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Influence of Amine Group on Highly Efficient Reversible Adsorption of Iodine in Two Novel Isoreticular Interpenetrated Pillared-Layer Microporous Metal-Organic Frameworks

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Two isoreticular microporous Zn(II)-MOF were constructed using a bipyridine-type linker mixed by two homologous ligands, 1,4-benzenedicarboxylate, [Zn₂(BDC)₂(4-bpdh)].3DMF (TMU-16) and amino-1,4-benzenedicarboxylate, [Zn₂(NH₂-BDC)₂(4-bpdh)].3DMF (TMU-16-NH₂). Both unmodified and amino functionalized MOFs can serve as host for encapsulating I₂. In particular, the amino functionalized MOF can find more applications in the encapsulation of iodine.

During the past few years the synthesis and characterization of supramolecular compounds and microporous metal-organic frameworks (MOFs), which are new types of zeolite analogues, is one of the most rapidly developing areas of chemical science.[1] These materials have unquestionably enormous potential for many practical structure-related applications. This includes the more traditional areas of storage, separation or controlled release of gases, catalysis, sensing, and drug delivery, as well as adsorptive removal of hazardous materials, which are based on the pore size and shape as well as the host-guest interactions involved.[2]

The research of iodine in the life sciences, marine atmosphere, materials science and nuclear industries has become a growing active field. So the study of enrichment of iodine is more valuable.[3] Driven by the recent successful encapsulation of functional species such as drugs, dyes, light emitters, explosives, etc. into the cavities, we [4] and others [5] were successfully used metal-organic frameworks for removal and recovery of iodine. In recently reported work, the non-interpenetrating microporous mixed-ligand MOF based on octahedral cage-like building units was used as a host for encapsulating I₂.[6] In another work, Su and coworkers used two isoreticular microporous polycatenane-like MOFs for rapid adsorption of iodine.[7]

A key to accessing advanced MOF materials suitable for more specialized applications is to introduce different functional groups into these networks. The ability to modify the physical environment of the pores and surfaces within MOFs would allow tuning of the interactions with guest species, and serve as a route to tailor the chemical reactivity of the framework.[8] The use of amine-tagged ligand may enhance the adsorbent-adsorbate interactions through host-guest hydrogen-bonding to enhance iodine adsorption.[9] There are some reports that show tuning of the chemical functionality of the pore walls in the MOFs by amine as a Lewis basic group increase CO₂ uptake and adsorption selectivity.[10] Herein we reported a detailed investigation that demonstrates the influence of amine group on the ad/desorption rates of iodine in two novel isoreticular two-fold interpenetrated pillared-layer microporous Zn(II) metal-organic frameworks (Scheme 1).
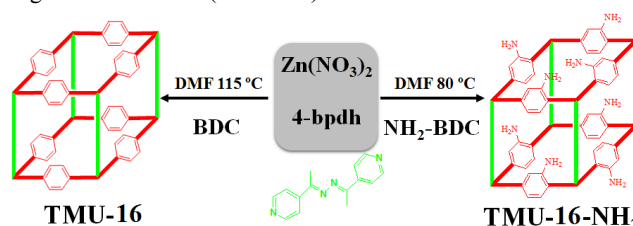
Scheme 1 Schematic view of comparative synthesis for TMU-16 and TMU-16 -NH₂.

Using long, rigid bipyridyl-based ligand, 2,5-bis(4-pyridyl)-3,4-diaza-2,4-hexadiene (4-bpdh), linear 1,4-benzenedicarboxylate (BDC) and Zn(NO₃)₂, a microporous MOF [Zn₂(BDC)₂(4-bpdh)].3DMF (**TMU-16**, TMU corresponds to **T**arbiat **M**odares

University) was designed to have a primitive cubic framework with pores that can be tuned by double interpenetration to have 1D channels of approximately 7.1 × 4.6 Å in cross section (including van der Waals radii). There is a considerable number of functional porous coordination polymers which have been synthesized using the 4-bpdh as a neutral azine or azo chromophore containing bipyridyl ligand,[11] in combination with dicarboxylate using the pillar-layer technique.[12] The pyridyl based spacer can act as a pillar to link the metal-carboxylate layer to produce higher dimensional crystalline novel topological frameworks containing the channels or cavities.[13] Furthermore, to investigate the influence of amine group on the adsorption and desorption rate of iodine, the pores in the MOF was successfully functionalized with potentially reactive groups ($-NH_2$) without changing the SBU or the underlying framework topology. And the amine-functionalized isoreticular framework, $[Zn_2(NH_2\text{-}BDC)_2(4\text{-}bpdh)].3DMF$ (**TMU-16-NH$_2$**) was synthesized by using amine substituted BDC ligand.

