LETTER

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Controlled hydrothermal synthesis of copper(II or I,II) coordination polymers *via* pH-dependent *in situ* metal/ligand redox reactions†

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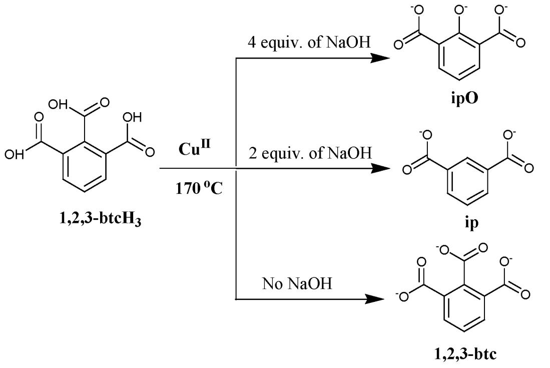
Three new coordination polymers synthesized from a mixture of $Cu(NO_3)_2$, NaOH, 4,4′-bipyridine (4,4′-bpy) and 1,2,3-benzenetricarboxylic acid (1,2,3-btcH_3) illustrate the pH dependence of *in situ* metal/ligand redox reactions.

The rational design of molecular architectures having different topologies and functions is one of the most important targets in crystal engineering.[1–3] Recently, hydrothermal synthesis is being widely used in this field to produce functional polymers such as zeolites, nanomaterials, and inorganic-organic materials. Meanwhile, a few novel *in situ* metal/organic reactions such as ligand oxidative coupling, hydrolysis, and substitution were uncovered during the hydrothermal process,[4–9] in which many factors, including the nature of the metal ion and the temperature, pressure and pH, have been found to significantly influence the reaction outcome.[6,8] Nevertheless, such ligand reactions, due to their role as a new bridge between inorganic and organic chemistry, require further understanding and expansion. Following our recent report on the *in situ* metal/ligand redox synthesis of $[Cu_2(ipO)(4,4'\text{-bpy})]_n$ (**1**; ipO = 2-hydroxyisophthalate, 4,4′-bpy = 4,4′-bipyridine),[8] we performed analogous reactions using 1,2,3-benzenetricarboxylic acid (1,2,3-btcH_3), which can be regarded as isophthalic acid (ip) with a carboxylic group in position 2.

Interestingly, the *in situ* metal/ligand redox reaction also occurs with 1,2,3-btc and is highly pH dependent, as shown in Scheme 1. When 1,2,3-btcH_3 was reacted with 4 equiv. of NaOH, the 2-carboxylate unit was replaced by a hydroxy group. In the reaction mixture consisting of $Cu(NO_3)_2$, 4,4′-bpy and 1,2,3-btcH_3, this resulted in the known polymer **1** in very high yields (95%) under these conditions, as well as a minor product $[Cu_3(ipO)_2(4,4'\text{-bpy})_{0.5}(H_2O)_2]_n$, **2** (yield *ca.* 2%). When reducing the amount of NaOH to 2 equiv, the 2-carboxylate was simply removed, giving rise to a new mixed-valence Cu(I)-Cu(II) polymer $[Cu_2(ip)(ipH)(4,4'\text{-bpy})_{1.5}]_n$ (**3**; ip = isophthalate). However, without addition of NaOH, the 2-carboxylate was retained, resulting in a 3D porous framework **4**, $\{[Cu_2(1,2,3\text{-btc})(4,4'\text{-bpy})(H_2O)_2](NO_3)\}_n$. We can, therefore, conclude that, under certain conditions, 1,2,3-btcH_3 gives either an ip or ipO containing polymer, while the ip based polymer can be further transformed into the ipO containing polymer. Accordingly, the ip system may be assumed to be an intermediate in the *in situ* metal/ligand redox reaction that occurs with 1,2,3-btcH_3. The reaction mechanism may involve the following steps: rapid decarboxylation at the 2-position of 1,2,3-btcH_3 due to steric hindrance, then metal/ligand redox reaction on this active site, leading to the formation of ip or ipO containing polymers at pH = 6–7 or 9–10, respectively, and where Cu^{2+} acts as an essential oxidant as illustrated previously.[6–9]

