

3D Porous Metal–Organic Framework Exhibiting Selective Adsorption of Water over Organic Solvents

Jin-Zhong Gu,^{†‡} Wen-Guan Lu,[†] Long Jiang,[†] Hong-Cai Zhou,[§] and Tong-Bu Lu^{*†}

MOE Key Laboratory of Bioinorganic and Synthetic Chemistry, State Key Laboratory of Optoelectronic Materials and Technologies, and School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou 510275, China, and Department of Chemistry & Biochemistry, Miami University, Oxford, Ohio 45056, and School of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, China

Received March 13, 2007

A 3D porous metal–organic framework (MOF) with 1D open channels has been constructed hydrothermally using Zn^{II} and a rigid planar ligand IDC³⁻ (imidazole-4,5-dicarboxylate). This MOF can adsorb water selectively over organic solvents and can be regenerated and reused. It also represents a rare example of a MOF with open channels that form/collapse reversibly upon hydration/dehydration.

In the past decade, much attention has been given to the design and synthesis of porous metal–organic frameworks (MOFs), owing to their potential applications in ion exchange,¹ gas adsorption/separation,^{2,3} and catalysis.⁴ One of the major hurdles in the construction of such porous materials is the prevention of interpenetration. The use of large secondary building units as vertices has proven to be beneficial.² Recently, we have demonstrated that a rigid planar ligand containing multiple coordination sites, imidazole-4,5-dicarboxylate (IDC³⁻), is effective in promoting non-interpenetrated MOFs.^{5a,b} We and others have used IDC³⁻ to construct a series of porous MOFs with a variety of metal ions.^{4d,5} In our continuing effort to construct porous

MOFs using the IDC³⁻ ligand, a new MOF, namely, [Zn₆(IDC)₄(OH)₂(Hprz)₂]_n (**1**), was obtained. MOF **1** can adsorb water selectively over organic solvents and can be regenerated and reused.^{3p,6} It also represents a rare example of a MOF with open channels that form/collapse reversibly upon hydration/dehydration.

A hydrothermal reaction of Zn(NO₃)₂·6H₂O, H₃IDC, prz (prz = piperazine), and water under 180 °C for 2 days gave pale-yellow needle-shaped crystals of **1**·13H₂O in 60% yield.⁷ An X-ray crystallographic study⁸ reveals that **1** crystallizes in *P*2₁/*n*. As shown in Figure 1, there exist three symmetry-independent Zn²⁺ ions in **1**. Each Zn²⁺ is five-coordinated in a slightly distorted trigonal-bipyramidal coordination

* To whom correspondence should be addressed. E-mail: lutongbu@mail.sysu.edu.cn.

[†] Sun Yat-Sen University.

[‡] Lanzhou University.

[§] Miami University.

- (1) (a) Manos, M. J.; Iyer, R.; Quarez, G. E.; Liao, J. H.; Kanatzidis, M. G. *Angew. Chem., Int. Ed.* **2005**, *44*, 3552. (b) Trikalitis, P. N.; Rangan, K. K.; Bakas, T.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **2002**, *124*, 12255.
- (2) (a) Rowsell, J. L. C.; Yaghi, O. M. *J. Am. Chem. Soc.* **2006**, *128*, 1304. (b) Sudik, A. C.; Millward, A. R.; Ockwig, N. W.; Cote, A. P.; Kim, J.; Yaghi, O. M. *J. Am. Chem. Soc.* **2005**, *127*, 7110. (c) Rosi, N. L.; Eckert, J.; Eddaoudi, M.; Vodak, D. T.; O’Keeffe, M.; Yaghi, O. M. *Science* **2003**, *300*, 1127. (d) Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; O’Keeffe, M.; Yaghi, O. M. *Science* **2002**, *295*, 469. (e) Férey, G.; Mellot-Draznieks, C.; Serre, C.; Millange, F. *Acc. Chem. Res.* **2005**, *38*, 217. (f) Férey, G.; Mellot-Draznieks, C.; Serre, C.; Millange, F.; Dutour, J.; Surblé, S.; Margiolaki, I. *Science* **2005**, *309*, 2040. (g) Férey, G.; Serre, C.; Mellot-Draznieks, C.; Millange, F.; Surblé, S.; Dutour, J.; Margiolaki, I. *Angew. Chem., Int. Ed.* **2004**, *43*, 6296.

