Efficient Cyano-Containing Electron-Transporting Polymers for Light-Emitting Diodes

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Poly(dialkylfluorene)s possess excellent thermal and chemical stability, high photoluminescence (PL) quantum efficiencies, and high hole mobilities.[1−4] However, these wide band gap materials have a relatively low electron affinity, which makes electron injection rather difficult with the use of conventional cathode materials.[5,6] The electron-transporting properties of polyfluorenes have been improved by incorporating electron-deficient comonomers, such as benzothiodiazole and cyano-substituted olefins into the polymer main chain.[7,8] However, the elongated conjugation length and charge transfer shifted the emission color of these two copolymers to the green region. In addition, the vinylenic linkage of the cyano-substituted olefins is intrinsically unstable and can very easily be photo-oxidized to form carbonyl groups, which will act as defect sites to trap electrons.[9] Recently, a fluorene-based alternating copolymer containing 2-cyanobenzene was also synthesized to modify the electronic properties of the fluorene.[10] Although this polymer possessed a quite high PL efficiency (48%), there is no information regarding its EL properties. Concurrent with that effort, we have introduced a dicyanobenzene unit into the fluorene system to enhance the electron affinity of the polyfluorene (Scheme 1). With variation of the ratio between two monomers (fluorene and dicyanobenzene), the electron affinity and mobility of the resulting polymers were significantly enhanced.

The synthetic route for the poly(9,9-di-*n*-hexylfluorene-*co*-2,5-dicyanophenylene) (PF−CNP) polymers is described in Scheme 1. A two-step oxidation process involving nitric acid followed by potassium permagnant as the oxidation reagents was adopted to afford the diacid **1** (overall yield: 40%).[11] Diacid **1** was converted into acid chloride and then further reacted with ammonium hydroxide to give diamide **2** in quantitative yield. The 1,4-dibromo-2,5-dicyanobenzene was obtained by the dehydration reaction of the diamide.[12] Monomer 9,9-di-*n*-hexylfluorene-2,7-di(ethylenyl boronate) was synthesized using fluorene as the starting material following literature procedures.[13,14] The polymerization is based on the Suzuki coupling reaction described in the literature.[15] The chemical structures of the polymers were confirmed by ^{1}H NMR and elemental analyses. These polymers are quite soluble in common organic solvents, such as toluene, tetrahydrofuran, and dichloroethane, etc.

The optical properties of these polymers were studied in thin films. Figure 1 compares the UV−vis absorption spectra of PF−CNP copolymers with that of the fluorene homopolymer, poly(9,9-di-*n*-hexylfluorene) (PHF). The absorption of PF−CNP (3:1) possesses a strong featureless $\pi-\pi^*$ transition that peaks at 380 nm, which is very similar to the absorption of PHF, except for a broader line width. Its optical band gap is estimated to be 2.85 eV from the onset of UV−vis absorption. The alternating copolymer, PF−CNP (1:1), exhibits a main absorption peak at 384 nm, identical to that of PHF, which is attributed to the fluorene building blocks, and an additional absorption peak at shorter wavelength, 328 nm, contributed from the 2,5-dicyanobenzene moieties. The optical band gap of this polymer is slightly larger (2.92 eV) due to a less planar structure. However, the PL spectra of both cyano-containing polymers (Figure 1) are red-shifted with respect to that of PHF owing to the intramolecular charge transfer between the fluorene and 2,5-dicyanobenzene rings. PF−CNP (3:1) emits pale blue light with an emission peak at 477 nm, showing a larger stokes shift than the PF−CNP (1:1). Because the higher content of 2,5-dicyanobenzene in PF−CNP (1:1) slightly twists the conjugation path out of plane compared to that in PF−CNP (3:1), with only 25% benzene units, it emits at a shorter wavelength around 447 nm. Both polymers are strongly fluorescent. The solid-state PL quantum efficiencies, as measured in an integrating sphere, were found to be 66% for PF−CNP (3:1) and 48% for PF−CNP (1:1), respectively.

Electrochemical data from cyclic voltammetry (CV) indicate that the introduction of cyano electron-withdrawing functionality leads to a significant increase in electron affinity (E_a) from the 2.12 eV for PHF[5] to 2.89 eV for PF−CNP (3:1) and 2.98 eV for PF−CNP (1:1). This demonstrates the effectiveness of dicyanobenzene in improving charge-injection properties of polymers. A crude estimation of the highest occupied molecular orbital (HOMO) levels of these two polymers was obtained from the subtraction of LUMO level values from the optical band gaps. The corresponding values

