Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Light-Induced Self-Assembly of Dithienylethene Bolaamphiphiles in water

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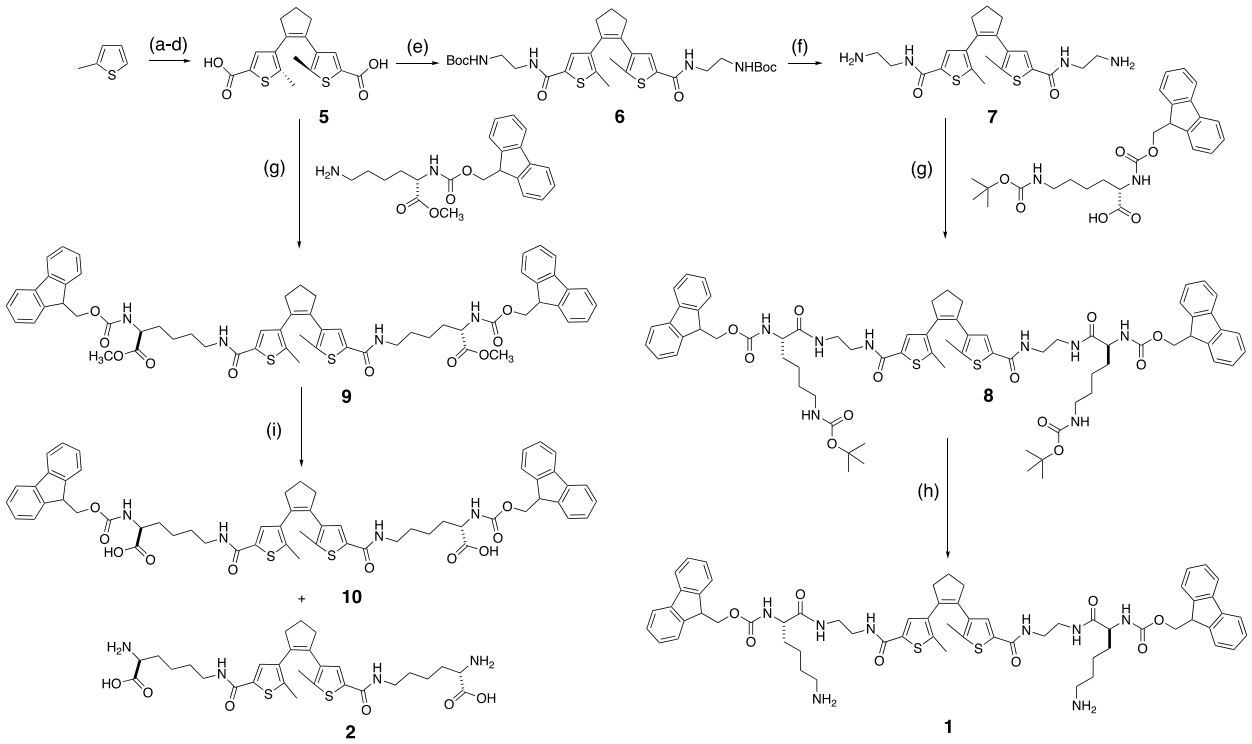
‡ Both authors contributed equally to this work.

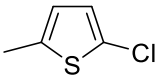
Keywords: bolaamphiphile, nanostructures, self-assembly, photoresponsive, dithienylethene



Scheme S1. Synthesis of monomers **1** and **2.** (a) *N*-chlorosuccinimide, benzene/acetic acid (1:1), reflux, 70%; (b) glutaryl chloride, $AlCl_3$, CH_3NO_2, 54%; (c) $TiCl_4$-Zn, pyridine-THF, reflux, 72%; (d) i. *n*-C_4H_9Li, THF; ii. CO_2, 85%; (e) *tert*-butyl(2-aminoethyl)carbamate, HOBT, HBTU, DIPEA, CH_3CN, 47%; (f) CF_3CO_2H, CH_2Cl_2, 99%; (g) Fmoc-Lys(Boc)-OH or Fmoc-Lys-OCH_3; HOBT, HBTU, DIPEA, CH_3CN,59% (**8**), 90% (**9**); (h) CF_3CO_2H, CH_2Cl_2, 89%; (i) $(CH_3)_3SnOH$, 1M $CaCl_2$ in 30% water/*i*-PrOH. 35% (**2**); 26% (**10**).

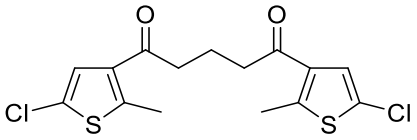
1. Experimental procedures

2-chloro-5-methyl thiophene



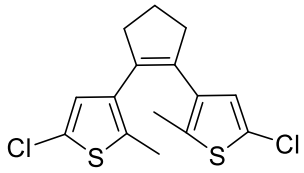
This compound was prepared as described in literature.[1] 2-Methyl thiophene (207 mmol, 20 mL, 1 eq) and *N*-chlorosuccinimide (227 mmol, 30 g, 1.1 eq) were added to a rigorously stirred mixture of benzene (125 mL) and glacial acetic acid (125 mL). This mixture was heated at reflux for 7 h, continuing to stir vigorously. The mixture was cooled to room temperature, then poured into ice-water (300 mL). Extracted with DCM (3 × 100 mL). The organic layers were combined, dried over Na_2SO_4, filtered, then purified by distillation to isolate a slightly brown liquid (143 mmol, 70%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.58 (d, =CH, *J* = 3.6 Hz, 1H), 6.44 – 6.39 (m, =CH, 1H), 2.30 (s, CH_3, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.4, 126.4, 125.7, 124.3, 15.2 ppm. Data is in accordance with literature.[1]

1,5-Bis(5-chloro-2-methylthiophen-3-yl)pentane-1,5-dione (3)



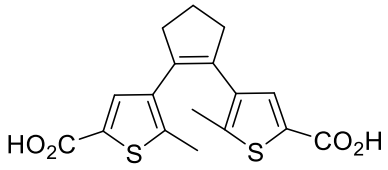
This compound was prepared as described in literature.[1] 2-chloro-5-methyl thiophene (30 mmol, 2.1 eq) and glutaryl dichloride (15 mmol, 1.8 mL, 1 eq) were added to dry $MeNO_2$ (120 mL) under N_2, then cooled to 0°C. $AlCl_3$ (30 mmol, 3.8 g, 2 eq) was carefully added to the mixture, and then it was stirred at room temperature for 4 h. The reaction mixture was poured into ice-water (100 mL). Crude product was extracted with CH_2Cl_2 (3 × 75 mL), dried over Na_2SO_4, filtered, and then concentrated in vacuo. Crude product was isolated with flash chromatography (10% EtOAc, Hexanes) to obtain a white solid of **3** (2.79 g, 7.7 mmol, 54%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.19 (s, =CH, 1H), 2.86 (t, *J* = 7.5 Hz, CH_2, 4H), 2.67 (s, CH_3, 6H), 2.01 (quint, *J* = 7.5 Hz, CH_2, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 194.7, 147.6, 134.7, 126.7, 125.2, 40.4, 18.1, 16.0 ppm. Data is in accordance with literature.[1]

1,2-bis(5-chloro-2-methylthiophen-3-yl)cyclopent-1-ene (4)



This compound was prepared as described in literature[1] with modification.[2] With all glassware flame-dried and in N_2 environment, $TiCl_4$ (4.2 mL, 4.2 mmol, 1M/toluene, 1.5 eq) was added carefully to 0°C freshly-distilled THF (20 mL) whereby a suspension formed. Zinc powder (0.55 g, 8.4 mmol, 3 eq) and dry pyridine (0.11 mL, 1.4 mmol, 0.5 eq) were added and the mixture brought to reflux (80°C) for 1 h. A solution of **3** (1.0 g, 2.8 mmol, 1 eq) in dry THF (3 mL) was added dropwise to the mixture and heated at reflux (80°C) for 5 h. The mixture was cooled to rt, added saturated K_2CO_3 solution (several drops) to quench, and filtered reaction over a celite cake while washing with EtOAc. Organic solvent was dried with Na_2SO_4, concentrated in vacuo, and crude product was purified with flash chromatographed (hexanes, 100%) to isolate a white crystalline solid (0.66 g, 2.0 mmol, 72% yield) **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.57 (s, =CH, 2H), 2.72 (t, *J* = 7.5 Hz, CH_2, 4H), 2.02 (quint, *J* = 7.5 Hz, CH_2, 2H), 1.89 (s, CH_3, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 135.8, 134.4, 133.3, 126.7, 125.2, 38.2, 22.8, 14.2 ppm. Data is in accordance with literature.[1]

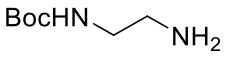
4,4'-(Cyclopent-1-ene-1,2-diyl)bis(5-methylthiophene-2-carboxylic acid) (5)



This compound was prepared as described in literature.[1] In a round-bottomed flask equipped with a stirring bar, **4** (2.0 g, 6.0 mmol, 1.0 equiv) was dissolved in dry THF (60 mL). Then *n*-BuLi (6.1 mL, 2.5 M in hexanes, 2.5 equiv) was added dropwise and the black mixture was stirred for 1 h. Solid CO_2 (dry ice, excess) was added, after which a brown suspension was formed which was stirred for 30 min. Water (60

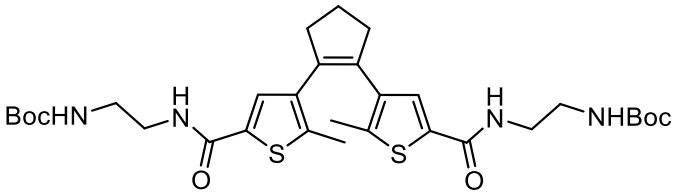
mL) was added slowly and the aqueous layer was washed with Et_2O (60 mL) and subsequently acidified to pH = 1 with HCl (1M). After extraction with CH_2Cl_2 (3 × 60 mL), the combined organic layers were dried over Na_2SO_4, filtered and concentrated to yield the title compound as a brown solid (1.8 g, 85%). The product was used without further purification. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 12.94 (bs, COOH, 2H), 7.42 (s, =CH, 2H), 2.78 (t, *J* = 7.5 Hz, CH_2, 4H) 2.02 (quint, *J* = 7.5 Hz, CH_2, 2H), 1.93 (s, CH_3, 6H) ppm. **^{13}C NMR** (100 MHz, DMSO-d_6): δ 162.6, 141.7, 136.4, 134.3, 133.8, 130.4, 37.8, 22.3, 14.3 ppm. Data is in accordance with literature.[1]

tert-Butyl (2-aminoethyl)carbamate



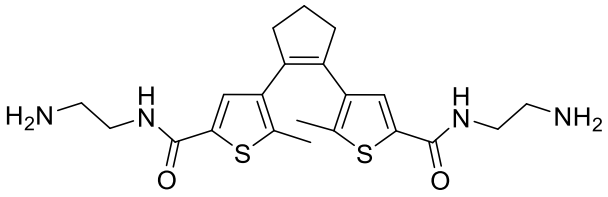
tert-Butyl (2-aminoethyl)carbamate was prepared as described in literature.[3] A solution of di-*tert*-butyl dicarbonate (5.0 g, 23 mmol) in 1,4-dioxane (7 mL) was added dropwise over 4 h min to a solution of ethane-1,2-diamine (4.6 mL, 69 mmol) in 1,4-dioxane (30 mL). A white precipitate formed slowly as the reaction was stirred at rt. After 19 h, the mixture was quenched with K_2CO_3 solution, and then extracted with DCM (3 × 100 mL). The combined organic layers were washed once with $NaHCO_3$ (saturated), dried with Na_2SO_4, then concentrated to yield *tert*-butyl (2-aminoethyl)carbamate as a white solid (3.20 g, 87%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 4.93 (bs, NH, 1H), 3.17 (q, *J* = 5.9 Hz, CH_2, 2H), 2.80 (t, *J* = 5.9 Hz, CH_2, 2H), 1.45 (s, CH_3, 6H), 1.22 (bs, NH_2, 2H) ppm. **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 156.2, 79.2, 43.5, 41.9, 28.4 ppm. Data is in accordance with literature.[3]

