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Cu(II) coordination polymers constructed by tetrafluoroterephthalic acid and varied imidazole-containing ligands: Syntheses, structures and properties

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ABSTRACT

Six new copper(II) coordination polymers combining 2,3,5,6-tetrafluoroterephthalatic acid (H_2tfBDC) and diverse imidazole-containing ligands, {[Cu(tfBDC)(1,2-bix)$_2$]·2(H_2O)}$_n$ (**1**), {Cu(tfBDC)(Im)$_2$}$_n$ (**2**), {[Cu(1,4-bmimb)$_2$(H_2O)]·(tfBDC)·2(H_2O)}$_n$ (**3**), {Cu(1,4-bimb)$_2$(H_2O)$_2$·(tfBDC)}$_n$ (**4**), {[Cu(1,3-bix)$_2$(H_2O)$_2$]·(tfBDC)·6(H_2O)}$_n$ (**5**) and {[Cu(1,4-bix)$_2$(H_2O)$_2$]·(tfBDC)·(1,4-bix)·4(H_2O)}$_n$ (**6**) (1,2-bix = 1,2-bis(imidazole-1-yl-methyl)-benzene, Im = imidazole, 1,4-bmimb = 1,4-bis((2-methyl-1H-imidazol-1-yl)methyl)benzene, 1,4-bimb = 1,4-bis(imidazol-1-yl)-butane, 1,3-bix = 1,3-bis(imidazole-1-ylmethyl)-benzene, 1,4-bix = 1,4-bis(imidazole-1-ylmethyl)-benzene), have been obtained and structurally verified by single-crystal X-ray diffraction analyses and further characterized by powder X-ray diffraction (PXRD), elemental analyses and infrared spectroscopy (IR). Single crystal X-ray diffraction analysis revealed that **1** is 2D 4-connected **sql** topology (point symbol: {4^4·6^2}) based on a single metal ion node. Compound **2** is characterized as an infinite 1D chain structure, which is further extended into a 2D layer through N-H···O hydrogen bonds and then a 3D supramolecular architecture *via* π···π stacking interactions. Note that **2** was prepared through an *in situ* ligand reaction in which N,N'-carbonyldiimidazole (cdi) broke up into imidazole ligand. Compound **3** possesses a 3D 4-fold interpenetrated architecture with 4-connected **dia** topology (Schläfli symbol: {6^6}) in which $tfBDC^{2-}$ is stabilized in the channel by hydrogen bonds. Compounds **4–6** are all linear 1D coordination polymers. In **4**, the free $tfBDC^{2-}$ ligand acts as a μ_4-bridge to link four coordinated water molecules from the chain to construct a 2D structure *via* hydrogen bonds. While in **5** and **6**, the uncoordinated $tfBDC^{2-}$ ligands and multimeric water clusters is responsible for the conversion of these 1D coordination polymers into 3D supramolecular assemblies through O–H···O hydrogen bonding interactions. Moreover, the UV–vis spectra and thermal stability of **1–6** are discussed in detail.

1. Introduction

An important focus of molecular crystals in recent years has been the area of molecular networks, which are produced by iteration of specific interactions between components [1–5]. For such materials, components are seen as building blocks or tectons and their interconnection as recognition events [6–10]. Both coordination [11–13] and hydrogen [14–17] bonds have been widely used for the construction of highly ordered crystalline architectures. Coordination frameworks are infinite 1-D, 2-D or 3-D skeletons which are extended, and sometimes porous, allowing for potential applications as solid framework hosts [18–23]. Similarly, hydrogen bonded networks of coordination compounds or organic molecules can also generate periodic structures [24–27]. Interestingly, these two approaches can intersect with both types of interactions working synergistically [28–36].

