CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200901412

Crown-Ether-Like Pb^{II}-Metal Framework with Dual- and Bimodal Emissive Properties Based on Its Photochromic Precursor by Leaching

You-Yun Jiang, Shu-Kui Ren, Jian-Ping Ma, Qi-Kui Liu, and Yu-Bin Dong*[a]

Owing to their potential as high-performing photochemical and photophysical materials, numerous studies of metal–organic frameworks (MOFs) have been reported.[1] For accessing to the dual (for example green and red emissions) and bimodal emission (UV/Vis and NIR emissions), significant effort has been afforded in design and synthesis of the heterometallic complexes, especially heterolanthanide-based complexes.[2] However, the preparation of f–f and f–d hybrids are very hard due to the inherent difficulty in synthesis of the organic ligands with specific recognizing sites required by the different metal ions.[3]

Motivated by our interest in tunable luminescent host–guest complexes,[4] we have initiated a synthetic program for preparation of the open heteroatom-rich MOFs, in which the flexible open-chain polyether-bridged organic spacers are chosen as the building blocks.[5] The porous metal–organic frameworks containing heteroatom-rich rungs would incorporate electrophilic species into a host–guest system in a crown ether manner. The synthesis of hollow MOFs based on long, flexible, open-chain polyether-bridged ligands, however, is extremely challenging, owing to an unavoidably large amount of framework interpenetration. Herein, we present a new leaching approach to prepare the hollow oxygen-rich frameworks. Our strategy for the construction of hollow oxygen-rich MOFs, lies with the recognition that the MOFs are designed to possess at least two different types of ligands with different coordinating functional groups (for example, with neutral and charged coordination donors) can be used to synthesize mixed-ligand coordination networks. In such a mixed-ligand framework, the weakly coordinating ligands might be selectively leached by solvent; meanwhile the robust joints consisting of stronger coordinating ligands and metal cations are intact. In this paper, we present the first example of such a mixed-ligand (BIPY: 4,4′-bipyridine and **L**:1,5-bis(*m*-carboxyphenoxy)-3-oxapentane) Pb^{II}-framework, furthermore, the hollow oxygen-rich framework $Pb_2\mathbf{L}_2$ by leaching of the coligand of BIPY under reflux in $CDCl_3$. Consequently, the $[Ln(H_2O)_8]^{3+}\subset Pb_2\mathbf{L}_2$ and $[Ln/Ln'(H_2O)_8]^{3+}\subset[Pb_2\mathbf{L}_2]$ ($Ln=Tb^{3+}$; $Ln'=Eu^{3+}$ or Nd^{3+}) host–guest f–d and f–f′–d hybrids were obtained by a reversible $[Ln(H_2O)_8]^{3+}$ encapsulation. As a result, the dual- and bimodal emissions are successfully realized originated from different Ln^{3+} emission colors (Scheme 1).

The flexible open-chain polyether-bridged bicarboxylate **L** and rigid BIPY (Scheme 2) are our ligands of choice for constructing oxygen-rich MOF of **1.** **L** is more extended and flexible than the open-chain polyether-bridged spacer previously reported by us.[5] The three bridging oxygen atoms and the two terminal carboxylate groups on **L** would result in the target oxygen-rich framework (Supporting Information). The complex $[Pb_2\mathbf{L}_2(bipy)]$ (**1**) was obtained as colorless crystals by treatment of $Pb(OAc)_2$ with **L**/BIPY under hydrothermal conditions (180 °C for 70 h) in high yield (93 %). The single-crystal analysis revealed that **1** crystallizes in the monoclinic space group $P2_1/c$. The Pb^{II} center lies in the four-coordinated $\{PbO_4\}$ coordination sphere consisting of four carboxylate O-donors. In addition, the Pb^{II} center still weakly coordinates to the N_{bipy}-donor with a long Pb–N distance of 2.629(7) Å (Scheme 2). As shown in Figure 1, the Pb^{II} centers extend along the crystallographic *b* axis through **L** to form a single-stranded helix with a period of separation of ≈24 Å. All the helices are further linked to each other by the co-ligands of BIPY to generate a "double-edged" parquet-like net[6] in the crystallographic *bc* plane, in which the right- and left-handed strands are arranged alternatively. Complex **1** is self-intercalated and 5-fold interpenetrated. When viewed down the crystallographic *c* axis, the rectangular channels are found, in which the BIPY co-ligands are located. The opposite oxygen distances in the channel are

