

一对手性铕(III)配合物的合成和铁电性质

刘 建^{*,1,2} 张小朋³ 李承辉²

⁽¹⁾ 南京林业大学化学工程学院, 江苏省生物质绿色燃料与化学品重点实验室, 南京 210037)

⁽²⁾ 南京大学化学化工学院, 配位化学国家重点实验室, 人工微结构科学与技术协同创新中心, 南京 210023)

⁽³⁾ 海南师范大学化学与化工学院, 海南省水环境污染治理与资源化重点实验室, 海口 571158)

摘要: 合成并表征了一对蒎烯修饰的稀土铕(III)配合物 $\text{Eu}(\text{TTA})_3\text{L}_{1a}$ (**1a**) 和 $\text{Eu}(\text{TTA})_3\text{L}_{1b}$ (**1b**) (TTA=2-噻吩甲酰三氟丙酮, $\text{L}_{1a}=(+)-4,5$ -双蒎烯-2,2'-联吡啶, $\text{L}_{1b}=(-)-4,5$ -双蒎烯-2,2'-联吡啶)。化合物的手性特征通过 X 射线单晶结构和圆二色光谱进行了表征。配合物 **1a** 结晶于极性空间群 $P1$, 中心 Eu(III) 离子呈现出严重扭曲的四方反棱柱体的配位环境。鉴于非中心对称结构的特性, 配合物 **1a** 也表现出明显的铁电性质。

关键词: 配位化学; 手性铕(III)配合物; 晶体结构; 铁电性质

中图分类号: O614.33*8

文献标识码: A

文章编号: 1001-4861(2017)11-2060-05

DOI: 10.11862/CJIC.2017.256

Syntheses and Ferroelectric Properties of a Couple of Chiral Europium(III) Complexes

LIU Jian^{*,1,2} ZHANG Xiao-Peng³ LI Cheng-Hui²

⁽¹⁾ Jiangsu Key Lab of Biomass-based Green Fuels and Chemicals, College of Chemical Engineering, Nanjing Forestry University, Nanjing 210037, China)

⁽²⁾ Collaborative Innovation Center of Advanced Microstructures, State Key laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210023, China)

⁽³⁾ Key Laboratory of Water Pollution Treatment & Resource Reuse of Hainan Province, College of Chemistry and Chemical Engineering, Hainan Normal University, Haikou 571158, China)

Abstract: A couple of pinene-containing europium(III) complexes, $\text{Eu}(\text{TTA})_3\text{L}_{1a}$ (**1a**) and $\text{Eu}(\text{TTA})_3\text{L}_{1b}$ (**1b**) (TTA=thenoyltrifluoroacetate, $\text{L}_{1a}=(+)-4,5$ -bis(pinene)-2,2'-bipyridine, $\text{L}_{1b}=(-)-4,5$ -bis(pinene)-2,2'-bipyridine), were prepared and characterized. The chiral characterization was confirmed by single crystal X-ray diffraction and distinct electronic circular dichroism (CD) signals. Complex **1a** crystallizes in the polar space group $P1$, and a strongly distorted square-antiprism environment around the Eu(III) ion is exhibited. Due to the non-centrosymmetric structure, distinct ferroelectric behavior of complex **1a** was observed as expected. CCDC: 818185, **1a**.

Keywords: coordination chemistry; chiral europium(III) complexes; crystal structure; ferroelectric properties

Recently, multifunctional materials based on lanthanide complexes have received much attention due to their potential applications in optoelectronics^[1-3].

The introduction of chiral environments in lanthanide complexes would lead to a diversification of configuration and crystallize in a polar space group.

收稿日期: 2017-09-20。收修改稿日期: 2017-10-16。

江苏省自然科学基金(No.BK20150569)、国家自然科学基金(No.201502088)、江苏省科技支撑计划(No.BE2014147-2)、国家教育部博士点专项基金(No.20120091130002)资助项目。

*通信联系人。E-mail: liu.jian@njfu.edu.cn

Thus, interesting properties, such as ferroelectricity, piezoelectricity, triboluminescence, circular polarized luminescence (CPL) and second harmonic generation (SHG) would be expected^[4-7].

