Supporting Information for

Synthesis of Conjugated Diacetylene, Metal-Chelating Monomers for Polymerizable Monolayer Assemblies

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Synthesis and Characterization Data:

Compound 9: The amine-thioester **7** (0.62 g, 4.0 mmol) in dry DMF (20 mL) was added dropwise to a solution of 10,12-docosadiynedioic acid (1.50 g, 4.0 mmol), Et_3N (2.5 mL, 17.9 mmol) and BOP reagent (1.77 g, 4.0 mmol) in dry $CHCl_3$ (30 mL) over a period of 8 h by syringe pump. The reaction mixture was stirred for another 8 h at room temperature and then quenched with saturated NaCl solution. The compound was extracted with ethyl acetate. The organic layer was successively washed with 4% citric acid, water, 4% $NaHCO_3$ solution and finally with water. The organic layer was dried over anhydrous Na_2SO_4 and solvent was removed in vacuo. The crude product was purified by silica gel column chromatography with 4% MeOH in $CHCl_3$ ($R_f = 0.2$) to obtain a white solid (1.35 g, 71%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.23-1.37 (m, 16H), 1.46-1.52 (m, 4H), 1.58-1.63 (m, 4H), 2.15 (t, 2H, J = 7.6 Hz), 2.21-2.25 (m, 4H), 2.31-2.36 (m, 5H), 3.02 (t, 2H, J = 6.3 Hz), 3.42-3.46 (m, 2H), 5.86 (bs, 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.23, 24.72, 24.74, 25.65, 28.32, 28.34, 28.75, 28.78, 28.83, 28.88, 28.94, 29.02, 29.09, 29.17, 29.19, 33.94, 36.64, 39.45, 65.40, 77.43, 173.45, 178.22, 178.45.

Thiol 1: The coupling of amine **10** (0.22 g, 0.34 mmol) and acid **9** (0.156 g, 0.34 mmol) was carried out with BOP reagent (0.15 g, 0.34 mmol) and Et_3N (0.15 mL, 1.78 mmol) in dry $CHCl_3$ at room temperature for 12 h. The reaction was quenched with saturated NaCl solution. Solvent was evaporated in vacuo. The white solid was filtered and washed with water. The pure product was obtained by silica gel column purification with 10% MeOH in $CHCl_3$ ($R_f = 0.3$) as a white solid (0.22 g, 60%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.21-1.27 (m, 24H), 1.32-1.37 (m, 4H), 1.47-1.53 (m, 4H), 1.59-1.66 (m, 4H), 2.14-2.19 (m, 4H), 2.22-2.24 (m, 4H), 2.36 (s, 3H), 2.98 (t, 2H, J = 5.5 Hz), 3.03 (t, 2H, J = 6.4 Hz), 3.42-3.47 (m, 4H), 3.52-3.55 (m, 6H), 3.58 (s, 4H), 3.61-3.64 (m, 10H), 3.94 (bs, 1H, NH), 4.14-4.17 (m, 8H), 5.87 (bs, 1H, NH), 6.83 (bs, 1H, NH), 7.53 (s, 1H), 7.76 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.44, 19.38, 25.79, 25.88, 28.51, 28.52, 28.94, 28.97, 29.07, 29.13, 29.26, 29.32, 29.36, 29.38, 29.46, 30.74, 36.84, 39.41, 39.64, 53.98, 54.67, 56.19, 57.96, 60.66, 65.58, 70.23, 70.44, 70.59, 77.64, 126.68, 128.84, 130.82, 139.27, 171.25, 171.60, 173.41.

