A carbazole–triphenylamine copolymer-bearing pendant europium complexes: Synthesis and luminescence properties

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ABSTRACT: A novel carbazole–triphenylamine copolymer-bearing pendant bipyridine PM1TPA and corresponding europium (III) complexed polymer PM1TPA–Eu–x, in which the values of x are 0.1, 0.5, and 1.0 representing the molar ratio of bipyridine ligands complexed with Eu(III), were designed and synthesized. Their chemical structures were confirmed by ^{1}H NMR, FT-IR, and elemental analysis. Both PM1TPA and PM1TPA–Eu shows good solubility in common organic solvents such as tetrahydrofuran (THF) and CHCl$_3$. The 5% weight loss temperature ($T_d^{5\%}$) of PM1TPA and PM1TPA–Eu–1.0 are 363°C and 306°C, respectively. The photoluminescence (PL) spectra of PM1TPA–Eu in solution consists of two emission bands, one in the 400–570 nm region and another at 612 nm, corresponding to the emission of polymer main chain and europium complexes, respectively. When the concentration of PM1TPA–Eu–1.0 in THF solution increases, the PL intensity in the 400–570 nm regions became more and more weaker. And only the characteristic emission of europium complex was observed in the solid film, which indicates that the excited energy absorbed by the polymer backbone was efficiently transferred to the europium complexes. Furthermore, nearly monochromatic red electroluminescence from europium complex was observed from the polymeric light-emitting diode using PM1TPA–Eu–1.0 as the emissive layer under 25 V forward bias. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42746.

INTRODUCTION

Lanthanide ions (Ln(III)) and their complexes are excellent chromophores because of their excellent luminescent properties such as narrow emission bands and long radiative lifetimes.[1] These special characters render their usage for extensive applications such as light-emitting diodes (LEDs), optical communications, luminescent probes for analyses, and bioanalytical sensors.[2,3] However, the f–f transitions that result in the emission of light from the lanthanide ions in the visible and near-infrared (NIR) regions of the spectrum are spin and parity-forbidden, requiring the use of antenna molecules to indirectly excite the metal center. In order to overcome these problems, the so-called antenna ligands which chelate to lanthanide ions have been developed. These antenna ligands can absorb and transfer energy efficiently to the central metal, and the lanthanide complex display the metal-to-ligand charge transfer (MLCT) emission. The antenna ligands may be small molecules, polymer backbones, or small molecules that have been incorporated into the polymer backbone.[4,5]

So far most of the small-molecule europium complexes with important β-diketone antenna ligands such as Eu(DBM)$_3$Phen, Eu(DBM)$_3$Bath, Eu(DBM)$_3$TPIP exhibit intense PL,[6–8] and were used as red light-emitting materials for OLEDs. However, to prepare LED devices, low-molecular-weight europium complexes have to be fabricated into thin solid films by high-cost techniques such as vapor deposition, which could limit its practical application in a large degree. After the europium complexes are doped into polymer matrices, the polymeric light-emitting diodes (PLEDs)[9–12] can be prepared by spin-coating method. But the doping technique always leads to concentration quenching and phase separation, which are the main factors affecting the performance of PLEDs.[13] Hence, to incorporate the europium complexes into a polymer main chain or side chain through covalent linkages would be a preferable option.

Up to now, a number of nonconjugated[14–17] and conjugated[18,19] polymers containing europium complexes have been reported. The europium (III) center is either tethered to the polymer backbone by a saturated organic linker, covalently coupled to
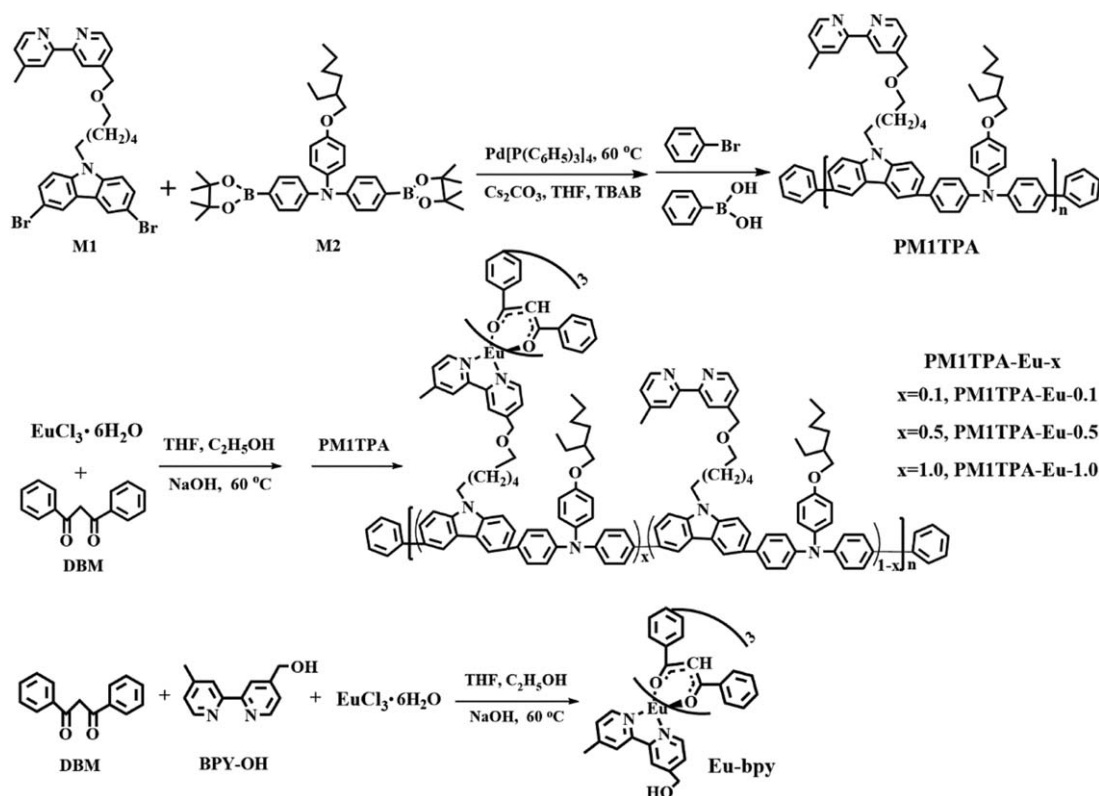
Scheme 1. Synthetic routes of **PM1TPA**, **PM1TPA–Eu–x** (x = 0.1, 0.5, and 1.0), and **Eu-bpy**.

