Selective gas sorption property of an interdigitated 3-D metal–organic framework with 1-D channels†

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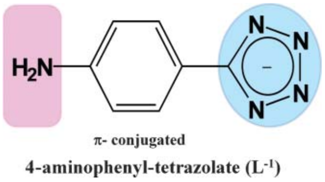
An interdigitated 3-D metal–organic framework, $[Cd_3(OH)_2L_4(H_2O)_2]$, with 1-D channels was prepared using 4-aminophenyl-1*H*-tetrazole (HL) and Cd(II) ions, where the host framework shows selective gas sorption behavior that is based on the different nature of the interactions between the gas and the framework rather than on the size-exclusion effect of the micropores.

Considerable effort has been devoted to the synthesis and characterization of microporous metal–organic frameworks (MOFs) composed of transition metal ions and bridging organic ligands because of their potential applications in many areas, including storage, separation, and exchange processes.[1] In contrast to conventional microporous materials such as zeolites and activated carbon materials, MOFs have pore surfaces that can be rationally designed and functionalized by their components.[1,2]

Several MOFs that exhibit selective gas sorption properties have been reported,[2a,3] and most of the selectivities are believed to be based on the size-exclusion effect.[4] Modulation of the sorption profiles of MOFs[5] is a challenging but attractive topic (because of their potential in practical applications such as specific sensing and separation of gas molecules). Recently, it was reported that an adsorption system for specific target molecules can be realized if there are multiple sites for specific interactions (hydrogen bonding and van der Waals forces) at suitable positions on the micropores.[2a,6] It is also known that adsorption will be affected by a change in the polarizabilities of guest molecules or the polarities of frameworks.[6c,7] The interactions between guest molecules and the MOF backbone (such as dipole–dipole interaction, donor–acceptor affinity, *etc.*) may make some contributions to the selective gas sorption. In order to test this hypothesis, a suitable MOF needs to be constructed. We selected 4-aminophenyl-1*H*-tetrazole (HL) (see ESI†) as a ligand for the following reasons: (1) it can act as a rigid building block to form robust MOFs with metal ions; (2) the amino group of the ligand can participate in either coordination or hydrogen bonding, which will play an important role in the assembly of MOFs;[5f,8] (3) the tetrazolate group and the amino group connected through a conjugated π-electron reservoir might provide polar environment in the resulting MOFs (Scheme 1).



Scheme 1 4-Aminophenyl-1*H*-tetrazole (HL).

$[Cd_3(OH)_2L_4(H_2O)_2]\cdot DMF$ (**1**) was prepared by solvothermal reaction of equivalent amounts of $Cd(NO_3)_2\cdot 3H_2O$ and the ligand HL in DMF–H_2O mixed solvent (see ESI†). The crystal structure of **1**‡ (see ESI†) is shown in Fig. 1. Two types of Cd^{2+} centers and two 4-aminophenyl-1*H*-tetrazolate ligands (Fig. S1, ESI†) lead to a 3-D network with 1-D channels. The coordination geometry around Cd1, which is on a crystallographic inversion center, is octahedral with four N atoms of the tetrazole groups from four different ligands occupying the corners of a square and two O atoms from two μ_3-OH^- groups at the apical positions (Table S2, ESI†). Cd2 is in a distorted octahedral environment and is coordinated to two nitrogen atoms of tetrazole groups from two different ligands, one nitrogen atom from the amino group of a ligand, one oxygen atom from water, and two oxygen atoms from two different μ_3-OH^- groups. The μ_3-OH^- groups link Cd1 and Cd2 to form a 1-D chain, $\{[Cd_3(OH)_2]^{4+}\}_n$, running along the *a*-axis (Fig. 1(a)). The two ligands in the asymmetric unit of **1** are in two different coordination modes. One is a tridentate ligand and

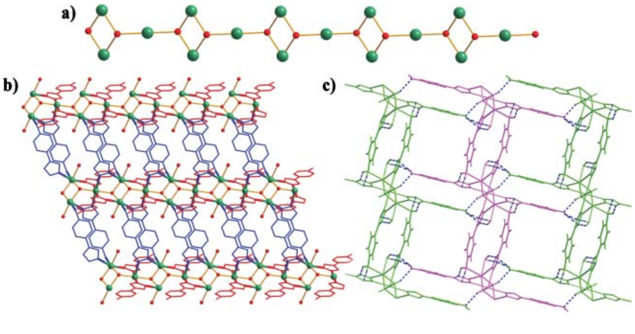


Fig. 1 The crystal structure of **1**. The solvent molecules in the 1-D channels and hydrogen atoms are omitted for clarity. (a) A 1-D $\{[Cd_3(OH)_2]^{4+}\}_n$ chain along the *a*-axis. (b) A 2-D sheet was constructed by the 1-D $\{[Cd_3(OH)_2]^{4+}\}_n$ chains interconnected by the tridentate ligands (blue), and the bidentate ligands (red) coordinated with 1-D chains forming ridge parts in the 2-D sheet along the *c*-axis. (c) Bidentate ligands in a 2-D sheet (pink) are interdigitated with those of neighboring 2-D sheets (differentiated in green) using hydrogen bonds (blue dotted line) and π–π interactions to form a 3-D structure.

