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Unprecedented $4^2 6^4$ Topological 2-D Rare-Earth Coordination Polymers from a Flexible Tripodal Acid with Additional Amide Groups

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Novel lanthanide(III) coordination polymers based on a flexible tripodal ligand with additional amide groups were obtained with interestingly unprecedented four-connected $4^2 6^4$ topology from the pyramidal nodes and reversible crystal-to-amorphous transformation properties.

In recent years, construction of coordination polymers is one of the most active areas of materials research driven by both their potential applications and interesting network topologies.[1−3] In particular, highly symmetrical multitopic ligands attract more attention because of the fact that in their self-assembly process various coordination modes can be adjusted to generate interesting structural motifs.[4] Among them, rigid ligands are often employed in a designed strategy to construct coordination complexes with special predictable topologies,[5] while flexible ligands with additional functional groups can adopt more types of conformations and coordination modes according to the geometric requirements of different metal ions compared with the rigid ones, which may lead to more intriguing topologies and properties.[6] However, only a few examples with flexible tripodal ligands have been reported.[7]

Four-connected topological coordination polymers have been intensively investigated. Generally, it is easier for the square nodes leading to a 2-D (4, 4)[8] square net rather than 3-D NbO ($6^4 8^2$),[9] $CdSO_4$ ($6^5 8$),[10] and lvt ($4^2 8^4$)[11] nets, while tetrahedral nodes always give rise to 3-D diamondoid (6^6)[12]

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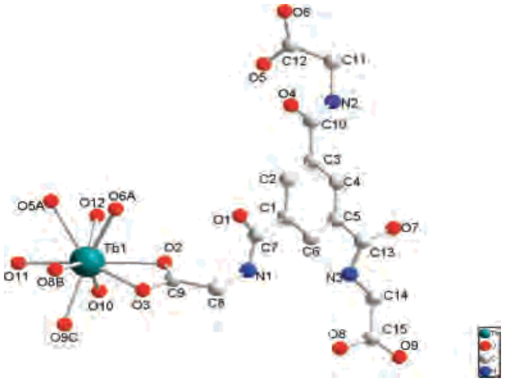

Figure 1. ORTEP plot of complex **1** showing the local coordination environment of Tb^{III} with thermal ellipsoids at 50% probability.

and $SrAl_2$ (4^26^38)[13] nets. Other four-connected nodal nets have less been reported. Moreover, those coordination polymers in which lanthanides, with their variable coordination numbers and flexible coordination environments, may provide unique opportunities for the discovery of unusual network topologies and have been scarcely investigated.[14] Usually, the rare-earth ions are always thought to be unsuitable for four-connected nodes, while very limited examples were reported to exhibit such topology.[15]

In order to expand our investigations on the assembly of symmetrical ligands,[16] we turned our attention to a flexible tripodal acid, *N*,*N*,′*N*′′-tris(carboxymethyl)-1,3,5-benzenetricarboxamide (TCMBT) containing amide groups, which may increase the flexibility of the ligand, lead to the formation of hydrogen bonds, and generate dynamic molecular solids as well.[17] Herein, we report four novel lanthanide coordination polymers: $\{[Ln(TCMBT)(H_2O)_3]\cdot 4H_2O\}_n$ [Ln = Tb (**1**), Gd (**2**), Nd (**3**)] and $\{[Ln(TCMBT)(C_2H_5OH)(H_2O)_2]\cdot 2.5H_2O\}_n$ [Ln = La (**4**)]. All of the complexes show 2-D bilayer structures and exhibit interesting crystal-to-amorphous transformation properties. It is worth noting that they are the first 2-D sheet molecular architectures with unprecedented 4^26^4 topology from the pyramidal nodes.

X-ray diffraction analyses indicate that complexes **1**−**3** are isostructural, and only the structure of complex **1** is described in detail. As shown in Figure 1, the central Tb^{III} is coordinated by nine O atoms, in which six are from four TCMBT ligands and three from coordinated water molecules, leading to a distorted monocapped square antiprism with one O atom of the monodentate ligand (O8) in the capped positions. The Tb−O distances range from 2.330(5) to 2.599(5) Å, and the cis angles vary from 50.68(18)° to 148.68(19)°. Each TCMBT ligand adopts a cis,cis,trans conformation, and three carboxylate groups adopt the μ^2-η^1:η^1 and μ^1-η^1:η^1 coordination fashions, coordinating to four metal centers.

