Crystal Structure, Thermal Decomposition Mechanism and Properties of Lanthanide Supramolecular Complexes Based on 2,4,6-Trimethylbenzoic Acid and 5,5'-Dimethyl-2,2'-bipyridine

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Abstract: Six ternary lanthanide complexes formulated as $[\text{Ln}(2,4,6\text{-TMBA})_3(5,5'\text{-DM-2,2'-bipy})]_2$ ($\text{Ln} = \text{Pr } \mathbf{1}$, $\text{Nd } \mathbf{2}$, $\text{Sm } \mathbf{3}$, $\text{Eu } \mathbf{4}$, $\text{Gd } \mathbf{5}$, $\text{Dy } \mathbf{6}$; 2,4,6-TMBA = 2,4,6-trimethylbenzoate; 5,5'-DM-2,2'-bipy = 5,5'-dimethyl-2,2'-bipyridine) have been synthesized under solvothermal conditions and characterized by single-crystal X-ray diffraction, elemental analysis, thermogravimetric analysis, etc. The results of crystal diffraction analysis show that complexes **1–6** are binuclear units, crystallizing in the triclinic *Pt* space group. Complexes **1–5** are isostructural, and each of the central metal ions has a coordination number of 9. The asymmetric unit of complexes **1–5** consists of one Ln^{3+} , one 5,5'-DM-2,2'-bipy ligand, and three 2,4,6-TMBA[−] moieties with three coordination modes: chelation bidentate, bridging bidentate, and bridging tridentate. The coordination geometry of Ln^{3+} is

distorted monocapped square antiprismatic. The binuclear units of complexes **1–5** form a one-dimensional (1D) supramolecular chain along the *c*-axis via π – π stacking interactions between the 2,4,6-trimethylbenzoic acid rings. The 1D chains are linked to form a supramolecular two-dimensional (2D) sheet in the *bc* plane via π – π stacking interactions between the pyridine rings. Although the molecular formulae of complex **6** and complexes **1–5** are similar, the coordination environment of the lanthanide ions is different in the two cases. The asymmetric unit of complex **6** contains a Dy^{3+} ion coordinated by a bidentate 5,5'-DM-2,2'-bipy and three 2,4,6-TMBA[−] ligands adopting bidentate and bridging bidentate coordination modes. The Dy^{3+} metal center has a coordination number of 8, with distorted square antiprismatic molecular geometry. The binuclear molecule of **6** is assembled into a six-nuclear unit by π – π weak staking interactions between two 5,5'-DM-2,2'-bipy ligands; then, adjacent six-nuclear units form a 1D chain via offset π – π interactions between 5,5'-DM-2,2'-bipy ligands on different adjacent units. The adjacent 1D chains are linked by C–H $\cdots$ O hydrogen bonding interactions to form a 2D supramolecular structure. The thermal stability and thermal decomposition mechanism of all the complexes are investigated by the combination of thermogravimetry and infrared spectroscopy (TG/FTIR) techniques under a simulated air atmosphere in the temperature range of 298–973 K at a heating rate of 10 K $\cdot$ min^{−1}. Thermogravimetric studies show that this series of complexes have excellent thermal stability. During the thermal decomposition of the complex, the neutral ligand is lost first, followed by the acid ligand, and finally, the complex is decomposed into rare earth oxides. The three-dimensional infrared results are consistent with the thermogravimetric results. The photoluminescence spectra of complex **4** show the strong characteristic luminescence of Eu^{3+} . The five typical emission peaks at 581, 591, 621, 651, and 701 nm correspond to the $^5\text{D}_0 \rightarrow ^7\text{F}_0$, $^5\text{D}_0 \rightarrow ^7\text{F}_1$, $^5\text{D}_0 \rightarrow ^7\text{F}_2$, $^5\text{D}_0 \rightarrow ^7\text{F}_3$, and $^5\text{D}_0 \rightarrow ^7\text{F}_4$ electronic transitions of Eu^{3+} , respectively. The emission at 621 nm is due to the electric dipole transition $^5\text{D}_0 \rightarrow ^7\text{F}_2$, while that at 591 nm is assigned to

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the $^5D_0 \rightarrow ^7F_1$ the magnetic dipole transition. The lifetime (τ) of complex **4** is calculated as 1.15 ms based on the equation $\tau = (B_1\tau_1^2 + B_2\tau_2^2)/(B_1\tau_1 + B_2\tau_2)$, and the intrinsic quantum yield is calculated to be 45.1%. Further, the magnetic properties of complex **6** in the temperature range of 2–300 K are studied under an applied magnetic field of 1000 Oe.

Key Words: Lanthanide supramolecular complexes; Crystal structure, Thermal behavior; Luminescence spectrum; 2,4,6-Trimethylbenzoic acid

2,4,6-三甲基苯甲酸与 5,5'-二甲基-2,2'-联吡啶构筑的系列镧系超分子配合物的晶体结构、热分解机理和性能

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摘要: 利用2,4,6-三甲基苯甲酸和5,5'-二甲基-2,2'-联吡啶配体在溶剂热的条件下成功合成出系列三元稀土超分子配合物 $[\text{Ln}(\text{2,4,6-TMBA})_3(5,5'\text{-DM-2,2'-bipy})]_2$ (Ln = Pr **1**, Nd **2**, Sm **3**, Eu **4**, Gd **5**, Dy **6**), 并对其进行了单晶X-射线衍射、元素分析、热重分析等一系列表征。研究结果表明配合物**1-5**同构, 中心离子的配位数为9, 配合物通过 π - π 堆积作用形成一维、二维的超分子结构。配合物**6**具有不同的结构, 中心离子的配位数为8, 分子间通过 π - π 堆积作用和 C—H $\cdots$ O氢键形成一维、二维的超分子结构。利用TG/FTIR技术研究了配合物的热稳定性和热分解机理, 荧光光谱表明配合物**4**可以发射出Eu³⁺离子的特征荧光, 同时对配合物**6**的磁性进行了初步探究。

