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A Highly Stable Porous Multifunctional Co(II) Metal-Organic Framework Showing Excellent Gas Storage Applications and Interesting Magnetic Properties

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A porous Co^{II} -metal-organic framework with unprecedented stability has been successfully synthesized, which displays excellent N₂ (292.0 cm³ g⁻¹), H₂ (181 cm³ g⁻¹, 1.6wt%), CO₂ storage capacity (123 cm³ g⁻¹, 24.3 wt% for 273 K, 73.3 cm³ g⁻¹, 14.4 wt% for 298 K), and interesting ferrimagnetic behavior

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A porous multifunctional Co(II)-metal organic framework with large BET and Langmuir surface areas, 911.0 and 1126.8 $\mbox{cm}^3\mbox{ g}^{-1}$ respectively, exhibits excellent N₂ (292.0 cm³ g⁻¹), H₂ (181 cm³ g⁻¹, 1.6 wt%), CO₂ storage capacity (123 cm³ g⁻¹, 24.3 wt%). Furthermore, it also exhibits interesting ferrimagnetic behavior.

Metal-organic frameworks (MOFs) are a burgeoning subclass of crystalline porous functional materials composed of metal-cluster or metal-ion connected by organic linkers.¹ They contain many attributes, such as, ultrahigh surface areas, pore size and shape, as well as tunable chemical composition². These characters make MOFs to be ideal materials for their associated exceptional wide range of applications in various fields such as gas storage and separation,³ luminescence,⁴ magnetism,⁵ and drug delivery,⁶ etc. The porosity is a key feature and plays a crucial role in these functional properties, typically in gas storage applications for various alternative energy source, such as H₂, CH₄, etc, as well as greenhouse gas, carbon dioxide capture.⁷ In recent years, the undesirable global warming and climate change have attracted increasing attention with the growing increase in the amount of CO₂ in the atmosphere, so ongoing attention and endeavours have been paid to designingly synthesize novel MOF materials with large and tunable free pore volumes to control the clean energy storage and capture of pollutant gases. The MOFs materials with flexibility framework will be a desirable select, since they can shrink or expand (breathing effect), leading to large accessible channel and high internal surface area, which are key for high gas adsorption capacity. At the same time, it is the most appealing aim to explore multifunctional MOFs materials, since multifunctional MOFs

ligands in porous MOFs. In large porous MOFs, metal chains or clusters are bridged by long organic linkers, so the inter-cluster magnetic interaction is very weak. Intra-cluster magnetic behavior plays the most important role, which is ascribed to the contribution of metal center. Based on the aforementioned considerations, a semi-rigid ligand hexa[4-(carboxyphenyl)oxamethyl]-3-oxapentane acid (H₆L) was selected as building block to construct new structures. Such conformational adjustable hexacarboxylate liganc space-directed auxiliary ligand adding 1,4-bis(1imidazolyl)benzene (dib) is proved to be effective and successful n improving the porosity of the resulting structure, because the use of two complementary ligands provides an additional level of control in the framework structure and charge density distribution. Co²⁺ salt as metal source reacts with H₆L in mixed solvent systems DMF/H₂O at 130 °C, resulting in one highly porous CoMOF 1. Its structure was characterized by elemental analysis, infrar d spectroscopy, TGA, and single-crystal X-ray diffraction, namely, Co₃(L)(dib)•2H₂O•6DMF (1). We describe detailedly its synthesis, crystal structure, gas adsorption and magnetic behavior. Single-crystal X-ray diffraction result reveals that CoMOF 1 crystallizes in monoclinic space group C2/c (Table S1) and possesses a two-fold interpenetrating topology with large channels. It is

