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Synthesis and Electroluminescent Properties of Soluble Poly(3,6-fluorene) and Its Copolymer

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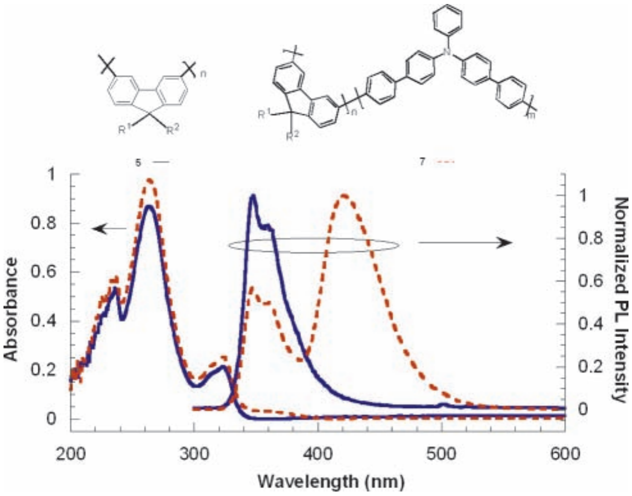
ABSTRACT



Soluble poly(3,6-fluorene) and its copolymer were synthesized by nickel-catalyzed coupling. Poly(3,6-fluorene) exhibited the optical band gap of 3.6 eV, the emission maximum at 347 nm, and the HOMO level of –6.05 eV. These results confirm that 3,6-linkage is an effective way to get wide band gap conjugated polymers. Furthermore, its copolymer containing triarylamine moieties emits deep-blue light, which means that the adjustable blue light emission can be obtained from their copolymers via energy transfer.

Wide band gap polymers are attracting more and more attention because they can be used as a host for blue electrophosphorescent dopants.[1] Their blends[2] and copolymers[3] can emit adjustable blue light with ease via energy transfer.[4] The most popular way to get wide band gap polymers at present is to synthesize unfully conjugated polymers.[5] Another way is to introduce the meta-linkage into the backbone.[6] It is well-known that poly(3,6-carbazole)[7] and

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poly(2,7-carbazole)[8] have different optical band gaps (3.25 eV for the former, 2.85 eV for the latter), although they have nearly identical photoluminescent (PL) spectra with the maximum at ca. 420 nm. We synthesized poly(3,6-silafluorene)[9] in 2005 and found that its band gap was much bigger than poly(2,7-silafluorene).[10] The latter is a typical blue light emitting polymer, while the former is a wide band gap polymer with a PL emission maximum at around 355 nm. In this work, we intended to synthesize poly(3,6-fluorene) and its copolymer, investigate their light-emitting properties, and compare the difference with poly(2,7-fluorene), etc.

Poly(2,7-fluorene)[11] is very important because of its high electroluminescent (EL) efficiency and high chemical stability. Unlike polysilafluorene, polyfluorene is only composed of C and H elements. It has a lower HOMO level compared with polycarbazoles (−5.4 eV for poly(3,6-carbazole)[7b] and −4.85/−5.14 eV for poly(*N*-octyl-2,7-carbazole)[8b]), which means that it is more stable against oxygen. If poly(3,6-fluorene) is a wide band gap polymer, it will be a stable host.

The synthetic strategy for poly(3,6-fluorene) **5** and its copolymer **7** is outlined in Scheme 1. 2,2′-Dibromo-5,5′-dichlorobibenzene **1**, which was prepared according to the literature,[9] was treated with *n*-BuLi at −78 °C, stirred at −60 °C with 2-ethylhexanoyl chloride, warmed up to room temperature, and worked up to give **2** as a yellowish oil (yield 78%). **2** reacted with $SOCl_2$ followed by reaction with $LiAlH_4$ at room temperature to afford **3** (yield 50%). **3** was treated with *n*-BuLi at −78 °C and stirred at −78 °C with *n*-bromooctane to give **4** (yield 62%). Polymerization of **4** by $NiCl_2$-catalyzed coupling reaction in dimethylacetamide (DMAc) gave poly(3,6-fluorene) **5** as a yellowish solid (yield 40%). Copolymer poly{[3,6-(9-(1-ethylpentyl)-9-octylfluorene)]-co-[bis(biphenyl-4-yl)phenylamine)-4′,4′-diyl]} **7** was prepared from **4** and bis(4-chlorobiphenyl-4-yl)phenylamine **6** with the same process as **5** (yield 40%). All the newly prepared compounds were confirmed by ^{1}H NMR, ^{13}C NMR, and elemental analysis.

