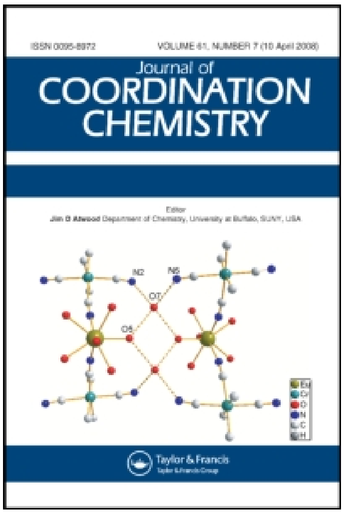

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Synthesis and characterization of two tetranuclear heterometallic Tb(III)–Zn(II) complexes

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Tetranuclear heterometallic complexes, $[Tb_2Zn_2(Bzo)_{10}(phen)_2]$ (**1**) and $[Tb_2Zn_2(TPA)_{10}(phen)_2]$ (**2**) ($Bzo^- = C_6H_5CO_2^-$, $TPA^- = o\text{-}C_4H_3SCO_2^-$, phen = 1,10-phenanthroline), were synthesized by the rheological phase reaction method and characterized by elemental analysis, IR and X-ray crystallography. Both complexes are tetrameric and the carboxylate ligands display three coordination modes, bidentate bridging, bidentate chelating and tridentate chelating-bridging. The Zn atoms in complexes **1** and **2** are coordinated by two nitrogen atoms from one phen ligand, four oxygen atoms from two bidentate bridging and a tridentate chelating-bridging carboxylate group. However the coordination spheres around the Tb atoms are different. The Tb atom in **1** is eight-coordinate, while the Tb atom in **2** is seven-coordinate. Both complexes **1** and **2** exhibit green luminescence when irradiated by UV light. Compared with binary terbium benzoate, the introduction of the Zn^{2+} ion and phen enhances the luminescence intensity dramatically.

Keywords: Terbium; Zinc; Heterometallic complexes; Crystal structure; Luminescence

1. Introduction

The design and synthesis of 4f–3d heterometallic complexes has been explored because of the fascinating structures and potential applications in magnetic, luminescent and other materials [1–11]. Magnetic exchange interactions between rare earth and transition metals are not only of theoretical interest, but have several possible applications [12–16]. Reports on 4f–3d heterometallic luminescent complexes are still relatively rare [1,2,17–21]. In this paper we report the synthesis and structures of two tetranuclear heterometallic Tb(III)–Zn(II) complexes, $[Tb_2Zn_2(Bzo)_{10}(phen)_2]$ (**1**) and $[Tb_2Zn_2(TPA)_{10}(phen)_2]$ (**2**) ($Bzo^- = C_6H_5CO_2^-$, $TPA^- = o\text{-}C_4H_3SCO_2^-$, phen = 1,10-phenanthroline), which were obtained by the rheological phase reaction method [22]. The Zn(II) ion is a sensitizer of Tb(III) ion luminescence [23], and the influences of the Zn(II) ion and the phen ligand on the luminescence are discussed here.

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2. Experimental

2.1. *Materials and methods*

All chemicals were of reagent grade. $TbCl_3 \cdot 5H_2O$ was prepared by dissolving Tb_4O_7 in hydrochloric acid followed by drying. The IR spectra were recorded on a Thermo Nicolet Avatar 360 FT-IR spectrophotometer using KBr pellets. Elemental analyses were carried out with a Perkin-Elmer 240B elemental analyzer. The excitation and emission spectra of the solid samples were measured on a Shimadzu RF-5301PC spectrofluorophotometer at room temperature with excitation and emission slit widths of 1.5, 1.5 nm and 3.0, 1.5 nm for complexes **1** and **2,** respectively.

2.1.1. Synthesis of $[Tb_2Zn_2(Bzo)_{10}(phen)_2]$ (1). 0.16 g (2.0 mmol) of ZnO, 0.35 g (1.0 mmol) of $TbCl_3 \cdot 5H_2O$, 0.86 g (7.0 mmol) of HBzo, 0.20 g (1.0 mmol) of phen H_2O and 2.0 cm^3 of H_2O were placed in a Teflon-lined stainless-steel vessel to obtain a rheological phase. The vessel was sealed and heated to 90°C for 3 d and then slowly cooled to room temperature. Colorless block-shaped crystals were obtained (0.33 g in a yield of 32.7% based on Tb). *Anal.* Calcd. for $C_{94}H_{66}N_4O_{20}Tb_2Zn_2$ (%): N, 2.77; C, 55.84; H, 3.27. Found: N, 2.67; C, 56.01; H, 3.44.

