Supporting Information

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Solution-Processable Donor-Acceptor-Donor Oligomers with Cross-Linkable Functionality

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Materials

All experiments involving air and/or water sensitive compounds were performed under inert atmosphere using a dual vacuum/nitrogen line and Schlenk techniques or in a glove box. All reagents were purchased from commercial suppliers (e.g. Aldrich) and were used as received and without further purification unless otherwise specified. All the solvents used under inert atmosphere were dried by refluxing over a suitable drying agent under nitrogen and deoxygenated before use by freeze-pump-thaw cycling. Diethyl ether and tetrahydrofuran were dried with sodium as drying agent and chloroform with calcium hydride. N-Bromosuccinimide (Aldrich) was recrystallized from water and dried under dynamic vacuum overnight at 40 °C prior to use. The intermediate compounds **7**, **8**, and **9** were prepared according to the procedures described in ref. 1 **(7)**, 2 **(8)**, and 3 **(9)**.

Measurements

NMR spectra were recorded on a Brucker "Advance II" spectrometer (300 MHz or 400 MHz) in $CDCl_3$. ^{1}H and ^{13}C NMR spectra are referenced to the residual solvent impurity peak of $CDCl_3$. Multiplicities were abbreviated as: singlet (s), doublet (d), triplet (t), quartet (q), quintet (quint), multiplet (m), doublet of doublets (dd), doublet of triplets (dt), triplet of doublets (td), broad signal (br).

Elemental analyses were performed by LAIST, IST elemental analysis services. Matrix-assisted laser desorption ionization (MALDI) mass spectra were performed on a Voyager-DE™ PRO Biospectrometry Workstation MALDI/TOF/MS analyzer (Applied Biosystems) by LAREQUIMTE.

Differential scanning calorimetry (DSC) was performed in the temperature range 0 °C to 340 °C at a heating rate of 10 °C/min in a 2920 Modulated DSC TA Instruments.

UV/Visible absorption spectra were recorded in a Cecil 7200 spectrophotometer. Thin films were prepared by spin-coating solutions of the compounds in toluene (30 mg/ml) onto quartz substrates at 1800 rpm for 45 seconds.

Cyclic voltammetry (CV) measurements were performed in a Solartron potentiostat using 0.1 M tetrabutylammonium tetrafluorborate/CH_3CN supporting electrolyte, at a scan rate of 50 mV/s. A saturated calomel reference electrode (SCE) calibrated against ferrocene, Fc/Fc^+ (0.42 V), a platinum wire as counter electrode and a platinum disk as working electrode were used. The compounds were drop cast from toluene solutions onto the working electrode. As the energy level of Fc/Fc^+ is at 4.8 eV below the vacuum level we calculate HOMO (eV) = – ($E_{onset,ox}$ (eV) + 4.38) and LUMO (eV) = - ($E_{onset,red}$ (eV) + 4.38).

Photoluminescence spectra were measured on a SPEX Fluorolog 212I spectrophotometer, at the right angle geometry, S/R mode, and corrected for instrumental wavelength dependence, optics and detector wavelength dependence. The measured wavelength range with this equipment, from 250 nm up to 800 nm. For each pair neat film- BHJ film, PL were measured in the same experimental conditions.

Current–voltage (I–V) characteristics of photovoltaic devices were measured under inert atmosphere (N2). Power conversion efficiencies (PCEs) were calculated using a solar simulator (Oriel instruments 92250A-1000) with simulated AM 1.5 G illumination. The light intensity was measured with a calibrated solar cell. The cell active area is 0.16 cm^2. External quantum efficiency (EQE) spectra were obtained under short-circuit conditions, using a homemade system with a Xe lamp as light source.

