Supporting Information for

5,11-Conjugation-Extended Low-Bandgap Anthradithiophene-Containing Copolymer Showing Enhanced Thin-Film Order and Field-Effect Transistor Mobility

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Experimental

Materials and characterization methods

Unless otherwise specified, all chemicals were of reagent grade obtained from Aldrich, Acros, or TCI Chemical Co. Anhydrous grade solvents were purchased from these commercial sources. ^{1}H and ^{13}C NMR spectra were recorded using Varian Inova 300, Merc 400 or Inova 500 in deuterated chloroform at 293 K. Chemical shifts for 1H and 13C NMR spectra were referenced to solvent peaks. Relative molecular weight was measured by gel-permeation chromatography (GPC) with tetrahydrofuran (THF) as the eluent and polystyrene as the standard, on a Malvern GPCMax unit affixed with three columns measuring molecular weights ranging from xx – xx. DSC thermographs were recorded on a Mettler DSC 822 and calibrated with a pure indium sample with a scan rate of 10.0 °C min^{-1}. Thermal gravimetric analyses (TGA) were performed using a Mettler TOLEDO TGA/SDTA 851e at a heating rate of 10 °C min^{-1} under a nitrogen flow of 20 mL/min.

Electrochemical and Photophysical Properties Measurement

Cyclic voltammetry (CV) experiments were performed under a stream of argon in anhydrous *o*-DCB with 0.05 M tetra-*n*-butylammonium hexafluorophosphate (^{n}Bu$_4$NPF$_6$) as a supporting electrolyte. Platinum electrodes were used at a scan rate of 100 mV s^{-1} with the Fc/Fc$^+$ redox system as an internal reference oxidation potential for **M5.3** (**CHOThADT**) and **P5.4**. Films for UV-vis were prepared by spin-casting 5 mg/ml polymer solutions from chloroform (at 800 rpm). Their thicknesses were measured on a Dektak 150 profilometer (Veeco Metrology Group). Film drop-cast from 1 mg/ml polymer solutions in chloroform were used for the measurement of onset ionization energy in a Riken AC-2 spectrometer.

OTFT fabrication and measurement

oADT-dTDPP was dissolved in chloroform (CHCl$_3$) and chlorobenzene (PhCl) at 5 mg mL^{-1} and 7 mg mL^{-1} respectively; the solutions were then spin-cast onto octadecyltrichlorosilane treated SiO$_2$ surfaces. The films were annealed at various temperatures for 15 min before 40-nm-thick gold source and drain electrodes were deposited through a shadow mask. I-V characterization was carried out using a Keithley 4200, four-channel semiconductor parametric analyzer with femtoamp resolution. All devices were electrically tested inside a nitrogen glovebox. Tapping mode atomic force microscopy (AFM) investigation of the solar cell films was done using a Multimode Nanoscope III with Extender electronics (Veeco Metrology Group).

Grazing-Incidence X-Ray Diffraction

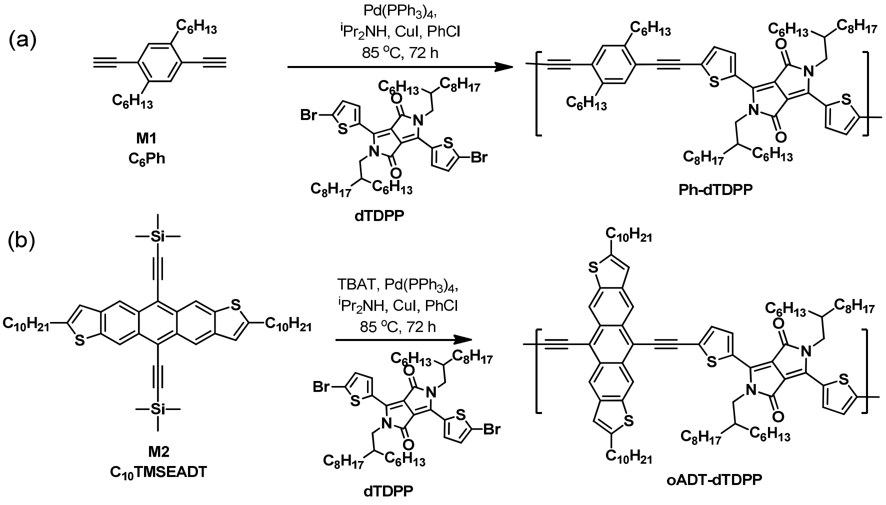
2D-GIXD images were collected in reflection mode with a planar area detector in a He atmosphere at beamline 11-3 of the Stanford Synchrotron Radiation Lightsource. The sample-detector distance was nominally set to 400 mm, and the incidence angle was 0.12 degrees; the X-ray wavelength was 0.9758 Angstroms. The beam size was defined by the slits to be 150 µm and 50 µm in the horizontal and vertical directions, respectively. GIXD images were analyzed using WxDiff software provided by Stefan Mannsfeld.[1] Details about the sample chamber could be found the reference previously published.[2]

