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Novel Electroluminescent Cationic Polyelectrolyte Based On Poly[(fluorene-2,7-diylvinylene)-*alt*-(1,4-phenylenevinylene)] and its Precursor

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ABSTRACT: A novel conjugated poly[(fluorene-2,7-vinylene)-*alt*-(1,4-phenylenevinylene)] derivative **2** with quaternizable tertiary amino groups was synthesized by Heck coupling of a substituted 2,7-dibromofluorene and 1,4-dialkoxy-2,5-divinylbenzene. The corresponding quaternary ammonium cationic polyelectrolyte **3** was obtained by the treatment of **2** with bromoethane. Both polymers were soluble in common organic solvents, like tetrahydrofuran, chloroform, and dichloromethane. Polymer **3** showed a limited solubility in alcohols and was insoluble in water. Photophysical and electrochemical properties of the resulting polymers were fully investigated. An intensive green photoluminescence (PL) with maxima at 550 and 545 nm was observed from thin films of **2** and **3** polymers, respectively, red-shifted compared with the PL emission spectra measured in the solution. The electrochemical band gaps were 2.38–2.45 eV. Single-layer and double-layer (with poly[3,4-(ethylenedioxy)thiophene]/poly(styrenesulfonate) (PEDOT:PSS)) light-emitting devices (LEDs) with ITO and Al electrodes were prepared and studied. They emitted a green light and their electroluminescence (EL) spectra were similar to those of PL thin films. The external EL efficiency was determined to be 0.43 and 0.32% for ITO/PEDOT:PSS/**2**/Al and ITO/PEDOT:PSS/**3**/Al LEDs, respectively. © 2006 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 45: 1016–1027, 2007

Keywords: conjugated polymers; electrochemical properties; electroluminescence; Heck polymerization; light-emitting diodes; light-emitting polymer; photophysics; polyelectrolyte; poly[(fluorene-2,7-vinylene)-*alt*-(1,4-phenylenevinylene)] derivative; synthesis

INTRODUCTION

Conjugated polyelectrolytes (CPs) are attractive series of polymers, which combine optoelectronic and redox properties of conventional conjugated polymers with aqueous solubility and ionic nature of polyelectrolytes, with possible uses in the electroluminescent and the electro-optical devices.[1] With appropriate substitution, numerous conjugated polymers have been prepared that are soluble in organic media. Water-soluble polyelectrolytes are known for their uses in the redox and the electroactive systems,[2] concentration control of ionic reactants in chemical reactions,[3] and photoinduced electron-transfer

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events.[4] Incorporation of anionic or cationic functionality into a CP yields a material which possesses the useful properties of a conjugated polymer with the aqueous solubility/processability of a polyelectrolyte.

CPs based on poly(phenylenevinylene) (PPV),[5] poly-*p*-phenylene, and polyfluorene (PF)[1(e),5(i–k)] present unique characteristics different from those of the original neutral polymer and therefore were widely investigated. Water-soluble CPs can be used as highly sensitive materials in biosensors for biological fluids in the living organisms.[6] The ionic groups of CPs can offer some new applications in the light-emitting diodes (LEDs). For example, they can be used as the active layers in LEDs prepared by layer-by-layer self-assembling.[7] Another advantage of CPs in LED application is that environment-friendly solvents such as water or alcohols can be used in device fabrication. In general, CPs have not been very successful as light-emitting layer in LEDs because the device performance and the color purity are poor. Cimrová et al.[8] reported the first LED based on a sulfonated poly(*p*-phenylene) as the emission layer in a single-layer device. The external quantum efficiencies of single-layer devices were in the range 0.5–0.8% with counterions H$^+$ or Na$^+$. Certain attempts were made to improve the performance of LEDs that are fabricated from CPs.[5(c),9,10] Recently, Cao and coworkers[1(e)] reported the first LEDs based on quaternary ammonium functioned polyfluorene electrolytes (PFN$^+$R$_3$). He found that these PF-based CPs could be used as the electron injection layer. Insertion of a thin layer of PFN$^+$R$_3$ between the high work-function metals and emitting layers greatly enhances the performance of the LEDs with a high work-function metal cathode. However, when these PF CPs are used as the active layer in LEDs, the external quantum efficiencies remain low (from 0.07 to 0.16%).[1(e)] Therefore, despite numerous efforts, high-efficiency polymer LEDs with good color purity based on the CP remain a great challenge in these days.

In this article we synthesized a conjugated poly[(fluorene-2,7-vinylene)-*alt*-(1,4-phenylenevinylene)] derivative and the corresponding cationic polyelectrolyte. The neutral copolymer was successfully synthesized by Heck coupling of 1,4-dialkoxy-2,5-divinylbenzene and a substituted 2,7-dibromofluorene bearing substituents with tertiary amino groups (quaternizable groups) at the C-9 position of fluorene. Quaternization of the

neutral polymer was carried out by the reaction with bromoethane to afford a cationic polyelectrolyte. The present polymers combine the interesting properties of PPVs and PFs. PPV derivatives are desirable as they have been proven to exhibit high-efficient green fluorescence and enhanced photostability. PFs and their derivatives have emerged as one of the most promising families of light-emitting materials because of their high photoluminescence (PL) quantum efficiency, good chemical and thermal stability, and facile color tunability. PFs have been widely synthesized and used in LEDs very recently.[11–17] The photophysical properties of both the quaternized polymer and its neutral precursor were systematically investigated in the solution and the solid state. LEDs were fabricated using the synthesized polymers as light-emitting layers. To our knowledge, this is the first report on the PL and electroluminescence (EL) properties of poly [(fluorene-2,7-vinylene)(1,4-phenylenevinylene)] cationic polyelectrolyte and its neutral precursor.

EXPERIMENTAL

Characterization Methods

IR spectra were recorded on a Perkin–Elmer 16PC FTIR spectrometer with KBr pellets. ^{1}H NMR (400 MHz) spectra were obtained using a Bruker spectrometer. Chemical shifts (δ values) are given in parts per million with tetramethylsilane as the internal standard. GPC analysis was conducted with a Waters Breeze 1515 series liquid chromatograph equipped with a differential refractometer (Waters 2410) as a detector using polystyrene as the standard and tetrahydrofuran (THF) as eluent. Elemental analyses were carried out on a Carlo Erba model EA1108 analyzer.

Reagents and Solvents

Dimethylformamide (DMF) and triethylamine were dried by distillation over CaH$_2$ and KOH, respectively. 2,7-Dibromofluorene was synthesized by a reported method.[18] The Stille reaction was used to prepare 1,4-bis(dodecyloxy)-2,5-divinylbenzene.[19] The latter was prepared by reacting 1,4-bis(dodecyloxy)-2,5-dibromobenzene with tributyl(vinyl)tin in the presence of the catalyst [PdCl$_2$(PPh$_3$)$_2$] and a few crystals of 2,6-di-*tert*-butylphenol using toluene as the solvent.