X-Ray single-crystal diffraction analysis reveals that the structure of **2** contains three crystallographically unique Cu(II) atoms, two ipO ligands, half a 4,4′-bpy ligand and two bound water molecules [Fig. 1(a)]. The Cu1 atom displays a square-pyramidal coordination geometry. The base of the square pyramid geometry is provided by two carboxylate oxygen atoms and two phenoxy oxygen atoms from two ipO ligands, with Cu1–O bond lengths in the range 1.894(2)–1.926(2) Å. The apical position of the square pyramid is occupied by one carboxylate oxygen atom from a third ipO ligand with a substantially longer Cu–O bond distance of Cu1–O3 2.420(3) Å. The Cu2 atom has a planar-square geometry sharing the basal edge of the Cu1 square-pyramid [Cu2–O1 1.902(3), Cu2–O6 1.923(2) Å] and is coordinated to two other oxygen atoms from the *anti-anti* [Cu2–O2 1.899(2) Å] and *anti-syn* [Cu2–O7 1.868(3) Å] bidentate carboxylate groups. Therefore, Cu1 and Cu2 are chelated by two ipO ligands to form a dinuclear $[Cu(II)_2(ipO)_2]^{2-}$ core [Cu1···Cu2 2.9420(9) Å]. The Cu3 atom is coordinated by one oxygen atom [Cu3–O8 2.071(3) Å] from the *anti-syn* bidentate carboxylate, two oxygen atoms [Cu3–O9 2.388(2), Cu3–O10 2.328(3) Å] from the bidentate-bridging carboxylates, as well as two binding water molecules [Cu3–O1w 1.939(3) and Cu3–O2w 2.100(4) Å] and one 4,4′-bpy nitrogen [Cu3–N1 1.995(3) Å], to form an elongated octahedron. The Cu3 atoms connect the $[Cu(II)_2(ipO)_2]^{2-}$ cores (Cu3···Cu1 4.018, Cu3···Cu2 4.355 Å) to form the 1D ribbons. Each pair of ribbons is linked *via* inter-ribbon carboxylate oxygen atoms interacting with Cu1 atoms belonging to opposite ribbons to generate a double-ribbon [Fig. 1(b)]. The



Scheme 1 Fate of 1,2,3-btcH_3 in media with different equivalents of NaOH.

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† Electronic Supplementary Information (ESI) available: TGA curve of **4**. See http://www.rsc.org/suppdata/nj/b4/b409696g/.

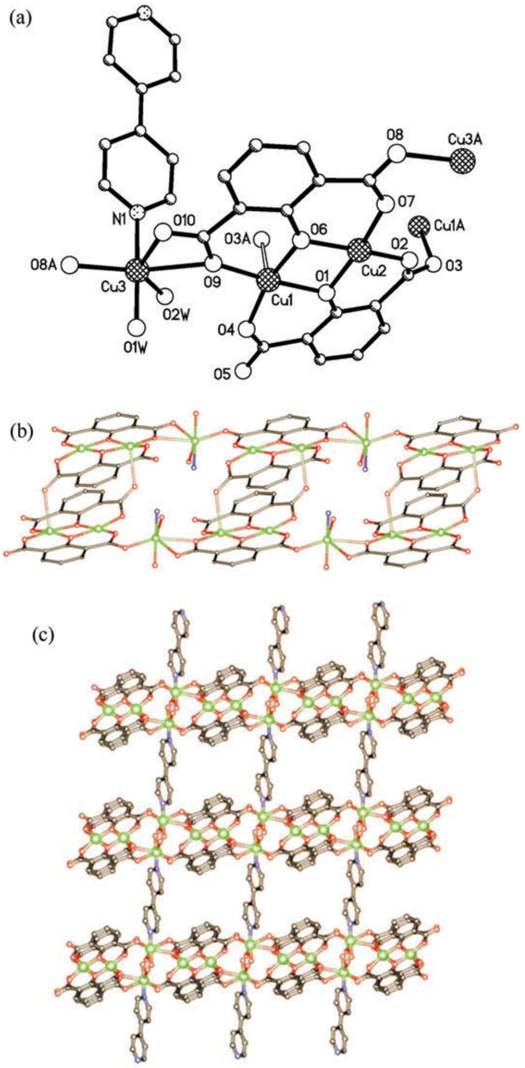

Fig. 1 Perspective view of the coordination environments of the metal atoms (a), the 1D double-ribbon (b) and the 2D network (c) of **2**.

