Electronic Supplementary Information

Dicyclopentadithienothiophene (DCDTT)-based Organic Semiconductor Assisted Grain Boundary Passivation for Highly Efficient and Stable Perovskite Solar Cells

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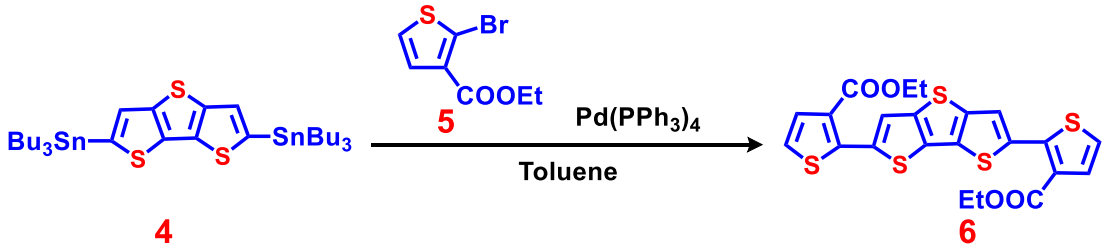
References

Experimental Section

Characterization

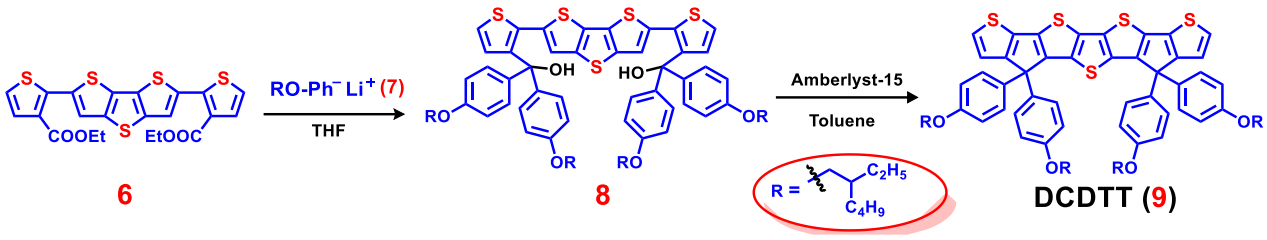
^{1}H and ^{13}C NMR spectra were recorded using a Bruker 500 or a 300 instrument, with reference to solvent signals. Differential scanning calorimetry (DSC) was carried out on a Mettler DSC 822 instrument at a scan rate of 10 K/min. Thermo gravimetric analysis (TGA) was performed on a Perkin Elmer TGA-7 thermal analysis system using dry nitrogen as a carrier gas at a flow rate of 40 mL/min. UV–Vis absorption and fluorescence spectra were obtained in the indicated solvents at room temperature using JASCO V-530 and Hitachi F-4500 spectrometers, respectively. Differential pulse voltammetry experiments were performed with a conventional three-electrode configuration (a platinum disk working electrode, an auxiliary platinum wire electrode, and a non-aqueous Ag reference electrode, with a supporting electrolyte of 0.1 M tetrabutylammonium hexafluorophosphate (dry $TBAPF_6$) in the specified dry solvent, using a CHI621C Electrochemical Analyzer (CH Instruments). Under N_2, the anhydrous OSC material was dissolved in above 0.1 M *o*-$C_6H_4Cl_2$ solution to prepare a 10^{-3} M test solution. In each DPV experiment, 5 mL of the test solution is scanned together with Fc^+/Fc (also 10^{-3} M; as internal standard) under N_2. Electrochemical potentials were referenced to an Fc^+/Fc internal standard (at +0.64 V). Mass spectrometric data were obtained with a JMS-700 HRMS instrument. Grazing incidence XRD data were collected in the 2θ range of 5−50 degree on a Bruker powder diffractometer (D8 Discover) using Cu $K\alpha_1$ radiation equipped with a 2D detector. UPS and X-ray photoelectron spectroscopy spectra were obtained from a Thermo VG-Scientific/VG-Sigma Probe spectrometer. UV/Vis and PL spectra were recorded using a Cary 300 Bio spectrometer and a Hitachi F-7000 fluorescence spectrophotometer, respectively, at room temperature. The nanosecond TRPL spectra were recorded with an opticalmicroscope-based system (UniRAM, Protrustech with the custom designed light path). The average power, wavelength, pulse duration, and repetition rate of the excitation are 20 μW, 405 nm, 150 ps, and 20 MHz, respectively. SEM was performed with a Hitachi S-800 microscope at 15 KV. Samples for SEM imaging were mounted on a metal stub with a piece of conducting tape and then coated with a thin layer of gold film to avoid charging. The cross-sectional SEM image was used for estimating

the film thickness and observing the interface contact between each layer of the cell. The contact angle was measured with a home-made set-up (Grandhand Ctag01, Taiwan) using water as a probe solvent. The contact angle is determined using the image of a sessile drop at the points of the intersection between the drop contour and the projection of the surface. Fourier transform infrared (FTIR) spectra were recorded for **IN^{X}-DCDTT** derivatives and **IN^{X}-DCDTT** derivatives+PbI_2 film in KBr using a Bio-Rad 155 FTIR spectrometer at ambient temperature with a resolution of 4 cm^{-1}. The electron-only devices were fabricated with the architecture FTO/c-TiO_2/m-TiO_2/various perovskite/ phenyl-C_{61}-butyric acid methyl ester (PCBM)/Ag, and measurement the dark I–V characteristics were evaluated to trap state density and charge mobility in the vertical direction of the various films.[1]



Scheme S1. Synthesis of Compound **6**

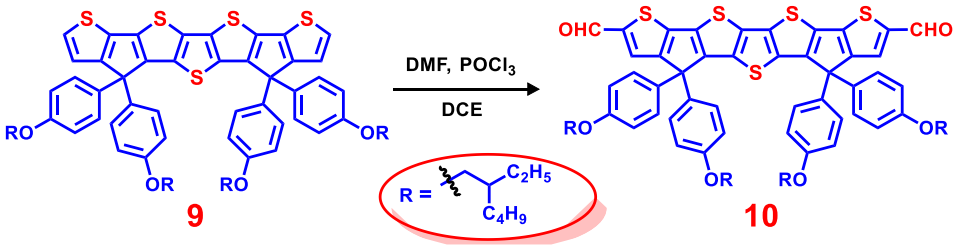
Synthesis of diethyl 2,2'-(dithieno[3,2-b:2',3'-d]thiophene-2,6-diyl)bis(thiophene-3-carboxylate) (6): Under anhydrous and deoxygenated conditions $Pd(PPh_3)_4$ (150 mg, 0.13 mmol) was added to the solution of bis(tributylstannyl)dithieno[3,2-b:2',3'-d]thiophene (**4**) (2.0 g, 2.7 mmol), ethyl 2-bromothiophene-3-carboxylate (**5**) (1.88 g, 8.1 mmol) and toluene (20 ml). The resulting mixture was refluxed for two days under nitrogen. After cooling to room temperature, the solvent was evaporated, the crude material was purified by column chromatography (15% EA/Hexane) to give product **6** as yellow solid, (1.0 g, 80%). ^{1}H NMR (300 MHz, $CDCl_3$) : δ (ppm) 7.74 (s, 2H), 7.52 (d, J = 5.4 Hz, 2H), 7.23 (d, J = 5.4 Hz, 2H), 4.32 (q, J = 7.2 Hz, 4H), 1.33 (t, J = 7.2 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.06, 142.96, 141.58, 135.00, 132.32, 130.75, 128.22, 124.24, 122.60, 60.90, 14.25. HRMS (MALDI, $[M]^+$) calcd for $C_{22}H_{16}O_4S_5$, 503.9652; Found: 503.9647.



Scheme S2. Synthesis of **DCDTT** (**9**)

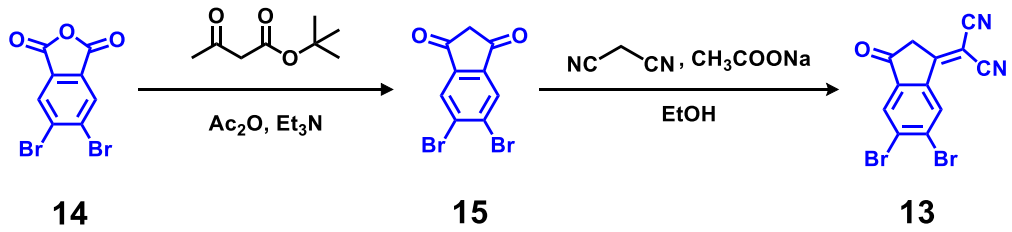
Synthesis of DCDTT (**9**)**:** 2.5 M *n*-BuLi (3.3 mL in Hexanes, 8.3 mmol) was slowely added to 1-bromo-4-((2-ethylhexyl)oxy)benzene (2.28 g, 8 mmol) at -78 °C in THF (30 ml) under anhydrous condition, the mixture was stirred for one hour and then it was warmed to 0 °C to remove the formed C_4H_9Br in the reaction by vacuum, then THF (30 mL) was added and transferred anion (**7**) slowly to reaction flask containing to solution of diethyl 2,2'-(dithieno[3,2-b:2',3'-d]thiophene-2,6-diyl)bis(thiophene-3-carboxylate (**6**) (0.5 g, 1 mmol) (70 mL) in THF (70 mL) under anhydrous condition at -78 ℃. Further, reaction mixture was slowly warmed to room temperature and heated to reflux for 2 hours. Further, reaction mixture was slowly warmed to room temperature and reaction was quenched by slow addition of deionized water and, THF was removed by rotary evaporator and reaction mixture was extracted by ether. Organic layer was dried over $MgSO_4$ and concentrated to give crude reaction mixture of benzylic alcohol **8** which was confirmed by ^{1}H NMR ((^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.15-7.13 (m,10H), 6.83-6.81 (m,10H), 6.50 (d, J = 5.5 Hz, 2H), 3.83 (d, J = 5.5 Hz, 8H), 3.23 (s, 2H), 1.70 (m, 4H), 1.40 (m, 16H), 1.30 (m, 16H), 0.8 (m, 24H)) (Note. benzylic alcohol **8** is not enough stable to collect useful ^{13}C NMR spectrum) and used for next step without further purification. To this crude reaction mixture toluene 30 ml followed by Amberlyst-15 was (0.5 g) was added under N_2 atmosphere and reaction mixture was refluxed for 4 hours. Further, reaction mixture was cool down to room temperature. toluene was removed under rotary evaporator and extracted with ethyl acetate and organic layer was dried over $MgSO_4$ and concentrated to give crude reaction mixture which is purified by column chromatography using DCM/Hexane (20:80) to give orange liquid (0.5 g, 41%). ^{1}H NMR (500 MHz, $CDCl_3$) : δ (ppm) 7.19 (d, J = 5 Hz, 2H), 7.12 (d, J = 8.5 Hz, 8H), 7.01 (d, J = 5 Hz, 2H), 6.74 (d, J = 9 Hz, 8H), 3.76 (m,

8H), 1.70 (m, 4H), 1.40 (m, 32H), 0.8 (m, 24H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.49, 157.93, 149.27, 136.40, 136.21, 135.37, 134.10, 132.18, 128.87, 125.72, 123.13, 114.44, 70.31, 61.46, 39.44, 30.54, 29.12, 23.86, 23.06, 14.10, 11.15. HRMS (MALDI, $[M]^+$) calcd for $C_{74}H_{88}O_4S_5$,1200.5286; Found: 1200.5281.



Scheme S3. Synthesis of compound **10**.

Synthesis of compound 10: Slowly $POCl_3$ (3 mL) was added to DMF (2 mL) in 30 mL DCE at 0°C and stirred for 30 min at same temperature. To this solution, **DCDTT** (**9**) (0.5 g, 0.19 mmol) was added 0°C and refluxed for 20 hours. Reaction mixture was cooled to room temperature and slowly saturated solution of $NaHCO_3$ was added at 0°C and warmed to RT. Reaction mixture was extracted with ethyl acetate, organic layer was concentrated and crude residue was purified by column chromatography (EA/Hexane 15:85) to obtain compound **10** as orange liquid (0.3 g 57%). ^{1}H NMR (300 MHz, $CDCl_3$) : δ (ppm) 9.80 (s, 2H), 7.62 (s, 2H), 7.10 (d, J = 8.7 Hz, 8H), 6.77 (d, J = 8.7 Hz, 8H), 3.76 (m, 8H), 1.68 (m, 4H), 1.44 (m, 16H), 1.41 (m, 16H), 0.90 (m, 24H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 182.30, 158.90, 158.45, 153.20, 146.49, 144.28, 136.79, 136.29, 136.12, 135.24, 132.56, 131.27, 128.67, 114.71, 70.42, 61.79, 39.39, 31.92, 30.50, 30.48, 30.33, 29.69, 29.65, 29.35, 29.07, 23.82, 23.01, 22.68, 14.09, 14.04, 11.10, 11.07. HRMS (MALDI, $[M]^+$) calcd for $C_{76}H_{88}O_6S_5$, 1256.5184 Found : 1256.5181.



Scheme S4. Synthesis of compound **13**.

