

Photoluminescence properties of eight coordinated terbium(III) complexes

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8배위 터븀 (III) 착화합물의 합성과 Photoluminescence 특성

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Abstract: Eight coordinated terbium(III) complexes, tris (2-pyrazinecarboxylato)(phenanthroline) terbium(III) [Tb (pzc)₃(phen)], tris (5-methyl-2-pyrazinecarboxylato) (phenanthroline) terbium(III) [Tb(mpzc)₃(phen)] and tris(2-picolinato) (phenanthroline) terbium(III) [Tb(pic)₃(phen)], have been synthesized and characterized by Fourier transform infrared (FT-IR), UV-Visible and X-ray photoelectron spectroscopy. Photoluminescence (PL) spectroscopy shows that these complexes emitted strong green luminescence. When powder samples of the Tb³⁺ complexes are examined using time-resolved spectroscopic analysis, the luminescence lifetimes are found to be 0.87 ms and 1.0 ms, respectively. Thermogravimetric analysis reveals the terbium complexes to have good thermal stability up to 333-379 °C. Cyclic voltammetry shows that HOMO-LUMO energy gap of the Tb³⁺ complexes ranges from 4.26~4.41 eV. These values are similar to those obtained from the UV-visible spectra. Overall, the synthesized Tb³⁺ complexes may be useful advanced materials for green light emitting devices.

요 약: 3종의 8배위 터븀 착화합물 [tris (2-pyrazinecarboxylato) (phenanthroline) terbium (III), tris (5-methyl-2-pyrazinecarboxylato) (phenanthroline) terbium(III) 및 tris (2-picolinato) (phenanthroline) terbium (III)]을 합성하고, 이 화합물을 FT-IR, UV 및 XPS 사용하여 특성평가 하였다. 또한, PL 스펙트라를 통하여 합성된 터븀 착화합물은 강한 녹색 형광을 방출하는 것을 확인하였으며, 시간 분해 분광분석기를 통하여 합성된 터븀 착화합물의 형광 반감기가 0.87 ms 및 1.0 ms임을 알았고, 열분석을 통하여 합성된 터븀 착화합물의 열안정성은 333-379 °C 나타내는 것을 확인하였다. CV를 통하여 합성된 터븀 착화합물의 경우 HOMO-LUMO 에너지 차이가 4.26~4.41 eV를 나타냈는데, 이것은 UV-visible 스펙트라에서 얻은 값과 유사한 값을 확인하였다. 따라서, 제조된 터븀 착화합물은 초록색을 발광하는 디바이스 재료로 사용할 수 있다.

Key words: pyrazinecarboxylato, picolinato, phenanthroline, eight coordinated terbium(III) complex, photoluminescence, green emission

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1. Introduction

Many research groups that studied lanthanide complexes as potential emitting materials have typically reported narrow emission bands, long decay times and high efficiency.¹⁻⁴ Since the emissions from lanthanide complexes are based on 4f electronic transitions, which are effectively shielded from the influence of external forces by filled 5s² and 5p⁶ orbitals, the various states arising from fⁿ configurations are split by external fields only to the extent of 100 cm⁻¹. On the other hand, the intensities of the absorption bands are usually weak because the f-f transitions of these ions are forbidden. In contrast, lanthanide complexes with organic ligands can exhibit extensive luminescence due to the high absorption capacity of the ligands in the ultraviolet region and efficient energy transfer from the ligands to the central rare earth ions.⁵ In terbium chelates, the major luminescent peaks originate from the ⁵D₄ → ⁷F_J (J=6,5,4,3) transition. The strongest transition, ⁵D₄ → ⁷F₅, normally occurs at approximately 546 nm with a narrow emission band, which produces the green color in these Tb(III) complexes.⁶ For many years, terbium and europium complexes with the β-diketone ligand were produced and shown to exhibit intense narrow band emission as well as high efficiency emission.^{7,8} Unfortunately, rare earth β-diketone complexes have only limited applications owing to their poor photostability.⁹ In contrast, lanthanide complexes containing carboxyl ligands tend to have desirable UV absorption properties, whereas those with phenanthroline ligands possess good photoluminescent properties⁹⁻¹¹ and thermal stability.¹² Therefore, this study designed and synthesized tris(2-pyrazinecarboxylato)(phenanthroline) terbium(III) Tb(pzc)₃(phen) (**a**), tris(5-methyl-2-pyrazinecarboxylato)(phenanthroline) terbium(III) Tb(mpzc)₃(phen) (**b**), and tris(2-picolinato)(phenanthroline) terbium(III) Tb(pic)₃(phen) (**c**) in an effort to realize both these two properties in a single complex, which will have applications as green emitters. These complexes, which represent novel Tb(III) emitting materials, were characterized by Fourier transform infrared

