ELSEVIER

Synthesis and luminescence properties of three novel polyfluorene copolymers

A. Charas[a,b], J. Morgado[a,*], J.M.G. Martinho[a], L. Alcácer[a], S.F. Lim[c], R.H. Friend[c], F. Cacialli[c,d]

[a]*Departamento de Engenharia Química, Instituto Superior Técnico, Avenida Rovisco Pais, P-1049-001 Lisboa, Portugal*
[b]*Instituto Tecnológico e Nuclear, P-2686 Sacavém, Portugal*
[c]*Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, UK*
[d]*Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK*

Abstract

We report on the synthesis and characterization (including structural, optical, electrochemical and electroluminescence properties) of three alternating F-*alt*-X copolymers, where F is 9,9-bis(2′-ethylhexyl)fluorene unit and the X comonomer varies from a phenylene, to a thiophene and to a thiophene-*S,S*-dioxide unit. Among these X comonomers, the phenylene group is at the origin of a blue-emitting copolymer with unitary luminescence efficiency in solution, while thiophene-*S,S*-dioxide promotes the highest electron affinity. These copolymers are also used in the fabrication of light-emitting diodes.
© 2003 Elsevier Science Ltd. All rights reserved.

Keywords: Polymer synthesis; Polymer physical chemistry; Luminescence

1. Introduction

The huge development of polymer-based light-emitting diodes, LEDs, since the report of electroluminescence, EL, observation in poly(*p*-phenylene vinylene), PPV [1], is the result of a successful combination of efforts in various areas, such as polymer chemistry, materials science and device physics. The driving force behind this evolution is the preparation of efficient devices, operating at low voltages and emitting in the full visible range of the spectrum (though, for full color displays, only the primary red, green and blue (RGB) colors are required). In order to optimize these parameters, different materials and combinations have been investigated. The ability to chemically modify the polymers (both the main chain and the pendant side groups) in a predictable way, when targeting color tuning, the control of the energetic position of the frontier levels (highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO)) and, to

some extent, the efficiency of light emission, is at the heart of the most significant progresses in this area [2]. Among the known luminescent polymers, polyfluorenes are presently the most attractive class of polymers for LEDs [3], and they are very promising also for fabrication of efficient photovoltaic diodes [4]. Advantages of these polymers include their capability to emit in the blue part of the visible spectrum, their chemical and photochemical stability, the high purity with which they can be synthesized, liquid crystalline properties and durability under operation in LEDs [5–7].

Various fluorene-based copolymers have been prepared, aiming at achieving color tunability over the visible spectrum and tuning of the frontier levels energetic position in order to minimize (possibly eliminate) the anodic and cathodic injection barriers of LED structures [3]. More specifically, the synthesis and properties of various fluorene–thiophene copolymers were reported by various groups [3,8–13]. Scherf et al. [14], have recently reported on the synthesis of a series of fluorene–oligothiophene alternating copolymers, and related their optical properties with the size of the oligothiophene unit.

* Corresponding author. Tel.: +351-21-841-8451; fax: +351-21-841-7675.
E-mail address: jmorgado@gcsi.ist.utl.pt (J. Morgado).

However, systematic studies on the effect of the comonomers combined with the fluorene units are still lacking. We have also been studying similar fluorene-based copolymers [15–17], combining thiophene-based units and 9,9-bis(2′-ethylhexyl)fluorene, looking for the systematic variation of the copolymers optical and electrochemical properties with the type of thiophene-based comonomer used. We chose 9,9-bis(2′-ethylhexyl)-fluorene, instead of the isomer with linear side groups, in an attempt to reduce solid state packing and the formation of low energy interchain states, such as aggregates or excimers, which have been suggested as responsible for the existence of a low energy emission peak in polyfluorenes [18–20]. Note that, recently, the existence of keto defects (fluorenone) was also suggested to be at the origin of such low energy emission [21].

The copolymerization of thiophene-S,S-dioxide with 9,9-bis(2′-ethylhexyl)fluorene was shown to increase both the ionization potential (IP) and the electron affinity (EA) of the copolymer in comparison with the use of thiophene [15]. The choice of this comonomer follows the report, by Barbarella et al., [22,23] showing that this thiophene functionalization was very effective at increasing EA of oligothiophenes. Note that, more recently, Beaupré and Leclerc [24] reported on the preparation and characterization of two new alternating copolymers combining 9,9-dihexylfluorene and oligothiophenes with the central thiophene unit functionalized to S,S-dioxide.

Here, we present a detailed report on the synthesis, characterization and properties of three F-alt-X alternating copolymers, where F is the 9,9-bis(2′-ethylhexyl)fluorene unit and X is either a phenylene, a thiophene or a thiophene-S,S-dioxide unit (see Scheme 1). These copolymers are members of a larger family of copolymers we have been studying [15–17]. They were prepared using Suzuki coupling [25] of the appropriate dibrominated and boron ester monomers (Scheme 1).
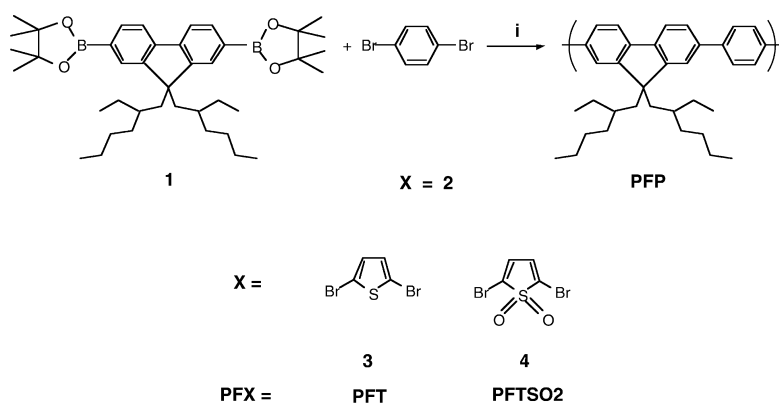
2. Experimental

