二乙酰对甲苯酒石酸构筑的三个镧系配合物的 合成、结构、荧光及光催化性质

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摘要:合成并通过红外光谱、元素分析、单晶及粉末衍射表征了3个一维配合物[Ln(HDTTA)₃(CH₃OH)₃]_n (Ln=Ce (1), Pr (2), Sm (3))的结构(D-H₂DTTA为(+)-二(对甲苯酰)-D-酒石酸)。单晶衍射结果表明,3个配合物同构,结晶于三方晶系手性空间群R3,在 c方向呈现一维链状结构。荧光光谱表明由于D-H₂DTTA配体的激发态能级与Pr³⁺和Sm³⁺离子激发态能级接近,所以可以敏化 2种离子的f电子在609 nm处的发光。此外,配合物1在紫外光照射下表现出良好的光催化降解染料亚甲基蓝的性质,在无外 加试剂条件下160 min内降解率可达76%。

关键词:镧配合物;二(对甲苯)酰酒石酸;晶体结构;荧光;光催化
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Synthesis, Structures, Luminescence and Photocatalytic Properties of Three Lanthanide Complexes Based on Ditoluoyl-Tartrate

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Abstract: Three one-dimensional (1D) lanthanide complexes $[Ln(HDTTA)_3(CH_3OH)_3]_n$ (Ln=Ce (1), Pr (2), Sm (3)) (D -H₂DTTA=(+)-di(*p*-toluoyl)-*D*-tartaric acid) were synthesized at room temperature and normal pressure. They were fully structurally characterized by IR, elemental analysis, single-crystal and powder X-ray diffraction. The structure analysis shows that complexes 1~3 are isomorphic. They belong to chiral *R*3 space group of trigonal system and display infinite 1D chains structure along *c* axis. Photoluminescence measurements indicated that D-H₂DTTA ligand can partly sensitize the *f*-*f* transition luminescence of Pr³⁺ and Sm³⁺ cations but Ce³⁺ at 609 nm, which is attributed to the mismatching between the excited state energy levels of metal cations and ligands. Additionally, Complex 1 exhibited photocatalytic property for the degradation of methylene blue under UV light irradiation in the solution. The photocatalytic performance was up to 76% within 160 min without any other reagents. CCDC: 2017862, 1; 2017863, 2; 2017864, 3.

Keywords: Ln³⁺ complexes; di(*p*-toluoyl) tartaric acid; crystal structure; luminescence; photocatalysis

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0 Introduction

During the past three decades, the design and synthesis of lanthanide complexes have attracted much attention due to their charming variety of topologies and architectures as well as potential applications in the areas of luminescence, electrochemistry, catalysis, magnetism and biomedical technologies^[1-4]. Among them, chiral lanthanide complexes are particularly attractive, especially the ones combined with natural chiral carboxylic acids, such as lactic acid, malic acid, camphoric acid and tartaric acid^[5-7], because the addition of natural chirality to lanthanide luminescence allows circularly polarized luminescence which can be used in bioscience fields such as biomarkers and biosensors^[8-11].

Organic dyes are one of the most common contaminants which have seriously affected on people's production and life^[12-13]. It is urgently to find effective solutions to remove dyes from the water. Numerous physicochemical approaches such as advanced oxidation, photo -Fenton oxidations and physical adsorption were reported in this field. Among them, photocatalytic degradation has been accepted as one effective technology for water treatment because of its low cost and benign nature^[14-16]. As a continuation of our research in materials and environmental chemistry, in this work, we focus on the ligand (+)-di(*p*-toluoyl)-*D*-tartaric acid (D-H₂DTTA), one of the derivates of tartaric acid. It is a flexible dicarboxylic acid with two equal chiral carbon atoms, and its abundant carboxyl groups provide the variable coordination modes, helping to construct versatile metallo-organic complexes^[17-18]. Several lanthanide complexes based L-H₂DTTA have been reported^[19-21], but the studies employing D-H₂DTTA are practically rare. Recently, our group firstly reported heavy lanthanide complexes (Ln=Eu, Tb~Ho) based on D-H₂DTTA, and studied their chiral, optical and magnetic properties^[22-23]. However, the structural features and physicochemical properties of D-H₂DTTA are still unexplored.

