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A Novel Photo and Thermal Stable Dysprosium Complex with Tetraphenylimidodiphosphinate Acid[1]

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Abstract—The first Dy(III) tetraphenylimidodiphosphinate complex $Dy(Tpip)_3$ was synthesized and characterized by elemental analysis, IR, TG, and X-ray diffraction analysis. The aryl-functionalised imidodiphosphinate ligand (Tpip) provides a bidentate anionic site that leads to a hexa-coordinate dysprosium complex $[Dy(Tpip)_3]$. The X-ray single-crystal structural analysis indicates that the structure crystallizes to a trigonal system with a space group $P\bar{3}$, $a = 23.4638(17)$, $c = 21.3207(18)$ Å, and $Z = 6$. It shows excellent thermal stability with no obvious weight loss below 400°C. The luminescence experiment shows that the complex exhibits the typical luminescence of Dy^{3+} ion in the visible region. The photo stability of $Dy(Tpip)_3$ is very good and the emission intensity remains above 94% as it of before excited upon excitation for 3600 s.

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INTRODUCTION

In recent years, the design and synthesis of lanthanide complexes (RE) are a research focus not only because of the intriguing variety of architectures and topologies in supramolecular chemistry and crystal engineering [1, 2], but also the special photo/electroluminescence [3–6], magnetism [7–9], and photocatalysis [10, 11]. Particularly, optical properties of lanthanide coordination complexes become a highly active and fast-growing research field owing to the strong fluorescence deriving from *f–f* transitions, which lead to long fluorescence lifetimes, large Stokes' shift and shark emission peaks. The intra-configuration of 4*f*–4*f* transitions in lanthanide ions are Laporte-forbidden, but organic ligands called as "antennas" [12] can absorb the excitation light and transfer the energy from their lowest triplet state energy level (*T*) to the resonance level of RE(III) ions, which makes the luminescence intensity of RE(III) ions stronger. By employing different organic ligands, large amount of rare earth complexes bearing unique luminescent properties have been synthesized, especially Sm(III), Eu(III), Tb(III) and Dy(III) complexes. A series of lanthanide metal-organic frameworks $[Ln(L)(Bpdc)_{0.5}(Phen)]_\infty$ (Ln = Eu, Gd, Tb, Dy; L = 4,4'-bis(2-sulfonatostyryl)biphenyl; Bpdc = 4,4'-biphenyldicarboxylate; Phen = 1,10-phenanthroline) were prepared in [13]. These compounds display intriguing fluorescent properties including strong intensity, bathochromic-shift and the variable and versatile emission bands. The Sm, Eu, Tb, and Dy complexes of the type $[Ln(Hfaa)_3(Phen)]$ (Hfaa = hexafluoropentanedione) were successfully synthesized, and the quantum yields (Φ = 46, 32, 2.7, and 2.1% for Eu, Tb, Sm, and Dy, respectively) of the complexes indicate that energy transfer from ligands (Hfaa and Phen) to Ln(III) is efficient [14].

We are interested in the development of neutral lanthanide complexes with ligands that completely encapsulate the ion forming a hydrophobic shell around the metal ion. In order to achieve this, we need strong binding sites that coordinate to the lanthanide and bulky aromatic units that are "independent/remote" from the binding site and which form the hydrophobic shell. We have chosen tetraphenylimidodiphosphinate (Tpip) as an ideal ligand, which can be regarded as the "inorganic analog" of 1,3-diketones providing O=P–N–P=O binding site [15]. We envisage that complexes with Tpip may have higher thermal stability due to its inorganic nature. The structure and luminescence properties of $Eu(Tpip)_3 \cdot 0.67H_2O$ and $Tb(Tpip)_3$ were reported in [16]. Two interesting bis-cyclometalated iridium complexes using Tpip as the ancillary ligand were synthesized in [17] and they are good green and blue-green phosphorescent materials having potential applications in OLEDs, particularly at high luminance and high current density. In this work, we used the ligand tetraphenylimidodiphosphinate acid (HTpip) to construct the compound $Dy(Tpip)_3$ (**I**). The structure of the Dy(III) complex was characterized by single crystal X-ray diffraction, the themal property and PL spectra of it were investigated too.

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[1] The article is published in the original.

