Supporting Information

Synthesis, characterization, and semiconducting properties of π conjugated polymers containing hydrogen bonded bis-pyridine-

thieno[3,2-b]thiophene moieties

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Experimental Section

Materials

The regents were purchased from Adamas, Sigma-Aldrich, *J&K* Scientific, Bide Pharmatech, SunaTech and Derthon. All chemicals were reagent grade and used as received. Thieno[3,2-b]thiophene-3,6-dicarboxylic was synthesized according to procedures reported in the literature.¹ (2,2'-((2Z,2'Z)-((12,13-Bis(2-ethylhexyl)-3,9diundecyl-12,13-dihydro-[1,2,5]-thiadiazolo-[3,4-e]thieno[2, "3": 4' 5']thieno[2', 3': 4, 5]pyrrolo[3,2-g]thieno[2', 3': 4, 5]thieno[3,2-b]indole-2,10-diyl)bis(methanyl-ylidene)) bis(5,6-difluoro-3-oxo-2,3-dihydro-1H-indene-2,1-diylidene))dimalono-nitrile (Y6) was purchased from Solarmer Materials Inc. Tetrahydrofuran (THF) and toluene were freshly distilled over sodium wires and benzophenone prior to use.

Synthesis of monomer and polymers

Synthesis of bis(2-octyldodecyl)thieno[3,2-b]thiophene-3,6-diyldicarbamate *(1a)*. Thieno[3,2-b]thiophene-3,6-dicarboxylic acid (1.20 g, 5.30 mmol), diphenylphosphoryl azide (DPPA) (3.50 g, 12.60 mmol) and triethylamine (1.30 g, 12.60 mmol) were added to a solution of 2-octyldodecan-1-ol (3.20 g, 10.80 mmol) in anhydrous toluene (15.0 mL). After refluxing overnight, the solution was cooled, and then was concentrated under reduced pressure. The residue was dissolved in diethyl ether and washed with 5% aqueous citric acid, deionized water, and brine. The solution was dried with anhydrous sodium sulfate, and the solvent was evaporated under reduced pressure. The crude product was purified by silica gel column chromatography with ethyl acetate/petroleum ether (1:20) as the eluent to give compound 1a (1.80 g, 42% yield) as a light-yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 7.37 (s, 2H), 6.90 (s, 2H), 4,13 (d, J = 6.0 Hz, 4H), 1.69 (m, 2H), 1.37 (m, 64H), 0.89 (m, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 153.90, 130.37, 128.57, 109.49, 68.64, 37.60, 31.95, 31.93, 31.13, 30.01, 29.70, 29.67, 29.65, 29.60, 29.38, 29.36, 26.73, 22.71, 22.70, 14.13. HRMS MALDI-TOF: *m*/*z* calcd for C₄₈H₈₆N₂O₄S₂, 818.6009; found, 818.6003.

Synthesis of bis(2-ethylhexyl) thieno[3,2-b]thiophene-3,6-diyldicarbamate (1b). The procedure used was same as that of 1a. The reagents used were thieno[3,2-b]thiophene-3,6-dicarboxylic acid (0.400 g, 1.75 mmol), diphenylphosphoryl azide DPPA (1.16 g, 4.20 mmol) and triethylamine (0.425 g, 4.20 mmol) were combined in 2-ethylhexan-1-ol (0.501 g, 3.85 mmol) and anhydrous toluene (5.0 mL). The crude was purified by silica gel column chromatography with ethyl acetate/petroleum (1:15) as the eluent to give the titled compound as a light yellow solid. (0.439 g, 52% yield) ¹H NMR (400 MHz, CDCl₃) δ 7.37 (s, 2H), 6.73 (s, 2H), 4,17 (m, 4H), 1.66 (m, 2H), 1.44 (m, 16H), 0.94 (m, 12H) ¹³C NMR (101 MHz, CDCl₃) δ 153.82, 130.38, 128.53, 109.52, 68.62, 39.00, 30.29, 28.94, 23.65, 23.01, 14.08, 10.98. HRMS MALDI-TOF: *m/z* calcd for C₂₄H₃₈N₂O₄S₂, 482.2273; found, 482.2270.

Synthesis of bis(2-octyldodecyl) (2,5-dibromothieno[3,2-b]thiophene-3,6diyl)dicarbamate (2a). A mixture of 1a (1.60 g, 2.00 mmol) and N-bromosuccinimide (NBS) (0.765 g, 4.40 mmol) in chloroform (60.0 mL) was stirred at room temperature for 1 hour. The reaction was quenched by addition of deionized water, and the mixture was extracted with dichloromethane. The organic layer was dried with anhydrous sodium sulfate. After removing the solvent, the crude product was purified by silica gel column chromatography using ethyl acetate/petroleum ether (1:20) as the eluent to afford compound **2a** (1.50 g, 70% yield) as white solid. ¹H NMR (400 MHz, CDCl₃) δ 6.76 (s, 2H), 4.15 (d, *J* = 6.0 Hz, 4H), 1.73 (m, 2H), 1.34 (m, 64H), 0.92 (m, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 153.50, 128.88, 127.79, 99.98, 69.23, 37.53, 31.94, 31.92, 31.08, 29.98, 29.69, 29.66, 29.63, 29.59, 29.37, 29.34, 26.69, 22.70, 14.13. HRMS MALDI-TOF: *m/z* calcd for C₄₈H₈₆N₂O₄S₂, 976.4203; found, 976.4199.

Synthesis of bis(2-ethylhexyl) (2,5-dibromothieno[3,2-b]thiophene-3,6diyl)dicarbamate (2b). The procedure used was same as that of 2a. The reagents used were 1b (0.400 g, 0.83 mmol), NBS (0.325 g, 1.83 mmol) and chloroform (30.0 mL). The product was purified by silica gel column chromatography with petroleum ether/ dichloromethane (3:2) as the eluent to give the titled compound as a light yellow solid. (0.399 g, 75% yield). ¹H NMR (400 MHz, CDCl₃) δ 6.76 (s, 2H), 4.19 (m, 4H), 1.69 (m, 2H), 1.46 (m, 16H), 0.97 (m, 12H) ¹³C NMR (101 MHz, CDCl₃) δ 153.52, 128.87, 127.77, 99.98, 68.82, 38.92, 30.21, 28.92, 23.59, 23.00, 14.08, 10.9. HRMS MALDI-TOF: *m/z* calcd for C₂₄H₃₆N₂O₄S₂Br₂, 640.0463; found,640.0460.

Synthesis of bis(2-octyldodecyl) (2,5-di(pyridin-2-yl) thieno[3,2-b]thiophene-3,6-diyl)dicarbamate (TTPY). The compound 2a (1.20 g, 1.20 mmol), 2-(tributylstannyl)pyridine (1.10 g, 2.90 mmol), and anhydrous toluene (24.0 mL) were placed in two-necked round bottomed flask under а nitrogen. Dichlorobis(triphenylphosphine)-palladium (0.129 g, 0.18 mmol), triphenylphosphine (0.097 g, 0.37 mmol), and cuprous iodide (0.047 g, 0.25 mmol) were added quickly. The mixture was refluxed under nitrogen atmosphere for 18 hours. After removal of the solvent, the residue was separated by column chromatography on silica gel with ethyl acetate/petroleum ether (1:20) as eluent to afford the crude product, and it was purified by recrystallization in ethanol to give the titled compound as yellow solid. (0.574 g, 48% yield) ¹H NMR (400 MHz, CDCl₃) δ 12.15 (s, 2H), 8.54 (d, J = 4.8 Hz, 2H), 7.69 (m, 4H), 7.11 (m, 2H), 4.15 (d, J = 6.0 Hz, 4H), 1.76 (m, 2H), 1.38 (m, 64H), 0.88 (m,

12H). ¹³C NMR (101 MHz, CDCl₃) δ 154.41, 154.33, 147.51, 137.16, 131.40, 130.76, 122.48, 120.67, 116.98, 68.74, 37.49, 31.93, 31.30, 30.04, 29.71, 29.67, 29.65, 29.60, 29.37, 26.75, 22.69, 14.12. HRMS MALDI-TOF: *m/z* calcd for C₅₈H₉₂N₄O₄S₂, 972.6540; found, 972.6536.

Synthesis of bis(2-ethylhexyl) (2,5-di(pyridin-2-yl) thieno[3,2-b]thiophene-3,6diyl)dicarbamate (TTPYa). The procedure used was same as that of TTPY. The reagents used were **2b** (0.300 g, 0.47 mmol), 2-(tributylstannyl)pyridine (0.414 g, 1.12 mmol). dichlorobis(triphenylphosphine)-palladium (0.049)0.07 g, mmol), triphenylphosphine (0.037 g, 0.14 mmol), CuI (0.018 g, 0.09 mmol) and toluene (6.0 mL). The product was purified by column chromatography of silica gel using petroleum ether/dichloromethane (2:1) as the eluent to afford the crude product, which was further purified by recrystallization in ethanol to give the titled compound as yellow solid. (0.134 g, 45% yield)¹H NMR (400 MHz, CDCl₃) δ 12.13 (s, 2H), 8.56 (d, J = 4.8 Hz, 2H), 7.72 (m, 4H), 7.14 (m, 2H), 4.16 (d, *J* = 6.0 Hz, 4H), 1.74 (m, 2H), 1.57 (m, 16H), 0.97 (m, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 154.34, 152.43, 147.50, 137.21, 131.37, 130.79, 122.53, 120.73, 116.61, 68.36, 38.90, 30.40, 28.95, 23.83, 23.03, 14.08, 11.07. HRMS MALDI-TOF: *m*/*z* calcd for C₃₆H₄₆N₂O₄S₂, 636.2804; found, 636.2802.

Synthesis of bis(2-octyldodecyl) (2,5-bis(5-bromopyridin-2-yl)thieno[3,2b]thiophene-3,6-diyl)dicarbamate (TTPY-Br₂). Bromine (0.1 mL, 1.95 mmol) in chloroform (10.0 mL) was added slowly to a solution of TTPY (0.50 g, 0.51 mmol) in chloroform (50.0 mL). After stirring the reaction at 60 °C for 15 hours, it was cooled to room temperature, and was quenched by addition of saturated aqueous solution of sodium carbonate. The mixture was extracted with dichloromethane and the combined organic layer was dried with anhydrous sodium sulfate. After removing the solvent, the crude product was separated by column chromatography of silica gel with ethyl acetate/petroleum ether (1:30) as the eluent to afford a yellow solid, which was further purified by recrystallization in ethanol to give the titled compound (0.233 g, 40% yield). ¹H NMR (400 MHz, CDCl₃) δ 11.65 (s, 2H), 8.60 (d, *J* = 2.2 Hz, 2H), 7.81 (dd, *J*₁ = 2.2 Hz, *J*₂ = 8.4 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 4.14 (d, *J* = 6.0 Hz, 4H), 1.77 (m, 2H), 1.42 (m, 64H), 0.89 (m, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 154.16, 152.70, 148.67, 139.69, 131.55, 130.87, 121.80, 121.74, 116.91, 68.92, 37.46, 31.93, 31.29, 30.04, 29.72, 29.67, 29.62, 29.37, 26.76, 22.70, 14.13. HRMS MALDI-TOF: *m/z* calcd for C₅₈H₉₀Br₂N₄O₄S₂, 1130.4750; found, 1130.4746.

The regio-chemistry of bromination reaction was confirmed by analyzing the splitting patterns and the coupling constants of ¹H NMR spectrum. The coupling constants of pyridine protons are as follows:

ortho-coupling $J_{3-4} = 7 \sim 9$ Hz, $J_{4-5} = 7 \sim 9$ Hz, $J_{5-6} = 5 \sim 6$ Hz; meta-coupling $J_{3-5} = 1 \sim 2$ Hz, $J_{4-6} = 1 \sim 2$ Hz; para-coupling $J_{3-6} = 1$ Hz. (page 198, "Spectrometric Identification of Organic Compounds" R. M. Silverstein; F. X. Webster; D. Kiemle, 7th Edition, John Wiley 2005.)

(i) If bromines were at position 3, J_{4-5} would be about 7-9 Hz, and J_{5-6} would be about 5-6 Hz, which contradicted with experimental observation. (ii) If bromines were at position 4, J_{5-6} would be about 5-6 Hz, and J_{3-5} would be about 1-2 Hz, which contradicted with experimental observation. (iii) If bromines were at position 6, J_{3-4} would be about 7-9 Hz, and J_{4-5} would be about 7-9 Hz, which contradicted with experimental observation. (iv) When bromines are at position 5, J_{3-4} is about 7-9 Hz, and J_{4-6} is about 1-2 Hz, which are consistent with the experimental observation.

*Synthesis of bis(2-ethylhexyl) (2,5-bis(5-bromopyridin-2-yl)thieno[3,2-b]thiophene-3,6-diyl)dicarbamate (TTPYa-Br*₂). The procedure used was same as that of **TTPY-Br**₂. The reagents used were bromine (0.1 mL, 1.95 mmol), **TTPYa** (0.107 g, 0.17 mmol) and chloroform (10.0 mL). The crude product was separated on silica gel column with petroleum ether/dichloromethane (2:1) as the eluent to afford a yellow solid, which was further purified by recrystallization in ethanol to give the titled compound (0.054 g, 45% yield). ¹H NMR (400 MHz, CDCl₃) δ 11.64 (s, 2H), 8.62 (d, J = 2.2 Hz, 2H), 7.82 (dd, $J_1 = 2.2$ Hz, $J_2 = 8.4$ Hz, 2H), 7.53 (d, J = 8.4 Hz, 2H), 4.16 (d, J = 6.0 Hz, 4H), 1.77 (m, 2H), 1.42 (m, 16H), 0.97 (m, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 154.16, 152.71, 148.68, 139.66, 131.53, 130.83, 121.80, 121.73, 116.89, 68.49, 38.88, 30.35, 28.94, 23.78, 23.03, 14.09, 11.04. HRMS MALDI-TOF: *m/z* calcd for C₃₆H₄₄N₂O₄S₂Br₂, 794.0974; found, 794.0970.

Synthesis of PTTPY-DPP. To a degassed solution of compound TTPY-Br₂(0.113

g, 0.100 mmol) and **3** (0.096 g, 0.100 mmol) in anhydrous toluene (2.0 mL) under nitrogen, Pd₂(dba)₃ (0.002 g, 0.0021 mmol) and P(*o*-tol)₃ (0.003 g, 0.084 mmol) were added. The mixture was then stirred at 120 °C for 15 hours. After cooling to room temperature, the reaction mixture was precipitated in methanol and was filtered. The residue was washed in a Soxhlet extractor with methanol, acetone, hexane, and chloroform sequentially under nitrogen and then was extracted with hot toluene. The toluene solution was concentrated under reduced pressure and was precipitated in methanol to give a black solid (0.120 g, 75% yield). Anal. Calcd for C₉₆H₁₄₆N₆O₆S₄: C 71.69, H 9.15, N 5.22; Found: C 71.51, H 8.97, N 4.89. GPC (TCB, 150 °C): $M_n =$ 153.5 kDa, PDI = 3.5.

Synthesis of PTTPY-BDT. The polymerization procedure was same as that of PTTPY-DPP. Compound TTPY-Br₂ (0.113 g, 0.100 mmol) and 4 (0.091 g, 0.100 mmol) were used to afford a moss green solid (0.110 g, 70% yield). Anal. Calcd for $C_{92}H_{132}N_4O_4S_6$: C 71.27, H 8.58, N 3.61; Found: C 70.87, H 8.46, N 3.40. GPC (TCB, 150 °C): $M_n = 86.6$ kDa, PDI = 4.0.

Characterization

Nuclear magnetic resonance (NMR) spectra were measured on a Bruker AV-400 MHz spectrometer at room temperature. Chemical shifts were recorded with tetramethylsilane (TMS) as the internal reference. Single crystal X-ray diffraction analysis was performed on a Bruker D8 VENTURE X-ray diffractometer. Electrospray ionization mass spectrometry analyses were performed on a Primer UPLC-Q-TOF mass spectrometer. Matrix-assisted laser desorption ionization time-off light mass spectrometry (MALDI-TOF MS) analyses were performed on a Bruker Autoflex system. Elemental analyses were carried out on an Elementar Vario EL Cube system. Gel permeation chromatography (GPC) analyses of polymers were carried out on a PL-GPC 220 high-temperature chromatography with 1,2,4-trichlorobenzene (TCB) as eluent at 150 °C and were calibrated with polystyrene standards. Thermogravimetric analysis (TGA) measurements were conducted on a PerkinElmer Pyris 1 at a heating rate of 20 °C/min under nitrogen. Differential scanning calorimetry (DSC)

measurements were performed on a Netzsch Instruments DSC 204f1 at a scan rate of 10 °C/min under nitrogen. UV-vis absorption spectra of polymers in chlorobenzene (CB) solution and polymer thin-films were acquired from a PerkinElmer Lambda 20 UV-vis spectrophotometer. Cyclic voltammetry (CV) measurements were performed on a CHI600 electrochemical workstation in a solution of tetrabutylammonium hexafluorophosphate (Bu₄NPF₆, 0.1 M) in acetonitrile at scan rate of 100 mV s⁻¹, platinum disk, platinum wire and Ag/Ag⁺ (AgNO₃, 0.01 M in acetonitrile) were used as counter electrode, working electrode and reference electrode, respectively. The cell was calibrated with the ferrocene/ferrocenium (Fc/Fc⁺) redox couple (4.8 eV below vacuum level) as an external standard which was measured under the same conditions before and after the measurement of samples. The polymer film was coated on the surface of a platinum disk electrode. Atomic force microscopy (AFM) images were acquired with a Bruker JPK atomic force microscope. The theoretical calculation was performed with density functional theory (DFT) at B3LYP/6-31G(d) basis set to study molecular geometries and energy levels. All the branched side chains were substituted with methyl to simplify calculation. Grazing-incidence wide-angle X-ray scattering (GIWAXS) characterizations were carried out at the beamline 14B1 of Shanghai Synchrotron Radiation Facility (SSRF).

OFET device fabrication and measurement

The bottom gate top contact (BGTC) OFET devices were used to evaluate the charge transport properties of the polymers. The channel length (*L*) and width (*W*) of the devices were 31 μ m and 273 μ m, respectively. The Si/SiO₂ substrates with a capacitance of 10 nF cm⁻² were used as the gate electrode and dielectric layer. The polymer films were deposited on octadecyl trichlorosilane (OTS) treated Si/SiO₂ substrates by spin-coating from hot chloroform solution (5.0 mg mL⁻¹) at 3000 rpm. The Au source and drain electrode were deposited on the active layer through a shadow mask under a high vacuum. The devices were measured in a glove box under a nitrogen atmosphere using a Keithley 4200-SCS analyzer. Field-effect mobility in saturation regime was calculated by the following equation:

$$\mu = \frac{2L}{WC_i} \left(\frac{\partial \sqrt{I_D}}{\partial V_G} \right)^2$$

Where L is the channel length, W is the channel width, C_i is the capacitance per unit area of gate dielectric layer, I_D is the drain-source current, V_G is the gate voltage.

Organic photovoltaic device fabrication and measurement

The device structure of solar cell was ITO/ZnO/Polymer:Y6/MoO₃/Ag. A layer of zinc oxide (30 nm) was deposited by spin-coating precursors (zinc acetate and ethanolamine in 2-metoxyethanol) on top of pre-cleaned ITO substrates and was annealed at 200 °C for 15 min in air. After deposition, the substrate was transferred to a glove box filled with nitrogen, and a thin layer of ZnO (sol-gel) was spin-coated at 5000 rpm for 30 s. The active layer was a blend of **PTTPY-BDT**:**Y6** (1:1.2 w/w, the total concentration of 10.3 mg mL⁻¹ in chloroform) spin-coated at different speeds. A layer of MoO₃ (15 nm)/Ag (70 nm) was deposited on the active layer by vacuum evaporation at a base pressure of 2×10^{-7} Torr. The effective device area was 4.1 mm² defined by shallow masks. The *J-V* characteristics were measured inside a nitrogen-filled glove box using Keithley 2400 source meter controlled by the LabVIEW program in dark and under illumination (AM 1.5G, 100 mW cm⁻²). Light intensity was calibrated with a silicon photodetector (Newport 818-UV). The external quantum efficiencies (*EQEs*) of the solar cells were measured on a system equipped with a 150 W xenon lamp fitted with a monochromator (Cornerstone 74004) as a monochromatic light source.



Scheme S1 The synthesis of pyridine-flanked dibrominated compounds $S1^2$, $S2^3$ and $S3^4$ from previous reports.



Fig. S1 Single crystal structures of TTPYa-Br₂.



Fig. S2 Calculated molecular geometries and frontier molecular orbitals of (a) **PTTPY-DPP** and (b) **PTTPY-BDT** trimers at B3LYP/6-31G(d) level.



Fig. S3 TGA curves of **PTTPY-DPP** and **PTTPY-BDT**.



Fig. S4 DSC traces of **PTTPY-DPP** and **PTTPY-BDT**.



Fig. S5 Absorption spectra of the polymer solutions at room temperature (a) **PTTPY-DPP** and (b) **PTTPY-BDT**, Absorption spectra of polymer solutions in variable temperature experiments: (c) **PTTPY-DPP** and (d) **PTTPY-BDT**.



Fig. S6 The ¹H NMR spectrum of compound **1a** in CDCl₃.



Fig. S7 The ¹³C NMR spectrum of compound **1a** in CDCl₃.



Fig. S8 The ¹H NMR spectrum of compound **1b** in CDCl₃.



Fig. S9 The ¹³C NMR spectrum of compound **1b** in CDCl₃.



Fig. S10 The ¹H NMR spectrum of compound **2a** in CDCl₃.



Fig. S11 The ¹³C NMR spectrum of compound **2a** in CDCl₃.



Fig S12. The ¹H NMR spectrum of compound **2b** in CDCl₃.



Fig. S13 The ¹³C NMR spectrum of compound **2b** in CDCl₃.



Fig. S14 The ¹H NMR spectrum of compound TTPY in CDCl₃.



Fig. S15 The ¹³C NMR spectrum of compound TTPY in CDCl₃.



Fig. S16 The ¹H NMR spectrum of compound TTPYa in CDCl₃.



Fig. S17 The ¹³C NMR spectrum of compound TTPYa in CDCl₃.



Fig. S18 The ¹H NMR spectrum of compound TTPY-Br₂ in CDCl₃.



Fig. S19 The ¹³C NMR spectrum of compound TTPY-Br₂ in CDCl₃.



Fig. S20 The ¹H NMR spectrum of compound TTPYa-Br₂ in CDCl₃.



Fig. S21 The ¹³C NMR spectrum of compound TTPYa-Br₂ in CDCl₃.



Fig. S22 The ¹H NMR spectrum of **PTTPY-DPP** in C₂D₂Cl₄ at room temperature.



Fig. S23 The ¹H NMR spectrum of **PTTPY-BDT** in C₂D₂Cl₄ at room temperature.



Fig. S24. GPC curves of (a) **PTTPY-DPP** and (b) **PTTPY-BDT** acquired using TCB as eluent at 150 °C.



Fig. S25 a) light intensity dependence of J_{sc} , and b) light intensity dependence of V_{oc} of the solar cells based on PM6 or PTTPY-BDT.

Empirical formula	$C_{34}H_{44}N_4O_4S_2$
Formula weight	636.85
Temperature	173(2) K
Wavelength	1.54178 Å
Crystal system, space group	Triclinic, P-1
	$a = 6.0334(2) \text{ Å} \alpha = 104.443(2)^{\circ}$
Unit cell dimensions	$b = 8.4344(3) \text{ Å } \beta = 91.287(2)^{\circ}$
	$c = 16.7937(5) \text{ Å } \gamma = 94.040(2)^{\circ}$
Volume	824.83(5) Å ³
Z, Calculated density	1, 1.282 mg/m ³
Absorption coefficient	1.810 mm ⁻¹
F(000)	340
Crystal size	$0.180 \times 0.160 \times 0.150 \text{ mm}^3$
Theta range for data collection	2.719 to 68.645°
Limiting indices	-6<=h<=7, -10<=k<=10, -20<=l<=20
Reflections collected / unique	15578 / 3023 [R(int) = 0.0580]
Completeness to theta	67.679 99.9 %

Table S1 Crystal data and structure refinement for TTPYa

Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3023 / 7 / 201
Goodness-of-fit on F ²	1.065
Final R indices [I>2sigma(I)]	R1 = 0.0800, wR2 = 0.2170
R indices (all data)	R1 = 0.0911, wR2 = 0.2288
Extinction coefficient	n/a
Largest diff. peak and hole	0.950 and -0.646 e.Å ⁻³

Table S2 Crystal data and structure refinement for TTPYa-Br₂

Empirical formula	$C_{34}H_{42}Br_2N_4O_4S_2$
Formula weight	794.65
Temperature	173(2) K
Wavelength	1.54178 Å
Crystal system, space group	Monoclinic, Pc
	$a = 10.8870(3) \text{ Å} \alpha = 90^{\circ}$
Unit cell dimensions	$b = 5.0282(2) \text{ Å } \beta = 96.568(2)^{\circ}$
	$c = 32.0053(10) \text{ Å } \gamma = 90^{\circ}$
Volume	1740.54(10) Å ³
Z, Calculated density	2, 1.516 mg/m ³
Absorption coefficient	4.428 mm ⁻¹
F(000)	816
Crystal size	$0.220 \times 0.200 \times 0.180 \text{ mm}^3$
Theta range for data collection	4.087 to 68.134°
Limiting indices	-13<=h<=11, -6<=k<=6, -38<=l<=36
Reflections collected / unique	20443 / 5443 [R(int) = 0.0539]
Completeness to theta	67.679 99.9 %
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	5443 / 6 / 425
Goodness-of-fit on F ²	1.063
Final R indices [I>2sigma(I)]	R1 = 0.0606, wR2 = 0.1666
R indices (all data)	D1 = 0.0712 w D2 = 0.1799
It malees (an adda)	K1 = 0.0713, WK2 = 0.1788
Extinction coefficient	n/a

Table S3	Selected	bond dista	nce and t	orsion	angles	for com	pound '	ГТРҮа
					0			

Bond type	Bond length (Å)	Torsion angles (°)
N(2)-H	0.88	
N(2)·····N(1)	2.71	
H·····N(1)	2.08	
N(1)-C(1)-C(6)-S(1A)		169.28

Bond type	Bond length (Å)	Torsion angles (°)
N(3)-H	0.96	
N(3)·····N(2)	2.73	
H·····N(2)	1.96	
N(4)-H	0.79	
N(4) ·····N(1)	2.70	
H·····N(1)	2.15	
N(2)-C(12)-C(11)-S(2)		175.09
N(1)-C(1)-C(6)-S(1)		-174.91

Table S4 Selected bond distance and torsion angles for compound TTPYa-Br₂

Table S5 Device performance of the **PTTPY-BDT:Y6** solar cells fabricated with different D/A ratio

Solvent	D:A	$V_{\rm oc}({ m V})$	$J_{\rm sc}$ (mA cm ⁻²)	FF	PCE (%)
	1:1	0.76	20.9	57.6	9.1
CF	1:1.2	0.79	22.2	61.7	10.8
	1:1.5	0.77	21.7	58.1	9.7

Table S6 Device performance of the **PTTPY-BDT:Y6** solar cells fabricated with different amount of chloronaphthalene (CN)

D:A	CN	$V_{\rm oc}\left({ m V} ight)$	$J_{\rm sc}$ (mA cm ⁻²)	FF	PCE (%)
	None	0.76	20.4	60.2	9.3
1.1.2	0.3%	0.77	21.8	62.0	10.4
1:1.2	0.5%	0.79	22.2	61.7	10.8
	1.0%	0.73	17.5	59.1	7.6

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