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Strong Hydrogen Binding within a 3D Microporous Metal−Organic Framework

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A 3D microporous cadmium(II) metal−organic framework based on 1*H*-tetrazole exhibits strong hydrogen binding with an initial enthalpy of adsorption of 13.3 kJ/mol, due to the smaller pore sizes and the high hydrogen binding affinity of the tetrazolyl-ring-decorated inner surface of the pores.

The possibility of hydrogen (H_2) extensively utilized as a clean energy substituting for fossil fuels mainly relies on the construction of the feasible storage system.[1] Among the various H_2 storage candidates, porous metal−organic frameworks (MOFs) are considered as the most promising materials, owing to their exceptionally high surface areas and chemically tunable structures of the pores.[2] It is more convincing that, in mass, some of the MOFs have arguably reached or even surpassed the U.S. DOE 2010 H_2 storage target except the low H_2 adsorption energies,[3] which means cryogenic temperatures are required to observe significant H_2 uptake (mostly at 77 K). Recent research indicates that H_2 adsorption energies of 22−25 kJ/mol have been predicted to maximize the amount of adsorbed H_2 at 298 K in the pressure range of 1.5−30 bar.[4] Therefore, increasing the H_2 binding energy within MOFs is the most important challenge for creating H_2 storage materials that operate at room temperature.

Recently, some strategies are employed for increasing the H_2 adsorption enthalpy. For instance, introduction of unsaturated metal coordination sites to the surfaces, which can significantly strengthen the H_2 molecule binding with the metal open sites, is considered as the most effective measure.[5,6] In addition, recent researches also showed that the H_2 isosteric heat of adsorption can also be increased by modifying the pore surface. Such an MOF with its inner pore surface decorated by aromatic-rich groups can heighten the H_2 adsorption enthalpy because of multiple interactions between H_2 molecules and aromatic rings.[7] However, it still lacks the instance exhibiting high H_2 adsorption enthalpy because the interactions between H_2 molecules and aromatic rings are relatively weak. Herein, we report the structure and H_2 adsorption property of a 3D microporous MOF, $[Cd_5(Tz)_9](NO_3)\cdot 8H_2O$ (**1**; Tz = tetrazolate), in which the strong H_2 binding property of **1** possibly results from its inner pore surface decorated by tetrazolyl rings.

The hydrothermal reaction of $Cd(NO_3)_2\cdot 4H_2O$ and ethyl tetrazolate-5-carboxylate (ETzc) in distilled water under 160 °C for 72 h obtained unexpected colorless block-shaped crystals of **1** in 63% yield (see the Supporting Information). Because the carboxylate group linking to the tetrazolyl ring is unstable under hydrothermal conditions,[8] the ligand Tzc underwent decarboxylation and produced 1*H*-tetrazole (HTz). It is worth noting that the structure of **1** is different from the one directly synthesized through the reaction of HTz and $Cd(NO_3)_2\cdot 4H_2O$ under the same reaction

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conditions,[9] which may ascribe to the mystery of the in situ reaction.

