A flexible tripodal ligand linking octametallic terbium rings into luminescent polymeric chains†

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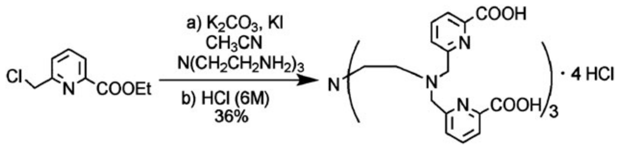
Six bidentate building blocks have been used to form a tripodal ligand with a flexible C_3 symmetric spacer to direct the assembly of large octametallic clusters covalently linked to form a 1-D highly luminescent terbium tube-like polymer.

Infinite metal–organic frameworks containing lanthanide ions are attracting increasing attention due to their fascinating structural topologies and the variety of potential technological applications.[1–6] In particular, the attractive light-emitting properties (characteristic sharp emission, long lifetime, large Stokes shift) of 4f elements make lanthanide-based coordination polymers particularly suitable for the development of optical devices and sensors.[7,8] However the design and control of lanthanide-based polymeric frameworks is very difficult due to the high coordination flexibility and the lack of preferential geometries of these 4f ions. By contrast, their flexible coordination environment can lead to unusual topologies and new framework families.[9,10] Most studies have so far been focused on the assembly of lanthanide polymers from low denticity rigid ligands (*e.g.* aromatic acids). Multidentate flexible linkers remain rare in the construction of lanthanide polymers, although some lanthanide frameworks isolated using flexible ligands display very attractive properties such as high thermal stability[11] or unusual structural and optical properties.[12,13] Moreover, flexibility, also called structural dynamism, in the functional porous framework is crucial for selective molecular recognition.[14]

We have recently shown that the use of four bidentate building blocks to form a multidentate linker through a flexible linear spacer directs the self-assembly of 1-D functional polymers.[15] Picolinates were chosen as building blocks for their efficient sensitization of lanthanide luminescence.[16,17] We are now investigating the possibility of extending this topological approach to the assembly of more sophisticated structures. The flexible C_3 symmetric [tris(2-aminoethyl)-amine] (tren) has been used as an anchor in various tripodal ligands to assemble mononuclear nonacoordinated lanthanide complexes.[18] We have previously shown that tren-based tripodal ligands with an increased overall ligand denticity (twelve) can be used to direct the assembly of discrete polymetallic arrays.[19] In order to promote the assembly of an infinite framework and to shed light on the factors determinating the assembly of discrete *versus* infinite polymetallic lanthanide arrays we have designed a ligand with increased flexibility and higher denticity. Here we describe the highly flexible potentially hexadecadentate tripodal ligand N,N,N',N',N'',N''-hexakis[(6-carboxypyridin-2-yl)methyl]-tris-(2-aminoethyl)amine (H_6trenpa)‡ in which six picolinate building blocks are connected by a tren spacer. The reaction of this flexible multidentate ligand with lanthanide salts yields large octametallic clusters covalently linked into 1-D chains. H_6trenpa is readily obtained in five steps from commercially available 2,6-dipicolinic acid and tren in a yield of 36% (Scheme 1).



Scheme 1 Synthesis of H_6trenpa·4HCl.

The slow diffusion of acetonitrile into a DMF–water mixture of $TbCl_3·6H_2O$ and H_6trenpa in a 2 : 1 ratio in the presence of KOH leads to the isolation of the 1-D polymer $[Tb_4(Htrenpa)(trenpa)(H_2O)_2]Cl·35H_2O$ (**1**) in ∼67% yield.§

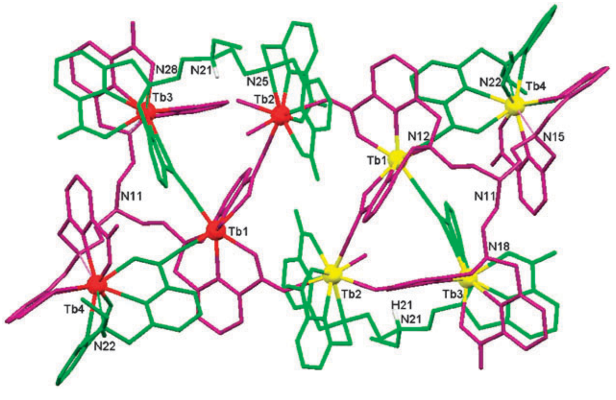


Fig. 1 Crystal structure showing the coordination mode of $Htrenpa^{5-}$ (green) and $trenpa^{6-}$ (purple) in the cationic octameric unit $[Tb_4(Htrenpa)(trenpa)(H_2O)_2]_2^{2+}$ in **1**. The inversion related Tb(n) ions in yellow and Tb(n) in red are at equivalent positions ($1 - x, -y, -z$).

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The X-ray diffraction analysis reveals a monoclinic polymer with a large unit cell volume (27 592.4(6) Å^3), close to that of a small protein. Elemental analysis is in good agreement with the structural results.

