Reorientable fluorinated aryl rings in triangular channel Fe-MOFs: an investigation on CO₂-matrix interactions

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1. Experimental Methods

Synthesis

All solvents and reagents were purchased from Sigma-Aldrich and used without any purification. Triethylamine (TEA) was distilled under reduced pressure before use.

Infrared spectroscopy

Infrared spectra were collected on a Jasco FT/IR 4100 equipped with an ATR PRO450-S module. The samples were treated in vacuum before analysis to ensure the complete removal of adsorbed chemical species. Spectra were collected between 600 and 4000 cm⁻¹ with a resolution of 2.0 cm⁻¹. In the following, signal intensities are denoted as br = broad, vs = very strong, s = strong, m = medium and w = weak.

Powder X-ray diffraction experiment (PXRD)

Microcrystalline MOF powder were casted on a silicon wafer sample holder. Diffraction data were collected at room temperature on a Rigaku Smartlab SE diffractometer operating with CuK α_1 radiation ($\lambda = 1.54060$ Å). The generator was set at 40 kV and 30 mA. Diffraction data for the refinement of the crystal structure of **Fe-PF1**, **Fe-PF2** and **Fe-PF4** were measured in the 2° - 70° 20 range, with steps of 0.02° and a scan speed of 0.3°/min.

Thermogravimetric analysis (TGA)

TGA measurements was performed using a Mettler Toledo Star System 1 equipped with a gas controller GC10. The analysis was conducted from 30 to 800 °C at 10 °C/min in dry air.

Differential scanning calorimetry (DSC)

Measurements were performed on a Mettler-Toledo StarE instrument from 25 to 450 °C, at a heating rate of 10 °C/min and under 80 mL/min flow of N_2 .

Gas adsorption measurements

 N_2 adsorption isotherms at 77 K were collected on a Micromeritics ASAP 2020 and Hiden-IGA instruments. The samples were treated overnight at 150 °C under vacuum before adsorption experiments. Surface area were calculated from the N_2 adsorption isotherm at 77 K using the data in the pressure range p/p° from 0.015 to 0.1, according to the Brunauer-Emmett-Teller (BET) and Langmuir models. Total pore volume were calculated from the N_2 adsorption isotherms at 77 K by the NLDFT method with the carbon slit pore model up to p/p° 0.98. The microporosity was calculated at p/p° = 0.1.

 CO_2 and N_2 adsorption isotherms at 298, 283 and 273 K and up to 10 bar were collected on a Micromeritics ASAP 2050 instrument, the temperature was controlled using a Julabo F12-ED refrigerated/heating circulator.

SEM images

Scanning electron microscopy (SEM) images were collected using Zeiss Gemini 500 scanning electron microscopy operating at 5 kV. MOF powders were dispersed in 2-propanol and deposited on a silicon wafer. The silicon wafers were stuck on SEM stubs with a conductive tape and were sputtered with a 10 nm layer of chromium in order to improve the electrical conductivity.

2 Indexing and Rietveld refinement

Indexing and Rietveld refinement were performed using the TOPAS-Academic-64 V6 software package.^{S1} The initial input structure used for the PXRD refinement was generated using the CASTEP code (DFT) within the Biovia Materials Studio software package.^{S2} The symmetries for these MOFs were lowered to remove disordered moieties for the purpose of performing the DFT and molecular mechanics calculations needed to solve the ligand ring orientations; *Cc* for **Fe-PF1** and **Fe-PF2**, and *Fdd2* for **Fe-PF4**. The periodic DFT optimizations had the unit-cell and all the atoms optimized using the applied symmetry in order to reduce the computational load. Optimizations were performed using the GGA PBE functional with Grimme's DFT-D dispersion correction, thresholds for geometry

optimization and SCF convergence were chosen as 2×10^{-6} eV. The unit-cell parameters were then refined against the PXRD trace and then kept fix while all the atoms where allowed to optimize using CASTEP. Following this the unit-cell parameters were kept fix for the remainder of the refinement process. The background was fitted and refined using a Chebyshev polynomial with 20 coefficients in the range of the PXRD trace from 4° to 70° 2theta and a baseline shift refinement was used. Other corrections include: Specimen Displacement, Divergence Sample Length, Absorption with Sample Thickness Shape Intensity and Specimen Tilt. The peaks were fitted using a modified Thompson-Cox-Hastings pseudo-Voigt "TCHZ" profile. Preferred orientation was considered using a sixth order Spherical Harmonics refinement.

Rigid body refinement was used to refine the relative orientation (rotation) of the central fluorinated benzene ring with no success. Therefore, the central ring orientation was determined computationally. Molecular Quench Dynamics was using to determine the possible orientations and combinations of ring orientations within the unit-cell which were then further optimized using DFT. The central rings were evaluated to elucidate the structural equivalent positions of the fluorine atoms thereby generating a disordered model for the three MOFs. The space-group was then redetermined using the materials studio visualizer and yielded *Fddd* for all three MOFs. Thereafter the rings were kept fix during the Rietveld refinement.

3 Solid state NMR

¹³C, ¹H and ¹⁹F 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. ¹³C{¹H} ramped-amplitude Cross Polarization (CP) experiments^{S3} were performed at a spinning speed of 12.5 kHz using a recycle delay of 5 s and contact time of 2 ms and 0.05 ms. The 90° pulse for proton was 2.9 μ s. 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 at a spinning speed of 12.5 kHz using a recycle delay of 20 s. The ¹H chemical shift was referenced to adamantane. ¹³C{¹⁹F} ramped-amplitude CP experiments were performed at a spinning speed of 12.5 kHz using a recycle delay of 8 s and contact time of 5 ms and 10 ms. The 90° pulse for fluorine was 2.5 μ s. Quantitative solid-state ¹⁹F MAS NMR spectra were performed at a spinning speed of 12.5 kHz using a recycle delay of 8 s and contact time of 5 ms and 10 ms. The 90° pulse for fluorine was 2.5 μ s. Quantitative solid-state ¹⁹F MAS NMR spectra were performed at a spinning speed of 12.5 kHz using a recycle delay of 20 s. The ¹⁹F chemical shift was referenced to solium fluorine was 2.5 μ s. Quantitative solid-state ¹⁹F MAS NMR spectra were performed at a spinning speed of 12.5 kHz using a recycle delay of 20 s. The ¹⁹F chemical shift was referenced to solium fluorine.

