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LETTER

A Novel 3-fold Interpenetration Metal–Organic Framework with Tunable Luminescence and Selective Adsorption of CO_2 Properties

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A novel acylamide MOF $Zn_2(L)(oba)_2$•2DMF•$2H_2O$ [1, H_2oba=4,4'-oxybis(benzoic acid), L=N^1,N^4-di (pyridin-4-yl)terephthalamide)] has been synthesized by solvothermal method. The adsorption study indicates that 1 shows higher selective adsorption behaviors of CO_2 rather than CH_4, CO, N_2 and significant isosteric heat (Qst) of CO_2(39.3 kJ mol^{-1}), which are attributed to nature from the acylamide groups holding unique affinity towards CO_2. Vapor adsorption studies indicate that 1 has higher selective adsorption of water vapor over ethanol and methanol vapor. In addition, tunable luminescence properties dependent on excitation wavelengths was observed.

In the last decade, great interest has been focused on acylamide metal–organic frameworks (MOFs) due to remarkable structural features and promising applications in gas storage and separation, catalysis, sensors, magnetism and luminescence.[1] Acylamide MOFs are tailorable materials and the structures and properties can be rationally designed and improved through many ways, which is derived from their special inorganic–organic combination, intrinsic tunability and modularity of their highly ordered structures.

Nowadays increasing efforts have been devoted to utilizing MOFs to separate CO_2 from other gases (N_2, CH_4, or CO). Therefore, MOFs possessing high selective adsorption behaviors of CO_2 over other gases becomes promising. Several methods such as incorporation of exposed metal cations, ligand functionalization, and framework interpenetration have been proved to be effective approaches to enhance the selectivity of CO_2. [2] The research of acylamide MOF has shown that these materials are highly efficient in the field of gas storage and separation, especially acylamide functional groups have larger affinity towards CO_2, making it being admirable materials for selective adsorption of CO_2. [1c] Furthermore, acylamide MOFs are also excellent candidates as tunable luminescence materials. [3] So far, a variety of luminescent acylamide MOFs with tunable emission have been designed and investigated. [4] It is reported that there are many cases of acylamide MOFs showing tunable luminescence properties by varying the excitation wavelength. [5] To our knowledge, zinc is an excellent transition metal to act as coordination center, and build stable compounds which make it fairly good choice to form coordination compounds.

We here present a novel acylamide MOF, which reveals distinct selective adsorption of CO_2 over other gases. Vapor adsorption studies indicated that it has higher selective adsorption of water vapor over ethanol and methanol vapor. Furthermore, the MOF shows extraordinary tunable luminescent properties from light blue to blue and then to green by means of direct variation of excitation wavelength.

Single crystal X-ray diffraction reveals that polymer **1** crystallizes in *P2(1)/c* space group. As shown in Fig. 1, the asymmetrical unit contains two crystallographic independent Zn(II) ions. Observing carefully the coordination environment, it is very obvious that Zn1 site takes the ZnO_3N tetrahedral geometry, finished by three oba^{2-} oxygen atoms and one L nitrogen [Zn–O = 1.929(3)–1.997(3) Å, Zn–N = 2.036(3) Å]. However, Zn2 site is five-coordinated in the pyramidal geometry completed by four oxygen atoms from three oba^{2-} ligands and one L nitrogen atom [Zn–O = 1.964(3)–2.474(3) Å, Zn–N = 2.025(3) Å]. [6] In addition, Zn1 and Zn2 atoms connect with each other through oba^{2-} carboxyl groups to form the dinuclear unit with the Zn-Zn distance of ca. 3.5 Å. The L ligand adopts the *trans* conformation which means that the two acylamide C=O groups are located on the opposite side, and the distortion degree of it can be traced by the dihedral angle between pyridine and benzene rings, giving ca. 61.2°or 37.7°. Whereas, a large distortion is observed for oba^{2-} ligand, as evidenced by the dihedral angel of ca.79.45° between two benzene rings, and it is common for oba^{2-} ligand due to the existence of flexibility. Each oba^{2-} ligand links to three Zn(II) ions in a μ_3:$\eta^1\eta^1\eta^1\eta^1$ mode, thus creating a 2D layer(Fig. S1). Further, the L ligands connect directly the two-dimensional layers by taking a bridging bidentate coordination mode, finally the overall pillar-layered 3D framework is formed (Fig. 2). Due to the interpenetration, there is only a small void space occupied by DMF and H_2O molecules in **1**. The topology analysis is performed by

