Coordination Polymers

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Solid Solutions of Soft Porous Coordination Polymers: Fine-Tuning of Gas Adsorption Properties

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Control of the physical and chemical properties of porous materials has been an ongoing challenge for the optimization of functions, such as gas storage, separation, and catalysis. For example, a high surface area is important for large-volume gas uptake, and the control of pore shape is also significant for molecular separation.[1] These requirements are also valid for porous coordination polymers (PCPs) or metal–organic frameworks (MOFs), which consist of metal ions and organic linkers.[2] This class of adsorbent has received attention because of its structural versatility and physical properties, such as magnetism and redox activity.[3] Among the PCP compounds, flexible frameworks have been identified as a unique type of porous material because of their guest-responsive transformations.[4] This structural transformation is often directly related to the functionality of these frameworks; gas recognition separation or slow drug release are good examples in this respect.[5]

The flexibility of the network must be modulated to precisely control these functions and to tailor the network performance, and much effort has been expended in creating flexible compounds.[6] However, there have been few reports on the rational incorporation of flexibility in the known PCP compounds as their synthesis is difficult.[7] Herein, we describe the preparation of ligand-based solid solutions of flexible PCPs and our attempts to overcome difficulties in the precise flexibility control and resulting gas sorption properties. A few approaches toward ligand-based solid solutions of robust metal–organic framework have been reported,[8] although corresponding structural information and control of their adsorptive functions has not been observed. We have synthesized two distinct interdigitated frameworks that contain different organic ligands, and have created a series of solid solutions based on these frameworks. These compounds exhibited a range of flexible adsorption properties, and their bimodal properties enabled them to show an improved performance compared with the two pure compounds CID-5 and CID-6 in the separation of a CO_2/CH_4 mixture.

The two flexible compounds with an interdigitation motif of 2D layers, $[\{Zn(5\text{-}NO_2\text{-}ip)(bpy)\}(0.5DMF{\cdot}0.5MeOH)]_n$ (CID-5⊃G; 5-NO_2-ip = 5-nitroisophthalate, bpy = 4,4′-bipyridyl, and CID = coordination polymer with an interdigitated structure), and $[\{Zn(5\text{-}MeO\text{-}ip)(bpy)\}(0.5\,DMF{\cdot}0.5\,MeOH)]_n$ (CID-6⊃G; 5-MeO-ip = 5-methoxyisophthalate), were prepared from $Zn(NO_3)_2{\cdot}6\,H_2O$ and either of the ligands in a 1:1 v/v DMF/MeOH mixture. The crystal structures are shown in Figure 1. For both compounds, two carboxylate groups coordinate to Zn^{2+} ions to form eight-membered rings, and the bpy groups coordinate to the axial position of the Zn^{2+} ions to create the 2D layered structure. The layers are assembled in an interdigitated fashion with micropores formed within the structure. Both frameworks can be

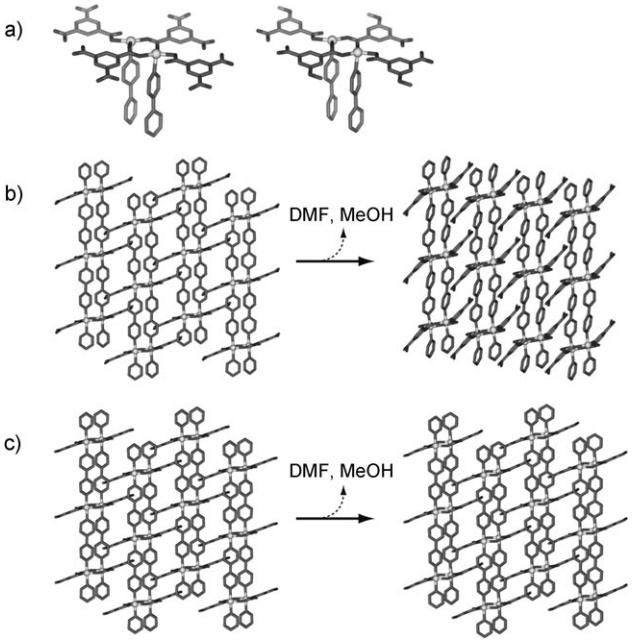

Figure 1. Partial crystal structures of a) CID-5⊃G (left) and CID-6⊃G (right), and the assembled structures of b) CID-5⊃G and CID-5 and c) CID-6⊃G and CID-6.

