinning at 30 kHz. The 90° pulse for proton was 2.9 μs. The ¹H chemical shift was referenced to adamantane.

Hyperpolarized ¹²⁹Xe NMR Spectroscopy

Hyperpolarization ¹²⁹Xe NMR experiments were performed by a home-built apparatus with a continuous-flow delivery of hyperpolarized xenon gas with a Bruker Avance 300 spectrometer operating at a Larmor Frequency of 83.02 MHz for ¹²⁹Xe. A diode array laser delivering 6 W at 795 nm was applied, circular polarization was achieved using a beam splitting cube and quarter wave plate. A stream of gas mixture containing 2% xenon, 2% nitrogen and 96% helium at 2 atm was used and the gas flow rate was maintained at 20 L/h. The samples were outgassed overnight at 120°C in vacuum, then were pressed in a glass tube before being inserted into the coil. A pulse duration of 7 μs was applied, with a recycle delay of 0.5 s. The ¹²⁹Xe NMR chemical shifts were referenced to xenon gas set at 0 ppm.

Scanning Electron Microscopy

Scanning electron microscopy (SEM) images were collected using Zeiss Gemini 500 scanning electron microscopy, operating at 10 kV.

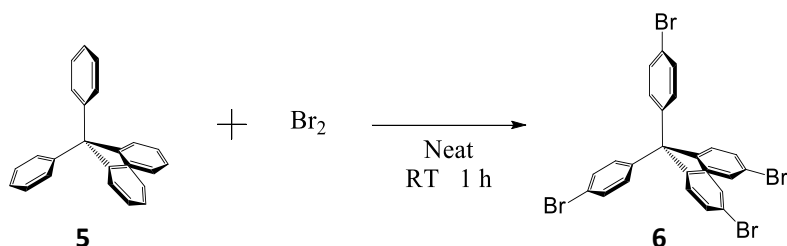
Helium Pycnometer

Helium pycnometer analyses were performed with a Micromeritics AccuPyc II 1340 Pycnometer with a 1 cm³ sample holder. The samples were previously treated in vacuum at 120 °C for 4 h.

2. Synthetic procedures

Chemicals and solvents were purchased from Sigma Aldrich or Alfa Aesar and used without further purification, unless otherwise specified.

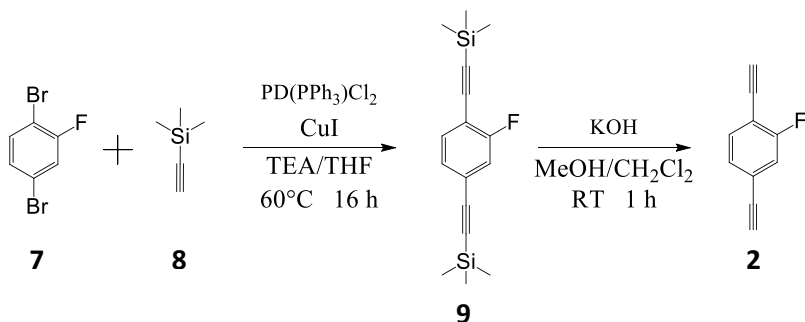
Synthesis of tetrakis(4-bromophenyl)methane (**6**)



Tetrakis(4-bromophenyl)methane was synthesized according to the procedure published in *J. Org. Chem.*, 69(5), 1524-1530, 2004. Commercial tetraphenylmethane (**5**) was further purified by sublimation at 180°C under vacuum before being used in this reaction. Then, Br₂ (12.8 ml, 250 mmol) was transferred to a 100 ml round-bottom flask. Purified tetraphenylmethane (2 g, 6.25 mmol) was added in small portions under vigorous stirring. The white smoke (HBr) produced by the reaction was driven towards a Drexel bottle filled with aqueous NaOH solution. The mixture was left at room temperature under stirring until no more white smoke was produced (approx. 60 minutes). Then, the mixture was cooled with an ice bath and EtOH (50 ml) was

slowly added. A white precipitate formed. The mixture was then stirred at RT for 2 hours; after that, the excess of bromine was quenched with a saturated aqueous sodium bisulfite solution. The white solid was recovered by filtration, washed with abundant water and EtOH. The crude product was crystallized from CHCl₃/EtOH to afford pure **1** as white crystalline needles (3.2 g, 80% yield).

Synthesis of 1,4-diethynyl-2-fluorobenzene (**2**)

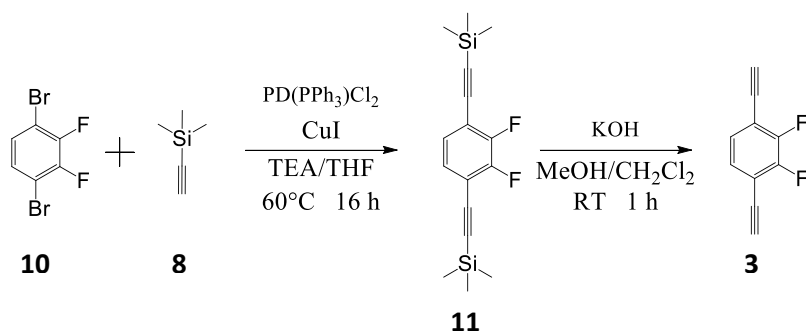


An oven-dried Schlenk was purged with N₂ and charged with N₂-purged triethylamine (TEA, 20 ml) by means of a syringe. Dry tetrahydrofuran (THF, 10 ml) was then added. Three freeze-pump-thaw cycles were performed on the solvents mixture. Then, 1,4-dibromo-2-fluoro-benzene (**7**) (1 g, 3.94 mmol), PdCl₂(PPh₃)₂ (70 mg, 0.1 mmol), CuI (20 mg, 0.1 mmol) and trimethylsilylacetylene (**8**) (TMSA, 1.50 ml, 10.6 mmol) were added. The resulting mixture was sealed under N₂ atmosphere, heated up to 60°C and kept at this temperature under stirring for 16 hours. After 16 hours, thin layer chromatography (TLC) analysis (hexane) showed complete consumption of **7**. The reaction mixture was cooled down to room temperature and filtered over Celite. The solid residue was washed with ethyl acetate (EtOAc) and all the organic fractions were combined and passed over a silica pad to obtain a clear, brown solution. This solution was dried over Na₂SO₄ and the solvent was removed by rotary evaporation to give a brown solid. This solid was recrystallized from hexane/ethanol to afford ((2-fluoro-1,4-phenylene)bis(ethyne-2,1-diyl))bis(trimethylsilane) (**9**) as a crystalline white solid (940 mg, 82.5% yield). ¹H-NMR (CDCl₃, 400 MHz, ppm): 7.36 (1H, dd, J = 8.4, 7.2 Hz), 7.16 (1H, dd, J = 7.2, 1.6 Hz), 7.14 (1H, dd, J = 10 Hz, 1.6 Hz), 0.26 (9H, s), 0.25 (9H, s). ¹³C-NMR (CDCl₃, 100 MHz, ppm): 163.8, 161.3, 133.7, 127.69, 127.66, 125.1, 125.0, 119.0, 118.7, 112.4, 112.3, 103.4, 102.24, 102.20, 0.0 (6 C). ¹⁹F-NMR (CDCl₃, 377 MHz, ppm): -110.3.

Intermediate (**9**) (500 mg, 1.74 mmol) was dissolved in CH₂Cl₂ (10 ml) in a 50-ml round-bottom flask and the obtained solution was cooled with an ice bath. In a beaker, KOH (2 g, 35.7 mmol) was dissolved in methanol (10 ml) and slowly added to the reaction mixture. Then, the ice bath was removed, and the mixture was left to react at room temperature. After 1 hour, TLC analysis (hexane/ethyl acetate, 8/2) showed complete consumption of (**9**). The product was extracted with CH₂Cl₂. The organic fractions were collected, dried with Na₂SO₄ and the solvent was removed under reduced pressure at 0°C. 1,4-diethynyl-2-fluorobenzene (**2**) was obtained as a white solid which was kept at -18 °C until needed (220 mg, 88% yield). IR (ATR, cm⁻¹): 3265 (vs), 2115 (w, sharp), 1908 (w), 1750 (w), 1615 (m), 1546 (s), 1489 (s), 1418 (s), 1405 (s), 1279 (m), 1246 (s), 1143 (m), 1104 (s), 949 (s), 871 (vs), 826 (vs), 707 (m). ¹H-NMR (400 MHz, CDCl₃): δ 7.42 (t, J = 8 Hz, 1

H), 7.22 (dd, $J = 8, 1.2$ Hz, 1 H), 7.20 (dd, $J = 10, 1.2$ Hz, 1 H), 3.38 (s, 1 H), 3.20 (s, 1 H). $^{13}\text{C-NMR}$ (CDCl_3 , ppm): 164.1 - 161.6 (d, C-F, $^1J_{\text{C-F}} = 250$ Hz) 134.00 (s, CH), 128(s, CH), 124.6 - 124.5 (d, C, $^3J_{\text{C-F}} = 10$ Hz), 119.3 - 119.1 (d, CH, $^2J_{\text{C-F}} = 20$ Hz), 111.8 - 111.6 (d, C, $^2J_{\text{C-F}} = 20$ Hz), 84.28 (C \equiv C), 82.00 (C \equiv C), 80.2 (C \equiv C), 76.7 (C \equiv C). $^{19}\text{F NMR}$ (377 MHz, CDCl_3 , ppm): -110.31.

