A Novel n-Type Conjugated Polymer DOCN-PPV: Synthesis, Optical, and Electrochemical Properties

Yingping Zou,[†,‡] Jianhui Hou,[†,‡] Chunhe Yang,[†] and Yongfang Li*[,†]

Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China, and Graduate University of Chinese Academy of Sciences, Beijing 100039, China

Received November 11, 2006
Revised Manuscript Received November 26, 2006

Conjugated polymers are currently the subject of a broad research area, especially for the application in electronic and electrochemical devices such as polymer light-emitting diodes (PLEDs),[1] polymer solar cells (PSCs),[2] sensors,[3] electrochromic devices, and field effect transistors (FETs).[4] For the applications in the optoelectronic devices, some special electron-donating or electron-accepting properties of the conjugated polymers are required. At present, the majority of the conjugated polymers in use are electron donor (hole-transporting) in character, i.e., p-type materials. In contrast, there are few reports on electron acceptor (n-type) of conjugated polymers which are with low-lying LUMO (the lowest unoccupied molecular orbital) energy level and high electron affinity (EA). The n-type conjugated polymers are important not only in OLEDs as electron transport materials for increasing electron injection from the cathode and as hole blockers but also in PSCs as polymer acceptors.[5,6]

One method to modulating the electronic properties of the conjugated polymers is the introduction of substituents with functional groups.[7,8] For obtaining n-type poly(phenylenevinylene) (PPV), the cyano group was generally connected on the vinylene units of the PPVs such as MEH-CN-PPV.[9] However, the cyano-substituted vinylene units are intrinsically unstable and can be easily photooxidized,[10] while the introduction of cyano group on the phenylene ring of the PPVs results in more stable polymers. Up to now, the phenylenevinylene units with the cyano groups on their phenylene rings were copolymerized with other monomers with flexible side chains to improve the solubility of the resulting polymers. In this work, we first synthesized a homopolymer poly[1,4-dioctyloxyl-*p*-2,5-dicyanophenylenevinylene] (DOCN-PPV) bearing two cyano units and two symmetrical alkoxyl groups on the phenyl ring by a facile synthesis method. Here, the cyano units were used to tune the electronic energy levels of the polymer, and the symmetrical alkoxyl groups were introduced to obtain the regioregularity which is very important in the solar cells and at the same time was used to improve the solubility of the polymer. Furthermore, the intramolecular interactions of the electron-donating alkoxyl groups and the electron-accepting cyano groups on the benzene could form a charge-transfer state which reduces the energy gap of the conjugated polymer. The polymer showed a promising n-type behavior with a reversible n-doping/dedoping process and an onset reduction potential of −1.06 V vs Ag/Ag$^+$ which is the highest value reported in the literature for the n-doping of conjugated polymers. The electrochromic properties of the polymer in n-doping process were also investigated.

The polymer DOCN-PPV was prepared by the Stille coupling reaction; the synthesis route is illustrated in Scheme 1. Monomer **3** was obtained from **2** by bromination of NBS under CF_3COOH and concentrated sulfuric acid conditions. The polymer was obtained as a dark-red powder and can be easily dissolved in conventional organic solvents such as chloroform, methylene chloride, and toluene. The good solubility can be partially attributed to the two octyloxy side chains attached to phenyl ring. The chemical structure of DOCN-PPV was confirmed by ^{1}H NMR and IR (KBr) spectroscopy and elemental analysis. In the ^{1}H NMR spectrum, electron-withdrawing cyano units result in the downfield shift of the vinylene peak (7.87 ppm); the ratio of hydrogen atoms is in complete agreement with the polymer structure. The IR spectrum (Figure 1) indicates that the carbonitrile functional group on the polymer was unaffected by the polymerization reaction with a sharp signal at around 2225 cm^{-1}; the vinyl(C=C) band together with the aromatic C=C band appears as a broad peak around 1600 cm^{-1} because of the inducement effect of the cyano group. The band of vinylene double bonds shifts to a higher wavenumber at 1007 cm^{-1}, which confirms the all-trans configuration of the vinylene double bonds. Elemental analysis also agrees with the structure of the polymer. The GPC result indicates that there are 25 average repeating units on the polymer main chains.

