

Hierarchically porous metal–organic frameworks with red topology for hydrogen and methane storage

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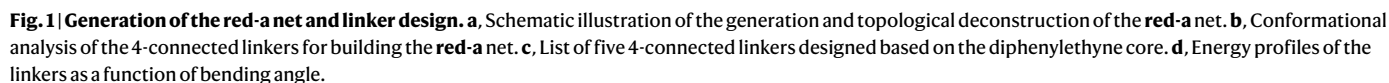
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The construction of highly porous metal–organic frameworks with complex topologies requires precise matching between linker conformation and node connectivity. Here we report the reticular design and synthesis of CU-6-M (M = Fe or Cr), assembled from conformationally adaptive diphenylethynyl linkers and six-connected trinuclear oxo-centred clusters. The ability of the linker to adopt multiple out-of-plane conformations satisfies the geometric requirements of a **red** topology, resulting in a highly interconnected hierarchical pore architecture. CU-6-Fe and CU-6-Cr exhibit an interconnected hierarchical pore system with Brunauer–Emmett–Teller surface areas up to 7,145 m² g^{−1}. This architecture enables total H₂ uptakes of up to 17.5 wt% and 45.4 g l^{−1} at 100 bar and 77 K. Under temperature–pressure swing conditions, CU-6-Fe and CU-6-Cr deliver up to 16.9 wt% and 44.1 g l^{−1} and also show record gravimetric CH₄ storage at ambient temperature. These results establish linker flexibility as a key design parameter for the realization of complex, highly porous topologies for high-capacity storage of clean-energy fuel gases.

Topology-guided design enables systematic expansion of metal–organic framework (MOF) structural diversity while providing control over framework connectivity and pore architecture to tune functional properties^{1,2}. Central to this approach is reticular chemistry, which enables the controlled assembly of multitopic organic linkers with inorganic nodes into crystalline structures with well-defined topology, geometry and connectivity^{3,4}. This ‘design by topology’ strategy allows key structural features to be encoded at the molecular level, thereby minimizing reliance on trial-and-error synthesis⁵. Topologically, the number of symmetry-independent vertices and edges are defined as the minimum possible based on the principle of minimal transitivity,

favouring simpler and more predictable framework topologies⁶. Trinodal nets with transitivity [3 2], containing three types of node and two types of edge, are particularly suitable for constructing MOFs from branched polytopic linkers^{2,7}. Their topological flexibility can accommodate large organic linkers and highly connected metal nodes, producing complex polyhedral pores and large void volumes⁸. Although many such nets can theoretically be derived from parent minimal edge-transitive nets with transitivity [2 1], their experimental realization remains challenging². Recent advances in the molecular building block and supramolecular building block (SBB) methods⁹, edge expansion strategies¹⁰ and merged-net approaches¹¹ have enabled access to

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Here we report the design and synthesis of a highly interconnected hierarchically porous MOF featuring a rare **red** topology. Guided by the analysis of structural requirements for constructing **red** nets, particularly focusing on the bending behaviour of organic linkers, we selected a semi-rigid diphenylethynyl-based linker capable of adopting multiple out-of-plane conformations. Although its ethynyl spacer is linear and rigid, rotation and bending of the adjacent phenyl rings provide sufficient conformational flexibility to accommodate different coordination geometries and framework curvatures. Combining this linker with a 6-connected oxo-centred metal cluster (M_6O) forms a

three-dimensional (3D) **red** net as the sole crystalline phase. Building on this design strategy, we synthesized **CU-6-Fe** and **CU-6-Cr** (CU stands for Cambridge University), exhibiting a high Brunauer–Emmett–Teller (BET) surface area of 7,145 m² g^{−1}. **CU-6-Fe** and **CU-6-Cr** show gravimetric H₂ uptakes of 17.5 and 15.9 wt%, respectively, at 100 bar and 77 K, while maintaining high volumetric uptakes of 45.4 and 45.5 g l^{−1}. In addition, computational analysis demonstrates that linker flexibility and precise control of metal-cluster connectivity are critical for constructing topologically complex, highly porous MOFs for clean energy storage.

Generation of red net and linker design

The augmented **red** (**red-a**) net with transitivity [4 9] can be theoretically derived from the parent **reo** net through edge expansion followed by face decoration of the 4-connected nodes²⁹. This topology contains rhombicuboctahedral (rco), cubic (cub) and cuboctahedral (cuo) cavities, and can be viewed as a corner-sharing assembly of alternating cubes, similar to MIL-hypo-1³⁰ (Fig. 1a). Topologically, it comprises both 4-connected and 6-connected nodes. Geometrical analysis shows that the 4-connected units adopt two conformations: planar and slightly bent. Although two different rigid 4-connected linkers could, in principle, realize this topology (Fig. 1b), this strategy often gives mixed phases. We therefore reasoned that a conformationally flexible linker could accommodate both geometries within one framework (Fig. 1b), enabling the targeted **red-a** net.

To test this hypothesis, we selected a conformationally adaptive diphenylethyne core (–Ph–C≡C–Ph–), which enables different bending angles depending on the molecular environment³¹. Five 4-connected linkers based on this core were designed with increasing lengths and evaluated by density functional theory (DFT) calculations, with total energy plotted as a function of bending angle relative to the linear configuration (Fig. 1c,d; more details in Supplementary Section 2). Linkers H₄L1, H₄L2 and H₄L4 exhibit monotonic energy increases on bending, indicating a preference for linear conformations. H₄L2, which contains only one triple bond, shows the steepest energy increase and therefore the lowest tolerance for angular distortion. By contrast, H₄L3 and H₄L5 initially decrease in energy on bending, reaching minima at 15° and 21°, respectively, before starting to increase. These profiles indicate that both linkers favour moderately bent conformations and can accommodate bending over defined angular ranges with minimal energetic penalty. The contrasting behaviour of H₄L3 and H₄L4 further shows that linker flexibility is not governed by length alone, but also by molecular geometry. H₄L3 and H₄L5 were therefore identified as promising candidates for constructing **red-a** net. We selected H₄L3 for subsequent synthesis because of its simpler preparation and potential to afford a higher-density framework (Supplementary Figs. 2–6). For clarity, H₄L3 is hereafter referred to as H₄L.

Synthesis and characterization

Heating H₄L, FeCl₃·6H₂O and 4-nitrobenzoic acid in a dimethylformamide (DMF) solution afforded red-coloured cubic single crystals, denoted as **CU-6-Fe**. Given the excellent hydrolytic stability of oxo-centred trinuclear Cr(III) cluster (Cr₃O) based-MOFs^{32,33}, we performed the postsynthetic Cr(II) metathesis on **CU-6-Fe** to give green cubic crystals of **CU-6-Cr** (Supplementary Fig. 11). Synchrotron single-crystal X-ray diffraction (SCXRD) analysis revealed that **CU-6-Cr** crystallizes in the cubic space group *P* $\bar{4}3m$ with *a* = 50.2563(1) Å (Supplementary Table 1), formulated as (Cr₃(μ₃-O)(H₂O)₂(OH)(L)₁₅). The linkers **L** adopt two crystallographically independent conformations, termed **L_a** and **L_b**, with out-of-plane bending angles of approximately 3° and 13° (Fig. 2a,b and Supplementary Figs. 15 and 18). Assembly of 4-connected linkers **L** and 6-connected Cr₃O clusters results in a distorted cube (cub) polyhedron (Fig. 2c), which serves as the basic SBB for **CU-6-Cr**. Each cub SBB consists of two **L_a** and four **L_b** linkers, with half of them adopting either horizontal or vertical

orientations (Fig. 2d). Such a spatial arrangement results in a geometric distortion to the cub SBB, highlighting the conformational flexibility of linker **L**. Adjacent corner-sharing cub SBBs are eclipsed and staggered (Fig. 2e). Six pairs of cub SBBs further assemble into a rco cavity (Fig. 2f and Extended Data Fig. 1), with twelve of its square faces capped by inward-bent **L_b** linkers. The remaining square and triangular faces remain open as guest-accessible windows (Supplementary Fig. 19). The triangular windows are framed by three planar **L_a** linkers, whereas the distorted square windows are defined by four bent **L_b** linkers (Fig. 2g,h and Supplementary Fig. 19). These non-planar square windows interconnect adjacent rco polyhedrons into a continuous 3D network (Fig. 2j and Supplementary Fig. 20). Each cub SBB connects to four surrounding rco polyhedrons through four of its six square faces, which are capped by bent linkers **L_b** (Fig. 2i). Further stacking of eight neighbouring rco polyhedrons produces the third polyhedron, cuo (Fig. 2j,k, Extended Data Fig. 1 and Supplementary Fig. 21), whose six square faces are capped by six **L_a** linkers, while the eight remaining triangular faces are shared with eight surrounding rco polyhedrons. These triangular openings act as interconnected channels between the rco and cuo polyhedrons, further enriching the hierarchical nature of **CU-6-Cr** (Fig. 2j,k, Extended Data Fig. 1 and Supplementary Fig. 22).

