

A NOVEL SAMARIUM COMPLEX WITH INTERESTING PHOTOLUMINESCENCE AND SEMICONDUCTIVE PROPERTIES

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ABSTRACT. $[\text{Sm}(\text{H}_2\text{O})_4(\text{NO}_3)_3](4,4'\text{-Hbipy})_2(\text{NO}_3)_2$ (**1**) (bipy = bipyridine) has been synthesized via hydrothermal reaction and characterized by X-ray diffraction. The title complex features an isolated structure, based on discrete 4,4'-Hbipy moieties, isolated nitrates and $[\text{Sm}(\text{H}_2\text{O})_4(\text{NO}_3)_3]$ species. The samarium ion is in a distorted bicapped square antiprism environment, coordinated by three bidentate nitrates and four coordination water molecules. The 4,4'-Hbipy moieties, isolated nitrates and $[\text{Sm}(\text{H}_2\text{O})_4(\text{NO}_3)_3]$ species are held together via hydrogen bonds and $\pi \dots \pi$ interactions to form a 3-D supramolecular framework. Luminescent investigation reveals a strong emission in blue region. Optical absorption spectrum of **1** reveals the presence of an optical gap of 3.60 eV.

KEY WORDS: Bipyridine, Crystal structure, Fluorescence, Hydrothermal reaction, Samarium

INTRODUCTION

Fluorescent materials, particularly blue fluorescent materials have gained strong interest because blue fluorescence is one of the key color components required for full-color EL displays and blue fluorescent materials are still rare up to now [1-5]. Recently, 4,4'-bipyridine (bipy) with delocalized π -electrons of the pyridyl rings obtains increasing attention in preparing light emitting complexes in different technical applications, such as emitting materials for organic light emitting diodes, sensitizers in solar energy conversion, chemical sensors and so forth [6-9]. The ability of bipy to act as a rigid, rod-like organic building block in the self-assembly of coordination frameworks is well-known, such as, acting as a charge-compensating cation, a pillar bonding to inorganic skeletal backbone, an uncoordinated guest molecule and organic template, a bridge connecting two metal complex moieties, or linking a metal and an inorganic framework [10-12]. Comparing with the neutral 4,4'-bipy, 4,4'-Hbipy cation is easier to form supramolecular frameworks through H-bonding. Our recent efforts in synthesizing novel complex have focused largely on the systems containing bifunctional molecule like 4,4'-bipy [13-19].

In this work, we describe the synthesis and characterization of $[\text{Sm}(\text{H}_2\text{O})_4(\text{NO}_3)_3](4,4'\text{-Hbipy})_2(\text{NO}_3)_2$ (**1**). It should be pointed out that the energy band gap of **1** is 3.60 eV, suggesting that compound **1** is a semiconductor.

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EXPERIMENTAL

Materials and measurements

Infrared spectra were carried out on a PE Spectrum-One FT-IR spectrometer using KBr discs. The UV-Vis spectrum was recorded at room temperature on a computer-controlled PE Lambda 35 UV-Vis spectrometer equipped with an integrating sphere in the wavelength range 190–1100 nm. BaSO₄ plate was used as a reference (100% reflectance), on which the finely ground powder of the samples were coated. The absorption spectrum was calculated from reflection spectra by the Kubelka-Munk function [20]: $\alpha/S = (1-R)^2/2R$, α is the absorption coefficient, S is the scattering coefficient which is practically wavelength independent when the particle size is larger than 5 μm , and R is the reflectance. The fluorescence study was conducted at room temperature on a JY Fluorolog-322 fluorescence spectroscopy instrument. All reactants of A.R. grade were obtained commercially and used without further purification.

Synthesis of complex 1

Sm(NO₃)₃·6H₂O (0.5 mmol, 222 mg), 4,4'-bipy(1 mmol, 156 mg), HNO₃ acid (1 mL) and distilled water (10 mL) were loaded into a Teflon-lined stainless steel autoclave (25 mL) and kept at 423 K for 10 days. After being slowly cooled to room temperature at a rate of 5 K/h, yellow crystals suitable for X-ray analysis were obtained. Yield: 61% (based on samarium). FT-IR peaks (KBr, cm⁻¹): 3447(m), 3063(m), 2462(w), 1950(w), 1847(w), 1613(vs), 1537(m), 1492(m), 1419(s), 1320(w), 1222(s), 1074(s), 1049(m), 1015(m), 862(w), 813(vs), 729(m), 641(s), 567(w) and 498(m).

