Tuning the optoelectronic properties of polyfluorenes by copolymerisation with thiophene moieties

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Abstract

A series of alternating copolymers of the type A-alt-B, where A is 9,9-bis(2\textsuperscript{-}ethylhexyl)fluorene and B is a thiophene-based moiety, was synthesised via the palladium-catalysed Suzuki coupling. These copolymers were characterised by optical and electrochemical methods and used in the fabrication of light-emitting diodes. We find that upon increasing the conjugation length of the B moiety, from a thiophene unit to 2,5-bis(2\textsuperscript{-}vinyl thiophen-3-yli)thiophene, the fluorescence quantum yields are reduced both in solution (from 51 to 11\%) and in solid state. Both absorption and emission are red-shifted, with the solid state emission maximum increasing from 476 nm (green) to 600 nm (orange). When the B unit is changed from thiophene to thiophene-5,S,S-dioxide, there is a significant increase in both the ionisation potential and electron affinity, and a concurrent reduction of the solution fluorescence efficiency (down to 16\%). These polymers appear promising materials for optoelectronic applications. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Polyfluorenes are presently the most attractive class of organic semiconducting materials for optoelectronic applications, such as long-lived polymeric full colour displays. They combine high chemical and photochemical stability with high luminescence efficiencies [1,2]. Furthermore, they have the capability to emit in the blue region of the visible spectrum as well as to allow a broad tunability of emission when copolymerised with low band gap monomers [3]. This copolymerisation approach is also an effective tool to alter the energetic position of the frontier levels [3], ionisation potential (IP) and electron affinity (EA), which are relevant for charge injection. We note that the control of charge injection into the electroluminescent (EL) polymer is of paramount importance for the preparation of highly efficient light-emitting diodes (LEDs). We have previously shown that the S,S-dioxide substitution on the thiophene moiety of a fluorene–thiophene alternating copolymer is effective at increasing both IP and EA [4]. In this communication, we report on the properties of well-defined alternating copolymers of the same type, A-alt-B, where A is 9,9-bis(2\textsuperscript{-}ethylhexyl)fluorene and B is an extended thiophene-based moiety, synthesised via palladium-catalysed Suzuki coupling (see Fig. 1). LEDs prepared with these copolymers show that they are potential candidates for display application.

2. Experimental

The details of the monomers synthesis will be reported in a forthcoming publication [5]. Fig. 1 shows a typical polymerisation reaction, leading to poly[2,7-(9,9-bis(2\textsuperscript{-}ethylhexyl)fluorene)-alt-2,5-thiophene] (PFT).

The polymerisation reactions were carried out in a refluxing tetrahydrofuran/aqueous potassium carbonate solution (2 M) containing equimolar amounts of the fluorene–boron ester and the adequate dibrominated monomers, in the presence of a catalytic amount of Pd(PPh\textsubscript{3})\textsubscript{4}, for several days, in the dark, under N\textsubscript{2} and vigorous stirring. Copolymers were precipitated by the addition of the reaction mixture to methanol under stirring. The collected solid was purified by dissolving in a minimum amount of CHCl\textsubscript{3}, filtration of the solution and precipitation into methanol. This dissolution/precipitation purification procedure was repeated two more times. The copolymers were finally dried under vacuum. Their chemical and structural characterisation was performed by elemental analysis (C, H, S), FT-IR,
${^1}$H NMR and ${^{13}}$C NMR. Number-average ($M_n$) and weight-averag ($M_w$) molecular weights were estimated by gel permeation chromatography (GPC), relative to monodisperse polystyrene standards.

Solution fluorescence quantum yields were determined in CHCl$_3$ dilute solutions (OD < 0.1) by comparison of the spectrally integrated fluorescence spectra with those of an adequate standard [6]. Details will be reported elsewhere [5]. PFT and PF3T were excited at their absorption maximum (408 and 440 nm, respectively), whereas PFTSO2 and PFVT were excited at the maximum of the lowest energy band of the absorption spectra. Solid state fluorescence (or photoluminescence, PL) quantum yields were determined using an integrating sphere, upon excitation with the blue line (442 nm) of a He–Cd laser, according to the procedure reported by de Mello et al. [7].

