Supporting information

Synthesis and application of near infrared dyes based on sulfur-substituted dicyanomethylene-4*H*-chromene and diarylethene

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Fig. **S40**: Cell imaging experiments of **S-DCM-4O@PEG@PLL** with the same concentration gradient (0-100 μg mL^{-1})

In order to better investigate the changes of the fluorophore of sulfur-substituted dicyanomethylene-4*H*-chromene binding with different diarylethene units, compound **S-DCM-1O**, **S-DCM-2O**, **S-DCM-3O**, and **S-DCM-4O** were synthesized. As shown in Scheme S1, the synthetic steps of compounds **2**-**10** have been extensively reported in the literature, so we mainly discussed the synthesis of compounds **1**, **1b**, **11**, and **S-DCM-1O**.[1]

General synthetic procedures

Synthesis of compound **1**. To a mixture of *p*-thiocresol (6.21 g, 50.0 mmol) and polyphosphoric acid (80 mL) was added ethyl acetoacetate (6.51 g, 50.0 mmol) dropwise at 363.15 K. After stirring for 0.5 h, the mixture was cooled to room temperature and stirred with ice water. The mixture was extracted with ethylacetate and dried over Na_2SO_4. Purification by silica gel column chromatography (petroleum ether/ethylacetate = 10:1, v/v) afforded compound **1** as white solids (7.30 g, 77%). M.p. 388-390 K; ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 8.25 (s, 1H), 7.39 (d, J = 10.0 Hz, 1H), 7.35-7.33 (m, 1H), 6.78 (s, 1H), 2.40 (s, 3H), 2.39 (d, J = 5.0 Hz, 3H) (Fig. S1).

Synthesis of compound **1b**. A mixture of compound **1** (0.35 g, 2.0 mmol) and malononitrile (1.32 g, 20.0 mmol) in acetic anhydride (7 mL) was stirred for 16 h at 413.15 K. After that, the mixture was cooled to 328.15 K, and methanol (11 mL) was added to stir for 3h. The solvent was removed by evaporation under reduced pressure, and the residue was subjected to silica gel chromatography (petroleum ether/ethylacetate = 20:1, v/v) as eluent, obtaining a yellow solid (0.10 g, 42%). M.p. 452-454 K; ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 8.79 (s, 1H), 7.53 (d, J = 10.0 Hz, 1H), 7.46-7.44 (m, 1H), 7.40 (s, 1H), 2.51 (s, 6H) (Fig. S2); HRMS (ESI^+) calcd for $C_{14}H_{11}N_2S$ $[M + H]^+$ 239.0643, found 239.0598 (Fig. S3).

Synthesis of compound **11**. Compound **10** (1.17 g, 2.2 mmol), pyridine (1 mL) and *p*-TsOH (0.29 g, 1.5 mmol) was added to a mixture of solution (acetone/water = 4:1, v/v, 7 mL). After stirring for 6 h, the solution obtained was concentrated. The resulting residue dissolved in ethylacetate and washed with H_2O. The organic layer was dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was subjected to silica gel chromatography, obtaining compound **11** (0.97 g, 91%). M.p. 382-384 K; ^{1}H NMR (500 MHz, CD_2Cl_2), δ (ppm): 9.94 (d, *J* = 10.0 Hz, 1H), 8.89 (s, 1H), 7.91-7.85 (m, 2H), 7.35 (d, *J* = 60.0 Hz, 1H), 6.72 (d, *J* = 50.0 Hz, 1H), 2.41 (d, *J* = 65.0 Hz, 3H), 1.91 (s, 3H), 1.80 (s, 3H) (Fig. S4); ^{13}C NMR (100 MHz, CD_2Cl_2), δ (ppm): 191.75, 146.05, 132.32, 124.89, 123.81, 120.99, 14.03, 13.64, 13.39 (Fig. S5); HRMS (ESI$^+$) calcd for $C_{22}H_{16}F_6NOS_2$ $[M + H]^+$ 488.0577, found 488.0552 (Fig. S6).

Synthesis of compound **S-DCM-1O**. A mixture of compound **11** (97 mg, 0.2 mmol), compound **1b** (48 mg, 0.2 mmol), piperidine (0.1 mL, 1.0 mmol) and acetic acid (0.1 mL, 2.0 mmol) in dry 10 mL toluene was stirred for 16 h at 383.15 K under N_2 atmosphere. The solution was removed by concentrated in vacuo under reduced pressure, and the residue was subjected to silica gel chromatography with a mixture of solution (petroleum ether/dichloromethane = 2:1, v/v) as eluent, obtaining compound **S-DCM-1O** as an orange solid (30 mg, 21%). M.p. 512-514 K; ^{1}H NMR (500 MHz, CD_2Cl_2), δ (ppm): 8.76 (s, 1H), 8.65 (s, 1H), 7.78 (d, *J* = 10.0 Hz, 1H), 7.66 (d, *J* = 20.0 Hz, 1H), 7.57 (t, *J* = 7.5 Hz, 2H), 7.42 (d, *J* = 10.0 Hz, 1H), 7.37 (d, *J* = 10.0 Hz, 1H), 7.32 (s, 1H), 7.23 (d, *J* = 20.0 Hz, 1H), 6.68 (s, 1H), 2.43 (s, 3H), 2.35 (s, 3H), 1.90 (s, 3H), 1.81 (s, 3H) (Fig. S7); ^{13}C NMR (100 MHz, CD_2Cl_2), δ (ppm): 154.95, 151.63, 146.48, 145.83, 142.77, 139.57, 138.49, 137.84, 137.40, 134.17, 132.95, 132.41, 131.35, 128.93, 128.55, 127.61, 126.80, 125.95, 124.83, 124.05, 123.80, 123.36, 122.48, 116.55, 115.20, 68.65, 29.15, 20.64, 14.26, 13.79, 13.55 (Fig. S8); HRMS (ESI$^+$) calcd for $C_{36}H_{24}F_6N_3S_3$ $[M + H]^+$ 708.1037, found 708.0967 (Fig. S9).

As shown in **Scheme S2**, the synthetic steps of compounds **2**-**10** have been extensively reported in the literature, so we mainly discussed the synthesis of compounds **11** and **S-DCM-2O**.[2]

General synthetic procedures

Synthesis of compound **11**. To compound **10** (2.33 g, 4.4 mmol) in a mixture of solution (acetone/water = 4:1, v/v, 14 mL) were added to pyridine (2 mL) and *p*-TsOH (0.58 g, 3.0 mmol).

After refluxing for 6 h, the solution obtained was concentrated. The resulting residue dissolved in ethylacetate and washed with H_2O. The solvent was removed by evaporation under reduced pressure. The residue was subjected to silica gel chromatography, obtaining compound **11** (1.80 g, 84%). M.p. 390-392 K; ^{1}H NMR (500 MHz, CD_2Cl_2), δ (ppm): 9.91 (s, 1H), 7.80 (d, J = 10.0 Hz, 2H), 7.63 (d, J = 10.0 Hz, 2H), 7.36 (s, 1H), 6.67 (s, 1H), 2.34 (s, 3H), 1.84 (d, J = 40.0 Hz, 6H) (Fig. S10); ^{13}C NMR (100 MHz, CD_2Cl_2), δ (ppm): 190.36, 142.80, 139.76, 139.34, 138.15, 137.59, 134.85, 129.55, 125.03, 123.88, 123.83, 14.03, 13.58, 13.31 (Fig. S11); HRMS (ESI$^+$) calcd for $C_{23}H_{17}F_6OS_2$ $[M + H]^+$ 487.0625, found 487.0613 (Fig. S12).

Synthesis of compound **S-DCM-2O**. To compound **11** (97 mg, 0.2 mmol) and compound **1b** (48 mg, 0.2 mmol) in a solution of toluene were added to piperidine (0.1 mL, 1.0 mmol) and acetic acid (0.1 mL, 2.0 mmol). After refluxing for 16 h at 383.15 K under N_2 atmosphere. The mixture was then cooled, and the solvent was removed under reduced pressure. The crude product was dissolved in CH_2Cl_2, extracted with water, and dried over sodium sulfate. The residue was subjected to silica gel chromatography with a mixture of solution (petroleum ether/dichloromethane = 3:1, v/v) as eluent, obtaining compound **S-DCM-2O** as an orange solid (61 mg, 43%). M.p. 532-534 K; ^{1}H NMR (500 MHz, CD_2Cl_2), δ (ppm): 8.74 (s, 1H), 7.64-7.58 (m, 6H), 7.50 (d, J = 10.0 Hz, 1H), 7.32 (t, J = 17.5 Hz, 2H), 7.20 (d, J = 15 Hz, 1H), 6.75 (s, 1H), 2.51 (s, 3H), 2.42 (s, 3H), 1.96 (s, 3H), 1.89 (s, 3H) (Fig. S13); ^{13}C NMR (100 MHz, CD_2Cl_2), δ (ppm): 154.89, 146.35, 141.73, 140.36, 139.34, 138.16, 137.51, 135.16, 134.04, 133.69, 132.68, 131.05, 127.52, 127.35, 126.54, 125.46, 125.14, 124.75, 124.64, 123.77, 123.52, 122.59, 121.11, 116.50, 115.25, 67.54, 28.94, 20.45, 14.09, 13.59, 13.37 (Fig. S14); HRMS (ESI$^+$) calcd for $C_{37}H_{25}F_6N_2S_3$ $[M + H]^+$ 707.1084, found 707.1026 (Fig. S15).

As shown in **Scheme S3**, the synthetic routes of compounds **2-9** have been extensively reported in the previous literature, so we mainly discussed the synthesis of compounds **10** and **S-DCM-3O**.[3]

General synthetic procedures

Synthesis of compound **10**. Compound **9** (1.30 g, 2.2 mmol), pyridine (1 mL) and *p*-TsOH (0.29 g, 1.5 mmol) was added to a mixture of solution (acetone/water = 4:1, v/v, 7 mL). After refluxing for 6 h, the mixture was cooled to room temperature and drained. The crude product was cleaned in a

mixed system of ethylacetate and water. The solvent was removed by evaporation under reduced pressure. The residue was subjected to silica gel chromatography, obtaining compound **10** (1.12 g, 93%). M.p. 397-399 K; ^{1}H NMR (500 MHz, CD_2Cl_2), δ (ppm): 10.01 (s, 1H), 7.95 (d, *J* = 10.0 Hz, 2H), 7.89 (d, *J* = 10.0 Hz, 2H), 7.77 (s, 1H), 7.64 (d, *J* = 10.0 Hz, 2H), 7.52 (s, 1H), 7.43 (t, *J* = 10.0 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 1H), 2.00 (d, *J* = 15.0 Hz, 6H) (Fig. S16); ^{13}C NMR (100 MHz, CD_2Cl_2), δ (ppm): 192.22, 143.18, 141.70, 141.19, 140.10, 137.81, 135.20, 132.40, 130.37, 129.16, 128.09, 125.62, 125.37, 125.22, 124.84, 124.80, 122.44, 14.07, 13.99 (Fig. S17); HRMS (ESI^+) calcd for $C_{28}H_{18}F_6OS_2$ $[M]^+$ 548.0703, found 548.0699 (Fig. S18).

Synthesis of compound **S-DCM-3O**. A mixture of compound **1b** (48 mg, 0.2 mmol), piperidine (0.1 mL, 1.0 mmol), compound **10** (110 mg, 0.2 mmol) and acetic acid (0.1 mL, 2.0 mmol) in dry 10 mL toluene was stirred for 16 h at 383.15 K under N_2 atmosphere. The mixture was removed by concentrated in vacuo under reduced pressure, and the crude product was subjected to silica gel chromatography with a mixture of solution (petroleum ether/dichloromethane = 3:1, v/v) as eluent, obtaining compound **S-DCM-3O** as an orange red solid (79 mg, 56%). M.p. 542-544 K; ^{1}H NMR (500 MHz, CD_2Cl_2), δ (ppm): 8.74 (s, 1H), 7.64-7.55 (m, 8H), 7.50 (d, *J* = 10.0 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 3H), 7.32-7.28 (m, 3H), 7.20 (d, *J* = 15.0 Hz, 1H), 2.51 (s, 3H), 2.01 (s, 6H) (Fig. S19); ^{13}C NMR (100 MHz, CD_2Cl_2), δ (ppm): 154.88, 146.34, 140.59, 138.16, 135.14, 133.98, 133.75, 132.68, 132.52, 131.05, 128.25, 127.53, 127.35, 127.21, 126.54, 125.18, 124.89, 124.79, 124.64, 123.98, 122.51, 121.63, 121.13, 115.24, 67.56, 28.93, 20.45, 13.64, 13.12 (Fig. S20); HRMS (ESI^+) calcd for $C_{42}H_{27}F_6N_2S_3$ $[M + H]^+$ 769.1241, found 769.1136 (Fig. S21).

In order to make a better comparison, the fluorophore of sulfur-substituted dicyanomethylene-4*H*-chromene combined with symmetric diarylethene compound was synthesized. As shown in **Scheme S4**, the synthetic routes of compounds **2**-**7** have been extensively reported in the previous literature, so we mainly discussed the synthesis of compounds **8** and **S-DCM-4O**.[4]

General synthetic procedures

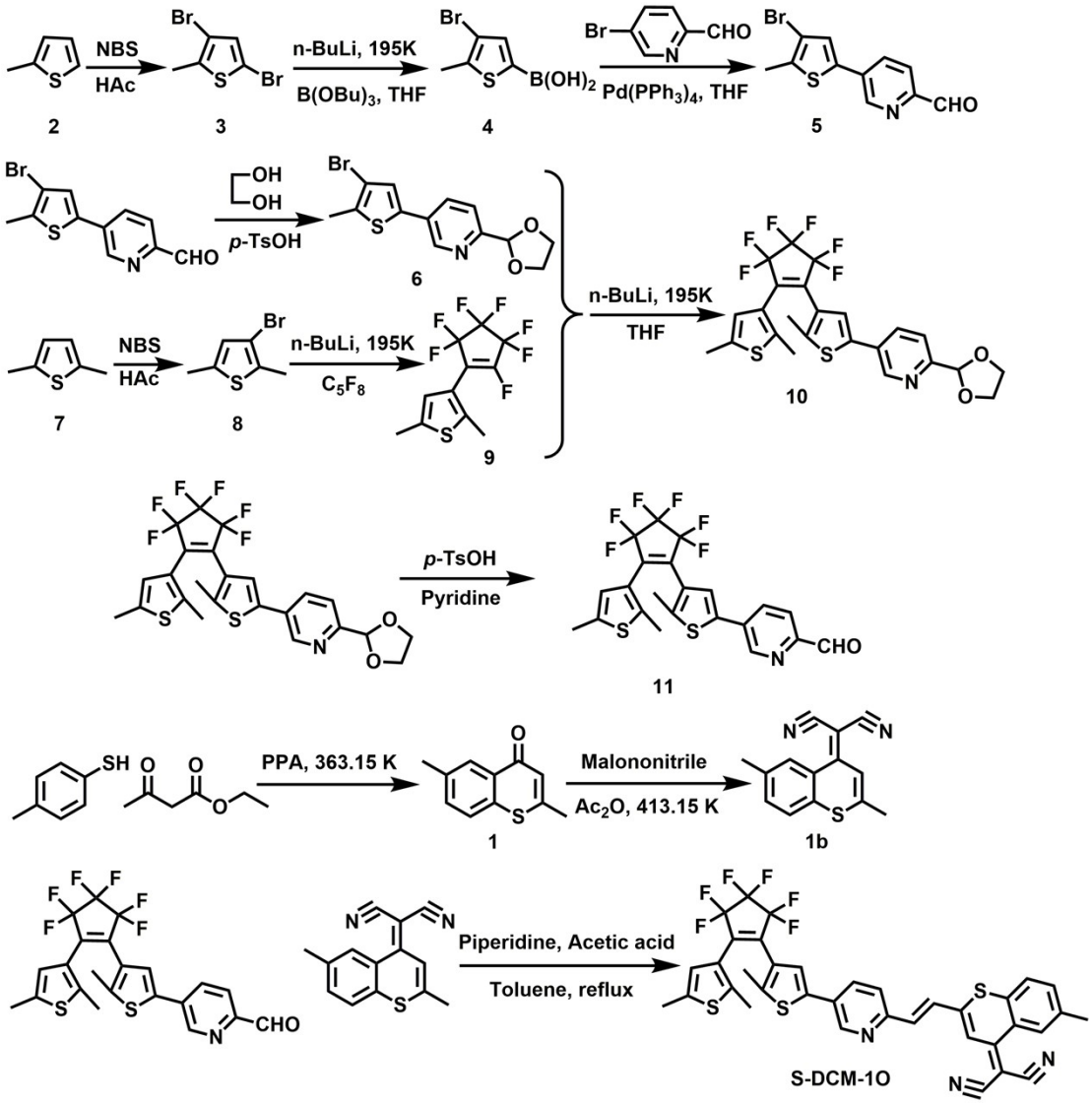
Synthesis of compound **8**. Pyridine (1 mL) and *p*-TsOH (0.29 g, 1.5 mmol) was dissolved in a mixture of solution (acetone/water = 4:1, v/v, 7 mL). Compound **7** (1.46 g, 2.2 mmol) was added to solvent and refluxed for 6 h. The mixture was cooled to room temperature and the solvent was

evaporated in vacuo to dryness. The crude product was cleaned in a mixed system (ethylacetate and water) and applied to silica gel chromatography, obtaining compound **8** (1.08 g, 85%). M.p. 473-475 K; ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 10.01 (s, 2H), 7.90 (d, J = 5.0 Hz, 4H), 7.69 (d, J = 10.0 Hz, 4H), 7.42 (s, 2H), 2.02 (s, 6H) (Fig. S22); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 190.28, 142.33, 139.78, 137.75, 134.47, 129.53, 125.24, 124.80, 123.30, 13.71 (Fig. S23); HRMS (ESI^+) calcd for $C_{29}H_{18}F_6O_2S_2Na$ $[M + Na]^+$ 599.0550, found 599.0543 (Fig. S24).

