Supporting Information

Ideal Alloys of Two Donor Isomers with Noncovalently Conformational Locking for Ternary Organic Solar Cells

Dan Deng, Hao Zhang, Qiong Wu, Muhammad Abdullah Adil, Chen Yang, Jianqi Zhang, Zhixiang Wei*

CAS Key Laboratory of Nanosystem and Hierarchical Fabrication, CAS Center for Excellence in Nanoscience, National Center for Nanoscience and Technology, Beijing 100190, China

University of Chinese Academy of Sciences, Beijing 100049, China

KEYWORDS Organic solar cells, conformation lock, alloy, isomers, ternary

1. Characterization method

(1) Molecular structure/properties characterization and calculation (NMR, MS spectra, DFT).

^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra were obtained on a Bruker DMX–400 NMR Spectrometer and using tetramethylsilane as internal standard. MS spectra (MALDI–TOF–MS) were determined on a Micromass GCT–MS spectrometer. The infrared spectrum (IR) was measured using microinfrared spectrometer (sp-200i) by transmission-mode. The melting point was obtained by differential scanning calorimetry (DSC) Q100 V9.0 Build 275 analyzer under purified nitrogen gas flow with a 10 ^{o}C min^{-1} heating rate. The calculated HOMO and LUMO levels, optimized conformations, and NBO charge distribution of the small molecules were optimized by density functional theory (DFT)/time-dependent density functional theory (TDDFT) at the B3LYP/6-31G (d, p) level; the relaxed potential surface energy (PSE) scans of rotamers were using modredundant at the wb97x/g-31G(d, p) level. All calculations were performed in the gas phase and with Gaussian 09 program.[1-3] UV-Vis spectra[1] were obtained with a JASCO–V570 spectrophotometer. Electrochemical cyclic voltammetry was conducted on an electrochemical work station (VMP3 Biologic, France), with a Pt disk coated with a molecular film, a Pt plate, and an Ag$^+$/Ag electrode as working, counter, and reference electrodes, respectively, in a 0.1 mol L^{-1} tetrabutylammonium phosphorus hexafluoride (Bu$_4$NPF$_6$) acetonitrile solution.

(2) Morphology characterization

All films for characterization are prepared under identical optimized conditions of device fabrication in the absence of special emphasis. The AFM images of the blended films on ZnO substrates were obtained on a Nanoscope Ia AFM (Digital Instruments) in tapping mode. The TEM images of the blended films were prepared under the same conditions as AFM: the sample on the ITO/ZnO substrate was transferred by floating in water.

(3) Solar cell fabrication and measurements

Devices were fabricated with a structure of glass/ITO/ZnO/MoO$_x$/Ag. The ITO-coated glass substrates were cleaned by the same procedure with inverted devices. The precursor solution of ZnO was spin-coated on the ITO at 4,000 r.p.m, then was annealed at 200 ºC for half an hour to obtain a thin layer of ZnO. The precursor solution was prepared by dissolving 0.14 g of zinc acetate dihydrate (Zn(CH$_3$COO)$_2$·2H2O, 99.9%, Aldrich, U.S.A.) and 0.5 g of ethanolamine (NH$_2$CH$_2$CH$_2$OH, 99.5%, Aldrich, U.S.A.) in 5 mL of 2-methoxyethanol (CH$_3$OCH$_2$CH$_2$OH, 99.8%, J&K Scientific, Canada). The substrates were transferred into a nitrogen-filled glove box. The mixture of small molecules/PC$_{71}$BM and additives with total concentration ca. 16.7 mg ml^{-1} stirred at 50 °C in chloroform for ca. 0.5 hour until they intensively dissolved. Subsequently, the active layer was spin-coated from blend chloroform solutions. Finally, a layer of ~5 nm MoO$_x$ and then 160 nm Ag layer was evaporated under high vacuum (<1 × 10^{-4} Pa).

Device *J–V* characteristics was measured under AM 1.5G (100 mWcm^{-2}) using a Newport Thermal Oriel 91159A solar simulator. Light intensity is calibrated with a Newport Oriel PN 91150 V Si-based solar cell. *J–V* characteristics were recorded using a Keithley 2400 source-measure unit. Typical cells have device areas of approximately 4 mm^2. EQEs were performed in air with an Oriel Newport system (Model 66902) equipped with a standard Si diode. Monochromatic light was generated from a Newport 300W lamp source. Mobility measurements of pristine films and blend films were characterized by a hole-only space-charge limited current (SCLC) method with the following diode structures: ITO/PEDOT:PSS/active layer/MoO$_x$/Ag for hole by taking current–voltage current in the range of 0–5 V and fitting the results to a space–charge-limited form.[4-5] Charge carrier motilities were calculated by using the SCLC model considering electric-field dependence, as described by

$$J = \frac{9}{8}\varepsilon_r \varepsilon \mu V^2 \exp\left(0.89\sqrt{\frac{V}{E_0 L}}\right)/L^3$$

where J is the current density (mA cm^{-2}), L is the film thickness of the active layer (cm), μ is the hole or electron mobility, ε_r is the relative dielectric constant of the transport medium, ε_0 is the permittivity of free space (8.85 × 10^{-14} F cm^{-1}), and V is the internal voltage in the device. V = V$_{appl}$ − V$_{bi}$, where V$_{appl}$ is the applied voltage to the device, and series resistance across the electrodes, and V$_{bi}$ is the built-in voltage owing to the relative work function difference of the two electrodes.

2. Materials and synthesis

All reagents and chemicals were purchased from Aldrich, Alfa and used as received. Solvents and other common reagents were obtained from the Beijing Chemical Plant. Toluene, chloroform and THF were freshly distilled prior to use. Other materials were used without further purification. 5-

bromo-4-(octyloxy)thiophene-2-carbaldehyde, 5-bromo-3-(octyloxy)thiophene-2- carbaldehyde, compound **1**, and compound **6** were synthesized according to literatures.[6-7]

Scheme S1 Synthesis routes of small molecules
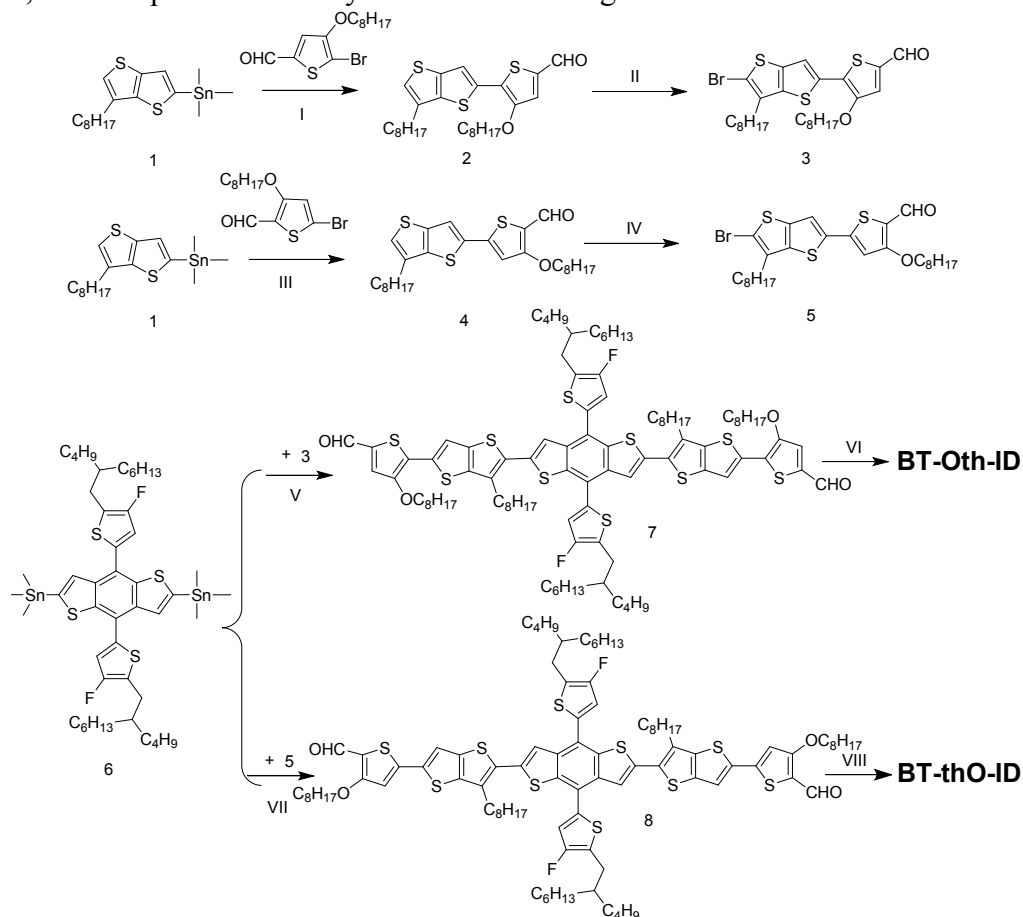
I Pd(PPh$_3$)$_4$, toluene, 100°C; II CF：HOAc=1:1, NBS; III Pd(PPh$_3$)$_4$, toluene, 100°C; IV CF：HOAc=1:1, NBS; V Pd(PPh$_3$)$_4$, toluene, 100°C; VI Triethylamine, CF; VII Pd(PPh$_3$)$_4$, toluene, 100°C; VIII Triethylamine, CF.

