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Hydroxyl Group Recognition by Hydrogen-Bonding Donor and Acceptor Sites Embedded in a Layered Metal−Organic Framework

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Supporting Information

ABSTRACT: One of the dominant types of interactions between host and guest molecules is hydrogen-bonding, and these interactions can work selectively for a guest molecule. Here, we demonstrate a metal−organic framework (MOF) having both hydrogen-bonding donor and acceptor sites that are quite effective for selective sorption. The MOF selectively interacts with hydroxylic guests in contrast to aprotic hydrogen-bonding guests and shows a sorption selectivity for protic H_2O, MeOH, and EtOH guests. Notably, this is the first compound that shows complete selectivity in adsorption not for MeCN and MeCHO but for EtOH, which has similar fundamental properties except for its proticity.

The rational design and construction of metal−organic frameworks (MOFs) is an active current topic in solid-state chemistry because of the specific properties of these compounds, such as their gas sorption,[1] heterogeneous catalysis,[2] magnetic,[3] and conductive properties.[4] The porous frameworks of designable MOFs have regular pores and internal surfaces, which provide the opportunity for them to interact with various guest molecules via optimally tuned hydrophilic, hydrophobic, and electrostatic interactions.[5] In particular, hydrogen-bonding has emerged as a promising interaction in MOFs and can confer unique properties, such as proton conductivity,[6] dielectricity,[7] and sorption selectivity.[1b,2d,5c,8]

We have focused on the selective sorption properties of MOFs using hydrogen-bonding interactions. Hydrogen bonds work selectively for specific molecules having hydrogen-bonding functional groups such as hydroxyl, carbonyl, and nitrile groups; their configuration depends on the combination of these groups. Well-designed MOFs having accessible hydrogen-bonding sites and a suitable geometry for the target molecule can selectively bind to these hydrogen-bonding guests. Therefore, they have the potential to recognize specific molecules independently of their fundamental properties, such as size, polarity, and boiling point. So far, sorption selectivity in MOFs has been investigated for functional-group recognition using two types of hydrogen bonds,[1b,2d,5c,8] those formed between a hydrogen-bonding donor site on the host and an acceptor site on the guest,[2d,5c] and those formed between an acceptor host and a donor guest.[8] However, MOFs containing either of these types of hydrogen bonds show only a size-dependent selectivity among polar solvents (e.g., MeOH over MeCN, and MeOH over EtOH).[8] It has been suggested that functional-group recognition in hydrogen-bonding MOFs requires a more elaborate design and construction of such MOFs to enhance the hydrogen-bonding interaction specific to the target functional group.

In this work, we have demonstrated hydroxyl group recognition of protic solvents by employing a layered MOF, $(H_2dab)[Zn_2(ox)_3]\cdot 6H_2O$ (ox = oxalate and dab = 1,4-diaminobutane), that has a combination of hydrogen-bonding donor and acceptor sites to provide a suitable geometry for hydroxylic guests. This system is selective toward the hydroxyl group of a guest in contrast to other potential hydrogen-bonding groups, such as carbonyl and nitrile groups, because the hydroxyl group has both hydrogen-bonding donor and acceptor sites that form two types of hydrogen bonds concurrently. This MOF clearly shows complete selectivity for protic guests of H_2O, MeOH, and EtOH over other hydrogen-bonding guests, such as MeCN and MeCHO, which are smaller than EtOH.

Single crystals of $(H_2dab)[Zn_2(ox)_3]\cdot 6H_2O$ (**$1\cdot 6H_2O$**) were hydrothermally synthesized from a mixture of zinc oxide, oxalic acid, and 1,4-diaminobutane with water as the solvent (details are provided in the Supporting Information (SI)). The crystal structure of **$1\cdot 6H_2O$** was determined using single-crystal X-ray diffraction (SCXRD) and is shown in Figure 1. The zinc ions are octahedrally coordinated by three oxalate ions, and the oxalate ligands bridge zinc ions to form an infinite two-dimensional (2-D) layer framework of $[Zn_2(ox)_3]^{2-}{}_{\infty}$. The H_2dab ions are incorporated as counterions in the voids of the honeycomb framework. As a result, the $-NH_3^+$ groups of the H_2dab dications and the O atoms of the ox ions are located between the 2-D layers as hydrogen-bonding donors and acceptors, respectively. From a thermogravimetric analysis, H_2dab ions were found to be stably trapped in the frameworks up to the decomposition temperature of the MOF, 300 °C. Therefore, the H_2dab ions are considered to be a part of the host.

