CrystEngComm

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Reaction vessel- and concentration-induced supramolecular isomerism in layered lanthanide-organic frameworks†

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**The self-assembly of the flexibly bonded dicarboxylate ligand, 2, 2′-(2,3,5,6-tetramethyl-1,4-phenylene)bis(methylene)bis(sulfanediyl) dibenzoic acid (H$_2$L^1), with La(NO$_3$)$_3$·6H$_2$O resulted in the formation of three layered coordination polymers. Interestingly, three complexes are supramolecular isomers and their structures are highly influenced by the concentration of the starting reagents and the reaction vessel, such as a glass tube or a Teflon-lined steel bomb.**

With the development of supramolecular chemistry and crystal engineering of coordination polymers (or metal–organic frameworks), it is possible to design and construct novel coordination polymers (CPs) with desired topologies and rationally predict the final structures of the product.[1,2] Unfortunately, this predictive ability is still limited to CPs containing rigid organic ligands and rigid secondary building units (SBUs). For flexible organic ligands, it is still difficult to predict the final structures, because flexible ligands may adopt several kinds of conformation when they coordinate to metal ions.[3] On the other hand, the recent advance of supramolecular isomerism has added more complexity in designing a desired complex and rationally predicting the final structure of a product.[4,5] The conformational change of a flexible ligand may generate conformational isomerism in CPs.[6] Hence, the studies of supramolecular isomerism with a flexible ligand may provide a good opportunity for seeking novel functional materials and a better understanding of the factors that influence the crystal growth.

Recently, we and other groups have become interested in utilizing flexible carboxylate or N-containing ligands to construct metal–organic frameworks.[7,8] The effect of conformation of flexible carboxylate ligands on the structures of metal–organic

supramolecules has also been studied.[9] It is evident that the use of flexible ligands in the construction of CPs may generate novel complexes with interesting topologies and attractive properties, because flexible ligands have variable coordination modes,[10] and can adopt a variety of conformations according to the restrictions imposed by the coordination geometry of the metal ion and the final 3D packing. Hence, studying the factors that influence the structure of CPs based on flexible ligands is helpful for the construction of CPs with desired topologies. Continuing our previous research,[8] in this communication, we report three layered supra molecular isomers, [La$_2$(H$_2$O)$_2$(EtOH)(dmf)$_2$(L^1)$_3$·3dmf·3H$_2$O]$_n$ (**1**), [La$_2$(H$_2$O)$_4$(L^1)$_3$·2H$_2$O]$_n$ (**2**), [La$_2$(H$_2$O)$_2$(dmf)$_4$(L^1)$_3$·2dmf·2H$_2$O]$_n$ (**3**) (H$_2$L^1 = 2,2′-(2,3,5,6-tetramethyl-1,4-phenylene)bis-(methylene)bis(sulfanediyl) dibenzoic acid, dmf = dimethylformamide), whose structures are highly influenced by the concentration and reaction vessel.

syn-conformation $anti$-conformation
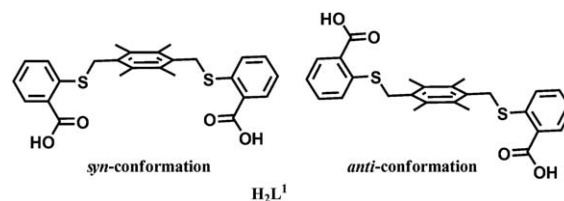
H$_2$L^1

Solvothermal reaction of H$_2$L^1, 1,3-di(pyridin-4-yl)propane, and La(NO$_3$)$_3$·6H$_2$O resulted in the formation of colorless crystals of **1**, **2** and **3**, which were not soluble in common organic solvents. Phase purities of **1**–**3** are substantiated by the powder X-ray diffraction patterns (Figure S1, see ESI†). For **1**–**3**, most peak positions of simulated and experimental patterns are in good agreement with each other. The dissimilarities in intensity may be due to the preferred orientation of the crystalline powder samples. The solid FT-IR spectra (Fig. S2, see ESI†) of **1** and **2** show characteristic absorption bands for carboxyl groups. Single-crystal X-ray diffraction‡ reveals that all three complexes possess 2D layered frameworks and, if the coordinated solvents in the La ions are ignored, they are supramolecular isomers.

