Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Significant enhancement of photovoltaic performance of organic small molecule acceptor *via* side-chain engineering

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Experimental Section

Measurements: ^{1}H NMR and ^{13}C NMR spectra were measured in $CDCl_3$ on Bruker AV 400 MHz FT-NMR spectrometer. Mass spectra were obtained with a Shimadzu QP2010 spectrometer. UV-vis absorption spectrum was recorded on a UV-Vis-NIR Spectrophotometer of Agilent Technologies Cary Series, in which the extinction coefficient was defined by the absorption intensity of the active layer with a thick of 1 cm (*ca.* 80 nm for IT-M, POIT-M and MOIT-M). The electrochemical cyclic voltammetry (CV) was taken on a Electrochemical Workstation of Zahner Ennium

IM6 in a acetonitrile solution with 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6), where glassy carbon disk, Ag/Ag^+ electrode, and Pt wire as working electrode, reference electrode and counter electrode, respectively. Photoluminescence (PL) spectra were taken on an Edinburgh Instrument FLS 980. Atomic force microscopy (AFM) measurements were performed on a Dimension 3100 (Veeco) Atomic Force Microscope in the tapping mode. Transmission electron microscopy (TEM) was performed using a Tecnai G2 F20 S-TWIN instrument at 200 kV accelerating voltage, where the PTZ1:acceptor films were prepared by the following processing techniques for the TEM measurement: The PTZ1:acceptor films were spin-cast on the ITO/PEDOT:PSS substrates, and then the resulting substrates with the PTZ1:acceptor films were submerged in deionized water to make these PTZ1:acceptor films float onto the water/air interface, and finally the floated PTZ1:acceptor films were picked up on unsupported 200 mesh copper grids. Grazing incidence wide-angle X-ray scattering (GIWAXS) measurements were performed at beamline 7.3.3 at the Advanced Light Source.[1] Samples were prepared on Si substrates using identical blend solutions as those used in devices. The 10 keV X-ray beam was incident at a grazing angle of 0.12°-0.16°, selected to maximize the scattering intensity from the samples. The scattered x-rays were detected using a Dectris Pilatus 2M photon counting detector. The crystal coherence length (CCL) was defined as $\mathrm{CCL} = 0.9 \times (2\pi/\mathrm{FWHM})$ (Å), where FWHM is the full width at half maximum of the corresponding diffraction peak.

Device Fabrication and characterization: The PSC devices structure was ITO/PEDOT:PSS/active layer/PFN-Br/Al. In an ultrasonic bath, the ITO-coated glass (10 Ω/sq) was cleaned with deionized water, acetone and isopropanol, respectively. After oxygen plasma cleaning for 10 min, and then a 30 nm thick poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (Bayer Baytron 4083) anode buffer layer was spin-cast onto the ITO substrate and then dried by baking in an oven at 150 ^{o}C for 15 min. In a nitrogen golve box containing less than 5 ppm moisture and oxygen, the active layers were then deposited atop the PEDOT:PSS layer by spin-coating a CB solution of PTZ1:acceptor (w:w, 1:1) with a blend concentration of 10 mg/mL. The thickness of the active layers was about 100 nm and controlled by adjusting the spin speed during the spin-coating process and measured by a KLA Tencor D-100 profilometer. The poly[(9,9-bis(3'-(*N*,*N*-dimethyl)-nethylammoiniumpropyl)-2,7-fluorene)-*alt*-2,7-(9,9-dioctylfluorene)]dibromide (PFN-Br) was then deposited on top of the active layer by spin-coating a ethanol solution with a concentration of 0.5 mg/mL. Finally, 80 nm Al was evaporated on the photosensitive layer under vacuum at a pressure of *ca.* 4×10^{-4} Pa, and through a shadow mask to determine the active area of the devices (~4×5 mm^2). The PCE values of the PSCs were measured under a illumination of AM 1.5G (100 mW/cm^2) using a SS-F5-3A solar simulator (AAA grade, 50×50 mm^2 photobeam size) of Enli Technology CO., Ltd. A 2×2 cm^2 monocrystalline silicon reference cell (SRC-00019) was purchased from Enli Technology CO., Ltd. Mask made by laser beam cutting technology with a defined area of 0.2 cm^2 was used to determine the effective area for accurate measurement. All the measurements with mask or without mask gave consistent results with relative errors within 2%. PCE statistics were obtained using 10 or 20 individual devices fabricated under the same conditions. The EQE was measured by Solar Cell Spectral Response Measurement System QE-R3011 of Enli Technology CO., Ltd. The light intensity at each wavelength was calibrated with a standard single crystal Si photovoltaic cell. To study the charge generation and dissociation processes of the PSCs, plots of the photocurrent (J_{ph}) versus effective voltage (V_{eff}) of the PSCs were measured. Here, J_{ph} and V_{eff} are defined as $J_{ph} = J_L - J_D$ and $V_{eff} = V_0 - V_{appl}$, respectively, where J_D and J_L are the photocurrent densities in the dark and under the illumination, and V_{appl} is the applied bias voltage and V_0 is the voltage at which $J_{ph} = 0$, respectively.[2] The J_{ph} reaches the saturation current density (J_{sat}) at high V_{eff} (≥ 2 V in this case).

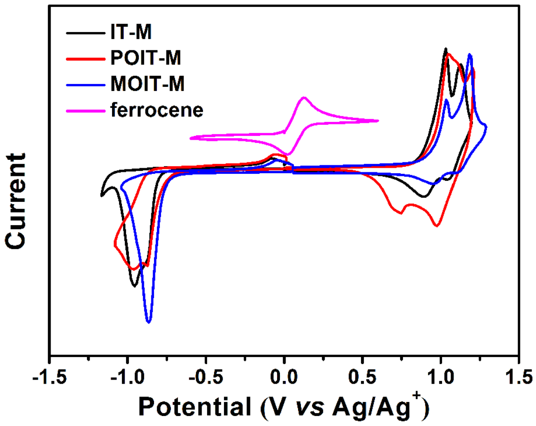


Fig. S1 Cyclic voltammograms of IT-M, POIT-M and MOIT-M films on a glassy carbon electrode measured in a 0.1 mol/L Bu_4NPF_6 acetonitrile solution at a scan rate of 50 mV/s.