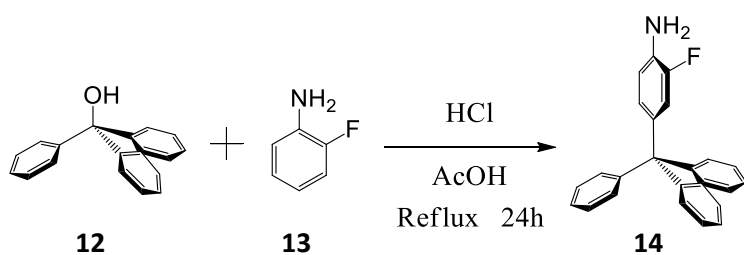
Synthesis of 1,4-diethynyl-2,3-difluorobenzene (**3**)



Intermediate (**11**) was obtained following a similar procedure to the one described for (**9**). In a typical synthesis, 1,4-dibromo-2,3-difluorobenzene (**10**) (1 g, 3.78 mmol) was dissolved in N_2 purged TEA (20 ml) and dry THF (10 ml). TMSA (**8**) (1.53 ml, 10.3 mmol), $\text{PdCl}_2(\text{PPh}_3)_2$ (70 mg, 0.1 mmol) and CuI (20 mg, 0.1 mmol) were used. After recrystallization, pure (**11**) was obtained as yellowish crystals (970 mg, 84 %). $^1\text{H-NMR}$ (CDCl_3 , 400 MHz, ppm): 6.87 (m, 1H), 0.03 (s, 18H). $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz, ppm): 152.39-149.85 (dd, $^1J_{\text{C-F}} = 240$ Hz, $^2J_{\text{C-F}} = 14.6$ Hz, 2C), 127.71 (t, $^3J_{\text{C-F}} = 2.4$ Hz, 2C), 114.05 (dd, $^2J_{\text{C-F}} = 9.2$ Hz, $^3J_{\text{C-F}} = 5.4$ Hz, 2C), 103.52 (s, 2C), 96.23 (d, $^3J_{\text{C-F}} = 2.1$ Hz, 2C), -0.32 (s, 6C). $^{19}\text{F NMR}$ (377 MHz, CDCl_3 , ppm): -134 (s, 2F).

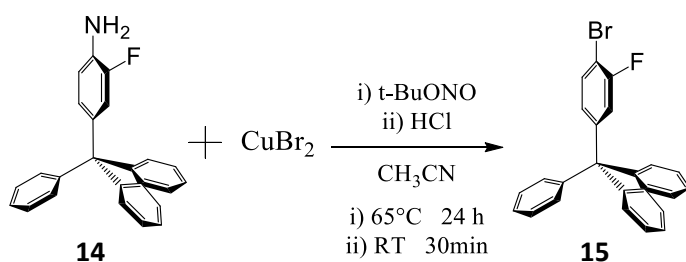
Compound (**3**) was obtained from (**11**) following a similar procedure to the one described for (**2**). In a typical synthesis, (**11**) (500 mg, 1.63 mmol), KOH (2g, 35.7 mmol), CH_2Cl_2 (10 ml), MeOH (10 ml) were used. Pure (**3**) was obtained as a pale yellow solid (235 mg, 89% yield) that was kept at -18°C until needed. $^1\text{H-NMR}$ (100 MHz, CDCl_3 , ppm): 7.18 (m, 2H), 3.44 (s, 2H). $^{13}\text{C-NMR}$ (400 MHz, CDCl_3 , ppm): 151.75-149.20 (dd, $^1J_{\text{C-F}} = 255$ Hz, $^2J_{\text{C-F}} = 14.9$ Hz, 2C), 127.01 (t, $^3J_{\text{C-F}} = 2.4$ Hz, 2C), 112.46 (dd, $^2J_{\text{C-F}} = 9$ Hz, $^3J_{\text{C-F}} = 5.1$ Hz, 2C), 84.27 (s, 2C), 74.42 (s, 2C). $^{19}\text{F NMR}$ (377 MHz, CDCl_3 , ppm): -134.05 (s, 2F)

Synthesis of 4,4',4''-((4-bromo-3-fluorofenyl)methantryl)tris(bromobenzene) (**4**)

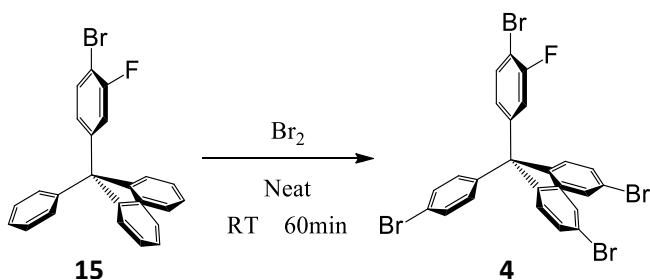


A 50 ml round-bottom flask was loaded with triphenylmethanol (2 g, 8.15 mmol) (**12**) and acetic acid (AcOH, 10 ml). Next, 2-fluoroaniline (**13**) (800 μl , 8.29 mmol) and hydrochloric acid (37% wt/wt, 800 μl , 26.3 mmol)

were added. The mixture was heated to reflux for 24 h. Full dissolution of solids only occurred after heating up. After 24 h, the heating was turned off and the mixture was allowed to slowly cool to room temperature. After a few hours, a white solid began to form. The resulting slurry was filtered on a Büchner funnel and washed with water. This intermediate is a mixture of the desired product and its chloride salt. To obtain pure 2-fluoro-4-tritylaniline, the crude product was suspended in ethanol (20 ml), and a solution of sodium hydroxide dissolved in a small amount of deionized water (approx. 2 g in 3 ml) was added. The mixture was heated, under stirring, to reflux for 12h. The mixture was then filtered on Büchner funnel and washed with water. The obtained solid was recrystallized from chloroform/hexane to give pure 2-fluoro-4-tritylaniline (**14**) as white crystals (885 mg, 33% yield). ¹H-NMR (DMSO-d₆, 400 MHz, ppm): 7.27 (6H, t, J = 7.6; 7.2 Hz), 7.16 (3H, t, J = 6.8; 6.8 Hz), 7.10 (6H, d, J = 7.6 Hz), 6.65 (1H, t, J = 8.8; 8.8 Hz), 6.60 (1H, s), 6.57 (1H, s); ¹³C-NMR (CDCl₃, 100 MHz, ppm): 152.68-150.798 (C-F, d, ¹J_{C-F} = 263 Hz), 147.61 (3C, s), 138.96-138.92 (C, d, ³J_{C-F} = 5 Hz), 132.85-132.74 (C, d, ²J_{C-F} = 12 Hz), 131.92 (6C, s), 128.35 (6C, s), 128.11-128.09 (C, d, ⁴J_{C-F} = 2 Hz), 126.82 (3C, s), 119.06-118.90 (C, d, ²J_{C-F} = 16 Hz), 116.72-116.70 (C, d, ³J_{C-F} = 3 Hz), 65.08 (C, s); ¹⁹F-NMR (CDCl₃, 377 MHz, ppm): -135.00 (dd, J = 8.9; 12.8 Hz). Melting point (DSC, ramp 10°C/min): 242 °C.

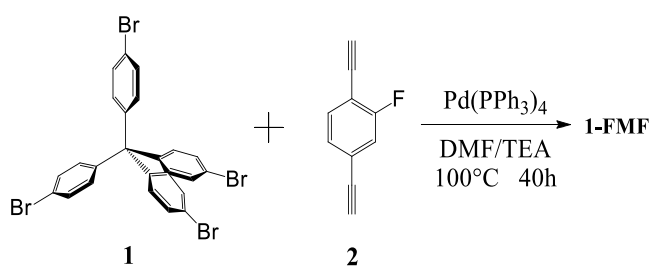


In a 100-ml round-bottom flask, intermediate **14** (670 mg, 1.97 mmol) was suspended in acetonitrile (30 ml). Next CuBr₂ (609 mg, 2.73 mmol) was added and the resulting green slurry was cooled with an ice bath. Then, tert-butyl nitrite (t-BuONO) (0.5 ml, 4.3 mmol) was added dropwise. The mixture was then heated to 65°C and kept at this temperature under stirring overnight. Next, 5 ml of HCl 2N were added and the color changed from deep green to bright yellow. The organic phase was extracted with dichloromethane and washed with water (100 ml) and aqueous ammonia solution (33% wt, 2 x 80 ml). All the organic layers were combined, dried over Na₂SO₄ and the solvent was removed by rotary evaporation yielding a yellow solid. This solid was recrystallized from chloroform/ethanol to give pure **15** as a white crystalline solid (532 mg, 67% yield). ¹H-NMR (CDCl₃, 400 MHz, ppm): 7.40 (1H, dd, J = 8.0; 1.0 Hz), 7.28-7.16 (15H, m), 7.04 (1H, dd, J = 11; 2.5 Hz), 6.90 (1H, dd, J = 8.5; 2.5 Hz). ¹³C-NMR (CDCl₃, ppm): 159.60-157.16 (C-F, d, ¹J_{C-F} = 244 Hz), 149.03-148.97 (C, d, ³J_{C-F} = 6 Hz), 145.80 (3C, s), 132.18 (C, s), 130.90 (3C, s), 128.31-128.28 (C, d, ³J_{C-F} = 7 Hz), 127.73 (3C, s), 126.31 (3C, s), 119.32-119.08 (C, d, ²J_{C-F} = 24 Hz), 106.50-106.29 (C, d, ²J_{C-F} = 21 Hz), 64.66 (C, s). ¹⁹F-NMR (CDCl₃, ppm): -107.6 (s). Melting point (DSC, ramp 10°C/min): 243 °C.



