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Dramatic improvement in photostability of luminescent Eu(III) complexes with tetraphenylimidodiphosphinate ligand

Wei Zheng, Shu-Jing Li, Cheng-Hui Li*, You-Xuan Zheng, Xiao-Zeng You*

State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing National Laboratory of Microstructures, Nanjing University, Nanjing 210093, PR China

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ABSTRACT

In this paper, we synthesized and characterized a new Eu(III) tetraphenylimidodiphosphinate complex with dimethyl sulfoxide (DMSO) as co-ligand. Moreover, we compared the photostability of a series of Eu(III) complexes containing tetraphenylimidodiphosphinate ligands, $Eu(tpip)_3$, $Eu(tpip)_3Phen$, $Eu(tpip)_3DMSO$, with their analogs of 1,3-dibenzoylmethanate, $Eu(dbm)_3\cdot 2H_2O$, $Eu(dbm)_3Phen$, $Eu(dbm)_3(DMSO)_2$. We found that the photostability of the luminescent Eu(III) complexes was significantly improved upon substitution of the 1,3-diketones with tetraphenylimidodiphosphinate ligands.

1. Introduction

Luminescent Eu(III) β-diketonate complexes have attracted intensive attention due to their intriguing luminescent properties (high emission quantum yield, narrow bandwidth, long-lived emission, and large stokes shifts, etc.) [1–3] which are useful in many applications such as luminescent labels [4,5], sensors [6–10], light-conversion materials [11–13] and organic light-emitting devices [14–19]. The photostability during prolonged illumination is an important factor to consider when the application of Eu(III) β-diketonate complexes in luminescent devices is assessed. Unfortunately, most of the Eu(III) β-diketonate complexes are unstable towards long-term UV irradiation [20], which restricts their application. It has been reported that the photostability of luminescent Eu(III) complexes can be improved by incorporating them into inert host matrices, such as silica-based materials [21–28], natural minerals [29,30], polymers [31–36], or ionic liquid [37]. The matrices act as protective cages for the luminescent Eu(III) complexes and therefore can strongly decrease the UV degradation rate [38]. However, in order to incorporate the Eu(III) complexes into inert host matrices, the ligands in the Eu(III) complexes or the surface of the host matrices have to be functionalized, such as anchoring with triethoxysilane, amino, carboxyl or hydroxyl groups, so that they can covalently grafted to each other, which require additional synthesizing efforts. Moreover, embedding the Eu(III) complexes into inorganic host matrices also lead to the insolubility or fluidity which makes it difficult for the subsequent processes. It is still a challenge to obtain intrinsically photostable luminescent Eu(III) complexes [39].

Recently, attention was drawn to the "inorganic analogs" of 1,3-diketones, namely tetraarylimidodiphosphinates (tpip) providing O=P–N–P=O binding site [40–47] (Scheme 1). We envisage that Eu(III) complexes with tpip ligand may have higher photostability due to the presence of strong and polar P=O bond. In this work, a new Eu(III) tetraphenylimidodiphosphinate complex with dimethyl sulfoxide (DMSO) as co-ligand was synthesized and characterized. Moreover, we compared the photostability of a series of Eu(III) complexes containing tetraphenylimidodiphosphinate ligands, $Eu(tpip)_3$, $Eu(tpip)_3Phen$, $Eu(tpip)_3DMSO$, with their analogs of 1,3-dibenzoylmethanate, $Eu(dbm)_3\cdot 2H_2O$, $Eu(dbm)_3Phen$, $Eu(dbm)_3(DMSO)_2$. Our results indicate that the photostability of the luminescent Eu(III) complexes can be significantly improved upon substitution of the 1,3-diketones with tetraphenylimidodiphosphinate ligands.

2. Experimental

2.1. Materials

$Eu(dbm)_3\cdot 2H_2O$, $Eu(dbm)_3Phen$, $Eu(dbm)_3(DMSO)_2$, $Eu(tpip)_3$, and $Eu(tpip)_3Phen$, were synthesized by the published methods [41,46]. Other reagents were purchased from commercial suppliers and used as received.