The structure of **CU-6-Cr** can be viewed as a 3D framework formed by the face-sharing assembly of cub, cuo and rco polyhedrons (Fig. 3a,d and Supplementary Fig. 23), generating a hierarchical pore architecture with three types of well-defined polyhedral cavities (Fig. 3b,d). The distorted cub pore adopts an ellipsoidal shape with dimensions of 1.6 × 2.4 × 2.4 nm³. The cuo cavity features a larger internal diameter of 2.6 nm and two distinct triangular apertures of 1.6 and 1.8 nm. The largest rco cavity has an internal diameter of 4.1 nm and three types of aperture: two are shared with the cuo cavities, while the third, measuring 1.8 nm, connects neighbouring rco cavities. The integration of these polyhedral cavities results in a highly interconnected 3D porous network (Fig. 3c and Supplementary Figs. 20 and 22). The calculated total solvent accessible volume is 89.7% using a probe radius of 1.2 Å (ref. 34). Topologically, **L_a** and **L_b** linkers can be simplified as two different 4-connected units (Fig. 3e). Their combination with 6-connected trigonal prismatic Cr₃O nodes forms an augmented 4,4,6-connected trinodal **red** net with the point symbol of {4⁴.6²}.₃{4⁶.6⁷.8²}.₂ (Fig. 3e and Supplementary Fig. 24). Natural tiling analysis shows five distinct types of tile with transitivity [3 2 5 5] (Fig. 3f and Supplementary Fig. 25). Each largest blue tile with the face symbol of [6⁸.8⁶], representing the largest cavity, connects to the adjacent identical tiles and green tiles [6⁸] via the purple [4⁴.8²] and pink tiles [4³.6²] (Fig. 3g and Supplementary Fig. 25). Although a previous theoretical study predicted the existence of the **red** topology²⁹, its experimental realization has not yet been reported. The successful construction of **CU-6-Cr** with such a complex topology while maintaining high phase purity highlights the importance of rational integration of a conformationally flexible linker backbone with a well-defined branch length in framework assembly. In particular, the incorporation of flexible ethynylene units into the linker proved essential for accommodating the geometric requirements of the **red** net structure.

Following transmetalation, inductively coupled plasma atomic emission spectroscopy (ICP-AES) confirmed nearly complete exchange of Fe³⁺ by Cr³⁺, with ~0.08 wt% Fe content detected. Although the synchrotron SCXRD data for **CU-6-Fe** remained insufficient for structure solution due to weak diffraction, its indexing yielded a cubic unit cell with *a* = 50.3292(1) Å, slightly larger than that of **CU-6-Cr** (Supplementary Figs. 29 and 30). We built a structural model for **CU-6-Fe** on the basis of the refined **CU-6-Cr** structure and the indexed unit cell parameters. In addition to synchrotron SCXRD, scanning transmission electron microscopy (STEM) enabled direct visualization of the highly porous structure of **CU-6-Fe**, despite its high electron-beam sensitivity³⁵. Under low-dose conditions, we imaged **CU-6-Fe** and **CU-6-Cr** using

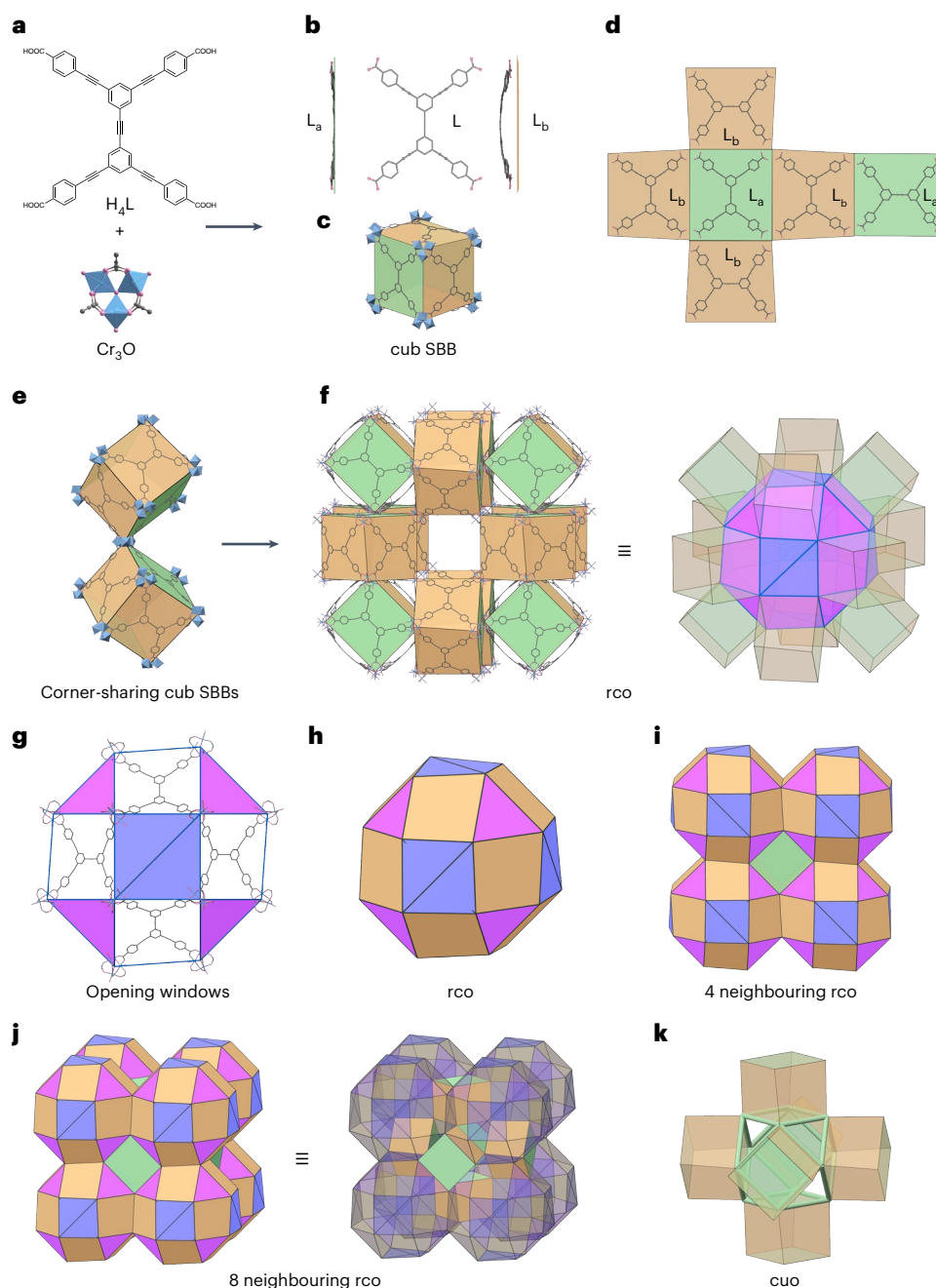


Fig. 2 | Structural assembly of CU-6-Cr by SBB approach. **a**, Representation of organic linker H_4L and Cr_3O cluster. **b**, Representation of the two distinct bending conformations of the linkers L . **c**, The cub SBB constructed by six linkers L and eight Cr_3O clusters. **d**, Two-dimensional projected net of cub SBB. Green squares: planar linkers L_a ; yellow squares: out-of-plane bent linkers L_b . **e**, Representation of the corner-sharing cub SBB. **f**, The rco polyhedron assembled by cub SBBs. **g**, Opening windows within rco. Pink triangles are formed by three linkers L_b ; blue

squares are formed by four linkers L_b . Note that blue squares can be seen as two adjacent triangular faces due to the slight non-coplanarity of its four vertices. **h**, The rco composed of six blue squares, eight pink triangles and twelve yellow squares, showing the opening windows and closed faces by linkers L_b . **i**, Face-sharing packing of four neighbouring rco, surrounding one centring cub SBB. **j**, Face-sharing packing of eight neighbouring rco, surrounding six centring cub SBBs and one cuo. **k**, Representation of cuo formed by six cub SBBs.

