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Synthesis, characterisation and luminescence properties of novel $Eu(TTA)_3$–co-polymer and $Tb(TPC)_3$–co-polymer

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This report describes the synthesis, characterisation and luminescence properties of $Eu(TTA)_3$–co-polymer (where TTA is 2-thenoyltrifluoroacetonate) and $Tb(TPC)_3$–co-polymer (where TPC is 2-thiophenecarboxylic acid).

Keywords: $Eu(TTA)_3$–co-polymer, $Tb(TPC)_3$–co-polymer, luminescence

Luminescent rare earth (RE) complexes, particularly europium and terbium complexes, have been intensively explored in the fields of photo-luminescent and electro-luminescent materials, due to their excellent luminescence characteristics, *i.e.,* high luminous intensity, long luminous lifetime and extremely sharp emission bands from the electronic transitions between the 4f energy levels.[1,2] However, rare earth complexes are unstable in organic solution, and it is not possible to form vacuum-vapor deposited films.[3]

Based upon the advantages of both the luminescence characteristics of rare earth ions and the material properties of a polymer, rare earth metal-containing polymers have also attracted attention in the past decade, since the first successful Eu-complex/PMMA(where PMMA is Polymethyl methacrylate)blending polymer was reported by Wolff and Pressley in 1963.[4] It is difficult to obtain rare earth polymers with the high fluorescence intensity and long fluorescence lifetime by directly dispersing a rare earth in the polymer matrix.[3,5] In contrast, the coordination of rare earth ions with carboxyl, bipyridine, or sulfo groups on the polymer chain may resolve the above problems.[6]

In order to overcome the drawbacks of conventional polymeric matrixes, the novel luminescent $Eu(TTA)_3$–co-polymer and $Tb(TPC)_3$–co-polymer were prepared from RE complexes and polymer **1** (which was reported in our previous study[7]), as shown in Scheme 1.