 $(H_{c}L)$





J. Name., 2013, 00, 1-3 | 1

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COMMUNICATION

isomorphous as our reported CdMOF.^{4d} Two crystallographically unique Co^{2+} ions exist in the fundamental unit (Fig. S1a). The characteristic linear trinuclear (Co^{II}₃) secondary building units (SBUs) was formed (Fig. 1a), in which Co(1) ion in an inversion centre with 50% occupancy, coordinated by six oxygen atoms from four different carboxylate ligands to form an octahedral coordination environment (Fig. S1b); Co(2) and its symmetry-related atom Co(2D) (symmetry code: D -x+3/2,-y+3/2,-z+1) in terminal positions adopt distorted triangular-prism coordination sphere, being ligated by five carboxylate oxygen atoms from three L⁶⁻ anions and one pyridyl nitrogen atom from dib (Fig. S1c). The Co(1) and Co(2) ions are linked by one O-C-O bridge and two oxygen atoms μ_2 -[O(4), and O(7)] (Fig. S1a) with a Co...Co interaction of 3.175(1) Å. The Co-O bonds vary from 1.987(4) Å to 2.364(6) Å, and Co-N bond length is 2.043(5) Å. Each L⁶⁻ ligand links ten Co(II) centers via four carboxylate groups adopting μ_2 - $\eta^1 \eta^2$ coordination modes, and two carboxylage groups adopting μ_2 - $\eta^1 \eta^1$ coordination modes (Fig. S1d), in which its central oxygen O(1) lies on a two-fold axis with 50% occupancy. It as a tetradentate linker links four adjacent Co^{II}₃ SBUs (Fig. S2a) into two-dimensional (2D) layers along *b*-direction by L⁶⁻ ligands (Fig. S2b). The dib ligand lies about another inversion centre and links two Co centers as a 2-connected node (Fig. S1e). A porous CoMOF framework with very large 1D nanochannels (18.52 × 13.60 $Å^2$) along *c*-axis is generated by a dib bridger (Fig. S2c). The spacious nature of the single network allows the other identical pts networks to penetrate it in a normal mode, resulting in a two-fold interpenetrating array (Fig. 1b), in which the large channels in CoMOF (1) were divided into four parts. PLATON analysis showed that the effective free volume in 1 is 44.7% of the crystal volume (4025.7 out of the 8999 (3) unit cell volume).⁸ Each $\text{Co}_{3}^{\text{II}}$ SBU is surrounded by four L^{6-} ligands. The whole interpenetrated framework can be simplified as a (4, 6)-connected 2-nodal fsc net with the point symbol of $\{4^4.6^{10}.8\}\{4^4.6^2\}$ by TOPOS software (Fig. 1c, Fig. S2e).9



Fig. 1 (a) The Co^{II}_{3} building unit. (b) The porous CoMOF (1) along *c*-axis. Free water and DMF molecules are omitted for clarity. (c) The simplified **fsc** net along [100] direction.

Such interpenetrated structure minimizes the whole empty space, but it can significantly enhance the stability of the framework. Especially, such interpenetration will be beneficial to the capture of small gas molecules, such as H_2 and CO_2 , because large pores are hard to lead to high uptake capacities. Therefore, we hypothesized that CoMOF (1) will be a potential gas sorption material. Firstly, the experimental PXRD pattern of the as-synthesized CoMOF (1) is basically identical to the respective simulated pattern, indicating the high phase purity of the solid products of 1 (Fig. 2, red line). Secondly, thermogravimetric analysis (TGA) shows that all free solvent molecules (containing two free water and six DMF molecules: calc. 25.9%, observ. 25.3%) below 235 °C in the channels of 1 can be completely released into guest-free 1a as expected, followed by a plateau from 235-345 °C (Fig. S3, black line). The resulting 1a can be stable to about 345 °C. In order to confirm that as-synthesized 1 can be activated into guest-free 1a, some preparative work was done, as follows: 1 was immersed in ethanol and dichloromethane alternately, followed by evacuation under vacuum at 130 °C for 8 h. Furthermore, the samples of activated 1a were characterized by TGA measurement to assure full activation (Fig. S3, red line), which clearly shows that the resulting **1a** does not exhibit obviously weight-loss and can be still thermally stable up to 350 °C. More supportively, FT-IR spectrum of 1a (Fig. S4) shows no absorption bands in 3417 and 1659 cm⁻¹ comparative to the one 1. which should be attributed to the asymmetric vibration from free water molecules and the characteristic stretching vibration of the C=O group of DMF. Moreover, the XRPD pattern (Fig. 2, blue line) of CoMOF 1a shows similar sharp peaks as CoMOF (1), verifying the maintenance of the framework and its crystallinity. Thus the compound will be an attractive candidate for gas adsorption applications.



Fig. 2 The PXRD patterns of **1** in different states.



Fig. 3 (a) Gas adsorption isotherm of N_2 at 77 K. Inset: the pore size distribution of **1** based N_2 sorption data. (b) H_2 at 77 K and (c) CO_2 at 273 and 298 K adsorption isotherms.

