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Visible-light excitable highly luminescent molecular plastic materials derived from Eu^{3+}-biphenyl based *β*-diketonate ternary complex and poly(methylmethacrylate)

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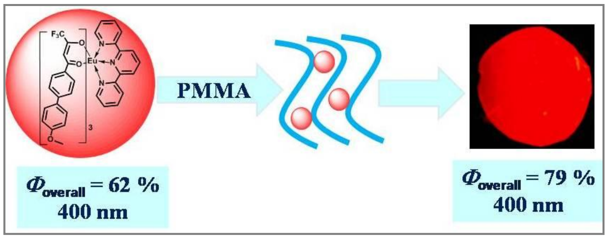
Graphical abstract



Luminescent molecular plastic materials derived from Eu^{3+}-biphenyl based β-diketonate ternary complex and poly(methylmethacrylate) display impressive quantum yield (79%) under blue-light excitation.

Highlights

- A fluorinated methoxy-substituted biphenyl based *β*-diketonate ligand was synthesized and well characterized.
- A blue-light excitable Eu^{3+}-tris(methoxy-substituted biphenyl *β*-diketonate)(terpyridine) ternary complex was developed with promising photoluminescence quantum yield.
- Visible-light excitable highly luminescent Eu^{3+} based molecular plastic materials designed with remarkable quantum yield as compared to many of the existing Eu^{3+}-*β*-diketonate doped polymer films.

Visible-light excitable highly luminescent molecular plastic materials derived from Eu^{3+}-biphenyl based *β*-diketonate ternary complex and poly(methylmethacrylate)

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Abstract

In the present work, a *β*-diketonate ligand, namely, 1-(4'-methoxy-[1,1'-biphenyl]-4-yl)-4,4,4-trifluoro-3-hydroxybut-2-en-1-one (HMeOBPhTFB), which contains a conjugated methoxy-substituted biphenyl unit, as well as a polyfluorinated alkyl group, was synthesized and utilized for the construction of two new Eu^{3+} complexes $[Eu(MeOBPhTFB)_3(H_2O)(C_2H_5OH)]$ **1** and $[Eu(MeOBPhTFB)_3(TPY)]$ **2** where TPY denotes 2,2':6',2''- terpyridine. The synthesized compounds are well characterized by various spectroscopic techniques, and their solid-state photophysical properties were investigated. For comparison, Eu^{3+} complexes {$[Eu(BPhTFB)_3(H_2O)(C_2H_5OH)]$ **3** and $[Eu(BPhTFB)_3(TPY)]$ **4**} were also designed involving an unsubstituted biphenyl based *β*-diketonate ligand, 1-[1,1'-biphenyl]-4-yl)-4,4,4-trifluoro-3-hydroxybut-2-en-1-one (HBPhTFB). The results disclosed that the methoxy-substituted biphenyl based polyfluorinated Eu^{3+}-*β*-diketonate complexes significantly red-shifted the excitation maximum to the visible region (λ_{ex} = 400 nm) with promising solid-state quantum yield ($\Phi_{overall}$ = 62 % for **2**) as compared to simple Eu^{3+}-biphenyl *β*-diketonate ternary complex (λ_{ex} = 382 nm for **3** and **4**). In the current work, attempts also have been made to isolate luminescent molecular plastic materials by incorporating the unique photophysical properties of the developed visible-light excitable Eu^{3+}-*β*-diketonate complex (**2**) with the mechanical, thermal and chemical stability, and flexibility and a film-forming tendency of poly(methylmethacrylate) [PMMA]. The developed molecular plastic materials were characterized and evaluated their photoluminescence properties. Most importantly, the newly constructed polymer films exhibit remarkable quantum yields (75-79%) under blue-light excitation as compared to many of the existing Eu^{3+} based polymeric materials.

Keywords: Visible-light excitable; Eu^{3+} based plastic materials; high quantum yields.

1. Introduction

Due to their excellent photophysical properties, Eu^{3+}-β-diketonate complexes are among the most meticulously studied class of coordination compounds. The considerable attention they have been attracting until now stems from their ease of synthesis, intense absorption transitions and the variety of potential practical applications ranging from biomedicine [1–5] to material sciences [6–10]. The forbidden nature of the f-f transitions in trivalent europium ions results in a very weak intensity of the metal-centered absorption bands. This weak absorbance can, however, be overcome by coordinating chromophore-containing ligands to the Eu^{3+} ion which, upon irradiation, transfer energy to the metal center, typically *via* the ligand triplet excited state, thereby populating the Eu^{3+} emitting levels in a process known as the "antenna effect" [11–16]. As a result, a significant number of Eu^{3+}-β-diketonate complexes have been isolated and investigated their photoluminescence properties [17–26]. However, the optical excitation window for many of the reported luminescent Eu^{3+}complexes are found to be limited to UV region (<390 nm) due to the energy constraints arose from the photophysics of Eu^{3+} ions as emphasized by Reinhoudt and co-workers [27]. For application in biosensing or bioimaging, over the years great efforts have been made on the development of luminescent Eu^{3+} complexes that are capable of being efficiently excited by visible-light, because the blue-light is less harmful to biological tissue, allowing deep penetration, causing less background fluorescence and thus lowering the interferences from biological samples [13]. Thus, one of the challenges in the photophysics of 4f elements is to design and develop visible-light excitable Eu^{3+}-β-diketonate complexes, which is in high demand for less-harmful labeling reagents in the field of life sciences. Indeed, some of the latest studies have revealed that the excitation window can be shifted to longer wavelengths in Eu^{3+}-β-diketonate complexes by appropriate molecular engineering and suitably expanded π-conjugation in the β-diketonate ligands [13, 28–38]. Reddy and coworkers reviewed recent advances on the development of visible-light sensitized luminescent Eu^{3+}-β-diketonate complexes and their applications towards bioprobes for cellular imaging [39–41]. In this context, Divya and Reddy have developed a novel visible-light excited red-emitting luminescent Eu^{3+}-phenathrene-based fluorinated β-diketonate complex with high solid-state quantum yield (75%) [41]. Recently, a new family of Eu^{3+} complexes based on aminophenyl polyfluorinated β-diketonate ligands in the absence and presence of a chelating phosphine oxide has been isolated in our laboratory and investigated their photophysical properties [42]. Among the developed compounds, the Eu^{3+}-triphenylamine based β-diketonate ternary complex displays intense red emission under blue-light excitation, (λ_{ex} = 400 nm) with an overall quantum yield of 40%. In the later studies, visible-light excited carbazole-based Eu^{3+}-β-diketonate complexes *via* molecular engineering have also been disclosed [43]. The results demonstrated that suitably expanded π-conjugation in the developed Eu^{3+}-carbazole based β-diketonate complexes with a red-shift in the excitation maximum to the visible region (λ_{ex} = 420 nm) with a moderate quantum yield (34-42%). Nevertheless, many of the visible-light excitable Eu^{3+}-β-diketonate complexes so far known display poor quantum yields. Thus there is a growing demand for the development of new Eu^{3+} complexes with high quantum yields that are based on robust visible-light excitable β-diketonate ligands.

The compounds with aromatic-aromatic bond appended with functional moieties have attracted considerable interest owing to their intriguing structural motifs and unique luminescence properties [44–47]. The intermolecular interactions in the solid state may promote the coplanar arrangements of aromatic rings in the biphenyl compounds, which may be accountable for the noted conjugation. Further, investigations disclosed that complexation with cations can control the conformation of the biphenyl [45]. It is also well documented that the incorporation of electron-donating methoxy group on the phenyl ring of the biphenyl system allows oxygen electrons to be part of the delocalized system through resonance and increases the conjugation of the chromophore [38,43,48,49]. The replacement of C-H bonds in a β-diketonate ligand with low-energy C-F oscillators reduces the vibrational energy and further promotes the spin-orbit coupling through heavy atom effect, which facilitates the intersystem crossing in lanthanide complexes and thus improves the photoluminescence quantum yield [39,50,51]. These factors have inspired us to incorporate simultaneously highly conjugated methoxy-substituted biphenyl and trifluoromethyl units into the β-diketonate ligand system and synthesize a β-diketonate ligand (Fig. 1). The resultant antenna molecule expected to display efficient luminescence under visible-light excitation upon coordination with trivalent Eu^{3+} ions. Therefore, in the current study a β-diketonate ligand, namely, 1-(4'-methoxy-[1,1'-biphenyl]-4-yl)-4,4,4-trifluoro-3-hydroxybut-2-en-1-one (HMeOBPhTFB) was designed and utilized for the synthesis of new visible-light excitable Eu^{3+}-β-diketonate complexes in the presence and absence of an ancillary ligand, 2,2':6',2''-terpyridine and investigated their solid-state photophysical properties. For comparison, Eu^{3+}-coordination compounds were also prepared involving an unsubstituted biphenyl based β-diketonate ligand system.