Compound 2
4-(octyloxy)-5-(6-octylthieno[3,2-b]thiophen-2-yl)thiophene-2-carbaldehyde
Under Ar protection, Pd(PPh$_3$)$_4$ was added to the solution of compound **1** (1.5 g, 3.6 mmol) and 5-bromo-4-(octyloxy)thiophene-2-carbaldehyde (1.15 g, 3.6 mmol) in 100 mL of toluene. Then, Ar gas was bubbled for 20 min; then, the mixture was heated to 100 °C and maintained at the temperature for 12 h. After being cooled to ambient temperature, the mixture was evaporated, and the crude product was purified using column chromatography on silica gel with petroleum and dichloromethane (2:1); the product was given as a yellow solid (1.20g) with a yield of 68%. MS (EI): calcd for C$_{27}$H$_{38}$O$_2$S$_3$ [M]$^+$ 490.2, found m/z 491.1. ^{1}H NMR (400 MHz, CDCl$_3$), δ: 9.77 (s, 1H), 7.61 (s, 1H), 7.48 (s, 1H), 7.01 (s, 1H), 4.17-4.21 (t, 2H, J=6.4), 2.71-2.75 (t, 2H, J=7.6), 1.88-1.92 (m, 2H), 1.75-1.78 (m, 2H), 1.26-1.56 (m, 20H), 0.86-0.89 (m, 6H)

Compound 3
5-(5-bromo-6-octylthieno[3,2-b]thiophen-2-yl)-4-(octyloxy)thiophene-2-carbaldehyde

In an ice bath, NBS (435 mg, 2.45 mmol) was added in portion to the solution of compound **2** (1.2 g, 2.45 mmol) in a mixed solvent of 30 mL of chloroform and 30 mL of acetic acid. After addition, the mixture was warmed to ambient temperature and left undisturbed overnight. The whole mixture was poured into 50 mL of chloroform: then, the organic layer was washed with water, saturated $NaHCO_3$, and water for three times and then dried over $MgSO_4$. After concentration, the crude product was purified with column chromatography on silica gel, with petroleum and dichloromethane (2:1) as eluent, and the product was obtained as a yellow solid (1.10 g, 79.5%). MS (EI): calcd for $C_{27}H_{37}BrO_2S_3$ [M]$^+$ 568.1, found m/z 569.0. ^{1}H NMR (400 MHz, CDCl$_3$), δ: 9.77 (s, 1H), 7.53 (s, 1H), 7.47 (s, 1H), 4.17-4.21 (t, 2H, J=6.4), 2.72-2.76 (t, 2H, J=7.6), 1.88-1.92 (m, 2H), 1.75-1.78 (m, 2H), 1.54-1.56 (m, 2H), 1.26-1.34 (m, 18H), 0.88-0.89 (m, 6H)

Compound 4

The procedure of the synthesis is the same with **compound 2**. The product was given as yellow solid with a yield of 70%. MS (EI): calcd for $C_{27}H_{38}O_2S_3$ [M]$^+$ 490.2, found m/z 491.1. ^{1}H NMR (400 MHz, CDCl$_3$), δ: 9.97 (s, 1H), 7.51 (s, 1H), 7.07 (s, 1H), 6.91 (s, 1H), 4.17-4.20 (t, 2H, J=6.8), 2.72-2.74 (t, 2H, J=7.6), 1.73-1.86 (m, 4H), 1.28-1.55 (m, 20H), 0.87-0.91(m, 6H)

Compound 5

The procedure of the synthesis is the same with **compound 3**. The product was given as yellow solid with a yield of 75%. MS (EI): calcd for $C_{27}H_{37}BrO_2S_3$ [M]$^+$ 568.1, found m/z 569.0. ^{1}H NMR (400 MHz, CDCl$_3$), δ: 9.97 (s, 1H), 7.42 (s, 1H), 6.90 (s, 1H), 4.17-4.20 (t, 2H), 2.71-2.75 (t, 2H), 1.80-1.87 (m, 2H), 1.67-1.74 (m, 22H), 0.86-0.91 (m, 6H)

Compound 7

Under Ar protection, Pd(PPh$_3$)$_4$ was added to the solution of compound **3** (400 mg, 0.70 mmol) and compound **6** (337 mg, 0.32 mmol) in 40 mL of toluene. Then, Ar gas was bubbled for 20 min; then, the mixture was heated to 100 °C and maintained at the temperature for 12 h. After being cooled to ambient temperature, the mixture was evaporated, and the crude product was purified using column chromatography on silica gel with petroleum and dichloromethane (1:1); the product was given as a red solid (290 mg) with a yield of 54%. MALDI–TOF MS calcd for $C_{96}H_{128}F_2O_4S_{10}$ 1702.7 found 1703.5, ^{1}H NMR (400 MHz, CHCl$_3$), δ: 9.77 (s, 2H), 7.69 (s, 2H), 7.59(s, 2H), 7.48 (s, 2H), 7.20 (s, 2H), 4.20-4.23 (t, 2H, J=6.4), 2.80-3.00(t, 4H, J=7.2), 2.80-2.81(d, 4H, J=6.4), 1.73-1.86 (m, 10H), 1.27-1.60 (m, 72H), 0.86-0.95 (m, 24H)

Compound 8

The procedure of the synthesis is the same with **compound 7**. The product was given as a red solid with a yield of 61%. MALDI–TOF MS calcd for $C_{96}H_{128}F_2O_4S_{10}$ 1702.7 found 1702.5, ^{1}H NMR (400 MHz, CDCl$_3$), δ: 9.95 (s, 2H), 7.65 (s, 2H), 7.40 (s, 2H), 7.18 (s, 2H), 6.87 (s, 2H), 4.15-4.18 (t, 4H, J=6.4), 2.93-2.97 (t, 4H, J=7.2), 2.81-2.82 (d, 4H, J=6.8), 1.73-1.85 (m, 10H), 1.26-1.38 (m, 72H), 0.85-0.93 (m, 24H)

BT-OT-ID

Under Ar protection, five drops of triethylamine was added into the mixture of compound **6** (200 mg, 0.12 mmol) and 1H-indene-1,3(2H)-dione (177 mg, 1.2 mmol). After being stirred for 24 h at ambient temperature, the mixture was poured into water and extracted using $CHCl_3$. The organic layer was washed with brine and water and then dried over $MgSO_4$. After being concentrated, the crude product was purified by using column chromatography on silica gel, with a mixture of $CHCl_3$ and petroleum (2:3) as eluent, and then recrystallized with chloroform and hexane to yield the target compound (150 mg, 45%) as a dark solid. IR (ATR):v_{max}/cm^{-1} : 3367, 3270,3092, 2957, 1714, 1670, 1596, 1560, 1534, 1469, 1439,1407, 1361,1342, 1308, 1286, 1234,1201, 1183, 1151, 1098, 1017, 991,978, 814,802, 728, 628, 603; m. p. (244°C); MALDI–TOF MS calcd for $C_{114}H_{136}O_6S_{10}$ 1958.8 found 1958.6, 1H NMR (400 MHz, $CDCl_3$): 8.02 (s, 2H), 7.75-7.83 (m, 4H), 7.54-7.60 (m, 4H), 7.47 (s, 2H), 7.41 (s, 4H), 7.22 (s, 2H), 4.24-4.27 (t, 4H), 2.86-2.89 (m, 8H), 1.95-2.02 (m, 4H), 1.61-1.83 (m, 10H), 1.37-1.46 (m, 68H), 0.93-1.00 (m, 24H). (Note: ^{13}C NMR has been operated for several times, but the peaks are too low for the insufficient solubility).