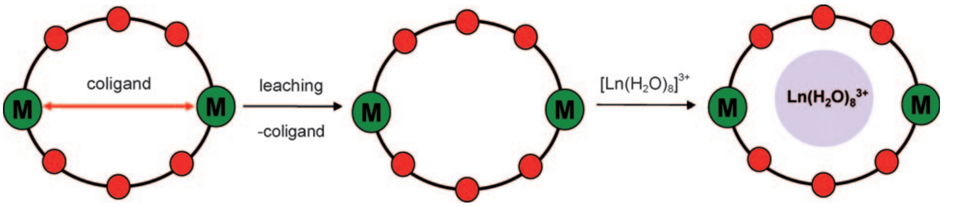
---

[a] Y.-Y. Jiang, S.-K. Ren, J.-P. Ma, Q.-K. Liu, Prof. Dr. Y.-B. Dong
College of Chemistry, Chemical Engineering and
Materials Science, Key Lab of Molecular and Nano Probes
Engineering Research Center of Pesticide and
Medicine Intermediate Clean Production
Ministry of Education, Shandong Normal University
Jinan, 250014 (P. R. China)
Fax: (+86) 531-82615258
E-mail: yubindong@sdnu.edu.cn

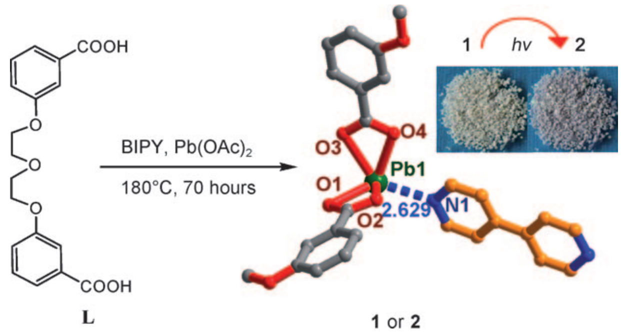
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200901412.

InterScience

© 2009 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



Scheme 1. The synthesis of crown-ether-like, f–d hybrid host–guest system generated from flexible oxygen-rich carboxylate ligand and rigid bipyridyl ligand. The red and green balls represent oxygen atoms and d-metal ions, respectively.



Scheme 2. Synthesis of **1** and **2**.

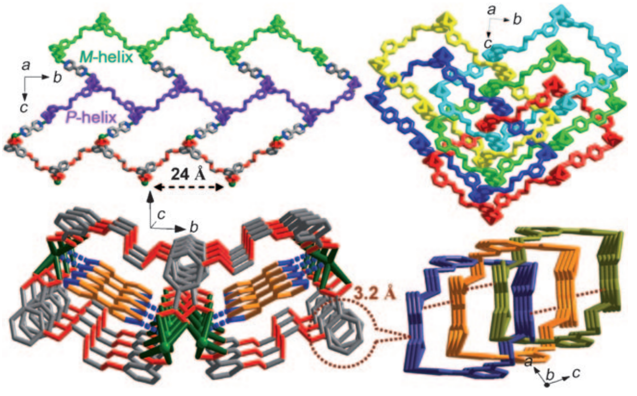


Figure 1. Single 2D and 5-fold interpenetrating network (top) and the π–π interaction-driven channels (bottom) in **1**. The *P* and *M* helices are highlighted in different colors.

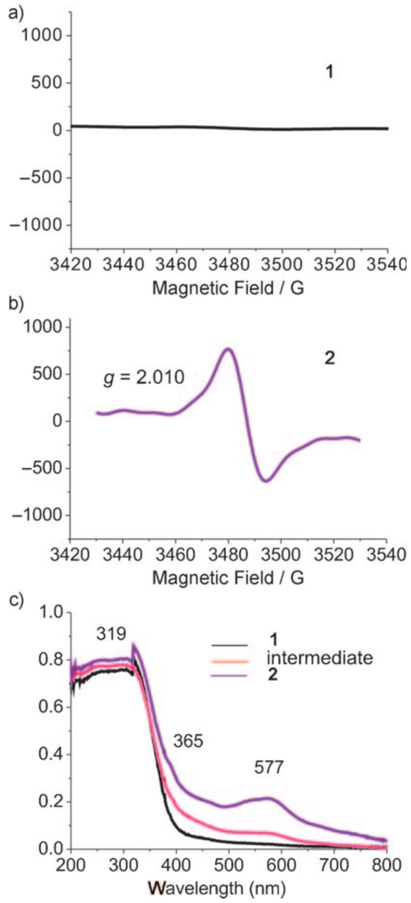


Figure 2. The ESR spectra of a) **1** and b) **2**. c) The UV/Vis spectra of the transition between **1** and **2**.