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uses the two nitrogen atoms (N2, N3) of its tetrazolate group to bridge two adjacent Cd atoms (Cd1, Cd2) in the 1-D chain and the nitrogen atom (N5) of the amino group to link atom Cd2 in the adjacent chain to form a 2-D sheet structure (Fig. 1(b) and Fig. S2, ESI†). The other as a bidentate ligand uses the two nitrogen atoms (N7, N8) of its tetrazolate group to bridge another two adjacent Cd atoms (Cd1, Cd2) in the 1-D chain and acts as the ridge part of the 2-D sheet motif (Fig. 1(b) and (c)). The ridges are interdigitated with those of neighboring 2-D sheets by hydrogen bonds to form a 3-D network with 1D channels. The hydrogen atoms of the amino group (N10) in the bidentate ligand act as hydrogen donors towards the nitrogen atoms (N1, N4) of the tetrazole residue, while the nitrogen atom (N10) of the amino group also acts as a hydrogen acceptor to form a hydrogen bond with a μ_3-OH$^-$ group (Fig. 1(c) and Table S3, ESI†).[8d,9] As shown in Fig. 1(c), the two neighboring bidentate ligands, which are almost parallel to each other, also contribute to the formation of the interdigitated 3D structure *via* the π–π interaction between phenyl and tetrazole groups (Fig. S5 and Table S4, ESI†). The 1-D channels are along the *a*-axis with a cross section of 5.4 × 5.4 Å^2 (the channel size is measured after considering van der Waals radii for constituting atoms) (Fig. 2). The cavity volume is 208.5 Å^3 per unit cell, which is *ca.* 20.2% of the total crystal volume (calculated by PLATON).[11]

Thermogravimetric analysis (TGA) of **1** (Fig. S3, ESI†) reveals a weight loss of 4.7% in the region 80–250 °C. This weight loss corresponds to 0.75 DMF molecules per formula unit (calc. 5.0%) and is consistent with the elemental analysis. Decomposition of the framework is observed above 300 °C. The solvent-free framework, **1a**, was obtained by heating a crystal of **1** at 200 °C for about 20 min.[12] The crystal structure of **1a**‡ is similar to that of **1**, except that the DMF and water molecules in the solvent channels are removed from the framework (see ESI†). The integrity of the microporous framework was also confirmed by measuring the powder X-ray diffraction (PXRD) pattern of **1a**, which shows sharp diffraction peaks similar to those of **1** even without solvent molecules (Fig. 3). The temperature-dependent PXRD patterns suggest the stability of the framework up to 300 °C (Fig. S4, ESI†), which is consistent with the TGA result.

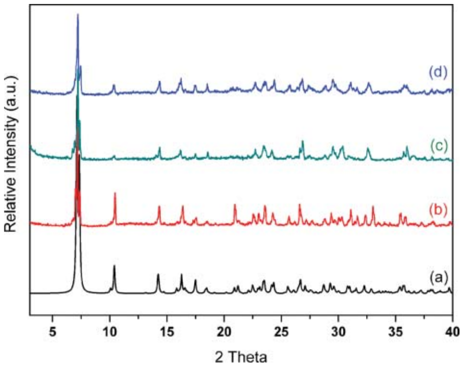

Fig. 3 PXRD patterns: (a) calculated **1**; (b) as-synthesized **1**; (c) **1a** prepared by heating **1** at 200 °C; (d) **1a** prepared by soaking **1** in acetonitrile and desolvating.[12]

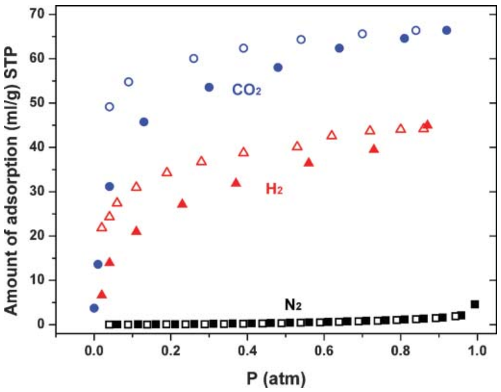

Fig. 4 Gas sorption isotherms of N_2 (77 K), H_2 (77 K) and CO_2 (195 K); ● and ○ represent the adsorption and desorption of CO_2; ▲ and △ H_2, and ■ and □ N_2, respectively.