(FT-IR) spectroscopy, UV-visible spectroscopy, X-ray photoelectron spectroscopy (XPS) and photoluminescence (PL) spectroscopy, and their thermal stability was evaluated by thermogravimetric analysis (TGA).

2. Experimental

2.1. Preparation of tris(2-pyrazinecarboxylato)(phenanthroline)terbium(III) (**a**)

Fig. 1 shows the method used to prepare Tb(III) complexes **a** and **b**. 2-Pyrazinecarboxylic acid (Hpzc, 0.372 g, 3 mmol) was dissolved in 30 mL of absolute ethanol. In a separate flask, 0.373 g of TbCl₃ (99.9%, Aldrich Co., 1 mmol) was dissolved in warm ethanol and added slowly to the ligand solution with constant stirring. The mixture was adjusted to pH 6-7 by the addition of NaOH (1 N water dissolution) and stirred at 78 °C for 30 min under nitrogen. Subsequently, 0.198 g of a phenanthroline (phen, 1 mmol) solution in ethanol was added to the reaction flask. The flask was stirred again at 78 °C for 2 h under nitrogen. Upon cooling, the resulting white precipitate was filtered and washed with warm ethanol and water, and dried under vacuum. The precipitate was then purified by train sublimation for 24 h to yield 0.4717 g (67%). Anal. Calcd for C₂₇H₁₇N₈O₆Tb: Calc. C, 45.78; H, 2.42; N, 15.82. Found: C, 45.3; H, 2.64; N, 15.42.

2.2. Preparation of tris(5-methyl-2-pyrazinecarboxylato)(phenanthroline)terbium(III)(**b**)

This complex was synthesized using the same

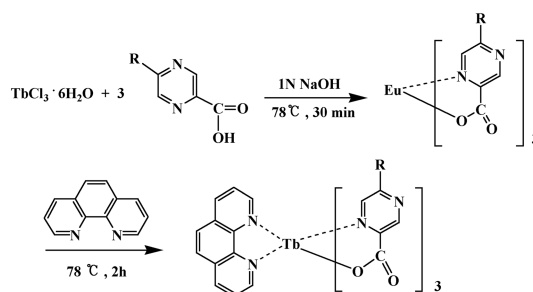


Fig. 1. Schematic synthesis of Tb(pzc)₃(phen) [R = H] and Tb(mpzc)₃(phen) [R = CH₃].

procedure as that for complex **a**, except its product did not precipitate as readily. After cooling the reaction flask, the product's precipitation was aided by the addition of ether. The white precipitate was purified by train sublimation for 24 h to yield 0.561 g (75%). Anal. Calcd for $C_{30}H_{23}N_8O_6Tb$: C, 48.01; H, 3.09; N, 14.93. Found: C, 47.89; H, 3.18; N, 14.77.

2.3. Preparation of tris(2-picolinato)(phenanthroline) terbium(III) (**c**)

This complex was synthesized using the same procedure used for complex **a**. After cooling the reaction flask, the product was again precipitated by the addition of ether. The white precipitate was purified by train sublimation for 24 h to yield 0.353 g (50%). Anal. Calcd for $C_{30}H_{20}N_5O_6Tb$: C, 51.08; H, 2.86; N, 9.93. Found: C, 51.03; H, 2.90; N, 9.94.