关键词: 镧系超分子配合物; 晶体结构; 热分析; 荧光光谱; 2,4,6-三甲基苯甲酸
中图分类号: O642

1 Introduction

Lanthanide complexes with various structures¹ have attracted extensive attention due to their excellent optical²⁻⁵, magnetic⁶⁻⁹, adsorption¹⁰ and catalytic properties^{11,12}. Due to the particularity of 4f electron layer structure of lanthanides, lanthanide complexes have special luminescent properties such as high color purity, long decay times, high quantum yields, and so on¹³. These optical properties of lanthanide complexes have potential applications in fluorescent probes¹⁴ and luminescent bioassays¹⁵. However, $f-f$ transition is prohibited by spin and parity¹⁶, it is necessary to select appropriate organic chromophores to enhance the luminescence of intensity, which is called "antenna effect"¹⁷. Lanthanide has strong affinity with nitrogen or oxygen atoms, so aromatic carboxylic acids ligands: 3,4-diethoxybenzoic acid¹⁸, 2,4-dichlorobenzoic acid¹⁹, 1,2,3,5-benzenetetracarboxylic acid²⁰, *etc.*, and nitrogen-containing rigid ligands: 1,10-phenanthroline²¹, 2,2'-bipyridine²², 2,2':6',2''-terpyridine²³, *etc.*, are usually selected as ligand to synthesize lanthanide complexes. The introduction of nitrogen-containing second ligand can not only improve the stability of the complex, but also replace the position of the solvent, reduce energy loss and enhance luminous efficiency. The second ligand can also act as an energy donor, absorbing energy and transferring to the central ion, improving the luminous intensity. Deprotonated 2,4,6-trimethylbenzoic acid anions have multiple

coordination modes, such as monodentate, bidentate, bridged bidentate, bridged tridentate, *etc.*, providing a possibility for the diversity structure of lanthanide complexes. 2,4,6-trimethylbenzoic acid as an aromatic carboxylic acid ligand combined with nitrogen-containing heterocyclic ligands 5,5'-dimethyl-2,2'-bipyridine as antenna ligands sensitizes lanthanide ions and improves luminescence efficiency. In recent years, the thermal stability, decomposition mechanism and kinetics of complexes have been significantly increased²⁴. TG/FTIR is usually used to monitor the mass loss in the process of gas escape and thermal decomposition at different temperatures, which provides valuable information for the structure of complexes. Moreover, the potential application of trivalent lanthanide ion coordination complexes in magnetic materials has attracted great attention²⁵. Owing to the unquenched orbital angular momentum of high spin 4f unpaired electrons in trivalent lanthanide ion, these lanthanide complexes show magnetic anisotropy²⁶. Therefore lanthanide complexes are the most promising magnetic materials.

In this paper, we utilize 2,4,6-trimethylbenzoic acid and 5,5'-dimethyl-2,2'-bipyridine to form six binuclear complexes, $[\text{Ln}(\text{2,4,6-TMBA})_3(5,5'\text{-DM-2,2'-bipy})]_2$ (Ln = Pr **1**, Nd **2**, Sm **3**, Eu **4**, Gd **5**, Dy **6**). All the prepared complexes were characterized *via* single-crystal X-ray diffraction, elemental analysis *etc.* The pyrolysis mechanisms of the complexes were

studied by the TG-DTG-DSC/FTIR technique. Solid state fluorescence and lifetime of complex **4** were studied. In addition, the magnetic property of **6** was also investigated.

2 Experimental section

2.1 Materials and methods

$\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ($\text{Ln} = \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Dy}$) (Alfa Aesar, 99.9%), 2,4,6-trimethylbenzoic acid (Alfa Aesar, 99%), and 5,5'-dimethyl-2,2'-bipyridine (Alfa Aesar, 98%) were received from commercial suppliers and used as received without further purification. The Vario-EL II analyser (Elementar, Germany) was used for elemental analyses (C, H and N) and the contents of lanthanide elements were titrated with ethylenediamine tetraacetic acid (EDTA). The TG-DTG/FTIR analyses were conducted in a simulated air atmosphere with the STA 449 F3 instrument (Netzsch, Germany) and the TENSOR 27 fourier transform infrared spectrometer (Bruker, Germany) at a heating rate of $10 \text{ K} \cdot \text{min}^{-1}$ with about 3–8 mg compounds. Excitation ($\lambda_{\text{em}} = 621 \text{ nm}$) and emission spectra ($\lambda_{\text{ex}} = 330 \text{ nm}$) and lifetimes of solid complexes were measured on a Fluorescence Spectrometer (Edinburgh Instruments Ltd., UK). In addition, magnetic susceptibilities of the complex **6** were performed on a MPMS XL-7 magnetometer (Quantum Design, USA) from 2 K to 300 K with an applied magnetic field of 1000 Oe.

2.2 Synthesis of complexes 1–6

Complexes **1–6** have the same synthetic conditions. A mixture of 2,4,6-trimethylbenzoic acid (0.098 g, 0.60 mmol) and 5,5'-dimethyl-2,2'-bipyridine (0.037 g, 0.20 mmol) was dissolved in 6 mL ethanol solution with stirring. Adjust the pH value of the mixture to 5–7 with $1.0 \text{ mol} \cdot \text{L}^{-1}$ NaOH, add the mixture drop to $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.20 mmol, $\text{Ln} = \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Dy}$)

aqueous solution by stirring. After stirring for 40 min, the suspension was sealed in a 25 mL Teflon-lined autoclave and heated to $120 \text{ }^\circ\text{C}$ for 7 days and then slowly cooled to room temperature, the crystals were collected by filtration, washed with ethanol and distilled water.