the backbone, or directly incorporated into the polymer backbone, respectively. The europium complexes could be dispersed evenly around the polymer chains, and the concentration quenching and phase separation could be effectively avoided,[18,20] which is very important for optical application. Interestingly, when the europium complex is tethered to the polymer chain via an electronically insulating organic linker, they have virtually the same electronic, optical, and chemical properties as the uncoupled complexes.[17,18] For example, Pei et al.[18] designed and synthesized a fluorene–phenylene conjugated polymer with a bipyridyl moiety at the side chain directly coordinating with Eu(III) chelates (β-diketone) to afford luminescent lanthanide-containing metallopolymers. Under the irradiation of UV light, the efficient Förster energy transfer processes from the backbone of the blue emitting conjugated polymer to the Eu(III) center happened both in solution and in films. Using this europium-containing polymer as luminescent materials, the corresponding PLEDs emitted pure red monochromic characteristic emission of europium complexes. Reddy and colleagues[21] reported a carboxylic functionalized poly(m-phenylenevinylene) containing two kinds of lanthanide complexes emitted white PL in solid state when the Eu(III) and Tb(III) of β-diketonate complexes were tethered to the polymer backbone in an equimolar ratio.

Herein, a novel carbazole–triphenylamine conjugated polymer-bearing pendant europium complex via a flexible linkage, **PM1TPA–Eu** (as shown in Scheme 1), was designed and synthesized. As the charge transport balance is very important in PLEDs device, carbazole and triphenylamine units are used to improve the hole-transporting ability[18,22] of the metallopolymers. As the europium complexes were linked to the conjugated main chain via an "inert" flexible spacer, both the conjugated main chain and the europium complex might emit light independently, and the PL of **PM1TPA–Eu** should probably be like that of the blends of **PM1TPA** and **Eu-bpy**. Therefore, the reported **PM1TPA–Eu** complex may not only inherit the good charge transferability of the conjugated polymer main chains, but also present the inherent sharp red emission of europium complexes. The PL properties of **PM1TPA–Eu** were invested both in solution and in solid state. The primary electroluminescence (EL) properties of **PM1TPA–Eu** were also invested.

EXPERIMENTAL

Materials
4,4′-Dimethyl-2,2′-bipyridine and EuCl₃·6H₂O were purchased from Acros. Monomer **M1** was firstly synthesized in our group, and the synthetic procedure has been reported elsewhere.[23] 4-Hydroxymethyl-4′-methyl-2,2′-bipyridine (BPY-OH)[24] and monomer **M2**[25] were synthesized according to the literature procedures. All other materials were used as received except the solvent THF was dried over and distilled from calcium hydride under dry nitrogen atmosphere.

Instruments
Melting point was measured with a WRS-1B melting point apparatus. ^{1}H NMR spectra were recorded on a Bruker DRX-400 (400 MHz) NMR spectrometer using CDCl₃ as solvent. FT-IR spectra were conducted with a Nicolet Protégé 460 infrared spectrometer on KBr discs. Elemental analyses were carried out

on an EA 1110 CHNSO elemental analysis system. Gel permeation chromatography (GPC) analysis was performed on HLC-8220 liquid chromatograph calibrated with polystyrene standards using THF as eluent. Thermogravimetric analysis (TGA) was determined by a NETZSCH TG 209 calorimeter at a heating rate of 10°C min^{-1} with a nitrogen flow from room temperature to 600°C. Differential scanning calorimetry (DSC) was carried out with a NETZSCH DSC 204 at a heating rate of 10°C min^{-1} from 20°C to 250°C under a nitrogen atmosphere. UV–visible absorption spectra were obtained on a Shimadzu UV-3010 instrument. The fluorescence spectra were collected on a PTI-QM40-Laser-NIR luminescence spectrometer.

Synthesis

Synthesis of PM1TPA. M1 (0.607 g, 1.00 mmol), M2 (0.625 g, 1.00 mmol), tetrabutylammonium bromide (0.200 g), and tetrakis(triphenylphosphine)palladium (28 mg) were mixed in a Schlenk tube under an argon atmosphere. THF (20 mL) was added and the mixture was degassed by three freeze-pump thaw cycles. Cesium carbonate aqueous solution (2.0 g in 3 mL water) was added, and the mixture was heated at 60°C for 5 days. Then the end groups were capped by refluxing for 12 h with phenylboronic acid (0.085 g, 0.70 mmol) and for another 12 h with bromobenzene (0.157 g, 1.00 mmol), sequentially. Then the reaction mixture was poured into methanol to induce precipitation, and the resulting solid was collected by filtration. The polymer was dissolved in THF and reprecipitated from methanol for three times, and finally dried in vacuum oven overnight. The resultant polymer was obtained as a white powder (0.697 g, yield: 82.1%). ^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm): 8.75–6.75 (ArH), 4.69–4.52 (Ar–CH$_2$O–), 4.43–4.17 (carbazole–NCH$_2$–), 3.92–3.71 (triphenylamine–OCH$_2$–), 3.61–3.40 (–CH$_2$O–), 2.63–2.42 (Ar–CH$_3$), 2.02–1.18 (–CH$_2$–, –CH–), 1.02–0.81 (–CH$_3$). GPC: $M_w = 6.67 \times 10^3$, polydispersity index (PDI) = 1.78. Anal. Calcd for [C$_{56}$H$_{60}$N$_4$O$_2$]: C, 81.91; H, 7.37; N, 6.82. Found: C, 82.42; H, 7.73; N, 6.80.

