Supporting Information

A Ring-locking Strategy to Enhance the Chemical and Photochemical Stability of A-D-A-type Non-Fullerene Acceptors

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1. Experimental Section

1.1. Instrumentations

^{1}H NMR and ^{13}C NMR spectra were measured using a Bruker 400 and 600 MHz instrument spectrometers. High-resolution mass spectrometry (HRMS) was performed by using Bruker Daltonics instrument, SolariX 7.0T. MALDI-TOF MS analysis was performed on an AB SCIEX MALDI TOF/TOF™ 5800 system (Applied Biosystems, Foster City, CA, USA). Cyclic voltammetry (CV) was measured on a CHI600E electrochemical analyzer (CH Instruments, Inc., China) using a conventional three-electrode cell with a platinum disk electrode (2 mm in diameter) as the working electrode, a platinum wire (0.5 mm in diameter), an Ag/AgCl as the reference electrode in an 0.1 M electrolyte containing tetrabutylammonium hexafluorophosphate in dichloromethane at a scan rate of 100 mV s^{-1}. Potentials were referenced to the ferrocenium/ferrocene ($FeCp_2^{+/0}$) couple by using ferrocene as an external standard. The HOMO/LUMO energy levels are calculated according to the equation of $E_{HOMO/LUMO} = -(E_{ox/red} + 4.8)$ eV. For HOMOs, they are mainly calculated based on the average potentials from the quasi-reversible oxidation peak, except those of IDT-R and IDTT-R based on the onset of first oxidation peak. For LUMOs, all values are calculated based on the onset of first reduction peak. Differential pulse voltammetry (DPV) was measured on a

CHI760E electrochemical analyzer (CH Instruments, Inc., China) using a same three-electrode cell as CV, and the $E_{ox/red}$ are obtained from the peak potential of the first oxidation/reduction wave.[1] UV−Vis−NIR absorption spectra were collected using a PerkinElmer LAMBDA 750S UV-VIS-NIR spectrophotometer. Current density-voltage (*J-V*) characteristics of the cells were measured using a Keithley 2400 SourceMeter. The cells were illuminated through an aperture area of 4.1 mm^2 from a 100 mW/cm^2 AM1.5 solar simulator (Newport, ORIEL, Sol3A, 450 W xenon lamp), and the device photostability was also measured under the same light sources. The photostability of solution and film was tested by using a solar light simulator (CEL-S500L, Beijing China Education Au-light Co., Ltd) based on a xenon lamp (500W).

1.2. Photovoltaic device fabrication

Device structure of organic solar cell with metal electrode is: glass/ITO/ZnO/ donor:acceptor/MoO_3/Ag. ITO glass substrates were cleaned in the ultrasound baths for 15 min with soapy water, deionized water, acetone and isopropanol, respectively. ITO substrates were blown dry with a nitrogen gun and treated by air plasma for 3 min. ZnO precursor solution was spin-coated on the ITO glass at 3500 rpm for 40 s, and then annealed at 200 ^oC for 15 min. The active layer was deposited on the ZnO at optimized speed for 45 s. The annealed process was at optimized temperature for 10 min in a N_2–filled glovebox. The detail preparation parameters of active layer were displayed in **Table S4**. The top electrode MoO_3 (7 nm)/Ag (70 nm) was deposited thermal evaporation system (Mini-Spectros, Kurt J. Lesker) at a base pressure of 2×10^{-6} Torr. The effective area was 4.1 mm^2.

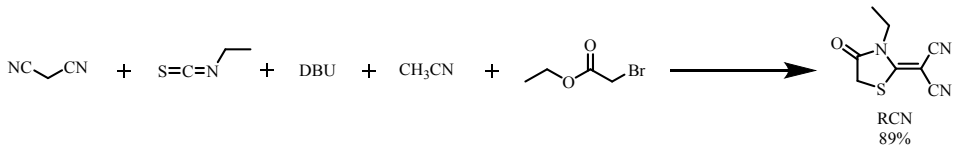
1.3. Materials and Synthesis

2-(1,1-dicyanomethylene)rhodanine (RCN)[2], thiobarbituric acid (TBA)[3], and 3-Bromocyclohex-2-enon[4] were synthesized according to the previous literatures. IDT-CHO,

IDTT-CHO, IDT-tin, and IDTT-tin were purchased from Derthon Optoelectronic Materials Science Technology Co., LTD. PBDB-T, PBDB-T-2F, PTB7-Th, ITIC, IT-4F, and IT-M were purchased from Solarmer Materials Inc. Both acetonitrile and dichloromethane (DCM) were dried and distilled from calcium hydride under an atmosphere of dry nitrogen. Chloroform was dried and distilled from anhydrous calcium chloride under an atmosphere of dry nitrogen. Toluene was dried and distilled from sodium with benzophenone as indicator under an atmosphere of dry nitrogen. All other reagents were used as received.

2. Organic synthesis

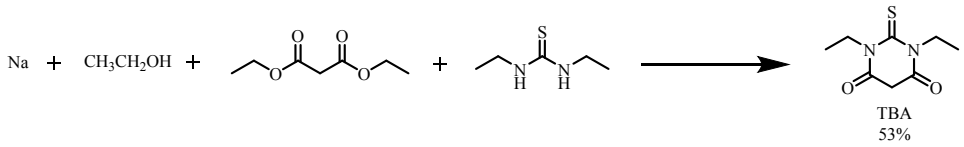
Synthesis of 2-(1,1-dicyanomethylene)rhodanine (RCN)



RCN
89%

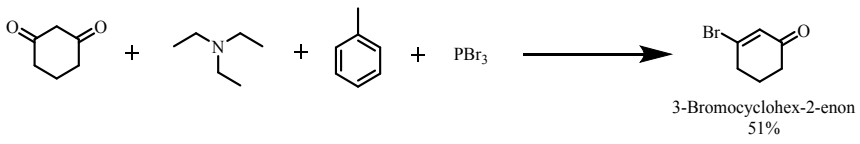
Under an argon atmosphere, a mixture of malononitrile (1.2 g, 18.6 mmol), ethyl isothiocyanate (1.9 mL, 20.5 mmol), 1,8-diazabicyclo[5.4.0]-7-undecene (DBU) (2.7 mL, 18.1 mmol), and anhydrous acetonitrile (60 mL) was stirred at room temperature for 0.5 h. Afterwards, ethyl bromoacetate (3.4 mL, 30.5 mmol) was added. The mixture was further stirred at room temperature for 1 h and then refluxed for 4 h. After the completion of reaction, the product was concentrated, acidified with aqueous 2 M hydrochloric acid (60 mL) and extracted with DCM. The organic extraction was dried over anhydrous sodium sulfate. After the solvent was removed under reduced pressure, the residue was purified by silica gel flash column chromatography using DCM as the eluent to afford the crude product. The crude product was purified by recrystallization from n-hexane to afford RCN as a pale yellow solid (3.1 g, 89%). ^{1}H NMR (600 MHz, chloroform–*d*, δ): 4.19 (q, J = 7.2 Hz, 2H, –CH_2CH$_3$), 4.00 (s, 2H, –CH$_2$–), 1.36 (t, J = 7.2 Hz, 3H, –CH$_3$).

Synthesis of thiobarbituric acid (TBA)



Under an argon atmosphere, sodium (4.6 g, 200 mmol) was first dissolved in absolute ethyl alcohol (200 mL) to prepare a solution of sodium ethylate. Then diethyl malonate (32.0 g, 200 mmol) and N,N'-Diethylthiourea (6.6 g, 50 mmol) were added to the solution, and the resulting mixture was allowed to stir at reflux for 48 h. After the completion of reaction as indicated by thin-layer chromatography (TLC), the reaction mixture was diluted with water (100 mL). Then most of the ethyl alcohol was removed under reduced pressure. The residue was poured into cold water (100 mL), chilled and filtered. The aqueous layer was washed with ether (2 × 50 mL) to remove any unreacted diethyl malonate. The aqueous layer was acidified with diluted hydrochloric acid, and the resulting solid was filtered off, washed with cold water and ether, and dried to afford TBA as a white solid (5.3 g, 53%). ^{1}H NMR (600 MHz, chloroform–*d*, δ): 4.19 (q, *J* = 7.2 Hz, 4H, –C*H*$_2$CH$_3$), 4.00 (s, 2H, –CH$_2$–), 1.36 (t, *J* = 7.2 Hz, 6H, –CH$_3$).

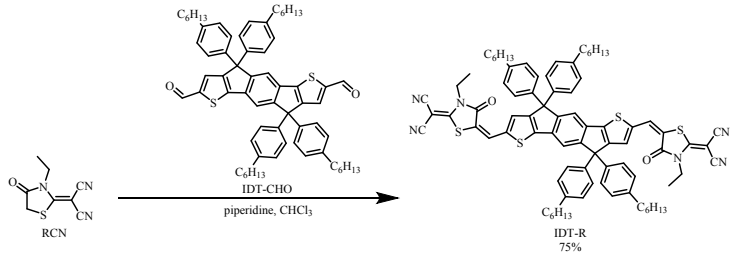
Synthesis of 3-Bromocyclohex-2-enon



Under an argon atmosphere, phosphorus tribromide (4.6 ml, 49.0 mmol) was added into a solution of 1,3-cyclohexanedione (5.0 g, 44.5 mmol) and triethylamine (6.8 mL, 49.0 mmol) in toluene (175 mL) at -10 °C. The reaction was then stirred at room temperature for 36 h and then poured into ice-water (200 mL). The mixture was extracted with ether, and the organic extraction was washed with saturated sodium bicarbonate solution (100 mL) and distilled water (3×100 mL) and dried over anhydrous sodium sulfate. After removing the solvent under reduced pressure, the residue was purified by silica gel flash column chromatography using

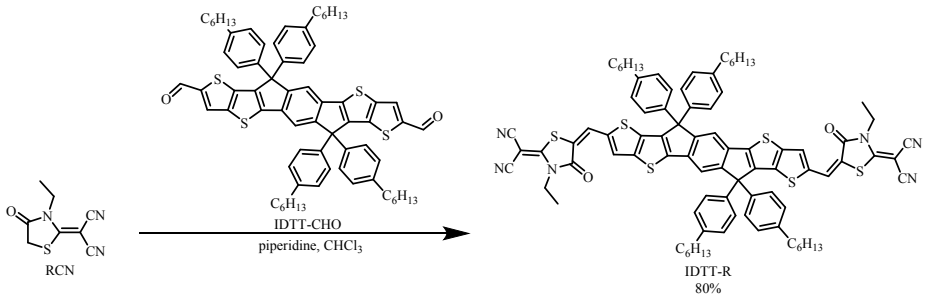
DCM/petroleum ether (PE) (1:1, V/V) as the eluent to afford 3-Bromocyclohex-2-enon as a colorless liquid (4.0 g, 51%). ^{1}H NMR (600 MHz, chloroform-*d*): δ 6.47 (s, 1H, =CH–), 2.82–2.80 (m, 2H, –CH_2–), 2.42–2.30 (m, 2H, –CH_2–), 2.10–2.05 (m, 2H, –CH_2–).

Synthesis of IDT-R



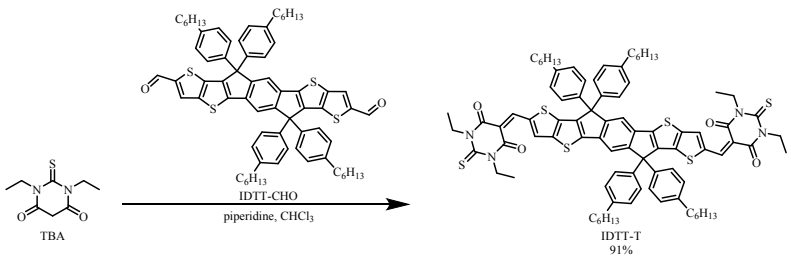
Under an argon atmosphere, IDT-CHO (96 mg, 0.1 mmol) and RCN (194 mg, 1.0 mmol) were dissolved in anhydrous chloroform (10 mL) containing 2 μL of piperidine, an then the mixture was refluxed for 48 h. After cooling to room temperature, the reaction was quenched with 20 mL of distilled water and extracted with DCM. The organic extraction was dried with anhydrous sodium sulfate, and the solvent was removed under reduced pressure. The residue was purified by silica gel flash column chromatography using DCM/PE (1:1, V/V) as the eluent to afford pure product IDT-R as a red solid (98 mg, 75%). ^{1}H NMR (600 MHz, chloroform-*d*): δ 8.06 (s, 2H, =CH–), 7.61 (s, 2H, ArH), 7.39 (s, 2H, ArH), 7.13 (d, J = 8.4 Hz, 8H, ArH), 7.10 (d, J = 8.4 Hz, 8H, ArH), 4.30 (q, J = 7.1 Hz, 4H, –CH_2–), 2.57 (t, J = 7.8 Hz, 8H, –CH_2Ar–), 1.61–1.58 (m, 8H, –CH_2–), 1.40 (t, J = 7.2 Hz, 6H, –CH_3), 1.34–1.27 (m, 24H, –CH_2–), 0.88–0.86 (m, 12H, –CH_3). ^{13}C NMR (101 MHz, chloroform-*d*): δ 165.91, 165.46, 158.32, 155.13, 150.54, 142.46, 140.50, 140.47, 135.87, 131.21, 129.82, 128.88, 127.75, 119.03, 113.44, 112.92, 112.38, 63.35, 55.77, 40.79, 35.68, 31.83, 31.44, 29.22, 22.72, 14.33, 14.23. HRMS (APCI): $[M + H]^+$ = 1313.5564 (calcd for $C_{82}H_{85}N_6O_2S_4^+$, 1313.5611)

Synthesis of IDTT-R



Under an argon atmosphere, IDTT-CHO (108 mg, 0.1 mmol) and RCN (117 mg, 0.6 mmol) were dissolved in anhydrous chloroform (10 mL) containing 0.1 mL of piperidine. After refluxing for 4 h, the reaction was cooled to room temperature, quenched with 20 mL of distilled water and then extracted with DCM. The organic extraction was dried with anhydrous sodium sulfate, and the solvent was removed under reduced pressure. The residue was purified by silica gel flash column chromatography using DCM as the eluent to afford pure product IDTT-R as a dark blue solid (106 mg, 80%). ^{1}H NMR (600 MHz, chloroform-*d*): δ 8.03 (s, 2H, =CH–), 7.66 (s, 2H, ArH), 7.59 (s, 2H, ArH), 7.17 (d, *J* = 8.4 Hz, 8H, ArH), 7.14 (d, *J* = 8.4 Hz, 8H, ArH), 4.31 (q, *J* = 7.1 Hz, 4H, –CH_2–), 2.58 (t, *J* = 7.8 Hz, 8H, –CH_2Ar–), 1.62–1.60 (m, 8H, –CH_2–), 1.40 (t, *J* = 7.2 Hz, 6H, –CH_3), 1.35–1.28 (m, 24H, –CH_2–), 0.87–0.85 (m, 12H, –CH_3). ^{13}C NMR (101 MHz, chloroform-*d*): δ 165.99, 165.45, 154.95, 149.03, 146.99, 143.67, 142.66, 139.88, 139.14, 137.86, 136.63, 129.56, 128.98, 128.05, 127.92, 118.08, 113.43, 113.05, 112.43, 63.28, 55.68, 40.83, 35.73, 31.82, 31.35, 29.31, 22.72, 14.32, 14.22. HRMS (APCI): $[M + H]^+$ = 1425.5004 (calcd for $C_{86}H_{85}N_6O_2S_6^+$, 1425.5053)

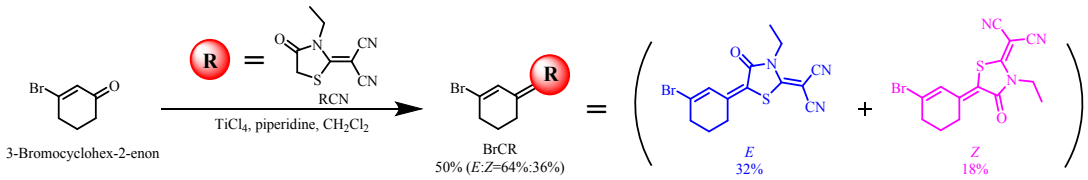
Synthesis of IDTT-T



Under an argon atmosphere, IDTT-CHO (108 mg, 0.1 mmol) and TBA (80 mg, 0.4 mmol)

were dissolved in anhydrous chloroform (10 mL) containing 0.1 mL of piperidine. After refluxing for 18 h, the reaction was cooled to room temperature, and quenched with 20 mL of distilled water and then extracted with DCM. The organic extraction was dried with anhydrous sodium sulfate and the solvent was removed under reduced pressure. The residue was purified by silica gel flash column chromatography using DCM/PE (1:1, V/V) as the eluent to afford pure product IDTT-T as a dark blue solid (131 mg, 91%). ^{1}H NMR (400 MHz, chloroform-*d*): δ 8.65 (s, 2H, =CH–), 8.16 (s, 2H, ArH), 7.62 (s, 2H, ArH), 7.22 (d, *J* = 8.4 Hz, 8H, ArH), 7.13 (d, *J* = 8.4 Hz, 8H, ArH), 4.62–4.52 (m, 8H, –CH_2–), 2.57 (t, *J* = 7.8 Hz, 8H, –CH_2–), 1.62–1.59 (m, 8H, –CH_2–), 1.39–1.29 (m, 36H, –CH_2–, –CH_3), 0.86 (t, *J* = 6.6 Hz, 12H, –CH_3). ^{13}C NMR (101 MHz, chloroform-*d*): δ 178.69, 161.14, 159.81, 155.72, 152.90, 149.79, 148.04, 147.66, 143.49, 142.61, 140.01, 139.13, 138.23, 136.95, 128.97, 128.04, 118.67, 110.28, 100.12, 63.46, 44.14, 43.28, 35.74, 31.83, 31.38, 29.31, 22.72, 14.22, 12.66, 12.53. HRMS (APCI): $[M + H]^+$ = 1439.5627 (calcd for $C_{86}H_{95}N_4O_4S_6^+$, 1439.5672)

