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Mixed Tb/Dy coordination ladders based on tetra(carboxymethyl)thiacalix[4]arene: a new avenue towards luminescent molecular nanomagnets†

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The macrocyclic ligand calix[4]arene (L1) and its sulphur-containing analogue thia[4]calixarene (L2) are promising precursors for functional molecular materials as they offer rational functionalization with various organic groups. Here, we present the first example of lanthanide-based coordination polymers built from the macrocyclic thiacalix[4]arene backbone bearing four carboxylic moieties, namely, ligand H₄L3. The combination of H₄L3 with the Tb³⁺ and Dy³⁺ cations led to the formation of 1D ladder-type coordination polymers with the formula [Ln^{III}HL3DMF₃](DMF) (where DMF = dimethylformamide and Ln = Tb or Dy, denoted as HL3–Tb and HL3–Dy), which resulted from the coordination of the lanthanide cations with the partially deprotonated ligand HL3³⁻ that behaved as a T-shape connector. The coordination sphere around the metal was completed by the coordinated DMF solvent molecules. By combining both Tb³⁺ and Dy³⁺ cations, isostructural heterobimetallic solid solutions HL3–Tb_{1-x}Dy_x were also prepared. HL3–Tb and HL3–Dy showed visible light photoluminescence originating from the f–f electronic transitions of pale green emissive Tb³⁺ and pale yellow emissive Dy³⁺ with efficient sensitization by the functionalized thia[4]calixarene ligand HL3. In the HL3–Tb_{1-x}Dy_x solid solutions, the Tb/Dy ratio governed both the emission colour as well as the emission quantum yield, which reached even 28% at room temperature for HL3–Tb. Moreover, HL3–Dy exhibited a slow magnetic relaxation effect related to the magnetic anisotropy of the dodecahedral Dy³⁺ complexes, which were well isolated in the crystal lattice by expanded organic spacers.

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Introduction

Coordination polymers (CPs),^{1,2} MOFs³ and molecular networks^{4,5} have molecular architectures that offer properties such as gas storage,^{6,7} catalysis,^{8,9} magnetism^{10,11} and luminescence.^{12–14} The

generation of such molecular species is based on the formation of coordination bonds between organic coordinating ligands and metal centres or complexes.¹⁵ A large number of coordination polymers that display different connectivity patterns have been generated using different types of polytopic ligands and metals.

Concerning the luminescence properties⁷ of CPs, special attention has been devoted to lanthanide-based CPs,^{16–18} owing to their outstanding photoluminescence originating from the triplet excited states of f–f transitions. Lanthanide-based CPs may find applications in luminescence sensing, light emission together with photonics,^{19–21} and as ligands presenting a strong antenna effect,²² allowing energy transfer from an organic ligand to the metal. The use of macrocyclic ligands for the formation of such assemblies has been documented;²³ however, most of the reports are mainly related to porphyrin-based lanthanide CPs.²⁴

Concerning the magnetic properties of lanthanide-based CPs, examples of molecular nanomagnets have been reported earlier.^{25–27} In addition, LnCPs may combine both SMM behaviour and tunable photoluminescence, as shown recently.^{28–30}

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For building new CPs based on macrocycles, the use of calixarene derivatives presents a nice alternative. Calix[4]arenes^{31–33} are macrocyclic compounds composed of four phenolic moieties bridged by methylene groups as in the “classic” calix[4]arene, CA, **L1** (Fig. 1), sulphur atoms in the case of thiacalix[4]arene, TCA, **L2** (Fig. 1),³⁴ or hydroxyl or mercapto groups as in tetramercaptothiacalix[4]arene (TMTCA).^{35,36} These molecules can be easily modified by the functionalization of the upper and/or lower rims of the macrocyclic scaffold. They can adopt four different conformations (cone, partial cone, 1,2-alternate and 1,3-alternate), which make these compounds attractive precursors for designing molecular networks. The generation of coordination polymers with various dimensionalities using tetrasubstituted (tetramercapto)(thia)calix[4]arene derivatives that bear different coordinating sites is well documented.³⁷

By combining functionalized calix[6]arene bearing amide groups, calix[8]arene,^{38,39} unsubstituted calix[4]arene and thiacalix[4]arene derivatives in cone conformation^{40–43} with lanthanides salts or mixtures of 3d/4f,^{44–51} different types of clusters have been obtained. Among them, the use of calixarenes bearing carboxylic coordinating sites, for which the lanthanides cations present great affinity, has been reported for the formation of isolated complexes.^{52,53}

It is important to note that, to date, only a few lanthanide-based coordination networks involving calixarene derivatives, which are mainly formed by the tetrasulfonate derivatives of (thia)calix[4]arenes in cone conformation,^{54–57} have been reported. To the best of our knowledge, no examples involving carboxylate derivatives or (thia)calix[4]arenes in 1,3-alternate conformation have been reported so far.

