

Syntheses, structures, photoluminescence and photocatalysis of 2D layered lanthanide-carboxylates with 2, 2'-dithiodibenzoic acid

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ARTICLE INFO

Keywords:

Lanthanide-carboxylates
In situ S–S reaction of 2-mercaptobenzoic acid
Structure
Luminescence.
Photocatalytic activity

ABSTRACT

Two series of lanthanide-carboxylates, $[\text{Ln}(2,2'\text{-dtba})(2,2'\text{-Hdtba})(\text{EtOH})]_n$ (**I**: Ln=Eu(**1a**), Dy(**1b**)) and $[\text{Ln}(2,2'\text{-dtba})(2,2'\text{-Hdtba})(4,4'\text{-bpy})_{0.5}]_n$ (**II**: Ln=Eu(**2a**), Dy(**2b**), Tb(**2c**)) 2,2'-H₂dtba=2,2'-dithiodibenzoic acid, 4,4'-bpy=4,4'-bipyridine) have been synthesized under hydrothermal conditions. Interestingly, the H₂dtba organic ligand was generated by *in situ* S–S reaction of 2-mercaptobenzoic acid. Compounds **I** and **II** possess different 2D layered structures based on similar 1D $[\text{Ln}(2,2'\text{-dtba})]^+$ chains. Photoluminescence studies reveal that compounds **I** and **II** exhibit strong lanthanide characteristic emission bands. Remarkably, Compounds **1b** and **2a** both exhibit good photocatalytic activity for degradation of Rhodamine-B (Rh-B) under the simulated sunlight irradiation.

1. Introduction

In recent years, the design and hydro(solvo)thermal *in situ* syntheses of metal-organic coordination polymers (MOCs) have attracted great interest in the field of coordination chemistry and organic chemistry owing to their intriguing architectures and topologies, as well as potential applications in catalysis, magnetism, luminescence and gas absorption [1–4]. Compared with the traditional synthesis method, hydrothermal and solvothermal method could create more chances for *in situ* syntheses of ligands due to the reaction conditions of high temperature and high pressure [5]. At the same time, the hydro(solvo)thermal method has demonstrated increasing success in providing alternative pathways to crystalline complexes with *in situ* synthesized ligands which are difficult to obtain by routine synthetic methods.

Obviously, *in situ* ligand formation depends on the condition of chemistry reaction, such as pH, catalysts, time and temperature [6,7]. Disulfide bond formation has been usually observed in mercapto aromatic systems under hydrothermal or solvothermal conditions [8]. Mercapto aromatic carboxylic acid is a kind of multifunctional ligand, which not only includes S coordinated atoms, but also includes carboxyl groups, such as 2-mercaptobenzoic acid, 2-mercaptocotinic acid or others. It is well known that those mercapto aromatic carboxylic acids can be changed to the disulfide aromatic carboxylic acids by *in situ* reactions under the proper conditions [8c]. The S–S bond extends the length of the ligand and gives more chances for building more excellent coordination polymers with new structures.

Lanthanide carboxylates have been attracted a lot of attention due to their potential applications in fluorescence materials, magnetic properties and photocatalysis fields [9–11]. It is worth mentioning that lanthanide ions possess high and variable coordination numbers and have high affinity for oxygen donor atoms. 2,2'-dithiodibenzoic acid (H₂dtba) ligand is a good ligand for the preparation of metal-organic complexes because of its flexibility and more O atoms as donor. Generally, H₂dtba ligand is used in the construction of metal-organic supramolecular complexes with both transition metal ions and alkali metal ions as nodes [12,13]. However, it is rare to introduce the H₂dtba ligand into the syntheses of lanthanide-carboxylates [14]. In this paper, we report two series of the lanthanide-carboxylates: $[\text{Ln}(2,2'\text{-dtba})(2,2'\text{-Hdtba})(\text{EtOH})]_n$ (**I**: Ln=Eu(**1a**), Dy(**1b**)) and $[\text{Ln}(2,2'\text{-dtba})(2,2'\text{-Hdtba})(4,4'\text{-bpy})_{0.5}]_n$ (**II**: Ln=Eu(**2a**), Dy(**2b**), Tb(**2c**)), which are 2D grid layered structures based on similar 1D $[\text{Ln}(2,2'\text{-dtba})]^+$ chains. The H₂dtba organic ligand was generated by *in situ* S–S reaction of 2-mercaptobenzoic acid under the hydrothermal method. Compounds **1b** and **2a** are both found to have good photocatalytic activity for degradation of Rh-B under the simulated sunlight irradiation.