Figure 1c shows the guest arrangement and hydrogen bonds between the host and the water molecules in interlayer space. The positions of hydrogen atoms were refined using SCXRD, and the results show a reasonable geometry (see the SI). These hydrogen bonds were classified into three types, as color-coded in Figure 1c: (1) to the donor site of $-NH_3^+$, (2) to the acceptor site of the oxalate, and (3) to neighboring guest molecules. The average hydrogen-bonding distances of $N-H\cdots O$ and $O-H\cdots O$ are 2.88 and 2.82 Å, respectively, indicating an effective interaction

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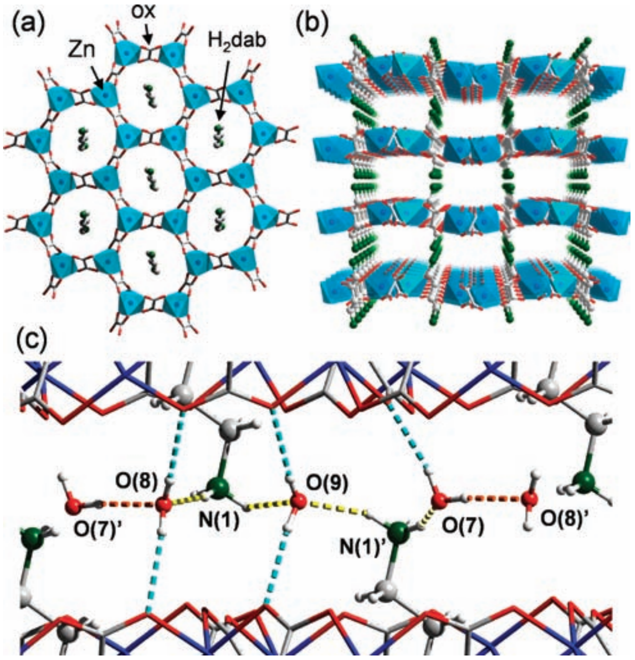


Figure 1. (a) Honeycomb layer framework of $[Zn_2(ox)_3]^{2-}{}_\infty$ and incorporated H_2dab ions. (b) Perspective view along a layer. The guest molecules are omitted. (c) Arrangement of hydrogen bonds around the guest molecules. The yellow, light blue, and brown dotted lines denote the hydrogen bonds to the donor sites of the host, to the acceptor sites of the host, and between the guests, respectively. Red, green, gray, blue, and white correspond to oxygen, nitrogen, carbon, zinc, and hydrogen atoms, respectively.

of the host with the hydroxyl groups, according to a previous report.[9] All the guest molecules concurrently form two types of hydrogen bonds according to (1) and (2) above (denoted by the yellow and light blue dotted lines in Figure 1c, respectively). This result indicates that hydroxyl groups can form both types of hydrogen bonds with this host, and the interlayer space of **1** potentially has the ability to recognize the hydroxylic groups of protic guests by the plural hydrogen bonds.

To examine the selectivity toward hydroxylic guests, we measured adsorption/desorption isotherms of several guests having various sizes, degrees of polarization, and functional groups (Figure 2). The fundamental parameters of the adsorbents are shown in Table 1.[1b,10] This compound showed a high degree of adsorption toward the protic guests H_2O, MeOH, and EtOH. However, no adsorption was observed for the other guests studied: H_2, N_2, MeCN, MeCHO, Me_2CO, Me_2CHOH, PrOH, and BuOH. This result indicates two tendencies for this compound. One is the clear tendency to bind specific guests having hydroxyl groups, independently of molecular size and polarity; the other is that **1** does not adsorb hydroxylic guests that are larger than EtOH. Notably, EtOH is well adsorbed in **1** compared with MeCN and MeCHO, which are smaller polar molecules. It should be also noted that MeCN and EtOH have similar boiling points (MeCN bp = 81.6 °C, EtOH bp = 78.3 °C). To the best of our knowledge, this is the first compound that shows complete selectivity in its adsorption of EtOH over MeCN and MeCHO. These results show the ability for hydroxyl group recognition in this MOF, and this can be explained by the ability of this MOF to form multiple hydrogen bonds with the hydroxyl groups. Thus, protic polar solvents can be successfully separated from aprotic solvents by their proticity.

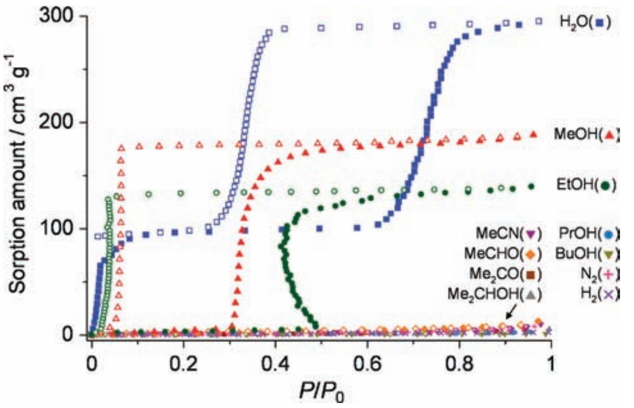
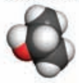


Figure 2. Sorption isotherms of **1** for several guest molecules. The measurements were performed at 298 K, except for H_2 (77 K), N_2 (77 K), and MeCHO (288 K).

