Tuning Redox Behavior and Emissive Wavelength of Conjugated Polymers by *p*−*n* Diblock Structures

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Since the discovery of electroluminescence of poly(*p*-phenylene vinylene) a conjugated polymer,[1] polymer light-emitting diodes (PLEDs) have drawn special attention because of the potential applications in developing large area and flexible displays.[2−4] The emission of PLEDs comes from the radiative decay of excitons resulting from the recombination of electrons and holes, which are injected from the two opposite electrodes, in the emitting layer.[3] Balanced injection and transport of electrons and holes are therefore crucial for achieving high quantum efficiency. Unfortunately, so far most of the electroluminescent polymers have unipolar character, showing greater tendency for transporting holes than for transporting electrons.[5] To overcome the problem of the unbalanced charge injection, three approaches have been developed. The first is adding an electron-transporting layer between the emitting layer and cathode to fabricate multilayer devices.[6,7] However, in practical applications one has to face some serious technical difficulties in fabricating such multilayer devices. The second is using metals with low work functions such as Ca and Mg as cathodes.[8] The problem of this approach is that such metals are highly susceptible to atmospheric degradation and are difficult to encapsulate. The third approach is making the emissive layer polar in nature to eliminate the charge buildup at the electrode−polymer interfaces.[9] Although this development results in a more balanced charge injection, some issues such as the slow charging time and operating stability have to be addressed before it can be widely employed. Therefore, it would be interesting and meaningful to develop new electroluminescent polymers with an intrinsically balanced tendency for injecting and transporting electrons and holes for the development of highly efficient and stable PLEDs. For this goal, the key is to develop a synthetic methodology to effectively adjust and control the HOMO and LUMO of conjugated polymers. Here we present a new molecular design and synthesis, i.e., *p*−*n* diblock conjugated copolymers, in which typical *p*-dope type and *n*-dope type segments are alternatively incorporated into one backbone of conjugated polymer, to adjust the HOMO and LUMO of the resulting polymers.

Seven *p*−*n* diblock conjugated copolymers were synthesized, and their chemical structures are illustrated in Figure 1. The oligothiophenes, which are π-excessive, act as *p*-dope type blocks, while the di(1,3,4-oxadiazole) phenylenes, which are π-deficient, act as *n*-dope type blocks. The variation of the length of the oligothiophene block affords the possibility of tuning redox behavior (related to the HOMO and LUMO of polymers) and emissive color of the resultant polymers. Actually, there are two series in these seven polymers. One includes polymers B, C, and D (series 1) with 1,4-bis(1,3,4-oxadiazolyl)-2,5-dioctoxybenzene as the *n*-dope type block. The other series comprises polymers E, F, and G (series 2) with 2,6-bis(1,3,4-oxadiazolyl)toluene as the *n*-dope type block. Polymer A was synthesized for comparison. All of these polymers show highly thermal stability with the starting decomposition temperatures higher than 300 °C in air according to the thermogravimetric analysis (TGA). Polymers C and F are completely soluble in chloroform, tetrahydrofuran (THF), *N*,*N*-dimethylformamide (DMF), and xylene. The average molecular weights (M_w) were measured to be higher than 15,000 against polystyrene standards with polydispersity around 1.8. The other five polymers are partially soluble in the above solvents, and the average molecular weights (M_w) of THF-soluble parts were measured to be 4000−10000 against polystyrene standards. All of the seven polymers are readily dissolved in chloroform with a small amount of trifluoroacetylacetone (TFA) to give clear solutions. The synthesis of polymers A and F has been published in our previous papers.[10,11] The other syntheses will be published elsewhere.