Synthesis of BrCR



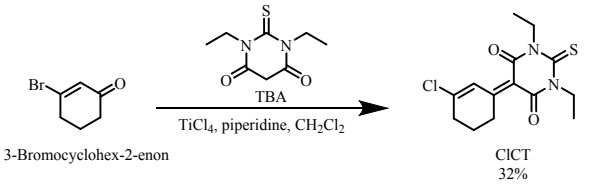
Under an argon atmosphere, 3-Bromocyclohex-2-enon (0.4 mL, 3.72 mmol) and RCN (476 mg, 2.48 mmol) were dissolved in anhydrous DCM (20 mL) at 0 °C, and then tetrachloride (0.4 ml, 3.72 mmol) and anhydrous pyridine (0.6 ml, 7.44 mmol) were added. After stirred at 0 °C for 1 h, the reaction was stirred at room temperature for another 36 h and then poured into distilled water (40 mL). The mixture was extracted with DCM, and the organic layer was dried over anhydrous sodium sulfate. After removing the solvent under reduced pressure, the residue was purified by silica gel flash column chromatography using DCM as the eluent to afford pure BrCR as a yellow solid (437 mg, 50%, *E*:*Z*=64%:36%). ^{1}H NMR (600 MHz,

chloroform-*d*): δ 8.26 (s, 0.56H, =CH–, *E*), 6.55 (s, 0.31H, =CH–, *Z*), 4.23–4.20 (m, 2H, –CH_2–), 3.19–3.16 (m, 0.71H, –CH_2–, *Z*), 2.80–2.77 (m, 2H, –CH_2–), 2.45–2.42 (m, 1.28H, –CH_2–, *E*), 2.04–1.97 (m, 1.28H, –CH_2–, *E*), 1.97–1.90 (m, 0.71H, –CH_2–, *Z*), 1.36 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, chloroform-*d*): δ 165.11, 164.77, 163.66, 148.02, 146.63, 142.56, 140.86, 129.28, 126.58, 113.53, 113.40, 112.77, 112.60, 112.54, 54.67, 54.18, 40.33, 36.60, 36.35, 30.63, 25.32, 23.21, 23.09, 14.18. HRMS (APCI): $[M - H]^-$ = 347.9811 (calcd for $C_{14}H_{11}BrN_3OS^-$, 347.9812)

BrCR (294 mg, 0.84 mmol) was dissolved in chloroform (10 mL) at room temperature, and then *n*-hexane (10 mL) was added slowly to the top of BrCR solution. After two days, light yellow crystals precipitated in the solution and were separated to afford pure Z-BrCR (80 mg, 27%) by filtration. ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.55 (s, 1H, =CH–), 4.30 (q, *J* = 7.2 Hz, 2H, –CH_2–), 3.18 (t, *J* = 6.6 Hz, 2H, –CH_2–), 2.78 (t, *J* = 6.6 Hz, 2H, –CH_2–), 1.96–1.91 (m, 1H, –CH_2–), 1.36 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 165.14, 164.78, 148.03, 142.57, 129.29, 113.54, 112.78, 112.61, 54.21, 40.35, 36.62, 25.34, 23.23, 14.23.

The above filtrate was concentrated and purified by silica gel flash column chromatography using DCM/PE (7:3, V/V) as the eluent to afford pure *E*-BrCR as a yellow powder (74 mg, 25%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.26 (s, 1H, =CH–), 4.23 (q, *J* = 7.2 Hz, 2H, –CH_2–), 2.78 (t, *J* = 6.6 Hz, 2H, –CH_2–), 2.44 (t, *J* = 6.6 Hz, 2H, –CH_2–), 2.03–1.98 (m, 1H, –CH_2–), 1.36 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 165.11, 163.65, 146.62, 140.87, 126.57, 113.53, 113.40, 112.54, 54.67, 40.33, 36.35, 30.63, 23.10, 14.19.

Synthesis of ClCT

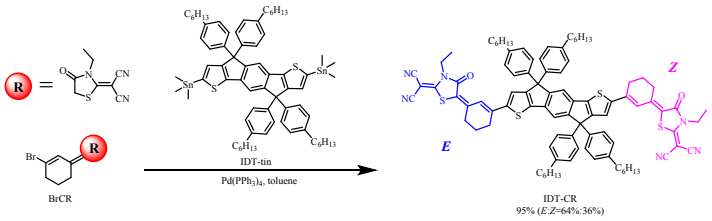


3-Bromocyclohex-2-enon ClCT 32%

Under an argon atmosphere, 3-Bromocyclohex-2-enon (0.6 mL, 5.52 mmol) and TBA

(1.10 g, 5.52 mmol) were dissolved in anhydrous DCM (30 mL) at 0 °C, and then titanium tetrachloride (0.6 ml, 5.52 mmol) and anhydrous pyridine (0.9 ml, 11.04 mmol) were added. After stirred at 0 °C for 1 h, the reaction was stirred at room temperature for another 28 h and then poured into distilled water (60 mL). The mixture was extracted with DCM, and the organic layer was dried over anhydrous sodium sulfate. After removing the solvent under reduced pressure, the residue was purified by silica gel flash column chromatography using DCM/PE (1:1, V/V) as the eluent to afford pure ClCT as a yellow solid (624 mg, 32%). ^{1}H NMR (400 MHz, chloroform-*d*): δ 8.29 (s, 1H, =CH–), 4.52–4.45 (m, 4H, –CH_2–), 3.17–3.14 (m, 2H, –CH_2–), 2.66–2.63 (m, 2H, –CH_2–), 1.98–1.92 (m, 2H, –CH_2–), 1.29–1.25 (m, 6H, –CH_3). ^{13}C NMR (101 MHz, chloroform-*d*): δ 178.43, 167.19, 160.74, 160.26, 156.86, 127.05, 113.91, 43.86, 43.75, 34.33, 28.98, 22.95, 12.64. HRMS (APCI): $[M + H]^+$ = 313.0769 (calcd for $C_{14}H_{18}ClN_2O_2S^+$, 313.0772)

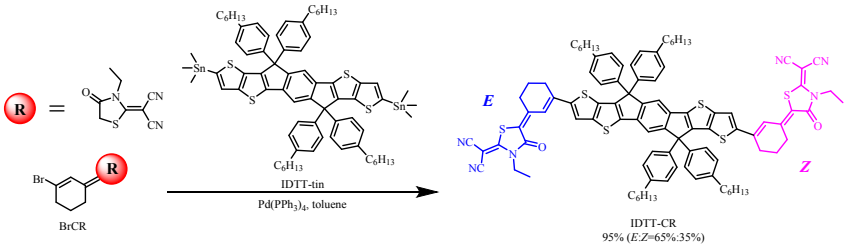
Synthesis of IDT-CR



Under an argon atmosphere, IDT-tin (160 mg, 0.13 mmol) and BrCR (116 mg, 0.33 mmol) and $Pd(PPh_3)_4$ (12 mg, 0.01 mmol) were added into anhydrous toluene (15 mL). After refluxing for 20 h, the reaction was cooled to room temperature, and quenched with 30 mL of distilled water and then extracted with DCM. The organic layer was dried with anhydrous sodium sulfate, and the solvent was removed under reduced pressure. The residue was purified by silica gel flash column chromatography using DCM/PE (7:3, V/V) as eluent to afford pure product IDT-CR as a dark blue solid (179 mg, 95%, *E*:*Z*=64%:36%). ^{1}H NMR (600 MHz, chloroform-*d*): δ 8.45 (s, 1.19H, =CH–, *E*), 7.48 (s, 0.27H, ArH, *Z*), 7.47 (s, 0.42H,

ArH, *Z*), 7.43 (s, 0.48H, ArH, *E*), 7.42 (s, 0.76H, ArH, *E*), 7.29 (s, 0.69H, ArH, *Z*), 7.27 (s, 1.25H, ArH, *E*), 7.15–7.08 (m, 16H, ArH), 6.51 (s, 0.67H, =CH–, *Z*), 4.27–4.21 (m, 4H, $–CH_2–$), 3.21–3.19 (m, 1.38H, $–CH_2–$, *Z*), 2.74–2.71 (m, 4H, $–CH_2–$), 2.58–2.55 (m, 8H, $–ArCH_2–$), 2.49–2.46 (m, 2.50H, $–CH_2–$, *E*), 2.02–1.98 (m, 2.47H, $–CH_2–$, *E*), 1.94–1.90 (m, 1.39H, $–CH_2–$, *Z*), 1.62–1.59 (m, 8H, $–CH_2–$), 1.39–1.29 (m, 30H, $–CH_3$, $–CH_2–$), 0.88–0.86 (m, 12H, $–CH_3$). ^{13}C NMR (101 MHz, chloroform-*d*): δ 165.31, 165.17, 164.60, 163.90, 157.73, 157.59, 154.44, 150.53, 149.41, 148.52, 147.78, 147.67, 146.56, 146.24, 145.47, 144.93, 142.02, 141.25, 135.73, 135.51, 128.67, 127.87, 123.14, 120.04, 118.37, 118.18, 114.09, 113.12, 111.52, 111.05, 63.28, 53.08, 52.71, 40.19, 35.70, 31.85, 31.67, 31.46, 29.26, 27.88, 26.89, 22.73, 21.79, 14.24. HRMS (APCI): $[M + H]^+$ = 1445.6527 (calcd for $C_{92}H_{97}N_6O_2S_4^+$, 1445.6550)

Synthesis of IDTT-CR



Under an argon atmosphere, IDTT-tin (175 mg, 0.13 mmol) and BrCR (116 mg, 0.33 mmol) and $Pd(PPh_3)_4$ (12 mg, 0.01 mmol) were added in anhydrous toluene (15 mL). After refluxing for 20 h, the reaction was cooled to room temperature, and quenched with 30 mL of distilled water and then extracted with DCM. The organic extraction was dried with anhydrous sodium sulfate and the solvent was removed under reduced pressure. The residue was purified by silica gel flash column chromatography using DCM/PE (7:3, V/V) as eluent to afford pure IDTT-CR[1] as a dark blue solid (179 mg, 96%, *E*:*Z*=65%:35%). ^1H NMR (600 MHz, chloroform-*d*): δ 8.35 (s, 1.19H, =CH–, *E*), 7.60 (s, 0.67H, ArH, *Z*), 7.58 (s, 1.24H, ArH, *E*), 7.54 (s, 0.23H, ArH, *Z*), 7.53(s, 0.42H, ArH, *Z*), 7.51 (s, 0.43H, ArH, *E*), 7.50 (s, 0.78H, ArH,

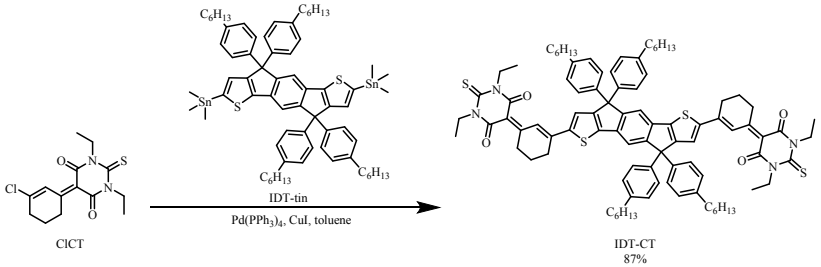
E), 7.19–7.10 (m, 16H, ArH), 6.44 (s, 0.63H, =CH–, *Z*), 4.28–4.22 (m, 4H, –CH_2–), 3.22–3.20 (m, 1.31H, –CH_2–, *Z*), 2.78–2.74 (m, 4H, –CH_2–), 2.58–2.55 (m, 8H, –ArCH_2–), 2.47–2.45 (m, 2.47H, –CH_2–, *E*), 2.03–1.99 (m, 2.56H, –CH_2–, *E*), 1.95–1.91 (m, 1.36H, –CH_2–, *Z*), 1.62–1.58 (m, 8H, –CH_2–), 1.40–1.28 (m, 30H, –CH_3, –CH_2–), 0.87–0.85 (m, 12H, –CH_3). ^{13}C NMR (101 MHz, chloroform-*d*): δ 165.32, 165.13, 164.63, 163.90, 154.51, 154.36, 150.49, 149.24, 148.23, 147.06, 146.84, 146.61, 145.94, 145.36, 144.27, 143.04, 142.32, 142.22, 139.71, 139.56, 136.34, 135.96, 128.77, 128.09, 120.74, 120.19, 118.47, 117.53, 114.01, 113.09, 111.82, 111.24, 63.16, 53.26, 52.73, 40.17, 35.75, 31.84, 31.41, 31.37, 29.34, 27.97, 26.96, 22.73, 21.81, 14.23. HRMS (APCI): $[M + H]^+$ = 1557.5970 (calcd for $C_{96}H_{97}N_6O_2S_6^+$, 1557.5991)

Use the same method with *Z*-BrCR as raw material to obtain IDTT-CR^2 (164 mg, 88%, *E*:*Z*=50%:50%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.36 (s, 1H, =CH–, *E*), 7.60 (s, 1H, ArH, *Z*), 7.59 (s, 1H, ArH, *E*), 7.53 (s, 0.6H, ArH, *Z*), 7.52(s, 0.4H, ArH, *Z*), 7.51 (s, 0.4H, ArH, *E*), 7.50 (s, 0.6H, ArH, *E*), 7.19–7.10 (m, 16H, ArH), 6.44 (s, 1H, =CH–, *Z*), 4.28–4.22 (m, 4H, –CH_2–), 3.21 (t, *J* = 6.6 Hz, 2H, –CH_2–, *Z*), 2.78–2.75 (m, 4H, –CH_2–), 2.58–2.55 (m, 8H, –ArCH_2–), 2.48 (t, *J* = 6.6 Hz, 2H, –CH_2–, *E*), 2.03–1.99 (m, 2H, –CH_2–, *E*), 1.95–1.91 (m, 2H, –CH_2–, *Z*), 1.61–1.59 (m, 8H, –CH_2–), 1.40–1.28 (m, 30H, –CH_2–), 0.86 (t, *J* = 6.6 Hz, 12H).

Use the same method with *E*-BrCR as raw material to obtain IDTT-CR^3 (173 mg, 93%, *E*:*Z*=84%:16%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.35 (s, 1.63H, =CH–, *E*), 7.60 (s, 0.32H, ArH, *Z*), 7.59 (s, 1.66H, ArH, *E*), 7.53 (s, 0.05H, ArH, *Z*), 7.52(s, 0.27H, ArH, *Z*), 7.51 (s, 0.33H, ArH, *E*), 7.50 (s, 1.31H, ArH, *E*), 7.19–7.10 (m, 16H, ArH), 6.44 (s, 0.31H, =CH–, *Z*), 4.28–4.22 (m, 4H, –CH_2–), 3.21 (t, *J* = 6.6 Hz, 0.62H, –CH_2–, *Z*), 2.78–2.74 (m, 4H, –CH_2–), 2.58–2.55 (m, 8H, –ArCH_2–), 2.47 (t, *J* = 6.6 Hz, 3.30H, –CH_2–, *E*), 2.03–1.99 (m, 3.29H,

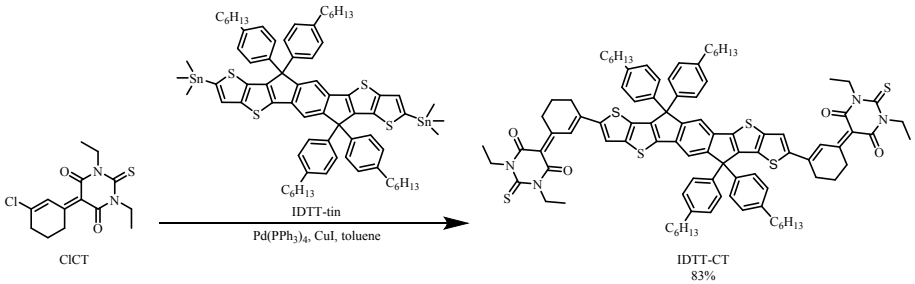
–CH_2–, *E*), 1.95–1.91 (m, 0.62H, –CH_2–, *Z*), 1.62–1.58 (m, 8H, –CH_2–), 1.40–1.27 (m, 30H, –CH_2–), 0.86 (t, *J* = 6.6 Hz, 12H).

