

Supporting Information for

Donor-Acceptor Conjugated Block Copolymer of Poly(arylenevinylene)s by Ring-Opening Metathesis Polymerization

Shu-Wei Chang and Masaki Horie*

Department of Chemical Engineering, National Tsing-Hua University
101, Sec. 2, Kuang-Fu Road, Hsin-Chu, 30013 Taiwan

E-mail: mhorie@mx.nthu.edu.tw

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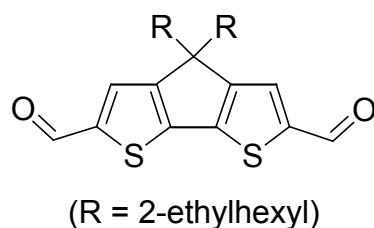
1. General methods and synthesis of compounds
2. Optical and electrochemical properties
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1. General methods and synthesis of compounds

General methods

Synthesis was performed under a nitrogen atmosphere using standard Schlenk techniques. Compounds were purified by preparative size exclusion chromatography (SEC) using JAI LC-9204 with a column GAIGEL-1H-40 eluted with chloroform. ^1H and ^{13}C NMR spectra were obtained using a Bruker 500 MHz spectrometer. Gas chromatography mass spectra were measured by Hewlett Packard 5972 series mass selective detector and 5890 series 2 plus gas chromatographer. High resolution mass spectra were recorded on Thermo Fisher Scientific LTQ Orbitrap XL. Low resolution ESI mass spectra were recorded on Thermo Finnigan Corporation LCQ ion-trap mass spectrometer. Polymer molecular weight was determined by GPC in tetrahydrofuran (THF) solution using a JASCO 880-PU pump, JASCO 870-UV/VIS detector, and Waters 410 differential refractometer (referenced to polystyrene standards). UV-Vis absorption spectra were recorded on a JASCO U-670 UV-Vis spectrophotometer. CV was performed at 0.10 V s^{-1} in a DY2300 electrochemical analyzer with a three-electrode cell, Ag/AgCl as reference electrode, platinum wire as counter electrode and platinum plate as the working electrode in nitrogen-purged anhydrous 0.10 M tetrabutylammonium hexafluorophosphate acetonitrile solution at room temperature. Onsets of oxidation and reduction peak potentials were used in the calculation of HOMO and LUMO energy levels.

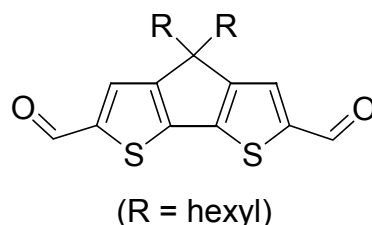
Synthesis of 4,4-bis(2-ethylhexyl)-4*H*-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene-2,6-dicarbaldehyde



To a solution of 4,4-bis(2-ethylhexyl)-4*H*-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene (1.2 g, 2.99 mmol, 1.0 equiv.) and anhydrous tetramethylethylenediamine (0.91 mL, 2.05 equiv.) in anhydrous diethyl ether (50 mL, 0.06 M), *n*-butyllithium (1.6 M in hexane, 3.83 mL, 2.05 equiv.) was slowly added via syringe at $-40\text{ }^{\circ}\text{C}$ under nitrogen. The mixture was stirred at $-40\text{ }^{\circ}\text{C}$ for an hour and was allowed to stir at room temperature for another 30 minutes. Then, anhydrous DMF (0.69 mL, 3.0 equiv.) was added at $-40\text{ }^{\circ}\text{C}$ and the mixture was stirred at room temperature overnight. The reaction mixture was quenched by water and extracted with NH_4Cl /ether. The concentrated organic layer was purified by chromatography on a silica gel column

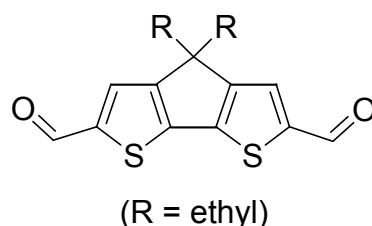
using hexane:ethyl acetate = 8:1 as eluent to give 4,4-bis(2-ethylhexyl)-4*H*-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene-2,6-dicarbaldehyde as yellow solid (1.24 g, 90%). ¹H NMR (500 MHz, CDCl₃): δ 9.89 (s, 2H, vinyl), 7.61 (t, 2H, *J* = 5.0 Hz, 3-CPDT, the ratio was 1:2:1 due to racemic 2-ethylhexyl groups), 1.94 (m, 4H, CH₂, due to racemic 2-ethylhexyl groups), 0.97-0.82 (m, 18H, CH₂), 0.72 (t, 6H, *J* = 7.0 Hz, CH₃), 0.60 (t, 6H, *J* = 7.0 Hz, CH₃). ¹³C {¹H} NMR (125 MHz, CDCl₃): δ 182.8 (CHO), 160.9, 146.3, 145.3 (C_{quart}), 130.2 (CH, 3-CPDT), 54.4 (4-CPDT), 43.0 (CH₂), 35.3 (CH), 34.2, 28.4, 27.3, 22.7 (CH₂), 14.0, 10.6 (CH₃). HRMS (ESI) calcd. for C₂₇H₃₉O₂S₂ [M+H]⁺ (*m/z*): 459.2391, found: 459.2400 (error 2.0 ppm).

Synthesis of 4,4-dihexyl-4*H*-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene-2,6-dicarbaldehyde



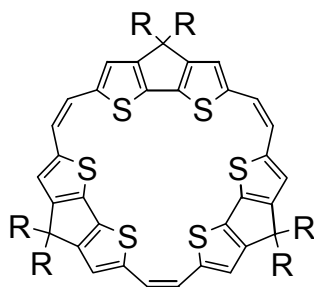
4,4-dihexyl-4*H*-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene-2,6-dicarbaldehyde was synthesized by the same method as that used to prepare 4,4-bis(2-ethylhexyl)-4*H*-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene-2,6-dicarbaldehyde, using 4,4-dihexyl-4*H*-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene (1.2 g, 3.468 mmol, 1.0 equiv.), anhydrous TMEDA (1.06 mL, 2.05 equiv.), anhydrous diethyl ether (80 mL, 0.04 M), *n*-butyllithium (1.6 M in hexane, 4.44 mL, 2.05 equiv.) and anhydrous DMF (0.80 mL). The mixture was purified by chromatography on a silica gel column using hexane:ethyl acetate = 4:1 as eluent. (1.11 g, 79%). ¹H NMR (500 MHz, CDCl₃): δ 9.89 (s, 2H, vinyl), 7.60 (s, 2H, 3-CPDT), 1.88 (m, 4H, CH₂), 1.20-1.12 (m, 12H, CH₂), 0.92 (m, 4H, CH₂), 0.79 (t, 6H, *J* = 7.0 Hz, CH₃). ¹³C {¹H} NMR (125 MHz, CDCl₃): δ 182.9 (CHO), 161.3, 146.6, 145.1 (C_{quart}), 129.5 (CH, 3-CPDT), 54.3 (4-CPDT), 37.5, 31.5, 29.5, 24.6, 22.5 (CH₂), 14.0 (CH₃). HRMS (ESI) calcd. for C₂₃H₃₁O₂S₂ [M+H]⁺ (*m/z*): 403.1765, found: 403.1765 (error 0.0 ppm).

Synthesis of 4,4-diethyl-4*H*-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene-2,6-dicarbaldehyde



4,4-diethyl-4*H*-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene-2,6-dicarbaldehyde was synthesized by the same method as that used to prepare 4,4-bis(2-ethylhexyl)-4*H*-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene-2,6-dicarbaldehyde, using 4,4-diethyl-4*H*-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene (0.5 mg, 2.19 mmol, 1.0 equiv.), anhydrous TMEDA (0.69 mL, 2.1 equiv.), anhydrous diethyl ether (45 mL, 0.05 M), *n*-butyllithium (1.6 M in hexane, 2.87 mL, 2.1 equiv.) and anhydrous DMF (0.51 mL). The mixture was purified by chromatography on a silica gel column using dichloromethane as eluent. (0.51 g, 80%). ¹H NMR (500 MHz, CDCl₃): δ 9.89 (s, 2H, vinyl), 7.61 (s, 2H, 3-CPDT), 1.96 (m, 4H, CH₂), 0.62 (t, 6H, *J* = 7.5 Hz, CH₃). ¹³C {¹H} NMR (125 MHz, CDCl₃): δ 182.9 (CHO), 160.6, 146.7, 145.4 (C_{quart}), 129.5 (CH, 3-CPDT), 55.3 (4-CPDT), 29.9 (CH₂), 9.1 (CH₃). HRMS (ESI) calcd. for C₁₅H₁₅O₂S₂ [M+H]⁺ (*m/z*): 291.0513, found: 291.0516 (error 1.0 ppm).

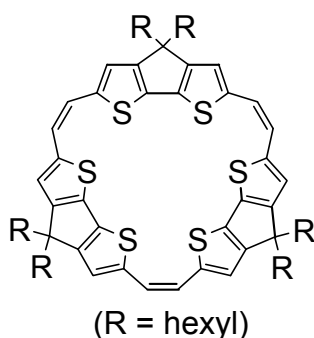
Synthesis of M1a



(R = 2-ethylhexyl)

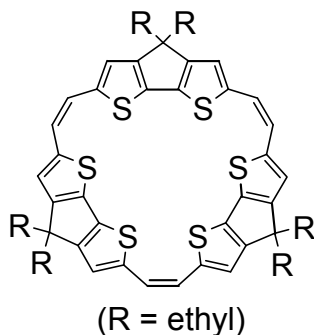
TiCl₄ (0.47 mL, 10 equiv.) was added to a suspension of zinc (0.8 g, 22.5 equiv.) in THF (70 mL, 0.009 M) at 0 °C under nitrogen with stirring over a period of 30 min, then the suspension was heated to reflux for 1 h. To the gently refluxing suspension, a solution of 4,4-bis(2-ethylhexyl)-4*H*-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene-2,6-dicarbaldehyde (200.0 mg, 0.434 mmol, 1.0 equiv.) and pyridine (0.5 mL) in THF (20 mL) was added by syringe. After a further hour at reflux, the reaction mixture was cooled to room temperature. The reaction mixture was firstly concentrated by rotary evaporator to remove THF, and the residue was then purified by the flash silica gel column with acetone as eluent. The residue was further purified by chromatography on a silica gel column using hexane as eluent as well as SEC to give **M1a** as orange oil (38 mg, 21 %). ¹H NMR (500 MHz, CDCl₃): δ 6.72-6.66 (m, 12H, vinyl and 3-CPDT), 1.80 (m, 12H, CH₂), 0.99-0.82 (m, 18H, CH and CH₂), 0.76-0.73 (m, 18H, CH₃), 0.59-0.54 (m, 18H, CH₃). ¹³C {¹H} NMR (125 MHz, CDCl₃): δ 156.7, 138.4, 124.9, 124.1, 122.6 (CPDT), 54.4 (4-CPDT), 43.0 (CH₂), 35.3 (CH), 34.2, 28.4, 27.3, 22.7 (CH₂), 14.0, 10.6 (CH₃). HRMS (ESI) calcd. for C₈₁H₁₁₄S₆ [M]⁺ (*m/z*): 1278.7245, found: 1278.7283 (error 2.9 ppm).

Synthesis of M1b



M1c was synthesized by the same method as that used to prepare **M1a**, using TiCl_4 (0.236 mL, 10 equiv.), zinc (0.42 g, 22.5 equiv.), THF (17 mL, 0.005 M), and another solution of 4,4-dihexyl-4*H*-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene-2,6-dicarbaldehyde (100.0 mg, 0.248 mmol, 1.0 equiv.), pyridine (0.3 mL), THF (2.5 mL). The mixture was purified by flash column on silica gel with chloroform and further by SEC. The first fraction of SEC gave **M1c** (11.0 mg, 12%). ^1H NMR (500 MHz, CDCl_3): δ 6.73 (s, 6H, vinyl or CPDT), 6.69 (s, 6H, vinyl or CPDT), 1.75 (m, 12H, CH_2), 1.17-1.11 (m, 48H, CH_2), 0.77 (t, $J = 7.5$ Hz, 18H, CH_3). ^{13}C NMR $\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 157.3, 138.7, 137.9 (C_{quart}), 124.7, 122.8 (CH), 54.2 (4-CPDT), 37.7, 31.6, 29.7, 24.5, 22.7 (CH_2), 14.0 (CH_3). HRMS (ESI) calcd. for $\text{C}_{69}\text{H}_{90}\text{S}_6$ $[\text{M}]^+$ (m/z): 1110.5367, found: 1110.5388 (error 1.9 ppm).

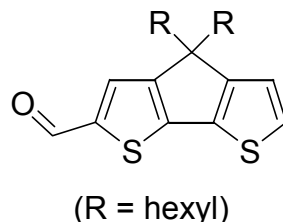
Synthesis of M1c



M1b was synthesized by the same method as that used to prepare **M1a**, using TiCl_4 (0.375 mL, 10 equiv.), zinc (0.67 g, 22.5 equiv.), THF (70 mL, 0.005 M), and another solution of 4,4-diethyl-4*H*-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene-2,6-dicarbaldehyde (100.0 mg, 0.345 mmol, 1.0 equiv.), pyridine (0.6 mL), THF (15.0 mL). The mixture was purified by flash column on silica gel with chloroform and further by SEC. The first fraction of SEC gave **M1b** (23 mg, 26%). ^1H NMR (500 MHz, CDCl_3): δ 6.72 (s, 6H, vinyl or CPDT), 6.70 (s, 6H, vinyl or CPDT), 1.80 (qua., $J = 7.5$ Hz, 12H, CH_2), 0.57 (t, $J = 7.5$ Hz, 18H, CH_3). ^{13}C NMR $\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 156.5, 138.9, 138.0 (C_{quart}), 125.0, 123.1 (CH), 55.3 (4-CPDT), 29.7

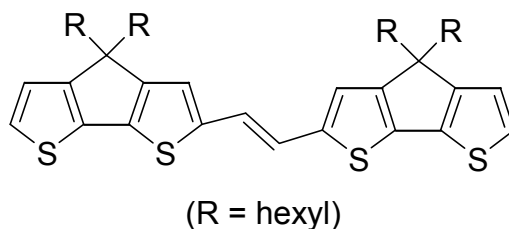
(CH₂), 9.2 (CH₃). HRMS (ESI) calcd. for C₄₅H₄₂S₆ [M]⁺ (*m/z*): 774.1611, found: 774.1625, (error 1.8 ppm).

Synthesis of 4,4-dihexyl-4*H*-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene-2-carbaldehyde



To a solution of 4,4-dihexyl-4*H*-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene (0.6 g, 1.732 mmol, 1.0 equiv.) and anhydrous tetramethylethylenediamine (0.25 mL, 1.0 equiv.) in anhydrous diethyl ether (40 mL, 0.04 M), *n*-butyllithium (1.6 M in hexane, 1.11 mL, 1.0 equiv.) was slowly added via syringe at -40 °C under nitrogen. The mixture was stirred at -40 °C for an hour and was allowed to stir at room temperature for another 30 minutes. Then, anhydrous DMF (0.27 mL, 2.0 equiv.) was added at -40 °C and the mixture was stirred at room temperature overnight. The reaction mixture was quenched by water and extracted with NH₄Cl/ether. The concentrated organic layer was purified by chromatography on a silica gel column using hexane:ethyl acetate = 12:1 as eluent to give 4,4-dihexyl-4*H*-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene-2-carbaldehyde as yellow-orange oil (0.44 g, 68%). ¹H NMR (500 MHz, CDCl₃): δ 9.81 (s, 1H, vinyl), 7.55 (s, 1H, 3-CPDT), 7.38 (d, 1H, *J* = 5.0 Hz, 5-CPDT), 6.96 (d, 1H, *J* = 5.0 Hz, 6-CPDT), 1.84 (m, 4H, CH₂), 1.19-1.10 (m, 12H, CH₂), 0.95-0.88 (m, 4H, CH₂), 0.79 (t, 6H, *J* = 7.0 Hz, CH₃). ¹³C {¹H} NMR (125 MHz, CDCl₃): δ 182.6 (CHO), 162.4, 158.1, 147.7, 143.1, 135.5 (C_{quart}), 130.2 (3-CPDT), 129.6 (5-CPDT), 121.8 (6-CPDT), 53.7 (4-CPDT), 37.5, 31.5, 29.5, 24.5, 22.5 (CH₂), 14.0 (CH₃). GC-MS: *m/z* = 374.6 [M]⁺.

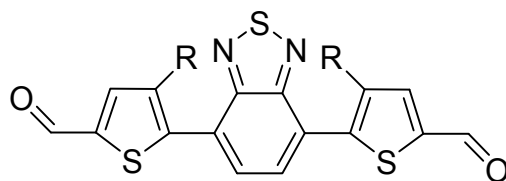
Synthesis of CPDT-CH=CH-CPDT



TiCl₄ (0.24 mL, 10 equiv.) was added to a suspension of zinc (0.42 g, 22.5 equiv.) in THF (17 mL, 0.016 M) at 0 °C under nitrogen with stirring over a period of 30 min, then the suspension was heated to reflux for 1 h. To the gently refluxing suspension, a solution of 4,4-dihexyl-4*H*-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene-2-

carbaldehyde (100.0 mg, 0.267 mmol, 1.0 equiv.) and pyridine (0.23 mL) in THF (2.0 mL) was added by syringe. After a further hour at reflux, the reaction mixture was cooled to room temperature. The reaction mixture was firstly concentrated by rotary evaporator to remove THF, and the residue was then purified by the flash silica gel column with chloroform as eluent. The residue was further purified by SEC to give CPDT-CH=CH-CPDT as fluorescent yellow solid (76 mg, 79 %). ^1H NMR (500 MHz, CDCl_3): δ 7.15 (d, 2H, $J = 5.0$ Hz, 6-CPDT), 6.97 (s, 2H, vinyl), 6.90 (d, 2H, $J = 5.0$ Hz, 5-CPDT), 6.84 (s, 2H, 3-CPDT), 1.81 (m, 8H, CH_2), 1.19-1.10 (m, 24H, CH_2), 0.97-0.91 (m, 8H, CH_2), 0.80 (t, 12H, $J = 7.0$ Hz, CH_3). ^{13}C $\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 158.5, 158.3, 143.0, 136.6, 135.4 (C_{quart}), 125.0 (6-CPDT), 121.6 (5-CPDT), 120.4 (vinyl or 3-CPDT), 120.3 (vinyl or 3-CPDT), 53.7 (4-CPDT), 37.5, 31.5, 29.5, 24.5, 22.5 (CH_2), 14.0 (CH_3). HRMS (ESI) calcd. for $\text{C}_{44}\text{H}_{60}\text{S}_4$ $[\text{M}]^+$ (m/z): 716.3578, found: 716.3591 (error 1.8 ppm).

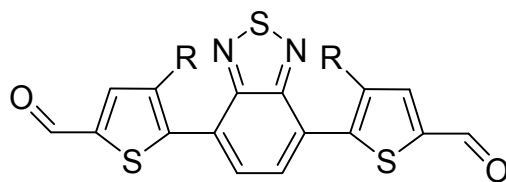
Synthesis of 5,5'-(2,1,3-benzothiadiazole-4,7-diyl)bis[4-(2-ethylhexyl)thiophen-2-carbaldehyde]



(R = 2-ethylhexyl)

To a solution of DMF (30 mL, excess) and 4,7-bis[3-(2-ethylhexyl)-2-thienyl]-2,1,3-benzothiadiazole (1.41 g, 2.68 mmol, 1.0 equiv.), phosphorous oxychloride (POCl_3) (14.1 mL, excess) were added at ambient temperature and then the mixture were heated to 95 °C with vigorous stirring for two hours under nitrogen. The reaction mixture was completed with the slow addition of water, and then the organic layer was extracted with chloroform. The crude product was then purified by column chromatography on silica gel with hexane:ethyl acetate = 4:1 to give 5,5'-(2,1,3-benzothiadiazole-4,7-diyl)bis[4-(2-ethylhexyl)thiophen-2-carbaldehyde] as orange solid (1.26 g, 81%). ^1H NMR (500 MHz, CDCl_3): δ 9.94 (s, 2H, CHO), 7.72 (s, 2H, Th), 7.71 (s, 2H, BT), 2.60 (d, $J = 7.0$ Hz, 4H, CH_2), 1.43 (m, 2H, CH), 1.18-0.92 (m, 16H, CH_2), 0.73 (t, $J = 7.5$ Hz, 6H, CH_3), 0.63 (t, $J = 7.5$ Hz, 6H, CH_3). ^{13}C $\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 183.0 (CHO), 153.4, 143.0, 142.6, 142.4, 138.3 (C_{quart}), 130.2, 127.7 (CH), 40.4 (CH_2), 33.4 (CH), 32.4, 28.6, 25.6, 22.8 (CH_2), 14.2, 10.7 (CH_3). HRMS (ESI) calcd. for $\text{C}_{32}\text{H}_{41}\text{O}_2\text{N}_2\text{S}_3$ $[\text{M}+\text{H}]^+$ (m/z): 581.2330, found: 581.2345 (error 2.6 ppm).