Journal Name

The accessible permanent openness and the architectural stability of CoMOF 1a was also proved by N2 adsorption isotherm at 77 K (Fig. 3a), which shows a characteristic type I behavior with a Brunauer-Emmett-Teller (BET) and Langmuir surface areas up to 911.0 and 1126.8 $\mbox{m}^2\mbox{ g}^{\mbox{-}1},$ respectively, as well as a micropore volume of 0.45 cm³ g⁻¹, demonstrating high porosity. The adsorption amount of N_2 at saturation is about 292.0 cm³ g⁻¹. A pore width of 6.12 Å is also calculated by applying the Horvath-Kawazoe method. This accessible porosity prompts us to further examine anthropogenic energy (or atmosphere) related gas sorption properties of H₂ and CO₂. The results display that the uptake of H_2 is ca. 1.62 wt % (181.1 cm³ g⁻¹) (Fig. 3b) at 1 atm and 77 K, which surpasses some well-known MOFs and ZIFs, ¹⁰ such as PCN-105 with mesoporous cages (1.51 wt%), the best zeolite ZSM-5 (0.7 wt%), ZIF-8 (1.27 wt%), MOF-5 (1.32 wt%), IRMOR-8 (1.45 wt%) as well as MOF-177 (1.25 wt%). It is very obvious that MOF-177 with very high BET surface area of 4526 m²/g is much larger than that of 1, but displays much lower H₂ uptake, interpenetrated 1a with interconnected micropore may effectively improve the gas adsorption capacity, which has been demonstrated by typical MOF-5 and interpenetrated MOF-5.¹¹ The classical MOF-5 with higher BET surface area of 3361 m^2/g displays much smaller H₂ adsorption capacity (1.32 wt%) than the corresponding interpenetrated MOF-5 (BET: 1130 m²/g and 2.0 wt% H₂ uptake). Then the CO₂ sorption properties of 1a were also investigated at 273 and 298 K under 1 bar. Notably, 1a also exhibits a particularly high CO2 uptake capacity of 123.1 cm³ g⁻¹ (24.3 wt%) at 273 K (Fig. 3c, black line) and 73.3 cm³ g⁻¹ (14.4 wt%) at 298 K (Fig. 3c, red line), which nearly outperforms all previously reported MOFs at 273 K,¹² except limited SNU-5 and Cu-EBTC¹³, and most of MOFs at 298 K.¹² Fitting the CO₂ adsorption isotherm gives an BET surface area of 2309.5 m² g⁻¹ and Langmuir surface areas was 2835.9 m² g⁻¹. Evidently, these surface areas are relatively high comparatively reported MOFs. Based on the experimental isotherm data of CO_2 at 273 and 298 K, the isosteric heat (Qst) on activated 1a was calculated from Virial analysis combined with the Clausius–Clapeyron equation.¹⁴ The complex 1 exhibits strong binding affinity for CO_2 with high enthalpies in the range of 16.0-29.0 kJ mol⁻¹ (Fig. S5).¹⁴ To evaluate the practical use of an adsorptive material, it is crucial and important standards for its regeneration and recycling properties. Keeping this in mind, the PXRD of 1a after three cycles was investigated, which is in good agreement with that of its original structural characteristics, revealing its good stability. The high H₂ and CO₂ uptakes as well good thermal stability make **1a** a promising candidate for industrial sorbent application. Comparing with its isomorphous CdMOF in our previous report,^{4d} CoMOF (1) displays excellent gas storage capacity for N₂, H₂ and CO₂ with high BET and Langmuir surface areas. CdMOF also displays type-I sorption behavior, but it exhibits much lower gas adsorption amount for N₂ (141 cm³ g⁻¹) and H₂ (47.8 cm³ g⁻¹) at 77 K and 1 atm with Langmuir and BET surface areas of 178 and 138 m² g⁻¹, respectively. Such different gas adsorption behaviour between CdMOF and CoMOF may be caused by two main reasons. (1) Activated temperature: CdMOF and CoMOF are activated under vacuum at 80 °C and 130 °C,

