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A hetero-supermolecular-building-block strategy for the assembly of porous (3,12,24)-connected uru metal–organic frameworks

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Supermolecular building block (SBB) approaches have been widely used for synthesizing highly connected metal-organic frameworks (MOFs). However, it remains a challenge to synthesize trinodal MOFs via SBB approaches. Here we report the assembly of (3,12,24)-connected uru-MOFs via a hetero-supermolecular-building-block (hetero-SBB) strategy, that is, using different types of highly connected metal-organic polyhedra (MOPs) as building units. This hetero-SBB strategy allows the facile synthesis of previously inaccessible uru-MOFs via 12-connected cuboctahedral and 24-connected rhombicuboctahedral MOPs. The uru-MOF-1, consisting of hierarchical microporous and mesoporous cages, exhibits a Brunauer-Emmett-Teller area of 3,170 m² g⁻¹. This MOF shows a high methane uptake of 339.6 cm³ (standard temperature and pressure) cm⁻³ at 159 K and 10 bar and is a promising candidate for low-temperature methane storage. The hetero-SBB strategy paves a way for the designed synthesis of highly connected MOFs, which are difficult to synthesize via traditional strategies, by taking advantage of the arsenal of synthetic MOPs.

Metal–organic frameworks (MOFs), a class of crystalline porous materials consisting of periodically linked inorganic metal ions/clusters and organic linkers, have been developed to address global challenges related to energy and environment^{1–5}. Highly porous MOFs, exhibiting ultrahigh porosity and surface area on account of their well-defined framework structures, are promising candidate materials for the reversible and high-capacity storage of natural gas and hydrogen^{6–11}. Supermolecular building block (SBB) approaches^{12,13} have been successfully deployed to design and synthesize highly porous MOFs based on the edge-transitive binodal nets–with one type of edge–such as (3,24)-connected rht net¹³, (4,12)-connected ftw net¹⁴ and 12-connected fcu net^{15,16}. For example, a group of highly porous rht-MOFs including rht-MOF-1 (ref. 13), NU-100 (ref. 17) and NU-110 (ref. 18) have been synthesized using SBB approaches from 24-connected metal-organic polyhedra (MOPs) based on metal-paddlewheel-based building blocks.

Minimal edge-transitive trinodal nets, consisting of two types of edge, are derived from the parent edge-transitive nets via the derived, related and merged approaches, aiming to precisely guide the assembly of MOFs from the pre-selected building units^{19–22}. These minimal edge-transitive trinodal nets, particularly highly connected nets, are ideal blueprints for the rational construction of MOFs and related framework materials^{23,24}. A group of trinodal MOFs have been rationally designed and synthesized via molecular building blocks (MBBs).

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Fig. 1 Generation and deconstruction of uru net. a. Generation of a (3,12,24)-connected uru net (transitivity [32]) from a (8,8)-connected bcu-b net (transitivity [21]) by replacing one 8-connected node with a group of nodes (one kind of 3-connected node and one 12-connected node). The

of the uru net exhibiting 3-connected, 12-connected and 24-connected nodes. c, Deconstruction of uru-a exhibiting triangle, cuboctahedron and rhombicuboctahedron forms.

For example, polynuclear metal-node-based MBBs allow the assembly of trinodal MOFs based on the minimal edge-transitive (3,4,12)-connected kce, (3,6,12)-connected kex, (3,6,12)-connected urx, (3,6,12)-connected aea, (3,6,12)-c sph and (3,8,12)-connected pek net^{21,23-25}. The use of MBB approach for the synthesis of highly connected MOFs remains difficult due to the limited numbers of MBBs with a connectivity higher than 12 (refs. 26-29). In this regard, SBB approaches provide an alternative way to achieve the designed synthesis of highly connected MOFs^{13,30}; however, it remains a challenge to synthesize trinodal MOFs via SBB approaches owing to the incompatibility of different types of MOP, in particular the high-connectivity ones, to form periodic framework structures.