X-ray crystallography study (see the Supporting Information) reveals that **1** is a 3D porous structure with open hexagonal channels modified by tetrazolyl rings. As shown in Figure 1a, the asymmetric unit in **1** contains two crystallographic independent Cd^{II} ions. Cd1 is coordinated with six nitrogen atoms from two individual μ_4-Tz and four individual μ_3-Tz ligands, forming an octahedral geometry. Cd2 also shows an octahedral coordination geometry by coordination with six nitrogen atoms from three individual μ_4-Tz and μ_3-Tz ligands, respectively. The Cd−N distances of 2.329(10)−2.361(10) Å are in good agreement with literature values in cadmium tetrazole complexes, and the C−C and C−N distances are unexceptional.[10] In **1**, six Cd1 and two Cd2 are connected via six μ_3-Tz and three μ_4-Tz ligands to form a trigonal-prismatic second building unit (SBU; Figure 1a), in which six Cd1 occupy the six apical sites, while two Cd2 locate at the 3-fold axis. The adjacent SBUs are further connected by an additional three μ_4-Tz anions along the *c* axis to form trigonal-prismatic SBUs with NO_3^- occupied cages (Figure 1c). Six previously described SBUs are connected by sharing Cd1 ions, resulting in a hexagonal channel with sizes of 4.9 Å × 4.9 Å (Figure 1b). Inside the channel, eight water molecules are connected through intermolecular hydrogen bonds to form an octamer water cluster with two-capped trigonal-prism geometry, and the octamer water clusters are further connected by the sharing of two-capped water molecules to generate a 1D water chain (Figure 1d), which is embedded in the surface of the channel. About 27% solvent-accessible volume is estimated by using *PLATON* software. It is worth noting that the inner surface of the hexagonal channel is modified with pairs of tetrazolyl rings directed toward the cavity interiors, resulting in a tetrazolyl-ring-decorated inner surface (Figures S1 and S2 in the Supporting Information).

Thermogravimetric analysis (TGA) indicates that the lattice water molecules in the hexagonal channels are easily lost under 100 °C and the framework of **1** is stable around 300 °C (Figure S3 in the Supporting Information). The results of variable-temperature powder X-ray diffraction (PXRD) measurements also elucidate that the framework of **1** is stable up to 300 °C (Figure S4 in the Supporting Information). N_2 sorption measurements for desolvated **1** measured at 77 K revealed a type I isotherm (Figure 2a), which is characteristic of a microporous material.[11] The uptake amount of N_2 increases abruptly at the start of the experiment and reaches a plateau of about 80 cm^3 (STP)/g, corresponding to 6.8 N_2 molecules in each unit cell, indicating a uniform microporous structure. Using the Brunauer−Emmett−Teller (BET) equation, a pore volume of 0.134 cm^3/g is estimated and is smaller than the pore volume of 0.218 cm^3/g calculated from the crystal structure. This discrepancy can be attributed to the fact that gas molecules are unable to fill the void space efficiently. Fitting the BET and Langmuir equations to the isotherm gave estimated surface areas of 310 and 338 m^2/g, respectively.

