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Synthesis, structure and photoluminescence properties of lanthanoid coordination polymers based on tetra(3,5-dicarboxyphenoxymethyl)methane

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Abstract

A series of isostructural lanthanoid coordination polymers with the formula $[Ln_2(H_6L)(H_4L)(H_2O)_2]_n$ (XL-Ln; $Ln = Sm^{III}$, Eu^{III} , Gd^{III} , Tb^{III} , Dy^{III} ; $H_8L = tetra(3,5-dicarboxyphenoxymethyl)methane)$ has been synthesized. The compounds (except XL-Gd) exhibit the characteristic emission of trivalent lanthanoid ions under UV irradiation. By using a mixture of Eu^{III}/Tb^{III} salts as starting material, color-tunable coordination polymers have been obtained of which the emission color can be changed from red to green with different Eu^{III}/Tb^{III} ratios.

Keywords: Coordination Polymers; Luminescence; Lanthanoids; Hydrothermal; Topology

Introduction

In recent years, luminescent lanthanoid coordination polymers (*Ln*-CPs) have attracted extensive research efforts due to their unique luminescence properties, such as long lifetime, high quantum yields, and characteristic sharp line emissions [1]. By rational selection of the organic and inorganic components, *Ln*-CPs can generate intense photoluminescence via the antenna effect [2-5]. Due to the similar chemical properties of the different lanthanoid metal ions, it is possible to synthesize coordination polymers with more than one kind of lanthanoid ions occupying the identical sites in the crystal structures [6-8]. By this strategy, multi-color emitting CPs have been obtained, which have been demonstrated to be potentially useful in applications such as ratiometric thermometers, ratiometric sensors of small organic molecules and ions, luminescence barcodes and white-light emitting phosphors [9-24].

Continuing our previous efforts in this field of research, we synthesized a series of new Ln-CPs using the potentially cross-linking ligand tetra(3,5-dicarboxyphenoxymethyl)methane (H₈L) shown in Figure 1. By using mixed Eu/Tb salts as starting material mixed Ln-CPs were obtained. The emission color of these

mixed *Ln*-CPs can be tuned from red to green under single-wavelength excitation by adjusting the Eu/Tb molar ratio.

Experimental Section

General

The ligand tetra(3,5-dicarboxyphenoxymethyl)methane was synthesized following literature procedures [25, 26]. All chemicals and solvents are commercially available and were used without further purification. Elemental analysis for C and H was performed at the Microanalytical laboratory Kolbe in Germany. IR spectra were recorded on a Perkin Elmer UATR Two FT-IR spectrometer set to a resolution of 4 cm⁻¹. The excitation and emission spectra were recorded on a Shimadzu RF-5301PC spectrofluoriphotometer. X-ray powder diffraction patterns were recorded on a Philips PW 1050 diffractometer using Cu Ka radiation ($\lambda = 1.54178$ Å). Inductively coupled plasma optical emission spectrometry (ICP-OES) was measured on a VISTA-MPX Simultaneous ICP-OES with Varian SPS 3 sample preparation system. Thermogravimetric analyses (TGA) spectra were recorded on a NETZSCH STA 499 instrument under argon atmosphere with heating rate of 3 °C per minute. The fluorescence lifetime was measured using a Hamamatsu R928P photomultiplier connected to a Tektronix DPO4054 digital scope, a Carl Zeiss M20 grating monochromator was used to select the emission wavelength. A Labview program was used to collect and to average the data. Excitation was done with an Ekspla NTB342B Nd:YAG laser equipped with a OPO and SHG to generate 5ns pulses at a 10 Hz rate.