Synthesis of PM1TPA–Eu–1.0. To a solution of DBM (0.67 g, 3 mmol) in 20 mL THF, aqueous NaOH (1 mol/L) was added carefully to control the pH value in the range of 7.0–8.0, and then followed by 5 mL ethanol solution containing EuCl$_3$·6H$_2$O (0.37 g, 1.0 mmol). After the reaction mixture was stirred at 60°C for 2 h, PM1TPA (0.62 g, 0.75 mmol repeating units) was added, followed by heating under nitrogen for 24 h. Then the mixture was dropped into methanol, and the solid was extracted with a mixed solvent of methanol and acetone (1/1, v/v) in a Soxhlet extractor for 2 days. The final product was dried in vacuum oven overnight to obtain a light yellow powder. (0.52 g, yield: 57%). IR (KBr disc): v (C=N): 1602 cm^{-1}, v (C=O-Eu): 1553 cm^{-1}, v (C=C): 1514 cm^{-1}, v(C–O–Eu): 1402 cm^{-1}, v (Eu–N): 728 cm^{-1}, v (Eu–O): 513 cm^{-1}. GPC: $M_w = 12.50 \times 10^3$, PDI = 2.04. Anal. Calcd for [C$_{101}$H$_{93}$N$_4$O$_8$Eu]: C, 73.84; H, 5.71; N, 3.41. Found: C, 74.03; H, 5.91; N, 4.01.

Synthesis of PM1TPA–Eu–0.5. The synthetic procedure is same as that of **PM1TPA–Eu–1.0**. DBM (0.335 g, 1.50 mmol), EuCl$_3$·6H$_2$O (0.185 g, 0.50 mmol), and PM1TPA (0.821 g, 1.00 mmol) were charged for the reaction. Light yellow powder (0.78 g, yield: 61%). IR (KBr disc): v (C=N): 1607 cm^{-1}, v (C=O–Eu):

1550 cm^{-1}, v (C=C): 1518 cm^{-1}, v (C–O–Eu): 1404 cm^{-1}, v (Eu–N): 728 cm^{-1}, v (Eu–O): 513 cm^{-1}. GPC: $M_w = 8.97 \times 10^3$, PDI = 1.87. Anal. Calcd for [C$_{78.5}$H$_{76.5}$N$_4$O$_5$Eu$_{0.5}$]: C, 76.59; H, 6.18; N, 4.55. Found: C, 76.87; H, 6.33; N, 4.71.

Synthesis of PM1TPA–Eu–0.1. The synthetic procedure is same as that of **PM1TPA–Eu–1.0**. DBM (0.067 g, 0.30 mmol), EuCl$_3$·6H$_2$O (0.037 g, 0.10 mmol), and PM1TPA (0.821 g, 1.00 mmol) were charged for the reaction. Light yellow powder (0.606 g, yield: 66%). IR (KBr disc): v (C=N): 1607 cm^{-1}, v (C=O–Eu): 1550 cm^{-1}, v (C=C): 1518 cm^{-1}, v (C–O–Eu): 1404 cm^{-1}, v (Eu–N): 728 cm^{-1}, v (Eu–O): 513 cm^{-1}. GPC: $M_w = 7.12 \times 10^3$, PDI = 1.74. Anal. Calcd for [C$_{60.5}$H$_{63.3}$N$_4$O$_{2.6}$Eu$_{0.1}$]: C, 80.61; H, 6.88; N, 6.22. Found: C, 80.17; H, 6.57; N, 6.38.

Synthesis of Eu-bpy. Eu-bpy was synthesized following the literature procedures.[26] To a solution of **DBM** (0.403 g, 1.80 mmol) and BPY-OH (0.120 g, 0.60 mmol) in 20 mL ethanol, 3 mL aqueous NaOH (0.072 g, 1.80 mmol) was added followed by an ethanol solution containing EuCl$_3$·6H$_2$O (0.220 g, 0.60 mmol). The reaction mixture was stirred at 60°C for 5 h and yellow precipitate was formed. The product was washed for several times with deionized water and ethanol, and dried in vacuum at 80°C for 24 h. **Eu-bpy** was obtained as a yellow powder (0.510 g, yield: 83.1%). M_p: 252–255°C. IR (KBr disc): v(C=N): 1607 cm^{-1}, v(C=O–Eu): 1550 cm^{-1}, v (C=C): 1518 cm^{-1}, v(Eu-N): 728 cm^{-1}, v (Eu–O): 513 cm^{-1}. Anal. Calcd for [C$_{57}$H$_{45}$EuN$_2$O$_7$]: C, 66.99; H, 4.44; N, 2.74. Found: C, 66.18; H, 4.47; N, 2.69.

Fabrication of EL Devices. Poly(3,4-ethylenedioxithiophene)/poly(styrene sulfonate) (PEDOT:PSS, 40 nm) films (Bayer Corporation) were deposited by spin-coating onto a patterned indium tin oxide (ITO) glass substrate (10 Ω sq^{-1}) and dried at 110°C for 30 min. A CHCl$_3$ solution of polymer **PM1TPA–Eu–1.**(6 mg mL^{-1}) was filtered and deposited by spin-coating at 1500 rpm over the PEDOT:PSS layer under dry nitrogen environment. The polymer film thickness was about 40 nm thick. A LiF layer (1 nm thickness) was deposited on the top of electronic transport layer (TPBI, 20 nm) by Thermal Evaporator System (ZHD-400) at 4×10^{-4} Pa, followed by about 120 nm aluminum layer as cathode on the top of the device. The final configuration of the device was ITO/PEDOT:PSS (40 nm)/**PM1TPA–Eu–x** (40 nm)/TPBI (20 nm)/LiF (1 nm)/Al (120 nm). Device characteristics were measured by Keithley 2400 and PR 715. All processes and measurements were carried out under atmosphere.