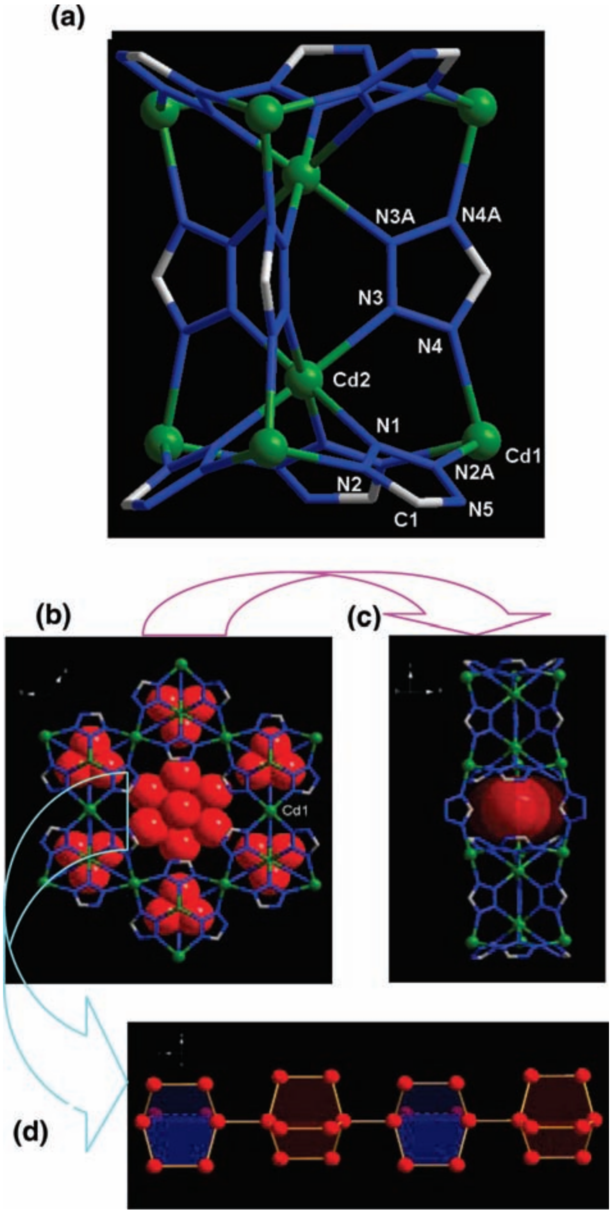

Figure 1. (a) Structure of a trigonal-prismatic SBU showing the coordination environments of Cd ions and bridging modes of μ_3-Tz and μ_4-Tz ligands. (b) Hexagonal channel composed of six trigonal-prismatic SBUs by sharing Cd1 vertexes (NO_3^- anions locate at the 3-fold axis) viewed along the *c* axis. (c) Trigonal-prismatic SBUs with a NO_3^- occupied cage. (d) 1D water chain consisting of octamer water clusters by the sharing of two vertical water molecules.

Considering the structural features of **1** with tetrazolyl-ring-modified narrow pores, H_2 uptake measurements were explored. It was found that the desolvated **1** can store up to 0.75 wt % (3.71 mmol/g) of H_2 at 760 Torr and 77 K (Figure 2b); this value is comparable to those of reported porous MOFs with larger surface areas. For instance, under similar conditions, Co_2(6-mna)$_2$) and Er_2(3,5-pdc)$_3$ display H_2 uptake of 0.66 and 0.68 wt %, respectively, with surface areas of 420 and 427 m^2/g, respectively (6-mna = 6-mercaptonicotinate; 3,5-pdc = pyridine-3,5-dicarboxylate).[12,13] The

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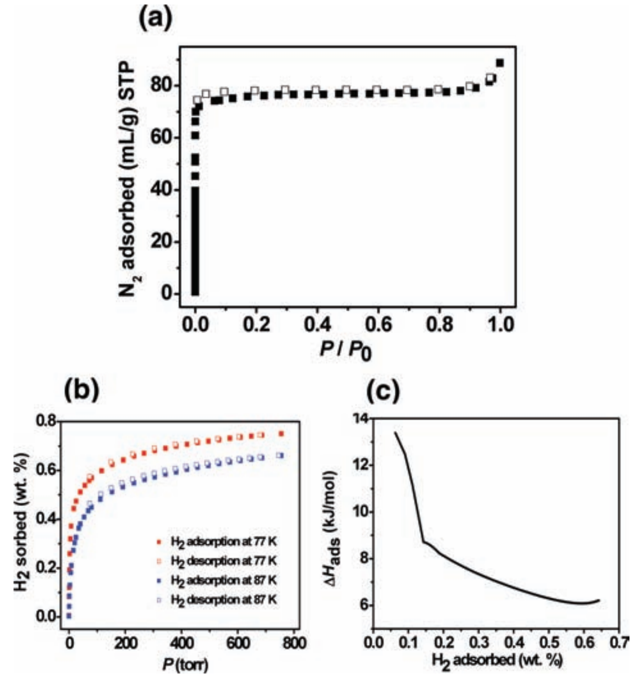

Figure 2. (a) N_2 sorption isotherm for desolvated **1** at 77 K. (b) H_2 sorption isotherms for desolvated **1** at 77 and 87 K. (c) Enthalpy of adsorption plots as a function of the amount of H_2 uptake in desolvated **1**.