Phase-modulated Lee–Goldburg (PMLG) heteronuclear ¹H-¹³C correlation (HETCOR) experiments coupled with fast magic angle spinning allowed the recording of the 2D spectra with a high resolution in both hydrogen and carbon dimensions.⁵⁴ Narrow hydrogen resonances, with line widths on the

order of 1–2 ppm, were obtained with homonuclear decoupling during t_1 ; this resolution permits a sufficiently accurate determination of the proton species in the system. The 2D ¹H - ¹³C PMLG HETCOR spectra were run with an LG period of 18.9 µs. The efficient transfer of magnetization to the carbon nuclei was performed by applying the RAMP-CP sequence. Quadrature detection in t_1 was achieved by the time proportional phase increments method (TPPI). The carbon signals were acquired during t_2 under proton decoupling by applying the two-pulse phase modulation scheme (TPPM).^{S5} The 2D ¹H-¹³C PMLG HETCOR NMR spectra of **Fe-PF2** were conducted at 298 K under magic-angle spinning (MAS) conditions at 12.5 kHz with a contact time of 2, 0.5 and 0.1 ms.

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.^{S6} 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 sample **Fe-PF2** was outgassed at 100°C for 1 h and overnight at rt in vacuum, then were pressed in a glass tube before being inserted into the coil. A pulse duration of 7 μ s was applied, with a recycle delay of 0.5 s. The experiments were conducted at variable temperature in the range 213–292 K. The ¹²⁹Xe NMR chemical shifts were referenced to xenon gas set at 0 ppm.

4 Enthalpy measurements by sorption-coupled micro-Calorimetry

Methodology for Qst from sorption-coupled micro-Calorimetry

A Micromeritics ASAP 2050 instrument were coupled to a Setaram high pressure μ DSC7 EVO instrument, similar to the pressure-scanning μ DSC setup employed by Barbour *et. al.*^{S7} The ASAP 2050 performs the gas dosing and calculates the amount of gas adsorbed while the μ DSC maintains the sample temperature (293 K) and measures the heat-flow of the sample cell against the reference cell.^{S8} Blanks measurements were performed to measure the contribution of slight asymmetric expansion of the gas between the sample and reference cells. CO₂ measurements were performed at 293 K up to 2 bar for both the samples and the blank. 293 K was chosen for the analysis temperature since the tube connecting the DSC to the sorption analyzer is at the temperature of the room, ca. 293 K. This reduces error in the free volume determination of the ASAP 2050 sorption analyzer.

The heat flow from sorption events, measured using the μ DSC, is integrated over time in seconds to yield the integral heat (Q^{int}) for each event. The differential heat (Q^{diff}) is obtained by differentiating

the integral heat in J/g with respect to the loading (N) in mmol/g, measured at the same time, to yield a value in kJ/mol^{S9, S10}:

$$\frac{\Delta Q^{int}}{\Delta N} = Q^{diff} \tag{eq. S2}$$

The isosteric heat is calculated by adding an appropriate thermodynamic term (zRT) to the resultant differential heat. z is the compressibility factor of the gas, which for CO_2 is negligible at 293 K up to 2 bar and thus reduces the thermodynamic term to RT:

$$Q_{st} = Q^{diff} + RT \tag{eq. S3}$$

The calorimetry experiments are performed in duplicate. The Q^{int} vs N data are averaged and then fitted with a polynomial which is used to smooth the data (8th order polynomial). Great care is taken to ensure that the fitting does not produce any artifacts and accurately represents the raw data. The total error of the experiment is determined by combining the averaging error with the polynomial regression error.

Methodology for Qst derived from adsorption isotherms

 $Q_{st}(CO_2)$ derived from adsorption isotherms collected at various temperatures were calculated using the Clausius-Clapeyron equation as displayed below^{S11}:

$$\frac{dP}{P} = \frac{\Delta H_{vap} dT}{R T^2}$$
(eq. S1)

where^{S12}:

$$\Delta H_{vap} = -\Delta H_{ads} \approx Q_{st} \tag{eq. S4}$$

The integrated form of (eq. S1) can be plotted as lines at constant loading concentrations. The Q_{st} , for each loading step can be determined from the gradient of the straight line fit of ln(P) vs 1/T as shown in eq. S3 below:

$$lnP = \frac{-Q_{st1}}{R T} + C \tag{eq. S5}$$

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

$$q = \frac{q_{max}bp^t}{1+bp^t}$$
(eq. S6)

where q is the adsorbed quantity at pressure p, q_{max} is the saturation loading and b and t are the Freundlich parameters. The model is used to obtain pressure values for each isotherm (collected at different temperatures) at predetermined loading values. These pressure and temperature data are used to construct the plots of ln(P) vs 1/T according the *eq. S5*. The total error of this process is determined by combining the regression errors of the Langmuir-Freundlich model and the straight line fit of the isosteres for each loading step.

5 Theoretical calculations and Modelling

CASTEP plane-wave DFT

Atomic coordinates were imported from the refined crystal structures. Only the hydrogen atoms in the frameworks were optimized as part of a periodic system using the CASTEP module of the Materials Studio software suite. The optimizations were performed using the GGA PBE functional with Grimme's DFT-D dispersion correction, and thresholds for geometry optimization and SCF convergence were chosen as 2×10^{-6} eV. Single point energy calculations were performed using the GGA PBE functional the GGA PBE functional with Grimme's DFT-D dispersion correction, and thresholds for geometry optimization and SCF convergence were chosen as 1×10^{-6} eV.

Atomic charges for Molecular Mechanics MM and Molecular Dynamics MD calculations: Single point calculations were performed using the GGA PBE functional with Grimme's DFT-D dispersion correction; thresholds for SCF convergence were chosen as 1×10^{-6} eV. The Milliken charges were calculated at the end of the SCF cycle. These atomic charges were used in all the Molecular Mechanics and Molecular Dynamics calculations.

Molecular mechanics and Molecular dynamics simulations

All MM and MD calculations were performed using the Forcite-Plus module within the Biovia Materials Studio software suite.^{S2} The Quench Dynamics (QD, Combination of MD and MM optimizations) protocol was used to perform a configurational search for the possible fluorinated ring orientations and arrangements. The resulting structures were further optimized using the CASTEP module and parameters as described above except for optimizing the entire unit-cell contents. The obtained structures were then used for Rietveld refinement against the PXRD traces of the MOFs.