Synthesis

2-(6-bromohexyl)thiophene (1a). Thiophene (0.40 ml, 5.00 mmol) was dissolved in dry THF, under nitrogen atmosphere. The solution was cooled to -78 °C and 0.8 ml (5.28 mmol) of TMEDA (N,N,N',N'-Tetramethylethane-1,2-diamine) was added. 3.3 ml (5.28 mmol) of N-butyllithium (1.6 M solution in hexanes) were added drop wise, and the mixture was left to stir at -40°C for 1 hour, and then at 0°C for 30 min. The mixture was re-cooled to -40°C and 1,6-dibromohexane (4.6 ml, 30 mmol) was added all at once. The cooling bath was left for one hour, and the mixture was left at room temperature for 2 more hours. Water and diethyl ether were added and phases were separated. The aqueous phase was extracted with diethyl ether, and the collected organic extracts were washed with water, dried with anhydrous $MgSO_4$, filtered, and concentrated. The excess 1,6-dibromohexane was distilled under reduced pressure, and the remaining mixture was purified by silica gel column chromatography, using petroleum ether 40/60 as eluent to yield the pure product as a colorless oil (0.62 g, 2.5 mmol). η=46 %. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.11 (dd, *J* = 5.0, 1.2 Hz, 1H), 6.92 (dd, *J* = 5.1, 3.4 Hz, 1H), 6.78 (ddt, *J* = 3.4, 1.1, 1.0 Hz, 1H), 3.41 (t, *J* = 6.9 Hz, 2H), 2.84 (td, *J* = 7.7, 1.0 Hz, 2H), 1.87 (quint, *J* = 7.0 Hz, 2H), 1.70 (quint, *J* = 7.5 Hz, 2H), 1.36 - 1.53 (m, 4H). ^{13}C-NMR (100 MHz, $CDCl_3$, δ): 145.39, 126.64, 123.99, 122.81, 33.85, 32.64, 31.51, 29.73, 28.13, 27.85.

5-(6-bromohexyl)-2,2´-bithiophene (2b). It was prepared analogously to **2a** starting from 2,2´-bithiofene (Aldrich). η=44 %. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.17 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.10 (dd, *J* = 3.6, 1.1 Hz, 1H), 6.97 (dd, *J* = 5.3, 3.6 Hz, 2H), 6.68 (dd, *J* = 3.6, 1.0 Hz, 1H), 3.41 (t, *J* = 6.8 Hz, 2H), 2.8 (t, *J* = 7.18 Hz, 2H), 1.87 (quint, *J* = 6.8 Hz, 2H), 1.70 (quint, *J* = 7.0 Hz, 2H), 1.35-1.52 (m, 4H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ ppm: 145.20,

138.20, 135.21, 128.01, 125.16, 124.10, 123.71, 123.36, 34.21, 32.98, 31.67, 30.31, 28.46, 28.46, 28.20. Anal. Calcd for $C_{14}H_{17}BrS_2$: C 51.10; H 5.09; S 19.94. Found: C 51.06; H 5.20; S 19.47.

2-bromo-5-(6-bromohexyl)thiophene (3a). **2a** (0.57 g, 2.30 mmol) was dissolved in 2 ml of chloroform and the solution was protected from light and cooled to 0 °C. Acetic acid (2 ml) was added and *N*-Bromossuccinimide (0.43 g, 2.40 mmol) was added. The mixture was left to stir in the ice bath for 30 minutes, and then overnight at room temperature. Water was added and the product was extracted several times with chloroform. The collected organic extracts were washed with an aqueous solution of $Na_2S_2O_5$, and water until neutral pH, dried over anhydrous $MgSO_4$, filtered, and concentrated. The mixture was then purified by silica gel column chromatography, using petroleum ether 40/60 as eluent to yield the pure product as a yellowish oil (0.57 g, 1.74 mmol). η=76 %, ^{1}H NMR (300 MHz, $CDCl_3$, δ): 6.84 (d, *J* = 3.6 Hz, 1H), 6.53 (dt, *J* = 3.6, 0.9 Hz, 1H), 3.40 (t, *J* = 6.8 Hz, 2H), 2.71 - 2.78 (m, 2H), 1.86 (quint, *J* = 7.2 Hz, 2H), 1.65 (quint, *J* = 7.5 Hz, 2H), 1.31-1.52 (m, 4H). ^{13}C-NMR (75 MHz, $CDCl_3$, δ): 147.59, 129.83, 124.89, 109.11, 34.24, 33.02, 31.60, 30.57, 28.44, 27.22.

5-bromo-5´-(6-bromohexyl)-2,2´-bithiophene (3b). It was prepared analogously to **3a** starting from **2b**. η = 76 %, ^{1}H NMR (300 MHz, $CDCl_3$, δ): 6.94 (d, *J* = 4.0 Hz, 1H), 6.92 (d, *J* = 3.6 Hz, 1H), 6.83 (d, *J* = 4.0, 0.9 Hz, 1H), 6.67 (dt, *J* = 3.6, 0.9 Hz, 1H), 3.42 (t, *J* = 6.8 Hz, 2H), 2.79 (t, *J* = 7.6 Hz, 2H), 1.87 (quint, *J* = 7.0 Hz, 2H), 1.69 (quint, *J* = 7.6 Hz, 2H), 1.52-1.31 (m, 4H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ ppm: 145.79, 139.73, 134.21, 130.83, 125.26, 124.05, 123.43, 110.55, 34.17, 32.98, 31.65, 30.32, 28.46, 28.19. Anal. Calcd for $C_{14}H_{16}Br_2S_2$: C 44.93; H 4.62; S 14.17. Found: C 41.19; H 3.95; S 15.71.

