Selective guest sorption in an interdigitated porous framework with hydrophobic pore surfaces†

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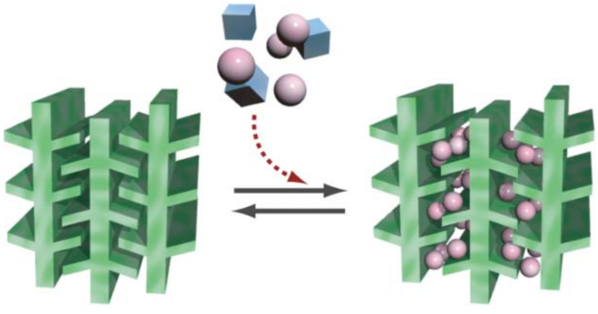
An interdigitated porous coordination polymer with hydrophobic pore surface shows size and affinity dependent selective gas sorption properties accompanying the reversible structure transformation.

One of the fronts of materials chemistry is the synthesis of crystalline compounds known as porous coordination polymers (PCPs) or metal–organic frameworks (MOFs) built from organic ligands and metal ions.[1] These compounds are tailorable, low-density solids with promise for use in gas storage, molecular sensing, and other materials applications. Systematic design and creation of robust PCPs have been developed by using a variety of coordination modes of metal ions and organic linkers, and demonstrated that its three-dimensional porous system can be functionalized with organic moieties and that its pore size can be controllable in the nanometer scale.[2]

In recent years, PCPs with flexible (or dynamic) structure have been highlighted as a new class of adsorbents.[3,4] Some flexible PCPs show unusual adsorption properties that are not observed in robust frameworks or other conventional porous solids.[5,6] The structural flexibility has also been observed in inorganic frameworks; however, the changes are not so drastic as those of PCPs. The flexibility is associated with weaker interactions, including coordination bonds, H-bonds, π-electron stacking and van der Waals interactions.[4,7,8] Adsorption properties of flexible PCPs are heavily dependent on both the structural transition mechanism and pore functionality, and therefore, such a flexible framework with specific pore environment can be suitable for selective sorption. We have realized a flexible PCP based on interdigitation with π-stacking, useful to construct a porous system with selective gas sorption *via* dynamic structure transformation (Scheme 1).[6] In this report, we employ an interdigitated Zn^{2+} compound (CID: coordination polymer with interdigitated structure) with hydrophobic pore surfaces by employing the carboxylate-bridged dinuclear metal structure, and elucidated the gas selectivity based on the pore shape and hydrophobicity.

A porous coordination polymer of $\{[Zn_2(ip)_2(bpy)_2]\cdot DMF\}_n$ (CID-1⊃DMF), was prepared from $Zn(NO_3)_2\cdot 6H_2O$, isophthalic acid (Hip) and 4,4′-bipyridine (bpy) in DMF solution.[9] Isomorphous salts with other guest molecules or other transition metals have been reported in recent years.[10,11] In compound CID-1⊃DMF, each Zn^{2+} atom is in a distorted octahedral geometry, being coordinated by two bpy ligands at the axial positions, two oxygen atoms from the chelate carboxylate end of the ip ligand and two oxygen atoms from the ip in the equatorial plane.‡ The Zn^{2+} and ip give rise to 1-D double-chain structures along the *a* axis and the further linkages of these chains *via* bpy ligands in the axial positions generate an infinite 2-D neutral layer (Fig. 1(a), (b)). Although the distance of 3.8 Å between the planes of the nearest-neighbor ip ligands is too large to form π-stacking interactions, the motifs are mutually interdigitated to create a stable 3D assembled framework (Fig. 1(c)). The void spaces are separated by bpy ligands, and zero-dimensional pores, which are isolated from the others and scattered in the solid, are created with a cross section of about 5 × 6 Å^2 (Fig. 2). The walls of these cavities consist of faces and edges of aromatic rings of bpy and ip to form a hydrophobic environment and one DMF molecule is trapped per cavity in this framework. The total potential solvent area of this cavity of CID-1⊃DMF (probe molecule radius = 1.20 Å) is 107.3 Å^3 and the void volume is 12.2% of the total crystal volume, as estimated by using PLATON.[12] Thermogravimetric analysis of CID-1⊃DMF shows the release of just one DMF molecule within the cavity with increasing temperature up to 130 °C to give the guest-free anhydrous phase. No obvious further weight loss was observed between 130 and 260 °C, that is, the guest-free phase is stable and guest evacuation occurs accompanying the structural transition from CID-1⊃DMF to CID-1. From the comparison of powder X-ray diffraction patterns between CID-1⊃DMF and CID-1 in Fig. 3, several peaks of CID-1 shift to higher 2θ values suggesting that the guest-free phase closely packs after the degas treatment.

The adsorption isotherm of CO_2 at 195 K on CID-1 displays a steep rise at the low relative pressure region and the isotherm can be categorized as Type I, indicative of a typical physisorption



Scheme 1 Representation of selective guest sorption of a coordination polymer with interdigitated structure (CID).