Herein, by choosing light lanthanide cations as metal centers, three lanthanide complexes $[Ln(HDTTA)_3(CH_3OH)_3]_n$ (Ln=Ce (1), Pr (2), Sm (3)) (Scheme 1) were synthesized successfully from D-H₂DTTA and structurally characterized by IR, elemental analysis (EA), single-crystal and powder X-ray diffraction (PXRD). The thermal stabilities and photoluminescence properties have also been systematically investigated. In addition, we found they have the potential applications in photocatalytic degradation of dyes in the solution.



Scheme 1 Synthesis routes of complexes 1~3

1 Experimental

1.1 Materials and measurements

The D - H_2DTTA ligand was bought from TCI (Shanghai) Development Co., Ltd. and used directly without further purification. All solvents and reagents were of standard commercial grade and used directly without further purification. The sample for EA was dried under vacuum and performed with the CHN-O-

Rapid instrument. IR spectra were obtained on KBr pellet with the BRUKER TENSOR27 spectrometer. PXRD patterns were collected on the Bruker D8 Advance X-ray diffractometer employing Cu $K\alpha$ radiation (λ =0.154 18 nm) with a 2 θ range of 5°~50°. The operating voltage and current are 40 kV and 25 mA, respectively. Thermogravimetric analyses (TGA) were performed on the Dupont thermal analyzer under a nitrogen atmosphere with the heating rate of 10 °C ·

min⁻¹. Luminescence analyses were performed on a Fluoromax-4 spectrofluorometer with a xenon arc lamp as the light source. The UV-visible spectra were obtained

with a JASCO V-570 spectrophotometer.**1.2 Preparations of complexes 1~3**

D-H₂DTTA (0.1 mmol, 0.038 6 g) was dissolved in 2.5 mL methanol solution and added to a 10 mL flask. Ce(NO₃)₃ · 6H₂O (0.066 mmol, 0.028 2 g) or Pr(NO₃)₃ · 6H₂O (0.066 mmol, 0.028 7 g) was dissolved in 2.5 mL aqueous solution, and gradually added to the solution. Then 200 μ L KOH (0.2 mol·L⁻¹) was added to the mixture, and the pH value was about 3. After stirring seven hours, the filtrate was maintained unperturbed for two days. Colorless prismatic crystals of **1** or light green prismatic crystals **2** were obtained in the yield of 27% or 24%, respectively (based on D-H₂DTTA).

Anal. Calcd. for $C_{63}H_{63}O_{27}Ce(1)(\%)$: C 54.35, H 4.56; Found(%): C 54.30, H 4.32. IR (KBr, cm⁻¹): 3 495 m, 2 949w, 1 735s, 1 708s, 1 670s, 1 611s, 1 509 w, 1 411 m, 1 341w, 1 301w, 1 266s, 1 180s, 1 109s, 1 020m, 906w, 841w, 752s, 689w, 654w, 609w, 564w, 477m.

Anal. Calcd. for $C_{63}H_{63}O_{27}Pr$ (2) (%): C 54.32, H 4.56; Found(%): C 54.38, H 4.51. IR (KBr, cm⁻¹): 3 487 m, 2 951w, 1 735s, 1 708s, 1 671s, 1 611s, 1 510w, 1 411 m, 1 339w, 1 301w, 1 268s, 1 180s, 1 109s, 1 020m, 906w, 841w, 752s, 689w, 655w, 608w, 594w, 477m.

D-H₂DTTA (0.1 mmol, 0.038 6 g) was dissolved in 2.5 mL methanol solution and added to a 10 mL flask. Sm(NO₃)₃·6H₂O (0.066 mmol, 0.022 2 g) was dissolved in 2.5 mL aqueous solution and gradually added to the solution. Then 150 μ L KOH (0.2 mol·L⁻¹) was added to the mixture, and the pH value was about 3. After stirring seven hours, the filtrate was maintained unperturbed for two days. Colorless prismatic crystals 3 were obtained in the yield of 20% (based on D-H₂DTTA).