X-ray data collection and structure refinement

X-ray diffraction data were collected on Rigaku Mercury CCD X-ray diffractometer with graphite monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) using a ω scan technique. Crystal Clear software was used for data reduction and empirical absorption correction. The structure was solved by the direct methods using the Siemens SHELXTL™ Version 5 package of crystallographic software. The difference Fourier maps based on the atomic positions yield all non-hydrogen atoms. The structure was refined using a full-matrix least-squares refinement on F^2 . All non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were generated theoretically, allowed to ride on their respective parent atoms and included in the structure factor calculations with assigned isotropic thermal parameters but not refined. The summary of crystallographic data and structure analysis is given in Table 1. The selected bond lengths are listed in Table 2. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 686904. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CBZ 1EZ, UK (Fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

RESULTS AND DISCUSSION

FT-IR spectroscopy

As for the title complex, its FT-IR bands are dominantly resided in the frequency range of 498–1613 cm⁻¹. The band at 3447 cm⁻¹ could be ascribed to the $\nu_{\text{O-H}}$ stretching vibration of the water molecules, while the band at 3063 cm⁻¹ could be assigned to the $\nu_{\text{C-H}}$ bent vibration mode

of the 4,4'-bipyridinium moieties. The strong intensity band locating at 1222 cm^{-1} could be attributed to the stretching mode of the pyridyl rings of the 4,4'-bipyridinium moieties. The band at 1074 cm^{-1} could be ascribed to the $\delta_{\text{C-H}}$ stretching vibration. The bands locating at the $641\text{--}1049\text{ cm}^{-1}$ region could be corresponded to the aromatic ring bending modes of the 4,4'-bipyridinium moieties. Two bands at 567 cm^{-1} and 498 cm^{-1} could be ascribed to the $\nu_{\text{Sm-O}}$ stretching vibration.

Table 1. Crystal data of $[\text{Sm}(\text{H}_2\text{O})_4(\text{NO}_3)_3](4,4'\text{-Hbipy})_2(\text{NO}_3)_2$.

Empirical formula	$\text{C}_{20}\text{H}_{26}\text{N}_9\text{O}_{19}\text{Sm}$
Formula weight	846.85
Crystal system	Triclinic
Space group	P_{-1}
Unit cell dimensions	$a = 8.1141(5)\text{ \AA}$ $b = 12.7860(8)\text{ \AA}$ $c = 15.1511(9)\text{ \AA}$ $\alpha = 95.050(1)^\circ$ $\beta = 101.689(1)^\circ$ $\gamma = 100.066(1)^\circ$
Z	2
V	$1503.1(2)\text{ \AA}^3$
D_x	1.871 Mg/m^3
Absorption coefficient	2.054 mm^{-1}
Crystal size	$0.48 \times 0.42 \times 0.27\text{ mm}$
No. of reflections collected/unique	9041/4903 [$R_{\text{int}} = 0.0184$]
Goodness-of-fit on F^2	1.095
Final R indices	$R_1 = 0.0251$, $wR_2 = 0.0645$
R indices (all data)	$R_1 = 0.0283$, $wR_2 = 0.0656$
Index ranges	$-9 \leq h \leq 9$, $-15 \leq k \leq 15$, $-18 \leq l \leq 18$
$(\Delta/\sigma)_{\text{max}}$	0.001

Table 2. Selected bond lengths of **1**.

Sm(1)-O(1W)	2.424(2)	Sm(1)-O(2)	2.493(2)
Sm(1)-O(2W)	2.429(2)	Sm(1)-O(4)	2.564(2)
Sm(1)-O(3W)	2.427(2)	Sm(1)-O(5)	2.509(2)
Sm(1)-O(4W)	2.479(2)	Sm(1)-O(7)	2.598(2)
Sm(1)-O(1)	2.797(3)	Sm(1)-O(8)	2.531(2)