3-({[6-(5-bromothiophen-2-yl)hexyl]oxy}methyl)-3-methyloxetane (4a). 8 ml of an aqueous saturated solution of NaOH was added to a solution of 1.0 ml (9.92 mmol) of 3-methyl-3-oxetanemethanol (Aldrich) in THF, containing 0.15 g (0.47 mmol) of TBABr and a few crystals of KI. The mixture was stirred for 30 minutes at 0 °C (ice-bath) and then added dropwise to a solution of 0.57 g (1.74 mmol) of **3a** in 10 ml of THF, at 0 °C, under stirring. The mixture was stirred for 30 minutes at 0 °C, and then warmed to reflux for 48 hours. The mixture was cooled to room temperature and the THF was evaporated under reduced pressure. Water and chloroform were added and the phases were separated. The aqueous phase was extracted with dichloromethane and the collected organic extracts were washed with water until neutral pH. The organic phase was dried over anhydrous $MgSO_4$, filtered and concentrated. The residue was purified by silica gel column chromatography, using petroleum ether/ethyl acetate (80/20, v/v) as eluent to yield the pure product as a pale yellow oil (0.17 g, 0.48 mmol). η = 28 %. ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 6.8 (d, *J* = 3.6 Hz, 1H), 6.5 (d, *J* = 3.6 Hz, 1H), 4.5 (d, *J* = 5.9 Hz, 2H), 4.3 (d, *J* = 5.7 Hz, 2H), 3.4 (t, *J* = 6.2 Hz, 2H), 3.5 (s, 2H) 2.7 (t, *J* = 7.6 Hz, 2H) 1.5-1.9 (m, 4H) 1.4 (quint, *J* = 3.4 Hz, 4H) 1.3 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$, δ):147.45, 129.39, 124.41, 108.60, 80.25, 76.08, 71.49, 39.91, 31.38, 30.26, 29.42, 28.74, 25.87, 21.39.

3-({[6-(5´-bromo-2,2´-bithiophen-5-yl)hexyl]oxy}methyl)-3-methyloxetane (4b). It was prepared analogously to **4a** starting from **3b**. η = 28 %. ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 6.94 (d, *J* = 3.8 Hz, 1H), 6.91 (d, *J* = 3.6 Hz, 1H), 6.83 (d, *J* = 3.8 Hz, 1H), 6.67 (dt, *J* = 3.6, 0.9 Hz, 1H), 4.50 (d, *J* = 5.9 Hz, 2H), 4.35 (d, *J* = 5.7 Hz, 2H), 3.47 (d, *J* = 4.2 Hz, 2H), 3.45 (d, *J* = 6.4 Hz, 2H), 2.78 (t, *J* = 7.9 Hz, 2H), 1.61-1.54 (m, 4H), 1.47-1.37 (m, 4H), 1.30 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$, δ): 16.07, 139.77, 134.12, 130.81, 125.18, 124.03, 123.38,

110.50, 80.58, 76.43, 71.85, 40.27, 31.83, 30.42, 29.78, 29.18, 26.24, 27.73. Anal. calcd for $C_{19}H_{25}BrO_2S_2$: C 52.90; H 5.80; S 14.69; found: C 53.14; H 5.87; S 14.93.

3-({[6-(5-tributylstannylthiophen-2-yl)hexyl]oxy}methyl)-3-methyloxetane (5a) A solution of **4a** (0.86 g, 2.4 mmol) in dry THF (15 ml) was cooled to -78 °C, and 2.8 ml (4.8 mmol) of *tert*-Butyllithium (1.7 M in pentane) were added dropwise. The mixture was left to stir at low temperature (-78 °C) for 2 h, after which 1.4 ml (4.8 mmol) of tributyltin chloride were added dropwise. The cool bath was removed and the mixture was left to stir for 12 h at room temperature. Water and diethyl ether were added and phases were separated. The aqueous phase was extracted with diethyl ether and the collected organic extracts were washed several times with water until neutral pH. The organic phase was then dried under anhydrous $MgSO_4$, filtered, and concentrated. The aromatic region of the ^{1}H-NMR (300 MHz, $CDCl_3$) shows only two doublets, at δ (ppm) 6.98 (d, *J* = 3.1 Hz, 1H) and 6.90 (d, *J* = 3.0 Hz, 1H), indicating complete conversion. Due to the instability of the tributyltin groups in silica, the compund was used without any further purification.

