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Short Communication

Metal Doping Induced Formation and Dynamic Gas Sorption of a Highly Porous Mesoporous Metal- Organic Framework

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Abstract

A new high-porosity MOF of $[\text{Ni}_{2.3}\text{Zn}_{0.7}(\text{tzba})_3(\text{H}_2\text{O})_6]\cdot 12\text{DMF}$ (**NiZn-MOF**) processes 2D (3,6)-grid layers constructed from rare $[\text{M}_2(\text{tz})_3(\text{H}_2\text{O})_3]$ and $[\text{M}(\text{COO})_3]$ nodes. The metal doping of Ni^{2+} and Zn^{2+} are crucial for the formation of the two kinds of metal nodes and subsequent synergistical assembly into the mesoporous MOF, in contrast to the formation of MIL-88-topology resembled compound of $\{(\text{Me}_2\text{NH}_2)[\text{Ni}_3(\mu_3\text{-OH})(\text{tzba})_3(\text{H}_2\text{O})_3]\cdot 8\text{DMF}$ (**Ni3-MOF**) using single Ni^{2+} as metal source. The regular 2D layers stacked in parallel and ABAB fashion through interlayer hydrogen bonding, leading to a neutral framework with void fraction up to 72.1% and 1D mesoporous hexagonal channels sized at 24.0 Å in diameter. The large gas accessible porosity was revealed by the saturated N_2 and CO_2 uptake of 720 and 708 $\text{cm}^3 \text{g}^{-1}$, at 77 K and 195 K, respectively, giving a high Langmuir surface area of 2066 $\text{m}^2 \text{g}^{-1}$. The varying gas sorption amounts dependent on accommodated solvents and activation temperature, as well as the gate-opening behaviors in sorption isotherms, well confirm the dynamic structure response to guest species of the flexible framework.

Introduction

Metal-organic frameworks (MOFs) exhibit unprecedented structure designability and are outstanding in their multi-functionalization than traditional porous materials [1]. The pursuing of high porosity and accessible surface area, based on rational design of the metal node, organic linker and topology net, was one of the persistent tasks in the area [2]. Indeed, known examples with void fraction exceeding 70% and experimental surface area exceeding 3000 $\text{m}^2 \text{g}^{-1}$, just shear a mere portion of the whole MOF database [3]. Mesoporous framework with even larger apertures than common microporous MOF was one effective strategy to achieve extremely high porosity. The seeking of new metal nodes and matched spatial orientation of the linkers to create mesoporous porosity, is a valuable topic to explore the limit to rational chemical synthesis [4]. Considering the diversified electronic structure and coordination tendency of different metal ions, an accompanying interest work is the heterometallic effect on framework differentiation, but far from well understanding [5]. The large internal void fraction and size in highly porous motifs further facilitate structural dynamism with diverse types and magnitudes. These mesoporous and flexible MOFs contribute to systematic study about the relevance between dynamic structural response and different guest inclusion behaviours [6].

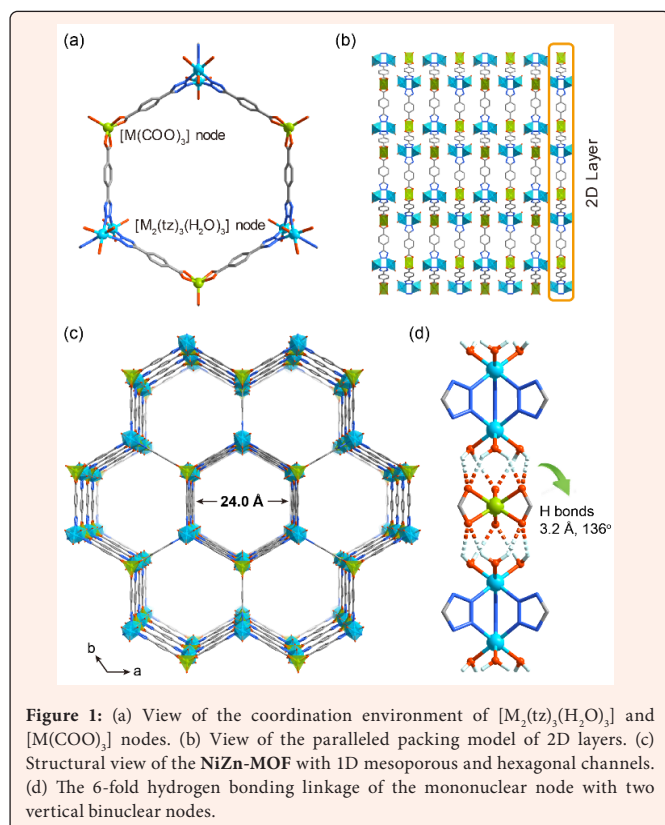
Synthesis Method

The **NiZn-MOF** crystals were prepared by dissolving $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ (0.25 mmol, 58.7 mg), $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (0.2 mmol, 59.5 mg), and H_2tzba (0.1 mmol, 19.0 mg) in mixed solution of dimethylformamide (DMF, 5 mL) and acetonitrile (CH_3CN , 2 mL), followed by stirring for 5 minutes and adding of 350 μL trifluoroacetic acid (TFA). The product was then placed in a 25 mL Teflon-lined steel bomb and heated at 433 K for 72 h. The reaction bomb was cooled to room temperature at a rate of 10 K/h. Pink block crystals were collected and washed with dried DMF, with yield of 43% based on Ni.

