Electronic Supplementary Information

Tuning the cavity properties of zirconium-based MIL-140 frameworks to modulate CO₂ adsorption

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Contents	Page number
S1 Syntheses.	S2
S2 X-ray powder diffraction (XRPD).	S3
S3 Nuclear magnetic resonance (NMR).	S7
S4 Thermogravimetric analysis (TGA).	S7
S5 Adsorption analysis.	S9
S6 Ideal adsorption solution theory (IAST) calculations.	S17
S7 Density Functional Theory (DFT) calculations for CO ₂ binding energy and location in MIL-	S18
140s	
S8 Parameter correlation study.	S20
S9 References.	S21

S1 Syntheses.

All chemicals and solvents were purchased from commercial sources and used as received without further purification.

S1.1 Ligand syntheses.

2-Fluoro-1,4-benzendicarboxylic acid (H_2bdc-F) ,¹ 2,2'-bipyridine-5,5'-dicarboxylic acid (H_2bpydc) ,² 3,3'-dimethylbiphenyl-4,4'-dicarboxylic acid $(H_2bpydc-Me)$,³ 3,3'-dichloro-4,4'-azobenzenedicarboxylic acid $(H_2azobdc-Cl)$,⁴ and azobenzene-4,4'-dicarboxylic acid $(H_2azobdc)^5$ were synthesised and characterised based on literature procedures.

S1.2 Microwave-assisted MIL-140 syntheses.

Powdered MIL-140 samples (MIL-140A, MIL-140A-NH₂, MIL-140A-F, MIL-140B, MIL-140C, MIL-140C-n (where n is the molar percentage of bpydc ligand in the MOF, n = 25, 50, 70, and 100), MIL-140C-Me and MIL-140D) were synthesised using a microwave-assisted solvothermal method in an Anton Paar Monowave 300 microwave oven as reported previously.^{1, 6} A 30-mL glass microwave vial was charged with 0.5 mmol ZrCl₄ (>99.5%, Sigma-Aldrich) and 0.5 mmol of the relevant ligand (refer to Table S1). Thereafter, acetic acid (99.9%, Ajax) and *N*,*N*-dimethylformamide (DMF, >99.5%, Ajax) were introduced. The mixture was heated with magnetic stirring to 220 °C within 1 min, and held at this temperature for 30 min before cooling to 55 °C within 2 min. The precipitates were isolated by vacuum filtration and washed with *N*,*N*-dimethylacetamide (DMA, >99.5%, Merck, 3 × 20 mL), and acetone (3 × 20 mL). The materials were subsequently solvent-exchanged with methanol by using a Soxhlet washing procedure for 16 h. The resulting powder was dried *in vacuo*.

A summary of the reaction conditions is provided in Table S1.

Compound	ZrCl ₄ [mmol]	mmol, Ligand ^b	DMF [mL]	Acetic acid [mL]	Temperature [°C]	Time [min]
MIL-140A	0.5	$0.5, H_2 bdc$	3	0.1	220	30
MIL-140A-NH ₂ ^a	0.5	0.5, H ₂ bdc-NH ₂	3	0.1	220	30
MIL-140A-F	0.5	0.5, H ₂ bdc-F	3	0.1	220	30
MIL-140B	0.5	$0.5, H_2$ ndc	3	0.1	220	30
MIL-140C	0.5	$0.5, H_2$ bpdc	3	0.25	220	30
MIL-140C-25	0.5	0.375, H ₂ bpdc/0.125, H ₂ bpydc	3	0.25	220	30
MIL-140C-50	0.5	0.5, H ₂ bpdc/0.5, H ₂ bpydc	3	0.25	220	30
MIL-140C-75	0.5	0.125, H ₂ bpdc/0.375, H ₂ bpydc	3	0.25	220	30
MIL-140C-100	0.5	0, H ₂ bpdc/0.5, H ₂ bpydc	3	0.25	220	30
MIL-140D	0.5	0.5, H ₂ azobdc-cl	3	0.2	220	30
MIL-140D-H	0.5	0.5, H ₂ azobdc	3	0.2	220	30

Table S1. Synthesis conditions for the MIL-140 samples.

