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A Free Tetrazolyl Decorated Metal−Organic Framework Exhibiting High and Selective CO_2 Adsorption

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Supporting Information

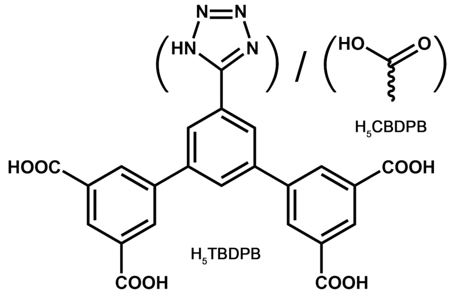
ABSTRACT: In this work, we employed a new tetrazolyl-functionalized ligand, 5-(1H-tetrazole-5-yl)-1,3-bis(3,5-dicarboxylphenyl)-benzene (H_5TBDPB), and successfully obtained an example of incorporating free tetrazolyl groups in transition-metal-based MOFs based upon an ideal MOF platform. With a BET surface area of 2070 m^2 g^{-1}, this new tetrazolyl-decorated MOF $[Cu_6(TBDPB)_3(H_2O)_6]\cdot9DMF\cdot15H_2O$ (HHU-5, HHU for Hohai University) exhibits a high CO_2 adsorption capacity of 37.1 wt % at 1 bar and 273 K and high CO_2 separation capacity toward N_2 and CH_4 as well.

A new type of crystalline porous material, Metal−Organic Frameworks (MOFs), has shown promising application in gas separation due to its modular nature in structures.[1−3] In order to achieve high gas storage capacity and separation efficiency in MOFs, various strategies were employed, especially preferential functionalization.[4−7] Aiming at CO_2, which is the critical factor that causes global warming, a number of functional groups with different natures were introduced to strengthen the CO_2-framework interaction, such as nitrogen bases (aniline,[8−11] pyridine,[12−14] and ethylenediamine,[15] for instance) and other polar functional groups ($-NO_2$, −F, −COOH, $-SO_3H$, $-CF_3$, etc.).[16−24]

MOFs containing azolate rings were widely regarded as showing amazing affinity to CO_2 molecules due to their abundance of aromatic −N(H)− donors.[25−37] The underlying mechanism is the interaction between uncoordinated N atoms and CO_2 molecules. The capability of keeping more N donors uncoordinated may lead to better CO_2 adsorption in MOFs. Tetrazolate with a comparably higher amount of nitrogen atoms was therefore widely used in the construction of new MOFs. However, with at least two N-donor sites participating in the building of a framework, only half of the open donor sites work during gas adsorption.[38−41] Meanwhile, tetrazolyl group always exhibits a high tendency of coordination during solvothermal reactions with transition metal ions. Therefore, keeping more N atoms uncoordinated in transition-metal-based MOFs is still a great challenge.[31]

Herein, we present the first example of incorporating free tetrazolyl groups in transition-metal-based MOFs. Mfj-type MOF is chosen as a platform for isoreticular functionlization due to its structural stability against various functional groups.[37−39] We supposed that in this type of MOF the location of the functional groups seldom interferes with the formation of the skeleton, and the introduction of an active tetrazolate group in this location may still be left uncoordinated. Therefore, by a new tetrazolyl-functionalized diisophthalate ligand, H_5TBDPB shown in Scheme 1, a new *mfj*-type MOF $[Cu_6(TBDPB)_3(H_2O)_6]\cdot9DMF\cdot15H_2O$ (HHU-5, HHU for Hohai University) with free tetrazolyl groups was successfully synthesized. With a BET surface area of 2070 m^2 g^{-1} and free tetrazolyl groups in the pores, this new MOF exhibits a highest CO_2 adsorption capacity of 37.1 wt % at 1 bar and 273 K (and 21.0 wt % at 1 bar and 298 K) among tetrazolate-based MOFs, and selective CO_2 adsorption toward N_2 and CH_4 as well.

Scheme 1. Schematic Structure of the Organic Linker H_5TBDPB (or H_5CBDPB)



HHU-5 was synthesized using $Cu(NO_3)_2\cdot3H_2O$ and H_5TBDPB and the phase purity of the bulk sample was independently confirmed using powder X-ray diffraction (PXRD, Figure S7 in the Supporting Information). In addition, carboxylic acid has comparable size as tetrazole, and their pK_a values are almost equal (∼4 for carboxylic acid and 4−5 for tetrazole). For a better interpretation of CO_2-framework interactions through comparison, we also synthesized an

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isoreticular analogue of HHU-5 with free carboxyl groups[42] decorated instead, named HHU-5C (Figures S4–S6).