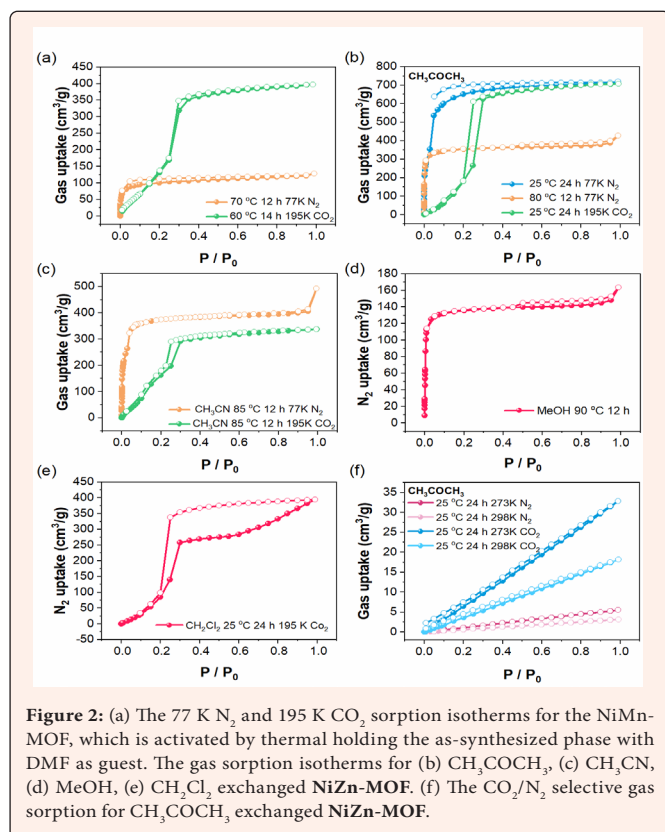
Crystal Structure

As we have confirmed, light blue need crystals of **Ni3-MOF** were obtained under solvothermal reaction between $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ and H_2tzba , which is a $[\text{Ni}_3(\mu_3\text{-OH})(\text{COO})_3(\text{tz})_3(\text{H}_2\text{O})_3]$ node based 3D negative framework, revealed by single crystal X-ray diffraction analyses. However, crystals with pink colour and hexagonal prisms shape were obtained for the **NiZn-MOF**, using Ni^{2+} and Zn^{2+} mixed salts as starting materials.

The solved crystal structure of **NiZn-MOF** crystallized at hexagonal $P6_3/mmc$ space group. Its asymmetric unit consists of a quarter of M^{2+} , a quarter of tzba linker, and half of coordinative H_2O . Two kinds of metal nodes of $[\text{M}_2(\text{tz})_3(\text{H}_2\text{O})_3]$ and $[\text{M}(\text{COO})_3]$ (Figure 1a), are linked through the $\mu_3\text{-}\eta^1, \eta^1, \eta^1, \eta^1$ fashion tzba . The two metal ions in the binuclear node were chelated by three tetrazole groups, giving $\text{M}\cdots\text{M}$ distance of 3.8 Å. Three terminal water further accomplish the coordination sphere. The geometry of metal ions can be assigned to Trigonal prism and Octahedron in the mononuclear and binuclear node, respectively. The binuclear and mononuclear node found here is quite rare, and only previously founded in isolated clusters. Their coexistence and well assemble matching played an unexpected role in molecular assembly, resulting to a thin, flat, regular and (3,6)-connected 2D layer (Figure 1b). There is large hexagonal aperture with side length of 12.0 Å and diagonal length of 24.0 Å (Figure 1c). The layers are stacked in a perfectly parallel and ABAB fashion, through 6-fold interlayer hydrogen bonding between the mononuclear node with two vertical binuclear nodes (Figure 1d). Based on PLATON calculation, the void fraction of the framework is up to 72.1%, which is quite high and comparable to some known typical high-porosity MOFs of IRMOF-177, MIL-101, DUT-32, NU-100, PCN-68 and others [7].