BT-TO-ID

The procedure of the synthesis is the same with BT-OT-ID, and the target compound was produced as dark red solid with a yield of 65%. IR (ATR):v_{max}/cm^{-1} : 3423, 3270, 3263, 3191, 3077, 2929, 2858, 2309, 2242, 1717, 1673, 1594, 1551, 1523, 1445, 1383, 1331,1314, 1276, 1230, 1206, 1154, 1129, 1065,1021, 994, 949, 876, 815, 798, 734, 680, 652; MALDI–TOF MS calcd for $C_{114}H_{136}O_6S_{10}$ 1958.8 found 1958.5, m. p (189 °C) 1H NMR (400 MHz, $CDCl_3$): 8.11 (s, 2H), 7.83-7.86 (m, 4H), 7.56-7.66 (m, 6H), 7.41 (s, 2H), 7.15 (s, 2H), 6.76 (s, 2H), 4.08-4.10 (t, 4H), 2.84-2.89 (m, 8H), 1.74-1.80 (m, 8H), 1.25-1.42 (m, 74H), 0.81-0.98 (m, 24H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.38, 143.30, 141.54, 140.48, 138.35, 136.19, 134.82, 134.16, 134.08, 122.45, 122.41, 122.37, 122.23, 122.10, 118.38, 109.98, 72.65, 50.91, 39.44, 38.87, 33.53, 33.23, 33.06, 31.99, 31.97, 31.85, 30.18, 30.07, 29.81, 29.72, 29.54, 29.42, 29.38, 29.25, 28.84, 26.75, 26.66, 25.86, 23.14, 22.76, 22.69, 14.29, 14.19, 14.17, 14.14, 10.90.
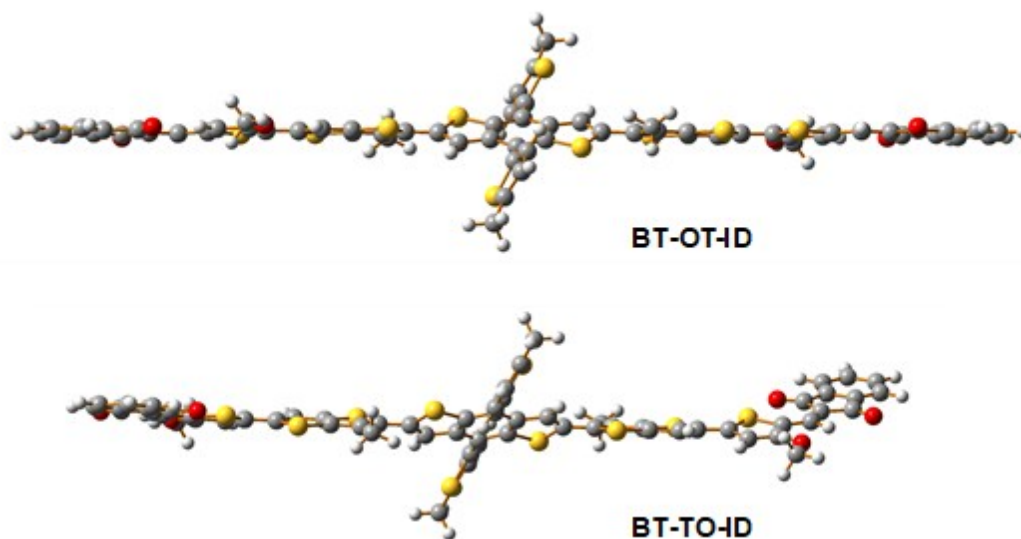
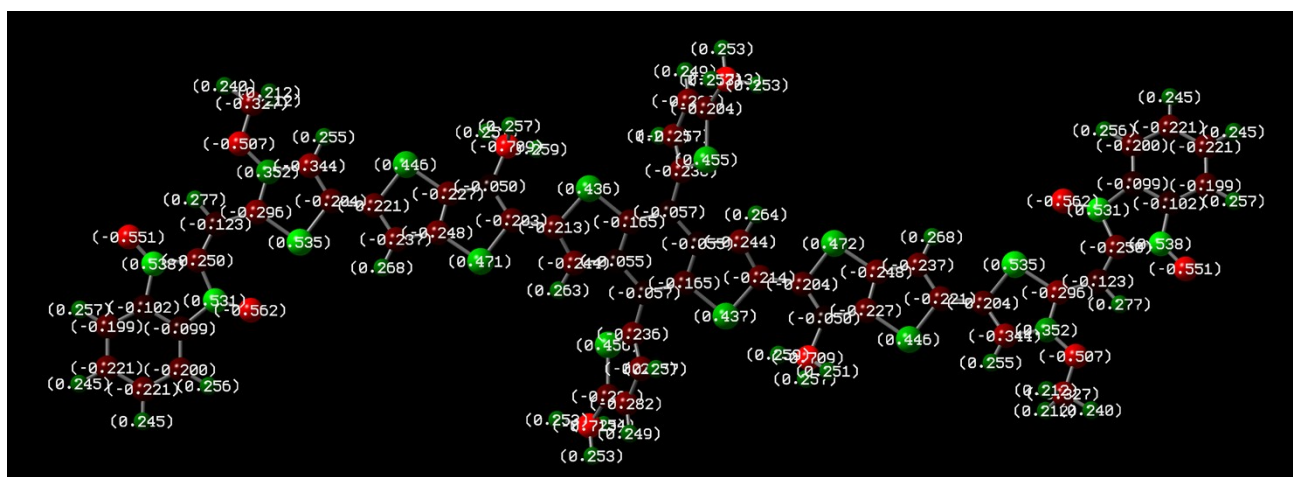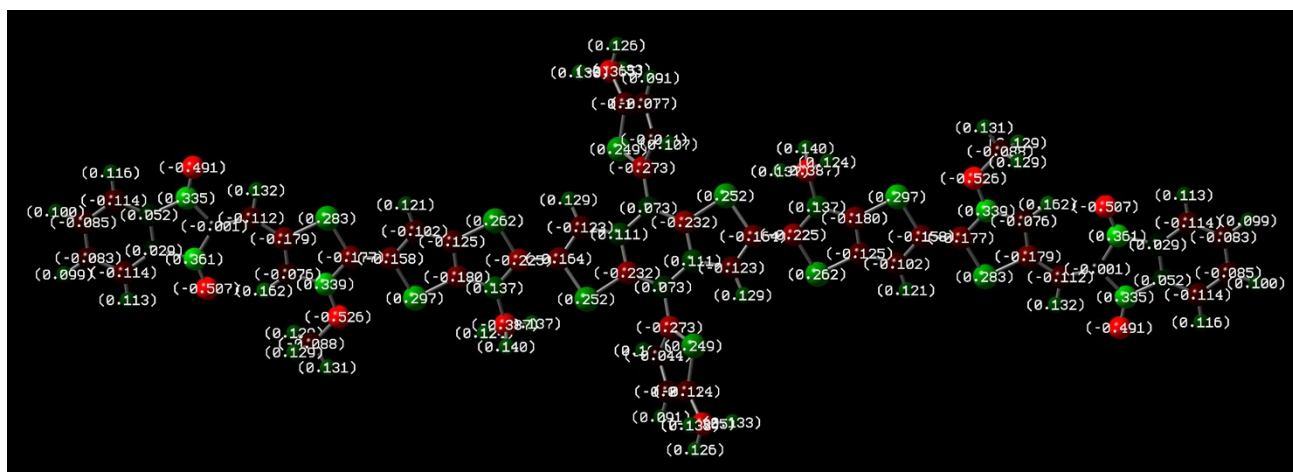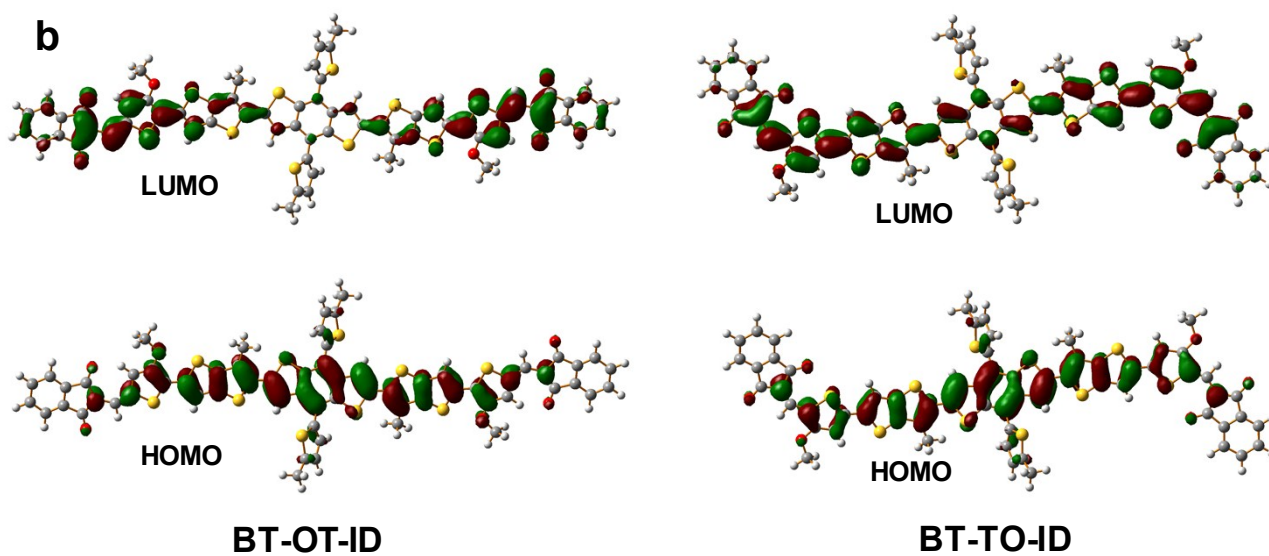# 3. Supporting figures

