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A unique magnesium-based 3D MOF with nanoscale cages and temperature dependent selective gas sorption properties[†]

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A porous Mg-based 3D metal-organic framework with unique nanoscale cages and two-fold interpenetrating pcu nets has been synthesized and characterized. It shows gas-uptake capacities for N_2 , H_2 , O_2 and CO_2 at low temperatures and selective adsorption of CO_2 over O_2 and N_2 at room temperature.

In the past decade, the design and synthesis of porous metalorganic frameworks (MOFs) have attracted widespread attention due to their intriguing structural diversities of architecture and potential applications such as gas separation and storage,¹ ionic/ molecular recognition,² heterogeneous catalysis,³ luminescence tuning,⁴ fabrication of metal nanoparticles,⁵ and so on. To date, a large number of porous MOFs have been constructed using transition metals and lanthanide ions as framework nodes.⁶ Recently, the coordination chemistry of MOFs based on light main group metal cations such as Li⁺, Mg²⁺, and Al³⁺ has been revealed and studied. With these lightweight main group elements, the MOFs have an advantage of low-density, which will be beneficial for on-board hydrogen storage application.⁷ Up to now, a number of research groups have done the previewing work on magnesiumbased MOFs.8 For example, Long et al. have found that a porous Mg-based MOF, $Mg_3(ndc)_3(DEF)_4$ (H₂ndc = 2,6-naphthalene dicarboxylic acid), shows strong hydrogen gas affinity. Matzger et al. have reported that MOF-74 (Mg₂(dobdc), H₄dobdc = 2,5-dihydroxyterephthalic acid) exhibits a high uptake capacity for CO₂ at room temperature. However, compared with large numbers of porous MOFs constructed using transition metals and lanthanide ions, Mg-based porous MOFs are still rare.

Herein, we report a novel Mg-based 3D porous MOF, $[Mg_{16}(PTCA)_8(\mu_2-H_2O)_8(H_2O)_{16}(dioxane)_8] \cdot (H_2O)_{13} \cdot (DMF)_{26}$ (1), which

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was constructed by the coordination of a tetracarboxylate ligand (pyrene-1,3,6,8-tetracarboxylic acid, H_4 PTCA) with Mg²⁺. Interestingly, this 3D porous MOF has nanoscale polyhedral cages and shows temperature dependent selective gas sorption properties.

The hydrothermal reaction of MgCl₂·6H₂O, H₄PTCA and HCl at 90 °C in a mixture solution of DMF-dioxane-H₂O (2 : 1 : 1) produced yellow block-shaped crystals of 1 in high yield (ESI⁺). The result of X-ray crystal structural analysis[‡] reveals that 1 crystallizes in the cubic space group $Im\bar{3}m$, in which there are two half crystallographically independent Mg(II) ions in one asymmetric unit (Fig. S2, ESI⁺), and Mg1 and Mg2 show similar distorted octahedral geometries. In addition, the PTCA ligand is located in a 4-fold axis, and the dioxane molecule is located both in a 2-fold axis and a mirror plane. In 1, the six oxygen atoms coordinated to Mg1 are from four PTCA ligands and two water molecules, while six oxygen atoms around Mg2 come from two PTCA ligands, three water molecules and one dioxane molecule. In 1, the inorganic brick consists of octahedral Mg dimers with a common corner corresponding to a µ2-H2O aquo ligand as a secondary building unit (SBU). As illustrated in Fig. 1, twelve PTCA ligands bridge a total of 24 Mg₂ SBUs to generate a large nanoscale cage with a diameter of 2.3 nm, and its calculated pore volume is 6.3 nm³. To the best of our knowledge, such a large cage based on main group metal ions has not been reported so far. On the surface of each cage, there are two types of windows: six square windows with dimensions of 7.9 \times 7.9 Å (Mg to Mg distances from SBUs) and eight triangular windows with dimensions of 7.4 \times 7.4 \times 7.4 Å (Mg to Mg distances from SBUs) (Fig. S3, ESI⁺). Furthermore, four PTCA ligands link four SBUs to form a tube with dimensions of 10.7 imes 10.7 Å (centroid–centroid distances from PTCA). The tubes connect the nanoscale cages to form a three-dimensional (3D) metal-organic framework of 1, in which each cage is surrounded by six neighboring cages connected by six tubes to generate a pcu topological net (Fig. 2). In the framework, large octagonal channels (2.4 \times 2.4 nm) are formed along a, b and c directions and are size-matchable with the nanoscale cages (2.3 nm in diameter), leading to a two-fold interpenetrating net (Fig. 3). As far as we know, analogous MOFs with a two-fold interpenetrating pcu net are still rare, and

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Fig. 1 A schematic illustration of the nanoscale cage containing 12 PTCA ligands and 24 Mg_2 dimer SBUs.



Fig. 2 Polyhedral representation of the pcu net in 1

only two analogous MOFs have been reported so far.⁹ The pores of **1** are filled with disordered DMF and H_2O molecules, and the solvent-accessible volume calculated using PLATON¹⁰ is 40.2%. Afterwards, soaking **1** in methanol leads to the exchange of DMF and H_2O guest molecules with methanol to give **1**'.

The results of thermogravimetric analysis (TGA) indicate that **1** shows continuous weight loss in the temperature range



Fig. 3 The two-fold interpenetration of 1 observed along the a axis.



