Design and solvothermal synthesis of luminescent copper(I)-pyrazolate coordination oligomer and polymer frameworks†

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Two luminescent coordination compounds, $[Cu(Pz)]_3$ (1) and $[Cu_2(Bpz)]_n$ (2), were isolated from solvothermal reactions of $Cu(NO_3)_2$ with 3,5-dimethylpyrazole (HPz) and 3,3′,5,5′-tetramethyl-4,4′-bipyrazole (H_2Bpz) respectively in the presence of NH_3, of which 1 was revealed to be a planar trimer and 2 a three-dimensional framework, presenting a rare 3-connected binodal $(6^2.10)(6.10^2)$ topology and eight-fold interpenetration.
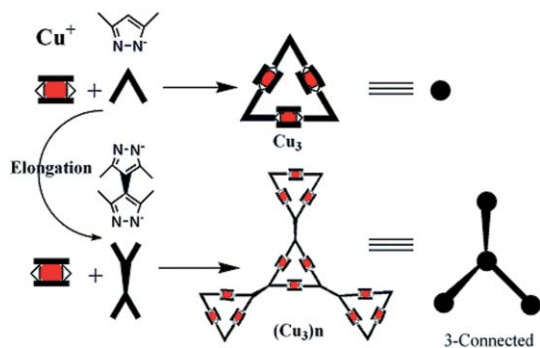
Bottom-up construction of metal–organic frameworks (MOFs), possessing desired structure and bulk nature, from selected metals and organic ligands, is the central mission of crystal engineering.[1] The endeavour directs the fabrication of functional materials *via* pre-designed setting up of molecular building blocks.[2] As preparation for this practice, rational design of the structures of MOFs has drawn considerable attention of current studies and has been thoroughly surveyed by reviews.[3] In general, the formulation of MOF structures is based on the coordination preference of building blocks and the prediction of properties relies on the presence of special functionalities. For instance, Yaghi *et al.* have produced MOFs with predesigned secondary building units (SBU) as structural and functional carriers.[4]

Enlightened by the success of Domasevitch *et al.* in constructing 3-D porous supramolecular network from H_2Bpz[5] and the finding of Dias *et al.* that the coordination trimer $[Cu((F_3C)_2Pz)]_3$[6] is room temperature photoluminescent,[7] we adopted $Cu(NO_3)_2$ as the metal source, HPz and H_2Bpz[8] as ligands, in our attempts to prepare the triangular Cu_3 (1) and the extended framework $[Cu_3]_n$ (2) in a strategy depicted in Scheme 1. Two products containing

Scheme 1

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Cu_3 centers with luminescent properties were obtained. As supposed, 2 is a 3-D extended, neutral and porous framework, similar to the network of solid H_2Bpz constructed by hydrogen-bonds with four-fold interpenetration.[5]

1 was readily obtained as yellowish crystals from heating a H_2O–CH_3OH solution of HPz and $Cu(NO_3)_2$ in the presence of NH_3,‡ whereupon the Hpz is deprotonated to Pz^- and Cu(II) is reduced to Cu(I) by NH_3.[9] Reaction of the *in situ* formed Cu(I) and Pz^- results in the triangular Cu_3,§ similar to the reported compound obtained from the reaction of $Cu(OH)_2$ and molten HPz under nitrogen atmosphere.[10] But the dimeric associations, in both cases, stack in a staggered way and present centrosymmetry, in which Cu1 is 3.277 Å away from the centroid of the (N1, N2, C2, C3, C4) ring at $(1 - x, 2 - y, 1 - z)$. The shortest intra- and inter-molecular Cu···Cu distances of 1 are 2.954 Å and 3.194 Å respectively (see ESI†), much closer than those of $[Cu((F_3C)_2Pz)]_3$[6] (3.221 Å and 3.879 Å), suggesting stronger intermetallic interactions in 1.

Similar treatment of $Cu(NO_3)_2$ and H_2Bpz in NH_3 solution‡ afforded the pale-yellow 2,§ which crystallized in orthorhombic space group *Ccca* and showed a MOF consisting of *in-situ* generated Cu(I) and Bpz^{2-}. To the best of our knowledge and according to a search of the results in the latest version of the CSD, this is the first case of Bpz^{2-} being used as a tecton in the construction of a MOF. As expected, 2 is porous and 3-D extended with Cu_3 as SBUs. By denoting the Cu_3 as 3-connected nodes and C–C bonds as spacers, the framework can be abstracted into a network in binodal topology of $(6^2.10)(6.10^2)$ nof ("nof" is a three-letter code, added to the Schlafli symbol of the topologic

Fig. 1 Topologic representation of 2 showing binodal connectivity ($\bullet$ $(6^2.10)$, $\bullet$ (6.10^2)).

network to specify the coordination sequence; the denotation system has been detailed by O'Keeffe, see: http://okeeffe-ws1.la. asu.edu/RCSR/home.htm)[11] (Fig. 1), a fashion that has only been illustrated by Fujita *et al.*[12] It can be seen in Fig. 1 that the network is composed of two independent short circuits, one containing six nodes and another containing ten. The decamer is analogous to the decameric pore (size 20 Å) in solid H_2Bpz,[5] but at a much larger size (35 Å) (see ESI†). The occurrence of the large pores in two cases illustrates the application of elongated ligands to the construction of porous networks.