Anal. Calcd. for $C_{63}H_{63}O_{27}Sm$ (**3**)(%): C 53.95, H 4.53; Found(%): C 54.02; H 4.38. IR (KBr, cm⁻¹): 3 485 m, 2 950w, 1 735s, 1 708s, 1 671s, 1 611s, 1 510w, 1 412 m, 1 339w, 1 301w, 1 268s, 1 180s, 1 109s, 1 020m, 906w, 841w, 752s, 689w, 656w, 609w, 565w, 477m.

1.3 X-ray crystallography

Single-crystal X-ray diffraction data for 1~3 were collected on a Bruker SMART APEX II diffractometer with a CCD area detector and Mo $K\alpha$ radiation λ = 0.071 073 nm at 120(2) K. Multi-scan program SADABS was used for absorption correction^[24]. The structures were solved by the direct method and refined by the full-matrix least-squares method on F^2 using SHELXS-2014^[25]. All the non-H atoms were refined anisotropically. Hydrogen atoms attached to C atoms were placed geometrically and refined by using a riding model approximation, with C-H of 0.093~0.096 nm. Hydrogen atoms in hydroxyl and methanol molecules were located from difference Fourier maps and refined using their global U_{iso} value with O—H of 0.082 nm. A summary of the crystallographic data for complexes 1~3 is provided in Table 1. Selected bond lengths and angles for **1~3** are provided in Table 2.

CCDC: 2017862, 1; 2017863, 2; 2017864, 3.

Complex	1	2	3
Formula	$\mathrm{C_{63}H_{63}CeO_{27}}$	$C_{63}H_{63}PrO_{27}$	$C_{63}H_{63}SmO_{27}$
Formula weight	1 392.29	1 393.08	1 402.53
Crystal system	Trigonal	Trigonal	Trigonal
Space group	<i>R</i> 3	R3	R3
<i>a</i> / nm	2.750 5(1)	2.749 0(1)	2.736 4(1)
<i>b</i> / nm	2.750 5(1)	2.749 0(1)	2.736 4(1)
<i>c</i> / nm	0.773 1(0)	0.769 8(0)	0.771 0(0)
V / nm^3	5.065 2(5)	5.038 3(5)	4.999 6(5)
Ζ	3	3	3
<i>F</i> (000)	2 145	2 148	2 157
$D_{\rm c} / ({ m Mg} \cdot { m m}^{-3})$	1.369	1.377	1.397

Table 1 Crystal data and structure refinement for complexes 1~3

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	Continued Table 1								
	μ / $ m mm^{-1}$		0.755			0.806		0.963	
	Reflection collected		9 358			13 054		5 555	
	Independent reflection		3 652			4 464		2 127	
	$R_{ m int}$		0.045 9			0.050 3	i	0.064 2	
	GOF		1.056			1.076		1.035	
	$R_1, wR_2 [I > 2\sigma(I)]$		0.032 2,	0.076 5		0.025 3	, 0.059 2	0.027 0, 0.027 4	
_	R_1, wR_2 (all data)		0.032 2,	0.076 5		0.025 4	, 0.059 2	0.052 7, 0.052 9	

Table 2 Selected bond lengths (nm), Ln…Ln distances (nm) and bond angles (°) for 1~3 $\,$