The asymmetric unit of **1** consists of two La ions, three L^1 ligands, one coordinated ethanol molecule, two coordinated dmf molecules, and two coordinated water molecules. All the L^1 ligands are deprotonated during the reaction, and there are two types of L^1 ligand with different conformation and coordination modes: one adopts the syn-conformation and connects three La ions, while the other adopts

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the *anti*-conformation and connects four La ions. The basic building unit in **1** is a binuclear lanthanum SBU engaged by six carboxylate groups from four *syn*-conformational **L**^{1} ligands and two *anti*-conformational **L**^{1} ligands (Fig. 1a). The remaining carboxylate groups of the four *syn*-conformational **L**^{1} ligands further link the adjacent binuclear SBU to generate a 1D ladder with the *syn*-conformational **L**^{1} ligands as the side rails and the binuclear SBUs as the rungs (Fig. 2a). The π⋯π interactions (3.79 Å) between the side benzene rings of the *syn*-conformational **L**^{1} ligands further stabilize the 1D ladder.

The 1D ladders extend along the *a* axis, with the nearest distance between the binuclear SBUs being 8.9 Å. Both carboxylate groups of the *anti*-conformational **L**^{1} ligand adopt a chelating mode to connect one of the La ions of the SBUs, and all the *anti*-conformational **L**^{1} ligands connect the ladders in the *ac* plane in the same direction to result in the formation of a 2D wave-like layer (Fig. 3a, 3b) with the nearest distance of the 1D ladders being 16.7 Å.

Complex **2** crystallizes in the triclinic *P*1̄ space group and the basic building block is a 1D rod-shaped SBU. The asymmetric unit of **2** consists of one La ion, one and half **L**^{1} ligands, two coordinated water molecules, and one uncoordinated water molecule. The La ion is coordinated by eight oxygen atoms, six from different **L**^{1} ligands and two from coordinated water molecules. Similar to that found in complex **1**, there are two types of **L**^{1} ligand with different conformations: *syn*- and *anti*-conformations (Fig. 1b), which play different roles in the formation of the 2D layer. The *syn*-conformational **L**^{1} ligand in a bis-bridging mode connect binuclear La unit to generate a 1D ladder with the *syn*-conformational **L**^{1} ligands as the side rails and the binuclear SBUs as the rungs (Fig. 2b). There are no π⋯π interactions between the side benzene rings of the *syn*-conformational **L**^{1} ligands. Both carboxylate groups of the *anti*-conformational **L**^{1} ligand adopt the bridging mode to connect two La ions in different binuclear units to generate a 1D rod-shaped SBU, and all the *anti*-conformational **L**^{1} ligands connect the ladders in the *ac* plane in an opposite direction to result in the formation of a 2D layer framework (Fig. 3c, 3d) with the nearest distance of the 1D ladders being 13.2 Å.

Single-crystal X-ray diffraction reveals that complex **3** crystallizes in the triclinic *P*1̄ space group, and the asymmetric unit consists of one La ion, one and half **L**^{1} ligands, two coordinated dmf molecules, one coordinated water molecule, one uncoordinated water molecule and one uncoordinated dmf molecule. The La ion is coordinated by nine oxygen atoms, six from four **L**^{1} ligands and three from coordinated solvents. The basic building unit is a binuclear SBU engaged by six carboxylate groups, similar to that found in **1**. All the ligands are deprotonated and adopt *anti*-conformation, which is different from those in **1** and **2**. Two types of coordination modes of **L**^{1} ligands are present: (a) one of the carboxylate groups adopts the monodentate
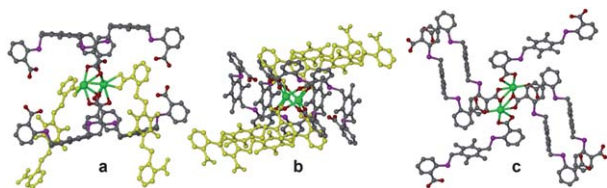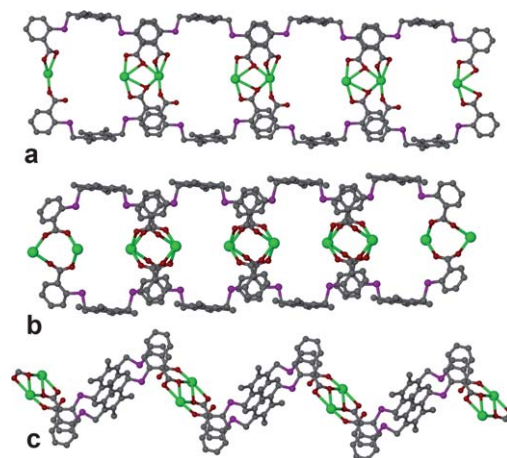

