Electronic Supplementary Information for:

A D-A-D swivel-cruciform oligothiophene based on 5,5'-bibenzothiadiazole

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Materials

Unless stated otherwise, starting materials were obtained from Aldrich or Acros and were used without further purification. THF and toluene was distilled from sodium benzophenone under nitrogen prior to use. 5,5'-Bibenzo[c][1,2,5]thiadiazole[1] and tributyl(5-(5-hexylthiophen-2-yl) thiophen-2-yl)stannane[2] were synthesized according to the literatures.

Characterization

The ^{1}H and ^{13}C NMR spectra were measured on a Bruker AVANCE 400 spectrometer. Mass spectra were measured on a GCT-MS micromass spectrometer using EI mode or on a Bruker Daltonics BIFLEX III MALDI-TOF Analyzer using MALDI mode. Elemental analyses were carried out using a FLASH EA1112 elemental analyzer. Solution (chloroform) and thin-film (on quartz substrate) UV-vis absorption spectra were recorded on a JASCO V-570 spectrophotometer. Solution ($CHCl_3$) and thin-film (on quartz substrate) emission spectra were collected on a Hitachi F-4500 spectrofluorophotometer. Electrochemical measurements were carried out under nitrogen on a deoxygenated solution of tetra-n-butylammonium hexafluorophosphate (0.1 M) in CH_2Cl_2 using a computer-controlled Zahner IM6e electrochemical workstation, a glassy-carbon working electrode, a platinum-wire auxiliary electrode, and an Ag/AgCl in 3M KCl reference electrode. Thermogravimetric analysis (TGA) measurements were performed on Shimadzu thermogravimetric analyzer (model DTG-60) under a nitrogen flow at a heating rate of 10 °C min^{-1}. DSC measurements were performed using an SII EXSAR6000 (DSC 6220) under a nitrogen atmosphere with a heating and cooling rate of 20 ^{o}C min^{-1}. XRD measurements were done on a RIGAKU RINT ultra X18SAXS-IP (Cu K$_a$: 1.5418 Å). All AFM images are captured by a Nano Navi II – Nano Cute from SII-Nanotechnology Inc. in tapping mode using a SiN cantilever (OMCL-AC200TS) with the spring constant of 200 N/m at 137.2 kHz from Olympus Co. Ltd.

Time-resolved microwave conductivity (TRMC) measurement

The nanosecond laser pulses from a Nd:YAG laser [third harmonic generation, THG (355 nm) from Spectra Physics, INDY-HG] have been used as excitation sources. The power density of the laser was set at 7.0 mW cm^{-2} (10 Hz). For time-resolved microwave conductivity (TRMC) measurements, the microwave frequency and power were set at ~ 9.1 GHz and 3 mW, respectively. Upon excitation to BBT-SC thin film (1.2 μm thick) on a quartz substrate cast from a 3 wt% chloroform solution, the TRMC signal picked up by a diode (rise time < 1 ns) is monitored by a Tektronix TDS 3032B digital oscilloscope. Transmittance of excitation light pulses at 355 nm for the film was measured by PE25 power meter of Ophir Optoronics Ltd. All of the above experiments were carried out at room temperature. The transient photoconductivity ($\Delta\sigma$) of the samples is related to the reflected microwave power ($\Delta P_r/P_r$) and sum of the mobilities of charge carriers via

$$\Delta\sigma = \frac{1}{A}\frac{\Delta P_r}{P_r}$$

$$\Delta\sigma = e\phi\Sigma\mu N$$

where A, e, ϕ, N, and $\Sigma\mu$ are the sensitivity factor, elementary charge of the electron, photo carrier generation yield (quantum efficiency), number of absorbed photons per unit volume, and sum of mobilities for negative and positive carriers, respectively. The details of the set of apparatus are described elsewhere.[3]

Determination of photo-carrier generation yield

Photo-current accumulation was carried out for BBT-SC thin solid film cast onto an Au interdigitated electrode with 5 μm gap. Excitation was carried out at 355 nm with the photon density of 9.1×10^{15} photons cm^{-2}, and under a variety of applied bias voltage, photo-current transients were accumulated directly by a Keithley 6514 electrometer, and by monitoring with Tektronix 3052B digital oscilloscope via an evolution with 10 kΩ terminate resistance.[4]

Transient absorption spectroscopy was performed under ambient conditions. The films (2.2 μm thick) of BBT-SC and BBT-SC with 3 wt% *N*,*N*'-bis(2,5-di-tert-butylphenyl)-3,4:9,10-perylenedicarboximide (PDI) were cast onto quartz substrate from a corresponding chloroform solution. The films were dried under vacuum for 1 h. Time-dependent absorption spectral changes were monitored by a Hamamatsu C7700 streak camera via a Hamamatsu C5094 spectrometer upon excitation with pulses from a Nd: YAG laser (Spectra Physics, INDY-HG). The excitation density was tuned at 2.2×10^{16} cm^{-2} photons per pulse. To correct a 2-dimensional time-wavelength correlation data of the transient absorption, the streak scope images were averaged over 2500 times.[5]