2.4. Measurement

Elemental analyses of the samples were performed using a Perkin-Elmer model 240 C.H.N analyzer. The IR and UV-VIS absorption spectra were obtained on a Perkin-Elmer Spectrum 1000FT-IR and Shimadzu UV-3101PC, respectively. PL spectroscopy of the solution and solid state samples were measured on an Edinburgh Instruments FS 920 fluorometer, whereas the luminescence lifetimes were evaluated using an Edinburgh Instruments FL 900 by monitoring the $^5D_4 \rightarrow ^7F_5$ emission line of Tb^{3+} at room temperature. XPS was performed using a Perkin-Elmer Phi 5500 ESCA system. TGA was carried out on a 951 Dupont thermogravimetric analyzer using a temperature program of 10 °C per min from room temperature to 700 °C

in a flowing N_2 atmosphere. Cyclic voltammetry was measured using a potentiostat/galvanostat (model 283, Ametek PAR, U.S.A.) in a conventional three-electrode system. The working, counter, and reference electrodes were a GC MWNT electrode, platinum wire, and Ag/AgCl (sat'd KCl), respectively.

3. Results and Discussion

3.1. IR spectra

Table 1 lists the principal bands observed and their assignments in the IR spectra of compounds **a** [$Tb(pzc)_3(phen)$], **b** [$Tb(mpzc)_3(phen)$] and **c** [$Tb(pic)_3(phen)$]. The carboxyl stretching frequency of the C-C(=O)-O moiety of the pzc, mpzc and pic ligands manifested itself as very strong absorptions at 1,668, 1,655 and 1,620 cm^{-1} , respectively, which demonstrates a shift to lower frequencies compared to 1721, 1729 and 1,720 cm^{-1} for the Hpzc, Hmpzc and Hpic free acid, respectively.¹³ The C=N stretching frequencies of the heterocycles underwent a shift upon coordination of the ligand. For the pyrazine ring, C=N stretching for compounds **a** and **b** was observed at 1,583 and 1,585 cm^{-1} , respectively, and at 1,394 and 1,379 cm^{-1} for the free acid (Hpzc and Hmpzc). For the picolin ring, the C=N stretching band was observed at 1,568 cm^{-1} for the $Tb(pic)_3(phen)$ complex and at 1,454 cm^{-1} for the free acid (Hpic), whereas for phenanthroline, it was observed at 1,628 cm^{-1} (**a,c**) and 1,626 cm^{-1} (**b**) for the three terbium complexes, and at 1,590 cm^{-1} for the free ligand (phen).¹⁴ These shifts in the stretching frequencies were attributed to the strong coordination of the ring nitrogen and

Table 1. Principal IR bands of the ligands and complexes

Compound	$\nu_{C=O}^a$	$\nu_{C=N}$ from pyrazine and picolin	$\nu_{C=N}$ from phen
Hpzc	1721	1394	
Hmpzc	1729	1379	
Hpic	1720	1454	
Phen		1315, 1154 1337, 1309	1590
$Tb(pzc)_3(phen)$	1668	1583	1628
$Tb(mpzc)_3(phen)$	1655	1585	1626
$Tb(pic)_3(phen)$	1620	1568	1628

^aall IR frequencies are given in cm^{-1}

carboxylate oxygen with Tb(III), supporting their assignment as chelating ligands.

3.2. XPS

By measuring the differences in kinetic energy of the photoelectrons, XPS can provide direct experimental evidence of important quantities, such as the energy of the molecular orbitals and the atomic charge distributions within the coordination sphere. The results are shown in Fig. 2. The 4d peak of Tb was shifted to 154.10 eV, which is higher than that of the pure Tb(III) peak, which is normally observed at 150.1 eV.¹⁵ In addition, the Tb³⁺ 3d signal depicts the spin-orbit splitting into Tb³⁺ 3d_{3/2} and Tb³⁺ 3d_{5/2}. The binding values of Tb³⁺ 3d in the chelate were increased from 1,276 (Tb³⁺ 3d_{3/2}) and 1,246 eV (Tb³⁺ 3d_{5/2}) to 1,278 and 1,245 eV, respectively. The binding energy of O1s (532 eV, standard) and N1s (399 eV, standard) were also increased to 535.91 eV (O1s) and 404.64

