

Control over Interpenetration in Lanthanide–Organic Frameworks: Synthetic Strategy and Gas-Adsorption Properties

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Two isostructural lanthanide–organic frameworks (**1** and **2**) with 2-fold interpenetrating nets have been synthesized based on 1,4-benzenedicarboxylic acid (H₂BDC). By application of an organic ligand with hindrance groups and a terminal chelating ligand to replace BDC and coordinated solvates, interpenetration has been effectively controlled. The gas-sorption properties of the noninterpenetrating net have been studied.

The rational design and synthesis of porous metal–organic frameworks (MOFs) received a great deal of attention because of their fascinating structures and intriguing potentials in applications such as separation, gas storage, etc.^{1–5}

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(1) For recent reviews, see: (a) Kitagawa, S.; Kitaura, R.; Noro, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334. (b) Ferey, G.; Mellot-Drazniak, C.; Serre, C.; Millange, F. *Acc. Chem. Res.* **2005**, *38*, 217. (c) Bradshaw, D.; Claridge, J. B.; Cussen, E. J.; Prior, T. J.; Rosseinsky, M. J. *Acc. Chem. Res.* **2005**, *38*, 273. (d) Murray, L. J.; Dinca, M.; Long, J. R. *Chem. Soc. Rev.* **2009**, *38*, 1294. (e) Phan, A.; Doonan, C. J.; Uribe-Romo, F. J.; Knobler, C. B.; O'Keeffe, M. O.; Yaghi, M. *Acc. Chem. Res.* **2010**, *43*, 58.

(2) (a) Moulton, B.; Lu, J. J.; Hajndl, R.; Hariharan, S.; Zaworotko, M. J. *Angew. Chem., Int. Ed.* **2002**, *41*, 2821. (b) Ma, L. Q.; Lin, W. B. *Angew. Chem., Int. Ed.* **2009**, *48*, 3637. (c) Liu, Y.; Eubank, J.; Cairns, A.; Eckert, J.; Kravtsov, V. Ch.; Luebke, R.; Eddaoudi, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 3278. (d) Fang, Q.; Zhu, G.; Xue, M.; Sun, J.; Wei, Y.; Qiu, S.; Xu, R. *Angew. Chem., Int. Ed.* **2005**, *44*, 3845. (e) Jin, C. M.; Zhu, Z.; Chen, Z. F.; Hu, Y. J.; Meng, X. G. *Cryst. Growth Des.* **2010**, *10*, 2054. (f) Zeng, M. H.; Wang, Q. X.; Tan, Y. X.; Hu, S.; Zhao, H. X.; Long, L. S.; Kurmoo, M. *J. Am. Chem. Soc.* **2010**, *132*, 2561.

(3) (a) Farha, O. K.; Mulfort, K. L.; Thorsness, A. M.; Hupp, J. T. *J. Am. Chem. Soc.* **2008**, *130*, 8598. (b) Banerjee, M.; Das, S.; Yoon, M.; Choi, H. J.; Hyun, M. H.; Park, S. M.; Seo, G.; Kim, K. *J. Am. Chem. Soc.* **2009**, *131*, 7524. (c) 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. (d) Guo, Z.; Cao, R.; Wang, X.; Li, H.; Yuan, W.; Wang, G.; Wu, H.; Li, J. *J. Am. Chem. Soc.* **2009**, *131*, 6894. (e) Zhang, J.; Chen, S.; Zingiryan, A.; Bu, X. H. *J. Am. Chem. Soc.* **2008**, *130*, 17246.

(4) (a) Zhang, J.; Wu, T.; Chen, S.; Feng, P.; Bu, X. H. *Angew. Chem., Int. Ed.* **2009**, *121*, 3538. (b) Ma, L. Q.; Mihalcik, D. J.; Lin, W. B. *J. Am. Chem. Soc.* **2009**, *131*, 4610. (c) Zhang, Y. B.; Zhang, W. X.; Feng, F. Y.; Zhang, J. P.; Chen, X. M. *Angew. Chem., Int. Ed.* **2009**, *48*, 5287. (d) Cui, H. B.; Zhou, B.; Long, L. S.; Okano, Y.; Kobayashi, H.; Kobayashi, A. *Angew. Chem., Int. Ed.* **2008**, *47*, 3376. (e) Jin, C. M.; Lu, H.; Wu, L. Y.; Huang, J. *Chem. Commun.* **2006**, 5039.