2.1.2. Synthesis of $[Tb_2Zn_2(TPA)_{10}(phen)_2]$ (2). 0.16 g (2.0 mmol) of ZnO, 0.35 g (1.0 mmol) of $TbCl_3 \cdot 5H_2O$, 0.90 g (7.0 mmol) of HTPA, 0.20 g (1.0 mmol) of phen H_2O and 2.0 cm^3 of H_2O were placed in a Teflon-lined stainless-steel vessel to obtain a rheological phase. The vessel was sealed and heated to 90°C for 7 d and then slowly cooled to room temperature. Colorless sheet-like crystals were obtained (0.60 g, yield of 52.7% based on Tb). *Anal.* Calcd. for $C_{74}H_{46}N_4O_{20}S_{10}Tb_2Zn_2$ (%): N, 2.69; C, 42.69; H, 2.21. Found: N, 2.58; C, 42.78; H, 2.35.

2.2. *Crystallographic measurements and structure solution*

The X-ray diffraction data of complexes **1** and **2** were collected on a RIGAKU R-AXIS IV imaging plate diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 291(2) K. The structures were solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXL-97 and SHELXS-97 programs [24]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were generated geometrically and treated by a mixture of independent and constrained refinements. A summary of the crystal parameters and refinement details is given in table 1. Selected bond lengths for **1** and **2** are listed in table 2. X-Ray crystallographic files in CIF format for complexes **1** and **2** have been deposited at the Cambridge Crystallographic Data Center, CCDC No. 222657 and 222658 for **1** and **2**, respectively.

3. Results and discussion

3.1. *Syntheses of complexes 1 and 2*

Synthesis of 4f–3d heterometallic complexes methods usually involves conventional solution reactions and hydro(solvo)thermal reactions. In this paper, the rheological phase reaction method has been used and two complexes, $Tb_2Zn_2(Bzo)_{10}(phen)_2$ (**1**) and

Table 1. Crystal data and structure refinement parameters for complexes **1** and **2**.

Compound	**1**	**2**
Empirical formula	$C_{47}H_{33}N_2O_{10}TbZn$	$C_{37}H_{23}N_2O_{10}S_5TbZn$
Formula weight	1010.04	1040.16
Temperature (K)	291(2)	291(2)
Wavelength (Å)	0.71073	0.71073
Crystal system, space group	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$
a (Å)	12.011(2)	11.117(2)
b (Å)	13.623(3)	12.711(3)
c (Å)	14.741(3)	15.438(3)
α (°)	107.69(3)	71.24(3)
β (°)	110.87(3)	73.96(3)
γ (°)	99.01(3)	81.98(3)
V (Å^3)	2050.0(7)	1982.2(7)
Z, D_c (g cm^{-3})	2, 1.636	2, 1.743
μ (mm^{-1})	2.360	2.696
$F(000)$	1008	1028
Crystal size (mm)	0.22 × 0.20 × 0.20	0.20 × 0.20 × 0.20
θ range (°)	1.61 to 27.51	1.69 to 27.53
Index ranges (°)	$15 \leq h \leq 14$	$-14 \leq h \leq 14$
	$-17 \leq k \leq 16$	$-16 \leq k \leq 0$
	$0 \leq l \leq 18$	$-19 \leq l \leq 16$
Reflections collected/unique	7869/7869	7560/7560
Completeness to $2\theta = 27.53$	88.3%	88.2%
Max. and min. transmission	0.6497 and 0.6248	0.6146 and 0.6146
Data/restraints/parameters	7869/0/551	7560/0/506
Goodness-of-fit on F^2	1.051	1.094
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0306$, $wR_2 = 0.0660$	$R_1 = 0.0393$, $wR_2 = 0.1078$
R indices (all data)	$R_1 = 0.0396$, $wR_2 = 0.0677$	$R_1 = 0.0486$, $wR_2 = 0.1108$
Extinction coefficient	0.00248(18)	0.0042(4)
Largest diff. peak and hole (e A^{-3})	0.603 and –0.933	1.511 and –0.977

Table 2. Selected bond lengths (Å) for **1** and **2**.