3-({[6-(5´-tributylstannyl-2,2´-bithiophen-5-yl)hexyl]oxy}methyl)-3-methyloxetane (5b). It was prepared analogously to **5a** starting from **4b**. The aromatic region of the ^{1}H-NMR (300 MHz, $CDCl_3$) shows two doublets and two doublets of doublets: δ (ppm): 7.21 (dd, *J* = 5.7, 3.2 Hz, 1H), 7.04 (d, *J* = 3.4 Hz, 1H), 6.97 (d, *J* = 3.4 Hz, 1H), 6.66 (dd, *J* = 4.2, 0.8 Hz, 1H), indicating complete conversion. Due to the instability of the tributyltin groups in silica, the compound was used without any further purification.

5,5''-di(tributylstannyl)-2,2':5',2''-terthiophene (6). 5,5"-dibromo-2,2':5',2"-terthiophene (0.403 g, 0.99 mmol) prepared accordingly to ref. 4 was dissolved in dried THF (20 ml). The solution was cooled down to -45 °C and *tert*-BuLi (2.54 ml, 4.32 mmol) were added

dropwise. The mixture was left to stir at -45 °C for 2 hours, and tributyltin chloride (1.1 ml, 3.92 mmol) was added dropwise. The mixture was left to warm to room temperature and stirred overnight, under N_2. Water was added and phases were separated. The aqueous phase was extracted with diethyl ether and the collected organic extracts were washed several times with water, dried over anhydrous $MgSO_4$, filtered, and concentrated. The resultant mixture was analyzed by ^{1}H-NMR. The aromatic region of the ^{1}H-NMR (300 MHz, $CDCl_3$) shows one singlet and two doublets: δ (ppm): 7.28 (d, *J* = 3.4 Hz, 2H), 7.07 (s, 2H), and 7.06 (d, *J* = 5.5 Hz, 2H), indicating complete conversion. Due to the instability of the tributyltin groups in silica, and since the contaminant species are unreactive towards the following reaction, the compound was used without purification.

General procedure for the Stille coupling reactions: 1.2 mmol of the oxetane-functionalized reactant (**4a**, **5a**, or **5b**) and 0.5 mmol of the central unit (**6**, **7**, **8**, or **9**) were dissolved in dry THF (4 ml) and the solution was degassed. The solution was added to a schlenk containing 8 mg (1.1×10^{-2} mmol) of bis(triphenylphosphine)palladium(II) dichloride ($PdCl_2(PPh_3)_2$) (Aldrich), charged with nitrogen, and was left to stir overnight, at 70 °C, under inert atmosphere.

SM0. The mixture was poured in methanol to precipitate the product. After washing with methanol, the pure product was obtained as a dark red solid. η = 47 %. ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 7.05 (s, 2H) 7.05 (d, *J* = 3.4 Hz, 2H) 7.00 (d, *J* = 3.8 Hz, 2 H) 6.98 (d, *J* = 3.6 Hz, 2H) 6.70 (d, *J* = 3.6 Hz, 2H) 4.51 (d, *J* = 5.7 Hz, 4H) 4.35 (d, *J* = 5.7 Hz, 4H) 3.47 (s, 4 H) 3.46 (t, *J* = 6.5 Hz, 4H) 2.80 (t, *J* = 7.5 Hz, 4H) 1.70 (quin, *J* = 7.3 Hz, 4H) 1.60 (m, 4 H) 1.41 (m, 8H), 1.31 (s, 6H). MALDI-TOF, *m/z* (Da): 780.21 (M^+). Calcd. for $C_{42}H_{52}O_4S_5$ 780.25.

