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Substituent Effect To Prevent Autoxidation and Improve Spectral Stability in Blue Light-Emitting Polyfluorenes

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Abstract: A group of fluorene-based polymers, **PF-1SOR** and **PF-2SOR**, were synthesized and characterized as blue light-emitting materials. **PF-1SOR** and **PF-2SOR** displayed nematic liquid crystalline mesophase in films cast from solution. Compared with conventional polyfluorene, **PF-1SOR** and **PF-2SOR** display blue-shifted UV absorption and structureless blue fluorescence. The photoluminescence spectra of **PF-1SOR** and **PF-2SOR** were found insensitive against thermal treatment in air up to 200° C and the blue electroluminescence in their light-emitting devices was independent of the driving voltage. Compared to the conventional polyfluorenes, the improved spectral stability of these polymers is attributed to the anti-oxidization effect of (3,5-di(*tert*-butyl)phenoxy)sulfonyl side groups attached to the backbone.

Keywords: electroluminescence · liquid crystals · luminescence · polymers

Introduction

Light-emitting polymers have found considerable interest because of their potential application in optoelectronics, for example, as functional components in polymer light-emitting diodes (PLEDs), solar cells, and thin film transistors.[1–3] Among all the light-emitting polymers of the three primary colors, blue light-emitting polymers are of special interest. Polymers available so far show insufficient efficiency and lifetime, despite intense research efforts. In addition to the typical blue luminescent poly(*p*-phenylene) (PPP),[4] and its derivatives, poly(2,7-(9,9-disubstituted)fluorene) (PF) and respective copolymers were found as another important series of blue light-emitting materials of high photoluminescent (PL) quantum yield, good solubility in common organic solvents and acceptable charge carrier mobility.[5–8] A number of fluorene-based homo- and copolymers have been reported and blue PLEDs have been fabricated using these polyfluorenes.[5–8] However, an undesired low-energy "green" band covering a broad range from 500 to 600 nm is frequently generated in both PL and electroluminescence (EL) of PFs during operation, which not only limits the emission efficiency but also damages the blue color purity and stability.[5–8,9] There have been two opposing popular points of view on the origin of this green emission in the literature.[10,11] One kind of interpretation assigned this green band to the emission of hypothetical interchain aggregates and/or excimer formation of PFs.[5a,8a,10] Consequently some strategies such as dendronization,[8b,12] introduction of spiro- or cross-links,[6e,8a,c] substitution with bulky side groups,[7b–e,13] and blending[8d] were applied to obtain light-emitting fluorene polymers or systems aiming to prevent the formation of aggregates or excimers by suppressing intermolecular interactions. Another kind of view insists that this green emission band is caused by keto defects of PFs which are generated during handling the materials in air, or by reaction with residual oxygen in the course of photophysical experimentation.[11] The latter interpretation was confirmed experimentally. By investigating the photophysical properties and energy transfer behavior of a series of monodisperse oligofluorenes and fluorenone-centered oligofluorenes, our group has demonstrated that highly pure oligofluorenes do not show the "green" emission and that oligofluorenes containing just one fluorenone group could act as model to reproduce the green emission of the PFs.[14] Lupton, Scherf, Jenekhe and their co-workers also clarified the origin of the green emission band as coming from a fluorenone moiety and contradicted experimentally the assumption that intermolecular aggregates or excimers play a role.[11,15]

With a better understanding of the origin of the green emission in fluorene-based polymers, it is possible to search for efficient strategies to avoid the formation of the keto defects to obtain pure blue emission, unless the green light

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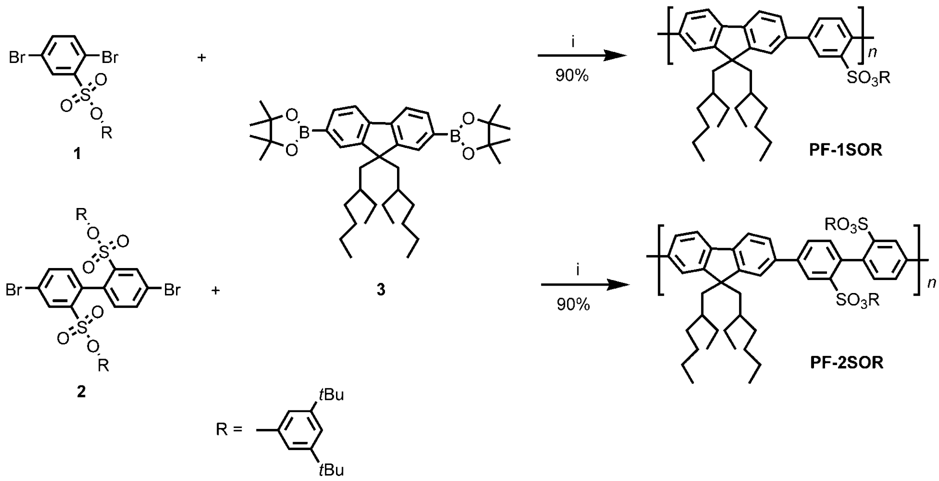
emission is deliberately provoked by means of energy transfer to or charge trapping by the fluorenone moieties.[15] It is safe to assume that the keto defect is formed by oxidation of the fluorene ring at the 9-position when it is exposed to intensive light, heat or electrical field, although the mechanism of the oxidation is not fully clear yet. Therefore, any method which aims to introduce anti-oxidation capability should help to suppress the green emission and to improve the color purity and stability of the blue emission. Common chemical sense tells us that, the oxidation probability of a reagent can be decreased by reducing the electron density on the reactive sites through proper substitution. Alternatively, one can introduce scavenging agents and deactivators for reactive intermediates such as hydroxy radicals, singlet oxygen and the like.

