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Adducts of lanthanide β-diketonates with 2,4,6-tri(2-pyridyl)-1,3,5-triazine: Synthesis, structural characterization, and photoluminescence studies

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Abstract

Adducts of lanthanide β -diketonates of the general formula LnL₃(TPTZ) were synthesized and structurally characterized by single crystal X-ray diffraction [Ln = Eu³⁺, Tb³⁺, Er³⁺; L is the conjugate base of dibenzoylmethane (DBM), 1-benzoylacetone (BA), thenoyl-trifluoroacetone (TTA), or 4,4,4-trifluoro-1-phenyl-1,3-butanedione (BTFA); TPTZ = 2,4,6-tri(2-pyridyl)-1,3,5-triazine, a rigid Lewis base with a large π system]. The lanthanide ion in each of these complexes is nonacoordinate with six β -diketonate oxygen atoms and three TPTZ nitrogen atoms, forming a coordination polyhedron best describable as a monocapped square antiprism. Characteristic red, green, and near infrared luminescence was observed for the Eu³⁺, Tb³⁺, and Er³⁺ complexes, respectively. All complexes showed significantly enhanced luminescence quantum yields when compared with the corresponding aqua analogues, with one of the Eu³⁺ complexes displaying a quantum yield of 69.7% in chloroform.

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1. Introduction

A number of lanthanide ions display characteristic luminescence, a consequence of the f–f electronic transitions, in the visible or near-infrared spectral regions upon ultraviolet excitation [1]. Such transitions are forbidden by parity, leading to long-lived excited states, in the micro- to millisecond range. The forbidden nature of such transitions is also reflected in the low molar absorptivities, making direct photo-excitation of the lanthanide ions difficult [2]. Nevertheless, this can be overcome by energy transfer from organic chromophores to the lanthanide ions; when ligands containing organic chromophores with suitable photophysical properties are employed, highly luminescent lanthanide complexes can be obtained. The commonly accepted mechanism of energy transfer from the organic ligands to a lanthanide ion is that of Crosby and Whan [3], which involves light absorption by the organic ligand to produce the singlet excited states, intersystem crossing to populate the ligand triplet states, and energy transfer from the triplet states to the lanthanide emissive levels for light emission. Though not nearly as prevalent, other mechanisms are possible [4], including one involving direct energy transfer from the ligand singlet state to the resonance levels of the lanthanide ion [5]. The vibronic perturbation to the f orbitals caused by ligand coordination is nevertheless limited as these orbitals are well shielded by the filled 5s and 5p orbitals. As such, characteristically narrow line-like emissions are observed for luminescent lanthanide complexes. Technologically significant applications have been realized or envisioned for these materials. These include their uses as fluorescent probes for bio-immunoassays, efficient and sharp-emitting materials in display technologies, and for optical conversion and amplification [1].

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Arguably the most extensively studied luminescent lanthanide complexes are those with β -diketonate ligands [6]. When three β -diketonate ligands coordinate a trivalent lanthanide ion, an electrically neutral complex is produced. Unless a sterically encumbering β -diketonate ligand is used, additional ligands such as water and other Lewis bases are necessary in order to fulfill the high coordination requirement of these large metal ions. For practical applications, non-aqua neutral ligands are typically used, as high phonon energy OH oscillators can bridge off at very high rates the energy of the excited states of a lanthanide ion, leading to low quantum efficiency of light emission [7].

The property of the Lewis base adduct of a lanthanide β -diketonate depends on not only the diketonate but also the accompanying neutral ligand(s). Specifically, while the wavelength of light emission is inherently metal-dependent, its quantum efficiency is heavily dependent on how well the energetic levels of the ligand singlet, triplet, and the lanthanide emissive states are matched, a direct consequence of the ligand-assisted transfer of excitation energy [3,4,8]. Other properties such as thermal stability, solubility, and film-forming characteristics (for the fabrication of light-emitting devices) are also strongly dependent on the nature of the ligands.

We have been interested in the design and synthesis of lanthanide β -diketonates for applications as light-emitting materials in organic electroluminescent devices, as they offer a number of advantages over the much studied conducting polymers and other non-lanthanide materials [9]. Specifically, we have been looking at ligand design as a fundamental means of enhancing the thermal stability of a complex and improving its charge-carrier transporting ability in a working device [10]. For example, a terbium complex with acetylacetonate ligand modified with an electron-withdrawing oxadiazolyl group has been shown to possess higher thermal stability than its unmodified counterpart. More importantly, significantly improved electroluminescence device performance was also achieved [10]. In comparison, the unmodified complex barely produced any green emission using an otherwise identically configured device. Work by others has also validated this ligand design approach for producing improved electroluminescent lanthanide materials [11].

The neutral ligands are equally important in modifying the properties of luminescent lanthanide β -diketonates. Just like the negatively charged ligands, neutral ligands contribute to the overall stability of the resulting complex. They may also serve to promote energy transfer for light emission. Based on such considerations, we have recently started the quest for adducts of lanthanide β -diketonates with unique neutral ligands [12]. One of the ligands of interest is 2,4,6-tri(2-pyridyl)-1,3,5-triazine (TPTZ), a bulky aromatic compound featuring three 2-pyridyl rings fixed on a central 1,3,5-triazine platform [13]. This ligand has been studied previously for its application in actinide–lanthanide group separations in a synergistic extraction system [14]. There also exist a few structurally characterized lanthanide complexes in which TPTZ acts as a tridentate ligand [15,16]. However, TPTZ adducts of lanthanide β -diketonates are unknown prior to our work. In addition to the novelty of such complexes, the bulky ligand, by offering three coordinating atoms, helps protect the lanthanide ion from interacting with solvent molecules, and therefore, suppressing solvent-based vibrational coupling and luminescence quenching [17]. Furthermore, the remaining nitrogen atoms allow for further coordination to other metals, transition metals in particular. Thus, structurally sophisticated heterometallic complexes may be envisioned, for which novel magnetic as well as luminescence properties can be expected [18,19].

As a first step to many of the research opportunities elaborated above, we have prepared the TPTZ adducts of several lanthanide β -diketonates, wherein the lanthanide ion is Eu³⁺, Tb³⁺, or Er³⁺, and the β -diketone is dibenzoylmethane (DBM), 1-benzoylacetone (BA), thenoyltrifluoroacetone (TTA), or 4,4,4-trifluoro-1-phenyl-1,3-butanedione (BTFA). The Eu³⁺ and Tb³⁺ complexes are synthesized as potential red- and green-emitting materials, respectively, while their Er³⁺ cognate is potentially useful in developing integrated lasers or fiber amplifiers due to its near infrared emission [20,21]. In this report, we describe in detail the synthesis, structural characterization by single-crystal diffraction, and photoluminescence studies of these new members of the lanthanide β -diketonate family.

2. Experimental

Reagents were of commercial origin (Aldrich) and were used as received. The recently reported procedure [12] for the synthesis of Eu(DBM)₃TPTZ was adopted with modifications where necessary. Elemental analysis (CHN) was performed by Desert Analytics Laboratory, Tucson, Arizona.