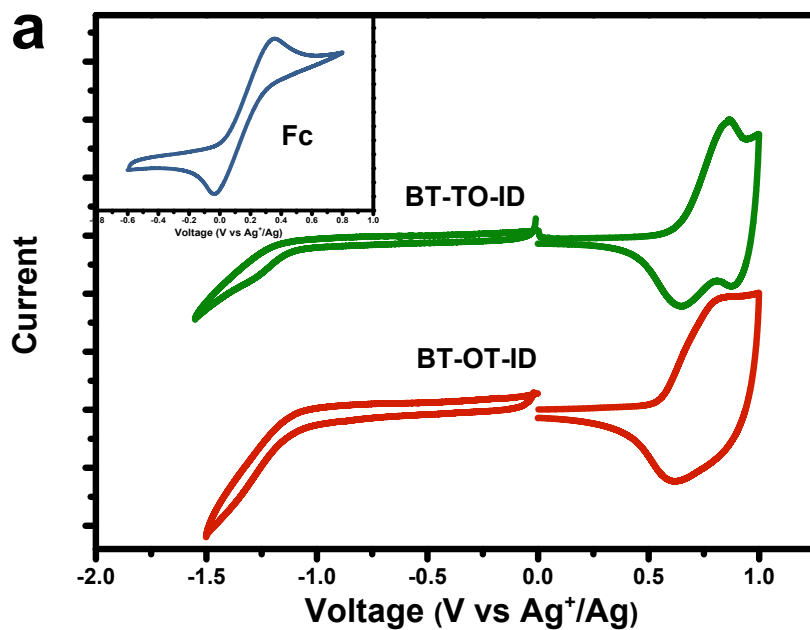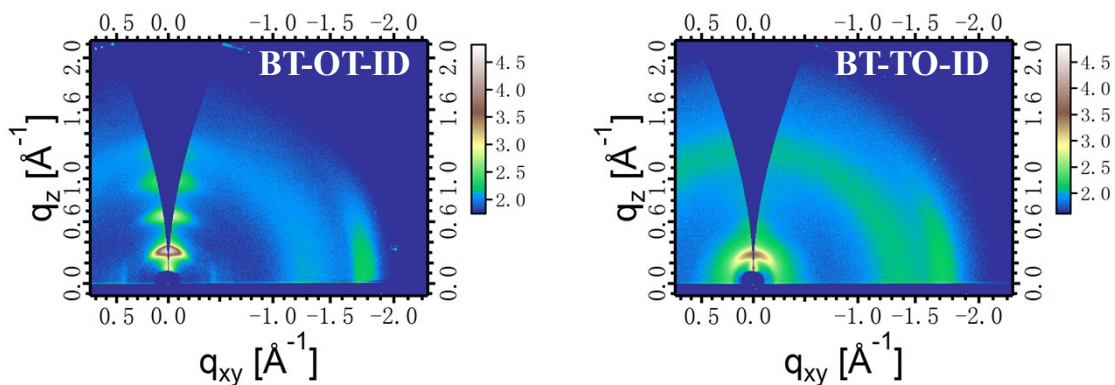Fig. S1 Side views of small molecules

Fig. S2 Calculated NBO charge distribution of the two optimized small molecules, top) BT-OT-ID; bottom) BT-TO-ID

Fig. S3 a) CV curves of the two small molecules, with the scan rate of 50 mV/s; The insert figure is the calibration CV curve of ferrocene b) Electron density distribution of calculated HOMO and LUMO based on the two isomers

**Fig. S4** Two dimensional GIWAXs images for isomers of pristine films
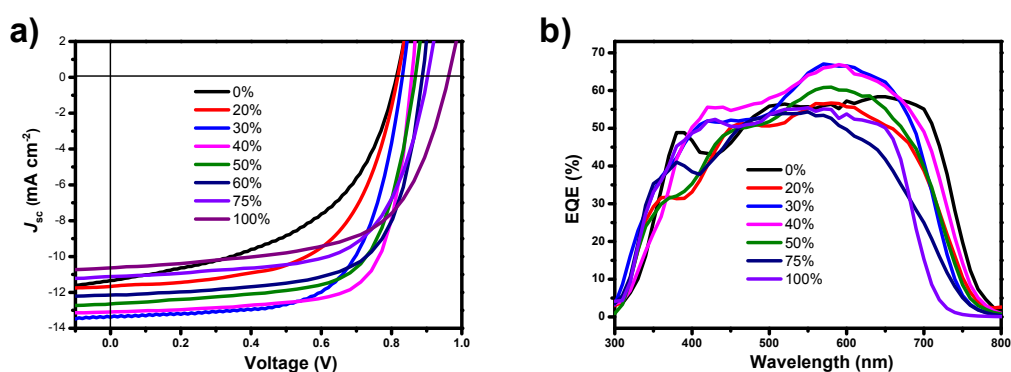
Fig. S5 a) J-V curves of TOSCs at different weight ratio of BT-TO-ID b) The corresponding EQE curves.
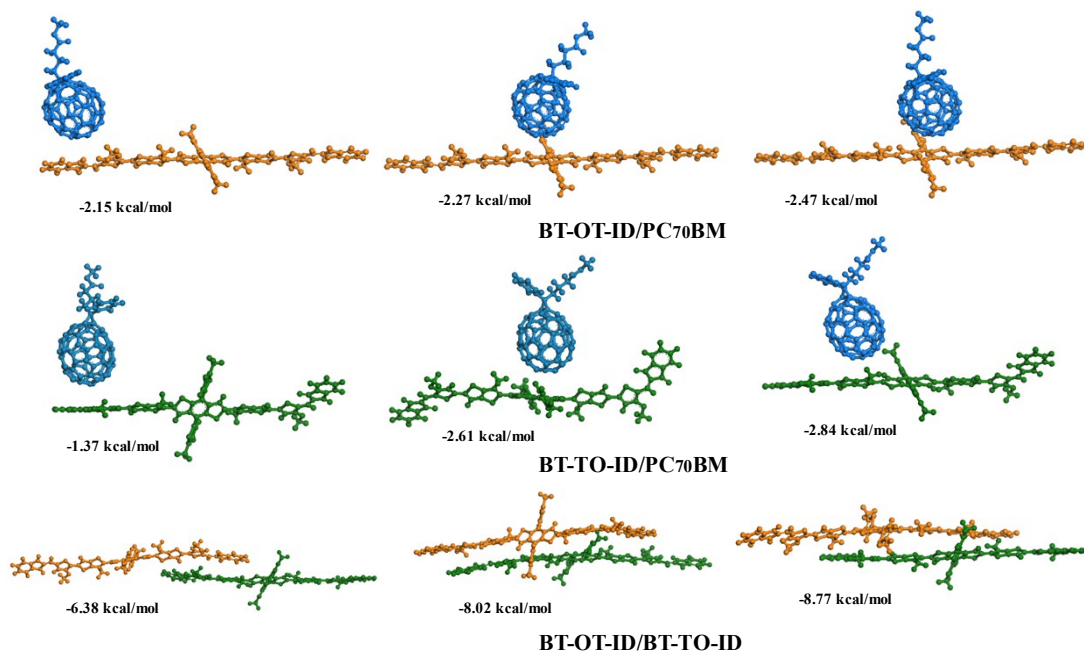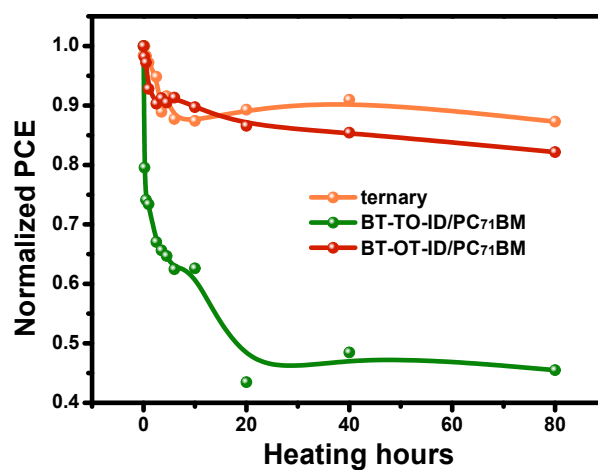

