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ARTICLE TYPE

Significant enhancement of gas uptake capacity and selectivity by judiciously increasing open metal sites and Lewis basic sites within two polyhedron-based metal-organic frameworks

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Two new isomorphous polyhedron-based MOFs (JLU-Liu20 and JLU-Liu21), with dual functionality of OMSs and LBSs, have been synthesized by using SBBs strategy. By judiciously avoiding the DABCO axial ligand, JLU-Liu21 possesses more OMSs than JLU-Liu20, and exhibits significant enhancement of CO₂ uptake capacity 210 versus 162 cm³ g⁻¹ for JLU-Liu20 at 273 K under 1 bar.

Metal-organic frameworks (MOFs), as one type of porous crystalline materials, have attracted extensive research interests for their diverse applications, such as gas storage and/or separation,¹ heterogeneous catalysis,² non-linear optics,³ magnetism,⁴ drug delivery,⁵ and molecular recognition.⁶

Carbon dioxide as anthropogenic greenhouse gas in the atmosphere has caused global warming which is considered as one of the greatest environmental issues facing our daily life. MOFs emerged as a new type of adsorbent materials have the enormous potential for effective capture and sequestration/separation of CO₂. Thus far, the efficient method of promoting the adsorption amount of MOFs for CO₂ can be summarized as the following aspects: 1) afford high internal surface areas and large pore volumes;⁷ 2) increase the coordinative unsaturated open metal sites (OMSs);⁸ 3) provide abundant N-rich Lewis basic sites (LBSs);⁹ 4) functionalize and control the framework by post-synthetic modification (PSM).¹⁰ The strategy of utilizing metal-organic polyhedra (MOP) as supermolecular building blocks (SBBs) to design polyhedron-based metal-organic frameworks (PMOFs) materials is an attractive way to obtain MOFs with hierarchical structures, high surface areas, large pore volumes, especially significant gas uptake capacity.¹¹ Meanwhile, incorporation isophthalate moieties with 120° angle afford the platform to design SBBs with familiar MOP and paddlewheel moieties with OMSs. In addition, introducing accessible N-rich sites can facilitate LBSs which drastically impact the affinity between the framework and CO₂.

On the basis of above considerations, we adopt 5, 5'-(1*H*-1, 2, 4-triazole-3, 5-diyl) diisophthalic acid (H₄TADIPA) as

ligand, which possess dual functionality of isophthalate and triazole moieties to construct the framework with MOP, OMSs and LBSs. Just as the design, [Cu₆(TADIPA)₃(DABCO)(H₂O)₂(DMF)₂]·13H₂O·7DMF (DABCO = 1,4-diazabicyclo[2.2.2]-octane) (JLU-Liu20) with high surface areas, multiple pore systems and high density of OMSs/LBSs is successfully prepared. Nevertheless, on account of the DABCO linkers are unnecessary to the formation of overall 3-periodic framework structure, we judiciously avoid the DABCO axial ligand to build a new PMOF [Cu₆(TADIPA)₃(H₂O)₆]·16H₂O·8DMF (JLU-Liu21) with higher surface areas and more OMSs/LBSs than JLU-Liu20, and exhibits significant enhancement of gas uptake capacity and selectivity.

Single-crystal X-ray diffraction analysis reveals that JLU-Liu20 crystallizes in tetragonal crystal system with space group of *P4/mnc*. As depicted in Fig. 1a, the framework is assembled by the typical Cu paddlewheel secondary building units (SBUs) and organic TADIPA⁴⁻ ligands which can be viewed as a pair of 3-c node or simplified as a linear rod. The DABCO as axial ligand is coordinated to two neighboring paddlewheels. JLU-Liu20 features three types of cages with different sizes and shapes (Fig. S2, ESI[†]): a well-known MOP-1 consisted of 12 paddlewheels and 24 TADIPA⁴⁻ ligands forms a cuboctahedron (cuo) geometry (M₁₂L₂₄) (Fig. 1b); a asymmetric cage with 12 paddlewheels and 6 TADIPA⁴⁻ ligands generates to a truncated tetrahedron (T-T_d) configuration (M₁₂L₆); a large cage built from 24 paddlewheels and 16 TADIPA⁴⁻ ligands outlines in truncated octahedron (T-O_h) (M₂₄L₁₆). The three types of polyhedron packing arrangements result in a novel PMOF with multiple pore systems (Fig. 1c), such as a 1D square channel with an approximate diameter of 6.7 × 6.7 Å² along the *a* axis (regardless of the van der Waals radii) (Fig. S5, ESI[†]). From a topological perspective, MOP-1 is corresponded to a 12 connected vertex and links 12 crystallographically equivalent nanocages through the linear rods to construct a porous 3D network with *fcu* topology (Fig. 1e and Fig. 1f). From another topological point of view, Cu paddlewheel SBUs with square