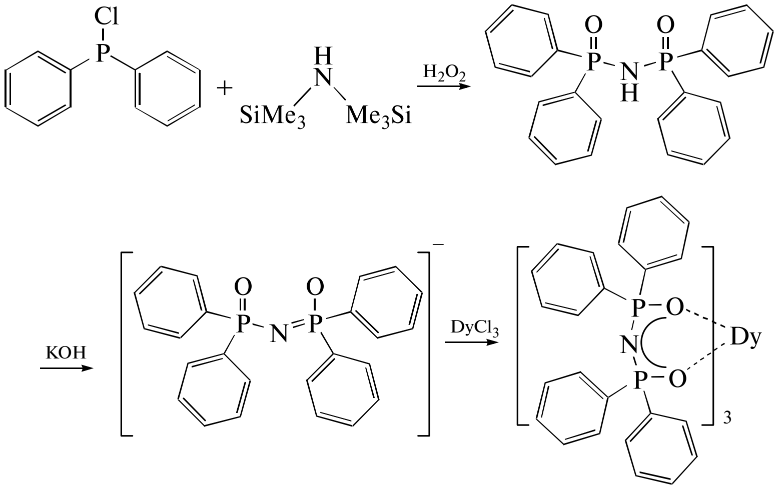
EXPERIMENTAL

Materials and methods. All chemicals of analytical grade were purchased from Sigma-Aldrich and used as received. Elemental analyses for C, H, and N were performed on a PerkinElmer 240C analyzer. Solid infrared spectrum was recorded on a Vector22 Bruker Spectrophotometer with KBr pellets in the 400–4000 cm^{-1} region. TG analyse was collected on a PerkinElmer Pyris 1 TG-DSC STA 499F3 analyzer from room temperature to 800°C with a heating rate of 10°C/min under nitrogen. The powder XRD pattern was recorded on a Shimadzu XD-3A X-ray diffractometer. Solid-state luminescence spectra were recorded on HITACHI F-4600 fluorescence spectrophotometer.

Synthesis. The ligand HTpip was synthesized by the reaction of chlorodiphenylphosphine and hexamethyldisilazane followed by oxidation with H_2O_2. KTpip was prepared by dissolving HTpip in methanolic KOH solution and then adding diethyl ether [15]. One equivalent of $DyCl_3 \cdot 6H_2O$ was added drop by drop to three equivalents of KTpip to afford complex **I**. The synthetic route of complex **I** is shown in Scheme 1. Colorless block crystals suitable for X-ray structure analysis were obtained in 76% yield by evaporation of a concentrated solution of complex **I** in dichloromethane and ethanol.

For $C_{72}H_{60}N_3O_6P_6Dy$			
anal. calcd., %:	C, 61.26;	H, 4.28;	N, 2.98.
Found, %:	C, 61.30;	H, 4.33;	N, 2.95.

The IR spectrum of $Dy(Tpip)_3$ shows strong absorptions at 1223 and 1127 cm^{-1}, which can be assigned to the stretching of the group P–N–P. And the ν(P–O) stretch appears at 1089 and 1064 cm^{-1}. No obvious absorptions in the region between 3100 and 4000 cm^{-1} indicates there are no water moleculars coordinated to Dy(III).



Scheme 1. The synthetic route of complex **I**.

X-ray crystallography. The crystal structure of **I** has been solved by X-ray diffraction analysis. Intensity data were collected on a Bruker SMART CCD diffractometer using monochromated MoK_α radiation ($\lambda = 0.71073$ Å) at room temperature. The collected frames were processed with the software SAINT [18]. The structure was solved by the direct method and refined by full-matrix least-squares on F^2 using the program SHELXTL-97 [19]. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated position or found in the difference Fourier maps. The main crystallographic data are summarised in Table 1. Selected bond lengths and angles are listed in Table 2. Crystallographic data for structure **I** has been deposited in the Cambridge Crystallographic Data Centre (no. 92707; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The crystal structure of **I** is shown in Fig. 1. There are three $Dy(Tpip)_3$ molecules in each unit cell. The center atom dysprosium coordinates to six oxygen atoms from the three Tpip ligands with mean Dy–O bond length 2.26 Å. The geometry around dysprosium is a distorted octahedron with ODyO angles 156.148(69)° and 80.837(69)°–112.424(72)°. The center dysprosium bonds with three sets of skeleton atoms O–P–N–P–O

