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A microporous Cu-MOF with optimized open metal sites and pore spaces for high gas storage and active chemical fixation of CO_2†

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A microporous Cu-MOF with optimized open metal sites and pore space was constructed based on a designed bent ligand; it exhibits high-capacity multiple gas storage under atmospheric pressure and efficient catalytic activity for chemical fixation of CO_2 under mild conditions.

CO_2, as an anthropogenic greenhouse gas, is considered to be one of the greatest environmental concerns of our age.[1] Such a serious issue mainly stems from the burning of fossil fuels, which bear around 86% of all energy used globally.[2] Solving this problem relies on alternative green sources[3] with low carbon consumption as well as carbon capture and sequestration.[4] H_2 is believed to be the ultimate fuel with water as the only by-product; CH_4 produces lower CO_2 emission and is seen as a transitional fuel; CO_2 capture is an immediate solution to the on-going climate change.[5] Consequently, storage of H_2, CH_4 and CO_2 has been an unfailing research hotspot in chemistry and material science for the last few decades.[6] Amongst various porous candidate groups of absorption materials, metal–organic frameworks (MOFs) hold the greatest potential for effective gas storage due to the modification of pore size/shape and surface area by elaborate selection and design of the linkers.[7] Although great progresses in gas storage capacity have been made based on MOF-adsorbents, most materials dominate high volumetric storage using a special gas uptake,[8–10] such phenomenon of which can be attributed to different kinetic diameters, quadrupole moments

and polarizabilities of H_2, CH_4 and CO_2. Realization of high-capacity multiple gas storage materials is essential to meet the urgent demand for clean energy and carbon capture, however, involved reports are very few especially under ambient pressure.[11]

Meanwhile, CO_2 being an inexpensive and abundant renewable C1 building block provides an alternative feedstock to fossil fuels. Converting CO_2 into high-value chemicals undoubtedly helps to mitigate global warming and conforms to green and sustainable chemistry. One of the most promising technologies is the coupling reaction of CO_2 and epoxides to form cyclic carbonates, which are widely applied in pharmaceutical and fine chemical industries.[12] What is more, the cycloaddition of CO_2 to an epoxide produces no side products in accordance with green chemistry and atomic economy.[13] Although homogeneous catalysis has been industrialized in the formation of cyclic carbonate, the process requires high temperatures and pressures as well as rigorous separation and purification of products.[14] For this application, it is desirable to develop efficient heterogeneous catalysts that operate under mild conditions.

With the above considerations in mind, our attention was paid to the creation of open metal sites in a MOF-material, which can be generated by removing metal-bound solvent molecules, as coordinatively unsaturated metal centers not only strengthen the gas–MOF interaction[15] but can also be utilized as heterogeneous Lewis acid catalysts for the efficient transformation of CO_2 into cyclic carbonate.[16] Herein, a semi-rigid tetracarboxylic acid ligand 5,5′-(dimethylsilanediyl) diisophthalic acid (H_4L in Fig. 1a, left) was designed and synthesized. The phenyl rings face each other and form an angle at the Si atom; such a conformation is conducive to the formation of cavity space so that the density of open metal sites of each gas-hosting void can be increased. To the best of our knowledge, the ligand H_4L is among never documented examples. Based on the bent ligand, a microporous MOF with a $[Cu_2(CO_2)_4]$-type paddlewheel cluster, $[Cu_2L(H_2O)_2]\cdot 4H_2O\cdot 2DMF$ **1** was successfully synthesized and structurally characterized. Remarkably, the activated phase **1a** displays high multiple gas uptake (H_2, CH_4 and CO_2) under atmospheric pressure and high catalytic activity for chemical fixation of CO_2 under mild conditions.

