Supporting information for

Synthesis of annulated thiophene perylene bisimide analogues : their applications to bulk heterojunction organic solar cells

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Contents of Supplementary Data

Scheme 1: Schematic diagram for the synthesis of the perylenes

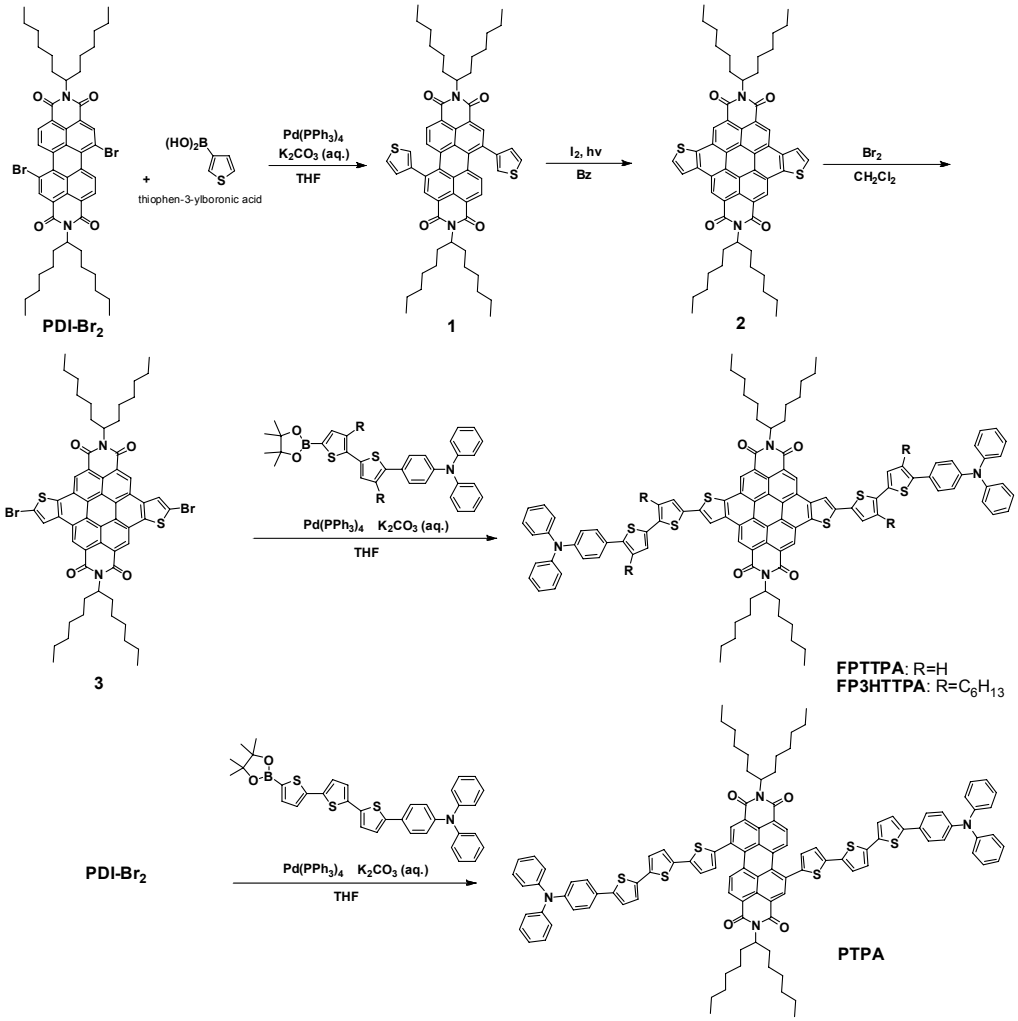
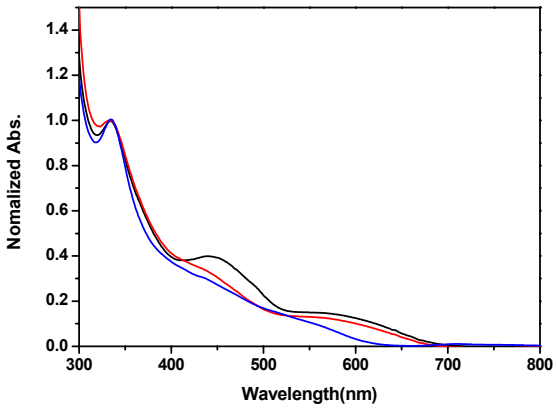