RESULTS AND DISCUSSION

Synthesis

The monomer **M1** is a dibromo-carbazole linked with a bipyridine group *via* a flexible spacer. As shown in Scheme 1, the conjugated polymer-bearing pendant bipyridine groups **PM1TPA** was prepared by Suzuki polycondensation between the dibromo-monomer **M1** and the diborate monomer **M2**. Monofunctional bromobenzene and phenylboronic acid were used as the end capping regents for the polymers. Figure 1 shows the ^{1}H NMR spectra of monomer **M1**, **M2**, and **PM1TPA** in CDCl$_3$.
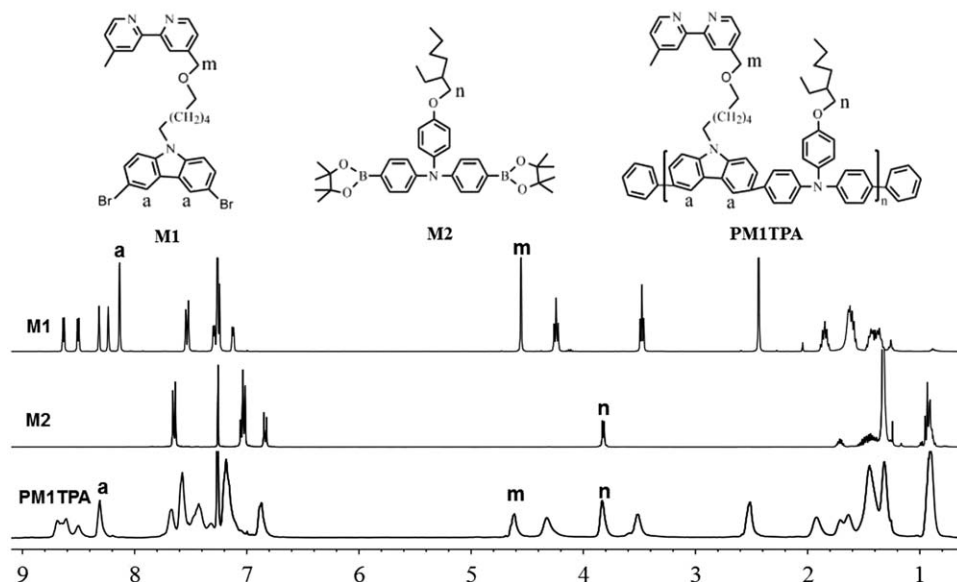
Figure 1. ^{1}H NMR spectra of monomer **M1**, **M2**, and **PM1TPA** in CDCl$_3$.

In the range of 0.80–4.60 ppm, the chemical shifts of **PM1TPA** were similar with those of monomers **M1** and **M2**. The content of related monomer units in the copolymer could be calculated from the integration ratios of the peaks at 4.60 ppm (bipyridine–CH$_2$–, marked m in Figure 1) and 3.85 ppm (isooctyl–CH$_2$–, marked n in Figure 1). The value of m/n was about 1 for the polymer **PM1TPA**, which indicated that the designed polymer was successfully synthesized. Furthermore, all the proton signals in **PM1TPA** showed a tendency for signal broadening due to polymerization. In addition, the elemental analysis result of **PM1TPA** was consistent with its calculated value, which further confirmed the successful polymerization. The weight-average molecular weight (M_w) and PDI of **PM1TPA** measured by GPC using THF as eluent calibrated with polystyrene standard were 6670 and 1.78, which are consistent with those polymers synthesized through Suzuki polycondensation using tetrakis(triphenyl-phosphine)palladium as catalyst in literatures.[27–29]

PM1TPA–Eu–x was synthesized by adding DBM and **PM1TPA** in sequence to the THF solution of EuCl$_3$·6H$_2$O. Then the crude product was extracted in a Soxhlet extractor to remove unreacted small molecules. When the molar ratio of chelate ligand bipyridine of **PM1TPA** to EuCl$_3$·6H$_2$O is 0.1, 0.5, and 1.0, the corresponding europium (III) complexed polymers are named as **PM1TPA–Eu–x**, in which the values of x are 0.1, 0.5, and 1.0 representing the molar percentage of bipyridine ligands complexed with Eu(III). **PM1TPA–Eu–x** shows good solubility in common organic solvents such as CH$_2$Cl$_2$, CHCl$_3$, and THF, indicating that the interchain crosslinking of macromolecular ligands **PM1TPA** have been successfully avoided by this one-pot postfunctionalization method.

As shown in Figure 2, in comparison with the metal-free polymer **PM1TPA**, some new strong absorptions appeared at approximately 1553 cm^{-1}, 1402 cm^{-1}, and 728 cm^{-1} in FT-IR spectrum of **PM1TPA–Eu–x**. These bands could be ascribed to

the stretching vibrations of C=O–Eu, C–O–Eu, and N–Eu groups in the europium complex, illustrating the successful introduction of the europium complexes onto the pendant bipyridine groups in **PM1TPA**. Furthermore, all the elemental analysis results of **PM1TPA–Eu–x** ($x = 0.1$, 0.5, and 1.0) were very close to their theoretical values, indicating that all the added Eu(III) ions have been completely complexed with the bipyridine ligands in the ligand polymers **PM1TPA**.

Thermal Stability

The thermal stabilities of **PM1TPA–Eu–x** ($x = 0.1$, 0.5, and 1.0), **PM1TPA,** and **Eu-bpy** were evaluated by TGA under nitrogen atmosphere, and the results are shown in Figure 3(a). The 5% weight loss temperature ($T_d^{5\%}$) of **PM1TPA-Eu-x** ($x = 0.1$, 0.5, and 1.0) is in the range of 306–349°C, which was higher than that (292°C) of the model compound (**Eu-bpy**) and lower than
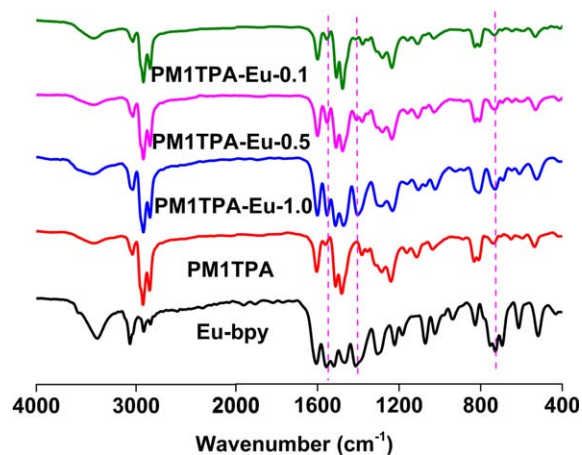

