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Poly(distyrylbenzene-*block*-sexi(ethylene oxide)), a highly luminescent processable derivative of PPV

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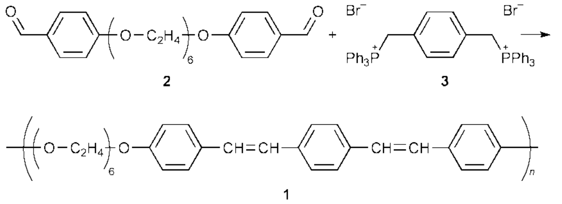
A block copolymer of distyrylbenzene with sexi(ethylene oxide) spacers displays high solid state photoluminescence efficiency (34%). Single layer light-emitting diodes with calcium or aluminium cathodes exhibit luminances over 2000 cd m^{-2} and efficiencies of 0.5 cd A^{-1}.

Electroluminescence in conjugated polymers was first observed in poly(*p*-phenylenevinylene),[1] PPV, which is made *via* a precursor route and has been the workhorse for investigations of the phenomenon.[2] Most unsubstituted conjugated polymers are insoluble and infusible and consequently not easily processed. Various protocols have been adopted to overcome this fundamental problem including the use of precursor routes, solubilising side chains, formation of block copolymers and polymers containing functional units in side chains.[3] Several groups have demonstrated the use of Wittig condensation as an effective route to copolymers with well-defined conjugated chromophores separated by a non-conjugated unit.[4] In this context oligo(ethylene oxide), OEO, spacers are attractive as they can provide a dramatic enhancement of solubility in both organic and aqueous solvents[5] and avoid the requirement to introduce solubilising side chains directly on the chromophore, which can disrupt planarity. In addition OEOs can provide a significant ionic conductivity that can, in principle, be exploited for fabricating light-emitting electrochemical cells, LECs. Sandman *et al.*[6] and Li *et al.*[7] have described the synthesis of copolymers of distyrylbenzene (DSB) and OEO, but found it difficult to report device characteristics owing to rapid device degradation.[6]

In contrast to these reports, we describe the synthesis and characterisation of a block copolymer of DSB with sexi(ethylene oxide), SEO, spacers (DSB-*block*-SEO) **1** which displays high solid state photoluminescence (PL) efficiency and good electroluminescence in device structures. In our approach SEO was activated as the bis-tosylate and reacted with 4-hydroxybenzaldehyde to give the flexible linker **2**. The reaction of triphenylphosphine with α,α′-dibromoxylene gave bis(triphenylphosphonium)xylylene dibromide **3** and Wittig condensation of **2** and **3** gave the polymer **1** (see Scheme 1).

The polymer is soluble in chloroform and robust free-standing films can be cast from solution. The ^{1}H-NMR-, ^{13}C-NMR-, FTIR and UV/vis spectra and elemental analysis were consistent with the assigned structure. The ^{1}H-NMR spectrum is reproduced in Fig. 1, in the inset four AB quartets can be identified and assigned;[8] the two with J_{AB} = 16 Hz are assigned to *trans* vinylenes in *trans,trans* and *trans,cis* DSB units and the two with J_{AB} = 12 Hz to *cis* vinylenes in *cis,cis* and *cis,trans* units, the relative intensities of these signals indicating a 50:50 *cis*:*trans* distribution of double bonds.



Scheme 1 Synthesis of polymer DSB-*block*-SEO **1**.

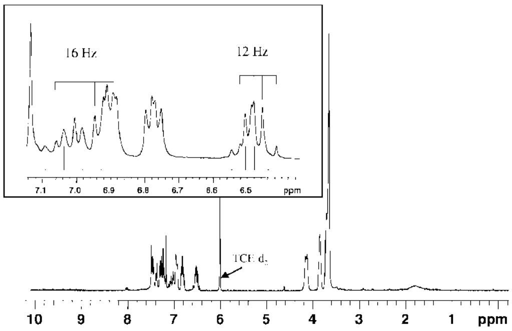


Fig. 1 ^{1}H NMR spectrum of DSB-*block*-SEO in Tetrachloroethane-d$_2$ (TCE-d$_2$).

Gel Permeation Chromatography (Viscoteck, RI detector, chloroform eluent, 2 × PL$_{gel}$ mixed bed D 30 cm columns, polystyrene standards, we thank RAPRA for this measurement) indicated a M_n of 5600, a polydispersity of 3 and a degree of polymerisation of about 10 with respect to polystyrene calibration. Ion chromatography (Dionex, DX 120) indicated no traces of Li$^+$, Na$^+$, K$^+$, Mg^{2+} or Ca^{2+} and ^{31}P-NMR showed no phosphorous.

