Electronic Supplementary Information (ESI)

**Polymorphism in 9,9-diarylfluorene-based organic semiconductors: influence on optoelectronic functions**

Jun Yun Kim, Takuma Yasuda, Yu Seok Yang, Naoki Matsumoto and Chihaya Adachi

\(^a\) Department of Applied Chemistry, Graduate School of Engineering, and Center for Organic Photonics and Electronics Research (OPERA), Kyushu University, Japan
\(^b\) International Institute for Carbon Neutral Energy Research (WPI-I2CNER), Kyushu University, Japan
\(^c\) PRESTO, Japan Science and Technology Agency (JST), Japan
\(^d\) Tosoh Corp., Nanyo Research Laboratory, Japan

E-mail: yasuda@cstf.kyushu-u.ac.jp; adachi@cstf.kyushu-u.ac.jp

Table of Contents:

Experimental details

- **Fig. S1** XRD patterns of SFPT films in the \(a\)-, \(b\)-, and \(c\)-phases.
- **Fig. S2** SCLC characteristics for hole-only devices based on BFPT films.
- **Fig. S3** VASE results for an as-deposited BFPT film.
- **Fig. S4** POM and AFM images of SFPT films in the \(a\)-, \(b\)-, and \(c\)-phases.
- **Fig. S5** ASE characteristics for an annealed SFPT film in the \(b\)-phase.
- **Fig. S6** Photoelectron yield spectra of SFPT and BFPT.
- **Fig. S7** Output and transfer characteristics of OFETs based on BFPT films.
- **Table S1** Summary of OFET properties of SFPT.
General.  $^1$H and $^{13}$C NMR spectra were recorded on a Bruker Avance III 500 spectrometer. Chemical shifts of $^1$H and $^{13}$C NMR signals were quoted to tetramethylsilane ($\delta = 0.00$) and CDCl$_3$ ($\delta = 77.0$) as internal standards. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were collected on a Bruker Daltonics Autoflex III spectrometer using dithranol as the matrix. Elemental analyses were carried out with a Yanaco MT-5 CHN corder. UV/Vis absorption and photoluminescence (PL) spectra were measured with a Shimadzu UV-2550 spectrometer and a Horiba Fluoromax-4 spectrophotometer, respectively. PL quantum yields were measured using an integration sphere system coupled with a photonic multichannel analyzer (Hamamatsu Photonics C9920-02, PMA-11). The HOMO energy levels were determined using a Riken-Keiki AC-3 ultraviolet photoelectron spectrometer. X-ray diffraction (XRD) patterns were obtained using a Rigaku Ultima IV diffractometer with CuK$\alpha$ radiation. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were performed on a Shimadzu DTG-60AH at a scanning rate of 10 °C min$^{-1}$ and a Netzsch DSC204 Phoenix calorimeter at a scanning rate of 5 °C min$^{-1}$, respectively, under N$_2$ atmosphere. AFM was performed using a JEOL JSPM-5400 scanning probe microscope with tapping-mode in air. X-ray crystallographic analysis was made on a Rigaku VariMax with a Saturn 724+ system with graphite monochromated MoK$\alpha$ radiation. The structures were solved by direct methods (SIR2008)$^1$ and refined by full-matrix least-square techniques based on $F^2$ (SHELXL-97).$^2$

Variable-angle spectroscopic ellipsometry (VASE). Thin films for the ellipsometry measurements were deposited onto Si (100) substrates, which were precleaned by detergent and organic solvents. VASE was performed using a fast spectroscopic ellipsometer (M-2000U, J. A. Woollam Co. Inc.). Seven different angles of the incident light from 45° to 75° with steps of 5° were used. At each angle, the experimental ellipsometric parameters $\Psi$ and $\Delta$ were obtained simultaneously in 1.6-nm steps from 245 to 1000 nm. The VASE data were analyzed using WVASE32 software.
**Amplified spontaneous emission (ASE) measurements.** Thin films of SFPT and BFPT (thickness = 100 nm) were deposited on glass substrates. The films were optically pumped using a N₂ gas laser (MNL200, Laser Technik) at a wavelength of 337 nm with a pulse width of 500 ps and a repetition rate of 20 Hz. The ASE measurements were conducted by focusing the excitation light with an irradiation area of 400 μm × 10 mm. A detector (PMA-11, Hamamatsu Photonics) to observe the photoluminescence spectra was located on the edge of the films.

