

含 Eu(III)和 Gd(III)共轭高分子配合物发光性质研究

缪 谦^{*,1} 张树伟² 黄小波^{1,2} 程亚倩¹ 宗利利² 成义祥^{*,2}

(¹温州大学化学与材料工程学院,温州 325027)

(²南京大学化学化工学院,南京 210093)

摘要: 线性共轭高分子 **P-1** 是由单体 1,4-二溴-2,3-二正丁氧基萘(**M-2**)和 5,5'-二乙烯-2,2'-联吡啶(**M-3**)通过 Pd 催化 Heck 偶合反应合成得到,高分子配合物 **P-2** 和 **P-3** 由高分子 **P-1** 和 Eu(TTA)₃·2H₂O 和 Gd(TTA)₃·2H₂O 反应生成。高分子 **P-1** 能发射强蓝绿色荧光。高分子配合物 **P-2** 和 **P-3** 发光性能测试表明,含有 Eu(III)的高分子配合物 **P-2** 不仅显示高分子荧光,而且还显示了 Eu(III)(⁵D₀ → ⁷F₂)特征荧光,含 Gd(III)的高分子配合物 **P-3** 仅发射高分子的荧光,其荧光波长相对 **P-1** 而言,呈现 13 nm 红移。

关键词: 共轭高分子配合物; 2,2'-联吡啶; Eu(III)和 Gd(III); Heck 反应; 荧光

中图分类号: O614.33*8; O614.33*9

文献标识码: A

文章编号: 1001-4861(2008)05-0723-08

Fluorescent Properties on Conjugated Polymer Complexes Incorporating Eu(III) and Gd(III)

MIAO Qian^{*,1} ZHANG Shu-Wei² HUANG Xiao-Bo^{1,2}

CHENG Ya-Qian¹ ZONG Li-Li² CHENG Yi-Xiang^{*,2}

(¹College of Chemistry and Materials Engineering, Wenzhou University, Wenzhou, Zhejiang 325027)

(²School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093)

Abstract: Linear conjugated polymer **P-1** showing strong blue-green fluorescence was synthesized by the polymerization of 1,4-dibromo-2,3-bisbutoxynaphthalene (**M-2**) with 5,5'-divinyl-2,2'-bipyridine (**M-3**) via Heck reaction. The polymer complexes **P-2** and **P-3** were obtained by the bipyridyl coordination of **P-1** with Eu(TTA)₃·2H₂O and Gd (TTA)₃·2H₂O (TTA=2-thenoyltrifluoroacetate). Based on the fluorescent property of the polymer and RE(III)-containing polymer complex, Eu(III)-containing polymer complex **P-2** can not only emit the polymer fluorescence, but also has the characteristic fluorescence of Eu(III) (⁵D₀ → ⁷F₂) under different excited wavelengths. Gd(III)-containing polymer complex **P-3** only emits the polymer fluorescence, but fluorescence wavelength has a redshift of about 13 nm with respect to **P-1**.

Key words: conjugated polymer complex; 2,2'-bipyridine; Eu(III) and Gd(III); Heck reaction; fluorescence

The conjugated polymers based on π -conjugated organic molecules and high fluorescence quantum efficiencies attracted much attention in the past decade. Those polymers with tunable optical and electronic properties can be prepared by careful combination of the designed monomers^[1~3]. They can also be used to prepare organic light-emitting diodes, molecular sensors

and other devices with colors ranging from blue to red^[4~7]. But it is still difficult to obtain pure emission color from conjugated polymers due to their full width emission spectra at half-maximum of 50~200 nm^[8]. As known, lanthanide complexes, especially Eu(III) and Tb(III) complex, have pure monochromatic characteristic emission, extremely long PL lifetime, chemical enviro-

收稿日期:2007-10-25. 收修改稿日期:2008-03-30.

浙江自然科学基金(No.Y406068);国家自然科学基金(No.20474028 和 20774042)资助项目。

*通讯联系人。E-mail:mq0577@yahoo.com.cn;E-mail:yxcheng@nju.edu.cn

第一作者:缪 谦,女,36 岁,副教授;研究方向:功能材料合成与有机分析化学。

mental stability, and potentially high internal quantum efficiency. The introduction of RE(III) compounds has been demonstrated as a potential approach to improve the emission purity because RE(III) compounds can exhibit intense fluorescence with a narrow spectral bandwidth (10~20 nm)^[9-12]. On the other hand, it has been shown that the introduction of charge injection or transporting moiety into the ligand can improve the fluorescent performance. Therefore, the conjugated polymers incorporating Eu(III) or Tb(III) complex moieties can fabricate the excellent pure emission color device with respect to the desired mechanical flexibility, solubility in organic solvents, and convenient processability for electro-optic sensors^[13-15]. Bazan and co-workers^[9,16] reported the polymeric organic light-emitting diodes based on Eu(III) complexes. Eu(III) complexes with β -diketonate and phenanthroline were incorporated in the polymer matrix, poly[2-(6'-cyano-6"-methylheptyloxy)-1,4-phenylene]. The result indicated that the efficient energy transfer from the polymer to the Eu(III) complex resulted in complete quenching of the broad emission of the polymer, and a pure red, Eu(III)-based fluorescence was observed. Huang and Wang et al.^[10,17] reported a new class of main-chain-type RE-containing conjugated polymers with oxetane side groups crosslinked photochemically to produce insoluble polymer networks. RE(III) complexes were located in the main chain of the conjugated polymers. The resulting conjugated polymer exhibited quite different fluorescence properties in the dilute solution and solid film. Cao et al.^[12] also reported a convenient approach to the novel Eu(III)-grafting conjugated polymers to achieve sharp red emission for polymeric light emitting diodes (PLEDs). The results showed that efficient intramolecular Föster energy transfer depended on the overlap between the fluorescent spectrum of conjugated polymers and absorption spectrum of Eu(III) chelates, and the efficiency of energy transfer relied on the content of Eu(III) in the complexes.

