Cite this: Chem. Commun., 2012, 48, 531-533

## COMMUNICATION

## Bright blue emissions with temperature-dependent quantum yields from microporous metal-organic frameworks<sup>†</sup>

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Received 18th August 2011, Accepted 25th October 2011 DOI: 10.1039/c1cc15138j

Two 2D microporous metal-organic frameworks have been assembled from a fluorophore ligand, whose quantum yields of strong blue emissions could vary from 40.3% to 74.5% and 13.7% to 25.8% with the decreasing temperature.

The luminescent properties of metal-organic frameworks (MOFs) have attracted considerable interest owing to numerous real and potential applications in chemical and biological detection, medical imaging, lighting, displays, and so forth.<sup>1</sup> The ordered nature of MOF structures which include both organic ligands and metal ions provides a powerful platform for the development and application of solid-state luminescent materials as they have a degree of structural predictability, in addition to two well-defined binding sites: metal-based binding sites and organic linkers in crystalline form.<sup>2</sup> On the one hand, the combination of lanthanide ions and conjugated organic ligands usually can produce an antenna effect and a pronounced increase in the luminescence intensity compared with the free lanthanide ions.<sup>3</sup> On the other hand, the MOFs containing d<sup>10</sup> metals and highly conjugated organic linking groups can emit intense linker-based luminescence, including intraligand emission as well as ligand-to-metal charge transfer (LMCT) and metalto-ligand charge transfer (MLCT).<sup>4</sup> A combination of stable porosity and intense luminescence in these materials is relatively uncommon.<sup>5</sup> Recently, detailed studies on porous luminescent MOFs have revealed that the network topology may heavily affect the color and intensity of luminescence.<sup>4</sup>

Herein we designed a novel tricarboxylate ligand, N,N',N''-1,3,-5-triazine-2,4,6-triyltris(4-aminomethylbenzoic acid) (H<sub>3</sub>TTAA),based on the optically active and strongly fluorescent C3N6 core as illustrated in Scheme 1 which was functionalized with 4-methylbenzote fragments. The C3N6 core was chosen as a linker, whose all atoms are totally coplanar to form the great  $\pi$ -conjugated

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 $\label{eq:scheme1} Scheme \ 1 \quad Coordination \ mode \ and \ the \ core \ structure \ of \ H_3 TTAA \ ligand.$ 

system. Triaminobenzene is nearly identical to the C3N6 core, however, the three nitrogen atoms of triaminobenzene show slight deviation from the central benzene ring, due to steric interactions between the hydrogen atoms of the amino groups and those of the central ring.<sup>6</sup> The ligands based on the C3N6 core also have been proven to be outstanding fluorophores in our previous work.<sup>7</sup> Meanwhile, H<sub>3</sub>TTAA is more extended than other tricarboxylate ligands, such as 1,3,5-tris(4-carboxyphenyl)benzene (H<sub>3</sub>BTB),<sup>8</sup> which is often used to prepare microporous MOFs. Thus, highly emissive porous framework structures from the self-assembly between the fluorophore ligand and suitable metal ions were anticipated.

As expected, a 2D porous framework with strong fluorescence,  $\{(H_2NMe_2)[Cd(TTAA)]\}\cdot 2H_2O$  (1), has been solvothermally synthesized. Under the same synthetic procedure except addition of 4,4'-bipy, another 2D fluorescent porous framework with different topological structures, {(H2NMe2)[Cd(TTAA)]}·H2O (2), was surprisingly obtained, despite the fact that the 4,4'-bipy did not coordinate to the Cd(II) ions. According to the sizes of 4,4'-bipy and the voids in 2, the hypothesis is put forward that the 4,4'-bipy plays a crucial template role in this synthesis. Although the ligands in the two frameworks are arranged in different geometry configurations, they possess the same coordination mode acting as  $\mu_7$ -bridges (Scheme 1). Each TTAA<sup>3-</sup> ligand in 1 and 2 connect four mononuclear Cd units forming chiral enantiomeric SBUs (Fig. S2 and S5, ESI<sup>†</sup>). The frameworks 1 and 2 are both based on the mononuclear seven-coordinated CdO<sub>6</sub>N units, in which each Cd(II) is bound to four ligands with three carboxylate groups and a triazine nitrogen atom. The bond lengths of Cd–O/N in 1 and 2 are in the ranges of 2.320(3)-2.488(4) and 2.320(6)-2.476(8) Å, respectively.<sup>‡</sup>

