

## Toward the Rational Design of Lanthanide Coordination Polymers: a New Topological Approach

Claire Marchal,<sup>†</sup> Yaroslav Filinchuk,<sup>‡</sup> Daniel Imbert,<sup>†</sup> Jean-Claude G. Bünzli,<sup>§</sup> and Marinella Mazzanti<sup>\*†</sup>

Laboratoire de Reconnaissance Ionique et Chimie de Coordination, Service de Chimie Inorganique et Biologique (UMR-E 3 CEA-UJF), CEA/DSM/DRFMC, CEA-Grenoble, 38054 Grenoble Cedex 09, France, Swiss Norwegian Beam Lines (SNBL) at the European Synchrotron Radiation Facility (ESRF), rue Jules Horowitz, 38043 Grenoble, France, and Ecole Polytechnique Federale de Lausanne (EPFL), BCH 1402, CH-1015 Lausanne, Switzerland

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The implementation of four bidentate building blocks into a high-denticity linker with a flexible spacer leads to a predisposed ligand that allows one to direct the self-assembly of 1D functional coordination polymers. This is illustrated by the assembly under mild conditions of the luminescent metal–organic framework [Tb(Htpabn)]·14H<sub>2</sub>O<sub>∞</sub> (1; H<sub>4</sub>tpabn = *N,N,N',N'*-tetrakis[(6-carboxypyridin-2-yl)methyl]butylenediamine). The X-ray crystal structure shows that the monoprotonated Htpabn binds two equivalent lanthanide ions to form a one-directional staircase chain. The high ligand denticity prevents solvent coordination and leads to a high luminescence quantum yield (*Q* = 39%), which is maintained after solvent removal.

Coordination polymers are presently playing a prominent role in material science, and their potential as functional materials is clearly recognized.<sup>1</sup> The construction of supramolecular networks containing lanthanide ions as connectors is particularly attractive because of the magnetic and electronic properties of 4f ions, which should result in the application of lanthanide polymers in sensors, lighting devices, and optical storage.<sup>2–10</sup> Lanthanide ions feature long

luminescence lifetimes and characteristically sharp line emissions, which span from infrared to blue. Efficient luminescence emission requires usually sensitization by suitable coordinated ligands (“antennae”). Accordingly, stable frameworks, which can act as porous solids, and networks with interesting luminescent properties have been synthesized<sup>11–15</sup> using lanthanide ions, demonstrating the potential of this field. However, the high coordination flexibility of lanthanide ions and their lack of preferential geometries make it very difficult to control or even to predict the final network architecture that will result from the combination of lanthanide ions with low-denticity organic linkers. Furthermore, the use of low-denticity linkers often results in the coordination of solvent molecules. This can lead to luminescence quenching and low thermal stability due to considerable structural changes associated with the removal of these molecules.

In order to better control the geometry and properties of the final lanthanide framework, we have chosen to use a new topological approach,<sup>16</sup> in which suitable building blocks are implemented<sup>17</sup> into a multidentate linker with a flexible spacer, which directs the geometry and dimensionality of the self-assembled network. Picolinates are efficient sensitizers of lanthanide luminescence,<sup>18,19</sup> and because of the

\* To whom correspondence should be addressed. E-mail: marinella.mazzanti@cea.fr. Fax: +33(4)38785090.

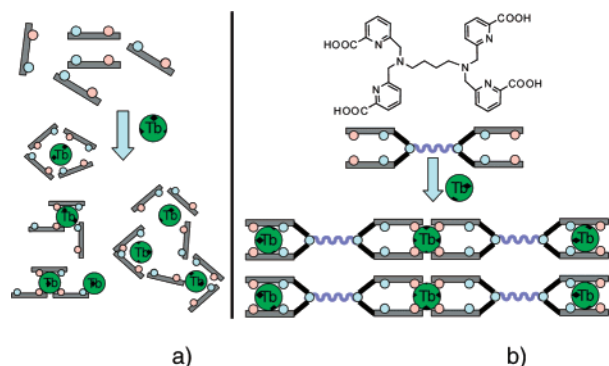
<sup>†</sup> Cea-Grenoble.

<sup>‡</sup> ESRF.

<sup>§</sup> EPFL.

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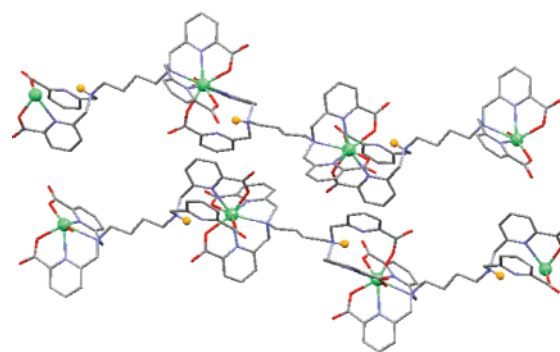
**Figure 1.** Schematic representation of the self-assembly of picolinate building blocks to produce (a) random or (b) ligand-controlled coordination networks.

versatile chemistry of pyridine, they form excellent building blocks for the construction of more sophisticated linkers. In this work, we have used a flexible linear spacer to connect four picolinate building blocks in order to produce 1D polymers (Figure 1).