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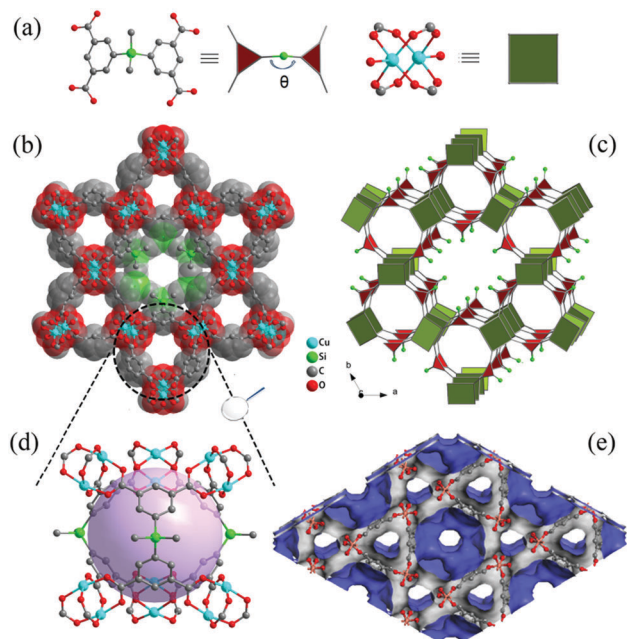
Fig. 1 (a) The organic ligand H_4L and the Cu paddlewheel SBU as well as their abstracted geometric shapes. A view of the 3D architecture of the framework (b) and the assembly of abstracted geometric shapes (c) in compound 1 along the c-axis. (d) The cage confined by six SBUs and three linkers. (e) Connolly surface representation showing the 3D structure. Colour scheme: C (black), O (red), Cu (blue) and Si (green). Guest molecules and hydrogen atoms have been omitted for clarity.

Single-crystal X-ray diffraction analysis reveals that compound 1 crystallizes in the hexagonal space group $P6(3)/mmc$ with one formula unit per unit cell. The framework is built from typical $Cu_2(CO_2)_4$ paddlewheel secondary building units (SBUs) and organic L^{4-} linkers (Fig. 1b); the former can be viewed as a four-coordinated node shown as a green square (Fig. 1a, right) and the latter can be simplified as a bent linker shown as a pair of red outstretched triangles (Fig. 1a, left). Such an arrangement extends infinitely to give rise to a (4,4)-connected network of **ssa** topology with a Schläfli symbol of $\{4^2 \cdot 6^4\}\{4^2 \cdot 8^4\}$ (Fig. 1c).[17] There are hexagon channels with methyl groups hanging inward-facing running along the c axis (Fig. 1b) and the apertures of which are about 9.5 Å at the widest and 7.0 Å at the narrowest spacing. Interestingly, six paddlewheels and three L^{4-} ligands form a cage with an approximate pore diameter of 8.0 Å (taking the van der Waals radii of atoms into consideration) (Fig. 1d and Fig. S9, ESI†); such cage voids afford beneficial circumstances for more favourable gas access and consequent host–guest interaction. The total effective free volume of 1 with removal of solvent molecules is 63.6% (3640.9 Å³ out of the 5727.3 Å³ unit cell volume) calculated by PLATON analysis.[18]

To confirm the porosity of the activated phase 1a, N_2 sorption–desorption isotherms were measured at 77 K and 1 bar, and showed a reversible type-I behaviour, characteristic of permanent microporous materials, with an uptake of 392 cm³ g⁻¹; there is a slight hysteresis between the sorption and desorption traces (Fig. S8, ESI†), which may be due to the cage effect of the network.[19] The Brunauer–Emmett–Teller (BET) surface area

was calculated to be 1145.9 m² g⁻¹ with a pore volume of 0.998 cm³ g⁻¹. Such porosity is moderate and even lower than those of early reported MOFs.[20] However, 1a takes up a significant amount of H_2, CH_4, and CO_2 under atmospheric pressure.

