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Supporting Information for

Efficient Modulation of End Groups for the Asymmetric Small Molecule Acceptors Enabling Organic Solar Cells with over 15% Efficiency

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Table of Contents

- 1. General information
- 2. Solar cell fabrication and characterization
- 3. Space charge-limited current (SCLC) device fabrication
- 4. Film and device characterization
- 5. Electrochemical Characterization.
- 6. AFM Characterization.
- 7. Computational studies
- 8. The calculation of exciton dissociation and charge extraction.
- 9. Synthetic details
- 10. Copy of characterization data
- 11. References

1. General information

All solvents and chemicals used were purchased from Energy Chemical, Aladdin, Innochem, Spake or other commercial resources and used as received. Toluene and THF were distilled from sodium benzophenone under nitrogen. Anhydrous DMF was distilled from CaH₂. IC^[1], IC-Cl^[2], IC-2Cl^[3] were synthesized according to literature. IC-Cl is a mixture of two isomers of 2-(5-chloro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)-malononitrile and 2-(6-chloro-3-oxo-2,3-dihydro-1H-inden-1-ylidene) malononitrile (75:25, w/w), which is difficult to separate. Thus, this mixture was used for the final condensation without further purification. ¹H and ¹³C NMR spectra were recorded on a Bruker AVIII-400M (400 MHz and 100 MHz, respectively) spectrometer at room temperature. ¹H and ¹³C NMR chemical shifts were determined relative to internal standard TMS at δ 0.0, CDCl₃(δ ¹H, 7.26 ppm; δ ¹³C, 77.16 ppm). The spectroscopic solvents were purchased from Cambridge Isotope Laboratories. Chemical shifts (δ) are reported in ppm. The following abbreviations are used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Analytical thin layer chromatography (TLC) was performed on 0.25 mm silica gel 60 F254 plates and viewed by UV light (254 nm). Column chromatographic purification was performed using 100-200 or 200-300 mesh silica gel. Mass spectra were measured on a Bruker Maxis UHR-TOF MS spectrometer. UV–vis absorption spectra were performed with a Beijing Purkinje General Instrument Co. Ltd. TU-1901 spectrophotometer. All steady-state measurements were carried out using a quartz cuvette with a path length of 1 cm. Thermogravimetric analysis (TGA) was carried out on a TA Instrument TA Q50 Thermogravimetric Analyzer at a heating rate of 10 °C /min up to 600 °C.

2. Solar cell fabrication and characterization

Solar cells were fabricated in a conventional device configuration of ITO/PEDOT: PSS/active layer/PNDIT-F3N/Ag. The ITO substrates were first scrubbed by detergent and then sonicated with deionized water, acetone and isopropanol subsequently, and dried overnight in an oven. The glass substrates were treated by UV-Ozone for 30 min before use. PEDOT: PSS (Heraeus Clevios P VP A 4083) layer was spin-cast onto the ITO substrates at 4000 rmp for 40s, and then dried at 150 °C for 15 min in air. The donor:acceptor blends with 1:1 ratio were dissolved in chloroform (the concentration of blend solutions are 16 mg/mL for all blend films), and stirred overnight in a nitrogen-filled glove box. The blend solution was spin-cast at 3000 rmp for 40s on the top of PEDOT: PSS layer followed by annealed at 100 °C for 3 mins to remove the residual solvent. A thin PNDIT-F3N layer (10 nm) and Ag layer (100 nm) were sequentially evaporated through a shadow mask under vacuum of 5×10^{-5} Pa. The area of each device was 5.90 mm² defined by a shadow mask. The optimal blend thickness was about 105 nm, measured on a Bruker Dektak XT stylus profilometer. Current density-voltage (J-V) curves were measured in a Keithley 2400 Source Measure Unit. Photocurrent was measured in an Air Mass 1.5 Global (AM 1.5 G) solar simulator (Class AAA solar simulator, Model 94063A, Oriel) with an irradiation intensity of 100 mW cm⁻², which was measured by a calibrated silicon solar cell and a readout meter (Model 91150V, Newport). IPCE spectra were measured by using a QEX10 Solar Cell IPCE measurement system (PV measurements, Inc.).

3. Space charge-limited current (SCLC) device fabrication

The structure of electron-only devices is ITO/ZnO/active layers / PNDIT-F3N /Ag and the structure of hole-only devices is ITO/MoOx/active layer/MoOx/Ag. The fabrication conditions

of the active layer films are same with those for the solar cells. The charge mobilities are generally described by the Mott-Gurney equation:

$$J = (9/8)\varepsilon_0 \varepsilon_r \mu_e V^2/L^3$$

where J is the current density, ε_0 is the permittivity of free space (8.85×10⁻¹⁴ F/cm), ε_r is the dielectric constant of used polymer materials, μ is the charge mobility, V is the applied voltage and L is the active layer thickness. We draw the curves of J-V (not J^{0.5}-V), and obtain the corresponding μ value.

4. Film and Device Characterization

The ultraviolet-visible (UV-Vis) absorption spectra of neat and blend films were obtained using a Shimadzu UV-3101 PC spectrometer. The current density-voltage (J-V) curves of all encapsulated devices were measured using a Keithley 2400 Source Meter in air under AM 1.5G (100 mW cm⁻²) using a Newport solar simulator. The light intensity was calibrated using a standard Si diode (with KG5 filter, purchased from PV Measurement to bring spectral mismatch to unity). Optical microscope (Olympus BX51) was used to define the device area (5.9 mm²). EQEs were measured using an Enlitech QE-S EQE system equipped with a standard Si diode. Monochromatic light was generated from a Newport 300W lamp source. The morphology of the active layers was investigated by atomic force microscopy (AFM) using a Dimension Icon AFM (Bruker) in a tapping mode.

5. Electrochemical Characterization.

Electrochemical measurements were performed under nitrogen in deoxygenated 0.1 M solutions of tetra-n-butylammonium hexafluorophosphate in dry dichloromethane using a CHI 660C electrochemical workstation, a glassy carbon working electrode, a platinum wire auxiliary electrode, and an Ag/AgCl reference electrode. Cyclic voltammograms were recorded at a scan rate of 50 mV s⁻¹. The lowest unoccupied molecular orbital (LUMO) levels were estimated based on the onset reduction potential (E_{red}), and the reduction potential was calibrated using ferrocene ($E_{Fc/Fc+}$) as a reference ($E_{red} = -[E_{measured} - E_{Fc/Fc+} + 4.8]$ eV). Ferrocene as an internal standard.

6. AFM Characterization.

AFM measurements were performed by using a Scanning Probe Microscope-Dimension 3100 in tapping mode. All films were coated on ITO glass substrates.

7. Computational Studies

The geometry was optimized by density functional theory (DFT) using the B3LYP hybrid functional with basis set 6-31G(d).^[4] Quantum chemical calculation was performed with the Gaussian09 package. The long alkyl chains were replaced with an isopropyl group for simplification.

8. The calculation of exciton dissociation and charge extraction.

The dependence of photocurrent density (J_{ph}) on the effective voltage (V_{eff}) was measured. J_{ph} is defined as $J_{ph} = J_L - J_D$, where J_L and J_D represent the photocurrent density under the illumination of AM 1.5 G, 100 mW cm⁻² and in the dark conditions, respectively. $V_{eff} = V_0 - V_{app}$, where V_0 is the voltage when $J_{ph} = 0$ and V_{app} is the applied bias voltage. At a high V_{eff} , the photocurrent is fully saturated, defined as V_{sat} , which is independent of temperature and voltage.



Figure S1. (a) Energy level diagrams for TPIC, TPIC-2Cl and TPIC-4Cl. (b) The OSCs devices diagram.



Figure S2. Absorption spectra of PM7 blended with TPIC, TPIC-2Cl and TPIC-4Cl films.



Figure S3. CV curves of TPIC, TPIC-2Cl and TPIC-4Cl in dichloromethane solutions.



Figure S4. Dark current density-voltage characteristics for electron-only devices with optimized TPIC, TPIC-2Cl and TPIC-4Cl films.



Figure S5. Dark current density-voltage characteristics for hole-only devices with optimized blend of PM7: TPIC, PM7: TPIC-2Cl and PM7: TPIC-4Cl films.



Figure S6. Film morphology images, AFM height (a, c, e, f) and phase (b, d, f, h) images. a, b) PM7, RMS = 0.920 nm; c, d) TPIC, RMS = 0.526 nm; e, f) TPIC-2Cl, RMS = 0.611 nm. g, h) TPIC-4Cl, RMS = 0.613 nm.



Figure S7. 2D GIWAXS patterns of PM7.



Figure S8. TGA profiles of TPIC, TPIC-2Cl and TPIC-4Cl under nitrogen atmosphere.

Samplas	НОМО	LUMO	Eg
Samples	(eV)	(eV)	(eV)
TPIC	-5.53	-3.47	2.06
TPIC-2Cl	-5.64	-3.62	2.02

Table S1. The calculated data of TPIC, TPIC-2Cl and TPIC-4Cl.

TPIC-4Cl	-5.73	-3.72	2.01	

Table S2. Hole and electron mobility of TPIC, TPIC-2Cl and TPIC-4Cl blend with PM7 BHJ

 films.

Samplag	Hole mobility	electron mobility		
Sampies	(cm ² V ⁻¹ s ⁻¹)	$(cm^2 V^{-1} s^{-1})$		
PM7: TPIC	6.97×10-4	3.66×10 ⁻⁴		
PM7: TPIC-2Cl	7.96×10-4	4.45×10^{-4}		
PM7: TPIC-4Cl	8.49×10-4	5.15×10 ⁻⁴		
TPIC	-	6.66×10 ⁻⁴		
TPIC-2Cl	-	7.53×10 ⁻⁴		
TPIC-4Cl	-	8.78×10 ⁻⁴		

Table S3. Key photovoltaic parameters calculated from the J_{ph} - V_{eff} curves of TPIC, TPIC-2Cl and TPIC-4Cl blended with PM7 based devices after annealing.

Samples	J <u>sat</u> (mA cm ⁻²)	J _{ph} ^b (mA cm ⁻²)	J _{ph} ^c (mA cm ⁻²)	J _{ph} ^b / J _{sat} (%)	J _{ph} ^c / J _{sat} (%)
PM7: TPIC	20.631	18.776	15.421	91.0	74.7
PM7: TPIC-2Cl	22.977	21.371	18.231	93.0	79.3
PM7: TPIC-4Cl	24.251	23.032	20.636	94.9	85.1

^aThe J_{ph} under condition of $V_{eff} = 3.0 \text{ V}$; ^bThe J_{ph} under short circuit condition; ^cThe J_{ph} under maximum power output condition.

Table S4. The corresponding data of 2D-GIWAXS characterization of TPIC, TPIC-2Cl andTPIC-4Cl blended with PM7 BHJ films.

Location FWHM d-spacing CL Location FWHM d-spacing CL	Samples	In plane				Out of plane			
	Samples	Location	FWHM	d-spacing	CL	Location	FWHM	d-spacing	CL

	(Å-1)		(Å)	(nm)	(Å-1)		(Å)	(nm)
PM7: TPIC	0.300	0.073	20.93	77.02	1.739	0.240	3.612	20.56
PM7: TPIC-2Cl	0.297	0.068	21.13	82.42	1.787	0.266	3.515	21.23
PM7: TPIC-4Cl	0.302	0.068	20.77	83.33	1.773	0.2470	3.543	23.89
PM7	0.288	0.114	21.77	49.46	1.690	0.302	3.716	18.70
TPIC	0.331	0.127	18.99	44.58	1.798	0.247	3.493	22.89
TPIC-2Cl	0.314	0.105	20.01	53.49	1.799	0.212	3.491	26.61
TPIC-4Cl	0.310	0.085	20.24	65.88	1.806	0.205	3.478	27.52

9. Synthetic procedures



3,3'-dibromo-2,2'-bithiophene^[5]. To a solution of 3-bromothiophene (15 g, 92 mmol) in freshly distilled THF (150 ml) at -78°C was added with lithium diisopropylamide (LDA, 46.4 ml, 2.0 M, 92 mmol) over 30 min. After 1h stirring at -78 °C, the reaction solution was added with anhydrous CuCl₂ (14.9 g, 110.4 mmol) in portions. After another 1h stirring at -78°C, the reaction mixture was then warmed to room temperature and stirred overnight. Quenched with saturated aqueous NH₄Cl, the organic layer was separated and the aqueous layer was extracted with CH₂Cl₂. The combined organic layers were washed with water and brine, dried over MgSO₄, and concentrated via rotary evaporation. The crude product was purified by silicon chromatography (petroleum ether) to get pure product as a pale yellow solid (9.5 g, 63.3%). ¹H NMR (400 MHz, CDCl₃): δ 7.41-7.39 (d, 2H), 7.08-7.07 (d, 2H). The ¹H NMR data is consistent with the literature report. ^[5]



N-(2-ethylhexyl)-dithieno[3,2-b:20,30-d]pyrrole^[6]. A solution of 3,3'-dibromo-2,2'bithiophene (4.2 g,13 mmol), sodium tert-butoxide (2.95 g, 31.56 mmol), Pd₂(dba)₃ (0.31 g, 3.38 mmol), and 2,2'-bis(diphenylphosphino)-1,10-binaphthyl (BINAP, 0.81 g, 1.302 mmol) in anhydrous toluene (93 ml) was purged with N₂ for 10 min and 2-ethylhexylamine (1.74 g, 13.39 mmol) was added via syringe. The mixture was allowed to reflux overnight under N₂ atmosphere. The reaction was quenched with 150 mL of cold water and the layers were separated. The aqueous phase was extracted with CH₂Cl₂ for three times. The combined organic layer was washed by water twice and then dried over anhydrous Na₂SO₄. After the removal of solvent under reduced pressure, the residue was purified by column chromatography on silica gel (eluent: CH₂Cl₂/petroleum ether, 1/6, v/v) to provide the title compound as a light yellow oil (3.53 g, 93.1%). ¹H NMR (400 MHz, CDCl₃): δ 7.12-7.10 (d, 2H), 6.98-6.97 (d, 2H), 4.10-4.00 (m, 2H), 1.96-1.93 (m, 1H), 1.32-1.26 (m, 8H), 0.91-0.86 (m, 6H). The ¹H NMR data is consistent with the literature report. ^[6]



Diethyl 2-bromo-5-(thiophen-2-yl)terephthalate (1) ^[7]: To a stirring solution of thiophene (1.0 g, 11.9 mmol) in dry THF (20 ml) was added dropwise n-butyllithium solution (n-BuLi) (4.75 ml, 2.5 M, 11.9 mmol) at -35°C under argon atmosphere. After one hour, a solution of anhydrous zinc chloride (1.6 g, 11.9 mmol) in dry THF (20 ml) was added dropwise to the resulting solution within 10 mins, and then the mixture was allowed to stir at -35 °C for another one hour. Diethyl 2,5-dibromoterephthalate (4.5 g, 11.9 mmol) and tetrakis (triphenylphosphine) palladium (Pd(PPh₃)₄, 275 mg, 0.238 mmol) were added into the solution of thiophen-2-ylzinc(II) chloride under the protection of argon, and then the mixture was refluxed with a refluxing device for 6 hours. After cooling to room temperature, water was added and the mixture was extracted with dichloromethane and washed with salt solution, dried with anhydrous Na₂SO₄ and concentrated. The residue was purified by silicon chromatography using petroleum ether/ ethyl acetate (12:1 v/v) as eluent to get the product as a light yellow oil

(2.1 g, 46.6%). ¹H NMR (400 MHz, CDCl₃): δ 7.98 (s, 1H), 7.85 (s, 1H), 7.40-7.38 (m, 1H), 7.07-7.06 (m, 2H), 4.45-4.40 (q, 2H), 4.24-4.19 (q, 2H), 1.43-1.39 (t, 3H), 1.17-1.14 (t, 3H). The ¹H NMR data is consistent with the literature report. ^[7]



dithieno[3,2-b:2',3'-d]pyrrol) Diethyl 2-(thiophen-2-yl)-5-(N-(2-ethylhexyl)terephthalate (2): To a stirring solution of N-(2-ethylhexyl)-dithieno[3,2-b:20,30-d]pyrrole (1.74 g, 5.96 mmol) in dry THF (20 ml) was added dropwise n-BuLi in hexane (2.84 ml, 2.5 M, 5.96 mmol) at -35°C under argon atmosphere. After one hour, a solution of anhydrous zinc chloride (0.8 g, 5.96 mmol) in dry THF (20 ml) was added dropwise to the resulting solution within 10 mins, and then the mixture was allowed to stir at -35°C for another one hour. Compound 1 (1.84 g, 4.81 mmol) and Pd(PPh₃)₄ (113 mg, 0.097 mmol) were added into the solution under the protection of argon, and then the mixture was refluxed with a refluxing device for 6 hours. After cooling to room temperature, water was added and the mixture was extracted with dichloromethane and washed with salt solution, dried with anhydrous Na2SO4 and concentrated. The residue was purified by silicon chromatography using petroleum ether/dichloromethane (3:1 v/v) as eluent to get the product as a light yellow solid (2.14 g)75%). ¹H NMR (400 MHz, CDCl₃): δ 7.89 (s, 1H), 7.77 (s, 1H), 7.39-7.38 (d, 1H), 7.17-7.15 (d, 1H), 7.10-7.06 (m, 2H), 7.04 (s, 1H), 6.99-6.98 (d, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 168.25, 168.20, 167.87, 145.20, 145.04, 140.62, 137.18, 134.19, 134.04, 134.00, 132.97, 131.71, 131.69, 127.43, 126.97, 126.50, 123.69, 115.80, 114.68, 111.12, 111.10, 61.78, 61.72, 53.55, 51.41, 40.51, 30.67, 28.76, 24.06, 23.06, 14.13, 14.00, 13.87, 10.75. MAIDI-TOF: C₃₂H₃₆NO₄S₃ (M+H⁺), calcd, 594.1806, found, 594.1798.



4-(2-ethylhexyl)-5,5,10,10-tetrakis(4-hexylphenyl)-5,10-dihydro-4H-thieno[2",3":5',6']-sindaceno[2',1':4,5]thieno[3,2-b]thieno[2,3-d]pyrrole-2,8-dicarbaldehyde (3): To a stirring solution of 1-bromo-4-hexylbenzene (3.26 g, 13.53 mmol) in dry THF (49 ml) was added dropwise n-BuLi in hexane (5.44 ml, 2.5 M, 13.6 mmol) at -78°C under argon atmosphere. After being stirred at -78oC for 1.5 hours, compound 5 (1 g, 1.68 mmol) in dry THF (33 ml) was added dropwise into the resulting solution within 10 mins, and then the mixture was allowed to warm up to room temperature naturally and stirred at room temperature overnight. After the reaction finished, the mixture was poured into water (150 ml) and extracted with ethyl acetate $(3 \times 100 \text{ ml})$, then washed with saturated salt water three times and dried over anhydrous Na₂SO₄. After removal of the solvent under reduced pressure, the brown crude product was obtained and then used in the next step without further purification. The crude product was dissolved in chloroform/glacial acetic acid (5:1 v/v), and 2 ml concentrated sulfuric acid in 5 ml glacial acetic acid was dropwise into the solution, then the mixture was refluxed for 30 min. After cooling to room temperature, the mixture was extracted with dichloromethane and washed with sodium carbonate and water. The collected organic layer was dried over anhydrous Na₂SO₄ and concentrated. The residue was purified by column chromatography on silica gel using a mixture solvent as eluent (petroleum ether/dichloromethane, v/v = 15/1) to give the crude light yellow solid (0.37 g). Then to a dry 100 mL two-necked round bottom flask, anhydrous N, Ndimethylformamide (DMF, 10 ml) was added, and the solution was cooled to 0°C and stirred when phosphorous oxychloride (POCl₃, 2 ml) was added by syringe under argon protection. The mixture kept at 0°C for 2 hours, and then crude light yellow solid in dry 1, 2-dichloroethane (20 ml) was added. Then, the mixture solution was allowed to reflux overnight. After cooling to room temperature, 100 ml water was added to quench the reaction. The mixture was extracted with dichloromethane, and the organic layer was collected, washed with water and dried with anhydrous Na₂SO₄. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel using a mixture solvent as eluent (petroleum ether/ethyl acetate, v/v = 1/15) to give a yellow solid (340 mg, 16%). ¹H NMR (400 MHz, CDCl₃): δ 9.84 (s, 1H), 9.79 (s, 1H), 7.61 (s, 1H), 7.52-7.51 (d, 2H), 7.42 (s, 1H), 7.30-7.28 (m, 6H), 7.14-7.07 (m, 10H), 3.67-3.64 (d, 2H), 2.58-2.54 (t, 8H), 1.58-1.55 (m, 8H), 1.34-1.25 (br, 26H), 0.88-0.56 (br, 25H). ¹³C NMR (100 MHz, CDCl₃): δ 182.79, 182.75, 157.55, 156.20, 154.86, 151.15, 145.55, 145.47, 144.79, 144.02, 142.40, 142.04, 140.85, 140.28, 139.96, 137.66, 137.62, 137.33, 134.42, 132.14, 128.85, 128.60, 128.56, 127.72, 124.69, 118.71, 117.74, 116.68, 62.84, 52.74, 39.13, 35.54, 35.52, 31.70, 31.41, 31.36, 31.31, 29.91, 29.71, 29.11, 28.87, 23.33, 22.88, 22.59, 22.58, 14.08, 13.95, 11.07. MAIDI-TOF: C₇₈H₉₁NO₂S₃ (M⁺), calcd, 1169.6212, found, 1169.6207.



2,2'-((2Z,2'Z)-((4-(2-ethylhexyl)-5,5,10,10-tetrakis(4-hexylphenyl)-5,10-dihydro-4Hthieno[2'',3'':5',6']-s-indaceno[2',1':4,5]thieno[3,2-b]thieno[2,3-d]pyrrole-2,8diyl)bis(methanylylidene))bis(3-oxo-2,3-dihydro-1H-indene-2,1-

dividene))dimalononitrile (TPIC): To a 100 ml round bottom flask, compound 3 (117 mg, 0.1 mmol), 1,1-dicyanomethylene-3-indanone (IC) (77.6 mg, 0.4 mmol), chloroform (30 ml) were added under argon protection and stirred for a while when pyridine (1 ml) was added. The mixture was kept stirring at 75 °C for 24 hours. After removal of chloroform of reaction mixture under reduced pressure, 100 ml methanol was added and the precipitate was collected by filtration. The residue was purified by column chromatography on silica gel using a mixture solvent as eluent (petroleum ether/dichloromethane, v/v = 1/1) to give a dark solid (100 mg, 65.7%). ¹H NMR (400 MHz, CDCl₃): δ 8.86 (s, 2H), 8.67-8.62 (m, 2H), 7.89-7.86 (m, 2H), 7.73-7.63 (m, 7H), 7.48 (s, 1H), 7.32-7.29 (m, 4H), 7.15-7.09 (m, 12H), 3.68-3.66 (d, 2H), 2.61-2.55 (q, 8H), 1.61-1.56 (m, 8H), 1.32-1.25 (br, 26H), 0.88-0.56 (br, 25H). ¹³C NMR (100 MHz, CDCl₃): δ 188.43, 188.27, 160.89, 160.41, 159.90, 158.59, 157.39, 156.17, 150.04, 147.74, 146.42, 142.71, 142.25, 140.71, 140.45, 140.42, 140.00, 139.95, 139.51, 138.48, 138.26, 137.10, 136.87, 136.85, 136.28, 135.36, 135.05, 134.64, 134.34, 133.96, 128.75, 128.70, 127.73, 126.37, 125.27, 124.96, 123.66, 123.40, 121.71, 120.55, 120.09, 118.58, 117.28, 115.38, 115.27, 114.73, 114.70, 68.79, 66.96, 62.91, 62.80, 52.96, 38.94, 35.56, 35.53, 31.71, 31.41, 31.38, 31.32, 29.94, 29.71, 29.10, 28.75, 23.39, 22.94, 22.59, 22.58, 14.10, 13.96, 10.99. MAIDI-TOF: C₁₀₂H₉₉N₅O₂S₃ (M⁺), calcd, 1522.6994, found, 1522.7099.



2,2'-((2Z,2'Z)-((4-(2-ethylhexyl)-5,5,10,10-tetrakis(4-hexylphenyl)-5,10-dihydro-4Hthieno[2'',3'':5',6']-s-indaceno[2',1':4,5]thieno[3,2-b]thieno[2,3-d]pyrrole-2,8diyl)bis(methanylylidene))bis(6-chloro-3-oxo-2,3-dihydro-1H-indene-2,1-

divlidene))dimalononitrile (TPIC-2Cl): To a 100 ml round bottom flask, compound 3 (117 mg, 0.1 mmol), 5-chloro-1,1-dicyanomethylene-3-indanone (IC-Cl) (91.4 mg, 0.4 mmol), chloroform (30 ml) were added under argon protection and stirred for a while when pyridine (1 ml) was added. The mixture was kept stirring at 75°C for 24 hours. After removal of chloroform of reaction mixture under reduced pressure, 100 ml methanol was added and the precipitate was collected by filtration. The residue was purified by column chromatography on silica gel using a mixture solvent as eluent (petroleum ether/dichloromethane, v/v = 1/1) to give a dark solid (100 mg, 62.9%). ¹H NMR (400 MHz, CDCl₃): δ 8.87-8.86 (m, 2H), 8.64-8.56 (m, 2H), 7.82-7.79 (m, 2H), 7.69-7.62 (m, 5H), 7.48 (s, 1H), 7.31-7.29 (d, 4H), 7.14-7.09 (m, 12H), 3.68-3.66 (d, 2H), 2.60-2.55 (q, 8H), 1.59-1.56 (m, 8H), 1.33-1.25 (br, 26H), 0.87-0.57 (br, 25H). ¹³C NMR (100 MHz, CDCl₃): δ 187.17, 187.03, 186.80, 160.63, 159.80, 159.31, 158.96, 158.71, 157.68, 156.37, 150.62, 148.17, 146.69, 142.77, 142.33, 141.71, 141.29, 141.19, 141.11, 140.80, 140.62, 140.48, 140.32, 139.91, 138.89, 138.39, 138.03, 136.98, 136.40, 135.38, 135.04, 134.42, 133.96, 128.79, 128.73, 127.71, 126.44, 126.09, 125.35, 125.06, 124.62, 124.32, 123.76, 123.50, 121.21, 120.27, 120.03, 118.73, 117.39, 115.22, 114.53, 69.48, 68.88, 67.47, 66.96, 62.90, 62.83, 52.98, 50.91, 38.95, 35.55, 35.53, 31.70, 31.41, 31.38, 31.31, 29.94, 29.71, 29.10, 28.75, 23.38, 22.93, 22.59, 14.09, 13.95, 10.99. MAIDI-TOF: C₁₀₂H₉₇Cl₂N₅O₂S₃ (M⁺), calcd, 1590.6215, found, 1590.6241.



2,2'-((2Z,2'Z)-((4-(2-ethylhexyl)-5,5,10,10-tetrakis(4-hexylphenyl)-5,10-dihydro-4Hthieno[2'',3'':5',6']-s-indaceno[2',1':4,5]thieno[3,2-b]thieno[2,3-d]pyrrole-2,8-

diyl)bis(methanylylidene))bis(5,6-dichloro-3-oxo-2,3-dihydro-1H-indene-2,1-

divlidene))dimalononitrile (TPIC-4Cl): To a 100 ml round bottom flask, compound 3 (120 mg, 0.1 mmol), 5,6-dichloro-1,1-dicyanomethylene-3-indanone (IC-2Cl) (105.6 mg, 0.403 mmol), chloroform (30 ml) were added under argon protection and stirred for a while when pyridine (1 ml) was added. The mixture was kept stirring at 75 °C for 24 hours. After removal of chloroform of reaction mixture under reduced pressure, 100 ml methanol was added and the precipitate was collected by filtration. The residue was purified by column chromatography on silica gel using a mixture solvent as eluent (petroleum ether/dichloromethane, v/v = 1/1) to give a dark solid (98 mg, 59%). ¹H NMR (400 MHz, CDCl₃): δ 8.87 (s, 1H), 8.85 (s, 1H), 8.76 (s, 1H), 8.72 (s, 1H), 7.91-7.89 (d, 2H), 7.68-7.65 (d, 2H), 7.49 (s, 1H), 7.30-7.26 (m, 5H), 7.14-7.09 (m, 12H), 3.68-3.66 (d, 2H), 2.61-2.55 (q, 8H), 1.60-1.57 (m, 8H), 1.33-1.25 (br, 26H), 0.88-0.56 (br, 25H). ¹³C NMR (100 MHz, CDCl₃): δ 186.13, 185.88, 161.32, 158.82, 158.52, 158.17, 157.92, 156.54, 151.17, 148.57, 146.91, 142.86, 142.40, 140.93, 140.53, 140.22, 139.64, 139.32, 139.16, 139.00, 138.87, 138.71, 138.61, 138.56, 136.88, 136.57, 136.01, 135.43, 128.81, 128.75, 128.72, 127.70, 126.97, 126.62, 125.09, 124.79, 120.82, 120.48, 119.53, 118.84, 117.50, 115.04, 114.89, 114.30, 69.39, 67.35, 62.91, 62.86, 53.02, 38.94, 35.55, 35.53, 31.70, 31.41, 31.38, 31.31, 29.94, 29.10, 28.75, 23.39, 22.93, 22.59, 22.58, 14.09, 13.95, 10.98. MAIDI-TOF: C₁₀₂H₉₅Cl₄N₅O₂S₃ (M⁺), calcd, 1660.5406, found, 1660.5339.

10. Copy of characterization data



Figure S10. ¹ H NMR spectrum of N-(2-ethylhexyl)-dithieno[3,2-b:20,30-d]pyrrole.





Figure S11.¹ H NMR spectrum of compound 1.



Figure S12. ¹H NMR spectrum of compound 2.



Figure S14. ¹H NMR spectrum of compound 3.



Figure S16. ¹H NMR spectrum of compound TPIC.



Figure S18. ¹H NMR spectrum of compound TPIC-2Cl.





Figure S20. ¹ H NMR spectrum of compound TPIC-4Cl.





Figure S22. HRMS profile of compound 2.









Figure S24. HRMS profile of compound TPIC.



Figure S25. HRMS profile of compound TPIC-2Cl.



Figure S26. HRMS profile of compound TPIC-4Cl.

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