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Synthesis and characterisation of poly(distyrylbenzene-*block*-hexa(ethylene oxide)) and its fluorinated analogue—two new block copolymers and their application in electroluminescent devices

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Dedicated to Professor Imanishi on the occasion of his retirement

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Abstract

Two new soluble block copolymers are reported in which chromophores and hexa(ethylene oxide) units alternate along the polymer backbone. In polymer **1** the chromophore was the distyrylbenzene unit. The polymer was synthesised via the Wittig reaction and the ionisation potential of 5.4 ± 0.2 eV was measured by cyclic voltammetry and photoelectron spectroscopy. Polymer **1** showed a high solid-state photoluminescence efficiency (34%) and was used to make efficient (0.5 cd/A) light emitting diodes (LEDs). Polymer **1** was also used in light emitting cells; these showed luminescence in reverse bias and a reduced turn-on voltage compared to the LEDs. Polymer **2**, in which the chromophore was dodecafluoro-distryrylbenzene, was prepared via the Horner–Wittig reaction and showed an ionisation potential of 6.25 ± 0.15 eV and a solid-state photoluminescence efficiency of 17%. It was used as electron-conducting layer in a LED but failed to give significant electroluminescence. The optical energy gap for both polymers was 3.0 eV. © 2002 Published by Elsevier Science Ltd.

Keywords: Synthesis; Fluoropolymer; Block-copolymer

1. Introduction

Electroluminescence in conjugated polymers was first observed in poly(*p*-phenylene vinylene) (PPV), [1] which is made via a precursor route and has been the workhorse for investigations of the phenomenon [2]. PPV itself emits in the yellow/green region of the spectrum but the colour can be altered by incorporation of electron-donating and electron-withdrawing substituents on the polymer backbone. Appropriate substituents on the polymer backbone also control the solubility and processability of PPV, which is otherwise insoluble and infusible.

An alternative approach to control of solubility and colour is the synthesis of block copolymers with alternating oligo(*p*-phenylene vinylene) chromophores and non-conjugated spacers [3]. In this approach the chromophores and the flexible linkers are well defined and there is no need to introduce solubilising groups directly onto the chromophore, a practice which can disrupt planarity. We have recently reported briefly the synthesis and characterisation of a block copolymer of alternating distyrylbenzene chromophores and hexa(ethylene oxide) spacers along with their photo and electroluminescence behaviour [4]. Poly(distyrylbenzene-*block*-hexa(ethylene oxide)) **1** is a highly efficient emitter and its optoelectronic properties will be discussed in detail in this paper. Fluorine is unique as a substituent, because of its relatively small size and exceptionally high electronegativity, and induces large effects. Intuitively, in the case of conjugated polymers, fluorine substituents are expected to increase the electron affinity. Other workers have reported that the introduction of one or two fluorine substituents per aromatic ring in PPV derivatives improves the efficiency of electroluminescent devices based on such polymers [5]. However, so far no PPV derivative has been prepared in which all the aromatic

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positions are substituted with fluorine. Here we report the synthesis of such a block copolymer with alternating fluorinated DSB units and hexa(ethylene oxide) spacer units; namely, poly(dodecafluoro-distyrylbenzene-*block*-hexa(ethylene oxide)) **2**. The syntheses, characterisation and optical properties of polymers **1** and **2** are reported. A range of light emitting diodes based on polymers **1** and **2** was prepared and tested and their properties and performances are reported, along with the properties of a light-emitting cell based on block copolymer **1**.

2. Experimental Section

2.1. General

All commercially available materials were used as received unless noted otherwise. Tetrahydrofuran (THF) was dried over alumina (EasyPureSystem). Hexa(ethylene oxide) ditosylate [6] (**3**), *p*-xylylene-bis(triphenylphosphonium bromide) [7] (**4**), 2,3,4,5,6-pentafluorobenzaldehyde diacetal [8] (**5**) and 2,3,5,6-tetrafluoroxylylene bis(dimethyl)phosphonate [9] (**6**) were prepared as described in the literature.

2.1.1. 1,17-Bis-(4-formylphenyloxy)-3,6,9,12,15-pentaoxaheptadecane (7)

Hexa(ethylene oxide) ditosylate (**3**) (25.0 g, 42.3 mmol), *p*-hydroxybenzaldehyde (11.0 g, 90.1 mmol) and K_2CO_3 (17 g, 123 mmol) were dissolved in DMF (70 ml) and heated at 90 °C for 48 h. The product was poured onto ice (100 g) and chloroform (200 ml) was added. The organic layer was washed three times with water, dried ($MgSO_4$) and the chloroform was removed under reduced pressure. The product was purified by column chromatography (silica gel, hexane/ethyl acetate 1:1 (800 ml), then ethyl acetate) yielding a white solid (14.5 g, 70%), m.p. 43–45 °C. Anal. Calcd. for $C_{26}H_{34}O_9$: C, 63.66%; H 6.99%. Found: C, 63.49%; H, 7.07%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.87 (s, 2H, –CHO), 7.81 (d, 4 H, $J = 9$ Hz, ArH), 7.01 (d, 4 H, $J = 9$ Hz, ArH), 4.20 (t, 4 H, $J = 4.5$ Hz CH_2), 3.88 (t, 4H CH_2), 3.68 (m, 16H); ^{13}C {^{1}H} NMR ($CDCl_3$, 63 MHz) δ 190.74, 163.80, 131.89, 130.01, 114.84, 70.86, 70.59, 69.41, 67.17.