Synthesis of 5,6-dibromo-1H-indene-1,3(2H)-dione (**15**): To the mixture of 4,5-dibromophthalic anhydride (1 g, 3.27 mmol), acetic anhydride (4 mL) and, triethylamine (2 mL) in volume ratio 2:1 was slowly added tertbutylacetoacetate (0.517 g, 6.32 mmol) and reaction mixture was stirred overnight. Further, reaction was quenched with ice and concentrated hydrochloric acid, then heated at 80°C for 1 hour. The reaction mixture was cooled to room temperature and precepitated solid was obtained by vaccum filtration, (0.89 g, 89%). ^{1}H NMR (300 MHz, $CDCl_3$) : δ (ppm) 8.22 (s, 2H), 3.25 (s, 2H).

2-(5,6-dibromo-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (**13**): Mixture of 5,6-dibromo-1,3-indandione (1 g, 3.29 mmol) and malononitrile (0.434 mg, 6.58 mmol) sodium acetate (0.405 g, 4.94 mmol), in ethanol (20 mL) was stirred at room temperature for 1 hour, and then heated for 3 hour. Further, reaction mixture added to water and ethanol mixture (20 mL) acidified with an aqueous hydrochloric acid, and precipitated solid was filtered by vaccum filtration and washed with hexane to get compound **13** (0.903 g, 78%). ^{1}H NMR (300 MHz, $CDCl_3$) : δ (ppm) 8.90 (s, 1H), 8.22 (s, 1H), 3.76 (s, 2H).

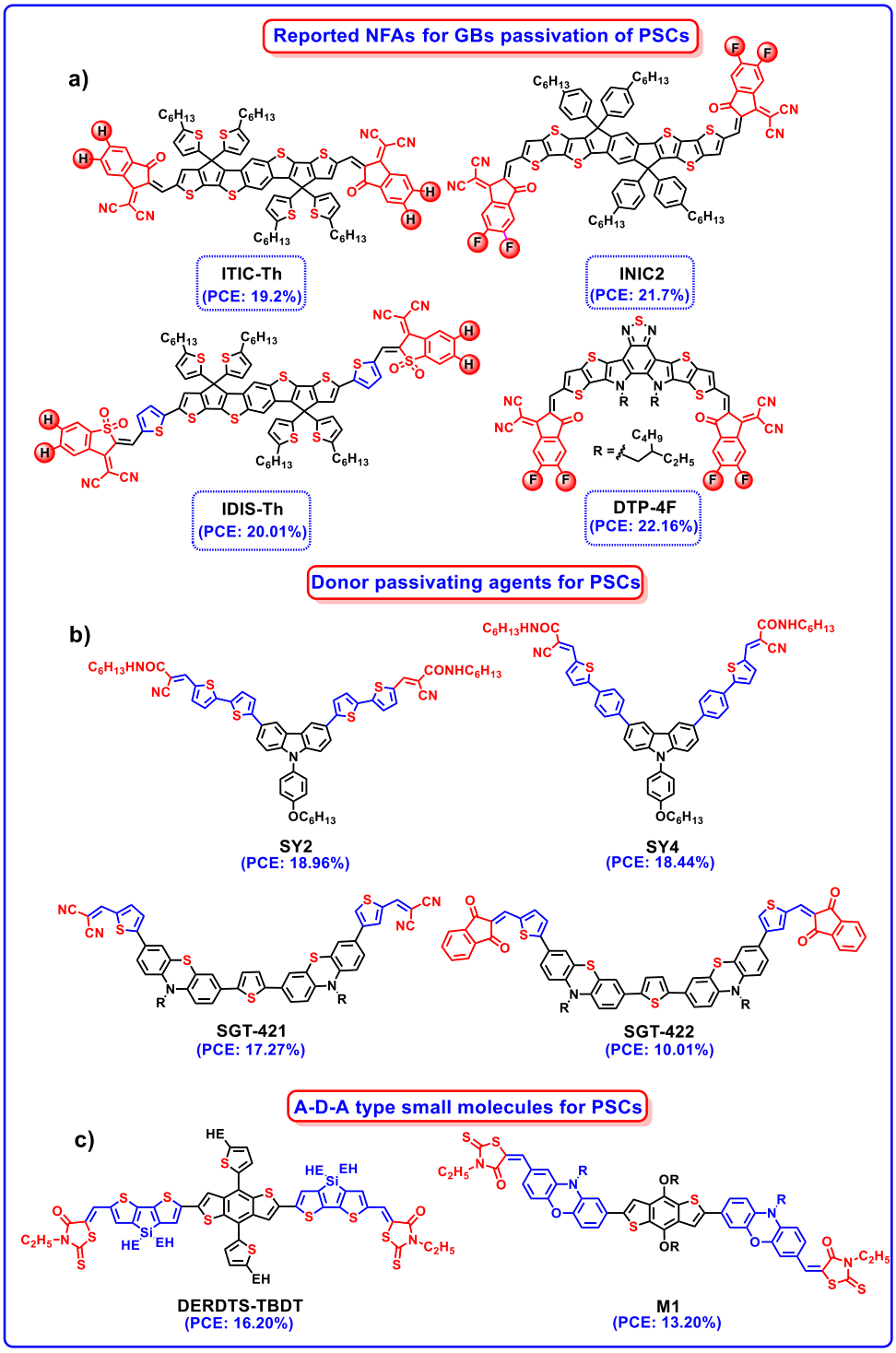


Figure S1. Reported molecular structures of (a) NFAs for grain boundary passivation of PSCs; (b) Donor passivating agents for PSCs; (c) A-D-A type small molecules for PSCs.

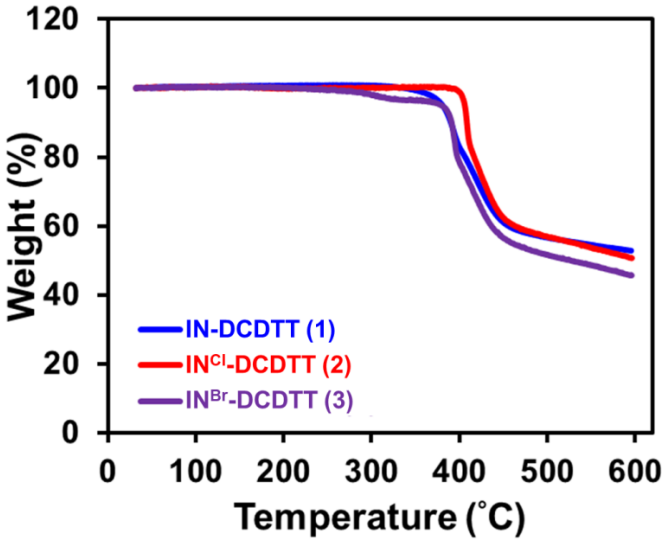


Figure S2. TGA curves of the studied compounds **1-3**.

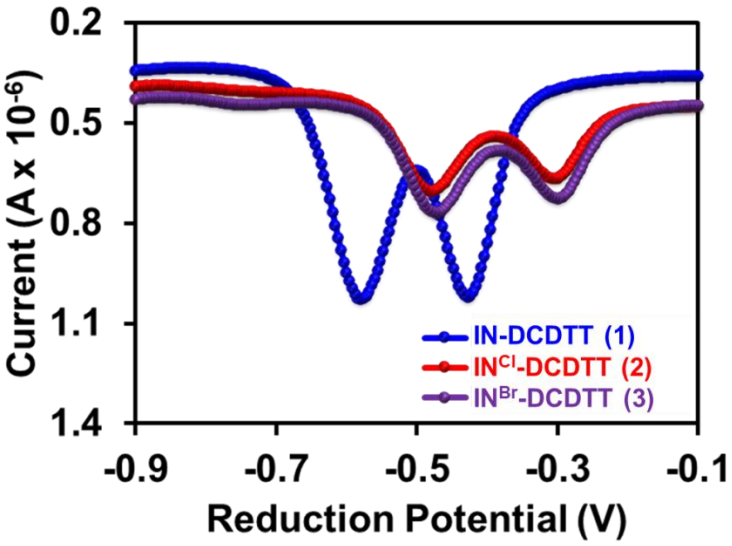


Figure S3. DPV curves of the studied compounds **1-3**.

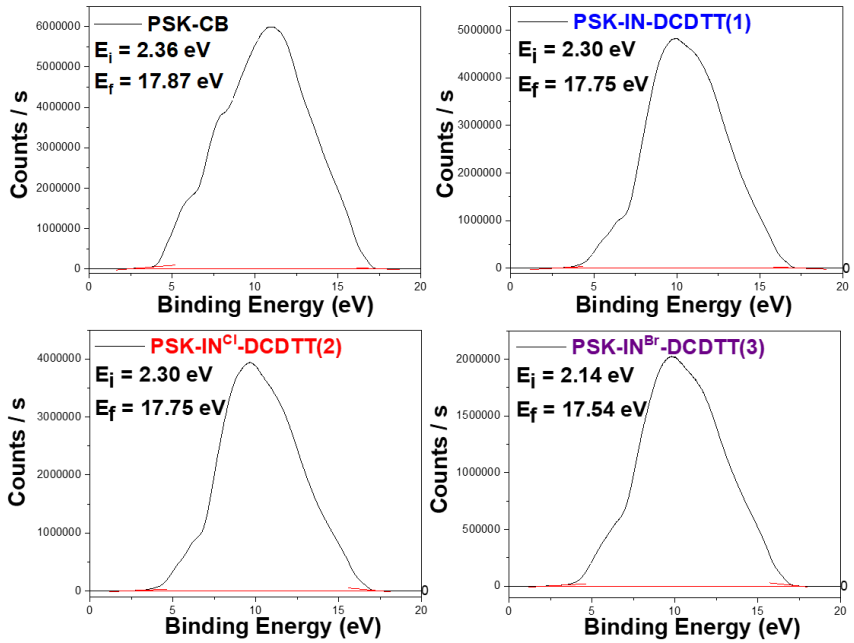


Figure S4. The UPS of the perovskite made by using pure CB (pristine perovskite), 0.2 wt% **IN-DCDTT** (**1**), 0.2 wt% **IN^{Cl}-DCDTT** (**2**) or 0.2 wt% **IN^{Br}-DCDTT** (**3**) in CB **as an anti-solvent (**0.2 wt% compounds 1-3 treated perovskite).

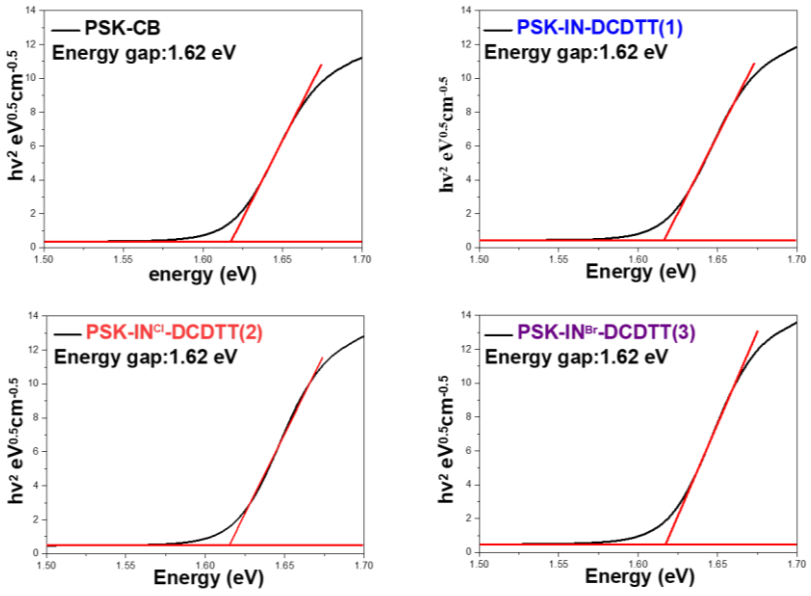


Figure S5. The tauc plot of the pristine perovskite and perovskite films treated with 0.2 wt% compounds **1**-**3**.

Table S1. The energy level of pristine perovskite and perovskite films treated with 0.2 wt% compounds **1**-**3**.