Several calixarene derivatives bearing carboxylic/ate coordinating groups have been described. Among them, the compound **H₄L3** has been used in the formation of coordination polymers with 3d metals, such as Co(II) or Mn(II), and ancillary ligands.^{58,59} An analogous ligand without the *tert*-butyl groups has been used for the formation of coordination polymers with Ag⁺, Ni²⁺, Co²⁺, and Zn²⁺ together with K⁺.^{60,61} TMTCA derivative-based coordination polymers using 3d metals have also been reported⁶² and shown to form hydrogen-bonded networks.⁶³

In this study, we report the structure of a series of isostructural new 1D lanthanide-based coordination networks,

derived from tetrasubstituted TCA in 1,3-alternate conformation bearing carboxylate moieties (**HL3³⁻**). A series of isostructural, homo and heterometallic lanthanide-based periodic architectures (Dy/Tb, because of the isostructurality of the related CPs) has been prepared. Mixing lanthanide cations in solid solution coordination networks can lead to the combination of two phosphorescent centres with large emission differences, which is a common strategy to gain self-referenced luminescence. Heteronuclear lanthanide Gd/Eu or La/Tb, Tb/Eu or Dy/Ln polymers are usually reported for the fine-tuning (colour and brightness) of the corresponding luminescence properties.^{64–66} Generally, the mixed Eu/Tb compounds allow energy transfer in the mixed coordination polymers due to the optimal energy match between the lanthanide cations.^{67–72} But tuneable emission can also arise when mixed Tb/Dy coordination compounds are used.⁷³

The ligand fluorescence and Dy³⁺ and Tb³⁺ phosphorescence were thoroughly studied in the solid-state in the corresponding (Dy/Tb) solid solutions. In addition, the magnetic properties of the anisotropic Dy³⁺ compound were investigated in detail.

Results and discussion

Synthesis and structural details

The synthesis of compound **H₄L3** was achieved following a previously reported procedure that involves a nucleophilic substitution reaction between TCA and ethyl bromoacetate in the presence of Cs₂CO₃ in acetone, followed by hydrolysis under basic conditions using LiOH in a THF/H₂O mixture.^{63,74,75} The combination of compound **H₄L3** with lanthanide(III) nitrate salts (Ln = Tb or Dy) under solvothermal conditions in DMF (see Experimental part) led to the formation of isostructural 1D coordination networks. The structural investigation of both single crystals of **HL3–Ln** (Ln = Dy and Tb) was carried out using X-ray diffraction. The formula derived from the crystallographic analysis was found to be [C₄₈H₅₃O₁₂S₄Ln(C₃H₇NO)₃]·(C₃H₇NO) ([Ln^{III}**HL3DMF**]³⁻·(DMF), Ln = Dy or Tb), as shown in Table 1. In the present CP, the ligand/metal ratio is 1/1.

The crystals were composed of **HL3³⁻** in its tris-deprotonated form (see Table 2 for C–O distances), the trivalent Ln cation (Ln(III)) and four DMF solvent molecules. The description of the structure in the solid-state is reported below only for **HL3–Tb**. The terbium atom was octacoordinated and surrounded by oxygen atoms. Two carboxylate moieties coordinated with the lanthanide in a bidentate mode and the third carboxylate presented a monodentate coordination mode. The 3 oxygen atoms belonging to three DMF molecules completed the coordination sphere of Tb (Fig. 2c). Using the SHAPE program,⁷⁶ the geometry around the Tb centres was found to be a deformed triangular dodecahedron, as shown in ESL†

The crystal also contained a non-coordinated DMF molecule occupying the interstices between antiparallel 1D coordination networks without forming any specific interactions with them. The terbium atoms acted as T-shaped connectors, connecting three carboxylate groups belonging to three adjacent **HL3³⁻** ligands, leading to a double chain ladder-like structure (Fig. 2a and b and schematically represented in d).

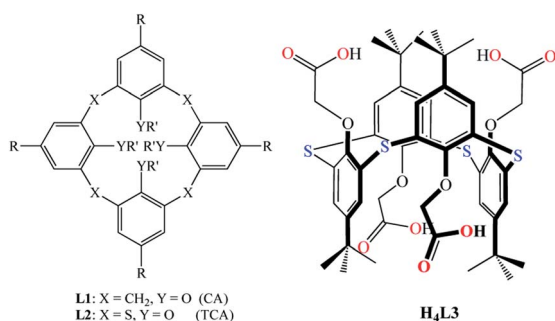


Fig. 1 Calix[4]arene (**L1**, CA) and thiacalix[4]arene (**L2**, CA) and tetramercaptothiacalix[4]arene (**H₄L3**) adopting a 1,3-alternate conformation.



