

Supporting information

Influence of Phenyl Perfluorination on Charge Transport Properties of Distyryl- Oligothiophenes in Organic Field-Effect Transistors.

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Experimental section

Synthesis: Methylenechloride, toluene, diethylether, tetrahydrofurane (THF), chloroform, cyclohexane, heptane were purchased from CarloErba and used as received. Tetrabutylammonium hexafluorophosphate (TBHP) was purchased from Fluka. Silica gel (240-400 mesh) was obtained from Merck. Tetrakis(triphenyl)phosphine palladium (0), bis(picolinato)diboron, palladium acetate (II), 2-carboxaldehyde-5-bromo-thiophene, were purchased from Sigma-Aldrich. 2',5'-di(tributylstannyl)-2,2'-bithiophene and 2,2'-bithienyl-2',5'-dicarboxaldehyde were prepared as described in the literature.^{1,2} Melting points are uncorrected and were obtained from an Electrothermal 9100 apparatus. ¹H NMR and ¹³C NMR spectra were recorded on Bruker AC 250 at respectively 250 MHz and 62.5 MHz.

From 2,2'-bithienyl-2',5'-dicarboxaldehyde, **DFS2T** was generated by Wittig olefination with pentafluorobenzyltri(phenyl)phosphonium bromide salt. **DFS4T** was obtained in two steps (Scheme 1). The first one is a Wittig olefination between commercial 2-carboxaldehyde-5-bromo-thiophene and pentafluorobenzyltri(phenyl)phosphonium bromide salt **1a** to give **2a**. The last step is a coupling between **2a** and 2',5'-di(tributylstannyl)-2,2'-bithiophene. **DFS4T** was purified by two successive Soxhlet extractions using heptane (24 h) and toluene (72 h) as solvents.

Pentafluorobenzyltri(phenyl)phosphonium bromide salt (1a). A mixture of pentafluorobenzylbromide (5.08 g, 19.50 mmol) and triphenylphosphine (5.62 g, 21.40 mmol) in toluene (30 mL) was refluxed during 20h. After cooling, the precipitate was filtered and washed with toluene and diethyl ether to give the title compound (10.08 g, 99%). Mp: 242-244°C. ¹H NMR (250 MHz, CDCl₃) δ: 5.65 (d, 2H, J = 14.00 Hz, CH₂-P), 7.60-8.00 (m, 15H, H_{phenyl}) ppm.

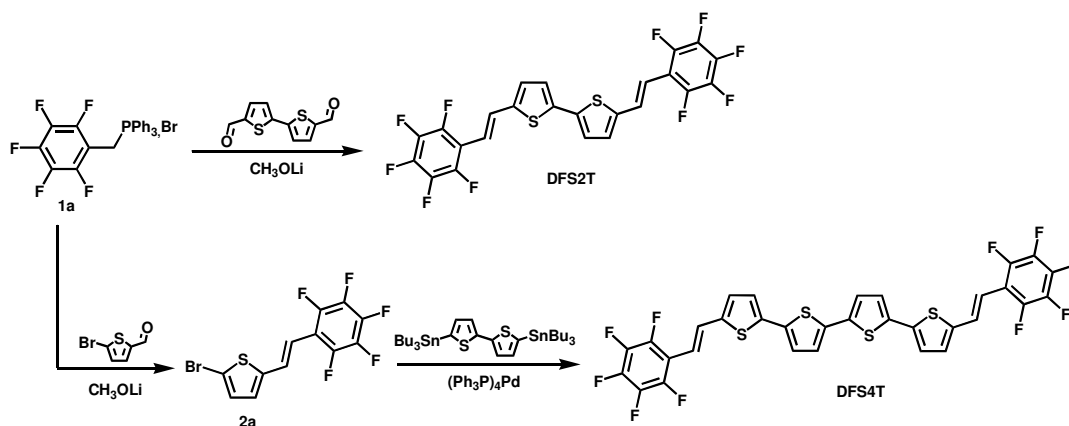
E,E-5,5'-bis(2-(pentafluorophenyl)-ethenyl)-2,2'-bithiophene (DFS2T). 2,2'-bithienyl-2',5'-dicarboxaldehyde (0.26 g, 1.15 mmol) and pentafluorobenzyltri(phenyl)phosphonium bromide salt **1a** (1.20 g, 2.30 mmol) were dissolved in 60 mL of anhydrous THF under argon. Lithium methoxide (3 mmol, 0.3 M in methanol solution) was added at 0°C and the reaction mixture was further stirred for 1h at room temperature. The solvent was evaporated in vacuum. The crude product was dissolved in methylenechloride and water was added. After extraction with methylenechloride, the combined organic phases were washed with water, dried over MgSO₄, and evaporated to dryness. The crude product was purified on a silica gel column, eluting with a methylenechloride/cyclohexane (1/4 v:v) solvent mixture to afford **DFS2T** as an orange solid (410 mg, 65% yield). Mp 224-226°C; ¹H NMR (250 MHz, CDCl₃) δ: 5.10 (d, 2H, J = 16.25 Hz, H_{eth}), 5.57(d, 2H, J = 4.00 Hz, H_{thio}), 5.53 (d, 2H, J = 4.00 Hz, H_{thio}), 5.82 (d, 2H, J = 16.25 Hz, H_{eth}) ppm. Elemental Analysis for C₂₄H₈F₁₀S₂ (1***DFS2T**/1*cyclohexane): calcd., C, 56.78; H, 3.18; F, 29.94; S, 10.11. Found: C, 55.82; H, 3.30; F, 30.49; S, 10.40.