The IDA-thioester (0.165 g, 0.15 mmol) was dissolved in degassed MeOH/THF (4/4 mL) and LiOH.H_2O (40 mg, 0.95 mmol) was added and stirred under nitrogen at room temperature for 10 h. The reaction mixture was then acidified with dilute, degassed HCl (pH = 3.0). The solvent was removed in vacuo and nanopure water was added. The white solid was filtered off, washed with plenty of water (50 mL) and then vacuum dried. Yield: 0.135 g, (81%, white solid). ^{1}H NMR (500 MHz, $CDCl_3$-CD_3OD-D_2O) δ 1.24-1.31 (m, 12H), 1.34-1.38 (m, 4H), 1.46-1.52 (m, 4H), 1.55-1.61 (m, 4H), 2.16-2.28 (m, 10H), 2.78 (t, 2H, J = 6.6 Hz), 3.36-3.39 (m, 2H), 3.48 (t, 2H, J = 6.5 Hz), 3.52 (t, 2H, J = 5.0 Hz), 3.57-3.63 (m, 6H), 3.65-3.75 (m, 10H), 3.85-3.87 (m, 2H), 3.89 (s, 1H), 7.49 (s, 1H), 7.82 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$-CD_3OD) δ 19.31, 24.49, 25.02, 25.87, 28.42, 28.45, 28.89, 28.94, 29.04, 29.07, 29.12, 29.21, 29.30, 29.33, 29.37, 34.12, 36.60, 36.72, 39.18, 42.42, 51.86, 54.25, 57.94, 65.42, 70.18, 70.24, 70.27, 77.68, 127.22, 132.74, 134.82, 138.93, 171.98, 172.01. Anal. Calcd. for $C_{47}H_{71}N_5O_{13}S$.HCl: C, 57.45; H, 7.28; N, 7.13. Found: C, 57.53; H, 7.67; N, 7.46.

Compounds 12 & 13 (DPTA pentaester-monoacid**)**: The selective mono deprotection of ester was carried out according to the literature procedure.[31] The mixture (**12** and **13**) was separated from other impurities by silica gel column chromatography with 20% MeOH in $CHCl_3$ (R_f = 0.3). Yield (overall): 60%. ^{1}H NMR (300 MHz, $CDCl_3$, **12** + **13**) δ 1.22-1.26 (m, 12H), 2.90-3.22 (m, 8H), 3.45-3.62 (m, 10H), 4.15-4.25 (m, 8H).

Compound 14 (Cbz-DPTA pentaester**):** The DTPA acid mixture (**12** and **13**, 2.12 g, 4.20 mmol) was coupled with Cbz-amine **20** (1.18 g, 4.20 mmol) in presence of BOP (1.85 g, 4.20 mmol) and Et_3N (1.2 mL, 8.4 mmol) in MeCN. The reaction was carried out at room temperature for 12 h. The reaction was quenched with saturated NaCl solution. Solvent was evaporated in vacuo. The white solid was filtered and washed with water. The pure product was obtained by silica gel column chromatography with 10% MeOH in $CHCl_3$ (R_f = 0.4). Yield: 1.89 g (56%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.23-1.26 (m, 12H), 2.73-2.78 (m, 6H), 2.81-2.85 (m, 2H), 3.25-3.28 (m, 2H), 3.37-3.42 (m, 6H), 3.45-3.47 (m, 2H), 3.52-3.56 (m, 8H), 3.59 (s, 4H), 4.10-4.17 (m, 8H), 5.10 (s, 2H), 5.43 (bs, 1H, NH), 7.34 (s, 5H), 7.90 (bs, 1H, NH). ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.44, 14.45, 14.77, 38.99, 41.10, 52.10, 52.42, 52.79, 53.13, 54.95, 55.32, 56.14, 58.94, 60.57, 60.71, 60.89, 66.81, 70.08, 70.31, 70.53, 128.27, 128.33, 128.70, 136.84, 156.74, 171.41, 171.45, 171.56, 171.81.

To a solution of Cbz-ester (1.60 g, 2.08 mmol) in MeOH (30 mL) was added conc. HCl (0.22 mL) and followed by the addition of a small portion of Pd-black and hydrogen was then bubbled through the solution. The reaction was achieved at room temperature for 16 h. The Pd-black was filtered, and solvent was removed in vacuo to give the product as yellowish viscous oil Yield: 1.47 g (98%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.19-1.23 (m, 9H), 1.27 (t, 3H, J = 7.5 Hz), 3.14-3.23 (m, 6H), 3.40-3.44 (m, 6H), 3.52 (s, 4H), 3.58-3.63 (m, 6H), 3.64-3.67 (m, 6H), 3.80-3.83 (m, 2H), 4.08-4.13 (m, 6H), 4.22 (q, 2H, J = 7.2 Hz), 4.56 (bs, 3H, NH), 8.41 (bs, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.25, 14.34, 14.36,39.57, 39.96, 49.83, 50.00, 50.64, 52.12, 53.04, 53.26, 54.95, 56.08, 56.93, 61.16, 61.21, 62.47, 66.62, 69.76, 70.05, 70.33, 171.28, 172.35, 171.66.