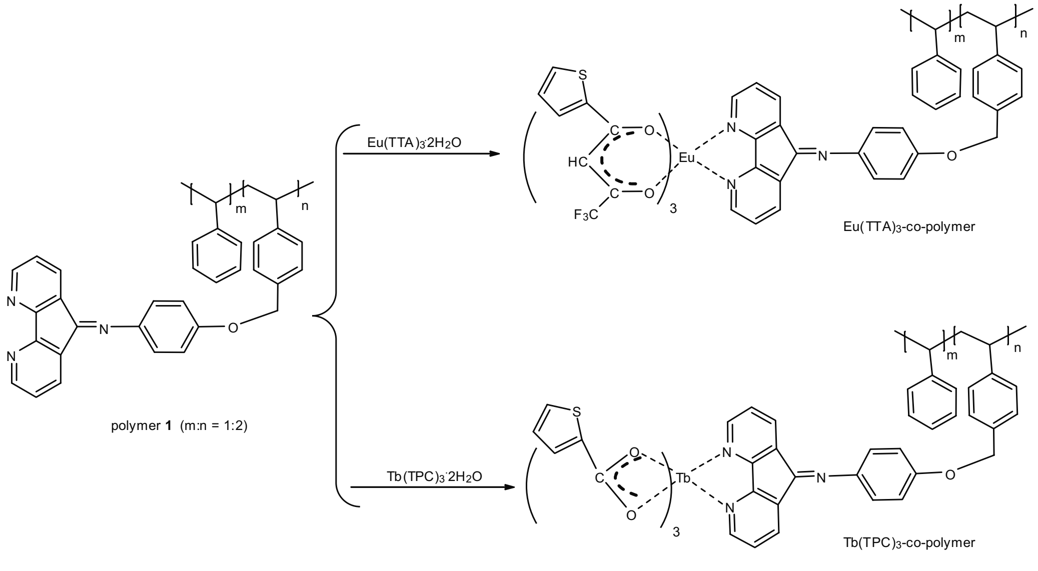
Experimental

All reagents and solvents were purchased commercially as AC grade and were used without further purification unless noted. Elemental analysis was made with Elementar Vario EL III. Eu and Tb content were determined by EDTA titration after Re^{3+} in the complexes were dissociated with 10% hydrochloric acid. The IR spectra were determined as potassium bromide pellet on a Bruker Equinox 55 FT-IR spectrophotometer. UV–vis absorption spectra were recorded on a Hitachi U-3010 UV–vis recording spectrophotometer. Luminescence spectra were recorded on a Perkin-Elmer LS55 luminescence spectrometer. TGA was carried out on a Netzsch STA 409 PG/PC and conducted with a heating rate of 10 °C min^{-1} under air atmosphere. X-ray diffraction (XRD) analysis was carried out using a D/MAX2500 VB2 + /PC with scanning angle (2θ) from 5° to 40°.

$Eu(TTA)_3 \cdot 2H_2O$: $Eu(TTA)_3 \cdot 2H_2O$: Opalescent solid following a literature method.[8] UV-vis ($CHCl_3$), λ_{max} (>235nm, ε): 338 (2.29×10^4), 269 (0.75×10^4). Anal Calcd for $Eu(C_8H_4O_2F_3S)_3 \cdot 2H_2O$: C, 33.8; H, 1.89; Eu, 17.9. Found: C, 33.7; H, 1.78; Eu, 18.3%. IR (KBr): 3412 (s, $\nu_{O\text{-}H}$), 3075 (w, $\nu_{=C\text{-}H}$), 1676 (s, $\nu_{C\text{-}O}$), 1621 (s, $\nu_{C\text{-}O}$), 1428 (s, $\nu_{C=C}$), 1234 (s, $\nu_{C\text{-}F}$), 1186 (s, $\nu_{C\text{-}F}$), 889 (w, $\delta_{C\text{-}H}$), 419 (w, $\nu_{Eu\text{-}O}$).

$Tb(TPC)_3 \cdot 2H_2O$: *$Tb(TPC)_3 \cdot 2H_2O$:* White solid. UV-vis ($CHCl_3$), λmax (>235nm, ε): 316 (2.78×10^4), 273 (0.98×10^4). Anal Calcd for $Tb(C_5H_3O_2S)_3 \cdot 2H_2O$: C, 31.3; H, 2.26: Tb, 27.6. Found: C, 31.1; H, 2.13; Tb, 27.2%. IR (KBr): 3419 (s, $\nu_{O\text{-}H}$), 3083 (w, $\nu_{=C\text{-}H}$), 1538 (s, ν_{asCOO^-}), 1426 (s, $\nu_{C=C}$), 1398 (s, ν_{sCOO^-}), 863 (w, $\delta_{C\text{-}H}$), 429(w, $\nu_{Tb\text{-}O}$).

$Eu(TTA)_3$-co-polymer: Polymer **1** (0.597 g, 1 mmol, m : n = 1 : 2)was dissolved in 5 mL DMF solution. Then a solution of $Eu(TTA)_3 \cdot 2H_2O$ (0.851 g, 1 mmol) in 5 mL of DMF was added. After refluxing for 5 h, the mixture was cooled to RT and purified by several solution-precipitation cycles using THF (4 mL) to dissolve and methanol (100 mL) to precipitate. The resulting pink solid was finally dried in a vacuum oven at 50 °C for 24 h. UV-vis ($CHCl_3$), λ_{max} (>235nm, ε): 336 (2.66×10^4), 272 (2.01×10^4), 247 (1.96×10^4). IR (KBr): 3091 (w, $\nu_{Ar\text{-}H}$), 3082 (w, $\nu_{Ar\text{-}H}$), 3036 (s, $\nu_{Ar\text{-}H}$), 2928 (w, $\nu_{asC\text{-}H}$), 2856 (w, $\nu_{sC\text{-}H}$), 1674 (s, $\nu_{C\text{-}O}$), 1651 (s, $\nu_{C=N}$), 1626 (s, $\nu_{C\text{-}N}$), 1619 (s, $\nu_{C\text{-}O}$), 1473 (s, $\nu_{C\text{-}N}$), 1428 (s, $\nu_{C=C}$), 1232 (s, $\nu_{C\text{-}F}$), 1187 (s, $\nu_{C\text{-}F}$), 860 (w, $\delta_{C\text{-}H}$), 468 (w, $\nu_{Eu\text{-}N}$), 421 (w, $\nu_{Eu\text{-}O}$). Anal Calcd for $[Eu(C_8H_4O_2F_3S)_3\ (C_{26}H_{19}N_3O)]_m(C_8H_8)_n$ (m : n = 1 : 2): C, 56.1; H, 3.33; N, 2.97; Eu, 10.8. Found: C, 56.7; H, 3.11; N, 2.71; Eu, 10.3%. The concentrations of the active constituent Eu^{3+} ($10.2/152.0 \times 100$)



