

Supporting Information

α,ω -Distyryl-Oligothiophenes: High Mobility Semiconductors for Environmentally Stable Organic-Thin Film Transistors

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Syntheses of oligomers DS-nT (n = 2, 3, 4)

Materials. 5-Bromo-2-thiophenecarboxaldehyde, benzyltriphenylphosphonium bromide, bis(picolinato)diboron, [PdCl₂(dppf)] (dppf = 1,1'-bis(diphenylphosphino)ferrocene) and tetrakis(triphenylphosphine)palladium are commercially available. 5-Formyl-2,2'-bithiophene, 5-bromo-5''-formyl-2,2'-bithiophene and 2,2'-bis(tri-*n*-butylstannyl)thiophene were synthesized according to published procedures.^{1,2} NMR spectra were collected on a Bruker 250 MHz spectrometer. Mass spectra were recorded on a MALDI TOF Bruker Biflex III.

Syntheses. The synthesis of the oligomers is outlined in Scheme S1. The shorter compound, **DS-2T** was obtained in a one-step Wittig reaction from benzyltriphenylphosphonium bromide and 2,2'-bithienyl-5,5'-dicarboxaldehyde using lithium methoxide as a base as published elsewhere.³ The longer oligomers, **DS-3T** and **DS-4T**, were synthesized according to a stepwise procedure involving a combination of Wittig reactions to produce the precursors **2_m** (m = 1, 2) and palladium-catalyzed coupling reactions in the final steps. **DS-4T** was obtained in a one-pot reaction upon treatment of **2** with bis(picolinato)diboron in the presence of [PdCl₂(dppf)] according to a published procedure.⁴ All compounds, and especially the quaterthiophene-containing oligomer, **DS-4T**, are poorly soluble in organic solvents at room temperature. The new compounds were purified by repetitive Soxhlet extraction using successively heptane and toluene as solvents. They precipitated from the cooled toluene solution and were used in the electrochemical, spectroscopic and physical studies as obtained after filtration and extensive drying under vacuum. The structures were characterized by mass spectrometry and elemental analyses. In the case of the more soluble oligomers, **DS-2T** and **DS-3T**, ¹H NMR spectroscopy allowed to confirm the all-*trans* configuration of the double bonds. Owing to the poor solubility of **DS-4T**, no such direct evidence could be obtained from ¹H NMR. However, it is believed that the *trans* precursor, **2₂**, does not undergo any *cis/trans* isomerization under the palladium-catalyzed coupling conditions.

5-Bromo-5'-styryl-thiophene (2₁). To a solution of 5-bromo-2'-formyl-thiophene (5 g, 28.6 mmol) and benzyltri(phenyl)phosphonium bromide (12.4 g, 28.6 mmol) in 50 mL of anhydrous THF at room temperature was added dropwise a solution of lithium methoxide (0.24 g; 34 mmol)

in methanol (25 mL). The mixture was stirred for 3 h at room temperature. After addition of water to neutralize excess of MeOLi and evaporation of THF, the mixture was taken up with diethyl ether. The organic layer was washed with water and dried over MgSO₄. After the solvent was removed, the solid was chromatographed on silica gel eluting with dichloromethane to give 4.5 g of **2₁** as a brown solid (59 %). ¹H NMR (CDCl₃): δ 7.4-7.2 (m, 5H), 7.10 (d, 16.0 Hz, 1H), 6.94 (d, 3.8 Hz, 1H), 6.91 (d, 3.8 Hz, 1H), 6.88 (d, 3.8 Hz, 1H), 6.85 (d, 3.8 Hz, 1H), 6.83 (d, 16.0 Hz, 1H).

5,5'''-distyryl-terthiophene (DS-3T). A solution of compound **2₁** (0.265 g, 1 mmol) and 2,2'-bis(tri-*n*-butylstannyl)thiophene (0.331 g, 0.5 mmol) in DMF (15 mL) was thoroughly deaerated with argon prior to the addition of tetrakis(triphenylphosphine)palladium (12 mg, 0.01 mmol, 10 mol %). The reaction mixture was heated at 70 °C for one night under argon. The suspension was cooled down to room temperature. After filtration, the solid residue was washed with water and diethyl ether before it was subjected to two successive Soxhlet extractions using heptane (24 h) and toluene (72 h) as solvents. Cooling of the toluene solution afforded **DS-3T** as an orange-red microcrystalline solid which was used without further purification (353 mg, 78 %). F = 259 °C. ¹H NMR (THF): δ 7.05 (d, 16.0 Hz, 2H), 7.12 (d, 3.8 Hz, 2H), 7.22 (d, 3.8 Hz, 2H), 7.25 (s, 2H), 7.38 (d, 16.0 Hz, 2H), 7.6-7.2 (m, 10H). Anal. Calcd for C₃₂H₂₂S₄: C 74.30, H 4.45, S 21.25. Found: C 74.57, H 4.97, S 20.55. MS (MALDI-TOF) *m/z*: (M⁺) calcd for C₂₈H₂₀S₃, 452.07; found 452.07.