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* Corresponding authors. Tel.: +86 25 8359 2969; fax: +86 25 8331 4502.
E-mail addresses: chli@nju.edu.cn (C.-H. Li), youxz@nju.edu.cn (X.-Z. You).

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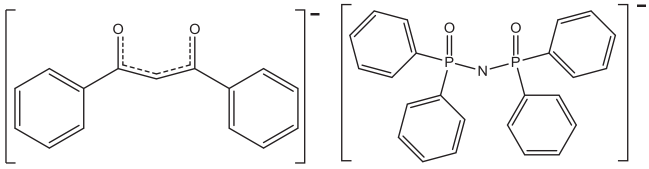

dbm **tpip**

Scheme 1. Structure of dbm and tpip ligands.

2.2. Measurements

Elemental analyses for C, H and N of the complexes were performed on a perkin-Elmer 240C analyzer. Thermogravimetric analysis were measured on a Hitachi TG/DTA7300 thermal analyzer. Infrared spectra were recorded in KBr pellet on a vector22 Bruker spectrophotometer in the range of 4000–400 cm^{-1}. UV–vis spectra were measured on a UV-3600 spectrophotometer. Fluorescent emission spectra and photostability measurement were performed on Hitachi 4600 luminescence spectrometer. The powder XRD patterns were recorded on a Shimadzu XD-3A X-ray diffractometer.

2.3. Synthesis of Eu(tpip)$_3$DMSO

0.14 g (0.1 mmol) Eu(tpip)$_3$ was dissolved in 10 mL DMSO and then heated to 150 °C for 24 h. The resultant solution was filtered and placed undisturbed for one week. Needle crystals of Eu (tpip)$_3$DMSO suitable for X-ray diffraction analysis were isolated (yield c.a. 45% based on Eu(tpip)$_3$). Anal Calc for Eu(tpip)$_3$DMSO ($C_{74}H_{68}N_3O_8P_6SEu$): C, 59.36; H, 4.58; N, 2.81%; Found: C, 59.50; H, 4.52; N, 2.77%. IR (KBr, cm^{-1}): 3406(m), 1611(s), 1533(m), 1461 (w), 1303(s), 1190(s), 1138(s), 977(m), 794(m), 572(w), 472(w).

2.4. X-ray crystallography

X-ray structure determination for Eu(tpip)$_3$DMSO was carried out on a Bruker SMART APEX CCD diffractometer at room temperature. The data integration and empirical absorption corrections were performed by SAINT program [48]. Absorption corrections were performed using the SADABS program [49]. The structure was solved by direct methods and refined anisotropically on F^2 by full-matrix least-squares techniques (SHELXL 97) [50]. Hydrogen atoms were generated geometrically and refined isotropically using the riding mode. Crystallographic data and details of the data collection and structure refinement are collected in Table 1, and selected bond distances and angles for Eu(tpip)$_3$DMSO are listed in Table 2. The crystallographic data has been deposited in the Cambridge Crystallographic Data Centre (CCDC 921899).

3. Results and discussions

3.1. Synthesis and crystal structure of Eu(tpip)$_3$DMSO

The new complex Eu(tpip)$_3$DMSO was prepared by heating the DMSO solution of Eu(tpip)$_3$ at 150 °C for one day. The resultant solution was filtered and placed undisturbed. Single crystals of Eu (tpip)$_3$DMSO suitable for X-ray analysis were obtained after several days. Unlike Eu(dbm)$_3$(DMSO)$_2$ which can be readily prepared by mixing the acetone solution of hydrated Eu(dbm)$_3$ complex and DMSO in 1:2 M ratio at room temperature, Eu(tpip)$_3$DMSO can only be prepared at high temperature in DMSO solution. Moreover, only one DMSO molecule can bind to Eu(tpip)$_3$ complex, in agreement with the bulky nature of the tpip ligand. Therefore, the coordination sphere of Eu(tpip)$_3$DMSO is composed of six oxygen atoms from tpip and one oxygen atom from DMSO. (Fig. 1). The Eu–O(tpip) bond lengths range from 2.316(7) to 2.379(2) Å (Table 2) which are typical in the literatures [40,41,46]. However, the Eu–O(DMSO) bond length in Eu(tpip)$_3$DMSO (2.463(3) Å) is significantly longer than those found in other Eu(III) complexes containing DMSO ligand [51,52]. The sulfur atoms are disordered in the crystal structure. CH–π interactions between adjacent molecules are observed (Fig. 2). The experimental XRD pattern is in good agreement with the simulated one from single crystal structures, manifesting the phase purity (Fig. 3)