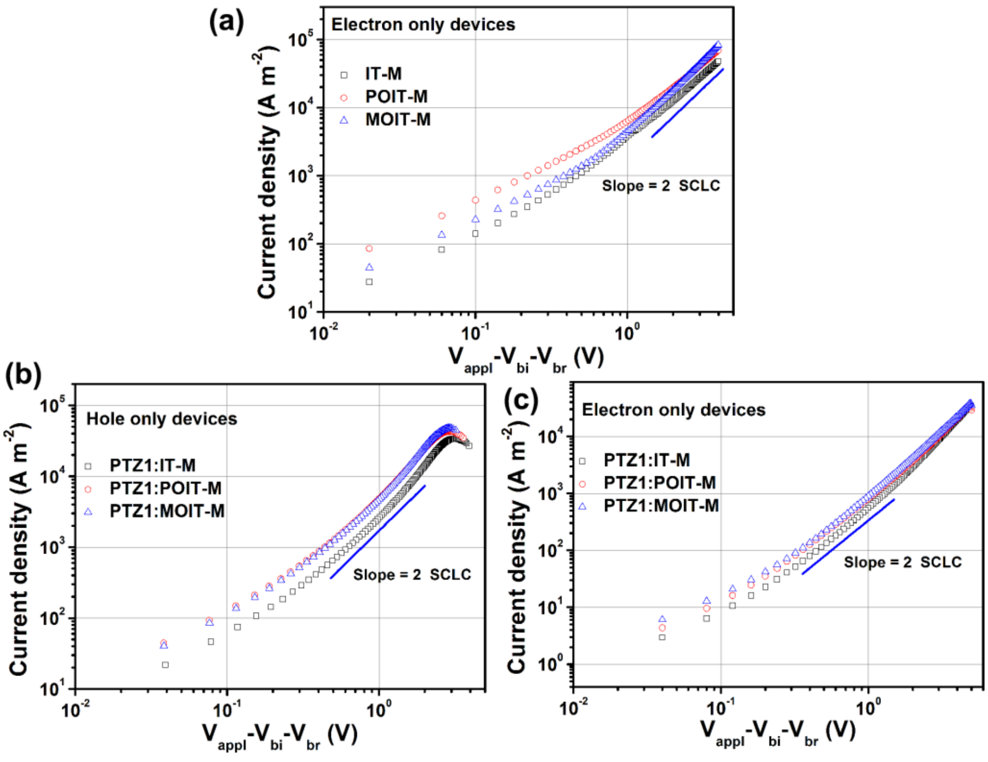


Fig. S2 The *J*-*V* curves of (a) and (c) the electron-only devices with a structure of ITO/ZnO/acceptor or PTZ1:acceptor/Ca/Al; (b) the hole-only devices with a structure of ITO/PEDOT:PSS/PTZ1:acceptor/MoO_3/Al according to the SCLC model.

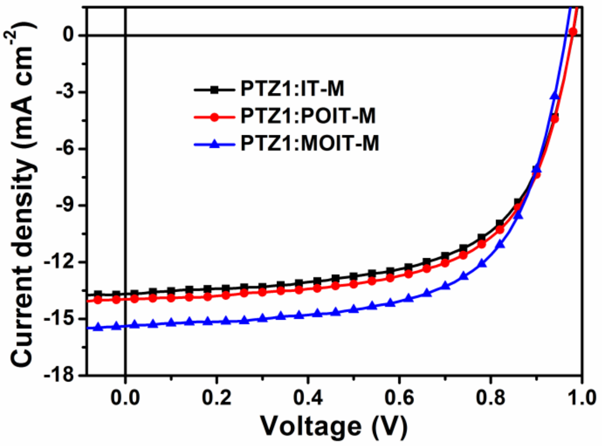


Fig. S3. *J*-*V* curves of the PSCs with Ca as buffer layer under the illumination of AM 1.5G, 100 mW/cm^2.

Table S1 Photovoltaic parameters of the PTZ1-based PSCs with Ca as buffer layer under the illumination of AM 1.5G, 100 mW/cm^2.

Acceptor	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE^a [%]
IT-M	0.98	13.6	62.6	8.3 (8.1)
POIT-M	0.98	14.0	63.3	8.7 (8.4)
MOIT-M	0.96	15.4	64.4	9.5 (9.3)

a) The PCE values in brackets are average efficiency from 10 devices.

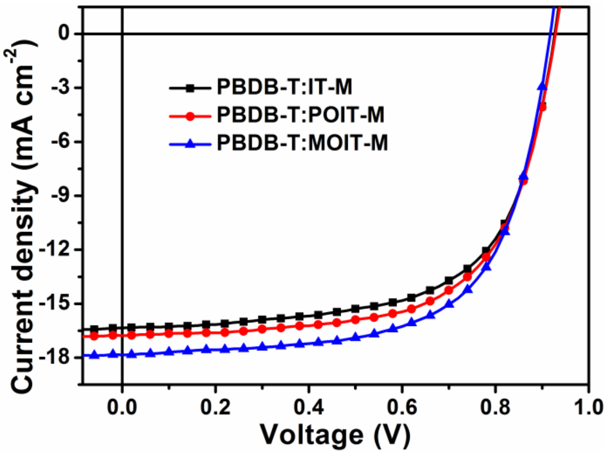
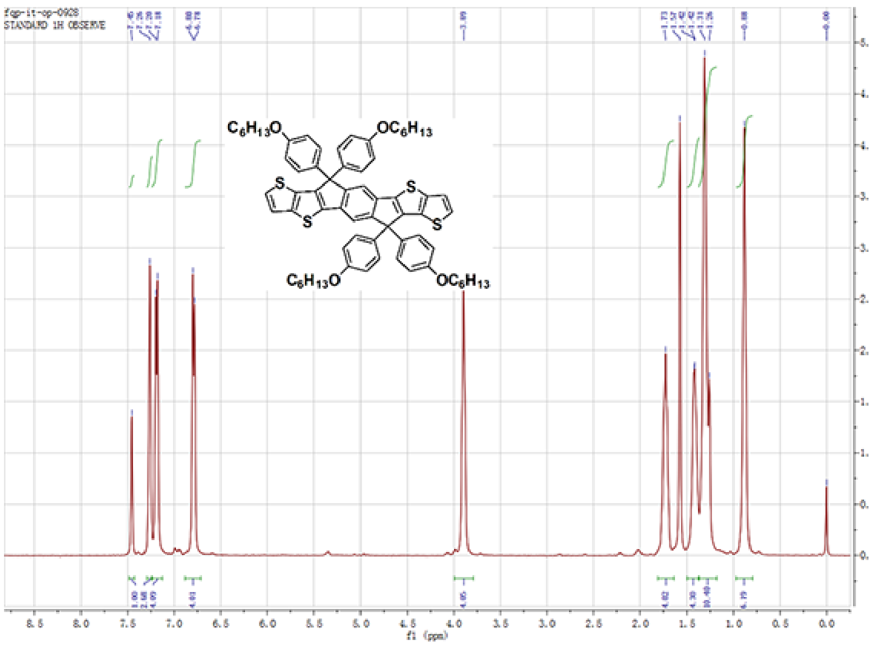