Di-*t*-butyl (((4,4'-(cyclopent-1-ene-1,2-diyl)bis(5-methylthiophene-4,2-diyl-2-carbonyl))bis(azanediyl))bis(ethane-2,1-diyl))dicarbamate (6)



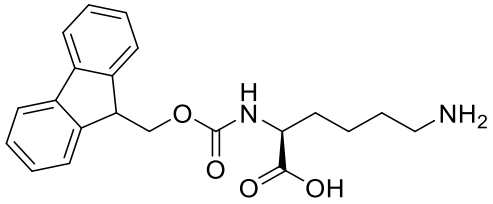
A solution of *tert*-butyl (2-aminoethyl)carbamate (290 mg, 1.80 mmol) in dry MeCN (5 mL) was added to a solution of HOBt (231 mg, 1.70 mmol), HBTU (653 mg, 1.70 mmol), DTE-diacid (**5**) (300 mg, 0.90 mmol), and DIEA (0.60 mL, 3.40 mmol) in dry MeCN (15 mL) under N_2 atmosphere. The reaction was stirred at room temperature for 12 h and then concentrated in vacuo. The residue was dissolved in EtOAc (100 mL) and washed with $NaHCO_3$ (saturated) (2 × 30 mL), citric acid (10%; 2 × 30 mL). The organic solution was dried (Na_2SO_4), filtered, and concentrated in vacuo. The residue was purified by silica gel chromatography (methanol: DCM; 3:97) to give the title compound as a pink solid (258 mg, 47% yield). M.p.: 123−124 °C. (acetone/hexane) **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 7.14 (s, =CH, 2H), 7.02 (bs, NH, 2H), 5.20 (bs, NH, 2H), 3.34 (dd, *J* = 10.9, 5.4 Hz, CH_2, 4H), 3.22 (dd, *J* = 10.9, 5.4 Hz, CH_2, 4H), 2.66 (t, *J* = 7.5 Hz, CH_2, 4H), 1.99 – 1.90 (quint, *J* = 7.5 Hz, CH_2, 2H), 1.83 (s, CH_3, 6H), 1.33 (s, CH_3, 18H) ppm. **^{13}C NMR** (100 MHz, CD_2Cl_2): δ 162.8, 157.7, 140.5, 136.8, 135.2, 134.9, 129.6, 79.9, 41.9, 40.5, 38.8, 28.5, 23.3, 14.8 ppm. **ESI-MS** calcd. for $C_{31}H_{44}N_4NaO_6S_2$: $[M+Na]^+$: 655.2600, found: 655.2610.

4,4'-(Cyclopent-1-ene-1,2-diyl)bis(*N*-(2-aminoethyl)-5-methylthiophene-2-carboxamide) (7)



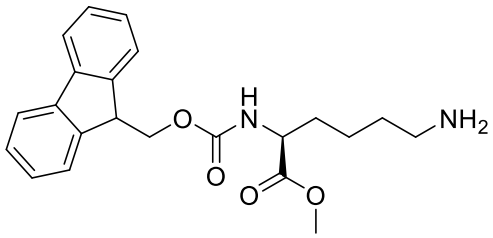
TFA (4 mL) was added to a solution of **7** (324 mg, 0.5 mmol) at room temperature in CH_2Cl_2 (4 mL). The reaction mixture was stirred at rt for 2 h. TFA was removed with addition of diethyl ether (3 × 25 mL) to the residue (red oil) followed by solvent removal in vacuo. The final product was obtained as a light red oil (220 mg, 99% yield). **^{1}H NMR** (250 MHz, CD_3OD): δ 7.39 (s, =CH, 2H), 3.50 (t, *J* = 5.9 Hz, CH_2, 4H), 3.04 (t, *J* = 5.9 Hz, CH_2, 4H), 2.72 (t, *J* = 7.4 Hz, CH_2, 4H), 2.07 – 1.93 (m, CH_2, 2H), 1.83 (s, CH_3, 6H) ppm. **^{13}C NMR** (100 MHz, DMSO-d_6): δ 162.6, 140.2, 137.1, 136.1, 135.1, 130.3, 80.1, 38.0, 31.7, 27.8, 15.2 ppm. **ESI-MS** calcd. for $C_{21}H_{29}N_4O_2S_2$: $[M+H]^+$: 433.1732, found: 433.1754.

((9*H*-Fluoren-9-yl)methoxy)carbonyl)-*L*-lysine (Fmoc-Lys-OH)



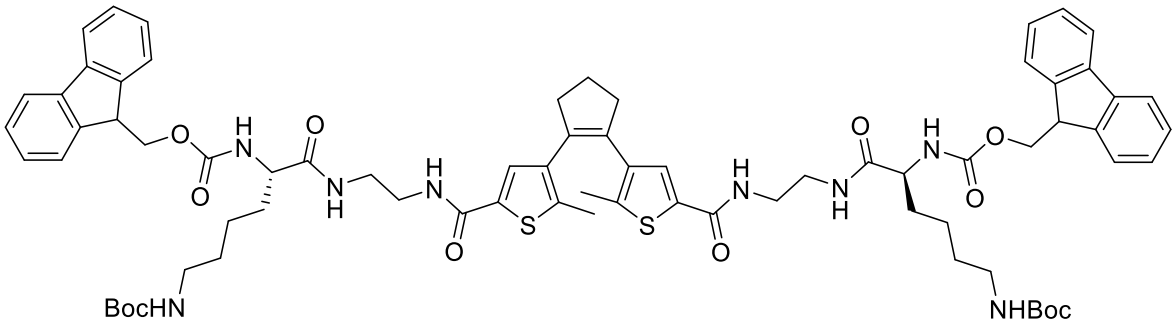
This compound was prepared as described in literature.[3] Fmoc-Lys(Boc)-OH (1.0 g, 2.10 mmol) was dissolved in a solution of TFA/CH_2Cl_2 (1:1, 50 mL) and stirred for 2 h at room temperature. Following evaporation and diethyl ether extraction of the residue, Fmoc-Lys-OH was obtained as a white powder (0.75 g, 95 % yield). **^{1}H-NMR** (400 MHz, DMSO-d_6): δ 7.99 (d, *J* = 7.5 Hz, =CH, 2H), 7.76-7.71 (m, =CH, 2H), 7.62 (d, *J* = 8.1 Hz, NH, 1H), 7.42 (t, *J* = 7.5 Hz, =CH, 2H), 7.33 (t, *J* = 7.5 Hz, =CH, 2H), 4.34-4.26 (m, CH_2, 2H), 4.23 (t, *J* = 6.5 Hz, CH, 1H), 3.97-3.91 (m, CH, 1H), 2.78 (dd, *J* = 12.6, 6.5 Hz, CH_2, 2H), 1.76-1.72 (m, CH_2, 2H), 1.64-1.51 (m, NH_2, CH_2, 4H), 1.39-1.35 (m, CH_2, 2H); **^{13}C-NMR** (100 MHz, DMSO-d_6): δ 173.8, 156.2, 143.8, 140.7, 127.6, 127.0, 125.2, 120.1, 65.6, 53.6, 46.6, 38.6, 30.1, 26.5, 22.5. Data is in accordance with literature.[3]

Methyl (((9*H*-fluoren-9-yl)methoxy)carbonyl)-*L*-lysinate (Fmoc-Lys-OMe)



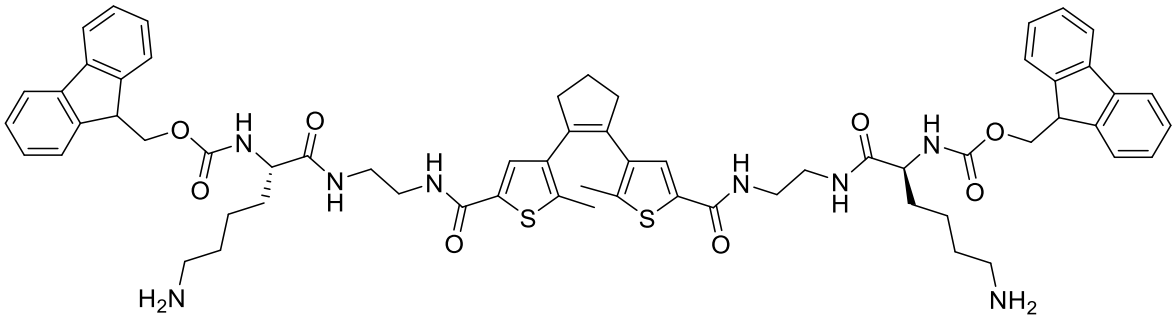
This compound was prepared as described in literature.[3] Thionyl chloride (0.5 mL, 5.1 mmol) was slowly added to a suspension of Fmoc-Lys-OH (500 mg, 1.4 mmol) in dry methanol (20 mL). The resulting clear solution was kept at room temperature for 2 h and then evaporated to dryness. Upon re-dissolving in methanol (10 mL) and dropwise addition into diethyl ether, the ester precipitated. A white solid (503 mg, 97 %) was obtained. Data is in accordance with literature.[3] **^{1}H NMR** (400 MHz, DMSO-d_6): δ 7.91-7.87 (m, =CH, NH, 3H), 7.78-7.70 (m, =CH, 2H), 7.43 (t, *J* = 7.5 Hz, =CH, 2H), 7.34 (t, *J* = 7.5 Hz, =CH, 2H), 4.38 – 4.26 (m, CH_2, 2H), 4.23 (t, *J* = 6.8 Hz, CH, 1H), 4.05 – 3.97 (m, CH, 1H), 3.63 (s, CH_3, 3H), 2.75 (bs, NH_2, 2H), 1.76 – 1.48 (m, CH_2, 6H), 1.43 – 1.27 (m, CH_2, 2H); **^{13}C-NMR** (100 MHz, DMSO-d_6): 172.8, 156.1, 143.8, 140.7, 127.6, 127.0, 125.2, 120.1, 66.6, 53.6, 51.9, 46.6, 38.4, 30.0, 26.4, 22.4.

