Design and Synthesis of 3d−4f Metal-Based Zeolite-type Materials with a 3D Nanotubular Structure Encapsulated "Water" Pipe

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The enormous current interest in designing and fabricating 3D metal-based coordination polymers with larger pores by self-assembly has been strongly stimulated by not only their impressive topological structures that are similar to those of zeolite-type materials, but also by versatile applications in the areas of gas storage, molecular sieves, and ion-exchange.[1] As a result, many spectacular porous 3D coordination polymers have been well documented.[1−4] However, the metals involved in these polymers focused mostly on the 3d block, and only three examples of zeolite-type complexes with 3d−4f heterometals including our previous work have been reported.[2] The preparation of 3d−4f metal-based zeolite-type materials has been a great challenge for the following reasons: (a) the variable and versatile coordination behavior of 4f metals frequently causes lattice interpenetration and, consequently, makes coordination polymers with no pores; (b) low stereochemical preferences for lanthanide limit their selective introduction into a highly ordered high dimensional structure; and (c) competitive reactions between 3d and 4f metals chelated to the same ligand often result in homometallic complexes rather than 3d−4f hetero-metallic ones. Here, we report how the 1D ladder-like mixed-metal polymer $\{[Yb(PDA)_3Mn_{1.5}(H_2O)_6]\cdot 6H_2O\}_n$ (1) (PDA = pyridine-2,6-dicarboxylic acid anion) can be transformed into a nanotubular 3D heterometallic zeolite-type complex $\{[Yb(PDA)_3Mn_{1.5}(H_2O)_3]\cdot 1.5H_2O\}_n$ (2) by simply controlling the number of coordinated water molecules without the aid of any auxiliary ligand.[5] To our knowledge, this is the first example of coordinated water tuned self-assembly of 3d−4f metal-based polymers from a 1D ladder to a 3D porous motif. The water molecules trapped within the nanotube were arranged into an unprecedented "water" pipe. Most importantly, the robust 2 retained intact networks after the removal of the guest water trapped in the nanotubes and after methanol replaced the guest water.

Indeed, the synthetic strategy employed for 2 was triggered and further designed only after complex 1 had been structurally characterized (Scheme 1). By taking into account the four water molecules and the two carboxyl O atoms coordinated to the Mn^{2+} in 1 (Figure 1), we wondered whether 1 could be transformed into a more interesting and different structure by decreasing the number of water molecules located on the Mn ion. The next problem was how to control the amount of coordinated water around the Mn^{2+}.

From the entropic point of view, synthesis at a higher temperature could reduce terminal ancillary ligands, such as water or other solvent molecules, and result in the formation of polymer frame-works with higher dimensionality.[1c] Using this idea, hydrothermal synthesis was used on the reagent system of complex 1, and, unexpectedly, a highly ordered nanoporous 3D complex 2 was formed. As compared to 1, the number of coordinated water molecules on the Mn^{2+} in 2 decreased from 4 to 2. This subtle divergence caused a significant difference in the structures.
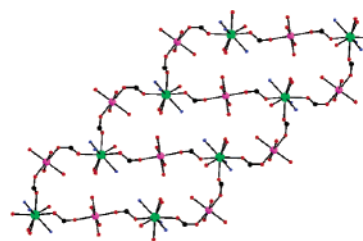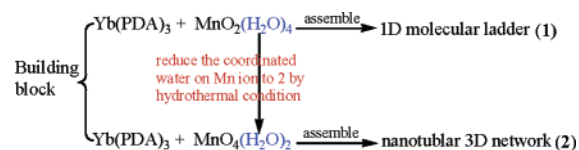

Figure 1. The subunit of a 32-membered square lattice with $Yb_4Mn_4C_8O_{16}$ and 1D molecular ladder motifs in 1; the carbon atoms in the pyridine ring and the H atoms were omitted for clarity. Yb, green; Mn, purple; C, black; O, red; N, blue.

