Inorganic Chemistry

COMMUNICATION

pubs.acs.org/IC

Ln−Co-Based Rock-Salt-Type Porous Coordination Polymers: Vapor Response Controlled by Changing the Lanthanide Ion

Atsushi Kobayashi,*[†] Yui Suzuki,[†] Tadashi Ohba,[†] Shin-ichiro Noro,[‡] Ho-Chol Chang,[†] and Masako Kato*[†]

[†]Division of Chemistry, Faculty of Science, Hokkaido University, North-10, West-8, Kita-Ku, Sapporo 060-0810, Japan

[‡]Research Institute for Electronic Science, Hokkaido University, North-20, West-10, Kita-ku, Sapporo 001-0020, Japan

S *Supporting Information*

ABSTRACT: We synthesized new porous coordination polymers (PCPs) $\{Ln^{III}[Co^{III}(dcbpy)_3]\cdot nH_2O\}$ ($Ln = La^{3+}$, Nd^{3+}, Gd^{3+}; H_2dcbpy = 4,4′-dicarboxy-2,2′-bipyridine) and characterized them by X-ray diffraction and vapor-adsorption measurements. These three Ln−Co-based PCPs have similar rock-salt types and highly symmetrical porous structure and show a reversible structural collapse−regeneration accompanied by water-vapor desorption−adsorption. Similar structural regeneration was also observed for the Gd−Co PCP upon exposure to MeOH and CH_3CN vapors, whereas the remaining two PCPs barely responded to organic vapors.

Porous coordination polymers (PCPs) have attracted considerable attention over recent decades because of their controllable frameworks, interesting gas- and vapor-adsorption properties, and catalytic activity, among other properties.[1−3] Until now, various metal ions and bridging ligands have been used to achieve large surface areas, to enhance host−guest interaction for hydrogen storage, and to introduce a catalytic active site inside their nanosized pores.[4−6] The use of a metal-complex ligand as a bridging ligand is also one of the most useful methods of building new multifunctional PCPs.[7] In addition, the stepwise synthesis of PCPs using metal-complex ligands may enable us to create new multifunctional materials more systematically owing to the versatile functions of the metal-complex ligand.[8]

In this study, to build new multifunctional PCPs on the basis of the versatility of the $[M(bpy)_3]$ (bpy = 2,2′-bipyridine) complex series, we used the cobalt(III) complex $[Co(dcbpy)_3]^{3-}$ (H_2dcbpy = 4,4′-dicarboxy-2,2′-bipyridine) as the metal-complex ligand. It is well-known that $[M(bpy)_3]$-type metal complexes exhibit several interesting properties, including photosensitizers and O_2-evolving catalysts of $[Ru(bpy)_n]$ derivatives, and spin crossover in the $[Co^{II}(trpy)_2]$ moiety (trpy = 2,2′,6′,2″-terpyridine), for example.[9,10] We chose lanthanide ions as connectors in the $[Co(dcbpy)_3]^{3-}$ complex ligands because of their flexible and variable coordination modes.[11] In this Communication, we report the syntheses, crystal structures, and vapor-adsorption properties of three PCPs, $\{La[Co(dcbpy)_3]\cdot 14H_2O\}$ (**La−Co**), $\{Nd[Co(dcbpy)_3]\cdot 14H_2O\}$ (**Nd−Co**), and $\{Gd[Co(dcbpy)_3]\cdot 14H_2O\}$ (**Gd−Co**), and demonstrate that the structural flexibilities and vapor-adsorption properties of these PCPs strongly depend on f metal ions, despite their similar crystal structures.