2.1.2. Poly(distyrylbenzene-block-hexa(ethylene oxide)) (1)

p-Xylylene-bis(triphenyl-phosphonium bromide) (**4**) (7.96 g, 10.1 mmol) and LiCl were dissolved in *N*,*N*-dimethylformamide (DMF) (60 ml). A solution of KO^{t}Bu in THF (1.0 M, 29.6 ml, 29.6 mmol) was added and the mixture stirred for 1 h. Compound **7** (4.95 g, 10.1 mmol) was dissolved in DMF (10 ml) and added to the mixture. After stirring at room temperature for 6 h the mixture was quenched with aqueous HCl (2 M, 20 ml). All solvents were removed under reduced pressure. The product was redissolved in chloroform (200 ml) and washed with water. The chloroform solution was concentrated (10 ml) and the polymer recovered by precipitation into methanol (60 ml). The reprecipitation was repeated once more yielding a yellow solid (3.8 g, 68%). Gel permeation chromatography (GPS) (Viscoteck, RI detector, chloroform eluent, $2 \times PL_{gel}$ mixed bed D 30 cm columns, polystyrene standards) M_n 5600 g/mol; M_w 16,700 g/mol; PDI 3.0. Anal. Calcd for $C_{34}H_{40}O_7$: C, 72.83%; H 7.19%. Found: C, 71.69%; H, 7.11%. ^{1}H NMR (TCE-d_2, 300 MHz) δ 7.5–7.1 (m, 8H, Ar*H*), 7.01 (AB q, $J = 16$ Hz, 1H, Vinyl *H*, *trans* coupling), 6.97 (AB q, $J = 16$ Hz, 1H, Vinyl *H*, *trans* coupling), 6.90 (m, 2H, Ar*H*), 6.77 (m, 2H, Ar*H*), 6.49 (AB q, $J = 12$ Hz, 1H, Vinyl H, *cis* coupling), 6.46 (AB q, $J = 12$ Hz, 1H, Vinyl *H*, *cis* coupling), 4.13 (m, 4H, C*H*$_2$), 3.84 (m, 4H, C*H*$_2$), 3.64 (m, 16H); ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz) δ 158.24, 157.60, 136.37, 135.89, 130.04, 130.00,129.76, 129.71, 129.56, 129.09, 128.55, 128.42, 127.79, 127.74, 127.66, 126.51, 126.15, 125.99, 114.77, 114.20, 114.15, 70.46, 70.21, 69.40, 67.31, 67.19.

2.1.3. 1,17-Bis(4-diethoxymethly-2,3,5,6-tetrafluorophenyloxy)-3,6,9,12,15-pentaoxaheptadecane (8)

Hexa(ethylene glycol) (9.7 g, 34.3 mmol) was dissolved in dry THF (300 ml). A solution of *n*-Butyllithium in hexane (1.6 M, 43.7 ml, 70 mmol) was added and the mixture stirred for 30 min under nitrogen. Then 2,3,4,5,6-pentafluorobenzaldehyde diethylacetal (**5**) (18.5 g, 68.6 mmol) was added. The mixture was refluxed for 14 h. After the addition of water (20 ml) the volatile components were removed under reduced pressure. Diethyl ether (200 ml) was added and the organic phase was washed twice with brine, twice with water and dried ($MgSO_4$). The diethyl ether was removed under reduced pressure and the product purified by column chromatography (silica gel, hexane/diethyl ether 1:1 followed by pure diethyl ether) yielding a colourless oil (11.3 g, 42%). Anal. Calcd for $C_{34}H_{46}F_8O_{11}$ C, 52.17% H, 5.92%. Found C: 52.26%; H, 5.95%; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 5.67 (s, 2H, OCHO), 4.35 (t, $J = 7$ Hz, 8H, CH_2), 3.62 (m, 24H CH_2), 1.23 (t, $J = 7$ Hz, 12H, CH_3); ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz) δ 144.77 (d, $J =$ 260 Hz), 140.91 (d, $J = 250$ Hz), 137.95, 111.46, 96.53, 74.37, 71.05, 70.81, 70.79, 70.76, 70.29, 63.44, 14.92; ^{19}F NMR ($CDCl_3$, 188 MHz) δ −144.89 (m, 4F), −157.26 (m, 4F).

