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SUPPLEMENTARY INFORMATION

Push-pull thiophene-based *small molecules* with donor and acceptor units of varying strength for photovoltaic application: beyond P3HT and PCBM.

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I. Methods

Synthesis & characterization. TLC was carried out with 0.2-mm thick of silica gel 60 F_{254} (Sigma). Preparative column chromatographies were carried out on glass columns with silica gel 60 (particle sizes 0.040-0.063 mm, Sigma). 3-hexylthiophene, 4,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[c][1,2,5]thiadiazole, 2,5-dibromothiophene, *N*-bromosuccinimide (NBS), *n*-butyllithium 2.5 M solution in hexane, tributyltin chloride, 3,4-thiophenedicarboxylic acid, acetic anhydride, hexan-1-amine, thionyl chloride, $NaHCO_3$, glacial CH_3COOH, CF_3COOH, H_2O_2 30% wt, tetrakis(triphenylphosphine)palladium(0) $Pd(PPh_3)_4$, [1,1′-Bis(diphenylphosphino)ferrocene] dichloropalladium(II) $Pd(dppf)Cl_2$ were purchased from Sigma-Aldrich Co. All reagents and solvents were used as received. Organic solvents were dried by standard procedures. Microwave experiments were carried out in a CEM Discover SP-Microwave Synthesizer reactor in a closed vessel (230W, fixed temperature at 80 °C, air, high stirring rate). Reactions with ultrasound were performed in a FALC LBS1 50KHz Ultrasonic bath at room temperature. All ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Mercury-400/500 spectrometer equipped with a 5-mm probe. Chemical shifts were calibrated using the internal $CDCl_3$ resonance, which were referenced to TMS. Mass spectra were collected on a Thermo Scientific TRACE 1300 gas chromatograph. Thermogravimetric analysis (TGA) of the heptamers was carried out by a TGA TA Instruments Q600 apparatus operating under nitrogen atmosphere, in the 25–600 °C temperature range at a heating scan rate of 10 °C min^{-1}. Differential scanning calorimetry (DSC) was performed under nitrogen on a DSC TA Instruments Q2000, operating in the -50 to 200 °C temperature range at a heating scan rate of 10 °C min^{-1}.

X-ray diffraction (XRD). WAXS patterns were obtained with CuKα radiation in reflection mode by means of an X'Pert PANalytical diffractometer equipped with a fast X'Celerator detector, step 0.05°, 100s /step. GIWAXS measurements were carried out with incidence angle set to 0.8°.

Density functional theory (DFT) calculations. DFT calculations were carried out using the B.01 revision of the Gaussian 16 program package,[1] in combination with the M06 global-hybrid meta-GGA exchange-correlation functional and, for some single-point TD-DFT calculations, its M06-2X version,[2-3] which has been specifically designed to work well with charge-transfer excitations having intermediate spatial overlap.[4] The Pople 6-31+G(d) basis set was adopted for all atoms unless otherwise stated.[5] The polarizable continuum model (PCM) was employed to take into account dichloromethane solvation effects.[6-8] TD-DFT calculations were used to compute Franck-Condon excitations and to fully optimize the lowest-energy excited state (S_1) of all the molecules.[9-11] The nature of the computed transitions with multiconfigurational character was assessed with the help of natural transition orbital (NTO) analysis.[12] All molecules were investigated within the C_2 or C_s symmetry point group and analytical frequency calculations were always carried out to confirm the nature of the minima found on the potential energy surfaces of both S_0 and S_1. All the pictures of molecular orbitals and density surfaces were created using GaussView 6.[13]

Photophysical characterization. UV–Vis absorption spectra were recorded at room temperature on a Perkin-Elmer Lambda 19 spectrophotometer in the 300–800 nm spectral region on CH_2Cl_2 solutions in 1 cm quartz cells. Solid thin film measurements were made on heptamers, alone or blended with PCBM/P3HT, casted from CH_2Cl_2/chlorobenzene solutions on quartz slides by the doctor-blade technique. Emission spectra of solutions and thin films on glass were recorded on a Perkin Elmer LS50B fluorescence spectrofluorometer. Emission lifetime measurements were performed on a Edinburgh FLS920 spectrofluorimeter equipped with a TCC900 card for data acquisition in time-correlated single-photon counting experiments (0.5 ns time resolution) with a LDH-P-C-405 pulsed diode laser. Longer lifetimes were measured by the PerkinElmer LS-50.

Cyclic Voltammetry (CV). Electrochemical experiments were performed by using an electrochemical system AMEL model 5000 in a three-compartment electrochemical cell, carefully purged with Ar, with an aqueous Satured Calomel reference Electorde (SCE) and a Pt wire auxiliary electrode in the same solution of the working electrode separated by glass frits. CVs of the heptamers, in solution 1 mmol L^{-1} carefully purged with Ar, were performed by an electrochemical system AMEL model 5000 at scan rates from 0.20 to 0.01 V s^{-1} and potential range -1.8 to 1.5 V vs. SCE in a three compartment electrochemical cell with Pt disk working electrode (diameter 1 mm) and Pt wire auxiliary electrode. For reversible and quasi-reversible waves, redox potential was evaluated as the average of direct and related reverse peak potential, when the voltammetric waves were irreversible, the half-wave potentials have been reported. HOMO and LUMO energy levels were evaluated according to reference [14]. The solvent was CH_2Cl_2 distilled over P_2O_5 and stored under Ar pressure. Supporting electrolyte was 1 mol L^{-1} $(C_4H_9)_4NClO_4$ recrystallized from CH_3OH and stored in a dryer filed with Cs_2Cl_2 under reduced pressure. In CH_2Cl_2 0.1 mol L^{-1} $(C_4H_9)_4NClO_4$, ferricinium/ferrocene potential is 0.47 vs. SCE. The thin films were drop casted on Indium Tin Oxide (Kintec 20 Ω/square, coverage 12 x 12 mm) and their CVs were performed in propylene carbonate (PC) 0.1 mol L^{-1} $(C_2H_5)_4NBF_4$ at scan rates 0.10 V s^{-1}.[15] PC (Sigma-Aldrich, anhydrous 99.7%) was used as received, $(C_2H_5)_4NBF_4$ (Sigma-Aldric for electrochemical analysis $\geq$ 99%) was used after storage in $CaCl_2$ dryer under reduced pressure. In PC 0,1mol L^{-1} $(C_2H_5)_4NBF_4$, ferricinium/ferrocene potential is 0.50 vs. SCE.

Atomic Force Microscopy (AFM), Kelvin Probe Force Microscopy (KPFM). AFM and KPFM measurements were obtained in air by employing a commercial microscope Multimode 8 (Bruker). We employed (k = 3 N/m) Pt/Ir coated cantilever silicon tips (Bruker) with oscillating frequencies in the range between 60-90 KHz. AFM and KPFM images are acquired in the same measurement: a topographic line scan is first obtained by AFM operating in Tapping Mode and then that same line is rescanned in Lift Mode with the tip raised to a lift height of 50 nm using the Amplitude Modulation (FM) mode. KPFM provides a voltage resolution of about 10 mV, while the lateral resolution amounts to a few tens of nanometers. Samples were prepared according to the procedure employed for the device fabrication, connecting the ITO substrate to the instrument electrical ground.

Device fabrication. BHJ solar cells were prepared according to the following procedure: the Indium Tin Oxide (ITO) glass substrate (2 × 2 cm, surface resistance 21 Ω/sq) was etched on one side by using a 10% wt aqueous solution of HCl and heated at 60 °C for 15 min in order to obtain an area of 1.5 × 1 cm covered by ITO. The glass was then rinsed with distilled water, 2-propanol and dried with a nitrogen flow. The final resistance of the ITO glass was 12 Ω/sq. Poly(3,4-ethylenedioxythiophene):polystyrene sulfonic acid (PEDOT:PSS, 2.8 wt% dispersion in water, viscosity 20 cps) was diluted 1:1 v/v with 2-propanol, sonicated for 15 min using an ultrasonic bath (Elmasonic S 30H), filtered on a Gooch G2 and the resulting solution (viscosity 12 cps) deposited over the previously treated ITO glass by the doctor blading technique using a Sheen Instrument Model S265674, leaving only a small (0.5 × 1 cm) area uncovered at the opposite side of the previously etched area. The PEDOT:PSS film was heated in a Buchi GKR-50 glass oven at 120 °C for 90 min under vacuum (10^{-3} mmHg). A solution made by mixing (i) 2.5 mg of **heptamer** and 2.5 mg of **PC$_{61}$BM** in 0.5 mL of chlorobenzene, (ii) 2.5 mg of **heptamer** and 2.5 mg of poly(3-hexylthiophene) (**P3HT**, HT 96%, Mn 30.0 kD, PDI 1.2, synthesized starting from 3-hexylthiophene through GRIM Method)[16] in 0.5 mL of chlorobenzene and (iii) 2.5 mg of **T7SBz-Bz$_2$** and 2.5 mg of **T7Bz-Dp$_2$** or **T7Bz-TSO$_2$** in 0.5 mL of chlorobenzene or THF, were sonicated for 15 min and deposited under ambient air conditions by doctor blading on the slide in order to cover the PEDOT:PSS layers. The active layers were then annealed in the glass oven under vacuum (10^{-3} mmHg) at 120 °C for 30 min. The Al electrode was finally deposited over the layer using an Edwards 6306A coating system operating at 10^{-6} mmHg. The prepared solar cells, having a final active area of 1.0 × 1.0 cm^2, were measured in air at room temperature using a Keithley 2401 source meter under the illumination of an Abet Technologies LS150 Xenon Arc Lamp Source AM 1.5 Solar Simulator (100 mW/cm^2) calibrated with an ILT 1400-BL photometer. The structure of the final devices was composed of: ITO (80 nm)/PEDOT:PSS (100 nm)/active layer (150 nm)/Al (50 nm). The solar cells spectral response was measured using a 7-SC Spec III Modularized Solar Cell Spectral Test System (SevenStar Optics, Beijing, PRC). Layer thickness were measured using a FTPAdvances FTPadv-2 Film Thickness Probe (Sentech GmbH, Germany) equipped with the FTPExpert software.

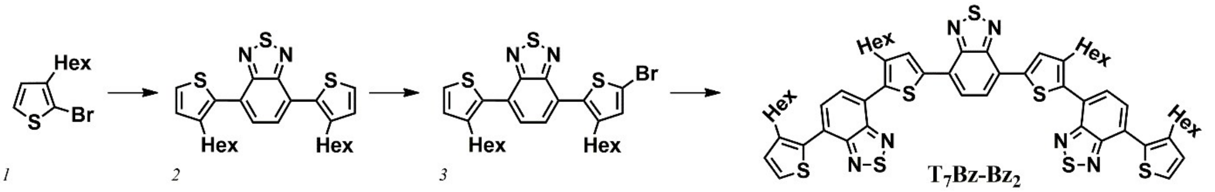
II. Synthesis of heptamers

General procedure for ultrasound-assisted bromination: to a stirring solution of thienyl derivative (1 mmol) in CH_2Cl_2 (≈ 10^{-3} M), 1 mmol NBS was added in small portions, under ultrasound irradiation, over a period of about 10-20 min. After completion the reaction mixture was extracted with CH_2Cl_2/H_2O and the combined organic phases were evaporated under reduce pressure.

General procedure for Stille cross-coupling: 2 mmol of bromide aryl derivative, 1 mmol of stannyl aryl derivative and 0.005 mmol of $Pd(PPh_3)_4$ were refluxed overnight in toluene at 110°C. The reaction mixture was extracted twice with CH_2Cl_2/H_2O and the solvent evaporated under reduced pressure.

General procedure for microwave-assisted Suzuki cross-coupling: 2 mmol of bromide thienyl derivative, 1 mmol of aryl boronic derivative, 6 mmol $NaHCO_3$, 0,01 mmol of $Pd(dppf)Cl_2$ were dissolved in 3 mL of THF/H_2O (2/1) and irradiated with microwave at 80°C for 25 min. After returning to room temperature the mixture was extracted with H_2O and the combined organic phases were evaporated under reduced pressure.

Scheme S1



2-bromo-3-hexylthiophene (1) → 3-hexythiophene (1 mmol) was dissolved in a CH_3COOH/CH_2Cl_2 (1:1) solution and 1 mmol of NBS was added in one way. The mixture was stirred overnight. The acetic acid was removed by extraction with a saturated solution of sodium bicarbonate and the combined organic phase were evaporated under reduced pressure. The residue was isolated by flash chromatography (Cyclohexane). Colorless oil. Yield: 98%. EI-MS *m/z* 246 (M^+). ^1H NMR (400 MHz, $CDCl_3$, TMS/ppm): δ 7.18 (d, J = 5.6, 1H), 6.80 (d, ^3J = 5.6, 1H), 2.58 (t, 2H), 1.61–1.55 (m, 2H), 1.41–1.32 (m, 6H), 0.91 (t, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS/ppm): δ 141.9, 128.2, 125.1, 108.8, 31.6, 29.7, 29.4, 28.9, 22.6, 14.1.

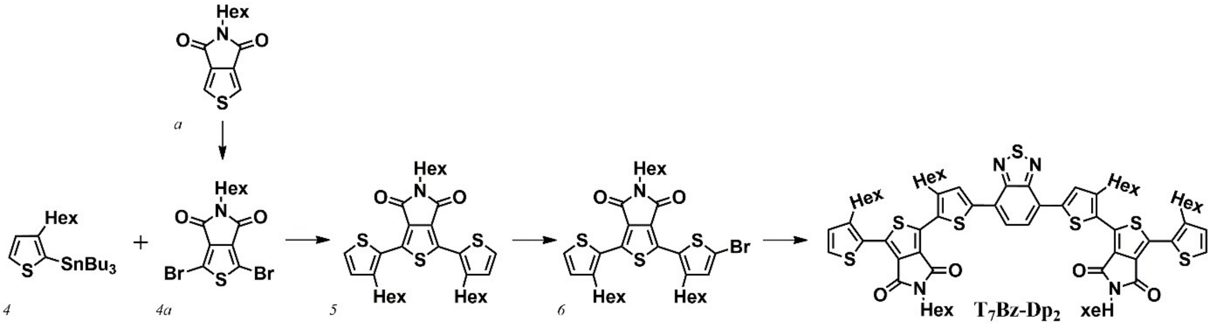
4,7-bis(3-hexylthiophen-2-yl)benzo[c][1,2,5]thiadiazole (2) → The compound was prepared following the general procedure for Suzuki Cross-coupling starting from **1** (2 mmol) and 4,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[c][1,2,5]thiadiazole (1 mmol). The residue was isolated by flash chromatography (Cyclohexane/CH_2Cl_2, 90:10). Pale yellow oil. Yield: 70%. EI-MS *m/z* 468 (M^+). ^1H NMR (400 MHz, $CDCl_3$, TMS/ppm): δ 7.65 (s, 2H), 7.44 (d, J = 5.2, 2H), 7.11 (d, J = 5.2, 2H), 2.67 (t, 4H), 1.66–1.56 (m, 4H), 1.31–1.17 (m, 12H), 0.82 (t, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS/ppm): δ 154.3, 141.7, 132.2, 129.9, 129.2, 127.4, 125.8, 31.5, 30.7, 29.3, 29.1, 22.5, 14.0.

4-(5-bromo-3-hexylthiophen-2-yl)-7-(3-hexylthiophen-2-yl)benzo[c][1,2,5]thiadiazole (3) → The compound was prepared following the general procedure for bromination starting from **2** (1 mmol) using 1 mmol of NBS. The residue was isolated by flash chromatography (Cyclohexane/CH_2Cl_2, 80/20). Yellow oil. Yield: 85%. EI-MS *m/z* 546 (M^+). ^1H NMR (400 MHz, $CDCl_3$, TMS/ppm): δ 7.62 (d, J = 7.2, 2H), 7.44 (d, J = 5.2, 1H), 7.10 (d, J = 5.2, 1H), 7.01 (s, 1H), 2.68-2.60 (m, 4H), 1.64–1.56 (m, 4H), 1.28–1.20 (m, 12H), 0.84-0.79 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$, TMS/ppm): δ 154.2, 153.9, 142.3, 141.8, 133.7, 131.99, 131.91, 129.8, 129.7, 129.2, 127.9, 129.1, 126.9, 31.6, 31.5, 30.6, 30.5, 29.4, 29.3, 29.1, 29.0, 22.5, 22.49, 14.0.

4,7-bis(4-hexyl-5-(7-(3-hexylthiophen-2-yl)benzo[c][1,2,5]thiadiazol-4-yl)thiophen-2-yl)benzo[c][1,2,5]thiadiazole (T_7Bz-Bz_2) → The compound was prepared following the general procedure for Suzuki Cross-coupling starting from **3** (2 mmol) and 4,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[c][1,2,5]thiadiazole (1 mmol). The residue was isolated by flash chromatography (Cyclohexane/CH_2Cl_2, 70:30). Red powder. Yield: 55%. EI-MS *m/z* 1068 (M^+). ^{1}H NMR (400 MHz, $CDCl_3$, TMS/ppm): δ 8.17 (s, 2H), 7.96 (s, 2H), 7.76 (d, J = 7.2, 2H), 7.69 (d, J = 7.2, 2H), 7.45 (d, J = 5.2, 2H), 7.12 (d, J = 5.2, 2H), 2.78 (t, 4H), 2.69 (t, 4H), 1.79–1.71 (m, 4H), 1.68–1.60 (m, 4H), 1.35–1.20 (m, 28H), 0.85-0.81 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS/ppm): δ 154.3, 154.1, 152.6, 142.8, 141.8, 139.5, 134.1, 132.1, 129.9, 129.8, 129.3, 127.7, 127.1, 125.9, 125.8, 125.5, 31.6, 31.5, 30.7, 29.7, 29.4, 29.2, 29.1, 22.6, 22.5, 14.0.