SM1. The mixture was poured in methanol to precipitate the product. After washing with methanol and ethanol, the pure product was obtained as a dark red solid. η = 37 %. ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 8.04 (d, *J* = 4.0 Hz, 2H), 7.84 (s, 2H), 7.20 (d, *J* = 3.8 Hz, 2H), 7.11 (d, *J* = 3.3 Hz, 2H), 6.73 (d, *J* = 3.5 Hz, 2H), 4.51 (d, *J* = 5.5 Hz, 4H), 4.36 (d, *J* = 5.8 Hz, 4H), 3.48 (s, 4 H), 3.47 (t, *J* = 6.5 Hz, 4H), 2.83 (t, *J* = 7.5 Hz, 4H), 1.69-1.76 (m, 4H), 1.58-1.65 (m, 4H), 1.40-1.45 (m, 8H), 1.31 (s, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$, δ): 152.55, 145.86, 139.37, 137.49, 134.71, 128.28, 125.55, 125.14, 125.07, 123.87, 123.80, 80.28, 77.23, 76.12, 71.55, 39.96, 31.53, 30.18, 29.46, 28.87, 25.93, 21.41. MALDI-TOF, m/z (Da): 832.25 (M+). Calcd. for $C_{44}H_{52}N_2O_4S_5$ 832.25.

SM2. The mixture was poured in n-hexane to precipitate the product. After washing with n-hexane, the pure product was obtained as a dark red solid.η = 83 %. ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 7.43 (d, *J* = 4.0 Hz, 2H), 7.19 (d, *J* = 4.0 Hz, 2H), 7.15 (d, *J* = 3.6 Hz, 2H), 6.74 (d, *J* = 3.4 Hz, 2H), 4.51 (d, *J* = 5.7 Hz, 4H), 4.36 (d, *J* = 5.7 Hz, 4H), 3.47 (t, *J* = 4.9 Hz, 8H), 2.83 (t, *J* = 10.0 Hz, 4H), 1.62-1.56 (m, 8H), 1.44-1.39 (m, 8H), 1.31 (s, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$, δ): 152.22, 147.68, 145.05, 141.59, 133.64, 132.22, 127.81, 125.64, 125.40, 124.02, 120.46, 80.56, 76.43, 71.84, 40.26, 31.80, 30.51, 29.78, 29.16, 26.23, 27.73. Anal. Calcd for $C_{44}H_{50}N_4O_8S_5$: C 57.24; H 5.45; N 6.07; S 17.36; found: C 56.02; H 5.28; N 6.00; S 17.18.

SM3. The mixture was poured in n-hexane to precipitate the product. After washing with n-hexane, and methanol, the pure product was obtained as a dark purple solid. η = 63 %. ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 7.52 (d, *J* = 4.2 Hz, 2H), 7.11 (d, *J* = 4.0 Hz, 2H), 6.72 (d, *J* = 3.6 Hz, 2H), 6.69 (s, 2H), 4.51 (d, *J* = 5.7 Hz, 4H), 4.35 (d, *J* = 5.7 Hz, 4H), 3.47 (t, *J* = 4.7 Hz, 8H), 2.81 (t, *J* = 7.4 Hz, 4H), 1.72-1.58 (m, 8H), 1.43-1.41 (m, 8H), 1.31 (s, 6H). ^{13}C-

NMR (100 MHz, $CDCl_3$, δ): 147.54, 141.20, 136.04, 134.10, 129.22, 128.36, 125.64, 125.22, 124.56, 118.05, 80.60, 76.46, 71.86, 40.29, 31.81, 30.53, 29.79, 29.19, 26.25, 21.74. Anal. calcd for $C_{42}H_{52}O_6S_5$: C 62.04; H 6.45; S 19.71; found: C 59.39; H 6.39; S 17.34 (differences between calculated values and experimentally determined are attributed to adsorbed water, ex: anal. calcd. for $C_{42}H_{52}O_6S_5.2H_2O$ is C 59.40; H 6.65; S 18.86).