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† Electronic supplementary information (ESI) available: Descriptions of synthesis and crystal structure, thermogravimetric analysis, solid-state ^{13}C NMR, adsorption isotherms and rate analyses. See DOI: 10.1039/b703502k

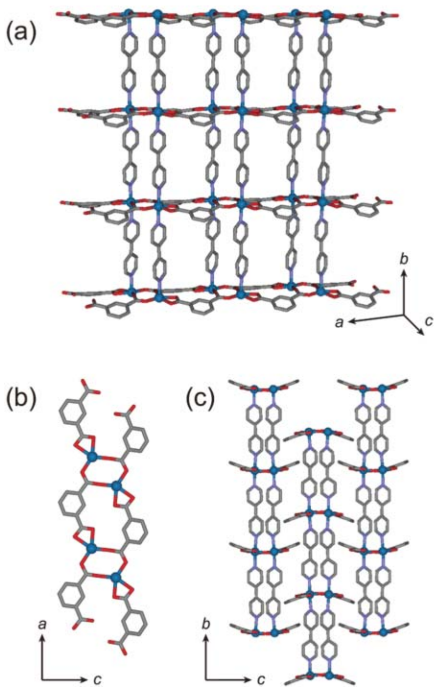

Fig. 1 (a) 2D layer structure, (b) bonding mode in the Zn–O plane and (c) 3D assembled structure of CID-1$\supset$DMF. Gray, purple, red, blue are C, N, O and Zn, respectively; H atoms are omitted.

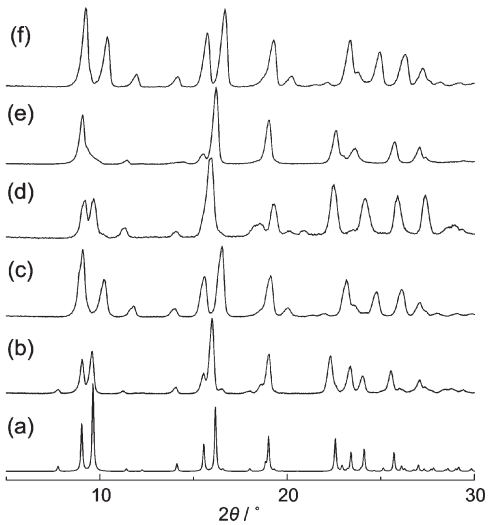

Fig. 3 XRPD patterns of (a) simulated CID-1$\supset$DMF from single-crystal analysis and experimental (b) CID-1$\supset$DMF (as synthesized), (c) CID-1 (d) CID-1$\supset$2MeOH, (e) CID-1$\supset$EtOH, (f) CID-1 with benzene vapor.

process of a microporous compound.[13] The saturation adsorbed amount of CO_2, 58 cm^3 (at STP) g^{-1}, corresponds to two CO_2 molecules trapped in the interstitial lattice cavity. This amount is appropriate by considering that the relationship between the volumes of the cavity and CO_2 molecule.[14] The specific surface area, determined by the Brunauer–Emmett–Teller (BET) method using the adsorption branches of the CO_2 isotherms, is 300 m^2 g^{-1}. On the other hand, CID-1 was found to be essentially non-porous to nitrogen and oxygen at 77 K, hence CO_2 was used to determine the BET surface area. This non-porosity toward N_2 and O_2 under these conditions is not uncommon in PCP systems prepared from 4,4′-bpy with pore sizes of less than 10 Å.[15,16]

We have examined the adsorption properties of several solvents at 298 K and results are shown in Fig. 4. These isotherms show good selectivity on the shape of guest molecules. In the case of ethanol (EtOH) as a guest, the adsorption profile is also Type I and the saturated amount of adsorption clearly shows a stoichiometry with just one guest molecule per cavity. Therefore the cavity incorporates just one EtOH molecule in a commensurate fashion with the CID-1 to CID-1$\supset$EtOH bulk phase transition.[10,17] On the other hand, by using methanol (MeOH) as a guest, the adsorption isotherm shows a sharp uptake with stepwise profile at $P/P_0 \leqslant 0.1$ region and the saturated amount is two MeOH per unit pore. The open circles in Fig. 5 represent the adsorption isotherm of MeOH at the low pressure region. The adsorption amount of the first step is about 29 mL g^{-1} (P = 8.8 mmHg) which is consistent with just one MeOH per unit pore. This stepwise isotherm suggests that the mechanism of methanol accommodation would be as follows; initially each cavity of CID-1 incorporates one MeOH molecule (CID-1$\supset$MeOH) and then, a second MeOH is introduced to each pore to complete the saturated adsorption structure of CID-1$\supset$2MeOH. Because of its shape-selective sorption abilities, this compound hardly adsorbs

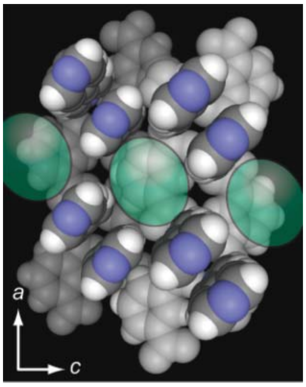

Fig. 2 Cross section of pore surfaces of CID-1$\supset$DMF. Dicarboxylates within the 2D layers are represented in light/dark grey and N, C, H are blue, grey, white, respectively. Cavities are highlighted in green.