2.1. Synthesis of $Tb(DBM)_3TPTZ$

A mixture of TPTZ (0.312 g, 1.00 mmol) and TbCl₃. 6H₂O (0.265 g, 1.00 mmol) in 15 mL of absolute ethanol was stirred under reflux for 30 min to afford a clear solution. To this mixture was added over 10 min a solution of $KOBu^{t}$ (0.800 g, 7.130 mmol) and DBM (0.672 g, 3.00 mmol) in 20 mL of absolute ethanol, and the resulting mixture was stirred at 50 °C for 1 h, and then at room temperature for an additional 30 min. Ethanol was removed under vacuum, and the residue was washed with copious de-ionized water. The crude product thus obtained was dissolved in a minimum amount of chloroform, and the solution was dried over anhydrous MgSO₄. The filtrate was collected, from which a yellow solid was obtained upon removal of the solvent. Upon recrystallization from ethanol/chloroform (v/v 2:1), analytically pure product was obtained as a yellow crystalline solid (0.73 g, 64.0%). Anal. Calc. for C₆₃H₄₅N₆O₆Tb: C, 66.32; H, 3.98; N, 7.36. Found: C, 66.44; H, 3.96; N, 7.08%.

2.2. Synthesis of $Er(DBM)_3TPTZ$

This compound was prepared by starting with $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$ (0.382 g, 1.00 mmol) and adopting otherwise identical preparative and purification procedures to those for Tb(DBM)₃TPTZ. The product was obtained as a pale yellow crystalline solid (1.02 g, 88.8%). *Anal.* Calc. for C₆₃H₄₆N₆O_{6.5}Er: C, 65.32; H, 4.00; N, 7.25. Found: C, 65.45; H, 4.33; N, 7.28%.

2.3. Synthesis of $Eu(BA)_3TPTZ$

A mixture of TPTZ (0.312 g, 1.00 mmol) and EuCl₃· $6H_2O$ (0.366 g, 1.00 mmol) in 20 mL of absolute ethanol was stirred at 50 °C for 10 min to afford a clear solution. To this mixture was added with stirring a solution of KOBu^t (0.600 g, 5.347 mmol) and BA (0.487 g, 3.00 mmol) in 15 mL of absolute ethanol. The resulting mixture was stirred at 60 °C for 0.5 h, and then at room temperature under nitrogen for an additional 1.5 h. Purification of the reaction mixture followed the procedures detailed above for Tb(DBM)₃TPTZ. Analytically pure product was obtained as a pale yellow crystalline solid (0.57 g, 60.0%) upon recrystallizing the crude product from ethanol: chloroform:hexane (v/v/v 2:1:1). *Anal.* Calc. for C₄₈H₄₀-N₆O_{6.5}Eu: C, 60.25; H, 4.11; N, 8.80. Found: C, 60.25; H, 4.34; N, 9.01%.

2.4. Synthesis of Eu(BTFA)₃TPTZ

EuCl₃·6H₂O was allowed to react with TPTZ as described above. To this mixture was added with stirring a solution of KOBu^t (0.336 g, 3.00 mmol) and BTFA (0.648 g, 3.00 mmol) in 20 mL of absolute ethanol. The resulting mixture was stirred at 60 °C for 30 min, and then at room temperature under nitrogen for an additional 3 h. The mixture was filtered and the solid was washed with copious de-ionized water to remove KCl byproduct. The crude product thus obtained was washed with hexane (3 mL), dissolved in acetone (50 ml), and the solution was dried over anhydrous MgSO₄. The filtrate was collected, from which a pale yellow solid was obtained upon removal of the solvent. Recrystallization from ethanol:acetone (v/v 1:1) afforded analytically pure product as a pale yellow crystalline solid (0.63 g, 57.0%). Anal. Calc. for C₄₈H₃₀N₆O₆F₉Eu: C, 51.95; H, 2.72; N, 7.57. Found: C, 51.56; H, 2.54; N, 7.37%.

2.5. Synthesis of $Eu(TTA)_3TPTZ$

Starting with EuCl₃6H₂O (0.366 g, 1.00 mmol) and adopting otherwise identical preparative and purification procedures described for Eu(BTFA)₃TPTZ, the product was obtained as a pale yellow crystalline solid (1.00 g, 78.0%). *Anal.* Calc. for C₄₂H₂₄N₆O₆F₉S₃Eu: C, 44.72; H, 2.14; N, 7.45. Found: C, 44.38; H, 2.20; N, 7.45%.

2.6. X-ray structure determinations

Single crystals of Tb(DBM)₃TPTZ and Er(DBM)₃-TPTZ suitable for X-ray diffraction studies were obtained by directly layering their respective saturated chloroform solutions with diethyl ether at room temperature. Single crystals of Eu(BTFA)₃TPTZ and Eu(TTA)₃TPTZ were produced by slow evaporation of their respective solutions in ethanol:acetone (v/v 1:1), while single crystals of Eu(BA)₃TPTZ were obtained from its solution in ethanol:chloroform:hexane (v/v/v 2:1:1).

The crystals were mounted on a glass fiber in a random orientation. Examination of the crystal was carried out on a Bruker SMART 1000 CCD detector X-ray diffractometer at 170(2) K and a power setting of 50 kV, 40 mA. Data were collected on the SMART1000 system using graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The frames were integrated using the Bruker SAINT [22] software package's narrow frame algorithm, and empirical absorption and decay corrections were applied using the program SADABS [23]. The structures were solved using SHELXS in the Bruker SHELXTL (Version 5.0) software package [22]. Refinements were performed using SHELXL and illustrations were made using XP.

Solution was achieved by using direct methods followed by Fourier synthesis. Hydrogen atoms were added at idealized positions, constrained to ride on the atom to which they are bonded and given thermal parameters equal to 1.2 or 1.5 times U_{iso} of that bonded atom. Details on data collection and structure refinements are given in Table 1.

2.7. Photophysical studies

Electronic absorption spectra in the solid state and chloroform solutions were recorded on a Perkin–Elmer Lambda 10 spectrophotometer. Photoluminescence studies were carried out with a Fluorolog-3 fluorometer. The measured solid-state and solution-phase luminescence for the Tb^{3+} and Eu^{3+} complexes was excited by the light from a Xe-Arc lamp and detected using a photo multiplier tube at an angle of 90° with respect to the incident beam. Near infrared emission spectrum of $Er(DBM)_3TPTZ$ was obtained at room temperature by excitation using a 980-nm laser diode (ADC Telecommunications), a grating monochromator, and an InGaAs detector (Thorlabs). A chopper and a lock-in amplifier were used for signal amplification.