Fmoc-*N*-BocLys-DTE-*N*-BocLys-Fmoc (8)

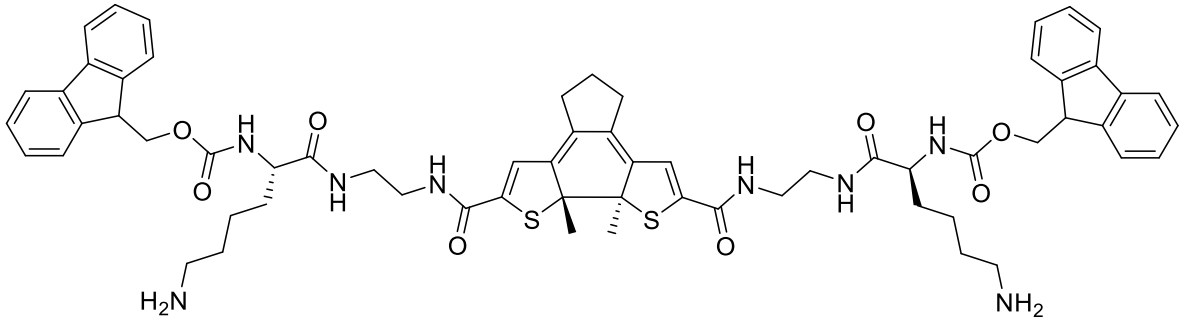


A solution of **7** (209 mg, 0.50 mmol) in dry THF (5 mL) was added to a solution of HOBt (131 mg, 1.0 mmol), HBTU (379 mg, 1.0 mmol), Fmoc-Lys(Boc)-OH (453 mg, 1.0 mmol), and DIEA (0.60 mL, 3.40 mmol) in dry MeCN under and N_2 atmosphere. The reaction was stirred at room temperature for 12 h then concentrated in vacuo. The residue was dissolved in EtOAc (100 mL) and washed with $NaHCO_3$ (saturated) solution (2 × 30 mL), citric acid (10 %; 2 × 30 mL). The organic solution was dried (Na_2SO_4), filtered, and concentrated in vacuo. The residue was purified by silica gel chromatography (3% MeOH in DCM) to give **8** as a pink solid (379 mg, 59 % yield). M.p.: 156−157 °C. (acetone/hexane). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 7.3 Hz, =CH, 4H), 7.56 (d, *J* = 7.3 Hz, =CH, 4H), 7.36 (t, *J* = 7.4 Hz, =CH, 4H), 7.30 – 7.23 (m, =CH, 6H), 7.17 (bs, NH, 2H), 6.09 (bs, NH, 2H), 4.87 (bs, NH, 2H), 4.41 – 4.07 (m, NH, CH, CH_2, 8H), 3.56 – 3.35 (m, CH_2, 8H), 3.03 – 3.02 (m, CH_2, 4H), 2.64 – 2.61 (m, CH_2, 4H), 1.96 (s, CH_3, 6H), 1.94 – 1.84 (m, CH_2, 2H), 1.83 – 1.50 (m, CH, CH_2, 8H), 1.41 (s, CH_3, 18H), 1.37 – 1.30 (m, CH_2, 4H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 173.4, 162.7, 156.5, 156.3, 143.8, 141.2, 140.3, 136.3, 135.0, 134.0, 130.0, 127.7, 127.1, 125.1, 120.0, 79.2, 67.1, 55.2, 54.0, 47.1, 42.2, 37.9, 28.4, 22.9, 22.7, 18.5, 17.4, 14.6, 11.9 ppm. **ESI-MS** calcd. for $C_{73}H_{88}N_8NaO_{12}S_2$: $[M+Na]^+$: 1355.5861, found: 1355.5884.

Fmoc-Lys-DTE-Lys-Fmoc (1)

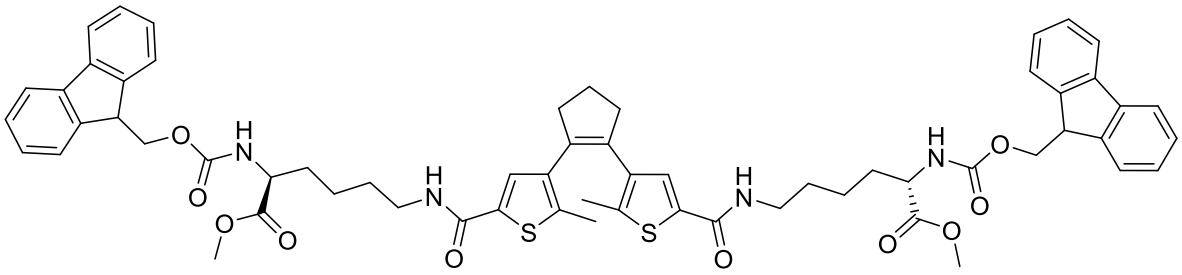


To a solution of **8** (330 mg, 0.3 mmol) in CH_2Cl_2 (10 mL), was added TFA (10 mL) at rt. The reaction mixture was stirred at rt for 2 h. The solvent was removed under reduced pressure and cold diethyl ether (25 mL) was added to the red oil. A red precipitate formed and was collected by centrifugation. The crude sediment was dissolved in water and dried by lyophilization, then further purified by reversed-phase HPLC to give **1** as light red solid (249 mg, 89 %). M.p.: 138−140 °C. (methanol). **^{1}H NMR** (500 MHz, CD_3OD): δ 7.80 (d, *J* = 7.5 Hz, =CH, 4H), 7.67 – 7.64 (m, =CH, 4H), 7.43 (s, =CH, 2H), 7.40 (t, *J* = 7.5 Hz, =CH, 4H), 7.31 (t, *J* = 7.5 Hz, =CH, 4H), 4.45 – 4.33 (m, CH_2, 4H), 4.21 (t, *J* = 6.6 Hz, CH, 2H), 4.08 – 4.00 (m, CH, 2H), 3.55 – 3.37 (m, CH_2, 8H), 2.93 (t, *J* = 6.6 Hz, CH_2, 4H), 2.72 – 2.69 (m, CH_2, 4H), 2.04 – 1.92 (m, CH_2, 2H), 1.84 (s, CH_3, 6H), 1.73 – 1.62 (m, CH_2, 8H), 1.52 – 1.37 (m, CH_2, 4H) ppm. **^{13}C NMR** (100 MHz, CD_3OD): δ 175.3, 164.7, 145.4, 145.3, 142.8, 141.8, 138.0, 136.3, 135.9, 131.1, 129.0, 128.3, 126.3, 121.1, 68.1, 56.6, 48.6, 40.6, 40.6, 40.4, 39.6, 32.5, 28.3, 24.0, 23.9, 14.9 ppm. **ESI-MS** calcd. for $C_{63}H_{73}N_8O_8S_2$: $[M+H]^+$: 1133.4993, found: 1133.4987.



^{1}H NMR (400 MHz, CD_3OD): δ 7.82 (d, *J* = 7.5 Hz, =CH, 4H), 7.69 (t, *J* = 7.5, =CH, 4H), 7.43-7.40 (m, =CH, 4H), 7.33 (dd, *J* = 4.5, 1.0 Hz, =CH, 4H), 6.64 (d, *J* = 2.8, =CH, 2H), 4.48-4.37 (m, CH_2, 4H), 4.25 (t, *J* = 6.7, CH, 2H), 4.06 – 4.03 (m, CH, 2H), 3.52 – 3.36 (m, CH_2, 8H), 2.95 (t, *J* = 6.8, CH_2, 4H), 2.35 (t, *J* = 6.9, CH_2, 4H), 1.91-1.63 (m, CH_2, CH_3, 16H), 1.52-1.39 (m, CH_2, 4H) ppm. **^{13}C NMR** (100 MHz, CD_3OD): δ 173.8, 163.9, 163.2, 157.1, 143.9, 143.8, 141.8, 138.9, 127.5, 126.8, 124.8, 119.6, 66.6, 65.6, 55.1 (2C), 39.1, 31.0 (2C), 29.2, 26.7, 26.3, 24.6, 22.5, 13.3 ppm.

Fmoc-Lys-OMe-DTE-OMe-Lys_Fmoc (9)



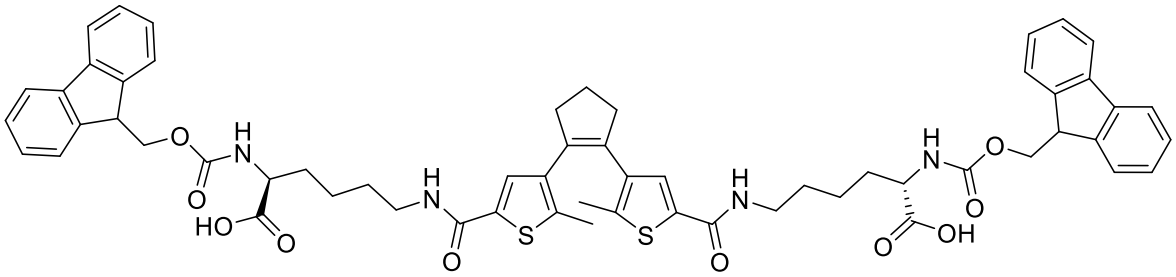
A solution of Fmoc-Lys-OMe (439 mg, 1.20 mmol) in dry DMF (3 mL) was added to a solution of HOBt (155 mg, 1.20 mmol), HBTU (435 mg, 1.20 mmol), DTE-diacid (200 mg, 0.60 mmol), and DIEA (0.40 mL, 2.30 mmol) in dry THF (15 mL) under N_2 atmosphere. The reaction was stirred at room temperature overnight and then concentrated in vacuo. The residue was dissolved in EtOAc (100 mL) and washed with $NaHCO_3$ (saturated) solution (2 × 30 mL), citric acid (10 %; 2 × 30 mL). The organic solution was dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by silica gel chromatography (Acetone/hexane, 3:7) to give title compound as a light pink solid (555 mg, 90 % yield). M.p.: 137−138 °C. (acetone/hexane)

^{1}H NMR (400 MHz, Acetone-d_6): δ 7.86 (d, *J* = 7.5 Hz, =CH, 4H), 7.71 (d, *J* = 7.5 Hz, =CH, 4H), 7.62 (t, *J* = 5.6 Hz, NH, 2H), 7.46 (s, =CH, 2H), 7.41 (t, *J* = 7.5 Hz, =CH, 4H), 7.35 – 7.29 (m, =CH, 4H), 6.88 (d, *J* = 8.2 Hz, NH, 2H), 4.39 – 4.19 (m, CH, CH_2, 6H), 3.68 (s, CH_3, 6H), 3.38 – 3.33 (m, CH_2, 4H), 2.73 (t, *J* = 7.4 Hz, 4H), 2.01 – 1.94 (m, CH_2, 2H), 1.89 (s, CH_3, 6H), 1.86 – 1.71 (m, CH, CH_2, 6H), 1.67 – 1.41 (m, CH_2, 8H) **^{13}C NMR** (100 MHz, Acetone-d_6): δ 173.7, 162.2, 157.1, 145.1, 142.1, 140.1, 137.2, 137.0, 135.5, 129.4, 128.6, 128.0, 126.2, 120.8, 67.2, 55.0, 52.3, 48.0, 39.9, 39.7, 32.0, 30.0, 23.9, 23.5, 14.7. **ESI-MS** calcd. for $C_{61}H_{64}N_4NaO_{10}S_2$: $[M+Na]^+$: 1099.3962, found: 1099.3956.

