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ARTICLE

Fluorescent and energy transfer properties of heterometallic lanthanide-titanium oxo clusters coordinated with anthracenecarboxylate ligand

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Two 9-anthracenecarboxylate (9-AC) coordinated heterometallic TOC compounds, $[\text{Ln}_2\text{Ti}_{10}\text{O}_{14}(\text{ClO}_4)_2(\text{O}^i\text{Pr})_{14}(9\text{-AC})_2(\text{CH}_3\text{CN})_2] \cdot 2\text{H}_2\text{O}$, Ln = Nd (**1**) and Eu (**2**), along with two benzoate (bza) analogues $[\text{Ln}_2\text{Ti}_{10}\text{O}_{14}(\text{ClO}_4)_2(\text{O}^i\text{Pr})_{14}(\text{bza})_2(\text{HO}^i\text{Pr})_2]$, Ln = Nd (**3**) and Eu (**4**) are prepared by one step in situ solvothermal synthesis, and characterized by single crystal analysis. Up to now, only about ten lanthanum-titanium oxo clusters were reported. Except two Ti28 clusters, the others are all small clusters ($\text{Ti} \leq 4$). The cluster structures of **1–4** adopt a $\text{Ti}_{10}\text{Ln}_2$ core structure with pseudo- C_i symmetry, which are similar to the fundamental structure of Ti12 clusters. Furthermore, except structures, the properties of lanthanum-titanium oxo clusters have not ever been studied. Herein the fluorescence properties of these compounds are detailedly studied. Metal centered emission of Eu(III) is completely quenched by 9-AC due to the lower triplet energy of the coordinated ligand. Enhanced ligand centered fluorescence is found for **2** in comparison with that of **1**.

Introduction

Titanium oxo-clusters (TOCs), especially $[\text{Ti}_n\text{O}_m(\text{OR})_x(\text{L})_y]$, are widely studied and their rich variations in structures have been characterized by different metal nuclearity, different kinds of the ligands (L), and different coordination modes of the L, which have been reviewed by Sanchez and Rozes.¹ The TOCs as the model compounds offer the opportunity to bridge the practical and the theoretical TiO systems in terms of both structures and chemical reactivities.² Recently, great attentions have been paid to derivatives of TOCs, because of their various properties and potential applications. Heterometallic TOCs with transition metals have been synthesized,³ inspired by the applications of transition metal doped titanium oxide materials, which have been proven to be an efficient route to improve both the photoactivity and catalytic activity of titania.⁴ Charge-transfer between chromophores and TOC clusters has been reported for some TOCs with catecholate or a nitrophenyl acetylacetonate ligand.⁵ TOCs with a monobenzenedicarboxylate were found to have good photocatalytic activity for hydrogen evolution from water.⁶ Very recently, it has been observed that some TOCs with carboxylates show selective sorption of carbon dioxide.⁷ We have also reported the first Co^{II} phen moiety fused TOC, and as the model compound of dye-sensitized solar cells (DSSC), photocurrent responsive property and complex-cluster electron transition were studied.⁸ However, in comparison with the reports on crystal structures, the researches on properties and applications of TOCs are still scarce.

Anthracene group is a well known fluorescent moiety, which has been used in photoactive systems.⁹ Theoretical

studies on the TiO-9-AC (9-AC = 9-anthracenecarboxylate) system¹⁰ and the solar energy cells with the 9-AC adsorbed TiO_2 electrode¹¹ have been carried out. Recently, using 9-AC as a functional organic ligand, TOC-9-AC model compounds (Ti6 clusters) were prepared for studies of the structures, optical and photocurrent responsive properties.¹² As a successive work, we herein prepared two new 9-AC coordinated heterometallic TOC compounds, $[\text{Ln}_2\text{Ti}_{10}\text{O}_{14}(\text{ClO}_4)_2(\text{O}^i\text{Pr})_{14}(9\text{-AC})_2(\text{CH}_3\text{CN})_2] \cdot 2\text{H}_2\text{O}$, Ln = Nd (**1**) and Eu (**2**), along with two benzoate (bza) analogues $[\text{Ln}_2\text{Ti}_{10}\text{O}_{14}(\text{ClO}_4)_2(\text{O}^i\text{Pr})_{14}(\text{bza})_2(\text{HO}^i\text{Pr})_2]$, Ln = Nd (**3**) and Eu (**4**). Their crystal structures and fluorescent properties are studied.