Herein, we use a hetero-SBB strategy to rationally synthesize a series of (3,12,24)-connected uru-MOFs using two types of MOP-12-connected cuboctahedron (cuo) and 24-connected rhombicuboctahedron (rco)-as building units. The (3,12,24)-connected uru net is a minimal edge-transitive trinodal net, which is related to the parent edge-transitive 8-connected bcu-b net²⁰. Certainly, constructing uru-type MOFs via a MBB approach is tremendously difficult because it is challenging to combine 12-connected and 24-connected cluster-based nodes with 3-connected linker into a crystalline framework. Interestingly, the use of a flexible linker-organic-cage-based carboxylates-allows the rational assembly of copper-paddlewheel-based cuo and rco MOPs into a three-dimensional uru framework. The resulting uru-MOF-1 shows hierarchical microporous and mesoporous cages, resulting in an accessible porosity with a Brunauer-Emmett-Teller area of 3,170 m² g⁻¹ and an experimental pore volume (PV) of 1.38 cm³ g⁻¹. As a result, the uru-MOF-1 displays a methane uptake of 339.6 cm³ (standard temperature and pressure, STP) cm⁻³ at 159 K and 10 bar and

is a promising candidate material towards low-temperature methane storage, with a working capacity of 309.4 cm³ (STP) cm⁻³ between 6 bar, 159 K and 5 bar. 298 K.

Results and discussion Generation of uru net

The uru net is generated from the bcu-b net by replacing one 8-connected node with a group of nodes (one kind of 3-connected node and one 12-connected node), and the coordination number of the other node in bcu-b net is transformed to 24 in uru net (Fig. 1a). The augmented net (uru-a) is used in MOF chemistry for ease of visualization. The uru net can be deconstructed into 3-connected node with triangle, 12-connected node (cuo) and 24-connected node (rco) (Fig. 1b,c). Further geometrical analysis revealed that the transposition of both SBBs into the anticipated uru-MOF platform requires the employment of hexacarboxylate organic ligands, encompassing two arms linking rco SBBs and one branch coordinating cuo SBBs. However, the highly symmetrical nature of most hexacarboxylate ligands hinders the inclusion of the aforementioned heterogeneous branches (Supplementary Fig. 12). Recently, the dynamic nature oxygen-bridged trigonal prismatic organic cages allowed the formation of diverse geometries under a variety of synthetic conditions and modifications³¹⁻³⁴, suggesting the possibility of using these linkers to construct uru-MOFs with heterogeneous SBBs.

Synthesis and crystal structures

Reactions between $Cu(NO_3)_2 \cdot xH_2O$ and peripherally extended bicyclooxacalixarene with -CF₃ substituents (Cage-6c-CF₃) (Supplementary Fig. 1a–d) in the presence of HNO₃ in an $N_{\gamma}N$ -dimethylformamide (DMF)



Fig. 2 | **A hetero-SBB strategy for the synthesis of uru-MOF. a**, A 12-connected cuo SBB is constructed by 12 functionalized pyridine-3,5-bis(phenyl-4-carboxylate (PDC) arms and 6 copper-paddlewheel-based clusters. **b**, A 24-connected rco SBB is constructed by 24 functionalized PDCs and 12 copper-

paddlewheel-based clusters. **c**, Triangular core of hexacarboxylate linker. **d**, The 12- and 24-connected SBBs are linked by a triangular core. Substituent groups in MOPs of A, B and D were omitted for clarity. Hydrogen atoms were omitted for clarity. Colour code for structure: dark blue, Cu; grey, C; red, O; blue, N; green, F.

solution yields blue truncated cube-shaped crystals (Supplementary Tables 1 and 2), formulated by single-crystal X-ray diffraction analysis (SCXRD) as [Cu₃(H₂O)₃(Cage-6c-CF₃)] (uru-MOF-1) (Fig. 2 and Supplementary Table 3). The SCXRD study reveals that uru-MOF-1 crystallizes in the cubic space group $Pm\bar{3}m$ with a = 40.8170(19) Å and V = 68002(5)Å³ at 193 K. Analysis of the resultant crystal structure of uru-MOF-1 reveals the in situ formation of 12-connected cuo and 24-connected rco copper-paddlewheel-based MOPs, and their subsequent co-polymerization yields a 3-periodic highly connected Cu-MOF (Supplementary Figs. 3 and 7). The main difference with rht-MOFs is that the symmetry of the 3-connected core is broken, resulting in the simultaneous formation of cuo and rco based on copper-paddlewheel-based clusters in the crystalline framework (Supplementary Figs. 12-15 and Supplementary Table 6). Close examination of the uru-MOF-1 reveals body-centred cubic packing of the cuo and rco SBBs (Supplementary Fig. 9). The resultant framework encloses three distinct cavities, cavity I (2.2 Å × 22.2 Å, 12.0 Å van der waals (vdw) sphere), cavity II (32.8 Å × 32.8 Å, 22.0 Å vdw sphere) and cavity III (4.9 Å × 18.6 Å, 15.0 Å vdw sphere) (Supplementary Fig. 6), and one type of interconnected infinite channels (Supplementary Fig. 8). The corresponding calculated total accessible volume for uru-MOF-1, upon removal of guest solvent molecules, was estimated to be 75.9%, by summing voxels more than 1.2 Å away from the framework using PLATON software³⁵. Further geometrical studies showed that the structure is theoretically expandable through three independent parameters, suggesting a high degree of tunability for the uru-MOF platform (Supplementary Fig. 11).