Fmoc-Lys-OMe-DTE-OH-Lys_Fmoc (10) and **Fmoc-Lys-DTE-Lys** and **Lys-DTE-Lys (2)**

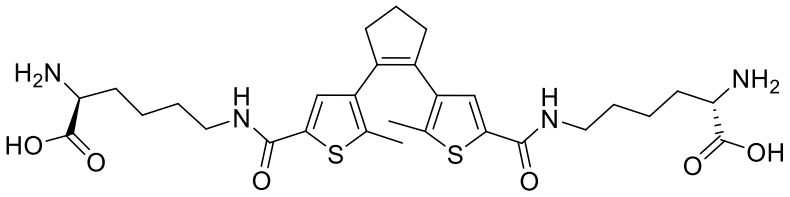
Trimethyltin chloride (370 mg, 1.9 mmol) was dissolved in MeOH (5 mL) treated with KOH (104 mg, 1.9 mmol) was added to the solution. Then, the mixture was stirred for 1 h at ambient temperature at which time potassium chloride precipitated as a white solid. The reaction mixture was subsequently filtered and the filtrate containing $(CH_3)_3SnOH$ was evaporated under vacuum. The solid $(CH_3)_3SnOH$ was added to a mixture of $CaCl_2$ in water and *i*-PrOH (20 mL) and. Fmoc-Lys-OMe-DTE-OMe-Lys-Fmoc (**9**; 100 mg, 0.1 mmol) was added to the $(CH_3)_3SnOH$ solution was stirred for 12 h at 100°C. The solvent was evaporated in vacuo and the crude residue was dissolved in water: CH_3CN (1:1) (40 mL) and purified by reversed-phase HPLC on preparative Varian Dynamax C18 column eluting with a linear gradient of acetonitrile/water with 0.1 % TFA (20/80 to 90/10 over 7 h) producing three products were obtained: Lys-DTE-Lys (**2**) (20 mg, 35 %), Fmoc-Lys-DTE-Lys (10 mg, 13 %) and Fmoc-Lys-DTE-Lys-Fmoc (**10**) (25 mg, 26 %) were obtained as white solids. M.p. for **10**: 135−136 °C. (acetone/hexane), M.p. for **2**: 125−126 °C. (acetone/hexane).

Fmoc-Lys-DTE-Lys-Fmoc (10)



^{1}H NMR (400 MHz, $CDCl_3/CD_3OD$ (1/1)): δ 7.96 – 7.92 (m, =CH, 4H), 7.81 – 7.74 (m, =CH, NH, 8H), 7.59 – 7.52 (m, =CH, 4H), 7.50 – 7.45 (m, =CH, 4H), 4.62 – 4.35 (m, CH, CH_2, 10H), 3.00 – 2.87 (m, CH_2, 4H), 2.28 – 2.15 (m, CH_2, 4H), 2.06 (s, CH_3, 6H), 1.99 – 1.36 (m, CH_2, 12H); **^{13}C-NMR** (100 MHz, $CDCl_3/CD_3OD$ (1/1)): δ 162.5, 156.6, 143.4, 143.3, 140.8, 139.7, 136.0, 134.2, 134.0, 129.0, 127.0, 126.5, 124.5, 119.3, 66.4, 53.3, 46.6, 38.9, 37.9, 31.0, 28.4, 22.4, 22.2, 13.7. **ESI-MS** calcd. for $C_{59}H_{61}N_4O_{10}S_2$: $[M+H]^+$: 1049.3829, found: 1049.3824.

Lys-DTE-Lys (2)



^{1}H NMR (400 MHz, D_2O/CD_3OD (1/1)): δ 7.40 (s, =CH, 2H), 4.01 – 3.83 (m, CH, CH_2, 6H), 3.02 – 2.95 (m, CH_2, 4H), 2.87 – 2.72 (m, CH_2, 4H), 2.11 – 1.89 (m, CH_2, 2H), 1.87 (s, CH_3, 6H), 1.71 – 1.36 (m, 8H); **^{13}C-NMR** (100 MHz, D_2O/CD_3OD (1/1)): δ 172.6, 164.7, 141.9, 138.1, 136.3, 135.7, 131.0, 54.1, 40.4, 39.6, 31.2, 30.1, 23.9, 23.4, 14.8. **ESI-MS** calcd. for $C_{29}H_{41}N_4O_6S_2$: $[M+H]^+$: 605.2468, found: 605.2256.

2. Circular Dichroism (CD) and Ultraviolet-Visible (UV-Vis) Spectroscopy.

CD spectra were recorded on a JASCO spectrometer under a nitrogen atmosphere. Experiments were performed in a quartz cell with a 1 mm or 1 cm path length over the range of 190-650 nm at 25 ºC. UV spectra were recorded on a Shimadzu UV-3200 spectrometer under an atmospheric condition. Experiments were performed in a quartz cell with a 1 mm or 1 cm path length over the range of 190-650 nm at 25˚C.

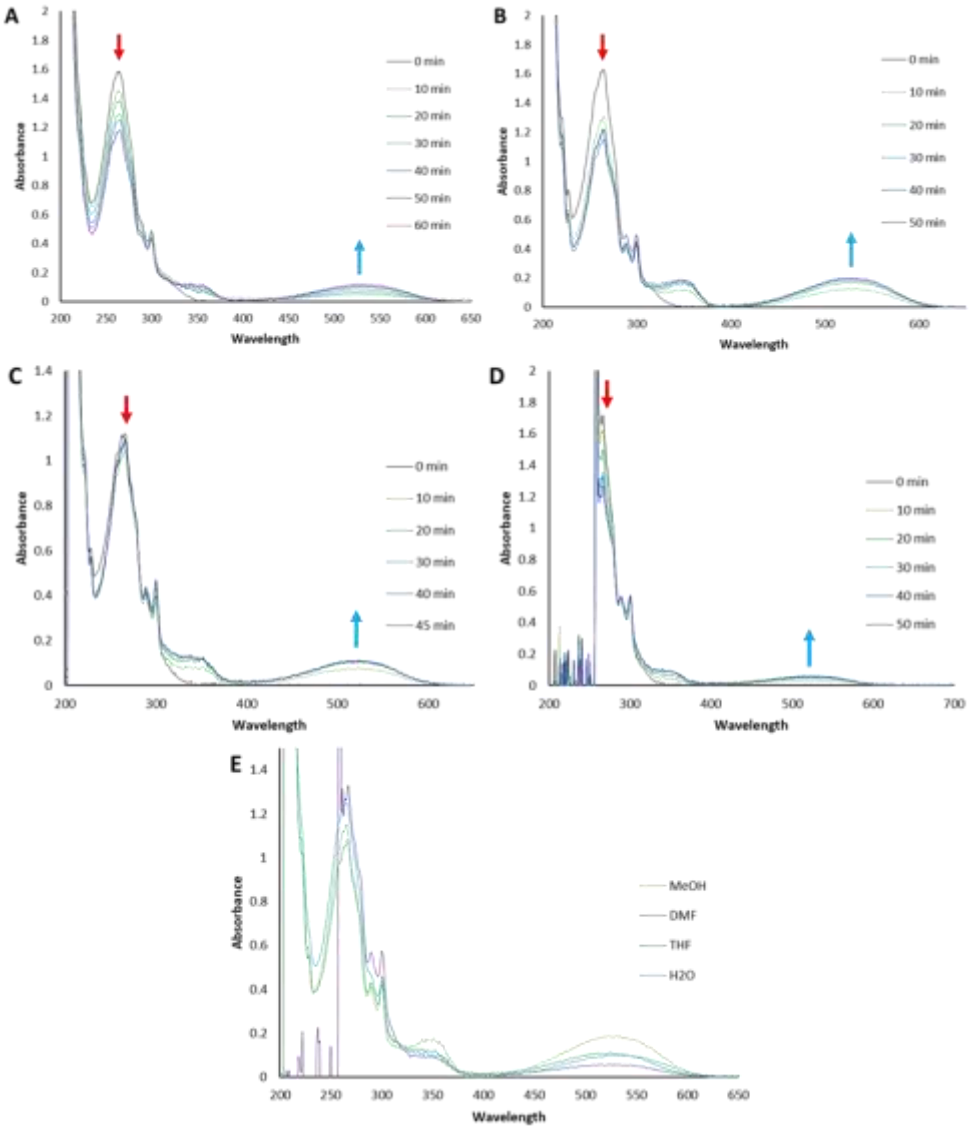


Figure S1: Photochromic behavior of **1**. 3 mM stock solutions of **1-open** in **A)** water, **B)** methanol, **C)** THF, and **D)** DMF were irradiated with 254 nm UV light over time, then dilute to 0.3 mM prior to analysis by UV-Vis. **E)** Comparison of all four solvents at the PSS (40 min in 254 nm UV light). UV-Vis spectroscopy was conducted on a Shimadzu UV-2450 Spectrometer with a TCC-240A temperature-controlled cell holder using a 1 mm path length quartz cuvette.

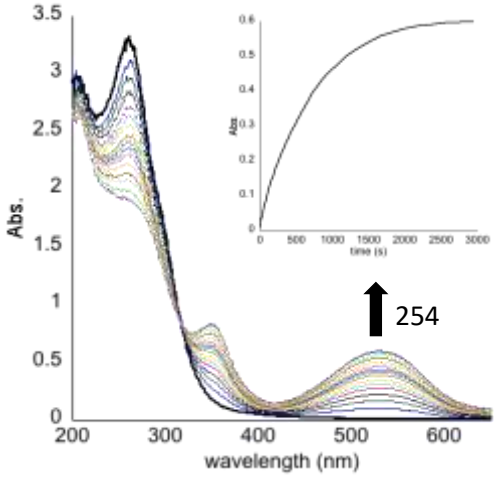


Figure S2. Photochromic behavior of **2**. UV/Vis absorption spectra in water (1 mM) during the course of irradiation at 254 nm from the open state to the photostationary state. Inset: time-dependent absorption changes at 524 nm.

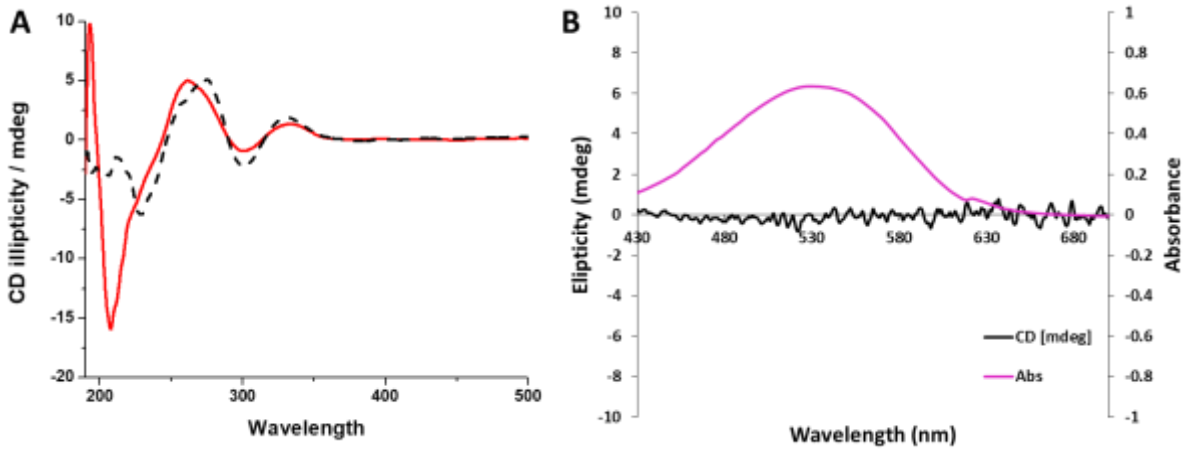


Figure S3: **A)** CD Spectra of **1** in water (1 mM) (solid-open, dash-closed). **B) 1-closed** extended UV-Vis and CD spectra showing a lack of CD signal correlating with DTE ring-closed form.

3. Photoisomerization

Photoisomerization of **1** was performed in quartz cuvettes by irradiation with 254 nm light in a Rayonet UV Chamber. The open:closed ratio of **1** was measured by ^{1}H NMR (in CD_3OD) by the ratio of the protons (4H, 2 × -CH_2- (cyclopentenyl) at ~2.35 ppm (closed-form) and 2.70 ppm (open-form). Samples were prepared by evaporation of the isomerization solvent and dissolution in CD_3OD for NMR analysis. The open/closed ratios were best determined by analytical reverse-phase HPLC, which provided more accurate ratios due to the ability to minimize sample handling prior to analysis.