In structures, they are new characterized heterometallic TOC compounds with lanthanide elements. Up to now only near ten lanthanide-titanium-oxo clusters were documented based on our knowledge.¹³ A $[(\text{Tb}/\text{Er})_4\text{TiO}(\text{OPr}^i)_{14}]$,^{13a} a $[\text{Er}_2\text{Ti}_4\text{O}_2(\text{OEt})_{18}] \cdot 2\text{EtOH}$,^{13b} two $[\text{Ce}_2\text{Ti}(\text{pin})_2(\text{OPr}^i)_8]$ and $[\text{Ce}_2\text{Ti}_2\text{O}_2(\text{pin})_4(\text{OPr}^i)_4] \cdot 2\text{Pr}^i\text{OH}$ (pin = pinacol),^{13c} a $[\text{Eu}_3\text{K}_3\text{TiO}_2(\text{OBu})_{12}]$,^{13d} and three $[\text{NdCITi}_2\text{O}(\text{OEt})_8(\text{HOEt})]$ and $[\text{LnCITi}_{28}\text{O}_{38}(\text{OEt})_{40}]$ (Ln = La and Ce)^{13e} were reported. Except the syntheses and crystal structural characterization, studies on their properties were not involved, and except two Ti28 clusters, the others are all small clusters ($\text{Ti} \leq 4$). The work described here is not only aimed at the synthesis and crystal structures of these fluorescent ligand grafted TOCs, but also aimed at exploring their fluorescence properties and energy transfer between the lanthanide hybrid TiO cluster and the organic substituent. It is found that the metal centered emission is completely quenched by the coordinated 9-AC ligand. More notable, the photo excited Eu(III) hybrid TiO cluster can

transfer the energy to singlet state of the 9-AC ligand and enhance the fluorescence emission of the 9-AC moiety.

Experimental section

General Remarks

All analytically pure reagents were commercially purchased and used without further purification. Elemental analyses of C, H and N were performed on a Varidel III elemental analyzer. Fourier transform infrared (FT-IR) spectra were recorded as KBr pellets on a Nicolet Magna 550 FT-IR spectrometer. Solid-state room-temperature optical diffuse reflectance spectra of the micro crystal samples were obtained with a Shimadzu UV-3150 spectrometer. Fluorescence was recorded on an Edinburgh FLS920 fluorescent photometer. Room-temperature X-ray diffraction data were collected using a D/MAX-3C diffractometer using a Cu tube source (Cu-K α , λ = 1.5406 Å). Thermoanalytical measurements were performed using a SDT 2960 microanalyzer and all the samples were heated under a nitrogen stream of 100 ml min⁻¹ with a heating rate of 5 °C min⁻¹.

Syntheses

[Nd₂Ti₁₀O₁₄(ClO₄)₂(OⁱPr)₁₄(9-AC)₂(CH₃CN)₂]·2H₂O (1). Analytically pure Ti(OⁱPr)₄ (0.1 mL, 0.26 mmol), Nd(ClO₄)₃·6H₂O (13 mg, 0.024 mmol) and 9-anthracenecarboxylic acid (6.0 mg, 0.027 mmol) were mixed in 1.0 mL anhydrous CH₃CN (CAUTION: All metal perchlorates must be regarded as potentially explosive. Only a small amount of compound should be prepared, and it should be handled with caution). The mixture was placed in a thick Pyrex tube (0.7 cm dia., 15 cm length) and quickly degassed by argon. The sealed tube was heated under autogenous pressure at 100 °C for 4 days, and then cooled to room temperature to yield greenish blue crystals (35 % yield based on Ti(OⁱPr)₄). The crystals were rinsed with isopropanol and preserved in a sealed glass tube. Anal. Calcd for C₇₆H₁₂₆Cl₂Nd₂N₂O₄₂Ti₁₀ (MW 2578.17): C, 35.41; H, 4.93; N, 1.09. Found: C, 35.26; H, 5.12; N, 1.23. Important IR data (KBr, cm⁻¹): 2970(m), 2928(w), 2865(w), 1625(w), 1544(m), 1430(w), 1391(m), 1314(m), 1120(s), 1009(m), 950(w), 733(m), 715(s), 656(s), 630(s), 474(s).