Compound				
Complex **1**	Tb(1)–O(6)	2.287(2)	Tb(1)–O(7)#1	2.680(3)
	Tb(1)–O(4)	2.291(3)	Zn(1)–O(3)	2.028(3)
	Tb(1)–O(7)	2.325(3)	Zn(1)–O(5)	2.031(3)
	Tb(1)–O(2)	2.351(3)	Zn(1)–N(1)	2.109(3)
	Tb(1)–O(10)	2.393(2)	Zn(1)–N(2)	2.181(3)
	Tb(1)–O(9)	2.421(3)	Zn(1)–O(1)	2.192(3)
	Tb(1)–O(8)#1	2.428(3)	Zn(1)–O(2)	2.343(3)
Complex **2**	Tb(1)–O(10)#1	2.264(3)	Zn(1)–O(3)	2.033(4)
	Tb(1)–O(6)	2.274(3)	Zn(1)–O(1)	2.046(4)
	Tb(1)–O(9)	2.277(4)	Zn(1)–O(4)	2.700(4)
	Tb(1)–O(4)	2.292(4)	Zn(1)–O(5)	2.087(4)
	Tb(1)–O(2)	2.334(4)	Zn(1)–N(2)	2.062(4)
	Tb(1)–O(7)	2.377(4)	Zn(1)–N(1)	2.197(5)
	Tb(1)–O(8)	2.407(4)		

$Tb_2Zn_2(TPA)_{10}(phen)_2$ (**2**), have been obtained at a lower temperature (90°C). In the past, some lanthanide carboxylates with novel structures have been obtained in our laboratory by this method [25–27]·

Selection of the starting materials is the key to the product. For complex **1**, when $TbCl_3 \cdot 5H_2O$ was replaced by $Tb_2(CO_3)_3$, only a polycrystalline powder was obtained; the presence of phen is also very important, perhaps serving as the nucleation site for crystal growth owing to its affinity for Zn(II). Confirmation of the role of the phen in the self-assembly process is demonstrated by the fact that an attempt to prepare the crystals of Tb(III)–Zn(II) carboxylates in the absence of phen failed. Both complexes are air stable and soluble in DMF and DMSO, but sparingly soluble in acetone, ethanol and methanol.

3.2. *IR spectra*

The IR spectra of the free ligands and complexes **1** and **2** were determined in the range 4000–400 cm^{-1}. The typical peaks expected for COOH groups at 1700–1650 cm^{-1} are absent indicating complete deprotonation of the carboxyl groups, whilst characteristic bands for carboxylate groups and phen are observed. The asymmetric and symmetric stretching bands for COO^- groups appear at 1593.9, 1554.2, and 1412.9 cm^{-1} for **1** and 1559.1, 1520.8, 1425.8, and 1396.2 cm^{-1} for **2**. The different splitting modes show that the COO^- groups have different coordination modes in complexes **1** and **2**. Compared to the free ligand, the vibration bands of phen are shifted to lower frequencies. The out-of-plane bending vibrations ($\delta_{C\text{–}H}$) at 855 and 735 cm^{-1} are shifted to 847.2 and 721.9 cm^{-1} for **1** and 849.2 and 725.6 cm^{-1} for **2**. The $\nu_{C=N}$ at 1588 cm^{-1} is shifted to about 1519 cm^{-1} due to coordination of N to Zn. The weak bands at 574.8 and 426.5 cm^{-1} for **1** and 518.0 and 427.7 cm^{-1} for **2** are attributed to M–O and Zn–N vibrations, respectively [28].