2.1. Measurements

^{1}H and ^{13}C NMR spectra were recorded on a Varian spectrometer (300 and 75 MHz, respectively), in CDCl$_3$ with tetramethylsilane as internal reference. FT-IR spectra were recorded using a Mattson 1000 spectrophotometer, dispersing the samples in KBr. Number-average (M_n) and weight-average (M_w) molecular weights were estimated by Gel Permeation Chromatography (GPC) in a Waters 51 chromatograph equipped with two Waters UltraStyragel columns (1000–500 Å) in series and with two detectors (a Water 410 Differential Refractometer and a Scanning Fluorescence Detector), at a flux rate of 1 ml/min. GPC analyses were performed on filtered solutions (0.45 μm, Millipore Millex HV) of the copolymers in tetrahydrofuran (THF) and using polystyrene standards.

UV–visible absorption spectra were recorded on a Jasco V500 spectrophotometer, both for dilute copolymers solutions in cyclohexane or chloroform ($\sim 10^{-6}$ M, based on the repeat unit) and for thin copolymers films spun coated on spectrosil substrates from concentrate chloroform solutions ($\approx 4\%$ by weight). Fluorescence (or photoluminescence) spectra, for both copolymers solutions and solid films, were obtained on a Spex Fluorog F112A spectrofluorimeter, by exciting the polymer samples at the wavelength corresponding to the absorption maximum, except for PFTSO2 where two absorption bands were observed, in which case the sample was excited at the two maximum absorption peaks.

Solution fluorescence quantum yields (or photoluminescence efficiencies, Φ_{PL}) were calculated by the relative method, based on the comparison of the areas of the fluorescence spectra of a reference and of the sample [26]. The experimental spectra were multiplied by a correction curve that considers the dependence of the spectrofluorimeter detecting system response on the photon energy.

(i) K$_2$CO$_3$ (aq)/THF, Pd[(PPh$_3$)$_4$], reflux, in the dark, under N$_2$, 3 days (minimum).

Scheme 1. Polymerization reaction, molecular structure of the various comonomers X combined with the fluorene unit and identification of the copolymers PFX or -(F-alt-X)$_n$-.

Several standards were used to cover the spectral range of the different light-emitting polymers in order to minimize the errors associated to this correction procedure. The copolymers solutions used in these studies, either in chloroform or cyclohexane, were saturated with argon, with polymer concentrations of about 10^{-6} M, so that their maximum absorbance values were below 0.1, in order to avoid inner-filter effects. As reference substances, we used 9,10-diphenylanthracene in cyclohexane ($\Phi_{PL} = 0.90$) [26], quinine sulphate in 0.1 M H_2SO_4 ($\Phi_{PL} = 0.546$) [27] and rhodamine 101 in acidified ethanol ($\Phi_{PL} = 0.89$) [28]. All solvents were spectroscopic grade. In Φ_{PL} calculations we have taken into account the refractive indexes of the (diluted) solutions, which were considered equal to those of the pure solvents. Solid state photoluminescence efficiencies were determined for thin films spun coated onto spectrosil discs, using an integrating sphere upon laser-excitation at 325 or 442 nm, depending on the sample absorption spectrum, according to the procedure reported by de Mello et al. [29].

Cyclic voltammetry (CV) was performed using a Solartron potentiostat (model 1285), in a cell containing tetra-n-butylammonium tetrafluoroborate (Bu_4NBF_4) in degassed acetonitrile (HPLC grade, Aldrich) as supporting electrolyte, at a scan rate of 50 mV/s. A set of three electrodes was used, namely, a saturated calomel reference electrode (SCE) (calibrated against ferrocene, Fc/Fc^+ 0.41 V), a platinum wire as counter electrode and a platinum disc as working electrode (working area $\approx 0.2\ cm^2$). The polymer films were deposited on the platinum-working electrode by solvent casting. As the energy level of Fc/Fc^+ is estimated at 4.8 eV below the vacuum level [30], we estimate the IP and EA according to the relations: IP (eV) $= E_{ox}^{onset} + 4.39$ and EA (eV) $= E_{red}^{onset} + 4.39$.

2.2. LEDs fabrication and characterization

ITO-coated glass substrates ($\sim 10\ \Omega$/square) were cleaned with oxygen–plasma for ten minutes, prior to use [31]. The luminescent copolymers were spun coated from their filtered (Whatman, PTFE 1 μm membranes) $CHCl_3$ solutions, yielding films of 100 nm thickness, measured with a DEKTAK profilometer. Calcium cathodes, with an additional protective layer of aluminum, were thermally evaporated at a bare pressure of about 5×10^{-6} mbar, defining pixel areas of $\sim 2\ mm^2$. The devices were tested under vacuum (~ 0.01 mbar), using a calibrated large area silicon photodiode to measure the electroluminescence (EL) intensity. EL spectra were recorded using a single grating UV-enhanced CCD spectrograph (Oriel Instaspec IV).

