

FLUORENE-BASED LIGHT-EMITTING POLYMERS

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Abstract Several series of fluorene-based light-emitting polymers with the emphasis on achieving efficient and stable blue light emission are reported. Spiro-functionalization may narrow the emission spectra (with smaller tail at longer wavelengths) of fluorene homopolymers to provide purer blue emission. The thermal spectral stability of the polymers could also be improved because of the elevation of the glass transition temperature caused by the spiro-functionalization. However, the excimer emission in fluorene homopolymers is not suppressed by the spiro-functionalization. Alternate copolymers of 9,9-dihexylfluorene and substituted phenylenes may emit efficient blue light both in solution and in film. The optical properties are dependent on the substitution on the phenylene ring. The alkoxy-substituted polymers displayed efficient PL and EL and good thermal spectral stability. The HOMO and LUMO energy levels of the polymers based on the backbone structure could be tuned in a wide range by attaching different functional groups on the phenylene ring. By attaching europium(III) complex at the ends of the side chains in the alternate copolymers, we have demonstrated a new approach to achieving red emission with a very narrow spectrum. The copolymers of 9,9-dihexylfluorene and thiophene and bithiophene with different substitutions were also synthesized to study the effect of substitution and regioregularity on the optical and other physical properties of the polymers.

Keywords Conjugated polymers, Light-emitting polymers, Polymer light-emitting diodes, Fluorene, Polyfluorene, Spiro-polyfluorene

INTRODUCTION

Since the publication of the first report on electroluminescence with a conjugated polymer in 1990^[1], considerable efforts have been devoted to the development of polymer light-emitting diodes (PLEDs) as a new display technology. Numerous conjugated polymers have been designed and synthesized as light-emitting materials in the last decade. The most popular chemical structures include poly(*para*-phenylene vinylene) and its derivatives (PPVs), substituted polythiophenes (PTs), poly(*para*-phenylene) and its derivatives (PPPs), and substituted polyfluorenes (PFs) (Fig. 1). Aiming to commercialize PLED, more efforts have recently been concentrated on two series of polymers, PPVs and PFs. As the first example of electroluminescent polymer, PPV and its derivatives still occupy an important position in the commercialisation of PLED. However, PPV based materials also suffer from some structure-related problems. For instance, the vinylene bonds are susceptible to photo-oxidation and thus cause the devices to be unstable. Most of the useful PPV-based materials are synthesized through the Gilch route. So far, no one has found an effective approach to completely avoid the structure defects arising from the irregular dehydrohalogenation in the Gilch reaction^[2]. The existence of structural defects is unhelpful for pursuing long lifetime of devices. In addition, it is difficult to realize efficient blue light emission, one of the three primary colors for fulfilling full color displays, with PPV backbone.

9,9-Disubstituted polyfluorenes were first synthesized as blue light-emitting materials^[3]. Initially, the polymers were synthesized through the approach of FeCl₃-oxidation, in which irregular coupling may be

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involved. Later, nickel-catalyzed polymerization of arene dihalides and Suzuki's coupling reaction between aryl bromide and aryl boronate were used to synthesize PFs^[4, 5]. Both synthetic methods provide regioregular polymerization through 2 and 7 positions of the fluorene ring and high molecular weight products. The defined structures involve no structural defects, and even the end groups can be carefully capped. These homopolymers display efficient blue photoluminescence and electroluminescence and have good chemical and photo-stability. Furthermore, the copolymerization of substituted fluorene units with other aromatic units produces a series of novel light-emitting polymers^[6]. These copolymers have emission spectra spanning the whole visible range, including the three primary colors. The PLED devices fabricated from some of these copolymers have high EL efficiency and commercially acceptable lifetime at the brightness level of monitors. Fluorene-based polymers have received increasing attention in the development of PLEDs, especially in the effort to commercialize PLED.

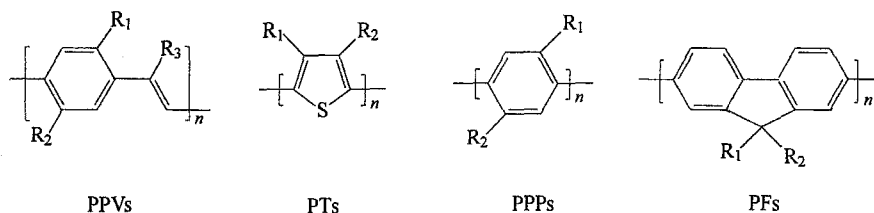


Fig. 1 Chemical structures of some light-emitting polymers

The development of efficient and stable blue light-emitting polymers is of particular interest, because there is a great demand for these commercially acceptable polymers. To date, fluorene-based polymers are the most popular candidates for blue PLEDs. However, the lifetime of the devices based on the PFs are still far from commercially satisfactory. Although the fluorene homopolymers exhibit high PL quantum efficiency (> 40%) and moderate level of EL efficiency (≈ 2 cd/A) together with good chemical stability and photostability, the polymers have a high tendency to aggregate in film form. The aggregation induces excimer formation, which results in the red shift of emission spectra and significant decrease of emission efficiency. Incorporation of a small amount of anthracene into the backbone of PF can effectively suppress the excimer emission^[7], but there is no report concerning the lifetime of the devices based on the modified polyfluorenes. It is also argued that the difficulty of hole injection and transfer because of the very low HOMO (highest occupied molecular orbital) level (generally around 5.5 eV below the vacuum level) is also responsible for the relatively poor device performance of the polymers. On the other hand, from the viewpoint of chemistry, the backbone structure of PF has little freedom to tune the electronic properties by chemical modification. The only available position for easily attaching different functional groups to the fluorene unit is the C-9 position, which does not affect the electronic properties of the resulting polymers. Some of our efforts aim to find solutions for the above mentioned problems in PFs.

