Triple-stranded helices and zigzag chains of copper(I) 2-ethylimidazolate: solvent polarity-induced supramolecular isomerism†

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The solvent effect of different polarities in hydro(solvo)thermal reaction of Cu^{II} and 2-ethylimidazole leads to the generation of two supramolecular isomers of triple-stranded helical and zigzag chain-like structures of Cu^I 2-ethylimidazolate.

Zaworotko and coworkers introduced the term 'supramolecular isomers'[1] which are actually widely encountered in the field of supramolecular chemistry and crystal engineering.[1–4] However, most reported examples in coordination networks have different solvent molecules in the structures,[1,3] and only a few are true supramolecular isomers with a fixed stoichiometry for all components.[4] Furthermore, though it is easy to predict the possible superstructure especially for the simple, low dimensional system, controlled synthesis of them is still a formidable task even for such supramolecular isomerism.[4c]

In our previous work we successfully designed and synthesized supramolecular isomeric polygons constructed by simple, bent, exo-bidentate 2-methylimidazolate and 2-coordinate Cu^I ions with 1 : 1 stoichiometry by utilizing organic solvent molecules as templates.[3c] Unfortunately, template molecules usually result in the final structures having guest molecules, and the helical structure among the three possible superstructures[2a] has not been observed for this system.[3c] Meanwhile the helix is one of the most significant coordination polymers in the context of spontaneous chiral resolution from achiral components.[5,6] A question which arises here is how to form the helical structures by this simple and feasible synthetic method? Since the final formation of a superstructure in a polymorphic system involves many factors including small differences of thermodynamic and kinetic stabilities and unpredictable crystal packing effects,[2] as well as the striking impact of the introduction of the methyl group to the simple imidazolate ligand in the formation of those polygons,[3c] we speculated that it may be useful to increase the length of the alkyl substituent. When the methyl groups are replaced by a longer alkyl substitutent, the planar cyclic structure should be difficult to be generated because of the larger spatial hindrance. Moreover, the stronger hydrophobic nature of the larger alkyl substitute groups has a significant structural response to the polarity of the reaction medium which is somewhat similar with self-assembly of amphiphilic molecules in solution. Thus we chose 2-ethylimidazolate as the bridging ligand for investigation of the hydro(solvo)thermal reaction. Fortunately, two superstructures (**1** and **2**) of copper(I) 2-ethylimidazolate were isolated from different solvent media, namely water, water–cyclohexane or water–benzene mixtures.‡

It is understandable that a water medium assists the aggregation of the hydrophobic ethyl groups, whereas the nonpolar solvent cyclohexane or benzene would weaken this tendency. As expected, the former medium resulted in the formation of isomer **1** with helical structural character and the latter led to the formation of isomer **2** with zigzag chain-like structural character. We also tried other solvents with different polarities, in which other polar solvents such as alcohols and acetonitrile led to the formation of the helical structure in relatively lower yields, whereas chloroform and THF did not give observable crystals of the helical structure. These observations suggest the significant effect of solvent polarity in the above conformation isomerism. It should be noted that except for the solvent polarity, the solubility and reactivity of the solvent molecules under hydro(solvo)thermal conditions would also influence the process of crystal growth and the mechanism needs to be further investigated.

Single-crystal X-ray analysis§ has revealed that **1** and **2** are conformational supramolecular isomers without any solvent molecule in the structures, where for both polymers, the local coordination environment is similar, *i.e.* Cu^I ions are linearly ligated by two N atoms from μ-bridged imidazolate anions (Cu–N 1.843(2)–1.868(2) Å, N–Cu–N 167.4(1)–178.1(1)°), which are also similar to those observed in the Cu^I 2-methylimidazolates,[3c] on the other hand, the orientations of the imidazolato rings in the two polymers are different which result in the different conformation of the chains.

In **1**, there are four crystallographically unique Cu^I ions and four eim (Heim = 2-ethylimidazole) anions in a *syn* manner with dihedral angles of *ca.* 10–43°, and followed by another four Cu^I ions and four *anti* eim anions to extend into a helical chain along the 2$_1$-axis with a long helical pitch of 33.28(1) Å (triple of the *b*-axis length) (Fig. 1, top). Every three helices further intertwine to generate a triple-stranded helix (Fig. 1, bottom) with the ethyl groups of eim ligands concentrated within the channel formed by the triple-stranded helix (Fig. 2). Since the shortest Cu···Cu distances (3.283(1) Å) inside the triple helix is much longer than the van der Waals radius sum of copper atom (2.8 Å),[7] the peculiar formation of such triple helices may be mainly ascribed to the hydrophobic nature of the ethyl groups in the relatively polar media. It should be noted that the formations of double- and triple-stranded helical coordination polymers directed uniquely by inter-strand supramolecular interactions within the multiple-stranded helices are still very rare,[6] and this phenomenon may be regarded as 'self-template assembly' by making use of the template effect from the ligand itself.
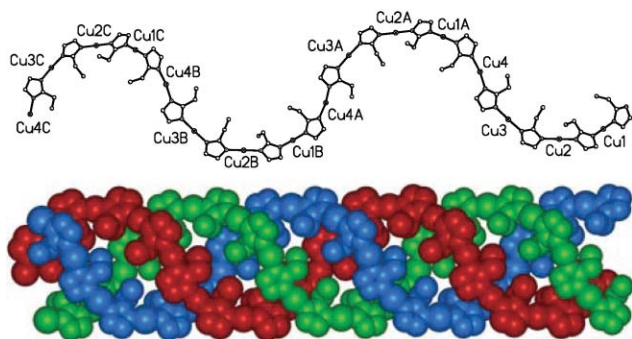
Fig. 1 A perspective view of a single-stranded 2_1 helix (top, A: $-x + 1/2$, $y + 3/2$, $-z + 1/2$; B: x, $y + 3$, z; C: $-x + 1/2$, $y + 9/2$, $-z + 1/2$) and a space-filling model of a triple-stranded helix (bottom) in **1**.
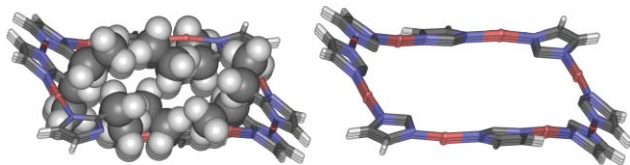