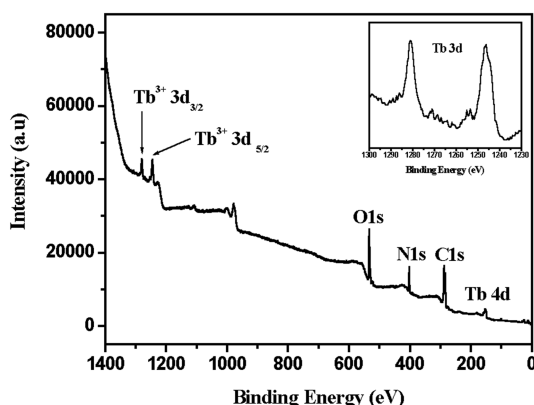


Fig. 2. XPS spectra of Tb(pzc)₃(phen).

eV (N1s)^{13,16} in the Tb(pzc)₃(phen) complex. From this data, it appears that the lone pair electrons from the nitrogen and oxygen atoms were shifted to the coordination sphere of the metal atom, which also supports the conclusion that the ligands strongly chelate to Tb(III).

3.3. TGA

Fig. 3 presents the TGA results for the complexes. The TGA curves essentially level up to >300 °C, except that the complexes experienced slight weight loss of approximately 1~2% near 100 °C. This weight loss is probably due to a small amount of physically adsorbed water. Therefore, Tb(pzc)₃(phen), Tb(mpzc)₃(phen) and Tb(pic)₃(phen) have good thermal stability with decomposition temperatures of 367, 334 and 379 °C, respectively.

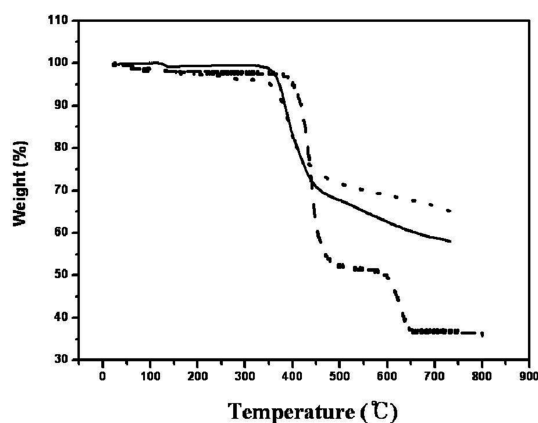


Fig. 3. The TGA plots of Tb(pzc)₃(phen) (solid line), Tb(mpzc)₃(phen) (dotted line) and Tb(pic)₃(phen) (dash line).

Table 2. Electronic absorption and photoluminescence data for Tb³⁺ complexes

	UV		PL			
	λ_{abs} (nm)	ϵ_{max} ($\times 10^4$)	λ_{em} (nm)	Intensity (Ratio %)	Lifetime, τ (ms)	Transition
Tb(pzc) ₃ (phen)	271.5 ^a	3.056 ^a	543.2 ^a	100 ^b	0.87 ^a	⁵ D ₄ → ⁷ F ₅
	319.0 ^b	0.306 ^b	544.4 ^b		1.96 ^b	
Tb(mpzc) ₃ (phen)	273.0 ^a	2.71 ^a	542.8 ^a	56.6 ^b	1.0 ^a	⁵ D ₄ → ⁷ F ₅
	317.0 ^b	0.339 ^b	543.3 ^b		1.89 ^b	
Tb(pic) ₃ (phen)	279.5 ^a	0.72 ^a	547.1 ^a			⁵ D ₄ → ⁷ F ₅

