# A novel 3D porous metal–organic framework based on trinuclear cadmium clusters as a promising luminescent material exhibiting tunable emissions between UV and visible wavelengths†

**Yong-Quan Huang, Bin Ding, Hai-Bin Song, Bin Zhao, Peng Ren, Peng Cheng,* Hong-Gen Wang, Dai-Zheng Liao and Shi-Ping Yan**

***Received (in Cambridge, UK) 17th July 2006, Accepted 31st August 2006***
***First published as an Advance Article on the web 9th October 2006***
**DOI: 10.1039/b610185b**

**A novel 3D porous MOF built with trinuclear cadmium clusters exhibiting rhombohedral topology has been synthesized and characterized as a promising luminescent material that can give tunable emissions between UV and visible wavelengths by controlling the number of guest molecules.**

Luminescent materials have been an active research field for decades because of their numerous applications, especially in light-emitting devices (LEDs). Ultraviolet light-emitting devices (UV-LEDs) are strong candidates in lighting equipment and optical storage devices,[1] while visible LEDs are applicable to fluorescent lamps, plasma display panels and optical switching.[2] But for fluorescent lamps and plasma display panels, luminescent materials are required for the efficient conversion of UV radiation to visible light. Therefore, luminescent devices which can give tunable emissions between UV and visible wavelengths are attractive targets for both fundamental research and practical applications. Although many chemical approaches have been focused on tuning luminescence properties,[3] we hope to find a more convenient route to control the luminescence properties without chemical reactions or intricate processes. This type of material is still very rare hitherto.[4] Metal–organic frameworks (MOFs) have emerged as a new class of materials, but there have been hardly any reports of the MOFs showing simultaneously permanent porosity, high thermal stability, and tunable luminescence.[5]

Herein, we reported a novel 3D porous MOF, $[Cd_3\mathbf{L}_6](BF_4)_2(SiF_6)(OH)_2\cdot 13.5H_2O$ (**1**) (abbreviated as $\mathbf{A\cdot 13.5H_2O}$, **L** = 2,6-di-(4-triazolyl)pyridine), where the guest species in the open channels can be removed and reintroduced reversibly without destroying the porous framework. It is important to note that the solid-state luminescence of this new material can be reversibly tuned *via* dehydration/rehydration treatment, exhibiting tunable emissions between UV and visible wavelengths.

Compound **1** crystallizes in the rhombohedral system, space group $R\bar{3}$, with two crystallographically different Cd atoms in the asymmetric unit.‡ Each Cd(II) unit has $[CdN_6]$ octahedral coordination geometry. The ligand **L** connects two such differently coordinated Cd atoms composing the $[Cd_3L_{12}]$ trinuclear cluster (Fig. 1, the coordination environment of Cd2A is the same as that of Cd2), where each terminal Cd2 (Cd2A) atom is linked by three N1, N2-bridged triazoles to the central Cd1 atom, which is located at an inversion center. The distance between the two metal centers [Cd1···Cd2] is 4.145(1) Å, which is slightly shorter than in previous triazole–metal structures.[6] The $[Cd_3L_{12}]$ trinuclear clusters are further connected to each other *via* **L** bridges to create a highly ordered 3D triangular-shaped channel system (Fig. 2a). A PLATON program analysis suggests that there is approximately 42.9% of the crystal volume accessible to solvents.[7] This value is very large among the reported cadmium MOFs.[8] Considering each Cd1 metal center of the $[Cd_3L_{12}]$ trinuclear cluster as a node, a rhombohedral coordination network can be obtained (Fig. S1†).

The channels are filled with disordered water molecules, $BF_4^-$ and $SiF_6^{2-}$ anions (generated from the decomposition of $BF_4^-$)[9] (Fig. 2b). There tends to be a significant number of hydrogen-bonding interactions between these anions and the surrounding water molecules. Two types of rings (8-membered and 10-membered rings) in quasi-planar and quasi-chair structures (Fig. 3a), respectively, array alternately to form an infinite