Fig. 2 The 1D ladders in **1** and **2** formed by *syn*-conformational **L**^{1} connecting the binuclear units and the 1D zig–zag chain in **3** formed by *anti*-conformational **L**^{1} connecting the binuclear units.

mode, coordinating to one La atom, whereas the other carboxylate group adopts the chelating-bridging mode, linking two La atoms (^{a}**L**^{1}); (b) both carboxylate groups adopt the chelating mode, coordinating to one La atom (^{b}**L**^{1}). Thus, the binuclear SBUs are first connected by double ^{a}**L**^{1} ligands to form a 1D zig–zag chain, as shown in Fig. 1c. There exist weak π⋯π interactions (3.97 Å) between the side benzene rings of the ^{a}**L**^{1} ligands. The 1D chains are further linked by single ^{b}**L**^{1} ligands to generate a 2D layer framework. If the double ^{a}**L**^{1} ligands and single ^{b}**L**^{1} ligands can be considered as a single linker, and the binuclear SBU as a 4-connect node, then the 2D layer possesses a (4,4) net.

It should be pointed out that the structures of **1**–**3** are highly influenced by the reaction vessel and the concentration of the starting reagents. Complexes **1** and **2** were synthesized in the same concentration of starting reagents and reaction times and temperatures, except that the reaction vessels were different. The reaction for complex **1** was run in a Teflon-lined steel bomb, whilst complex **2** was run in a glass tube. The different reaction vessels resulted in different SBUs in **1** and **2**: binuclear SBU *vs.* 1D rod-shaped SBU. To the best of our knowledge, this is the first example of reaction vessel-induced formation of a supramolecular isomer, although temperature-, solvent-, template-, guest-, catenation- or concentration-induced
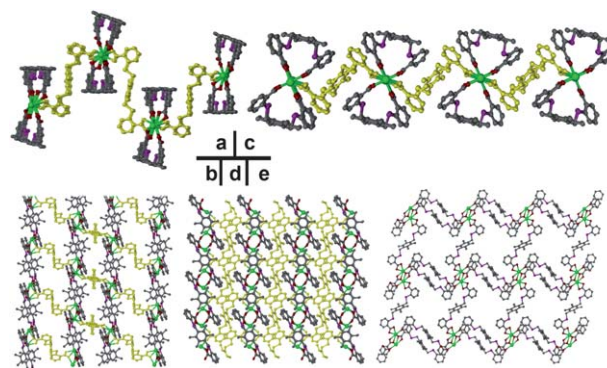

Fig. 3 The 2D layers of **1** and **2** in different directions (a, b for **1** and c, d for **2**, the *anti*-conformational **L**^{1} ligands are shown in yellow) and the 2D (4,4)-net of **3** (e).

Fig. 1 The coordination environment of the binuclear units in **1**–**3**, respectively. The **L**^{1} ligands in *anti*-conformation are shown in yellow in a and b.

supramolecular isomerism have been reported.[11] Complexes **2** and **3** were synthesized in similar conditions, except the concentration of the starting reagents were different. At low reaction concentration **2** was formed with two types of conformation of **L**[1] ligands, while complex **3** with a single conformation of **L**[1] ligand was formed at high concentration of the starting reagents. Interestingly, the conformations of **L**[1] ligands in **2** and **3** are highly controlled by the reaction concentration of the starting reagents, which is different from our previous results that the conformation of flexible ligands is controlled by the reaction solvent.[12] Although the 1,3-di(pyridin-4-yl)propane does not exist in the final crystal structures, it plays an important role in the formation of **1**–**3**. Without addition of 1,3-di(pyridin-4-yl)propane in the reaction, only some unknown precipitates were formed. Although detailed studies are still needed, 1,3-di(pyridin-4-yl)propane may play a base or template role in the formation of **1**–**3**.

TGA measurement reveals that all complexes can be stable up to 300 °C. For **1**, the first weight loss of 4.5% from 45 to 135 °C is in accordance with the loss of three uncoordinated water molecules and one coordinated EtOH molecule (calcd: 4.6%); the second weight loss of 10.3% from 135 to 178 °C is in accordance with the loss of three uncoordinated dmf molecules and two coordinated water molecules (calcd: 11.7%); the third weight loss of 7.3% from 178 to 348 °C is in accordance with the loss of two coordinated dmf molecules (calcd: 6.7%), and after 348 °C, **1** starts to decompose. For **2**, the first weight loss of 2.5% from 50 to 118 °C corresponds to the loss of two uncoordinated water molecules (calcd: 2.0%); the second weight loss of 4.0% from 118 to 195 °C corresponds to the loss of four coordinated water molecules (calcd: 4.0%). There is no further weight loss until 340 °C, where **2** starts to decompose. For **3**, the first weight loss of 10.2% from 50 to 125 °C is in accordance with the loss of two coordinated water molecules, two uncoordinated water molecules and two uncoordinated dmf molecules (calcd: 10.0%); the gradual weight loss of 13.3% from 125 to 337 °C corresponds to the loss of four coordinated dmf molecules (calcd: 13.4%). After 338 °C, **3** starts to decompose.

