New efficient blue light emitting polymer for light emitting diodes

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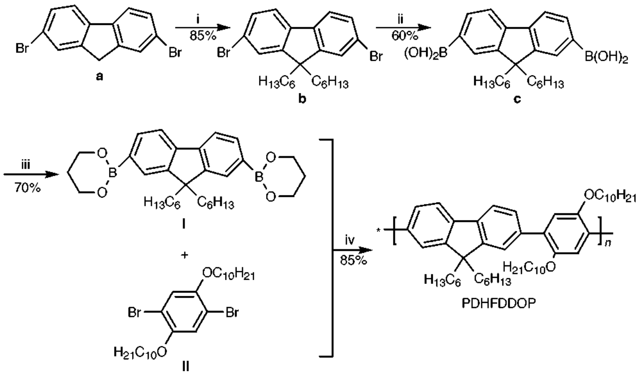
The synthesis, by the Suzuki coupling reaction, of a novel soluble blue light emitting polymer, poly{(9,9-dihexyl-2,7-fluorene–*alt-co*-[2,5-bis(decyloxy)-1,4-phenylene]} (PDHFDDOP) is reported. PDHFDDOP exhibits photoluminescence (PL quantum efficiency of 40% in neat films) and electroluminescence (EL) with deep blue emission.

The design and synthesis of light emitting polymers have received attention in the last decade following the discovery of EL in conjugated polymers and the development of polymer light emitting diodes (PLEDs) as a display technology.[1–4] Although the three primary colors have been demonstrated in PLEDs, only red (orange) and green PLEDs have sufficient efficiencies and lifetimes to be of commercial value.[3,4] Thus, to achieve full color polymer emissive displays, there is a need for stable blue-emitting conjugated polymers with high photoluminescence efficiency.

The first blue PLED was fabricated from poly(*para*-phenylene) (PPP),[5] which is not soluble in its conjugated form. Subsequently, soluble substituted PPPs were synthesized and high external EL quantum efficiencies were demonstrated.[6] However, low molecular weight and poor stability have limited the application of blue-emitting conjugated polymers. Blue EL has also been demonstrated in poly(*para*-phenylene vinylene) derivatives,[7] 3,4-disubstituted polythiophenes,[8] copolymers with and without non-conjugated segments,[9,10] and other structures.[11,12] Recently, the 9,9-disubstituted polyfluorenes have drawn attention as efficient blue-emitting polymers.[13–16]

We report here, the synthesis of a new blue light emitting conjugated polymer and preliminary data which characterize the emission from this polymer. As depicted in Scheme 1, poly{(9,9-dihexyl-2,7-fluorene)–*alt-co*-[2,5-bis(decyloxy)-1,4-phenylene]} (PDHFDDOP) comprises alternating fluorene and phenylene units. The long hydrocarbon chains at the fluorene bridge (‘9’) methylene and on the phenylene ring ensure the solubility of the polymer. PDHFDDOP was synthesized through the Suzuki coupling reaction.[17] The monomer 9,9-dihexylfluorene-2,7-bis(trimethylene boronate) **I**, was synthesized from 2,7-dibromofluorene **a** as starting material.† The monomer 1,4-dibromo-2,5-bis(decyloxy)benzene **II**, was prepared from hydroquinone by reaction with 1-bromodecane in a solution of NaOEt in ethanol, followed by bromination. Polymerization was performed in a refluxing toluene/aqueous potassium carbonate solution (2 M) containing 1.0–1.5 mol% of $Pd(PPh_3)_4$ under vigorous stirring for 48 h. The polymer was isolated by pouring the reaction mixture into methanol. After being purified and dried under dynamic vacuum at room temperature, the polymer was obtained as a white solid with the yield of *ca*. 85%. The structure was confirmed by NMR and elemental analysis.‡

PDHFDDOP readily dissolves in solvents, such as THF, chloroform, toluene and xylene. Uniform colorless films were prepared with thicknesses of *ca*. 750 Å on quartz and ITO coated glass substrates by spin coating from solution in toluene (3%) at a spin rate of 1500 rpm. Upon exposure to UV radiation, the films emitted intense blue fluorescence. The UV–VIS absorption and PL spectra obtained from the films on quartz are displayed in Fig. 1. The PL spectrum of poly(9,9-dihexyl-2,7-fluorene) (PDHF) is also given in Fig. 1 for comparison. The PL spectrum of PDHFDDOP has a maximum at 420 nm with a well defined vibronic feature at 448 nm. The emission peaks in the blue are very similar to those of PDHF. However, PDHF also emits at longer wavelengths (486, 534 nm). This longer wavelength emission is common in 9,9-disubstituted polyfluorenes and has been attributed to interchain excimer formation.[13,16] By contrast, the PL spectrum of PDHFDDOP does not include the longer wavelength components. The absolute PL efficiency of PDHFDDOP in neat films, as measured in an integrating sphere at room temperature, was found to be *ca*. 40%.



