A Novel Series of Copolymers Containing 2,5-Dicyano-1,4-phenylenevinylene—Synthetic Tuning of the HOMO and LUMO Energy Levels of Conjugated Polymers

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Abstract: A series of copolymers of 2,5-dicyano-1,4-phenylenevinylene and 2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene were synthesized by Wittig reaction. The HOMO and LUMO energy levels of copolymers can be easily tuned by controlling the feed ratio of co-monomers.

Keywords: cyclic voltammetry · polymers · redox · synthetic methods · Wittig reactions

Introduction

Conjugated polymers for polymer light-emitting diodes (PLEDs) have been extensively studied recently due to their potential for practical applications.[1] It is known that balanced charge injection from both electrodes, and the comparable mobility of both types of charge carriers within the polymer are crucial for high device efficiencies.[2] Higher efficiencies can be achieved when the rate of electron injection matches the rate of hole injection.[3] Typically, for poly(*para*-phenylenevinylene) (PPV), and poly(thiophene), as well as their respective derivatives, electron injection is more difficult than hole injection,[4] which means the energy barrier for electron injection from the cathode is normally larger than that for hole injection from the anode. A couple of strategies have been established to balance the injection of the two types of electrical charges. One of the approaches uses low work function metals (such as calcium) as the cathode material.[5] However, such devices have to be hermetically encapsulated, since low work function metals are very sensitive to air and moisture. Alternatively, an electron-transporting layer can be inserted between the emissive layer and the cathode.[6, 7] From the viewpoint of commercialization, such a process is not economical. In addition, another approach has been developed by increasing the electron affinity of polymers to decrease the energy barrier for electron injection.[2, 8] A more attractive way for chemists and materials scientists to achieve high efficiency in PLEDs is by developing new conjugated polymers, with intrinsically balanced injection ability of electrons and holes from stable electrodes. To succeed, it is necessary to find an effective synthetic methodology to adjust the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of conjugated polymers.

Herein, we report a new synthetic strategy capable of tuning the redox behavior of conjugated polymers so as to match the energy barriers of electron injection from the metal electrode, such as Al, into the LUMO of polymers, and hole injection from the ITO electrode into HOMO of polymers. This is achieved by copolymerization of an electron-deficient, or *n*-dope type unit, of 2,5-dicyano-1,4-phenylenevinylene (DCN-PV) with an electron-rich, or *p*-dope type unit, of 2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene (MEH-PV)[9] by varying the feed ratio of three comonomers by a Wittig reaction. DCN-PV was chosen as the *n*-dope type segment because of the high electron affinity of the cyano group. CN-PPV (cyano groups attached to the vinylene bonds of PPV derivatives) has exhibited high electron affinity and excellent electron-transport properties.[3] Double layer devices fabricated with CN-PPV as the electron-transport layer and PPV as the hole-transport layer exhibited high internal quantum efficiency (4%) using ITO as the anode, and aluminum as the cathode.[4] A theoretical investigation has shown that the LUMO of the pentamer of DCN-PV is -1.17 eV, which is lower than that of the pentamer of CN-PPV by -0.55 eV.[10]. Thus, DCN-PV is supposed to have stronger electron affinity than CN-PPV. It is most likely that by copolymerizing these two types of monomers at different feed ratios, one should be able to adjust the HOMO and LUMO energy levels of copolymers and thereby to approach the target.

Results and Discussion

Compound **A** (Scheme 1) was obtained by bromomethylation of 1-methoxy-4-(2′-ethylhexyloxy)benzene with paraform-