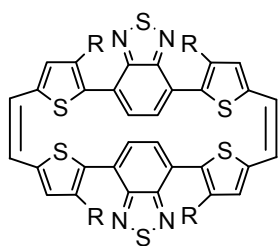
Synthesis of 5,5'-(2,1,3-benzothiadiazole-4,7-diyl)bis(4-ethylthiophen-2-carbaldehyde)



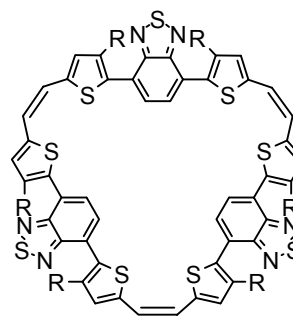
(R = ethyl)

5,5'-(2,1,3-benzothiadiazole-4,7-diyl)bis(4-ethylthiophen-2-dicarbaldehyde) was synthesized by the same method as that used to prepare 5,5'-(2,1,3-benzothiadiazole-4,7-diyl)bis[4-(2-ethylhexyl)thiophen-2-carbaldehyde], using DMF (45 mL, excess), POCl₃ (23 mL, excess), and 4,7-bis(3-ethyl-2-thienyl)-2,1,3-benzothiadiazole (1.6 g, 4.49 mmol). The reaction mixture was heated at 95 °C for 2 h under nitrogen. The crude product was purified by column chromatography on silica gel with chloroform to give 5,5'-(2,1,3-benzothiadiazole-4,7-diyl)bis(4-ethylthiophen-2-carbaldehyde) as yellow solid (1.98 g, 76%). ¹H NMR (500 MHz, CDCl₃): δ 9.94 (s, 2H, CHO), 7.79 (s, 2H, Th or BT), 7.72 (s, 2H, Th or BT), 2.69 (qua., *J* = 7.5 Hz, 4H, CH₂), 1.26 (t, *J* = 7.5 Hz, 6H, CH₃). ¹³C {¹H} NMR (125 MHz, CDCl₃): δ 183.0 (CHO), 153.4, 144.6, 143.3, 141.6, 137.3 (C_{quart}), 130.0, 127.4 (CH), 22.7 (CH₂), 14.8 (CH₃). HRMS (ESI) calcd. for C₃₂H₄₁O₂N₂S₃ [M+H]⁺ (*m/z*): 581.2330, found: 581.2345 (error 2.6 ppm).

Synthesis of M2a and M3a



(R = 2-ethylhexyl)



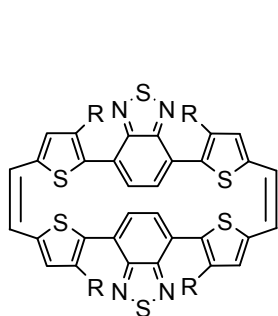
(R = 2-ethylhexyl)

TiCl₄ (0.75 mL, 40 equiv.) was added to a suspension of zinc (0.26 g, 22.5 equiv.) in THF (19 mL, 0.009 M) at 0 °C under nitrogen with stirring over a period of 30 min, then the suspension was heated to reflux for 1 h. To the gently refluxing suspension, a solution of 5,5'-(2,1,3-benzothiadiazole-4,7-diyl)bis[4-(2-ethylhexyl)thiophen-2-carbaldehyde] (100.0 mg, 0.172 mmol, 1.0 equiv.) and pyridine (0.2 mL) in THF (5 mL) was added by syringe. After a further hour at reflux, the reaction

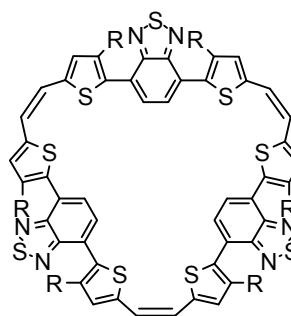
mixture was cooled to room temperature. The reaction mixture was firstly concentrated by rotary evaporator to remove THF, and the residue was then purified by the flash silica gel column with hexane:dichloromethane = 1:1 as eluent. The residue was further purified by chromatography on a silica gel column using hexane:dichloromethane = 2:1 as eluent as well as SEC. The first fraction of SEC gave **M2a** as orange oil (11.3 mg, 12 %). ^1H NMR (500 MHz, CDCl_3): δ 7.52 (s, 6H, BT), 7.01 (s, 6H, Th), 6.67 (s, 6H, vinyl), 2.48 (m, 12H, CH_2), 1.38 (m, 6H, CH), 1.12–0.97 (m, 48H, CH_2), 0.74 (t, J = 7.0 Hz, 18H, CH_3), 0.64 (t, J = 7.0 Hz, 18H, CH_3). ^{13}C NMR $\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 153.9, 140.5, 138.9, 133.9 (C_{quart}), 132.1 (CH, Th), 130.0 (CH, BT), 127.6 (C_{quart}), 123.6 (CH, vinyl), 40.3 (CH_2), 33.3 (CH), 32.4, 29.4, 25.5, 22.7 (CH_2), 14.0, 10.6 (CH_3). HRMS (ESI) calcd. for $\text{C}_{96}\text{H}_{120}\text{N}_6\text{S}_9$ $[\text{M}]^+$ (m/z): 1644.7061, found: 1644.7102 (error 1.7 ppm).

The second fraction of SEC gave **M3a** as orange oil (8.5 mg, 9 %). ^1H NMR (500 MHz, CDCl_3): δ 7.34 (s, 4H, Th), 6.86 (s, 4H, BT), 6.71 (s, 4H, vinyl), 2.77 (m, 8H, CH_2), 1.41 (m, 4H, CH), 1.17–1.06 (m, 32H), 0.72 (t, J = 7.0 Hz, 12H, CH_3), 0.67 (t, J = 7.0 Hz, 12H, CH_3). ^{13}C NMR $\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 153.8, 140.3, 139.3, 135.7 (C_{quart}), 131.6 (CH, BT), 130.2 (CH, Th), 127.6 (C_{quart}), 124.5 (CH, vinyl), 40.5 (CH_2), 33.7 (CH), 32.5, 28.7, 25.7, 22.9 (CH_2), 14.1, 10.7 (CH_3). HRMS (ESI) calcd. for $\text{C}_{64}\text{H}_{80}\text{N}_4\text{S}_6$ $[\text{M}]^+$ (m/z): 1096.4707, found: 1096.4728 (error 1.9 ppm).

Synthesis of **M2c** and **M3c**



(R = ethyl)



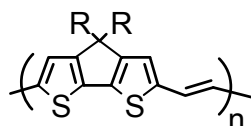
(R = ethyl)

M2c and **M3c** were synthesized by the same method as that used to prepare **M2a** and **M3a**, using TiCl_4 (1.04 mL, 40 equiv.), zinc (0.34 g, 22.5 equiv.), THF (45 mL, 0.005 M), and another solution of 5,5'-(2,1,3-benzothiadiazole-4,7-diyl)bis(4-ethylthiophen-2-carbaldehyde) (100.0 mg, 0.243 mmol, 1.0 equiv.), pyridine (0.275 mL), THF (5.0 mL). The mixture was purified by flash column on silica gel with chloroform and further SEC. The first fraction of SEC gave **M2c** (13.8 mg, 15%). ^1H NMR (500 MHz, CDCl_3): δ 7.53 (s, 6H, BT), 7.13 (s, 6H, Th), 6.67 (s, 6H, vinyl),

2.60 (qua., $J = 7.5$ Hz, 12H, CH₂), 1.38 (t, $J = 7.5$ Hz, 18H, CH₃). ¹³C NMR {¹H} NMR (125 MHz, CDCl₃): δ 154.0, 142.5, 139.3 (C_{quart}), 132.9 (CH, Th), 131.4 (CH, BT), 129.6, 127.1 (C_{quart}), 123.4 (CH, vinyl), 29.7 (CH₂), 22.6 (CH₃). HRMS (ESI) calcd. for C₆₀H₄₈N₆S₉ [M]⁺ (m/z): 1140.1427, found: 1140.1447 (error 1.8 ppm).

The second fraction of SEC gave **M3c** (9.2 mg, 10%). ¹H NMR (500 MHz, CDCl₃): δ 7.33 (s, 4H, Th), 6.93 (s, 4H, BT), 6.73 (s, 4H, vinyl), 2.83 (qua., $J = 7.5$ Hz, 8H, CH₂), 1.23 (t, $J = 7.5$ Hz, 12H, CH₃). ¹³C NMR {¹H} NMR (125 MHz, CDCl₃): δ 153.8, 142.7, 139.9, 134.9 (C_{quart}), 130.7 (CH, BT), 129.9 (CH, Th), 127.3 (C_{quart}), 124.8 (CH, vinyl), 29.7 (CH₂), 23.0 (CH₃). HRMS (ESI) calcd. for C₄₀H₃₃N₄S₆ [M+H]⁺ (m/z): 761.1029, found: 761.1040 (error 1.4 ppm).

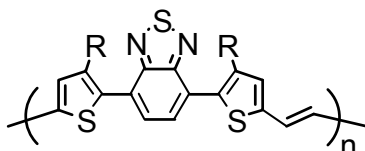
Synthesis of P1



(R = 2-ethylhexyl)

Second-generation Grubbs catalyst (2.65 mg, 12.5mol%) was dissolved in anhydrous *p*-xylene (0.5 mL, 0.05 M) in a 10 mL Schlenk tube under nitrogen. This solution was added to **M1a** (33 mg, 0.025 mmol, 1.0 equiv.) in a 5 mL Schlenk tube. After the reaction mixture was stirred at 120 °C for 6 minutes, ethyl vinyl ether (1.0 mL) was added to quench the reaction and stirred at room temperature for 10 minutes. 1.0 mL *p*-xylene was added to the reaction mixture and the resulting mixture was stirred at 120 °C for an hour to isomerize *cis*-form to *trans*-form. The mixture was then poured into MeOH (60 mL). The precipitate was washed with MeOH and acetone, then dried in vacuum to give **P1** as the blue fiber (25 mg, 78%). ¹H NMR (500 MHz, CDCl₃): δ 6.95 (s, 2H, vinyl), 6.83 (s, 2H, 3-CPDT), 1.84-1.80 (br, 4H, CH₂), 1.02-0.92 (m, 18H, CH and CH₂), 0.76 (br, 6H, CH₃), 0.63 (s, 6H, CH₃). GPC (polystyrene standards in THF): $M_n = 19100$, $M_w/M_n = 1.94$.

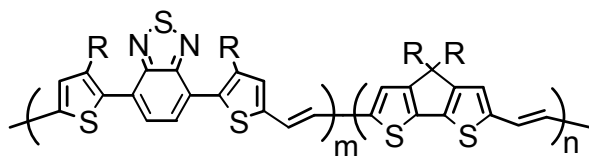
Synthesis of P2



(R = 2-ethylhexyl)

The synthesis of **P2** was carried out using the same method as described above, using **M2a** (12.4 mg, 0.008 mmol, 1.0 equiv.), second-generation Grubbs catalyst (1.06 mg, 16.7mol%), anhydrous *p*-xylene (0.15 mL, 0.05 M). Red-orange fiber (10 mg, 81%). ¹H NMR (500 MHz, CDCl₃): δ 7.68 (s, 2H, BT), 7.09 (s, 2H, Th), 7.01 (s, 2H, vinyl), 2.60 (broad, 4H, CH₂), 1.23-1.01 (m, 18H, CH and CH₂), 0.74 (br, 6H, CH₃), 0.66 (br, 6H, CH₃). GPC (polystyrene standards in THF): $M_n = 18600$, $M_w/M_n = 1.74$.

Synthesis of P3



(R = 2-ethylhexyl)

Second-generation Grubbs catalyst (0.97 mg, 20 mol%) was dissolved in anhydrous *p*-xylene (0.13 mL, 0.05 M) in a 10 mL Schlenk tube under nitrogen. This solution was added to **M2a** (9.4 mg, 0.006 mmol, 1.0 equiv.) in a 5 mL Schlenk tube and the reaction mixture was stirred at 120 °C for 6 minutes. **M1a** (10.9 mg, 1.5 equiv.) was then added into the reaction mixture. After the reaction mixture was stirred at 120 °C for 6 minutes, the mixture was cooled to room temperature. Ethyl vinyl ether (1.0 mL) was added and stirred at room temperature for 10 minutes. 1.0 mL *p*-xylene was added and the reaction mixture was stirred at 120 °C for an hour. The mixture was then poured into MeOH (60 mL). The precipitate was washed with MeOH and acetone, then dried in vacuum to give **P3** as the purple fiber (12 mg, 60 %). ¹H NMR (500 MHz, CDCl₃): δ 7.68 (s, 2H, BT), 7.09 (s, 2H, Th), 7.01 (s, 2H, vinyl of **P2** block), 6.95 (s, 2H, vinyl of **P1** block), 6.83 (s, 2H, 3-CPDT), 2.61 (br, 4H, CH₂ of **P2** block), 1.84 (br, 4H, CH₂ of **P1** block), 1.23-0.85 (m, 36H, CH and CH₂), 0.76 (m, 12H, CH₃), 0.64 (m, 12H, CH₃). GPC (polystyrene standards in THF): $M_n = 35600$, $M_w/M_n = 2.10$.

2. Optical and electrochemical properties

Table S-1. Optical and electrochemical properties

Compound	$\lambda_{\text{max}}/\text{nm}^{\text{a}}$	$\lambda_{\text{onset}}/\text{nm}^{\text{a}}$	$E_{\text{opt}}/\text{nm}^{\text{b}}$	HOMO /eV ^c	LUMO /eV ^d	E_{cv}/eV
M1a	385	441	2.90	-	-	-
M2a	438	538	2.38	-	-	-
M3a	438	538	2.38	-	-	-
CPDT-CH=CH-CPDT	478	516	2.48	-	-	-
P1	655/609	749	1.71	-4.83	-2.79	2.04
P2	490/377	640	2.00	-5.44	-3.18	2.26
P3	649/603/528/379	740	1.73	-4.95	-3.17	1.78

^a UV-vis spectra were measured in CHCl_3 solution. ^b Optical energy gap was calculated from onset of the absorption spectra. ^c $\text{HOMO} = -(4.8 + E_{\text{pa}}^{\text{onset}} - E_{\text{Fc}})$, where the half potential of ferrocene ($\text{Fc}/\text{Fc}^+ = 0.68 \text{ V vs. Ag/AgCl}$). ^d $\text{LUMO} = -(4.8 + E_{\text{pc}}^{\text{onset}} - E_{\text{Fc}})$.

3. ^1H and ^{13}C and HSQC NMR and ESIMS spectra

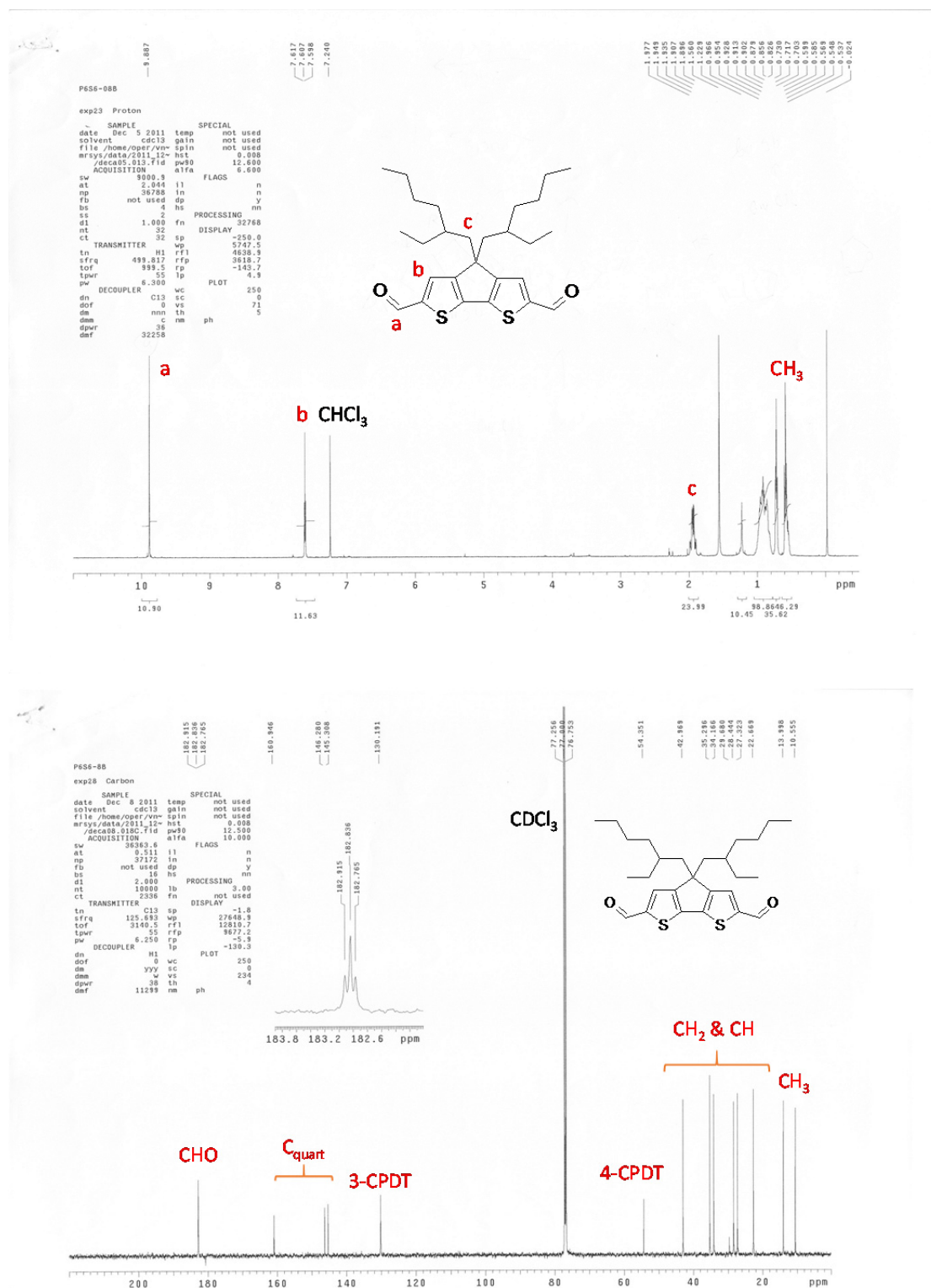


Figure S-1. ^1H and ^{13}C NMR spectra of 4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b']dithiophene-2,6-dicarbaldehyde in CDCl_3 .

02-1 #1-30 RT: 0.00-0.09 AV: 30 NL: 3.70E6
T: ITMS + c ESI Full ms [150.00-2000.00]

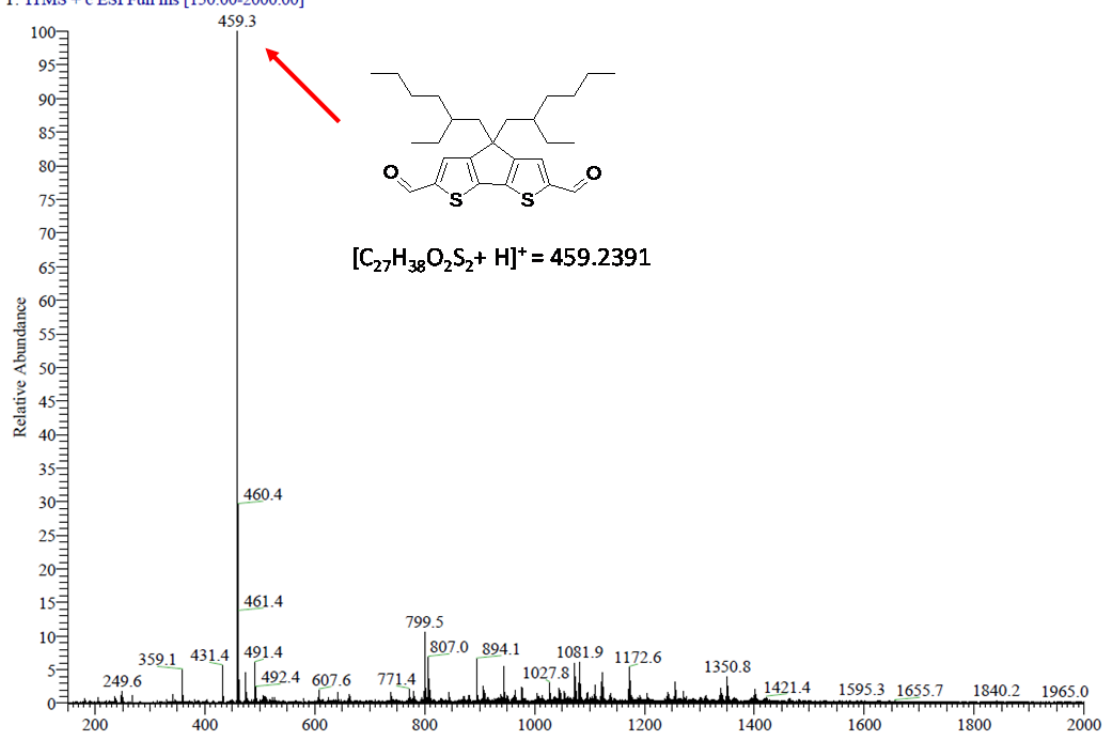


Figure S-2. ESIMS of 4,4-bis(2-ethylhexyl)-4*H*-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene-2,6-dicarbaldehyde.