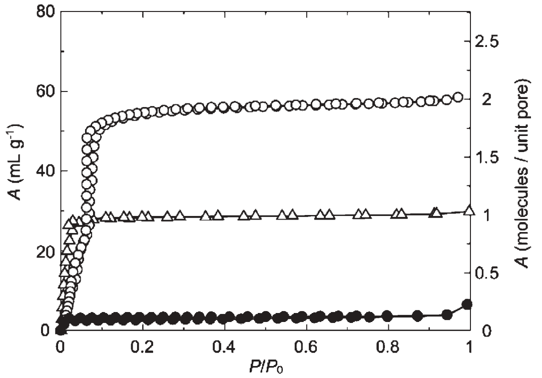

Fig. 4 (a) Adsorption and desorption isotherms of methanol (open circles), ethanol (open triangles) and benzene (closed circles) for CID-1 at 298 K.

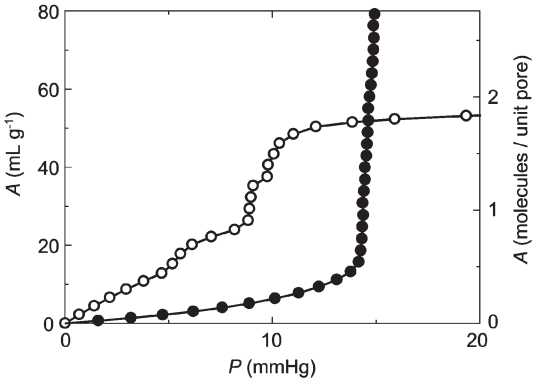

Fig. 5 Adsorption isotherms of methanol (open circles) and water (closed circles) at 298 K in the range from 0 to 20 mmHg.

benzene molecules (6.63 × 7.34 × 3.28 Å^3)[14] whose shape does not fit the host framework (Fig. 4, closed circles).

These guest-responsive sorption properties accompanied with structural transition are proved by the XRPD patterns (Fig. 3). The powder patterns for CID-1$\supset$EtOH and CID-1$\supset$2MeOH show almost identical structure to CID-1$\supset$DMF (as synthesized). Differences of peak intensity at about $2\theta = 10°$ are because of the guest species and flexibility of ip ligands that are easily disordered. CID-1 shows good affinity for these alcohol molecules and affords stable guest-inclusion phases in a commensurate fashion without any stresses. Meanwhile, as expected, the XRPD pattern for CID-1 exposed to benzene vapour does not change at all, because of low adsorption property at 298 K (Fig. 3(f)).

Interestingly, in the case of water as a guest, the sorption isotherm at 298 K does not show adsorption uptake until P = 14 mmHg (P/P_0 = 0.59 at 298 K) despite the small size of the guest, and then shows an abrupt rise and reaches the saturation point of approximately 160 mL g^{-1} with a large hysteresis loop (Fig. 5, closed circles). The XRPD pattern after the water adsorption/desorption measurement is identical to original CID-1, suggesting that no collapse occurs during the water accommodation.[18] This water isotherm can be classified as Type V which has been hardly observed in other PCP compounds,[13] which is indicative of weak adsorbent–adsorbate interactions as a consequence of the hydrophobic pore surfaces of CID-1.[19] As a result, in the pressure range from zero to 14 mmHg, we can observe an obvious selectivity between MeOH and H_2O. Thus CID-1 shows not only the size-selectivity described above, but also hydrophobicity-dependent selectivity with the structural transformation.

We also analyzed the adsorption phenomena from the kinetic point of view. In this interdigitated structure, two kinds of barriers can be considered; one is diffusion through the windows between two cavities and the other is along the cavities.[8] In fact, the obtained kinetic profiles for both MeOH and H_2O adsorption on CID-1 follow the double exponential model with good accuracy. This suggests that though the hydrophobicity of CID-1 interferes with the water accommodation below P = 14 mmHg, once the adsorption occurs, the mechanism of the two kinetic processes is identical to that of other adsorbents.

In this report, we have demonstrated the size and affinity-based selective sorption properties of interdigitated coordination polymer (CID) with a hydrophobic porous framework *via* dynamic structural transformation. This result suggests to us that the guest-driven dynamics of PCP framework with characteristic pore surfaces would provide a new type of selectivity toward applications such as sensor systems or purification.

Notes and references

‡ CCDC 639850. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b703502k

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