3.2. Thermal properties

The thermogravimetric analysis (TGA) curves of Eu(tpip)$_3$, Eu (tpip)$_3$Phen and Eu(tpip)$_3$DMSO are shown in Fig. 4. The complexes

Table 1
Crystal and structure refinement data of Eu(tpip)$_3$DMSO.

Formula	$C_{74}H_{68}N_3O_8P_6SEu$
Mr	1497.15
Crystal system	Triclinic
Space group	*P*-1
a/Å	10.922(3)
b/Å	13.755(3)
c/Å	24.133(6)
α/°	87.408(4)
β/°	89.135(4)
γ/°	78.881(4)
V/Å^3	3558.9(15)
Z	2
T/K	296(2)
D_{calcd}, g/cm^{-3}	1.397
μ/mm^{-1}	1.102
F(000)	1532
Reflections measured	24 088
Unique reflections	15 957
R_{int}	0.0166
Number of parameters	836
Goodness-of-fit on F^2	1.039
R_1[a],wR_2[b][$I > 2\sigma(I)$]	0.0405, 0.1095
R_1,wR_2 (all data)	0.0468, 0.1141
$\Delta\rho_{max}$, $\Delta\rho_{min}$/eÅ^{-3}	1.077, −2.268

[a] $R_1 = \Sigma(|Fo|-|Fc|)/\Sigma|Fo|$,
[b] $wR_2 = [\Sigma w(Fo^2-Fc^2)^2/\Sigma w(Fo^2)^2]^{1/2}$.

Table 2
Selected bond lengths (Å) and angles (°) for Eu(tpip)$_3$DMSO.

Bond distance	(Å)	Bond angle	(°)
Eu(1)–O(1)	2.331(2)	O(1)–Eu(1)–O(2)	76.70(9)
Eu(1)–O(2)	2.379(2)	O(1)–Eu(1)–O(3)	80.97(9)
Eu(1)–O(3)	2.328(2)	O(1)–Eu(1)–O(4)	128.79(9)
Eu(1)–O(4)	2.358(2)	O(1)–Eu(1)–O(5)	119.93(10)
Eu(1)–O(5)	2.316(2)	O(1)–Eu(1)–O(6)	72.75(9)
Eu(1)–O(6)	2.368(2)	O(1)–Eu(1)–O(7)	143.14(9)
Eu(1)–O(7)	2.463(3)	O(2)–Eu(1)–O(3)	92.53(10)
		O(2)–Eu(1)–O(4)	150.05(9)
		O(2)–Eu(1)–O(5)	84.31(10)
		O(2)–Eu(1)–O(6)	130.47(9)
		O(2)–Eu(1)–O(7)	73.46(9)
		O(3)–Eu(1)–O(4)	78.65(9)
		O(3)–Eu(1)–O(5)	157.14(10)
		O(2)–Eu(1)–O(4)	150.05(9)
		O(3)–Eu(1)–O(6)	119.38(10)
		O(3)–Eu(1)–O(7)	79.24(10)
		O(4)–Eu(1)–O(5)	92.86(10)
		O(4)–Eu(1)–O(6)	77.48(9)
		O(4)–Eu(1)–O(7)	76.77(9)
		O(5)–Eu(1)–O(6)	78.50(9)
		O(5)–Eu(1)–O(7)	78.16(10)
		O(6)–Eu(1)–O(7)	144.03(9)