$[\text{Pr}(\text{2,4,6-TMBA})_3(\text{5,5'-DM-2,2'-bipy})_2]$ (**1**), Elemental Anal. Calcd. for $\text{C}_{84}\text{H}_{90}\text{N}_4\text{O}_{12}\text{Pr}_2$: C, 61.96; H, 5.61; N, 3.42; Pr, 17.35, Found: C, 61.92; H, 5.57; N, 3.44; Pr, 17.30. $[\text{Nd}(\text{2,4,6-TMBA})_3(\text{5,5'-DM-2,2'-bipy})_2]$ (**2**), Elemental Anal. Calcd. for $\text{C}_{84}\text{H}_{90}\text{N}_4\text{O}_{12}\text{Nd}_2$: C, 62.13; H, 5.61; N, 3.49; Nd, 17.66, Found: C, 62.14; H, 5.54; N, 3.42; Nd, 17.63. $[\text{Sm}(\text{2,4,6-TMBA})_3(\text{5,5'-DM-2,2'-bipy})_2]$ (**3**), Elemental Anal. Calcd. for $\text{C}_{84}\text{H}_{90}\text{N}_4\text{O}_{12}\text{Sm}_2$: C, 61.23; H, 5.49; N, 3.44; Sm, 18.25, Found: C, 61.21; H, 5.50; N, 3.40; Sm, 18.24. $[\text{Eu}(\text{2,4,6-TMBA})_3(\text{5,5'-DM-2,2'-bipy})_2]$ (**4**), Elemental Anal. Calcd. for $\text{C}_{84}\text{H}_{90}\text{N}_4\text{O}_{12}\text{Eu}_2$: C, 61.06; H, 5.52; N, 3.37; Eu, 18.45, Found: C, 61.09; H, 5.49; N, 3.39; Eu, 18.40. $[\text{Gd}(\text{2,4,6-TMBA})_3(\text{5,5'-DM-2,2'-bipy})_2]$ (**5**), Elemental Anal. Calcd. for $\text{C}_{84}\text{H}_{90}\text{N}_4\text{O}_{12}\text{Gd}_2$: C, 60.73; H, 5.50; N, 3.36; Gd, 18.97, Found: C, 60.70; H, 5.46; N, 3.37; Gd, 18.92. $[\text{Dy}(\text{2,4,6-TMBA})_3(\text{5,5'-DM-2,2'-bipy})_2]$ (**6**), Elemental Anal. Calcd. for $\text{C}_{84}\text{H}_{90}\text{N}_4\text{O}_{12}\text{Dy}_2$: C, 60.30; H, 5.44; N, 3.39; Dy, 19.48; Found: C, 60.32; H, 5.42; N, 3.35; Dy, 19.43.

2.3 Single-crystal X-ray diffraction

Crystallographic data for complexes **1–6** were collected on a Smart-1000 diffractometer (Bruker, Germany) using graphite-monochromated with Mo- K_α radiation ($\lambda = 0.71073 \text{ \AA}$, $1 \text{ \AA} = 0.1 \text{ nm}$, the same below) at the temperature of 298 K. Structures of complexes **1–6** were solved by means of direct methods and refined by full-matrix least-squares techniques on F^2 using the SHELXL-97 program. The detailed crystallographic data and

Table 1 Crystal data and structure refinement for complexes **1–6** ($1 \text{ \AA} = 0.1 \text{ nm}$).

Complex	1	2	3
Empirical formula	$\text{C}_{84}\text{H}_{90}\text{N}_4\text{O}_{12}\text{Pr}_2$	$\text{C}_{84}\text{H}_{90}\text{N}_4\text{O}_{12}\text{Nd}_2$	$\text{C}_{84}\text{H}_{90}\text{N}_4\text{O}_{12}\text{Sm}_2$
Formula weight/($\text{g} \cdot \text{mol}^{-1}$)	1629.42	1636.08	1648.30
Temperature/K	298(2)	298(2)	298(2)
Wavelength/ $\text{\AA}$	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions			
$a/\text{\AA}$	12.4109 (11)	12.1605 (13)	12.3684 (11)
$b/\text{\AA}$	13.4486 (12)	13.1382 (13)	13.3244 (11)
$c/\text{\AA}$	13.4944 (13)	13.2316 (14)	13.4910 (12)
$\alpha/^\circ$	107.863 (3)	107.790 (2)	107.653 (2)
$\beta/^\circ$	108.458 (3)	108.686 (2)	108.945 (2)
$\gamma/^\circ$	91.858 (2)	91.7080 (10)	91.5490 (10)
Volume/ $\text{\AA}^3$	2012.4 (3)	1887.6 (3)	1984.4 (3)
Z, calculated density/($\text{mg} \cdot \text{m}^{-3}$)	1, 1.344	1, 1.439	1, 1.379
Absorption coefficient/ mm^{-1}	1.257	1.425	1.526
$F(000)$	836	838	842
Crystal size/ mm^3	$0.13 \times 0.08 \times 0.05$	$0.16 \times 0.08 \times 0.06$	$0.15 \times 0.08 \times 0.05$

