Supporting Information

Decyloxy-substituted BTBT derivative for highly efficient and stable thinfilm organic (opto)electronic devices

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S1. Calculations details

a)





Fig. S1. HOMO (a) and LUMO (b) for DPBTBT.

Table S1. HOMO (E_H) and LUMO (E_L) energies, optical gap for absorption E_g^{abs} and emission E_g^{em} , and oscillator strengths for S₀-S₁ and S₁-S₀ transitions.

	E_H , eV	E_L , eV	E_g^{abs} , eV	E_g^{lum} , eV	fso-si	fs1-s0
DPBTBT	-5.19	-1.35	3.50	3.00	1.38	1.75
DOPBTBT	-5.04	-1.24	3.45	2.95	1.50	1.86

S2. Synthesis details

Below, details of the synthesis of the compounds from Fig. 2 are described.

Compound 1: A mixture of phenol (7.0 g, 74.6 mmol) and potassium carbonate (15.4 g, 111.9 mmol) in DMF was stirred for 40 minutes at 65 °C, after which 1-bromododecane (11.0 g, 49.7 mmol) was added and the reaction was stirred at 70 °C for 18 hours. The reaction mixture was then extracted in ethyl acetate-water system. The organic phase was combined, the solvent was evaporated under reduced pressure and the residue was dried at 1 Torr. The product was purified by column chromatography on silica gel (eluent: petroleum ether) to give pure compound 1 (9.5 g, 81 %) as a colorless liquid. ¹H NMR (300 MHz, CDCl₃): δ [ppm] 0.89 (t, 3H, J = 6.9 Hz), 1.26-1.51 (overlapping peaks, 14H), 1.73-1.83 (m, 2H), 3.95 (t, 2H, J = 6.6 Hz), 6.86-6.98 (overlapping peaks, 3H), 7.23-7.34 (m, 2H). ¹³C NMR (75 MHz, CDCl₃): δ [ppm] 14.10, 22.67, 26.05, 29.30, 29.31, 29.40, 29.56, 29.58, 31.89, 67.86, 114.47, 120.41, 129.37, 159.12. Anal. calcd (%) for C₁₆H₂₆O: C, 81.99; H, 11.18. Found: C, 81.37; H, 11.42.

Compound 2: Liquid bromine (Br₂) (1.95 mL, 38.0 mmol) was added dropwise to a solution of compound 1 (8.9 g, 38.0 mmol) in 100 mL dichloromethane (DCM) at 0 °C. The reaction mixture was then stirred for 2 days at room temperature. After completion of the reaction, an aqueous solution of sodium sulfite (4.8 g, 38.0 mmol) was added to the reaction mixture and the mixture was extracted. The combined organic phases were dried over sodium sulfate and filtered. The

solvent was evaporated in vacuum and the residue was dried at 1 Torr. This crude product was purified by column chromatography on silica gel (eluent: petroleum ether) to give pure compound 2 (11.5 g, 97%) as a colorless liquid. ¹H NMR (300 MHz, CDCl₃): δ [ppm] 0.88 (t, 3H, J = 6.8 Hz), 1.25-1.47 (overlapping peaks, 14H), 1.71-1.80 (m, 2H), 3.90 (t, 2H, J = 6.6 Hz), 6.76 (d, 2H, J = 8.9 Hz), 7.35 (d, 2H, J = 8.9 Hz). ¹³C NMR (75 MHz, CDCl₃): δ [ppm] 14.12, 22.67, 25.97, 29.15, 29.31, 29.36, 29.54, 31.89, 68.22, 112.50, 116.25, 132.15, 158.22. Anal. calcd (%) for C₁₆H₂₅BrO: C, 61.34; H, 8.08. Found: C, 61.85; H, 8.31.

