

Supplementary Materials: Investigations of New Phenothiazine-Based Compounds for Dye-Sensitized Solar Cells with Theoretical Insight

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Synthesis of Compounds 1a-1c

7. -[(Dibenzothiophen-2-yl)ethynyl]-10-octyl-10H-phenothiazin-3-carbaldehyde (1a)

A mixture of 7-(2-[(trimethylsilyl)ethynyl]-10-octyl-10H-phenothiazin-3-carbaldehyde (II) 1.4 g (2.38 mmol) and 2-bromodibenzothiophene 480 mg (1.84 mmol) dissolved in 90 mL of dry tetrahydrofuran (THF). The mixture was stirred under argon for 30 minutes. The catalytic mixture of [Pd(PPh₃)₄] 424 mg (0.36 mmol) and CuI 35 mg (0.36 mmol) were added and then 1M solution of tetrabutylammonium fluoride (TBAF) in THF 2.4 mL (2.4 mmol) was injected through the septum and the mixture was heated at 75 °C for 24h. After being cooled to room temperature, the reaction mixture was evaporated under reduced pressure. The crude product was purified by column chromatography using CHCl₃ as eluent. Yield: 40% (384 mg).

¹H NMR (400 MHz, CDCl₃) δ 9.80 (s, 1H), 8.29 (m, 1H), 8.15 (m, 1H), 7.86 (m, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.63 (dd, *J* = 7.6 Hz, 1.6 Hz, 1H), 7.58 (m, 2H), 7.48 (m, 2H), 7.35 (dd, *J* = 7.6 Hz, 1.6 Hz, 1H), 7.31 (s, 1H), 6.90 (d, *J* = 8.4 Hz, 1H), 6.84 (d, *J* = 8.4 Hz, 1H), 3.88 (t, *J* = 6.8 Hz, 2H), 1.81 (m, 2H), 1.26 (m, 10H), 0.88 (m, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 189.91, 150.02, 143.39, 139.76, 139.48, 135.70, 134.94, 131.35, 130.99, 130.25, 130.11, 129.65, 128.42, 127.16, 124.68, 124.63, 124.48, 123.93, 122.87, 122.77, 121.73, 119.31, 118.44, 115.66, 114.97, 90.07, 88.36, 48.16, 31.71, 29.18, 29.13, 26.77, 26.69, 22.61, 14.08.

HRMS (ESI): *m/z* calcd. for C₃₅H₃₁NOS₂: 545.1842 [M]; found 545.1840.

7. -{2-[(2,2'-bithiophen-5-yl)ethynyl]}-10-octyl-10H-phenothiazin-3-carbaldehyde (1b)

A mixture of 7-bromo-10-octyl-10H-phenothiazin-3-carbaldehyde (I) 2.5 g (5.97 mmol), 5-(2-[(trimethylsilyl)ethynyl]-2,2'-bithiophene 2.2 g (8.37 mmol) in 120 mL dry tetrahydrofuran (THF) was stirred under argon for 15 minutes. The catalytic mixture of [Pd(PPh₃)₄] 1.38 g (1.19 mmol) and CuI 0.23 g (1.19 mmol) was added and then 1M solution of tetrabutylammonium fluoride (TBAF) in THF (8.4 mL, 8.4 mmol) was injected through the septum and the mixture was heated at 65 °C for 24h. After being cooled to room temperature, the mixture was filtered and the filtrate was evaporated under reduced pressure. The crude product was purified by column chromatography using CHCl₃ as eluent. Yield 77% (2.43 g).

¹H NMR (400 MHz, CDCl₃) δ 9.81 (s, 1H), 7.64 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.57 (d, *J* = 1.6 Hz, 1H), 7.29 (dd, *J* = 5.2, 2.4 Hz, 1H), 7.24 (dd, *J* = 4.0, 1.6 Hz, 2H), 7.19 (dd, *J* = 3.6, 0.8 Hz, 1H), 7.14 (d, *J* = 3.6 Hz, 1H), 7.06 (d, *J* = 3.6 Hz, 1H), 7.02 (dd, *J* = 5.2, 3.6 Hz, 1H), 6.90 (d, *J* = 8.6 Hz, 1H), 6.82 (d, *J* = 8.6 Hz, 1H), 3.91 – 3.85 (m, 2H), 1.86 – 1.75 (m, 2H), 1.33 – 1.23 (m, 8H), 0.90 – 0.83 (m, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 189.88, 149.89, 143.53, 138.88, 136.74, 132.65, 131.38, 130.81, 130.11, 129.95, 128.40, 127.97, 125.01, 124.39, 124.23, 123.93, 123.57, 121.89, 117.94, 115.64, 114.99, 93.15, 83.18, 48.16, 31.72, 29.18, 29.12, 26.76, 26.66, 22.62, 14.10.

HRMS (ESI): m/z calcd. for $C_{31}H_{30}NOS_3$: 528.1484 $[MH^+]$; found 528.1483.

7. -[2-(9,9'-dibutylfluoren-2-yl)ethynyl]-10-octyl-10H-phenothiazin-3-carbaldehyde (1c)

Compound 1c was prepared from 7-bromo-10-octyl-10H-phenothiazin-3-carbaldehyde (I) (500 mg, 1.2 mmol) and 670 mg (1.79 mmol) 2-(2-trimethylsilyl)ethynyl-9,9'-dibutylfluorene according to the synthetic route described for 1b. Compound 1c was purified by column chromatography using hexane/dichloromethane (10:3), and then dichloromethane. Yield: 63% (482 mg).

1H NMR (400 MHz, $CDCl_3$) δ 9.81 (s, 1H), 7.67 (m, 3H), 7.58 (d, J = 1.6 Hz, 1H), 7.51 – 7.47 (m, 2H), 7.38 – 7.29 (m, 5H), 6.90 (d, J = 8.4 Hz, 1H), 6.83 (d, J = 8.4 Hz, 1H), 3.89 (t, J = 6.8 Hz, 2H), 1.98 (t, J = 8.3 Hz, 4H), 1.88 – 1.77 (m, 2H), 1.44 (m, 2H), 1.28 (m, 8H), 1.09 (m, 4H), 0.90 – 0.85 (m, 4H), 0.68 (t, J = 7.3 Hz, 6H), 0.60 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.89, 151.03, 150.80, 150.04, 143.27, 141.46, 140.42, 131.34, 130.93, 130.53, 130.22, 130.11, 128.42, 127.54, 126.90, 125.86, 124.50, 123.88, 122.91, 121.34, 120.00, 119.65, 118.64, 115.65, 114.97, 91.06, 88.36, 55.06, 48.16, 40.20, 31.72, 29.18, 29.13, 26.77, 26.69, 25.92, 23.07, 22.62, 14.09, 13.82.

HRMS (ESI): m/z calcd. for $C_{44}H_{49}NOS$: 639.3535 $[M]$; found 639.3529.