Scheme S2



(3-hexylthiophen-2-yl)trimethylstannane (4) → To a stirring solution of 2-bromo-3-hexylthiophene (1 mmol) in $THF_{(dry)}$ (10^{-2} M) at -78°C, *n*Buli (1 mmol) was added dropwise under nitrogen atmosphere. The resulting mixture was stirred for 1 hour, quenched with $Sn(Bu)_3Cl$ (1,1 mmol) and then stirred overnight. The reaction mixture was extracted with CH_2Cl_2/H_2O, the organic phases were combined and evaporated under reduced pressure. The crude product was used without further purifications. Brown oil. Yield: 95%. EI-MS *m/z* 332 (M^+). ^{1}H NMR (400 MHz, $CDCl_3$, TMS/ppm): δ 7.53 (d, J = 4.7, 1H), 7.10 (d, J = 4.7, 1H), 2.60 (t, 2H), 1.63–1.50 (m, 8H), 1.38–1.32 (m, 12H), 1.14-1.10 (m, 6H), 0.90 (t, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS/ppm): 150.7, 130.8, 130.6, 129.1, 32.9, 32.2, 31.8, 29.4, 29.1, 29.0, 28.9, 27.3, 22.6, 14.0, 13.6, 10.8.

5-heptyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (a) → In a dried three-neck round-bottom flask 3,4-thiophenedicarboxylic acid (1 mmol) was dissolved in acetic anhydride (10^{-1} M) and the resulting solution was refluxed 24 hours at 140°C under nitrogen atmosphere. The acetic anhydride was removed by *in-situ* vacuum distillation, the resulting residue was dissolved in toluene (10^{-1} M) and, then, hexan-1-amine (1,5 mmol) was added. The reaction mixture was heated to 110 °C for 24 hours. Toluene and the excess of amine were distilled off under vacuum, and the resulting solid was dissolved in thionyl chloride (10^{-1} M). The reaction mixture was refluxed at 80°C for 24 hours. The excess of thionyl chloride was removed by vacuum distillation and the resulting residue was purified by flash chromatography (cyclohexane/CH_2Cl_2, 60:40). Sandy crystalline solid. Yield: 50%. EI-MS m/z 251 (M^+). ^{1}H

NMR (400 MHz, $CDCl_3$, TMS/ppm): 7.81 (s, 2H), 3,61 (t, 2H) 1.66-1.60 (m, 2H), 1.35-1.31 (m, 6H), 0,88 (t, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS/ppm): 162.6, 136.7, 125.4, 38.5, 31.4, 28.4, 26.5, 22.5, 13.9.

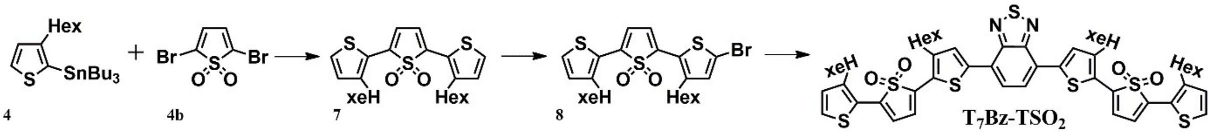
1,3-dibromo-5-heptyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (4a) → To a solution of **a** (1 mmol) in sulfuric acid and trifluoroacetic acid (1/3, 10^{-1} M), NBS (3 mmol) was added in one portion and the resulting mixture was kept in dark under stirring for 48 h. The resulting mixture was extracted with CH_2Cl_2 and a saturated aqueous solution of sodium bicarbonate, and the combined organic phases were evaporated under reduced pressure. The residue was isolated by flash chromatography (Cyclohexane/CH_2Cl_2, 50/50). Sand-colored powder. Yield: 90%. EI-MS *m/z* 395 (M^+). ^1H NMR (400 MHz, $CDCl_3$, TMS/ppm): δ 3.60 (t, 2H), 1.68–1.62 (m, 2H), 1.34–1.26 (m, 6H), 1.14-1.09 (m, 6H), 0.89 (t, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS/ppm): 160.4, 134.8, 112.9, 38.8, 31.3, 28.2, 26.4, 22.4, 14.0.

5-hexyl-1,3-bis(3-hexylthiophen-2-yl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (5) → The compound was prepared following the general procedure for Stille Cross-coupling starting from **4** (2 mmol) and **4a** (1 mmol). The residue was isolated by flash chromatography (Cyclohexane/CH_2Cl_2, 70:30). Dark magenta solid. Yield: 70%. EI-MS *m/z* 569 (M^+). ^1H NMR (400 MHz, $CDCl_3$, TMS/ppm): δ 7.40 (d, J = 5.2, 2H), 7.00 (d, ^3J = 5.2, 2H), 3.61 (t, 2H), 2.80 (t, 4H), 1.68–1.61 (m, 6H), 1.35–1.27 (m, 18H), 0.87 (t, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS/ppm): δ 162.3, 144.3, 137.0, 130.6, 129.8, 127.6, 124.9, 38.4, 31.6, 31.4, 30.5, 29.6, 29.2, 28.4, 26.6, 22.6, 22.5, 14.1, 14.0.

1-(5-bromo-3-hexylthiophen-2-yl)-5-hexyl-3-(3-hexylthiophen-2-yl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (6) → The compound was prepared following the general procedure for bromination starting from **5** (1 mmol) using 1 mmol of NBS. The residue was isolated by flash chromatography (Cyclohexane/CH_2Cl_2, 70/30). Dark magenta powder. Yield: 75%. EI-MS *m/z* 647 (M^+). ^1H NMR (400 MHz, $CDCl_3$, TMS/ppm): δ 7.40 (d, J = 5.2, 1H), 7.00 (d, J = 5.2, 1H), 6.97 (s, 1H), 3.61 (t, 2H), 2.80-2.72 (m, 4H), 1.65–1.60 (m, 6H), 1.34–1.25 (m, 18H), 0.88-0.84 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS/ppm): δ 162.2, 162.1, 144.7, 144.3, 137.2, 136.2, 132.5, 130.8, 130.4, 129.8, 127.8, 126.5, 124.7, 115.2, 38.5, 31.6, 31.5, 31.4, 30.5, 30.2, 29.7, 29.6, 29.2, 29.1, 28.4, 26.6, 22.61, 22.58, 22.50, 14.09, 14.07, 14.04.

3,3'-(5,5'-(benzo[c][1,2,5]thiadiazole-4,7-diyl)bis(3-hexylthiophene-5,2-diyl))bis(5-hexyl-1-(3-hexylthiophen-2-yl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione) (T_7Bz-Dp_2) → The compound was prepared following the general procedure for Suzuki Cross-coupling starting from **6** (2 mmol) and 4,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[c][1,2,5]thiadiazole (1 mmol). The residue was isolated by flash chromatography (Cyclohexane/CH_2Cl_2, 50:50). Dark red powder. Yield: 55%. EI-MS *m/z* 1270 (M^+). ^1H NMR (500 MHz, $CDCl_3$, TMS/ppm): δ 8.07 (s, 2H), 7.90 (s, 2H), 7.43 (d, J = 5.2, 2H), 7.03 (d, J = 5.2, 2H), 3.66 (t, 4H), 2,91 (t, 4H), 2,84 (t, 4H), 1.79–1.68 (m, 12H), 1.43–1.27 (m, 36H), 0.90-0.89 (t, 18H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS/ppm): δ 162.3, 162.2, 152.4, 145.2, 144.3, 140.7, 137.1, 136.5, 130.7, 130.4, 129.8, 127.7, 126.8, 125.9, 125.6, 124.9, 38.5, 31.7, 31.6, 31.4, 30.5, 30.0, 29.7, 29.3, 29.2, 28.4, 26.6, 22.7, 22.6, 22.5, 14.1, 14.0.

Scheme S3



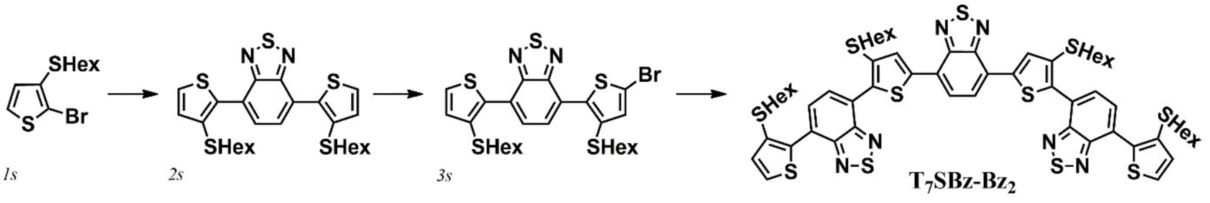
2,5-dibromothiophene 1,1-dioxide (4b) → To a solution of 2,5-dibromothiophene (1 mmol) in CH_2Cl_2/CF_3COOH (2:1), 2 mmol of H_2O_2 (as a solution in H_2O 30 wt. %) were added drop by drop. The reaction mixture was sonicated for 15 min in a closed vessel by immersion in an ultrasonic bath. The crude product was extracted with a saturated aqueous solution of sodium bicarbonate and the organic layers were collected. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography (Cyclohexane/CH_2Cl_2/AcOEt, 80:15:5). Pale yellow solid. Yield: 60%. EI-MS *m/z* 274 (M^+); ^1H NMR (400 MHz, $CDCl_3$, TMS/ppm): δ 6.89 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS/ppm): 128.6, 119.0.

3,3''-dihexyl-[2,2':5',2''-terthiophene] 1',1'-dioxide (7) → The compound was prepared following the general procedure for Stille Cross-coupling starting from **4** (2 mmol) and **4b** (1 mmol). The residue was isolated by flash chromatography (Cyclohexane/CH_2Cl_2, 60:40). Dark burgundy oil. Yield: 65%. EI-MS *m/z* 448 (M^+). ^1H NMR (400 MHz, $CDCl_3$, TMS/ppm): δ 7.43 (d, J = 5.2, 2H), 7.01 (d, J = 5.2, 2H), 6.76 (s, 2H), 2.75 (t, 4H), 1.68–1.60 (m, 6H), 1.39–1.32 (m, 10H), 0.94–0.87 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS/ppm): δ 145.9, 136.2, 129.9, 128.2, 122.3, 121.8, 31.7, 30.4, 29.9, 29.2, 22.6, 14.1.

5-bromo-3,3''-dihexyl-[2,2':5',2''-terthiophene] 1',1'-dioxide (8) → The compound was prepared following the general procedure for bromination starting from **7** (1 mmol) using 1 mmol of NBS. The residue was isolated by flash chromatography (Cyclohexane/CH_2Cl_2, 70/30). Dark red solid. Yield: 50%. EI-MS *m/z* 526 (M^+). ^1H NMR (400 MHz, $CDCl_3$, TMS/ppm): δ 7.45 (d, J = 5.2, 1H), 7.03 (d, J = 5.2, 1H), 6.99 (s, 1H), 6.75-6.72 (m, 1H), 2.76-2.68 (m, 4H), 1.69–1.58 (m, 6H), 1.39–1.28 (m, 10H), 0.89 (t, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS/ppm): δ 146.5, 146.2, 136.6, 136.1, 130.0, 128.5, 123.8, 122.5, 122.1, 121.3, 115.9, 31.7, 31.6, 30.4, 30.3, 29.97, 29.92, 29.2, 29.1, 22.6, 22.5, 14.05, 14.04.

5,5'''-(benzo[c][1,2,5]thiadiazole-4,7-diyl)bis(3,3''-dihexyl-[2,2':5',2''-terthiophene] 1',1'-dioxide) (T_7Bz-TSO$_2$) → The compound was prepared following the general procedure for Suzuki Cross-coupling starting from **8** (2 mmol) and 4,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[c][1,2,5]thiadiazole (1 mmol). The residue was isolated by flash chromatography (Cyclohexane/CH_2Cl_2, 60:40). Purple crystalline solid. Yield: 50%. EI-MS *m/z* 1028 (M^+). ^1H NMR (400 MHz, $CDCl_3$, TMS/ppm): δ 8.11 (s, 2H), 7.91 (s, 2H), 7.46 (d, J = 5.2, 2H), 7.05 (d, J = 5.2, 2H), 6.86 (d, J = 5.2, 2H), 6.80 (d, J = 5.2, 2H), 2.86-2.76 (m, 8H), 1.79–1.64 (m, 12H), 1.47–1.35 (m, 20H), 0.93-0.88 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS/ppm): δ 152.3, 146.9, 146.0, 141.5, 136.1, 136.0, 130.6, 129.9, 128.4, 125.9, 125.5, 124.0, 122.4, 121.8, 121.4, 31.7, 31.6, 30.4, 30.3, 30.2, 30.0, 29.7, 29.3, 29.2, 22.6, 22.5, 14.1, 14.0.

Scheme S4



2-bromo-3-(hexylthio)thiophene (1s) → The compound was prepared following the general procedure for bromination starting from 3-(hexylthio)thiophene (1 mmol) using 1 mmol of NBS. The residue was isolated by flash chromatography (Cyclohexane). Pale yellow oil. Yield: 70%. EI-MS *m/z* 280 (M^+). ^{1}H NMR (400 MHz, $CDCl_3$, TMS/ppm): δ 7.23 (d, *J* = 5.7, 1H), 6.91 (d, *J* = 5.7, 1H), 2.83 (t, 2H), 1.60–1.53 (m, 2H), 1.43–1.22 (m, 6H), 0.87 (t, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS/ppm): δ 133.1, 130.1, 125.8, 113.6, 36.1, 31.3, 29.5, 28.2, 22.5, 14.0.

4,7-bis(3-(hexylthio)thiophen-2-yl)benzo[c][1,2,5]thiadiazole (2s) → The compound was prepared following the general procedure for Suzuki Cross-coupling starting from **1s** (2 mmol) and 4,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[c][1,2,5]thiadiazole (1 mmol). The residue was isolated by flash chromatography (Cyclohexane/CH_2Cl_2, 80:20). Pale orange oil. Yield: 75%. EI-MS *m/z* 532 (M^+). ^{1}H NMR (400 MHz, $CDCl_3$, TMS/ppm): δ 7.98 (s, 2H), 7.52 (d, *J* = 5.2, 2H), 7.20 (d, *J* = 5.2, 2H), 2.85 (t, 4H), 1.55–1.48 (m, 4H), 1.28–1.16 (m, 12H), 0.83-0.79 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS/ppm): δ 153.7, 134.9, 131.6, 130.0, 129.9, 126.6, 126.2, 36.7, 31.3, 29.3, 28.3, 22.4, 13.9.

4-(5-bromo-3-(hexylthio)thiophen-2-yl)-7-(3-(hexylthio)thiophen-2-yl)benzo[c][1,2,5]thiadiazole (3s) → The compound was prepared following the general procedure for bromination starting from **2s** (1 mmol) using 1 mmol of NBS. The residue was isolated by flash chromatography (Cyclohexane/CH_2Cl_2, 80/20). Orange oil. Yield: 90%. EI-MS *m/z* 612 (M^+). ^{1}H NMR (400 MHz, $CDCl_3$, TMS/ppm): δ 8.01-7.96 (m, 2H), 7.53 (d, *J* = 5.3, 1H), 7.20 (d, *J* = 5.3, 1H), 7.14 (s, 1H), 2.87-2.83 (m, 4H), 1.56–1.50 (m, 4H), 1.30-1.15 (m, 12H), 0.84-0.79 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS/ppm): δ 153.6, 153.4, 136.3, 134.7, 132.1, 131.8, 130.0, 129.8, 129.7, 126.7, 126.5, 125.1, 114.0, 36.8, 36.7, 31.3, 31.2, 29.3, 29.2, 28.3, 28.2, 22.4, 13.9.

4,7-bis(4-(hexylthio)-5-(7-(3-(hexylthio)thiophen-2-yl)benzo[c][1,2,5]thiadiazol-4-yl)thiophen-2-yl)benzo[c][1,2,5]thiadiazole ($T_7SBz\text{-}Bz_2$) → The compound was prepared following the general procedure for Suzuki Cross-coupling starting from **3s** (2 mmol) and 4,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[c][1,2,5]thiadiazole (1 mmol). The residue was isolated by flash chromatography (Cyclohexane/CH_2Cl_2, 70:30). Deep red solid. Yield: 55%. EI-MS *m/z* 1196 (M^+). ^{1}H NMR (400 MHz, $CDCl_3$, TMS/ppm): δ 8.32 (s, 2H), 8.14 (d, *J* = 7.5, 2H), 8.03 (d, *J* = 7,5 2H), 7.98 (s, 2H), 7.54 (d, *J* = 5.3, 2H), 7.21 (d, *J* = 5.3, 2H), 3.01 (t, 4H), 2.87 (t. 4H), 1.66–1.51 (m, 10H), 1.37-1.17 (m, 22H), 0.84-0.81 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS/ppm): δ 153.7, 153.5, 152.5, 139.9, 136.9, 134.9, 133.1, 131.8, 130.6, 130.0, 129.9, 129.8, 126.7, 126.4, 125.9, 125.6, 36.8, 36.7, 31.3, 31.2, 29.4, 29.3, 28.4, 28.3, 22.5, 22.4, 13.9.