Figures

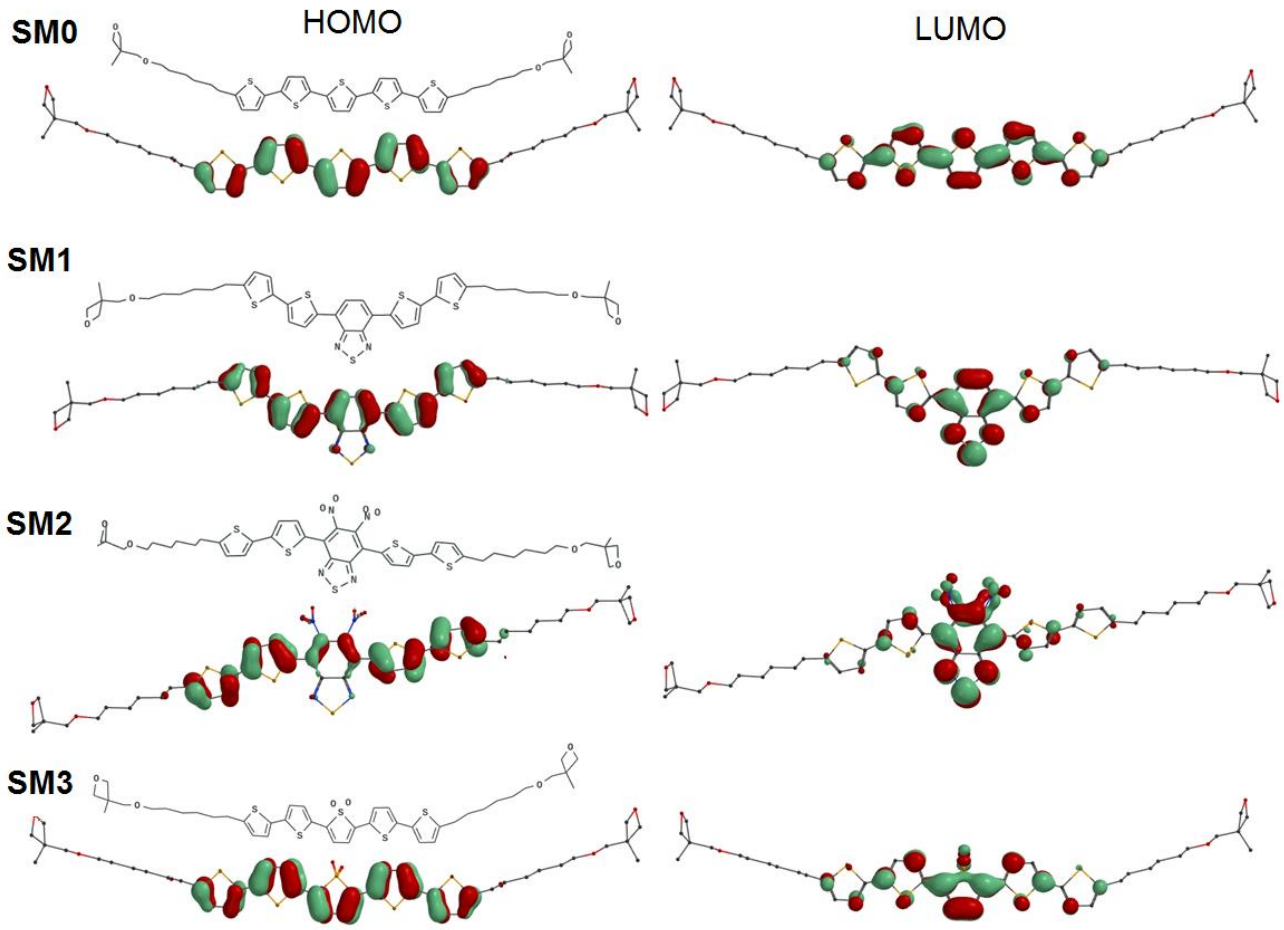

Figure S1 – (Color figure) Optimized ground-state (S0) geometric structures and HOMO and LUMO wavefunctions representation for the molecules SM0-SM3 as determined at the B3LYP/6-31G* DFT.