Synthesis of Compounds 2a-2c

2. -Cyano-3-[7-(dibenzothiophen-2-yl)ethynyl]-10-octyl-10H-phenothiazin-3-yl)acrylic acid (2a)

A mixture of 7-[dibenzothiophen-2-yl)ethynyl]-10-octyl-10H-phenothiazin-3-carbaldehyde (1a) 0.06 g (0.11 mmol) and cyanoacetic acid 0.04 g (0.46 mmol) were dissolved in 10 mL of chloroform. The mixture was stirred under argon for 30 minutes. Then 0.1 mL of piperidine 0.087 g (1.00 mmol) was added and the mixture was heated at 60 °C for 24 h. After being cooled to room temperature, the water was added (30 mL) and the mixture was extracted with chloroform (3 times with 15 mL). The organic layers were collected and dried over anhydrous $MgSO_4$. After filtration, the solvent was removed under reduced pressure and the crude product was purified by chromatography ($CHCl_3/MeOH$, 15:1) to give a dark red solid of 2a. Yield: 52%.

1H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 8.15 (s, 1H), 8.01 (s, 1H), 7.84 (m, 3H), 7.58 (m, 2H), 7.48 (m, 2H), 7.35 (d, J = 8.8 Hz, 1H), 7.24 (m, 1H), 6.79 (m, 2H), 3.82 (m, 2H), 1.80 (m, 2H), 1.28 (m, 10H), 0.89 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.57, 154.17, 149.13, 142.52, 139.73, 139.50, 135.68, 134.91, 131.84, 131.53, 131.08, 130.30, 130.10, 129.67, 127.16, 125.62, 124.69, 124.63, 123.87, 123.19, 122.85, 122.79, 121.75, 119.25, 118.70, 115.91, 115.56, 114.97, 98.02, 90.32, 88.30, 48.30, 31.73, 29.19, 29.15, 26.79, 26.57, 22.62, 14.10. Anal. Calcd for $C_{38}H_{32}N_2O_2S_2$: C 74.48, N 4.57, H 5.26; Found: C 74.12, N 4.37, H 5.13. DSC: (I run) T_m = 68 °C; (II run) T_g = 64 °C.

2. -Cyano-3-(7-(2,2'-bithien-5-yl)ethynyl)-10-octyl-10H-phenothiazin-3-yl)acrylic acid (2b).

Compound 2b was prepared from 7-(2-(5,5'-bithienyl)ethynyl)-10-octyl-10H-phenothiazin-3-carbaldehyde (1b) (160 mg, 0.30 mmol) according to the synthetic route described for 2a. Compound 2b was purified by column chromatography ($CHCl_3/MeOH$, 20:1) afforded a dark red solid. Yield: 45%.

1H NMR (400 MHz, DMSO) δ 7.98 (s, 1H), 7.82 (d, J = Hz, 1H), 7.73 (s, 1H), 7.58 (m, 1H), 7.49 – 7.36 (m, 2H), 7.36 – 7.25 (m, 3H), 7.17 – 7.05 (m, 3H), 3.99 – 3.87 (m, 2H), 1.68 (m, 2H), 1.35 (m, 2H), 1.21 (m, 8H), 0.82 (m, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.03, 142.71, 139.25, 138.83, 136.76, 134.25, 132.66, 132.43, 131.94, 130.72, 129.66, 129.52, 128.83, 127.97, 125.88, 124.98, 124.20, 123.57, 123.18, 121.88, 114.92, 114.16, 103.19, 93.18, 83.29, 38.91, 31.75, 29.72, 29.18, 24.00, 22.99, 22.65, 14.14. Anal. Calcd for $C_{34}H_{30}N_2O_2S_3$: C 68.65, N 4.71, H 5.08; Found: C 68.38, N 4.56, H 5.01. DSC: (I run) T_m = 56 °C; (II run) T_g = 43 °C.

2. -Cyano-3-(7-[(2-(9,9'-dibutylfluoren-2-yl)ethynyl)]-10-octyl-10H-phenothiazin-3-yl)acrylic acid (2c).

Compound 2c was prepared from compound 1c (55 mg, 0.088 mmol) according to the synthetic route described for 2a. Compound 2c was purified by column chromatography (CHCl₃/MeOH, 20:1) afforded a dark red solid. Yield: 55%.

¹H NMR (400 MHz, DMSO) δ 7.90 (s, 1H), 7.85 (d, J = 3.6 Hz, 1H), 7.82 (d, J = 4.8 Hz, 1H), 7.79 (d, J = 8.8 Hz, 1H), 7.71 – 7.68 (m, 4H), 7.49 (d, J = 8.0 Hz, 1H), 7.45 (m, 1H), 7.41 (d, J = 8.8 Hz, 1H), 7.36 (s, 1H), 7.15 (d, J = 8.4 Hz, 1H), 7.09 (d, J = 8.8 Hz, 1H), 3.94 (m, 2H), 2.01 (m, 4H), 1.63 (m, 4H), 1.25 (m, 4H), 1.02 (m, 4H), 0.86 (m, 8H), 0.62 (m, 6H), 0.44 (m, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 165.99, 150.99, 150.77, 142.86, 141.38, 140.40, 134.20, 130.81, 130.60, 129.95, 129.51, 128.83, 127.50, 126.89, 126.36, 125.78, 123.24, 122.90, 121.41, 120.00, 119.67, 118.36, 118.26, 115.74, 115.20, 114.87, 114.10, 95.11, 91.04, 88.49, 55.02, 48.11, 40.22, 38.92, 31.75, 29.72, 29.68, 29.27, 29.18, 29.00, 26.85, 26.48, 25.92, 23.08, 22.64, 14.13, 13.85. Anal. Calcd for C₄₇H₅₀N₂O₂S: C 79.85, N 3.96, H 7.13; Found: C 79.57, N 3.74, H 7.08. DSC: (I run) T_m = 58 °C; (II run) T_g = 59 °C.