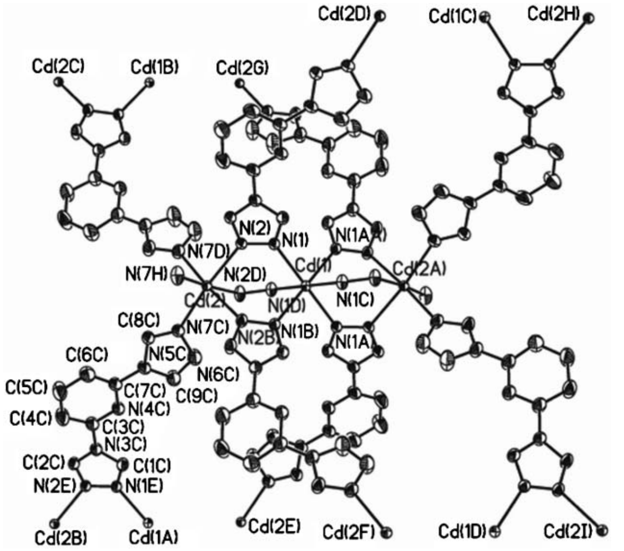

**Fig. 1** Asymmetric unit representation of **1**. Thermal ellipsoids are drawn with 50% probability and hydrogen atoms, lattice water molecules and anions have been omitted for clarity. Selected bond lengths (Å ) and angles (°): Cd(1)–N(1), 2.366(3), Cd(2)–N(7), 2.324(4), Cd(2)–N(2), 2.351(3); N(1)–Cd(1)–N(1), 90.14(11), N(1)–Cd(1)–N(1), 180.00(13), N(7)–Cd(2)–N(2), 89.63(13), N(7)–Cd(2)–N(7), 95.52(12), N(7)–Cd(2)–N(2), 173.83(13), N(2)–Cd(2)–N(2), 87.20(12).

---

*Department of Chemistry, Nankai University, Tianjin, 300071, P. R. China. E-mail: pcheng@nankai.edu.cn*

† Electronic supplementary information (ESI) available: Synthesis, crystal data, additional figures, TGA analysis and PXRD patterns. See DOI: 10.1039/b610185b

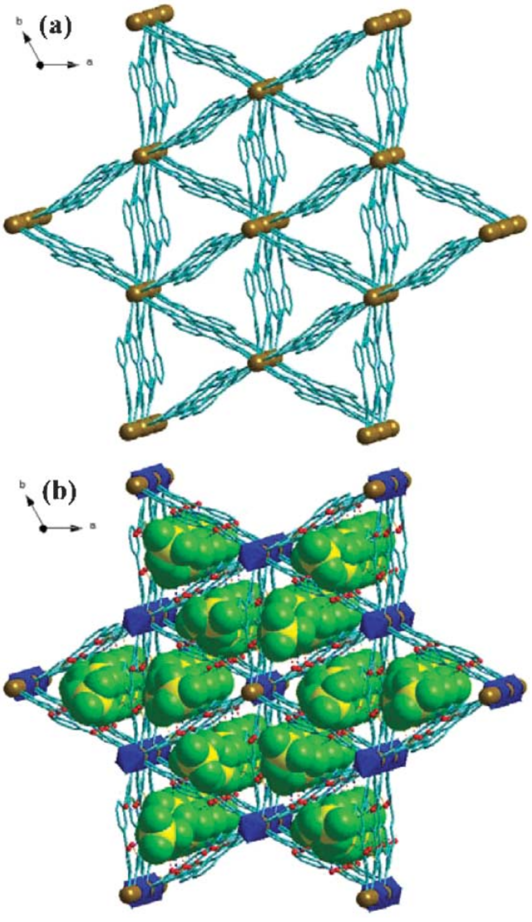

**Fig. 2** Perspective views of the 3D framework of **1** without (a) and with the guest water molecules and anions (b) in the cavities. The hydrogen atoms are omitted for clarity. Color code: Cd, brown; O, red; $SiF_6^{2-}$, polyhedron, blue; $BF_4^-$, space filling, green and yellow.