geometry and TADIPA⁴⁻ simplified as a pair of triangle geometries, make up a novel (3, 4)-connected network with a Schläfli symbol of $\{6^2.8^2.9^2\}_2\{6^2.8\}_4\{6^2.9\}_2\{6^3.8.10^2\}$, which is different to other related MOFs based on tetracarboxylate ligands and MOP-1 SBBs (Table S2 and S3, ESI†).

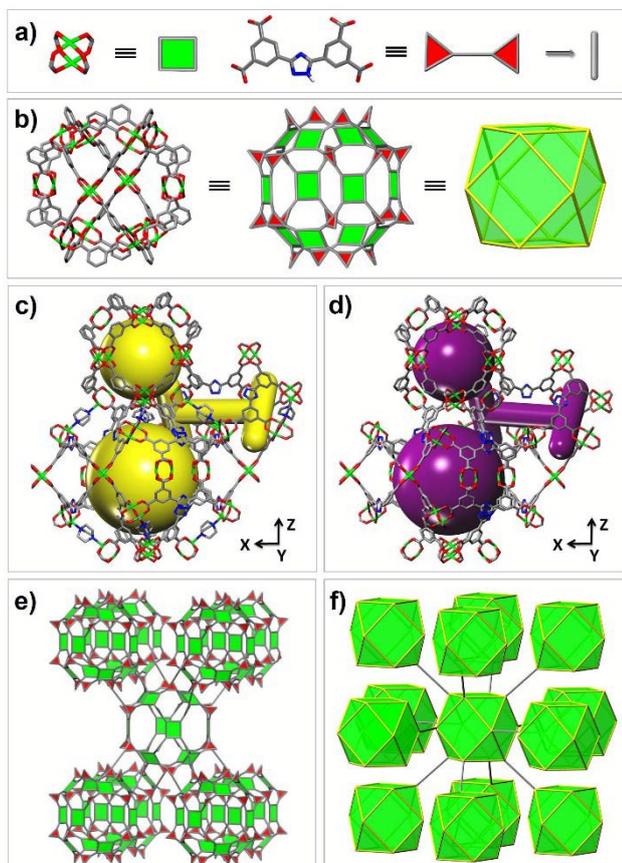


Fig. 1 Description of the structure of **JLU-Liu20** and **JLU-Liu21**: a) Cu paddlewheel SBUs, and organic TADIPA⁴⁻ ligand viewed as a pair of 3-c node; b) MOP-1 and cuo cage; c) three types of cages in **JLU-Liu20**; d) three types of cages in **JLU-Liu21**; e) polyhedral view of the net; f) the **fcu** topology for **JLU-Liu20** and **JLU-Liu21**. Color scheme: carbon = gray, oxygen = red, copper = green. Guest molecules and H atoms have been omitted for clarity.

On account of the DABCO linkers located at the center of two Cu paddlewheel SBUs do not contribute to the formation of the overall framework structure, we expect to synthesize a similar framework without DABCO linker. Fortunately, the presumptive PMOF **JLU-Liu21** with more open framework and high density of LBSs/OMSs is successfully prepared (Fig. 1d), which possesses same structure with **JLU-Liu20** (Fig. S3-8, ESI†). The total accessible volume of **JLU-Liu20** (63.7%) and **JLU-Liu21** (68.6%) calculated by PLATON prove that **JLU-Liu21** owns more open framework.

Both of **JLU-Liu20** and **JLU-Liu21** exhibit moderate thermal stability, which can be stable up to 200 °C (Fig. S9, S10, ESI†). Permanent porosity of activated **JLU-Liu20** and **JLU-Liu21** were confirmed by N₂ sorption-desorption isotherms at 77 K which showed a reversible type-I isotherm characteristic of microporous material (Fig. S14, ESI†). The Brunauer-Emmett-Teller (BET) surface areas for **JLU-Liu20**

and **JLU-Liu21** are calculated to be 1807 and 2080 m² g⁻¹, respectively, which indicates that **JLU-Liu21** possesses higher surface areas, larger pore volumes, more OMSs and LBSs (Table S4, ESI†).