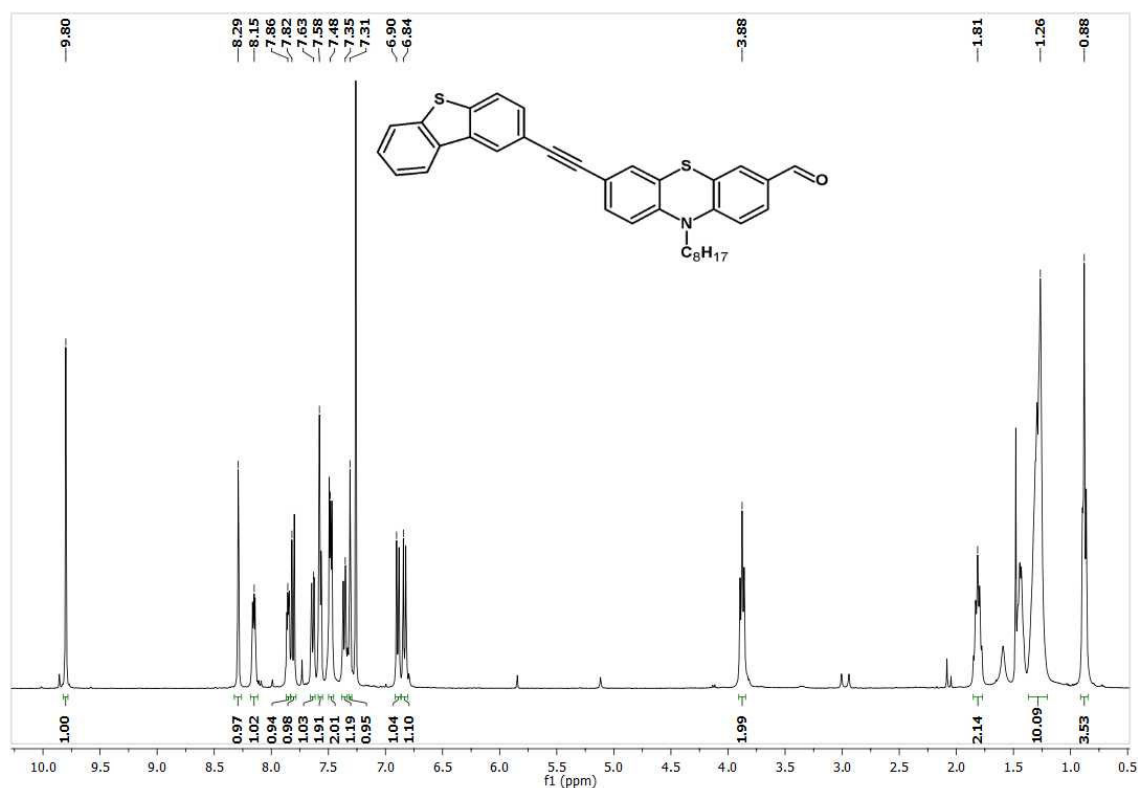
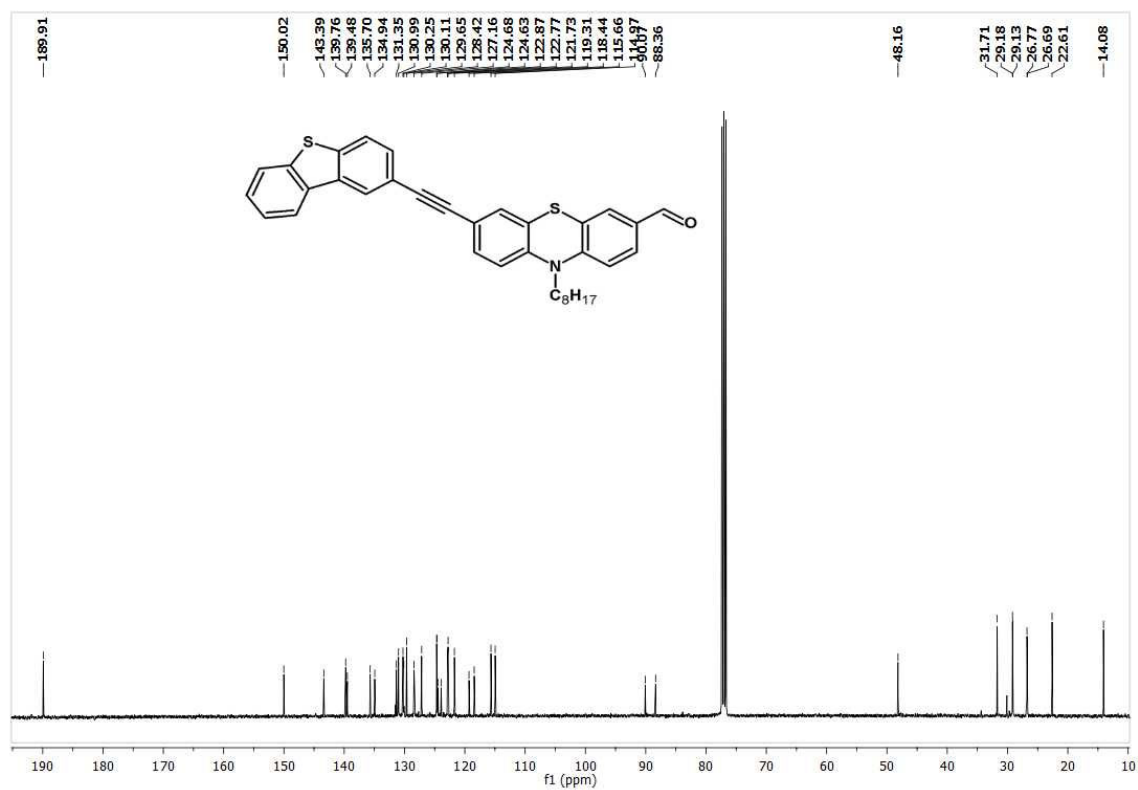
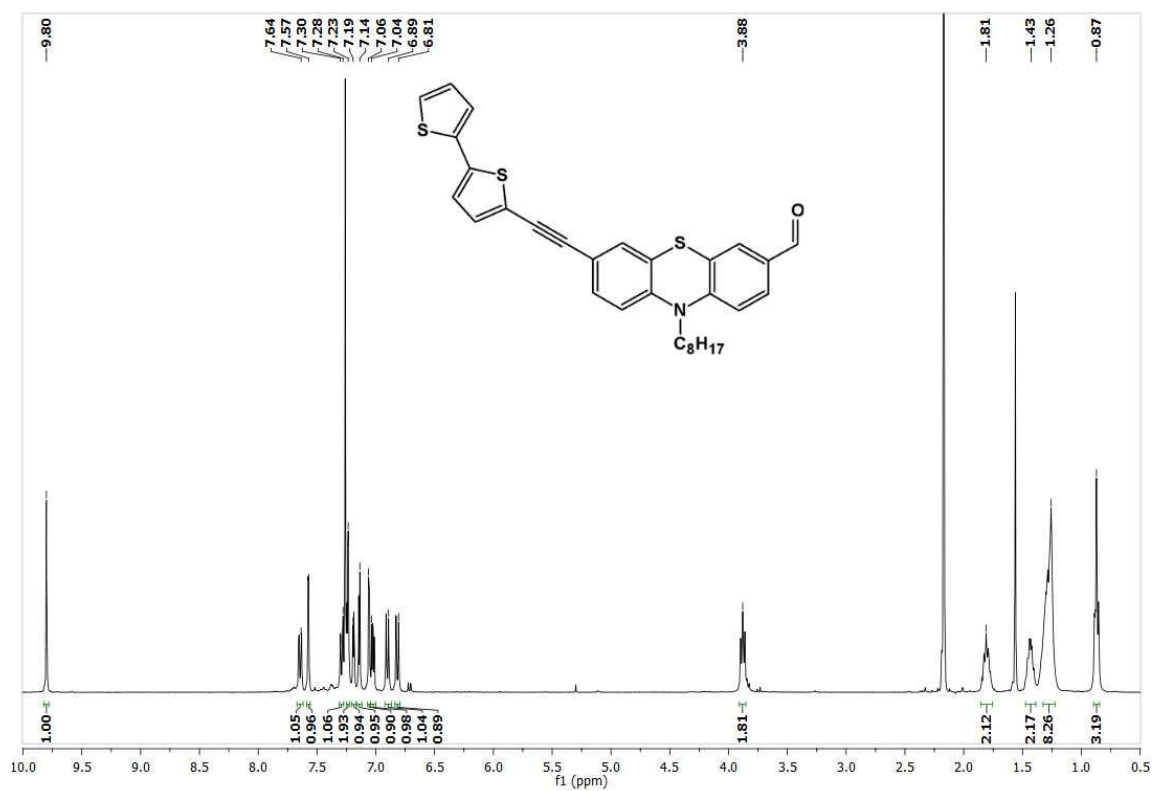