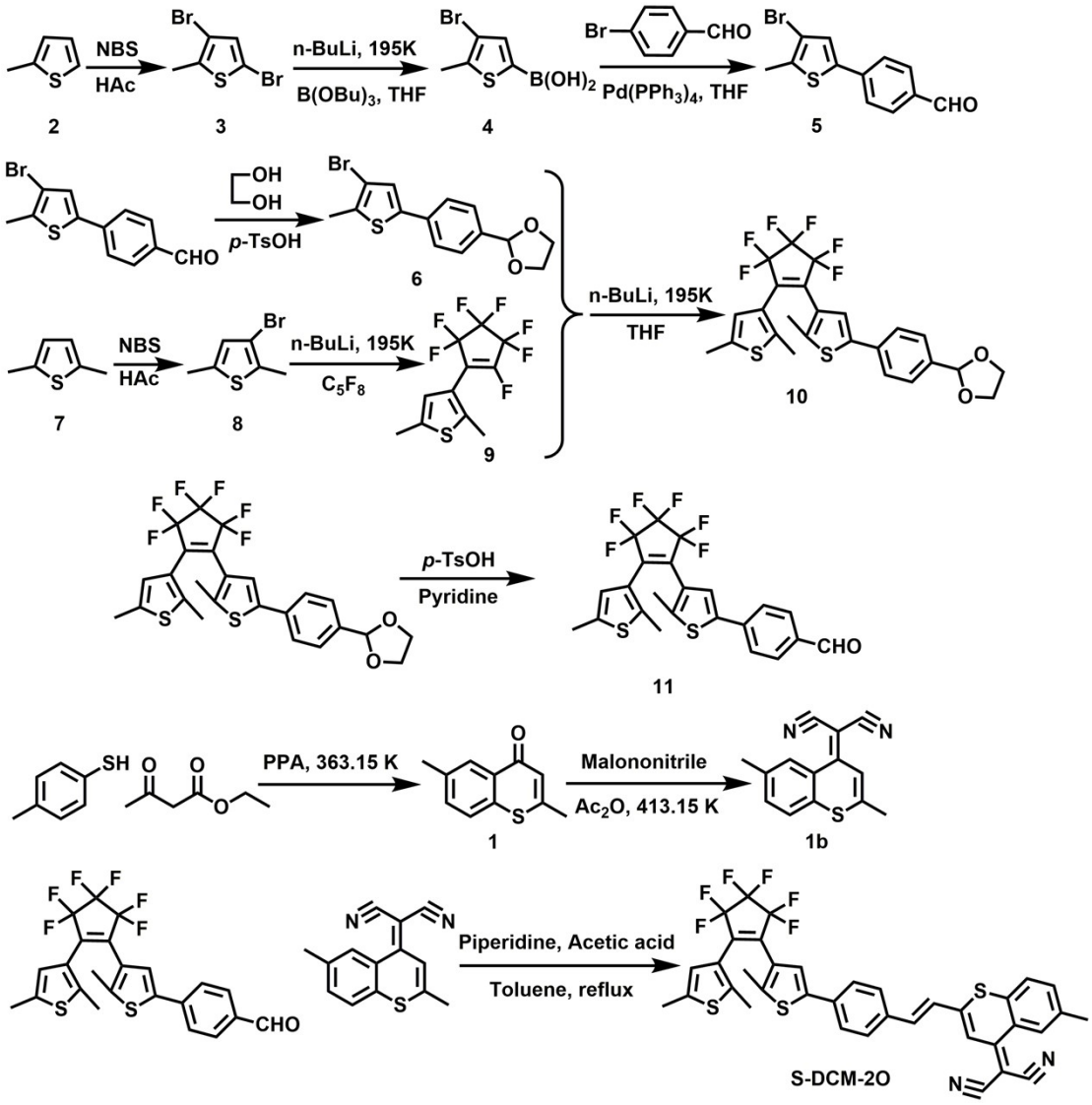
Synthesis of compound **S-DCM-4O**. To compound **1b** (96 mg, 0.4 mmol) and compound **8** (115 mg, 0.2 mmol) in toluene (10 mL) were added to piperidine (0.1 mL, 1.0 mmol) and acetic acid (0.1 mL, 2.0 mmol), the reaction mixture was refluxed for 16 h at 383.15 K under N_2 atmosphere. The mixture was then cooled, and the solvent was removed under reduced pressure. The crude product was subjected to silica gel chromatography with a mixture of solution (petroleum ether/dichloromethane = 2:1, v/v) as eluent to afford an orange red solid (134 mg, 66%). M.p. 552-554 K; ^{1}H NMR (500 MHz, DMF-d_7), δ (ppm): 8.73 (s, 2H), 7.95 (d, J = 10.0 Hz, 6H), 7.91 (s, 1H), 7.88 (s, 1H), 7.82 (d, J = 5.0 Hz, 4H), 7.75 (d, J = 5.0 Hz, 4H), 7.72 (d, J = 10 Hz, 2H), 7.55 (s, 1H), 7.52 (s, 1H), 2.52 (s, 6H), 2.15 (s, 6H) (Fig. S25); ^{13}C NMR (100 MHz, DMF-d_7), δ (ppm): 148.90, 143.17, 142.24, 139.50, 136.87, 135.97, 134.95, 134.62, 132.62, 129.66, 128.63, 128.42, 127.13, 126.49, 125.61, 124.60, 122.44, 118.27, 116.66, 79.62, 67.82, 21.24, 14.56 (Fig. S26); HRMS (ESI^+) calcd for $C_{57}H_{34}F_6N_4S_4Na$ $[M + Na]^+$ 1039.1468, found 1039.1332 (Fig. S27).

References

1. H.L. Liu, S.Q. Cui, F. Shi, S.Z. Pu, *Tetrahedron*, 2019, **75**, 3772-3778.
2. X.X. Zhang, R.J. Wang, C.B. Fan, G. Liu, S.Z. Pu, *Dyes Pigments*, 2017, **139**, 208-217.
3. S. Yamamoto, K. Matsuda, M. Irie, *Org. Lett.*, 2003, **5**, 1769-1772.
4. S. Yamamoto, K. Matsuda, M. Irie, *Chem. Eur. J.*, 2003, **9**, 4878-4886.



Scheme 1. Synthetic route to compound **S-DCM-1O**.



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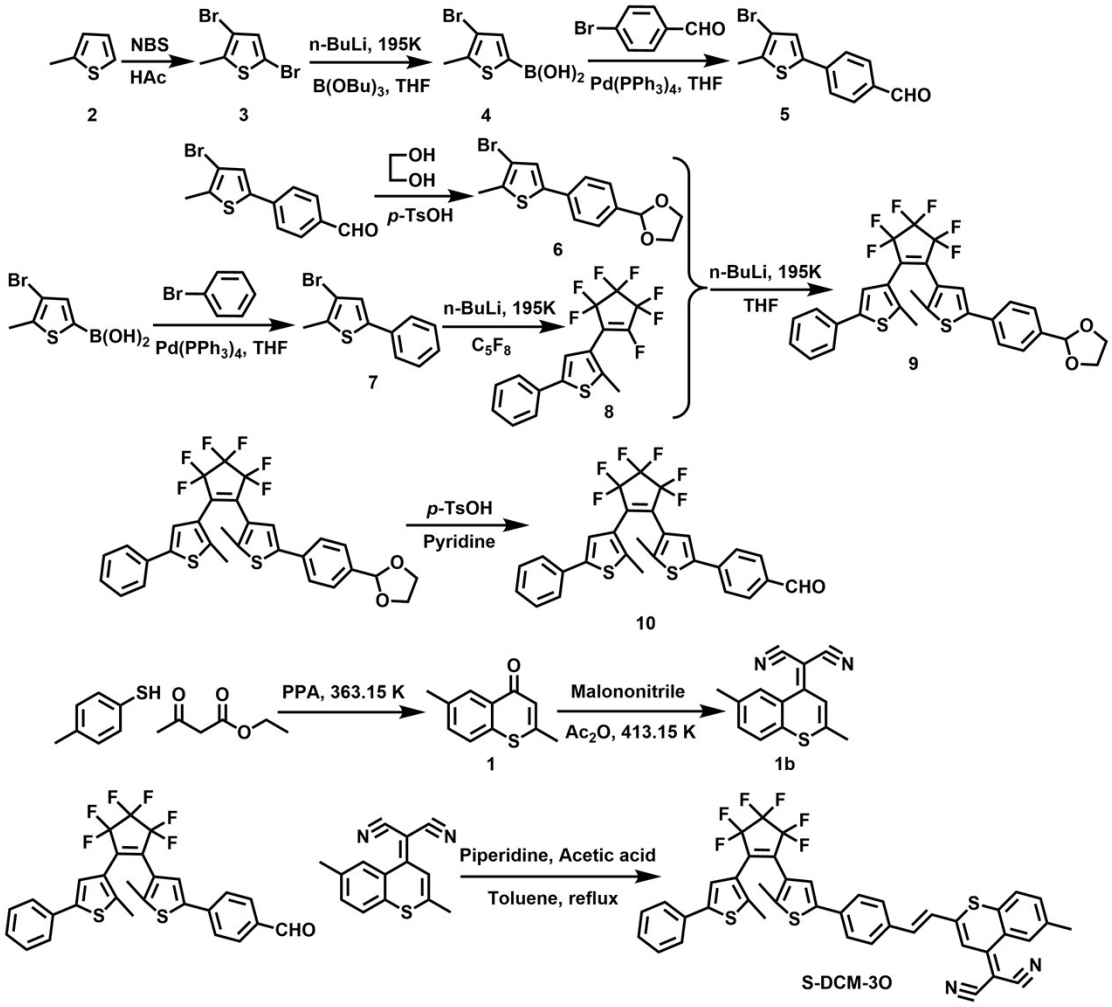

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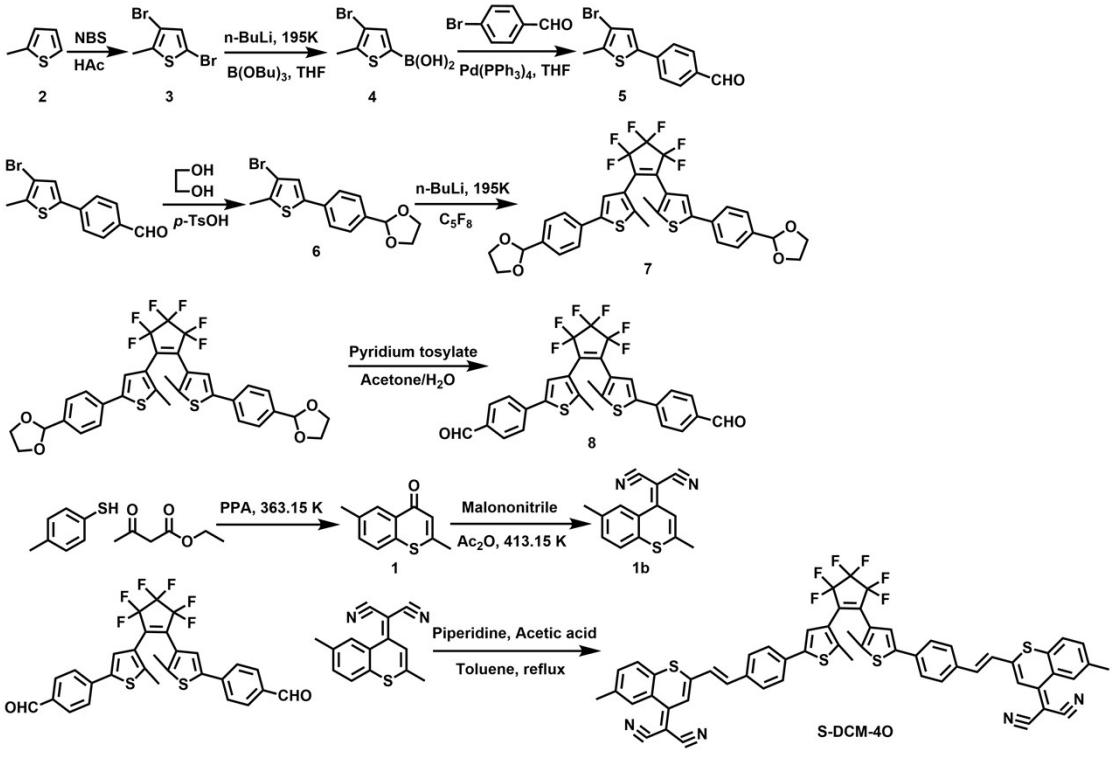