5-bromo-2-(pentafluorophenyl)-ethenyl-thiophene (2a). Pentafluorobenzyltri(phenyl)phosphonium bromide salt **1a** (10.08 g, 19.30 mmol) and 5-bromo-2-thiophenecarboxaldehyde (3.87 g, 20.20 mmol) were dissolved in 60 mL of anhydrous tetrahydrofurane under argon. Lithium methoxide (12.6 mL, 0.3 M in methanol solution) was added dropwise. The mixture was stirred for 1h at room temperature and then water was added. The mixture was extracted with

methylenechloride. The combined organic phases were washed with water, dried over MgSO_4 , and evaporated in vacuum. The product was purified on a silica gel column, eluting with a mixture of chloroform and heptane mixture (5/95 v:v). Compound **2a** was obtained as a yellow solid (2.84 g, 41 %). Mp: 106-108°C; ^1H NMR (250 MHz, CDCl_3) δ : 6.62 (d, 1H, $J = 16.50$ Hz, H_{eth}) , 6.79 (d, 1H, $J = 4.00$ Hz, H_{thio}) , 6.89 (d, 1H, $J = 4.00$ Hz, H_{thio}) , 7.31 (d, 1H, $J = 15.75$ Hz, H_{eth}) ppm.

E,E-5,5''-bis(2-(pentafluorophenyl)-ethenyl)-2,2':5',2'':5'',2'''-quaterthiophene (DFS4T). A mixture of compound **1a** (1 g, 2.82 mmol), tetrakis(triphenylphosphine) palladium-bis(picolinato)diboron (16 mg, 0.013 mmol) and 5,5'-bis(tri-*n*-butylstannyl)-2,2'-dithiophene (1 g, 1.34 mmol) in 25 mL of DMF was degassed under argon for 15 minutes prior to heating at 80°C for 20h. After cooling and filtration, the solid residue was washed with water, heptane and diethylether before it was subjected to two successive Soxhlet extractions using heptane (24h) and toluene (72h) as solvents. Cooling of the toluene solution afforded the title compound as an orange microcrystalline powder which was filtered and used without further purification (490 mg, 51 %). Mp: 234-236°C; Solid ^{13}C NMR (400 MHz) δ : 140.8, 136.3, 131.3, 124.7, 111.5 ppm; Solid ^{19}F NMR (400 MHz) δ : -139.0, -143.2, -146.0, -156.0, -159.0 ppm; Elemental Analysis for $\text{C}_{32}\text{H}_{12}\text{F}_{10}\text{S}_4$ (2***DFS4T**/3*toluene): calcd C, 59.85; H, 2.84; F, 22.28; S, 15.04; found: C, 59.81; H, 2.81; F, 21.26; S, 15.00.