2.1.4. 1,17-Bis(4-formyl-2,3,5,6-tetrafluorophenyloxy)-3,6,9,12,15-pentaoxaheptadecane (9)

Compound **8** (11.3 g, 14.4 mmol) was dissolved in a mixture of THF and water (100 ml/50 ml) and conc. H_2SO_4 (1 ml) was added. The mixture was stirred over night at 55 C. The THF was removed under reduced pressure and diethyl ether (100 ml) was added. The organic phase was washed with water, aqueous $NaHCO_3$ and twice with water. It was dried ($MgSO_4$) and the solvent removed under reduced pressure yielding a colourless oil

(8.9 g, 97%) Anal. Calcd for $C_{26}H_{26}F_8O_9$: C, 49.22%, H, 4.13% Found: C, 48.86%; H, 4.14%; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 10.18 (s, 2H, –CHO), 4.52 (m, 4H, CH_2), 3.83 (m, 4H, CH_2), 3.59 (m, 16H, CH_2); ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz) δ 182.09, 147.52 (d, $J = 260$ Hz), 143.10, 140.26 (d, $J = 250$ Hz), 108.90, 74.21, 70.80, 70.50, 70.44, 70.03; ^{19}F NMR ($CDCl_3$, 188 MHz) δ −146.75 (m, 4F), −157.03 (m, 4F).

2.1.5. Poly(dodecafluoro-distyrylbenzene-block-hexa(ethylene oxide)) (**2**)

A mixture of 2,3,5,6-tetrafluoroxylylene bis(dimethyl)-phosphonate (**6**) (6.46 g, 16.4 mmol) and NaH (3.8 g, 60% in oil, 95 mmol) was dissolved in dry THF (300 ml) under nitrogen and stirred for 30 min. Compound **9** (10.4 g, 16.4 mmol) was dissolved in dry THF (40 ml) under nitrogen and added to the reaction mixture. The reaction temperature was increased from 50 to 65 °C over 13 days. The reaction was followed by NMR spectroscopy (^{1}H, ^{19}F). The solution was then quenched with water (150 ml) and the THF removed under reduced pressure. Chloroform (500 ml) was added and the mixture washed with brine. The chloroform solution was filtered through Celite and concentrated (150 ml). The product was recovered by precipitation into methanol (450 ml) yielding a white polymer (8.0 g, 62%). The polymer was fractionated by gel-chromatography (Bio-Beads S-X1, BIORAD, chloroform as eluent) and the chloroform solution reprecipitated into hexane. GPC (Viscoteck, RI detector, chloroform eluent, $2 \times PL_{gel}$ mixed bed D 30 cm columns, polystyrene standards) fraction 1: M_n 12,500 g/mol; M_w 44,700 g/mol; PDI 3.6; fraction 2: M_n 7200 g/mol; M_w 32,000 g/mol; PDI 4.4. Fraction 1 was used for further analysis and experiments. Anal. Calcd for $C_{34}H_{28}F_{12}O_7$: C, 52.59%; H 3.36% Found: C, 51.76%; H, 3.63%. ^{1}H NMR ($CDCl_3$, 300 MHz) ABq δ_A 7.39 ($J = 16$ Hz, 2H, Vinyl H, *trans* coupling), δ_B 7.33 ($J = 16$ Hz, 2H, Vinyl *H*, *trans* coupling), 4.43 (t, $J = 4.2$ Hz, 4H, CH_2), 3.86 (t, $J = 4.2$ Hz, 4H, CH_2), 3.67 (m, 16H, CH_2); ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz) δ 145.20 (d, $J = 249$ Hz), 144.71 (d, $J = 249$ Hz), 138.62 (d, $J = 246$ Hz), 137.41, 122.51, 120.79, 115.46, 109.99, 74.25, 70.84, 70.58, 70.13; ^{19}F {^{1}H} NMR ($CDCl_3$, 188 MHz) δ −143.80 (m, 8F), −157.83 (m, 4F).

2.2. Cyclic voltammetry

ITO electrodes were coated with polymers **1** and **2** the oxidation potential were recorded by cyclic voltammetry using a EGE potentostat/galvanostat instrument 263A. The experiment used one cell containing three electrodes; a working electrode and counter electrode of Pt, a reference electrode of Ag/AgCl and an electrolyte of 1 M tetrabutyl-ammonium perchlorate in acetonitrile. The apparatus was purged with dry, oxygen free nitrogen. The polymer films were approximately 80 nm thick and the scan rate was 20 mV/s. Ferrocene was used as a reference.

2.3. Photoelectronspectroscopy

A helium discharge lamp (He II radiation, 40.8 eV) with monochromator was used. The spectrometer was designed and constructed in Linköping.