1,10-phenanthroline (phen) and 2,2'-bipyridyl (bpy) have been used extensively as neutral metal chelating ligands in a variety of approaches dealing with structural coordination chemistry or functional

systems. These two kinds of ligands can show redox active behavior, luminescent properties, supramolecule-forming reactivity, and ease of functionalization^[9,18-21]. But so far, there have been no reports on the conjugated polymers incorporating 2,2'-bipyridyl moiety into the main-chain backbone to afford their corresponding polymer complexes with Eu(III) and Gd(III). In this paper, we describe fluorescent properties on the linear conjugated polymer **P-1** and Eu(III)- and Gd(III)-containing polymer complexes **P-2** and **P-3**. Based on fluorescent properties of the conjugated polymer and RE(III)-containing polymer complexes, **P-1** can emit strong blue-green fluorescence. **P-2** can show both the polymer fluorescence and the characteristic fluorescence of Eu(III) ($^5D_0 \rightarrow ^7F_2$). The relative fluorescence intensity of the conjugated polymer and Eu(III) complex moiety can be tuned by using the different excited wavelengths. Moreover, **P-3** can only show blue-green polymer fluorescence. The result shows that the fluorescence emission wavelength of **P-3** has an obvious redshift of 13 nm with respect to **P-1**.

1 Experimental

1.1 General

^1H , ^{13}C NMR spectra were recorded on a 300-Bruker spectrometer. Deuterated chloroform was used as NMR solvent and chemical shifts were reported as δ -values in parts per million relative to tetramethylsilane (TMS), J -values are in Hz. IR spectra were taken on a Nexus 870 FTIR spectrometer (400~4 000 cm^{-1}) with KBr pellets. UV-Vis spectra were obtained from a Perkin-Elmer Lambda 25 spectrometer. Thermogravimetric analyses (TGA) was preformed on a Perkin-Elmer Pyris-1 instrument under a N_2 atmosphere at a heating rate of 10 $^\circ\text{C} \cdot \text{min}^{-1}$. Fluorescent spectra were obtained from a 48000 DSCF spectrometer. Mass spectrometry (MS) was determined on a Micromass GCT in methanol solution. C, H, N and S of elemental analyses were performed on an Elementar Vario MICRO analyzer. Molecular weight was determined by gel permeation chromatography (GPC) with Waters-244 HPLC pump and tetrahydrofuran (THF) was used as an eluent, and polystyrenes were used as external

standards. Thenoyltrifluoroacetate (HTTA) was purchased from Sigma. All solvents and reagents were commercially available A.R. grade. All reactions were performed under a N_2 atmosphere using Schlenk techniques.

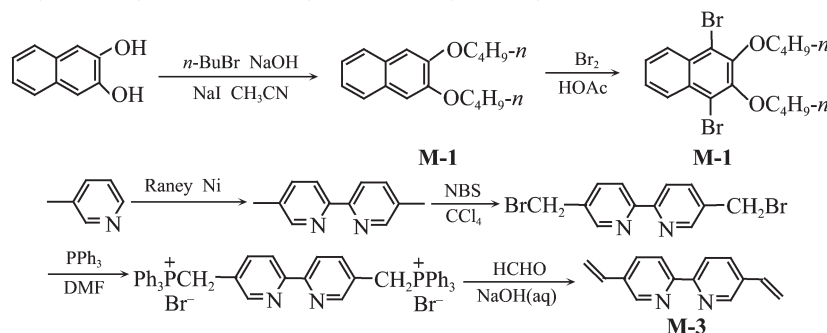
1.2 Preparation of monomers (M-1 and M-2)

$Eu(TTA)_3 \cdot 2H_2O$, $Gd(TTA)_3 \cdot 2H_2O$ and the repeating unit $Eu(TTA)_3 \cdot (M-3)$ were prepared and purified according to literature reports^[15,22].

The repeating unit 2,3-bisbutoxynaphthalene (**M-1**) and the monomer 1,4-dibromo-2,3-bisbutoxynaphthalene (**M-2**) were synthesized according to the literatures^[23,24], the overall yield of **M-2** was 90% (Scheme 1). 1H NMR: δ 8.25 (dd, $J=6.5, 3.3$ Hz, 2H), 7.56 (dd, $J=6.6, 3.2$ Hz, 2H), 4.15 (t, $J=6.6$ Hz, 4H), 1.85~1.94 (m, 4H), 1.56~1.67 (m, 4H), 1.04 (t, $J=7.3$ Hz, 6H); FTIR

(cm^{-1}): 3 057, 2 958, 2 934, 2 872, 1 577, 1 541, 1 454, 1 360, 1 336, 1 325, 1 117, 1 021, 961, 754.