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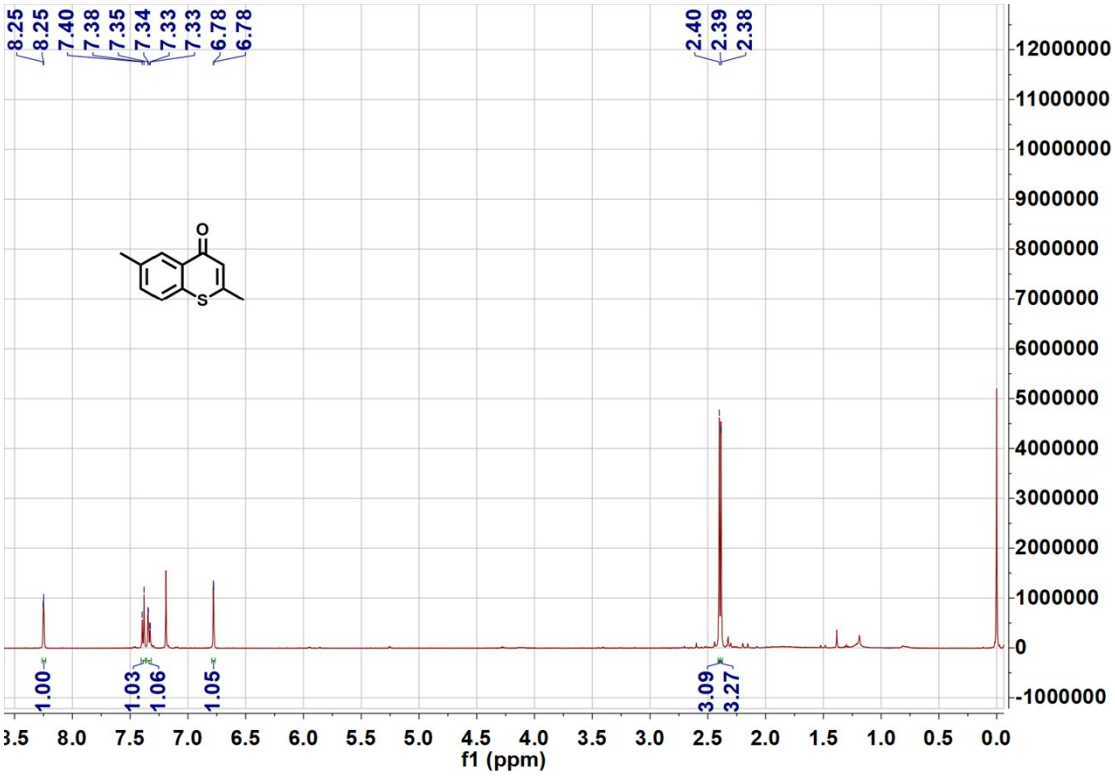
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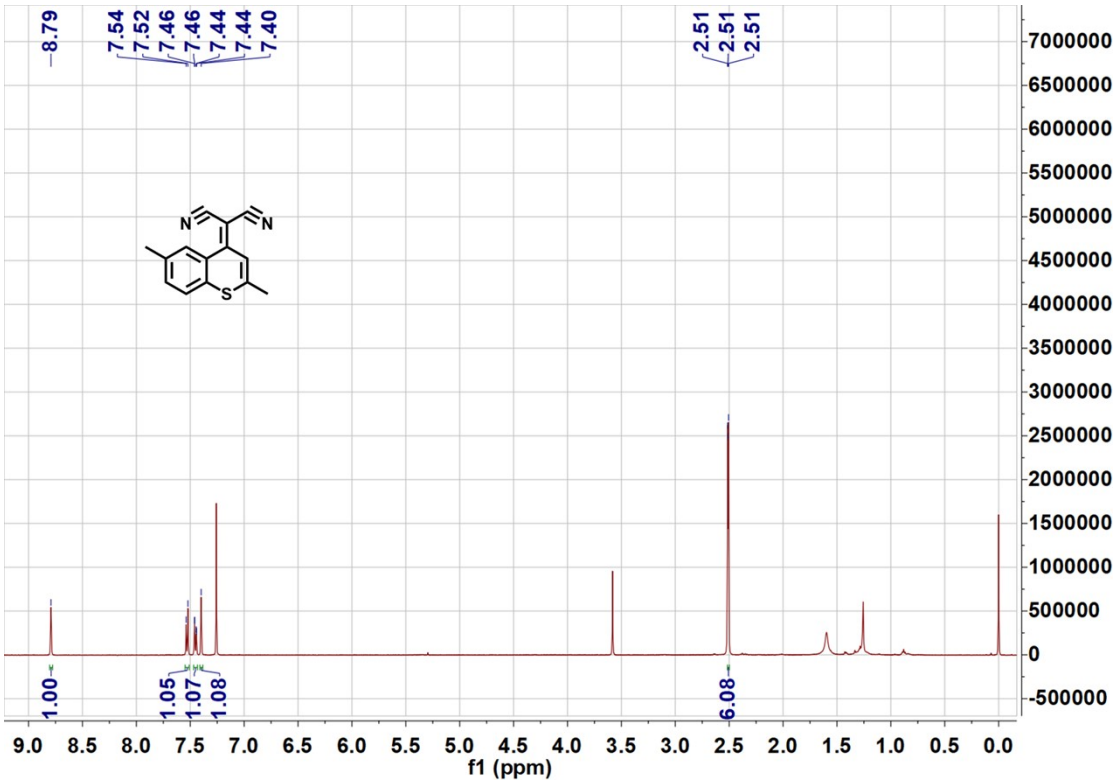
Fig. S1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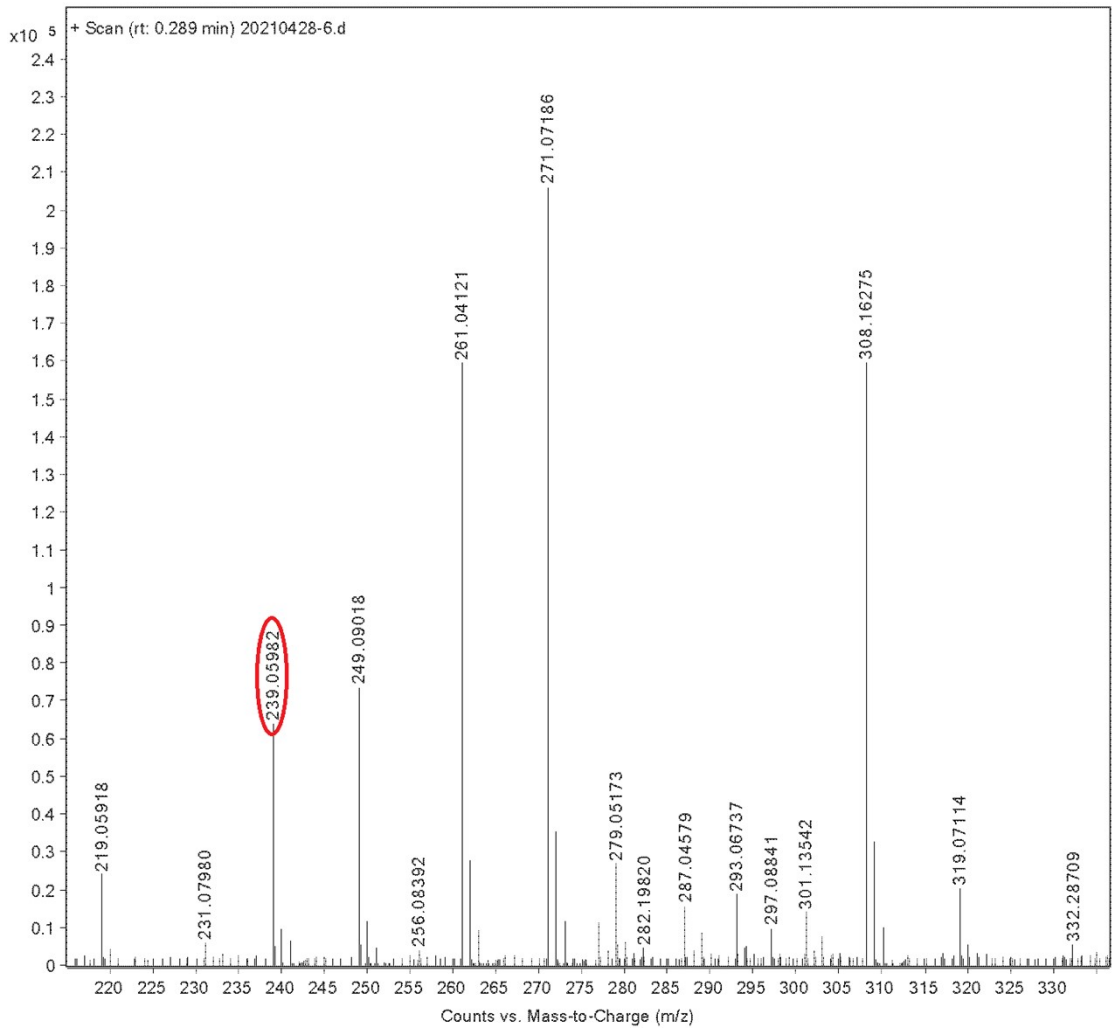
f1 (ppm)

Fig. S2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Counts vs. Mass-to-Charge (m/z)

Fig. S3

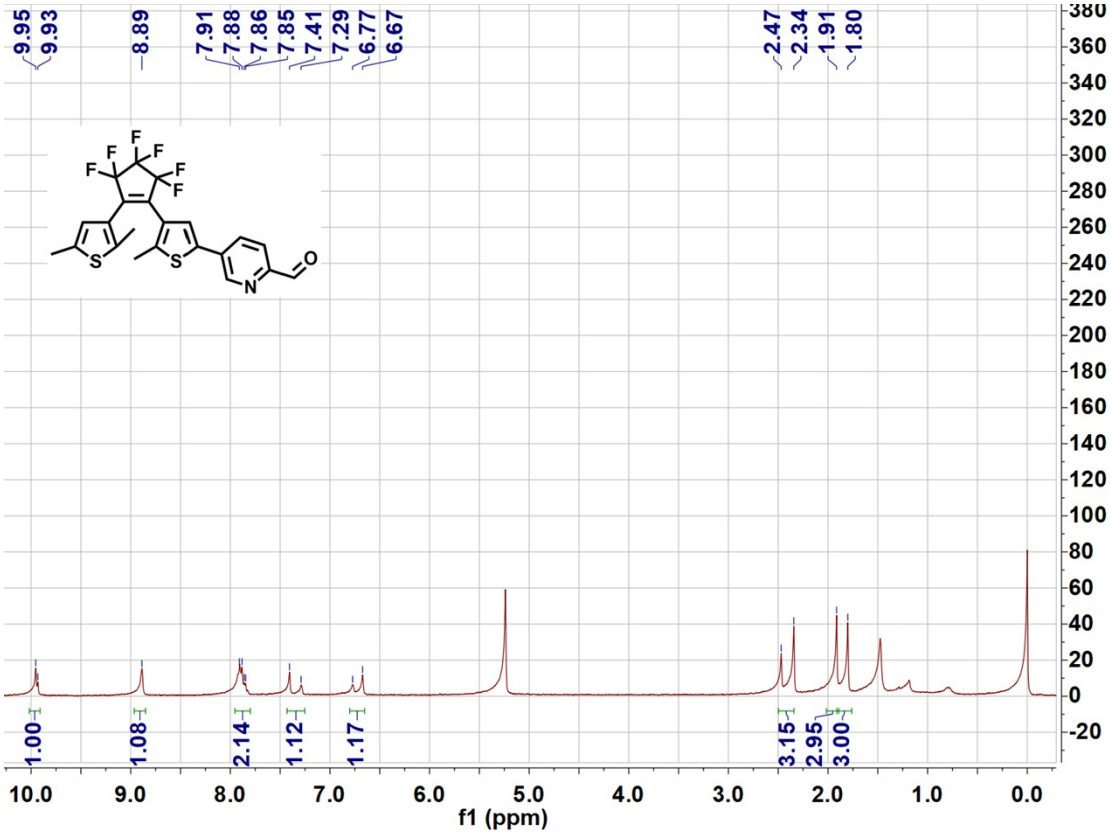
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Fig. S4

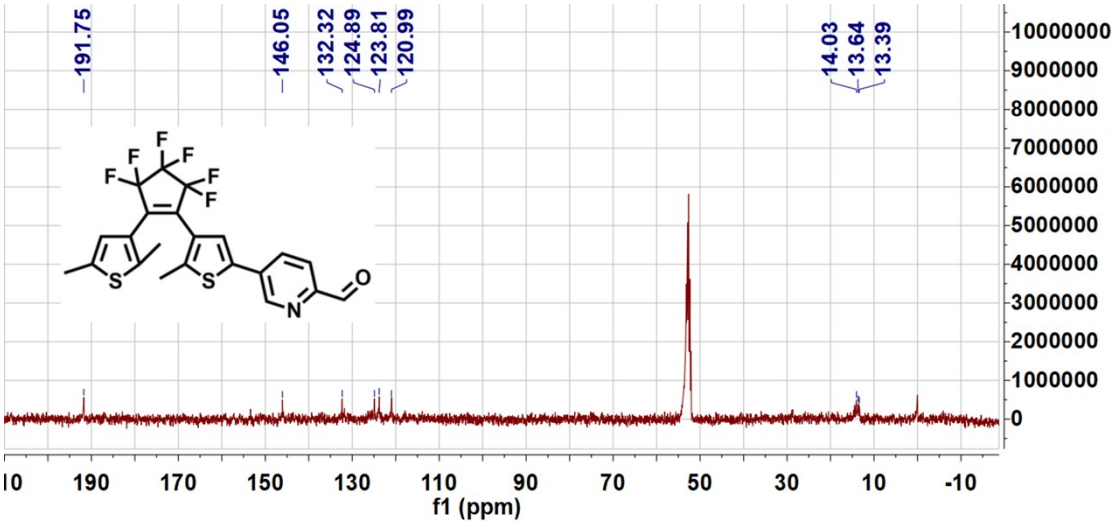
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Fig. S5

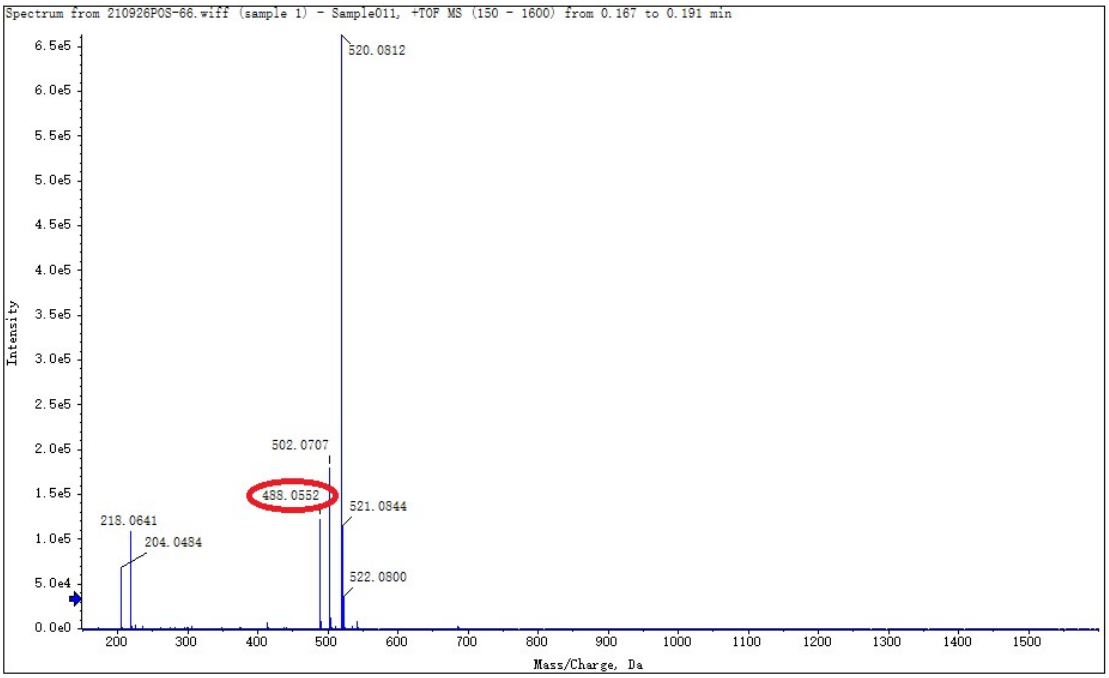
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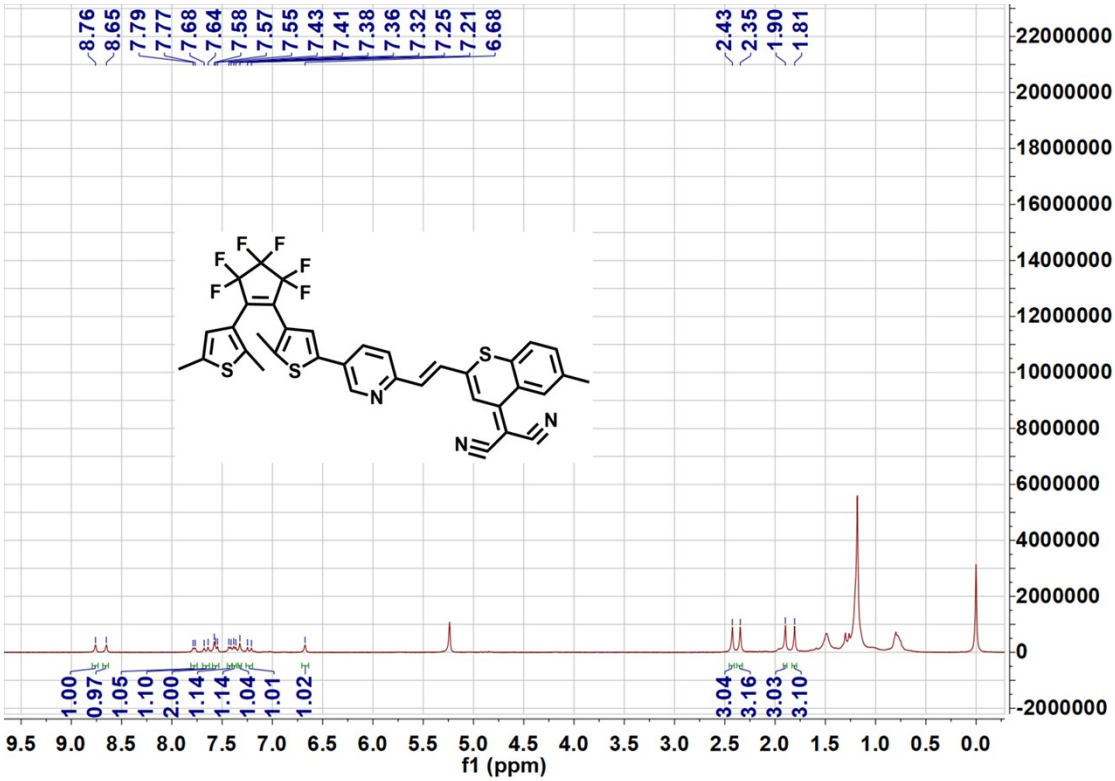
Fig. S6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f1 (ppm)