- (3) (a) Kitagawa, S. *Nature* **2006**, *441*, 584. (b) Uemura, T.; Hoshino, Y.; Kitagawa, S. *Chem. Mater.* **2006**, *18*, 992. (c) Spencer, E. C.; Howard, J. A. K.; McIntyre, G. J. *Chem. Commun.* **2006**, 278. (d) Kitagawa, S.; Noro, S.; Nakamura, T. *Chem. Commun.* **2006**, 701. (e) Latroche, M.; Surble, S.; Serre, C.; Mellot-Draznieks, C.; Llewellyn, P. L.; Lee, J. H.; Chang, J. S.; Jung, S. H.; Férey, G. *Angew. Chem., Int. Ed.* **2006**, *45*, 8227. (f) Llewellyn, P. L.; Bourrelly, S.; Serre, C.; Filinchuk, Y.; Férey, G. *Angew. Chem., Int. Ed.* **2006**, *45*, 7751. (g) Surble, S.; Millange, F.; Serre, C.; Duren, T.; Latroche, M.; Bourrelly, S.; Llewellyn, P. L.; Férey, G. *J. Am. Chem. Soc.* **2006**, *128*, 14889. (h) Loiseau, T.; Lecroq, L.; Volklinger, C.; Marrot, J.; Férey, G.; Haouas, M.; Taulelle, F.; Bourrelly, S.; Llewellyn, P. L.; Latroche, M. *J. Am. Chem. Soc.* **2006**, *128*, 10223. (i) Wang, X. S.; Ma, S. Q.; Sun, D. F.; Parkin, S.; Zhou, H. C. *J. Am. Chem. Soc.* **2006**, *128*, 16475. (j) Ma, S. Q.; Zhou, H. C. *J. Am. Chem. Soc.* **2006**, *128*, 11734. (k) Sun, D. F.; Ma, S. Q.; Ke, Y. X.; Collins, D. J.; Zhou, H. C. *J. Am. Chem. Soc.* **2006**, *128*, 3896. (l) Sun, D. F.; Ke, Y. X.; Mattox, T. M.; Ooro, B. A.; Zhou, H. C. *Chem. Commun.* **2005**, 5447. (m) 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. (n) Kubota, Y.; Takata, M.; Matsuda, R.; Kitaura, R.; Kitagawa, S.; Kato, K.; Sakata, M.; Kobayashi, T. C. *Angew. Chem., Int. Ed.* **2005**, *44*, 920. (o) Kitagawa, S.; Uemura, K. *Chem. Soc. Rev.* **2005**, *34*, 109. (p) Serre, C.; Millange, F.; Thouvenot, C.; Nogues, M.; Marsolier, G.; Louër, D.; Férey, G. *J. Am. Chem. Soc.* **2002**, *124*, 13519.
- (4) (a) Schweiger, M.; Yamamoto, T.; Stang, P. J.; Blaser, D.; Boese, R. *J. Org. Chem.* **2005**, *70*, 4861. (b) Yoshizawa, M.; Kusukawa, T.; Kawano, M.; Ohhara, T.; Tanaka, I.; Kurihara, K.; Niimura, N.; Fujita, M. *J. Am. Chem. Soc.* **2005**, *127*, 2798. (c) Wu, C. D.; Hu, A.; Zhang, L.; Lin, W. B. *J. Am. Chem. Soc.* **2005**, *127*, 8940. (d) Zou, R. Q.; Sakurai, H.; Xu, Q. *Angew. Chem., Int. Ed.* **2006**, *45*, 2542. (e) Pan, L.; Olson, D. H.; Ciemnomolnski, L. R.; Heddy, R.; Li, J. *Angew. Chem., Int. Ed.* **2006**, *45*, 616.