All other reagents and solvents were commercial of analytical-grade quality and were used without further purification.

Preparation of Monomers and Polymers

N,N,N′,N′-Tetraisopropyl-2,2′-(2,7-Dibromo-9H-fluorene-9,9-diyl)Diethan-1-amine(1)

A catalytic amount of tetrabutylammonium bromide (phase transfer catalyst) and 50 wt % aqueous solution of NaOH (3 mL) were added to a stirred mixture of 2,7-dibromofluorene (1.00 g, 3.08 mmol) and dimethyl sulfoxide (DMSO) (20 mL) under N_2. N-(2-chloroethyl)-N-isopropyl-propan-2-amine hydrochloride (1.60 g, 8.00 mmol) dissolved in DMSO (15 mL) was added dropwise, and the mixture was stirred at room temperature for 15 h under N_2. Then, it was diluted with water to dissolve the salts. The product was extracted with dichloromethane (3 × 15 mL), and the combined organic layer was washed with 10% NaOH and water. The solution was dried with anhydrous Na_2SO_4, filtered and concentrated to yield the crude product. It was purified by chromatography on a silica gel using n-hexane as eluent. A whitish pure product was obtained with a yield of 74% (1.32 g).

IR (KBr, cm^{-1}): 2964, 2870, 1452, 1384, 1318, 1242, 1200, 1118, 1060, 992, 880, 806, 750. ^{1}H NMR (CDCl$_3$, ppm): 7.55–7.46 (m, 6H); 2.76 (br, 4H); 2.12 (br, 4H); 1.58 (br, 4H); 0.76 (d, J = 6.27 Hz, 24H). Anal. Calcd for $C_{29}H_{42}Br_2N_2$: C, 60.21; H, 7.32; N, 4.84. Found: C, 59.83; H, 7.41; N, 4.78.

Polymer 2

A flask was charged with one (0.3640 g, 0.629 mmol), 1,4-bis(dodecyloxy)-2,5-divinylbenzene (0.3134 g, 0.629 mmol), Pd(OAc)$_2$ (0.0059 g, 0.026 mmol), and P(o-tolyl)$_3$ (0.0440 g, 0.145 mmol). The flask was degassed and purged with N_2. DMF (10 mL) and triethylamine (3 mL) were added, and the mixture was stirred and heated at 110 °C for 24 h under N_2. It was then filtered, and the filtrate was poured into a mixture of MeOH/H$_2$O (1:2 v/v). The orange precipitate was filtered off, washed with a MeOH/H$_2$O mixture, and dried to afford polymer **2**. The polymer was purified by dissolving in THF and precipitate into methanol (0.48 g, yield 83%).

IR (KBr, cm^{-1}): 2922, 2852, 1600, 1464, 1386, 1200, 1128, 1034, 970, 814, 750, 566, 486. ^{1}H NMR (CDCl$_3$, ppm): 7.56–7.47 (m, 6H); 7.17–6.98 (m, 6H); 4.04 (br, 4H); 2.81 (br, 4H); 2.17 (br, 4H); 2.79 (br, 4H); 1.63 (br, 4H); 1.48 (br, 4H); 1.26 (m, 32H); 0.88 − 0.79 (m, 30H). Anal. Calcd for $(C_{63}H_{98}N_2O_2)_n$: C, 82.65; H, 10.79; N, 3.06. Found: C, 82.28; H, 10.83; N, 2.95.

Polymer 3

A flask was charged with a solution of polymer **2** (100 mg) in THF (20 mL). To this solution bromoethane (5 mL) was added on excess and the mixture was stirred at room temperature for 5 days under N_2. Then, THF and bromoethane were evaporated. Polymer **3** was obtained as a sticky solid (94 mg, yield 76%).

IR (KBr, cm^{-1}): 3410, 2922, 2854, 1632, 1464, 1386, 1206, 1126, 1034. ^{1}H NMR (CDCl$_3$, ppm): 7.58–7.49 (m, 6H); 7.20–6.97 (m, 6H); 4.05 (br, 4H); 3.52 (br, ~4H); 2.83 (br, 4H); 2.18 (br, 4H); 2.81 (br, 4H); 1.62 (br, 4H); 1.48 (br, 4H); 1.26 (m, 32H); 1.07 − 0.78 (m, ~36H). Anal. Calcd for $C_{63}H_{98}N_2O_2$ 1.7C_2H_5Br H_2O: C, 72.49; H, 9.69; N, 2.55. Found: C, 69.60; H, 9.32; N, 2.41.

Sample Preparation

Thin polymer films were prepared by spin coating from THF or chloroform solutions. All solutions were filtered using 0.45-μm Millex-FH$_{13}$ Millipore syringe filters prior to the spin-coating. Thin films for optical studies were spin-coated onto the fused silica substrates. Polymer LEDs with a hole-injecting indium-tin oxide (ITO) electrode and an electron-injecting aluminum electrode were fabricated. Two types of the devices were prepared: the polymer layers were spin coated (1) onto ITO-covered glass substrates, (2) onto ITO substrates covered with a thin layer of poly[3,4-(ethylenedioxy)thiophene]/poly(styrenesulfonate) (PEDOT:PSS). The ITO glass substrates were purchased from Merk (Germany) and PEDOT:PSS Baytron-P from Bayer AG (Germany). The 50 nm thick PEDOT:PSS layers were prepared by spin coating and dried in vacuum at 396 K for 3 h prior to the polymer film deposition. Finally, 60–80 nm thick aluminum (Al) electrodes were vacuum-evaporated on the top of polymer films to form LED devices. Typical active area of the LEDs was 4 mm^2. All polymer films were dried in vacuum (10^{-3} Pa) at 323 K for 6 h. Layer thicknesses were measured using

a KLA-Tencor P-10 profilometer. All the thin film preparation and the LED fabrication were done under ambient laboratory conditions.

Cyclovoltammetric Measurements

Cyclic voltammetry (CV) was performed using a PA4 polarographic analyzer (Laboratory Instruments, CZ) with a three-electrode cell. Platinum wire electrodes were used as both counter and working electrodes, and silver/silver ion (Ag in 0.1 M $AgNO_3$ solution) electrode was used as the reference electrode. CV measurements were made in solution of 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile. All solutions in the cell were purged with argon before measurement. Typical scan rates were 50 mV s^{-1}.