III. ^{1}H and ^{13}C Spectra

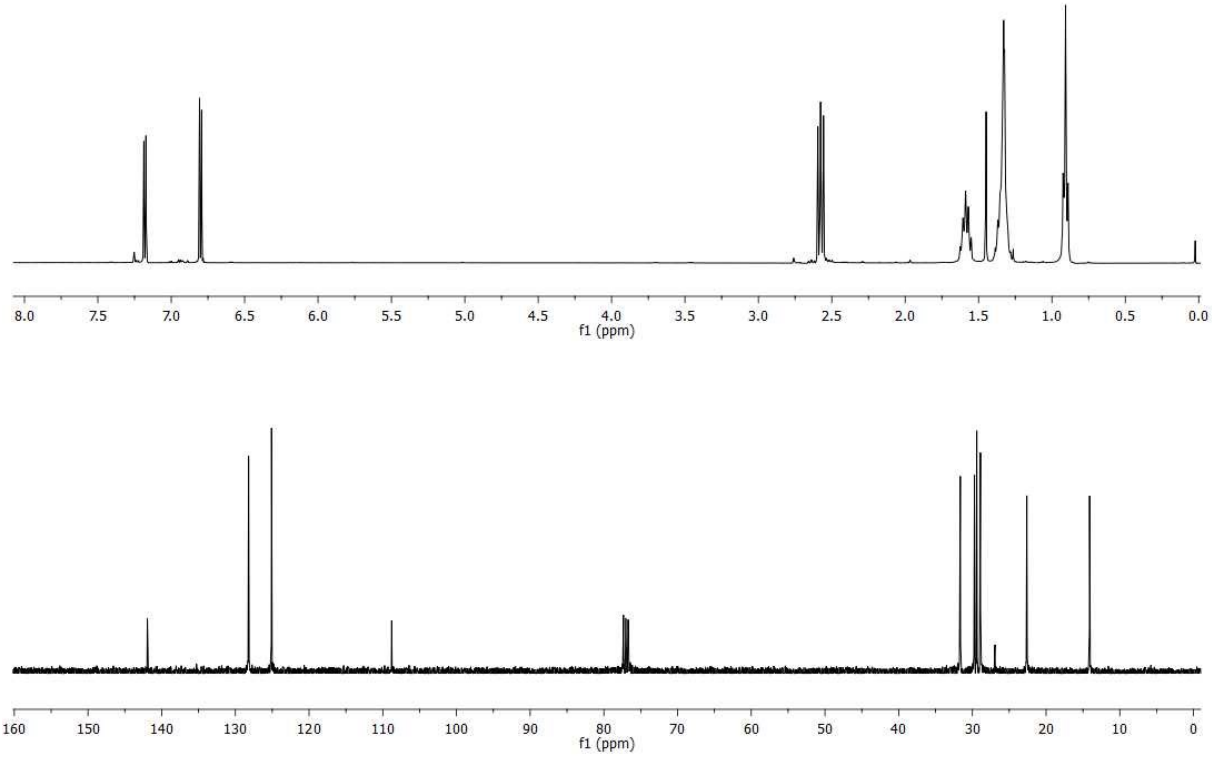


Figure S1. ^{1}H and ^{13}C NMR spectra of compound **1**.

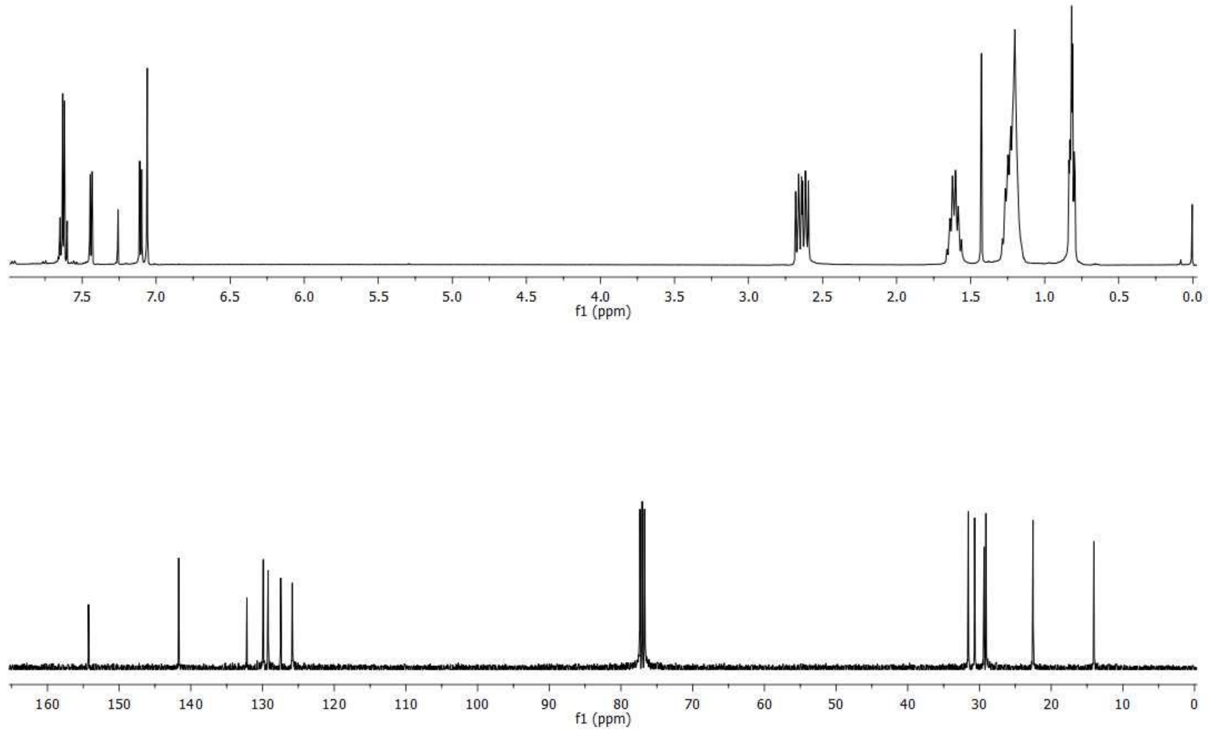


Figure S2. ^{1}H and ^{13}C NMR spectra of compound **2**.

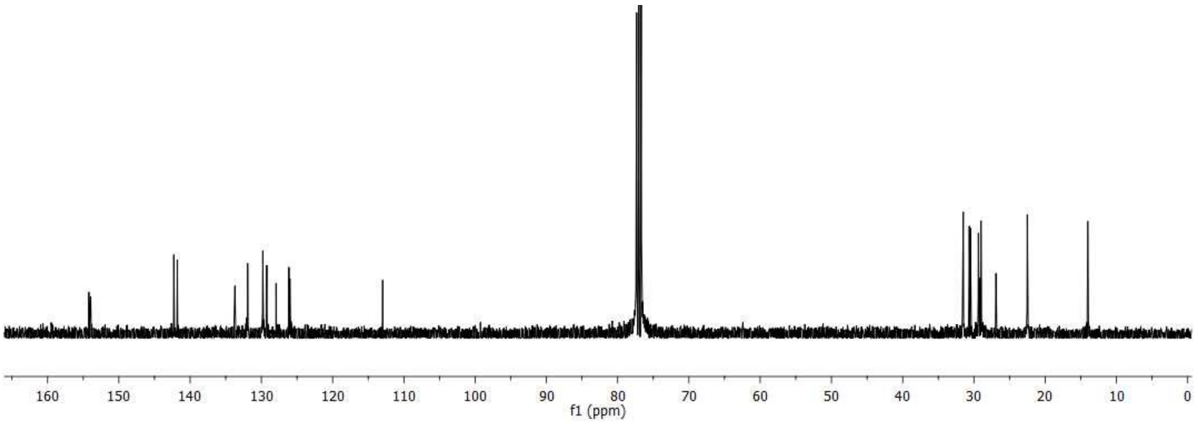


Figure S3. ^{1}H and ^{13}C NMR spectra of compound **3**.

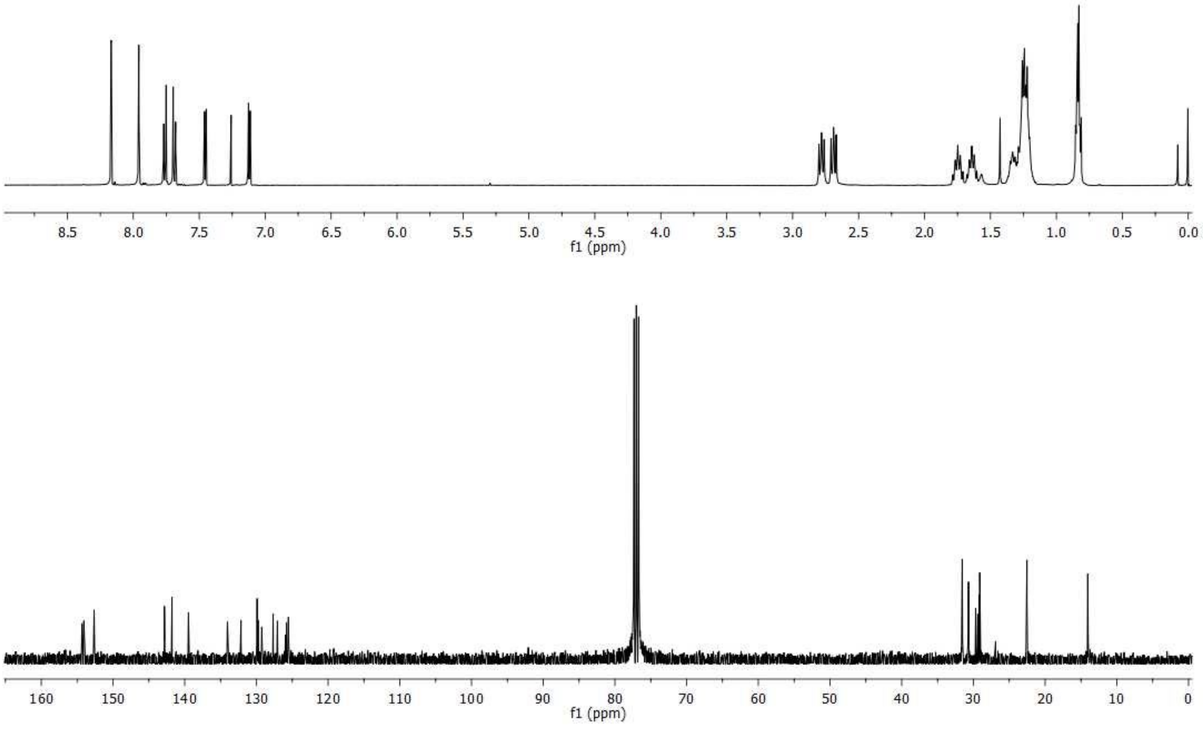


Figure S4. ^{1}H and ^{13}C NMR spectra of compound **T_7Bz-Bz_2**.

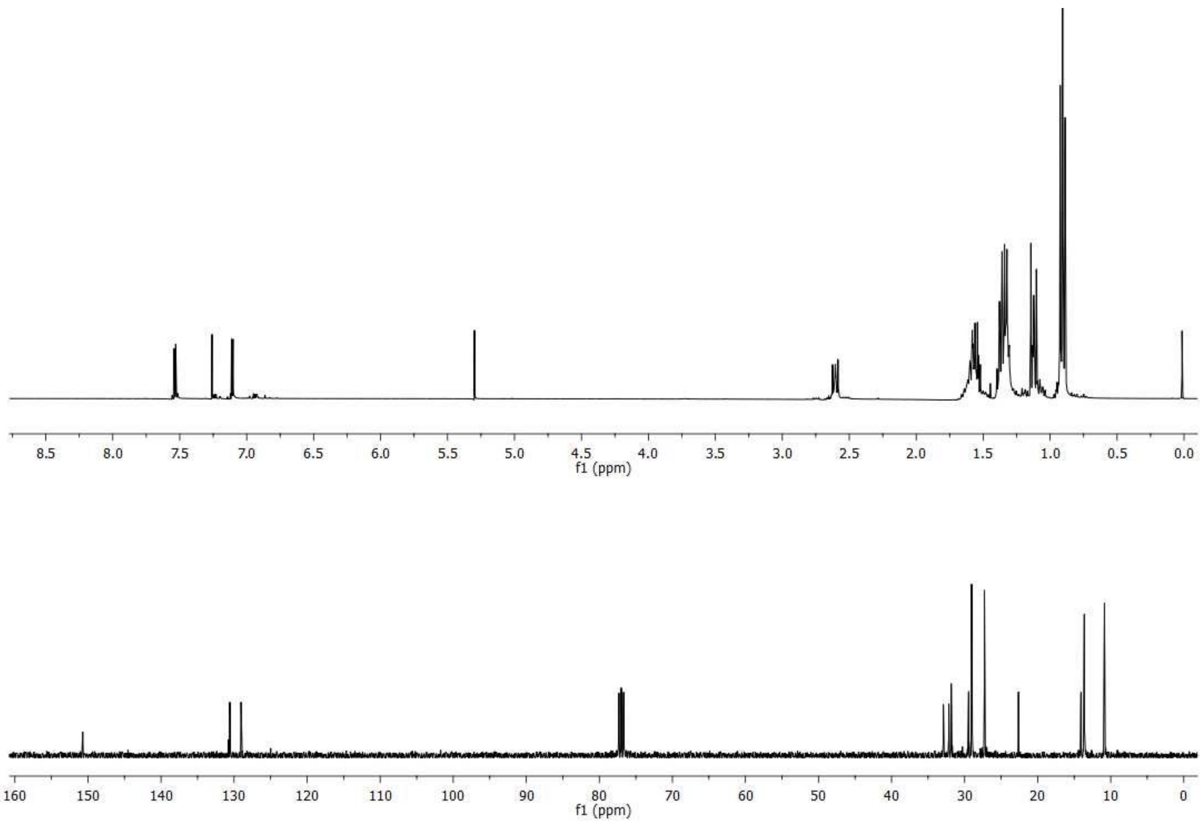


Figure S5. ^{1}H and ^{13}C NMR spectra of compound **4**.

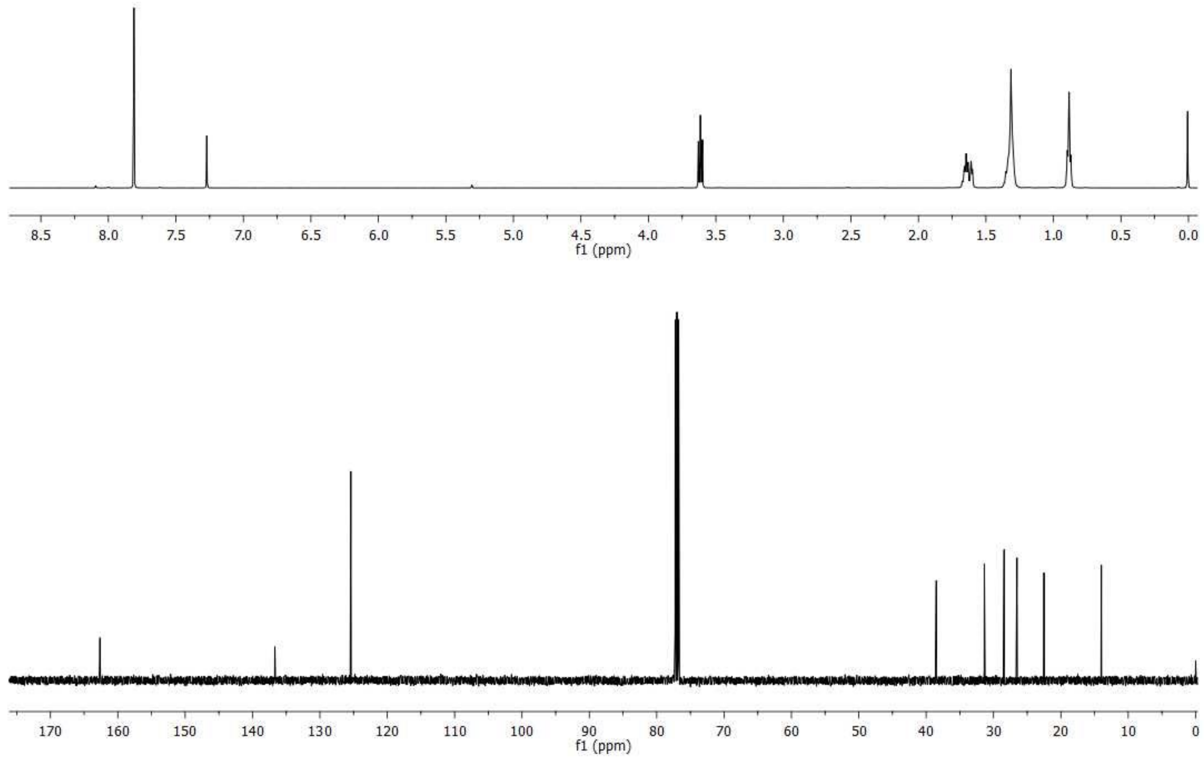


Figure S6. ^{1}H and ^{13}C NMR spectra of compound **a**.

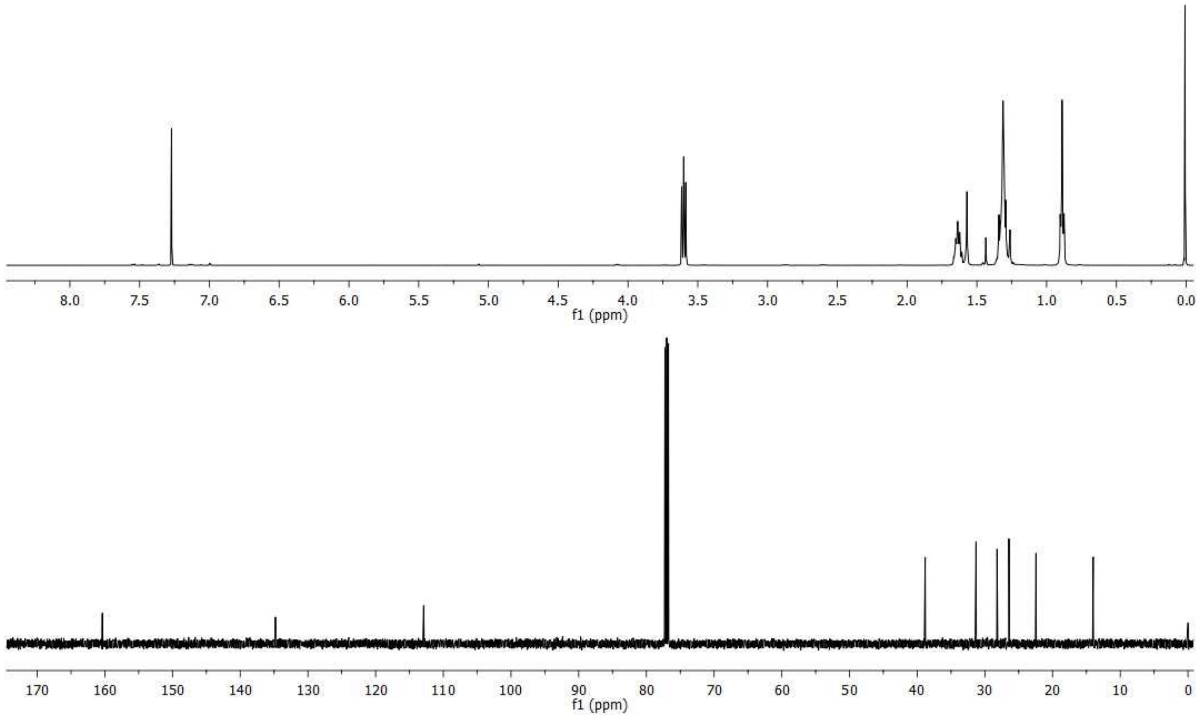


Figure S7. ^{1}H and ^{13}C NMR spectra of compound **4a**.