Single-crystal X-ray diffraction analysis reveals that HHU-5 crystallizes in orthorhombic *Cmcm*. The asymmetric unit of HHU-5 consists of one-half and a quarter TBDPB-ligand, three crystallographically unique Cu^{2+} ions, and three coordinated water molecules (Figure S1). HHU-5 is isostructural to PCN-306 and therefore can be simplified to a (3,3,4,4)-c 4-nodal *mfj*-type net. Two types of ligands have different dihedral angles of 89.0° (type A in Figure 1a) and 42.7° (type B in Figure 1a) between central and terminal benzene rings, respectively. No matter which type they belong to, all the tetrazolyl groups are uncoordinated and can act as Lewis-base sites. Of note, tetrazolyl groups in type B ligands tend to link in pairs by hydrogen bonds (Figure S2), which may limit the accessibility of the Lewis-base sites. Up to now, HHU-5 is the first transition-metal-based MOF with free tetrazolyl groups and the free tetrazolyl groups in HHU-5 work either in pairs or singly to block the channels along the *c* axis and decorate on the surface of channels along the *a* axis with a diameter of 7.4 Å (Figure 1c). Using PLATON, the total potential solvent accessible volume of HHU-5 was calculated to be 66.9%. As an isostructural analogue of both HHU-5 and PCN-306, HHU-5C crystallizes in a slightly different orthorhombic space group of $Cmc2_1$, and the asymmetric unit of HHU-5C consists of one and a half CBDPB ligands, four crystallographically unique Cu^{2+} ions, and four coordinated water molecules (Figure S4). Similar to HHU-5, the channels along the *c* axis in HHU-5C are blocked by free carboxyl groups, and the channels along the *a* axis also have a diameter of about 7.4 Å and are decorated by free carboxyl groups (Figure S6). The similarity of the pore structures of both MOFs makes the contrast in gas adsorption be more concentrated on the different electrostatic fields of functional groups rather than pore-structural differences.

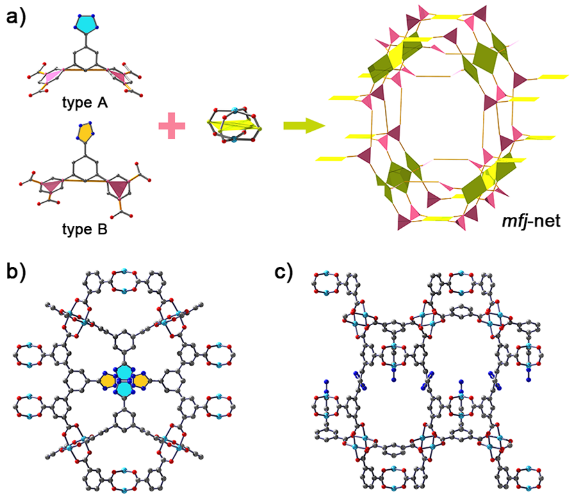

Figure 1. (a) Two types of TBDPB ligands and the Cu-paddlewheel clusters assembled into a *mfj*-type MOF HHU-5. (b) HHU-5 viewed along *c* axis. (c) HHU-5 viewed along *a* axis.

The bulky identity and thermal stability of HHU-5 and HHU-5C were investigated by PXRD measurements and TGA. The TG curve of HHU-5 (Figure S19a) shows that the as-synthesized HHU-5 lost ~36% of its weight because of H_2O and DMF guest molecules filling in the pores, and the framework can be thermally stable up to 260 °C. For HHU-5C, the TG curve shows a ~35% weight loss, and it can be stable up to 250 °C. The as-synthesized sample of HHU-5 (or HHU-5C) was solvent-exchanged with dry methanol and then evacuated at 100 °C for 12 h under a high vacuum to yield the activated sample. Obviously, the PXRD pattern of desolvated HHU-5 (or HHU-5C) indicates that it still maintains crystallinity (Figures S7 and S8). As shown in Figure 2, HHU-5 exhibits reversible type-I sorption behavior, characteristic of microporous materials with saturated adsorption amount of N_2 of 515.6 $cm^3\ g^{-1}$ at 77 K. The Brunauer–Emmett–Teller (BET) surface area and Langmuir surface area of HHU-5 were calculated to be 2070 and 2240 $m^2\ g^{-1}$, respectively. Meanwhile, the BET surface area and Langmuir surface area of HHU-5C were also measured and calculated, with values of 2082 and 2280 $m^2\ g^{-1}$, respectively. In comparison with the BET surface area of PCN-306 (2772 $m^2\ g^{-1}$), similar decreases were found in HHU-5 and HHU-5C, which confirms the comparable size of tetrazolyl group and carboxyl group.