5-Bromo-5''-styryl-bithiophene (2₂). To a solution of 5-bromo-5''-formyl-2,2'-bithiophene (0.16 g, 0.59 mmol) and benzyltri(phenyl)phosphonium bromide (0.25 g, 0.59 mmol) in 10 mL of anhydrous DMF at room temperature was added dropwise a solution of lithium methoxide in methanol. The mixture was stirred for 1 h at room temperature. After addition of water, the mixture was extracted with chloroform. The organic layer was separated, washed with brine and dried over MgSO₄. After the solvent was removed, the solid was chromatographed on silica gel eluting with dichloromethane to give 0.13 g of **2₂** as a brown solid (63%). ¹H NMR (CDCl₃): δ 7.4-7.2 (m, 5H), 7.1 (d, 16.0 Hz, 1H), 6.94 (d, 3.8 Hz, 1H), 6.91 (d, 3.8 Hz, 1H), 6.88 (d, 3.8 Hz, 1H), 6.85 (d, 3.8 Hz, 1H), 6.83 (d, 16.0 Hz, 1H).

5,5''''-distyryl-quaterthiophene (DS-4T). A mixture of **2**₂ (0.167 g, 0.48 mmol), bis(picolinato)diboron (0.134 g, 0.53 mmol), potassium acetate (0.142 g, 1.4 mmol) and [PdCl₂(dppf)] (0.012 g, 0.014 mmol) in 10 mL of DMF were heated at 80 °C under argon for 2 h. To this mixture was added a degassed solution of **2**₂ (0.334 g, 0.96 mmol) and [PdCl₂(dppf)] (0.012 g, 0.014 mmol) in 10 mL of DMF and then a degassed solution of Na₂CO₃ (5 mg) in 1.2 mL of water. The reaction mixture was heated at 80 °C under argon for one night. After cooling and filtration, the solid residue was washed with water, and diethyl ether before it was subjected to two successive Soxhlet extractions using heptane (24 h) and toluene (72 h) as solvents. Cooling of the toluene solution afforded **DS-4T** as an orange microcrystalline solid which was used without further purification (115 mg, 45 %). F > 300 °C. Anal. Calcd for C₃₂H₂₂S₄.(1/3 toluene molecule): C 72.92, H 4.40, S 22.68. Found: C 72.88, H 4.46, S 22.65. MS (MALDI-TOF) *m/z*: (M⁺) calcd for C₃₂H₂₂S₄, 534.06; found 534.04.

Spectroscopic, electrochemical, and physical methods

Solution measurements. Uv-vis absorption and fluorescence emission spectra were obtained on a Varian Cary 1E spectrophotometer and a Varian Cary Eclipse spectrofluorimeter, respectively. Corrected emission spectra were obtained on diluted solution (CH_2Cl_2 , conc. $< 10^{-5}$ M) upon excitation at the absorption maximum wavelength. Cyclic voltammetry was performed using a BAS 100 Potentiostat (Bioanalytical Systems) operated with BAS 100W (v2.3) software. A three-electron setup based on a Pt working electrode (diameter 0.1 mm), a Pt counter electrode, and a Ag/AgCl (filled with 3 M NaCl) was used. Tetrabutylammonium hexafluorophosphate (TBAPF_6) was used as received as electrolyte (0.1 M). All experiments were carried out in *o*-dichlorobenzene at 50°C. Ferrocene used as internal standard.

OTFTs fabrication. The “top contact” configuration (Figure S1) was used for the OTFT devices based on **DS-nT** derivatives. Highly n-doped silicon wafers (gate), covered with thermally grown silicon oxide SiO_2 (3000 Å, insulator layer), were purchased from A.C.M (France) and used as device substrates. In order to change the surface property of the SiO_2 layer from hydrophilic to hydrophobic, SiO_2 -covered substrates were treated by immersion for several hours in a 1.5×10^{-1} M CH_2Cl_2 solution of hexamethyldisilazane (HMDS). The capacitance per unit area of either untreated or HMDS-modified silicon dioxide dielectric layers was $1.2\text{-}1.3 \times 10^{-8}$ F/cm². The semiconductor layer was then vacuum deposited onto the substrates, using a Edwards Auto 306 apparatus, at a rate of 4-7 nm/min under a pressure of $1\text{-}2 \times 10^{-6}$ mbar to a nominal thickness of 50 nm as determined with a in situ quartz crystal monitor. Substrate temperature (T_{sub}) during deposition was controlled by heating the block on which the substrates are mounted. The Au source and drain electrodes (channel length $L = 50$ μm, channel width $W = 1$ mm) were evaporated on top of the organic thin film through a shadow mask. Current-voltage characteristics were obtained at room temperature under ambient conditions with a Hewlett-Packard 4140B pico-amperemeter-DC voltage source. The source-drain current (I_{DS}) in the saturation regime is governed by the equation:

$$(I_{\text{DS}})_{\text{sat}} = WC_i\mu/2L (V_{\text{GS}} - V_t)^2 \quad (1)$$

where C_i is the capacitance per unit area of the gate insulator layer, V_{GS} is the gate voltage, V_t is the threshold voltage, and μ is the field-effect mobility. In the plot of $(|I_{\text{DS}}|)^{1/2}$ versus V_{GS} in the

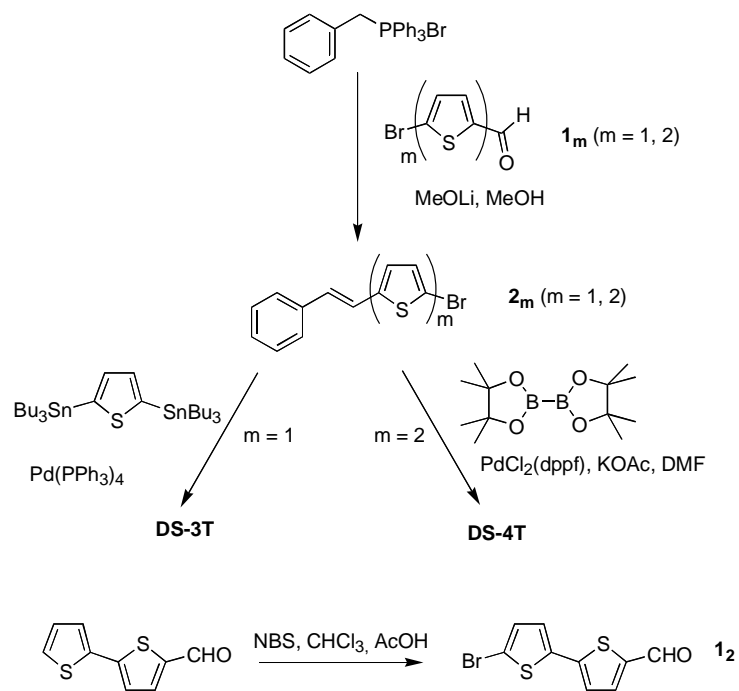
saturation regime, μ was calculated from the slope of the measured data while V_t was extracted from the extrapolation of the data at $I_{DS} = 0$. The on/off ratio values given in Tables 1 and S2 were determined from the current I_{DS} at $V_{GS} = -100$ V to the current I_{DS} at $V_{GS} = +100$ V under a constant drain-source voltage $V_{DS} = -30$ V. For comparison, Table S1 gives on/off ratio values between $V_{GS} = -100$ V and $V_{GS} = +10$ V. All the data in Table 1, Tables S1 and S2 were obtained by randomly measuring 10 individual OTFTs for each substrate temperature.

AFM characterization. Atomic force microscopy (AFM) measurements were done on thin films in air with a Nanoscope III Multimode (Instrument, Inc.), operating in the tapping mode.

X-Ray diffraction. Thin films of **DS-4T** were fabricated by vacuum deposition in a pressure of 5×10^{-5} Pa using K-cell type crucible. Si wafer (covered by SiO_2 layer 300 nm thick) was used as substrates which were kept at room temperature. The deposition rate and final film thickness were 0.1 nm/s and 100 nm, respectively. The as-deposited thin films were characterized using X-ray diffraction in air using an X-ray diffractometer (Regaku Co., ATX-G) which was specially designed for characterization of thin films. A parabolic multilayer positioned next to the laboratory X-ray source produces high intensity parallel beam ($\text{Cu K}\alpha$). The goniometer has not only usual $\omega/2\theta$ axes but also in-plane $\phi/2\theta\chi$ axes for measuring both in-plane and out of plane diffraction. The details of the diffractometer and characterization method were described elsewhere⁵.

References

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Scheme S1. Synthetic routes toward **DS-3T** and **DS-4T** oligomers.

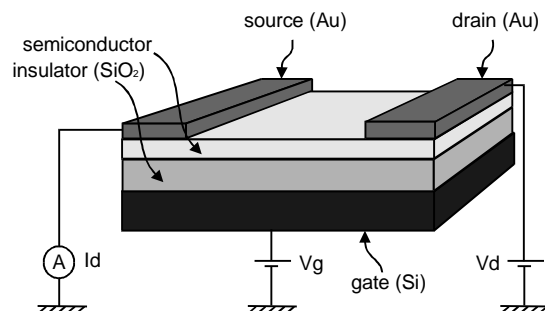


Figure S1. Schematic “top contact” configuration used for OTFT measurements.