Fig. S4. *J*-*V* curves of the PSCs based on PBDB-T as donor under the illumination of AM 1.5G, 100 mW/cm^2.

Table S2 Photovoltaic parameters of the PSCs based on PBDB-T as donor under the illumination of AM 1.5G, 100 mW/cm^2.

Acceptor	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE^a [%]
IT-M	0.93	16.3	63.8	9.7 (9.5)
POIT-M	0.93	16.8	64.3	10.0 (9.7)
MOIT-M	0.92	17.8	65.5	10.7 (10.4)

a) The PCE values in brackets are average efficiency from 10 devices.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7.25
7.20
7.18
6.80
6.78
3.89
1.73
1.57
1.42
1.40
1.31
1.26
0.88
0.00
1.00
2.98
4.09
4.01
4.05
4.02
4.30
10.40
6.19
$C_6H_{13}O$
OC_6H_{13}
S
$C_6H_{13}O$
OC_6H_{13}
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
f1 (ppm)
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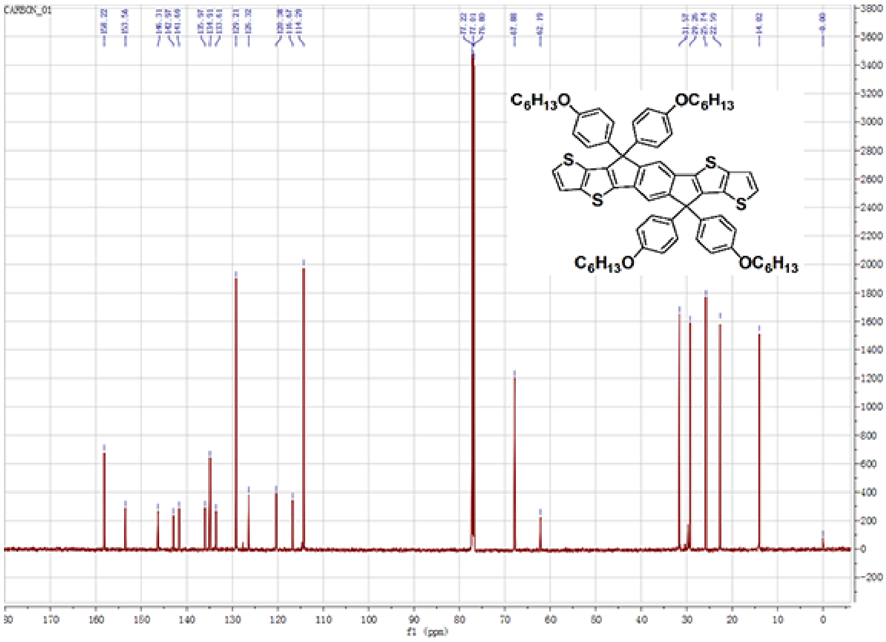
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0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129.21
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116.67
114.29
77.22
77.01
76.80
67.88
62.19
31.52
29.26
25.74
22.59
14.02
0.00
$C_6H_{13}O$
OC_6H_{13}
S
$C_6H_{13}O$
OC_6H_{13}
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
3800
3600
3400
3200
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2800
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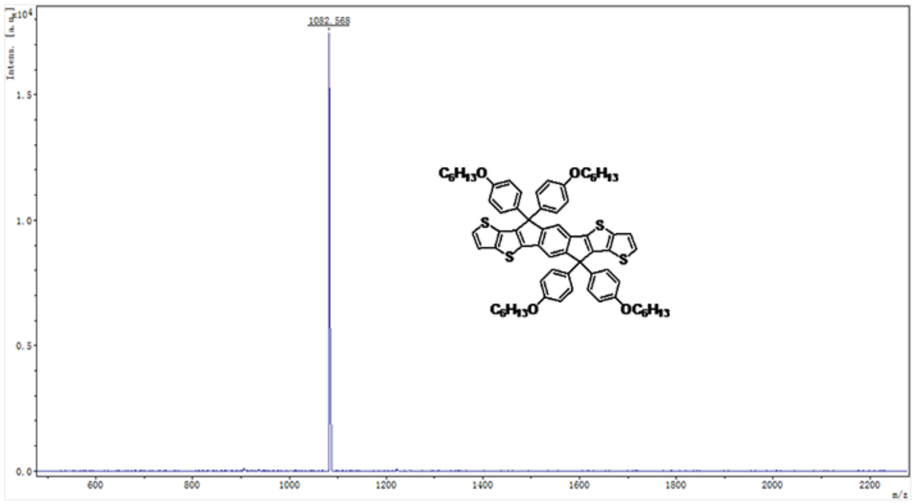
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200