^aThe addition of 0.1 mmol 1,3,5-benzentricarboxylic acid to the reaction medium for the synthesis of MIL-140A-NH₂ can greatly improve the purity and crystallinity of the product, as well as the reproducibility of the procedure. ^bH₂bdc (1,4-benzendicarboxylic acid, 99%, Sigma-Aldrich), H₂bdc-NH₂ (2-amino-1,4-benzenedicarboxylic acid, 99%, Sigma-Aldrich), H₂bdc-F, H₂ndc (2,6-naphthalenedicarboxylic acid, 99%, Sigma-Aldrich), H₂bpdc (biphenyl-4,4'-dicarboxylic acid, 97%, Sigma-Aldrich), H₂bpydc, H₂bpdc-Me, H₂azobdc-Cl, or H₂azobdc.

S2 X-ray powder diffraction (XRPD).

XRPD measurements were carried out on a PANalytical X'pert Pro diffractometer fitted with a solid-state PIXcel detector (45 kV, 40 mA, 1° divergence and anti-scatter slits, and 0.3 mm receiver and detector slits) using Cu-K α (λ = 1.5406 Å) radiation. Profile fits were performed using the *Le Bail* extraction method in GSAS.⁷



Figure S1. XRPD patterns of MIL-140C-n (n = molar percentage of bpydc linkers within the structure, bpydc = 2,2'-bipyridine-5,5'-dicarboxylate) and of the same batch of samples after a 4-d exposure to air.



Figure S2. XRPD patterns of activated MIL-140D, MIL-140D after a 4-d air-exposure, activated MIL-140D-H, MIL-140D-H after a 4-d air-exposure, and the collapsed MIL-140D-H sample after attempted re-solvation with DMF at room temperature for 24 h.



Figure S3. XRPD patterns of activated MIL-140A, MIL-140A-NH₂, MIL-140A-F, MIL-140B, MIL-140C, MIL-140C-25, MIL-140C-Me, and MIL-140D.

Table S2. Simulated *Le Bail* cell parameters for MIL-140A, MIL-140A-NH₂, MIL-140A-F, MIL-140B, MIL-140C, MIL-140C-25, MIL-140C-Me, and MIL-140D.

			Cell parameters							
Compound	Space group	<i>a</i> [Å]	<i>b</i> [Å]	с [Å]	α [°]	β [°]	γ [°]	Volume [Å ³]	Density [g.cm ⁻³] ^a	wRp [%] ^b
MIL-140A	C 2/c	24.37(1)	11.20(1)	7.84(1)	90	104.07(1)	90	2075.7(1)	1.74	11.55
MIL-140A-NH ₂	C 2/c	24.45(1)	11.21(1)	7.84(1)	90	104.19(1)	90	2085.0(1)	1.67b	7.40
MIL-140A-F	C 2/c	24.37(1)	11.24(1)	7.84(1)	90	103.69(1)	90	2086.7(1)	1.84	8.76
MIL-140B	Сс	26.79(1)	13.46(1)	7.84(1)	90	93.91(1)	90	2821.7(1)	1.51	12.16
MIL-140C	I 2/a	31.30(1)	15.64(1)	7.57(1)	90	84.51(1)	90	3689.1(3)	1.25	13.92
MIL-140C-25	I 2/a	30.49(1)	15.32(1)	8.47(1)	90	84.97(1)	90	3940.4(1)	1.05c	13.04
MIL-140C-Me	I 2/a	33.82(1)	15.56(1)	8.44(1)	90	112.62(1)	90	4098.4(2)	1.01d	9.37
MIL-140D	Сс	34.78(1)	17.60(1)	7.96(1)	90	93.17(1)	90	4866.1(4)	1.21	12.73

$$M_{L=140} = \frac{M_{cell}}{M_{cell}} \times 10^{24}$$

 $\rho_{MIL-140} = \frac{\rho_{MIL-140}}{N_A V_{cell}} \times 10^{24}$ a The density ($\rho_{MIL-140}$) can be expressed as: of MIL-140, M_{cell} = 8 × M_{MIL-140}, where M_{MIL-140} is the molecular weight of the corresponding sample (Table S3)), N_A is Avogadro's number (6.022 × 10²³), and V_{cell} is the volume of one unit cell as extracted from *Le Bail* method in GSAS; ^bwRp represents the initial weighted R-factor.