1							
Ce1—01 ⁱ	0.241 6(3)	Ce1—O3 ⁱ	0.249 2(3)	Ce1—O9 ⁱⁱ	0.267 3(2)		
Ce1—01 ⁱⁱ	0.241 6(3)	Ce1—O3 ⁱⁱ	0.249 2(3)	Ce1-09	0.267 3(2)		
Ce1-01	0.241 6(3)	Ce1-03	0.249 2(3)	Ce1-09 ⁱ	0.267 3(2)		
$Ce1\cdots Ce1^{iv}$	0.773 10(5)						
01 ⁱ —Ce1—O1 ⁱⁱ	80.76(10)	01—Ce1—03	84.57(9)	03 ⁱ —Ce1—O9	70.02(8)		
01 ⁱ —Ce1—O1	80.76(10)	03 ⁱ —Ce1—O3	78.80(9)	03 ⁱⁱ —Ce1—O9	134.46(9)		
01 ⁱⁱ —Ce1—O1	80.76(10)	03 ⁱⁱ —Ce1—O3	78.80(9)	03—Ce1—O9	63.47(8)		
01 ⁱ —Ce1—O3 ⁱ	84.57(9)	01 ⁱ —Ce1—O9 ⁱⁱ	140.89(9)	09 ⁱⁱ —Ce1—O9	119.815(10)		
01 ⁱⁱ —Ce1—O3 ⁱ	132.98(9)	01 ⁱⁱ —Ce1—O9 ⁱⁱ	70.10(8)	01 ⁱ —Ce1—O9 ⁱ	70.10(8)		
$01 - Ce1 - 03^{i}$	140.11(9)	01—Ce1—O9 ⁱⁱ	69.52(8)	01 ⁱⁱ —Ce1—O9 ⁱ	69.52(8)		
01 ⁱ —Ce1—O3 ⁱⁱ	140.11(9)	03 ⁱ —Ce1—O9 ⁱⁱ	134.46(9)	01-Ce1-09 ⁱ	140.89(9)		
01 ⁱⁱ —Ce1—O3 ⁱⁱ	84.57(9)	03 ⁱⁱ —Ce1—O9 ⁱⁱ	63.47(8)	03^{i} —Ce1—O9 ⁱ	63.47(8)		
01—Ce1—O3 ⁱⁱ	132.98(9)	03—Ce1—O9 ⁱⁱ	70.02(8)	03 ⁱⁱ —Ce1—O9 ⁱ	70.02(8)		
03 ⁱ —Ce1—O3 ⁱⁱ	78.80(9)	01 ⁱ —Ce1—O9	69.52(8)	03—Ce1—O9 ⁱ	134.46(9)		
01 ⁱ —Ce1—O3	132.98(9)	01 ⁱⁱ —Ce1—O9	140.89(9)	09 ⁱⁱ —Ce1—O9 ⁱ	119.818(10)		
01 ⁱⁱ —Ce1—O3	140.11(9)	01—Ce1—09	70.10(8)	09—Ce1—O9 ⁱ	119.813(9)		
-		2					
Pr1-01 ⁱ	0.238 7(2)	Pr1—O3 ⁱⁱ	0.245 6(2)	Pr1-09	0.266 1(2)		
Pr1-01	0.238 7(2)	Pr1-03 ⁱ	0.245 6(2)	Pr1—09 ⁱⁱ	0.266 1(2)		
Pr1—O1 ⁱⁱ	0.238 7(2)	Pr1-03	0.245 6(2)	Pr1—09 ⁱ	0.266 1(2)		
$Pr1\cdots Pr1^{iv}$	0.769 84(5)						
01 ⁱ —Pr1—01	80.49(9)	01 ⁱⁱ —Pr1—03	133.07(8)	03 ⁱⁱ —Pr1—09 ⁱⁱ	63.40(8)		
01 ⁱ —Pr1—01 ⁱⁱ	80.49(9)	03 ⁱⁱ —Pr1—03	78.50(9)	03 ⁱ —Pr1—09 ⁱⁱ	70.32(8)		
01—Pr1—01 ⁱⁱ	80.49(9)	03 ⁱ —Pr1—03	78.50(9)	03—Pr1—09 ⁱⁱ	134.30(8)		
01 ⁱ —Pr1—03 ⁱⁱ	133.07(8)	01 ⁱ —Pr1—09	140.65(9)	09—Pr1—09 ⁱⁱ	119.824(9)		
01—Pr1—03 ⁱⁱ	140.29(8)	01—Pr1—09	69.98(8)	$O1^i$ —Pr1— $O9^i$	69.98(8)		
O1 ⁱⁱ —Pr1—O3 ⁱⁱ	84.95(9)	01 ⁱⁱ —Pr1—09	69.69(8)	$01 - Pr1 - 09^{i}$	69.69(8)		
$O1^{i}$ —Pr1— $O3^{i}$	84.95(9)	03 ⁱⁱ —Pr1—09	70.32(8)	01 ⁱⁱ —Pr1—09 ⁱ	140.66(9)		
01-Pr1-03 ⁱ	133.07(8)	03 ⁱ —Pr1—09	134.30(8)	03 ⁱⁱ —Pr1—09 ⁱ	134.30(8)		
O1 ⁱⁱ —Pr1—O3 ⁱ	140.29(8)	03—Pr1—09	63.40(8)	03 ⁱ —Pr1—09 ⁱ	63.40(8)		
03 ⁱⁱ —Pr1—03 ⁱ	78.50(9)	01 ⁱ —Pr1—O9 ⁱⁱ	69.69(8)	03—Pr1—09 ⁱ	70.32(8)		
01 ⁱ —Pr1—03	140.29(8)	01—Pr1—09 ⁱⁱ	140.65(9)	09—Pr1—09 ⁱ	119.826(9)		
01—Pr1—03	84.95(9)	O1 ⁱⁱ —Pr1—O9 ⁱⁱ	69.98(8)	09 ⁱⁱ —Pr1—09 ⁱ	119.825(9)		

