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Syntheses, Structures, and Electroluminescence of Ln$_2$(acac-azain)$_4$(μ-acac-azain)$_2$ [acac-azain = 1-(*N*-7-azaindolyl)-1,3-butanedionato, Ln = Tb(III) and Y(III)]

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Two new luminescent lanthanide complexes Ln$_2$(acac-azain)$_4$(μ-acac-azain)$_2$ [acac-azain = 1-(*N*-7-azaindolyl)-1,3-butanedionato, Ln = Tb(III), **1**, Y(III), **2**] have been synthesized and structurally characterized. These two dinuclear complexes are isostructural with the two lanthanide ions being bridged by two acac-azain ligands. Each of the two metal ions is further chelated by four oxygen atoms from two acac-azain ligands, resulting in a coordination number eight for each metal ion. **1** displays characteristic Tb(III) emission bands while **2** displays weak blue luminescence attributable to the ligand. Single-layer and double-layer electroluminescent devices for compound **1** were fabricated, where compound **1** doped PVK layer functions as both the emitting layer and the hole transport layer and PBD functions as an electron transport layer (in the double-layer device), demonstrating that compound **1** is a promising green emitter in electroluminescent devices.

Introduction

Organic light-emitting diodes (OLEDs) have attracted intense research interest from both academia and industry recently due to their potential use in the development of energy-efficient, low-cost, full-color, flat-panel displays and other emissive products.[1−3] Owning to the unique f-electronic configuration, lanthanide luminescent materials have been demonstrated recently to be promising electroluminescent (EL) emitters, attributable to their very narrow emission bands and the potential high device efficiency, in comparison to fluorescent organic emitters.[3] However, the low f−f emission intensity of lanthanide ions demands activators, i.e. appropriate ligands that can enhance the f−f electronic transitions through an intersystem energy transfer process, to be present in the lanthanide compounds in order for the lanthanide compounds to be useful for the EL display.[3]

Our recent studies demonstrated that 7-azaindole can form a variety of blue luminescent organic and organometallic compounds, which typically have a large excitation band gap in the UV region, making 7-azaindole a potentially useful ligand as activators for lanthanide ions.[1i−k,2e] However, as a neutral ligand, 7-azaindole is not a good donor for lanthanide ions. Acetylacetonato (acac) and its derivatives (acac*) are well-known for forming stable and highly soluble or volatile

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lanthanide complexes. Some lanthanide complexes based on acac* ligands have been shown recently to be very bright emitters.[3e,j,4] However, lanthanide complexes that have been demonstrated to be useful emitters in EL devices are still rare. We therefore designed and synthesized the new ligand 1-(*N*-7-azaindolyl)-1,3-butanedione (Hacac-azain),[5] which combines the chelation capability of 1,3-butanedionato with the potential activator capability of 7-azaindole. When bound to a B(III) or a Al(III) center, the acac-azain ligand produces a blue emission.[5] We report herein the synthesis, structure, and electroluminescent properties of a new Tb(III) complex using acac-azain ligands as the activator. For comparison, the Y(III) analogue compound was also investigated.

Experimental Section

All starting materials were purchased from Aldrich Chemical Co. and used without further purification. All solvents were reagent grade and used without further purification. The Canadian Microanalytical Service Ltd., Delta, British Columbia, performed the elemental analyses. Excitation and emission spectra were recorded on a Photon Technologies International QuantaMaster model C-60 spectrometer. The decay lifetime of the compounds was recorded on a Time Master spectrometer of Photon Technologies International. UV−vis spectra were measured on a Varian Cary 3 UV−vis spectrophotometer. The quantum yield of complex **1** was determined by using $Tb(acac)_3$ ($\Phi = 0.19$) as the standard.[6] The quantum yield of **2** was obtained by using 9,10-diphenylanthracene as the standard. The synthesis of 1-(*N*-7-azaindolyl)-1,3-butanedione (Hacac-azain) was carried out according to the previously reported procedure.[5] The measurements of luminescent properties for all compounds were carried out under a nitrogen atmosphere.