In a 20-ml round-bottom flask, Br₂ (2.1 ml, 40.1 mmol) was added; 340 mg of intermediate (**15**) (340 mg, 0.84 mmol) were added in small portions under vigorous stirring. The mixture was kept under stirring at room temperature until no more white smoke (HBr) evolved from the reaction mixture (approximately 1 hour). Then, the mixture was cooled with an ice bath and ethanol (15 ml) was added. The mixture was left under stirring at room temperature for 1 hour. Next, the mixture was poured in a saturated solution of sodium bisulfite in water (50 ml) and the precipitated solid was collected by filtration. This solid was purified by recrystallization from THF/hexane giving **4** as a white crystalline solid (270 mg, 50% yield). ¹H-NMR (CDCl₃, 400 MHz, ppm): 7.48-7.15 (7H, m), 7.04-7.01 (6H, m), 6.96 (1H, dd, J = 10.4; 2.4 Hz), 6.83 (1H, dd, J = 8.4; 2.0 Hz); ¹³C-NMR (CDCl₃, 100 MHz, ppm): 159.87-157.41 (C-F, d, ¹J_{C-F} = 246 Hz), 147.36-147.31 (C, d, ³J_{C-F} = 6 Hz), 143.98 (3C, s), 132.81 (C, s), 132.26 (6C, s), 131.24 (6C, s), 127.76-127.73 (C, d, ³J_{C-F} = 3 Hz), 121.08 (3C, s), 118.92-118.68 (C, d, ²J_{C-F} = 24 Hz), 107.44-107.23 (C, d, ²J_{C-F} = 21 Hz), 63.69-63.68 (C, d, ⁴J_{C-F} = 1.8 Hz); ¹⁹F-NMR (CDCl₃, 377 MHz, ppm): -106.18 (dd, J = 7.3; 10.0 Hz). Melting point (DSC, ramp 10 °C/min): 284 °C

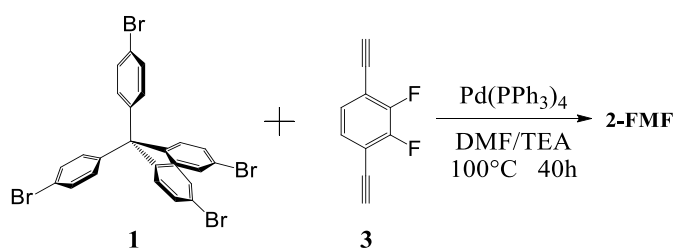
Synthesis of 1-FMF



Anhydrous dimethylformamide (DMF, 100 ml) and anhydrous triethylamine (TEA, 40 ml) were poured into an oven-dried 250 ml two-neck round-bottom flask equipped with a nitrogen inlet and put under a flux of nitrogen. Two freeze-pump-thaw cycles were performed. Then (**2**) (181 mg, 1.26 mmol), (**1**) (400 mg, 0.63 mmol) and Pd(PPh₃)₄ (38.8 mg, 0.034 mmol) were added. Another freeze-pump-thaw cycle was performed before heating the mixture at 100°C under stirring. After a few hours, a voluminous solid formed from the reaction mixture. After 40 hours at 100°C, the mixture was slowly cooled to room temperature and the precipitate was collected by filtration and washed with methanol (2 X 30 ml), tetrahydrofuran (2 X 30 ml), water (2 X 50 ml) and chloroform (2 X 30 ml). A voluminous yellow powder was recovered from the filter.

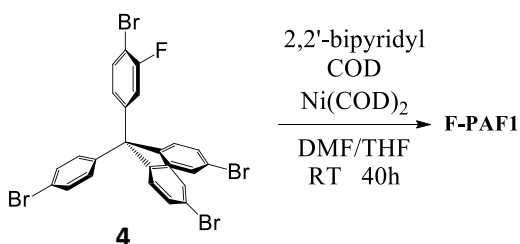
This product was further purified by Soxhlet extraction with methanol for 24 h. Then the solid was dried under vacuum overnight at room temperature. A massive reduction of the powder's volume was observed after complete drying. Compound **1-FMF** was finally recovered as a yellow-brown powder (340 mg, 89 %). IR (KBr pellet, cm⁻¹): 3060(w, br), 2212(w), 1916(w), 1686(m), 1611(s), 1545(s), 1508(vs), 1414(s), 1270(w), 1209(s), 1191(s), 1113(m), 1015(m), 957(m), 871(m), 820(vs), 745(m), 717(m), 693(m), 621(w). Elemental analysis: 1-FMF C 88.81% (calc 89.98%), H 4.15% (calc 3.69%).

Synthesis of 2-FMF



2-FMF was synthesized following a similar procedure to the one described for the preparation of **1-FMF**. In this case, the following reagents quantities were used: (**3**) (205 mg, 1.26 mmol), (**1**) (400 mg, 0.63 mmol), $\text{Pd}(\text{PPh}_3)_4$ (38.8 mg, 0.034 mmol). After purification and drying, **2-FMF** was recovered as a red-brown powder (361 mg, 90 %). IR (KBr pellet, cm⁻¹): 3029(w, br), 2214(w), 1917(w), 1715(m), 1621(m), 1617(m), 1562(w), 1506(s), 1486(s), 1459(vs), 1401(w), 1361(w), 1291(w), 1217(m), 1077(w), 1008(s), 955(w), 916(w), 817(vs), 734(w). Elemental analysis: 2-FMF C 82.90% (84.90%), H 3.07% (calc 3.17%).

Synthesis of F-PAF1



All the glassware used in this reaction was oven-dried overnight. Inside a glovebox, anhydrous DMF (100 ml) and anhydrous THF (20 ml) were transferred in a 250 ml two-neck round-bottom flask equipped with a nitrogen inlet. Then, 2,2'-bipyridyl (600 mg, 3.84 mmol) and cyclooctadiene (COD) (0.6 ml, 4.89 mmol) were added. A solution of (**8**) (450 mg, 0.703 mmol) in anhydrous THF (30 ml) was transferred in a dripping funnel and mounted over the round-bottom flask. Lastly, $\text{Ni}(\text{COD})_2$ (1 g, 3.64 mmol) was added to the round-bottom flask. A deep violet solution formed. The apparatus was sealed under N_2 , quickly brought outside the glovebox

and immediately reconnected to fluxing nitrogen. The mixture was cooled to 0 °C with an ice bath and the monomer solution was slowly added over 20 minutes under vigorous stirring, while fluxing N₂ from the inlet. At the end of the addition, the dripping funnel was removed and the reaction mixture was sealed under nitrogen. The flask was left in the cooling bath for 60 minutes and then allowed to warm to room temperature. The reaction was left in these conditions for 48 hours. Then, 15 ml of HCl (10% wt) were added and the mixture was stirred at room temperature until the colour changed from violet to light blue. The mixture was filtered and the solid washed with methanol (2 X 30 ml), THF (2 X 30 ml), water (2 X 50 ml), and chloroform (2 X 30 ml). The solid was recovered and dried in vacuum overnight at room temperature. A massive reduction in the solid volume was observed after complete drying. **F-PAF1** was recovered as a yellowish powder (192 mg, yield 85%). IR (ATR, cm⁻¹): 3033 (w, br), 1616 (w), 1489 (s), 1395 (m), 1259 (w), 1229 (w), 1190 (w), 803 (vs), 740 (s), 702 (s). Elemental analysis: F-PAF1 C 89.06% (calc 89.8%), H 4.65% (calc 4.49%).

Density of FMs

The density of the framework walls, as calculated by He Pycnometer analysis, corresponds to 1.51, 1.35 and 1.44 g cm⁻³ for F-PAF1, 1-FMF and 2-FMF, respectively. The density of the samples was calculated considering the density of the framework walls and the pore volume from the N₂ adsorption isotherms: 0.38 g cm⁻³, 0.80 g cm⁻³ and 0.93 g cm⁻³ for F-PAF1, 1-FMF and 2-FMF, respectively. The volumetric density of F groups is 0.021, 0.054 and 0.131 g cm⁻³ for F-PAF1, 1-FMF and 2-FMF, respectively.

3. IR spectroscopy

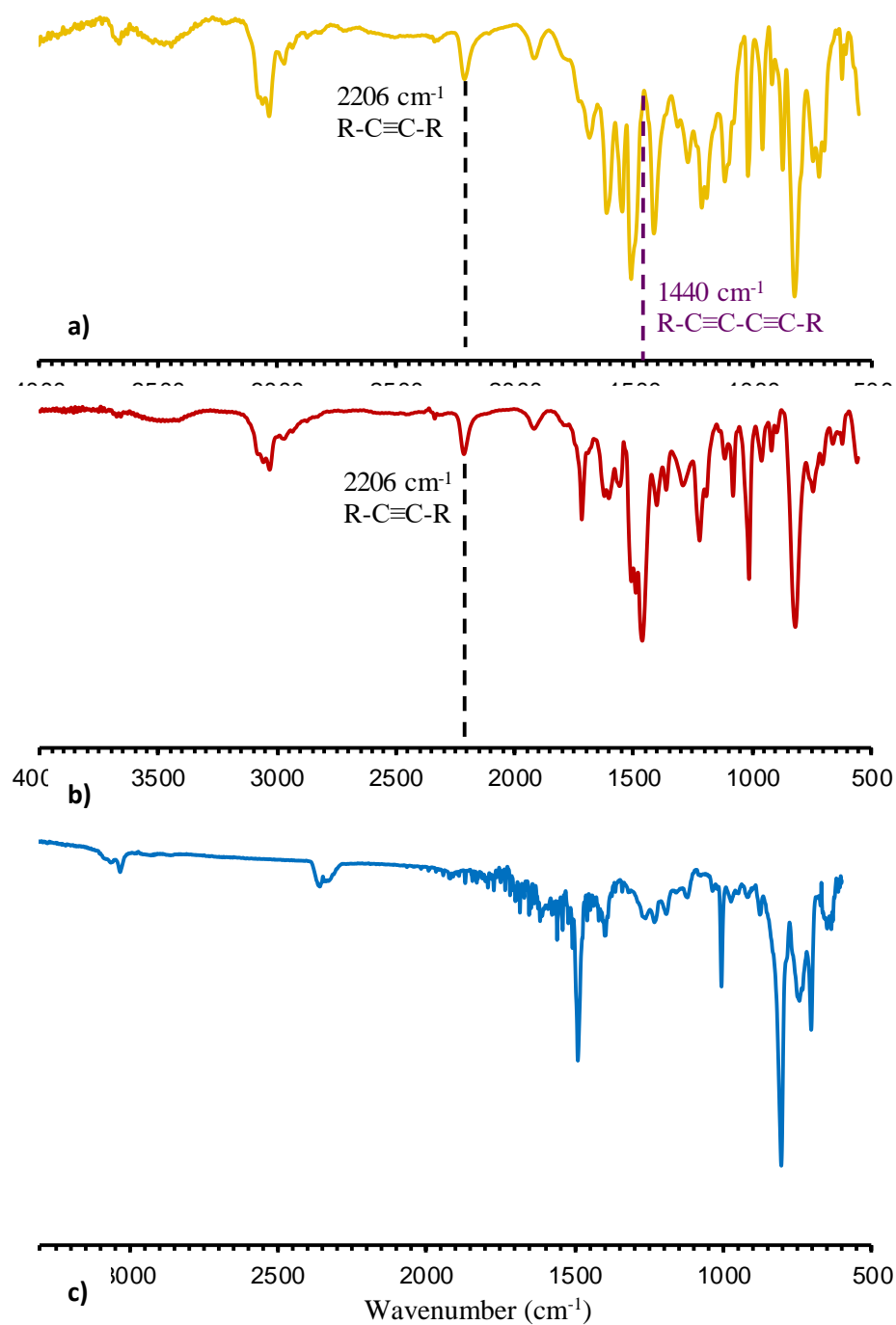


Figure S1. IR spectra of **a) 1-FMF** (yellow trace), **b) 2-FMF** (red trace) and **c) F-PAF1** (blue trace) collected in the $600\text{-}4000 \text{ cm}^{-1}$ range.