[Eu₂Ti₁₀O₁₄(ClO₄)₂(OⁱPr)₁₄(9-AC)₂(CH₃CN)₂]·2H₂O (2). Compound **2** was prepared by the same procedure as that for **1** except the neodymium salt was replaced by europium salt. pale greenish yellow crystals were obtained (30 % yield based on Ti(OⁱPr)₄). Anal. Calcd for C₇₆H₁₂₆Cl₂Eu₂N₂O₄₂Ti₁₀ (MW 2593.61): C, 35.20; H, 4.90; N, 1.08. Found: C, 34.91; H, 5.37; N, 0.86. Important IR data (KBr, cm⁻¹): 2970(m), 2924(w), 2865(w), 1625(w), 1544(s), 1442(w), 1395(m), 1318(m), 1127(s), 1012(s), 949(w), 733(m), 711(s), 656(s), 630(s), 478(m).

[Nd₂Ti₁₀O₁₄(ClO₄)₂(OⁱPr)₁₄(bza)₂(HOⁱPr)₂] (3). Analytically pure Ti(OⁱPr)₄ (0.1 mL, 0.26 mmol), Nd(ClO₄)₃·6H₂O (15 mg, 0.027 mmol) and benzoic acid (8.0 mg, 0.065 mmol) were mixed in 0.5 mL anhydrous isopropanol. The mixture was placed in a thick Pyrex tube and quickly degassed by argon. The sealed tube was heated under autogenous pressure at 80 °C for 7 days, and then cooled to room temperature to yield light blue crystals (25 % yield based on Ti(OⁱPr)₄). The crystals were rinsed with isopropanol and preserved in a sealed glass tube. Anal. Calcd for

C₆₂H₁₂₄Cl₂Nd₂O₄₂Ti₁₀ (MW 2379.83): C, 31.29; H, 5.25. Found: C, 30.89; H, 5.57. Important IR data (KBr, cm⁻¹): 2970(m), 2935(w), 2864(w), 1597(w), 1554(m), 1390(s), 1120(vs), 1090(w), 1011(m), 947(w), 720(m), 661(s), 632(s), 630(s), 472(m).

[Eu₂Ti₁₀O₁₄(ClO₄)₂(OⁱPr)₁₄(bza)₂(HOⁱPr)₂] (4). Compound **4** was prepared by the same procedure as that for **3** except the neodymium salt was replaced by europium salt. Colorless crystals were obtained (15 % yield based on Ti(OⁱPr)₄). Anal. Calcd for C₆₂H₁₂₄Cl₂Eu₂O₄₂Ti₁₀ (MW 2395.27): C, 31.09; H, 5.22. Found: C, 30.78; H, 5.13. Important IR data (KBr, cm⁻¹): 2970(m), 2932(w), 2864(w), 1595(w), 1558(m), 1390(s), 1120(vs), 1090(w), 1015(m), 945(w), 716(m), 660(s), 636(s), 602(w), 480(m).

X-ray Crystallographic Study

The measurements were carried out on a Rigaku Mercury charge-coupled device (CCD) diffractometer with graphite monochromated Mo K α (λ = 0.71075 Å) radiation. X-ray crystallographic data for all compounds were collected and processed by use of CrystalClear (Rigaku).¹⁴ The structures were solved by direct methods with SHELXS-97 program and the refinements were performed against F^2 with SHELXL-97.¹⁵ All non-hydrogen atoms are refined anisotropically. The hydrogen atoms are positioned with idealized geometry and refined with fixed isotropic displacement parameters. CCDC 1026005–1026007 contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Detailed crystal data and structural refinement parameters for **1–3** are listed in Table S1 in Supporting Information.

Results and Discussion

Preparation and Characterization

Crystals of clusters **1–4** were prepared directly by one step in situ solvothermal synthesis at 80–100 °C for 4–7 days in anhydrous acetonitrile or isopropanol. The perchlorate salts were suitable for the synthesis and crystallization, because the coordination of perchlorate can complement the high coordination number of the lanthanide ions. Acetonitrile was found to be a favourable solvent for 9-AC in preparing high quality crystals of compounds **1** and **2**. FTIR data of clusters **1–4** are listed in experimental section and given in Figure S1. The IR spectra of these compounds are very similar to each other. The very strong bands around 1110 cm⁻¹ are the characteristic of perchlorate anion. The vibrations at about 1625 and 1435 cm⁻¹ for **1** and **2** and 1595 cm⁻¹ for **3** and **4** indicate the coordinated carboxyl groups of the AC and bza. The bands at about 1545, 1328 (only for anthracene of **1** and **2**) and 710 cm⁻¹ are assigned to the characteristic bands of the C-H vibrations of the aromatic planes. Isopropoxy groups are detected by the ν_{C-H} (between 2865–2970 cm⁻¹) and ν_{Ti-O-C} (about 1010 cm⁻¹) vibrations. The bands around 630–670 cm⁻¹ are attributed to the Ti–O vibrations. The XRD patterns of the bulk microcrystal samples **1–4** are mainly in agreement with those simulated from the data of single-crystal analysis (Figure S2) and the slightly deviation in some weak peaks is aroused due to the lost of solvent molecules and somewhat hydrolysis in air. Thermogravimetric analyses of **1–4** are measured (Figure S3).