In the present paper, we report the synthesis of two new fluorene-based polymers, **PF-1SOR** and **PF-2SOR**, and their application for blue photoluminescence (PL) and electroluminescence (EL). Polymers and copolymers composed of fluorene and phenylene segments have been reported previously.[8a] However, fluorene-based polymers having phenylene sulphonate groups incorporated are reported here for the first time. Besides to improve the solubility and to avoid interchain aggregation, the (3,5-di(*tert*-butyl)phenoxy)sulfonyl side groups attached to the phenylene ring on the backbone are expected to improve the oxidative stability of the fluorene moieties by taking away electron density from the fluorene to the phenylene ring and by the scavenging activity of the 3,5-di(*tert*-butyl)phenoxy residues. The photophysics, phase transition and liquid crystalline properties of these new copolymers are investigated. Moreover, their thermal spectral stability is studied by monitoring the PL of their thin solid films and the electrical spectral stability by EL of light-emitting devices built from them. For comparison, the spectral stabilities of a conventional fluorene homopolymer, poly(9,9-di(ethylhexyl)-fluorene) (**PF**), is also studied under the same conditions.



Scheme 1. Chemical structure and preparation of polymers **PF-1SOR** and **PF-2SOR**. i: [Pd(PPh_3)$_4$] THF/H_2O, $NaHCO_3$, reflux.

Table 1. Summary of the spectroscopic data of polymers **PF-1SOR**, **PF-2SOR** and **PF**.

			Film		Toluene solution			
Polymer	M_n [gmol^{-1}]	PD	$\lambda_{max(UV)}$ [nm]	$\lambda_{max(PL)}$ [nm]	$\lambda_{max(UV)}$ [nm]	$\lambda_{max(PL)}$ [nm]	Stoke shift [nm]	Φ_{FL}
PF-1SOR	21 000	1.60	350	419	349	413	64	0.58
PF-2SOR	28 000	1.87	347	416	349	410	61	0.56
PF	15 000	1.79	388	423	383	413	30	1

Results and Discussion

Synthesis: Scheme 1 illustrates the chemical structure and the preparation of the polymers **PF-1SOR** and **PF-2SOR**. They were synthesized by Suzuki polycondensation reaction of monomer **1** or **2** with **3** by using [Pd(PPh_3)$_4$] as catalyst in a mixture of tetrahydrofuran and aqueous $NaHCO_3$ solution. The syntheses of the monomers **1**, **2** and **3** have been reported previously.[16,17] Polymers **PF-1SOR** and **PF-2SOR** were obtained as white solids in over 90% yields after repeated precipitation with methanol. They dissolve in common organic solvents such as tetrahydrofuran, chloroform and toluene. Gel permeation chromatography (GPC), by using poly(*p*-phenylene) (PPP) based standard, gave number-average molecular weights (M_n) and weight-average molecular weights (M_w) as 21 000 and 35 000 for **PF-1SOR**, and 28 000 and 53 000 for **PF-2SOR**, respectively. These results correspond to a polydispersity index (PD, PD $= M_w/M_n$) of 1.6 and a number-average degree of polymerization (DP_n) of 28 for **PF-1SOR**, 1.87 and 26 for **PF-2SOR**, respectively. Table 1 gives a brief summary of these parameters. Full characterization of both polymers is obtained by ^{1}H NMR, ^{13}C NMR, spectroscopy and elemental analysis as mentioned in the Experimental Section.