about 8–11 Å. Notably, the channel-frame is significantly reinforced by the interlayer π–π interactions (Figure 1).

Interestingly, **1** is photochromic. Upon exposure to sunlight (≈2 days), **1** undergoes a radical-based single-crystal-to-single-crystal transformation from the colorless to the purple of **2**. To our knowledge, the photochromic MOFs are very rare.[7] Notably, the structures of **1** and **2** are identical (Supporting Information); confirmed by the single-crystal analysis and IR spectra. However, the variations of the solid-state UV/Vis adsorption and ESR spectra demonstrate the essential difference between **1** and **2**. As shown in Figure 2, the ESR spectrum of **1** shows no signal, but a single peak radical signal appears after irradiation. In the UV/Vis spectra, compound **1** exhibits only one π–π* absorption peak at $\lambda = 319$ nm, while compound **2** presents additional two peaks at $\lambda = 365$ and 577 nm, which are attributed to the purple appearance and the radicals of **2**, respectively. The red trace in the UV/Vis spectrum indicates the solid-state transformation occurred gradually. For confirming of **1** to **2** is a photoinduced process instead of an oxidation process, the crystals of **1** were kept in dark in oxygen, however, no coloration occurred. On the other hand, when the crystals of **1** were kept in an inert atmosphere but exposed to light, the coloration occurred as usual. In addition, no coloration happened by heating the crystals of **1** in either air or inert atmosphere without light.

To explore the origin of the radicals of **2**, a parallel experiment was carried out. When the crystals of **1** were refluxed in $CDCl_3$, the weakly coordinated BIPY was selectively extracted to generate the hollow oxygen-rich framework of **3** (Figure 3). Such selective solid–liquid extraction is equivalent to the wet-chemical etching technique, which is

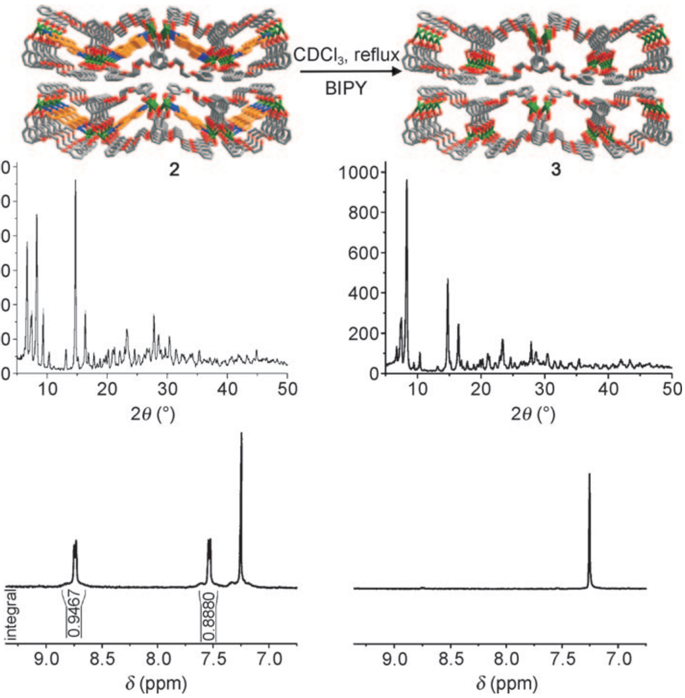


Figure 3. The synthesis of **3** from **2** by leaching and their corresponding XRPD patterns and ^{1}H NMR spectra.

widely used in preparation of the inorganic nano-materials.[8] This leaching process was monitored by ^{1}H NMR spectrum. The XRPD pattern indicates that the framework is maintained upon leaching, which clearly benefits from the strong interchain π–π interactions. The corresponding ESR spectrum of **3**, however, exhibits no signal, which demonstrates the radicals originated from the Pb^{II}-bipy electron transfer (Supporting Information).