Compounds **1** and **2** show clearly a stage for the loss of water and acetonitrile molecules (about 4%), but no such stage appears for **3** and **4**. The **1** and **2** are more stable than **3** and **4** for the higher decomposition temperature (loss of $\text{O}(\text{Pr})_2$: 35%, vigorous decomposition temperature 240 °C for the former and 43% 200 °C for the latter, respectively). The decomposition of aromatic ligand is a multi-step process that ranges from 250 °C (**1** and **2**) or 230 °C (**3** and **4**) to above 840 °C.

Crystal Structures

The structures of **1–4** are similar, characterized by single crystal X-ray analysis. Compounds **1** and **2** are isostructure except the lanthanide atoms, therefore only **1** is discussed. Figure S4 gives the structures of **1** and **2** with the ellipsoid presentation, respectively. Crystal **1** is triclinic with $P\bar{1}$ space group and the unit cell includes one cluster and two cocrystallized water molecules. Figure 1 gives the ball-stick and partial polyhedron views of cluster **1**, $[\text{Nd}_2\text{Ti}_{10}\text{O}_{14}(\text{ClO}_4)_2(\text{O}^i\text{Pr})_{14}(9\text{-AC})_2(\text{CH}_3\text{CN})_2]$, in different directions. The cluster adopts a $\text{Ti}_{10}\text{Nd}_2$ core with pseudo- C_i symmetry and is similar to the Ti_{12} fundamental structure. A number of reported Ti_{12} TOCs, $[\text{Ti}_{12}\text{O}_{16}(\text{O}^i\text{Pr})_{16}]$, have the similar core structure to **1**.¹⁶ Six Ti atoms are octahedral coordinated and assembled to two Ti_3O_{13} subunits by sharing edges and a $\mu_3\text{-O}$ atom, which act as the top and bottom of the cluster. In Ti_{12} core, six pentacoordinated Ti atoms assemble to a cycle that is sandwiched by the top and bottom Ti_3O_{13} subunits. In **1**, two of the Ti atoms are replaced by the Nd(III) atoms in opposite position (Figure 1 bottom). The Nd atoms take a NdNO_7 eight-coordinated geometry with one chelating perchlorate anion (OO), one acetonitrile (N), an oxygen from carboxylate group of 9-AC and four oxygen atoms from the TiO skeleton. Another unique characteristic of **1** is the two coordinated groups of anthracene that is chelated through the $\mu_2\text{-}\eta^1\text{:}\eta^1$ carboxylate group, which adds new fluorescent property to the TOCs.

The structures of compounds **3** and **4** are similar to those of **1** and **2**, but the 9-AC ligand is replaced by a benzolate ligand and the acetonitrile is replaced by an isopropanol (Figure 2 and Figure S5). The crystal of **3**, $[\text{Nd}_2\text{Ti}_{10}\text{O}_{14}(\text{ClO}_4)_2(\text{O}^i\text{Pr})_{14}(\text{bza})_2(\text{HO}^i\text{Pr})_2]$, is monoclinic, $P2_1/n$, and the unit cell includes two clusters and no cocrystallized solvent molecule exists. Figure 2a gives the ball-stick and polyhedron views. The core of **3** is also a $\text{Ti}_{10}\text{Ln}_2$ cluster, and the Nd atom takes a NdO_8 eight-coordinated biccapped triangular prism geometry (Figure 2b) with one

chelating perchlorate anion (OO), an isopropanol oxygen (O), an oxygen from carboxylate group of 9-AC and four oxygen atoms from the TiO skeleton. The coordination mode of benzolate is the same as that of the 9-AC. Compound **4** is isostructural to **3**, and the data are not good enough to be published and only used as a reference material.