Thermal characterization: The thermal properties of **PF-1SOR** and **PF-2SOR** were first investigated by polarized optical microscopy of the materials in form of their films which were cast from solution and were observed directly or after they had been subjected to thermal annealing. Figure 1 shows the optical micrographs of **PF-1SOR** and **PF-2SOR** films between crossed polarizers on glass substrates. The films were obtained from their dilute chloroform solutions by very slow evaporation of the solvent at room temperature. Details of the sample preparation have been described elsewhere.[18] The **PF-1SOR** film displayed a typical Schlieren texture, as shown in Figure 1a, indicating a nematic liquid crystal mesophase. This Schlieren texture persisted even after the solvent was evaporated and the film was fully dry, implying that the liquid crystalline mesophase was frozen in. A similar LC texture was revealed under same conditions for films of **PF-2SOR**.

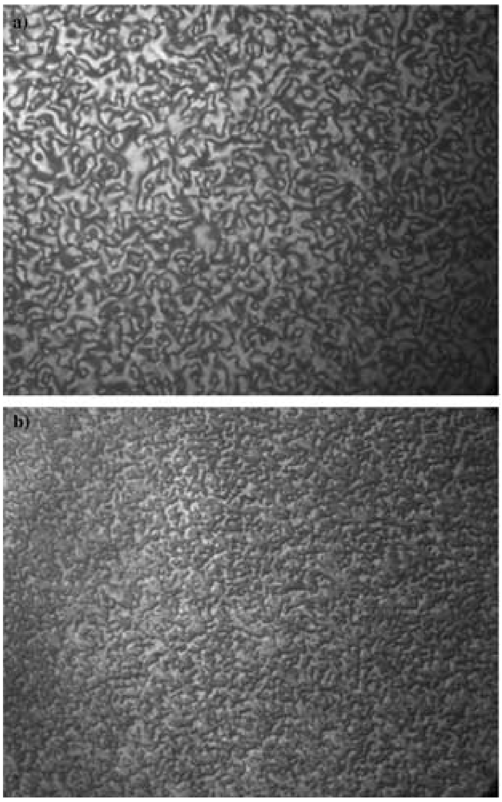


Figure 1. Optical micrographs under crossed polarizers of **PF-1SOR** a) and **PF-2SOR**, b) films developed from dilute chloroform solutions.

The LC mesophase of **PF-1SOR** and **PF-2SOR** was also observed in case where the solution was rapidly evaporated which gave rise to a thin film of unspecified initial structure that turned into a mesophase characterized by a Schlieren texture upon annealing at elevated temperature. Upon heating at 10 K min^{-1}, the **PF-1SOR** film on a glass substrate displayed the same Schlieren texture as in Figure 1a when the temperature reached about 155° C; this suggests that a nematic LC mesophase was formed. Increasing the temperature, this texture persisted and no isotropization was observed even when heating to 350° C. In the subsequent cooling at 10 K min^{-1} to room temperature, the LC texture still persisted, implying that the LC mesophase is frozen persistently. The fact that the LC mesophases of polyconjugated polymers can be quenched and kept either by cooling from the thermally treated films or by evaporating solvent from the lyotropic phases was reported by our group as early as 1993.[18]

Formation of a nematic LC mesophase of **PF-1SOR** was also identified by differential scanning calorimetry (DSC). Figure 2 shows the DSC trace on heating (solid line) of **PF-1SOR** after it had been quenched from the melt. As the temperature was increased, an endothermic peak was detected at 155° C, which is identified as the melting of **PF-1SOR** into a liquid crystalline mesophase according to the observation of the Schlieren texture by polarized optical microscopy. Further transitions were not observed on further heating, indicating that the isotropization temperature lies above the decomposition temperature. Thermogravimetry showed that **PF-1SOR** started to decompose at 360° C.

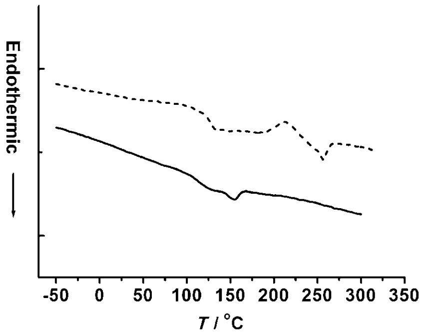


Figure 2. DSC traces of **PF-1SOR** (——) and **PF-2SOR** (-----) (second heating at 10 K min^{-1}).