Compound 3: 2.5 M solution of n-butyllithium (n-BuLi) (4.1 mL, 10.3 mmol) in hexane was added drop wise to a solution of compound 2 (3.06 g, 9.8 mmol) in 92 mL of dry THF at -60 °C. Afterwards the reaction mixture was stirred for 1 hour at -60 °C and then IPTMDOB (1.9 g, 10.3 mmol) was added in one portion. The reaction mixture was stirred for 1 hour at -70 °C, then the cooling bath was removed, and the stirring was continued for 1h. After completion of the reaction, freshly distilled diethyl ether, distilled water and aqueous 1 M HCl solution were added to the reaction mixture. The organic phase was separated, washed with water, and dried over sodium sulfate and filtered. The solvent was evaporated to give 3.36 g (95%) of compound 3 as a white solid, which was used in next stage without any purification. ¹H NMR (300 MHz, CDCl₃): δ [ppm] 0.87 (t, 3H, J = 6.8 Hz), 1.24-1.34 (overlapping peaks, 24H), 1.40-1.48 (m, 2H), 1.72-1.80 (m, 2H), 3.96 (t, 2H, J = 6.6 Hz), 6.87 (d, 2H, J = 8.8 Hz), 7.73 (d, 2H, J = 8.6 Hz). ¹³C NMR (75 MHz, CDCl₃): δ [ppm] 14.12, 22.67, 24.83, 26.00, 29.18, 29.31, 29.37, 29.55, 31.88, 67.76, 83.48, 113.82, 136.45, 161.72. Anal. calcd (%) for C₂₂H₃₇BO₃: C, 73.33; H, 10.35. Found: C, 73.87; H, 10.21.

DOPBTBT: To 2,7-dibromo[1]benzothieno[3,2-b][1]benzothiophene (Br-BTBT) (0.4 g, 1 mmol), 2-(4-(decyloxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3) (0.87 g, 2.4 mmol), and tetrakis(triphenylphosphine)palladium(0) Pd(PPh₃)₄ (58 mg, 0.1 mmol) in inert atmosphere were added degassed toluene (34 mL), ethanol (5 mL), and 2M K₂CO₃ aqueous solution (3.6 mL). The reaction mixture was stirred under reflux for 19 h. After cooling, the reaction mixture was poured into water and toluene. The organic phase was separated, and solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: toluene) and recrystallization in toluene to give pure DOPBTBT (0.47 g, 66 % yield) as a light green solid. ¹H NMR (300 MHz, CDCl₃): δ [ppm] 0.90 (t, 6H, J = 6.9 Hz), 1.28-1.36 (overlapping peaks, 24H), 1.47-1.54 (m, 4H), 1.78-1.87 (m, 4H), 4.03 (t, 4H, J = 6.4 Hz), 7.00 (d, 4H, J = 8.8 Hz), 7.60 (d, 4H, J = 8.8 Hz), 7.65 (dd, 2H, J₁ = 1.5 Hz, J₂ = 8.3 Hz), 7.89 (d, 2H, J = 8.1 Hz), 8.06 (d, 2H, J = 1.1 Hz). Anal. calcd (%) for C₄₆H₅₆O₂S₂: C, 78.36; H, 8.01; S, 9.09. Found: C, 78.94; H, 8.20; S, 9.01. MALDI-TOF MS: found m/z 704.67; calculated for [M]⁺ 704.37.

DPBTBT: To 2,7-dibromo[1]benzothieno[3,2-b][1]benzothiophene (Br-BTBT) (0.4 g, 1 mmol), 2-(4-decylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.83 g, 2.4 mmol), and Pd(PPh3)4 (58 mg, 0.1 mmol) in inert atmosphere were added degassed toluene (34 mL), ethanol (5 mL), and 2M K₂CO₃ aqueous solution (3.6 mL). The reaction mixture was stirred under reflux for 20 h. After cooling, the reaction mixture was poured into water and toluene. The organic phase was separated, and solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: toluene) and recrystallization in toluene to give pure DPBTBT (0.54 g, 80 % yield) as a light green solid. ¹H NMR (300 MHz, CDCl3): δ [ppm] 0.89 (t, 6H, J = 7.0 Hz), 1.24-1.41 (overlapping peaks, 28H), 1.63-1.74 (m, 4H), 2.68 (t, 4H, J = 7.9 Hz), 7.28 (d, 4H, J = 8.4 Hz), 7.60 (d, 4H, J = 8.2 Hz), 7.69 (dd, 2H, J₁ = 1.6 Hz, J₂ = 8.2 Hz), 7.91 (dd, 2H, J₁ = 0.4 Hz, J₂ = 8.2 Hz), 8.11 (d, 2H, J = 1.6 Hz). Anal. calcd (%) for C₄₆H₅₆S₂: C, 82.09; H, 8.39; S, 9.53. Found: C, 82.01; H, 8.36; S, 9.56. MALDI-TOF MS: found m/z 672.62; calculated for [M]⁺ 672.38.