Synthetic scheme for the **DFS_nT** oligomers.



- [1] Wei T.; Yang Y.; Yeh J.-M ., *Chem. Mater.* **1996**, 8, 2659.
 [2] Curtis R.F.; Phillips G.Y., *Tetrahedron* **1967**, 23, 4419.

Film characterizations: Atomic force microscopy (AFM) measurements were done on thin films in air with a Nanoscope III Multimode (Instrument, Inc.), operating in the tapping mode. Scanning electronic microscopy (SEM) pictures were realized by a JEOL field emission gun scanning electron microscope (FEG-SEM, model JSM 6320F). Furthermore, thin films were analyzed by X-ray film diffractometry (XRD) where thin films of **DFS_nT** were fabricated by vacuum deposition in a pressure of 5×10^{-5} Pa using K-cell type crucible. Si wafer (covered by SiO₂ layer 300 nm thick) was used as substrates which were kept at room temperature. The deposition rate and final film thickness were 6 nm/min 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. The used wavelength of X-ray in the experiments was 0.1542 nm.

OTFTs fabrication: The “top-contact” configuration was used for the OTFT devices based on **DFS2T** and **DFS4T** derivatives. Highly n-doped silicon wafers (gate), covered with thermally grown silicon oxide SiO₂ (3000 Å, insulating layer), were purchased from A.C.M. (France) or Vegatec (France) and used as device substrates. Hexamethyldisilazane (HMDS) treatment was carried out by immersing the Si/SiO₂ in a pure solution HMDS at room temperature overnight. 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. A second “top-contact” configuration was used for the OTFT devices. It comprises a glass substrate, onto which the gate electrode (aluminum, Al) was first evaporated. The insulating layer is made of spin-coated polymethylmethacrylate (PMMA) with a capacitance per unit area of 8×10^{-9} F/cm². The semiconductor layer was then vacuum deposited onto the insulating layers, using an 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 an 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 with a Hewlett-Packard 4140B pico-amperemeter-DC voltage source at room temperature in air and/or under moderate vacuum (270-300 mTorr). The source-drain current (I_D) in the saturation regime is governed by the equation:

$$(I_D)_{\text{sat}} = (W/2L) C_i \mu (V_G - V_t)^2 \quad (1)$$

where C_i is the capacitance per unit area of the gate insulator layer, V_G is the gate voltage, V_t is the threshold voltage, and μ is the field-effect mobility. The on/off ratio values given in Table 1 were determined from the current I_D at $V_G = -100$ V to the current I_D at $V_G = +100$ V under a constant drain-source voltage $V_D = -30$ V. All the data in Table 1 were obtained by randomly measuring 5-7 individual OTFTs for each substrate temperature.

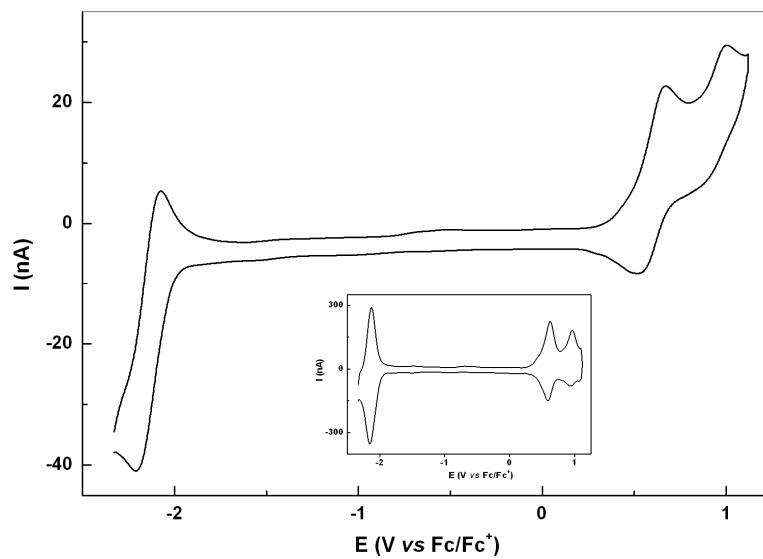
Physicochemical measurements in solution: UV-visible absorption and fluorescence emission spectra were obtained on a Varian Cary 1E spectrophotometer and a Varian Cary Eclipse spectrofluorimeter, respectively. Corrected emission spectra were obtained on diluted solution (CH₂Cl₂, conc. $< 10^{-5}$ M) upon excitation at the absorption maximum wavelength.