Figure 2. FT-IR spectra of **PM1TPA–Eu–x**, **PM1TPA**, and **Eu-bpy** in KBr disc. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
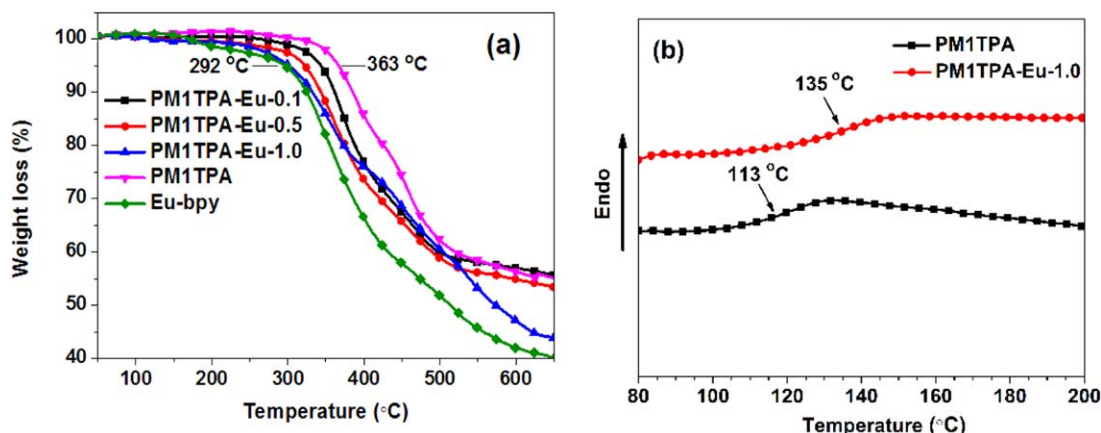
Figure 3. (a) TGA curves of **PM1TPA–Eu–x** (x = 0.1, 0.5, and 1.0), **PM1TPA**, and **Eu-bpy**; (b) DSC curves of **PM1TPA** and **PM1TPA–Eu–1.0** under nitrogen atmosphere at a heating rate of 10°C min^{-1}. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

that (363°C) of **PM1TPA**. With the content of europium increase, its $T_d^{5\%}$ decrease. The weight loss at this temperature was mainly due to the decomposition of **Eu–bpy** complexes in the copolymer. The glass transition temperature (T_g) was measured as 113°C for **PM1TPA** (bipyridine-containing polymer) and 135°C for **PM1TPA–Eu** (complex-containing polymer), respectively, as determined by DSC under nitrogen atmosphere shown in Figure 3(b). The introduction of europium complexes rendered the polymer backbone more rigid, since the bulkiness of the complexed site required a higher energy for rotation.[30]

UV–Vis Absorption Properties

The UV–vis absorption spectra of **PM1TPA–Eu–x**, **PM1TPA**, and **Eu-bpy** in THF solutions and in solid state at room temperature are shown in Figure 4. The polymer thin films for UV–vis absorption and PL measurements were prepared by spin-coating their THF solution (6 mg/mL) onto quartz substrates with a rotating speed of 1200 rpm at room temperature and dried in oven under vacuum. The maximum absorption of the UV–vis spectra (λ_{abs}) is summarized in Table I.

As shown in Figure 4a, all of them exhibited a series of broad absorption peaks in the region from 250 to 420 nm in THF

solution, which could be attributed to the energy levels undergoing reorganization and π–$\pi^\star$ electronic transitions of the conjugated main chain or the low molar mass organic ligands.[31] Furthermore, as the absorption of conjugated main chain overlapped with the europium complex, the absorption intensity of **PM1TPA–Eu–x** at about 350 nm was higher than that of europium-free polymer **PM1TPA** at the same concentration. Compared with the UV–vis absorption spectra in solution, the absorption spectra of all the five materials in films (Figure 4b) had undergone a red shift to long wavelengths due to the molecules aggregation.[32] The red shift values of **Eu-bpy** and **PM1TPA–Eu–1.0** are 15 nm and 5 nm, respectively, indicating that the molecular aggregation of small molecule europium complexes could be avoided in a large extent after the introduction to the polymer pendant groups.

Photoluminescence Properties

All the PL spectra of **PM1TPA–Eu–x** (x = 0.1, 0.5, and 1.0), **PM1TPA**, and **Eu-bpy** were excited by 360 nm light both in solution and in films. The emission spectra of **PM1TPA–Eu–x**, **PM1TPA**, and **Eu-bpy** in solutions and in solid state at room temperature are shown in Figures 5 and 6, respectively. The maximum emission of PL spectra (λ_{em}) is also summarized in
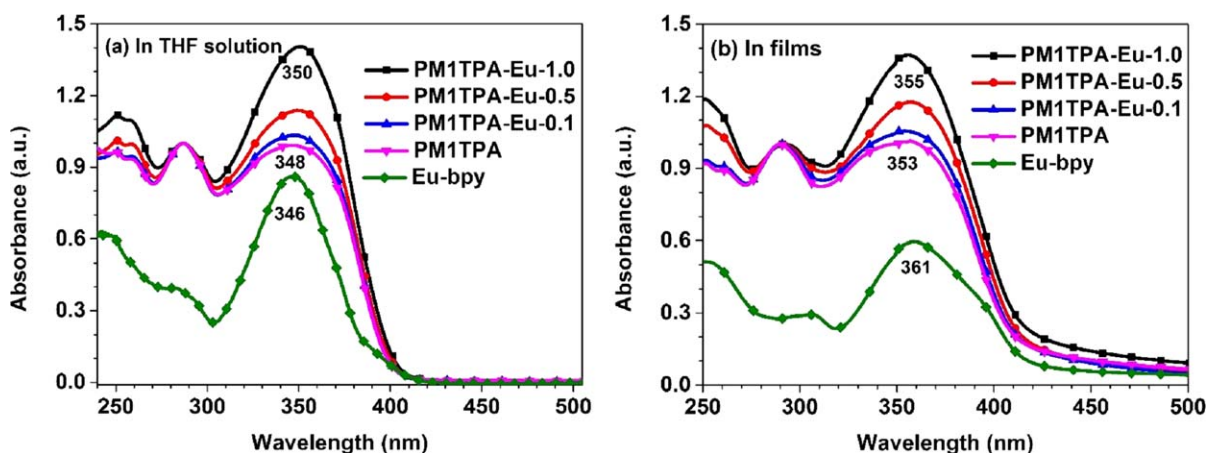

Figure 4. UV–vis absorption spectra of **PM1TPA–Eu–x** (x = 0.1, 05, and 1.0), **PM1TPA** and **Eu-bpy** in THF solution (a) and in thin films (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Data of UV–Vis and PL Measurements for PM1TPA, PM1TPA–Eu–*x*, and Eu-bpy

Compounds	λ_{abs} (nm) (in solution)	λ_{abs} (nm) (in films)	λ_{em} (nm) (in solution)	λ_{em} (nm) (in films)
PM1TPA	348	353	423	428
PM1TPA-Eu-0.1	348	354	430, 612	470, 612
PM1TPA-Eu-0.5	348	354	433, 612	472, 612
PM1TPA-Eu-1.0	350	355	465, 612	612
Eu-bpy	346	361	612	612

Table I. Additionally, the PL spectra of **PM1TPA–Eu–1.0** in films annealed at different temperature are shown in Figure 7.

