Microporous Materials

Expanding and Shrinking Porous Modulation Based on Pillared-Layer Coordination Polymers Showing Selective Guest Adsorption**

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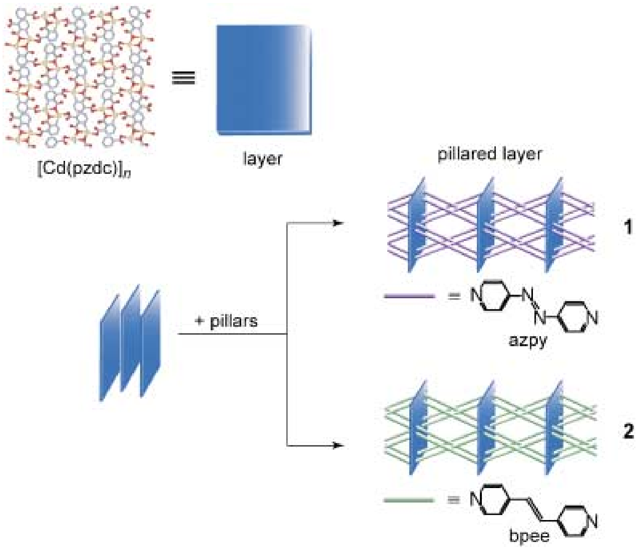
The design and construction of coordination polymers are of great interest due to their intriguing new structural topologies and potential application as functional materials.[1–5] Their microporous frameworks have a large surface area, which is relevant for storage of large quantities of natural gas or hydrogen, and this is becoming a new field of research.[6–12] In addition, it has been shown that these frameworks display unique dynamic behavior, that is, crystal-to-crystal or crystal-to-amorphous transformations, which are characteristic of metal–organic motifs. Therefore, their selective-sorption profiles are fascinating,[13–18] and pave the way for practical applications such as specific sensing and separation of gas molecules. Recently, several coordination polymers that exhibit selective gas adsorption were reported; $\{Er_2(PDA)_3\}_n$ (PDA = $OOCCH_2PhCH_2COO$) selectively adsorbs CO_2 but not Ar or N_2,[10] while $\{Mn(HCO_2)_2\}_n$ adsorbs H_2 and CO_2 but not N_2.[12] This selectivity is attributed to the fact that the apertures of the channels are smaller than the molecules attempting pass through them.

For the rational construction of porous frameworks with controlled channel dimensions, the “pillared-layer” motif has so far been employed, because simple modification of the pillars can control not only the channel size but also chemical functionality.[19–21] Here, we selected $\{Cd(pzdc)\}_n$ (pzdc = pyrazine-2,3-dicarboxylate) as a layer, and py-N=N-py (azpy)/py-CH=CH-py (bpee; py is pyridine) as pillar ligands, and obtained similar prototype structures, $\{[Cd(pzdc)(azpy)]\cdot 2\,H_2O\}_n$ (**1**) and $\{[Cd(pzdc)(bpee)]\cdot 1.5\,H_2O\}_n$ (**2**; Scheme 1). Despite the slight difference in the spacer groups (-N=N-/-CH=CH-) found between azpy and bpee, the observed adsorption/desorption behavior of **1** and **2** were distinct. We show them in detail below.



Scheme 1. Simplified representation of the network topology of complex **1** and **2**. The second carboxy group on each pzdc ligand has been omitted for clarity.