It is noteworthy to mention that the Eu^{3+}-β-diketonate complexes have always been excluded from the practical applications, mainly due to their low thermal stability, limited photostability and poor mechanical properties. The polymers are ideal matrices for Eu^{3+} complexes, because their several attractive features including mechanical strength, flexibility, ease of processing and controllable cost [20,23,52–56]. To overcome the above-cited limitations, in the present study, the newly developed visible-light excitable Eu^{3+}-β-diketonate compound was embedded into a PMMA matrix and developed molecular plastic materials and studied their thermal and photophysical properties.

2. Experimental Section

2.1. Materials

The reagents used in this study were commercially available and used as purchased: Europium(III) nitrate hexahydrate, 99.9% (Alfa Aesar); gadolinium(III) nitrate hexahydrate, 99.999% (Sigma-Aldrich); (4-acetylphenyl)boronic acid, 97% (Sigma-Aldrich), iodobenzene, 98% (Sigma-Aldrich), iodoanisole, 96% (Sigma-Aldrich); ethyl trifluoroacetate, 99% (Sigma-Aldrich); poly(methylmethacrylate), 98% (Sigma-Aldrich); sodium hydride 60% dispersion in mineral oil (Sigma-Aldrich); sodium carbonate, 99.5% (Sigma-Aldrich).

2.2. Characterization techniques

Elemental analyses were performed with an Elementar - vario MICRO cube elemental analyzer. IR spectra were recorded on a Perkin-Elmer Spectrum two FT-IR spectrometer using KBr pellets. The synthesized compounds were characterized by ^1H NMR (500MHz) and ^{13}C NMR (125.7MHz) using a Bruker 500 MHz NMR spectrometer in chloroform-d solution. The chemical shifts are reported in parts per million relative to tetramethylsilane, $SiMe_4$ for ^1H NMR and ^{13}C NMR spectra. Electro spray ionization (ESI) mass spectra were recorded on a Thermo Scientific Exactive Benchtop LC/MS Orbitrap Mass Spectrometer and the thermogravimetric analyses were performed on a TG/DTA-6200 (SII Nano Technology Inc., Japan). The absorbances of the ligands were measured in acetonitrile solution on a UV-vis spectrophotometer (Shimadzu, UV-2450). The photoluminescence (PL) spectra were recorded on a Spex-Fluorolog FL22 spectrofluorimeter equipped with a double grating 0.22 m Spex 1680 monochromator and a 450W Xe lamp as the excitation source operating in the front face mode. The lifetime and phosphorescence measurements were carried out by using a SPEX 1040 D phosphorimeter. The phosphorescence spectra were monitored after a delay after flash of 0.05 ms. The overall quantum yield (Φ_{overall}) was measured using an integrating sphere in a SPEX Fluorolog spectrofluorimeter as previously reported in literature [42,57–59]. The estimated error for the quantum yields is (± 10%).

2.3. Synthetic procedures

2.3.1. Synthesis of ketones. The corresponding ketone was prepared by Suzuki-Miyaura coupling reaction. In a round bottom flask, one equivalent of iodoanisole or iodobenzene was taken and dissolved in 25 ml of dry THF. To that 1.2 equivalents of (4-acetylphenyl)boronic acid and 0.06 equivalents of tetrakis-(triphenylphosphine)palladium(0) were added. A solution of 5% Na_2CO_3 (10 mL) was added to that mixture and refluxed with stirring for 24 h, under the nitrogen atmosphere. After cooling to room temperature, the mixture was poured into water, and extracted with dichloromethane. The organic layer was dried over Na_2SO_4. The solvent was removed and the crude product was purified by silica column chromatography with ethyl acetate: *n*-hexane as the eluent (1:99) to give the final product.

2.3.1.1. 1-([1,1'-biphenyl]-4-yl)ethanone. Yield: 72%. ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.89 (m, 2H), 7.68 (m, 4H), 7.44 (m, 2H), 7.13 (m, 1H), 2.53 (s, 3H). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ (ppm): 197.77, 145.79, 139.88, 135.86, 128.96, 128.92, 128.24, 127.28, 115.23, 26.66. *m/z* = 197 $(M+1)^+$.

2.3.1.2. 1-(4'-methoxy-[1,1'-biphenyl]-4-yl)ethanone. Yield: 60%. ^{1}H NMR ($CDC1_3$, 500 MHz): δ (ppm) 8.03 (m, 2H), 7.64 (m, 4H), 7.01 (m, 2H), 3.87 (s, 3 H) 2.63 (s, 3H). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ (ppm): 196.48, 159.81, 145.51, 135.78, 132.92, 131.03, 129.34, 128.60, 114.96, 55.84, 25.53. *m/z* = 227 $(M+1)^+$.

2.3.2. Synthesis of ligands. The ligands, 1-([1,1'-biphenyl]-4-yl)-4,4,4-trifluoro-3-hydroxybut-2-en-1-one (HBPhTFB) and 1-(4'-methoxy-[1,1'-biphenyl]-4-yl)-4,4,4-trifluoro-3-hydroxybut-2-en-1-one (HMeOBPhTFB) were synthesized by Claisen condensation reaction as reported in literature [20,42].

2.3.2.1. 1-([1,1'-biphenyl]-4-yl)-4,4,4-trifluoro-3-hydroxybut-2-en-1-one (HBPhTFB). Yield: 64%. Elemental analysis (%): calculated for $C_{16}H_{11}F_3O_2$ (292.25): C 65.76, H 3.59 ; Found: C 66.01, H 3.86, ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm): 15.15 (broad, enol–OH), 8.03 (d, 2H, J = 8.5 Hz), 7.74 (d, 2H, J = 8.5 Hz), 7.65 (m, 2H), 7.48 (m, 3H), 6.62 (S, 1H). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ (ppm): 185.66, 177.50, 146.91, 131.50, 129.07, 128.61, 128.23, 127.61, 127.2, 116.05, 92.23, 77.26-76.76 ($CDCl_3$). FT-IR (KBr) ν_{max} (cm^{-1}): 3033, 2918, 2849, 1605, 1486, 1319, 1288, 1213, 1150, 1066, 772, 689. m/z = 293 $(M+1)^+$.

2.3.2.2. 1-(4'-methoxy-[1,1'-biphenyl]-4-yl)-4,4,4-trifluoro-3-hydroxybut-2-en-1-one (HMeOBPhTFB). Yield: 52%. Elemental analysis (%): calculated for $C_{17}H_{13}F_3O_3$ (322.08): C 63.06, H 4.07 ; Found: C 63.31, H 3.97, ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm): 15.31 (broad, enol–OH), 8.00 (d, 2H, J = 8.5 Hz), 7.69 (d, 2H, J = 8.5 Hz), 7.60 (m, 2H), 7.01 (m, 2H), 6.60 (S, 1H), 3.88 (s, 3H). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ (ppm): 185.68, 182.10, 160.24, 146.52, 136.42, 131.74 130.79, 128.42, 128.28, 126.96, 114.53, 92.10, 55.42, 77.27-76.76 ($CDCl_3$). FT-IR (KBr) ν_{max} (cm^{-1}): 3038, 2970, 2917, 2846, 1600, 1496, 1296, 1217, 1150, 1108, 799, 669. m/z = 323 $(M+1)^+$.

2.3.3. Synthesis of binary complexes. NaOH (3.0 mmol) in water was added to a solution of corresponding β-diketonate ligand (3.0 mmol) in ethanol and stirred for 10 min. To this mixture, $Ln(NO_3)_3 \cdot 6(H_2O)$ (where Ln = Eu^{3+}, Gd^{3+}) (1.0 mmol) in ethanol was added drop wise and stirred for 12 h at room temperature. A light yellow coloured precipitate was formed by adding excess amount of water. The resultant precipitate was filtered off, washed with water and dried. The products were purified by recrystallization from dichloromethane solution and used for further analysis and photophysical studies.

