Supporting Information

The influence of alkyl side chains on molecular packing and solar cell performance of dithienopyrrole-based oligothiophenes

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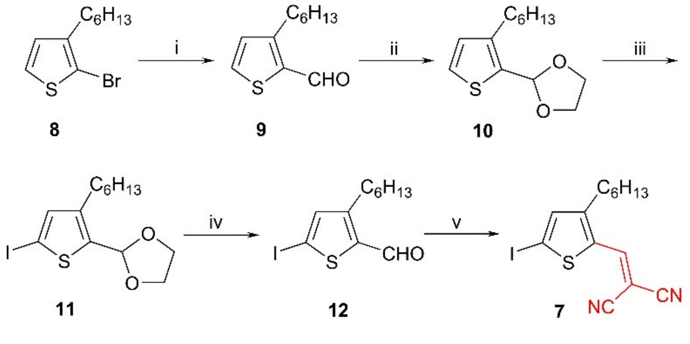
Synthesis: All reactions were performed under an argon atmosphere in dry solvents. Compounds **8**,[1,2] **9**,[3] and **10**[4] were synthesized according to the literature procedures.



Scheme S1. (i) ^{n}BuLi-THF, DMF, -78 °C – 40 °C, 84%. (ii) $C_2H_4(OH)_2$, p-TSA, toluene, reflux, 18 h, 95%. (iii) ^{n}BuLi-THF, I_2, -78 °C – r.t., 15h, 82%. (iv) HCl·aq. (25%), ^{n}PrOH, 90 °C, 6 h, 98%. (v) $CH_2(CN)_2$, NH_4OAc, 1,2-DCE-EtOH, 60 °C, 16h, 94%.

2-(3-Hexyl-5-iodo-2-thienyl)-[1,3]dioxolane (11). To a solution of 2-(3-hexyl-2-thienyl)-[1,3]dioxolane **10** (24.2 g, 100.6 mmol) in 150 ml THF was added *n*-butyl lithium (72 ml, 115 mmol, 1.6 molar in *n*-hexane), at -80 °C. After maintaining the temperature for about 20 minutes a solution of iodine (30.46 g, 115 mmol) in 150 ml THF was added. A pale yellow precipitate formed and the mixture became viscous. The mixture was stirred for further 45 minutes. The temperature was increased slowly to -15 °C, the cooling bath was removed and the reaction mixture stirred at room temperature for 14 hrs. The mixture was quenched with water, NH_4Cl (1M) solution and aqueous $NaHSO_3$ solution. The aqueous phase was extracted twice with diethyl ether and the combined organic layers were washed successively with water, satd. $NaHCO_3$ solution, and brine. Removal of the solvent furnished a crude product, which was purified by column chromatography on silica with petroleum ether-DCM (1:1,v/v). Yield: 30.05 g (82%) of pale yellow oil; ^{1}H-NMR ($CDCl_3$, 400 MHz): $\delta = 0.88$ (t, $J = 6.8$ Hz, 3H, CH_3), 1.29 (m, 6H, CH_2), 1.55 (tt, J= 7.6 Hz, 2H, CH_2), 2.58 (t, $J = 7.8$ Hz, 2H, CH_2), 3.92-4.02 (m, 2H, OCH_2), 4.05-4.15 (m, 2H, CH_2O), 6.06 (s, 1H, C*H*), 6.99 (s, 1H, Th-*H*). ^{13}C-NMR ($CDCl_3$, 100 MHz): $\delta = 14.1$, 22.5, 28.1, 29.0, 30.7, 31. 6, 65.2, 73.8, 98.6, 138.8, 140.8, 143.5. Elemental analysis for $C_{13}H_{19}IO_2S$: calcd. C, 42.63; H, 5.23; S, 8.75%; found: C, 42.73; H, 5.29; S, 8.67.

3-Hexyl-5-iodothiophene-2-carbaldehyde (12). A mixture of **11** (5.0 g, 14 mmol) and hydrochloric acid (25 wt%, 50 ml) was heated to 90 °C under vigorous stirring. After 5 hrs the mixture is cooled and the phases separated. The aqueous phase was extracted twice with pentane. The combined organic layers were washed with water and satd. $NaHCO_3$, dried over Na_2SO_4. After removal of the solvent the dark brown oil was passed over silica using DCM – petrol ether (9:1, v/v) to obtain the desired aldehyde **12** as a pale yellow oil in 4.31 g (98%). The analytical data match with the known literature values.[5]