Fig. S7

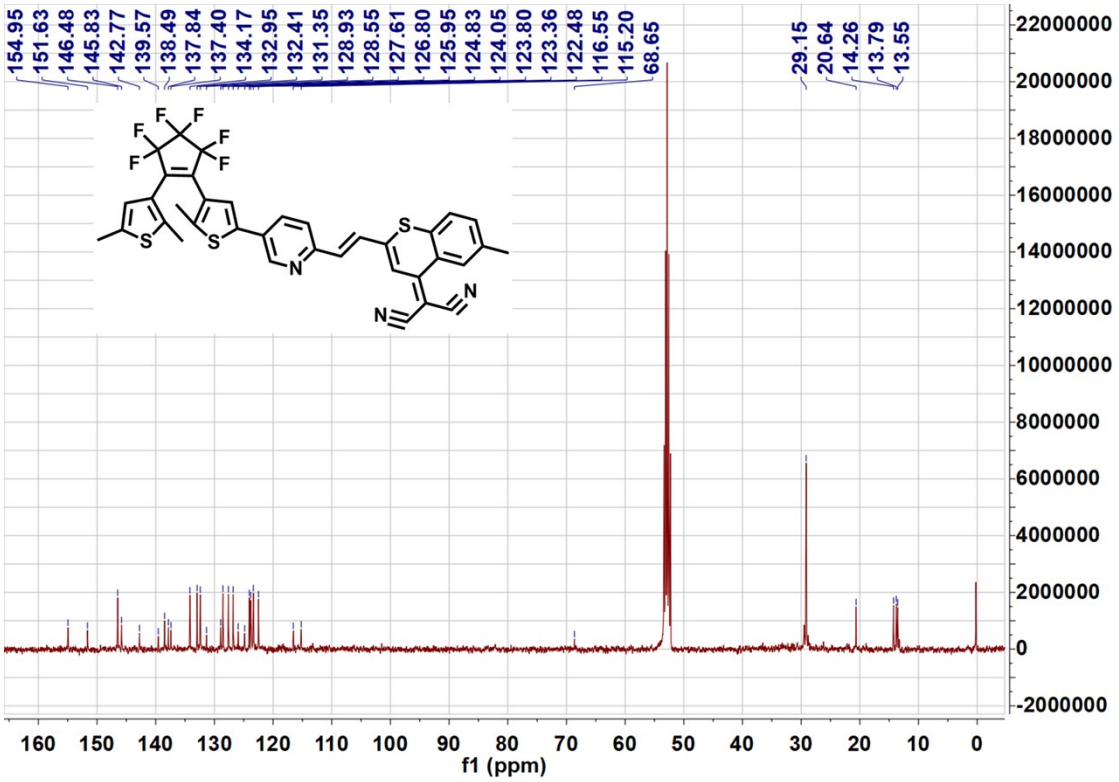
154.95
151.63
146.48
145.83
142.77
139.57
138.49
137.84
137.40
134.17
132.95
132.41
131.35
128.93
128.55
127.61
126.80
125.95
124.83
124.05
123.80
123.36
122.48
116.55
115.20
68.65
29.15
20.64
14.26
13.79
13.55
F
F
F
F
F
S
S
N
S
N
N
22000000
20000000
18000000
16000000
14000000
12000000
10000000
8000000
6000000
4000000
2000000
0
-2000000
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Fig. S8

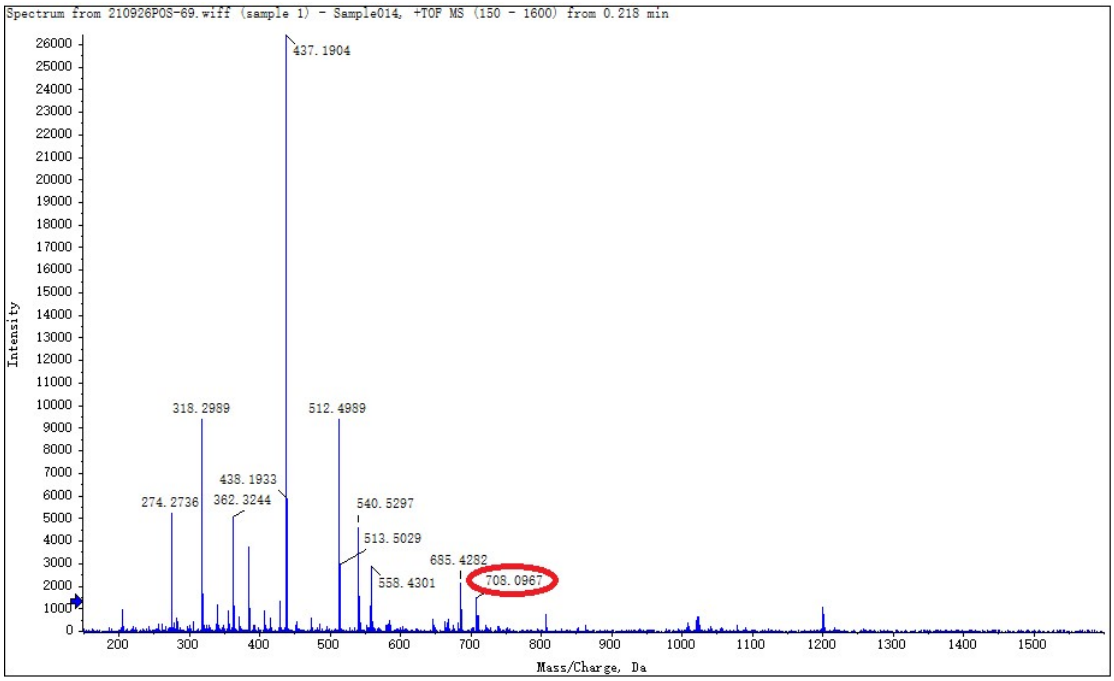
Spectrum from 210926POS-69.wiff (sample 1) - Sample014, +TOF MS (150 - 1600) from 0.218 min
Intensity
Mass/Charge, Da
437.1904
318.2989
512.4989
438.1933
274.2736
362.3244
540.5297
513.5029
685.4282
558.4301
708.0967

Fig. S9

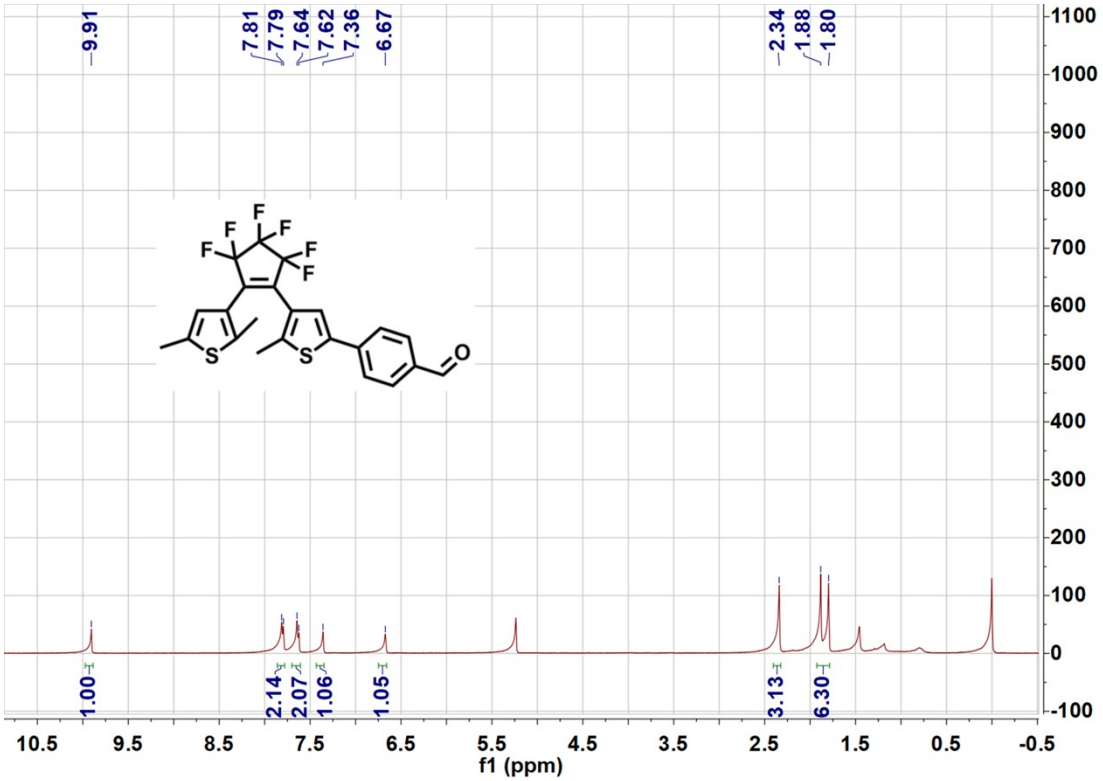
9.91
7.81
7.79
7.64
7.62
7.36
6.67
2.34
1.88
1.80
1.00
2.14
2.07
1.06
1.05
3.13
6.30
F
F
F
F
F
F
S
S
O
f1 (ppm)

Fig. S10

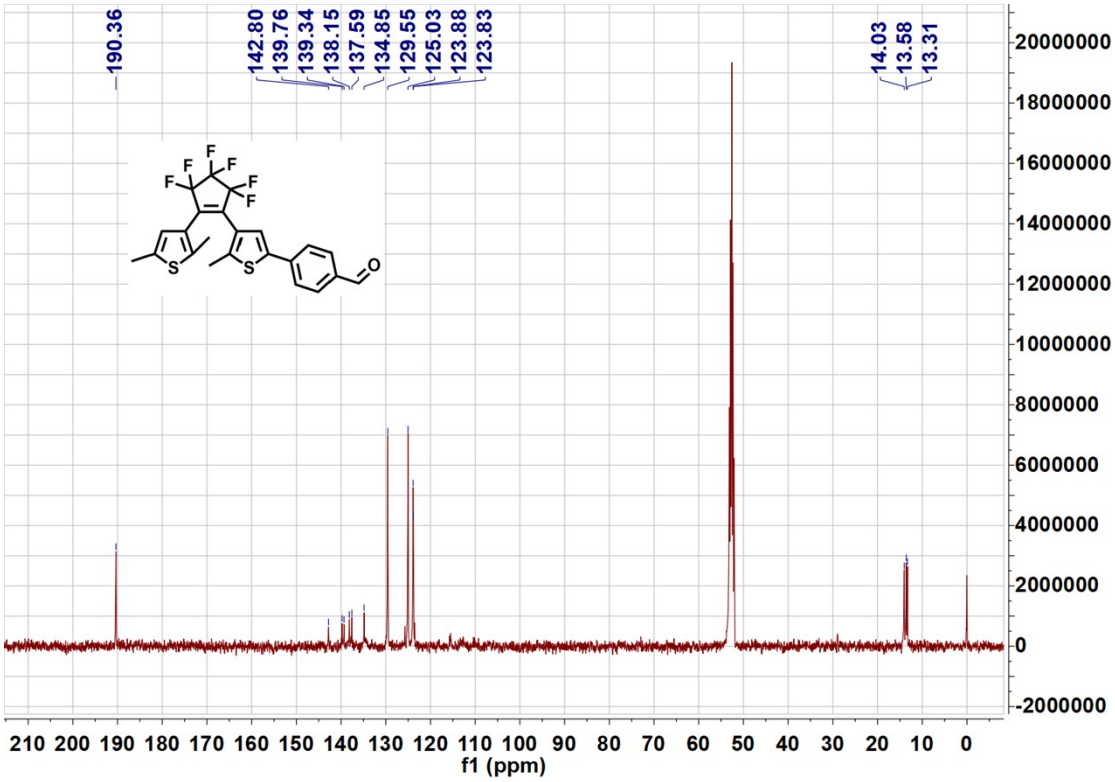
190.36
142.80
139.76
139.34
138.15
137.59
134.85
129.55
125.03
123.88
123.83
14.03
13.58
13.31
F
F
F
F
F
F
S
S
O
20000000
18000000
16000000
14000000
12000000
10000000
8000000
6000000
4000000
2000000
0
-2000000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Fig. S11

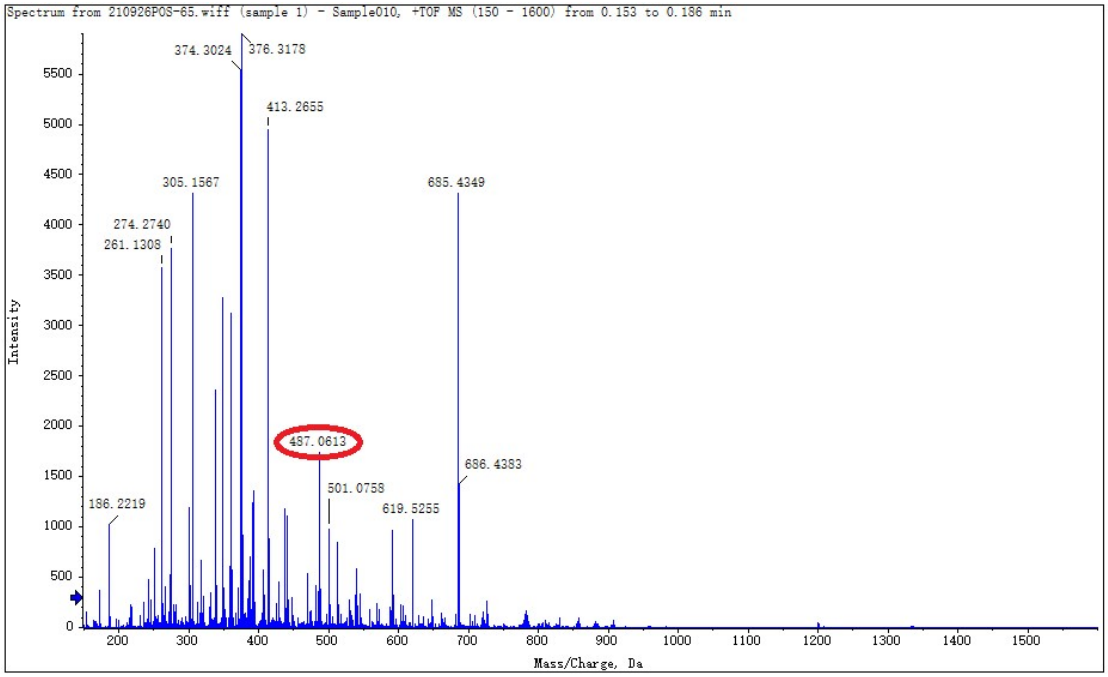
Spectrum from 210926POS-65.wiff (sample 1) - Sample010, +TOF MS (150 - 1600) from 0.153 to 0.186 min
374.3024
376.3178
413.2655
305.1567
685.4349
274.2740
261.1309
487.0613
686.4383
501.0758
619.5255
186.2219
Intensity
Mass/Charge, Da

Fig. S12

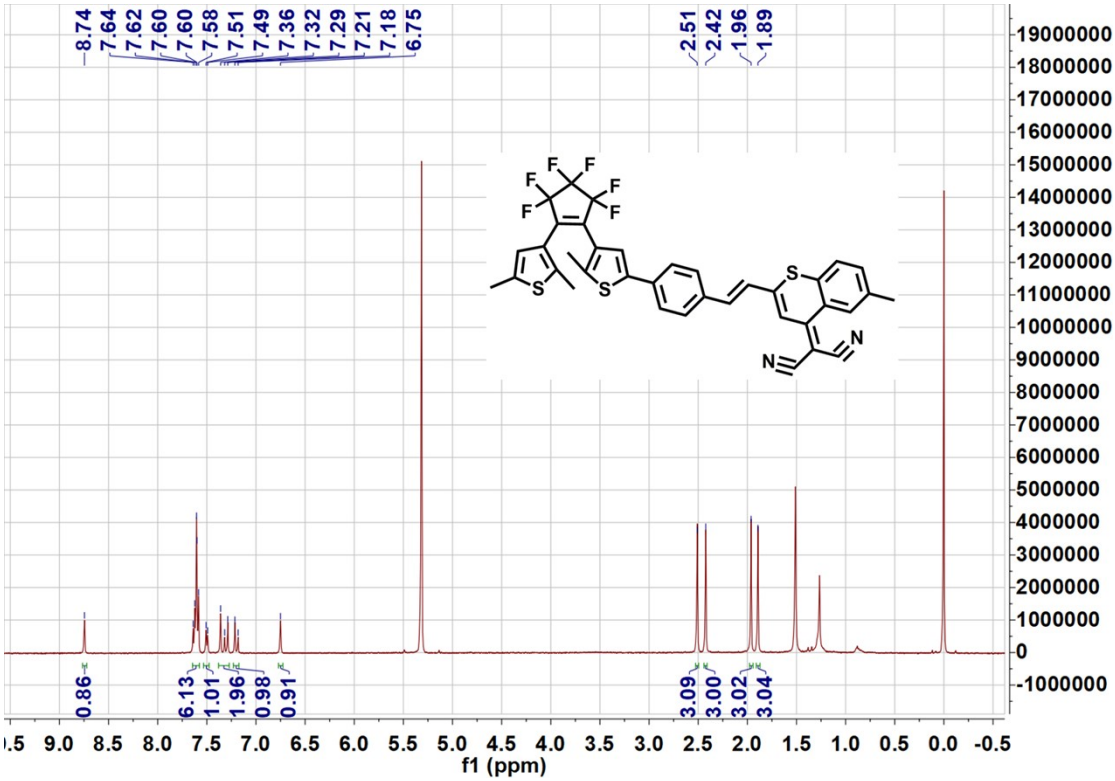
8.74
7.64
7.62
7.60
7.60
7.58
7.51
7.49
7.36
7.32
7.29
7.21
7.18
6.75
2.51
2.42
1.96
1.89
0.86
6.13
1.01
1.96
0.98
0.91
3.09
3.00
3.02
3.04
f1 (ppm)