2.3.3.1. $Eu(MeOBPhTFB)_3(H_2O)(C_2H_5OH)$ (1). Elemental analysis (%): calculated for $C_{53}H_{44}F_9O_{11}Eu$ (1179.86): C 53.95, H 3.76; Found: C 54.23, H 3.94. FT-IR (KBr) ν_{max}

(cm^{-1}): 3419, 3036, 2959, 2911, 2839, 1615, 1602, 1557, 1530, 1496, 1299, 1199, 1138, 793, 667. *m/z* = 1116 [Eu(MeOBPhTFB)$_3$]$^+$.

2.3.3.2. Eu(BPhTFB)$_3$(H$_2$O)(C$_2$H$_5$OH) (3). Elemental analysis (%): calculated for $C_{50}H_{38}F_9O_8Eu$ (1089.78): C 55.11, H 3.51; Found: C 54.93, H 3.68. FT-IR (KBr) ν_{max} (cm^{-1}): 3411, 3031, 2928, 1618, 1603, 1557, 1486, 1319, 1296, 1196, 1140, 1073, 766, 689. *m/z* = 1025 [Eu(BPhTFB)$_3$-1]$^+$.

2.3.3.3. Gd(MeOBPhTFB)$_3$(H$_2$O)(C$_2$H$_5$OH) (5). Elemental analysis (%): calculated for $C_{53}H_{44}F_9O_{11}Gd$ (1185.15): C 53.71, H 3.74; Found: C 54.03, H 3.81. FT-IR (KBr) ν_{max} (cm^{-1}): 3418, 3061, 2961, 2921, 2841, 1614, 1602, 1560, 1530, 1495, 1317, 1296, 1193, 1138, 790, 667. *m/z* = 1122 [Gd(MeOBPhTFB)$_3$+1]$^+$.

2.3.3.4. Gd(BPhTFB)$_3$(H$_2$O)(C$_2$H$_5$OH) (6). Elemental analysis (%): calculated for $C_{50}H_{38}F_9O_8Gd$ (1095.07): C 54.84, H 3.50; Found: C 54.87, H 3.46. FT-IR (KBr) ν_{max} (cm^{-1}): 3418, 3032, 2922, 1617, 1601, 1556, 1486, 1316, 1296, 1196, 1140, 1073, 766, 689. *m/z* = 1054 [Gd(BPhTFB)$_3$+Na+1]$^+$.

2.3.4. Synthesis of ternary Eu^{3+} complexes 2 and 4. Like earlier literature reports [21], ternary complexes were synthesized by refluxing equimolar solutions of corresponding binary complexes and terpyridine in chloroform solution for 12 h at 70°C. Solvent was removed in rotary-evaporator and purified by recrystallization from a chloroform solution. The synthesis procedure is illustrated in scheme 3.

2.3.4.1. Eu(MeOBPhTFB)$_3$(TPY) (2). Elemental analysis (%): calculated for $C_{66}H_{47}O_9F_9N_3Eu$ (1349.04): C 58.76, H 3.50, N 3.11; Found: C 58.72, H 3.84, N 2.82. FT-IR (KBr) ν_{max} (cm^{-1}): 3034, 2958, 2917, 2847, 1640, 1620, 1602, 1581, 1556, 1492, 1298, 1248, 1184, 1137, 786, 665. *m/z* = 1027 [Eu(MeOBPhTFB)$_2$(TPY)]$^+$.

2.3.4.2. Eu(BPhTFB)$_3$(TPY) (4). Elemental analysis (%): calculated for $C_{63}H_{41}O_6F_9N_3Eu$ (1258.97): C 60.10, H 3.28, N 3.34; Found: C 59.82, H 3.47, N 3.08. FT-IR (KBr) ν_{max} (cm^{-1}): 3030, 2919, 2849, 1638, 1621, 1602, 1580, 1555, 1484, 1316, 1295, 1188, 1138, 1071, 764, 687. *m/z* = 968 [Eu(BPhTFB)$_2$(TPY)]$^+$.

2.4. Preparation of luminescent polymer films

PMMA powder and required amount of Eu(MeOBPhTFB)$_3$(TPY) (3, 5, 7 and 9% (w/w)) were dissolved in 10 mL of chloroform solution. After stirring for 30 minutes at 70ºC, the solution was dried at room temperature to obtain the transparent polymer films. The prepared polymer films were represented as PMMA@3Eu, PMMA@5Eu, PMMA@7Eu and PMMA@9Eu.

3. Results and discussion

3.1. Synthesis and characterization of ligands and their corresponding lanthanide complexes

The ligands 1-([1,1'-biphenyl]-4-yl)-4,4,4-trifluoro-3-hydroxybut-2-en-1-one (HBPhTFB) and 1-(4'-methoxy-[1,1'-biphenyl]-4-yl)-4,4,4-trifluoro-3-hydroxybut-2-en-1-one (HMeOBPhTFB) were successfully synthesized in two steps starting from commercially available 4-acetylphenylboronic acid as summarized in Scheme 1. The designed biphenyl based *β*-diketonate ligands were identified by ^{1}H NMR and ^{13}C NMR spectroscopy, electrospray ionization mass spectrometry (ESI-MS), FT-IR spectroscopy and elemental analysis (Figs. S1-S8 in the Supplementary data). ^{1}H NMR analysis indicates that both the *β*-diketonate ligands exist as enol form in chloroform-d solution. The protocols used for the syntheses of binary and ternary lanthanide complexes (Ln = Eu^{3+} and Gd^{3+}) are outlined in the Schemes 2 and 3, respectively. The elemental analysis and ESI-MS data of all the lanthanide complexes revealed that in each case Ln^{3+} ion has reacted with the corresponding *β*-diketone ligand in a metal-to-ligand mole ratio of 1:3. In the case of ternary Eu^{3+}-*β*-diketonate complexes (**2** and **4**), one molecule of terpyridine is also present in the coordination sphere. The FT-IR spectra of the binary complexes (**1, 3, 5** and **6**) show a broad absorption band in the 3000-3500 cm^{-1} region, indicating the presence of solvent molecules in the coordination sphere of the Ln^{3+} ion. The presence of coordinated water molecule in the case of binary Eu^{3+}-*β*-diketonate complexes has been further ascertained by ^{1}H NMR analysis (a broad peak noted at about 3.02 ppm in **1** of Fig. S9 and 2.50 ppm in **3** of Fig.S10 in the Supplementary data). However, the absence of the above broadband in the case of Eu^{3+} ternary complexes implies that the ancillary ligand, terpyridine displaced the solvent molecules successfully. Also, the strong bands at 1581, 1436 and 736 cm^{-1} noted in the ternary complexes confirm the presence of coordinated terpyridine [60,61]. The carbonyl stretching frequency of the biphenyl based *β*-diketonate ligands (1605 cm^{-1} for HBPhTFB and 1600 cm^{-1} for HMeOBPhTFB) are shifted to higher wavenumbers (1615 cm^{-1} in **1**, 1620 cm^{-1} in **2**, 1618 cm$^{\mathbf{-1}}$ in **3** and 1621cm^{-1} in **4**) in all the Eu^{3+} complexes indicating the involvement of carbonyl oxygen in the complex formation with the Eu^{3+} ion.

The thermal stabilities of the synthesized biphenyl based Eu^{3+}-*β*-diketonate complexes (**1**-**4**) were evaluated by thermogravimetric analysis (30-1000^{o}C range in a nitrogen atmosphere), and the corresponding thermograms are depicted in Fig. S11 (in Supplementary data). It is evident from the thermogravimetric analysis that both the binary Eu^{3+} complexes **1** and **3** undergoes a mass loss about ~5.3% (calculated ~5.4%) in the first step (90-140^{o}C), which corresponds to the loss of coordinated solvent and water molecules. In contrast, Eu^{3+} ternary complexes **2** and **4** are more stable than binary complexes, and they undergo decomposition only above 220^{o}C, indicating that there are no coordinated solvent molecules in these complexes. These trends are in good agreement with the FT-IR spectral data. The total weight loss noted in the thermal analysis of the complexes is found to be much lower than the calculated value for the non-volatile europium oxide, implying the partial sublimation of these compounds under atmospheric pressure which is well documented in many of the lanthanide fluorinated *β*-diketonate complexes [21,42,62].