Figure 1 shows the crystal structures of **La−Co** and **Gd−Co** PCPs. These PCPs were synthesized by the simple reaction of $[Co(Hdcbpy)_3]$ and $LnCl_3$ in basic aqueous solutions (see the Supporting Information, SI). The structures of all three PCPs are essentially of the rock-salt type. Among the three Ln−Co-based PCPs, only **La−Co** crystallized in the orthorhombic *Fddd* space group, while the others crystallized in the cubic $Fm\bar{3}m$ group. The metal-complex ligand $[Co(dcbpy)_3]^{3-}$ coordinated to six Ln^{3+} ions to form a three-dimensional porous framework. The Co−N bond distances (1.89−1.94 Å) indicate that the Co ion remains in the trivalent oxidation state. Interestingly, two enantiomers of Λ- and Δ-$[Co(dcbpy)_3]^{3-}$ were disordered in **Nd−Co** and **Gd−Co**, but they were ordered in **La−Co** (Figure S1 in the SI) despite their almost identical synthetic procedures except for the difference in the f metal sources. In our preliminary results of the other Ln−Co PCPs, only two PCPs with La^{3+} and Ce^{3+} ions adopted the ordered *Fddd* structures, implying that the structural ordering of two enantiomers may be related to the ionic radius of the Ln^{3+} ion. Two of the six carboxyl groups in **La−Co** coordinated to La^{3+} ions in a monodentate fashion, while the other four coordinated in a bidentate fashion. By contrast, all of the carboxyl groups in **Nd−Co** and **Gd−Co** coordinated to the Ln^{3+} ion in a bidentate fashion. Thus, the coordination number of the La^{3+} ion was 10, while those of Nd^{3+} and Gd^{3+} were 12. It is noteworthy that all three PCPs have a large void space, approximately 55%, 51%, and 50% PCP volume in the unit cell (calculated using the *PLATON* SQUEEZE program[12]), for the **La−Co**, **Nd−Co**, and **Gd−Co** PCPs, respectively, which are probably occupied by water molecules in each case. Although the hydration numbers of these PCPs could not be determined by X-ray structural analyses owing to disorder of the water molecules, elemental analysis suggests that the hydration numbers of all three Ln−Co PCPs are 14.

To investigate the rigidity of the porous framework of the three PCPs, powder X-ray diffraction (PXRD) patterns were measured. As shown in Figure 2, the PXRD patterns of the **La−Co** and **Gd−Co** PCPs obtained after drying under vacuum are featureless amorphous patterns. IR spectra of the original and dried **La−Co** were almost identical with each other (see Figure S2 in the SI), suggesting that desorption of water did not affect the local structure around the $[Co(dcbpy)_3]^{3-}$ anion. Thus, the porous frameworks of these PCPs are not sufficiently rigid to retain the porous structure without crystal water molecules.

Received: November 29, 2010
Published: February 21, 2011

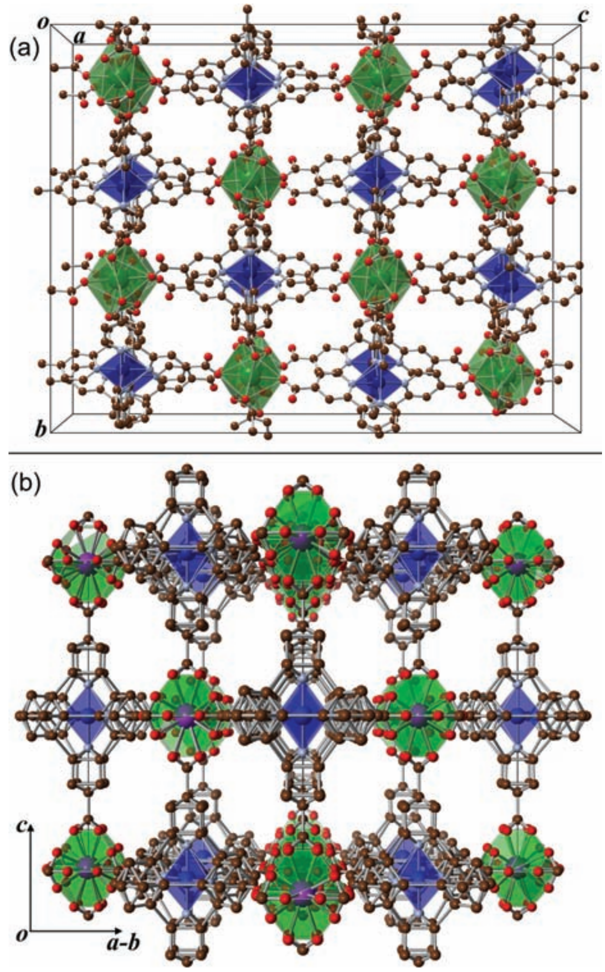

Figure 1. Perspective views of the crystal structures of (a) the **La−Co** PCP along the *a* axis and (b) the **Gd−Co** PCP along the *a* + *b* axis. Solvated water and H atoms are omitted for clarity. Blue and green polyhedra represent the coordination spheres of the Co^{3+} and Ln^{3+} ions, respectively. Brown, light-blue, and red balls represent C, N, and O atoms, respectively.[13]