The large porosity of **2** allows the high interpenetration of the networks. Fig. 2 exhibits the entanglement of the networks. According to the translation equivalence, eight interpenetrated nets can be categorized into two subsets.[13] Each subset of four nets is related by the translation vector [1/2, 1/2, 0] (25.02 Å). Interestingly the configuration and bond parameters of **Cu₃** unit in **2** are not significantly different from those in **1**. Moreover, the closest two **Cu₃** units, belonging to different nets, are stacked also in a staggered way like in **1** (see ESI†) and the inter-net Cu···Cu distance (3.331Å) is close to the intermolecular Cu···Cu contact in **1**. The observation implies that the intermetallic interaction dominates not only the stacking of **1**, but also the interpenetration of **2**.

As expected, the presence of luminophor **Cu₃** in both **1** and **2** results in room temperature photoluminescence. Irradiated at 305 nm, these two solids give broad emission bands in the visible region with maxima at 542 and 598 nm respectively (Fig. 3). In the light of the attribution to the emission of $[(3,5-(CF_3)_2Pz)Cu]_3$ (550 nm),[7] the bands are assigned to metal-based phosphorescence. The assignment should be more proper for **1** and **2** because they have much shorter intra- and inter-molecular Cu···Cu distances than $[(3,5-(CF_3)_2Pz)Cu]_3$.[6] As shown in Fig. 3, the band of **1** is bathochromically shifted from that of **2**, in principle indicating a stronger Cu···Cu interaction in **1**.[7] In comparison, the inter-molecular Cu···Cu contacts (2.954 Å (**1**); 3.331 Å (**2**)) of two compounds are more diverse than the intramolecular ones (3.194 Å; 3.022 Å). Therefore, the shift may largely arise from
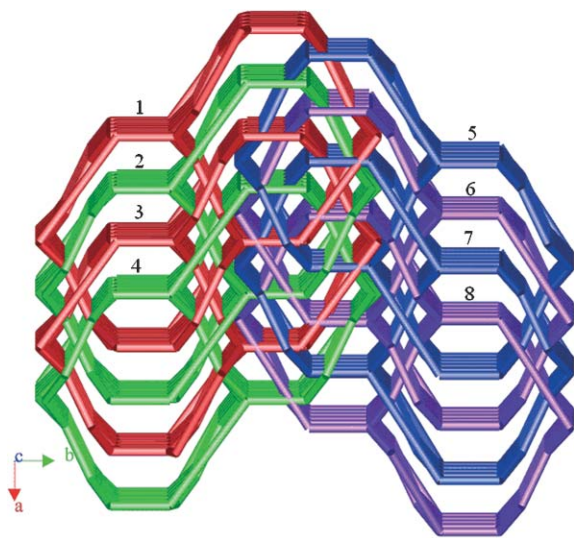

Fig. 3 Photoluminescence spectra of **1** and **2** at room temperature.

the difference in intermolecular Cu···Cu interaction,[7] in agreement with the observation that the emission of $[(3,5-(CF_3)_2Pz)Cu]_3$ is more sensitive to solution concentration than to temperature.[7] In addition, the smaller Stokes shift of **2** can be related to its distorted excited state.[7,14] This is reasonable because the luminophor in **2** is more rigid for the fixation by the MOF.

The thermogravimetric (TG) plot of **2** shows a multistep weight-loss from *ca* 395 °C to 905 °C in N_2 atmosphere (Fig. 4), during which a total weight loss of 55.4% (59.5% for calculated Bpz^{2-} content) was measured, and ascribed to the loss of the organic component. In the differential thermal (DT) curve, the slope corresponds (Fig. 4) to a process indicating exothermal decomposition. Besides, below the temperature of decomposition, an exothermal process occurs in the region 270–395 °C. The large enthalpy change (-13.84 kJ g^{-1}) is likely caused by a solid phase transition because it is accompanied by no weight change.