2.3. Materials

The palladium(0) tetrakis(triphenylphosphine), $Pd(PPh_3)_4$, catalyst was purchased from Aldrich and handled in a glove box. Column chromatography was carried out on silica gel 60 (Merck). All the solvents were purified according standard methods [32,33] and were degassed prior to use. Deionized water used in the polymerization reactions was degassed by bubbling Ar for 3–4 h at about 70 °C. Thiophene, fluorene, 1,4-dibromo-benzene (**2**) and 2,5-dibromothiophene (**3**) were purchased from Aldrich and used as received. 2,5-dibromothiophene-S,S-dioxide (**4**) was prepared from thiophene according to the procedure reported by Furukawa et al. [34], though two steps (instead of a one-step reaction), each comprising lithiation and sililation, were required to obtain the 2,5-bis(trimethylsilil)thiophene intermediate from thiophene. 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-bis(2′-ethylhexyl)fluorene (**1**) was obtained from fluorene, according to the method reported by Ranger and Leclerc [35] for the preparation of analogous compounds. All reactions were carried out under inert atmosphere (Ar or N_2).

2.4. General procedure of the polymerization reactions

The polymerization reactions were carried out in a refluxing THF/aqueous potassium carbonate (or sodium carbonate) (2 M) medium containing equimolar amounts of the carefully purified boron ester and dibrominated monomers and a catalytic amount of $Pd(PPh_3)_4$, for a long period (3–7 days), in the dark and vigorous stirring under N_2. The copolymers were precipitated by drop wise addition of the cooled reaction mixture to a five-fold volume of methanol and were collected by filtration. The purification was performed by dissolution of the collected solid in a minimum amount of $CHCl_3$ and by the addition of the filtered solution to methanol. This procedure was repeated two more times. The collected copolymers were dried under vacuum for 24 h.

2.4.1. Poly[2,7-(9,9-bis(2′-ethylhexyl)fluorene)-alt-1,4-phenylene] (PFP)

The product, prepared according to the general procedure, was further purified by Soxhlet extraction with acetone (24 h) to remove traces of catalyst and low molecular weight compounds. The copolymer was isolated as a pale yellow powder, in 58% yield (0.81 g starting from 1.93 g (3 mmol) of the fluorene boron ester). Anal. calcd for $(C_{35}H_{44})_n$: C: 90.46%, H: 9.54%. Exp. C: 89.31%, H: 11.36%. ^{1}H NMR: δ (ppm): 7.85–7.78 (6H, m, aromatic), 7.70 (4H, m, aromatic), 2.13 (4H, m, $-CH_2$) 0.91–0.88 (16H, m, aliphatic), 0.66–0.58 (14H, m, aliphatic). ^{13}C NMR: δ (ppm): 151.35, 140.38, 139.04, 127.45, 127.05, 126.03, 122.68, 120.01, 55.11, 44.60, 34.70, 33.86, 28.24, 27.13, 22.76, 14.01, 10.39. FT-IR (KBr, cm^{-1}): 2956, 2925, 2872, 1460, 1380, 810.

2.4.2. Poly[2,7-(9,9-bis(2′-ethylhexyl)fluorene)-alt-2,5-thiophene] (PFT)

The product obtained by the general procedure, was further purified from traces of catalyst and low molecular weight compounds by Soxhlet extraction with acetone. The copolymer was isolated as a bright yellow powder, in 58% yield (0.82 g starting from 1.93 g (3 mmol) of the fluorene boron ester). Anal. calcd for $(C_{33}H_{42}S)_n$: C: 84.20%, H: 8.99%, S: 6.81%. Exp. C: 83.83%, H: 8.76%, S: 6.20%. ^{1}H NMR: δ (ppm): 7.71–7.66 (6H, m, fluor.), 7.38 (2H, s, thiop.), 2.10 (4H, m, $-CH_2$) 0.91 (16H, m, aliphatic), 0.68–0.58 (14H, m, aliphatic). ^{13}C NMR: δ (ppm): 151.53, 144.21, 140.43, 132.75, 124.69, 123.72, 121.15, 120.08, 55.08, 44.48, 34.78, 33.88, 28.24, 27.20, 22.81, 14.06, 10.42. FT-IR (KBr, cm^{-1}) 2956, 2923, 2856, 1608, 1460, 1380, 880, 795.

2.4.3. Poly[2,7-(9,9-bis(2′-ethylhexyl)fluorene)-alt-2,5-thiophene-S,S-dioxide] (PFTSO2)

It was isolated as an orange powder in 58% yield (0.87 g starting from 1.93 g (3 mmol) of the fluorene boron ester). Anal. calcd for $(C_{33}H_{42}SO_2)_n$: C: 78.84%, H: 8.42%, S: 6.38%. Exp. C: 80.44%, H: 9.07%, S: 6.35%. ^{1}H NMR: δ (ppm): 7.84–7.64 (6H, m, aromatic), 7.11 (2H, s, thiophene), 2.11 (4H, m, $-CH_2$), 0.89–0.56 (30H, m, aliphatic). ^{13}C NMR: δ (ppm): 151.09, 150.08, 140.99, 127.44, 125.38, 124.58, 120.76, 119.26, 54.27, 43.40, 33.71, 32.84, 27.13, 26.00, 21.69, 12.99, 9.28. FT-IR (KBr, cm^{-1}): 2956, 2923, 2871, 1606, 1459, 1379, 1309 (SO$_2$), 1138 (SO$_2$), 890, 816.