Gas Sorption



For the thermogravimetry result of NiZn-MOF, there is a large weight loss of 51.9% below 200 °C, which is ascribed to the departure of guest DMF, followed by sustaining weight decrease and obvious decomposition above 300 °C. To reveal the structure flexibility and acquire porosity, the as-synthesized sample was directly vacuumized at 60~70 °C for 12~14 h. The obtained saturated N_2 uptake is 128 $cm^3 g^{-1}$, at the maximum sorption pressure under 77 K (Figure 2a). This value is far below the calculated saturated N_2 uptake of 836 $cm^3 g^{-1}$. In contrast, the obtained CO_2 maximum uptake at 195 K is higher to 398 $cm^3 g^{-1}$, comparing to the simulated maximum CO_2 uptake of 728 $cm^3 g^{-1}$. Particularly, the CO_2 adsorption is sluggish and progressive below P/P_0 of 0.30. Large adsorption jumps of 177 $cm^3 g^{-1}$ occurred in a narrow pressure range of 0.25~0.35 P/P_0 . These results indicate the flexible characteristic of the NiZn-MOF and framework shrinkage during guest-removal processes.

Subsequently, the original DMF guest was exchanged by different volatile solvent, so as to decrease the structure distortion induced by the surface tension during guest removal. For CH_3COCH_3 exchanged NiZn-MOF, just the long-time vacuum treatment for 24 h under room temperature is appropriate to realize full activation and porosity maintenance. The resulting N_2 sorption isotherms shows type-I curves (Figure 2b), with saturated uptake of 720 $cm^3 g^{-1}$, slightly lower than the simulated value. There is sorption jump in the pressure range of 0.01~0.05 P/P_0 , as well as small desorption hysteresis. For 195 K CO_2 sorption, the gradual adsorption leads to uptake of 268 $cm^3 g^{-1}$ till P/P_0 of 0.25. Then, a large jump to 628 $cm^3 g^{-1}$ at P/P_0 of 0.29 was observed. The saturated CO_2 uptake is 708 $cm^3 g^{-1}$, which is highly close to the theoretical maximum CO_2 uptake. However, the framework rigidity is sensitive to high temperature. When the CH_3COCH_3 exchanged NiZn-MOF was activated under 80 °C, the N_2 uptake will heavily decrease to 427 $cm^3 g^{-1}$. For CH_3CN exchanged NiZn-MOF, the resulting N_2 and CO_2 uptake were 492 and 337 $cm^3 g^{-1}$ (Figure 2c). For MeOH exchanged NiZn-MOF, the observed N_2 uptake were only 148 $cm^3 g^{-1}$ (Figure 2d). For CH_2Cl_2 exchanged NiZn-MOF, the 195 K CO_2 sorption isotherms shows similar tendency and comparable maximum uptake (Figure 2e), comparing to the thermal activated as-synthesized phase. The fully activated CH_3COCH_3 exchanged NiZn-MOF shows better adsorption of CO_2 over N_2 , with selectivity of 6.0 (273 K) and 5.8 (298 K) (Figure 2f), respectively.

Conclusion

A vivid example showing large structure orientation effect of metal doping was built, based on two solvothermal generated compounds of Ni_3 -MOF and NiZn-MOF. The great differentiation on metal node, topology net, pores shape, aperture size were stemmed from metal doping and slight coordination tendency diversity between Ni^{2+} and Zn^{2+} during MOF self-assembly. New mixed-metal nodes of binuclear $[M_2(tz)_3(H_2O)_3]$, and single-metal $[M(COO)_3]$ nodes were observed, and found to be effective secondly building units in the construction of highly porous mesoporous MOF. The findings are instructive for metal coordination directed MOF construction, and suggest the great potential to rational construct targeted MOFs by metal doping. The various structure response to departure/inclusion of different solvent and gas, confirm and arouse potential function application like smart sensing of highly porous flexible MOFs.

References

1. Furukawa H, Cordova KE, O'Keeffe M (2013) The chemistry and applications of metal-organic frameworks. *Science* 341(6149): 1230444.
2. Zhang WX, Liao PQ, Lin RB, Wei YS, Zeng MH, et al. (2015) Metal cluster-based functional porous coordination polymers. *Coord Chem Rev* 293: 263-278.
3. Furukawa H, Ko N, Go YB, Aratani N, Choi SB, et al. (2010) Ultrahigh porosity in metal-organic frameworks. *Science* 329(5990): 424-428.
4. Kitagawa S (2017) Future porous materials. *Account Chem Res* 50: 514-516.
5. Zeng MH, Wang B, Wang XY, Zhang WX, Chen XM, et al. (2006) Chiral magnetic metal-organic frameworks of dimetal subunits: magnetism tuning by mixed-metal compositions of the solid solutions. *Inorg Chem* 45(18): 7069-7076.
6. Zhang JP, Zhou HL, Zhou DD, Liao PQ, Chen XM (2018) Controlling flexibility of metal-organic frameworks, *Nat Sci Rev* 5: 907-919.
7. Zhang X, Chen Z, Liu X, Hanna SL, Wang X, et al. (2020) A historical overview of the activation and porosity of metal-organic frameworks. *Chem Soc Rev* 49: 7406-7427.