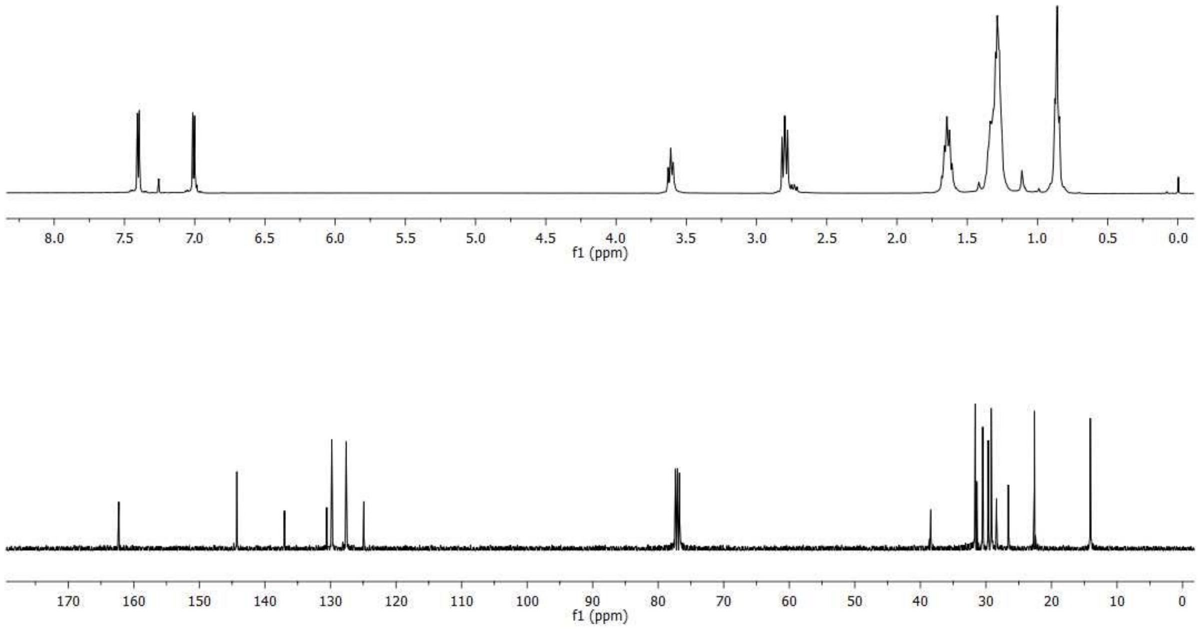


Figure S8. ^{1}H and ^{13}C NMR spectra of compound **5**.

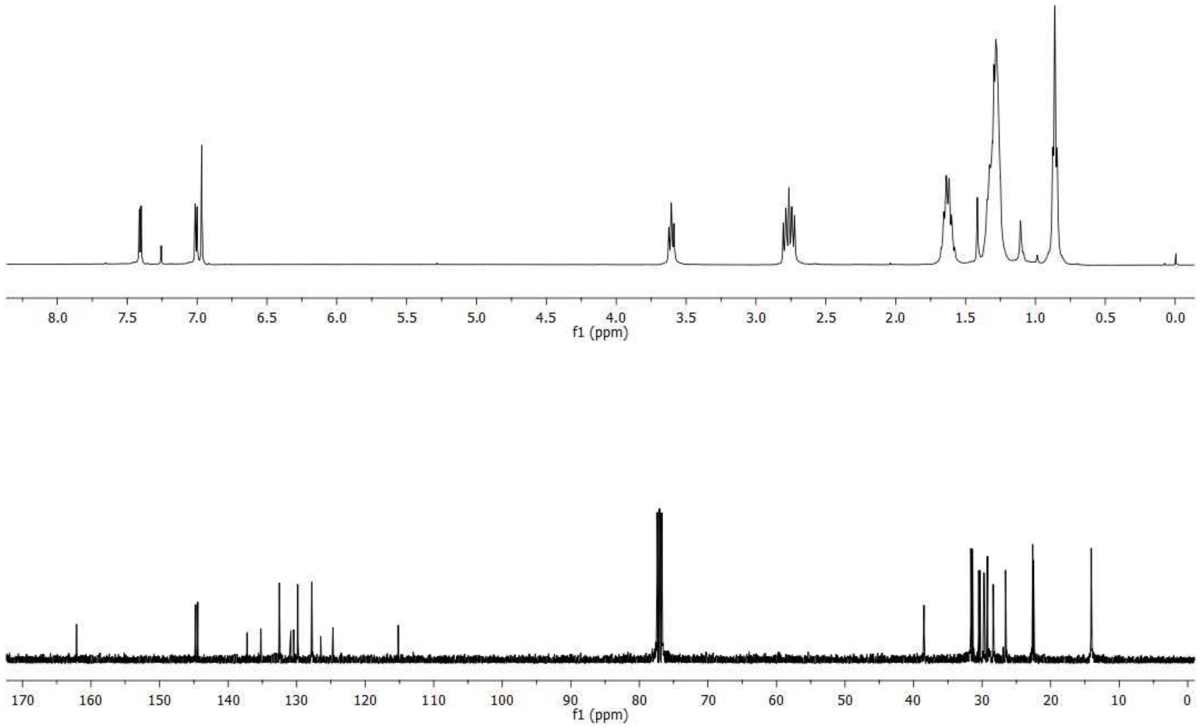


Figure S9. ^{1}H and ^{13}C NMR spectra of compound **6**.

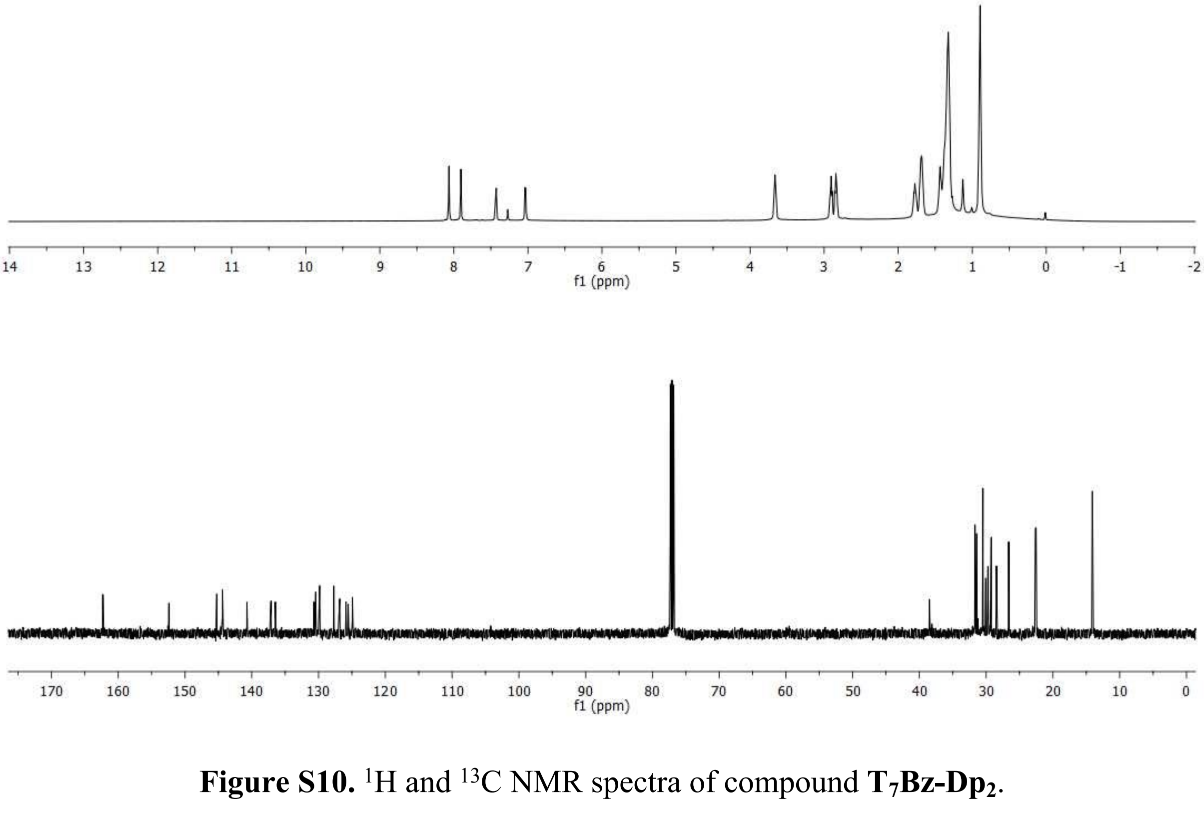


Figure S10. ^{1}H and ^{13}C NMR spectra of compound **T_7Bz-Dp$_2$**.

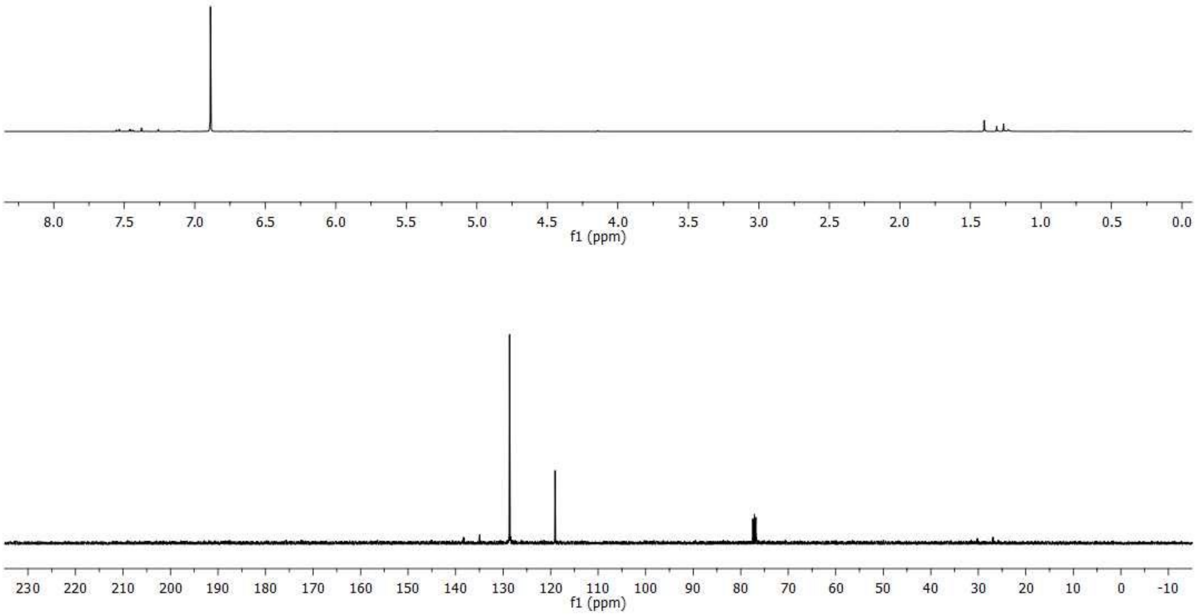


Figure S11. ^{1}H and ^{13}C NMR spectra of compound **4b**.

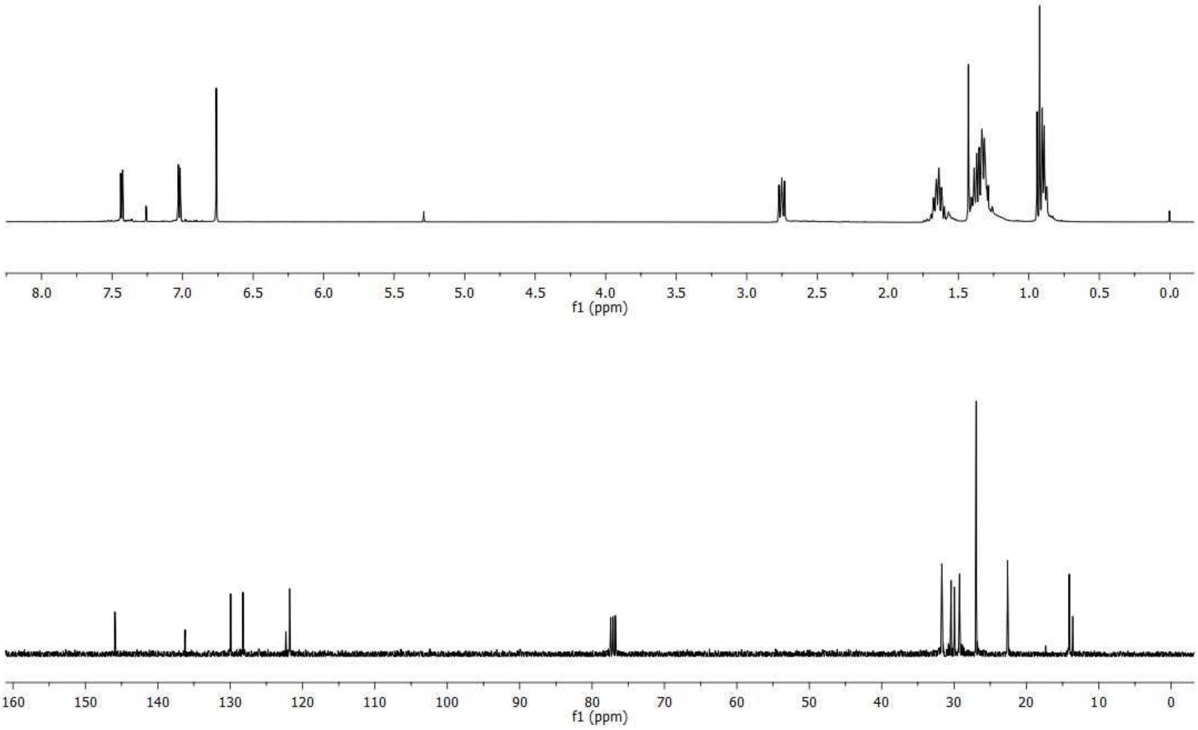


Figure S12. ^{1}H and ^{13}C NMR spectra of compound **7**.

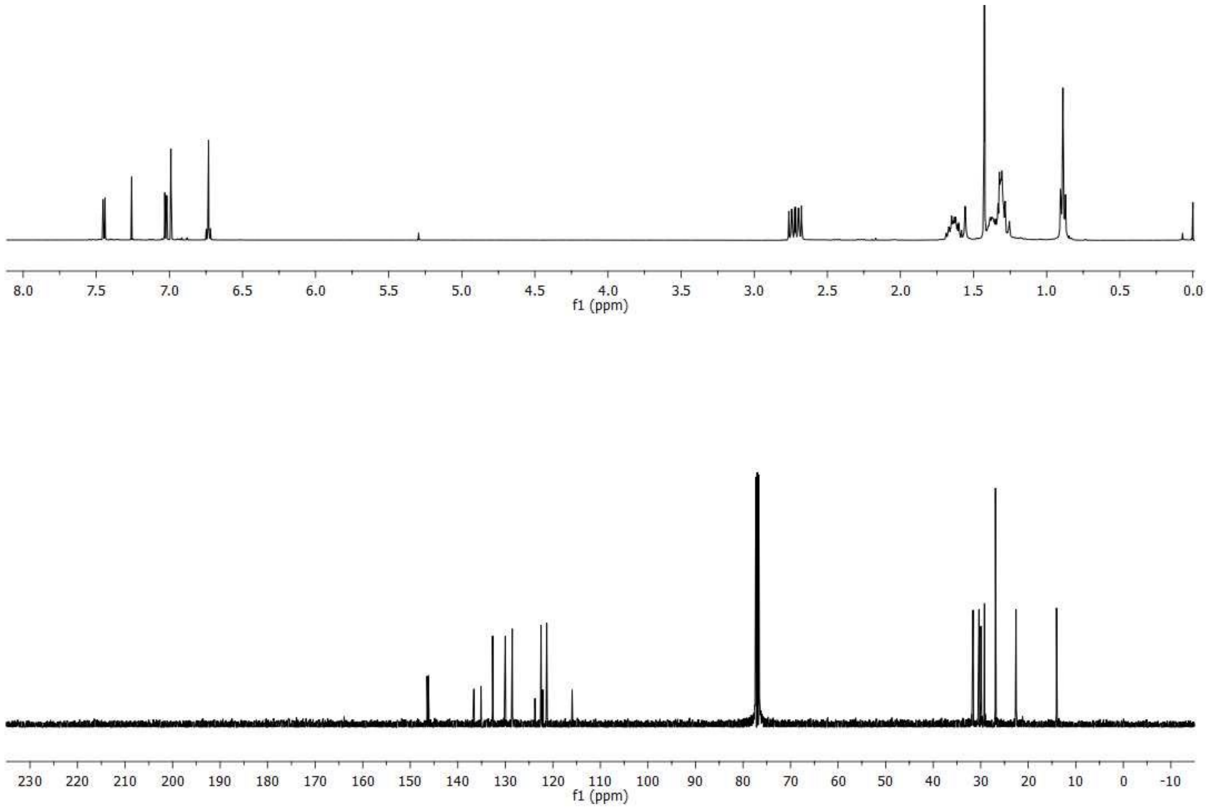


Figure S13. ^{1}H and ^{13}C NMR spectra of compound **8**.