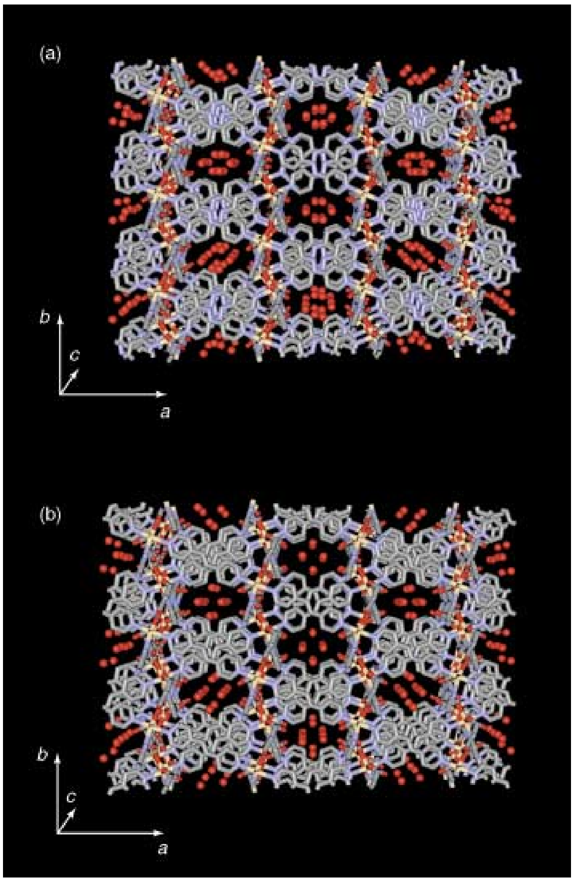


Figure 1. Crystal structures of a) $\{[Cd(pzdc)(azpy)]\cdot 2\,H_2O\}_n$, **1**, and b) $\{[Cd(pzdc)(bpee)]\cdot 1.5\,H_2O\}_n$, **2**, along the *c* axis. Hydrogen atoms are omitted for clarity.

The crystal structures of **1** and **2** were determined by X-ray crystallography as shown in Figure 1. In **1**, each Cd^{II} center is hexacoordinated, residing in a distorted octahedral environment, surrounded by three oxygen atoms, one nitrogen atom in the equatorial position from one of possibly three

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different pzdc ligand and two nitrogen atoms from the two azpy ligands ligated in axial positions to give a CdO_3N_3 chromophore. Each pzdc ligand is coordinated to three Cd^{II} centers through three oxygen and one nitrogen atoms, forming a 2D corrugated layer, $\{Cd(pzdc)\}_n$, in the *bc* plane. $\{Cd_2(\mu\text{-}O)_2\}$ units ($\angle Cd^{II}\text{-}O\text{-}Cd^{II} = 111.7(2)°$, $Cd^{II}\cdots Cd^{II} = 3.883(1)$ Å) in the layers are pillared with the axial coordination of azpy, forming a 3D network. An interesting aspect of the structure is that azpy ligands connect the layers in a criss-cross fashion, which facilitates the formation of π–π interactions ($C\cdots C = 3.71$–4.89 Å, dihedral angle = 0.3–1.7°) among the pyridine planes. Such a criss-cross pattern resembles topologically the α-polonium net, a topology that has been generated via $\{M(CN)_2\}$ sheets linked by pyrazine ligands.[22]

The framework has interlayer spaces (volume of the void $V_{void} = 20.3\,\%$),[23] affording 1D microchannels along the *c* axis with window dimensions of 3.5×6.1 Å^2 (Figure 1a).[24] Each pore is surrounded by four perpendicular pyridine planes and two internal panels of pzdc plane, and filled with four water molecules. In the channel walls two oxygen atoms of the carboxylate moiety in pzdc protrude, thus allowing hydrogen-bonding interactions with water (w) molecules ($C{=}O\cdots O(w) = 2.66(3)$ Å). Moreover, the four water molecules are hydrogen bonded to each other ($(O(w)\cdots O(w')) = 2.40(3)$ Å, 3.03(2) Å).

The unit cell parameters of **2** are very close to those of **1** and structure determination reveals that they are isostructural. In **2**, the corrugated $\{Cd(pzdc)\}_n$ layers in the *bc* plane are pillared through axial coordination of bpee in a criss-cross fashion, thus forming a 3D network. Compound **2** also contains 1D channels along the *c* axis with window dimensions of 3.5×4.5 Å^2 ($V_{void} = 19.3\,\%$; Figure 1b) and each pore is occupied by three water molecules. The water molecules form hydrogen bonds with protruding carboxylate moieties of pzdc ligands ($C{=}O\cdots O(w) = 2.68(4)$ Å).