Scheme 1

The crystal structure[6] of 1 is assembled from two distinct types of building blocks, $Yb(PDA)_3$ and $MnO_2(H_2O)_4$. The Yb ion coordinates to three PDA anions, which are tridentate (ONO) with each carboxy group attached by one oxygen atom. The three N atoms and six carboxylic O atoms complete the coordination sphere of the Yb^{3+}, which conforms most closely to a tricapped trigonal prism. Four water molecules and two carboxylic O atoms form the slightly distorted octahedral environment of the Mn ion. Each PDA anion has an identical coordination mode, chelated to one Yb atom and linked to only one Mn atom. Thus, each Yb^{3+} is surrounded by three Mn^{2+} as the nearest neighbors, while each Mn^{2+} has two Yb^{3+} in its vicinity (Figure 1), which is consistent with the Mn/Yb molar ratio. Yb and Mn atoms alternate and are linked by carboxy groups to construct a 32-membered square lattice of $Yb_4Mn_4C_8O_{16}$. This lattice as a subunit, which consists of an octanuclear 3d−4f metal macrocycle, is extremely rare,[7] and it further assembles into an infinite 1D molecular ladder.

As mentioned above, complex 2[8] was crystallized under hydro-thermal conditions based on the reagents of 1. 2 is fabricated from two types of building blocks, $Yb(PDA)_3$ and $MnO_4(H_2O)_2$. The coordination environment of Yb^{3+} is the same as that of 1, whereas the coordination sphere of the Mn^{2+} is completed by four carboxyl O atoms and two water molecules. The subtle distinction in the building blocks between 1 and 2 resulted in the fascinating topological structure of 2, which exhibits nanotubular 3D networks (Figure 2a) rather than the 1D ladder of 1. Each PDA anion chelated to Yb^{3+} also bonds to two Mn^{2+} through carboxyl O bridges. Thus, six Mn^{2+} exist around one Yb^{3+} as the nearest neighbors, whereas each Mn^{2+} has four Yb^{3+} in its vicinity.

The adjacent Yb and Mn atoms are connected by carboxyl bridges, and, most importantly, each carboxy group also bridges
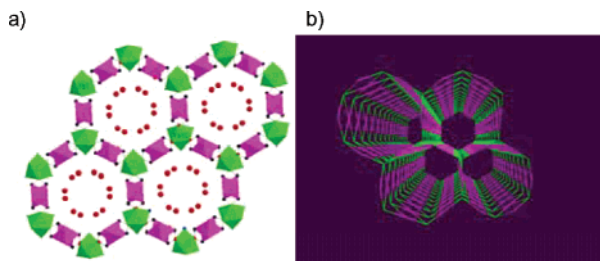
Figure 2. (a) The [Yb$_6$Mn$_6$] section structures of a nanotube with C_6 symmetry and a "water" pipe within the nanotube. The carbon atoms in the pyridine ring and the H atoms were omitted for clarity. (b) Perspective of the nanotube in **2**, showing the square [Yb$_2$Mn$_2$] unit in the wall of the nanotube. The lines between the Yb and Mn atoms stand for carboxyl bridges. Yb, green; Mn, purple; O, red.
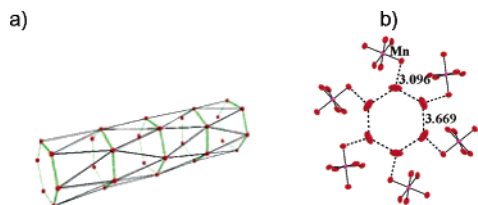

Figure 3. (a) Side view of a "water" pipe in a nanotube with C_6 symmetry. (b) The distance between the adjacent water in the nanotube and hydrogen bonds between the water in the nanotube and the coordinated water on Mn ions. O, red; Mn, purple.

