

Structure-property relationships of a semiconducting polymer based on naphthobisthiadiazole

There has been considerable attention focused on semiconducting polymers in the field of organic electronics because their solution processability, thermal stability, and mechanical properties are expected to lead to the realization of large-area, flexible next-generation devices [1]. Organic field-effect transistors and solar cells are of particular current interest in the field. Recent advances in the development of new materials, mostly small bandgap polymers with donor-acceptor systems, have brought about great improvements in device performances [2]. A key issue for the materials is to build a strong π - π stacking structure, which facilitates charge carrier transport through the π -orbital overlaps between the cofacially stacked polymer backbones. Thus, the choice of building unit to ensure strong π - π stacking is crucial for the development of high-performance polymers.

In this report, we present the structure-property relationships of a novel semiconducting polymer based on naphthobisthiadiazole (PNTz4T, Fig. 1) in comparison with those of an analogue polymer based on benzothiadiazole (PBTz4T, Fig. 1) [3]. Naphthobisthiadiazole (NTz) is a doubly benzothiadiazole (BTz)-fused heterocycle [4]. Since NTz is expected to be a more rigid π -extended ring than BTz, its incorporation into the polymer main chain should enhance the intermolecular interaction and thereby promote a strong π - π stacking structure due to the more coplanar and better arranged backbone structure than that of 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 (Fig. 2). The red-shift of the absorption range for PNTz4T compared with that for PBTz4T should be due to the stronger electron-accepting nature of the NTz moiety than BTz, which would lower the level of the lowest occupied molecular orbital and thus the bandgap.

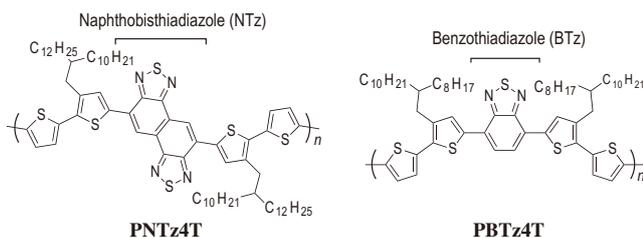


Fig. 1. Chemical structures of a naphthodithiophene-based semiconducting polymer (PNTz4T) and a benzothiadiazole-based analogue (PBTz4T).

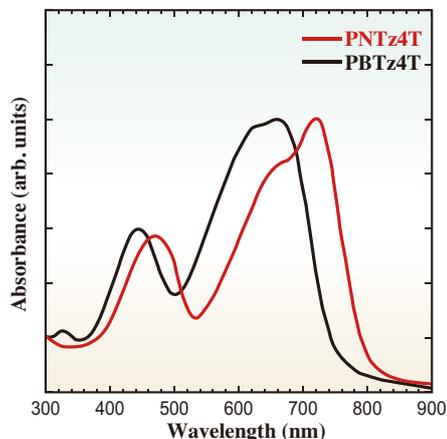


Fig. 2. UV-vis absorption spectra of PNTz4T and PBTz4T in thin films.

Transistor devices 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 3(a) 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 the range of 0.2–0.4 cm²/Vs with current on/off ratios of $\sim 10^7$. The mobility of PNTz4T is one order of magnitude higher than that of PBTz4T, typically 0.05 cm²/Vs, indicating the high potential of the NTz core.

Bulk-heterojunction solar cells are fabricated by spin coating a solution of the polymer blended with [6,6]-phenyl C₆₁-butyric acid methyl ester (PC₆₁BM) in DCB. Current density-voltage curves of the devices under one sun of simulated AM 1.5 G solar irradiation (100 mW/cm²) are displayed in Fig. 3(b). While PBTz4T shows power conversion efficiencies (PCEs) of $\sim 2.6\%$ with a polymer to PC₆₁BM weight ratio (p:n) of 1:1, in which the short circuit current (J_{SC}) is 5.6 mA/cm², the open-circuit voltage (V_{OC}) is 0.74 V, and the fill factor (FF) is 0.63, PNTz4T shows a maximum PCE of 6.3% with $J_{SC} = 12.0$ mA/cm², $V_{OC} = 0.76$ V, and FF = 0.69 at p:n = 1:1.5. The significantly higher J_{SC} for the devices with PNTz4T than for those with PBTz4T is likely to be partly a result of 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 grazing incidence X-ray diffraction measurements with a two-dimensional detector. The diffraction images of the polymer-only films and polymer/PC₆₁BM