Ferroelectric materials possessing a spontaneous electric polarization that can be reversed by the application of an external electric field, are of great interest in the field of optics and electronics^[8]. Compared to the typical inorganic ABO_3 -type ferroelectrics, molecular-based ferroelectric materials show some advantages: larger spontaneous polarization, facile chemical vapor deposition (CVD) and convenient structural modification. Furthermore, owing to the high coordination numbers and the interaction between a central metal ion and its ligand field (LF), the structures of lanthanide complexes could be easily distorted and spontaneous dipole moments can be induced, possibly resulting in interesting multi-ferroic properties.

In previous studies, we have studied multifunctional properties (luminescence, ferroelectricity, magnetism and so on) of chiral lanthanide complexes incorporated pinene functionalized with aromatic amine derivatives as well as solvent-induced or temperature-induced switching of configurations and properties of these complexes^[9-12]. A novel Eu(III) complex $\text{Eu}(\text{TTA})_3\text{L}_{1a}$ (**1a**) (TTA=thenoyltrifluoroacetate, L_{1a} =(+)-4,5-bis(pinene)-2,2'-bipyridine) with a bispinene-containing bipyridyl ligand was used as high efficient luminescent down-shifting material and lead to a significant improvement of the spectral response of c-Si PV module in the UV region^[13].

As an extension of these work, the crystal structure and ferroelectric property of **1a** has been studied in this paper. The compound **1a** crystallizes in a noncentrosymmetric space group ($P1$), and a distorted square-antiprism configuration exists around the central Eu(III) ion, satisfying the prerequisites of ferroelectrics. As expected, complex **1a** shows a distinct electric hysteresis loop, making it as potential multifunctional molecular materials. The enantiomer $\text{Eu}(\text{TTA})_3\text{L}_{1b}$ (**1b**) (L_{1b} =(-)-4,5-bis(pinene)-2,2'-bipyridine) was also prepared, and chiral environments are

confirmed by a mirror symmetry of circular dichroism (CD) spectra of **1a** and **1b**.

1 Experimental

1.1 Chemicals and synthesis

All reagents were purchased from commercial suppliers and used as received. Compounds **1a** and **1b** were prepared according to our published methods as follows^[13]: L_{1a} or L_{1b} (344 mg, 1 mmol) was added to a stirred solution of $\text{Eu}(\text{TTA})_3 \cdot 2\text{H}_2\text{O}$ (851 mg, 1 mmol) in ethanol (40 mL). The resulting mixture was stirred at room temperature for 24 h. The precipitate was collected by filtration to yield the desired product. Crystals of compound **1a** suitable for X-ray crystallographic analysis were obtained by slow evaporation over a period of 3 weeks of their $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CH}_2\text{OH}$ solution.

