Efficient Photoluminescence and Electroluminescence from a Soluble Polyfluorene

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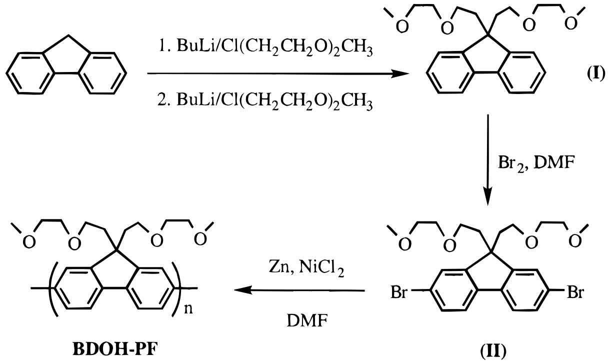
Light-emitting diodes (LEDs) using luminescent conjugated polymers as the emissive medium are currently under active development for display applications. The quantum efficiency of the LEDs is determined by the photoluminescent (PL) efficiency of the emissive polymer and by the balanced injection of electrons and holes.[1,2] Solid-state light-emitting electrochemical cells (LECs) provide an alternative opportunity for light emission from thin polymer films.[3] An ideal material for LECs would have an interpenetrating network morphology: one network to provide the channels for ion transport and the other network to provide the pathways for transport of electronic charge carriers.[3b] Such a bicontinuous network morphology has been obtained by using a bipolar liquid surfactant in the blend of a hydrophobic poly(2,5-dialkoxy-1,4-phenylenevinylene) and a hydrophilic poly(ethylene oxide) complex with lithium triflate.[4] In this communication, we report the synthesis of a high-efficiency luminescent polymer, poly[9,9-bis(3,6-dioxaheptyl)-fluorene-2,7-diyl] (BDOH-PF). The conjugated poly(1,4-phenylene) main chain is capable of transporting electrons and holes, while the bis(3,6-dioxaheptyl) side groups function to solvate ions and promote ion transport as required for high-performance LECs.[5,6]

BDOH-PF was synthesized starting from fluorene. Fluorene was reacted with equimolar butyllithium at −50 °C in THF. The resulting 9-lithiofluorene was reacted with equimolar 1-chloro-2-(2-methoxyethoxy)ethane at −40 to 20 °C, yielding 9-(3,6-dioxaheptyl)fluorene. This process was repeated to obtain (**I**) which was separated by vacuum distillation at 160 °C/0.06 mmHg. The overall yield was 80%. Direct oxidative polymerization of (**I**) using 4:1 molar iron(III) chloride as the oxidant in chloroform yielded a brown polymer.[7] Residual iron chloride in the polymer was difficult to remove completely. Therefore, an alternative route involving 2,7-dibromo-9,9-bis-(3,6-dioxaheptyl)fluorene (**II**) was used. Bromination of (**I**) with excess amount of bromine in DMF was completed at 22 °C within 10 min. The product (**II**) was separated by flash chromatography using hexane/ether (1:1) as the eluent. The yield was 72%. Reductive polymerization of (**II**) in DMF using zinc as the reductant and reactive nickel(0) as the catalyst produced light-yellow powders of BDOH-PF after repeated dissolution in THF and precipitation in methanol.[8] The yield was 35%.



BDOH-PF as-obtained was characterized by FT-IR, ^{1}H NMR, and elemental analysis. The molecular weight determined by GPC is Mw = 215 000, Mn = 94 000, calibrated to a polystyrene standard, and the polydispersity is 2.3. This molecular weight is higher than those of soluble poly(2-substituted-1,4-phenylene)s synthesized by a similar method, probably because the side groups in BDOH-PF are farther away from the coupling 2,7-carbons of the fluorene ring and do not sterically interfere with the coupling polymerization.