to be continued

continued Table 1

Complex	1	2	3
Theta range for data collection/(°)	2.34 to 25.02	2.38 to 25.02	2.34 to 25.02
Limiting indices	$-14 \leq h \leq 14$ $-15 \leq k \leq 15$ $-12 \leq l \leq 16$	$-14 \leq h \leq 14$ $-11 \leq k \leq 15$ $-15 \leq l \leq 15$	$-14 \leq h \leq 14$ $-15 \leq k \leq 15$ $-10 \leq l \leq 16$
Reflections collected/unique	10173/6956 [<i>R</i> (int) = 0.0564]	9719/6570 [<i>R</i> (int) = 0.0655]	10125/6888 [<i>R</i> (int) = 0.0494]
Completeness to theta = 25.02°	98.3%	98.5%	98.5%
Max. and min. transmission	0.9398 and 0.8537	0.9194 and 0.8041	0.9276 and 0.8034
Data/restraints/parameters	6956/0/460	6570/0/471	6888/0/471
Goodness-of-fit on <i>F</i> ²	1.072	1.033	1.014
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0681 <i>wR</i> ₂ = 0.1529	<i>R</i> ₁ = 0.0650 <i>wR</i> ₂ = 0.1490	<i>R</i> ₁ = 0.0533 <i>wR</i> ₂ = 0.0929
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0929 <i>wR</i> ₂ = 0.1634	<i>R</i> ₁ = 0.0901 <i>wR</i> ₂ = 0.1621	<i>R</i> ₁ = 0.0832 <i>wR</i> ₂ = 0.1004
Complex	4	5	6
Empirical formula	C ₈₄ H ₉₀ N ₄ O ₁₂ Eu ₂	C ₈₄ H ₉₀ N ₄ O ₁₂ Gd ₂	C ₂₅₂ H ₂₇₀ N ₁₂ O ₃₆ Dy ₆
Formula weight/(g·mol ⁻¹)	1651.52	1662.10	5017.80
Temperature/K	298 (2)	298 (2)	298 (2)
Wavelength/Å	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
Unit cell dimensions			
<i>a</i> /Å	12.3030 (11)	11.8539 (12)	13.8471 (12)
<i>b</i> /Å	13.1940 (12)	12.6869 (13)	16.3534 (14)
<i>c</i> /Å	13.4110 (12)	12.9280 (14)	28.649 (3)
<i>α</i> /(°)	107.599 (2)	107.535 (3)	78.807 (2)
<i>β</i> /(°)	109.113 (4)	109.358 (3)	77.3610 (10)
<i>γ</i> /(°)	91.4870 (10)	91.3950 (10)	78.530 (2)
Volume/Å ³	1941.7 (3)	1732.3 (3)	6126.5 (9)
<i>Z</i> , calculated density/(mg·m ⁻³)	1, 1.412	1, 1.593	1, 1.360
Absorption coefficient/mm ⁻¹	1.663	1.968	1.875
<i>F</i> (000)	844	846	2550
Crystal size/mm ³	0.20 × 0.11 × 0.10	0.11 × 0.07 × 0.04	0.41 × 0.37 × 0.13
Theta range for data collection/(°)	2.36 to 25.02	2.67 to 25.02	2.30 to 25.02
Limiting indices	$-14 \leq h \leq 14$ $-15 \leq k \leq 15$ $-15 \leq l \leq 12$	$-7 \leq h \leq 14$ $-14 \leq k \leq 15$ $-15 \leq l \leq 14$	$-8 \leq h \leq 16$ $-18 \leq k \leq 19$ $-34 \leq l \leq 33$
Reflections collected/unique	9927/6752 [<i>R</i> (int) = 0.0280]	8934/6028 [<i>R</i> (int) = 0.1072]	31411/21320 [<i>R</i> (int) = 0.0620]
Completeness to theta = 25.02°	98.5%	98.9%	98.5%
Data/restraints/parameters	6752/0/471	6028/0/471	21320/37/1378
Goodness-of-fit on <i>F</i> ²	1.025	1.082	0.778
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0369 <i>wR</i> ₂ = 0.0688	<i>R</i> ₁ = 0.0917 <i>wR</i> ₂ = 0.2045	<i>R</i> ₁ = 0.0592 <i>wR</i> ₂ = 0.0973
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0532 <i>wR</i> ₂ = 0.0744	<i>R</i> ₁ = 0.1293 <i>wR</i> ₂ = 0.2209	<i>R</i> ₁ = 0.1234 <i>wR</i> ₂ = 0.1125
Largest diff. peak and hole (e ⁻ ·Å ⁻³)	1.858 and -0.644	2.959 and -2.296	2.028 and -0.891
Largest diff. peak and hole (e ⁻ ·Å ⁻³)	2.276 and -1.794	1.922 and -1.438	1.357 and -0.851

1 Å = 0.1 nm, the same below.

structure refinements for all compounds are presented in Table 1.

3 Results and discussion

3.1 Crystal structure description of complexes 1–6

The results of crystal diffraction analysis show that although

the molecular ratio of complexes 1–6 is the same, there are two different structures due to the contraction effect of lanthanide elements. Among them, complexes 1–5 are isostructural, the central ions are all nine-coordinated, while complex 6 is different with a coordination number of eight. So as a representative, the

Fig. 1 (a) The molecular structure of complex 4;
(b) coordination polyhedron of Eu^{3+} center.

Fig. 2 Different coordination modes of 2,4,6-TMBA⁻ ligand for complex 4.

A: bridging tridentate, B: bridging bidentate, C: bidentate.

crystal structures of complexes **4** and **6** are employed to be discussed in detail.