Synthesis of Ln_2(acac-azain)$_4$(μ-acac-azain)$_2$ [Ln = Tb(III) (1); Y(III) (2)]. To a mixture of 0.50 mmol of $LnCl_3$ and 0.33 g (1.65 mmol) of Hacac-azain in 20 mL of acetone−water (1:1) was added 3.0 mL of 0.5 M sodium hydroxide solution dropwise under stirring at ambient temperature. The mixture was stirred for 1 h after the completion of the addition. Most of the acetone solvent was removed on a rotatory evaporator. The residual was extracted with CH_2Cl_2 (5 × 5 mL). The organic layer was collected, dried over Na_2SO_4 anhydrous, and filtrated. The filtrate was concentrated and layered by hexane. Colorless prism crystals suitable for X-ray single-crystal structural determination were obtained in 2−4 days. The yields are 70% and 50% for **1** and **2**, respectively. Anal. Calcd for Tb_2(acac-azain)$_4$(μ-acac-azain)$_2$·0.5CH_2Cl_2: C, 50.90; H, 3.54; N, 10.72. Found: C, 50.70; H, 3.53; N, 10.67. Anal. Calcd for Y_2(acac-azain)$_4$(μ-acac-azain)$_2$·0.5CH_2Cl_2: C, 55.96; H, 3.86; N, 11.78. Found: C, 55.20; H, 3.61; N, 11.67.

X-ray Diffraction Analyses. Crystals used for the data collections were sealed in glass capillaries to keep them from losing solvents. Data collections were performed at ambient temperature (298 K) on a Smart CCD 1000 X-ray diffractometer with Mo Kα radiation, operating at 50 KV and 30 mA.The data collection range over 2 Å is 2.96−56.78° for complex **1**. No significant decay was observed during the data collection. The reflection data were processed on a Pentium PC with use of the Bruker AXS SHELXTL NT software package (Version 5.10).[7] Neutral atom scattering factors were taken from Cromer and Waber.[8] Compounds **1** and **2** are isostructural and isomorphous, belonging to the monoclinic space group $P2_1/n$ (unit cell parameters for **2**: $a = 22.455(6)$ Å, $b = 15.893(6)$ Å, $c = 22.643(8)$ Å, $\alpha = 90°$, $\beta = 104.951(6)°$, $\gamma = 90°$, $V = 7812(21)$ Å^3). Therefore, no data collection for compound **2** was carried out. The structure of **1** was solved by direct methods. All non-hydrogen atoms were located directly from the difference Fourier maps and refined anisotropically. CH_2Cl_2 solvent molecules with partial occupancy factors were located and refined successfully. All hydrogen atoms were located by calculation and refined isotropically. The crystallographic data of **1** are given in Table 1.

Table 1. Crystal Data for **1**

formula	$C_{66}H_{54}N_{12}O_{12}Tb_2·H_2O·2.4\ CH_2Cl_2$
fw	1746.9
crystal system	monoclinic
space group	$P2_1/n$
a (Å)	22.413(5)
b (Å)	15.843(4)
c (Å)	22.678(5)
β (deg)	104.949(6)
V (Å^3)	7780(3)
Z	4
D_c (g cm^{-3})	1.491
T (K)	295
μ (mm^{-1})	2.033
λ (Å)	0.71073
2θ range (deg)	3.08−55.66
reflns collected	56471
independent reflns	18756
parameters	889
final R [$I > 2\sigma(I)$]	$R_1{}^a = 0.0738$
	$wR_2{}^b = 0.1652$
R (all data)	$R_1 = 0.2657$
	$wR_2 = 0.2139$
goodness-of-fit on F^2	0.753

[a] $R_1 = \sum|F_o|^2 - |F_c|^2/\sum|F_o|^2$. [b] $wR_2 = [\sum w[(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]]^{1/2}$. $w = 1/[\sigma^2(F_o{}^2) + (0.075P)^2]$, where $P = [\max(F_o{}^2,0) + 2F_c{}^2]/3$.