Molecular Simulation

Simulation was carried out with a Gaussian03 software package, employing density functional theory at a level of B3LYP and a basis set of 6-31G*.

Synthesis

Solvents and chemicals were purchased from Sigma-Aldrich Co. and used as received unless otherwise stated. The synthesis of **M2** (as a mixture of syn and anti isomers) was carried out according to literature procedures.[3,4] The synthesis of **Ph-dTDPP** and **oADT-dTDPP** is described.



Scheme 1. Synthesis of (a) control polymer **Ph-dTDPP** via Sonogashira Coupling and (b) target polymer **oADT-dTDPP** via *in situ* desilylation.

Ph-dTDPP synthesis In a flame-dried, argon-filled Schlenk tube, **M1** (87.0 mg, 0.10 mmol, 1.0 equiv), **dTDPP** (95.1 mg, 1.0 equiv), $Pd(PPh_3)_4$ (12.1 mg, 0.1 equiv) and CuI (1.4 mg, 0.07 equiv) were dissolved in chlorobenzene (5.2 ml, 0.02 M) and diisopropylamine (2.6 ml). The mixture was immediately degassed via the freeze-pump-thaw procedure, and then heated to 80 °C for 72 hr. The mixture was poured into 500 ml of methanol and filtered. The polymer residue was washed sequentially with hot acetone, hexanes and chloroform in a soxhlet setup. The chloroform fraction was stirred with a metal scavenger for 2 hr at room temperature, then concentrated and re-precipitated in methanol. A final filtration afforded 270 mg of the polymer in 88.3 % yield. M_n = 22,500 g/mol, PDI = 4.8. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.98 – 8.86 (br), 7.44 – 7.30 (br), 4.16 – 3.88 (br), 2.86 – 2.64 (br), 1.62 – 1.52 (br), 1.46 – 1.14 (br), 0.94 – 0.78 (br). Anal. Calcd. for $(C_{68}H_{98}N_2O_2S_2)_n$: C, 78.56; H, 9.50; N, 2.69; O, 3.08; S, 6.17. Found: C, 77.90; H, 9.58, N: 2.61.

oADT-dTDPP synthesis In a flame-dried, argon-filled Schlenk tube, **M2** (80.0 mg, 0.10 mmol, 1.0 equiv), **dTDPP** (95.1 mg, 1.0 equiv), TBAT (226.3 mg, 4.0 equiv), Ph(PPh3)4 (12.1 mg, 0.1 equiv) and CuI (1.4 mg, 0.07 equiv) were dissolved in chlorobenzene (5.2 ml, 0.02 M) and diisopropylamine (2.6 ml). The mixture was immediately degassed via the freeze-pump-thaw procedure, and then heated to 80 °C for 72 hr. The mixture was poured into 300 ml of methanol and filtered. The polymer residue was washed sequentially with hot acetone, hexanes and chloroform in a soxhlet setup. The chloroform fraction was stirred with a metal scavenger for 2 hr at room temperature, then concentrated and re-precipitated in methanol. A final filtration afforded 88.9 mg of the polymer in 62.2% yield. M_n = 22,500 g/mol, PDI = 4.8. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 – 7.88 (br), 7.56 – 7.50 (br), 3.53 – 3.49 (br), 1.70 – 1.50 (br), 1.40 – 1.17 (br), 0.90 – 0.71 (br). Anal. Calcd. for $(C_{88}H_{118}N_2O_2S_4)_n$: C, 77.48; H, 8.72; N, 2.05 Found: C, 75.96; H, 8.22, N: 1.90.

