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Systematic Construction of Porous Coordination Pillared-layer Structures and Their Sorption Properties

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Two novel coordination polymers, $\{[Cu_2(pzdc)_2L]\cdot mH_2O\}_n$ where pzdc is pyrazine-2,3-dicarboxylate and L is 2,7-diazapyrene (**CPL-3**) and 1,2-azopyridine (**CPL-4**), respectively, having 3D pillared-layer structure were prepared and the compounds showed gas adsorption properties depending on L.

Porous coordination polymers (PCPs) constructed from transition-metal ions and bridging ligands are known to be a new class of microporous materials with great potential for applications such as gas storage, separation, and heterogeneous catalysis.[1] One of the advantages of PCPs over conventional porous materials is the feasibility of rational design, that is, their pore size, shape, and functionality can be systematically and predictably controlled through synthetic modification of their components.[2] One example demonstrating the features of PCPs is a series of coordination pillared-layer (CPL) structures, which consists of neutral 2D layers composed of Cu^{II} and pyrazine-2,3-dicarboxylate (pzdc) and various dipyridyl bridging ligands as pillars.[3] The channel dimensions and surface functionalities can be systematically controlled by modification of the pillar ligands (L). (Scheme 1.) Previously, some CPLs have been reported to exhibit unique properties along with their crystal structures, for example, formation of crystalline arrays of gas molecules in **CPL-1** (L = pyrazine),[4] guest shape-responsive fitting of **CPL-2** (L = 4,4′-bipyridine),[5] and nanochannel-promoted polymerization of substituted acetylenes in **CPL-2** and **CPL-5** (L = 1,2-

di(4-pyridyl)ethylene).[6] Moreover, there must remain plenty of uncharted ground in the nanospace of CPLs, so it is worth trying to prepare new CPLs with different pillar ligands and investigate their unique properties.

In this report, we report further availability of the systematic design of new CPLs, which are formulated as $\{[Cu_2(pzdc)_2L]\cdot mH_2O\}_n$ where L is 2,7-diazapyrene (**CPL-3**, $m = 4$), and 1,2-azopyridine (**CPL-4**, $m = 6$), respectively. The porous properties of the compounds were investigated by synchrotron X-ray diffraction measurements and gas sorption measurements.

CPL-3 and **CPL-4** were prepared by adding an ethanol–water (1:1) mixed solution of $Cu(ClO_4)_2\cdot 6H_2O$ to an ethanol–water (1:1) mixed solution of Na_2pzdc and L. After allowing the reaction mixture to stir at rt for 24 h, **CPL-3** and **CPL-4** were obtained as orange and green powders, respectively. Their crystal structures were determined by the Rietveld analysis of synchrotron X-ray powder diffraction patterns measured on the BL02B2 beam line in SPring-8.[7] As a result of indexing and the Le Bail fitting, we determined the crystal systems (monoclinic) and cell parameters were the same as those of **CPL-1** except for the b axis which corresponds to the interlayer distance. Hence, we expected that they had 3-D structure adopted by the prototype **CPL-1** in which the same neutral 2D layer structure $\{[Cu(pzdc)]_n\}$ is bridged by pillar ligand to give a 3D porous pillared layer structure with the space group $P2_1/c$. From these considerations, structural models for **CPL-3** and **CPL-4** were built by simulated annealing and used for initial atomic coordinates in the Rietveld fitting.[8]