Forcite energy parameters

Fine
COMPASS
Current (obtained from CASTEP)
Ewald
Ewald
1.0e-5 kcal/mol

Forcite Geometry optimization parameters

Geometry optimization				
Quasi-Newton				
1.0e-4 kcal/mol				
0.005 kcal/mol/Å				
750				

Forcite Quench Dynamics parameters				
Ensemble	NVT (constant V and T)			
Temperature	298 K			
Time step	1 fs			
Simulation time	500 ps			
Thermostat	Velocity scale (2 K)			
Quench	Every 5000 frames			

Molecular Electrostatic maps

The electrostatic potentials were calculated using the VAMP module of the Materials Studio Software suite as a single point energy calculation using the ZINDO Hamiltonian type and the INDO/2 Hamiltonian. A SCF convergence threshold of 5×10^{-7} kcal/mol was used and the grid size for the imported electrostatic potential was set to 0.1 Å. The electron density data were calculated as a single point energy calculation, for the CO₂ molecule in the absence of the surrounding host using the DMOI³ module^{S13-S14} of the Materials Studio Software suite, employing the GGA PBE functional ^{S15} with Grimme's DFT-D dispersion correction^{S16}, and thresholds for geometry optimization and SCF convergence were chosen as 1×10^{-6} eV. An all-electron core treatment was used in conjunction with the DNP numerical basis-set ^{S13} and the grid size for the imported electron density was set to 0.1 Å. The electron density data obtained were used to construct the three-dimensional 0.01 e^{-/}Å³ electron density contours of the CO₂ molecules. The molecular electrostatic potential calculated for the host was then mapped onto the electron density contours of the CO₂ molecules.

Simulations for determination of the gas arrangements and interaction energies

Gas (CO₂ and Xe) arrangements were determined using GCMC fixed loading simulations using one molecule per unit-cell. This yields CO₂ and Xe occupational density distribution as well as initial localized CO₂ positions within the MOFs. DFT optimizations (CASTEP) were performed to obtain the energies used to determine the most probable CO₂ arrangements. The optimizations were performed using the GGA PBE functional with Grimme's DFT-D dispersion correction, and thresholds for geometry optimization and SCF convergence were chosen as 2×10^{-6} eV. Single point energies, calculated using CASTEP, were used to determine the interaction energies which were calculated as follows:

$$\begin{split} E(host + CO_2) &: The \ full \ crystal \ structure \ with \ the \ guest \ molecules \ included. \\ E(host) &: The \ guest \ molecules \ are \ removed \ from \ the \ periodic \ model. \\ E(CO_2) &: The \ host \ molecules \ are \ removed \ from \ the \ periodic \ model. \\ E_{int}(host - CO_2) &: The \ host - \ guest \ interaction \ energy_{.} \\ E_{int}(host - CO_2) &= \ E(host \ + \ CO_2) - (E(host) \ + \ E(CO_2)) \end{split}$$

6 MOFs preparation

6.1 Synthesis of Fe-PF1



The fluorinated bis(pyrazole), namely, 1,4-bis(1*H*-pyrazol-4-ylethynyl)-2-fluorobenzene (H_2PF1), were synthesized by Sonogashira-Hagihara coupling reactions with Pd(PPh₃)₂Cl₂ and CuI, starting from 1,4-diethynyl-2-fluorobenzene and 4-iodio-(1-ethoxyethyl)pyrazole, followed by deprotection with 6M HCl. An oven dried Schlenk tube was purged with nitrogen and loaded with H₂PF1 (150 mg, 0.54 mmol). The solid was dissolved in DMF (15 mL) and iron(III) chloride (48 mg, 0.27 mmol) was added. The bright yellow solution was heated at 60 °C and TEA (1.8 mL) was added dropwise. The deep orange mixture was heated at 110 °C for 24 hours under stirring. After cooling at room temperature, the suspension was centrifuged and the black solid was separated from the liquid. The residue was washed three times with fresh DMF and twice with MeOH. The solid was dried under vacuum at 150 °C overnight. **Fe-PF1** was obtained as a black powder (131 mg, 0.14 mmol) in 94% yield. Elemental analysis: exp. C 58.82%, H 2.67%, N 16.94%; calc. C 61.70%, H 2.27%, N 17.99%. IR (ATR, cm⁻¹): 2222 (w), 1613 (w), 1540 (w), 1487 (vs), 1414 (w), 1387 (s), 1352 (s), 1284 (w), 1223 (w), 1164 (s), 1110 (w), 1069 (vs), 1020 (m), 998 (w), 943 (m), 850 (m), 845 (s), 843 (m), 785 (w), 746 (s), 714 (w), 636 (vs).

6.2 Synthesis of Fe-PF2



The fluorinated bis(pyrazole), namely, 1,4-bis(1H-pyrazol-4-ylethynyl)-2,3-difluorobenzene (**H**₂**PF2**), were synthesized by Sonogashira-Hagihara coupling reactions with Pd(PPh₃)₂Cl₂ and CuI, starting from 1,4-diethynyl-2,3-difluorobenzene and 4-iodio-(1-ethoxyethyl)pyrazole, followed by

deprotection with 6M HCl. An oven dried Schlenk tube was purged with nitrogen and loaded with H_2PF_2 (120 mg, 0.4 mmol). The solid was dissolved in dimethylacetamide (DMA, 24 mL) and iron acetylacetonate (72 mg, 0.2 mmol) was added. TEA (1.4 mL) was added and the solution was heated at 165 °C for 72 hours under stirring. After cooling at room temperature, the suspension was centrifuged and the black solid was separated from the liquid. The residue was washed three times with DMF and twice with MeOH. The solid was dried under vacuum at 150 °C overnight. Fe-PF2 was obtained as a black powder (51.7 mg, 0.05 mmol) in 51% yield. Elemental analysis: exp. C 54.26%, H 2.37%, N 15.20%; calc. C 58.33%, H 1.84%, N 17.01%.

IR (ATR, cm⁻¹): 2230 (w), 1666 (w), 1614 (w), 1548 (w), 1488 (vs), 1466 (vs), 1364 (s), 1355 (s), 1276 (m), 1261 (m), 1228 (w), 1162 (vs), 1077 (vs), 1033 (vs), 847 (vs), 819 (w), 768 (s), 635 (vs).

6.3 Synthesis of Fe-PF4



The fluorinated bis(pyrazole), namely, 1,4-bis(1*H*-pyrazol-4-ylethynyl)-tetrafluorobenzene (H_2PF4), were synthesized by Sonogashira-Hagihara coupling reactions with Pd(PPh₃)₂Cl₂ and CuI, starting from 1,4-diethynyl-tetrafluorobenzene and 4-iodio-(1-ethoxyethyl)pyrazole, followed by deprotection with 6 M HCl. An oven dried Schlenk tube was purged with nitrogen and loaded with H₂PF4 (48 mg, 0.145 mmol). The solid was suspended in benzonitrile (PhCN, 10 mL) and Fe(acac)₃ (26 mg, 0.073 mmol) was added. TEA (0.5 mL) was added and the solution was heated at 150 °C for 24 hours under stirring. After cooling at room temperature, the solution was centrifuged, and the black precipitate was separated from the liquid. The residue was washed three times with DMF and twice with MeOH. The black solid was dried under vacuum at 150 °C overnight. Fe-PF4 was obtained as a black powder in 70% yield. Elemental analysis: exp. C 49.40%, H 2.76%, N 13.12%; calc. C 52.58%, H 1.10%, N 15.33%.