Fig. 4 Gas adsorption isotherms of **1d** for (a) H_2 , N_2 and O_2 at 77 K; CO_2 at 195 K, (b) CO_2 , N_2 and O_2 at 273 K and 298 K. Filled shapes = adsorption, open shapes = desorption.

from 30 to 550 °C, while 1' shows plateaus from 60 to 400 °C (Fig. S4, ESI⁺). Unfortunately, the results of variable temperature PXRD measurements of $\mathbf{1}'$ show that the powder diffraction peaks disappeared after 70 °C (Fig. S5, ESI⁺), indicating the collapse of the framework structure. Fortunately, the methanol molecules in 1' can be removed under high vacuum at room temperature to obtain a desolvated sample 1d. The gas adsorption measurements of 1d show that it can adsorb N_2 , H_2 , O_2 and CO₂ at low temperatures (Fig. 4a). At 77 K, the sorption isotherm of N₂ shows a typical Type-I curve, with the amounts of N₂ uptake increasing abruptly at the beginning and then gradually reaching a plateau of 123.7 cm³ (STP) g⁻¹ at 1.0 atm. Fitting the Langmuir and BET equations to the N₂ adsorption isotherm gave estimated surface areas of 532.9 and 438.1 m² g⁻¹, respectively. The H₂ and O₂ adsorption isotherms reveal that 1d can store up to 92.2 cm³ (STP) g⁻¹ hydrogen at 77 K/1.0 atm and 200.1 cm³ (STP) g^{-1} oxygen at 77 K/0.19 atm. It is worth noting that the adsorption capacity for O_2 is higher than that for N_2 , which may be due to the smaller kinetic diameter and lower critical temperature of O_2 (3.47 Å, 33.2 K) than those of N_2 (3.64 Å, 126.2 K), which allows the O_2 adsorption in a more condensable manner in the cages with smaller windows.^{1e} In addition, the CO₂ adsorption isotherm of 1d measured at 195 K and 1.0 atm shows two-step sorption. From 0 to 0.1 atm, 1d can adsorb 97.2 cm³ (STP) g^{-1} of CO₂, and then it adsorbs more CO₂ and reaches a plateau of 160.5 cm^3 (STP) g^{-1} .



The CO_2 , N_2 and O_2 sorptions were also performed at near room temperature. Interestingly, 1d shows selective gas adsorption for CO₂ over N₂ and O₂ at 273 and 298 K. The amounts of CO_2 uptake by 1d are 44.2 cm³ (STP) g⁻¹ at 273 K and 23.6 cm³ (STP) g^{-1} at 298 K, while almost no N₂ and O₂ adsorptions are observed for 1d under the same conditions. The ideal adsorbed solution theory (IAST) method¹¹ was used to estimate the adsorption selectivity of CO2 over N2 and O2 (Fig. S11 and S12, ESI[†]). The predicted adsorption selectivity of CO₂-N₂ for an equimolar mixture of CO₂-N₂ is 30.9 at 273 K and 28.3 at 298 K, respectively, and the predicted CO₂-O₂ selectivity for an equimolar mixture of CO2 and O2 is 24.7 at 273 K and 22.1 at 298 K, respectively. 1d exhibits better CO₂-N₂ selectivity than PCN-61 $(\sim 15)^{11c}$ and SNU-100' $(26.5)^{1h}$ at 298 K, indicating that 1d may have potential applications in the separation of the CO2-O2 mixture and the CO2-N2 mixture. The selective sorption of CO_2 rather than N_2 and O_2 can be attributed to the quadrupole moment of CO_2 (-1.4 × 10⁻³⁹ cm²), which generates specific interactions with the framework.¹² To better understand the interactions between CO₂ and the framework of 1d, we calculated the isosteric heat Q_{st} of CO_2 adsorption for 1d at 273 K by the Clausius-Clapeyron method.9a As shown in Fig. 5, the adsorption enthalpy for 1d at zero loading is approximately 31.3 kJ mol⁻¹, which is higher than the values of the PCN-6X series (PCN-61, 21.0 kJ mol⁻¹; PCN-66, 26.2 kJ mol⁻¹; PCN-68, 21.2 kJ mol⁻¹)¹³ and SNU-100' (29.3 kJ mol⁻¹),^{1h} implying relatively strong interactions between the CO₂ and the pore surface of 1d.

In conclusion, we have successfully constructed a novel twofold interpenetrating Mg-based 3D MOF containing large nanoscale cages with a diameter of 2.3 nm. The desolvated solid **1d** exhibits selective gas adsorption for CO_2 over N_2 and O_2 around room temperature, indicating that the present material can be potentially applied in a CO_2 capture process.

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Notes and references

‡ Crystal data for 1 (C₂₇₀H₃₆₈N₂₆O₁₄₃Mg₁₆): cubic, space group $Im\bar{3}m$, a = b = c = 35.1938(1) Å, V = 43591.2(2) Å³, $M_r = 6654.86$, Z = 6, $\rho_{calcd} = 1.521$ g cm⁻³, $\mu = 1.352$ mm⁻¹, T = 150(2) K, $R_1 = 0.1487$, w $R_2 = 0.2497$, GOF = 1.010 for 3203 reflections with $I > 2\sigma(I)$. CCDC 913523 (1).

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