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Phase transfer catalyst supported, room-temperature biphasic synthesis: a facile approach to the synthesis of coordination polymers†

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A facile approach, named phase transfer catalyst supported, room temperature biphasic synthesis, has been developed to synthesize a new type of coordination polymers. Compared to the traditional biphasic solvothermal synthesis that was run at high temperature (100–200 °C), the new approach introduced here can be operated under a mild condition (room temperature) with the support of phase transfer catalyst. With the application of this new approach, two copper coordination complexes with 1D metal–organic nanotube and 1D coordination polymer containing large water clusters have been successfully synthesized and characterized. Furthermore, the synthetic approach presented here can be extended to synthesize other coordination polymers, including porous lanthanide–organic frameworks.

The design and synthesis of new types of coordination polymers (or metal–organic frameworks) has received intense research interest because of the potential applications of the polymers in gas storage and catalysis.[1,2] As a result of research on the correlations among their synthetic conditions, structures and properties, coordination polymers have been developed and constructed over the past three decades using various synthetic methods. Compared with traditional solution methods under bench-top conditions (20–80 °C, 1 atm),[3] hydro- and solvothermal synthesis can favour the condensation of M–OH into M–O–M bonds, and provide multidimensional functional materials.[4] These synthetic methods have been widely used in the construction of porous metal–organic frameworks and inorganic zeolites.[5–7] Iono- and urothermal synthesis have recently been developed to yield crystalline porous materials[8,9] because ionic liquids or urea derivatives have advantages in acting as structure

directing agents or pendant ligands to template the formation of solids.

To reduce reaction speeds and avoid the formation of precipitates, Cheetham *et al.* developed a method of biphasic solvothermal synthesis for the assembly of hybrid inorganic–organic materials.[10] Where traditional hydro- or solvothermal synthesis reactions are run in homogeneous solutions, biphasic solvothermal reaction are run at the interface of two immiscible solvents, thus favoring the growth of single crystals. We previously reported the biphasic solvothermal synthesis of a new Cu(I) coordination polymer (**BPS-1**) with the $CdSO_4$ structure type.[11] Cu(II) ions were slowly reduced to Cu(I) ions during the biphasic solvothermal reaction, which may result from the use of nitrobenzene with higher boiling point and the longer reaction time. These conditions allow the redox reaction to proceed during the reaction. Herein, we describe a new method for preparing of new types of coordination polymers. The reactions are carried out in biphasic conditions in the presence of a phase transfer catalyst. With the support of the phase transfer catalyst, the biphasic reaction can be run at room temperature. Our new approach is illustrated with applications to a single-walled metal–organic nanotube, $\{[Cu(py)_4Cl\cdot Cl][Cu_8(H_2O)_8(py)_{14}(BTMIPA)_4]\cdot 56-H_2O\}_n$ (**BPS-2**), and a 1D coordination polymer with large water clusters, $\{[Cu_2(BTMIPA)(phen)_2(H_2O)]\cdot 12H_2O\}_n$ (**BPS-3**, **BPS** = biphasic synthesis, $H_4BTMIPA$ = 5,5′-methylenebis(2,4,6-trimethylisophthalic acid)).

Metal–organic nanotubes (MONTs), as a special kind of functional coordination polymers, have received much attention from chemists because of their unique tubular properties and potential applications in storage, delivery, and catalysis among others. To assemble discrete MONTs, the linking mode of the organic ligand must meet the coordination geometry of the metal ion. In our previous work, we designed and synthesized a novel non-interpenetrating MONT based on mixed organic ligands.[12] In this work, we focus our attention on the synthesis of 1D MONT based on a tetracarboxylate ligand. We selected the ligand 5,5′-methylenebis(2,4,6-trimethylisophthalic acid) ($H_4BTMIPA$) because of its special conformation, in which the twist between two benzene rings causes the four carboxylate groups to link metal ions in different directions.