The host framework, **1a**, was subjected to gas sorptions using CO_2, H_2 and N_2. It was observed that **1a** adsorbs CO_2 and H_2, but not N_2 (Fig. 4). A steep rise was observed at relatively low pressure in the adsorption branch of CO_2, this early uptake indicating the presence of permanent micropores in **1a**. Calculations based on the T-method[13] from H_2 isotherm gave a pore opening of *ca.* 5.5 Å, consistent with the single-crystal structure analysis. The pore volume for **1a** (0.056 mL g^{-1}) measured from H_2 isotherm indicates that less than a half of the available pore volume (0.120 mL g^{-1}, calculated using PLATON) was filled at 77 K. The BET surface areas estimated from the CO_2 and H_2 sorption isotherms are 210 and 90 m^2 g^{-1}, respectively (see ESI†). The difference in the surface areas indicates that the effect of the framework polarity is significant. The framework host, which contains Cd^{2+} ions, ligated water molecules, the polar residues and the π-electrons of the ligand, gives rise to an electric field that induces a dipole in CO_2. Besides such dipole-induced dipole interactions, the quadrupole moment of CO_2 (3.3–3.4 × 10^{-26} e.s.u.) would interact with the electric field gradient, providing a further contribution to the potential energy of adsorption.[5f,7] In addition, there may be some donor–acceptor affinity between the CO_2 molecules and the Lewis acidic Cd^{2+} ions.[4c]

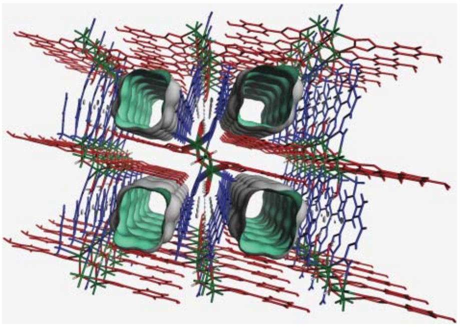

Fig. 2 The top view of **1** with 2 × 2 arrays of the 1-D channels.[10] The outside surfaces of the channels appear in dark grey, and the inside surfaces in cyan.

Hysteresis was observed in **1a** gas sorption isotherms for H_2 at 77 K, and for CO_2 at 195 K. Similar hysteresis behavior was also observed for various MOFs.[4f,4g,14] The mechanism for hysteresis in the adsorption/desorption isotherms of MOFs is not well understood currently. However, guest-directed framework rearrangements have been proposed for some coordination networks.[9a,14c,15,16] It is unlikely that this mechanism operates in the hysteresis described here, since **1a** keeps its robust framework up to 300 °C. The hindrance of some residual solvent molecules and metal hydroxide fragments at the pores for the diffusion of the gas molecules is also unlikely to be the cause of the hysteresis,[4f] because the sample for sorption study was prepared by repeatedly soaking and desolvating **1** in low-boiling acetonitrile, and by subsequent drying under vacuum at 100 °C overnight. We speculate that such behavior is a result of the increased sorbate–sorbent interactions as the gas molecules access pore region around the metal centers.[14a]

Most of the reported gas sorption selectivities in MOFs are related to the size-exclusion effect.[4] In principle, guests with kinetic diameters smaller than the pore windows can diffuse through the window and reach any point of the pore in the framework. Although the kinetic diameter of N_2 (3.54 Å)[17] is much smaller than that of the effective pore window of **1a** (5.5 Å), N_2 sorption at 77 K was not observed. This sorption behavior is not due to lower kinetic energy of N_2, because the result at 193 K was similar to that at 77 K (Fig. S12, ESI†). Such a phenomenon is rare for microporous MOFs.[18] A similar behavior was recently reported in Kitagawa's microporous Ni-MOF.[18a] It is likely that some nitrogen molecules interact very strongly with the pore windows around the metal centers having polar environment, which prevents other nitrogen molecules from entering the micropores, because the framework has no additional open channels along the *a*- and *b*-axes (Fig. 2).[19]

We have synthesized Cd-containing interdigitated 3-D MOF **1** using a rigid tetrazole ligand. We observed that the solvent molecules in the channels of **1** can be removed without disturbing the framework structure, yielding microporous MOF **1a**. The framework is highly robust, retaining its stability up to 300 °C. **1a** adsorbs H_2 and CO_2, but does not adsorb N_2, not because of size selectivity but because of the different nature of the host–guest interactions.

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‡ CCDC 656711–656713. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b712485f

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19 The possibility of a 'bottle-neck effect' for sorption selectivity can not be ruled out completely. However, a change of the crystal structure such as shifting of layers is unlikely to be the cause of the 'bottle-neck effect', because the 'guest-free' crystal structure **1a** does not show any indications of a layer shift or the formation of a 'bottle-neck' in the channel, and the powder X-ray diffraction pattern of the sample prepared for the sorption study was very similar to that simulated from the single crystal structure. Even though the sample for sorption study was prepared by repeated soaking and desolvation in acetonitrile, and followed by under vacuum it at 100 °C overnight, there might be some residual solvent molecules in the channel that are responsible for reduction of the effective pore size, and subsequent the sorption selectivity.