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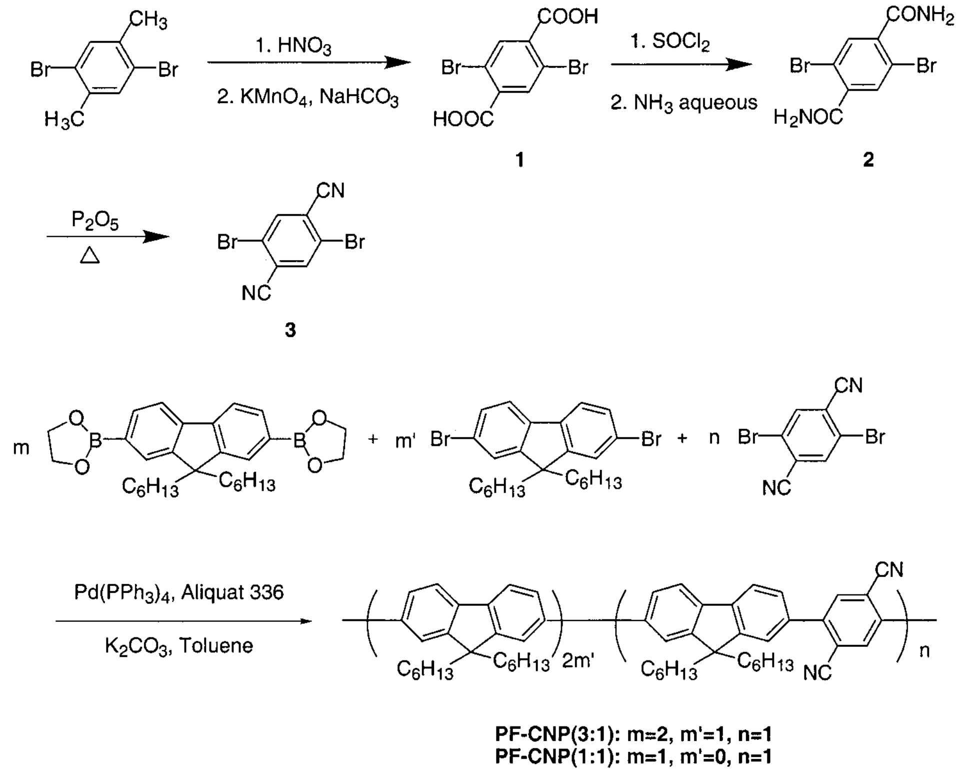
Scheme 1. Synthetic Route of CN-Containing Polyfluorenes



PF-CNP(3:1): m=2, m'=1, n=1
PF-CNP(1:1): m=1, m'=0, n=1

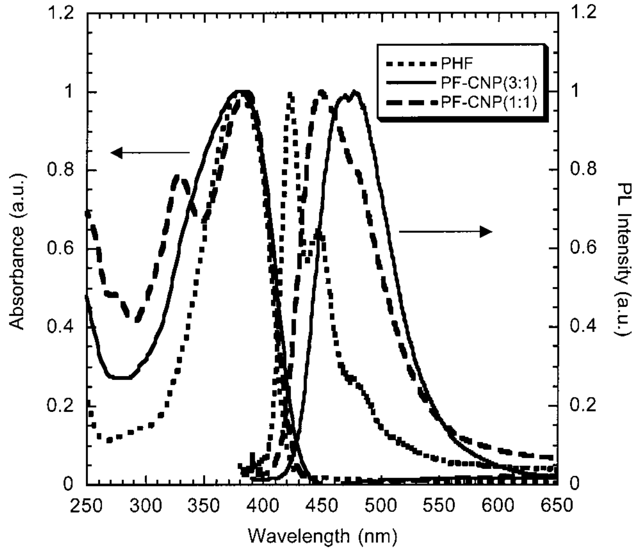


Figure 1. Optical absorption and PL spectra of PF–CNP (3:1) and PF–CNP (1:1) thin films on quartz substrate. The absorption and PL spectra of PHF thin films are also shown for comparison.

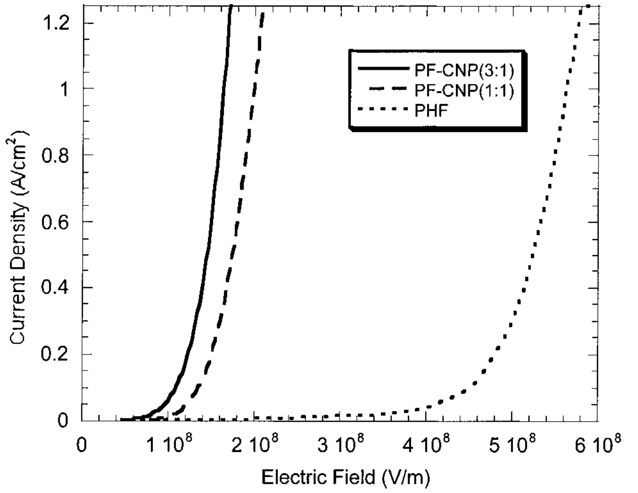


Figure 2. I–V characteristics of "electron-only" devices.

for PF–CNP (3:1) and PF–CNP (1:1) are -5.74 and -5.90 eV, respectively.