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classified as members of a previously reported series of flexible PCPs.[5c,9] Because the size of the substituent groups (NO_2 and MeO) in the dicarboxylates is comparable, the unit cell parameters obtained for CID-5⊃G and CID-6⊃G are not markedly different. The thermogravimetric analysis (TGA) profiles of these samples indicate that DMF and MeOH can be released on incorporation of a guest to afford a stable guest-free framework that remains intact up to 300 °C. The weight loss of each compound was 10.8 and 11.5 wt %, respectively, which is reasonable when their crystal structures are taken into account.

We investigated the crystal structures of the guest-free CID-5 and CID-6 forms to obtain direct information on their contraction behavior. Although the cell parameters of the as-synthesized compounds are similar, the guest-free structures were different after degassing. As the guest molecule exits, the flatness of the Zn^{2+} eight-membered rings is disturbed because of the flexibility of this core module, and consequently, a reorientation of the interdigitation for mutual packing occurs (Figure 1b). There is no guest-accessible void volume in CID-5, thus a "porous" to "nonporous" transformation occurs. CID-6⊃G shows contrasting behavior. Even after complete degassing of the guest molecules, the crystal structure of CID-6 shows only a small difference when compared to the as-synthesized structure (Figure 1c), and the change in void volume decreases from 15.8 % to 14.6 %. The Zn^{2+} eight-membered ring in CID-6 does not show a large distortion and therefore a small structural change. The characteristics of the substituent group, such as electronic properties or shape are the cause of the different behavior of CID-6.

Based on the information obtained for CID-5⊃G and CID-6⊃G, we prepared ligand-based solid solutions. Careful mixing of $H_2$5-NO_2-ip and $H_2$5-MeO-ip with $Zn(NO_3)_2{\cdot}6H_2O$ in molar ratios of 1:1:2 in a 1:1 v/v DMF/MeOH solution resulted in a white powder containing 48 % of 5-NO_2-ip and 52 % of 5-MeO-ip, as confirmed by elemental analysis and ^{1}H NMR spectroscopy after degradation of the powder with H_2SO_4 in DMSO (the product $[\{Zn(5\text{-}NO_2\text{-}ip)_{1-x}(5\text{-}MeO\text{-}ip)_x(bpy)\}(DMF{\cdot}MeOH)]_n$ is denoted as CID-5/6⊃G (x = 0.52), where x is the content of 5-MeO-ip ligand in the sample) To exclude the possibility that the powder was just the mixture of pure microcrystals of CID-5 and CID-6, X-ray powder diffraction data was obtained (Figure 2). The resulting pattern was different from either of the pure compounds, in particular, the peaks that occur at around $2\theta = 7.2°$ and $2\theta = 8°$ represent an original phase when compared with the peak positions of CID-5⊃G and CID-6⊃G. To find out if the powder pattern was representative of a single crystalline phase, we prepared a single crystal of CID-5/6⊃G ($x = 0.52$), and succeeded in solving its structure (Figure 3). Two types of ligand, which are disordered with a dihedral angle of 38.2°, were observed around the Zn^{2+} centers. The mixed-ligand Zn^{2+} eight-membered rings are connected by bpy ligands to form the 2D layers, thus resulting in the formation of an interdigitated framework. The unit-cell parameters and volume obtained lie between the values obtained for CID-5⊃G and CID-6⊃G. This result is reasonable if we consider that both the 5-NO_2-ip and 5-MeO-ip ligands are evenly dispersed and form a single-phase crystal. The simulated powder X-ray pattern of CID-5/6⊃G ($x = 0.52$) generated from the single crystal structure and the experimental pattern (Figure 2) are in good agreement, and we concluded that the obtained powder sample could be regarded as a ligand-based solid solution of CID-5⊃G and CID-6⊃G.[10]

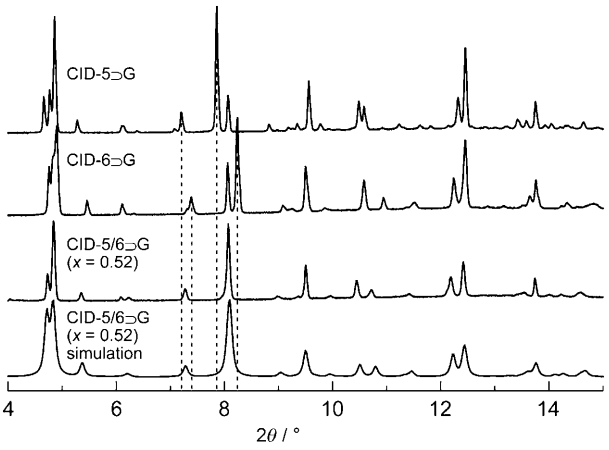

Figure 2. XRPD patterns of CID-5⊃G, CID-6⊃G, and CID-5/6⊃G ($x = 0.52$), and simulated pattern of CID-5/6⊃G ($x = 0.52$).