blend films are displayed in Fig. 4, where they reflect the ordering structures in the transistors and solar cells, respectively. In the polymer-only film of PNTz4T (Fig. 4(a)), diffractions assignable to the lamellar ($q_z \approx 0.25 \text{ \AA}^{-1}$) and π - π stacking structures ($q_{xy} \approx 1.7 \text{ \AA}^{-1}$) appear on the q_z and q_{xy} axes, respectively, indicating the predominant edge-on orientation, i.e., the polymer backbones are oriented vertically on the substrate surface [5]. In addition, the π - π stacking distance of PNTz4T is determined to be 3.5 \AA , which is very narrow for semiconducting polymers and clearly explains 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 (Fig. 4(b)). PBTz4T does not show clear diffraction corresponding to the π - π 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/PC₆₁BM blend film, it is interesting that PNTz4T is mainly oriented in a face-on manner, i.e., the polymer backbones lie on the substrate, as the diffraction corresponding to the π - π stacking appears on the q_z axis (Fig. 4(c)). It should also be noted that PNTz4T still has the narrow π - π stacking distance of 3.5 \AA in the blend film. Meanwhile, PBTz4T results in much lower crystallinity in the blend film, where there

is no π - π stacking diffraction. The predominant face-on orientation and the preserved narrow d_p 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 why PNTz4T shows a high PCE exceeding 6% and greater performances than PBTz4T.

In summary, the structure-property relationships of a novel semiconducting polymer based on NTz are presented. A striking structural feature of the polymer is the strong π - π stacking structure with a narrow distance of 3.5 \AA , most likely owing to its π -extended rigid structure, allowing better arrangement of the main chain and the side chain. In addition, the polymer spontaneously orients in the desired directions for transistors and solar cells in the corresponding films. These results are in good agreement with high mobilities and high photovoltaic properties of PNTz4T.

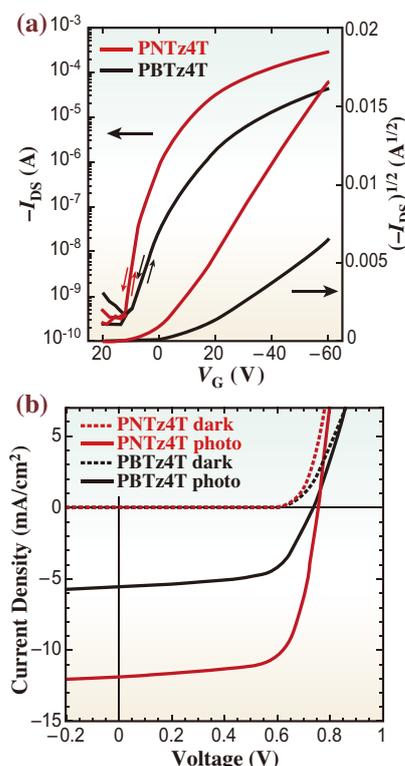


Fig. 3. Current-voltage curves of the transistor devices (a) and solar cells (b) using the polymers.

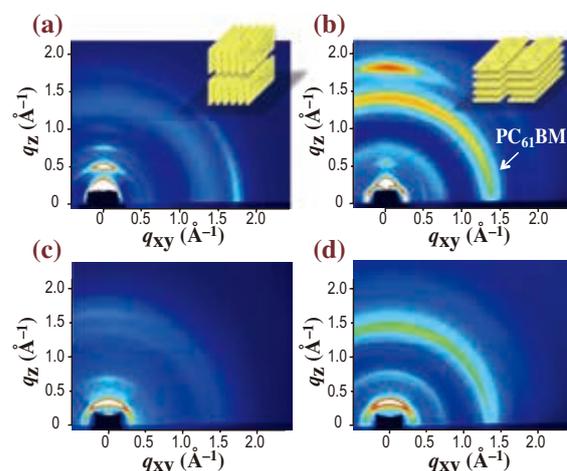


Fig. 4. 2D-GIXD images of the PNTz4T thin film (a), PNTz4T/PC₆₁BM blend film (b), PBTz4T thin film (c), and PBTz4T/PC₆₁BM blend film (d). The illustrations shown in (a) and (b) depict motifs of the edge-on and face-on orientations, respectively.

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