3							
Sm1-01 ⁱ	0.235 6(3)	Sm1-03 ⁱ	0.241 1(3)	Sm1-09 ⁱ	0.261 8(3)		
Sm1—01 ⁱⁱ	0.235 6(3)	Sm1-03	0.241 1(3)	Sm1-09 ⁱⁱ	0.261 8(3)		
Sm1-01	0.235 6(3)	Sm1-03 ⁱⁱ	0.241 1(3)	Sm1-09	0.261 8(3)		
$Sm1{\cdots}Sm1^{iv}$	0.771 00(5)						
01 ⁱ —Sm1—01 ⁱⁱ	79.58(10)	01—Sm1—03 ⁱⁱ	133.85(9)	03 ⁱ —Sm1—09 ⁱⁱ	134.06(10)		
01 ⁱ —Sm1—O1	79.58(10)	03 ⁱ —Sm1—03 ⁱⁱ	77.80(10)	03—Sm1—09 ⁱⁱ	70.24(9)		
01 ⁱⁱ —Sm1—01	79.58(10)	03—Sm1—03 ⁱⁱ	77.80(10)	03 ⁱⁱ —Sm1—09 ⁱⁱ	64.03(9)		
01^{i} —Sm1— 03^{i}	85.98(9)	01^{i} —Sm1— 09^{i}	70.05(9)	09 ⁱ —Sm1—09 ⁱⁱ	119.849(9)		
01 ⁱⁱ —Sm1—03 ⁱ	133.85(9)	01 ⁱⁱ —Sm1—09 ⁱ	69.84(9)	01 ⁱ —Sm1—09	69.84(9)		
$01 - Sm1 - 03^{i}$	140.28(9)	$01 - Sm1 - 09^{i}$	139.88(10)	01 ⁱⁱ —Sm1—09	139.88(10)		
01 ⁱ —Sm1—03	133.85(9)	03^{i} —Sm1— 09^{i}	64.03(9)	01—Sm1—09	70.05(9)		
01 ⁱⁱ —Sm1—03	140.28(9)	$03 - Sm1 - 09^{i}$	134.06(10)	03 ⁱ —Sm1—09	70.24(9)		
01—Sm1—03	85.99(9)	03 ⁱⁱ —Sm1—09 ⁱ	70.24(9)	03—Sm1—09	64.03(9)		
03 ⁱ —Sm1—O3	77.80(10)	01^{i} —Sm1— 09^{ii}	139.88(10)	03 ⁱⁱ —Sm1—09	134.06(10)		
01 ⁱ —Sm1—03 ⁱⁱ	140.28(9)	01 ⁱⁱ —Sm1—09 ⁱⁱ	70.05(9)	09 ⁱ —Sm1—09	119.850(9)		
01 ⁱⁱ —Sm1—03 ⁱⁱ	85.98(9)	01—Sm1—09 ⁱⁱ	69.84(9)	09 ⁱⁱ —Sm1—09	119.849(9)		

Symmetry codes: $^{i} -x+y+1$, -x+1, z; $^{ii} -y+1$, x-y, z; $^{iii} x$, y, z-1; $^{iv} x$, y, z+1.