SPIRO-FUNCTIONALIZED POLYFLUORENES

Spiro-annulated molecules make use of their spiro-bridge to connect two conjugated moieties. The tetrahedral bonding atom at the center of a spiro-annulated molecule maintains a angle of 90° between the connected conjugated moieties via the σ -bonded network. This structural feature minimizes the close packing of spiro-annulated molecules in the solid state. A series of spiro-annulated molecules based on 9,9'-spirobifluorene have been synthesized. Thin films of the materials were demonstrated to be completely amorphous with a high glass transition temperature (*T_g*) and good optical properties^[8]. Our objective is to enhance the amorphous morphology of the polymers in the film states and thus to improve the optical properties by introducing the 9,9'-spirobifluorene structure into the backbone of conventional polyfluorene.

The chemical structures of the spiro-functionalized polyfluorenes are depicted in Fig. 2. The backbone structure is still polyfluorene, but at the C-9 position of every other repeat fluorene unit, the two alkyl chains are replaced by a fluorene ring, which is connected to the backbone through the spiro-bridge. The polymers are

synthesized through Suzuki's coupling reaction between a 9,9-dialkylfluorene-2,7-bis(trimethylene boronate) and 2,7-dibromo-9,9'-spirobifluorene. In order to ensure their solubility in organic solvents, the attached alkyl groups should be long enough. For example, when the alkyl group is *n*-hexyl, the resulting polymer has very poor solubility in THF and chloroform, and can only be dissolved in hot chlorobenzene. When the alkyl is lengthened to *n*-octyl, the resulting polymer, poly[(9,9-di-*n*-octyl-fluorene-2,7-diyl)-*alt-co*-(9,9'-spirobifluorene-2,7-diyl)] (**P1**) becomes partially soluble in THF and chloroform and can be completely dissolved in chlorobenzene. Uniform and pinhole-free films can be prepared by spin-casting the chlorobenzene solution.

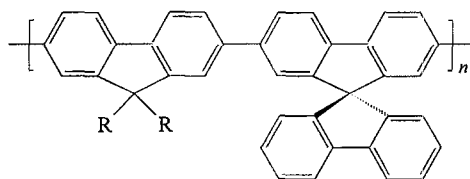


Fig. 2 Chemical structure of spiro-functionalized polyfluorenes

The UV-Vis absorption and PL spectra of **P1** film (cast on quartz plate) are displayed in Fig. 3. The corresponding spectra of a conventional polyfluorene, poly(9,9-di-*n*-hexylfluorene-2,7-diyl) (**P2**), are also placed in Fig. 3 for comparison. The absorption spectrum of **P1** is featureless and coincides with that of **P2** with the onset of absorption at 430 nm (2.88 eV) and the absorption peak at 379 nm. These results indicate that the spiro-functionalization does not change the electronic structure of the backbone. However, their PL spectra are noticeably different. **P2** exhibits strong vibronic structures (sub-peak at 428 nm and shoulder peaks at 480 and 520 nm), a broad spectrum, and a long tail extended to longer wavelength region in the PL spectrum. In comparison with **P2**, **P1** displays very weak vibronic structures, a narrower spectrum, and a shorter tail to the longer wavelength region in the PL spectrum, indicating that **P1** produces purer blue emission. The purer blue emission of **P1** as compared with **P2** is ascribed to the improved amorphous structure and to the weaker interchain interaction of polymer in solid states as a result of the steric hindrance of the spiro-structure. The absolute PL quantum efficiency of the polymer in neat film was measured in an integrating sphere to be $45\% \pm 3\%$.

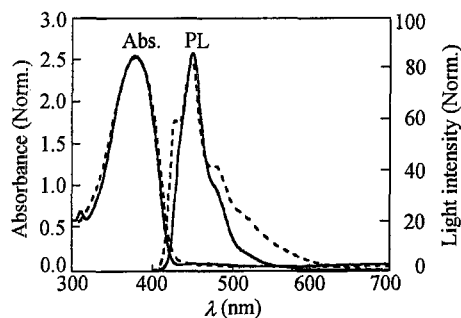


Fig. 3 UV-visible and PL spectra of **P1** (solid lines) and **P2** (dotted lines) in film states

