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Integration of open metal sites and Lewis basic sites for construction of a Cu MOF with rare chiral O_h type of cage for high performance of methane purification

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Abstract: A Cu MOF $[Cu_4(PMTD)_2(H_2O)_3] \cdot 20H_2O$, **1**, (Where PMTD is (1,4-phenylenebis(5-methyl-4H-1,2,4-triazole-3,4-diyl))bis(5-carboxylato-3,1-phenylene))bis(hydroperoxymethanide) with rare chiral O_h type of cage and dual functionalities of open metal sites and Lewis basic sites based on a designed U-shaped ligand was synthesized by hydrothermal method. It exhibits high-capacity of CO_2 , C_2 and C_3 hydrocarbon storage capacity under atmospheric pressure as well as high H_2 (1.96% wt) adsorption capacity at 77K. Methane purification capacity was tested and verified step by step. Isothermic heats (Qst) study reveals that CH_4 has the weakest van der Waals host-guest interactions among the seven gases at 298K. Ideal adsorbed solution theory (IAST) calculation reveals that compound **1** is more selective toward CO_2 , C_2H_6 and C_3H_8 over CH_4 in further calculating its separation capacity, as exemplified for CO_2/CH_4 (50:50, 5:95), C_2H_6/CH_4 (50:50, 5:95) or C_3H_8/CH_4 (50:50, 5:95) binary gas mixtures. Breakthrough experiments show that **1** has a significantly higher adsorption capacity for CO_2 , C_2H_6 and C_3H_8 than CH_4 . The selective adsorption properties of **1** make it a promising candidate for methane purification.

Introduction

Methane, the primarily component of natural gas (NG), is not only an alternative eco-friendly energy source for fossil fuels replacement, but also an important chemical raw material for production of various C_1 and C_2 chemicals, such as formaldehyde, carbon monoxide and acetylene.^[1] Unfortunately, mined NG from deep inside the earth has a remaining fraction (5%) with a mixture of ethane, heavier hydrocarbons and carbon dioxide,^[2] which

requires further purification prior to various chemical processes. For example, carbon dioxide poisons the Li/MgO catalyst that converts methane into ethane and ethylene.^[3] Two traditional common methods of NG purification currently used are (1) liquefaction at low temperature and (2) compression to 200-300 bar at room temperature. Both of them waste energy and costly. Therefore, porous adsorbents which can preferentially absorb carbon dioxide, ethane and heavier hydrocarbons over methane are highly desirable. Such porous materials can also be used to screen starting materials in industrial methane conversion processes.

Metal-organic frameworks (MOFs) have attracted considerable attention as advanced porous materials in the past decades.^[4] and have found use in gas storage and separation.^[5] So far, effective strategies for designing and synthesizing MOFs with excellent gas separation capabilities have been frequently employed to (1) afford high internal surface areas and large pore volumes; (2) increase the coordinative unsaturated open metal sites (OMSs); and (3) provide abundant N-rich Lewis basic sites (LBSs).^[6] Therefore, Integration of dual functionalities of OMSs and LBSs as supermolecular building units (SBUs) is an attractive way to obtain MOFs with hierarchical structures, high surface areas, large pore volumes and achieve high gas uptake.^[7] For example, Krautscheid and co-workers have successfully synthesized a triazol-functionalized microporous metal-organic framework with high H_2 (3.05 wt%) and CO_2 (40.5 wt%) adsorption at ambient pressure^[8]. Our group has fully used and designed two *rht* topology MOFs containing high density triazine or s-heptazine LBSs with excellent gas storage and separation properties.^[6d, 6e] Moreover, the introduction of accessible N-rich sites can facilitate LBSs, which drastically impacts the affinity between the framework and CO_2 .

On the basis of the above considerations, we carefully designed and synthesized a new U-shaped ligand (5,5'-(1,4-phenylenebis(5-methyl-4H-1,2,4-triazole-3,4-diyl))diisophthalic acid) (H_4PMTD) which contains carboxylate and triazol groups to construct a hierarchical 3D porous framework $[Cu_4(PMTD)_2(H_2O)_3] \cdot 20H_2O$, **1**, with dual functionalities of OMSs and LBSs. We found it is rare that adjacent O_h type of cages in **1** are mirror images of each other but not identical. Notably, compound **1** has large surface areas and high storage capacity of CO_2 , C_2 and C_3 hydrocarbons under atmospheric pressure and room temperature. Besides, compound **1** exhibits high selectivity of methane from CO_2 , C_2 and C_3 hydrocarbons, making it a promising candidate for methane purification.