5,5'-divinyl-2,2'-bipyridine (**M-3**) could be synthesized from 3-methylpyridine by a four-step reaction according to literatures (Scheme 1)^[7,15,25,26]. **M-3** needs to be kept in the dark at $-4^\circ C$ before using. MP: $56\sim58^\circ C$; 1H NMR: δ 8.68~8.69 (d, 2H, $J=1.9$ Hz), 8.37~8.39 (d, 2H, $J=8.3$ Hz), 7.87~7.91 (dd, 2H, $J=8.3, 2.2$ Hz), 6.74~6.83 (dd, 2H, $J=17.7, 11.0$ Hz), 5.89~5.95 (d, 2H, $J=17.6$ Hz), 5.42~5.46 (d, 2H, $J=11.0$ Hz). ^{13}C NMR ($CDCl_3$): δ 155.34, 148.17, 133.94, 133.67, 133.42, 121.85, 116.82. Anal. Calcd. for $C_{14}H_{12}N_2$: C, 80.74; H, 5.82; N, 13.45. Found: C, 80.76; H, 5.75; N, 13.37. FTIR (cm^{-1}): 3 002, 1 629, 1 589, 1 542, 1 468, 1 367, 1 250, 1 023, 911, 846, 750. MS (EI, m/z): 208 (M^+ , 100).



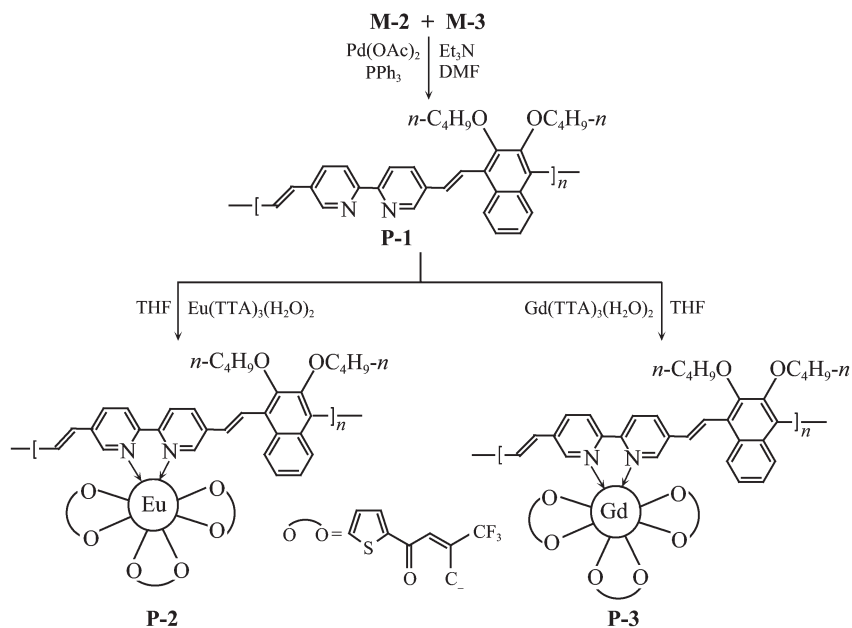
Scheme 1 Synthesis procedures for **M-1**, **M-2**, and **M-3**

1.3 Preparation of P-1, P-2 and P-3 (Scheme 2)

Preparation of **P-1**: A mixture of **M-2** (225 mg, 0.52 mmol) and **M-3** (109 mg, 0.52 mmol) was dissolved in the mixed solvent of DMF (6 mL) and Et_3N (0.8 mL). The solution was first degassed with N_2 for 15 min before 5mol% $Pd(OAc)_2$ (5.9 mg, 0.026 mmol) and 25mol% PPh_3 (34.3 mg, 0.13 mmol) were added to the above solution. The temperature of the mixture was kept at $120^\circ C$ for 12 h under N_2 . After the reaction mixture was refluxed at $140^\circ C$ for 2 h, styrene (10.4 mg, 0.10 mmol) was added for endcapping the polymer for an additional 2 h. The mixture was cooled to room temperature, and then was filtered through a short silica gel column, and the filtrate was dropped into methanol (50 mL) to precipitate out the crude polymer. The resulting polymer was filtered and washed with methanol several times. Further purification could be conducted by dissolving the polymer in CH_2Cl_2 and then

precipitating in methanol again. **P-1** was dried in vacuum to give 207 mg in 83.6% yield. 1H NMR: 8.89 (br, s, 2H), 8.53 (br, s, 2H), 8.27 (br, s, 2H), 8.12 (br, s, 2H), 7.73 (br, s, 2H), 7.54 (br, s, 2H), 7.37~7.28 (m, 2H), 4.19~4.06 (m, 4H), 1.81 (br, s, 4H), 1.61 (br, s, 4H), 1.08~0.95 (m, 6H). Anal. Calcd. for $C_{32}H_{32}N_2O_2$: C, 80.67; H, 6.72; N, 5.88. Found: C, 78.75; H, 6.57; N, 5.79. FTIR (cm^{-1}): 3 037, 3 005, 2 956, 2 870, 1 628, 1 589, 1 466, 1 421, 1 371, 1 269, 1 213, 1 021, 965, 755.