Photoluminescence Measurements

PL spectra were measured using a home-made spectrofluorimeter with a single photon-counting detection (SPEX, RCA C31034 photomultiplier). PL spectra were taken perpendicularly to the sample surface and the angle of incidence for the excitation beam was 30°, with respect to the sample surface normal to minimize reabsorption. A 300-W Xenon lamp (Oriel) was used as the excitation source. The measured PL emission spectra were corrected for the spectral response of the detection system. PL and absorption measurements were performed under ambient laboratory conditions.

Electroluminescence Measurements

EL spectra were measured using a home-made spectrofluorimeter with single photon-counting detection (SPEX, RCA C31034 photomultiplier), the same setup as for PL measurements. LEDs were supplied from a Keithley 237 source measure unit, which served for simultaneous recording of the current flowing through the sample. Current- and luminance-voltage characteristics were recorded simultaneously using the Keithley 237 source measure unit and a silicon photodiode with integrated amplifier (EG and G HUV-4000B) for the detection of total light output. A voltage signal from the photodiode was recorded with a Hewlett–Packard 34401A multimeter. The LED characteristics were measured in a vacuum chamber to prevent any electrode degradation. Photostability was followed by UV–vis spectroscopy. PL and absorption mea-

surements were performed under ambient laboratory conditions.

The EL quantum efficiencies were evaluated from the measurements of EL spectra and the total light output. The external EL efficiency is expressed by the relation $\eta_{\mathrm{ext}} = n_{\mathrm{ph}}/n_{\mathrm{el}}$, where n_{ph} and n_{el} are the total number of photons emitted from the LED and the total number of electrons injected into the polymer per second, respectively. n_{el} was evaluated from the current, I, passing through LED as $n_{\mathrm{el}} = I/e$, where $e = 1.6 \times 10^{-19}$ C. The total light output was measured with a calibrated silicon photodiode with a built-in amplifier. n_{ph} was determined from the photocurrent, I_{ph}, because of the emitted photons using the relation

$$n_{\mathrm{ph}} = \frac{I_{\mathrm{ph}}}{\int n(\lambda)\frac{hc}{\lambda}S(\lambda)\mathrm{d}\lambda} \qquad (1)$$

where λ is the wavelength of the emitted photons, $n(\lambda)$ the fraction of photons with wavelength λ, hc/λ photon energy, and $S(\lambda)$ the sensitivity of the photodiode (A W^{-1}). I_{ph} was evaluated from the measured voltage signal U using $I_{\mathrm{ph}} = U/G$, where G (V A^{-1}) is the gain of the built-in amplifier. $n(\lambda)$ was calculated from the EL spectrum. For the estimation of the internal EL quantum efficiency, η_{EL}, the external EL efficiency, η_{ext}, was multiplied by the factor $2n^2$, where n is the refractive index of the polymer.[20] The value $n = 1.67$ was used in our evaluation of the η_{EL}.

RESULTS AND DISCUSSION

Synthesis and Characterization

The polymers were prepared according to the reaction sequence of Scheme 1. In particular, the key dibromide **1** was synthesized from the reaction of 2,7-dibromofluorene with (2-chloroethyl)di-isopropylamine hydrochloride in a two-phase mixture of water and DMSO in the presence of excess NaOH and a phase-transfer catalyst. The required dibromide **1** was purified by column chromatography and obtained in a satisfactory yield (74%). Its structure was confirmed by IR, ^{1}H NMR, and ^{13}C NMR spectroscopy (Fig. 1).

Polymer **2** was prepared from dibromide **1** and 1,4-bis(dodecyloxy)-2,5-divinylbenzene by Heck coupling. It was obtained in 83% yield, its num-
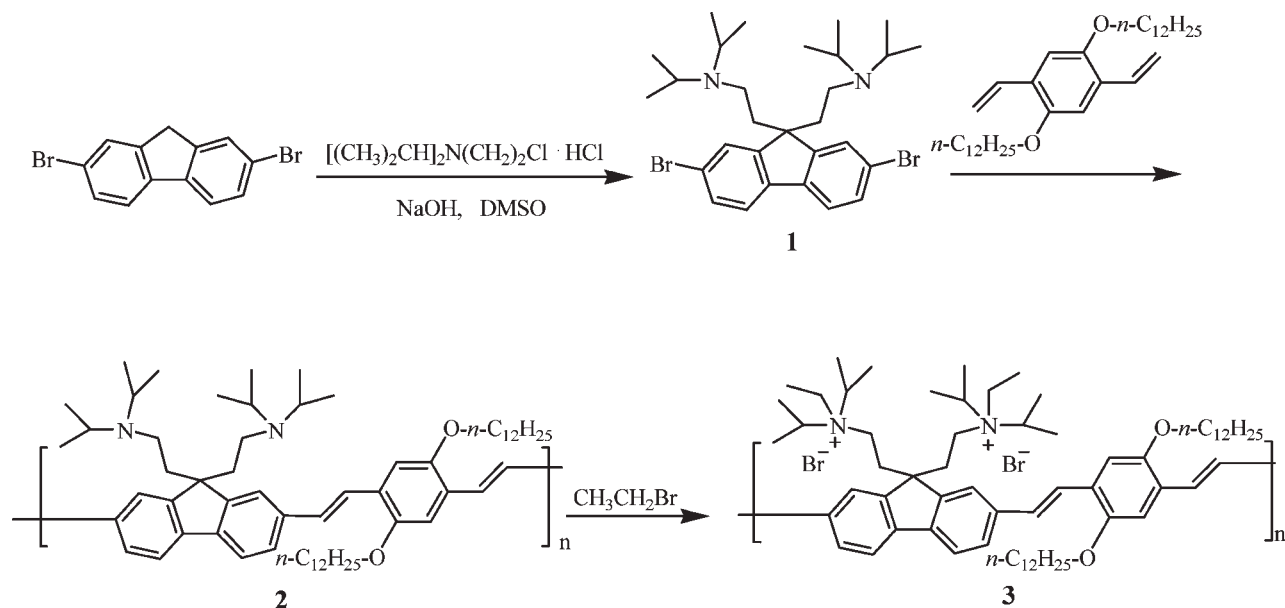
Scheme 1

ber-average molecular weight (M_n) was 8600, and polydispersity 2.3. Polymer **2** was readily soluble in common organic solvents such as: THF, chloroform, and dichloromethane.