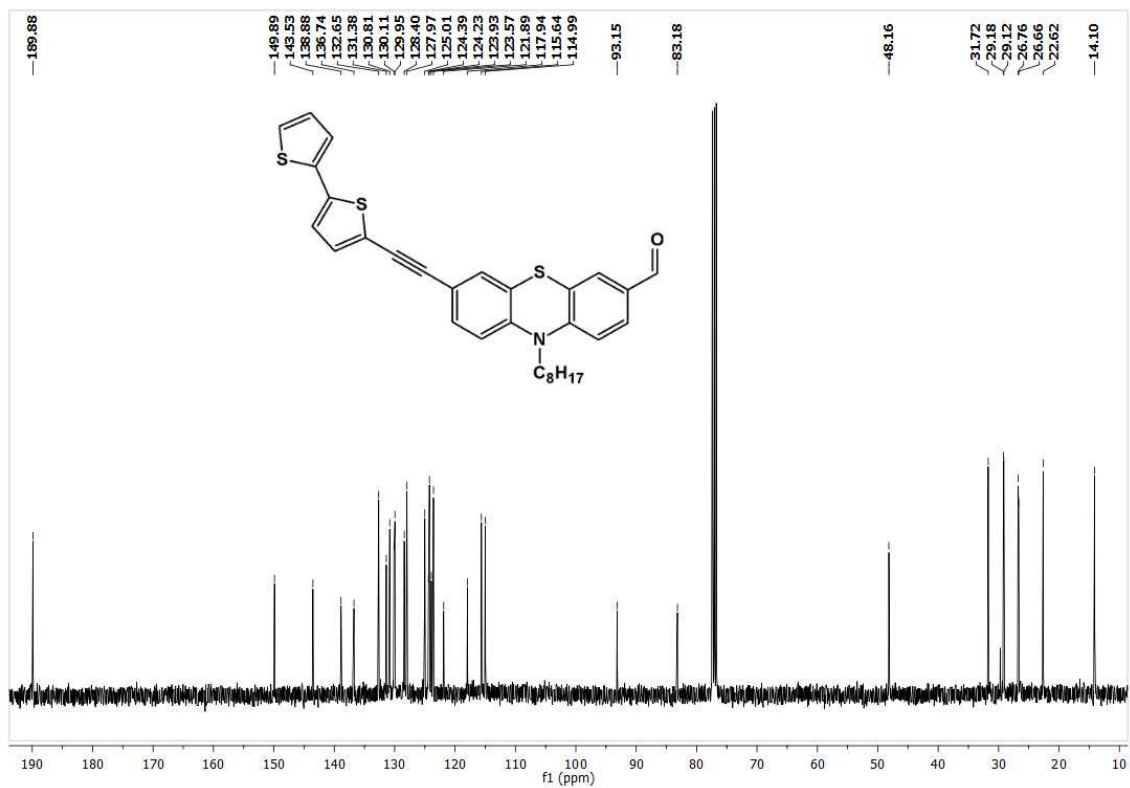
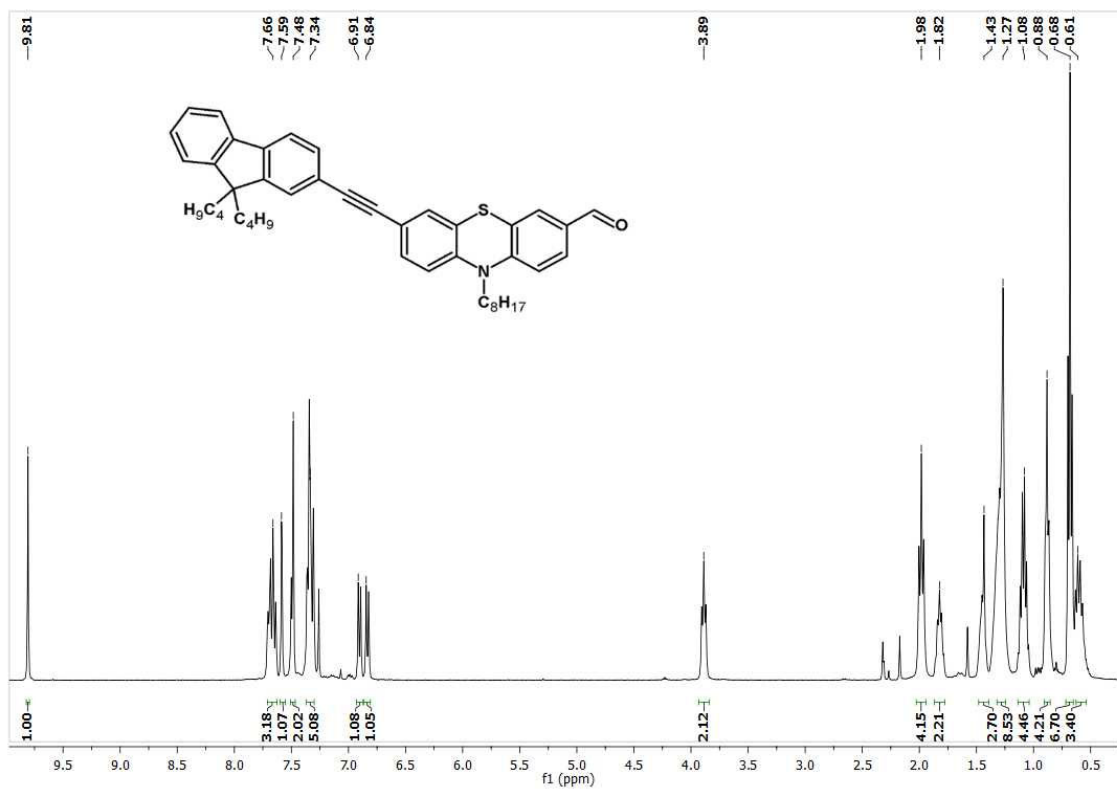
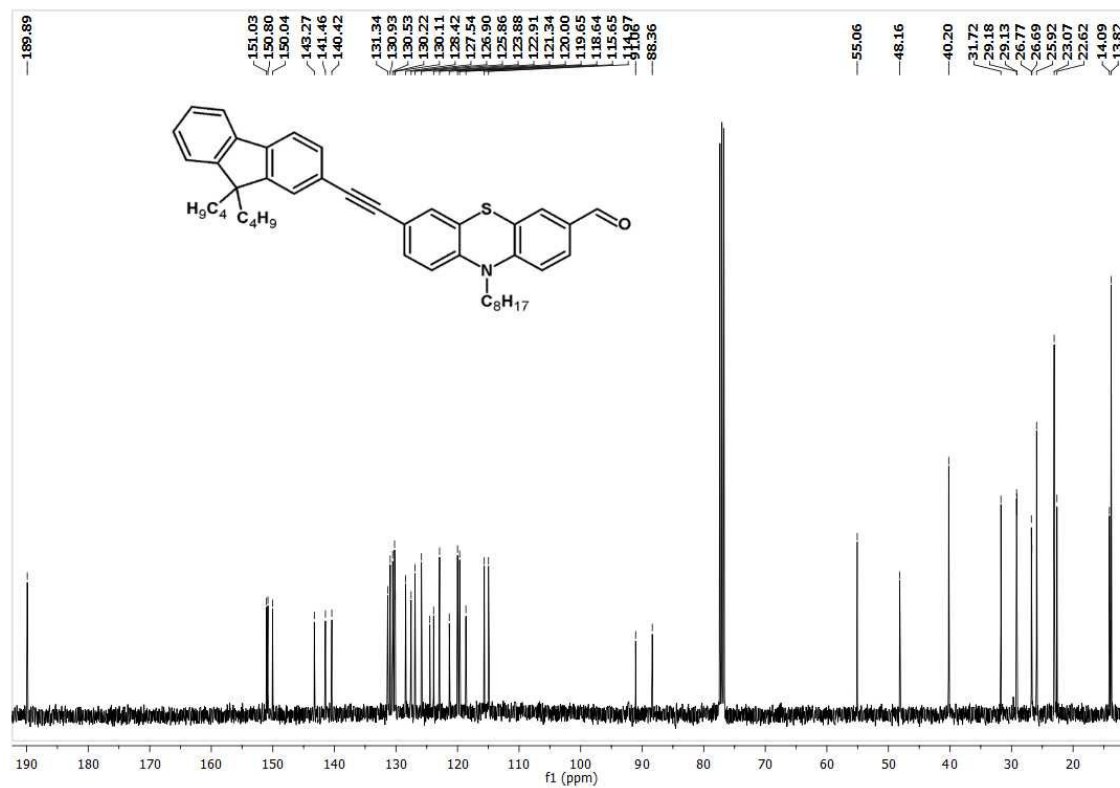