2-[3-Hexyl-5-iodo-2-thienyl(methane-1-yl-1-ylidene)]malononitrile (7). To a solution of **12** (4.31 g, 13 mmol) in 1,2-dichloroethane (50 mL), a solution of malonodinitrile (1.33 g, 20 mmol) and ammonium acetate (0.17 g, 2.2 mmol) in 50 ml ethanol was added and the reaction mixture was stirred at 65 °C for 16 hrs. After cooling to room temperature the product precipitated. The solid was filtered with suction, washed with ethanol and dried under vacuum. Yield: 4.37 g (88%) of a red solid. M.p. 154-155 °C. ^{1}H-NMR ($CDCl_3$, 400 MHz): $\delta = 0.90$ (t, J= 6.8 Hz, 3H, CH_3), 1.31 (m, 6H, CH_2), 1.59 (tt, $J = 7.6$ Hz, 2H, CH_2), 2.72 (t, $J = 7.9$ Hz, 2H, CH_2), 7.26 (s, 1H, Th-*H*), 7.80 (s, 1H, C*H*). ^{13}C-NMR ($CDCl_3$, 100 MHz): $\delta = 14.0$, 22.5, 28.7, 28.9, 31.3, 31.4, 76.9, 89.6, 113.4, 114.3, 136.0, 140.1, 147.1, 156.5. IR (KBr, cm^{-1}): 2928 (s, CH assym.), 2858 (s, CH sym.), 2227/ 2214 (s/m, CN), 1571 (s, CC). Elemental analysis for $C_{14}H_{15}IN_2S$: calcd. C, 45.42; H, 4.08; N, 7.57; S, 8.66%; found: C, 45.57; H, 4.02; N, 7.59; S, 8.50%.

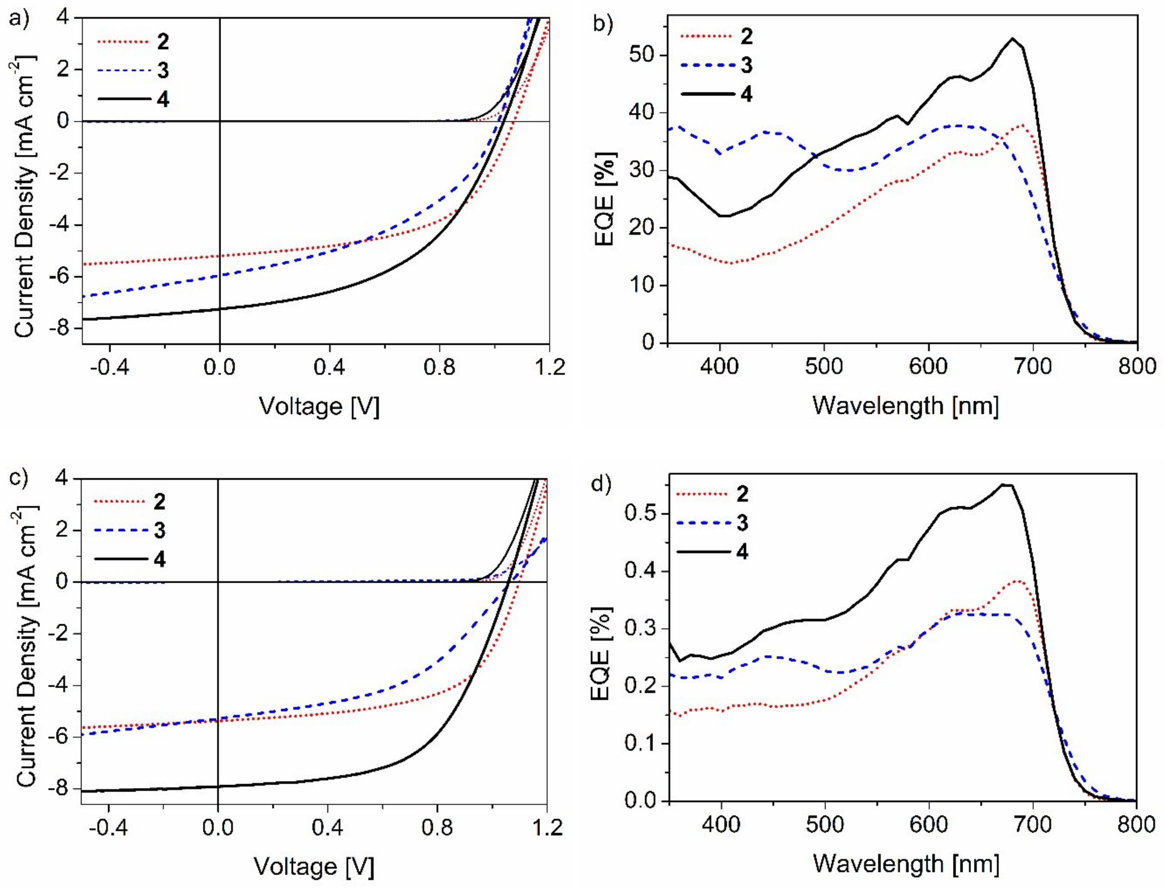


Figure S1. Comparison of the *J-V* and EQE curves of the best solar cell performance of devices with the optimized structure: (a and b) ITO|PEDOT:PSS|Donor:$PC_{61}BM$|LiF|Al. (c and d) ITO|V_2O_5|Donor:$PC_{61}BM$|LiF|Al.