3.2. Electronic spectra of the Eu^{3+}-β-diketonate complexes

The UV-vis absorption spectra of the *β*-diketonate ligands and their corresponding Eu^{3+} complexes, which were recorded in acetonitrile solution ($c = 5 \times 10^{-6}$ M) at 298 K, are displayed in Figs. 2 and 3. The pertinent spectral features are summarized in Table S1. The absorption maxima at 345 and 358 nm noted for the ligands HBPhTFB and HMeOBPhTFB are attributable to the singlet-singlet $^{1}\pi$-$\pi*$ enolic transition assigned to the *β*-diketonate moiety [17,18,43,62]. It is notable that the UV-vis absorption maximum band is red-shifted (13 nm) in the case of methoxy-substituted biphenyl based *β*-diketonate ligand, thus pointing out that the degree of conjugation enhances and that the $^{1}\pi$-$\pi*$ energy level is lowered by the introduction of electron-donating methoxy moiety at the 4' position of the biphenyl based *β*-diketonate ligand [38,42,43,48]. Besides, the molar absorption coefficient of the HMeOBPhTFB ligand also significantly enhanced as compared to the parent ligand (ε = 34463 M^{-1} cm^{-1} for HBPhTFB and 46945 M^{-1}cm^{-1} for HMeOBPhTFB, calculated at their absorption maximum). The absorption profiles of the Eu^{3+}-*β*-diketonate complexes are found to be identical to that one observed for the free ligands, indicating that the singlet excited states of the ligands are not significantly affected upon coordination to the Eu^{3+} ion. However, a small blue shift that is detectable in the absorption maximum of all the complexes is a consequence of perturbation induced by the coordination of

Eu^{3+} ion to the ligand [20,24,35,63,64]. The absorption coefficients for the complexes are three times larger than those of the free ligands, thus indicating the presence of three β-diketonate ligands in the coordination sphere of the lanthanide ion. Furthermore, the large molar absorption coefficients noted for the developed ligands disclose that the β-diketonate ligands have a strong potential to absorb light.

3.3. Steady state photoluminescence

To understand the energy transfer mechanism in the developed Eu^{3+}-biphenyl based β-diketonate complexes it is required to determine the singlet and triplet energy levels of the β-diketonate ligands. The singlet (S_1) energy levels of these ligands are estimated by reference to the wavelengths of the UV-vis absorption edges of the Gd^{3+} biphenyl based β-diketonate complexes (**5** and **6**) [65–68]. The relevant values are found to be 26178 cm^{-1} (382 nm) and 25641 cm^{-1} (390 nm) for HBPhTFB and HMeOBPhTFB, respectively (Fig. S12a in the supplementary data). The triplet energy levels (T_1) of the developed β-diketonate ligands were calculated by reference to the lower wavelength emission edges (480 nm: 20833 cm^{-1}, 492 nm: 20325cm^{-1} for HBPhTFB and HMeOBPhTFB, respectively) from the low-temperature phosphorescence spectra of the Gd^{3+} complexes of the pertinent β-diketonates (Fig. S12b in the supplementary data) [65–68]. Because there is a large gap (32000 cm^{-1}) between the $^8S_{7/2}$ ground state and the first $^6P_{7/2}$ excited state of the Gd^{3+} ion, it cannot accept any energy from the first excited triplet state of the ligand *via* intramolecular ligand-to-metal energy transfer. Thus, the phosphorescence spectra of the Gd^{3+} complexes reveal the triplet energy levels of the β-diketonate ligand in the Eu^{3+} complexes. It is also noticed that the energy gap between the S_1 and T_1 levels are 5345, 5316 cm^{-1} for HBPhTFB and HMeOBPhTFB, respectively. These values are in accordance with the Reinhoudt's empirical rule [27], that the intersystem crossing process becomes effective when $\Delta E(S_1\text{-}T_1)$ is around 5000 cm^{-1}. Thus, the intersystem crossing processes are efficient for these ligands. The energy gaps between the Eu^{3+} core ($^5D_0$ ~17250 cm^{-1}) and the donor ligand's T_1 levels turns out to be 3583, 3075 cm^{-1} for HBPhTFB and HMeOBPhTFB, respectively. According to the empirical rule pointed out by Latva, for an optimal ligand-to-metal energy transfer process $2500 < \Delta E(T_1\text{-}^5D_0) < 4000$ cm^{-1} for Eu^{3+} [69]. It is interesting to note that the triplet energy levels of the developed β-diketonate ligands lay above the energy of the main emitting level of $^5D_0$ for Eu^{3+}, thus demonstrate that these ligands can act as antenna molecules for the sensitization of Eu^{3+} ions.

The room-temperature (298 K) solid-state excitation spectra of Eu^{3+}-*β*-diketonate complexes (**1**-**4**) recorded by monitoring the intense $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} are depicted in Figs. 4a and 5a, respectively. The excitation profiles of unsubstituted biphenyl based Eu^{3+} complexes **3** and **4** exhibit a broad band in the 300-475 nm region (centered at 382 nm) because of the π-π* electronic transitions of the coordinated *β*-diketonate ligand. In addition, a sharp band corresponding to f-f transition is also seen at 464 nm ($^5D_2 \leftarrow {}^7F_{0,1}$) [21]. Most importantly, in the case of Eu^{3+} complexes **1** and **2** upon substitution of electron-donating methoxy group at 4' position of the biphenyl based *β*-diketonate ligand strikingly shifts the excitation window to visible region (300-490 nm) with an excitation maximum 400 nm. The red-shift observed in the excitation window can be attributed to the donating methoxy group on the phenyl ring, which allows the oxygen electrons as a part of the whole delocalization process and enhances conjugation of the chromophore molecule [38,43,48]. These findings specify that methoxy-substituted biphenyl based *β*-diketonate Eu^{3+} complexes (**1** and **2**) are propitious red-emitting materials for luminescent applications such as bioimaging and solid-state lighting without UV radiation.

The emission spectra of Eu^{3+}-*β*-diketonate complexes (**1-4**) (Figs. 4b and 5b) excited at their corresponding excitation maxima (λ_{ex} = 382 nm for **3** and **4** and 400 nm for **1** and **2**) show characteristics of the metal ion emissions in the 550-725 nm wavelength region, and displays well resolved peaks that are due to the transitions from the metal-centered $^5D_0$ excited state to the ^7F_J ground state multiplet. Maximum peak intensities at 579, 593, 615, 653 and 697 nm were noted for the J = 0, 1, 2, 3, 4 transitions, respectively. The so-called 'hypersensitive transition' (J = 2) observed at 615 nm is found to be intense, and is responsible for the observed red emission in these complexes. Further, the intensity of the $^5D_0 \rightarrow {}^7F_2$ transition (electric-dipole) is greater than that of the $^5D_0 \rightarrow {}^7F_1$ transition (magnetic-dipole), which indicates that the coordination environment of the Eu^{3+} ion is devoid of an inversion center [32,70–77]. It can also be noted from the emission spectra that the luminescence intensity of the Eu^{3+} ternary complexes (**2** and **4**) significantly enhanced as compared to the Eu^{3+} binary complexes (**1** and **3**) by the displacement of solvent molecules from the complexes by the ancillary ligand terpyridine [74-77]. Further, no broad emission bands related to *β*-diketonate ligands are observed in the blue region, indicating the efficient energy transfer from the ligand to the emitting level of the metal ion. It is worth mentioning that the emission intensity specifically at 615 nm of the Eu^{3+} ternary complex (**2**) with a methoxy-substitution at the 4' position (9.03 × 10^8) has been greatly enhanced (about three fold) as compared to Eu^{3+}-biphenyl based β-diketonate complex (**4**) without a methoxy substitution (3.05 × 10^8). This enhancement is easily understood by the modification of the molecular structure of the ligand. The substitution of 4' positional hydrogen atom with methoxy moiety leads to increase in electron density in the biphenyl ring and thus increases the electron transition probability [48-49]. Based on their emission spectra, the CIE chromaticity coordinates (Fig. 6) for all the Eu^{3+} complexes are calculated to be the same, x = 0.67 and y = 0.32, which are very close to the NTSC standard CIE values for red (x = 0.67, y = 0.33) [48,73].