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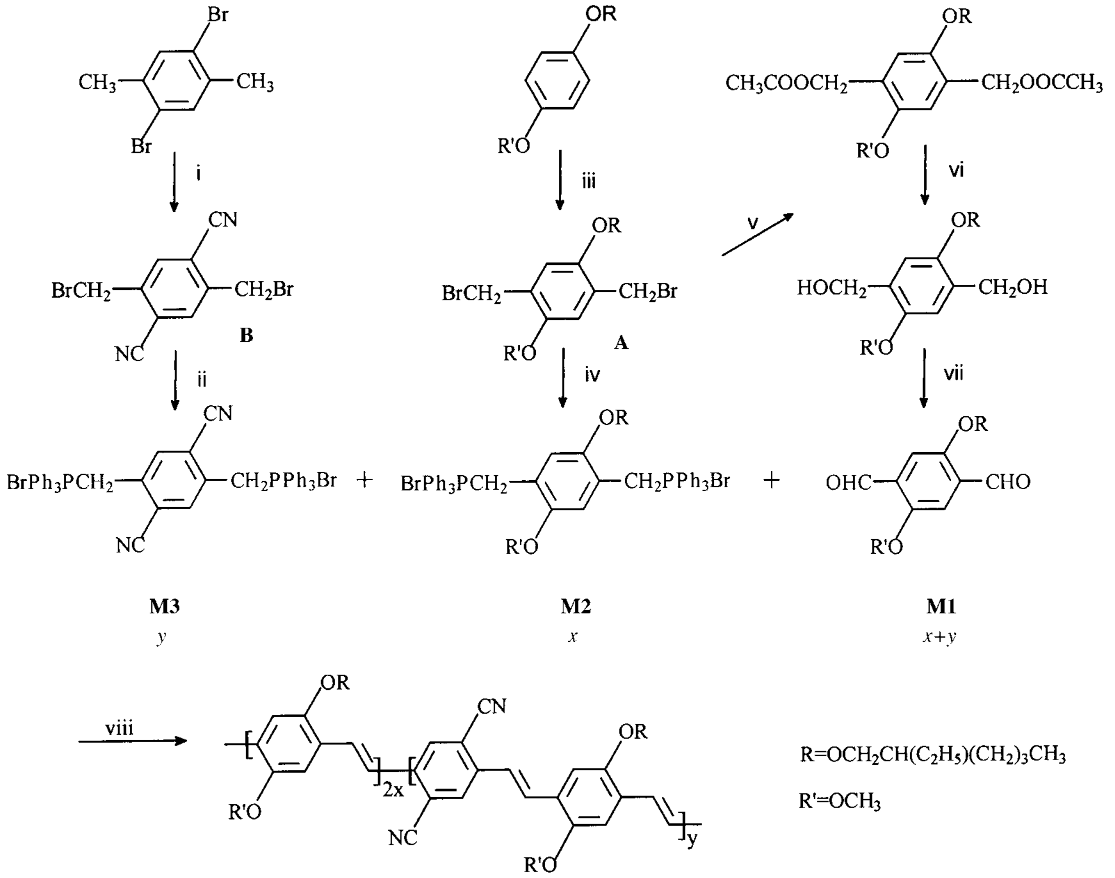

Scheme 1. The reaction pathways and conditions: i) a. CuCN, DMF, reflux, b. NBS, CCl_4, reflux; ii) PPh_3, DMF; iii) $(CH_2O)_n$, HBr; iv) PPh_3, DMF; v) NaOAc; vi) NaOH, EtOH; vii) PCC, CH_2Cl_2; and viii) EtONa, EtOH, $CHCl_3$.

aldehyde and hydrogen bromide. It was allowed to react with sodium acetate in a solution of glacial acetic acid and acetic anhydride to give 2-methoxy-5-(2′-ethylhexyloxy)-1,4-bis-acetoxymethylbenzene. This was hydrolyzed in a solution of sodium hydroxide in ethanol, followed by oxidation with pyridinium chlorochromate (PCC) in dichloromethane to give monomer 1 (**M1**). Then compound **A** was allowed to react with triphenylphosphane in *N*,*N*-dimethylformamide (DMF) to give monomer 2 (**M2**). Compound **B** was obtained by the reaction of 2,5-dibromo-1,4-xylene with CuCN in DMF,[11] followed by bromination with *N*-bromosuccinimide (NBS) in carbon tetrachloride to give pale yellow crystals. Monomer 3 (**M3**) was obtained by the reaction of compound **B** with triphenylphosphane in DMF. The copolymerization was performed by adding an excess of sodium ethoxide solution in ethanol into the mixture of **M1**, **M2**, and **M3** in specific proportions,[12] in a mixed-solvent system of dry ethanol and dry chloroform, at room temperature for 24 h. The reaction mixture was poured into methanol, and the crude product was precipitated and collected by filtration. The polymer was redissolved in chloroform and precipitated in methanol. After filtration, the final dark reddish copolymer was dried under reduced pressure at room temperature.