Synthesis of IDT-CT



Under an argon atmosphere, IDT-tin (123 mg, 0.10 mmol) and ClCT (109 mg, 0.30 mmol), $Pd(PPh_3)_4$ (12 mg, 0.01 mmol) and copper(I) iodide (CuI, 1.8 mg, 0.01 mmol) were added in anhydrous toluene (10 mL). After refluxing for 24 h, the reaction was cooled to room temperature, and quenched with 20 mL of distilled water and then extracted with DCM. The organic layer was dried with anhydrous sodium sulfate and the solvent was removed under reduced pressure. The residue was purified by silica gel flash column chromatography using DCM/PE (1:1, V/V) as the eluent to afford pure product IDT-CT as a dark blue solid (128 mg, 87%). ^{1}H NMR (600 MHz, chloroform-*d*): δ 8.90 (s, 2H, =CH–), 7.49 (s, 2H, ArH), 7.39 (s, 2H, ArH), 7.15–7.13 (m, 8H, ArH), 7.10–7.09 (m, 8H, ArH), 4.58–4.50 (m, 8H, –CH_2–), 3.24–3.22 (m, 4H, –CH_2–), 2.76–2.74 (m, *J* = 6.0 Hz, 4H, –CH_2–), 2.57 (t, *J* = 7.8 Hz, 8H, –ArCH_2–), 1.95–1.91 (m, 4H, –CH_2–), 1.62–1.59 (m, 8H, –CH_2–), 1.34–1.27 (m, 36H, –CH_3, –CH_2–), 0.88–0.86 (m, 12H, –CH_3). ^{13}C NMR (101 MHz, chloroform-*d*): δ 178.21, 170.75, 161.11, 160.91, 158.02, 154.85, 154.27, 148.29, 147.12, 142.13, 141.07, 135.98, 128.73, 127.89, 124.76, 123.23, 118.61, 111.73, 63.31, 43.74, 35.72, 31.86, 31.47, 31.17, 29.26, 28.04, 22.74, 22.35, 14.24, 12.78, 12.71. MALDI-TOF MS: $[M + H]^+$ = 1459.66 (calcd for $C_{92}H_{107}N_4O_4S_4^+$, 1459.72)

Synthesis of IDTT-CT



Under an argon atmosphere, IDTT-tin (134 mg, 0.10 mmol) and ClCT (109 mg, 0.30 mmol), $Pd(PPh_3)_4$ (12 mg, 0.01 mmol) and CuI (1.8 mg, 0.01 mmol) were added into anhydrous toluene (10 mL). After refluxing for 24 h, the reaction was cooled to room temperature, and quenched with 20 mL of distilled water and then extracted with DCM. The organic layer was dried with anhydrous sodium sulfate and the solvent was removed under reduced pressure. The residue was purified by silica gel flash column chromatography using DCM/PE (1:1, V/V) as the eluent to afford pure product IDTT-CT as a dark blue solid (129 mg, 83%). ^{1}H NMR (600 MHz, chloroform-*d*): δ 8.83 (s, 2H, =CH–), 7.78 (s, 2H, ArH), 7.53 (s, 2H, ArH), 7.19–7.17 (m, 8H, ArH), 7.12–7.11 (m, 8H, ArH), 4.59–4.50 (m, 8H, $–CH_2–$), 3.24–3.22 (m, 4H, $–CH_2–$), 2.77 (t, J = 6.0 Hz, 4H, $–CH_2–$), 2.57 (t, J = 7.8 Hz, 8H, $–ArCH_2–$), 1.96–1.92 (m, 4H, $–CH_2–$), 1.62–1.59 (m, 8H, $–CH_2–$), 1.34–1.28 (m, 36H, $–CH_3$, $–CH_2–$), 0.87–0.85 (m, 12H, $–CH_3$). ^{13}C NMR (101 MHz, chloroform-*d*): δ 178.20, 170.65, 161.09, 160.90, 154.56, 153.88, 147.63, 146.95, 145.84, 143.52, 142.33, 139.62, 137.51, 136.47, 128.83, 128.05, 123.24, 122.11, 117.74, 111.88, 63.21, 43.73, 35.75, 31.84, 31.39, 31.19, 29.33, 28.43, 22.73, 22.41, 14.23, 12.77, 12.71. MALDI-TOF MS: $[M + H]^+$ = 1571.56 (calcd for $C_{96}H_{107}N_4O_4S_6^+$, 1571.66)

3. Supporting Figures and Tables

Table S1 Crystal data and structure refinement for *Z*-BrCR.

***Z*-BrCR**	
Empirical formula	$C_{14}H_{14}BrN_3OS$
Formula weight	352.25
Temperature / K	296(2)
Wavelength / Å	0.71073
Crystal system	Orthorhombic
Space group	Pnma
a / Å	15.716(4)
b / Å	7.1522(17)
c / Å	12.863(3)
deg	90
deg	90
deg	90
Volume / $Å^3$	1445.9(6)
Z	4
Density (calculated) / Mg/m^3	1.618
Absorption coefficient / mm^{-1}	2.986
F(000)	712
Crystal size / mm^3	0.3 x 0.2 x 0.2
Theta range for data collection	2.046 to 25.500°
Index ranges	-19<=h<=17, -8<=k<=8, -15<=l<=15
Reflections collected	10242
Independent reflections	1461 [R(int) = 0.0727]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7460 and 0.5582
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1461 / 3 / 134
Goodness-of-fit on F^2	1.060
Final R indices [I>2sigma(I)]	R1 = 0.0512, wR2 = 0.1476
R indices (all data)	R1 = 0.0755, wR2 = 0.1661
Extinction coefficient	n/a
Largest diff. peak and hole / $e.Å^{-3}$	0.602 and -0.513

Table S2 Crystal data and structure refinement for ClCT.

ClCT	
Empirical formula	$C_{14}H_{17}ClN_2O_2S$
Formula weight	312.80
Temperature / K	293(2)
Wavelength / Å	0.71073
Crystal system	Triclinic
Space group	P-1
a / Å	9.049(3)
b / Å	9.739(3)
c / Å	9.862(3)
□□□□deg	67.129(5)
□□□□deg	82.299(5)
□□□□□deg	67.966(5)
Volume / $Å^3$	742.2(4)
Z	2
Density (calculated) / Mg/m^3	1.400
Absorption coefficient / mm^{-1}	0.400
F(000)	328
Crystal size / mm^3	0.150 x 0.120 x 0.100
Theta range for data collection	2.242 to 26.997°
Index ranges	-9<=h<=11, -12<=k<=12, -12<=l<=12
Reflections collected	6100
Independent reflections	3205 [R(int) = 0.0363]
Completeness to theta = 25.242°	98.9 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3205 / 0 / 183
Goodness-of-fit on F^2	0.941
Final R indices [I>2sigma(I)]	R1 = 0.0494, wR2 = 0.1365
R indices (all data)	R1 = 0.0704, wR2 = 0.1572
Extinction coefficient	n/a
Largest diff. peak and hole / $e.Å^{-3}$	0.330 and -0.266

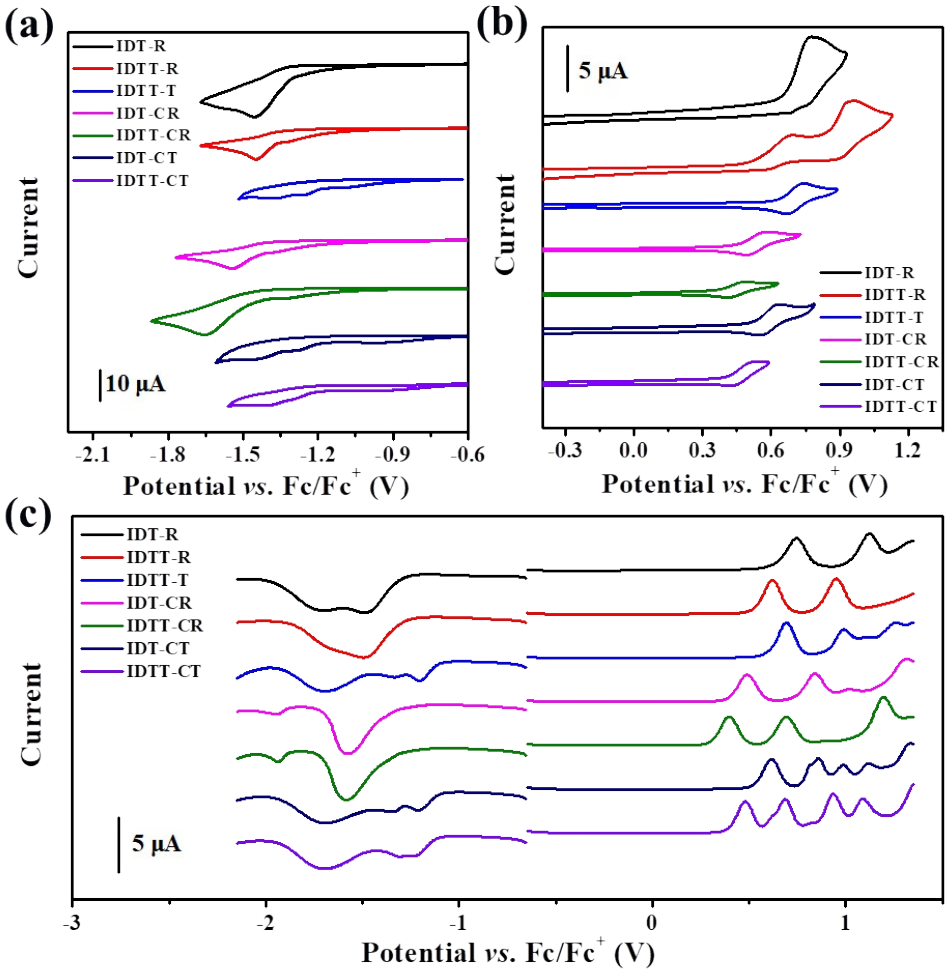


Fig. S1 Cyclic voltammograms (CVs) (a-b) and differential pulse voltammograms (DPVs) (c) for NFAs (IDT-R, IDTT-R, IDTT-T, IDT-CR, IDTT-CR, IDT-CT and IDTT-CT) in dichloromethane/0.1 M Bu_4NPF_6 solution.

Table S3. Electrochemical data based on DPVs.

NFAs	E_{HOMO}[a] (eV)	E_{LUMO}[a] (eV)	$E_{g,ec}$[b] (eV)
IDT-R	-5.55	-3.32	2.23
IDTT-R	-5.42	-3.31	2.11
IDTT-T	-5.49	-3.60	1.89
IDT-CR	-5.29	-3.23	2.06
IDTT-CR	-5.20	-3.22	1.98
IDT-CT	-5.42	-3.59	1.83
IDTT-CT	-5.28	-3.56	1.72

[a]The HOMO and LUMO energy levels are calculated according to the equation of $E_{HOMO/LUMO} = -(E_{ox/red}+4.8)$ eV. [b]Calculated according to the equation of $E_{g,ec} = E_{LUMO} - E_{HOMO}$.

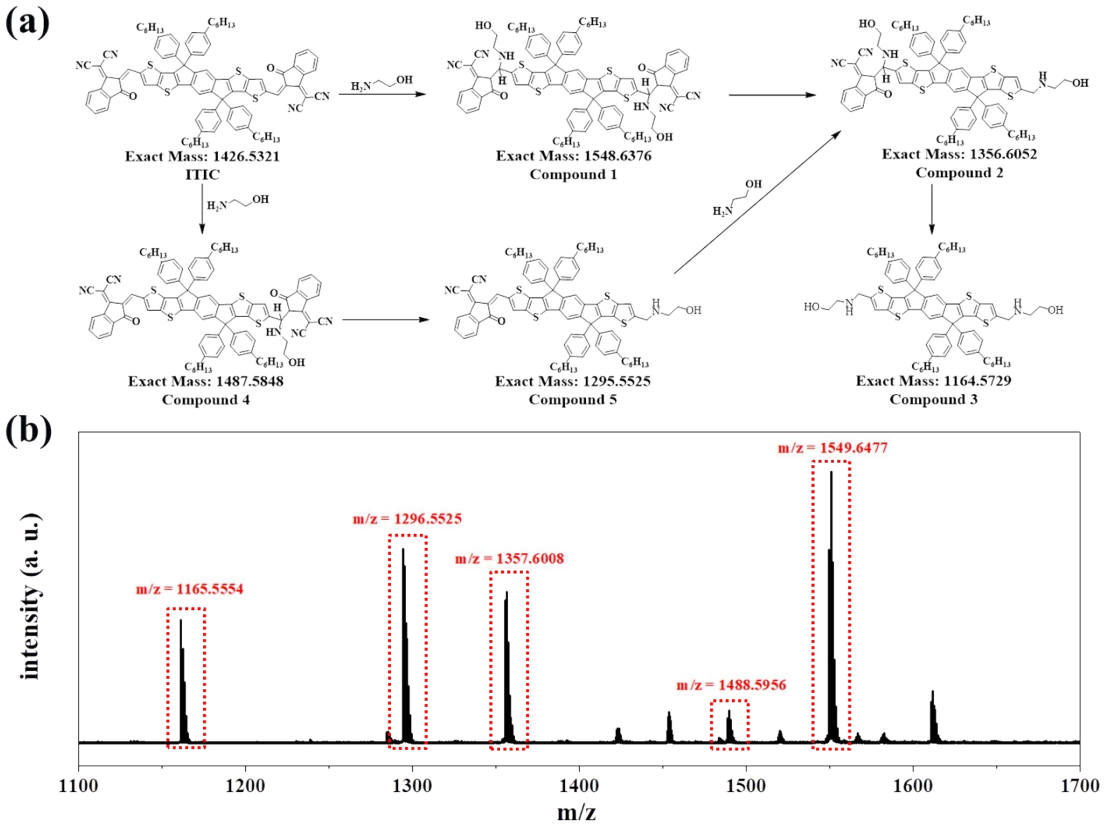


Fig. S2 (a) The illustration of nucleophilic addition reaction of ITIC with ethanolamine (EA) after 10 min reaction in dichloromethane. (b) HRMS spectrum of products of ITIC with EA after 10 min reaction in dichloromethane.

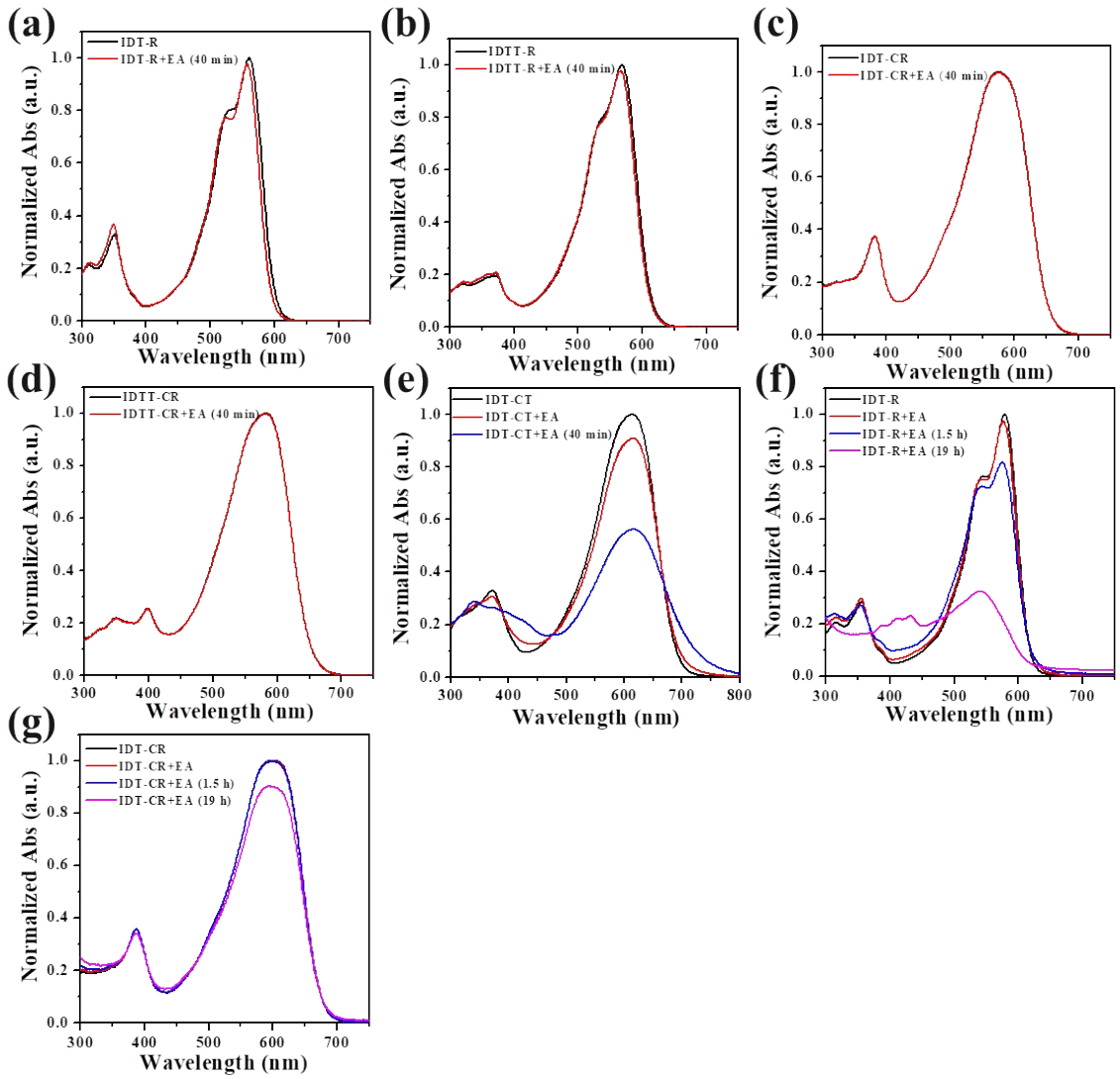


Fig. S3 Normalized UV–Vis absorption spectra of NFAs, (a) IDT-R, (b) IDTT-R, (c) IDT-CR, (d) IDTT-CR, (e) IDT-CT, (f) IDT-R and (g) IDT-CR, before and after adding ethanolamine (EA) in THF:H_2O (96:4, V/V). The concentration of NFAs is controlled at 10^{-5} M, while that of EA is 10^{-3} M (a, b, c, d, e) and 0.15 M (f, g), respectively.

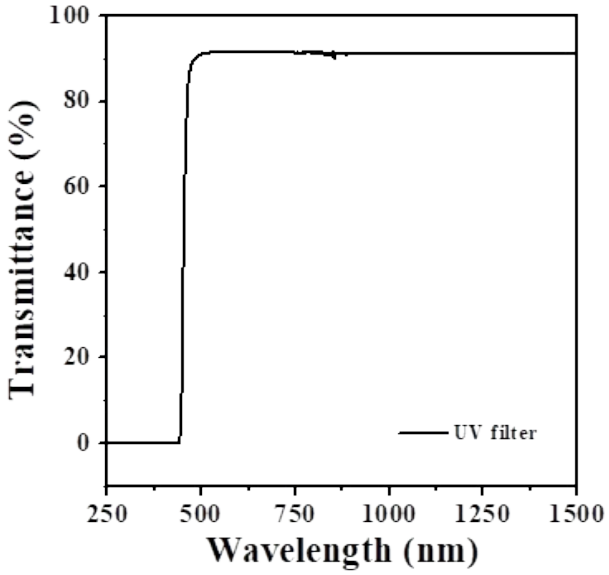


Fig. S4 Transmission spectrum of UV filter.

