A new Cu(I) coordination polymer with the CdSO₄ structure type prepared *via* biphasic solvothermal reaction†

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Biphasic solvothermal reaction of Cu(NO₃)₂·6H₂O and 2,3,5,6-tetramethyl-1,4-benzenedicarboxylic acid (H₂TBDC) resulted in the formation of a novel coordination polymer, [Cu(TBDC)₁/₂]·H₂O (BPS-1). BPS-1 possesses a 3D framework containing 1D Cu(I)–COO helical chains. The use of an organic solvent with a high boiling point and an extension of the reaction time play important roles in the reduction of Cu(II) ions to Cu(I) ions and the formation of BPS-1.

In the past decade, hybrid inorganic–organic materials have received much attention from chemists due to the fact that these materials may incorporate functionality from both inorganic and organic components.[1,2] Compared to other metal–organic frameworks that are synthesized with conventional methods under bench-top conditions (20–80 °C, 1 atm),[3–5] hybrid inorganic–organic materials are normally generated under hydro- or solvothermal conditions,[6] which is an effective method for preparing rapidly developed metal–organic frameworks and inorganic zeolites.[7–10] Hydro- or solvothermal synthesis can favor condensation of M–OH into M–O–M bonds, providing multidimensional functional materials.[11] Most of the hydro- or solvothermal syntheses were run in homogeneous solution and moderate temperature, which can increase the reaction speed and reduce the reaction time. However, sometimes, insoluble precipitates or microcrystals can be obtained when a hydro- or solvothermal synthesis was used to prepare hybrid inorganic–organic materials based on carboxylate ligands due to the high coordination ability of the carboxylate to metal ions,[12] leading to difficulties in crystal growth.

Recently, biphasic solvothermal synthesis has been applied to prepare hybrid inorganic–organic materials based on carboxylate ligands. Different from the traditional hydro- or solvothermal synthesis in that the reaction was run in homogeneous solution, for the biphasic solvothermal synthesis, the reaction was run at the interface of two immiscible solvents, which can reduce the reaction speed and favor the growth of single crystals. Cheetham and coworkers[13] have prepared copper and nickel coordination polymers by use of the advantages of biphasic solvothermal synthesis.

However, from then on, reports on coordination polymers synthesized by biphasic solvothermal synthesis are quite rare, which may derive from the fact that most of the organic carboxylate ligands are not soluble in the organic solvents that are immiscible with water. Recently, we began to apply biphasic solvothermal synthesis to prepare functional coordination polymers. In this communication, we report a new coordination polymer, [Cu(TBDC)₁/₂]·H₂O (denoted as **BPS-1**) (H₂TBDC = 2,3,5,6-tetramethyl-1,4-benzenedicarboxylic acid), with a 3D framework prepared by biphasic solvothermal synthesis in nitrobenzene and water solvents.

As is well known, a lot of organic solvents, such as chloroform, dichloromethane, benzene, nitrobenzene *etc.*, are immiscible with water. However, most of the carboxylate ligands are not soluble in these solvents. Recently, we synthesized a new dicarboxylate ligand, 2,3,5,6-tetramethyl-1,4-benzenedicarboxylate (H₂TBDC).[14] Compared to benzenedicarboxylic acid, the additional four methyl groups enhance its solubility in organic solvents, such as nitrobenzene. Thus, the biphasic solvothermal reaction‡ of H₂TBDC in nitrobenzene and Cu(NO₃)₂·6H₂O in water at 130 °C resulted in the formation of blue prismatic crystals of **BPS-1**. As expected, the crystals were formed at the interface of nitrobenzene and water. The formula of [Cu(TBDC)₁/₂]·H₂O was further confirmed by elemental analysis and TGA.

Single-crystal X-ray diffraction§ reveals that **BPS-1** is a 3D coordination polymer. The asymmetric unit of **BPS-1** consists of two halves of Cu(I) ions and a half TBDC ligand. Surprisingly, Cu(II) ions were reduced to Cu(I) ions during the biphasic solvothermal reaction, which is quite different from the previous reported results that the biphasic solvothermal synthesis can effectively avoid the reduction of the copper by the carboxylic acid.[13]