IR (ATR, cm⁻¹): 2224 (w), 1557 (w), 1540 (w), 1475 (vs), 1385 (w), 1361 (w), 1299 (s), 1260 (s), 1029 (s), 979 (vs), 822 (m), 795 (vs), 665 (s), 633 (s).

7 Powder X-ray diffraction (PXRD) – Structural refinement



7.1 Rietveld refinement results

Figure S1. Rietveld fits of X-ray data for **Fe-PF1** using the TOPAS-Academic-64 V6 software package [S1]. The HKL indices are indicated as green markers and the difference plot are shown below. The black and red represent the observed and calculated traces respectively while the dotted yellow line represent the background plot.



Figure S2. Rietveld fits of X-ray data for **Fe-PF2** using the TOPAS-Academic-64 V6 software package [S1]. The HKL indices are indicated as green markers and the difference plot are shown below. The black and red represent the observed and calculated traces respectively while the dotted yellow line represent the background plot.



Figure S3. Rietveld fits of X-ray data for **Fe-PF4** using the TOPAS-Academic-64 V6 software package [S1]. The HKL indices are indicated as green markers and the difference plot are shown below. The black and red represent the observed and calculated traces respectively while the dotted yellow line represent the background plot.

Table S1. Crystallographic data for Fe-PF1, Fe-PF2 and Fe-PF4.

Identification code	Fe-PF1	Fe-PF2	Fe-PF4
Empirical formula C ₂₄ H _{9.5} N ₆ F _{1.5} Fe		C ₂₄ H ₉ F ₃ FeN ₆	C ₂₄ H ₆ F ₆ FeN ₆
Formula weight	466.225	494.21	548.20
Crystal system	orthorhombic	orthorhombic	orthorhombic
Space group	Fddd	Fddd	Fddd
<i>a</i> /Å 7.461		7.497	8.089
<i>b</i> /Å 36.247		36.474	36.391
c/Å 63.653		63.258	61.878
Volume/Å ³ 17214.8		17298.5	18215.3
Z	16	16	16
$\rho_{calc}g/cm^3$	0.71954	0.75905	0.79955
Rp 3.8 %		8.4%	3.9 %
Rwp	4.9 %	12.2%	5.6 %
CCDC number	1998739	1998740	1998739

7.2 Crystal structure analysis



Figure S4. The disorder and tilts angles of the central fluorinated rings for a) side 1 and b) sides 2 and 3 of the triangular channel for **Fe-PF1**. The disordered moieties occupy equal occupancy.



Figure S5. The disorder and tilts angles of the central fluorinated rings for a) side 1 and b) sides 2 and 3 of the triangular channel for **Fe-PF2**. The disordered moieties occupy equal occupancy.



Figure S6. The disorder and tilts angles of the central fluorinated rings for a) side 1 and b) sides 2 and 3 of the triangular channel for **Fe-PF4**. The disordered moieties occupy equal occupancy.

Table S2. The free volumes calculated for the structures of **Fe-PF1**, **Fe-PF2** and **Fe-PF4**. A probe radius of 1.82 Å (N₂ kinetic diameter is 3.64 Å) was used with a grid resolution of 0.15 Å.

Identification code	Fe-PF1	Fe-PF2	Fe-PF4
Unit-cell Formula weight / g.mol ⁻¹	7475.76	7907.34	8771.2
Volume /Å ³	17214.8	17298.5	18215.3
V_{free} / Å ³	10406.19	10851.8	10465.2
Volume %	60.4	61	59
V _{free} / cm ³ .g ⁻¹	0.84	0.83	0.72
$V_{\rm free}$ (N ₂)/ cm ³ .g ⁻¹	0.70	0.67	0.71



Figure S7. a) and b) A face-on view of the channel walls of Fe-PF1 with the L--L distance. The ligand angle with respect to the *c*-axis indicated along with the F \cdots H distances for the hydrogen bonds present. The channel walls propagate along the crystallographic *c*-axis. The ligands are shown in ball-and-stick while the metal coordination nodes are shown in polyhedron representation.



Figure S8. a) and b) A face-on view of the channel walls of Fe-PF2 with the L--L distance. The ligand angle with respect to the *c*-axis indicated along with the F \cdots H distances for the hydrogen bonds present. The channel walls propagate along the crystallographic *c*-axis. The ligands are shown in ball-and-stick while the metal coordination nodes are shown in polyhedron representation.



Figure S9. a) and b) A face-on view of the channel walls of Fe-PF4 with the L--L distance. The ligand angle with respect to the *c*-axis indicated along with the F \cdots H distances for the hydrogen bonds present. The channel walls propagate along the crystallographic *c*-axis. The ligands are shown in ball-and-stick while the metal coordination nodes are shown in polyhedron representation.



Figure S10. The solvent-accessible volume determined using a probe radius of 1.82 Å (kinetic diameter of N_2 is 3.64 Å) for **Fe-PF1** (a), **Fe-PF2** (b) and **Fe-PF4** (c) as view along (1 0 0). The black arrows indicate the length of the base and height of the triangular accessible space which can be used to calculate the triangular cross-sectional area. The reference distance is from the centre of one metal node to another and is exactly half of the crystallographic *b*-axis. The metal node is shown in polyhedron representation while the fluorinated phenyl rings are shown in space-filling representation and the rest as ball-and-stick.

7.3 Cross-sectional area and pore diameters of the triangular channels

The cross-sections of Fe-MOFs were calculated as $A = \frac{1}{2}bh$, b – the base length and h – the height of the triangular cross-section as obtained from the evaluation of the guest-accessible volume using a probe radius of 1.82 Å (kinetic diameter of N₂ is 3.64 Å). The cross-sectional areas are 57, 60 and 57 Å² for **Fe-PF1**, **Fe- PF2** and **Fe- PF4**, respectively.

8 Thermal analyses

8.1 Thermal gravimetric analysis (TGA)



Figure S11. TGA analysis of Fe-PF1 performed in dry air.



Figure S12. TGA analysis of Fe-PF2 performed in dry air.



Figure S13. TGA analysis of Fe-PF4 performed in dry air.

Assuming the final weight losses to be due to complete combustion of ligands with the formation of iron oxide as residue, ligand/iron stoichiometries were evaluated for the three materials and found to be consistent with the theoretical value of 1.5.

 Table S3. Comparison between theoretical ligand/metal ratios and values calculated from TGA analyses.

