Supplementary Materials for

Polymerized Fluorescent Liposomes Incorporating Lanthanide Ions

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Experimental Details for the synthesis of lipid 1:

Compound 5: To a stirred solution of EDTA-triester-**3** (1.03 g, 2.66 mmol and Cbz-amine **4** (0.75 g, 2.66 mmol) in $CHCl_3$ (25 mL) was added BOP reagent (1.17 g, 2.66 mmmol) followed by the addition of Et_3N (0.8 mL, 5.75 mmol). The mixture was stirred for 10 h at room temperature. The reaction was then quenched with saturated solution of NaCl. The organic solvent was removed in vacuo. The product was extracted in ethyl acetate. Ethyl acetate layer was successively washed with 4% aq. citric acid, water, 4% aq. $NaHCO_3$ and water. The organic layer was dried over anhydrous Na_2SO_4 and then evaporated to obtain the crude product. Purification was achieved by silica gel column chromatography using $CHCl_3$/MeOH (9:1, R_f = 0.5) to afford **Cbz-EDTA** as a yellow viscous liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.22-1.24 (m, 9H), 2.62-2.89 (m, 4H), 3.33-3.37 (m, 4H), 3.42-3.46 (m, 4H), 3.52 (s, 8H), 3.56-3.58 (m, 4H), 4.10-4.13 (m, 6H), 5.08 (s, 2H), 5.58 (s, 1H), 7.32-7.34 (m, 5H), 8.14 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.41, 38.90, 41.07, 53.00, 55.00, 55.81, 58.65, 60.85, 60.99, 66.75, 69.98, 70.27, 70.47, 128.24, 128.28, 128.67, 136.84, 156.71, 171.36.

The Cbz-protected compound was dissolved in MeOH (40 mL) with 0.4 mL of conc. HCl. A small portion of Pd-black was added and hydrogen was bubbled through the solution at room temperature for 12 h. Pd-black was filtered off and solvent was removed in vacuo to give **5** (1.18 g, 93%, R_f = 0.2, 10% MeOH in $CHCl_3$) as a yellowish viscous liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.22 (t, 9H, J = 7.1 Hz), 2.73-2.80 (m, 4H), 3.19 (t, 2H, J = 4.8 Hz), 3.33-3.37 (m, 2H), 3.40 (s, 4H), 3.51 (s, 4H), 3.56-3.61 (m, 4H), 3.64-3.66 (m, 2H), 3.79 (t, 2H, J = 4.8 Hz), 4.12 (q, 6H, J = 7.1 Hz), 8.36 (bs, 1H).

Compound 6: 2,3-Diaminopropanoic acid (3.0 g, 21.43 mmol) and PTSA monohydrate (14.25 g, 75.00 mmol) were dissolved in dry MeOH and refluxed for 24 h. The solvent was removed under vacuo. The crude product was recrystallized with ether/EtOH. Yield: 8.5 g (74%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.34 (s, 6H), 3.45 (dd, 1H, J = 5.4 and 13.7 Hz), 3.58 (dd, 1H, J = 8.0 and 13.7 Hz), 3.83 (s, 3H), 4.48 (dd, 1H, J = 5.4 and 8.0 Hz), 7.27 (d, 4H, J = 8.2 Hz), 7.61 (d, 4H, J = 8.2 Hz).

Compound 7: To a stirred solution of **6** (2.0 g, 3.74 mmol) in 30 mL of dry $CHCl_3$ with Et_3N (3.1 mL, 22.3 mmol) was added acid (10,12-pentacosadiynoic acid, 2.89 g, 7.47 mmol) and BOP reagent (3.31 g, 7.47 mmol). The stirring was continued for 15 h at room temperature. Work up procedure was the same as **5** (Cbz-EDTA). The solvent was then evaporated in vacuo and compound **7** (3.0 g, 96%) was obtained as a gray-white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.87 (t, 6H, J = 7.0 Hz) 1.21-1.38 (m, 52H), 1.48-1.52 (m, 8H), 1.58-1.62 (m, 4H), 2.16 (t, 2H, J = 7.7 Hz), 2.21-2.25 (m, 10H), 3.61-3.66 (m, 2H), 3.76 (s, 3H), 4.58-4.60 (m, 1H), 6.01 (bs, 1H),

6.73 (d, 1H, J = 6.7 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.37, 19.41, 19.42, 19.43, 22.92, 25.69, 25.83, 28.52, 28.54, 28.58, 28.99, 29.01, 29.09, 29.15, 29.17, 29.34, 29.36, 29.39, 29.58, 29.71, 29.84, 29.86, 29.88, 32.15, 36.63, 36.75, 41.87, 52.99, 53.76, 65.41, 65.42, 65.50, 65.52, 77.64, 77.67, 77.83, 77.86, 170.97, 174.07, 174.95.