Fig. S6 Optimized complex structures and calculated binding energies of **BT-OT-ID**/PC$_{71}$BM, **BT-TO-ID/**PC$_{71}$BM and **BT-TO-ID/BT-OT-ID**, using DFT methods with long-range corrected functional CAM-
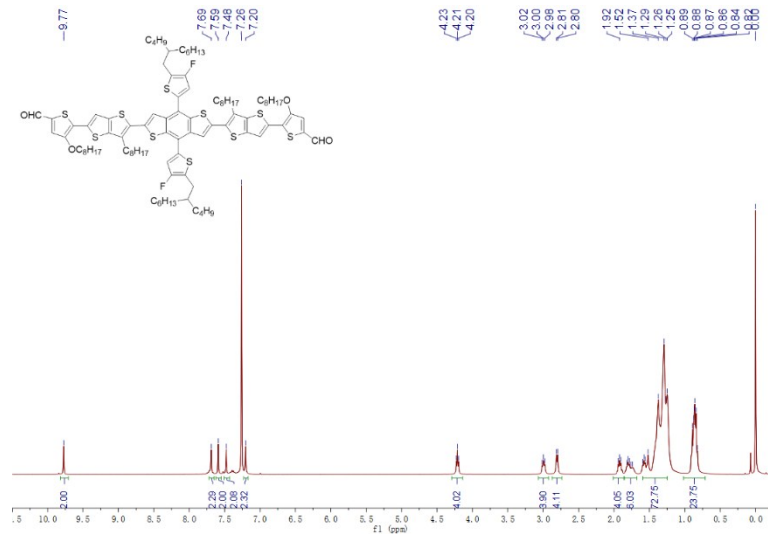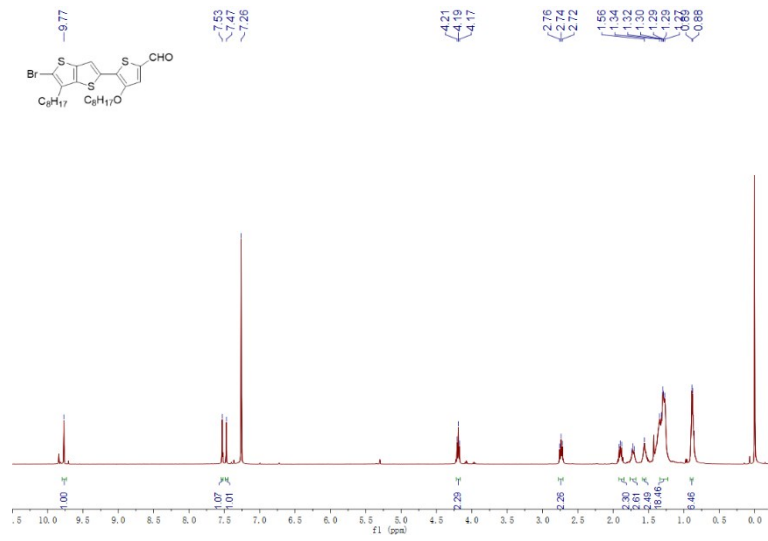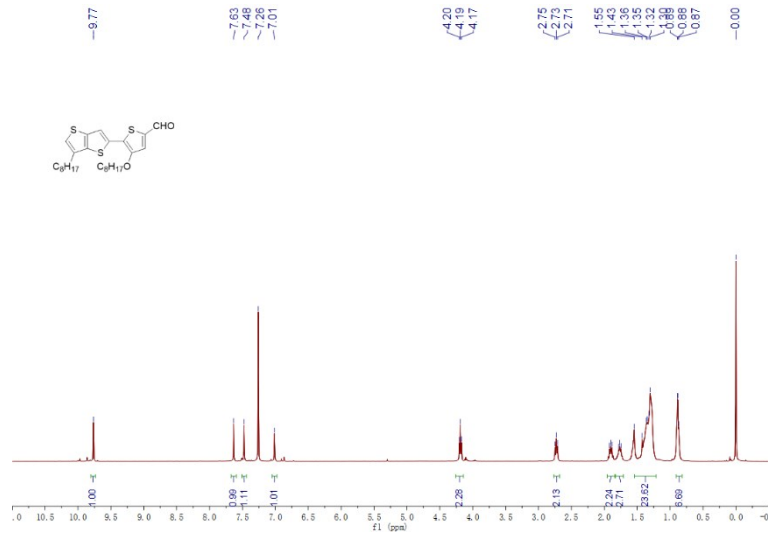
B3LYP and the 6-31G (d, p) basis set
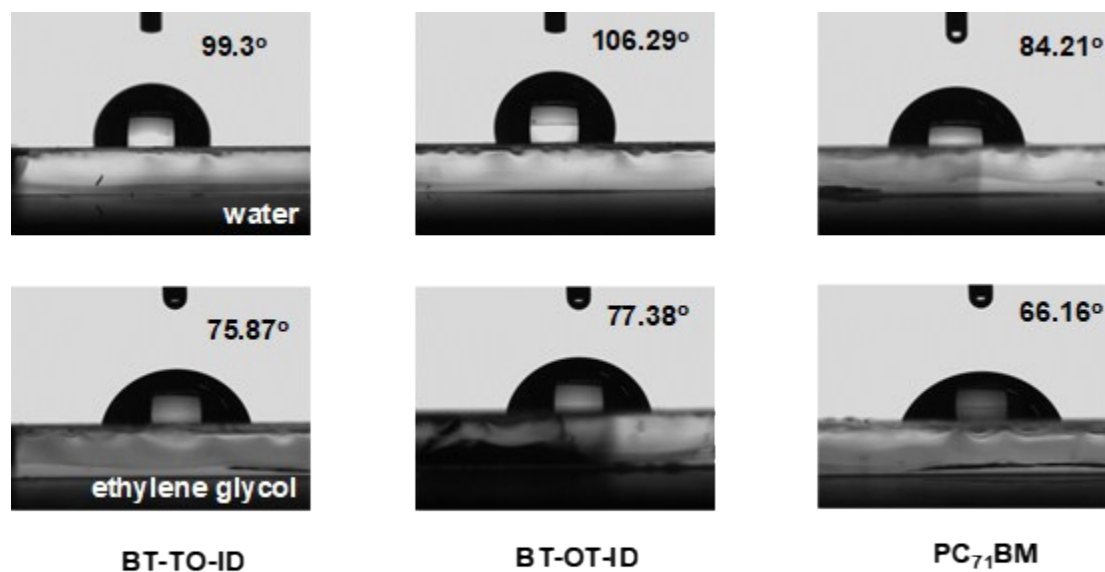
Fig. S7 Examples of contact angle measurement on the substrate of pristine isomers or $PC_{71}BM$ substrate