Fig. S13

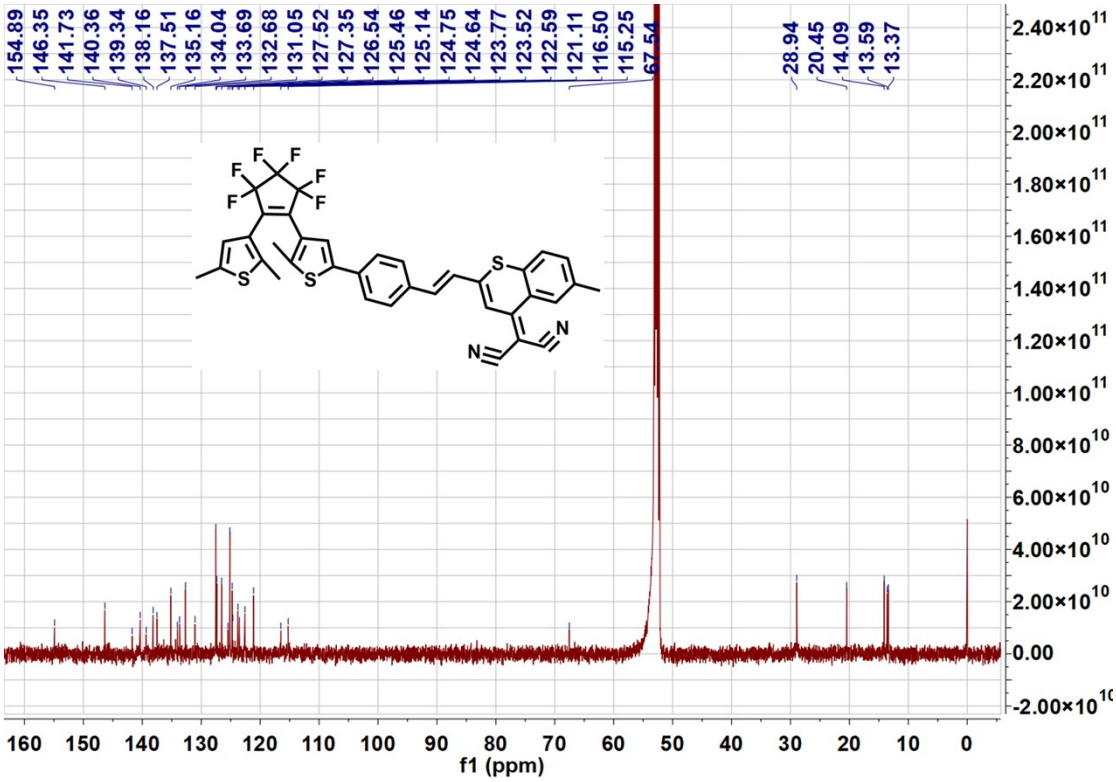
154.89
146.35
141.73
140.36
139.34
138.16
137.51
135.16
134.04
133.69
132.68
131.05
127.52
127.35
126.54
125.46
125.14
124.75
124.64
123.77
123.52
122.59
121.11
116.50
115.25
67.54
28.94
20.45
14.09
13.59
13.37
F
F
F
F
F
F
S
S
S
N
N
2.40×10^11
2.20×10^11
2.00×10^11
1.80×10^11
1.60×10^11
1.40×10^11
1.20×10^11
1.00×10^11
8.00×10^10
6.00×10^10
4.00×10^10
2.00×10^10
0.00
-2.00×10^10
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Fig. S14

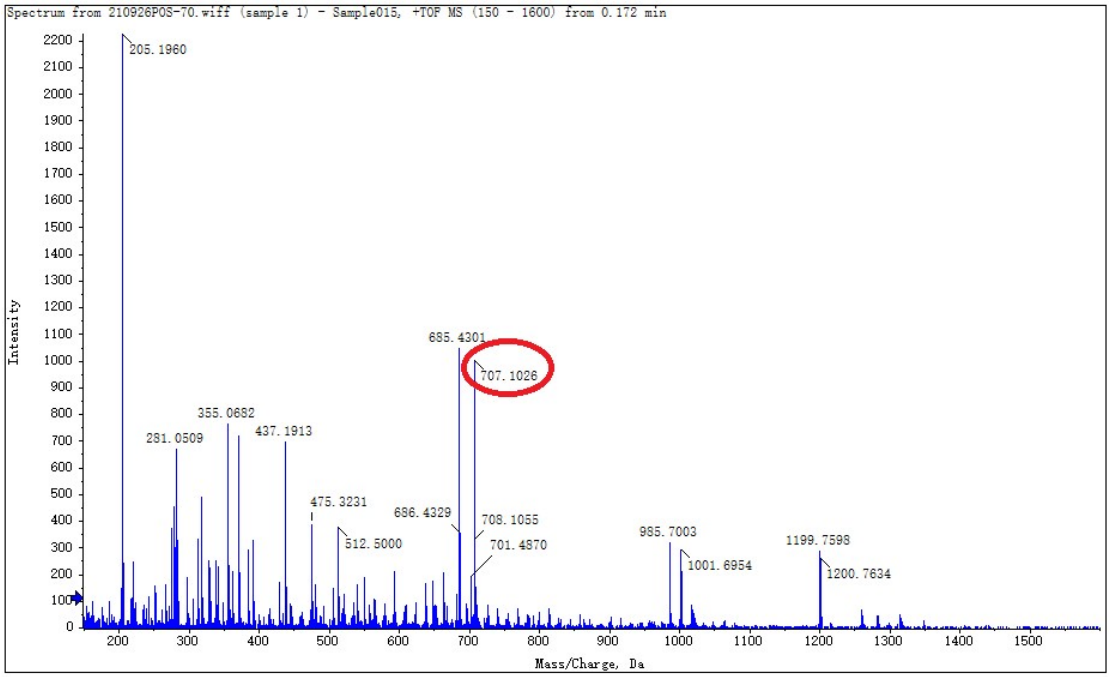
Spectrum from 210926POS-70.wiff (sample 1) - Sample015, +TOF MS (150 - 1600) from 0.172 min
Intensity
Mass/Charge, Da
205.1960
685.4301
707.1026
355.0682
281.0509
437.1913
475.3231
686.4329
708.1055
512.5000
701.4870
985.7003
1001.6954
1199.7598
1200.7634

Fig. S15

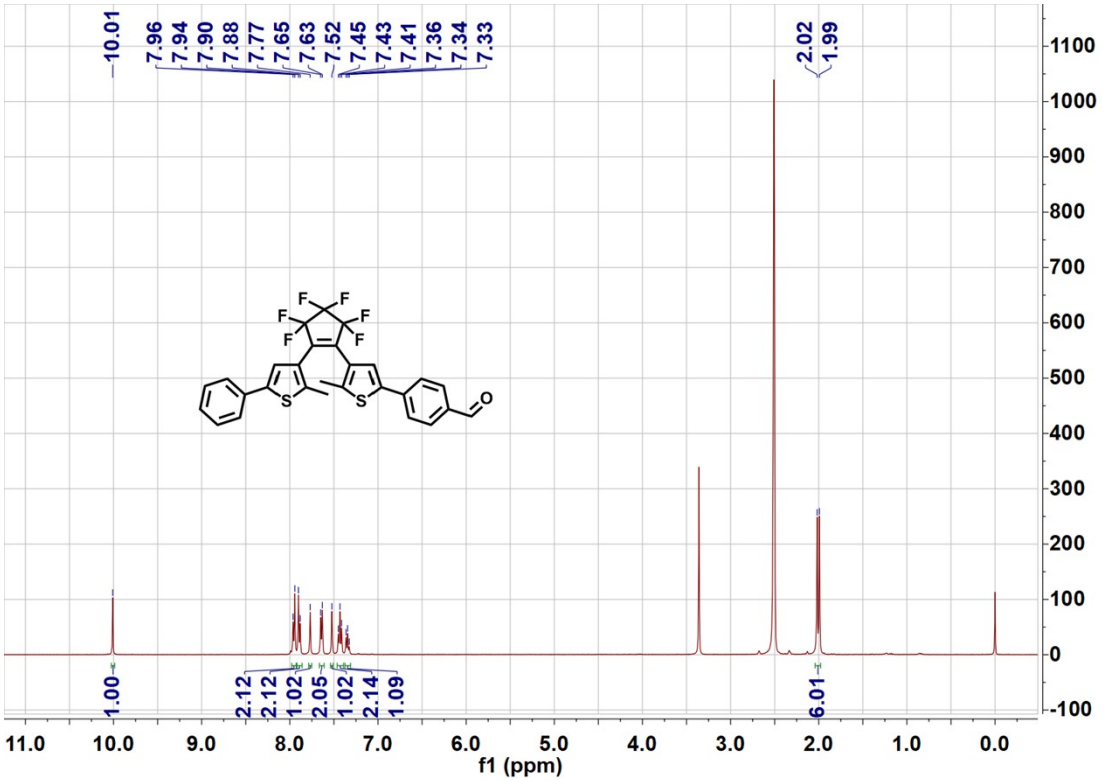
10.01
7.96
7.94
7.90
7.88
7.77
7.65
7.63
7.52
7.45
7.43
7.41
7.36
7.34
7.33
2.02
1.99
1.00
2.12
2.12
1.02
2.05
1.02
2.14
1.09
6.01
f1 (ppm)

Fig. S16

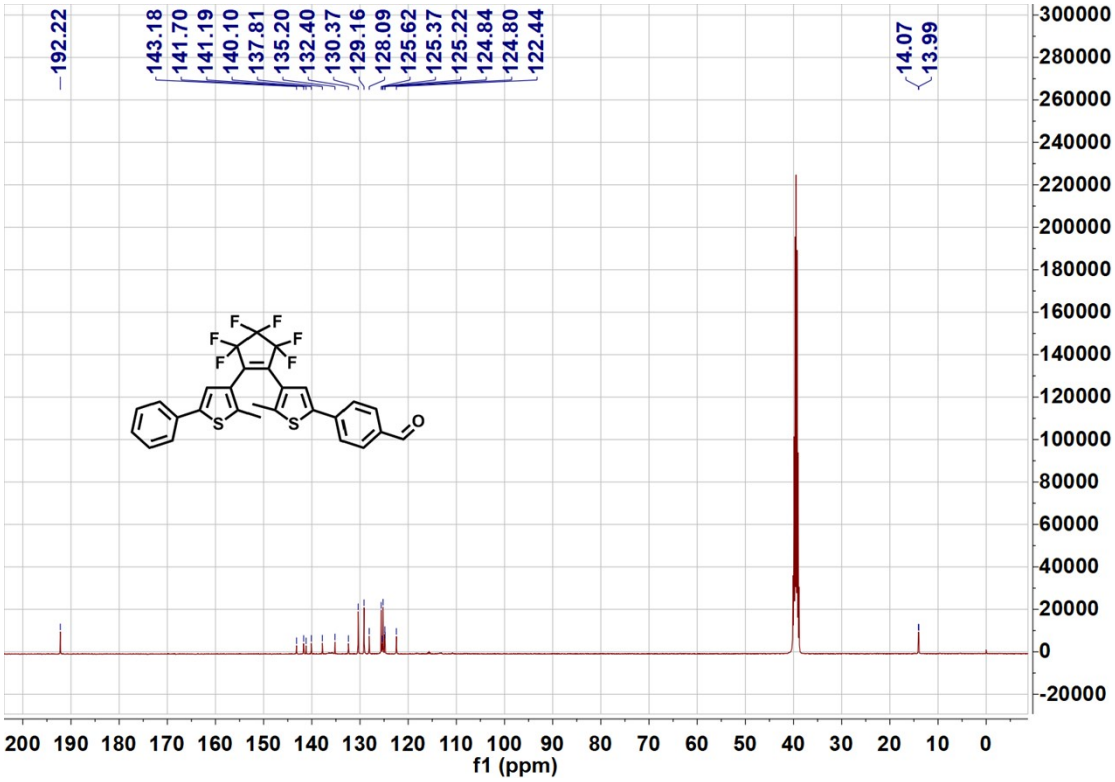
192.22
143.18
141.70
141.19
140.10
137.81
135.20
132.40
130.37
129.16
128.09
125.62
125.37
125.22
124.84
124.80
122.44
14.07
13.99
F
F
F
F
F
S
S
O
300000
280000
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
-20000
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Fig. S17

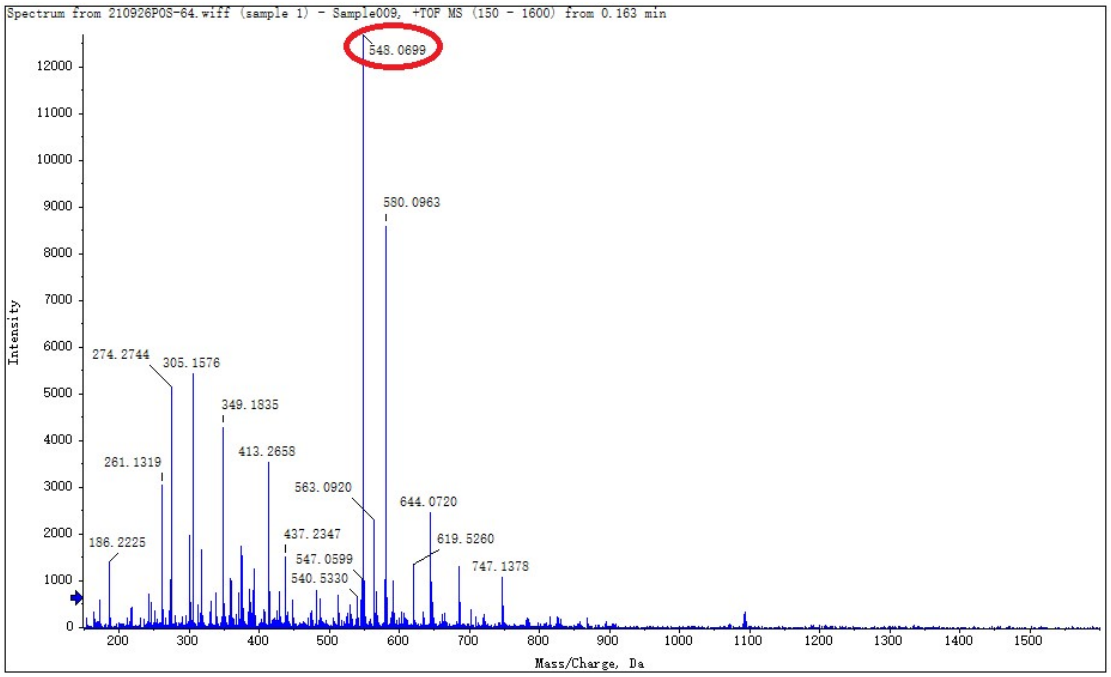
Spectrum from 210926POS-64.wiff (sample 1) - Sample009, +TOF MS (150 - 1600) from 0.163 min
548.0699
580.0963
274.2744
305.1576
349.1835
413.2658
261.1319
563.0920
644.0720
437.2347
619.5260
186.2225
547.0599
747.1378
540.5330
Intensity
Mass/Charge, Da