Film	CB (eV)	Eg (eV)	VB (eV)
PSK-CB	-5.69	1.62	4.07
PSK-IN-DCDTT-(1)	-5.75	1.62	4.13
PSK-IN^{Cl}-DCDTT-(2)	-5.81	1.62	4.19
PSK-IN^{Br}-DCDTT-(3)	-5.80	1.62	4.18

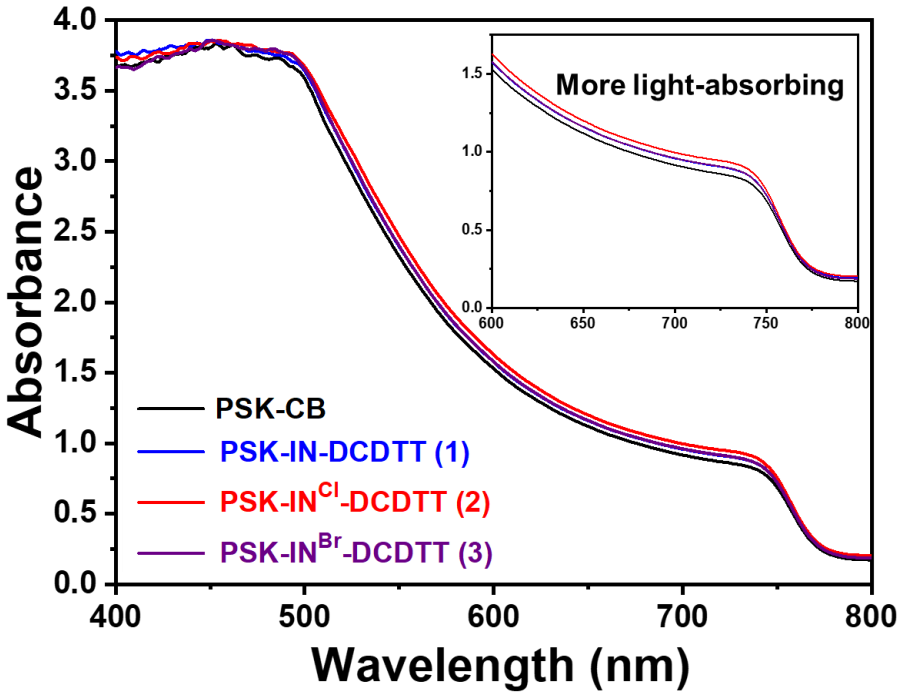
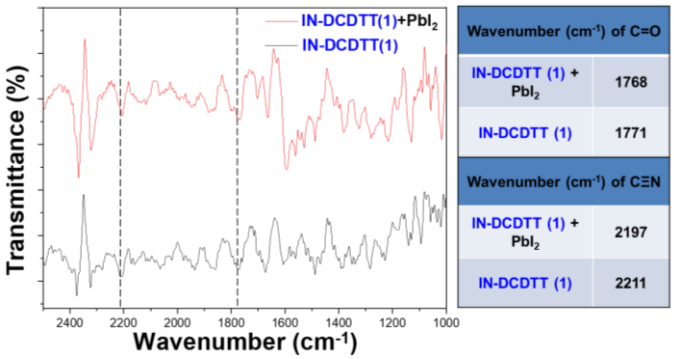
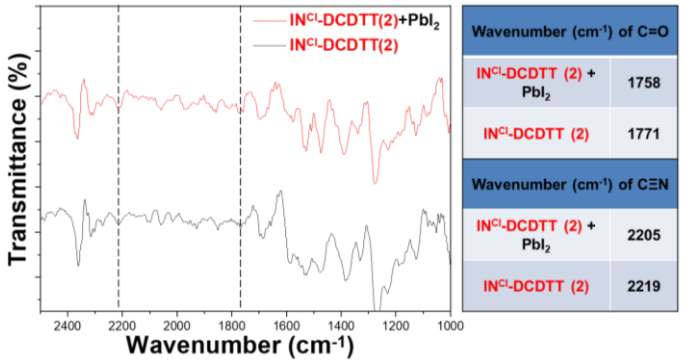


Figure S6. UV-Vis absorption spectra of pristine perovskite and perovskite films treated with 0.2 wt% compounds **1**-**3**.



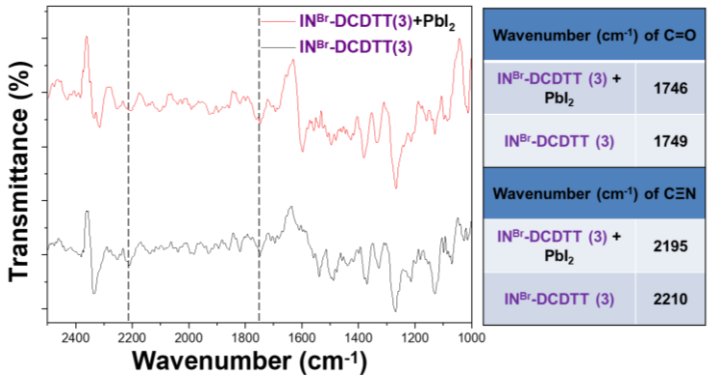
Wavenumber (cm^{-1}) of C=O	
IN-DCDTT (1) + PbI_2	1768
IN-DCDTT (1)	1771
Wavenumber (cm^{-1}) of C≡N	
IN-DCDTT (1) + PbI_2	2197
IN-DCDTT (1)	2211

Figure S7a. FTIR spectrum of **IN-DCDTT (1)** and **IN-DCDTT (1)** mixed with PbI_2.



Wavenumber (cm^{-1}) of C=O	
IN^{Cl}-DCDTT (2) + PbI_2	1758
IN^{Cl}-DCDTT (2)	1771
Wavenumber (cm^{-1}) of C≡N	
IN^{Cl}-DCDTT (2) + PbI_2	2205
IN^{Cl}-DCDTT (2)	2219

Figure S7b. FTIR spectrum of IN^{Cl}-**DCDTT** (**2**) and IN^{Cl}-**DCDTT** (**2**) mixed with PbI_2.



Wavenumber (cm^{-1}) of C=O	
IN^{Br}-DCDTT (3) + PbI_2	1746
IN^{Br}-DCDTT (3)	1749
Wavenumber (cm^{-1}) of C≡N	
IN^{Br}-DCDTT (3) + PbI_2	2195
IN^{Br}-DCDTT (3)	2210

Figure S7c. FTIR spectrum of IN^{Br}-**DCDTT** (**3**) and IN^{Br}-**DCDTT** (**3**) mixed with PbI_2.

Table S2. PL spectra of perovskite films on glass and FTO/TiO_2 substrates.

Sample	PL intensity	[a]Charge injection/transfer efficiency (η_{inj})
CB on glass	70	--
0.2 wt% IN-DCDTT$_{(CB)}$ on glass	145	--
0.2 wt% IN^{Cl}-DCDTT$_{(CB)}$ on glass	242	--
0.2 wt% IN^{Br}-DCDTT$_{(CB)}$ on glass	198	--
CB onTiO_2	47	33%
0.2 wt% IN-DCDTT$_{(CB)}$ onTiO_2	35	76%
0.2 wt% IN^{Cl}-DCDTT$_{(CB)}$ onTiO_2	3	99%
0.2 wt% IN^{Br}-DCDTT$_{(CB)}$ onTiO_2	27	86%

[a] Charge injection efficiency (ηinj) = (△PL)/PL

Table S3. TRPL spectra of pervoskite films with **Spiro-OMeTAD** overlayer.

Films	A1	τ_1 lifetime (ns)	A2	τ_2 lifetime (ns)	τ_{av} (ns)
PSK-CB with Spiro-OMeTAD	0.65	0.94	0.35	3.19	1.73
PSK- IN-DCDTT (1) with Spiro-OMeTAD	0.69	0.62	0.31	2.68	1.26
PSK- IN^{Cl}-DCDTT (2) with Spiro-OMeTAD	0.78	0.22	0.22	1.21	0.44
PSK- IN^{Br}-DCDTT (3) with Spiro-OMeTAD	0.73	0.31	0.27	2.23	0.83

$y = A_1*\exp(-t/T_1) + A_2*\exp(-t/T_2)$

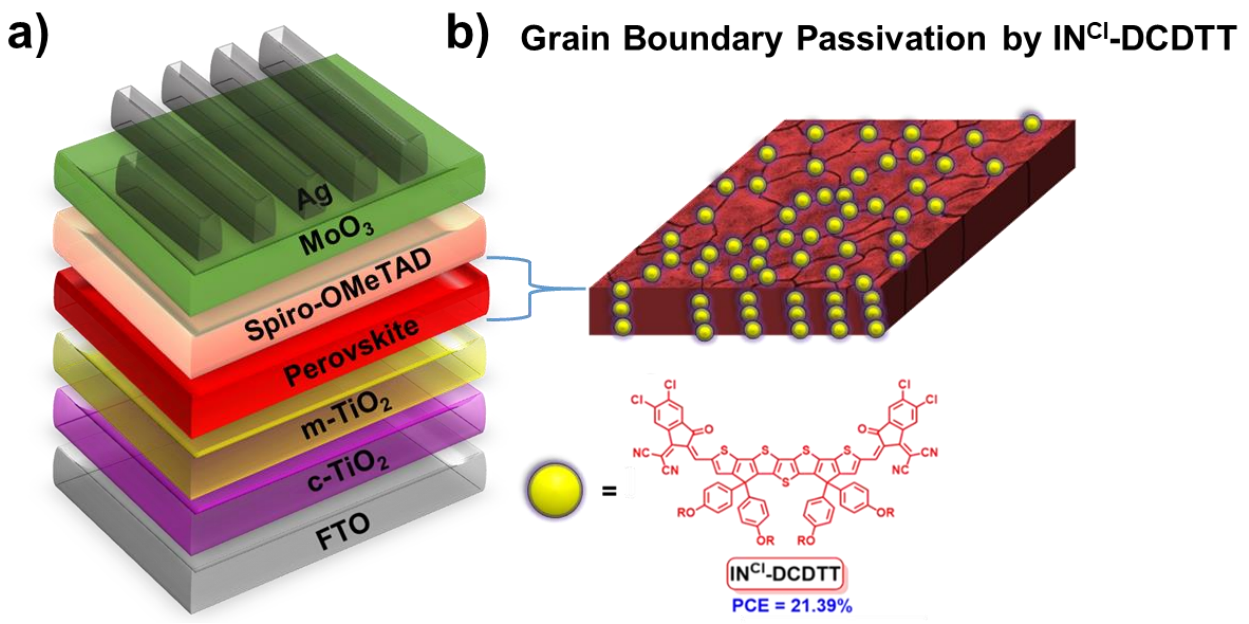


Figure S8. (a) Device architecture of PSCs and (b) Schematic of grain boundary passivation by **IN^{Cl}-DCDTT** (**2**).

Table S4. The I-V curves of the cell based on I**N^{Cl}-DCDTT** (**2**) treated perovskite measured with two voltage scan directions.

Hysteresis index = $(PCE_{reverse} - PCE_{forward})/PCE_{reverse}$

Direction	Jsc (mA/cm^2)	Voc (V)	FF	FF%	Hysterisis Index
Negative to positive bias	23.71	1.10	0.82	21.39	**0.5%**
Positive to negative bias	23.67	1.11	0.81	21.28	

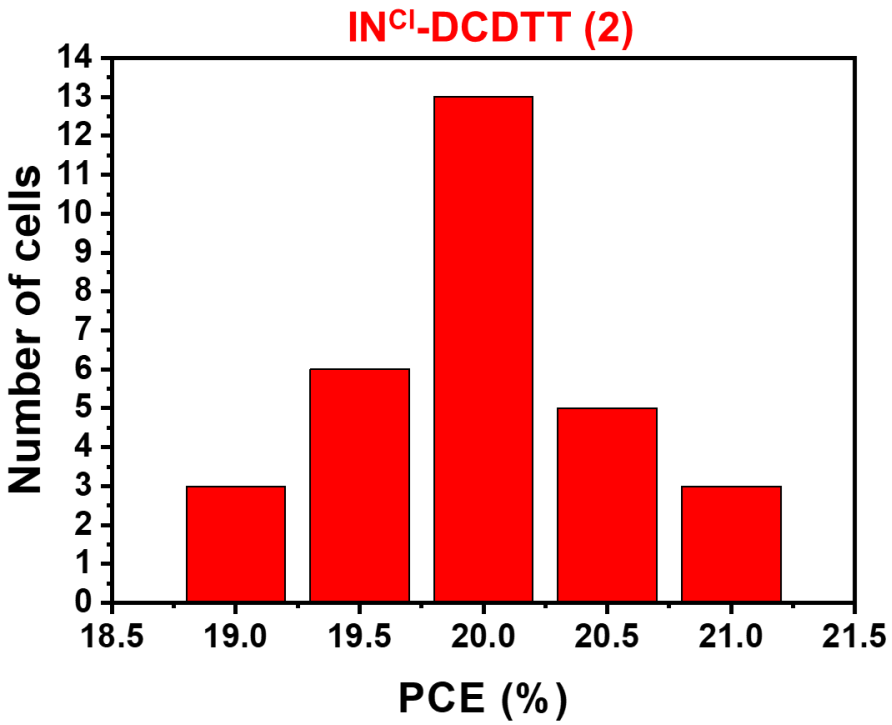
Table S5. The I-V curves of the cell based on pristine perovskite measured with two voltage scan directions.

