Crystalline conjugated polymers for organic electronics

Itaru Osaka and Kazuo Takimiya

RIKEN Center for Emergent Matter Science, Wako, Saitama 351-0198, Japan

E-mail: itaru.osaka@riken.jp

Abstract. We reported the characterization of a series of semiconducting polymers based on naphthodithiophenes (NDTs) and naphthobisthiadiazole (NTz). Four different isomeric NDTs are selectively synthesized using the similar synthetic protocol. The isomeric NDTs provide quite distinct electronic structures and crystallinity of the corresponding polymers and thus the device performances. Polymers with one of the NDT isomers, NDT3, showed high hole mobilities in excess of 0.5 cm²/Vs. On the other hand, an NTz-based polymer exhibited high hole mobility of >0.5 cm²/Vs in OFETs and power conversion efficiencies of >7% in OPVs. These high performances of the present polymers are found to originate in their highly crystalline structures in the thin films.

1. Introduction
With their great electrical and optical properties and ease of fabrication process using their solutions, π-conjugated polymers, namely, semiconducting polymers have been attracting considerable attentions for applications to various organic electronic devices such as field-effect transistors (OFETs) and photovoltaics (OPVs) [1-2]. A key to develop high-performance semiconducting polymers is to achieve strong π–π stacking structures that determines the charge transport property in the active layer films [3-6]. Therefore, the incorporation of π-cores into the backbones and/or the use of donor–acceptor backbones that can promote strong intermolecular interaction are important design strategies [1]. In parallel, understanding the structure–property relationships, i.e., correlation between polymer structures and their optical, physical, and device properties, is also crucial for the development of polymers.

In this paper, we reported on a series of semiconducting polymers based on naphthodithiophenes (NDTs) [7-11] and naphthobisthiadiazoles (NTz) [12], both four-ring-fused heteroaromatics. These polymers afford higher crystalline structures in the thin films, which are beneficial to OFETs and OPVs.

2. Naphthodithiophene-based polymers
Figure 1 shows the chemical structure of the NDT-based polymers. All polymers were soluble in hot chlorobenzene, o-dichlorobenzene, and 1,2,4-trichlorobenzene, where the solubility was PNDT2BT > PNDT1BT > PNDT3BT > PNDT4BT from the highest, and the polymers with C20H41 (C20) side chains showed better solubility than those with C16H33 (C16) side chains. Molecular weights (Mn) of the polymers evaluated by high-temperature (140 °C) GPC calibrated with polystyrene standard were 21000–52000 g/mol.
In the UV-vis absorption spectra, room temperature solutions of PNDT1BT-16, PNDT3BT-16, and PNDT4BT-16 gave two peaks at 532 and 571 nm, 506 and 540 nm, and 492 and 529 nm, respectively, which are mostly identical with those in the as-spun thin film. PNDT2BT-16, on the other hand, gave a single peak with $\lambda_{\text{max}}$ of 487 nm in the solution, which slightly broadens toward the longer wavelength region in the as-spun thin film. Photoelectron spectroscopy in air was carried out to evaluate the ionization potential (IP) of the polymers in the thin film. The IPs were 5.1, 5.2, 5.0, and 5.2 eV for PNDT1BT–PNDT4BT, respectively. Interestingly, the IP of PNDT1BT was larger than that of PNDT3BT, and similar to PNDT4BT. Interestingly IP of PNDT1BT was larger than that of PNDT3BT despite the fact that PNDT1BT had a smaller bandgap than PNDT3BT. A plausible explanation can be described by taking into account the calculated HOMOs of corresponding model compounds (Figure 2). In PNDT1BT, the HOMOs are apparently localized within the NDT cores.