$_1$H-NMR: 9.0 (b, 2H), 7.5 (b, 4H), 7.1 (b, 2H), 4.0 (b, 4H), 1.9 (b, 2H), 1.20-1.00 (b, 48H) , 0.80-0.70 (b, 12H).

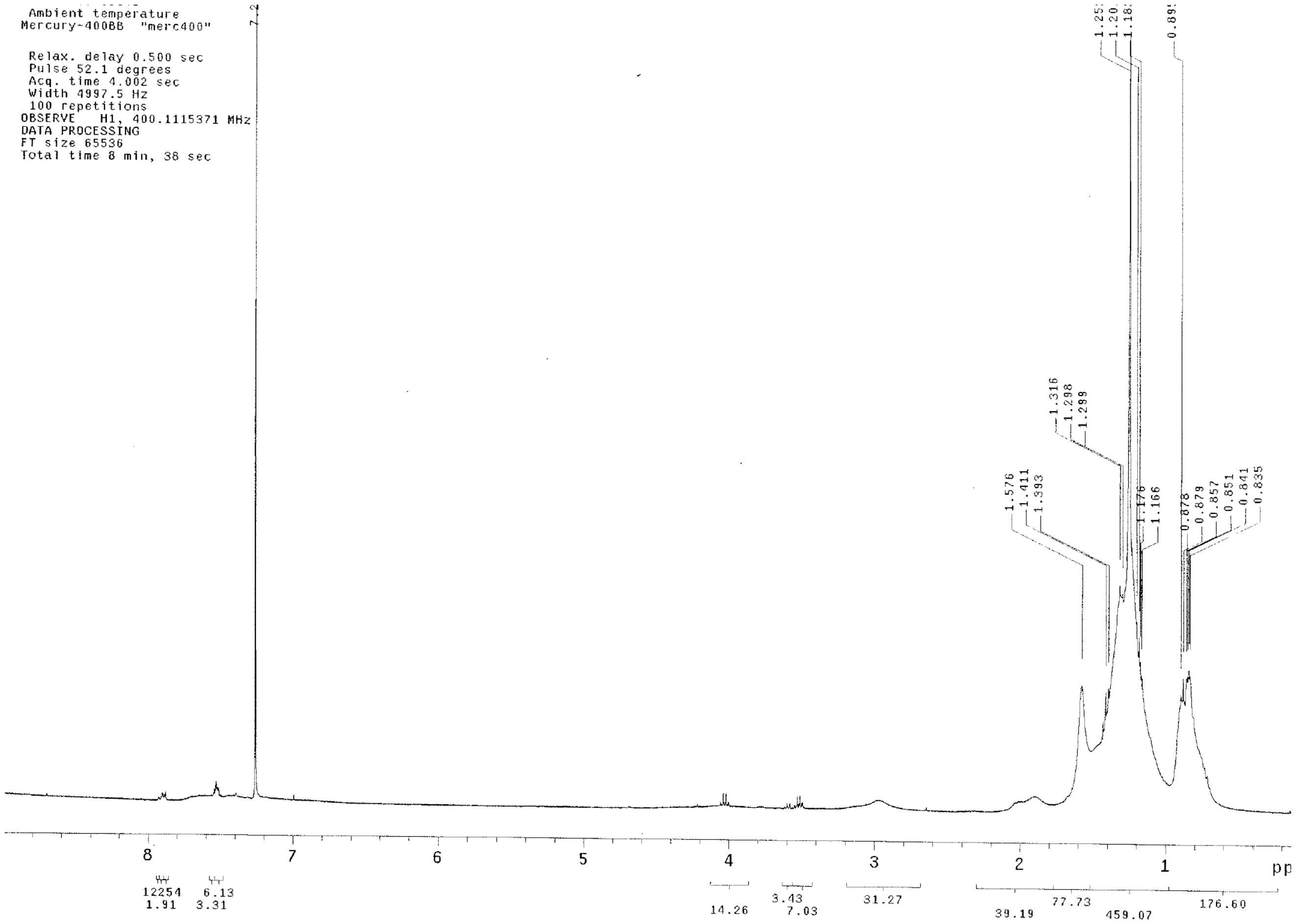
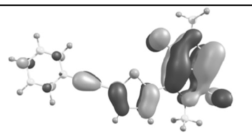
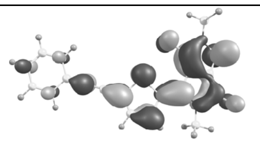


Figure S1. ^{1}H NMR of **oADT-dTDPP**.