Thiol 2: The coupling of acid **9** (0.32 g, 0.69 mmol) and amine **14** (0.23 g, 0.69 mmol) was achieved as described for the **thiol 1**. The purification was done by silica gel column chromatography with 6% MeOH in $CHCl_3$ (R_f = 0.2). Yield: 0.22 g (59%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.23-1.35 (m, 28H), 1.45-1.52 (m, 4H), 1.57-1.62 (m, 4H), 2.11-2.25 (m, 8H), 2.35 (s, 3H), 2.74-2.83 (m, 6H), 3.02 (t, 2H, J = 6.4 Hz), 3.27-3.30 (m, 2H), 3.40-3.47 (m, 10H), 3.51-3.62 (m, 14H), 4.11-4.18 (m, 8H), 5.84 (bs, 1H, NH), 6.28 (bs, 1H, NH), 8.05 (bs, 1H, NH). ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.51, 19.43, 25.87, 25.97, 28.53, 28.56, 29.01, 29.06, 29.10, 29.16, 29.21, 29.40, 29.50, 29.55, 30.90, 36.87, 36.93, 39.06, 39.40, 39.69, 39.74, 52.13, 52.47, 52.85, 53.20, 55.02, 55.39, 56.20, 59.01, 60.64, 60.77, 60.97, 65.53, 65.57, 70.05, 70.32, 70.32, 70.61, 77.45, 77.77, 171.44, 171.51, 171.99, 173.62, 180.

The selective hydrolysis of ester (0.15 g, 0.14 mmol) with LiOH (46 mg, 1.1 mmol) was carried as described for the **thiol 1**. Yield: 0.10 g (78%). ^{1}H NMR (500 MHz, $CDCl_3$-CD_3OD) δ 1.34-1.46 (m, 16H), 1.56-1.62 (m, 4H), 1.65-1.72 (m, 4H), 2.27-2.38 (m, 10H), 2.90 (t, 2H, J = 6.5 Hz), 3.35-3.42 (m, 16H), 3.46-3.51 (m, 4H), 3.59-3.71 (m, 10H), 3.81 (s, 1H), 3.88 (bs, 1H, NH), 4.10-4.16 (bs, 2H, NH), 7.50 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$-CD_3OD) δ 19.24, 25.01, 25.88, 28.42, 28.87, 28.90, 29.02, 29.09, 29.19, 19.24, 29.33, 29.81, 34.23, 36.23, 36.47, 37.78, 38.49, 39.14, 65.37, 69.92, 70.04, 70.20, 70.28, 174.9, 176.83. Anal. Calcd. for $C_{44}H_{74}N_6O_{13}S.HCl$: C, 54.82; H, 7.78; N, 8.72. Found: C, 55.00; H, 7.63; N, 8.54.

Compound 16: The Cbz-amine **20**[32] (0.75 g, 2.66 mmol) and EDTA-ester **15** (1.00 g, 2.66 mmol) were dissolved in dry MeCN (25 mL) followed by the addition of Et_3N (0.80 mL, 5.75 mmol) and BOP reagent (1.17 g, 2.66 mmol). The reaction was carried out at room temperature for 12 h. The workup procedure was the same as described for **9**. The purification was done by silica gel column chromatography with 10% MeOH in $CHCl_3$ (R_f = 0.5) as the elutant to afford a yellowish viscous liquid (1.50 g, 92%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.25 (t, 9H, J = 7.0 Hz), 2.77 (t, 2H, J = 6.0 Hz), 2.82 (t, 2H, J = 6.0 Hz), 3.26-3.30 (m, 2H), 3.36-3.40 (m, 4H), 3.35 (q, 2H, J = 5.7 Hz), 3.52 (s, 4H), 3.54-3.56 (m, 4H), 3.59 (s, 4H), 4.13 (q, 6H, J = 7.1 Hz), 5.09 (s, 2H), 5.58 (bs, 1H, NH), 7.34 (s, 5H), 8.02 (bs, 1H, NH).

