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Self-assembly of a novel 3D copper(I)-tetrazolate supramolecular framework *via* interpenetration of porous 2D double-layer motifs

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The self-assembly of CuCN and 1*H*-TAZ ligand under hydrothermal conditions generated a novel three-dimensional hybrid supramolecular framework, namely, $[Cu_6(TAZ)_4(CN)_2]_n$ (**1**) (TAZ = tetrazole). Single-crystal X-ray diffraction show that $[Cu_2(TAZ)_2]$ binuclear subunits are linked by μ_2- and μ_3-CN groups to give a 2D double-wave-shaped network, which possesses 1D channels with four open-windows. The 2D bilayers interpenetrated each other to form the 3D supramolecular framework of **1**.

In the past decade, much attention has been paid to the design and synthesis of coordination polymers because of their interesting molecular topologies and crystal packing motifs, alongside their potential applications in many areas including gas storage, magnetism, luminescence, as well as electrical conductivity [1–6]. In this process, some latest investigations show that the application of polyazaheteroaromatic compounds as donor groups gives the possibility to tune the properties of the organic ligands by the careful selection of the polyazole donors or by the type and position of the substituent in the five-membered ring [7–11]. Among polyazaheteroaromatic compounds, tetrazole and its derivatives are very interesting ligands because they almost combine the possible bridging fashions of pyrazoles (N_1,N_2-), imidazoles(N_1,N_4-), 1,2,3-triazoles (N_1,N_2,N_3-) and 1,2,4-triazoles (N_1,N_2,N_4-) with regard to the arrangement of their four nitrogen atoms (Scheme 1). On the other hand, it is well known that the azide ion can easily undergo cycloaddition with the cyano groups of organic nitriles to yield tetrazole rings [7,12]. Especially, Sharpless and Demko have reported the preparation of a variety of 5-substituted 1*H*-tetrazoles in water and investigated the mechanism by which zinc(II) catalyzes the union of an azide ion with organic nitriles to form tetrazoles [13]. On the base of this report, a number of coordination polymers with interesting structural and/or physical properties, such as luminescence, non-linear optics, ferroelectricity, magnetism and porosity, have been synthesized from in situ generated ligands bearing one or more tetrazoles under hydro- or solvothermal conditions [14–20].

As an extension of our previous study of the family of Cu(I)/Ag(I)/1,2,4-triazole/polyoxometalate hybrids [21,22], we have embarked on a program in which hydro(solvo)thermal synthesis are used to discover new hybrid solids based on inorganic CuX (X = Cl, Br, I, CN, SCN) subunits and polyazaheteroaromatic compounds, such as 1,2,4-triazole, benzotriazole, tetrazole and their derivatives [23,24]. To our knowledge, despite the extensive studies on the 5-substituted-1*H*-tetrazoles, the coordination chemistry of the non-substituted tetrazole ligand remains largely unexplored [25–28]. Herein, using the non-substituted tetrazole ligand, we report a novel 3D hybrid supramolecular compound, namely, $[Cu_6(TAZ)_4(CN)_2]_n$ (**1**) (TAZ = tetrazole), which was characterized *via* X-ray single-crystal diffraction, elemental analysis, FT-IR, Raman spectrum, DT/TGA and solid state photoluminescence measurements.

Heating a mixture of 1*H*-TAZ, CuCN and $K_3Fe(CN)_6$ in 10 ml H_2O at 180 °C for 5 days [29] followed by slowly cooling down to ambient temperature produced golden block crystals of compound **1**. In this process, the $K_3Fe(CN)_6$ was selected as a precursor instead of KCN to provide CN^- because the slow release of CN^- might play an important role in the formation of such hybrid materials. The IR spectrum exhibits multiple bands at 2100, 2089, 2071 and 2048 cm^{-1}, assigned to the cyanide groups. These bands are higher than that of terminal cyanide ions and are typical for bridging cyanide groups [30]. These results are consistent with the single-crystal structure of **1**, which shows μ_2 and μ_3 two types of bridging cyanide groups. The other two series of bands in the ranges of 660–1715 and 3130–3377 cm^{-1} are ascribed to the vibrations of

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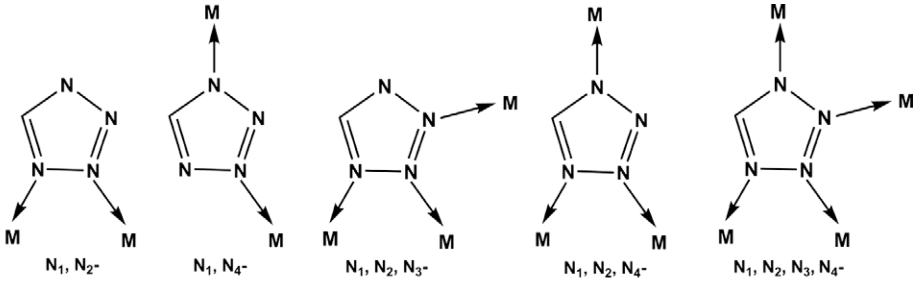

Scheme 1.

organic ligands. Similarly, the Raman spectrum also exhibits three bands at 2103, 2077 and 2051 cm^{-1} associated with bridging CN groups and displays several bands from 1000 to 1510 cm^{-1} attributed to the TAZ ligands. Since the thermal stability is important for the hybrid materials, TG/DTA experiments were also carried out on crystalline samples of compound **1** under a nitrogen atmosphere from 40 to 1000 °C. The weight loss curve showed that it was stable up to *ca.* 280 °C. Over the range 280–850 °C, a continuous weight losses were due to the decomposition of organic ligands and cyanide groups (exptl: 47.7%, calcd: 46.3%), and the residue should be copper powder.