$\times10^4$
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0.5
0.0
600
800
1000
1200
1400
1600
1800
2000
2200
m/z
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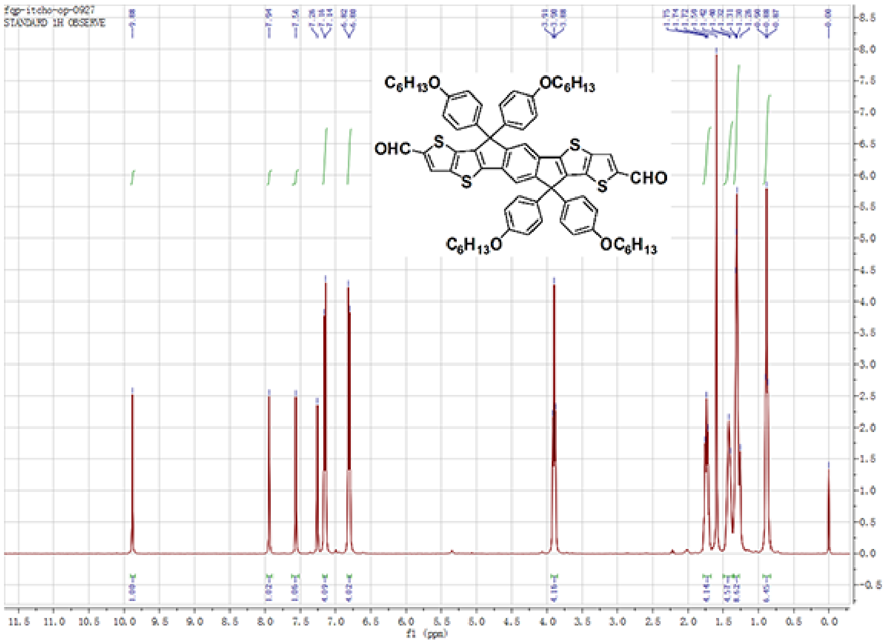
OC_6H_{13}
S
$C_6H_{13}O$
OC_6H_{13}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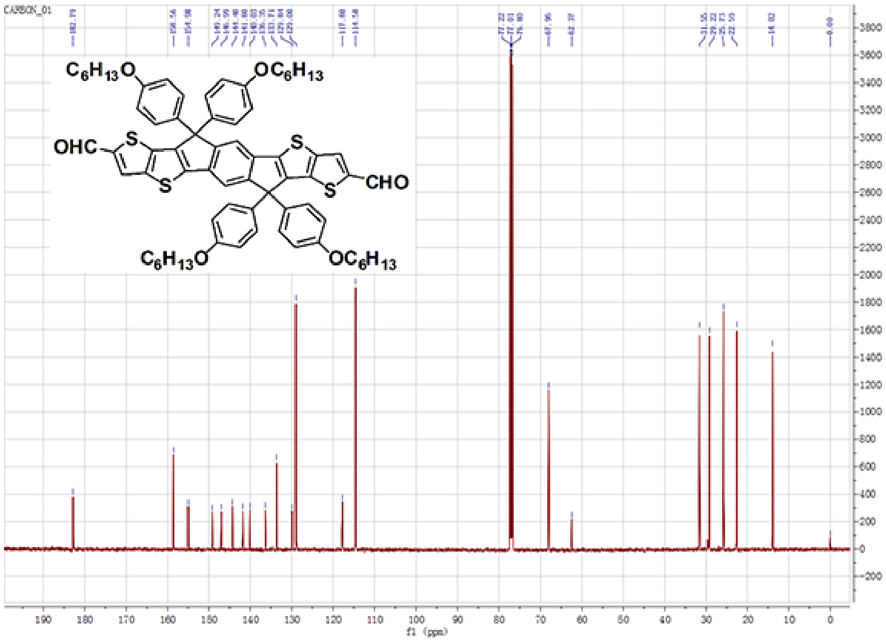
7.94
7.56
7.26
7.16
7.14
6.82
6.80
3.91
3.90
3.88
1.75
1.74
1.72
1.59
1.42
1.40
1.32
1.31
1.30
1.28
0.90
0.88
0.87
0.00
$C_6H_{13}O$
OC_6H_{13}
OHC
S
S
S
S
CHO
$C_6H_{13}O$
OC_6H_{13}
1.00
1.02
1.06
4.09
4.02
4.16
4.14
4.57
8.62
6.45
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
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 -0.5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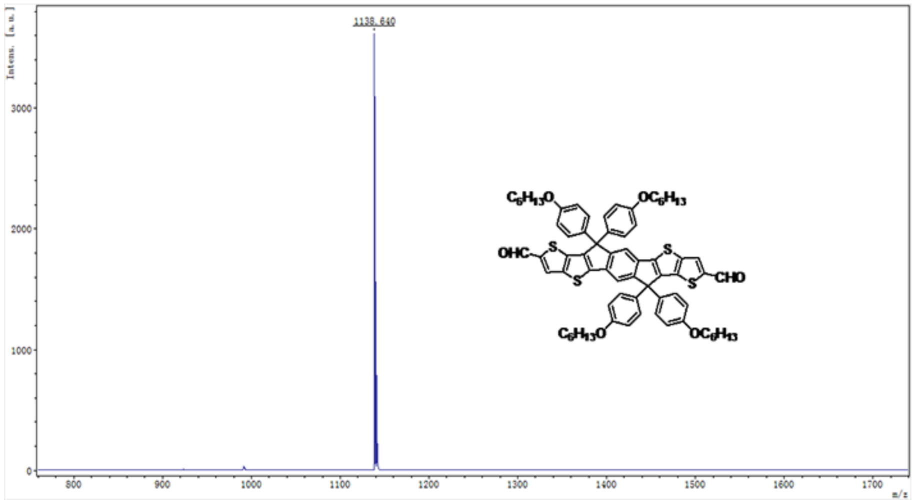
149.24
146.99
144.46
141.88
140.03
136.35
133.71
129.84
129.08
117.88
114.58
77.22
77.01
76.80
67.95
62.37
31.55
29.22
25.73
22.59
14.02
0.00
$C_6H_{13}O$
OC_6H_{13}
OHC
S
S
S
S
CHO
$C_6H_{13}O$
OC_6H_{13}
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
3800 3600 3400 3200 3000 2800 2600 2400 2200 2000 1800 1600 1400 1200 1000 800 600 400 200 0 -200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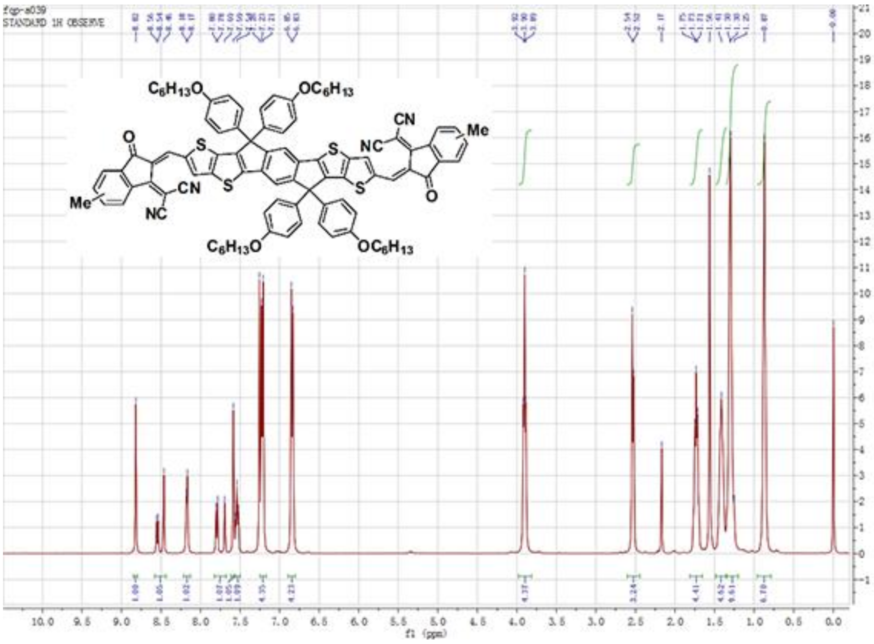
2000
1000
0
800 900 1000 1100 1200 1300 1400 1500 1600 1700
m/z
$C_6H_{13}O$
OC_6H_{13}
OHC
S
S
S
S
CHO
$C_6H_{13}O$
OC_6H_{13}


