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Three mixed-ligand coordination networks modulated by flexible N-donor ligands: Syntheses, topological structures, and temperature-sensitive luminescence properties

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Fig. S1: The powder XRD patterns and the simulated one from the single-crystal diffraction data for compounds 1-3

**Compound 1**

**Compound 2**

**Compound 3**
Fig. S2 IR spectrum of 1-3.

Compound 1

Compound 2

Compound 3
(3) Fig. S3: The infinite 1D zig-zag chain formed by Zn(II) cation centers and tbtpa ligands.
(4) Fig. S4: TG curves of compounds 1-3
(5) Fig. S5: The emission decay curves for 2 and 3.
<table>
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<tr>
<th>Different N-donor ligands</th>
<th>Structures</th>
<th>Literature/synthesis condition</th>
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| ![Diagram 1](image1.png) | ![Diagram 2](image2.png) | **CrystEngComm, 2013, 15, 5552–5560.**
Synthesis of 1: A mixture of Cd(NO$_3$)$_2$·4H$_2$O (123.4 mg, 0.4 mmol), tib (110.4 mg, 0.4 mmol) and H$_2$tbtpa (192.7 mg, 0.4 mmol), KOH (1.2 mg, 0.02 mmol) were dissolved in 10 mL methanol–H$_2$O (v:v = 1 : 1) in a 25 mL Teflon-lined stainless steel vessel. The mixture was sealed and heated at 120 °C for 72 min. After the mixture was cooled to room temperature, the pale yellow block crystals were collected.

Synthesis of 2: Synthesis of 2 was similar to that of 1, but the ratio of Cd(NO$_3$)$_2$·4H$_2$O/tib/H$_2$tbtpa is 1 : 1 : 2. Yellow crystals of 2 were obtained.

Synthesis of 3: Synthesis of 3 was similar to that of 1, but the ratio of Cd(NO$_3$)$_2$·4H$_2$O/tib/ H$_2$tbtpa is 1 : 1 : 3. |
| ![Diagram 3](image3.png) | ![Diagram 4](image4.png) | **CrystEngComm, 2012, 14, 7856–7860.**
Synthesis of 2: A mixture Zn(NO$_3$)$_2$·6H$_2$O (5.9 mg, 0.02 mmol), bmimbp (3.42 mg, 0.01 mmol) and H$_2$tbtpa (14.5 mg, 0.03 mmol), NaOH (0.8 mg, 0.02 mmol) were dissolved in 1 mL DMF-H$_2$O (v:v = 1:1) and heated in a sealed Perex tube at 120 °C for 83 hours. After the mixture was cooled to room temperature, pale-yellow crystals of 2 were obtained. |
Many synthetic conditions have been tried, but no crystalline products could be obtained yet.

**Synthesis method:** In this system, not only the solvent systems have been changed, example DMSO-H$_2$O ($\nu\nu = 1:1$), NMP-H$_2$O ($\nu\nu = 1:1$), DMF-EtOH-H$_2$O ($\nu\nu \nu = 5:2:1$), CH$_3$CN-H$_2$O ($\nu\nu = 2:1$) and so on, but also different temperatures of the system have been tried, example 90 °C, 110 °C, 120 °C, 130 °C, 150 °C. Nevertheless, these experiments were all failed; we have not obtained any crystalline products.

Summary

There are several coordination complexes that have been structurally characterized using H$_2$tbtpa ligands with entangled features. In addition, a careful selection of N-donor ligands with different conformations as secondary auxiliary ligands is a key step for the rational design of structures with specific physical and chemical properties. In our previous report (CrystEngComm, 2013, 15, 5552–5560), we use the rigid ligand N-donor (tib) and H$_2$tbtpa ligand to construct three new entangled coordination polymers [Cd(tib)(tbtpa)(H$_2$O)]$_n$ (1) and [Cd(Htib)(tbtpa)·Htbtpa·2CH$_3$OH]$_n$ (2) and [Cd$_2$(tib)$_2$(tbtpa)$_2$(H$_2$O)$_2$·10H$_2$O]$_n$ (3) by adjusting the molar ratio of the reactant metal salt and ligands. Complex 1 is a 2-fold interpenetrated three-dimensional (3D) 8-connected uninodal net with rare hex topology. Complex 2 presents a 2D 6$_3$-hcb network, which is interdigitated with each other to form the 3D supramolecular framework. Complex 3 is a complicated 3D self-penetrated framework, which can be seen as a pair of 2-fold interpenetrated networks by breaking bidentate-bridging tib ligand.

In another paper (CrystEngComm, 2012, 14, 7856–7860), when the semi-rigid bmimbp ligand was introduced instead of the rigid tib ligand. A novel entangled coordination polymers namely [Zn(bmimbp)(tbtpa)]$_n$ (bmimbp= 4,4’-bis(2-methylimidazol-1-ylmethyl)biphenyl) was synthesized, and the most striking feature of the complex is that two identical 2D single 6$_3$-hcb sheets are interlocked with each other in a 2D → 2D parallel fashion thus directly leading to the formation of a 2D polyrotaxane-like structure containing rotaxane-like motifs.
In this assembly system, previous work mainly focused on rigid or semi-rigid N-donor ligands, whereas flexible ligands have been rarely explored. In order to explore the influence of flexible N-donor ligands on the tuning of entangled networks and achieve different topological structures, here we have adopted three such flexible N-donor ligands viewing their difference of length and configuration and influence on the final structures. In addition, as shown in above table, several other N-donor ligands were also selected in this system, but no crystalline products could be obtained yet, although many synthetic conditions have been tried.