1.4 Photocatalytic activity study

Continued Table 2

The photocatalytic activity of the sample was evaluated by the degradation of methylene blue (MB) in aqueous solution. A MB aqueous solution (12 μ mol· L⁻¹, 15 mL) was mixed with 1.5 mg of complex **1**, and the mixture was stirred in the dark for 30 min to reach the adsorption - desorption equilibrium, then it was exposed to the illumination. Then, the samples were periodically removed from the reactor and immediately centrifuged to separate any suspended solids. The transparent solution was transferred to trace cuvette and analyzed by a UV - Vis spectrometer. A 300 W medium pressure mercury lamp served as a source of ultraviolet light. The distance between the light and the solution was about 30 cm.

2 Results and discussion

2.1 IR spectra

IR spectra of $D-H_2DTTA$ and complexes 1~3 were examined at room temperature, and the main characteristic absorption peaks present the typical stretching vibrations of COO⁻ and O—H groups. The broad band at 3 485~3 495 cm⁻¹ shows O—H stretching vibrations of the coordinated methanol molecules and hydroxy groups in the complexes^[26-27]. The strong bands at 1 109 and 1 735 cm⁻¹ are attributed to the ester C—O and acyl C == O stretching vibrations, respectively^[28]. The corresponding peaks of symmetric stretching vibrations of the carboxylate groups in complexes 1~3 (1 341 cm⁻¹ for 1, 1 339 cm⁻¹ for 2 and 1 339 cm⁻¹ for 3) were weaker than those of D-H₂DTTA, suggesting the coordination of carboxylate groups with Ln³⁺ in the complexes^[29-30]. These structural features are in accord with the results of the X-ray diffraction analysis.

2.2 Crystal structures description

X-ray single-crystal diffraction analysis indicates that complex **1** belongs to the trigonal system with *R3* space group, and the asymmetric unit includes one HDTTA⁻ ligand, 33% crystallographically independent Ce³⁺ cation and one coordinated methanol molecule. Each Ce³⁺ cation inside the unit is nine-coordinated with oxygen atoms, displaying the tri-capped trigonal prism geometry. Three partly deprotonated HDTTA⁻ ligands link neighboring Ce³⁺ cations via monodentate carboxyl groups in a η^1 - η^1 - μ_2 coordination mode, forming 1D infinite chains along *c* axis with Ce····Ce distance of 0.773 10(5) nm (Fig. 1). The bond lengths of Ce—O and bond angles of O—Ce—O are within the

报

range of 0.241 $6(3)\sim0.267$ 3(2) nm and $63.47(8)^{\circ} \sim$ 140.89(9)°, respectively, in accordance with those reported in the literatures^[31-32]. Complexes **1~3** are isomorphic with our previously reported Ln³⁺ compounds (Ln=Eu, Tb, Dy, Ho)^[22-23]. Cell parameters and intermetallic distances of these isomorphic structures almost gradually decrease from Ce³⁺ to Ho³⁺, due to the contraction of the lanthanide cation radius.

Using the CrystalExplorer software^[33], we found that besides O—H····O hydrogen bonds, C—H···· π weak interactions also play important roles in stabilizing the structures (Fig. 2a), which link the 1D chains giving rise to the 3D network (Fig. 3). The percentages of contacts contributed to the total Hirshfeld surface area of molecules are shown in Fig. 2. The proportions of



Symmetry codes: ' -y+1, x-y, z; '' -x+y+1, -x+1, z; '' x, y, z+1

Fig.1 Coordination structure of complex 1



Fig.2 (a) Hirshfeld surfaces of compound **1** mapped with d_{norm} property, the molecule in tube/licorice representation within the transparent surface maps, O—H…O (1) and C—H… π (2); Fingerprint plots of compound **1**: (b) O—H…O and (c) C—H… π contacts, listing the percentages of contacts contributed to the total Hirshfeld surface area of the molecule