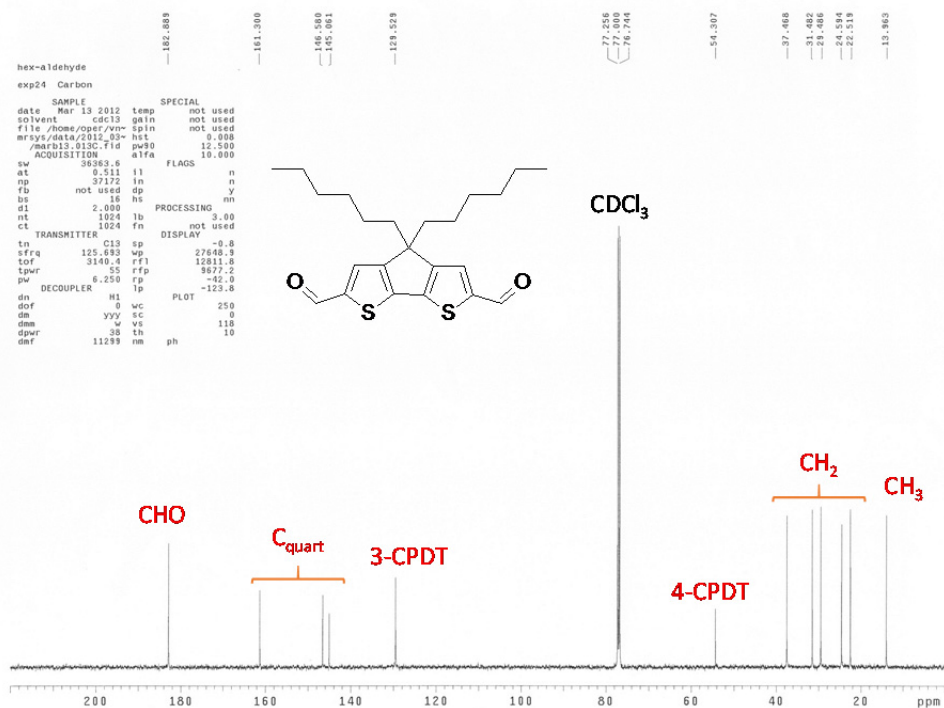
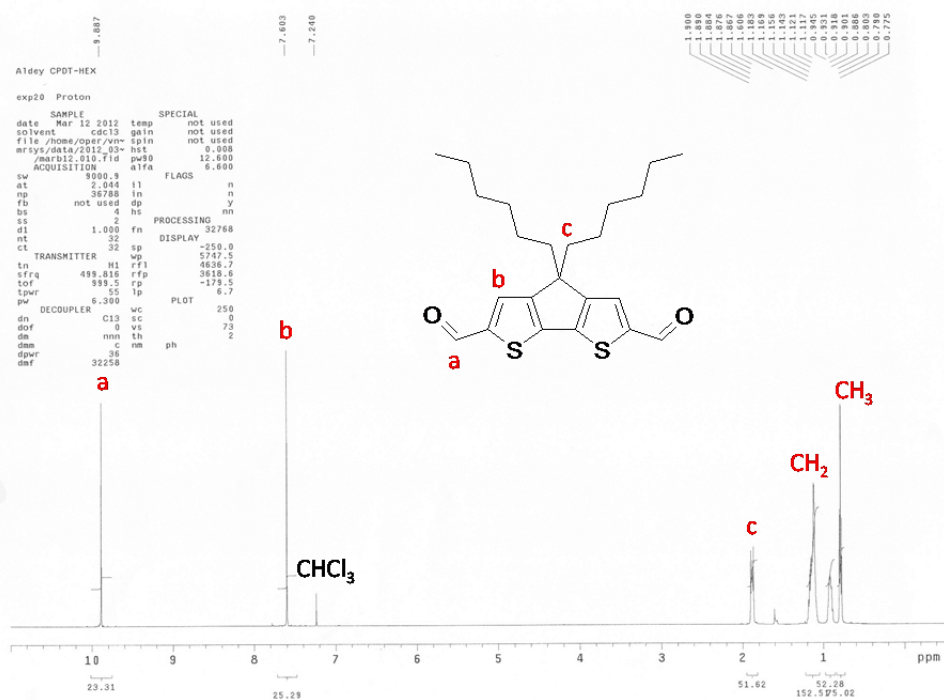


Figure S-3. ^1H and ^{13}C NMR spectra of 4,4-dihexyl-4*H*-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene-2,6-dicarbaldehyde in CDCl_3 .

21-3 #1-30 RT: 0.00-0.09 AV: 30 NL: 6.23E5
T: ITMS + e ESI Full ms [150.00-2000.00]

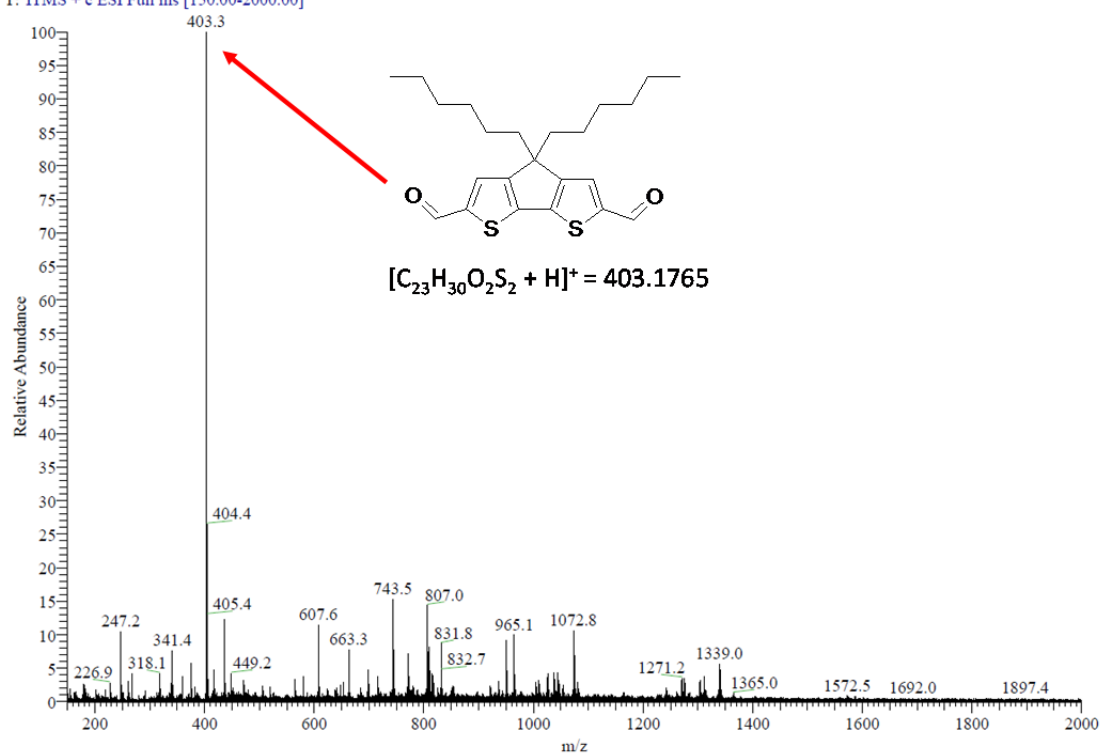


Figure S-4. ESIMS of 4,4-dihexyl-4*H*-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene-2,6-dicarbaldehyde.

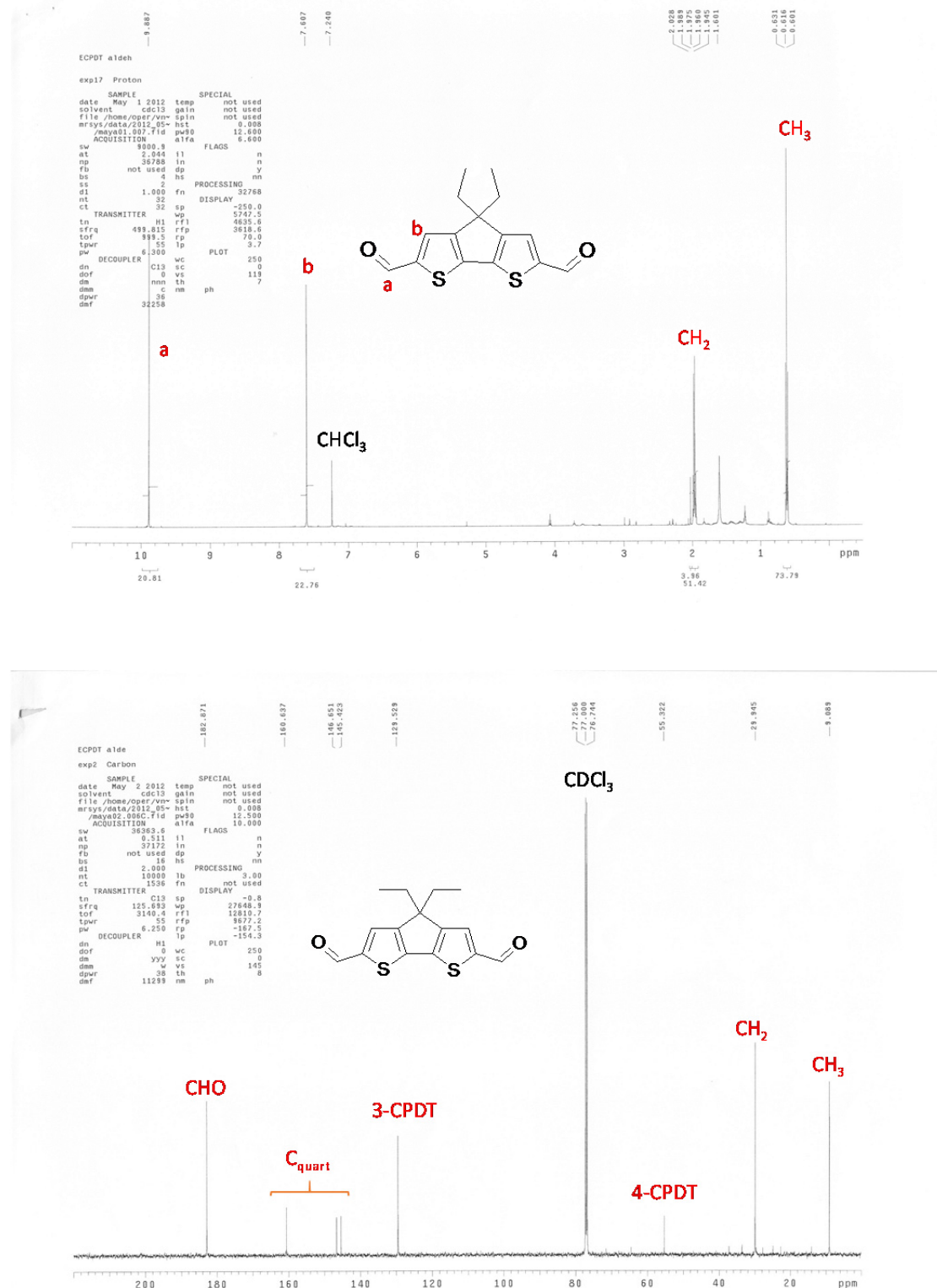


Figure S-5. ¹H and ¹³C NMR spectra of 4,4-diethyl-4H-cyclopenta[2,1-b;3,4-b']dithiophene-2,6-dicarbaldehyde in CDCl₃.

09-2 #1-30 RT: 0.00-0.09 AV: 30 NL: 1.05E7
T: ITMS + e ESI Full ms [150.00-2000.00]

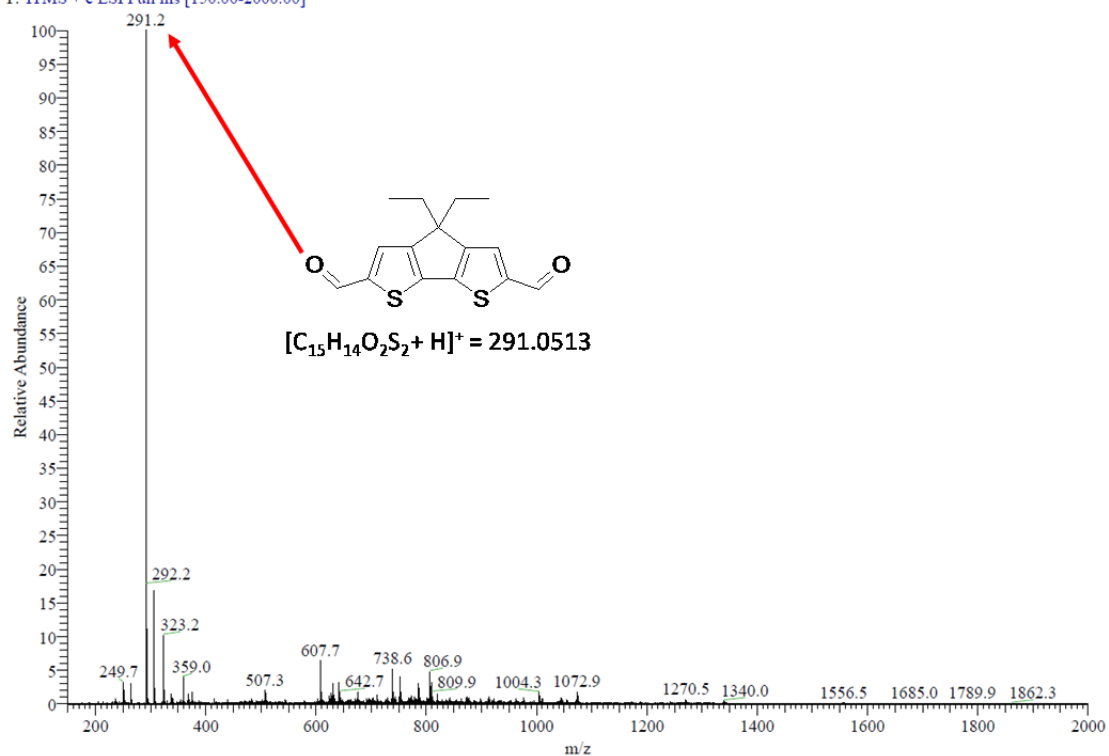


Figure S-6. ESIMS of 4,4-diethyl-4*H*-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene-2,6-dicarbaldehyde.

36-5 #1-30 RT: 0.00-0.09 AV: 30 NL: 1.21E6
T: ITMS + c ESI Full ms [150.00-2000.00]

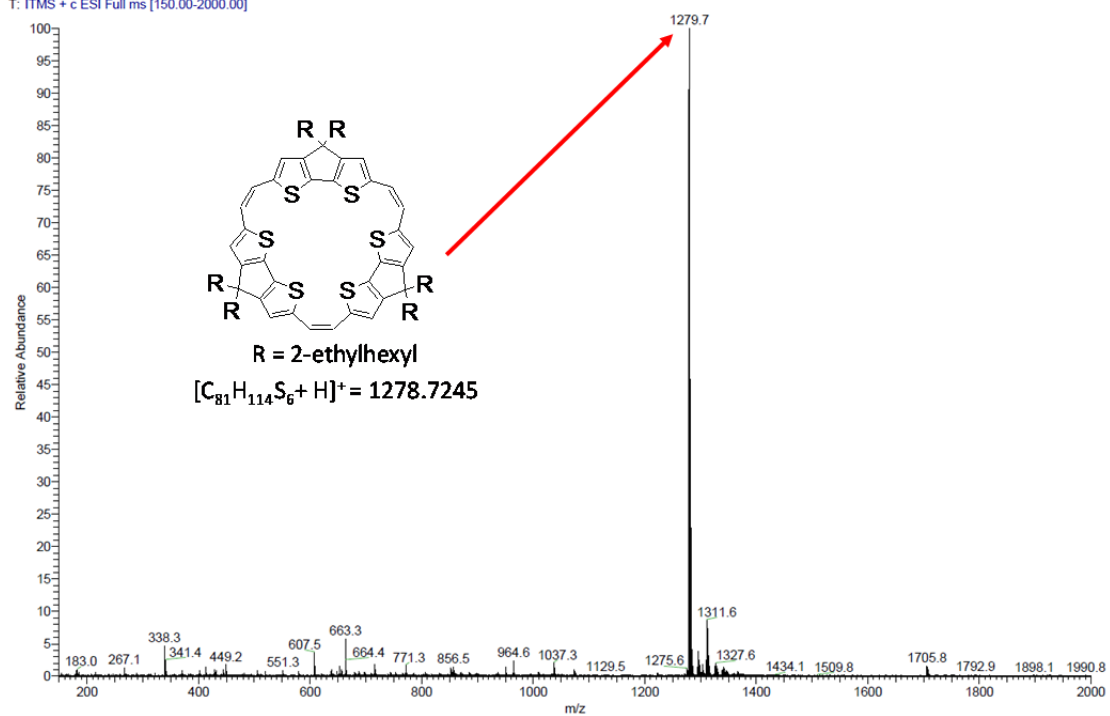


Figure S-8. ESIMS of M1a.

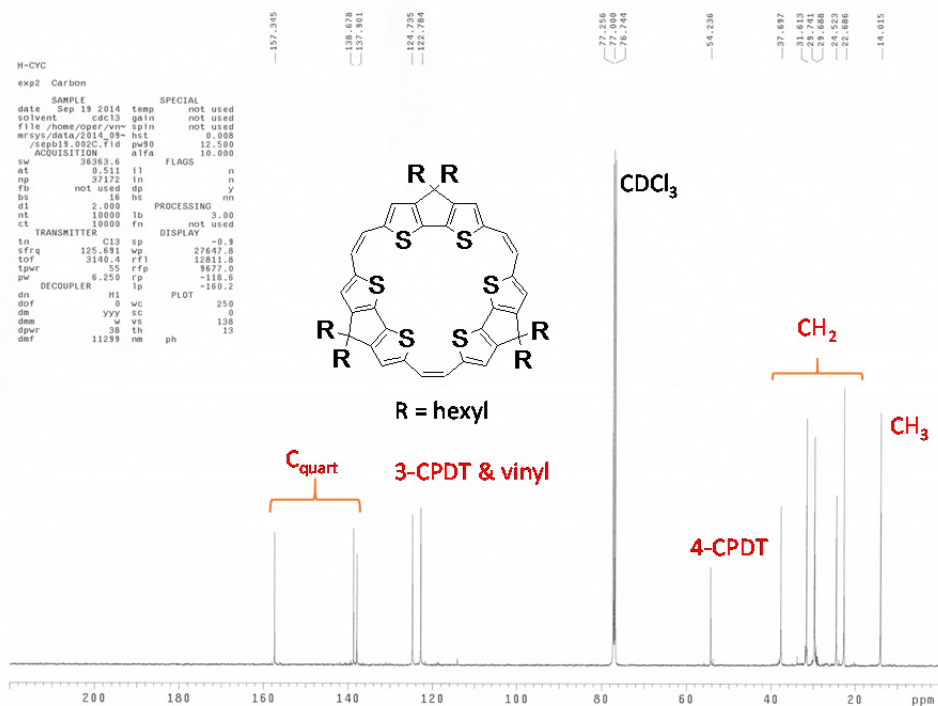
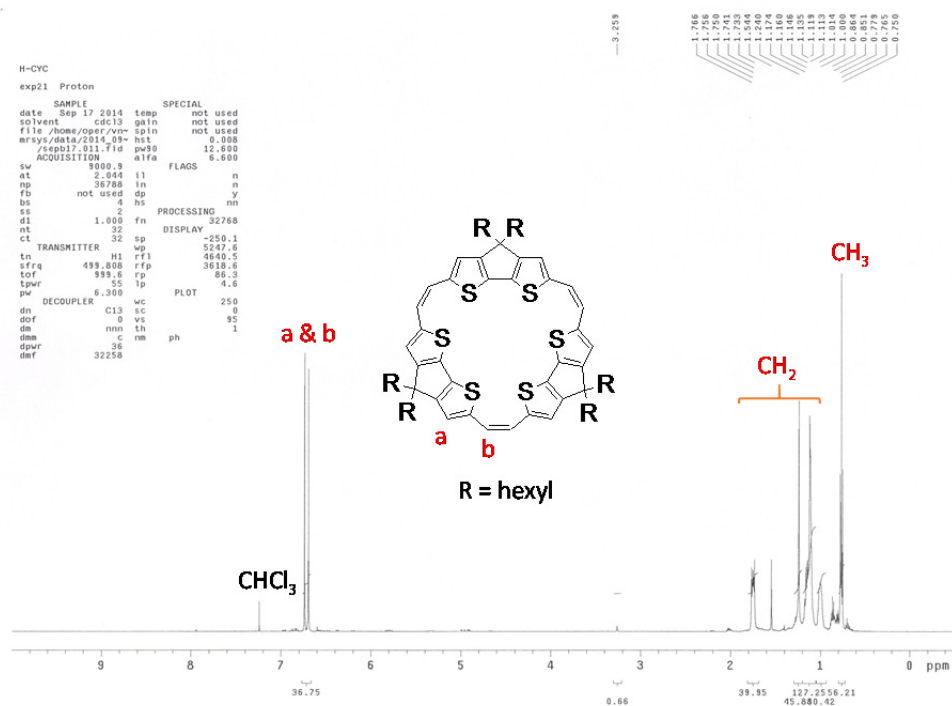


Figure S-9. ¹H and ¹³C NMR spectra of M1b in CDCl₃.