S3. Characterization methods details

NMR spectroscopy: ¹H and ¹³C NMR spectra were recorded using a "Bruker Avance II 300" spectrometer at 300.17 MHz and 75.48 MHz, respectively, and utilizing CDCl₃ signal (7.25 ppm and 77.00 ppm, for ¹H and ¹³C NMR, respectively) as the internal standard.

Elemental analysis: of C, N and H elements was carried out using a CHN automatic analyzer (CE 1106). The settling titration using BaCl₂ was applied to analyze the S element. The experimental error for elemental analysis is 0,30-0,50%.

Mass-spectra: mass-spectra (MALDI-TOF) were registered on the "Autoflex II Bruker" (resolution FWHM 18000), equipped with a nitrogen laser (work wavelength 337 nm) and time-of-flight mass-detector working in reflections mode. The accelerating voltage was 20 kV. Samples were applied to a polished stainless steel substrate. Spectrum was recorded in the positive ion mode. The resulting spectrum was the sum of 300 spectra obtained at different points of sample. 2,5-Dihydroxybenzoic acid (DHB) (Acros, 99%) and α -cyano-4-hydroxycinnamic acid (HCCA) (Acros, 99%) were used as matrices.

Gel permeation chromatography (GPC): analysis was performed on a "Shimadzu" instrument with a RID-10A refractometer and an SPD-M10AVP diode matrix as detectors using 7.8×300 mm Phenomenex columns (USA) filled with the Phenogel sorbent with pore sizes of 500 and 103 Å and THF as the eluent.

The solubility: of compounds was measured using their saturated solutions in odichlorobenzene, which were prepared by stirring of an excess of solid material in the solvent. For this purpose, the compounds were added in small portions to 5 mL of pure solvent. As prepared, the saturated solution was filtered through 0.22 μ m PTFE syringe filters, and the solvent was evaporated. Afterwards the residue was dried in vacuum at 135 °C until reaching its constant weight, which was used to calculate the solubility value.

Cyclic voltammetry (CV) measurements: were carried out using solid compact layers of the oligomers, which in turn were made by electrostatically rubbing the materials onto a work glassy carbon electrode using IPC-Pro M potentiostat. Measurements were made using 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) in acetonitrile as supporting electrolyte. The scan rate was 200 mV s⁻¹. Potentials were measured relative to a saturated calomel electrode (SCE). The highest occupied molecular orbital (HOMO) energies were evaluated using the first standard oxidation (φ_{ox}) potentials obtained from CV experiments as E(HOMO) = $-e(\varphi_{ox} + 4.40)(eV)$, where *e* is the elementary charge¹⁻³. DPBTBT and DOPBTBT lack reduction centers and their CVs do not show cathodic peaks up to background discharge potentials (E=-1.60 eV).

Thermogravimetric analysis (TGA): was conducted in dynamic mode within the temperature range of 30 to 700 °C using a "Mettler Toledo TG50" system equipped with an M3 microbalance. This system enabled the measurement of sample weights within a range of 0–150 mg with a precision of 1 μ g. The heating and cooling rates were set at a constant rate of 10 °C/min. Each compound was studied in both air and an N₂ flow of 200 mL/min.

Differential scanning calorimetry (DSC): scans were obtained using a "Mettler Toledo DSC30" system, with a heating/cooling rate of 10 °C/min within a temperature range of 0-350 °C for all compounds. The N₂ flow rate was set at 50 mL/min.

Polarization optical images were obtained by employing a polarization microscope (Axioskop 40 A Pol, Zeiss AG, Germany) with a Lincam camera (Carl Zeiss, Germany) and a heating stage (THMS600, Linkam Scientific Instruments, UK).

Absorption spectroscopy: the absorption spectra of the corresponding compounds were recorded with a SILab u-Violet R (China) spectrophotometer in the standard 10 mm photometric quartz cuvette. Absorption spectra were recorded using THF solutions with a concentration of 10^{-5} M. Thin films were deposited in vacuum on glass substrates (22×22 mm). All measurements were carried out at room temperature.