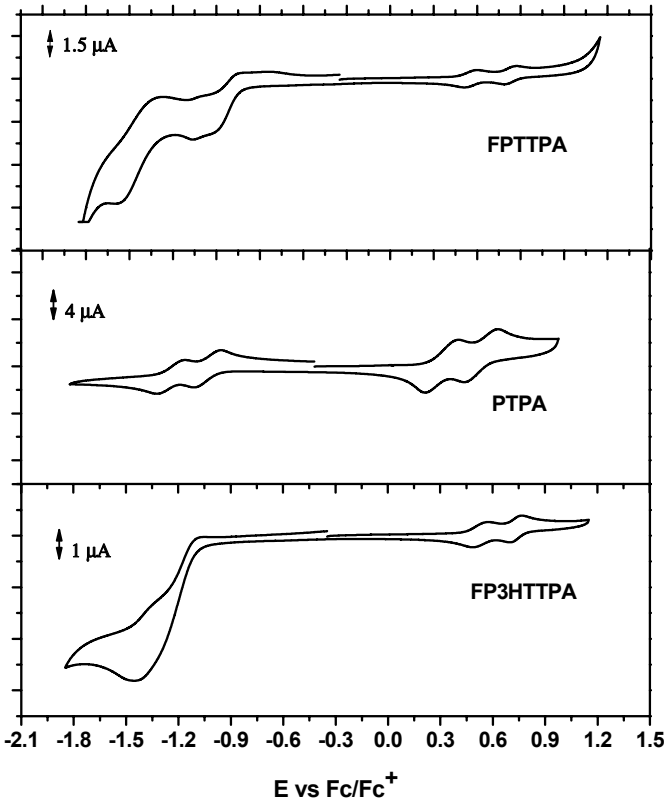
Table 1. Optical, redox parameters of the compounds

Compunds	λ_{abs}[a]/nm (ε/$M^{-1}cm^{-1}$)	$E_{onset, ox}$(V) / HOMO (eV)[b]	$E_{onset, red}$(V) / LUMO (eV)[b]	$E_{0\text{-}0}$ (eV)[c]
FPTPA	438 (136 000), 573 (38 000)	0.56 / -5.27	-1.17 / -3.54	1.73
FP3HTTPA	420 (103 200), 563 (35 000)	0.53 / -5.24	-1.38 / -3.33	1.91
PTPA	420 (134 000), 523 (60 900)	0.28 / -4.98	-1.16 / -3.55	1.44