STEM through both annular dark-field (ADF) and integrated differential phase contrast (iDPC) modes (Fig. 3h–k and Supplementary Figs. 32 and 33). Both ADF and iDPC images overlaid well with the simulated **CU-6-Fe** structure (Fig. 3i,k), confirming the high structural order of the crystals. STEM images collected along the [100] direction possess the plane group symmetry $p4mm$, and the corresponding selected area electron diffraction pattern has $4mm$ Laue symmetry in 2D (insets in Fig. 3h,j), which are both consistent with the space group $P43m$. The phase purity of the bulk **CU-6-Cr** was confirmed by the well-matched simulated and experimental powder X-ray diffraction patterns

(Supplementary Fig. 35). **CU-6-Fe** shows similar characteristic diffraction peaks, although with weaker overall intensities (Supplementary Fig. 35). To examine the role of linker flexibility in forming **red-a** net, we tested the ability of the less flexible H_4L2 linker to form Fe-based MOFs. Despite extensive synthetic efforts, it consistently produced competing mixed phases and resulted in only a low yield of the **red-a** net. Together, these contrasting outcomes for H_4L2 and H_4L linkers support the predictive potential of the topology-guided design strategy (Fig. 1 and Supplementary Figs. 7–10, 12, 13, 26–28, 31, 34 and 36; more details in Supplementary Note 1).

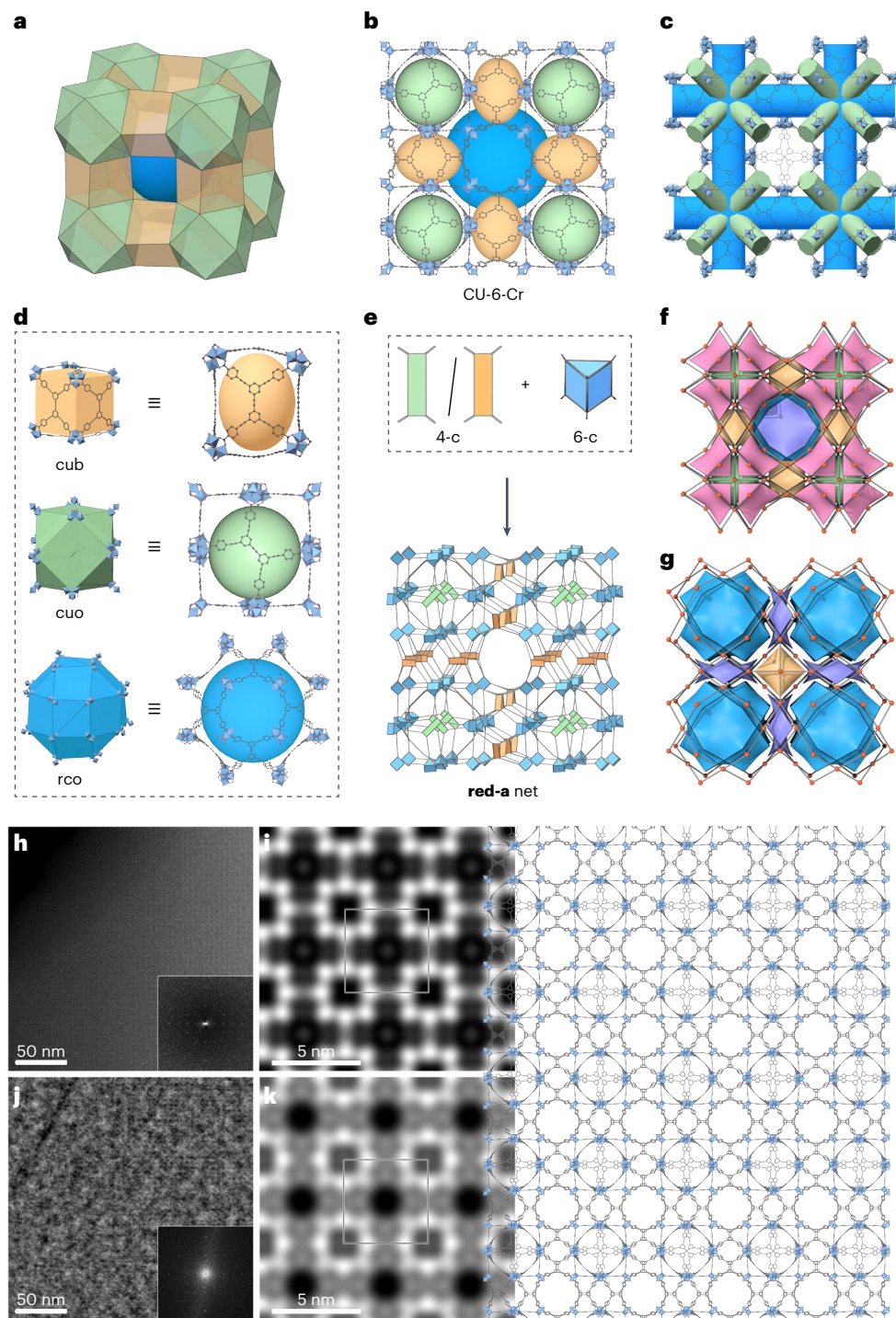


Fig. 3 | Structural description of CU-6. **a, b**, Representation of the hierarchical cub, cuo and rco cavities for the **red-a** framework (**a**) and within CU-6-Cr (**b**). Colour code: yellow, cub; green, cuo; blue, rco. **c**, 3D interconnected channels connecting adjacent rco cavities (in blue), and cuo and rco cavities (in green). **d**, Representation of the cub, cuo and rco polyhedrons and related cavities. Cavity size is determined by the diameter of the largest sphere or ellipsoid that fits into the cavity. **e**, Simplified 4-connected linkers, 6-connected trigonal prismatic cluster and 4,4,6-connected augmented red topology of CU-6-Cr. Colour code: Cr₃O, blue polyhedron; linker L, green and yellow polyhedrons; C, grey; O, pink; H atoms are omitted for clarity. **f**, Natural tiling of the **red-a** net.

g, Packing of the adjacent tiles [$6^8.8^6$]. **h, j**, ADF (**h**) and iDPC STEM (**j**) images of a crystal of CU-6-Fe viewed along the [100] orientation, as well as the overlaid CU-6-Fe structure. Insets in **h** and **j** show the Fourier transformations of each respective STEM image. **i, k**, Lattice-averaged projected potential maps obtained from the images in **h** (**i**) and **j** (**k**), with $p4mm$ plane group symmetry imposed. Both images are in good correspondence with the crystal structure of CU-6-Fe viewed along [100]. The ADF image emphasizes heavier elements, clearly highlighting the positions of Fe ions in the crystal structure, while the iDPC image provides more contrast to lighter atoms such as carbon and oxygen, accentuating the linker molecules.

Porosity and high-pressure H₂ and CH₄-storage performance

The well-defined hierarchical and interconnected pores within CU-6-Fe and CU-6-Cr are expected to promote high gas uptake.

Screening of activation conditions showed that supercritical CO₂ activation was required to achieve the highest N₂ uptakes at 77 K (Supplementary Fig. 37). As shown in Fig. 4a, b, CU-6-Fe and CU-6-Cr exhibit identical multi-stepped isotherms, with CU-6-Fe consistently