Topological analysis of the uru-MOF-1 reveals that the hexacarboxylate ligand can be deconstructed into a 3-connected node, which combines with the aforementioned 12- and 24-connected SBBs to afford an unprecedented highly connected Cu-MOF with the underlying (3,12,24)-connected uru net (Supplementary Figs. 18 and 19). It is worth noting that the trinodal uru net with a minimal transitivity of [3 2] has only two kinds of edges. Additionally, the uru-MOF-1 can alternatively be described as the complex (3,3,3,4,4)-connected tru net with transitivity [5 4], considering the linkers as two 3-connected nodes and copper-paddlewheel-based clusters as 4-connected nodes (Supplementary Fig. 17). However, the complexity of this pentanodal net suggests the difficulty of using square and triangular MBBs to construct such highly connected MOFs. Therefore, the effectiveness of the hetero-SBB strategy and reticular chemistry allow the synthesis of this



Fig. 3 | **Isoreticular synthesis of uru-MOFs. a**, Functionalized cage-based hexacarboxylate ligands used for the assembly of uru-MOFs. Colour code: cyan, Cage-6c-CF₃; pink, Cage-6c-Me; green, Cage-6c-F. **b**, Optical images of MOF crystals isolated showing their variability in size. **c**, Structures of the uru-MOFs

family showing the changes in pore functionalization and the cavities accessible. Hydrogen atoms were omitted for clarity. Colour code: dark blue, Cu; grey, C; red, O; blue, N; green, F. **d**, Natural tilings of the uru-a net.

flexibility. The porosity of uru-MOF-1 was examined by N₂ adsorption-

highly connected uru-MOF-1 (Supplementary Fig. 16), which is among the most highly connected framework materials^{13,28–30}.

Low-pressure gas sorption studies

The discovery of minimal edge-transitive uru-MOF-1 offers a viable platform for the isoreticular synthesis. The -CF₃ groups were further replaced by -Me and -F groups to give Cage-6c-Me and Cage-6c-F ligands, respectively. As anticipated, truncated cube-shaped crystals were obtained using these ligands, and the SCXRD studies revealed the successful construction of two isoreticular uru-MOFs–that is, uru-MOF-2 and uru-MOF-3 (Fig. 3). The phase purity of bulk MOF samples is confirmed by the well-matched as-synthesized and simulated powder X-ray diffraction patterns (Supplementary Figs. 22–24). Thermogravimetric analysis of activated uru-MOF-1, uru-MOF-2 and uru-MOF-3 revealed a mass loss occurring at 270 °C, at which point the material decomposes (Supplementary Fig. 20). The decomposition temperature is lower than that of NU-100, NU-110 and rht-MOF-1 (refs. 13,17,18), reflecting a relatively higher degree of framework

desorption measurements. The N₂ adsorption isotherm at 77 K exhibits a type IV isotherm with a steep increase at $P/P_0 \approx 0.15$, indicating the existence of small mesopores (Fig. 4). The apparent BET surface area of uru-MOF-1 was calculated to be 3,170 m² g⁻¹, after satisfying the four consistency criteria with a correlation coefficient higher than 0.995 (Supplementary Fig. 26). The experimental total PV was estimated to be ~1.38 cm³ g⁻¹, corresponding to 95% of the theoretical PV calculated from single-crystal structure. The pore size distribution (PSD) plot calculated using a suitable nonlocal density functional theory kernel (NLDFT) reveals that three peaks centred at 11.4 Å, 14.8 Å and 20.3 Å match the cuboctahedral, octahedral and rhombcuboctahedral cavities from crystal structure, respectively. In addition, we performed the N₂ sorption experiments at 77 K under various activated temperatures (Supplementary Fig. 28). The results showed that uru-MOF-1 was able to maintain 83% volume adsorbed at an activation temperature of 200 °C, which indicated that uru-MOF-1 has high thermal stability. After numerous trials, we are still unable to fully activate uru-MOF-2