In summary, the structural definition and luminescence of two compounds suggest the possibility of predetermining the connectivity of a MOF on the basis of the coordination preference of the building blocks and the properties of a bulky solid by the presence of functional sites. Polymer **2** presents the first example of a MOF with bipyrazolate as the tecton and also the unprecedented [4 + 4] type of eight-fold interpenetration of $(6^2.10)(6.10^2)$ networks.[15]

Fig. 2 Eight-fold interpenetrating frameworks of **2** in unusual [4 + 4] mode with 4 nets of one subset colored in red and green and the other subset in blue and purple.
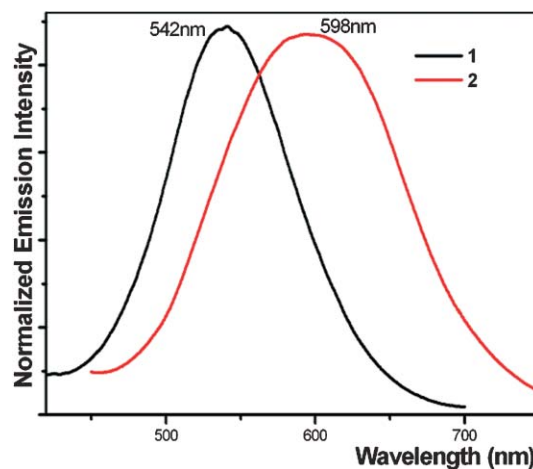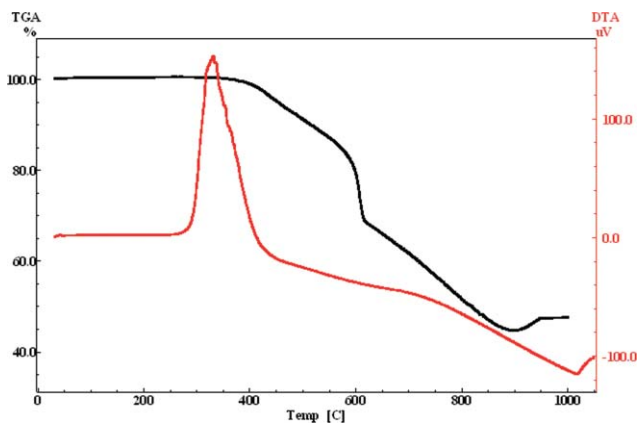

Fig. 4 Thermogravimetric and differential thermal curves of **2**.

Notes and references

‡ Synthesis of **1**: a mixture of Cu $(NO_3)_2 \cdot 3H_2O$ (0.241 g, 1.0 mmol), HPz (0.096 g, 1.0 mmol), aqueous ammonia (25%, 5 mL) and methanol (5 mL) was stirred for 10 min in air, then transferred to and sealed in a 23 mL Teflon-lined reactor, heated in an oven to 180 °C for 80 h. The resulting yellowish block crystals were filtered, washed, and dried in air; yield 0.10 g, *ca.* 65%. Elemental analysis calcd (%) for **1** $C_{15}H_{21}Cu_3N_6$: C 37.86, H 4.45, N 17.65; found: C 37.78, H 4.51, N 17.72%. Synthesis of **2** was similar to that of **1** using H_2Bpz (0.190 g, 1.0 mmol) in place of HPz; yield 0.12 g, *ca.* 70%. Elemental analysis calcd (%) for **2** $C_{60}H_{72}Cu_{12}N_{24}$: C 38.09, H 3.84, N 17.77; found: C 37.98, H 3.92, N 17.82%. IR data (KBr, cm^{-1}) for **2**: 2908 m, 1641 w, 1552 w, 1489 m, 1425 s, 1335 m, 1142 s, 1051 s.

§ Crystal data for **1**: $C_{15}H_{21}Cu_3N_6$, $M_r = 476.00$, triclinic, space group $P\bar{1}$ (no. 2), $a = 8.5774(8)$ Å, $b = 10.2884(10)$ Å, $c = 11.4238(11)$ Å, $\alpha = 69.5260(10)°$, $\beta = 75.178(2)°$, $\gamma = 81.239(2)°$, $V = 910.82(15)$ Å^3, $Z = 2$, $D_c = 1.736$ g cm^{-3}, $F(000) = 480$, $\mu = 3.479$ mm^{-1}, 7160 reflections measured, 3092 unique ($R_{int} = 0.0226$), final $R_1 = 0.0327$, $wR_2 = 0.0873$, $S = 1.014$ for all data. **2**: $C_{60}H_{72}Cu_{12}N_{24}$, $M_r = 1891.90$, orthorhombic, space group $Ccca$ (no. 68), $a = 18.6363(13)$ Å, $b = 46.435(3)$ Å, $c = 34.874(3)$ Å, $V = 30179(4)$ Å^3, $Z = 16$, $D_c = 1.666$ g cm^{-3}, $F(000) = 15168$, $\mu = 3.359$ mm^{-1}, 153632 reflections measured, 10779 unique ($R_{int} = 0.0735$), final $R_1 = 0.0487$, $wR_2 = 0.1181$, $S = 1.013$ for all data. Data collections were performed on a Bruker Smart Apex CCD diffractometer with MoKα radiation ($\lambda = 0.71073$ Å), using frames of 0.3° oscillation ($2\theta \leqslant 56°$). The structures were solved by direct methods and all anisotropic refinement by full-matrix least-squares on F^2 using SHELXTL programs.[16] CCDC 295579 and 286905. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b601009a

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