However, interestingly, crystalline patterns identical with simulations based on the crystal structures were recovered upon exposure of the amorphous PCPs to water vapor. Similar changes in the PXRD pattern were observed for the **Nd−Co** PCP (Figure S3 in the SI). These results clearly show that the long-range structural ordering of Ln−Co-based PCPs is reversibly destroyed and regenerated by desorption and adsorption of water. It should be noted that the structure of the **Gd−Co** PCP could also be regenerated by exposure to methanol and acetonitrile vapors, but, surprisingly, such structural regeneration by these vapors was hardly observed for the **La−Co** PCP despite their similar structures. The **Nd−Co** PCP showed slightly similar structural regeneration under exposure to both methanol and acetonitrile vapors (Figure S3 in the SI). Under exposure to other organic vapors, including ethanol, acetone, chloroform, *n*-hexane, and diethyl ether, the three Ln−Co PCPs failed to show structural regeneration (Figures S3−S5 in the SI). These results suggest that the radius of the f metal ion and disorder of the two enantiomers of $[Co(dcbpy)_3]^{3-}$ significantly affect the flexibility of the crystal lattice and its adsorption properties.

For greater insight into this structural flexibility, we measured the water-vapor-adsorption isotherms of these three Ln−Co PCPs, as shown in Figure 3. As expected from the results of the PXRD measurements, these PCPs can adsorb considerable amounts of water vapor, approximately 16.1, 14.5, and 13.5 $mol \cdot mol^{-1}$ for the **La−Co**, **Nd−Co**, and **Gd−Co** PCPs at saturated vapor pressure, respectively. These saturated amounts are close to the hydration numbers estimated from elemental analyses and seem to be proportional to the relative size of the void. It is interesting to note that the **La−Co** PCP can adsorb water vapor more effectively at a very low pressure, whereas the other two PCPs adsorb it above $P/P_0 = 0.04$ (inset of Figure 3). This difference may be related to disorder of the two $[Co(dcbpy)_3]^{3-}$

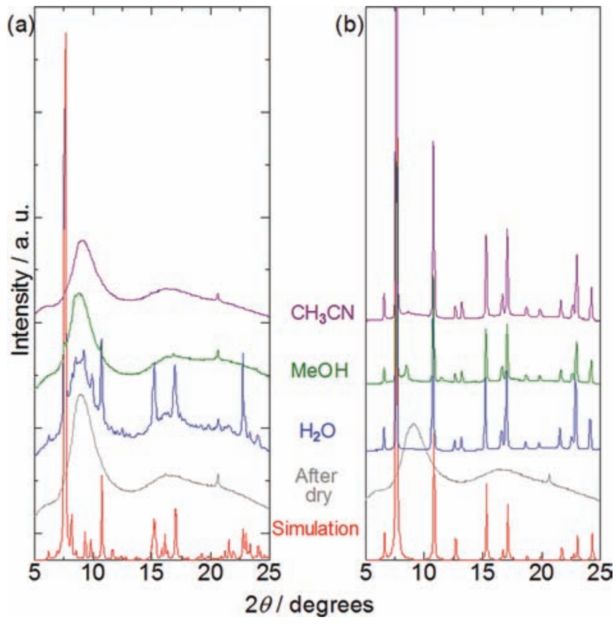

Figure 2. Changes of the PXRD patterns [$\lambda = 1.200(1)$ Å] of (a) **La−Co** and (b) **Gd−Co** PCPs. Gray, blue, green, and purple lines represent the PXRD patterns of dried Ln−Co under vacuum and the dried Ln−Co PCPs exposed to water, methanol, and acetonitrile vapors for 8 days, respectively. The bottom patterns in red are simulations calculated from the crystal structures of the Ln−Co PCPs.

