Electrochromic Behavior of Donor-Acceptor Polymers Containing Diketopyrrolopyrrole Unit

Wei Li and Tsuyoshi Michinobu*

Department of Materials Science and Engineering, Tokyo Institute of Technology
2-12-1 Ookayama, Meguro-ku, Tokyo 152-8552, Japan
*michinobu.t.a@ms.titech.ac.jp

Donor-acceptor polymers composed of the electron-rich fluorene or triphenylamine unit and electron-deficient diketopyrrolopyrrole (DPP) unit were investigated. These polymers showed an intense low-energy visible absorption in their neutral film states. The films of all the polymers displayed both oxidation and reduction waves in their cyclic voltammograms due to their narrow bandgaps. Both the anodic and cathodic electrochemical behaviors were investigated and compared to those of the reported DPP-based polymers. The results were explained by the difference in the comonomer structures. In addition, the switching times during the cathodic electrochromism were reported.

Keywords: Diketopyrrolopyrrole, Donor-acceptor polymer, Electrochromism, Switching time

1. Introduction

As a member of the brilliant red pigments, 3,6-dithiophen-2-yl-2,5-dihydropyrrole[3,4-c]pyrrole-1,4-dione (DPP) has been applied to paints, plastic ink, fluorescent probes, and semiconducting components in organic electronic devices, such as organic transistors and organic solar cells [1-5]. The DPP unit has a compact but highly polarized conjugated structure possessing a self-assembling nature via π-π interactions [6]. The two lactam moieties make DPP a strong electron-acceptor, and hence most DPP derivatives display n-type or ambipolar-type charge transport properties in the thin film states [7-12]. This feature is probably most significantly highlighted in the field of semiconducting polymers; DPP-based narrow bandgap polymers have been synthesized and employed as promising materials in polymer transistors and solar cells. On the other hand, as compared to the semiconducting applications, the electrochromic properties of the DPP-based polymers have rarely been investigated. Most of the reported electrochromic DPP-based polymers were the copolymers with thiophene-based comonomers, and accordingly, they showed only an anodic electrochromism [13-18].

Organic electrochromic materials are redox active conjugated molecules or polymers, which can be applied to smart windows [19], wearable sensors [20] and electronic displays [21]. From a materials point of view, it is significant to understand the structure-property relationship that determines the colors in both the neutral and doped states and their switching rates [22-28]. However, as already mentioned, examples of electrochromic DPP-based polymers are limited, and most of them are composed of alternating structures of thiophene-based donors and DPP acceptors.

We now, for the first time, report the electrochromic behavior of DPP-based polymers with fluorene or triphenylamine donors. Due to the intramolecular charge-transfer interactions, the polymers showed a
strong visible absorption. Interestingly, they were redox active in both the anodic (p-dope) and cathodic (n-dope) directions. The reversibility and switching times were also determined.

2. Experimental

2.1. Materials

The DPP-based polymers were synthesized by direct arylation polymerization between 2,5-bis(2-ethylhexyl)-3,6-di(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione and the aryl dibromide comonomers (Chart 1). The detailed procedure will be reported elsewhere. All the polymers showed the number-average molecular weights ($M_n$) of 7.9-12.6 kg mol$^{-1}$ and the polydispersity ($M_w/M_n$) of 2.2-2.8 as determined by GPC (eluent: o-dichlorobenzene at 40 °C).

2.2. Measurements

The UV-vis absorption spectra were measured by a JASCO V-670 spectrophotometer or an Agilent 8453 UV-vis spectrophotometer. The electrochemical measurements were carried out under flowing Ar by a BAS electrochemical analyzer model 612C at 25 °C in dehydrated CH$_3$CN containing 0.1 M $(nC_6H_5)_4NPF_6$ in a three-electrode cell. The working, reference, and auxiliary electrodes were a glassy carbon electrode, Ag/AgCl/CH$_3$CN/$(nC_6H_5)_4NPF_6$, and a Pt wire, respectively. The ferrocene/ferrocinium (Fc/Fc$^+$) couple was 0.09 V (vs Ag/AgCl). For the spectroelectrochemistry experiments, indium-tin-oxide (ITO) coated glass plate electrodes were used as a transparent electrode.