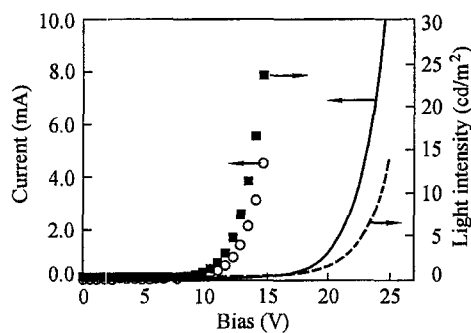


Fig. 4 The current (*I*)-voltage (*V*) and brightness (*L*)-voltage (*V*) curves of the devices prepared from ITO/**P1**/Ca (solid and dotted lines) and ITO/CuPc/**P1**/Ca (circle and square)

The blue electroluminescence of **P1** was demonstrated with the single-layered, ITO/**P1**/Ca, and double-layered, ITO/CuPc/**P1**/Ca EL cells. The current-voltage (*I-V*) and light output-voltage (*L-V*) characteristics of the devices are given in Fig. 4. The maximum external EL quantum efficiency measured from the single-layered device is 0.12%. After the addition of copper phthalocyanine (CuPc), the turn-on voltage was lowered from

≈ 15 V to less than 10 V, and the external EL quantum efficiency was increased to 0.54%. The EL spectra exhibited by the devices are identical to the PL spectrum.

To investigate the thermal spectral stability of the polymers, the films spin-cast on quartz plates were annealed at different temperatures for 2 h. After the films cooled down to room temperature, their absorption and PL spectra were recorded. The results are shown in Fig. 5. When the film of **P2** was annealed below its T_g (80 °C), both the absorption and PL spectra remained unchanged. When the polymer film was heated at temperatures above the T_g (i.e. 100 and 150 °C), a strong additional emission band appeared in the PL spectrum, but the absorption spectra did not exhibit a corresponding change. The appearance of such an additional emission band upon heating is a common phenomenon for fluorene-based polymers and has been attributed to the excimer emission. For the films of **P1**, the PL spectra remained unchanged up to a temperature of 100 °C, just below its T_g (105 °C). When the heating temperature was raised to 150 °C, an additional emission band appeared between 500 and 600 nm similar to the observation on **P2** films. After the **P1** film was annealed at 200 °C, the additional emission band became more pronounced. It is evident, that the formation of the additional emission peak upon heating may be related to the T_g of polymers. When the polymer films are heated above T_g , the polymer chains can rearrange (by diffusion), resulting in closer packing.

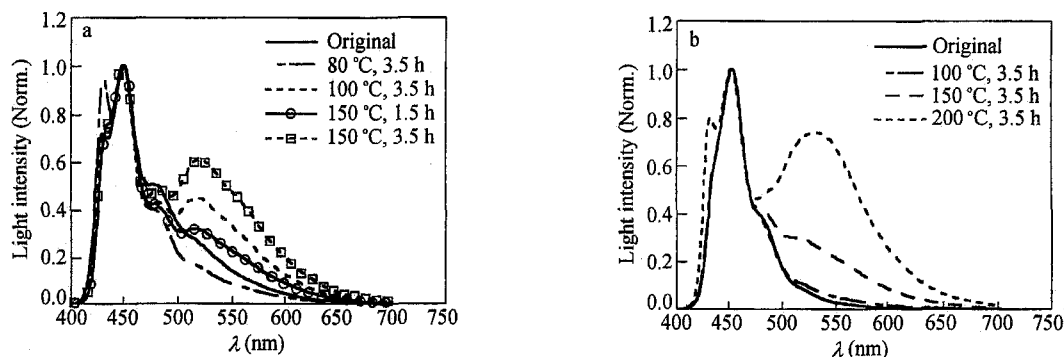


Fig. 5 PL spectra of annealed films of **P2** (a) and **P1** (b)

The results in Fig. 5 also indicate that the spiro-functionalization does not solve the problem of excimer emission in PFs. This is probably associated with the good co-planarity of the polyfluorene backbone^[9], which favors the cofacial close packaging between polymer main chains. In order to examine our assumption, we investigated the thermal spectral stability of a substituted poly(*para*-phenylene) (PPP), poly[(2-(6'-cyano-6'-methyl-heptyloxy)-1,4-phenylene)] (CN-PPP). In substituted PPP, the adjacent phenylene rings are highly twisted (with the twist angles up to 45°)^[10]. The poor co-planar feature will minimize the tendency to form close cofacial packaging between polymer chains, and thus better thermal spectral stability could be expected. Indeed, we found that the PL spectrum of CN-PPP could be stable up to 200 °C. This finding encouraged us to modify the PF backbone with phenylene units.

ALTERNATED COPOLYMERS WITH SUBSTITUTED PHENYLENES

We modified the backbone of PF by alternately inserting substituted phenylene units. The chemical structures and the molecular weights as well as the optical parameters of the copolymers with different substituents are summarized in Table 1. When the substituents are hydrogen and alkoxy groups (**P3**–**P6** as shown in Table 1), the resulting polymers emit pure deep blue PL and EL with high quantum efficiencies (> 40% for PL and > 0.5% for EL)^[11]. We noted that **P3** shows strong and well-defined vibronic structures in the PL spectrum. When methoxy groups are attached to the 2- and 5-position of the phenylene ring (**P4**), the vibronic structures are dramatically reduced. With the increase of length of the alkoxy side chains, the vibronic structures are further weakened. For **P6**, the PL spectrum is almost featureless. Correspondingly, the full width at half maximum (FWHM) of the fluorescence spectrum is also decreased from 62 nm for **P3** to 46 nm for **P6** (see the last column in Table 1).