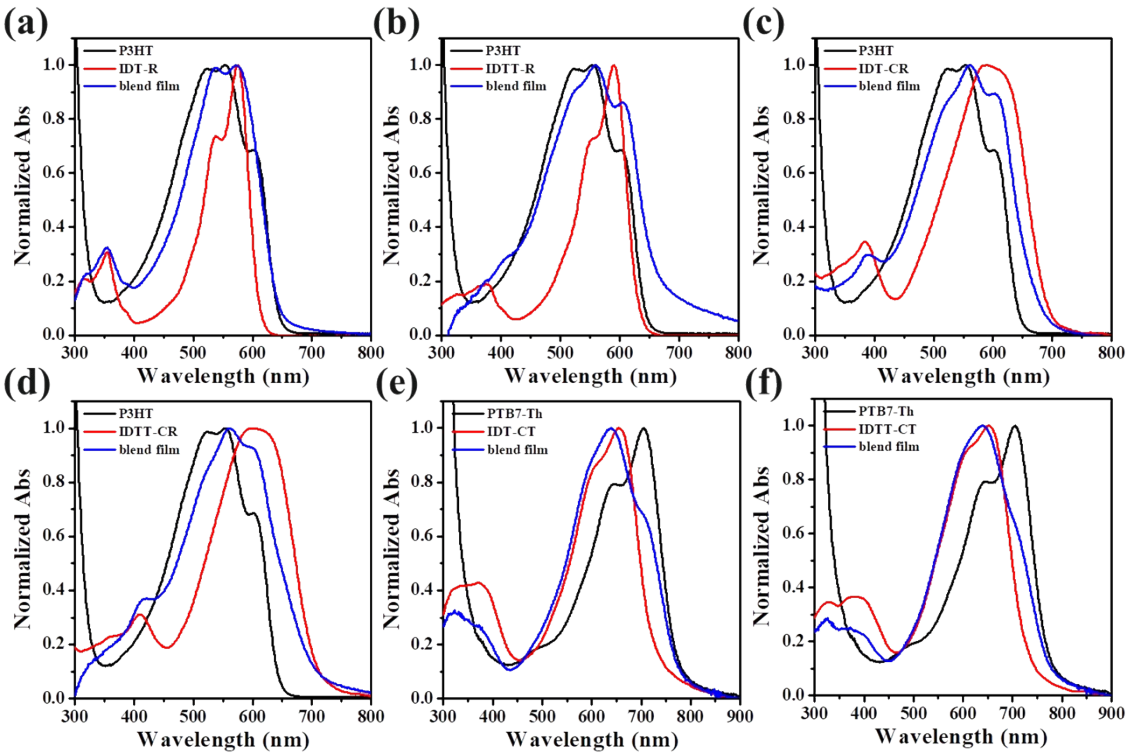


Fig. S5 Normalized UV–Vis absorption spectra of films, (a) P3HT, IDT-R, and P3HT:IDT-R blend, (b) P3HT, IDTT-R, and P3HT:IDTT-R blend, (c) P3HT, IDT-CR, and P3HT:IDT-CR blend, (d) P3HT, IDTT-CR, and P3HT:IDTT-CR blend, (e) PTB7-Th, IDT-CT, and PTB7-Th:IDT-CT blend, (f) PTB7-Th, IDTT-CT, and PTB7-Th:IDTT-CT blend.

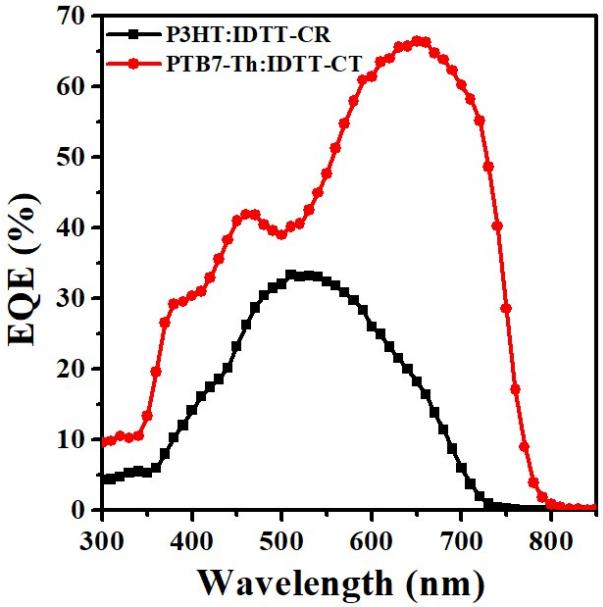


Fig. S6 EQE spectra of the P3HT:IDTT-CR and PTB7-Th:IDTT-CT -based devices.

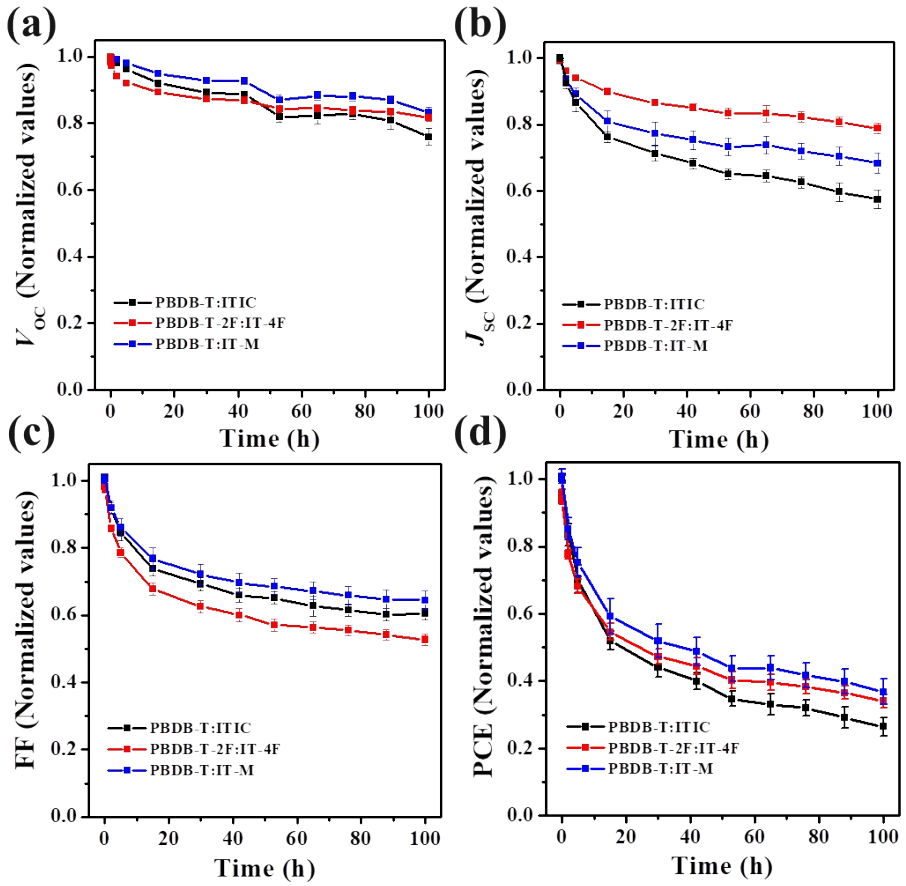


Fig. S7 The photovoltaic parameters variation of ITIC, IT-4F, and IT-M -based solar cells in a glovebox with dry nitrogen atmosphere under one-sun continuous irradiation: (a) V_{OC}, (b) J_{SC}, (c) FF, and (d) PCE.

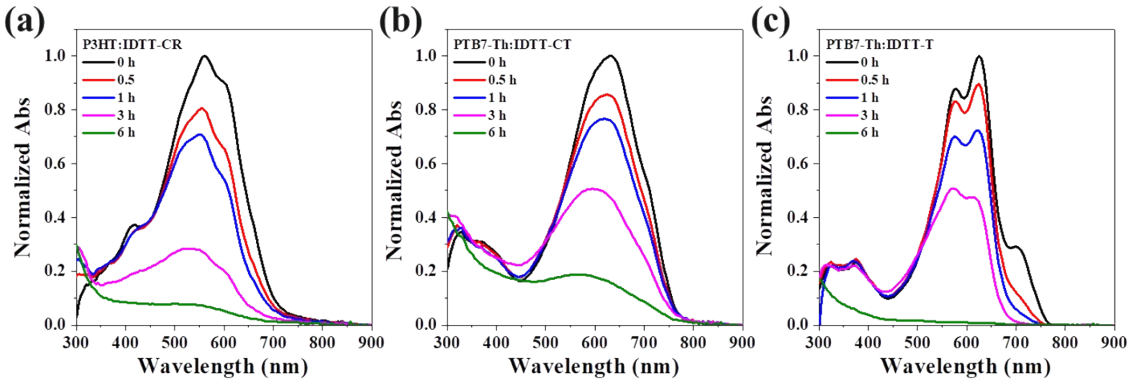


Fig. S8 Normalized UV–Vis absorption spectra of films in air under continuous light irradiation (100 mW/cm^2) for 6 h, (a) P3HT:IDTT-CR blend, (b) PTB7-Th:IDTT-CT blend, (c) PTB7-Th:IDTT-T blend, and (d) PTB7-Th:ITIC blend.

Table S4. The optimal photovoltaic parameters of solar cells based on the PBDB-T donor under the irradiation (AM 1.5G, 100 mW/cm^2).

Donor:acceptor	V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)	PCE (%)
PBDB-T:IDTT-CR	0.84±0.01	1.74 ±0.21	40.2±1	0.59±0.1 (0.69)
PBDB-T:IDT-CT	0.86±0.01	6.02 ±0.15	40.4 ±1.6	2.09 ±0.08 (2.17)
PBDB-T:IDTT-CT	0.8 ±0.01	5.22±0.22	35.5 ±1.5	1.48 ±0.15 (1.63)

Data obtained from the average of 15 individual devices, and the best PCEs are shown in brackets.

Table S5. The preparation parameters of OSC devices based on different photoactive layers.

Active laver	D:A by wt	solvent	Concentration mg/ml	Speed (rpm)	Anneal Temperature (°C)
P3HT:IDT-R	1:1	CB	30.0	1000	100
P3HT:IDTT-R	1:1	CB	30.0	2000	100
P3HT:IDT-CR	1:1	CB	30.0	1000	100
P3HT:IDTT-CR	1:1.3	CB	18.4	1000	140
PTB7-Th:IDTT-T	1:1.2	CB	25.0	2500	100
PTB7-Th:IDT-CT	1:1.4	CB	16.8	2500	W/O
PTB7-Th:IDTT-CT	1:1.4	CB	16.8	3000	W/O
PBDB-T:ITIC	1:1	CB	20.0	2500	150
PBDB-T-2F:IT-4F	1:1	CB	20.0	1500	100
PBDB-T:IT-M	1:1.2	CB	17.6	1200	120

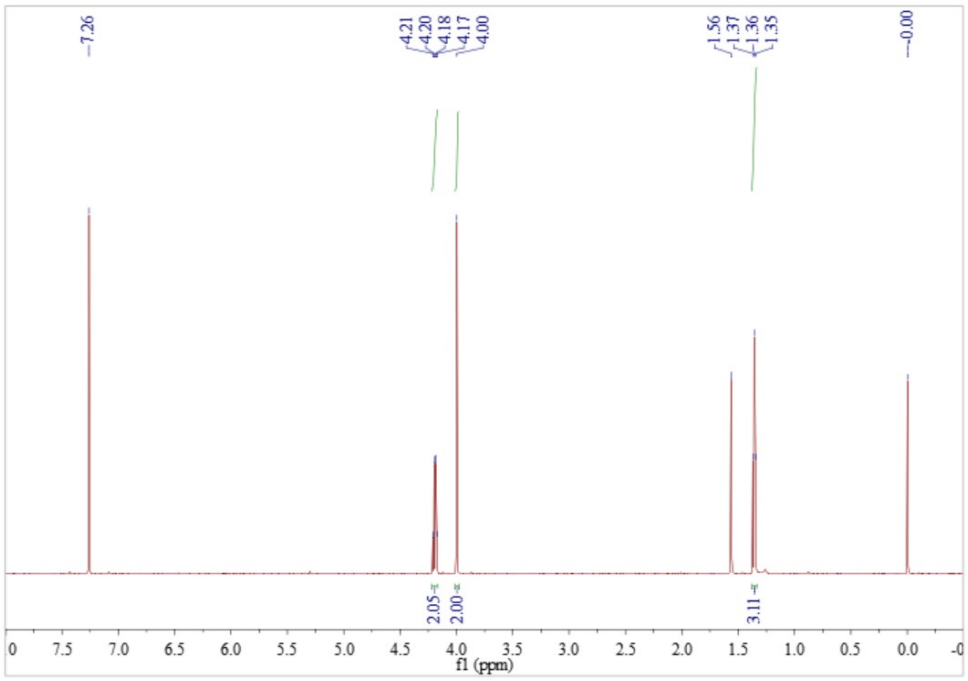


Fig. S9 [1]H NMR spectrum of RCN conducted in chloroform-*d*.

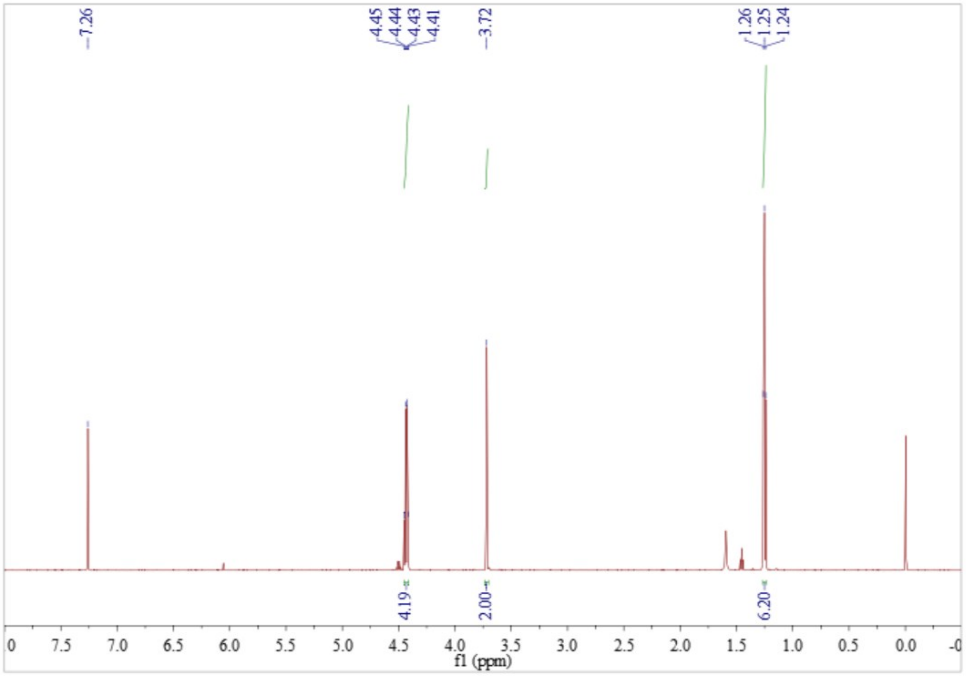


Fig. S10 [1]H NMR spectrum of TBA conducted in chloroform-*d*.

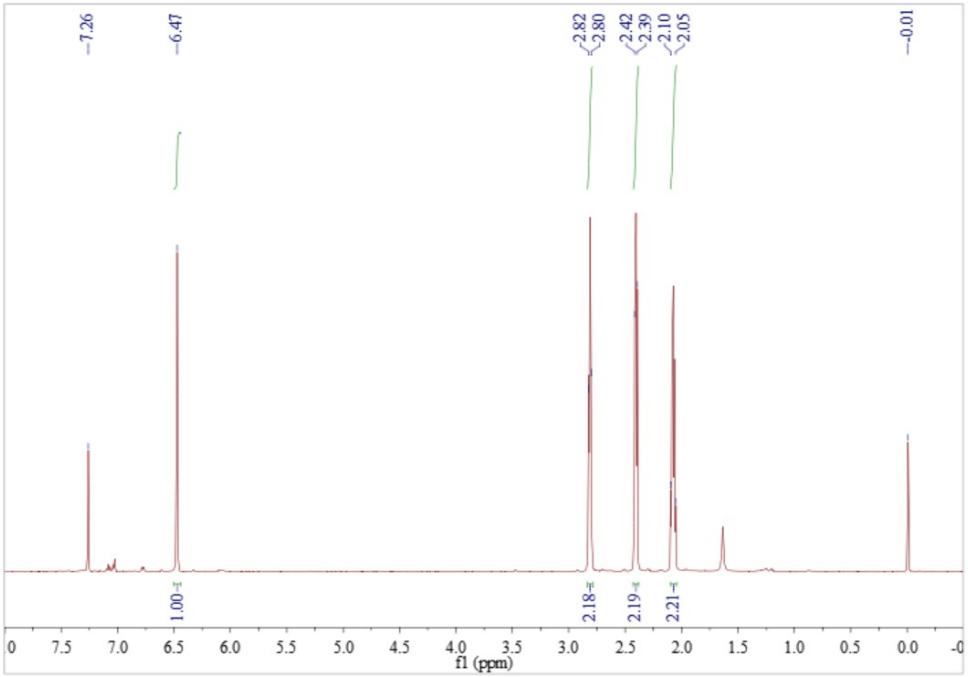


Fig. S11 [1]H NMR spectrum of 3-Bromocyclohex-2-enon conducted in chloroform-*d*.