The electron-transporting properties of these polymers were investigated using an "electron-only" configuration that contains a polymer layer sandwiched between Al and Ca electrodes.[16] By replacement of the high work function ITO (4.7 eV) with a lower work function metal Al (4.3 eV), the energy barrier for hole injection is increased. Hole injection becomes very difficult, and only electron injection becomes dominant due to the Ohmic contact between the Ca cathode and polymer. As a result, the current density–electric field (J–E) characteristics are only related to the electron conduction of the bulk polymer films. The J–E characteristics of these devices showed that both polymers bearing cyano groups possess much higher electron conduction than PHF; the current increased dramatically at low electric field (Figure 2). The highest electron conduction was achieved in the PF–CNP (3:1), whose LUMO level is 0.1 eV higher than that of PF–CNP (1:1). This may be due to the higher content of the cyano substituents in the PF–CNP (1:1) that stabilizes the radical anion and slows down the electron motion. In addition, the less planarity of PF–CNP (1:1) will also hinder the electron transport.

EL measurements were performed on a simple device structure ITO/polymer/Ca. In general, the EL spectra

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Table 1. Performance of Single-Layer and Double-Layer LEDs Based on PF−CNP (3:1) and PF−CNP (1:1)

device structure	d[a] (nm)	V_{on}[b] (V)	B_{max}[c] (cd/m^2)	η_{max}[d] (%)
ITO/ PF−CNP (3:1)/Ca	60	4.6	223	0.018
ITO/ PF−CNP (1:1)/Ca	70	8.0	31	0.0028
ITO/PEDOT/PF−CNP (3:1)/Ca	90	3.4	5430	0.50
ITO/PEDOT/PF−CNP (1:1)/Ca	80	3.9	677	0.057
ITO/PEDOT/PHF/Ca	85	4.5	717	0.044

[a] Thickness of the emitting layer. The thickness for the PEDOT layer is 40 nm for all double-layer devices. [b] Turn-on voltage, defined as the voltage required to give a luminance of 1 cd/m^2. [c] Maximum brightness. [d] Maximum external quantum efficiency.

of the polymers are similar to their corresponding PL spectra. Pale blue light was observed with an onset of 4.6 V for PF−CNP (3:1) (Table 1). While the device based on PF−CNP (1:1) showed uniform blue emission with a turn-on voltage of 8.0 V. The single-layer devices based on these two polymers suffer low brightness and efficiency due to a large energy barrier for hole injection. The excessive electrons injected from Ca will reach the ITO electrode without recombining with holes. Considerable improvements for EL efficiency and luminance were achieved in the devices with the configuration of ITO/PEDOT/polymer/Ca in which a conducting polymer, poly(3,4-ethylene dioxythiophene), was employed as the hole-injecting layer to lower the barrier for hole injection (Table 1). For comparison, the device with PHF as the active layer was also fabricated using the same configuration. The efficiencies of the devices are improved by a factor of 20 and are higher than PHF due to much more balanced charge injection and transport for both holes and electrons. The ITO/PEDOT/PF−CNP (3:1)/Ca device has the best performance with a turn-on voltage of 3.4 V and high brightness of 5430 cd/m^2 at a bias voltage of 7.4 V (current density of 0.964 A/cm^2), corresponding to an external quantum efficiency of 0.38%. The maximum external quantum efficiency of PF−CNP (3:1) (0.5%) is much higher than that of polymer PF−CNP (1:1) (0.057%). This could be attributed to optimized electron affinity and electron conduction as well as higher PL efficiency of PF−CNP (3:1). In addition, the PF−CNP (1:1) has a HOMO 0.16 eV lower than that of PF−CNP (3:1), which makes the injection of holes even more difficult. As a result, it pushes the recombination interface closer to PEDOT, which quenches exciton emission.

In conclusion, two copolymers PF−CNP (3:1) and PF−CNP (1:1) composed of 9,9-di-*n*-hexylfluorene and 2,5-dicyanobenzene have been synthesized. Efficient blue emission and good electron affinity and conduction have been demonstrated in these two polymers. The device employing the cyano-containing copolymer, PF−CNP (3:1) as the emitting layer showed a low turn-on voltage (3.4 V), improved EL efficiencies (0.5%), and high brightness (5430 cd/m^2) compared with the PHF device with the same configuration. This is due to improved electron injection from the cathode to the polymers and higher electron conduction.

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Supporting Information Available: Experimental data for PF-CNP (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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