1.2 Chemical and physical characterizations

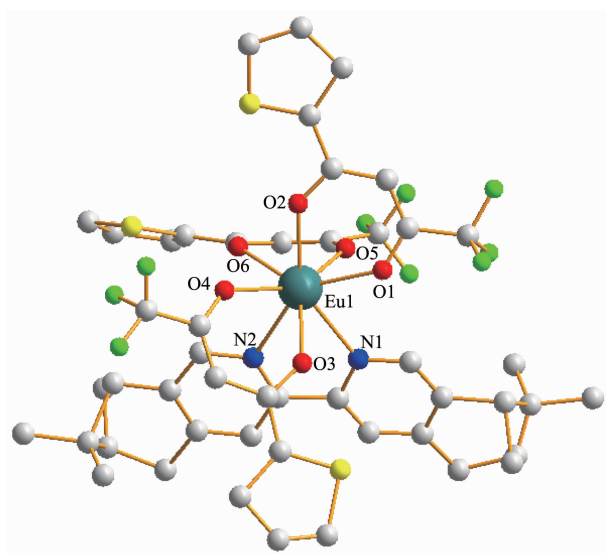
Single-crystal X-ray diffraction measurements were carried out on a Bruker SMART APEX CCD based on diffractometer operating at room temperature. Intensities were collected with graphite monochromatized Mo $K\alpha$ radiation ($\lambda=0.071\ 073\ \text{nm}$) operating at 50 kV and 30 mA, using ω - 2θ scan mode. The data reduction was made with the Bruker SAINT package^[14]. Absorption corrections were performed using the SADABS program^[15]. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares using SHELXL-97 with anisotropic displacement parameters for all non-hydrogen atoms in all two structures^[16]. Hydrogen atoms bonded to the carbon atoms were placed in calculated positions and refined as riding mode, with $d_{\text{C-H}}=0.093\ \text{nm}$ (methane) or $0.096\ \text{nm}$ (methyl) and $U_{\text{iso}}(\text{H})=1.2U_{\text{eq}}(\text{C}_{\text{methane}})$ or $U_{\text{iso}}(\text{H})=1.5U_{\text{eq}}(\text{C}_{\text{methyl}})$. All computations were carried out using the SHELXTL-97 program package^[16-17]. The absorption spectra of complexes **1a** and **1b** in CH_2Cl_2 solution were recorded on a Shimadzu UV-3100 spectrometer. CD spectra were recorded by a Jasco J-810 spectropolarimeter. The Electric hysteresis loops were recorded by a Ferroelectric Tester Precision Premier II by using powder samples in pellets at room temperature.

CCDC: 818185, **1a**.

2 Results and discussion

2.1 Crystal structure

The crystal data and structure refinements for compound **1a** are provided in Table 1. Similar to those europium(III) complexes reported previously^[4,12], compound **1a** is a mononuclear neutral europium(III) compound and crystallizes in triclinic system, space group *P*1. As shown in Fig.1, each molecule contains three β -diketonate anions, one (+)-4,5-bis(pinene)-2,2'-bipyridine, and one eight-coordinated Eu(III) ion. Each of the three diketonate anions provides two donor O atoms to coordinate to the Eu(III) ion. The other two



H atoms are omitted for clarity

Fig.1 Molecular structure of **1a**

coordination sites of the Eu(III) ion are occupied by two N atoms of the chiral bipyridine derivative to complete the eight-coordinate configuration.

Selected bond lengths and angles are summarized in Table 2. The Eu-O bond lengths range from 0.231 8 to 0.238 5 nm, while the two Eu-N bond lengths are 0.258 7(16) and 0.255 6(15) nm, respectively. Eight bonds with different lengths give rise to a strongly distorted square-antiprism environment around the Eu(III) ion (Fig.2). The O1-O2-O3-O4 (bottom plane) and O5-O6-N1-N2 atoms (top plane) comprise the two square-basic planes of the antiprism with mean deviations of 0.002 78 and 0.013 97 nm from each plane, and their dihedral angle is 3.442°. For a regular square antiprism, two square planes are parallel to each other and one square rotates 45° from the other. However, in **1a**, the top plane rotates only 41.4° from the bottom plane.