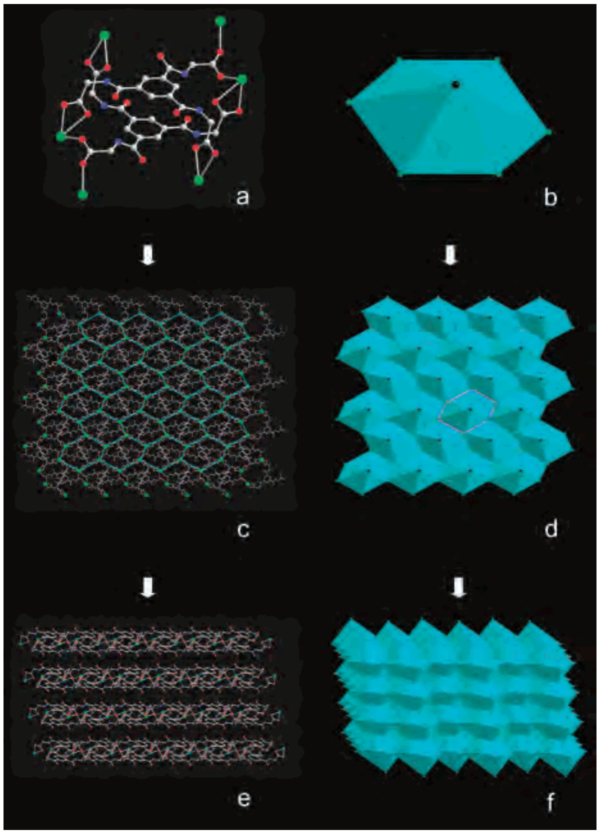

Figure 2. (a) View of the $M_6(TCMBT)_2$ entity in complex **1**. (b) Perspective view of the dodecahedron of a single building unit for $Tb_6(TCMBT)_2$ (the geometrical centers of the benzene ring of TCMBT ligands, black; Tb atoms, blue). (c) View of the 2-D sheet along the *c* axis. (d) Perspective view of the sheet in a dodecahedronal representation. (e) View of the packing mode along the *b* axis. (f) Packing of complex **1** in a polyhedral representation.

The basic building block of this strucuture is the hexanuclear $M_6(TCMBT)_2$ entity, in which a rare 28-membered ring is observed with two ligands linking two metal centers in a head-to-tail mode, with the Tb1···Tb1A (symmetry codes: $-x$, $1 - y$, $1 - z$) distance being 5.867 Å (Figure 2a). Two TCMBT ligands are antiparallel with a face-to-face distance of 3.613 Å, suggesting the existence of significant $\pi\cdots\pi$ interactions between them. Notably, this building block can be rationalized as a distorted dodecahedron if the metal centers and the geometry centers of the aromatic ring of the ligand are considered as vertexes (Figure 2b). Furthermore, by sharing the edges of dodecahedrons, compact undulating 2-D sheets are formed parallel to the *bc* plane in an ...ABAB... fashion (Figure 2c,d). Within the sheets, there exist complicated hydrogen-bonding interactions between the coordinated carboxylate O atom and the N atom

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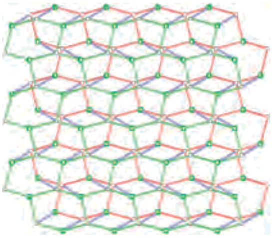

Figure 3. View of the $4^2 6^4$ nets: the connectors of TCBMT ligands and Tb atoms are colored in gray and green, respectively.

of the amide group as well as the coordinated water molecules, which extend the 2-D sheets into a 3-D supramolecular network (Figure 2e,f).