Thus, long alkoxy side chains enhance the amorphism of the resulting polymers in solid states.

Table 1. Chemical structures, molecular weights, and optical properties (in film form) of substituted fluorene and phenylene alternate copolymers

Polymers	M_n^a ($\times 10^{-3}$)	λ_{abs}^b (nm)	E_{BG}^c (eV)	λ_{em}^b (nm)	$\Delta\lambda^d$ (nm)
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$R_1 = R_2 = H$	P3	11.8 (1.70)	371	2.92	442	62
$R_1 = R_2 = OCH_3$	P4	27.7 (1.78)	373	2.95	425	52
$R_1 = R_2 = OC_6H_{13}$	P5	50.5 (2.00)	372	2.94	426	49
$R_1 = R_2 = OC_{10}H_{21}$	P6	41.4 (2.08)	373	2.94	424	46
$R_1 = R_2 = C_6H_{13}$	P7	9.4 (1.54)	324	3.32	404	58
$R_1 = H, R_2 = CN$	P8	22.8 (1.52)	370	2.93	424	48
$R_1 = R_2 = COOEt$	P9	48.1 (1.91)	351	3.04	443	69

^a Numerical values in parentheses are the polydispersity indexes (M_w/M_n)

^b Main peak wavelengths in absorption (λ_{abs}) and fluorescence (λ_{em}) spectra

^c Band gap energy is obtained from the onset wavelengths in absorption spectra

^d Full width at half maximum (FWHM) in fluorescence spectra

Polymers **P4–P6** all exhibit much better thermal spectral stability than **P2** and **P1**, because their absorption spectra and the PL spectra are stable up to 150°C. In DSC heating scans, the samples were quenched from 250°C before scanning. As shown in Fig. 6, **P5** exhibited a clear crystallization exothermal peak at 123°C and a melting endothermal peak at 137°C. Similarly, **P6** showed a sharp crystallization exothermal peak at 66°C and a melting endothermal peak at 148°C. This means the spectra of the polymers are stable even above their melting temperatures. Interestingly, it was found that the PL efficiency of the polymer films could be remarkably enhanced by the annealing treatment. For example, after being annealed at 100°C (in N₂), the PL efficiency of the spin-cast **P5** film was increased by 14%. When the film was annealed at 170°C, the increment of PL efficiency was about 50%. This finding is interesting for the application in polymer LEDs, in which high PL efficiency of the light-emitting polymers is always pursued. It is believed that the phenomenon is associated with the formation of ordered structures in the film. We have demonstrated that **P5** and **P6** have a pronounced tendency to crystallize. The crystal structures in the drop-cast films of the polymers have been carefully studied. The results will be published elsewhere. When the annealed films of **P5** and **P6** were examined under a polarized light microscope, clear birefringence images were observed. This is an indication of thermotropic liquid crystalline states. The polarized light microscopy (PLM) image of **P6** is shown in Fig. 7. Further study of the ordered structures to understand the relationship between the ordered structures and the optical properties is ongoing in our lab.

The backbone of poly(fluorene-*alt-co*-phenylene) has another advantage over the backbone of PF because the protons at the 2- and 5-positions of phenylene ring can be easily substituted by various functional groups so that the electronic properties of the resulting polymers can be tuned. When the 2- and 5-positions are substituted by alkyl groups (**P7**), the band gap is extended to 3.32 eV due to the steric effect, which results in an obvious spectral blue shift as compared with **P3–P6**. When strong electron-withdrawing groups, such as cyano (**P8**) and ester (**P9**) groups, are attached to the phenylene ring, the resulting polymers are still blue emissive (the band gap energies are close to those of **P3–P6**, see Table 1). However, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels of the polymers are tuned in a wide range because of the different substitutions, as demonstrated by cyclic voltammetry (CV). The cyclic voltammograms of **P3**, **P5**, **P7–P9** are displayed in Fig. 8. The oxidation and reduction peaks of **P5** locate at 1.18 and -2.70 V (versus SCE),

respectively. For **P9**, an ester-substituted polymer, the oxidation and reduction peak potentials are 1.42 and -1.92 V, indicating **P9** is much easier to reduce but more difficult to oxidize than **P5**. The oxidation and reduction onset potentials of **P5** were determined to be 0.96 and -1.97 V, from which the HOMO and LUMO energy levels of **P5** can be estimated to be -5.36 eV and -2.43 eV, respectively. The HOMO and LUMO of **P9** were determined to be -5.72 and -2.78 eV. The controllable adjustment for HOMO and LUMO energy levels is especially useful for developing efficient blue EL polymers, because hole-injection is normally a limiting factor in fluorene-based blue light-emitting polymers. However, the attachment of strong electron-withdrawing groups, such as cyano and ester groups, seems to be a wrong approach for enhancing hole injection in the resulting polymers. Our other efforts were devoted to the triphenyl-modified polymers.

