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Short communication

A new microporous metal-organic framework with a novel trinuclear nickel cluster for selective CO_2 adsorption

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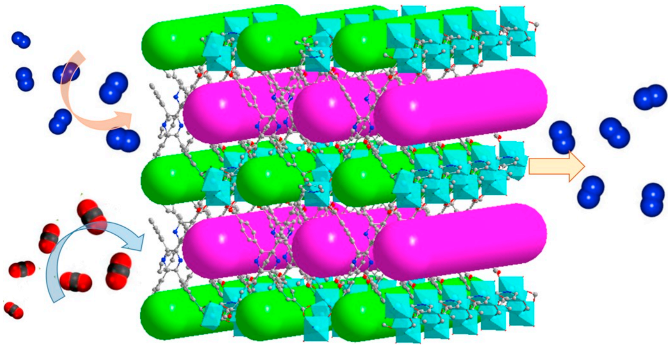
GRAPHICAL ABSTRACT

A new Ni-based metal-organic framework with a novel $Ni_3(OH)_2(COO)_4(HCOO)_4$ clusters was reported which exhibits high selectivity for CO_2 adsorption from CO_2/N_2 gas mixtures.



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ABSTRACT

A new microporous Ni-based metal-organic framework (Ni-MOF-1) was synthesized by reaction of Ni $(NO)_3$·$6H_2O$ with the binary ligands of tetracarboxylic 2,3,5,6-tetrakis(4-carboxyphenyl)pyrazine (H_4TCPP) and 4,4′-bipyridine under solvothermal reaction. The single crystal X-ray diffraction indicates that Ni-MOF-1 possesses a three-dimensional porous network with novel trinuclear $Ni_3(OH)_2(COO)_4(HCOO)_4$ clusters, exhibiting high CO_2 uptakes of 37.57 $cm^3\ g^{-1}$ and high selectivity of CO_2 over N_2 (42.89) at 273 K.

The increasing CO_2 emissions that accompany rapidly industrial and economic development are leading to greenhouse effect and worsening environmental pollution [1]. Therefore, how to reduce the ultrahigh concentration of carbon dioxide has become an urgent and serious issue. There are still some unavoidable bottlenecks for the traditional alkylamine-containing chemical CO_2 capture techniques, such as corrosion, high regeneration cost and chemical decomposition, in which an alternative physical adsorption of CO_2 based on porous solids has aroused people's great interest [2]. Compared with amorphous organic polymers, molecular sieves and activated carbon, metal-organic frameworks (MOFs) have attracted more attention for CO_2 capture in virtue of their superhigh surface area, tunable porosity, rich surface

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chemical environment and remarkable stability [3–9], which enable MOFs for widely potential applications in gas adsorption/separation [10–13], including CO_2 adsorption and separation [14–16]. For example, the well-known Mg-MOF-74 [17] exhibits excellent CO_2 adsorption performance because of its high surface area and highly exposed Mg(II) sites for CO_2. Due to their advantages in high structural tenability and faster kinetic responses with lower regeneration energy for selective capture of CO_2 [18], many functionalized MOF materials are rationally designed and prepared for enhanced CO_2 adsorption and separation. Recently, researchers construct a series of MOFs with active coordination sites of ligands and the polarized pore environment, resulting in high CO_2 uptakes and selectivities [19]. Furthermore, the pore walls decorated by functional groups can also improve the adsorption capacity and selectivity of CO_2 [20]. Herein we report a novel Ni-based MOF (Ni-MOF-1) with binary ligands of 2,3,5,6-tetrakis(4-carboxyphenyl)pyrazine (H_4TCPP) and 4,4′-bipyridine (BPY) under solvothermal condition, in which the formula was defined as $Ni_3(OH)_2(H_2TCPP)_2(BPY)$. The ligand H_4TCPP is easy to produce in batches using a new method different from the reported [1] (see Supporting information).

Single crystal X-ray diffraction (XRD) analysis reveals that Ni-MOF-1 crystallized in orthorhombic *Pmna* space group. As shown in Fig. 1a, there are two crystallographic independent Ni(II) in an asymmetry unit, which further assemble into a trinuclear Ni_3 cluster bridged by two free OH^- anions and eight carboxylate groups from separate H_2TCPP linkers. The two crystallographic independent Ni(II) both adopt typical octahedral coordination modes, in which the centroid Ni(II) coordinates to two OH^- groups and four *syn-syn* bridging carboxylates while the terminal one has a more complicated coordination environment with an OH^- group, two undeportonated carboxyl groups, two *syn-syn* bridging carboxylates and a pyridinic N atom. To the best of our knowledge, the typical $M_3(COO)_6$ (M = Zn, Co, Ni) clusters are widely presented in previous published MOF structures while the target $Ni_3(OH)_2(COO)_4(HCOO)_4$ clusters are rarely reported [21]. Furthermore, Each H_2TCPP linker connects six Ni(II) ions from four separate Ni_3 clusters (Fig. 1b&c), resulting in a three dimensional (3D) porous network (Fig. 1d). There are two main types of molecular channels with dimensions of 9.07 × 13.06 and 7.82 × 9.95 $Å^2$ along the c-axis direction, respectively (Fig. 1d, Fig. S2a, Supporting Information) and one type of channels with dimensions of 7.1 × 9.03 $Å^2$ along the b axis (Fig. S2b).