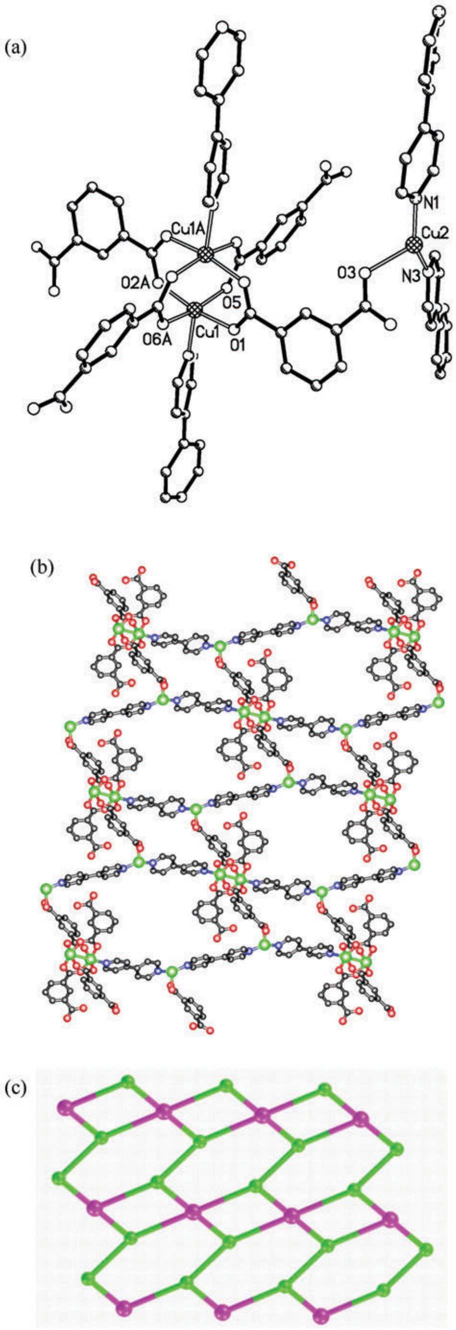

Fig. 2 Perspective view of the coordination environments of the metal atoms (a), the 2D network (b) and the topological (3,4)-connected 2D net (c) in **3** [purple spheres: 4-connected Cu$_2$(μ-O$_2$CR)$_4$ node, green spheres: 3-connected Cu(I) node].

double-ribbons are further interconnected into a 2D layer by the 4,4′-bpy spacers [Fig. 1(c)].

The structure of **3** contains two crystallographically independent Cu(II) atoms, one and a half 4,4′-bpy ligands, and two isophthalates [Fig. 2(a)]. Cu1 displays a square-pyramidal geometry surrounded by four oxygen atoms [Cu–O 1.953(8)–1.969(8) Å] from four *syn-syn* bidentate carboxylate groups at the base and one 4,4′-bpy nitrogen atom [Cu–N 2.156(9) Å] at the axial position. A pair of inversely related Cu1 atoms is bridged by four *syn-syn* carboxylate ends to form a dinuclear subunit [Cu···Cu 2.642(2) Å]. Cu2 adopts a T-shaped geometry with one carboxylate oxygen atom [Cu–O 2.168(8) Å] from the monodentate end of one bidentate-monodentate ip ligand and two nitrogen atoms [Cu–N 1.917(9), 1.918(8) Å] from two 4,4′-bpy ligands. Obviously, Cu1 is bivalent and Cu2 is monovalent. Two isophthalates are involved in different coordination modes, one being bidentate-monodentate to bridge Cu1 and Cu2, and the other bidentate (the protonated ipH) to bridge two Cu1 atoms. The network of **3** is a 2D coordination framework. Topological analysis shows that **3** is a novel example of the 2D (3,4)-connected nets predicted by Wells,[10] as shown in Fig. 2(b,c), which can be characterised by a short vertex symbol $(4.6^2)_2(4^26^28^2)$ with each Cu$_2$(μ-O$_2$CR)$_4$ core as a 4-connected node, each Cu(I) as a 3-connected node; the ratio of the number of 3-connected to 4-connected nodes is 2 : 1.[11] Usually, the (3,4)-connected nets form Catalan-type or Archimedean-type 3D nets,[10] and such 2D nets with both 4- and 6-membered rings, as well as both 3- and 4-connections, are rarely observed because the 4-connected nodes generally favour the formation of 3D nets.[12] Obviously, the Cu$_2$(μ-O$_2$CR)$_4$ node is essential to keep the planar structure observed in **3**.[13]