To identify the topology of the whole network, the metal ions and geometry centers of the phenyl ring of the ligand are assumed as four-connected nodes (Figure 3). The whole topology shows a novel 2-D bilayer net with the Schläfli symbol of $4^2 6^4$ and the vertex symbols of $4.6.4.6_3.6_2.6_4$. This unusual 2-D topology can also be described as a result of connection of two undulating honeycomb networks, which is different from common 2-D topology in which the projections down the *c* axis are non-superimposable. Moreover, this topological difference from those of other known four-connected nets, square and tetrahedron, is a pyramidal arrangement.[8−13] According to the classification, the present net belongs to 2-D nets with the feature of a 3-D net.[18] In other words, it displays similar planar arrangement of the nodes as well as potential extension of the dimensionality through additional connecting between nodes in a common plane. Ultimately, this special assembly may be related to the flexible coordination of the lanthanide centers and flexible conformations of the ligand. Thus, a novel network based upon the pyramidal four-connected nodes has been generated, and it is the first molecular architecture with unprecedented topology of a $4^2 6^4$ net.

Complexes **2** and **3** are isostructural to **1**. The selected bond lengths and angles and other related parameters about the structure are listed in Table S2 in the Supporting Information). All of these values increase from **1** to **3**, indicating the radius contraction of the metal centers. It is notable that complex **4** is very similar, except that the coordinated water molecules are replaced by the ethanol molecules, which may also be attributed to the difference in the lanthanide ion radii.

The luminescent properties of complex **1** at room temperature were also investigated. Upon excitation at 340 nm, the complex exhibits bright-green luminescence, and the narrow nature of the bands and the positions of the principal transitions are characteristic of the f−f transitions of Tb^{III}.[19]

To further identify the stability and dynamic properties of the whole frameworks, thermal gravimetric analysis (TGA) and powder X-ray diffraction (PXRD) measurements were performed. All complexes show similar properties, and thus complex **1** was selected as an example. TGA data of complex **1** indicate that the release of guest and coordinated water molecules occurs before 85 and 135 °C, respectively. The remaining solids can be heated to 280 °C without any additional weight loss. As expected, hydrogen-bonding interactions between the layers induce interesting reversible crystal-to-amorphous transformation of the complexes. The white residue obtained by heating the crystals of **1** to 120 °C was confirmed as the dehydrated amorphous form of [Tb(TCMBT)]$_n$ by elemental analysis and PXRD analysis (Figure 4). Interestingly, when this solid was suspended in water, the same PXRD patterns as those of the original crystal were regenerated. Thus, the dehydrated solids of these complexes may be potential reversible adsorbent materials for water molecules.

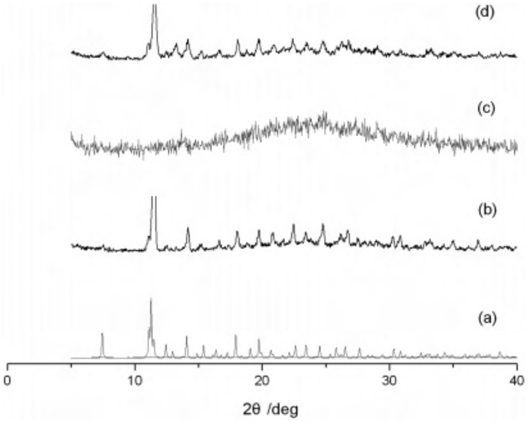

Figure 4. PXRD of complex **1** and [Tb(TCMBT)]$_n$: (a) simulated for **1**; (b) as-synthesized **1**; (c) [Tb(TCMBT)]$_n$; (d) restored **1** from [Tb(TCMBT}]$_n$.

In summary, four novel lanthanide(III) coordination polymers have been synthesized by the agar gel method from a new flexible tripodal ligand with additional amide groups. They have 3-D networks constructed from novel 2-D layers through hydrogen bonds induced by additional amide groups in the ligands, which also lead to interesting crystal-to-amorphous properties. To the best of our knowledge, they are the first molecular architectures with unprecedented topology of a four-connected $4^2 6^4$ net.

CCDC 648760−648763 for complexes **1**−**4** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Supporting Information Available: Crystal data and structure refinement parameters, bond lengths and angles, hydrogen-bonding interactions, and TGA curves for compounds **1**−**4**, solid-state excitation−emission spectrum for **1**, and PXRD of compounds **2** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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