**OFET device fabrication and measurements.** SFPT and BFPT were incorporated into OFETs with a bottom-gate and top-contact geometry. For all of the OFET devices, heavily doped n-type Si wafers with a thermally grown 300-nm-thick SiO₂ layer were used as substrates. The SiO₂/Si substrates were pretreated with a piranha solution at 90 °C for 0.5 h, and then copiously cleaned by sonication in deionized water, acetone, and isopropanol in that order. The SiO₂/Si surface was treated with a self-assembled monolayer of hexamethyldisilazane (HMDS) by thermal evaporation for 1 h in air. The organic semiconductor layer of SFPT and BFPT was thermally evaporated on the substrates under high vacuum conditions. The devices were completed by evaporating gold (thickness = 50 nm) through a shadow mask to define the source and drain electrodes with a channel length of 20–100 μm on top of the organic layer. The output and transfer characteristics of the OFETs were measured using an Agilent B1500A semiconductor parameter analyzer under ambient conditions at room temperature. Field-effect mobilities (μ_{FET}) of the OFET devices were calculated in the saturation regime using the following equation: \( I_D = (W/2L)\mu_{FET} C_i (V_G - V_{th})^2 \), where \( I_D \) is the source–drain current, \( W \) and \( L \) are channel width and length, respectively, \( C_i \) is the capacitance per unit area of the gate dielectric (11 nF/cm²), \( V_G \) is the gate voltage, and \( V_{th} \) is the threshold voltage.

**Materials and syntheses.** Commercially available reagents and solvents were used without further purification unless otherwise noted. All of the reactions were performed under an N₂ atmosphere in dry solvents. The synthetic routes for SFPT and BFPT are outlined in Scheme S1. 2,7-Dibromo-9,9'-spirobifluorene (1) and 2,7-dibromofluorenone (2) were purchased from TCI.
Scheme S1. Synthesis of SFPT and BFPT.

Synthesis of SFPT. To a mixture of 1 (2.00 g, 4.2 mmol) and 2-phenylthiophen-5-yl-boronic acid (1.82 g, 11.2 mmol) in dry THF (40 mL) were added Pd(PPh3)4 (0.30 g, 0.26 mmol) and aqueous Na2CO3 (2.0 M, 15 mL; Ar bubbled before use). The mixture was vigorously stirred under reflux for 48 h. After cooling to room temperature, the formed precipitate was collected by filtration and then washed with water and ethanol. The product was recrystallized from THF/methanol, and dried under vacuum to afford SFPT as a yellow solid (yield = 1.50 g, 56%). This compound was further purified by repetitive temperature-gradient sublimation before use. 1H NMR (500 MHz, CDCl3): δ 7.90 (d, J = 8.0 Hz, 2H), 7.84 (d, J = 8.0 Hz, 2H), 7.65 (dd, J = 7.5 Hz, 1.5 Hz, 2H), 7.54 (dd, J = 7.5 Hz, 1.0 Hz, 4H), 7.41 (d, J = 7.5 Hz, 2H), 7.33 (t, J = 7.5 Hz, 4H), 7.24 (t, J = 7.0 Hz, 2H), 7.16 (d, J = 4.0 Hz, 2H), 7.14 (t, J = 7.0 Hz, 2H), 7.11 (d, J = 4.0 Hz, 2H), 6.94 (d, J = 1.5 Hz, 2H), 6.82 (d, J = 7.5 Hz, 2H). 13C NMR (125 MHz, CDCl3): δ 149.97, 148.30, 143.50, 143.46, 141.82, 140.72, 134.22, 134.05, 128.85, 128.04, 127.93, 127.44, 125.61, 125.54, 124.26, 124.14, 123.85, 120.94, 120.44, 120.14, 65.99. MS (MALDI-TOF): m/z 633.37 [M+H]+. Anal. calcd (%) for C45H28S2: C 85.41, H 4.46; found: C 85.51, H 4.34.

Synthesis of 2,7-dibromo-9-biphenyl-9-hydroxyfluorene (3). 4-Biphenyl magnesium bromide was prepared from magnesium powders (694 mg, 28.6 mmol) 4-bromobiphenyl (6.15 g, 26.4 mmol) in dry THF (40 mL). The obtained Grignard solution was diluted with dry THF (50 mL), and 2 (7.51 g, 22.0 mmol) was then added into the solution. The mixture was refluxed for 5 h. After cooling to room temperature, the reaction mixture was quenched with an aqueous NH4Cl solution (10%). The organic layer was washed with brine and dried over anhydrous MgSO4. After filtration
and evaporation, the crude product was recrystallized from toluene to give 3 as pale yellow crystals (yield = 7.60 g, 70%). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.32-7.57 (m, 15H), 2.49 (s, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 151.82, 140.64, 140.51, 137.48, 132.45, 128.72, 128.39, 127.31, 127.26, 127.04, 125.66, 122.52, 121.53, 83.21.

Synthesis of 2,7-dibromo-9,9-bis(biphenyl)fluorene (4). To a mixture of 3 (1.60 g, 3.2 mmol), biphenyl (4.92 g, 32 mmol), and acetic acid (15 g) were added dropwise H$_2$SO$_4$ (0.94 g, 9.6 mmol) at room temperature. The mixture was stirred for 3 h at 80 °C. After cooling to room temperature, the reaction mixture was poured into a large amount of water. The formed precipitate was collected by filtration, washed with water and ethanol, and recrystallized from ethanol/THF to yield 4 as colorless crystals (1.20 g, 62%). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.23-7.63 (m, 24H).