3. Results and discussion

3.1. Synthesis and characterization

The copolymers were obtained in reasonably good yields (after purification) and with moderate average molecular weights (Table 1), as typically obtained by the Suzuki type of polymerization reaction. The copolymers show good solubility in common organic solvents, such as chloroform, tetrahydrofuran, toluene or xylene.

3.2. Optical and electrochemical properties

Fig. 1 shows the absorption and fluorescence spectra of

Table 1
Number-average (M_n) and weight-average (M_w) molecular weights and polydispersities (PD)

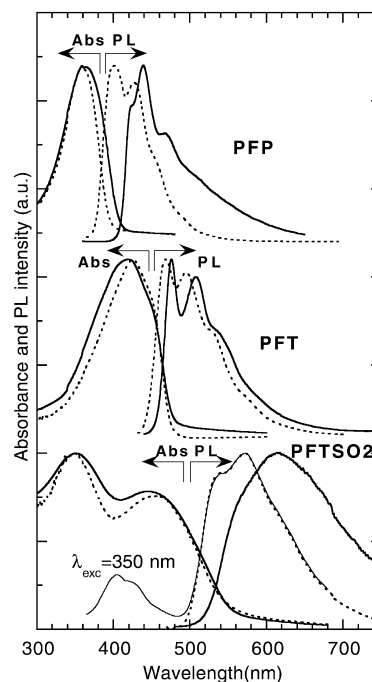| Polymer	Yield (%)	M_n; M_w	PD
PFP	58	12,700; 50,230	3.9
PFT	58	14,100; 48,200	3.4
PFTSO2	58	8700; 27,400	3.1

Fig. 1. Optical absorbance and emission spectra of the copolymers PFP, PFT and PFTSO2 in cyclohexane solution (doted line) and in solid state (continuous line). Excitation was at the absorption maximum. In case of PFTSO2 in solution, two excitation wavelengths were used (corresponding to the two absorption bands) with the solid thinner line corresponding to the emission spectrum obtained upon excitation at the lower wavelength (350 nm).

the three copolymers in dilute cyclohexane solutions and as solid films. On going from PFP to the copolymers incorporating thiophene units there is a significant red-shift of the emission color, both in solution and solid state, which follows the decrease of the optical gap, $E_{g,opt.}$, taken as the absorption onset of the solid films (see Table 2).

The solution absorption spectrum of PFT is red-shifted in relation to that of PFP, and the emission is shifted from blue to the blue-green region of the visible range ($\lambda_{max} = 468$ nm). The decrease of the $\pi-\pi^*$ transition energy upon substitution of the phenylene by a thiophene unit is attributed to inductive effects (thiophene is an electron rich system), which contribute to the reduction of the optical gap, and to an increase of the polymer chain planarity and the consequent increase of the effective conjugation length (increased delocalization). Note that the twist angle in a phenylene–thiophene block is predicted to be smaller than in a phenylene–phenylene unit [36]. A similar red-shift of the emission spectrum, upon substitution of a phenylene by thiophene unit in alternating copolymers based on 9,9-dioctylfluorene, was also observed by Ranger and Leclerc [35]. Interestingly, the dioxide functionalization of the S atom in the thiophene unit lowers the optical gap and red-shifts the emission of the resulting copolymer (PFTSO2) in relation to PFT. A similar red-shift, upon such modification of the thiophene unit, was previously observed in oligothiophenes by Barbarella et al. [22,23].

Table 2
Optical and electrochemical properties of the copolymers

Polymer	$E_{g,opt.}$ (eV)	$\lambda_{max,emiss.}$ film (nm)	Φ_{PL} (%) soln. (C_6H_{12})	Φ_{PL} (%) soln. ($CHCl_3$)	Φ_{PL} (%) film	E_{ox}^{onset} (V)	E_{red}^{onset} (V)	IP (eV)	EA (eV)
PFP	2.94	439	100[dpa]	96[dpa]	9.4	1.45	−2.00	5.84	2.39
PFT	2.54	476	61[sq]	51[sq]	3.2	1.10	−1.55	5.49	2.84
PFTSO2	2.19	615	19[rhd]	16[rhd]	0.5	1.23	−1.45	5.62	2.94

dpa, 9,10-diphenyl-anthracene as standard; sq, quinine sulphate as standard; rhd, rhodamine 101 as standard.

The absorption spectrum of PFTSO2 shows two distinct maxima between 600 and 300 nm (see Fig. 1). The band occurring at lower energy is attributed to a $\pi-\pi^*$ transition. Beaupré and Leclerc [24] have recently reported on the properties of fluorene-based copolymers incorporating TSO2 units, which show also two absorption bands in the same spectral region. While they attributed the low energy band to a $\pi-\pi^*$ transition, the higher energy maximum (at 394 nm), was attributed to a n,σ_{S-O}^* transition. We could not definitely conclude about the origin of the higher energy band of PFTSO2 absorption spectra. We observed that, on going from non-polar (cyclohexane) to a polar solvent (chloroform), there is a red-shift of the lower energy band of PFTSO2 absorption spectra, suggesting it is indeed associated to $\pi-\pi^*$ transition [37]. However, the higher energy band is very slightly blue-shifted when changing from non-polar to the polar solvent, suggesting a different origin or mixed contributions. We further note that short conjugation segments absorption can also contribute to the higher energy absorption bands.

