Electronic Supplementary Information (ESI) for *CrystEngComm*

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

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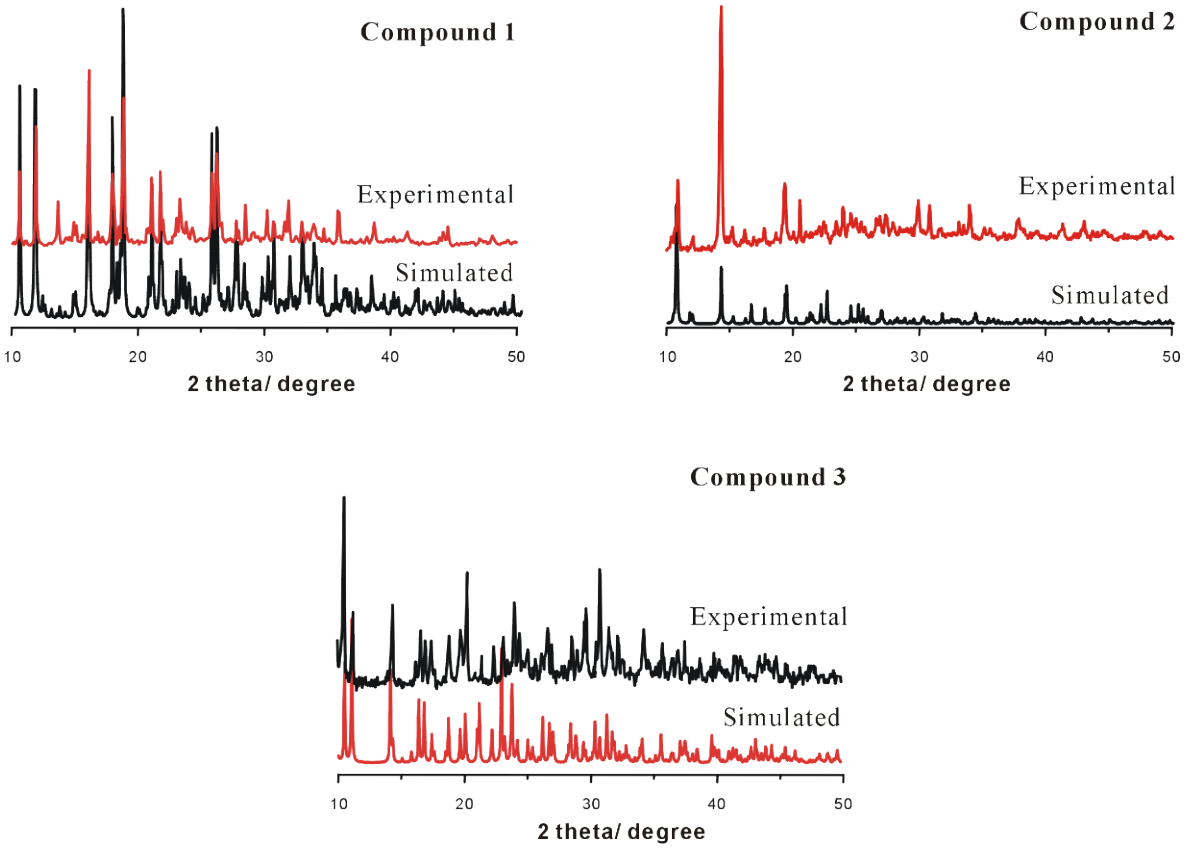
(1) Fig. S1: The powder XRD patterns and the simulated one from the single-crystal diffraction data for compounds 1-3



(2) Fig. S2 IR spectrum of 1-3.