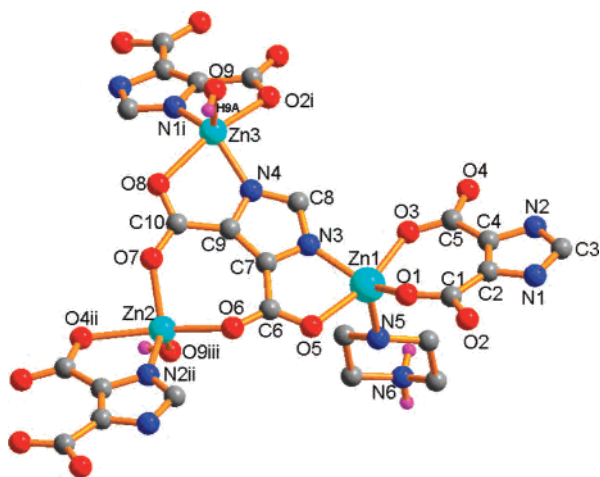


Figure 1. Coordination environments of three Zn^{2+} ions, including $\mu_3\text{-IDC}^{3-}$ and prz in **1**. H atoms and water molecules were omitted for clarity (symmetry code: (i) $-x + 1/2, y + 1/2, -z + 3/2$; (ii) $x - 1, y, z$; (iii) $x - 1/2, -y + 3/2, z - 1/2$).

environment. Zn1 coordinates one N and three O atoms from two discrete $\mu_3\text{-IDC}^{3-}$ ligands and one N atom from the Hprz^+ bridge, with O1, N3, and N5 occupying the equatorial positions and O3 and O5 residing in the axial positions. Zn2 also coordinates one N and three O atoms from two separate $\mu_3\text{-IDC}^{3-}$ ligands and one O atom from a $\mu_2\text{-OH}^-$ bridge, but the atom connectivity is not the same as that of Zn1, with O7, N2ii, and O9iii occupying the equatorial positions and O4ii and O6 sitting on the axial positions. Zn3 coordinates two N and two O atoms from two distinct $\mu_3\text{-IDC}^{3-}$ ligands and one O atom from a $\mu_2\text{-OH}^-$ bridge, with

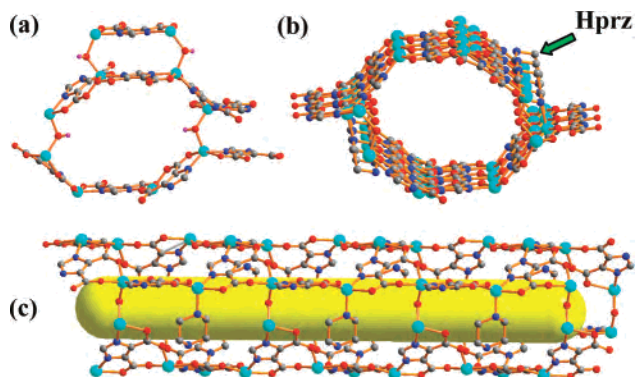


Figure 2. (a) Large $[\text{Zn}_8(\text{IDC})_6(\text{OH})_2]$ ring and small $[\text{Zn}_4(\text{IDC})_2(\text{OH})_2]$ ring. (b) View of an open channel down the a axis. (c) View of the open channel along the b axis (the yellow bar represents free space inside the open channel).

N4, O9, and N1i occupying the equatorial positions and O8 and O2i dwelling in the axial positions. In all three symmetry-independent Zn^{II} atoms, the axial Zn–O bonds are longer than the equatorial Zn–O and Zn–N bonds. Each $\mu_2\text{-OH}^-$ anion bridges two Zn^{II} ions, with the distances and an angle of $1.935(5)\text{--}1.936(5)\text{ \AA}$ and $120.9(2)^\circ$, respectively. Each $\mu_3\text{-IDC}^{3-}$ connects three Zn^{II} in a symmetrical coordination mode with a pseudo- C_2 axis going through Zn2 and C8.