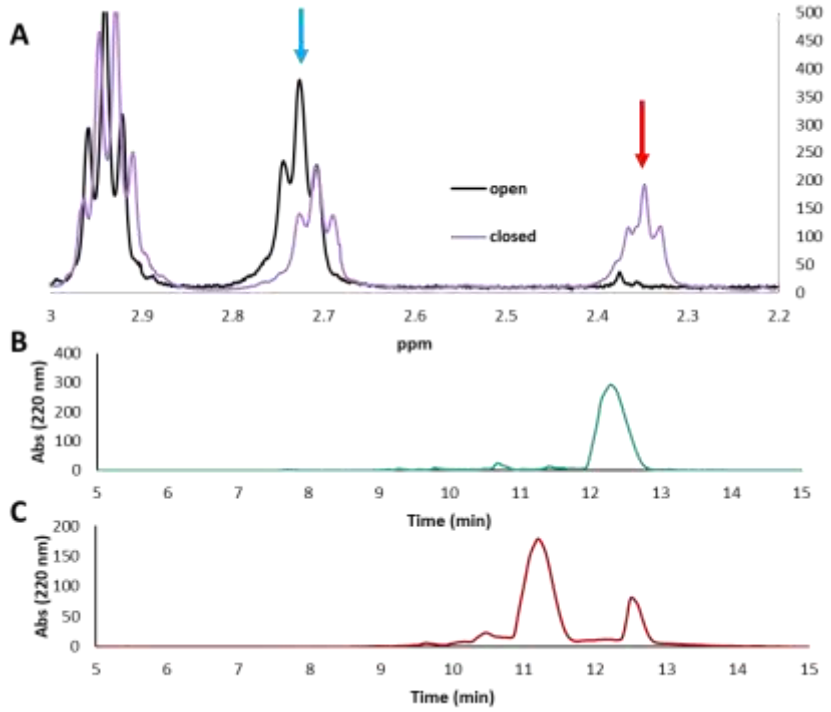


Figure S4: ^{1}H NMR of **A)** (blue arrow) **1-open** and (red arrow) **1-closed** irradiated with 254 nm UV light (45 min) in water (switched to CD_3OD for ^{1}H NMR). Reverse-phase analytical HPLC of **B) 1-open** prior to irradiation and **C) 1**, after irradiation at 254 nm at the PSS (closed:open 4:1).

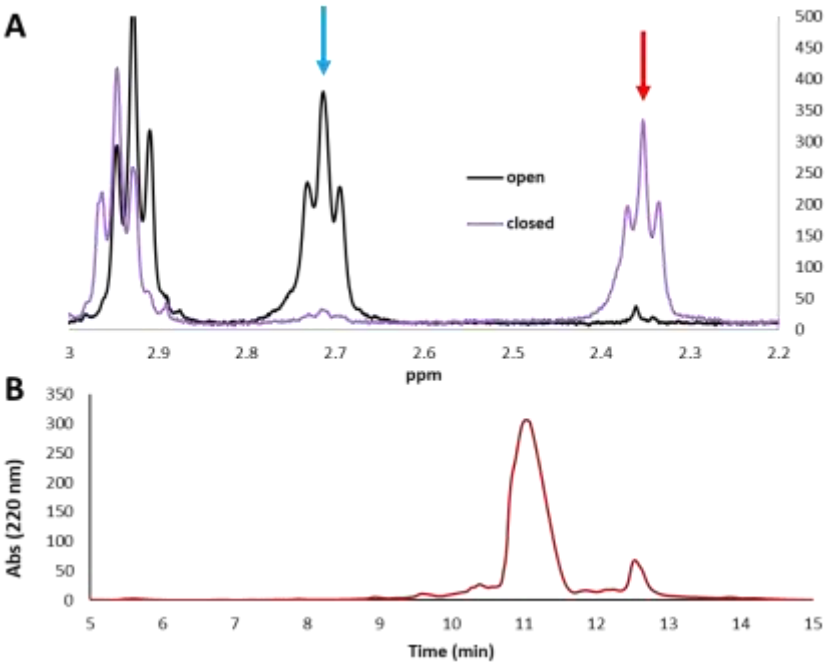


Figure S5: **A)** ^{1}H NMR of (blue arrow) **1-open** and (red arrow) **1-closed** via 254 nm UV light (45 min) in CD_3OD. **B)** Reverse-phase analytical HPLC of **1** at the PSS after irradiation at 254 nm light (45 min) in CD_3OD [closed:open = 18:1].

4. Atomic Force Microscopy (AFM)

AFM images were collected on a NanoScope IIIa device at ambient temperature in tapping mode using silicon tips (NSC14/AIBS, MikroMasch). 10 μL of the sample solution (250 μM) was diluted and placed on freshly cleaved mica. After adsorption for 30 min under moist conditions, excess solution was removed by absorption onto filter paper. The sample was allowed to dry fully before being scanned. The scanning speed was at a line frequency of 1.0 Hz, and the original images were sampled at a resolution of 512 x 512 pixels.

5. Transmission Electron Microscopy Measurement (TEM)

Using clean parafilm for aqueous samples, a copper grid (200 mesh) was floated on 50 uL drops of diluted samples for 3-5 min. After removal of the excess solution with filter paper by tapping the edge of the grid to a chem-wipe, the grid was floated on 50 μL drops of 2 % wt uranyl acetate solution for negative stain for 30 seconds. The excess solution was removed by tapping the edge of the grid to a chem-wipe. The dried specimen was observed with the Technai G2 Spirit instrument operating at 80 kV. The data were analyzed with Image-Pro Software.

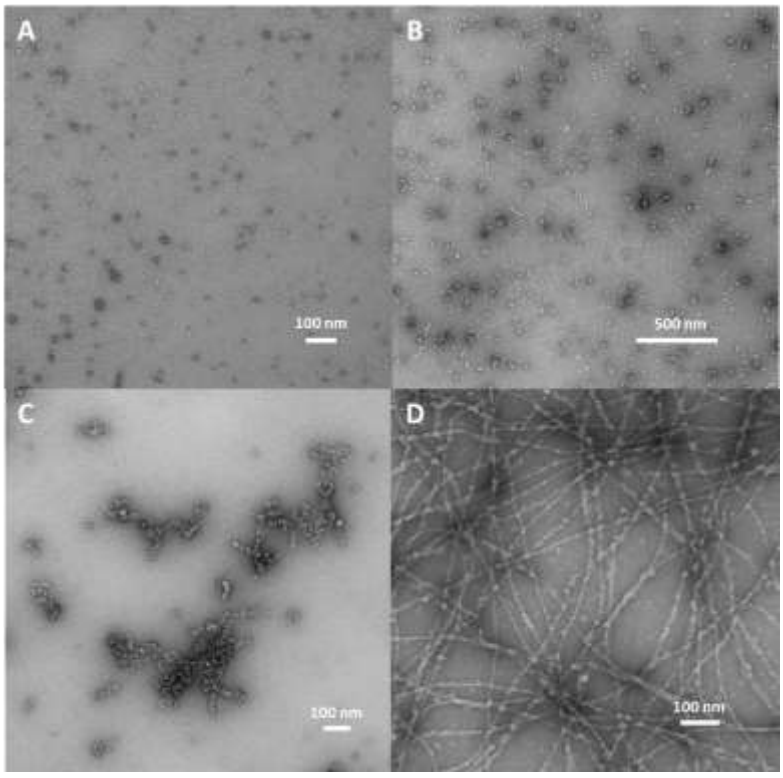


Figure S6: TEM images of aqueous solutions (10 mM) of **1-open: A)** after 24 h and **B)** 24 h after sonication (20% 1 min, pulsed 10s on, 5s off) and of **1-closed**: **C)** after 24 h in darkness and **D)** 24 h (in darkness) after sonication (20% 5 min, pulsed 10s on, 5s off). TEM images were recorded after diluting in water (1 mM) and evaporating onto a carbon-coated copper grid with uranyl acetate as a negative stain. Fiber diameters were 11.9 nm ± 2.3 nm (analyzed with ImageJ Pro Software).