2. Experimental section

2.1. Materials and physical measurements

Commercially available solvents and chemicals were used without further purification. IR spectra were recorded using KBr pellets on a Perkin-Elmer Spectrum 2000 FT-IR in the range of 400–4000 cm^{−1}.

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Table 1Crystal data and structural refinement parameters for **1a**, **1b**, **2a**, **2b** and **2c**.

	1a	1b	2a	2b	2c
Formula	C ₃₀ H ₂₃ O ₉ S ₄ Eu	C ₃₀ H ₂₃ O ₉ S ₄ Dy	C ₃₃ H ₂₁ NO ₈ S ₄ Eu	C ₃₃ H ₂₁ NO ₈ S ₄ Dy	C ₃₃ H ₂₁ NO ₈ S ₄ Tb
fw	807.68	818.22	839.75	850.25	846.67
Crystal System	triclinic	triclinic	Triclinic	Triclinic	Triclinic
Space Group	<i>P</i> –1	<i>P</i> –1	<i>P</i> –1	<i>P</i> –1	<i>P</i> –1
<i>a</i> (Å)	9.191(4)	9.086(4)	9.528(4)	9.4783(17)	9.471(10)
<i>b</i> (Å)	11.581(2)	11.517(4)	10.518(5)	10.4894(19)	10.484(16)
<i>c</i> (Å)	15.798(3)	15.755(7)	16.030(9)	16.024(3)	15.988(3)
α (deg)	90.241(5)	91.025(15)	82.874(19)	82.800(6)	82.752(7)
β (deg)	100.443(5)	99.644(19)	81.967(18)	81.839(7)	81.828(5)
γ (deg)	109.126(4)	109.028(17)	78.512(15)	78.812(7)	78.795(4)
<i>V</i> (Å ³)	1558.8(11)	1532.0(11)	1551.1(13)	1539.4(5)	1533.0(3)
<i>Z</i>	2	2	2	2	2
<i>D_c</i> (g/cm ³)	1.721	1.774	1.798	1.834	1.834
<i>F</i> (000)	804	810	834	840	838
GOOF on <i>F</i> ²	0.958	1.158	1.041	1.062	1.058
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e·Å ^{−3})	1.826–1.626	0.792–0.772	4.386–1.456	2.253–1.286	2.190–1.160
<i>R</i> ₁ ^a , <i>wR</i> ₂ ^b (<i>I</i> > 2σ(<i>I</i>))	0.0395, 0.0709	0.0190, 0.0450	0.0507, 0.1051	0.0398, 0.0841	0.0474, 0.1161
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0629, 0.0772	0.0209, 0.0524	0.0659, 0.1121	0.0426, 0.0859	0.0658, 0.01273

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$.^b $wR_2 = \{\sum [w(F_o^2 - F_c^2)]^2 / \sum [w(F_o^2)^2]\}^{1/2}$.

The powder X-ray diffraction (PXRD) patterns were recorded on a D/MXA-2500 diffractometer equipped with Cu K α radiation ($\lambda = 1.54056$ Å) at room temperature. The C, H and N elemental analyses were performed with an elemental Analysis Vario EL III elemental analyzer. Thermo-gravimetric analyses were recorded in Mettler Toledo TGA thermal analyzer at a heating rate of 10 °C/min. The steady fluorescence spectra with solid sample of compounds **I** and **II** were obtained on Edinburgh-Instrument F920 Spectra-Fluorimeter.