Figure S4. *Le Bail* refinements of MIL-140A, MIL-140A-NH₂, MIL-140A-F, MIL-140B, MIL-140C, MIL-140C-25, MIL-140C-Me, and MIL-140D showing the experimental (black), refined (red), and difference (blue) patterns. The positions of the Bragg peaks are indicated by the pink bars.



Figure S5. XRPD patterns of MIL-140A, MIL-140A-NH₂, MIL-140A-F, MIL-140B, MIL-140C, MIL-140C-25, MIL-140C-Me, and MIL-140D after 24-h liquid water treatment at room temperature

S3 Nuclear magnetic resonance (NMR).

¹H NMR spectra were recorded in deuterated solvents using a Bruker AVANCE200 or Bruker DPX400 NMR Spectrometer. The MIL-140C-25 (~20 mg) sample was digested in KOH/D₂O. The actual bpydc ligand loading was calculated by integrating the proton signals (as indicated in Figure S6) of the ligands in the ¹H NMR.



Figure S6. ¹H NMR spectrum of alkaline-digested (KOH/D₂O) MIL-140C-25. Molecular ratio between bpdc and bpydc ligands is 2.7 (bpdc = 4,4'-biphenyldicarboxylate; bpydc = 2,2'-bipyridine-5,5'-dicarboxylate). The theoretical value is 3.

S4 Thermogravimetric analysis (TGA).

TGA measurements were performed on a DISCOVERY TGA Thermogravimetric Analyzer. Approximately 10 mg of sample was placed on a platinum pan, which was heated under a flow of instrument air (20 mL.min^{-1}) at a rate of 5 °C.min⁻¹ up to 700 °C.

Compound	Formula	Molecular weight [g.mol ⁻¹]
MIL-140A	$[ZrO(C_8H_4O_4)]$	271.224
MIL-140A-NH ₂	$[ZrO(C_8H_5NO_4)]$	286.224
MIL-140A-F	$[ZrO(C_8H_3O_4F)]$	289.224
MIL-140B	$[ZrO(C_{12}H_6O_4)]$	321.224
MIL-140C	$[ZrO(C_{14}H_8O_4)]$	347.224
MIL-140C-25	$[ZrO(C_{14}H_8O_4)_{0.75}(C_{12}H_6N_2O_4)_{0.25}]$	347.224
MIL-140C-Me	$[ZrO(C_{16}H_{12}O_4)]$	375.224
MIL-140D	$[ZrO(C_{14}H_6N_2O_4C_{12})]$	444.224

Table S3. Formulae and molecular weights for MIL-140 samples.



Figure S7. Thermogravimetric analysis showing the weight loss (relative to ZrO_2) for MIL-140 frameworks upon heating in air. Dashed lines indicate the theoretical weight (relative to ZrO_2) for a given MIL-140 sample.



Figure S8. Thermogravimetric analysis (air environment) showing the weight loss (blue line) and derivative weight loss (green line) for activated MIL-140A, MIL-140A-NH₂, MIL-140A-F, MIL-140B, MIL-140C, MIL-140C-25, MIL-140C-Me and MIL-140D.

S5. Adsorption analysis.

