The synthesis and characterization of an efficient green electroluminescent conjugated polymer: poly[2,7-bis(4-hexylthienyl)-9,9-dihexylfluorene]

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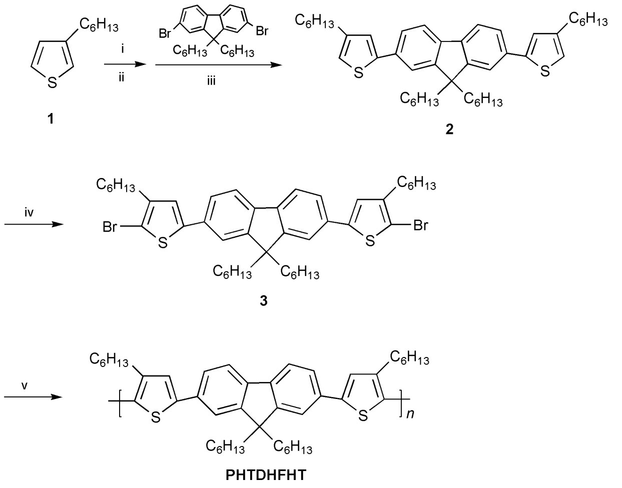
A novel soluble electroluminescent (EL) material, poly[(4-hexylthiophene-2,5-diyl)(9,9-dihexyl-9*H*-fluoren-2,7-ylene)(4-hexylthiophene-2,5-diyl)] (PHTDHFHT), with high absolute photoluminescence (PL) quantum efficiency (32 ± 3%) compared with other polythiophene derivatives, was synthesized and a green EL is observed.

During the past decade, design and synthesis of novel conjugated polymers as low-cost materials with high potential for electronic and optoelectronic applications have received considerable attention.[1–3] The development of novel highly efficient materials that emit primary color lights is particularly attractive due to the requirement for full-color displays. Among conjugated polymers, polythiophene (PT) and its processable derivatives are an important class of representatives as electrically conductive and optoelectronic materials because of their high electrical conductivity and environmental and thermal stability in both neutral and doped states, as well as their interesting electronic and optical properties.[4–6] However, the low PL quantum efficiency of PTs in solid films, typically 1–3%, has limited the application of PTs in polymer light-emitting diodes (PLEDs).[7] In our previous reports, a significant increase in PL efficiency of PTs by modifying the backbone structure with phenylene groups was demonstrated.[8,9] Recent progress made in our group demonstrates that 9,9-disubstituted polyfluorene copolymers with arylene groups, such as a phenylene ring, may exhibit relatively high PL and EL efficiencies as well as good EL performances.[10,11] Here we present a novel conjugated polymer, PHTDHFHT, in which thiophene moieties are introduced into the backbone of poly(9,9-dihexyl-9*H*-fluoren-2,7-ylene) in place of phenylene units. The resultant polymer emits green PL and EL with high quantum efficiencies.

The synthetic approach towards PHTDHFHT is outlined in Scheme 1. Compound **2** is synthesized through the coupling reaction between thienylzinc chloride and 2,7-dibromo-9,9-dihexylfluorene catalyzed by Pd(PPh$_3$)$_4$ in a high yield (89%). The bromination of compound **2** with NBS produces monomer **3**, 2,7-bis(5-bromo-4-hexylthienyl)-9,9-dihexyl-9*H*-fluorene. The polymer, PHTDHFHT, was obtained through a nickel-catalyzed reductive polymerization. Usually the preparation of PFs and PTs can also employ direct oxidative polymerization using ferric chloride as an oxidant. It was found that residual iron in the polymers was difficult to remove completely, which could affect the performance of devices.[12] Metal-catalyzed coupling reactions of dihalo compounds in place of the oxidative polymerization by ferric chloride was employed in our synthesis. The reductive polymerization also avoids irregular coupling or branching that easily happens in conventional electrochemical and oxidative polymerization. After careful purification,† the polymer was obtained as a light-yellow solid in a yield of 60%.

PHTDHFHT is highly soluble in common organic solvents, *e.g.*, THF, toluene, xylene, and CHCl$_3$. Uniform and transparent films on substrates, such as ITO-coated glasses and microslides, can be obtained by spin-casting the solutions. The molecular structure and purity of the polymer are verified by ^{1}H and ^{13}C NMR, FT-IR, and elemental analysis.‡ The molecular weights of the polymer determined by gel permeation chromatography (GPC) against the polystyrene standards in THF are $M_w = 2.1 \times 10^4$, $M_n = 1.3 \times 10^4$ (polydispersity, 1.67). Thermal gravimetry analyses (TGA) (heating at 10 °C min^{-1} in nitrogen) indicate that the polymer is stable up to 300 °C. Differential scanning calorimetry (DSC) reveals an exothermic phase transition around 70 °C, which is higher than those of our previously reported poly[bi(thienyl)phenylene] derivatives.