Photoluminescence quantum yields were measured and calculated using cresyl violet perchlorate (quantum yield $\varphi = 0.54$ in methanol [24]) and rhodamin 6G ($\varphi = 0.95$ in ethanol [25]) as the standards. Corrections were made for the instrumental parameters and differing refractive indices of the solvents used [26,27]. The relative quantum yields were calculated using the following established equation where Abs, A, and n denote the absorbance at the excitation wavelength, integrated area of the corrected emission

Table 1

 $Crystal \ data \ and \ structure \ refinement \ for \ Er(DBM)_3(TPTZ), \ Tb(DBM)_3(TPTZ), \ Eu(TTA)_3(TPTZ) \ , \ Eu(BA)_3(TPTZ), \ and \ Eu(BTFA)_3(TPTZ) \ , \ Eu(BA)_3(TPTZ), \ and \ Eu(BTFA)_3(TPTZ) \ , \ Eu(BA)_3(TPTZ), \$

		Er(DBM) ₃ (TPTZ)		Tb(D	BM) ₃ (TPTZ)
Empirical formula		C ₆₅ H ₅₀ ErN ₆ O ₆		C ₆₃ H	45TbN6O6
Formula weight $(g mol^{-1})$		1186.37		1140.9	97
Temperature (K)		170(2)		170(2)
Wavelength (Å)		0.71073		0.710	73
Crystal system		monoclinic		mono	clinic
Space group		I2/a		P21/c	
Unit cell dimensions					
$a(\mathbf{A})$		25 3385(12)		9 588	0(10)
$h(\mathbf{A})$		17.0616(8)		23.06	2(3)
$c(\mathbf{A})$		26 3956(13)		23.002	2(3)
β (°)		109 8140(10)		96.61	7(2)
p() Volumo (Å ³)		109.8140(10) 10725.7(0)		5277	7(2)
Volume (A)		8		1	5(10)
$D \qquad (m \alpha/m^3)$		1 469		1 400	
$D_{\text{calc}}(\text{IIIg/III})$		1.408		1.409	
Absorption coefficient (mm)		1.025		1.3/4	
F(000)		4816		2312	0.00
Crystal size (mm ³)		$0.19 \times 0.19 \times 0.18$		$0.30 \times$	(0.20×0.10)
θ Range for utilized data (°)		1.45-28.32		1.22-2	26.00
Limiting indices		$-33 \leqslant h \leqslant 33, -22$	$\leq k \leq 22, -35 \leq l \leq 35$	-11 <	$\leqslant h \leqslant 11, -28 \leqslant k \leqslant 28, -30 \leqslant l \leqslant 30$
Reflections utilized		67 549		57456)
Independent reflections $[R_{int}]$		13252 [0.1232]		10559	9 [0.1650]
Completeness to $\theta = 28.32^{\circ}$ (%)		99.1		100.0	
Absorption correction		semi-empirical from	1 equivalents	semi-	empirical from equivalents
Maximum and minimum transmiss	sion	0.7567 and 0.7470		0.8749 and 0.6834	
Refinement method		full-matrix least-squ	lares on F^2	full-matrix least-squares on F^2	
Data/restraints/parameters		13251/250/730		10559	9/243/685
Goodness-of-fit on F^2		0.905		0.980	
Final <i>R</i> indices $[I \ge 2\sigma(I)]$		$R_1 = 0.0346, wR_2 =$	0.0717	$R_1 =$	$0.0634, wR_2 = 0.1143$
R indices (all data)		$R_1 = 0.0559, wR_2 =$	0.0765	$R_1 =$	$0.1292, wR_2 = 0.1356$
Largest difference in peak and hole	$e (e Å^{-3})$	1.260 and -0.586		1.162	and -1.425
RMS difference in density (e $Å^{-3}$)		0.109		0.134	
	Eu(TTA) ₃ (TPTZ)		Eu(BA) ₃ (TPTZ)		Eu(BTFA) ₃ (TPTZ)
Empirical formula	C46H36EuF9N6O8	S ₃	$C_{48}H_{39}EuN_6O_6$		C ₅₀ H ₃₆ EuF ₉ N ₆ O ₇
Formula weight $(g mol^{-1})$	1219.95	2	947.81		1155.81
Temperature (K)	170(2)		170(2)		170(2)
Wavelength (Å)	0 71073		0 71073		0 71073
Crystal system	orthorhombic		monoclinic		triclinic
Space group	P212121		P21/n		
Unit cell dimensions	1 212121				P1
enn een annensions			121/1		<i>P</i> 1
$a(\mathbf{\dot{A}})$	10.4683(8)		12 265(3)		<i>P</i> 1 11.0603(10)
$a(\mathbf{A})$ $b(\mathbf{A})$	10.4683(8)		12.265(3) 27.548(6)		P1 11.0603(10) 15.0588(13)
$a(\mathring{A})$ $b(\mathring{A})$	10.4683(8) 15.5897(12) 20.022(2)		12.265(3) 27.548(6)		P1 11.0603(10) 15.0588(13) 15.2027(14)
$ \begin{array}{c} a (\mathring{A}) \\ b (\mathring{A}) \\ c (\mathring{A}) \\ \end{array} $	10.4683(8) 15.5897(12) 30.023(2)		12.265(3) 27.548(6) 12.472(3)		P1 11.0603(10) 15.0588(13) 15.3027(14) 02.666(2)
$ \begin{array}{c} a (\mathring{A}) \\ b (\mathring{A}) \\ c (\mathring{A}) \\ \beta (\circ) \\ \end{array} $	10.4683(8) 15.5897(12) 30.023(2) 90		12.265(3) 27.548(6) 12.472(3) 93.576(5) 4205 9(17)		P1 11.0603(10) 15.0588(13) 15.3027(14) 92.666(2) 2418.8(4)
$a (Å)b (Å)c (Å)\beta (°)Volume (Å3)$	10.4683(8) 15.5897(12) 30.023(2) 90 4899.7(7)		12.265(3) 27.548(6) 12.472(3) 93.576(5) 4205.9(17)		P1 11.0603(10) 15.0588(13) 15.3027(14) 92.666(2) 2418.8(4)
a (Å) b (Å) c (Å) $\beta (°)$ Volume (Å ³) Z P = (a (A3))	10.4683(8) 15.5897(12) 30.023(2) 90 4899.7(7) 4		12.265(3) 27.548(6) 12.472(3) 93.576(5) 4205.9(17) 4		P1 11.0603(10) 15.0588(13) 15.3027(14) 92.666(2) 2418.8(4) 2 1.507
$a (\mathring{A})$ $b (\mathring{A})$ $c (\mathring{A})$ $\beta (°)$ Volume (\mathring{A}^{3}) Z $D_{calc} (mg/m^{3})$	10.4683(8) 15.5897(12) 30.023(2) 90 4899.7(7) 4 1.654		12.265(3) 27.548(6) 12.472(3) 93.576(5) 4205.9(17) 4 1.497		P1 11.0603(10) 15.0588(13) 15.3027(14) 92.666(2) 2418.8(4) 2 1.587
$a (Å)b (Å)c (Å)\beta (°)Volume (Å3)ZDcalc (mg/m3)Absorption coefficient (mm-1)$	10.4683(8) 15.5897(12) 30.023(2) 90 4899.7(7) 4 1.654 1.5014		12.265(3) 27.548(6) 12.472(3) 93.576(5) 4205.9(17) 4 1.497 1.549		P1 11.0603(10) 15.0588(13) 15.3027(14) 92.666(2) 2418.8(4) 2 1.587 1.390
$a (Å)b (Å)c (Å)\beta (°)Volume (Å3)ZDcalc (mg/m3)Absorption coefficient (mm-1)F(000)$	10.4683(8) 15.5897(12) 30.023(2) 90 4899.7(7) 4 1.654 1.5014 2440		12.265(3) 27.548(6) 12.472(3) 93.576(5) 4205.9(17) 4 1.497 1.549 1920		P1 11.0603(10) 15.0588(13) 15.3027(14) 92.666(2) 2418.8(4) 2 1.587 1.390 1156
$a (Å)b (Å)c (Å)\beta (°)Volume (Å3)ZDcalc (mg/m3)Absorption coefficient (mm-1)F(000)Crystal size (mm3)$	10.4683(8) 15.5897(12) 30.023(2) 90 4899.7(7) 4 1.654 1.5014 2440 0.294 × 0.174 × 0.0)71	$12.265(3)$ $27.548(6)$ $12.472(3)$ $93.576(5)$ $4205.9(17)$ 4 1.497 1.549 1920 $0.228 \times 0.223 \times 0.101$		P1 11.0603(10) 15.0588(13) 15.3027(14) 92.666(2) 2418.8(4) 2 1.587 1.390 1156 0.269 × 0.310 × 0.370