Fabrication and characterization of OFETs

Field-effect transistors based on BBT-SC films were fabricated in the top contact configuration at ambient atmosphere. Highly n-doped silicon and thermally grown silicon dioxide (500 nm) were used as back gate and gate dielectric, respectively. The substrates were cleaned with pure water, hot concentrated sulfuric acid-hydrogen peroxide solution (concentrated sulfuric acid/hydrogen peroxide = 2:1), pure water, and pure isopropyl alcohol. Solutions of BBT-SC in chlorobenzene were spin coated onto substrates to form thin films. The thin films were thermally annealed at 150 °C for 10 min under nitrogen. Gold contacts (25 nm) for source and drain electrodes were vacuum-deposited at a rate of 0.1 Å/s through a metal shadow mask that defined a series of transistor devices with a channel length (*L*) of 50 μm and a channel width (*W*) of 3 mm. The characterization was accomplished by keithley 4200 SCS with a micromanipulator 6150 probe station in a clean shielded box at ambient atmosphere. Then field-effect mobility was calculated from the standard equation for saturation region in metal-dioxide-semiconductor field effect transistors: $I_{DS} = (W/2L)\mu C_i(V_G - V_T)^2$, where I_{DS} is drain-source current, μ is field-effect mobility, W and L are the channel width and length, C_i is the capacitance per unit area of the dielectric layer (C_i = 7.5 nF cm^{-2}), V_G is the gate voltage and V_T is the threshold voltage.

Synthesis

4,4',7,7'-Tetrabromo-5,5'-bibenzo[c][1,2,5]thiadiazole: To a suspension of BBT (540 mg, 2 mmol) in 8 mL HBr aqueous solution was added Br_2 (4.8 g, 30 mmol) dissolved in 6 mL HBr aqueous solution slowly while stirring vigorously. After refluxing at 110 °C for 48 h, the mixture was cooled to room temperature, then poured into saturated $NaHSO_3$ aqueous solution. The precipitate was filtered, washed with water, and dried under vacuum. The crude product was purified by column chromatography on silica gel (CH_2Cl_2/hexanes = 3:1) to give a pale yellow solid (1.0 g, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (s, 2H). HRMS (EI): 585.6417 (calcd for $C_{12}H_2N_4S_2Br_4$, 585.6413). Anal. Calcd for $C_{12}H_2N_4S_2Br_4$: C, 24.60; H, 0.34; N, 9.56. Found: C, 24.36; H, 0.30; N, 9.70%.

4,4',7,7'-Tetra(2-hexylbithiophene-2'-yl)-5,5'-bibenzo[c][1,2,5]thiadiazole (BBT-SC): To a solution of 4,4',7,7'-tetrabromo-5,5'-bibenzo[c][1,2,5]thiadiazole (586 mg, 1 mmol) and tributyl(5-(5-hexylthiophen-2-yl)thiophen-2-yl)stannane (3.23 g, 6 mmol) in 15 mL anhydrous toluene was added $Pd(PPh_3)_4$ (115 mg, 0.1 mmol) under a N_2 atmosphere. The mixture was stirred at 110 °C for 48 h. After cooling to room temperature, a 10 mL aqueous solution of KF (5 g) was added and stirred for 2 h. The organic layer was extracted with CH_2Cl_2, and washed subsequently with 10% HCl aqueous solution and saturated $NaHCO_3$ aqueous solution. The extracts were dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was purified by column chromatography on silica gel (CH_2Cl_2/hexanes = 1:1) to give a black solid (320 mg, 25%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 2.8 Hz, 2H), 7.72 (s, 2H), 7.12 (d, *J* = 2.4 Hz, 2H), 7.09 (d, *J* = 2.8 Hz, 2H), 6.97 (d, *J* = 2.9 Hz, 2H), 6.87 (d, *J* = 2.4 Hz, 2H), 6.82 (d, *J* = 2.8 Hz, 2H), 6.65 (d, *J* = 2.4 Hz, 2H), 6.56 (d, *J* = 2.7 Hz, 2H), 2.80 (t, *J* = 7.5 Hz, 4H), 2.73 (t, *J* = 7.5 Hz, 4H), 1.71 (q, *J* = 6.8 Hz, 4H), 1.63 (q, *J* =7.3 Hz, 4H), 1.39～1.29 (m, 24H), 0.91 (t, *J* = 7.1 Hz, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.76, 151.70, 146.04, 145.87, 140.99, 139.76, 139.14, 136.80, 134.70, 134.54, 134.36, 131.37, 128.96, 128.85, 125.64, 124.96, 124.72, 124.62, 123.92, 123.84, 123.77, 122.96, 31.65, 30.29, 29.67, 29.00, 22.76, 14.15. MS (MALDI): 1263 (M^+). Anal. Calcd for $C_{68}H_{70}N_4S_{10}$: C, 64.62; H, 5,58; N, 4.43. Found: C, 64.29; H, 5.60; N, 4.42%.