To examine the thermal stability of these porous networks, thermal gravimetric (TG) analyses and X-ray powder diffraction pattern (XRPD) measurements were carried out. The TG curve of **1** and **2** indicates the release of guest water molecules up to 105 °C for **1** and 100 °C for **2** to give their dehydrated forms, **1a** and **2a**, respectively. At 265 °C for **1** and 260 °C for **2**, the ligand molecules start to be released. No chemical decomposition was observed between the dehydration and ligand-release temperatures. Figure 2 shows the observed XRPD patterns of **1**, **1a**, **2**, and **2a**. XRPD patterns of **1a** and **2a** show sharp diffraction peaks indicating that the porous framework is maintained even without guest molecules. XRPD shifts of the (200) reflections demonstrate the elongated (or shrunken) *a* axes. In the process of "**1**→**1a**", the peak (200) at 7.50° for **1** moves to 7.40° for **1a**, exhibiting a slight increase in the interlayer distance (Figure 2b). Whereas, in the process of "**2**→**2a**", the peak (200) at 7.28° for **2** slightly moves to the higher angle 7.34° in dehydrated **2a** indicating that slight decrease in the inter-layer distance (Figure 2e).

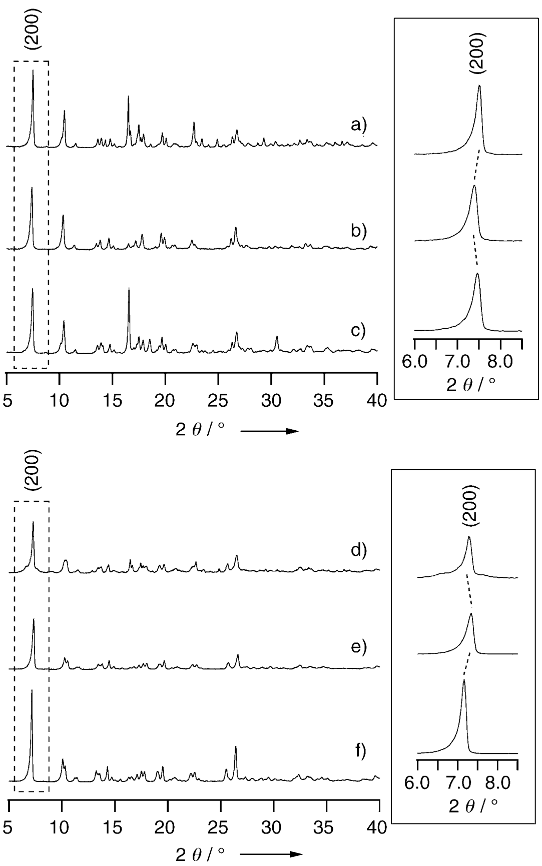


Figure 2. Powder XRD pattern of a) as-synthesized **1**, b) drying of **1** in vacuo at 130 °C for 30 minutes (**1a**), c) **1a** exposed to H_2O, d) as-synthesized **2**, e) drying **2** in vacuo at 130 °C for 30 minutes (**2a**), f) **2a** exposed to H_2O. (inset; enlarged view of the 200 peak position in hydrated, dehydrated, and rehydrated state.)

It is worth mentioning that we succeeded in obtaining single crystals of guest-free **1a** by heating **1** at 130 °C for 30 minutes to completely remove the water molecules. The structure determination of **1a** shows that the crystal system and space group remain the same as those of **1**, but there is a significant increase in the cell volume. **1a** is isostructural to **1**, the only difference being the distance between the pendant oxygen atom of pzdc and the nitrogen atom of azpy; $C{=}O(2)\cdots N{=}N$ (azpy) = 4.57(1) Å (**1**) and $C{=}O(2)\cdots N{=}N$ (azpy) = 4.721(8) Å (**1a**; Figure 3a and b). Moreover, $V_{void} = 21.2\,\%$ of the total crystal volume for **1a**, with effective dimensions of the pore size being 3.7×6.4 Å^2, which is larger than the original **1** ($V_{void} = 20.3\,\%$, 3.5×6.1 Å^2), thus indicating that **1a** has expanded relative to **1**. This expansion is attributed to lone pair–lone pair electronic repulsion from the pendant oxygen atom of the carboxylate and nitrogen atom of the azo group. In contrast, the interlayer distance of **2** decreases upon the removal of water molecules. In case of **2** the pendant oxygen (O2) atoms are in close contact with ethylene hydrogen atoms ($C\text{-}O(2)\cdots HC{=}CH$ (bpee) = 3.46 Å; Figure 3c), and after dehydration of **2** to give **2a** the $C{-}O(2)\cdots HC{=}CH$ hydrogen-bonding interaction results in a more closely packed structure, which is responsible for the shrinking.[25] These results coincide with the results of XPRD. Thus, the different phenomena of adsorption/desorption, expanding and shrinking, have been realized in **1** and **2**, respectively (Scheme 2). In both **1a** and **2a**, the original