The thermal properties of **PF-2SOR** are similar. Heating a film of **PF-2SOR** on a glass substrate a similar LC texture (see Figure 1b) was generated when the temperature reached about 260° C. It should be noted that formation of the LC texture in **PF-2SOR** films was much slower than in **PF-1SOR** even at the high temperature of 300° C. Figure 2 also illustrates the DSC trace of **PF-2SOR** (dash line). When the glassy **PF-2SOR** quenched from its melt was reheated for the second run, an endothermic transition phenomenon was detected at 133° C, which corresponds to a transition of **PF-2SOR** from a glassy to a rubbery state. On further heating, an exothermic process, probably corresponding to the formation of a crystalline phase, was observed at 212° C. Further increasing the temperature, this phase melted at 256° C into a mesophase, consistent with the observation of the LC mesophase by polarized microscopy.

Optical properties: The normalized electronic absorption and fluorescence spectra of **PF-1SOR** and **PF-2SOR** in dilute toluene solution are shown in Figure 3. For comparison, the absorption and fluorescence spectra of the neat poly(fluorene) **PF** in dilute toluene solution are also displayed. For the sake of comparison and accurate data acquisition, the optical density of all solutions was adjusted to a value of 0.1. **PF-1SOR** and **PF-2SOR** exhibit structureless absorption bands with identical absorption maximum at 349 nm, which is associated to the π–π* transition of the polymer backbone. Compared to **PF**, the absorption of **PF-1SOR** and **PF-2SOR** is blue-shifted by 30 nm, implying that the presence of the phenylenes segments with the bulky sulphonate side groups does change the electronic structure of the polymer backbone only slightly and increases the energy band gap. Despite the same absorption maximum in solution and the similar spectral shape, the absorption of **PF-2SOR** starts at a shorter wavelength than **PF-1SOR**; this indicates a higher energy band gap of **PF-2SOR**. The band gaps of **PF-1SOR** and **PF-2SOR** were determined by the absorption onset of the corresponding solid films on quartz substrates as 3.22 and 3.30 eV, respectively.

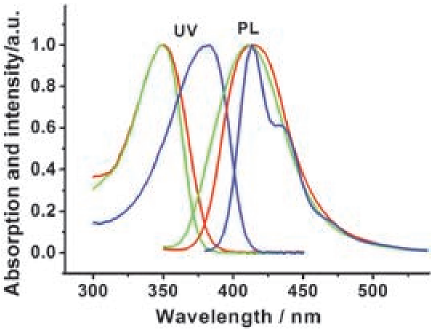


Figure 3. UV-VIS absorption and fluorescence spectra of **PF-1SOR** (——), **PF-2SOR** (——) and **PF** (——) solutions in toluene.

The fluorescence spectra of **PF-1SOR**, **PF-2SOR** and **PF** in dilute toluene solution with the same concentration to those for above absorption measurement are also shown in Figure 3. Under excitation at 350 nm, **PF-1SOR** and **PF-2SOR** exhibit unstructured blue fluorescence with emission peaks at 413 and 410 nm, respectively. Compared with the well-resolved fluorescence bands of 413, 435 and 472 nm of **PF**, the absence of any vibronic structure in the fluorescence spectra of **PF-1SOR** and **PF-2SOR** probably contributes to the color purity of their blue emission. Notably, the Stoke's shift of polymer **PF-1SOR** (64 nm) and **PF-2SOR** (61 nm) determined as the difference between the absorption and fluorescence maximum is double in magnitude compared to that of PF (30 nm). The fluorescence quantum yields (Φ_{FL}) of polymer **PF-1SOR** and **PF-2SOR** in toluene solution were measured related to **PF** as 0.58 and 0.56, respectively, assuming that the quantum yield of **PF** in dilute toluene solution is unity. All the involved photophysical parameters of **PF-1SOR**, **PF-2SOR** and **PF** are summarized in Table 1.

Spectral stability: The blue light emission in conventional PFs is in most cases reported in literature accompanied by a broad and structureless green band if the material has ever been exposed to air during preparation or operation. It is, therefore, of interest to test the polymers described in this paper with regard to their response towards exposure to oxygen under harsh conditions.

The spectral stability of **PF-1SOR** and **PF-2SOR** was probed by annealing their films in air at various temperatures for two and a half hours and then measuring the fluorescence spectra after cooling to room temperature. For comparison, films of **PF** were treated and tested in the same way. In order to avoid any possible effect on the fluorescence from residual solvent or film thickness, all films were fabricated by spin coating on same kind of quartz substrate from toluene solution and the film thickness of all samples was adjusted to 70 nm. The films were dried in a vacuum oven at room temperature for 10 hrs. Three polymers were also annealed in form of powder at various temperatures and then subjected to FT-IR measurement to detect the possible formation of keto groups. Only fresh films and powders were used as starting materials for these experiments. Figure 4 shows the absorption spectra of these polymers in form of films before and after annealing. The absorption maxima and the spectral shape of **PF-1SOR** and **PF-2SOR** are almost identical after annealing even at 200° C, except that the absorption spectra of **PF-1SOR** films became a little broader, indicating a possible physical change, for example, in film morphology. This notion is supported by the increase in the absorption in the long wavelength region outside the true absorption band due to scattering. Those of the **PF** films also broaden and the absorption maximum shifts to the red by 4 nm after annealing, implying some minor physical and/or chemical change.

