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COMMUNICATION

A stable,pillar-layermetal−organic framework containing uncoordinated carboxyl groups for separation oftransition metal ions

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A 3D pillar-layer framework (1) withuncoordinated carboxyl groupsexhibits exceptional stability. It can effectively and selectively adsorb Cu^{2+}ionsand has been applied as chromatographic column for separating Cu^{2+}/Co^{2+}ions.

Metal−organic frameworks (MOFs), composed of metal ions (or cluster) as nodes and multitopic organic ligands as linkers have received tremendous attention not only owing to their fascinating structures but also for their potential applications in gas storage,[1]chemical separation,[2] optical sensing/detection,[3] catalysis[4] and drug delivery.[5] Despite this, stability of MOFs against the external environment has being recognized as a crucial issue for practical applications. However, MOFs are frequently air/moisture-sensitive,[6] which could be one of the key limitations to meet the needs of various applications. To data, MOFs possessingmoisture resistanthas seldom been reported.[7] Thus, there are urgent needs for the development of stable MOFs towards external environment to meet the future practical applications.

An especially notable characteristic of some MOFs is their extra-large cavity, which enables their exploration in applications composed of high adsorption capacities and selectivity separation for gas molecules, dye molecules, organic isomers and even fullerene molecules.[8]For example,M-MOF-74 materials with high densities of open metal sitesexhibit good selective adsorption of propene over propane.[1b-d, 8a]However, only few MOFs reported possess selective adsorption and separation ability for transition metal ions.[9]Due to their similar sizes and charge, transition metal ions cannot be separated effectively only by utilizing size-exclusion effect of MOFs. The interactions between metal ions and skeletons of MOFs might be a key factor to capture and separate metal ions, which has been demonstrated by researchers. Zhou and coworkers have made use of PCN-100 to capture heavy metal ions (Cd(II) and Hg(II)), which may be because of chelating coordination between PCN-100 and heavy metal ions.[9b]On the basis of the above reports, selection of the ligand plays a crucial role in the design and construction of such

MOFs. We selected 1,2,4-Triazole (trz), pyromellitic acid (H_4betc) ligands and Zn(II) to synthesize MOFs for selective adsorption and separation of transition metal ions based on the following considerations: i) both of the ligands prefer to favoring the generation of porous architectures with high rigidity for encapsulating metal ions and without a tendency to interpenetrate; ii) both of the ligands possess the abundant coordinated sites, which means MOFs may possess open uncoordinated sites. Does this promote metal ions adsorbance or not? This inspires us to employ it serve as a model system for capture metal ions; iii) the crystals constructed from Zn(II) ions are usually colorless, and the change of the crystal colors can be easily detected by naked-eye if colored metal ions enter into the pores. Herein, we reported a pillar-layer MOF, which exhibits exceptional stability. Furthermore, it contains uncoordinated free carboxyl groups and can be used to selectively adsorb Cu^{2+} ions and separate Cu^{2+}/Co^{2+} ions.

Solvothermal reaction of Zn(NO_3)$_2$, trz, andH_4betc in DMF solution afforded colorless block crystals of**1**, which was formulated as [Zn(trz)(H_2betc)$_{0.5}$]·DMF (DMF = dimethylformamide).Single-
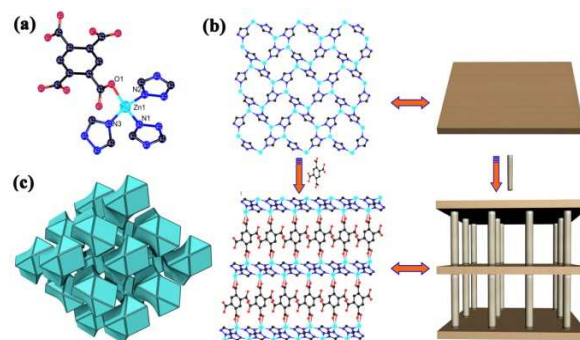

Fig. 1 (a) The coordination environment of the Zn(II) center; (b) The 2D layers pillared by the H_2btec ligand generate a 3D pillar-layer framework (*b*-axis); (c) The (3,4)-connected augmented net as a natural tiling.