Figure 2a shows the UV−vis absorption spectra of the polymer and monomer solutions and polymer film. It can be seen that the absorption maxima of the monomer solution is 342 nm, while that of the polymer solution is 457 nm, red-shifted by 115 nm than the monomer. In comparison with the absorption spectrum of the polymer solution, the absorption spectrum of DOCN-PPV film red-shifted further and shows a rather broad band from 400 to 625 nm. The absorption band edge of the polymer is at 625 nm, corresponding to a band gap of ca. 2.0 eV, which is smaller than that of poly(2,5-di-*n*-octyloxy-1,4-phenylenevinylene) (DO-PPV) without the cyano units. (DO-PPV exhibits an absorption edge at ca. 590 nm, corresponding to a band gap of ca. 2.10 eV.[11]) The reduction of a band gap from DO-PPV to DOCN-PPV does confirm that the interaction between the electron-donating octyloxy groups and the electron-accepting cyano groups resulted in the band gap reduction of the polymer.

PL spectra of the polymer and monomer solutions in $CHCl_3$ and the polymer film are shown in Figure 2b. The PL spectra were measured under the excitation at the absorption peak wavelength. The PL peaks of the monomer and DOCN-PPV solutions are at 399 and 536 nm, respectively. The PL peak of the DOCN-PPV film red-shifted to 615 nm with a full width at half-maximum (fwhm) of 91 nm. The PL quantum efficiency of the DOCN-PPV solution is 0.69 with fluorescein as standard.

Figure 3 shows the thermal gravimetric analysis (TGA) curve of DOCN-PPV under a nitrogen atmosphere with a heating rate of 10 °C min^{-1}. Thermal decomposition of DOCN-PPV starts at about 230 °C, and 5% weight loss was recorded at 313 °C. The results indicate that the thermal stability of the polymer is enough for the application in optoelectronic devices.

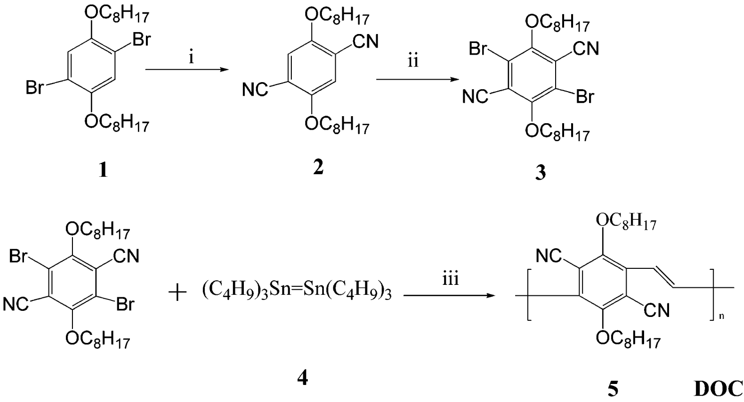
Cyclic voltammetry (CV) of DOCN-PPV film on a Pt electrode was performed to investigate its electrochemical behavior and to estimate its electronic energy levels. The cyclic voltammogram of DOCN-PPV, as shown in Figure 4, displays a distinct reversible reduction/reoxidation (n-doping/dedoping) process. The onset reduction potential of DOCN-PPV is

---

* Corresponding author: e-mail liyf@iccas.ac.cn, Fax 86-10-62559373.
[†] Chinese Academy of Sciences.
[‡] Graduate University of Chinese Academy of Sciences.

10.1021/ma0626057 CCC: $33.50

Scheme 1. Synthetic Routes of Monomer and Polymer[a]



[a] (i) CuCN, DMF, 140 °C, 24 h, 87%; (ii) NBS, CF_3COOH/concentrated sulfuric acid, rt, 5 h, 91%; (iii) $Pd(PPh_3)_4$, toluene, reflux, 48 h, 71%.

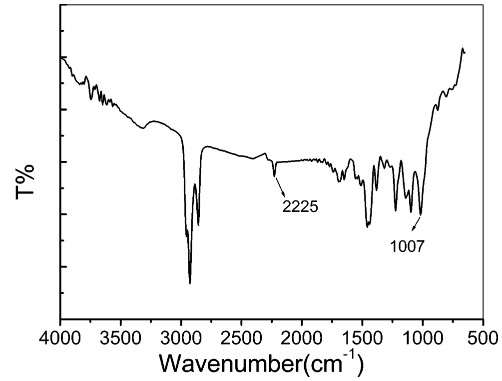


Figure 1. IR spectrum of DOCN-PPV.