In the current study, the various photophysical parameters summarized in Table 1 of the newly developed Eu^{3+} complexes were calculated by the procedures described in our previous publications [40,42,57]. The observed luminescence decay profiles (τ_{obs}) for all the Eu^{3+}-β-diketonate complexes at 298 K (Fig. 7, Figs. S13 in the supplementary data) are found to be single exponential functions, indicating the presence of only one emissive Eu^{3+} center [42,56]. The relatively shorter lifetime observed for binary Eu^{3+} complexes (**1** and **3**) may be caused by dominant non-radiative decay channels associated with the vibronic coupling due to the presence of solvent molecules, as well documented in many of the binary Eu^{3+}-β-diketonate complexes [39-43,78]. On the other hand, longer lifetime values have been noted for ternary Eu^{3+} complexes (**2** and **4**) because of the absence of solvent molecules. These trends are in good agreement with the observed radiative and non-radiative decay rates of the complexes (Table 1).

The substitution of solvent molecules in the Eu^{3+}-tris(1-(4'-methoxy-[1,1'-biphenyl]-4-yl)-4,4,4-trifluoro-3-hydroxybut-2-en-1-one) complex **1** by a chelating ancillary ligand, 2,2':6',2"-terpyridine leads to an approximately 3-fold enhancement in the absolute quantum yield (from 19 to 62%). The substantial contribution of the chelating terpyridine ligand to the overall sensitization of the Eu^{3+}-centered luminescence in **2** is confirmed by (i) an increase in the intrinsic quantum yield by a factor of 3, which results from removal of quenching effect of the O-H vibrations and (ii) the significant enhancement of Φ_{sens} from 95 to 100 %. Furthermore, due to the extended conjugation induced by the substitution of the electron-donating methoxy group at 4' position of biphenyl based β-diketonate ligand, Eu^{3+} complex **2** notably exhibits visible-light sensitized red luminescence with an overall quantum yield 62 ± 6 % when excited at 400 nm. Indeed, this overall quantum yield also found to be superior to that of parent Eu^{3+} ternary complex (Φ_{overall} = 53 ± 5 % at 400 nm). Most significantly, the overall quantum yield obtained in the present investigation is found to be promising as compared to many of the recently reported visible-light excited Eu^{3+}- β-diketonate complexes (Table S2 in supplementary data).

3.4. Characterization and photophysical properties of Eu(MeOBPhTFB)$_3$(TPY) doped PMMA polymer films

PMMA displays superior mechanical and optical properties that aid its application in optical devices. In addition, PMMA comprises carbonyl groups along with its carbon-chain that can strongly interact with Eu^{3+} ions and displace ligand water molecules. Therefore, in the present study visible-light excitable Eu^{3+}-tris(methoxy-substituted biphenyl-β-diketonate)(terpyridine) complex has been embedded into PMMA polymer films with a view to improving its mechanical and emission properties [23,52,53,79–81].

PMMA was doped with a ternary Eu^{3+} complex **2** in proportions of 3, 5, 7 and 9% (w/w), and characterized by FT-IR spectroscopy and the results are shown in Fig. S14 (supplementary data). For the PMMA film and the samples (PMMA@3Eu, PMMA@5Eu PMMA@7Eu PMMA@9Eu), the absorption bands noted in the range 2900-3000 cm^{-1} corresponds to C-H vibrations. The band at 1726 cm^{-1} for the PMMA film belongs to C=O vibration, whereas for the Eu^{3+} complex doped PMMA films, it shifts to 1733 cm^{-1} [53,82]. Fig. S15 displays the TGA thermograms for PMMA film (solution casting) and PMMA film doped with 7% of Eu^{3+} complex (solution casting). It is observed that the solution cast PMMA film shows ~10% weight loss at 166ºC, which is attributed to the entrapped solvent removal from the polymer matrix. Further, Eu^{3+} complex doped PMMA film exhibits ~10% weight loss at 238ºC [52]. Thus, TGA infers that the Eu^{3+} complex doped films have improved thermal stability as compared to precursor PMMA film.

Fig. 8a illustrates the room temperature (298 K) excitation profiles of PMMA polymer films embedded with Eu^{3+} complex **2** at different concentrations (3, 5, 7 and 9 w/w%), by monitoring the emission at $^5D_0 \rightarrow {}^7F_2$ (615 nm) transition. The excitation spectra are dominated by an intense broad band in the region 300-450 nm (λ_{ex} = 385 nm) which can be ascribed to absorptions of both PMMA and methoxy-substituted biphenyl based β-diketonate ligand. However, the excitation spectra of the polymer film doped with complex **2** are blue-shifted (~15 nm) as compared to solid state spectrum of the Eu^{3+} complex **2**. This behavior may be due to a change of symmetry of the complex [56]. The emission spectra of PMMA doped with Eu^{3+} complex **2** at variety of concentrations (3, 5, 7 and 9 w/w%), and excited at 400 nm exhibit well defined emission peaks characteristic of the $^5D_0 \rightarrow {}^7F_J$ (J = 0-4) transition of Eu^{3+} ion in the wavelength region 550-715 nm (Fig. 8b). As can be noted from the emission profiles, the luminescence intensity at 615 nm increases with increase in the concentration of Eu^{3+} compound **2** and reaches a maximum at 7 w/w% (1.7 times). Further, an increase in the Eu^{3+} concentration decreases the luminescence intensity [20,56,62]. This may be due to the energy transfer between the Eu^{3+} ions themselves is a non-radiative process, which is responsible for the decrease in the Eu^{3+} emission, especially at 9 w/w%. The overall quantum yield, radiative and non-radiative decay rates, intrinsic quantum yield and energy transfer efficiencies of the PMMA film doped with Eu^{3+} complex **2** at different concentration are summarized in Table 2. The overall quantum yield of the polymer films (75-79%) excited under blue light (400 nm) was found to be remarkably enhanced as compared to the precursor Eu^{3+} complex **2** (Φ_{overall} = 62%). To the best of our knowledge, no reports have been seen in the open literature regarding investigations on the photophysical properties of Eu^{3+}-compounds doped PMMA polymer films, especially excited under visible-light, which exhibit exceptionally high photoluminescence quantum yields as noted in the current study. Further, the intrinsic quantum yields noted in the current hybrid polymer films are found to be exceptionally higher than that reported elsewhere [83] for Eu^{3+}-tris(1-(4'-methoxy-[1,1'-biphenyl]-4-yl)-4,4,4-trifluoro-3-hydroxybut-2-en-1-one)(phen) complex doped into silicone rubber (38.8 %). The quantum yields of the polymer films also have been calculated at the excitation maximum 385 nm and the corresponding excitation and emission profiles are given in Fig. S16. Exceptionally very high quantum yield of about 98% has been noted for the 7 w/w% Eu^{3+} complex doped PMMA polymer film when excited at 385 nm. The $^5D_0$ lifetimes of the Eu^{3+} complex doped films (Fig. 9) are higher than that of the parent compound **2**. In addition, the non-radiative decay rates have been significantly lowered in the doped films and hence the intrinsic quantum yields also greatly improved (78-81%) in the doped polymer films. The Photograph of the PMMA film doped with 7 w/w% $Eu(MeOBPhTFB)_3(TPY)$ under normal light and after UV irradiation is shown in Fig. 10.

4. Conclusions

In summary, we have successfully developed a new visible-light excited (λ_{ex} = 400 nm) Eu^{3+}-tris(1-(4'-methoxy-[1,1'-biphenyl]-4-yl)-4,4,4-trifluoro-3-hydroxybut-2-en-1-one)(2,2':6',2''-terpyridine) ternary complex which display intense metal centered luminescence with remarkable solid-state quantum yield (62%). Consequently, the synthesized Eu^{3+} ternary complex may find potential applications in bioimaging and organic light emitting diodes (OLEDs). Additionally, the newly designed Eu^{3+} ternary complex incorporated PMMA polymer films exhibit exceptionally high photoluminescence quantum yield under wide excitation wavelengths (PL quantum yield 98% at λ_{ex} = 385 nm and 79% at λ_{ex} = 400 nm). This indicates that the PMMA with high molecular weight enwraps the Eu^{3+} ternary complex and keeps the donor-acceptor close, which results in the effective intermolecular energy transfer and, consequently, the high quantum yields. Most importantly, the photoluminescence quantum yields noted for the Eu^{3+} compound doped PMMA polymer films under blue light excitation are found to be promising as compared to earlier reports. Thus, the derived luminescent molecular plastic materials show considerable promise for use in polymer light emitting diodes and active polymer optical fibers.

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Table 1 The radiative (**A_{RAD}, s^{-1}**) and non-radiative (**A_{NR}, s^{-1}**) decay rates, $^5D_0$ lifetime (**τ_{obs}, μs**), intrinsic quantum yield (**Φ_{Ln}, %**), energy transfer efficiency (**Φ_{sen}, %**), overall quantum yield (**Φ_{overall}, %**) and colour coordinates for Eu^{3+} complexes in the solid-state (λ_{ex} = 400 nm).

