Supplementary Information

for

Bis[1]benzothieno[2,3-d:2',3'-d']anthra[1,2-b:5,6-b']dithiophene: synthesis, characterization, and application to organic field-effect transistors

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1. General.

Instrumentation

All the reactions were carried out under an Ar atmosphere using standard Schlenk techniques. Glassware was dried in an oven (130 °C) and heated under reduced pressure before use. For thin layer chromatography (TLC) analyses throughout this work, Merck precoated TLC plates (silica gel 60 F254, 0.25 mm) were used. Silica gel column chromatography was carried out using Silica gel 60 (spherical, 40-100 μm) from Kanto Chemicals Co., Ltd. NMR spectra (1H and 13C{1H}) were recorded on Varian INOVA-600 (600 MHz), Mercury-400 (400 MHz) and 300-NMR ASW (300 MHz) spectrometers. Chemical shifts (δ) are in parts per million relative to CDCl3 at 7.26 ppm for 1H and at 77.0 ppm for 13C{1H} NMR spectra. Infrared spectra were recorded on a Shimadzu IRPrestige-21 spectrophotometer and reported in wave numbers (cm⁻¹). HRMS were determined on a JEOL JMS-700 MStation. Dynamic force-mode atomic force microscopy (AFM) was carried out using an SPA 400-DFM (SII Nano Technologies). X-ray diffraction (XRD) was measured using a Smart Lab-Pro (Rigaku) with an X-ray wavelength of 1.5418 Å (CuKα source). Thermogravimetric analysis (TGA) was carried out at a heating rate of 10 °C/min from 25 °C to 600 °C under a nitrogen flow rate of 100 mL/min using a Thermo Plus TG8120 thermogravimetric analyzer (Rigaku Corp.). Differential scanning calorimetry (DSC) measurement was performed at the rate of 10 °C/min for both heating and cooling steps under a nitrogen flow using a SSC5200H (Seiko Instruments). Elemental analyses were carried out with a Perkin-Elmer 2400 CHN elemental analyzer.

Chemicals

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Benzo[b]thiophene (TCI), bromine (Kanto chemicals), n-butyllithium (TCI), ethyl thioglycolate (TCI), potassium carbonate (Nacalai Tesque), copper (I) oxide (Aldrich), 1,4-benzenedimethanol (TCI), acetic anhydride (Wako), iodine (Nacalai Tesque), orthoperiodic acid (Wako), pyridinium chlorochromate (TCI), trimethylsulfonium iodide (Aldrich), potassium hydroxide (Nacalai Tesque), and indium chloride (TCI) were used as received.
2. Experimental Procedures and Spectroscopic Data for New Compounds.

Benzo[\textit{b}]thieno[2,3-\textit{d}]thiophene (1), \cite{1} 2,5-diiodo-1,4-benzendicarboxaldehyde (2), \cite{2} 2,3-dibromobenzo[\textit{b}]thiophene (6), \cite{3} 3-bromobenzo[\textit{b}]thiophene-2-carboxaldehyde (7), \cite{1} ethyl benzo[\textit{b}]thieno[2,3-\textit{d}]thiophene-2-carboxylate (8), \cite{1} benzo[\textit{b}]thieno[2,3-\textit{d}]thiophene-2-carboxylic acid (9), \cite{1} 1,4-phenylenebis(methylene)diacetate (11), \cite{4} (2,5-diiodo-1,4-phenylene)bis(methylene)diacetate (12), \cite{4} (2,5-diiodo-1,4-phenylene)dimethanol (13) \cite{4} showed the identical spectra reported in the literature. Synthetic procedure of compound 1 and 2 are shown in Scheme S1 and S2.