H atoms not employed in the weak interactions have been omitted for clarity; Symmetry code: "-x+y+1, -x+1, z

Fig.3 C—H \cdots π weak intermolecular interactions in complex 1

O—H···O and C—H··· π interactions are 24.5% and 21.3% of the total Hirshfeld surfaces for **1**, respectively (Fig.2b and 2c), which also proves the important role of C—H··· π weak interactions in the structure. The inter-

atomic distance of C8—H8…Cgⁱⁱ (Cg is the centroid of the C6~C11 ring; Symmetry code: ⁱⁱ -x+y+1, -x+1, z) is 0.347 0(5) nm. The information of hydrogen bonds and C—H… π weak interactions of **1~3** are given in Table 3.

D—H····A	$d(\mathrm{D}\text{H})$ / nm	$d(\mathbf{H}\cdots\mathbf{A})$ / nm	$d(\mathbf{D}\cdots\mathbf{A})$ / nm	∠DHA / (°)
		1		
04—H4…02 ^{iv}	0.082	0.170	0.249 1(4)	162
09—H9A…08 ^v	0.086	0.213	0.290 5(4)	149
$C8$ — $H8$ ···· Cg^{vi}	0.093	0.259	0.347 0(5)	158
		2		
09—H9A…08 ^v	0.086	0.214	0.291 2(4)	149
04—H4…02 ^{iv}	0.082	0.168	0.247 7(4)	162
$C8$ — $H8$ ···· Cg^{vi}	0.093	2.60	0.348 4(6)	160
		3		
04—H4…02 ^{iv}	0.082	0.169	0.248 3(4)	162
09—H9A…08 ^v	0.086	0.214	0.292 1(4)	151
$C8$ — $H8$ ···· Cg^{vi}	0.093	0.257	0.344 2(6)	157

Table 3 Hydrogen bonds and C—H··· π weak interactions parameters for complexes 1~3

Symmetry codes: ⁱⁱ -y+1, x-y, z; ^{iv} x, y, z+1; ^v -x+y+1, -x+1, z-1; ^{vi} -x+y+1, -x+1, z.

2.3 PXRD patterns and thermal analysis

To verify the phase purity of complexes 1~3, PXRD data were collected. The experimental PXRD patterns were in consistent with the calculated ones based on the X-ray single-crystal data, certifying the high phase purity of the complexes (Fig.4). In order to estimate the thermal stabilities of the complexes, TGA was performed in a range of 25~800 °C (Fig.5). Due to the isomorphic structures of complexes $1\sim3$, the TGA curve of 1 is discussed in detail as a representative. For 1, the weight loss of 6.80% from 25~175 °C is equivalent to the loss of three coordinated methanol







Fig.5 TGA curves of complexes 1 (a), 2 (b) and 3 (c)

molecules (Calcd. 6.90%). Then with the temperature further increasing the framework decomposed gradually without displaying any plateau.

2.4 Luminescence properties

The solid - state photoluminescent properties of D-H₂DTTA and complexes $1 \sim 3$ were investigated at room temperature. The $D-H_2DTTA$ ligand exhibited a broad fluorescence emission band at 350 nm upon excitation at 300 nm (Fig.6), which is attributed to the intramolecular charge-transfer process between the ground state and excited states^[34-35]. For the complexes, the emission spectrum of 1 exhibited two weak bands at about 337 and 636 nm, and 2 and 3 exhibited strong fluorescence emission bands at 312 and 609 nm, respectively under excitation at 300 nm. Their luminescence emission spectra in the UV region were dominated by ligand-based emission and exhibited blue-shift compared with D-H₂DTTA ligand, which may be caused by ligand-to-metal charge transfer (LMCT)^[22] because of the coordination of the HDTTA- ligand to the Ln³⁺ cation. However, the intensities of the energy transitions from D-H₂DTTA ligand to the similar light lanthanide cations were different, mainly due to inherently diverse band gaps of various Ln³⁺ cations. Our recent research indicates that the energy of the excited state of D-H₂DTTA can be effectively transferred to Eu³⁺ center during the luminescence process^[23], so D-H₂DTTA ligand is an excellent antenna chromophore for sensitizing the fluorescence of Eu^{3+} cation (⁵ D_0 $\rightarrow^7 F_J$, J=1, 2, 3 and 4). The electronic excited-state energies of $Pr^{3+}({}^{1}D_{2})$ and $Sm^{3+}({}^{4}G_{5/2})$ are close to that of



