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Electrochemical and luminescent properties of poly(fluorene) derivatives for optoelectronic applications

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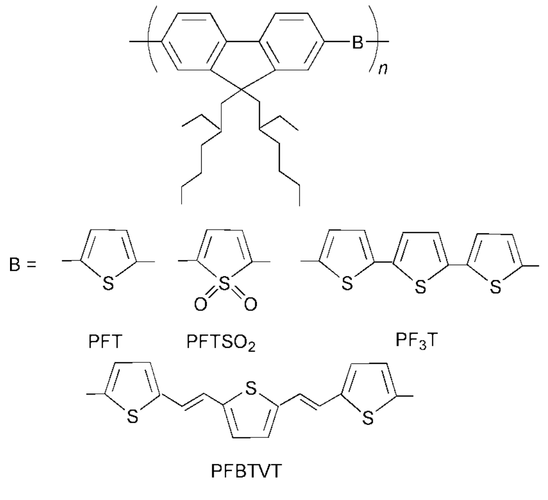
We report the synthesis of novel alternating copolymers of the kind A-*alt*-B, where A is a dialkylfluorene unit and B is an aromatic moiety unit which is varied in order to change the position of the frontier energy levels; in particular we find that the B unit thiophene *S,S*-dioxide is particularly effective at increasing the polymer electron affinity and ionisation potential.

Poly(9,9-dialkylfluorene)s and derivatives are attracting significant interest in the context of polymer-based optoelectronic devices and in particular for the fabrication of efficient and long-lived light-emitting diodes.[1] Both colour tunability and control of the position of the frontier energy levels (electron affinity, EA, and ionisation potential, IP) are important in order to extend the applicability of this class of polymers, with a view to fabrication of full-colour displays and also to optimisation of charge injection from environmentally stable electrodes. From the synthetic point of view, a successful strategy to achieve this goal is the preparation of copolymers combining the fluorene moiety with other electroactive ones, in an alternating coupling pattern (A-*alt*-B). For example, a moiety of interest is the thiophene *S,S*-dioxide, which has been shown to produce an effective increase of EA in oligothiophenes.[2,3]

Here, we report the synthesis and the electrochemical and optical properties of a variety of well-defined A-*alt*-B copolymers, where A is a 9,9-bis(2′-ethylhexyl)fluorene unit and B is either a thiophene unit, a thiophene derivative, an oligothiophene or an oligothienylenevinylene (Scheme 1).

We synthesised the copolymers *via* palladium-catalysed Suzuki coupling[4] from the appropriate dibrominated and boron ester monomers, with a polymerisation yield in the range of 47–58%. The choice of the bulkier 2-ethylhexylfluorene solubilizing substituents, at variance with the more commonly used dioctyl or dihexyl linear chains, is aimed at reducing interchain interactions and ordering. The detrimental role of the interchain excited states on the luminescent polymer properties has been widely reported, in particular for polyfluorenes.[5,6] The polymerisation was carried out in a refluxing tetrahydrofuran–aqueous potassium carbonate solution (2 M) containing $Pd(PPh_3)_4$ as catalyst, for several days, in the dark and under N_2. Copolymers were then purified by dissolution in the minimum amount of $CHCl_3$ and by addition of the filtered solution to a non-solvent (methanol). This process was repeated at least three times, after which the copolymers were dried under vacuum. Monomers and polymers were characterised by standard spectroscopic techniques and elemental analysis. Details of the synthesis and structural characterisation will be reported in a future publication. The molecular weight of the polymers was determined by gel permeation chromatography of their THF solutions, relative to polystyrene standards. The obtained values (Table 1) are typical of the Suzuki type polymerisation reaction.



Scheme 1 Molecular structure of the synthesised copolymers.

We investigated the electrochemical behaviour of the copolymer films by cyclic voltammetry. The ionisation potential (IP) and electron affinity (EA) were estimated from the oxidation and reduction onset potentials determined against a saturated calomel electrode (calibrated against ferrocene, Fc/Fc$^+$ 0.41 V), considering that the energy level of Fc/Fc$^+$ is 4.8 eV below the vacuum level.[7] These values are summarised in Table 1. On going from PFT to the copolymers with longer B segments (PF3T and PFBTVT), we observe a decrease of IP whereas EA remains nearly constant. The most significant alteration of these two parameters occurs when the sulfur atom of PFT is functionalised to SO_2; namely, a significant increase of both IP and EA is observed in going from PFT to PFTSO2. The stabilisation of the frontier levels upon such functionalisation was previously reported for oligothiophenes,[2] though, for those systems, the increase of EA was larger than the increase of IP.

The UV-vis absorption of the copolymer films is also dependent on the B unit (Fig. 1). The copolymers'optical gap values, E_g, estimated from the onset of the UV-vis absorption spectra, are given in Table 1. E_g decreases on going from PFT

Table 1 Number-average molecular weight (M_n), polydispersity (M_w/M_n), ionisation potential (IP), electron affinity (EA), optical gap (E_g) and fluorescence quantum yields (Φ_{FL}) determined in solution and in solid films of the investigated copolymers

Polymer	M_n	M_w/M_n	IP[a]/eV	EA[a]/eV	E_g/eV	Φ_{FL} Soln.	Φ_{FL} Film
PFT	14100	3.4	5.49	2.84	2.5	0.51	0.032
PFTSO2	8700	3.1	5.62	2.94	2.2	0.16	0.008
PF3T	2800	1.5	5.39	2.81	2.3	0.37	0.081
PFBTVT	5300	3.5	5.24	2.89	2.2	0.11	0.005

[a] CV in MeCN–NBu_4BF_4 (0.2 M) at 50 mV s^{-1}.