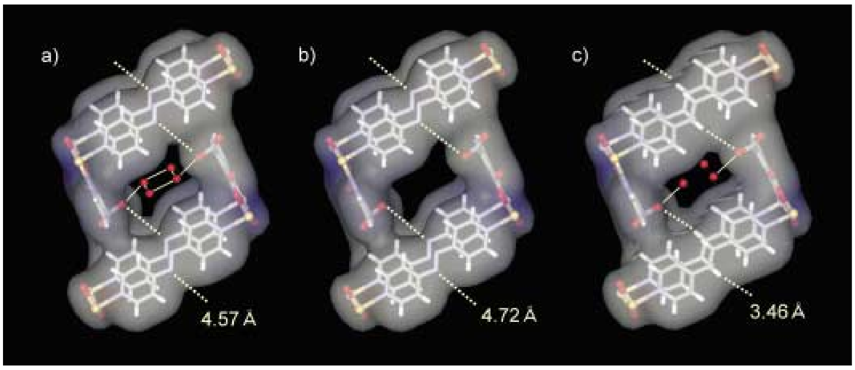
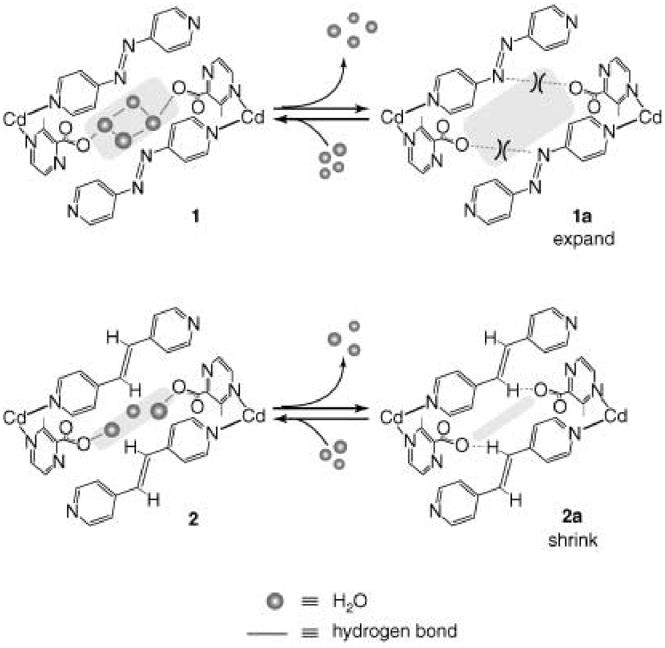


Figure 3. Views of pores in a) **1**, b) **1a**, and c) **2**, along the *c* axis. In **1** and **2**, water molecules are accommodated by hydrogen bonds.



Scheme 2. Schematic diagram of expansion and shrinking of complex **1** and **2**.

framework completely reformed when exposed to water vapor for several hours (Figure 2c and f).