Almost all of the applications are highly determined by the porosity and stability of the porous MOFs. One effective way to increase the porosity of an MOF is to extend the size of the ligand sustaining the framework.⁶ However, extending the size of the ligand may lead to interpenetration of the framework and/or partial collapse of the framework upon guest molecule removal.⁷ Hence, how to control interpenetration to synthesize stable MOFs with high porosity becomes one of the most compelling challenges to chemists.

Although several examples on controlling the interpenetration of MOFs have been reported,⁸ two mainly efficient methods can be achieved: one is to apply an organic ligand containing large hindrance groups to prevent the formation of interpenetration (Scheme 1), which has been reported less in the literature; the other is to use in situ generated rod-shaped secondary building units (SBUs). Recently, Yaghi and co-workers have reported a series of porous MOFs based on rod-shaped SBUs,⁹ in which the rigidity of the rod-shaped SBUs has efficiently avoided interpenetration and thus improved the porosity of the resulting frameworks. Very recently, temperature and concentration control over interpenetration in a cadmium–organic framework has been

(5) (a) Fang, Q. R.; Zhu, G. S.; Xue, M.; Sun, J. Y.; Wei, Y.; Qiu, S. L.; Xu, R. R. *Angew. Chem., Int. Ed.* **2005**, *117*, 3913. (b) Lan, A. J.; Li, K. H.; Wu, H. H.; Olson, D. H.; Emge, T. J.; Ki, W.; Hong, M. C.; Li, J. *Angew. Chem., Int. Ed.* **2009**, *48*, 2334. (c) Ohara, K.; Marti-Rujas, J.; Haneda, T.; Kawano, M.; Hashizume, D.; Izumi, F.; Fujita, M. *J. Am. Chem. Soc.* **2009**, *131*, 3860. (d) Wang, X. L.; Qin, C.; Wu, S. X.; Shao, K. Z.; Lan, Y. Q.; Wang, S.; Zhu, D. X.; Su, Z. M.; Wang, E. B. *Angew. Chem., Int. Ed.* **2009**, *48*, 5291. (e) Goto, Y.; Sato, H.; Shinkai, S.; Sada, K. *J. Am. Chem. Soc.* **2008**, *130*, 14354.

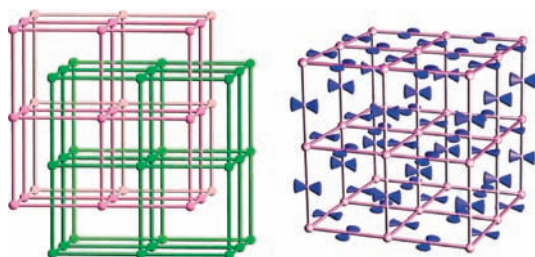
(6) (a) Sun, D.; Ke, Y.; Mattox, T. M.; Parkin, S.; Zhou, H.-C. *Inorg. Chem.* **2006**, *45*, 7566. (b) Zhao, D.; Yuan, D. Q.; Sun, D. F.; Zhou, H.-C. *J. Am. Chem. Soc.* **2009**, *131*, 9186.

(7) (a) Chen, B. L.; Eddaoudi, M.; Hyde, S. T.; O'Keeffe, M.; Yaghi, O. M. *Science* **2001**, *291*, 1021. (b) Sun, D.; Ma, S.; Ke, Y.; Collins, D. J.; Zhou, H.-C. *J. Am. Chem. Soc.* **2006**, *128*, 3896.

(8) (a) Shekhah, O.; Wang, H.; Paradinis, M.; Ocal, C.; Schupbach, B.; Terfort, A.; Zacher, D.; Fischer, R. A.; Woll, C. *Nat. Mater.* **2009**, *8*, 481. (b) Ma, L. Q.; Lin, W. B. *J. Am. Chem. Soc.* **2008**, *130*, 13834. (c) Ma, S.; Sun, D.; Ambrogio, M.; Fillinger, J. A.; Parkin, S.; Zhou, H.-C. *J. Am. Chem. Soc.* **2007**, *129*, 1858. (d) Wang, Q.; Zhang, J. Y.; Zhuang, C. F.; Tang, Y.; Su, C. Y. *Inorg. Chem.* **2009**, *48*, 287.

(9) Rosi, N. L.; Kim, J.; Eddaoudi, M.; Chen, B. L.; O'Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* **2005**, *127*, 1504.