The structure of **4** is composed of one crystallographicaly independent Cu(II) atom, half a 1,2,3-btc ligand and half a 4,4′-bpy ligand. Each Cu atom has a square-pyramidal geometry, being coordinated by two chelating carboxylate oxygen atoms [Cu–O 1.994(2), 2.039(2) Å], one *syn-syn* bidentate carboxylate oxygen atom [Cu–O 1.948(2) Å] and one 4,4′-bpy nitrogen atom [Cu–N 1.968(2) Å] at the basal positions, and one binding water molecule [Cu–O 2.216(2) Å] at the apical position, as shown in Fig. 3(a). The overall structure is a 3D porous coordination network [Fig. 3(b)] with 1D channels parallel to the *c* axis, with effective dimensions of *ca.* 11.5 × 6.5 Å^2 and which constitute 21.5% of the unit cell volume according to the PLATON program. The NO$_3^-$ ions and the

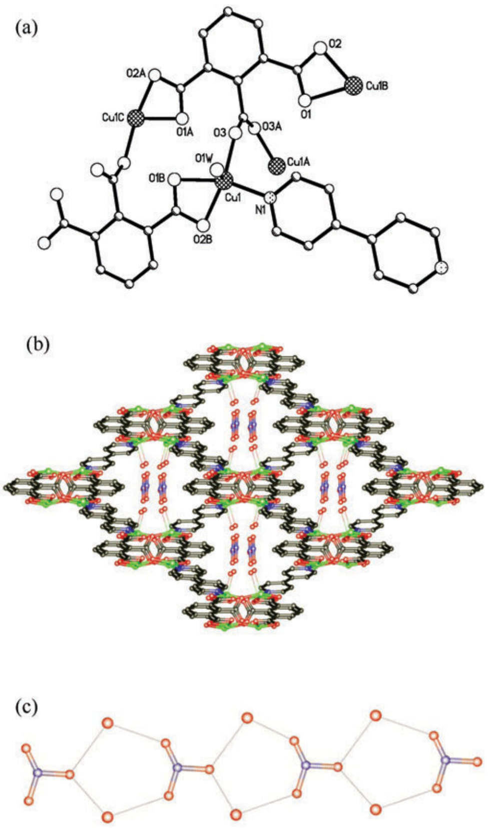

Fig. 3 Perspective views of the coordination environments of the metal atoms (a), the 3D network (b) and the 1D hydrogen-bonded chain (c) in **4**.

weakly coordinated water molecules occupy these channels in which they form 1D hydrogen-bonded chains [Fig. 3(c)]. The topological analysis of the network has been performed by considering each 1,2,3-btc ligand as a 4-connected node [Fig. 4(a)] and each Cu(II) as a 3-connected node because each 1,2,3-btc ligand connects with four equivalent Cu(II) atoms and each Cu(II) atom connects with two 1,2,3-btc and one 4,4′-bpy ligand; the ratio of the number of 3-connected to 4-connected nodes is also 2 : 1.[11] Such a net structure can be characterised by a short vertex symbol $(4.10^2)_2(4^2 10^4)$, which is a 3D (3,4)-connected net, as shown in Fig. 4(b). Therefore, **4** represents an unusual 3D AB_2 (A = 4-connected vertices, B = 3-connected vertices) composition compared to the usual A_3B_4 nets constructed by the Catalan or Archimedean types.[10,14]