The single-crystal structure analysis [31] shows that compound **1** presents a 3D hybrid supramolecular architecture generated by interpenetrated 2D double wave-like layers with TAZ and cyanide group acting as two kinds of tridentate bridging ligands. As depicted in Fig. 1, the structure of **1** possesses six unique copper sites, two anionic TAZ ligands and two cyanide groups. Six independent Cu^{I} atoms are of 2- [Cu(1) and Cu(6)], 3- [Cu(2), Cu(3) and Cu(4)] and 4-coordinated [Cu(5)], respectively. The linear geometries of Cu(1) and Cu(6) are finished by two nitrogen atoms from different TAZ ligands with Cu–N bonds and N–Cu–N bond angles of 1.855(3) and 1.868(3) Å, 178.4(2)° and 176.5(2)°, respectively. The distorted trigonal coordination environments of Cu(2), Cu(3) and Cu(4) atoms are different in detail. Cu(2) and Cu(4) are coordinated by two TAZ ligands and one μ_2-bridging cyanide group, while Cu(3) is coordinated by two TAZ ligands and one μ_3-cyanide group, with Cu–N bond lengths ranging from 1.967(3) to 1.995(3) Å, and Cu–C/N bond length of 1.881(5)–1.886(6) Å. The corresponding bond angles are in the range of 110.55(18)–124.20(10)°. The remaining Cu(5) is in a tetrahedral geometry and is coordinated by two nitrogen atoms from different TAZ ligands [Cu–N = 2.021(3) Å] and two C atoms from two μ_3-CN groups [Cu–C = 2.246(6) Å], the Cu–C bond being much longer than that to the μ_2-bridging cyanide group. Each TAZ ligand firstly links adjacent copper atoms [Cu(2) and Cu(3) or Cu(4) and Cu(5)) utilizing the pyrazole-like fashion to give two kinds of [Cu_2N_4] dinuclear rings, and the Cu···Cu separations are 3.5336(17) [Cu(2)···Cu(3)] and 3.5684(17) [Cu(4)···Cu(5)], respectively. It is noted that the absences of a second anion bridging ligand to 'ease' the repulsion of the two metal ions make the two dinuclear units are nonplanar, and the dihedral angles are of about 20°. The [$Cu_2(TAZ)_2$] motifs linked each other through Cu(1) or Cu(6) atoms to give two linear chains along the *b*-axis, with Cu(1), Cu(2), and Cu(3) in one chain and Cu(4), Cu(5), and Cu(6) in the other. Two different 1D chains are further connected by cyanide groups alternately to form 2D wave-like layer structure. In addition, the C(4)N(5) cyanide groups further act as μ_3-bridges to link two Cu(5) from different layers, which ultimately form a novel 2D double-layer framework of **1** as depicted in Fig. 2. It should be pointed out that two C(4)N(5) cyanide groups take the μ_3-1,2κC:3κN fashion linking two Cu(5) and two Cu(3) centers to

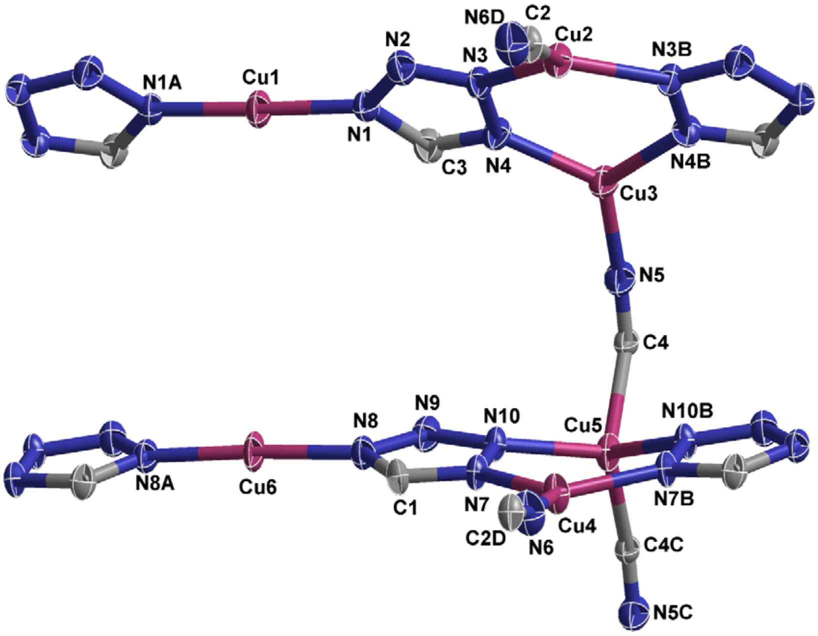

Fig. 1. ORTEP diagram of compound **1** showing the local coordination environment of copper(I) centers in the asymmetric unit and 30% thermal ellipsoids (Symmetry codes: A: *x*, −*y*, *z*; B: *x*, 1 − *y*, *z*; C: 1 − *x*, 1 − *y*, 1 − *z*; D: −*x*, *y*, −*z*).