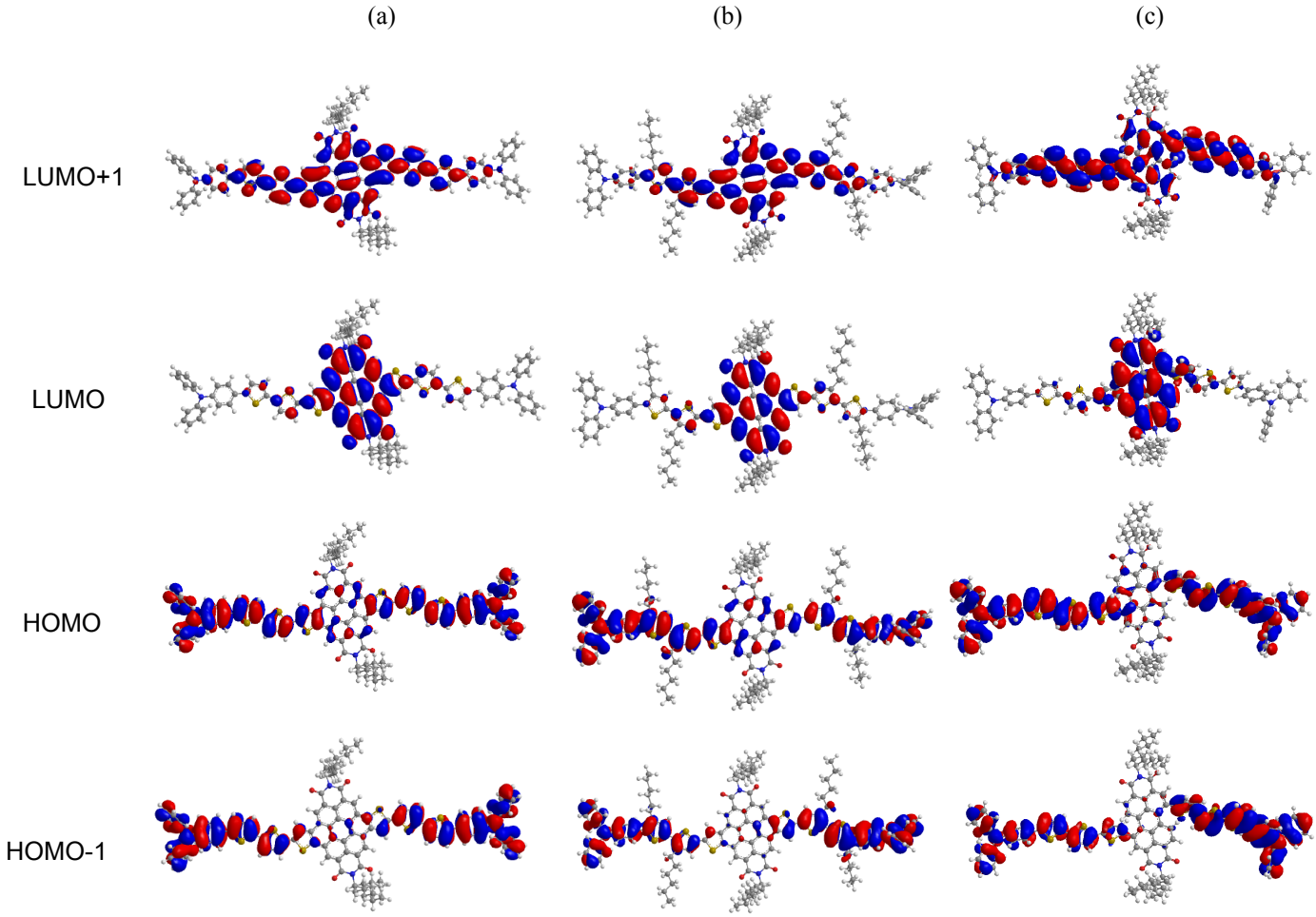
[a] Absorption spectra were measured in CH_2Cl_2 solution. [b] Redox potential of the compounds were measured in CH_2Cl_2 with 0.1M $(n\text{-}C_4H_9)_4NPF_6$ with a scan rate of 100 mVs^{-1} (*vs*. Fc/Fc^+). [c] $E_{0\text{-}0}$ was calculated from the absorption thresholds from absorption spectra of spincoating film on quartz substrate.



SI 1. UV-Visible absorption spectra of **FPTPA**/C_{61}-PCBM films (black solid line), **FP3HTTPA**/C_{61}-PCBM films (red solid line), and **PTPA**/C_{61}-PCBM films (blue line).

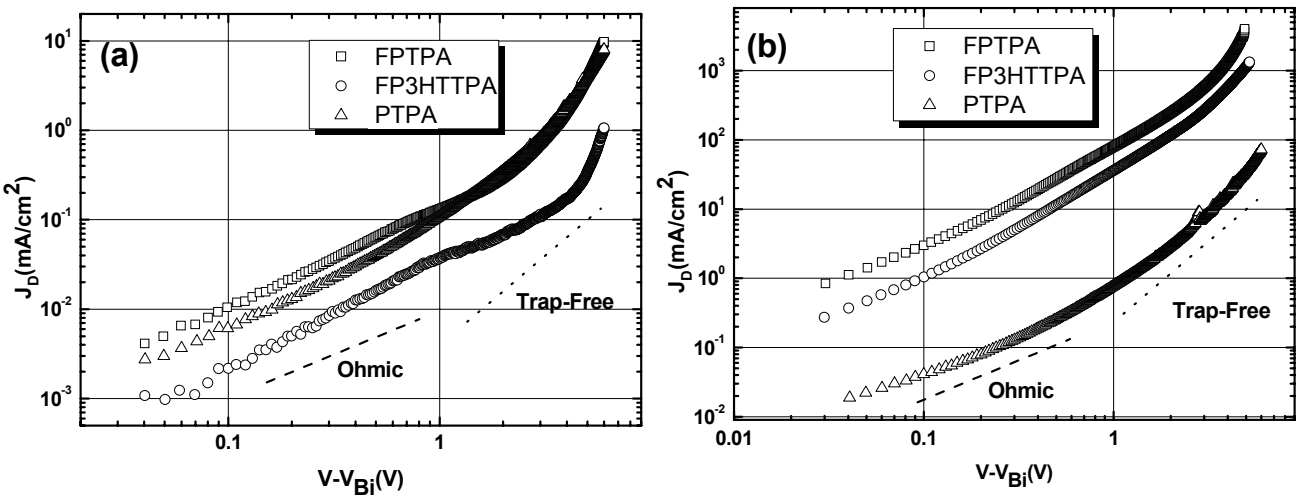


SI 2. Electrochemical characterization of the perylenes in dichloromethane/TBAHFP (0.1 M), scan speed 100 mV/s, potentials vs. Fc/Fc^{+}.