the Mn−OCO−Yb unit, which assembles into the highly ordered 3D structure with a tubular channel of about 17.8 Å diameter (defined by the separation between Yb1 and Yb1D) (Figure 2a). This section of nanotube possesses a C_6 symmetry and displays a dodecanuclear heterometallic macrocycle of Yb$_6$Mn$_6$C$_{12}$O$_{24}$, in which Yb and Mn atoms alternate and are connected via O−C−O bridges. The wall of the nanotube consists of tetranuclear hetero-metallic squares of Yb$_2$Mn$_2$C$_4$O$_8$ (approx 6.0 × 6.0 Å^2) (Figure 2b). Remarkably, the water molecules trapped in the nanotube form a spectacular hollow "water" pipe with a diameter of 7.3 Å (Figure 3a). This section of the pipe consists of six water molecules, which are rigidly coplanar and form a hexagon with equal edge lengths of 3.6 Å. Water hexamers[9a,b] reported previously display a chair configuration rather than plane. The "water" pipe in the nanotube is stabilized by hydrogen bonds between the water molecules in the tube and the coordinated water molecules on the Mn atoms (Figure 3b). Although water polymer encapsulated in the void spaces of coordination polymers has been observed,[9] this kind of "water" pipe in a nanotube based on 3d−4f mixed metals has not been reported.

Thermal gravimetric analyses (TGA) and elemental analyses (EA) of **2** support that, per YbMn$_{1.5}$ unit, **2** adsorbs three water molecules. Further investigation was conducted to determine whether **2** would adsorb other small molecules such as methanol. {[Yb(PDA)$_3$Mn$_{1.5}$(H$_2$O)$_3$]·3CH$_3$OH}$_n$ (**2a**) was obtained by removal of the uncoordinated and adsorbed water in **2** by immersing **2** in methanol for 12 h. This was demonstrated by TGA and EA (see Supporting Information).

We also explored whether the framework would break down on removal of the guest water molecules (uncoordinated and adsorbed H$_2$O) or after the adsorption of methanol. Water molecules can be removed by heating **2** at 120 °C for 12 h. Powder XRD spectra of hydrated and dehydrated **2** as well as **2a** were nearly identical, supporting the idea that the crystal lattice remains intact after the guest water molecules are removed and even after methanol replaces the guest water.

The magnetic susceptibilities measurements show that the $\chi_M T$ values for **1** and **2** at room temperature are 9.04 and 8.97 cm^3 K mol^{-1}, respectively. These are slightly lower than the theoretical value of 9.14 cm^3 K mol^{-1} that is expected for 1.5 isolated Mn^{2+} and 1 Yb ions in the ^{2}F$_{7/2}$ ground state ($g = {}^8/_7$).[10] Although the $\chi_M T$ values for **1** and **2** smoothly decrease on cooling, the nature of the magnetic coupling between adjacent Yb and Mn ions could not be interpreted as an anti-ferromagnetic interaction due to the existence of strong spin−orbit coupling for lanthanide atoms.

In summary, nanotubular **2** was successfully designed and synthesized by simply controlling the amount of coordinated water on the Mn ion in **1** under hydrothermal conditions. As far as we know, this is the first attempt to fabricate 3d−4f heterometallic zeolite-type complexes by this method. These results provide a new route to synthesize porous 3D polymers containing 3d−4f mixed metals and enrich a promising field of lanthanide-transition metal-based zeolitic materials.

Supporting Information Available: Complete experimental procedures and characterization data (PDF and CIF) and plots. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; O'Keeffe, M.; Yaghi, O. M. *Science* **2002**, *295*, 469. (b) Seo, J. S.; Whang, D.; Lee, H.; Jun, S. I.; Oh, J.; Jeon, Y. J.; Kim, K. *Nature* **2000**, *404*, 982. (c) Forster, P. M.; Eckert, J.; Chang, J. S.; Park, S. E.; Férey, G.; Cheetham, A. K. *J. Am. Chem. Soc.* **2003**, *125*, 1309. (d) Aoyagi, M.; Biradha, K.; Fujita, M. *J. Am. Chem. Soc.* **1999**, *121*, 7457.

(2) (a) Zhao, B.; Cheng, P.; Dai, Y.; Cheng, C.; Liao, D. Z.; Yan, S. P.; Jiang, Z. H.; Wang, G. L. *Angew. Chem., Int. Ed.* **2003**, *42*, 934. (b) Ren, Y. P.; Long, L. S.; Mao, B. W.; Yuan, Y. Z.; Huang, R. B.; Zheng, L. S. *Angew. Chem., Int. Ed.* **2003**, *42*, 532. (c) Baggio, R.; Garland, M. T.; Moreno, Y.; Peña, O.; Perec, M.; Spodine, E. *Dalton Trans.* **2000**, 2061.