Based on well-defined **1a** and **2a**, the adsorption isotherms for N_2, H_2O, MeOH, EtOH, THF, and Me_2CO were measured. The adsorption isotherm of N_2 (surface area; 16.3 Å^2)[26,27] at 77 K for both **1a** and **2a** reveals only surface adsorption occurs, indicating that N_2 molecules cannot diffuse into the channel at low temperature (77 K; see Supporting Information). On the other hand, at 298 K, H_2O (10.5 Å^2), MeOH (18.0 Å^2), EtOH (23.1 Å^2), THF (28.7 Å^2), and Me_2CO (26.8 Å^2) can diffuse into the micropores of **1a**, irrespective of whether or not it is similar in size to N_2 (Figure 4), and all the adsorption profiles show hysteretic adsorption (see Supporting Information). The amount of adsorption was calculated by using the Langmuir analysis and which shows that for every Cd atom, 1.62 of H_2O, 1.11 of MeOH, 0.28 of EtOH, 0.62 of THF, and 0.44 of Me_2CO molecules can be adsorbed.

The adsorption properties of **2a** were also studied (Figure 4); the adsorption of molecules per Cd atom calculated from the Langmuir analysis is as follows: 1.12 for H_2O, 0.72 for MeOH, 0.08 for EtOH, 0.02 for THF, and 0.04 for Me_2CO. It is note worthy that **2a** adsorbs selectively; H_2O and MeOH are adsorbed, whereas EtOH, THF and Me_2CO molecules are not. As it is the larger molecules that are not adsorbed, it is clear that this selectivity arises from the size of the channel windows in **2a**, that is the channel windows are smaller than the adsorbates.[12]

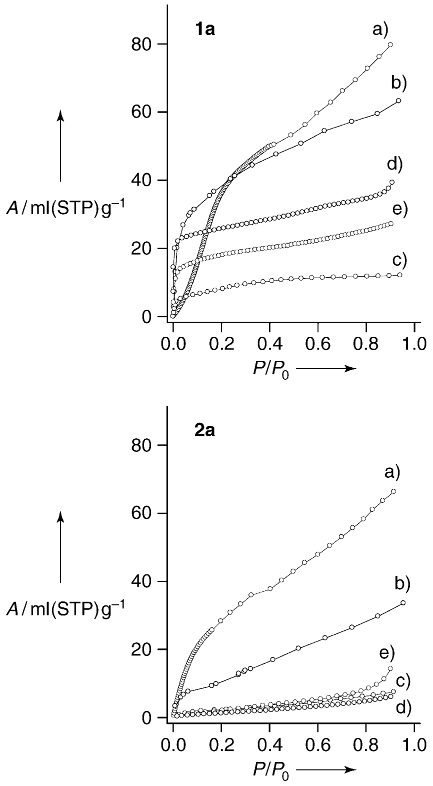


Figure 4. Isotherm for a) H_2O, b) MeOH, c) EtOH, d) THF, e) Me_2CO vapor adsorption, *A*, at 298 K of **1a** (top) and **2a** (bottom). P_0 is the saturated vapor pressure at 298 K; 3.17 kPa (H_2O), 16.94 kPa (MeOH), 7.87 kPa (EtOH), 23.45 kPa (THF), and 30.59 kPa (Me_2CO). STP is standard temperature and pressure.

In conclusion, we have synthesized new pillared-layer porous coordination polymers with different properties: the ability to expand or shrink, and by doing so we have shown that the coordination polymer is much softer than generally believed. **2a** selectively adsorbs H_2O and MeOH, which is due to the small aperture of the channels. The adsorption selectivity exhibited by these new zeolite-like materials arises from a simple change in the organic pillar module, and may well find useful applications in molecular separation techniques.

Experimental Section

Synthesis of **1:** An aqueous solution of $Cd(NO_3)_2{\cdot}4H_2O$ (2 mL, 0.5 mmol; 0.154 g, in 50 mL) was slowly and carefully layered to a solution of azpy (2 mL, 0.5 mmol, 0.92 g) and Na_2pzdc (0.5 mmol, 0.107 g) in $MeOH/H_2O$ (1:1; 50 mL). Dark red diamond-shaped crystals were obtained after one week. The crystals were separated and washed with a methanol/water (1:1) mixture and dried. Yield 80%.

Synthesis of **2:** An aqueous solution of $Cd(ClO_4)_2{\cdot}$hydrate (2 mL, 0.5 mmol; 0.156 g, in 50 mL) was slowly and carefully layered to a solution of bpee (2 mL, 0.5 mmol, 0.91 g) and Na_2pzdc (0.5 mmol, 0.107 g) in $MeOH/H_2O$ (1:1; 50 mL). Colorless square crystals were obtained after one month. The crystals were separated and washed with a methanol/water (1:1) mixture and dried. Yield 60%.