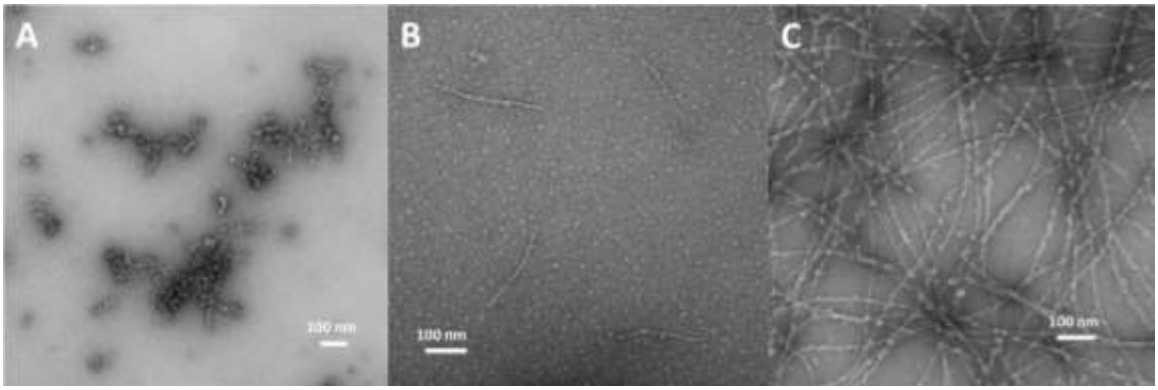
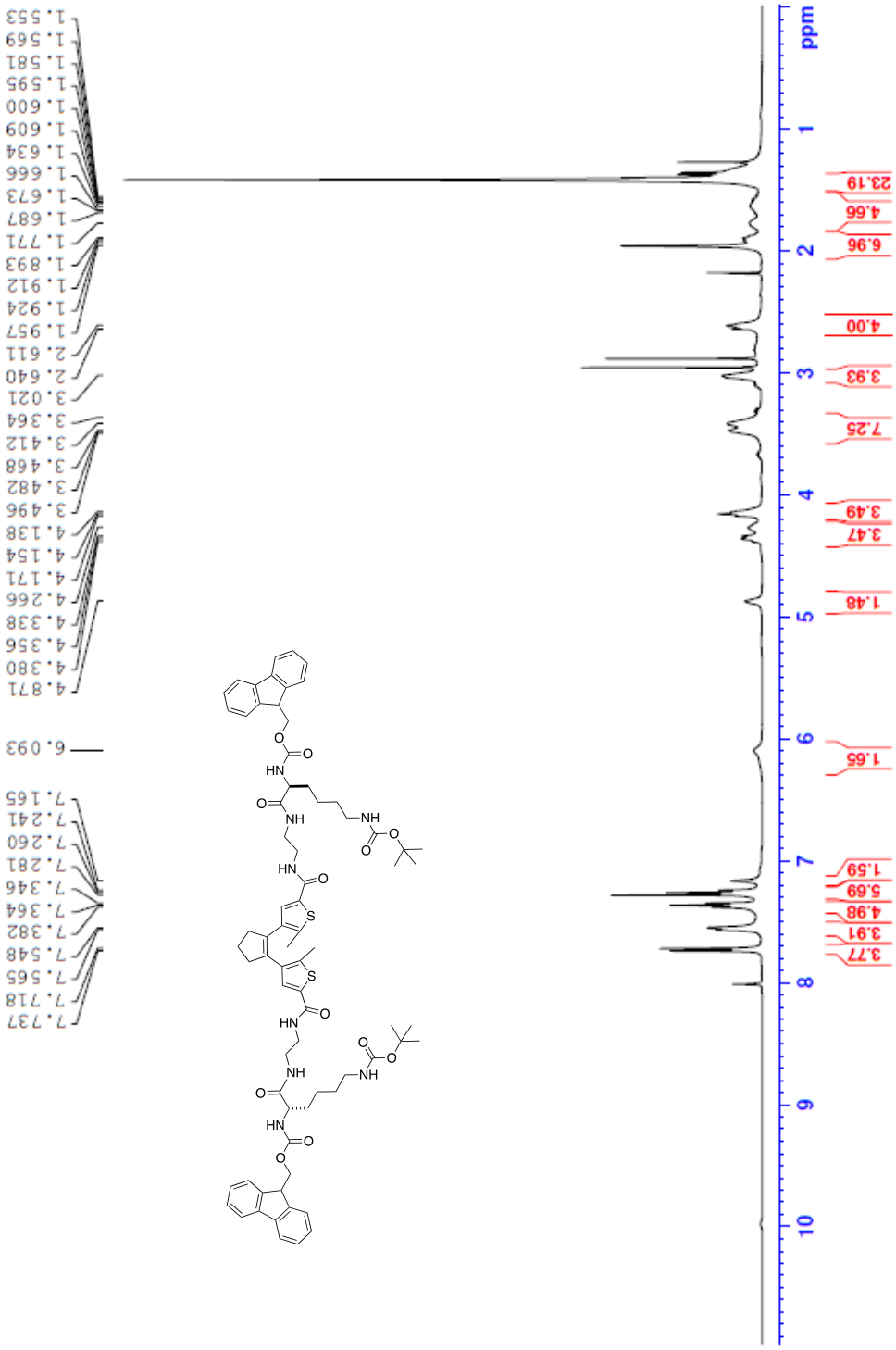
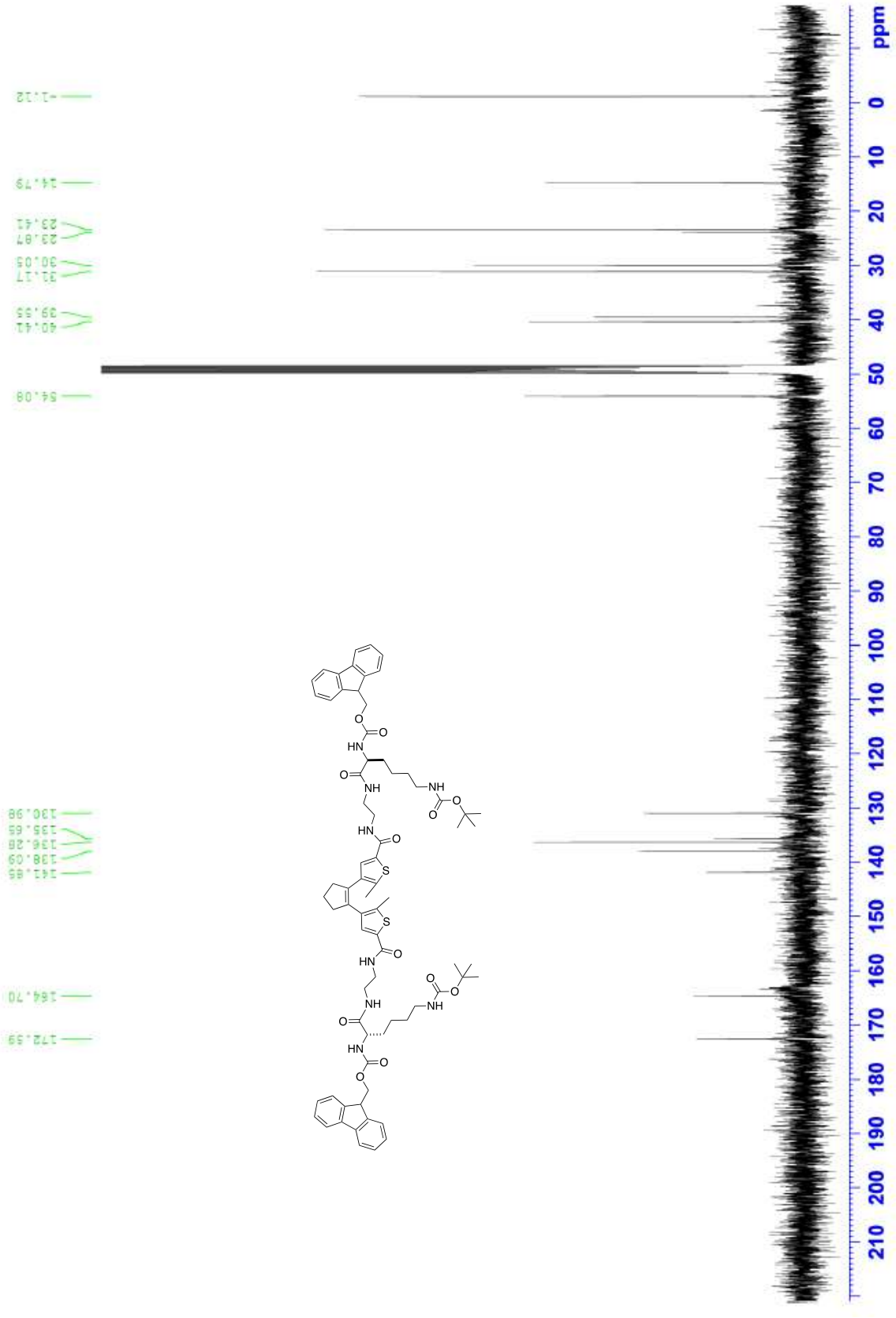


Figure S7. TEM images of aqueous solutions (10 mM) of **1-closed** after irradiation in MeOH, then evaporated and dispersed in water. **A)** 24 h/darkness w/o ultrasonication, **B)** 10 min/darkness after 5 min ultrasonication (20% pulsed, 10s on, 5s off), and **C)** 24 h/darkness after 5 min ultrasonication (20% pulsed, 10s on, 5s off). TEM images were recorded after diluting in water (1 mM) and evaporating onto a carbon-coated copper grid with uranyl acetate as a negative stain.