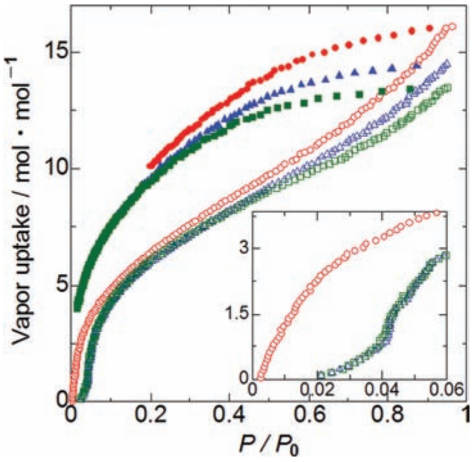

Figure 3. Water-vapor-adsorption isotherms of **La−Co** (red circle), **Nd−Co** (blue triangle), and **Gd−Co** (green square) PCPs at 298 K. Open and closed symbols show the adsorption and desorption processes, respectively. The inset shows magnification of the low-vapor-pressure region below $P/P_0 = 0.06$.

enantiomers in the crystal structure, which might serve as a barrier to prevent vapor-molecule diffusion into the lattice.

In summary, we synthesized three new rock-salt-type PCPs using lanthanide ions, Ln^{3+}, and a [Co(dcbpy)$_3$]$^{3-}$ metal-complex ligand and demonstrated a structural collapse—regeneration accompanied by water-vapor desorption—adsorption. Interestingly, substitution of the lanthanide ion allowed us to modify the structural flexibilities and adsorption properties dramatically, despite their similar rock-salt-type structures. Further studies focused on structural tuning using other lanthanide ions and functionalization of this PCP system by replacement of the [Co(dcbpy)$_3$]$^{3-}$ metal-complex ligand are now in progress.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental details regarding the syntheses and characterizations, IR spectra of the dried and water-vapor-adsorbed **La—Co**, crystallographic data (CIF), and PXRD patterns under exposure to various organic vapors for **La—Co**, **Nd—Co**, and **Gd—Co** PCPs. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: akoba@sci.hokudai.ac.jp (A.K.), mkato@sci.hokudai.ac.jp (M.K.).

■ ACKNOWLEDGMENT

This work is supported by a Grant-in-Aid for Scientific Research (Grant 21021001), Young Scientists (B) (19750050), Elements Science and Technology Project "Nano-hybridized Precious-Metal-Free Catalysts for Chemical Energy Conversion", and the Global COE Program (Project B01: Catalysis as the Basis for Innovation in Materials Science) from the Ministry of Education, Culture, Sports, Science, and Technology, Japan.

■ REFERENCES

(1) (a) Li, H.; Eddaoudi, M.; O'Keeffe, M.; Yaghi, O. M. *Nature* **1999**, *402*, 276–279. (b) Eddaoudi, M.; Moler, D. B.; Li, H.; Chen, B.; Reineke, T. M.; O'Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2001**, *34*, 319–330. (c) Rosi, N. L.; Kim, J.; Eddaoudi, M.; Chen, B.; O'Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* **2005**, *127*, 1504–1518. (d) Louseau, T.; Férey, G. *J. Fluorine Chem.* **2007**, *128*, 413–422. (e) Banerjee, R.; Phan, A.; Wang, B.; Knobler, C.; Furukawa, H.; O'Keeffe, M.; Yaghi, O. M. *Science* **2008**, *319*, 939–943. (f) Férey, G.; Serre, C. *Chem. Soc. Rev.* **2009**, *38*, 1380–1399. (g) Tranchemontagne, D. J.; Mendoza-Cortes, J. L.; O'Keeffe, M.; Yaghi, O. M. *Chem. Soc. Rev.* **2009**, *38*, 1257–1283.