Cyclic voltammetric (CV) data were acquired using a BAS 100 Potentiostat (Bioanalytical Systems) and a PC computer containing BAS100W software (v2.3). A three-electrode system based on a platinum (Pt) working electrode (diameter 1.6 mm),

a Pt counter electrode and an Ag/AgCl (with 3 M NaCl filling solution) reference electrode was used. Tetrabutylammonium hexafluorophosphate (TBHP) (Fluka) was used as received and served as supporting electrolyte (0.1 M). All experiments were carried out in anhydrous 1,2-dichlorobenzene (electronic grade purity) at 20°C. $E_{1/2}$ values are determined from the cyclic voltammogram at a concentration of $1 \times 10^{-3} \text{ M}$ with a scan rate of 50 mV.s^{-1} . Ferrocene was used as internal standard.

Figure S1: Cyclic voltammograms for **DFS2T** (a) and **DFS4T** (b) at 1.10^{-3}M in 10^{-1}M Bu_4NPF_6 /1,2-dichlorobenzene. Insert cyclic voltammogram deconvoluted.

(a)



(b)

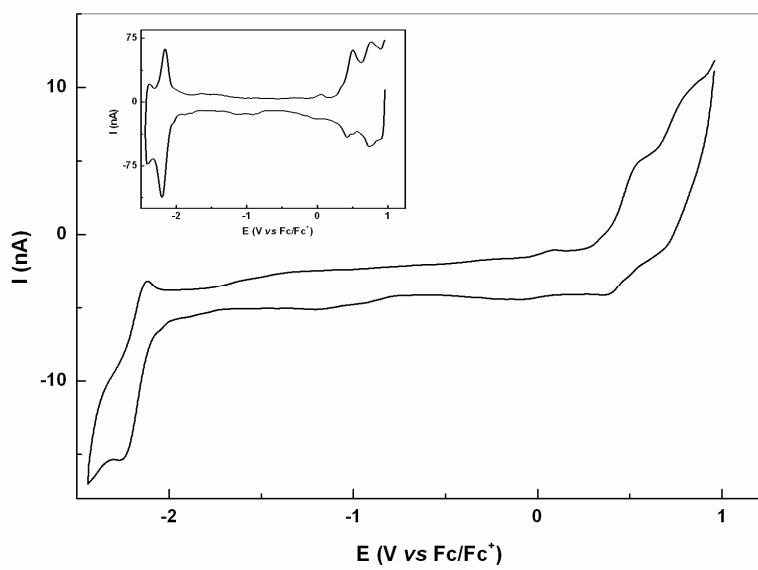
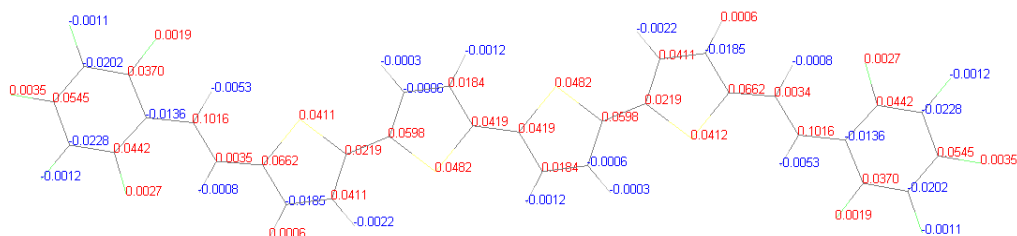
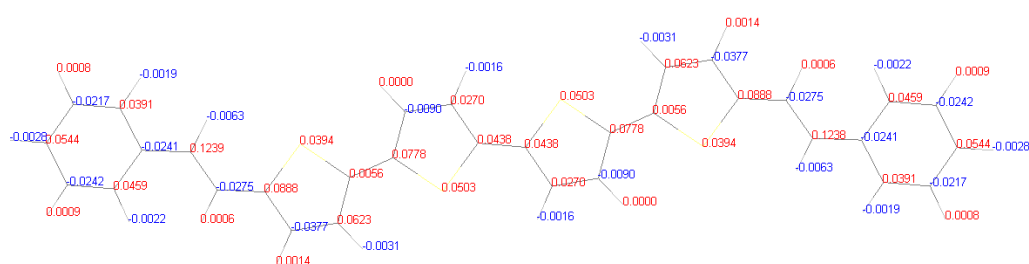