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† Electronic Supplementary Information (ESI) available: Crystallographic data, Selected geometric parameters, and additional structural figures, PXRD patterns. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x

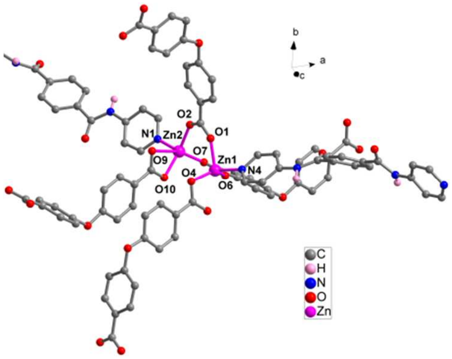

Fig. 1 The asymmetrical unit of polymer **1** and the coordination surrounding around the metal ions.

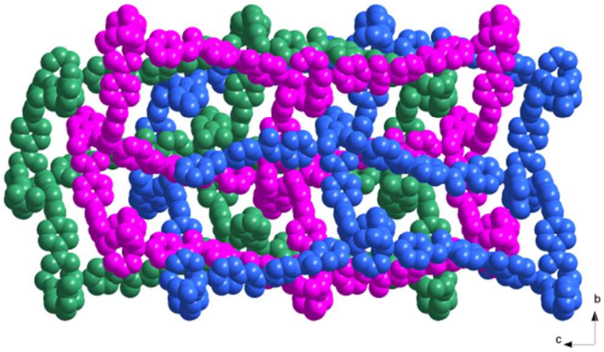

Fig. 2 Viewed down *a* axis, the 3D stacking architecture displays the microporous channels that host DMF and water molecules.

Topos40 program, giving a six-connecting **α-Po** net with $4^{12}6^{3}$ topology symbol. As shown in Fig. S2, each Zn_2 dinuclear unit links with adjacent six identical Zn2 units through two L ligands and four oba^{2-} groups, giving the six-connectivity and thus being seen as a six-connected node. It is noteworthy that every three identical **α-Po** nets interpenetrate with each other, and finally a threefold interpenetrating mode is generated. Moreover, the potential solvent-accessible volume is estimated by Platon program, giving 22.3% of cell volume.

At room temperature, we examined the luminescence emission spectra of polymer **1** in the solid state, which is highlighted in Fig. 3. As it is shown, when excited at 285 nm, a clear emission is observed with a maximum intensity around 431 nm. Along with the rising of the excitation wavelength, another emission at 494 nm appears and increases gradually along with the rising of the excitation wavelength. Two emission peaks are observed clearly with a similar maximum intensity at approximately 431 and 492 nm when adjusting the excitation light to around 310 nm. When polymer **1** is excited at around 350 nm, the emission intensity at around 431 nm almost disappear, whereas the emission intensity at around 468 nm is observed with a blue-shift about 24 nm, in contrast to the 492 nm emission intensity. The same phenomenon can also be seen when excitation is at above 350 nm. The luminescence details are shown in Fig. S3, based on the studies of Commission International de l'Eclairage (CIE) chromaticity coordinates of the emissions spectrum. It is obvious that the luminescence of **1** is tunable from light blue to blue by means of the variation of excitation light. Only when excitation wavelength is at 320nm, the luminescence colour of **1** emerges green. Compared to other methods of producing luminescence, such as modulating chemical factors (Ln^{3+} types and concentration, ligand structure, coordination status, guest species), the way of variation of excitation light appears very convenient. Similar tunable luminescence of acylamide MOFs dependent on excitation wavelength were observed in some cases, such as a direct white-light-emitting MOF $[AgL]_n{}^{\cdot}nH_2O$ with tunable yellow to white luminescence by variation of excitation light was reported by Wang et al; [6a] a acylamide MOF Zn(L) $(HBTC)^{\cdot}(H_2O)_2$ shows tunable luminescence properties from yellow to white and then to blue by means of the variation of excitation light and A 3-fold interpenetrating porous acylamide MOF Zn(bdc)(L)·solvents excited at 320−410 nm suggests that the luminescence of it is tunable from yellow to white and then to blue reported by Luo et al. [1c,6b] However, polymer **1** changes colour only in monochromatic light range from light blue to blue and then to green when excited at 285-380 nm. In addition, the luminescence property of **1** is possible derived from the acylamide groups and ether acid, as both of which are luminous.