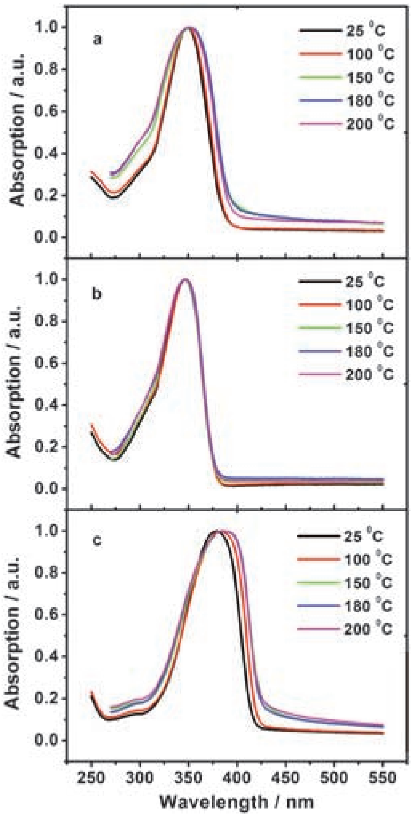


Figure 4. UV-VIS absorption spectra of a) **PF-1SOR**, b) **PF-2SOR** and c) **PF** films before and after thermal annealing in air at various temperatures.

Figure 5 shows the fluorescence spectra of these polymer films before and after annealing. It is clear that the emission

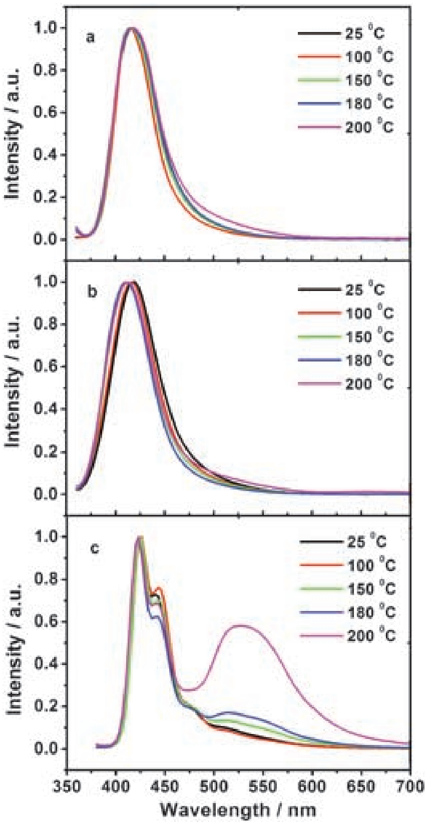


Figure 5. Fluorescence spectra of a) **PF-1SOR**, b) **PF-2SOR** and c) **PF** films before and after thermal annealing in air at various temperatures. The spectra in (c) are normalized with regard to the "blue" band.

spectra of copolymers **PF-1SOR** and **PF-2SOR** remain nearly identical, except for the discernable spectral position change which is probably due to the same physical factors as in the absorption spectra. The emission at 410 or 413 nm were stable, even after annealing at such a high temperature as 200 °C for 2.5 h. The absence of any new emission band excludes the formation of any new emissive species in **PF-1SOR** and **PF-2SOR**. However, under identical thermal treatment, the **PF** films exhibited the well-known "green" band at 500–600 nm after annealing at and over 150° C. The ratio of the emission intensities of the "blue" and the "green" band increased in favor of the latter. The green emission in **PF** films is assigned to the fluorenone defects which were generated by oxidation of fluorene units when **PF** was exposed to oxygen at high temperature, although no typical absorption band at around 1718 cm^{-1} was found in the FT-IR spectra of this material. The absence of the keto vibration peak seems reasonable if we make a reference to Jenekhe's report of the FT-IR data of a series of well-defined fluorene–fluorenone copolymers.[15c] In his report, the copolymer with 10 mol% fluorenone (10-FO) showed a strong absorption at 1718 cm^{-1} that is the region of the C=O stretch. This intensity decreased dramatically with decreasing the fluorenone content in the copolymer and only left a small peak in copolymer with 5 mol% fluorenone (5-FO). It is deduced that, although not shown in that report, the keto vibration signal may be too low to be captured in FT-IR spectra for polymer having only around 1 mol% of fluorenone group (1-FO). However, the green emission from the fluorenone moiety in 1-FO films is five times stronger than the blue emission, which reveals the important contribution of the keto moieties to the undesired green emission even at tiny concentration.