**Figure 1.** Chemical structures of NDT-based semiconducting polymers.

**Figure 2.** Calculated HOMOs and LUMOs of NDTs and the model compounds (NDT$m$BTs).
whereas in PNDT3BT the HOMOs are delocalized over the whole molecule structures (including attached thiophene rings). Therefore, the elevation of the $E_{\text{HOMO}}$ ($\Delta E_{\text{HOMO}}$) from the parent NDTs to NDTmBTs is more significant in the angular NDT system as compared to the linear NDT system; for example, in the NDT1 system $\Delta E_{\text{HOMO}} (= |E_{\text{HOMO}} (\text{NDTm}) - E_{\text{HOMO}} (\text{NDTmBT}) |)$ is ca. 0.10 (=$|-5.09 - (-4.99)|$) eV, whereas in the NDT3 system $\Delta E_{\text{HOMO}}$ is ca. 0.46 ($= |-5.66 - (-5.20)|$) eV. Assuming that this estimation can be adapted in the actual polymer system, the $E_{\text{HOMO}}$ of the linear and angular NDT systems would get closer as the molecular chains extend to end up with the similar or possibly reversed $E_{\text{HOMO}}$, which well agrees with the results observed for the present polymer system.

OFET characteristics of the polymers were evaluated by top contact, bottom gate devices fabricated by using polymer thin films spin-coated from $o$-dichlorobenzene solutions onto hexamethyldisilazane (HMDS)- and 1H,1H,2H,2H-perfluorodecyltriethoxysilane (FDTS)-modified Si/SiO$_2$ surfaces, respectively, which were subsequently annealed at 150 °C. Mobilities were calculated from the saturation regime and are summarized in Table 1. PNDT3BT-20 on the FDTS-modified devices exhibited the highest mobility of 0.77 cm$^2$V$^{-1}$s$^{-1}$ (average 0.38 cm$^2$V$^{-1}$s$^{-1}$) with high on/off ratios of $\sim$10$^7$ (Figure 3). This value is among the highest observed so far for semiconducting polymers. The mobilities obtained for these polymers are PNDT3BTs > PNDT4BTs > PNDT1BTs > PNDT2BTs, e.g., the average mobility of the C20 polymers on the HMDS-modified devices are 0.18, 0.093, 0.027,

![Figure 3.](image_url)

**Table 1.** Mobilities and on/off ratios

| Polymer | Side chain | $\mu$ (cm$^2$ V$^{-1}$ s$^{-1}$)/ maximum (average) | Ion/Ioff |
|---------|------------|-----------------------------------------------|---------|
| PNDT1BT | C16        | 0.029 (0.025) 0.024 (0.020) | $\sim$106 |
|         | C20        | 0.037 (0.027) 0.055 (0.032) | $\sim$104 |
| PNDT2BT | C16        | 0.0059 (0.0039) 0.0033 (0.0019) | $\sim$105 |
|         | C20        | 0.0066 (0.0037) 0.026 (0.0016) | $\sim$103 |
| PNDT3BT | C16        | 0.54 (0.20) 0.26 (0.12) | $\sim$107 |
|         | C20        | 0.32 (0.18) 0.77 (0.38) | $\sim$107 |
| PNDT4BT | C16        | 0.086 (0.043) 0.030 (0.022) | $\sim$107 |
|         | C20        | 0.15 (0.093) 0.19 (0.14) | $\sim$107 |

whereas in PNDT3BT the HOMOs are delocalized over the whole molecule structures (including attached thiophene rings). Therefore, the elevation of the $E_{\text{HOMO}}$ ($\Delta E_{\text{HOMO}}$) from the parent NDTs to NDTmBTs is more significant in the angular NDT system as compared to the linear NDT system; for example, in the NDT1 system $\Delta E_{\text{HOMO}} (= |E_{\text{HOMO}} (\text{NDTm}) - E_{\text{HOMO}} (\text{NDTmBT}) |)$ is ca. 0.10 (=$|-5.09 - (-4.99)|$) eV, whereas in the NDT3 system $\Delta E_{\text{HOMO}}$ is ca. 0.46 (=$|-5.66 - (-5.20)|$) eV. Assuming that this estimation can be adapted in the actual polymer system, the $E_{\text{HOMO}}$ of the linear and angular NDT systems would get closer as the molecular chains extend to end up with the similar or possibly reversed $E_{\text{HOMO}}$, which well agrees with the results observed for the present polymer system.