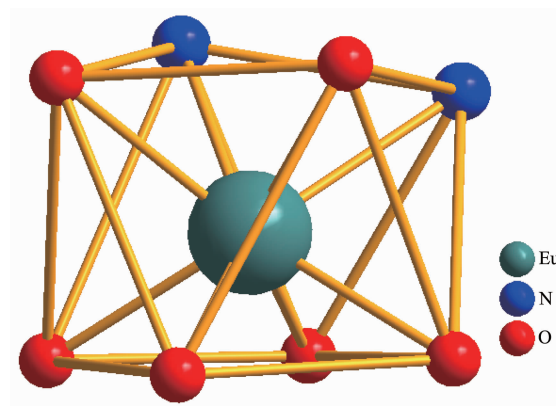


Fig.2 Coordination environments of **1a**

Table 1 Crystal data and structure refinements for complex **1a**

Empirical formula	C ₄₈ H ₄₀ EuF ₉ N ₂ O ₆ S ₃	<i>V</i> / nm ³	2.474 0(19)
Formula weight	1 159.96	<i>Z</i>	2
Crystal system	Triclinic	<i>D_c</i> / (Mg·m ⁻³)	1.557
Space group	<i>P</i> 1	<i>F</i> (000)	1 164
<i>T</i> / K	293(2)	Collected reflection	10 292
<i>a</i> / nm	1.066 9(5)	Unique reflection	7 702
<i>b</i> / nm	1.076 9(5)	Parameter	1 142
<i>c</i> / nm	2.354 9(10)	<i>R</i> ₁ , <i>wR</i> ₂ ^a [<i>I</i> >2σ(<i>I</i>)]	0.078, 0.188
α / (°)	88.832(6)	μ / mm ⁻¹	1.477
β / (°)	89.872(5)	GOF	1.133
γ / (°)	66.146(5)		

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

Table 2 Selected bond lengths (nm) and angles (°) for **1a**

Eu(1)-O(1)	0.233 2(12)	Eu(1)-O(2)	0.235 4(16)	Eu(1)-O(3)	0.236 4(13)
Eu(1)-O(4)	0.231 8(12)	Eu(1)-O(5)	0.232 6(12)	Eu(1)-O(6)	0.238 5(13)
Eu(2)-O(7)	0.234 3(13)	Eu(2)-O(8)	0.235 3(14)	Eu(2)-O(9)	0.234 6(13)
Eu(2)-O(10)	0.241 1(13)	Eu(2)-O(11)	0.236 7(13)	Eu(2)-O(12)	0.234 8(12)
Eu(1)-N(1)	0.258 7(16)	Eu(1)-N(2)	0.255 6(15)	Eu(2)-N(3)	0.263 9(16)
Eu(2)-N(4)	0.255 9(16)				
O(1)-Eu(1)-O(2)	7.07(6)	O(1)-Eu(1)-O(3)	8.37(5)	O(1)-Eu(1)-O(6)	13.93(5)
O(1)-Eu(1)-N(2)	14.07(5)	O(1)-Eu(1)-N(1)	7.93(5)	O(2)-Eu(1)-O(3)	11.80(6)
O(2)-Eu(1)-O(6)	8.20(6)	O(2)-Eu(1)-N(2)	14.84(6)	O(2)-Eu(1)-N(1)	14.65(5)
N(2)-Eu(1)-N(1)	6.23(5)	O(3)-Eu(1)-O(6)	13.67(4)	O(3)-Eu(1)-N(2)	7.71(5)
O(3)-Eu(1)-N(1)	7.19(5)	O(4)-Eu(1)-N(1)	13.40(5)	O(4)-Eu(1)-O(5)	14.79(5)
O(4)-Eu(1)-O(1)	12.02(5)	O(4)-Eu(1)-O(2)	7.62(5)	O(4)-Eu(1)-O(3)	7.00(5)
O(4)-Eu(1)-O(6)	7.96(5)	O(4)-Eu(1)-N(2)	8.47(5)	O(5)-Eu(1)-O(1)	7.84(5)
O(5)-Eu(1)-O(2)	8.77(5)	O(5)-Eu(1)-O(3)	14.16(5)	O(5)-Eu(1)-O(6)	7.06(5)
O(5)-Eu(1)-N(2)	9.59(5)	O(5)-Eu(1)-N(1)	7.16(5)	O(6)-Eu(1)-N(2)	6.99(5)
O(6)-Eu(1)-N(1)	11.36(5)	O(7)-Eu(2)-O(9)	7.76(5)	O(7)-Eu(2)-O(12)	12.03(5)
O(7)-Eu(2)-O(8)	7.14(5)	O(7)-Eu(2)-O(11)	8.13(5)	O(7)-Eu(2)-O(10)	14.22(5)
O(7)-Eu(2)-N(4)	13.69(5)	O(7)-Eu(2)-N(3)	7.82(5)	O(8)-Eu(2)-O(10)	8.64(5)
O(8)-Eu(2)-N(4)	15.12(5)	O(8)-Eu(2)-O(11)	11.80(5)	O(8)-Eu(2)-N(3)	14.48(5)
O(9)-Eu(2)-O(8)	8.48(5)	O(9)-Eu(2)-O(11)	14.17(4)	O(9)-Eu(2)-O(12)	14.72(5)
O(9)-Eu(2)-O(10)	7.01(5)	O(9)-Eu(2)-N(4)	10.45(5)	O(9)-Eu(2)-N(3)	7.14(5)
O(10)-Eu(2)-N(4)	7.19(5)	O(10)-Eu(2)-N(3)	10.84(5)	O(11)-Eu(2)-O(10)	13.65(4)
O(11)-Eu(2)-N(4)	7.09(5)	O(11)-Eu(2)-N(3)	7.31(5)	O(12)-Eu(2)-O(8)	7.68(4)
O(12)-Eu(2)-O(11)	7.10(4)	O(12)-Eu(2)-O(10)	8.16(5)	O(12)-Eu(2)-N(4)	8.14(5)
O(12)-Eu(2)-N(3)	13.57(5)	N(4)-Eu(2)-N(3)	6.27(5)		