Fluorescence spectroscopy: a scanning spectrofluorometer Zolix OmniFluo-990 (China) with registration in the single photon counting mode at successive time intervals and automatic adjustment of the measured emission intensity was used for the registration of photoluminescence (PL) spectra. Measurements were carried out for 10⁻⁵ M solutions in the 10 mm quartz cuvette and for thin films on glass substrates, the measurement geometry was 90°. The PL quantum yield (PLQY) of solutions in THF was carried out using an integrating sphere integrated in the spectrofluorimeter. All measurements were carried out at room temperature.

Substrate pretreatment: silicon substrates with a SiO_2 layer thickness of 300 nm were cleaned using the following procedure. First, the substrates were washed in acetone to remove the protective photoresist layer. Then, in an ultrasonic bath, the substrates were cleaned for 10 minutes in isopropanol at 10 °C. After this, they were washed in distilled water, dried in a stream of nitrogen and placed under ultraviolet radiation for 15 minutes (PL16-110, SenLights).

S4. NMR data



Fig. S2. ¹H NMR spectrum of compound 1 in Chloroform-d.



Fig. S3. ¹³C NMR spectrum of compound 1 in Chloroform-d.



Fig. S4. ¹H NMR spectrum of compound 2 in Chloroform-d.



Fig. S5. ¹³C NMR spectrum of compound 2 in Chloroform-d.



Fig. S6. ¹H NMR spectrum of compound 3 in Chloroform-d.



Fig. S7. ¹³C NMR spectrum of compound 3 in Chloroform-d.



Fig. S8. ¹H NMR spectrum of compound DOPBTBT in Chloroform-d.



Fig. S9. ¹H NMR spectrum of compound DPBTBT in Chloroform-d.

S5. CV data



Fig. S10. Cyclic voltammogram of a DPBTBT(a) and DOPBTBT(b) films. No reduction peaks were observed up to the background discharge potentials.



Fig. S11. Molar extinction spectra for DPBTBT and DOPBTBT in THF solution (a); absorption and PL spectra for DPBTBT and DOPBTBT thin films excited at 372 nm and 400 nm, respectively

(b).

S6. Optical spectroscopy data

The difference between the absorption/PL spectra in solution and films for both oligomers could be tentatively assigned to H-aggregation in the solid state. In fact, the main absorption band in solution at ~360 nm is strongly suppressed, and PL is considerably red shifted (by ~0.4 eV) in the films. Such differences between the optical spectra of isolated (solution) and aggregated (films) molecules are signatures of H-aggregates observed for various conjugated oligomers⁴. The PL QY in thin films of DOPBTBT and DPBTBT were found to be 1% and 4%, respectively, and these values are considerably lower than those in solution. The lower PL QY could be also reasonably assigned to H-aggregation, which considerably decreases the radiative constant and hence can enhance non-radiative relaxation. The further analysis of the photophysics in these oligomers in the solid state is a subject of a separate study.





Fig. S12. DSC scan of DPBTBT (a) and DOPBTBT (b) powder.

	TGA		DSC								
Compound	$T_{\rm d}$, °C		1-st ł	neating	coo	oling	2-nd heating				
	in air	in inert	T _{trans} , °C	$\Delta H_{\text{trans}}, J/g$	T _{trans} , °C	$\Delta H_{\text{trans}}, J/g$	T _{trans} , °C	$\Delta H_{trans}, J/g$			
DPBTBT	271	385	26	-7	280	21	26	-3			
			55	-17	133	22	55	-14			
			145	-22	39	17	141	-21			
			283	-21			283	-22			
DOPBTBT	355	397	163	-48	286	20	156	-36			
			194	-9	189	10	198	-8			
			287	-20	108	48	288	-19			

Table S2. Phase behavior of DPBTBT and DOPBTBT.

Notes: T_d is the decomposition temperature calculated for the 5% weight-loss; T_{trans} is temperature of endothermic phase transitions according to the first heating, cooling and second heating; ΔH_{trans} is enthalpies of endothermic phase transitions according to the first heating, cooling and second heating.



Fig. S13. Optical polarizing microscopy of compound DPBTBT at room temperature (a) and at 285 $^{\circ}$ C (c); and compound DOPBTBT at room temperature (b) and at 290 $^{\circ}$ C (d).

S8. PXRD data



Fig. S14. PXRD data for DOPBTBT (red curve) and DPBTBT (violet curve).

Table S3. Position of peaks q (nm⁻¹) and the interplanar distance $d=2\pi/q$ (Å) for DPBTBT and DOPBTBT.