3.1.1 Crystal structure of $[\text{Eu}(\text{2,4,6-TMBA})_3(5,5'\text{-DM-2,2'-bipy})_2]$

The complex **4** is a binuclear unit, crystallizing in the triclinic $P\bar{1}$ space group. As shown in Fig. 1a, the asymmetric unit of **4**

consists of one Eu^{3+} , one 5,5'-DM-2,2'-bipy ligand, three 2,4,6-TMBA⁻ with three coordination modes: chelation bidentate, bridging bidentate and bridging tridentate (Fig. 2). The Eu^{3+} is nine coordinated and displays a distorted monocapped square antiprismatic coordination geometry (Fig. 1b). In the polyhedron $\text{Eu1O}_7\text{N}_2$, seven oxygen (O1, O2, O3, O4, O3A, O5 and O6) atoms are derived from 2,4,6-TMBA⁻ ligand with different coordination modes, and two nitrogen (N1, N2) atoms are derived from the bidentate 5,5'-DM-2,2'-bipy ligand. The average bond distances of $\text{Eu1}-\text{O}$ to Eu1 is 2.451 Å, while the bond distances of $\text{Eu1}-\text{N}$ (bound through N1, N2) is 2.653 Å. The $\text{Eu1}-\text{O}$ and $\text{Eu1}-\text{N}$ bond length ranges (Table 2) are similar to the bond lengths previously reported²⁷.

As shown in Fig. 3a, the binuclear unit of **4** forms a one-dimensional (1D) supramolecular chain along the c -axis via π - π stacking interactions between 2,4,6-trimethylbenzoic acid rings with the distance of 3.726 Å. The 1D chain is linked to form a supramolecular two-dimensional (2D) sheet in about the bc plane via π - π stacking interactions between pyridine rings with the distance of 3.772 Å (Fig. 3b).

3.1.2 Crystal structure of $\text{Dy}(\text{2,4,6-TMBA})_3(5,5'\text{-DM-2,2'-bipy})_2$

The complex **6** is also a binuclear molecule, crystallizing in the triclinic $P\bar{1}$ space group. Although the molecular formula of complex **6** and **4** are similar, the coordination environment of lanthanide ions is different. As shown in Fig. 4a, the asymmetric unit of complex **6** contains a Dy^{3+} coordinated by a bidentate

Table 2 The main bond lengths for complexes 1–6.

	Pr(1)	Bond length/Å	Nd(2)Ln-O/Å	Bond length/Å	Sm(3)	Bond length/Å
Ln-O	Pr(1)-O(1)	2.461	Nd(1)-O(1)	2.401	Sm(1)-O(1)	2.396
	Pr(1)-O(2)	2.581	Nd(1)-O(2)	2.515	Sm(1)-O(2)#1	2.403
	Pr(1)-O(3)	2.455	Nd(1)-O(3)	2.380	Sm(1)-O(3)	2.366
	Pr(1)-O(4)#1	2.458	Nd(1)-O(4)#1	2.383	Sm(1)-O(4)#1	2.574
	Pr(1)-O(5)	2.440	Nd(1)-O(5)	2.374	Sm(1)-O(5)	2.402
	Pr(1)-O(6)#1	2.617	Nd(1)-O(6)#1	2.557	Sm(1)-O(6)	2.528
	Pr(1)-O(5)#1	2.702	Nd(1)-O(5)#1	2.633	Sm(1)-O(3)#1	2.666
Average Ln-O		2.531		2.463		2.476
Ln-N	Pr(1)-N(1)	2.722	Nd(1)-N(1)	2.646	Sm(1)-N(1)	2.677
	Pr(1)-N(2)	2.737	Nd(1)-N(2)	2.678	Sm(1)-N(2)	2.694
Average Ln-N		2.730		2.662		2.686
	Eu(4)	Bond length/Å	Gd(5)	Bond length/Å	Dy(6)	Bond length/Å
Ln-O	Eu(1)-O(1)	2.367	Gd(1)-O(1)	2.271	Dy(1)-O(1)	2.394
	Eu(1)-O(2)#1	2.372	Gd(1)-O(2)#1	2.288	Dy(1)-O(3)	2.274
	Eu(1)-O(3)	2.346	Gd(1)-O(3)	2.246	Dy(1)-O(5)	2.374
	Eu(1)-O(4)#1	2.535	Gd(1)-O(4)#1	2.417	Dy(1)-O(7)	2.326
	Eu(1)-O(5)	2.381	Gd(1)-O(5)	2.276	Dy(1)-O(9)	2.409
	Eu(1)-O(6)	2.503	Gd(1)-O(6)	2.413	Dy(1)-O(10)	2.461
	Eu(1)-O(3)#1	2.651	Gd(1)-O(3)#1	2.566		
Average Ln-O		2.451		2.354		2.373
Ln-N	Eu(1)-N(1)	2.637	Gd(1)-N(1)	2.501	Dy(1)-N(1)	2.565
	Eu(1)-N(2)	2.668	Gd(1)-N(2)	2.571	Dy(1)-N(2)	2.588
Average Ln-N		2.653		2.536		2.577

Symmetry transformations used to generate equivalent atoms: #1 - $x + 1, -y + 1, -z + 1$.

Fig. 3 (a) The supramolecular 1D chain structure of **4** along the *c* axis; (b) The supramolecular 2D sheet of **4** in about the *bc* plane.

Fig. 4 (a) The molecular structure of complex **6**; (b) Coordination polyhedron of Dy^{3+} center.

5,5'-DM-2,2'-bipy and three 2,4,6-TMBA[−] ligand adopting bidentate and bridging bidentate coordination modes. The Dy^{3+} metal center has a coordination number of eight with a distorted square antiprismatic molecular geometry (Fig. 4b). $\text{Dy1}-\text{O}$ bond distances for the bidentate 2,4,6-TMBA[−] ligand (O9 and O10) are 2.409 Å and 2.461 Å. $\text{Dy1}-\text{O}$ bond distances for the bridging bidentate 2,4,6-TMBA[−] ligand (O1, O3, O5 and O7) are 2.394 Å, 2.274 Å, 2.374 Å and 2.326 Å, respectively. The $\text{Dy1}-\text{N1}$ and $\text{Dy1}-\text{N2}$ bond distances are 2.565 Å and 2.588 Å. The Ln—O, Ln—N distances and their average distances for complexes **1–6** are listed in Table 2. Obviously, the shrinkage

effect of lanthanides is reflected in the decrease of average Ln—O bond length and average Ln—N bond length with the increase of atomic number²⁸.