4. ThermoGravimetric Analysis

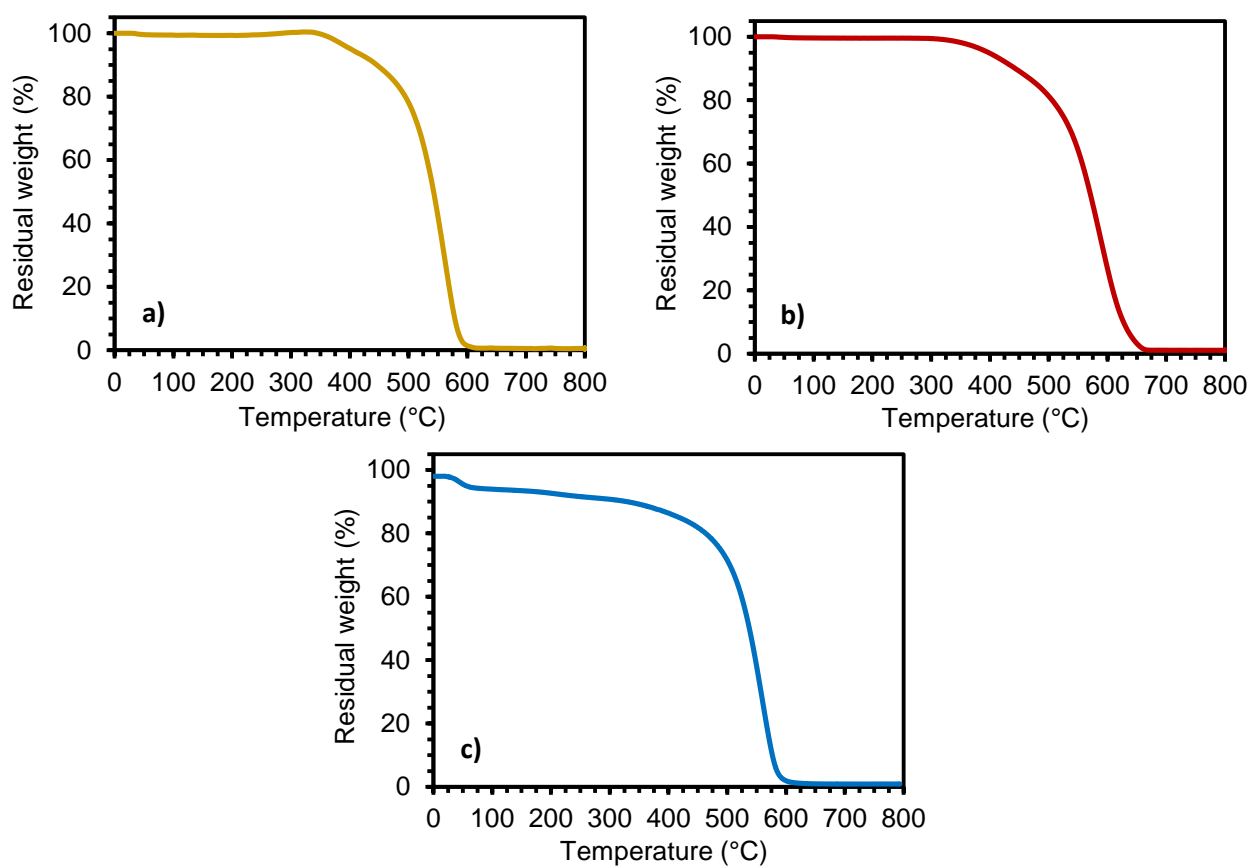


Figure S2. TGA traces of **a) 1-FMF** (yellow trace); **b) 2-FMF** (red trace); **c) F-PAF1** (blue trace) collected from 0 to 800 °C with a heating rate of 20 °C/min. High thermal stability of all fluorinated materials can be appreciated.

5. Differential Scanning Calorimetry

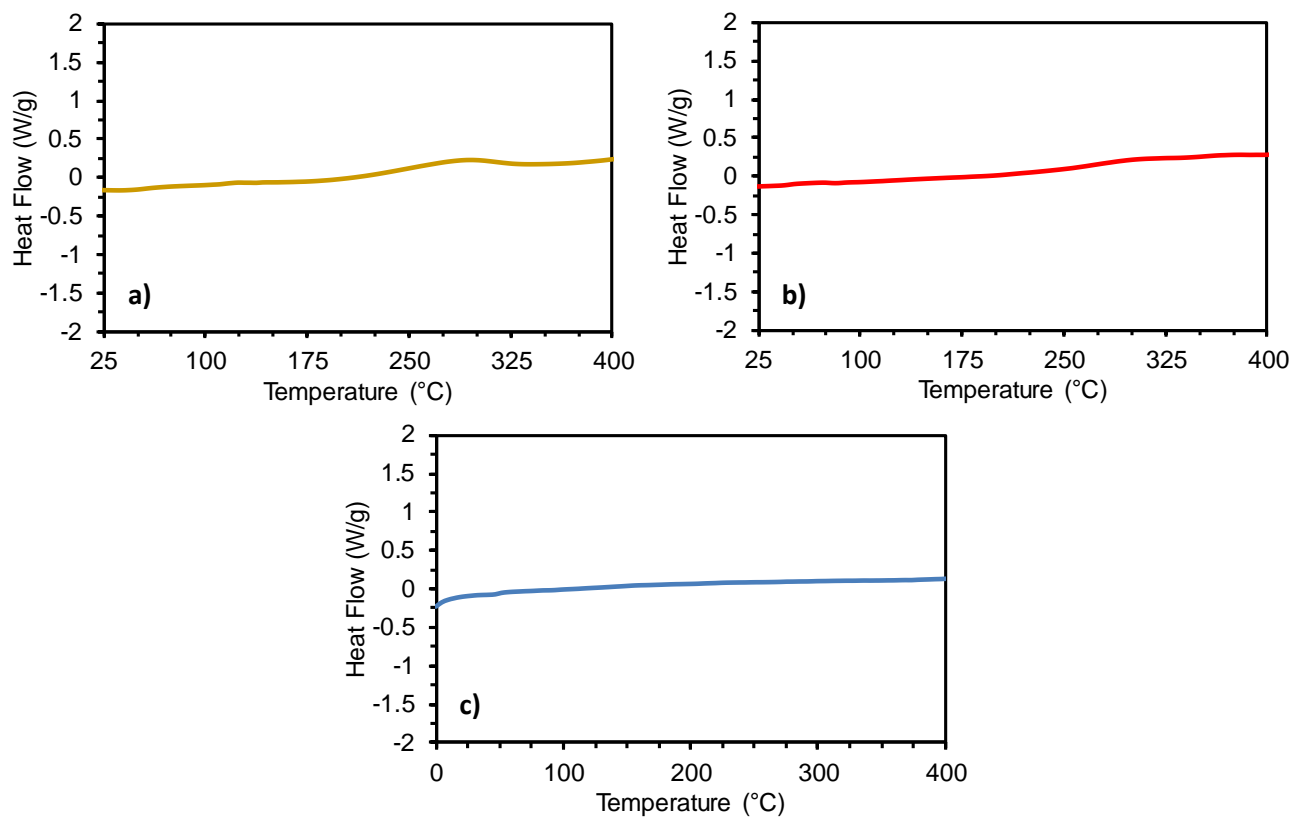


Figure S3. DSC traces of **a) 1-FMF** (yellow trace); **b) 2-FMF** (red trace); **c) F-PAF1** (blue trace) collected from 25 to 400 °C with a heating rate of 10 °C/min under an 80 ml/min flux of N₂. No relevant thermal phenomena can be observed.