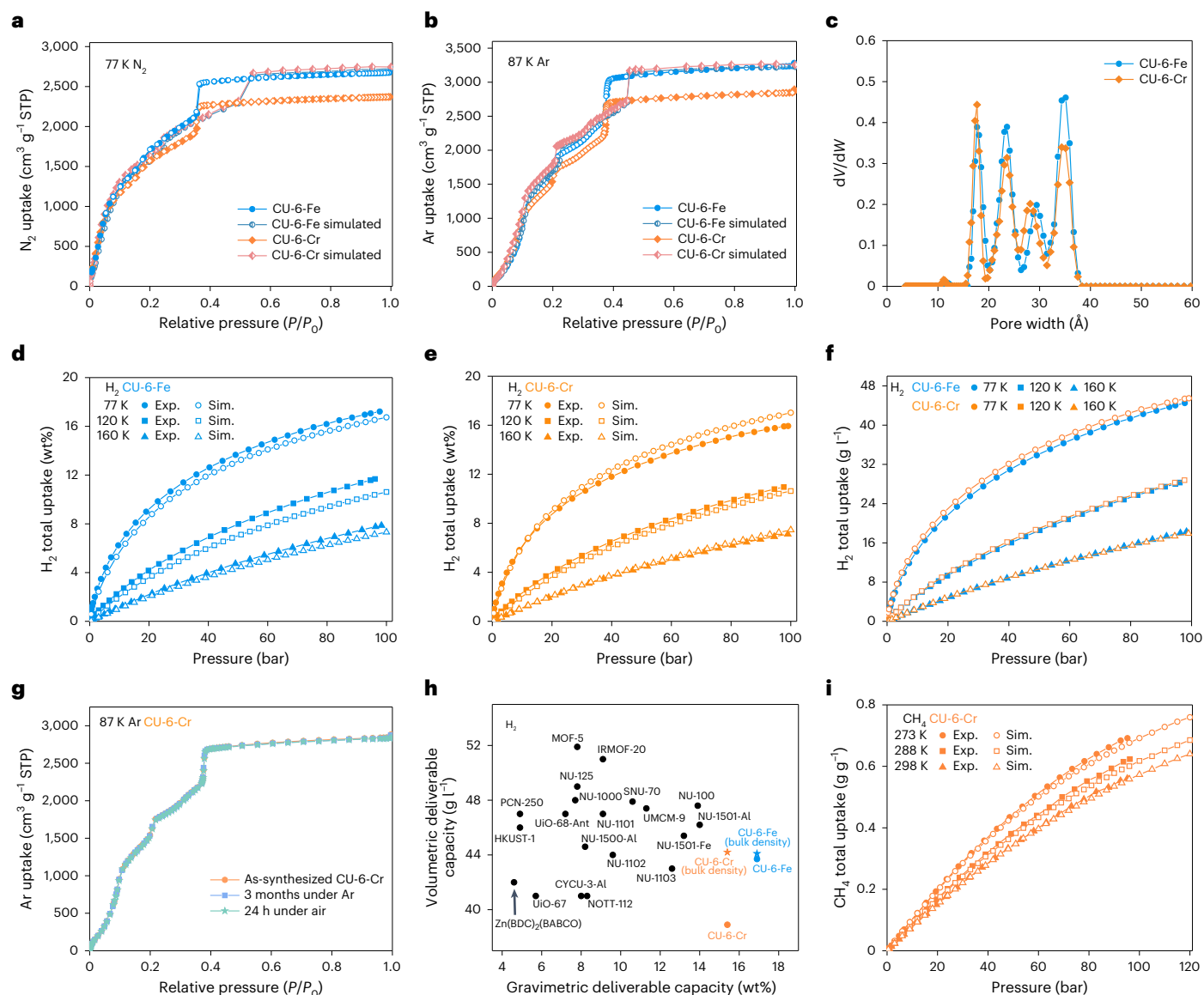


Fig. 4 | Porosity characterization and high-pressure gas-storage performance of CU-6-Fe and CU-6-Cr. **a**, Experimental (Exp.) and simulated (Sim.) 77 K N_2 isotherms. **b**, Experimental and simulated 87 K Ar isotherms. **c**, Pore-size distribution calculated from Ar adsorption isotherms. V and W denote the cumulative pore volume and pore width, respectively. **d**, **e**, Simulated and total gravimetric H_2 -adsorption isotherms measured at 77, 120 and 160 K: CU-6-Fe (**d**) and CU-6-Cr (**e**). **f**, Total volumetric H_2 -adsorption isotherms measured at

77, 120 and 160 K. **g**, 87 K Ar adsorption isotherms of CU-6-Cr after exposure to Ar and air. **h**, Comparison between the total gravimetric and volumetric deliverable H_2 capacity under temperature–pressure swing conditions: 77 K–100 bar to 160 K–5 bar. Bulk-density-based data points for CU-6-Fe and CU-6-Cr are also included. **i**, Simulated and total gravimetric CH_4 -adsorption isotherms for CU-6-Cr measured at 273, 288 and 298 K.

showing higher uptake than CU-6-Cr in both 77 K N_2 and 87 K Ar adsorption measurements. Among them, the steps present in the 87 K Ar adsorption isotherm are better defined than in the 77 K N_2 isotherm³⁶. Thus, our subsequent pore-size analyses are based on 87 K Ar isotherms. Both materials display a combination of type I and IV isotherms, characterized by four clear, well-defined adsorption steps at relative pressures $P/P_0 = 0.0001$, 0.10, 0.21 and 0.38, along with a minor step at $P/P_0 = 0.30$. Non-local DFT analysis reveals identical hierarchical pore-size distributions for the two frameworks, with four main maxima centred at approximately 1.7, 2.3, 2.9 and 3.5 nm, and an additional minor peak at around 1.2 nm for CU-6-Fe (Fig. 4c).

We then performed grand canonical Monte Carlo (GCMC) simulations of 77 K N_2 and 87 K Ar isotherms (Fig. 4a,b and Supplementary Figs. 39–42). For CU-6-Fe, the simulated isotherms agree closely with the experimental data and reproduce the five

characteristic steps observed experimentally. By contrast, the simulations overestimate the uptake of CU-6-Cr, despite its unit cell parameters being nearly identical to those of CU-6-Fe. Such discrepancies are commonly associated with inaccessible porosity, non-porous impurities or defects, which can arise during transmetalation^{37–39}. In our case, consistent 77 K N_2 isotherms obtained across three independent batches of CU-6-Cr (Supplementary Fig. 43) confirmed reproducibility. Although powder X-ray diffraction showed no evidence of crystalline Cr_2O_3 phases in CU-6-Cr, the reduced capacity may be rationalized by the presence of dispersed amorphous chromium species within the framework or other potential defects. Analysis of the simulated 87 K Ar adsorption isotherm of CU-6-Cr reveals sequential filling of cub, cuo and rco pores (Extended Data Fig. 2a). Extended Data Figs. 2c and 3 and Supplementary Video 1 show these spatial volumes occupied by Ar at each adsorption step inside the relevant cavity as well as their