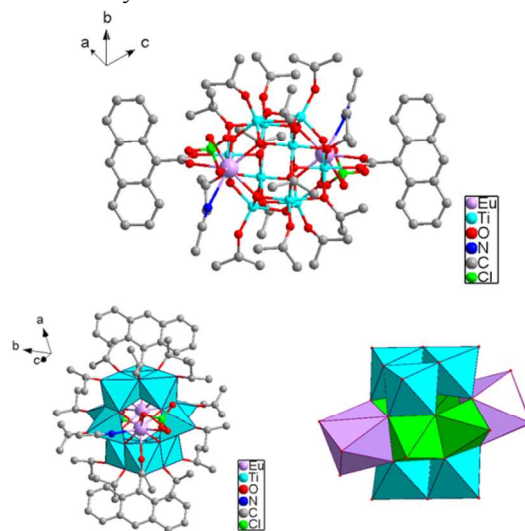


Figure 1. Ball-stick and polyhedron views of cluster **1** in different directions. Hydrogen atoms and the cocrystallized water molecules are omitted for clarity.

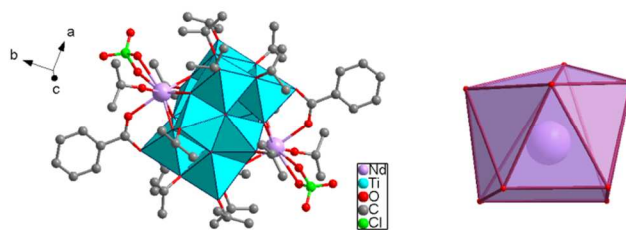


Figure 2. Ball-stick and polyhedron view of cluster **3** and the NdO_8 eight-coordinated geometry. Hydrogen atoms are omitted for clarity.

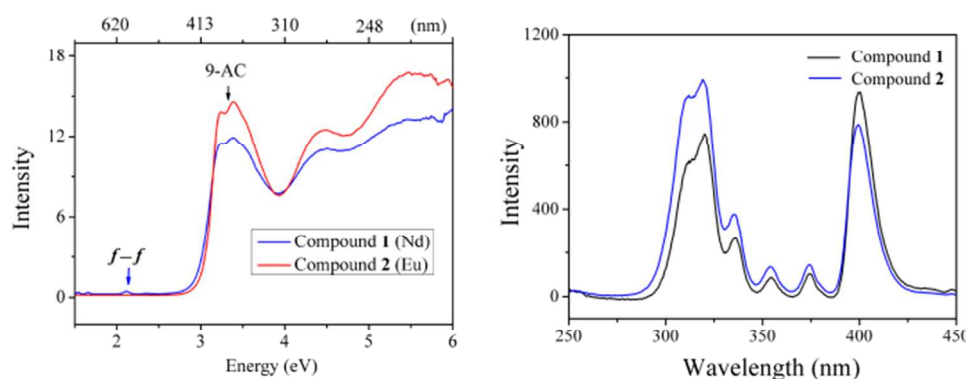


Figure 3. Left: Solid-state UV-vis absorption spectra of **1** (blue) and **2** (red); Right: Fluorescence exciting spectra of **1** (black) and **2** (blue).

Spectral properties

Solid-state UV-vis absorption spectra of the clusters **1** and **2**, calculated from the diffuse-reflection spectra, show a broad absorption band around 3.3 eV (320–430 nm), which is the representative band of the 9-AC (Figure 3 left). The on-set energy of the strong AC absorption bands of **1** is 2.9 eV (428 nm), which partially extends into visible light range and thus improves the absorption property of the clusters, because the on-set energy of pure TOCs is about 3.5 eV.⁸ Some very weak bands appear in low energy visible range, which are *f-f* electron transition of the Nd atoms. The spectrum of **2** is similar to that of **1**. Its *f-f* transition bands are covered by intense AC band.^{17a} Fluorescence exciting spectra of **1** and **2** are shown in Figure 3 right. They are similar to the absorption spectra with two intense bands at about 320 nm and 400 nm, but better band splits appear in comparison with those absorption spectra.