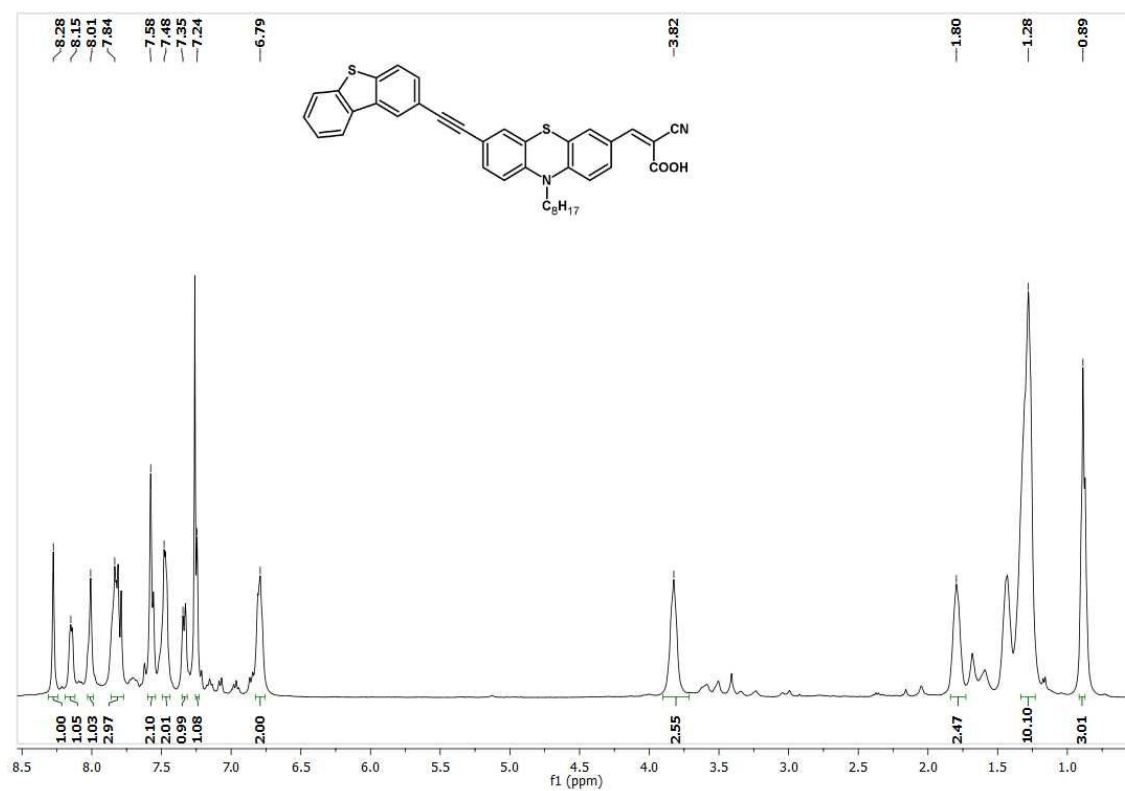
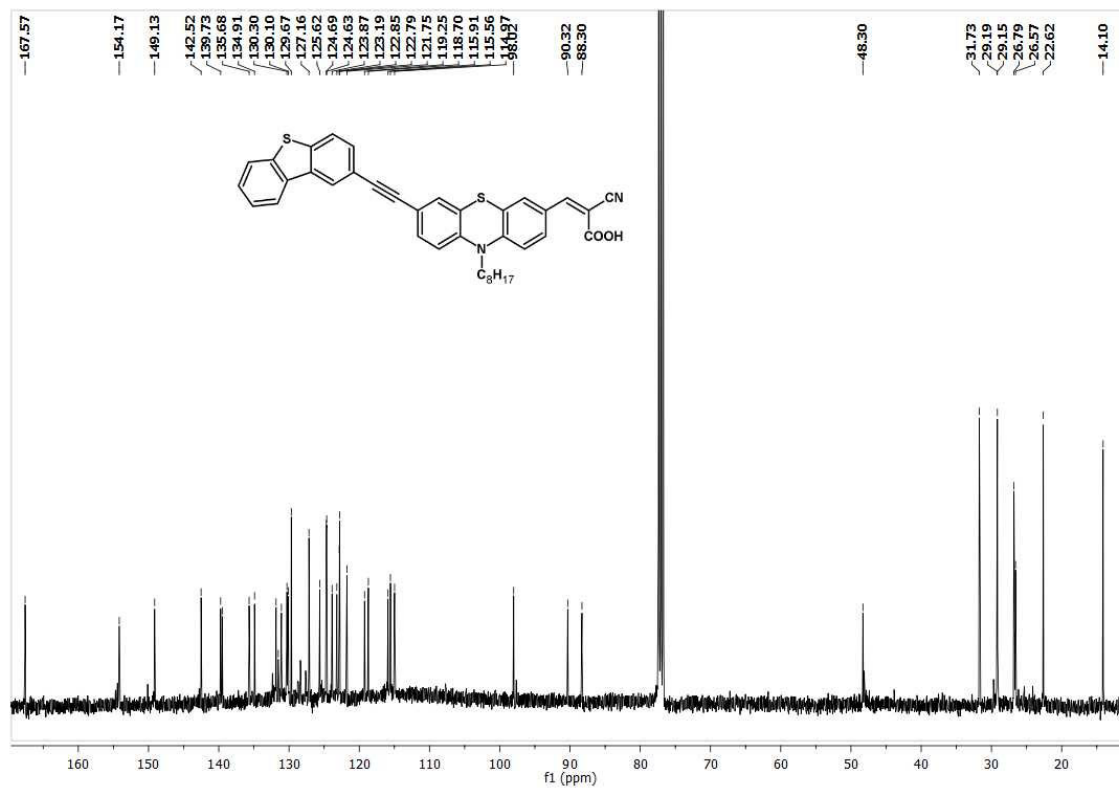
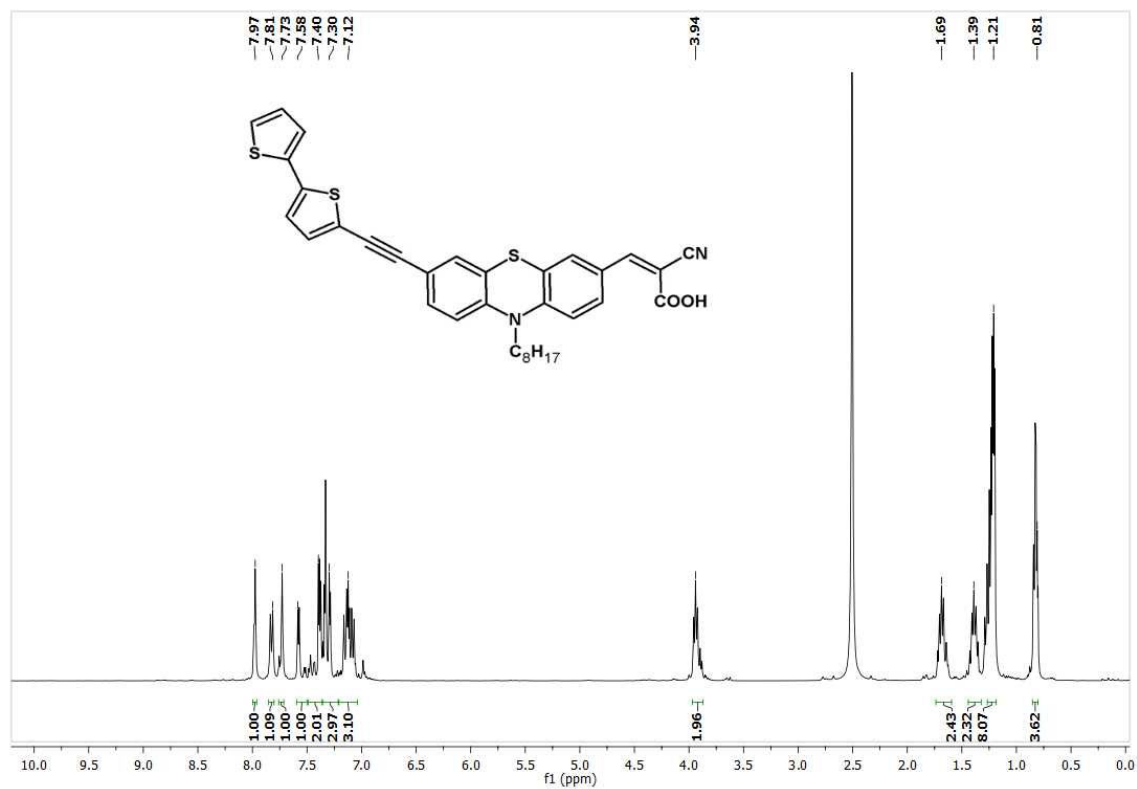