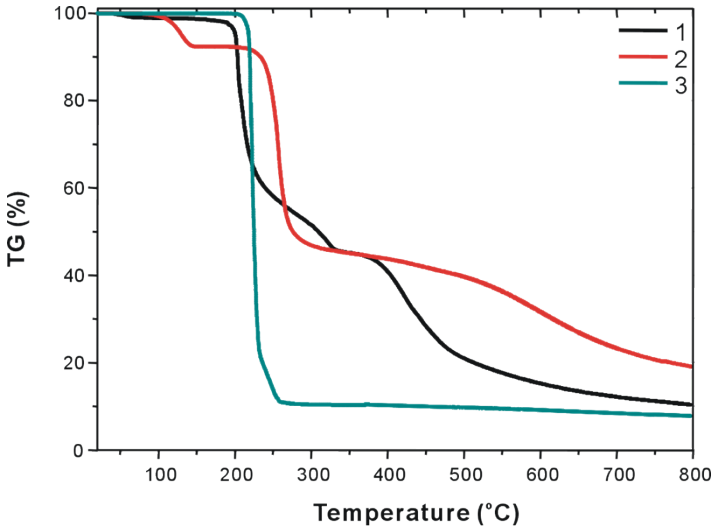
Compound **1**

Compound **2**

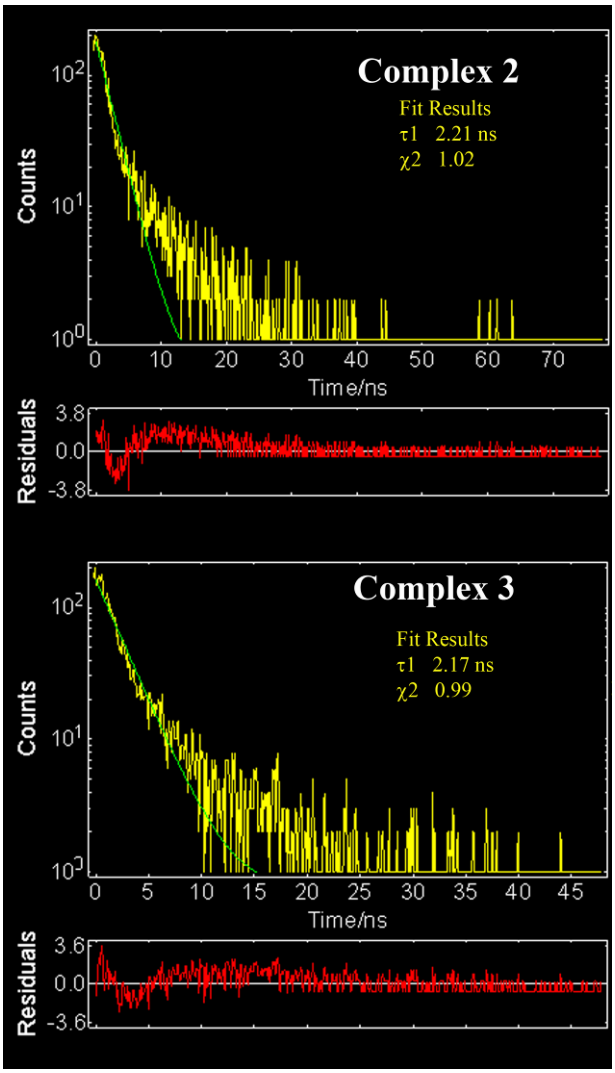
Compound **3**

(3) Fig. S3: The infinite 1D zig-zag chain formed by Zn(II) cation centers and tbtpa ligands.

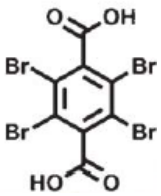
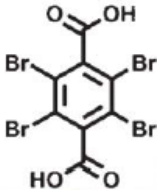
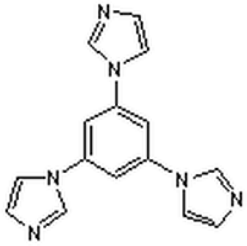
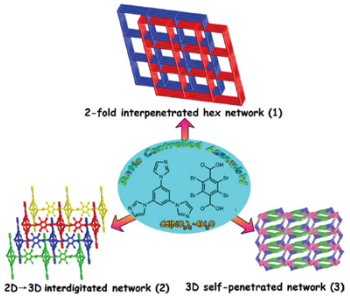
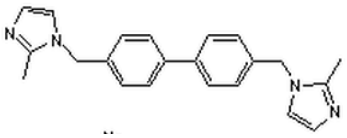
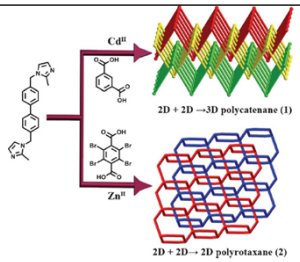
(4) Fig. S4: TG curves of compounds 1-3