2.2 Circular dichroism (CD) spectra

The chirality of complexes **1a** and **1b** is confirmed by measuring circular dichroism (CD) spectra (Fig.3). Two distinct Cotton effect at 245 and

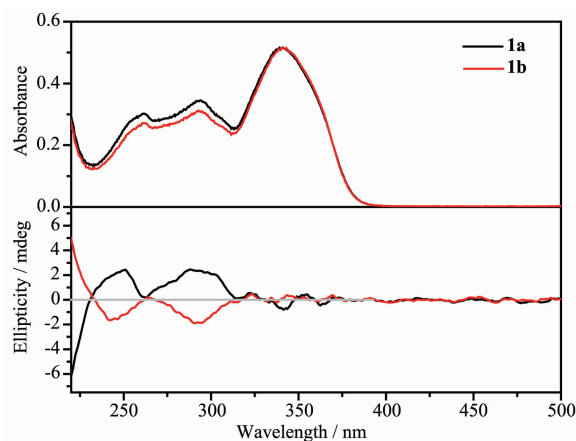


Fig.3 UV-Vis and CD spectra of **1a** and **1b** in 2×10^{-5} mol·L⁻¹ dichloromethane solution

292 nm can be observed, and the spectra of **1a** and **1b** are almost mirror-symmetric. These features indicate that **1a** and **1b** are chiral and enantiomeric to each other.

2.3 Ferroelectric properties

Since complexes **1a** crystalizes in a polar space group (*P*1), the ferroelectric properties of **1a** were investigated at 298 K with compressed powder samples as shown in Fig.4. The ferroelectric measurements reveal that complex **1a** indeed displays an obvious ferroelectric behavior and almost reaches the saturated polarization status with a remnant polarization (*P_r*) of *ca.* 0.27 μC·cm⁻² and *E_c* of *ca.* 7.2 kV·cm⁻¹ by applying an electric field of 15 kV·cm⁻¹ at 4 Hz. The saturation spontaneous polarization (*P_s*) is about 0.43 μC·cm⁻², which exceeds the value of typical ferroelectrics NaKC₄H₄O₆·4H₂O (Rosal salt,

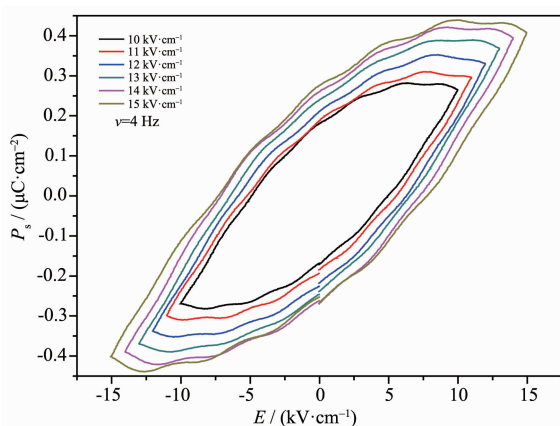


Fig.4 Ferroelectric hysteresis loop for complex **1a** at 298 K

$P_s = 0.25 \mu\text{C} \cdot \text{cm}^{-2}$).