Synthesis of the Ligand (H₈L)

The ligand was synthesized via a slightly modified procedure from literature [25]. To a solution of dimethyl-5-hydroxyisophthalate (9.2 g, 44 mmol) and K₂CO₃ (16.6 g, 120 mmol) in DMF (50 ml), pentaerythrityl tetrabromide (3.87g, 10.0 mmol) was added slowly. The solution was stirred at room temperature for 20 min, then heated up to 100 °C for 72 h. The reaction was then cooled to room temperature, all the solvent was evaporated. The resulting white residue was added to a solution of KOH (10.24 g, 80 mmol) in a water/ethanol mixture (50 ml/50 ml) and refluxed for 6 h. The reaction mixture was cooled down to room temperature, and concentrated HCl was added until pH=1. The resulting white precipitate was filtered and dried in vacuo. Yield 6.0 g, 91%. ¹H NMR (300 MHz, DMSO): δ =8.06 (s, 4H), 7.72 (s, 8H), 4.50 (s, 8H) ppm. ¹³C NMR (75 MHz, DMSO): δ = 166.8, 159.1, 133.1, 123.1, 119.8, 66.9, 45.2 ppm. IR (*v*): 3083 (br), 2626 (br), 1690 (vs), 1594 (s), 1459 (m), 1413 (m), 1327 (m), 1211 (s), 1123 (m), 1041 (m), 998 (w), 904 (w), 882 (w), 759 (s), 726 (s), 489 (w) cm⁻¹.

Synthesis of $[Ln_2(H_6L)(H_4L)(H_2O)_2]_n$ (XL-*Ln*; *Ln* = Sm, Eu, Gd, Tb, Dy) and the Mixed Lanthanoid Compounds XL-Eu_xTb_{1-x} (x = 0.2, 0.4, 0.6, 0.8).

The ligand H₈L (21 mg, 26.5 mmol) was mixed with TbCl₃•6H₂O (20 mg, 53 mmol) in 10 ml H₂O and the reaction mixture was transferred to a 20 ml Teflon-lined stainless-steel vessel, which was heated to 170 °C for 3 days. Then the vessel was cooled down to room temperature at a rate of 20 °C per hour. The colorless flat crystals were collected by filtration and dried in vacuo. Yield: 6 mg (24 %, based on ligand). XL-Tb. Elemental analysis found (calc) for $C_{37}H_{27}O_{21}Tb$: C, 45.78 (45.98); H, 2.92 (2.82). Selected IR data (*v*, cm⁻¹): 2929 (br), 2528 (br), 1643 (vs), 1598 (m), 1541 (m), 1447 (m), 1377 (s), 1263 (s), 1209 (m), 1133 (m), 1043 (m), 906 (m), 754 (vs), 679 (m), 663 (m), 596 (w), 555 (w), 508 (w).

XL-Ln (Ln = Sm, Eu, Gd, Dy) and the mixed lanthanoid compounds were made following a similar procedure, but using Sm, Eu, Gd, Dy salts or a mixture of Eu and Tb salts. ICP-OES was used to determine the Eu/Tb molar ratio in the final products.

XL-Sm. Selected IR data (*v*, cm⁻¹): 2923 (br), 2520 (br), 1642 (vs), 1599 (m), 1536 (m), 1433 (m), 1374 (s), 1256 (s), 1208 (m), 1136 (m), 1029 (m), 906 (m), 754 (vs), 655 (m), 595 (w), 552 (w), 508 (w).

XL-Eu. Selected IR data (v, cm⁻¹): 2934 (br), 2535 (br), 1642 (vs), 1590 (m), 1540 (m), 1431 (m), 1374 (s), 1261 (s), 1212 (m), 1137 (m), 1029 (m), 905 (m), 754 (vs), 677 (m), 595 (w), 508 (w).

XL-Gd. Selected IR data (*v*, cm⁻¹): 2933 (br), 2553 (br), 1643 (vs), 1596 (m), 1538 (m), 1443 (m), 1375 (s), 1260 (s), 1211 (m), 1131 (m), 1030 (m), 906 (m), 754 (vs), 677 (m), 664 (m), 596 (w), 506 (w).

XL-Dy. Selected IR data (*v*, cm⁻¹): 2929 (br), 2524 (br), 1644 (vs), 1600 (m), 1543 (m), 1450 (m), 1376 (s), 1263 (s), 1203 (m), 1134 (m), 1043 (m), 905 (m), 755 (vs), 683 (m), 656 (m), 596 (w), 509 (w).