Figure 5 shows the normalized PL spectra of **PM1TPA–Eu–*x*** (*x* = 0.1, 0.5, and 1.0), **PM1TPA** and **Eu-bpy** in 4 mg/mL THF solution. The ligand polymer **PM1TPA** showed blue light emission of the maximum emission wavelength 423 nm with FWHM of 70 nm. The broad emission of **PM1TPA** indicates the conjugation between the carbazole moiety and triphenylamine moiety formed. **Eu-bpy** exhibits the typical emission of a europium (III) complex. The main emission centered at 612 nm was assigned to $^5D_0 \rightarrow ^7F_2$ transition, and the other emissions such as peaks at approximately 580, 593, 649, and 701 nm correspond to $^5D_0 \rightarrow ^7F_0$, $^5D_0 \rightarrow ^7F_1$, $^5D_0 \rightarrow ^7F_3$, $^5D_0 \rightarrow ^7F_4$ electronic transition of europium (III), respectively.[33] While the complexed polymer **PM1TPA–Eu–1.0** exhibited two main emission peaks centered at 458 nm and 612 nm, compared with the PL spectra of **PM1TPA** and **Eu-bpy**, the peaks of **PM1TPA–Eu–1.0** centered at 465 nm and 612 nm originated from the emission from the conjugated main chain and from the europium complex, respectively. Compared with the ligand polymer **PM1TPA**, 42 nm red shift of the emission from the conjugated main chain of **PM1TPA–Eu–1.0** was observed.

Figure 6(a) shows the PL spectra of **PM1TPA–Eu–1.0** in the concentrations from 2 mg/mL to 14 mg/mL. With the solution concentration increase, the fluorescence intensity of the emission peak from the conjugated backbone gradually decreased, and about 47 nm red shift from the dilute solution (2 mg/mL) to concentrated solution (14 mg/mL) is observed. While the fluorescence intensity of the emission peak from the europium complexes firstly increased, then decreased and finally increased again with the increase in solution concentration. When the concentration reached to 14 mg/mL, the PL emission of **PM1TPA–Eu–1.0** was dominated by the emission from the europium complexes, and the emission from the conjugated backbone almost disappeared. As expected, the PL spectrum of **PM1TPA–Eu–1.0** in thin film (Figure 6b) was similar to that in concentrated solution (14 mg/mL) and also same as that of **Eu-bpy**. On the other hand, the PL spectrum of PM1TPA in films was similar to that in solution, only 5 nm red shifted. Considered that only the emission from the europium complex was observed, and the emission from the conjugated main chain completely vanished, the efficient energy transfer from the conjugated main chain to europium complex must have occurred.

As shown in Figure 6c, the emission spectrum of **PM1TPA** in film overlapped with the absorption spectrum of **Eu-bpy**, thus **Eu-bpy** could accept the emission energy from **PM1TPA**.[34] As europium complexes were linked to the polymer chain *via* an "inert" flexible linkage, the two chromophores could emit light independently, and the PL of **PM1TPA–Eu** probably like that of the blends of **PM1TPA** and **Eu-bpy**. Therefore, the intramolecular and/or intermolecular Förster energy transfer from the main chain to the europium complexes of **PM1TPA–Eu** could also occur. With the europium complexes content of **PM1TPA–Eu–*x*** (*x* = 0.1, 0.5, and 1.0) increase, the energy transfer became more effective both in solution (Figure 5) and in films (Figure 6b). As the europium complexes were directly bonded to the main chain of the copolymer, and the distance between the donor (main chain) and the acceptor (europium complex) was fixed, the energy transfer should not be influenced by the solution concentration. However, with the concentration of **PM1TPA–Eu-1.0** increase (Figure 6a), the energy transfer also became more and more efficiently. Therefore, it seems more reasonable to attribute this process to the combined action of the intermolecular and intramolecular energy transfer in **PM1TPA–Eu–*x*** rather than to the intramolecular process.[35] As for the PL process, the polymer backbones are excited by absorption of light, and the excited states are created on polymer backbones and then transfer to the europium complexes. With the **PM1TPA–Eu–1.0** concentration increase [Figure 6(a)], the distance between polymer backbones and europium complex is getting shorter and shorter, the Förster energy transfer from the polymer backbones to europium complex is getting more and more effective, and the emission from the polymer backbones gradually become weak. Compared with the PL spectra (Figure 5) of three europium-containing **PM1TPA–Eu–*x*** (*x* = 0.1, 0.5, and 1.0) in solution, the emission of polymer backbone become more and more weak with the increase of the europium content, which indicates that the energy transfer from the backbone to the europium complexes was enhanced with the increase of the europium content. Previously, Pei[18] and Ling[35] also reported the complete energy transfer from the
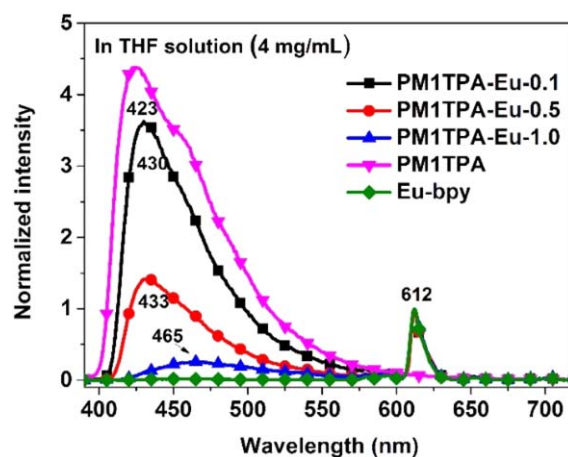