Photos of the fluorescence of **2** and **4** are shown in Figure 4a. The cluster **2** gives ligand centered blue emission and cluster **4** gives typical Eu(III) red emission, respectively. Fluorescence spectra of **1** and **2** are shown in Figure 4b. The

460 nm peak is assigned to the emission of 9-AC.¹² It is found that the emission intensity of **2** (Eu) is about 1.6 times higher than that of **1** (Nd) in the same solvent (CH₃OH:CH₂Cl₂, 1:5 by volume) and concentration (1.0×10^{-4} mol·L⁻¹). Using the mixed solvent is due to the consideration of two aspects: solubility and higher fluorescence intensity. The intensity of the fluorescence is solvent-related and changes largely in different ratios of CH₃OH:CH₂Cl₂. Figure 4c gives the results of **2** in 1:5 and 1:2 CH₃OH:CH₂Cl₂ mixed solvents. The intensity decreases significantly when the content of methanol increases due to the energy dissipation caused by the polar solvent.¹⁸ In the meantime a new peak appears at about 410 nm, which should be assigned to the new solvated state. The relationship between fluorescence intensities and compound concentrations is illustrated in Figure 4d. The intensity increases along with an increase of the concentration and then reaches a maximum at concentration about 1.0×10^{-4} mol·L⁻¹, and then decreases gradually when the concentration further increases. Thus in general, concentration 1.0×10^{-4} mol·L⁻¹ and CH₃OH:CH₂Cl₂, 1:5 by volume are used as the standard system for further studies.

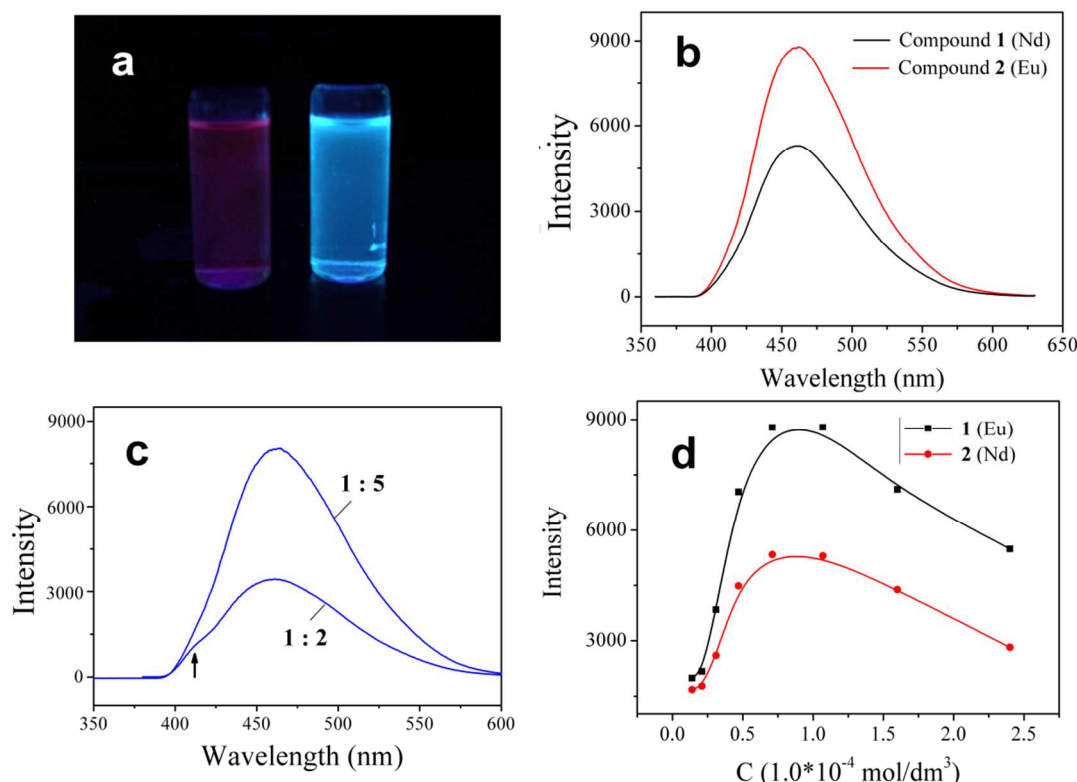


Figure 4. (a) Photos of the fluorescence emission of **2** (right) and **4** (left). (b) Fluorescence spectra of compounds **1** and **2** in $1.0 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$ concentration and mixed solvent ($\text{CH}_3\text{OH}:\text{CH}_2\text{Cl}_2$, 1:5 by volume), excited at 320 nm. (c) Emission spectra of **2** in 1:5 and 1:2 $\text{CH}_3\text{OH}/\text{CH}_2\text{Cl}_2$ mixed solvents. (d) Plots of fluorescence intensities vs compound concentrations.