In virtue of the high BET surface areas, multiple pore systems and high density of OMSs/LBSs, we investigate their adsorption performance for some small gases (Table S5, ESI†). Both **JLU-Liu20** and **JLU-Liu21** exhibit excellent H₂ storage capacity at 77 K and 1 bar (ca. 2.3 and 2.5 wt %) in comparison to other highly porous materials (Fig. S15, Table S6, ESI†). Meanwhile, the CO₂ uptake of **JLU-Liu20** and **JLU-Liu21** are also explored to be 162 (31.8 wt%) and 210 (41.2 wt%) cm³ g⁻¹ at 273 K under 1 bar, respectively. The values at 298 K are 88 (17.3 wt%) and 118 (23.2 wt%) cm³ g⁻¹, respectively (Fig. 2a). It is worth noting that the CO₂ storage capacity of **JLU-Liu21** is among the highest values for porous MOFs (Table S7, S8, ESI†). The outstanding performance is mainly due to its high density of LBSs and OMSs that provide abundant positions and force sites toward CO₂. This result suggests that **JLU-Liu20** and **JLU-Liu21** may be good candidate materials for the storage of H₂ and CO₂.

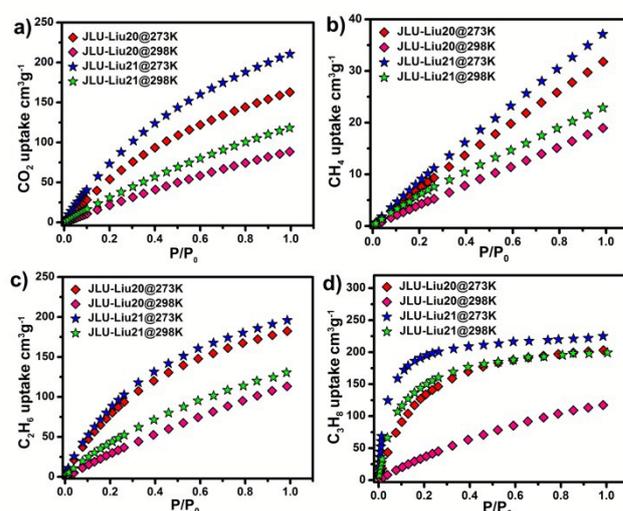


Fig. 2 (a), CO₂; (b), CH₄; (c), C₂H₆; (d) C₃H₈ gas sorption isotherms for **JLU-Liu20** and **JLU-Liu21** at 273 and 298 K under 1 bar.

Additionally, CH₄, C₂H₆ and C₃H₈ are also selected as probe molecules to appraise their gas adsorption properties (Fig. 2b-d). Although both compounds have multiple pore systems, the involving of DABCO which alter the surface areas of the cavities and the sizes of the windows leads to **JLU-Liu21** possessing more excellent adsorption capability than **JLU-Liu20**. **JLU-Liu20** exhibits notable adsorption capacities to CH₄ (31, 18 cm³ g⁻¹), C₂H₆ (182, 113 cm³ g⁻¹) and C₃H₈ (202, 117 cm³ g⁻¹) at 273 and 298 K. Meanwhile, **JLU-Liu21** shows higher performance for adsorption capacities to CH₄ (37 and 22 cm³ g⁻¹), C₂H₆ (195 and 130 cm³ g⁻¹) and C₃H₈ (224 and 199 cm³ g⁻¹) at 273 and 298 K. At zero loading, the isosteric heats (Q_{st}) of CO₂ for the two compounds are 32 (**JLU-Liu20**) and 28 kJ mol⁻¹ (**JLU-Liu21**), respectively (Fig. S18, ESI†), which were calculated by virial method. The Q_{st} of **JLU-Liu20** and **JLU-Liu21** are similar to NTU-111 and NTU-112^{12c}, which exhibits different

framework structures with **JLU-Liu20** and **JLU-Liu21** while the ligand is similar.

To mimic the separation behaviour of **JLU-Liu20** and **JLU-Liu21** under a more real-world setting, the gas selectivities of CO_2/CH_4 ,¹² $\text{C}_2\text{H}_6/\text{CH}_4$ and $\text{C}_3\text{H}_8/\text{CH}_4$ were calculated using ideal solution adsorbed theory (IAST)¹³ (Fig. 3, S19, ESI†). The selectivity of CO_2/CH_4 (50% and 50%, 5% and 95%) is 5.9 and 5.5 for **JLU-Liu20**.