Photocatalytic activities of the prepared samples were evaluated by the degradation of RhB (10 mg L^{−1}) under simulated irradiation. A 300 W high-pressure xenon lamp (type:PLS-SXE) was used as the light source. Before the irradiation, compounds **1b** or **2a** as a photocatalyst were dispersed into the solution of RhB by magnetically stirring in the dark for about 2 h to reach an adsorption/desorption equilibrium between the photocatalyst and RhB. Then, the suspensions were exposed to simulated sunlight irradiation. 3 mL of the suspension was sampled every 30 min and centrifuged to separate the photocatalyst. The filtrate was analyzed by using a UV–vis spectrophotometer (Shimadzu UV1750), and the concentration of RhB was monitored at 552 nm. The range of wavelength scanning is 450–650 nm.

2.2. Synthesis of [Ln(2,2′-dtba)(2,2′-Hdtba)(EtOH)]_n (**I**: Ln=Eu(**1a**), Dy(**1b**))

A mixture of 2-mercaptobenzoic acid (0.8 mmol, 0.1233 g), Ln₂O₃ (0.1 mmol, Eu₂O₃ 0.0358 g, Dy₂O₃ 0.0373 g), 2 mL EtOH and 8 mL distilled water were placed in 23 mL Teon-lined stainless steel vessels. After being stirred for 1.5 h, the pH was adjusted to 3.5 via 1 M H₂SO₄ aqueous solution. The mixture was sealed in 25 mL Parr Teflon-lined stainless steel auto-clave and heated to 160 °C for 3 days for **1a** while 140 °C for 1 d for **1b**, then cooled to the room temperature naturally. The colorless crystals (**1a**) or yellow block crystals (**1b**) were obtained in 47% (**1a**, based on Eu₂O₃) and 53% yield (**1b**, based on Dy₂O₃). Anal. Calc for C₃₀H₂₃EuO₉S₄ (**1a**): C, 44.61; H, 2.87 wt%; Found: C, 44.51; H, 2.78 wt%. Anal. Calc for C₃₀H₂₃DyO₉S₄ (**1b**): C, 44.04; H, 2.83 wt%; Found: C, 44.14; H, 2.78 wt%. The IR data (KBr, cm^{−1}): 3400(w), 3058(w), 2925(m), 1670(w), 1612(m), 1579(s), 1402(s), 852(m), 768(s), 746 (s) (Fig. S1).

2.3. Synthesis of [Ln(2,2′-dtba)(2,2′-Hdtba)(4,4′-bipy)_{0.5}]_n (**II**, Ln=Eu(**2a**), Dy(**2b**), Tb(**2c**))

2-Mercaptobenzoic acid (0.8 mmol, 0.1233 g), 4,4′-bipyridi-

ne (0.8 mmol, 0.1239 g), Ln₂O₃ (0.2 mmol, Eu₂O₃ 0.0704 g; Dy₂O₃ 0.0746 g; Tb₄O₇, 0.0747 g) and distilled water (10 mL) were placed in a 23 mL Teflon-lined stainless. The mixture was stirred for 60 min and adjusted the value of pH to 3.5–4.0 via 1 M H₂SO₄ aqueous solution. After being stirred for 30 min, the mixture was sealed in 25 mL Teflon-lined stainless steel auto-clave and heated to 160 °C for 7 days, and then cooled to room temperature naturally. Yellow columnar crystals were obtained. Yield: 73% (**2a**), 77% (**2b**), 60% (**2c**) (based on Ln₂O₃). Anal. calcd. for C₃₃H₂₁EuNO₈S₄ (**2a**): C, 47.20; H, 2.52; N, 1.67 wt%. Found: C, 47.48; H, 2.41; N, 1.72 wt%. Anal. calcd. for C₃₃H₂₁DyNO₈S₄ (**2b**): C, 46.61; H, 2.49; N, 1.65 wt%. Found: C, 46.76; H, 2.51; N, 1.67 wt%. Anal. calcd. for C₃₃H₂₁TbNO₈S₄ (**2c**): C, 46.81; H, 2.50; N, 1.65. Found: C, 46.86; H, 2.51; N, 1.58 wt%. The IR data (cm^{−1}): 3086(w), 1676(m), 1593(s), 1539(w), 1462(s), 1400(s), 852(m), 738(s) (Fig. S2).