Scheme S1. Synthetic procedure of benzo[\textit{b}]thieno[2,3-\textit{b}]thiophene (1)

\begin{center}
\begin{tikzpicture}
\node [draw] (1) {\textbf{5 \hspace{1cm} Br$_2$ (2 equiv)}};
\node [draw, below of=1, yshift=-1cm] (2) {\textbf{6 \hspace{1cm} 'BULI (1.2 equiv)}};
\node [draw, below of=2, yshift=-1cm] (3) {\textbf{7 \hspace{1cm} DMF (2.5 equiv)}};
\node [draw, below of=3, yshift=-1cm] (4) {\textbf{8 \hspace{1cm} NaOH (4 equiv)}};
\node [draw, below of=4, yshift=-1cm] (5) {\textbf{9 \hspace{1cm} CuO (10 mol \%)}};
\node [draw, below of=5, yshift=-1cm] (6) {\textbf{1 \hspace{1cm} quinoline reflux, 5 h \hspace{3cm} 94\%}};
\node [draw, above of=1, yshift=1cm] (7) {\textbf{5 \hspace{1cm} CHCl$_3$ 0\^\circ C \hspace{1cm} to \hspace{1cm} rt \hspace{1cm} 12 h \hspace{1cm} 97\%}};
\node [draw, above of=2, yshift=1cm] (8) {\textbf{6 \hspace{1cm} THF, 0\^\circ C \hspace{1cm} 30 min \hspace{1cm} 95\%}};
\node [draw, above of=3, yshift=1cm] (9) {\textbf{7 \hspace{1cm} -78 \^\circ C \hspace{1cm} to \hspace{1cm} rt \hspace{1cm} 2 h \hspace{1cm} 90\%}};
\node [draw, above of=4, yshift=1cm] (10) {\textbf{8 \hspace{1cm} ETOH, H$_2$O reflux, 4 h \hspace{1cm} 93\%}};
\node [draw, above of=5, yshift=1cm] (11) {\textbf{9 \hspace{1cm} CuO (10 mol \%)}};
\node [draw, above of=6, yshift=1cm] (12) {\textbf{1 \hspace{1cm} quinoline reflux, 5 h \hspace{1cm} 94\%}};
\end{tikzpicture}
\end{center}

Scheme S2. Synthetic procedure of 2,5-diiodo-1,4-benzendicarboxaldehyde (2)

\begin{center}
\begin{tikzpicture}
\node [draw] (1) {\textbf{10 \hspace{1cm} Ac$_2$O (1 equiv) pyridine (3 equiv) \hspace{1cm} THF, rt \hspace{1cm} overnight \hspace{1cm} 92\%}};
\node [draw, below of=1, yshift=-1cm] (2) {\textbf{11 \hspace{1cm} I$_2$ (0.8 equiv) H$_2$O reflux, 15 h \hspace{1cm} 64\%}};
\node [draw, below of=2, yshift=-1cm] (3) {\textbf{12 \hspace{1cm} PCC (4 equiv) \hspace{1cm} CH$_2$Cl$_2$ reflux, 5 h \hspace{1cm} 85\%}};
\node [draw, above of=1, yshift=1cm] (4) {\textbf{11 \hspace{1cm} Ac$_2$O \hspace{1cm} MeOH, reflux, 12 h \hspace{1cm} 91\%}};
\node [draw, above of=2, yshift=1cm] (5) {\textbf{12 \hspace{1cm} I$_2$ (0.5 equiv) H$_2$O reflux, 15 h \hspace{1cm} 64\%}};
\node [draw, above of=3, yshift=1cm] {\textbf{13 \hspace{1cm} PCC (4 equiv) \hspace{1cm} CH$_2$Cl$_2$ reflux, 5 h \hspace{1cm} 85\%}};
\end{tikzpicture}
\end{center}

\textbf{Synthesis of 2,5-Bis(benzo[\textit{b}]thieno[2,3-\textit{b}]thiophene-2-yl)benzendicarboxaldehyde (3)}