Transparent thin films of the polymers on glass substrates (microscopy slides or quartz plates) were prepared by spin coating from the polymer solutions. The UV−vis absorption and fluorescence spectra of series 1 polymer films are displayed in Figure 2, and the optical data of all of the polymers are summarized in Table 1. For both series 1 and 2, the absorption and luminescence spectra of the polymers shift to longer wavelength with the increase of the length of the oligothiophene segments. The emissive colors are blue, green, and orange for the polymers with one, two, and three thiophene rings in the oligothiphene segments, respectively. This indicates that the *p*−*n* diblock structure is an effective approach for tuning the emissive color of conjugated polymers. Comparison between the polymers with the same oligothiophene segments in series 1 and 2 shows that the polymers in series 1 exhibit longer wavelength of absorption and fluorescence. This can be attributed to the electron-donating character of alkoxy groups and coplanarity in 2,6-bis(1,3,4-oxadiazolyl)toluene lower than that in 1,4-bis(1,3,4-oxadiazolyl)-2,5-dioctoxybenzene, which can be demonstrated by the spectral comparisons between polymers A and B and polymers A and E. These results suggest that the electronic properties of the *p*−*n* diblock conjugated copolymers can be finely tuned by attaching different functional groups on the phenylene ring or by changing the steric configuration in the *n*-dope type segments.

The redox behavior of the polymers (as coated films on a 1 cm^2 Pt electrode) was studied by cyclic voltammetry in a CH_3CN solution of n-Bu_4NClO_4 (0.1 M) using a Pt wire as counter electrode and a $Ag/AgNO_3$ (0.1 M) electrode as reference electrode. When scanning cathodically, all of these polymers displayed reversible reduction peaks around −1.8 V (−1.86 to −1.73 V) vs SCE, and the corresponding reoxidation peaks appeared around −1.6 V (−1.75 to −1.53 V). Thus, the reduction potentials of the polymers can be determined to be ca. −1.7 V. The detailed data are listed in Table 1 and the cyclic voltammograms of series 2 polymers are given in Figure 3. Generally, the increase of the thiophene ring number in the oligothiophene blocks does not change the reduction potential of the polymers remark-

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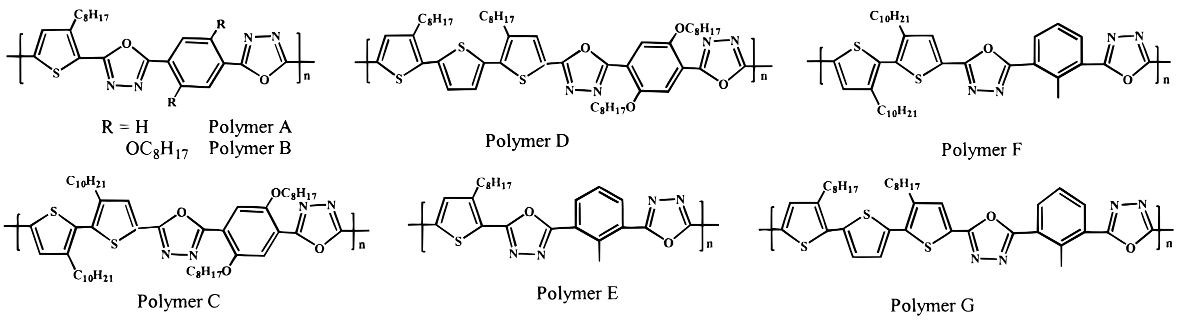

Figure 1. Chemical structures of the polymers.

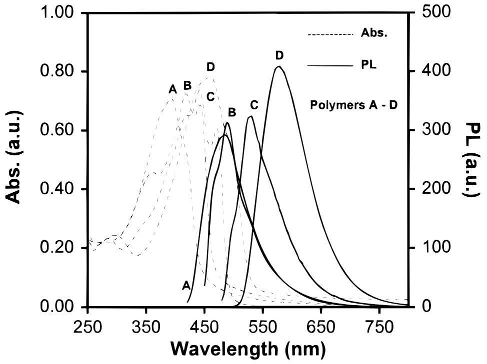

Figure 2. Absorption and fluorescence spectra of polymers A−D as films at room temperature.

Table 1. Optical and Electrochemical Data of the Polymers

polymer	absorption λ_{max}^a (nm)	fluorescence λ_{max}^a (nm)	oxidative E_{pa}/E_{pc}^b (V)	reductive E_{pc}/E_{pa}^b (V)
A	393 (358, 416)	458	1.96/—	−1.77/−1.62
B	420 (360, 443)	489	1.75/—	−1.83/−1.60
C	441 (419, 471)	530	1.70/—	−1.82/−1.70
D	461 (439, 494)	580	1.30/1.20	−1.79/−1.70
E	360 (388)	460	1.95/—	−1.73/−1.53
F	380 (358, 416)	497 (526)	1.64/—	−1.86/−1.75
G	430 (456, 470)	570	1.38/1.24	−1.76/−1.67

[a] Obtained from solid films, numbers in parentheses are the wavelengths of subpeaks or shoulders. [b] Peak potential of anodic (E_{pa}) and cathodic (E_{pc}) peak, respectively (vs SCE) measured between neutral and oxidized (oxidative) or reduced (reductive) states on a square platinum electrode (1.0 cm^2) in 0.1 M Bu_4NClO_4 solution in acetonitrile at a scan rate of 50 mV/s.

