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 104 were synthesized according to the literature procedures.

\[ \text{Scheme S1.} \] (i) \( \text{aBuLi-THF, DMF, } -78 \, ^\circ \text{C} \rightarrow 40 \, ^\circ \text{C}, 84\%. \) (ii) \( \text{C}_2\text{H}_4(\text{OH})_2, \) p-TSA, toluene, reflux, 18 h, 95%. (iii) \( \text{aBuLi-THF, I}_2, -78 \, ^\circ \text{C} \rightarrow \text{r.t.}, 15h, 82\%. \) (iv) HCl·aq. (25%), \( \text{aPrOH, 90 } ^\circ \text{C, 6 h, 98\%.} \) (v) \( \text{CH}_3(\text{CN})_2, \) NH₄OAc, 1,2-DCE-EtOH, 60 \, ^\circ \text{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, NH₄Cl (1M) solution and aqueous NaHSO₃ solution. The aqueous phase was extracted twice with diethyl ether and the combined organic layers were washed successively with water, satd. NaHCO₃ 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; ¹H-NMR (CDCl₃, 400 MHz): δ = 0.88 (t, J = 6.8 Hz, 3H, CH₃), 1.29 (m, 6H, CH₂), 1.55 (tt, J= 7.6 Hz, 2H, CH₂), 2.58 (t, J = 7.8 Hz, 2H, CH₂), 3.92-4.02 (m, 2H, OC₂H₂), 4.05-4.15 (m, 2H, C₂H₂O), 6.06 (s, 1H, CH), 6.99 (s, 1H, Th-H). ¹³C-NMR (CDCl₃, 100 MHz): δ = 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 C₁₃H₁₉IO₂S: 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. NaHCO₃, dried over Na₂SO₄. 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.

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. ¹H-NMR (CDCl₃, 400 MHz): δ = 0.90 (t, J = 6.8 Hz, 3H, CH₃), 1.31 (m, 6H, CH₂), 1.59 (tt, J = 7.6 Hz, 2H, CH₂), 2.72 (t, J = 7.9 Hz, 2H, CH₂), 7.26 (s, 1H, Th-H), 7.80 (s, 1H, CH). ¹³C-NMR (CDCl₃, 100 MHz): δ = 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),
Elemental analysis for $\text{C}_{14}\text{H}_{15}\text{IN}_2\text{S}$: 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$_2$O$_5$|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:PC₆₁BM using different concentration of PDMS additive. D:A ratio was 1:2. Device structure: ITO|V₂O₅|Donor:PC₆₁BM|LiF|Al.

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<th>Soln conc. [mg/mL]</th>
<th>T [°C]</th>
<th>Soln/Sub</th>
<th>Jₛₚ [mA cm⁻²]</th>
<th>Vₒᶜ [V]</th>
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Figure S3. AFM height (a-c) and phase (a’-c’) images of samples with 4:PC₆₁BM spin-coated on (a and a’) ITO|PEDOT:PSS| from CHCl₃, (b and b’) ITO|V₂O₅| from CHCl₃ and (c and c’) ITO|V₂O₅| from CHCl₃/PDMS. Image size: 1 x 1 μm.

References