$a (Å)b (Å)c (Å)\beta (°)Volume (Å3)ZDcalc (mg/m3)Absorption coefficient (mm-1)F(000)Crystal size (mm3)\theta Range for utilized data (°)$	10.4683(8) 15.5897(12) 30.023(2) 90 4899.7(7) 4 1.654 1.5014 2440 0.294 × 0.174 × 0.0 1.36-26.47)71	$12.265(3)$ $27.548(6)$ $12.472(3)$ $93.576(5)$ $4205.9(17)$ 4 1.497 1.549 1920 $0.228 \times 0.223 \times 0.101$ $1.80-23.27$		P1 11.0603(10) 15.0588(13) 15.3027(14) 92.666(2) 2418.8(4) 2 1.587 1.390 1156 $0.269 \times 0.310 \times 0.370$ 1.33-26.42
$a (Å)b (Å)c (Å)c (Å)\beta (°)Volume (Å3)ZDcalc (mg/m3)Absorption coefficient (mm-1)F(000)Crystal size (mm3)\theta Range for utilized data (°)Limiting indices$	$\begin{array}{c} 10.4683(8)\\ 15.5897(12)\\ 30.023(2)\\ 90\\ 4899.7(7)\\ 4\\ 1.654\\ 1.5014\\ 2440\\ 0.294\times 0.174\times 0.0\\ 1.36-26.47\\ -13\leqslant h\leqslant 13, -1 \end{array}$	071 9 $\leq k \leq 19$,	$12.265(3)$ $27.548(6)$ $12.472(3)$ $93.576(5)$ $4205.9(17)$ 4 1.497 1.549 1920 $0.228 \times 0.223 \times 0.101$ $1.80-23.27$ $-13 \leqslant h \leqslant 13, -28 \leqslant k \leqslant 30,$		P1 11.0603(10) 15.0588(13) 15.3027(14) 92.666(2) 2418.8(4) 2 1.587 1.390 1156 0.269 \times 0.310 \times 0.370 1.33–26.42 $-13 \leq h \leq 13, -18 \leq k \leq 18,$
a (Å) b (Å) c (Å) β (°) Volume (Å ³) Z $D_{calc} (mg/m3)$ Absorption coefficient (mm ⁻¹) F(000) Crystal size (mm ³) θ Range for utilized data (°) Limiting indices	$\begin{array}{c} 10.4683(8)\\ 15.5897(12)\\ 30.023(2)\\ 90\\ 4899.7(7)\\ 4\\ 1.654\\ 1.5014\\ 2440\\ 0.294\times 0.174\times 0.0\\ 1.36-26.47\\ -13\leqslant h\leqslant 13, -1\\ -37\leqslant l\leqslant 37 \end{array}$	071 9 $\leq k \leq 19$,	$12.265(3)$ $27.548(6)$ $12.472(3)$ $93.576(5)$ $4205.9(17)$ 4 1.497 1.549 1920 $0.228 \times 0.223 \times 0.101$ $1.80-23.27$ $-13 \le h \le 13, -28 \le k \le 30,$ $-13 \le l \le 12$		P1 11.0603(10) 15.0588(13) 15.3027(14) 92.666(2) 2418.8(4) 2 1.587 1.390 1156 0.269 \times 0.310 \times 0.370 1.33–26.42 $-13 \leq h \leq 13, -18 \leq k \leq 18,$ $-19 \leq l \leq 19$
$a (Å)b (Å)c (Å)c (Å)\beta (°)Volume (Å3)ZDcalc (mg/m3)Absorption coefficient (mm-1)F(000)Crystal size (mm3)\theta Range for utilized data (°)Limiting indicesReflections utilized$	$\begin{array}{c} 10.4683(8)\\ 15.5897(12)\\ 30.023(2)\\ 90\\ 4899.7(7)\\ 4\\ 1.654\\ 1.5014\\ 2440\\ 0.294\times 0.174\times 0.0\\ 1.36-26.47\\ -13\leqslant h\leqslant 13, -1\\ -37\leqslant l\leqslant 37\\ 54175 \end{array}$	071 9 $\leq k \leq 19$,	$12.1/n$ $12.265(3)$ $27.548(6)$ $12.472(3)$ $93.576(5)$ $4205.9(17)$ 4 1.497 1.549 1920 $0.228 \times 0.223 \times 0.101$ $1.80-23.27$ $-13 \le h \le 13, -28 \le k \le 30,$ $-13 \le l \le 12$ 25900		P1 11.0603(10) 15.0588(13) 15.3027(14) 92.666(2) 2418.8(4) 2 1.587 1.390 1156 0.269 × 0.310 × 0.370 1.33–26.42 $-13 \le h \le 13, -18 \le k \le 18,$ $-19 \le l \le 19$ 26593
$a (Å)b (Å)c (Å)c (Å)\beta (°)Volume (Å3)ZDcalc (mg/m3)Absorption coefficient (mm-1)F(000)Crystal size (mm3)\theta Range for utilized data (°)Limiting indicesReflections utilizedIndependent reflections$	$\begin{array}{c} 10.4683(8)\\ 15.5897(12)\\ 30.023(2)\\ 90\\ 4899.7(7)\\ 4\\ 1.654\\ 1.5014\\ 2440\\ 0.294\times 0.174\times 0.0\\ 1.36-26.47\\ -13\leqslant h\leqslant 13, -1\\ -37\leqslant l\leqslant 37\\ 54175\\ 10075 \end{array}$	071 9 $\leq k \leq 19$,	$12.1/n$ $12.265(3)$ $27.548(6)$ $12.472(3)$ $93.576(5)$ $4205.9(17)$ 4 1.497 1.549 1920 $0.228 \times 0.223 \times 0.101$ $1.80-23.27$ $-13 \le h \le 13, -28 \le k \le 30,$ $-13 \le l \le 12$ 25900 6045		P1 11.0603(10) 15.0588(13) 15.3027(14) 92.666(2) 2418.8(4) 2 1.587 1.390 1156 0.269 × 0.310 × 0.370 1.33–26.42 $-13 \le h \le 13, -18 \le k \le 18,$ $-19 \le l \le 19$ 26593 9826
$\begin{array}{c} a (\mathring{A}) \\ b (\mathring{A}) \\ c (\mathring{A}) \\ \beta (\circ) \end{array}$ Volume (\mathring{A}^3) $\begin{array}{c} Z \\ D_{calc} (mg/m^3) \\ Absorption coefficient (mm^{-1}) \\ F(000) \\ Crystal size (mm^3) \\ \theta \text{ Range for utilized data (}^{\circ}) \\ Limiting indices \\ \end{array}$ Reflections utilized Independent reflections $[R_{int}]$	$\begin{array}{c} 10.4683(8)\\ 15.5897(12)\\ 30.023(2)\\ 90\\ 4899.7(7)\\ 4\\ 1.654\\ 1.5014\\ 2440\\ 0.294\times 0.174\times 0.0\\ 1.36-26.47\\ -13\leqslant h\leqslant 13, -1\\ -37\leqslant l\leqslant 37\\ 54175\\ 10075\\ [0.1213] \end{array}$	071 9 $\leq k \leq 19$,	$12.265(3)$ $27.548(6)$ $12.472(3)$ $93.576(5)$ $4205.9(17)$ 4 1.497 1.549 1920 $0.228 \times 0.223 \times 0.101$ $1.80-23.27$ $-13 \le h \le 13, -28 \le k \le 30,$ $-13 \le l \le 12$ 25900 6045 $[0.1742]$		P1 11.0603(10) 15.0588(13) 15.3027(14) 92.666(2) 2418.8(4) 2 1.587 1.390 1156 0.269 × 0.310 × 0.370 1.33–26.42 $-13 \le h \le 13, -18 \le k \le 18,$ $-19 \le l \le 19$ 26593 9826 [0.0329]
$a (Å)$ $b (Å)$ $c (Å)$ $c (Å)$ $\beta (°)$ Volume (Å ³) Z $D_{calc} (mg/m3)$ Absorption coefficient (mm ⁻¹) $F(000)$ Crystal size (mm ³) θ Range for utilized data (°) Limiting indices Reflections utilized Independent reflections $[R_{int}]$ Completeness to $\theta = 28.32^{\circ}$ (%)	10.4683(8) 15.5897(12) 30.023(2) 90 4899.7(7) 4 1.654 1.5014 2440 0.294 × 0.174 × 0.0 1.36-26.47 $-13 \le h \le 13, -1$ $-37 \le l \le 37$ 54175 10075 [0.1213] 99.6	071 $9 \leq k \leq 19,$	$12.1/n$ $12.265(3)$ $27.548(6)$ $12.472(3)$ $93.576(5)$ $4205.9(17)$ 4 1.497 1.549 1920 $0.228 \times 0.223 \times 0.101$ $1.80-23.27$ $-13 \le h \le 13, -28 \le k \le 30,$ $-13 \le l \le 12$ 25900 6045 $[0.1742]$ $99.9 (\theta = 23.27^{\circ})$		P1 11.0603(10) 15.0588(13) 15.3027(14) 92.666(2) 2418.8(4) 2 1.587 1.390 1156 0.269 × 0.310 × 0.370 1.33–26.42 $-13 \le h \le 13, -18 \le k \le 18,$ $-19 \le l \le 19$ 26593 9826 [0.0329] 98.8