Photoluminescence measurements of **1**–**3** in the solid state at room temperature show that all three coordination networks exhibit similar luminescence at λ_{max} = 384, 375, and 385 nm, respectively, upon excitation at 320 nm (Fig. 4). These emissions can be assigned to an intraligand $\pi \rightarrow \pi^*$ transition, as free H_2L^1 possesses similar
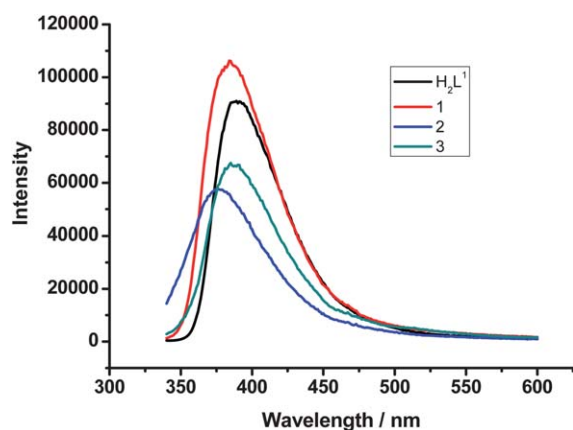
emission in the solid state (λ_{max} = 389 nm), though the intensity is slightly different.

In conclusion, three lanthanide supramolecular isomers based on a flexible dicarboxylate ligand have been synthesized and characterized. All complexes have 2D layered frameworks, whose structures are highly controlled by the reaction vessel and the concentration of the starting reagents. In **1** and **2**, both *syn*- and *anti*-conformational ligands are present, while only an *anti*-conformational ligand is found in **3**. Interestingly, the conformation of the flexible ligand in **2** and **3** is controlled by the concentration of the starting reagents. Our research results reveal that by control of the reaction conditions, such as reaction vessel and concentration, different conformations of flexible ligands may be present in the structures and further lead to the formation of supramolecular isomerism.

Acknowledgements

Notes and references

‡ *Crystal data* for **1**–**3**: **1**: $C_{86}H_{95}La_2N_2O_{17}S_6$, M = 1898.82, monoclinic, space group $P2_1/c$, a = 13.036(3), b = 34.721(6), c = 23.393(5) Å, β = 92.699(4)°, U = 10576(3) Å³, Z = 4, D_c = 1.193 g cm⁻³, μ = 0.969 mm⁻¹, F(000) = 3884; 44869 reflections were measured with 15049 unique reflections (R_{int} = 0.0821). Final R_1 (wR_2) = 0.0591 (0.1567) [I > 2.0 $\sigma(I)$]. **2**: $C_{39}H_{42}LaO_9S_3$, M = 889.82, triclinic, space group $P\bar{1}$, a = 9.8233(5), b = 13.2039(7), c = 15.9391(8) Å, α = 113.863(1), β = 96.308(1), γ = 92.677(1)°, U = 1869.74(17) Å³, Z = 1, D_c = 1.566 g cm⁻³, μ = 1.363 mm⁻¹, F(000) = 898; 9305 reflections were measured with 6479 unique reflections (R_{int} = 0.0216). Final R_1 (wR_2) = 0.0323 (0.0830) [I > 2.0 $\sigma(I)$]. **3**: $C_{48}H_{61}LaN_3O_{11}S_3$, M = 1091.09, triclinic, space group $P1$, a = 12.668(2), b = 14.585(3), c = 17.323(3) Å, α = 113.754(2), β = 109.044(2), γ = 90.263(2)°, U = 2734.7(9) Å³, Z = 1, D_c = 1.325 g cm⁻³, μ = 0.951 mm⁻¹, F(000) = 1126; 19200 reflections were measured with 9506 unique reflections (R_{int} = 0.0197). Final R_1 (wR_2) = 0.0379 (0.1152) [I > 2.0 $\sigma(I)$].

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Fig. 4 The photoluminescence spectra for **1**–**3** as well as free ligand H_2L^1.

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