 N_2 sorption isotherms were recorded on a 3Flex Surface Characterisation Analyser (Micromeritics Instruments Inc.). Prior to analysis, the materials were washed with MeOH as described in section S1.2. Then, approximately 100 mg of the powdered solid was loaded into a glass analysis tube and outgassed for 16 h under dynamic vacuum (~10⁻⁶ bar) at 220 °C. N_2 adsorption and desorption isotherms were measured at 77 K and the surface areas were calculated using the Brunauer–Emmett–Teller (BET)⁸ or Langmuir⁹ models. CO₂ adsorption and desorption isotherms were measured at 293, 303, and 313 K.



Figure S9. N_2 adsorption (filled circle) and desorption (open circle) isotherms, measured at 77 K.

The general BET equation can be expressed as shown in equation 1:8,10

$$\frac{P/P_0}{Q(1-\frac{P}{P_0})} = \frac{c-1}{Q_m c} P/P_0 \frac{1}{Q_m c}$$
(1)

In this equation, Q is the excess amount of N₂ adsorbed under a given equilibrium pressure P at 77 K, P/P_0 is the relative pressure (where $P_0 = 1$ atm and P is the saturation vapor pressure of N₂ at 77 K), Q_m is the monolayer adsorbed N₂ amount and c is the BET constant. The BET surface areas of MIL-140 samples were calculated with two consistency criteria suggested by Rouquerol and Snurr:^{10, 11} (i) within the pressure range chosen for the S_{BET} calculation, $Q(1-P/P_0)$ should always increase with increasing P/P_0 ; and (ii) the straight line fitted to the BET plot must have a positive intercept to yield a meaningful value for the c parameter (c > 0). The so-obtained value of Q_m is used to calculate the surface area from equation 2.

$$S_{BET} = \frac{Q_m S_0 N_a}{V_{STP}}$$

where N_A is Avogadro's number and S_0 is the cross-sectionional area of one nitrogen molecule in the liquid state (16.2 Å²).¹⁰ V_{STP} is the molar volume of N₂ at standard temperature and pressure (273 K, 1 atm), its value being 2.24 x 10⁴ cm³.mol⁻¹.

The general Langmuir equation can be expressed as shown in equation 3:12, 13

(2)

$$Q = \frac{bP}{1+bP}Q_m$$

(3)

In this equation, Q is the quantity of N₂ adsorbed at a given equilibrium pressure P at 77 K, Q_m is the quantity of N₂ gas molecules adsorbed when the entire surface is covered with a monolayer, and b is an empirical constant. If the model applies then a plot of P/Q vs. P gives a straight line from which b and Q_m can be determined from the slope and Y intercept. The Langmuir surface area (S_{Langmuir}) is then calculated from equation 4:

$$S_{Langmuir} = \frac{Q_m S_0 N_a}{m V_{STP}}$$

(4)

where N_A is Avogadro's number and S_0 is the cross-sectionional area of one nitrogen molecule in the liquid state (16.2 Å²).¹⁰ V_{STP} is the molar volume of N₂ at standard temperature and pressure (273 K, 1 atm), its value being 2.24 x 10⁴ cm³.mol⁻¹, and m is the mass of the adsorbing sample.



Figure S10. Consistency plot (a), BET fit (b), and Langmuir fit for MIL-140A ([ZrO(C₈H₄O₄)]).



Figure S110. Consistency plot (a), BET fit (b), and Langmuir fit (c) for MIL-140A-NH₂ ([ZrO(C₈H₅NO₄)]).



Figure S12. Consistency plot (a), BET fit (b), and Langmuir fit (c) for MIL-140A-F ([ZrO(C₈H₃FO₄)]).



Figure S13. Consistency plot (a), BET fit (b) and Langmuir fit (c) for MIL-140B ([ZrO(C₁₂H₆O₄)]).



Figure S14. Consistency plot (a), BET fit (b) and Langmuir fit (c) for MIL-140C ([ZrO(C₁₄H₈O₄)]).



Figure S15. Consistency plot (a), BET fit (b) and Langmuir fit (c) for MIL-140C-25 $([ZrO(C_{14}H_8O_4)_{0.75}(C_{12}H_6N_2O_4)_{0.25}]).$



Figure S16. Consistency plot (a), BET fit (b), and Langmuir fit (c) for MIL-140C-Me ([ZrO(C₁₆H₁₂O₄)]).



