Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Isostructural compartmentalized spin-crossover coordination polymers for gas confinement

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Supporting information

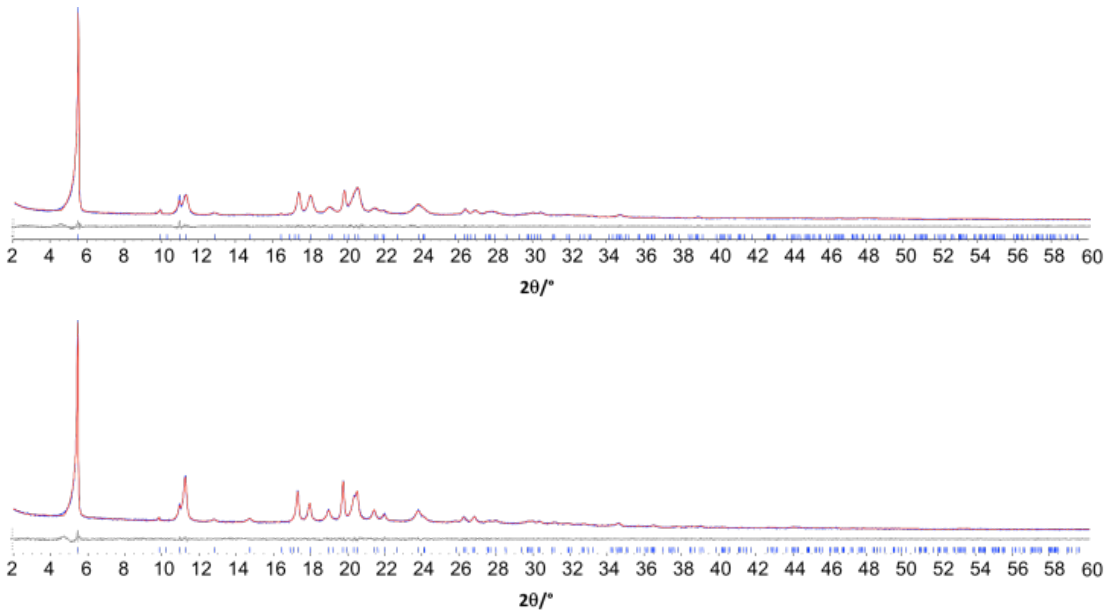


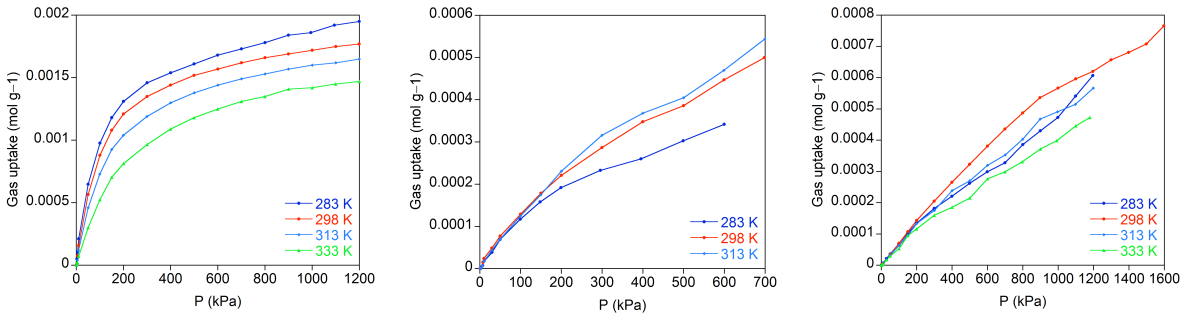
Figure S1. Observed (blue) and calculated (red) profiles and difference plot [(I_{obs} – I_{calcd})] (grey) of the Pawley refinements for compounds **CCP-3** (top) and **CCP-4** (bottom) (2θ range 2.0–60 °; maximum resolution 1.54 Å)

Table S1. Selected bond lengths (Å) and angles (°) for **CCP-4-HS** and **CCP-4-LS**

	CCP-4-HS (240 K)	**CCP-4-LS** (120 K)
Fe-N	2.16(3)	2.01(3)
N-Fe-N	86.54	88.02
	90.50	89.23
	91.30	91.27
	91.75	91.49
	176.54	179.14