Fig. 2 A view of the triple-stranded helices with the ethyl groups highlighted in space-filling model (left) and without (right) along the *b*-axis in **1**.


Fig. 3 Schematic presentation of a single 3D net of **1** constructed *via* ligand-unsupported cuprophilic attractions (yellow sticks) viewed along the *b*-axis. Red spheres (Cu atoms), blue and green sticks (eim ligands, blue: right handed, green: left handed).

Fig. 4 A perspective view of a zigzag chain in **2** (A: x, $y + 1$, z).

The helices with the same helicity in **1** are associated through short Cu⋯Cu contacts (Cu1⋯Cu1 2.834(1) Å, N–Cu⋯Cu–N *ca.* 87°) along the *a*-axis to give homochiral layers, and these layers with opposite helicity are further alternatively extended by longer Cu⋯Cu contacts (Cu2⋯Cu4 3.034(1) Å, N–Cu⋯Cu–N *ca.* 72°) to furnish the final racemic structure. There is no other obvious intermolecular metal–ligand (shortest Cu⋯N 3.350(1) Å) or ligand–ligand interaction found to support the Cu⋯Cu contacts, therefore this is also an example of ligand-unsupported cuprophilicity which is important, yet rarely documented for identification of these weak interactions.[8]

To understand the complicated 3D structure of **1**, the network was simplified in Fig. 3, in which only single-stranded helices were presented for clarity, and eim ligands are represented by blue (right handed) and green (left handed) sticks whereas yellow ones represent the shorter Cu⋯Cu contacts. From the topological point of view, this 3D network can be regarded as a binodal 3-connected $(4.8.12)_2(8.12.14)$ net with the Cu^I atoms as T-shaped nodes, and eim ligands as well as short Cu⋯Cu contacts as linkers, in which Cu1 and Cu4 act as one kind of node (4.8.12) and Cu2 acts as another. Large channels in this net are occupied by other two identical nets to form a three-fold interpenetrating net the same way as individual triple-stranded helices.

In **2**, there are two crystallographically unique Cu^I ions and two eim anions in an *anti* manner with dihedral angles of 36° which result in a typical zigzag chain-like structure (Fig. 4). All these chains are extended along the *b*-axis and there is no obvious interchain Cu⋯Cu interaction (shortest Cu⋯Cu *ca.* 3.678(2) Å). The crystal packing of **2** is dominated by van der Waals interactions since no other strong supramolecular interaction is observed (Fig. S1 of ESI†). As may be expected, the crystal densities of these two polymers are rather similar (**1**, 1.723 g cm^{-3}; **2**, 1.747 g cm^{-3}).
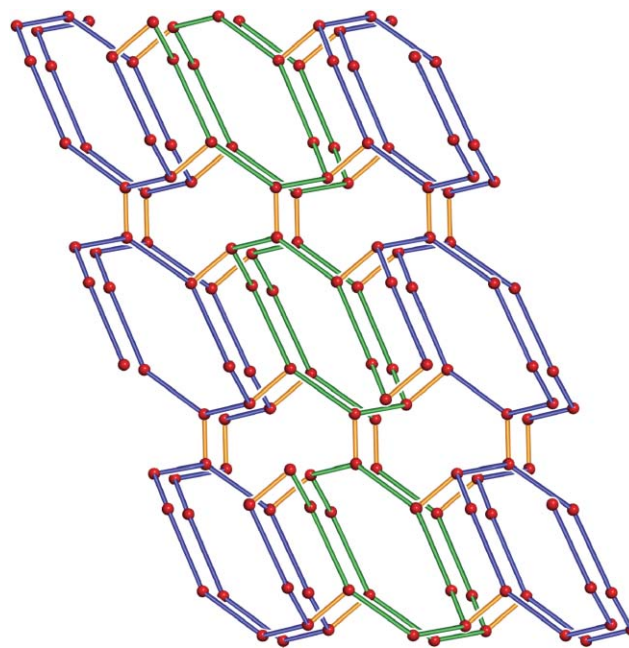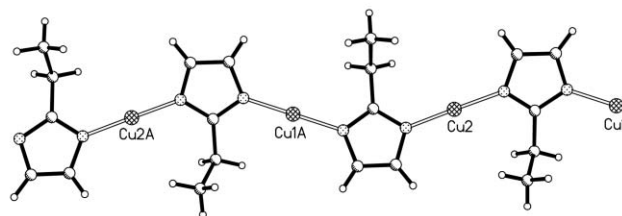
Both **1** and **2** show strong photoluminescence at room temperature with the emission maxima at 524 nm and 532 nm, respectively (Fig. 5). Moreover, the long-lived luminescence of both **1** (11.3 μs,) and **2** (12.7 μs) is indicative of a spin-forbidden triplet parentage.[9] The similar emission spectra and lives of excited
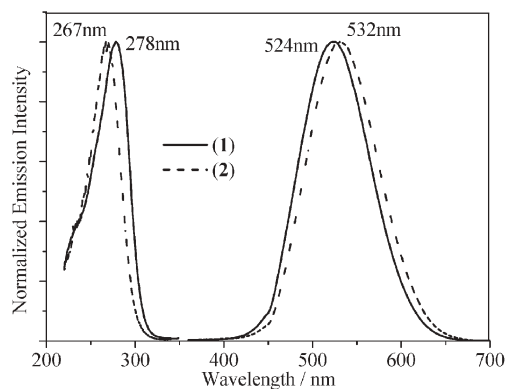
Fig. 5 Solid-state emission spectra of **1** (solid line) and **2** (dashed line) at room temperature.