fqp-a039
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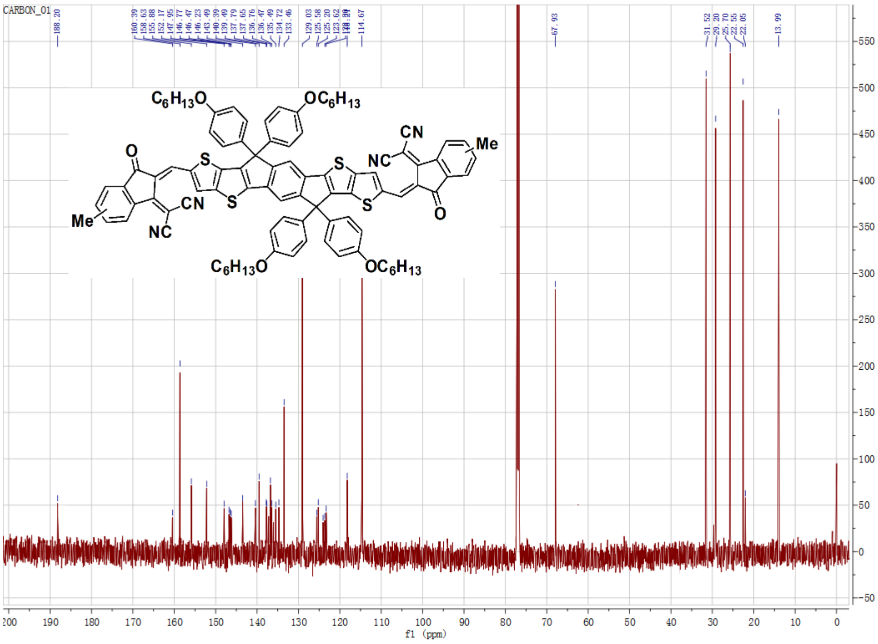
C6H13O
OC6H13
CN
NC
Me
O
S
CN
NC
Me
O
C6H13O
OC6H13
1.00
1.05
1.02
1.07
1.05
1.09
4.35
4.21
4.37
3.24
4.41
4.52
9.61
6.70
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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139.49
137.79
137.65
136.76
136.47
135.49
134.72
133.46
129.03
125.58
125.20
123.62
114.67
67.93
31.52
29.20
25.70
22.55
22.05
13.99
C6H13O
OC6H13
CN
NC
Me
O
S
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
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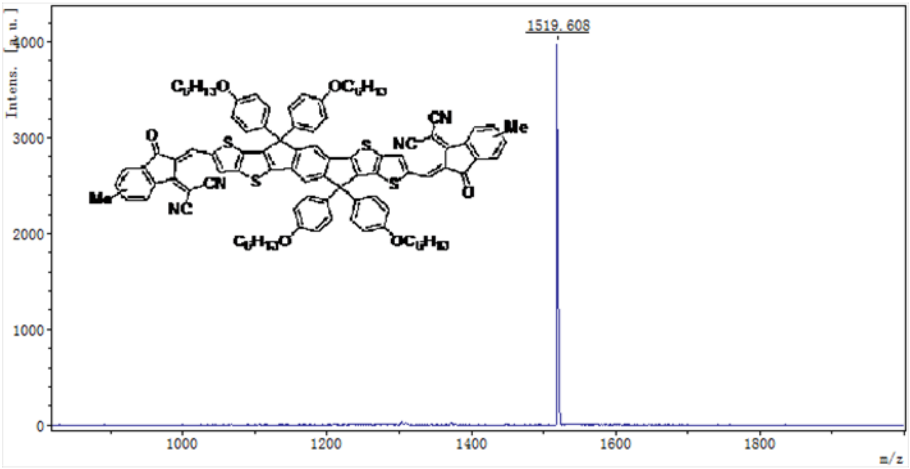
450
400
350
300
250
200
150
100
50
0
-50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1600
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m/z
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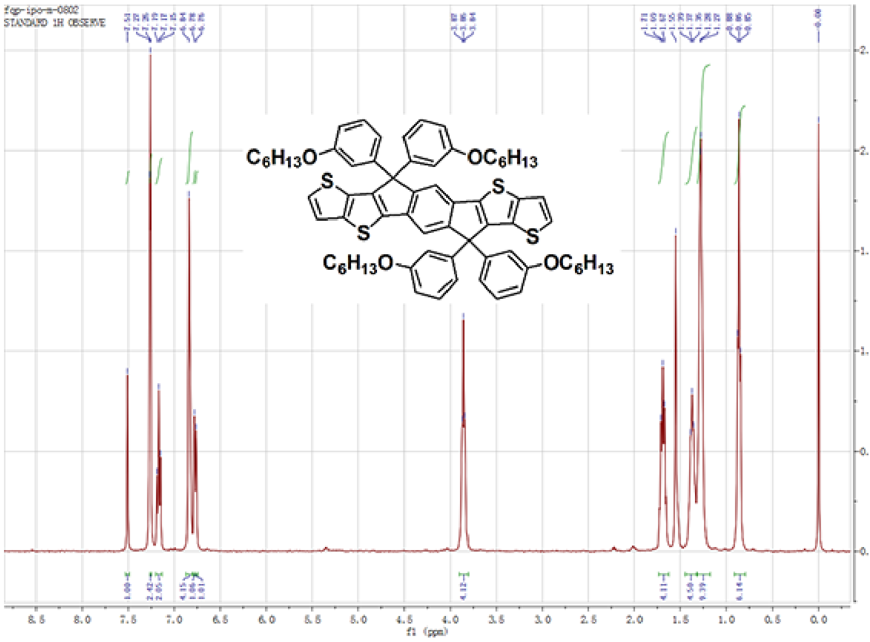
OC6H13
CN
NC
Me
O