^{1}H, ^{13}C NMR and HRMS Spectra

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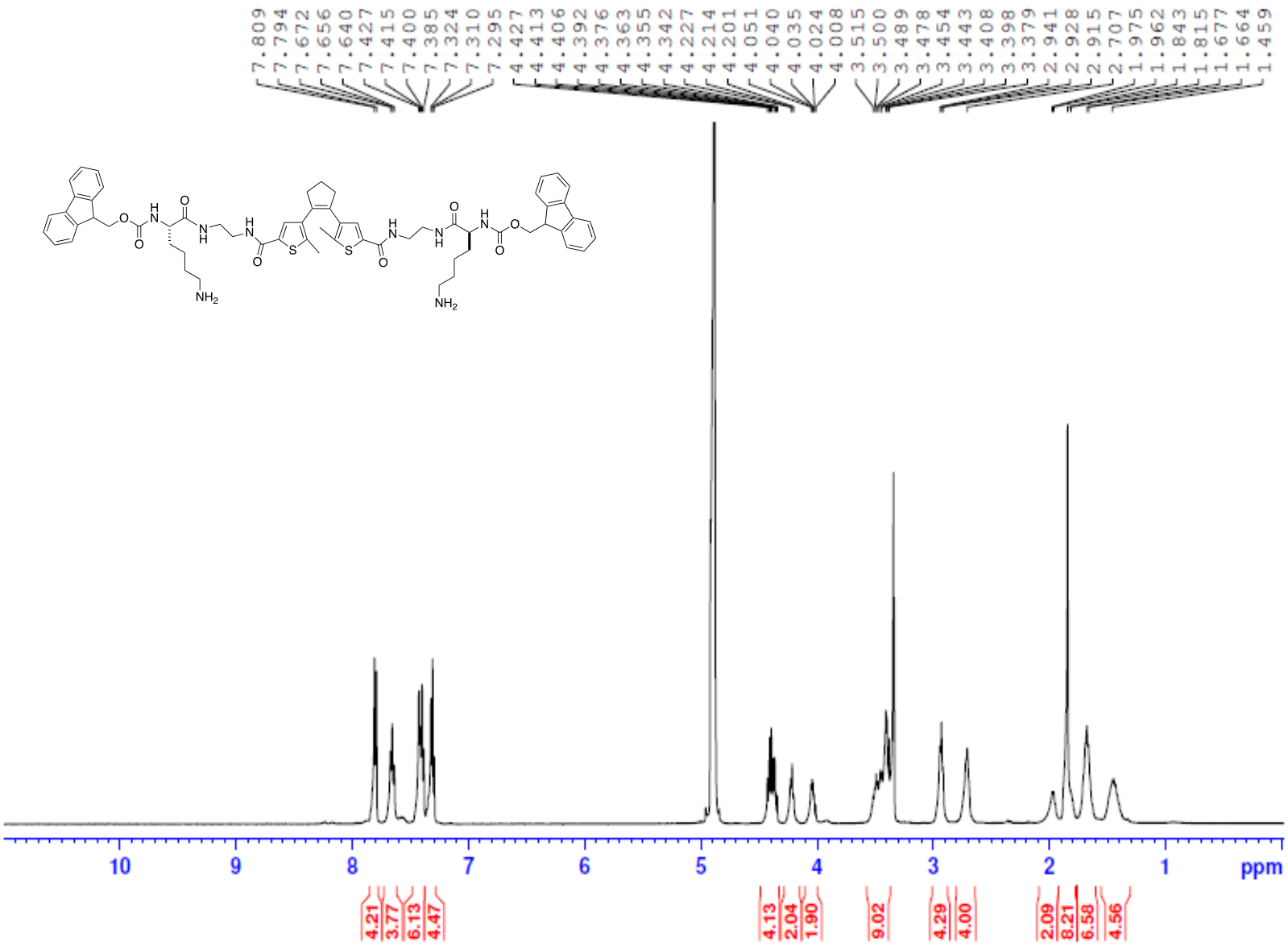
S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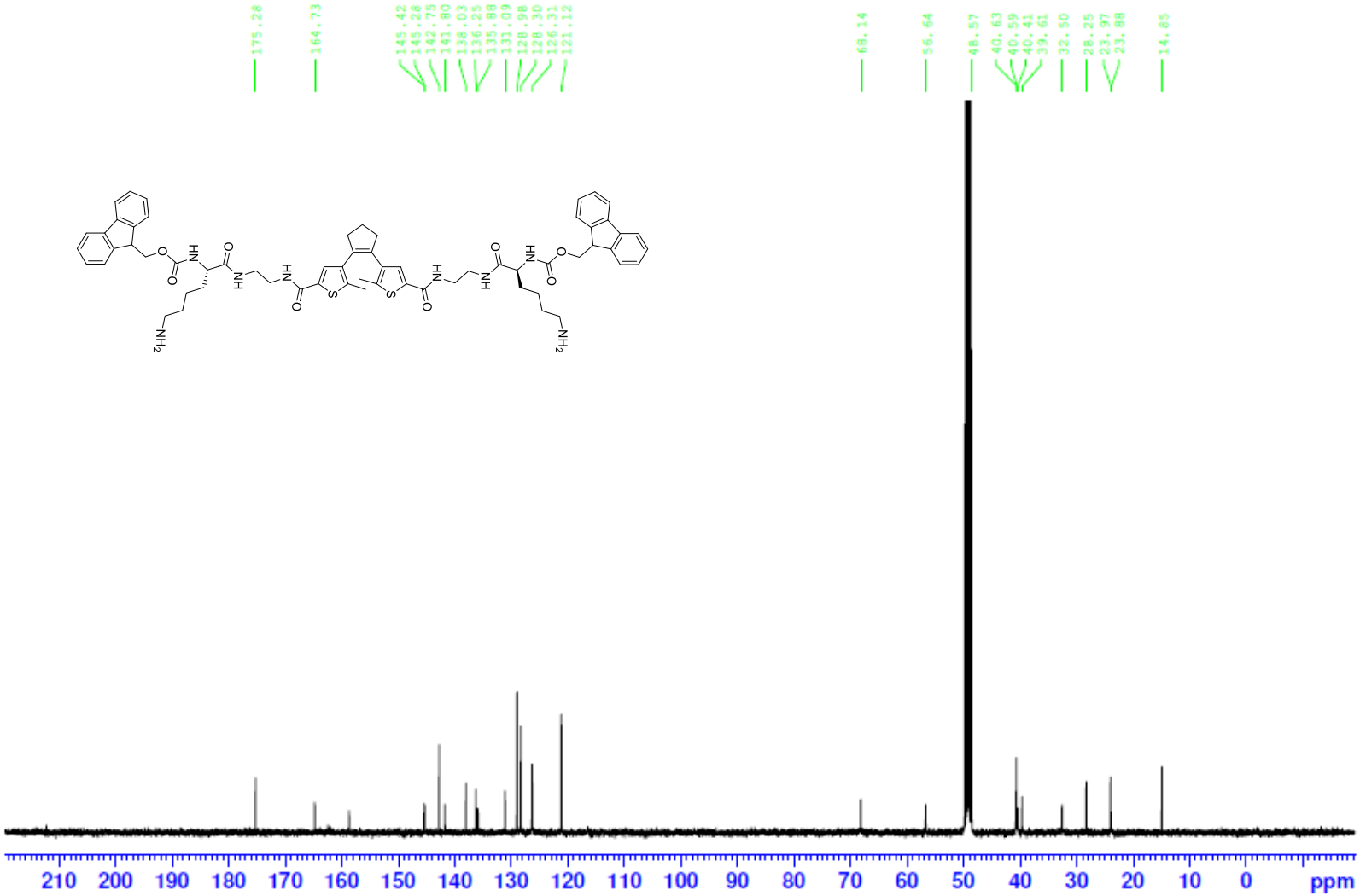
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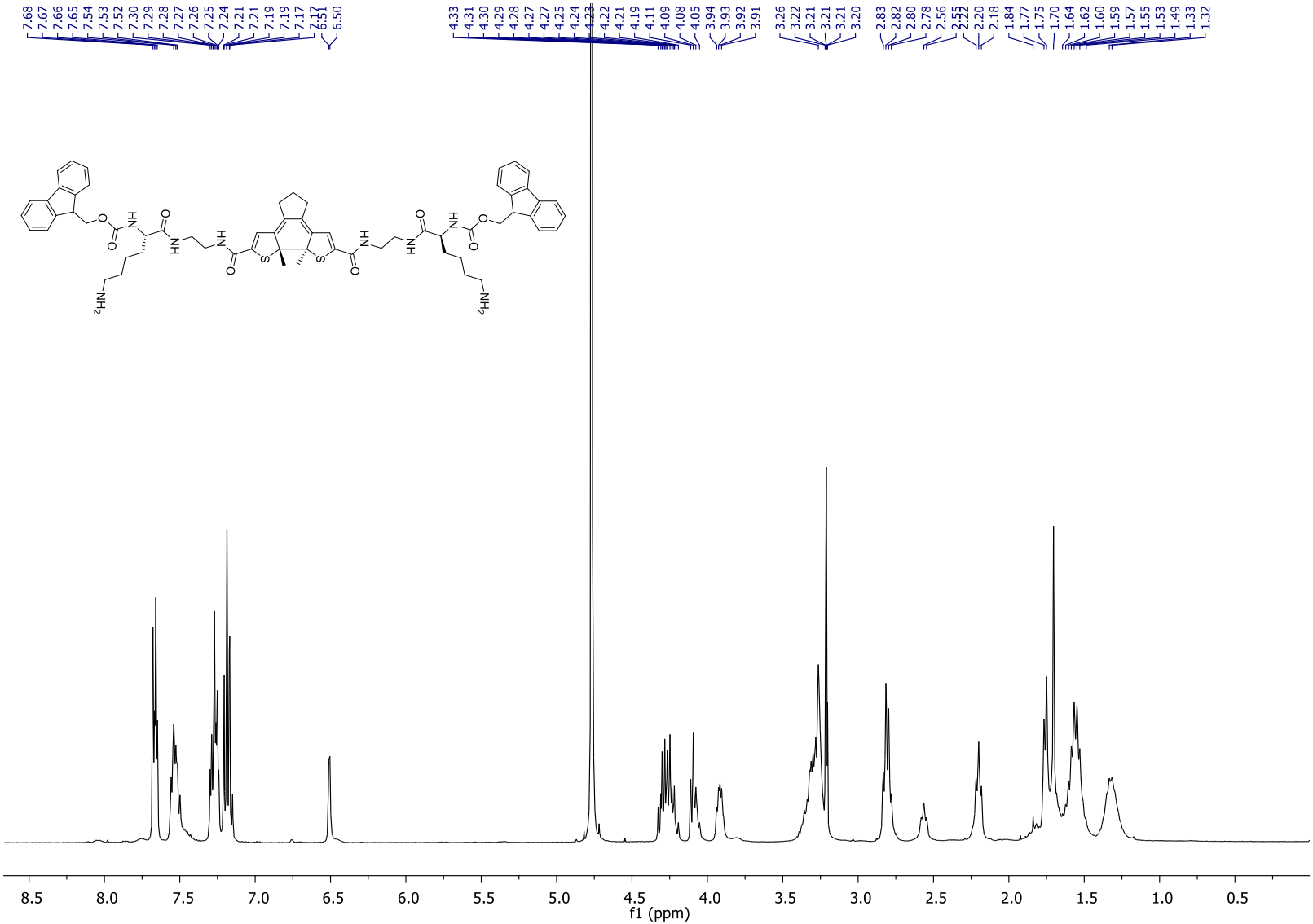
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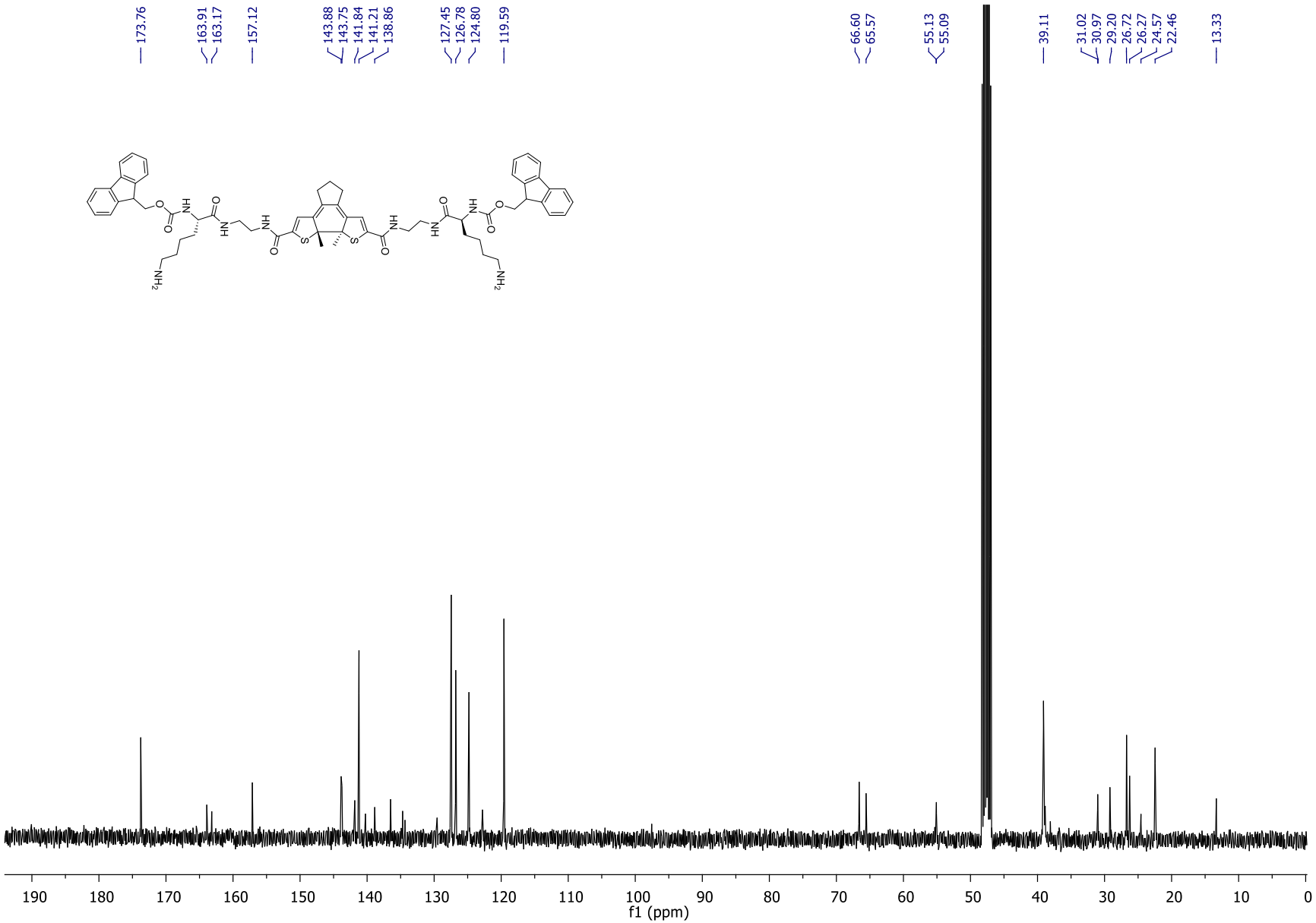
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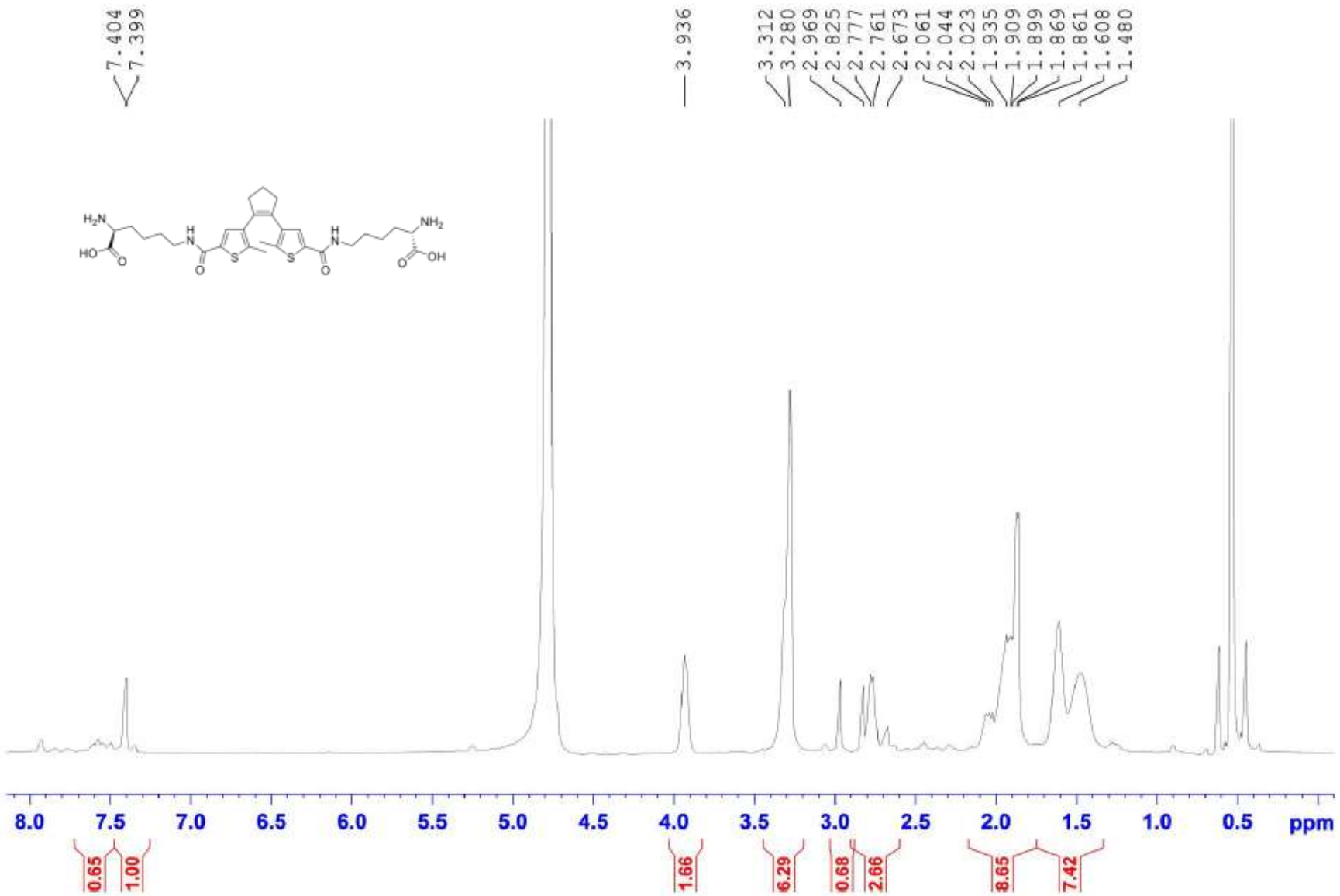
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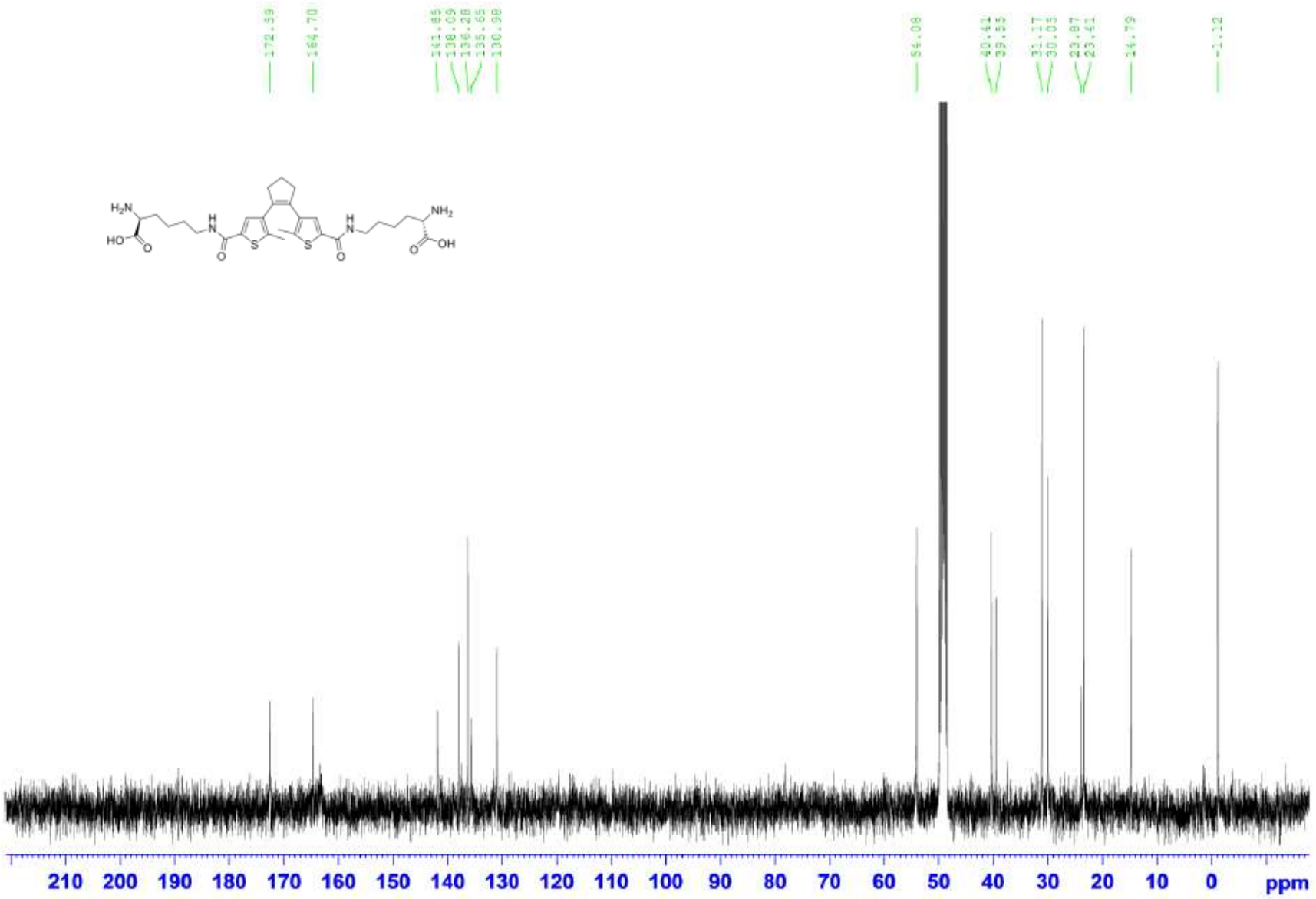