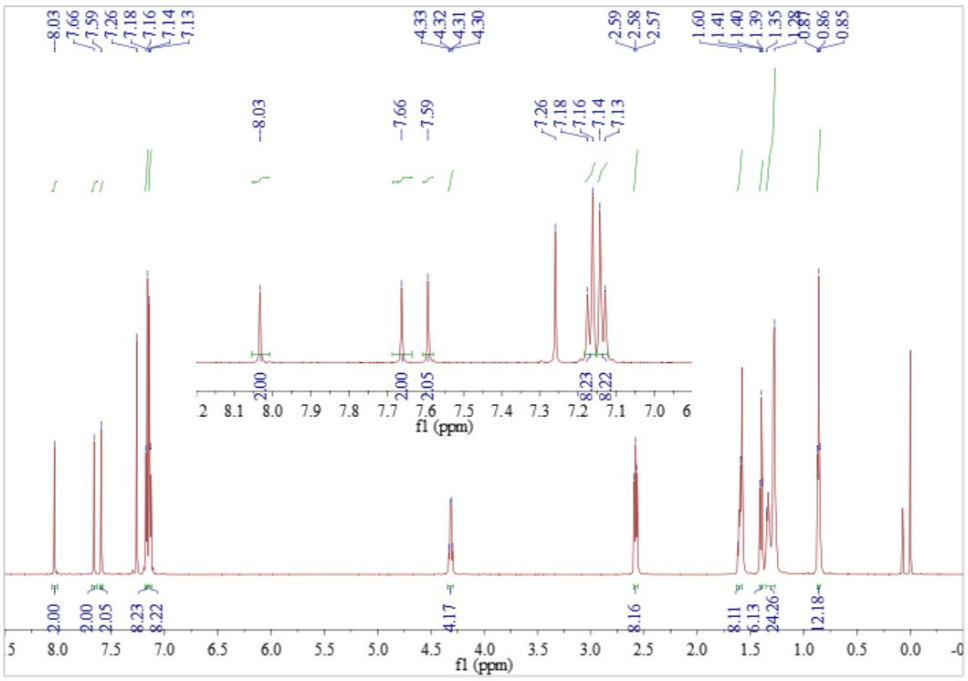


Fig. S12 ^{1}H NMR spectrum of IDT-R conducted in chloroform-*d*.

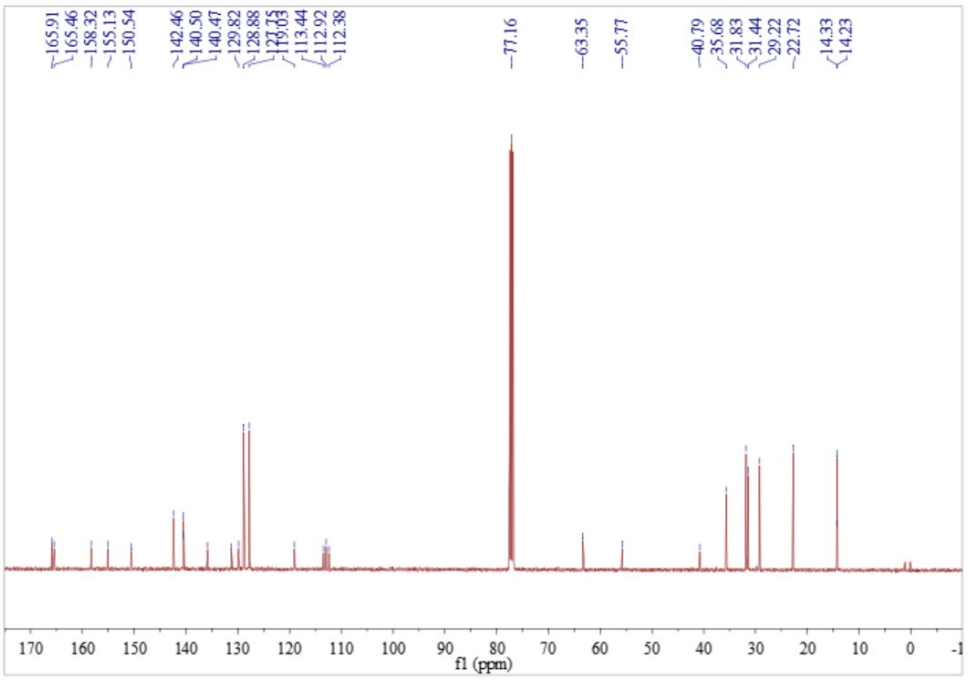


Fig. S13 ^{13}C NMR spectrum of IDT-R conducted in chloroform-*d*.

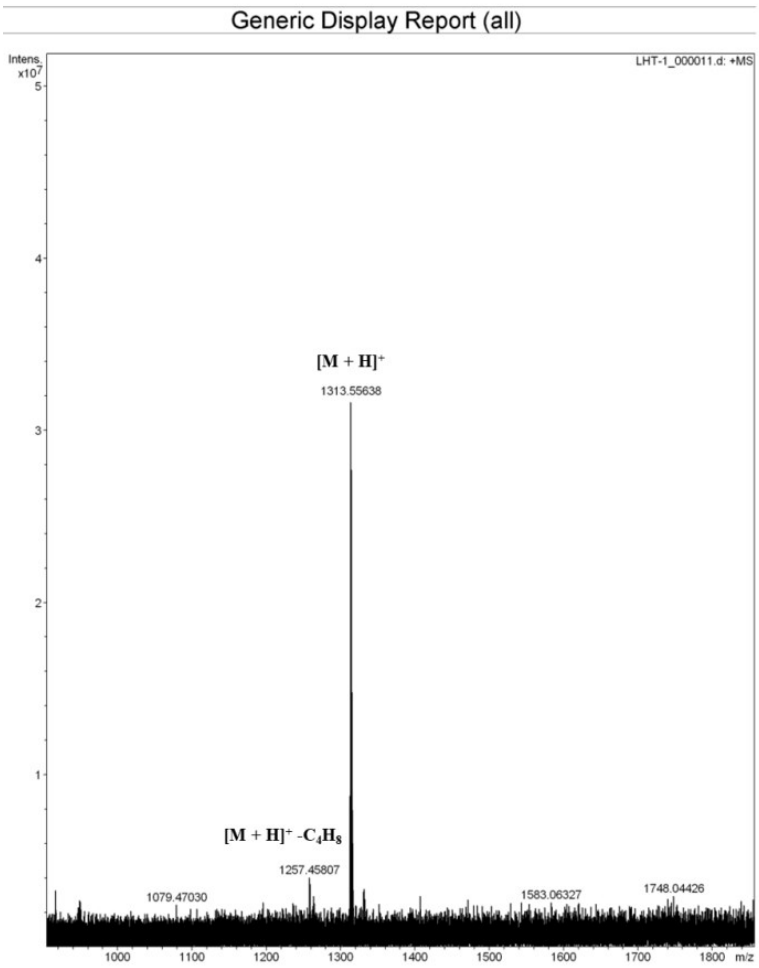


Fig. S14 The HRMS spectrum spectrum of IDT-R.

Fig. S15 ^{1}H NMR spectrum of IDTT-R conducted in chloroform-*d*.

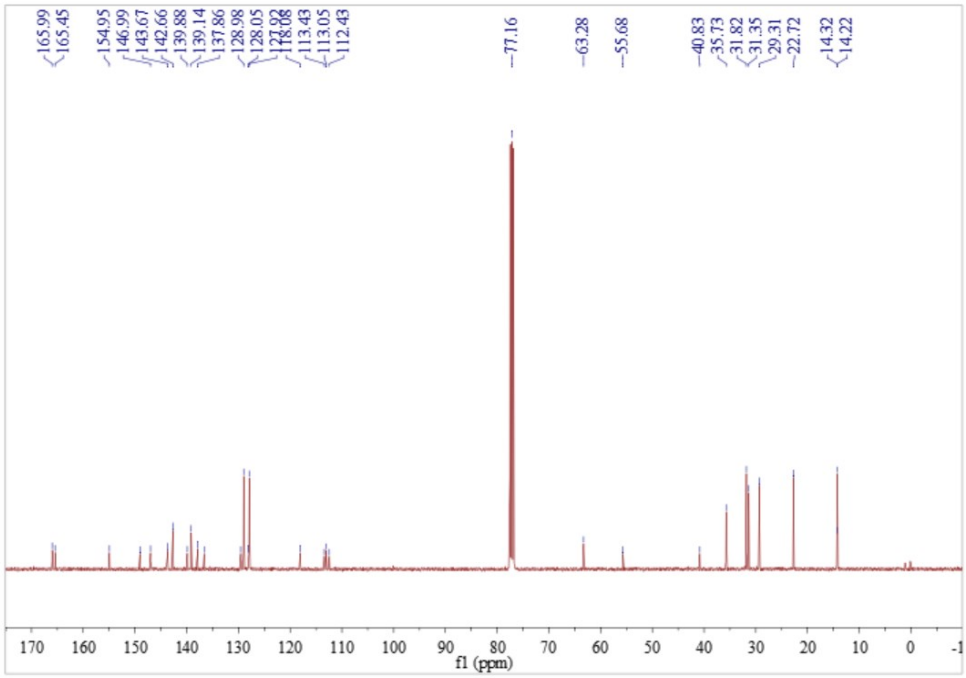


Fig. S16 ^{13}C NMR spectrum of IDTT-R conducted in chloroform-*d*.

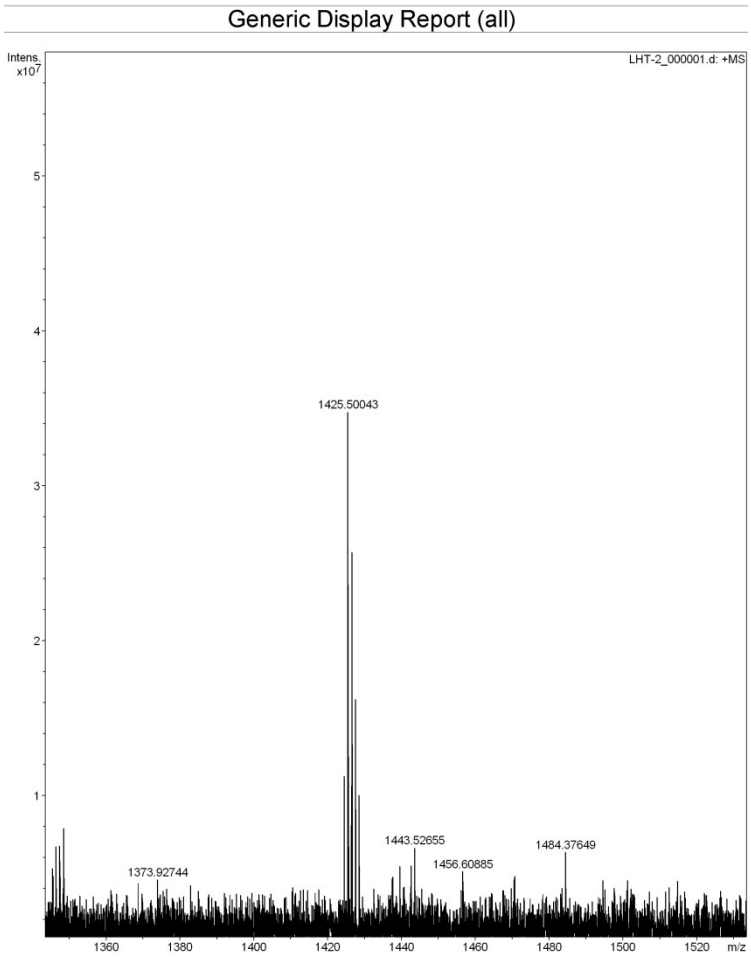


Fig. S17 The HRMS spectrum of IDTT-R.

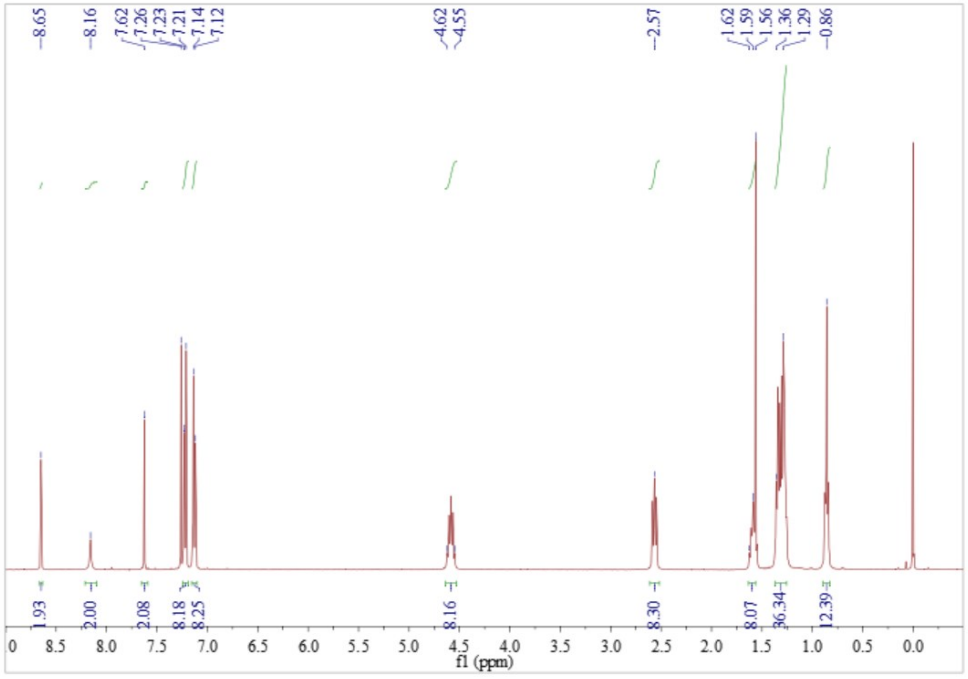


Fig. S18 ^{1}H NMR spectrum of IDTT-T conducted in chloroform-*d*.

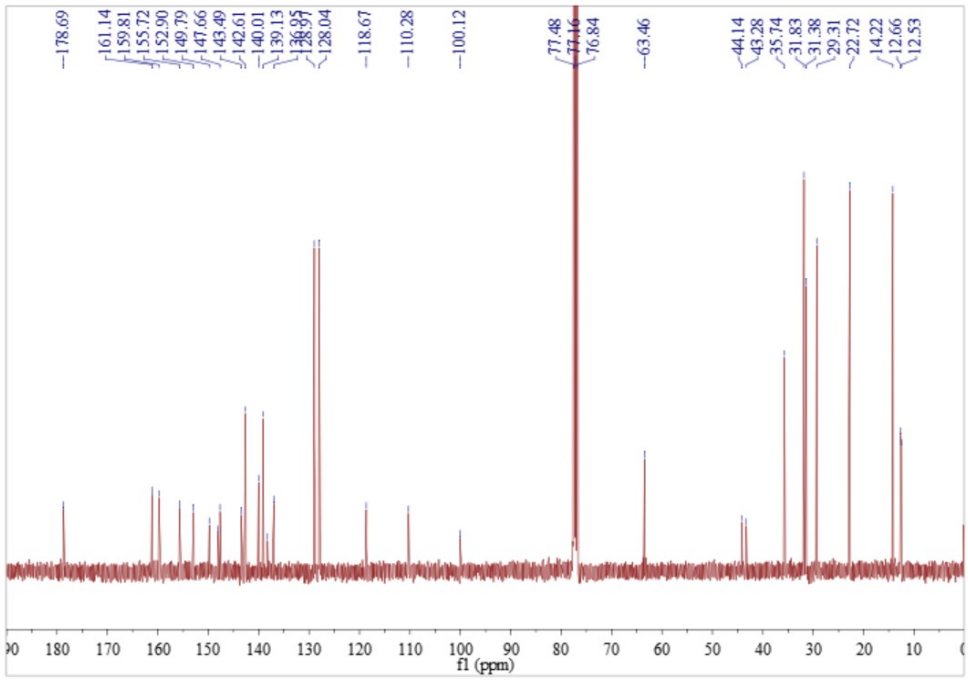


Fig. S19 ^{13}C NMR spectrum of IDTT-T conducted in chloroform-*d*.

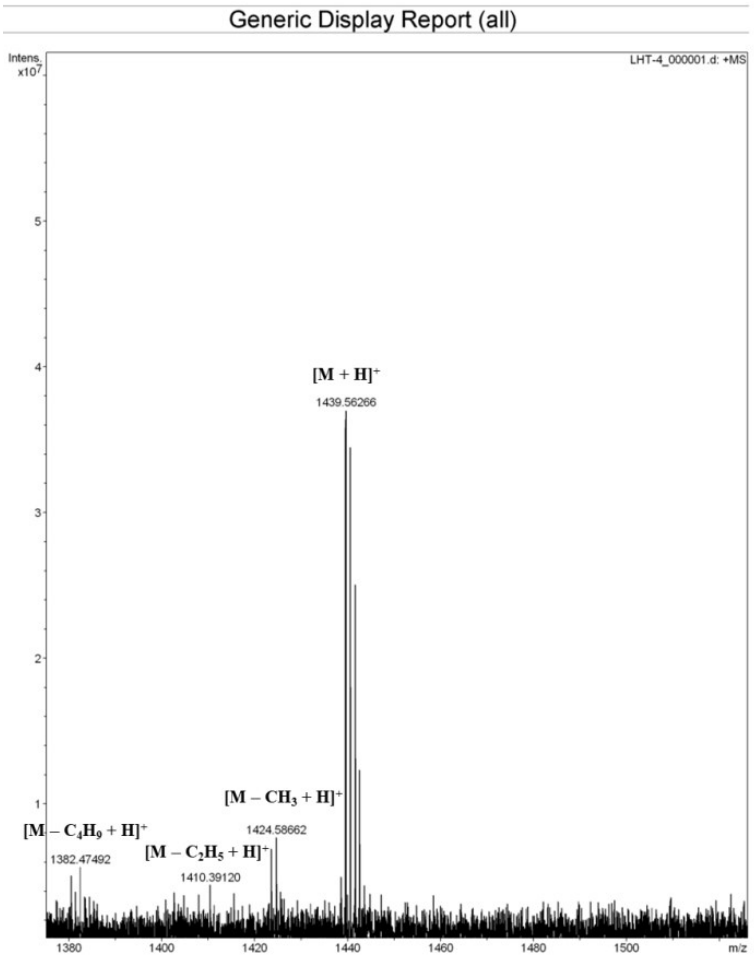


Fig. S20 The HRMS spectrum of IDTT-T.