Fig S8 Thermal stability of the devices under the best optimized conditions
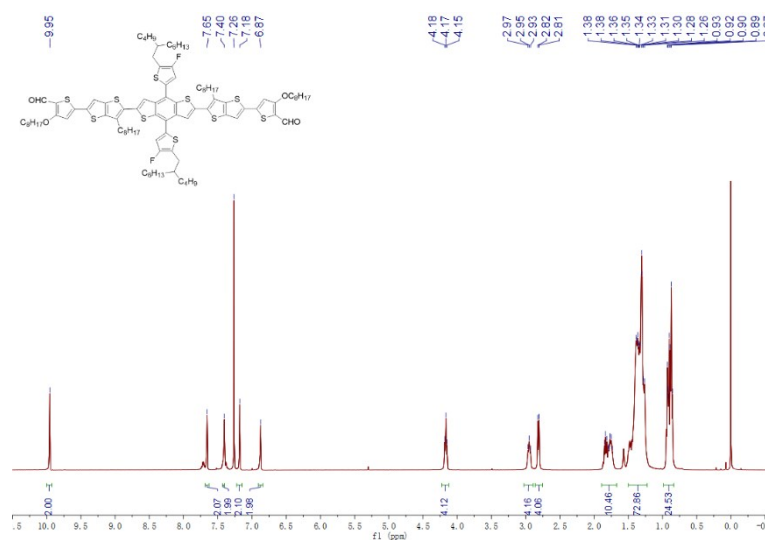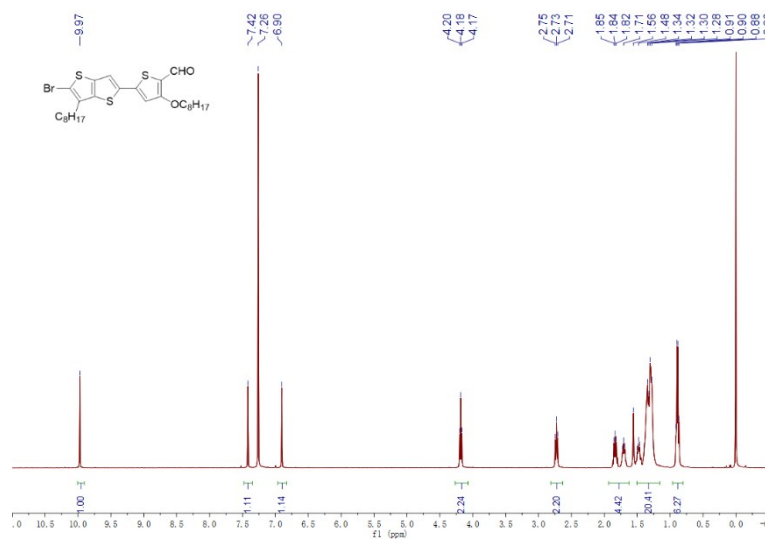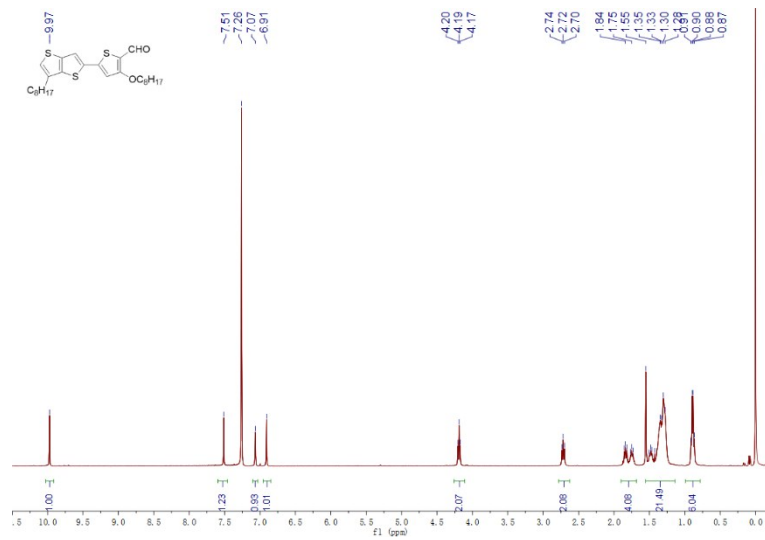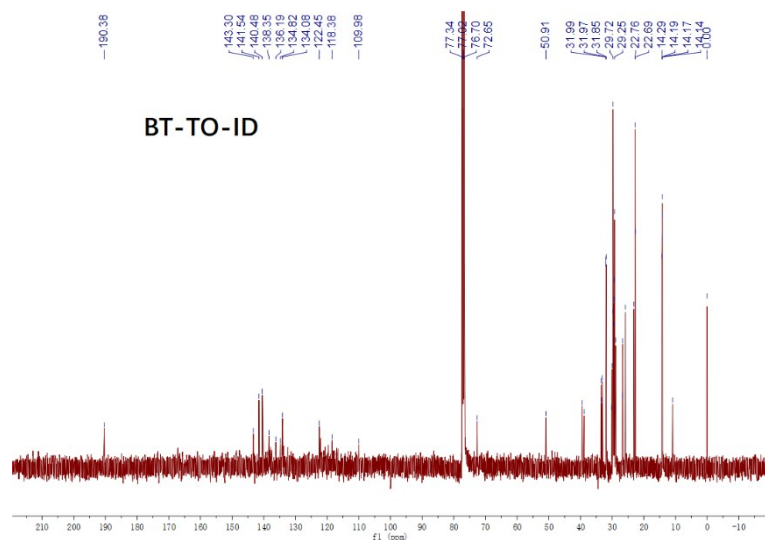
Spectrum 1 (top):

9.77

7.63
7.48
7.26
7.01

4.20
4.19
4.17

2.75
2.73
2.71

1.55
1.43
1.36
1.35
1.32
1.29
0.88
0.87

0.00

Structure: thienothiophene with S, S, C₈H₁₇, C₈H₁₇O, CHO

Integrations: 1.00 | 0.99 1.11 1.01 | 2.28 | 2.13 | 2.24 2.71 23.62 | 3.69

f1 (ppm): 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0

Spectrum 2 (middle):

9.77

7.53
7.47
7.26

4.21
4.19
4.17

2.76
2.74
2.72

1.56
1.34
1.32
1.30
1.29
0.88

Structure: Br, S, S, C₈H₁₇, C₈H₁₇O, CHO

Integrations: 1.00 | 1.07 1.01 | 2.29 | 2.26 | 2.30 2.61 2.49 18.46 | 6.46

f1 (ppm): 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

Spectrum 3 (bottom):

9.77

7.69
7.59
7.48
7.26
7.20

4.23
4.21
4.20

3.02
3.00
2.98
2.81
2.80

1.92
1.52
1.37
1.29
1.26
1.25
0.89
0.88
0.87
0.86
0.84

Structure labels: C₄H₉, C₆H₁₃, F, S, C₈H₁₇, C₈H₁₇O, OHC, S, S, S, S, OC₈H₁₇, C₈H₁₇, CHO, S, F, C₆H₁₃, C₄H₉