Table 1. Crystallographic data and structure refinement for complex **I**

Parameter	Value
Formula weight	1411.55
Temperature, K	296(2)
Crystal system	Trigonal
Space group	$P\bar{3}$
a, Å	23.4638(17)
b, Å	23.4638(17)
c, Å	21.3207(18)
α, deg	90
β, deg	90
γ, deg	120
Volume, Å^3	10165.5(13)
Z	6
ρ_{calcd}, mg m^{-3}	1.383
Absorption coefficient, mm^{-1}	1.297
F(000)	4302
θ Range for data collection, deg	1.00–27.55
Index ranges	$-30 \le h \le 29$, $-27 \le k \le 30$, $-21 \le l \le 27$
Reflections collected/unique	70183/15657
R_{int}	0.0339
Absorption correction	None
Max and min transmission	0.7814 and 0.7127
Data/restraints/parameters	15657/0/793
Goodness-of-fit on F^2	1.027
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0310$, $wR_2 = 0.0846$
R indices (all data)	$R_1 = 0.0463$, $wR_2 = 0.0945$
Largest diff. peak and hole, e Å^{-3}	2.472 and –0.718

to form three six-numbered rings, and the twelve phenyl groups surround them to construct a hydrophobic cage. In the powder XRD patterns for **I**, the diffraction peaks of simulated and experimental patterns match well at the relevant positions, indicating the phase purity. The difference in reflection intensities between the simulated and experimental patterns is due to the preferred orientation of the crystals in the powder sample.

The thermogram of complex **I** was recorded under nitrogen atmosphere at a heating rate of 10°C/min (Fig. 2). Before 400°C, the thermogram does not display any inflexion point, which indicates that it does not contain any kind of water (crystalliferous or coordinated). The complex has excellent thermal reliability, probably due to the high binding energy of O=P and N=P bonds. At 400°C, it begins to decompose and loses a fraction of weight corresponding to the decomposition of the ligands. The decomposition takes place in two stages, and the total weight loss for the complex is 72.6%.

Considering the excellent luminescent properties of Dy(III), the solid-state photoluminescent spectra were measured at room temperature. The solid-state excitation and emission spectra of **I** are shown in Fig. 3. Dy(Tpip)$_3$ exhibits emission bands at 487, 576, and 667 nm (λ_{ex} = 274 nm), which correspond to the $^4F_{9/2} \to {}^6H_{15/2}$, $^4F_{9/2} \to {}^6H_{13/2}$, $^4F_{9/2} \to {}^6H_{11/2}$ transitions, respectively. These are characteristic of Dy(III) and result in the typical yellow luminescence [20].

In order to investigate the photo stability of **I**, the Dy(III) complex with Dbm (dibenzoylmethane) ligand [21] was choosed as contrast. The photo stability of Dy(Tpip)$_3$ and Dy(Dbm)$_3$ was studied by successive scans of the solid sample for 3600 s under the same experimental conditions. The average intensity was re-

Table 2. Selected bond lengths (Å) and angles (deg) for **I***

Bond	d, Å	Bond	d, Å
Dy(1)–O(1)	2.2593(19)	Dy(1)–O(2)	2.2656(18)
O(1)–P(1)	1.518(2)	O(2)–P(2)	1.5140(18)
N(1)–P(1)	1.591(3)	N(1)–P(2)	1.594(2)
Angle	**ω, deg**	**Angle**	**ω, deg**
O(1)$^{\#1}$Dy(1)O(1)	87.82(7)	O(1)Dy(1)O(2)$^{\#1}$	80.86(7)
O(1)$^{\#2}$Dy(1)O(2)$^{\#2}$	156.21(7)	O(2)Dy(1)O(2)$^{\#1}$	84.21(7)
O(1)$^{\#1}$Dy(1)O(2)	112.39(8)	P(1)N(1)P(2)	120.46(15)
O(1)$^{\#2}$Dy(1)O(2)	80.86(7)	P(1)$^{\#1}$O(1)Dy(1)	133.37(12)
O(1)Dy(1)O(2)	156.21(7)	P(2)O(2)Dy(1)	132.38(11)
O(2)$^{\#2}$Dy(1)O(2)	84.21(7)	O(1)$^{\#2}$P(1)N(1)	116.55(12)
O(1)$^{\#1}$Dy(1)O(2)$^{\#1}$	156.21(7)	O(2)P(2)N(1)	116.11(12)
O(1)$^{\#2}$Dy(1)O(2)$^{\#1}$	112.39(7)		

* Symmetry code: $^{\#1}$ $-x + y, -x + 1, z$; $^{\#2}$ $-y + 1, x - y + 1, z$.