XL-Eu_{0.2}Tb_{0.8} analyzed as [Eu_{0.66}Tb_{1.34}(H₆L)(H₄L)(H₂O)₂]_n. Selected IR data (*v*, cm⁻¹): 2929 (br), 2517 (br), 1641 (s), 1600 (m), 1543 (m), 1450 (m), 1433 (m), 1375 (s), 1256 (s), 1198 (m), 1134 (m), 1031 (m), 906 (m), 877 (w), 800 (w), 754 (vs), 677 (m), 655 (m), 595 (w), 552 (w), 506 (w).

XL-Eu_{0.4}Tb_{0.6} analyzed as [Eu_{1.10}Tb_{0.90}(H₆L)(H₄L)(H₂O)₂]_n. Selected IR data (*v*, cm⁻¹): 3073 (br), 2529 (br), 1643 (s), 1601 (m), 1544 (m), 1455 (m), 1433 (m), 1377 (s), 1264 (s), 1211 (m), 1135 (m), 1043 (m), 906 (m), 875 (w), 799 (w), 756 (vs), 679 (m), 595 (w), 553 (w), 507 (w).

XL-Eu_{0.6}Tb_{0.4} analyzed as [Eu_{1.44}Tb_{0.56}(H₆L)(H₄L)(H₂O)₂]_n. Selected IR data (*v*, cm⁻¹): 2929 (br), 2526 (br), 1642 (s), 1599 (m), 1539 (m), 1448 (m), 1436 (m), 1375 (s), 1256 (s), 1207 (m), 1133 (m), 1031 (m), 905 (m), 876 (w), 801 (w), 754 (vs), 681 (m), 656 (m), 595 (w), 553 (w), 508 (w).

XL-Eu_{0.8}Tb_{0.2} analyzed as [Eu_{1.74}Tb_{0.26}(H₆L)(H₄L)(H₂O)₂]_n. Selected IR data (*v*, cm⁻¹): 2934 (br), 2535 (br), 1645 (s), 1599 (m), 1544 (m), 1453 (m), 1433 (m), 1376 (s), 1264 (s), 1213 (m), 1135 (m), 1046 (m), 906 (m), 877 (w), 798 (w), 756 (vs), 678 (m), 664 (m), 595 (w), 552 (w), 509 (w).

Single Crystal X-ray Crystallography

All reflection intensities were measured at 110(2) K using a SuperNova diffractometer (equipped with Atlas detector) with Cu $K\alpha$ radiation ($\lambda = 1.54178$ Å) under the program CrysAlisPro (Version 1.171.36.32 Agilent Technologies, 2013). The same program was used to refine the cell dimensions and for data reduction. The structure was solved with the program SHELXS-2014/7 and was refined on F^2 with SHELXL-2014/7 [27]. Analytical numeric absorption correction based on a multifaceted crystal model was applied using CrysAlisPro. The temperature of the data collection was controlled using the system Cryojet (manufactured by Oxford Instruments). The H atoms were placed at calculated positions (unless otherwise specified) using the instructions AFIX 23, AFIX 43 or AFIX 147 with isotropic displacement parameters having values 1.2 or 1.5 Ueq of the attached C or O atoms. The H atoms attached to O1W (coordinated water molecule) were found from difference Fourier maps, and their coordinates were refined freely. The O–H and H…H bond distances for the coordinated water molecule were restrained using the DFIX instructions. The structure is ordered. The organic moiety has twofold axial symmetry as C101 and C103 are located at sites of twofold axial symmetry.

Additional notes: (i) the displacement ellipsoids for atoms O53 and O54 are somewhat elongated, most likely suggesting slight disorder. An attempt to model the disorder was not successful as the refinement was not stable. Thus, both atoms were left ordered in the final refinement.

(ii) There is one residual electron density Q peak of 0.54 e^- Å⁻³ found at 0.96 Å from O23. This peak cannot be an H atom because it is not located within the plane defined by C73, O13 and O23, and because there are no potential O acceptors around O23 except for O11.