S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7.27
7.26
7.19
7.17
7.15
6.84
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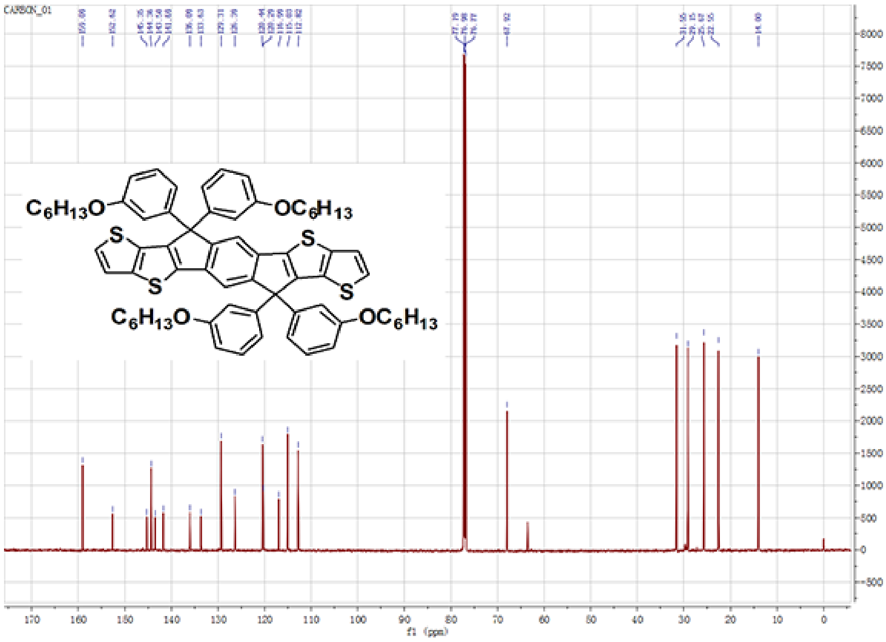
6.76
3.87
3.85
3.84
1.73
1.70
1.67
1.55
1.39
1.37
1.36
1.28
1.27
0.88
0.86
0.85
0.00
1.00
2.42
2.05
4.15
1.06
1.01
4.12
4.11
4.50
9.39
6.14
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
2.5
2.0
1.5
1.0
0.5
0.0
$C_6H_{13}O$
OC_6H_{13}
S
S
S
S
$C_6H_{13}O$
OC_6H_{13}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152.62
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144.36
143.58
141.68
136.09
133.63
129.31
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116.98
115.03
112.82
77.19
76.98
76.77
67.92
31.55
29.15
25.67
22.55
14.00
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
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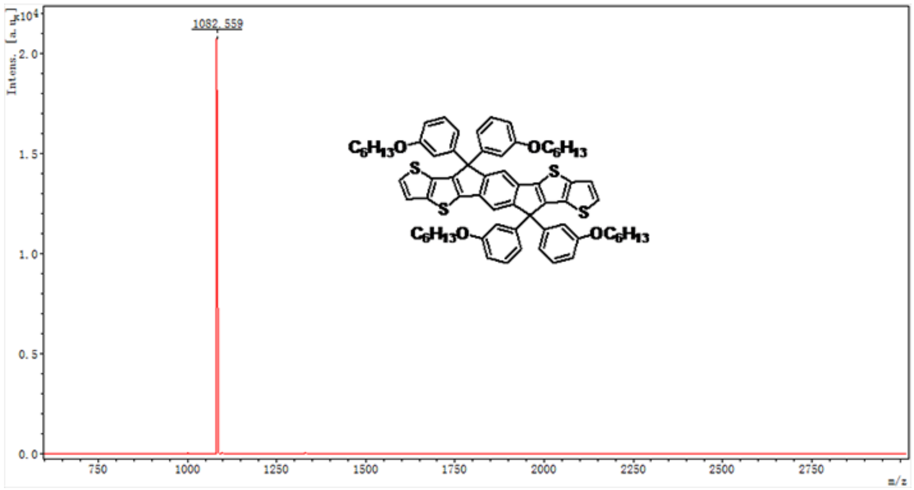
OC_6H_{13}
S
S
S
S
$C_6H_{13}O$
OC_6H_{13}