3 Conclusions

In summary, a couple of pinene-containing chiral europium(III) complexes **1a** and **1b** were prepared. The chirality of complexes **1a** and **1b** is confirmed by measuring circular dichroism (CD) spectra. Complexes **1a** crystallizes in *P1* space group of triclinic system. The coordination polyhedron of the Eu(III) ion in **1a** can be described as a significantly distorted square-antiprism. The complex **1a** exhibited distinct ferroelectric behaviors with a remnant polarization (P_r) of *ca.* $0.27 \mu\text{C} \cdot \text{cm}^{-2}$ and E_c of *ca.* $7.2 \text{ kV} \cdot \text{cm}^{-1}$ by applying an electric field of $15 \text{ kV} \cdot \text{cm}^{-1}$ at 4 Hz.

Acknowledgements: This work was supported by the Jiangsu Province Science Foundation for Youths (Grant No. BK20150569), the National Natural Science Foundation of China (Grant No.201502088), the project of Scientific and Technological Support Program in Jiangsu province (Grant No. BE2014147-2), and the Doctoral Fund of the Ministry of Education of China for financial support (Grant No. 20120091130002).

References:

- [1] Walton J W, Bourdolle A, Butler S J, et al. *Chem. Commun.*, **2013**,**49**(16):1600-1602
- [2] Kotova O, Kitchen J A, Lincheneau C, et al. *Chem. Eur. J.*, **2013**,**19**(48):16181-16186
- [3] Carr R, Di Bari L, Lo Piano S, et al. *Dalton Trans.*, **2012**,**41**(42):13154-13158
- [4] Li D P, Li C H, Wang J, et al. *Eur. J. Inorg. Chem.*, **2009**(32):4844-4849
- [5] Bozoklu G, Gateau C, Imbert D, et al. *J. Am. Chem. Soc.*, **2012**,**134**(20):8372-8375
- [6] Harada T, Tsumatori H, Nishiyama K, et al. *Inorg. Chem.*, **2012**,**51**(12):6476-6485
- [7] Li X L, Chen C L, Xiao H P, et al. *Dalton Trans.*, **2013**,**42**(43):15317-15325
- [8] Hang T, Zhang W, Ye H Y, et al. *Chem. Soc. Rev.*, **2011**,**40**(7):3577-3598
- [9] Li D P, Wang T W, Li C H, et al. *Chem. Commun.*, **2010**,**46**(17):2929-2931
- [10] Li D P, Zhang X P, Wang T W, et al. *Chem. Commun.*, **2011**,**47**(24):6867-6869
- [11] Liu J, Zhang X P, W T, et al. *Inorg. Chem.*, **2012**,**51**(16):8649-8651
- [12] Li X L, Chen K, Liu Y, et al. *Angew. Chem. Int. Ed.*, **2007**,**46**(36):6820-6823
- [13] Liu J, Wang K, Zheng W, et al. *Prog. Photovoltaics Res. Appl.*, **2013**,**21**(4):668-675
- [14] SAINT-Plus, Ver. 6.02, Bruker Analytical X-ray System, Madison, WI, **1999**.
- [15] Sheldrick G M. *SADABS, an Empirical Absorption Correction Program*, Bruker Analytical X-ray Systems, Madison, WI, **1996**.
- [16] Sheldrick G M. *SHELXL-97, Program for Crystal Structure Refinement*, University of Göttingen, Germany, **1997**.
- [17] Sheldrick G M. *Acta Crystallogr. Sect. A: Found. Crystallogr.*, **2008**,**64**:112-122