Scheme 1 *Reagents and conditions*: i, 1-bromohexane, 50% NaOH aqueous solution, TBACl, 80 °C; ii, (1) Mg, THF, (2) $B(OMe_3)_3$, THF, −78 °C to room temp., 48 h, (3) H_2SO_4 (5% in ice); iii, Propane-1,3-diol, toluene, reflux, 3 h; iv, Toluene/aqueous potassium carbonate solution (2 M), $Pd(PPh_3)_4$, reflux, 48 h.

Cyclic voltammetry (CV) was performed with a polymer film on a glassy carbon disc working electrode (*ca*. 0.2 cm^2) using a platinum wire as counter electrode and a silver wire as a quasi-reference electrode (electrochemical potential *ca*. 0.01 V *vs*.

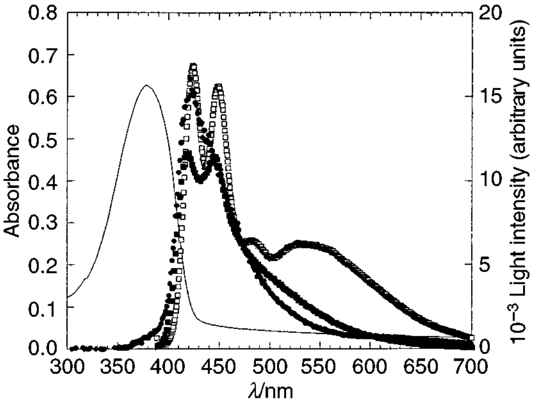


Fig. 1 Absorption (○), photoluminescence (■) and electroluminescence (●) spectra of PDHFDDOP. The photoluminescence spectrum of PDHF (□) is also given for comparison.

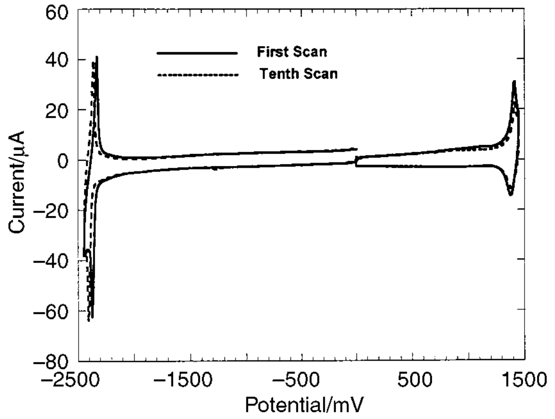


Fig. 2 Cyclic voltammograms of PDHFDDOP recorded from the first scan (——) and the tenth scan (– – – –) in a solution of TBAPF$_6$ (0.10 mol L^{-1}) in MeCN at room temp. Scan rate = 40 mV s^{-1}.

SCE). The data are shown in Fig. 2. Both the oxidative and the reductive reactions are reversible. The onset of reduction occurs at *ca.* −1.78 V above which the cathodic current quickly increases, and a cathodic peak appears at −2.38 V. A corresponding re-oxidation peak appears at −2.33 V. The n-doping potential, $E_{\mathrm{Red}}{}^{1/2}$, is −2.36 V. For oxidation, the onset potential is *ca.* 1.22 V and an anodic peak occurs at 1.42 V with the corresponding re-reduction peak at 1.37 V. The oxidation potential, $E_{\mathrm{Ox}}{}^{1/2}$, is 1.39 V. The difference between the p- and n-doping onset potentials is 3.00 V, implying that the π–π* band gap of the polymer is 3.00 eV; the same as the value determined from the onset of optical absorption. The HOMO and LUMO energy levels of the polymer were estimated from the p- and n-doping onset potentials[18] to be 5.66 and 2.62 eV, respectively. As shown in Fig. 2, after ten scans for the same polymer film, both the potentials and the current intensities of the redox peaks remain almost unchanged.