Direction	Jsc (mA/cm^2)	Voc (V)	FF	FF%	Hysterisis Index
Negative to positive bias	21.98	0.73	17.00	17	**18.94%**
Positive to negative bias	21.36	0.68	13.72	13.72	

Hysteresis index = $(PCE_{reverse} - PCE_{forward})/PCE_{reverse}$

Table S6. The integrated photocurrent density from IPCE and short-circuit current density from J-V of the reference cell and cells based on compounds **1**-**3**-treated perovskite films

Anti-solvent	Integrated Photocurrent Density from IPCE (mA/cm^2)	Short-circuit Current from J-V
CB	19.75	21.98
0.2wt% IN-DCDTT (1)	20.98	22.52
0.2wt% IN^{Cl}-DCDTT (2)	22.22	23.71
0.2wt% IN^{Br}-DCDTT (3)	21.77	23.32



Figures S9. The efficiency distribution for perovskite solar cells based on I**N^{Cl}-DCDTT** (**2**) treated perovskite absorbers (30 devices, average PCE of 20.15 ± 0.46)

The trap density was determined using the following equation:

$$n_{trap} = \frac{2\varepsilon_0 \varepsilon_r V_{TFL}}{eL^2}$$

Where ε_0 is the vacuum permittivity, ε_r is the relative dielectric constant, V_{TFL} is the onset voltage of the trap-filled limit region, *e* is the elementary charge, and *L* is the distance between the electrodes. The electron mobility was further extracted using Mott-Gurney Law.[2]

Film	n_{trap}
PSK-CB	**1.61 x 10^{16} cm^{-3}**
PSK-IN^{Cl}-DCDTT (2)	**7.14 x 10^{15} cm^{-3}**

The electron mobility

The electron mobility can be by the following version of the Mott–Gurney equation:

$$J = \frac{9\,\varepsilon\,\varepsilon_0\,\mu\,V^2}{8L^3}$$

Here, ε_0 is the permittivity of free space, e is the dielectric constant of the material, L is the thickness of the perovskite film, and V is the applied voltage.[3]

Film	Mobility
PSK-CB	**3.50 x 10^{-4}**
PSK-IN^{Cl}-DCDTT (2)	**7.47 x 10^{-3}**

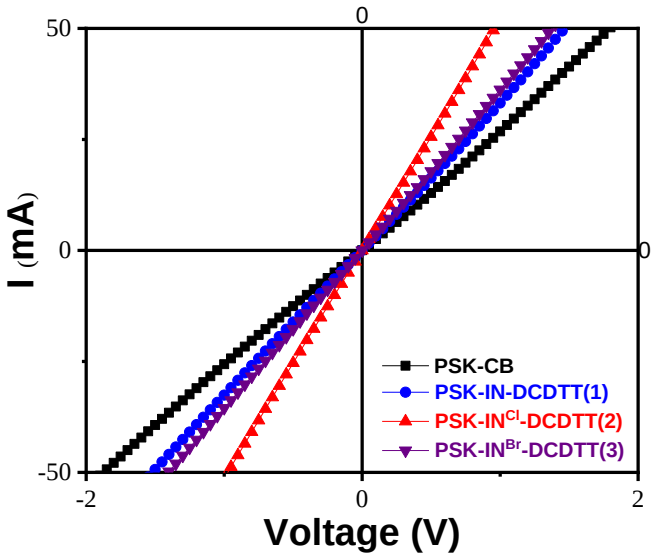


Figure S10. The I-V curves of the perovskite films made by using CB, 0.2 wt% **IN-DCDTT** (**1**)$_{(CB)}$**,** 0.2 wt% **IN^{Cl}-DCDTT** (**2**)$_{(CB)}$ or 0.2 wt% **IN^{Br}-DCDTT** (**3**)$_{(CB)}$ as an anti-solvent.

σ_0=Id/AV

σ_0 : Conductivity

I: Current

A: Detected area (0.1 cm^2)

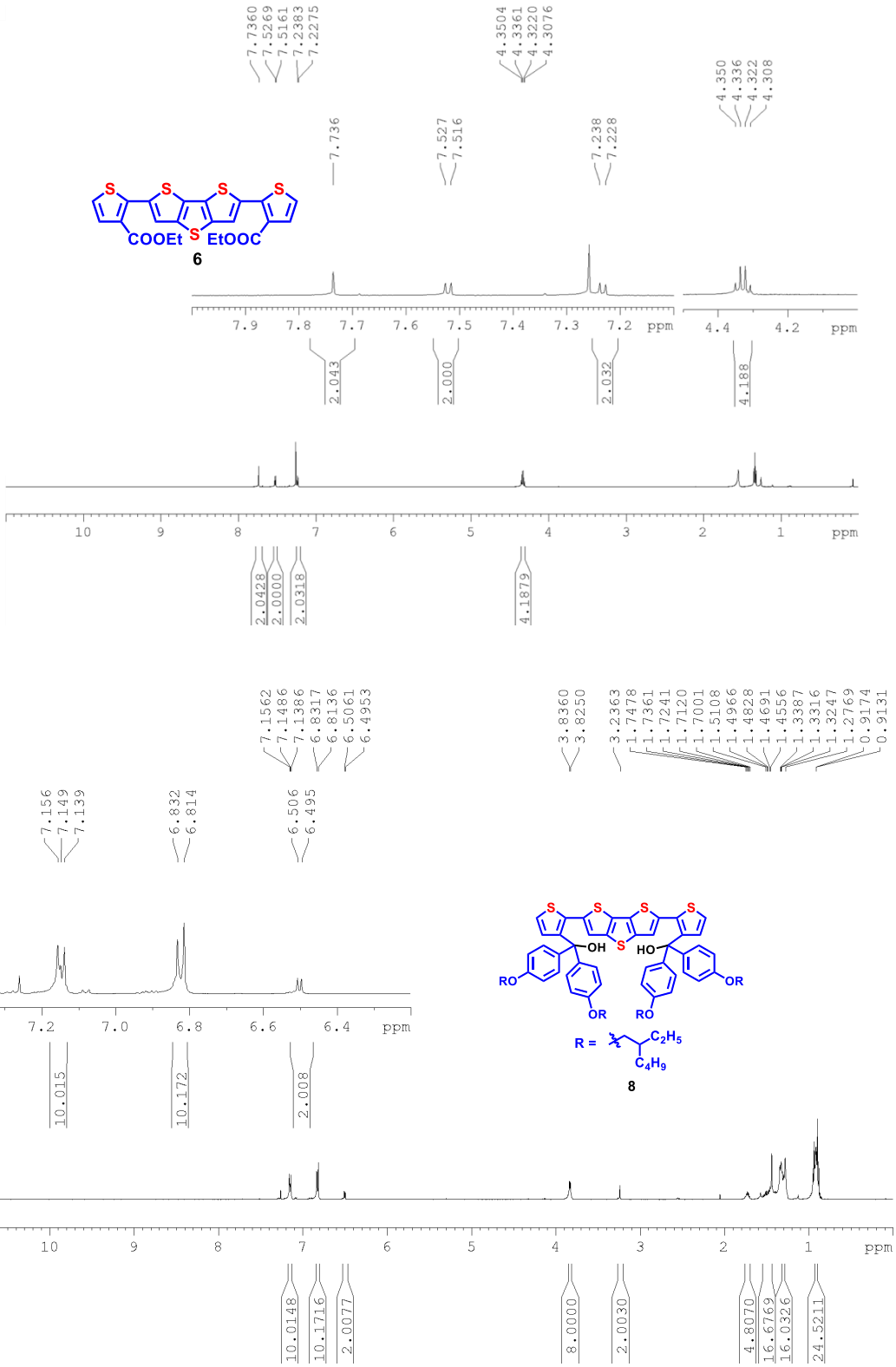
d: Thickness of the film

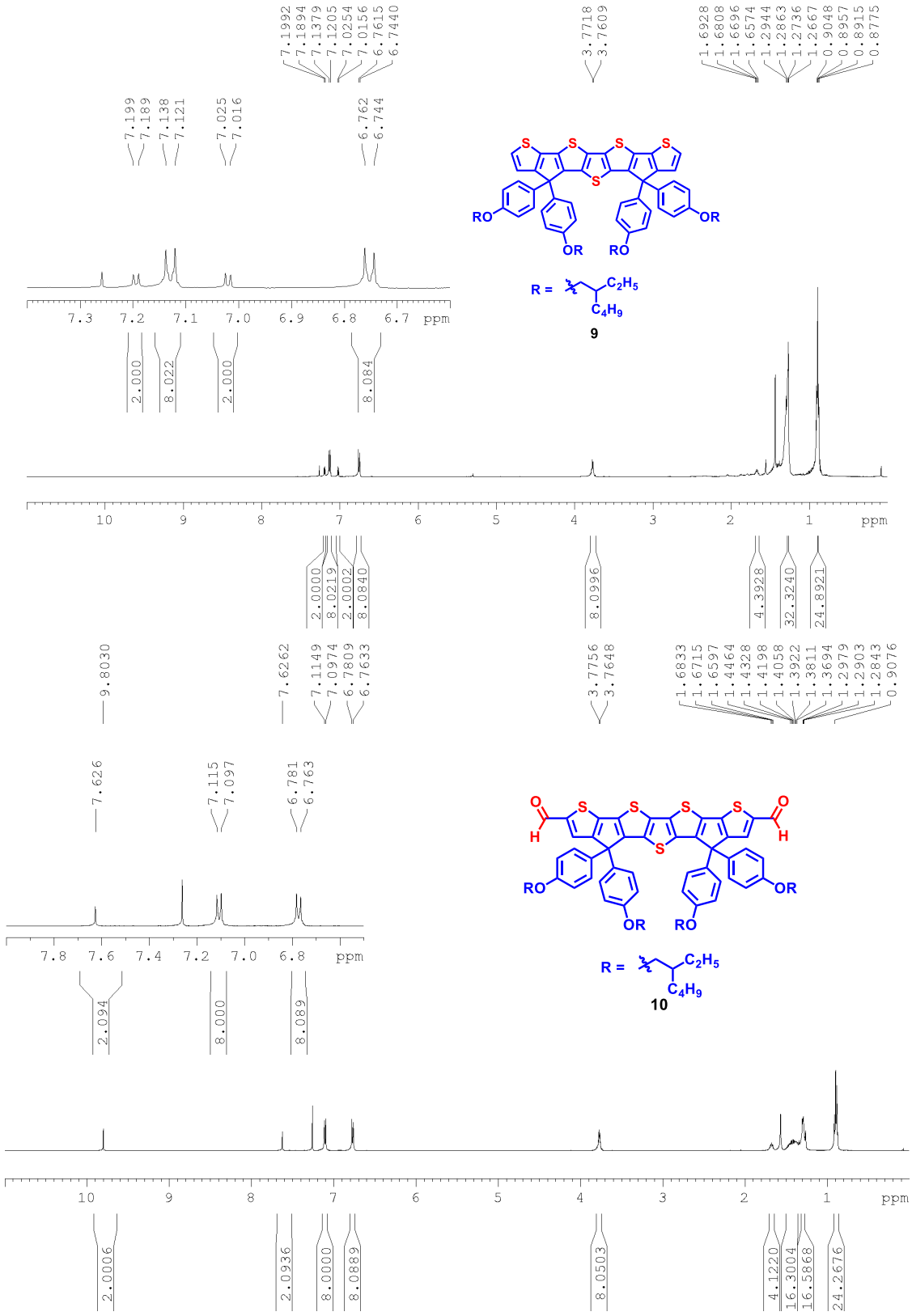
Device: FTO/c-TiO$_2$/m-TiO$_2$/Perovskite/Au

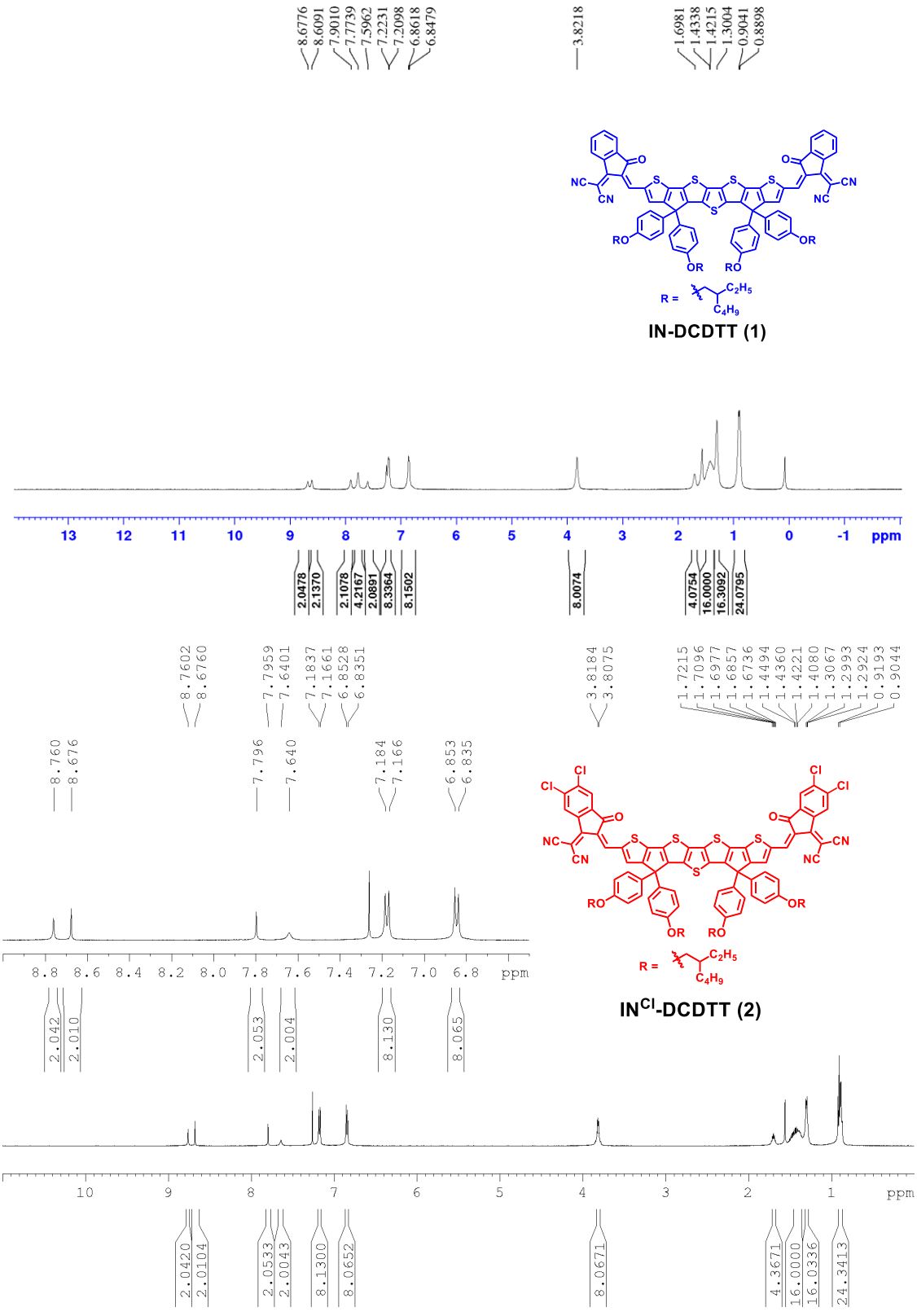
Table S7. The conductivity of the perovskite film made by using CB, 0.2 wt% **IN-DCDTT** (**1**)$_{(CB)}$**,** 0.2 wt% **IN^{Cl}-DCDTT** (**2**)$_{(CB)}$ or 0.2 wt% **IN^{Br}-DCDTT** (**3**)$_{(CB)}$ as an anti-solvent.