SI 3. Isodensity surface plots of (a) **FPTPA**, (b) **FP3HTTPA** and (c) **PTPA.**

Density Functional Theory (DFT). Optimized structures calculated by TD-DFT using the B3LYP functional and the 3-21G* basis set. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energies were determined using minimized singlet geometries to approximate the ground state



SI 4. (a) Hole-only devices (ITO/PEDOT:PSS/perylenes: C_{61}-PCBM /Au) with a thickness L = 90 ± 5 nm and (b) electron-only devices (Al/perylenes: C_{61}-PCBM /Al) with a thickness L = 150 ± 5 nm.

To investigate the space-charge effects, we extracted the hole and electron mobilities from the SCLC *J-V* characteristics obtained in the dark for hole- and electron-only devices. SI 3 (a)shows the dark-current characteristics of **ITO/PEDOT**:**PSS/perylenes**:**C_{61}-PCBM/Au** devices as a function of the bias corrected by the built-in voltage determined from the difference in work function between **Au** and the HOMO level of perylenes. In the same manner, we also fabricated electron-only devices (**Al/perylenes**:**C_{61}-PCBM/Al**) and investigated their *J-V* characteristics in the dark (see SI 3 (b)). We can expect that Ohm's law will be observed at low voltages as an effect of thermal free carriers. For the presence of carrier traps in the active layer, there is a trap-filled-limit (TFL) region between the ohmic and the trapfree SCLC regions. The SCLC behavior in the trap-free region can be characterized using the Mott-Gurney square law where ε is the static dielectric constant of the medium and μ is carrier mobility.

$J = (9/8)\varepsilon\mu(V^2/L^3)$

Table 2. Hole and Electron Mobility of perylenes:PCBM Films Evaluated Using the Mott-Gurney Law ($\varepsilon = 3\varepsilon_0$)

Film	μ_h	μ_e	μ_e/μ
FPTPA:C_{61}-PCBM	3.64×10^{-6}	6.42×10^{-4}	176
FP3HTTPA:C_{61}-PCBM	1.01×10^{-6}	2.74×10^{-4}	271
PTPA: C_{61}-PCBM	1.28×10^{-6}	2.74×10^{-6}	

Cell fabrication Method

The BHJ films were prepared under optimized conditions according to the following procedure reported previously: The 55 indium tin oxide (ITO)-coated glass substrate was first cleaned with detergent, ultrasonicated in acetone and isopropyl alcohol, and subsequently dried overnight in an oven. PEDOT : PSS (Baytron PH) in aqueous solution was spin-cast to form a film with thickness of approximately 40 nm. The substrate was dried for 10 min at 140 ºC in air, then transferred into a glove-box to spin-cast the photoactive layer. The perylenes:PCBM blend solutions (weight ratio, 1:2) were prepared in chlorobenzene at a concentration of 30 mg/mL. The perylenes:PCBM blend solutions were then spin-cast on top of the PEDOT layer. Then, the device was pumped down to lower than 10–7 torr and a ~100 nm thick Al electrode was deposited on top.

Measurement. Solar cells efficiencies were characterized under simulated 100 mW/cm^2 AM 1.5G irradiation from a Xe arc lamp with an AM 1.5 global filter. Simulator irradiance was characterized using a calibrated spectrometer and illumination intensity was set using an NREL certified silicon diode with an integrated KG1 optical filter: spectral mismatch factors were calculated for each device in this report to be less than 5%. Short circuit currents were also found to be with 5% of values calculated using the integrated external quantum efficiency (EQE) spectra and the solar spectrum. The EQE was measured by underfilling the device area using a reflective microscope objective to focus the light output from a 75 watt Xe lamp, monochromator, and optical chopper; photocurrent was measured using a lock-in amplifier and the absolute photon flux was determined by a calibrated silicon photodiode.