2.4. X-ray Crystallography

Suitable size and clean single crystals were selected and mounted on a glass fiber. All the data for compounds **I** and **II** were collected on a Rigaku Saturn724 CCD diffractometer with graphite-monochromated MoK α ($\lambda = 0.71073$ Å) radiation in the ω scanning mode 293 (2) K. The structures were solved by direct methods and refined by full-matrix least squares on *F*² using the SHELXTL-97 program package [15,16]. Hydrogen atoms bound to N and C were generated geometrically (C–H = 0.93 Å, N–H = 0.86 Å) and refined with fixed isotropic displacement parameters. Crystallographic data for the reported structures have been deposited with the Cambridge Crystallographic Data Center. Selected crystal parameters, data, and structural refinements are summarized in Table 1.

3. Results and discussion

3.1. In situ reaction analysis

In compounds of **I** and **II**, it is interesting to note that *in situ* S–S function reaction occurred and 2-mercaptobenzoic acid was transformed into 2,2′-H₂dtba under hydrothermal conditions in the presence of Ln(III) ions when the pH value of the reactant was 3.5–4.0 (Scheme 1).

Scheme 1. *In situ* S-S function reaction of 2-mercaptobenzoic acid.

3.2. Structural description of $[Ln(2,2'\text{-dtba})(2,2'\text{-Hdtba})(\text{EtOH})]_n$ (I : $Ln = \text{Eu}(\mathbf{1a})$, $\text{Dy}(\mathbf{1b})$)

As shown in Fig. S3, the PXRD patterns of compounds of **I** agree with the calculated from the structures, indicating that compounds of **I** are pure phase. In addition, compounds **1a** and **1b** are isostructural, respectively. The unit cell similarity index ($\Pi = 0.0058$) between **1a** and **1b** are close to unity, indicating high degree of isostructurality [17]. Herein, complex **1a** is taken as an example to depict the structure in detail.

Compound **1a** crystallizes in the triclinic space group $P\bar{1}$. Single-crystal X-ray analysis reveals that compound **1a** is described as a novel 2-D bamboo-raft-like layered network. The asymmetric unit of **1a** contains one independent $\text{Eu}(\text{III})$, one $2,2'\text{-dtba}^{2-}$ ligand, one $2,2'\text{-Hdtba}^-$ ligand and one EtOH molecule (Fig. 1). The coordination geometry for eight-coordinated $\text{Eu}(\text{III})$ is close to dodecahedron: five oxygen atoms from four $2,2'\text{-dtba}^{2-}$ ligands, two oxygen atoms from two $2,2'\text{-Hdtba}^-$ ligands and one oxygen atom from EtOH . The $\text{Eu}-\text{O}$ bond lengths range from 2.319(4) to 2.724(4) Å. The $2,2'\text{-H}_2\text{dtba}$ ligand exhibit two kinds of distinctly different bridging modes: one $2,2'\text{-dtba}^{2-}$ ligand behaves as $\mu_5-\eta^2:\eta^1:\eta^1:\eta^1$ mode linking four $\text{Eu}(\text{III})$ centers (Scheme 2a), the other $2,2'\text{-Hdtba}^{2-}$ ligand act as $\mu_2-\eta^1:\eta^1$ mode connecting two $\text{Eu}(\text{III})$ centers (Scheme 2b).

Two centrosymmetric $\text{Eu}(\text{III})$ centers are bridged by two $\mu_2-\text{O}$ atoms of $2,2'\text{-dtba}^{2-}$ ligand to form a $[\text{Eu}_2\text{O}_2]$ rhombic unit with the $\text{Eu}\cdots\text{Eu}$ distance of 3.868 Å. These units are double-linked up *via* two carboxyls of 2, $2'\text{-Hdtba}^-$ ligand to give rise to a linear ribbon running along a axis (Fig. 2a). Two linear ribbons are weaved by 2, $2'\text{-dtba}^{2-}$ ligands to generate a tube with double-arrow-like cross section (Fig. 2b). The ethanol molecules are hang by coordinating to $\text{Eu}(\text{III})$ centers in the tube. These tubes are connected with $[\text{Eu}_2\text{O}_2]$ units functioning as hinges. As a result, a 2D bamboo-raft-like layered structure forms in the ab plane (Fig. 2c). The $2,2'\text{-Hdtba}^-$ ligands are above or below the tubular layers. The strong $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds ($d(\text{O}\cdots\text{O}) = 2.654(4)$ Å) between the 2, $2'\text{-Hdtba}^-$ ligands from adjacent layers link the layers into a 3D supra-molecular network (Fig. 3).