Scheme 1. Schematic Representation of the Interpenetrating Net (Left) and the Noninterpenetrating Net Constructed with an Organic Ligand with a Large Steric-Hindrance Group (Right)



reported by the Zaworotko group,¹⁰ and control over catenation via the rational design of an organic building block has also been reported by Hupp and co-workers.¹¹ Control over interpenetration in lanthanide–organic frameworks has never been explored, although many lanthanide–organic frameworks have been widely reported.^{12–14} In this Communication, we mainly focus on the construction of porous lanthanide–organic frameworks, $\text{Er}_2(\text{BDC})_3(\text{phen})_2 \cdot 3\text{H}_2\text{O}$ (**3**), $\text{Tm}_2(\text{TBDC})_3(\text{DMF})_2(\text{H}_2\text{O})_2 \cdot 4\text{H}_2\text{O}$ (**4**; DMF = *N,N*-dimethylformamide), and $\text{Er}_2(\text{TBDC})_3(\text{phen})_2 \cdot 4\text{DMF} \cdot 2\text{H}_2\text{O}$ (**5**), through control over the interpenetrating nets, $\text{Ln}(\text{BDC})_{1.5}(\text{DMF})(\text{H}_2\text{O})$ [$\text{Ln} = \text{Er}$ (**1**), Tm (**2**)], via the first strategy mentioned above.

The solvothermal reaction of 1,4-benzenedicarboxylic acid (H_2BDC) and $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$ or $\text{Tm}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ in DMF/EtOH/ H_2O resulted in the formation of a large amount of prismatic crystals of **1** or **2**. Single-crystal X-ray diffraction reveals that complexes **1** and **2** are isostructural and both crystallize in triclinic space group $P\bar{1}$. The following discussions on the structural aspects will mainly be focused on complex **1**. The asymmetric unit of **1** consists of one erbium ion, three halves of BDC ligands, one coordinated DMF molecule, and one coordinated H_2O molecule. The central erbium ion is eight-coordinated by six oxygen atoms from different BDC ligands, two oxygen atoms from one coordinated DMF molecule, and one coordinated H_2O molecule with an average Er–O distance of 2.366(3) Å. Two erbium ions are bridged by two carboxylate groups to generate a binuclear SBU, which is further coordinated by four carboxylate groups from different BDC ligands in a chelating mode. Thus, the binuclear SBUs are further bridged by BDC ligands in different directions to give rise to a 3D porous framework containing 3D channels. The dimensions of the channels are 11.3×14.7 Å. Because of the existence of large channels in **1**, the final structure is a 2-fold interpenetrating framework. Two such porous nets interpen-

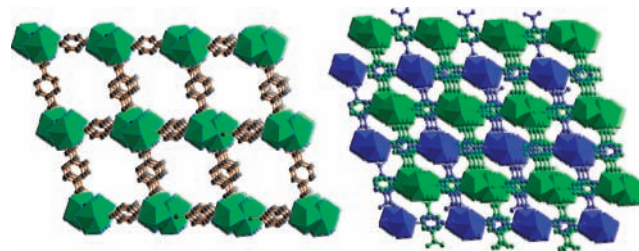


Figure 1. Single net (left) and the 2-fold interpenetrating net (right) of complex **1** along the [1 0 1] direction.

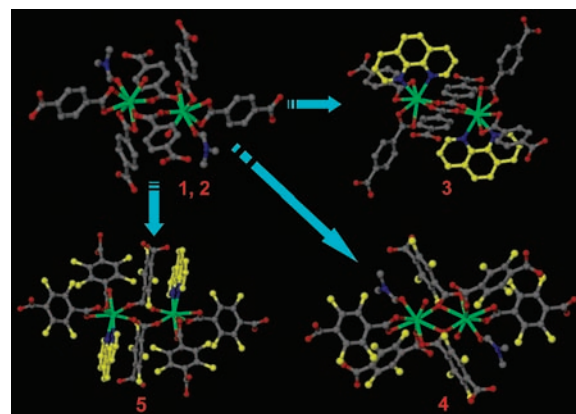


Figure 2. Binuclear SBUs in complexes **1–5** showing coordination environments similar to those of the erbium or thulium ions. The atoms with yellow color in complexes **3–5** represent the hindrance groups to prevent the formation of interpenetrating nets.

trate each other, providing a 3D nonporous framework (Figure 1). If the binuclear SBU can be considered as a single node and the BDC ligand as a linear linker, then complex **1** would be a 2-fold interpenetrating pcu net.

Interpenetration in **1** has limited porosity and application such as in gas storage, etc. To improve the porosity of the framework, the key is to control interpenetration to construct a noninterpenetrating MOF. Interpenetration may derive from the existence of large channels without any sustenance.¹⁵

After careful analysis of the structure of **1**, we found that the coordinated H_2O and DMF molecules locate in a position adjacent to the $\text{O}_{\text{H}_2\text{O}}\text{--Er--O}_{\text{DMF}}$ angle of 78.56° . Hence, to control interpenetration, the following strategies can be achieved: (i) replacing the coordinated solvates by other chelating ligands such as phen, (ii) replacing the BDC ligand by another analogical ligand with a hindrance group, or (iii) their combination.