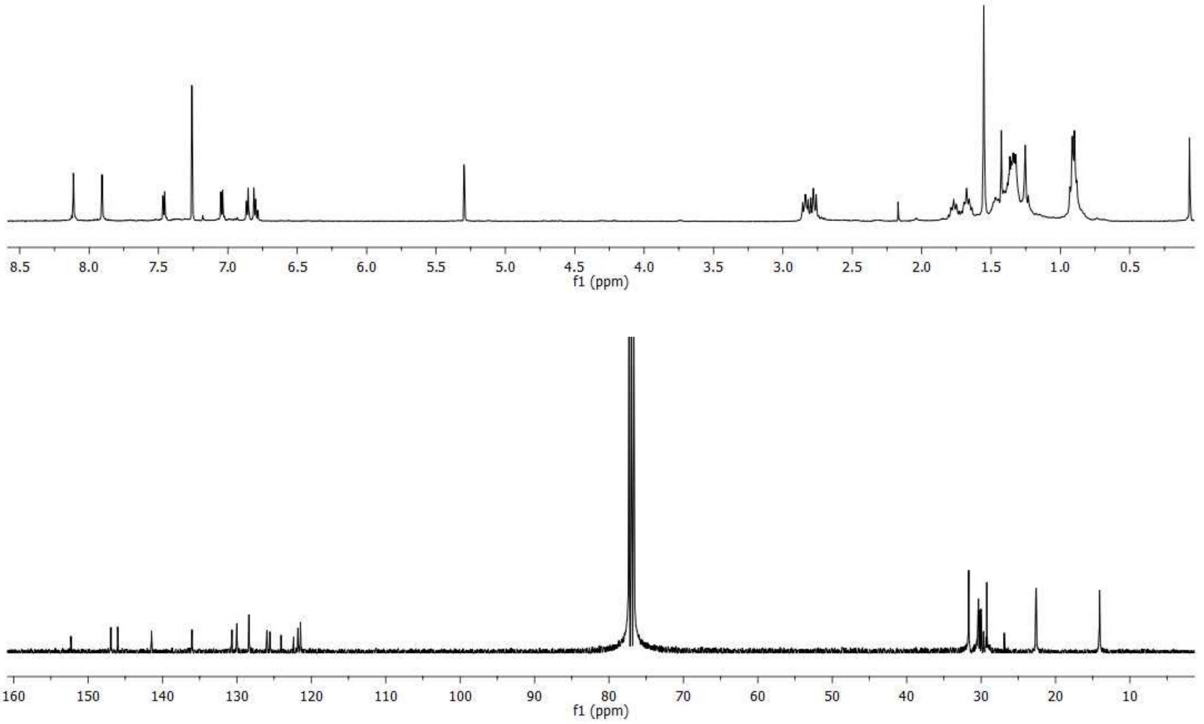


Figure S14. ^{1}H and ^{13}C NMR spectra of compound **T_7Bz-TSO$_2$**.

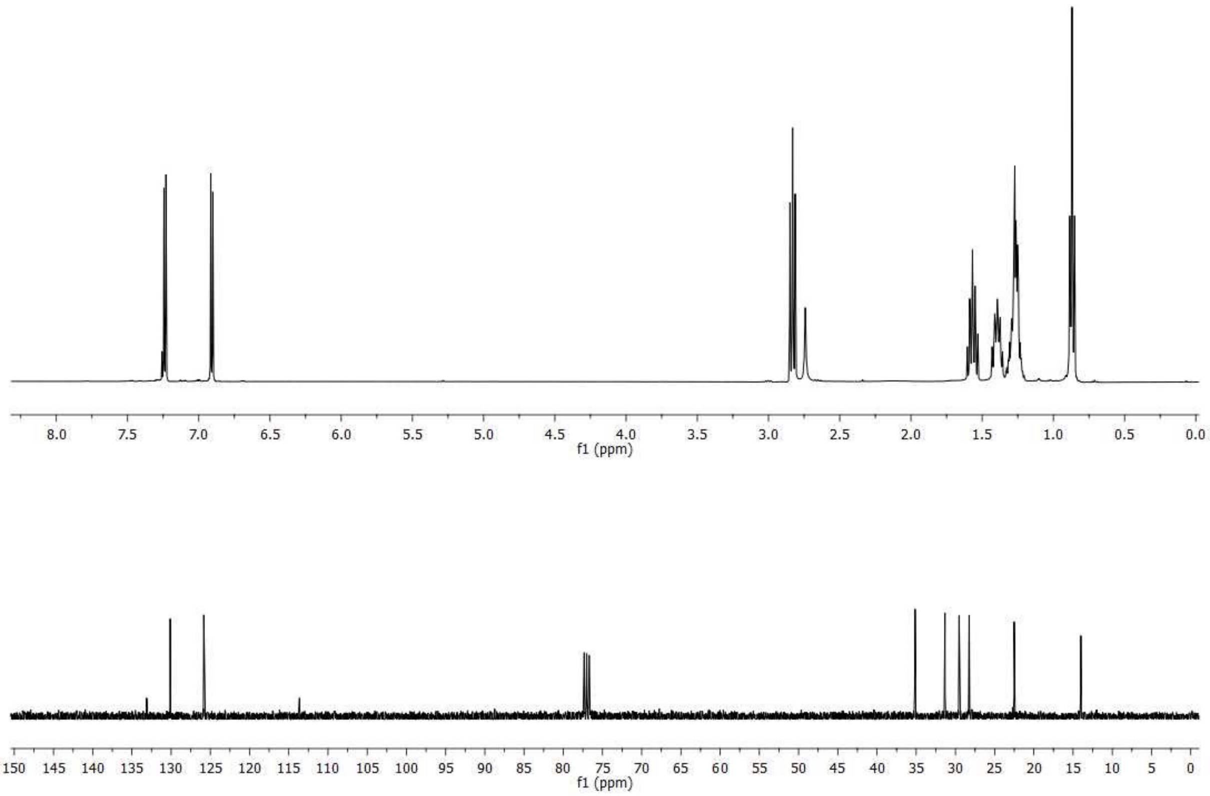


Figure S15. ^{1}H and ^{13}C NMR spectra of compound **1s**.

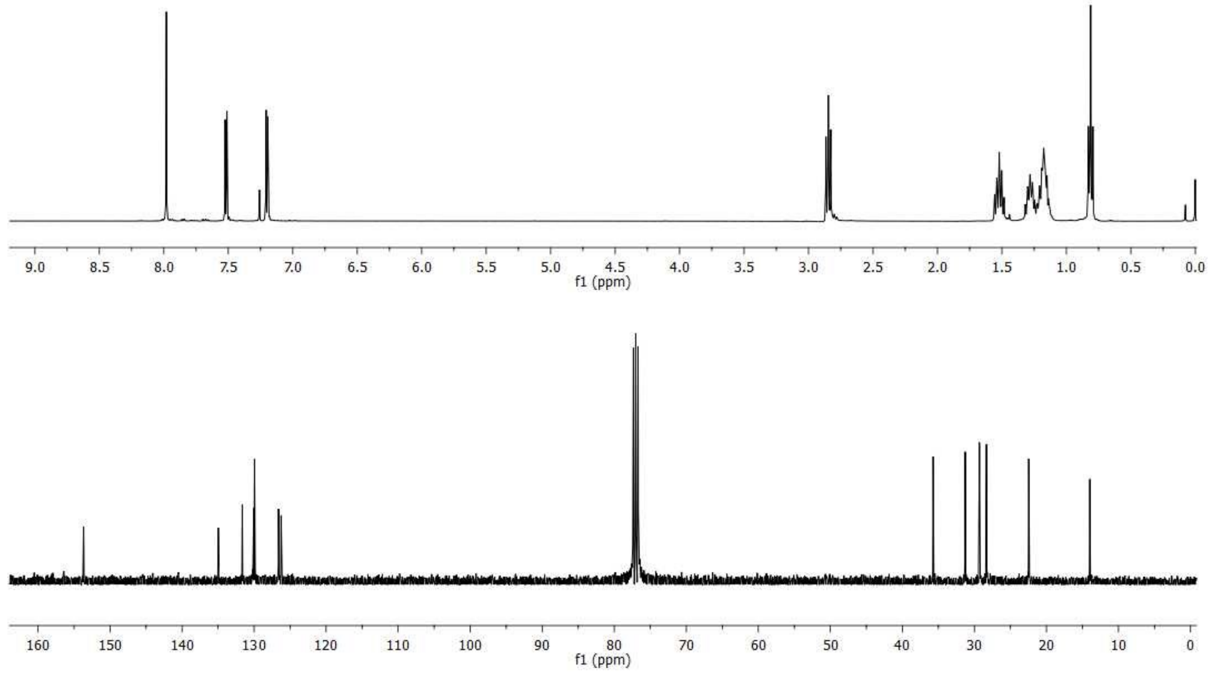


Figure S16. ^{1}H and ^{13}C NMR spectra of compound **2s**.

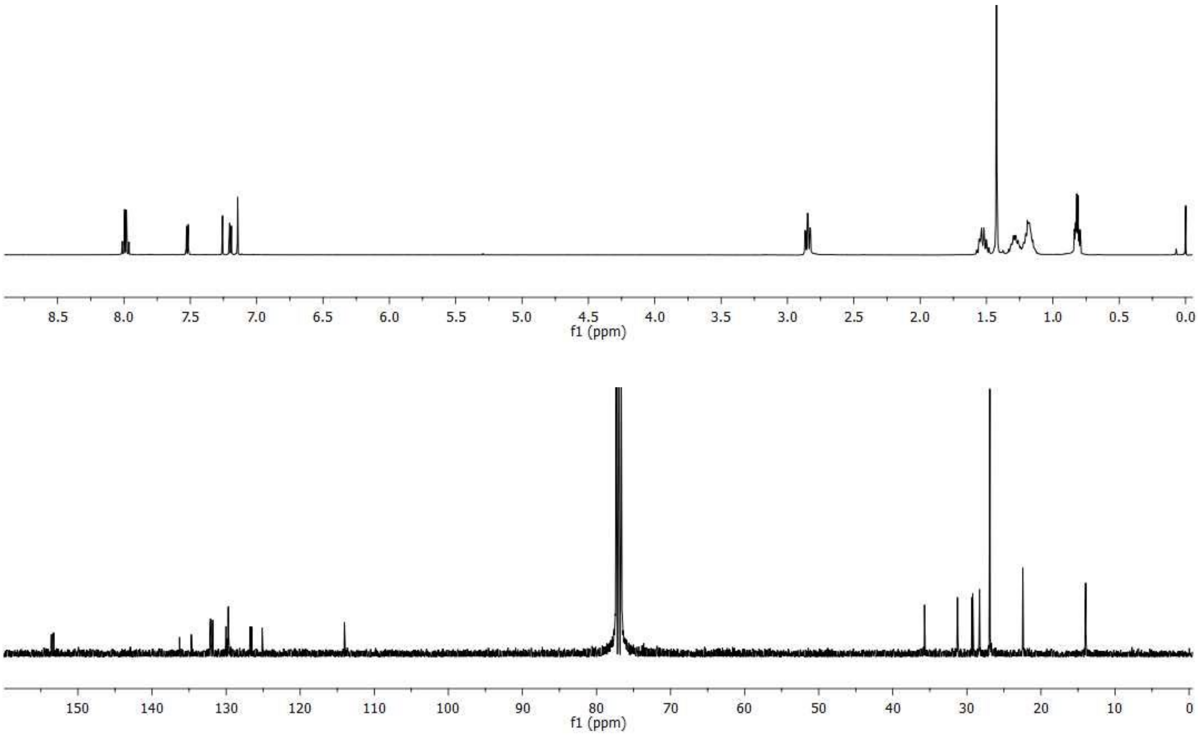


Figure S17. ^{1}H and ^{13}C NMR spectra of compound **3s**.

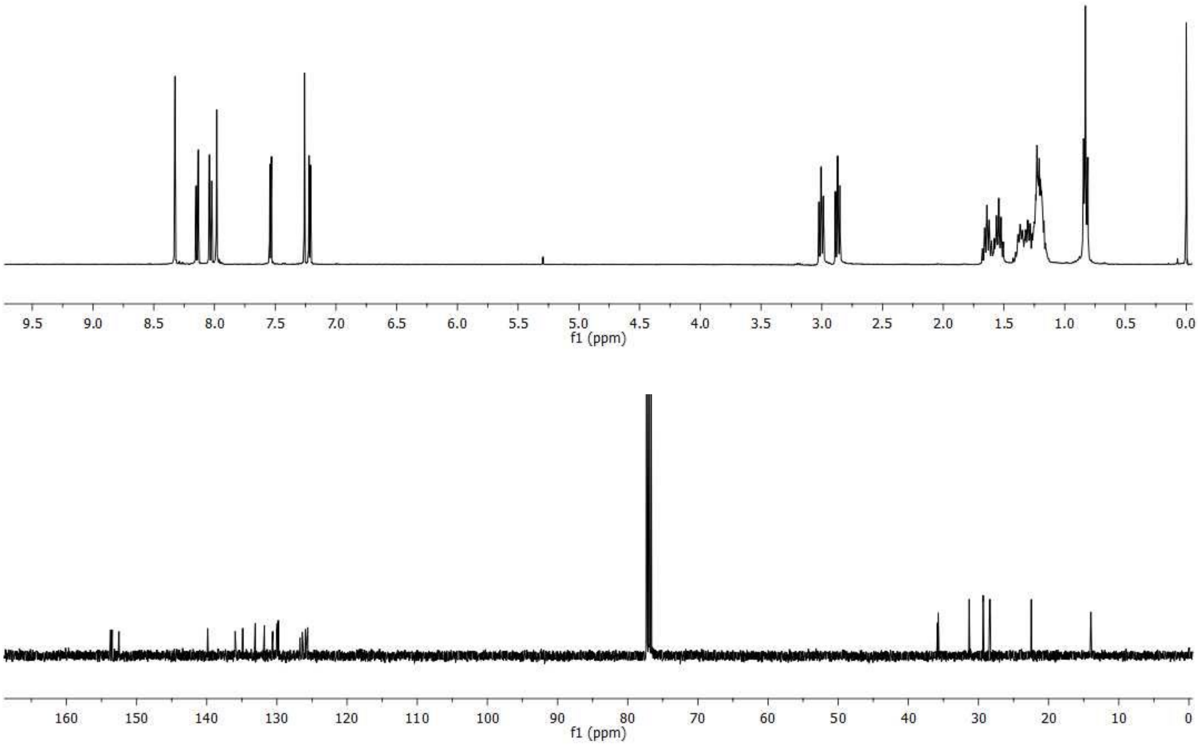


Figure S18. ^{1}H and ^{13}C NMR spectra of compound **T_7SBz-Bz$_2$**.

IV. DCS and TGA Analysis

Table S1: DSC data

	Heating 2nd scan				*Cooling*	
	T_g (°C)	**Dc_p (J/g)**	**T_m (°C)**	**DH_m (J/g)**	**Tcc**	**DH_{cc} (J/g)**
T7Bz-Bz$_2$	11.3	0.286	/		/	
T7Bz-Dp$_2$	/		146	38.4	117	37.5
T7Bz-TSO$_2$	17.5	0.255	150, 167	2.95, 29.7	133	37.1
T7SBz-Bz$_2$	/		81, 93	14.2, 4.01	39	10.0

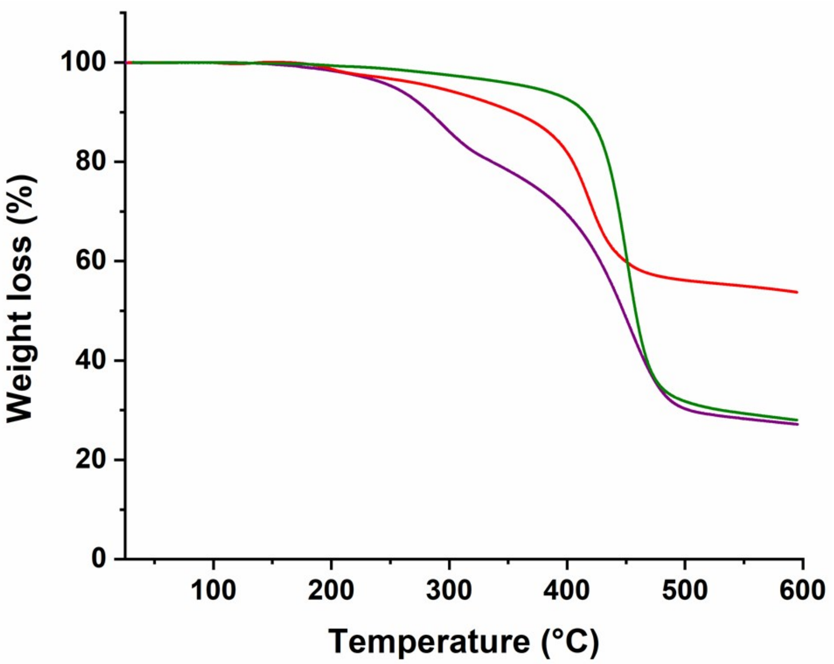
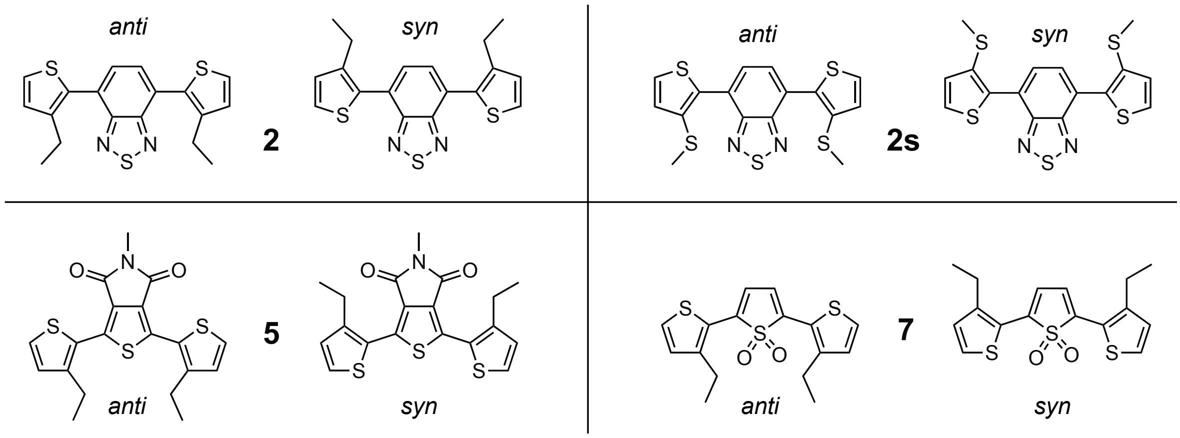
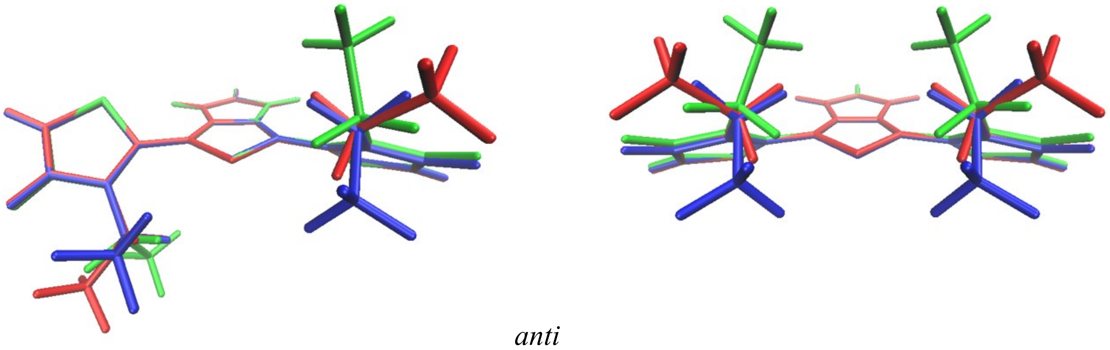


Figure S19. TGA curves of heptamers T7Bz-TSO$_2$ (purple line), T7SBz-Bz$_2$ (red line), and T7Bz-Dp$_2$ (green line).