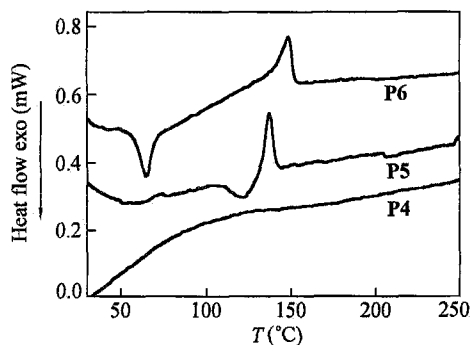


Fig. 6 DSC traces of polymers **P4–P6**

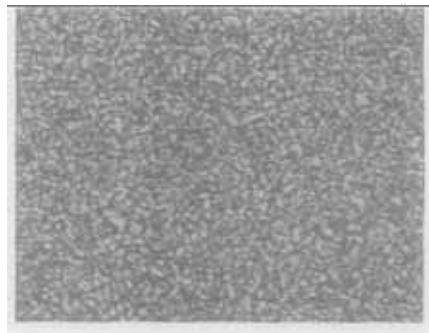


Fig. 7 Polarized microscopic image recorded from the annealed (170°C) **P6** film

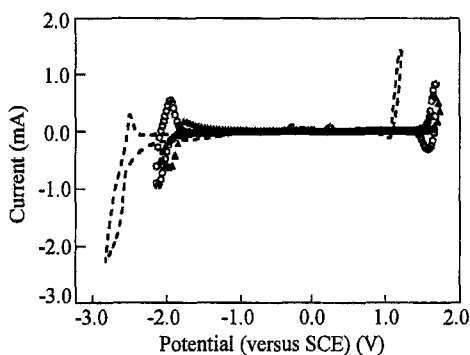


Fig. 8 Cyclic voltammograms of **P5** (dotted line), **P8** (circle), and **P9** (triangle) in film form on Pt electrode in CH_3CN solution of Bu_4NClO_4 (0.1 mol) at a scan rate of 50 mV/s

One example (**P10**) of the triphenyl-containing fluorene-based polymers is shown in Fig. 9. This polymer exhibits a similar PL spectrum in film states with CN-PPP (Fig. 9). The cyclic voltammogram of **P10** is compared with that of **P6** in Fig. 10. The oxidation onset potential was determined to be 0.72 V, about 0.4 V lower than that of **P6**. From the oxidation onset potential, the HOMO level of **P10** could be estimated to be -5.1 eV, a value that could be expected to provide good hole-injection.

A NEW APPROACH TO ACHIEVING PURE RED EMISSION

With respect to the three primary emission colors, red is the most difficult one to be achieved for polymer LEDs, because the emission spectra of the conjugated polymers are normally broad and the visual activity of human eyes is much more sensitive to orange than to red. Currently, pure red emission from PLEDs is obtained by

filtering out the orange component from the emission or by using polymers whose emission starts at the red end and extends to the infrared region. However, such LEDs are inefficient because only part of the emission is usable. It is well known that rare earth ions have very sharp emission spectra and can give pure color emission. Rare earth complexes obtained by chelating with suitable organic ligands are an important class of light emission and laser materials. A number of rare earth *beta*-diketonate complexes, such as *tris*(2,4-pentanediono)-1,10-phenanthroline terbium(III) and *tris*[4,4,4-trifluoro-1-(2-thienyl)-1,3-butanidiono]-1,10-phenanthroline europium(III), have been used successfully as emitting materials to provide pure green ($\lambda_{\text{max}} = 545 \text{ nm}$) and red emissions ($\lambda_{\text{max}} = 615 \text{ nm}$) in organic light-emitting diodes (OLEDs)^[12]. Recently, Heeger's group obtained efficient pure red electroluminescence by blending a blue light-emitting polymer, CN-PPP, with europium(III) *beta*-diketonate complexes^[13]. The blending system works through a Förster energy transfer: the blue polymer is first electrically pumped and emits blue light which is then absorbed by the complex to give the emissive light characterized by the europium(III) ion. The blending approach, however, has inherent problems of inhomogeneity of the rare earth complexes in polymer matrix, aggregation of rare earth complexes, and phase separation. A would-be ideal material as inspired by this idea would be a one-component material. We report here an approach of chemically grafting the rare earth onto the side chains of suitable blue light-emitting polymers.