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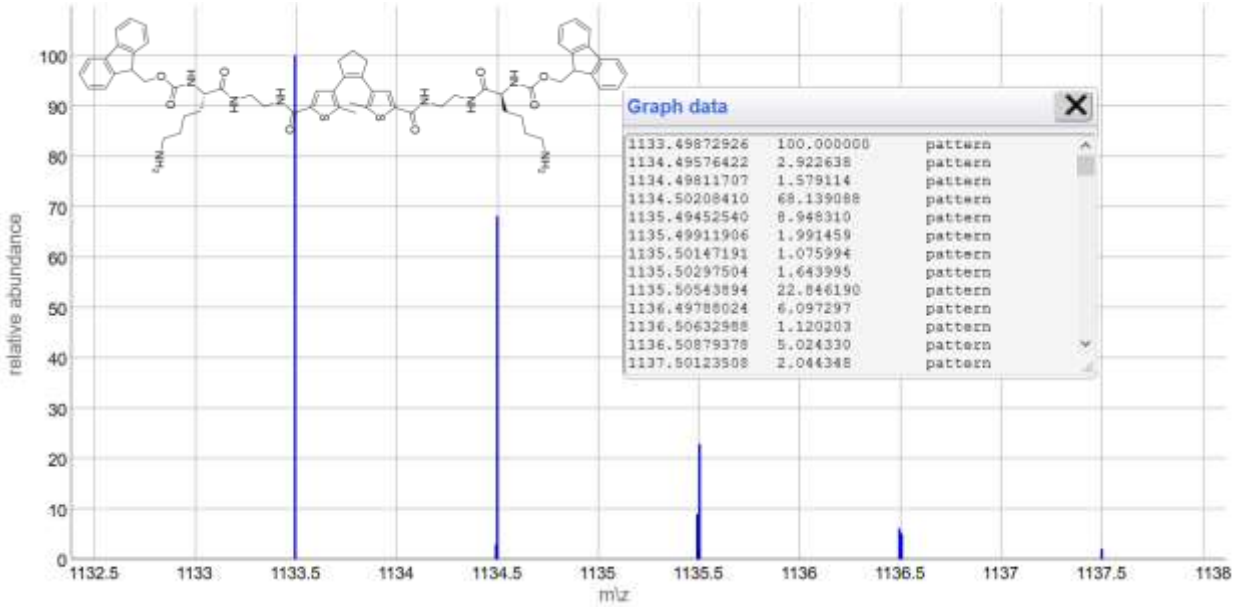
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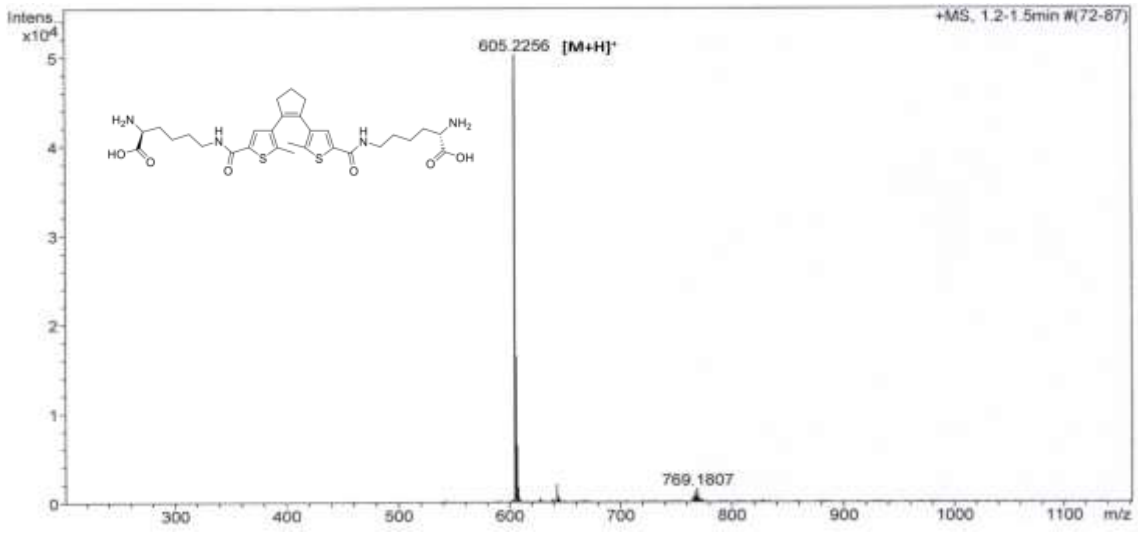
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References

1. D. J. Dijken, J. M. Beierle, M. C. A. Stuart, W. Szymanski, W. R. Browne and B. L. Feringa, *Angew. Chem.*, 2014, **53**, 5073-5077.
2. P. Rajakumar, M. Gayatri Swaroop, S. Jayavelu and K. Murugesan, *Tetrahedron*, 2006, **62**, 12041-12050.
3. R. B. Hamed, L. Henry, J. R. Gomez-Castellanos, A. Asghar, J. r. Brem, T. D. W. Claridge and C. J. Schofield, *Org. Biomol. Chem.*, 2013, **11**, 8191-8196.