Ligand $H_4BTMIPA$ was synthesized according to the route shown in Scheme 1. The room temperature biphasic reaction of $Cu(NO_3)_2\cdot 5H_2O$, pyridine or 1,10-phenanthroline (phen), and $H_4BTMIPA$ in water–cyclohexanol–toluene in the presence of

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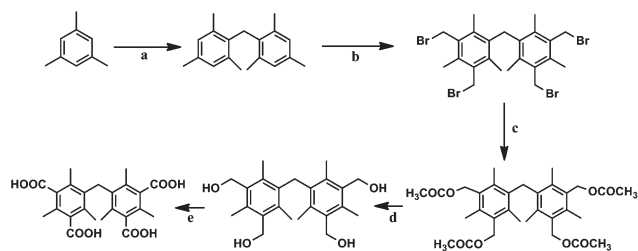
Scheme 1 Synthetic procedures of the H$_4$BTMIPA. (a) Paraformaldehyde and formic acid; (b) paraformaldehyde, HBr–acetic acid solution; (c) anhydrous sodium acetate; (d) LiOH; (e) Jones reagent.
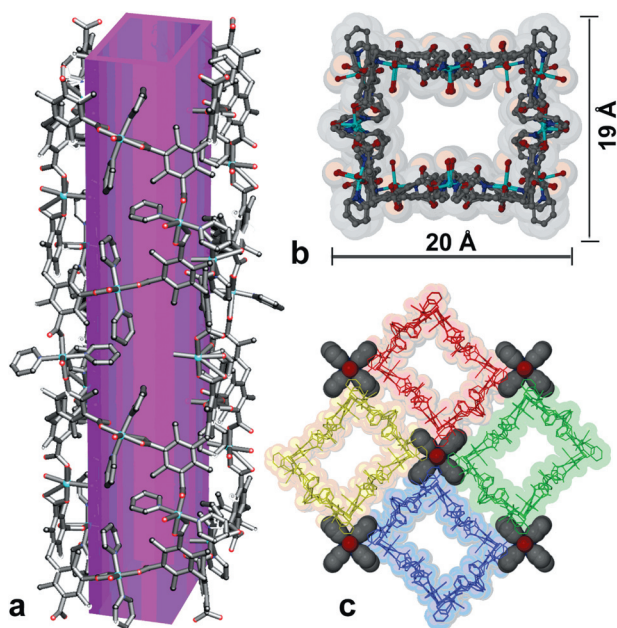

Fig. 1 (a) Side view of **BPS-2**; (b) top view of **BPS-2**; (c) the 3D packing of **BPS-2**, showing the [Cu(py)$_4$Cl·Cl] locating among the nanotubes, red balls represent chlorine ions.

the phase-transfer catalyst 18-crown-6 resulted in the formation of large, blue crystals of **BPS-2** and **BPS-3** in the water phase. The phase-transfer catalyst played an important role in the formation of large crystals. The effect of the phase-transfer catalyst on the formation of **BPS-2** is discussed.

Single crystal X-ray diffraction‡ reveals that **BPS-2**, which crystallizes in tetragonal space group $P42_1/c$, is a tubular coordination polymer. The two benzene rings of BTMIPA ligand are twisted with an average dihedral angle of 83.3°. The carboxyl groups are almost vertical with respect to the benzene ring because of the steric hindrance between the carboxyl and methyl groups. All the carboxyl groups of the BTMIPA ligand are deprotonated, and each adopts monodentate coordination mode to coordinate with a copper ion. The most intriguing feature of **BPS-2** is that there is a non-interpenetrating MONT with [Cu(py)$_4$Cl·Cl] as the space filler among the tubes (Fig. 1). Hence, two kinds of copper ions are found to play different roles in the formation of **BPS-2**: one is connected by the BTMIPA ligands to generate a 1D MONT, and another is coordinated by pyridine and chlorine ions to avoid interpenetration.

Four copper ions are linked by four BTMIPA ligands to form a rectangular subunit, in which each BTMIPA uses its two opposite carboxyl groups to coordinate with copper ions (ESI,† Fig. S1). The subunits are further connected to each other along the [001] direction through the two remaining opposite carboxyl groups of BTMIPA ligands coordinating with the copper ions, resulting in the formation of the 1D MONT. In the MONT, each copper ion in a square planar geometry is linearly coordinated by two carboxyl oxygen atoms from different BTMIPA ligands and the remaining coordination sites are occupied by coordinated pyridine and water molecules. The coordinated water molecules point toward the centre of the nanotube, resulting in a hydrophilic cavity. The dimensions of the MONT are 18.7 × 11.5 Å (from copper to copper atom), and a large amount of uncoordinated water molecules reside in the nanotube, in agreement with the IR data, which shows strong and wide absorption peak at around 3500 cm^{-1} for H$_2$O (ESI,† Fig. S7).