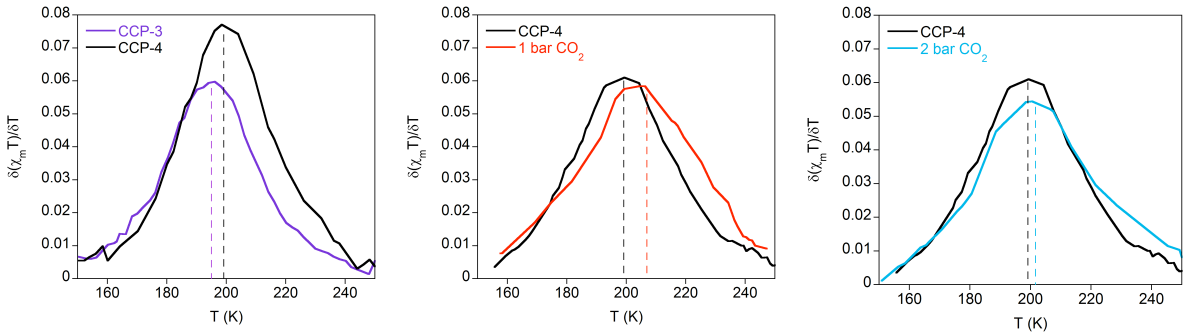
Table S2. Structural parameters for Pawley refinements for **CCP-3** and **CCP-4** at 298 K and those for single crystal refinement of **CCP-4** at 240 K

Compound	**CCP-3**	**CCP-4**	**CCP-4** (single crystal)
a (Å)	10.3551(7)	10.3633(5)	10.3650(10)
b (Å)	10.3551(7)	10.3633(5)	10.3650(10)
c (Å)	32.487(7)	32.303(5)	32.289(5)
α (°)	90	90	90
β (°)	90	90	90
γ (°)	120	120	120



a) b) c)

Figure S2. Adsorption isotherms for **CCP-4** collected at different temperatures for a) CO_2, b) CH_4 and c) N_2



a) b) c)

Figure S3. Derivative of the product $\chi_M T$ for a) **CCP-3** and **CCP-4** as synthesized, b) activated **CCP-4** and the same material with one molecule of CO_2 loaded and c) activated **CCP-4** and the same material with two molecules of CO_2 loaded

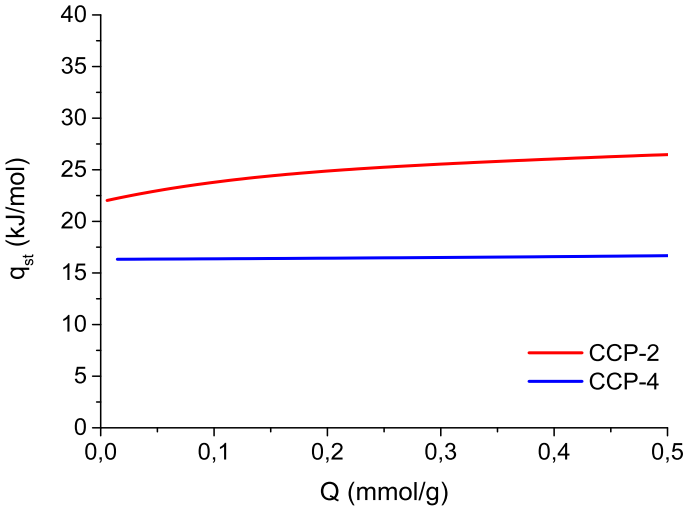


Figure S4. Plot of the isosteric heats of adsorption of CO_2 in **CCP-2** and **CCP-4**.