(3) (a) Carlucci, L.; Ciani, G.; Proserpio, D. M.; Porta, F. *Angew. Chem., Int. Ed.* **2003**, *42*, 317. (b) Carlucci, L.; Ciani, G.; Porta, F.; Proserpio, D. M.; Santagostini, L. *Angew. Chem., Int. Ed.* **2002**, *41*, 1907. (c) Ciurtin, D. M.; Smith, M. D.; zur Loye, H. C. *Chem. Commun.* **2002**, 74. (d) Dong, Y. B.; Smith, M. D.; zur Loye, H. C. *Angew. Chem., Int. Ed.* **2000**, *39*, 4271.

(4) (a) Kitaura, R.; Seki, K.; Akiyama, G.; Kitagawa, S. *Angew. Chem., Int. Ed.* **2003**, *42*, 428. (b) Wang, X.; Liu, L.; Jacobson, A. J. *Angew. Chem., Int. Ed.* **2003**, *42*, 2044. (c) Noro, S.; Kitaura, R.; Kondo, M.; Kitagawa, S.; Ishii, T.; Matsuzaka, H.; Yamashita, M. *J. Am. Chem. Soc.* **2002**, *124*, 2568. (d) Kim, J.; Chen, B. L.; Reineke, T. M.; Li, H. L.; Eddaoudi, M.; Moler, D. B.; O'Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* **2001**, *123*, 8239. (e) Bourne, S. A.; Lu, J. J.; Mondal, A.; Moulton, B.; Zaworotko, M. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 2111.

(5) Syntheses of **1**, **2**: The mixture of Yb(SCN)$_3$·6H$_2$O (0.4 mmol), MnCO$_3$ (0.2 mmol), MnSO$_4$·H$_2$O (0.4 mmol), PDA (0.6 mmol), H$_2$O (6 mL), and ethanol (6 mL) was refluxed for 4 h, and then crystals of **1** were obtained after the filtrate was allowed to stand at room temperature for 2 months. The same mixture was conducted in a 20 mL acid digestion bomb at 155 °C for 3 days. The crystals of **2** were collected after washing by H$_2$O (2 × 5 mL). The yields of **1** and **2** (based on Yb) were 37% and 29%, respectively.

(6) {[Yb(PDA)$_3$Mn$_{1.5}$(H$_2$O)$_6$]·6H$_2$O}$_n$, M_r = 966.95, triclinic, P-1, a = 9.304-(4), b = 12.170(4), c = 16.243(3) Å, α = 104.048(6)°, β = 90.555(5)°, γ = 107.490 (5)°, V = 1694.9(11) Å^3, Z = 2, T = 293 (2) K. R1 = 0.0359 ($I > 2\sigma(I)$). GOF = 1.131.

(7) Guillou, O.; Bergerat, P.; Kahn, O.; Bakalbassis, E.; Boubekeur, K.; Batail, P.; Guillot, M. *Inorg. Chem.* **1992**, *31*, 110.

(8) {[Yb(PDA)$_3$Mn$_{1.5}$(H$_2$O)$_3$]·1.5H$_2$O}$_n$, M_r = 831.84, hexagonal, $P6/mcc$, $a = b$ = 15.440(5), c = 16.254(12) Å, γ = 120°, V = 3356(3) Å^3, Z = 4, T = 293 (2) K, R1 = 0.0503 ($I > 2\sigma(I)$). GOF = 1.093.

(9) (a) Doedens, R. J.; Yohannes, E.; Khan, M. I. *Chem. Commun.* **2002**, 62. (b) Noro, S.; Kitaura, R.; Kondo, M.; Kitagawa, S.; Ishii, T.; Matsuzaka, H.; Yamashita, M. *J. Am. Chem. Soc.* **2002**, *124*, 2568. (c) Custelcean, R.; Afloroaei, C.; Vlassa, M.; Polverejan, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 3094.

(10) Benelli, C.; Gatteshi, D. *Chem. Rev.* **2002**, *102*, 2369.

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