Fig. 1. The coordination environments of Eu^{3+} in **1a**, with thermal ellipsoids at 50% probability. Atoms having “A”, “B”, “C” or “D” in their labels are symmetry-generated. A: 1-x, -y, 1-z; B: 2-x, -y, 1-z; C: x, -1+y; D: 2-x, 1-y, 1-z. Hydrogen atoms are omitted for clarity. Color code: Eu, purple; S, yellow; O, red; C, black; H, green. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Scheme 2. The coordination modes of $2,2'\text{-H}_2\text{dtba}$ ligands in compounds of **I** (a and b) and **II** (a and c).

Fig. 2. (a) The 1D linear ribbon running along a axis in **1a**; (b) The 2D bamboo-raft-like layered structure of **2a** viewed along a axis showing the double-arrow-like cross section; (c) View of the 2D bamboo-raft-like layer in **2a** along c axis. Color code: Eu, purple; S, yellow; O, red; C, black. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 3. The 3D supra-molecular network formed by $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds between the layers in **1a** viewed along a axis.

Fig. 4. The coordination environments of Eu^{3+} in **2a**, with thermal ellipsoids at 50% probability. Atoms having “A” and “B” in their labels are symmetry-generated. A:1-x, -y, 1-z; B:1-x, 1-y, 1-z. Some hydrogen atoms are omitted for clarity. Color code:Eu, purple; O, red; N, blue; C, black. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 5. (a) View of 1D double-chain consisting of two twined sinusoidal-like chains in **2a**; (b) 2D (4,4) layer structure in **2a**. Color code:Eu, purple; O, red; N, blue; C, black. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3.3. Structural description of $[\text{Ln}(2,2'\text{-dtba})(2,2'\text{-Hdtba})(4,4'\text{-bipy})_{0.5}]_n$ ($\text{Ln}=\text{Eu}(\text{2a}), \text{Tb}(\text{2b}), \text{Dy}(\text{2c})$)

Compounds **2a**, **2b** and **2c** are isomorphous (Fig. S4), The unit cell similarity index (II) among **2a**, **2b** and **2c** are close to unity (Table S1), indicating high degree of isostructurality. so only the structure of **2a** is described here.

Compound **2a** crystallizes in the triclinic system, $P\bar{1}$ space group. The structure of **2a** is a 3D lanthanide-organic supra-molecule structure based on a 2D (4, 4) layer. The asymmetric unit of **2a** contains one independent $\text{Eu}(\text{III})$, one $2,2'\text{-dtba}^{2-}$ ligand, one $2,2'\text{-Hdtba}^-$ ligand and 0.5 $4,4'\text{-bpy}$ molecule (Fig. 6). The $\text{Eu}(\text{III})$ center is eight-coordinated by one N atom from $4,4'\text{-bpy}$, five O atoms from four $2,2'\text{-dtba}^{2-}$ ligands and two O atoms from one $2,2'\text{-Hdtba}^-$ ligand which forming a distorted dodecahedron (Fig. 4). The bond lengths of $\text{Eu}-\text{O}$ bond distances are in the ranges of 2.336(4)–2.607(4) Å and the $\text{Eu}-\text{N}$ bond distance is 2.591(4) Å. The $2,2'\text{-H}_2\text{dtba}$ ligand adopt two types of distinctly different bridging modes: one $\mu_5\text{-}\eta^2\text{:}\eta^1\text{:}\eta^1\text{:}\eta^1\text{:}\eta^1$ mode of $2,2'\text{-dtba}^{2-}$ are also observed in **1a** (Scheme 2a), the other $2,2'\text{-Hdtba}^{2-}$ ligand act as $\mu_2\text{-}\eta^2$ mode connecting one $\text{Eu}(\text{III})$ center (Scheme 2c).