Results and discussion

Description of the Structure

The structure of XL-Tb was determined by single crystal X-ray crystallography and was shown to have the formula $[Tb_2(H_6L)(H_4L)(H_2O)_2]_n$; all compounds proved to be isostructural as deduced from powder XRD (discussed below). X-ray quality single crystals of XL-Tb were obtained from the hydrothermal synthesis [28]. XL-Tb crystallized in the monoclinic space group P2/c (Table S1); the asymmetric unit contains two half parts of two ligands with different coordination modes, one terbium ion and one coordinated water molecule (Figure 1a and Figure S1). The Tb^{III} ion is coordinated by seven O atoms from six carboxylate groups and one O atom from water, forming a geometry best described as a distorted bicapped trigonal prism. There are no O atoms shared by Tb^{III} ions. The Tb-O bond lengths are found in the range of 2.254(2) – 2.582(2) Å, which can be considered normal for this type of bonds (Table S2) [9, 14, 16, 29, 30]. The ligands show two different kinds of coordination modes. In the first coordination mode the ligand is twice deprotonated and coordinated to six different Tb^{III} ions (Figure 1c). In the second

coordination mode the ligand is four times deprotonated and coordinated to four different Tb^{III} ions (Figure 1d). In both cases the ligand has twofold rotational symmetry with the axis passing through the central carbon atom of the ligand. Hydrogen bonds can be found in the crystal structure which may enhance the structure stability (Table S2). The structure is tightly packed and does not contain any solvent-accessible voids.



Figure 1. Impression of the crystal structure of $[Tb_2(H_6L)(H_4L)(H_2O)_2]_n$ and coordination modes of the ligand. a) asymmetric unit; b) Projection of the structure of XL-Tb along the *c* axis; c) coordination mode of the ligand H₆L; d) coordination mode of the ligand H₄L. Green = terbium, red = oxygen, grey = carbon, hydrogen is omitted for clarity.

Topology Studies

The free software programme TOPOS was used to analyze the structure [31-33]. The ligand is coordinated to either six Tb^{III} or four Tb^{III} ions, and thus are considered as a six or four connected nodes (Figure 2a and 2b). Each Tb^{III} ion is bound by five different ligands and thus treated as a five-connected node (Figure 2c). Due to the absence of bridging O atoms, the coordination polyhedra of the metal ions share neither an edge nor a point. Thus, the use of SBUs is not suitable in this structure analysis and in the topology

structure analysis only the coordination polyhedron itself is treated as a node. The point symbol of this topology is $\{4^4 \cdot 6^2\}\{4^6 \cdot 6^4\}^2\{4^8 \cdot 6^7\}$ (Figure 2d).



Figure 2. Topological structure of XL-Tb. a) the six-connected node (ligand H_6L^{2-}); b) the four-connected node (ligand H_4L^{4-}); c) the five-connected node (Tb^{III}); d) topology structure. (Gray node = Tb^{III}; yellow node = six connected ligand; blue node = four connected ligand)

Powder XRD and IR Spectroscopic Studies

Powder XRD was used to confirm the phase purity of XL-Ln (Ln = Sm, Eu, Gd, Tb and Dy) and the mixed-lanthanoid samples. As shown in Figures S2 and S3, the PXRD pattern of all samples are highly similar to the simulated pattern from the single crystal structure of XL-Tb, confirming the phase purity of all samples and their being isomorphous. The highly similar IR spectra further confirm that all the compounds are isostructural (Figure S4 and S5).

Luminescent Properties

When illuminated with a laboratory high-pressure Hg lamp (366 nm), the compounds XL-Sm, XL-Eu, XL-Tb and XL-Dy show orange, red, green and white luminescence, respectively, whereas XL-Gd shows

no luminescence emission at room temperature. Solid-state photoluminescence spectra for all compounds are shown in Figure 3. The CIE (Commission Internationale de l'Éclairage) coordinates have been calculated on the basis of the emission spectra; the emission colors of all four compounds are depicted in the CIE chromaticity diagram shown in Figure 4.



Figure 3. The excitation and emission spectra of a) XL-Sm; b) XL-Eu; c) XL-Tb; d) XL-Dy.