Fabrication of Electroluminescent Devices. The EL devices with compound **1** as the emitting layer were fabricated on a patterned indium−tin oxide (ITO) substrate, which was cleaned by an ultraviolet ozone cleaner immediately before use. The solution for spin-coating was made up of 10 g of chlorobenzene, 100 mg of PVK, and 20 mg of compound **1** (1 wt % solution, 20% doped Tb complex). This solution was stirred for about 2 h, then filtered to remove any undissolved material or insoluble impurities. It was then spin-cast onto an ITO glass at 1600 rpm for about 45 s, producing a film about 400−500 Å thick. The electron transport material PBD (2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole) layer was deposited in a vacuum. The cathode composed of LiF and Al was deposited on the substrate by conventional vacuum thermal deposition. A single-layer device with the structure of ITO/PKV + **1** (∼50 nm)/LiF (1.5 nm)/Al (150 nm) and a double-layer device with the structure of ITO/PKV + **1** (∼50 nm)/PBD (30 nm)/LiF (1.5 nm)/Al (150 nm) were fabricated. The active device area is 1.0 × 5.0 mm^2. The current/voltage characteristics were measured with a Keithley 238 Source Measure Unit. The EL spectra and the

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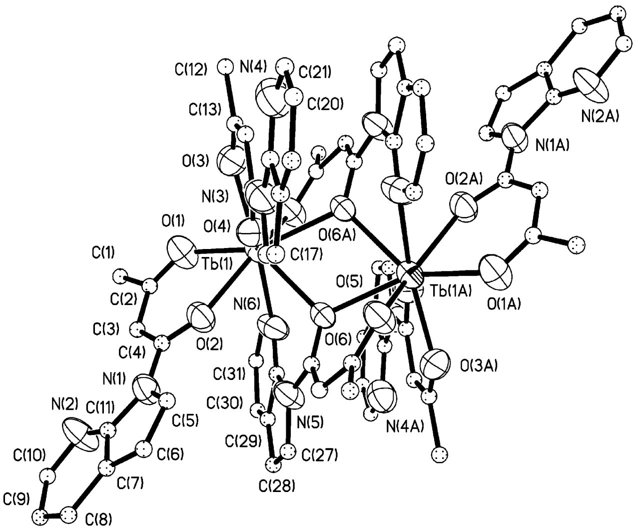


Figure 1. A diagram showing the molecular structure of **1** with 50% thermal ellipsoids and labeling schemes. Hydrogen atoms were omitted for clarity.

Table 2. Selected Bond Lengths and Angles for One of the Independent Molecules of **1**

Tb(1)−O(3)	2.314(8)	Tb(1)−O(2)	2.340(8)
Tb(1)−O(4)	2.328(10)	Tb(1)−O(6A)	2.404(7)
Tb(1)−O(5A)	2.329(9)	Tb(1)−O(6)	2.451(7)
Tb(1)−O(1)	2.337(9)	Tb(1)−N(6)	2.599(12)
O(3)−Tb(1)−O(4)	72.3(3)	O(2)−Tb(1)−O(6A)	138.5(3)
O(3)−Tb(1)−O(5A)	79.0(3)	O(3)−Tb(1)−O(6)	140.5(3)
O(4)−Tb(1)−O(5A)	139.6(3)	O(4)−Tb(1)−O(6)	78.5(3)
O(3)−Tb(1)−O(1)	82.7(3)	O(5A)−Tb(1)−O(6)	109.0(3)
O(4)−Tb(1)−O(1)	121.0(3)	O(1)−Tb(1)−O(6)	136.1(3)
O(5A)−Tb(1)−O(1)	81.8(3)	O(2)−Tb(1)−O(6)	77.7(3)
O(3)−Tb(1)−O(2)	118.2(3)	O(6A)−Tb(1)−O(6)	67.9(3)
O(4)−Tb(1)−O(2)	74.8(3)	O(3)−Tb(1)−N(6)	149.0(4)
O(5A)−Tb(1)−O(2)	145.2(3)	O(4)−Tb(1)−N(6)	138.3(4)
O(1)−Tb(1)−O(2)	71.7(3)	O(5A)−Tb(1)−N(6)	76.0(4)
O(3)−Tb(1)−O(6A)	79.3(3)	O(1)−Tb(1)−N(6)	75.9(4)
O(4)−Tb(1)-O(6A)	76.0(3)	O(2)−Tb(1)-N(6)	76.0(3)
O(5A)-Tb(1)−O(6A)	71.1(3)	O(6A)-Tb(1)−N(6)	109.0(3)
O(1)−Tb(1)-O(6A)	149.8(3)	O(6)−Tb(1)-N(6)	66.5(4)