BDOH-PF is soluble in THF, toluene, DMF, cyclopentanone, and other common organic solvents. Thin films cast from the solutions are colorless and optically transparent. Figure 1 displays the optical absorption and PL spectra of a solution of BDOH-PF in THF (1 mg/100 mL) and of a thin film spin-cast from a concentrated solution (20 mg/mL). The absorption spectrum of the dilute solution has a relatively sharp peak at 385 nm, with an onset of absorption at 430 nm. The absorption spectrum of the thin film is similar except that the peak is broader. This small change in absorption spectrum from a dilute solution to thin film is in contrast to other soluble conjugated polymers such as poly(3-alkylthiophene) where large solvatochromism has been observed.[9] In BDOH-PF, the side groups that render the polymer soluble are well separated from the side groups on the adjacent fluorene unit. Therefore, the steric interaction between side groups that twists the conjugated repeating units from planar configuration and causes the solvatochromism in poly(3-alkylthiophene)s is negligible in BDOH-PF.

The band gap of BDOH-PF (taken from the onset of the absorption spectrum) is 2.8 eV, smaller than that of poly(2-(decyloxy)-1,4-phenylene) (DO-PPP).[8] The negligible steric interaction of the side groups between adjacent fluorene units and the locking of the two phenylene rings in a planar configuration by the 9-carbon of fluorene account for the smaller band gap of BDOH-PF.

The PL spectrum of the dilute solution of BDOH-PF pumped by UV light ($\lambda = 367$ nm) has two sharp peaks at 430 and 450 nm, with minor shoulders at 482 and 520 nm. The quantum yield was measured to be 77%,[10] comparable to many laser dyes in dilute solutions.[11] The PL spectrum of the thin film also has two sharp peaks in the blue region. In addition, a broad and intense peak appears in the green region. This broad peak is probably from interchain excimer emission.[12] In the dilute solution, the polymer chains are separated from each other, and

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(10) The 367 nm line of a mercury lamp is used as the excitation source. The luminescence is collected with an integrating sphere. Coumarin 102 in a dilute solution in ethanol with a reported PL yield of 93% (Fletcher, A. N.; Bliss, D. E., *Appl. Phys.* **1978**, *16*, 289) is used as the standard. This solution was purged with argon prior to measurement. The measurement of the photoluminescent yield of the dilute solution and the thin film of BDOH-PF was carried out in air.

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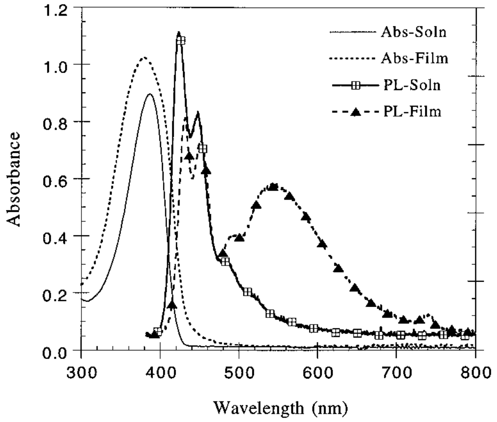

Figure 1. Optical absorption and PL spectra of BDOH-PF in a dilute solution in THF (1 mg/100 mL) and in a thin film spin-cast from a solution in THF (20 mg/mL). The 367 nm line of a mercury lamp is used as the excitation source.

excimer emission is suppressed. The color of the PL emission from the film appears sky blue, and the quantum yield was measured to be 73%,[10] higher than the other known luminescent conjugated polymers.[8,13] Photochemical stability of BDOH-PF is high: the PL intensity of the thin films showed negligible degradation in 1 h under irradiation of 1 mW/cm^2 of 367 nm UV light in air. On the other hand, the thermal stability of the PL is not high; the emission color shifted to white and the emission efficiency decreased to ~50% when the films were heated at 110 °C in an inert gas or air for 1 h. This thermal degradation probably resulted from enhanced excimer emission due to a spatial rearrangement of the polymer chains.

Since the side groups of BDOH-PF are hydrophilic, all light-emitting devices were fabricated and tested in a dry box. An LED was fabricated by sandwiching a thin film of BDOH-PF (~1200 Å thick, spin-cast from a solution in cyclopentanone) between an ITO-coated glass (as anode) and a vacuum-evaporated calcium film (as cathode). This diode turned on at 9 V and reached a brightness of 100 cd/m^2 at 30 V. The external quantum efficiency of the diode was approximately 0.3%, lower than that of a similar device using DO-PPP as the emissive layer, even though DO-PPP has a PL efficiency which is approximately half of that of BDOH-PF.[8] The lower efficiency implies that the injection of electrons and holes into the BDOH-PF film is not balanced.