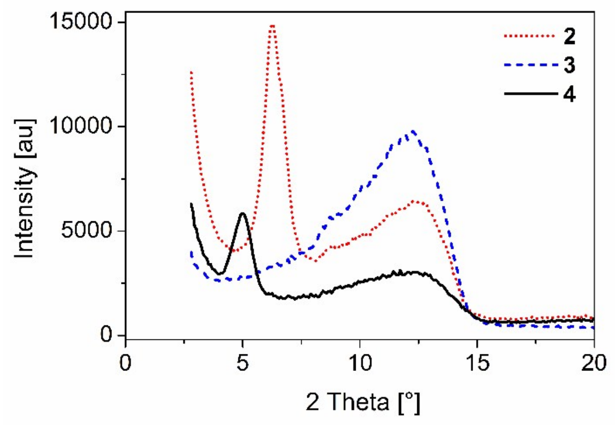


Figure S2. 1D-GIXRD patterns of oligomer:$PC_{61}BM$ blends deposited from $CHCl_3$ on PEDOT:PSS coated glass substrate.

Table S1. Photovoltaic performance of DTP-**4**:$PC_{61}BM$ using different concentration of PDMS additive. D:A ratio was 1:2. Device structure: ITO|V_2O_5|Donor:$PC_{61}BM$|LiF|Al.

Donor	HTL spin speed	Additive [%]	Soln conc. [mg/mL]	T [˚C] Soln/Sub	J_{SC} [mA cm^{-2}]	V_{OC} [V]	FF	PCE [%]
4	5750	-	15	60/60	7.9	1.06	0.57	4.8
4	5750	0.1	15	60/60	7.6	1.06	0.64	5.2
4	5750	0.2	15	60/60	7.9	1.07	0.63	5.3
4	5750	0.4	15	60/60	7.3	1.06	0.61	4.7

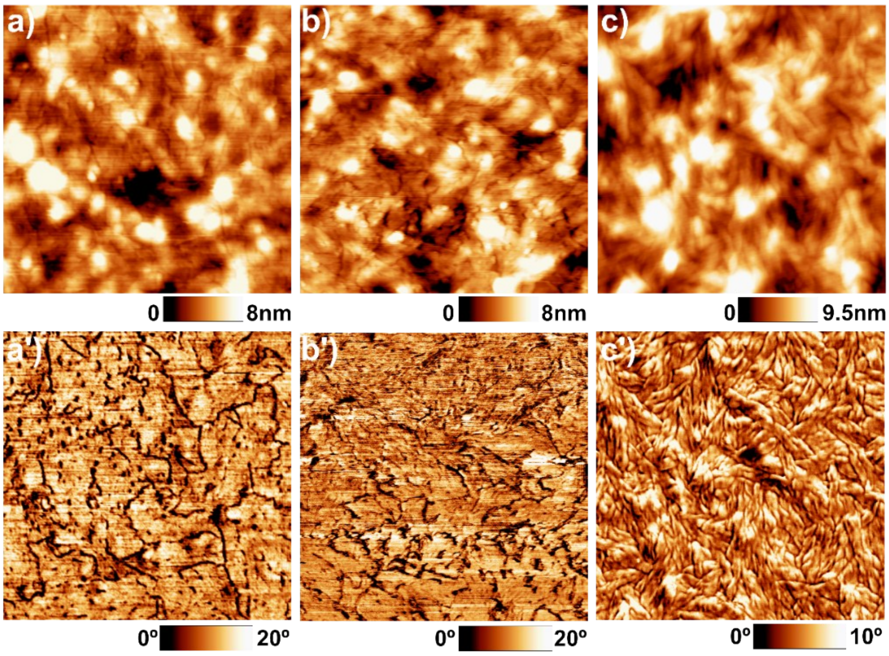


Figure S3. AFM height (a-c) and phase (a'-c') images of samples with **4**:$PC_{61}BM$ spin-coated on (a and a') ITO|PEDOT:PSS| from $CHCl_3$, (b and b') ITO|V_2O_5| from $CHCl_3$ and (c and c') ITO|V_2O_5| from $CHCl_3$/PDMS. Image size: 1 x 1 μm.

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