The final step in the synthesis was the conversion of the neutral polymer **2** to the quaternized ammonium polymer **3** by reacting with bromoethane in the THF solution at room temperature for several days. During the reaction no precipitation was observed, and polymer **3** remained soluble in the THF owing to the long and/or the branched hydrophobic side groups of the polymer. For the same reason, this polymer exhibited a limited solubility in methanol or ethanol and was insoluble in water although it possesses an ammonium structure. It has been well established that it is difficult to achieve a full quaternization for the conversion of the neutral amine polymer into a quaternized ammonium salt.[1(e)] The quaternization degree is affected by the conditions of the reaction with bromoethane such as: solvent, temperature, and reaction time. The reproducibility of the quaternization degree is not very satisfactory. A typical degree of quaternization for polymer **3** was about 85% as estimated by elemental analysis. This conforms to literature data since a degree of quaternization of 80–90% has been reported for related polymers.[1(e)] The TGA thermograms of **3** showed that it retained a residual water of about 4% even on extensive drying. It was difficult to

determine the molecular weight of **3** by GPC because of the polymer aggregation on the column fillers induced by the ionic nature of polymer side chains.[1(e)] Since the quaternization reaction took place under mild conditions, the molecular weight of **3** is expected to be comparable with that of the starting polymer **2**.

The IR and ^{1}H NMR spectra of the neutral polymer **2** were consistent with its chemical structure (Fig. 2). Specifically, the IR spectrum showed characteristic absorption bands at 2922, 2852 (aliphatic C—H stretching); 1600, 1464 (aromatics), 1200 (ether), and 970 cm^{-1} (*trans*-alkene). In the ^{1}H NMR spectrum the resonances at 7.56–6.98 ppm are assigned to the aromatic and the alkene protons whereas those in the region 4.04–0.79 ppm are assigned to the aliphatic protons. Polymer **3** displayed essentially the same absorptions as the parent polymer **2**. Moreover, polymer **3** exhibited an additional broad absorption band at 3410 cm^{-1} associated with the residual water and the ammonium salt structure. The ^{1}H NMR spectrum of **3** supported its quaternized structure since the ratio of aliphatic protons to the sum of the aromatic and the alkene protons was higher than the corresponding ratio of **2**.

Polymer **2** exhibited a satisfactory thermal stability with a 5% weight loss above 300 °C. In contrast, polymer **3** started to lose weight at significantly lower temperatures because of the
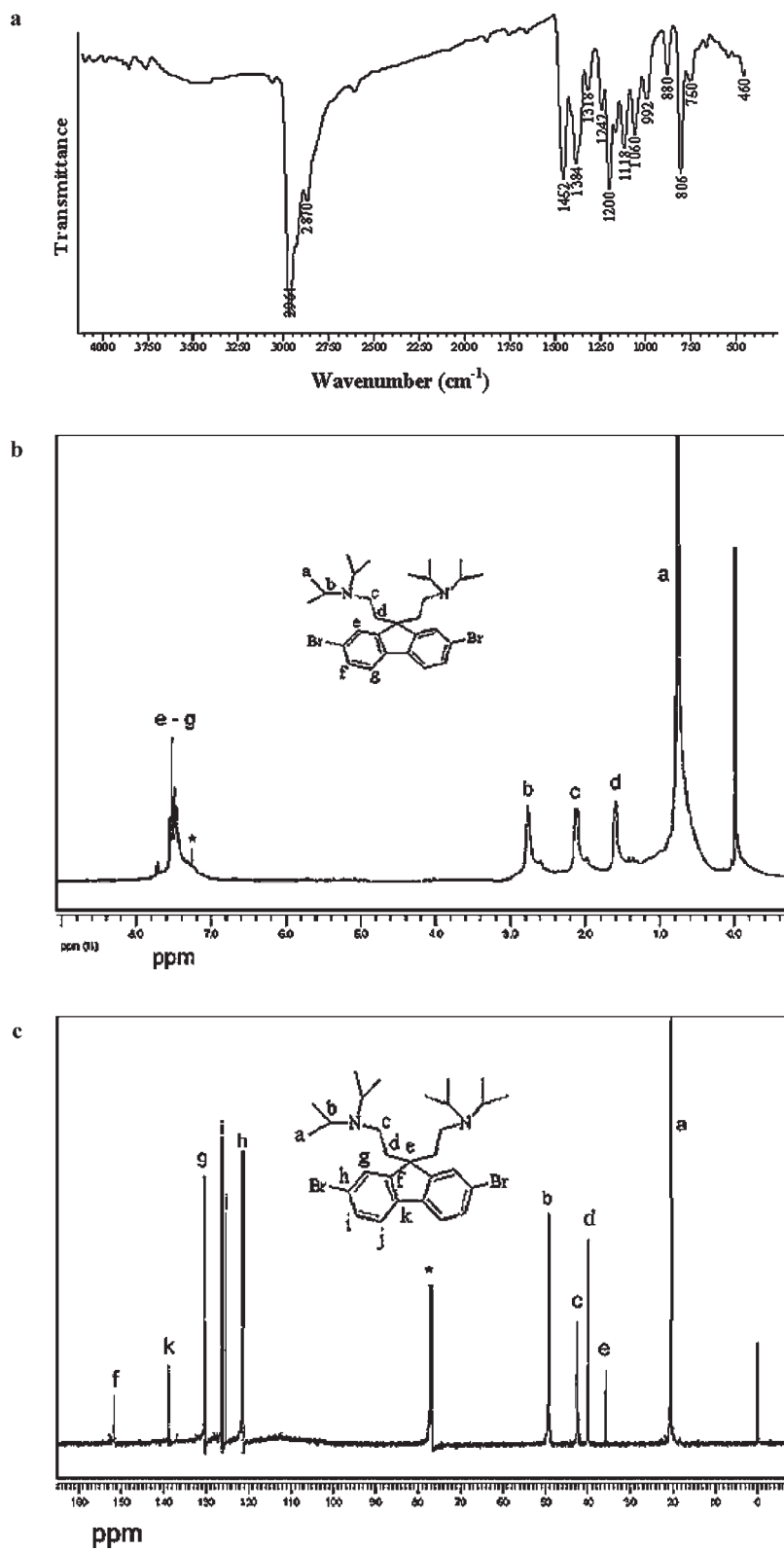
Figure 1. (a) FTIR, (b) ^{1}H NMR, and (c) ^{13}C NMR spectra of fluorene derivative **1**. ^{1}H NMR and ^{13}C NMR spectra were obtained in CDCl$_3$ solution. The peak of the solvent is marked with asterisk.
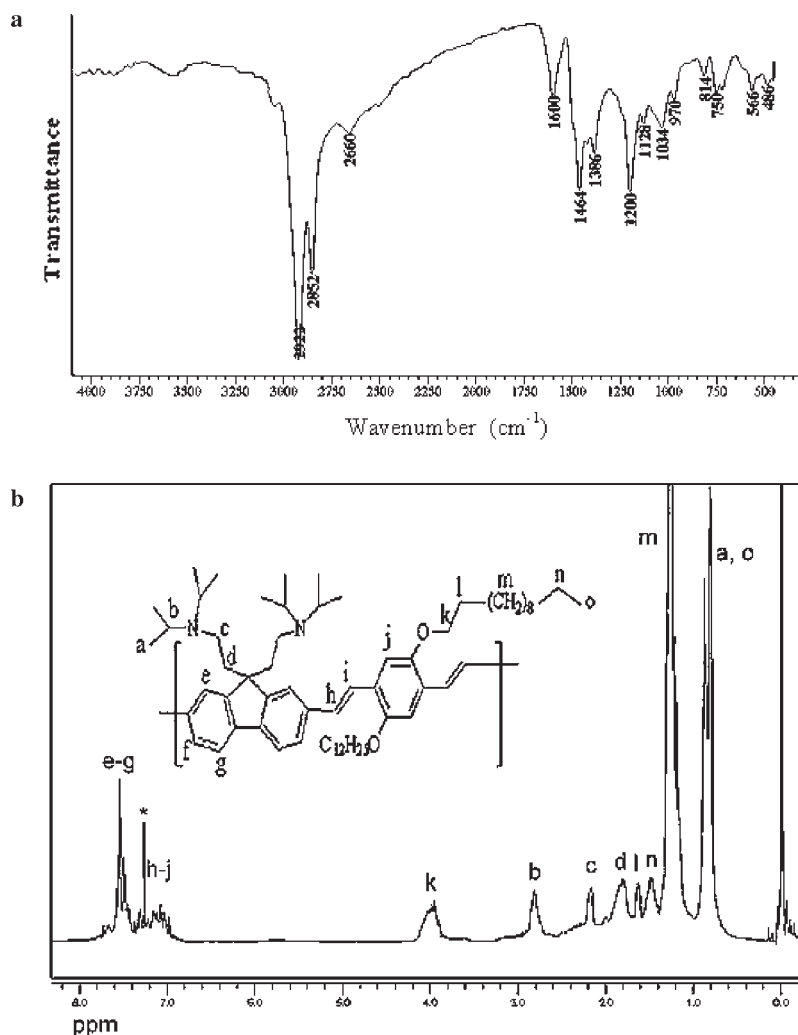
Figure 2. (a) FTIR and (b) ^{1}H NMR spectra of polymer **2**. ^{1}H NMR spectrum was obtained in CDCl$_3$ solution. The peak of the solvent is marked with asterisk.