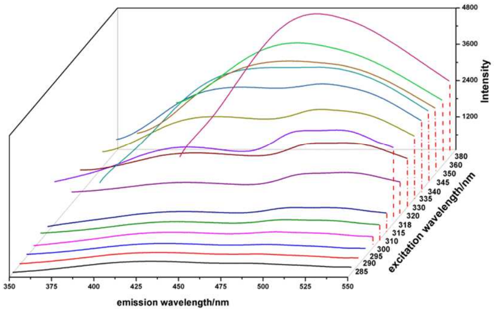

Fig.3 The emission spectrum of **1** under different excitation wavelengths.

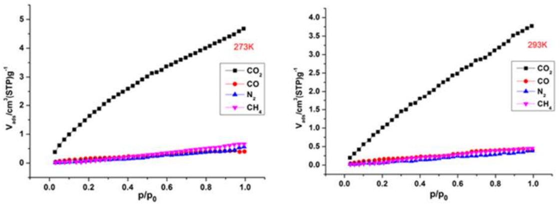

Fig. 4 Comparison of gas adsorption isotherms of **1** for CO_2/CO/N_2/ CH_4 at 273 K (left) and 293 K (right). The kinetic diameters of these gases: 3.3, 3.76, 3.64, and3.8 Å respectively.

Before gas adsorption tests, we carried on the pretreatment of crystal samples of **1** by heating under a vacuum for removing the guest molecules and coordinated solvent molecules from the pores at a first-rank temperature of 100 °C for 8 h. Specific surface area and pore volume were determined by N_2 adsorption at 77 K using a BEL SORP gas adsorption analyzer. The specific surface areas were calculated using the Brunauer−Emmett− Teller (BET) equation by assuming the section area of nitrogen molecule to be 0.162 nm. The total pore volume was determined as the volume of liquid nitrogen adsorbed at a relative pressure of 0.99. The BET surface area and the total pore volume of **1** are 0.97 m^2/g and 0.0035 cm^3/g. The nitrogen adsorption isotherm of **1** at 77 K is shown in Fig. S4, and the desolvated microporous MOF **1** shows no obvious sorption of N_2, which can be attributed to the fact that its aperture is smaller than the kinetic diameter of N_2 (3.64–3.80 Å). [7]

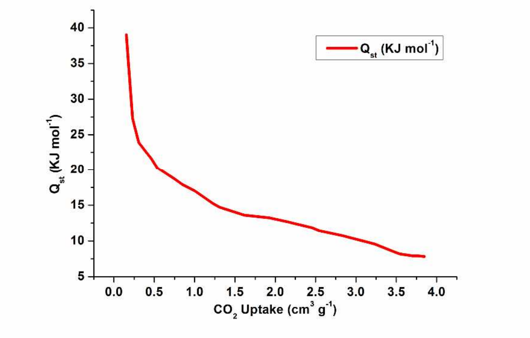

Fig. 5 The adsorption enthalpies of CO_2 calculated by isotherms at 273 and 293 K.