Both central copper(I) ions are two-coordinated by two oxygen atoms from different TBDC ligands (see Fig. 1) in linear geometries with the average Cu–O distance of 1.8434(5) Å, which is significantly shorter than that found in other Cu(II) complexes (1.9–2.2 Å).[14] Both
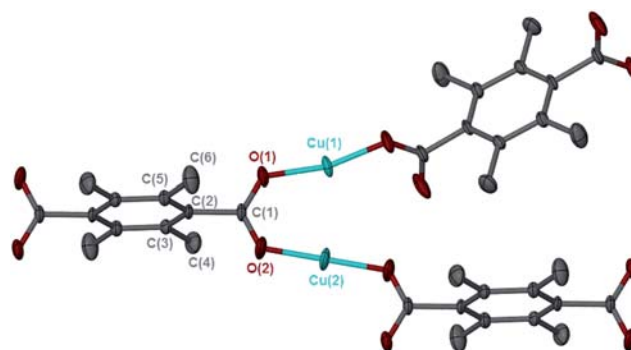
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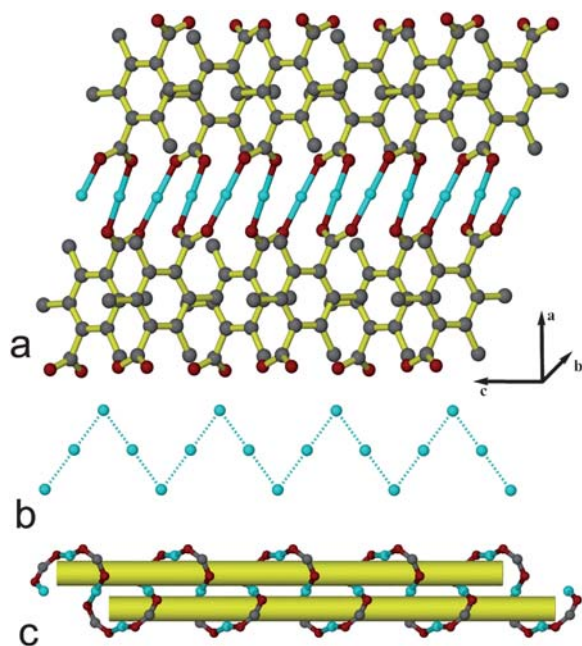
Fig. 1 The coordination environment of the central Cu(I) ions.

Fig. 2 (a) the 1D Cu(I)–TBDC chain; (b) the arrangement of Cu(I) ions in the 1D chain; (c) the helical Cu(I)-(COO) chain.

Fig. 3 Ball-stick (top) and space-filling (bottom) representation of the 3D framework of **3**.

carboxylate groups of TBDC ligands are deprotonated during the reaction and each adopts a bidentate bridging mode to connect two Cu(I) ions. As found in our previous reported $Zn(TBDC^1)_{1/2}(TBDC^2)_{1/2}$,[15] the TBDC ligand is nonplanar due to the space hindrance between the carboxylate groups and the methyl groups, with the dihedral angle between the carboxylate group and the benzene ring of 94.2°.

Thus, every Cu(I) ion is connected by two carboxylate groups of different TBDC ligands and each carboxylate group of the TBDC ligand bridges two Cu(I) ions to generate a 1D Cu(I)–TBDC chain, as shown in Fig. 2a. The Cu(I) ions in the chain have a zigzag chain arrangement (Fig. 2b) with the Cu–Cu distance of 2.816(6) Å. Every three Cu3 units is in a linear arrangement and all the Cu(I) are connected by the carboxylate groups of different TBDC ligands to form a 1D Cu(I)-(COO) helical chain, as shown in Fig. 2c. The 1D Cu-carboxylate chains are further connected by the spacer of TBDC in different directions to give rise to a three-dimensional framework (Fig. 3). The dimensions of the small channel along the *c* axis are 3.0 × 4.2 Å (from atom to atom), in which uncoordinated water molecules reside. The gas sorption isotherm did not indicate any appreciable amount of adsorption, presumably due to the limited pore size.

As mentioned above, each TBDC connects four Cu(I) ions, which can be considered as a planar four-connected node; each Cu(I) ion is attached to two TBDC ligands in a linear geometry, which can be considered as a linear node between two TBDC ligands. On the basis of the simplification, **BPS-1** possesses a CdSO4 structure type, as shown in Fig. 4.

Thermal gravimetric analysis (TGA) of **BPS-1** was performed under a N₂ atmosphere. The gradual weight loss of 9.1% from 50 to 255 °C corresponds to the loss of one uncoordinated water molecule (calcd: 9.4%), and after 255 °C, **BPS-1** starts to decompose.