Compared with **PF**, the blue fluorescence of **PF-1SOR** and **PF-2SOR** is surprisingly stable, even after annealing at a high temperature of 200° C. This supports our initial hypothesis that introduction of the bulky (3,5-di(*tert*-butyl)phenoxy)sulfonyl groups would prevent the undesired oxidation of the fluorene segments.

Electroluminescence: The EL properties of **PF-1SOR** and **PF-2SOR** were investigated using double-layer light-emitting diodes (LEDs) with the device configuration of ITO/PEDOT:PSS(40 nm)/polymer(70 nm)/Ca(50 nm)/Al(100 nm), in which ITO is indium tin oxide and acts as anode, PEDOT:PSS is poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) as hole injection layer, polymer stands for the present **PF-1SOR**, **PF-2SOR** or **PF** and as active emitting layer, and Ca as cathode and is protected by a layer of Al. The EL spectra of these devices under various driving voltages are shown in Figure 6. It is clear that both **PF-1SOR** and **PF-2SOR** devices emit in the blue exhibiting a single peak at 445 (Figure 7a) and 435 nm (Figure 7b), respectively.

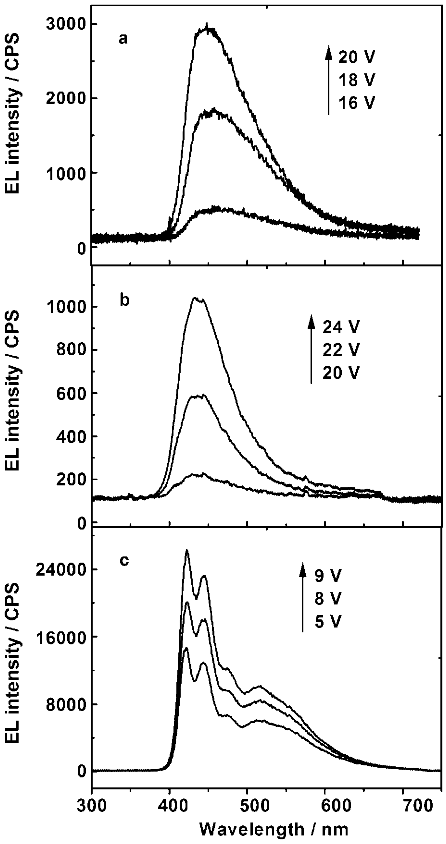


Figure 6. EL spectra of a) **PF-1SOR**, b) **PF-2SOR** and c) **PF** under various driving voltages in their double-layer LEDs.

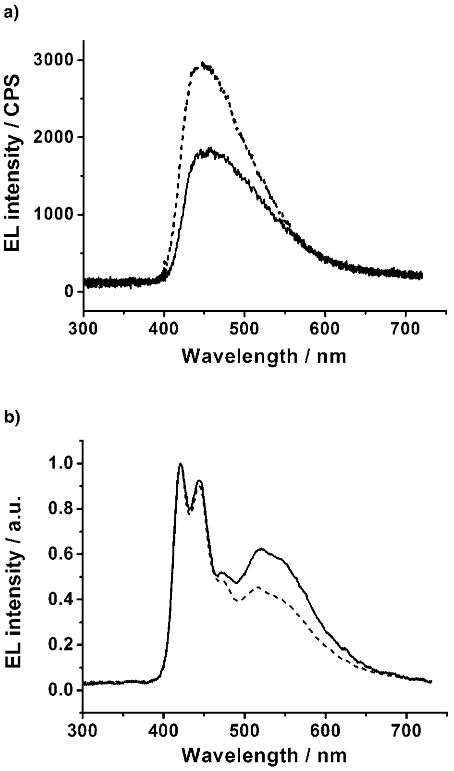


Figure 7. EL spectra of a) **PF-1SOR** and b) **PF** in their double-layer LEDs before (-----) and after (——) continuous operation at 5 mA cm^{-2} for 1 h. The spectra in b) are normalized with regard to the "blue" band.