The absorption and photoluminescence (PL) spectra of the polymer as film (spun-cast from a solution in xylene at the concentration of 30 mg ml^{-1}) on microslides are shown in Fig. 1. The absorption onsets at 490 nm and gives a broad spectrum with the maximum at 396 nm. From the onset wavelength, the optical band gap of the polymer can be estimated to be 2.53 eV. The film emits intensive green light when it is exposed to UV light. The PL spectrum exhibits a peak at 493 nm with a shoulder at 515 nm, corresponding to green emission (CIE: $x = 0.24$, $y = 0.51$). The absolute PL quantum yield of the neat polymer film was measured to be 32 ± 3% in an integrated sphere at rt in air using an argon ion laser line of 358 nm as the excitation source according to the procedure described by Greenham *et al.*[13] The PL efficiency is quite high compared with conventional PTs, and is also higher than those of our previously reported polythiophene derivatives modified by the phenylene group in their backbones, although it is still lower than those measured from 9,9-disubstituted polyfluorenes which are highly efficient blue light-emitting polymers.[14] The photochemical stability of PHTDHFHT is also high. The fluorescence intensity of the thin film shows negligible degradation in 5 h under irradiation of UV light (367 nm) in air. This is similar to other polyfluorene and polythiophene



Scheme 1 *Reagents and conditions*: i, LDA, THF, −78 °C, 2 h; ii, ZnCl$_2$, THF, −78 °C, 2 h; iii, Pd(PPh$_3$)$_4$, THF, reflux, 20 h; iv, NBS, CHCl$_3$–AcOH, 10 h; v, NiCl$_2$, Zn, PPh$_3$, 2,2′-dipyridyl, DMAC, 20 h.

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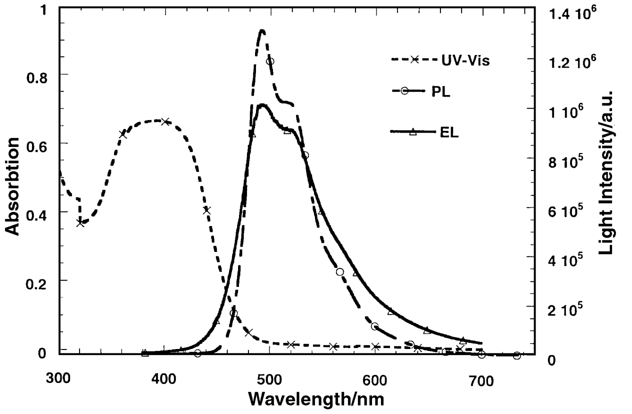

Fig. 1 UV-visible absorption (film), photoluminescence (film), and electroluminescence spectra of PHTDHFHT.

derivatives. These results indicate that PHTDHFHT is an efficient and stable green emissive material.

Cyclic voltammetry (CV) was performed on a thin polymer film of PHTDHFHT coated onto a glassy carbon disc electrode in a 0.1 mol L^{-1} tetrabutylammonium hexylfluorophosphate (n-Bu$_4$NPF$_6$) solution in acetonitrile by using platinum wire as a counter electrode and a silver wire as a quasi-reference electrode. All the experiments were performed in a glove-box under an argon atmosphere at rt. As shown in Fig. 2, in the anodic scan, the oxidation started at about 0.90 V and gave a sharp oxidation peak at 1.21 V. The re-reduction peak appeared at 1.15 V. On sweeping the polymer cathodically, the reduction (n-doping) began at -1.60 V and then the cathodic current increased quickly and produced a cathodic peak at -1.81 V, and a corresponding re-oxidation peak occurred at -1.75. The oxidation and reduction reactions are reversible. The clear redox behavior and the good doping reversibility prove that the polymer may be a good candidate of EL materials for applications in polymer light emitting diodes and polymer light-emitting electrochemical cells (LECs).[15] The electrochemically measured band gap is 2.5 V, which agrees well with the HOMO–LUMO energy gap of 2.53 eV as determined from the absorption onset. The HOMO and LUMO energy levels of this polymer were estimated from the oxidation and reduction onset potentials to be -5.30 and -2.85 eV, respectively.