EL devices with the configuration of ITO|PVK (900 Å)|PDHFDDOP (750 Å)|Ca were fabricated, where PVK is poly(*N*-vinylcarbazole). Because of the low HOMO energy of PDHFDDOP, 5.66 eV below vacuum there is a large energy barrier for hole injection from ITO into the polymer layer. Here we use PVK as hole transporting layer. A typical device emits visible blue light at *ca.* 10 V forward bias (ITO wired positive) and reaches the brightness of 115 cd m^{-2} for a bias of 23.8 V. This gives an efficiency of 0.34 cd A^{-1} and a luminosity of 0.045 lm W^{-1}. The maximum external quantum efficiency was 0.60%. The current and light output characteristics are given in Fig. 3. The EL spectrum is displayed in Fig. 1. As noted for other polymer LED devices,[11] the HOMO level of PL (6.1 eV below vacuum) causes a large barrier for hole injection. Nevertheless, the external quantum efficiency is three times higher than that of the blue polymer LED device of 9,9-dioctylpolyfluorene, in which a polymeric triphenyldiamine is used as hole transporting layer and the thickness of the emissive polymer layer has been optimized.[14]

In summary, a new light emitting polymer, poly{(9,9-dihexyl-2,7-fluorene)–*alt-co*-[2,5-bis(decyloxy)-1,4-phenylene]}, has been synthesized. The polymer emits deep blue light without longer wavelength components in the emission spectrum. Relatively high PL and EL efficiences have been demonstrated. Improved EL performance, lower operating voltage and higher efficiency can be expected by further improving the hole-injection. The results demonstrate that this new polymer is a promising candidate for blue-emitting polymer LEDs.

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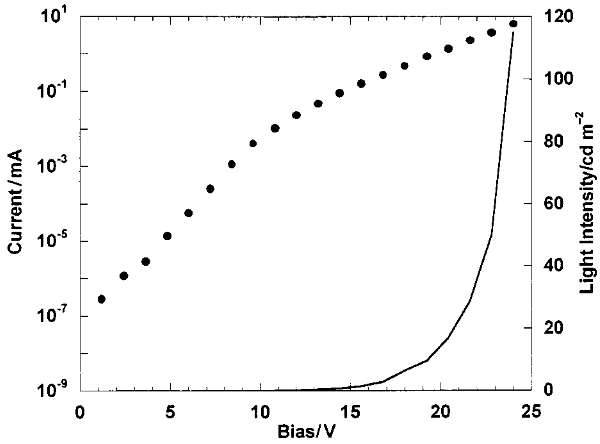

Fig. 3 Light output and *I–V* characteristics of a device in the ITO|PVK|PDHFDDOP|Ca configuration.

Notes and references

† The reaction of 2,7-dibromofluorene with 1-bromohexane in 50% NaOH aqueous solution in the presence of tetrabutylammonium chloride at 80 °C afforded 2,7-dibromo-9,9-dihexylfuorene **b** as white crystals after purification by recrystallization from ethanol. 2,7-Dibromo-9,9-dihexylfuorene **b** was treated with magnesium (turnings) in THF to form the Grignard reagent. The Grignard reagent solution was slowly dropped into a sitrred solution of trimethyl borate in THF at −78 °C. The mixture was stirred at −78 °C for 2 h and then at room temperature for two days. The reaction mixture was then poured into crushed ice containing sulfuric acid (5%) while stirring. The mixture was extracted with diethyl ether and the combined extracts were evaporated to give a white solid. Recrystallization of the crude product from hexane–acetone (80 : 20) afforded pure 9,9-dihexylfuorene-2,7-diboronic acid **c** as a white solid. The diboronic acid **c** was then reacted with propane-1,3-diol in toluene under reflux to produce monomer **I**.

‡ PDHFDDOP, ^{1}H NMR (CDCl$_3$, 200 MHz) δ 7.80 (d, 2H), 7.74 (s, 2H), 7.58 (d, 2H), 7.14 (s, 2H), 3.99 (t, 4H), 2.05 (br, 4H), 1.72 (t, 4H), 1.50–0.97 (m, 44H), 0.82 (t, 12H). Anal. Found: C, 84.50; H, 10.59. Calc. for $C_{51}H_{76}O_2$: C, 84.94; H, 10.62%.

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