Although both complex **6** and complex **4** are binuclear molecules with similar molecular ratios, the coordination numbers of the central rare earth ions are different, furthermore, the 1D and 2D supramolecular structures are quite different. The binuclear molecule of **6** is assembled into a six-nuclear units by $\pi-\pi$ weak stacking interactions between two 5,5'-DM-2,2'-bipy ligands with the distance of 3.752 Å, then adjacent six-nuclear units *via* offset $\pi-\pi$ interactions between 5,5'-DM-2,2'-bipy ligands on different adjacent units forms a 1D chain, where the distance is 3.614 Å (Fig. 5a). The adjacent 1D chains are linked by $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonding interactions with the distance of 3.456 Å to construct two-dimensional supramolecular structure (Fig. 5b).

3.2 Thermal analysis

To investigate the pyrolytic dissociation mechanism and thermal stability of ternary lanthanide complexes, we measured the thermal behavior using TG-DTG-DSC under a simulated air atmosphere in the temperature range of 298–973 K with a heating rate of 10 $\text{K}\cdot\text{min}^{-1}$. Thermal analysis curves of **1–6** are shown in Fig. S1(a–f) (in Supporting Information). The details of the pyrolysis steps (mass losses, temperature ranges, probable expelled groups and peak temperatures of DTG) are exhibited in Table 3. The complexes **1–5** have the similar pyrolysis steps, the complex **4** as a representative will be discussed in detail.

The thermal decomposition temperature of complex **4** is 454.15 K, which has certain thermal stability. The first mass loss between 454.15–547.15 K, is connected with symmetry peak on DTG curves centered at 497.25 K (experiment value of mass loss = 22.16%, calculated value of mass loss = 22.31%). The mass loss percent is close to the theoretical value of two 5,5'-DM-2,2'-dipy losses. Additionally, in the DSC curves of complex **4**, a low endothermic peak is observed. Over 547.15K, the DTG curve of complex **4** shows that the mass loss is divided into three overlapping steps. The first one is centered at 615.85 K with mass loss of 26.76%. The second one is centered at 658.95 K with mass loss of 5.65%. The third one is centered at 710.45 K with mass loss of 23.86%. These steps are corresponding to the loss of six 2,4,6-TMBA ligands (experiment value of mass loss = 56.27%, calculated value of mass loss = 56.38%). In the meantime, three exothermic peaks on the DSC curve can be

Fig. 5 (a) Supramolecular 1D chain in **6** along the *c* axis; (b) Supramolecular 2D sheet in **6** about the *bc* plane.

Table 3 Thermal data for the complexes 1-6 at pressure 101.3 kPa.

	Step	Temperature range/K	DTG T_p /K	Mass loss rate/%		Probable expelled groups	Intermediate and residue
				Found	Calcd.		
1	I	454.15–555.15	512.95	22.59	22.61 ^a	2(5,5'-DM-2,2'-dipy)	[Pr ₂ (2,4,6-TMBA) ₆]
	II	555.15–678.15	630.05	32.20		<i>x</i> 2,4,6-TMBA	[Pr ₂ (2,4,6-TMBA) _{6-<i>x</i>}]
	III	678.15–716.15	690.95	4.50		<i>y</i> 2,4,6-TMBA	[Pr ₂ (2,4,6-TMBA) _{6-<i>x-y</i>}]
	IV	716.15–873.15	761.35	19.80	56.49 ^b	(6- <i>x-y</i>) 2,4,6-TMBA	Pr ₆ O ₁₁
				79.09	79.10 ^c		
2	I	457.15–554.15	507.35	22.22	22.52 ^a	2(5,5'-DM-2,2'-dipy)	[Nd ₂ (2,4,6-TMBA) ₆]
	II	554.15–681.15	633.35	32.28		<i>x</i> 2,4,6-TMBA	[Nd ₂ (2,4,6-TMBA) _{6-<i>x</i>}]
	III	681.15–716.15	689.75	4.78		<i>y</i> 2,4,6-TMBA	[Nd ₂ (2,4,6-TMBA) _{6-<i>x-y</i>}]
	IV	716.15–973.15	752.85	18.91	56.91 ^b	(6- <i>x-y</i>) 2,4,6-TMBA	Nd ₂ O ₃
				78.19	79.43 ^c		
3	I	455.15–548.15	496.45	22.26	22.35 ^a	2(5,5'-DM-2,2'-dipy)	[Sm ₂ (2,4,6-TMBA) ₆]
	II	548.15–682.15	632.45	33.07		<i>x</i> 2,4,6-TMBA	[Sm ₂ (2,4,6-TMBA) _{6-<i>x</i>}]
	III	682.15–731.15	691.85	8.21		<i>y</i> 2,4,6-TMBA	[Sm ₂ (2,4,6-TMBA) _{6-<i>x-y</i>}]
	IV	731.15–973.15	763.25	15.19	56.49 ^b	(6- <i>x-y</i>) 2,4,6-TMBA	Sm ₂ O ₃
				78.73	78.84 ^c		
4	I	456.15–547.15	497.25	22.16	22.31 ^a	2(5,5'-DM-2,2'-dipy)	[Eu ₂ (2,4,6-TMBA) ₆]
	II	547.15–647.15	615.85	26.76		<i>x</i> 2,4,6-TMBA	[Eu ₂ (2,4,6-TMBA) _{6-<i>x</i>}]
	III	647.15–675.15	658.95	5.65		<i>y</i> 2,4,6-TMBA	[Eu ₂ (2,4,6-TMBA) _{6-<i>x-y</i>}]
	IV	675.15–973.15	710.45	23.86	56.38 ^b	(6- <i>x-y</i>) 2,4,6-TMBA	Eu ₂ O ₃
				78.43	78.69 ^c		
5	I	454.15–548.15	485.15	22.11	22.12 ^a	2(5,5'-DM-2,2'-dipy)	[Gd ₂ (2,4,6-TMBA) ₆]
	II	548.15–682.15	633.45	32.11		<i>x</i> 2,4,6-TMBA	[Gd ₂ (2,4,6-TMBA) _{6-<i>x</i>}]
	III	682.15–737.15	693.05	9.39		<i>y</i> 2,4,6-TMBA	[Gd ₂ (2,4,6-TMBA) _{6-<i>x-y</i>}]
	IV	737.15–973.15	764.25	14.10	56.11 ^b	(6- <i>x-y</i>) 2,4,6-TMBA	Gd ₂ O ₃
				77.71	78.23 ^c		
6	I	432.15–460.15	456.85	5.15		<i>x</i> (5,5'-DM-2,2'-dipy)	[Dy ₂ (2,4,6-TMBA) ₆](5,5'-DM-2,2'-dipy) _{2-<i>x</i>}]
	II	460.15–540.15	469.25	16.95	22.03 ^a	2- <i>x</i> (5,5'-DM-2,2'-dipy)	[Dy ₂ (2,4,6-TMBA) ₆]
	III	540.15–687.15	621.25	29.97		<i>y</i> 2,4,6-TMBA	[Dy ₂ (2,4,6-TMBA) _{6-<i>y</i>}]
	IV	687.15–736.15	702.45	8.22		<i>z</i> 2,4,6-TMBA	[Dy ₂ (2,4,6-TMBA) _{6-<i>y-z</i>}]
	V	736.15–873.15	763.85	15.99	55.67 ^b	(6- <i>y-z</i>) 2,4,6-TMBA	Dy ₂ O ₃
				76.28	77.70 ^c		