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Fig. 4 | **Gas sorption experiments. a**, Nitrogen sorption isotherms of uru-MOF-1 recorded at 77 K. The inset shows the corresponding NLDFT calculated PSD curves. **b**, High-pressure methane isotherm of uru-MOF-1 recorded at the indicated temperature. **c**, Low-pressure methane isotherm of uru-MOF-1

and uru-MOF-3 owing to the collapse of the frameworks, even using supercritical carbon dioxide activation (Supplementary Fig. 27).

High-pressure gas sorption and storage studies

The interesting structural features and high porosity nature of uru-MOF-1 make it a very promising candidate for natural gas storage. Natural gas, mostly composed of methane, is widely considered as an environmentally friendly transportation fuel. Liquefied natural gas (LNG), a common way to store and transport natural gas, requires an expensive cryogenic cooling system³⁶. The boil-off gases should inevitably be addressed in LNG tanks to prevent the emission of greenhouse natural gas into air, and to reduce safety risks. The coupling of LNG regasification and the adsorbed natural gas (ANG) charging process (LNG–ANG coupling) offers a feasible solution to the current challenge by utilizing the cold energy from LNG and reducing carbon emission^{37–40}. The LNG–ANG coupling technology requires high-performance adsorbents in ANG systems. Thus, highly porous MOFs with high methane capacities under cryogenic conditions are ideal candidate materials for this LNG–ANG technology, although



recorded at the indicated temperature. The inset shows the corresponding isosteric heat of the adsorption curve as a function of the CH_4 uptakes. **d**, The working capacity of uru-MOF-1 under LNG–ANG conditions.

low-temperature methane sorption is rarely studied in the MOF field⁴¹. To this end, we decided to investigate the methane sorption performance of uru-MOF-1 at low-temperature and ambient conditions—relevant to LNG–ANG applications.

High-pressure methane sorption experiments show that the methane uptake of uru-MOF-1 achieves 647 cm³ (STP) g⁻¹ (339.6 cm³ (STP) cm⁻³) at 159 K and 10 bar, which makes it a promising candidate material towards low-temperature methane storage (Fig. 4 and Supplementary Figs. 29–33). Under LNG–ANG conditions, the methane uptakes of uru-MOF-1 are 330.2 cm³ (STP) cm⁻³ and 20.8 cm³ (STP) cm⁻³ at low temperature (159 K and 6 bar) and room temperature (298 K and 5 bar), respectively. The resulting CH₄ working capacity between 6 bar and 159 K to 5 bar and 298 K is estimated to be 309.4 cm³ (STP) cm⁻³. This working capacity is comparable to those in MIL-53(Al) (262.3 cm³ (STP) cm⁻³)³⁹ and is lower than those in DUT-23(Cu) (373.1 cm³ (STP) cm⁻³)⁴⁰. To evaluate the strength of the interaction between CH₄ and uru-MOF-1, the CH₄ sorption isotherms were recorded at 278, 288, 298 and 308 K (Fig. 4 cm⁴)

Article

Supplementary Fig. 34). The isosteric heat of adsorption (Q_{st}) at high CH₄ loading was estimated to be 14.8 kJ mol⁻¹, reflecting the physical adsorption interaction between methane and framework.

Conclusions and outlook

In summary, we report the implementation of the hetero-SBB strategy for the discovery and rational synthesis of isoreticular (3,12,24)-connected uru-MOFs by assembling heterogeneous 12- and 24-connected SBBs. The highly porous uru-MOF-1, exhibiting hierarchical microporous and mesoporous cages, is considered a promising material for methane storage and LNG–ANG applications. Our results suggest the validity of the hetero-SBB strategy to expand the bounda-ries of high-connectivity nets in MOF crystal chemistry. Finally, we envision that our reported strategy introduces a route to rationally access non-interpenetrated made-to-order materials with an unreached level of high porosity for high-capacity gas storage purposes.