48-7 #1-30 RT: 0.00-0.09 AV: 30 NL: 6.73E5
T: ITMS + e ESI Full ms [150.00-2000.00]

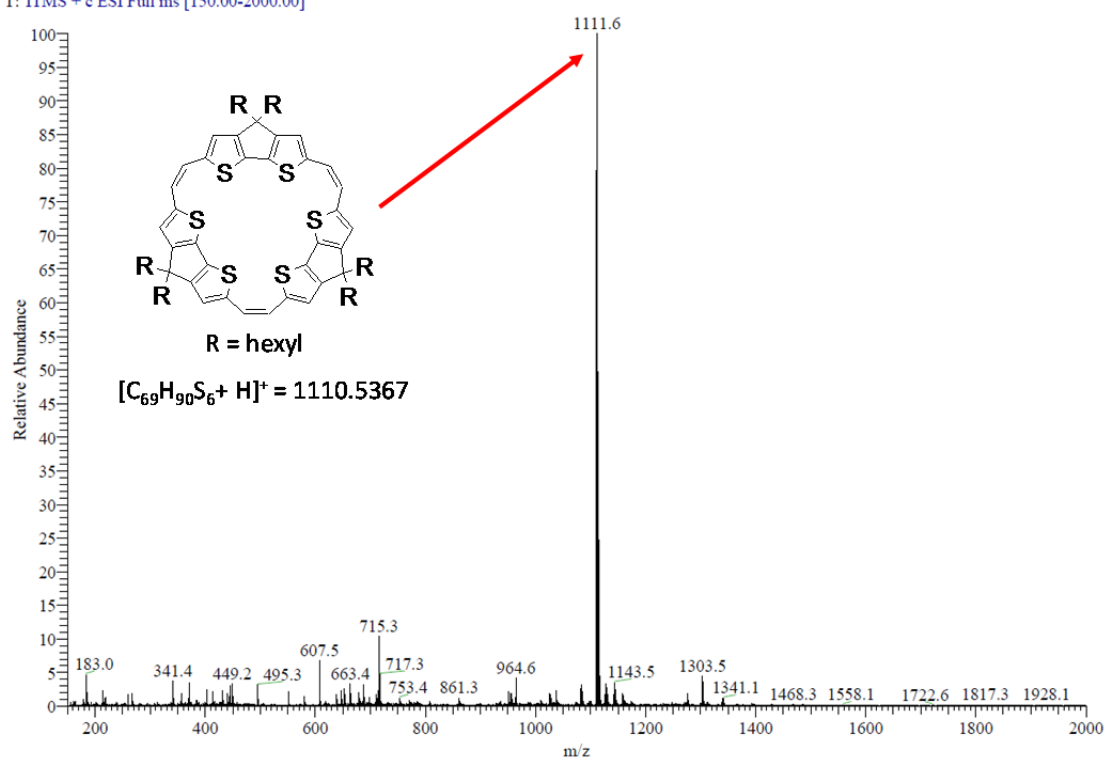


Figure S-10. ESIMS of M1b.

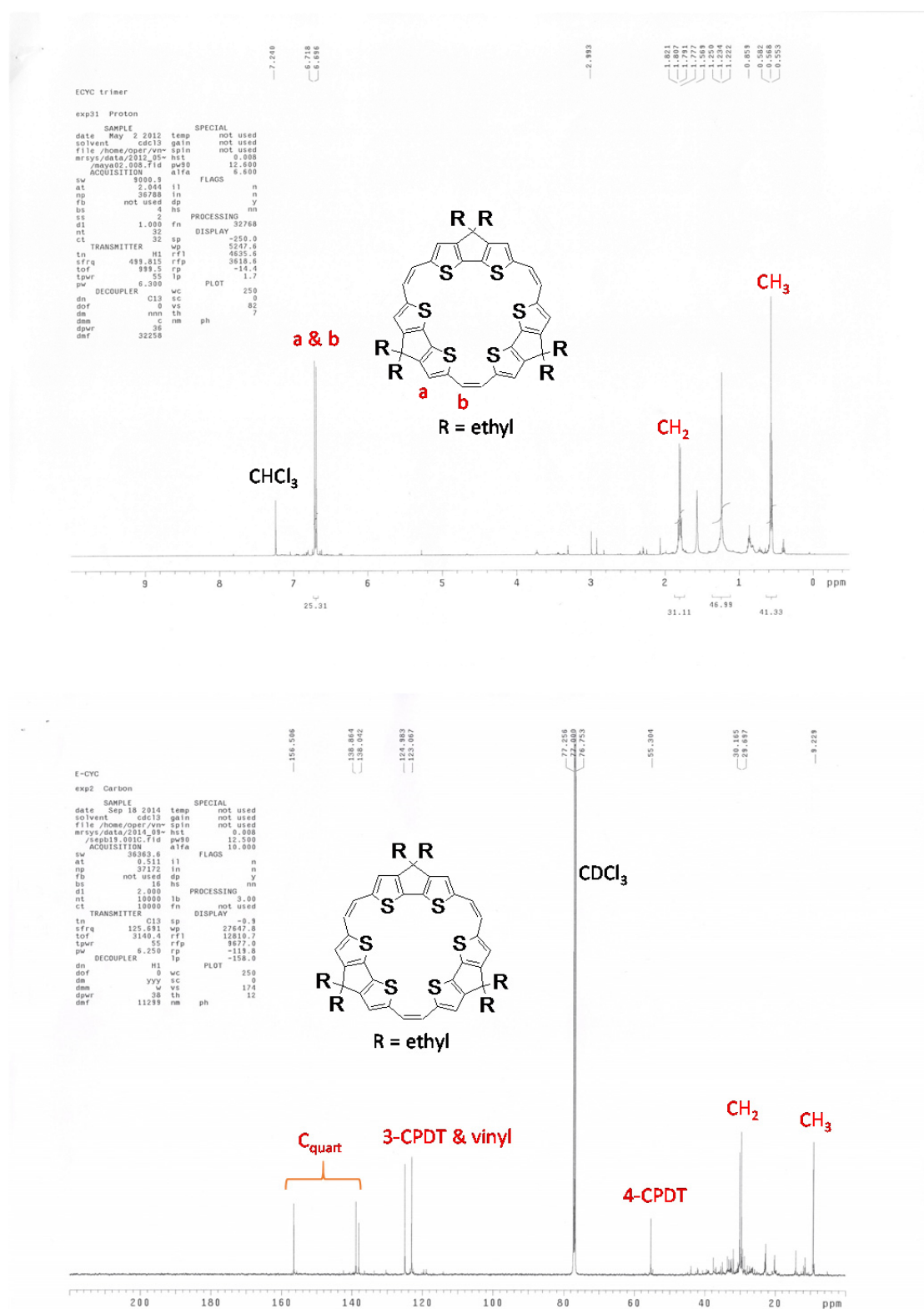


Figure S-11. ¹H and ¹³C NMR spectra of M1c in CDCl₃.

42-6 #1-30 RT: 0.00-0.09 AV: 30 NL: 1.73E6
T: ITMS + e ESI Full ms [150.00-2000.00]

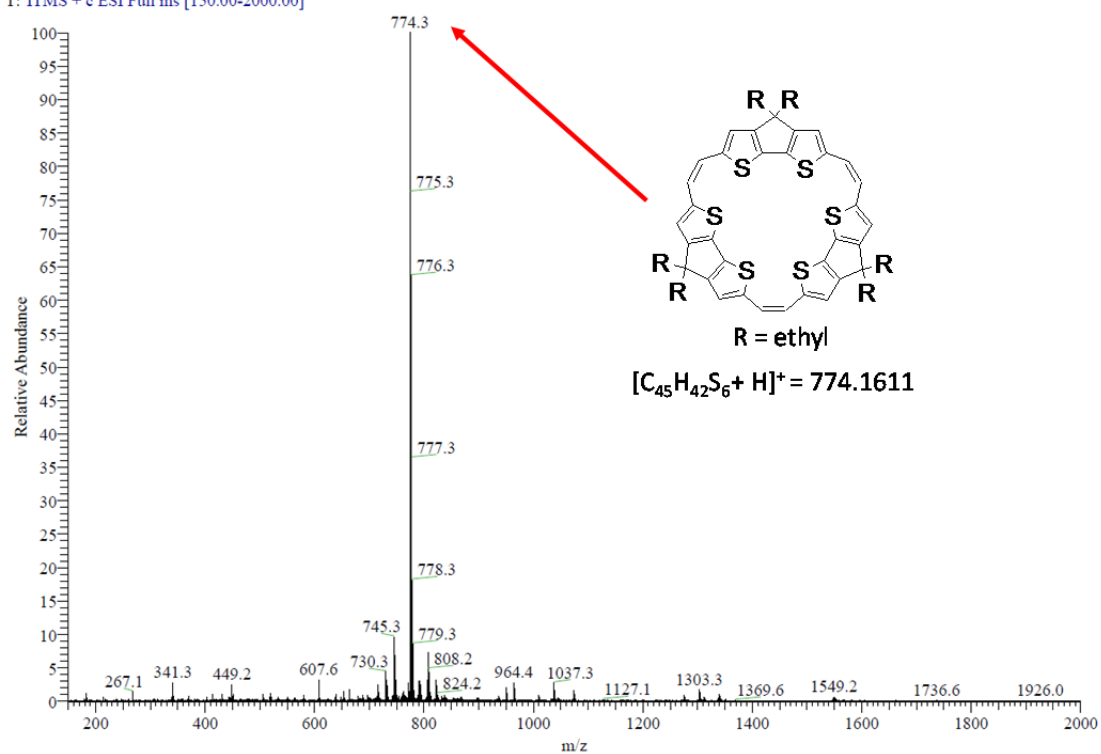


Figure S-12. ESIMS of M1c.

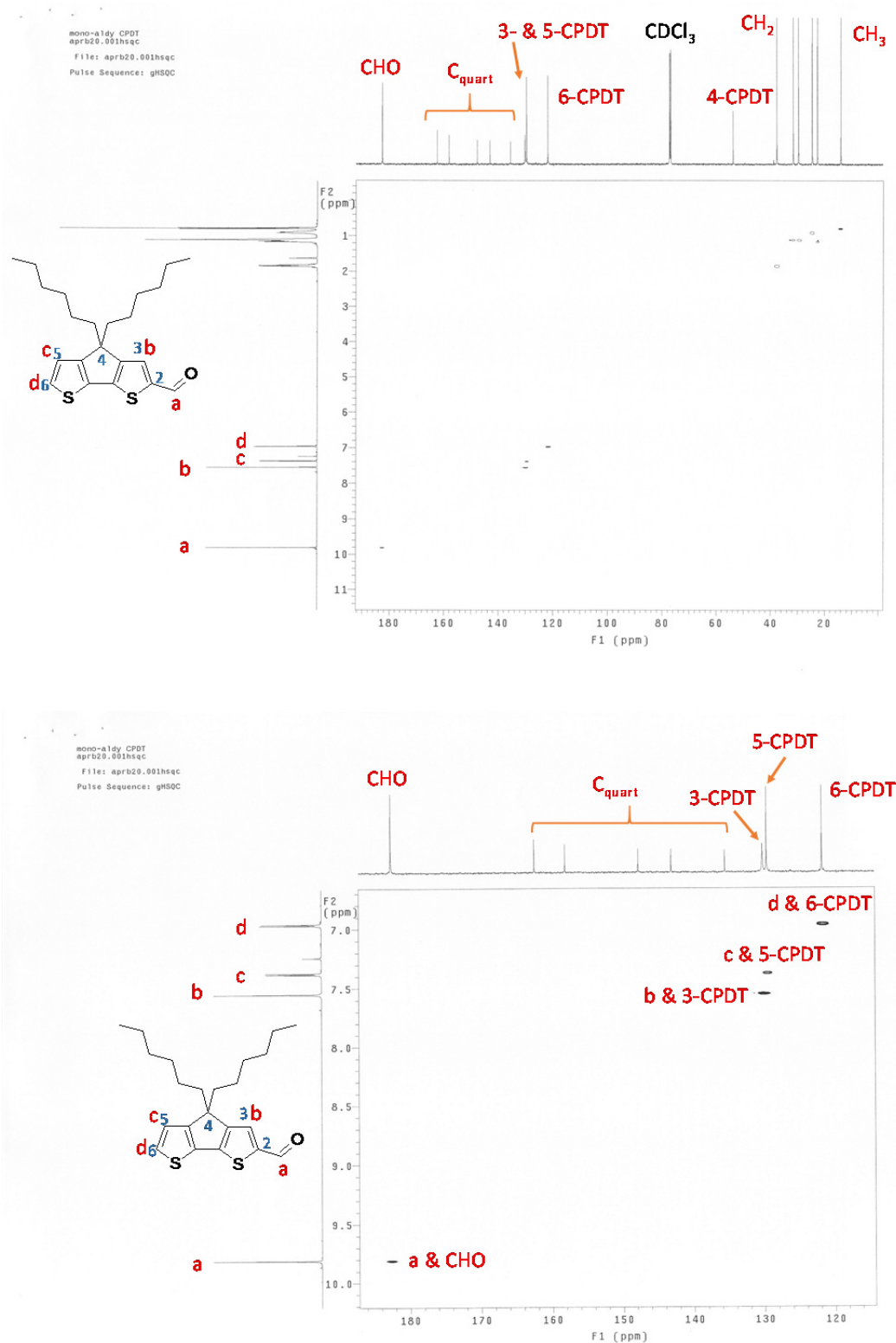


Figure S-14. ^1H - ^{13}C HSQC NMR spectra of 4,4-dihexyl-4*H*-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene-2-carbaldehyde in CDCl_3 .

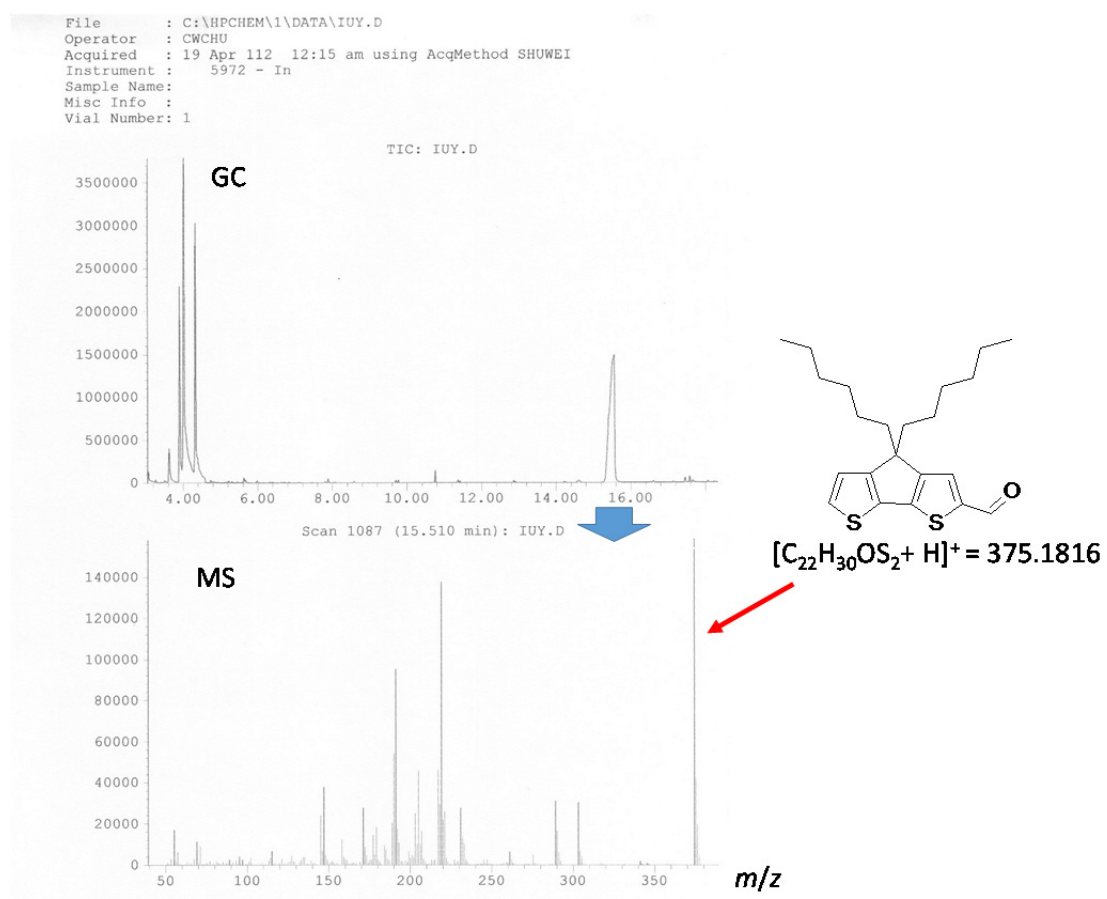


Figure S-15. GCMS of 4,4-dihexyl-4*H*-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene-2-carbaldehyde.

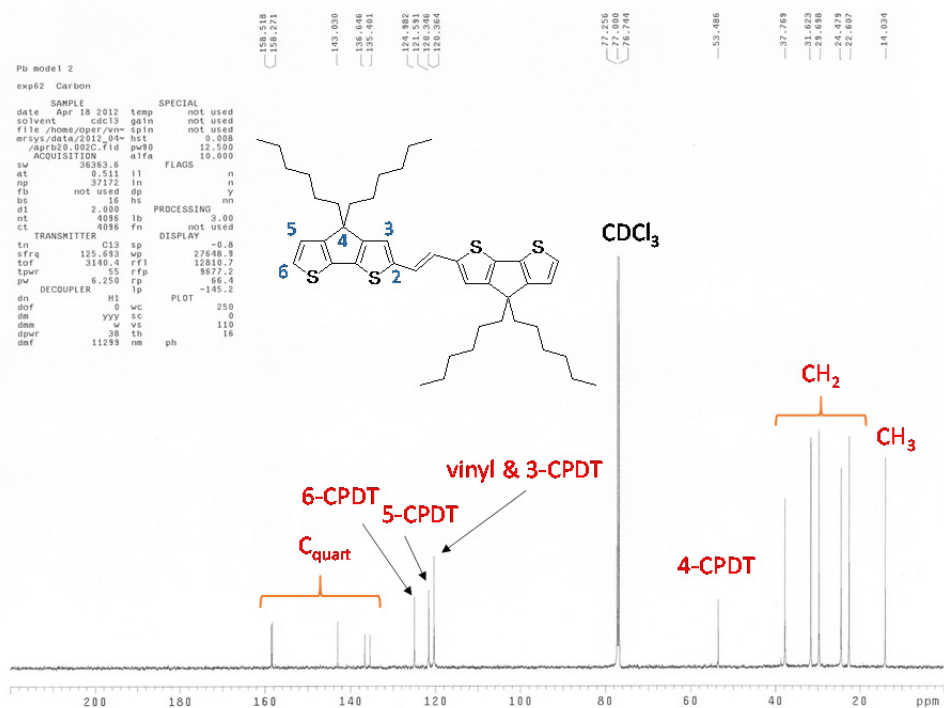
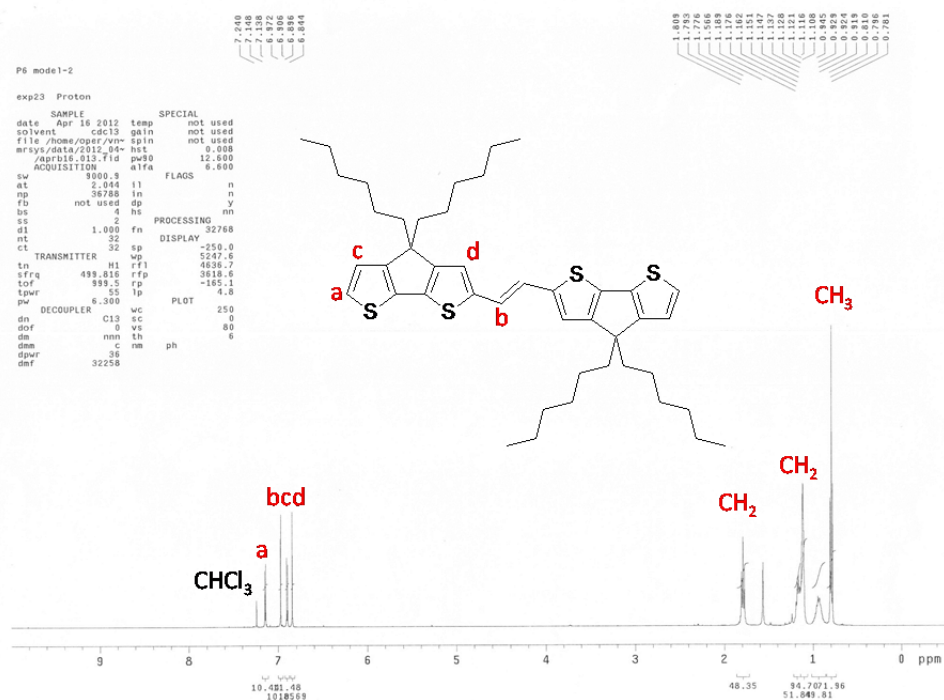


Figure S-16. ¹H and ¹³C NMR spectra of CPDT-CH=CH-CPDT in CDCl₃.