Figure 5. PL spectra of **PM1TPA–Eu–*x*** (*x* = 0.1, 0.5, and 1.0), **PM1TPA**, and **Eu-bpy** in 4 mg/mL THF solution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
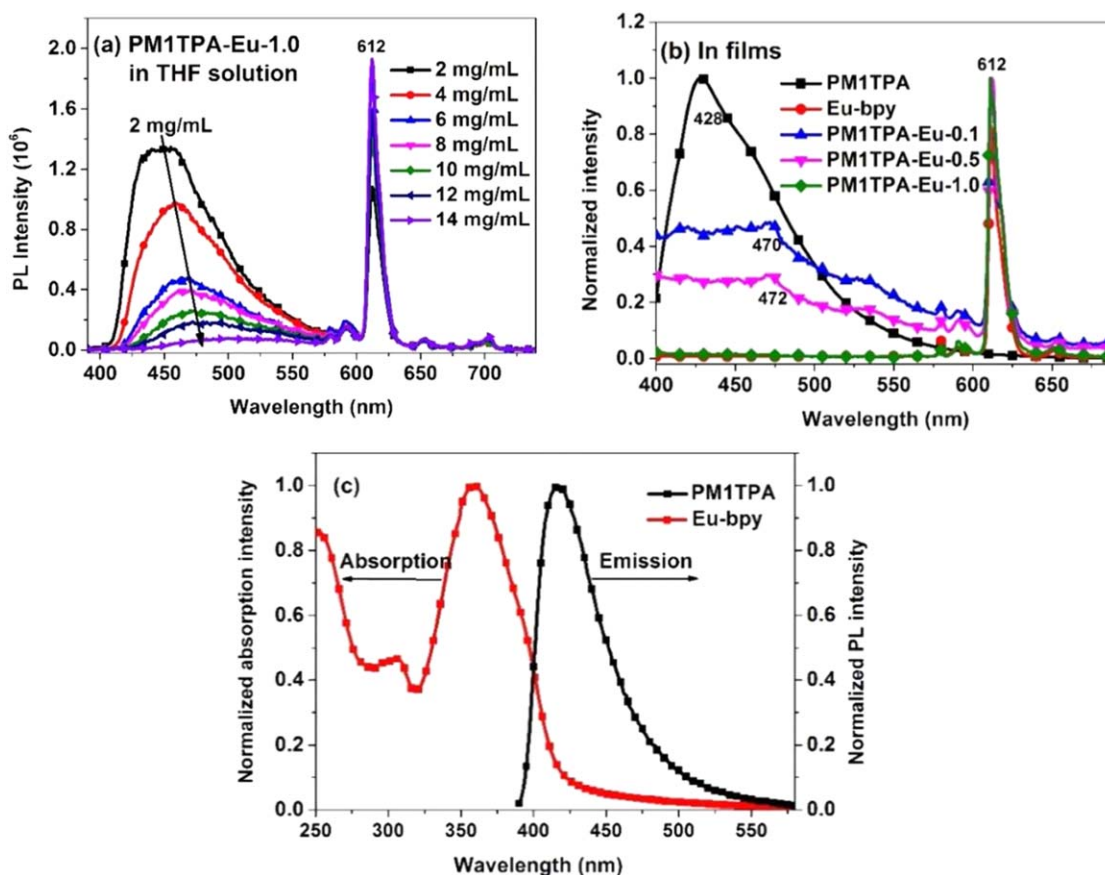
Figure 6. (a) PL spectra of **PM1TPA–Eu–1.0** in different THF concentrations; (b) PL spectra of **PM1TPA**, **PM1TPA–Eu–x** ($x = 0.1$, 0.5, and 1.0) and **Eu-bpy** in films; and (c) the normalized absorption spectra of **Eu-bpy** and the emission spectra of **PM1TPA** in films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

main chain to the europium complexes in the copolymers bearing pendant europium complexes. While for a europium-complexed fluorene–bipyridine copolymer reported by Turchetti,[36] as europium complexes were complexed directly with the polymer main chain, no energy transfer from the polymer backbone (polyfluorene) to the metal complex was observed, and the europium complexed polymer emitted strong light from the polymer main chain and weak light from the europium complexes.

In order to study the effect of temperature on the luminescent stability, the thin films of **PM1TPA–Eu–1.0** was annealed at different temperatures for 30 min and cooled down to room temperature. The corresponding PL spectra are shown in Figure 7. The emission of **PM1TPA–Eu–1.0** was kept stable until after being annealed at 100°C and the emission intensity decreased severely after being annealed at 120°C. As the annealed temperature of 120°C was close to its T_g (Figure 3b), the morphology of **PM1TPA–Eu–1.0** film would vary, which made the PL intensity of **PM1TPA–Eu–1.0** film decayed greatly.[35] The results suggested that the working temperature of device using **PM1TPA–Eu–1.0** as luminescent material should be lower than its T_g. Of course, the above temperature was high enough to satisfy the demand of practical application.

Electroluminescence Properties
To investigate the EL properties of **PM1TPA–Eu–x** ($x = 0.1$, 0.5, and 1.0) and to understand internal energy transfer within the

whole molecule under the electric field, three multilayer devices using **PM1TPA–Eu–x** as light-emitting layer with the configuration of ITO/PEDOT:PSS (40 nm)/**PM1TPA–Eu–x** (40 nm)/TPBI (20 nm)/LiF (1 nm)/Al (120 nm) were fabricated. As shown in Figure 8a, the maximum luminance of the devices using **PM1TPA–Eu–0.1**, **PM1TPA–Eu–0.5**, and **PM1TPA–Eu–1.0** as emissive layer are 69, 27, and 28 cd/m², respectively.
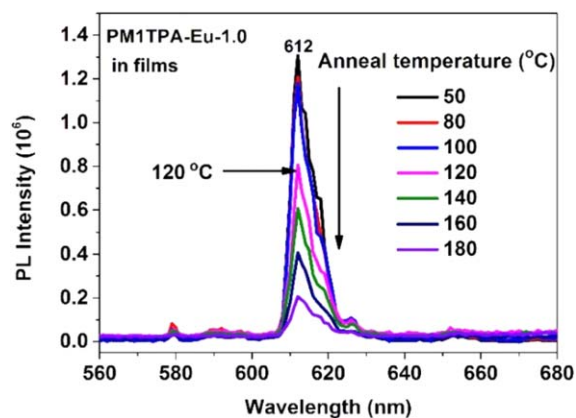