Generally, the selection of organic ligands is a tremendously significant because the coordination modes, configuration and flexibility of organic ligands have been considered to be the most crucial to the fine-tuning of molecular nets. Moreover, employment of a secondary organic ligand in the 'bottom-up' assembly would offer an opportunity to adjust the structural complexity and flexibility of the resulting mixed-ligand coordination polymers (CPs). Thus CPs comprising mixed ligands, especially a combination of dicarboxylates and N-donors, represent an important subset [37–44]. In previous studies, 2,3,5,6-tetrafluoroterephthalatic acid (H_2tfBDC), as a perfluorinated counterpart of terephthalic acid (H_2BDC), is receiving increasing

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attention [45–50], for its versatile coordination ability and considerable flexibility introduced by the torsion angles between the carboxylate groups and the benzene ring (45–60°). In addition, our group recently found out that H_2tfBDC is a good candidate for constructing supramolecular structures through hydrogen bonds [51]. As a result, H_2tfBDC has a variable bridging conformation and can diversify the structures and dimensionalities of the resulting networks. Likewise, imidazole and its derivatives, especially the bis(imidazole) ligands, have been regarded as a versatile and efficient building blocks for construction of CPs [52–55].

The self-assembly process which fabricates crystallized CPs materials from solution is widely known as an exquisite interplay of abundant competing interactions. For this reason, while the formation of CPs from single-ligand with a few sites of strong secondary interaction is very well understood now, the same cannot be said for the case of mixed-ligands system and/or those ligands containing extra hydrogen-bonded sites or regions with other strong intermolecular interactions. Herein, we report the mixed-ligands system of tetrafluoroterephthalic acid and varied imidazole-containing ligands and its use in the formation of copper(II) coordination polymers, namely, $\{[Cu(tfBDC)(1,2\text{-bix})_2]\cdot 2(H_2O)\}_n$ (**1**), $\{Cu(tfBDC)(Im)_2\}_n$ (**2**), $\{[Cu(1,4\text{-bmimb})_2(H_2O)]\cdot(tfBDC)\cdot 2(H_2O)\}_n$ (**3**), $\{Cu(1,4\text{-bimb})_2(H_2O)_2\cdot(tfBDC)\}_n$ (**4**), $\{[Cu(1,3\text{-bix})_2(H_2O)_2]\cdot(tfBDC)\cdot 6(H_2O)\}_n$ (**5**) and $\{[Cu(1,4\text{-bix})_2(H_2O)_2]\cdot(tfBDC)\cdot(1,4\text{-bix})\cdot 4(H_2O)\}_n$ (**6**). Among them, compound **1** and **3** possess **sql** [56] and **dia** [57] topology, respectively. The crystal structures are presented and discussed (Scheme 1). Furthermore, UV–vis spectra and thermal stability were also investigated.

2. Experimental

2.1. Materials and measurements

All reagents used in the syntheses were of analytical grade and used without further purification. The diffraction data collection was performed with Mo-Kα radiation (λ = 0.71073 Å) on a Rigaku RAXIS-RAPID area-detector diffractometer. IR spectrum was measured in KBr pellets on a Bruker IFS-66V/S FT-IR spectrometer. The elemental analyses (C, H and N) were carried out on a Perkin-Elmer 240 C elemental analyzer. The thermogravimetric measurement was performed on pre-weighed samples in a nitrogen stream using a Netzsch STA449C apparatus with a heating rate of 10 °C/min. Powder X-ray diffraction (PXRD) data were obtained using a Rigaku D/Max2550 automated diffractometer (CuKα, 1.5418 Å). UV–vis measurements (in diffuse reflectance mode) were carried out on a Hitachi U-4100 UV–vis–NIR spectrophotometer at 298 K. The magnetic measurements of the compounds were carried out by use of Quantum Design SQUID MPMS-VSM magnetometer in the temperature range of 2–300 K for and fields up to 5 T.