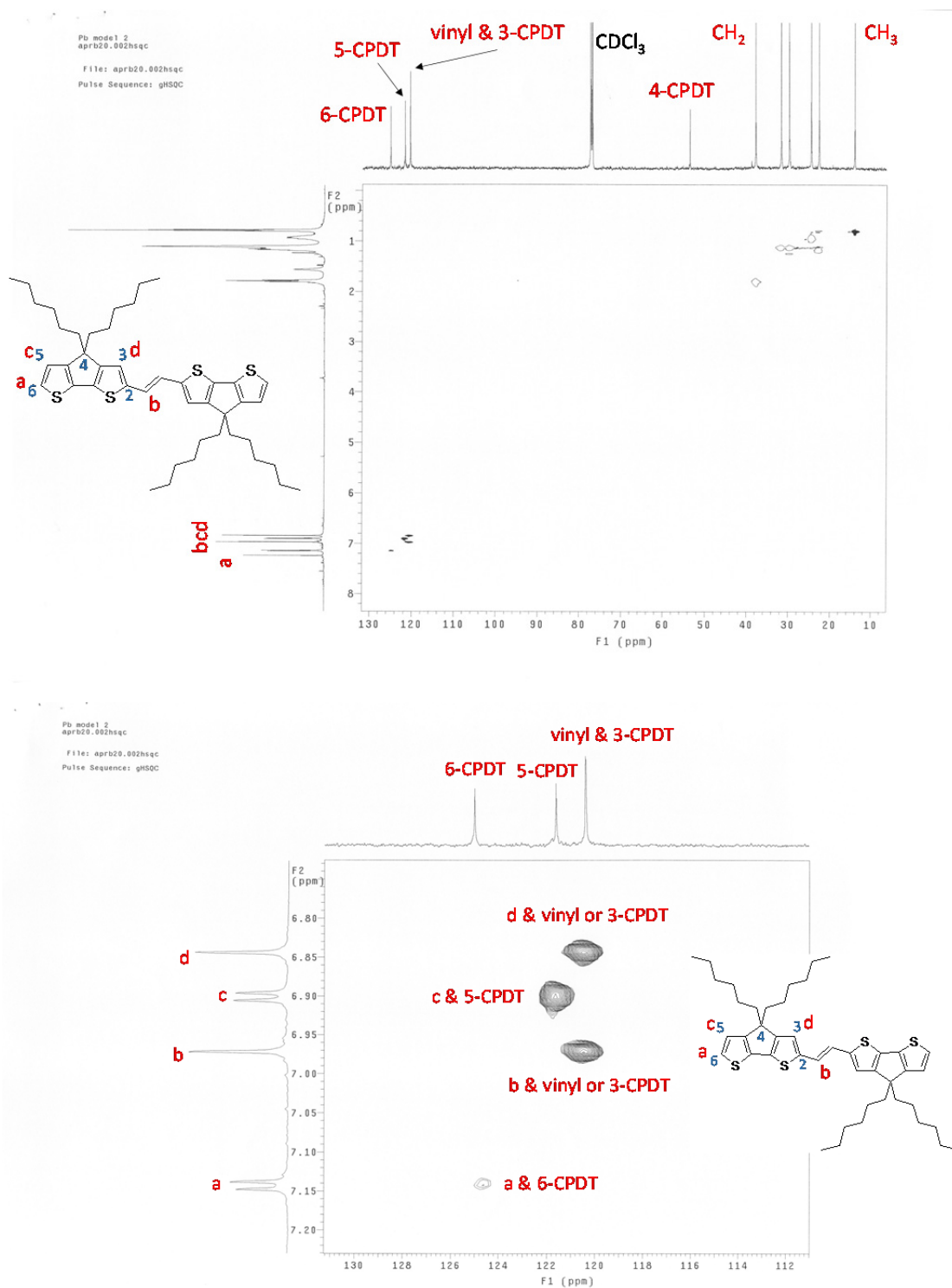


Figure S-17. ^1H - ^{13}C HSQC NMR spectra of CPDT-CH=CH-CPDT in CDCl_3 .

30-4 #1-30 RT: 0.00-0.09 AV: 30 NL: 7.40E5
T: ITMS + e ESI Full ms [150.00-2000.00]

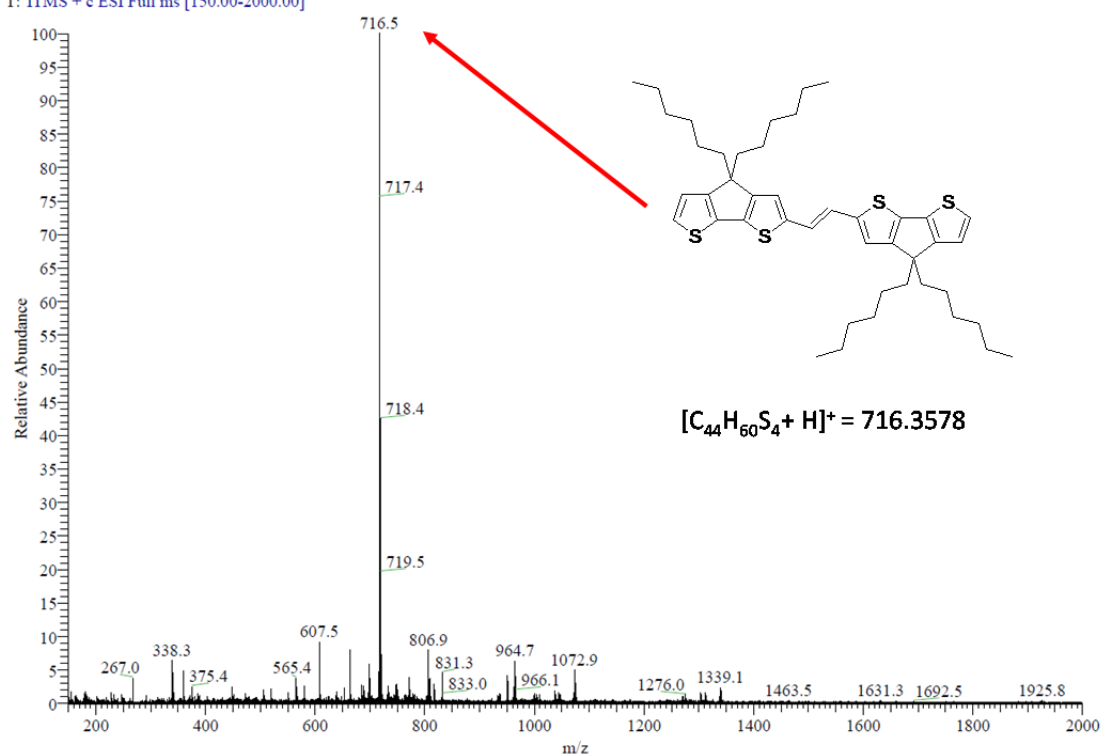


Figure S-18. ESIMS of CPDT-CH=CH-CPDT.

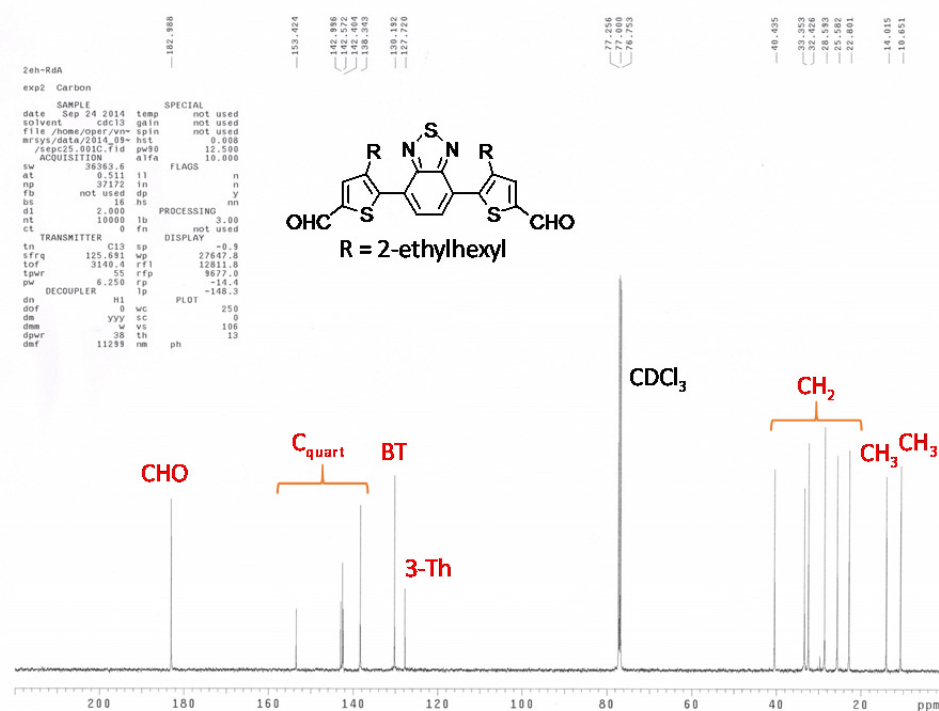
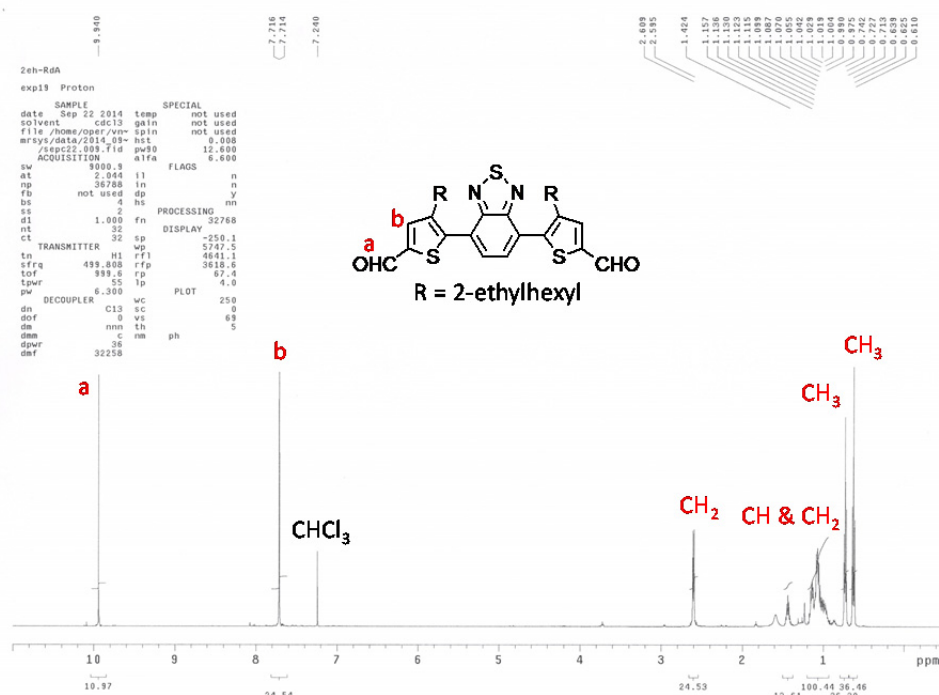


Figure S-19. ¹H and ¹³C NMR spectra of 5,5'-(2,1,3-benzothiadiazole-4,7-diyl)bis [4-(2-ethylhexyl)thiophen-2-carbaldehyde] in CDCl₃.

54-S #1-30 RT: 0.00-0.09 AV: 30 NL: 4.65E5
T: ITMS + e ESI Full ms [150.00-2000.00]

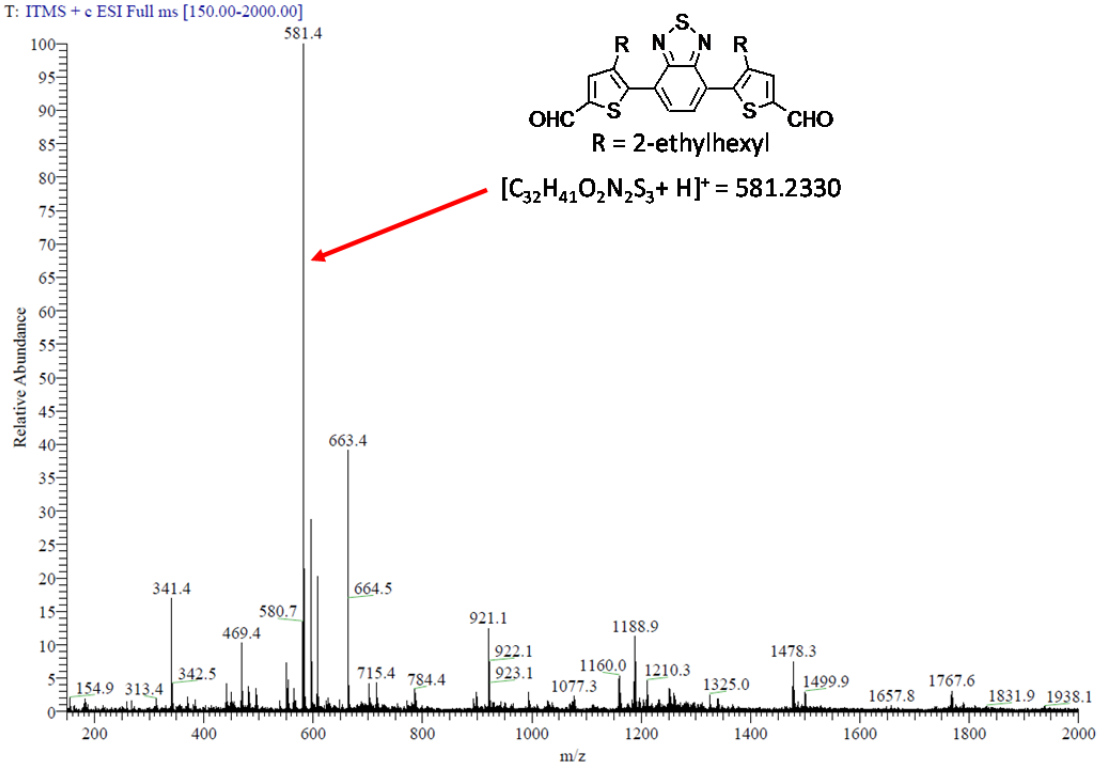


Figure S-20. ESIMS of 5,5'-(2,1,3-benzothiadiazole-4,7-diyl)bis[4-(2-ethylhexyl)thiophen-2-carbaldehyde].

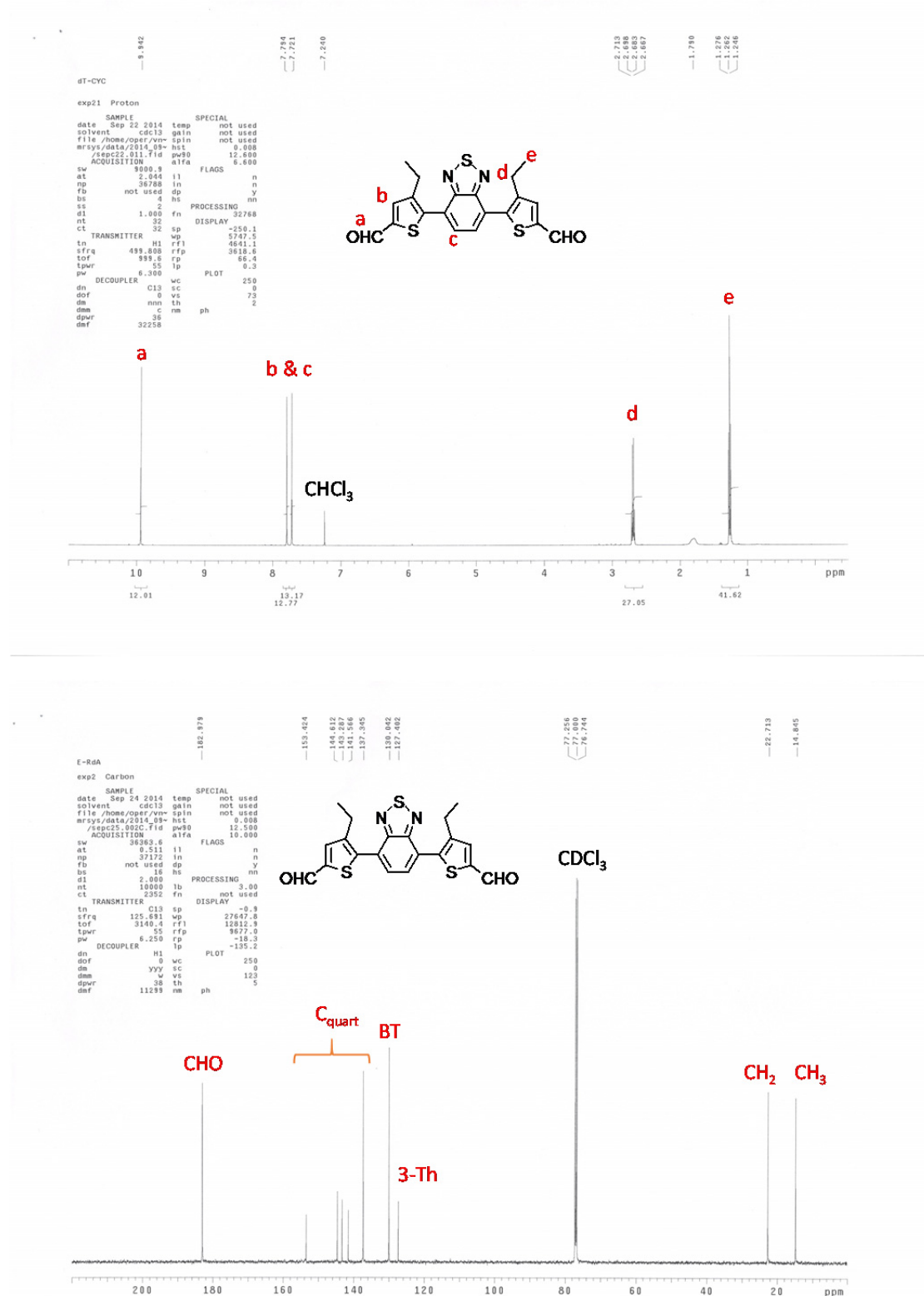


Figure S-21. ¹H and ¹³C NMR spectra of 5,5'-(2,1,3-benzothiadiazole-4,7-diyl)bis(4-ethylthiophen-2-carbaldehyde) in CDCl₃.

58-9 #1-30 RT: 0.00-0.09 AV: 30 NL: 6.88E5
T: ITMS + e ESI Full ms [150.00-2000.00]

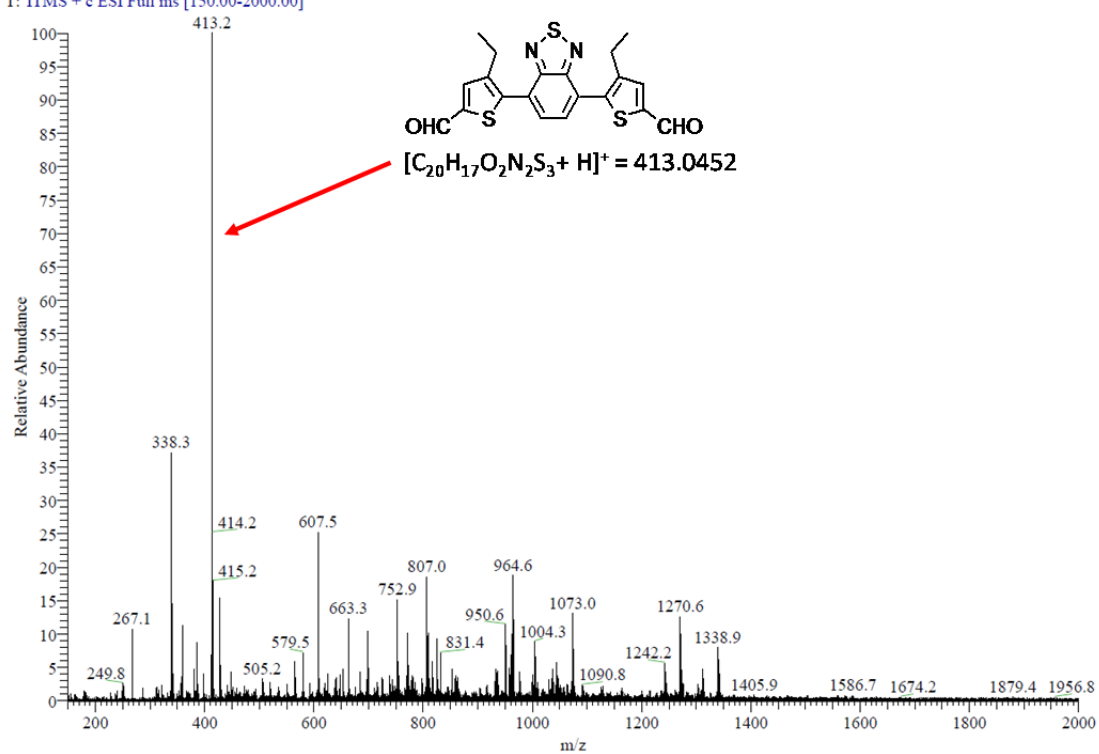


Figure S-22. ESIMS of 5,5'-(2,1,3-benzothiadiazole-4,7-diyl)bis(4-ethylthiophen-2-carbaldehyde).