Fig. S18

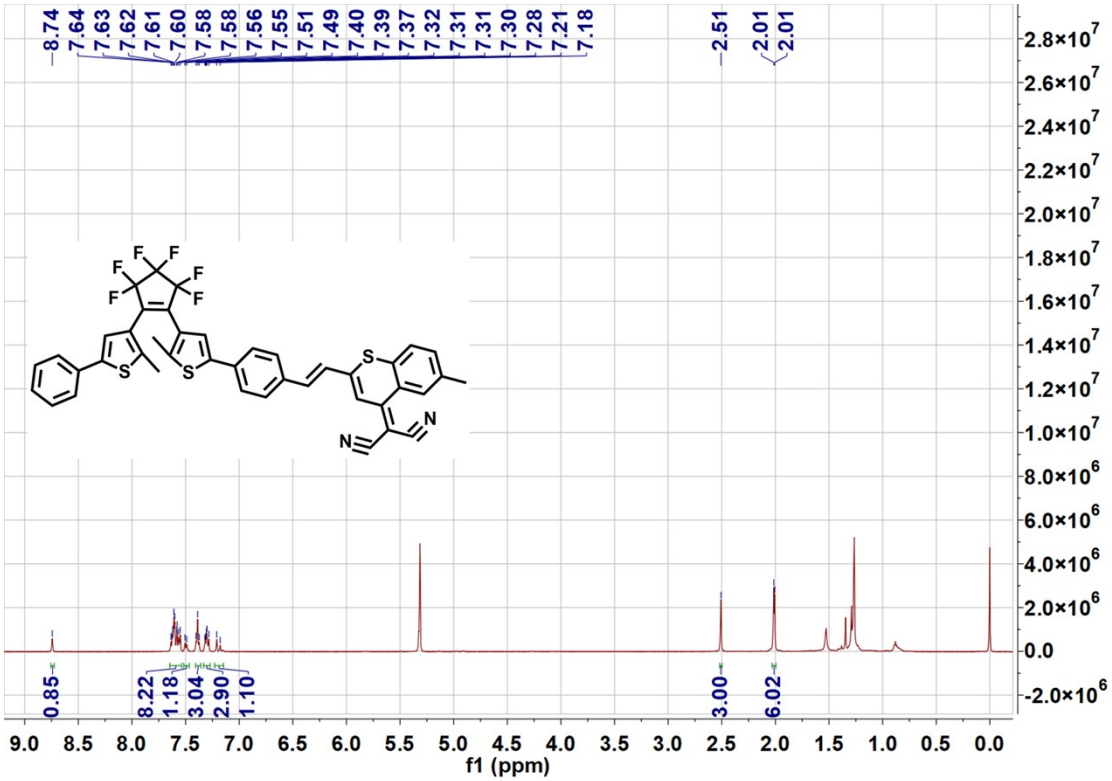
8.74
7.64
7.63
7.62
7.61
7.60
7.58
7.58
7.56
7.55
7.51
7.49
7.40
7.39
7.37
7.32
7.31
7.31
7.30
7.28
7.21
7.18
2.51
2.01
2.01
F
F
F
F
F
F
S
S
S
N
N
2.8×10^7
2.6×10^7
2.4×10^7
2.2×10^7
2.0×10^7
1.8×10^7
1.6×10^7
1.4×10^7
1.2×10^7
1.0×10^7
8.0×10^6
6.0×10^6
4.0×10^6
2.0×10^6
0.0
-2.0×10^6
0.85
8.22
1.18
3.04
2.90
1.10
3.00
6.02
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)

Fig. S19

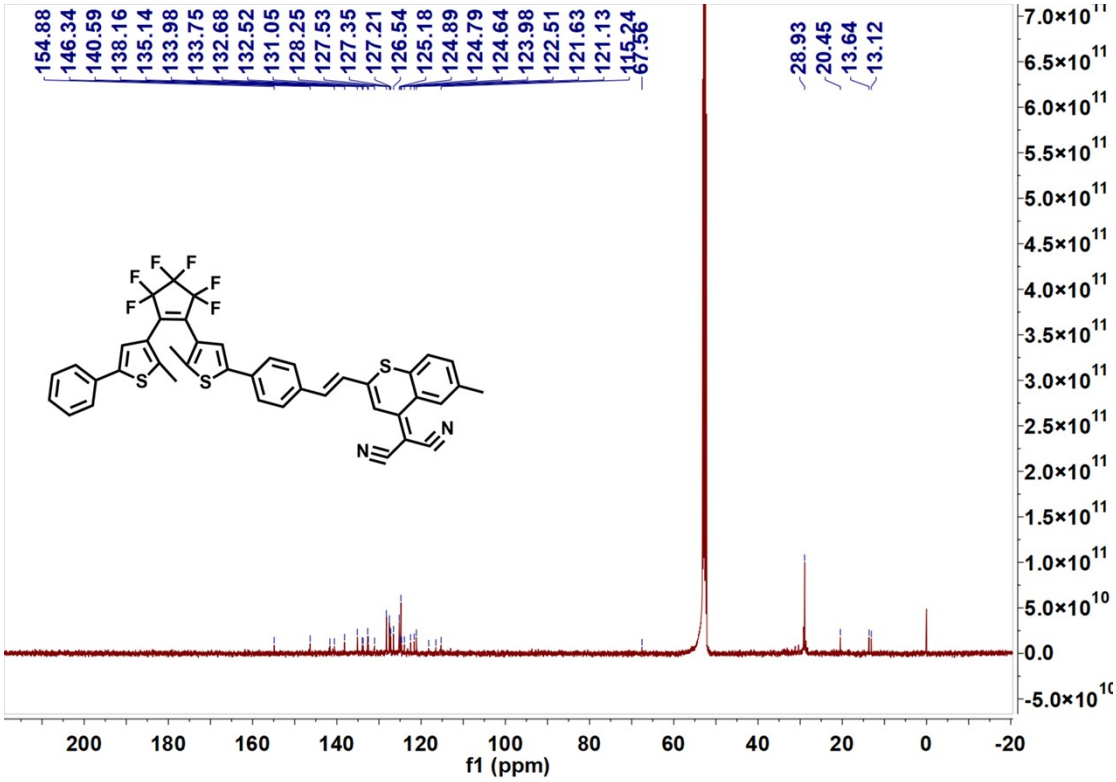
154.88
146.34
140.59
138.16
135.14
133.98
133.75
132.68
132.52
131.05
128.25
127.53
127.35
127.21
126.54
125.18
124.89
124.79
124.64
123.98
122.51
121.63
121.13
115.24
67.56
28.93
20.45
13.64
13.12
F
S
N
7.0×10^11
6.5×10^11
6.0×10^11
5.5×10^11
5.0×10^11
4.5×10^11
4.0×10^11
3.5×10^11
3.0×10^11
2.5×10^11
2.0×10^11
1.5×10^11
1.0×10^11
5.0×10^10
0.0
-5.0×10^10
200
180
160
140
120
100
80
60
40
20
0
-20
f1 (ppm)

Fig. S20

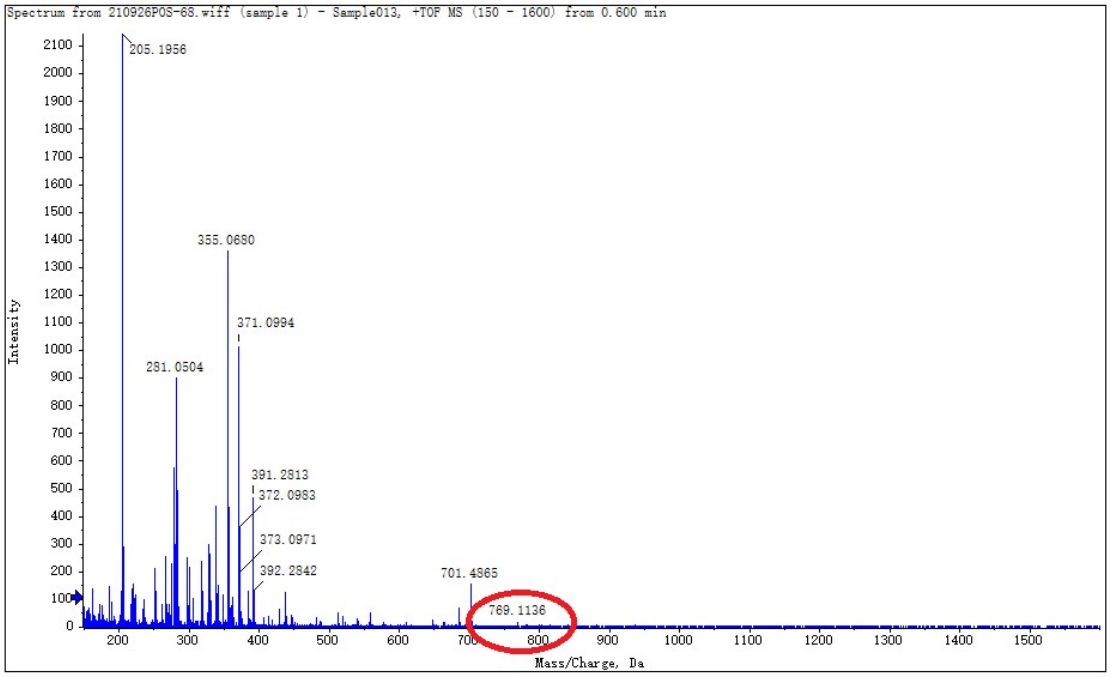
Spectrum from 210926POS-68.wiff (sample 1) - Sample013, +TOF MS (150 - 1600) from 0.600 min
Intensity
205.1956
355.0680
371.0994
281.0504
391.2813
372.0983
373.0971
392.2842
701.4865
769.1136
Mass/Charge, Da

Fig. S21

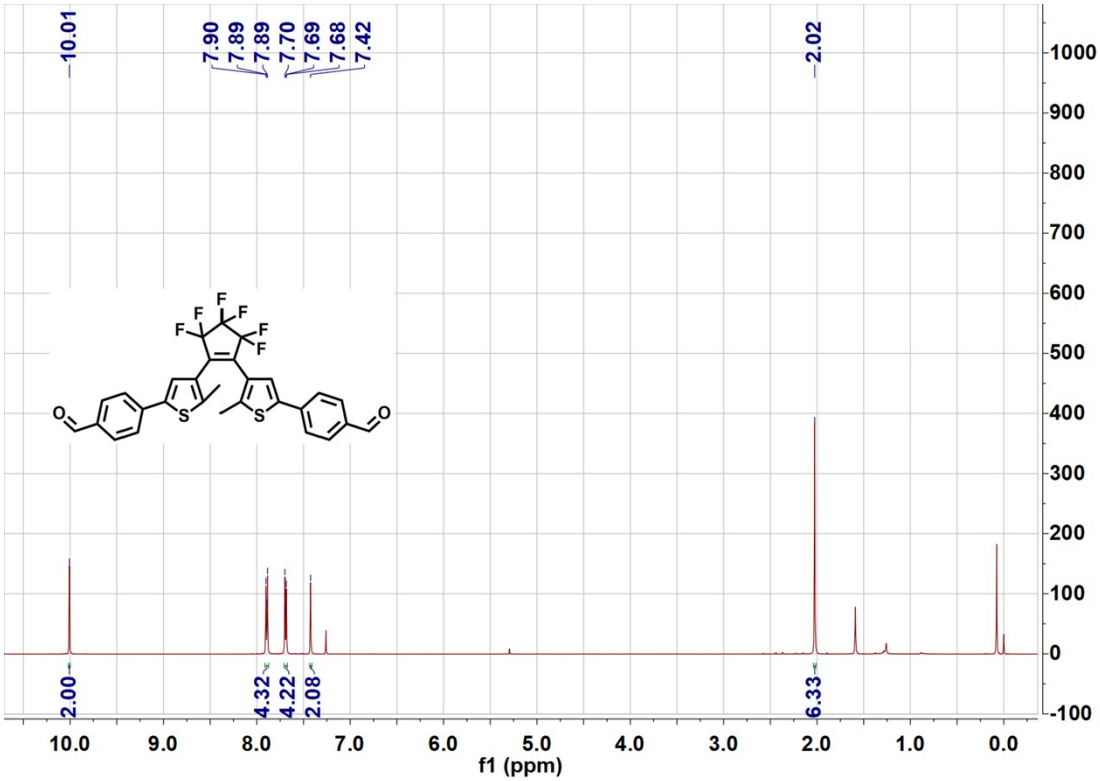

Fig. S22

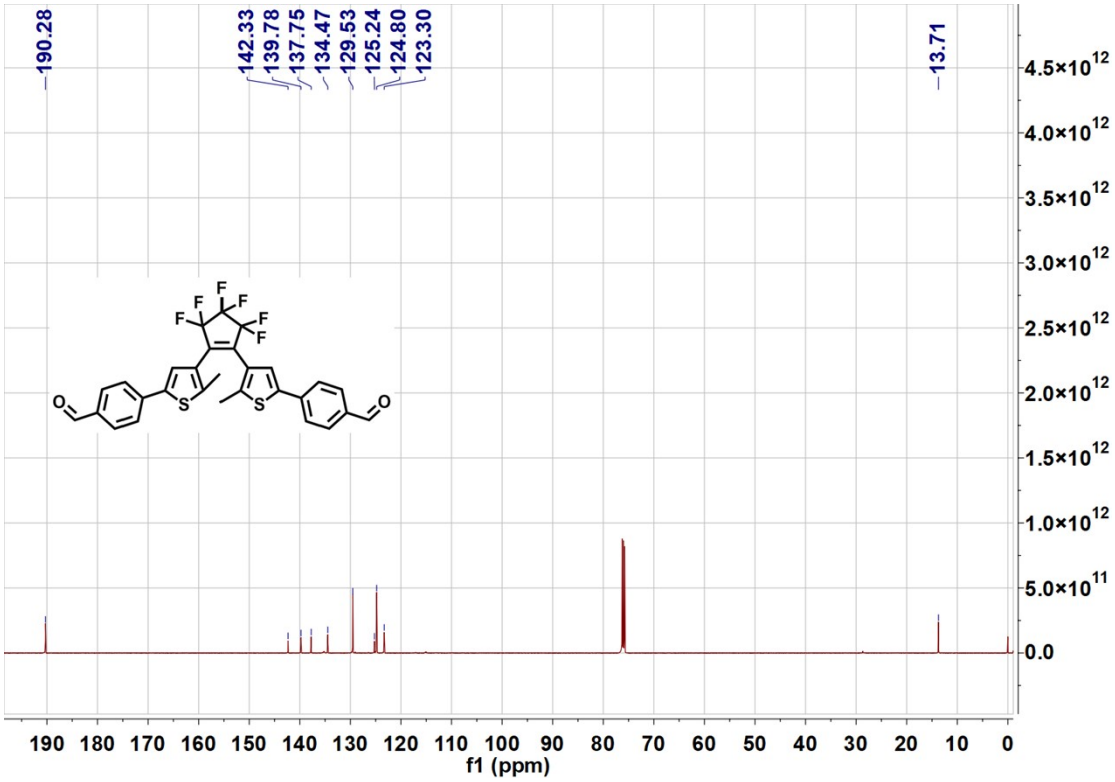
190.28
142.33
139.78
137.75
134.47
129.53
125.24
124.80
123.30
13.71
4.5×10^12
4.0×10^12
3.5×10^12
3.0×10^12
2.5×10^12
2.0×10^12
1.5×10^12
1.0×10^12
5.0×10^11
0.0
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
F
F
F
F
F
F
S
S
O
O

Fig. S23

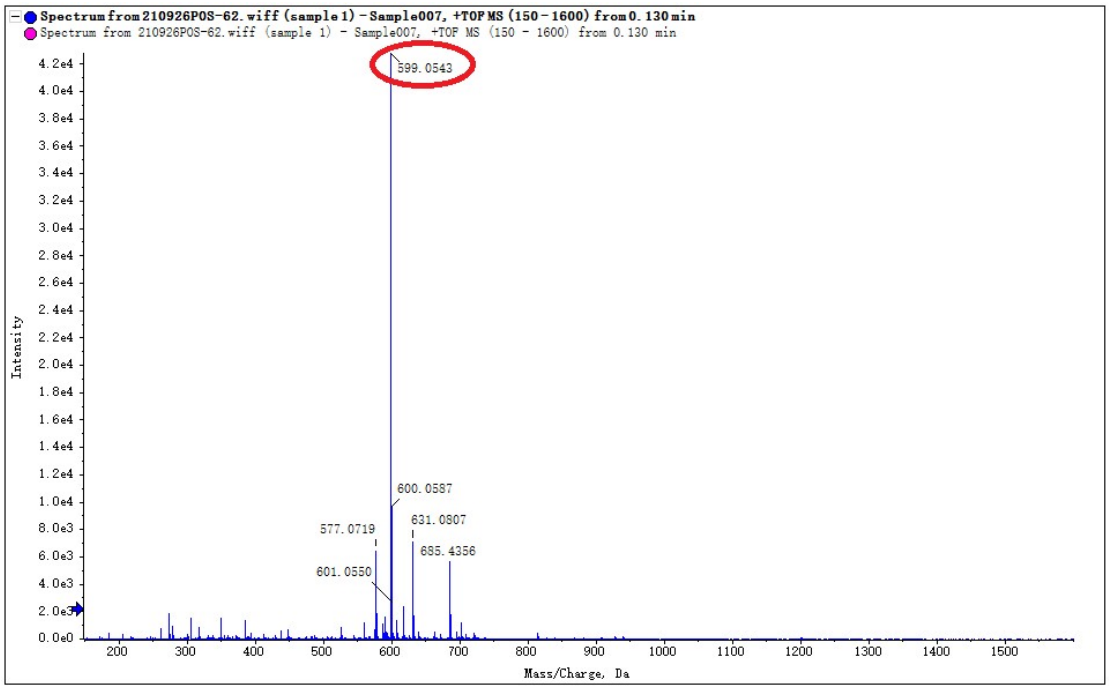
Spectrum from 210926POS-62.wiff (sample 1) - Sample007, +TOF MS (150 - 1600) from 0.130 min
Spectrum from 210926POS-62.wiff (sample 1) - Sample007, +TOF MS (150 - 1600) from 0.130 min
599.0543
600.0587
631.0807
577.0719
685.4356
601.0550
Intensity
Mass/Charge, Da