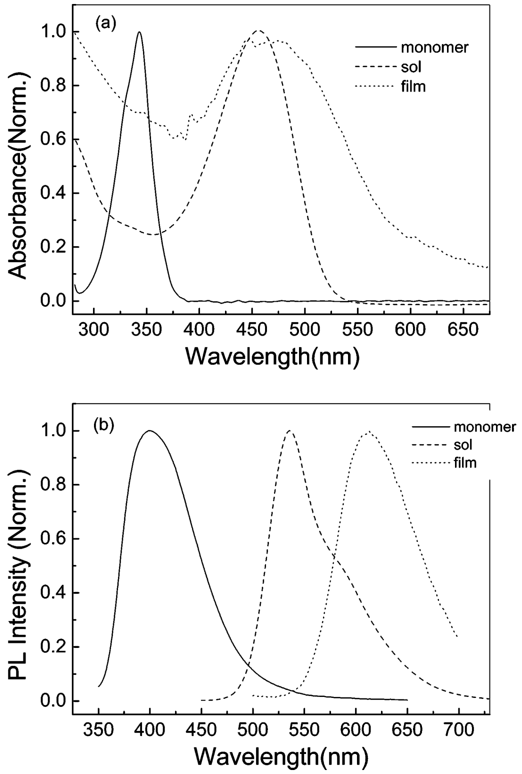


Figure 2. (**a**) Absorption spectra and (**b**) photoluminescence (PL) spectra of DOCN-PPV and monomer dilute solutions in chloroform and DOCN-PPV film on a quartz plate.

−1.06 V vs Ag/Ag$^+$, which corresponds to the lowest unoccupied molecular orbital (LUMO) energy level of −3.65 eV according to the equation LUMO = $-e(E_{\mathrm{on}}^{\mathrm{red}} + 4.71)$ (eV).[12]

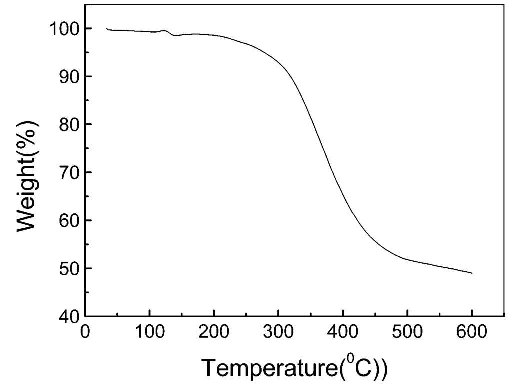


Figure 3. TGA curve of DOCN-PPV with a heating rate of 10 °C/min.

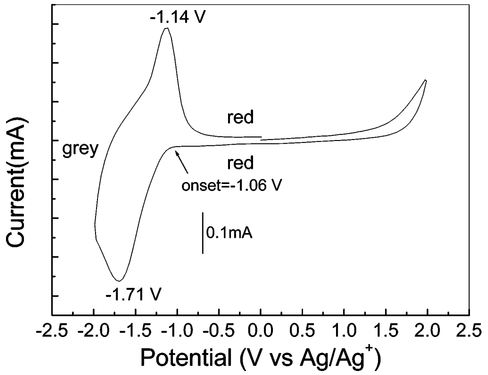


Figure 4. Cyclic voltammogram of the DOCN-PPV film on platinum plates in an acetonitrile solution of 0.1 M $[Bu_4N]PF_6$ (Bu = butyl) with a potential scan rate of 50 mV/s.

The LUMO level of DOCN-PPV is much lower than that of other n-type conjugated polymers such as poly(cyanoterephthalyidene) (CN-PPV) with the LUMO of −3.11 eV.[13] The reduction (n-doping) peak potential of DOCN-PPV is −1.71 V vs Ag/Ag$^+$, and the corresponding n-dedoping peak appears at −1.14 V. The reproducibility of the cyclic voltammograms in the potential range of 0 to −2.0 V is very good, indicating a good electrochemical stability for the n-doping/dedoping processes of DOCN-PPV. In contrast with the n-doping/dedoping process, the current associated with the p-doping in the oxidation process of DOCN-PPV is very small (see Figure 4). The results suggest that DOCN-PPV is a strong electron acceptor and a pure n-type conjugated polymer. Such an n-type conjugated polymer is quite rare and highly desired for the application in PSCs.[14]

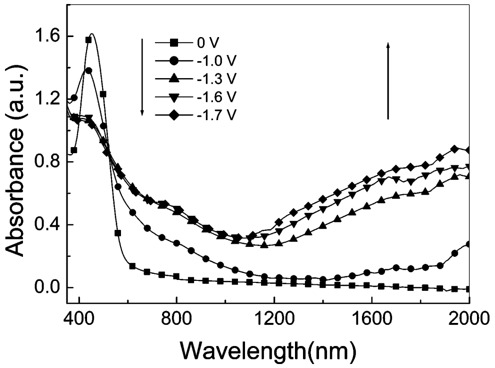


Figure 5. In-situ vis−NIR absorption spectra of DOCN-PPV film on ITO glass electrode in acetonitrile solution containing 0.01 M [Bu_4N]-PF_6 (Bu = butyl), at different potentials (Ag/AgCl as reference electrode).