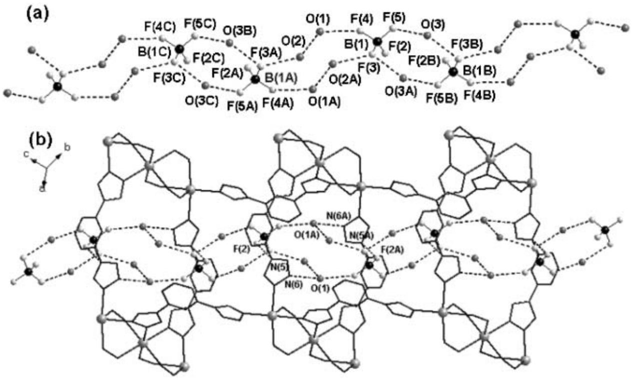

**Fig. 3** (a) Fragment of the 1D infinite chains formed by the water molecules and anions present in the crystal lattice of **1**. (b) A close view showing part of the hydrogen bonding interactions between the water molecules, anions and the host molecules. The hydrogen atoms of the water molecule have not been located and therefore have not been included in this drawing. Typical nonbonding distances (Å) and angles (°) in compound **1**: O(1)···O(2), 2.763(3), O(1)···F(4), 2.972(2), O(2)···F(3), 2.811(4), O(3)···F(3), 2.661(5), O(3)···F(5), 2.835(8), O(1)···N(6), 2.901(9), F(2)···N(5), 2.891(5); O(1)···O(2)···F(3), 108.79(98), O(2)···O(1)···F(4), 137.01(36), F(3)···O(3)···F(5), 121.02(50), O(2)···O(1)···N(6), 96.32(54).

hydrogen-bonded chain by sharing the edge of the $BF_4^-$ anions. No distinct interaction between $SiF_6^{2-}$ and water molecule can be found (Fig. S2†). It is helpful to note that hydrogen bonds can be observed between two nitrogen atoms of ligand **L** and the O(1) atom and the F(2) atom belonging to the $BF_4^-$ anion, as indicated by the N(6)···O(1) and N(5)···F(2) distances (Fig. 3b). The weak forces play a crucial role in stabilizing the expanded three dimensional network.

Thermogravimetric analysis (TGA) indicates that **1** is stable up to 300 °C (Fig. S3†), while the first weight loss of 11.52% from room temperature to 110 °C corresponds to the loss of all the guest water molecules (calculated 11.00%). When compound **1** was heated at different temperatures (180, 200, 225, 250 °C) for 1 day, a series of dehydrated products **A**·$\boldsymbol{x}$**H$_2$O** (**2–5**) were obtained in air. Although the crystal quality of the heat-treated samples was reduced, the unit cell parameters of **2–5** are almost identical with **1** and the framework structures remain intact after the guests have been removed as evidenced by powder X-ray diffraction (PXRD) (Fig. S4†). However, the number of guest water molecules is difficult to determine accurately using single-crystal X-ray diffraction and elemental analysis, but was deduced by TGA ($T$, $x$H$_2$O, compound reference number: *180*, *11.5*, **2**; *200*, *10.5*, **3**; *225*, *6.5*, **4**;

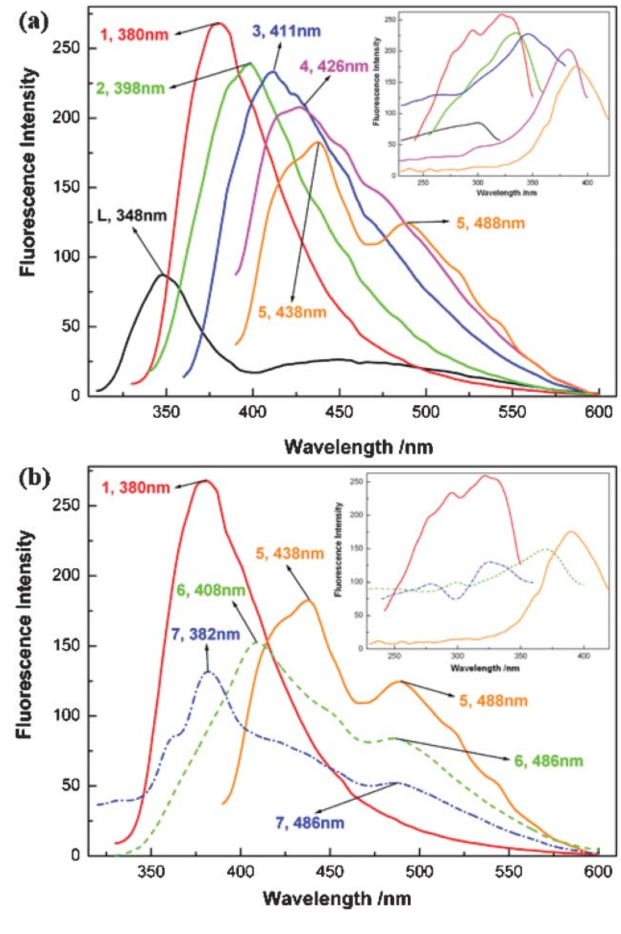

**Fig. 4** (a) Luminescence spectra of complexes **L**, **1–5** in the solid state at room temperature. Color code: **L**, black; **1**, red; **2**, green; **3**, blue; **4**, magenta; **5**, orange. (b) Luminescence spectra of complexes **1**, **5**, **6** and **7** in the solid state at room temperature. Color code: **1**, red; **5**, orange; **6**, dash line, green; **7**, dash-dot line, blue. The inset pictures represent the excitation spectra.