Figure S17. Consistency plot (a), BET fit (b), and Langmuir fit (c) for MIL-140D ([ZrO(C₁₄H₆N₂Cl₂O₄)]).

The pore-size-distribution calculations were carried out using the MicroActive software DFT package (non-local density functional theory calculations, NLDFT, based on the N_2 -Cylindrical Pores – Oxide Surface DFT model in the MicroActive software package, Micromeritics Instruments Inc.).



Figure S18. Goodness of fit and log goodness of fit plots of N₂ adsorption isotherm for MIL-140A ([ZrO(C₈H₄O₄)]).



Figure S19. Goodness of fit and log goodness of fit plots of N_2 adsorption isotherm for MIL-140A-NH₂ ([ZrO(C₈H₅NO₄)]).



Figure S20. Goodness of fit and log goodness of fit plots of N₂ adsorption isotherm for MIL-140A-F ([ZrO(C₈H₃FO₄)]).



Figure S21. Goodness of fit and log goodness of fit plots of N₂ adsorption isotherm for MIL-140B ([ZrO(C₁₂H₆O₄)]).



Figure S22. Goodness of fit and log goodness of fit plots of N2 adsorption isotherm for MIL-140C ([ZrO(C14H8O4)]).



Figure S23. Goodness of fit and log goodness of fit plots of N_2 adsorption isotherm for MIL-140C-25 ([ZrO(C₁₄H₈O₄)_{0.75}(C₁₂H₆N₂O₄)_{0.25}]).



Figure S24. Goodness of fit and log goodness of fit plots of N_2 adsorption isotherm for MIL-140C-Me ([ZrO(C₁₆H₁₂O₄)]).



Figure S25. Goodness of fit and log goodness of fit plots of N_2 adsorption isotherm for MIL-140D ([ZrO(C₁₄H₆N₂Cl₂O₄)]).

Calculation of the CO_2 heat of adsorption involves the generation of an interpolated curve by spline fitting of data points using MicroActive software (version 3.00, Micromeritics Instrument Corporation). This was used to fit data for CO_2 adsorption isotherms at 293, 303, and 313 K to the Clausius–Clapeyron equation, which was used to determine the isosteric enthalpy of adsorption at specific surface coverage.



Figure S26. CO₂ (filled circle) and N₂ (open circle) adsorption isotherms at 293, 303 and 313 K.



Figure S27. Isosteric heat (Q_{st}) of CO₂ adsorption.



Figure S28. Isostere plots (calculated from CO₂ adsorption isotherms at 293, 303, and 313 K) for MIL-140A, MIL-140A-NH₂, MIL-140A-F, MIL-140B, MIL-140C, MIL-140C-25, MIL-140C-Me, and MIL-140D.

Table S4. Comparison of physical properties and CO₂ adsorption performance for MIL-140 MOFs.

Compound	$\begin{array}{c} S_{BET} \\ [m^2.g^{\text{-1}}]^a \end{array}$	$\begin{array}{c} S_{Langmuir} \\ [m^2.g^{-1}]^a \end{array}$	$\begin{array}{c} V_{total} \\ [cm^3.g^{\text{-1}}]^a \end{array}$	d _{pore width} [Å] ^b	CO ₂ /N ₂ Selectivity ^c	$ Q_{st}^{0} $ [kJ.mol ⁻¹] ^d	$n_{\rm CO2}$ [mmol.cm ⁻³]
MIL-140A	396.4(0.9)	436.5(0.3)	0.16	5.6	32.9	29.98	1.54
MIL-140A-NH ₂	269.3(0.6)	322.8(1.6)	0.14	5.2	34.8	33.98	1.83
MIL-140A-F	350.3(0.7)	384.9(0.4)	0.16	5.4	12.6	36.21	0.88
MIL-140B	429.1(1.1)	467.1(1.8)	0.19	8.1	18.7	25.08	1.52
MIL-140C	660.8(0.5)	726.3(0.8)	0.27	9.9	12.9	22.19	1.58
MIL-140C-25	665.9(0.5)	724.4(1.8)	0.28	9.5	22.2	29.18	2.11
MIL-140C-Me	574.4(1.3)	657.8(2.0)	0.26	9.9	13.3	20.51	1.47
MIL-140D	830.6(1.9)	946.2(2.0)	0.37	10.6	8.6	13.30	1.14