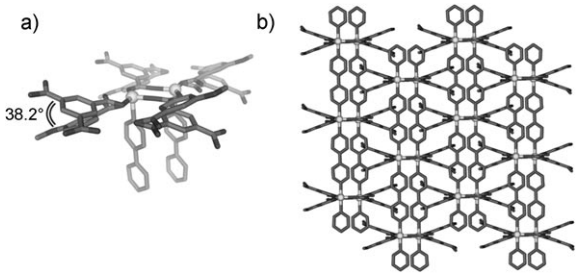

Figure 3. a) Partial crystal structure (around the Zn^{2+} center) and b) interdigitated structure of the solid solution CID-5/6⊃G ($x = 0.52$).

We subsequently synthesized a series of CID-5/6⊃G solid solutions with different ratios of 5-NO_2-ip and 5-MeO-ip in the range $0.06 < x < 0.92$. We observed that the as-synthesized compounds had unique XRPD patterns, not all of which are a mixture of the two types of crystal, as shown in Figure 4. Determination of the content of each ligand in the compounds was carried out using ^{1}H NMR spectroscopy and elemental analysis. The actual 5-MeO-ip content for all the compounds was slightly higher than the theoretical value calculated from the mixed ligand ratio. From the XRPD patterns, the crystal structure gradually shifted to the pattern of CID-6⊃G as the value of x increased. For these compounds, we determined the cell parameters using the LeBail fitting procedure, and these values also gradually shifted from those of CID-5⊃G to CID-6⊃G. The thermal stability of the solid solutions determined from the TGA data was checked, and the profiles were similar to other CID frameworks, thus indicating that the solid solutions can be used as flexible porous coordination polymers, similar to pure CID-5⊃G and CID-6⊃G. The key for the successful preparation of solid

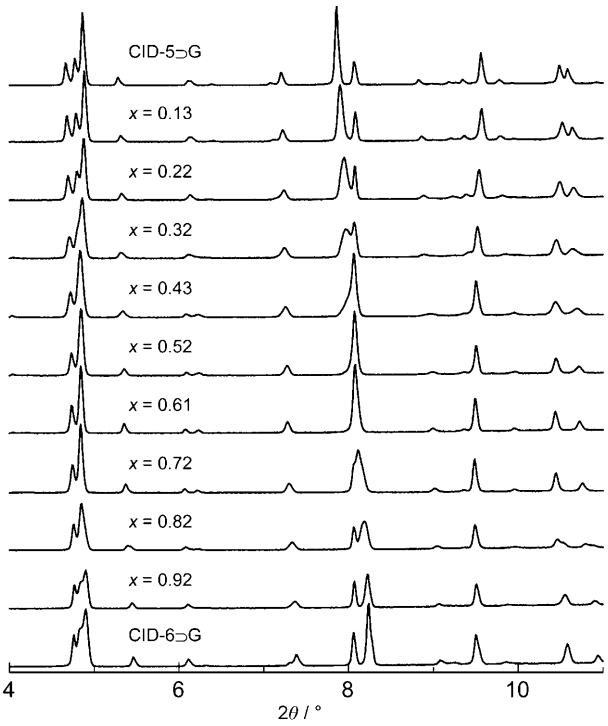

Figure 4. XRPD patterns of CID-5⊃G, CID-6⊃G, and solid solutions of CID-5/6⊃G ($x = 0.13$–0.92).

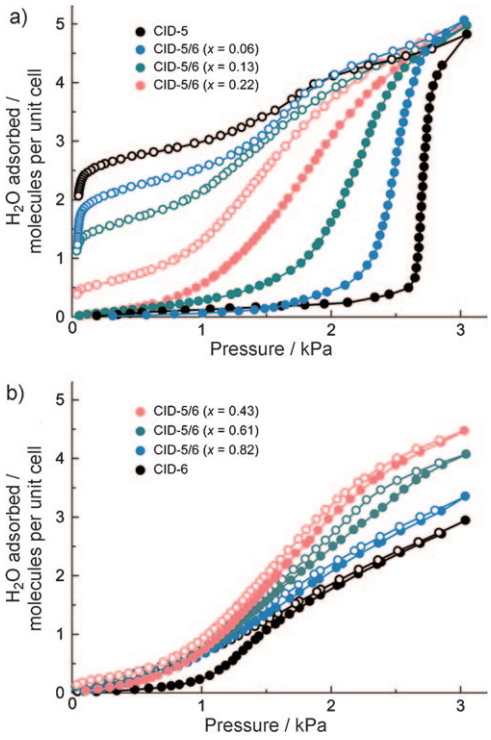

Figure 5. Adsorption isotherms (closed circles) and desorption isotherms (open circles) of H_2O at 298 K for: a) CID-5 and solid solution CID-5/6 ($x = 0.06$–0.22) and b) CID-5/6 ($x = 0.43$–0.82) and CID-6.