^aFor powder sample

^bFor 5×10^{-5} M solution in DMSO

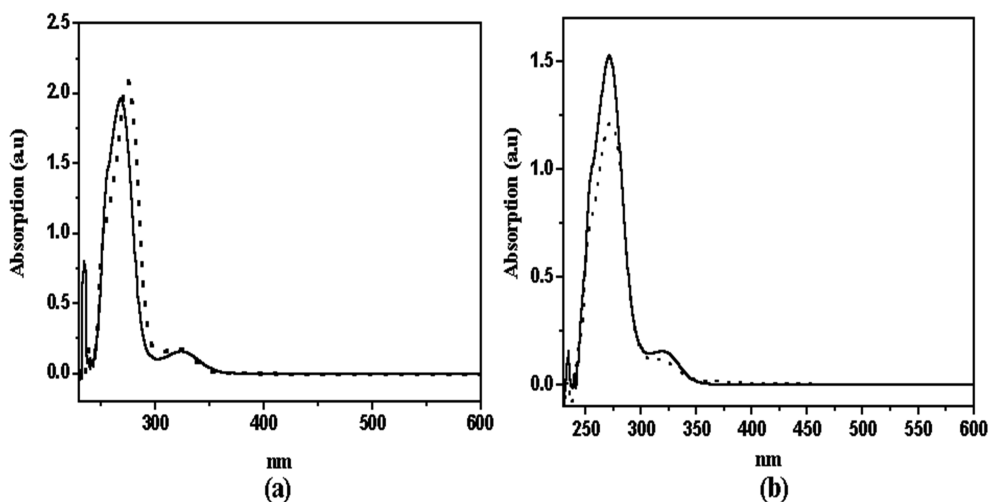


Fig. 4. Electronic absorption spectra of (a) Hpzc (solid line) and Hmpzc (dotted line), 1×10^{-4} M (DMSO) and (b) Tb(pzc)₃(phen) (solid line) and Tb(mpzc)₃(phen) (dotted line), 5×10^{-5} M (DMSO).

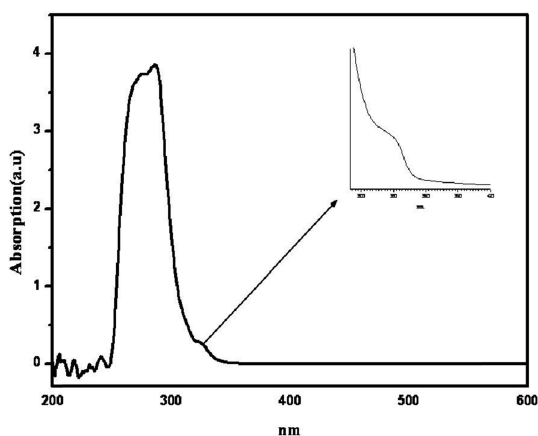


Fig. 5. Electronic absorption spectra of Tb(pic)₃(phen), 5.0×10^{-4} M (DMSO).

3.4. UV absorption spectra

Fig. 4 and Fig. 5 show the electronic absorption (EA) spectrum for each complex and anion ligand in DMSO, respectively. The spectral data are summarized in Table 2. The absorption maxima for compounds **a**, **b** and **c** at 271.5, 273.0 and 279.5 nm, respectively, are associated with the $\pi \rightarrow \pi^*$ transitions in the aromatic rings and have absorption coefficients of 3.06×10^4 , 2.71×10^4 and 0.72×10^4 $\text{M}^{-1} \text{cm}^{-1}$, respectively. For each complex, compounds **a**, **b** and **c** showed a weaker absorption band at 319.0, 317.0 and 326, respectively, which can be assigned to the

$n \rightarrow \pi^*$ transition of the non-bonding electrons of the heterocyclic nitrogen. The small “blue-shift” in the $n \rightarrow \pi^*$ bands of these complexes was also observed between pyrazine-2-carboxylic acid and 5-methylpyrazine-2-carboxylic acid, which might be due to the presence of an electron donating methyl substituent.¹⁷⁻¹⁹ The EA spectra of these lanthanide complexes strongly resemble that of their anionic ligand, which suggests that the absorption process of these complexes is strongly dependent on the nature of these ligands.

3.5. Luminescence properties

Luminescence in rare earth complexes is produced by the relatively weak f-f transitions of the metal ion, and the intensities of Tb³⁺ are the weakest of the whole lanthanide series.²⁰ On the other hand, in lanthanide chelates, the ligand energy is transferred from the lowest triplet state of the ligand to an appropriate ⁵D_j level on the metal ion. In order for energy transfer to be effective, the triplet state of the ligand must be higher in energy than the emissive excited state of the metal ion, and for terbium chelates, the ligand energy is mostly transferred to the ⁵D₄ level because of the high position of the ⁵D₃ level. The efficiency of this energy transfer process depends on the relative forward and reverse transfer