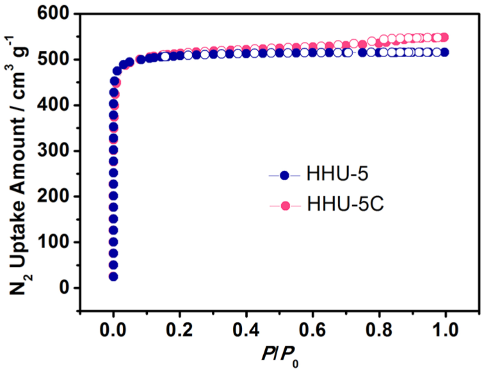

Figure 2. N_2 adsorption isotherms of HHU-5 and HHU-5C at 77 K.

The free tetrazolyl groups in HHU-5 make us believe that HHU-5 may have good performance in CO_2 adsorption. Thus, we further measured the CO_2 adsorption of it. As shown in Figure 3a, at 1 bar, the CO_2 uptake capacities of HHU-5 at 273

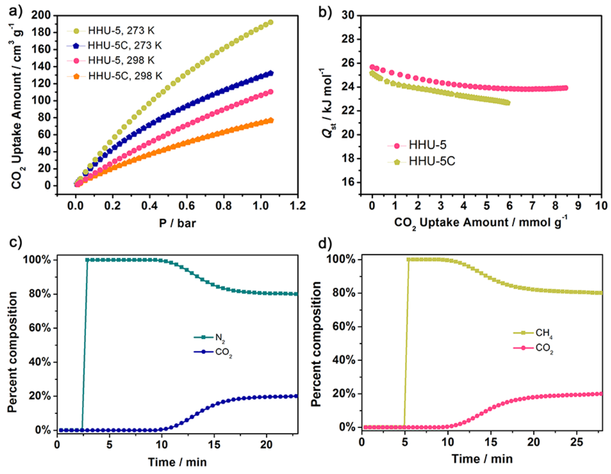

Figure 3. (a) CO_2 adsorption isotherms of HHU-5 and HHU-5C at 273 and 298 K. (b) CO_2 adsorption enthalpy of HHU-5 and HHU-5C. (c and d) Breakthrough curves of HHU-5 initially saturated with CO_2: (c) gas mixture containing 20% of CO_2 and 80% of N_2, (d) gas mixture containing 20% of CO_2 and 80% of CH_4.