As shown in Figure 2a, eight Zn^{II} ions, six $\mu_3\text{-IDC}^{3-}$ ligands, and two $\mu_2\text{-OH}^-$ bridges form a large $[\text{Zn}_8(\text{IDC})_6(\text{OH})_2]$ ring, and four Zn^{II} ions, two $\mu_3\text{-IDC}^{3-}$ ligands, and two $\mu_2\text{-OH}^-$ bridges form a small $[\text{Zn}_4(\text{IDC})_2(\text{OH})_2]$ ring. The rings are further connected by the coordination interactions of the $\mu_3\text{-IDC}^{3-}$ ligands and Zn^{II} ions to generate a novel MOF containing nanotubular open channels as shown in Figure 3. Parts b and c of Figure 2 show the framework structure surrounding a single tubular channel. The tubular channel extends along the a axis, with a 2_1 axis going through the center of each channel. The Hprz^+ cations are located within the wall of the channel (Figures 2b and 3a), and the protonated N atom of each Hprz^+ points toward the open channel, which may serve as potential acidic catalytic sites. The dimension of each channel is $9.38 \times 9.67\text{ \AA}$ measured by atom-to-atom distances ($\text{H9}\cdots\text{H9}^a = 9.38$, $\text{C1}\cdots\text{C4}^b = 9.67\text{ \AA}$, $a = -x, 1 - y, 2 - z$, $b = 1 - x, 1 - y, 2 - z$). The channels are filled with guest water molecules interacting with the $\mu_2\text{-OH}^-$ bridge and the NH group of Hprz^+ on the surface of the channel through hydrogen bonding (Figure S1 in the Supporting Information).

A solid of **1** displays a strong ligand-to-metal charge-transfer^{5b} photoluminescence emission band at 573 nm at room temperature (Figure S2 in the Supporting Information). A thermal gravimetric analysis (TGA) study (Figure S3 in the Supporting Information) indicates that **1** loses its water solvates under $100\text{ }^\circ\text{C}$, with the weight loss of 15.9% being consistent with that of the calculated value ($1\cdot 13\text{H}_2\text{O}$, 16.2%). After the loss of water molecules, there is no other weight loss before $340\text{ }^\circ\text{C}$, indicating the presence of a stable dehydrated framework over a wide range of temperatures. X-ray powder diffraction (XRPD) was used to check the structural identity and possible phase transition of the

- (5) (a) Lu, W. G.; Su, C. Y.; Lu, T. B.; Jiang, L.; Chen, J. M. *J. Am. Chem. Soc.* **2006**, *128*, 34. (b) Lu, W. G.; Jiang, L.; Feng, X. L.; Lu, T. B. *Cryst. Growth Des.* **2006**, *6*, 564. (c) Fang, R. Q.; Zhang, X. H.; Zhang, X. M. *Cryst. Growth Des.* **2006**, *6*, 2637. (d) Sun, Y. Q.; Zhang, J.; Yang, G. Y. *Chem. Commun.* **2006**, 4700. (e) Li, C. J.; Hu, S.; Li, W.; Lam, C. K.; Zheng, Y. Z.; Tong, M. L. *Eur. J. Inorg. Chem.* **2006**, 1931. (f) Fang, R. Q.; Zhang, X. M. *Inorg. Chem.* **2006**, *45*, 4801. (g) Majji, T. K.; Mostafa, G.; Chang, H. C.; Kitagawa, S. *Chem. Commun.* **2005**, 2436. (h) Sun, Y. Q.; Zhang, J.; Chen, Y. M.; Yang, G. Y. *Angew. Chem., Int. Ed.* **2005**, *44*, 5814. (i) Wang, Y. L.; Yuan, D. Q.; Bi, W. H.; Li, X.; Li, X. J.; Li, F.; Cao, R. *Cryst. Growth Des.* **2005**, *5*, 1849. (j) Cheng, A. L.; Liu, N.; Zhang, J. Y.; Gao, E. Q. *Inorg. Chem.* **2007**, *46*, 1034. (k) Liu, Y. L.; Kravtsov, V.; Larsen, R.; Eddaoudi, M. *Chem. Commun.* **2006**, 1488. (l) Liu, Y. L.; Kravtsov, V.; Walsh, R. D.; Poddar, P.; Srikanth, H.; Eddaoudi, M. *Chem. Commun.* **2004**, 2806. (m) Brant, J. A.; Liu, Y. L.; Sava, D. F.; Beauchamp, D.; Eddaoudi, M. *J. Mol. Struct.* **2006**, *796*, 160.
- (6) (a) Kitagawa, S.; Kitaura, R.; Noro, S. I. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334. (b) Uemura, K.; Matsuda, R.; Kitagawa, S. *J. Solid State Chem.* **2005**, *178*, 2420. (c) Kitagawa, S.; Uemura, K. *Chem. Soc. Rev.* **2005**, *34*, 109.
- (7) Synthesis of compound **1**: A mixture of $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (0.5 mmol), H_3IDC (0.5 mmol), prz (piperazine; 1.5 mmol), and water (10 mL) was sealed in a 25 mL Teflon-lined stainless steel vessel and heated at $180\text{ }^\circ\text{C}$ for 2 days, followed by cooling to room temperature at a rate of $10\text{ }^\circ\text{C/h}$. Pale-yellow needle-shaped crystals of $\text{1}\cdot 13\text{H}_2\text{O}$ were isolated and washed with distilled water. Yield: 72 mg, 60%. The starting and final pH values of the solutions are 8.5 and 7.5, respectively. Elem. anal. Calcd for $\text{C}_{28}\text{H}_{32}\text{N}_{12}\text{O}_{20}\text{Zn}_6$ ($\text{1}\cdot 2\text{H}_2\text{O}$): C, 26.92; H, 2.58; N, 13.46. Found: C, 27.04; H, 2.85; N, 13.28. IR (KBr, cm^{-1}): ν_{OH} 3391, ν_{NH} 3213, $\nu_{\text{as}}(\text{CO}_2)$ 1583 and 1540, $\nu_s(\text{CO}_2)$ 1476 and 1386.
- (8) Crystal data: $\text{C}_{28}\text{H}_{34}\text{N}_{12}\text{O}_{31}\text{Zn}_6$, $M = 1447.05$, monoclinic, space group $P2_1/n$, $a = 11.690(3)\text{ \AA}$, $b = 17.998(4)\text{ \AA}$, $c = 14.173(3)\text{ \AA}$, $\beta = 111.013(5)^\circ$, $V = 2783.7(11)\text{ \AA}^3$, $Z = 2$, $D_c = 1.726\text{ Mg/m}^3$, $\mu = 2.641\text{ mm}^{-1}$, $F(000) = 1468$. A total of 12 924 reflections collected, 5437 independent reflections ($R_{\text{int}} = 0.0674$) with 3192 [$I > 2\sigma(I)$] observed data, 406 parameters, $R1 = 0.0540$, $wR2 = 0.1328$ [$I > 2\sigma(I)$] and $R1 = 0.1100$, $wR2 = 0.1597$ (all data) with $S = 1.005$.