Table S1. Energy levels and frontier molecular orbital visualization for model compounds **C1** and **C2**.

Structure	**HOMO (eV)**		**LUMO (eV)**		**E_g (eV)**
C1		-5.14		-2.55	2.59

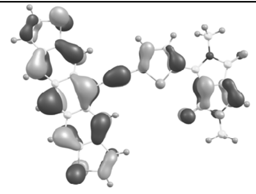
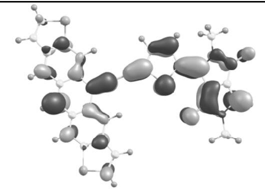
C2		-4.8		-2.7	2.1

Table S2. Molecular weight distributions, optical and electrochemical properties of **Ph-dTDPP** and **oADT-dTDPP**.

Polymer	**M_n[a] / PDI[a] (g/mol)**	**In solution**		**In film**		
		HOMO[b] (eV)	**LUMO[b] (V)**	**$E_{g,\ opt}$[c] (eV)**	**E_{onset}[d] (eV)**	**$E_{g,\ opt}$[c] (eV)**
Ph-dTDPP	18700 / 3.5	-5.20	-3.41	1.80	5.41	1.60
oADT-dTDPP	23,500 / 4.8	-	-	1.36	5.00	1.30

[a] Determined from GPC using THF soluble part. [b] Determined from CV oxidation and reduction onsets in *o*-DCB with ferrocene as the standard. [c] Estimated from the onset of film absorption. [d] Determined from the onset of ionization of film in air.

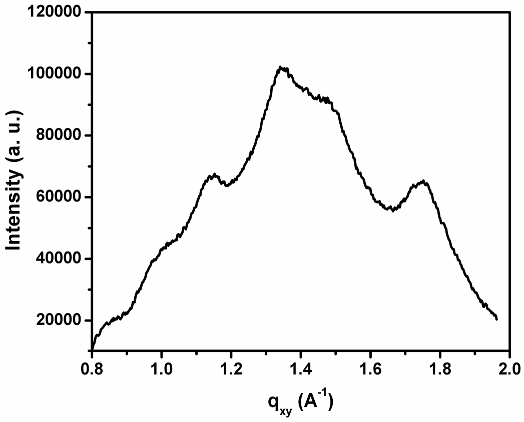


Figure S2. Diffraction intensity profile along q_{xy} indicates many poorly defined peaks with d-spacings of 3.6 – 5.5 Å.

Table S3. Summary of **oADT-DTDPP**'s TFT charge transport properties for various device fabrication conditions. Average mobility values are tabulated, with maximum values in parentheses.

Solvent	**T_{anneal} (°C)**	**Hole or electron mobility, μ_h or μ_e ($cm^2\ V^{-1}\ s^{-1}$)**	**I_{on} / I_{off}**	**V_{th} (V)**
$CHCl_3$	150	$\mu_h = 0.044 \pm 0.004$ (0.051)	10^5	+2 ~ +20
CB		$\mu_h = 0.060 \pm 0.027$ (0.12)	$10^4 - 10^5$	-10 ~ +10
	210	$\mu_h = 0.007 \pm 0.001$ (0.009)	10^4	-20 ~ +4
		$\mu_e = 2.7 \times 10^{-5} \pm 1.9 \times 10^{-5}$ (4.8×10^{-5})	10^5	+30 ~ +60

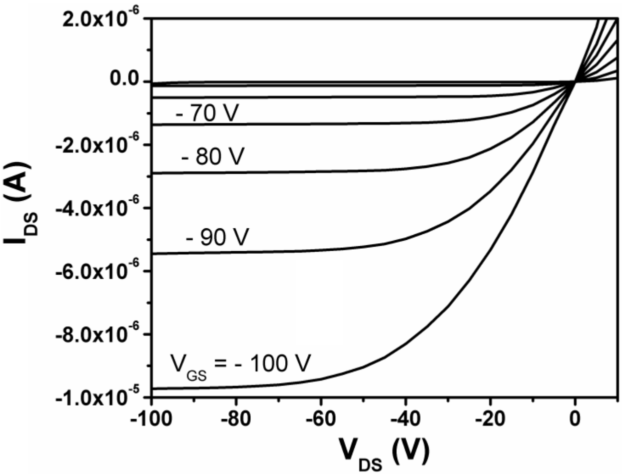


Figure S3. P-type output characteristics of a representative **oADT-dTDPP** device spin-cast from CB on OTS-treated SiO_2, annealed at 150 °C.