Energy transfer in Eu-TiO-AC cluster

Energy transfer in Eu(III) complexes has been studied extensively owing to their important luminescent properties. The aim of this work is to study the energy transfer between the lanthanide hybrid TiO cluster and the fluorescent ligand AC moiety, which has not been researched yet based on our knowledge. Compounds **3** and **4** are prepared to serve as controls, because they have the same heterometallic lanthanide-titanium oxo cluster structures, except the 9-AC ligand being replaced by non fluorescence active benzoate. Neither metal centred nor ligand centred fluorescence is observed in visible range for compound **3** (Nd, near-infrared emission).^{17b,c} Figure 5a shows the fluorescence spectra of the europium compounds **2** and **4**. When the solution of compound **4** is subjected to 320 nm irradiation, a red emission from the excited Eu(III) ion is observed with the peaks at 556, 578, 591, 614, 652 nm (blue line), which are well characterized for Eu(III) complexes. When the Eu(III)

complexes having organic ligand with suitable excited triplet state are exposed to light, the ligand absorbs light and transfers the photoenergy to the central Eu(III) ion to give enhanced red luminescence.^{17d} In contrast to that found for **4**, the fluorescent spectrum of **2** only shows an intense ligand centred band with the highest peak at 460 nm and no any Eu(III) emission is found (black line). To be more cautious, the concentrations of **2** and **4** are controlled strictly identical and a 540 nm filter was applied to minimize the effect of the strong ligand centred fluorescence on the weak metal centred emission. The result (red line) indicates no Eu(III) centred emission detected. This phenomenon has been explained as the energy level matching problem. The triplet energy level (T_1) of the ligand is lower than the metal centered excited levels.¹⁹ Solid state fluorescent spectra are also measured to confirm the energy transfer phenomenon found in solution spectra (Figure S6), which give the same results and conclusion.

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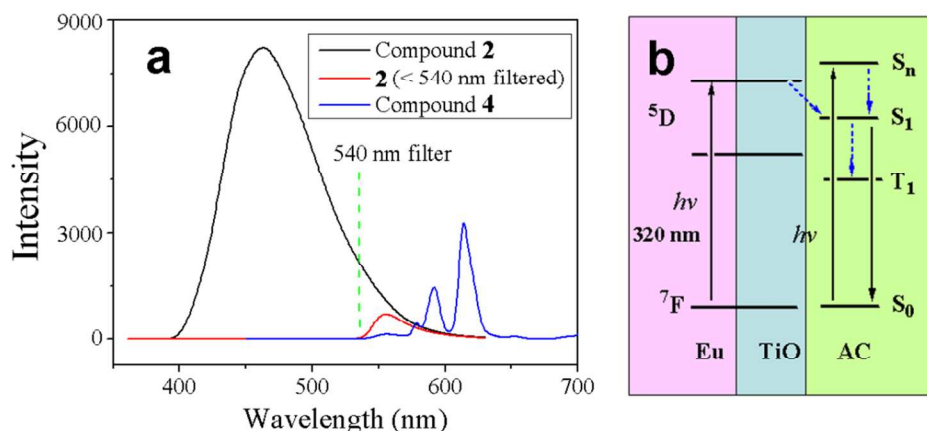


Figure 5. (a) Fluorescence spectra of **2** and **4** (1.0×10^{-4} mol·L $^{-1}$), illustrating the result of energy transfer within the cluster. (b) Proposed energy transfer processes in compound **2**.

We have found the different intensity of the two lanthanide TiO clusters, and those are in the order **2** > **1** (Figure 4b and 4d). The relative fluorescence quantum yields are determined by a standard method (eqn. 1) and the anthracene quantum yield (0.27) is used as a reference.²⁰ The results shows that the quantum yield of compounds **1** and **2** are 0.023 and 0.060, respectively, and **2** is 1.26 times of **1**. Solid state fluorescent spectra of **1** and **2** are given in Figure S7 that shows the same result.

$$\frac{\varphi_{em,s}}{\varphi_{em,r}} = \left(\frac{A_r}{A_s} \right) \left(\frac{F_s}{F_r} \right) \left(\frac{n_s^2}{n_r^2} \right) \quad \text{Eqn. 1}$$