(2) (a) Halder, G. J.; Kepert, C. J.; Moubaraki, B.; Murray, K. S.; Cashion, J. D. *Science* **2002**, *298*, 1762–1765. (b) Kitagawa, S.; Kitaura, R.; Noro, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334–2375. (c) Matsuda, R.; Kitaura, R.; Kitagawa, S.; Kubota, Y.; Belosludov, R. V.; Kobayashi, T. C.; Sakamoto, H.; Chiba, T.; Takata, M.; Kawazoe, Y.; Mita, Y. *Nature* **2005**, *436*, 238–241. (d) Yaghi, O. M. *Nat. Mater.* **2007**, *6*, 92–93. (e) Chandler, B. D.; Enright, G. D.; Udachin, K. A.; Pawsey, S.; Ripmeester, J. A.; Cramb, D. T.; Shimizu, G. K. H. *Nat. Mater.* **2008**, *7*, 229–235. (f) Tanaka, D.; Nakagawa, K.; Higuchi, M.; Horike, S.; Kubota, Y.; Kobayashi, T. C.; Takata, M.; Kitagawa, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 3914–3918. (g) Li, J.-R.; Kuppler, R. J.; Zhou, H.-C. *Chem. Soc. Rev.* **2009**, *38*, 1477–1504. (h) Horike, S.; Shimomura, S.; Kitagawa, S. *Nat. Chem.* **2009**, *1*, 695–704. (i) Higuchi, M.; Tanaka, D.; Horike, S.; Sakamoto, H.; Nakamura, K.; Takashima, Y.; Hijikata, Y.; Yanai, N.; Kim, J.; Kato, K.; Kubota, Y.; Takata, M.; Kitagawa, S. *J. Am. Chem. Soc.* **2009**, *131*, 10336–10337. (j) Fukushima, T.; Horike, S.; Inabushi, Y.; Nakagawa, K.; Kubota, Y.; Takata, M.; Kitagawa, S. *Angew. Chem., Int. Ed.* **2010**, *49*, 4820–4824.

(3) (a) Hong, D.-Y.; Hwang, Y. K.; Serre, C.; Férey, G.; Chang, J.-S. *Adv. Funct. Mater.* **2009**, *19*, 1537–1552. (b) Shultz, A. M.; Farha, O. K.; Hupp, J. T.; Nguyen, S. T. *J. Am. Chem. Soc.* **2009**, *131*, 4204–4205. (c) Yang, L.; Kinoshita, S.; Yamada, T.; Kanda, S.; Kitagawa, H.; Tokunaga, M.; Ishimoto, T.; Ogura, T.; Nagumo, R.; Miyamoto, A.; Koyama, M. *Angew. Chem., Int. Ed.* **2010**, *49*, 5348–5351. (d) Dhakshinamoorthy, A.; Alvaro, M.; Garcia, H. *Chem. Commun.* **2010**, *46*, 6476–6478.

(4) (a) Koh, K.; Wong-Foy, A. G.; Matzger, A. J. *J. Am. Chem. Soc.* **2009**, *131*, 4184–1485. (b) Zhao, D.; Yuan, D.; Sun, D.; Zhou, H.-C. *J. Am. Chem. Soc.* **2009**, *131*, 9186–9188.

(5) (a) Dinca, M.; Long, J. R. *J. Am. Chem. Soc.* **2005**, *127*, 9376–9377. (b) Dinca, M.; Long, J. R. *Angew. Chem., Int. Ed.* **2008**, *47*, 6766–6779. (c) Panella, B.; Hönes, K.; Müller, U.; Trukhan, N.; Schubert, M.; Pütter, H.; Hirscher, M. *Angew. Chem, Int. Ed.* **2008**, *47*, 2138–2142. (d) Zhou, W.; Wu, H.; Yildirim, T. *J. Am. Chem. Soc.* **2008**, *130*, 15268–15269. (e) Lee, W. R.; Ryu, D. W.; Lee, J. W.; Yoon, J. H.; Koh, E. L.; Hong, C. S. *Inorg. Chem.* **2010**, *49*, 4723–4725.