	Theoretical	Experimental
	L/M ratio	L/M ratio
Fe-PF1	1.5	1.6
Fe-PF2	1.5	1.4
Fe-PF4	1.5	1.6

9 Water stability

The **Fe-MOFs** were soaked in deionized water for 24 hours. The samples were filtered and PXRD analyses were performed. Then, the samples were activated under high vacuum ($1x10^{-1}$ mmHg) at 150°C and PXRD patterns were collected.



Figure S14. Powder X-ray diffraction pattern of pristine **Fe-PF1** (top, light green), **Fe-PF1** soaked in water for 24 hours and filtered (middle, dark green) and **Fe-PF1** activated under high vacuum for 12 hours at 150°C.

Experimental procedure: **Fe-PF1** (15 mg) was dispersed in deionized water for 24 hours at room temperature. Then, the powder was filtered on a PTFE filter (0.2 μ m) and the PXRD pattern of wet **Fe-PF1** was recorded. The sample was activated under high vacuum for 12 hours at 150°C (recovered mass=11.7 mg) and the PXRD pattern was collected.



Figure S15. Powder x-ray diffraction pattern of **Fe-PF2** (top, dark blue) and **Fe-PF2** after soaking in water for 24 h and activation under high vacuum for 12 hours at 150°C (bottom, light blue).



Figure S16. Powder X-ray diffraction pattern of **Fe-PF4** (Top, dark red), and **Fe-PF4** after soaking in water for 24 h and activation under high vacuum for 12 hours at 150°C (bottom, light red).

10 Solid state NMR



Figure S17. ¹³C{¹H} CP MAS NMR spectra of Fe-PF1, Fe-PF2 and Fe-PF4 recorded with contact time of 2 ms. The comparison with the ${}^{13}C{}^{1}H$ CP MAS of the ligands (contact time of 0.5 and 2 ms) has been reported.



Figure S18. ¹³C{¹⁹F} CP MAS and ¹³C{¹H} CP MAS spectra of H_2 -PF2 ligand, recorded, respectively, with contact times of 5 and 2 ms.



Figure S19. ¹³C{¹⁹F} CP MAS spectra of **Fe-PF2**, recorded with contact times of 5 and 10 ms, are compared to ${}^{13}C{}^{1}H$ CP MAS NMR spectra obtained at a contact time of 2 ms.



Figure S20. ¹³C{¹⁹F} CP MAS spectra of **Fe-PF2**, recorded with contact times of 5 and 10 ms, are compared to ${}^{13}C{}^{1}H$ CP MAS NMR spectra obtained at a contact time of 2 ms.



Figure S21. ¹H MAS NMR spectra of H_2 -PF2 (above) and Fe-PF2 (below) recorded at 300.13 MHz and spinning speed of 12.5 kHz.



Figure S22. ¹⁹F MAS NMR spectra of Fe-PF4, Fe-PF2 and H₂-PF2 recorded at 282 MHz and spinning speed of 12.5 kHz.

H ₂ -PF2	Assignment	δ (ppm) ¹³ C{ ¹ H} CPMAS	δ (ppm) ¹³ C{ ¹⁹ F} CPMAS
	C _{1,1} ,	136.5	-
	C ₂	102.9	104.0
	C ₃	90.6	90.5
	C ₄	84.4	84.2
	C ₅	113.9	113.5
	C ₆	152.0-149.0 (¹ J _{C-F} ~226 Hz)	150.3
	C ₇	127.3	-
	Assignment	δ (ppm) 'Η MAS	
	Н	14.7	
	Н	7.7	
	Н	6.4	
н н н		δ (ppm) ¹⁹ F MAS	
	F	-134.5	

Table S4. ¹³C, ¹H and ¹⁹F chemical shifts of H_2 -PF2 from solid state NMR spectra collected at 7.04 T.

Table S5. ¹³C, ¹H and ¹⁹F chemical shifts of Fe-PF2 from solid state NMR spectra collected at

/.04 1.	7.	.04	T.
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Fe-PF2	Assignment	δ (ppm) ¹³ C{ ¹ H} CPMAS	δ (ppm) ¹³ C{ ¹⁹ F} CPMAS	Δδ (ppm) ^{a)}
	C ₁	-50.4	-	93.2 134.3 (Fe _α) ^{b)}
	C ₂	-1.5	-	52.2
F F	C ₃	48.7	-	21.0
	C4	~60	-	12.2
	C ₅	90.1	89.8	
	C ₆	-	153.9	
	\mathbf{C}_7	130.2	133.5	
	Assignment	δ (p 'H M	pm) MAS	Δδ (ppm)
HEFH	Н	-2	2.1	9.8
	Н	4.2		2.1
		δ (p ¹⁹ F 1	pm) MAS	
	F	-14	2.3	

a) The ¹³C pseudocontact paramagnetic shift per Fe ion $\Delta\delta$ (ppm) is equal to the difference between the carbon chemical shifts of the **H**₂-**PF2** and those of the **Fe-PF2** divided by 2. The factor 2 derives from the presence of two effective Fe atoms.

b) The upfield shift for C1 from the closest iron (Fe_{α}) of 134.3 ppm is calculated by subtracting from the experimental value of 186.5 ppm, the shift value of 52.2 ppm due to the farther Fe (Fe_{β}).



Figure S23. 2D ¹H–¹³C HETCOR phase-modulated Lee–Goldburg (PMLG) MAS NMR spectra of **Fe-PF2** at contact times of: a) 2, b) 0.5 and c) 0.1 ms.

¹²⁹ Xe δ (ppm)	T (K)
93.2	292
102.9	256
107.3	243
114.0	229
129.4	213

 Table S6.
 129Xe NMR chemical shifts of Fe-PF2 loaded with xenon gas.



Figure S24. The Xe distribution density within **Fe-PF2** calculated using fixed loading GCMC simulations with one Xe atom per unit-cell. The red color represents high and the blue color low Xe density. The MOF is shown in ball-and-stick representation. In the inset Xe atoms localized in the most probable positions within a channel of **Fe-PF2** as determined by the GCMC simulations. The pyrazole hydrogens have been omitted for clarity. The black lines highlight the triangular channel.

11 Scanning Electron Microscopy



Figure S25. Scanning electron microscope images of Fe-PF1 drop-casted on a silicon substrate.



Figure S26. Scanning electron microscope images of Fe-PF2 drop-casted on a silicon substrate.



Figure S27. Scanning electron microscope images of Fe-PF4 drop-casted on a silicon substrate.

12 Gas adsorption measurements

12.1 N₂ adsorption isotherms



Figure S28. N₂ adsorption isotherms collected at 77 K and up to 1 bar for **Fe-PF1** (green circles). The desorption branches are depicted as empty symbols.