Methods

All reagents were obtained from commercial sources and used without further purification (unless otherwise noted in 'Synthesis of ligands' section in Supplementary Information). No metal salt nor ligand stock solutions were prepared.

Synthesis of single crystals of uru-MOF-1

A DMF solution (5.0 ml) of Cage-6c-CF₃ (12.5 mg) and a DMF solution of Cu(NO₃)₂:xH₂O (25 mg, 5.0 ml) were combined in a 15 ml, 22 × 70 mm glass vial. Then, 3.5 M nitric aqueous solution (2.0 ml) was added. The mixture was sonicated for 2 min and sealed and heated to 75 °C for 48 h and cooled to room temperature. The green crystals were collected and washed with DMF (3 × 5 ml) to remove any impurities (yield: 40% based on Cu). Selected attenuated total reflectance Fourier transform infrared (ATR-FTIR) peaks (4,000 to 400 cm⁻¹): 3,422 (br), 3,069 (w), 2,923 (w), 2,866 (w), 1,650 (vs), 1,598 (vs), 1,582 (s), 1,500 (m), 1,378 (vs), 1,311 (vs), 1,222 (vs), 1,091 (vs), 1,040 (s), 977 (s), 852 (m), 789 (m), 659 (s), 549 (w) and 476 (m).

Synthesis of single crystals of uru-MOF-2

A DMF solution (5.0 ml) of Cage-6c-Me (12.5 mg) and a DMF solution of $Cu(NO_3)_2 xH_2O$ (25 mg, 5.0 ml) were combined in a 15 ml, 22 × 70 mm glass vial. Then, 3.5 M nitric aqueous solution (2.0 ml) was added. The mixture was sonicated for 2 min and sealed and heated to 70 °C for 48 h and cooled to room temperature. The green crystals were collected and washed with DMF (3 × 5 ml) to remove any impurities (yield: 40% based on Cu). Selected ATR-FTIR peaks (4,000 to 1,000 cm⁻¹): 3,398 (br), 3,059 (w), 2,929 (w), 2,850 (w), 1,650 (vs), 1,598 (vs), 1,572 (s), 1,499 (m), 1,384 (vs), 1,311 (vs), 1,232 (vs), 1,091 (vs), 1,040 (s), 977 (s), 877 (m), 783 (m), 732 (m), 648 (s), 554 (m) and 481 (m).

Synthesis of single crystals of uru-MOF-3

A DMF solution (1.0 ml) of Cage-6c-F (30 mg) and a DMF solution of $Cu(NO_3)_2 \cdot xH_2O$ (60 mg, 1.0 ml) were combined in a 15 ml vial. Then, 3.5 M nitric DMF solution (0.4 ml) was added. The mixture was sonicated for 2 min and sealed and heated to 85 °C for 12 h and cooled to room temperature. The green crystals were collected by centrifugation and washed with DMF. Crystals were immersed in dichloromethane for 3 days, during which time the dichloromethane was replaced two times per day (yield: 60% based on Cu). Selected ATR-FTIR peaks (4,000 to 1,000 cm⁻¹): 3,424 (br), 3,059 (w), 3,075 (w), 2,929 (w), 2,865 (m), 1,650 (vs), 1,603 (vs), 1,577 (s), 1,499 (w), 1,384 (vs), 1,311 (s), 1,238 (vs), 1,086 (vs), 982 (s), 851 (m), 794 (m), 643 (s), 554 (m) and 486 (m).

Note that the use of nitric acid in solvothermal reaction was found to have the potential to produce brown impurities.

Data availability

Data supporting the findings of this investigation are available from the Article and its Supplementary Information. The X-ray crystallographic coordinates for structures reported in this study have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition numbers CCDC 2343936 (uru-MOF-1), 2343937 (uru-MOF-2) and 2343938 (uru-MOF-3). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/cif. Source data are provided with this paper.