Compounds	**A_{RAD} (s^{-1})**	**A_{NR} (s^{-1})**	**τ_{obs} (μs)**	**Φ_{Ln} (%)**	**Φ_{sen} (%)**	**Φ_{overall} (%)**	**CIE$_{(x,y)}$**
Eu(MeOBPhTFB)$_3$(H$_2$O)(C$_2$H$_5$OH)(**1**)	1152	4608	174 ± 1	20	95	19 ± 2	0.67, 0.32
Eu(MeOBPhTFB)$_3$(TPY)(**2**)	1171	813	506 ± 2	59	~100	62 ± 6	0.67, 0.32
Eu(BPhTFB)$_3$(H$_2$O)(C$_2$H$_5$OH)(**3**)	948	2698	282 ± 1	26	77	20 ± 2	0.66, 0.33
Eu(BPhTFB)$_3$(TPY)(**4**)	1165	843	499 ± 2	58	91	53 ± 5	0.66, 0.33

Table 2 The radiative (**A_{RAD}, s^{-1}**) and non-radiative (**A_{NR}, s^{-1}**) decay rates, $^5D_0$ lifetime (**τ_{obs}, μs**), intrinsic quantum yield (**Φ_{Ln}, %**), energy transfer efficiency (**Φ_{sen}, %**), overall quantum yield (**$\Phi_{overall}$, %**) of 3%, 5%, 7% and 9% Eu^{3+} complex doped PMMA films (λ_{ex} = 400 nm).

Compounds	**A_{RAD} (s^{-1})**	**A_{NR} (s^{-1})**	**τ_{obs} (μs)**	**Φ_{Ln} (%)**	**Φ_{sen} (%)**	**$\Phi_{overall}$ (%)**
PMMA@3Eu	994	280	788 ± 4	78	96	75 ± 8
PMMA@5Eu	972	290	792 ± 5	77	99	76 ± 8
PMMA@7Eu	980	230	823 ± 4	81	98	79 ± 8
PMMA@9Eu	982	420	714 ± 5	70	100	70 ± 7

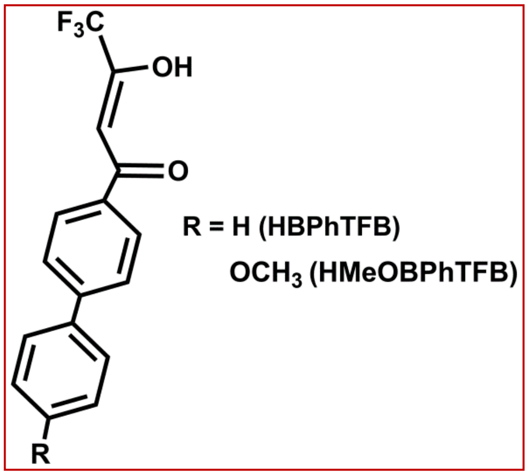


Fig. 1. Structure of the ligands.

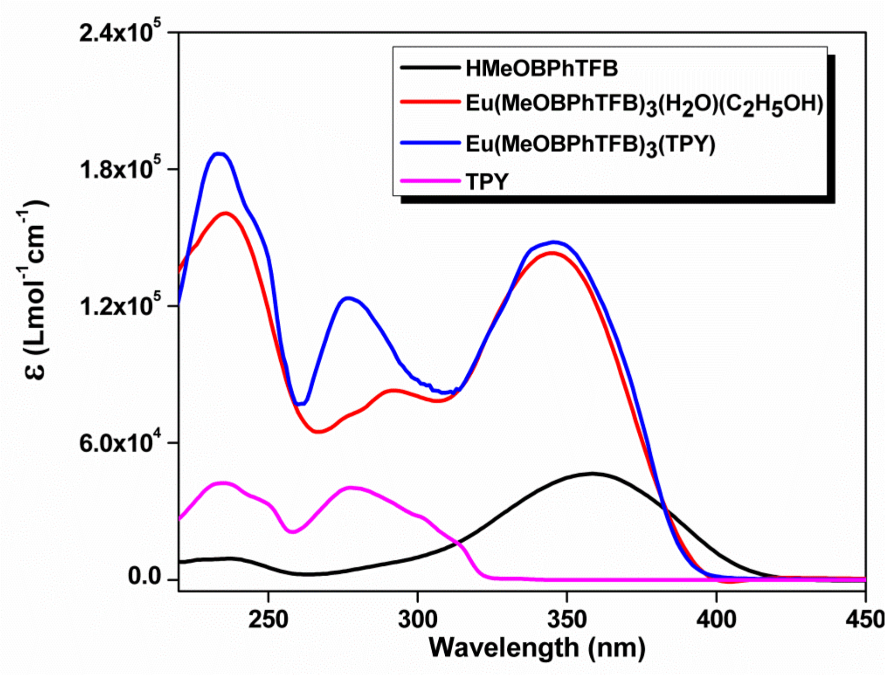


Fig. 2. UV-visible absorption spectra of the ligands, HMeOBPhTFB, TPY and corresponding Eu^{3+} complexes (**1**-**2**) in acetonitrile ($c = 5\times10^{-6}$ M).

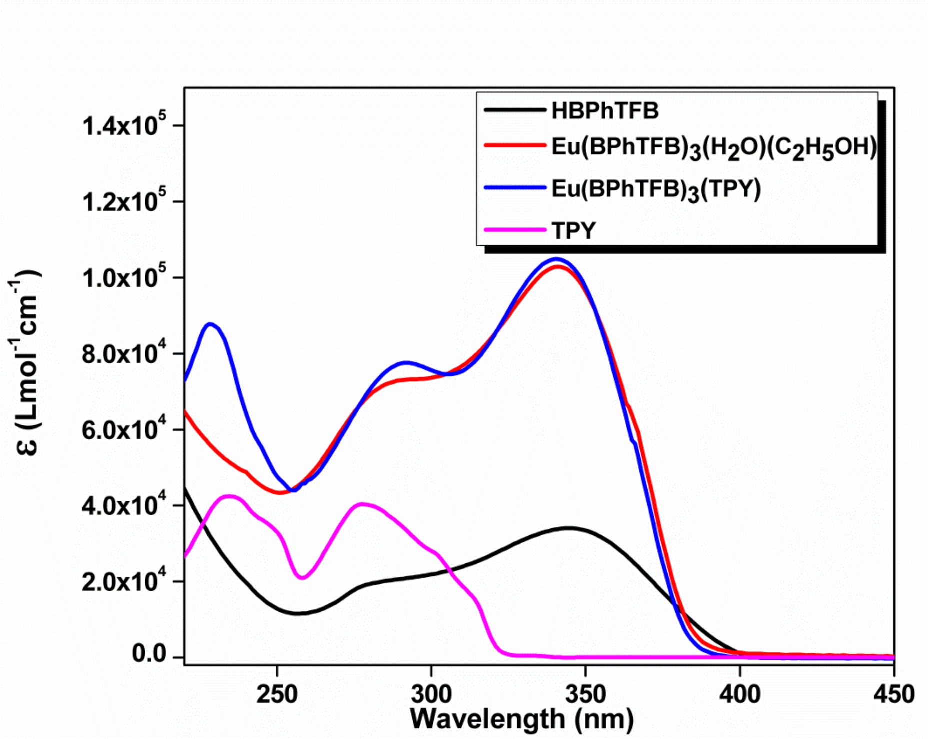


Fig. 3. UV-visible absorption spectra of the ligand, HBPhTFB, TPY and corresponding Eu^{3+} complexes (**3-4**) in acetonitrile ($c = 5\times10^{-6}$ M).

