Supporting Information

Benzobisthiadiazole-based conjugated donor-acceptor polymers for organic thin film transistors: effects of π -conjugated bridges on ambipolar transport

Yang Wang, Tomofumi Kadoya, Lei Wang, Teruaki Hayakawa, Masatoshi Tokita, Takehiko Mori and Tsuyoshi Michinobu*

Department of Organic and Polymeric Materials, Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8552, Japan

*Corresponding address: Tsuyoshi Michinobu Tel/Fax: +81-3-5734-3774, E-mail: michinobu.t.aa@m.titech.ac.jp



Fig. S1 ¹H NMR spectrum of compound **1**.



Fig. S2 ¹³C NMR spectrum of compound **1**.



Fig. S3 ¹H NMR spectrum of compound 2.



Fig. S4 ¹³C NMR spectrum of compound **2**.



Fig. S5 ¹H NMR spectrum of compound **3**.



Fig. S6¹³C NMR spectrum of compound **3**.



Fig. S7 ¹H NMR spectrum of compound **4**.



Fig. S8 ¹³C NMR spectrum of compound 4.



Fig. S9 ¹H NMR spectrum of compound **5**.



Fig. S10 ¹³C NMR spectrum of compound **5**.



Fig. S11 ¹H NMR spectrum of PBBT-FT.



Fig. S12 ¹H NMR spectrum of PBBT-T-FT.



Fig. S13 ¹H NMR spectrum of PBBT-Tz-FT.



Fig. S14 (a) TGA of the polymers under nitrogen flow (50 mL min⁻¹) at the heating rate of 10 °C min⁻¹ and DSC curves of (b) PBBT-FT, (c) PBBT-T-FT, and (d) PBBT-Tz-FT. All the DSC curves are the second heating and cooling processes under nitrogen flow (50 mL min⁻¹) at the scan rate of 10 °C min⁻¹.



Fig. S15 Normalized absorption spectra of (a) PBBT-FT and (b) PBBT-T-FT in dilute CHCl₃, as-cast thin film, and annealed film at 150 °C for 30 min.



Fig. S16 (a) Current–voltage (*I–V*) characteristics of TFTs fabricated by spin-coating in air. Comparison of transfer characteristics for (a),(b) PBBT-FT; (c),(d) PBBT-T-FT; (e),(f) PBBT-Tz-FT films under optimized conditions stored in air (hole-enhancement operation with $V_{\rm DS}$ = -80 V and electron-enhancement operation with $V_{\rm DS}$ = 80 V; *L* = 100 µm and *W* = 1 mm).



Fig. S17 Tapping-mode AFM topography images (left: as-cast, right: after thermal annealing at 200 °C for 10 min) of the PBBT-T-FT films spin-cast from a chloroform solution. AFM size: $10 \times 10 \ \mu m^2$.



Fig. S18 Comparison of the TFT performances (a: average hole mobility values from 5 to 10 devices, b: average electron mobility values from 5 to 10 devices) of the devices fabricated in air and in a glove box under optimized conditions.



Fig. S19 Current–voltage (I-V) characteristics of TFTs fabricated by spin-coating in a glove box under optimized conditions. Transfer characteristics for PBBT-FT films (a: hole, b: electron), for PBBT-T-FT films (c: hole, d: electron), and for PBBT-Tz-FT films (e: hole, f: electron) at the carrier-enhancement operation with $V_{\rm DS} = -80$ and +80 V, respectively ($L = 100 \ \mu m$ and $W = 1 \ mm$, all the measurements were done under vacuum (10^{-4} - $10^{-5} \ mbar$)).

Polymer	$\mu_{\rm h} ({\rm cm}^2{\rm V}^{-1}{\rm s}^{-1})$	$\mu_{\rm e} ({\rm cm}^2{\rm V}^{-1}{\rm s}^{-1})$	$I_{\rm on}/I_{\rm off}$
PBBT-FT	$1.3 \times 10^{-1} (9.2 \times 10^{-2})$	$3.1 \times 10^{-3} (2.3 \times 10^{-3})$	$p:10^4-10^5; n:10^2-10^3$
One week	$1.0 \times 10^{-1} (5.9 \times 10^{-2})$	$2.6 \times 10^{-3} (2.0 \times 10^{-3})$	$p:10^4-10^5; n:10^1-10^2$
Two weeks	9.5×10 ⁻² (5.6×10 ⁻²)	$2.4 \times 10^{-3} (1.9 \times 10^{-3})$	p:10 ⁴ -10 ⁵ ; n:10 ² -10 ³
Four weeks	$9.0 \times 10^{-2} (5.5 \times 10^{-2})$	$2.1 \times 10^{-3} (1.6 \times 10^{-3})$	$p:10^4-10^5$; $n:10^1-10^2$
PBBT-T-FT	$6.5 \times 10^{-3} (4.8 \times 10^{-3})$	$1.2 \times 10^{-3} (8.3 \times 10^{-4})$	$p:10^2-10^3$; $n:10^1-10^2$
One week	$6.0 \times 10^{-3} (5.6 \times 10^{-3})$	$7.7 \times 10^{-4} (5.1 \times 10^{-4})$	$p:10^2-10^3$; $n:10^1-10^2$
Two weeks	4.8×10 ⁻³ (3.7×10 ⁻³)	$6.0 \times 10^{-4} (3.8 \times 10^{-4})$	$p:10^3-10^4$; $n:10^1-10^2$
Four weeks	$4.4 \times 10^{-3} (3.5 \times 10^{-3})$	$3.8 \times 10^{-4} (1.5 \times 10^{-4})$	$p:10^3-10^4; n:10^1-10^2$
PBBT-Tz-FT	$6.8 \times 10^{-3} (5.8 \times 10^{-3})$	$1.5 \times 10^{-2} (1.3 \times 10^{-2})$	$p:10^1-10^2$; $n:10^2-10^3$
One week	3.8×10 ⁻³ (2.0×10 ⁻³)	$1.6 \times 10^{-3} (1.4 \times 10^{-3})$	$p:10^2-10^3$; $n:10^3-10^4$
Two weeks	2.9×10 ⁻³ (1.9×10 ⁻³)	$6.8 \times 10^{-4} (4.1 \times 10^{-4})$	$p:10^2-10^3$; $n:10^2-10^3$
Four weeks	$1.7 \times 10^{-3} (1.3 \times 10^{-3})$	5.5×10 ⁻⁴ (3.0×10 ⁻⁴)	p:10 ² -10 ³ ; n:10 ² -10 ³

Table S1 Summary of TFT device performances stored in air

^a Maximum values of the hole/electron mobilities measured under vacuum $(10^{-4}-10^{-5} \text{ Pa})$. The average values are in parentheses (from 5 to 10 devices).