A pair of centrosymmetric $\text{Eu}(\text{III})$ centers are bridged by two $\mu_2\text{-O}$ atoms of $2,2'\text{-dtba}^{2-}$ ligand to form a $[\text{Eu}_2\text{O}_2]$ rhombic units with $\text{Eu}\cdots\text{Eu}$ distance of 3.860 Å which are found in **1a**. The $[\text{Eu}_2\text{O}_2]$ cluster

Fig. 6. The 3D supra-molecular network formed by $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds between the layers in **2a** viewed along b axis. Color code:Eu, purple; O, red; N, blue; C, black. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 7. Emission spectra of **1a** ($\lambda_{\text{ex}}=395\text{ nm}$) and **2a** ($\lambda_{\text{ex}}=394\text{ nm}$).

units are linked by $2,2'\text{-dtba}^{2-}$ ligands to form a 1D double-chain structure consisting of two twined sinusoidal-like chains (Fig. 5a). The double-chains are bridged by $4,4'\text{-bpy}$, generating a 2D layer structure in the ab plane (Fig. 5b). From the topological point of view, the 2D layer of **2a** is a (4,4) network. Each $[\text{Eu}_2\text{O}_2]$ cluster unit acts as a four-

Fig. 8. Emission spectra of **1b** (λ_{ex} =298 nm) (a), **2b** (λ_{ex} =300 nm) (b) and **2c** (λ_{ex} =309 nm).

connected node and the 2,2'-dtba²⁻ and 4,4'-bpy ligands are bridging ligands. The 2, 2'-Hdtba⁻ ligands are hanged above or below the layers. All the layers adopt an AAAA arrangement along the *c* axis in **2a**. There are strong O–H...O hydrogen bonds (*d* (O...O) = 2.713 (7) Å) between the 2, 2'-Hdtba⁻ ligands from adjacent layers, linking the layers into a 3D supra-molecular network (Fig. 6).

3.4. Influence of second ligands on the structures

Complexes **I** and **II** were obtained from H₂dtba ligand and different second ligands. Since the H₂dtba ligand has shown stronger coordination ability to Ln ions than the EtOH, the structures of **I** are mainly determined by the nature of the H₂dtba ligand. The Ln(III) ions in **I** are linked by H₂dtba ligands, forming a bamboo-raft-like layered network. The similar layered structure in compound [Yb(2,2'-dtba)(2,2'-

Fig. 9. Absorption spectra of the RhB aqueous solution during the photodegradation under 300 W high pressure Xe lamp irradiation with compound **1b** (a) or **2a** (b).

Hdtba)]_n are reported by us [14]. The structure difference lies in the coordination modes of H₂dtba ligand in compounds **I** and [Yb(dtba)(Hdtba)]_n. The 2,2'-dtba²⁻ ligand adopts $\mu_4-\eta^1:\eta^1:\eta^1:\eta^1$ coordination mode in [Yb(dtba)(Hdtba)]_n and behaves as $\mu_5-\eta^2:\eta^1:\eta^1:\eta^1$ mode in Compound **I**. By introducing 4,4'-bpy bridge ligand, the 4, 4'-bpy ligands link the double-chains into a 2D (4,4) layer structure.