^aCalculated from N₂ adsorption isotherm measured at 77 K; ^bcalculated from non-local density functional theory calculations, NLDFT, based on the N_2 -Cylindrical Pores – Oxide Surface DFT model in the MicroActive software package, Micromeritics Instruments Inc.; ^ccoadsorption selectivity at 293 K, $\alpha_{CO2/N2} = (Q_{CO2,0.15 \text{ bar}}/Q_{N2, 0.75 \text{ bar}})/(p_{CO2}/p_{N2})$; ^dcalculated from the CO₂ adsorption isotherms measured at 293, 303, and 313 K ^d At 293 K.

S6. Ideal adsorption solution theory (IAST) calculations.

A dual-site Langmuir-Freundlich (DSLF) equation:

$$N = N_A + N_B = \frac{N_{A,sat}k_A P^{n_A}}{1 + k_A P^{n_A}} \frac{N_{B,sat}k_B P^{n_B}}{1 + k_B P^{n_B}}$$

was used to fit the adsorption isotherm of pure CO₂ and N₂ gas, where *P* is the pressure of bulk gas at equilibrium with adsorbed phase, N_i is maximum loading in site (*i* = A and B), k_i is the affinity constant, and n_i is used to characterize the deviation from the simple Langmuir equation. The fitted parameters will then used to predict the adsorption of mixture based on ideal-adsorbed solution theory (IAST).²⁰ There is no restriction on the choice of the model to fit the adsorption isotherm, but data over the pressure range under study should be fitted very precisely.



Figure S29. IAST-predicted selectivity toward CO₂ and N₂ in a 15:85 mixture at 293 K.

		N _{i,A,sat}	k _{i,A}	n _{i,A}	N _{i,B,sat}	k _{i,B}	n _{i,B}
		mol kg ⁻¹	mbar-1	dimensionless	mol kg ⁻¹	mbar-1	dimensionless
MIL-140A	CO ₂	5.48	3.6778E-04	0.8812	-	-	-
	N ₂	3.02E-02	9.436E-14	4.34	1.42E+01	8.842E-07	1.089
MIL-140A-F	CO ₂	7.83E-01	1.149E-02	0.956	8.948E-02	1.120E-09	4.45
	N ₂	2.435	3.206E-05	1.459	-	-	-
MIL-140A-NH ₂	CO ₂	1.403	2.195E-02	0.887	3.671E-01	3.847E-06	2.514
	N ₂	3.974E03	1.687E-08	1.481	-	-	-
MIL-140B	CO ₂	1.221	5.213E-06	1.58	1.202	1.035E-03	0.992
	N ₂	2.50E-02	6.561E-15	4.705	2.239E01	1.163E-06	1.115
MIL-140C	CO ₂	1.155	1.171E-03	0.964	2.531	3.415E-06	1.623
	N ₂	1.512E01	5.857E-06	0.997	1.974E-02	4.692E-14	4.459
MIL-140C-25	CO ₂	3.628E01	1.156E-04	0.758	3.628E01	1.156E-04	0.758
	N ₂	3.99E-02	3.493E-05	1.841	1.954E-01	2.750E-10	3.164
MIL-140C-Me	CO ₂	2.212	3.563E-04	0.980	2.212	3.563E-04	0.980
	N ₂	2.11E-02	1.905E-14	4.619	1.929E01	3.199E-06	1.065
MIL-140D	CO ₂	3.26E-01	3.225E-09	2.697	1.530E03	4.536E-07	0.992
	N ₂	1.762E01	2.027E-06	1.105	1.774E-02	1.714E-14	4.665

Table S5. Fitted parameters using dual-site Langmuir-Freundlich (LF) for CO₂ and N₂.