Scheme 1

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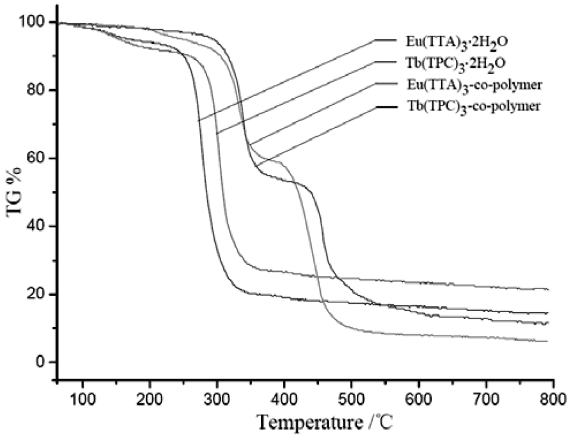

Fig. 1 The TGA curves of Re compounds.

and bipyridine [2.77(14.0 × 3) × 100] were 6.71 mmol g^{-1} and 6.59 mmol g^{-1} in the Eu-containing polymer, respectively. The molar ratio of Eu^{3+}: bipyridine was very close to 1 : 1.

Synthesis of Tb(TPC)$_3$-co-polymer: Tb(TPC)$_3$-co-polymer was obtained as grey solid following the synthetic procedure of Eu(TTA)$_3$-co-polymer. UV-vis (CHCl$_3$), λmax (>235nm, ε): 318 (2.48 × 10^4), 275 (2.25 × 10^4), 245 (1.89 × 10^4). IR(KBr): 3089 (w, $\nu_{\text{Ar-H}}$), 3033 (s, $\nu_{\text{Ar-H}}$), 2930 (w, $\nu_{\text{asC-H}}$), 2855 (w, $\nu_{\text{sC-H}}$), 1536 (s, ν_{asCOO^-}), 1649 (s, $\nu_{\text{C=N}}$), 1625 (s, $\nu_{\text{C-N}}$), 1620 (s, $\nu_{\text{C-O}}$), 1473 (s, $\nu_{\text{C-N}}$), 1428 (s, $\nu_{\text{C=C}}$), 1341 (s, ν_{sCOO^-}), 862 (w, $\delta_{\text{C-H}}$), 476 (w, $\nu_{\text{Tb-N}}$), 431 (w, $\nu_{\text{Tb-O}}$). Anal Calcd for $[Tb(C_5H_3O_2S)_3\ (C_{26}H_{19}N_3O)]_m(C_8H_8)_n$ (m : n = 1 : 2): C, 60.2%; H, 3.87%; N, 3.69%; Tb, 14.0%. Found: C, 60.9%; H, 3.56%; N, 3.48%; Tb, 13.1%. The molar ratio of Tb^{3+} (13.4/159.0 × 100 = 8.43 mmol g^{-1}):bipyridine [3.48/(14.0 × 3) × 100 = 8.29 mmol g^{-1}] was also very close to 1 : 1 in the Tb-containing polymer.