The adsorption isotherms of CO_2 show a gradual increase from P/P_0=0 to 1.0 and reach the maximal amounts of 4.7 cm^3g^{-1}(0.92 wt%) at 273 K and 3.8 cm^3g^{-1}(0.75 wt%) at 293 K (Fig. 4), Both isotherms present typical type-I curves as defined by the IUPAC classification, which is the characteristic of a microporous material. In contrast, the capture capacities of **1** for CH_4, CO, and N_2 are extremely poorer, the adsorption amounts are less than 0.7 cm^3g^{-1} at all tested temperatures. The selective adsorption behaviors of CO_2 over other gases are attributed to the fact that the acylamide functional groups have larger affinity towards CO_2, making a contribution to the potential energy of adsorption, nevertheless, other gases are without this feature. In order to better understand the affinity between the pore surface of MOFs and CO_2, the isosteric heat (Qst) of CO_2 adsorption was calculated by the virial method (Fig. 5). [8] The Qst of CO_2 in **1** is 39.3 kJ mol^{-1} at the onset of adsorption. Compared with some famous MOFs examples such as MOF-5, [9] bio-MOF-1, [10] MIL-53(Al) (34-36 kJ mol^{-1}), [11] the Qst value is relatively high. The high Qst may indicate strong interactions between acylamide functional groups and CO_2 molecule. As the adsorption proceeds, the Qst value decreases gradually, and ultimately tends to be parallel, which means the acylamide adsorption sites are saturated, the adsorption process of CO_2 changes the physisorption in nature.

Careful observation on the adsorption isotherms of vapor, we can discover that the maximal amounts of water vapor reaches 23.3 cm^3g^{-1}, as shown in Fig. S5. In comparison, the capture capacities of **1** for ethanol and methanol vapour are fairly weak, the adsorption amounts are no more than 6.3 cm^3g^{-1} at 293K. The behavior of desolvated **1** for relative selective adsorption of water vapor over ethanol and methanol vapour indicates that the pore size in desolvated **1** is less than the kinetic diameter of ethanol(4.3 Å) and methanol vapour (3.8 Å), demonstrating that the micropore structure in desolvated **1** is suitable for water vapor to pass through. Additionally, compound **1** may have certain affinity of water.

In summary, we have successfully synthesized a new acylamide MOF by solvothermal method. Fascinatingly, this polymer presents distinct selective adsorption behaviors of CO_2 over CH_4, CO, N_2 and the high isosteric heat (Qst) of CO_2 (39.3 kJ mol^{-1}), the adsorption amounts of **1** of water vapor is higher than ethanol and methanol vapour. In addition, an obvious tunable luminescence property by varying the excitation wavelength was observed. To some extent, these results may benefit the research in the construction of new acylamide MOFs with pore structures and excellent sorption properties.

Experimental section

Syntheses of 1: $Zn(NO_3)_2$ (0.2 mmol), 4,4'-oxybis(benzoic acid) (0.2 mmol) and L ligand(0.2 mmol) were sealed in a Teflon reactor with 2 mL DMF and 1 mL H_2O, and heated at 115°C for 3 day, and then cooled to room temperature at 6˚C/h, and colorless crystal of **1** was obtained in the yield of 69%, based on Zn. EA analysis (%): calc. C/52.44, N/11.12,H/4.40; exp. C/51.97, N/10.98, H/4.32. Thermogravimetric analysis of 1 reveals that all guest water and DMF molecules are released at 290 °C, with a mass loss of approximately 16.82% (cal. 17.61%), and no further loss up to 410 °C. Then the framework gradually collapses with increasing temperature (Fig. S6). The powder X-ray diffraction (PXRD) pattern of the as-synthesized compound matched the simulated pattern well, indicating that the polycrystalline sample is in the pure phase (Fig. S7).

Single-Crystal X-ray Structure Analyses: Single-crystal diffraction intensity data were collected on Bruker Smart Breeze CCD with MoKα radiation (0.71073 Å) at 298K, the measurement method is phi and omega scans, and corrected with SADABS program. The structures were solved by direct methods and all non-hydrogen atoms were subjected to anisotropic refinement by full matrix least-squares on F2 using the SHELXTL program.[12] Crystal data for 1: Monoclinic, space group $P2(1)/c$, a = 14.5740(7) Å, b = 23.5585(11) Å, c = 15.4557(7) Å, β = 110.801(3)˚, V = 4960.7(4) $Å^3$, Z = 2, GOF = 1.051, all data final $R1$ = 0.0474, $\omega R2$ = 0.1164. Crystallographic data of **1** is summarized in Table S1; Selected geometric parameters are given in Table S2. CCDC-1059599 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

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Graphical Abstract

A novel acylamide metal–organic framework(MOF) with 3-fold interpenetration has been synthesized, which shows high selective adsorption behaviors of CO_2 and tunable luminescence properties dependent on excitation wavelengths.