S7. Density Functional Theory (DFT) calculations.

(a) Models for MIL-140s

Based on the parent structure of MIL-140A, the corresponding functionalized structures are built as described below. The hydrogen atom on the phenyl rings are substituted with the different functional groups studied in this work. Further, several initial models were generated by grafting the functional groups onto all the position positions on the BDC linkers. These models were then optimised using the Forcite module implemented in Material Studio software,²¹ based on the Universal force field (UFF)²² and the charges calculated based on Electronegativity Equalization method. For each modified form, the locations for the functional groups were identified by selecting those in the optimised structure with the lowest energy. Similarly procedure is employed to build the functionalized model for MIL-140C and MIL-140D structures respectively. Finally, density functional theory (DFT) geometry optimization procedure was further employed to refine the models using the experimentally obtained lattice parameters. Our DFT calculations were performed using density functional theory (DFT) as implemented in software package VASP. Electron exchange and correlation were described using the generalized gradient approximation form and the projector-augmented wave potentials were used to treat core and valence electrons. In all cases, we used a plane-wave kinetic energy cutoff of 600 eV and a Gamma-point mesh for sampling the Brillouin zone. The supercell vectors as well as all the ionic coordinates were relaxed until the Hellman-Feynman ionic forces were less than 0.02 eV/Å.

(b) Location and energy of CO₂ binding in MIL-140s

Static binding energies for CO₂ at 0 K were calculated using the van der Waals density functional (vdW-DF2) method.¹⁴ All calculations were performed using Vienna *ab initio* simulation package (VASP)^{15, 16} with a plane-wave energy cut-off of 600 eV and k-point sampling at the gamma-point. The interactions between core and valence electrons were described by the projector-augmented-wave (PAW) method and rPW86¹⁷ was used to parameterize the exchange-

correlation functional. The initial location of CO_2 in the periodic cell was obtained from the classical simulated annealing technique. In the simulated annealing method, the temperature was lowered stepwise, allowing the gas molecule to reach a desirable configuration based on different moves such as rotation, translation and re-positioning with preset probabilities of occurrence. This process of heating and cooling the system was repeated in several heating cycles to find the local minima. Forty heating cycles were performed where the maximum temperature and the final temperature were 10^5 K and 100 K, respectively. Static binding energies (ΔE) at 0 K were calculated using the following expression;

$$\Delta E = E_{MOF + gas} - E_{MOF} - E_{gas}$$

where E_x refers, respectively, to the total energies of the MOF + gas complex, the MOF alone, and gas molecule. In order to enable comparisons with experimental measurements of CO₂ adsorption enthalpies made at room temperature, both zero point and thermal energy corrections were included (~4 kJ/mol).^{18, 19}





(c) MIL-140A_NH₂, $BE_{CO2} = -37.97 \text{ kJ/mol}$

Figure S30. DFT-optimized locations of CO₂ in MIL-140A, MIL-140A_F, MIL-140A_NH₂, as well as the associated binding energies (BEs) calculated using vdW-DF2 method. Color code; C, grey; H, white; N, blue; F, cyan.

S8. Parameter-correlation study.



Figure S31. Relationships between $\alpha_{CO2/N2}$ and pore size (a); $\alpha_{CO2/N2}$ and pore volume (b); $\alpha_{CO2/N2}$ and BET surface area (c); $|Q_{st}^{0}|$ and pore size (d); $|Q_{st}^{0}|$ and pore volume (e); $|Q_{st}^{0}|$ and BET surface area (f); $|Q_{st}^{0}|$ for MIL-140 frameworks. MIL-140A-NH₂, MIL-140A-F, MIL-140C-25, and MIL-140D are not included in the linear regression.

S9. References.

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