2.4. Optical measurements and device preparation

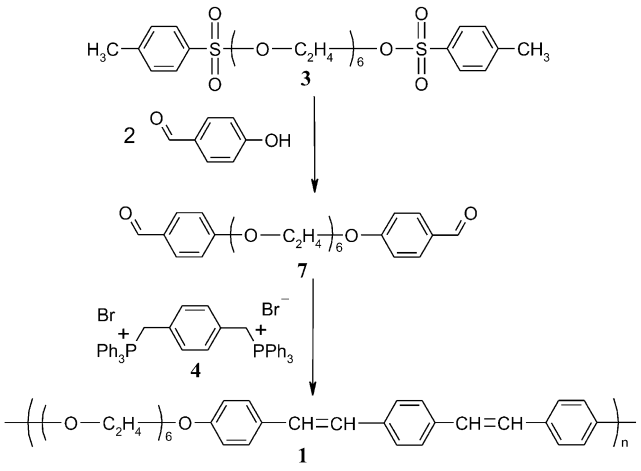
All optical and device investigations were carried out at room temperature with thin films of polymer prepared by spin-coating (60 s, 2000 rpm) from a chloroform solution (approximately 2 wt%, filtered through a Millipore membrane with a pore size of 1 μm). Film thicknesses were determined with a Dektak IIa stylus profiler and concentrations adjusted so that 90–100 nm thick films were obtained. Spectrosil substrates were used for solid state absorption PL experiments. The PL efficiencies of thin solid films were determined using an integrating sphere, purged with nitrogen to avoid photo-oxidation.

Commercially available ITO-coated glass substrates (Asahi) were used for the fabrication of LEDs. The ITO substrates were cleaned in an ultrasonic bath with acetone and 2-propanol, each for 15 min and then treated for 10 min with oxygen plasma at approximately 300 W [10]. For double layer LEDs with PEDOT/PSS (Bayer AG) the commercially available PEDOT/PSS was spin-cast from an aqueous solution [11]. It was dried and conditioned by thermal treatment for 1 h at 100 °C under nitrogen. A thin calcium or aluminium layer was subsequently deposited over the substrate through a shadow mask at a pressure below 10^{-6} mbar. The calcium layer was covered with an aluminium layer in the same way in order to slow down oxidation of the anode and improve the mechanical integrity of the device for the measurements. All processing of LEDs was carried out in a glove box under a nitrogen atmosphere with less than 20 ppm residual water vapour and 5 ppm oxygen.

Measurements were carried out in a sample holder specially designed to allow the transfer of the sample from the glove box to the measuring station without exposure to air. The luminous output was measured with a calibrated silicon photodiode. Spectral characterisation was performed by means of an Oriel CCD-matrix spectrograph, with a spectral resolution better than 5 nm.

3. Results and discussion

Several groups have demonstrated the use of the Wittig condensation as an effective route to block copolymers with well-defined conjugated chromophores such as DSB separated by a non-conjugated unit [3,12]. We choose DSB as the emissive chromophore since it is the simplest oligo(phenylene vinylene) that emits in the visible region. Oligo(ethylene oxide) spacers are attractive as they can provide a dramatic enhancement of solubility in both organic and aqueous solvents and avoid the requirement to introduce



Scheme 1. Synthetic route to polymer **1**.

solubilising side chains directly on the chromophore. Hexa(ethylene glycol) is commercially available as a monodisperse compound and this spacer is expected to be sufficiently long to render the DSB units soluble.

To prepare polymer **1** hexa(ethylene glycol) was activated as the bistosylate and reacted with two equivalents of *p*-hydroxybenzaldehyde to give compound **7** (Scheme 1). The Wittig condensation of the latter with *p*-xylylene-bis(triphenylphosphonium bromide) (**4**) in DMF gave a yellow polymer **1** in 68% yield after purification by reprecipitation. Ion chromatographic analysis of an aqueous extract (polymer boiled in pure water) showed no traces of Na^+, K^+, Li^+, Ca^{2+} or Mg^{2+} ions. GPC indicated a M_n of 5600, a polydispersity of 3 and a degree of polymerisation of 10 with respect to polystyrene calibration. As shown previously the ^{1}H-NMR spectrum indicates a 50:50 distribution of *cis*- and *trans*-double bonds in the DSB units [4]. The FT-IR spectrum of a thin film of polymer **1** shows C–H out-of-plane deformations for *cis* and *trans*-double bonds at, respectively, 968 and 837 cm^{-1}, confirming the proposed structure (Fig. 1). Similar *cis*/*trans* ratios have been reported for 4,4′-dialkoxy substituted distyrylbenzenes prepared by the Wittig reaction [13].