The electrochemical properties were evaluated by cyclic voltammetry (CV), using a tetra-n-butylammonium tetrafluoroborate/CH$_3$CN supporting electrolyte, at a scan rate of 50 mV/s. A saturated calomel reference electrode (SCE) (calibrated against ferrocene, Fe/Fe$^+$ 0.41 V), a platinum wire as counter electrode and a platinum disc as working electrode were used. As the energy level of Fe/Fe$^+$ is estimated to lie at 4.8 eV below the vacuum level [8], we calculate the IP and the EA, as IP (eV) = $E_{ox}^{\text{opz}} + 4.39$ and EA (eV) = $E_{red}^{\text{opz}} + 4.39$, respectively.

LEDs were prepared by depositing the polymers, by spin coating, from CHCl$_3$ solutions, onto ITO-coated glass substrates, previously treated with oxygen plasma [9]. The final polymer layer thickness is of about 100 nm. Ca cathodes were thermally evaporated at ca. $5 \times 10^{-6}$ mbar (pixel area ~2 mm$^2$) and protected with an overlayer of Al. The devices were tested under vacuum (ca. $5 \times 10^{-2}$ mbar).

3. Results and discussion

We obtained well defined and soluble copolymers in reasonably good yields (47–58%, after purification). Their molecular weight and polydispersity (PDI) (see Table 1) are typical of the palladium-catalysed Suzuki-type polymerisation [10]. The lower molecular weight of PF3T and PFVT is due to their low solubility in the reaction mixture, which lead to their precipitation during the polymerisation reaction. According to the FT-IR spectra, the vinylene units between the thiophene rings in PFVT are mostly in trans configuration, as indicated by the relative intensity of the bands assigned to the CH vibration, occurring at 930 cm$^{-1}$, for the trans, and at 700 cm$^{-1}$ for the cis configurations. A similar relative intensity is found in the synthesized monomer 2,5-bis(2′-bromo-5-vinyl thiophenyl)thiophene.

The IP and the EA of the copolymers are shown in Table 1. As we reported in a previous publication [4], the S,S-dioxide functionalisation of the thiophene ring leads to a stabilisation of the frontier levels, as inferred from the increase of both IP and EA in going from PFT to PFTSO2. This is in

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_n$</th>
<th>PDI</th>
<th>IP (eV)</th>
<th>EA (eV)</th>
<th>$E_g$ (eV)</th>
<th>$\Phi_{PL}$ (solution)</th>
<th>$\Phi_{PL}$ (film)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFTSO2</td>
<td>8700</td>
<td>3.1</td>
<td>5.62</td>
<td>2.94</td>
<td>2.2</td>
<td>0.16</td>
<td>0.008</td>
</tr>
<tr>
<td>PFT</td>
<td>14100</td>
<td>3.4</td>
<td>5.49</td>
<td>2.84</td>
<td>2.5</td>
<td>0.51</td>
<td>0.032</td>
</tr>
<tr>
<td>PF3T</td>
<td>2800</td>
<td>1.5</td>
<td>5.39</td>
<td>2.81</td>
<td>2.3</td>
<td>0.37</td>
<td>0.081</td>
</tr>
<tr>
<td>PFVT</td>
<td>5300</td>
<td>3.5</td>
<td>5.24</td>
<td>2.89</td>
<td>2.2</td>
<td>0.11</td>
<td>0.005</td>
</tr>
</tbody>
</table>
agreement with the results first reported by Barbarella et al. [11] on the effect of such functionalisation in oligothiophenes. The increase of the thiophene-based moiety extension, in the series PFT, PF3T and PFBVT, leads instead to a decrease of the IP, whereas the EA is not significantly altered. A similar decrease of the IP was reported by Donat-Bouillud et al. [12], for an alternating copolymer, when a dithienylene, instead of a thienylene unit, is combined with 9,9-diocytfluorene.