As shown above, the encapsulated BIPY can be selectively leached to generate the hollow the oxygen-rich framework of **3**, which contains channels with hydrophilic inner surfaces. The cavity size ($d_{O\cdots O}=8$–11 Å) and hydrophilic nature are perfect for binding $[Ln(H_2O)_8]^{3+}$ species through hydrogen-bonding interactions (Supporting Information).[4] Indeed, when **3** was stirred in an aqueous solution of $Tb(ClO_4)_3$ (excess) for 3 h, the solid-state photoinduced-emission monitoring indicates that the maximal emission intensity of Tb^{3+} was obtained (Figure 4a), which reflects that the absorption of $[Tb(H_2O)_8]^{3+}$ is basically saturated. The ICP (inductively coupled plasma) measurement indicates that the doped amount of Tb^{3+} is 3.24%. Interestingly, the encapsulated $[Ln(H_2O)_8]^{3+}$ can be reversibly displaced. As shown in Figure 4b–c, when the obtained $[Tb(H_2O)_8]^{3+}\subset[Pb_2\mathbf{L}_2]$ was treated with excess of $Eu(ClO_4)_3$ in water for two days, the emission spectrum indicated that the original encapsulated $[Tb(H_2O)_8]^{3+}$ were partially replaced by $[Eu(H_2O)_8]^{3+}$, generating a heterometallic host–guest system $[Tb/Eu(H_2O)_8]^{3+}\subset[Pb_2\mathbf{L}_2]$. The ICP measurement indicates that the doped amount of Tb^{3+} and Eu^{3+} are 2.10 and 4.88%, respectively. As shown in Figure 4b, the corresponding emission intensity originated from Eu^{3+} is stronger than that of Tb^{3+}. On the other hand, when the sample of (b) was treated in water for two days with an excess of Tb^{3+}, the emission intensity of Tb^{3+} recovered, and the emission intensity originated from Eu^{3+} was correspondingly depressed (Figure 4c). Thus, the emission intensities originate from the different lanthanide species and can be tuned by controlling the Eu/Tb displacement. The XRPD monitoring indicates that the original structure remains intact during the displacing course (Supporting Information). By this gust-driven approach, two different lanthanide cations (Eu^{3+} and Tb^{3+}) were successfully incorporated into a single probe host–guest system and afford an interesting dual-emission within the UV/Vis region upon a single excitation wavelength. It is well known that the hydration states of the lanthanide complexes have a very significant effect on their metal-centered luminescent behaviors resulted from the vibrational quenching. The intense emission of $[Ln(H_2O)_8]^{3+}$ herein reasonably indicates that the strong coupling of O–H vibrations on the coordinated water molecules is efficiently reduced within the confining space by the host–guest O–H···O hydrogen-bonding interactions (Supporting Information).[4,9]

Besides UV/Vis emitter, the encapsulated $[Tb(H_2O)_8]^{3+}$ can also be displaced by the NIR-lanthanide emitter such as Nd^{3+}. For example, treatment of $[Tb(H_2O)_8]^{3+}\subset[Pb_2\mathbf{L}_2]$ with an excess of $Nd(ClO_4)_3$ resulted in the formation of heterometallic host–guest system $[Tb/Nd(H_2O)_8]^{3+}\subset[Pb_2\mathbf{L}_2]$. As shown in Figure 5, the typical Nd^{3+} emission bands in the NIR region increased at the expense of Tb^{3+} emission as the reaction going on. The ICP analysis indicates that the adsorbed amount of Nd^{3+} is up to 4.48% and corresponding