solutions in this system is that the unit cell parameters of CID-5⊃G and CID-6⊃G are not markedly different, and there would be little stress in the crystal, even if the two types of ligand are mixed with arbitrary ratios in the coordination networks.

We also measured the XRPD patterns of these samples after degassing (CID-5/6). Each pattern showed some changes, which were attributed to the flexibility, and the patterns of CID-5/6 showed a gradual shift from CID-5 to CID-6 as the value x increased, thus suggesting that each solid solution has unique cell parameters even after a degassing procedure. However, we were not successful in determining the unit-cell parameters of these degassed solid solutions.

We investigated the gas sorption properties of these compounds and, in particular, control of the "gate-opening" type sorption behavior, in which a sudden adsorption occurs at a given pressure point (not zero).[11] This behavior is observed when the closed phase of a flexible PCP changes to the open phase as a guest molecule is accommodated. The gate-opening pressure P_{go} is often sensitive to the affinity of the framework to the gas molecule, and is regarded as an important factor for gas separation, especially for gases that have similar properties.[12] As CID-5 is nonporous, it exhibits a gate-opening sorption behavior for H_2O and CO_2 molecules, as shown in Figure 5 and 6, respectively. The value of P_{go} is 2.48 kPa for H_2O at 298 K and 1.32 kPa for CO_2 at 195 K.[13] On the other hand, the porous CID-6 does not show a gate-opening-type behavior, but shows a linear uptake for H_2O and typical Type I isotherms for CO_2.[14] We tried to produce various gate-opening isotherms with different values of P_{go} by making use of the complementary sorption behaviors of CID-5 and CID-6 in their solid solutions. In the case of CID-5, the intrusion of H_2O occurred at a pressure of $P_{go} = 2.48$ kPa, and desorption occurred at a low pressure. We observed a large hysteresis in this process, which is denoted as a Type V profile using the IUPAC classification (Figure 5a).[14] The total uptake at 3 kPa was just five H_2O molecules per unit pore; this value suggests the formation of water clusters in the cavities.[15] In contrast, the data from CID-6 shown in Figure 5b shows a gradual uptake from low pressures without a large hysteresis curve. The total uptake was three H_2O molecules per unit pore, which is lower than that of CID-5. Meanwhile, the H_2O isotherms of the solid solutions of CID-5/6 represent unique profiles. For CID-5/6 ($x = 0.06$), whose structure is close to that of CID-5, gate-opening adsorption takes place at 2.42 kPa, which is lower than CID-5, and the width of the hysteresis was narrower than that of CID-5. The uptake was the same as CID-5; this result suggests that CID-5/6 ($x = 0.06$) not only has similar sorption properties to CID-5 but also possesses some characteristics of CID-6. The shift of P_{go} to lower values is attributed to an increase in the framework's affinity for H_2O because of the presence of a small amount of 5-MeO-ip ligands. The narrowing of the hysteresis width also arises from the decrease in the framework cooperativity and a decrease in the activation energy for the structural transformation from the degassed state to the adsorbed state. As the value of x increased, we observed a gradual shift in P_{go}, and the gradient of the profile also decreased, thus resulting in a narrowing of the hysteresis width. In the range $0.06 < x < 0.22$ (Figure 5a), the total

uptake was five molecules per unit pore, and for these solid solutions, this water cluster would stabilize the overall framework. At higher values of x (Figure 5b), the sorption profiles became more gentle with a decrease in the total uptake, which finally reached the value of CID-6.