Figure S29. N_2 adsorption isotherms collected at 77 K and up to 1 bar for **Fe-PF2** (blue diamonds). The desorption branches are depicted as empty symbols. Pore volumes distribution calculated with NLDFT, considering a cylindrical pore model and adopting the Tarazona method, are reported in the inset.



Figure S30. N_2 adsorption isotherms collected at 77 K and up to 1 bar for **Fe-PF4** (red triangles). The desorption branches are depicted as empty symbols. Pore volumes distribution calculated with NLDFT, considering a cylindrical pore model and adopting the Tarazona method, are reported in the inset.



Figure S31. Left: Differential pore size distributions (PSD) calculated from the N_2 adsorption isotherms at 77 K by the NLDFT method with Tarazona cylindrical pore model **Fe-PF1** (green line), **Fe-PF2** (blue line) and **Fe-PF4** (red line). Right: cumulative pore size distributions. Pore size distributions displayed the main peak between 6.5 and 8.5 Å, in good agreement with pore sizes calculated from crystallographic data.

Table S7. Textural parameters of Fe(III) MOFs as derived from N_2 adsorption isotherms at 77 K expressed by grams.

	S _{BET} ^a (m ² /g)	${{{\rm S}_{{\rm Langmuir}}} \over {{{\rm (m}^2/g)}}}$	Experimental V _{total} (cm ³ /g)	Experimental V _{micro} (cm ³ /g)	Calculated V_{total}^{d} (cm^{3}/g)	$\frac{Q_{1 \text{ bar}}(N_2)}{(\text{cm}^3/\text{g})}$	Q _{1 bar} (N ₂) (mmol/g)
Fe ₂ (BPEB) ₃ ^f	1273	1598	0.79	0.79	-	448.8	20.0
Fe-PF1	1415	1595	0.70	0.65	0.84	425.9	19.0
Fe-PF2	1500	1660	0.67	0.63	0.83	428.1	19.1
Fe-PF4	1470	1645	0.71	0.63	0.72	468.5	20.9

^a calculated using adsorption data in p/p° range from 0.015 to 0.1.

^b calculated using Non-Local Density Functional Theory and the Tarazona model on cylindrical pores.

^c calculated considering the total volume of pores less than 20 Å wide.

^d calculated from crystal structures using a probe radius of 1.82 Å.

^f J. Mater. Chem. A 2014,2,122018.

Table S8. Textural parameters of Fe(III) MOFs as derived from N_2 adsorption isotherms at 77 K expressed by mmoles of chemical formula.

	S _{BET} ^a (m ² /mmol)	S _{Langmuir} (m ² /mmol)	Experimental V _{total} ^b (cm ³ /mmol)	
Fe-PF1	661.14	745.24	0.32	
Fe-PF2	741.30	829.39	0.33	
Fe-PF4	805.85	901.79	0.39	

12.2 CO₂ adsorption isotherms

	Q _{max} (mmol/g)	V _{CO2} ^a (cm ³ /g)	V _P total ^b (cm ³ /g)
Fe-PF1	15.3	0.87	0.70
Fe-PF2	15.2	0.87	0.67
Fe-PF4	14.8	0.85	0.71

Table S9. Quantity adsorbed and filling percentage of CO₂ at 195 K and 1 bar.

^a dCO_{2(l)} = 0.77 g/cm³ was considered

^b calculated from N₂ isotherm with NLDFT considering a cylindrical pore model and adopting the Tarazona method



Experimental CO₂ 195K

Figure S32. The experimental CO₂ adsorption isotherms at 195 K for Fe-PF1 (green circles), Fe-**PF2** (blue diamonds) and **Fe-PF4** (red triangles). The insets expand the region from $0 - 0.005 \text{ p/p}^{\circ}$ and 0 - 4 mmol/g.

12.3 High pressure adsorption isotherms

	Т (К)	Q _{1 bar} (CO ₂) (mmol/g)	$\begin{array}{l} Q_{1 \ bar} \ (CO_2) \\ (cm^3/g \ STP) \end{array}$	Q _{10 bar} (CO ₂) (mmol/g)	Q _{10 bar} (CO ₂) (cm ³ /g STP)
Fe-PF1	195	15.3	342.9	/	/
	273	5.1	113.5	12.4	277.5
	283	4.1	91.0	11.9	266.0
	298	2.8	61.7	9.9	222.3
Fe-PF2	195	15.2	340.7	/	/
	273	6.2	138.2	12.8	287.4
	283	4.5	99.9	12.0	269.1
	298	3.1	69.6	10.7	240.1
Fe-PF4	195	14.8	331.7	/	/
	273	5.3	118.8	12.9	289.1
	283	4.1	91.9	11.8	264.5
	298	3.2	71.7	11.2	251.0

Table S10. CO_2 adsorption capacities of the three MOFs at 1 and 10 bar reported as mmol/g and cm³/g at Standard Temperature and Pressure conditions.



Figure S33. IAST selectivity for the adsorption of CO_2 over N_2 from a 15:85 mixture calculated at 273 K (a) and 298 K (b) for Fe-PF1 (green circles), Fe-PF2 (blue diamonds) and Fe-PF4 (red triangles).

Table S11. CO_2/N_2 selectivity calculated for **Fe-PF1**, **Fe-PF2** and **Fe-PF4** at different pressures (0.1 bar, 1 bar and 2 bar) at 273 K.

Sample	Selectivity at 0.1 bar	Selectivity at 1 bar	Selectivity at 2 bar
Fe-PF1	20	22	24
Fe-PF2	18	21	23
Fe-PF4	27	26	26

Value calculated applying the IAST theory to a 15:85 CO_2/N_2 mixture

Table S12. CO₂/N₂ selectivity calculated for **Fe-PF1**, **Fe-PF2** and **Fe-PF4** at different pressures (0.1 bar, 1 bar and 2 bar) at 298 K.

Sample	Selectivity at 0.1 bar	Selectivity at 1 bar	Selectivity at 2 bar
Fe-PF1	16	16	17
Fe-PF2	14	16	17
Fe-PF4	21	20	20

Value calculated applying the IAST theory to a 15:85 CO₂/N₂ mixture

	Surface area (BET) (m²/g)	Pore Volume (cm ³ /g)	Т (К)	P (bar)	Q(CO ₂) (mmol/g)	Wt(Q) %	CO ₂ /N ₂ Selectivity	Q _{st} (kJ/mol)
Fe ₂ (BPEB) ₃	1070	0.79	273	1	4.7	20.7	25	26
				10	12.0	52.8		
	12/3		298	1	2.9	12.8	20	
				10	9.2	40.5		

Table S13. Textural and CO₂ adsorption parameters of known MOFs

13 CO₂ Isosteric Heat

13.1 HKUST-1 test case for Qst determination



Figure S34. Results of the fitting process for **HKUST-1** to CO₂ sorption isotherms collected, using the Micromeritics ASAP 2020 instrument, at 298 K, 303 K, 308 K, 313 K and 318 K. The fitting trace is shown as a solid red line and the fitting parameters and statistics are reported in Table S13.