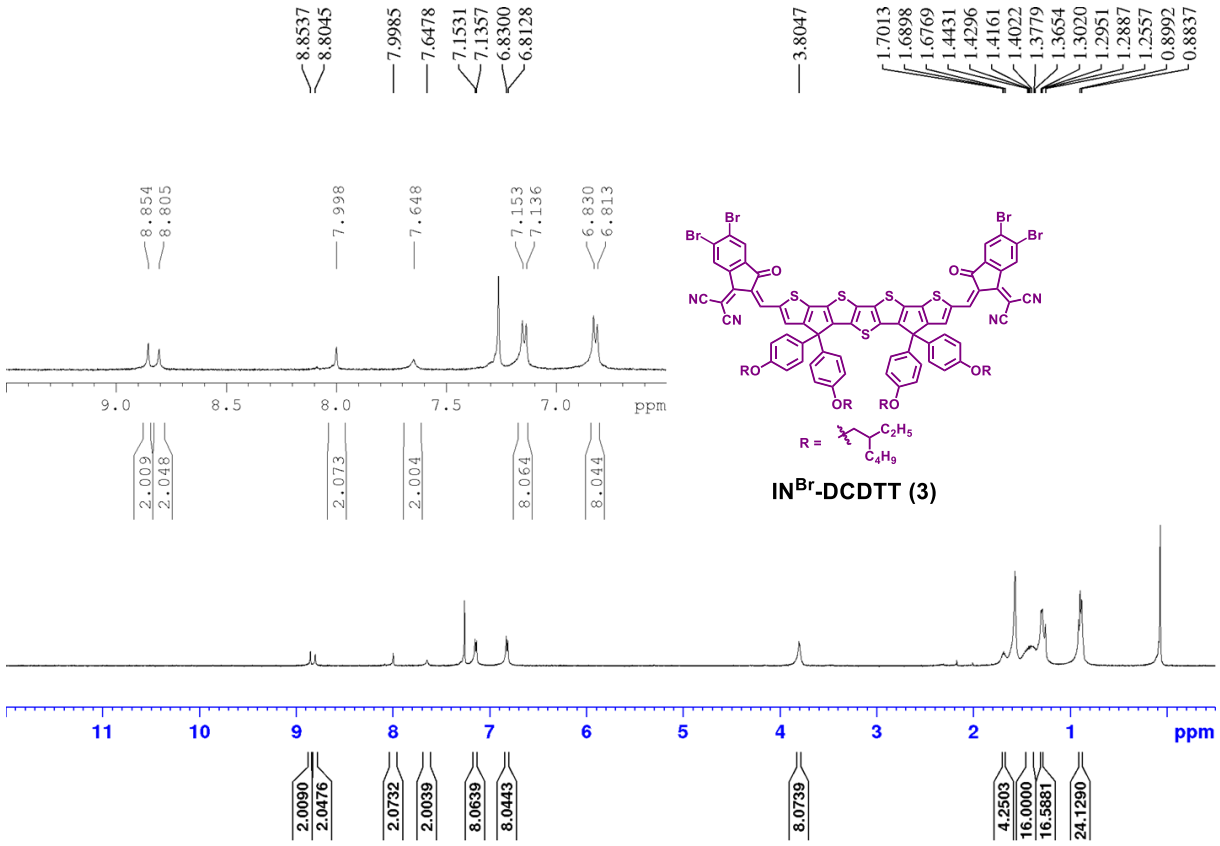
Films	Thickness of film (nm)	I/V (mA/V)	Conductivity (mS/cm)
PSK-CB	~490	27.24	1.33 x 10^{-2}
PSK-IN-DCDTT	~520	33.48	1.75 x 10^{-2}
PSK-IN^{Cl}-DCDTT	~510	51.77	2.64 x 10^{-2}
PSK-IN^{Br}-DCDTT	~490	35.93	1.75 x 10^{-2}

^{1}H NMR spectra of synthesized compounds

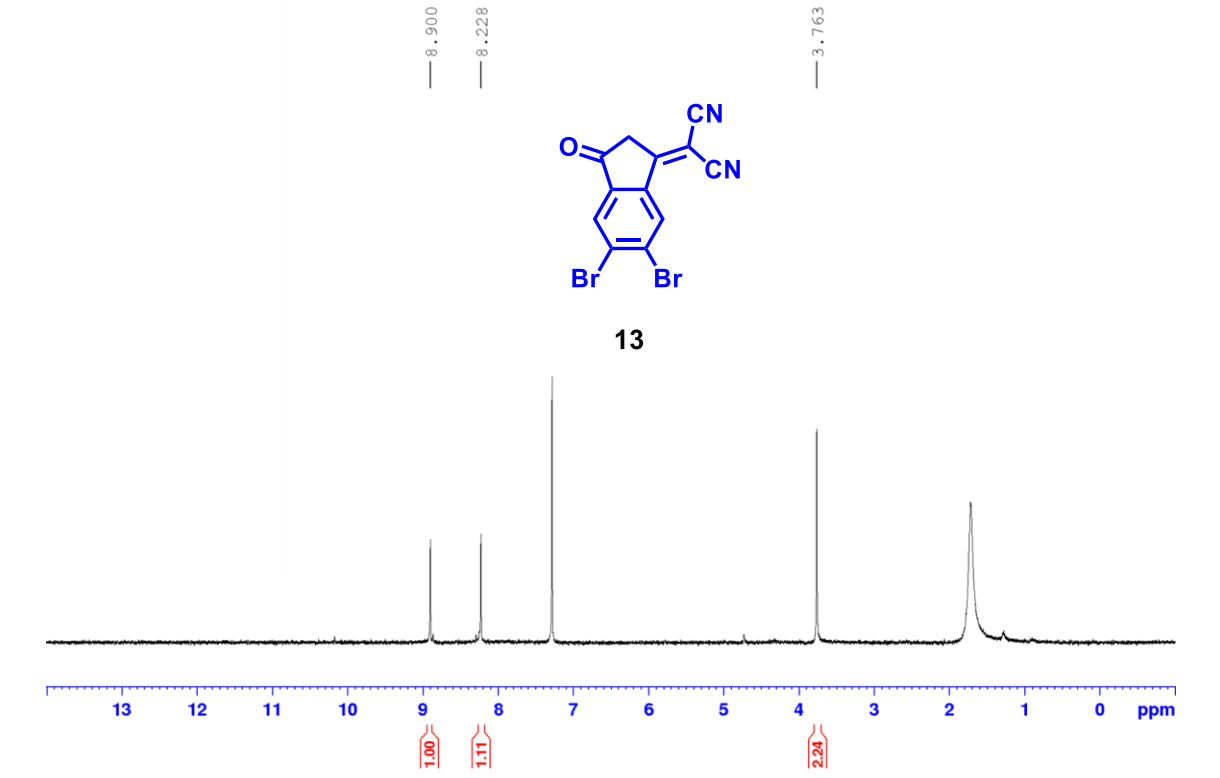


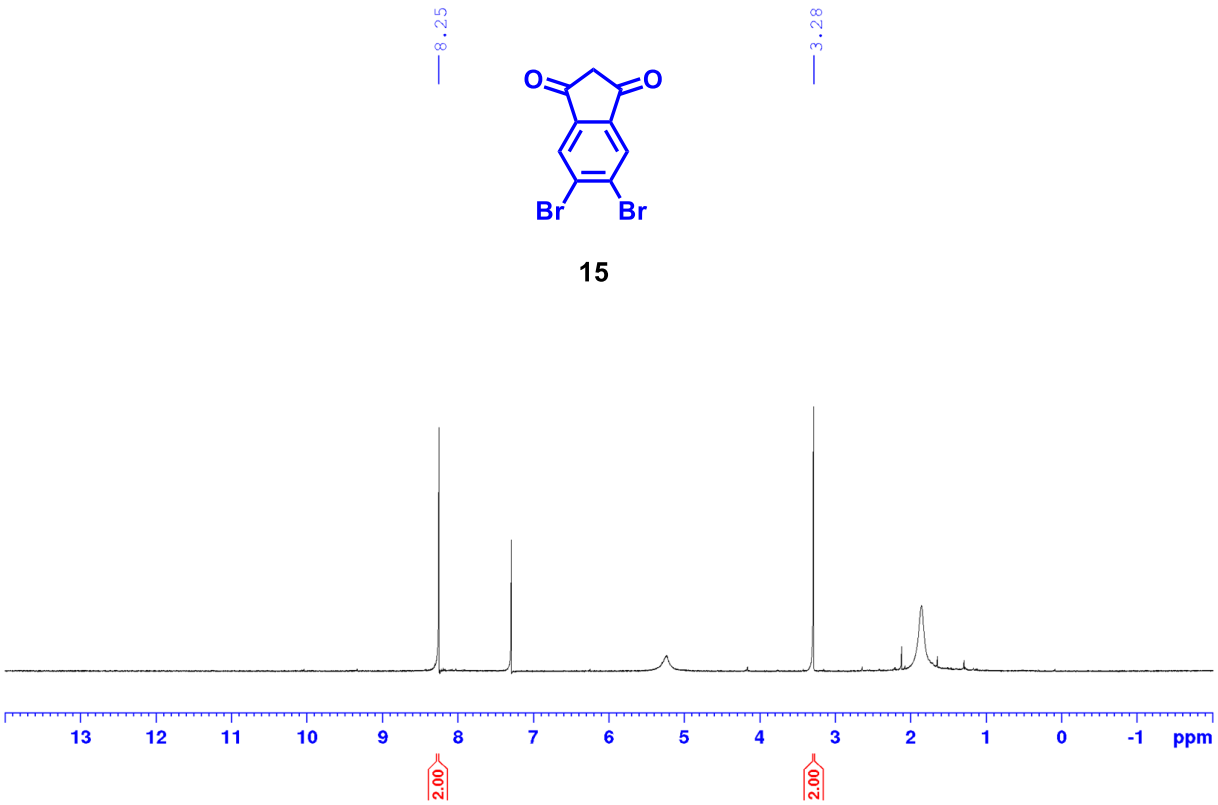

7.1992
7.1894
7.1379
7.1205
7.0254
7.0156
6.7615
6.7440
3.7718
3.7609
1.6928
1.6808
1.6696
1.6574
1.2944
1.2863
1.2736
1.2667
0.9048
0.8957
0.8915
0.8775
7.199
7.189
7.138
7.121
7.025
7.016
6.762
6.744
S
RO
OR
R =
C2H5
C4H9
9
7.3 7.2 7.1 7.0 6.9 6.8 6.7 ppm
2.000
8.022
2.000
8.084
10 9 8 7 6 5 4 3 2 1 ppm
2.0000
8.0219
2.0002
8.0840
8.0996
4.3928
32.3240
24.8921
9.8030
7.6262
7.1149
7.0974
6.7809
6.7633
3.7756
3.7648
1.6833
1.6715
1.6597
1.4464
1.4328
1.4198
1.4058
1.3922
1.3811
1.3694
1.2979
1.2903
1.2843
0.9076
7.626
7.115
7.097
6.781
6.763
O
H
10
7.8 7.6 7.4 7.2 7.0 6.8 ppm
2.094
8.000
8.089
10 9 8 7 6 5 4 3 2 1 ppm
2.0006
2.0936
8.0000
8.0889
8.0503
4.1220
16.3004
16.5868
24.2676