residual water and the loss of bromoethane. No phase transitions of both polymers were recorded by DSC, even after repeated scans, thus supporting their amorphous character.

Polymer **3**, as was mentioned above, did not dissolve freely in alcohols and was insoluble in water because of the hydrophobic side groups. Work is in progress for replacing the dodecyloxy side groups of the benzene ring with quaternizable tertiary amino groups to obtain a water- and alcohol-soluble cationic polyelectrolyte.

Photophysical Properties

The UV–vis absorption spectra of polymer **2** and its salt **3** in thin films displayed in Figure 3 (dashed lines) are similar to those in their THF solutions (Fig. 4). The lowest energy absorption maxima corresponding to the absorption of the π–π* conjugated backbone in **2** and **3** films were located at 424 and 428 nm, respectively, and were slightly shifted to longer wavelengths (5–10 nm) compared with those in solution. The thin film PL spectra of the polymers are also shown in Figure 3. The shapes of PL excitation spectra followed the absorption ones. Thin films of **2** and **3** exhibited an intense green PL broad band emission with maxima at 550 and 540 nm, respectively. Compared with the PL emission spectra measured in THF solutions (see Fig. 4), where the PL emission maximum in a solution of **2** was located at 500 nm and of **3** at 495 nm, the maxima in thin films were significantly red-shifted by 50 nm. Behaviors like the red shifts,
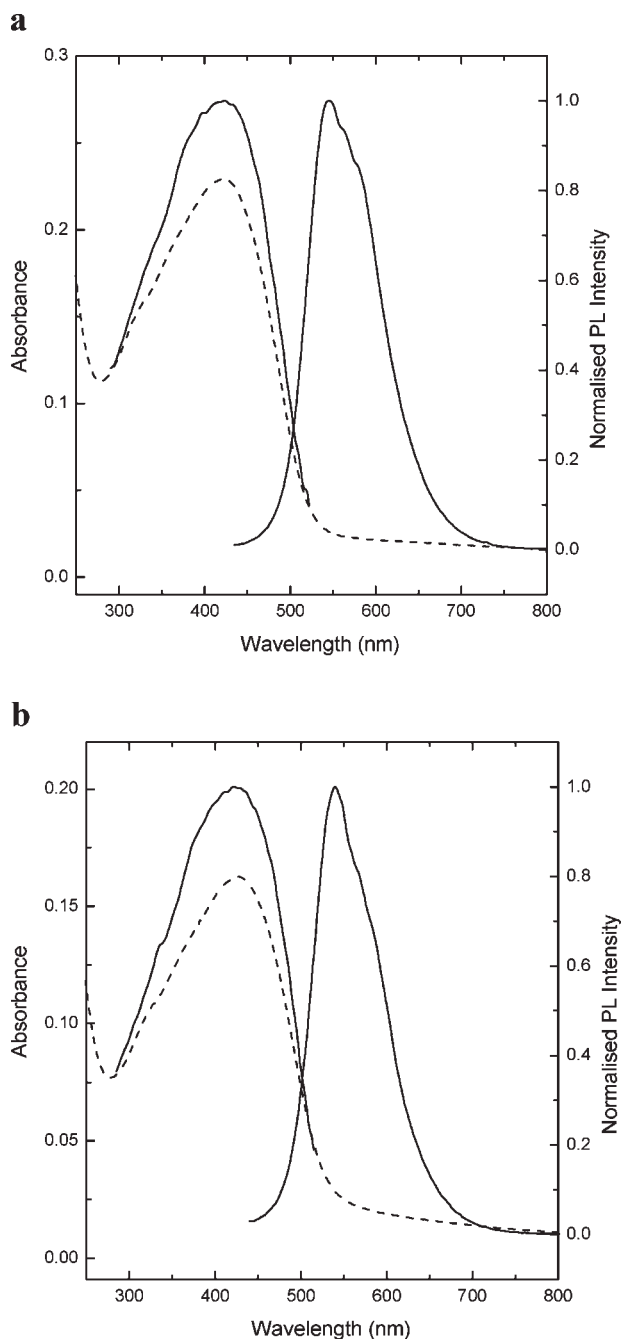
a

b

Figure 3. UV–vis absorption spectra (dashed), PL excitation (measured at emission wavelength λ_{em}) and emission (excitation wavelength λ_{exc}) spectra of polymers **2** and **3** in thin films. (a) **2**: $\lambda_{em} = 550$ nm and $\lambda_{exc} = 420$ nm, (b) **3**: $\lambda_{em} = 540$ nm and $\lambda_{exc} = 425$ nm.