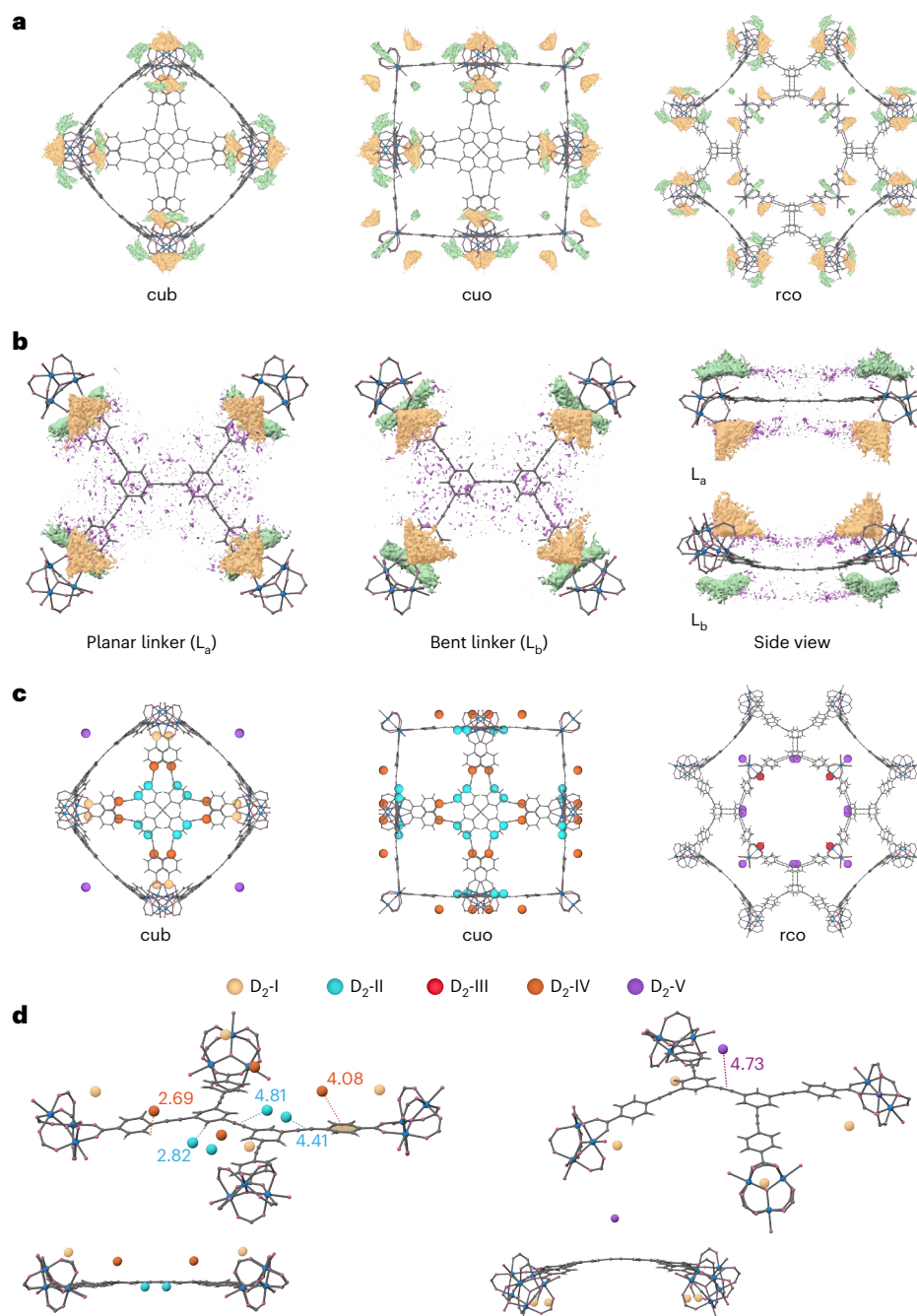


Fig. 5 | Theoretical and experimental insights on H₂ binding sites. a, 3D probability maps of H₂ binding sites I and II, revealed by GCMC simulations, in cub, cuo and rco cavities. **b**, 3D probability maps of H₂ binding sites I, II and III around the planar (L_a) and bent (L_b) linkers. **c**, Views of NPD-derived adsorption

sites within the cub, cuo and rco cavities. **d**, NPD-derived adsorption sites adjacent to the planar linker (L_a) and bent linker (L_b). GCMC colour code: site I in yellow; site II in green and site III in purple; NPD colour code: site D₂-I in yellow, site D₂-II in cyan, site D₂-III in red, site D₂-IV in brown and site D₂-V in purple.

corresponding locations within the unit cell (more details in Supplementary Note 2).

The BET surface areas of **CU-6-Fe** and **CU-6-Cr**, determined from 77 K N₂ adsorption isotherms using BETSI⁴⁰, are 7,145 and 6,488 m² g⁻¹, respectively (Supplementary Figs. 44 and 45). Meeting all five extended-Rouquerol criteria implemented in BETSI⁴⁰—guidelines for reliable and consistent BET surface area determination—**CU-6-Fe** ranks among MOFs with the highest BET surface areas reported so far, alongside DUT-60 (8,890 m² g⁻¹)⁴¹, NU-1501-Al (7,241 m² g⁻¹)²³ and MOF-210 (6,341 m² g⁻¹)²⁴. These benchmark values were recalculated from digitized 77 K N₂ isotherms using BETSI⁴² (Supplementary Table 7). Encouraged by the exceptional porosity, we evaluated the high-pressure H₂-adsorption

performance at 77, 120 and 160 K up to 100 bar (Fig. 4d–f). The excess H₂-adsorption isotherms exhibit the type I shape, as expected for supercritical gases, reaching maxima at around 60 bar before decreasing slightly at higher pressures⁴³ (Supplementary Figs. 46 and 47). Such a high saturation pressure, compared with most porous adsorbents⁴⁴, reflects the synergistic effect of microporous and mesoporous networks of the frameworks. Maximum excess uptakes of 8.4 and 8.0 wt% were obtained for **CU-6-Fe** and **CU-6-Cr**, respectively. When translated to total uptake, **CU-6-Fe** and **CU-6-Cr** exhibit gravimetric H₂ uptakes of 17.5 and 15.9 wt% at 100 bar and 77 K (Fig. 4d,e), along with volumetric H₂ uptakes of 45.4 and 45.5 g l⁻¹, respectively, calculated using bulk densities derived from 77 K N₂ isotherms (Fig. 4f). These values represent

very high gravimetric H_2 uptake, surpassing values reported for some benchmark adsorbents (Fig. 4h and Supplementary Table 7), including NU-1501-Al²³ and NU-100⁴². The total pore volumes of **CU-6-Fe** and **CU-6-Cr**, calculated from the N_2 adsorption isotherms at $P/P_0 = 0.99$, were 4.14 and 3.67 $cm^3 g^{-1}$, resulting in bulk densities of 0.214 and 0.240 $g cm^{-3}$, respectively. The slightly higher density of **CU-6-Cr** compensates for its lower gravimetric uptake, giving similar volumetric H_2 uptake (45.5 versus 45.4 $g l^{-1}$) under identical conditions (100 bar, 77 K) (Fig. 4f and Supplementary Table 7). Unless otherwise stated, all reported volumetric values herein are calculated using the corresponding bulk densities.

In practical fuel-cell vehicles, H_2 adsorbed below 5 bar is considered unrecoverable due to insufficient pressure to drive flow to the engine. Under a temperature–pressure swing from 77 K and 100 bar to 160 K and 5 bar, **CU-6-Fe** and **CU-6-Cr** achieve gravimetric deliverable capacities of 16.9 and 15.4 wt%, with corresponding volumetric capacities of 44.1 and 44.2 $g l^{-1}$, exceeding the DOE's 2025 target, albeit at cryogenic temperatures²⁸. Their performances are comparable to benchmark H_2 -storage adsorbents such as NU-1501-Al²³, NU-100⁴² and RP-H101⁴⁵ (Fig. 4h and Supplementary Table 7). Besides the adsorption capacity, adsorbent stability is critical for practical refuelling applications. **CU-6-Cr** retains its porosity after 3 months of storage in an inert Ar atmosphere and after 24 h of exposure to ambient air (Fig. 4g). Powder X-ray diffraction further shows that its framework remains largely intact after exposure to water vapour (Supplementary Fig. 35). By contrast, **CU-6-Fe** shows a ~20% reduction in N_2 uptake after 1 month of storage in an Ar glovebox (Supplementary Fig. 48). Nevertheless, the Fe K-edge extended X-ray absorption fine structure experiments confirm that the local coordination environment of Fe^{3+} ions remained intact before and after the H_2 -storage measurements (Supplementary Fig. 49 and Supplementary Table 4).

Owing to the exceptional H_2 uptakes of **CU-6-Fe** and **CU-6-Cr**, we also tested high-pressure CH_4 adsorption at 273, 288 and 298 K. At 80 bar, **CU-6-Fe** and **CU-6-Cr** show total gravimetric CH_4 uptakes of 0.67, 0.59 and 0.53 $g g^{-1}$, and 0.63, 0.56 and 0.50 $g g^{-1}$, at 273, 288 and 298 K, respectively, which are among the highest gravimetric CH_4 storage capacities reported (Fig. 4i, Extended Data Fig. 4a,d and Supplementary Figs. 50 and 52). The uptake capacity of **CU-6** surpasses the DOE's gravimetric target (0.5 $g g^{-1}$) at 80 bar at room temperature. The working capacity from 80 bar to 5 bar is 0.62, 0.54 and 0.49 $g g^{-1}$ for **CU-6-Fe**, and 0.58, 0.51 and 0.46 $g g^{-1}$ for **CU-6-Cr**, at 273, 288 and 298 K, respectively, comparable to the benchmark materials such as NU-1501-Al (0.44 $g g^{-1}$ at 296 K)²³ and 3D-TFB-COF-Me (0.35 $g g^{-1}$ at 298 K)⁴⁶. However, it is important to note that, due to their lower densities, the volumetric capacities of **CU-6-Cr** and **CU-6-Fe** (211, 188 and 168 $cm^3 (STP) cm^{-3}$, and 200, 175 and 159 $cm^3 (STP) cm^{-3}$ at 273, 288 and 298 K, respectively, and 80 bar) are lower than those of benchmark MOFs (Supplementary Tables 8 and 9, Extended Data Fig. 4b,c and Supplementary Figs. 51 and 53). The inherent trade-off between gravimetric and volumetric CH_4 capacities is often observed in highly porous MOF adsorbents^{23,24}, as increased pore volume and surface area lead to lower bulk density and reduced volumetric capacity.

Insights on H_2 uptake and binding sites

To further investigate H_2 adsorption in **CU-6-Fe** and **CU-6-Cr**, we performed GCMC simulations at 77, 120 and 160 K. The simulated isotherms closely reproduce the experimental adsorption profiles for **CU-6-Cr** and slightly underestimate the uptake for **CU-6-Fe** (Fig. 4d,e), supporting the structural integrity of the materials and validating the high-pressure adsorption measurements. The low-coverage isosteric heats of adsorption (Q_{st}) obtained from Clausius–Clapeyron analysis are 3.2 and 3.4 $kJ mol^{-1}$ for **CU-6-Fe** and **CU-6-Cr**, respectively, in strong agreement with the corresponding fluctuation-method values of 3.23 and 3.34 $kJ mol^{-1}$ obtained from GCMC simulations (Supplementary Figs. 56–61 and Supplementary Table 10), confirming weak host–guest interactions.