To a solution of Cbz-triester (1.50 g, 2.34 mmol) in MeOH (30 mL) was added conc. HCl (0.23 mL) and followed by the addition of a small portion of Pd-black and hydrogen was then bubbled through the solution. The reaction was achieved at room temperature for 16 h. The Pd-black was filtered, and solvent was removed in vacuo to give the product as yellowish viscous oil (R_f = 0.2, 12% MeOH in $CHCl_3$). Yeild: 1.18 g (96%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.22 (t, 9H, J = 7.1 Hz), 2.74-2.81 (m, 4H), 3.19 (t, 2H, J = 4.8 Hz), 3.34-3.37 (bs, 2H), 3.40-3.45 (m, 4H), 3.51 (s, 4H), 3.55-3.61 (m, 6H), 3.63-3.65 (m, 2H), 3.79 (t, 2H, J = 4.8 Hz), 4.11 (q, 6H, J = 7.1 Hz), 8.06-8.46 (bs, 4H, NH).

Thiol 3: The EDTA-amine **16** (0.29 g, 0.54 mmol) and acid-thioester **9** (0.25g, 0.54 mmol) was dissolved in dry MeCN/$CHCl_3$ (10 mL/10 mL), and the BOP reagent (0.24 g, 0.54 mmol) and Et_3N (0.30 mL, 2.15 mmol) were added. The resulting reaction mixture was stirred at room temperature for 18 h, then quenched with saturated NaCl solution. Solvent was evaporated in vacuo. The white solid was filtered and washed with water. The crude product was purified by silica gel column chromatography with 6% MeOH in $CHCl_3$ (R_f = 0.3) to afford a white solid (0.39 g, 76%). ^{1} H NMR (400 MHz, $CDCl_3$, 50 ^{0}C) δ 1.23-1.34 (m, 25H), 1.44-1.50 (m, 4H), 1.57-1.62 (m, 4H), 2.14-2.24 (m, 8H), 2.34(s, 3H), 2.78-2.81(m, 4H), 3.01(t, 2H, J = 6.5 Hz), 3.28-3.31 (m, 2H), 3.41-3.48 (m, 8H), 3.50-3.53 (m, 6H), 3.55-3.59 (m, 6H), 4.13 (q, 6H, J = 7.1 Hz), 5.82 (bs, 1H, NH), 6.30 (bs, 1H, NH), 8.18 (bs, 1H, NH). ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.45, 19.35, 25.08, 25.84, 25.92, 28.47, 28.94, 28.97, 29.11, 29.14, 29.36, 29.42, 29.46, 30.29, 36.73, 36.77, 39.02, 39.35, 39.55, 52.34, 52.96, 54.98, 55.88, 58.70, 60.84, 60.93, 65.50, 69.95, 70.23, 70.48, 77.68, 171.36, 171.44, 172.19, 173.84, 176.57.