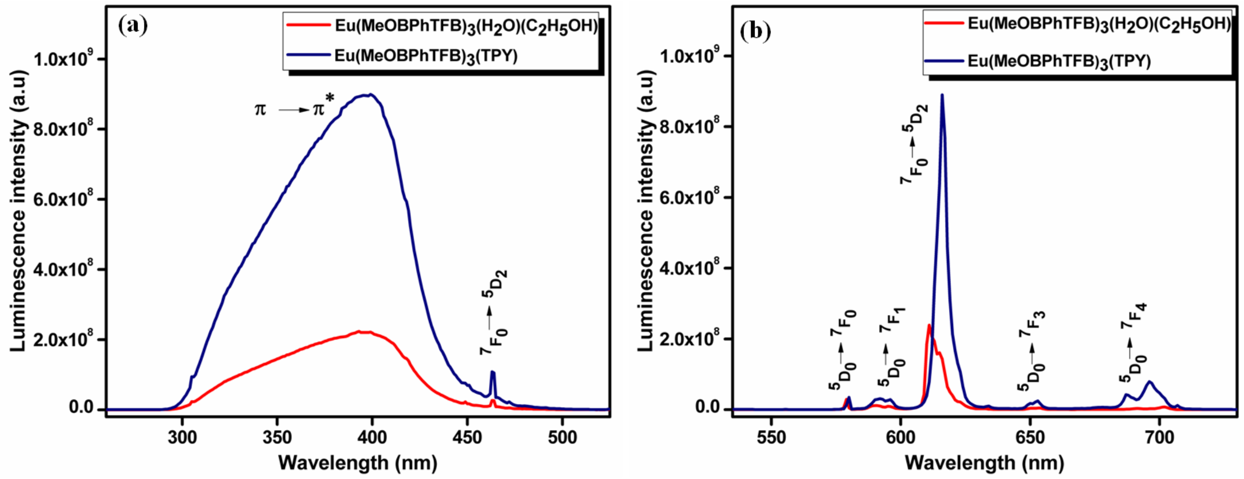


Fig. 4. 298 K (a) excitation and (b) emission spectra of Eu^{3+} complexes $Eu(MeOBPhTFB)_3(H_2O)(C_2H_5OH)$ (**1**) and $Eu(MeOBPhTFB)_3(TPY)$ (**2**) in solid-state.

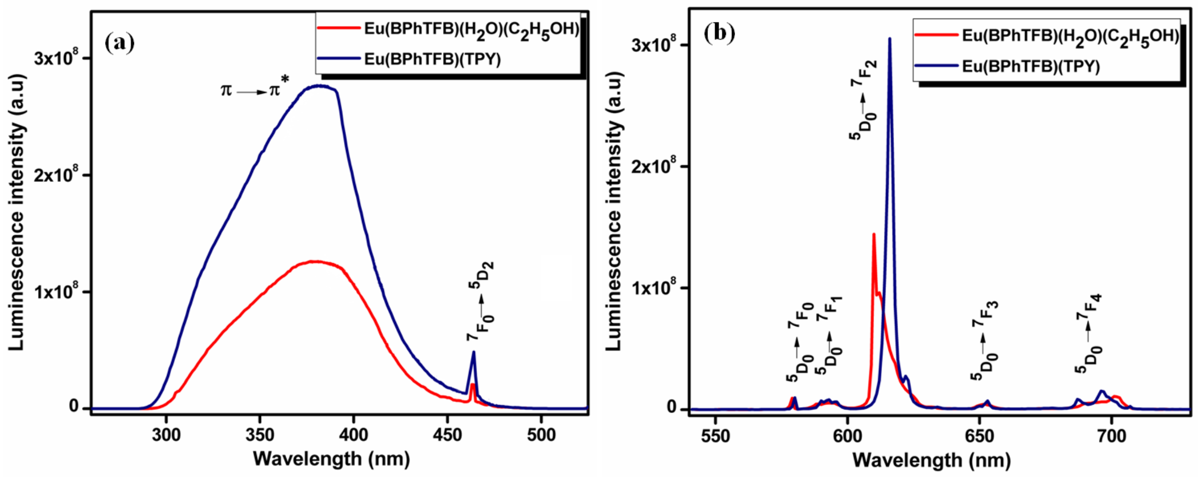


Fig. 5. 298 K (a) excitation and (b) emission spectra (b) of Eu^{3+} complexes $Eu(BPhTFB)_3(H_2O)(C_2H_5OH)$ (**3**) and $Eu(BPhTFB)_3(TPY)$ (**4**) in solid-state.

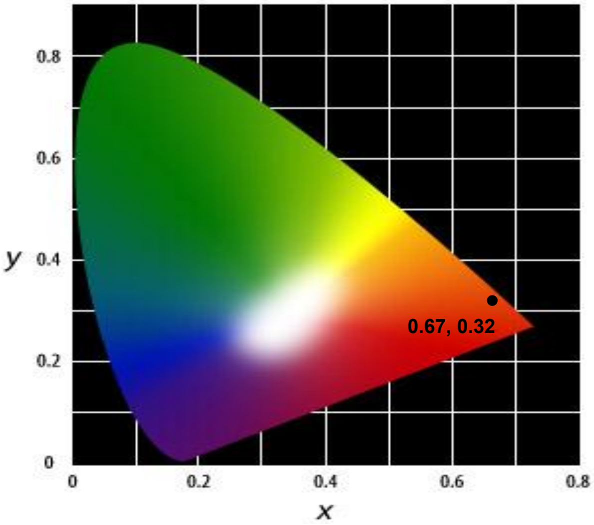


Fig. 6. CIE chromaticity diagram showing the colour of the Eu(MeOBPhTFB)$_3$(TPY) complex (**2**).

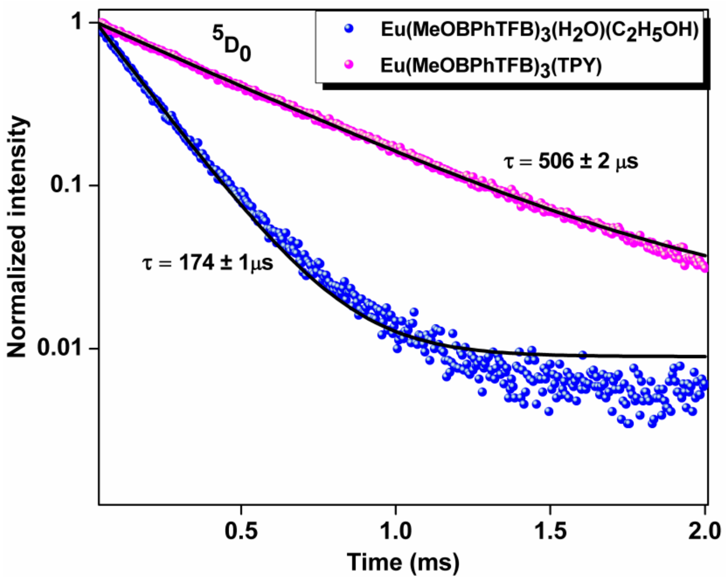


Fig. 7. $^5D_0$ decay profiles for complexes Eu(MeOBPhTFB)$_3$(H$_2$O)(C$_2$H$_5$OH) (**1**) and Eu(MeOBPhTFB)$_3$(TPY) (**2**) (solid-state) where emission monitored around 615 nm. The straight lines are the best fits ($r^2 = 0.999$) considering single-exponential behavior.

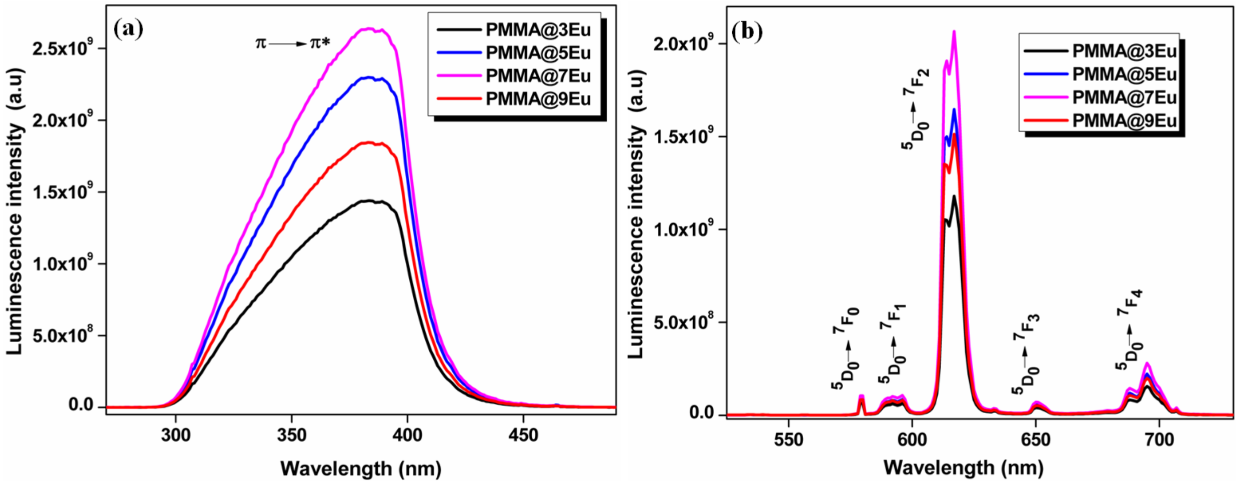


Fig. 8. 298 K (a) excitation and (b) emission spectra of 3%, 5%, 7% and 9% Eu(MeOBPhTFB)$_3$(TPY) doped PMMA films.