Results and Discussion

Crystal Structure of **1**

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Supporting information including material and methods, crystal data, XRD, TGA, H_2 adsorption property, Breakthrough experiment. CCDC 1549573 is given.

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Functional U-shaped ligand H_4PMTD was synthesized for the first time by four step organic reactions (Scheme S1†). Single crystal X-ray diffraction analysis reveals that **1** crystallizes in orthorhombic space group $pbam$. The asymmetric unit of **1** has four Cu (II) atoms, two crystallographically independent ligand, three coordinated water molecules and twenty guest water molecules. Cu1 and Cu2 are chelated by four carboxylate groups from two separate ligands to form paddlewheel configuration SBUs. Cu3 is tetracoordinated by two nitrogen atoms from diverse ligands and two oxygen atoms belonging to the same carboxylate groups of separate ligands to finish a capped tetrahedron geometry. The coordination geometry of Cu4 can be regarded as five-coordination tetragonal cone containing two oxygen atoms from different ligands, one coordinated oxygen atom and two nitrogen atoms.

Figure 1. The coordination environment of Cu(II); C; grey, N; blue, O; red, Cu; green. All H atoms are omitted for clarity.

Because of the tendency of the distorted ligand to attain stable configuration. The outstanding structural feature of **1** is the presence of three types of cages with different sizes and shapes, namely, octahedron (O_h), truncated octahedron ($T-O_h$) and cuboctahedron ($cub-O_h$). O_h type of cage (Fig. 2a) with the edge distance of 11.1 and 9.8 Å is formed by two copper paddlewheel SBUs occupying the apex position and four other Cu atoms linked with two different ligands to comprise the equatorial plane and surfaces. It is interesting to note that all these linkers are only rigid fragment units of $PMTD^{4-}$ ligands and do not involve chiral units. However, O_h type of cage is still a chiral cage, because we can't find any necessary symmetry operations in it. Adjacent O_h type of cages are reciprocal enantiomers for each other to further testify its chirality (Fig. 2e). A symmetric cage with four copper paddlewheel SBUs, four tetraconnected Cu SBUs, four five-connected Cu SBUs and 16 organic linkers generates a truncated octahedron ($T-O_h$) configuration ($M_{16}L_{16}$) (Fig. 2b); $cub-O_h$ type of cage (Fig. 2c) has the same kinds and amount of copper SBUs as $T-O_h$ and has 12 $PMTD^{4-}$ ligands to construct cuboctahedron configuration ($M_{16}L_{12}$). Each O_h type of cage interconnects via the paddlewheel SBUs to generate 1D chain along a axis. These chains are weaved by five-connected Cu SBUs to compose 2D

layers along the ab plane, which assemble the 3D framework via the $PMTD^{4-}$ ligand. The three types of cages packing arrangements result in a multiple pore system, such as 1D channel with approximate diameter of 10.1×9.5 Å along the c axis (Fig. 2d) (regardless of the van der Waals radii).

Figure 2. (a) O_h type of cage; (b) $T-O_h$ type of cage; (c) $cub-O_h$ type of cage; (d) A portion of **1** built on $PMTD^{4-}$; (e) Topological features of **1** displayed by tiling; (f) Topological features of **1** displayed by tiling; C; grey, N; blue, O; red, Cu; green, H; light grey.

To achieve better insights into the 3D framework structure of compound **1**, topological analysis was carried out. Each simple framework in **1** can be topologically represented as a novel 4-nodal (2, 4, 5, 8)-connected network with a Schläfli symbol of $(4^{16} \cdot 6^{12})(4^3 \cdot 6^2 \cdot 8)_4(4^6 \cdot 8^4)_2(8)$. The topological feature displayed by tiling is shown in Fig. 2f.