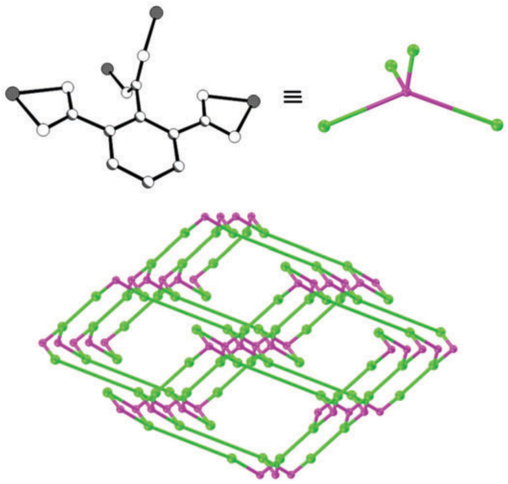

Fig. 4 Perspective views of the 4-connected ligand node (a) and the 3D (3,4)-connected topological net (b) in **4** (purple spheres: 4-connected ligand node, green spheres: 3-connected metal node).

Thermogravimetric analysis (TGA) was performed on a polycrystalline sample of **4** under a nitrogen atmosphere (see Electronic Supplementary Information). A first weight loss of 6.3% occurred in the temperature range of 100–130 °C, corresponding to the removal of two weakly coordinated water molecules per unit (theoretical weight loss, 6.1%). No weight loss was observed at 130–245 °C, suggesting that the framework is stable in this temperature range. The framework began to collapse above 245 °C.

In summary, we have successfully synthesised three new coordination polymers under hydrothermal conditions, which demonstrate pH-controlled metal/ligand *in situ* redox reactions and represent a feasible route to design topological networks and porous polymers in hydrothermal synthesis.

Experimental

Synthesis

The single crystals of **1**, **2**, **3** and **4** were prepared analogously by heating the mixture of $Cu(NO_3)_2 \cdot 3H_2O$ (0.242 g, 1.0 mmol), 1,2,3-btc$H_3 \cdot 2H_2O$ (0.123 g, 1.0 mmol), 4,4′-bpy (0.078 g, 0.5 mmol), water (10 cm^3) and NaOH (0.16 g, 4.0 mmol for **1**, **2**; 0.08 g, 2.0 mmol for **3**; none for **4**), in a 15 cm^3 autoclave with auto-generated pressure at 170 °C for 3 days. Dark blue block crystals of **1** were manually isolated from a small amount of green plate crystals of **2**. Both were washed by deionised water and ethanol (yield **1** 95%, **2** *ca.* 2% based on 4,4′-bpy) Anal. calcd for **2** $C_{21}H_{14}Cu_3NO_{12}$: C, 38.04; H, 2.13, N 2.11; found: C, 37.96; H, 2.05; N, 2.08 %. **3** (yield 65% based on 4,4′-bpy) and **4** (yield 55% based on 1,2,3-btcH_3) were isolated as green block crystals. Anal. calcd for **3** $C_{31}H_{21}Cu_2N_3O_8$: C, 53.91; H, 3.06, N 6.08; found: C, 53.56; H, 2.95, N, 6.03%; anal. calcd for **4** $C_{19}H_{15}Cu_2N_3O_{11}$: C, 38.78; H, 2.57, N 7.14; found: C, 38.56; H, 2.45, N, 7.03%.

X-Ray crystallography

The data were collected at 20 °C on a Bruker Smart CCD diffractometer with graphite-monochromated MoKα radiation (λ = 0.71073 Å). The structures were solved with direct methods and refined with full-matrix least-squares (SHELX-97).‡

Crystal data for **2**: $C_{21}H_{14}Cu_3NO_{12}$, M = 662.95, triclinic, space group $P{-}1$, $a = 7.868(1)$, $b = 10.356(2)$, $c = 13.390(2)$ Å, $\alpha = 85.43(1)°$, $\beta = 78.60°$, $\gamma = 72.67(1)°$, $U = 1020.7(3)$ Å^3, $Z = 2$, $D_c = 2.157$ g cm^{-3}, μ(MoKα) = 31.74 cm^{-1}, 8077 collected reflections, 4476 unique reflections ($R_{int} = 0.0328$), $R_1 = 0.0392$ and $wR_2 = 0.1046$.