The H_2 adsorption capacity of the activated phase 1a was measured at 77 K and 87 K. As shown in Fig. 2, the H_2 sorption isotherms show no hysteresis on adsorption and desorption, indicating that H_2 sorption is reversible physisorption. The H_2 uptake capacity of 1a reaches 209.5 cm³ g⁻¹ (9.35 mmol g⁻¹, 1.87 wt%) at 87 K and 1 bar, and its H_2 adsorption capability is up to 303.6 cm³ g⁻¹ (13.6 mmol g⁻¹, 2.7 wt%) at 77 K and 1 bar, being among the highest values known to date and significantly higher than those of some highly porous MOFs with much larger surface areas, such as MOF-177 (4526 cm² g⁻¹, 1.23 wt%),[21] IRMOF-6 (2476 cm² g⁻¹, 1.46 wt%),[22] and PCN-68 (5109 cm² g⁻¹, 1.87 wt%).[23] The above results indicate that the optimized pore size plays a dominant role in reducing the fraction of under-utilized void space, which consequently increases the high density of open metal sites and attractive adsorbate–adsorbent interactions.[24] Noticeably, there is only a small number of MOFs which exhibit over 2.0 wt% H_2 uptake under the same conditions (Table S3, ESI†).[25,26]

The sorption behaviours of 1a toward CH_4 and CO_2 were studied at 273 and 298 K at 1 bar, all of which are fully reversible and do not reach saturated adsorption (Fig. 2). 1a shows a maximum CH_4 uptake of 18 cm³ g⁻¹ (0.8 mmol g⁻¹, 1.29 wt%) at 298 K, and 69 cm³ g⁻¹ (3.1 mmol g⁻¹, 4.9 wt%) at 273 K. These values are much higher than most of those reported at 1 bar, such as CPM-33b (41.3 cm³ g⁻¹, at 273 K), L'_{Cu} (36.97 cm³ g⁻¹, 273 K) and [Zn(btz)] (0.57 at 273 K and 1.57 mmol g⁻¹ at 298 K),[27] and even higher than or comparable to some well-known MOFs such as MOF-200 (41 cm³ g⁻¹, at 290 K and 35 bar) and MOF-210 (53 cm³ g⁻¹, at 290 K and 35 bar) measured at high pressures.[28] It is interesting that 1a exhibits a high CO_2 uptake capacity of 149 cm³ g⁻¹ (6.65 mmol g⁻¹, 29.3 wt%) at 273 K and 115 cm³ g⁻¹ (5.2 mmol g⁻¹, 22.7 wt%) at 298 K; such uptake values at both temperatures are impressive as there are few MOFs exhibiting a
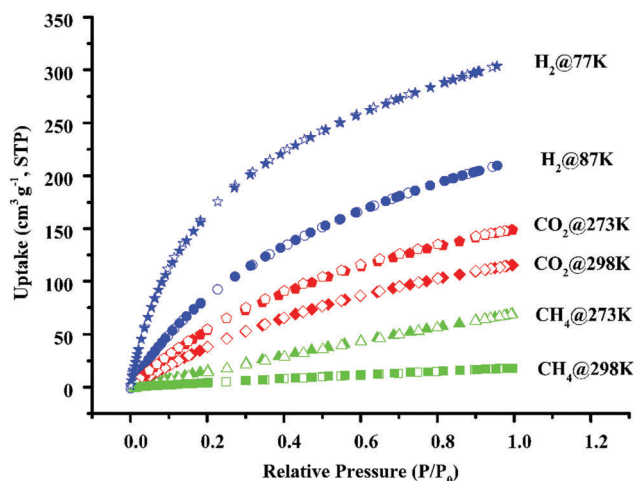

Fig. 2 H_2, CH_4 and CO_2 sorption isotherms. STP = standard temperature and pressure.

CO_2 uptake of more than 20.0 wt% under ambient conditions,[29] even though numerous MOF structures have been reported. The CO_2 absorption amount of Zn-MOF-74 (17.6 wt%), $Cu_3(BTC)_2$ (18.4 wt%) and PCN-6 (15.9 wt%) at 273 K and 1 bar is higher among reported MOFs,[30] which are lower than that of **1a**. The superior CO_2 capture of **1a** may be attributed to the overlap of potential fields of the pore walls and high density of open metal sites in small pores.