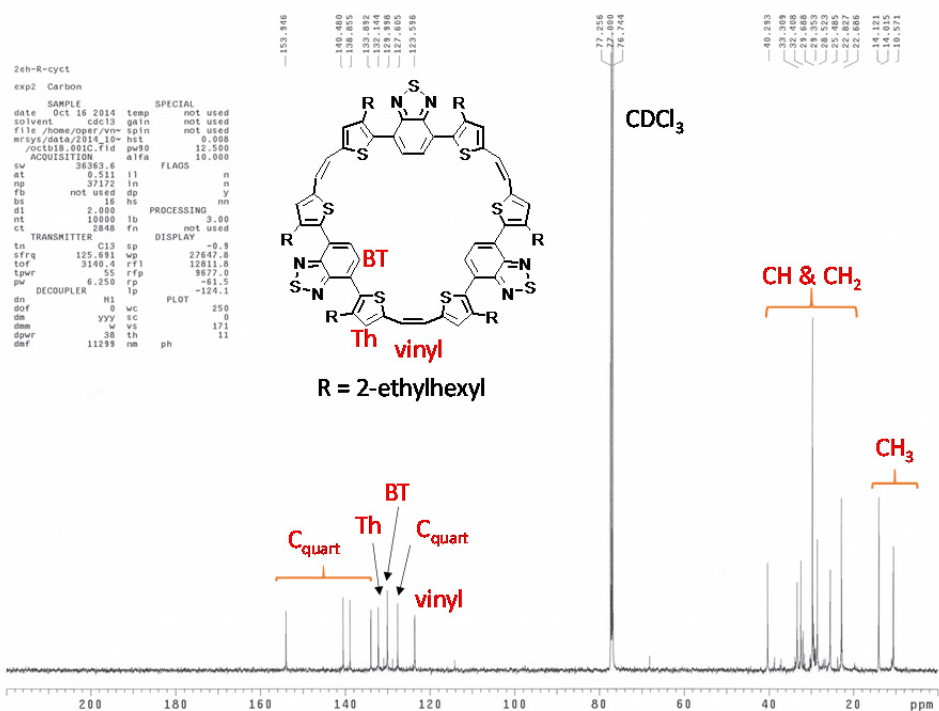
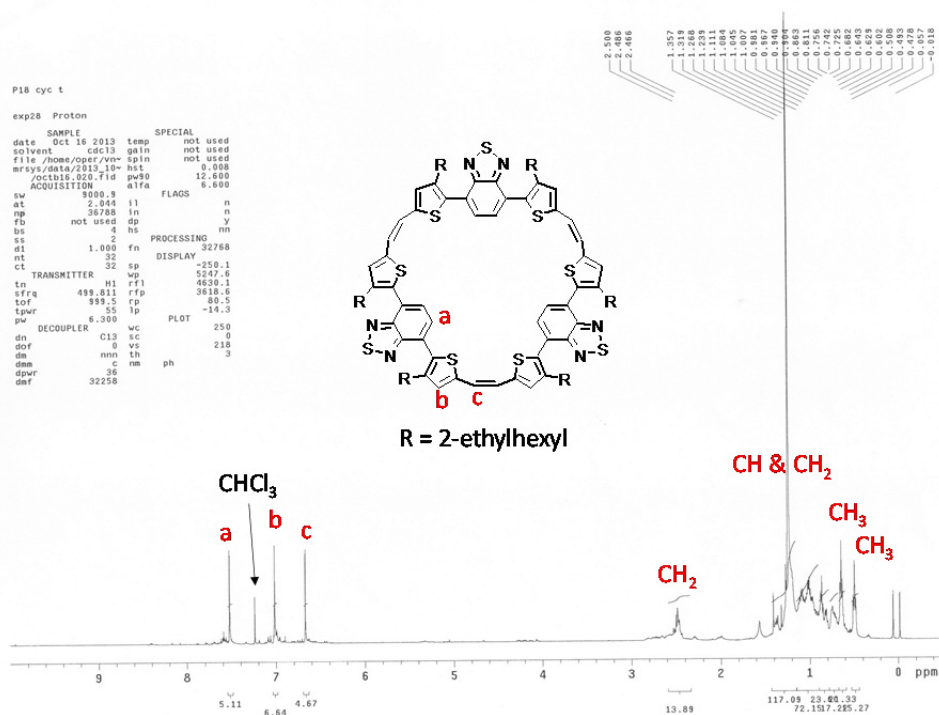


Figure S-23. ^1H and ^{13}C NMR spectra of M2a in CDCl_3 .

15-10 #1-30 RT: 0.00-0.10 AV: 30 NL: 6.22E4
T: ITMS + c ESI Full ms [150.00-2000.00]

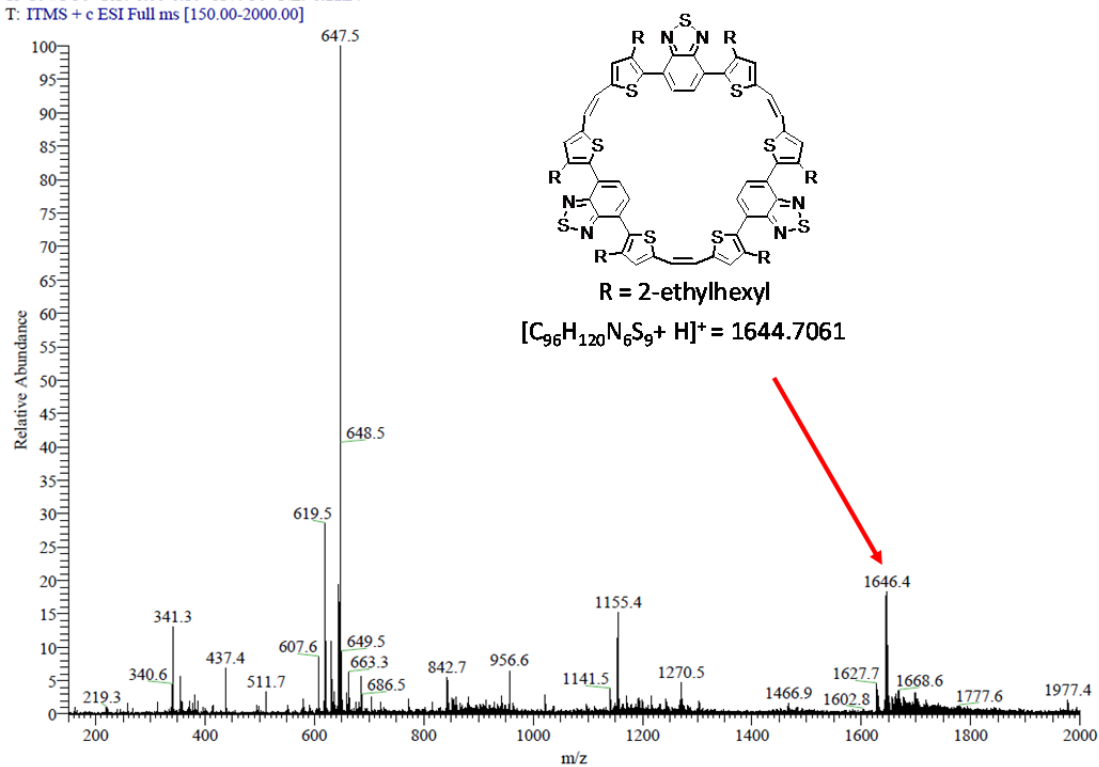


Figure S-25. ESIMS of M2a.

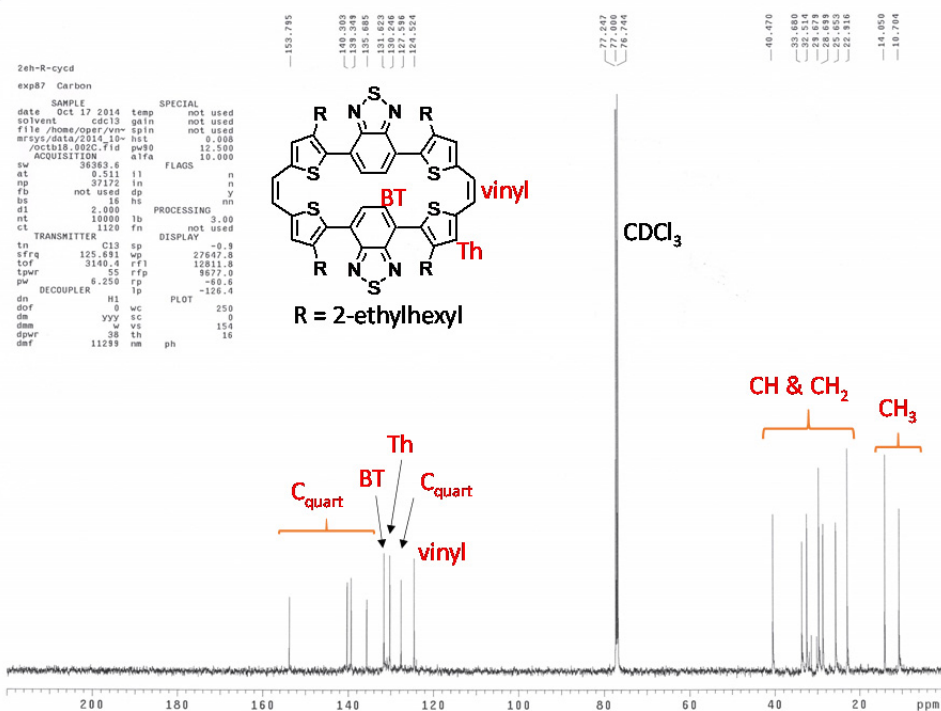
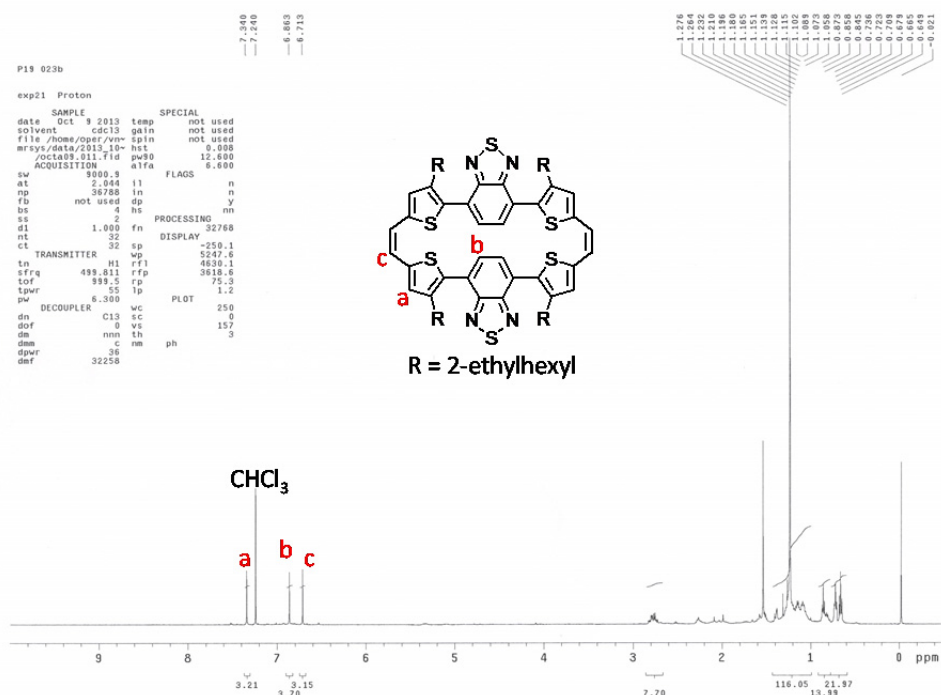


Figure S-26. ¹H and ¹³C NMR spectra of M3a in CDCl₃.

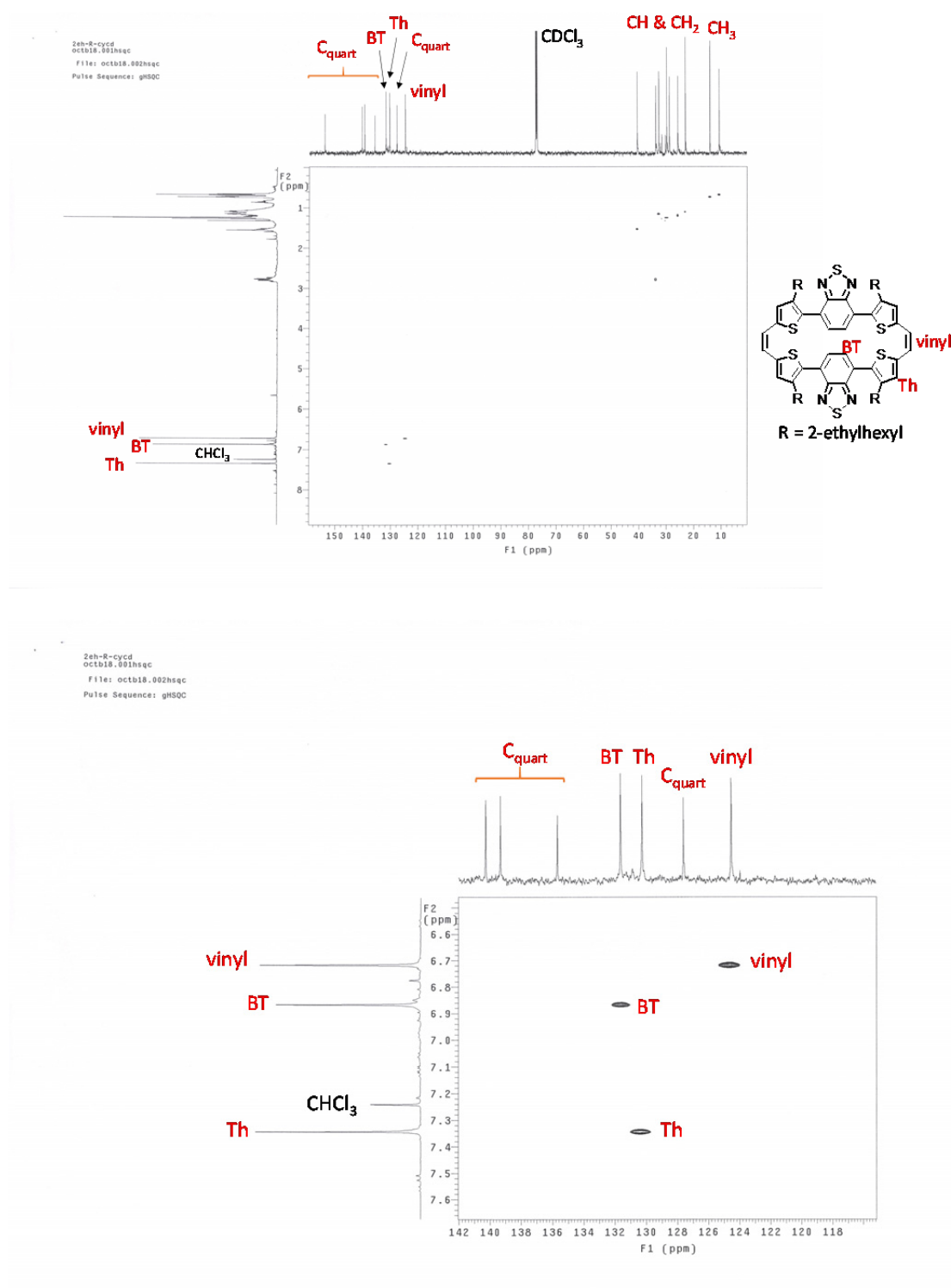


Figure S-27. ^1H - ^{13}C HSQC NMR spectra of **M3a** in CDCl_3 .

10-12 #1-30 RT: 0.00-0.10 AV: 30 NL: 4.18E4
T: ITMS + c ESI Full ms [150.00-2000.00]

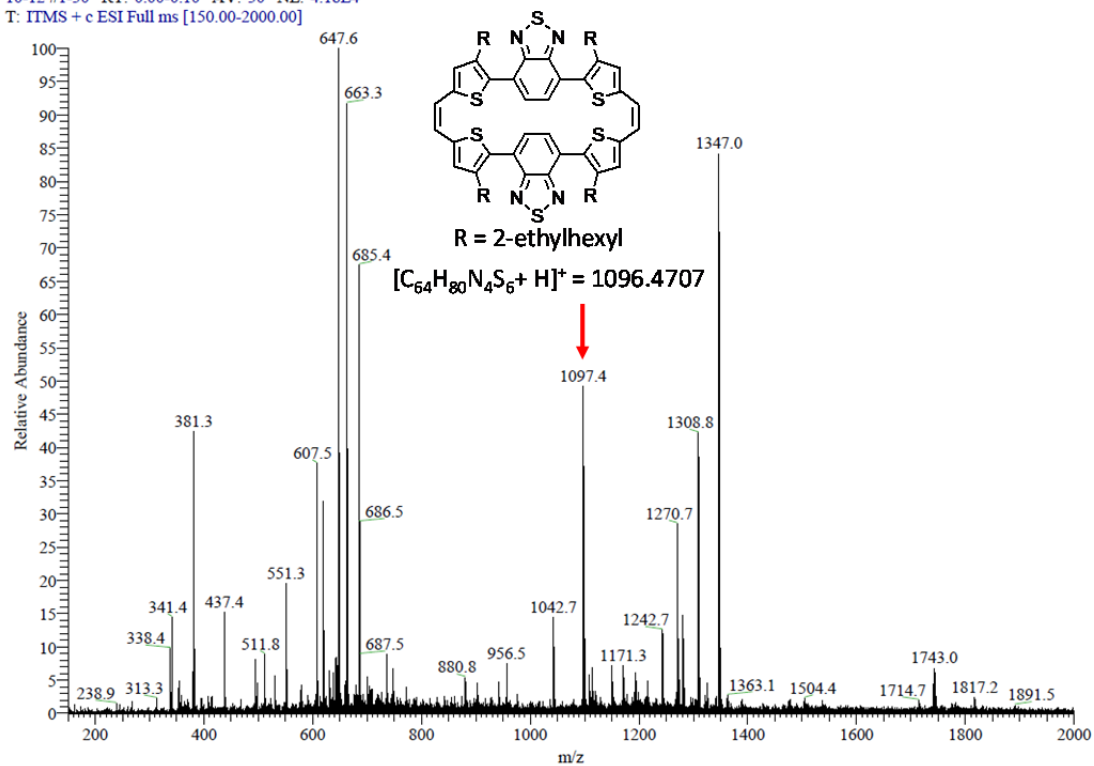


Figure S-28. ESIMS of M3a.

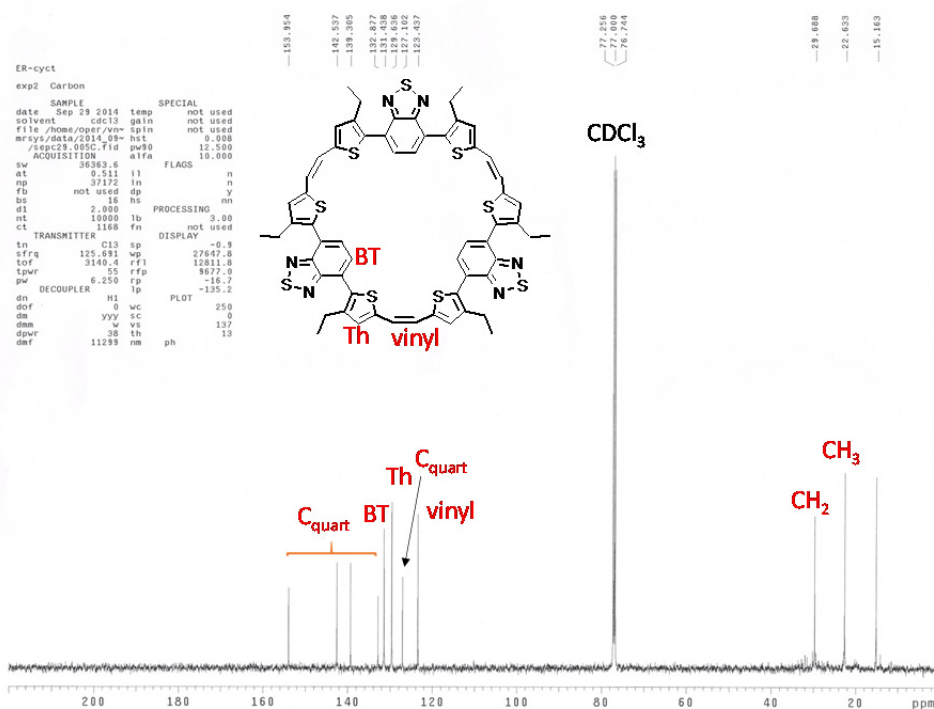
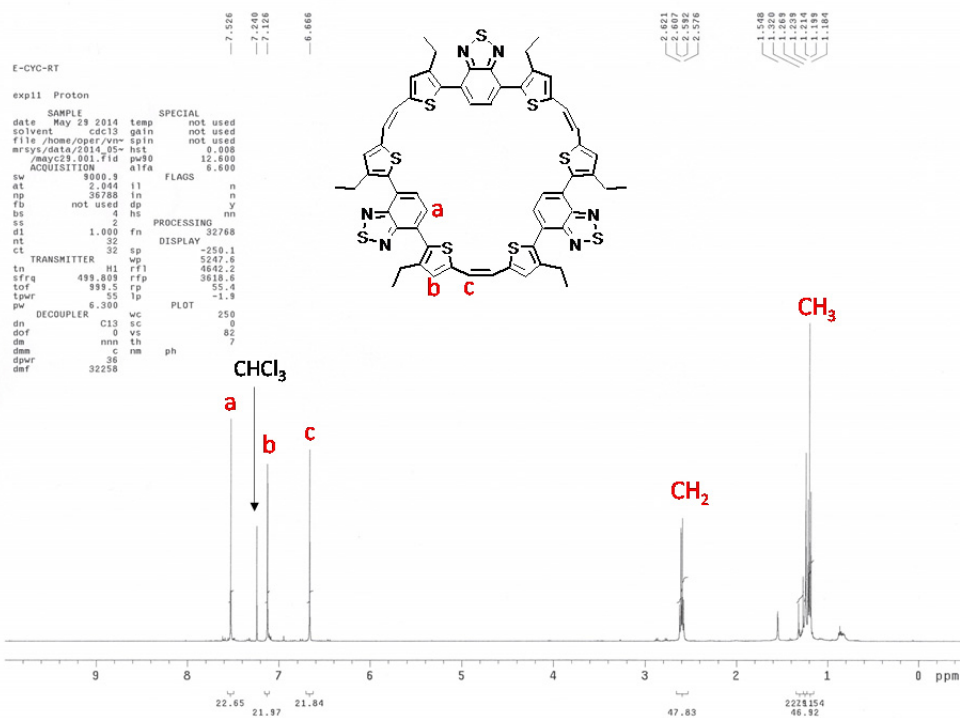


Figure S-29. ¹H and ¹³C NMR spectra of M2c in CDCl₃.

