doi:10.1246/cl.2012.425

Synthesis and Adsorption Properties of Azulene-containing Porous Interdigitated Framework

Keisuke Kishida,[1] Satoshi Horike,[2,3] Keiji Nakagawa,[2] and Susumu Kitagawa*[2,4,5]
[1]*Research and Development Center, Showa Denko K. K.,*
2 Oaza Nakanosu, Oita 870-0189
[2]*Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering,*
Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510
[3]*PRESTO, Japan Science and Technology Agency, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012*
[4]*Institute for Integrated Cell-Material Sciences (WPI-iCeMS), Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-8501*
[5]*Kitagawa Integrated Pores Project, ERATO, Japan Science and Technology Agency,*
Kyoto Research Park Bldg #3, Shimogyo-ku, Kyoto 600-8815

(Received January 17, 2012; CL-120045; E-mail: kitagawa@icems.kyoto-u.ac.jp)

A porous interdigitated 2D coordination framework {[Zn(azdc)(bpy)]·DMF}$_n$ (azdc: 1,6-azulenedicarboxylate; bpy: 4,4′-bipyridyl; DMF: *N*,*N*-dimethylformamide) was synthesized and structurally characterized. By comparing with its constitutional isomer, [Zn(azdc)(bpy)]$_n$ showed stronger H_2O interaction which was induced by polarized azulene moiety.

In recent years, a number of coordination polymers with permanent porosity; porous coordination polymers (PCPs) or metal–organic frameworks (MOFs) have been synthesized. They are providing a variety of properties such as molecular adsorption, heterogeneous catalysis, magnetism, and electron/ion conductivity.[1–5] One ongoing challenge to construct the frameworks is fine tuning of structures by systematic modulation by metal ions or ligands.[6–9] For instance, control of isomerism of ligand or framework is regarded as a key to precise design of the pore characteristics.[10] Although there are various framework isomers of PCPs such as conformational isomer and interpenetrated isomer, it has been difficult to synthesis isostructures of porous framework by use of ligand isomers.

Recently, PCPs having a structural motif of 2D layer stacking have been reported.[11–14] These are constructed from 3d/4d-metal ion, dicarboxylate having 120° coordination geometry and linear pyridine-based linker. The frameworks show unique gas adsorption properties that depend on its ligand.[15–17] By use of this structure platform, we tried synthesizing isostructure with ligand isomers. One of the structures is [Zn(ndc)(bpy)]$_n$ (**CID-3**, ndc: 2,7-naphthalenedicarboxylate; bpy: 4,4′-bipyridyl) which represents flexible pore structure and highly selective sorption on CO_2 from $CO_2/O_2/N_2$ gas mixture.[16] Azulene is an isomer of naphthalene, but with different properties.[18–22] Similar to naphthalene, it is a planar hydrocarbon possessing 10π electrons, but has a relatively large dipole moment of 0.8–1.08 D due to its asymmetric structure. In this study, we approached a synthesis of isostructure of naphthalene-based framework by ligand isomer, azulenedicarboxylate as a building block.

An azulene-containing porous interdigitated framework of {[Zn(azdc)(bpy)]·DMF}$_n$ (**CID-13**$\supset$DMF) was prepared from $Zn(NO_3)_2\cdot 6H_2O$, 1,6-azulenedicarboxylic acid (H_2azdc), and bpy in DMF/MeOH solution. H_2azdc was synthesized by Ziegler–Hafner synthesis as reported procedures.[23–26]

As shown in Figure 1,[27] each Zn^{2+} atom of **CID-13** is in a distorted trigonal-bipyramidal geometry, being coordinated by

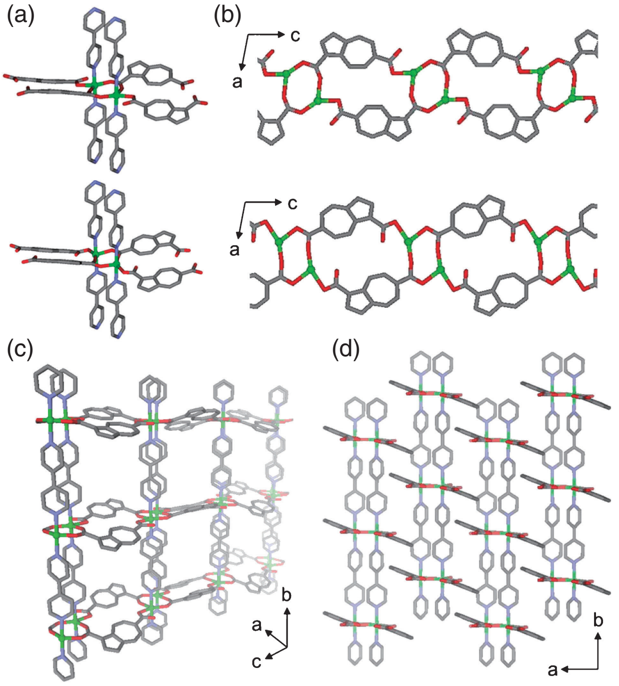

Figure 1. Perspective views of (a) the coordinating environments, (b) infinite [Zn(azdc)]$_n$ chain units, (c) two-dimensional [Zn(azdc)(bpy)]$_n$ sheet, and (d) the layer stacking mode (green: zinc, gray: carbon, blue: nitrogen, red: oxygen).