luminance for the devices were measured by using a Photo Research-650 Spectra Colorimeter.

Results and Discussions

Syntheses and Structures of Complexes 1 and 2. The syntheses of complexes **1** and **2** were carried out in acetone−water solution by the reaction of $LnCl_3$ with a 10% excess of Hacac-azain in good yields. Because the Hacac-azain ligand was found to be unstable in methanol or ethanol in the presence of base even at ambient temperature,[5] these solvents must be avoided in the synthesis. Both complexes are soluble in CH_2Cl_2, $CHCl_3$, THF, acetone, or acetonitrile, but insoluble in water.

Complexes **1** and **2** are isostructural and thus only the structure of complex **1** will be addressed in detail here. Selected bond lengths and angles are given in Table 2. There are two independent molecules in the asymmetric unit of **1**, each of which possesses an inversion center of symmetry. The structures of these two independent molecules are similar, one of which is shown in Figure 1. The corresponding selected bond lengths and angles are provided in Table 2. The complex contains two Tb(III) ions which are separated by 4.060(1) or 4.027(1) Å. Each Tb(III) ion is chelated by two acac-azain ligands through the diketone oxygen atoms. The remaining two acac-azain ligands display an interesting chelating and bridging bonding mode-chelate to one of the Tb(III) ions through the nitrogen atom of the 7-azaindolyl group and one of the oxygen atoms of the diketone and chelate to the second Tb(III) ion by using two oxygen atoms of the diketone, resulting in coordination number 8 for each metal center (Scheme 1). The coordination geometry of the metal can be described as distorted square antiprism with the four oxygen atoms from the two chelating ligands in one square plane and two oxygen atoms and two nitrogen atoms from the two bridging ligands in another square plane. The two types of acac-azain ligands in **1** adopt two different conformations, **A** (the chelate-bridging mode) and **B** (the chelate mode), as shown in Chart 1. Despite the different bonding models of the acac-azain ligands in the complex, the corresponding C−C, C−O, and C−N bond lengths of the chelate-bridging ligand and the chelate ligands are comparable. The Tb−O and Tb−N bond lengths are typical for lanthanide compounds,[3h,i,9] although the Tb−O bond length of the bridging acac-azain ligand is slightly longer than those of the chelating acac-azain ligands, attributable to steric hindrance. Molecules of **1** display extensive π stacking in the crystal lattice as shown by the unit cell packing diagram given in Figure 2.