The emission spectrum of XL-Sm contains the four characteristic peaks for the Sm^{III} ion at 562, 598, 644 and 713 nm, which are ascribed to the ${}^{4}G_{5/2}\rightarrow{}^{6}H_{J}$ transitions (J = 5/2, 7/2, 9/2 and 11/2) [34-36]. The dominant orange color of emission is due to the most intense peak of the ${}^{4}G_{5/2}\rightarrow{}^{6}H_{9/2}$ transition. The ${}^{4}G_{5/2}\rightarrow{}^{6}H_{5/2}$ transition is magnetic dipole (MD) in nature and its intensity is less sensitive to the coordination environment of the Sm^{III} ion. As a comparison, the ${}^{4}G_{5/2}\rightarrow{}^{6}H_{9/2}$ transition is electric dipole (ED) in nature, and its emission intensity is more sensitive to the coordination environment [37-39]. The fact that the ${}^{4}G_{5/2}\rightarrow{}^{6}H_{9/2}$ transition is more intense than the ${}^{4}G_{5/2}\rightarrow{}^{6}H_{5/2}$ transition indicates that the Sm^{III}

ion occupies a non-centrosymmetric site [34, 40, 41], which is in agreement with the single crystal structure. When excited by 330 nm UV light, the compound XL-Eu exhibits the four typical peaks of the Eu^{III} ion at 585, 615, 649 and 702 nm, assigned to the ${}^{5}D_{0}\rightarrow{}^{7}F_{J}$ transitions (J = 1-4). The emission spectrum is dominated by the ${}^{5}D_{0}\rightarrow{}^{7}F_{2}$ transition. The compound XL-Tb displays the characteristic emission peaks of Tb^{III} at 486, 542, 587 and 622 nm, related to the ${}^{5}D_{4}\rightarrow{}^{7}F_{J}$ (J = 6-3) transitions upon excitation with 333 nm light [21, 22]. The emission spectrum of XL-Dy comprises three peaks at 485, 574 and 660 nm, corresponding to the transitions of ${}^{4}F_{9/2}\rightarrow{}^{6}H_{J}$ (J = 15/2, 13/2 and 11/2) of the Dy^{III} ion [16].



Figure 4. The luminescence colors of XL-Sm, XL-Eu, XL-Tb and XL-Dy in a CIE chromaticity diagram. CIE coordinates: XL-Sm (X = 0.4332, Y = 0.2945); XL-Eu (X = 0.5691, Y = 0.3134); XL-Tb (X = 0.3189, Y = 0.6000); XL-Dy (X = 0.3662, Y = 0.3788).

The lowest singlet excited state of the ligand is 32260 cm^{-1} as estimated from the room temperature solidstate absorption spectrum of XL-Gd (Figure S6; 310 nm). The energy level of the triplet excited state of the ligand H₈L is 23200 cm^{-1} (431 nm), as estimated from the phosphorescence spectrum of XL-Gd at 77 K (Figure S7). The energy gap between the singlet and triplet excitation states of ligand thus is calculated to be 9060 cm⁻¹, which is suitable for efficient intersystem crossing according to Reinhoudt's rules [42]. Due to the small energy gaps between the emitting level and highest energy levels of the ground state of the Sm^{III} and Dy^{III} ions, their emission is easily quenched by non-radiative processes [43]. For XL-Tb and XL-Eu, the energy differences between the triplet state of the ligand and the Ln^{III} emitting level (for Tb^{III}, ⁵D₄, 20.5 × 10³ cm⁻¹; for Eu^{III}, ⁵D₀, 17.2 × 10³ cm⁻¹) are 2700 cm⁻¹ and 6000 cm⁻¹, respectively. This

suitable energy gap makes the energy transfer from the ligand triplet state to these Ln^{III} exited states efficient and without significant back transfer [6, 43, 44].