broad featureless emission bands, and large Stokes shifts (>100 nm) are the characteristic of excimers or aggregates in the solid state.[21,22] Similar behavior was observed with several PPV-based polymers as shown in our previous article.[23,24]

Electrochemical Properties and Electronic Structure

CV was used to study the redox properties of the polymers. The ionization potential (HOMO level), E_{IP}, and electron affinity (LUMO level), E_A, were estimated from the onset potentials on the basis of the reference energy level of ferro-
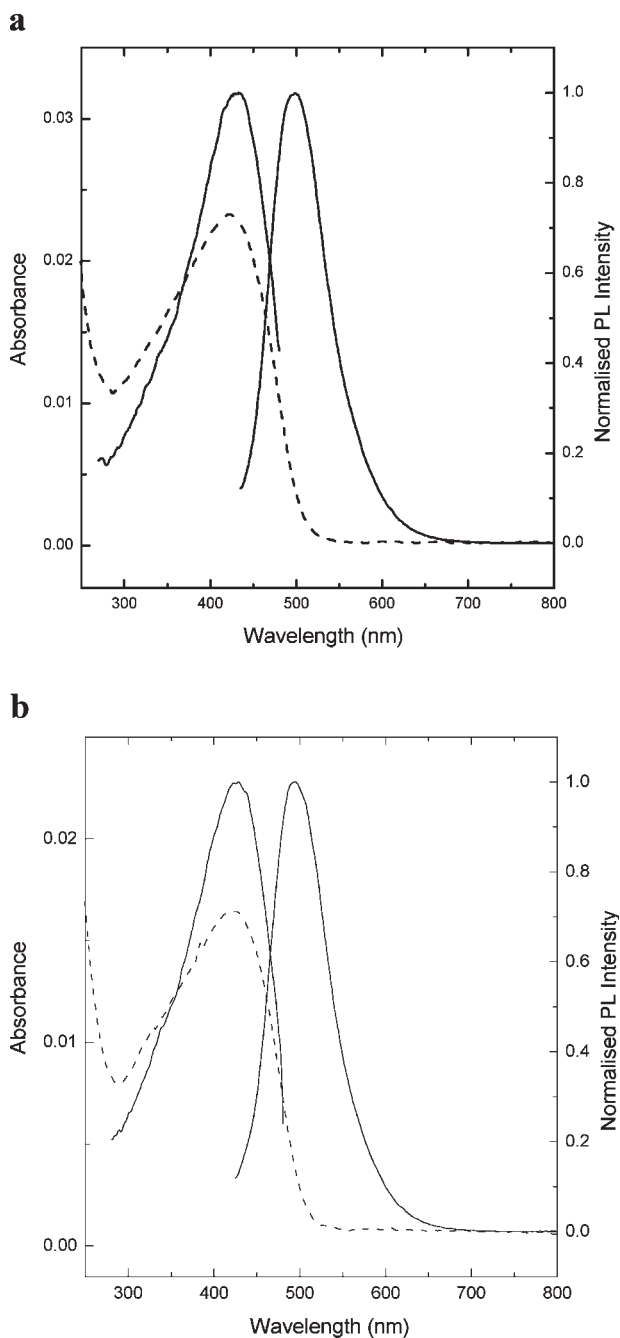
a

b

Figure 4. UV–vis absorption (dashed) and photoluminescence spectra of polymers **2** and **3** in THF solution (10^{-4} wt %). (a) **2**: $\lambda_{em} = 500$ nm and $\lambda_{exc} = 420$ nm, (b) **3**: $\lambda_{em} = 495$ nm and $\lambda_{exc} = 410$ nm.
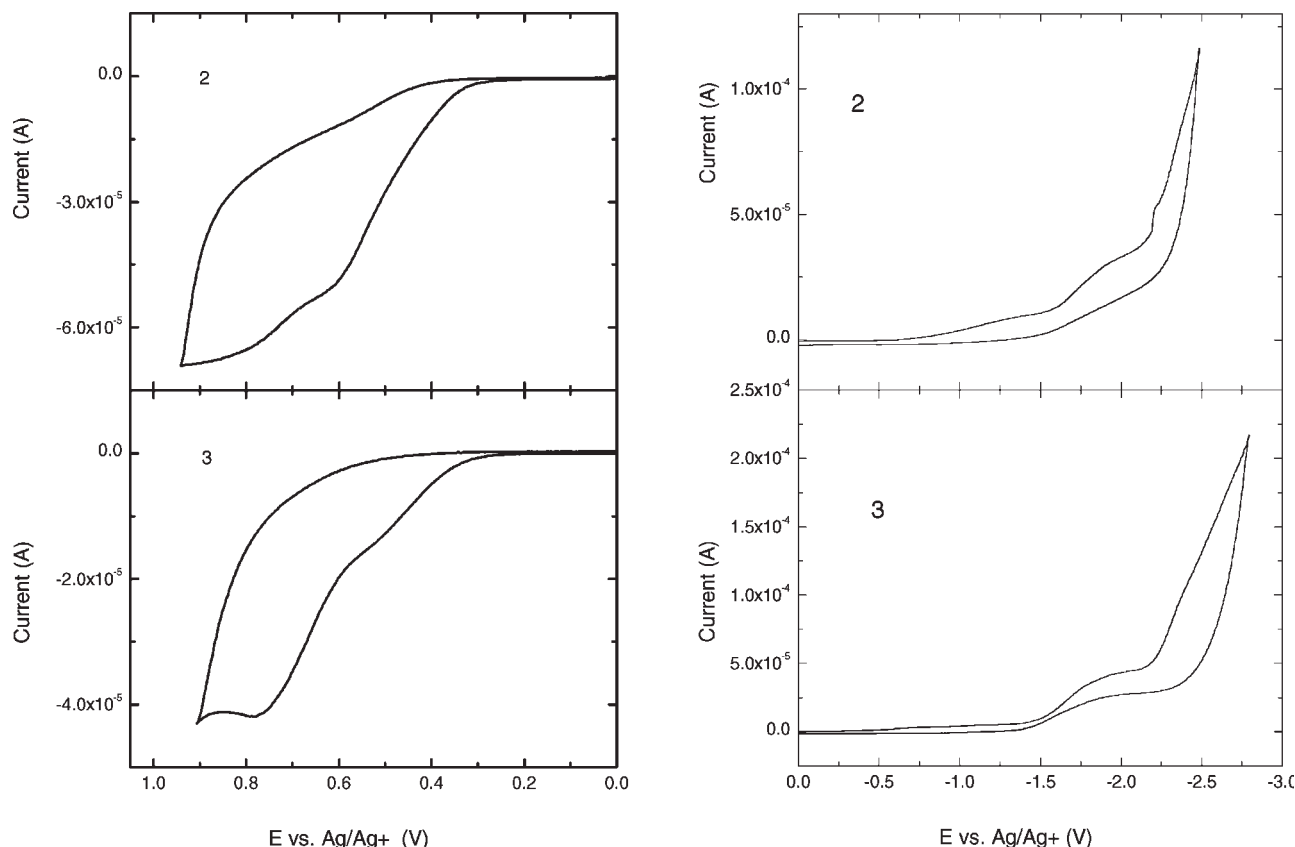
Figure 5. Cyclic voltammograms of the oxidation (left) and of the reduction (right) of polymers **2** and **3**.