Scheme 1

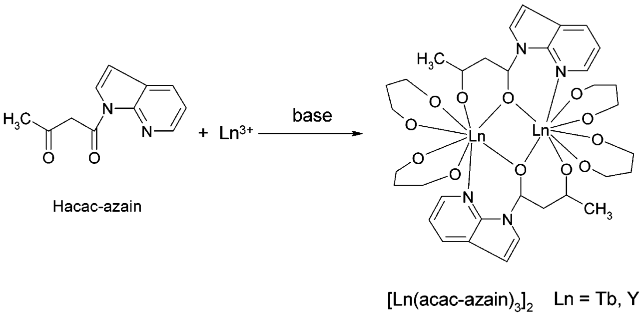
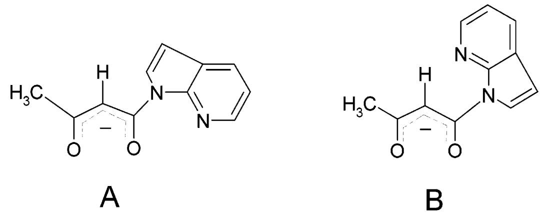


Chart 1



Due to the high molecular weight of compound **1**, it cannot be sublimed by vacuum. Attempts to prepare mononuclear complexes with the formula of [Tb(acac-azain)$_3$L] where L is a chelate ligand such as 2,2′-bipyridine or 1,10-phenanthroline so that the resulting complex may be sublimable were not successful. In fact, complex **1** was always isolated from the attempted syntheses of mononuclear compounds,

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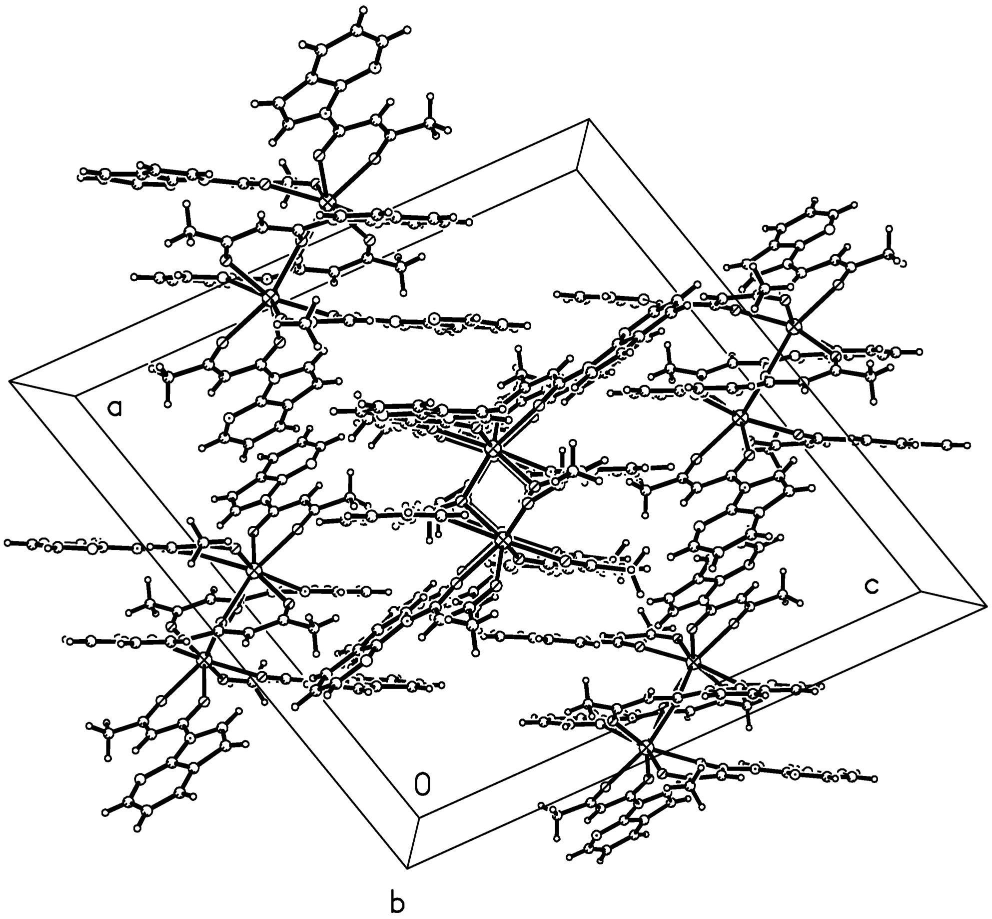

Figure 2. Unit cell packing diagram of **1**. Solvent molecules were omitted for clarity.