The EL spectra are similar to the PL in spectral shape, despite a red shift of 32 nm for **PF-1SOR** and 24 nm for **PF-2SOR** and the presence of band tailing in the long wavelength region. The EL spectral red shift compared with PL is commonly observed in most organic and polymeric LEDs. Apparently, the EL spectra of both **PF-1SOR** and **PF-2SOR** devices are independent of the driving voltage, indicating a stable emission color with respect to the excitation intensity. However, the EL spectra of the **PF** device always consist of the blue parts at 422, 445 and 475 nm which are consistent with those in PL of the fresh **PF** films and a broad green component with a peak at 518 nm, even at low driving voltage of 5 V (Figure 6c). The green emission could be observed in EL of the fresh **PF** LED, but not in PL of the fresh **PF** films. There have been similar reports that the green emission from the fluorenone is stronger in EL than in PL.[11c,15] This is because the low-energy keto defects can be excited not only by energy transfer from the fluorene moieties but also by direct charge trapping in the EL device made of **PF**, while only by energy transfer in PL of **PF** films. It should be noted that the EL intensity and current density (not shown) of **PF-1SOR** and **PF-2SOR** devices are lower than those of the **PF** device under same experimental conditions, due to the lower fluorescence quantum yields and possibly lower charge carrier mobilities of these two polymers. This may be caused by the bulky side groups which give rise to a dilution effect.

The spectral stability at high voltages of **PF-1SOR** and **PF-2SOR** was investigated by comparing the EL spectra of their LEDs before and after continuous operation under a constant current density in vacuo. To evaluate the spectral stability of these polymers, the **PF** device was studied similarly. Figure 7a and b illustrates the EL spectra of **PF-1SOR**, as an example, and a **PF** double-layer devices before and after continuous operation under a constant current density of 5 mA cm^{-2} for 1 h in vacuo. Except for the decrease in light intensity, no significant change in spectral characteristic was found in the **PF-1SOR** device after continuous operation, indicating an electrically stable blue emission of **PF-1SOR**. However, the intensity of the green band at 518 nm in **PF** device increased dramatically on expense of that of the blue emission at 422 nm after the same continuous operation, resulting in further deviation of the overall emission color from the initial blue one.

Conclusion

Novel fluorene- and phenylene-based polymers with sulphonate side groups, **PF-1SOR** and **PF-2SOR**, were synthesized by Suzuki polycondensation as blue light-emitting materials. They display a nematic liquid crystalline phase after proper temperature treatment and do not show isotropization up to a temperature close to their decomposition. **PF-1SOR** and **PF-2SOR** have higher energy band gaps than the comparable fluorene homopolymer **PF** and emit structureless blue fluorescence in both solution and film form. The spectral stability was studied by annealing the fresh films in air at various temperatures and monitoring the absorption and fluorescence spectra. Unlike **PF**, the films of **PF-1SOR** and **PF-2SOR** never showed the well-known green emission band that is seen in **PF** even if these materials were annealed at a temperature of 200 °C for 2.5 h in air. Instead the pure blue fluorescence was maintained. **PF-1SOR** and **PF-2SOR** display blue electroluminescence in their double-layer LEDs independent of the driving voltage. In contrast to a continuous increase during operation in the intensity of the green emission band in the **PF** device, the EL spectra of **PF-1SOR** did not show any significant change after continuous operation under 5 mA cm^{-2} for 1 h; this confirms a high electrically spectral stability of **PF-1SOR**. The better spectral stability of **PF-1SOR** and **PF-2SOR** is attributed to a combination of the strong electron-withdrawing nature of the sulphonate side groups and the scavenging effect of the 3,5-di(*tert*-butyl)phenoxy moieties in the side groups. Although the fluorescence quantum yield of the polymers **PF-1SOR** and **PF-2SOR** is lower than **PF** and the electroluminance and current density of the LEDs of these polymers are not as high as those of **PF**, the present study definitely provides a strategy to design pure blue light-emitting fluorene-based polymers by introducing suitable side groups.

Experimental Section

Materials and methods: Reactions requiring an inert gas atmosphere were conducted under argon, and the glassware was dried with a heat-gun. Commercial grade reagents were used without further purification. **PF** was purchased from American Dye Sources. THF was distilled from sodium prior to use. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DPX 250 and a Bruker DRX 500 spectrometer. Chemical shifts are given in ppm, referenced to residual proton resonance of the solvents. Elemental analysis was performed on an Elemental Analysis system vario EL II (Hanau Germany). UV/Vis spectra were recorded at room temperature with a Perkin-Elmer Lambda 9 UV/VIS/NIR spectrometer. Photoluminescence spectra were obtained on a Spex Fluorolog II (212) apparatus. Differential scanning calorimetry was measured on a Mettler DSC 30 with a heating and cooling rate of 10 K min^{-1}.