COMMUNICATION

respectively. Some solvent molecules may remain in the channel of CdMOF, but CoMOF can release completely its solvents, demonstrated by IR and TGA analyses of activated sample; (2) Metal center: Co^{II}-framework with d⁷ electron configuration is more active and displays stronger interactions between framework and gas molecules over CdMOF with d¹⁰ electron configuration.⁷

Considering the structure information of linear Co^{II}₃ subunits in the framework of 1, its magnetic property is detailedly investigated on its polycrystalline sample. As shown in Fig. 4, χ_{m}^{-1} (χ_{m} is molar magnetic susceptibity), and $\chi_m T$ versus T plot were obtained over 2-300 K and a magnetic field of 1000 Oe. The study of the temperature dependent magnetic susceptibilities revealed that 1 displays a typical ferrimagnetic interaction between the Co^{II} ions. The $\chi_{\rm m}$ T value at 300 K is equal to 8.23 cm³ K mol⁻¹, significantly larger than the spin-only value of 5.61 cm³ mol⁻¹ K for three spins with S = 3/2 and g = 2.00, being attributed to the orbi contribution of high spin Co(II) ions in an octahedral environment, but is consistent with the values observed in many other high spin octahedral Co(II) complexes.¹⁵ On lowering the temperature, $\chi_m T$ firstly decreases gradually, and reaches a minimum of 7.3 cm³ mol⁻¹ K at 35 K, which does not imply an antiferromagnetic coupling between Co(II) ions, as it is mainly due to the single ion behaviour of Co(II) ion. Then it passes through the minimum, sharply increases to the value of 8.49 cm^3 mol⁻¹ at about 3.4 K, then falls again, probably due to the saturation effect or zero-field splitting. The reciprocal molar susceptibility (χ_{m}^{-1}) plot as a function of temperature obeys the Curie–Weiss law $\chi_m = C/(T-\vartheta)$ for Co^{II} centers with the Curie constant $C = 8.21 \text{ cm}^3 \text{ K mol}^{-1}$ and Weiss temperature artheta = -3.02 K, covering the whole temperature range. The negative value of ϑ and the initial decrease of $\chi_{\rm m}$ T at high temperature a likely related to the effect of spin-orbit coupling that stabilizes an effective spin doublet state. The steep rise in $\chi_m T$ between 35 and 3 K indicates that a mechanism of ferromagnetic-like correlations within the μ_2 -O-bridged Co(II) ions may exist and develops into a long-range ordering. The shape of the $\chi_m T$ versus T plot, with its (shallow) minimum, may be a typical of ferrimagnetic behavior or spin-canting effects.



Fig. 4 (a) Temperature dependence of $\chi_m T$ and χ_m^{-1} for 1 at H = 1000 Oe from 2 to 300 K (b) The field dependent isothermal magnetization for 1 at 2 K and 300 K.

To gain more insight into the magnetic behaviour at low temperature, zero-field-cooled and field-cooled magnetic (ZFC, FC) and alternating-current (ac) magnetic susceptibility measurements were performed for **1** (Fig. S6). The ZFC and FC plots (Fig. S6a) display reversibility between the ZFC/FC curves, and the temperature dependences of the susceptibilities in different applied magnetic fields are compatible with the ferrimagnetism, at the same time the out-of-phase part of ac susceptibility (Fig. S6b) does not show clear frequency dependence, suggesting spin-canting behaviour may be excluded. Furthermore, a rapid saturation and large remnant magnetization at 2 K also verify a ferromagnetic long-range ordering, suggesting that **1** is rather a ferrimagnetic system.

Conclusions

A highly stable porous CoMOF (1) with 2-fold interpenetrated architecture has been designedly synthesized. Such interpenetration partitions the large pore space into small domains, which is effective enough to enhance the interaction between the framework and gas molecules, thus it displays excellent H₂ (181 cm³ g⁻¹, 1.6 wt%), CO₂ (123 cm³ g⁻¹, 24.3 wt%) capture capacity. Its magnetic property is also determined by the spin-orbit coupling between Co^{II} ions and a ferrimagnetic system was demonstrated. Taking into account both large porous and good magnetic exchange bridges, multinuclear subunits will be wise select. In continuation of our research interest in multifunctional MOFs, the most fascinating outcome of this work successfully combines gas capture and magnetic properties. Especially, its permanent porosity and adsorption properties are particularly useful to exploit potential sorption materials.

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4 | J. Name., 2012, 00, 1-3

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