x10^4
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1500
1750
2000
2250
2500
2750
m/z
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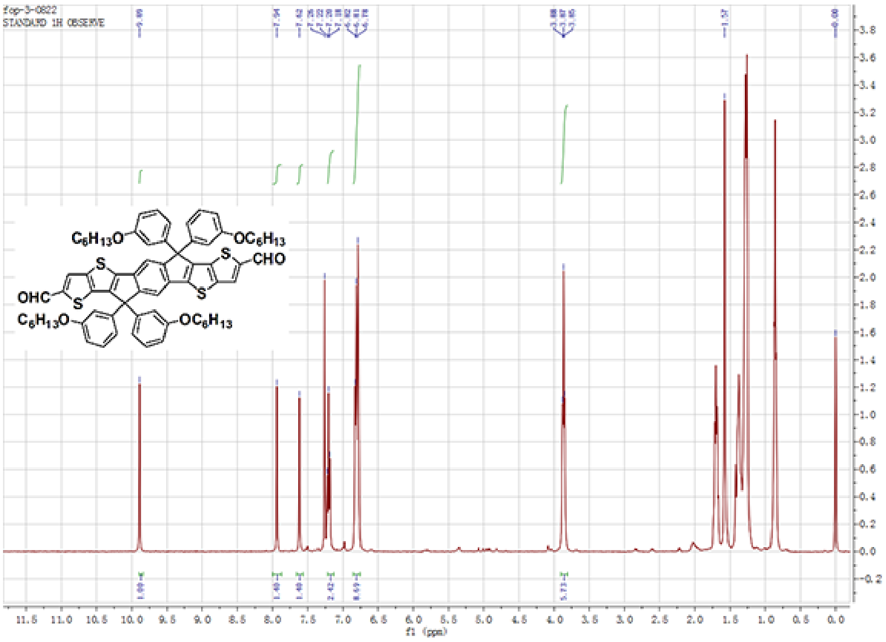
OC_6H_{13}
S
S
S
S
$C_6H_{13}O$
OC_6H_{13}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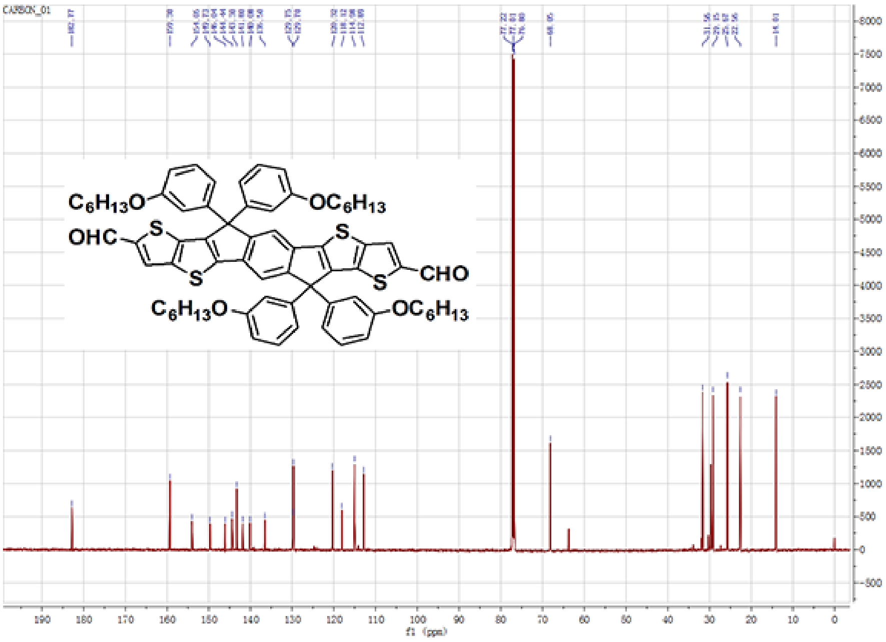
7.22
7.20
7.18
6.82
6.81
6.78
3.88
3.87
3.85
1.57
0.00
1.00
1.40
1.40
2.42
8.69
5.73
$C_6H_{13}O$
OC_6H_{13}
S
CHO
OHC
f1 (ppm)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159.38
154.05
149.73
146.04
144.44
143.30
141.88
140.08
136.50
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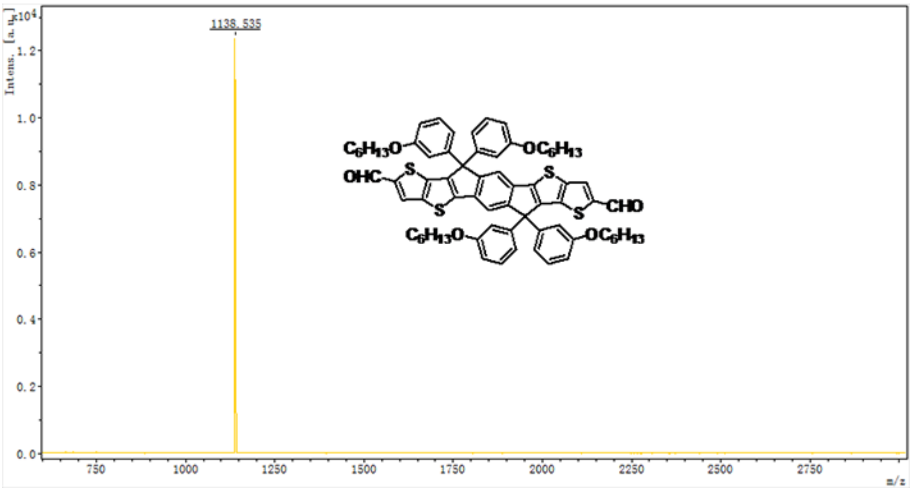
129.70
120.52
118.12
114.98
112.89
77.22
77.01
76.80
68.05
31.56
29.15
25.67
22.56
14.01
$C_6H_{13}O$
OC_6H_{13}
OHC
S
CHO
f1 (ppm)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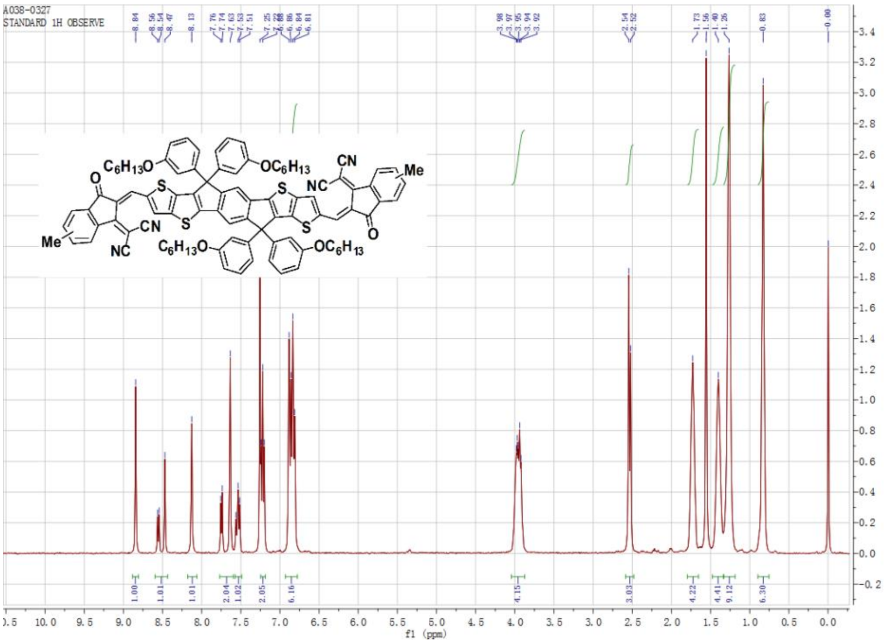
OHC
S
CHO
m/z