The fabrication of LED devices was carried out in a glove box under a nitrogen atmosphere. The thickness of the PHTDHFHT film was about 100 nm and the thickness of the calcium electrode, which was thermally evaporated onto the polymer film under 10^{-6} Torr, as about 200 nm. First, the single devices with the configuration ITO–PHTDHFHT–Ca were fabricated. In forward bias, the single-layer devices turned on at about 20 V for current and emitted green light at about 21 V. Considering the energy barrier for hole injection at the anode, double-layer devices with the configuration ITO–PVK–PHTDHFHT–Ca were also fabricated. By employing a PVK layer (90 nm) between the ITO and the polymer film the turn-on voltage for light output was reduced to about 8 V, and the maximum external quantum efficiency was increased from 0.05 to 0.6%. It indicates that PVK as hole-transporting layer can reduce the turn-on voltage of the devices and improve their efficiency.

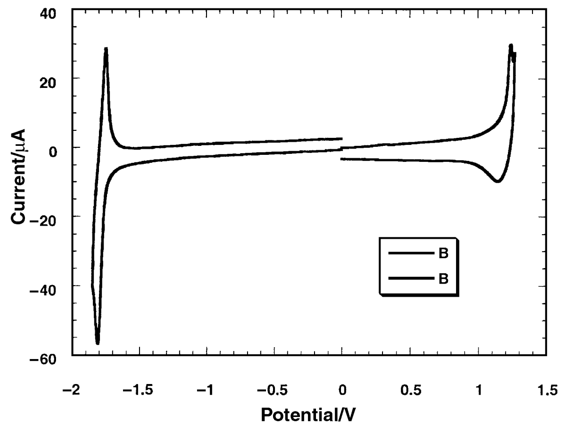

Fig. 2 Cyclic voltammograms of PHTDHFHT recorded in a solution of TBAPF6 (0.1 M) in acetonitrile at rt.

In conclusion, a novel poly(fluorene-*co*-bithiophene) conjugated polymer, PHTDHFHT, was prepared through metal-catalyzed coupling polymerization in place of ferric chloride oxidative reaction. This polymer shows good thermal stability and photostability. Efficient green PL and EL are demonstrated with the polymer.

Notes and references

† The polymer was precipitated from the reaction mixture by pouring it into MeOH. The precipitate was washed with MeOH and was then re-dissolved in THF. The THF solution was vigorously stirred together with the 50% aqueous solution of hydrazine monohydrate (v:v 1:1) at rt for 24 h. The THF solution was separated and filtered. The solution was then poured into MeOH to precipitate the polymer. The polymer was collected by filtration and was washed with MeOH. Finally, the polymer was washed with acetone in a Soxhlet apparatus for 24 h and then dried under vacuum at rt.

‡ *Selected data* for the monomer (compound **3**): δ_H(CDCl$_3$, 200 MHz, ppm) 7.64–7.68 (2H, d, J = 7.93 Hz, Ar-H), 7.45–7.64 (4H, m, Ar-H), 7.06 (2H, s, Th-H), 2.56–2.63 (4H, t, J = 7.2 Hz, CH$_2$), 1.96–2.04 (4H, m, CH$_2$), 1.61–1.65 (4H, m, CH$_2$), 1.25–1.35 (14H, m, CH$_2$), 1.00–1.10 (10H, m, CH$_2$), 0.89–0.95 (6H, m, CH$_3$), 0.76–0.85 (6H, m, CH$_3$); EI-MS (*m/z*): 824, 822, 820 (M$^+$); for PHTDHFHT: δ_H(CDCl$_3$, 200 MHz, ppm): 7.58–7.74 (6H, m, Ar-H), 7.31 (2H, s, Th-H), 2.59–2.65 (4H, t, J = 7.2 Hz, CH$_2$), 2.00–2.11 (4H, m, CH$_2$), 1.61–1.75 (4H, m, CH$_2$), 1.21–1.42 (12H, m, CH$_2$), 1.00–1.20 (12H, m, CH$_2$), 0.82–0.95 (6H, m, CH$_3$), 0.74–0.81 (6H, m, CH$_3$); δ_C(CDCl$_3$, 50 MHz, ppm): 151.69, 144.40, 143.53, 140.29, 133.08, 128.03, 124.53, 124.48, 120.07, 119.60, 55.31, 31.68, 31.48, 30.78, 29.68, 29.21, 23.78, 23.72, 22.60, 14.10, 14.01. Anal. Calc. For $C_{45}H_{60}S_2$: C, 81.26; H, 9.09; S, 9.64. Found: C, 81.44; H, 9.16; S, 9.47%.

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