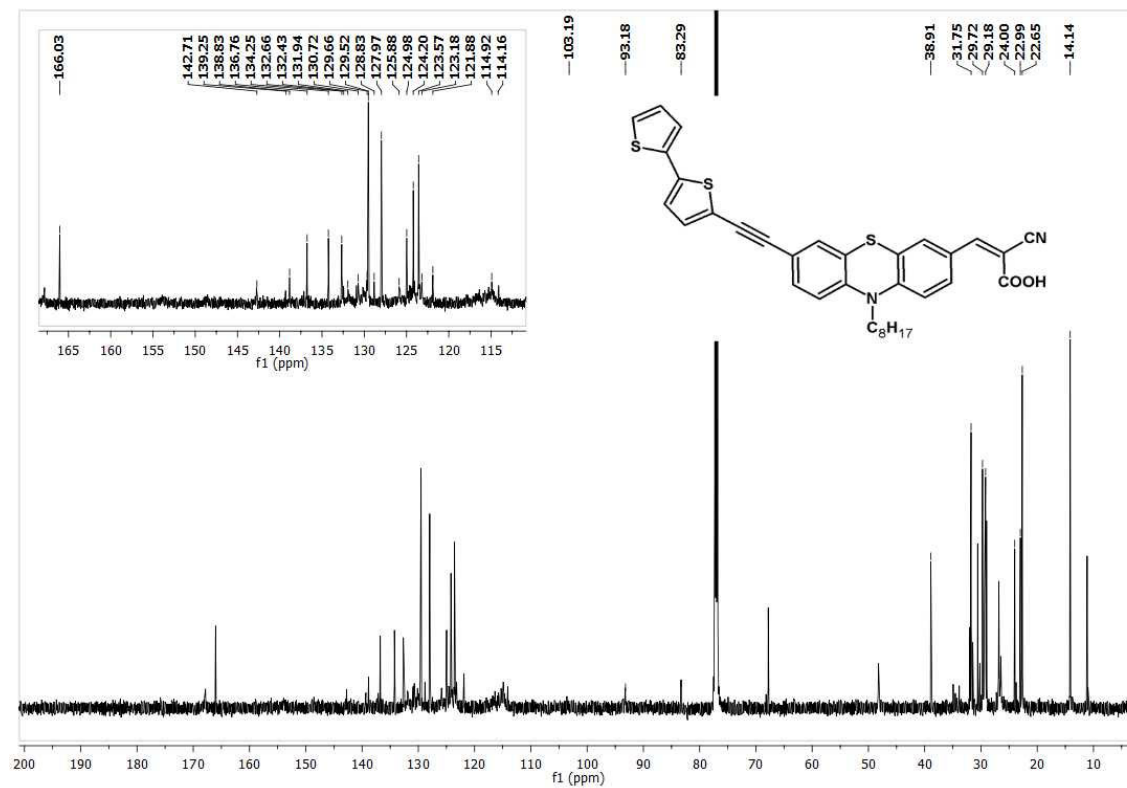
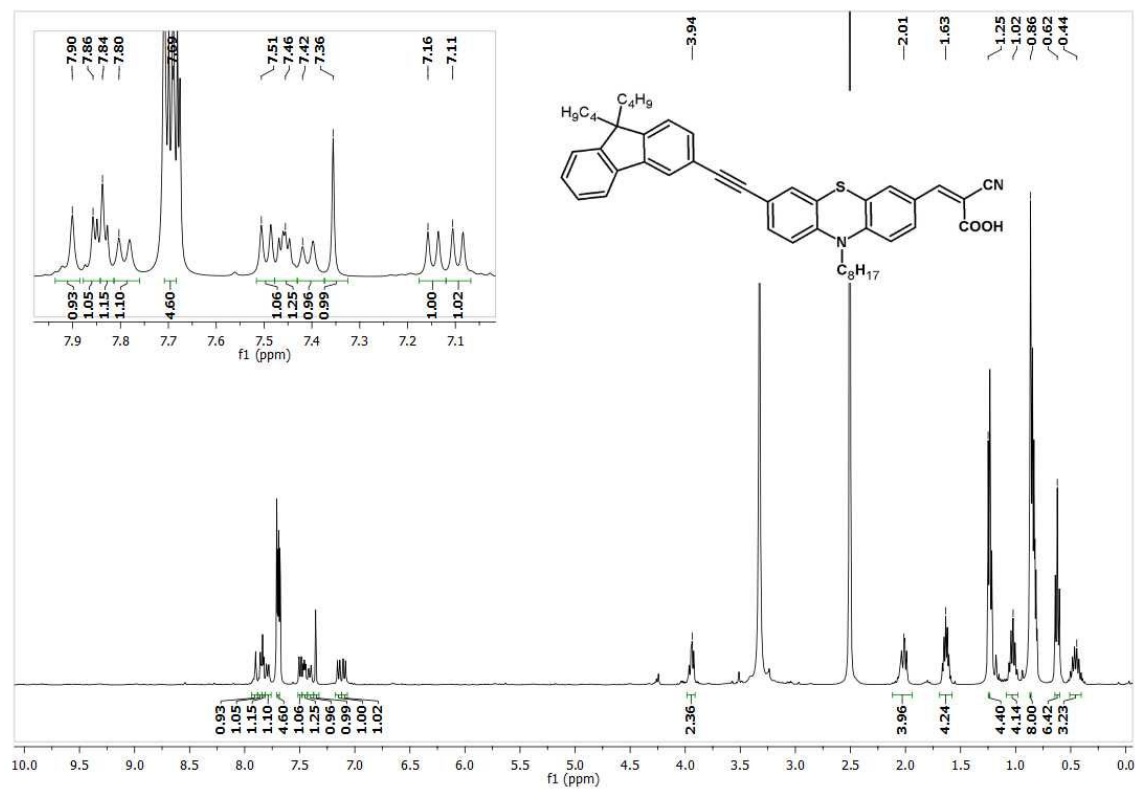
Figure S1. The ¹H spectrum of 1a in CDCl₃.