Preparation of **P-2**: A mixture of **P-1** (80.0 mg, 0.16 mmol) and $Eu(TTA)_3 \cdot 2H_2O$ (201 mg, 0.24 mmol) was dissolved in 15 mL of THF. The temperature of the solution was kept at $70^\circ C$ for 24 h under N_2 , and then the reaction mixture was cooled to room temperature. After removal of solvent, the residual solid was dissolved in 2 mL of CH_2Cl_2 , and the solution was dropped into 30 mL of methanol to precipitate out the crude red polymer complex **P-2**, which was washed with

Scheme 2 Synthesis procedures for **P-1**, **P-2**, and **P-3**

methanol several times. Further purification could be conducted by dissolving the polymer complex **P-2** in CH_2Cl_2 and then precipitating in methanol again. The resulting **P-2** was dried under vacuum to give 110 mg in 51.1% yield. Found: C, 56.41; H, 5.66; N, 3.16; S, 8.40; Eu, 10.52 (complexometric titration with EDTA). FTIR (cm^{-1}): 3 072, 3 039, 2 920, 2 849, 1 601, 1 538, 1 505, 1 467, 1 413, 1 308, 1 230, 1 187, 1 141, 1 061, 965, 787, 751, 581.

P-3 was synthesized by using the same way as **P-2**. Found: C, 49.73; H, 3.52; N, 2.63; S, 5.24; Gd, 11.05 (complexometric titration with EDTA). FTIR (cm^{-1}): 3 073, 3 038, 2 958, 2 933, 2 872, 1 602, 1 538, 1 504, 1 469, 1 412, 1 357, 1 308, 1 187, 1 141, 1 061, 965, 934, 859, 787, 717, 641, 581.

2 Results and discussion

2.1 Features of **P-1**, **Eu(III)**-/**Gd(III)**-containing polymer complexes **P-2** and **P-3**

Heck coupling reaction is one of the most important C-C coupling reactions in organic synthesis^[27,28]. Compared to the Wittig method, the Pd-catalyzed Heck polycondensation is relatively mild and gives an easy access to various monomers in the preparation of functionalized PPVs^[29-33]. In this paper, a typical Heck reaction condition was applied to the polymerization. The C-C cross coupling process was

easily carried out in DMF in the presence of a catalytic amount (5mol%) of $\text{Pd}(\text{OAc})_2$ with Et_3N and triphenylphosphine (PPh_3) under N_2 . The polymerization went on in a good yield (83.6%). GPC analysis results and yields of **P-1**, **P-2** and **P-3** are listed in Table 1. M_w of **P-1**, **P-2** and **P-3** was determined by gel permeation chromatography using polystyrene standard in THF . The molecular weights of **P-1**, **P-2** and **P-3** are normally smaller than the actual molecular weights of these polymers. The real molecular weight could be corrected by multiplying the measured values by a factor of approximately 1.4 to 2.5 and lies in the range from 4 500 to 8 200 (**P-1**), 4 980 to 8 900 (**P-2**) and 5 500 to 9 800 (**P-3**)^[34,35]. GPC analysis result of **P-1** indicates that an average degree of polymerization of the resulting linear conjugated polymer lies in the range from 10~17. The **Eu(III)**-/**Gd(III)**-containing polymer complexes **P-2** and **P-3** could be obtained by the bipyridyl units of **P-1** directly coor-dinating with $\text{Eu}(\text{TTA})_3$ and $\text{Gd}(\text{TTA})_3$. The resulting **P-2** and **P-3** can dissolve in CH_2Cl_2 , THF

Table 1 Polymerization results of **P-1**, **P-2**, and **P-3**

	Yield / %	M_w^a	M_n^a	PDI
P-1	83.6	3 280	1 780	1.84
P-2	51.1	3 560	1 990	1.79
P-3	41.7	3 920	1 850	2.11

^a M_w , M_n and PDI of **P-1**, **P-2**, and **P-3** were determined by gel permeation chromatography using polystyrene standard in THF .

and DMF, but they can be precipitated from methanol solution. Bipyridyl units in the main-chain backbone of **P-1** do not completely coordinate with RE (TTA)₃ according to their elemental analysis results and RE(III) content results in the polymer complexes **P-2** and **P-3**. Since elemental N is only in bipyridyl moiety and S is just included in RE (TTA)₃ moiety, the calculated molar ratios of S and N indicate that the **P-2** composition of **P-1** and Eu(TTA)₃ is 0.78 [8.40/(32.01×3): 3.16/(14.01×2)], and that of **P-3** is 0.84 [5.83/(32.01×3): 2.02/(14.01×2)]^[15].