^a Theoretical total mass loss of two 5,5'-DM-2,2'-bipy; ^b Theoretical total mass loss of six 2,4,6-TMBA; ^c The total loss rate.

found. Complex **4** was eventually completely collapsed into Eu₂O₃.

The decomposition temperature of complex **6** is 432.15 K. In the range of 432.15–540.15 K, the DTG curve of complex **6** shows the mass loss in the two overlapping steps. The first one is centered at 456.85 K with mass loss of 5.15%. The second one is centered at 469.25 K with mass loss of 16.95%. The DSC curve has no obvious endothermic peak in this temperature range. Between 540.15–873.15 K, the DTG curve for complex **6** shows mass losses in three overlapping steps, they are centered at 621.25, 702.45 and 763.85 K and corresponds to mass loss of 29.97%, 8.22% and 15.99%, respectively. Compared with complexes **1–5**, the exothermic peak on the DSC curve of complex **6** is significantly lower at 540.15–873.15 K. Complex **6** was eventually completely collapsed into Dy₂O₃.

3.3 Evolved gas analysis

In order to further study the pyrolysis behavior of complexes, the TG/FTIR spectra were obtained by thermogravimetry

followed by Fourier transform infrared spectroscopy system. The 3D stacked plots of the FTIR spectra are presented in Fig. 6a–f and the 2D IR spectra are shown in Fig. 7a–f. We take complex **4** as an example to give a detailed explanation. It can be seen from Fig. 7d that there are four infrared absorption peaks at different temperatures ($T = 500.44, 616.48, 653.26, 710.44$ K), which are consistent with the strongest absorption peaks of gases escaping from four temperature ranges (456.15–547.15, 547.15–647.15, 647.15–675.15, 675.15–973.15 K). In the first stage, at 500.44 K, the characteristic signal of $\nu_{C=C}$ at 1469 and 1600 cm^{-1} , $\nu_{C=N}$ at 1558 cm^{-1} , ν_{C-N} at 1130 and 1218 cm^{-1} , ν_{C-H} at 2881–3036 cm^{-1} , γ_{C-H} at 826, 1029 and 1061 cm^{-1} were observed. This indicates the loss of the neutral ligands in the first step. In the second IR spectrum at 616.48 K, the sharp absorption peak at 1797 cm^{-1} is $\nu_{C=O}$ from the carboxylic acid group, and the absorption peak in the region between 2258–2360 cm^{-1} and 669 cm^{-1} were attributed to the absorption peak of CO₂. The absorption peaks of ν_{C-H} at 2889–3025 cm^{-1} , δ_{C-H} at 849 and

Fig. 6 The 3D IR image of the gas escaping from the complexes 1–6 (a–f) during pyrolysis.

Fig. 7 The 2D IR spectra of the gaseous mixtures for complexes 1–6 (a–f).

1036 cm^{-1} , $\nu_{\text{C}=\text{C}}$ at 1615 cm^{-1} , and weak water peak at 3600–3800 cm^{-1} was observed. The results were consistent with the loss of the aromatic carboxylic acid ligand in the second step of the thermogravimetric analysis. In the infrared spectrum of the third and fourth steps, only the strong absorption peak of CO_2 at 2258–2360 cm^{-1} and 669 cm^{-1} and the weak water peak at 3600–3800 cm^{-1} were left on the infrared spectrum. This indicates that the carboxylic acid ligands have been completely cleaved.