OFET characteristics of the polymers were evaluated by top contact, bottom gate devices fabricated by using polymer thin films spin-coated from $o$-dichlorobenzene solutions onto hexamethyldisilazane (HMDS)- and 1H,1H,2H,2H-perfluorodecyltriethoxysilane (FDTS)-modified Si/SiO$_2$ surfaces, respectively, which were subsequently annealed at 150 °C. Mobilities were calculated from the saturation regime and are summarized in Table 1. PNDT3BT-20 on the FDTS-modified devices exhibited the highest mobility of 0.77 cm$^2$V$^{-1}$s$^{-1}$ (average 0.38 cm$^2$V$^{-1}$s$^{-1}$) with high on/off ratios of $\sim$10$^7$ (Figure 3). This value is among the highest observed so far for semiconducting polymers. The mobilities obtained for these polymers are PNDT3BTs > PNDT4BTs > PNDT1BTs > PNDT2BTs, e.g., the average mobility of the C20 polymers on the HMDS-modified devices are 0.18, 0.093, 0.027,
This trend is quite different from our initial expectation; we expected that PNDT1BT would give the best performance, since NDT1 showed the highest mobility among the four NDT isomers in the small molecular systems. To understand the difference of the mobility in these polymers and their unexpected trend, we carefully studied the ordering structures using grazing incidence X-ray diffraction (GIXRD) measurements.

The out-of-plane GIXRD patterns gave sharp peaks assignable to (h00), where (100) peaks appeared at around \( \theta = 4.2° \), d-spacings \( \langle d \rangle \) of 20–22 Å, which correspond to the lamellar structure along with side chain interdigitation (Figure 4a). Since these (h00) peaks were not seen in the in-plane patterns, the polymers are dominantly edge-on oriented respective to the substrate. It was found that, interestingly, each polymer gave quite distinct diffraction features in the out-of-plane direction. PNDT3BT-16 provides (h00) peaks up to the fourth order, the third order for PNDT4BT-16, the second order for PNDT1BT-16, and only the first order for PNDT2BT-16, indicating that PNDT3BT-16 forms the most highly ordered structure in the thin film and the rest of the polymers follow in this order. It is also clear from the in-plane diffractions (Figure 4b) that PNDT3BT-16 forms the most ordered structure. PNDT3BT-16 exhibited a very strong (010) peak at \( \theta = 24.5° \) corresponding to the \( \pi \)-stacking order between facing backbones with a distance \( \langle d \rangle \) of 3.6 Å, along with a small peak at \( \theta = 20.0° \) most likely assignable to (004), the backbone repeat unit. PNDT4BT-16 also showed a sharp (010) peak \( \langle d \rangle = 3.6 \) Å, but without a diffraction peak corresponding to the backbone repeat unit. It is noteworthy that this \( \langle d \rangle \) of 3.6 Å for these two polymers are smaller than those of so far reported high-performance semiconducting polymers that typically possess 3.7–3.8 Å. These indicate that PNDT3BT has a more ordered backbone structure than PNDT4BT, though the \( \pi \)-stacking crystallinity seems to be comparable. On the other hand, in PNDT1BT-16 a diffraction corresponding to (010) was barely seen at around \( \theta = 24.0° \) \( \langle d \rangle = ca. 3.7 \) Å, indicative of very weak \( \pi \)-stacking crystallinity. In PNDT2BT-16, although some unassignable diffraction peaks appeared at \( \theta = 16–22° \), no peak was found at around \( \theta = 24–25° \), indicating that the \( \pi \)-stacking order is absent. The ordering structure is one of the most important parameter for the charge carrier transport, and it is mostly accepted that the higher mobility would be achieved as the ordering structure enhances. Hence, these results perfectly agree with the order of the mobility for these polymers as shown above.
3. Naphthobisthiadiazole-based polymer