This compound showed sharp increases in its sorption isotherms for H_2O, MeOH, and EtOH, with large hysteresis. In the case of H_2O, a two-step adsorption/desorption isotherm was observed that had a hysteresis loop in each step. The amounts of adsorbent in these steps were 99 and 291 cm^3 g^{-1}, which correspond to 2.1 and 6.3 water molecules per formula, respectively, suggesting the existence of stoichiometric dihydrate and hexahydrate phases. This is consistent with the results of our SCXRD analysis, which indicated that **1** could adsorb six water molecules in its interlayer. We also confirmed the structure of **$1\cdot 2H_2O$** from our SCXRD measurements performed after air drying of **$1 \cdot 6H_2O$**. As shown in Figure S1, two water molecules were also bound by the hydrogen-bonding donor and acceptor sites of the host, and this may contribute to the adsorption observed in the low-pressure region. In addition, the $-NH_3^+$ groups of the host formed hydrogen bonds with the ox ions of the neighboring layers in **$1\cdot 2H_2O$**, resulting in a shrinking of the periodic distance between the layers of **$1\cdot 2H_2O$** (6.34 Å) compared to **$1\cdot 6H_2O$** (7.45 Å). It is suggested that there is competition between the two different trends. The first is the shrinking of interlayer spacing on the formation of hydrogen bonds between the hosts, and this also contributes to the electrostatic stabilization of the framework. The second trend is the expansion induced by the inclusion of the hydroxylic guests and the formation of hydrogen bonds to them. From a void analysis using PLATON software package,[11] no accessible pore was found in the host in **$1\cdot 2H_2O$**, whereas **$1\cdot 6H_2O$** showed a void volume of 22.1% per unit volume, owing to a narrowing of the interlayer space.

In the case of MeOH and EtOH, single-step adsorption profiles with a sharp rise were observed, and the amounts of MeOH (186 cm^3 g^{-1}) and EtOH (139 cm^3 g^{-1}) adsorbed corresponded to 4.0 and 3.0 molecules per formula, respectively. Each sample with these guests showed sharp X-ray powder diffraction (XRPD) patterns that were different from those of the other samples, indicating the existence of a separate crystalline phase of **$1\cdot$4MeOH** and **$1\cdot$3EtOH**. We confirmed the crystal structure of **$1\cdot$4MeOH** from a Rietveld analysis (see the SI), which indicates that the MeOH molecules were adsorbed in the interlayer and triggered an expansion of the layers accompanied by the formation of hydrogen bonds with the ox and H_2dab ions. Although the XRPD pattern of **$1\cdot$3EtOH** was

Table 1. Fundamental Parameters of the Adsorbents[a]

	H_2O	H_2	N_2	MeOH	MeCN	MeCHO	EtOH	Me_2CO	Me_2CHOH	PrOH	BrOH
											
Kinetic diameter (Å)	2.64–2.9	2.827–2.89	3.64–3.80	3.626–4.0	4.3	4.5	4.3–4.53	4.6–4.7	4.7	4.7	5.0
Dipole moment (D)	1.86	0	0	1.69	3.81	2.64	1.71	2.82	1.56	1.49	1.52
Protisity	P	A	A	P	A	A	P	A	P	P	P

[a] Dipole moments were estimated using DFT calculations, except for water. "P" and "A" in proticity indicate "protic" and "aprotic", respectively.

similar to that of **1·4MeOH**, it was not well fitted using the crystal data of **1·4MeOH**. This may be because the odd number of EtOH molecules gives a different unit cell for **1·3EtOH**.

Anhydrate **1** did not show any adsorption behavior toward small gaseous molecules, such as H_2 and N_2, and the structure of **1** was assumed to be nonporous. From the XRPD data, all the phases under each adsorption condition were found to be crystalline. A Pawley fitting of the XRPD data (see the SI) indicates that the unit cell of **1** shrank compared to that of **1·2H$_2$O**, whose framework does not have enough space to allow adsorption to occur, and the space between the layers in **1** is assumed to be too narrow to adsorb any guests. Thus, the absorption behavior of this MOF can be recognized as a gate-open type, with a closed–open structural transformation that enhances selectivity by prohibiting the adsorption of nontarget molecules.[12] Large protic guests such as propanol and butanol did not transform **1** into the open form and so were not adsorbed. The loss of electrostatic energy derived from the expansion process is considered to exceed the energy gain from the formation of hydrogen bonds to the guests. Both a large molecular size and a small number of hydroxyl groups per molecular volume are assumed to be unfavorable to the adsorption process in this MOF.

In summary, we have demonstrated that a layered MOF having hydrogen-bonding donor and acceptor sites in its interlayer space clearly shows a sorption selectivity for hydroxyl guest molecules. This MOF is an important example of a hydrogen-bonding MOF showing an ability for hydroxyl group recognition. Notably, this is the first compound to indicate a complete selectivity in its adsorption of EtOH over MeCN and MeCHO.

■ ASSOCIATED CONTENT

S Supporting Information. Synthetic procedure, physical measurements, and XRD measurements; X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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