For complex 6, the formation of complex can be divided into five steps according to the 3D IR spectrum of evolved gas. The five IR spectra at different temperatures ($T = 452.00$, 504.89, 623.81, 702.35 and 764.32 K) were shown in Fig. 7f. At 452.00 and 504.89 K, the 2D infrared spectra were similar. The characteristic peak of $\nu_{\text{C}=\text{C}}$, $\nu_{\text{C}=\text{N}}$ and $\nu_{\text{C}-\text{H}}$ at 1469, 1558 and 2889–3025 cm^{-1} can be observed respectively, indicating that the bipyridine ligands was lost in the first two steps. At 623.81

and 702.35 K, the similar 2D infrared spectra were also found. The characteristic peak of CO₂, $\nu_{\text{C=O}}$ and $\nu_{\text{C-H}}$ were observed at (2255–2347, 669 cm⁻¹), 1798 and (2893–3017) cm⁻¹ respectively, indicating the loss of carboxylic acid ligands. At 764.32 K, there are only strong absorption peak of CO₂ and H₂O in the infrared spectrum. This indicates that the carboxylic acid ligands have been completely decomposed.

3.4 Luminescence measurements

The luminescent properties of solid-state complex **4** were studied at room temperature. The excitation and emission spectra of **4** are shown in Fig. 8a. The fluorescence decay curve was shown in Fig. 8b. From the excitation spectrum, we can see a wide absorption band, that is, the absorption peak of electron transition from ligand to metal ion. The strength of the absorption band proves that carboxylic acid ligand as an antenna can effectively sensitize lanthanide ions²⁹.

For complex **4**, the emission spectrum was scanned at the excitation wavelength of 330 nm. It exhibits five emission peaks of Eu³⁺: $^5D_0 \rightarrow ^7F_j$ ($j = 0-5$) (581, 591, 621, 651, 701 nm). The emission at 621 nm was the electric dipole transition $^5D_0 \rightarrow ^7F_2$, while the emission at 591 nm was magnetic dipole transition $^5D_0 \rightarrow ^7F_1$. The highest peak $^5D_0 \rightarrow ^7F_2$ appears at 621 nm, which is the reason why the complex presents strong red light under the UV lamp. Moreover, $^5D_0 \rightarrow ^7F_2$ is higher than $^5D_0 \rightarrow ^7F_1$ indicated that the Eu³⁺ was located in an asymmetric coordination. According to the Judd-Ofelt theory, the $^5D_0 \rightarrow ^7F_0$ transition occurs only in asymmetric environments³⁰. While, this transition was observed at 581 nm indicating that the Eu³⁺ is

Fig. 8 (a) Emission and excitation spectrum of complex **4** in the solid state; (b) The fluorescence attenuation curves of the complex **4**.

Fig. 9 Temperature dependence of the $\chi_M T$, and $1/\chi_M T$ susceptibility for complex **6** in the range of 2–300 K.

at the asymmetric center. The lifetime (τ) of complex **4** can be calculated by the following equation:

$$\tau = (B_1\tau_1^2 + B_2\tau_2^2)/(B_1\tau_1 + B_2\tau_2)$$

τ_1 and τ_2 are the decay times and B_1 and B_2 are the fitting constants³¹. Finally, the lifetime (τ) of **4** is 1.15 ms. Using the calculation formula proposed by Bunzli³² *et al.*, the intrinsic quantum yield is calculated to be 45.1%.

3.5 Magnetic properties

The magnetic properties of **6** in the temperature range of 2–300 K were studied under the applied magnetic field of 1000 Oe. The $\chi_M T$ and $1/\chi_M$ vs T of complex **6** are shown in Fig. 9.

For complex **6**, the $\chi_M T$ value of 28.08 cm³·K·mol⁻¹ at room temperature is similar to the calculated value 28.34 cm³·K·mol⁻¹ of two isolated Dy³⁺ ($^6H_{15/2}$, $J = 15/2$, $g = 4/3$). With the decrease of temperature, the $\chi_M T$ value of **6** decreased slowly in the temperature range of 300–50 K, but with the continuous decrease of temperature, the $\chi_M T$ value decreased sharply and reached the minimum value of 14.93 cm³·K·mol⁻¹ at 2 K, which can be attributed to the antiferromagnetic interaction between Dy³⁺³³.

4 Conclusions

In conclusion, six new ternary lanthanide complexes formulated as [Ln(2,4,6-TMBA)₃(5,5'-DM-2,2'-bipy)]₂ (Ln = Pr **1**, Nd **2**, Sm **3**, Eu **4**, Gd **5**, Dy **6**) have been synthesized under the solvothermal conditions. The structural analyses revealed that complexes **1–5** are isostructural and each center metal ion is nine-coordinated, while complex **6** is different with another structures and each center metal ion is eight-coordinated. Complexes **1–5** are packed into 2D sheet via the π - π stacking interactions while complex **6** forms a 2D sheet through the π - π stacking interactions and C—H $\cdots$ O hydrogen bond interaction. Thermal analysis show that complexes **1–6** have similar thermal decomposition mechanisms and high thermal stability. The study of photoluminescence shows that solid complex **4** emits strong red light in the visible region, which indicates that 2,4,6-tmhbbs are highly effective sensitizers and are expected to become luminescent materials. The magnetic properties of complex **6** show that there is antiferromagnetic interaction in the synthesized complex.

Supplementary data: Crystallographic data for the structure reported in this paper are deposited in the Cambridge Crystallographic Data Center (CCDC 1906870(1); CCDC 1906869(2); CCDC 1906871(3); CCDC 1906867(4); CCDC 1906868(5); CCDC 1906865(6).)

Supporting Information: Thermal analysis curves of 1–6 are included. This information is available free of charge via the internet at <http://www.whxb.pku.edu.cn>.

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