Table 1 Crystallographic parameters for HL3–Dy and HL3–Tb recorded at 173 K

Formula	C ₄₈ H ₅₃ O ₁₂ S ₄ Dy(C ₃ H ₇ NO) ₃ , C ₃ H ₇ NO, C ₆₀ H ₈₁ DyN ₄ O ₁₆ S ₄ , HL3–Dy	C ₄₈ H ₅₃ O ₁₂ S ₄ Tb(C ₃ H ₇ NO) ₃ , C ₃ H ₇ NO, C ₆₀ H ₈₁ TbN ₄ O ₁₆ S ₄ , HL3–Tb
Molecular weight	1405.02	1401.44
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	15.0091(17)	15.0160(17)
<i>b</i> (Å)	15.9798(18)	15.9630(14)
<i>c</i> (Å)	16.7401(18)	16.7660(16)
α (deg)	62.217(5)	62.226(3)
β (deg)	67.626(5)	67.513(3)
γ (deg)	79.181(6)	79.132(4)
<i>V</i> (Å ³)	3284.5(7)	3285.2(6)
<i>Z</i>	2	2
Colour	Colourless	Colourless
Crystal dim (mm ³)	0.090 × 0.100 × 0.100	0.090 × 0.100 × 0.100
<i>D</i> _{calc} (g cm ⁻³)	1.421	1.417
<i>F</i> (000)	1454	1452
μ (mm ⁻¹)	1.332	1.270
Wavelength (Å)	0.71073	0.71073
Number of data meas	83 469	36 284
Number of data with <i>I</i> > 2 σ (<i>I</i>)	17 032 [<i>R</i> (int) = 0.0752]	17 822 [<i>R</i> (int) = 0.0558]
<i>R</i>	<i>R</i> ₁ = 0.0557, <i>wR</i> ₂ = 0.1391	<i>R</i> ₁ = 0.0494, <i>wR</i> ₂ = 0.1073
<i>R</i> _w	<i>R</i> ₁ = 0.0756, <i>wR</i> ₂ = 0.1559	<i>R</i> ₁ = 0.0708, <i>wR</i> ₂ = 0.1186
GOF	1.057	1.011
Largest peak in final difference (eÅ ⁻³)	1.740 and –1.406	1.411 and –1.140

Consequently, the fourth carboxylic group remained protonated without interactions with the other components of the crystal.

As expected, different C–O distances were observed for the carboxylic moieties of HL3³⁻, revealing the presence of one non-coordinated carboxylic group and three coordinated carboxylate moieties (see Table 2).

Within the 1-D arrays, the shortest Tb–Tb distance was equal to 11.879(3) Å, and the packing of the 1D networks in the *yOz* plane (Fig. 2b, packing along the *a*-axis) led to a shorter Tb–Tb distance of 7.836(4) Å between two Tb atoms belonging to two different chains.

Since both compounds HL3–Dy and HL3–Tb were isostructural (which is not the case for Gd and Eu analogues, for example), solid solutions of formula HL3–Tb_{1-x}Dy_x were

prepared using the same synthetic procedure as the one used for HL3–Dy and HL3–Tb (see Experimental section). Meanwhile, in our case, the related Eu compound obtained with H₄L3 was not isostructural with HL3–Tb or HL3–Dy.

Starting with different experimental Dy/Tb ratios, microcrystalline compounds of the following formula were obtained: HL3–Tb_{0.07}Dy_{0.93}, HL3–Tb_{0.20}Dy_{0.80}, HL3–Tb_{0.42}Dy_{0.58}, HL3–Tb_{0.67}Dy_{0.33} and HL3–Tb_{0.95}Dy_{0.05}.

The structure of the solid solution was investigated by XRPD, as shown in Fig. 3 (for the determined cell parameters of the corresponding single crystals, see Table S1, ESI†). XRPD clearly demonstrated the structural homogeneity of the phase of the formed coordination compounds. All the HL3–Tb_{1-x}Dy_x solid

Table 2 Selected bond distances (Å) for HL3–Dy and HL3–Tb

	HL3–Dy	HL3–Tb
C–O (carboxyl-ate/-ic)	1.232(5) and 1.273(5)	1.215(4) and 1.269(4)
	1.239(5) and 1.268(4)	1.253(4) and 1.258(4)
	1.254(5) and 1.261(5)	1.243(4) and 1.259(4)
	1.189(5) and 1.323(5) (carboxylic)	1.194(5) and 1.320(5) (carboxylic)
Ln–O (DMF)	2.354(3)	2.355(3)
	2.366(3)	2.369(2)
	2.380(3)	2.395(3)
	2.380(3)	2.393(3)
Ln–O (carboxylate)	2.256(3)	2.277(2)
	2.380(3)	2.393(3)
	2.393(3)	2.411(3)
	2.404(3)	2.418(3)
	2.438(3)	2.440(2)