A solution of $LiOH.H_2O$ (0.15 g, 3.57 mmol) in H_2O was added to a solution of **7** (2.0 g, 2.40 mmmol) in MeOH/THF/CH_2Cl_2 (20: 10:10). The mixture was then stirred at 40 ^oC for 24 h, then 30 mL of water was added in the solution and acidified (pH = 3.0) with 1 N HCl. The organic solvents were removed under vacuo. The solid was filtered and washed with water. Yield: 1.9 g (97%). ^{1}H NMR (500 MHz, $CDCl_3$-DMSO-d_6) δ 0.89 (t, 6H, J = 7.0 Hz), 1.22-1.39 (m, 52H), 1.43-1.54 (m, 12H), 2.07 (t, 2H, J = 7.4 Hz), 2.13 (t, 2H, J = 7.4 Hz), 2.27 (t, 8H, J = 6.9 Hz), 3.35-3.42 (m, 2H), 4.47-4.49 (m, 1H), 7.73 (bs, 1H). ^{13}C NMR (125 MHz, $CDCl_3$-DMSO-d_6) δ 13.87, 18.35, 22.08, 25.10, 25.15, 27.72, 27.77, 28.17, 28.23, 28.37, 28.39, 28.42, 28.58, 28.69, 28.86, 28.95, 28.99, 31.28, 35.29, 35.39, 65.28, 77.04, 77.42, 77.45, 177.35, 177.58, 178.13.

Lipid 1: The acid **7** (0.5 g, 0.61 mmol) was coupled with the amine **5** (0.33 g, 0.61 mmol) in presence of BOP reagent (0.27 g, 0.61 mmol) in DMF-$CHCl_3$ mixture (1:9, 15 mL) as the solvent. The work up procedure is the same as described for **5** (Cbz-EDTA). The crude product was purified by silica gel column chromatography with 5% MeOH in $CHCl_3$ (R_f = 0.4) as the eluant to afford the pure product as a waxy solid (88%). ^{1}H NMR (500 MHz, $CDCl_3$-CD_3OD) δ 0.89 (t, 6H, J = 7.0 Hz), 1.22-1.35 (m, 53H), 1.38-1.42 (m, 8H), 1.45-1.54 (m, 8H), 1.57-1.62 (m, 4H), 2.18 (t, 2H, J = 7.7 Hz), 2.22-2.25 (m, 10H), 2.78-2.87 (m, 4H), 3.36-3.39 (m, 2H), 3.42-3.48 (m, 4H), 3.52-3.54 (m, 4H), 3.58-3.62 (m, 12H), 4.16 (q, 6H, J = 7.0 Hz), 4.46-4.48 (m, 1H), 7.78 (bs, 1H), 7.95 (bs, 1H), 8.03 (bs, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.36, 14.47, 19.41, 19.42, 22.91, 25.73, 25.88, 28.54, 28.55, 28.57, 29.03, 29.09, 29.18, 29.33, 29.42, 29.43, 29.45, 29.49, 29.71, 29.84, 29.85, 29.87, 32.14, 36.74, 39.05, 39.50,, 42.50, 52.43, 53.01, 55.02, 55.93, 58.77, 60.84, 60.92, 65.41, 65.42, 65.49, 65.51, 69.79, 69.99, 70.38, 70.63, 77.48, 77.63, 77.65, 77.81, 77.83, 170.36, 171.40, 171.50, 172.13, 174.52, 175.40.

A solution of $LiOH.H_2O$ (53 mg) in 2 ml of water was added to the solution of the ester (0.3 g, 0.23 mmol) in THF-MeOH (5/2 mL). The reaction was continued for 10 h at room temperature. Another 10 mL of water was added there and acidified with 1 N HCl (pH = 3.0). The white solid was filtered and washed with plenty of water. Yield: 0.22 g (77%). ^{1}H NMR (500 MHz, DMSO-d_6) δ 0.85 (m, 6H, J = 7.0 Hz), 1.22-1.35 (m, 52H), 1.40-1.46 (m, 12H), 2.03 (t, 2H, J = 7.6 Hz), 2.09 (t, 2H, J = 7.3 Hz), 2.25 (t, 8H, J = 6.8 Hz), 2.69-2.71 (m, 2H), 2.73-2.75 (m, 2H), 3.22-3.28 (m, 8H), 3.36 (s, 2H), 3.38-3.43 (m, 8H), 3.50 (s, 4H), 4.27-4.31 (m, 1H), 7.62 (bs, 1H), 7.69 (bs, 1H), 7.76 (bs, 1H), 7.96 (bs, 1H). ^{13}C NMR (125 MHz, $CDCl_3$-CD_3OD) δ 14.30, 19.37, 22.88, 25.74, 25.89, 28.56, 29.07, 29.21, 29.30, 29.44, 29.48,, 29.54, 29.68, 29.81, 29.82, 29.84, 31.12, 32.10, 36.45, 36.50, 36.56, 39.12, 39.31, 41.54, 50.93, 52.40, 54.37, 56.30, 57.01, 65.38, 65.47, 69.44, 69.52, 70.08, 70.14, 77.58, 77.80, 170.72, 170.95, 175.08, 175.95. Anal. Calcd. for $C_{69}H_{116}N_6O_{12}$: C, 67.84; H, 9.57; N, 6.88. Found: C, 68.10; H, 9.70; N, 6.52.

Complex 1.Tb^{3+}: Lipid **1** (80 mg, 0.064 mmol) was dissolved in $CHCl_3$-MeOH (10 mL, 1:9) and a solution of $TbCl_3.6H_2O$ (24 mg, 0.064 mmol) in MeOH (5 mL) was added. The resulting clear solution was stirred at room temperature for 12 h and the solvents were removed in vacuo to obtain a white solid. This solid was finely grounded and washed repeatedly with ether and then dried to afford the complex. Anal. Calcd. for $C_{69}H_{113}N_6O_{12}.Tb^{3+}.3H_2O$: C, 57.83; H, 8.31; N, 5.86. Found: C, 58.12; H, 8.38; N, 5.61.

Fluorescence spectra for Tb^{3+} and EDTA-Tb^{3+} (10 mM each, 50 mM HEPES buffer, pH = 8.0):