The molecular weights of poly(3,6-fluorene) **5** and its copolymer **7** are around 25 000/16 000 (M_w/M_n) and 24 000/14 000, respectively. All these polymers can form thin polymer films by spin coating with their solution in common organic solvents, such as toluene, THF, and chloroform.

Scheme 1. Synthesis of Poly(3,6-fluorene) and Its Copolymer

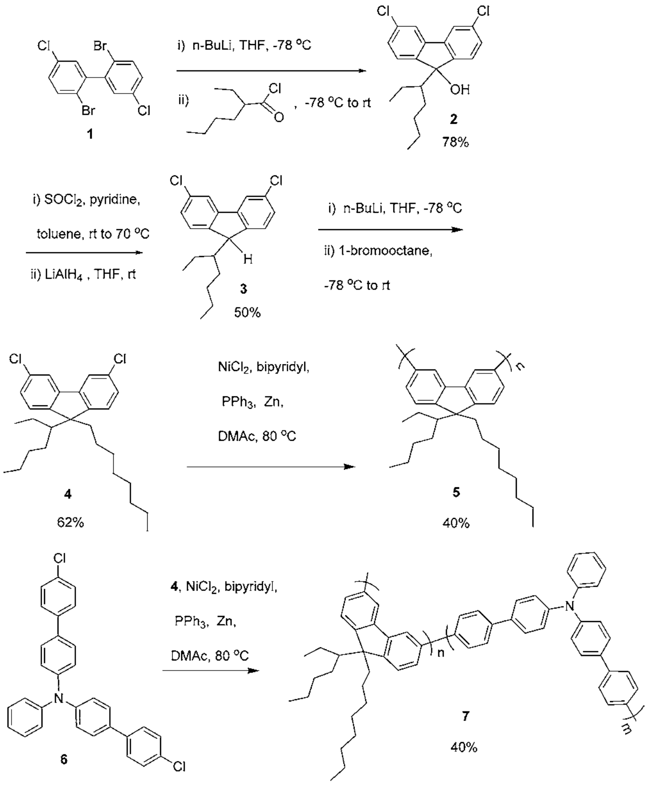

Figure 1 shows the absorption spectra of **5** and **7**. All these polymers exhibit the absorption maximum at 263 nm with a shoulder at 323 nm in both solution and film. The absorption onset of **5** is around 342 nm, so the optical band gap (Eg) of poly(3,6-fluorene) **5** is estimated at ca. 3.6 eV. The spectrum of the copolymer **7** is nearly identical to that of **5** except that the absorption onset is red-shifted to over 400 nm due to the triarylamine moieties in the copolymer. It is obvious that the absorption maximum value of poly(3,6-fluorene) is

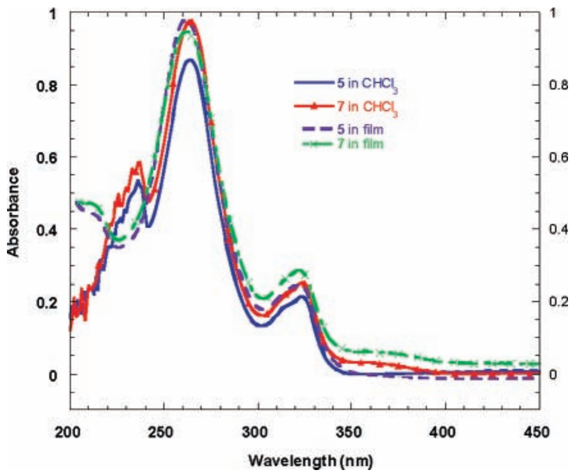

Figure 1. Absorption spectra of **5** and **7** in chloroform and in thin films.

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much smaller than that of poly(2,7-fluorene), e.g., 260 nm for the former and 380 nm for the latter.[11] The results confirm that meta-linkage is a very effective way to get wide band gap conjugated polymers.[6,9]

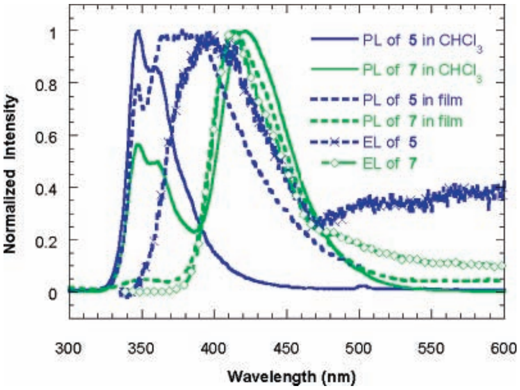

Figure 2. PL and EL spectra of **5** and **7** in chloroform and in thin films.