Though not shown in Fig. 1, solution fluorescence excitation spectra at emission maximum of all copolymers are identical to the corresponding absorption spectra. This is particularly relevant in the case of PFTSO2, as this similarity indicates that both absorption bands contribute to the lower energy emission band.

In solution, upon excitation at the higher-energy band of PFTSO2 (350 nm), a low intensity emission band at about 400 nm is observed, besides the intense emission band at lower energies, as shown in Fig. 1. In solid state, this high energy emission nearly disappears, suggesting the existence of an efficient energy transfer process to the lower energy excited state, as a result of shorter interchain distances. Supporting evidence for such an energy transfer process
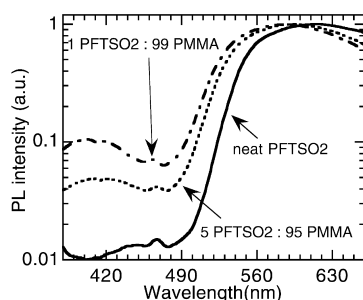

Fig. 2. Comparison of the emission spectra of PFTSO2: PMMA blends (composition expressed as the luminescent polymer content, by weight) with that of neat PFTSO2 in solid film. Excitation was at 350 nm.

comes from studies in blends of PFTSO2 and polymethyl-metacrilate (PMMA), with 1 to 5%, by weight, content of the luminescent polymer. As shown in Fig. 2, the dilution of PFTSO2 in the PMMA matrix leads to an increase of the high energy emission band, resulting from a decrease of the energy transfer efficiency, owing to an increased separation between donor and acceptor sites. Furthermore, there is a blue-shift of the PL spectrum on going from the neat PFTSO2 to the PFTSO2:PMMA blends, which follows the trend found when comparing solid state and dilute solution PL spectra of PFTSO2 (see Fig. 1).

The origin of the higher energy emission of PFTSO2 is not yet clear. It is probably due to emission from confined chromophores, possibly associated to chain defects. It is worth noting that this band closely overlaps with the emission spectrum of an oligo(9,9-bis(2′-ethylhexyl)fluor-ene), with average polymerization degree of 6[1]. The fact that this high energy emission band is clearly observed in dilute solution, evidencing that intrachain excitation migration or energy transfer is not complete within the lifetime of the excited state, suggests it is associated with a disruption of the π system (broken conjugation), and/or to a misorientation of the transition dipole moments associated with transitions between the 'localized defects' and the lower energy π^* delocalized state. The presence of much shorter oligomers may also contribute to a high energy emission, though it does not explain the 'bimodal' distribution (two bands) of the emission spectrum, as this would be expected to give origin to a broader band extending to higher energies.

The chain defects, which are likely associated to the higher energy localized states of PFTSO2, could have been left after the polymerization reaction and/or could result from degradation of the polymer. We note that, in spite of the efforts to minimize the exposure of the polymer solutions to daylight during their purification, it is possible that some photo-oxidation has still occurred. Solution fluorescence aging studies, by exposure of PFTSO2 cyclohexane solutions to daylight, do not fully support the possibility that the high energy emission is entirely due to confined chromophores formed as a result of photodegrada-tion. Fig. 3 compares the aging effect of diluted PFTSO2/cyclohexane solutions on the luminescence spectra, when

---

[1] We have prepared this oligomer by the general polymerization process followed in the preparation of the copolymers.
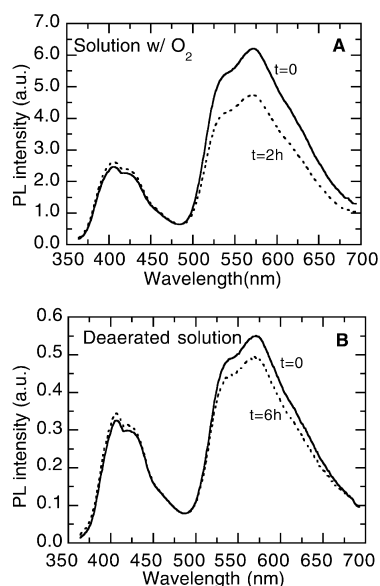
Fig. 3. Aging of fluorescence spectra of PFTSO2 diluted solutions in cyclohexane, both saturated with oxygen (A) and deaerated (B), upon exposure to daylight. Excitation was at 350 nm.

the solutions were either saturated with air (an oxygen) or when they were carefully deaerated.

As shown in Fig. 3(A), the aging of oxygen-saturated solutions for two hours induces a strong quenching of the low energy emission band of PFTSO2, which is attributed to photodegradation. A small increase of the high energy emission band is observed. In terms of integrated intensities, the low energy emission band decreases to about 76% (of the initial value), while the high energy emission band increases by about 7% only. If the solution is carefully deaerated, after 6 h exposure to day light, the lower energy emission band integrated intensity decreases to about 91% (of the initial value) and the higher energy band integrated intensity increases by about 6%. These results show that, even for carefully deaerated solutions, there is a small decrease of the lower energy emission with time. The aging effect on the higher energy emission intensity, which does not appear to be as oxygen sensitive as the lower energy emission, is consistent with a minor contribution from photodegradation-induced 'emissive defects'.