Figure S2: Spin density, alpha and beta contribution, per atom for **DFS4T**, **DS4T**, **DFS2T**, **DS2T**, **DF-4T** and **D-4T**.

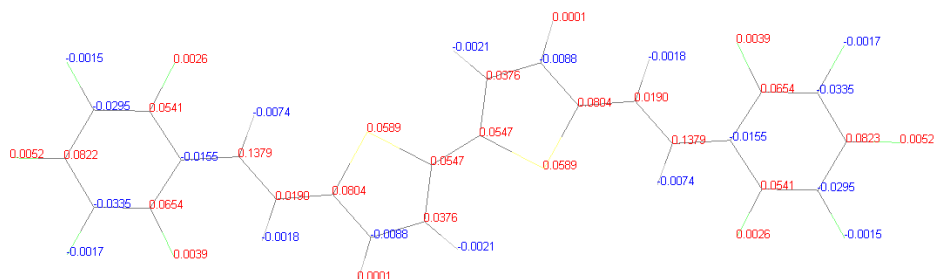
DFS4T



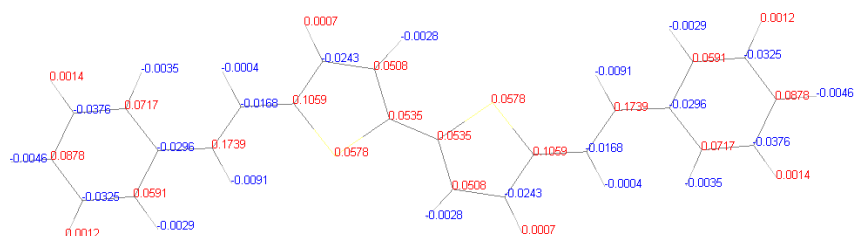
DS4T

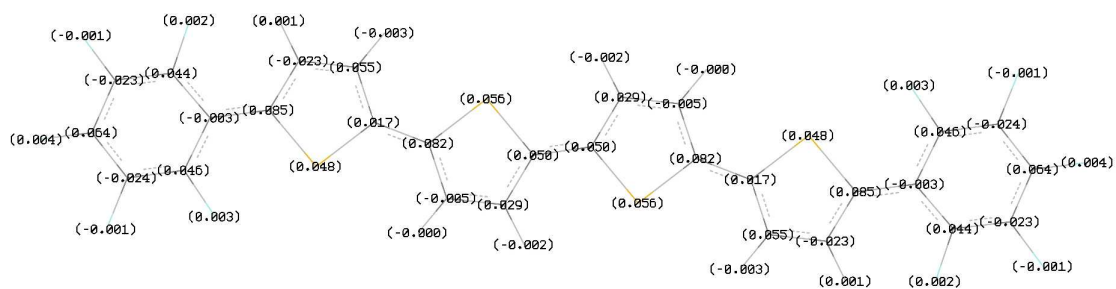


DFS2T



DS2T



DF-4T

D-4T