two bpy ligands at the axial positions and three oxygen atoms from the carboxylates of both 5-membered ring and 7-membered ring of azdc ligand in the equatorial plane. Because of the symmetry, azdc linkages are disordered over two sites with equal site occupancies and these are related to each other in mirror reversed manner. The Zn^{2+} and azdc give 1D chain structures along the *c* axis and the further linkages of these chains via bpy ligands in the axial positions generate an infinite 2D neutral layer. The azulene part locates both sides of the 1D chains in a *trans*-arrangement, and these 2D layers run along the *c* axis stack with the plane of azdc ligands of adjacent layers. The void spaces are surrounded by azdc and bpy ligands and 1D, zig-zag channels are created. The void volume calculated from PLATON software is 22.9%.[28] TGA profile of **CID-13**$\supset$DMF indicates that the guest-free phase is stable even at 250 °C under N_2

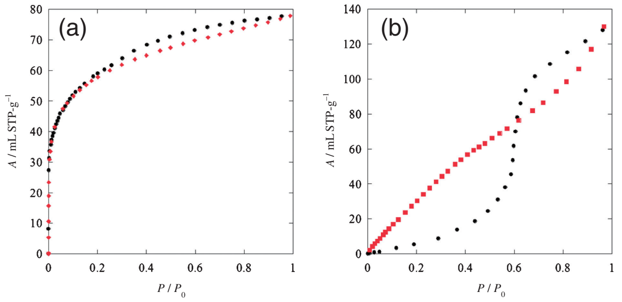

Figure 2. Adsorption isotherms of **CID-13** (red) and **CID-3** (black) for (a) CO_2 at 195 K and (b) H_2O at 298 K.

atmosphere. Solvent guests in the as-synthesized form are removed by evacuation at 150 °C overnight. Powder X-ray diffraction pattern and TGA curve of guest-free **CID-13** confirm that it retains crystallinity after guest removal.

The constitutional isomers **CID-13** and [Zn(ndc)(bpy)] (**CID-3**) show similar structures, including space group and cell parameters. Void volume of **CID-3** is 25.8% and it is close to that of **CID-13**. From the viewpoint of pore structure, **CID-13** and **CID-3** have the same 1D pore surrounded by "polar" azulene and "nonpolar" naphthalene, respectively. To demonstrate how polar π character of the azulene moiety makes a difference in the host–guest interactions compared with **CID-3**, we investigated gas adsorption behaviors of these compounds for nonpolar CO_2 (0 D) and polar H_2O (1.87 D). As shown in Figure 2a, both compounds reveal Type-I sorption behaviors for CO_2 at 195 K with the same adsorption amounts.[29] This indicates that these compounds have similar gas-accessible void volumes. On the other hand, adsorption isotherms for polar H_2O exhibit different behaviors in the isomer pairs (Figure 2b). **CID-3** shows Type-V sorption behavior for H_2O, while **CID-13** adsorbs H_2O in the low-pressure region. Type-V sorption isotherm of **CID-3** indicates weak host–guest interactions as a consequence of the hydrophobic pore surfaces, therefore, stronger host–guest interaction is expected in the case of **CID-13** having azulene moiety. Computational studies also estimated that the interaction energy of azulene with H_2O is stronger than that of naphthalene and the present result experimentally supports the behavior.[30,31] In the high-pressure region, the adsorption amounts of H_2O for both compounds are almost the same because of the similar guest-accessible void volumes as is the case with CO_2.

In summary, a new 2D interdigitated porous coordination polymer was synthesized and structurally characterized. By utilizing the isomeric ligand, we successfully prepared the constitutional isomer of PCP that showed the same interdigitated framework previously reported. We carried out comparative studies on gas adsorption and showed that these constitutional isomers exhibited different adsorption behaviors for polar H_2O, suggesting its distinct surface character in host–guest interaction. The use of ligand isomers for construction of PCP frameworks is an effective approach for fine tuning of pore characteristics.