We should add that, twisted intramolecular charge transfer states (TICT) are proposed to be at the origin of dual fluorescence of some molecules, which combine electron-donating and electron-withdrawing groups [38]. We believe this is not the case for PFTSO2, as such dual fluorescence is observed only in polar solvents (as the stabilization of the excited charge transfer state is due to a relaxation of the solvent molecules), while in the case of PFTSO2 the two emission bands are observed, with similar intensity, in both cyclohexane and chloroform.

The absorption spectra are not significantly red-shifted on going from solution to solid state (see Fig. 1). The solid state emission spectra of all copolymers are red-shifted in comparison with dilute solution, leading to emission in the orange region of the spectra for PFTSO2. This red-shift of the emission is attributed to the combined effect of interchain interactions and increased packing in the solid state, that leads to a lowering of the energy of the excited state from which emission occurs. The spectral distribution of the solid state emission spectra of either PFP or PFT is similar to that of the corresponding solution emission spectra, apart from the above mentioned red-shift. This is more pronounced for PFT, where there is an almost perfect overlap, when the solution PL spectrum is red-shifted by about 45 meV. In case of PFP, this shift is of about 254 meV, indicating a more pronounced stabilization of the excited state when going from solution to solid state. In addition, the intensity of the longer-wavelength tail of PFP PL spectrum appears to be slightly higher in solid state, which is attributed to a small contribution of interchain excited states to the total fluorescence emission. In the case of PFTSO2, besides the red-shift of the lower energy emission band, in going from solution to solid state (of about 148 meV), there is also a decrease of vibronic structure resolution. Excitation spectra of PFTSO2 films were recorded for emission at 570, 612 and 680 nm and they were found to be identical. These results provide evidence for very small or even absent contribution of interchain states, such as excimers or aggregates, for the solid state PL spectra of these copolymers. This is an interesting result as significant contribution of such interchain states is usually observed in copolymers based on the 9,9-dioctylfluorene unit [35], an isomer of the 9,9-bis(2'-etylhexyl)fluorene unit used in this study. We consider that the use of the branched 2-ethylhexyl as substituent of the fluorene unit promotes a reduction of conformational ordering and/or packing in solid state.

Table 2 shows photoluminescence quantum yields, Φ_{PL}, for the synthesized copolymers, both in cyclohexane and chloroform solutions and in solid state. A very strong PL quenching occurs in going from solution to solid state, as commonly observed, as a result of stronger interchain interactions caused by the denser packing, and a reduction of the free-volume available for structural rearrangement of the molecular geometry, that is often more planar than in solution. Both the planarized geometry and the increased interchain interactions lead to a higher exciton mobility, and therefore to a higher probability of collisions between excitons and quenching sites. Interchain interactions also tend to reduce the oscillator strength of the transition. However, in our case, and as we discussed above, we consider that the formation of distinct species such as aggregates or excimers is negligible.

In Table 2, we also compare Φ_{PL} values obtained in cyclohexane and in chloroform solutions. The Φ_{PL} values are significantly higher in the non-polar solvent (cyclohexane) [39]. The fluorescence quantum yield of PFP is about 100% in both cyclohexane and chloroform solutions. To the best of our knowledge, this value is the highest among those

reported for blue-emitting fluorene-based copolymers in solution. The modification of the X unit from a phenylene to a thiophene unit, brings about a reduction of Φ_{PL} down to 61% in cyclohexane solution. This variation is attributed to the heavy-atom effect of sulfur in the thiophene unit, which facilitates the intersystem crossing to triplet excited states. Note that, intersystem crossing has been identified as the main deactivation pathway of oligothiophenes [40]. In agreement with our findings, Ranger and Leclerc [35] reported a similar reduction of Φ_{PL} in 9,9-dioctylfluorene copolymers, when thiophene-based units were used instead of phenylene comonomers. In fact, these authors observed a decrease of Φ_{PL} from 86 to 49% when the unit copolymerized with 9,9-dioctylfluorene is changed from a phenylene to a thiophene unit.

We further note that the relevance of the sulfur heavy atom effect in the intersystem crossing rate in polythiophenes was recently addressed by Cadby et al. [41]. It was found that by reducing the sulfur content, for instance by replacing every third thienyl ring with a furanyl ring, there is a decrease of such intersystem crossing rate. When a phenyl ring is used instead, such reduction is even more pronounced. These results are also in agreement with the variation of Φ_{PL} with the chemical nature of the X comonomer we have discussed above.

The cause of the significant reduction of Φ_{PL} upon *S,S*-dioxide functionalization of the thiophene ring, that is, in going from PFT to PFTSO2, is not yet clear. In fact, this modification, by removing the sulfur lone-pairs from the thienyl π system (dearomatization) [22,23], was expected to lead to a decrease of sulfur heavy atom effect and an increase of Φ_{PL}, at variance with the experimental results. Note, however, that two dihexylfluorene-based copolymers, which incorporate oligothiophene comonomers with sulfones, show a maximum solution fluorescence quantum yield of 5% [24], which is significantly lower than the value of 19% we obtained for PFTSO2.