(6) (a) Doonan, C. J.; Morris, W.; Furukawa, H.; Yaghi, O. M. *J. Am. Chem. Soc.* **2009**, *131*, 9492–9493. (b) Farrusseng, D.; Aguado, S.; Pinel, C. *Angew. Chem., Int. Ed.* **2009**, *48*, 7502–7513. (c) Sato, H.; Matsuda, R.; Sugimoto, K.; Takata, M.; Kitagawa, S. *Nat. Mater.* **2010**, *9*, 661–666.

(7) (a) Noro, S.; Kitagawa, S.; Yamashita, M.; Wada, T. *Chem. Commun.* **2002**, 222–223. (b) Kitaura, R.; Onoyama, G.; Sakamoto, H.; Matsuda, R.; Noro, S.; Kitagawa, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 2684–2687.

(8) (a) Chandler, B. D.; Cramb, D. T.; Shimizu, G. K. H. *J. Am. Chem. Soc.* **2006**, *128*, 10403–10412. (b) Kobayashi, A.; Hara, H.; Noro, S.; Kato, M. *Dalton Trans.* **2010**, *39*, 3400–3406.

(9) (a) Kiwi, J.; Grätzel, M. *Nature* **1979**, *281*, 657–658. (b) Magnuson, A.; Anderlund, M.; Johansson, O.; Lindblad, P.; Lomoth, R.; Polivka, T.; Ott, S.; Stensjö, K.; Styring, S.; Sundström, V.; Hammarström, L. *Acc. Chem. Res.* **2009**, *42*, 1899–1909. (c) Masaoka, S.; Sakai, K. *Chem. Lett.* **2009**, *38*, 182–183. (d) Concepcion, J. J.; Jurss, J. W.; Norris, M. R.; Chen, Z.; Templeton, J. L.; Meyer, T. J. *Acc. Chem. Res.* **2009**, *42*, 1954–1965.

(10) (a) Hayami, S.; Murata, K.; Urakami, D.; Kojima, Y.; Akita, M.; Inoue, K. *Chem. Commun.* **2008**, 6510–6512. (b) Hayami, S.; Urakami, D.; Kojima, Y.; Yoshizaki, H.; Yamamoto, Y.; Kato, K.; Fuyuhiro, A.; Kawata, S.; Inoue, K. *Inorg. Chem.* **2010**, *49*, 1428–1432.

(11) (a) Reineke, T. M.; Eddaoudi, M.; Fehr, M.; Kelley, D.; Yaghi, O. M. *J. Am. Chem. Soc.* **1999**, *121*, 1651–1657. (b) Pan, L.; Adams, K. M.; Hernandez, H. E.; Wang, X.; Zheng, C.; Hattori, Y.; Kaneko, K. *J. Am. Chem. Soc.* **2003**, *125*, 3062–3067. (c) Mahata, P.; Sankar, G.; Madras, G.; Natarajan, S. *Chem. Commun.* **2005**, 5787–5789. (d) Chem, B.; Wang, L.; Zapata, F.; Qian, G.; Lobkovsky, E. B. *J. Am. Chem. Soc.* **2008**, *130*, 6718–6719. (e) White, K. A.; Chengelis, D. A.; Gogick, K. A.; Stehman, J.; Rosi, N. L.; Petoud, S. *J. Am. Chem. Soc.* **2009**, *131*, 18069–18071. (f) Allendorf, M. D.; Bauer, C. A.; Bhakta, R. K.; Houk, R. J. T. *Chem. Soc. Rev.* **2009**, *38*, 1330–1352. (g) Gustafsson, M.; Bartoszewicz, A.; Martin-Matute, B.; Sun, J.; Grins, J.; Zhao, T.; Li, Z.; Zhu, G.; Zou, X. *Chem. Mater.* **2010**, *22*, 3316–3322. (h) Lin, Z.-J.; Xu, B.; Liu, T.-F.; Cao, M.-N.; Lu, J.; Cao, R. *Eur. J. Inorg. Chem.* **2010**, 3842–3849.

(12) *PLATON*: Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7–13.

(13) These pictures were drawn by the *VESTA* computer program. Momma, K.; Izumi, F. *J. Appl. Crystallogr.* **2008**, *41*, 653–658.