DPBTBT	q, nm ⁻¹	19.4	16.1	15.3	14.7	14.1	13.7	13.4	7.5	4.5	3.0	1.5
	d, Å	3.24	3.90	4.11	4.27	4.46	4.59	4.69	8.38	14.0	20.9	41.7
DOPBTBT	q, nm ⁻¹	19.8	16.7	15.6	14.8	-	13.8	13.4	7.3	4.3	2.9	1.4
	d, Å	3.17	3.76	4.03	4.25	-	4.55	4.69	8.61	14.1	21.7	44.9

S9. AFM data

Fig. S15 illustrates atomic-force microscopy maps for vacuum-deposited DOPBTBT and DPBTBT thin-film surfaces in two different scales. Average roughness is rather higher for DOPBTBT than that for DPBTBT, however the lateral dimensions of grains are about tens of nm for DOPBTBT which is lower than that for DPBTBT – about hundreds of nm.



Fig. S15. AFM maps of vacuum-deposited DOPBTBT (a,b) and DPBTBT (c,d) thin-film surfaces in $10x10 \ \mu m$ (a,c) and $2x2 \ \mu m$ (b,d) scales.

S10. OFET details



Thin films transistors with top MoO3/Ag electrodes.

Fig. S16. OFET images and electrical characteristics for the best silver top electrode devices: DOPBTBT (a,c), DPBTBT (b,d). Output characteristics (a, b), insets show optical images of the devices; transfer characteristics in the linear regimes (c, d).

For both oligomers, the charge carrier mobility for transistors with silver electrodes was lower than for similar devices with PEDOT:PSS electrodes (cf. Fig. 4 and Fig. S15). This may be connected with procedure of fabrication device. Heavy silver atoms damaged the semiconductor during deposition, worsening charge injection. However, charge carriers mobility for DOPBTBT for MoO3/Ag electrodes is significantly higher than for devices with asymmetric electrodes, which is probably due to the larger effective injection area for holes.

Oligomer	Linear regime	Saturation regime	
	μ_{lin} , cm ² V ⁻¹ s ⁻¹	μ_{sat} , cm ² V ⁻¹ s ⁻¹	$V_{\rm T}, {\rm V}$
DPBTBT	0.26±0.03	0.24±0.03	-7.7
DOPBTBT	0.74±0.07	0.64±0.06	7.6

Table S4. OFET data for the best devices with PEDOT:PSS top electrodes based on both oligomers.

Monolayer OFETs

The worse solubility of DOPBTBT compared to DPBTBT forced us to carry out growth while maintaining a temperature of about 50 degrees in order to slow down the crystallization of the supersaturated solution. Temperature cooling after growth is complete can cause microcracks to form, which reduce film homogeneity and, consequently, reduce the measured charge carrier mobility. This was the reason why we were unable to obtain multilayer 2D films with charge carrier mobility more than 1.5 cm²V⁻¹s⁻¹. Perhaps this problem can be solved in the future by selecting another solvent and growing at room temperature.

Optical microscopic image of monolayer DOPBTBT-based OFET and AFM map and height profile at the edge of monolayer are given in Figure S17. According to the AFM data the thickness of monolayer is 3.9 ± 0.5 nm (average value among three points) which is close to estimated length of DOPBTBT molecule. The presence of pronounced clearly defined straight boundaries of monolayer suggests that the monolayer can appear to be a two-dimensional single crystal.





Fig. S17. (a) Optical microscope image of monolayer DOPBTBT-based OFET with small red square area denoting the place of AFM measurements at the edge of monolayer. (b) AFM map of the edge of monolayer (on the bottom), (c) height profile along the vertical blue line in panel (b).

When rotating the CDIC prism, domains are observed in multilayer films. The domain structure is a sign of crystallinity. Thus, oligomers of DOPBTBT are capable of forming a crystalline structure. The presence of a crystalline structure in multilayer films is not at all proof of its presence in monolayer films, but it indicates that it is possible.



Fig. S18 Optical microscopy images of few-layer films grown at a concentration of 0.1 g L-1 captured at different angles of the CDIC prism (pictures **a**) and **b**) correspond to different angles).

S11. Photoelectric effect



Fig. S19. Dependences of photocurrent I_{PH} (the difference between drain currents under light and in dark) on drain (a) and gate (b) voltages under incident illumination at wavelength of 400 nm and intensity of 2.75 W/m².

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