In the crystal structure of **1**,¶ two fully deprotonated trenpa^{6-} and two Htrenpa^{5-} ligands protonated on the apical nitrogen (which remains non coordinating in both species) bind eight terbium ions to form a bicapped hexameric ring (1.7 nm long and 6.5 Å wide). (Fig. 1 and Fig. S1†) The protonation of the non-coordinating nitrogen has been previously observed in related lanthanide complexes and found to favour crystallization.[20] The asymmetric unit of **1** contains four independent terbium ions (Tb1–Tb4), one trenpa^{6-} and one Htrenpa^{5-} ligand. Inversion by a symmetry center generates an octameric Tb$_8$ motif where six terbium ions are located on the same hexagonal plane (mean deviation ranges from 0.057 to −0.057 Å), while the two symmetry related Tb4 ions are situated 2.97 Å below and above the plane. Each deprotonated trenpa^{6-} ligand binds the four independent terbium ions and one symmetry related Tb2 ion within the same octamer. Two picolinate arms of each protonated ligand Htrenpa^{5-} bind three Tb ions (Tb1, Tb2, Tb3) from one octamer, the third picolinate arm binds the Tb4 and Tb1 ions from an adjacent octameric unit leading to the formation of an infinite 1-D tube-like polymeric chain running along the *b* axis. The Tb octamers are linked by the symmetry of a two-fold axis parallel to *b* (Fig. 2a).

The polymer **1** has an original porous structure with two different cavities filled up by water molecules. The Tb···Tb distances in the triangles formed by Tb1, Tb2, and Tb3 vary from 6.091 to 6.694 Å, while the longest Tb···Tb distance in the flat hexagons is 17.682 Å. The four Tb centers can be divided into three groups (Fig. S2–S5†): (1) Tb4 and Tb3 ions are ten-coordinated by two pentadentate dipodal aminodipicolinate units, one from the Htrenpa^{5-} and one from the trentpa^{6-} ligand. Tb1 ions are eight-coordinated by the five donor atoms of one pentadentate aminodipicolinate unit of trenpa^{6-}, one water molecule and two picolinate oxygens from two different Htrenpa^{5-} ligands (where the other picolinate O binds in one case Tb4 and in the other case Tb3). Finally, Tb2 ions are nine-coordinated by the five donor atoms of one pentadentate aminodipicolinate unit of Htrenpa^{5-}, one water molecule and three picolinate oxygens, two from different arms of one trenpa^{6-} (already bound, respectively to Tb3 and Tb1) and one from the symmetry related trenpa^{6-} in the same octamer. The average Tb–O and Tb–N distances are in the range of previously reported distances,[15] with relatively long Tb–N distances (3.005(6)–3.081(6) Å) found for the tertiary amine atoms. The strong hydrogen bonding between the polymer chains and lattice water molecules and the weak hydrogen bonding (C–H···O and C–H···π) between polymer chains generate an extended 3-D network with large 1.5 nm wide cavities filled with water molecules (Fig. 2b).

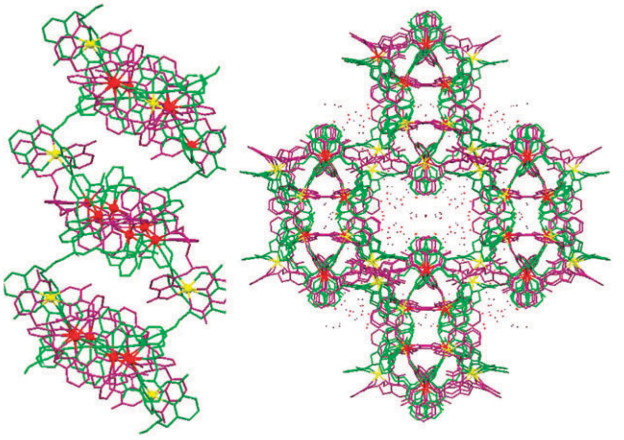

Fig. 2 (Left) View along the *b* axis of the polymeric chain in **1**. Hydrogen atoms and lattice water molecules are omitted for clarity (Tb1, Tb2, Tb3 in red, Tb4 in yellow). (Right) View along the *c* axis of the crystal packing. A small pore filled up by water molecules is situated in the middle of the polymeric chains.

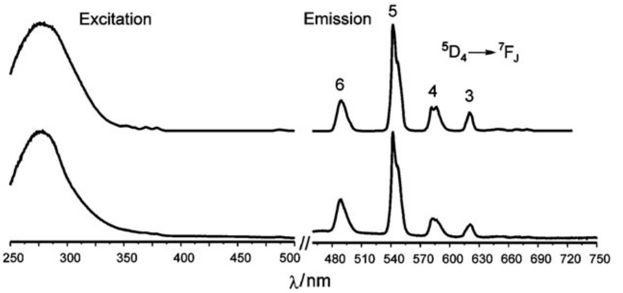

Fig. 3 Normalized excitation (left, λ_{em} = 545 nm) and emission spectra (right, λ_{exc} = 290 nm) of the hydrated (top) and dehydrated (bottom) terbium polymer (**1**) at 295 K.