Fig. S24

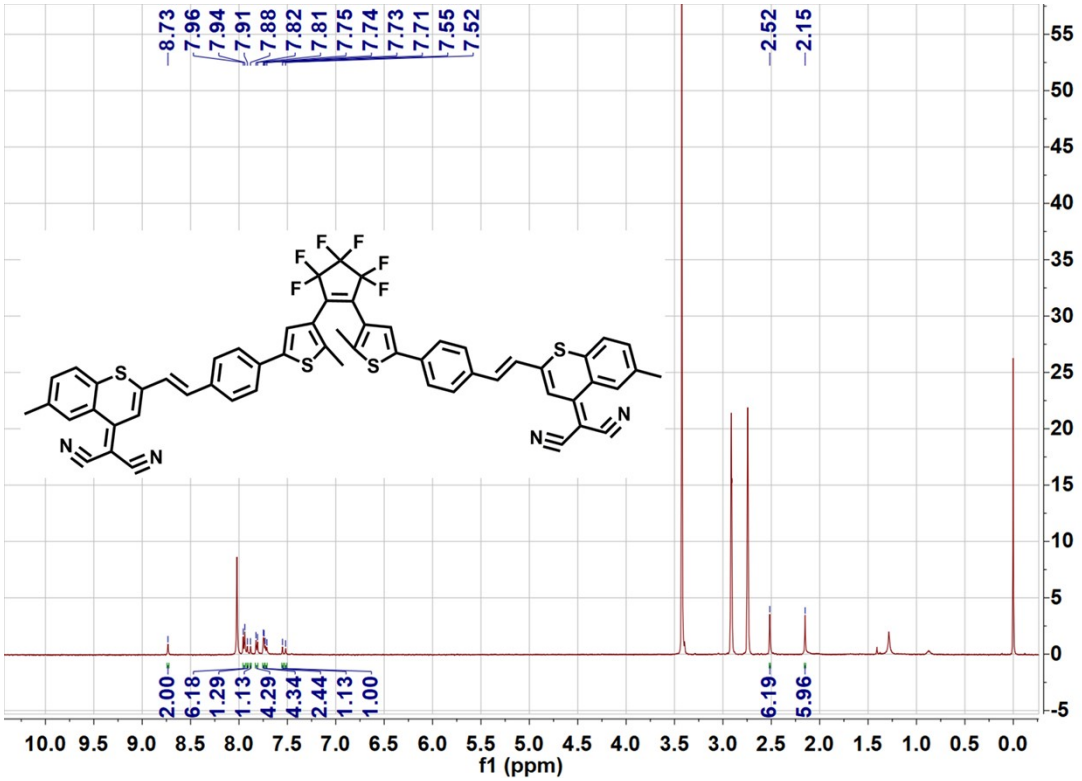
8.73
7.96
7.94
7.91
7.88
7.82
7.81
7.75
7.74
7.73
7.71
7.55
7.52
2.52
2.15
2.00
6.18
1.29
1.13
4.29
4.34
2.44
1.13
1.00
6.19
5.96
f1 (ppm)

Fig. S25

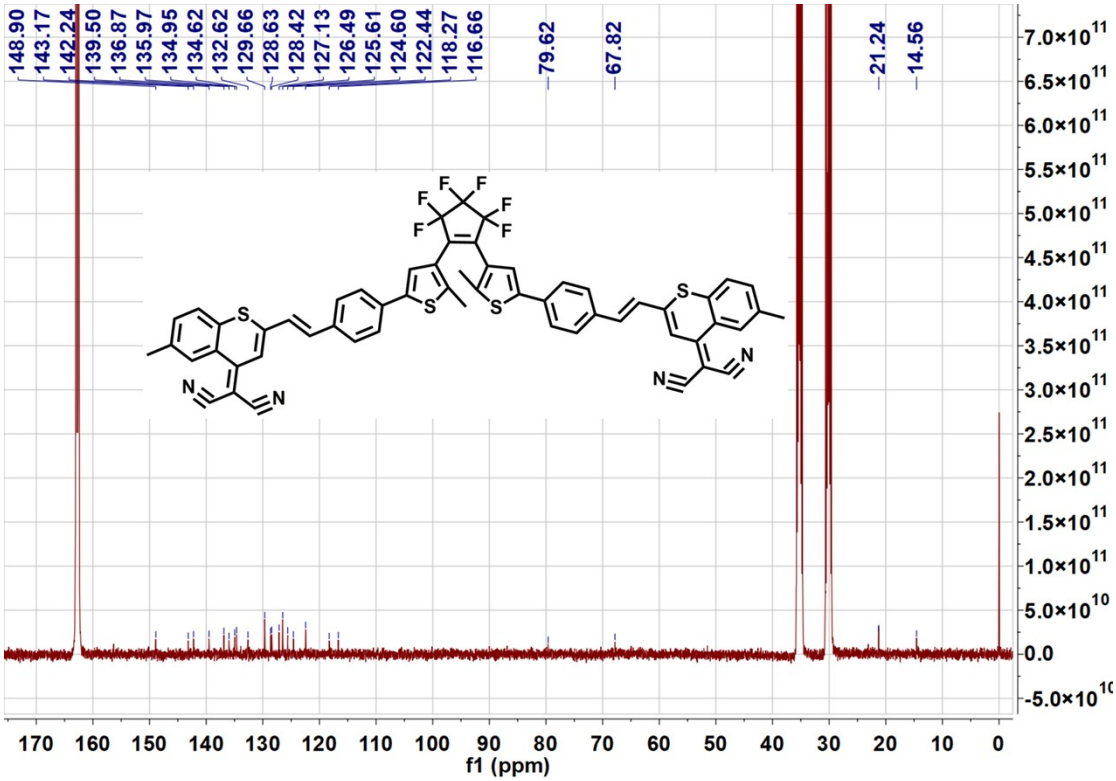
148.90
143.17
142.24
139.50
136.87
135.97
134.95
134.62
132.62
129.66
128.63
128.42
127.13
126.49
125.61
124.60
122.44
118.27
116.66
79.62
67.82
21.24
14.56
F
S
N
7.0×10^11
6.5×10^11
6.0×10^11
5.5×10^11
5.0×10^11
4.5×10^11
4.0×10^11
3.5×10^11
3.0×10^11
2.5×10^11
2.0×10^11
1.5×10^11
1.0×10^11
5.0×10^10
0.0
-5.0×10^10
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Fig. S26

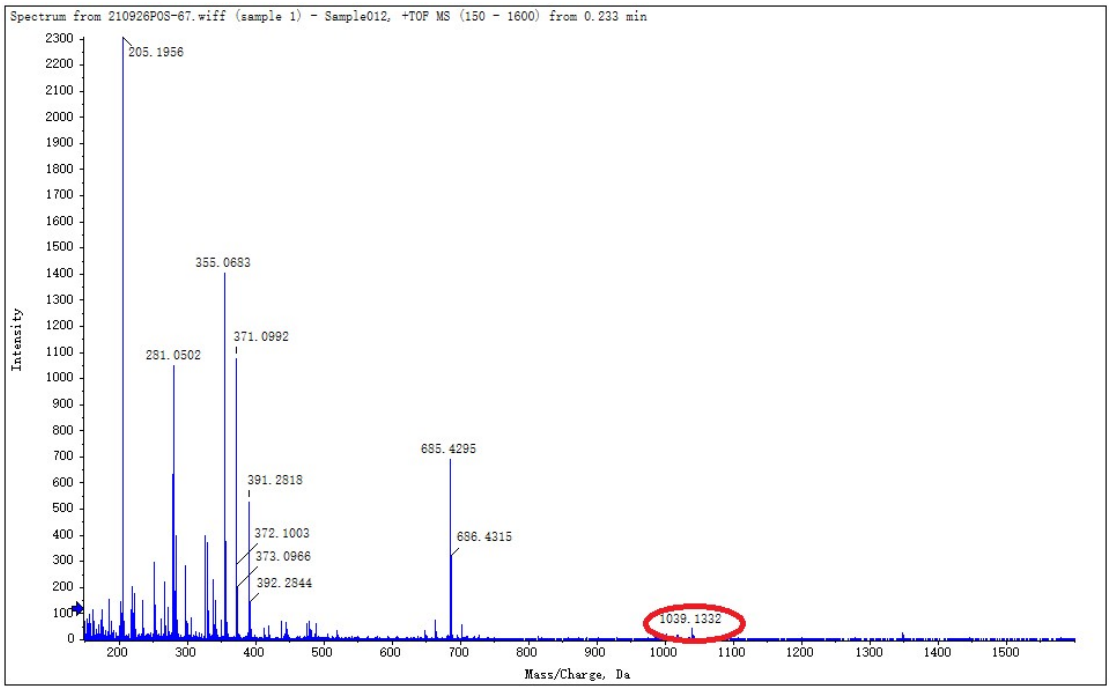
Spectrum from 210926POS-67.wiff (sample 1) - Sample012, +TOF MS (150 - 1600) from 0.233 min
Intensity
Mass/Charge, Da
205.1956
355.0683
371.0992
281.0502
685.4295
391.2818
372.1003
373.0966
392.2844
686.4315
1039.1332

Fig. S27

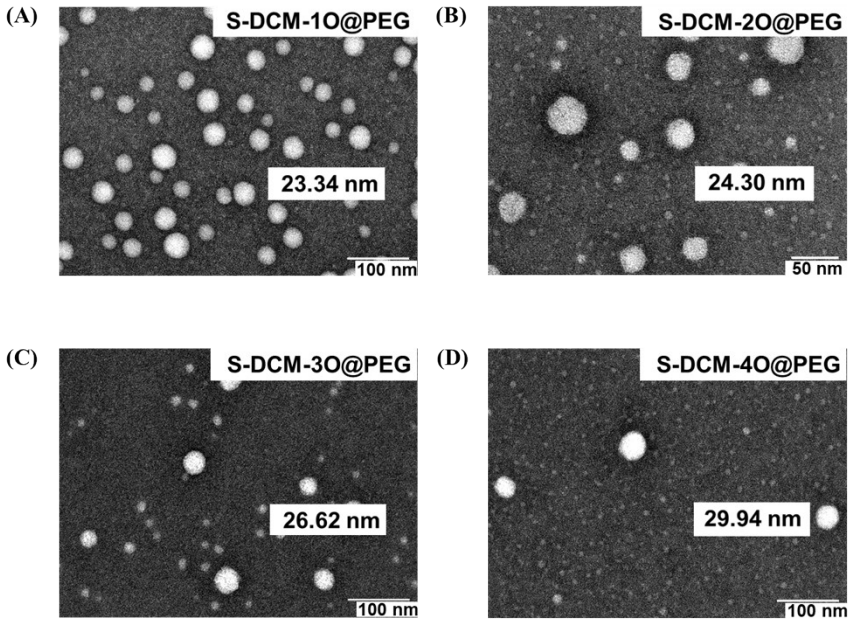
(A)
S-DCM-1O@PEG
23.34 nm
100 nm
(B)
S-DCM-2O@PEG
24.30 nm
50 nm
(C)
S-DCM-3O@PEG
26.62 nm
100 nm
(D)
S-DCM-4O@PEG
29.94 nm
100 nm

Fig. S28

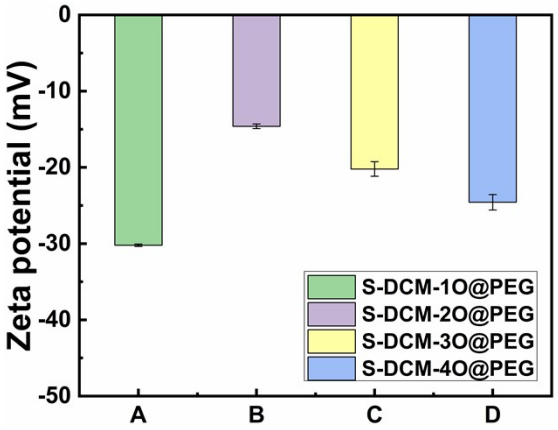
Zeta potential (mV)
0
-10
-20
-30
-40
-50
A
B
C
D
S-DCM-1O@PEG
S-DCM-2O@PEG
S-DCM-3O@PEG
S-DCM-4O@PEG

Fig. S29

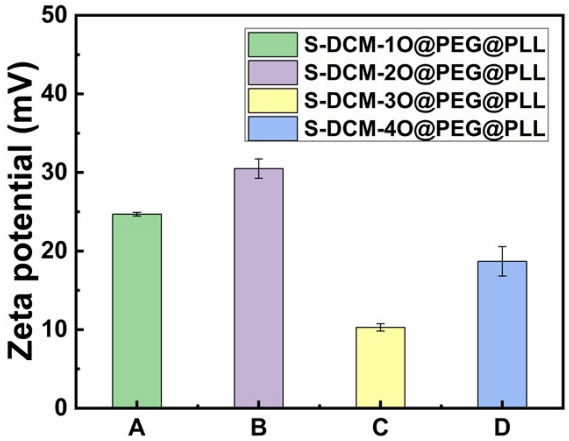
Zeta potential (mV)
50
40
30
20
10
0
A
B
C
D
S-DCM-1O@PEG@PLL
S-DCM-2O@PEG@PLL
S-DCM-3O@PEG@PLL
S-DCM-4O@PEG@PLL

Fig. S30

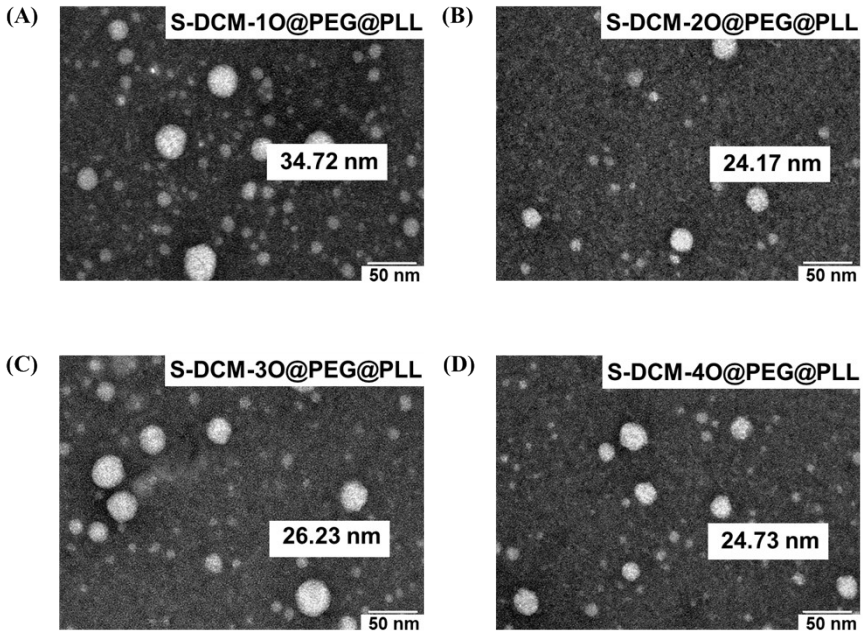
(A)
S-DCM-1O@PEG@PLL
34.72 nm
50 nm
(B)
S-DCM-2O@PEG@PLL
24.17 nm
50 nm
(C)
S-DCM-3O@PEG@PLL
26.23 nm
50 nm
(D)
S-DCM-4O@PEG@PLL
24.73 nm
50 nm