In solid state, a similar evolution of the Φ_{PL} values with the modifications of the X unit, just described, is observed. The lower Φ_{PL} value for PFTSO2 in relation to that of PFT contrasts with the improvement of the solid-state luminescence efficiency of oligothiophenes, upon similar *S,S*-dioxide functionalization of thiophene, reported by Gigli et al. [42]. Such enhancement of the solid-state Φ_{PL} was related to a reduction of non-emissive aggregates formation. However, due to the presence of the long alkyl groups on the fluorene unit, the role played by the sulfone groups in reducing intermolecular interactions/aggregation in the copolymers here reported is expected to be less important than in oligothiophenes.

The oxidation and reduction onset potentials, E_{ox}^{onset} and E_{red}^{onset}, respectively, and the calculated values of the IP and EA for the copolymers, are shown in Table 2. The ionization potential decreases from PFP to PFT, reflecting the substitution by a π-electron rich unit copolymerized with fluorene. An increase of both the IP (by 0.13 eV) and the EA

(by 0.10 eV) is found when going from PFT to PFTSO2. This stabilization of the frontier levels (LUMO and HOMO, as measured by EA and IP, respectively) upon the *S,S*-dioxide functionalization of the thiophene ring is in agreement with the reported trend for oligothiophenes, though in such systems a more significant increase of EA was found [42].

It was shown [43] that the effect of the *S,S*-dioxide functionalization of the thiophene ring on the stabilization of the LUMO of oligothiophenes is strongly dependent on both the relative position of the sulfone unit and on the extension of the oligothiophene, being smaller for longer oligothiophenes. This attenuation of the sulfone effect on the LUMO energy with the chain length increase is probably at the origin of its relatively smaller effect on the EA of PFTSO2.

3.3. Application in light-emitting diodes

Table 3 summarizes the electro-optical characteristics of the single-layer (ITO/copolymer/Ca) LEDs. For each device, we calculated the η_{EL}/Φ_{PL} ratio, in which η_{EL} is the internal quantum electroluminescence efficiency, estimated as 4.5 times the external quantum electroluminescence efficiency [44], and Φ_{PL} is the solid state fluorescence quantum yield (Table 2). This ratio is used to assess the efficiency of the device structure in making use of the intrinsic emissive properties of the active copolymer [45].

LEDs based on PFP exhibit the highest EL efficiency, while the maximum luminance is obtained for LEDs based on PFT. In general the EL efficiency values are low, which mainly reflect the low solid state PL efficiencies. The fact that the η_{EL}/Φ_{PL} ratio is also small allows us to anticipate that there is still room for EL efficiency improvement if, for instance, multi-layer device structures and/or blending with better charge transport materials are used. For instance, we have observed that by blending PFTSO2 with poly(9,9-dioctylfluorene), which is a good hole transporting material, a significant increase of both EL efficiency and maximum luminance is observed [46].

Finally, we should mention that the maximum luminance values shown in Table 3 are higher than the values reported for single-layer LEDs fabricated with analogous 9,9-dioctylfluorene-based copolymers [47].

4. Conclusion

Three novel, well defined, alternating copolymers F-*alt*-X, derivatives of the poly[2,7-(9,9-bis(2′-ethylhexyl)fluorene)], were prepared by the Suzuki-coupling type of polymerization. We show that the unit X, copolymerized with the fluorene moiety, effectively controls the optical, luminescence and electrochemical properties of the copolymers. In the design of new materials for full-color displays, the copolymerization is a very good strategy to

Table 3
Characteristics of the single-layer LEDs based on the prepared copolymers

ITO/polymer/Ca	V^{onset} (V)	L_{max} (cd/m^2)	Max. EL efficiency (cd/A)	η_{EL} (%)	η_{EL}/Φ_{PL}
PFP	20	8	0.012 (65 mA/cm^2)	5×10^{-2}	0.005
PFT	19	55	0.004 (393 mA/cm^2)	9×10^{-3}	0.003
PFTSO2	20	0.2	0.0003 (48 mA/cm^2)	1×10^{-3}	0.002

realize color tuning, but its influence on other polymer properties, which ultimately control the EL efficiency and the LEDs operating voltage, cannot be fully anticipated. The use of the thiophene-*S*,*S*-dioxide comonomer was shown to have a lower influence on the energetic position of the copolymers frontier levels than observed in oligothiophenes. In order to gain a better understanding of the optical and luminescence properties of PFTSO2 additional studies are currently in progress.

Acknowledgements

References

[1] Burroughes JH, Bradley DDC, Brown AR, Marks RN, Mackay K, Friend RH, Burn PL, Holmes AB. Nature 1990;347:539.

[2] Friend RH, Gymer RW, Holmes AB, Burroughes JH, Marks RN, Taliani C, Bradley DDC, dos Santos DA, Brédas J-L, Lögdlund M, Salaneck WR. Nature 1999;397:121.

[3] Bernius MT, Inbasekaran M, O'Brien J, Wu W. Adv Mater 2000;12: 1737.

[4] Arias AC, Corcoran N, Banach M, Friend RH, MacKenzie JD, Huck WTS. Appl Phys Lett 2002;80:1695.

[5] Grice AW, Bradley DDC, Bernius MT, Inbasekaran M, Wu WW, Woo EP. Appl Phys Lett 1998;73:629.

[6] Ho PKH, Kim JS, Burroughes JH, Becker H, Li SFY, Brown TM, Cacialli F, Friend RH. Nature 2000;404:481.