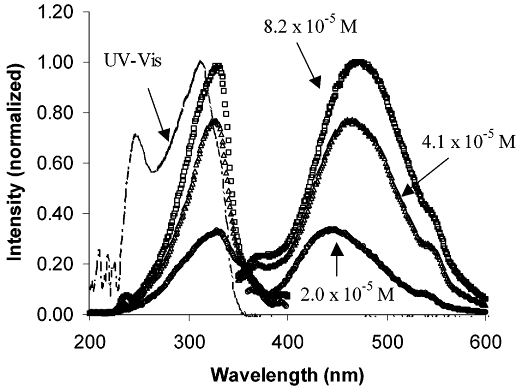

Figure 3. UV−vis, excitation, and emission spectra of **2** in CH_2Cl_2 at ambient temperature.

indicating that the dinuclear complex is the favored product, perhaps due to kinetic factors.

Luminescent and EL Properties of 1 and 2. When irradiated by UV light, the free ligand Hacac-azain emits a blue color in solution ($\lambda = 429$ nm, CH_2Cl_2) and the solid state ($\lambda = 420$ nm).[5] The Y(III) complex **2** also emits a weak blue color in solution and the solid state ($\lambda = \sim 490$ nm) with a broad emission band. At 298 K, the emission maximum of **2** shifts to lower energy as the concentration of the solution increases (450 to 476 nm, Figure 3), an indication that compound **2** exists likely as a mixture of monomer and dimer in solution. Since the Y(III) ion is nonemissive, the blue emission of compound **2** is attributed to the acac-azain ligand. The decrease of emission energy is likely caused by interligand $\pi-\pi$ interactions. The 77 K spectrum of compound **2** in CH_2Cl_2 solution displays a broad emission peak at $\lambda = 476$ nm with a decay lifetime of 6.20(1) μs, indicating that the emission from the ligand in compound **2** is most likely phosphorescent. The emission spectrum of **2** at the same concentration in solution at 298 K resembles that at 77 K with an emission lifetime of 5.48(1) μs, supporting that the emission of **2** at ambient temperature is also likely phosphorescent in nature. In fact, a number of ligands based on acac have been demonstrated previously that only phosphorescene from the acac ligands is detectable due to the presence of the carbonyl group that promotes efficient singlet-to-triplet intersystem crossing.[11]

The excitation and UV−vis spectra of Tb(III) complex **1** are similar to those of **2**. However, the emission spectrum of Tb(III) complex **1** consists of entirely characteristic emission bands of Tb(III) and no emission band from the acac-azain ligand was observed (Figure 4), an indication that the energy transfer from the ligand to the Tb(III) center may be efficient. The total quantum yield of compound **1** was determined to be 0.11 by using $Tb(acac)_3$ as the standard ($\Phi = 0.19$). The decay lifetime of **1** was determined to be 670(14) μs in the solid state and 677(11) μs in CH_2Cl_2

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Table 3. Spectroscopic Data for 1 and 2

compd	UV−vis (nm) (ϵ, M^{-1} cm^{-1})	excitation λ_{max} (nm)	emission λ_{max} (nm)	φ	τ (μs)
1 (CH_2Cl_2), RT	245 (27 740), 312 (38 000)	337	550	0.11	677(11)
1 (CH_2Cl_2), 77 K		334	550		962(17)
1, solid, RT		362	550		670(14)
1, solid, 77 K		350	550		877(16)
2, (CH_2Cl_2), RT	250 (38 380), 314 (55 000)	398	476	0.0043	5.48(1)
2, (CH_2Cl_2), 77 K		398	476		6.20(1)
2, solid, RT		418	485		4.56(3)
2, solid, 77 K		411	484		8.0(3)