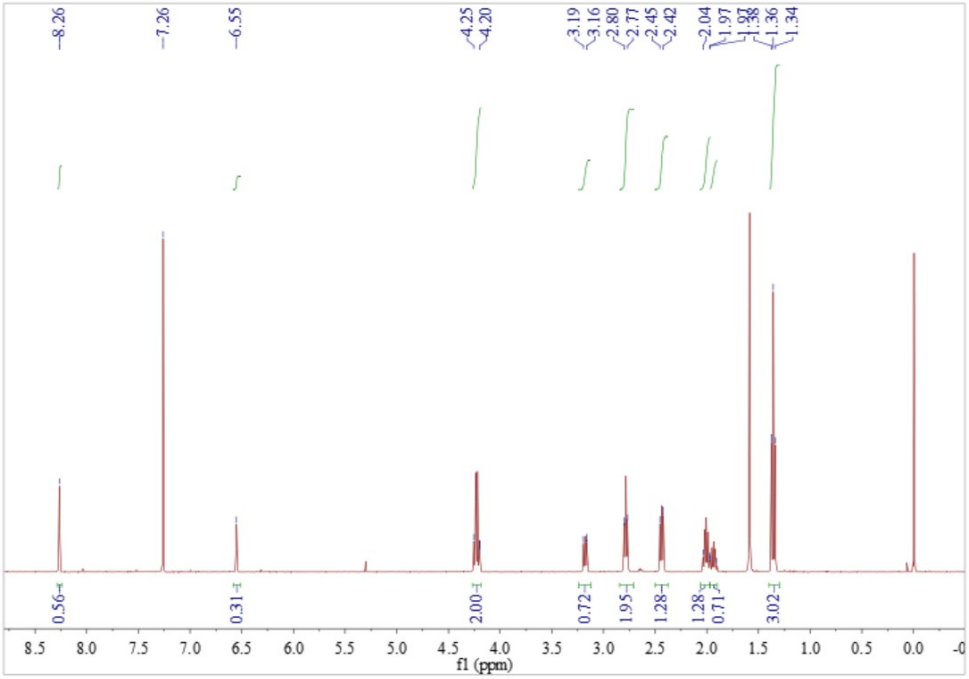


Fig. S21 ^{1}H NMR spectrum of BrCR conducted in chloroform-*d*.

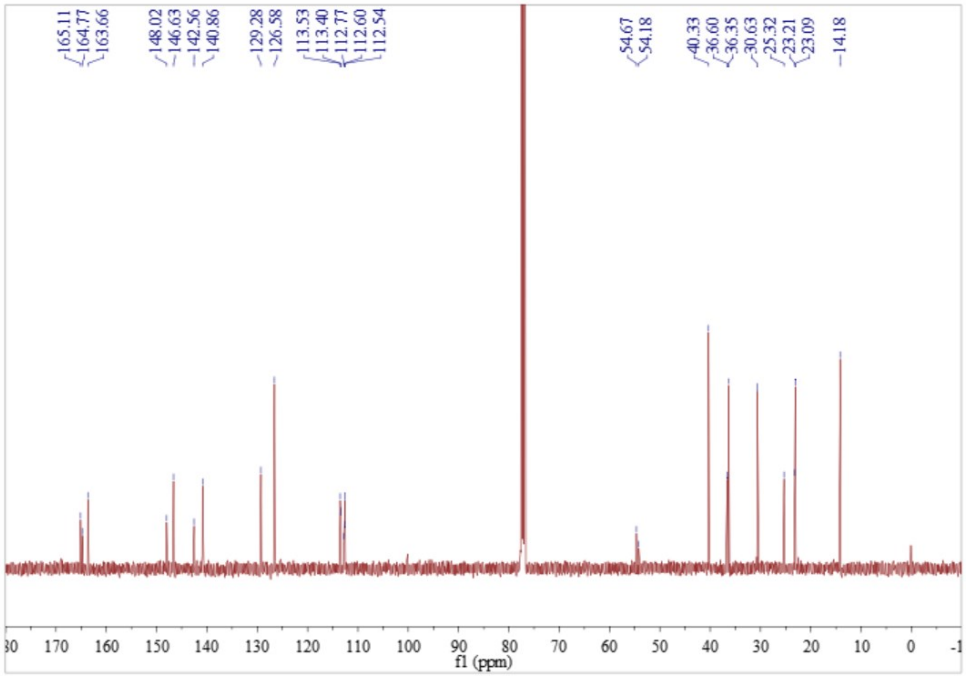


Fig. S22 ^{13}C NMR spectrum of BrCR conducted in chloroform-*d*.

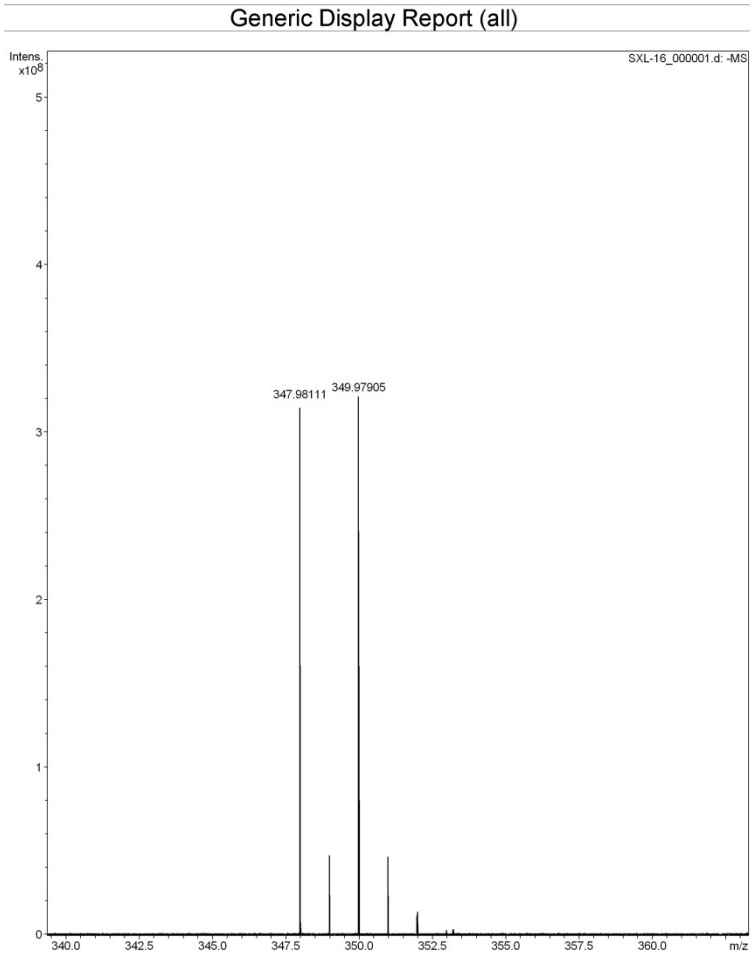


Fig. S23 The HRMS spectrum of BrCR.

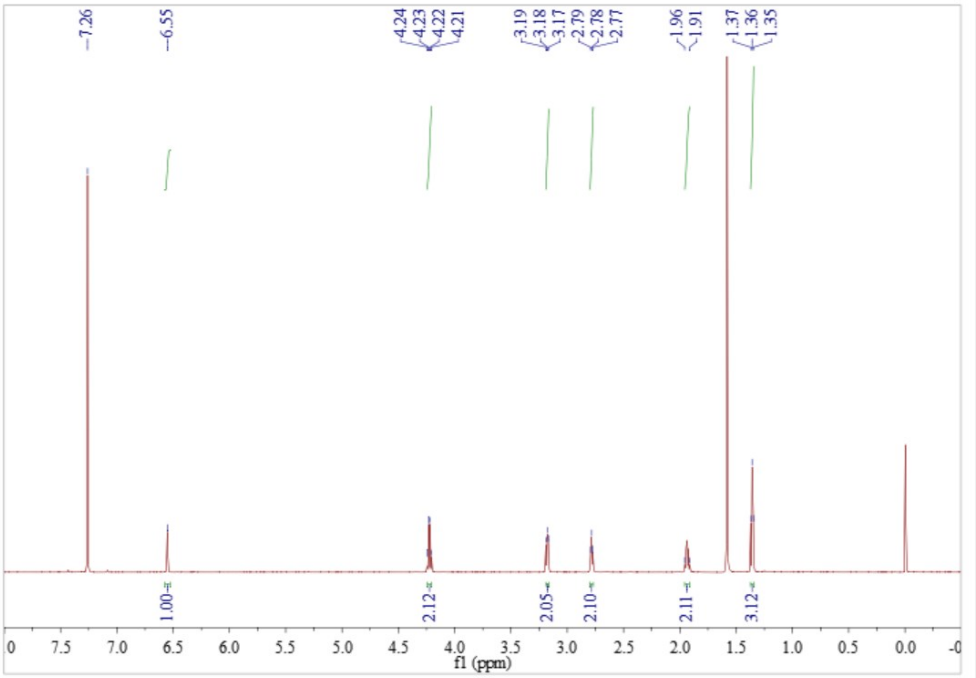


Fig. S24 ^{1}H NMR spectrum of *Z*-BrCR conducted in chloroform-*d*.

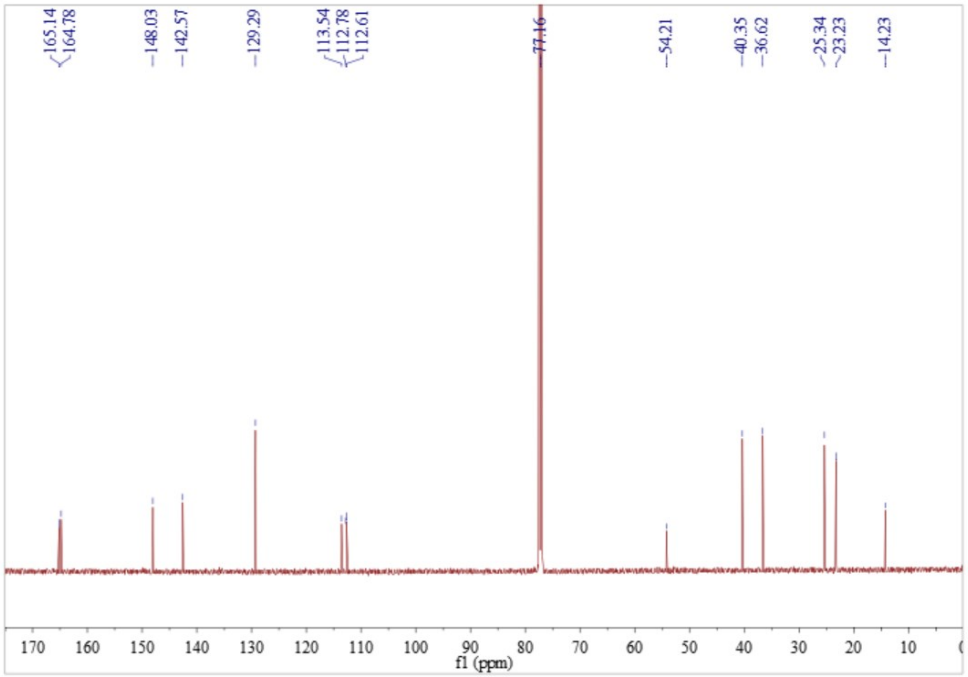


Fig. S25 ^{13}C NMR spectrum of *Z*-BrCR conducted in chloroform-*d*.

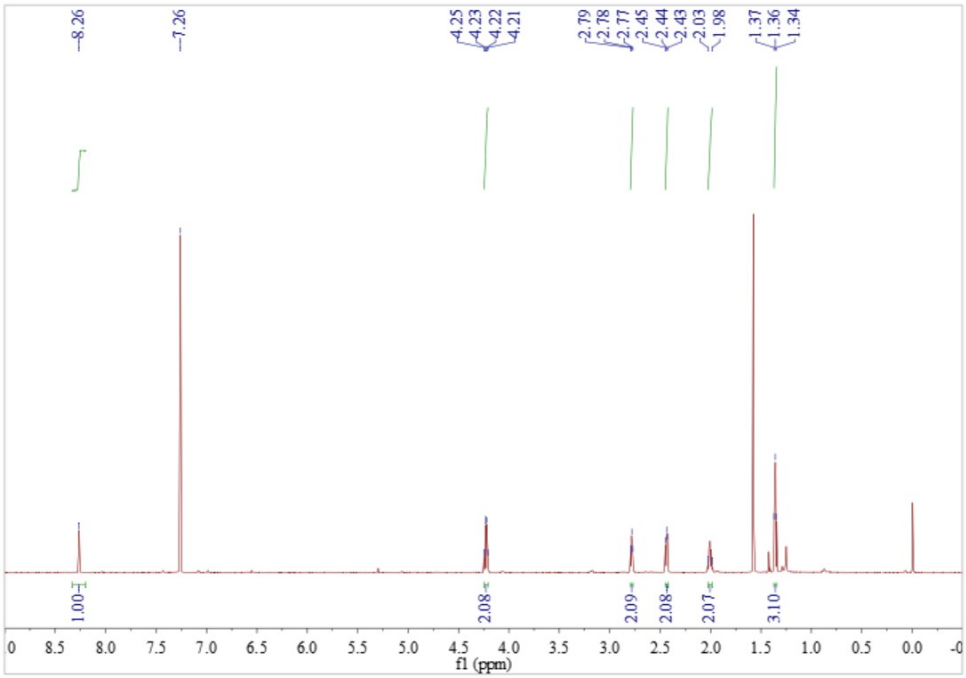


Fig. S26 ^{1}H NMR spectrum of *E*-BrCR conducted in chloroform-*d*.

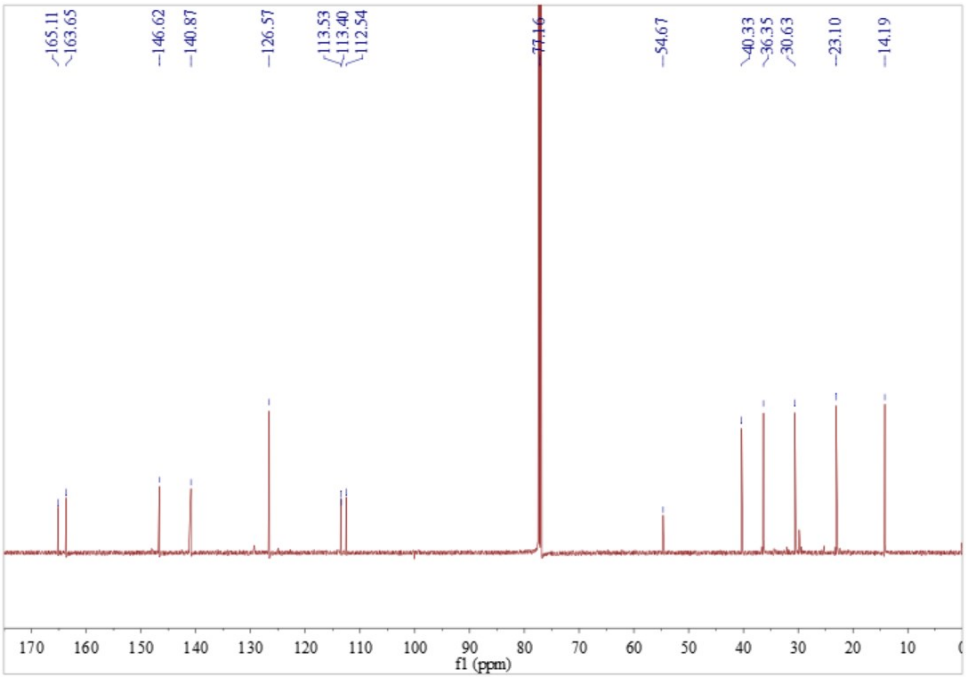


Fig. S27 ^{13}C NMR spectrum of *E*-BrCR conducted in chloroform-*d*.

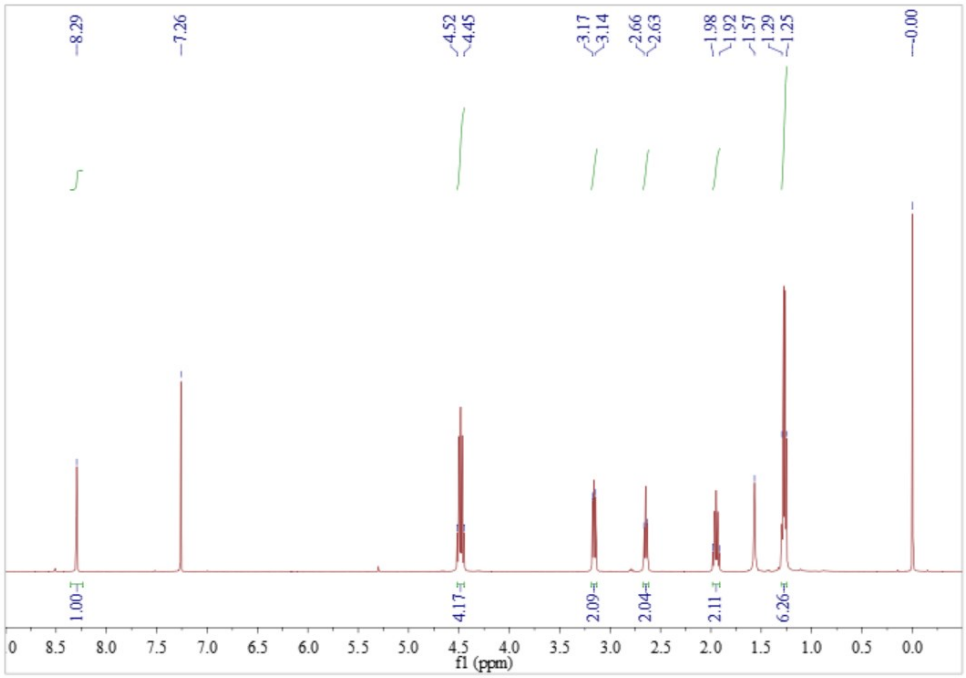


Fig. S28 ^{1}H NMR spectrum of ClCT conducted in chloroform-*d*.