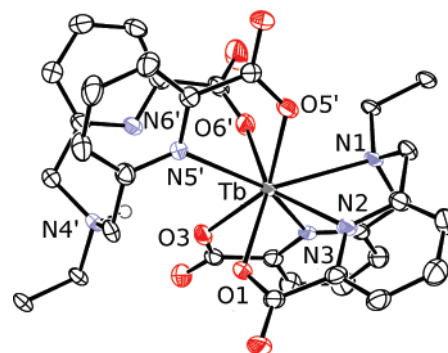
1D chains are the simplest type of coordination arrays and therefore are a good starting point in the development of new synthetic strategies. The choice of high-density coordination sites (five potential donor atoms on each side) allows for a good predictability of the final structure even in the presence of flexible spacers. Flexible linkers are of potential interest for the design of thermoplastic polymers.<sup>20</sup>

The potentially decadentate ligand *N,N,N',N'*-tetrakis[(6-carboxypyridin-2-yl)methyl]butylenediamine ( $H_4$ tpabn) was easily obtained in 40% yield from the reaction of 6-(chloromethyl)pyridine-2-carboxyl ethyl ester with 1,4-diaminobutane dihydrochloride in the presence of  $K_2CO_3$  followed by hydrolysis in 6 M HCl.<sup>21</sup> The protonation constants were measured by potentiometry to be  $pK_{a,1} = 3.2(3)$ ,  $pK_{a,2} = 3.7(2)$ ,  $pK_{a,3} = 6.99(4)$ , and  $pK_{a,4} = 8.082(3)$ . The highest  $pK_a$  was assigned by NMR titration to the aliphatic amine nitrogen.

Slow diffusion of an EtOH/water (4:1) solution of 1 equiv of  $TbCl_3 \cdot xH_2O$  into a 2:1 water solution of  $H_4$ tpabn and  $TbCl_3$  at pH = 6.5 (adjusted with triethylamine) produces small crystals suitable for X-ray diffraction.<sup>22</sup> The very small size of the crystals required the use of synchrotron radiation for structural studies. The structural analysis revealed the presence of a 1D coordination polymer  $[Tb(Htpabn)] \cdot 14H_2O_\infty$



**Figure 2.** Directional polymeric chains and crystal packing in **1**. Hydrogen atoms protonating aliphatic amine atoms are shown in orange. Other hydrogen atoms and water molecules are not shown for clarity (Mercury 1.4.1).



**Figure 3.** ORTEP view of the coordination environment of the terbium ion. Ellipsoids are shown at the 50% probability level. Bond lengths (Å): Tb–N(av)2,3, 2.485(3); Tb–N1, 2.672(3); Tb–N5, 2.691(3); Tb–N6, 3.796(3); Tb–N4, 4.206(3); Tb–O(av)5,7, 2.292(3); Tb–O(av)1,3, 2.335(3).

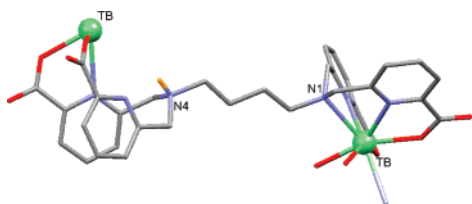
(**1**; Figure 2).<sup>23</sup> The polymer was prepared in 58% yield. Elemental analysis is in good agreement with the structural results. The structure contains eight-coordinate terbium ions with distorted bicapped trigonal-prismatic coordination geometry (Figure 3). The terbium atom is coordinated by two carboxylate oxygens, two pyridine nitrogens, and one aliphatic nitrogen from one ligand molecule and by two