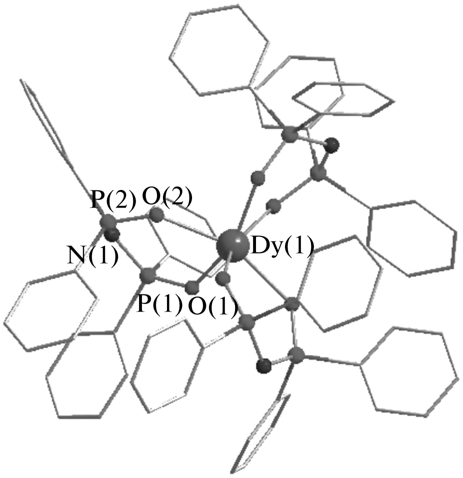


Fig. 1. The X-ray structure of Dy(Tpip)$_3$ (H atoms are omitted for clarity).

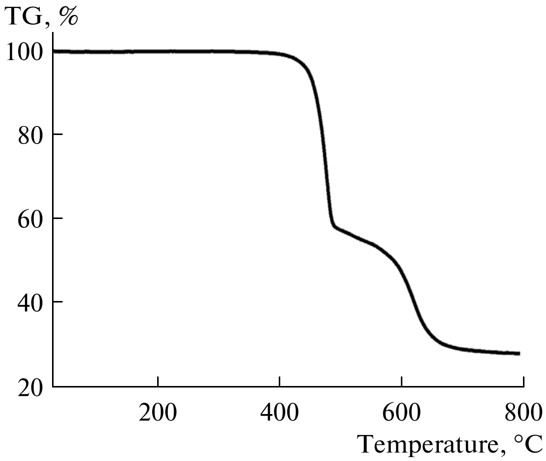


Fig. 2. TG curve of complex **I**.

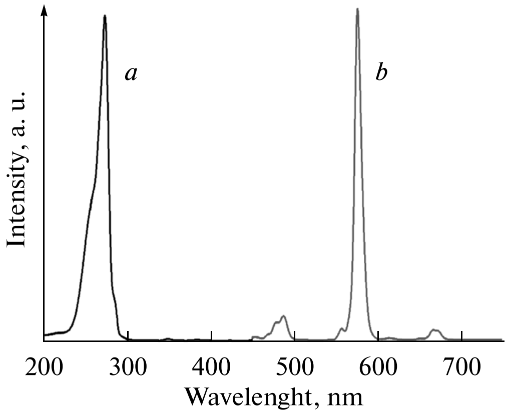


Fig. 3. Solid-state excitation (*a*) and emission (*b*) spectra of **I**.

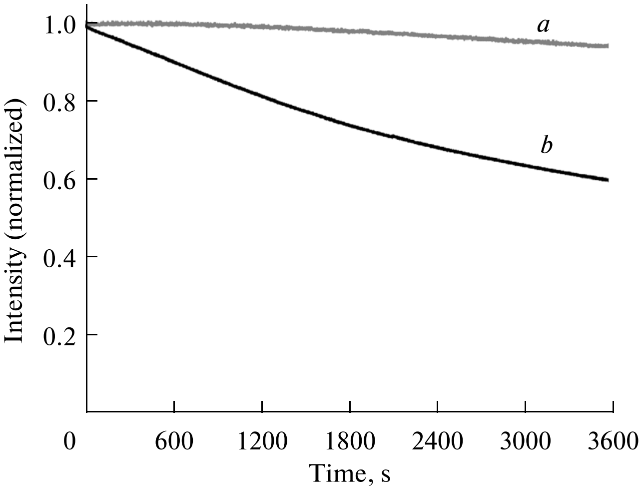


Fig. 4. Emission intensity on irradiation time for Dy(Tpip)$_3$ (*a*) and Dy(Dbm)$_3$ (*b*).

corded and normalized to its initial value. It is evident from Fig. 4 that the Dy(III) complex with Dbm ligand decays quickly upon successive photoexcitation to 59%. However, Dy(III) complex with Tpip ligand has excellent photostability. Upon excitation for 3600 s, the emission intensity of it remains above 94% as it of before excited.

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