Spectroelectrochemical measurement has been widely used to study the p-doping/dedoping processes and electrochromic properties of conjugated polymers.[15−17] But there is no report in the literature on the spectral change during n-doping/dedoping processes of PPV derivatives. Based on the stable and reversible n-doping/dedoping properties of DOCN-PPV, here the spectroelectrochemical measurement of DOCN-PPV was performed to investigate its n-doping process. Figure 5 shows the in-situ vis−NIR absorption spectra of DOCN-PPV film in a 0.1 mol/L [Bu_4N]PF_6 (Bu = butyl) acetonitrile solution at different cathodic potentials with units of V vs Ag/AgCl. It can be seen that when the potential was decreased to −1.0 V vs Ag/AgCl (corresponding to ca. −1.3 V vs Ag/Ag^+), the absorption peak in the visible region decreased, and the near-infrared (NIR) absorption increased, indicating the occurrence of the n-doping of the polymer. At −1.3 V vs Ag/AgCl (corresponding to ca. −1.6 V vs Ag/Ag^+), the visible absorption peak decreased further, and two absorption peaks at ca. 800 and 2000 nm in the near-infrared (NIR) region appeared. Moreover, the spectral changes were reversible; as the potential returned to 0 V vs Ag/AgCl, the absorption spectrum of DOCN-PPV resumed to the original spectrum at its neutral state. The spectral changes in the cathodic potential range confirmed that the reduction/reoxidation processes in Figure 4 do correspond to the n-doping/dedoping reactions of DOCN-PPV. The DOCN-PPV film shows a red color at its neutral state; it turned to gray at its n-doped state after reduction. This electrochromism showed good reversibility and fast response, which indicates that DOCN-PPV could be a novel electrochromic material in the n-doping potential region.

In summary, we have synthesized a soluble n-type conjugated polymer DOCN-PPV containing two cyano units and alkoxyl groups alternatively attached onto the phenyl ring through the Stille coupling for the first time. The electrochemical cyclic voltammogram of the polymer showed a distinct reversible reduction/reoxidation redox peaks with a quite higher onset reduction potential of −1.06 V vs Ag/Ag^+ and an irreversible and weak oxidation peak in the potential region higher than 1.0 V vs Ag/Ag^+. In-situ absorption spectra of DOCN-PPV film revealed that the visible absorption peak decreased, and two NIR absorption peaks at ca. 800 and 2000 nm appeared after the reduction, confirming the reversible and stable n-doping/dedoping processes of the polymer. The polymer film also showed a reversible color change between red at neutral state and gray at reduced (n-doped) state. The results indicate that DOCN-PPV is a novel n-type conjugated polymer with strong electron-accepting ability and electrochromic property in the n-doping potential region; moreover, the polymer should be very stable against the photooxidation degradation. DOCN-PPV can be used as an n-type conjugated polymer in the polymer optoelectronic devices such as in all polymer solar cells as an electron acceptor polymer as well as used as a novel electrochromic material in the negative potential region.

Acknowledgment. This work was supported by NSFC (Nos. 50373050, 20373078, 20474069, 20421101, 20574078, 50633050, and 60440420149) and the Ministry of Science and Technology of China (973 Project, No. 2002CB613404).

Supporting Information Available: Experimental details, synthesis of the monomers and polymer, instrumentation, and characterization procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Morin, J.-F.; Leclerc, M. *Macromolecules* **2002**, *35*, 8413−8417. (b) Cho, N. S.; Park, J.-H.; Lee, S.-K.; Lee, J.; Shim, H.-K.; Park, M.-J.; Hwang, D.-H.; Jung, B.-J. *Macromolecules* **2006**, *39*, 177−183.

(2) (a) Hou, J. H.; Tan, Z.; Yan, Y.; He, Y.; Yang, C. H.; Li, Y. F. *J. Am. Chem. Soc.* **2006**, *128*, 4911−4916. (b) Sun, B.; Marx, E.; Greenham, N. C. *Nano Lett.* **2003**, *3*, 961−963. (c) Zhou, E. J.; Tan, Z.; Yang, C. H.; Li, Y. F. *Macromol. Rapid Commun.* **2006**, *27*, 793−798. (d) Coakley, K. M.; McGehee, M. D. *Chem. Mater.* **2004,** *16, 4533*−4542.