Experimental procedure and characterization of compounds

All reactions were carried out under an argon atmosphere. Solvents were distilled from appropriate reagents. Thiophen-3-ylboronic acid was purchased from Sigma-Aldrich. PDI-Br_2[1] and *N,N*-diphenyl-4-(5'-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2'-bithiophen-5-yl)aniline[2] and 4-(3',4-dihexyl-5'-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2'-bithiophen-5-yl)-*N,N*-diphenylaniline[2] were synthesized using a modified procedure of previous references. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 300 spectrometer. Elemental analyses were performed with a Carlo Elba Instruments CHNS-O EA 1108 analyzer. Mass spectra were recorded on a JEOL JMS-SX102A instrument. The absorption and photoluminescence spectra were recorded on a Perkin-Elmer Lambda 2S UV-visible spectrometer and a Perkin LS fluorescence spectrometer, respectively.

Cyclic voltamogram

CV of the fused perylenes was measured in dichloromethane solution with 0.1 M tetrabutyl ammonium hexafluorophosphate (n-Bu_4NPF_6) as the supporting salt. The platinum working electrode consisted of a platinum wire sealed in a soft glass tube with a surface of 0.785 mm^2, which was polished down to 0.5 μm with Buehler polishing paste prior to use in order to obtain reproducible surfaces. The counter electrode consisted of a platinum wire and the reference electrode was an Ag/AgCl secondary electrode.

PDI-Br_2. were synthesized using a bromination procedure modified from a previously reported method. To a Schlenk tube charged with a solution of PDI_2 (10 g, 13.2 mmol) in $CHCl_3$ (200 mL) was added bromine (27 mL). The tube was sealed and reaction mixture was refluxed for 48h. After the excess of bromine was removed by a gentle steam of air. After the solvents removed in vacuo, the residue was purified with column chromatography over

silica gel, eluted with dichloromethane (DCM) / petroleum ether (PE) (1:3 to 1:1, v/v) to afford a regio-isomeric mixture of 1,6- and 1,7-PDI-Br_2(11 g, 12.0 mmol, 92%) Pure 1,7-PDI-Br_2 was obtained by recrystallization of THF solution with MeOH at room temperature (THF:MeOH=1:3) to give 1,7-PDI-Br_2 in 8% yield. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm) δ 9.47 (d, J=8.2 Hz), 8.92 (br s), 8.71 (br m) 5.17 (m, 2H), 2.24-2.26 (m, 4H), 1.83-1.85 (m, 4H), 1.24-1.32 (m, 32H), 0.83-0.85 (m, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 164.2, 163.7, 163.1, 162.6, 138.6, 137.8, 132.9, 132.8, 130.6, 129.8, 129.3, 128.5, 127.3, 123.8, 123.4, 123.1, 122.7, 120.8, 55.1, 32.5, 31.9, 29.4, 27.0, 22.7, 14.3. Anal.: Calc. For $C_{50}H_{60}Br_2N_2O_4$: C, 65.79; H, 6.63;. Found: C, 65.41; H, 6.48.

Compound (1). A mixture of **PDI-Br_2** (1 g, 1.09 mmol), thiophen-3-ylboronic acid (0.308 g, 2.41 mmol), $Pd(PPh_3)_4$ (0.126g, 0.11 mmol) and 2 M K_2CO_3 aqueous solution (5 ml) in THF (30 ml) was refluxed for 12 h. After cooling the solution, H_2O (20 ml) and brine were added to the solution. The organic layer was separated and dried in $MgSO_4$. The solvent was removed *in vacuo*. The pure product **1** was obtained by chromatographic work-up (eluent MC : Hx = 1 : 3, R_f = 0.4) as a purple solid in 70% yield. Mp: 205 ^{o}C. ^{1}H NMR ($CDCl_3$, 100 MHz, ppm): δ 8.65 (m, 2H), 8.21 (m, 2H), 7.94 (d, J = 4.8 Hz, 2H), 7.62 (s, 2H), 7.44 (s, 2H), 6.88 (d, J = 4.8 Hz, 2H), 5.16 (m, 2H), 2.25-2.19 (m, 4H), 1.82-1.80 (m, 4H), 1.50-1.20 (m, 32H), 0.83-0.81 (m, 12H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, ppm): δ 164.9, 162.9, 142.8, 137.8, 136.5, 135.5, 134.2, 133.8, 129.5, 129.2, 128.5, 128.1, 127.7, 125.8, 124.3, 118.8, 117.7, 54.9, 32.5, 31.9, 29.4, 27.0, 22.7, 14.2. MS: *m/z* 918 [M^+]. Anal. Calc. for $C_{58}H_{66}N_2O_4S_2$: C, 75.78; H, 7.24. Found: C, 75.34; H, 7.03.