3.3. *Crystal structure descriptions*

The molecular structure of complex **1** is shown in figure 1. It consists of two $[TbZn(Bzo)_5(phen)]$ subunits linked together by two tridentate chelating-bridging Bzo^- groups with a Tb···Tb separation of 4.153 Å, which is nearly identical to the Gd···Gd distance in the $[Gd_2Zn_2(O_2CC_2H_5)_8\ (C_9H_7N)_2(NO_3)_2(H_2O)_2]$ [4]. The Zn and Tb centers in the subunit are connected by two bidentate bridging and one tridentate chelating-bridging Bzo^- group with a Zn···Tb distance of 3.794 Å. The Bzo^- ligands exhibit three coordination modes, bidentate chelating, bidentate bridging and tridentate chelating-bridging.

Each Tb atom is eight-coordinate, bonded by four oxygen atoms (O2, O7, O7A, O8A) from three tridentate chelating-bridging Bzo^- groups mentioned above, two oxygen atoms (O4, O6) from two bidentate bridging Bzo^- groups and two oxygen atoms (O9, O10) from one bidentate chelating Bzo^- group. The Tb–O bonds range from 2.287 to 2.680 Å and the O–C–O angles vary from 120.1 to 124.8°. As expected, the average Tb–O bond length of the chelating (2.407 Å) and tridentate chelating-bridging (2.478 Å) Bzo^- groups are much longer than those of the bidentate bridging (2.290 Å) ones.

Each Zn atom is in an distorted octahedral geometry, surrounded by two nitrogen atoms [Zn–N 2.109, 2.181 Å] from one chelating phen ligand, two oxygen atoms [Zn–O 2.028, 2.031 Å] from two bidentate bridging Bzo^- groups and two oxygen atoms [Zn–O 2.192, 2.343 Å] from one tridentate chelating-bridging Bzo^- group.

The four metal atoms in the sequence of Zn(1)···Tb(1)···Tb(1A)···Zn(1A) make a zigzag line with the Zn(1)···Tb(1)··· Tb(1A) angle being 147.8°, smaller than that in $[Gd_2Zn_2(O_2CC_2H_5)_8(C_9H_7N)_2(NO_3)_2(H_2O)_2]$ [4].

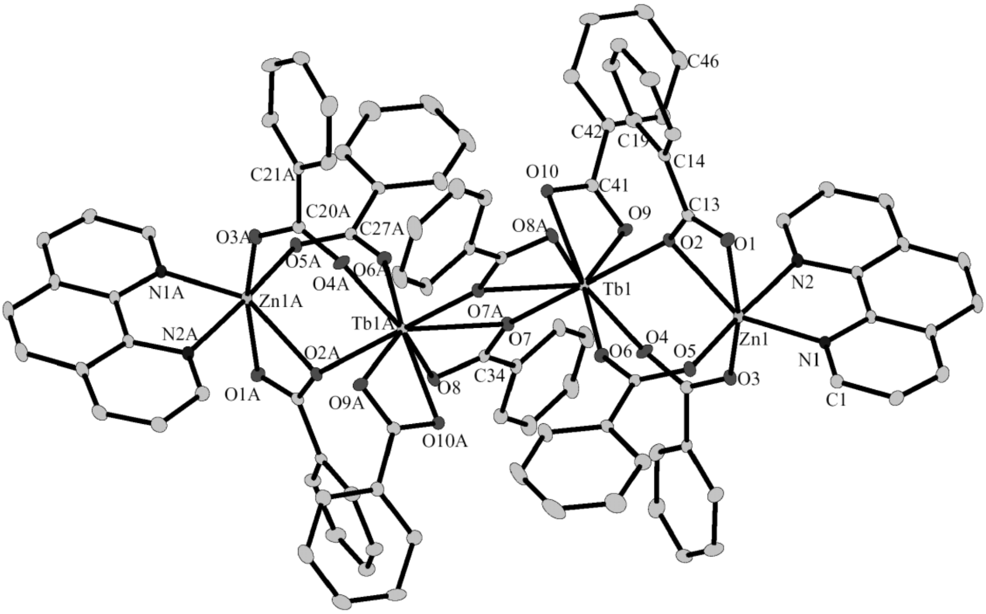

Figure 1. The molecular structure of complex **1** with 10% thermal ellipsoids.