LECs were fabricated using a blend of BDOH-PF with lithium triflate, at a weight ratio of 4.72/1, as the emissive material. A thin film of this blend (1500 Å thick) was sandwiched between an ITO-coated glass and a vacuum-evaporated aluminum film (400 Å thick). When a bias of 3.1V was applied between the two electrodes, the devices slowly turned on and emitted bright sky blue light. Figure 2 displays the current and light intensity as a function of time over a period of 5 h. The current and light intensity curves follow the same pattern. Both turn on rapidly, continue to increase in the first hour, reach a maximum in approximately 2 h, and then gradually decrease. The initial increase of current and emission intensity is probably due to the continuous growth of the p-type and n-type doped regions at the anode and cathode sides, respectively. At 3.1 V, the emission intensity reached a maximum brightness of 190 cd/m^2. The external quantum efficiency was 4% photons/electron, and the power efficiency was 12 lm/W. At 3.5 V, the emission intensity was 1000 cd/m^2 at a power efficiency of 8.6 lm/W.

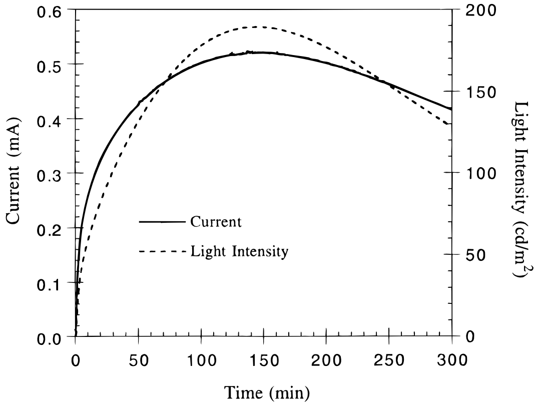

Figure 2. Current and light intensity as a function of time of an ITO/BDOH-PF + LiCF$_3$SO$_3$/Al LEC biased at 3.1 V.

The electroluminescent spectrum was similar to the PL spectrum of the thin film of BDOH-PF, although in the EL spectrum, the green peak was enhanced somewhat relative to the blue peaks.

The decrease of the current and emission intensity after 3 h of operation was not reversible. One possible mechanism is the thermal degradation of the polymer layer, as the emission color changed from sky blue to white during the operation. To suppress this degradation, a device was cooled to a constant temperature of 0 °C. The current and emission intensity at 3.1 V both substantially decreased. The EL efficiency remained unchanged, while the lifetime increased to about 20 h (light intensity dropping to half). Other degradation processes cannot be ruled out, such as degradation of the polymer/electrode interfaces and decomposition of the added lithium triflate.

In summary, we have successfully synthesized a high molecular weight, fully conjugated polyfluorene with bis(3,6-dioxaheptyl) side groups. While the conjugated main chain is electroactive and serves as an electronic conductor, the side groups can dissolve a lithium salt and serve as an ionic conductor. This polymer is sky blue fluorescent with a quantum yield of 73% in solid-state thin films. Solid-state light-emitting electrochemical cells based on this polymer and a dissolved lithium salt efficiently emitted bright blue light at low operating voltages. Studies are under way to address the problems of slow response and rapid degradation of the devices.

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(12) Interchain excimer formation has already been observed in other conjugated polymers with fused aromatic ring units (Jenekhe, S. A.; Osaheni, J. A. *Science* **1994**, *265*, 765). As added proof, in alkyl-PFs we have found that the PL color of the thin films is dependent on the size of the side groups: 9-hexyl-PF, pure green; 9,9-dihexyl-PF, blue-green; 9-hexyl-9-(2-ethylhexyl)-PF, sky blue (with green component); 9-(2-ethylhexyl)-9-(3,6,9-trioxadecyl)-PF, pure blue. All these polymers in solutions emit the same blue color.

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