2.2. Synthesis of $\{[Cu(tfBDC)(1,2\text{-bix})_2]\cdot 2(H_2O)\}_n$ (1)

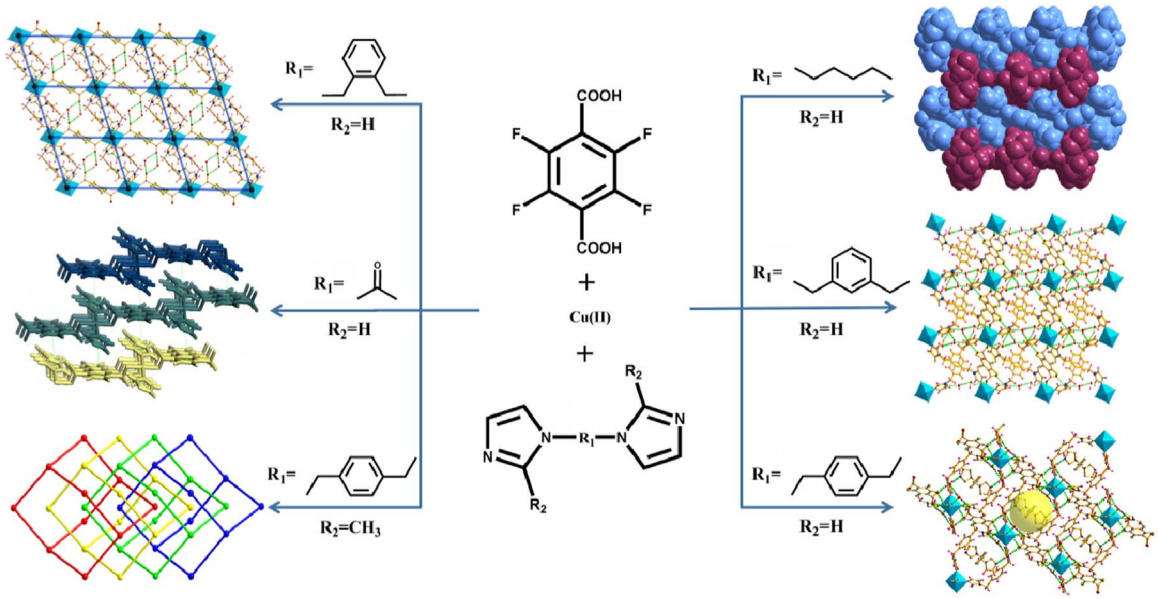
A mixture of $Cu(OH)_2$ (9.8 mg, 0.1 mmol), H_2tfBDC (47.6 mg, 0.2 mmol), 1,2-bix (23.8 mg, 0.1 mmol), EtOH (5 ml) and distilled water (5 ml) were loaded into a 25 ml beaker, and were slowly added ammonia under the condition of ultrasonic until a clear homogeneous solution was obtained. Then the solution was allowed to stand at room temperature for slow evaporation over 3 days. Blue crystals of **1** were isolated after washed with acetone, and dried in the air. Yield: 83%. Anal. calcd for $C_{36}H_{32}CuF_4N_8O_6$ (%): C 53.23, H 3.97, N 13.80. Found: C 53.20, H 3.92, N 13.84. IR (KBr disc, cm^{-1}): 3431 (s), 3143 (m), 3113 (m), 1619 (s), 1519 (m), 1461 (m), 1402 (w), 1359 (m), 1285 (w), 1237 (m), 1110 (m), 1086 (m), 1027(w), 976 (m), 948 (w), 905 (w), 838 (w), 727 (s), 670 (m), 621 (w), 459 (w), 438 (w).

2.3. Synthesis of $\{Cu(tfBDC)(Im)_2\}_n$ (2)

Compound **2** was obtained by following a similar procedure to that of **1**, but cdi (16.2 mg, 0.1 mmol) was used instead of 1,2-bix. Then the solution was allowed to stand at room temperature for slow evaporation over 3 days. Blue crystals of **2** were isolated after washed with acetone, and dried in the air. Note that **2** was prepared through an *in situ* ligand reaction in which N,N'-carbonyldiimidazole(cdi) broke up into imidazole ligand [58,59]. Yield: 52%. Anal. calcd for $C_{14}H_8CuF_4N_4O_4$ (%): C 38.59, H 1.85, N 12.86. Found: C 38.52, H 1.92, N 12.92. IR (KBr disc, cm^{-1}): 3429 (w), 3200 (s), 3084 (w), 2969 (w), 2875 (w), 1622 (s), 1541 (w), 1503 (m), 1467 (s), 1379 (s), 1327 (m), 1246 (m), 1143 (w), 1106 (w), 1076 (s), 978 (s), 863 (w), 787 (m), 737 (s), 648 (m), 627 (m), 518 (m).

2.4. Synthesis of $\{[Cu(1,4\text{-bmimb})_2(H_2O)]\cdot(tfBDC)\cdot 2(H_2O)\}_n$ (3)

Compound **3** was obtained by following a similar procedure to that of **1**, but 1,4-bmimb (26.6 mg, 0.1 mmol) was used instead of 1,2-bix.



Scheme 1. The summary of crystal structures in compounds **1–6**.