Figure 5. The decay curves of a) XL-Sm; b) XL-Eu; c) XL-Tb; d) XL-Dy. (λ_{ex} =325 nm; XL-Sm, monitored at 644 nm, τ =0.719 µs; XL-Eu, monitored at 615 nm, τ =0.363 ms; XL-Tb, monitored at 542 nm, τ =0.814 ms; XL-Dy, monitored at 574 nm, τ = 8.431 µs)

The emission lifetimes of the compounds XL-Sm, XL-Eu, XL-Tb and XL-Dy were recorded (Figure 5). The decay curves of all four compounds show monoexponential behavior, in agreement with the Ln^{III} emitting centers sharing identical coordination environments in the compounds. The lifetimes of the compounds XL-*Ln* (*Ln* = Sm, Eu, Tb and Dy) are 0.719 µs, 0.363 ms, 0.814 ms and 8.431 µs, which are normal values compared to the reported values of *Ln* compounds [11, 21, 41].



Figure 6. The emission spectra of XL-Eu_xTb_{1-x} (x = 0.2, 0.4, 0.6, 0.8) (λ_{exc} = 335 nm).

The luminescence emission spectra of the lanthanoid coordination polymer can be tuned by changing the molar ratio of Eu/Tb ions present in the compound (Figure 6). The Eu:Tb ratio was varied from 2:8 to 8:2; a CIE diagram showing the emission colors of the resulting compounds is displayed in Figure 7. With increasing Eu:Tb ratio, the emission color of the mixed-lanthanoid compound changes from green to red. Furthermore, the lifetime of Tb^{III} emission monitored at 544 nm (${}^{5}D_{4}$) decreases, indicating the occurrence of energy transfer from Tb^{III} to Eu^{III}, and confirming the compounds to be truly heterometallic and not just a physical mixture of two compounds. The energy-transfer efficiency from the Tb^{III} exited state to Eu^{III} in the mixed-lanthanoid sample is calculated with $\eta = 1-\tau/\tau_0$, where τ_0 and τ are the lifetime of the Tb^{III} emission in XL-Tb and the mixed-lanthanoid compounds, respectively. The results are presented in table S3. The energy-transfer efficiency increases from Tb^{III} to Eu^{III} concentrations. Compared to our previous work, the energy transfer from Tb^{III} to Eu^{III} is less efficient in this series of material due to the longer Ln-Ln distances (for this work, Ln-Ln = 6.898 Å; four our previous work, Ln-Ln = 4.212 Å and 4.532 Å) [22].



Figure 7. CIE diagram showing the luminescence colors of XL-Tb, XL-Eu and XL-Eu_xTb_{1-x} (x = 0.2, 0.4, 0.6, 0.8). CIE coordinates: XL-Eu_{0.2}Tb_{0.8} (X = 0.371, Y = 0.563); XL-Eu_{0.4}Tb_{0.6} (X = 0.424, Y = 0.516); XL-Eu_{0.6}Tb_{0.4} (X = 0.0532, Y = 0.381); XL-Eu_{0.8}Tb_{0.2} (X = 0.569, Y = 0.313).

Conclusions

For the first time, lanthanoid coordination polymers have been prepared using the inherently crosslinking ligand tetra(3,5-dicarboxyphenoxymethyl)methane and the compounds were fully characterized. The studies revealed that XL-Sm, XL-Eu, XL-Tb and XL-Dy exhibit the typical luminescent emission of the trivalent lanthanoid ions under UV irradiation. Tunable red-to-green emission is achieved by using a mixture of Eu/Tb salts as starting material in the hydrothermal synthesis of the coordination polymer. These multicolor emission materials are potentially useful for ratiometric sensors, optoelectronic devices and labeling applications [9].

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Appendix A. Supplementary data

CCDC 1422060 contains the supplementary crystallographic data for the compound. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the

Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-

336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Spectroscopic details in the supplementary data include: Powder XRD pattern of XL-Sm, XL-Eu, XL-Gd, XL-Tb and XL-Dy and the simulated pattern from the single crystal structure of XL-Tb. Powder XRD patterns of XL-Eu_xTb_{1-x} (x = 0.2, 0.4, 0.6, 0.8). FTIR spectra of XL-Sm, XL-Eu, XL-Gd, XL-Tb and XL-Dy. FTIR spectra of XL-Eu_xTb_{1-x} (x = 0.2, 0.4, 0.6, 0.8). Solid-state absorption spectrum of XL-Gd. Phosphorescence spectrum of XL-Gd at 77 K and its deconvolution with Gaussians.