Integrations: 2.00 | 2.29 2.00 2.08 2.32 | 4.02 | 3.90 4.11 | 4.05 5.03 72.75 | 23.75

f1 (ppm): 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

Fig. S9 NMR spectrums of intermediates

Fig. S10 NMR spectrums of final products
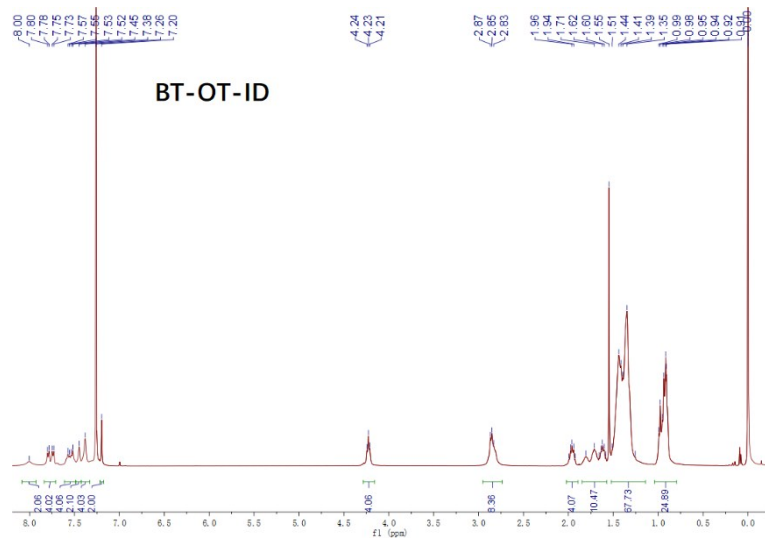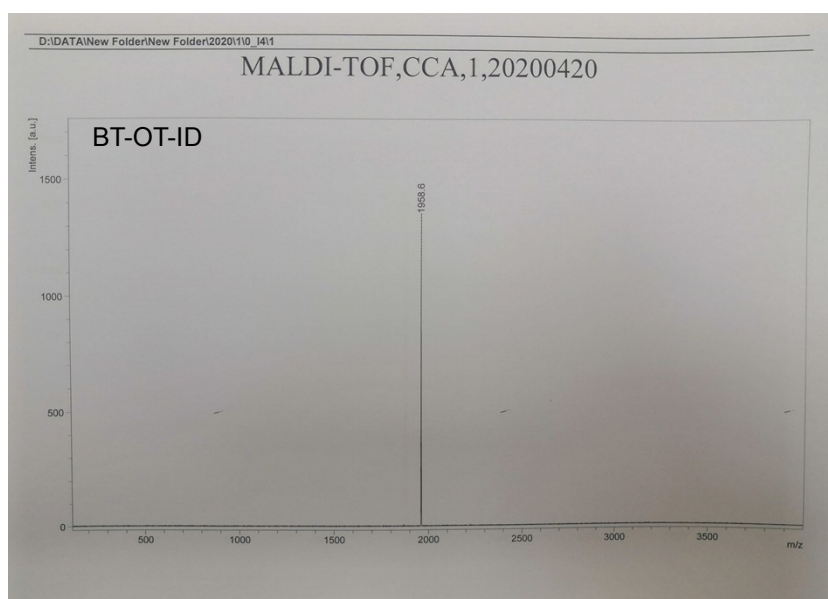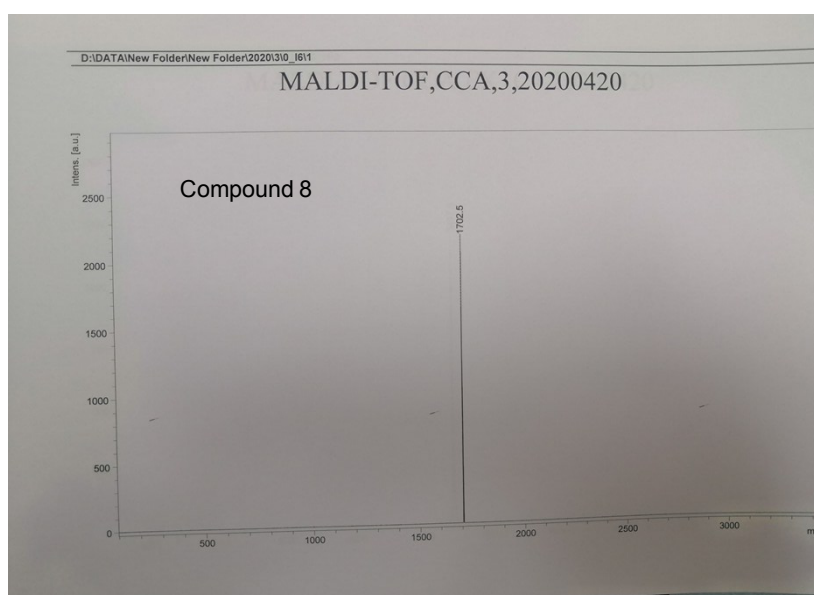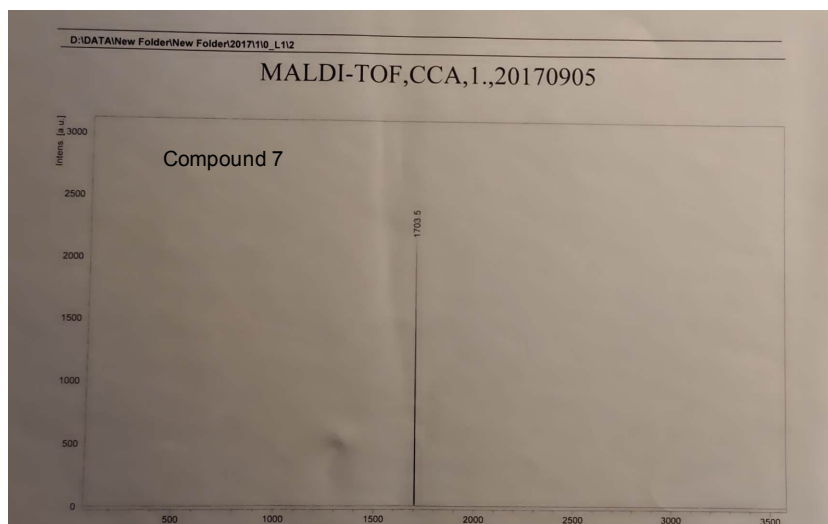
MALDI-TOF,CCA,1.,20170905

Compound 7

1703.5

MALDI-TOF,CCA,3,20200420

Compound 8
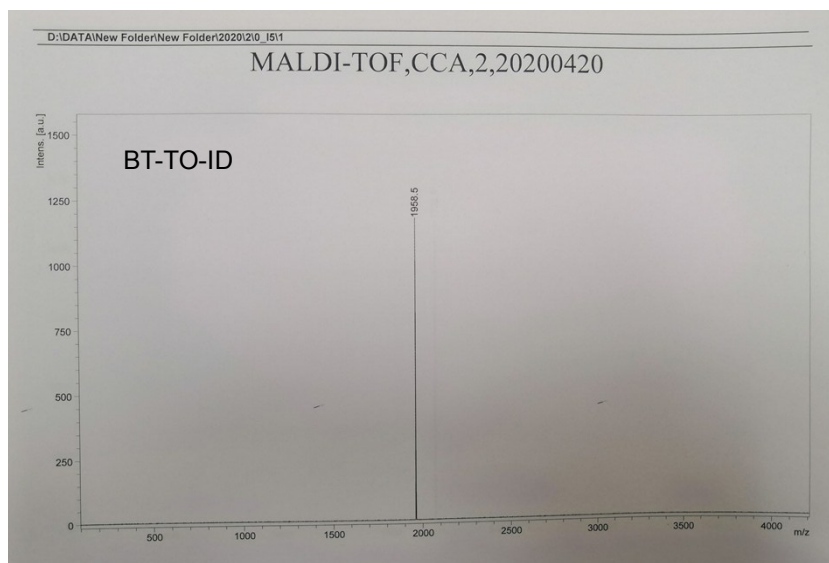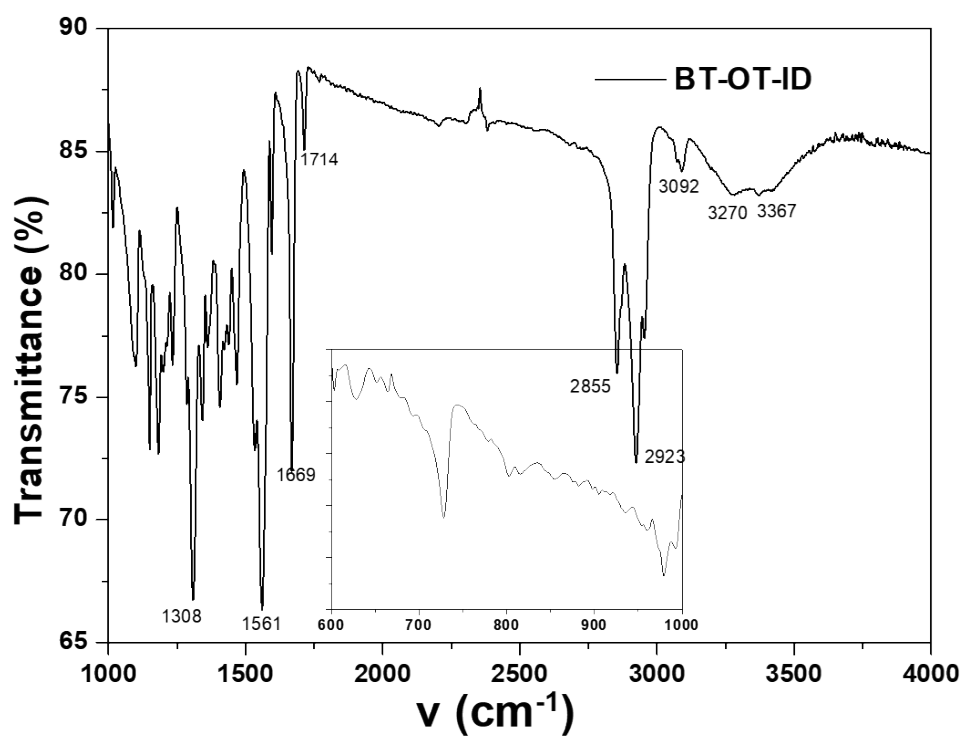
1702.5