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$\begin{array}{c} a (\mathring{A}) \\ b (\mathring{A}) \\ c (\mathring{A}) \\ c (\mathring{A}) \\ \beta (\circ) \end{array}$ Volume (\mathring{A}^3) $\begin{array}{c} Z \\ D_{calc} (mg/m^3) \\ Absorption coefficient (mm^{-1}) \\ F(000) \\ Crystal size (mm^3) \\ \theta Range for utilized data (\circ) \\ Limiting indices \end{array}$ Reflections utilized Independent reflections $\begin{bmatrix} R_{int} \end{bmatrix} \\ Completeness to \theta = 28.32^{\circ} (\%) \\ Absorption correction \\ Maximum and minimum \\ transmission \end{array}$	10.4683(8) 15.5897(12) 30.023(2) 90 4899.7(7) 4 1.654 1.5014 2440 0.294 \times 0.174 \times 0.0 1.36-26.47 -13 $\leq h \leq 13$, -1 -37 $\leq l \leq 37$ 54175 10075 [0.1213] 99.6 semi-empirical fron 1.0 and 0.895317)71 9 $\leq k \leq$ 19, om equivalents	12.265(3) 27.548(6) 12.472(3) 93.576(5) 4205.9(17) 4 1.497 1.549 1920 0.228 × 0.223 × 0.101 1.80–23.27 $-13 \le h \le 13, -28 \le k \le 30,$ $-13 \le l \le 12$ 25900 6045 [0.1742] 99.9 ($\theta = 23.27^{\circ}$) semi-empirical from equivalents 1.0 and 0.633047		P1 11.0603(10) 15.0588(13) 15.3027(14) 92.666(2) 2418.8(4) 2 1.587 1.390 1156 0.269 × 0.310 × 0.370 1.33-26.42 $-13 \le h \le 13, -18 \le k \le 18,$ $-19 \le l \le 19$ 26.593 98.26 [0.0329] 98.8 semi-empirical from equivalents 0.7062 and 0.6274
$\begin{array}{c} a (\mathring{A}) \\ b (\mathring{A}) \\ c (\mathring{A}) \\ c (\mathring{A}) \\ \beta (\circ) \end{array}$ Volume (\mathring{A}^3) $\begin{array}{c} Z \\ D_{calc} (mg/m^3) \\ Absorption coefficient (mm^{-1}) \\ F(000) \\ Crystal size (mm^3) \\ \theta Range for utilized data (\circ) \\ Limiting indices \end{array}$ Reflections utilized Independent reflections $\begin{bmatrix} R_{int} \end{bmatrix} \\ Completeness to \theta = 28.32^{\circ} (\%) \\ Absorption correction \\ Maximum and minimum \\ transmission \\ Refinement method \end{array}$	10.4683(8) 15.5897(12) 30.023(2) 90 4899.7(7) 4 1.654 1.5014 2440 0.294 \times 0.174 \times 0.0 1.36-26.47 -13 $\leq h \leq 13$, -1 -37 $\leq l \leq 37$ 54175 10075 [0.1213] 99.6 semi-empirical fron 1.0 and 0.895317 full-matrix least-set)71 $9 \leq k \leq 19$, om equivalents quares on F^2	12.265(3) 27.548(6) 12.472(3) 93.576(5) 4205.9(17) 4 1.497 1.549 1920 0.228 × 0.223 × 0.101 1.80–23.27 $-13 \le h \le 13, -28 \le k \le 30, -13 \le l \le 12$ 25900 6045 [0.1742] 99.9 ($\theta = 23.27^{\circ}$) semi-empirical from equivalents 1.0 and 0.633047 full-matrix least-squares on F^2		P1 11.0603(10) 15.0588(13) 15.3027(14) 92.666(2) 2418.8(4) 2 1.587 1.390 1156 0.269 × 0.310 × 0.370 1.33-26.42 -13 $\leq h \leq 13$, -18 $\leq k \leq 18$, -19 $\leq l \leq 19$ 26593 9826 [0.0329] 98.8 semi-empirical from equivalents 0.7062 and 0.6274 full-matrix least-squares on F^2
$\begin{array}{c} a (\mathring{A}) \\ b (\mathring{A}) \\ c (\mathring{A}) \\ c (\mathring{A}) \\ \beta (\circ) \end{array}$ Volume (\mathring{A}^3) $\begin{array}{c} Z \\ D_{calc} (mg/m^3) \\ Absorption coefficient (mm^{-1}) \\ F(000) \\ Crystal size (mm^3) \\ \theta Range for utilized data (\circ) \\ Limiting indices \end{array}$ Reflections utilized Independent reflections $\begin{bmatrix} R_{int} \end{bmatrix} \\ Completeness to \theta = 28.32^{\circ} (\%) \\ Absorption correction \\ Maximum and minimum \\ transmission \\ Refinement method \\ Data/restraints/parameters \end{array}$	10.4683(8) 15.5897(12) 30.023(2) 90 4899.7(7) 4 1.654 1.5014 2440 0.294 \times 0.174 \times 0.0 1.36-26.47 -13 $\leq h \leq 13$, -1 -37 $\leq l \leq 37$ 54175 10075 [0.1213] 99.6 semi-empirical fron 1.0 and 0.895317 full-matrix least-so 10075/855/725	171 $9 \le k \le 19$, om equivalents quares on F^2	12.265(3) 27.548(6) 12.472(3) 93.576(5) 4205.9(17) 4 1.497 1.549 1920 0.228 × 0.223 × 0.101 1.80–23.27 $-13 \le h \le 13, -28 \le k \le 30, -13 \le l \le 12$ 25900 6045 [0.1742] 99.9 ($\theta = 23.27^{\circ}$) semi-empirical from equivalents 1.0 and 0.633047 full-matrix least-squares on F^2 6045/115/554		P1 11.0603(10) 15.0588(13) 15.3027(14) 92.666(2) 2418.8(4) 2 1.587 1.390 1156 0.269 × 0.310 × 0.370 1.33-26.42 -13 $\leq h \leq 13$, -18 $\leq k \leq 18$, -19 $\leq l \leq 19$ 26593 9826 [0.0329] 98.8 semi-empirical from equivalents 0.7062 and 0.6274 full-matrix least-squares on F^2 9826/0/662
$\begin{array}{l} a (\mathring{A}) \\ b (\mathring{A}) \\ c (\mathring{A}) \\ c (\mathring{A}) \\ \beta (\circ) \end{array}$ Volume (\mathring{A}^3) $\begin{array}{l} Z \\ D_{calc} (mg/m^3) \\ Absorption coefficient (mm^{-1}) \\ F(000) \\ Crystal size (mm^3) \\ \theta Range for utilized data (\circ) \\ Limiting indices \end{array}$ Reflections utilized Independent reflections $\begin{bmatrix} R_{int} \end{bmatrix} \\ Completeness to \theta = 28.32^{\circ} (\%) \\ Absorption correction \\ Maximum and minimum \\ transmission \\ Refinement method \\ Data/restraints/parameters \\ Goodness-of-fit on F^2 \end{array}$	10.4683(8) 15.5897(12) 30.023(2) 90 4899.7(7) 4 1.654 1.5014 2440 0.294 × 0.174 × 0.0 1.36-26.47 -13 $\leq h \leq 13, -1$ -37 $\leq l \leq 37$ 54 175 10075 [0.1213] 99.6 semi-empirical from 1.0 and 0.895317 full-matrix least-so 10075/855/725 1.108	171 9 $\leq k \leq$ 19, om equivalents quares on F^2	12.265(3) 27.548(6) 12.472(3) 93.576(5) 4205.9(17) 4 1.497 1.549 1920 0.228 × 0.223 × 0.101 1.80–23.27 $-13 \le h \le 13, -28 \le k \le 30, -13 \le l \le 12$ 25900 6045 [0.1742] 99.9 ($\theta = 23.27^{\circ}$) semi-empirical from equivalents 1.0 and 0.633047 full-matrix least-squares on F^2 6045/115/554 1.095		P1 11.0603(10) 15.0588(13) 15.3027(14) 92.666(2) 2418.8(4) 2 1.587 1.390 1156 0.269 × 0.310 × 0.370 1.33-26.42 $-13 \le h \le 13, -18 \le k \le 18,$ $-19 \le l \le 19$ 26.593 98.8 semi-empirical from equivalents 0.7062 and 0.6274 full-matrix least-squares on F^2 9826/0/662 1.080