Figure 2 shows the photoluminescence spectra of **5** and **7** under excitation of 260 nm. In solution, **5** shows an emission maximum of 347 nm with a shoulder at 362 nm, which is much shorter than poly(2,7-fluorene) (422 nm)[11] and close to poly(3,6-silafluorene) (355 nm).[9] The PL efficiency of **5** in 1,2-dichloroethane is 30%, which is a little higher than that of poly(3,6-silafluorene).[9] In film, the PL spectrum of **5** is quite different from that in solution. An additional broad PL emission band (highland) from 350 to 400 nm appeared. The repeated syntheses of the polymers confirmed that it was not due to the contamination. This might have resulted from the excimer emission, but we cannot explain why this phenomenon did not happen in either poly(2,7-fluorene) or poly(3,6-silafluorene), which should be further studied. It does not seem that the 3,6-linkage of fluorene causes PL quenching. The PL quantum efficiency of **5** and **7** in film (ca. 100 nm) was about 7.3% and 41%, respectively, via an integral sphere excited by a 325 nm laser (see table S1 in Supporting Information).

The copolymer **7** shows the typical PL features of energy transfer (Figure 2). **7** in CHCl$_3$ (ca. 5 ppm) shows an emission maximum of 420 nm together with the emission of poly(3,6-fluorene) segments, while nearly one single PL peak at 420 nm can be observed due to the full energy transfer in solid film.

We fabricated the electroluminescent devices of **5** and **7** and measured their EL spectra (Figure 2). The EL efficiency of **5** is hard to obtain because the intensity is quite low. **7** can emit blue light with low efficiency (0.3%) and with no obvious red shift compared with the PL spectra in film. This unexpected result may originate from the strong excimer phenomena of the PL spectra.

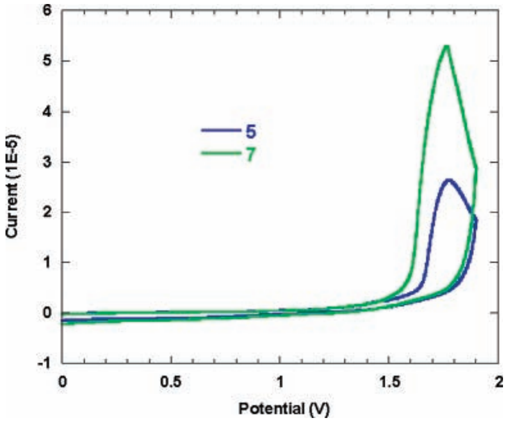

Figure 3. Cyclic voltammograms of **5** and **7** in 0.1 M Bu$_4$NPF$_6$/CH$_3$CN solution at a scan rate of 50 mV/s.

Figure 3 shows the cyclic voltammograms of **5** and **7** in film cast on a platinum electrode. The onset of the irreversible oxidation wave of **5** is recorded at about +1.65 V, which is much higher than that of poly(2,7-fluorene) (+1.3 V).[11] So the HOMO level of **5** is −6.05 eV according to the empirical formula, $E_{\mathrm{HOMO}} = -(E_{\mathrm{ox}} + 4.4)$ (eV).[12] The LUMO levels were calculated to be about −2.45 eV from the HOMO level and the optical band gap of poly(3,6-fluorene) because we cannot get the reduction potential. As for **7**, the oxidation potential was estimated at about +1.61 V, which is slightly less than that of the homopolymer. We might suppose that the difference between **5** and **7** is due to the hole-transporting units in the main chain of **7**.

In summary, soluble poly(3,6-fluorene) **5** and its copolymer **7** were prepared by a nickel-catalyzed coupling reaction as the key reaction. **5** shows the optical band gap of 3.6 eV, the emission maximum at 347 nm, and the HOMO level of −6.05 eV. The copolymer containing triarylamine units emits deep-blue light peaked at 420 nm. These results confirm that 3,6-linkage is a very effective way to get wide band gap conjugated polymers, and the adjustable blue light emission can be obtained from their copolymers via energy transfer.

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Supporting Information Available: Experimental procedures and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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