High CO_2 uptake together with the exposed copper metal sites within the framework of **1a** inspired us to investigate its heterogeneous catalytic activity for the cycloaddition reaction of CO_2 with epoxides (Table 1). Typically, the reactions were carried out using the epoxide (20 mmol) and carbon dioxide in the presence of a co-catalyst, tetrabutylammonium bromide (TBAB, 0.3 mmol), at 373 K and 1 MPa; while the loading of the catalyst (0.01 mmol) is a 0.5 mol‰ ratio based on the Cu_2 cluster. Remarkably, **1a** performed with high efficiency in the CO_2 cyclo-addition especially with small-sized epoxides (Table 1): the glycidol was completely converted to cyclic carbonate within 2 h with a turnover number (TON) of 2000 per mole of catalyst and a turnover frequency (TOF) as high as 1000 per mole of catalyst per hour. A small decrease in the conversion (95.2%) was observed when the hydroxyl was substituted for a chloride substituent and the corresponding TON and TOF values were 1904 and 952 h^{-1}; such values are very impressive, to the best of our knowledge, as the TON and TOF values are far greater than the previously reported ones for MOF catalysts under similar conditions (Table S7, ESI†).[31] To check the generality of the CO_2 cycloaddition in this work, larger epoxide substrates were employed and the experiment conducted under similar conditions. The reaction yields catalyzed by **1a** from related epoxides are almost complete for 1,2-epoxy-3-phenoxypropane and 64.1% for styrene oxide (SO) within 6 h with corresponding TOF values of 333 and 214 h^{-1} per Cu_2 cluster. Despite there being a certain decrease compared with values for small substrates under the same conditions, the TOF values of larger ones are still among the highest known to date (Tables S8 and S9, ESI†). To examine its recyclability, taking the CO_2

cycloaddition with glycidol as an example, the catalyst **1a** was successively reused in 3 runs without significant decrease in the catalytic efficiency (Fig. S13, ESI†). Additionally, the structural integrity of **1a** after catalysis was proved by powder X-ray diffraction (PXRD) measurements (Fig. S3, ESI†). Both high activity and recyclability make **1a** an excellent heterogeneous catalyst for chemical CO_2 fixation.

Accordingly, a tentative mechanism for the **1a**-catalyzed cycloaddition of epoxide and CO_2 into cyclic carbonate was proposed based on some previous reports,[26] and is shown in Fig. S14 (ESI†). The coupling reaction is initiated by binding the epoxide with the Lewis acidic copper site in the activated phase. Once binding with copper, the C–O bond of the epoxide is weakened, partly due to electron transfer from the oxygen atom to copper. Subsequently, the less-hindered carbon atom of epoxide is attacked by the Br generated from nBu$_4$NBr, which opens the epoxy ring, as a consequence of its lower steric effect and higher positive charge. This is followed by the interaction of an oxygen atom from CO_2 with the positively charged carbon of the epoxide and that of the O atom of the epoxide with the C atom of CO_2. The succedent ring closure gives the production of cyclic carbonate.
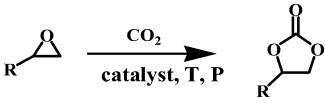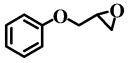
In summary, a microporous novel Cu-MOF has been successfully designed and synthesized based on a bent silicon-centered ligand. The title compound features optimized cavity space and a high density of embedded Lewis acid metal sites; such an intrinsic structure motif endows it with excellent gas storage performance under atmospheric pressure and heterogeneous catalytic activity for chemical fixation of CO_2 under mild conditions. The generation of a high density of active metal centres within confined cages through crystal engineering has been proved to be an applicable way to develop preponderant materials for gas uptake and chemical CO_2 fixation.

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Table 1 **1a**-catalyzed coupling of epoxides with CO_2

Entry	Substrate	Conversion (%)	TON	TOF
1[a]	(glycidol, R–OH)	>99	2000	1000
2[a]	(R–Cl)	95.2	1904	952
3[b]	(1,2-epoxy-3-phenoxypropane)	>99	2000	333
4[b]	(styrene oxide)	64.1	1282	214

Reaction conditions: epoxide (20 mmol), catalyst (0.01 mmol, based on $[Cu_2(CO_2)_4]$ cluster), and TBAB (0.3 mmol) under carbon dioxide (1 MPa) at 373 K. The yields were determined by ^{1}H NMR analysis. [a] 2 h. [b] 6 h.

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