Crystal data for **3**: $C_{31}H_{21}Cu_2N_3O_8$, M = 690.61, triclinic, space group $P{-}1$, $a = 10.725(1)$, $b = 10.840(1)$, $c = 14.797(2)$ Å, $\alpha = 91.429(2)°$, $\beta = 94.101(2)°$, $\gamma = 118.737(2)°$, $U = 1501.1(3)$ Å^3, $Z = 2$, $D_c = 1.528$ g cm^{-3}, μ(MoKα) = 14.72 cm^{-1}, 9083 collected reflections, 4448 unique reflections (R_{int} = 0.1245), $R_1 = 0.0858$ and $wR_2 = 0.2386$.

Crystal data for **4**: $C_{19}H_{15}Cu_2N_3O_{11}$, M = 588.42, monoclinic, space group $C2/c$, $a = 11.3502(8)$ Å, $b = 16.150(1)$, $c = 11.3658(8)$ Å, $\beta = 101.935(1)°$, $U = 2038.4(2)$ Å^3, $Z = 4$, $D_c = 1.917$ g cm^{-3}, μ(MoKα) = 21.59 cm^{-1}, 8679 collected reflections, 2401 unique reflections ($R_{int} = 0.0203$), $R_1 = 0.0289$ and $wR_2 = 0.0832$.

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‡ CCDC reference numbers 240358–240360. See http://www.rsc.org/suppdata/nj/b4/b409696g/ for crystallographic data in .cif or other electronic format.

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References

1 (*a*) B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629; (*b*) S. Kitagawa, R. Kitaura and S.-I. Noro, *Angew. Chem., Int. Ed.*, 2004, **43**, 2334.

2 (*a*) S.-L. Zheng, M.-L. Tong and X.-M. Chen, *Coord. Chem. Rev.*, 2003, **246**, 185; (*b*) S. R. Batten and K. S. Murray, *Coord. Chem. Rev.*, 2003, **246**, 103; (*c*) L. Carlucci, G. Ciani and D. M. Proserpio, *Coord. Chem. Rev.*, 2003, **246**, 247.

3 C. N. R. Rao, S. Natarajan and R. Vaidhyanathan, *Angew. Chem., Int. Ed.*, 2004, **43**, 1466.

4 C.-M. Liu, S. Gao and H.-Z. Kou, *Chem. Commun.*, 2001 1670.

5 R.-G. Xiong, X. Xue, H. Zhao, X.-Z. You, B. F. Abrahams and Z.-L. Xue, *Angew. Chem., Int. Ed.*, 2002, **114**, 3800.

6 X.-M. Zhang, M.-L. Tong and X.-M. Chen, *Angew. Chem., Int. Ed.*, 2002, **41**, 1029.

7 M.-L. Tong, L.-J. Li, K. Mochizuki, H.-C. Chang, X.-M. Chen, Y. Li and S. Kitagawa, *Chem. Commun.*, 2003, 428.

8 J. Tao, Y. Zhang, M.-L. Tong, X.-M. Chen, T. Yuen, C.-L. Lin, X.-Y. Huang and J. Li, *Chem. Commun.*, 2002, 1342.

9 J.-P. Zhang, S.-L. Zheng, X.-C. Huang and X.-M. Chen, *Angew. Chem., Int. Ed.*, 2004, **43**, 206.

10 A. F. Wells, *Three Dimensional Nets and Polyhedra*, Wiley, New York, 1977.

11 O. V. Dolomanov, A. J. Blake, N. R. Champness and M. Schröder, *J. Appl. Crystallogr.*, 2003, **36**, 1283.

12 M. O'Keeffe and S. T. Hyde, *Zeolite*, 1997, **19**, 370.

13 B. Moulton, J. Lu and M. J. Zaworotko, *J. Am. Chem. Soc.*, 2001, **123**, 9224.

14 M. O'Keeffe, M. Eddaoudi, A. Hailian Li, T. Reineke and O. M. Yaghi, *J. Solid State Chem.*, 2000, **152**, 3.