Figure 5 shows chemical structure of novel semiconducting polymers based on naphthobisthiadiazole (PNTz4T) and benzothiadiazole (PBTz4T) [12]. Naphthobisthiadiazole (NTz) is a doubly benzothiadiazole (BTz)-fused heterocycle [12-14]. Since NTz is expected to be a more rigid \( \pi \)-extended ring as compared to BTz, the incorporation into the polymer main chain should enhance intermolecular interaction and thereby promote a strong \( \pi-\pi \) stacking structure due to the more coplanar and the better arranged backbone structure compared to the BTz-analogue. In fact, the UV-vis absorption spectra of the polymer thin films show that PNTz4T gives a more defined structure, in which the absorption peak is more sharpened, than PBTz4T (Figure 6). The red-shift of the absorption range for PNTz4T than that for PBTz4T should be due to the stronger electron-accepting nature of the NTz moiety than BTz, which would lowers the level of the lowest occupied molecular orbital and thus the bandgap.

OFETs of the polymers are fabricated and evaluated using top-contact, bottom-gate devices using the polymer thin films spin-coated from \( o \)-dichlorobenzene (DCB) solutions, which are subsequently annealed at 200 °C. Figure 7a depicts the typical current–voltage curves of the transistor devices based on PNTz4T and PBTz4T. Mobilities evaluated from the saturation regime for PNTz4T are as high as 0.6 cm²/Vs, and typically in a range of 0.2~0.4 cm²/Vs with current on/off ratios of \( \sim 10^7 \). The mobility of PNTz4T is 1 order of magnitude higher than that of PBTz4T, typically 0.05 cm²/Vs, indicating the high potential of the NTz core.

OPV cells are fabricated by spin coating the solution of the polymer blended with \([6,6]\)-phenyl...
C61-butyric acid methyl ester (PC$_{61}$BM) in DCB. Current density–voltage curves of the devices under one sun of simulated AM 1.5G solar irradiation (100 mW/cm$^2$) are displayed in Figure 7b. While PBTz4T shows power conversion efficiencies (PCE) of ~2.6% with the polymer to PC$_{61}$BM weight ratio (p:n) of 1:1, in which the short circuit current ($J_{SC}$) = 5.6 mA/cm$^2$, open-circuit voltage ($V_{OC}$) of 0.74 V, and fill factor (FF) of 0.63, PNTz4T shows a maximum PCE of 6.3% with $J_{SC}$ = 12.0 mA/cm$^2$, $V_{OC}$ = 0.76 V, and FF = 0.69 at p:n = 1:1.5. Significantly higher $J_{SC}$ for the devices with PNTz4T than with PBTz4T is most likely as a result of, in part, the wider absorption range of PNTz4T.

In order to further understand these higher performances of PNTz4T in transistors and solar cells, the ordering structures of the polymers are investigated by the grazing incidence X-ray diffraction measurements with a two dimensional detector. The diffraction images of the polymer-only films and

Figure 7. Current–voltage curves of the transistors (a) and solar cells (b) using the present polymers.

Figure 8. 2D-GIXD images of the PNTz4T thin film (a), PNTz4T/PC$_{61}$BM blend film (b), PBTz4T thin film (c), and PBTz4T/PC$_{61}$BM blend film (d). The illustrations shown in Figure 8a and 8b depict the motif of edge-on and face-on orientation, respectively.
polymer/PC_{61}BM blend films are displayed in Figure 8, where they reflect the ordering structures in the transistors and solar cells, respectively. In the polymer-only film of PNTz4T (Figure 8a), diffractions assignable to the lamellar \( q_z \approx 0.25 \, \text{Å}^{-1} \) and the \( \pi-\pi \) stacking structures \( q_{xy} \approx 1.7 \, \text{Å}^{-1} \) appear on the \( q_z \) and \( q_{xy} \) axes, respectively, indicating the predominant edge-on orientation, i.e., the polymer backbones stand on the substrate surface [12]. In addition, the \( \pi-\pi \) stacking distance of PNTz4T is determined to be 3.5 Å, which is very narrow for semiconducting polymers, and thus this well rationalizes the high mobilities of PNTz4T in transistors. In contrast, PBTz4T shows largely arcing diffraction corresponding to the lamellar structure, indicating that there is no preferential orientation (Figure 8b). PBTz4T does not show clear diffraction corresponding to the \( \pi-\pi \) stacking structure, indicative of the much lesser crystalline nature of PBTz4T in the thin film. This large difference in the ordering structure between PNTz4T and PBTz4T is in good agreement with the fact that the transistor performances are quite distinct.