3. Results and discussion

3.1. Optical and electrochemical properties

The UV-vis absorption spectra of the DPP-based polymers were measured in the thin film states. All the polymers showed similar absorption spectra with two absorption bands; one in the range of 300~500 nm ascribed to the $\pi-\pi^*$ transitions and the other in the range of 500~700 nm originating from the intramolecular charge-transfer. Thus, the color of all the polymer films was dark blue. The optical bandgaps ($E_{g\text{opt}}$), calculated from the onset absorption ($\lambda_{\text{onset}}$), were in the range of 1.66-1.75 eV (Table 1).

The redox properties of the DPP-based polymers were studied using cyclic voltammetry (CV). The thin films of all the polymers showed quasi-reversible oxidation and reduction waves with the onset oxidation potentials ($E_{\text{ox}}$) at around 0.4~0.6 V (vs Ag/AgCl) and onset reduction potentials ($E_{\text{red}}$) at around -1.1 V. The oxidation behavior was similar to the reported DPP-based polymers [15]. The $E_{\text{ox}}$ values suggested that the triphenylamine derivatives are stronger donors than the fluorene unit and that the substitution of the methoxy group at the para-position with respect to the nitrogen atom facilitated the oxidation, whereas the cyano group substitution made it more difficult. This result is consistent with the redox behavior of the reported triphenylamine oligomers and polymers without the DPP unit [29-33]. In contrast, the $E_{\text{red}}$ values originating from the DPP unit were not affected by the electron-donating comonomer structures. As a result, the difference in the electrochemical bandgaps ($E_{g\text{ec}}$) was derived from the $E_{\text{ox}}$ values. The $E_{g\text{ec}}$ of all the polymers were in the range of 1.51-1.73 eV, and there was a clear correlation with the $E_{g\text{opt}}$ (see Table 1).

| Polymer | $\lambda_{\text{onset}}$ (nm)$^a$ | $E_{g\text{opt}}$ (eV)$^b$ | $E_{g\text{ec}}$ (eV)$^c$ |
|---------|-------------------------------|----------------------------|-------------------|
| DPP-F   | 714                           | 1.74                       | 1.73              |
| DPP-CN  | 710                           | 1.75                       | 1.68              |
| DPP-TPA | 735                           | 1.69                       | 1.58              |
| DPP-OMe | 748                           | 1.66                       | 1.51              |

$^a$ Onset wavelength of the polymer films; $^b$ Optical bandgap estimated from the onset wavelength of the polymer films; $^c$ Electrochemical bandgap determined from the $E_{\text{ox}}$ and $E_{\text{red}}$ potentials.

3.2. Anodic electrochromism

The electrochromic activity of the DPP-based polymers was investigated in the
spectroelectrochemistry setup. The polymer thin films were prepared by spray-coating on the ITO-coated glass plate, then it was immersed in the CH$_3$CN solution containing 0.1 M ($n$C$_4$H$_9$)$_4$NPF$_6$ together with the reference and counter electrodes in a 1-cm cuvette. The UV-vis-near IR spectra were measured at 20 °C with the applied potentials of 0~1.5 V. All the polymers showed almost the same spectral changes, although the potential responses were slightly different. As can be seen in Fig. 1, the initial low-energy absorption at around 600 nm started to decrease and a new broad absorption band appeared in the near-IR region when the potentials higher than the $E_{ox}$ were applied. This result suggested the formation of cationic radicals at the electron-donating fluorene or triphenylamine moieties. DPP-OMe displayed the most active response probably due to the lowest $E_{ox}$ value among the four polymers. In the fully oxidized states, the color of the polymer films bleached from dark blue to transparent. However, when the potentials higher than 0.7 V were applied, the electrochromic reversibility dramatically decreased. This was probably due to the intrinsic instability of the dication states of these polymers, which was in sharp contrast to the reported electrochromism of the DPP-thiophene based copolymers.

