Supporting Information

Synthesis, Characterization, and Transistor and Solar Cell Applications of A Naphthobisthiadiazole-Based Semiconducting Polymer

Itaru Osaka,^{*,†,‡} Masafumi Shimawaki,[†] Hiroki Mori,[†] Iori Doi,[†] Eigo Miyazaki,[†]
Tomoyuki Koganezawa,[§] Kazuo Takimiya^{*,†,¶}

[†]*Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, 1-4-1 Kagamiyama, Higashi-Hiroshima, Hiroshima 739-8527, Japan*

[‡]*Precursory Research for Embryonic Science and Technology (PRESTO), Japan Science and Technology Agency, Chiyoda-ku 102-0075, Japan*

[§]*Japan Synchrotron Radiation Research Institute, 1-1-1, Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5198, Japan*

[¶]*Institute for Advanced Materials Research, Hiroshima University, Higashi-Hiroshima 739-8530, Japan*

E-mail: iosaka@hiroshima-u.ac.jp, ktakimi@hiroshima-u.ac.jp

Complete list of the authors for reference 2f:

Bronstein, H.; Chen, Z.; Ashraf, R. S.; Zhang, W.; Du, J.; Durrant, J. R.; Tuladhar, P. S.; Song, K.; Watkins, S. E.; Geerts, Y.; Wienk, M. M.; Janssen, R. A. J.; Anthopoulos, T.; Sirringhaus, H.; Heeney, M.; McCulloch, I. *J. Am. Chem. Soc.* **2011**, *133*, 3272–3275.

Single crystal X-ray analysis of NTz2T-Me and BTz2T-Me.

Single crystals of NTz2T-Me and BTz2T-Me for X-ray structural analysis were obtained by sublimation and recrystallization from ethyl acetate, respectively. The X-ray crystal structural analysis was performed on a Rigaku CCD Mercury (Mo *K* α radiation, $\lambda = 0.71070$ Å, graphite monochromator, $T = 293$ K, $2\theta_{\max} = 55.0^\circ$). The structure was solved by the direct method using SHELXS-97.^{S1} Non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were included in the calculations but not refined. All calculations were performed using the crystallographic software of SHELXL-97.^{S1}

Crystal data for NTz2T-Me: C₂₀H₁₂N₄S₄, $M = 436.60$, red plate, $0.8 \times 0.5 \times 0.1$ mm³, *monoclinic*, space group *C2/c*, $a = 11.7955(15)$, $b = 8.5619(9)$, $c = 18.814(2)$ Å, $\beta = 106.7224(13)^\circ$, $V = 1819.7(4)$ Å³, $T =$

293 K, $Z=4$, $D_{\text{calc}}=1.594 \text{ g/cm}^3$, GOF = 0.745, reflections measured 6722, 2068 unique ($R_{\text{int}} = 0.0448$) which were used in all calculations. The final R_1 was 0.0398, and the final wR on F_2 was 0.1123 (all data). Crystal data for BTz2T-Me: $\text{C}_{16}\text{H}_{12}\text{N}_2\text{S}_3$, $M=328.47$, red needle, $0.8 \times 0.1 \times 0.1 \text{ mm}^3$, *orthorhombic*, space group *Pbca*, $a = 19.562(12)$, $b = 20.298(13)$, $c = 7.523(5) \text{ \AA}$, $V=2987(3) \text{ \AA}^3$, $T = 293 \text{ K}$, $Z = 8$, $D_{\text{calc}} = 1.461 \text{ g/cm}^3$, GOF = 0.946, reflections measured 20831, 3294 unique ($R_{\text{int}} = 0.0731$) which were used in all calculations. The final R_1 was 0.0599, and the final wR on F_2 was 0.1656 (all data).

Reference

(S1) SHELXS-97 and SHELXL-97: G. M. Sheldrick, Programs for the Determination and the Refinement of Crystal Structures. University of Goettingen, Germany, 1997.

Figure S1. GPC chromatograms of the polymers.

Figure S2. Calculated HOMOs and LUMOs of the model compounds of PNTz4T and PBTz4T.

Figure S3. Transistor properties of the polymer-based devices with the HMDS-modified substrate: (a) transfer and (b) output curves of PNTz4T-device, (c) transfer and (b) output curves of PBTz4T-device.

Figure S4. Changes in mobility (μ) and on/off ratio ($I_{\text{on}}/I_{\text{off}}$) with time.

Figure S5. J-V curves of (a) PNTz4T- and (b) PBTz4T-based solar cells with different p:n ratios.

(a)

(b)

Figure S6. AFM topographic images of the polymer thin films on FDTS-modified OFET devices;

(a) PNTz4T, (b) PBTz4T.

(a)

(b)

Figure S7. AFM topographic images of the polymer/PC₆₁BM thin films on solar cells;

(a) PNTz4T, (b) PBTz4T.