The EDTA-thioester (0.20 g, 0.21 mmol) was dissolved in degassed MeOH/THF (5 mL/5 mL) and $LiOH.H_2O$ (60 mg, 1.43 mmol) in H_2O/ MeOH (1 mL/3 mL) was added. The resulting mixture was stirred under nitrogen at room temperature for 10 h. It was acidified with dilute, degassed HCl (pH = 3.0). The solvent was removed in vacuo and nanopure water was added. The white solid was filtered off. Yield: 0.13 g (75%). ^{1}H NMR (500 MHz, DMSO-d_6) δ 1.25-1.41 (m, 16H), 1.47-1.54 (m, 8H), 2.10 (t, 4H, J = 7.3 Hz), 2.23 (t, 2H, J = 7.3 Hz), 2.29-2.32 (m, 4H), 2.78-2.82 (m, 4H), 3.23-3.26 (m, 2H), 3.29-3.33 (m, 4H), 3.34-3.39 (m, 2H), 3.43-3.46 (m, 4H), 3.47-3.49 (m, 2H), 3.50 (s, 4H), 3.56 (s, 4H), 3.63 (s, 1H), 7.67 (bs, 1H, NH), 7.84 (bs, 1H, NH), 7.99 (bs, 1H, NH). ^{13}C NMR (125 MHz, $CDCl_3$-DMSO-d_6) δ 18.53, 24.58, 25.46, 27.91, 27.93, 28.37, 28.42, 28.52, 28.58, 28.70, 28.80, 28.87, 33.80, 35.46, 38.34, 38.54, 51.69, 52.00, 54.71, 55.01, 57.44, 65.54, 69.06, 69.29, 69.69, 69.72, 78.07, 170.40, 172.17, 172.84, 174.74. Anal. Calcd. for $C_{40}H_{67}N_5O_{11}S$: C, 58.16; H, 8.18; N, 8.48. Found: C, 58.35; H, 8.30; N, 8.63.

Compound 18 (cyclen derivatives): The anhydrous K_2CO_3 (22.0 g, 157.00 mmol) was suspended in dry MeCN and sonicated (probe sonicator) for 15 min. at room temperature. Cyclen (3.00 g, 17.41 mmol) was then added. After refluxing for 30 min., ethylbromoacetate (7.27 g, 43.53 mmol) dissolved in 50 mL of MeCN was added dropwise by syringe pump (5 mL/h). The mixture was allowed to reflux another 12 h, and cooled to room temperature. Solids were filtered and solvent was evaporated to dryness. The crude product was purified by silica gel column chromatography with 10% MeOH in $CHCl_3$ (R_f = 0.5) to afford a yellowish viscous oil 4.10 g (66%). ^{1}H NMR (400 MHz, DMSO-*d*$_6$, 50 ^{o}C) δ 1.24 (t, 9H, J = 7.1 Hz), 2.69-2.72 (m, 4H), 2.74-2.77 (m, 4H), 2.90-2.93 (m, 4H), 3.01-3.04 (m, 4H), 3.45 (s, 2H), 3.53 (s, 4H), 4.10-4.14 (m, 6H).

The triester cyclen (1.68 g, 3.91 mmol) and benzylbromoacetate (0.89 g, 3.91 mmol) were dissolved in dry MeCN and large excess K_2CO_3 (1.60 g, 11.42 mmol) was added. The resulting mixture was sonicated (125 W bath sonicator) at room temperature for 14 h. The solids were then filtered off and the solvent was removed in vacuo. The purification was done with silica gel column chromatography (R_f = 0.2, 10% MeOH in $CHCl_3$) to afford an yellowish viscous oil. Yeild: 1.80 g (80%). ^{1}H NMR (400 MHz, $CDCl_3$-D_2O) δ 1.21-1.27 (m, 9H), 2.23-2.61 (m, 4H), 2.80-2.86 (m, 8H), 3.01-3.27 (m, 6H), 3.41-3.62 (bs, 6H), 4.10-4.17 (m, 6H), 4.73 (s, 2H). 7.35 (s, 5H).

The cyclen-tetraester (1.65 g, 2.85 mmol) was dissolved in MeOH (25 mL) in presence of small portion of Pd-black. The reaction condition was the same as described for **16**. Yield: 1.35 g (97%, viscous oil). ^{1}H NMR (500 MHz, DMSO-*d*$_6$, 70 ^{o}C) δ 1.22 (t, 9H, J = 7.1 Hz), 2.85-3.05 (bs, 12H), 3.63-3.67 (bs, 4H), 3.74 (s, 6H), 3.90 (s, 2H), 4.13 (q, 6H, J = 7.1 Hz).