Figure 1 shows the crystal structures of **CPL-3** and **CPL-4** along the channel direction.[9] The 2D sheets parallel to the ac plane constructed from pzdc and Cu^{II} with the same connectivity as those of previously reported CPLs are linked by L as pillar ligands, forming a 3D framework based on a pillared-layer motif. There are 1D uniform channels with cross sections of $8\,\text{Å} \times 3\,\text{Å}$ and $10\,\text{Å} \times 6\,\text{Å}$ along the b axis, respectively. In the channels, water molecules are included as crystallization solvent. The numbers of the guest water molecule were confirmed by thermogravimetric analysis. The void volume in **CPL-3** and **CPL-4** were calculated by PLATON[10] to be 20.4% and 32.7% of the total volume, respectively (Guest H_2O molecules are omitted for calculation.). In particular, the cell parameters of **CPL-4** are almost the same as those of **CPL-5**. The structural difference between them is only in the linker part of the pillar ligands, that is, –N=N– and –CH=CH–, respectively.
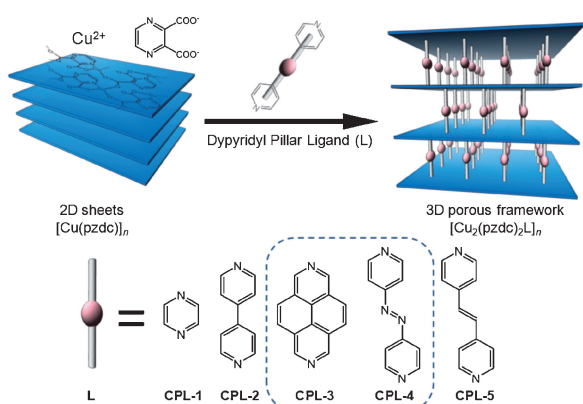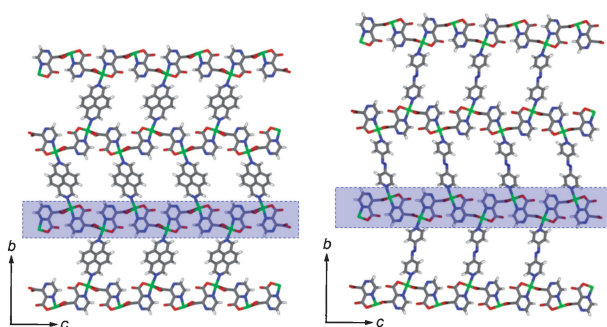

Scheme 1.

Figure 1. Crystal structures of **CPL-3** (left) and **CPL-4** (right) down from *a* axis. Guest water molecules are omitted for clarity. Shadowed parts indicate the 2D layers.
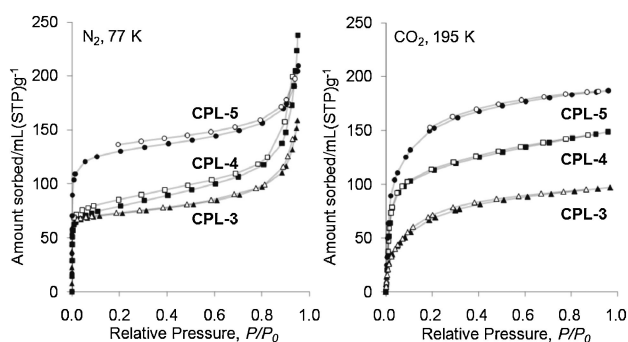
Table 1. Micropore parameters of **CPL-3**, **-4**, and **-5** by nitrogen adsorptions from DR analysis

	W_0 /mL g^{-1}	V_m (V_m') /mL g^{-1}	βE_0 /kJ mol^{-1}	$q_{st,\Phi=1/e}$ /kJ mol^{-1}
CPL-3	72.1	0.112 (0.129[a])	9.59	15.17
CPL-4	78.6	0.122 (0.244[a])	6.67	12.25
CPL-5	134.8	0.209 (0.247[a])	6.33	11.91

[a] V_m' values are calculated from the crystal structures.

In summary, two new isostructural PCPs were systematically prepared based on coordination pillared-layer (CPL) structure. They were structurally characterized by Rietveld analysis of synchrotron X-ray powder diffraction patterns. Their sorption properties were controlled by choice of the pillar ligands with different size and functional groups, exhibiting pore size and surface dependency. We have shown that the pores of CPL structures can be topologically and electrostatically controlled by changing pillar ligands.

Figure 2. Adsorption/desorption isotherm N_2 at 77 K (left) and CO_2 at 195 K (right) on **CPL-3**, **-4**, and **-5**.

The sorption isotherms of N_2 (77 K) and CO_2 (195 K) on **CPL-3**, **CPL-4**, and **CPL-5** were measured.[11] All isotherms are typically representative of Type I with no hysteresis, indicating the presence of permanent microporosity in the samples shown in Figure 2. The abrupt increase of the N_2 adsorption isotherms at low relative pressures indicates that the sizes of micropores are uniform.