V. DFT calculations

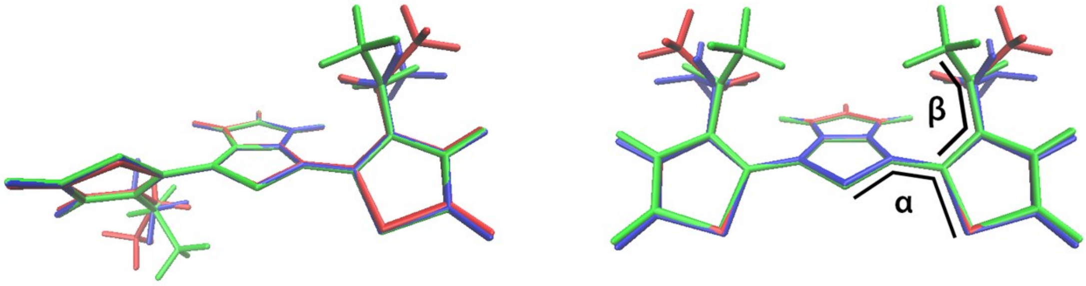


Scheme S5. Molecular structures of the investigated trimers used to locate the most stable minima of the related heptamers. Beyond the *syn*/*anti* isomerization, also the conformational freedom of the side chains was explored (see Figure S20 and Table S2).



anti
-**5** in C_2 symmetry

ant
i-**5** in C_s symmetry



syn-**5** in C_2 symmetry

syn-**5** in C_s symmetry

Figure S20. Optimized geometries of the *syn*/*anti* conformers of **5**, taken as a representative example of the investigated trimers reported in Scheme S5. All conformers were explored within the C_2 or C_s symmetry point groups. For each of the two pairs of conformers, three further classes of minima were found, depending on the orientation of the alkyl side chains (*i.e.*, rotamers a, b and c, in red, blue and green, respectively). For the sake of clarity, the α and β dihedral angles mentioned in Table S1F are highlight for the C_s-symmetry *syn*-**5** conformer (bottom right).

Table S2. Conformational study on selected trimers. Optimizations were performed, within the C_2 or C_s symmetry point groups, in dichloromethane at the PCM-M06/6-31++G(d,p) level of theory.[a] Three sets of conformers (*i.e.*, a–c) were investigated for each *syn*/*anti* and C_2/C_s pairs in order to map all possible conformations of the lateral chains (see Figure S1F as example).

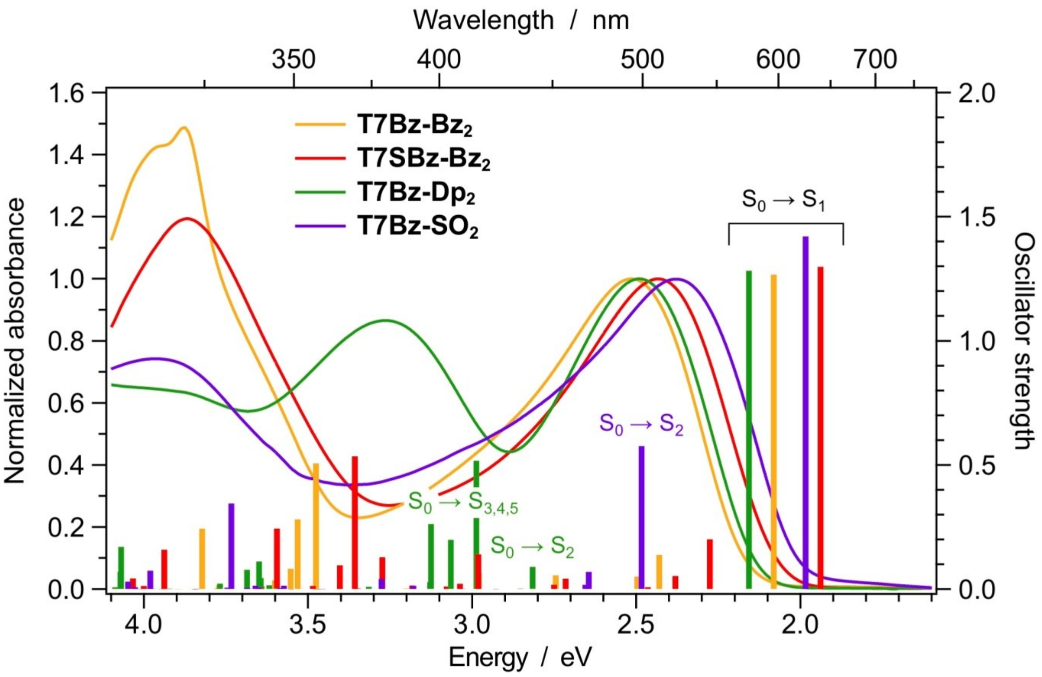
***anti* conformation**

	C_2 symmetry Energy meV (%)	α °	β °	C_s symmetry Energy meV (%)	α °	β °
2 [**T-Bz-T**]	54 (3)	126	–120	49 (4)	127	–128
	17 (13)	128	120	13 (15)	129	121
	50 (4)	128	–63	34 (7)	130	–59
2s [**TS-Bz-TS**]	43 (6)	130	–137	40 (6)	131	–135
	39 (7)	120	117	36 (8)	122	117
	116 (0)	122	–41	104 (1)	124	–40
5 [**T-Dp-T**]	87 (1)	139	–153	86 (1)	139	–152
	10 (15)	140	102	**3 (19)**	**140**	**101**
	79 (1)	137	–71	52 (3)	138	–67
7 [**T-TSO-T**]	98 (1)	134	–157	183 (0)	148	–170
	16 (18)	132	103	92 (1)	129	105
	50 (5)	142	–78	106 (0)	157	–86

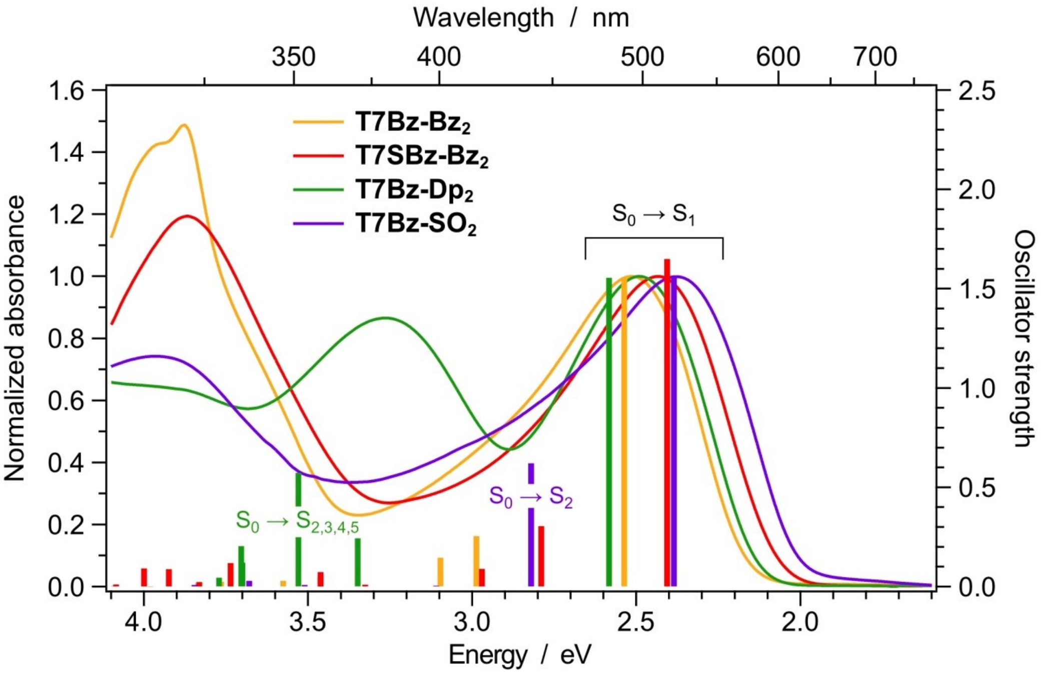
***Syn* conformation**

	C_2 symmetry Energy meV (%)	α °	β °	C_s symmetry Energy meV (%)	α °	β °
2 [**T-Bz-T**]	54 (3)	42	142	52 (3)	42	141
	2 (22)	43	–109	**0 (25)**	**42**	**–109**
	76 (1)	**58**	**87**	80 (1)	57	69
2s [**TS-Bz-TS**]	**1 (29)**	**37**	**154**	**0 (31)**	**36**	**153**
	70 (2)	44	–114	71 (2)	44	–115
	58 (3)	52	56	45 (5)	52	57
5 [**T-Dp-T**]	18 (11)	47	142	**0 (22)**	**45**	**143**
	46 (4)	50	–126	28 (7)	47	–126
	38 (5)	51	71	13 (13)	50	67
7 [**T-TSO-T**]	35 (8)	27	161	39 (7)	26	161
	0 (32)	**34**	**–97**	**6 (25)**	**31**	**–97**
	76 (2)	47	74	83 (1)	45	72

[a] Such more flexible basis set, if compared to the one adopted for the general investigation (*i.e.*, 6-31+G(d), with no polarization and diffuse functions on hydrogen atoms) was adopted to better take into account intermolecular hydrogen interactions, if any.



(a) M06/6-31+G(d)



(b) M06-2X/6-31+G(d)

Figure S21. Comparison between the experimental absorption spectra in dichloromethane at 298 K (full lines) of all the investigated heptamers and their lowest singlet vertical excitations (bars) computed at different levels of theory (a, b) in the same solvent, using PCM in combination with the linear-response formalism.

Table S3. Calculated NTOs couples describing the first three singlet excitations for **T7Bz-Bz$_2$** in dichloromethane at the M06-2X/6-31+G(d) level of theory. The *f* value is the oscillator strength of each transition, while λ value is the natural transition orbital eigenvalue associated with each NTOs couple; orbital isovalue: 0.04 e$^{-1/2}$ bohr$^{-3/2}$.

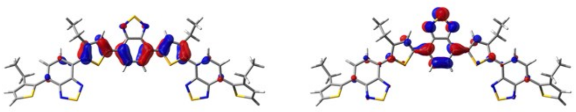
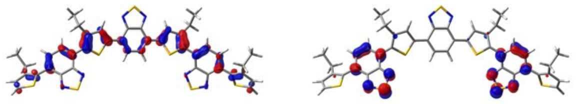
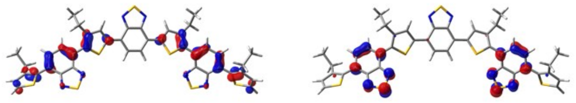
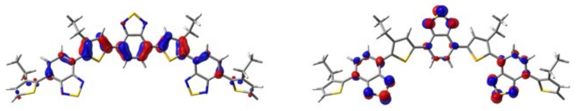
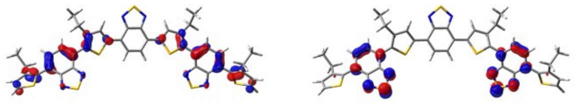
	Transition energy [eV (nm)]	NTO couple hole → electron (λ)
$S_0 \rightarrow S_1$	2.54 (489) *f* = 1.559	 (91.4%)
$S_0 \rightarrow S_2$	2.99 (415) *f* = 0.255	 (62.6%)
		 (36.3%)
$S_0 \rightarrow S_3$	3.10 (400) *f* = 0.146	 (67.0%)
		 (25.2%)

Table S4. Calculated NTOs couples describing the first three singlet excitations for **T7SBz-Bz$_2$** in dichloromethane at the M06-2X/6-31+G(d) level of theory. The *f* value is the oscillator strength of each transition, while λ value is the natural transition orbital eigenvalue associated with each NTOs couple; orbital isovalue: 0.04 e$^{-1/2}$ bohr$^{-3/2}$.

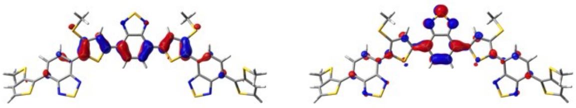
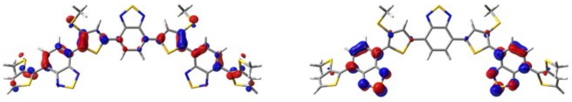
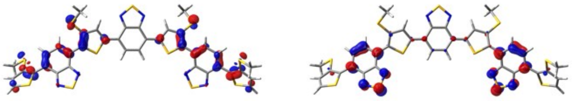
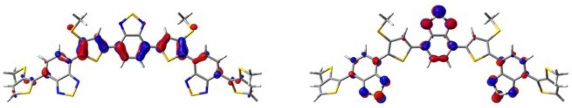
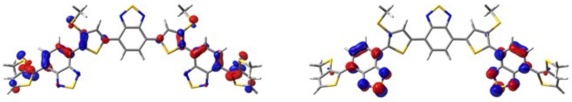
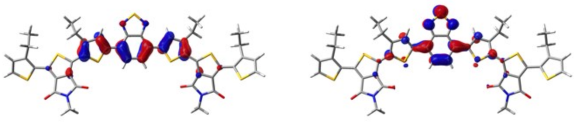
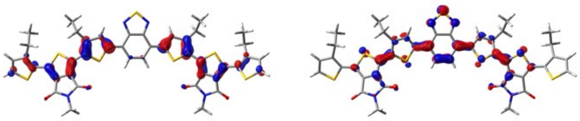
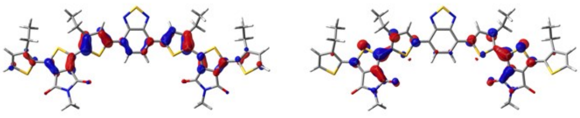
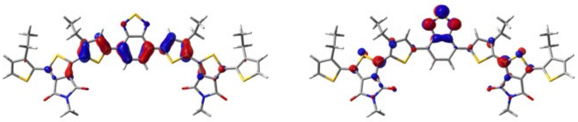
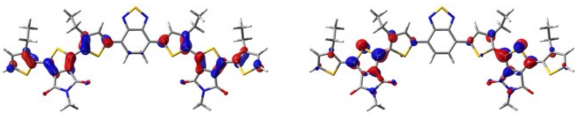
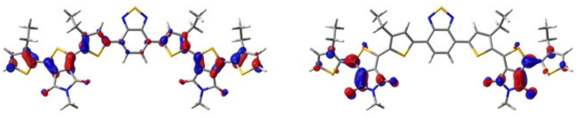
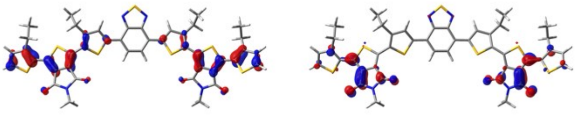
	Transition energy [eV (nm)]	NTO couple hole → electron (λ)
$S_0 \rightarrow S_1$	2.41 (515) *f* = 1.650	 (88.1%)
$S_0 \rightarrow S_2$	2.79 (444) *f* = 0.305	 (55.3%)
		 (43.3%)
$S_0 \rightarrow S_3$	2.97 (417) *f* = 0.089	 (63.5%)
		 (26.6%)

Table S5. Calculated NTOs couples describing the first five singlet excitations for **T7Bz-Dp$_2$** in dichloromethane at the M06-2X/6-31+G(d) level of theory. The f value is the oscillator strength of each transition, while λ value is the natural transition orbital eigenvalue associated with each NTOs couple; orbital isovalue: 0.04 e$^{-1/2}$ bohr$^{-3/2}$.