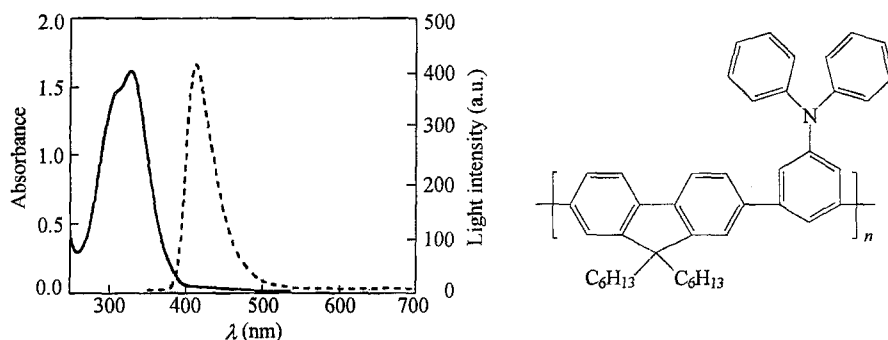


Fig. 9 Chemical structure and UV-visible absorption and PL spectra of P10 in film form

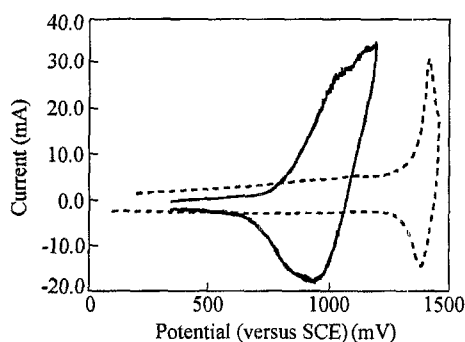


Fig. 10 Cyclic voltammograms of P6 (dotted line), P10 (solid line) in film form on Pt electrode in CH_3CH solution of Bu_4NClO_4 (0.1 mol/L) at a scan of 40 mV/s

The newly designed and synthesized polymers are exemplified in Fig. 11. The europium(III) complexes are chemically attached to the ends of side chains of a blue polymer, an alternate copolymer of fluorene-and-phenylene. Through such a chemical grafting, the europium complexes are dispersed in the blue polymer on a molecular level. The aggregation and phase separation tendency could be minimized. The grafted copolymers are soluble in common organic solvents, such as THF, chloroform, toluene, and xylenes. From their solutions,

uniform and transparent films could be spin-cast on various substrates. Figure 12 illustrates the UV-Vis absorption and PL spectra of the two exemplified polymers in film states. Their absorption spectra are the same and are characterized by the blue polymer. The PL spectrum of the polymer **P11** is still dominated by the blue emission from the backbone of the polymer although there is a component in the red region (≈ 615 nm) which comes from the emission of the europium ion. For the polymer **P12**, the blue emission derived from the polymer backbone almost completely disappears and the PL spectrum is characterized by the europium ion, centered at 615 nm with the FWHM of ≈ 10 nm. We presume that the light-emitting mechanism of the grafting copolymer is the same as that of the blends of blue polymers and europium complexes. The *beta*-diketonate ligand absorbs the light derived from the backbone of the polymer and undergoes intersystem crossing into a triplet state, and then transfers its energy to the europium ion. In order to transfer energy from a conjugated polymer to the ligands of a europium complex by Förster energy transfer (dipole coupling), the emission spectrum of the polymer must overlap with the absorption spectrum of the ligand. The overlap between the emission spectrum of blue polymer without the graft of the europium complexes and the absorption of the ligand TTA (**P11**) is very small. This results in an inefficient energy transfer from the polymer backbone to the ligand. However, a good spectral overlap exists between the backbone polymer and the ligand DBM (**P12**). This gives an almost complete energy transfer and achieves a pure red emission. The red electroluminescence with the EL spectrum being identical to the PL spectrum has been demonstrated by the polymer **P12**.

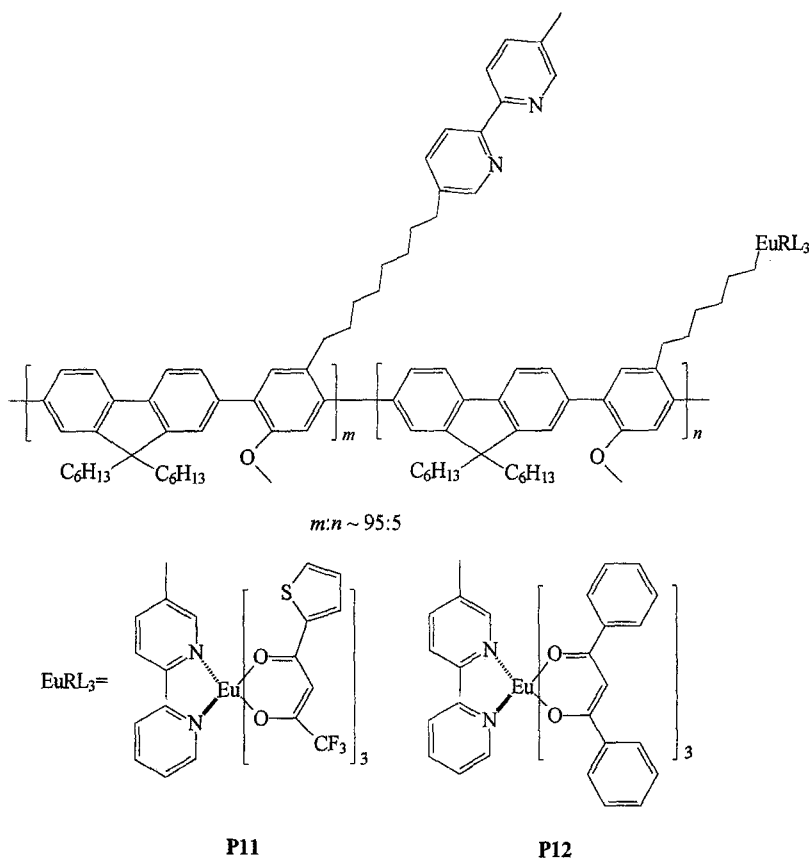


Fig. 11 Chemical structures of the polymers grafted with europium (III) complexes