Thermal properties: The thermal stability of RE complexes and copolymers was evaluated by means of TGA under an air atmosphere, as shown in Fig. 1. The thermal degradation of Eu(TTA)$_3$·2H$_2$O and Tb(TPC)$_3$·2H$_2$O started at about 100 °C, which can be assigned to loss of water. Whereas, the thermal degradation of copolymers started at about 250 °C, which indicated that copolymer have good thermally stability. The thermal stability of Eu(TTA)$_3$-co-polymers can be divided into three regions: 220–370 °C, 370–520 °C, and above 520 °C. The weight loss of up to 41.2% in the range 220–370 °C is probably caused by the elimination of polymer **1**, where the weight loss is close to the content of polymer **1**, 42.3%. The weight loss of up to 48.4% in the range between 370 and 520 °C may be caused by thermal degradation of the TTA groups (47.0% in theory), and the copolymer decomposed completely at 520 °C.[9] The similar degradation step of Tb(TPC)$_3$-co-polymer also was found in Fig. 1.

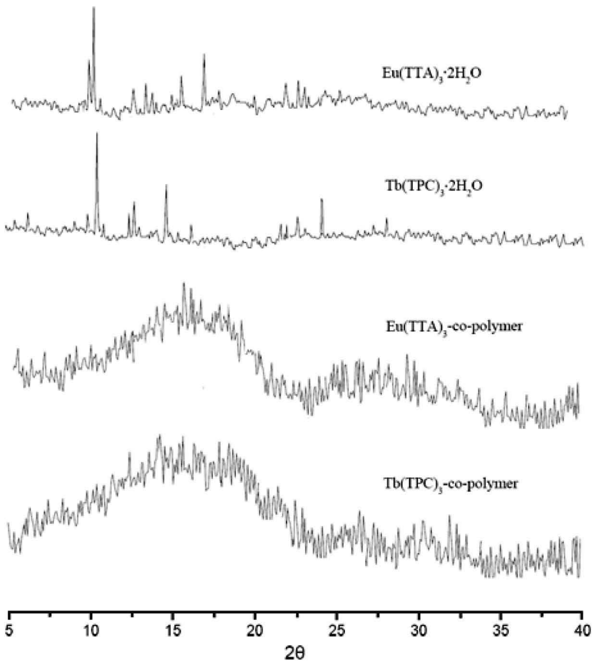

Fig. 2 The XRD curves of Re compounds.

XRD spectra analysis: XRD spectra of Eu^{3+} compounds are shown in Fig. 2. The curve of Eu(TTA)$_3$·2H$_2$O showed extremely strong diffraction peaks at 2*θ* angles of 8.7°, 9.3° and 16.3°, indicating the perfect crystal lattice structure of Eu(TTA)$_3$·2H$_2$O. However, in the XRD pattern of Eu(TTA)$_3$-co-polymer, all the sharp peaks corresponding to Eu(TTA)$_3$·2H$_2$O disappeared and only showed the amorphous structure, which proved that the rare earth ions were not simply doped in polymer system, but coordinated with bipyridine by the bond of Eu–N, leading to a homogeneous distribution of Eu^{3+} within the polymer host.[10] Similar information of Tb^{3+} complex and copolymer was also found in Fig. 2.

Fluorescence properties: The data in Table 1 showed that the two copolymers could emit the characteristic fluorescence of Eu^{3+} ($^5D_0 \rightarrow {}^7F_2$ at 612 nm) and Tb^{3+} ($^5D_4 \rightarrow {}^7F_5$ at 545 nm) with better monochromaticity (η) than that of complexes. In comparison with the complexes, the fluorescence emission intensities of Eu(TTA)$_3$-co-polymer and Tb(TPC)$_3$-co-polymer are stronger because of the influence of the bipyridine within the polymer chain.[11,12]

Eu(TTA)$_3$-co-polymer and Tb(TPC)$_3$-co-polymer were synthesised by coordination of rare earth ions with bipyridine groups on the polymer chain, and characterised by UV-vis, IR, elemental analysis,