Although interpenetration is a common phenomenon in the design and synthesis of low-density MOFs,[13] it is interesting to point out that **BPS-2** is non-interpenetrating, probably because of the steric hindrance effect of the methyl groups of the BTMIPA ligands and the coordinated pyridine molecules. Furthermore, [Cu(py)$_4$Cl·Cl], which locates among the MONTs, also prevents the formation of interpenetrating nets. Although many MONTs have recently been designed and synthesized, most of them are interpenetrating nets,[14] and non-interpenetrating MONTs with large voids remain rather rare.[15] The packing of MONTs along the *ab* plane is loose, and the nanotubes are about 6.7 Å apart because of the presence of [Cu(py)$_4$Cl·Cl]. The solvent-accessible volume of **BPS-2** is 45.9%, through an analysis using the PLATON software.[16]

When phen was added to a similar reaction system, blue block crystals of **BPS-3** were obtained. Single-crystal X-ray diffraction‡ reveals that **BPS-3** is a 1D coordination polymer. All the carboxyl groups of BTMIPA are deprotonated and each adopts a monodentate coordination mode to link copper ions. Thus, each BTMIPA ligand connects four copper ions, and every copper ion attaches to two BTMIPA ligands to generate a 1D coordination polymer with two types of metallocycles (ESI,† Fig. S6). The moderate π···π stacking (3.67 and 3.76 Å) between the phen ligands in different chains further connect the 1D chains into a 3D supramolecular architecture containing 1D channels along the *b* axis.

It is interesting to observe that 1D novel water tape with an 8-membered ring as the basic unit resides in the supramolecular channels. As shown in Fig. 2b, the basic unit of the water chain consists of 26 water molecules linked by hydrogen bonds. The average O···O distance in the large cluster is about 2.80 Å, which is shorter than that observed in liquid water (2.85 Å),[17] and longer than the corresponding value in hexagonal ice (I_h) (2.76 Å)[18] and other reported complexes containing large water clusters.[19] More interestingly, the coordinated water molecules and the carboxyl groups of BTMIPA ligand have strong hydrogen bonding interactions with the uncoordinated water molecules in the 1D water chains with an average O···O distance of 2.80 Å. These hydrogen bonding interactions further connect the 1D water cluster chains to generate a 3D water supramolecular architecture (Fig. 2c), which is quite different from other reported complexes containing 3D water clusters.[20]
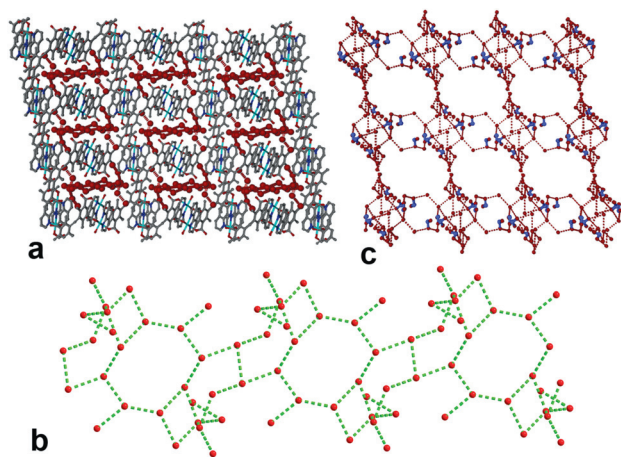
Fig. 2 The 3D supramolecular architecture with 1D water clusters in the channels (a), the 1D water tape (b) and the 3D water supramolecular architecture connected by carboxylate groups (c).

As mentioned above, the addition of a phase-transfer catalyst in the reaction is crucial to the formation of large, high-quality crystals of **BPS-2** and **BPS-3**. The role of the phase-transfer catalyst was further tested by carrying out various reactions for the synthesis of **BPS-2** at different conditions. When no phase-transfer catalyst was added to the reaction system, the crystals formed at the interface of the two immiscible solvents after two days, but the crystals were too small to be determined through single-crystal X-ray diffraction. When the phase-transfer catalyst 18-crown-6 was added to the reaction system, blue crystals appeared throughout the water phase after only two hours. In addition, the size of the largest crystal is about 0.4 mm × 0.4 mm × 0.35 mm, which is quite rare in porous coordination polymers with large cell units. The yield and the quality of the products were significantly improved, indicating that 18-crown-6 plays an important role in the reaction, similar to findings in other organic reactions.[21] Whilst other reactions have shown that the quantity of the phase-transfer catalyst has no direct effect on the yield and quality of the final product, our findings indicate that the type of the phase-transfer catalyst had a significant influence on the quality of the product. For example, when 18-crown-6 was replaced by tetrabutylammonium bromide (TBAB) in the reaction, fine crystals suitable for single-crystal X-ray diffraction were obtained but the crystals were significantly smaller than those obtained in the presence of 18-crown-6 (Fig. 3). The organic solvents used also had a significant influence on the product. The use of mixed organic solvents, such as cyclohexanol–toluene or cyclohexanol–benzene, yielded high-quality crystals; the use of other organic solvents yielded unknown precipitates that formed at the interface of the two immiscible solvents.