ALTERNATE COPOLYMER OF THIOPHENES

Previously, we have demonstrated that the alternate copolymer of 9,9-dihexylfluorene and bithiophene is an

efficient PL and EL material^[13]. Recently, a Bell labs group disclosed that the oligomer of fluorene and bithiophene shows much better photostability over other organic semiconducting materials. One of the most striking features of thiophene-containing polymers is the extended electronic tunability through side chain modification. Moreover, different structural regularities arising from side chain substitution on thiophene ring offer additional opportunities for tuning electronic properties by controlling the coupling configurations. Understanding the effects of the substitution and the regioregularity on the electronic properties is essential for developing efficient and stable light-emitting materials using the backbone structures. For this purpose, we have designed and synthesized four polymers with the structures shown in Fig. 13.

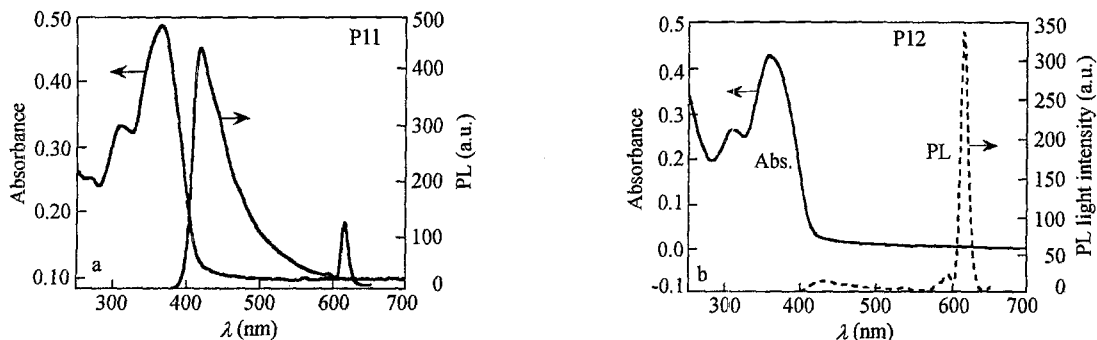


Fig. 12 UV-Vis absorption and PL spectra of **P11** and **P12** in film form

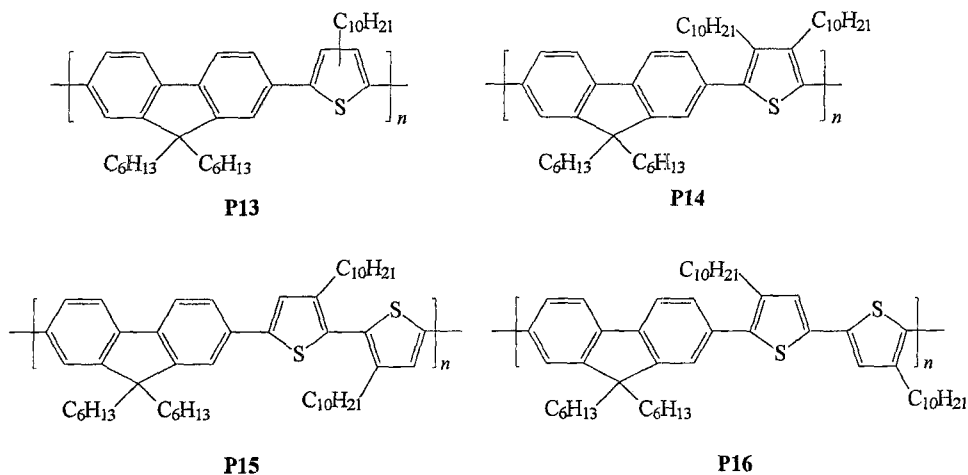


Fig. 13 Chemical structures of the fluorene-thiophene copolymers

All these polymers were synthesized through Suzuki's coupling reaction. The molecular weights, glass transition temperatures (T_g), and the optical properties of the polymers are summarized in Table 2. The copolymer of the mono-substituted thiophene (**P13**) emits green light both in solution and in film states. Its PL efficiency is very high, 65% in solution and 40% in film. When the thiophene ring is di-substituted (**P14**), the emission is shifted to the blue region, but the PL efficiency of the polymer is obviously decreased. For the copolymers of substituted bithiophenes, there are two manners of connecting the two substituted thiophene rings — head-to-head (**P15**) and tail-to-tail (**P16**) — to provide different regioregularities. Unlike in polythiophenes, the different regioregularities do not cause obvious differences in the optical properties of the polymers. Both the optical (absorption and emission) spectra and the PL efficiency of the two polymers are very close. This is probably because the poorer co-planarity between the adjacent thiophene rings is compensated by the better co-planarity between the fluorene and thiophene rings in **P15** in comparison with **P16**. However, **P15** has higher T_g

and better stability than **P16**. The chloroform solution of **P15** changed from yellow to deep brown upon standing in ambient conditions overnight. With the change of color, the emissive intensity of the solution was dramatically decreased. When the solution was laid aside for several days, its UV-Vis absorption spectrum showed a slight blue shift. In contrast, the solution of **P16** kept its color and spectra (both in shape and in intensity) unchanged, even if it was stored over one month.