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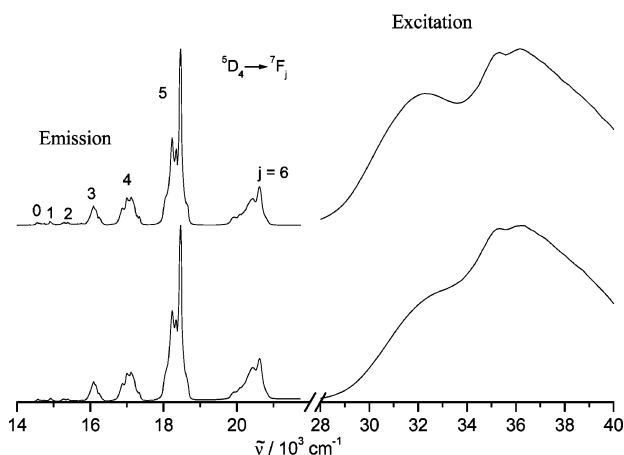
(21) To a solution of 6-(chloromethyl)pyridine-2-carboxyl ethyl ester (2.95 g, 14.8 mmol) in anhydrous acetonitrile (50 mL) were successfully added 1,4-diaminobutane dihydrochloride (0.582 g, 3.6 mmol) and  $K_2CO_3$  (3.45 g, 25 mmol). After refluxing for 20 h, the mixture was filtered. The solvent was evaporated to yield a yellow oil, which was dissolved in dichloromethane. The resulting solution was washed with water ( $2 \times 100$  mL) and then dried over anhydrous  $Na_2SO_4$ . After evaporation of the solvent, the resulting yellow oil (2.86 g) was refluxed overnight in a 6 M HCl solution (50 mL). After evaporation of the solvent to  $\sim 5$  mL, the solution was stored at 5 °C overnight. A white solid was formed that was filtered, washed with 6 M HCl, and dried under vacuum to yield  $H_4$ tpabn $\cdot 2HCl \cdot 6H_2O$  (1.13 g, global yield 27%). Elem anal. Calcd for  $H_4$ tpabn $\cdot 2HCl \cdot 6H_2O$  ( $C_{32}H_{46}N_6O_8Cl_2$ ): C, 47.49; H, 5.73; N, 10.38. Found: C, 47.81; H, 5.24; N, 10.76.  $^1H$  NMR ( $D_2O$ , 200 MHz,  $pD = 6.3$ ):  $\delta$  1.91 (4H, br s,  $-CH_2CH_2-$ ), 3.32 (4H, br s,  $2NCH_2$ ), 4.46 (8H, s,  $4NCH_2py$ ), 7.27 (4H, m, 4CH), 7.65 (m, 8H, 8CH).

(22) Synthesis of complex **1**: A solution of  $TbCl_3 \cdot 6H_2O$  (18.58 mg, 0.050 mmol) in 4:1 EtOH/water (5 mL) was allowed to slowly diffuse into a 2:1 solution of  $TbCl_3 \cdot 6H_2O$  (18.58 mg, 0.050 mmol) and  $H_4$ tpabn (80.56 mg, 0.10 mmol) in water (9.0 mL) adjusted at pH = 6.5 (by the addition of  $Et_3N$ ). Three days later crystals suitable for X-ray diffraction formed. The crystals were filtered, washed with water, and dried under vacuum to yield  $[Tb(Htpabn)] \cdot 6H_2O$  as a white crystalline powder (51.7 mg, 58%). Elem anal. Calcd for  $[Tb(Htpabn)] \cdot 6H_2O$  ( $C_{32}H_{41}N_6O_{14}Tb$ ): C, 43.06; H, 4.63; N, 9.41. Found: C, 43.1; H, 4.52; N, 9.49. A fraction of the solid was dried under vacuum at 130 °C for 6 days to remove all of the water molecules. Calcd for  $[Tb(Htpabn)]$  ( $C_{32}H_{29}N_6O_8Tb$ ): C, 48.99; H, 3.73; N, 10.71. Found: C, 48.90; H, 3.81; N, 10.73.

(23) Crystal data for **1**:  $[Tb(Htpabn)] \cdot 14H_2O$ ;  $C_{32}H_{57}N_6O_{22}Tb$ ,  $M = 1036.76$  g/mol, monoclinic, space group  $P2_1/n$ ,  $a = 16.0957(2)$  Å,  $b = 14.2869(1)$  Å,  $c = 18.4787(2)$  Å,  $\beta = 94.515(1)^\circ$ ,  $V = 4236.13(7)$  Å<sup>3</sup>,  $Z = 4$ ,  $\rho_c = 1.626$  g/cm<sup>3</sup>,  $\mu = 1.76$  mm<sup>-1</sup>,  $T = 100$  K,  $R_{int} = 0.0384$ . Synchrotron radiation with  $\lambda = 0.71076$  Å and a MAR345 detector were used for data collection (SNBL at the ESRF). The structure was solved by direct methods and refined by a full-matrix least-squares technique on  $F^2$  using the *SHELXL97* program: 597 refined parameters,  $R1 = 0.0382$  and  $wR2 = 0.0902$  for 8800 independent reflections with  $I > 2\sigma(I)$ ;  $R1 = 0.0454$  and  $wR2 = 0.0951$  for all 40951 reflections,  $GOF = 1.017$ . H(C) atoms were modeled in the riding model, while the H(N) atom was located from a difference Fourier map and refined independently. A total of 10 out of 28 H(O) atoms of water molecules were also located.