References

[1] Z.S. Dou, J.C. Yu, Y.J. Cui, Y. Yang, Z.Y. Wang, D. Yang, G.D. Qian, J. Am. Chem. Soc., 136 (2014) 5527-5530.

[2] B. Alpha, R. Ballardini, V. Balzani, J.M. Lehn, S. Perathoner, N. Sabbatini, Photochem. Photobiol., 52 (1990) 299-306.

[3] M.C. Heffern, L.M. Matosziuk, T.J. Meade, Chem. Rev., 114 (2013) 4496-4539.

- [4] A. D'Aléo, F. Pointillart, L. Ouahab, C. Andraud, O. Maury, Coord. Chem. Rev., 256 (2012) 1604-1620.
- [5] K. Binnemans, Chem. Rev., 109 (2009) 4283–4374.

[6] S. Freslon, Y. Luo, G. Calvez, C. Daiguebonne, O. Guillou, K. Bernot, V. Michel, X. Fan, Inorg. Chem., 53 (2014) 1217-1228.

[7] N. Kerbellec, D. Kustaryono, V. Haquin, M. Etienne, C. Daiguebonne, O. Guillou, Inorg. Chem., 48 (2009) 2837-2843.

[8] Y.J. Cui, F.L. Zhu, B.L. Chen, G.D. Qian, Chem. Commun., 51 (2015) 7420-7431.

[9] J.M. Zhou, W. Shi, N. Xu, P. Cheng, Inorg. Chem., 52 (2013) 8082-8090.

[10] Y. Lu, B. Yan, Chem. Commun., 50 (2014) 15443-15446.

[11] D. Ma, X. Li, R. Huo, J. Mater. Chem. C, 2 (2014) 9073-9076.

- [12] A.R. Ramya, S. Varughese, M.L.P. Reddy, Dalton Trans., 43 (2014) 10940-10946.
- [13] X.Y. Xu, B. Yan, Dalton Trans., 44 (2015) 1178-1185.

[14] A. Cadiau, C.D.S. Brites, P.M.F.J. Costa, R.A.S. Ferreira, J. Rocha, L.D. Carlos, ACS Nano, 7 (2013) 7213-7218.

[15] R.F. D'Vries, S. Alvarez-Garcia, N. Snejko, L.E. Bausa, E. Gutierrez-Puebla, A. de Andres, M.A. Monge, J. Mater. Chem. C, 1 (2013) 6316-6324.

[16] X.T. Rao, T. Song, J.K. Gao, Y.J. Cui, Y.Y. Yang, C.D. Wu, B.L. Chen, G.D. Qian, J. Am. Chem. Soc., 41 (2013) 15559-15564.

[17] Y.J. Cui, W.F. Zou, R.J. Song, J.C. Yu, W.Q. Zhang, Y. Yang, G.D. Qian, Chem. Commun., 50 (2014) 719-721.

[18] Y. Zhou, B. Yan, F. Lei, Chem. Commun., 50 (2014) 15235-15238.

[19] S.N. Zhao, L.J. Li, X.Z. Song, M. Zhu, Z.M. Hao, X. Meng, L.L. Wu, J. Feng, S.Y. Song, C. Wang, H.J. Zhang, Adv. Funct. Mater., 25 (2015) 1463-1469.

[20] Y. Zhou, B. Yan, J. Mater. Chem. C, 3 (2015) 9353-9358.

[21] X. Liu, S. Akerboom, S.H.C. Askes, I. Mutikainen, E. Bouwman, Inorg. Chem. Commun., 61 (2015) 60-63.

[22] X. Liu, S. Akerboom, M. de Jong, I. Mutikainen, S. Tanase, A. Meijerink, E. Bouwman, Inorg. Chem., 54 (2015) 11323-11329.