A guest-filled phase, **TMU-16**, was synthesized by the solvothermal reaction of BDC, 4-bpdh, and $Zn(NO_3)_2\cdot6H_2O$ in DMF at 115 °C for 72 h, and isolated as yellow block-shaped crystals. The analogues one, **TMU-16-NH$_2$**, was synthesized using NH_2-BDC under the same conditions but at lower temperature, 80 °C. The formula of the compounds was determined to be $[Zn_2(BDC)_2(4\text{-}bpdh)].3DMF$ and $[Zn_2(NH_2\text{-}BDC)_2(4\text{-}bpdh)].3DMF$, for **TMU-16** and **TMU-16-NH$_2$**, by elemental microanalysis and single-crystal X-ray diffraction studies. The phase purity of the bulk materials were independently confirmed by both powder X-ray diffraction (PXRD) and thermal gravimetric analysis (TGA).

TMU-16 and **TMU-16-NH$_2$** are isostructural and crystallize in the monoclinic space group *C*2c. **TMU-16** is composed of paddle-wheel dinuclear zinc carboxylate units $\{Zn_2(COO)_4\}$ (Figure S1a in the SI), which are bridged by the BDC ligands to form a distorted 2D square grid. The 2D square grids are pillared by 4-bpdh molecules, whose nitrogen atoms occupy the axial sites of the $\{Zn_2(COO)_4\}$ paddle wheels (**Figure 1**a and S1b, S1c in the SI), to form a 3D framework with a topology that can be described as primitive cubic lattice (RCSR symbol pcu)[14] (**Figure 1**b). Two of the 3D frameworks interpenetrate in **TMU-16**, reducing the pore size. A 1D channel occurs in the direction of the rectangular diagonal of the paddle-wheel clusters (**Figure 1**c and S1d-f in the SI). This channel has a cross section of approximately 7.1 × 4.6 Å (including van der Waals radii), thus suggesting microporous characteristic of **TMU-16** and **TMU-16-NH$_2$** (**Figure 1**d and Figure S2 in the SI). Moreover, the powder X-ray diffraction data show the two compounds are isotypic with each other (**Figure 1**e). Comparison of the calculated free volume in fully desolvated crystals of the compounds by PLATON shows that it varies in decrements from 3648.4 Å^3 per unit cell (42.7% of the cell volume) in **TMU-16** to 2286.1 Å^3 (27.6%) in **TMU-16-NH$_2$**.[15]
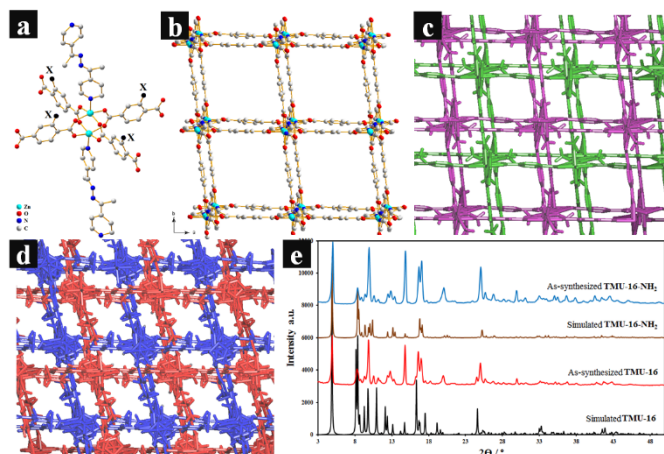

Figure 1. (a) Asymmetrical paddle wheel $Zn_2(X\text{-}BDC)_2(4\text{-}bpdh)$ unit and its coordination geometry in (**TMU-16**; X = H, **TMU-16-NH$_2$**; X = NH$_2$), (b) an elongated primitive cubic net of **TMU-16** viewed along c axis which contains 1D channels of 13.4 × 11.8 Å. Representations of the structures of the open phase **TMU-16** (c) and **TMU-16-NH$_2$** (d), which contains 1D channels of 7.1 × 4.6 Å, viewed along the rectangular diagonal of the paddle-wheel clusters. The two interpenetrating frameworks are shown in purple and green for **TMU-16**, and blue and red for **TMU-16-NH$_2$** . All hydrogen atoms and the disordered guest molecules are omitted for clarity. (e) PXRD of simulated and as-synthesized **TMU-16** and **TMU-16-NH$_2$**.