In spite of the large number of water molecules present in the structure, solid state photophysical studies show that the terbium polymer (**1**) is highly luminescent (Fig. 3) with an emission quantum yield of 26.2(4)% (λ_{ex} = 290 nm) and a long excited-state lifetime of τ = 1.52(8) ms.‖ The luminescence spectrum shows exclusively Tb emission with seven lines corresponding to transitions from $^5D_4 \rightarrow {}^7F_{6-0}$. The luminescence of the ligand $^1\pi\pi^*$ and $^3\pi\pi^*$ states disappears completely, indicating an efficient sensitization of the metal ion *via* a ligand-to-metal energy transfer. Thermal gravimetric analysis (TGA) data show that a continuous release of guest water molecules occurs between 30 and 330 °C. Decomposition occurs above 330 °C.

Surprisingly, the luminescence quantum yield of the terbium polymer after complete removal of water molecules (**1a****) decreases dramatically to 5.9(5)%. The abrupt change in the quantum yield presumably indicates that the polymeric structure collapsed after the removal of coordinated and guest water molecules probably leading to luminescence deactivation through inter-center energy transfer. This observation highlights the importance of including lanthanide ions in specifically designed networks to optimize the photoluminescence performance. The work in progress is directed to study the reversibility of the observed structural collapse in presence of different guest molecules.

In conclusion, the combination of the flexibility with the high denticity in the "predisposed" tripodal ligand H$_6$trenpa results in a lanthanide-based coordination polymer with an unprecedented topology consisting of large octanuclear terbium clusters covalently linked into a 1-D tube-like chain.

This unique structure anticipates other fascinating topologies when using multidentate flexible ligands in the assembly of lanthanide polymers. Moreover, the interesting luminescence properties of this polymer make attractive the use of flexible polydentate ligands in the development of luminescent materials. Future work will be directed to investigate the effect of lanthanide size on the polymer structure and to tune the ligand flexibility and denticity in order to obtain more robust topologies.

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Notes and references

‡ Elemental analysis (%) calc. for H_6trenpa·4HCl ($C_{48}H_{52}N_{10}O_{12}Cl_4$): C 52.28, H 4.75, N 12.70; found: C 52.37, H 4.64, N 13.11. ^{1}H NMR (D_2O, 400 MHz, 298 K, pD = 6): δ = 3.56 (s, 12H, NCH_2CH_2N), 4.45 (s, 12H, NCH_2py), 7.51 (d, 4H, CH), 7.80 (d, 4H, CH), 7.92 (t, 4H, CH). ^{13}C NMR (D_2O, 100 MHz, 298 K, pD = 6) δ = 49.64 (CH_2); 50.75 (CH_2); 59.86 (CH_2); 123.06 (CHpy); 125.87 (CHpy); 138.75 (CHpy); 153 (Cpy); 156.43 (Cpy); 172.57 (COOH). Mass spectrum shows the peak of $(L + 2H)/2^+$ at 479.6.

§ Elemental analysis (%): calc. for {[Tb_4(Htrenpa)(trenpa)$(H_2O)_2$]$_n$Cl$_n$}·24H_2O + 2.6KCl, $C_{96}H_{137}N_{20}O_{50}Cl_{3.6}K_{2.6}Tb_4$, C, 35.63; H, 4.27; N, 8.66; found C, 35.71; H, 4.20; N, 8.66.

¶ Crystal data: [Tb_4(Htrenpa)(trenpa)$(H_2O)_2$]Cl·35H_2O (**1**), $C_{96}H_{159}N_{20}O_{61}ClTb_4$, T = 100 K, M = 3240.56, monoclinic, space group $C2/c$, a = 30.5311(5), b = 33.6509(3), c = 27.1283(3) Å, β = 98.116(1)°, V = 27592.4(6) Å^3, Z = 8, D_c = 1.560 g cm^{-3}, μ = 2.141 mm^{-1}. Synchrotron radiation with λ = 0.71076 Å and MAR345 detector were used for data collection (SNBL at the ESRF). The structures were solved by direct methods and refined by a full-matrix least-squares technique on F^2 using the SHELXH97 program. R_1 = 0.0604 and wR_2 = 0.1597 for 22 512 independent reflections and 1644 refined parameters. CCDC 680329. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b803505a.

‖ The photoluminescence measurements were carried out on powder samples inside capillary tubes on a Fluorolog FL 3-22 spectrometer from Spex-Jobin Yvon-Horiba. Quantum yields were determined by an absolute method using a home-built integration sphere.

** Complex **1a** was prepared as follows: the complex **1** was dried under vacuum at 130 °C for 6 days to remove all the water molecules. Elemental analysis (%): calc. for [Tb_4(Htrenpa)(trenpa)]Cl + 2.6KCl, $C_{96}H_{85}N_{20}O_{24}Cl_{3.6}K_{2.6}Tb_4$, C, 41.66; H, 3.10; N, 10.12%, found C, 41.52; H, 3.28; N, 10.27.

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