It is well known that whilst most open coordination polymers are stable in organic solvents, they are also moisture-sensitive. Porous coordination polymers or metal–organic frameworks (MOFs) soaked in water decompose slowly. However, **BPS-2** is stable in water, a rarity in porous coordination polymers. Thus, it may catalyse some organic reactions in the water phase because of its unique tubular channels. Although many organic reactions catalyzed by porous MOFs in organic solvents have been
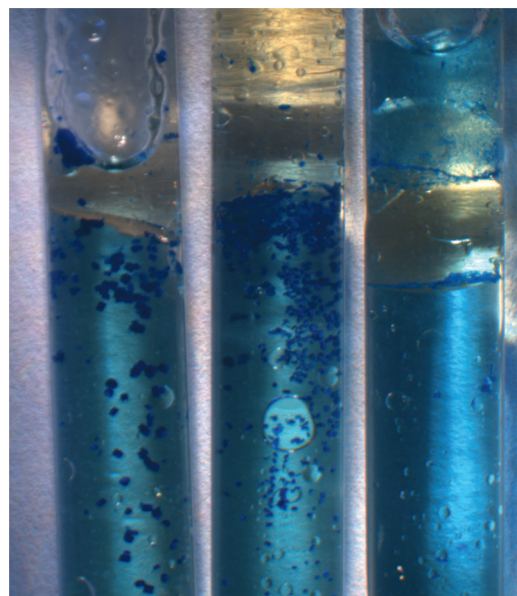

Fig. 3 The comparison of the crystals formed in different conditions. (Left) with 18-crown-6 as the catalyst; (middle) with tetrabutylammonium bromide as the catalyst; (right) without catalyst.

reported,[22] it is rare that the catalysis reaction is run in water solutions. This subject is currently being investigated in our lab.

In summary, a novel MONT and a 1D coordination polymer with large water clusters are obtained and characterized *via* a new synthetic approach: phase-transfer catalyst supported, room-temperature biphasic synthesis. The new nanotubular material (**BPS-2**) is non-interpenetrating because of the large template of [Cu(py)$_4$Cl·Cl]. To the best of our knowledge, **BPS-2** represents the first non-interpenetrating MONT obtained through the new synthetic approach introduced here. The application of biphasic synthesis at room temperature is crucial to the formation of large crystals of **BPS-2** and **BPS-3**. Our research provides a new approach for the synthesis of functional coordination polymers. Furthermore, the synthesis method presented here can be extended to synthesize other functional coordination complexes, and the temperature of the reaction can also fall into the range from room temperature to 160 °C. The results indicate that biphasic synthesis is an efficient strategy for the construction of functional coordination polymers. Further studies will focus on the synthesis of other porous materials based on this biphasic approach.

Notes and references

‡Crystal data for **BSP-2**: C$_{182}$H$_{280}$Cl$_2$Cu$_9$N$_{18}$O$_{96}$, M = 4899.05 g mol^{-1}, tetragonal, space group $P42_1/c$, 173 K, Z = 4, $a = b$ = 31.010(4), c = 28.765(6) Å, V = 27661(8) Å^3, 112 966 reflections collected of which 19 468 are independent [R_{int} = 0.0774], R_1 = 0.0801, wR_2 =

0.2348, $[I > 2\sigma(I)]$, $\mu = 0.749$ mm^{-1}, $S = 1.078$. Crystal data for **BSP-3**: $C_{47}H_{62}Cu_2N_4O_{21}$, $M = 1146.09$ g mol^{-1}, triclinic, space group $P\bar{1}$, $Z = 2$, $a = 11.4190(7)$, $b = 12.9822(8)$, $c = 17.2565(11)$ Å, $\alpha = 89.9860(10)$, $\beta = 79.2290(10)$, $\gamma = 80.3940(10)°$, $V = 2476.6(3)$ Å^3, 17 084 reflections collected of which 8438 are independent $[R_{int} = 0.0214]$, $R_1 = 0.0680$, $wR_2 = 0.1938$, $\mu = 0.945$ mm^{-1}, $S = 1.114$. For **BSP-2**, the SQUEEZE routine in the PLATON software[23] was applied to subtract the diffraction contribution from the disordered solvent molecules.

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