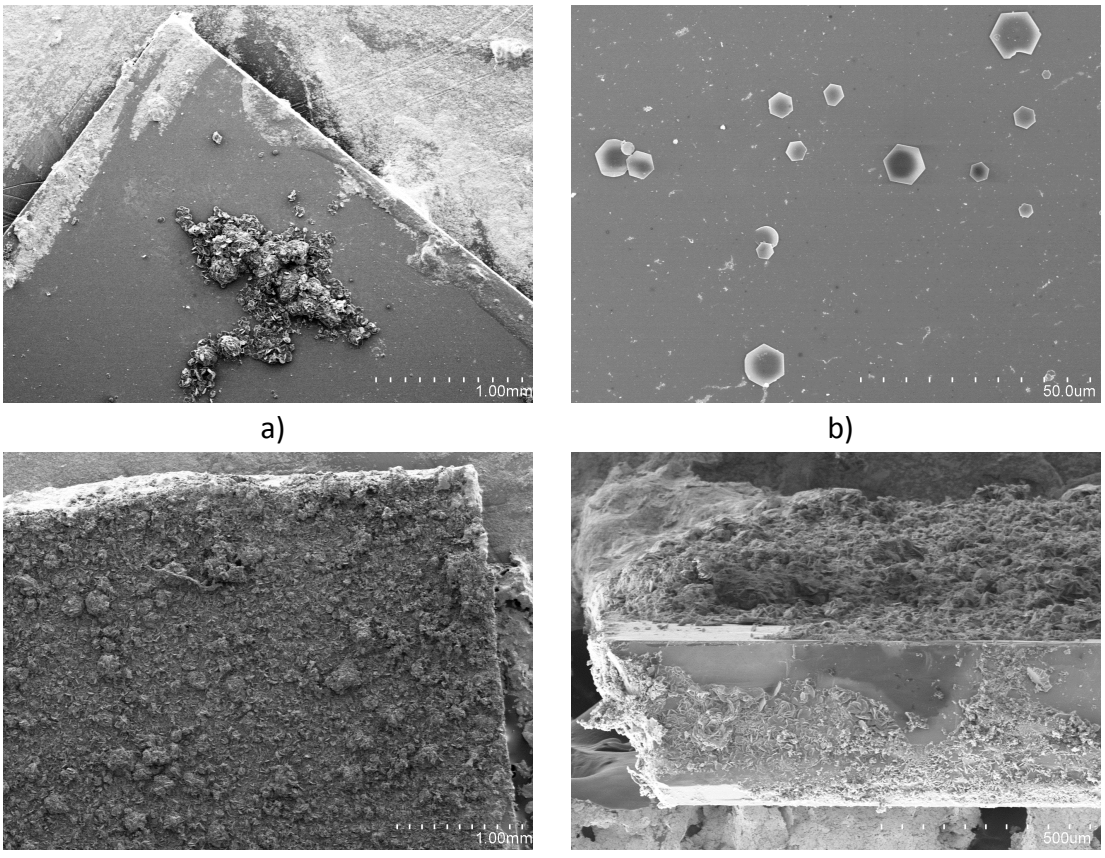


Figure S5. SEM images for the deposition of **CCP-4**. a) Uncomplete deposition in quartz substrate, b) hexagonal microcrystals in quartz substrate, c) complete deposition in silicon substrate and d) lateral view of the silicon substrate, the 400 µm layer of **CCP-4** can be seen.

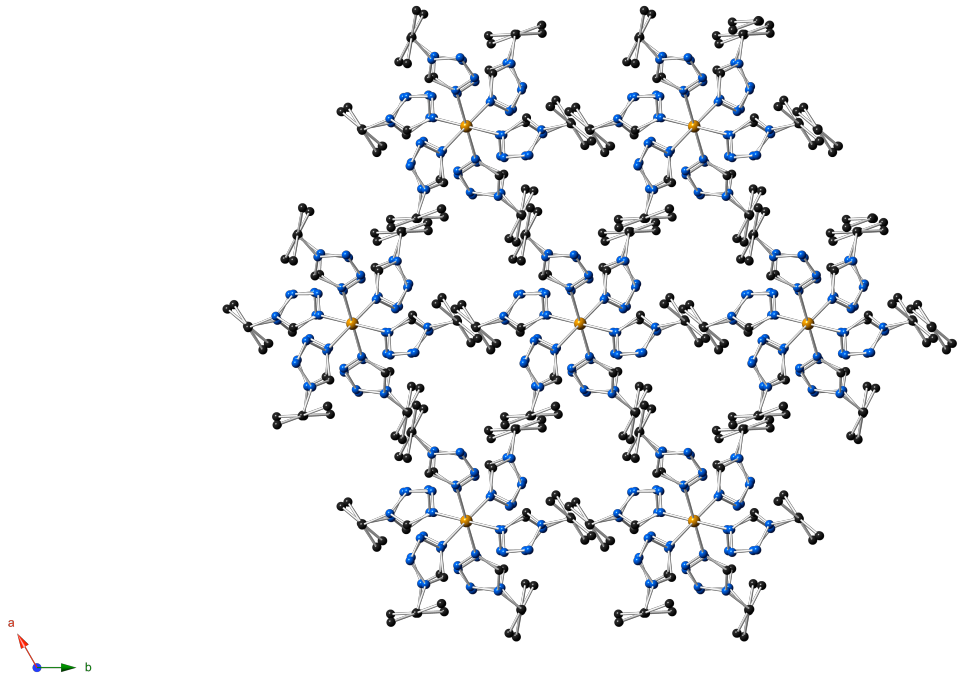


Figure S6. Hexagonal packing of **CCP-4** viewed along the *c*-axis. The BF_4^- anions and hydrogen atoms have been removed for clarity. Key: Fe, orange; C, gray; N, blue.

X-ray crystal analysis of compound CCP-4

The issues on the structural refinement are likely due to the weak diffraction data at high angles (see Figure S7.left), which is caused by the tiny size of the crystals (Figure S7.right).

Restraints on all aromatic rings and on chemical bonds have been applied to maintain chemical sense, and only the Fe centre has been refined anisotropically. All attempts to crystallize larger crystals have been unsuccessful. The high R_{int} could be indicative of the wrong space group, although in this case it is caused by the weak diffraction at high angles. This has been confirmed by performing the data reduction with a resolution of 1.5 Å, for which the R_{int} is reduced to 0.11 (**CCP-4-LS**) and 0.14 (**CCP-4-HS**).