rates of the energy exchange process between the ligand and 5D_j level to which the energy is primarily transferred.^{21,22} Therefore, although the emitting color of a rare earth complex depends on the metal ion, the energy transfer properties of the organic ligands are critical to the quantum yield of luminescent emission of the lanthanide complexes because the absorption coefficients of the ligands are many orders of magnitude larger than the trivalent lanthanide ions.^{23,24} As predicted, pzc and mpzc were found to be good energy transfer ligands for Tb^{3+} with respect to the photoluminescence. In addition, the incorporation of a neutral ligand, such as phenanthroline, may well have helped facilitate effective energy transfer through its good electron transport properties.²⁵

Figs. 6 and Fig. 7 present the emission and excitation spectra for the solids and DMSO solutions of complexes **a**, **b** and **c**, respectively. For each of the **a** and **b** complexes, the PL spectrum of the solid showed better resolved emission features than that in solution, suggesting that energy transfer from the anionic ligand to the Tb^{3+} is more efficient in the solid state than in solution.²⁵ Sharp emission peaks were observed for solid **a** at 488.9 nm ($^5D_4 \rightarrow ^7F_6$), 543.8 nm ($^5D_4 \rightarrow ^7F_5$), 582.8 nm ($^5D_4 \rightarrow ^7F_4$), and 619.9 nm ($^5D_4 \rightarrow ^7F_3$), and for solid **b** at 489.0 nm ($^5D_4 \rightarrow ^7F_6$) and 543.7 nm ($^5D_4 \rightarrow ^7F_5$). The luminescence spectra of the solid samples of both complexes

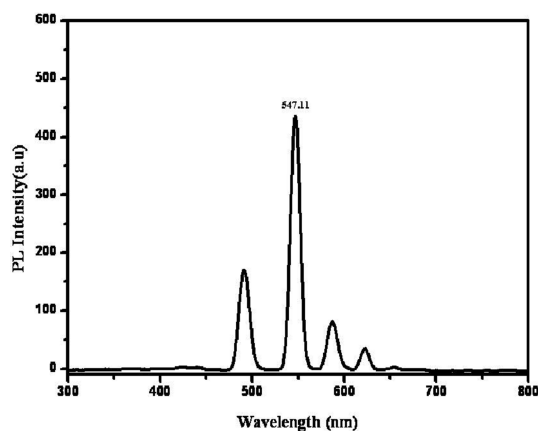


Fig. 7. Fluorescence spectrum of $Tb(pic)_3(phen)$ in DMSO solution.

showed a half spectral bandwidth of only approximately 8.8 nm. This indicates that the observed luminescence of these samples is almost monochromatic and filters may not be necessary for many applications.²⁶ In addition, sharp emission peaks were observed for the $Tb(pic)_3(phen)$ complex at approximately 547.1 nm ($^5D_4 \rightarrow ^7F_5$), which corresponds to green emission.

The luminescence lifetimes of solid samples of the Tb^{3+} complexes **a** and **b** were measured by time-resolved spectroscopy. The results and data are shown in *Fig. 8* and *Table 2*, respectively. The decay curves were fitted to a single exponential function, $y = y_0 + A_1 \exp(-x/\tau)$, and the luminescence lifetimes