17-11 #1-30 RT: 0.00-0.09 AV: 30 NL: 9.70E4
T: ITMS + c ESI Full ms [150.00-2000.00]

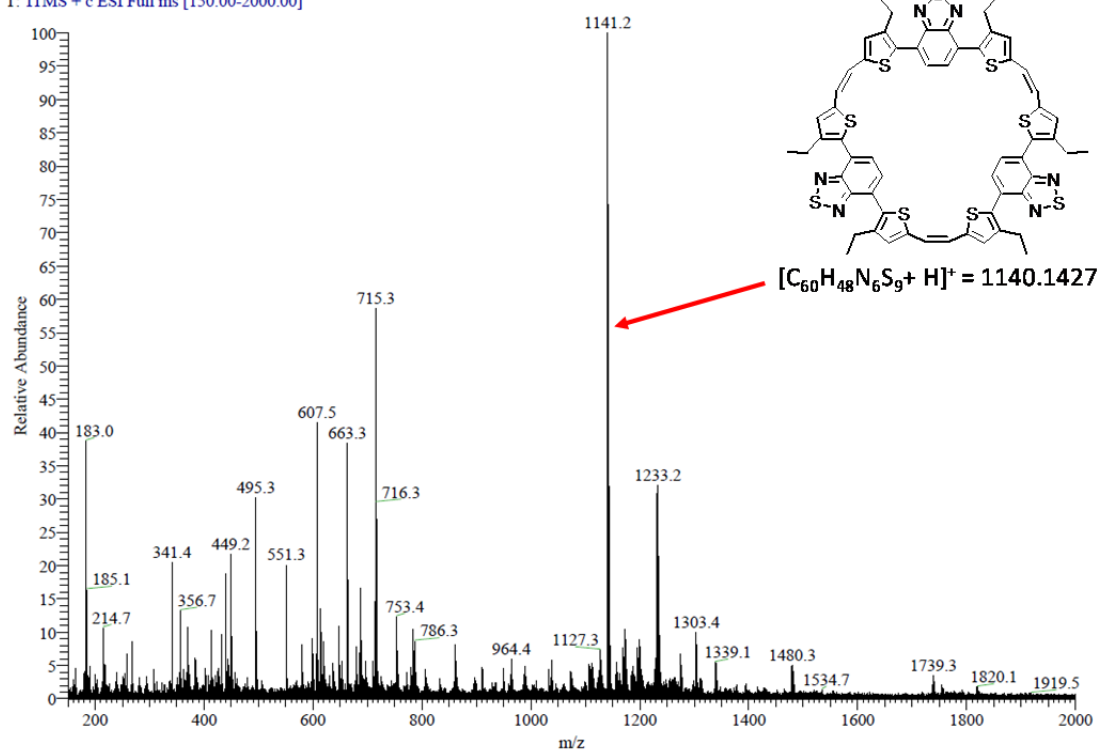


Figure S-30. ESIMS of M2c.

03-13 #1-30 RT: 0.00-0.10 AV: 30 NL: 8.73E4
T: ITMS + c ESI Full ms [150.00-2000.00]

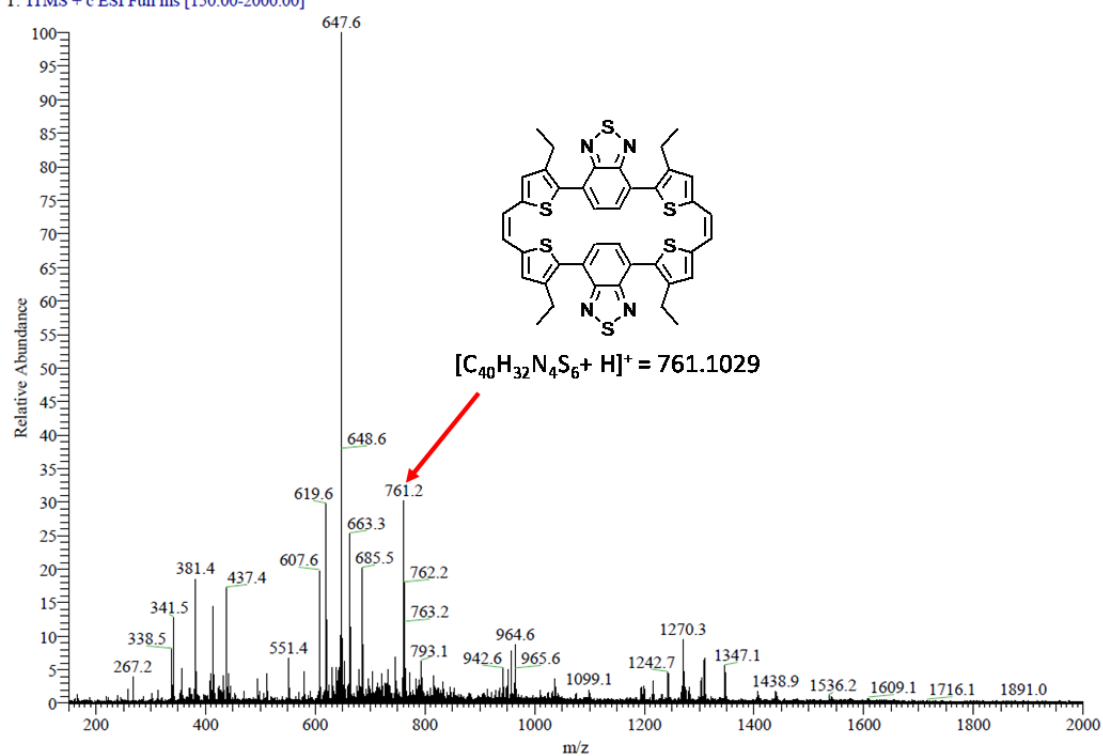


Figure S-32. ESIMS of M3c.

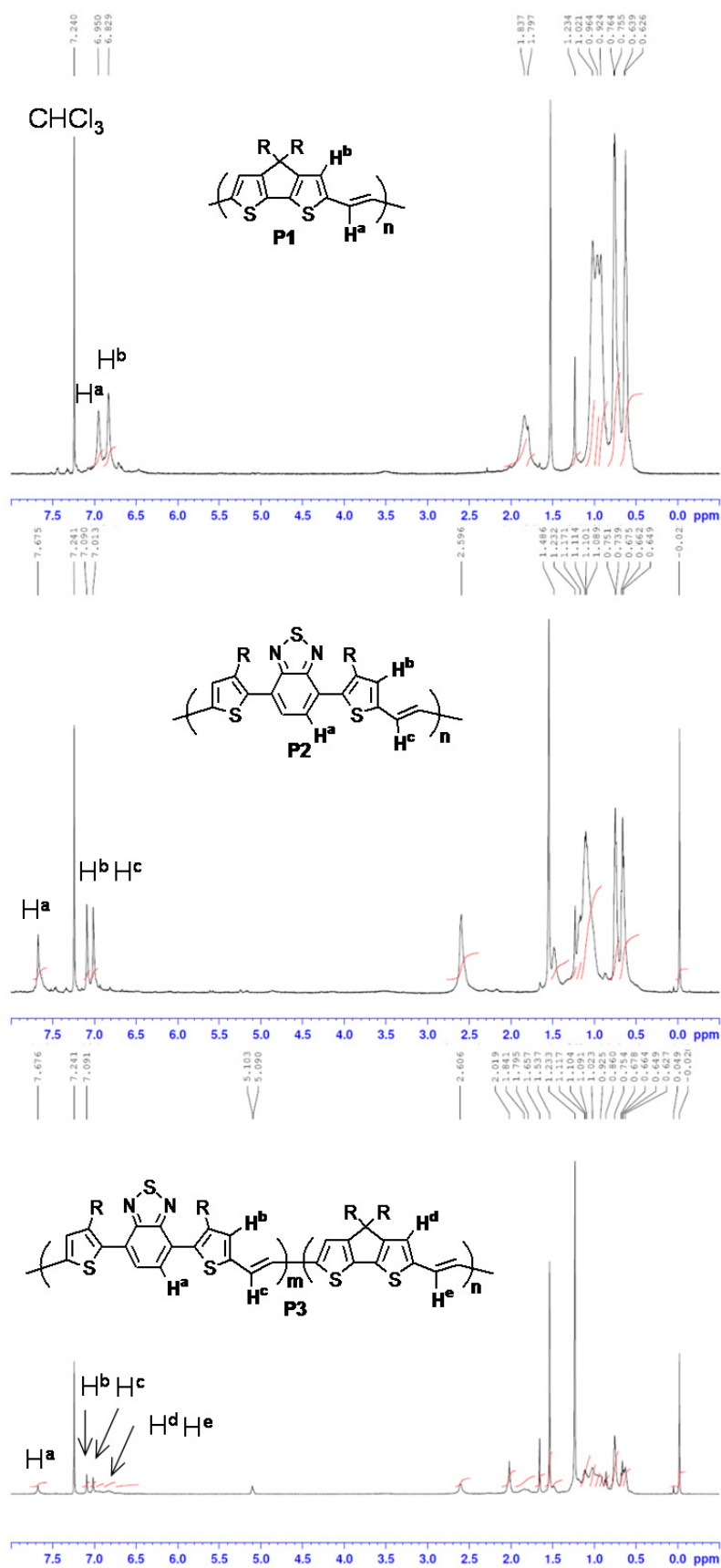


Figure S-33. 1H NMR spectra of **P1**, **P2**, and **P3** in $CDCl_3$.

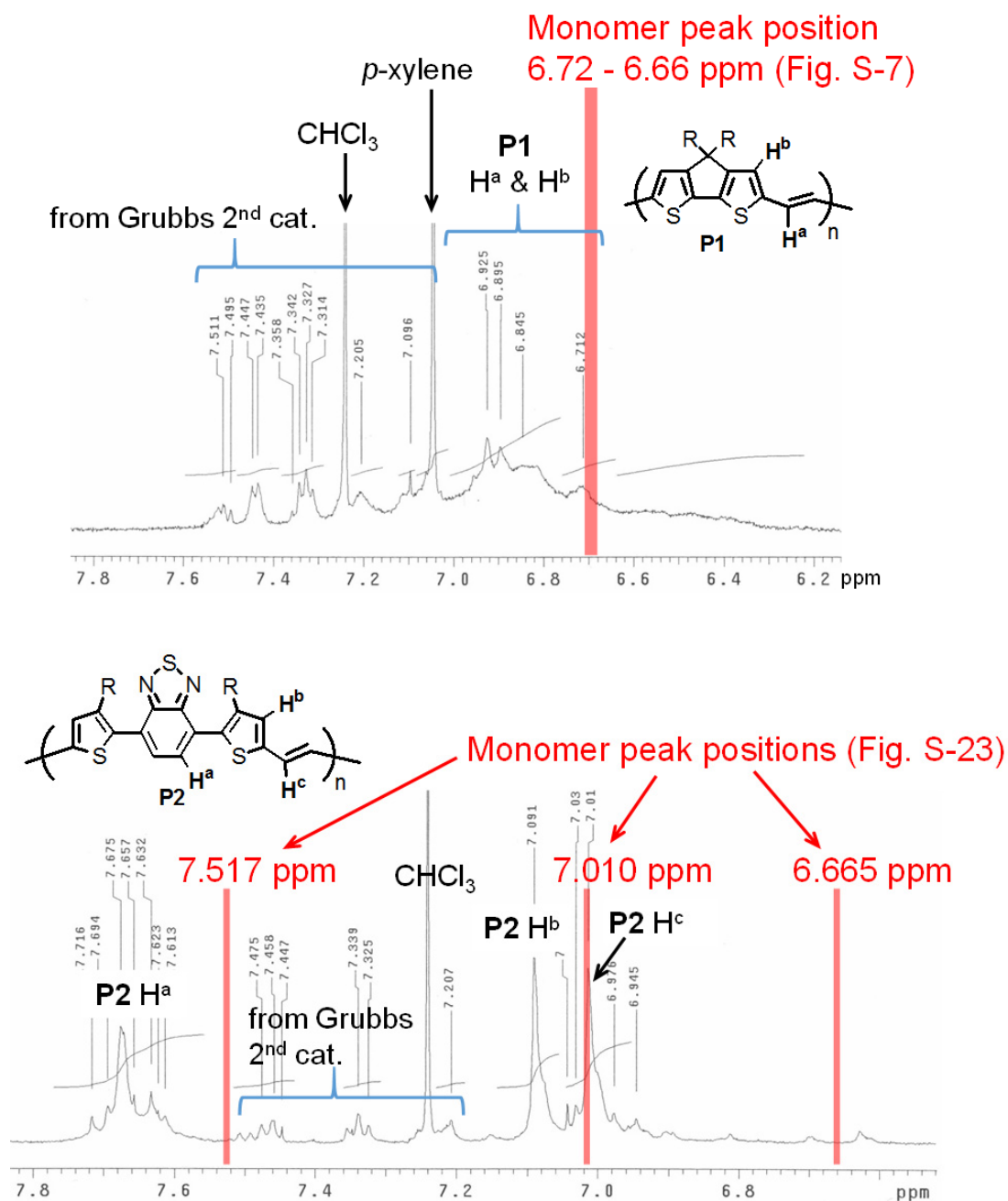


Figure S-34. ^1H NMR spectra of **P1** (top) and **P2** (bottom) in CDCl_3 . These spectra were measured immediately after the polymerization without purification. Note that monomer peaks in **P2** are completely disappeared, showing completion of the ROMP reaction. In the spectrum for **P1**, the monomer peak decreased; however, exact conversion is unclear due to broad peaks of **P1** which are possibly due to existence of cis and trans forms.

4. GPC traces

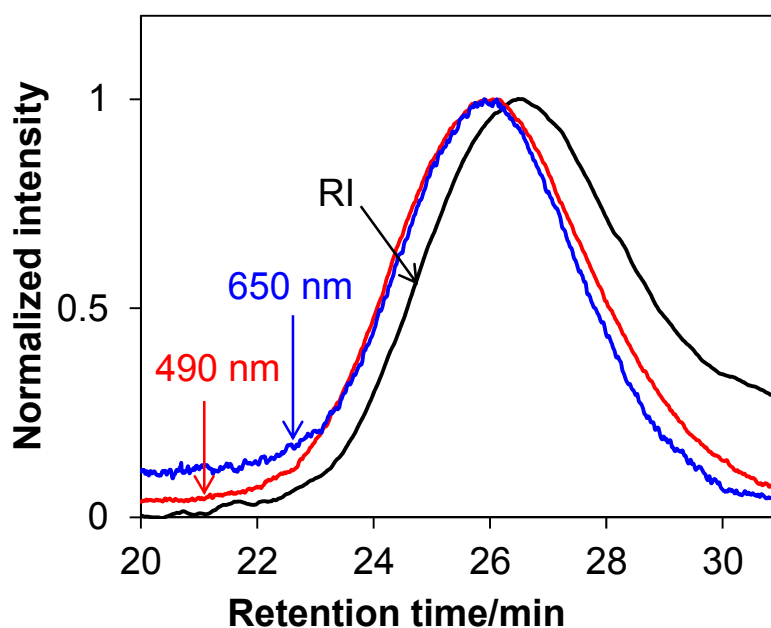


Figure S-35. GPC traces of **P3** detected using a UV-vis detector at 490 nm and 650 nm and refractive index (RI) detector (THF eluent, flow rate = 1.0 mL/min). RI signal delays 20 seconds after UV-vis signal due to sequence of the detectors. Estimated molecular weight and PDI from these signals are consistent with the values measured at 254 nm ($M_n = 35600$ and PDI = 2.10).

5. Crystallographic data

CCDC 1030718 contains the supplementary crystallographic data for **M1c**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

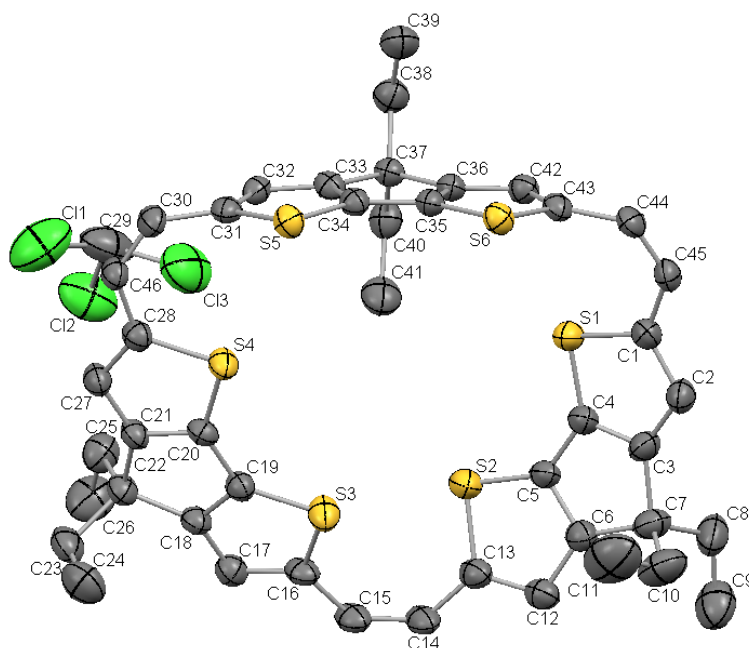


Figure S-36. X-ray crystallographic structure of **M1c**.

Table S-2. Crystal data and structure refinement for **M1c**.

Empirical formula	$\text{C}_{46}\text{H}_{43}\text{Cl}_3\text{S}_6$	
Formula weight	894.51	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	$a = 9.4165(4)$ Å	$\alpha = 90^\circ$
	$b = 19.7949(7)$ Å	$\beta = 90^\circ$
	$c = 45.5880(19)$ Å	$\gamma = 90^\circ$
Volume	8497.5(6) Å ³	
Z	8	
Density (calculated)	1.398 g cm ⁻³	
Absorption coefficient	0.544 mm ⁻¹	
$F(000)$	3728	
Crystal size	0.59 x 0.55 x 0.11 mm ³	
Theta range for data collection	0.89 to 25.09°	
Index ranges	$-9 < h < 11$, $-23 < k < 23$, $-53 < l < 32$	
Reflections collected	28795	
Independent reflections	7420 [$R(\text{int}) = 0.0794$]	
Completeness to theta = 25.09°	98.1 %	
Absorption correction	multi-scan	
Max. and min. transmission	0.9425 and 0.7395	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7420 / 0 / 496	
Goodness-of-fit on F^2	1.038	
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0590$, $wR_2 = 0.1473$	
R indices (all data)	$R_1 = 0.1246$, $wR_2 = 0.2002$	

Table S-3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **M1c**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U(eq)</i>
C(1)	-3616(6)	4992(2)	812(1)	38(1)
C(2)	-4406(6)	5204(2)	1049(1)	44(1)
C(3)	-3679(6)	5158(2)	1317(1)	42(1)
C(4)	-2317(6)	4931(2)	1278(1)	39(1)
C(5)	-1636(6)	4844(2)	1560(1)	39(1)
C(6)	-2611(6)	4991(2)	1777(1)	44(1)
C(7)	-4021(6)	5252(3)	1646(1)	51(2)
C(8)	-4222(7)	6014(3)	1718(1)	69(2)
C(9)	-4221(8)	6200(3)	2039(2)	83(2)
C(10)	-5309(7)	4851(3)	1736(2)	81(2)
C(11)	-5276(9)	4152(4)	1665(2)	115(3)
C(12)	-2096(6)	4819(2)	2062(1)	45(1)
C(13)	-731(6)	4529(2)	2046(1)	43(1)
C(14)	105(6)	4302(2)	2296(1)	49(2)
C(15)	1087(6)	3814(2)	2328(1)	47(1)
C(16)	1646(6)	3291(2)	2134(1)	41(1)
C(17)	2841(5)	2896(2)	2187(1)	42(1)
C(18)	3096(6)	2431(2)	1959(1)	38(1)
C(19)	2089(5)	2473(2)	1743(1)	37(1)
C(20)	2466(5)	2033(2)	1505(1)	35(1)
C(21)	3672(5)	1687(2)	1576(1)	37(1)
C(22)	4254(6)	1918(2)	1873(1)	41(1)
C(23)	4413(6)	1342(3)	2100(1)	55(2)
C(24)	3080(7)	979(3)	2166(2)	75(2)
C(25)	5692(6)	2257(3)	1819(1)	55(2)
C(26)	6416(7)	2564(3)	2084(2)	81(2)
C(27)	4121(6)	1278(2)	1343(1)	42(1)
C(28)	3291(5)	1331(2)	1095(1)	38(1)
C(29)	3489(5)	993(2)	816(1)	39(1)
C(30)	2995(5)	1157(2)	557(1)	41(1)
C(31)	2210(5)	1786(2)	486(1)	37(1)
C(32)	2734(5)	2428(2)	463(1)	33(1)

C(33)	1689(5)	2912(2)	397(1)	34(1)
C(34)	360(5)	2632(2)	369(1)	34(1)
C(35)	-681(5)	3171(2)	332(1)	34(1)
C(36)	29(5)	3782(2)	339(1)	32(1)
C(37)	1621(5)	3682(2)	370(1)	34(1)
C(38)	2390(6)	3935(3)	93(1)	48(2)
C(39)	1824(7)	3666(3)	-195(1)	59(2)
C(40)	2241(6)	4036(2)	640(1)	47(1)
C(41)	1642(7)	3829(3)	931(1)	64(2)
C(42)	-899(6)	4335(2)	313(1)	38(1)
C(43)	-2304(5)	4147(2)	293(1)	37(1)
C(44)	-3615(5)	4552(2)	293(1)	40(1)
C(45)	-4127(5)	4914(2)	513(1)	38(1)
C(46)	7309(8)	2722(4)	1021(2)	89(2)
S(1)	-1908(2)	4759(1)	922(1)	44(1)
S(2)	-86(2)	4527(1)	1689(1)	50(1)
S(3)	818(2)	3063(1)	1809(1)	48(1)
S(4)	1881(2)	1888(1)	1155(1)	41(1)
S(5)	388(1)	1772(1)	418(1)	40(1)
S(6)	-2472(1)	3268(1)	290(1)	39(1)
Cl(1)	7424(3)	1854(1)	985(1)	127(1)
Cl(2)	8213(2)	3010(1)	1324(1)	98(1)
Cl(3)	5534(2)	2984(1)	1021(1)	112(1)

Table S-4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$).