The molecular structure of complex **2** (figure 2) has an analogous structure to complex **1**, in which eight TPA$^-$ groups form bridges between the central Tb(III) ions and outer Zn(II) ions and phen ligands are attached terminally to the outer Zn(II) ions. The two Tb atoms, at a distance of 5.161 Å, are linked together by two bidentate bridging TPA$^-$ groups. The Zn and Tb atoms are connected by two bridging and one chelating-bridging TPA$^-$ group with a Zn···Tb separation of 3.930 Å, slightly longer than that in **1**. The TPA$^-$ groups are in three coordination modes as in complex **1**. The parent thiophene rings and the carboxyl groups are coplanar for all the TPA$^-$ groups, unlike in Eu(TPA)$_3$(HTPA)$_2$ and Eu(TPA)$_3$(H$_2$O)$_3$ · 0.5H$_2$O [27].

Each Zn atom in complex **2** is also six-coordinate with two nitrogen atoms (N1, N2) from one phen ligand and four oxygen atoms, two (O1, O5) from two bridging TPA$^-$ groups and the other two (O3, O4) from a tridentate chelating-bridging one; the Zn–N (2.062 and 2.197 Å) and Zn–O (2.033–2.700 Å) distances are slightly longer than those in complex **1**.

However, in complex **2** each Tb atom is seven-coordinate, bonded two oxygen atoms (O7, O8) from a chelating TPA$^-$ group, four oxygen atoms (O2, O6, O9, O10A) from four bridging TPA$^-$ groups and one oxygen atom (O4) from one tridentate chelating-bridging TPA$^-$ group. The lower coordination is probably due to the replacement of Bzo$^-$ groups by TPA$^-$ groups, which results in more steric hindrance between the phen ligands and carboxylate groups. Accordingly all the corresponding Tb–O bonds are slightly shorter than those in **1**. Two kinds of intramolecular hydrogen bonds (C15–H···O8 2.517 Å, C35A–H···O6 2.550 Å) are formed in complex **2**, which cause deformation of the TPA$^-$ groups containing O1, O2 and O9, O10, as shown in figure 2.

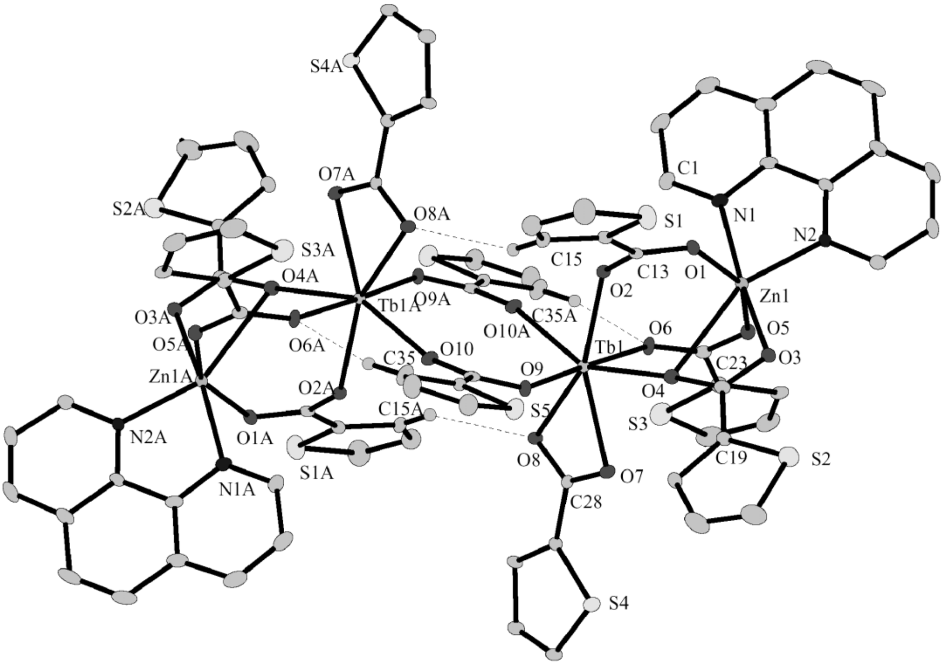

Figure 2. The molecular structure of complex **2** with 10% thermal ellipsoids.

For the Zn(1)···Tb(1)···Tb(1A)···Zn(1A) zigzag line in **2**, the Zn(1)···Tb(1)···Tb(1A) angle is 134.8°, much smaller than in **1**.