3.3. Cathodic electrochromism

The same spectroelectrochemical setup was employed to study the cathodic electrochromism. It is generally known that the electrochemical reduction is more difficult than the corresponding oxidation because the formed anionic radicals are very sensitive towards oxygen and water. However, the DPP-based polymers showed well-defined spectral changes upon the potential application of 0~2.0 V (Fig. 2). In contrast to the anodic electrochromism in which DPP-OMe was the most active, DPP-CN displayed quick spectral changes at the lowest applied potential of -1.4 V. The initial absorption at around 600 nm started to decrease and a new sharp band appeared at around 770 nm. This spectral change continued when the applied potentials were increased in the cathodic direction. The initial absorption ascribed to the neutral state eventually disappeared at the applied potential of -1.7 V. The film color changed from deep blue to grey. The presence of an isosbestic point indicated that only two optically different species (possibly the neutral and anionic radical states) existed within the films, which mutually interconverted without any undesirable side reactions. The other DPP-based polymers exhibited more or less the same behavior. However, it was necessary to apply higher negative potentials to promote the spectral changes especially in the case of DPP-F. This was probably due to the fluorene comonomer unit, which served as a spacer between the adjacent DPP units. The resulting dimer unit was inclined to readily form dianion species as compared to the other DPP-based polymers with the triphenylamine comonomers [34]. In addition to this reason, the overall...
reversibility of the cathodic electrochromism was unfortunately limited.

3.4. Switching time

To gain more insights into the film stability and coloring/discoloring mechanism, the response time and switching processes were investigated. The excellent reversibility was previously reported for the anodic electrochromism of the DPP-thiophene copolymers [13-18]. Unfortunately, the DPP-based polymers with the fluorene or triphenylamine donors in this study did not show such a reversible electrochromism in the anodic direction. However, there have been, to the best of our knowledge, no detailed reversibility studies for the cathodic electrochromism of the DPP-based polymers. Thus, despite the limited performances, the original absorbance at around 600 nm was carefully monitored as a function of time. The pulse time was 20 s, and the switching time was determined to be 90% of the full reduction. All the DPP-based polymers displayed relatively fast switching times on the order of 5-6 s (Fig. 3). There were no clear differences between the four polymers, indicating that the cathodic electrochromism mainly occurred at the DPP unit.

Fig. 3. Absorbance changes at 662 nm upon electrochromic switching between 0 and −2.0 V of (a) DPP-F, (b) DPP-CN, (c) DPP-TPA, and (d) DPP-OMe films on the ITO-coated glass plate.

4. Conclusion

The electrochromic behavior of a new series of DPP-based polymers with fluorene or triphenylamine comonomer units was investigated. All the polymers possessed visible absorptions with a deep blue color in the neutral film states and showed electrochemical oxidation and reduction waves. During both the oxidation and reduction processes, the original absorption at around 600 nm decreased and a new low-energy band appeared, resulting in the dramatic shift from a highly colored to almost a transparent state. The redox activities were dependent on the comonomer structures, which determined the $E_{ox}$ values, but not the $E_{red}$ values. Thus, the switching times of all the polymers during the cathodic electrochromism were almost the same.

Acknowledgements

This work was partially supported by the Heiwa Nakajima Foundation, the Ogasawara Foundation for the Promotion of Science and Engineering, and the Support for Tokyotech Advanced Researchers.