Gas Adsorption Property of **1**

The activated samples were prepared by exchanging the solvent in the as-synthesized **1** with C_2H_5OH , followed by evacuation under high vacuum at $120^\circ C$ for 10h. A comparison of PXRD patterns of as-synthesized and simulated **1** was made carefully (Fig. S2). Permanent porosity of activated **1** was confirmed by N_2 adsorption-desorption isotherms at 77 K which showed a reversible type-I isotherm. The Langmuir and BET surface areas are 1602 and $1185 m^2 g^{-1}$, respectively. The total pore volume calculated from the N_2 isotherm is $0.58 cm^3 g^{-1}$. A pore size distribution analysis by non-local density functional theory (NLDFT) utilizing N_2 gas at 77K shows that compound **1** exhibits a narrow distribution of micro-pores of around $5-10$ Å (Fig. 3).

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Figure 3. N₂ sorption isotherms at 77K (filled symbols: adsorption; open symbols: desorption); inset: pore size distribution analysed using the NLDFT method.

By virtue of the high BET surface areas, large pore volume and high density of OMSs (1.29 nm³)/LBSs (1.29 nm³), we investigate the adsorption performance of compound **1** for some small gases. Compound **1** exhibits high H₂ uptake (220 cm³ g⁻¹, 1.96 wt%) at 77K and 1 bar which is slightly lower than that of Mn₃[(Mn₄Cl)₃(BTT)₈(CH₃OH)₁₀]₂ with high density of OMSs and SBSs (2.1 wt%).^[9] The CO₂ low-pressure adsorption isotherms of **1** were measured at 273 and 298K (0–1 atm). At 273K, the uptake amount is 157 cm³ g⁻¹ (30.8 wt%), and the value at 298K is 94 cm³ g⁻¹ (18.5 wt%). The outstanding performance is mainly due to the high density of SBSs and OMSs that provides abundant positions and interaction sites toward CO₂.

Moreover, with multiple pore systems and diverse sizes of windows, compound **1** also exhibits notable adsorption capacities for C₂s (C₂H₂, C₂H₄ and C₂H₆) and C₃s (C₃H₆ and C₃H₈) hydrocarbons. The uptake capacities at 1 atm and 273K for C₂H₂, C₂H₄, C₂H₆, C₃H₆ and C₃H₈ are 125.8, 124.1, 147.3, 133.1 and 149.7 cm³ g⁻¹, respectively, while those at 1 atm and 298 K are 100.9, 76.3, 109.9, 118.9 and 134.3 cm³ g⁻¹. It was observed that more propane was adsorbed than ethane although propane has a larger collision diameter of (4.3 Å) than ethane (3.8 Å), which is mainly because propane has stronger binding with the adsorbent than ethane as well as significant dipole moments. These results suggest that **1** may become a good candidate material for storage of H₂, CO₂, C₂ and C₃ hydrocarbons.

On the contrary, the storage capacity of CH₄ exhibits diametrically opposed behavior compared to other small gases. Although the cavities and the window is large enough for methane to go in, the uptake of CH₄ at 273 and 298K is only 28.8 and 15.8 cm³ g⁻¹. It exhibits evident “channel gate” phenomenon for CH₄ and therefore **1** is expected to be a suitable material for CH₄ purification purposes.

Figure 4. (a) CH₄ and CO₂ sorption isotherm at 273K; (b) CH₄ and CO₂ sorption isotherm at 298K; (c) C₂H₆, C₂H₄, C₂H₂, C₃H₈ and C₃H₆ sorption isotherm at 273K; (d) C₂H₆, C₂H₄, C₂H₂, C₃H₈ and C₃H₆ sorption isotherm at 298K. STP= standard temperature and pressure.

Isosteric heats (Q_{st})

To evaluate the affinity of compound **1** for small gas molecules, the isosteric heats (Q_{st}) of **1** for the seven gases (CO₂, CH₄, C₂H₂, C₂H₄, C₂H₆, C₃H₆ and C₃H₈) are calculated using the virial method,^[10] which is a well-established and reliable methodology fitting from their adsorption isotherms at 273 and 298 K (Fig.5). The low coverage Q_{st} value of C₃H₆ adsorption in **1** (61.9 kJ mol⁻¹) is at top rank of values among the reported MOFs, while MIL-100(Fe) exhibits the highest value (70 kJ mol⁻¹) so far.^[11] The isosteric heats for CO₂, CH₄, C₂H₂, C₂H₄, C₂H₆ and C₃H₈ are 27.3, 20.4, 41.4, 44.2, 20.9 and 46 kJ mol⁻¹, respectively. The adsorption enthalpies for CO₂, C₂ and C₃ hydrocarbons are all greater than that for CH₄, which certify the weak van der Waals host-guest interactions to further explain the “channel gate” phenomenon for CH₄ uptake.