Table 1 (continued)

	Eu(TTA) ₃ (TPTZ)	Eu(BA) ₃ (TPTZ)	Eu(BTFA) ₃ (TPTZ)
<i>R</i> indices (all data)	$R_1 = 0.1236, wR_2 = 0.1786$	$R_1 = 0.1777, wR_2 = 0.2247$	$R_1 = 0.0633, wR_2 = 0.1180$
Largest difference in peak and hole (e $Å^{-3}$)	2.304 and -1.069	2.004 and -1.680	1.674 and -0.639
RMS difference in density (e $Å^{-3}$)	0.183	0.172	0.096

spectrum, and refractive index of the solvent, respectively. Subscript R and S refer to the reference and the unknown sample, respectively [28,29]. The experiments were performed using chloroform solutions $(1-5 \times 10^{-5} \text{ M})$ of the title complexes whose absorbance values are less than 0.2. The experimental uncertainty for the quantum efficiency calculations was found to be 10%.

$\varphi_{\rm S} = \varphi_{\rm R} ({\rm Abs}_{\rm R}/{\rm Abs}_{\rm S}) (A_{\rm S}/A_{\rm R}) (n_{\rm S}^2/n_{\rm R}^2)$

The stoichiometry of each of the title complexes in the solution phase was evaluated by titration of the specific lanthanide chloride solution $(1-5 \times 10^{-5} \text{ M})$ with TPTZ and the corresponding β -diketone. A stock solution of the ligand was freshly prepared by deprotonation of the β -diketone using a stoichiometric amount of KOBu^t. Following each addition of the ligand (both TPTZ and β -diketonate) solution, the integrated emission intensities of the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ (for Eu³⁺ at 614 nm) and ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ (for Tb³⁺ at 544 nm) transitions were monitored. Details of the experiments can be found in Supporting Information. The lanthanide (Eu³⁺ or Tb³⁺):TPTZ ratio was found to be 1:1, while the ratio of Eu³⁺:diketonate (BTFA, TTA, or BA) were found to be 1:3. However, the sensitization of Tb^{3+} luminescence by DBM is too weak to allow a reliable determination of the Tb³⁺:DBM ratio. This finding is consistent with the results, presented below, of the spectroscopic and luminescence studies of Tb(DBM)₃TPTZ in chloroform.