Thermogravimetric analysis (TGA) of as synthesized Ni-MOF-1 shows a continuous weight loss from room temperature to 200 °C, indicating the loss of solvent molecules. After that, the solvent-free framework could be stable up to 400 °C, and then the host framework start to decompose upon further calcination. In the TGA curve of the activated sample, there is no obvious weight loss observed until 400 °C, implying its effective activation prior to TGA (Fig. 2a). As shown in the powder XRD patterns (Fig. 2b), the peak positions of the as synthesized and activated are both well agreement with that of the simulated from

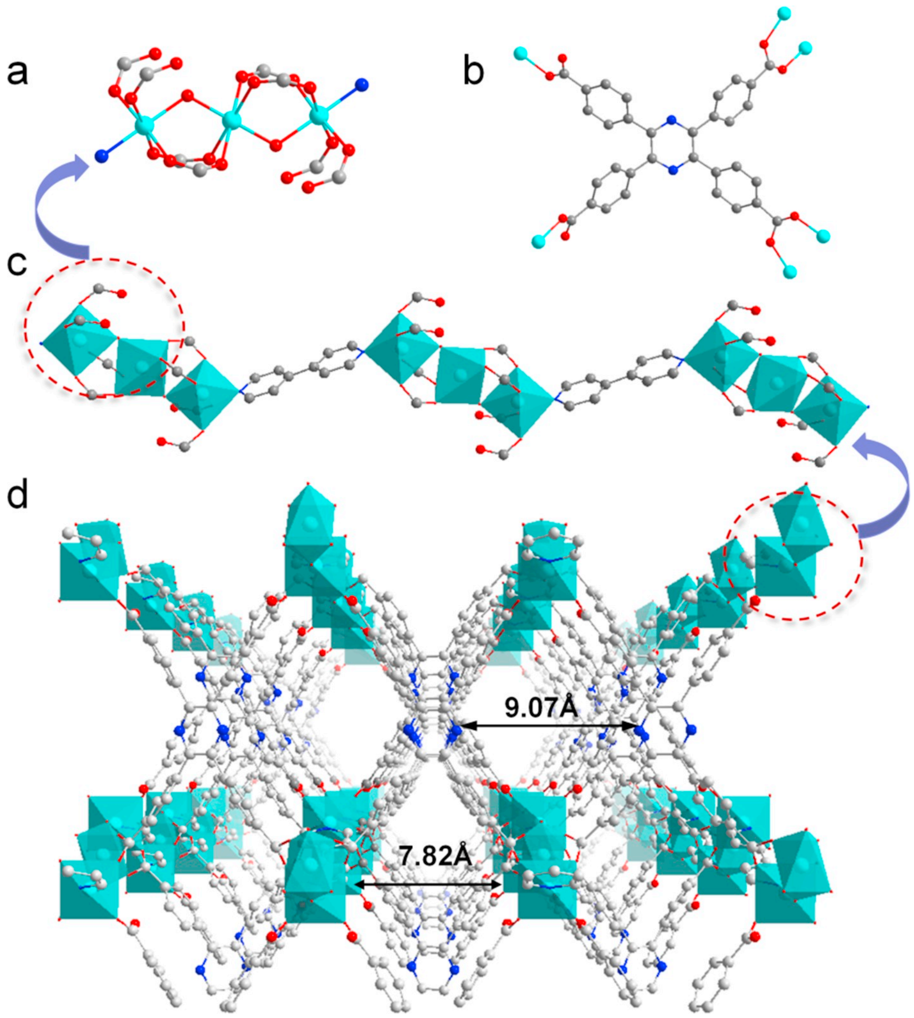

Fig. 1. (a) The coordination surroundings for the Ni(II) ions; (b) The coordination mode of the H_4TCPP ligand; (c) A quasi-one-dimensional chain along the c axis; (d) Pore channels of about 9.07 × 13.06 $Å^2$ and 7.82 × 9.95 $Å^2$ along the c axis. All hydrogen atoms were omitted for clarity.