solution at ambient temperature. Φ_{Tb} of **2** in solution was estimated[12] to be 0.19 by using the equation of $\Phi_{Tb} = \tau_{obs}/\tau_R$, where τ_{obs} =0.677 ms and τ_R = 3.5 ms. By using the total quantum yield of 0.11 of **1** and Φ_{Tb}, the intersystem energy transfer efficiency[12] or the efficiency of sensatization by the ligand to the Tb(III) center in **1** was estimated to be 0.57. By using the same method, Φ_{Tb} of **1** in the solid state was calculated to be 0.19 based on its lifetime at room temperature. Since there is no solvent quenching and the molecule is locked in a rigid crystal lattice in the solid state, the overall quantum yield of **1** in the solid state is expected to be bigger than 0.11 but smaller than 0.19. The triplet state energy of the ligand based on our measurement of compound **2** was found to be 22 220 cm^{-1}, which is 1720 cm^{-1} above the $^5D_4$ of Tb(III) (20 500 cm^{-1}). Sato indicated[13] that, to efficiently sensitize Tb(III) fluorescence, the triplet state of the ligand has to be 2400 ± 300 cm^{-1} above the $^5D_4$ of Tb(III). The triplet energy level of our ligand is slightly lower than the ideal energy level suggested by Sato, which may account for the low quantum yield of **1**. UV−vis and photoluminescent data of **1** and **2** are summarized in Table 3.

Because compound **1** cannot be sublimed, it cannot be used as an emitter in OLEDs by vacuum deposition. However, it may be possible to dope compound **1** into a suitable polymer matrix and deposit it to the substrate by spin cast. Therefore, we examined the photoluminescent properties of compound **1** in PVK. The choice of PVK as the host material is based on two reasons: (a) the PVK emission band overlaps with the excitation band of compound **1**, hence it may be able to transfer energy to the Tb(III) complex efficiently, and (b) PVK is a well-known hole transport material, hence it may facilitate the charge transport in EL devices. Compound **1** doped PVK film (20% weight) displays characteristic emission bands of compound **1** and a small fraction (~6% of overall integrated emission intensity) of emission at ~400 nm by PVK (Figure 5), supporting that PVK is an effective host for the Tb(III) compound and that the energy transfer from PVK to Tb(III) centers is efficient.

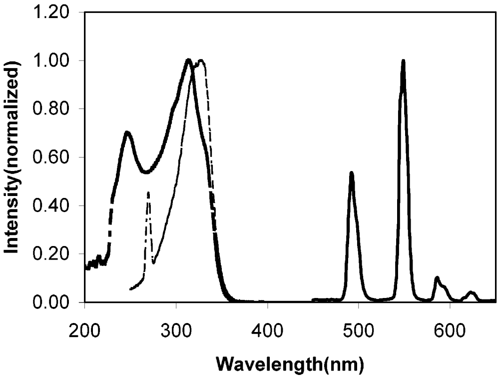

Figure 4. UV−vis, excitation and emission spectra of **1** in CH_2Cl_2 at ambient temperature.

Two types of electroluminescent devices were fabricated. The first type consists of a single layer of compound **1** doped PVK film (20%, ~50 nm) sandwiched between the ITO anode and the LiF(1.5 nm)/Al(150 nm) cathode. The second type consists of a layer of compound **1** doped PVK film (20%, ~50 nm) and a layer of vacuum deposited PBD (2-(4-biphenylyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole, 30 nm) sandwiched between the ITO anode and the LiF(1.5 nm)/Al(150 nm) cathode. Characteristic emission bands of Tb(III) were observed for both devices, which matches PL of compound **1** (Figure 5). A weak emission band at ~400 nm due to PVK was also observed. The *L*−*V*−efficiency diagrams of the single-layer device are shown in Figure 6, respectively. The single-layered device is clearly not efficient. The device performance was improved significantly when a PBD layer was included as shown by the *L*−*V*−efficiency characteristics of the double-layered device in Figure 7. PBD is an electron-transport material. The inclusion of the PBD layer in the double-layered device clearly facilitates the electron transport from cathode to anode, and forms a hole barrier at the PVK/PBD interface, hence improving the efficiency of the device. Using PVK as the host/hole transport layer and PBD as the electron transport layer for lanthanide emitters and phosphorescent transition metal complex emitters in electroluminescent devices has been well-documented