states of these two complexes imply that the properties of the excited state are just related to the local coordination geometry and irrelevant to the intermolecular interactions such as weak cuprophilic interactions. Because the ligands display no photoluminescence, the possibility of an MLCT [Cu → eim] excited state in both supramolecular isomers may be suggested.[10]

In summary, we have demonstrated that two unique, conformational supramolecular isomers can be assembled from the same components with the same ratio in solvents of different polarities, and the solvent effect of different polarities can be exploited to tune the conformations of the polymer structure. Such a phenomenon strongly implies that the supramolecular interaction between the organic ligands and solvent molecules may be important in tuning the conformation of the polymer structure during the formation or crystallization process, when the ligands have groups sensitive to the solvent molecules.

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Notes and references

‡ Synthesis of **1**: In a typical procedure, a mixture of $Cu_2CO_3(OH)_2$ (0.110 g, 1.0 mmol), Heim (0.095 g, 1.0 mmol), aqueous ammonia (25%, 5 mL) and water (2 mL) was stirred for 15 min in air, then transferred and sealed in a 23 mL Teflon reactor, which was heated in an oven to 160 °C for 80 h. The resulting yellow block crystals were filtered, washed, and dried in air, yield 0.11 g, *ca.* 70%. Elemental analysis calcd (%) for **1** $C_5H_7CuN_2$: C 37.85, H 4.45, N 17.66; found: 37.73, H 4.53, N 17.68%. Synthesis of **2** was similar to that of **1** using cyclohexane (3 mL) in place of water, yield 0.05 g, *ca.* 35%. Elemental analysis calcd (%) for **2** $C_5H_7CuN_2$: C 37.85, H 4.45, N 17.66; found: 37.64, H 4.89, N 17.52%.
§ Crystal data for **1**: monoclinic space group $C2/c$ (no. 15), $a = 26.6065(13)$ Å, $b = 11.0944(5)$ Å, $c = 17.0945(9)$ Å, $\beta = 106.9610(10)°$, $V = 4826.5(4)$ Å^3, $Z = 32$, $D_c = 1.747$ g cm^{-3}, $F(000) = 2560$, $\mu = 3.501$ mm^{-1}, 14503 reflections measured, 5616 unique ($R_{int} = 0.0254$), final $R_1 = 0.0387$, $wR_2 = 0.0720$, $S = 1.071$ for all data. **2**: monoclinic space group $C2/c$ (no. 15), $a = 19.5680(18)$ Å, $b = 11.4672(11)$ Å, $c = 13.5953(13)$ Å, $\beta = 126.6890(10)°$, $V = 2446.3(4)$ Å^3, $Z = 16$, $D_c = 1.723$ g cm^{-3}, $F(000) = 1280$, $\mu = 3.454$ mm^{-1}, 8050 reflections measured, 2881 unique ($R_{int} = 0.0216$), final $R_1 = 0.0405$, $wR_2 = 0.0887$, $S = 1.044$ for all data. Data collections of **1** and **2** were performed with MoKα radiation ($\lambda = 0.71073$ Å) on a Bruker SMART Apex CCD diffractometer, using frames of 0.3° oscillation ($2\theta \leqslant 56°$), the structures were solved by direct methods and all non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least-squares on F^2 using the SHELXTL program.[11] CCDC 238972 and 262126. See http://www.rsc.org/suppdata/cc/b5/b501071c/ for crystallographic files in CIF or other electronic format.

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