It has been reported that biphasic solvothermal synthesis can effectively avoid the reduction of the copper ion by the carboxylic
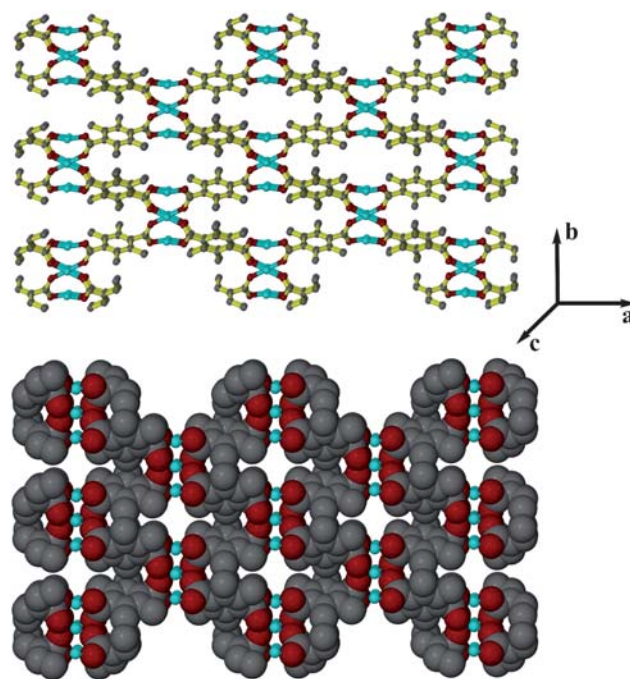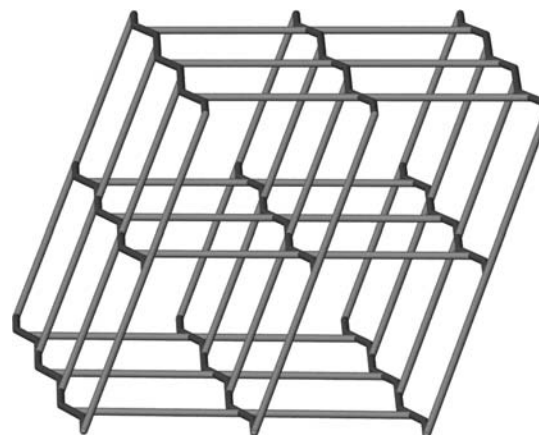

Fig. 4 The CdSO4 structure type of **BPS-1**.

acid.[13] However, in our case, the Cu(II) ion was reduced to Cu(I) ion during the biphasic solvothermal reaction, which may result from the use of nitrobenzene with a higher boiling point and longer reaction time, during which the Cu(II) ions were slowly reduced to Cu(I) ions. In order to prepare MOFs with various structural topologies, different organic solvents such as cyclohexanol, toluene *etc.* were used in the Cu–TBDC system, however, only some precipitates were obtained, indicating nitrobenzene with a high boiling point plays an important role in the reduction of Cu(II) to Cu(I) and formation of the porous coordination polymer of **BPS-1**.

In summary, a new Cu(I) coordination polymer (**BPS-1**) constructed from a nonplanar dicarboxylate ligand *via* biphasic solvothermal reaction, has been synthesized and characterized. **BPS-1** possesses a 3D porous framework containing helical Cu(I)-(COO) chains. Current research indicates that the use of organic solvents

with a high boiling point and extending the reaction time resulted in the reduction of Cu(II) ions to Cu(I) ions in the biphasic solvothermal synthesis. Further studies will focus on the synthesis of other coordination polymers *via* biphasic solvothermal synthesis.

Acknowledgements

Notes and references

‡ Preparation of **BPS-1**: H₂TBDC (10 mg, 0.045 mmol) was dissolved in 1 mL nitrobenzene. The resulting solution was placed in the bottom of a glass tube. Cu(NO₃)₂·6H₂O (20 mg, 0.085 mmol) was dissolved in 1 mL H₂O and carefully layered above the organic solution. The glass tube was sealed and heated to 130 °C for 5 days. The blue block crystals at the interface of the two phases were collected by filtration. Yield: 34%. Calc. for **BPS-1**: C 37.60, H 4.21%; Found: C 37.89, H 4.09%. IR (KBr, cm⁻¹): 3305(br, vs), 1700(vs), 1650(s), 1500(s), 1254(m), 1018(m), 788(s), 547(m).
§ Crystal data for **BPS-1**: $C_6H_6CuO_2$, monoclinic, space group $C2/c$, $a = 19.183(4)$, $b = 10.025(2)$, $c = 6.6486(15)$ Å, $\beta = 105.274(4)°$, $U = 1233.5(5)$ Å³, $T = 273$ K, $Z = 8$, $D_c = 1.870$ g/cm³, $\lambda = 0.71073$ Å, 3521 reflections measured, 1403 unique which are used in all calculations. $R1 = 0.0277$ ($R1$ all data = 0.0360) and $wR2 = 0.0696$ ($wR2$ all data = 0.0759).

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