In this paper, an electron-deficient heterocyclic ligand 5,5'-divinyl-bipyridine used as the conjugated molecular linker was introduced into the polymer backbone by Heck cross-coupling reaction. The electron transporting property within the main chain backbone may be improved. Furthermore, the polymer containing vinylene linkage between naphthyl and bipyridyl groups can reduce steric hindrance between backbone rings and groups, and can also have a beneficial effect on the corresponding polymer stability^[4,36,37]. 2,2'-bipyridine can orient in a well-defined spatial arrangement in the main chain backbone of the conjugated polymer **P-1**, and can act as a ligand by chelating coordination with Eu(TTA)₃·2H₂O and Gd(TTA)₃·2H₂O to afford the corresponding RE(III)-containing polymer complexes **P-2** and **P-3**.

2.2 Thermal analysis

P-1, **P-2** and **P-3** are air stable solid with red color and show good solubility in THF, CH₂Cl₂, CHCl₃ and DMF. Attachment of the flexible butoxy substituents on naphthyl rings as side chain of the polymer can not only modify the electronic property of the conjugated polymer, but can also dramatically improve solubility in organic solvents. The TGA plot of **P-1** is different with that of **P-2** and **P-3**. But the TGA plots of **P-2** and **P-3** are similar. According to Fig.1, **P-1** shows higher thermal stability than its corresponding polymer complexes **P-2** and **P-3**. Under a N₂ atmosphere, the obvious two-step degradation of **P-1** was observed, the first step is observed from 315 to 420 °C, and there is about 32% weight loss. The second step appears from 450 to 730 °C, and there is about 13% weight loss. Both

P-2 and **P-3** show three-step degradations. The first step shows a slow degradation process for **P-2** and **P-3** at temperature ranging from 160 to 310 °C, there are about 11% and 12% weight loss, respectively. It can be regarded as the coordination cleavage of RE(TTA)₃ with bipyridyl ligand. The second step appears a fast degradation from 330 to 420 °C, there are about 36% weight loss. The third step appears from 450 to 730 °C, and there is about 9% weight loss. The second and third degradation processes of **P-2** and **P-3** are similar with the polymer **P-1**. **P-1**, **P-2** and **P-3** tend to complete decomposition at 750 °C. There is a total loss of about 39.5%, 51.3% and 49.3% for **P-1**, **P-2** and **P-3** when heated to 800 °C.

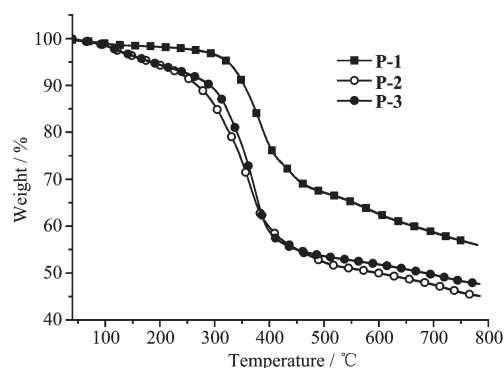


Fig.1 TGA curves of **P-1**, **P-2**, and **P-3**

2.3 Optical properties

Optical properties of the repeating unit 2,3-bisbutoxynaphthalene (**M-1**), **M-3**, Eu(TTA)₃·(**M-3**), and **P-1**, **P-2**, **P-3** in CH₂Cl₂ are summarized in Table 2. Fig.2 illustrates the UV-Vis absorption spectra of **M-1**, **M-3**, Eu(TTA)₃·(**M-3**), and **P-1**, **P-2**, **P-3**. According to Fig.2, UV-Vis spectra of **P-2** and **P-3** are similar due to the same repeating units of the chain backbone except the difference from coordination metal of Eu(III) and Gd(III). The strongest absorption wavelengths λ_{\max} of **M-1**, **M-3** and Eu(TTA)₃·(**M-3**) appear at 236, 321 and 341 nm. **P-1**, **P-2** and **P-3** UV-Vis absorption spectra display great red shifts. The absorption maxima λ_{\max} of **P-1**, **P-2** and **P-3** in CH₂Cl₂ appear at 394, 420 and 423 nm. **P-1** shows a broader absorption at the region from 340 to 430 nm. However, **P-2** and **P-3** show a stronger and broader absorption at the region from 310 to 475 nm. A large redshift in the electronic absorptions of **P-1**, **P-2** and **P-3** can be attributed to the effective π - π^*

conjugated segment of the linker unit **M-1** and 2,2'-bipyridyl group via vinylene bridge along the main-chain backbone^[15,25]. The strongest absorption peaks of **P-2** and **P-3** appear at about 338 nm, which can be regarded as the absorption of the repeating unit of $\text{Eu}(\text{TTA})_3 \cdot (\text{M-3})$ in the RE(III)-containing polymer backbone.