3.4. *Photoluminescence*

Under the excitation of UV light, both complexes **1** and **2** show intense green luminescence. The luminescence spectra of the solid-state samples recorded at room temperature are shown in figure 3. Both the excitation and the emission bands of the two complexes are similar. The broad excitation bands in the range 220–380 nm are attributed to the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions of the ligands (aromatic carboxylates and phen). The emission bands at 486, 542, 583 and 617 nm for **1** or 485, 545, 579 and 614 nm for **2** are assigned to the characteristic $^5D_4 \rightarrow ^7F_j$ ($j = 6, 5, 4, 3$) transitions of the Tb(III) ion, respectively. From figure 3, it can be seen that band splitting occurs for both complexes and the luminescence of **1** is much more intense than that of **2**, probably due to the different ligands. In comparison with **1**, the emission bands of **2** are red-shifted or blue-shifted from the different ligand field influence on the ^7F_j energy levels.

In order to investigate the influence of Zn(II) ion and phen on the luminescence properties, the binary and ternary complexes [Tb(Bzo)$_3$] and [Tb(Bzo)$_3$(phen)$_2$] were prepared by the rheological phase reaction method. Their luminescence properties were studied under the same conditions and the luminescence data are listed in table 3. The luminescence intensity order is: complex **1** > [Tb(Bzo)$_3$(phen)$_2$] > [Tb(Bzo)$_3$], indicating that the introduction of Zn(II) and phen influences the luminescence properties dramatically, possibly owing to the antenna effect of phen and the synergistic

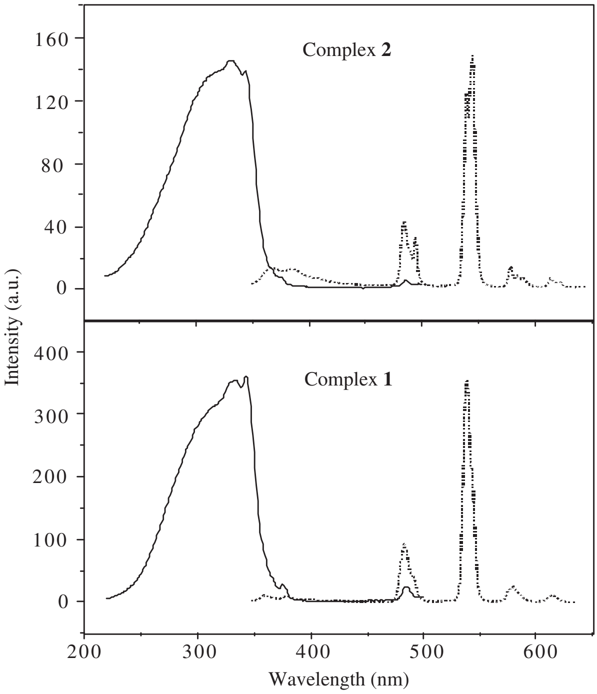

Figure 3. The excitation (solid line) and emission (dotted line) spectra of complexes **1** and **2** (complex **1**: $\lambda_{em} = 541$ nm, $\lambda_{ex} = 334$ nm; complex **2**: $\lambda_{em} = 545$ nm, $\lambda_{ex} = 330$ nm).

Table 3. Luminescence data*.

Compound	Ex (nm)	Em (nm)
[Tb(Bzo)$_3$]	290 (204.329)	485 (76.121)
	341 (53.107)	542 (203.997)
	350 (99.902)	583 (21.674)
	368 (109.285)	618 (10.118)
	453 (3.122)	
	486 (126.158)	
[Tb(Bzo)$_3$(phen)$_2$]	332 (ca.340)	486 (146.203)
	346 (361.095)	542 (370.582)
	487 (53.497)	583 (39.037)
		617 (19.914)
Complex 1	334 (1016.22)	486 (313.277)
	343 (ca.1026)	542 (1016.22)
	485 (100.70)	583 (76.939)
		618 (35.045)

*The numbers in the parentheses represent the peak intensities.

luminescence effect of Zn(II) [29], which is based on energy transfer from the chelates of Zn(II) ions to the chelates of Tb(III) ions.

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