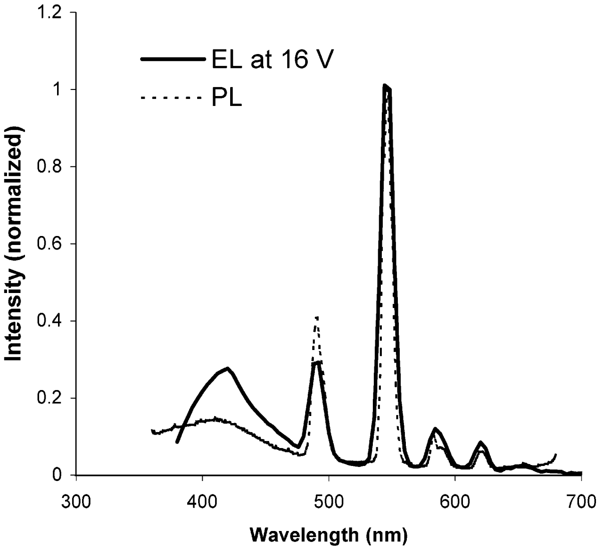

Figure 5. PL of **1** in PVK film and EL of the double-layered device.

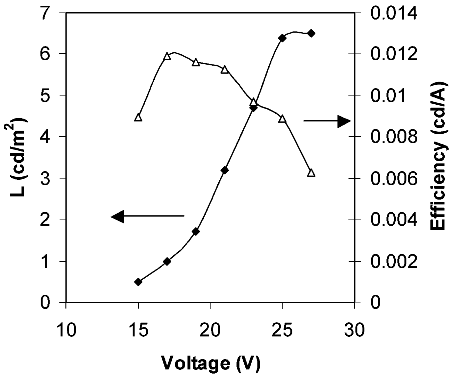

Figure 6. $L-V-$efficiency diagram of the single-layered device.

previously.[2–3,5e,10] The turn-on voltage for the double-layered device is ~11 V and the highest efficiency (0.65 cd/A) for the double-layered device was achieved at 13 V and 1.72 mA/cm^2. Compared with the previously known EL devices of Tb(III) compounds where a polymer host such as PVK was used, our double-layered EL device is certainly among the most efficient, if not the best.[3,4] EL devices with Tb(acac)$_3$ as the emitter and PVK as the host and hole transport layers have been demonstrated previously.[4e] The efficiency of those Tb(acac)$_3$ devices with PVK as the host is at least 10 times less than our device, hence demonstrating that the 7-azaindolyl group in complex **1** clearly plays an important role in promoting energy transfer from the ligand to the metal center.

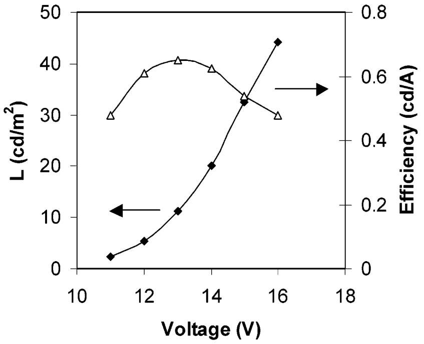

Figure 7. $L-V-$efficiency diagram of the double-layered device.

In summary, we demonstrated the synthesis and the structure of a new Tb(III) dinuclear compound based on 7-azaindolylacetylacetonato ligands. Preliminary study on electroluminescent properties of this compound shows that it is a very promising green emitter for light-emitting devices. Further optimization of the EL devices is being conducted.

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Supporting Information Available: Tables of crystal data, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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