X-ray structure determination for **1**, **1a**, and **2**: Measurements were recorded on a Rigaku mercury CCD diffractometer with graphite monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71069$ Å) and a CCD two-dimensional detector. All the structures were solved by direct methods by using SIR97 program and expanded by using Fourier techniques. For all compounds, the non-hydrogen atoms were refined anisotropically and all hydrogen atoms were placed in the ideal positions. Crystal data of **1**: $CdC_{16}H_{10}N_6O_6$, $M_r = 494.71$, Monoclinic, Space group $C2/c$ (no. 15); $a = 25.02(7)$, $b = 11.44(2)$, $c = 13.78(2)$ Å, $\beta = 104.58(4)°$, $V = 3817(14)$ Å^3, $Z = 8$, $\rho_{calc} = 1.722\ g\,cm^{-3}$, $\mu(Mo_{K\alpha}) = 1.191\ mm^{-1}$, $F(000) = 1952$, $T = 253$ K; $\lambda(Mo_{K\alpha}) = 0.71069$ Å, $\theta_{max} = 29.5°$, Total data = 16580, Unique data = 5155, $R_{int} = 0.065$, Observed data $[I > 2\sigma(I)] = 3096$, $R = 0.0398$, $R_w = 0.0845$. Crystal data of **1a**: $CdC_{16}H_{10}N_6O_4$, $M_r = 462.70$, Monoclinic, Space group = $C2/c$ (no. 15), $a = 25.09(3)$, $b = 11.472(3)$, $c = 13.762(6)$ Å, $\beta = 102.94(2)°$, $V = 3861(5)$ Å^3, $Z = 8$, $\rho_{calc} = 1.592\ g\,cm^{-3}$, $\mu(Mo_{K\alpha}) = 1.167\ mm^{-1}$, $F(000) = 1824$, , $T = 323$ K; $\lambda(Mo_{K\alpha}) = 0.71069$ Å, $\theta_{max} = 30.6°$, Total data = 16620, Unique data = 5150, $R_{int} = 0.025$, Observed data $[I > 2\sigma(I)] = 3809$, $R = 0.0390$, $R_w = 0.0616$. Crystal data of **2**: $CdC_{18}H_{12}N_4O_{5.5}$, $M_r = 484.73$, Monoclinic, Space group = $C2/c$ (no. 15), $a = 25.650(10)$, $b = 11.215(5)$, $c = 13.983(9)$ Å, $\beta = 105.60(10)°$, $V = 3874(4)$ Å^3, $Z = 8$, $\rho_{calc} = 1.662\ g\,cm^{-3}$, $\mu(Mo_{K\alpha}) = 1.167\ mm^{-1}$, $F(000) = 1920$, $T = 193$ K, $\lambda(Mo_{K\alpha}) = 0.71069$ Å, $\theta_{max} = 31.6°$, Total data = 19172, Unique Data = 5620, $R_{int} = 0.058$, Observed data $[I > 2\sigma(I)] = 1733$, $R = 0.0773$, $R_w = 0.1257$. The oxygen atoms O5, O6 of water molecules in case of **1** and **2** were refined isotropically. In case of **1** the oxygen atom O6 was found in the final stage, and thus its atom position was isotropically refined under rigid condition. CCDC-230071 (**1**), CCDC-230072 (**2**), and CCDC-230073 (**1a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

Gas adsorption measurement: The sorption isotherm measurements for N_2, O_2 gases and solvents H_2O, MeOH, EtOH were carried out at 77 K and 298 K respectively by using an automatic volumetric adsorption apparatus (BELSORP 18; BEL inc). A known weight (150–200 mg) of the as-synthesized sample was placed in the quartz tube, then, prior to measurements, the sample was dried under high vacuum at 403 K for 5 h to remove the solvated water molecules. The adsorbate was placed into the sample tube, then the change of the pressure was monitored and the degree of adsorption was determined by the decrease of the pressure at the equilibrium state.

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