To a solution of benzo[\textit{b}]thieno[2,3-\textit{d}]thiophene (1) (95 mg, 0.5 mmol, 2 equiv) in anhydrous THF (10 mL) in a 20 mL of Schlenk tube under an argon atmosphere were added \textit{n}-butyllithium (1.6 M in hexane, 0.34 mL, 0.55 mmol, 2.2 equiv) at 0 \^\circ C and stirred for 40 minutes. Then, zinc chloride (1 M in THF, 0.55
mL, 0.55 mmol, 2.2 equiv) was added to the reaction mixture and allowed to warm at room temperature and
stirred for 1 h. 2,5-diodo-1,4-benzendicarboxaldehyde (2) (97 mg, 0.25 mmol, 1 equiv), Pd(dba)2 (14 mg,
0.025 mmol, 5 mol %), and [HPt-Bu3]BF4 (15 mg, 0.05 mmol, 10 mol %) were added at room temperature.
The resulting reaction mixture was stirred at reflux for 3 hours, quenched with water (5 mL), and the reaction
mixture was then poured into MeOH (200 mL) and filtered. The filter cake was rinsed with water (50 mL),
hexane (50 mL), and ethyl acetate (50 mL). Drying in vacuo afforded the titled product 3 (95 mg, 0.19
mmol, 74%) as a yellow solid.
Mp > 270 °C.
FT-IR (KBr, cm−1): 3101 (s), 3068 (s), 2922 (s), 2877 (s), 2853 (s), 2361 (m), 2343 (m), 1684 (w), 1444 (m),
1391 (m), 1287 (m), 1169 (m), 1153 (m), 812 (m), 738 (m), 719 (m).
1H NMR (600 MHz, CDCl3, rt): δ 7.45 (m, 6H), 7.92 (d, J = 7.8 Hz, 4H), 8.29 (s, 2H), 10.40 (s, 2H).
13C{1H} NMR (150 MHz, C2D4Cl2, 70 °C) was not obtained due to the poor solubility.
Anal. Calcd for C28H14O2S4: C, 65.86; H, 2.76%. Found: C, 65.68; H, 2.48%.

Synthesis of 2,2′-[2,5-Bis(benzo[b]thieno[2,3-d]thiophene-2-yl)-1,4-phenylene]bis(oxirane) (4).

To a solution of dialdehyde 3 (77 mg, 0.15 mmol, 1 equiv) in anhydrous acetonitrile (7.2 mL) in a 20 mL
of Schlenk tube under an argon atmosphere were added trimethylsulphonium iodide (73 mg, 0.36 mmol, 2.4
equiv) and powdered KOH (46 mg, 0.15 mmol, 5.5 equiv) at room temperature. The reaction mixture was
vigorous stirred at 60 °C for 3 h, quenched with water (10 mL), and the reaction mixture was then poured
into MeOH (200 mL) and filtered. The filter cake was rinsed with water (50 mL), and hexane (50 mL),
then drying in vacuo afforded the titled product 4 (71 mg, 0.13 mmol, 88%) as a yellow-green solid.
Mp > 270 °C.
FT-IR (KBr, cm−1): 2993 (s), 3960 (s), 2918 (s), 1281 (m), 1150 (m), 974 (s), 907 (s), 881 (m), 831 (m), 752
(w), 743 (w), 633 (m).
1H NMR (600 MHz, CDCl3, rt): δ 2.89 (dd, J = 5.4, 3 Hz, 1H), 2.95 (dd, J = 5.4, 3 Hz, 1H), 3.26-3.28 (m,
2H), 4.21 (t, J = 3 Hz, 2H), 7.38-7.46 (m, 6H), 7.60 (d, J = 1.2 Hz, 2H), 7.88 (t, J = 7.8 Hz, 4H).
13C{1H} NMR (150 MHz, CDCl3, rt): was not obtained due to the poor solubility.
Synthesis of Bis[1]benzothieno[2,3-d:2',3'-d']anthra[1,2-b:5,6-b']dithiophene (BBTADT).