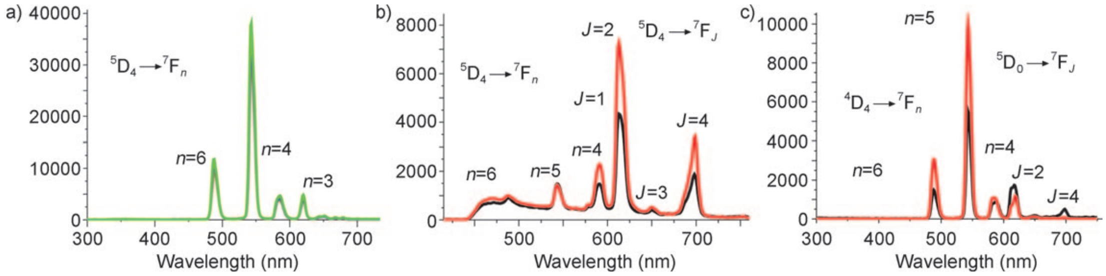


Figure 4. Emission spectra of a) **3** stirred in aqueous solution of $Tb(ClO_4)_3$ taken after 3 h ($\lambda_{ex}=303$ nm); b) sample of a) stirred in aqueous solution of $Eu(ClO_4)_3$ at 1 (black) and 2 (red) days ($\lambda_{ex}=303$ nm); c) sample of b) stirred in aqueous solution of $Tb(ClO_4)_3$ at 1 (black) and 2 (red) days ($\lambda_{ex}=303$ nm).

© 2009 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

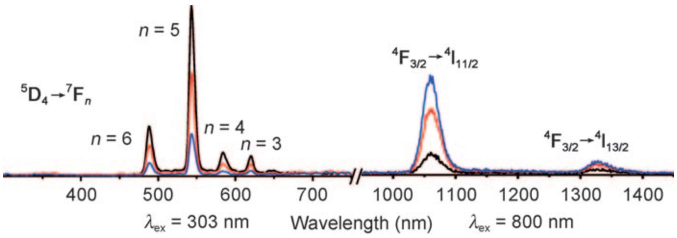


Figure 5. Emission spectra of $[Tb(H_2O)_8]^{3+} \subset [Pb_2\mathbf{L}_2]$ stirred in aqueous solution of $Nd(ClO_4)_3$ at 2 (black), 3 (red) and 4 (blue) days.

residual Tb^{3+} is 1.62 % after four days. Thus, the ion-exchange between Nd^{3+} and Tb^{3+} did lead to the tunable emission between UV/Vis and NIR regions, consequently, the bimodal-emission but excited at different wavelengths. Again, the XRPD monitoring confirms that the original structure remains intact during the reaction course (Supporting Information). The Pb^{II}-polymeric complexes herein are insoluble in water, so the possibility of a dissolution-recrystallization mechanism for explaining such ion-exchange reaction is certainly impossible. In addition, the resulted crystalline $[Ln/Ln'(H_2O)_8]^{3+} \subset [Pb_2\mathbf{L}_2]$ sample was adequately washed by water, EtOH and Et_2O, so the surface adsorption was avoided.

In summary, a crown-ether-like, open Pb^{II}-framework is generated from its photochromic precursor by a leaching approach. Furthermore, the dual- and bimodal-emission are successfully realized by intercalation of the different Ln^{3+} hydrates based on guest-driven approach. In addition, the results herein demonstrate that the guest species within the confining space exhibit the different behaviors from that of unconfined state.[10] We believe that this method can be applied to other coordination frameworks and can give rise to new hollow heteroatom-rich MOFs, which are not easy obtained by the common synthetic methods.

Experimental Section

Synthesis of L: A mixture of corresponding polyether-bridged bisbenzaldehyde (1.256 g, 4.0 mmol) and $AgNO_3$ (2.58 g, 15 mmol) was stirred in a NaOH (7 %) aqueous solution at 80 °C for 24 h. After neutralization by HCl, the product was obtained as white solids (85 %). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 12.99$ (s, 2 H, -COOH), 7.53–7.50 (d, 2 H, $-C_6H_4-$), 7.43–7.36 (m, 4 H, $-C_6H_4-$), 7.19–7.17 (d, 2 H, $-C_6H_4-$), 4.17 (s, 4 H, $-OCH_2CH_2O-$), 3.84 ppm (s, 4 H, $-OCH_2CH_2O-$); IR (KBr pellet): $\tilde{\nu} = 2956$(w), 2360(w), 1743(s), 1604(s), 1488(s), 1458(s), 1391(s), 1297(s), 1223(s), 1168(m), 1138(s), 1092(m), 1039(s), 939(s), 910(m), 870(w), 832(w), 750(s), 690(s), 646(m), 525 cm^{-1} (w); elemental analysis (%) calcd for $C_{22}H_{14}N_4O_2$: C 62.43, H 5.20; found: C 62.64, H 5.54.