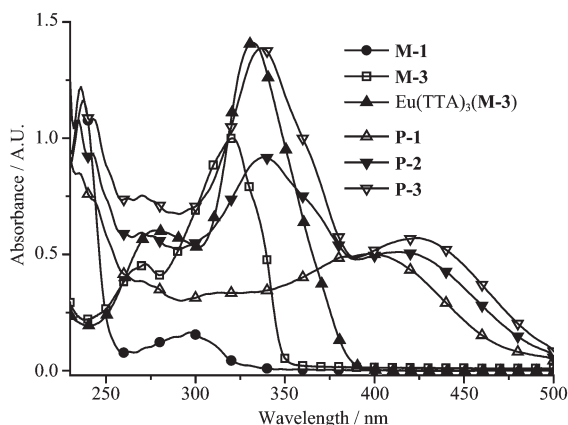


Fig.2 UV-Vis spectra of the repeating units and **P-1**, **P-2**, and **P-3**

Fluorescent spectra of **M-1**, **M-3**, $\text{Eu}(\text{TTA})_3 \cdot (\text{M-3})$, **P-1**, **P-2** and **P-3** in CH_2Cl_2 are shown in Fig.3. The polymer **P-1** can emit blue-green light under ultraviolet light (340 nm) or sunlight even in low concentration. **M-1** and **M-3** do not show fluorescence in the visible region. The maximum fluorescent wavelength $\lambda_{\text{max}}^{\text{F}}$ of **P-1** in CH_2Cl_2 solution is 521 nm. **P-1** shows strong blue-green fluorescence with higher fluorescence quantum efficiency ($\Phi_{\text{PL}}=0.27$) due to the conjugated structure between 2,3-bisbutoxynaphthyl group and the linker 2,2'-bipyridyl unit via vinylene bridge. Based on the fluorescent properties of the Eu(III)- and Gd(III)-containing polymer complexes **P-2** and **P-3**, it could be seen that **P-2** can not only emit the conjugated polymer fluorescence, but also show intense Eu(III)-centered characteristic fluorescence. Since $f-f$ transitions of Lanthanide(III) are forbidden, excitation usually relies on energy transfer from the host matrix or from the ligands surrounding the lanthanide ion (antenna effect). The triplet state energy level of β -diketonate anion ligand TTA^- is $20\,300\text{ cm}^{-1}$, and the resonance level of Eu(III) 5D_0 is $17\,200\text{ cm}^{-1}$. Eu(III) complex can have strong fluorescence due to the intramolecular energy transfer from electronic states associated with the anion ligand TTA^- to $4f$ energy states of Eu(III). The repeating unit

$\text{Eu}(\text{TTA})_3 \cdot (\text{M-3})$ has red fluorescence of Eu(III) electron dipole transition ($^5D_0 \rightarrow ^7F_2$) at 613 nm^[38,39]. However, the resonance level of Gd(III) $^6P_{7/2}$ is $32\,200\text{ cm}^{-1}$ ^[10,21,40,41]. The excitation energy could not be transferred from the ligand to the rare earth ion if the triplet state of the ligand was below the resonance level of the rare earth ion. Gd(III) has a stable electron structure with half-full in its outmost electronic shell, so **P-3** does not have characteristic emission color. As is evident from Fig.3 (b) and Table 2, the maximum fluorescent wavelength $\lambda_{\text{max}}^{\text{F}}$ of **P-3** appears at 534 nm, which can be regarded as the polymer fluorescence. But there is a redshift of about 13 nm with respect to **P-1**. It may be attributed to the intramolecular energy transfer from the anion ligand TTA^- to the π -extended conjugated polymer.

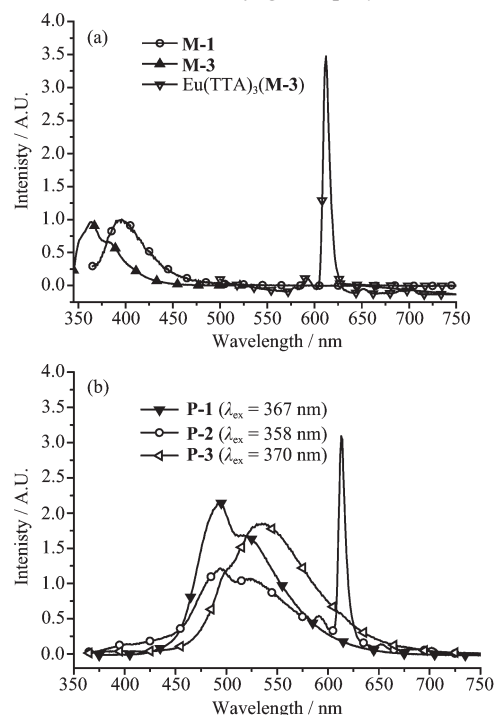


Fig.3 Fluorescent spectra of the repeating units (a) and **P-1**, **P-2**, **P-3** (b)

In order to investigate the energy transfer relationship between the polymer conjugated structure and fluorescent properties of Eu(III)-containing polymer complex **P-2**, we chose the different excited wavelengths from 320 to 390 nm. It is found **P-2** can not only emit the conjugated polymer fluorescence, but also has Eu(III)-centered characteristic fluorescence. The results indicate that the relative fluorescence intensity of **P-2** can be changed by using different excited

Table 2 Optical properties of the repeating units and **P-1**, **P-2**, and **P-3**

	UV-Vis (λ_{max}) ^a / nm	PL (λ_{max}) ^a / nm		Stokes shift ^b / nm	Φ_{PL} ^c
		λ_{ex}	λ_{em}		
M-1	236	352	394	—	—
M-3	272(w), 321	346	364	—	—
Eu(TTA) ₃ (M-3)	275(w), 341	388	591, 613	—	—
P-1	235, 394	367	494, 521	127	0.27
P-2	235, 338, 420	358	613, 494(w), 523(sh)	103	0.13
	—	399	494, 523	103	—
P-3	236, 337, 423	370	534	111	0.2