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	40(3)	38(2)	37(3)	4(2)	1(3)	3(2)
C(2)	40(3)	46(3)	46(4)	-2(2)	-3(3)	10(2)
C(3)	40(3)	44(3)	42(4)	-1(2)	10(3)	3(2)
C(4)	44(4)	39(2)	35(3)	4(2)	5(3)	3(2)
C(5)	49(4)	37(2)	32(3)	4(2)	7(3)	3(2)
C(6)	51(4)	41(3)	38(4)	0(2)	2(3)	4(2)
C(7)	46(4)	67(3)	40(4)	-3(3)	10(3)	-1(3)
C(8)	71(5)	74(4)	62(5)	-11(3)	-8(4)	33(3)
C(9)	92(6)	75(4)	83(6)	-21(4)	-11(5)	20(4)
C(10)	80(5)	93(5)	71(5)	-4(4)	31(4)	-5(4)
C(11)	127(8)	88(5)	130(8)	13(5)	47(6)	-21(5)
C(12)	55(4)	43(3)	38(4)	4(2)	1(3)	-2(2)
C(13)	57(4)	36(2)	36(3)	-1(2)	3(3)	2(2)
C(14)	76(4)	44(3)	28(3)	-5(2)	1(3)	11(3)
C(15)	67(4)	44(3)	29(3)	-5(2)	-3(3)	2(3)
C(16)	56(4)	42(3)	25(3)	-3(2)	-4(3)	-1(2)
C(17)	42(4)	45(3)	40(3)	2(2)	-4(3)	0(2)
C(18)	45(3)	41(2)	28(3)	1(2)	-5(3)	3(2)
C(19)	43(3)	33(2)	35(3)	1(2)	-3(3)	3(2)
C(20)	39(3)	37(2)	27(3)	2(2)	-5(3)	-3(2)
C(21)	43(3)	38(2)	31(3)	2(2)	-9(3)	5(2)
C(22)	42(3)	47(3)	35(3)	0(2)	-8(3)	5(2)
C(23)	63(4)	58(3)	44(4)	3(3)	-15(3)	13(3)
C(24)	89(5)	62(4)	73(5)	16(3)	-5(4)	-6(4)
C(25)	45(4)	63(3)	57(4)	-9(3)	-8(3)	-1(3)
C(26)	67(5)	99(5)	76(6)	-26(4)	-12(4)	-11(4)
C(27)	48(4)	36(2)	40(4)	0(2)	-7(3)	9(2)
C(28)	45(3)	32(2)	37(3)	0(2)	-3(3)	1(2)
C(29)	45(3)	33(2)	38(3)	-4(2)	-5(3)	9(2)
C(30)	50(4)	35(2)	39(3)	-6(2)	-1(3)	10(2)
C(31)	40(3)	45(3)	26(3)	-3(2)	-1(3)	4(2)
C(32)	27(3)	41(2)	30(3)	-6(2)	-1(2)	1(2)
C(33)	39(3)	32(2)	30(3)	-2(2)	-5(3)	-3(2)
C(34)	39(3)	33(2)	30(3)	-2(2)	-2(3)	0(2)

C(35)	35(3)	37(2)	28(3)	2(2)	1(3)	1(2)
C(36)	34(3)	33(2)	29(3)	2(2)	2(2)	1(2)
C(37)	37(3)	34(2)	31(3)	1(2)	0(3)	-2(2)
C(38)	48(4)	45(3)	53(4)	4(3)	6(3)	-3(2)
C(39)	61(4)	63(3)	52(4)	8(3)	13(4)	3(3)
C(40)	46(4)	41(3)	54(4)	-5(3)	-5(3)	0(2)
C(41)	71(5)	70(4)	49(4)	-10(3)	-13(4)	6(3)
C(42)	42(3)	34(2)	36(3)	1(2)	4(3)	0(2)
C(43)	43(3)	39(2)	28(3)	0(2)	-6(3)	5(2)
C(44)	39(3)	48(3)	33(3)	5(2)	-8(3)	5(2)
C(45)	33(3)	37(2)	43(4)	5(2)	-5(3)	5(2)
C(46)	77(6)	136(7)	54(5)	23(4)	-10(4)	-18(4)
S(1)	42(1)	57(1)	33(1)	3(1)	2(1)	8(1)
S(2)	60(1)	55(1)	34(1)	5(1)	3(1)	13(1)
S(3)	57(1)	47(1)	41(1)	-10(1)	-13(1)	12(1)
S(4)	48(1)	42(1)	34(1)	-6(1)	-9(1)	9(1)
S(5)	44(1)	31(1)	44(1)	1(1)	-2(1)	-3(1)
S(6)	37(1)	41(1)	40(1)	2(1)	-4(1)	-2(1)
Cl(1)	118(2)	138(2)	124(2)	-51(2)	27(2)	-12(1)
Cl(2)	89(2)	121(2)	84(2)	10(1)	-26(1)	-39(1)
Cl(3)	82(2)	165(2)	88(2)	19(1)	-23(1)	11(1)

Table S-5. Bond lengths [Å] and angles [°].

C(1)-C(2)	1.374(7)	C(16)-S(3)	1.732(5)
C(1)-C(45)	1.455(7)	C(17)-C(18)	1.410(7)
C(1)-S(1)	1.747(5)	C(17)-H(17)	0.9300
C(2)-C(3)	1.406(7)	C(18)-C(19)	1.370(7)
C(2)-H(2)	0.9300	C(18)-C(22)	1.540(7)
C(3)-C(4)	1.370(7)	C(19)-C(20)	1.436(6)
C(3)-C(7)	1.543(7)	C(19)-S(3)	1.699(5)
C(4)-C(5)	1.450(7)	C(20)-C(21)	1.364(6)
C(4)-S(1)	1.702(5)	C(20)-S(4)	1.713(5)
C(5)-C(6)	1.379(7)	C(21)-C(27)	1.400(7)
C(5)-S(2)	1.693(5)	C(21)-C(22)	1.532(7)
C(6)-C(12)	1.429(7)	C(22)-C(25)	1.531(7)
C(6)-C(7)	1.546(8)	C(22)-C(23)	1.547(7)
C(7)-C(10)	1.508(8)	C(23)-C(24)	1.476(8)
C(7)-C(8)	1.556(8)	C(23)-H(23A)	0.9700
C(8)-C(9)	1.507(9)	C(23)-H(23B)	0.9700
C(8)-H(8A)	0.9700	C(24)-H(24A)	0.9600
C(8)-H(8B)	0.9700	C(24)-H(24B)	0.9600
C(9)-H(9A)	0.9600	C(24)-H(24C)	0.9600
C(9)-H(9B)	0.9600	C(25)-C(26)	1.513(8)
C(9)-H(9C)	0.9600	C(25)-H(25A)	0.9700
C(10)-C(11)	1.421(10)	C(25)-H(25B)	0.9700
C(10)-H(10A)	0.9700	C(26)-H(26A)	0.9600
C(10)-H(10B)	0.9700	C(26)-H(26B)	0.9600
C(11)-H(11A)	0.9600	C(26)-H(26C)	0.9600
C(11)-H(11B)	0.9600	C(27)-C(28)	1.380(7)
C(11)-H(11C)	0.9600	C(27)-H(27)	0.9300
C(12)-C(13)	1.410(7)	C(28)-C(29)	1.451(7)
C(12)-H(12)	0.9300	C(28)-S(4)	1.748(5)
C(13)-C(14)	1.458(7)	C(29)-C(30)	1.306(7)
C(13)-S(2)	1.738(5)	C(29)-H(29)	0.9300
C(14)-C(15)	1.345(7)	C(30)-C(31)	1.484(6)
C(14)-H(14)	0.9300	C(30)-H(30)	0.9300
C(15)-C(16)	1.460(7)	C(31)-C(32)	1.368(6)
C(15)-H(15)	0.9300	C(31)-S(5)	1.743(5)
C(16)-C(17)	1.391(7)	C(32)-C(33)	1.406(6)

C(32)-H(32)	0.9300	C(1)-C(2)-H(2)	123.2
C(33)-C(34)	1.375(6)	C(3)-C(2)-H(2)	123.2
C(33)-C(37)	1.530(6)	C(4)-C(3)-C(2)	111.3(5)
C(34)-C(35)	1.459(6)	C(4)-C(3)-C(7)	111.2(5)
C(34)-S(5)	1.717(4)	C(2)-C(3)-C(7)	137.4(5)
C(35)-C(36)	1.384(6)	C(3)-C(4)-C(5)	109.7(5)
C(35)-S(6)	1.708(5)	C(3)-C(4)-S(1)	113.7(4)
C(36)-C(42)	1.406(6)	C(5)-C(4)-S(1)	136.3(4)
C(36)-C(37)	1.519(6)	C(6)-C(5)-C(4)	108.4(5)
C(37)-C(40)	1.528(7)	C(6)-C(5)-S(2)	113.9(4)
C(37)-C(38)	1.541(7)	C(4)-C(5)-S(2)	137.1(4)
C(38)-C(39)	1.517(8)	C(5)-C(6)-C(12)	112.1(5)
C(38)-H(38A)	0.9700	C(5)-C(6)-C(7)	111.4(5)
C(38)-H(38B)	0.9700	C(12)-C(6)-C(7)	136.4(5)
C(39)-H(39A)	0.9600	C(10)-C(7)-C(3)	111.7(5)
C(39)-H(39B)	0.9600	C(10)-C(7)-C(6)	114.1(5)
C(39)-H(39C)	0.9600	C(3)-C(7)-C(6)	99.0(4)
C(40)-C(41)	1.499(8)	C(10)-C(7)-C(8)	110.8(5)
C(40)-H(40A)	0.9700	C(3)-C(7)-C(8)	110.4(5)
C(40)-H(40B)	0.9700	C(6)-C(7)-C(8)	110.3(4)
C(41)-H(41A)	0.9600	C(9)-C(8)-C(7)	116.3(5)
C(41)-H(41B)	0.9600	C(9)-C(8)-H(8A)	108.2
C(41)-H(41C)	0.9600	C(7)-C(8)-H(8A)	108.2
C(42)-C(43)	1.377(7)	C(9)-C(8)-H(8B)	108.2
C(42)-H(42)	0.9300	C(7)-C(8)-H(8B)	108.2
C(43)-C(44)	1.472(7)	H(8A)-C(8)-H(8B)	107.4
C(43)-S(6)	1.746(5)	C(8)-C(9)-H(9A)	109.5
C(44)-C(45)	1.326(7)	C(8)-C(9)-H(9B)	109.5
C(44)-H(44)	0.9300	H(9A)-C(9)-H(9B)	109.5
C(45)-H(45)	0.9300	C(8)-C(9)-H(9C)	109.5
C(46)-Cl(2)	1.720(7)	H(9A)-C(9)-H(9C)	109.5
C(46)-Cl(1)	1.729(8)	H(9B)-C(9)-H(9C)	109.5
C(46)-Cl(3)	1.750(8)	C(11)-C(10)-C(7)	115.6(6)
C(46)-H(46)	0.9800	C(11)-C(10)-H(10A)	108.4
C(2)-C(1)-C(45)	126.0(5)	C(7)-C(10)-H(10A)	108.4
C(2)-C(1)-S(1)	110.8(4)	C(11)-C(10)-H(10B)	108.4
C(45)-C(1)-S(1)	123.0(4)	C(7)-C(10)-H(10B)	108.4
C(1)-C(2)-C(3)	113.5(5)	H(10A)-C(10)-H(10B)	107.4

C(10)-C(11)-H(11A)	109.5	C(18)-C(22)-C(21)	99.7(4)
C(10)-C(11)-H(11B)	109.5	C(25)-C(22)-C(23)	110.2(4)
H(11A)-C(11)-H(11B)	109.5	C(18)-C(22)-C(23)	112.6(4)
C(10)-C(11)-H(11C)	109.5	C(21)-C(22)-C(23)	114.0(4)
H(11A)-C(11)-H(11C)	109.5	C(24)-C(23)-C(22)	114.2(5)
H(11B)-C(11)-H(11C)	109.5	C(24)-C(23)-H(23A)	108.7
C(13)-C(12)-C(6)	111.0(5)	C(22)-C(23)-H(23A)	108.7
C(13)-C(12)-H(12)	124.5	C(24)-C(23)-H(23B)	108.7
C(6)-C(12)-H(12)	124.5	C(22)-C(23)-H(23B)	108.7
C(12)-C(13)-C(14)	125.2(5)	H(23A)-C(23)-H(23B)	107.6
C(12)-C(13)-S(2)	111.7(4)	C(23)-C(24)-H(24A)	109.5
C(14)-C(13)-S(2)	123.0(4)	C(23)-C(24)-H(24B)	109.5
C(15)-C(14)-C(13)	132.6(5)	H(24A)-C(24)-H(24B)	109.5
C(15)-C(14)-H(14)	113.7	C(23)-C(24)-H(24C)	109.5
C(13)-C(14)-H(14)	113.7	H(24A)-C(24)-H(24C)	109.5
C(14)-C(15)-C(16)	133.8(5)	H(24B)-C(24)-H(24C)	109.5
C(14)-C(15)-H(15)	113.1	C(26)-C(25)-C(22)	116.5(5)
C(16)-C(15)-H(15)	113.1	C(26)-C(25)-H(25A)	108.2
C(17)-C(16)-C(15)	125.7(5)	C(22)-C(25)-H(25A)	108.2
C(17)-C(16)-S(3)	111.5(4)	C(26)-C(25)-H(25B)	108.2
C(15)-C(16)-S(3)	122.7(4)	C(22)-C(25)-H(25B)	108.2
C(16)-C(17)-C(18)	112.1(5)	H(25A)-C(25)-H(25B)	107.3
C(16)-C(17)-H(17)	124.0	C(25)-C(26)-H(26A)	109.5
C(18)-C(17)-H(17)	124.0	C(25)-C(26)-H(26B)	109.5
C(19)-C(18)-C(17)	111.8(4)	H(26A)-C(26)-H(26B)	109.5
C(19)-C(18)-C(22)	110.4(4)	C(25)-C(26)-H(26C)	109.5
C(17)-C(18)-C(22)	137.6(5)	H(26A)-C(26)-H(26C)	109.5
C(18)-C(19)-C(20)	109.5(4)	H(26B)-C(26)-H(26C)	109.5
C(18)-C(19)-S(3)	113.7(4)	C(28)-C(27)-C(21)	114.0(5)
C(20)-C(19)-S(3)	136.5(4)	C(28)-C(27)-H(27)	123.0
C(21)-C(20)-C(19)	109.4(4)	C(21)-C(27)-H(27)	123.0
C(21)-C(20)-S(4)	113.9(4)	C(27)-C(28)-C(29)	127.8(5)
C(19)-C(20)-S(4)	136.5(4)	C(27)-C(28)-S(4)	110.5(4)
C(20)-C(21)-C(27)	111.3(5)	C(29)-C(28)-S(4)	121.8(4)
C(20)-C(21)-C(22)	110.9(4)	C(30)-C(29)-C(28)	129.1(5)
C(27)-C(21)-C(22)	137.3(5)	C(30)-C(29)-H(29)	115.4
C(25)-C(22)-C(18)	112.2(4)	C(28)-C(29)-H(29)	115.4
C(25)-C(22)-C(21)	107.8(4)	C(29)-C(30)-C(31)	125.6(5)

C(29)-C(30)-H(30)	117.2	H(39B)-C(39)-H(39C)	109.5
C(31)-C(30)-H(30)	117.2	C(41)-C(40)-C(37)	116.2(4)
C(32)-C(31)-C(30)	128.1(4)	C(41)-C(40)-H(40A)	108.2
C(32)-C(31)-S(5)	110.8(3)	C(37)-C(40)-H(40A)	108.2
C(30)-C(31)-S(5)	121.1(4)	C(41)-C(40)-H(40B)	108.2
C(31)-C(32)-C(33)	113.4(4)	C(37)-C(40)-H(40B)	108.2
C(31)-C(32)-H(32)	123.3	H(40A)-C(40)-H(40B)	107.4
C(33)-C(32)-H(32)	123.3	C(40)-C(41)-H(41A)	109.5
C(34)-C(33)-C(32)	112.4(4)	C(40)-C(41)-H(41B)	109.5
C(34)-C(33)-C(37)	110.9(4)	H(41A)-C(41)-H(41B)	109.5
C(32)-C(33)-C(37)	136.5(4)	C(40)-C(41)-H(41C)	109.5
C(33)-C(34)-C(35)	109.1(4)	H(41A)-C(41)-H(41C)	109.5
C(33)-C(34)-S(5)	112.0(3)	H(41B)-C(41)-H(41C)	109.5
C(35)-C(34)-S(5)	138.6(4)	C(43)-C(42)-C(36)	113.1(4)
C(36)-C(35)-C(34)	108.2(4)	C(43)-C(42)-H(42)	123.5
C(36)-C(35)-S(6)	112.4(3)	C(36)-C(42)-H(42)	123.5
C(34)-C(35)-S(6)	139.4(4)	C(42)-C(43)-C(44)	131.1(4)
C(35)-C(36)-C(42)	112.3(4)	C(42)-C(43)-S(6)	111.0(3)
C(35)-C(36)-C(37)	111.4(4)	C(44)-C(43)-S(6)	117.8(4)
C(42)-C(36)-C(37)	136.4(4)	C(45)-C(44)-C(43)	126.9(5)
C(36)-C(37)-C(33)	100.3(4)	C(45)-C(44)-H(44)	116.6
C(36)-C(37)-C(40)	113.1(4)	C(43)-C(44)-H(44)	116.6
C(33)-C(37)-C(40)	112.1(4)	C(44)-C(45)-C(1)	130.4(5)
C(36)-C(37)-C(38)	110.2(4)	C(44)-C(45)-H(45)	114.8
C(33)-C(37)-C(38)	111.7(4)	C(1)-C(45)-H(45)	114.8
C(40)-C(37)-C(38)	109.3(4)	Cl(2)-C(46)-Cl(1)	112.0(4)
C(39)-C(38)-C(37)	115.6(4)	Cl(2)-C(46)-Cl(3)	112.0(5)
C(39)-C(38)-H(38A)	108.4	Cl(1)-C(46)-Cl(3)	110.8(4)
C(37)-C(38)-H(38A)	108.4	Cl(2)-C(46)-H(46)	107.3
C(39)-C(38)-H(38B)	108.4	Cl(1)-C(46)-H(46)	107.3
C(37)-C(38)-H(38B)	108.4	Cl(3)-C(46)-H(46)	107.3
H(38A)-C(38)-H(38B)	107.4	C(4)-S(1)-C(1)	90.6(3)
C(38)-C(39)-H(39A)	109.5	C(5)-S(2)-C(13)	91.2(3)
C(38)-C(39)-H(39B)	109.5	C(19)-S(3)-C(16)	90.8(2)
H(39A)-C(39)-H(39B)	109.5	C(20)-S(4)-C(28)	90.4(2)
C(38)-C(39)-H(39C)	109.5	C(34)-S(5)-C(31)	91.3(2)
H(39A)-C(39)-H(39C)	109.5	C(35)-S(6)-C(43)	91.3(2)