6. Scanning Electron Microscopy

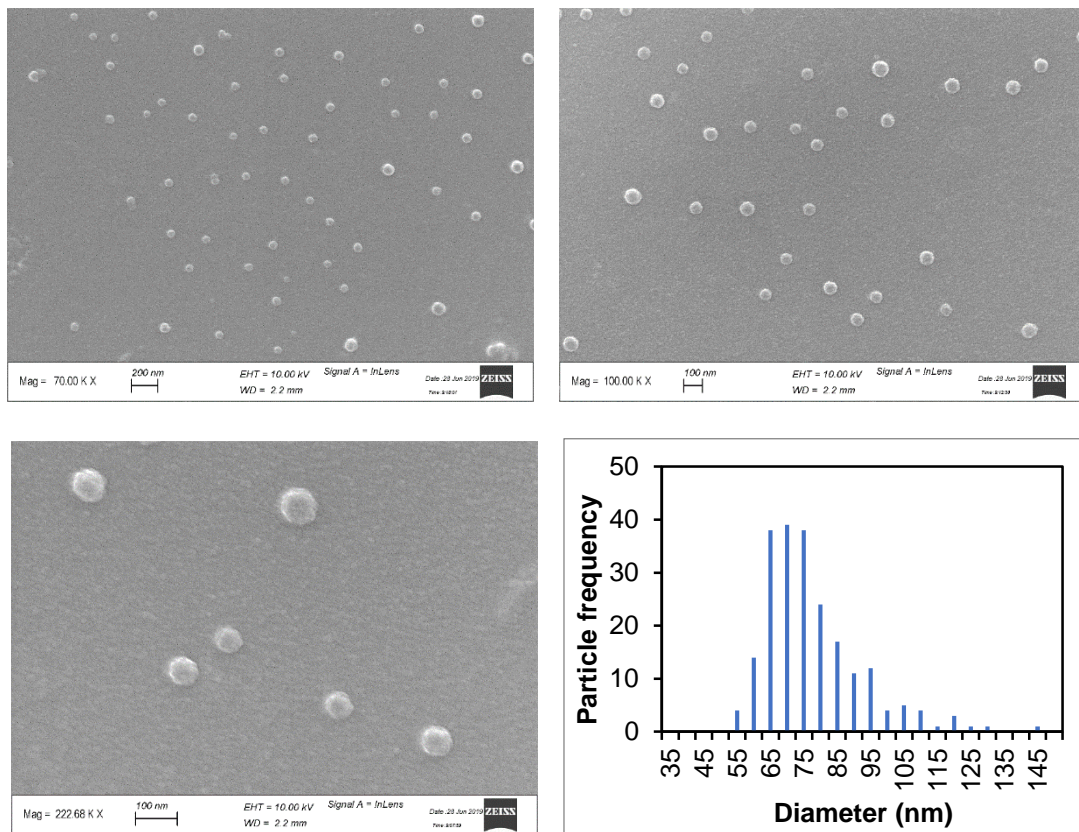


Figure S4. Scanning electron microscope images of **F-PAF1** sample drop-casted on a silicon substrate.

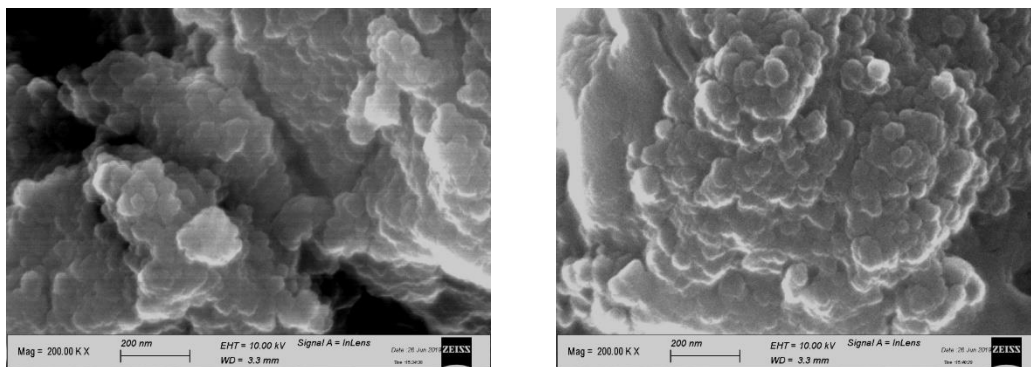


Figure S5. Scanning electron microscope images of **1-FMF** drop-casted on a silicon substrate.

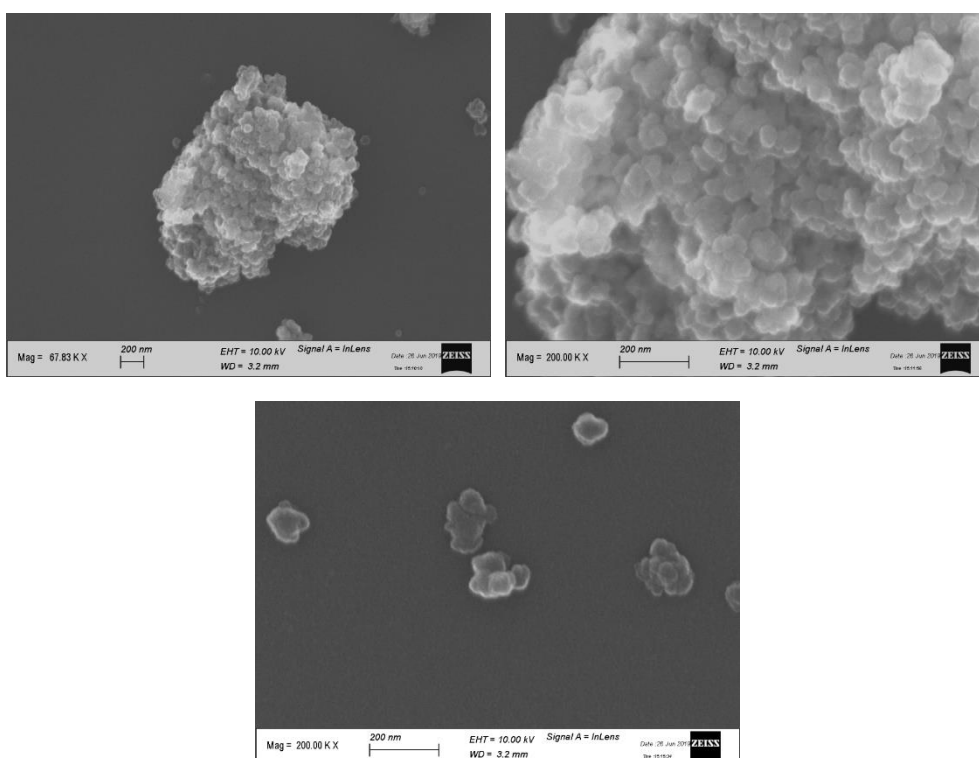
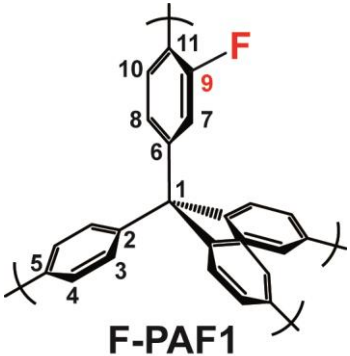
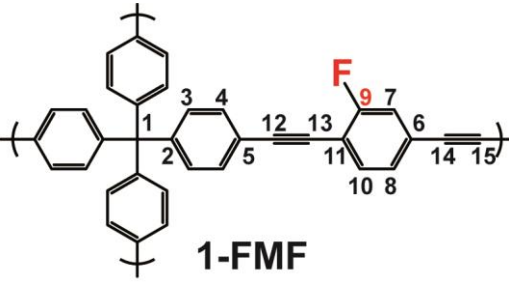
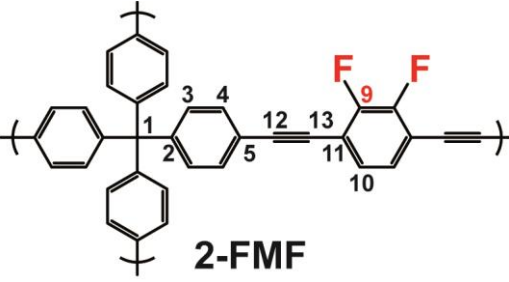


Figure S6. Scanning electron microscope images of **2-FMF** drop-casted on a silicon substrate.

7. Solid State NMR

Table S1. ^{13}C and ^1H chemical shifts of FMFs.

FMFs	Assignment	δ (ppm)	
 <p>F-PAF1</p>	C ₉	161.4 – 158.3 ($^1J_{\text{C-F}} = 234$ Hz)	
	C ₆	148.8	
	C ₂	145.8	
	C ₅	140.2	
	C ₈	134.5	
	C ₃	131.0	
	C ₄	127.3	
	C ₁₀	125.7	
	C ₇	118.2	
	C ₁₁	112.5	
	C ₁	65.0	
	Arom H	7.0 (FWHM = 1.3 ppm)	
	 <p>1-FMF</p>	C ₉	161.2 – 158.7 ($^1J_{\text{C-F}} = 189$ Hz)
C ₂ C ₅		146.9 144.8	
C ₆		138.0	
C ₃ C ₄		131.1 127.8	
C ₈		125.4	
C ₁₀		121.7	
C ₇		117.4	
C ₁₁		112.5	
C ₁₂ C ₁₃ C ₁₄ C ₁₅		95.3 91.8 89.2 83.5	
C ₁		65.3	
Arom H		6.9 (FWHM = 1.7 ppm)	
 <p>2-FMF</p>		C ₉	152.5 – 150.0 ($^1J_{\text{C-F}} = 189$ Hz)
		C ₂ C ₅	147.0 144.7
	C ₃ C ₄	131.0 127.0	
	C ₁₀	121.2	
	C ₁₁	113.9	
	C ₁₂ C ₁₃	96.5 83.1	
	C ₁	64.6	
	Arom H	6.9 (FWHM = 1.6 ppm)	

8. N₂, CO₂ and CH₄ adsorption isotherms

Table S2. Textural parameters obtained from N₂ adsorption isotherms and carbon dioxide adsorption isotherms at distinct temperatures for **1-FMF**, **2-FMF** and **F-PAF1**.

	S _{BET} (m ² /g)	S _{Langmuir} (m ² /g)	V _{total} ^a (V _{micro}) ^b (cm ³ /g)	Q _{ads} (CO ₂) ^c (mmol/g)	Q _{ads} (CH ₄) ^d (mmol/g)
1-FMF	1132	1285	0.51 (0.40)	2.4	3.3
2-FMF	853	970	0.38 (0.30)	1.8	2.3
F-PAF1	2054	2338	1.96 (0.63)	2.7	5.0

^a calculated using Density Functional Theory and the N₂@carbon slit pore model; ^b calculated considering the cumulative pore volume up to pore 20 Å wide; ^{c, d} adsorbed quantity at 273 K and 1 bar.