	Transition energy [eV (nm)]	NTO couple hole → electron (λ)
$S_0 \rightarrow S_1$	2.58 (480) f = 1.556	 (94.5%)
$S_0 \rightarrow S_2$	3.35 (470) f = 0.243	 (59.4%)  (37.6%)
$S_0 \rightarrow S_3$	3.53 (351) f = 0.573	 (69.6%)  (19.6%)
$S_0 \rightarrow S_4$	3.70 (335) f = 0.121	 (56.7%)  (38.8%)

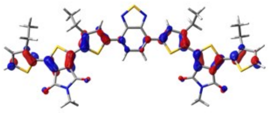
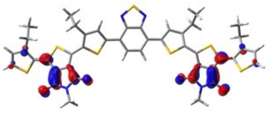
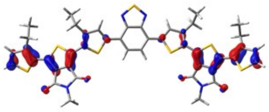
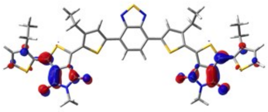
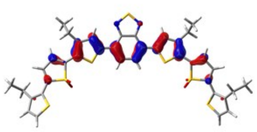
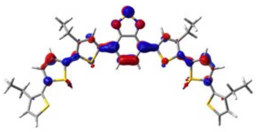
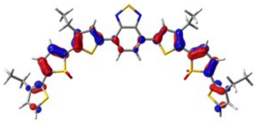
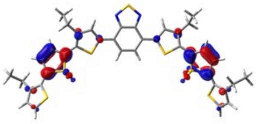
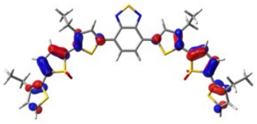
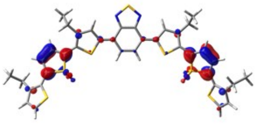
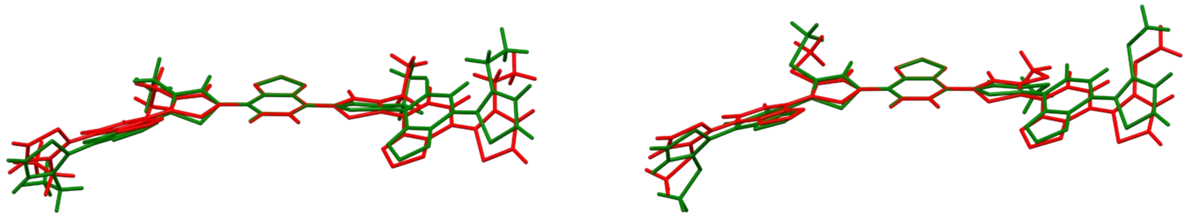
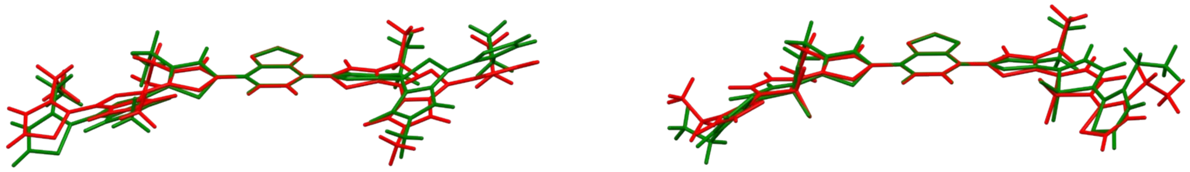
$S_0 \rightarrow S_5$	3.70 (335) $f = 0.205$	  (59.1%)   (34.4%)

Table S6. Calculated NTOs couples describing the first two singlet excitations for **T7SBz-TSO$_2$** in dichloromethane at the M06-2X/6-31+G(d) level of theory. The *f* value is the oscillator strength of each transition, while λ value is the natural transition orbital eigenvalue associated with each NTOs couple; orbital isovalue: 0.04 $e^{-1/2}$ $bohr^{-3/2}$.

	Transition energy [eV (nm)]	NTO couple hole → electron (λ)
$S_0 \rightarrow S_1$	2.39 (520) $f = 1.562$	  (86.2%)
$S_0 \rightarrow S_2$	2.82 (440) $f = 0.621$	  (55.4%)   (43.4%)



(a) **T7Bz-Bz$_2$** (b) **T7SBz-Bz$_2$**



(c) **T7Bz-Dp$_2$** (d) **T7Bz-TSO$_2$**

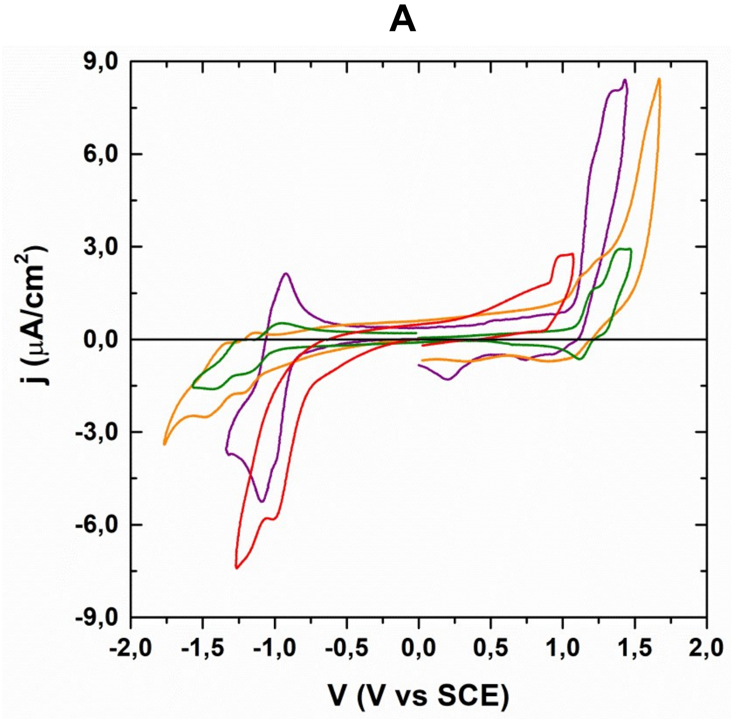
Figure S22. Structural overlay between the optimized ground-state (S_0, green) and excited-state (S_1, red) geometries of all the investigated heptamers. Molecules are overlapped by minimizing the root-mean-square deviation of the atoms of the benzothiadiazole central core. Due to excited-state relaxation, in the S_1 minimum-energy geometry, the central core and the nearby thiophene moieties become virtually coplanar (see Table S7 for numerical data). Optimizations were performed at the PCM-TD-M06/6-31+G(d) level of theory in dichloromethane, within the C_2 symmetry point group.

Table S7. Dihedral angles between the D–A'–D–A–D–A'–D moieties both of the optimized ground-state and S_1 excited-state geometries for all the investigated heptamers. Structures are reported in Figure S22. Optimizations were performed at the PCM-TD-M06/6-31+G(d) level of theory in dichloromethane, within the C_2 symmetry point group.

	S_0 geometry			S_1 geometry		
	D–A' (lateral)	A'–D (middle)	D–A (central)	D–A' (lateral)	A'–D (middle)	D–A (central)
T7Bz-Bz$_2$	41.20°	40.03°	16.97°	35.74°	23.90°	1.91°
T7SBz-Bz$_2$	35.82°	34.13°	14.82°	28.66	19.34°	1.35°
T7Bz-Dp$_2$	41.18°	37.82°	18.96°	34.21°	18.78°	2.02°
T7Bz-TSO$_2$	32.65°	31.24°	15.03°	20.34°	10.20°	2.05°

TD-DFT optimizations carried out on S_1 indicate that, upon relaxation, all the molecules undergo a generalized flattening distortion which leads to a virtually complete planarization of their central D–A–D unit, with a dihedral angle between the Bz central core and the nearby thiophene units of about 1.8° ± 0.3°, to be compared to an average dihedral of 16° ± 2° in the ground state. In Figure S22 and Table S7 are reported the molecular overlay of the optimized geometries of S_1 and S_0 and all the dihedral angles between the different moieties in both states, respectively (Table S7).

VI. CV measurements



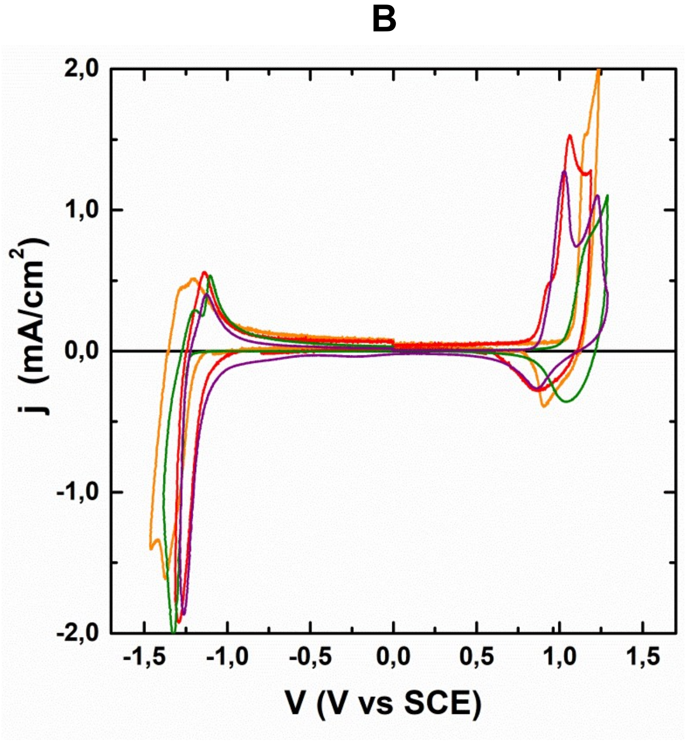


Figure S23. Cyclic Voltammetries of the heptamers in CH_2Cl_2 solution (A) and as thin films drop casted on ITO substrates (B). (T7Bz-Bz_2: orange line, T7Bz-Dp_2: green line, T7Bz-TSO_2: purple line, T7SBz-Bz_2: red line).

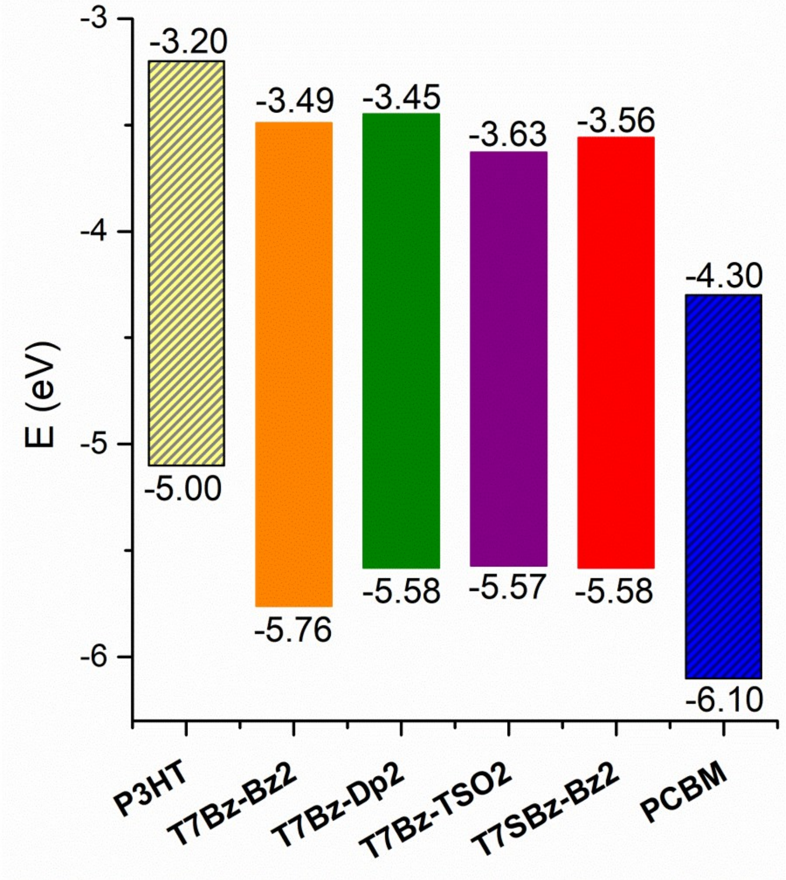


Figure S24. HOMO/LUMO energy levels of the investigated compounds as obtained from the electrochemical analysis in thin film.

VII. Optical characterizations

Table S8.

	λ_{em} [nm]	*eps* [$M^{-1}\cdot cm^{-1}$]	Stokes' shift [eV]	*PLQY* [%]*	*Lifetime [ns]*	K_r [s^{-1}]	K_{nr} [s^{-1}]	K_r/K_{nr}
T7Bz-Bz$_2$	625	37000	0.536	10.5	1.08	9.72E+07	8.29E+08	0.12
T7Bz-Dp$_2$	635	36000	0.537	37.9	2.63	1.44E+08	2.36E+08	0.61
T7Bz-TSO$_2$	590	37000	0.273	0.9	5.84	1.48E+06	1.70E+08	0.01
T7SBz-Bz$_2$	652	37000	0.529	8.9	0.92	9.63E+07	9.91E+08	0.10

*Dichloromethane, air-equilibrated

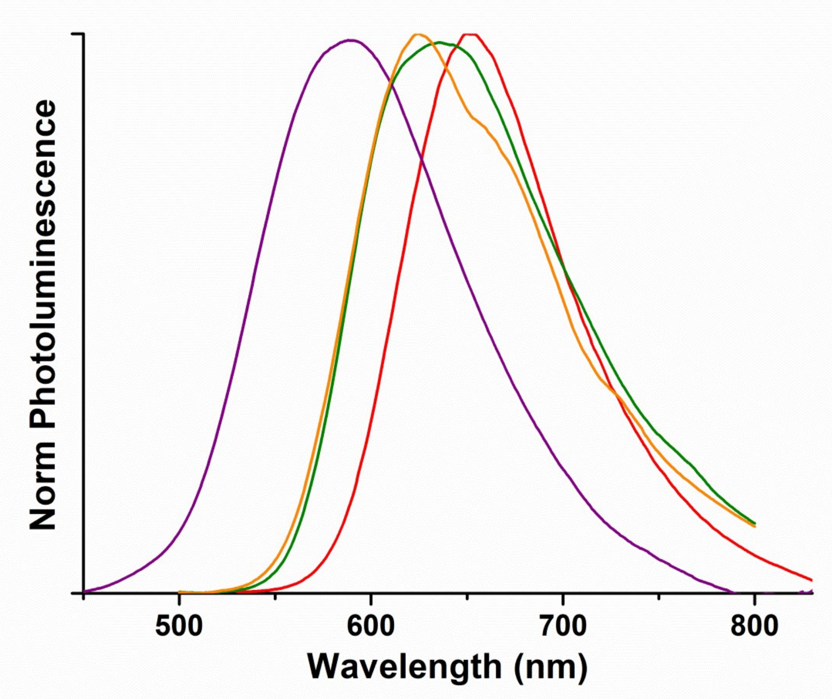


Figure S25. Normalized emission spectra of the heptamers in CH_2Cl_2 solution (T7Bz-Bz$_2$: orange line, T7Bz-Dp$_2$: green line, T7Bz-TSO$_2$: purple line, T7SBz-Bz$_2$: red line).

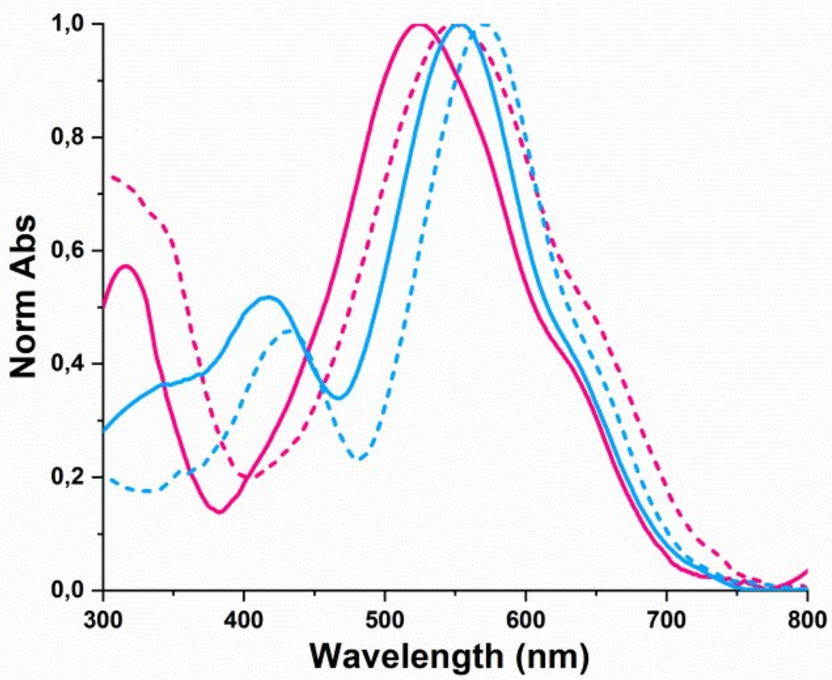


Figure S26. Normalized absorption spectra of the T7SBz-Bz$_2$:T7Bz-TSO$_2$ (pink line) and T7SBz-Bz$_2$:T7Bz-Dp$_2$ blue line) blends as thin film deposited from chlorobenzene (solid line) and THF (dashed line).