A038-0327
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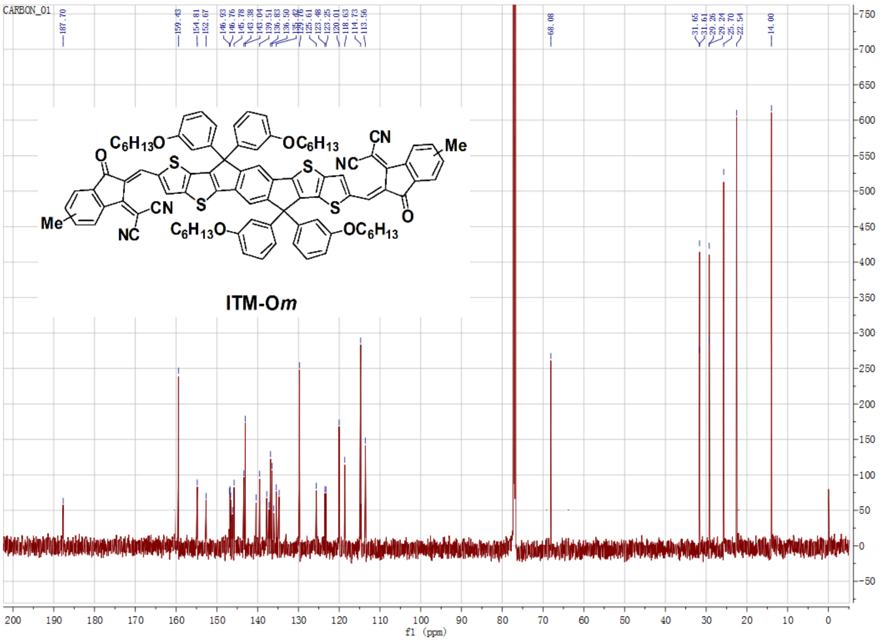
8.56
8.54
8.47
8.13
7.76
7.74
7.63
7.53
7.51
7.25
7.22
6.88
6.86
6.84
6.81
3.98
3.97
3.95
3.94
3.92
2.54
2.52
1.73
1.56
1.40
1.26
0.83
0.00
1.00
1.01
1.01
2.04
1.02
2.05
6.16
4.15
3.03
4.22
4.41
9.12
6.30
f1 (ppm)
C6H13O
OC6H13
CN
NC
Me
O
S
NC
CN
Me
O
C6H13O
OC6H13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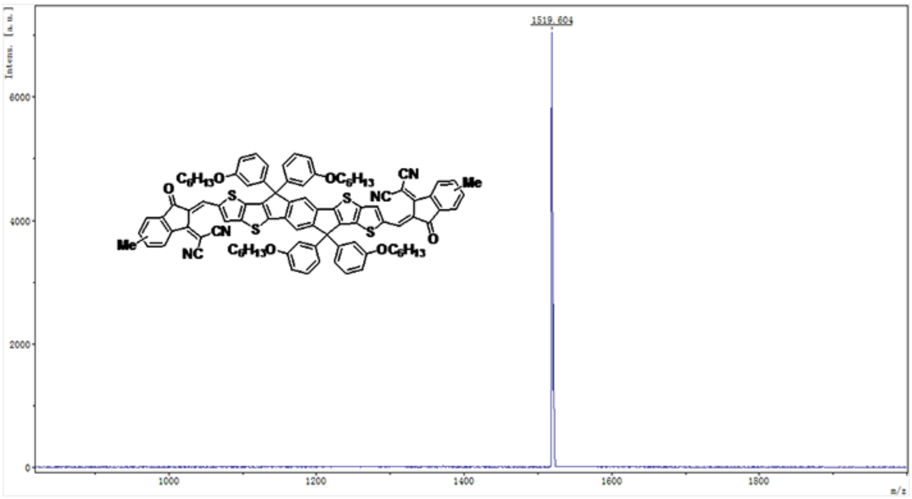
187.70
159.43
154.81
152.67
146.93
146.76
145.78
143.38
143.04
139.51
136.83
136.50
135.42
129.76
125.61
123.48
123.25
120.01
118.63
114.73
113.56
68.08
31.65
31.61
29.26
29.24
25.70
22.54
14.00
f1 (ppm)
ITM-Om


Intens. [a.u.]
1519.604
m/z

Notes and references

[1] W. Ma, J. R. Tumbleston, M. Wang, E. Gann, F. Huang and H. Ade, *Adv. Energy Mater.*, 2013, **3**, 864.

[2] P. W. M. Blom, V. D. Mihailetchi, L. J. A. Koster, D. E. Markov, *Adv. Mater.*, 2007, **19**, 1551.