The Dubinin–Radushkevich (DR) plots (Figure S6 in Supporting Information[13]) showed a linear relationship at a higher P/P_0 region, from which the micropore volume, W_0, the value of βE_0, and the isosteric heat of adsorption, $q_{st,\Phi=1/e}$, were obtained.[12] The micropore volume, V_m, was calculated from the value of W_0 and the density of the adsorbate by assuming that the molecules were adsorbed as a liquid. These micropore parameters are summarized in Table 1. The V_m values were also calculated from the crystal structures (V_m'). For **CPL-3** and **CPL-5**, the micropore volume calculated from different methods, V_m and V_m', has a good coincidence, well indicating pore size dependency on the adsorption. On the other hand, V_m of **CPL-4** is much lower than expected value from the crystal structure (V_m'). The azo group (–N=N–) has one pair on each nitrogen atom and is exposed on the pore surface of **CPL-4**. This low sorption amount on **CPL-4** can be attributed to lone pair–lone pair electronic repulsion between the azo group and N_2/CO_2. Therefore the effective void space for guest accomodation is smaller than that of **CPL-5** regardless of the similar crystal structures. Similar values of $q_{st,\Phi=1/e}$ for **CPL-4** and **CPL-5** with the same size pore indicate that the sites for initial accommodation of N_2 molecules are chemically the same in the two CPLs, the Cu(pzdc) layer.

References and Notes

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1 S. Kitagawa, R. Kitaura, S.-i. Noro, *Angew. Chem., Int. Ed.* **2004**, *43*, 2334.
2 O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi, J. Kim, *Nature* **2003**, *423*, 705.
3 M. Kondo, T. Okubo, A. Asami, S. Noro, T. Yoshitomi, S. Kitagawa, T. Ishii, H. Matsuzaka, K. Seki, *Angew. Chem., Int. Ed.* **1999**, *38*, 140.
4 R. Kitaura, S. Kitagawa, Y. Kubota, T. C. Kobayashi, K. Kindo, Y. Mita, A. Matsuo, M. Kobayashi, H.-C. Chang, T. C. Ozawa, M. Suzuki, M. Sakata, M. Takata, *Science* **2002**, *298*, 2358; R. Kitaura, R. Matsuda, Y. Kubota, S. Kitagawa, M. Takata, T. C. Kobayashi, M. Suzuki, *J. Phys. Chem. B* **2005**, *109*, 23378; R. Matsuda, R. Kitaura, S. Kitagawa, Y. Kubota, R. V. Belosludov, T. C. Kobayashi, H. Sakamoto, T. Chiba, M. Takata, Y. Kawazoe, Y. Mita, *Nature* **2005**, *436*, 238.
5 R. Matsuda, R. Kitaura, S. Kitagawa, Y. Kubota, T. C. Kobayashi, S. Horike, M. Takata, *J. Am. Chem. Soc.* **2004**, *126*, 14063.
6 T. Uemura, S. Horike, S. Kitagawa, *Chem. Asian J.* **2006**, *1*, 36.
7 E. Nishibori, M. Takata, K. Kato, M. Sakata, Y. Kubota, S. Aoyagi, Y. Kuroiwa, M. Yamakata, N. Ikeda, *J. Phys. Chem. Solids* **2001**, *62*, 2095.
8 H. M. Rietveld, *J. Appl. Cryst.* **1969**, *2*, 65; F. Izumi, T. Ikeda, *Mater. Sci. Forum* **2000**, *321–324*, 198.
9 Crystal data for **CPL-3**: C$_{26}$H$_{12}$Cu$_2$N$_6$O$_{12}$, $T = 298$ K, fw 727.24, monoclinic, space group $P2_1/c$, $Z = 4$, $a = 4.717(1)$ Å, $b = 26.797(4)$ Å, $c = 11.101(2)$ Å, $\beta = 96.52(2)°$, $V = 1392.9(5)$ Å^3, $R1 = 0.012$, Rwp = 0.037, CCDC 758167; for **CPL-4**: C$_{22}$H$_{12}$Cu$_2$N$_8$O$_{14}$, $T = 298$ K, fw 739.21, monoclinic, space group $P2_1/c$, $Z = 4$, $a = 4.083(4)$ Å, $b = 31.011(2)$ Å, $c = 10.980(1)$ Å, $\beta = 96.145(8)°$, $V = 1593.9(2)$ Å^3, $R1 = 0.027$, Rwp = 0.029, CCDC 758168.
10 A. L. Spek, *J. Appl. Cryst.* **2003**, *36*, 7.
11 D. Li, K. Kaneko, *J. Phys. Chem. B* **2000**, *104*, 8940.
12 M. M. Dubinin, *Chem. Rev.* **1960**, *60*, 235.
13 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.