[23] Y. Lu, B. Yan, J. Mater. Chem. C, 2 (2014) 7411-7416.

- [24] Y. Zhou, B. Yan, J. Mater. Chem. C, 3 (2015) 8413-8418.
- [25] Y.Q. Lan, H.L. Jiang, S.L. Li, Q. Xu, Inorg. Chem., 51 (2012) 7484-7491.

[26] Z.J. Lin, T.F. Liu, X.L. Zhao, J. Lü, R. Cao, Cryst. Growth Des., 11 (2011) 4284-4287.

[27] G.M. Sheldrick, Acta Crystallogr. Sect. A, A64 (2008) 112-122.

[28] CCDC 1422060 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <u>www.ccdc.cam.ac.uk/data_request/cif</u>.

[29] P.R. Matthes, C.J. Holler, M. Mai, J. Heck, S.J. Sedlmaier, S. Schmiechen, C. Feldmann, W. Schnick, K. Muller-Buschbaum, J. Mater. Chem., 22 (2012) 10179-10187.

[30] Y.M. Li, Z.F. Ju, B.L. Wu, D.Q. Yuan, Cryst. Growth Des., 13 (2013) 4125-4130.

- [31] V.A. Blatov, A.P. Shevchenko, D.M. Proserpio, Cryst. Growth Des., 14 (2014) 3576-3586.
- [32] V.A. Blatov, Struct. Chem., 23 (2012) 955-963.

[33] E.V. Alexandrov, V.A. Blatov, A.V. Kochetkov, D.M. Proserpio, Cryst.Eng. Comm., 13 (2011) 3947-3958.

[34] S. Akerboom, M.S. Meijer, M.A. Siegler, W.T. Fu, E. Bouwman, J. Lumin., 145 (2014) 278-282.

[35] S. Biju, D.B.A. Raj, M.L.P. Reddy, C.K. Jayasankar, A.H. Cowley, M. Findlater, J. Mater. Chem., 19 (2009) 1425-1432.

[36] E. Pavitra, G.S.R. Raju, Y.H. Ko, J.S. Yu, PCCP, 14 (2012) 11296-11307.

[37] B. Sharma, J. Vipin Prasad, S.B. Rai, D.K. Rai, Solid State Commun., 93 (1995) 623-628.

[38] H.F. Brito, O.L. Malta, M.C.F.C. Felinto, E.E.S. Teotonio, J.F.S. Menezes, C.F.B. Silva, C.S. Tomiyama, C.A.A. Carvalho, J. Alloys Compd., 344 (2002) 293-297.

[39] G. Lakshminarayana, S. Buddhudu, Physica B: Condensed Matter, 373 (2006) 100-106.

[40] J.H.S.K. Monteiro, I.O. Mazali, F.A. Sigoli, J Fluoresc, 21 (2011) 2237-2243.

[41] X.L. Li, C.L. Chen, H.P. Xiao, A.L. Wang, C.M. Liu, X. Zheng, L.J. Gao, X.G. Yang, S.M. Fang, Dalton Trans., 42 (2013) 15317-15325.

[42] F.J. Steemers, W. Verboom, D.N. Reinhoudt, E.B. van der Tol, J.W. Verhoeven, J. Am. Chem. Soc., 117 (1995) 9408-9414.

[43] S.V. Eliseeva, J.C.G. Bunzli, Chem. Soc. Rev., 39 (2010) 189-227.

[44] M. Latva, H. Takalo, V.M. Mukkala, C. Matachescu, J.C. Rodriguez-Ubis, J. Kankare, J. Lumin., 75 (1997) 149-169.

Synthesis, structure and photoluminescence properties of lanthanoid coordination polymers based on tetra(3,5-dicarboxyphenoxymethyl)methane

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Graphical abstract

A series of isostructural lanthanoid coordination polymers with the ligand tetra(3,5-dicarboxyphenoxymethyl)methane) has been synthesized and characterized. The emission colors of coordination polymers can be tuned by using a mixture of Eu^{III}/Tb^{III} salts.