Compound (2). A mixture of **1** (1 g, 1.08 mmol), iodine (0.055 g, 0.21 mmol) in benzene (30 ml) was exposed for 2 h. The solvent was removed *in vacuo*. The pure product 2 was

obtained by chromatographic work-up (eluent MC : Hx = 1 : 3, R_f = 0.2) as a red solid in 80% yield. Mp: 198 ^{o}C. ^{1}H NMR ($CDCl_3$, 100 MHz, ppm)): δ 8.68 (s, 2H), 8.46 (s, 2H), 8.00 (d, J = 4.8 Hz, 2H), 7.94 (d, J = 4.8 Hz, 2H), 5.25 (m, 2H), 2.43-2.41 (m, 4H), 2.27-2.22 (m, 4H), 1.60-1.40 (m, 32H), 0.98-0.94 (m, 12H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, ppm): δ 164.2, 163.3, 137.1, 136.7, 135.2, 134.4, 129.8, 128.2, 123.6, 122.8, 122.3, 120.4, 119.5, 118.8, 118.1, 117.7, 55.2, 32.8, 32.2, 29.7, 27.8, 23.0, 14.4. MS: *m/z* 914 [M^+]. Anal. Calc. for $C_{58}H_{62}N_2O_4S_2$: C, 76.11; H, 6.83. Found: C, 75.89; H, 6.63.

Compound (3). To a cold solution of compound **2** (1 g, 1.09 mmol) in dry CH_2Cl_2 (50 mL) at 0 ^{o}C was added a bromine (1.2 mL). The mixture was stirred at 40 ^{o}C for 2 h. After the excess of bromine was removed by a gentle steam of air and washed with hot toluene/MC. The pure product **3** was obtained.

FPTTPA. A mixture of **3** (0.40 g, 0.37 mmol), N,N-diphenyl-4-(5'-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2'-bithiophen-5-yl)aniline (0.49 g, 0.93 mmol), $Pd(PPh_3)_4$ (0.043g, 0.037 mmol) and 2 M K_2CO_3 aqueous solution (3 ml) in THF (40 ml) was sonicated for 2 h and refluxed for 12 h. After cooling the solution, H_2O (20 ml) and brine were added to the solution. The organic layer was separated and dried in $MgSO_4$. The solvent was removed *in vacuo*. The pure product **FPTTPA** was obtained by chromatographic work-up (eluent MC : Hx = 1 : 2, R_f = 0.4) as a dark green solid in 70% yield. Mp: 192 ^{o}C. ^{1}H NMR ($CDCl_3$):): δ 9.19 (s, 2H), 8.19 (s, 2H), 8.01 (s, 2H), 7.32 (d, J = 4.8 Hz, 2H), 7.31 (d, J = 4.8 Hz, 2H), 7.29 (d, J = 7.8 Hz, 8H), 7.22-7.13 (m, 16H), 7.05 (d, J = 7.8 Hz, 8H), 5.42 (m, 2H), 2.63-2.53 (m, 4H), 2.24-2.20 (m, 4H), 1.65-1.37 (m, 32H), 0.91-0.87 (m, 12H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, ppm): δ 165.9, 163.8, 147.9, 147.3, 143.7, 142.3, 140.4, 139.2, 137.8, 136.8, 135.7, 135.0, 133.8, 132.6, 131.1, 130.4, 129.2, 128.7, 127.8, 126.7, 125.4, 124.6,

123.7, 123.2, 123.0, 122.7, 121.7, 120.5, 120.1, 119.7, 118.1, 117.6, 54.8, 32.5, 31.9, 29.4, 27.1, 22.7, 14.2. MS: *m/z* 1729 [M^+]. Anal. Calc. for $C_{110}H_{96}N_4O_4S_6$: C, 76.35; H, 5.59. Found: C, 75.94; H, 5.33.