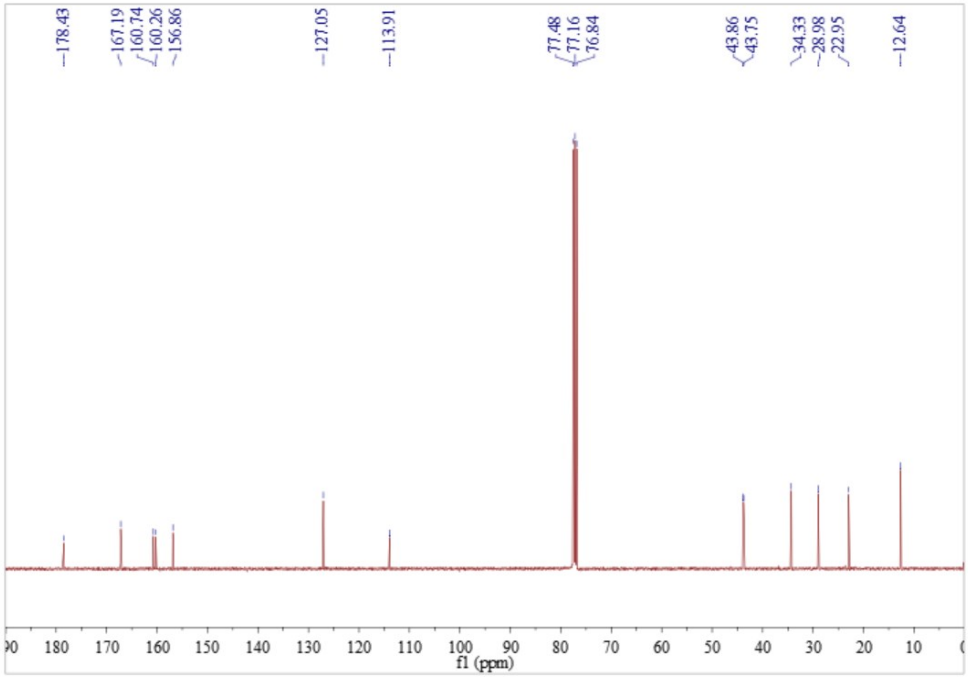


Fig. S29 ^{13}C NMR spectrum of ClCT conducted in chloroform-*d*.

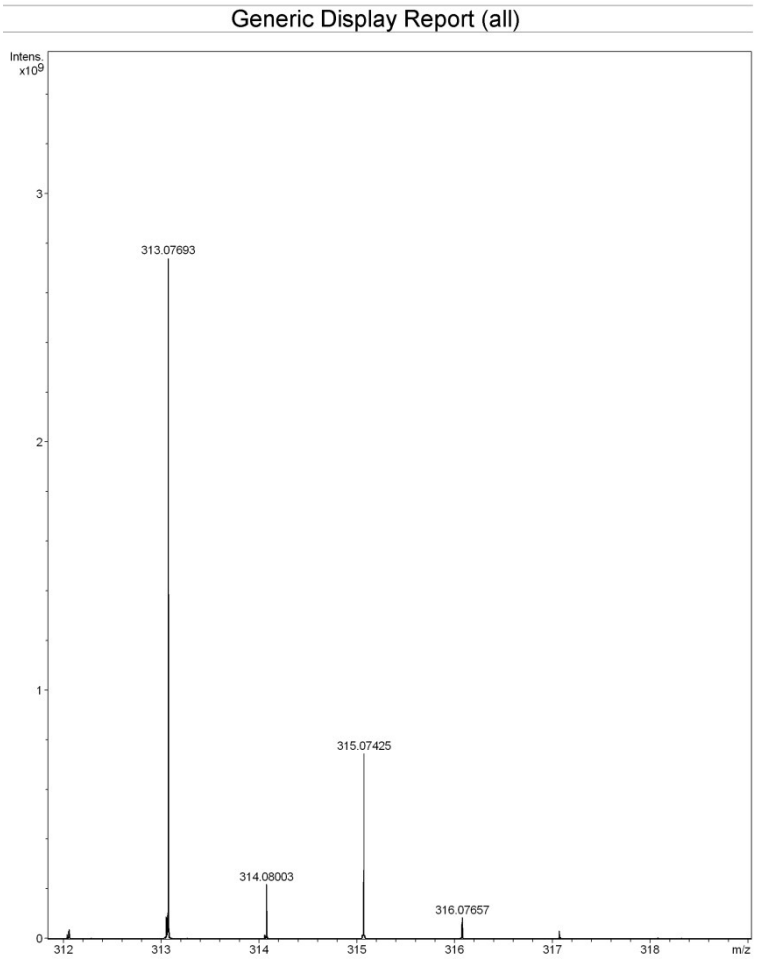


Fig. S30 The HRMS spectrum of ClCT.

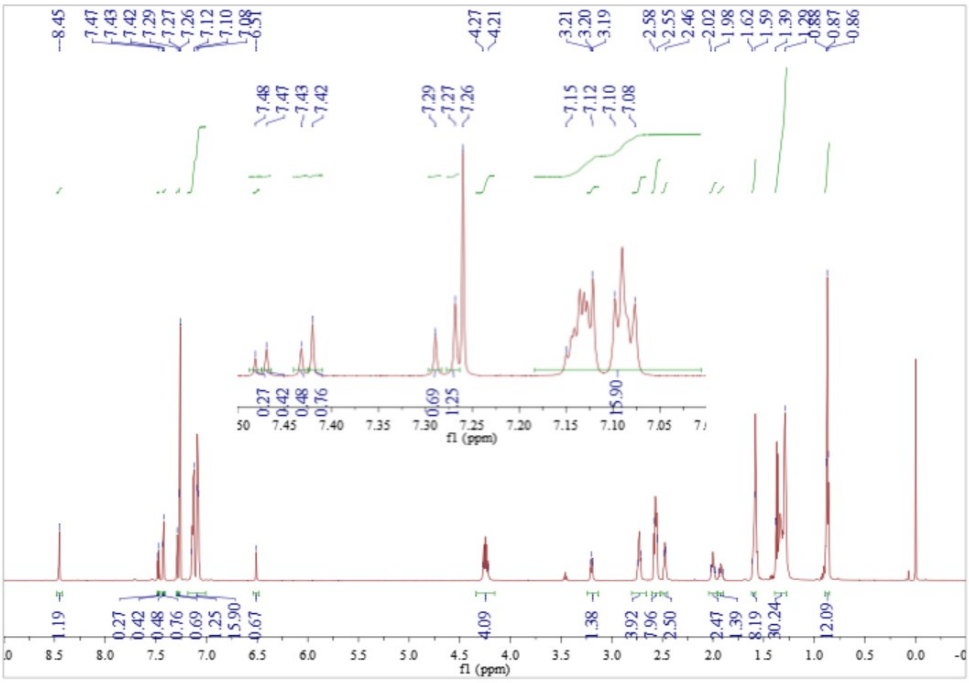


Fig. S31 ^{1}H NMR spectrum of IDT-CR conducted in chloroform-*d*.

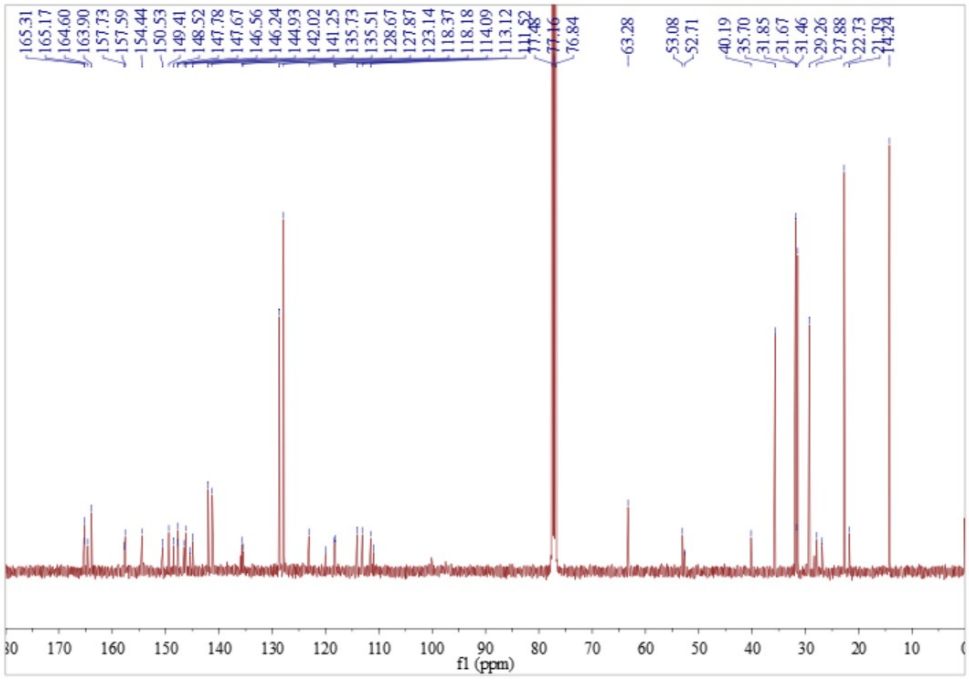


Fig. S32 ^{13}C NMR spectrum of IDT-CR conducted in chloroform-*d*.

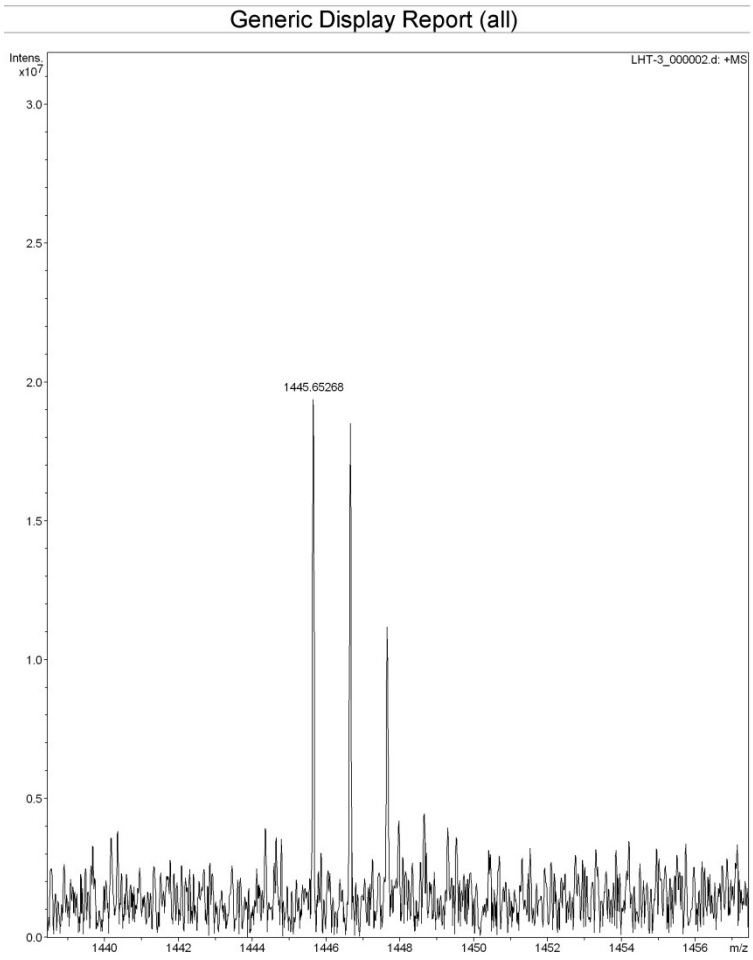


Fig. S33 The HRMS spectrum of IDT-CR.

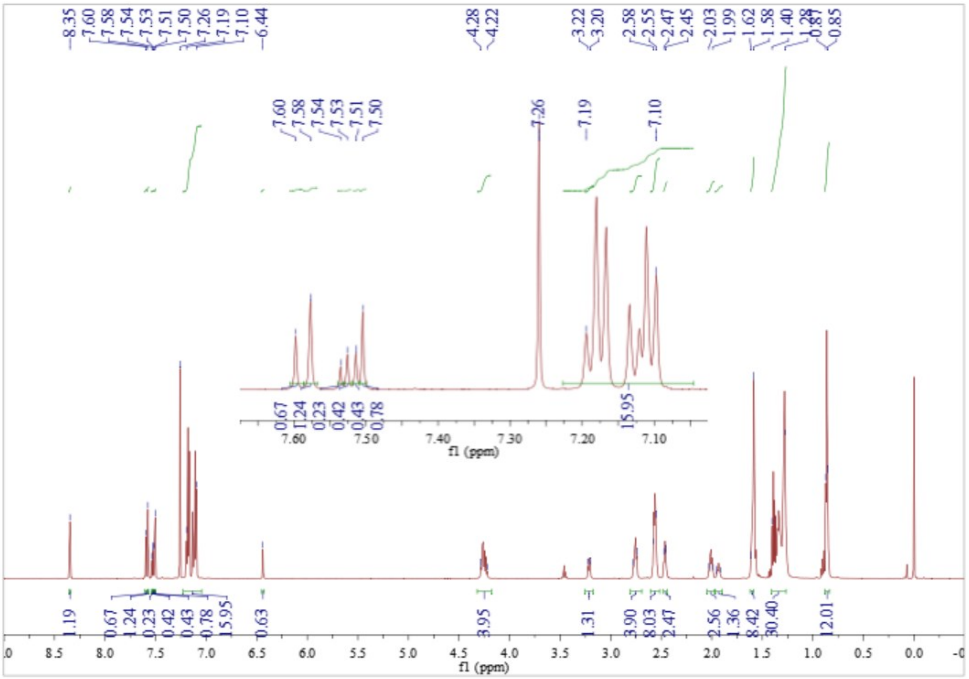


Fig. S34 ^{1}H NMR spectrum of IDTT-CR[1] conducted in chloroform-*d*.

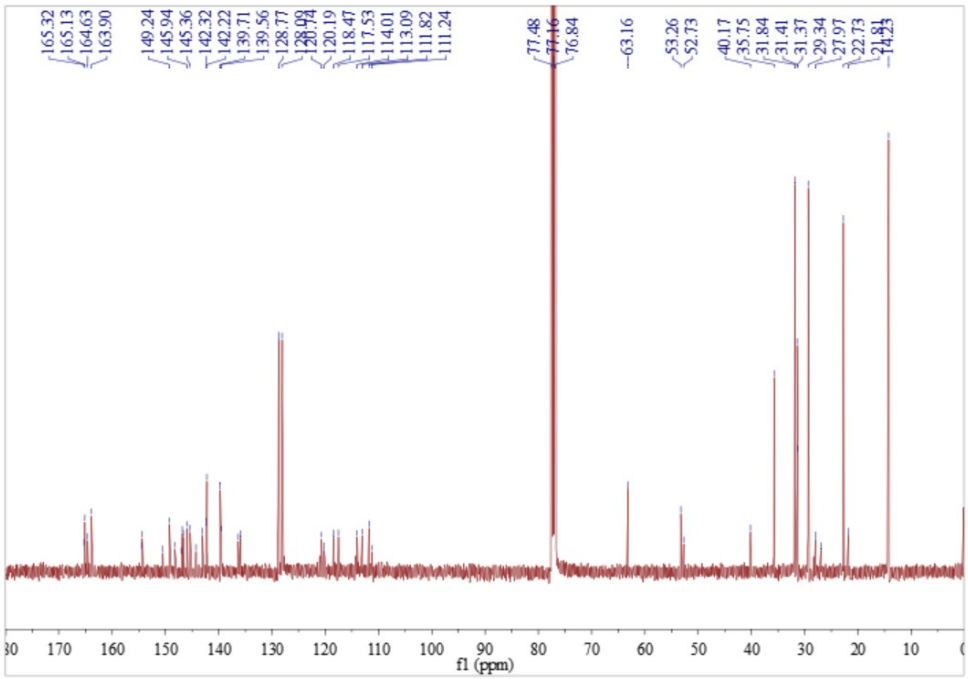


Fig. S35 ^{13}C NMR spectrum of IDTT-CR[1] conducted in chloroform-*d*.

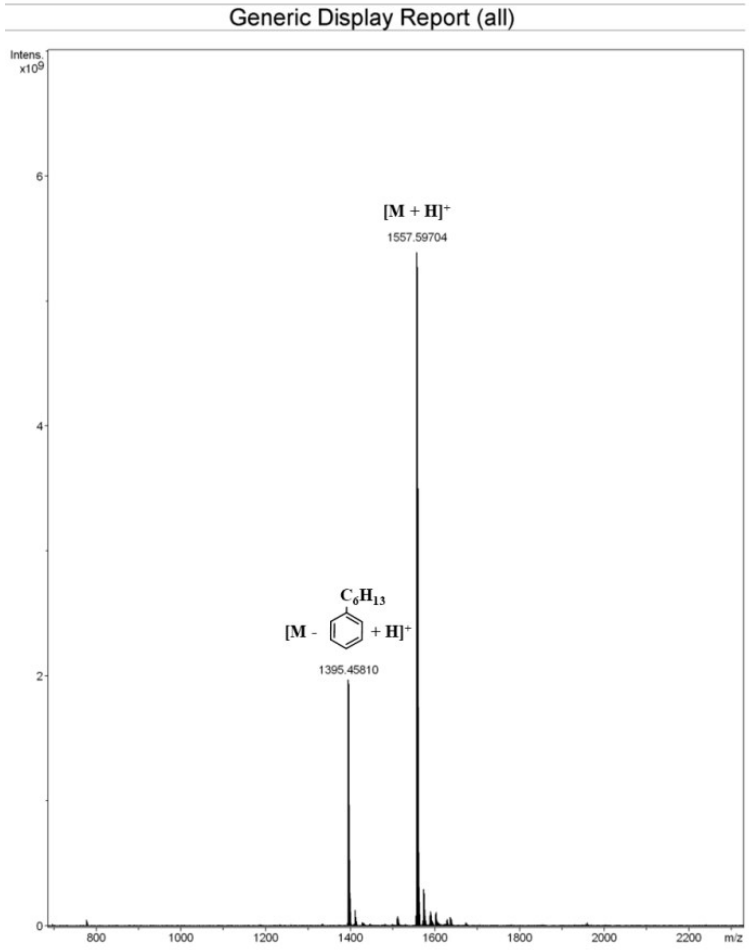


Fig. S36 The HRMS spectrum of IDTT-CR[1].