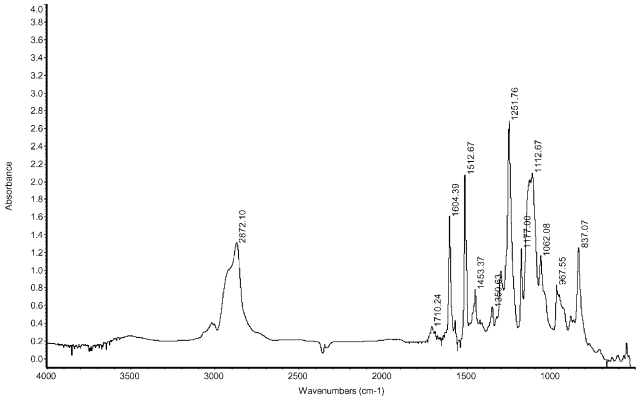
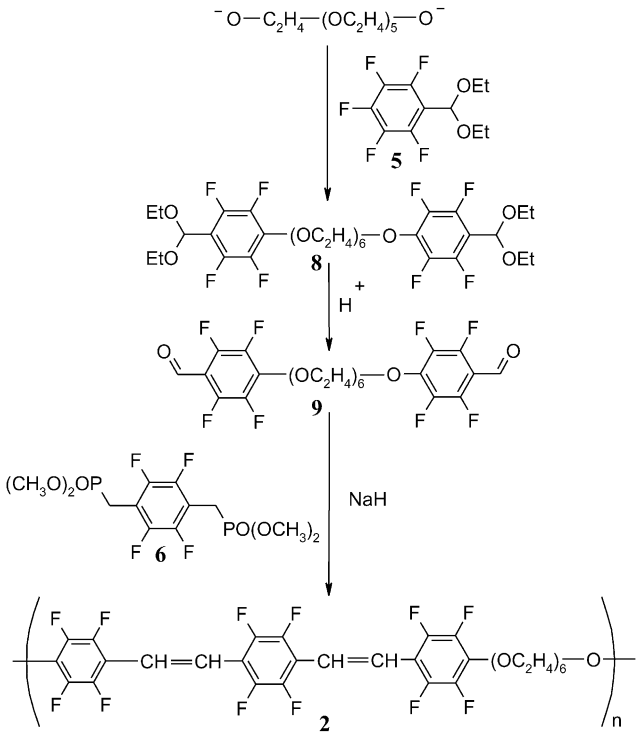


Fig. 1. FT-IR spectrum of polymer 1 (thin film).



Scheme 2. Synthetic route to polymer **2**.

We were also able to prepare a fluorinated analogue of polymer **1** in which all aromatic positions are substituted with fluorine. Hexa(ethylene glycol) was deprotonated with *n*-butyllithium and reacted with pentafluorobenzaldehyde diethylacetal (**5**) to give the protected comonomer **8** (Scheme 2). The nucleophilic substitution takes place selectively in the position *para* to the acetal group [14]. The acetal protecting group was removed by treatment with aqueous acid yielding the comonomer **9**. The Horner–Wittig reaction of 2,3,5,6-tetrafluoroxylylene bis(dimethyl)-phosphonate [9] (**6**) with comonomer **9** required relatively high temperatures (50–65 °C) over 13 days. When more forcing conditions were examined it was found that reflux of the reaction mixture resulted in a side reaction which led to a black product. When the temperature was kept between 50 and 65 °C for 13 days polymer **2** was obtained as a white solid in 62% yield after purification. The polymer was fractionated by gel chromatography (Bio-Beads S-X1 Beads, chloroform). GPC indicates for the first fraction a M_n of 12,600, a polydispersity of 3.5 and a degree of polymerisation of 17 with respect to polystyrene. For the second fraction GPC shows a high content of oligomers, a M_n of 7000, a polydispersity of 4.1 and a degree of polymerisation of about 9. Ion chromatography of an aqueous extract of the polymer obtained by boiling with pure water indicated the absence of any Na^+, K^+, Mg^{2+} or Li^+ ions and a trace (0.008%) of Ca^{2+} ions. The ^{1}H NMR spectrum of polymer **2** shows an AB quartet with a coupling constant of 16 Hz typical for *trans*-olefinc protons (Fig. 2). Only a very small signal is observed for *cis*-olefinic protons at δ 6.75

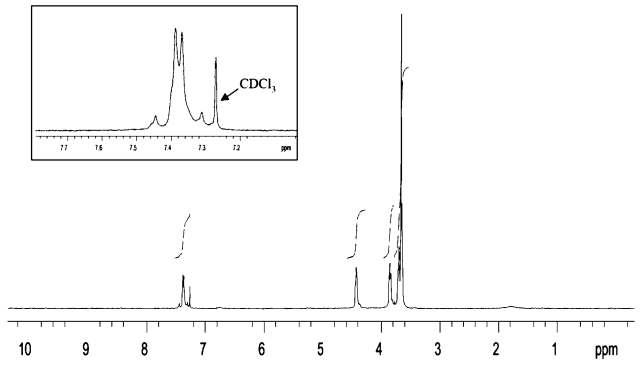


Fig. 2. ^{1}H NMR spectrum of polymer **2** in $CDCl_3$. The inset shows the expanded region between δ 7.1 and 7.7.