References

- 1. Furukawa, H., Cordova, K. E., O'Keeffe, M. & Yaghi, O. M. The chemistry and applications of metal–organic frameworks. *Science* **341**, 1230444 (2013).
- Horike, S. & Kitagawa, S. The development of molecule-based porous material families and their future prospects. *Nat. Mater.* 21, 983–985 (2022).
- Wang, W., Chen, D., Li, F., Xiao, X. & Xu, Q. Metalorganic-framework-based materials as platforms for energy applications. *Chem* 10, 86–133 (2024).
- 4. Shi, L., Kirlikovali, K. O., Chen, Z. & Farha, O. K. Metal–organic frameworks for water vapor adsorption. *Chem* **10**, 484–503 (2024).
- Shi, L., Yang, Z., Sha, F. & Chen, Z. Design, synthesis and applications of functional zirconium-based metal-organic frameworks. Sci. China Chem. 66, 3383–3397 (2023).
- Chen, Z., Kirlikovali, K. O., Li, P. & Farha, O. K. Reticular chemistry for highly porous metal–organic frameworks: the chemistry and applications. Acc. Chem. Res. 55, 579–591 (2022).
- 7. Guillerm, V. & Eddaoudi, M. The importance of highly connected building units in reticular chemistry: thoughtful design of metal-organic frameworks. *Acc. Chem. Res.* **54**, 3298–3312 (2021).
- 8. Chen, Z. et al. Balancing volumetric and gravimetric uptake in highly porous materials for clean energy. *Science* **368**, 297–303 (2020).
- Chen, Z., Kirlikovali, K. O., Idrees, K. B., Wasson, M. C. & Farha, O. K. Porous materials for hydrogen storage. *Chem* 8, 693–716 (2022).
- 10. Li, B., Wen, H.-M., Zhou, W., Xu, JeffQ. & Chen, B. Porous metalorganic frameworks: promising materials for methane storage. *Chem* **1**, 557–580 (2016).
- 11. Zhang, M. et al. Fine tuning of MOF-505 analogues to reduce low-pressure methane uptake and enhance methane working capacity. *Angew. Chem. Int. Ed.* **56**, 11426–11430 (2017).
- Guillerm, V. et al. A supermolecular building approach for the design and construction of metal-organic frameworks. *Chem.* Soc. Rev. 43, 6141–6172 (2014).
- Nouar, F., Eubank, J. F., Till Bousquet, L. W., Zaworotko, M. J. & Eddaoudi, M. Supermolecular building blocks (SBBs) for the design and synthesis of highly porous metal–organic frameworks. J. Am. Chem. Soc. 130, 1833–1835 (2008).
- 14. Stoeck, U., Senkovska, I., Bon, V., Krause, S. & Kaskel, S. Assembly of metal–organic polyhedra into highly porous frameworks for ethene delivery. *Chem. Commun.* **51**, 1046–1049 (2015).
- 15. Krause, S. et al. A pressure-amplifying framework material with negative gas adsorption transitions. *Nature* **532**, 348–352 (2016).
- 16. Krause, S. et al. Towards general network architecture design criteria for negative gas adsorption transitions in ultraporous frameworks. *Nat. Commun.* **10**, 3632 (2019).
- 17. Farha, O. K. et al. De novo synthesis of a metal–organic framework material featuring ultrahigh surface area and gas storage capacities. *Nat. Chem.* **2**, 944–948 (2010).
- Farha, O. K. et al. Metal–organic framework materials with ultrahigh surface areas: is the sky the limit?. J. Am. Chem. Soc. 134, 15016–15021 (2012).
- Li, M., Li, D., O'Keeffe, M. & Yaghi, O. M. Topological analysis of metal-organic frameworks with polytopic linkers and/or multiple building units and the minimal transitivity principle. *Chem. Rev.* 114, 1343–1370 (2014).