Table S1. On-off ratio* at low V_{GS} of OTFTs based on **DS-nT** deposited at different substrate temperatures on silicon oxide layers.

Material	T_{sub} (°C)	on/off
DS-2T	30	$1.6\text{-}2 \times 10^4$
	80	$0.8\text{-}1 \times 10^4$
DS-3T	30	$1.3\text{-}1.8 \times 10^4$
	80	$5\text{-}8 \times 10^3$
DS-4T	30	$3\text{-}6 \times 10^2$
	80	$1.2\text{-}3 \times 10^2$
	110	$1\text{-}1.2 \times 10^3$
	140	$1.1\text{-}1.5 \times 10^3$

* The on/off ratio was determined from the current I_{DS} at $V_{GS} = -100$ V to the current I_{DS} at $V_{GS} = +10$ V at a drain-source voltage $V_{DS} = -40$ V.

Table S2. OTFT data of the semiconductors **DS-nT** deposited at different substrate temperatures on HMDS modified silicon oxide layers.

Material	T_{sub} (°C)	μ (cm ² /Vs)	on/off	V_t (V)
DS-2T	30	0.003-0.009	$1.5\text{-}3.3\times 10^5$	(-2)-(-7)
	80	0.01-0.02	$2.1\text{-}2.8\times 10^5$	(-1.2)-(-4)
DS-3T	30	0.005-0.007	$0.8\text{-}1.4\times 10^4$	(-2)-(-5)
	80	0.01-0.02	$2.2\text{-}3.3\times 10^4$	(-1)-(-3)
DS-4T	30	0.01-0.06	$2.2\text{-}3\times 10^2$	0.7-5
	80	0.06-0.08	$1.2\text{-}2.1\times 10^3$	2.5-5.5
	110	0.08-0.1	$1.7\text{-}2.4\times 10^3$	3-11
	140	0.04-0.06	$1\text{-}1.8\times 10^3$	5-10

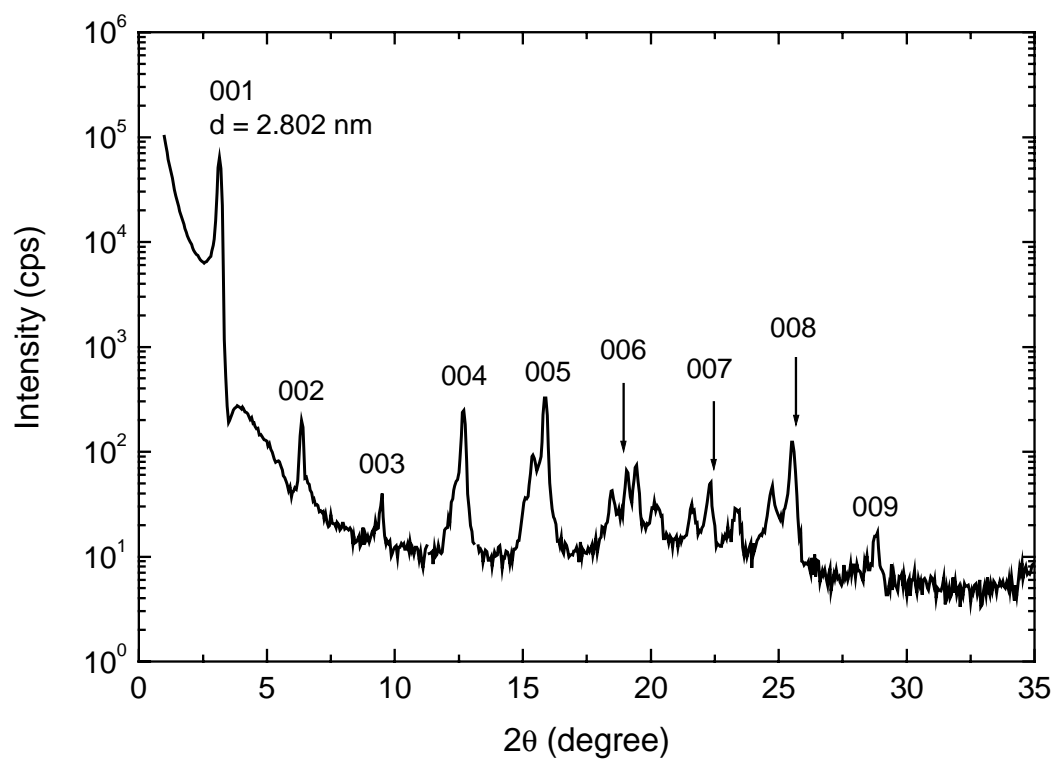


Figure S2. X-ray diffraction pattern of $\theta/2\theta$ scan of **DS-4T** films deposited onto SiO_2/Si substrates.