The optical energy gap values, $E_g$ (see Table 1), exhibit also a systematic decrease with the extension of the thiophene-based moiety, more specifically in going from PFT to PF3T and to PFBVT, from 2.5 down to 2.2 eV. Such decrease reflects the importance of the conjugation length of the B unit (Fig. 1), despite the lower molecular weight. We further note that the existence of trans vinylene groups between the thiophene units in BTVT is expected to favour a more planar (delocalised) structure in relation to 3T, contributing to the reduction of $E_g$. Quite interestingly, the SO$_2$ functionalisation of the thiophene unit leads to a similar decrease of $E_g$ down to 2.2 eV. A similar red-shift of the absorption spectra, due to this functionalisation, was previously reported by Barbarella et al. [11] for oligothiophenes. As shown in Fig. 2B, the PL spectra of PF3T and PFBVT are increasingly red-shifted in relation to that of PFT, as expected form the observed red-shift of the absorption features. Solution fluorescence quantum yields, given in Table 1, decrease in the same series PFT, PF3T, PFBVT, that is with the increase of conjugation of the thiophene-based moiety. This variation is likely to be associated to a lower intrinsic probability of the radiative decay (for example, due to higher intersystem crossing, ISC) although the occurrence of a higher exciton quenching resulting from a higher intra-chain mobility cannot be ruled out. Due to the low concentration of these solutions (<10$^{-6}$ M, based on the repeat unit), the effect of aggregation (either in the ground or excited states) is not expected to contribute to the observed reduction of fluorescence efficiency. These results are in agreement with the report by Ranger and Leclerc [13] that the solution PL efficiency decreases, from 49 to 30%, if a dithienylene unit, instead of a thienylene unit, is copolymerised with 9,9-diocytfluorene.

A strong reduction of the solution PL efficiency is also observed upon S,S-dioxide functionalisation of the thiophene unit: $\Phi_{PL}(\text{PFTSO}_2) = 16\%$, while $\Phi_{PL}(\text{PFT}) = 51\%$. For all polymers shown in Table 1, a strong reduction of fluorescence quantum yields is observed on going from solution to the solid state, exhibiting PF3T the highest solid state $\Phi_{PL}$ (8.1%). This luminescence quenching is associated to the interchain interactions and/or the increase of delocalisation, with the concomitant increase of excitons mobility and their probability of finding quenching sites [14]. On going from solution to solid state, we also find a red-shift of both the absorption spectra onset and of PL spectra. The shift of the PL spectra is not accompanied by a significant change of the spectral distribution. Among the four polymers, such a shift is more pronounced for PF3T, for which the PL spectrum is shifted by about 55 nm, whereas the shift of the absorption-onset is about 20 nm. This red-shift is attributed to a more planar molecular conformation in solid state, brought about by intermolecular interactions and packing mainly induced by the thiophene-based moiety. This increase of planarity in going from solution to solid state is also consistent with the observed smaller red-shift of both PL and absorbance of PFBVT (in relation to PF3T). Due to the presence of the vinyl unit between the thiophene rings, we expect the steric hindrance to be reduced and a more planar conformation to be favoured even in solution, leading to a less pronounced red-shift when going to the solid state.

Fig. 3 shows current–voltage and light intensity–voltage characteristics for LEDs based on PF3T and PFBVT. The electroluminescence, EL, spectra, shown in Fig. 3, are similar to the corresponding PL spectra, indicating that the same excited state is responsible for light-emission.

External EL efficiencies are in the order of 4 x 10$^{-3}$% for the PF3T and of 2 x 10$^{-3}$% for PFBVT. This is not unexpected considering the low solid state PL efficiencies. However, we believe that there is still room for improvement of these EL efficiencies, either using multilayer structures or by doping these polymers with charge transport molecules/polymers.
4. Conclusions

A series of novel alternating copolymers of the type A-alt-B, where A is 9,9-bis(2'-ethylhexyl)fluorene and B is a thiophene-based moiety, was synthesised. We find that we can tune the emission colour from green to orange, by increasing the extent of conjugation of the B unit, from a thiophene to 2,5-bis(2'-vinyl thiényl)thiophene, though at the expense of a fluorescence efficiency reduction. Among the B units we have used, the S,S-dioxide functionalisation of the thiophene promotes an increase of both IP and EA, with respect to the use of a single thiophene unit, that makes the polymer interesting, especially for improving electron injection from stable cathodes. The functionalisation also reduces the optical energy gap to 2.2 eV, the same value that we find for PFBTVT. We have reported EL from non-optimised, single-layer LEDs based on such polymers and we note that these materials are also interesting candidates for other optoelectronic devices, such as photovoltaic cells.

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