crystal X-ray diffraction analysis reveals that compound **1**crystallizes in the monoclinic space group $P2_1/c$. As shown in Fig.1a, the asymmetric unit of **1** contains one zinc ion, one trz ligand, one half H_2betc ligand, and one DMF solvent molecule. The central zinc ion adopts a distorted tetrahedron geometry and is coordinated by three oxygen atoms from three different H_2betc ligands and one nitrogen atom from one trz ligand. The average Zn–N and Zn–O distances are 1.995 and 1.961Å,which are within theexpected ranges, respectively. As shown in Fig. 1b top, four Zn atoms and four trz ligands generate a 16-membered macrometallocycle. The adjacent macrometallocycles link together through sharing trz ligands giving birth to the 2D sheet, {Zn(trz)}$_n$.The 2D sheet stack in the *bc* plane, pillared by the H_2betcligand in longitudinal axes, and generate a 3D pillar-layer framework (Fig. 1b bottom). From the topological point of view,Zn atoms and trz ligandsact as a 4-connected and 3-connected nodes respectively, and thus the whole framework can be described as a (3,4)-connected net withnoninterpenetratednetwork(Fig.1c). It is remarkable thatthere exist two kinds ofchannelsin **1**. The smallchannel with size of 6.8 Å×6.8 Å (viewing along the*a* directionwithout taking van der Waals radius into consideration) in quadrangle shape issurrounded by four Zn atoms and four trz ligands, whereas the larger one with size of 6.7 Å×7.8 Å in pear-like shape (along the*c* direction) iscomprised of twoZn(trz) units and two H_2betc ligands (Fig.S1†).The effective free volumeof **1**is calculated by PLATON analysis[10] to be 40.4% of the crystal volume (516 Å^3 of the unit-cell volume of 1276.4Å^3).

Structural stability of MOFsagainst theexternal environment is very important to meet the future practical applications.To demonstrate the stability ofthe compound **1**, it was immersed in boiling methanol, ethanol, DMA, dichloromethane, THF, acetonitrile, hexane, and dimethyl sulfoxide for 12 h.The PXRD confirms the structural stability of the framework of**1**(Fig.S4†).Considering future practical applications,material must be stable toward air. Thus, exposure of fresh prepared compound **1**to air for two weeks, it retain its structure bythe evidence of PXRD. In addition, we also determine the water stability of the compound **1**. Immersion of**1** in water for 4 h,no significant change of the PXRD patternwas found(Fig.S2†).In *situ* variable temperature PXRD patternsshowedthat**1**was thermally stable up to 250 °C(Fig. S5†).

We investigated the metal ion adsorption experiments of compound **1**. In the initial try, 0.03 g crystals of **1** were introduced into 10 mL, 0.1 mol/L^{-1}M(NO$_3$)$_2$·nH$_2$O (M^{2+} = Cu^{2+}, Co^{2+}, Ni^{2+}, or Cd^{2+}) DMF solution for 5.5 h. ICP results reveal that**1** has highest adsorption amount for Cu^{2+} ions compared to others (Co^{2+}, Ni^{2+}, or Cd^{2+}). Despite this, a very low uptake for metal ionsdisappoints us. In our case, uncoordinated free carboxyl groups stand on the pore surface ofMOFs.In general, this can favor the uptake of metal ions. Why the uptake is very low? After careful consideration, a hypothesis can be used to explain this result. The metal ions enter into the pore may be assisted by the solvent molecule. The small pores and the big size of DMF molecular restricts the move of the metal ions, which may lead to the very low uptakes in limited time. How is the metal ions uptake of **1**if the solvent is changed? Does this promote metal ions adsorbance or not? This inspired us to employ other solvent toexamine metal ions uptake. Methanol and water with small size were selected, and the metal ions adsorption experiments

were also determined using them. The experimental results reveal that compound **1** have the highest uptake for Cu^{2+}, no matter what the solvent was used, and the sorption amount increase exponentially, especially in water (Table S1†). There is a direct correlation between sorption amount and the size of solvent (H$_2$O<MeOH<DMF). The size of solvent may be a key factor for sorption amount. The competition adsorption experiments of compound **1** inM(NO$_3$)$_2$·nH$_2$O (M = Cu^{2+}, Co^{2+}, and Ni^{2+}) mixed solution were also investigated. ICPresults reveal that compound **1** has a high selectivityfor Cu^{2+} ions over other ions and the photographs are given in Fig. S6†. In order to clearly show this trend, 0.2 g crystals of compound **1** were immersed into 2 mL 0.1 mol/L Cu(NO$_3$)$_2$/Co(NO$_3$)$_2$ DMF/CH$_3$OH/H$_2$O solution. The photographsat the given time were collected and given in Fig. S7†.The colorless crystals turnedlight blue very slowly in DMF, and the color of crystals gradually became blue in methanol. In water, the crystal turned deep blue rapidly. The experimental phenomenon also demonstrates that the solvent can influence the adsorption of metal ions. It is worth mentioning that, as shown by powder XRD, the framework remains unchanged after the sorption experiment (Fig.S10†, Fig.S11† and Fig.S12†).