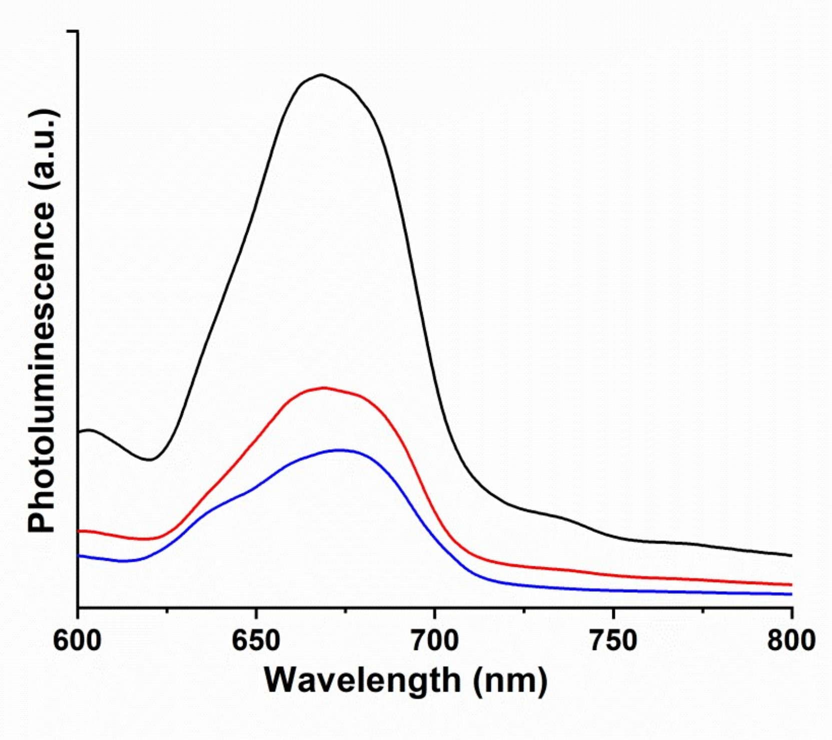


Figure S27. Emission spectra of T7SBz-Bz$_2$ in thin film (black line) and in blend (1:1 w/w) with P3HT (red line) and PCBM (blue line).

VIII. AFM

Table S9

	Roughness [nm]	Thickness [nm]
T7Bz-Bz$_2$:P3HT	19	100±30
T7Bz-Dp$_2$:P3HT	32	120±20
T7Bz-TSO$_2$:P3HT	10	100±20
T7SBz-Bz$_2$:P3HT	12	100±20
T7Bz-Bz$_2$:PCBM	2	190±10
T7Bz-Dp$_2$:PCBM	16	210±20
T7Bz-TSO$_2$:PCBM	4	210±30
T7SBz-Bz$_2$: PCBM	2	230±30

Table S10

	Roughness [nm]	Thickness [nm]
T7Bz-TSO$_2$:T7SBz-Bz$_2$ (chlorobenzene)	21	390 ± 40
T7Bz-TSO$_2$:T7SBz-Bz$_2$ (THF)	36	140 ± 40
T7Bz-Dp$_2$:T7SBz-Bz$_2$ (chlorobenzene)	53	400 ± 70
T7Bz-Dp$_2$:T7SBz-Bz$_2$ (THF)	28	260 ± 40

IX. WAXS and GIWAXS measurements

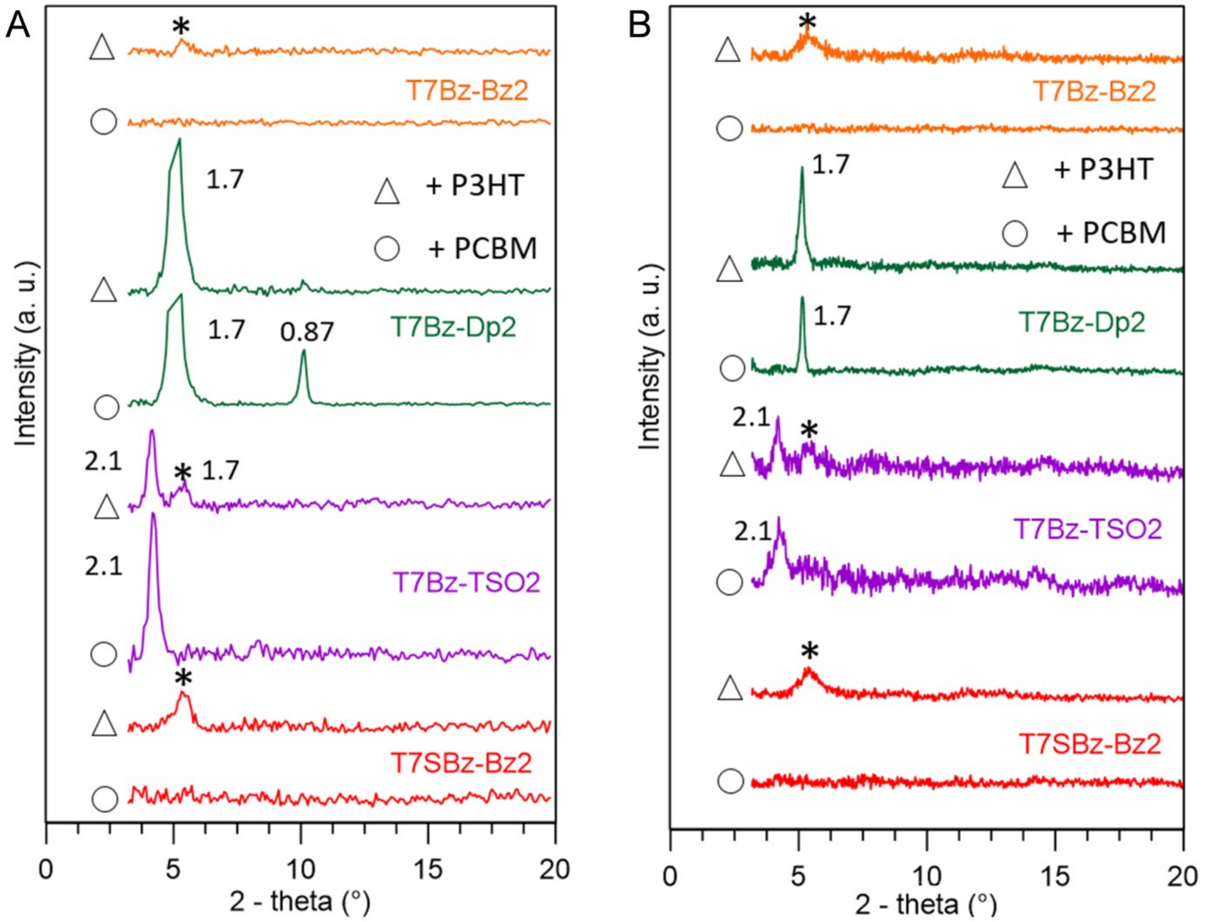


Figure S28. WAXS (A) and GIWAXS (B) scans of the films of heptamers blended with P3HT (triangle) or PCBM (circle). Peaks with asterisk identify P3HT reflection due to *1 0 0* plane.

Heptamers:P3HT and PCBM blends

Table S11. Size of the coherent crystalline domains (nm) calculated from Full Width at Half Maximum (FWHM) by Scherrer equation. e.s.d. ± 5.

	from WAXS		from GIWAXS	
	+P3HT	**+PCBM**	**+P3HT**	**+PCBM**
T7Bz-Bz$_2$	18	–	17	–
T7Bz-Dp$_2$	30	47	47	60
T7Bz-TSO$_2$	28	26	26	20
T7SBz-Bz$_2$	13	–	13	–

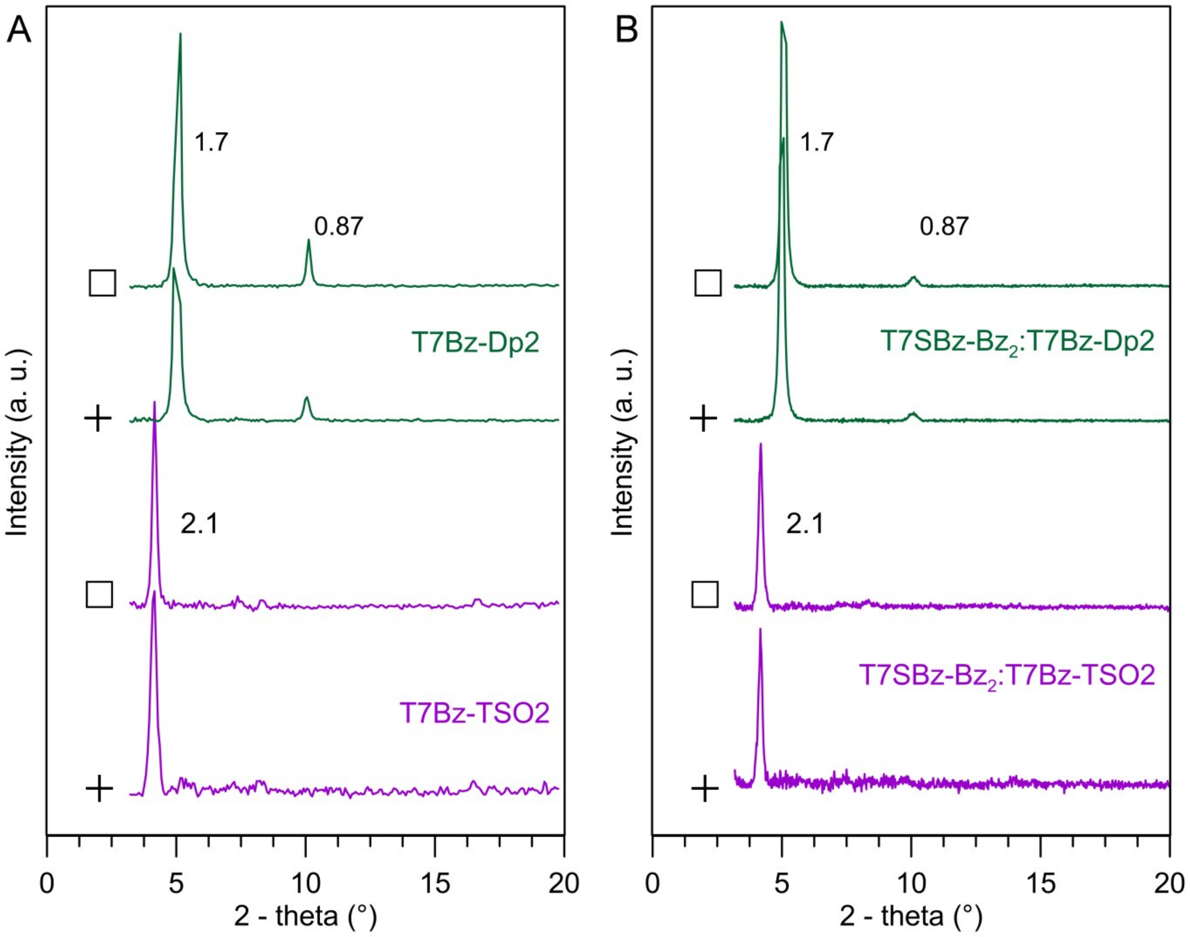


Figure S29. WAXS (A) and GIWAXS (B) scans of heptamer:heptamer blends; film processed from chlorobenzene (square) and from THF (cross). Interlayer distances of the peaks are reported in nm.

Heptamer:heptamer blends

Table S12. Size of the coherent crystalline domains (nm) calculated from Full Width at Half Maximum (FWHM) by Scherrer equation. e.s.d. ± 5.

	from WAXS		from GIWAXS	
T7SBz-Bz$_2$ *with*	**chlorobenzene**	**THF**	**chlorobenzene**	**THF**
T7Bz-Dp$_2$	62	63	63	59
T7Bz-TSO$_2$	47	33	47	52

X. BHJ solar cell

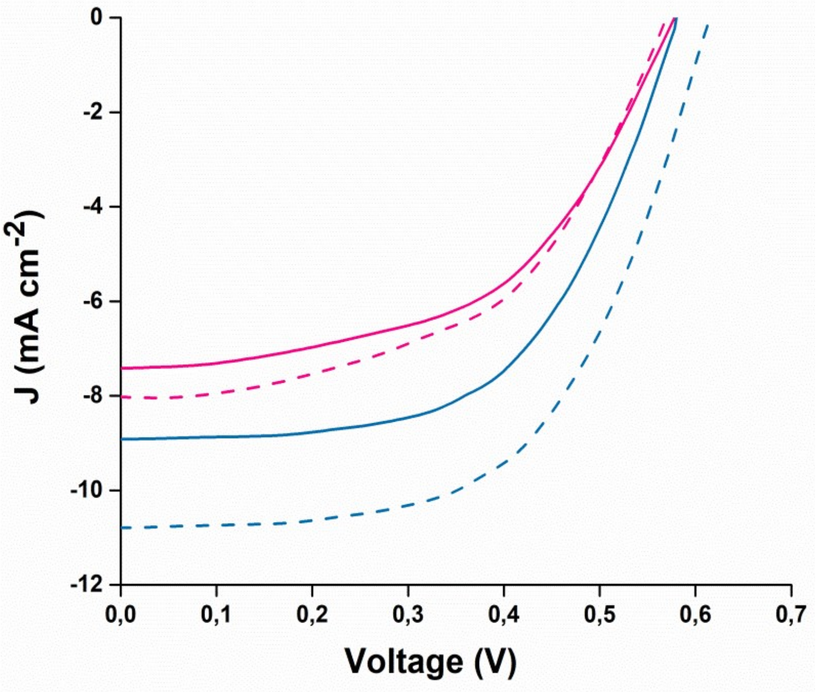


Figure S30. J–V curves of the cells prepared with blends of T7SBz-Bz$_2$:T7Bz-TSO$_2$ (pink line) and T7SBz-Bz$_2$:T7Bz-Dp$_2$ (blue line) from chlorobenzene (solid line) and THF (dashed line).

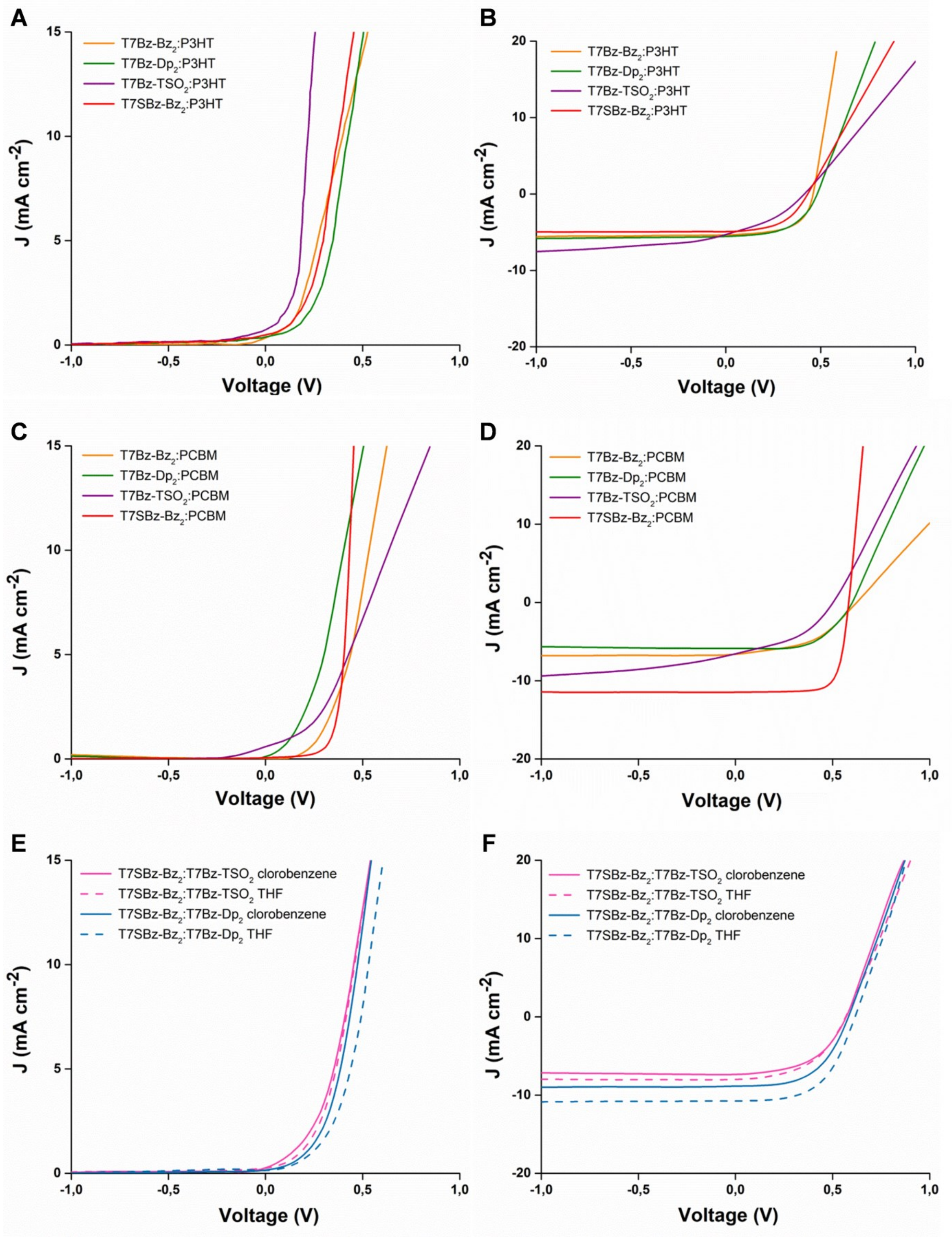


Figure S31. J–V curves in dark (left) and under illumination in the range -1.0/+1.0 V and +20/-20 mA·cm^{-2} (right) for the cells prepared with blends of heptamers:P3HT (A, B), heptamers:PCBM (C, D) (orange line T7Bz-Bz$_2$; red line T7SBz-Bz$_2$; green line T7Bz-Dp$_2$; purple line T7Bz-TSO$_2$) and heptamers:heptamers (E, F) (pink line T7S-Bz-Bz$_2$:T7-Bz-TSO$_2$; blue line T7S-Bz-Bz$_2$:T7-Bz-Dp$_2$) from chlorobenzene (solid line) and THF (dashed line).

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