We obtained molecular-level insight into low-coverage adsorption by analysing the probability density distributions of H_2 molecules in **CU-6-Cr** at 77 K and 0.04 bar (Fig. 5a,b, Supplementary Figs. 62 and 63a and Supplementary Videos 2–4). The simulations reveal three main adsorption regions, denoted sites I, II and III. Sites I and II are localized around the Cr_3O clusters, whereas site III is distributed around the organic linkers. Site I is positioned near the corner of the cub cavities, while site II is located near the corners of the cuo and rco cavities (Supplementary Fig. 63b). By contrast, site III is more diffuse and surrounds both the planar (L_a) and bent (L_b) linkers, with enhanced probability density near the phenyl and ethyne groups (Fig. 5b). In situ neutron powder diffraction (NPD) measurements on D_2 -loaded **CU-6-Cr** revealed five adsorption sites within the framework cavities, denoted D_2 -I to D_2 -V (Supplementary Figs. 64–67 and Supplementary Table 6). Figure 5c and Supplementary Fig. 63e,f show the centre-of-mass positions of these D_2 adsorption sites within the cub, cuo and rco cavities. Among them, D_2 -I shows the highest occupancy of 0.73(3) and is located near the Cr_3O cluster within the cub cavity [D_2 -I... $O_{Cr3O} = 4.15 \text{ \AA}$] (Supplementary Fig. 63e), indicating that it acts as the primary adsorption site. This position is fully consistent with site I identified from the GCMC simulations (Fig. 5b). By contrast, no experimental equivalent of simulated site II is directly observed in the NPD data.

The lower-occupancy NPD sites reveal the contribution of the organic linkers to secondary H_2 adsorption. D_2 -II, with an occupancy of 0.17(2), lies close to the planar linker L_a separating neighbouring cub and cuo cavities. This site sits nearly coplanar with the linker and interacts closely with the phenyl group of the diphenylethyne core [D_2 -II... $H_{\text{Phenyl-L}_a} = 2.82 \text{ \AA}$] (Fig. 5d). D_2 -IV, with an occupancy of 0.13(2), lies within the cub cavity near linker L_a and interacts with the phenyl group of the diphenylethyne arm [D_2 -IV... $H_{\text{Phenyl-L}_a} = 2.69 \text{ \AA}$; D_2 -IV... $\pi_{\text{Phenyl-L}_a} = 4.08 \text{ \AA}$] (Fig. 5d). Site D_2 -V, with an occupancy of 0.093(15), lies within the rco cavity near the centre of the bent linker L_b , 4.73 $\text{\AA}$ from the ethyne group (Fig. 5e). D_2 -III, with an occupancy of 0.161(12), lies along the small diagonal channel connecting neighbouring rco and cuo cavities through triangular openings (Figs. 3c and 5c and Supplementary Figs. 22 and 63f). Overall, the linker-associated adsorption sites (D_2 -II, D_2 -IV and D_2 -V) fall within the diffuse probability cloud of simulated site III (Fig. 5b), demonstrating strong agreement between the GCMC and NPD analyses, despite the absence of a direct NPD counterpart for simulated site II. DFT calculations were used to establish the energetic hierarchy of the H_2 adsorption sites, showing that adsorption near the Cr_3O clusters ($-11.10 \text{ kJ mol}^{-1}$) is favoured over linker-associated sites ($-2.42 \text{ kJ mol}^{-1}$) (more details in Supplementary Section 21 and Supplementary Note 3). Together, the GCMC, NPD and DFT analyses indicate that H_2 adsorption in **CU-6-Cr** is dominated at low loading by weak but preferential interactions around the Cr_3O clusters, followed by weaker adsorption around the organic linkers, enabling a favourable balance between high total uptake and deliverable capacity.

Conclusions

We report the reticular design and synthesis of **CU-6**, a highly porous MOF with a **red** topology and an interconnected hierarchical pore system. Computational analysis establishes linker flexibility as a key requirement for satisfying the geometric constraints of the **red** net, providing a rational basis for ligand selection. Beyond the structural characteristics, **CU-6** combines an exceptionally high BET surface area and pore volume with a favourable balance between gravimetric and volumetric porosity, resulting in considerable H_2 and CH_4 storage. In particular, **CU-6** shows one of the highest gravimetric BET surface areas reported among all highly porous MOFs, while retaining a high volumetric capacity and substantial deliverable capacity under temperature–pressure swing conditions. These results demonstrate how topology, linker conformation and hierarchical porosity can be jointly engineered to optimize gas storage, and establish the **red** net

as a promising platform for developing high-performance adsorbents for clean energy applications.

Methods

All reagents were purchased from commercial sources and used without further purification.

Synthesis of CU-6-Fe

$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (150 mg, 0.56 mmol), H_4L (125 mg, 0.17 mmol) and 4-nitrobenzoic acid (1.25 g, 7.49 mmol) were dissolved in DMF (30 ml) by sonication. The resulting clear solution was divided into two 30-ml black-capped glass, sealed and heated in a 130 °C oven for 48 h. Red cubic crystals were formed and then washed with fresh DMF five times over 2 days. The resulting crystals were either stored in DMF for subsequent Cr-exchange reactions or exchanged with dry ethanol for supercritical CO_2 activation. Yield: 92 mg, 60%.

Synthesis of CU-6-Cr

Approximately 50 mg of CU-6-Fe crystals were immersed in 5 ml of degassed, anhydrous DMF inside a glovebox. A solution of anhydrous CrCl_3 (300 mg) in 10 ml of anhydrous DMF was then added. The vial was sealed and removed from the glovebox, then placed in a preheated oven at 120 °C for 48 h. After cooling to room temperature, the resulting green crystals were collected and washed with fresh DMF six times over 2 days. The crystals were then soaked in dry ethanol for 3 days, with the solvent replaced twice per day. Yield: 34 mg, 87%.

Data availability

All data are available in the article or its Supplementary Information. Crystallographic data for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under the deposition numbers [2521553](#) (CU-6-Cr), [2551031](#) (CU-3-1), [2551030](#) (CU-3-2), [2551944](#) (CU-6-Cr_Bare) and [2551946](#) (CU-6-Cr-D2). Copies of these data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif. Source data are provided with this paper.

Code availability

The code used to investigate the pore-filling process is available via GitHub at https://github.com/fairen-group/Pore-filling_Mechanism_Study_in_Adsorption. Coordinate files of the optimized geometries used in the linker-flexibility energy analysis and binding-energy calculations are available via GitHub at https://github.com/fairen-group/CU-6_MOF_red_topology_source_data.

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Author contributions

X.C., Y.C. and D.F.-J. conceived of the idea for this project. X.C. and L.H.W. synthesized and characterized the materials. M.R.A.K. performed all the Monte Carlo and DFT calculations. C.T. and T.S. performed gas sorption experiments and analysis. X.C., L.H.W., M.R.A.K., M.A., D.M. and W.S. performed single-crystal X-ray diffraction analysis. Y.Z., E.Z. and T.W. performed STEM experiments and analysis. L.L.K. conducted X-ray absorption spectroscopy experiments and analysis. X.C., L.H.W., M.R.A.K., H.W.M., B.J.M., P.M. and F.O. performed in situ NPD experiments. J.F. and S.Y. analysed NPD data. X.C., L.H.W., M.R.A.K. and D.F.-J. wrote multiple drafts of the paper. All authors contributed to the preparation of the paper.

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Competing interests

D.F.-J. is founder and Chief Strategy Officer of Immaterial, a company working on the commercialization of MOFs for energy applications. The other authors declare no competing interests.