Figure 7. The PL spectra of **PM1TPA–Eu–1.0** in films after annealed at different temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
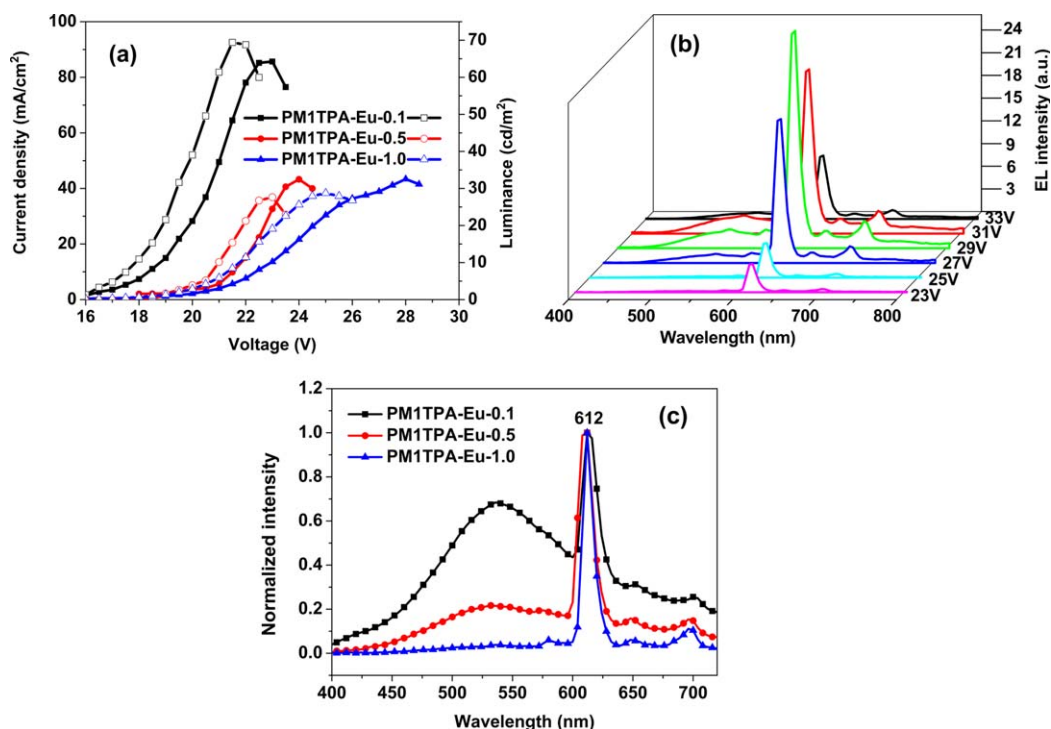
Figure 8. (a) Current density–voltage–brightness (J–V–B) characteristics of the PLEDs using **PM1TPA–Eu–x** (x = 0.1, 0.5, and 1.0) as luminescent layer; (b) EL spectra of PLED using **PM1TPA–Eu–1.0** as luminescent layer under different voltage; (c) normalized EL spectra PLED using **PM1TPA–Eu–x** as luminescent layer. (Note: PM1TPA–Eu–0.1 at 21 V, PM1TPA–Eu–0.5 at 23 V, and PM1TPA–Eu–1.0 at 25 V.). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 8b shows the EL spectra of PLED using **PM1TPA–Eu–1.0** as luminescent layer under different voltage. Under low forward bias, the EL spectra exhibits the characteristic emission of europium complex, and no emission from the conjugated polymer is observed, which is consistent with the PL spectra of **PM1TPA–Eu–1.0** in films. This implied that the emission from the conjugated backbone was quenched by the europium complexes in the EL emission of the device.[37] The CIE color coordinates of EL spectrum at 25 V calculated according to 1931 standards was $x = 0.618$, $y = 0.312$, which demonstrated that **PM1TPA–Eu–1.0** could emit nearly pure red light under the electric field. With the applied voltage raised, the emission peak from the conjugated polymer emerged. This reason may be that the europium complex was excited by injecting electrons from the cathode and hole from the anode, so the neutral excitations may be formed directly in the europium complexes. When the injected electrons and holes exceeded the need of europium complexes, some electrons and holes could encounter in the polymer main chain, so the emission of the polymer can also be observed. Furthermore, as the lower europium complex content, the EL spectra (Figure 8c) of PLED device using **PM1TPA–Eu–0.1** and **PM1TPA–Eu–0.5** as light-emitting layer consist of both the characteristic emission of europium complex and the emission from the conjugated polymer under different voltage. The reason may also result from the deficiency of acceptors (europium complex) in the **PM1TPA–Eu–0.1** or **PM1TPA–Eu–0.5** emissive layer, some excitons formed in the main chain emitted light directly.

CONCLUSIONS

The designed carbazole–triphenylamine conjugated polymer-bearing pendant bipyridine units *via* a flexible linkage, **PM1TPA**, was successfully synthesized by Suzuki polycondensation. Then **PM1TPA–Eu–x** (x = 0.1, 0.5, and 1.0) were prepared by adding DBM and **PM1TPA** in sequence to different amount of EuCl$_3$·6H$_2$O solution. **PM1TPA** and **PM1TPA–Eu–x** showed good solubility and high thermal stability. As the europium complexes were linked to the conjugated main chain *via* an "inert" flexible spacer, both the conjugated main chain and the europium complex emitted light independently, and the energy transfer from the backbone to the europium complexes happened efficiently. The ligand polymer **PM1TPA** in solution shows blue light emission at 423 nm with FWHM of 70 nm. While the europium-containing metallopolymer **PM1TPA–Eu–1.0** exhibits two main emission peaks centered at 458 nm and 612 nm, originating from the emission from the conjugated main chain and from the europium complex, respectively. The PL intensity, peak shape, and energy transfer of **PM1TPA–Eu–x** (x = 0.1, 0.5, and 1.0) are strongly influenced by the europium complex content in the copolymer and the solution concentration. In thin solid films, the PL spectra of **PM1TPA–Eu–1.0** had a sharp peak at 612 nm with a FWHM of about 10 nm, no emission from the conjugated polymer backbone was observed. Under forward bias, the device using **PM1TPA–Eu–1.0** as emissive layer emitted red light with the CIE coordinates at (0.618, 0.312) from europium (III) complex at 25 V voltage. The current efficiency obtained was about 0.09 cd/A when the

maximum luminance was about 28 cd/m^2 at 25 V. In order to obtain higher luminance and lower applied voltage, other methods such as selecting more suitable functional materials, optimizing the device configuration, reducing the device thickness, could be used. Furthermore, as **PM1TPA**-bearing pendant bipyridine units show good solubility and high thermal stability, it may be also used as macromolecular ligands to coordinate with different metals to prepare other new metallopolymers for solar cells, bioanalytical sensors, photocatalysts, etc.

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