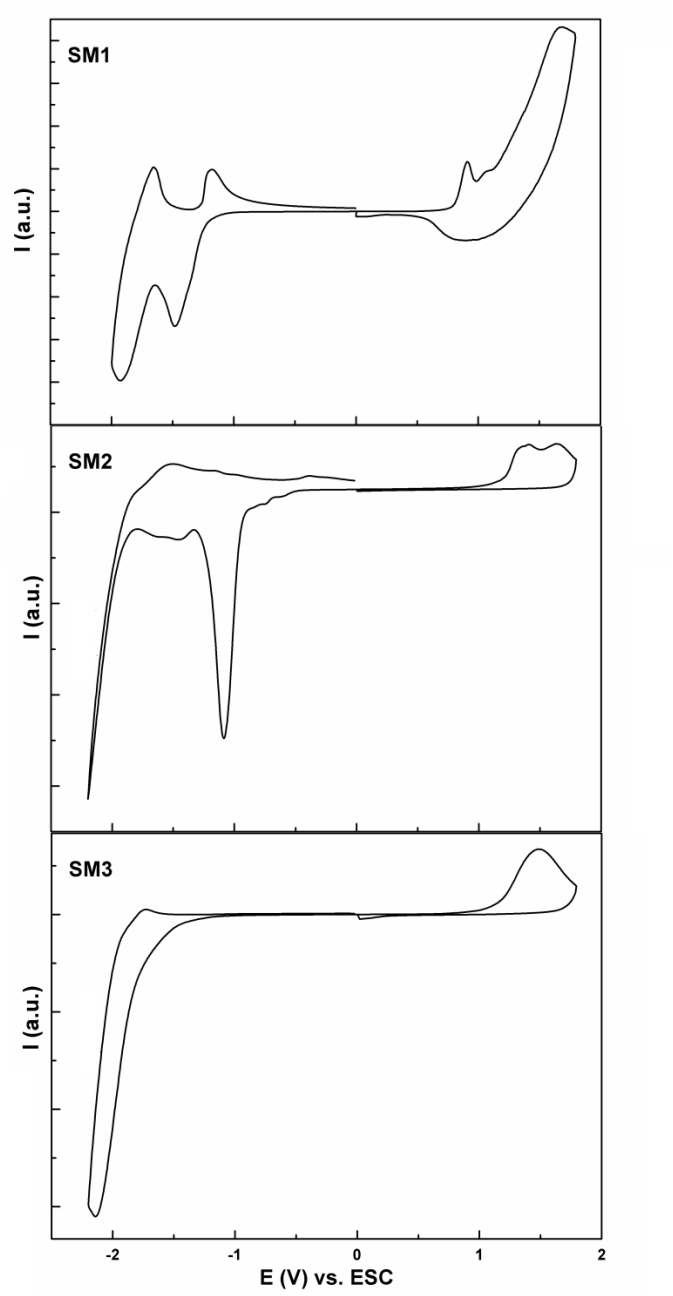

Figure S2 - Cyclic voltamograms obtained at 50 mV/s in a 0.1 M tetrabutylammonium tetrafluoroborate/acetonitrile electrolyte for SM1-SM3 drop cast over a Pt working electrode.