Table S14. Fitting paran	meters obtained	d for carbor	dioxide	adsorption	for I	HKUST-1	applying	the
Langmuir-Freundlich mo	odel.							

Model	Langmuir_Freundlich (User)							
Equation		q=Qsat*K*(c^n)/(1+K*(c^n))						
Plot	298 K	298 K 303 K 308 K 313 K 318 K						
q _{max} (Fixed)	17.8 ± 0	17.8 ± 0	17.8 ± 0	17.8 ± 0	17.8 ± 0			
b	0.34731 ± 1.05786E-4	0.299 ± 1.00589E-4	0.2547 ± 9.47125E-5	0.20735 ± 8.92244E-5	0.17941 ± 8.87073E-5			
t	0.99769 ± 3.14943E-4	1.0275 ± 3.67557E-4	1.01292 ± 4.116E-4	1.01945 ± 4.95229E-4	1.0169 ± 7.23198E-4			
Reduced Chi-Sqr*	1.54E-05							
R-Square(COD)	1	0.99998	0.99999	0.99995	0.99997			



Figure S35. HKUST-1 heat flow measured using the ASAP 2050 and μ DSC7 coupled system. (a) Full timeline and (b) an expanded timeline (1 – 5 hours).



Figure S36. HKUST-1 Qst results. (a) The sorption isotherms collected at 298 K, 303 K, 308 K, 313 K and 318 K. up to 1.1 bar using the Micromeritics ASAP 2020 instrument. The green circles represent the adsorption isotherm collected using the ASAP 2050 and μ DSC7 coupled system at 293 K up to 2 bar. (b) The Sorption derived Qst and Calorimetry determined Qst plotted against the CO₂ loading.



Figure S37. Results of the fitting process for **Fe-PF1** (a), **Fe-PF2** (b) and **Fe-PF4** (c) to CO₂ sorption isotherms collected at 273 K, 283 K and 298 K. The fitting trace is shown as a solid red line and the fitting parameters and statistics are reported in Table SX.

Fe-PF1						
Temperature	273 K	283 K	298 K			
q _{max}	15.85 ± 0	15.85 ± 0	15.85 ± 0			
b	0.44662 ± 0.00375	0.32213 ± 0.00319	0.20365 ± 0.00262			
t	0.90671 ± 0.00592	0.96674 ± 0.00658	0.94148 ± 0.00777			
Reduced Chi-Sqr*	0.0137					
R-Square (COD)	0.99849	0.9994	0.99919			
Fe-PF2						
Temperature	273 K	283 K	298 K			
q _{max}	14.99 ± 0	14.99 ± 0	14.99 ± 0			
b	0.62072 ± 0.00566	0.41193 ± 0.0047	0.24728 ± 0.00371			
t	1.00621 ± 0.00755	1.02189 ± 0.00818	1.03914 ± 0.0095			
Reduced Chi-Sqr*	0.01963					
R-Square (COD)	0.9981	0.99889	0.99943			
	Fe-	·PF4				
Temperature	273 K	283 K	298 K			
q _{max}	15.7599 ± 0	15.7599 ± 0	15.7599 ± 0			
b	0.48043 ± 0.00505	0.33488 ± 0.0042	0.25279 ± 0.00369			
t	0.9051 ± 0.00758	0.94168 ± 0.00847	1.00823 ± 0.0095			
Reduced Chi-Sqr*	0.01429					
R-Square (COD)	0.99846	0.99946	0.99993			

Table S15. Fitting parameters obtained for carbon dioxide adsorption for Fe-PF1, Fe-PF2 and Fe-**PF4** applying the Langmuir-Freundlich model.



Figure S38. Sorption derived Qst(CO₂) plot calculated at increasing loading values for **Fe-PF1** (green circles), **Fe-PF2** (blue diamonds) and **Fe-PF4** (red triangles). These Qst curves were calculated using CO₂ sorption data measured at 283 K, 283 K and 298 K.



13.3 Q_{st} from sorption-coupled micro-Calorimetry for Fe-PF1, Fe-PF2 and Fe-PF4

Figure S39. Heat flow measured of the adsorption of CO_2 for Fe-PF1 using the ASAP 2050 and μ DSC7 coupled system. The top and bottom are the duplicate experiments and the insets shows an expanded timeline of 1 – 3.5 hours. Each peak represents a gas dose and therefor an adsorption point.



Figure S40. Heat flow measured of the adsorption of CO_2 for **Fe-PF2** using the ASAP 2050 and μ DSC7 coupled system. The top and bottom are the duplicate experiments and the insets shows an expanded timeline of 1 – 3.5 hours. Each peak represents a gas dose and therefor an adsorption point.



Figure S41. Heat flow measured of the adsorption of CO₂ for **Fe-PF4** using the ASAP 2050 2050 (sorption analyzer) and μ DSC7 coupled system. The top and bottom are the duplicate experiments and the insets shows an expanded timeline of 1 – 3.5 hours. Each peak represents a gas dose and therefore an adsorption point.



Figure S42. CO_2 adsorption isotherms collected at 293 K up to ca. 2 bar in the ASAP 2050 (sorption analyzer) and μ DSC7 coupled system. The symbols with and without the dot represent the duplicate experiments pairs.



Figure S43. (a), (c) and (e) – The integral Heat (Qint in J/g) vs CO₂ Loading (N in mmol/g) of the duplicate experiments and their average for **Fe-PF1**, **Fe-PF2** and **Fe-PF4** respectively. (b), (d) and (f) – The 8th order polynomial fitting to the average Qint vs N data for **Fe-PF1**, **Fe-PF2** and **Fe-PF4** respectively. The derivatives of the fitted polynomials are used to calculate the Qst curve.