MALDI-TOF,CCA,1,20200420

BT-OT-ID

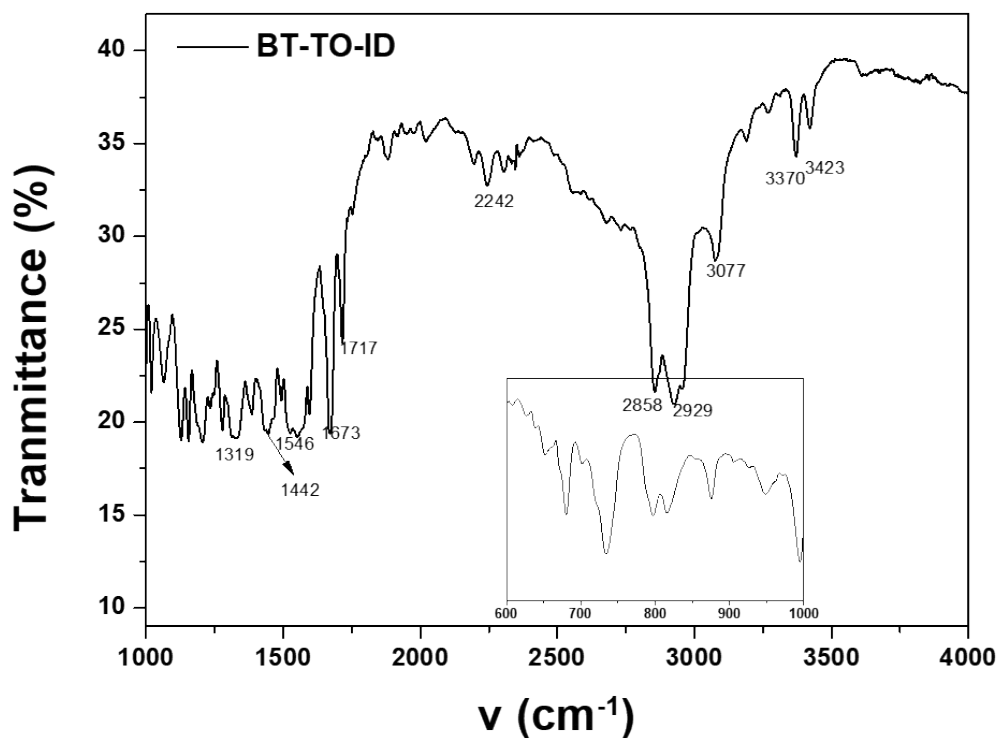1958.6

Fig. S11 Maldi-TOF spectras

Fig. S12 IR spectrums of final products

Table S1 opo-physical properties of the small molecules

Molecule	$\varepsilon_{max}^{(sol.)}$ [l mol^{-1}cm^{-1}]	$\varepsilon_{max}^{(film)}$ [cm^{-1}]	E_g^{opt} (eV)	HOMO^{CV} (eV)	LUMO^{CV} (eV)	E_g^{CV} (eV)	HOMO^{cal} (eV)	LUMO^{cal} (eV)	E_g^{cal} (ev)
BT-OT-ID	7.3×10^4	10.5	1.66	−5.23	−3.60	1.63	−5.05	−2.71	-2.34
BT-TO-ID	1.3×10^5	5.2	1.80	−5.31	−3.54	1.77	−5.07	−2.68	-2.39

Table S2 Additives optimization of reference binary organic solar cells [a](BT-OT-ID: PC$_{71}$BM)

Additives	Weight ratio (D: A)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)
None	1.5:1	0.79	10.84	48.26	4.11
0.6% CP	1.5:1	0.81	11.34	49.96	4.61
0.6% CN	1.5:1	0.81	8.22	53.37	4.02
0.6% DIO	1.5:1	0.70	6.21	37.44	1.83
0.6% DPE	1.5:1	0.80	8.16	58.48	4.30

[a] The total concentration is 16.7 mg/ml, at the speed rotation of 2000 rpm

Table S3 Concentration of additives and speed rotation optimization of ternary solar cell [a]

Concentration of additives (volume)	Rotation speed (rpm)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)
	1500	0.88	11.29	66.16	6.57
0.4%	2000	0.88	11.74	66.47	6.88
	2500	0.88	11.29	65.42	6.51
	1500	0.86	13.49	66.81	7.71
0.6%	2000	0.86	13.27	71.34	8.10
	2500	0.86	13.36	68.9	7.93
	1500	0.85	12.14	61.22	6.30
0.8%	2000	0.86	11.90	62.33	6.34
	2500	0.85	11.85	60.90	6.20

[a] The total concentration is 16.7 mg/ml, at the ratio of BT-OT-ID:BT-TO-ID: PC$_{71}$BM is 0.9:0.6:1

Table S4 Ratios and concentration optimization of ternary solar cells [a]

Total concentration（mg/ml)	Ratio (BT-OT-ID:BT-TO-ID : PC$_{71}$BM)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)
16.7	0.9:0.6:1	0.86	13.27	71.34	8.10
17.9	0.9:0.6:1	0.85	13.20	70.91	7.97
19.5	0.9:0.6:1	0.86	13.02	68.72	7.69
21.4	0.9:0.6:1	0.86	12.98	72.27	8.05
24	0.9:0.6:1	0.86	12.83	71.24	7.89
16.7	0.75:0.75:1	0.89	12.49	67.26	7.46
17.9	0.75:0.75:1	0.89	12.53	68.26	7.62
19.5	0.75:0.75:1	0.90	12.48	67.70	7.56
21.4	0.75:0.75:1	0.89	12.34	68.34	7.49
24	0.75:0.75:1	0.86	12.77	68.15	7.49
28	0.75:0.75:1	0.88	11.66	65.90	6.75

[a] The rotation speed is 2000 rpm, with 0.6% CP as additive

Supplementary References

1   Gaussian 09 D.01, F., M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg,

J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A., 2010.

2   Karolewski, A.; Stein, T.; Baer, R.; Kummel, S. Communication: Tailoring the optical gap in light-harvesting molecules. *J. Chem. Phys.* **2011**, 134, 151101.

3   Stein, T.; Eisenberg, H.; Kronik, L.; Baer, R. Fundamental Gaps in Finite Systems from Eigenvalues of a Generalized Kohn-Sham Method. *Phys. Rev. Lett.* **2010**, 105, 266802.

4   G. Malliaras, J. Salem, P. Brock, C. Scott, Electrical characteristics and efficiency of single-layer organic light-emitting diodes. *Physical Review B*, **1998**, 58, R13411.

5   A. B. Tamayo, B. Walker, T.-Q. Nguyen, *J. Phys. Chem. C*. **2008**, 112, 11545.

6   Yao, H.; Cui, Y.; Yu, R.; Gao, B.; Zhang, H.; Hou, J., Design, synthesis, and photovoltaic characterization of a small molecular acceptor with an ultra-narrow band gap. *Angew. Chem.* **2017,** *129* (11), 3091.

7   Zhang, M.; Guo, X.; Zhang, S.; Hou, J., Synergistic effect of fluorination on molecular energy level modulation in highly efficient photovoltaic polymers. *Adv. Mater.* **2014,** *26* (7), 1118.