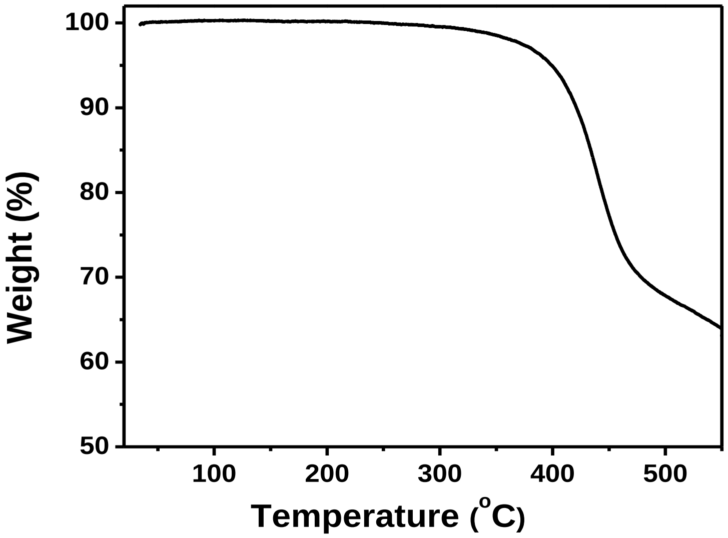

Figure S1. TGA curve of BBT-SC.

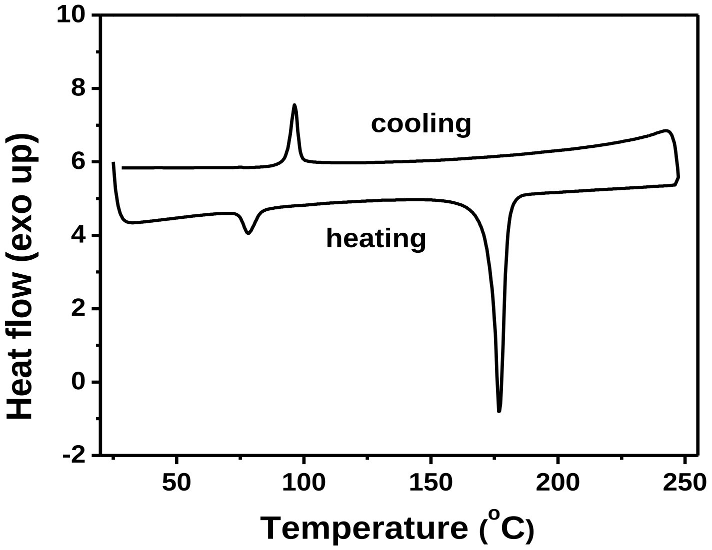

Figure S2. DSC curves of BBT-SC.

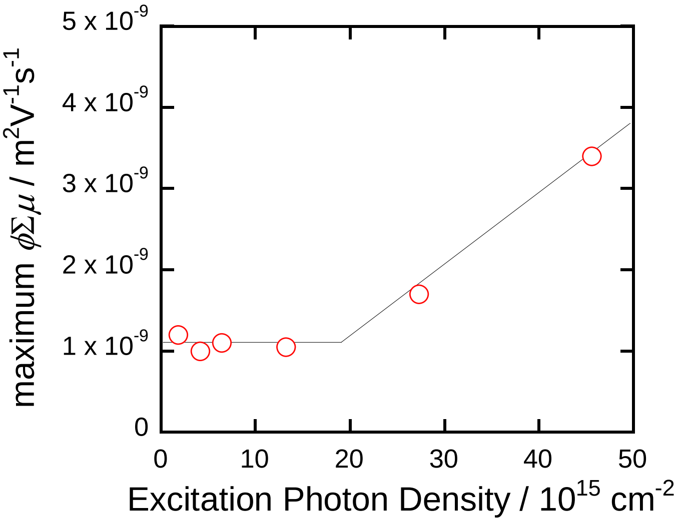

Figure S3. Dependence of observed maximum photoconductivity (maximum $\phi\Sigma\mu$ values in the conductivity transients) on excitation photon density.