3. Results and discussion

3.1. Synthesis and structural characterization

As noted in our previous work, the Lewis base ligand (TPTZ) is introduced prior to the coordination of DBM. BA, TTA, or BTFA ligands (Scheme 1) to avoid possible adventitious hydrolysis which has been shown to produce unexpected polynuclear oxo/hydro complexes [30]. The pre-occupation of part of the coordination sphere by the rather bulky TPTZ ligand also helps prevent more than three β -diketonate ligands from being incorporated [31]. Thus, electrically neutral and coordinatively saturated complexes were obtained. All compounds were produced in good to excellent yields. They are readily soluble in solvents such as acetone, chloroform, and dichloromethane, but sparingly soluble in alcohols. Product purification by recrystallization from alcohol and one of these solubilizing solvents proved to be facile. Satisfactory microanalysis results (CHN) were obtained for all complexes.

The crystal structures of all five complexes have been established by single crystal X-ray diffraction, and are shown in Figs. 1–5, respectively. Selected metric values of bond distances and angles are summarized in Table 2.

In each of these complexes, the lanthanide ion is situated in a coordination sphere composed of six oxygen atoms of the β -diketonate ligands and three nitrogen atoms of the TPTZ ligand. The coordination polyhedron can be best



Scheme 1. Synthesis of LnL₃TPTZ (Ln = Eu, Tb, Er; L = DBM, BA, TTA, BTFA).



Fig. 1. An ORTEP view of the crystal structure of $Tb(DBM)_3(TPTZ)$ with partial atomic labeling. Thermal ellipsoids are drawn at the 30% probability level.



Fig. 2. An ORTEP view of the crystal structure of $Er(DBM)_3(TPTZ)$ with partial atomic labeling. Thermal ellipsoids are drawn at the 30% probability level.

described as a distorted square antiprism monocapped by the central coordinating nitrogen atom. The rather crowded coordination environment effectively protects the lanthanide center from any substantial interactions with potentially luminescence-quenching solvent molecules.

The aromatic rings of the TPTZ ligand are nearly coplanar in each of the five complexes. Within the same complex, the Ln–N bond to the central coordinating N is the shortest (indicated in bold face in Table 2), in agreement with our previous observation [12,32] and those made by



Fig. 3. An ORTEP view of the crystal structure of $Eu(TTA)_3(TPTZ)$ with partial atomic labeling. Thermal ellipsoids are drawn at the 50% probability level.

others [14-16,33]. It is also of interest to note that the Eu–N(central) bonds [2.6757(16) Å for Eu(DBM)₃TPTZ; 2.618(11) Å for Eu(BA)₃TPTZ; 2.580(7) Å for Eu(TTA)₃-TPTZ; 2.607(3) Å for Eu(BTFA)₃TPTZ] are all noticeably longer than that of [Eu(TPTZ)Cl₃(MeOH)₂] [2.555(4) Å], the only other Eu–TPTZ complex [14]; the TPTZ ligand is understandably forced further away from the metal center by the bulkier diketonate ligands than if it is in a less coordinatively congested environment. By a similar argument, the presence of a bulky TPTZ ligand causes noticeably longer Eu-O distance (average) in the present adducts than those of closely related complexes with smaller neutral ligands. For example, the average Eu-O distance of Eu(DBM)₃(TPTZ) is 2.384 Å versus 2.348 Å of Eu(DBM)₃L [L = 2-(4'-dimethylaminophenyl)imidazo-[4,5-f]1,10-phenanthroline] [34]; the corresponding value for Eu(BTFA)₃TPTZ is 2.405 Å versus 2.360 Å for Eu(BTFA)₃(2,2'-dipyridyl) [35].

The non-coordinating "arm" of the TPTZ ligand in $Eu(BA)_3TPTZ$ and $Eu(BTFA)_3TPTZ$ is close in space to a corresponding arm of a second molecule. As such, π -dimers are formed, with a separation between two TPTZ ligands of 3.155 and 3.285 Å, shown in Figs. 4 and 5, respectively. The formation of such π -dimers raises an interesting question of whether excimers can form in the solid state, a point inviting further investigation.

3.2. Electronic spectroscopic and photoluminescence studies

Electronic spectroscopic and photoluminescence studies have been carried out for the title complexes in both chloroform solutions and the solid state, from which very similar results have been obtained. In addition, luminescence titration experiments utilizing solutions with concentrations comparable to those for the luminescence quantum



Fig. 4. The TPTZ ligands stack to form a centrosymmetric "dimer" in the crystal structure of $Eu(BA)_3TPTZ$. The closest contact between the TPTZ ligands is 3.155 Å.



Fig. 5. The TPTZ ligands stack to form a centrosymmetric "dimer" in the crystal structure of $Eu(BTFA)_3TPTZ$. The closest contact between the TPTZ ligands is 3.285 Å.

yield measurements were also conducted. The observed ratio of 1:1:3 (TPTZ:Ln³⁺:diketonate) is consistent with the molecular and crystal structures of the title complexes. In other words, the complexes remained un-dissociated in solution, even at the relatively low concentrations utilized.

The electronic absorption spectra of $Er(DBM)_3TPTZ$ and $Tb(DBM)_3TPTZ$ in chloroform each show three maxima at 250, 285, and 353 nm, independent of the central lanthanide metal. This observation is consistent with ligand-based absorptions [DBM (250 and 352 nm) and TPTZ (250 and 285 nm)] of these complexes. Complexes $Eu(BA)_3TPTZ$, $Eu(TTA)_3TPTZ$, and $Eu(BTFA)_3TPTZ$ also show ligand-based absorption in the range of 230– 385 nm (Supporting Information).

The electronic excitation and photoluminescence of $Tb(DBM)_3TPTZ$, $Eu(BA)_3TPTZ$, $Eu(TTA)_3TPTZ$, and $Eu(BTFA)_3TPTZ$ were also studied in chloroform solutions.

It is clear that the excitation of these complexes is mostly ligand based. The maximum emission of the terbium complex was observed when the complex was excited at 290 nm, suggesting that ligand-to- Tb^{3+} energy transfer is mainly mediated by the TPTZ ligand (Fig. 6). In contrast, the strongest emissions of Eu(BA)₃TPTZ, Eu(TTA)₃TPTZ, and Eu(BTFA)₃TPTZ were observed when the complexes were excited at 345, 355, and 342 nm, respectively. These excitation wavelengths match the absorption spectra of the corresponding β -diketonate ligands [12] (Supporting Information), suggesting that energy transfer originates from the β -diketonate ligands to Eu³⁺ ion. Only the excitation and emission spectra of Eu(BA)₃TPTZ are shown in Fig. 7 as representatives. Those for Eu(TTA)₃TPTZ and Eu(BTFA)₃TPTZ are deposited in Supporting Information. These observations are in line with the commonly accepted notion of "antenna effect" for lanthanide luminescence [36,37].