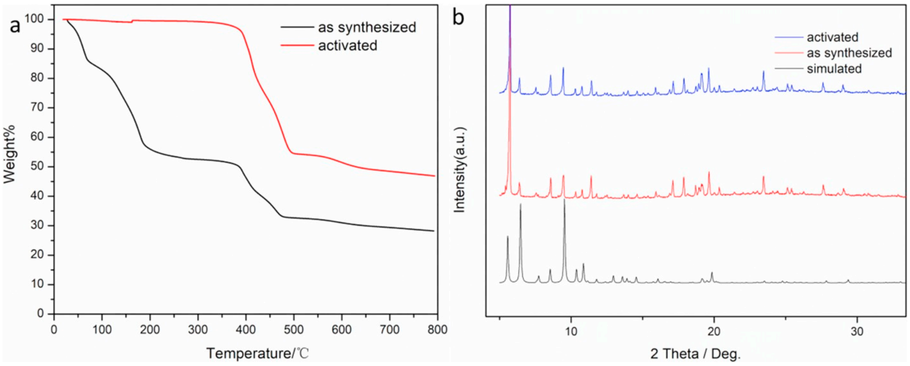

Fig. 2. Characterization of Ni-MOF-1: (a) The TGA curves of the as synthesized (black) and activated (red); (b) The powder XRD patterns of the simulated (black), the as synthesized (red) and activated (blue) sample. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the single crystal data, indicating the porous framework keeps intact after the removal of solvent molecules. The hydro-stability of Ni-MOF-1 has also been investigated, and the result indicated the framework decomposition after soaking the sample in the water for 12 h, as shown in Fig. S3 (Supporting information).

To investigate the porosity of Ni-MOF-1, N_2 adsorption isotherm was carried out at 77 K. The as synthesized sample (ca. 0.204 g, Supporting Information) was activated under vacuum at 373 K for 12 h prior to the adsorption measurements (see Supporting Information). As shown in Fig. 3a, the Brunauer-Emmett-Teller (BET) surface area of guest-free framework is 152 $m^2 g^{-1}$ with a pore volume of 0.07 $cm^3 g^{-1}$. Because the N_2 kinetic diameter does not match the ultramicropores, the partial pore space cannot be detected, resulting in the experimental pore volume smaller than the theoretical value of 0.74 $cm^3 g^{-1}$ [22]. Moreover, the analysis of pore width distribution by the method of Density Functional Theory(DFT)is 0.57 and 0.81 nm (inset in Fig. 3a), which is consistent with the calculated result from the single crystal data.

To systematically evaluate the potential of selective gas adsorption, we investigate the adsorption ability of Ni-MOF-1 for CO_2 and N_2 at various temperatures. The largest uptake amount of CO_2 is 37.57 $cm^3 g^{-1}$ (1.68 mmol g^{-1})at 1 atm and 273 K, while that of N_2 (3.59 $cm^3 g^{-1}$) is quite lower under the same conditions (Fig. 3b), indicating poor intermolecular interactions between MOF host framework and N_2 molecules. Furthermore, the molecular sieve effects depending on the pore sizes of MOF also have some contribution for CO_2/N_2 separation [23], because the diameter of N_2 (0.36 nm) molecule is larger than that of CO_2 (0.33 nm).

The significant difference of uptake amounts encouraged us to explore the gas selectivity based on the Ideal Adsorbed Solution Theory (IAST) method [24]. Unary equilibrium isotherms for CO_2 and N_2 were used to predict the behavior in a binary gas mixture (50:50 and 15:85 CO_2/N_2), where this ratio of 15:85 was chosen to simulate flue gas conditions [25]. Experimental isotherms of pure CO_2 and N_2 are fitted by single or dual site Langmuir model (Fig. S5-S8, Supporting Information). As shown in Fig. 4a, The CO_2/N_2 separation factors are higher than 42 for 15:85 CO_2/N_2 gas mixtures and 23 for 50:50 CO_2/N_2 gas mixtures at 273 and 298 K, respectively. It is noteworthy that the selectivity is superior to some recently reported results under the same conditions (Table 1), which are sufficient to achieve the benchmarked 99% purity (selectivity > 30) during separation at 273 K [26].

The ability of regeneration for MOFs is an important evaluation criterion. The higher binding energy of CO_2 and MOFs means the higher cost for the MOF regeneration. Proper binding energy can meet separation requirements while improving energy efficiency. Heat of adsorption (HOA) of CO_2 was calculated by using the adsorption isotherms at 273, 293 and 298 K with the Clausius-Clapeyron equation to reflect the binding energy. As shown in Fig. 4b, HOA at zero-coverage CO_2 is 36.57 kJ mol^{-1}, which is comparable to those of Tb-FTZBP (36.7 kJ mol^{-1}) [16], PCN-200(38 kJ mol^{-1}) [27], Cu-ATT(37.51 kJ mol^{-1}) [28] and HNUST-1(31.2 kJ mol^{-1}) [29], indicating the preferential CO_2 adsorption is firstly located at the active sites of Ni-MOF-1 such as hydroxyl and pyrazine groups [30]. After saturated adsorption toward active sites, the HOA smoothly decrease to 25.91 kJ mol^{-1} at relatively high pressure values, implying a weak physical CO_2 adsorption. It gives an almost unchanged constant of interaction energy between CO_2 and adsorbent along with the increasing of adsorption for the second step, which is beneficial to the CO_2 desorption and facile regeneration [31].