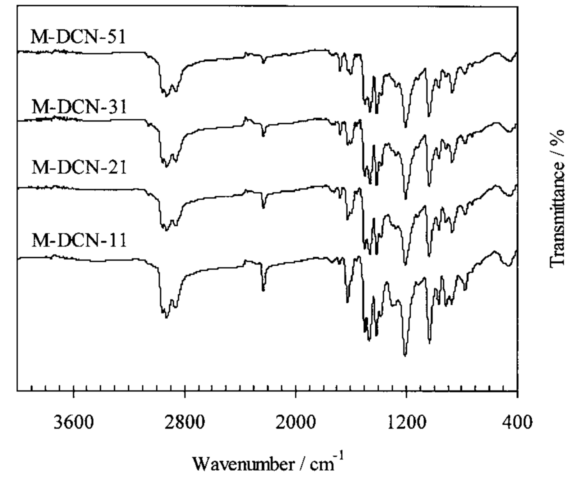

Figure 1. FT-IR spectra of copolymers.

The FT-IR spectra of the copolymers (Figure 1) indicate the existence of DCN-PV through an absorption at 2228 cm^{-1} corresponding to the C≡N stretching mode[13]. The absorption peak increases as the DCN-PV content increases. The DCN-PV content in the copolymers can be controlled by varying the feed ratio of **M1** to **M3**. Because the aldehyde-ending monomer links to the phosphoranylidene-ending monomer in the Wittig reaction, a DCN-PV unit must be inserted separately into the backbone of the copolymers. A series of copolymers with MEH-PV:DCN-PV ratios from 5:1 to 1:1 (molar ratio in the final polymers) were obtained in our experiments in yields of 60–86%. The average molecular weights (M_w), measured by gel permeation chromatography

(GPC), were in the range of 13000 to 19000, with polydispersity indexes ranging from 1.4 to 3.6 (measured against polystyrene standards using THF as eluent). Some properties of the copolymers are summarized in Table 1. The elemental analyses indicated that the DCN-PV contents in the final polymers were almost the same as the feed ratios, which means the average segment lengths of MEH-PV are 5 to 1 units, corresponding to the polymers from M-DCN-51 to M-DCN-11.

The UV/Vis absorption spectra and photoluminescence (PL) spectra of the copolymers as thin films were measured. The films were spin-cast onto glass substrates from chloroform solutions. The absorption spectra of the copolymer films are blue-shifted compared to that of MEH-PPV (λ_{max} of MEH-PPV: 524 nm, λ_{max} of the copolymers: 460–480 nm). The PL spectra of the copolymer films were red-shifted to 640–610 nm compared to 590 nm for MEH-PPV. The larger energy difference between the absorption and the corresponding PL bands, compared to that of MEH-PPV, is attributable to the formation of excimers in the films, due to the introduction of the electron-deficient DCN-PV groups into the polymer chain. This is in good agreement with the result for CN-PPV.[14]

The redox behavior of the copolymers (as films on a 1.0 cm^2 square Pt electrode) was studied by cyclic voltammetry with a three-electrode cell in a solution of Bu_4NBF_4 (0.10 M) in CH_3CN, using a Pt wire as the counter electrode and Ag/$AgNO_3$ (0.10 M) as the reference electrode. The scans towards the anodic and cathodic directions were performed separately at a scan rate of 20 mV s^{-1} at room temperature.

All of the copolymers exhibit reversible oxidation processes when scanned anodically. The oxidation potential increases as a function of the percentage composition of DCN-PV in the copolymers. The peak position for the polymers increases from 0.74 V (vs. SCE) for MEH-PPV to 0.91 V (vs. SCE) for M-DCN-31, and further to 1.4 V (vs. SCE) for M-DCN-11 (Figure 2). The onset of the oxidation processes also moves towards higher potentials, from 0.3 V (vs. SCE) for MEH-PPV to 0.6 V (vs. SCE) for M-DCN-31, and to 1.1 V (vs. SCE) for M-DCN-11, as the DCN-PV content increases.

The situation was even more interesting when the copolymers were scanned cathodically: All of the copolymers showed reversible reduction processes, but varied in terms of the peak positions according to the DCN-PV content (Figure 3). MEH-PPV has only one reduction peak potential at −1.83 V (vs. SCE), while the copolymers exhibit three reduction potential peaks at −1.51, −1.67, and −1.83 V (vs. SCE), respectively. The dominating processes shift negatively to lower potentials when the DCN-PV content increases (Figure 3). Notably, the onset of the first reduction process of M-DCN-11 was at −0.93 V (vs. SCE), shifted by 0.80 V compared to that of MEH-PPV. This value is more negative than that of CN-PPV which is well known as an electron-transport material, with the onset of reduction 0.4 V lower than that of MEH-PPV.[15] Evidently, the polymer changes