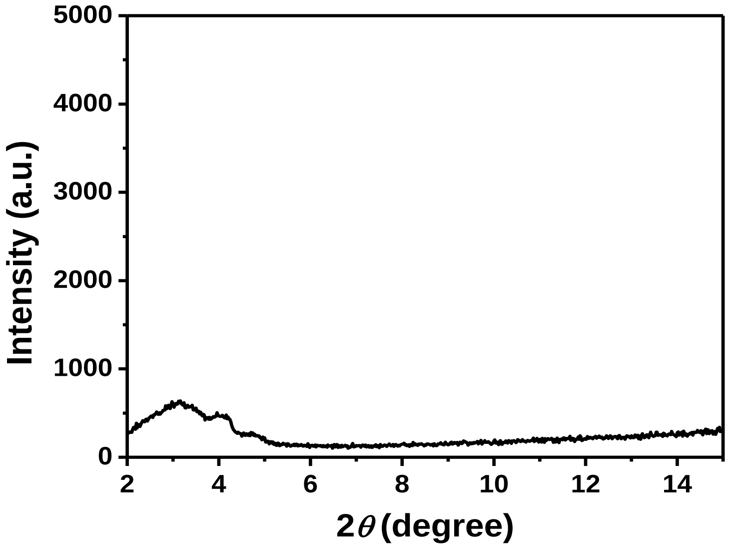

Figure S4. XRD pattern of BBT-SC film casted from a 1 wt% chloroform solution on a quartz substrate.

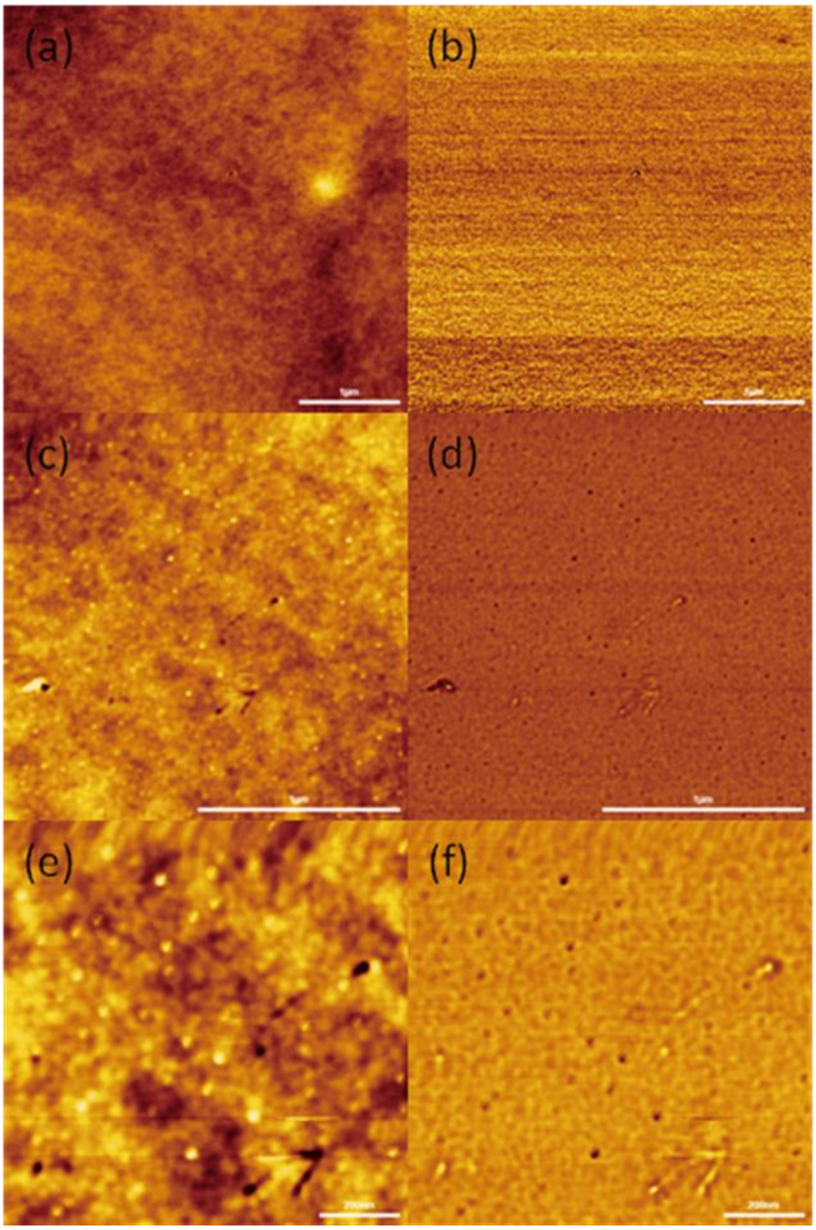

Figure S5. AFM images of a BBT-SC film casted on a quartz substrate (an identical film for XRD measurement). Images (a), (c), and (e) are topographic images with the color-height scale of 7.94, 5.03, and 2.81 nm, respectively. Images (b), (d), and (f) are the corresponding phase images of the film.

Reference and notes

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