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Figure 5. Coverage-dependent isosteric heat of adsorption.

IAST Calculation

To imitate the separation behaviour of **1** under a more real world setting, representative gas selectivities (CO_2/CH_4 , $\text{C}_2\text{H}_6/\text{CH}_4$ and $\text{C}_3\text{H}_8/\text{CH}_4$) in a binary mixture were calculated employing the ideal adsorbed solution theory (IAST) method^[12] based on the experimental single-component isotherms fitted by the dual site Langmuir Freundlich (DSLFF) model^[13] at 298 K under 1 bar. As shown in (Fig. 6), the model fits the isotherms at 298 K very well. The fitting parameters were then used to predict multicomponent adsorption with IAST (see S2 in the ESI†). The selectivity of CO_2/CH_4 (50% and 50%, 5% and 95%) is 13.5 and 16.1, which can be classified as the top rank of the MOF materials,^[14] and higher than the attractive $[\text{Cu}_2(\text{HBTB})_2(\text{H}_2\text{O})(\text{EtOH})]\cdot\text{H}_2\text{O}$ with open Cu sites (selectivity of CO_2/CH_4 is 12 under the same conditions).

Furthermore, the selectivity of $\text{C}_2\text{H}_6/\text{CH}_4$ and $\text{C}_3\text{H}_8/\text{CH}_4$ is 11.6 and 122.2 (50% and 50%), 12.8 and 187.3 (5% and 95%), respectively. Compound **1** exhibiting excellent separation performance for CH_4 can be attributed to many reasons: (1) multiple pore systems and high density of OMSs and LBSs can enhance framework- CO_2 interactions through charge-induced forces owing to its greater quadrupole moment and polarizability compared to CH_4 ; (2) the uptake capacity of hydrocarbons increases with polarizability ($\text{CH}_4 = 25 \times 10^{-25}$, $\text{C}_2\text{H}_6 = 44 \times 10^{-25}$, and $\text{C}_3\text{H}_8 = 63 \times 10^{-25} \text{ cm}^3$); (3) CH_4 is the smallest molecule and therefore has the weakest interactions with the adsorbent

Figure 6. 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 and e); gas mixture adsorption selectivity are predicted by IAST at 298 K and 100 KPa for Cu-PMTD (b, d and f).

Breakthrough separation experiments

To evaluate the feasibility of using compound **1** as a candidate for methane purification under conditions that mimic real-world situations, breakthrough experiments were performed in which equimolar four mixture containing CH_4 , CO_2 , C_2H_6 and C_3H_8 was flowed over a packed bed of the solid with a total flow of 4 mL/min at 298 K (Fig. 7). CH_4 was detected downstream shortly after the gas mixture was introduced into the column (43s), then CO_2 and C_2H_6 were detected at 191s and 198s respectively, whereas C_3H_8 was not detected until a breakthrough time of 721s was reached. Breakthrough times are based on adsorption capacity of the four gases, agreeable with the IAST selectivity derived from the single gas adsorption isotherms. We also carried out breakthrough experiment at room temperature on a more real proportion (95: 1.67: 1.67: 1.67) to further test the separation capacity (Fig. S5). The results indicate that **1** shows high methane selectivity not only at equilibrium, but also under kinetic flow conditions, suggesting that it is a promising candidate for methane separation from gas mixtures.

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Figure 7. Column breakthrough experiment for equimolar four component mixture containing CH₄, CO₂, C₂H₆ and C₃H₈ at 298 K and 1 atm in Cu-PMTD.

Conclusions

In summary, by Integrating OMSs and LBSs into the framework, a rare chiral-cage MOF **1** with high surface areas has been successfully synthesized. Compound **1** exhibits outstanding adsorption for seven gases (H₂, CO₂, C₂H₂, C₂H₄, C₂H₆, C₃H₆ and C₃H₈) and very little adsorption for CH₄. The methane purification capacity was tested and verified step by step. Isothermic heats (*Q*_{st}) study reveals that CH₄ has the weakest van der Waals host-guest interactions among the seven gases at 298K. According to IAST calculations, compound **1** shows highest selectivity of 16.1 for CO₂-CH₄ and 187.3 for C₃H₈-CO₂ at 298K. Moreover, breakthrough experiments show that compound **1** has a significantly higher adsorption capacity for CO₂, C₂S and C₃S than CH₄. The selective adsorption properties of **1** make it a promising candidate for methane purification.