	Fe-PF1	Fe-PF2	Fe-PF4
Data	Average Qint vs Loading	Average Qint vs Loading	Average Qint vs Loading
Model	Poly8 (User)	Poly8 (User)	Poly8 (User)
Equation	$y = A0 + A1^{*}x + A2^{*}x^{2} + A3^{*}x^{3} + A4^{*}x^{4} + A5^{*}x^{5} + A6^{*}x^{6} + A7^{*}x^{7} + A8^{*}x^{8}$	$y = A0 + A1*x + A2*x^2 + A3*x^3 + A4*x^4 + A5*x^5 + A6*x^6 + A7*x^7 + A8*x^8$	$y = A0 + A1*x + A2*x^2 + A3*x^3 + A4*x^4 + A5*x^5 + A6*x^6 + A7*x^7 + A8*x^8$
A0	0.05169 ± 0.00234	0.01215 ± 0.00296	$0.00205 \pm 9.8362E-4$
A1	25.31678 ± 0.0595	25.260 ± 0.0583	30.39142 ± 0.0536
A2	-4.68024 ± 0.1729	-4.9109 ± 0.1481	-17.94861 ± 0.23317
A3	2.63075 ± 0.1951	2.6016 ± 0.13847	16.21445 ± 0.35952
A4	-0.89143 ± 0.1054	-0.7495 ± 0.05976	-8.27832 ± 0.24916
A5	0.17999 ± 0.0304	0.1230 ± 0.01359	2.44284 ± 0.09011
A6	-0.02102 ± 0.0048	-0.01148 ± 0.00169	-0.41311 ± 0.0177
A7	$0.0013 \pm 3.96181-4$	$5.644E-4 \pm 1.081E-4$	0.03714 ± 0.00179
A8	$-3.340E-5 \pm 1.316E-5$	$-1.136E-5 \pm 2.8E-6$	-0.00138 ± 7.2998E-5
Reduced Chi-Sqr	0.0052	0.01532	0.01009
R-Square (COD)	1	1	1
Adj. R-Square	1	1	1

Table S16. The fitting parameters for an 8th order polynomial fit to the average integral Heat (Qint in J/g) vs CO₂ Loading (mmol/g).



Figure S44. Qst plots calculated from the micro-Calorimetry data, collected at 293 K up to 2 bar, for **Fe-PF1** (green circles), **Fe-PF2** (blue diamonds) and **Fe-PF4** (red triangles). Below is a plot of the total, measurement and regression, errors (in %) for each FeMOF plotted with the corresponding colours and symbols.



Figure S45. Comparison of Sorption-Derived and Calorimetry determined Qst curves for (a) **Fe-PF1** (circles), (b) **Fe-PF2** (diamonds) and (c) **Fe-PF4** (triangles). The red colour represents the Sorption-Derived Qst curves while the blue colour represents the Calorimetry determined Qst curves.

	Т (К)	Q _{10 bar} (CO ₂) (mmol/g)	Q _{1 bar} (CO ₂) (mmol/g)	Q _{st} ^a (kJ/mol)	Q _{st} ^b (kJ/mol)	Selectivity ^c CO ₂ /N ₂
19 27 Fe-PF1 28 29 29	195	-	15.3			_
	273	12.4	5.1			22
	283	11.9	4.1	27.6 ± 7.8	28.9 ± 0.19	-
	298	9.9	2.8	(0.05 mmol/g)	(0.039 mmol/g)	16
	293	-	3.0 ^b			-
	195	-	15.2	28.3±1.2 (0.05 mmol/g)	27.7±0.60 (0.052 mmol/g)	-
	273	12.8	6.2			20
Fe-PF2	283	12.0	4.5			-
	298	10.7	3.1			16
	293	-	3.5 ^b			-
	195	-	14.8		32.6±0.07 (0.057 mmol/g)	-
	273	12.9	5.3			25
Fe-PF4	283	11.8	4.1	32.3 ± 2.8		-
	298	11.2	3.2	(0.05 mmol/g)		26
	293	-	3.9 ^b			-

Table S17. CO₂ adsorption capacity, isosteric heat and selectivity values for Fe-PF1, Fe-PF2 and Fe-PF4 at 195, 273, 283 and 298 K.

^a calculated applying the calculated using the Clausius-Clapeyron relation to the experimental isotherms fitted with a Langmuir-Freundlich model; the loading is indicated in mmol/g in brackets.

^b directly measured from the µDSC7 EVO calorimeter coupled to an ASAP 2050 sorption analyser. the loading is indicated in mmol/g in brackets.

 $^{\rm c}$ calculated applying the IAST theory to a 15:85 CO_2/N_2 mixture; values reported at 1 bar

14 Computational Details



14.1 GCMC CO₂ density distribution

Figure S46. The CO_2 distribution density, within Fe-PF1, calculated using GCMC simulations. The red represents high and the blue represents low CO_2 density. The MOF is shown in ball-and-stick representation.



Figure S47. The CO_2 distribution density, within **Fe-PF2**, calculated using GCMC simulations. The red color represents high and the blue color represents low CO_2 density. The MOF is shown in ball-and-stick representation.



Figure S48. The CO_2 distribution density, within **Fe-PF4**, calculated using GCMC simulations. The red color represents high and the blue color represents low CO_2 density. The MOF is shown in ball-and-stick representation. The distance between the two closest sites are show in yellow.

14.2 CO₂ localization



Figure S49. (a) The CO₂ distribution density as viewed along the channel axis, within **Fe-PF1**, calculated using GCMC simulations. The red color represents high and the blue color represents low CO₂ density. (b) The CO₂ localized in the channel as determined by plane-wave DFT optimizations. (c) The perspective view of the CO₂ molecule interacting with the **H**₂-**PF1** molecules as indicated by the yellow arrow in (b). The red dotted lines indicate the most significant interactions with their distances shown.



Figure S50. (a) The CO₂ distribution density as viewed along the channel axis, within **Fe-PF2**, calculated using GCMC simulations. The red color represents high and the blue color represents low CO₂ density. (b) The CO₂ localized in the channel as determined by plane-wave DFT optimizations. (c) The perspective view of the CO₂ molecule interacting with the **PF2** molecules as indicated by the yellow arrow in (b). The red dotted lines indicate the most significant interactions with their distances shown.



Figure S51. (a) The CO_2 distribution density as viewed along the channel axis, within **Fe-PF4**, calculated using GCMC simulations. The red color represents high and the blue color represents low CO_2 density. (b) The CO_2 localized in the channel as determined by plane-wave DFT optimizations.

14.3 Electrostatic potential maps



Figure S52. Molecular electrostatic potential of CO₂.



Figure S53. Electrostatic potential of the H_2 -PF1 ligands projected onto the CO₂ density isosurface. The CO₂ molecules were localized by DFT calculations. The yellow arrows indicate the 3 different points of view shown as 1, 2 and 3 for better visualization of the 3D electrostatic map.



Figure S54. Electrostatic potential of the H_2 -PF2 ligands projected onto the CO₂ density isosurface. The CO₂ molecules were localized by DFT calculations. The yellow arrows indicate the 3 different points of view shown as 1, 2 and 3 for better visualization of the 3D electrostatic map.



Figure S55. Electrostatic potential of the **PF4** ligands projected onto the CO_2 density isosurface. The CO_2 molecules were localized by DFT calculations. The yellow arrows indicate the 3 different points of view shown as 1, 2 and 3 for better visualization of the 3D electrostatic map.

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