Compound 19: The coupling of Cbz-diamine **20** (0.865 g, 3.07 mmol) and cyclen-acid **18** (1.50 g, 3.07 mmol) was achieved in presence of BOP reagent (1.36 g, 3.07 mmol) and Et_3N (1.30 mL, 9.34 mmol) in dry MeCN. The work up procedure was the same as described for **9**. The crude product was purified by column chromatography with 10% MeOH in $CHCl_3$ (R_f = 0.4) to give yellowish viscous liquid (2.19g, 95%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.19-1.43 (m, 9H), 2.10-2.64 (bs, 8H), 2.72-3.19 (m, 8H), 3.38-3.43 (m, 8H), 3.47-3.75 (m, 12H), 4.12-4.31 (m, 6H), 5.08 (s, 2H), 5.48 (bs, 1H, NH), 6.65 (bs, 1H, NH), 7.34 (s, 5H).

The cyclen derivative (1.30 g, 1.73 mmol) from the above reaction was dissolved in MeOH (50 mL). A small portion of Pd-C (5%) and 0.25 mL of conc. HCl were added. The same reaction condition was followed as described for **16**. Yield: 1.15 g (96%). ^{1}H NMR (500 MHz, DMSO-*d*$_6$, 80 ^{o}C) δ 1.20-1.23 (m, 9H), 2.81-2.88 (bs, 4H), 2.92-2.96 (m, 4H), 3.15-3.18 (m, 2H), 3.27-3.31 (m, 4H), 3.41 (t, 2H, J = 5.7 Hz), 3.50 (t, 2H, J = 5.7 Hz), 3.55-3.59 (m, 8H), 3.62 (s, 4H), 3.65-3.76 (m, 4H), 3.72-3.75 (bs, 2H), 3.88 (bs, 1H, NH), 4.11-4.16 (m, 6H), 8.12 (bs, 3H, NH).

Thiol 4: The coupling between cyclen-amine derivative **19** (0.33 g, 0.47 mmol) and acid **9** (0.22 g, 0.47 mmol) was achieved with BOP reagent (0.21 g, 0.47 mmol) and Et_3N (0.33 mL, 2.37 mmol) in $CHCl_3$/MeCN (10 mL/3 mL). The reaction condition and work up procedure were the same as described for **thiol 3**. The purification was done by silica gel column chromatography with 6% MeOH in $CHCl_3$ (R_f = 0.3). Yield: 0.32 (67%). ^{1}H NMR (500 MHz, DMSO-*d*$_6$, 80^{o}C) δ 1.21-1.26 (m, 21H), 1.31-1.37 (m, 4H), 1.45-1.51 (m, 8H), 2.03-2.08 (m, 4H), 2.27 (t, 4H, J = 7.0 Hz), 2.32 (s, 3H), 2.65-2.75 (bs, 8H), 2.93 (t, 2H, J = 6.7 Hz), 2.91-3.09 (bs, 4H), 3.15-3.22 (m, 8H), 3.26-3.29 (m, 6H), 3.39-3.46 (m, 6H), 3.52 (s, 6H), 4.12-4.15 (m, 6H), 5.82 (bs, 1H, NH), 7.84 (bs, 1H, NH), 7.69 (bs, 1H, NH). ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.33, 14.40, 19.39, 25.84, 25.95, 28.49, 28.95, 28.97, 29.05, 29.12, 29.17, 29.37, 29.45, 30.86, 36.68, 36.82, 36.86, 39.19, 39.27, 39.37, 39.50, 39.62, 40.09, 55.32, 55.41, 56.54, 61.50, 61.54, 65.50, 69.58, 70.09, 70.17, 70.36, 70.93, 77.30, 172.07, 173.37, 173.70.