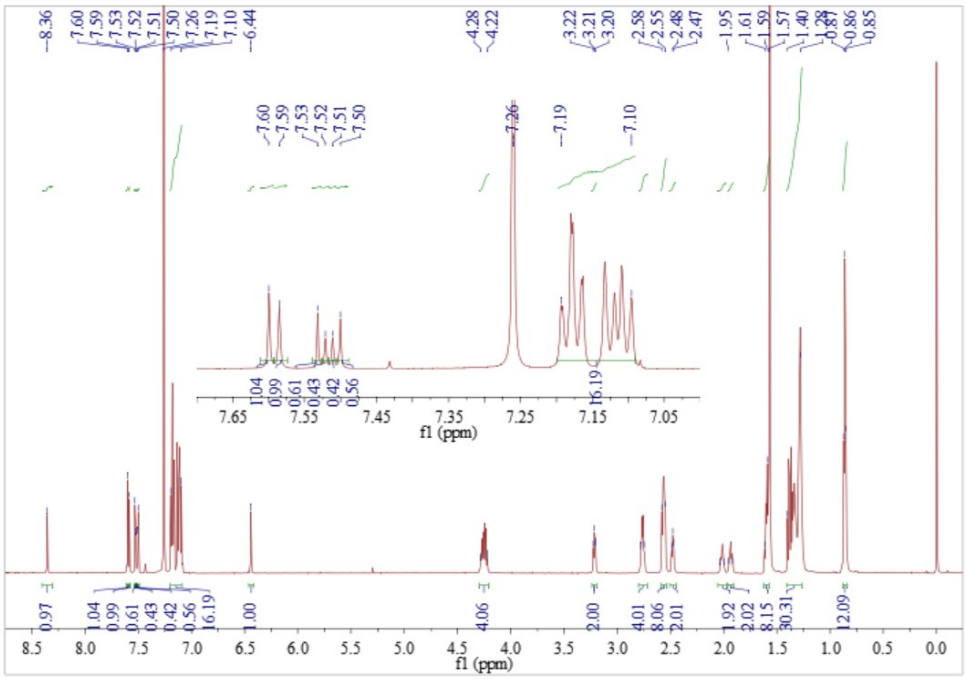


Fig. S37 [1]H NMR spectrum of IDTT-CR[2] synthesized from pure *Z*-BrCR conducted in chloroform-*d*.

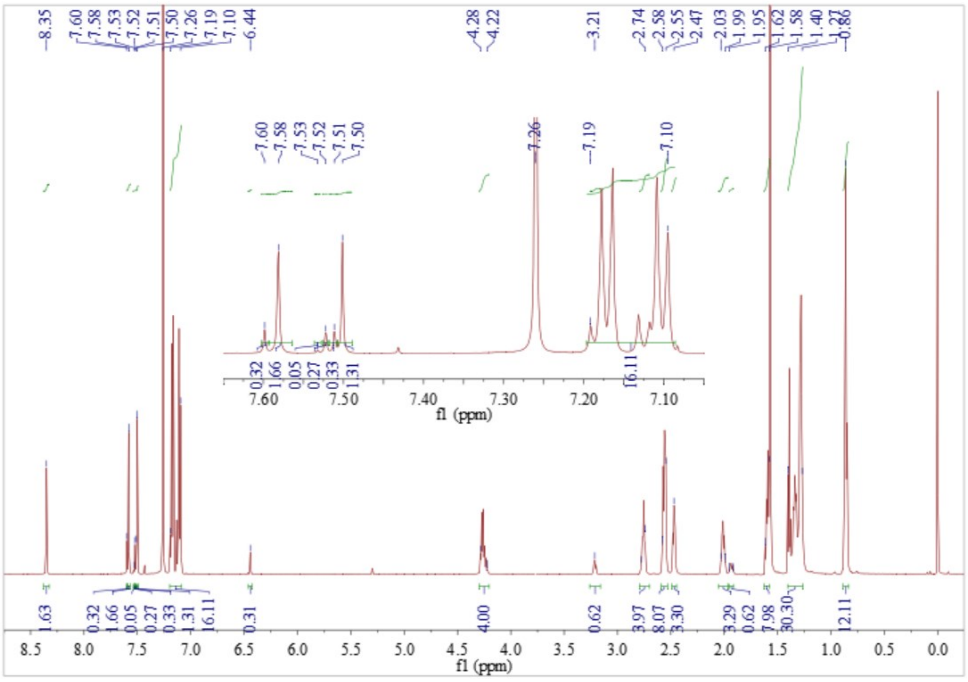


Fig. S38 ^{1}H NMR spectrum of IDTT-CR[3] synthesized from pure *E*-BrCR conducted in chloroform-*d*.

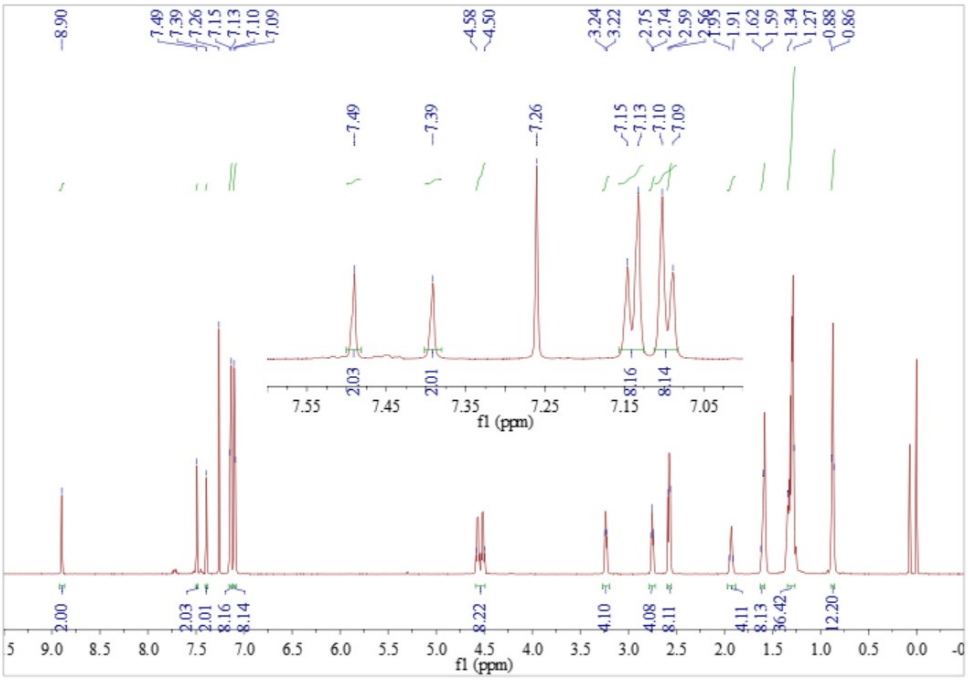


Fig. S39 ^{1}H NMR spectrum of IDT-CT conducted in chloroform-*d*.

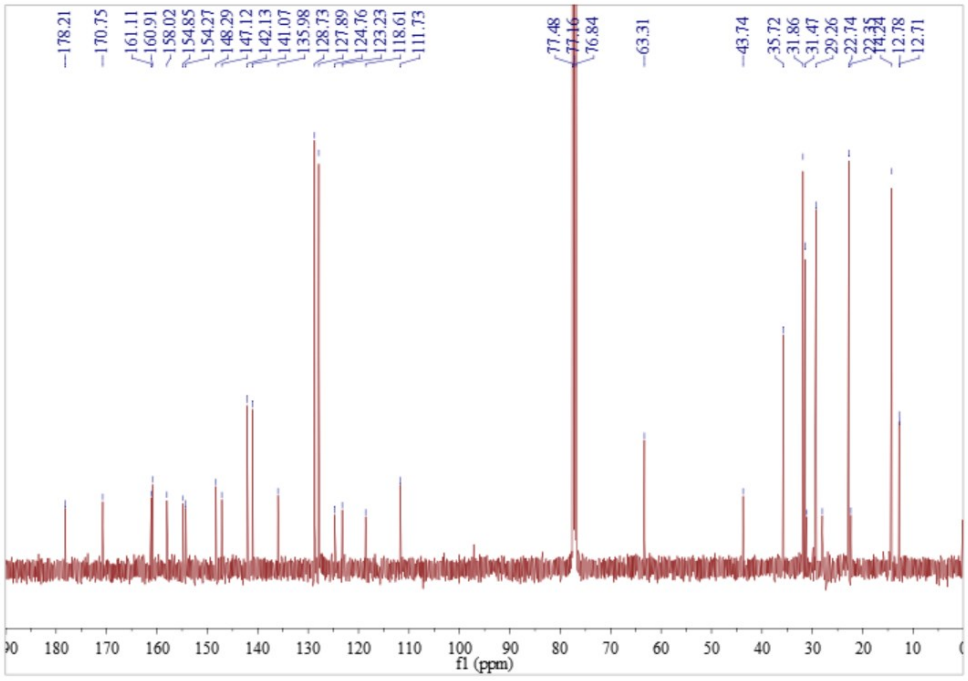


Fig. S40 ^{13}C NMR spectrum of IDT-CT conducted in chloroform-*d*.

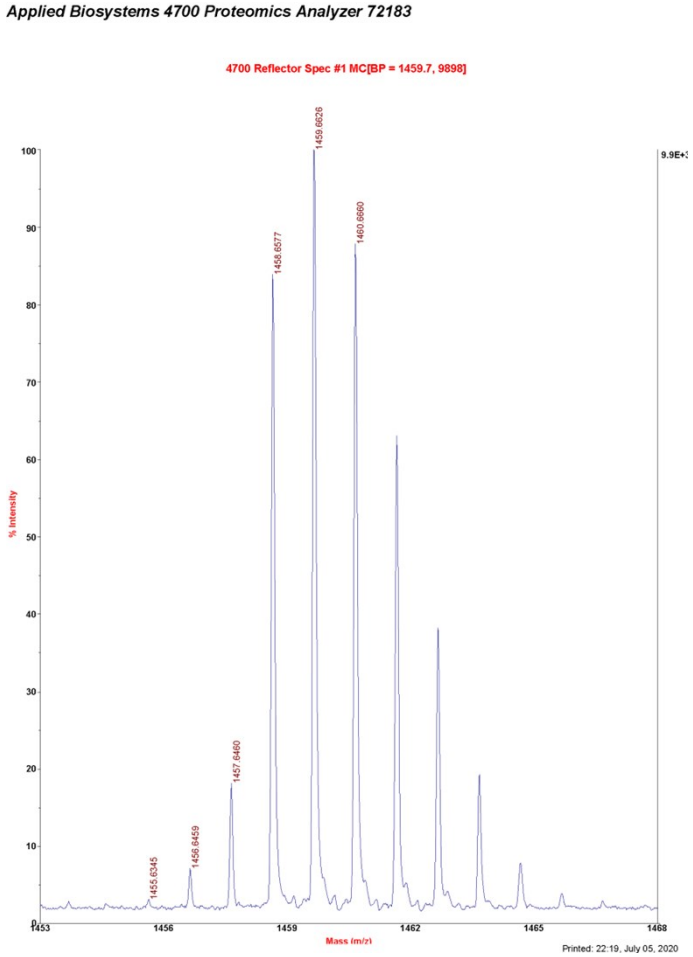


Fig. S41 The HRMS spectrum of IDT-CT.

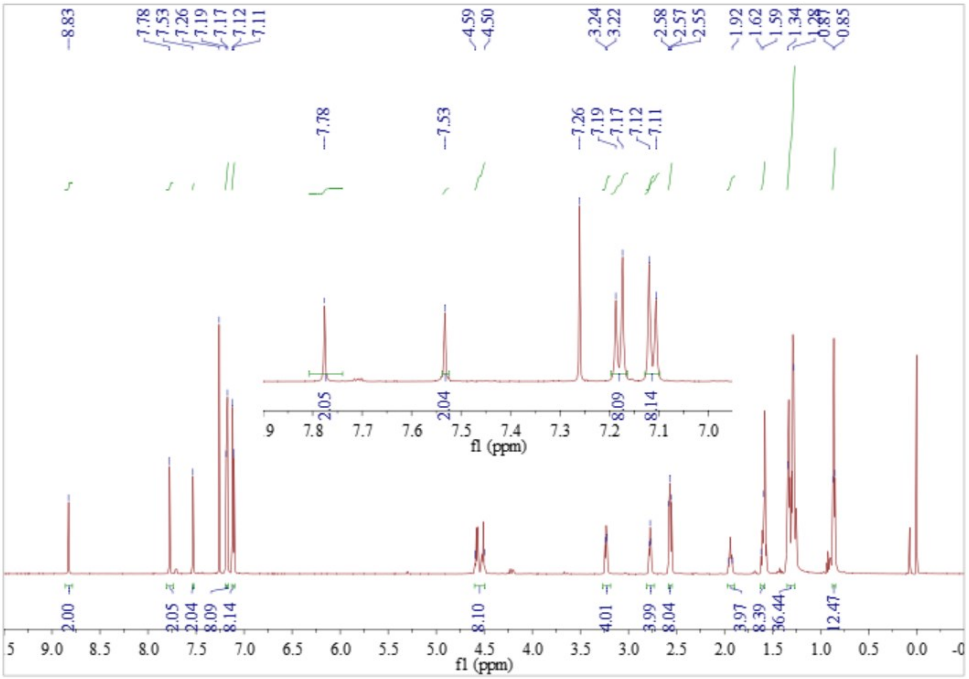


Fig. S42 ^{1}H NMR spectrum of IDTT-CT conducted in chloroform-*d*.

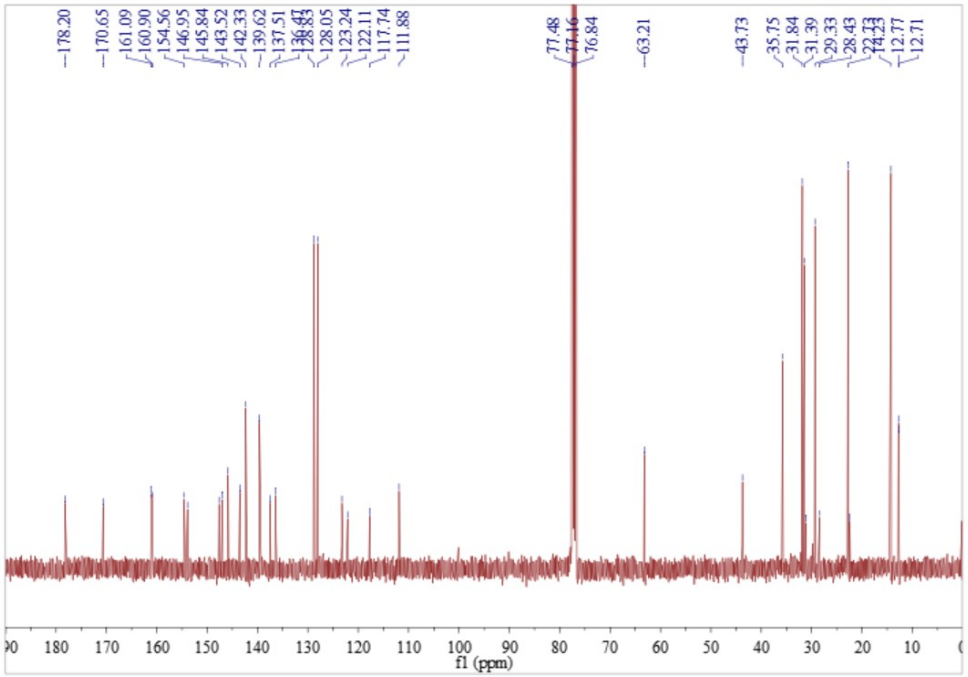


Fig. S43 ^{13}C NMR spectrum of IDTT-CT conducted in chloroform-*d*.

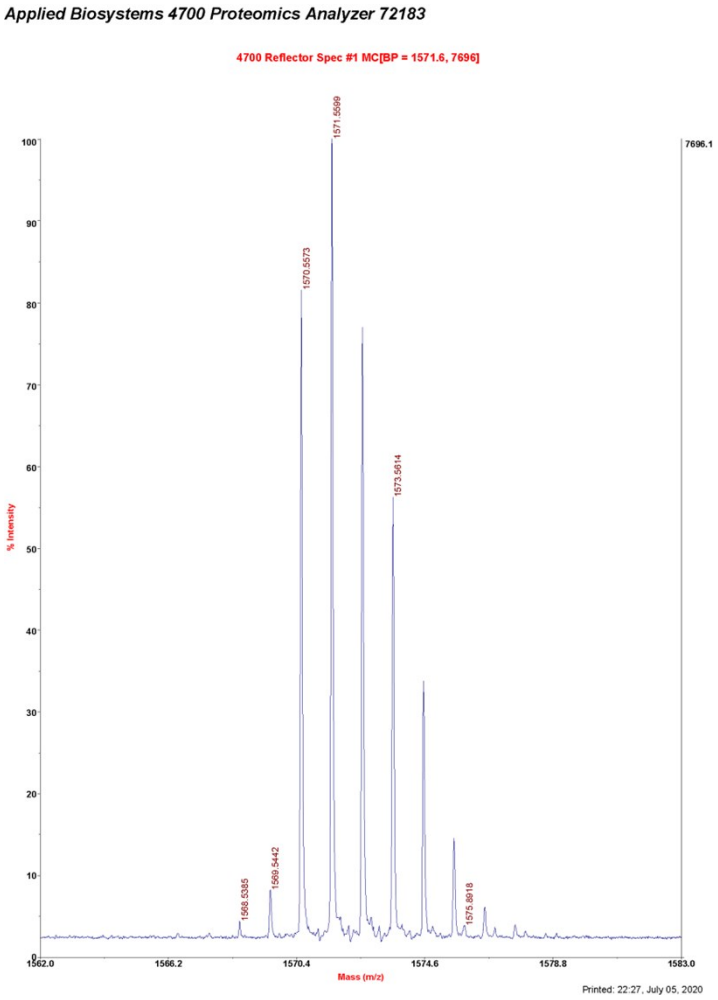


Fig. S44 The HRMS spectrum of IDTT-CT.

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