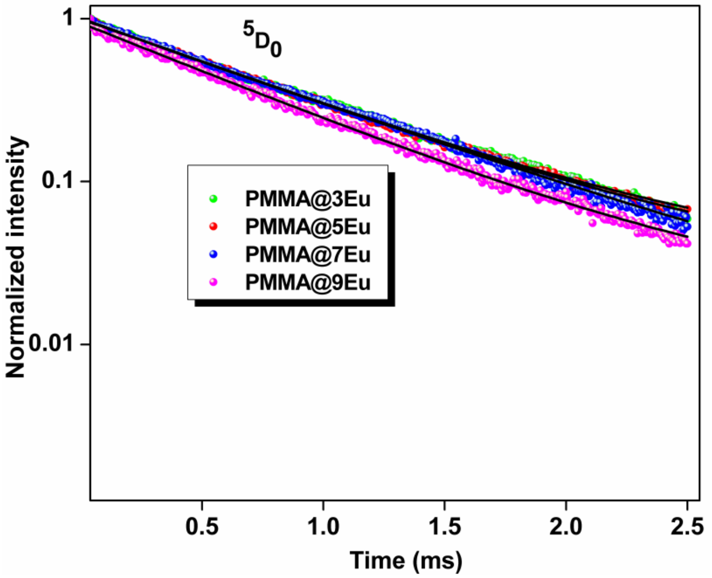


Fig. 9. $^5D_0$ decay profiles for 3, 5, 7 and 9 w/w% Eu(MeOBPhTFB)$_3$(TPY) doped PMMA films, where emission monitored around 615 nm. The straight lines are the best fits (r^2 = 0.999) considering single-exponential behavior.

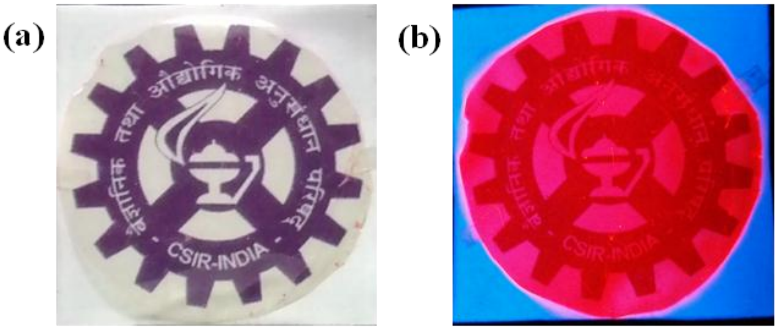
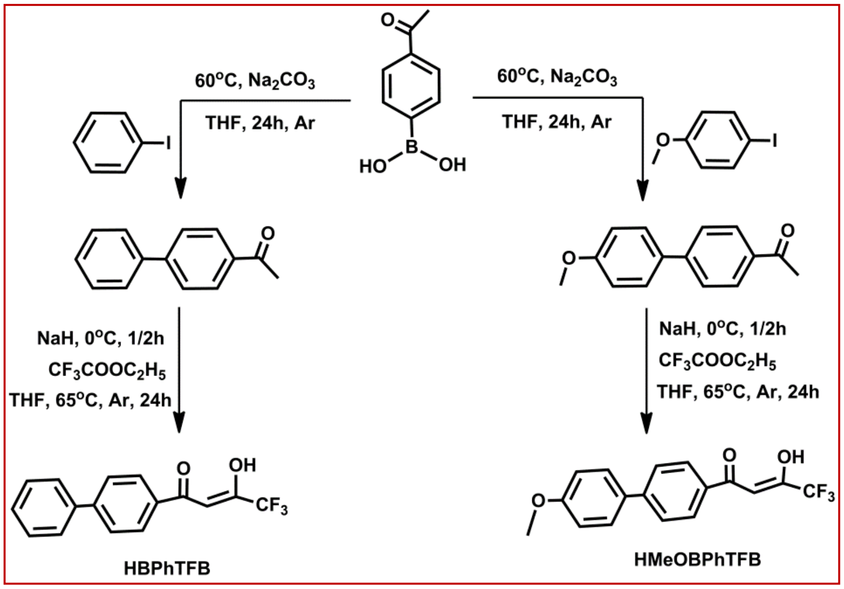
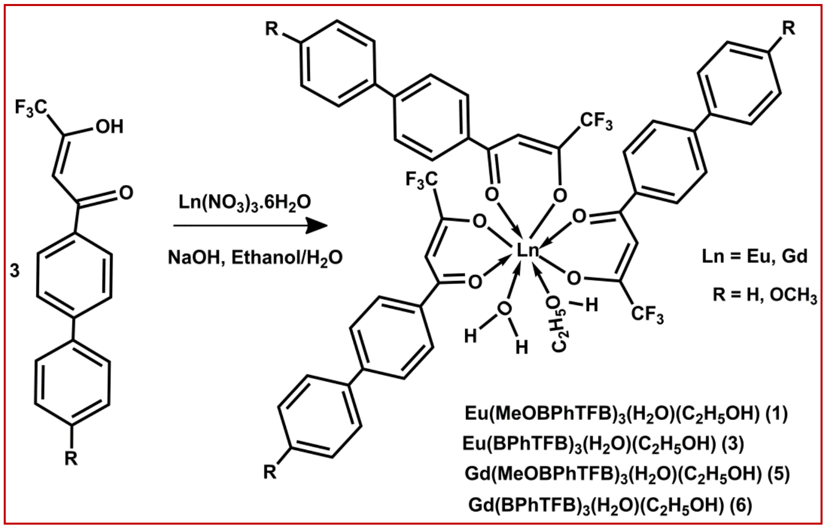


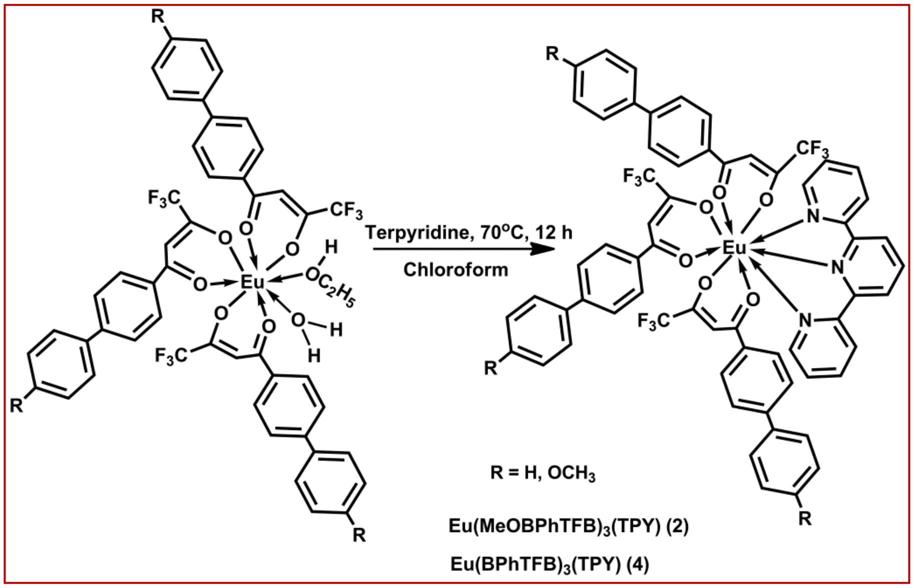
Fig. 10. Photograph of the transparent PMMA film doped with 7 w/w% Eu(MeOBPhTFB)$_3$(TPY) a) before UV irradiation and b) after UV irradiation.



Scheme 1. Synthesis of the ligands.



Scheme 2. Synthesis of the Ln^{3+} (Ln = Eu, Gd) binary complexes.



Scheme 3. Synthesis of the Eu^{3+} ternary complexes **2** and **4**.