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<sup>&</sup>lt;sup>†</sup> Electronic supplementary information (ESI) available: Synthesis, crystallographic information, supplementary figures, IR, TGA and XRD. CCDC 838864 and 838865. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1cc15138j



**Fig. 1** View of 2D layer comprising alternating right- and left-handed helical chains in **1**.

In 1, the three benzoate groups of the ligand are located at one side of the central C3N6 plane with the angles between the lines and the plane of  $67.7^{\circ}$ ,  $57.9^{\circ}$  and  $43.2^{\circ}$ , restraining it from extending in the other direction, which may be the cause of the 2D layer structure. The convex of one layer is immersed into the concave of the adjacent layer to get a tightly packed structure through aromatic  $\pi \cdot \cdot \pi$  stacking interactions (Fig. S2, ESI<sup>†</sup>). When viewed down the b axis, the structure presents two different channels alternately with dimensions of ca.  $7.0 \times 10.0 \text{ Å}^2$ and 7.2  $\times$  17.0 Å<sup>2</sup> based on the distances of the opposite atoms (Fig. 1). In the latter channels, with two arms of each ligand linking two metal ions, helical chains along the b axis are formed, in which the two-fold right- and left-handed helical chains are in an alternate array. One full turn of the helical chain contains two Cd(II) centers with a pitch of 12.33 Å. These double chains are further interlinked by the coordination interactions between the triazine rings and the metal ions.

The structure of **2** features a 2D rectangular grid-like network containing large cavities of *ca*.  $10.4 \times 17.5$  Å<sup>2</sup> based on the distances of the opposite atoms (Fig. 2). Two benzoate groups of the ligand are arranged above the central C3N6 plane with the angles of  $11.2^{\circ}$  and  $12.0^{\circ}$  between the lines and the plane, while another one is arranged below the plane with the angle of  $60.6^{\circ}$ . Intriguingly, because of the nonplanarity of ligands, the basic rectangular grid is puckered, different from the reported grid-like structures in which the basic grids are usually coplanar or quasi-coplanar.<sup>9</sup> Accordingly, the layer based on the grids is wave-like. The crystalline water molecules and protonated dimethylamine occupy the large cavities and



Fig. 2 Packing arrangement representation of the two adjacent layers in 2.



Fig. 3 Schematic descriptions of the two (4,4)-connected 2D networks of (a) 1 and (b) 2 (blue balls represent the Cd atoms; red balls represent the centers of ligands). The two kinds of helices reflected in the network of 1 are highlighted.

interact with the adjacent layers by hydrogen bonds, contributing to an extending 3D framework.

By PLATON/SOLV<sup>10</sup> analysis, the solvent accessible volumes are as high as 35.5 and 41.2% in frameworks **1** and **2**, respectively. Better insight into such elegant frameworks can be achieved by the employment of a topology method. From the connectivity considerations, Cd(II) centers and TTAA<sup>3-</sup> ligands in **1** and **2** are both viewed to be four-connected nodes. Thus, the framework **1** can be symbolized as an unusual 2D (4,4)-connected topology with a Schläfli symbol ( $4^{2} \cdot 6^{4}$ ) in which two kinds of helices can be observed easily (Fig. 3a). The framework **2** also can be interpreted topologically as a honeycomb-like 2D (4,4)-connected network with a Schläfli symbol ( $4^{3} \cdot 6^{3}$ ) (Fig. 3b).

The most remarkable feature of the two frameworks is their bright blue emissions at different temperatures under near-UV excitation. The solid-state emission spectrum of 1 at room temperature displays an intense emission band centered at 432 nm with excitation maximum at 318 nm (Fig. 4). The luminescent quantum yield was determined by means of an integrating sphere and was found to be 40.3%; and the lifetime of the emission is consistent with the nanosecond scale of fluorescence (Table 1). As the temperature is decreased to 77 K, a blue shift of 8 nm is observed with respect to the emission band of 1 at room temperature, whereas its full width at half-maximum (fwhm) undergoes no change. Surprisingly, the intensity of the



**Fig. 4** Relative emission spectra of framework **1** with the variation of its fluorescent quantum yields collected under excitation at 318 nm in the solid state at 77 and 298 K. Inset: fluorescent image of the bright blue luminescing framework **1** at 298 K.