indicating that at least 95% of double bonds have a *trans*-configuration. The roughly 50:50 *cis*/*trans* distribution of vinylenes in polymer **1** is consistent with expectation for this kind of synthesis, Wittig coupling at room temperature over 6 h, and in agreement with similar syntheses in Ref. [13] by contract, the more forcing conditions required for the synthesis of polymer **2**, Horner–Wittig modification at 50–65 °C over 13 days, lead to a predominance of the thermodynamically favoured **trans** vinylene in polymer **2**.

The ionisation potentials of both polymers were determined by cyclic voltammetry (CV) and UV-photolelectron-spectroscopy (UPS). The values obtained are self-consistent (see Table 1). The average values of both methods relative to the vacuum level are 5.4 ± 0.2 eV for **1** and 6.25 ± 0.15 eV for **2**. Kang et al. have reported an increase of the IP of 0.17 eV when one hydrogen atom per aromatic ring of PPV was substituted by fluorine [15]. In our case four positions on each aromatic ring are substituted by fluorine and an increase of the IP of 0.85 eV is observed indicating that the effect of fluorine is not linearly additive in this case.

The solid-state absorption spectra of **1** and **2** are shown in Fig. 3. The onset of absorption in the solid state for both polymers is at 415 nm, indicating a HOMO–LUMO gap for

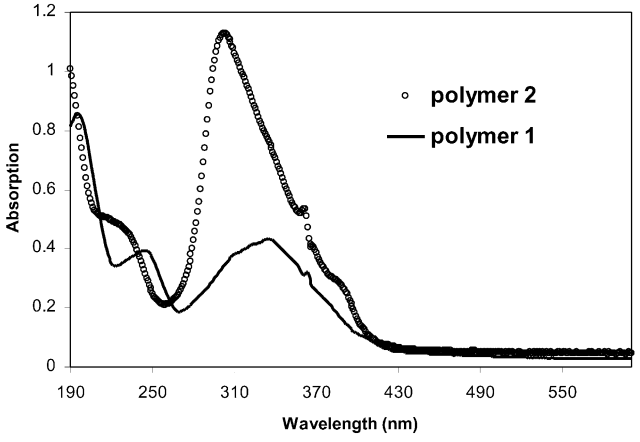


Fig. 3. Solid state absorption spectra of polymer **1** and **2** as thin films on spectrosil substrates.

Table 1
Ionisation potentials and electron affinities of polymers **1** and **2**

	IP_{UPS} (eV)	IP_{CV} (eV)	$IP_{average}$ (eV)	$EA_{calcd.}$ (eV)
Polymer **1**	5.5 ± 0.1	5.3 ± 0.1	5.4 ± 0.2	2.4 ± 0.2
Polymer **2**	6.2 ± 0.1	6.3 ± 0.1	6.25 ± 0.15	3.25 ± 0.15

both polymers in the solid state of 3.0 eV. It can be concluded that the size of the optical energy gap remains unchanged when 12 fluorine substituents are introduced; and that the IP (the potential of the HOMO relative to the vacuum level) and the electron affinity (potential of the LUMO relative to the vacuum level) are altered to the same extent. These data allow the electron affinities (EA) of **1** and **2** to be calculated; for 1 the EA is at 2.4 ± 0.2 eV and for **2** the EA is at 3.25 ± 0.15 eV. The shape of the absorption curve for polymer **2** suggests the presence of H-aggregates; a maximum absorption is found at 301 nm, strongly blue shifted relative to the solution state maximum (354 nm), and second weak absorption is found at 388 nm. Differential scanning calorimetry (DSC) analysis of polymer **2** shows three phase transitions at 78, 98 and 123 °C, indicative of the presence of ordered structures in polymer **2** at room temperature.

The photoluminescence efficiencies of both polymers were measured using an integrating sphere. The solid state PL efficiency of polymers **1** and **2** are 34 and 17%, respectively. This difference in efficiency might be due to one or more of the following factors: the substitution of hydrogen by fluorine, the different structures (*cis*/*trans* content) of the chromophores or different degrees of order in the polymers.

Light-emitting diodes (LEDs), were prepared on ITO substrates treated with an oxygen plasma prior to spin-coating in order to increase the work function and surface energy [10]. The polymers were spun-cast from a chloroform solution and the device fabrication completed by thermal evaporation of a calcium and/or aluminium cathode.