TGA data indicate that **TMU-16** and **TMU-16-NH$_2$** release their guest molecules over the temperature range 25-280 and 25-230 °C to form the guest-free phases, $[Zn_2(BDC)_2(4\text{-}bpdh)]$ and $[Zn_2(NH_2\text{-}BDC)_2(4\text{-}bpdh)]$, respectively (Figure S3 in the SI). Weight losses of about 23% were measured for both MOFs, which are attributed to the loss of 3 DMF (Calc.: ~24%). The networks **TMU-16** and **TMU-16-NH$_2$** are thermally stable to 360 and 320 °C, respectively, as evidenced by the fact that no additional weight loss were observed at those temperatures, after which the frameworks eventually decompose.

To explore the absorption ability of compounds to I_2, the fresh samples of **TMU-16** and **TMU-16-NH$_2$** (100 mg) were immersed in a hexane (3 mL) solution of I_2 (0.005 mol L^{-1}) and were monitored in real time with a camera. For the amine contained network, **TMU-16-NH$_2$**, the color of the crystals intensified from orang to dark brown (30 min) quickly. And the dark brown solutions of I_2 faded quickly to colorless in less than 30 minutes (Figure 2a and S4 in the SI). While, in non-functionalized analogue, **TMU-16**, the dark brown solutions of I_2 faded slower to colorless in about 2 hours (Figure 2b and S5 in the SI). Gravimetric analysis and TGA curves show that each formula units in **TMU-16** and **TMU-16-NH$_2$** can adsorb about 0.6 I_2 (4.8 I_2 molecules per each unit cells) (Figure S6 in the SI). The entry of I_2 into the **TMU-16** and **TMU-16-NH$_2$** host frameworks lead to a distinct decrease of the intensity of the adsorption band at 520 nm that correspond to the concentration of I_2 (Figure 2c, d). The rapid decline of the UV/vis peak also proves that **TMU-16-NH$_2$** can 1.4 times faster adsorb iodine compared with non-functionalized analogue (Figure S7 in the SI). The adsorption amount of I_2 was the same for both networks (~45%). The amount of the adsorption is the fifth highest compared to the reported MOFs.[6] The exceptional affinity of both **TMU-16** and **TMU-16-NH$_2$** for I_2 may be attributed to the structural character of the regular π-electron walls made of 4-bpdh. That is, there is a striking difference compared to conventional adsorbent materials that are lacking an accessible interaction between I_2 and host.
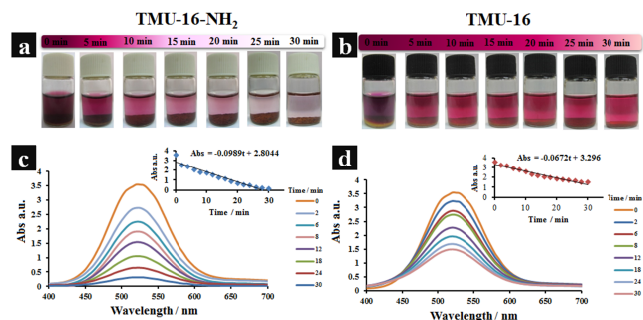
Figure 2. Photographs showing the color change when 100 mg of (a) **TMU-16-NH$_2$** and (b) **TMU-16** were soaked in hexane solutions of I$_2$ (3 mL, 0.005 mol L^{-1}). The UV/vis spectrum of (c) **TMU-16-NH$_2$** and (d) **TMU-16** for the adsorption process of iodine.