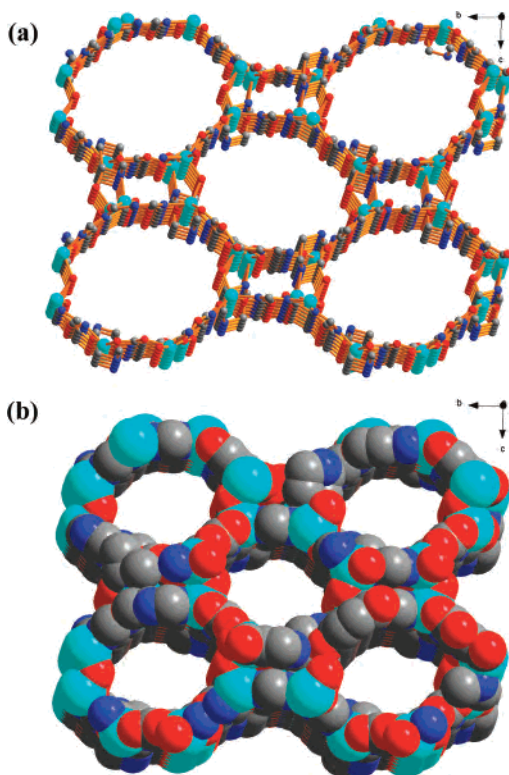


Figure 3. (a) 3D framework of **1**, showing the nanotubular channels along the *a* axis (water molecules and H atoms are omitted for clarity). (b) Space-filling model of the open channels.