Thus, the solvothermal reaction of H_2BDC or H_2TBDC and $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$ or $\text{Tm}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ in DMF/EtOH/ H_2O gave rise to complexes **3–5** (Figure 2). Compared to complex **1**, complex **3** is synthesized by replacing coordinated DMF and H_2O molecules in complex **1** with chelating phen ligands, and complex **4** is based on H_2TBDC , instead of H_2BDC , but the coordinated solvates are unchanged, while in complex **5**, both H_2BDC and coordinated solvates are replaced by H_2TBDC and chelating phen ligands, respectively. Complexes **3–5** possess the same topology with complex **1**, but no interpenetrating frameworks. The following discussions on the structural aspects will mainly be focused on complex **5**.

(10) Zhang, J. J.; Wojtas, L.; Larsen, R. W.; Eddaoudi, M.; Zaworotko, M. J. *J. Am. Chem. Soc.* **2009**, *131*, 17040.

(11) Farha, O.; Malliakas, C. D.; Kanatzidis, M. G.; Hupp, J. T. *J. Am. Chem. Soc.* **2010**, *132*, 950.

(12) (a) Chen, X.-Y.; Zhao, B.; Shi, W.; Xia, J.; Cheng, P.; Liao, D.-Z.; Yan, S.-P.; Jiang, Z.-H. *Chem. Mater.* **2005**, *17*, 2866. (b) de Lill, D. T.; Cahill, C. L. *Chem. Commun.* **2006**, 4946. (c) Liang, Y.; Cao, R.; Su, W.; Hong, M.; Zhang, W. *Angew. Chem., Int. Ed.* **2000**, *112*, 3442.

(13) (a) Zhao, X.; Zhu, G.; Fang, Q.; Wang, Y.; Sun, F.; Qiu, S. *Cryst. Growth Des.* **2009**, *9*, 737. (b) Huang, W.; Wu, D.; Zhou, P.; Yan, W. B.; Guo, D.; Duan, C. Y.; Meng, Q. J. *Cryst. Growth Des.* **2009**, *9*, 1361. (c) Zhou, Y. F.; Jiang, F. L.; Yuan, D. Q.; Wu, B. L.; Wang, R. H.; Lin, Z. Z.; Hong, M. C. *Angew. Chem., Int. Ed.* **2004**, *43*, 5665.

(14) (a) Luo, J.; Xu, H.; Liu, Y.; Zhao, Y.; Daemen, L. L.; Brown, C.; Timofeeva, T. V.; Ma, S.; Zhou, H.-C. *J. Am. Chem. Soc.* **2008**, *130*, 9626. (b) Ma, S. Q.; Wang, X. S.; Yuan, D. Q.; Zhou, H.-C. *Angew. Chem., Int. Ed.* **2008**, *47*, 4130.

(15) Losier, P.; Zaworotko, M. J. *Angew. Chem., Int. Ed.* **1996**, *35*, 2779.

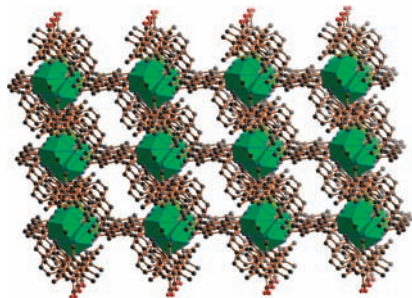


Figure 3. 3D porous framework of **5** along the *c* axis.

The asymmetric unit of **5** consists of one erbium ion, three halves of TBDC ligands, and one coordinated phen molecule. The coordination environment of the central erbium ion remains unchanged with that in complex **1**, except that the two coordinated solvates in complex **1** are replaced by the chelating ligand of phen in complex **2** (Figure 2), with the N–Er–N angle being 65.7° , which is smaller than the $\text{O}_{\text{H}_2\text{O}}\text{--Er--O}_{\text{DMF}}$ angle in complex **1**. The coordination modes of carboxylate groups of TBDC also remain unchanged with those of BDC in complex **1**.