8.6776
8.6091
7.9010
7.7739
7.5962
7.2231
7.2098
6.8618
6.8479
3.8218
1.6981
1.4338
1.4215
1.3004
0.9041
0.8898
IN-DCDTT (1)
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 ppm
2.0478
2.1370
2.1078
4.2167
2.0891
8.3364
8.1502
8.0074
4.0754
16.0000
16.3092
24.0795
8.7602
8.6760
7.7959
7.6401
7.1837
7.1661
6.8528
6.8351
3.8184
3.8075
1.7215
1.7096
1.6977
1.6857
1.6736
1.4494
1.4360
1.4221
1.4080
1.3067
1.2993
1.2924
0.9193
0.9044
8.760
8.676
7.796
7.640
7.184
7.166
6.853
6.835
IN^Cl-DCDTT (2)
8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 ppm
2.042
2.010
2.053
2.004
8.130
8.065
10 9 8 7 6 5 4 3 2 1 ppm
2.0420
2.0104
2.0533
2.0043
8.1300
8.0652
8.0671
4.3671
16.0000
16.0336
24.3413


8.8537
8.8045
7.9985
7.6478
7.1531
7.1357
6.8300
6.8128
3.8047
1.7013
1.6898
1.6769
1.4431
1.4296
1.4161
1.4022
1.3779
1.3654
1.3020
1.2951
1.2887
1.2557
0.8992
0.8837
8.854
8.805
7.998
7.648
7.153
7.136
6.830
6.813
9.0
8.5
8.0
7.5
7.0
ppm
2.009
2.048
2.073
2.004
8.064
8.044
Br
NC
CN
O
S
RO
OR
R =
C_2H_5
C_4H_9
11
10
9
8
7
6
5
4
3
2
1
ppm
2.0090
2.0476
2.0732
2.0039
8.0639
8.0443
8.0739
4.2503
16.0000
16.5881
24.1290

IN^{Br}-DCDTT (3)


8.900
8.228
3.763
CN
O
CN
Br
Br
13
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.11
2.24



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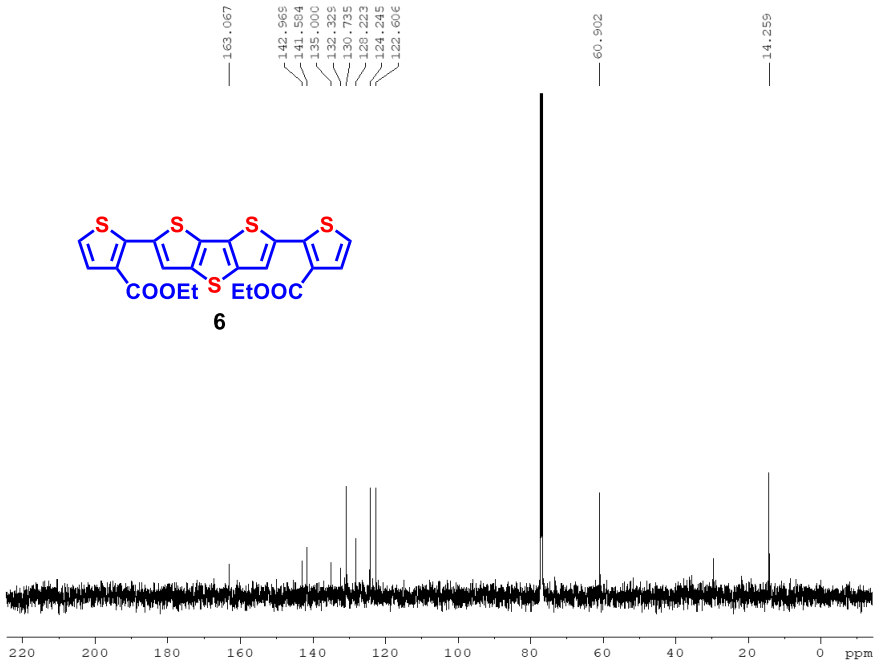
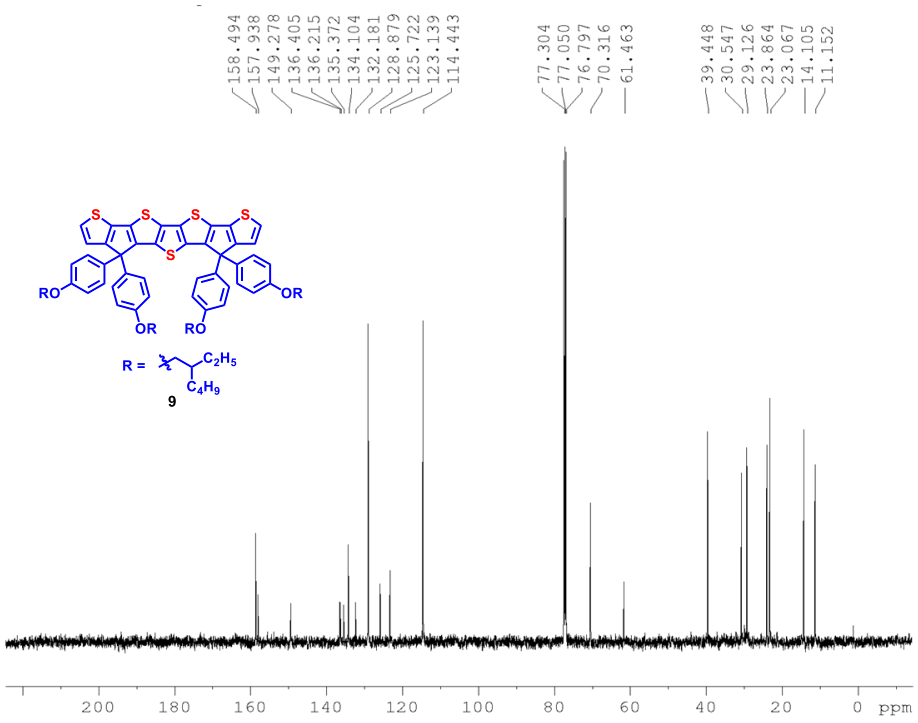
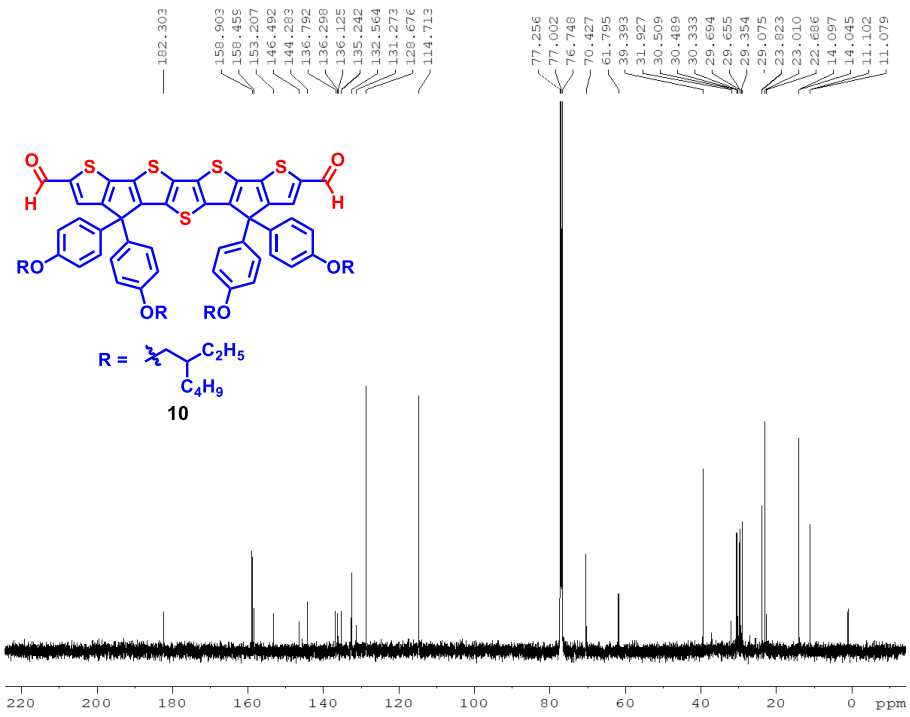
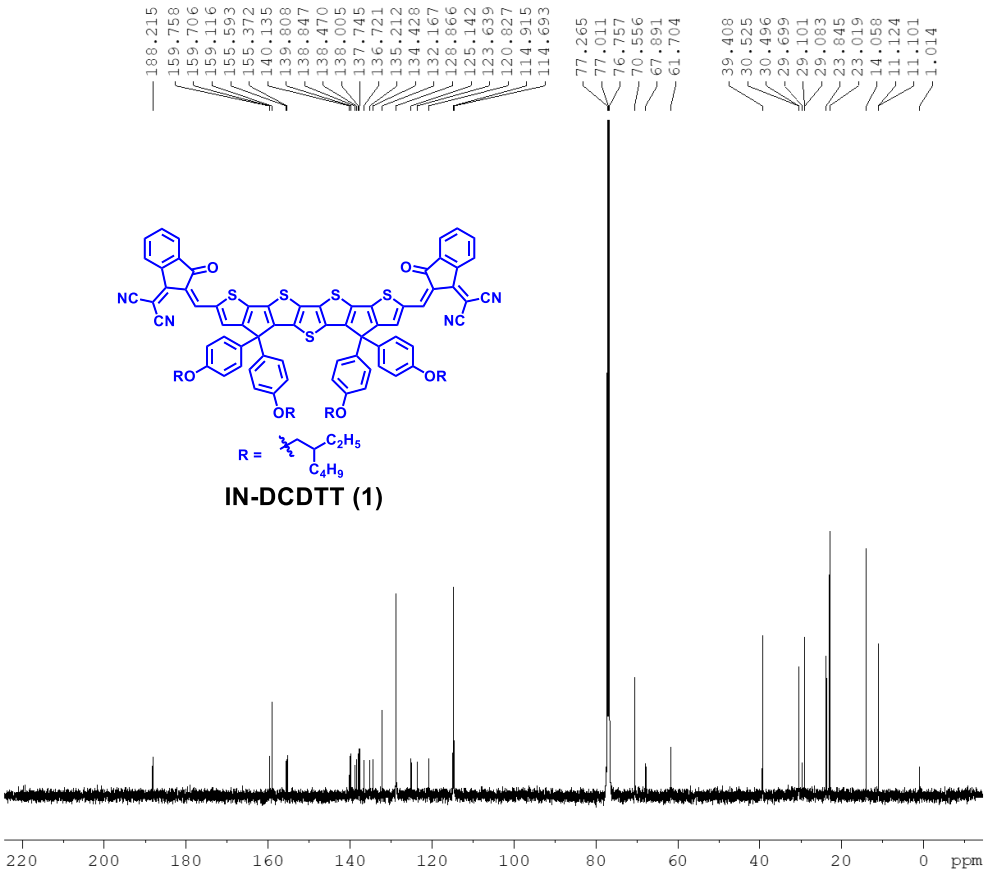
^{13}C NMR spectra of synthesized compounds



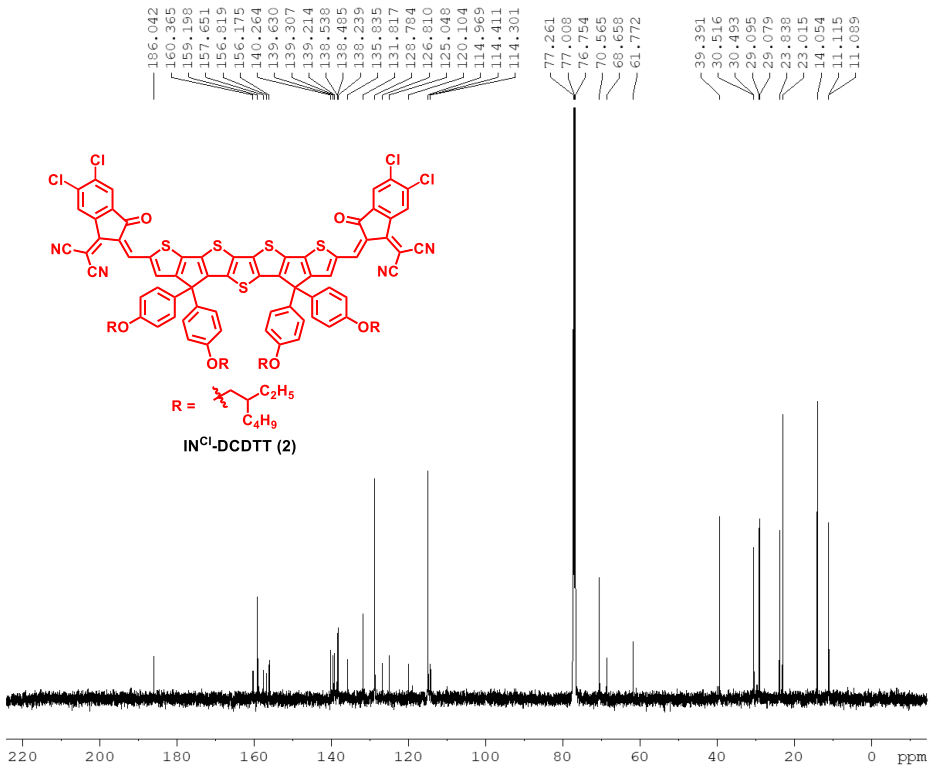



182.303
158.903
158.455
153.207
146.492
144.283
136.792
136.290
136.125
135.242
132.564
131.273
128.676
114.713
77.256
77.002
76.748
70.427
61.795
39.393
31.927
30.509
30.489
30.333
29.694
29.655
29.354
29.075
23.823
23.010
22.686
14.097
14.045
11.102
11.079
O
H
S
RO
OR
R =
C_2H_5
C_4H_9
220
200
180
160
140
120
100
80
60
40
20
0
ppm