- Chen, Z., Jiang, H., Li, M., O'Keeffe, M. & Eddaoudi, M. Reticular chemistry 3.2: typical minimal edge-transitive derived and related nets for the design and synthesis of metal–organic frameworks. *Chem. Rev.* **120**, 8039–8065 (2020).
- Jiang, H. et al. Enriching the reticular chemistry repertoire: merged nets approach for the rational design of intricate mixed-linker metal-organic framework platforms. J. Am. Chem. Soc. 140, 8858–8867 (2018).
- 22. Fang, H. et al. Ligand-Conformer-induced formation of zirconium–organic framework for methane storage and MTO product separation. *Angew. Chem. Int. Ed.* **60**, 16521–16528 (2021).
- Chen, Z. et al. Enriching the reticular chemistry repertoire with minimal edge-transitive related nets: access to highly coordinated metal-organic frameworks based on double six-membered rings as net-coded building units. J. Am. Chem. Soc. 141, 20480–20489 (2019).
- 24. Alezi, D. et al. Quest for highly connected metal–organic framework platforms: rare-earth polynuclear clusters versatility meets net topology needs. *J. Am. Chem.* Soc. **137**, 5421–5430 (2015).
- Jiang, H. et al. Reticular chemistry for the rational design of mechanically robust mesoporous merged-net metal-organic frameworks. *Matter* 6, 285–295 (2023).
- Guillerm, V. et al. Discovery and introduction of a (3,18)-connected net as an ideal blueprint for the design of metal–organic frameworks. *Nat. Chem.* 6, 673–680 (2014).
- Hurlock, M. J. et al. Evolution of 14-connected Zr6 secondary building units through postsynthetic linker incorporation. ACS Appl. Mater. Interfaces 13, 51945–51953 (2021).
- Froudas, K. G. et al. Expanding the reticular chemistry building block library toward highly connected nets: ultraporous MOFs based on 18-connected ternary, trigonal prismatic superpolyhedra. J. Am. Chem. Soc. 146, 8961–8970 (2024).
- Du, D.-Y. et al. An unprecedented (3,4,24)-connected heteropolyoxozincate organic framework as heterogeneous crystalline Lewis acid catalyst for biodiesel production. *Sci. Rep.* 3, 2616 (2013).
- Park, J. et al. A versatile metal-organic framework for carbon dioxide capture and cooperative catalysis. *Chem. Commun.* 48, 9995–9997 (2012).
- Zhu, Q. et al. 3D cage COFs: a dynamic three-dimensional covalent organic framework with high-connectivity organic cage nodes. J. Am. Chem. Soc. 142, 16842–16848 (2020).
- Zhu, Q. et al. Soft hydrogen-bonded organic frameworks constructed using a flexible organic cage hinge. J. Am. Chem. Soc. 145, 23352–23360 (2023).
- 33. Ji, C. et al. Tunable cage-based three-dimensional covalent organic frameworks. CCS Chem. **4**, 3095–3105 (2022).
- Shi, L., Xiong, Z., Wang, H., Cao, H. & Chen, Z. Quasicrystal approximants in isoreticular metal–organic frameworks via cairo pentagonal tiling. *Chem* 10, 2464–2472 (2024).
- 35. Spek, A. L. Structure validation in chemical crystallography. Acta Crystallogr. Sect. D **65**, 148–155 (2009).
- Mason, J. A., Veenstra, M. & Long, J. R. Evaluating metal-organic frameworks for natural gas storage. *Chem. Sci.* 5, 32–51 (2014).
- Kayal, S., Sun, B. & Chakraborty, A. Study of metal–organic framework MIL-101(Cr) for natural gas (methane) storage and compare with other MOFs (metal–organic frameworks). *Energy* 91, 772–781 (2015).
- Roszak, E. A. & Chorowski, M. Exergy analysis of combined simultaneous liquid natural gas vaporization and adsorbed natural gas cooling. *Fuel* 111, 755–762 (2013).

- 39. Kim, S.-Y., Kang, J. H., Kim, S.-I. & Bae, Y.-S. Extraordinarily large and stable methane delivery of MIL-53(Al) under LNG–ANG conditions. *Chem. Eng. J.* **365**, 242–248 (2019).
- 40. Kim, S. Y. et al. Discovery of high-performing metal-organic frameworks for on-board methane storage and delivery via LNG– ANG coupling: high-throughput screening, machine learning, and experimental validation. *Adv. Sci.* **9**, 2201559 (2022).
- 41. He, Y., Zhou, W., Yildirim, T. & Chen, B. A series of metal-organic frameworks with high methane uptake and an empirical equation for predicting methane storage capacity. *Energy Environ. Sci.* **6**, 2735–2744 (2013).

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Author contributions

The original idea was conceived by Z.C.; the synthesis of organic linkers and MOFs was performed by L.S.; SCXRD analysis was conducted by Z.C. and L.S.; low-pressure sorption measurements were performed by H.C., H.W. and K.W.; high-pressure sorption measurements were conducted by Y.Z. and Z.X.; and the paper was drafted by Z.C., L.S. and H.S. All authors have given approval to the paper.

Competing interests

The authors declare no competing interests.

Additional information

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