FP3HTTPA. **FP3HTTPA** was synthesized by a procedure to **FPTTPA** except that 4-(3',4-dihexyl-5'-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2'-bithiophen-5-yl)-*N,N*-diphenylaniline (0.327 g, 0.465 mmol) was used in place of *N,N*-diphenyl-4-(5'-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2'-bithiophen-5-yl)aniline. Yield: 72%. Mp: 193 ^oC. ^1H NMR ($CDCl_3$): δ 9.14 (s, 2H), 8.39 (s, 2H), 8.16 (s, 2H), 7.39 (d, J = 8.1 Hz, 4H), 7.31 (d, J = 7.8 Hz, 8H), 7.30 (s, 2H), 7.23 (s, 2H), 7.17 (d, J = 7.8 Hz, 8H), 7.12 (d, J = 8.1 Hz, 4H), 7.05 (t, J = 7.2 Hz, 4H), 5.42 (m, 2H), 2.93 (t, J = 7.2 Hz, 4H), 2.74 (t, J = 7.2 Hz, 4H), 2.57-2.53 (m, 8H), 2.24-2.20 (m, 8H), 1.65-1.37 (m, 56H), 0.98 (t, J = 7.2 Hz, 6H), 0.93 (t, J = 7.2 Hz, 6H), 0.91-0.87 (m, 12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, ppm): δ 164.9, 163.6, 147.9, 147.5, 143.7, 142.4, 140.4, 139.3, 137.8, 136.7, 135.7, 135.2, 133.5, 132.6, 131.3, 130.1, 129.6, 128.3, 127.8, 126.7, 125.8, 125.1, 124.7, 124.3, 123.9, 123.0, 122.1, 121.5, 120.1, 119.7, 118.9, 117.9, 54.8, 32.8, 32.1, 32.0, 31.9, 31.2, 30.8, 29.7, 29.5, 29.1, 27.8, 27.7, 27.6, 22.9, 22.8, 22.7, 14.4, 14.3, 14.2. MS: *m/z* 2065 [M^+]. Anal. Calc. for $C_{134}H_{144}N_4O_4S_6$: C, 77.86; H, 7.02. Found: C, 77.44; H, 6.73.

PTPA. A mixture of **PDI-Br$_2$** (1 g, 1.09 mmol), N,N-diphenyl-4-(5'-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2',2''-terthiophen-5-yl)aniline (1.48 g, 2.410 mmol), $Pd(PPh_3)_4$ (0.12g, 0.11 mmol) and 2 M K_2CO_3 aqueous solution (5 ml) in THF (30 ml) was refluxed for 12 h. After cooling the solution, H_2O (20 ml) and brine were added to the solution. The organic layer was separated and dried in $MgSO_4$. The solvent was removed *in vacuo*. The pure product **PTPA** was obtained by chromatographic work-up (eluent MC : Hx = 1 : 3, R_f =

0.4) as a grown solid in 70% yield. Mp: 205 ^{o}C. ^{1}H NMR ($CDCl_3$, 600 MHz, ppm): δ 8.65 (m, 2H), 8.21 (m, 2H), 7.62 (s, 2H), 7.43 (d, J = 4.8 Hz, 2H), 7.28 (d, J = 7.8 Hz, 8H), 7.26 (d, J = 4.8 Hz, 2H), 7.23 (d, J = 4.8 Hz, 2H), 7.16-7.08 (m, 16H), 7.03 (d, J = 7.8 Hz, 8H), 7.01 (d, J = 4.8 Hz, 2H), 5.17 (m, 2H), 2.23-2.18 (m, 4H), 1.82-1.80 (m, 4H), 1.40-1.20 (m, 32H), 0.83-0.79 (m, 12H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, ppm): δ 164.9, 162.9, 147.7, 147.5, 143.9, 142.3, 140.4, 138.2, 137.6, 136.8, 135.2, 135.0, 133.1, 132.5, 131.1, 130.8, 129.5, 128.7, 127.9, 126.6, 125.4, 125.1, 124.8, 124.2, 123.6, 123.1, 122.7, 121.7, 120.1, 119.8, 118.1, 117.7, 55.0, 32.5, 31.9, 29.4, 27.1, 22.7, 14.2. MS: *m/z* 918 [M^{+}]. Anal. Calc. for $C_{110}H_{100}N_4O_4S_6$: C, 76.18; H, 5.81. Found: C, 75.84; H, 5.63.

Reference

1. Yan, Q.; Zhao, D. *Org. Lett.* **2009**, *11*, 3426.
2. Li, W.; Du, C.; Li, F.; Zhou, Y.; Fahlman, M.; Bo, Z.; Zhang, F. *Chem. Mater*. **2009**, *21*, 5327.