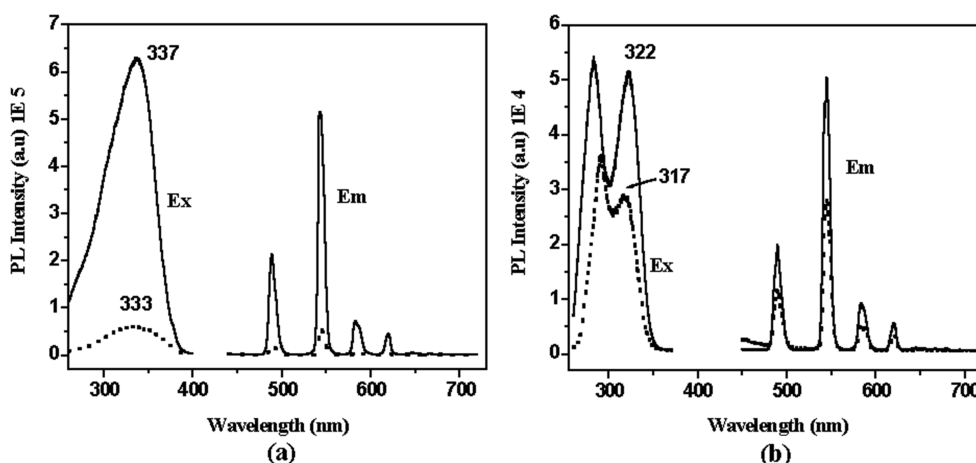


Fig. 6. Emission (Em) and excitation (Ex) spectra of (a) $Tb(pzc)_3(phen)$ (solid line), and $Tb(mpzc)_3(phen)$ (dotted line) in the solid state (b) $Tb(pzc)_3(phen)$ (solid line) and $Tb(mpzc)_3(phen)$ (dotted line) in solution, 5×10^{-5} M (DMSO).

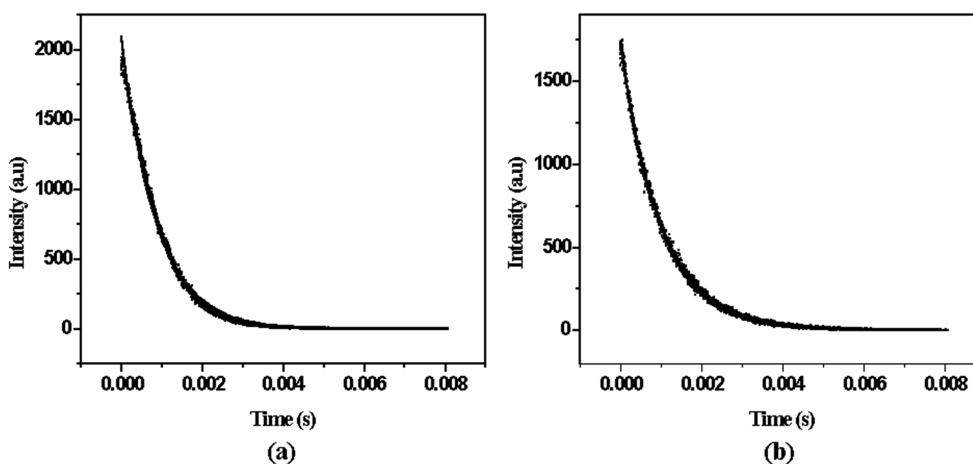


Fig. 8. Time-resolved spectra for (a) $\text{Tb}(\text{pzc})_3(\text{phen})$ and (b) $\text{Tb}(\text{mpzc})_3(\text{phen})$ in the solid state. The symbol curves represent experimental lifetime decay, and the solid line curves represent first order exponential decay.

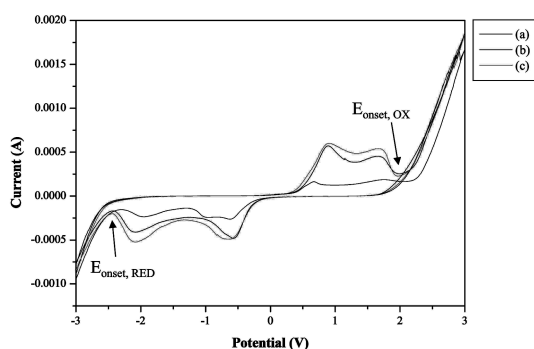


Fig. 9. Cyclic voltammograms (CV) of $\text{Tb}(\text{pzc})_3(\text{phen})$ (a), $\text{Tb}(\text{mpzc})_3(\text{phen})$ (b) and $\text{Tb}(\text{pic})_3(\text{phen})$ (c) in phosphate buffer solution (pH=7.0) with scan rate of 100 mV/s.