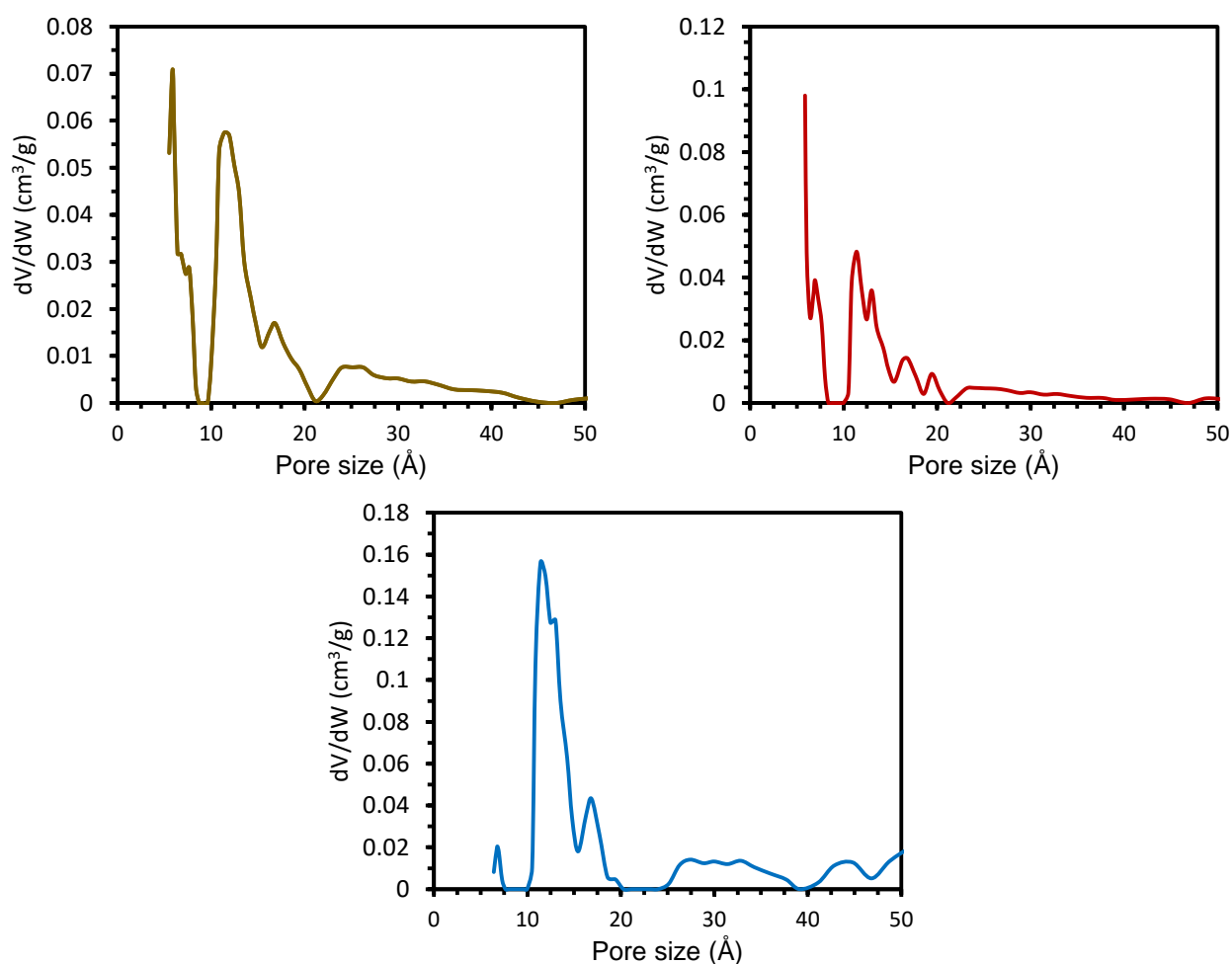


Figure S7. Pore size distribution graphs of **1-FMF** (yellow trace), **2-FMF** (red trace) and **F-PAF1** (blue trace) calculated by NLDFT adopting the N₂@77K carbon slit pore model.

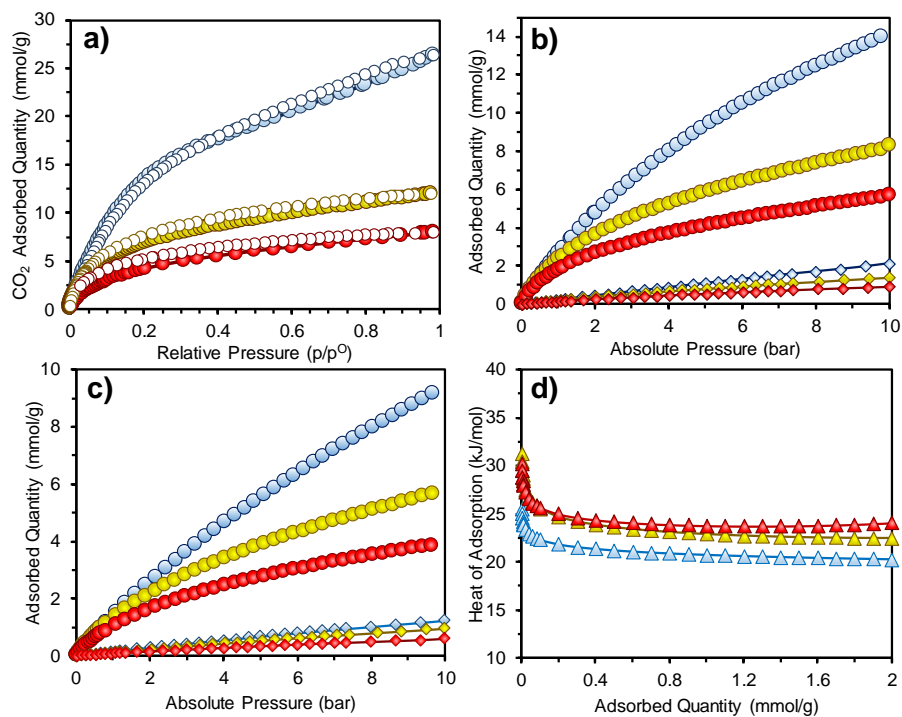


Figure S8. CO₂ isotherms at 195 K (a), 273K (b) and 298 K (c) for F-PAF1, 1-FMF and 2-FMF (blue, yellow and red circles, respectively); d) CO₂ isosteric heat of adsorption.

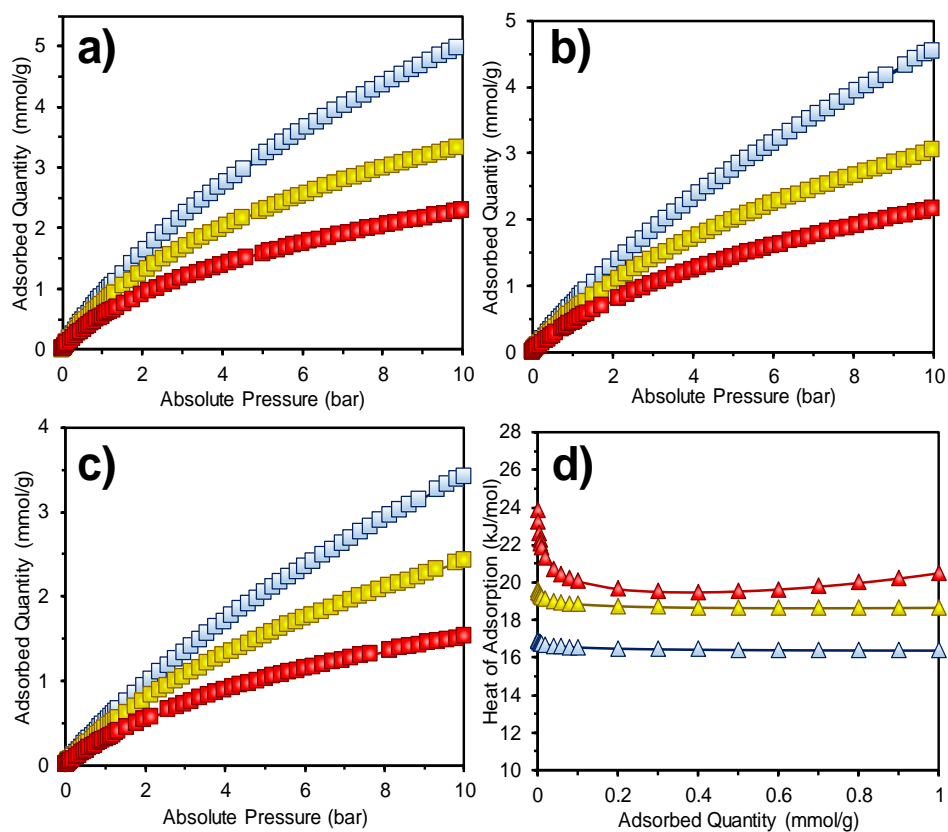


Figure S9. CH₄ (squares) adsorption isotherms of F-PAF1 (blue traces), 1-FMF (yellow traces) and 2-FMF (red traces) collected up to 10 bar at a) 273 K, b) 283 K and c) 298 K. d) $Q_{st}(\text{CH}_4)$ versus adsorbed quantity.