3.5. IR spectra

As shown in Fig. S1 and S2,[†] the similarities between the IR spectra of **1a** and **1b**, **2a** and **2b**, **2c** suggests that **1a** and **1b**, **2a** and **2b**, **2c** are isostructural, respectively. For **I** (**1a** and **1b**), the IR spectra exhibit wide and medium absorption peaks at 3385 and 3058 cm⁻¹ are associated with the $\nu(\text{O-H})$ and $\nu(\text{Ar-H})$, respectively. The sharp peaks at 2962 and 2870 cm⁻¹ correspond to the stretching bands of C-H of EtOH. For **II** (**2a**, **2b** and **2c**), the broad bands at 3060 cm⁻¹ correspond to the stretching bands of Ar-H. There is a peak observed at 1670 cm⁻¹ for **I** and 1676 cm⁻¹ for **II**, indicating that the carboxyl groups of 2, 2'-H₂dtba ligand are not completely deprotonated, which are good agreement with the crystallographic data. The strong bands at 1532, 1402 cm⁻¹ for **I** and 1539, 1405 cm⁻¹ for **II** are associated with $\nu_{\text{asym}}(\text{C=O})$ and $\nu_{\text{sym}}(\text{C=O})$ respectively. The disappearance of S-H stretching vibration over 2500 cm⁻¹ and the existence of S-S stretching vibration at 865 cm⁻¹ in **I** and 852 cm⁻¹ in **II** indicate that 2-mercaptobenzoic acid has been changed to 2,2'-dithiodibenzoic acid (H₂dtba) ligand *via* the *in situ* S–S function reaction in **I** and **II** complexes. These facts are consistent with the X-ray diffraction results.

emission peaks appear at 483 nm and 577 nm, are assigned to the characteristic emission of ${}^4F_{9/2} \rightarrow {}^6H_{15/2}$ and ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$ transitions of Dy^{3+} respectively. (Fig. 8a and b). Complex **2c** emits green light when excited 309 nm and exhibits only characteristic narrow bands of Tb^{3+} at 488, 544, 583, 619 nm that originated from the ${}^5D_4 \rightarrow {}^7F_6, {}^7F_5, {}^7F_4, {}^7F_3$ transitions (Fig. 8c).

3.8. Photocatalytic properties

To investigate the photocatalytic activity of complexes **1b** and **2a** as a catalyst, the photodecomposition of Rhodamine-B (RhB) in aqueous solution is evaluated under simulated sunlight irradiation via Xenon lamp. The target substrate RhB contains four N-ethyl groups at either side of the xanthene ring, which is stable in aqueous solutions upon visible-light irradiation. The characteristic absorption band of RhB at 554 nm was used to monitor the degradation process as a function of irradiation time. Figs. 9 and 10 and Fig. S8–S9 show the temporal evolution of the absorption spectra of the RhB solution degraded by compound **1b** or **2a** under the simulated sunlight irradiation. The decomposition rate of RhB (K) can be expressed as $K = (I_0 - I_t)/I_0$, where I_0 presents the UV–vis absorption intensity of RhB at the initial time ($t=0$) and the I_t is the intensity at a given time (t).

When the RhB solution was kept under simulated sunlight irradiation from a 300 W high pressure Xe lamp either in the presence of or in the absence of **1b** or **2a**, the photodegradation reactions of RhB happened and was detected. It is found that the absorbance of UV–vis spectra decreases as the irradiation time increases, which indicates that RhB gradually photodegrades and the amount of RhB in solution is less and less. The results show that the maximum absorbance at 554 nm of the blank RhB aqueous solution decreases from 2.312 to 1.807 after the 150 min simulated sunlight irradiation while those in the presence of **1b** or **2a** decrease from 2.357 to 0.596, 2.157 to 0.732, respectively, after the same time simulated sunlight irradiation (Fig. 9, S8 and S9). The decline of the absorption peak of RhB in the presence of **1b** or **2a** is faster than that of in the absence of **1b** or **2a**, and the hypsochromic shifts of the absorption band are considerably insignificant in the presence of **1b** or **2a**. On the basis of the experimental results, the decomposition rate of RhB reach 22.3% without catalyst, 74.7% with compound **1b** and 74.7% with compound **2a** (150 min the simulated sunlight irradiation) (Fig. 9), respectively. These results demonstrate that the photocatalyst **1b** or **2a** can effectively enhance the photodegradation of RhB. As a result, it can predict that complex **1b** and **2a** can be used as a potential photocatalytic materials of RhB degradation.