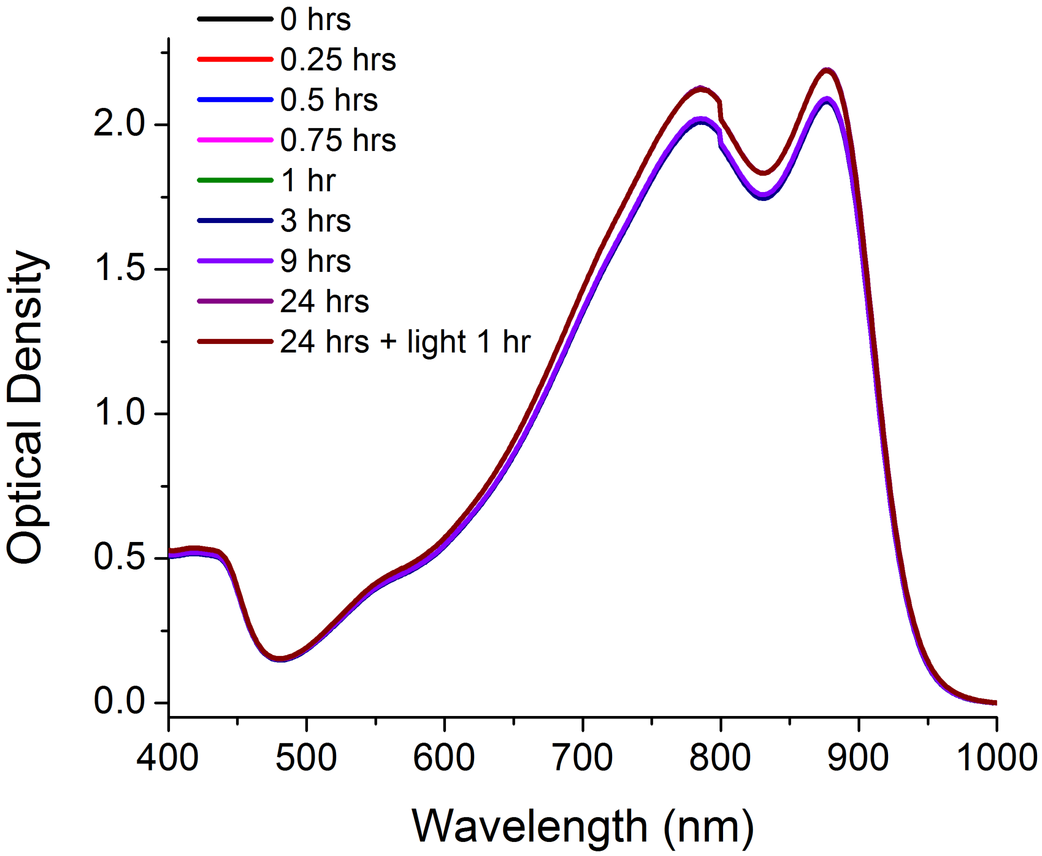


Figure S4. UV-Vis absorption profile over 24 h for an **oADT-dTDPP** film in dark followed by 1 h exposure to room light. The absorption intensity essentially remained constant.

(1) Mannsfeld, S. C. *Stanford Synchrotron Radiation Lightsource* **2009**.

(2) Verploegen, E.; Mondal, R.; Bettinger, C. J.; Sok, S.; Toney, M. F.; Bao, Z. *Advanced Functional Materials* **2010**, *20*, 3519.

(3) Mössinger, D.; Jester, S.-S.; Sigmund, E.; Müller, U.; Höger, S. *Macromolecules* **2009**, *42*, 7974.

(4) Laquindanum, J. G.; Katz, H. E.; Lovinger, A. J. *Journal of the American Chemical Society* **1998**, *120*, 664.