A plot of proposed energy transfer process in compound **2** is illustrated in Figure 5b, that might be able to explain the Eu(III) fluorescence silent and ligand fluorescence enhancement of **2**, in comparison with that of **1** and **4**. A Eu-Ti-O cluster-assisted energy transfer process is suggested. When excited by 320 nm irradiation, the Eu(III) hybrid TiO cluster is excited, and then the electron energy transfers from conductive bands of the cluster to S₁ state of AC that enhance the fluorescence of the AC ligand. The long lifetime ⁵D excited state of Eu(III) plays an important role for the energy process. That is also the reason why the energy transfer process does not happen in compound **1**. The lifetime of Nd(III) is 0.2–0.5 ms significantly shorter than 1–11 ms of Eu(III).^{17e}

Conclusions

In summary, four heterometallic TOC compounds with lanthanide elements Nd(III) and Eu(III) are prepared by one step in situ solvothermal synthesis, and two of them are coordinated by 9-AC ligand. The cluster structures of these

compounds adopt a Ti₁₀Ln₂ core structure with pseudo-C_i symmetry, similar to the fundamental structure of Ti₁₂ cluster. The Ln atoms take an eight-coordinated geometry and directly coordinated by 9-AC or benzoate ligands. The fluorescence spectra of **1** and **2** are solvent dependent and concentration related. The optimized condition is 1.0×10^{-4} mol·L $^{-1}$ in 1:5 CH₃OH:CH₂Cl₂ (v/v). Energy transfer between the Eu(III) hybrid TiO cluster and the organic AC substituent is studied. Metal centered emission of Eu(III) is completely quenched by the coordinated 9-AC due to the lower triplet energy of the ligand. More notable, enhanced ligand centered fluorescence is found for the Eu(III) cluster in comparison with that of the Nd(III) analogue. A Eu-TiO cluster to ligand energy transfer mechanism is proposed. The work is the first study of the fluorescence properties of lanthanide hybrid TOC compounds and may be helpful in developing material chemistry of TOC and lanthanides.

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Notes and references

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† Electronic Supplementary Information (ESI) available: X-ray crystallographic data of **1–3** in CIF format. Crystal data and structural

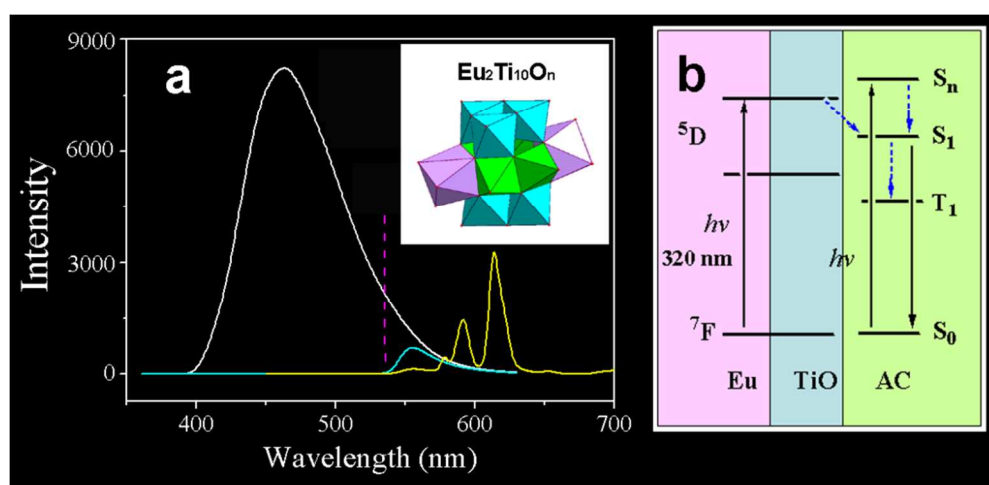
refinement parameters for 1–3. Figures of FTIR, XRD, Thermogravimetry analysis and degradation experiments. See DOI: 10.1039/b000000x/

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TOC

Fluorescent and Energy Transfer Properties of Heterometallic Lanthanide-titanium Oxo Clusters Coordinated with Anthracenecarboxylate Ligand

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Fluorescence quenching and enhancement due to energy transfer between heterometallic lanthanide-titanium oxo cluster and 9-anthracenecarboxylate ligand are studied.