[7] Bernius M, Inbasekaran M, Woo E, Wu W, Wujkowski L. J Mater Sci: Mater Electron 2000;11:111.

[8] Lévesque I, Donat-Bouillud A, Tao Y, D'Iorio M, Beaupré S, Blondin P, Ranger M, Bouchard J, Leclerc M. Synth Meth 2001;122:79. references there in.

[9] Sirringhaus H, Wilson RJ, Friend RH, Inbasekaran M, Wu W, Woo EP, Grell M, Bradley DDC. Appl Phys Lett 2000;77:406.

[10] Liu B, Yu W-L, Lai Y-H, Huang W. Macromolecules 2000;33:8945.

[11] Pei J, Yu W-L, Ni J, Lai Y-H, Huang W, Heeger AJ, Macromolecules 2001; 34: 7241.

[12] Cho NS, Hwang D-H, Lee J-I, Jung B-J, Shim H-K. Macromolecules 2002;35:1224.

[13] Scherf U, List EJW. Adv Mater 2002;14:477.

[14] Asawapirom U, Güntner R, Forster M, Farrell T, Scherf U. Synthesis 2002;1136.

[15] Charas A, Morgado J, Martinho JMG, Alcácer L, Cacialli F. Chem Commun 2001;1216.

[16] Charas A, Barbagallo N, Morgado J, Alcácer L. Synth Meth 2001; 122:23.

[17] Charas A, Morgado J, Martinho JMG, Alcácer L, Cacialli F. Synth Met 2002;127:251.

[18] Bradley DDC, Grell M, Long X, Mellor H, Grice A. SPIE Proc 1997; 3145:254.

[19] Lee J, Klaerner G, Miller RD. Synth Meth 1999;101:126.

[20] Lemmer U, Heun S, Mahrt RF, Scherf U, Hopmeier M, Siegner U, Göbel EO, Müllen K, Bässler H. Chem Phys Lett 1995;240:373.

[21] List EJW, Guentner R, de Freitas PS, Scherf U. Adv Mater 2002;14: 374.

[22] Barbarella G, Pudova O, Arbizzani C, Mastragostino M, Bongini A. J Org Chem 1998;63:1742.

[23] Barbarella G, Favaretto L, Sotgiu G, Zambianchi M, Antolini L, Pudova O, Bongini A. J Org Chem 1998;63:5497.

[24] Beaupré S, Leclerc M. Adv Funct Mater 2002;12:192.

[25] Ishiyama T, Murata M, Miyaura N. J Org Chem 1995;60:7508.

[26] Meech SR, Phillips D. J Photochem 1983;23:195.

[27] Melhuish WH. J Phys Chem 1961;65:229.

[28] Pereira EJN, Berberan-Santos MN, Fedorov A, Vincent M, Gallay J, Martinho JMG. J Chem Phys 1999;110:1600.

[29] de Mello JC, Wittmann HF, Friend RH. Adv Mater 1997;9:230.

[30] Pommerehne J, Vestweber H, Guss W, Mahrt RF, Bässler H, Porsh M, Daub J. Adv Mater 1995;7:551.

[31] Kim JS, Granström M, Friend RF, Johansson N, Salaneck WJ, Daik R, Feast WJ, Cacialli FJ. J Appl Phys 1998;84:6859.

[32] Perrin DD, Armarego WLF. Purification of laboratory chemicals, 3rd ed. Oxford: Pergamon; 1988.

[33] Casey M, Leonard J, Lygo B, Procter G. Advanced practical organic chemistry, 1st ed. New York: Blackie, Chapman and Hall; 1990.

[34] Furukawa N, Hoshiai H, Shibutani T, Higaki M, Iwasaki F, Fujihara H. Heterocycles 1992;34:1085.

[35] Ranger M, Leclerc M. Can J Chem 1998;76:1571.

[36] Kang BS, Kim DH, Lim SM, Kim J, Seo M-L, Bark K-M, Shin SC, Nahn K. Macromolecules 1997;30:7196.

[37] Turro NJ. Modern molecular photochemistry. California: Benjamin/Cummings; 1978. p 107.

[38] Valeur B. Molecular fluorescence—principles and applications. Weinheim: Wiley-VCH; 2002. p 62.

[39] Bark K-M, Forcé RK. Spectrochim Acta 1993;49A:1605.

[40] Becker RS, de Melo JS, Maçanita AL, Elisei F. J Phys Chem 1996; 100:18683.

[41] Cadby AJ, Yang C, Holdcroft S, Bradley DDC, Lane PA. Adv Mater 2002;14:57.

[42] Gigli G, Barbarella G, Favaretto L, Cacialli F, Cingolani R. Appl Phys Lett 1999;75:439.

[43] Caldas MJ, Pettenati E, Goldoni G, Molinari E. Appl Phys Lett 2001; 79:2505.

[44] Greenham NC, Friend RH, Bradley DDC. Adv Mater 1994;6:491.

[45] Cacialli F, Li XC, Friend RH, Moratti SC, Holmes AB. Synth Meth 1996;75:161.

[46] Charas A, Morgado J, Martinho JMG, Fedorov A, Alcácer L, Cacialli F. J Mater Chem 2002;12:3523.

[47] Donat-Bouillud A, Lévesque I, Tao Y, D'Iorio M, Beaupré S, Blondin P, Ranger M, Bouchard J, Leclerc M. Chem Mater 2000;12:1931.