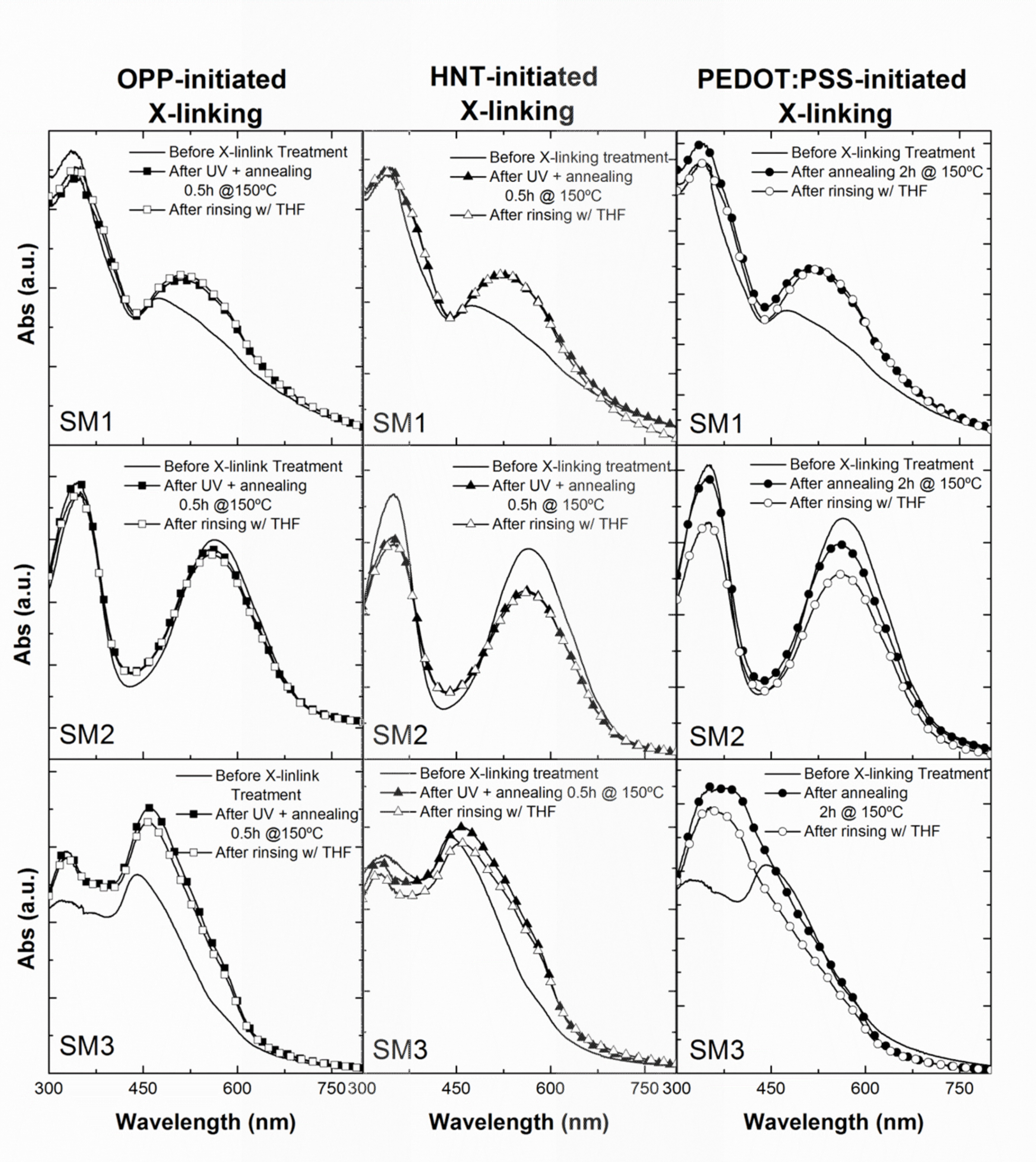

Figure S3 - Comparison between absorption spectra (non-normalized) of films of SM1-SM3 submitted to the three crosslinking treatments at the several stages: before crosslinking treatment; after UV (for OPP and HNT – initiated crosslinking) and temperature annealing; and after rinsing with THF.

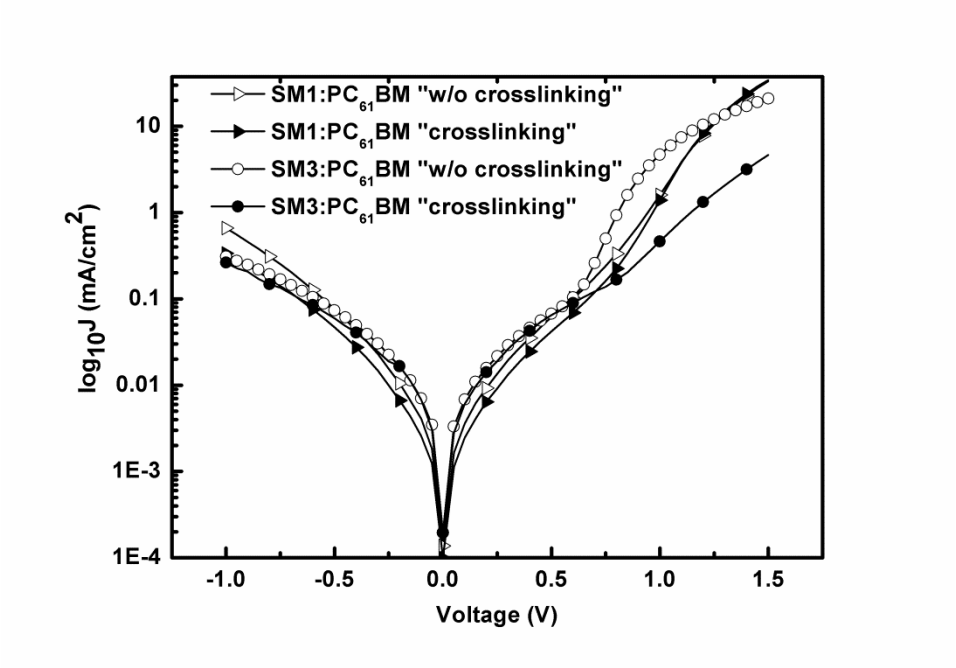

Figure S4 – Dark J-V curves for the BHJ cells made with SM1:PCBM and SM3:PCBM without and with crosslinking treatment.

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Solution-processable donor-acceptor-donor oligomers with crosslinkable functionality

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