Table 2

Selected bond distances (Å) and angles (°) of Tb(DBM)₃(TPTZ), Er(DBM)₃(TPTZ), Eu(BA)₃TPTZ, Eu(TTA)₃TPTZ, and Eu(BTFA)₃TPTZ

Tb(DBM)3TPTZ			Er(DBM)	3TPTZ	
Tb(1)–O(1)		2.380(4)	Er(1)-O(1)	2.308(2)
Tb(1)–O(2)		2.335(4)	Er(1)-O(2)		2.373(2)
Tb(1)–O(3)		2.394(5)		Er(1)-O(3)	
Tb(1)–O(4)	, ,	2.327(4)	Er(1)-O(4	2.314(2)	
Tb(1)-O(5)	2.322(4)		Er(1)-O(5	2.294(2)	
Tb(1)-O(6)	2.421(4)		Er(1)–O(6)		2.326(2)
Tb(1)-N(1)	2.626(5)		Er(1)-N(1	2.655(2)	
Tb(1)-N(2)	2.596(5)		Er(1)–N(2)		2.568(2)
Tb(1)–N(3)	2	2.640(5)	Er(1)–N(3)	2.582(2)
Eu(BA) ₃ TPTZ		Eu(TTA) ₃ TPTZ		Eu(BTFA)3TPTZ	
Eu(1)–O(34)	2.324(10)	Eu(1)–O(12)	2.602(7)	Eu(1)–O(1)	2.418(3)
Eu(1)–O(14)	2.349(9)	Eu(1) - O(14)	2.347(6)	Eu(1)-O(2)	2.397(3)
Eu(1)–O(24)	2.385(9)	Eu(1)–O(22)	2.404(6)	Eu(1) - O(3)	2.394(4)
Eu(1)–O(12)	2.406(9)	Eu(1)–O(24)	2.397(6)	Eu(1)-O(4)	2.433(3)
Eu(1)–O(32)	2.426(10)	Eu(1)–O(32)	2.399(6)	Eu(1)–O(5)	2.416(3)
Eu(1)–O(22)	2.466(9)	Eu(1)–O(34)	2.425(6)	Eu(1)–O(6)	2.373(3)
Eu(1)–N(41)	2.661(11)	Eu(1) - N(41)	2.602(7)	Eu(1) - N(1)	2.631(4)
Eu(1)-N(412)	2.618(11)	Eu(1)-N(48)	2.580(7)	Eu(1)–N(3)	2.607(3)
Eu(1)-N(418)	2.684(11)	Eu(1)-N(414)	2.634(8)	Eu(1)–N(2)	2.629(4)
Tb(DBM)3TPTZ			Er(DBM) ₃ T	PTZ	
O(1)-Tb(1)-O(2)	71.0(2)		O(1)-Er(1)-	O(2)	70.7(1)
O(3)-Tb(1)-O(4)	73.0(2)		O(3) - Er(1) - O(4)		70.6(1)
O(5)-Tb(1)-O(6)	70.6(1)		O(5) - Er(1) - O(6)		75.1(1)
O(1)-Tb(1)-N(2)	113.5(2)		O(1) - Er(1) - N(2)		138.0(1)
O(3)-Tb(1)-N(2)	66.4(2)		O(3) - Er(1) - N(2)		69.7(1)
O(5)-Tb(1)-N(2)		114.0(2)	O(5)–Er(1)–	N(2)	132.6(1)
Eu(BA) ₃ TPTZ		Eu(TTA) ₃ TPTZ		Eu(BTFA)3TPTZ	
O(12)-Eu(1)-O(14)	73.3(3)	O(12)–Eu(1)–O(14)	72.5(2)	O(1)-Eu(1)-O(2)	71.0(1)
O(22)–Eu(1)–O(24)	70.1(3)	O(22) - Eu(1) - O(24)	68.9(2)	O(3) - Eu(1) - O(4)	68.0(1)
O(32)–Eu(1)–O(34)	70.1(3)	O(32)-Eu(1)-O(34)	70.6(2)	O(5)-Eu(1)-O(6)	71.5(1)
O(12)-Eu(1)-N(412)	68.9(3)	O(12)-Eu(1)-N(48)	67.0(2)	O(1)-Eu(1)-N(2)	138.7(1)
O(22)-Eu(1)-N(412)	109.6(3)	O(22)-Eu(1)-N(48)	72.9(2)	O(3)-Eu(1)-N(2)	79.8(1)
O(32)-Eu(1)-N(412)	116.3(3)	O(32)-Eu(1)-N(48)	143.8(2)	O(5)-Eu(1)-N(2)	82.4(1)



Fig. 6. The excitation (---) and emission (—) spectra of $Tb(DBM)_3TPTZ$ in $CHCl_3.$



Fig. 7. The excitation (---) and emission (—) spectra of $\rm Eu(BA)_3TPTZ$ in $\rm CHCl_3.$



Fig. 8. The emission spectrum of Er(DBM)₃TPTZ in CHCl₃.

The photoluminescence quantum yields of Tb(DBM)₃-TPTZ, Eu(DBM)₃TPTZ, Eu(BA)₃TPTZ, Eu(TTA)₃TPTZ, and Eu(BTFA)₃TPTZ were found to be 3.4%, 17.4%, 15.5%, 40.2%, and 69.7% respectively. As expected, these lanthanide β -diketonate adducts with TPTZ display higher emission quantum yields than their aqua analogs [17,38]. In terms of photoluminescence quantum yield, Eu(BTFA)₃-TPTZ is among the most efficient Eu³⁺ complexes that are without substitution of H for D.

When the chloroform solution of $\text{Er}(\text{DBM})_3\text{TPTZ}$ was excited by a 980-nm pump laser, near infrared emission, shown in Fig. 8, was observed. The maximum intensity peak is located at 1527 nm, assigned to ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$, with a full width at half-maximum (FWHM) of about 81 nm. The value is greater than those of erbium-doped phosphate glass (55 nm) [39] and an erbium complex doped in epoxy resin polymers (47 nm) [40], but comparable to those of erbium polydentate cage complexes (70 nm) in organic solutions [41] and erbium tris(8-hydroxy)quinoline (73 nm) doped in sol-gels [20]. A broad spectrum enables a wide gain bandwidth for optical amplification in telecommunication systems.

4. Conclusion

Several new lanthanide β -diketonate adducts with the neutral ligand TPTZ were synthesized and their structures were established using single crystal X-ray diffraction. In each case, the lanthanide center is coordinatively saturated with three β -diketonate ligands and a TPTZ ligand. π - π interactions involving TPTZ ligands were observed with the formation of dimers of both Eu(BA)₃TPTZ and Eu(BTFA)₃TPTZ. Photoluminescence studies confirmed that excitation of the complexes is originated from the ligand absorption of photons, and the emission is characteristic of the lanthanide ion of the complex. It is likely that the bulky TPTZ ligand enhances the luminescence efficiency of the title complexes over their aqua species by

effectively shielding the lanthanide ions from interacting with luminescence-quenching solvent molecules.

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Appendix A. Supplementary material

Details of spectroscopic and photoluminescence studies in both solution and the solid states. CCDC 238124, 238125, 618401, 618402 and 618403 contain the supplementary crystallographic data for Tb(DBM)₃TPTZ, Er(DBM)₃TPTZ, Eu(TTA)₃TPTZ, Eu(BA)₃TPTZ, and Eu(BTFA)₃TPTZ. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving. html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2006. 10.049.

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