Early work demonstrated many complexes especially transition metal [18] such as Cu(II)/(Co(II))/Zn(II)/Cd(II)-based MOFs showed excellent photocatalytic activity for degradation on different organic pollutants under different light source and the reaction mechanism for enhancing the photodegradation of RhB could be discussed based on semiconductor theory [19] and HOMO–LUMO theory [20]. However, the main reasons why **1b** and **2a** can inhibit the photodegradation of RhB may be as follows: (i) compounds **1b** and **2a** can work as absorbers of the Hg lamp irradiation; (ii) the hydrogen bonding interactions between donors and acceptors in RhB substrates ($N(C_2H_5)_2$, COOH) and **1b** and **2a** (free COOH of 2,2'-H₂dtba ligands) and the weak π – π stacking interactions between phenyl cycles on RhB substrates and aromatic rings of 2,2'-dithiodibenzoic acid in **1b** and **2a** enhance the chemical stability of RhB substrates in the solutions, which leads to the slow photodegradation of RhB substrates. The profound study on the mechanism of photocatalysis of RhB in the presence of **1b** and **2a** as the photocatalyst is in progress.

4. Conclusions

In summary, we have successfully constructed two series of 2D lanthanide–carboxylates based on the 2,2'-dithiodibenzoic acid.

Fig. 10. Conversion rate of RhB (K) with the reaction time (t) with compound **1b** (a) or **2a** (b) and without catalyst.

3.6. Thermogravimetric analyses

Thermal analysis was carried out from 30 °C to 1200 °C for compounds **I** and compound **II** under N_2 atmosphere (Fig. S5). Compound **1a** and **1b** is stable until the temperature reaches 240 °C. The first weight loss of 5.71% (calcd, 5.70%) for **1a** and 5.67% (calcd, 5.62%) for **1b** in the temperature range of 240–270 °C can be assigned to the release of EtOH molecules. The second weight loss in the range of 350–550 °C corresponds to the decomposition of the Hdtba²⁻ and dtba²⁻ ligands. The remaining weight may be attributed to the formation of Eu_2O_3 for **1a** and $Dy_2(CO_3)_3$ for **1b** (Fig. S7). Compounds **II** are stable up to 320 °C. The TG curves of Compounds **II** exhibit one step weight loss, corresponding to decomposition of the Hdtba²⁻ and dtba²⁻ ligands when the temperature is higher than 200 °C. The remaining weight is attributed to the formation of Eu_2O_3 for **2a** (obsd, 20.65%, calcd, 21.06%), Dy_2O_3 for **2b** (obsd, 22.42%, calcd, 22.10%) and Tb_4O_7 for **3b** (obsd, 23.44%, calcd, 22.07%) (Fig. S8).

3.7. Luminescent properties

The room-temperature luminescent properties of the compounds **I** and **II** in the solid state were measured. Compounds **1a** and **2a** show characteristic emissions of Eu^{3+} ion in which bands at 580, 594, 618, 653, 700 nm correspond to ${}^5D_0 \rightarrow {}^7F_0$, ${}^5D_0 \rightarrow {}^7F_1$, ${}^5D_0 \rightarrow {}^7F_2$, ${}^5D_0 \rightarrow {}^7F_3$, ${}^5D_0 \rightarrow {}^7F_4$ transitions, respectively (Fig. 7a and b). The intensities of the ${}^5D_0 \rightarrow {}^7F_2$ transitions (electric dipole) are stronger than that of the ${}^5D_0 \rightarrow {}^7F_1$ transitions (magnetic dipole) of compounds **1a** and **2a**, which indicate the low symmetrical coordination environment of Eu^{3+} ions and which are agreed with the crystallographic analyses. In the emission spectra of compounds **1b** and **2b**, excited at 300 nm, the

Interestingly, 2,2'-dithiodibenzoic acid comes from the *in situ* S–S reaction of 2-mercaptobenzoic acid under the hydrothermal conditions. Compounds **I** and **II** exhibit strong lanthanide characteristic emission bands, which could be anticipated as good candidates for luminescent materials. The photocatalytic activity studies indicate that complexes **1a** and **2b** show the good photocatalytic activity in RhB degradation.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grants 21473030 and 21003020).

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.jssc.2016.11.002>.

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