Synthesis of $[Pb_2L_2(bipy)]$ (1) and (2): **L** (6.0 mg, 0.017 mmol), $Pb(OAc)_2$ (9.7 mg, 0.026 mmol), 4,4′-bipyridine (5.3 mg, 0.034 mmol) and water (2 mL) were sealed in a 5 mL glass tube. The mixture was heated at 180 °C for 70 h under autogenous pressure. After the mixture was allowed to cool to room temperature (40 h), colorless cubic crystals were isolated from the tube in 93 % yield. IR (KBr pellet): $\tilde{\nu} = 2915$(w), 2866(w), 1600(vs), 1538(vs), 1489(s), 1437(s), 1390(vs), 1281(s), 1239(s), 1143(m), 1120(m), 1079(m), 1060(s), 1024(w), 998(w), 964(m), 926(w), 904(w), 881(m), 864(m), 793(s), 763(vs), 676(s), 620(s), 412 cm^{-1} (w); elemental analysis (%) calcd for $C_{46}H_{40}N_2O_{14}Pb_2$: C 43.88, H 2.97, N 2.22; found: C 43.73, H 2.78, N 2.35. When **1** was exposed to sunlight in air for ≈2 days, compound **2** was generated. The IR spectrum of **2** is the same as that of **1**.

Synthesis of $[Pb_2L_2]$ (3): Complex **2** was refluxed in $CDCl_3$ till the BIPY signals of the $CDCl_3$ extract disappeared from the ^{1}H NMR spectrum, the resultant crystalline solids were collected and washed by water, MeOH and $CDCl_3$, and dried in air. IR (KBr pellet): $\tilde{\nu} = 2919$(w), 2229(w), 1681(w), 1600(w), 1538(s), 1438(m), 1391(s), 1314(w), 1281(w), 1241(m), 1119(w), 1059(w), 1024(w), 965(w), 881(w), 793(w), 763(m), 677(w), 621(w), 466 cm^{-1} (w); elemental analysis (%) calcd for $C_{36}H_{32}O_{14}Pb_2$: C 39.16, H 2.90, N 0.00; found: C 39.08, H 2.85, N 0.07.

Typical ion-exchange reaction: $G1 \subset Ln^{III}{}_2L_4$ (180 mg, $G1 = [Ln(H_2O)_8]^{3+}$) was stirred in an aqueous solution containing excess of G2 ($G2 = Ln'(ClO_4)_3 \cdot 6H_2O$). The resulted crystalline solids were collected and washed by water (5 mL × 4) and EtOH (5 mL × 2), Et_2O (5 mL × 1), and dried in air.

Crystal data for 1: $C_{46}H_{40}N_2O_{14}Pb_2$, monoclinic, $P21/c$, $M_r = 1259.18$, $a = 12.2792(3)$, $b = 24.8799(5)$, $c = 6.9753(2)$ Å, $V = 2117.26(9)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.975$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 8.015$ mm^{-1}, $F(000) = 1212$, $T = 298(2)$ K, $\lambda(Mo_{K\alpha}) = 0.71073$ Å, θmax = 25.50°, Reflections collected/unique: 13688/3947 [$R(int) = 0.1040$], R_1 ($I > 2\sigma(I)$) = 0.0381, wR_2 ($I > 2\sigma(I)$) = 0.0977.

Crystal data for 2: $C_{46}H_{40}N_2O_{14}Pb_2$, monoclinic, $P21/c$, $M_r = 1259.18$, $a = 12.263(16)$, $b = 24.96(3)$, $c = 6.987(9)$ Å, $V = 2124(5)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.968$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 7.988$ mm^{-1}, $F(000) = 1212$, $T = 298(2)$ K, $\lambda(Mo_{K\alpha}) = 0.71073$ Å, θmax = 25.35°, Reflections collected/unique: 10052/3885 [$R(int) = 0.0576$], R_1 ($I > 2\sigma(I)$) = 0.0400, wR_2 ($I > 2\sigma(I)$) = 0.0823. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC- 688537 (**1**) and 688538 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223–336–033; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

We are grateful for financial support from NSFC (Grant Nos. 20871076 and 20671060), Shangdong Natural Science Foundation (Grant No. JQ200803) and Ph.D. Programs Foundation of Ministry of Education of China (Grant No. 200804450001).