Polymer **1** was highly efficient as an electroluminescent material in LEDs. As reported previously the turn-on voltage of the device ITO/polymer **1**/Al was at 6.5 V and we obtained luminance values over 2000 cd m^{-1} at 19 V, with luminescence efficiencies up to 0.5 cd A^{-1} [4]. When Ca was used as cathode instead of Al the current density/voltage/luminescence curves (IVL) and the efficiency in particular were very similar (Fig. 4 and Table 2). This was unexpected since Ca has a much lower work-function (2.8 eV) than Al (4.2–4.3 eV), and for most organic semiconductors, for which transport is hole-dominated, use of Ca cathodes results in a higher luminescence efficiency. Although precise identification of the causes of this unusual behaviour is beyond the scope of this work we note that: (a) such moieties are more difficult to purify from contaminants and thus their presence might favour a higher unintentional doping of the polymer and thus higher currents in the Al devices; (b) the same moieties may favour Ca diffusion and

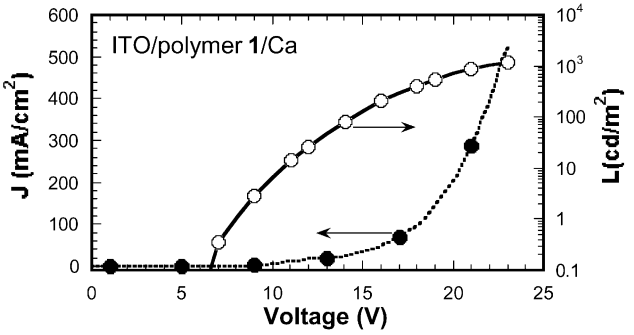


Fig. 4. Current density and luminance vs. voltage characteristics of an ITO/polymer **1**/Ca device.

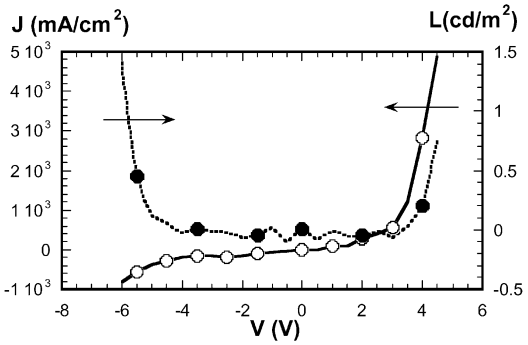


Fig. 5. Current density and luminance vs. voltage characteristics of an ITO/polymer **1**(LiTf)/Al device in reverse and forward bias.

doping of the active layer, and thus quenching of the photoluminescence, in the devices with Ca cathodes. The EL spectra of devices based on polymer **1** show two maxima at 523 and 494 nm similar to the PL maxima at 530 and 494 nm [4]. Sandman et al. have prepared a similar block copolymer with DSB units and oligo(ethylene oxide), which only contained *trans*, *trans* DSB units [16]. This polymer showed two absorption maxima at about 455 and 485 nm. These results are somewhat surprising since *cis*, *cis* and *cis*, *trans* units in polymer **1** might give rise to steric hindrance and a decrease in conjugation with a consequent blue shift relative to the absorptions of the *trans*, *trans* units described by Sandman et al. These polymers not only differ in their geometries but also in the chromophore content; the DSB units constitute 50 wt% in polymer **1** and only 24 wt% in the polymer by Sandman et al. Li et al. have also prepared block copolymers with DSB units and oligo(ethylene oxide) units [17] However, Li et al. and Sandman et al. found it difficult to report device characteristics due to rapid degradation of their devices. This is in strong contrast to the results described here for polymer **1**. We have also fabricated double layer devices with polymer **1** as emissive layer and PEDOT/PSS as a hole-injection layer since this frequently helps carrier injection into the emissive layer and improves device performance; however, the additional layer did not improve device performance in terms of efficiency, turn-on voltage and durability.

Light emitting cells (LECs) use an electroluminescent polymer, an ion transporting polymer (such as PEO) and a salt in order to aid charge injection at the electrodes. The combination of oligo(ethylene oxide) units and oligo (phenylene vinylene) units in one polymer avoids the risk of phase separation. Indeed, Huang et al. have prepared a conjugated polymer with a PPV backbone and two tri(ethylene oxide) side chains per aromatic ring with the avoidance of phase segregation in mind [18]. The authors showed that a LEC based on a complex of this polymer with lithium triflate has a low threshold voltage of 2.5 V and the device can be used in reverse bias. In contrast to this report, our polymer is a block copolymer and the chromophore as well as the oligo(ethylene oxide) unit are within the polymer backbone. We prepared a complex of polymer **1** and lithium triflate. A LEC with ITO and Al as electrodes based on this complex showed a reduced threshold of 3.8 V. We were also able to observe electroluminescence under reverse bias. (Forward bias means that ITO is the anode and Al the cathode) Fig. 5 shows an IVL curve with luminescence between −6.5 and −4.0 V and between 3.8 and 5.0 V. Furthermore, we were able to observe during the establishing of the electrochemical equilibrium that the current density decreases over time at constant voltage (4 V) while the luminescence increases.