High selective adsorption for metal ions inspired us to study compound 1 as an ion chromatographic column (Fig. S8†, Fig.S9†, and Fig. 2). A mixed solution (2 mL) containing the sameconcentration of Cu^{2+} and Co^{2+} ions (0.1 mol/L) were injected into
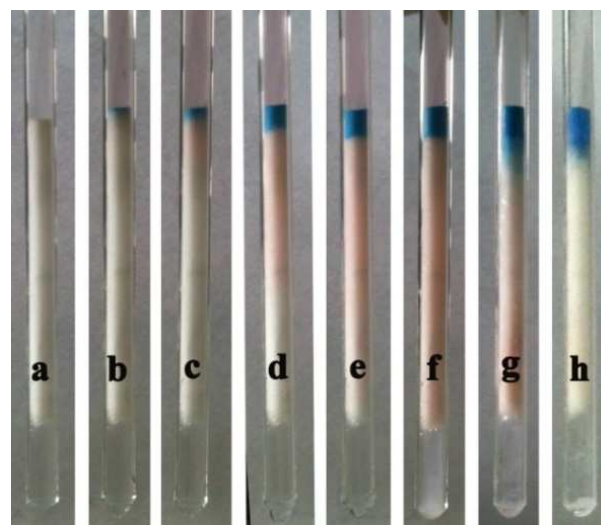

Fig. 2 Separation process of Cu^{2+} and Co^{2+} ions by the MOF-based chromatographic column (water as solvent). a) blank; b) 1 min; c) 2 min; d) 4 min; e) 7 min; f) 10 min; g) 30 min; h) 1 h.

the MOF-based separation column (60 mm × 4 mm), and thecorresponding solvent was used as the eluting agent (DMF/MeOH/H$_2$O). Different solvent were used, and the different experimental phenomena were observed. Due to the larger size of DMF, M^{2+} ions enter into the pores of the compound **1** very slowly. Most of two kinds of ions rapidly transport through the column along with the DMF stream, and the color of the separation column has no observable change (Fig. S8†). When MeOH acts as solvent, a part of Cu^{2+} ions are encapsulated in the crystals, and the whole

column exhibits light green (Fig. S9†). While water as solvent, due to its smaller size and the different interactions between two kinds of ions and the uncoordinated carboxyl groups from the framework of **1**, Cu^{2+} ions are quickly adsorbed into compound **1** and retain at the top of the separation column, while Co^{2+} ions transport the column along with the eluting agent (Fig. 2).The ICP result of the total eluting agent reveals that Co/Cu mole ratio is 99.995/0.005 and the fraction eluted from the column is almost pure Co ions.Compared to **1**, MOF-5 possesses no obviousadsorption selectivity forCu^{2+}/Co^{2+} ions.[9c] To date, only little work has been focused on systemically studying the selective adsorption experiments of MOFs for different metal ions in different solvent. To the best of our knowledge, it is the first example that a MOF is used for separation and purification of metal ions in water.

Where is the adsorption site for Cu^{2+} ions in **1**? A possible hypothesis is proposed. The uncoordinated oxygen atoms from carboxyl groups may facilitate Cu^{2+} ions adsorption in **1**, and the selective adsorption of different metal ions could be due to different binding energies between oxygen atoms and metal ions. The Cu^{2+} ions inside the framework of **1** did not escape into fresh DMF solution, which indicates that Cu^{2+} ions interact with this framework strongly. On the basis of rational length and orientation of a covalent bond, the possible adsorption sites have been calculated using density functional theory (DFT). DFT calculations show that Cu^{2+} ions are bonded to the O•••O in chelated coordination mode ($R_{Cu–O}$ = 1.98/2.01 Å) (Fig. S17†). Furthermore, the O•••Co•••O chelated coordination model was also optimized. The interaction energies (ΔE) of the Cu^{2+} and Co^{2+} ions with the framework are -129.77 and -66.34 kcal/mol, respectively. The results suggest that Cu^{2+} has strong interaction with O•••O chelated coordination site, which demonstrate that **1** including uncoordinated carboxyl groups possess the selective adsorption ability for Cu^{2+} ions.

In summary, a 3D pillar-layer framework (**1**) has been constructed. It exhibits exceptional stability and contains uncoordinated carboxyl groups. It can effectively and selectively adsorb Cu^{2+} ion, especially in water. It has been applied as chromatographic column for separating Cu^{2+}/Co^{2+} ions. DFT calculations suggest that Cu^{2+} ion might be bonded on O•••M•••O chelated coordination sites and Cu^{2+} ions have a stronger interaction energy with the framework than Co^{2+} ions, which is according with the experimental results. This work will open up a promising way to prepare MOFs for practice application in separation.

Notes and references

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† Electronic Supplementary Information (ESI) available: Syntheticdetails,X-ray powder diffraction data,TGA plot, and experimental details of the stability, separation and computational. See DOI: 10.1039/b000000x/

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