cene (4.8 eV below the vacuum level) using the following equation[25]

$$E_{IP}(E_A) = -(E_{onset} - E_{ferr}) - 4.8 \; (eV) \qquad (2)$$

where E_{ferr} is the measured value for ferrocene versus Ag/Ag+. Figure 5 shows cyclic voltammograms of the oxidation (left) and of the reduction (right). In both polymers an irreversible oxidation and reduction were observed. The oxidation onset potential (E_{onset}) 0.35 V for **2** and 0.34 V for **3** and the reduction onset potential (E_{onset}) $-$ 2.17 V for **2** and $-$ 2.05 V for **3** were detected. Using these values, HOMO and LUMO levels were estimated as E_{IP} = 5.07 eV and E_A = 2.62 eV for **2**, and E_{IP} = 5.06 eV and E_A = 2.68 eV for **3**, respectively. The determined values of the electrochemical band gap, 2.45 and 2.38 eV for **2** and **3**, respectively, are in very good agreement with the optical band gap values evaluated from the absorption edge, 2.46 and 2.42 eV for **2** and **3**, respectively.

Electroluminescence

Single-layer LEDs with a ITO and electron-injecting aluminum (Al) electrodes were prepared and studied. The EL efficiency of the LEDs increased by introducing the PEDOT:PSS layer between the hole-injecting ITO electrode and the polymer layer to smooth the ITO surface and improve the LED performance. Therefore, we focused our attention on the study of double-layer devices, ITO/PEDOT:PSS/polymer/Al. EL spectra of ITO/PEDOT:PSS/**2**/Al and ITO/PEDOT:PSS/**3**/Al LEDs are shown in Figure 6. Both the LEDs made of **2** and **3** exhibited broad band green EL emission with maxima at 537 and 531 nm, respectively, slightly shifted to short wavelengths compared with the positions of the corresponding PL maxima. The shapes of the EL spectra of the devices without PEDOT:PSS layer were the same. Typical dependences of the current and the EL intensity on the applied electric field measured on the LEDs are shown in Figure 7. A lower onset of the EL
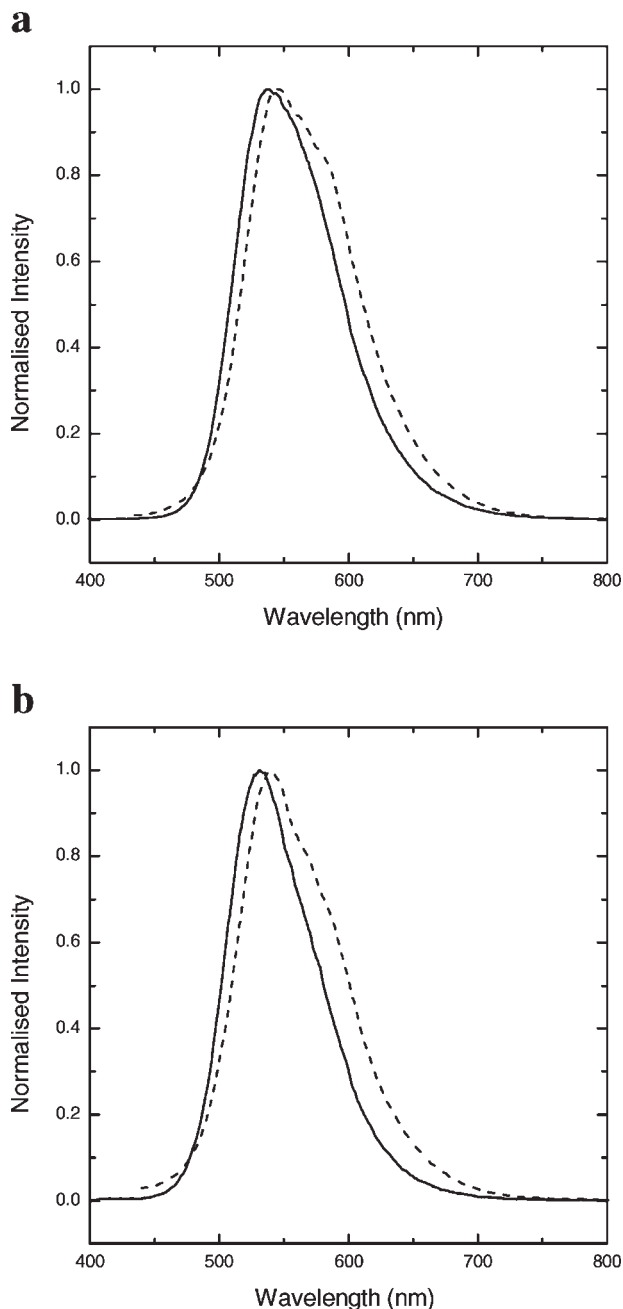
Figure 6. EL spectra (solid lines) of polymer LEDs: (a) ITO/PEDOT:PSS/**2**/Al and (b) ITO/PEDOT:PSS/**3**/Al. Dashed lines PL spectra of thin films.