As expected, because of the steric hindrance of the methyl groups in the TBDC ligand as well as the rigid phen ligand, complex **5** is a noninterpenetrating porous framework with the methyl groups of TBDC and the coordinated phen ligand pointing toward the pores to partly block the channels (Figure 3). The resulting dimensions of the channels are 6.9×5.09 , 6.0×5.09 , and 8.1×5.13 Å (from atom to atom) along the $[1\ 0\ 0]$, $[0\ 1\ 0]$, and $[0\ 0\ 1]$ directions, respectively, with a solvent-accessible volume of 38.9% calculated with PLATON.

In order to check the permanent porosity of complex **5**, various gas-adsorption studies have been performed (Figure 4). The gas-adsorption behaviors of the activated complex **5**, which had been vacuum-dried at 120°C after soaking in methanol, have been studied for N_2 , Ar, and H_2 at 77 K and for CO_2 at 195 K. The N_2 and Ar (kinetic diameter: 3.64 Å for N_2 and 3.54 Å for Ar) sorption isotherms did not indicate any appreciable amount of adsorption, presumably because of the limited pore size. However, the activated complex **5** can adsorb a moderate amount of CO_2 ($51\ \text{cm}^3\ \text{g}^{-1}$) and H_2 ($56\ \text{cm}^3\ \text{g}^{-1}$, 0.49% wt%), with type I behavior. Derived from the CO_2 adsorption data, complex **5** has a Langmuir surface area of $141\ \text{m}^2\ \text{g}^{-1}$. Considering the kinetic diameters of 2.89 Å for H_2 , 3.3 Å for CO_2 , and 3.54 Å for Ar, it can be speculated that the pore opening of activated **5** should fall into the range from 3.3 to 3.54 Å, which only allows CO_2 and H_2 to enter the channels.

In summary, we have synthesized two 3D interpenetrating lanthanide–organic frameworks (**1** and **2**) with pcu nets based on binuclear lanthanide SBUs. By application of steric hindrance effects, three types of porous noninterpenetrating lanthanide–organic frameworks (**3–5**) have been constructed. To the best of our knowledge, this is the first systemic

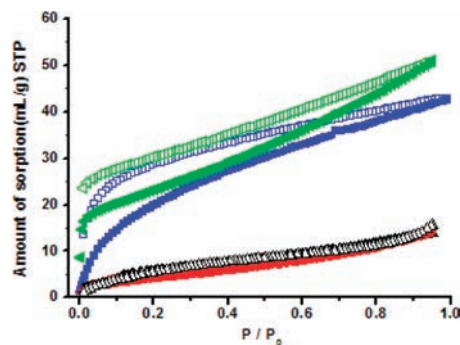


Figure 4. Gas-sorption isotherm of complex **5**: black, N_2 ; red, Ar; green, CO_2 ; blue, H_2 .

research on control over interpenetration in lanthanide–organic frameworks. The results and conclusions of these investigations are summarized as follows: (i) the replacement of 1,4-benzenedicarboxylic acid with its derivative 2,3,5,6-tetramethyl-1,4-benzenedicarboxylic acid containing hindrance groups or coordinated solvates with chelating phen ligands has effectively controlled the interpenetration without changing the original topology; (ii) owing to the use of a carboxylate ligand with a hindrance group and the large terminal ligand in the construction of complex **5**, the pore opening is limited to a narrow scale, which makes complex **5** possess adsorption selectivity of CO_2 and H_2 over N_2 and Ar, although the selectivity is lower compared to other reported results.¹⁶ Our research provides an effective strategy on control over interpenetration in MOFs. In particular, the strategy of using ligands with hindrance groups to block interpenetration may generate porous MOFs with wavy channels and a limited size of free passage, which may possess excellent gas storage capability or selectivity.¹⁷

The gas-adsorption measurement for complexes **3** and **4**, as well as synthesis of other noninterpenetrating lanthanide–organic frameworks with high thermal stability, is currently underway and will be reported in a full paper.

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Supporting Information Available: Experimental procedures and structural figures for all complexes and thermogravimetric analysis and gas-sorption curves. This material is available free of charge via the Internet at <http://pubs.acs.org>.

(16) (a) Li, J.; Kuppler, R.; Zhou, H.-C. *Chem. Soc. Rev.* **2009**, *38*, 1477. (b) Kitaura, R.; Seki, K.; Akiyama, G.; Kitagawa, S. *Angew. Chem., Int. Ed.* **2003**, *42*, 428. (c) Chen, B.; Ma, S.; Zapata, F.; Fronczek, F.; Lobkovsky, E.; Zhou, H.-C. *Inorg. Chem.* **2007**, *46*, 1233.

(17) Chun, H.; Dybtsev, D. N.; Kim, H.; Kim, K. *Chem.—Eur. J.* **2005**, *11*, 3521.