The solid state PL quantum efficiency of polymer **1** is 34%, as measured by exciting a 100 nm thick film on spectrosil inside an integrating sphere, with laser excitation at 325 nm (He-Cd laser). The solid state absorption spectrum is reported in Fig. 2 and shows a maximum at 3.71 eV (334 nm), whereas the solid state PL spectrum (Fig. 3) shows two maxima at 2.34 eV (529 nm) and 2.50 eV (496 nm), *i.e.* in the green region of the visible range. The substantial red-shift (~0.25 eV) with respect to distyrylbenzene oligomers can be explained by taking into

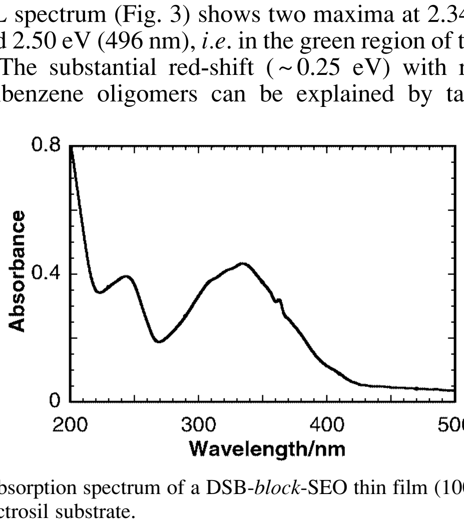


Fig. 2 Absorption spectrum of a DSB-*block*-SEO thin film (100 nm thick) on a spectrosil substrate.

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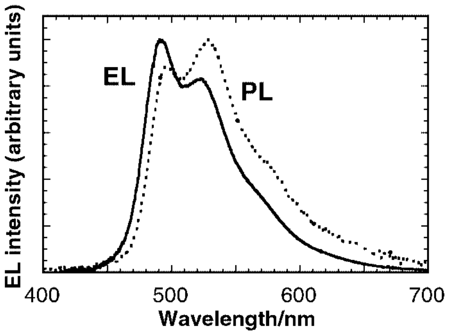

Fig. 3 EL and PL spectra of DSB-*block*-SEO. The EL spectrum is from an ITO/DSB-*block*-SEO/Al diode (2 mm^2 area; 100 nm thick layer). The PL spectrum is obtained by exciting with a He-Cd laser (325 nm) a 100 nm thick film on spectrosil. The relatively broad spectrum with respect to previous reports[6] is likely to be due to a greater disorder, induced by the significant *cis*-content.

account the electron-donating properties of the alkoxy groups in the 4 and 4′ positions.[9] The Stokes shift between absorption and emission is substantial (162 nm).

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 active material was spin-coated from a chloroform solution, and the device fabrication completed by thermal evaporation of a calcium and/or aluminium cathode.

Typical current density and luminance *vs.* voltage (IVL) curves for a diode with ITO and Al electrodes are reported in Fig. 4. The turn-on voltage is at 6.5 V, and we obtained luminance values over 2000 cd m^{-2} at 19 V, with luminescence efficiencies up to 0.5 cd A^{-1}. Interestingly, we observed no significant improvement when replacing Al cathodes by Ca cathodes in spite of a much lower work function (2.8 eV *vs.* 4.2–4.3 eV for Al). This is unexpected in view of the position of the frontier levels, found at 5.5 ± 0.1 eV (ionisation potential, IP) and 2.5 ± 0.1 eV (electron affinity, EA), determined by cyclic voltammetry with ferrocene as reference. Relatively high turn-on voltages, even when a poly(ethylenedioxythiophene)–poly(styrenesulfonic acid), PEDOT:PSS, hole-injection layer was used in order to try to increase the anode work function,[11] are consistent with the presence of a significant energy barrier at the anodic interface.

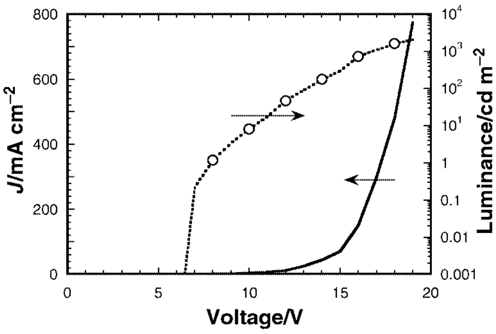

Fig. 4 Current density and luminance *vs.* voltage characteristics of the same ITO/DSB-*block*-SEO/Al device used for the EL spectrum of Fig. 3.

LECs use an electroluminescent polymer, an ion transporting polymer (such as poly(ethylene oxide)) and a salt in order to aid charge injection at the electrodes.[12] Since our polymer comprises both OEO and DSB within its backbone we were able to prepare LECs with active layers made of DSB-*block*-SEO blended with lithium triflate (10 wt%) (ITO/DSB-*block*-SEO(LiTf)/Al). The turn-on voltage was reduced to 3.8 V with emission, as before, in the green and we could observe electroluminescence under reverse bias.

In summary, we have prepared and characterised a solution processable polymer containing distyrylbenzene units having a 50:50 *cis*:*trans* vinylene distribution linked at the 4,4′-positions by sexi(ethylene oxide) units. In contrast to earlier reports on related materials this polymer can be used to construct very efficient LEDs.

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