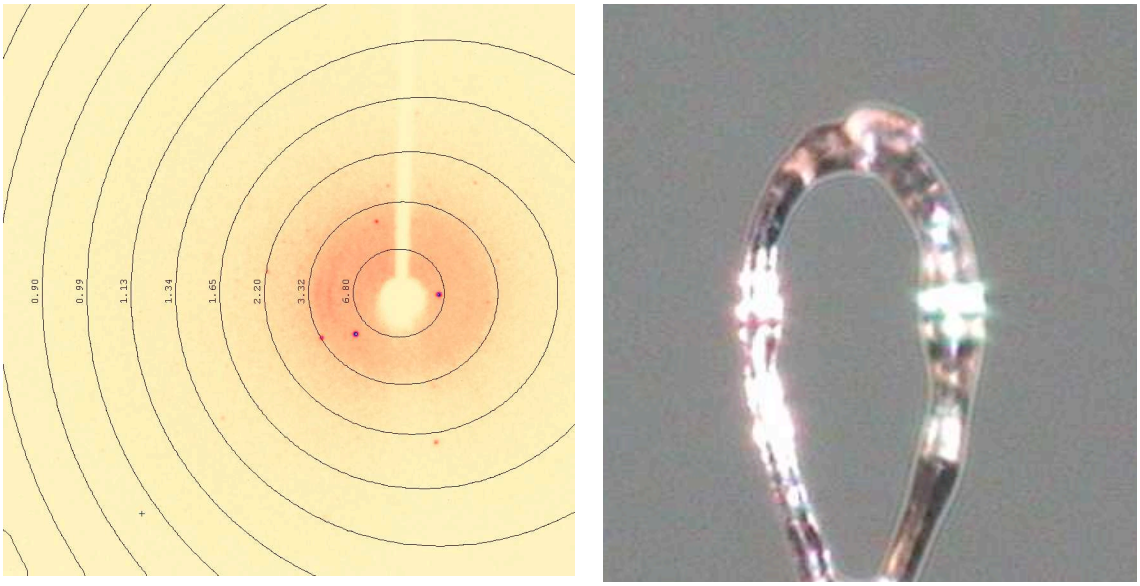


Figure S7. (left) diffraction data of compound **CCP-4-LS**. (right) Picture of the solved crystal.

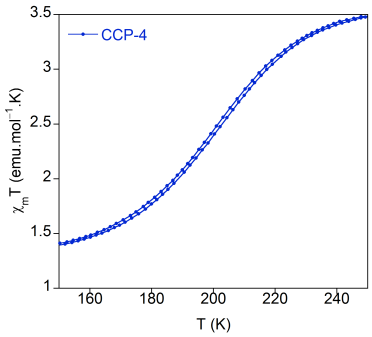


Figure S8. Magnetic behavior of **CCP-4** deposited on a silicon substrate.

Table S3. Crystallographic data for **CCP-2–HS** and **CCP-2–LS**.

Compound	**CCP-4–HS**	**CCP-4–LS**
Empirical formula	$C_{48}H_{42}N_{24}B_2F_8Fe$	$C_{48}H_{42}N_{24}B_2F_8Fe$
Formula weight	1184.53	1184.53
Crystal color	Colorless	Pink
Crystal size (mm^3)	0.06 × 0.06 × 0.01	0.05 × 0.05 × 0.02
Temperature (K)	240(2)	120(2)
Crystal system, Z	Hexagonal, 2	Hexagonal, 2
Space group	$P6_3$	$P6_3$
a (Å)	10.3650(10)	10.2235(14)
b (Å)	10.3650(10)	10.2235(14)
c (Å)	32.289(5)	31.903(8)
α (°)	90.00	90.00
β (°)	90.00	90.00
γ (°)	120.00	120.00
V ($Å^3$)	3004.2(6)	2887.8(11)
ρ_{calc} (Mg/m^3)	1.309	1.362
$\mu(Mo_{K\alpha})$ (mm^{-1})	0.330	0.344
θ range (°)	3.39 – 25.02	2.99 – 25.03
Reflns collected	24825	11791
Independent reflns (R_{int})	3571 (0.4179)	3408 (0.2722)
Reflns used in refinement, n	3571	3408
L. S. parameters, p/ restraints, r	90/46	60/46
$R1(F)$,[a] $I>2\sigma(I)$	0.2271	0.2157
$wR2(F^2)$,[b] all data	0.5406	0.5271
$S(F^2)$,[c] all data	1.232	1.150

[a] $R1(F) = \Sigma(||F_O| - |F_C||)/\Sigma|F_O|$; [b] $wR2(F^2) = [\Sigma w(F_O^2 - F_C^2)^2/\Sigma wF_O^4]^{1/2}$; [c] $S(F^2) = [\Sigma w(F_O^2 - F_C^2)^2/(n + r\text{—} p)]^{1/2}$