^a Determined in CH₂Cl₂ solution; ^b Stokes shift=PL λ_{max} (nm)-UV-Vis λ_{max} (nm); ^c These values were estimated by using the quinine sulfate solution ($1.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$) in $0.5 \text{ mol} \cdot \text{L}^{-1} \text{ H}_2\text{SO}_4$ ($\Phi_{\text{f}}=55\%$) as a standard.

wavelengths. According to Fig.4, **P-2** can emit strong fluorescence of the conjugated polymer at 494 and 521 nm, and very weak Eu(III) characteristic fluorescence ($^5D_0 \rightarrow ^7F_2$) at 613 nm if 390 nm is chosen as the excited wavelength. On the contrary, **P-2** appears weaker fluorescence of the polymer and Eu(III) ($^5D_0 \rightarrow ^7F_2$) under the excited wavelength at 320 nm. The intensities of Eu(III) characteristic fluorescence ($^5D_0 \rightarrow ^7F_2$) show the gradual increase as the change of the excited wavelength from 320 to 340 nm. **P-2** shows the strongest emission intensity of Eu(III) fluorescence ($^5D_0 \rightarrow ^7F_2$) under the excited wavelength at 340 nm which is the strongest absorption region of β -diketonate anion TTA⁻. The emission wavelength of the polymer moiety of **P-2** is similar with that of **P-1**, but the relative intensity shows the obvious change under the different excited wavelengths (Fig.4). It can also be concluded that the Eu(III) characteristic fluorescence of **P-2** is mainly arisen from the intramolecular energy transfer from the anion

ligand TTA⁻ coordinated with Eu(III). Furthermore, we can further draw a conclusion that the linear conjugated polymer does not transfer energy to Eu(III) complex and emits its own fluorescence. The results can provide an understanding of energy transfer relationship between the π -extended conjugated backbone of the polymer and fluorescent properties of the Eu(III)-containing polymer complexes. In addition, **P-2** also shows other weaker emission peaks assigned to the $^5D_0 \rightarrow ^7F_0$ (582 nm), $^5D_0 \rightarrow ^7F_1$ (593 nm), $^5D_0 \rightarrow ^7F_3$ (654 nm) and $^5D_0 \rightarrow ^7F_4$ (705 nm) transitions.

3 Conclusions

The Pd-catalyzed Heck reaction offers a simple access to the conjugated polymer. The polymer is air stable and shows good solubility in some organic solvents. **P-1** can emit strong blue-green fluorescence due to the extended π -electronic conjugated structure between the repeating 2,3-bisbutoxynaphthyl group and 2,2'-bipyridyl unit via vinylene bridge. **P-2** shows the strongest emission intensity of Eu(III) fluorescence and weaker polymer fluorescence if 340 nm is chosen as the excited wavelength. **P-3** only shows polymer fluorescence, but fluorescence wavelength has an obvious redshift of 13 nm with respect to **P-1**. Based on our study, it can be concluded that the Eu(III) characteristic fluorescence of **P-2** is mainly arisen from the intramolecular energy transfer from the anion ligand TTA⁻ coordinated with Eu(III). Furthermore, we can further draw a conclusion that the linear conjugated polymer does not transfer energy to Eu(III) complex and emits its own fluorescence. These kinds of polymer

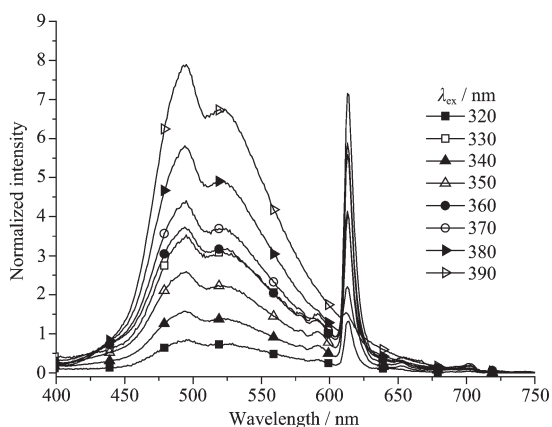


Fig.4 Fluorescent spectra of **P-2** under the different excited wavelengths

complexes incorporating bipyridyl and Eu(III) or Gd(III) moieties are expected to provide an understanding of the energy transfer relationship between the conjugated structure of the polymer and fluorescent properties of the RE(III)-containing polymer complexes.