The control of P_{go} is important for gas molecules because we have to deal with a range of relative pressures of the target gas from gas mixtures requiring separation. The sorption isotherms of CO_2 at 195 K were measured for these compounds (Figure 6). As observed for H_2O, CID-5 showed a

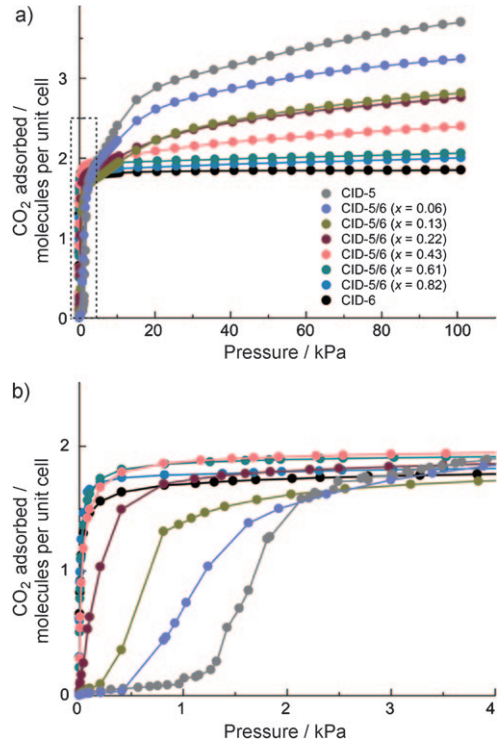

Figure 6. Adsorption isotherms of CO_2 at 195 K for CID-5, CID-6, and their solid solution CID-5/6 ($x = 0.06$–0.82) in the range a) $P = 0$–100 kPa and b) expansion of the range $P = 0$–4 kPa.

clear gate-opening-type uptake, although the value of P_{go} occurred at a lower pressure (1.60 kPa) and CID-6 showed a common Type I isotherm (Figure 6b). For CID-5/6, there was also a gradual shift in the gate-opening pressure and the gradient of the uptake was in the range $0.06 < x < 0.43$. The total amount adsorbed was also dependent on the value of x: as x increased, the total amount decreased. CID-5/6 with $x >$ 0.61 showed almost the same isotherms as CID-6. The results of the adsorption experiments suggest that solid solutions of CID-5/6 exhibit a range of gate-opening profiles based on the complementary sorption properties of CID-5 and CID-6.

A target for PCP solid solutions is to incorporate the advantageous properties of both compounds in the overall adsorption functionality. The present system provides one example in this respect: the improvement of gas separation properties. The selective adsorption uptake of CO_2 from a CO_2/CH_4 mixture ($CO_2/CH_4 = 1{:}1$ by volume) under the conditions of $P = 101.3$ kPa and $T = 273$ K was investigated (Figure 7). CID-5 has a closed-pore system, and so only CO_2 could be captured with negligible uptake (2.5 mL g^{-1}). On the other hand, CID-6, which has an open-pore system, can adsorb more CO_2 (40 mL g^{-1}), but it also simultaneously

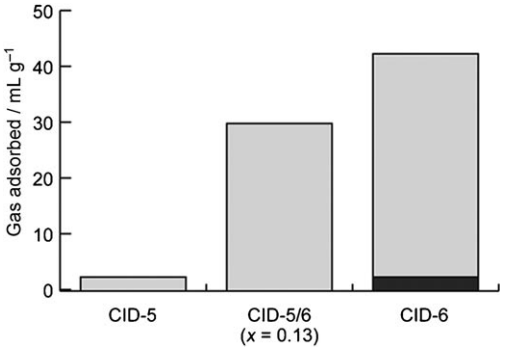

Figure 7. Total uptake of CO_2 (gray) and CH_4 (black) for CID-5, CID-5/6 ($x = 0.13$), and CID-6 from a CO_2/CH_4 (1:1) gas mixture at a total pressure of 101.3 kPa at 273 K.

adsorbs some CH_4 (2 mL g^{-1}), thus resulting in an unsatisfactory separation for each compound. We utilized a solid solution of CID-5/6 ($x = 0.13$) to take advantage of these properties. CID-5/6 ($x = 0.13$) retained the advantages of CID-6 and adsorbed 30 mL g^{-1} of CO_2. Moreover, CID-5/6 ($x = 0.13$) also had the characteristics of CID-5, and so did not adsorb CH_4 at all. The overall selectivity towards CO_2/CH_4 was clearly improved compared with that of pure CID-5 and CID-6. The low concentration of the 5-MeO-ip ligand in the solid solution optimized the selective accommodation of CO_2 into the pores.

In conclusion, we have synthesized two interdigitated frameworks and a series of their ligand-based solid solutions for the control of their adsorption isotherms. The crystallographic properties of the solid solutions were dependent on the ligand ratio; the gate-opening pressure P_{go}, the gradient of the sorption profile, and the total gas uptake were dependent on the inherent framework flexibility. Optimization of the gas-separation performance from a mixture of CO_2 and CH_4 using the solid solutions was demonstrated. This approach provides potential for the design of functional porous coordination polymers or metal–organic frameworks, even though these systems have a flexible nature.

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