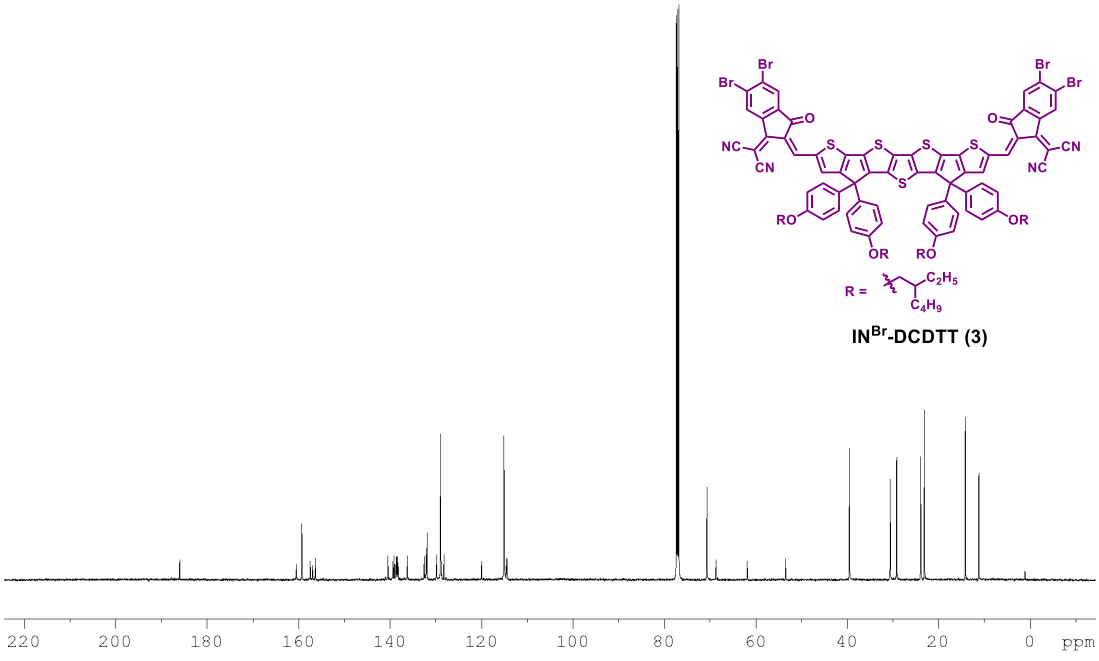
10


188.215
159.758
159.706
159.116
155.593
155.372
140.135
139.808
138.847
138.470
138.005
137.745
136.721
135.212
134.428
132.167
128.866
125.142
123.639
120.827
114.915
114.693
77.265
77.011
76.757
70.556
67.891
61.704
39.408
30.525
30.496
29.699
29.101
29.083
23.845
23.019
14.058
11.124
11.101
1.014
O
NC
CN
S
RO
OR
R =
C_2H_5
C_4H_9
220
200
180
160
140
120
100
80
60
40
20
0
ppm

IN-DCDTT (1)



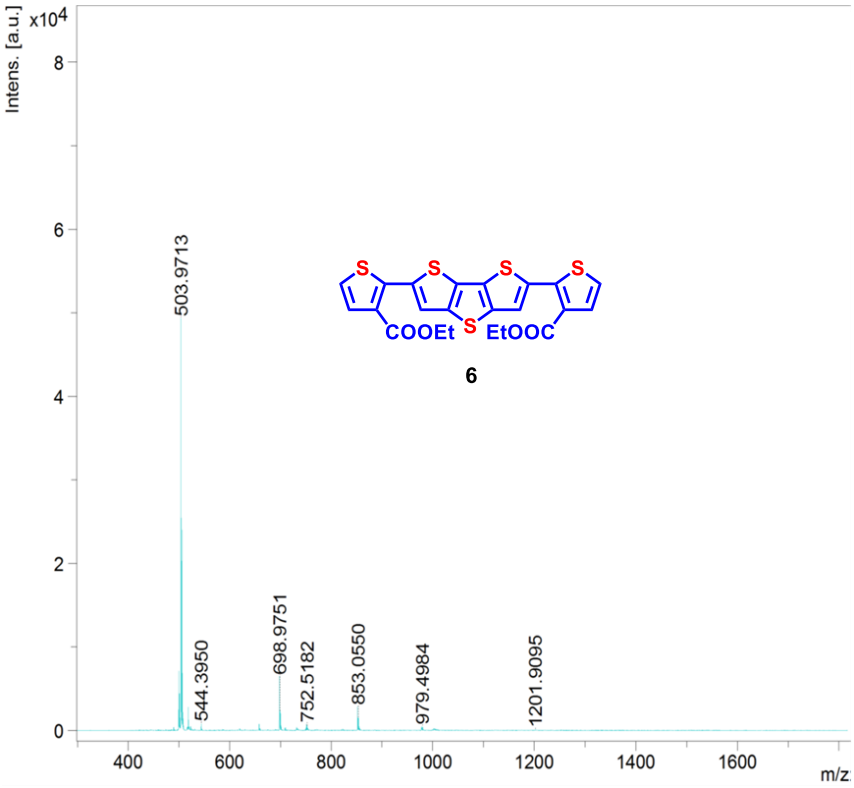
IN^{Cl}-DCDTT (2)



IN^{Br}-DCDTT (3)

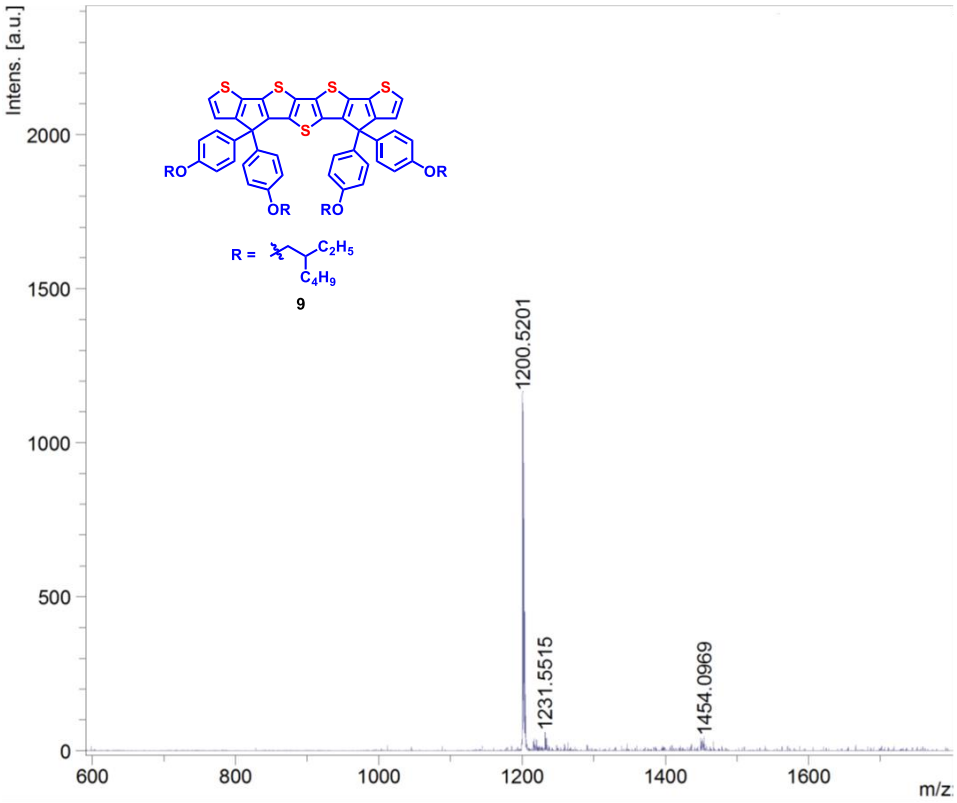
HRMS spectra of synthesized compounds

Formula	Mass	Error	mSigma	DblEq	N rule	Electron Configuration
C 22 H 16 O 4 S 5	503.9647	13.1081	800.7537	15.00	ok	odd