Table 1	PL data of	frameworks 1	and 2 at	10, 77	and 298 K
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	$\lambda_{\rm em}^{\ a}$ , fwhm <sup>b</sup> /nm			$\Phi_{ m f}{}^c(\%)$			
Compd	10 K	77 K	298 K	10 K	77 K	298 K	$\tau^d/\mathrm{ns}$
1 2	424, 70 431, 76	424, 70 432, 75	432, 72 432, 74	74.5 25.8	74.0 25.4	40.3 13.7	5.49 6.47
$\lambda_{\rm em} = 0$	emission uantum yi	band. <sup>b</sup> f eld. <sup>d</sup> $\tau =$	whm = lifetime a	full wid at 298 K	dth at	half-max	imum.



**Fig. 5** Relative emission spectra of framework **2** with the variation of its fluorescent quantum yields collected under excitation at 313 nm in the solid state at 77 and 298 K. Inset: fluorescent image of the bright blue luminescing framework **2** at 298 K.

emission response sharply rises to  $\Phi_{\rm f} = 74.0\%$ , suggesting its high sensitivity to temperature. Upon further cooling to 10 K, the intensity and fwhm of 1 show no essential change compared with those at 77 K, which indicates that the total intensity of 1 enhances continuously with decreasing temperature up to a maximum at a certain temperature above 77 K. Irradiation of framework 2 at 313 nm results in a similar emission at  $\lambda_{\rm em} = 432$  nm with an absolute quantum yield of 13.7%. When measurement temperature is reduced to 77 K, the quantum yield mounts up to 25.4% while no shift is observed (Fig. 5).

The emission features of 1 and 2 closely match to that of the fluorophore ligand (Fig. S7, ESI<sup>+</sup>), indicating the metalperturbed intraligand charge transfers. Thus, the intense fluorescence of the two frameworks should be mainly contributed from the well planar and  $\pi$ -conjugated C3N6 cores of ligands. Till now, few blue luminescent MOFs exhibiting high quantum yields have been reported.<sup>2a,11</sup> Temperature-dependence of emission intensity has been observed for the luminescent spectra of each framework studied herein. Cold conditions should be favorable for the rigidity of ligands, thereby the radiationless decay of the intraligand  $(\pi \cdot \cdot \pi^*)$  excited state could be reduced to some extent and the increase of the quantum yields should be observed eventually by lowering the temperature. So far, fluorescent intensity modulation has been encountered in some MOFs containing d<sup>10</sup> metals,<sup>12</sup> while the investigations of the very strong fluorescent MOFs exhibiting tunable emission intensity with temperature have been rarely studied.7c,12a

In summary, two novel microporous MOFs have been hydrothermally synthesized from a fluorophore ligand based

on the fluorescent C3N6 core. The two frameworks both display (4,4)-connected 2D networks with fascinating architectures. In particular, they show bright blue fluorescence both under ambient and freezing conditions, and drastic fluorescence enhancement when the temperature is lowered.

This work was supported by grants from the 973 Program (2007CB815301), the National Science Foundation of China (21073192, 20733003, 20801055 and 20871114), the Science Foundation of CAS (KJCX2-YW-H20) and of Fujian Province (2009HZ0006-1 and 2006L2005).

## Notes and references

‡ Crystal data for 1: CdC<sub>29</sub>H<sub>33</sub>N<sub>7</sub>O<sub>8</sub>,  $M_r = 719.77$ , monoclinic, space group  $P2_1/c$ , a = 12.943(4) Å, b = 12.329(3) Å, c = 23.867(5) Å,  $\beta = 108.881(12)^\circ$ , V = 3603.6(16) Å<sup>3</sup>, Z = 4, T = 293(2) K,  $\rho_{calcd} = 1.327$  g cm<sup>-3</sup>,  $R_1 = 0.0522$  and  $wR_2 = 0.1645$  for 27.237 reflections collected, 6911 observed reflections ( $I > 2\sigma(I)$ ) of 7817 ( $R_{int} = 0.0346$ ) unique reflections and 381 parameters, GooF = 0.975. Crystal data for 2: CdC<sub>29</sub>H<sub>31</sub>N<sub>7</sub>O<sub>7</sub>,  $M_r = 702.01$ , monoclinic, space group C2/c, a = 29.28(2) Å, b = 14.524(10) Å, c = 20.084(15) Å,  $\beta = 115.414(11)^\circ$ , V = 7714(10) Å<sup>3</sup>, Z = 8, T = 293(2) K,  $\rho_{calcd} = 1.209$  g cm<sup>-3</sup>,  $R_1 = 0.0758$  and  $wR_2 = 0.2071$  for 25 354 reflections collected, 5749 observed reflections ( $I > 2\sigma(I)$ ) of 8737 ( $R_{int} = 0.0666$ ) unique reflections and 393 parameters, GooF = 1.104.

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