Fig. S31

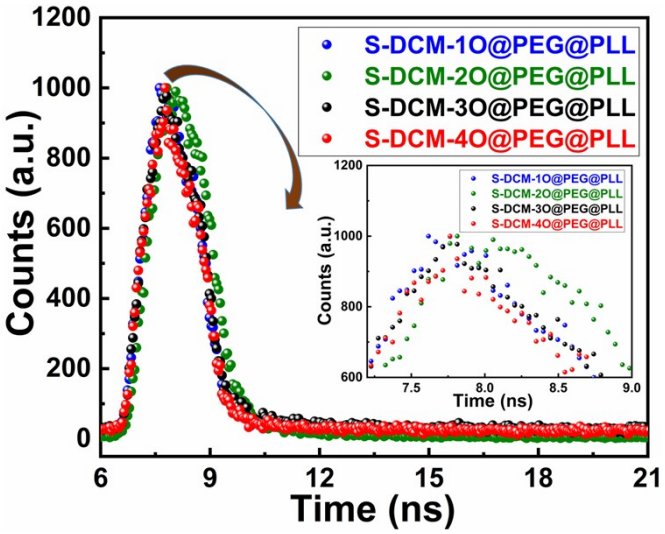
S-DCM-1O@PEG@PLL
S-DCM-2O@PEG@PLL
S-DCM-3O@PEG@PLL
S-DCM-4O@PEG@PLL
Counts (a.u.)
Time (ns)
1200
1000
800
600
400
200
0
6
9
12
15
18
21
7.5
8.0
8.5
9.0

Fig. S32

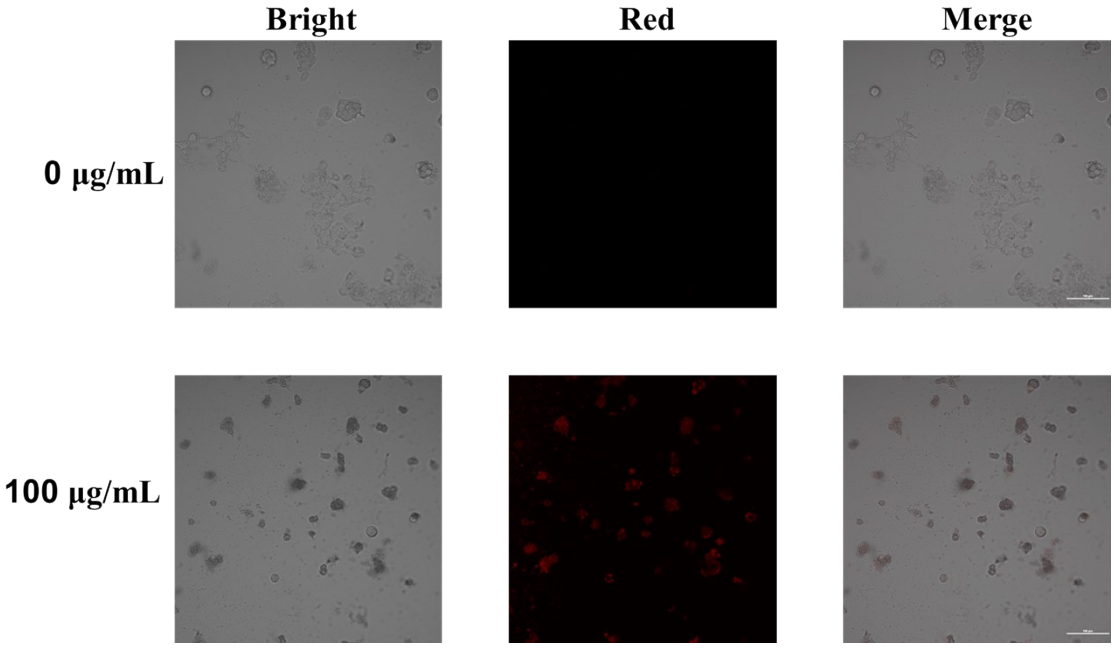

Fig. S33

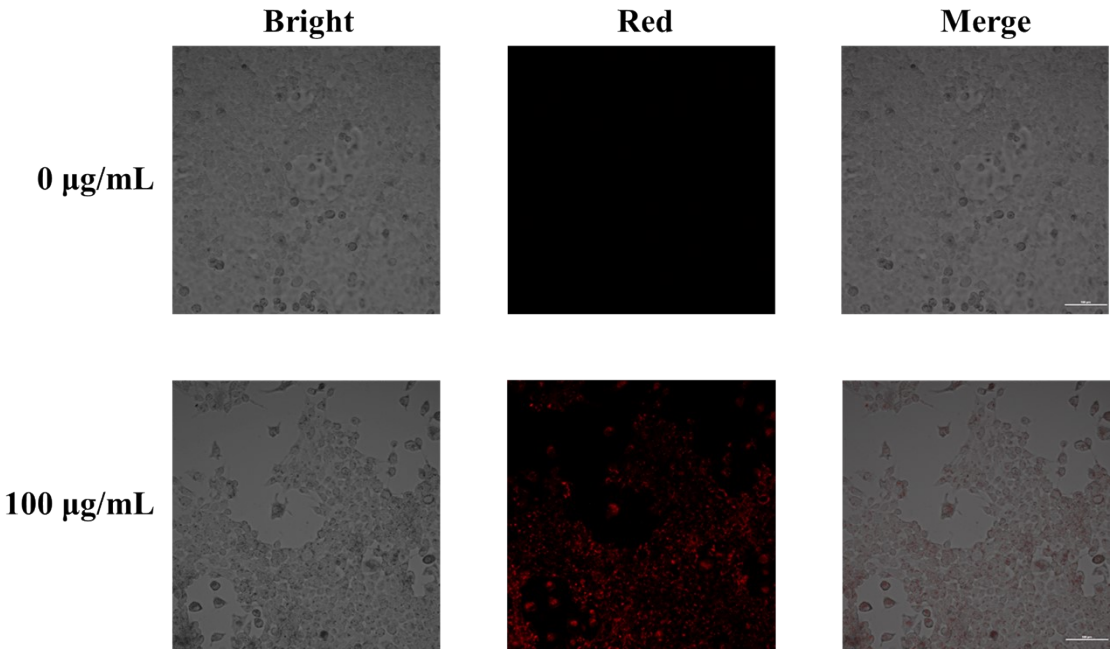

Fig. S34

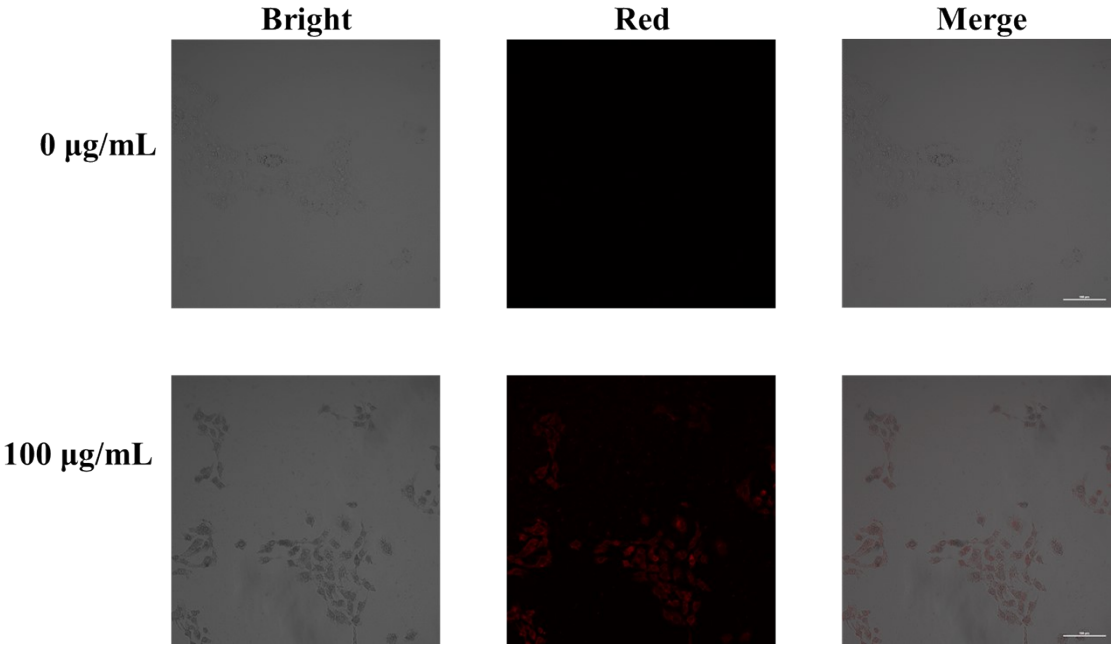

Fig. S35

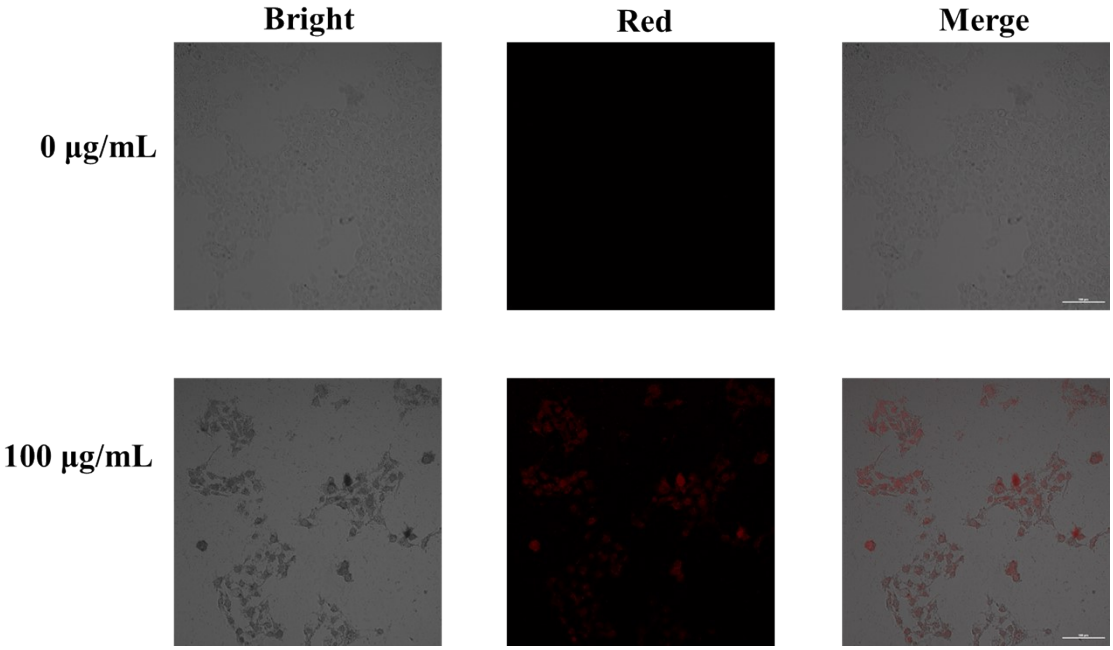

Fig. S36

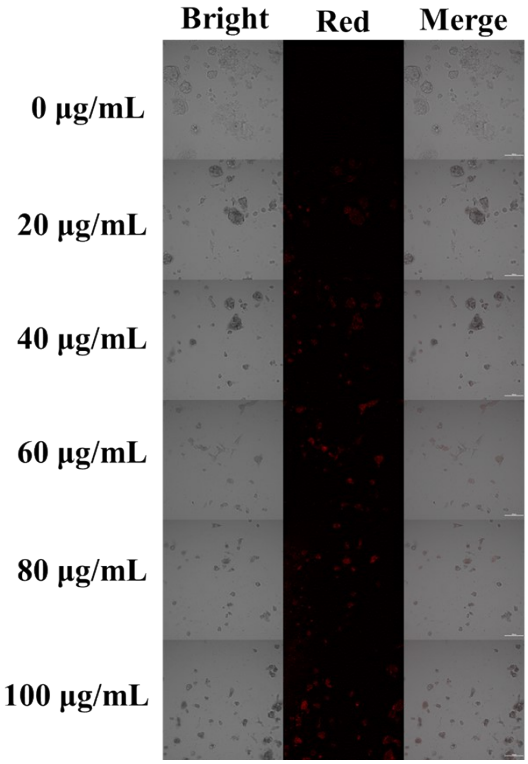
Bright
Red
Merge
0 μg/mL
20 μg/mL
40 μg/mL
60 μg/mL
80 μg/mL
100 μg/mL

Fig. S37

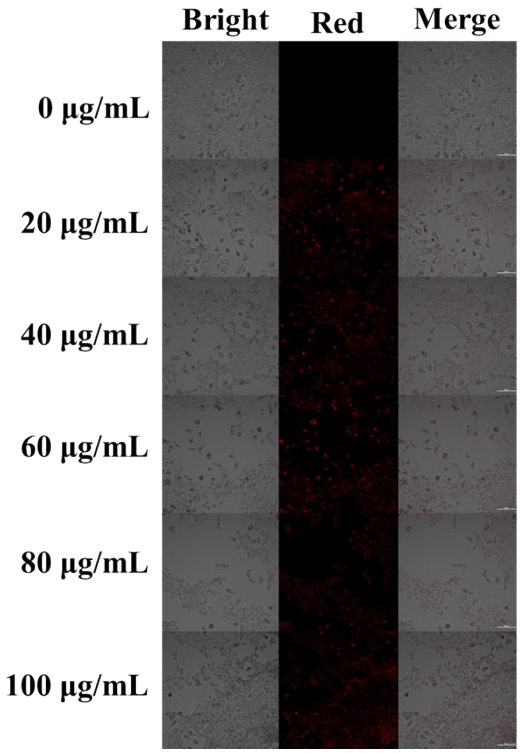
Bright
Red
Merge
0 μg/mL
20 μg/mL
40 μg/mL
60 μg/mL
80 μg/mL
100 μg/mL

Fig. S38

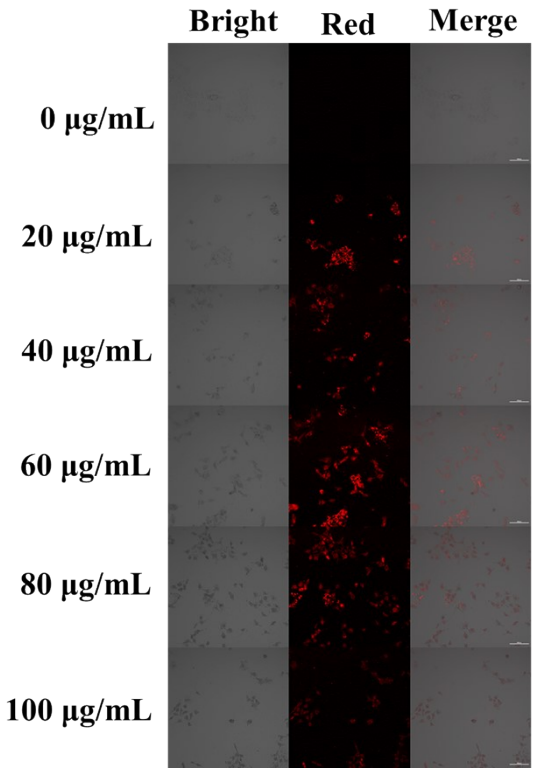
Bright
Red
Merge
0 μg/mL
20 μg/mL
40 μg/mL
60 μg/mL
80 μg/mL
100 μg/mL

Fig. S39

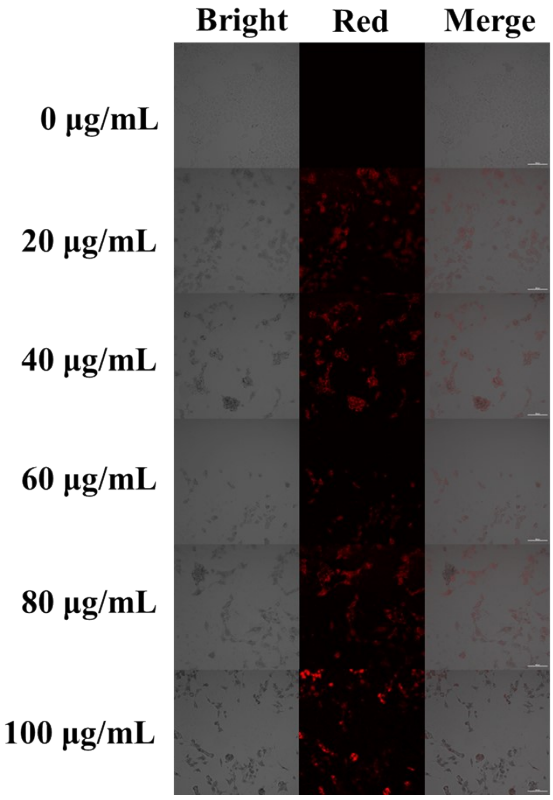
Bright
Red
Merge
0 μg/mL
20 μg/mL
40 μg/mL
60 μg/mL
80 μg/mL
100 μg/mL

Fig. S40