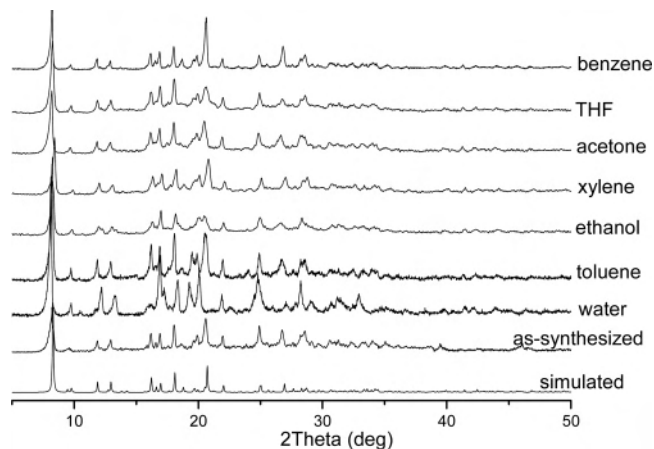


Figure 4. XRPD patterns of simulated, as-synthesized, and immersed dried crystals for 24 h in different solvents.

samples. The measured XRPD pattern closely matches the one simulated from single-crystal diffraction data (Figures 4 and S4 in the Supporting Information), indicating that a single phase of **1** is formed. However, the XRPD patterns at higher temperatures (50–300 °C) are different from those of the as-isolated sample, indicating a structural change upon guest water removal. In addition, a nitrogen adsorption measurement indicates that the dehydrated **1** becomes nonporous after removal of guest water molecules at 120 °C (Figure S5 in the Supporting Information).

To check the adsorption properties of **1** and to examine if the framework can be reversibly formed upon dehydration and hydration, a crystalline sample of **1** was dried under vacuum at 120 °C for 2 h and then immersed in a variety of *wet* solvents (water, ethanol, acetone, tetrahydrofuran, benzene, toluene, and xylene). All of the XRPD patterns are almost the same as those of the as-isolated **1**, indicating the recovery of the original framework after guest molecule adsorption. Elemental analyses, IR spectra, TGA, and TGA-MS measurements all indicate that the adsorbed guest molecules by dehydrated **1** from all of the tested solvents are water molecules (see the Supporting Information). The maximum number of adsorbed water molecules by a $[\text{Zn}_6(\text{IDC})_4(\text{OH})_2(\text{Hprz})_2]$ unit is 14 (17.2%). In the meantime, the water contents of the tested organic solvents were reduced after treatment with a dehydrated sample of **1** (see the Supporting Information), demonstrating that the dehydrated sample **1** can selectively adsorb water over organic solvents. This can be ascribed to the highly hydrophilic nature of **1** with its channel wall being built mainly from $\mu_2\text{-OH}^-$, Hprz^+ , and $\mu_3\text{-IDC}^{3-}$ groups (Figures 3 and S1 in the Supporting Information). The desorption/adsorption experiments can be repeated many times, indicating that the framework of **1** is resilient toward dehydration/hydration. Although 3D porous MOFs similar to that of **1** have also been constructed with other rigid planar ligands containing multiple coordination sites,⁹ their 3D frameworks remain after guest removal. Compound **1** represents a rare example of a MOF with open channels that form/collapse reversibly upon hydration/dehydration. It can be used as a desiccant that adsorbs water molecules very selectively. Compared to traditional molecular sieves that are widely used as desiccants for organic solvents, **1** possesses the following advantages: first, the adsorbed water molecules can be removed under relatively lower temperatures and, second, **1** can selectively adsorb water molecules over organic solvents.

Acknowledgment. This work was supported by the National Science Fund for Distinguished Young Scholars of China (Grant 20625103), NSFC (Grant 20371051), NSF of Guangdong Province (Grant 04205405), and the U.S. NSF (Grant CHE 0449634 to H.-C.Z.). We thank Li Gong and Jian Chen for assistance with TGA-MS measurements.

Supporting Information Available: X-ray crystallographic file in CIF format, complementary drawings, selected bond distances and angles, TGA, XRD patterns, nitrogen isotherm, and adsorption water experiments from organic solvents. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC7004908

(9) (a) Su, C. Y.; Goforth, A. M.; Smith, M. D.; Pellechia, P. J.; zur Loye, H. C. *J. Am. Chem. Soc.* **2004**, *126*, 3576. (b) Zhao, B.; Cheng, P.; Chen, X. Y.; Cheng, C.; Shi, W.; Liao, D. Z.; Yan, S. P.; Jiang, Z. H. *J. Am. Chem. Soc.* **2004**, *126*, 3012.