(3) (a) Cheng, F.; Zhang, G. W.; Lu, X. M.; Huang, Y. Q.; Chen, Y.; Zhou, Y.; Fan, Q. L.; Huang, W. *Macromol. Rapid Commun.* **2006**, *27*, 799−803. (b) Lee, K.; Cho, J. C.; Heckb, J. D.; Kim, J. *Chem. Commun.* **2006**, 1983−1985.

(4) (a) Kim, Y. M.; Lim, E.; Kang, I.-N.; Jung, B.-J.; Lee, J.; Koo, B. W.; Do, L.-M.; Shim, H.-K. *Macromolecules* **2006**, *39*, 4081−4085. (b) Li, Y.; Wu, Y.; Ong, B. S. *Macromolecules* **2006**, *39*, 6521−6527.

(5) Veenstra, S. C.; Verhees, W. J. H.; Kroon, J. M.; Koetse, M. M.; Sweelssen, J.; Bastiaansen, J. J. A. M.; Schoo, H. F. M.; Yang, X.; Alexeev, A.; Loos, J.; Schubert, U. S.; Wienk, M. M. *Chem. Mater.* **2004**, *16*, 2503−2508.

(6) Kietzke, T.; Egbe, D. A. M.; Horhold, H. H.; Neher, D. *Macromolecules* **2006**, *39*, 4018−4022.

(7) Ashraf, R. S.; Klemm, E. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 6445−6454.

(8) Wong, M. S.; Li, Z. H.; Tao, Y.; D'Iorio, M. *Chem. Mater.* **2003**, *15*, 1198−1203.

(9) Yu, Y.; Lee, H.; VanLaeken, A.; Hsieh, B. R. *Macromolecules* **1998**, *31*, 5553−5555.

(10) Liu, M. S.; Jiang, X.; Herguth, P.; Jen, A. K.-Y. *Chem. Mater.* **2001**, *13*, 3820−3822.

(11) (a) Chen, S. H.; Su, A. C.; Han, S. R.; Chen, S. A.; Lee, Y. Z. *Macromolecules* **2004**, *37*, 181−186. (b) Hsu, J. H.; Hayashi, M.; Lin, S. H.; Fann, W.; Rothberg, L. J.; Perng, G. Y.; Chen, S. A. *J. Phys. Chem. B* **2002**, *106*, 8582−8586.

(12) Sun, Q. J.; Wang, H. Q.; Yang, C. H.; Li, Y. F. *J. Mater. Chem.* **2003**, *13*, 800−806.

(13) Li, X.-C.; Kraft, A.; Cervini, R.; Spencer, G. C. W.; Cacialli, F.; Friend, R. H.; Gruener, J.; Holmes, A. B.; C De Mello, J.; Moratti, S. C. *Mater. Res. Soc. Symp. Proc.* **1996**, *413*, 13−25.

(14) Babel, A.; Jenekhe, S. A. *J. Am. Chem. Soc.* **2003**, *125*, 13656−13657.

(15) (a) Li, Y. F.; Qian, R. Y. *J. Electroanal. Chem.* **1993**, *362*, 267−272. (b) Li, Y. F.; Yan, B. Z.; Yang, J.; Cao, Y.; Qian, R. Y. *Synth. Met.* **1988**, *25*, 79−88.

(16) (a) Sonmez, G.; Shen, C. K. F.; Rubin, Y.; Wudl, F. *Angew. Chem., Int. Ed.* **2004**, *43*, 1498−1502. (b) Sonmez, G.; Meng, H.; Wudl, F. *Chem. Mater.* **2004**, *16*, 574−580. (c) Meng, H.; Tucker, D.; Chaffins, S.; Chen, Y.; Helgeson, R.; Dunn, B.; Wudl, F. *Adv. Mater.* **2003**, *15*, 146−149.

(17) (a) Schwendeman, I.; Hickman, R.; Sönmez, G.; Schottland, P.; Zong, K.; Welsh, D. M.; Reynolds, J. R. *Chem. Mater.* **2002**, *14*, 3118−3122. (b) Kumar, A.; Welsh, D. M.; Morvant, M. C.; Piroux, F.; Abboud, K. A.; Reynolds, J. R. *Chem. Mater.* **1998**, *10*, 896−902.

MA0626057