**Figure 4.** Detail of the crystal structure of **1** showing the coordination mode of the ligand  $H_4tpabn$  (Mercury 1.4.1).



**Figure 5.** Normalized excitation (right,  $\lambda_{an} = 18\,469\text{ cm}^{-1}$ ) and emission spectra (left,  $\lambda_{ex} = 36\,000\text{ cm}^{-1}$ ) of the hydrated (top) and dehydrated (bottom)  $Tb^{III}$  polymer at room temperature.

carboxylate oxygens and one pyridine nitrogen from another ligand molecule. Water molecules do not coordinate the metal atom. Because of the high  $pK_{a,4}$  value, one aliphatic nitrogen of the tetrapod is protonated under the reaction conditions, yielding a potentially nonadentate unsymmetrical ligand. Each potentially nonadentate  $Htpabn$  ligand acts as an octadentate ligand in **1** and binds two symmetry-related (by the  $n$ -glide plane) terbium ions (Figure 4), leading to the formation of a 1D staircase chain running along the  $a + c$  diagonal of the unit cell.

The presence of two different coordination sites leads to the formation of directional chains,<sup>24</sup> which are packed into a centrosymmetric structure (Figure 2). An introduction of chiral centers into the ligand is underway in order to promote the formation of polar crystals. The solvate water molecules are hydrogen-bonded to form a 2D framework situated in the  $(1,0,-1)$  plane. The 1D lanthanide–picolate chains run across these water layers and are connected to them by hydrogen bonds through the carboxylate oxygen atoms, resulting in a 3D framework.

The thermogravimetric analysis performed under an argon flow in the temperature range 30–800 °C showed that all of the water molecules can be removed from the crystal without decomposition in the temperature range 30–110 °C, while decomposition of the complex occurs above 250 °C.

The terbium polymer displays efficient luminescence in the solid state (Figure 5) with a measured luminescence quantum yield of 39% ( $\lambda_{exc} = 320\text{ nm}$ ) and a long excited-

state lifetime of  $\tau = 1.89(2)\text{ ms}$ .<sup>25</sup> Only the metal emission is observed, suggesting an efficient ligand-to-metal energy transfer. The value of the solid-state luminescence quantum yield of **1** is higher than the one found in solution for the monomeric tris(dipicolinate)terbium complex (24%)<sup>18</sup> and similar to the value found for the complex  $[Tb(tpaen)]$  ( $H_4tpaen = N,N,N',N'$ -tetrakis[(6-carboxypyridin-2-yl)methyl]ethylenediamine; 45% in water).<sup>19</sup> The luminescence quantum yield remains unchanged after removal of all of the solvate water molecules, indicating the absence of significant structural modification of the network. Preliminary luminescence studies on an isostructural erbium polymer show that the hydrated polymer does not display a detectable luminescence in the near-IR region. Conversely, the dehydrated form is luminescent in the solid state with a measured luminescence quantum yield of  $2.9 \times 10^{-3}$  ( $\lambda_{exc} = 335\text{ nm}$ ).

The terbium ions in the polymeric chain are 12.2 Å apart, with  $Tb-Tb-Tb$  angles of 149.4°. The shortest interchain  $Tb-Tb$  distance is 9.74 Å. Significantly shorter metal–metal distances of 4–6 Å are often found in polymeric networks formed by bidentate aromatic carboxylates through carboxylate bridges. The ligand design allows one to tune the distance between lanthanide centers and prevent luminescence deactivation through intercenter energy transfer. This should make possible the development of polymeric systems containing different independent lanthanide emitters. Notably, the controlled slow diffusion synthetic method used to prepare the terbium polymer **1** is particularly suitable for the preparation of heterometallic multicolor emissive polymers.

In conclusion, we note that a new rational synthetic strategy combining in one ligand high-denticity binding sites and a flexible linker has led to the preparation of a highly luminescent supramolecular 1D polymer. X-ray diffraction studies revealed that an isostructural coordination polymer is obtained for the smaller  $Er^{III}$  ion, confirming the predictability of this synthetic approach. An extensive study of polymer formation with differently sized lanthanides and under different reaction conditions is in progress. Future work will also be directed toward the development of spacers, which should lead to higher dimensionality networks and tune the flexibility and the optical properties of the final network.

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**Supporting Information Available:** Crystallographic data and CIF file for complex **1**, Figure S1 showing the thermogravimetric analysis of **1**, and Figures S2 and S3 showing the 2D layers of solvate water molecules. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(25) Luminescence measurements were made on a Fluorolog FL 3-22 spectrometer from Spex-Jobin Yvon-Horiba, and quantum yields were determined by an absolute method using a home-built integration sphere.

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