References

1. Y. Ki, P. Sonar, L. Murphy, and W. Hong, *Energy Environ. Sci.*, 6 (2013) 1684.
2. M. A. Naik and S. Patil, *J. Polym. Sci., Part A: Polym. Chem.*, 51 (2013) 4241.
3. M. Kaur and D. H. Choi, *Chem. Soc. Rev.*, 44 (2015) 58.
4. Z. Yi, S. Wang, and Y. Liu, *Adv. Mater.*, 27 (2015) 3589.
5. W. Li, K. H. Hendriks, M. M. Wienk, and R. A. J. Janssen, *Acc. Chem. Res.*, 49 (2016) 78.
6. O. Wallquist and R. Lenz, *Macromol. Symp.*, 187 (2002) 617.
7. J. H. Park, E. H. Jung, J. W. Jung, and W. H. Jo, *Adv. Mater.*, 25 (2013) 2583.
8. J. Lee, A. Han, H. Yu, T. J. Shin, C. Yang, and J. H. Oh, *J. Am. Chem. Soc.*, 135 (2013) 9540.
9. B. Sun, W. Hong, Z. Yan, H. Aziz, and Y. Li, *Adv. Mater.*, 26 (2014) 2636.
10. H.-J. Yun, S.-J. Kang, Y. Xu, S. O. Kim, Y.-H. Kim, Y.-Y. Noh, and S.-K. Kwon, *Adv. Mater.*, 26 (2014) 7300.
11. J. Lee, A. Han, S. M. Lee, D. Yoo, J. H. Oh, and C. Yang, *Angew. Chem. Int. Ed.*, 54 (2015) 4657.
12. Y. Gao, X. Zhang, H. Tian, J. Zhang, D. Yan, Y. Geng, and F. Wang, *Adv. Mater.*, 27 (2015) 6753.
13. Y. Zhu, K. Zhang, and B. Tieke, *Macromol. Chem. Phys.*, 210 (2009) 431.
14. W. T. Neo, Z. Shi, C. M. Cho, S.-J. Chua, and J. Xu, ChemPlusChem, 80 (2015) 1298.
15. J. Z. Low, W. T. Neo, Q. Ye, W. J. Ong, U. H. K. Wong, T. T. Lin, and J. Xu, J. Polym. Sci., Part A: Polym. Chem., 53 (2015) 1287.
16. E. M. Sanford, M. E. Tori, T. M. Smeltzer, C. K. Beaudoin, B. H. Bowser, M. E. Anderson, and K. L. Brown, Electrochemistry, 83 (2015) 1061.
17. Z. Shi, W. T. Neo, H. Zhou, and J. Xu, Aust. J. Chem., 69 (2016) 403.
18. W. T. Neo, C. M. Cho, Z. Shi, S.-J. Chua, and J. Xu, J. Mater. Chem. C, 4 (2016) 28.
19. C. G. Granqvist, A. Azens, A. Hjelm, A. L. Kullman, G. A. Niklasson, D. Rœnnow, M. S. Mattsson, M. Veszelei, and G. Vaivars, Sol. Energy, 63 (1998) 199.
20. P. A. Ersman, J. Kawahara, and M. Berggren, Org. Electron., 14 (2013) 3371.
21. P. Andersson, R. Forchheimer, P. Tehrani, and M. Berggren, Adv. Funct. Mater., 17 (2007) 3074.
22. P. M. Beaupège and J. R. Reynolds, Chem. Rev., 110 (2010) 268.
23. H.-J. Yen and G.-S. Liou, Polym. Chem., 3 (2012) 255.
24. Y. Li and T. Michinobu, J. Polym. Sci., Part A: Polym. Chem., 50 (2012) 2111.
25. M. Higuchi, J. Mater. Chem. C, 2 (2014) 9331.
26. M. Kanao and M. Higuchi, J. Photopolym. Sci. Technol., 28 (2015) 363.
27. M. Kanao and M. Higuchi, J. Photopolym. Sci. Technol., 29 (2016) 295.
28. W. Li and T. Michinobu, Polym. Chem., 7 (2016) 3165.
29. T. Michinobu, J. Inui, and H. Nishide, Org. Lett., 5 (2003) 2165.
30. M. Kivala, T. Stanoeva, T. Michinobu, B. Frank, G. Gescheidt, and F. Diederich, Chem. Eur. J., 14 (2008) 7638.
31. T. Michinobu, J. Inui, and H. Nishide, Polym. J., 42 (2010) 575.
32. T. Michinobu, N. Satoh, J. Cai, Y. Li, and L. Han, J. Mater. Chem. C, 2 (2014) 3367.
33. Y. Yuan, T. Michinobu, N. Satoh, M. Ashizawa, and L. Han, J. Nanosci. Nanotechnol., 15 (2015) 5856.
34. C. Wang, Y. Zang, Y. Qin, Q. Zhang, Y. Sun, C.-a. Di, W. Xu, and D. Zhu, Chem. Eur. J., 20 (2014) 13755.