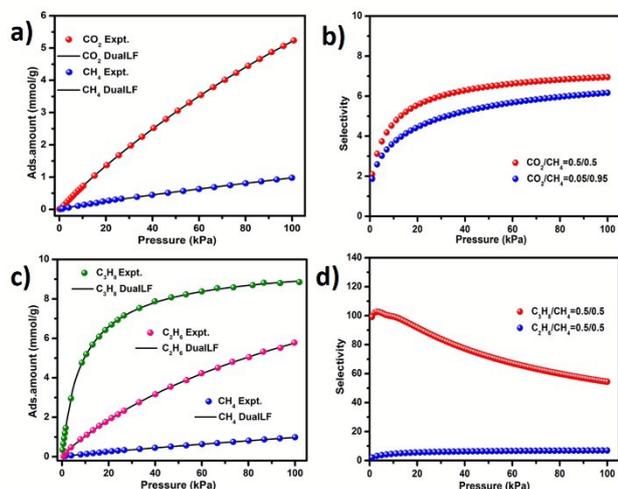


Fig. 3 CO_2 , CH_4 , C_2H_6 and C_3H_8 adsorption isotherms at 298 K along with the Dual-site Langmuir Freundlich (DSLFF) fits (a, c); Gas mixture adsorption selectivities are predicted by IAST at 298K and 100 kPa for **JLU-Liu21** (b, d).

In comparison, the selectivity of CO_2/CH_4 (50% and 50%, 5% and 95%) is 6.9 and 6.2 for **JLU-Liu21**. Furthermore, the selectivity of equimolar mixtures $\text{C}_2\text{H}_6/\text{CH}_4$ and $\text{C}_3\text{H}_8/\text{CH}_4$ are 7.0 and 11.1 for **JLU-Liu20**, respectively. The selectivity for **JLU-Liu21** of equimolar mixtures $\text{C}_2\text{H}_6/\text{CH}_4$ and $\text{C}_3\text{H}_8/\text{CH}_4$ are 7.0 and 99.2, which shows much higher $\text{C}_3\text{H}_8/\text{CH}_4$ selectivity than **JLU-Liu20**. It is worth mentioning that the selectivity of $\text{C}_3\text{H}_8/\text{CH}_4$ for **JLU-Liu21** is comparable to the higher values for UTSA-35a (80), FJI-C1 (78.7) and FIR-7a-ht (80).¹⁴ The PMOFs **JLU-Liu20** and **JLU-Liu21** with significant separation for CH_4 can be mainly attributed to the following reasons: (i) their multiple pore systems, high density of OMSs and LBSs enhance the interactions between the framework and CO_2 owing to its greater polarizability and quadrupole moment compared to CH_4 ; (ii) the uptake capacity of hydrocarbons promotes with polarizability increasing ($\text{CH}_4 = 25 \times 10^{-25}$, $\text{C}_2\text{H}_6 = 44 \times 10^{-25}$, and $\text{C}_3\text{H}_8 = 63 \times 10^{-25} \text{ cm}^3$); (iii) the Q_{st} of CH_4 is lowest in the gases indicating the weakest interactions with the adsorbent.

In summary, by utilizing the SBBs strategy, two PMOFs **JLU-Liu20** and **JLU-Liu21** with OMSs and LBSs have been successfully synthesized. Both compounds with high surface areas exhibit outstanding adsorption capacity for the H_2 , CO_2 , C_2H_6 and C_3H_8 . Moreover, **JLU-Liu21** showed a high CO_2 uptake capacity of 210 (41.2 wt%) $\text{cm}^3 \text{ g}^{-1}$ at 273 K under 1 bar, and higher $\text{C}_3\text{H}_8/\text{CH}_4$ selectivity (99.2), it may be a promising material for the storage of CO_2 , and the separation of C_3H_8 over CH_4 .

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Notes and references

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- † Electronic Supplementary Information (ESI) available: [materials and methods, crystal data and structure refinement, structure information, XRD, TGA, gases adsorption properties of **JLU-Liu20** and **JLU-Liu21** CCDC 1436216 and 1435683]. See DOI: 10.1039/b000000x/
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