Crystal structure of **1**

An ORTEP drawing of **1** is shown in Figure 1. X-ray diffraction analysis reveals that the title complex features an isolated structure, consisting of two 4,4'-Hbipy moieties, two isolated nitrates and one $[\text{Sm}(\text{H}_2\text{O})_4(\text{NO}_3)_3]$ species. The samarium atom is in a distorted bicapped square antiprism environment, coordinated by three bidentate nitrates and four coordination water molecules (Figure 1). The bond lengths of Sm(1)-O(1W), Sm(1)-O(2W), Sm(1)-O(3W) and Sm(1)-O(4W) are 2.424(2), 2.429(2), 2.427(2) and 2.479(2) Å, respectively, with an average value of 2.439(2) Å which is comparable with those reported [21-25]. In the three bidentate nitrate groups, the Sm-O_{nitrate} distances range from 2.493(2) to 2.797(3) Å (Table 2) with a mean value of 2.582(3) Å. The Sm-O_{nitrate} distances are comparable with those reported in the literature [26-30]. The average bond length of Sm-O_{water} is obviously shorter than that of Sm-O_{nitrate}, indicating that water has a stronger affinity to Sm^{III} ion than that of nitrate.

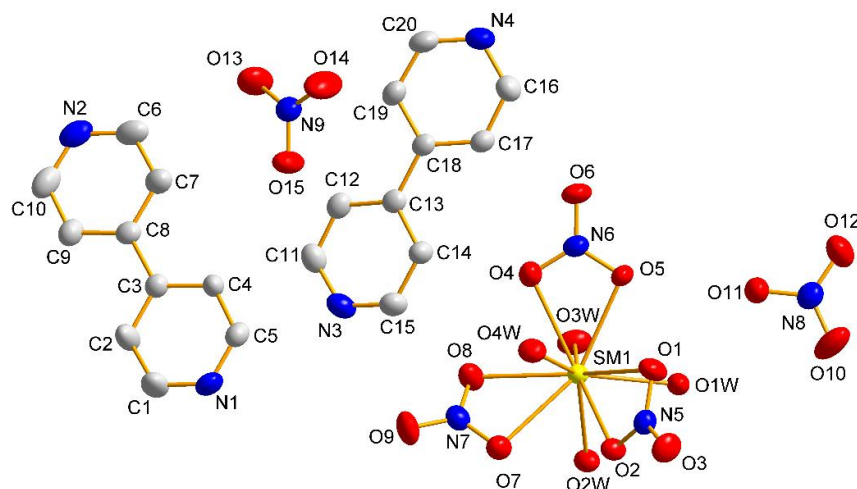


Figure 1. ORTEP drawing of **1** with 50% thermal ellipsoids. Hydrogen atoms were omitted for clarity.

There are two kinds of 4,4'-Hbipy moieties in the title complex. For one of them, the two pyridyl rings are twisted with a dihedral angle of *ca.* 3.91°, which is comparable with that previously documented [31, 32]; For another, the two pyridyl rings have a larger dihedral angle of *ca.* 14.75°, comparable with that previously documented [33-35]. In the title complex, some weak $\pi \dots \pi$ stacking interactions are established between the 4,4'-Hbipy moieties. The rings of the 4,4'-Hbipy moieties involved in the $\pi \dots \pi$ stacking interactions are arranged in such a way that the six atoms of each ring do not completely eclipse those of the other ring, meaning that the interaction is not “perfect face alignment” but “offset or slipped stacking”.

For clarity, we define the pyridyl rings involved into the $\pi \dots \pi$ stacking interactions as R1, R2 and R3, containing N2, N3 and N4 atoms, respectively. The R1 ring in one 4,4'-Hbipy moiety has a $\pi \dots \pi$ contact with a R1' ring in one adjacent 4,4'-Hbipy moiety; the R2 and R3 rings in one 4,4'-Hbipy moiety connects to a R3' and R2' ring in another adjacent 4,4'-Hbipy moiety via $\pi \dots \pi$ interaction. The centroid-to-centroid distance is 3.936 Å for rings R1 and R1', while it is 3.785 Å from R2 to R3' or R3 to R2'. The perpendicular distance from R1 to R1' is 3.473 Å, while it is 3.608 Å from R2 to R3' or R3 to R2'. R1 slides from R1' for about 1.852 Å, while R2 slides from R3' or R3 slides from R2' for about 1.143 Å. The dihedral angle is 0.02° between R1 and R1' while it is 14.75° between R2 and R3' or R3 and R2'. The [Sm(H₂O)₄(NO₃)₃] species interconnect to each other via O(3W) ... O(3) hydrogen bonds to yield a chain. The 4,4'-Hbipy moieties containing rings R2 and R3 link two such chains to form a ladder like structure through hydrogen bonds and $\pi \dots \pi$ contacts (Figure 2). The isolated nitrates and 4,4'-Hbipy moieties containing ring R1 bridge two neighboring ‘ladders’ via hydrogen bonds to give a 2-D layer. The 2-D layers are further interconnected via hydrogen bonds and $\pi \dots \pi$ contacts to construct a 3-D supramolecular framework (Figure 2).