Fig.6 Luminescence spectra of D-H₂DTTA ligand and complexes **1~3** at 298 K in the solid-state

Eu³⁺ (⁵ D_0), so the *f*-*f* transition can be seen in **2** and **3** at 636 nm during the luminescence process. In contrast, the electronic excited - state energy of Ce³⁺ cation is much lower than that of Eu³⁺, so the D-H₂DTTA ligand cannot sensitize Ce³⁺ cation effectively^[36]. The difference of luminescence property is related to the inherent variety of Ln³⁺ cations, and the luminescence sensitization to Ln³⁺ cations via *f*-*f* absorption is significantly different even for the same ligand^[37-38].

2.5 Photocatalytic properties

Since lanthanide metals have many stable valence states as well as luminescent properties, the lanthanide complexes may have good photocatalytic activity. So, the photocatalytic property was evaluated by the degradation of MB. The results showed that complex 1 displayed good specific degradation of MB under UV light irradiation. As shown in Fig. 7a, the variation of UVvisible adsorption spectra of MB dye solution in the presence of 1 was measured at each 20 min interval. The spectra displayed that the characteristic absorption peak of MB at 665 nm decreased as the radiation time increased, and the degradation of MB was about 76% when the UV light illumination time reached 160 min. Controlled experiments were also performed to ensure the results obtained from the photocatalytic experiments were consistent. Fig. 7b showed the variation of MB concentration (c/c_0) with reaction time under different experimental conditions (where c_0 is the initial concentration of the MB solution, and c is the concentration of the MB solution after the catalysis). Under the same experimental conditions, the degradation of MB in the absence of catalysts was negligible, implying that MB was relatively stable under illumination conditions. While the degradation of MB by 1 was about 64% when the illumination time reached 160 min under visible light, which is not as good as that under ultraviolet light. The PXRD and IR spectra of complex 1 before and after the photocatalytic reaction were performed to verify the dye removal mechanism. They match well with each other, which indicates that MB is not degraded by adsorption of 1, and as a photocatalyst, complex **1** has good stability during the heterogeneous catalytic reaction in the solution.



Fig.7 (a) Variation in UV-Vis adsorption spectra of MB solution in the presence of 1 irradiated by a UV lamp;
(b) Photocatalytic degradation rates of MB by 1

3 Conclusions

Three novel complexes featuring 1D chain structures and C—H··· π weak interactions were synthesized by light Ln3+ cations (Ln=Ce, Pr and Sm) and (+)-di(p-toluoyl)-D-tartaric acid $(D-H_2DTTA)$. Their structures were fully characterized. The structural analvsis reveals that Ln³⁺ cation is nine-coordinated in these complexes and adjacent Ln³⁺ cations are connected by triplex bridged ligands. The thermal analysis indicates that the complexes exhibited thermal stability up to ~175 °C after solvent elimination. Photoluminescence spectra reveal that the D-H₂DTTA ligand can partly sensitize the f-f transition luminescence of Pr^{3+} and Sm³⁺ cations. Still, the sensitization efficiency was lower than that of isomorphic heave Ln³⁺ (Ln=Eu, Tb and Dy) complexes, which is due to the different band gaps of various Ln³⁺ cations. Moreover, complex 1 exhibited relatively high photocatalytic efficiency for the degradation of MB under UV light irradiation in the solution. The photocatalytic performance was up to 76% for the degradation of MB within 160 min without any other reagents. The research indicates that these complexes may be good potential candidates for chiral, luminescent photocatalytic and multifunctional materials.

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