Table 1 Solid fluorescent data of the Re complexes and copolymers

Re complexes	Ex $_{max}$ /nm	Em		
		/nm	Energy transfer/Int./a.u	η^a
Eu(TTA)$_3$·2H$_2$O	335	539	$^5D_0 \rightarrow {}^7F_0$ (7.8)	11.3
	591		$^5D_0 \rightarrow {}^7F_1$ (74.6)	
	613		$^5D_0 \rightarrow {}^7F_2$ (842.9)	
	650		$^5D_0 \rightarrow {}^7F_3$ (62.8)	
Eu(TTA)$_3$-co-polymer	336	539	$^5D_0 \rightarrow {}^7F_0$ (10.1)	17.9
	591		$^5D_0 \rightarrow {}^7F_1$ (85.0)	
	613		$^5D_0 \rightarrow {}^7F_2$ (1526.5)	
	650		$^5D_0 \rightarrow {}^7F_3$ (32.3)	
	702		$^5D_0 \rightarrow {}^7F_4$ (73.2)	
Tb(TPC)$_3$·2H$_2$O	316	491	$^5D_4 \rightarrow {}^7F_6$ (210.9)	2.24
	545		$^5D_4 \rightarrow {}^7F_5$ (471.4)	
	583		$^5D_4 \rightarrow {}^7F_4$ (33.1)	
	620		$^5D_4 \rightarrow {}^7F_3$ (20.2)	
Tb(TPC)$_3$-co-polymer	320	490	$^5D_4 \rightarrow {}^7F_6$ (552.2)	2.83
	545		$^5D_4 \rightarrow {}^7F_5$ (1562.7)	
	584		$^5D_4 \rightarrow {}^7F_4$ (109.6)	
	620		$^5D_4 \rightarrow {}^7F_3$ (56.3)	
	652		$^5D_4 \rightarrow {}^7F_2$ (78.4)	

[a] η = Int.($^5D_0 \rightarrow {}^7F_2$):Int.($^5D_0 \rightarrow {}^7F_1$) for Eu^{3+} compound; η = Int.($^5D_4 \rightarrow {}^7F_5$):Int. ($^5D_4 \rightarrow {}^7F_6$) for Tb^{3+} compound;

TGA and XRD. The improvement of the luminescence properties for RE-containing polymers was attributed to the efficient intramolecular energy transfer from the triplet state level of the low organic ligand and polymer to RE^{3+} as well as the microenvironment effects.

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References

1 B. Yan and X.F. Qiao, *J. Phys. Chem. B.*, 2007, **111**, 12362.
2 C.J. Liang, D. Zhao, Z.R. Hong, D.X. Zhao, X.Y. Liu and W.L. Li, *Appl. Phys. Lett.*, 2000, **76**, 67.
3 L.H. Wang, W. Wang, W.G. Zhang, E.T. Kang and W. Huang, *Chem. Mater.*, 2000, **12**, 2212.
4 N.E. Wolff and R. Pressley, *J. Appl. Phys. Lett.*, 1963, **2**, 152.
5 Y. Okamoto, *J. Macromolec. Sci. Chem.*, 1987, **24**, 455.
6 Q.D. Ling, E.T. Kang, K.G. Neoh and W. Huang, *Macromolecules*, 2003, **36** 6995.
7 H. Cang, S.Q. Wang, W.Z. Yang and J.T. Wang, *J. Chem. Res.*, 2009, 101.
8 R.G. Charles and R.C. Ohlmann, *J. Inog. Nucl. Chem.*, 1965, **27**, 255.
9 W.L. Mo, H.T. Liu, H. Xiong, M. Li and G.X. Li, *Appl. Catal.s A: General*, 2007, **333** 172.
10 D. Liu and Z. Wang, *Polymer*, 2008, **49**, 4960.
11 D. Ling, M.J. Yang, W.G. Zhang, H.Z. Lin, G. Yu and F.L. Bai, *Thin Solid Films*, 2002, **47**, 127.
12 Y.X. Cheng, X.W. Zou, D. Zhu, T.S. Zhu, Y. Liu, S.W. Zhang and H. Huang, *J. Polym. Sci. Part A: Polym. Chem.*, 2007, **45**, 650.