Photoluminescence properties

The solid-state emission spectra of the title complex are investigated at room temperature. The emission spectrum of the title complex is given in Figure 3. The fluorescent spectrum study shows that the title complex exhibits a broad and strong blue-light emission band with a

maximum wavelength of 457 nm upon photo-excitation at 366 nm. The luminescent spectra of pure bipy were also measured under the same condition. For pure bipy, the emission spectra show one intense emission band in blue region with the maximum wavelength of 438 nm upon photo-excitation at 357 nm (inner plot of Figure 3). Thus, this complex may be a candidate in blue-light luminescent materials.

A search from the Cambridge Crystallographic Data Centre (CCDC) shows that there are dozens of complexes containing samarium [36-40]. However, among these complexes, only several are samarium-containing complex with bipy [41-45].

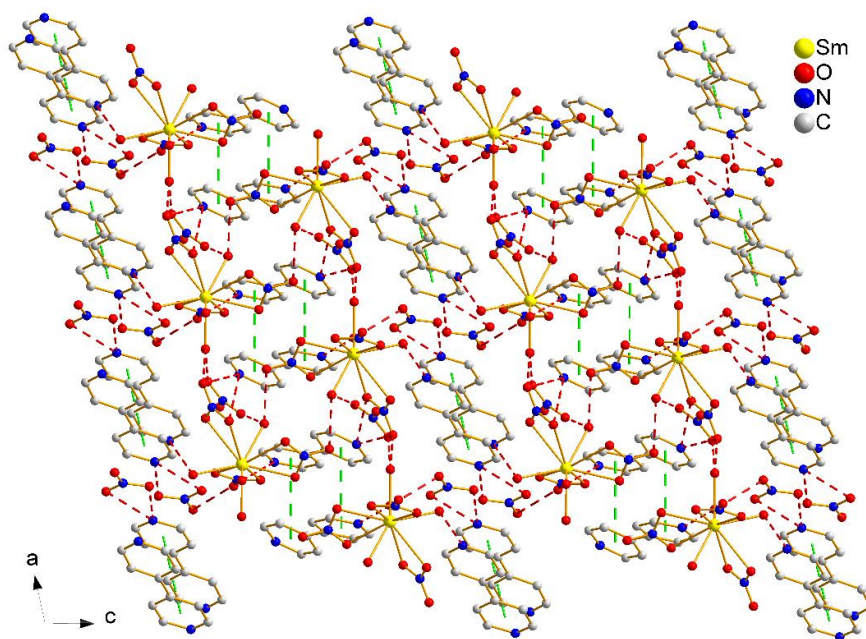


Figure 2. Packing diagram of **1** with the green and red dashed lines representing $\pi\cdots\pi$ interactions and hydrogen bonds, respectively. Hydrogen bonds(\AA): O1W...N1(-x, -y, -z) 2.786(4), O2W...N4(x, -1+y, z) 2.763(4), O2W...O10(1-x, -y, 1-z) 2.934(4), O3W...O3(1+x, y, z) 2.898(4), O3W...O13(1-x, 1-y, -z) 2.742(4), O4W...O14(-x, 1-y, -z) 2.681(4), O4W...O9(-x, -y, -z) 2.878(4), O2...N3(-x, -y, -z) 2.994(4), O3...N3(-x, -y, -z) 2.963(4), O11...N2(1-x, 1-y, -z) 2.796(4) and O12...N2(1-x, 1-y, -z) 3.040(4).