References:

- [1] Yu W L, Meng H, Pei J, et al. *Macromolecules*, **1998**,**31**:4838~4844
- [2] Wang B, Wasielewski M R. *J. Am. Chem. Soc.*, **1997**,**119**:12~21
- [3] Peng Z H, Gharavi A R, Yu L P. *J. Am. Chem. Soc.*, **1997**,**119**:4622~4632
- [4] Hwang S W, Chen Y. *Macromolecules*, **2002**,**35**:5438~5443
- [5] Bredas J L, Beljonne D, Coropceanu V, et al. *Chem. Rev.*, **2004**,**104**:4971~5004
- [6] Zhan X W, Liu Y Q, Wu X, et al. *Macromolecules*, **2002**,**35**:2529~2537
- [7] Liu B, Yu W L, Pei J, et al. *Macromolecules*, **2001**,**34**:7932~7940
- [8] Kido J, Okamoto Y. *Chem. Rev.*, **2002**,**102**:2357~2368
- [9] McGehee M D, Bergstedt T, Zhang C, et al. *Adv. Mater.*, **1999**,**11**:1349~1354
- [10] Wen G A, Zhu X R, Wang L H, et al. *J. Polym. Sci.: Part A: Polym. Chem.*, **2007**,**45**:388~394
- [11] Wang J F, Wang R Y, Yang J, et al. *J. Am. Chem. Soc.*, **2001**,**123**:6179~6180
- [12] Pei J, Liu X L, Cao Y, et al. *Macromolecules*, **2002**,**35**:7274~7280
- [13] Gao X C, Cao H, Huang C H, et al. *Appl. Phys. Lett.*, **1998**,**72**:2217~2219
- [14] Dirr S, Wiese S, Johannes H H, et al. *Synth. Met.*, **1997**,**91**:53~56
- [15] Cheng Y X, Zou X W, Zhu D, et al. *J. Polym. Sci. A: Polym. Chem.*, **2007**,**45**:650~660
- [16] Robinson M R, O'Regan M B, Bazan G C. *Chem. Commun.*, **2000**:1645~1646
- [17] Wang L H, Wang W, Zhang W G, et al. *Chem. Mater.*, **2000**,**12**:2212~2218
- [18] Kokil A, Yao P, Weder C. *Macromolecules*, **2005**,**38**:3800~3807
- [19] Kimura M, Horai T, Hanabusa K, et al. *Adv. Mater.*, **1998**,**10**:459~462
- [20] Murphy C B, Zhang Y, Troxler T, et al. *J. Phys. Chem. B*, **2004**,**108**:1537~1543
- [21] Yasuda T, Yamaguchi I, Yamamoyo T. *Adv. Mater.*, **2003**,**15**:293~296
- [22] Charles R G, Ohlmann R C. *J. Inorg. Nucl. Chem.*, **1965**,**27**:255~259
- [23] SONG Jin-Feng(宋金峰), ZOU Xiao-Wei(邹小伟), CHENG Yi-Xiang(成义祥), et al. *Acta Polimerica Sinica(Gaofenzi Xuebao)*, **2006**,**8**:1007~1012
- [24] Lau K, Foster J, Williams V. *Chem. Comm.*, **2003**,**17**:2172~2173
- [25] Liu Y, Zhang S W, Miao Q, et al. *Macromolecules*, **2007**,**40**:4839~4847
- [26] Ebmeyer F, Vogtle F. *Chem. Ber.*, **1989**,**122**:1725~1727
- [27] Heck R F, Nolleyjr J P. *J. Org. Chem.*, **1972**,**37**:2320~2325
- [28] Heck R F. *Acc. Chem. Res.*, **1979**,**12**:146~151
- [29] Meijere A D, Meyer F E. *Angew. Chem. Int. Ed. Engl.*, **1994**,**33**:2379~2411
- [30] Scherf U, Mullen K. *Synthesis*, **1992**,**1**:23~38
- [31] Cheng Y X, Liu T D, Chen L W. *Chin. J. Polym. Sci.*, **2004**,**22**:327~331
- [32] Cheng Y X, Chen L W, Song J F, et al. *Polym. J.*, **2005**,**17**:355~362
- [33] You W, Wang L M, Wang Q, et al. *Macromolecules*, **2002**,**35**:4636~4645
- [34] Pautzsch T, Klemm E. *Macromolecules*, **2002**,**35**:1569~1575
- [35] CHEN Ling-Wu(陈令武), CHENG Yi-Xiang(成义祥), SONG Jin-Feng(宋金峰), et al. *Chem. J. Chinese Univ. (Gaodeng Xuexiao Huaxue Xuebao)*, **2005**,**26**:1747~1751
- [36] Song J F, Cheng Y X, Chen L W, et al. *Euro. Polym. J.*, **2006**,**42**:663~674
- [37] Pan M, Bao Z N, Yu L P. *Macromolecules*, **1995**,**28**:5151~5153
- [38] CHENG Yi-Xiang(成义祥), WANG Yun-Chu(王韵初), TAO Zhong-Dong(陶中东), et al. *Chinese J. Inorg. Chem. (Wuji Huaxue Xuebao)*, **2000**,**16**:523~526
- [39] CHENG Yi-Xiang(成义祥), XU Duan-Jun(徐端钧), XU Yuan-Zhi(徐元植). *Chinese J. Inorg. Chem. (Wuji Huaxue Xuebao)*, **1998**,**14**:181~184
- [40] Sato S, Wada M. *Bull. Chem. Soc. Jpn.*, **1970**,**43**:1955~1962
- [41] Wong K S, Sun T, Liu X L, et al. *Thin Solid Films*, **2002**,**417**:85~89