The light-emitting devices with a configuration of ITO/PEDOT:PSS-(40 nm)/polymer(70 nm)/Ca(50 nm)/Al(100 nm) were fabricated by spin coating of the polymer layers on ITO anode. The ITO substrates were patterned and then cleaned by successive 5 min ultrasonications in detergent, de-ionized water, ethanol, and chloroform, followed by treatment with oxygen plasma. PEDOT/PSS (Bayer AG) was spin-coated on pretreated ITO substrate from aqueous dispersion and baked at 120 °C for 1 h. Subsequently the active polymer layer was spin-coated on PEDOT/PSS film from toluene solution after passing through a 0.45 μm PTFE filter, the thickness of which was controlled as 70 nm by adjusting the solution concentration and the spin rate. The Ca/Al cathode was deposited on the polymer layer by thermal evaporation at a rate of 0.5 nm s^{-1} in a vacuum chamber. The emitting area of each pixel is determined by overlapping of the two electrodes as 7 mm^{2}. Electrical and optical measurements of all LEDs were made under high vacuum (10^{-5} mbar) at room temperature. The EL spectra were recorded with an optical multichannel analyzer (EG&G OMA II) after dispersing the light through a digital triple grating spectrograph (EG&G Model 1235). The current and brightness characteristics of the LEDs were measured using computer-controlled Keithley 236 source measure unit and a photomultiplier (Products For Research Inc. Model R928P/1179/1179).

Synthesis of PF-1SOR and PF-2SOR: The intermediate **1**, **2** and **3** were synthesized according to the literature.[16,17] Under an argon atmosphere, equimolar amounts of **1** (4.51 g, 5.31 mmol) or **2** (5.31 mmol) and **3** (3.41 g, 5.31 mmol) were dissolved in a mixture composed of THF (54 mL) and aqueous $NaHCO_3$ solution (32 mL). $[Pd(PPh_3)_4]$ was added in 5×10^{-3} molar equivalents of **1** or **2**. The resulting mixture was stirred for 48 h under reflux. Bromobenzene (0.04 g, 0.3 mmol) was added to end cap the polymer. After additional 24 h under reflux the polymer was precipitated by pouring the reaction mixture into methanol [1 L]. The product was dried and redissolved in toluene. The filtered solution was precipitated in methanol and dried to give polymer **PF-1SOR** or **PF-2SOR** as a colorless solid (95 %).

PF-1SOR: GPC (THF, PPP standard): $M_n = 21000$ g mol^{-1}, $M_w = 35000$ g mol^{-1}, PD = 1.6; ^{1}H NMR (250 MHz, CD_2Cl_2): $\delta = 8.17$ (s, 1 H), 7.89 (brs, 1 H), 7.78–7.76 (d, 2 H), 7.59 (s, 1 H), 7.51–7.50 (d, 4 H), 7.22 (s, 1 H), 6.69 (s, 2 H), 1.98 (brs, 4 H), 1.13 (s, 18 H), 0.96–0.41 (m, 30 H); ^{13}C NMR (250 MHz, $CDCl_3$): $\delta = 151.5$, 149.7, 148.2, 140.2, 136.5, 134.4, 132.7, 130.5, 128.0, 125.4, 121.6, 119.8, 118.2, 115.5, 54.3, 43.8, 33.9, 33.7, 33.0, 30.2, 27.2, 26.1, 21.6, 12.9, 9.3; elemental analysis calcd (%) for $[C_{49}H_{64}O_3S]_n$ ($[733.1]_n$): C 80.28, H 8.80, S 4.37; found: C 79.66, H 8.49, S 4.45.

PF-2SOR: GPC (THF, PPP standard): $M_n = 28000$ g mol^{-1}, $M_w = 53000$ g mol^{-1}, PD = 1.87; ^{1}H NMR (250 MHz, CD_2Cl_2): $\delta = 8.16$ (brs, 2 H), 7.80–7.77 (m, 4 H), 7.63 (s, 2 H), 7.43 (brs, 2 H), 7.30 (s, 2 H), 6.98 (brs, 2 H), 6.72 (s, 4 H), 2.05 (brs, 4 H), 1.15 (s, 36 H), 0.95–0.43 (m, 30 H); ^{13}C NMR (250 MHz, $CDCl_3$): $\delta = 152.6$, 152.0, 149.3, 142.0, 141.0, 137.0, 134.9, 133.0, 130.7, 128.7, 126.5, 122.5, 120.8, 117.1, 55.2, 44.8, 34.96, 34.8, 33.7, 31.3, 28.2, 26.9, 22.7, 14.0, 10.4; elemental analysis calcd (%) for $[C_{69}H_{88}O_6S_2]_n$ ($[1077.6]_n$): C 76.91, H 8.23, S 6.45; found: C 76.87, H 8.08, S 6.35.

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