Semiconductive properties

Optical absorption spectrum of complex **1** discovers the presence of a wide optical band gap of 3.60 eV (Figure 4), which indicates that complex **1** is a potential semiconductor and this is consistent with the color of the crystals [46, 47]. The steep slope of the optical absorption edges for complex **1** is indicative of the existence of direct transitions [48]. It should be pointed out that the energy band gap of 3.60 eV of complex **1** is obviously larger than those of CuInS_2 (1.55 eV), CdTe (1.5 eV), CuInSe_2 (1.04 eV), and GaAs (1.4 eV), all of them are highly efficient photovoltaic materials [49-50]. The wide optical band gap of 3.60 eV of complex **1** is probably because of the 4,4'-Hbipy moieties which is an organic ligand and can enlarge the optical band gap.

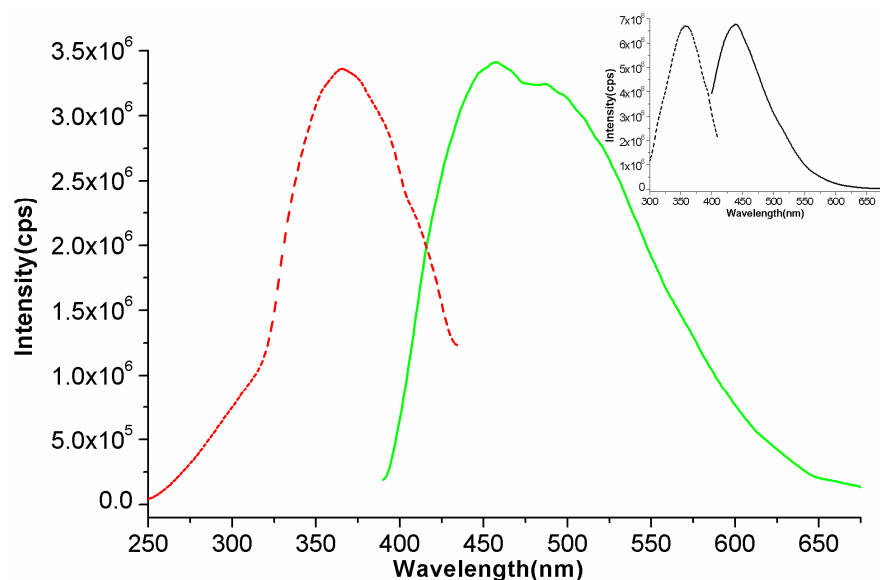


Figure 3. Solid-state emission and excitation spectra of **1** at room temperature (Inner plot: pure bipy). Solid line: emission spectrum; dashed line: excitation spectrum.

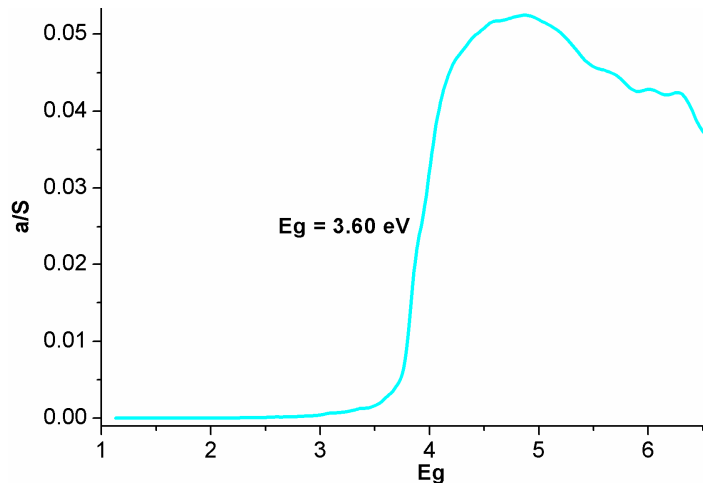


Figure 4. Solid-state diffuse reflectance spectrum of **1**.

CONCLUSION

In brief, a new complex, $[\text{Sm}(\text{H}_2\text{O})_4(\text{NO}_3)_3](4,4'\text{-Hbipy})_2(\text{NO}_3)_2$ (**1**), has been synthesized via hydrothermal reaction. It should be pointed out that the energy band gap of **1** is 3.60 eV,

suggesting that compound **1** is a wide optical band gap semiconductor. This complex exhibits a broad and strong fluorescent emission band, and it may be used as a blue-light material. Further investigations on this field are in progress in our laboratory.

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