mined from the cyclovoltammetric measurement $E_{IP} = 5.06 - 5.07$ eV. The ITO work function usually varies from 4.7 to 4.9 eV, so the expected height of the injection barrier for holes is lower than 0.4 eV and was further reduced by using PEDOT:PSS. On the other hand, the injection barrier for electrons is several times higher. Because of the small barrier height at the ITO/polymer interface, the LEDs are typical hole-
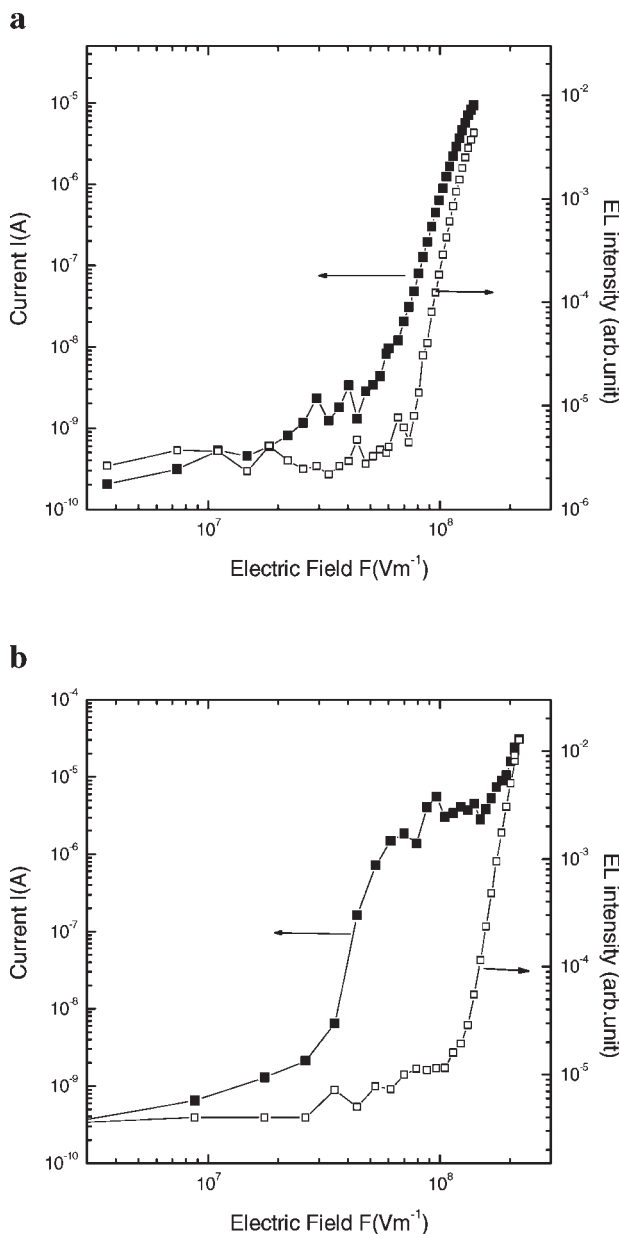
emission was observed in **2** (at 7.3×10^7 V m^{-1}) than in **3** (at 1.1×10^8 V m^{-1}). The onset was associated with a current increase at high electric fields. In the LEDs made of **3** an increase in the current was observed at lower electric field, which was not accompanied with any increase in EL emission. The ionization potential corresponding to the HOMO energy level, was deter-

Figure 7. Dependence of the current (solid squares) and integrated EL intensity (open squares) on the applied electric field measured on polymer LEDs: (a) ITO/PEDOT:PSS/**2**/Al and (b) ITO/PEDOT:PSS/**3**/Al.

Table 1. Photophysical, Electrochemical, and Electroluminescent Properties of Polymers

Polymer	λ_{absmax} in Solution (nm)	λ_{absmax} in Thin Film (nm)	λ_{PLmax} in Solution (nm)	λ_{PLmax} in Thin Film (nm)	Optical Band Gap (eV)	Electrochemical Band Gap (ev)	λ_{ELmax} (nm)	External EL Efficiency (%)
2	423	424	500	550	2.46	2.45	537	0.43
3	419	428	495	540	2.42	2.38	531	0.32

only devices. However, significant hole trapping at the radiative centers near the polymer/Al interface can improve the electron injection due to the space charges produced by trapped holes.

The external EL efficiencies 0.43 and 0.32% for LEDs made of **2** and **3** were determined, respectively. A relatively high value of η_{ext} = 0.2% was obtained as well in a single layer LED made of **2**. The photophysical, electrochemical, and electroluminescent properties of polymers are summarized in Table 1.

The measured η_{ext} values are several times higher than the values reported for LEDs based on bis(dodecyloxy) PPV-based polymers[24] or the EL efficiency measured in the double-layer devices composed of hole-transporting (triphenylamine) and light-emitting (random copolymer of 9,9-dihexylfluorene and anthracene) layers.[26] Our η_{EL} value also exceeds the η_{EL} value of a bilayer LED made of PF with a hole transport layer[27] and of bilayer LEDs based on thermally-cross-linked hole-transporting polyarylamine and PFs.[28]

Our values of the EL efficiency belong to the high ones measured on LEDs made of cationic polyelectrolytes in comparable configuration. They are about one order of magnitude higher than the values reported for the LEDs based on quaternary ammonium PFN$^+$R$_3$[1(e)] and also than that ($\eta_{\text{ext}} \sim 0.017\%$) reported for LEDs prepared from poly(p-phenylene-co-thiophene) layer by layer assembling with the polyanion poly(styrene sulfonic acid).[29] They are even slightly higher than those in the LEDs made of PFN$^+$R$_3$ (or its precursor) with an additional poly(N-vinylcarbazole) layer.[1(e)] Compared with the devices made of aminoalkyl-substituted PF copolymers with benzothiadiazole in the same configuration[1(f)] higher values of EL efficiency were observed in the neutral precursor **2** only. Our new cationic polyelectrolyte is due to the solubility in organic solvents and insolubility in water promising for the multilayer with water-soluble anionic polyelectrolytes or its precursor could

be used in blends devices to improve the device performance.

CONCLUSIONS

New electroluminescent cationic polyelectrolyte **3** based on poly[(fluorene-2,7-vinylene)-alt-(1,4-phenylenevinylene)] and its polymer precursor **2** were synthesized. They are soluble in common organic solvents. Thin films made of **2** and **3** exhibited an intense green broad band PL with maxima at 550 and 545 nm, respectively. Compared with the PL emission spectra measured in THF solutions, a red shift was observed indicating aggregate formation in the solid state. Both the polymers oxidized and reduced irreversibly. The values of ionization potential (HOMO level) were similar 5.07 and 5.06 eV for **2** and **3**, respectively. A slightly higher value of electron affinity (LUMO level) was evaluated for **3** (E_A = 2.68 eV) than for **2** (E_A = 2.62 eV). LEDs with an indium-tin oxide hole-injecting and aluminum electron-injecting electrodes were prepared and studied. LEDs emitted green light and EL spectra were similar to PL spectra of thin films. The external EL efficiency was determined to be 0.43 or 0.32% photons/electrons in LEDs made of **2** or LEDs made of **3**, respectively.

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