9. Isothermic heats of adsorption and IAST calculations

$Q_{st}(\text{CO}_2)$ and $Q_{st}(\text{CH}_4)$ were derived from CO_2 and CH_4 adsorption isotherms, respectively, collected at 273, 283 and 298 K up to 10 bar of pressure using the van't Hoff equation:

$$Q_{st} = RT^2 \left(\frac{\partial \ln p}{\partial T} \right) \quad [\text{E1}]$$

First, the three experimental isotherms were fitted adopting a Langmuir-Freundlich model isotherm, which has the general form

$$q = \frac{q_{max} b p^t}{1 + b p^t} \quad [\text{E2}]$$

where q is the adsorbed quantity at pressure p , q_{max} is the saturation loading and b and t are the Freundlich parameters. Parameter b can be written

$$b = b_0 e^{E/RT} \quad [\text{E3}]$$

where b_0 is a pre-exponential factor related to the gas saturation pressure p^0 and E can be considered as the mean adsorbent-adsorptive interaction energy calculated from $p = 0$ to p_{max} . In our fitting procedure, we used Langmuir-Freundlich model to fit simultaneously the three experimental curves. We allowed the saturation loading q_{max} and the Freundlich parameters t to vary independently for each experimental isotherm, while the pre-exponential factor b_0 and the energy E had to be the same for all the isotherms. We had then a total of eight fitting parameters: b_0 , E , Q_{273} , t_{273} , Q_{283} , t_{283} , Q_{298} and t_{298}

Calculations were run using Matlab software. The calculated fitting parameters are reported in **Table S3** for CO_2 and **Table S4** for CH_4 , while **Figures S5 and S6** show the fitted curve versus the experimental isotherms for CO_2 and CH_4 , respectively. From the Langmuir-Freundlich equation it is possible to obtain the analytical expression of p as a function of q

$$p = \left(\frac{q}{b(q_{max} - q)} \right)^{1/t} \quad [\text{E4}]$$

We calculated Q_{st} via the van't Hoff equation. In the case of CO_2 adsorption, we considered experimental values up to 2 mmol/g of adsorbed quantity, while for methane adsorption the experimental points up to 10 bar were included in the fitting calculations.

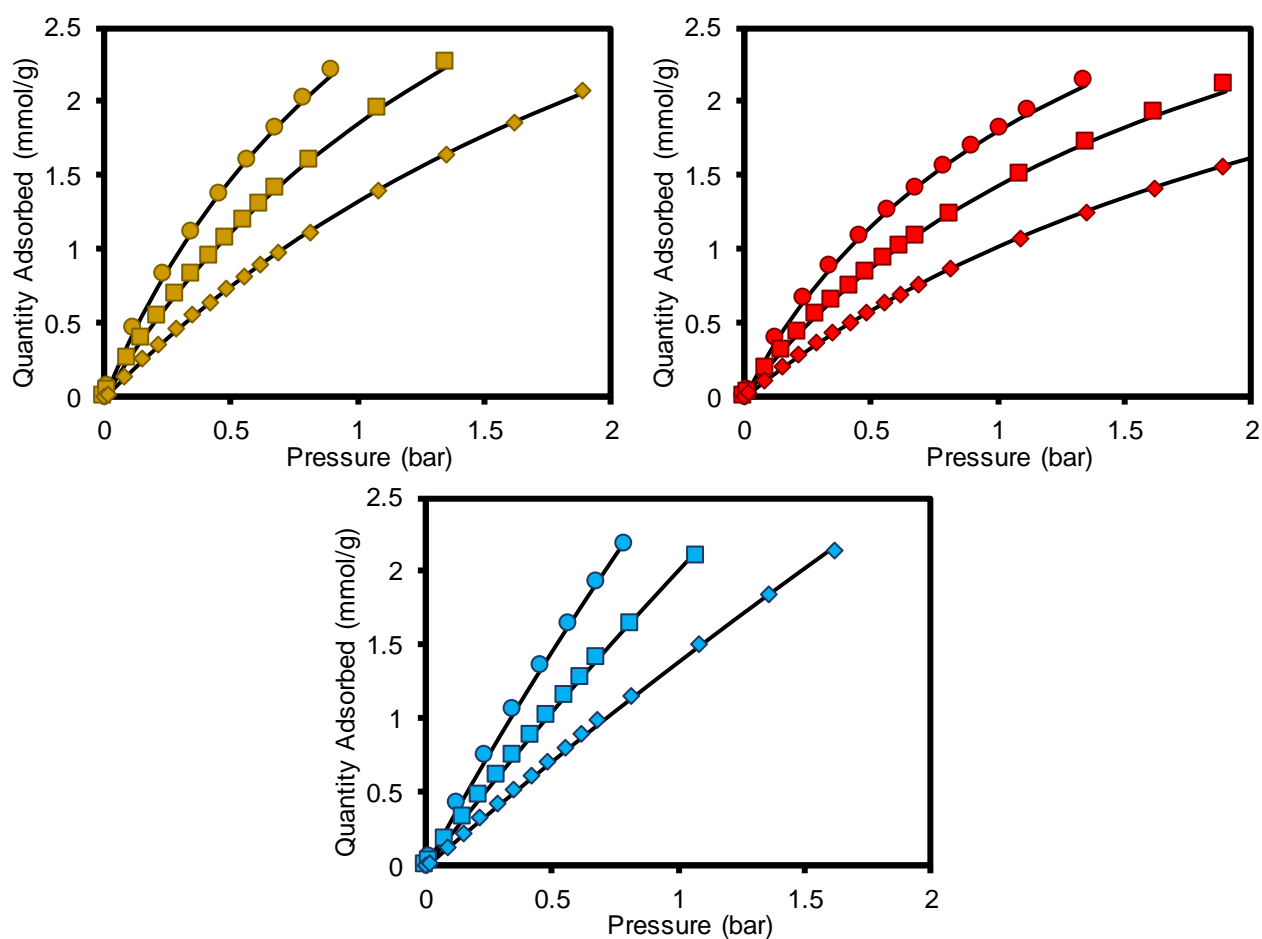


Figure S10. Results of the carbon dioxide isotherm fitting procedure for **1-FMF** (yellow traces), **2-FMF** (red traces) and **F-PAF1** (blue traces) using the parameters reported in **Table S3** and the Langmuir-Freundlich model. CO₂ isotherms at 273 K (dots), 283 K (squares), 298 K (diamonds) and fitting (solid black line).

Table S3. Fitting parameters obtained for carbon dioxide adsorption for **1-FMF**, **2-FMF** and **F-PAF1** using a Langmuir-Freundlich model and considering experimental points up to $Q(\text{ads}) = 2 \text{ mmol/g}$

	Q_{273} (mmol/g)	Q_{283} (mmol/g)	Q_{298} (mmol/g)	t_{273}	t_{283}	t_{298}	b_0 (bar ⁻¹)	E (kJ/mol)
1-FMF	5.9076	5.7085	5.442	0.9555	0.9766	1	$1.65 \cdot 10^{-4}$	18.7676
2-FMF	4.4966	4.3197	4.1298	0.9416	0.9604	0.9761	$1.31 \cdot 10^{-4}$	19.3811
F-PAF1	25.3882	24.4427	24.4427	0.9743	0.9937	1	$2.83 \cdot 10^{-5}$	18.9671

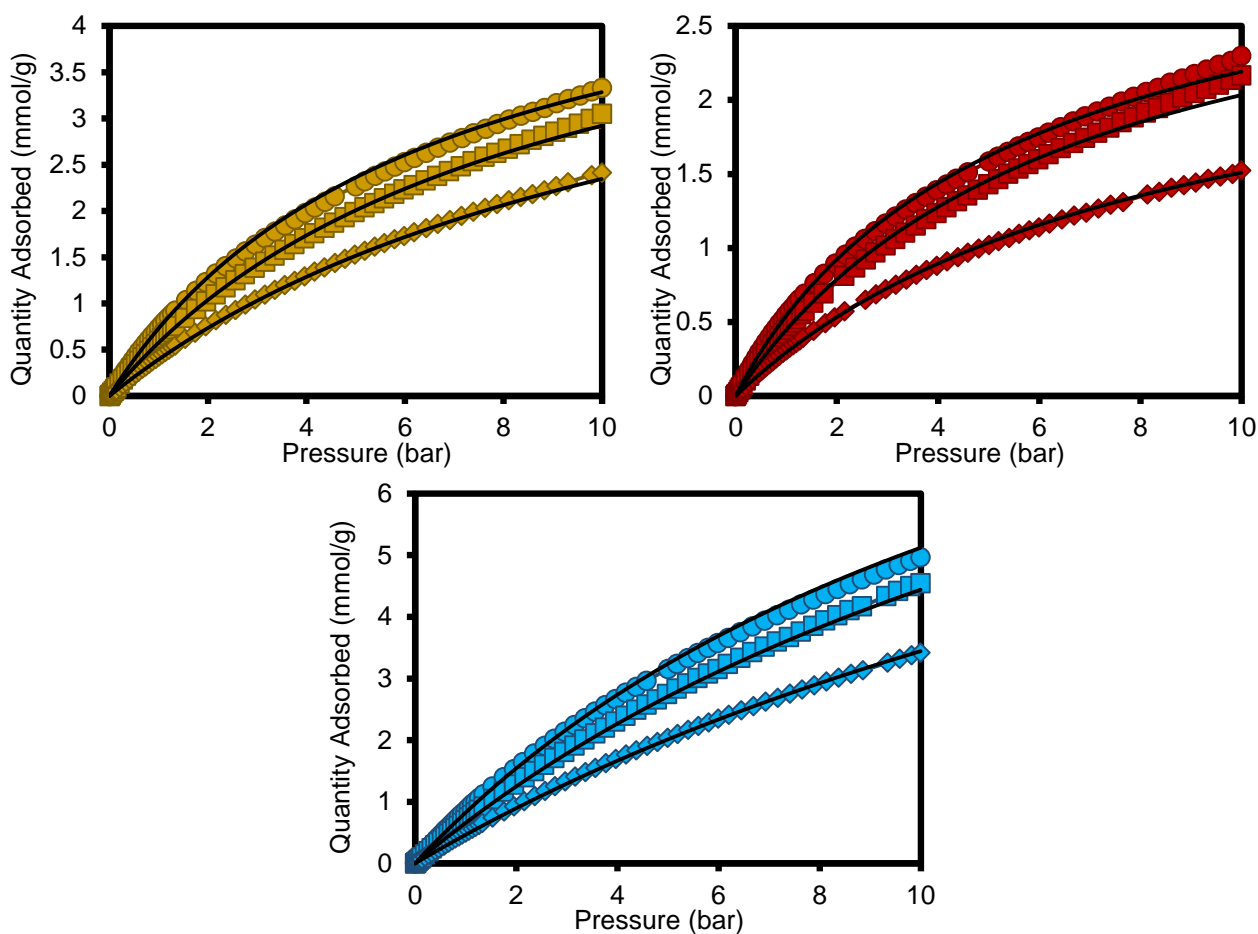


Figure S11. Results of the methane isotherm fitting procedure for **1-FMF** (yellow traces), **2-FMF** (red traces), and **F-PAF1** (blue traces) using the parameters reported in **Table S4** and the Langmuir-Freundlich model. CH₄ isotherms at 273 K (dots), 283 K (squares), 298 K (diamonds) and fitting (solid black line).