The encapsulated I$_2$ could be easily removed from the frameworks upon immersion of **I$_2$@MOFs** in organic solvents. When the crystals of **I$_2$@TMU-16** and **I$_2$@TMU-16-NH$_2$** were soaked in dry ethanol, the color of the both crystals changed gradually from dark brown to orange and yellow about 30 min, respectively, and the color of the ethanol solutions deepened gradually from colorless to darker yellow (**Figure 3**a, b and S8, S9 in the SI). To further investigate the kinetics of I$_2$ delivery of non- and amine-functionalized networks, UV/vis spectra were recorded at room temperature. For both hosts frameworks the absorbance of I$_2$ in ethanol increase linearly with time (**Figure 3**c, d). The photographs and UV spectra for both **I$_2$@MOFs** releasing I$_2$ demonstrate that the I$_2$ sorption process of compounds are reversible. Interestingly, **TMU-16** is released iodine 1.8 times faster than amine-functionalized analog (Figure S10 in the SI).
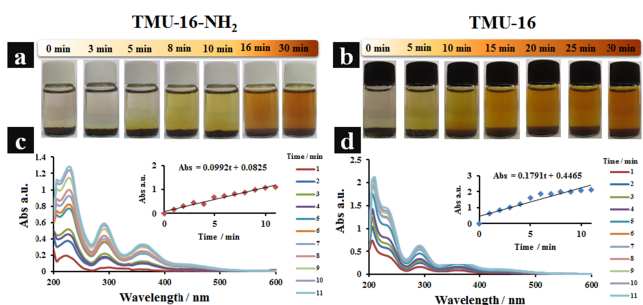

Figure 3. Photographs showing the I$_2$ release process when 50 mg of (a) **I$_2$@TMU-16-NH$_2$** and (b) **I$_2$@TMU-16** were immersed in EtOH (3 ml). The UV/vis spectra of (c) **I$_2$@TMU-16-NH$_2$** and (d) **I$_2$@TMU-16** for the releasing process of iodine.

Temporal evolution of the UV/vis spectra of iodine in ethanol solution shows λ_{max} at 210, 280 and 360 nm, which become stronger with increasing I$_2$ content (Figure 3 c, d). The intensity of the absorption band at 210 nm is proportional to the concentration of I$_2$, and the absorption bands at 280 and 360 nm correspond to polyiodide ions (I^{3-}), which are generally stabilized by H$^+$ ions and obtained from the reaction of I$_2$ with decomposed iodide.[16] Once these interactions fade out with increasing I$_2$ extrusion, the delivery in the second stage is mainly governed by a free diffusion process, and a complete I$_2$ release from **I$_2$@MOFs** needs more than one week to attain the equilibrium state. The regular confined micropores combining abundant π-electron walls may cumulate the advantages to achieve a better controlled release of I$_2$, in contrast to conventional adsorbents.[17] The differences in adsorption and desorption rates between the non- and amine-functionalized

frameworks probably resulted from the different host-guest interactions as well as different pore volume of the networks. The amine-functionalized cavities and surfaces of **TMU-16-NH$_2$** make a weak N-H…I interactions, so leads to faster sorption and of course lower desorption rates compared with **TMU-16**. On the other hand, the non-functionalized larger cavities of **TMU-16** results to the faster desorption rate. Further, the integrity of the frameworks is confirmed by the IR and the PXRD data (Figures S11-S16 in the SI). It was worth to say that when the crystals were soaked in the solution for about 30 minutes, most of the peaks in the PXRD distinctly weakened, but when the I$_2$ was removed from the frameworks upon immersing of the crystals in ethanol the peaks appeared again (Figures S11, S13 in the SI). The unusual phenomenon can be well explained by the high amount of iodine in **TMU-16** and **TMU-16-NH$_2$** which has a significant impact on the sensitivity of X-ray.

Conclusions

In summary, two isostructural two-fold interpenetrated microporous MOFs have been successfully synthesized based on zinc cations, rigid bipyridyl-based ligand and non-/amine-functionalized ligands. The ad/desorption rates of iodine from **TMU-16** and **TMU-16-NH$_2$** were compared. Our results further support the idea that judicious selection of building blocks in the assembly process can not only give a predictable new structure but also incorporate interesting properties. So, assembling MOFs with NH$_2$ group tagged on linker of the framework **TMU-16-NH$_2$** as hydrogen bond donor, can find more applications in the encapsulation of iodine. While, amine-functionalized network shows the faster adsorption rate, the delivery of iodine from the non-functionalized homolog is faster. However, the iodine contents were very close for both networks.

Notes and references

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