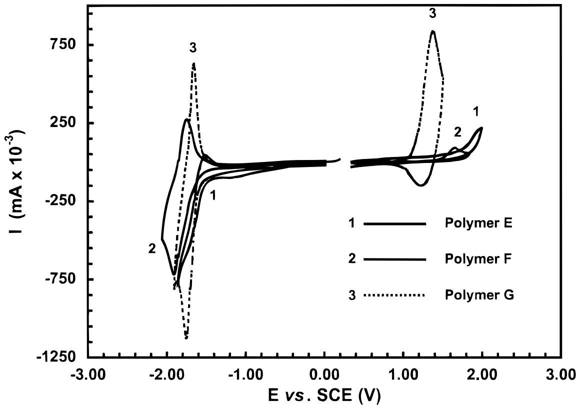

Figure 3. Cyclic voltammograms of polymers E−G as films on Pt electrode in CH_3CN solution of Bu_4NClO_4 (0.1 M) at a scan rate of 50 mV/s.

ably. This implies that the reduction properties of the polymers are dominated by the 2,6-bis(1,3,4-oxadiazolyl)phenylene segments. These reduction potentials are lower than those of 2-(4-biphenylyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) (−1.95 to −1.94 V vs SCE),[7,12] one of the most widely used electron-transporting/hole-blocking materials, and other 1,3,4-oxadiazole-containing materials,[13,14] and are comparable with those of some good electron-transporting materials.[7] The reduction onset potentials of the polymers were measured to be −1.2 to −1.4 V. These values are comparable with that of poly(cyanoterephthalyidene) (CN−PPV) [−1.6 V vs Ag/Ag^+ (0.1 M)],[15] which shows good electron-transporting ability in PLED devices.[16] Cyclic voltammetric reduction potential values can be used as a surrogate for LUMO energy levels.[7] Thus, the results suggest that the LUMO energy levels of the polymers may be lower than those of conventional *p*-dope type electroluminescent polymers and PBD and may be comparable with that of CN−PPV. Such energy levels may provide a closer match to the work function of Al when they are used as active materials in PLEDs.

On sweeping anodically, the polymers A, B, C, E, and F showed irreversible oxidation with the half wave oxidation peaks at 1.96, 1.75, 1.70, 1.95, and 1.64 V vs SCE, respectively. Polymers D and G exhibited a reversible oxidation process with the oxidation peaks at 1.30 and 1.38 V and the corresponding rereduction peaks at 1.20 and 1.24 V, respectively. Unlike their reduction potentials, the oxidation potential of the polymers is sensitive to the variation of the thiophene ring number in the oligothiophene segments. The oxidation peak potential is reduced by 0.45 V for series 1 and 0.57 V for series 2, respectively, with increasing the thiophene ring number in the oligothiophene segments from 1 to 3. For polymers D and G, the oxidation potentials are 1.25 and 1.31 V with the onset potentials of 1.00 and 1.04 V vs SCE, respectively. These values are lower than that of PPV[15] and are close to those of electroluminescent substituted polythiophenes,[17] which are hole-injection favorable electroluminescent materials. It is demonstrated that the HOMO level of the *p*−*n* diblock copolymers can be effectively adjusted by changing the thiophene ring number in the oilothiophene segments and it can be lower than that of PPV and are comparable with those of substituted polythiophenes.

In conclusion, the present idea of *p*−*n* diblock structure in conjugated polymers has afforded an efficient approach of tuning emissive color of conjugated polymers. According to the electrochemical studies, it provides a promising synthetic route to adjust the HOMO and LUMO of electroluminescent polymers to balance the injections of electrons and holes from the opposite contacts. Intensive studies on the charge transporting properties of these polymers in PLED devices are in progress.

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