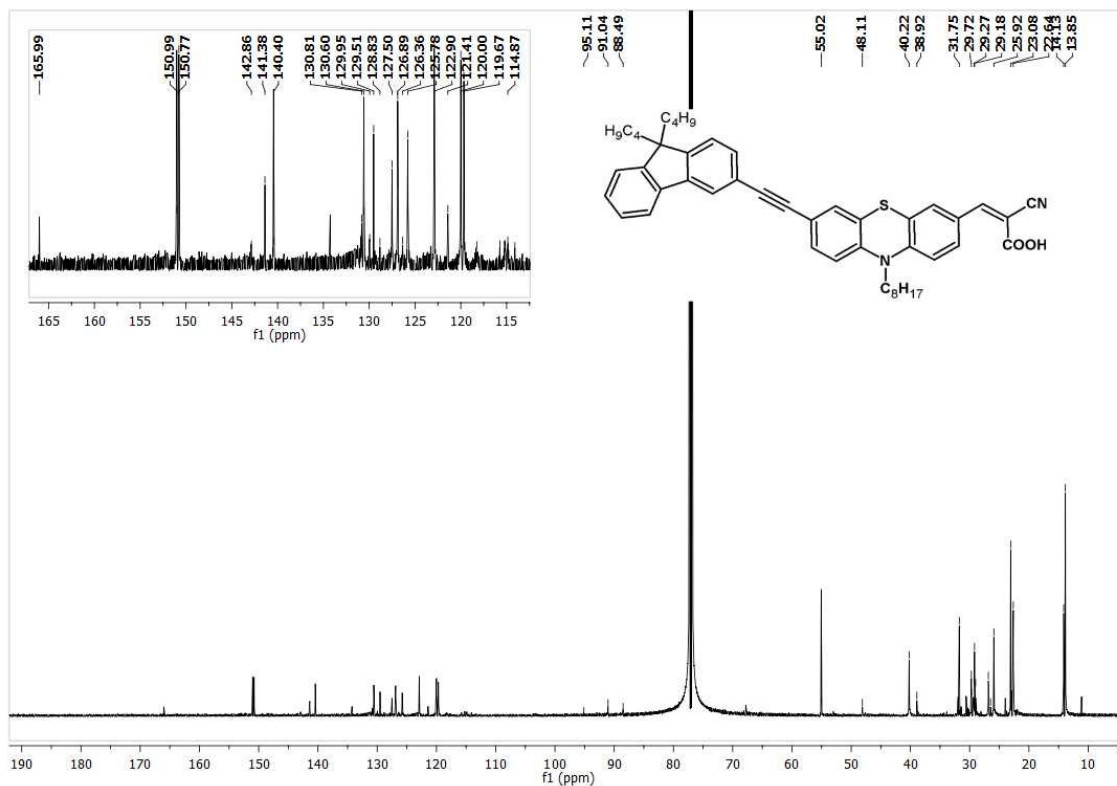
Figure S2. The ^{13}C spectrum of 1a in CDCl_3 .Figure S3. The ^1H spectrum of 1b in CDCl_3 .