References and Notes

1 S. Kitagawa, R. Kitaura, S.-i. Noro, *Angew. Chem., Int. Ed.* **2004**, *43*, 2334.
2 R. E. Morris, P. S. Wheatley, *Angew. Chem., Int. Ed.* **2008**, *47*, 4966.
3 G. Férey, *Chem. Soc. Rev.* **2008**, *37*, 191.
4 S. Horike, S. Shimomura, S. Kitagawa, *Nat. Chem.* **2009**, *1*, 695.
5 O. K. Farha, J. T. Hupp, *Acc. Chem. Res.* **2010**, *43*, 1166.
6 M. Kondo, T. Okubo, A. Asami, S.-i. Noro, T. Yoshitomi, S. Kitagawa, T. Ishii, H. Matsuzaka, K. Seki, *Angew. Chem., Int. Ed.* **1999**, *38*, 140.
7 Z. Wang, S. M. Cohen, *J. Am. Chem. Soc.* **2007**, *129*, 12368.
8 R. Banerjee, A. Phan, B. Wang, C. Knobler, H. Furukawa, M. O'Keeffe, O. M. Yaghi, *Science* **2008**, *319*, 939.
9 T. Devic, P. Horcajada, C. Serre, F. Salles, G. Maurin, B. Moulin, D. Heurtaux, G. Clet, A. Vimont, J.-M. Grenèche, B. Le Ouay, F. Moreau, E. Magnier, Y. Filinchuk, J. Marrot, J.-C. Lavalley, M. Daturi, G. Férey, *J. Am. Chem. Soc.* **2010**, *132*, 1127.
10 T. A. Makal, A. A. Yakovenko, H.-C. Zhou, *J. Phys. Chem. Lett.* **2011**, *2*, 1682.
11 J. Tao, X.-M. Chen, R.-B. Huang, L.-S. Zheng, *J. Solid State Chem.* **2003**, *170*, 130.
12 Y.-H. Wen, J.-K. Cheng, Y.-L. Feng, J. Zhang, Z.-J. Li, Y.-G. Yao, *Inorg. Chim. Acta* **2005**, *358*, 3347.
13 G. Tian, G. Zhu, Q. Fang, X. Guo, M. Xue, J. Sun, S. Qiu, *J. Mol. Struct.* **2006**, *787*, 45.
14 S. Horike, D. Tanaka, K. Nakagawa, S. Kitagawa, *Chem. Commun.* **2007**, 3395.
15 D. Tanaka, A. Henke, K. Albrecht, M. Moeller, K. Nakagawa, S. Kitagawa, J. Groll, *Nat. Chem.* **2010**, *2*, 410.
16 K. Nakagawa, D. Tanaka, S. Horike, S. Shimomura, M. Higuchi, S. Kitagawa, *Chem. Commun.* **2010**, *46*, 4258.
17 T. Fukushima, S. Horike, Y. Inubushi, K. Nakagawa, Y. Kubota, M. Takata, S. Kitagawa, *Angew. Chem., Int. Ed.* **2010**, *49*, 4820.
18 M. Beer, H. C. Longuet-Higgins, *J. Chem. Phys.* **1955**, *23*, 1390.
19 A. G. Anderson, Jr., B. M. Steckler, *J. Am. Chem. Soc.* **1959**, *81*, 4941.
20 R. J. Buenker, S. D. Peyerimhoff, *Chem. Phys. Lett.* **1969**, *3*, 37.
21 J. O. Morley, *J. Am. Chem. Soc.* **1988**, *110*, 7660.
22 J. O. Morley, *J. Chem. Soc., Perkin Trans. 2* **1989**, 103.
23 K. Hafner, *Angew. Chem.* **1958**, *70*, 419.
24 L. J. Mathias, C. G. Overberger, *J. Org. Chem.* **1980**, *45*, 1701.
25 K. Rudolf, D. Robinette, T. Koenig, *J. Org. Chem.* **1987**, *52*, 641.
26 L. L. Tolstikova, B. A. Shainyan, *Russ. J. Org. Chem.* **2006**, *42*, 1068.
27 fw 435.72, monoclinic, space group $C2/c$ (No. 15), $a = 16.399(10)$ Å, $b = 11.380(6)$ Å, $c = 24.014(14)$ Å, $\beta = 103.333(10)°$, $V = 4360(4)$ Å^3, $Z = 8$, $\rho_{\mathrm{calcd}} = 1.327$ g cm^{-3}. Of 15325 reflections collected, 4869 were independent with $R_{\mathrm{int}} = 0.104$, 4869 reflections with $I > 2\sigma(I)$, final $R_1[I > 2\sigma(I)] = 0.075$, wR_2(all data) $= 0.237$, $GOF = 1.10$.
28 A. L. Spek, *J. Appl. Crystallogr.* **2003**, *36*, 7.
29 K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquérol, T. Siemieniewska, *Pure Appl. Chem.* **1985**, *57*, 603.
30 E. M. Cabaleiro-Lago, J. Rodríguez-Otero, Á. Peña-Gallego, *J. Phys. Chem. A* **2008**, *112*, 6344.
31 E. M. Cabaleiro-Lago, J. Rodríguez-Otero, Á. Peña-Gallego, *J. Chem. Phys.* **2008**, *129*, 084305.