monolayer coverages in the pores predicted by the fitting of the Langmuir equation to the N_2 and H_2 isotherms were nearly identical (3.57 mmol/g for N_2 and 3.71 mmol/g for H_2), suggesting that the same number of binding sites are accessible in each case.[14]

The most striking feature of **1** is the steep slope in the H_2 sorption isotherm at an initial pressure and 77 K, indicating that the pores in desolvated **1** strongly interact with H_2 molecules. This fact prompts us to study the enthalpies of H_2 adsorption. Consequently, a second set of H_2 isotherms were measured at 87 K (Figure 2b), and enthalpies of adsorption were calculated using the modified Clausius–Clapeyron equation.[15] As shown in Figure 2c, the initial enthalpy of adsorption at very low pressure reaches up to 13.3 kJ/mol. To our knowledge, this value is only a little lower than the one of 13.5 kJ/mol, the highest enthalpy of adsorption observed in the reported MOFs.[5b] The porous MOF (CPO-27) with the highest enthalpy of adsorption possesses exposed Ni^{II} sites.[5b] In addition, this value is also higher than those (8–10 kJ/mol) observed in the significant polytetrazole-based porous MOFs reported by Long and co-workers.[6] According to the nature of the pore structure, we consider that the high H_2 binding affinity observed in desolvated **1** can be mainly attributed to decoration of the pores with tetrazolyl rings. It has been reported that the aromatic rings in microporous aromatic-rich MOFs, especially when the aromatic system was supplemented with electron-pushing groups, can strengthen the interactions of H_2 molecules with pore walls through multiple contacts.[16] In comparison with the aromatic ring, the tetrazolyl ring possesses more electrons to form an electron-rich conjugate π system; thus, the interaction between H_2 and the tetrazolyl ring should be stronger than the interaction between H_2 and the aromatic ring, which is in accordance with the fact that the value of the adsorption enthalpy of desolvated **1** is higher than any one of the reported aromatic- and tetrazolyl-rich microporous MOFs. In addition, the smaller size of the tetrazolyl-ring-decorated inner surface, which can overlap the potential energy fields of the pore walls,[17] may also contribute to the enhancement of the H_2 binding energy. Because of the above-mentioned reasons, a large enthalpy of sorption at low pressure was observed. Along with the augmentation of the amount of H_2 adsorption, the adsorption enthalpy reduces to 6.08 kJ/mol. This can be attributed to the monolayer coverage in the pores that prevents the latter H_2 molecules from touching the pore walls completely. In comparison with the initial enthalpy of adsorption of 13.3 kJ/mol for the desolvated **1**, the relatively lower values of 8–10 kJ/mol observed in the polytetrazole-based porous MOFs may be attributed to their large cage-shaped pores. The results of TGA indicate that there are no obvious plateau regions in these polytetrazole-based porous MOFs,[6] demonstrating that the guest molecules within the pores are hardly to fully removed for prevention of framework collapse, or the frameworks will partly collapse if all of the guest molecules are desolvated, and this will weaken the interactions between the pores and the H_2 molecules.

In conclusion, we have hydrothermally synthesized a 3D microporous MOF with tetrazolyl-ring-decorated pores. The desolvated **1** shows high H_2 binding affinity, with an initial adsorption enthalpy of 13.3 kJ/mol, which is close to the highest value of 13.5 kJ/mol observed in a porous MOF of CPO-27 with open metal sites. The tetrazolyl rings in the pores play a key role in the high H_2 binding affinity because of its electron-rich nature. The results presented here provide an efficient approach for increasing the H_2 adsorption enthalpy. Our future efforts will focus on the design and synthesis of stable MOFs with relatively larger tetrazolyl-ring-decorated pores to enhance the H_2 sorption capacity.

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Supporting Information Available: Crystallographic data in CIF format, synthesis, ΔH_{ads} calculations, crystallographic data, structural figures, TGA, and variable-temperature PXRD patterns. This material is available free of charge via the Internet at http://pubs.acs.org.

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