Figure S4. The ¹³C spectrum of 1b in CDCl₃.Figure S5. The ¹H spectrum of 1c in CDCl₃.

Figure S6. The ¹³C spectrum of 1c in CDCl₃.Figure S7. The ¹H spectrum of 2a in CDCl₃.

Figure S8. The ¹³C spectrum of 2a in CDCl₃.Figure S9. The ¹H spectrum of 2b in CDCl₃.

Figure S10. The ¹³C spectrum of 2b in CDCl₃.Figure S11. The ¹H spectrum of 2c in CDCl₃.

Figure S12. The ^{13}C spectrum of 2c in CDCl_3 .

Thermal Properties

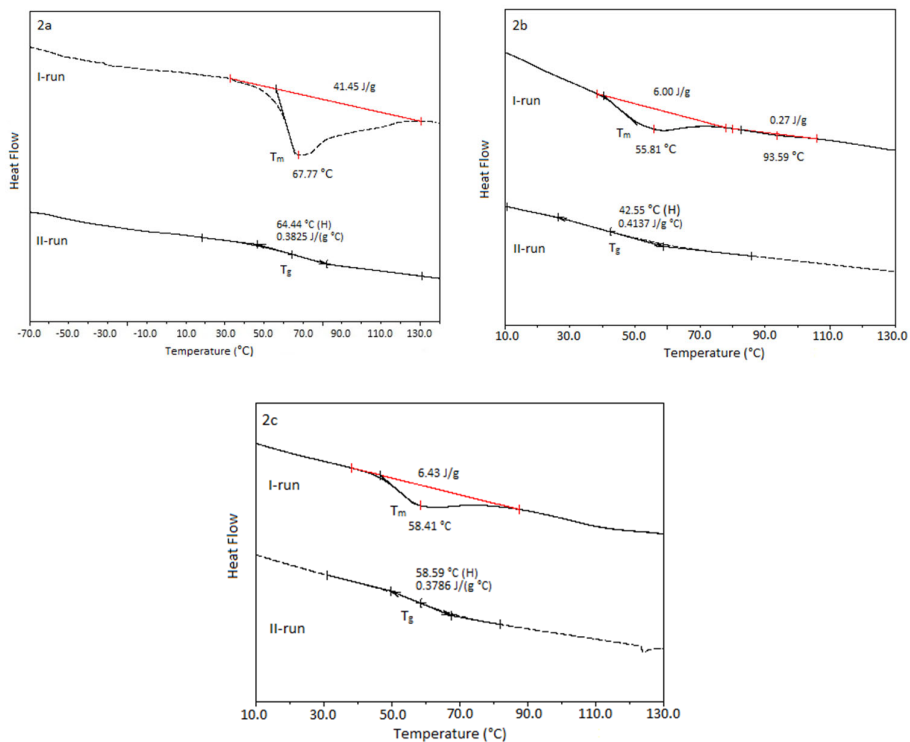


Figure S13. DSC thermograms of 2a-2c registered during the first and the second heating scan.

Electrochemical Properties

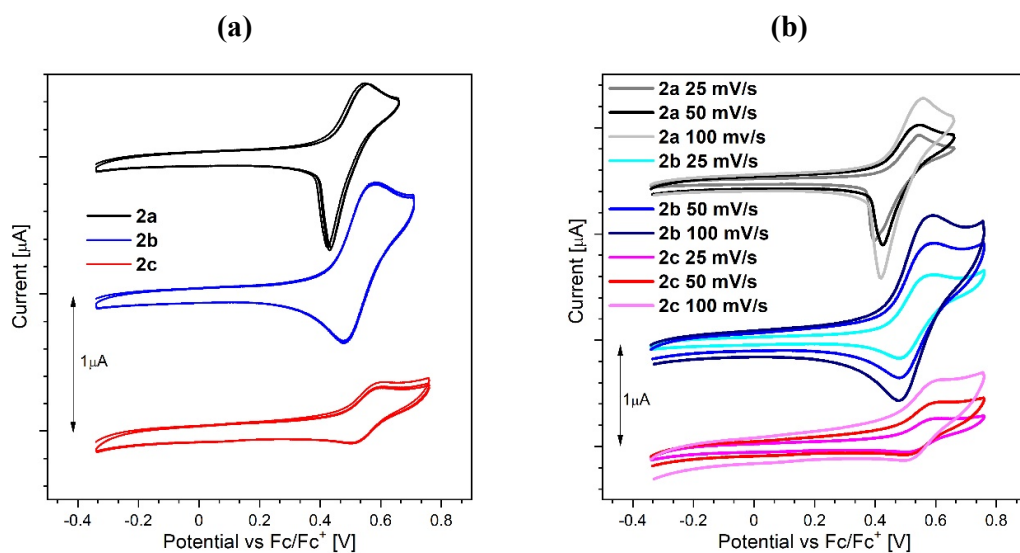


Figure S14. (a) CV scans of investigated compounds 2a-2c and (b) CV curves of the oxidation process with different scan rates.

Table S1. Peak to peak separation data of investigated compounds 2a-2c.

Code	Scan rate (mV/s)	Potential of peak separation (V)	Number of electrons
2a	25	0.1216	2.0610
	50	0.1241	2.1033
	100	0.1233	2.0898
2b	25	0.1206	2.0440
	50	0.1180	2.0000
	100	0.1192	2.0203
2c	25	0.1182	2.0033
	50	0.1227	2.0796
	100	0.1183	2.0508

Photovoltaic Properties

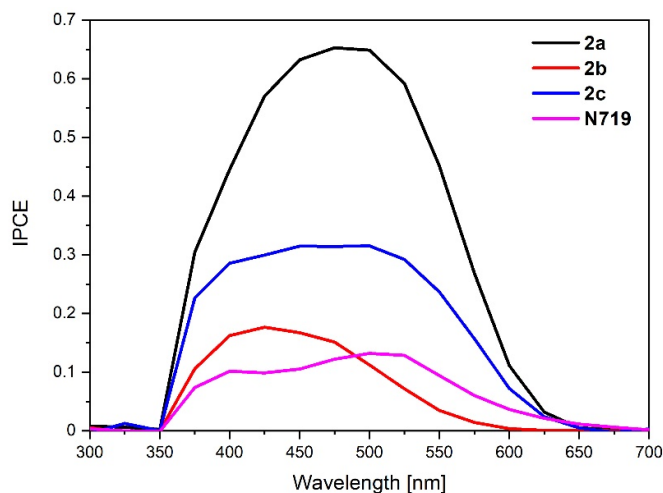


Figure S15. The combined IPCE spectra of devices containing photoanode sensitized with phenothiazine derivatives 2a-2c and N719.



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