Table 2. Parameters of the copolymers with thiophenes

Polymers	$M_w^a (\times 10^{-3})$	T_g (°C)	Solution (chloroform) ^b			Film ^b		
			λ_{abs} (nm)	λ_{em} (nm)	η_{PL}	λ_{abs} (nm)	λ_{em} (nm)	η_{PL}
P13	26.6 (1.4)	–	403	461 (490)	0.65	412	492 (477)	0.40
P14	29.3 (1.6)	78	367	447	0.39	378	458 (475)	0.29
P15	39.4 (1.7)	77	398	483 (520)	0.28	401	493 (520)	0.23
P16	29.1 (1.9)	63	401	482 (515)	0.31	403	490 (520)	0.21

^a Numerical values in parentheses are the polydispersity indexes (M_w/M_n).
^b The wavelength data are the peak wavelengths and the numbers in the parentheses are the wavelengths of shoulders or subpeaks.
The PL efficiency in solution was obtained by comparison with the standard of quinine sulfate (ca. 1×10^{-5} mol/L solution in 0.1 mol/L H_2SO_4). The efficiency in film states is measured against the standard of 9,10-diphenylanthracene dispersed in PMMA.

Table 3. Characteristics of the EL cells based on the polymers **P13–P16**

EL polymer (thickness, nm)	Anode buffer	Performance of device			
		Bias (V)	Current (mA)	Light intensity (cd/m ²)	QE (%) ^a
P1 (77)	PEDOT	8.0	12.4	356	0.38
P1 (77)	PVK	25.0	6.77	325	0.64
P2 (69)	PEDOT	8.0	66.7	824	0.16
P2 (74)	PVK	20.0	9.00	252	0.37
P3 (74)	PEDOT	6.0	20.5	144	0.09
P3 (74)	PVK	24.0	17.9	405	0.30
P4 (72)	PEDOT	8.0	75.4	388	0.07
P4 (72)	PVK	30.0	13.5	252	0.25

^a External quantum efficiency

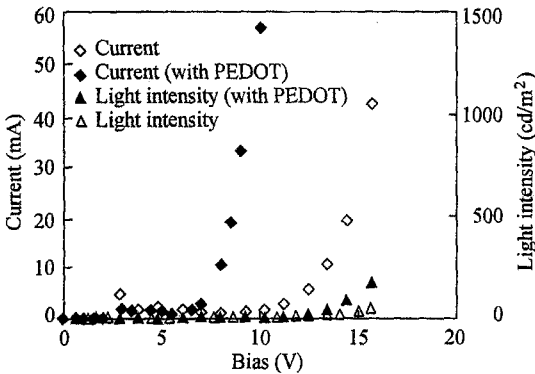


Fig. 14 The current (I)-voltage (V) and brightness (J)-voltage (V) curves of the EL cells based on **P13** with the configurations of ITO/**P13**/Ca and ITO/PEDOT/**P13**/Ca

P13–P16 are all used to fabricate EL cells with the following configurations: ITO/PEDOT/Polymer/Ca and ITO/PVK/Polymer/Ca. All the devices emit visible green light above certain positive (ITO wired positively) bias. The EL spectra are identical to their PL spectra except **P14**, whose EL spectrum red shifts by ≈ 40 nm with respect to its PL spectrum. The EL characteristics are summarized in Table 3. **P13** gives the best EL performance in terms of the efficiency. The I - V and J - V curves of the single-layered and double-layered devices based on **P13**

are shown in Fig. 14.

CONCLUSIONS

Spiro-functionalization is a promising approach to improve the blue light emission of fluorene homopolymers. The modification does not affect the electronic feature of the polyfluorene backbone, but probably changes the radiative process involved because of the amorphous enhancement in the polymer films. Modification imposed on the polyfluorene backbone by alternately inserting substituted phenylene units can significantly improve the thermal spectral stability of the resulting polymers. In comparison with the backbone of the fluorene homopolymers, the backbone of the alternate copolymers offers the possibility of tuning the electronic properties of the resulting polymers in a wide range by attaching different functional groups on the phenylene ring while the blue emission is retained. Chemically grafting europium(III) complexes onto the side chains of efficient blue light-emitting polymers achieves red light emission characterized by europium(III) ion. This may be a promising approach for developing efficient red light-emitting polymeric materials. In the copolymers of fluorene and thiophene, the substituent on the thiophene units and the manner of connection between thiophene units plays an important role in determining the optical and other physical properties of the polymers.

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