of Tb^{3+} ($^5\text{D}_4$) in $\text{Tb}(\text{pzc})_3(\text{phen})$ and $\text{Tb}(\text{mpzc})_3(\text{phen})$ were determined to be 0.87 and 1.0 ms, respectively. Because the excited state energy transition is inversely proportional to the lifetime, the transition probability of Tb^{3+} in $\text{Tb}(\text{pzc})_3(\text{phen})$ is apparently higher than that in $\text{Tb}(\text{mpzc})_3(\text{phen})$.²⁷ Arnaud *et al.* took this one step further and reported that it is possible to relate the luminescence lifetimes to the energy gap between the triplet state of the ligand and the acceptor level of the metal ion.²⁸ For these complexes, the lifetime of complex **a** is clearly shorter than that of complex **b** in the solid state. This is also in agreement with the PL intensity results with the luminescence intensity of complex **a** being almost

double that of complex **b** in solution (see Fig. 4b). Therefore, both the shorter luminescence lifetime and higher luminescence intensity of complex **a** suggest that the energy gap between the ligand triplet state and the $^5\text{D}_4$ state of Tb^{3+} is smaller for complex **a** than for complex **b**, resulting in more efficient energy transfer. Hence, in terms of the luminescence properties, pzc is clearly a better anionic ligand for $\text{Tb}(\text{phen})$ -type complexes than mpzc.

3.6. Electrochemical properties

Fig. 9 shows the cyclic voltammograms (CV) of Tb^{3+} complexes, recorded in PBS (pH=7.0) with scan rates at 100 mV. Table 3 lists the oxidation and reduction onset potentials of the synthesized Tb^{3+} complexes for the Ag/AgCl reference electrode. The ionization potential (I_p) and electron affinity (E_a) were obtained using an electrochemical method and are listed in Table 3. The HOMO-LUMO energy gap of $\text{Tb}(\text{pzc})_3(\text{phen})$, $\text{Tb}(\text{mpzc})_3(\text{phen})$, and $\text{Tb}(\text{pic})_3(\text{phen})$ were 4.26, 4.4, and 4.42 eV, respectively, using an electrochemical method. On the other hand, the HOMO-LUMO energy gap of $\text{Tb}(\text{pzc})_3(\text{phen})$, $\text{Tb}(\text{mpzc})_3(\text{phen})$, and $\text{Tb}(\text{pic})_3(\text{phen})$ were 3.52, 3.52, and 3.58 eV, respectively, using a UV-visible method. The energy gap of the Tb^{3+} complexes obtained from electrochemical method were larger than that of the Tb^{3+} complexes obtained from the UV-visible method.

Table 3. HOMO-LUMO energy gap analysis for the synthesized Tb³⁺ complexes via cyclic voltammogram and UV-visible spectrum

Tb ³⁺ complex	E _{onset} ^{OX} (V)	E _{onset} ^{RED} (V)	I _p (HOMO) (eV)	E _a (LUMO) (eV)	ΔE ¹ (eV)	ΔE ² (eV)
Tb(pzc) ₃ (phen)	1.89	-2.37	6.29	2.03	4.26	3.52
Tb(mpzc) ₃ (phen)	1.99	-2.42	6.39	1.98	4.41	3.52
Tb(pic) ₃ (phen)	1.97	-2.45	6.37	1.95	4.42	3.58

Ionization potential (I_p) = E_{onset}^{OX} + 4.4; Electron affinity (E_a) = E_{onset}^{RED} + 4.4; Electrochemical band gap (ΔE¹) = E_{onset}^{RED} - E_{onset}^{OX}; Photochemical band gap (ΔE²) = hc/eλ(nm) [*h* = 6.626 × 10⁻³⁴ (JS); *e* = 1.602 × 10⁻¹⁹ (C); *c* = 2.998 × 10⁸ (m/s)].

4. Conclusions

Eight coordinated terbium complexes, Tb(pzc)₃(phen), Tb(mpzc)₃(phen) and Tb(pic)₃(phen) were synthesized and characterized. These complexes showed similar emission patterns with the strongest emission being a strong, narrow band in the range, 543-547 nm. The luminescence lifetime of complex **a** was shorter than that of complex **b**. Thermal stability was good with decomposition of these complexes not occurring until 333-379 °C. This suggests that Tb(pzc)₃(phen), Tb(mpzc)₃(phen) and Tb(pic)₃(phen) have considerable potential as green emitting materials for future generations of electro-luminescence devices. This complex may have applications as an advanced material for green light emitting devices.

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