*250*, *4.5*, **5**). Notably, the dehydrated complex **5** can be rehydrated when exposed to $H_2O$ vapor for 1 or 2 days, obtaining **6** or **7** ($x$ = *9.5* for **6** and *12.5* for **7**), respectively. It was significant to note that almost all the features of the PXRD pattern of **7** were restored to those of **1**, demonstrating that the dehydration/rehydration process is reversible without destroying the channels.

The solid-state luminescence of complexes **1–7**, as well as free ligand **L** were investigated at room temperature and are shown in Fig. 4. **1** exhibits an intense UV radiation with $\lambda_{\max}$ at 380 nm upon excitation at 320 nm. Since a weakly similar emission ($\lambda_{\max}$ = 348 nm) is also observed for **L**, the luminescence of **1** is tentatively assigned to the intraligand fluorescent emissions. Compared with **L**, the enhancement and red-shift in **1** is probably due to the unique coordination of **L** to the Cd centre increasing the ligand conformational rigidity, thereby reducing the non-radiative decay of the intraligand ($\pi$–$\pi^*$) excited state. The original compound **1** and the series of dehydrated samples **2–5** display intense luminescence with emission maxima $\lambda_{\max}$ ranging from UV (380 nm) to visible light (438 nm). The emission spectrum for **5** shows a main peak at 438 nm and a shoulder peak at 488 nm with $\lambda_{\text{ex}}$ = 390 nm. The shoulder peak is probably due to ligand donation because a very weak, similar peak at 470 nm also appears for the free ligand. This is presumably owing to the framework architecture of **5**, which is more flexible than that of **1**. In addition, according to the previous literature,[10] the main peak at 438 nm may be assigned to ligand-to-metal charge-transfer (LMCT) bands.

Most interestingly, the fluorescent emissions of **5**, **6** and **7** shift back from visible light (438 nm) to the UV region (382 nm). This phenomenon may be attributed to the extent of the weak interactions. In the original crystal, abundant lattice water molecules and anions fill the network, forming important weak forces, which not only stabilize the supramolecular structures, but also absorb the UV light, preventing the transfer of energy effectively from **L** to the metal centre. Accordingly, the luminescence of **1** is merely assigned to intraligand fluorescence. Some guest molecules are removed from the MOF when heated, undoubtedly decreasing the weak interactions. Therefore, effective energy can be transferred from the ligand to the metal centre and the emission peaks for **5** may be assigned to LMCT bands. When **5** was rehydrated, the fluorescent emissions of **6** and **7** would spontaneously convert from visible light back to UV.

In summary, a novel 3D porous MOF built with trinuclear cadmium clusters has been synthesized and the framework can be described as a rhombohedral coordination network. This novel MOF is a promising luminescent device that can give tunable emissions between UV and visible wavelengths by controlling the number of guest molecules. The work provides a convenient and effective route for tuning luminescent properties without chemical reactions or intricate processes and will be helpful for the design and fabrication of multifunctional luminescent materials.

This work was supported by the National Natural Science Foundation of China (Nos. 90501002 and 20425103), the NSF of Tianjin (No. 06YFJZJC009000) and the State Key Project of Fundamental Research of MOST (2005CCA01200), P. R. China.

## Notes and references

‡ *Crystal data:* compound **1**, $C_{54}H_{71}B_2Cd_3F_{14}N_{42}O_{15.5}Si$, $M$ = 2209.44, rhombohedral, $R\bar{3}$, $a$ = 20.1077(11), $b$ = 20.1077(11), $c$ = 20.234(2) Å, $\alpha$ = 90°, $\beta$ = 90°, $\gamma$ = 120°, $V$ = 7085.1(9) Å$^3$, $T$ = 294(2) K, $Z$ = 3, $\mu$ = 0.787 mm$^{-1}$, $D_c$ = 1.553 Mg m$^{-3}$, $F(000)$ = 3321, $R_{\text{int}}$ = 0.0317, 13502 reflections, 3224 with $I > 2\sigma(I)$ for 252 parameters, $R_1$ = 0.0413 for $I > 2\sigma(I)$, $R_1$ = 0.0495 and $wR_2$ = 0.1357 for all data, GOF = 1.009. The structures were solved by direct methods and refined with the full-matrix least-squares technique using the SHELXS-97 and SHELXL-97 programs. CCDC 614743. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b610185b