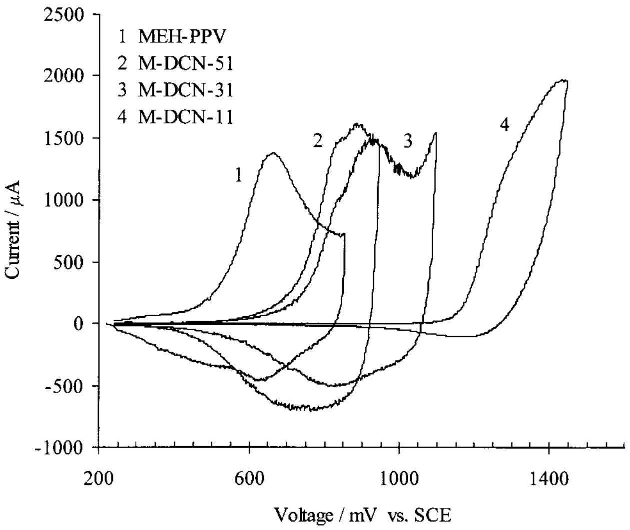

Figure 2. Cyclic voltammograms of *p*-dope processes of polymers.

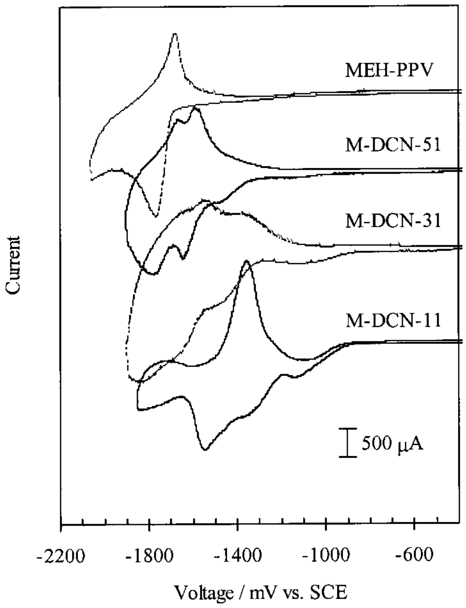

Figure 3. Cyclic voltammograms of *n*-dope processes of polymers.

Table 1. Elemental and GPC analyses of copolymers.

Polymer	Feed ratio M1:M2:M3	DCN-PV mol% (found)	Elemental analysis C% calcd (found)	H% calcd (found)	N% calcd (found)	M_w ($\times 10^4$)	Polydispersity
M-DCN-51	3:2:1	19	78.51 (77.41)	8.54 (8.64)	1.93 (2.19)	1.3	1.6
M-DCN-31	2:1:1	28	78.54 (76.66)	8.15 (8.51)	3.00 (3.43)	1.9	3.6
M-DCN-21	3:1:2	33	78.57 (77.45)	7.74 (7.94)	4.17 (4.13)	1.6	3.4
M-DCN-11	1:0:1	50	78.64 (77.48)	6.80 (6.80)	6.80 (6.87)	1.6	1.9

from a typical hole-transport material to a typical electron-injection material after the DCN-PV content reaches a certain level following incorporation of DCN-PV into the backbone of MEH-PPV.

The HOMO and LUMO energy levels of the copolymers can be calculated from the onsets of the oxidation and reduction processes.[15] The HOMO and LUMO energy levels of the copolymers can be easily adjusted in the range of 0.7 to 0.8 V by varying the feed ratio of **M1** against **M3** (Table 2).

Table 2. Estimated HOMO and LUMO values of copolymers.

Polymer V (vs. SCE) [eV]	$[E_{\text{onset}}]^{\text{ox}}$ V (vs. SCE) [eV]	$[E_{\text{onset}}]^{\text{red}}$ [eV]	HOMO	LUMO	Band gap
MEH-PPV	0.40	− 1.70	4.80	2.70	2.10
M-DCN-51	0.55	− 1.28	4.95	3.12	1.83
M-DCN-31	0.59	− 1.26	4.99	3.14	1.85
M-DCN-21	0.60	− 1.22	5.00	3.18	1.82
M-DCN-11	1.10	− 0.82	5.50	3.58	1.92

Conclusions

In summary, a series of copolymers containing 2,5-dicyano-1,4-phenylenevinylene and 2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene have been obtained by Wittig reaction. The HOMO and LUMO energy levels of the copolymers can be easily tuned in the range of 0.7 to 0.8 V and the polymer can be changed from a typical hole-transport material to a typical electron-transport material by varying the feed ratio of monomers. This methodology opens a novel way to the design and synthesis of light-emitting polymers with desired properties by controlling the feed ratio of selected monomers.

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