and 298 K are 188.8 $cm^3\ g^{-1}$ (37.1 wt %; wt % = 100(mass of adsorbed gas)/(mass of MOF)) and 107.1 $cm^3\ g^{-1}$ (21.0 wt %). These values are the highest among tetrazolate-based MOFs (Table S2) and also make HHU-5 one of the most reported top copper-diisophthalate framework materials with the highest CO_2 uptake at 1 bar (Table S3). The isoreticular analogue without any functional group (PCN-306) possesses a CO_2 uptake of 84.7 $cm^3\ g^{-1}$ under conditions of 298 K and 1 bar. Clearly, a great improvement of CO_2 uptake was observed due to free tetrazolyl groups being functioned as CO_2 preferred sites. To exclude the effect of narrow pore effect induced by the incorporation of large functional groups, a comparison was conducted to the isoreticular analogue with similar BET surface area, HHU-5C, possessing CO_2 adsorption capacities of 128.3 $cm^3\ g^{-1}$ at 273 K and 74.1 $cm^3\ g^{-1}$ at 298 K. Transparently, great improvement of CO_2 uptake was noticed. To further understand the interactions, we calculated the CO_2 adsorption enthalpies of both, as shown in Figure 3b. The zero-coverage CO_2 adsorption enthalpy of HHU-5 is 25.6 kJ mol^{-1}, which is quite comparable with that of HHU-5C (25.1 kJ mol^{-1}) but higher than that of PCN-306 (24.1 kJ mol^{-1}). Althrough the improvment of CO_2 adsorption enthalpy in either HHU-5 or HHU-5C is not significant, it still implies to some extent that both tetrazolyl and carboxyl groups can enhance the interactions between CO_2 molecules and MOFs, and tetrazolyl with uncoordinated N atoms works better than polar carboxyl group in the whole range and especially in the higher loading range. Theoretically, all four uncoordinated N atoms are able to act as electron-rich sites to attract the electropositive carbon atoms of CO_2 molecules and form Lewis acid−base pairs. However, due to the hydrogen bonding between tetrazolyl groups from every pair of ligand B, the accessibility of these N atoms is limited, and therefore the CO_2 adsorption enthalpy of HHU-5 at initial uptake does not show significant improvement. As the pressure increases, more CO_2 molecules enter into the pore, and the access-limited N atoms begin to work and then guarantee a high CO_2 uptake in the higher pressure range. Meanwhile, although tetrazolyl group has a similar pK_a value to carboxyl groups, more uncoordinated nitrogen atoms in tetrazolyl groups can form more Lewis acid−base pairs with CO_2 molecules, which leads to a continuously higher CO_2 adsorption enthalpy in HHU-5 than that in HHU-5C. In general, the gentle but continuous improvement in CO_2 enthalpy not only endows HHU-5 a high CO_2 adsorption capacity but also indicates that it may be a potentially energy-efficient adsorbent for CO_2. Very interestingly, if every N-donor site as well as unsaturated metal site in HHU-5 was regarded as a CO_2 favored site and was occupied by a CO_2 molecule, the CO_2 uptake of HHU-5 would be ∼60 molecules per unit cell, which is coincidently equal to the experimental CO_2 uptake of HHU-5 at 273 K.

The high CO_2 uptake of HHU-5 encouraged us to further investigate its CO_2 separation properties against N_2 and CH_4. Therefore, the N_2 and CH_4 adsorption isotherms were collected at 298 K (Figure S13). In contrast with the high CO_2 uptake, the N_2 and CH_4 adsorption capacities of HHU-5 are 7.0 $cm^3\ g^{-1}$ and 22.4 $cm^3\ g^{-1}$, respectively. Such discrepancies indicate a selective CO_2 adsorption toward N_2 and CH_4. Therefore, we evaluated the CO_2 selectivity of HHU-5 via the Ideal Adsorption Solution Theory (IAST), and the result in Figure S17 shows that the CO_2/N_2 selectivity of HHU-5 at 1 bar is 21.2, while the CO_2/CH_4 selecitivity of it is 6.2. We further conducted the transient breakthrough experiments on HHU-5 by applying the feed gases of CO_2/N_2 (or CO_2/CH_4). The breakthrough curves of HHU-5 for the CO_2/N_2 and CO_2/CH_4 separation at 298 K are shown in Figure 3c,d. When a gas mixture containing 20% CO_2 and 80% N_2 (or 20% CO_2 and 80% CH_4) was fed into the adsorption column, N_2 (or CH_4) initially saturated and broke through the column. The outlet concentration of N_2 (or CH_4) nearly reached 100% due to the preferred adsorption of CO_2 in HHU-5. The breakthrough results indicate that the separation of these two gas mixtures can be efficiently achieved, and CO_2 was detected until a breakthrough time of about 10 min was reached with an adsorption of 2.92 mmol g^{-1} during the $0\sim\zeta$ break. Such an efficient separation of CO_2 may make HHU-5 a potential material for carbon capture and methane purification.

In summary, via a new tetrazolyl-attached diisophthalate ligand, the first transition-metal-based MOF with free tetrazolyl groups was successfully synthesized. This new MOF HHU-5 exhibits the highest CO_2 adsorption capacity of 37.1 wt % at 1 bar and 273 K (and 21.0 wt % at 1 bar and 298 K) among tetrazolate-based MOFs and also shows a selective CO_2 adsorption toward N_2 and CH_4. The high CO_2 adsorption property, good CO_2 separation performance, and moderate CO_2 adsorption enthalpy may make HHU-5 a potential energy-efficient material for CO_2 capture.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.8b02031.

Experimental details, PXRD patterns, crystallographic data, additional gas adsorption isotherms (PDF)

Accession Codes

CCDC 1830113−1830114 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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