Keywords: lanthanides · leaching · lead · metal–organic frameworks · photochromism

---

[1] a) B. Moulton, M. J. Zaworotko, *Chem. Rev.* **2001**, *101*, 1629; b) O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi, J. Kim, *Nature* **2003**, *423*, 706; c) S. Kitagawa, R. Kitaura, S.-I. Noro, *Angew. Chem.* **2004**, *116*, 2388; *Angew. Chem. Int. Ed.* **2004**, *43*, 2334.

[2] a) M. Li, P. Selvin, *J. Am. Chem. Soc.* **1995**, *117*, 8132; b) M. S. Tremblay, D. Sames, *Chem. Commun.* **2006**, 4116; c) S. Faulkner, S. Pope, *J. Am. Chem. Soc.* **2003**, *125*, 10526; d) R. A. Poole, F. Kielar, S. L. Richardson, P. A. Stenson, D. Parker, *Chem. Commun.* **2006**, 4084; e) J.-P. Costes, F. Dahan, A. Dupuis, J.-P. Laurent, *Chem. Eur. J.* **1998**, *4*, 1616.

[3] C. Piguet, J.-C. G. Bünzli, *Chem. Soc. Rev.* **1999**, *28*, 347.

[4] a) Y.-B. Dong, P. Wang, J.-P. Ma, X.-X. Zhao, B. Tang, R.-Q. Huang, *J. Am. Chem. Soc.* **2007**, *129*, 4872; b) P. Wang, J.-P. Ma, Y.-B. Dong, R.-Q. Huang, *J. Am. Chem. Soc.* **2007**, *129*, 10620; c) P. Wang, J.-P. Ma, Y.-B. Dong, *Chem. Eur. J.* **2009**, DOI: 10.1002/chem.200900435.

[5] Y.-B. Dong, Y.-Y. Jiang, J. Li, J.-P. Ma, F.-L. Liu, B. Tang, R.-Q. Huang, S. R. Battern, *J. Am. Chem. Soc.* **2007**, *129*, 4520.

© 2009 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

[6] Y.-B. Dong, R. C. Layland, N. G. Pschirer, M. D. Smith, U. H. F. Bunz, H.-C. zur Loye, *Chem. Mater.* **1999**, *11*, 1413.

[7] M.-S. Wang, G.-C. Guo, W.-Q. Zou, W.-W. Zhou, Z.-J. Zhang, G. Xu, J.-S. Huang, *Angew. Chem.* **2008**, *120*, 3621; *Angew. Chem. Int. Ed.* **2008**, *47*, 3565.

[8] Z. Liu, D. Zhang, S. Han, C. Li, B. Lei, W. Lu, J. Fang, C. Zhou, *J. Am. Chem. Soc.* **2005**, *127*, 7.

[9] K.-L. Wong, G.-L. Law, Y.-Y. Yang, W.-T. Wong, *Adv. Mater.* **2006**, *18*, 1051.

[10] It is well-known that the free $[Ln(H_2O)_8]^{3+}$ species is non-luminescent or weak luminescent. The $[Ln(H_2O)_8]^{3+}$ species within the restricting space herein, however, is strong luminescent because the O−H oscillators in the coordinated water molecules are significantly restricted through the host–guest H-bonding interactions. Several recent examples show that the encapsulated guest species in the restricting space exhibits some unusual properties which are resulted from the intriguing host–guest interactions. See a) D. H. Leung, R. G. Bergman, K. N. Raymond, *J. Am. Chem. Soc.* **2007**, *129*, 2746; b) K. Nakabayashi, Y. Ozaki, M. Kawano, M. Fujita, *Angew. Chem.* **2008**, *120*, 2076; *Angew. Chem. Int. Ed.* **2008**, *47*, 2046; c) S. Hasegawa, S. Horike, R. Matsuda, S. Furukawa, K. Mochizuki, Y. Kinoshita, S. Kitagawa, *J. Am. Chem. Soc.* **2007**, *129*, 2607; d) S. Horike, M. Dincă, K. Tamaki, J. R. Long, *J. Am. Chem. Soc.* **2008**, *130*, 5854; e) C.-D. Wu, A. Hu, L. Zhang, W. Lin, *J. Am. Chem. Soc.* **2005**, *127*, 8940.

Received: May 26, 2009
Published online: September 10, 2009

© 2009 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim