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Supporting Information

Investigation of Isomerization Effects on Photovoltaic Performance of Fused Ring Electron Acceptors via Manipulating Side-Chain Position

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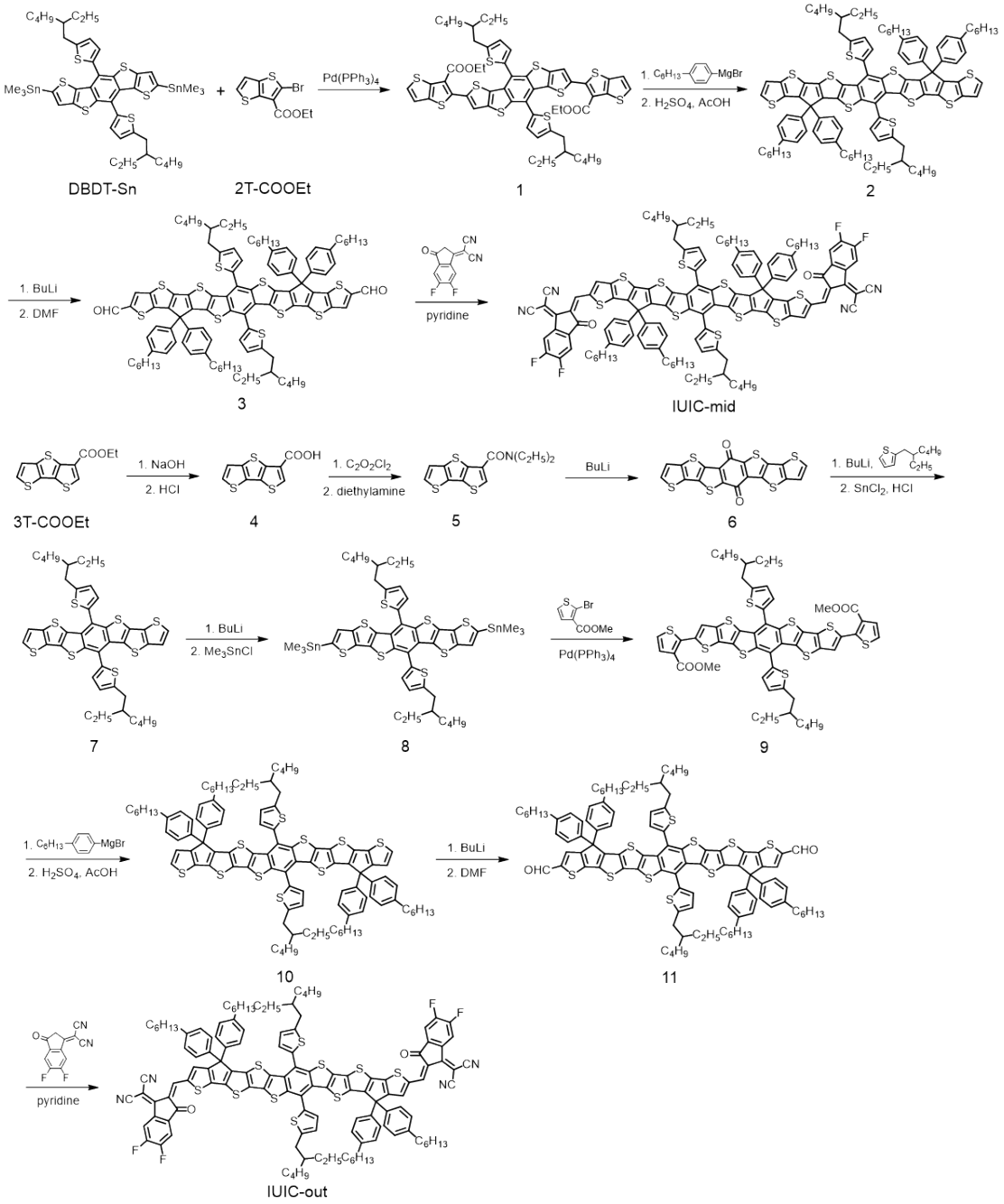
1. General characterization

^{1}H and ^{13}C NMR spectra were measured on a Bruker Avance-400 spectrometer. The MALDI-TOF mass spectrometry experiments were performed on an autoflex III instrument (Bruker Daltonics, Inc.). Absorption spectra were recorded on a Lambda 950 spectrophotometer (PerkinElmer, U.S.A.). Cyclic voltammetry was done by using a Shanghai Chenhua CHI660C voltammetric analyzer under argon in a mixture solution (acetonitrile:*o*-dichlorobenzene=1:1) of tetra-*n*-butylammonium hexafluorophosphate (0.1 M). A glassy-carbon electrode was used as the working electrode, a platinum-wire was used as the counter electrode, and a Ag/AgCl electrode was used as the reference electrode. All potentials were corrected against Fc/Fc^{+} redox couple (Fc represents ferrocene.). AFM was performed on a Bruker Dimension icon by using tapping mode. The *J-V* curves were measured by using a Keithley 2450 source-measure unit in the nitrogen-filled glove box along the reverse scan direction from -0.2 V to 1 V at room temperature. The scan speed and dwell times were fixes at 0.02 V per step and 0 ms, respectively. The photocurrent was measured under AM 1.5G illumination at 100 mW cm^{-2} by using a 3A solar simulator (LSS-55, Lightsky Technology Co., Ltd). Light intensity is calibrated with a standard photovoltaic cell equipped with a KG5 filter (certificated by the National Institute of Metrology). The EQE measurements of devices were carried out in the air with a solar cell spectral response measurement system (QE-R3018, Enli Technology Co., Ltd). The light intensity at each wavelength was calibrated by a standard single-crystal Si photovoltaic cell. The thickness of all films were measured by the Bruker Dektak-XT.

2. Synthesis

All reagents were purchased from J&K Co., Innochem Co., HWRK Chem Co., SunaTech Inc., and other commercial suppliers. The polymer donor, PM6, was purchased from Derthon Co.. All reactions dealing with air- or moisture-sensitive compounds were carried out using standard Schlenk techniques. The IUIC-in, 2T-COOEt and 3T-COOEt were prepared according to the literatures.[1-3]



Scheme S1. The synthetic routes of IUIC-mid and IUIC-out.

Compound 1. To a solution of DBDT-Sn (762 mg, 0.75 mmol) and 2T-COOEt (480 mg, 1.65 mmol) in fresh distilled toluene (30 mL) in a two-necked flask was added $Pd(PPh_3)_4$ (80 mg) under Ar. The mixture was heated to reflux and stirred overnight. Then it was cooled down to room temperature and the solvent was removed under reduced pressure. The crude product was re-dissolved in the mixture solvent of CH_2Cl_2/hexane (1:1, v/v) and purified via silica gel column chromatography by using CH_2Cl_2/hexane (1:1, v/v) as eluent to give compound **1** (775 mg, 93%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.74 (s, 2H), 7.46 (d, J = 5.3 Hz, 2H), 7.20 (m, 4H), 6.99 (d, J = 3.2 Hz, 2H), 4.37 (q, J = 7.1 Hz, 4H), 2.93 (d, J = 6.7 Hz, 4H), 1.72 (m, 2H), 1.54-1.25 (m, 22H), 0.96 (t, J = 7.4 Hz, 6H), 0.86 (t, J = 6.9 Hz, 6H). ^{13}C NMR ($CDCl_3$,

100 MHz, δ/ppm): 161.88, 147.33, 144.50, 143.27, 141.29, 139.32, 138.21, 136.07, 135.37, 134.13, 130.41, 129.36, 128.58, 125.93, 124.09, 122.25, 120.96, 118.62, 61.18, 41.60, 34.36, 32.49, 28.95, 25.71, 23.06, 14.20, 14.12, 10.99.

Compound 2. To a solution of 1-bromo-4-hexylbenzene (1.45 g, 6 mmol) in dry THF (8 mL) was added magnesium (158 mg, 6.6 mmol) under argon, and the mixture was heated to reflux for ~1 h until magnesium almost disappeared. Then the Grignard reagent was added to a suspension of compound **1** (667 mg, 0.6 mmol) in THF (10 mL) at room temperature under argon. The mixture was heated to reflux overnight and then allowed to cool down to room temperature. It was poured into diluted HCl (50 mL, 1M) and extracted with CH_2Cl_2 twice. The organic phase was dried over anhydrous Na_2SO_4. After removing the solvent, the residue was re-dissolved in octane (20 mL) and acetic acid (2 mL) again, and the concentrated H_2SO_4 (0.2 mL) was added dropwise. The solution was heated to reflux for ~1 h and then quenched with water. It was extracted with CH_2Cl_2 twice and the combined organic phase was dried over anhydrous Na_2SO_4. After removing the solvent, the crude product was purified via column chromatography (silica gel) using hexane/CH_2Cl_2 (4:1, v/v) as eluent to give compound **2** as a yellow solid (274 mg, 28%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.13 (m, 10H), 7.03 (m, 10H), 2.95 (dd, *J* = 6.5, 4.0 Hz, 4H), 2.56-2.46 (m, 8H), 1.74 (dd, *J* = 12.5, 6.3 Hz, 2H), 1.41-1.17 (m, 48H), 1.02 (t, *J* = 7.4 Hz, 6H), 0.93 (t, *J* = 6.8 Hz, 6H), 0.85 (t, *J* = 6.8 Hz, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 147.98, 147.69, 147.45, 142.68, 141.98, 141.05, 140.88, 138.49, 137.84, 134.53, 134.35, 134.04, 130.50, 128.63, 128.48, 127.91, 126.80, 126.01, 125.94, 122.63, 120.20, 62.36, 41.84, 35.59, 34.62, 32.49, 31.77, 31.18, 29.70, 29.44, 29.12, 28.93, 25.95, 23.18, 22.63, 14.23, 14.06, 11.19.

Compound 3. To a solution of compound **2** (240 mg, 0.15 mmol) in dry THF (20 mL) was added 1.6M *n*-butyllithium (0.38 mL, 0.60 mmol) at -78 °C under argon, and it stirred at the temperature for ~1 h. Then the solution was warmed to -50 °C. Anhydrous DMF (0.4 mL) was added to the solution and it continued to stir at -50 °C for ~1 h. Afterwards it was quenched with water and extracted with CH_2Cl_2 three times. The organic phase was dried over anhydrous Na_2SO_4. After removing the solvent, the crude product was purified via column chromatography (silica gel) using hexane/CH_2Cl_2 (1:1, v/v) as eluent to give compound **3** as an orange solid (215 mg, 87%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 9.87 (s, 2H), 7.91 (s, 2H), 7.16-6.99 (m, 20H), 2.97 (s, 4H), 2.53 (t, *J* = 7.1 Hz, 8H), 1.75 (s, 2H), 1.67-1.16 (m, 48H), 1.03 (t, *J* = 7.1 Hz, 6H), 0.93 (s, 6H), 0.86 (s, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 182.58, 150.35, 147.82, 147.77, 145.33, 143.53, 143.17, 142.47, 140.54, 140.32, 140.15, 136.90, 136.51, 134.24, 133.99, 130.66, 129.70, 128.89, 128.60, 127.69, 126.07, 123.27, 62.47, 41.83, 35.57, 34.59, 32.46, 31.75, 31.18, 29.41, 29.11, 28.89, 25.93, 23.18, 22.63, 14.24, 14.06, 11.20.

IUIC-mid. To a solution of compound **3** (80 mg, 47 μmol) in $CHCl_3$ (10 mL) were added 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (65 mg, 0.28 mmol) and pyridine (1 mL). It was heated to reflux for 1.5 h and then cooled down to room temperature. The solution was poured into column chromatography (silica gel)

directly and the crude product was purified by using $CHCl_3$ as eluent to give IUIC-mid a dark-green solid (84 mg, 84%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 8.80 (s, 2H), 8.50 (dd, *J* = 9.8, 6.5 Hz, 2H), 8.11 (s, 2H), 7.66 (t, *J* = 7.5 Hz, 2H), 7.15 (q, *J* = 8.3 Hz, 18H), 7.04 (d, *J* = 3.1 Hz, 2H), 2.96 (d, *J* = 5.5 Hz, 4H), 2.68-2.40 (m, 8H), 1.79-1.69 (m, 2H), 1.62-1.18 (m, 48H), 1.02 (t, *J* = 7.3 Hz, 6H), 0.94 (d, *J* = 6.0 Hz, 6H), 0.84 (t, *J* = 6.2 Hz, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 185.80, 158.19, 155.72, 152.67, 150.25, 148.50, 148.14, 143.75, 142.92, 142.77, 140.29, 138.69, 138.59, 138.01, 137.47, 136.62, 136.49, 134.69, 134.39, 133.56, 130.88, 129.05, 128.77, 127.74, 126.16, 123.81, 120.92, 114.97, 114.75, 114.42, 114.32, 112.59, 112.41, 99.98, 69.00, 62.58, 41.83, 35.60, 34.58, 32.48, 31.76, 31.18, 29.46, 29.11, 28.90, 25.96, 23.20, 22.62, 14.23, 14.05, 11.19. MALDI-TOF MS (m/z): 2113.7 ($M + H^+$).

Compound 4. A mixture of 3T-COOEt (1.5 g, 5.59 mmol) and sodium hydroxide (1.79 g, 44.7 mmol) in ethanol/THF/water (20 mL/20 mL/20 mL) was refluxed overnight. Half of solvent was evaporated under vacuum, then water (40 mL) was added to the solution. The resulting mixture was treated with diluted HCl. The precipitate was filtered and washed with water to give compound **4** as a pale-yellow solid (1.26 g, 94%). ^{1}H NMR (THF-d_8, 400 MHz, δ/ppm): 11.60 (broad, 1H), 8.22 (s, 1H), 7.52 (d, *J* = 5.2 Hz, 1H), 7.40 (d, *J* = 5.2 Hz, 1H). ^{13}C NMR (THF-d_8, 100 MHz, δ/ppm): 163.18, 145.10, 142.84, 133.67, 131.42, 131.31, 128.93, 127.83, 121.99.

Compound 5. To the suspension of compound **4** (1.20 g, 5.0 mmol) in dry CH_2Cl_2 (40 mL) were added oxalyl chloride (4 mL, 47 mmol) and 1 drop of DMF. The mixture was stirred at room temperature overnight. The volatile was removed under reduced pressure to obtain dithieno[3,2-*b*:2',3'-*d*]thiophene-3-carbonyl chloride, which was used in next step without purification. Dithieno[3,2-*b*:2',3'-*d*]thiophene-3-carbonyl chloride was re-dissolved in dry CH_2Cl_2 (30 mL) and diethylamine (1.46 g, 20 mmol) in dry CH_2Cl_2 (30 mL) was slowly added into the solution under 0 °C. The mixture was stirred at room temperature overnight. Then the mixture was poured into water and extracted with hexane three times. The organic phase was dried over anhydrous Na_2SO_4. After removal of the solvent, the crude product was purified by silica gel column chromatography with hexane/CH_2Cl_2 (3:2) as eluent to give compound **5** (1.45 g, 98%) as a pale yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.49 (s, 1H), 7.38 (d, *J* = 5.2 Hz, 1H), 7.31 (d, *J* = 5.2 Hz, 1H), 3.59 (q, *J* = 7.1 Hz, 4H), 1.28 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 163.96, 143.00, 142.28, 130.34, 130.10, 129.81, 126.31, 124.48, 120.87, 41.76, 13.71.

Compound 6. Compound **5** (1.40 g, 4.74 mmol) was put into a dried flask with 30 mL of THF under Ar. The solution was cooled down by an ice-water bath, and 1.6 M n-butyllithium (3 mL, 4.80 mmol) was added into the flask dropwise within ~10 min. Then the reactant was stirred at ambient temperature for 1 h. The mixture was poured into ice water and stirred for another hour. The mixture was filtrated. The precipitate was washed by 100 mL water, 50 mL methanol, and 50 mL hexane, successively, and dried under vacuum to give compound **6** (727 mg, 69%) as a dark red solid. It is used for next step without further purification. The product suffers from extremely poor solubility in common solvent and thus NMR data cannot be obtained.

Compound 7. In a 100 mL argon purged flask, 1.6 M n-butyllithium (3.5 mL, 5.60 mmol) was added dropwise to a solution of 2-ethylhexylthiophene (1.24 g, 6.30 mmol) in THF (40 mL) at 0 °C. The mixture was then warmed to 50 °C and stirred for about 1 h. Subsequently, compound **6** (700 mg, 1.57 mmol) was added to the reaction mixture, which was then stirred for another hour at 50 °C. After cooling the reaction mixture to ambient temperature, a mixture of $SnCl_2 \cdot 2H_2O$ (2.84 g, 12.6 mmol) in 36% HCl (4 mL) was added and the mixture was stirred for additional 1.5 h, after which it was poured into ice water. The mixture was extracted with CH_2Cl_2 three times, and the organic phases were combined. After removing solvent under vacuum, the residue was purified by silica gel column chromatography with hexane as eluent to give compound **7** (731 mg, 58%) as a yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.38 (d, J = 5.2 Hz, 2H), 7.23-7.16 (m, 4H), 7.02 (d, J = 3.3 Hz, 2H), 3.06-2.84 (m, 4H), 1.74 (dd, J = 12.4, 6.2 Hz, 2H), 1.57-1.33 (m, 16H), 0.98 (dt, J = 13.3, 7.1 Hz, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 147.53, 143.47, 142.67, 135.56, 133.96, 131.28, 130.93, 130.86, 128.75, 127.34, 125.80, 123.74, 120.58, 41.76, 34.45, 32.50, 29.02, 25.86, 23.13, 14.22, 11.01.

Compound 8. Compound **7** (700 mg, 0.87 mmol) was added into 20 ml THF in a flask under Ar. The solution was cooled down to -78 °C and 1.6 M n-butyllithium (1.25 mL, 2 mmol) was added dropwise. After being stirred at -78 °C for 2 h, 1.0 M trimethylchlorostannane in hexane (2.2 mL, 2.2 mmol) was added in one portion. The mixture was stirred at this temperature for 30 min and then the cooling bath was removed. The reactant was allowed to warm to room temperature for another hour. Then ~100 ml water was added and the mixture was extracted by diethyl ether three times and the organic phases were combined. After removing solvent under vacuum, the residue was recrystallized from methanol to give compound **8** (874 mg, 89%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.21 (s, 4H), 7.01 (d, J = 3.2 Hz, 2H), 2.95 (qd, J = 14.7, 6.8 Hz, 4H), 1.74 (dd, J = 12.2, 6.1 Hz, 2H), 1.52-1.33 (m, 16H), 1.06-0.90 (m, 12H), 0.41 (s, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 147.35, 145.57, 142.62, 142.04, 136.70, 135.52, 134.12, 131.07, 130.43, 128.70, 127.49, 125.77, 123.66, 41.76, 34.44, 32.52, 29.06, 25.84, 23.15, 14.24, 11.00, -8.12.

Compound 9. To a solution of compound **8** (850 mg, 0.75 mmol) and methyl 2-bromothiophene-3-carboxylate (400 mg, 1.80 mmol) in fresh distilled toluene (30 mL) in a two-necked flask was added $Pd(PPh_3)_4$ (85 mg) under Ar. The mixture was heated to reflux and stirred overnight. Then it was cooled down to room temperature and the solvent was removed under reduced pressure. The crude product was re-dissolved in the mixture solvent of CH_2Cl_2/hexane (1:1, v/v) and purified via silica gel column chromatography by using CH_2Cl_2/hexane (1:1, v/v) as eluent to give compound **9** (772 mg, 95%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.65 (s, 2H), 7.50 (d, J = 5.4 Hz, 2H), 7.24-7.20 (m, 4H), 7.03 (d, J = 3.2 Hz, 2H), 3.84 (s, 6H), 2.96 (m, 4H), 1.75 (dd, J = 12.3, 6.1 Hz, 2H), 1.57-1.31 (m, 16H), 1.01 (t, J = 7.4 Hz, 6H), 0.96 (t, J = 6.5 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm):163.42, 147.65, 143.22, 143.09, 143.05, 136.15, 135.67, 133.77, 132.79, 130.92, 130.88, 130.70, 128.87, 127.76, 125.84, 124.33, 123.93, 122.45, 51.82, 41.74, 34.44, 32.54, 29.03, 25.85, 23.14, 14.23, 11.01.

Compound 10. To a solution of 1-bromo-4-hexylbenzene (1.57 g, 6.5 mmol) in dry THF (10 mL) was added magnesium (168 mg, 7.0 mmol) under argon, and the mixture was heated to reflux for ~1 h until magnesium almost disappeared. Then the Grignard reagent was added to a suspension of compound **1** (700 mg, 0.65 mmol) in THF (10 mL) at room temperature under argon. The mixture was heated to reflux overnight and then allowed to cool down to room temperature. It was poured into diluted HCl (50 mL, 1M) and extracted with CH_2Cl_2 twice. The organic phase was dried over anhydrous Na_2SO_4. After removing the solvent, the residue was re-dissolved in octane (20 mL) and acetic acid (2 mL) again, and the concentrated H_2SO_4 (0.2 mL) was added dropwise. The solution was heated to reflux for ~1 h and then quenched with water. It was extracted with CH_2Cl_2 twice and the combined organic phase was dried over anhydrous Na_2SO_4. After removing the solvent, the crude product was purified via column chromatography (silica gel) using hexane/CH_2Cl_2 (4:1, v/v) as eluent to give compound **10** as a yellow solid (327 mg, 31%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.22 (d, *J* = 4.9 Hz, 2H), 7.14-7.06 (m, 12H), 7.03 (d, *J* = 7.9 Hz, 8H), 6.97 (s, 2H), 2.96 (ddd, *J* = 21.8, 14.6, 6.3 Hz, 4H), 2.54 (t, *J* = 7.2 Hz, 8H), 1.71 (s, 2H), 1.56 (d, *J* = 7.4 Hz, 8H), 1.42-1.23 (m, 48H), 1.00-0.75 (m, 24H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 157.89, 149.84, 148.81, 146.77, 142.35, 141.69, 139.45, 138.45, 138.22, 136.62, 134.62, 133.87, 131.70, 131.47, 130.62, 128.44, 127.63, 126.09, 125.76, 123.33, 123.13, 62.09, 41.17, 35.59, 33.70, 32.57, 31.72, 31.28, 29.69, 29.14, 25.19, 23.02, 22.59, 14.23, 14.07, 10.56.

Compound 11. To a solution of compound **10** (240 mg, 0.15 mmol) in dry THF (20 mL) was added 1.6M *n*-butyllithium (0.38 mL, 0.60 mmol) at -78 °C under argon, and it stirred at the temperature for ~1 h. Then the solution was warmed to -50 °C. Anhydrous DMF (0.4 mL) was added to the solution and it continued to stir at -50 °C for ~1 h. Afterwards it was quenched with water and extracted with CH_2Cl_2 three times. The organic phase was dried over anhydrous Na_2SO_4. After removing the solvent, the crude product was purified via column chromatography (silica gel) using hexane/CH_2Cl_2 (1:1, v/v) as eluent to give compound **11** as an orange solid (203 mg, 82%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 9.80 (s, 2H), 7.68 (s, 2H), 7.11 (d, *J* = 3.2 Hz, 2H), 7.09-7.02 (m, 16H), 6.97 (d, *J* = 3.1 Hz, 2H), 2.95 (ddd, *J* = 22.0, 14.6, 6.5 Hz, 4H), 2.55 (t, *J* = 7.4 Hz, 8H), 1.70 (s, 2H), 1.61-1.49 (m, 8H), 1.41-1.20 (m, 40H), 0.92 (t, *J* = 6.6 Hz, 6H), 0.86 (t, *J* = 6.3 Hz, 12H), 0.80 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 182.30, 157.87, 152.83, 147.17, 147.01, 144.08, 142.83, 142.34, 138.26, 137.98, 137.05, 136.78, 134.95, 133.40, 131.66, 131.51, 130.77, 129.03, 128.71, 127.49, 125.84, 123.76, 62.41, 41.20, 35.58, 33.71, 32.59, 31.70, 31.25, 29.09, 28.99, 25.22, 23.01, 22.58, 14.21, 14.05, 10.56.

IUIC-out. To a solution of compound **11** (80 mg, 47 μmol) in $CHCl_3$ (10 mL) were added 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (65 mg, 0.28 mmol) and pyridine (1 mL). It was heated to reflux for 1.5 h and then cooled down to room temperature. The solution was poured into column chromatography (silica gel) directly and the crude product was purified by using $CHCl_3$ as eluent to give IUIC-out a dark-green solid (92 mg, 92%). ^{1}H NMR ($C_2D_2Cl_4$, 400 MHz, δ/ppm): 8.82 (s, 2H), 8.38 (s, 2H), 7.76 (s, 2H), 7.67 (t, *J* = 7.3 Hz, 2H), 7.30 (d, *J* = 22.1 Hz, 2H), 7.22 (d, *J*

= 34.0 Hz, 16H), 7.07 (s, 2H), 3.03 (ddd, *J* = 21.5, 14.6, 6.1 Hz, 4H), 2.65 (s, 8H), 1.78 (s, 2H), 1.66 (d, *J* = 6.5 Hz, 8H), 1.49-1.32 (m, 40H), 1.01 (dd, *J* = 18.7, 12.2 Hz, 6H), 0.97-0.85 (m, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 185.21, 158.48, 155.67, 152.90, 149.62, 149.31, 146.63, 145.56, 142.49, 142.37, 139.82, 139.70, 139.31, 137.78, 137.58, 136.98, 136.27, 135.63, 132.86, 131.01, 129.96, 129.04, 128.97, 128.09, 127.30, 126.53, 123.45, 120.43, 114.51, 114.35, 113.86, 112.42, 112.32, 107.71, 62.48, 35.84, 35.67, 35.62, 31.72, 31.39, 31.25, 29.59, 29.23, 29.19, 23.11, 22.62, 14.29, 14.08, 10.24. MALDI-TOF MS (m/z): 2112.4 (M^+).

3. NMR spectra

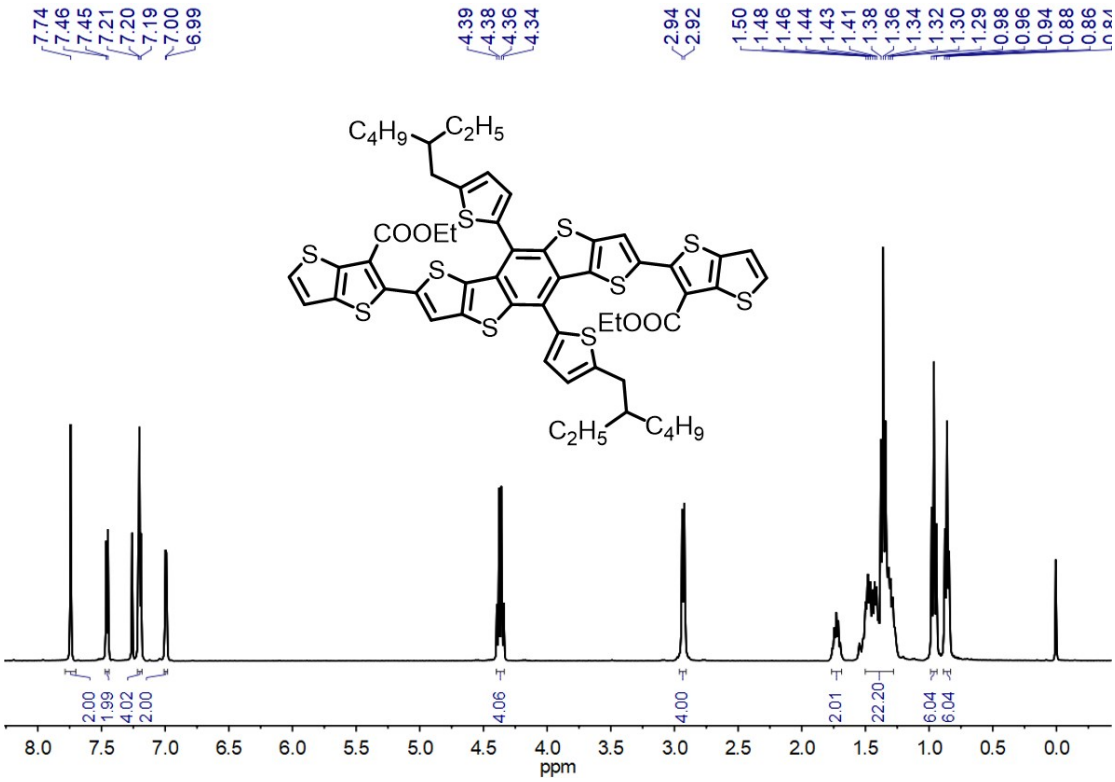


Fig. S1 ^{1}H spectrum of compound **1** in $CDCl_3$.

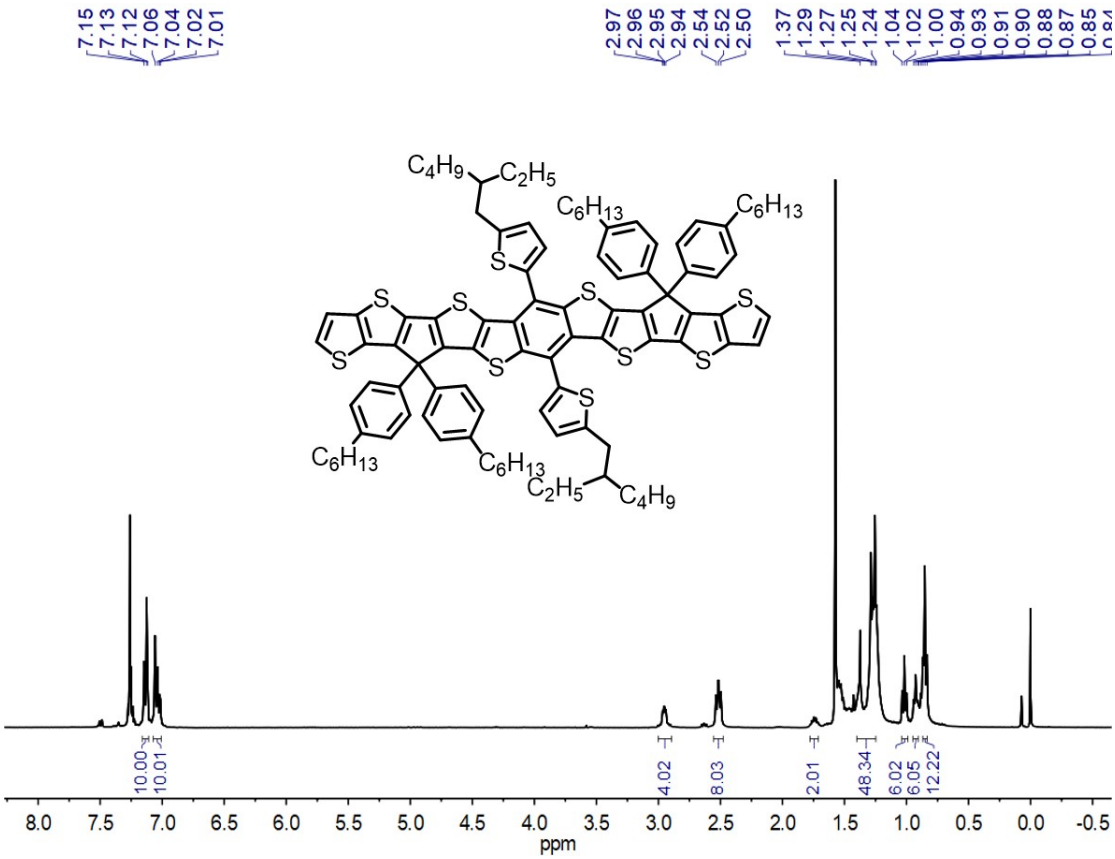


Fig. S2 ^{1}H spectrum of compound **2** in $CDCl_3$.

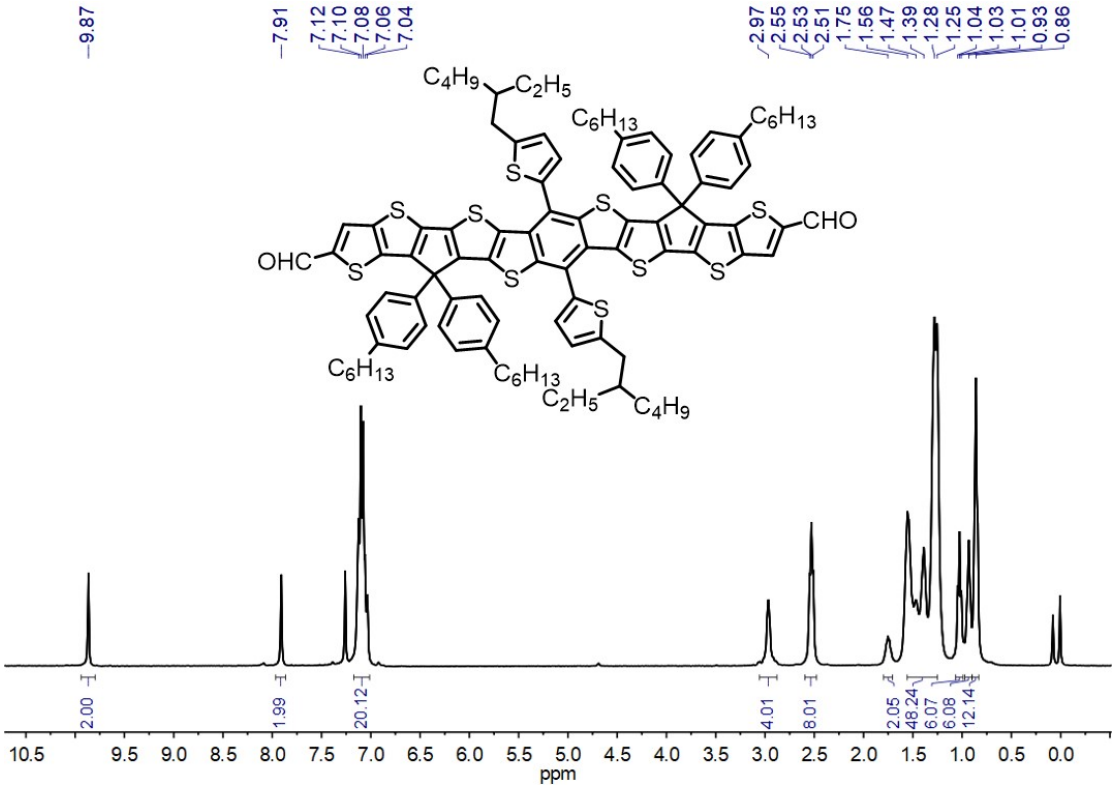


Fig. S3 ^{1}H spectrum of compound **3** in $CDCl_3$.

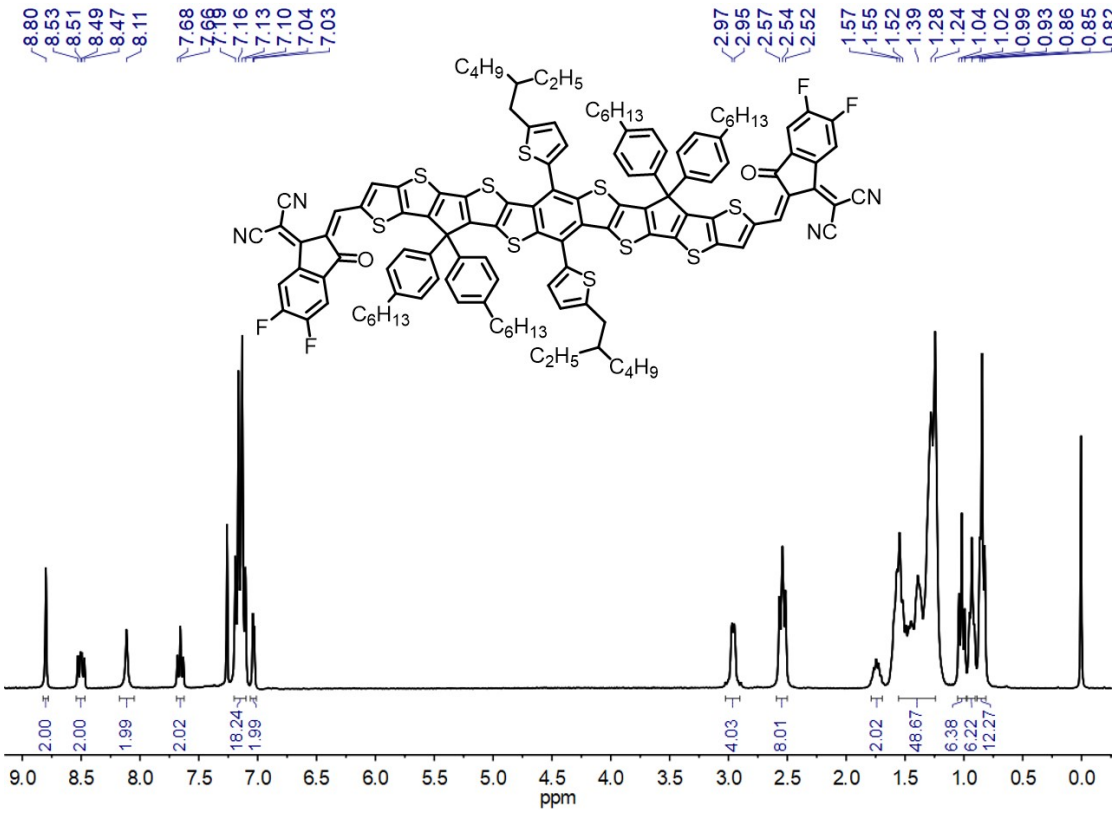


Fig. S4 ^{1}H spectrum of IUIC-mid in $CDCl_3$.

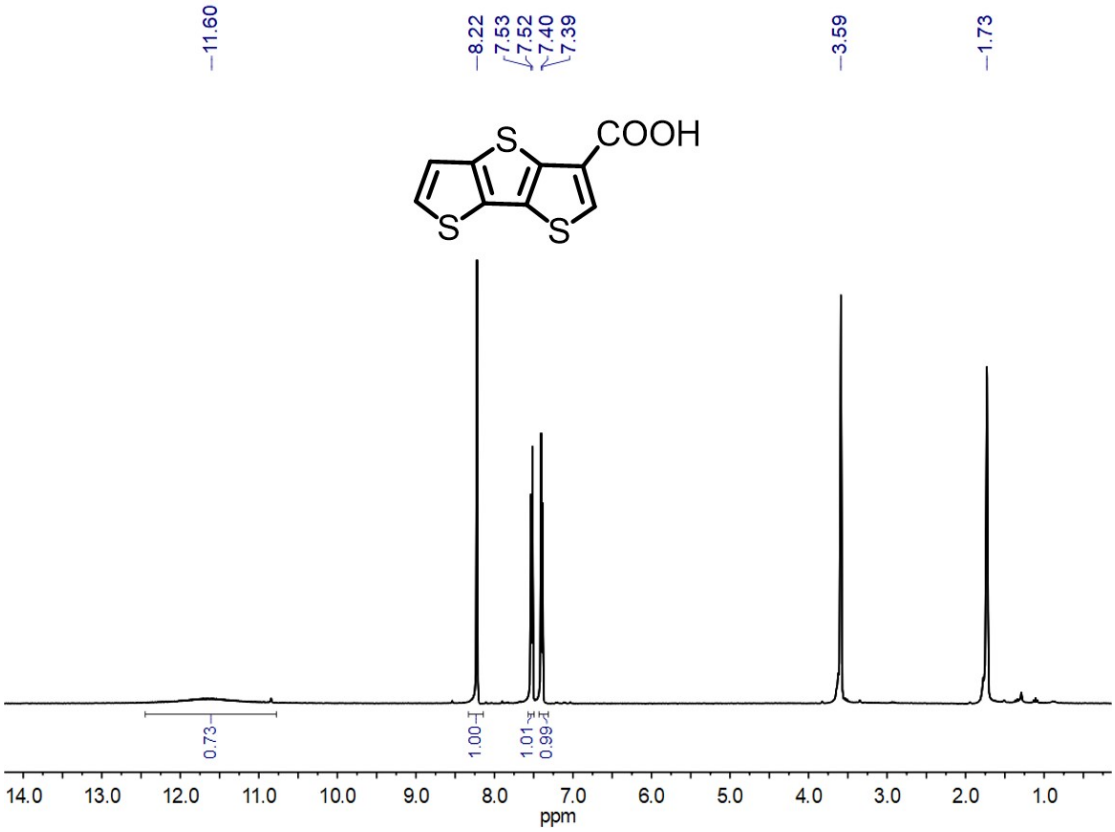


Fig. S5 ^{1}H spectrum of compound **4** in THF-d_8.

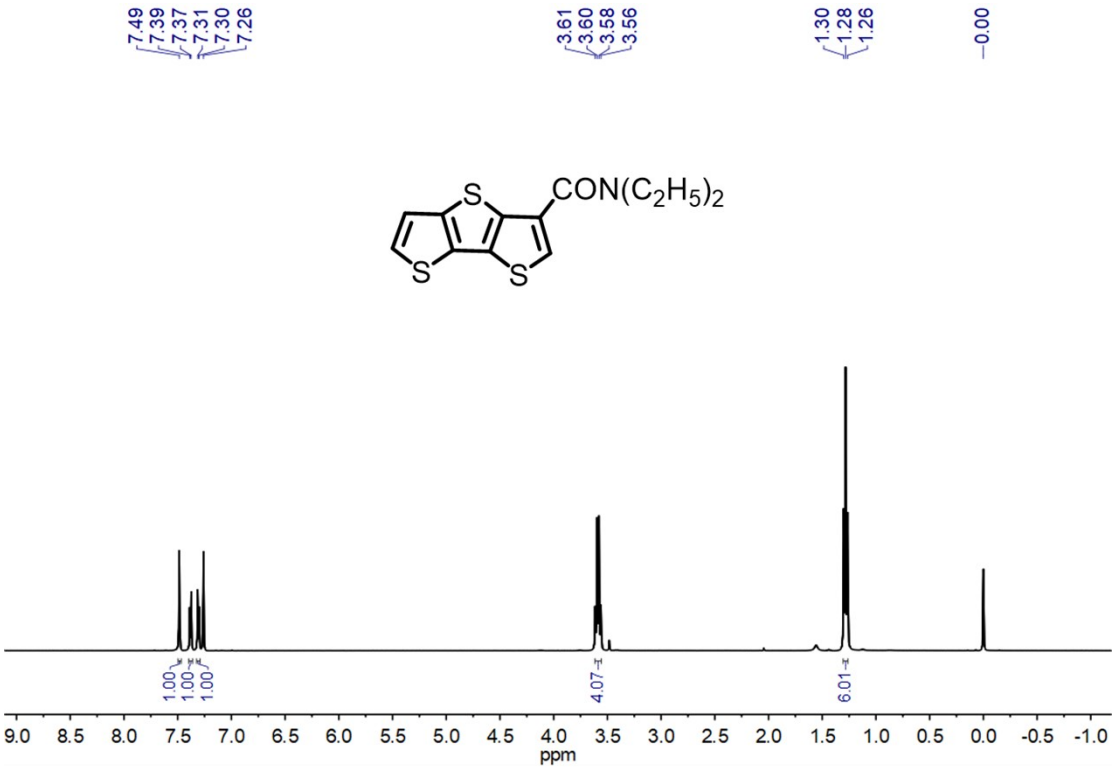


Fig. S6 ^{1}H spectrum of compound **5** in $CDCl_3$.

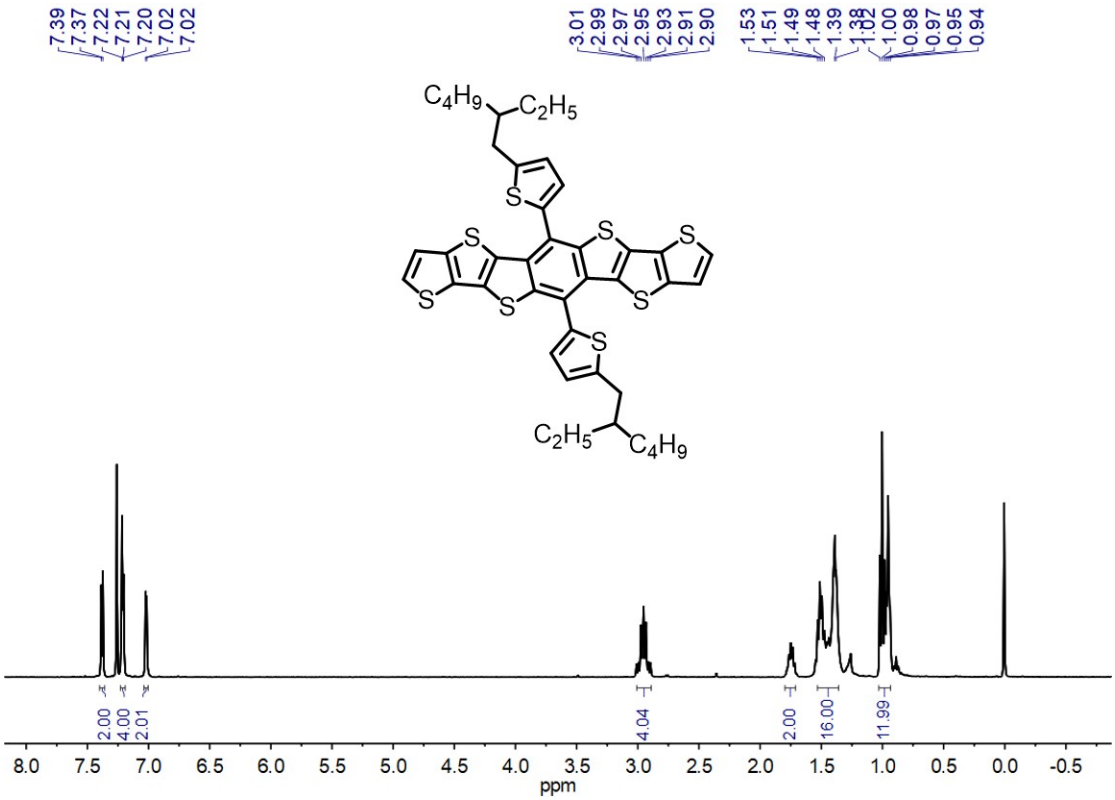


Fig. S7 ^{1}H spectrum of compound **7** in $CDCl_3$.

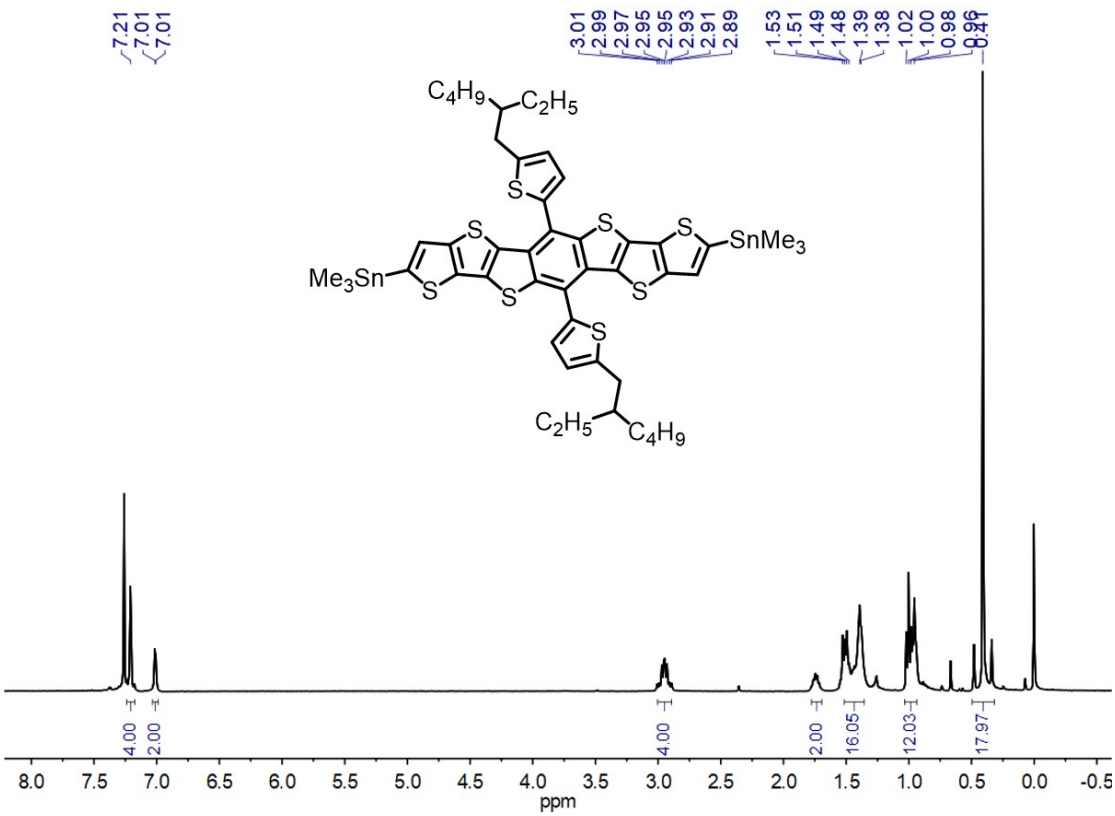


Fig. S8 ^{1}H spectrum of compound **8** in $CDCl_3$.

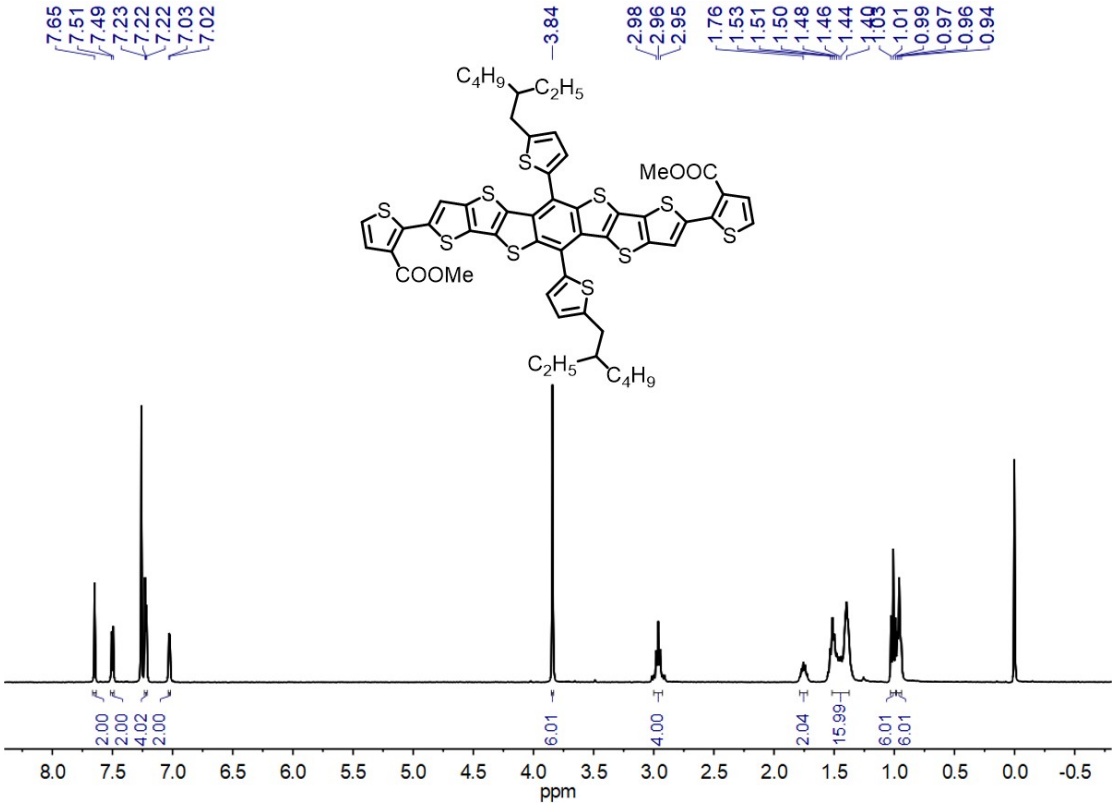


Fig. S9 ^{1}H spectrum of compound **9** in $CDCl_3$.

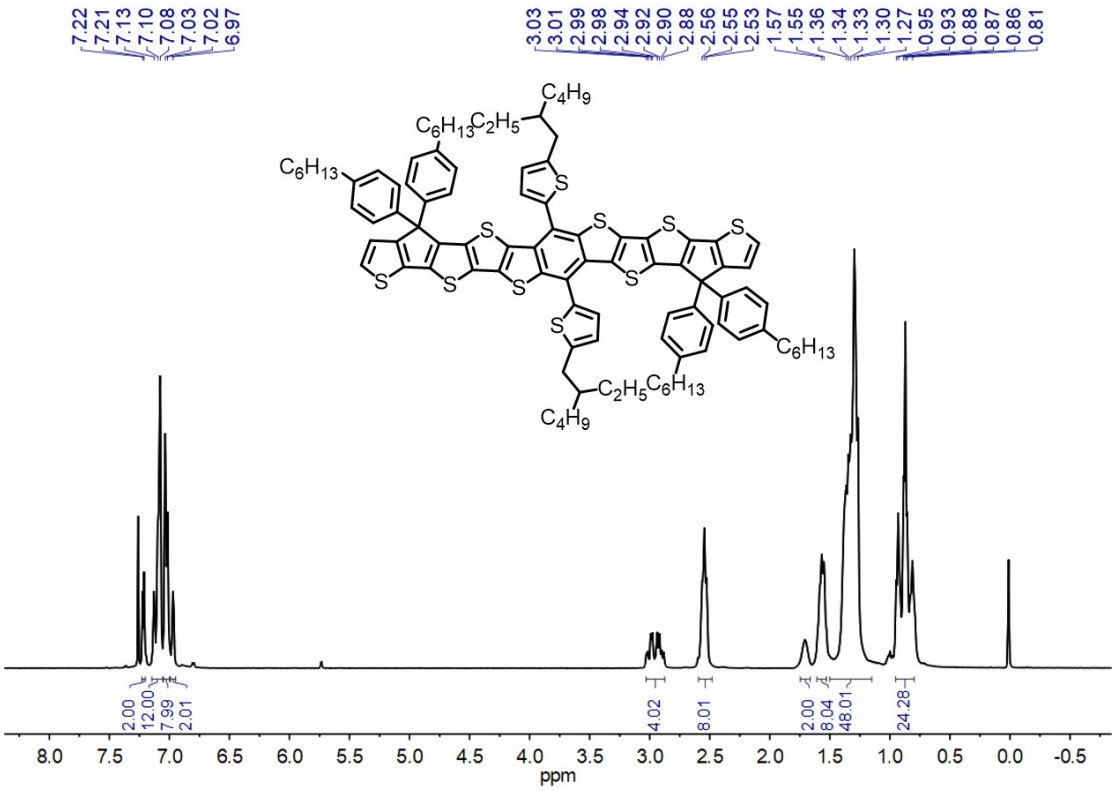


Fig. S10 ^{1}H spectrum of compound **10** in $CDCl_3$.

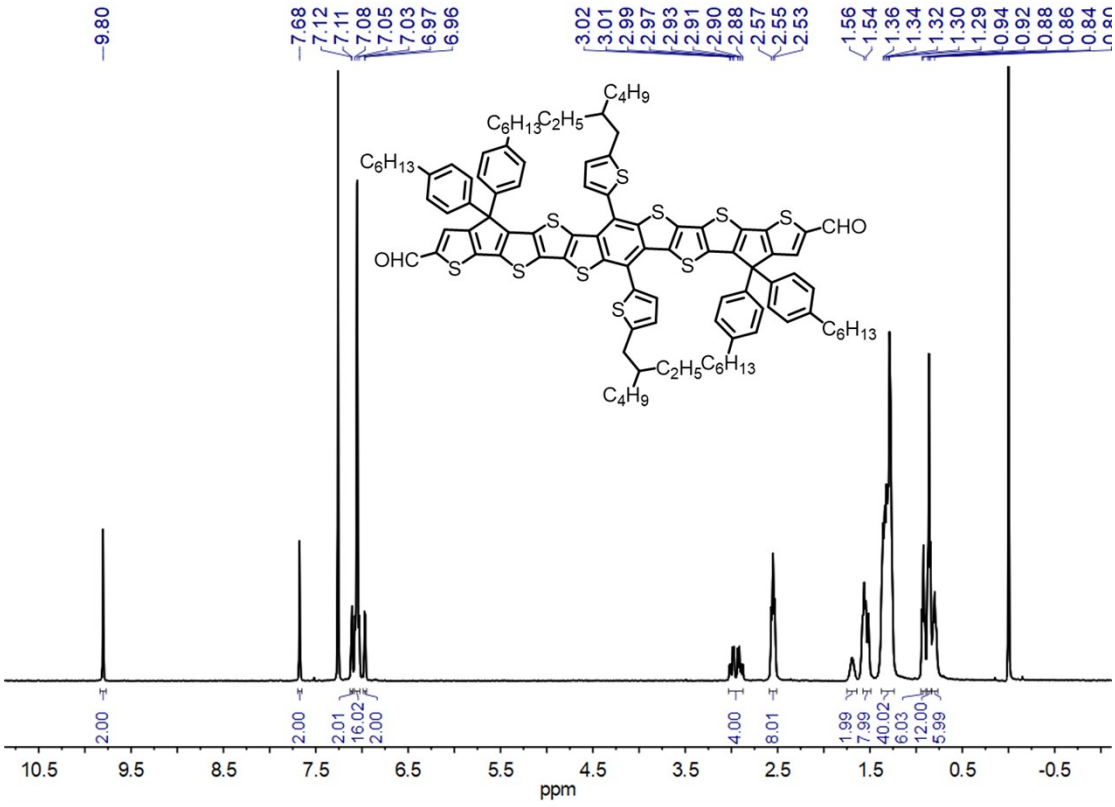


Fig. S11 ^{1}H spectrum of compound **11** in $CDCl_3$.

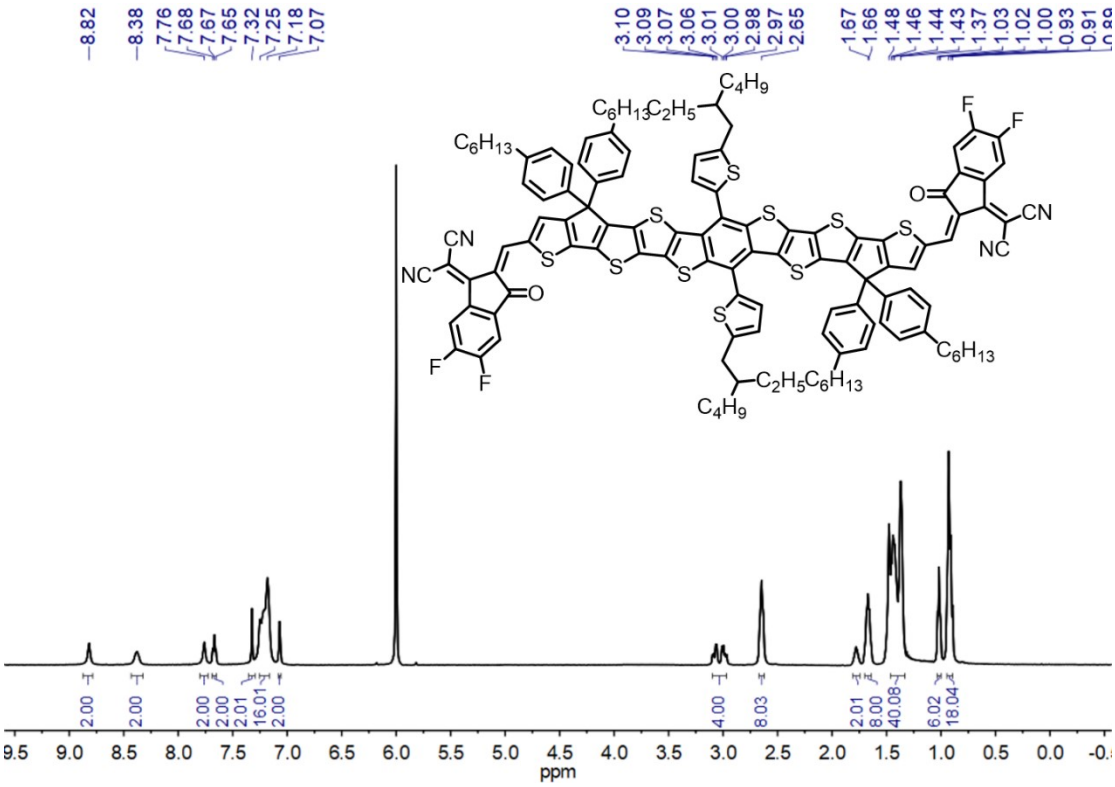


Fig. S12 ^{1}H spectrum of IUIC-out in $C_2D_2Cl_4$.

4. Absorption

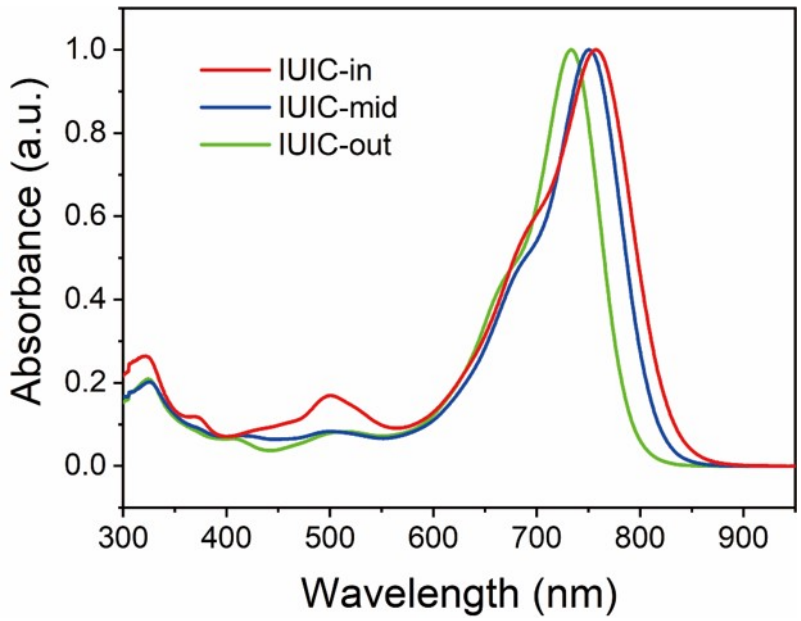


Fig. S13 Absorption spectra of IUIC-in, IUIC-mid and IUIC-out in $CHCl_3$ (10^{-5} M).

5. Cyclic voltammetry

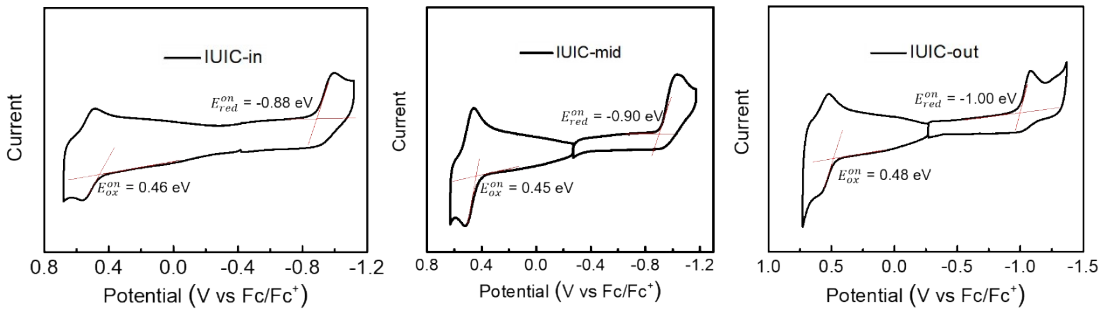


Fig. S14 Cyclic voltammograms of IUIC-in, IUIC-mid and IUIC-out.

Table S1. Optical and electrochemical data of IUIC-in, IUIC-mid and IUIC-out.

	$\lambda_{sol.}$ [nm]	λ_{film} [nm]	λ_{onset} [nm]	E_g^{opt} [eV]	HOMO [eV]	LUMO [eV]	E_g^{ec} [eV]
IUIC-in	757	795	913	1.36	-5.26	-3.92	1.34
IUIC-mid	751	790	908	1.37	-5.25	-3.90	1.35
IUIC-out	734	779	860	1.44	-5.28	-3.80	1.48

E_g^{opt} = 1240/λ_{onset}; HOMO = -(E_{ox}^{on} + 4.8); LUMO = -(E_{red}^{on} + 4.8); E_g^{ec} = LUMO-HOMO.

6. Contact angle

Contact angles of water and glycerol on donor (PM6), and acceptors (IUIC-in, IUIC-mid and IUIC-out) were measured by JY-82C contact angle analyzer. The surface tension can be evaluated by using the equation:[4]

$$\gamma_{LV}(1+cos\theta) = 4\frac{\gamma_S^d\gamma_L^d}{\gamma_S^d+\gamma_L^d} + 4\frac{\gamma_S^p\gamma_L^p}{\gamma_S^p+\gamma_L^p}$$

where γ_{LV} represents the surface tension of water/glycerol in equilibrium with its vapor. γ_L^d and γ_L^p represent the dispersion and polar components of the liquid surface tension, respectively, while γ_S^d and γ_S^p represent the dispersion and polar components of the solid surface tension, respectively. γ_S^d and γ_S^p can be calculated by using the contact angles with water and glycerol. The surface tension of donor and acceptors are calculated by equation: $\gamma = \gamma_S^d + \gamma_S^p$. The closer the surface tension, the better compatibility between two materials.

7. Device fabrication

OSCs were fabricated with the structure of ITO/PEDOT:PSS/active layer/PDINN/Ag. The ITO glass substrates were cleaned by an ultrasonic cleaner in

water with detergent, deionized water, acetone and isopropyl alcohol for 15 min, successively, and subsequently treated with UV-ozone for 20 min. Then, the PEDOT:PSS layer was spin-coated onto the ITO substrate at 4000 rpm for 30 s, and then annealed at 150 °C for 10 min. PM6:IUIC-in, PM6:IUIC-mid, and PM6:IUIC-out (w/w = 1:1.2, totally 15mg ml^{-1}) were dissolved in chlorobenzene (CB) at 60 °C before spin-coating, respectively. Subsequently, the solution of PM6:FREA was spin-coated onto the top of PEDOT: PSS at 1000 rpm for 60 s. Then the electron transport layer PDINN (1.0 mg/mL in methanol) was spin-coated onto the top of active layer with 4000 rpm for 20 s. Finally, Ag (~100 nm) was evaporated onto the active layer under vacuum (ca. 10^{-5} Pa) to form the top electrode. The effective area of the device is 0.04 cm^2.

Table S2. Optimization of D/A ratio for PM6:IUIC-in based OSCs.[a]

D/A [w/w]	V_{OC} [V]	J_{SC} [mA cm^{-2}]	FF [%]	PCE[b] [%]
1:0.8	0.92	13.8	65.0	8.2 (7.8)
1:1	0.92	13.8	63.2	8.0 (7.6)
1:1.2	0.92	14.0	63.8	8.2 (8.0)
1:1.5	0.88	13.7	64.8	7.8 (7.4)

[a]Blend solution: 15 mg/mL in CB with 0.25 vol% 1,8-diiodooctane (DIO); spin-coating: 1000 rpm for 60 s; thermal annealing: 100℃ 10min. [b]Data in parentheses stand for the average PCE for 10 cells.

Table S3. Optimization of additive content for PM6:IUIC-in based OSCs.[a]

DIO [v/v, %]	V_{OC} [V]	J_{SC} [mA cm^{-2}]	FF [%]	PCE[b] [%]
0	0.92	12.6	63.5	7.4 (7.0)
0.25	0.92	14.0	63.8	8.2 (8.0)
0.5	0.90	13.9	66.8	8.3 (8.0)
0.75	0.90	11.7	63.6	6.7 (6.4)

[a]Blend solution: 15 mg/mL in CB with D/A ratio: 1:1.2 (w/w); spin-coating: 1000 rpm for 60 s; thermal annealing: 100℃ 10min. [b]Data in parentheses stand for the average PCE for 10 cells.

Table S4. Optimization of thermal annealing temperature for PM6:IUIC-in based OSCs.[a]

Temperature [℃]	V_{OC} [V]	J_{SC} [mA cm^{-2}]	FF [%]	PCE[b] [%]
25	0.93	13.5	61.2	7.7 (7.4)
90	0.92	13.9	62.2	8.0 (7.6)
100	0.90	13.9	66.8	8.3 (8.0)
110	0.90	14.4	62.2	8.2 (7.8)

[a]Blend solution: 15 mg/mL in CB with D/A ratio: 1:1.2 (w/w) and 0.5 vol% DIO; spin-coating: 1000 rpm for 60 s. [b]Data in parentheses stand for the average PCE for 10 cells.

Table S5. Optimization of D/A ratio for PM6:IUIC-mid based OSCs.[a]

D/A [w/w]	V_{OC} [V]	J_{SC} [mA cm^{-2}]	FF [%]	PCE[b] [%]
1:0.8	0.88	21.6	67.4	12.8 (12.5)
1:1	0.87	21.4	68.1	12.7 (12.5)
1:1.2	0.87	21.4	70.2	13.1 (12.9)
1:1.5	0.86	21.7	61.8	11.5 (11.4)

[a]Blend solution: 15 mg/mL in CB with 0.25 vol% DIO; spin-coating: 1000 rpm for 60 s; thermal annealing: 100℃ 10min. [b]Data in parentheses stand for the average PCE for 10 cells.

Table S6. Optimization of additive content for PM6:IUIC-mid based OSCs.[a]

DIO [v/v, %]	V_{OC} [V]	J_{SC} [mA cm^{-2}]	FF [%]	PCE[b] [%]
0	0.90	20.4	60.9	11.3 (11.2)
0.25	0.87	21.4	70.2	13.1 (12.9)
0.5	0.86	21.4	66.7	12.5 (12.2)
0.75	0.86	20.9	65.2	11.9 (11.6)

[a]Blend solution: 15 mg/mL in CB with D/A ratio: 1:1.2 (w/w); spin-coating: 1000 rpm for 60 s; thermal annealing: 100℃ 10min. [b]Data in parentheses stand for the average PCE for 10 cells.

Table S7. Optimization of thermal annealing temperature for PM6:IUIC-mid based OSCs.[a]

Temperature [℃]	V_{OC} [V]	J_{SC} [mA cm^{-2}]	FF [%]	PCE[b] [%]
25	0.90	20.7	60.5	11.3 (11.0)
90	0.88	21.3	66.4	12.6 (12.4)
100	0.87	21.4	70.2	13.1 (12.9)
110	0.87	20.9	69.2	12.6 (12.4)

[a]Blend solution: 15 mg/mL in CB with D/A ratio: 1:1.2 (w/w) and 0.25 vol% DIO; spin-coating: 1000 rpm for 60 s. [b]Data in parentheses stand for the average PCE for 10 cells.

Table S8. Optimization of D/A ratio for PM6:IUIC-out based OSCs.[a]

D/A [w/w]	V_{OC} [V]	J_{SC} [mA cm^{-2}]	FF [%]	PCE[b] [%]
1:0.8	0.98	12.8	46.5	5.9 (5.6)
1:1	0.98	13.6	49.0	6.1 (5.8)
1:1.2	0.97	14.9	49.2	7.1 (6.9)
1:1.5	0.96	14.7	45.8	6.5 (6.1)

[a]Blend solution: 15 mg/mL in CB with 0.25 vol% DIO; spin-coating: 1000 rpm for 60 s; thermal annealing: 100℃ 10min. [b]Data in parentheses stand for the average PCE for 10 cells.

Table S9. Optimization of additive content for PM6:IUIC-out based OSCs.[a]

DIO [v/v, %]	V_{OC} [V]	J_{SC} [mA cm^{-2}]	FF [%]	PCE[b] [%]
0	0.99	14.2	52.5	7.4 (7.0)
0.25	0.97	14.9	49.2	7.1 (6.9)
0.5	0.96	14.8	49.4	7.1 (6.8)
0.75	0.95	14.5	45.2	6.3 (6.0)

[a]Blend solution: 15 mg/mL in CB with D/A ratio: 1:1.2 (w/w); spin-coating: 1000 rpm for 60 s; thermal annealing: 100℃ 10min. [b]Data in parentheses stand for the average PCE for 10 cells.

Table S10. Optimization of thermal annealing temperature for PM6:IUIC-out based OSCs.[a]

Temperature [℃]	V_{OC} [V]	J_{SC} [mA cm^{-2}]	FF [%]	PCE[b] [%]
25	0.99	12.2	45.8	5.5 (5.3)
90	0.99	13.7	53.0	7.2 (6.8)
100	0.99	14.2	52.5	7.4 (7.0)
110	0.98	13.9	50.6	6.9 (6.6)

[a]Blend solution: 15 mg/mL in CB with D/A ratio: 1:1.2 (w/w) and without additive; spin-coating: 1000 rpm for 60 s. [b]Data in parentheses stand for the average PCE for 10 cells.

8. Space charge limited current (SCLC)

Charge carrier mobility was obtained by using SCLC method. Electron-only devices were fabricated by using the architecture of ITO/ZnO/active layer/Ca/Al. Hole-only devices were fabricated by using the architectures of ITO/PEDOT:PSS/active layers/MoO_3/Ag. The mobility was determined by fitting the dark current to the model of a single carrier SCLC, which can be described as:

$$J = \frac{9}{8}\varepsilon_0\varepsilon_r\mu\frac{V^2}{d^3}$$

where J is the current density, μ is the zero-field mobility of electron (μ_e) or hole (μ_h), ε_0 is the permittivity of the vacuum, ε_r is the relative permittivity of the material, d is the thickness of the blend film, and V is the effective voltage, $V = V_{appl}$-V_{bi}, where V_{appl} is the applied voltage, and V_{bi} is the built-in potential determined by electrode work function difference.

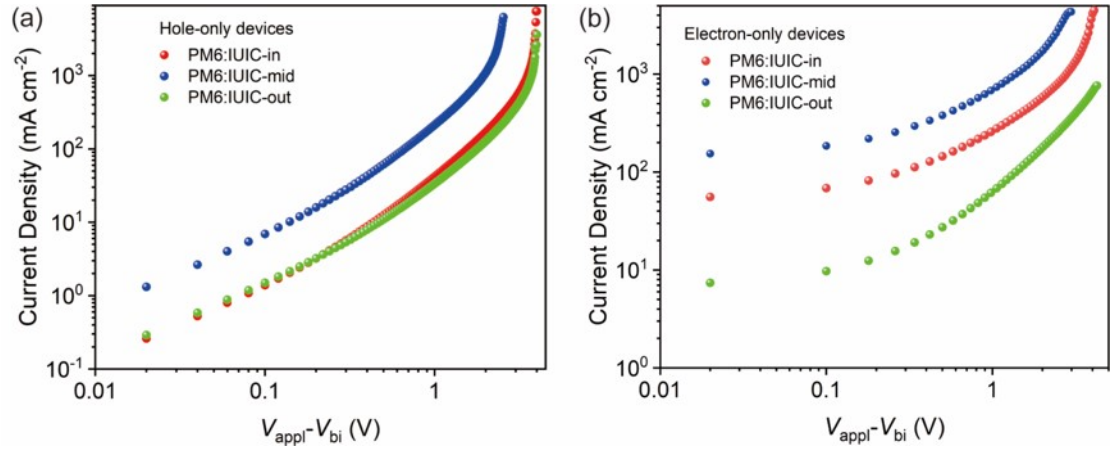


Fig. S15 (a) SCLC curves of hole-only devices based on PM6:IUIC-in, PM6:IUIC-mid and PM6:IUIC-out blend films. (b) SCLC curves of electron-only devices based on PM6:IUIC-in, PM6:IUIC-mid and PM6:IUIC-out blend films.

Table S11. Charge mobilities of PM6:FREA blend films measured by SCLC method.

Active layer	μ_h (10^{-4} cm^2 V^{-1} S^{-1})	μ_e (10^{-4} cm^2 V^{-1} S^{-1})
PM6:IUIC-in	2.32	5.73
PM6:IUIC-mid	12.2	19.1
PM6:IUIC-out	1.80	1.76

References

[1] D. He, L. Qian, L. Ding, *Polym. Chem.* **2016**, 7, 2329.
[2] W. Hu, Z. Zhang, Y. Xu, J. Cao, S. Liu, Z. Tang, B. Zhao, J. Zhang, *J. Mater. Chem. C* **2018**, 6, 6911.
[3] F. Zhao, D. He, J. Xin, H. Zhang, J. Zhou, B. Lin, Y. He, J. Li, W. Ma, B. Li, F. Gao, Y. Li, C. Wang, *Mater. Chem. Front.* **2021**, 5, 2001.
[4] J. Comyn, *Int. J. Adhes. Adhes.* **1992**, 12, 145.