Synthesis of BFPT. This compound was prepared in a fashion similar to SFPT, using 4 (2.00 g, 3.2 mmol), 2-phenylthiophen-5-yl-boronic acid (1.82 g, 8.9 mmol), and Pd(PPh$_3$)$_4$ (0.25 g, 0.22 mmol). The product was obtained as a yellow solid (yield = 1.60 g, 64%). This compound was further purified by repetitive temperature-gradient sublimation before use. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.79 (d, $J = 8.0$ Hz, 2H), 7.72 (d, $J = 1.5$ Hz, 2H), 7.68 (dd, $J = 8.0$ Hz, 1.5 Hz, 2H), 7.61 (dd, $J = 8.0$ Hz, 2.0 Hz, 4H), 7.56 (dd, $J = 8.0$ Hz, 2.0 Hz, 4H), 7.52 (dd, $J = 8.0$ Hz, 1.5 Hz, 4H), 7.25-7.42 (m, 26H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 145.69, 144.06, 143.84, 143.66, 140.73, 140.41, 137.67, 132.05, 131.40, 131.37, 131.34, 127.62, 127.59, 127.57, 126.40, 126.33, 126.27, 125.34, 122.45, 65.19. MS (MALDI-TOF): $m/z$ 787.75 [$M+H]^+$. Anal. calcd (%) for C$_{57}$H$_{38}$S$_2$: C 86.99, H 4.87; found: C 87.02, H 4.73.

References
**Fig. S1** XRD patterns of SFPT films in $a$-phase (bottom), $b$-phase (middle), and $c$-phase (top). Insets show (a) molecular length, (b) interlayer distance (1.84 nm) and tilted molecular orientation with respect to the substrate normal, calculated from XRD and X-ray crystallography data, and (c) crystal packing structure of SFPT.

**Fig. S2** Double logarithmic plots of $J$–$V$ characteristics of hole-only devices comprising ITO/MoO$_3$ (0.8 nm)/BFPT (300 nm)/MoO$_3$ (10 nm)/Al (70 nm). The solid lines represent the best fits to the SCLC model. The inset shows the electric-field dependence of hole mobility ($\mu_{SCLC}$) for the BFPT films before and after thermal treatment at 140 °C for 10 min.
**Fig. S3** Ordinary (solid lines) and extraordinary (dashed lines) extinction coefficients ($k_o$ and $k_e$) and refractive indices ($n_o$ and $n_e$) determined by VASE measurements for an as-deposited BFPT film.

**Fig. S4** POM (top panels) and AFM images (bottom panels) of SFPT films on Si/SiO$_2$ substrates: (a,d) at room temperature ($a$-phase) and after thermal treatment at (b,e) 140 °C ($b$-phase) and (c,f) 180 °C for 10 min ($c$-phase).
Fig. S5  (a) PL emission and ASE spectra of a 100-nm-thick SFPT film in the $b$-phase after thermal annealing at 140 °C for 10 min.  (b) Emission intensity and full width at half-maximum (FWHM) of PL as a function of excitation fluence.

Fig. S6  Photoelectron yield spectra of (a) SFPT and (b) BFPT.
Fig. S7  Output (left panels) and transfer characteristics (right panels) of OFETs based on SFPT films in (a,b) $a$-phase, (c,d) $b$-phase, and (e,f) $c$-phase. The insets show the optical microscopic images of the devices (scale bar = 100 μm).

Table S1  Summary of OFET properties of SFPT

<table>
<thead>
<tr>
<th>polymorph</th>
<th>orientation</th>
<th>$\mu_{\text{FET}}$ (cm$^2$/Vs)</th>
<th>$V_{\text{th}}$ a) (V)</th>
<th>$I_{\text{on}}/I_{\text{off}}$ b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$-phase</td>
<td>horizontal</td>
<td>$1.2 \times 10^{-3}$</td>
<td>$-57$</td>
<td>$10^4$</td>
</tr>
<tr>
<td>$b$-phase</td>
<td>random</td>
<td>$1.1 \times 10^{-4}$</td>
<td>$-64$</td>
<td>$10^4$</td>
</tr>
<tr>
<td>$c$-phase</td>
<td>crystalline</td>
<td>$3.7 \times 10^{-3}$</td>
<td>$-20$</td>
<td>$10^5$</td>
</tr>
</tbody>
</table>

a) Threshold voltage was determined by extrapolating the $|I_D|^{1/2}$ vs $V_G$ plot to $I_D = 0$
b) On/off ratio was determined from the $I_D$ at $V_G = 0$ V ($I_{\text{off}}$) and $V_G = -100$ V ($I_{\text{on}}$).