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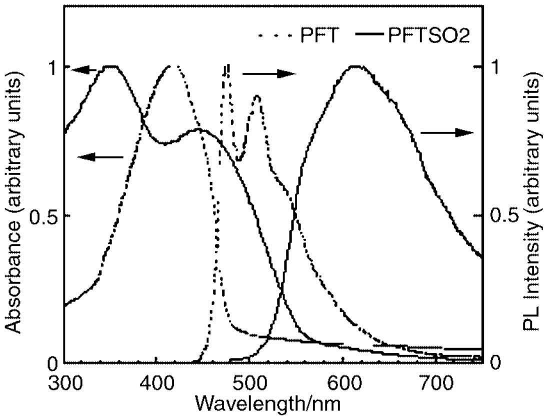

Fig. 1 Normalised UV-vis absorption and photoluminescence (PL) spectra of PFT (λ_{exc} = 408 nm) and PFTSO2 (λ_{exc} = 445 nm) thin films deposited on spectrosil.

to the copolymers with longer conjugated B units, PF3T and PFBTVT, indicating an increase of the conjugation length, despite the decrease of the molecular weight. A similar decrease of E_g is observed upon S to SO_2 functionalisation, showing that such chemical modification of the thiophene unit has a comparable effect to the increase of the number of thiophene rings in the B unit. Furthermore, two distinct bands are observed in the PFTSO2 absorption spectra while a single one is observed for PFT (Fig. 1). Correspondingly, a red-shift of the photoluminescence, PL, spectra is also observed on going from PFT to the other copolymers. Namely, while PFT fluorescence occurs in the green region (λ_{max} = 476 nm), PFTSO2 emits in the orange region of the visible spectrum (λ_{max} = 604 nm). Fluorescence quantum yields (Φ_{FL}) of these polymers were determined both for chloroform solutions and films. Solution Φ_{FL} were calculated by the relative method,[8] by comparing the corrected areas of the fluorescence spectra of a standard and of the sample. As reference substances, we used quinine sulfate in 0.1 M H_2SO_4 (Φ_{FL} = 0.546[9]) and rhodamine 101 in ethanol (Φ_{FL} = 0.89[10]). Solid state Φ_{FL} was determined following the procedure of de Mello *et al.*,[11] using an integrating sphere, upon excitation with the blue line (442 nm) of a He–Cd laser. As shown in Table 1, PFT has the highest solution Φ_{FL}, whereas PF3T shows the highest solid state efficiency. All polymers show a strong reduction of efficiency on going from solution to the solid state, which is indicative of the quenching effects associated to the interchain interactions. We further note that the fluorescence efficiency of PFTSO2 is lower than that of PFT, both in solution and solid state, indicating a detrimental effect of the *S,S*-dioxide functionalisation of the thiophene unit.

Φ_{FL} for PFT in solution, 0.51, is comparable to the value of 0.49 reported by Ranger and Leclerc[12] for a similar alternating copolymer combining 9,9-dioctylfluorene and an unsubstituted thiophene unit, prepared by Suzuki coupling. They reported also a decrease of Φ_{FL} to 0.30 when two thiophene rings are used instead of one. Interestingly, we find a higher value of 0.37 for PF3T (which has three thiophene rings), though this value is lower than that of PFT.

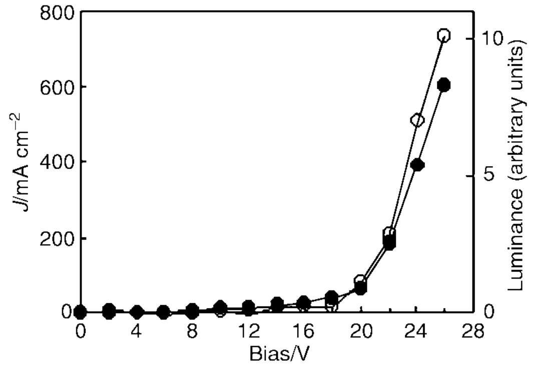

Fig. 2 Current density (*J*) (-●-) and luminance (-○-), as a function of the applied voltage (*V*) for an ITO/PEDOT(40 nm)/PFTSO2 (100 nm)/Ca device. The active area of the device is *ca.* 0.02 cm^2.

We fabricated light-emitting diodes using the copolymers shown in Scheme 1 as electroluminescent materials, with Ca cathodes and indium–tin oxide, ITO, or ITO/PEDOT:PSS anodes (where PEDOT:PSS is polyethylenedioxythiophene, doped with polystyrene sulfonic acid) and we found that the electroluminescence spectra are similar to the fluorescence spectra. Fig. 2 shows current density (*J*) and luminance (*L*) as a function of the applied voltage (*V*) for an ITO/PEDOT:PSS/PFTSO2/Ca device. Light-emission starts at about 14 V, and typical external electroluminescence efficiencies of these PFTSO2-based devices are on the order of 10^{-3}%.

In summary, we synthesised well defined alternating copolymers combining fluorene and thiophene-based moieties whose colour emission and position of frontier levels can be tuned upon structural modifications in the thiophene-based aromatic block.

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