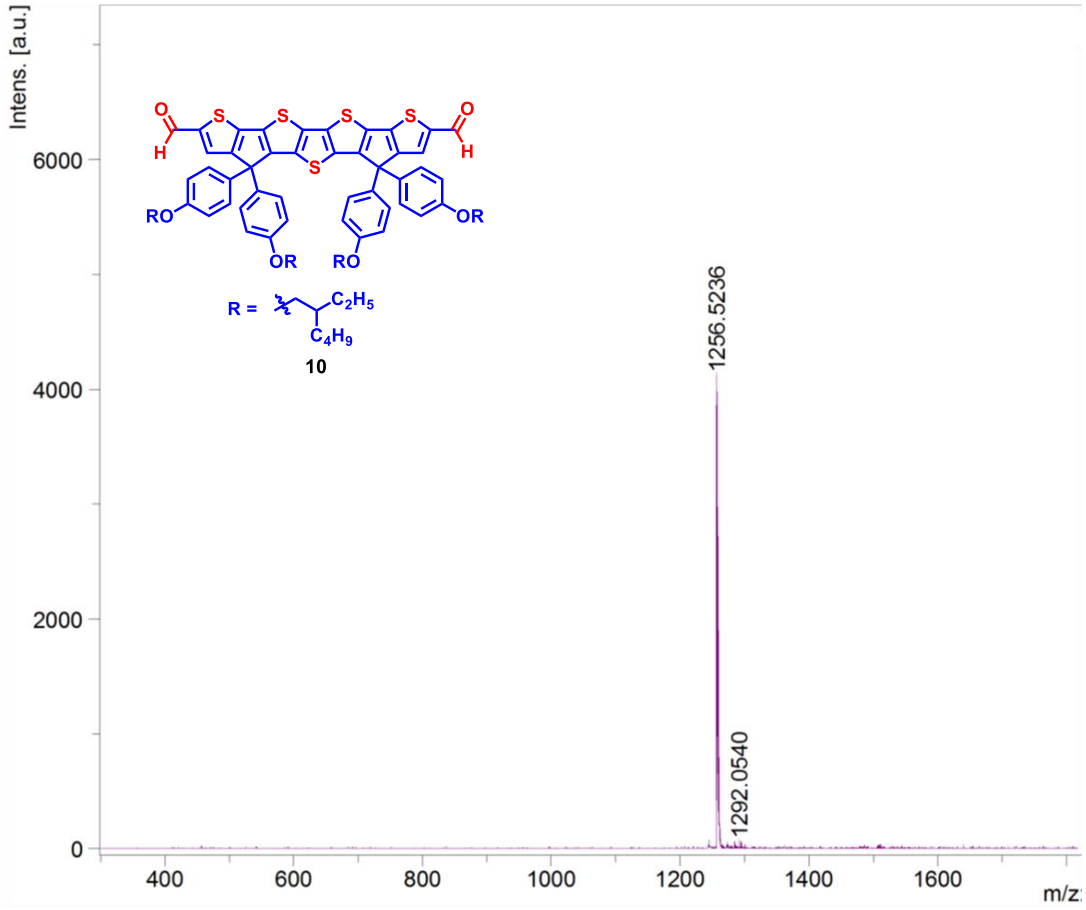


6

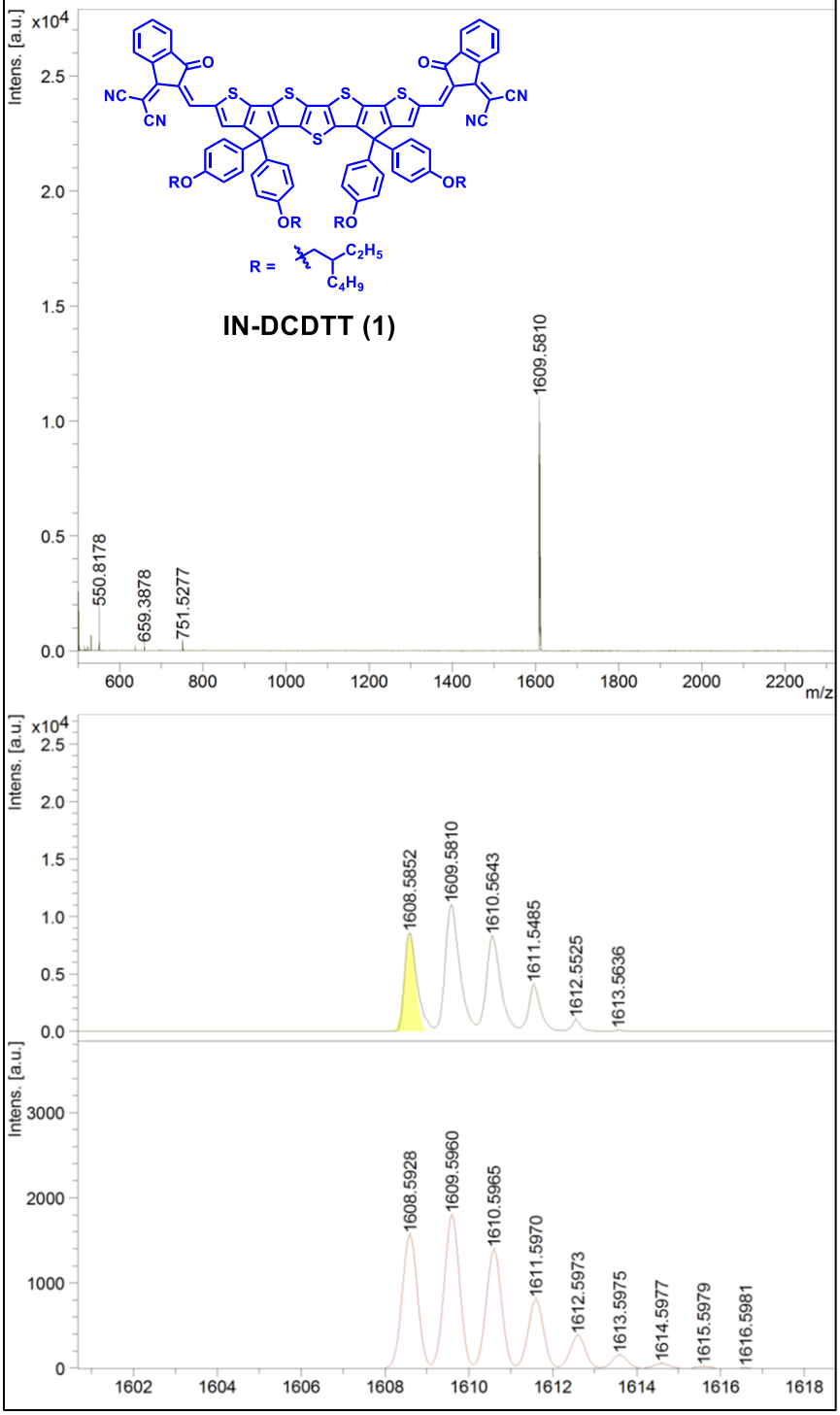
Formula	Mass	Error	mSigma	DblEq	N rule	Electron Configuration
C 74 H 88 O 4 S 5	1,200.5281	6.6369	174.3293	31.00	ok	odd



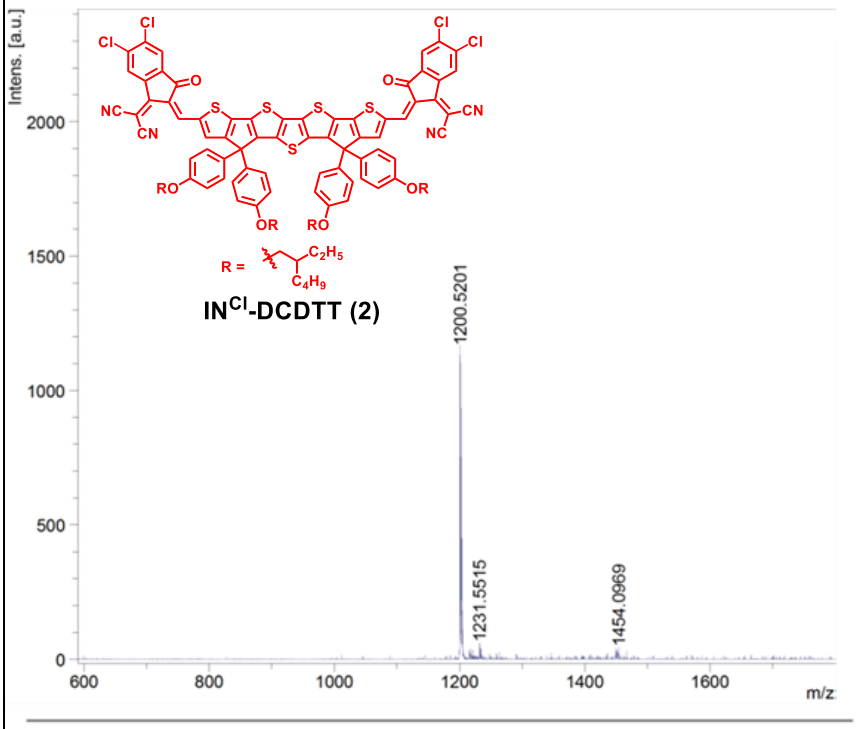
Formula	Mass	Error	mSigma	DblEq	N rule	Electron Configuration
C 76 H 88 O 6 S 5	1,256.5179	4.5387	176.1464	33.00	ok	odd



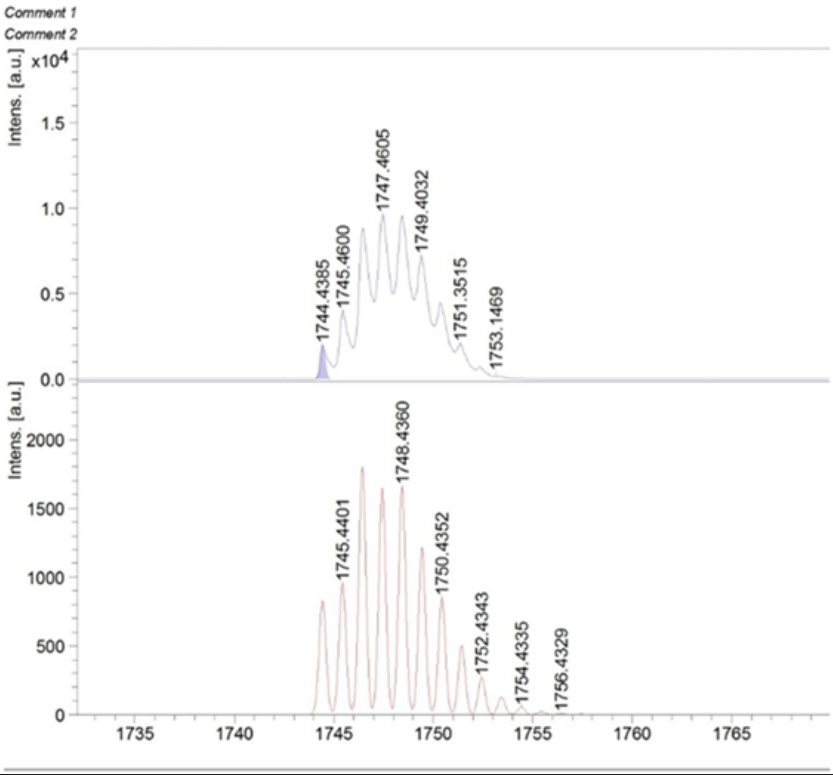
Formula	Mass	Error	mSigma	DblEq	N rule	Electron Configuration
C 100 H 96 N 4 O 6 S 5	1,608.5928	4.7485	66.5103	55.00	ok	odd



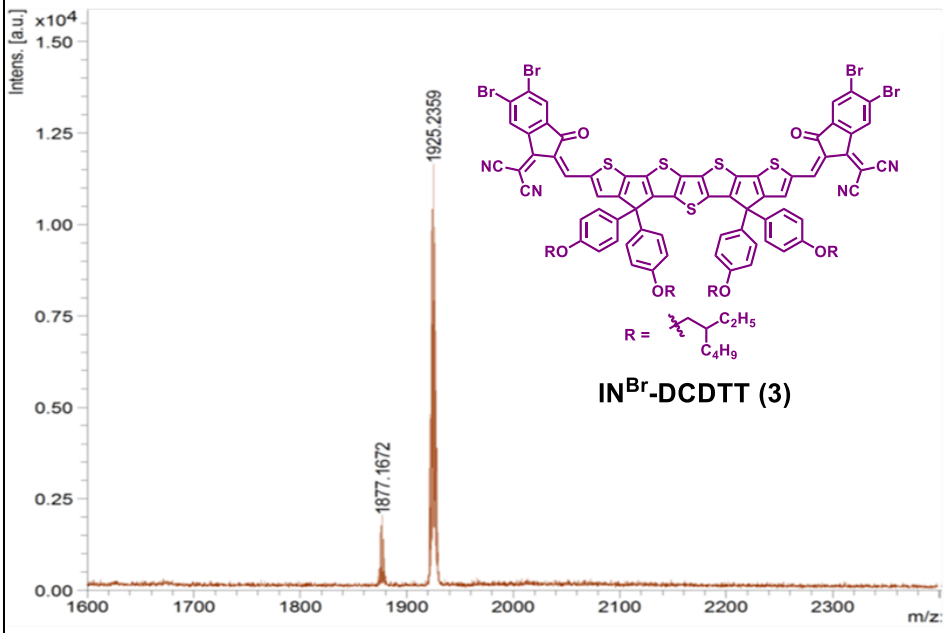
Formula	Mass	Error	mSigma	DblEq	N rule	Electron Configuration
C 100 H 92 Cl 4 N 4 O 6 S 5	1,744.4369	0.9218	94.3430	55.00	ok	odd



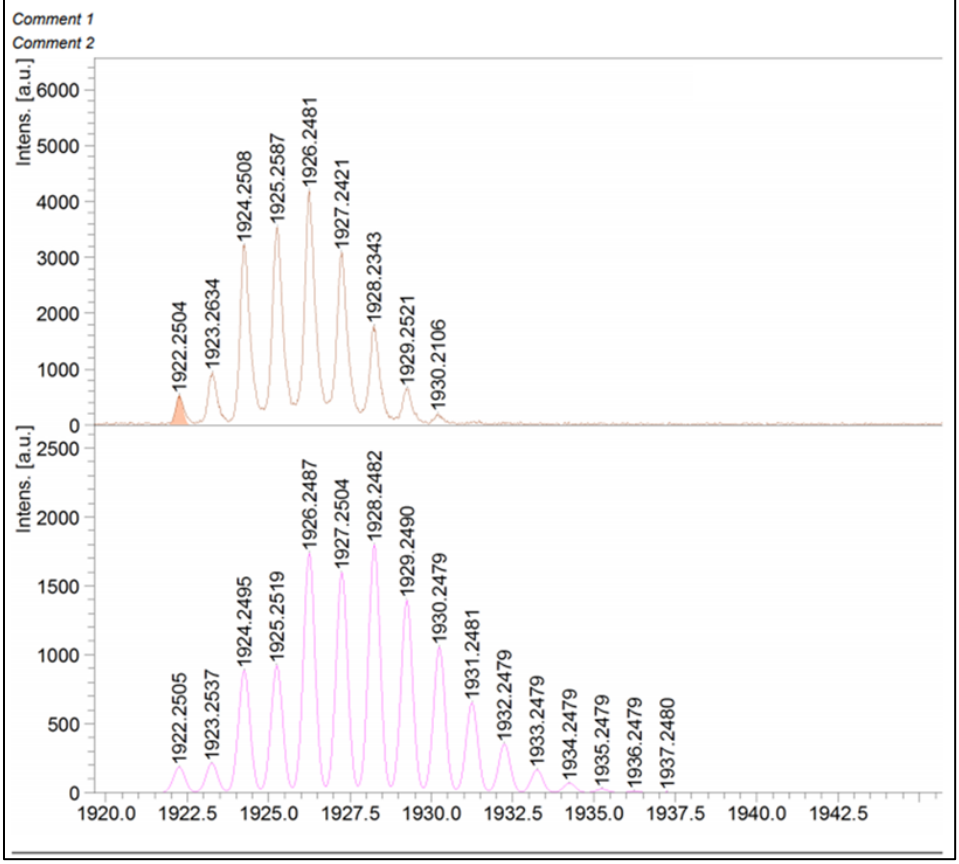
IN^{Cl}-DCDTT (2)



Formula	Mass	Error	mSigma	DblEq	N rule	Electron Configuration
C 100 H 93 Br 4 N 4 O 6 S 5	1,921.2427	0.0002	270.2197	54.50	ok	even



IN^{Br}-DCDTT (3)



References

1. Y. Zhang, P. Wang, M.-C. Tang, D. Barrit, W. Ke, J. Liu, T. Luo, Y. Liu, T. Niu, D.-M. Smilgies, Z. Yang, Z. Liu, S. Jin, M. G. Kanatzidis, A. Amassian, S. F. Liu and K. Zhao, *J. Am. Chem. Soc.*, 2019, **141**, 2684-2694.
2. F. N. Mott and R. W. Gurney, *Electronic Process in Ionic Crystals,*, 1940, 1st ed, Oxford University Press.
3. A. G. Baradwaj, L. Rostro, M. A. Alam and B. W. Boudouris, *Appl. Phys. Lett.*, 2014, **104**, 213306.