Experimental Section

Materials and methods

All reagents were purchased commercially and used without further purification. The hydrothermal reaction was performed in a 15 mL Teflon-lined stainless steel bomb. Powder X-ray diffraction (PXRD) data were obtained using a Rigaku D/Max 2550 automated diffractometer (Cu K α , 1.5418 Å). IR spectra were measured with KBr pellets on a Bruker IFS-66 V/S FT-IR spectrometer. Thermogravimetric measurement was performed on pre-weighed samples in a nitrogen stream using a Netzsch STA 449C apparatus with a heating rate of 10°C min⁻¹. ¹H NMR was carried out on a Bruker Avance III spectrometer at 400 MHz.

Synthesis of compound 1

Cu(NO₃)₂·3H₂O (12mg, 0.05mmol) and H₄PMTD (14mg, 0.025mmol) were mixed in 7mL ethanol/water (5:2, v/v). The mixture was placed in a Teflon-lined stainless steel vessel and heated at 100°C for 24h, then cooled to room temperature over 24h. Blue crystals of **1** were obtained and collected by filtration, washed with ethanol and then dried in air. Yield: 57% (based on H₄PMTD). Anal. Calcd (%): C, 41.45; H, 2.30; N, 8.06. Found (%): C, 40.85; H, 2.42; N, 8.34. IR (KBr, cm⁻¹): 3494(s), 3037(s), 2342(m), 1977(s), 1888(m), 1853(s), 1633(s), 1570(m), 1529(m), 1488(m), 1405(w), 1356(m), 1019(m), 936(s), 874(w), 839(m), 791(s), 764(w), 729(s), 591(s), 543(s), 467(s).

Single crystal X-ray crystallography

Diffraction data collection was performed with Ga-K α radiation (λ = 1.34139 Å) on Bruker PHOTON100 area-detector diffractometer. All data were collected at a temperature of 20±2°C. The structures were solved by direct methods and refined with full-matrix least squares technique using the SHELXTL^[15] crystallographic software package. Basic information pertaining to crystal parameters and structure refinement is summarized in Table S1. The unit cell includes a large region of disordered solvent molecules, which could not be modelled as discrete atomic sites. PLATON/SQUEEZE^[16] was employed to calculate the diffraction contribution of the solvent molecules and, thereby, to produce a set of solvent-free diffraction intensities; the SQUEEZE calculations showed nearly 20 molecules of H₂O per unit cell.

Gas adsorption measurements

Low-pressure N₂ gas sorption experiments at 77 K were carried out on a Micrometrics ASAP 2420 volumetric gas sorption instrument. Low-pressure H₂, CO₂, CH₄, C₂H₆, C₂H₄, C₂H₂, C₃H₈ and C₃H₆ experiments at 273K and 298K were performed on a Micrometrics ASAP 2020 surface area analyzer. Before gas adsorption measurements, the samples were washed with fresh EtOH 5 times for 3 days to completely remove the non-coordinative solvent molecules, which can be proved by TGA analysis (Fig. S3†).

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A Cu MOF with dual functionalities and rare chiral O_h type of cage has been designed and synthesized for methane purification. Owing to high density of OMSs (1.2nm^{-3}) and LBSs (1.29nm^{-3}). The MOF exhibits high adsorption capacity for seven C_1 , C_2 and C_3 hydrocarbons and little adsorption for methane. Isothermic heats (Q_{st}) study reveals that CH_4 has the weakest van der Waals host-guest interactions (20.4 KJ mol^{-1}). Ideal adsorbed solution theory (IAST) calculation and Breakthrough experiments testify the Cu MOF is a promising candidate for methane purification.

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Lingkun Meng, Ziyuan Niu, Chen Liang, Xinglong Dong, Kang Liu, Guanghua Li, Chunguang Li, Yu Han, Zhan Shi,* and Shouhua Feng

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Layout 2:

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