Table S4. Fitting parameters obtained for methane adsorption for **1-FMF**, **2-FMF** and **F-PAF1** and using a Langmuir-Freundlich model and considering experimental points up to $p = 10$ bar

	Q_{273}	Q_{283}	Q_{298}	t_{273}	t_{283}	t_{298}	b_0	E
	(mmol/g)	(mmol/g)	(mmol/g)				(bar ⁻¹)	(kJ/mol)
1-FMF	5.4189	5.4189	5.2003	0.9942	0.9921	1	$7.58 \cdot 10^{-5}$	17.3193
2-FMF	3.4618	3.3561	2.785	0.9674	1	1	$8.74 \cdot 10^{-4}$	12.2401
F-PAF1	25.3882	24.4427	24.4427	0.9743	0.9937	1	$2.83 \cdot 10^{-5}$	18.9671

For IAST calculations, N_2 isotherms were fitted up to 10 bar adopting the Langmuir-Freundlich model. We calculated spreading pressures (the integrals were solved using Wolfram Alpha) and applied the standard equations for IAST.

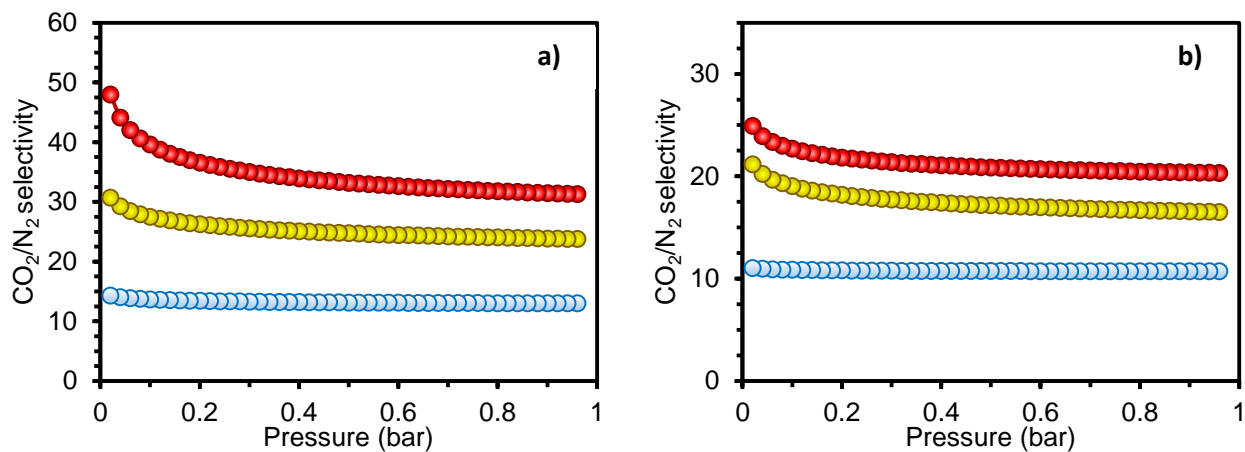


Figure S12. IAST selectivity for the adsorption of CO_2 over N_2 from a 15:85 mixture calculated at **a)** 273 K and **b)** 298 K for **1-FMF** (yellow trace), **2-FMF** (red trace), **F-PAF1** (blue trace).

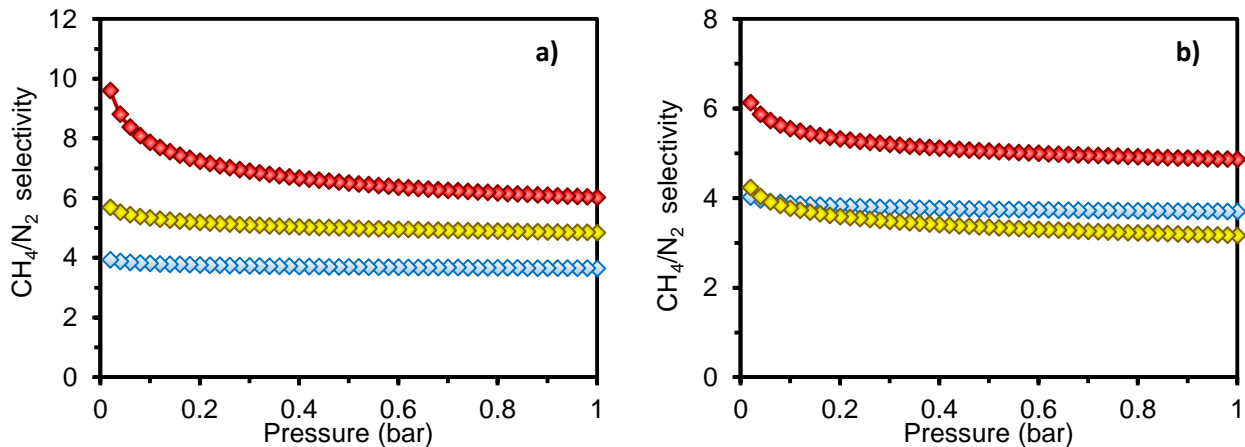


Figure S13. IAST selectivity for the adsorption of CH_4 over N_2 from a 50:50 mixture calculated at **a)** 273 K and **b)** 298 K for **1-FMF** (yellow trace), **2-FMF** (red trace), **F-PAF1** (blue trace).

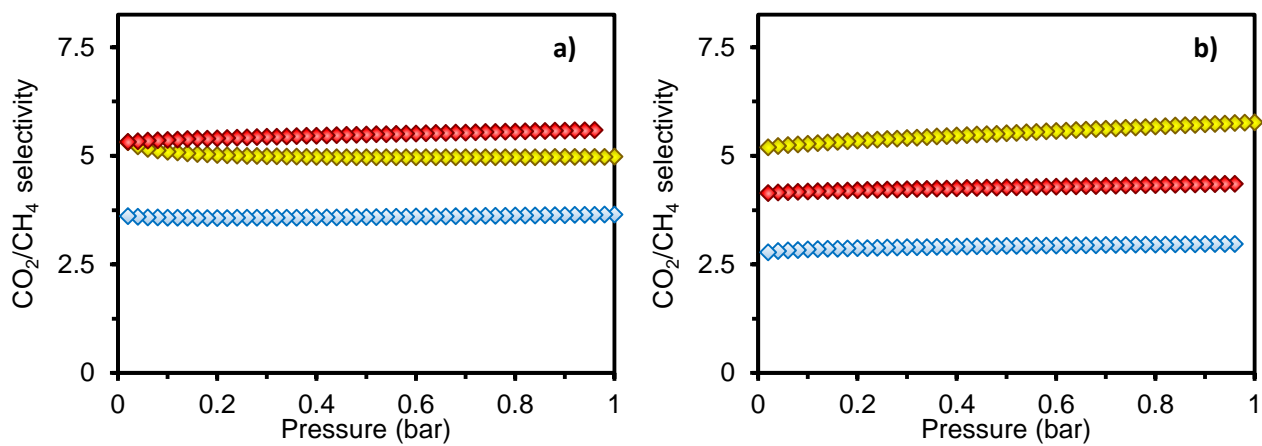


Figure S14. IAST selectivity for the adsorption of CO₂ over CH₄ from a 50:50 mixture calculated at **a)** 273 K and **b)** 298 K for **1-FMF** (yellow trace), **2-FMF** (red trace), **F-PAF1** (blue trace).

Table S5. CO₂ and CH₄ parameters of some MOFs, COFs and PAFs

Material	S _{Langmuir} (m ² /g)	S _{BET} (m ² /g)	V _{tot} (cm ³ /g)	Q _{st} (CO ₂) (kJ/mol)	Q _{st} (CH ₄) (kJ/mol)	Reference
MOF						
PCN-14	2176	1753	0.87	22.1	30	[1][2]
NOTT-140		2620	1.08	24.8	16.6	[3]
Co-MOF-74	2120	1404	0.82	51	19.6	[1][4]
Ni-MOF-74	1756	1115	0.86		20.2	[1]
Mn-MOF-74		1102	0.50		19.1	[1]
Mg-MOF-74		1332		38.4	18.5	[1][2]
HKUST-1	2216	1502	0.57	25.4	18.2	[1][2]
MIL-120	432	308	0.11		27	[1]
COF						
COF-1		1230	0.38		25.1	[5]
COF-102		4940	1.81		10.5	[5]
COF-102-Ant		2720	0.75		18.4	[5]
COF-102-Eth-trans		4640	1.20		13.1	[5]
CTF-1		746		27.5		[6]
PTCF-4		1090	0.75	27		[6]
fl-CTF-350		1235	0.67	32.7		[6]
ACOF-1		1776	0.94	27.6		[6]
PAF						
PAF1		4100	2.23	15.6		[7]
PAF1-CH ₃		3007	2.01			[7]
PAF1-CH ₂ N=CMe ₂		1302	0.73	18.2		[7]
PAF1-CH ₂ OH		1727	1.77	19.3		[7]
PAF1-CH ₂ NH ₂		1363	0.74	57.6		[7]

9. References

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