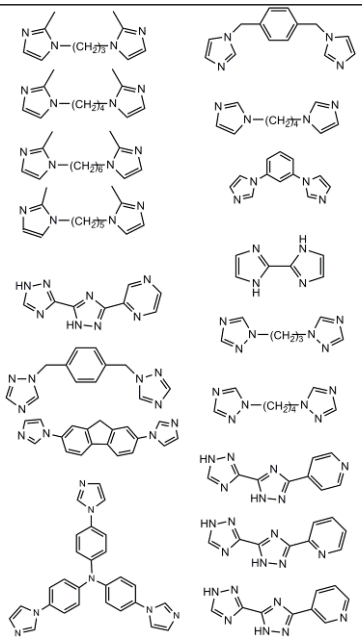
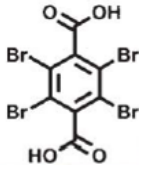
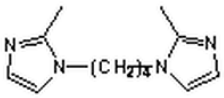
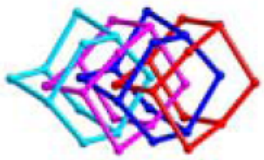
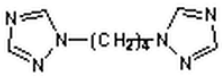
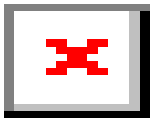
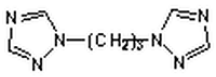
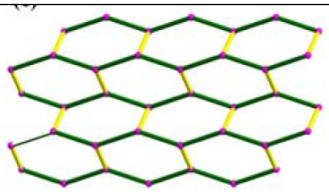


(5) Fig. S5: The emission decay curves for 2 and 3.



(6) Table S1: Summary of the synthesis of tbtpa-based coordination networks.

	Different N-donor ligands	Structures	Literature/synthesis condition
 			**CrystEngComm, 2013, 15, 5552–5560.** Synthesis of **1**: A mixture of $Cd(NO_3)_2{\cdot}4H_2O$ (123.4 mg, 0.4 mmol), tib (110.4 mg, 0.4 mmol) and H_2tbtpa (192.7 mg, 0.4 mmol), KOH (1.2 mg, 0.02 mmol) were dissolved in 10 mL methanol–H_2O (*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 $Cd(NO_3)_2{\cdot}4H_2O$/tib/H_2tbtpa 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 $Cd(NO_3)_2{\cdot}4H_2O$/tib/ H_2tbtpa is 1 : 1 : 3.
			**CrystEngComm, 2012, 14, 7856–7860.** Synthesis of **2**: A mixture $Zn(NO_3)_2{\cdot}6H_2O$ (5.9 mg, 0.02 mmol), bmimbp (3.42 mg, 0.01 mmol) and H_2tbtpa (14.5 mg, 0.03 mmol), NaOH (0.8 mg, 0.02 mmol) were dissolved in 1 mL DMF-H_2O (*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_2O (*v:v* = 1 : 1), NMP-H_2O (*v:v* = 1 : 1), DMF-EtOH-H_2O (*v:v :v*= 5 : 2 : 1), CH_3CN-H_2O (*v:v* = 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.
		 3-fold interpenetration **dia** of class **IIIa**	**In this paper**
		 2D-**sql**	
		 2D-**hcb**	
Summary	There are several coordination complexes that have been structurally characterized using H_2tbtpa 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_2tbtpa ligand to construct three new entangled coordination polymers $[Cd(tib)(tbtpa)(H_2O)]_n$ (1) and $[Cd(Htib)(tbtpa)\cdot Htbtpa\cdot 2CH_3OH]_n$ (2) and $[Cd_2(tib)_2(tbtpa)_2(H_2O)\cdot 10H_2O]_n$ (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.