Additional information

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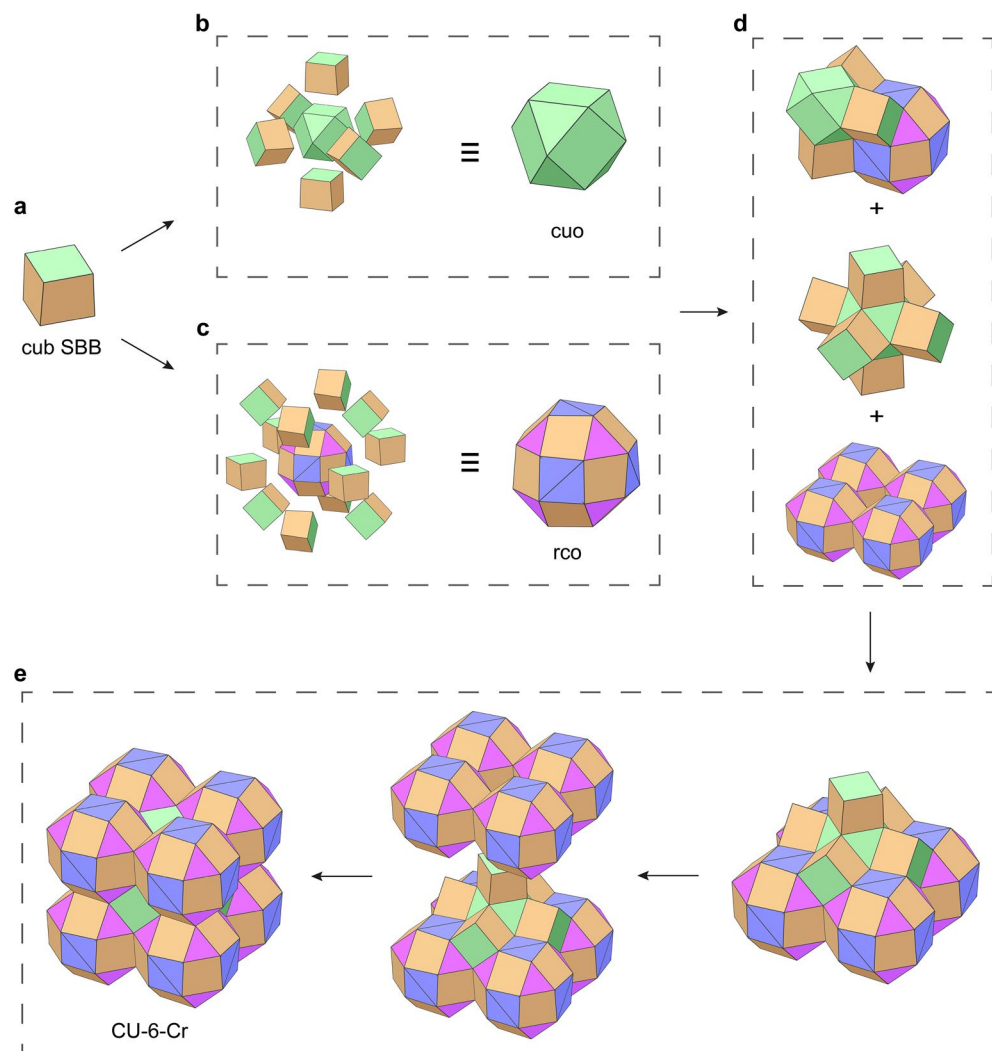
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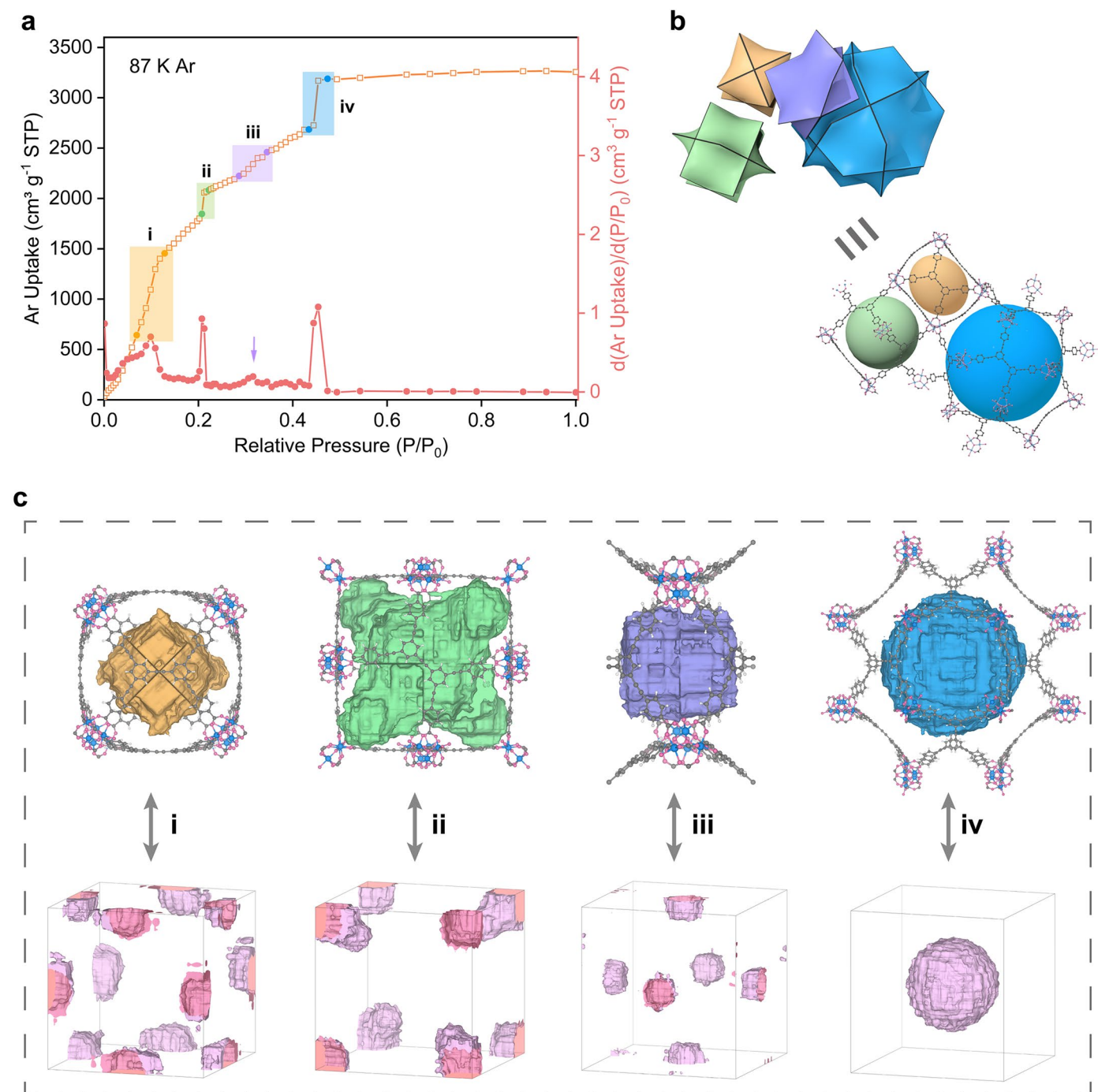
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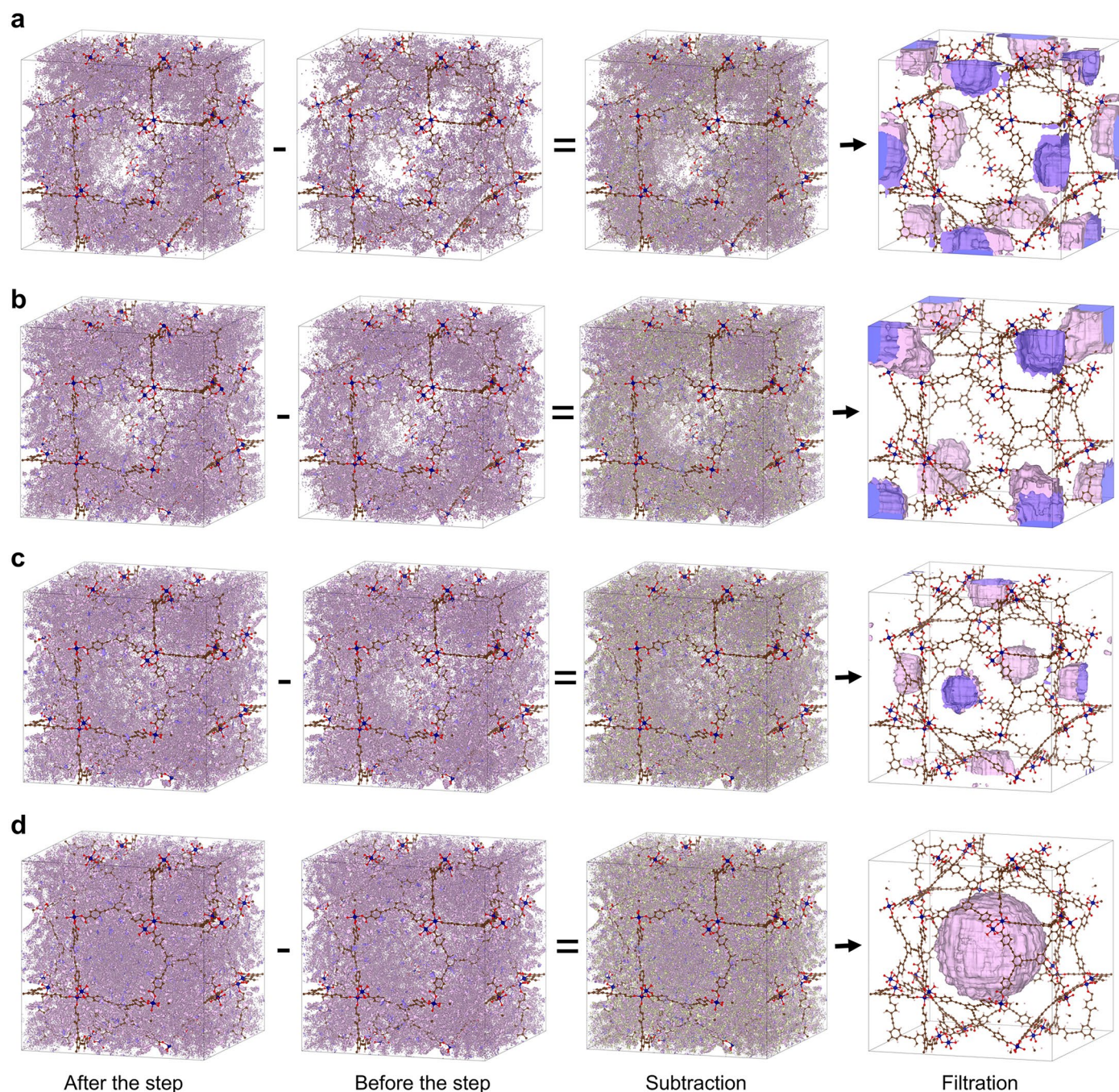
Extended Data Fig. 1 | Schematic illustration for the assembly of CU-6 from cubic (cub) supramolecular building block (SBB). **a**, cub SBB. **b**, Formation of cuboctahedral (cuo) polyhedron by the planar faces (green square faces) from six cub SBBs. **c**, Formation of rhombicuboctahedral (rco) polyhedron by the bent faces (yellow square faces) from twelve cub SBBs. **d**, Stacking styles for cub, cuo,