The selective hydrolysis of ester (0.24 g, 0.22 mmol) with LiOH.H_2O (60 mg, 1.43 mmol) in degassed MeOH/THF was crried out as described for **thiol 3**. Yield: 0.16 g (78%, white solid). ^{1}H NMR (500 MHz, DMSO-*d*$_6$, 100 ^{o}C) δ 1.23-1.28 (m, 12H), 1.32-1.36 (m, 4H), 1.43-1.58 (m, 8H), 2.07 (t, 4H, J = 7.4 Hz), 2.26 (t, 4H, J = 6.8 Hz), 2.54 (q, 2H, J = 7.2, 14.3 Hz), 2.76-2.88 (m, 4H), 2.89-3.11 (m, 8H), 3.12-3.17 (m, 2H), 3.19-3.23 (m, 6H), 3.28-3.36 (m, 2H), 3.40-3.45 (m, 6H), 3.49-3.60 (m, 9H), 3.64-3.67 (m, 2H), 5.76 (bs, 1H, NH), 7.37 (bs, 1H, NH), 7.55 (bs, 1H, NH). ^{13}C NMR (125 MHz, DMSO-*d*$_6$) δ 18.52, 23.52, 24.51, 24.56, 25.37, 28.36, 28.39, 28.83, 28.87, 29.01, 29.05, 29.24, 29.31, 33.47, 33.75, 35.50, 35.56, 37.57, 37.97, 37.99, 38.11, 38.54, 38.66, 42.01, 51.20, 61.34, 65.50, 69.06, 69.25, 69.65, 69.69, 77.86, 172.19, 172.75, 172.83. Anal. Calcd. for $C_{46}H_{79}N_7O_{11}S$.2THF: C, 59.95; H, 8.85; N, 9.06. Found: C, 60.36; H, 8.83; N, 8.83.

Thiol 5: The coupling of amine **10** (0.55 g, 0.55 mmol) and the thioester $CH_3S_2C(CH_2)_{11}COOH$ (0.15 g, 0.55 mmol, prepared following the procedure reported in: Finklea, H. O.; Ravenscroft, M. S.; Punturi, S. *J. Phys. Chem*. **1996**, *28*, 18851-18858) was carried out using BOP reagent (0.24 g, 0.55 mmol) in presence of Et_3N (0.23 mL, 1.65 mmol) in CH_3CN solvent (10 mL). The workup procedure was the same as described for **9**. Yield: 0.38 g (76%). ^{1}H NMR (400 MHz, $CDCl_3$-D_2O) δ 1.22-1.27 (m, 26H), 1.49-1.59 (m, 4H), 2.13 (t, 2H, J = 7.5 Hz), 2.30 (s, 3H), 2.83 (t, 2H, J = 7.5 Hz), 3.43 (t, 2H, J = 5.1 Hz), 3.50 (s, 8H), 3.55 (t, 2H, J = 5.1 Hz), 3.61 (m, 8H), 3.90 (s, 4H), 4.14 (q, 8H, J = 7.2 Hz), 7.48 (s, 1H), 7.83 (s, 2H).

The thioester and the ester groups were hydrolyzed (0.27 g, 0.29 mmol) with LiOH.H_2O (0.12 g, 2.86 mmol) in MeOH/THF solvent (5 mL/5mL). The workup procedure was the same as described for **thiol 1**. Yield: 0.18 g, 79% (white solid). ^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ 1.15-1.28 (m, 14H), 1.30-1.34 (m, 2H), 1.42-1.47 (m, 2H), 1.59-1.61 (m, 2H), 2.03 (t, 2H, J = 7.5 Hz), 2.67 (t, 2H, J = 7.5 Hz), 3.15-3.19 (m, 2H), 3.36-3.42 (m, 10H), 3.51-3.53 (m, 7H), 3.87 (s, 4H), 7.47 (s, 1H), 7.68 (s, 2H), 7.84 (t, 1H, J = 5.5 Hz, NH), 8.50 (t, 1H, J = 5.5 Hz, NH). ^{13}C NMR (125 MHz, DMSO-*d*$_6$) δ 25.95, 28.41, 28.19, 29.27, 29.34, 29.48, 29.58, 29.60, 35.96, 38.47, 39.09, 40.41, 54.15, 57.59, 69.59, 69.86, 70.22, 127.23, 132.50, 135.24, 139.58, 167.11, 172.92. Anal. Calcd for $C_{35}H_{56}N_4O_{12}S$: C, 55.54; H, 7.46; N, 7.40. Found: C, 55.24; H, 7.66; N, 7.59.