In summary, a new Ni-based MOFs with novel $Ni_3(OH)_2(COO)_4(HCOO)_4$ clusters is synthesized and structurally characterized, exhibiting high CO_2 uptakes and high selectivity of CO_2 over N_2, which may act as the potential porous material to separate carbon dioxide from nitrogen.

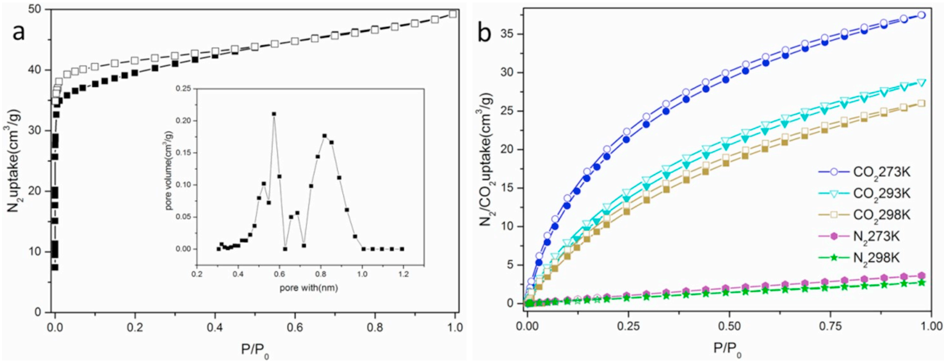

Fig. 3. Gas adsorption properties of Ni-MOF-1: (a) the N_2 isotherm at 77 K (The inset represents the pore size distribution) and (b) CO_2 and N_2 adsorption isotherms of Ni-MOF-1 at 273, 293 and 298 K, respectively.

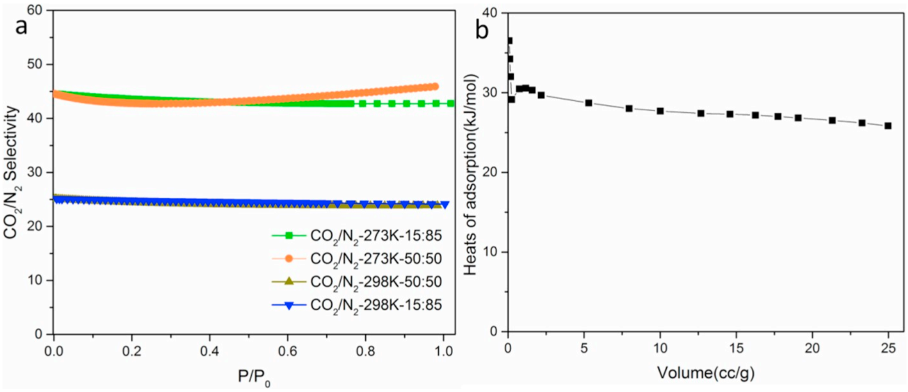

Fig. 4. (a) CO_2/N_2 selectivity of Ni-MOF-1 calculated by using IAST model employing a nominal composition of 15 (CO_2):85 (N_2) and 50 (CO_2):50 (N_2). (b) Heats of CO_2 adsorption.

Table 1
CO_2 separation properties of Ni-MOF-1 and some reported MOFs.

Sample	Selectivity CO_2/N_2	CO_2 concentration%	$S_{BET}/m^2\,g^{-1}$	Temperature K	Pressure bar	Referece
$[Zn_3L_2(HCOO)_{1.5}][(CH_3)_2NH_2]_{1.5}$	25	15	569.5	273	1	[32]
PCN-88	15.2	15	> 3000	296	1	[33]
	23.1	15		273		
	27.4	50		273		
SU-MAC-600	22	10	1500	298	1	[34]
SU-MAC-800	11	10	2369	298	1	
CN-950	12	10	1979	298	1	[35]
NC-1-700	13	10	1503	298	1	[36]
NJU-Bai18	49.2	15	852	273	1	[37]
Ni-MOF-74	30	40	1218	298	1	[38]
Ni-AG9	41	15	817	273	1	[39]
Ni-AG15	32	15	723	273		
MOF-76-Cs-ds	15.4	15	754	298	1	[40]
Ni-MOF-1	42.75	15	658.49	273	1	This work
	24.16	15		298	1	
	46.06	50		273	1	
	23.87	50		298	1	

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.inoche.2019.03.029.

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