1 (*a*) T. C. Chao, Y. T. Lin, C. Y. Yang, T. S. Hung, H. C. Chou, C. C. Wu and K. T. Wong, *Adv. Mater.*, 2005, **17**, 992; (*b*) X. Hu, J. Deng, J. P. Zhang, A. Lunev, Y. Bilenko, T. Katona, M. S. Shur, R. Gaska, M. Shatalov and A. Khan, *Phys. Status Solidi A*, 2006, **203**, 1815; (*c*) S. Mochizuki, S. Minami and F. Fujishiro, *J. Lumin.*, 2005, **112**, 267.

2 (*a*) C. D. Müller, A. Falcou, N. Reckefuss, M. Rojahn, V. Wiederhirn, P. Rudati, H. Frohne, O. Nuyken, H. Becker and K. Meerholz, *Nature*, 2003, **421**, 829; (*b*) E. Hosono and S. Fujihara, *Chem. Commun.*, 2004, 2062; (*c*) M. Q. Zhu, L. Zhu, J. J. Han, W. Wu, J. K. Hurst and A. D. Q. Li, *J. Am. Chem. Soc.*, 2006, **128**, 4303; (*d*) J. C. G. Bünzli and C. Piguet, *Chem. Soc. Rev.*, 2005, **34**, 1048.

3 (*a*) A. M. Stadler, F. Puntoriero, S. Campagna, N. Kyritsakas, R. Welter and J. M. Lehn, *Chem.–Eur. J.*, 2005, **11**, 3997; (*b*) S. Zhang, *IEEE Trans. Plasma Sci.*, 2006, **34**, 294; (*c*) W. Sun, H. Zhu and P. M. Barron, *Chem. Mater.*, 2006, **18**, 2602.

4 (*a*) Y. Mizobe, N. Tohnai, M. Miyata and Y. Hasegawa, *Chem. Commun.*, 2005, 1839; (*b*) T. Gunnlaugsson and J. P. Leonard, *Dalton Trans.*, 2005, 3204; (*c*) G. T. Hwang, H. S. Son, J. K. Ku and B. H. Kim, *J. Am. Chem. Soc.*, 2003, **125**, 11241.

5 (*a*) E. Y. Lee, S. Y. Jang and M. P. Suh, *J. Am. Chem. Soc.*, 2005, **127**, 6374; (*b*) T. M. Reineke, M. Eddaoudi, M. Fehr, D. Kelley and O. M. Yaghi, *J. Am. Chem. Soc.*, 1999, **121**, 1651.

6 B. Ding, L. Yi, Y. Wang, P. Cheng, D. Z. Liao, S. P. Yan, Z. H. Jiang, H. B. Song and H. G. Wang, *Dalton Trans.*, 2006, 665.

7 The accessible void volume was calculated with the program PLATON by using a probe with a radius of 1.2 Å.A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7.

8 (*a*) J. Fan, H. F. Zhu, T. Okamura, W. Y. Sun, W. X. Tang and N. Ueyama, *New J. Chem.*, 2003, **27**, 1409; (*b*) Q. Fang, G. Zhu, M. Xue, J. Sun, Y. Wei, S. Qiu and R. Xu, *Angew. Chem., Int. Ed.*, 2005, **44**, 3845.

9 (*a*) J. Klingele, B. Moubaraki, K. S. Murray, J. F. Boas and S. Brooker, *Eur. J. Inorg. Chem.*, 2005, 1530; (*b*) K. Sakai, M. Takeshita, Y. Tanaka, T. Ue, M. Yanagisawa, M. Kosaka, T. Tsubomura, M. Ato and T. Nakano, *J. Am. Chem. Soc.*, 1998, **120**, 11353; (*c*) P. J. van Koningsbruggen, J. G. Haasnoot, R. A. G. de Graaff and J. Reedijk, *J. Chem. Soc., Dalton Trans.*, 1993, 483.

10 (*a*) *Photochemistry and Photophysics of Coordination Compounds*, ed. H. Yersin and A. Vogler, Springer, Berlin, 1987; (*b*) B. Valeur, *Molecular Fluorescence: Principles and Applications*, Wiley-VCH, Weinheim, Germany, 2002; (*c*) J. Dai, X. Wu, Z. Fu, S. Hu, W. Du, C. Cui, L. Wu, H. Zhang and R. Sun, *Chem. Commun.*, 2002, 12.