and rco polyhedrons. e, Assembly of cub, cuo, and rco polyhedrons into CU-6. (Color code: yellow, shared faces between cub and rco polyhedrons, green, shared faces between cub and cuo polyhedrons, blue, shared faces between adjacent rco polyhedrons, and pink, shared faces between cuo and rco polyhedrons).



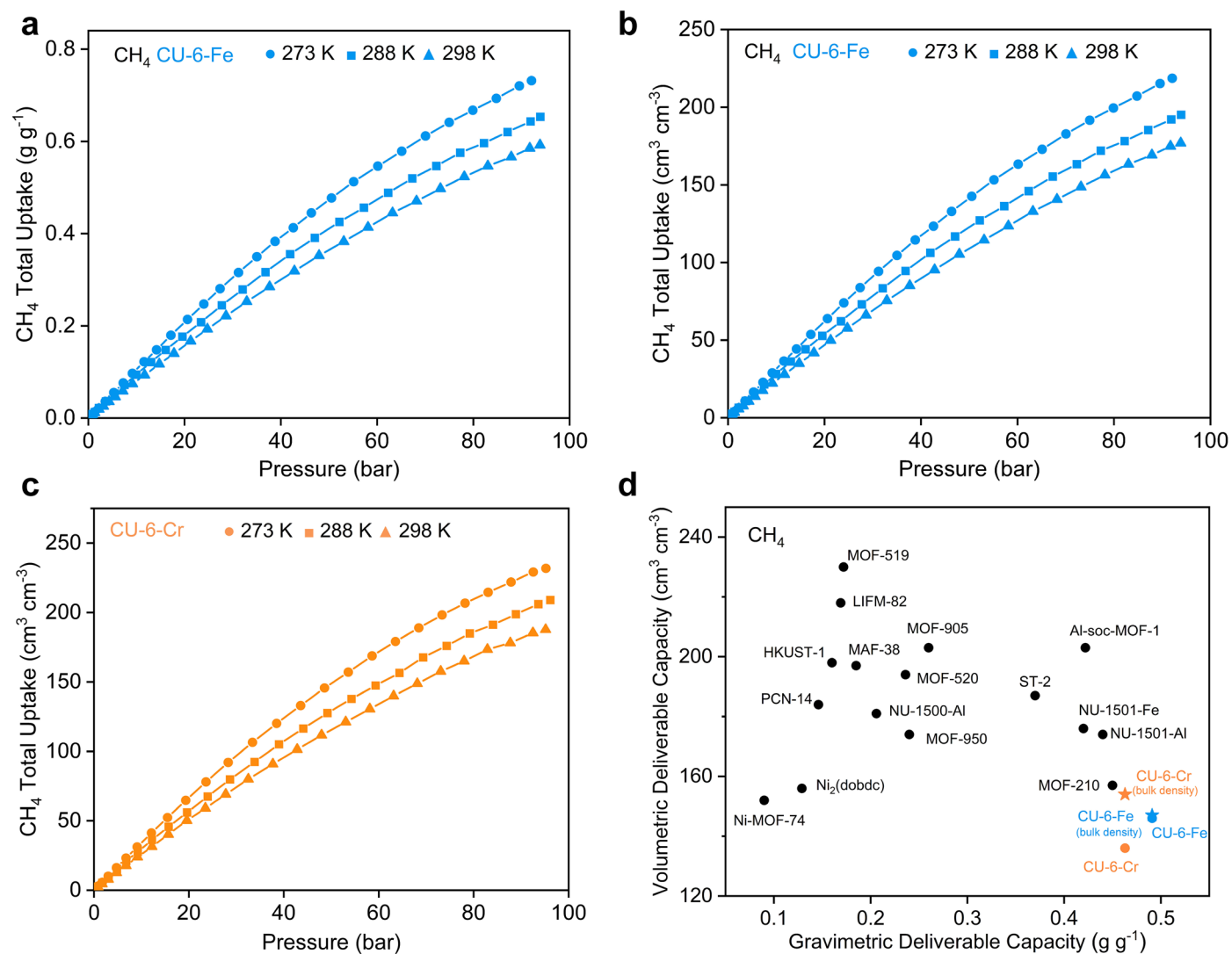
Extended Data Fig. 2 | Simulated 87 K Ar isotherm of CU-6-Cr showing the pore filling mechanism. **a**, Simulated 87 K Ar isotherm with highlighted pore filling adsorption steps. **b**, Representation of the natural tilings and the relevant pore cavities within the framework. **c**, 3D volume profile of the spatial volumes occupied by Ar at each adsorption step inside the relevant cavity as well as their corresponding locations within the unit cell. The first step in the isotherm at very low pressure corresponds to the adsorption of Ar in the vicinity of the

Cr_3O clusters, followed by the three major steps at 0.10, 0.21, and 0.45, which correspond to the sequential filling of the cubic (cub), cuboctahedral (cuo), and rhombicuboctahedral (rco) cavities. The minor step at $P/P_0 = 0.31$ is related to the adsorption within short, channel-like pores that connect the neighbouring rco cavities. Note the correlation of colors and numbering with steps i–iv (Color code: yellow for cub, green for cuo, purple for small channel-like cavity, and blue for rco).



Extended Data Fig. 3 | Sequential pore filling process revealed by simulated Ar adsorption. Process sequence to identify the spatial domains filled during: **a**, step i corresponding to cubic (cub) cavity. **b**, step ii corresponding to cuboctahedral (cuo) cavity. **c**, step iii corresponding to the channel connecting

two adjacent rhombicuboctahedral (rco) cavities. **d**, step iv corresponding rco cavity, along the simulated Ar adsorption isotherm. The process includes the subtraction of the probability density before the step from the probability density after the step, followed by a filtering stage for noise cancellation.



Extended Data Fig. 4 | High-pressure CH₄ storage performance of CU-6-Fe and CU-6-Cr, and comparison with benchmark materials. a, Total gravimetric CH₄ adsorption isotherms for CU-6-Fe measured at 273, 288 and 298 K. **b,** Total volumetric CH₄ adsorption isotherms for CU-6-Fe measured at 273, 288 and

298 K. **c,** Total volumetric CH₄ adsorption isotherms for CU-6-Cr measured at 273, 288 and 298 K. **d,** Comparison between the total gravimetric and volumetric deliverable CH₄ capacity under pressure swing conditions: 298 K/80 bar to 298 K/5 bar.