In the PNTz4T/PC_{61}BM blend film, it is interesting that PNTz4T mainly orients in a face-on manner, i.e., the polymer backbones lie on the substrate, as the diffraction corresponding to the \( \pi-\pi \) stacking appears on the \( q_z \) axis (Figure 8c). It should also be noted that PNTz4T still has the narrow \( \pi-\pi \) stacking distance of 3.5 Å in the blend film. In the meantime, PBTz4T provides much less crystalline feature in the blend film, where there is no \( \pi-\pi \) stacking diffraction (Figure 8d). The predominant face-on orientation and the preserved narrow \( d_{\pi} \) of PNTz4T in the blend film should allow efficient charge transport in the cells, where the films are sandwiched between the electrode, which could be one of the main reasons that PNTz4T shows high PCE of exceeding 6% and greater performances as compared to PBTz4T.

4. Summary

In summary, structure–property relationships of a novel semiconducting polymer based on NDTs and NTz are presented. A striking structural feature of these polymers is the strong \( \pi-\pi \) stacking structure with a narrow distance of 3.5–3.6 Å, most likely owing to its \( \pi \)-extended rigid structure, allowing better arrangement of the main chain and the side chain. As a result, these polymers showed high mobilities in transistor devices, and, in particular, together with the broad absorption spectrum, PNTz4T provided high photovoltaic properties in solar cells.

References

[1] Facchetti A 2011 Chem. Mater. 23 733
[2] Beaujuge P M, Fréchet, J M J 2011 J. Am. Chem. Soc. 133 20009
[3] McCulloch R D 1998 Adv. Mater. 10 93
[4] Sirringhaus H, Brown P J, Friend R H, Nielsen M M, Bechgaard K, Langeveld-Voss B M W, Spiering A J H, Janssen R A J, Meijer E W, Herwig P, De Leeuw D M 1999 Nature 401 685
[5] Osaka I, McCulloch R D 2008 Acc. Chem. Res. 41 1202
[6] McCulloch I, Heeney M, Chabinyc M L., DeLongchamp D, Kline R J, Colle M, Duffy W, Fischer D, Gundlach D, Hamadani B, Hamilton R, Richter L, Salleo A, Shkunov M, Sparrowe D, Tierney S, Zhang W 2009 Adv. Mater. 21 1091
[7] Shinamura S, Miyazaki E, Takimiya K 2010 J. Org. Chem. 75 1228
[8] Shinamura S, Osaka I, Miyazaki E, Nakao A, Yamagishi M, Takeya J, Takimiya K 2011 J. Am. Chem. Soc. 133 5024
[9] Osaka I, Abe T, Shinamura S, Miyazaki E, Takimiya K 2010 J. Am. Chem. Soc. 132, 132, 5000
[10] Osaka I, Abe T, Shinamura S, Takimiya K 2011 J. Am. Chem. Soc. 133 6852
[11] Osaka I, Shinamura S, Abe T, Takimiya K 2013 J. Mater. Chem. C 1 1297
[12] Osaka I, Shimawaki M, Mori H, Doi I, Miyazaki E, Koganezawa T, Takimiya K 2012 J. Am. Chem. Soc. 134 3498
[13] Wang M, Hu X, Liu P, Li W, Gong X, Huang F, Cao Y 2011 J. Am. Chem. Soc. 133 9638
[14] Mataka S, Takahashi K, Ikekazi Y, Hatta T, Tori-i A, Tashiro M 1991 Bull. Chem. Soc. Jpn. 64 68