To a solution of epoxide 4 (149 mg, 0.3 mmol, 1 equiv) in anhydrous 1,2-dichloroethane (30 mL) in a 50 mL of Schlenk tube under an argon atmosphere were added indium chloride (13 mg, 0.06 mmol, 20 mol %) at room temperature. The reaction mixture was stirred at 100 °C for 48 h, quenched with water (10 mL), and the reaction mixture was then poured into MeOH (200 mL) and filtered. The filter cake was rinsed with water (50 mL), hexane (50 mL), acetone (50 mL), and hot chloroform (50 mL). Drying in vacuo afforded the titled product (BBTADT) as a green solid, which was further purified by sublimation (source temperature, 380 °C under 10^{-3} Pa) to give analytically pure samples (49 mg, 0.1 mmol, 33%) as a yellow solid. Mp > 270 °C.

FT-IR (KBr, cm^{-1}): 3067 (s), 3048 (s), 3013 (s), 1445 (s), 1429 (s), 1341 (s), 1300 (s), 1288 (s), 1256 (s), 866 (w), 793 (m), 743 (w), 721 (m), 685 (s).

^1H NMR (300 MHz, CDCl3, rt) was not obtained due to the poor solubility.

^13C{^1H} NMR (150 MHz, CDCl3, rt): was not obtained due to the poor solubility.

Anal. Calcd for C\(_{30}\)H\(_{14}\)S\(_4\): C, 71.68; H, 2.81%. Found: C, 71.67; H, 2.60%.
3. Copies of $^1$H NMR Chart for the New Compounds

**Figure S1.** The $^1$H NMR spectrum of compound 3 (in CDCl$_3$).
**Figure S2.** The $^1$H NMR spectrum of compound 4 (in CDCl$_3$).
4. Calculation and OFET Device Fabrication

The molecular geometries were optimized using density functional theory (DFT) at the B3LYP/6-31G (d) level using Gaussian 09, Revision A. 02. Typical bottom-gate top-contact OFET devices were fabricated as follows. All processes, except for a substrate cleaning, were performed under a nitrogen atmosphere. A heavily doped $n$-Si wafer with 200 nm thick thermally grown SiO$_2$ ($C_i = 17.3$ nF cm$^{-2}$) as the dielectric layer was used as the substrate. The Si/SiO$_2$ substrates were carefully cleaned using ultrasonication with acetone and isopropanol for 10 min, respectively. After being dried, the substrates were irradiated by UV-O$_3$ for 20 min, and then treated with the solution of 0.1 M $n$-octyltrichlorosilane (OTS) in anhydrous toluene to form a self-assembled monolayer (SAM). The active layers were deposited on the treated substrate by vapor deposition at the rate of 0.1 Å/s. Thermal annealing was performed at 100, 150, and 200 °C for 30 minutes on the hotplate in glove box. After treatment, gold electrodes (50 nm thick) was deposited through a shadow mask on the top of the active layer under reduced pressure ($5 \times 10^{-5}$ Pa). The current-voltage characteristics of the OFET devices were measured at room temperature in air on a Keithley 6430 sub-femto ampere remote source meter combined with Keithley 2400 measure-source unit. Field-effect mobilities were calculated in the saturation regime of the $I_D$ using following equation,

$$I_D = \frac{WC_i}{2L} \mu (V_G-V_{th})^2$$

Where $C_i$ is the capacitance of the SiO$_2$ insulator. $I_D$ is the source-drain current, and $V_D$, $V_G$, and $V_{th}$ are the source-drain, gate, and threshold voltages, respectively. Current on/off ratio ($I_{on/off}$) was determined from a minimum $I_D$ at around $V_G = -60$ V. The parameters of all devices were collected from more than five different devices.
5. TGA and DSC measurements of BBTADT

Figure S3. (a) TGA and (b) DSC curves of BBTADT
6. Parameters on Morphology of BBTADT Thin Films

Figure S4. (a) Optimized molecular geometry of BBTADT using DFT method at the B3LYP/6-31G (d) level, and (b) Schematic images of molecular orientation.
7. References