Table 2
The maximum efficiency of the different LEDs using polymer **1** as the electroluminescent layer

Device	EL efficiency (cd/A)
ITO/POLYMER **1**/Al	0.48
ITO/POLYMER **1**/Ca	0.43
ITO/PEDOT/POLYMER **1**/Al	0.47
ITO/PEDOT/POLYMER **1**/Ca	0.40

Devices based on polymer **2** as the emissive layer were prepared in the same way as those with polymer **1**. Both calcium and aluminium were used as cathodes. In general, these devices were disappointing with respect to their electroluminescent properties. The devices were unstable and the faint electroluminescence faded away within a few seconds of passing current through the device. The weak electroluminescence spectrum shows a maximum at 502 nm (2.47 eV) similar to the PL spectrum; both are shown in Fig. 6. The maxima are in the same region of the spectrum as those of polymer **1**, whose PL and EL spectra are published as fig. 3 in Ref. [4], but in this case no fine structure can be observed. The current density vs. voltage curve shows that very little current passes through the device (Fig. 7). Sarker et al. have found also that block copolymers with fluorinated DSB units are very poor emitters [9]. They attributed the loss of efficiency compared to the pure hydrocarbon analogue to π-stacking in the solid state.

We prepared a double layer device of the structure ITO/PPV/polymer **2**/Al and compared it to a single layer device

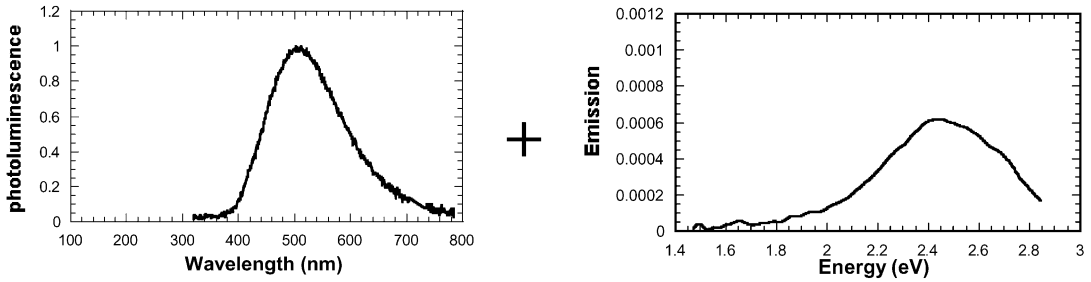


Fig. 6. EL and PL spectra of polymer **2**. The EL spectrum is from an ITO/polymer **2**/Al diode. The PL spectrum is obtained by exciting with a He–Cd laser (325 nm).

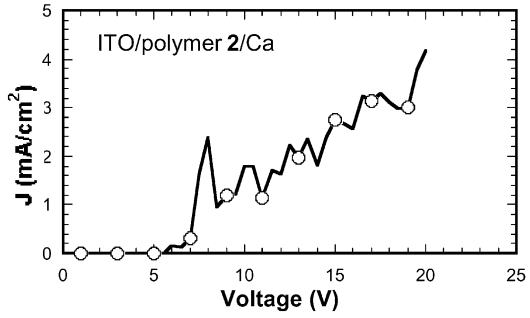


Fig. 7. Current density vs. voltage characteristics of an ITO/polymer **2**/Ca device.

based on PPV (ITO/polymer **2**/Al). Both devices show the typical emission spectrum of PPV and have the same efficiency. This indicates that, although polymer **2** is a poor emitter, it is a relatively good electron-carrier since the increase in thickness of this device is compensated for by the beneficial effect of an additional electron-injection layer.

We also prepared a blend of polymer **1** (50 wt%) and polymer **2** (50 wt%) and we found that the PL efficiency of this blend was reduced to 10%. This decrease might be due to a quenching process based on π, π-stacking, which is a well established behaviour of mixtures of aromatics and perfluoroaromatics. LEDs based on this blend such as ITO/**1** + **2**/Al showed a very high current density but no electroluminescence. The high current density can also be explained by π, π-stacking which allows the rapid transport of charge through the polymer layer so that no charge recombination can occur.

4. Conclusions

We have prepared two soluble block copolymers with alternating chromophores and hexa(ethylene oxide) spacers. In the first case, distyrylbenzene was the chromophore and the polymer showed high photoluminescence quantum efficiency. LEDs with ITO as the anode and aluminium or calcium as the cathode were very efficient. We have also used a complex of this polymer with lithium triflate in a LEC which showed a reduction in turn-on voltage. Substitution of all aromatic hydrogens by fluorines did not improve the emissive properties of the polymer, the material with dodecafluoro-distyrylbenzene as the chromophore was a poor emitter but it can be used as an electron-conducting layer due to its high electron affinity and ionisation potential.

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