Photophysical Properties of Newkome-Type Dendrimers in Aqueous Medium

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All chemicals were reagent grade. Tetrahydrofuran (THF) used was freshly distilled from sodium-benzophenone. Column chromatography was performed on silica gel (100-200 mesh) while TLC was performed on aluminium- backed plates coated with 0.25 mm silica gel.

Synthesis of *N-Tris* {[2-(*tert*-butoxy carbonyl)ethoxy] methyl}-methyl-}-4-pyren-1yl-butyramide (1GB): To a solution of 4-(1-Pyrene)butyric acid (318 mg, 1.1 mmol) in THF (5 mL) was added HOBt (149 mg, 1.1mmol). The reaction mixture was stirred for 5 min. after which Et_3N (153 μL, 1.1 mmol) was added followed by EDCl (210 mg, 1.1 mmol). *tris*[2-(*tert*-butoxycarbonyl) ethoxy]methyl}-methylamine (505 mg, 1 mmol) was added drop wise to the reaction mixture. The reaction mixture was then allowed to stir at room temperature. After the completion of reaction the THF was removed under vacuum and the crude mass was diluted with ethyl acetate (10 mL). The organic layer was then washed successively with 0.5 M HCl (5 mL) and saturated brine solution (5 mL). The organic layer was separated, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to yield the crude compound which was purified over silica gel using gradient elution of 20-30% EtOAc in hexane to afford the pure compound (600 mg) in 77 % yield. **IR** (neat): 3392, 2998, 1721, 1657, 1257 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 1.2 (s, 9H), 2.10 (bs, 4H), 3.27 (t, *J* = 6.9 Hz, 2H), 5.15 (s, 1H), 7.16-8.20 (m, 9H). **^{13}C NMR** ($CDCl_3$, 100MHz) δ 27.5, 28.3, 32.6, 36.8, 51.2, 123.4, 124.7, 124.9, 125.0, 125.1, 125.9, 126.7, 127.3, 127.4, 127.5, 128.8, 129.9, 130.9, 136.0, 172.0. MS (LRMS): 344 (M+1), 343 (M^+)

Synthesis of *N-Tris* {[2-(carboxyethoxy] methyl}-methyl-}-4-pyren-1yl-butyramide (1GA) : The amide1GB (0.30 g, 0.38 mmol) was stirred in 10 mL of 96% formic acid for 24 hrs. Then the formic acid was removed at reduced pressure to produce the titled compound in quantitative yield. **IR** (neat): 3344, 3056, 2912, 1728, 1628, 1523, 1264,

1196, 1113, 1065, 844 cm^{-1}; **^{1}H NMR** (CD_3COCD_3, 400 MHz): δ 2.08 - 2.13 (m, 2H), 2.34 (t, *J* = 6.8 Hz, 2H), 2.55 (t, *J* = 6.3 Hz, 6H), 3.72 (t, *J* = 6.3 Hz, 6H), 3.8 (s, 6H), 6.6 (bs, 1H), 7.96 – 8.47 (m, 9H); **^{13}C NMR** (CD_3COCD_3, 100 MHz): δ 28.6, 33.3, 35.2, 36.8, 60.7, 67.7, 69.9, 124.6, 125.6, 125.7, 125.8, 125.9, 126.8, 127.4, 128.1, 128.4, 128.5, 129.6, 130.7, 131.9, 132.3, 137.8, 173.0, 173.3; MS (ESI): *m/z* 608 $(M+1)^+$.

Synthesis of *N*-Tris[(2-{[(tris{[2-(*tert*-butoxycarbonyl)ethoxy]methyl}-methyl)amino]- carbonyl} ethoxy) methyl] methyl }-4-pyren-1yl-butyramide (2GB): To a solution of 4-(1-Pyrene)butyric acid (58 mg, 0.2 mmol) in dry THF (1mL) was added EDCl (46 mg, 0.2 mmol), HOBt (27 mg, 0.2 mmol) and Et_3N (34 μL, 0.2 mmol). To the stirred solution at rt was added *N*-Tris-[(2-{[(tris{[2-(*tert*-butoxycarbonyl)-ethoxy]methyl}-methyl)amino] carbonyl}ethoxy)-methyl]methylamine (360 mg, 0.2 mmol) dissolved dry THF (3 mL). The reaction was stirred at room temperature and after the completion of reaction, as indicated by TLC, THF was removed under vacuum and the reaction mixture was diluted with EtOAc (10 mL), washed with water (5 mL), 0.5M HCl solution (5 mL) and then with saturated solution of brine (5 mL). The organic layer was separated, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to yield the crude compound, which was purified over silica gel using 50-80 % gradient elution of EtOAc in hexane to yield the pure pyrene attached dendrimer, tetraamide 2 (200 mg) in 48% yield. **IR** (neat): 3440, 2912, 1728, 1667, 1523, 1369, 1257 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 1.42 (s, 81H); 2.20 - 2.44 (m, 28H); 3.57 - 3.75 (m, 52H); 6.35 (bs, 3H); 7.72 – 8.30 (m, 9H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 27.9, 28.0, 36.0, 37.0, 59.8, 60.0, 60.3, 67.0, 67.4, 69.0, 80.4, 123.4, 124.6, 124.7, 124.8, 124.9, 125.0, 125.6, 125.7, 126.4, 127.2, 127.3, 127.4, 128.6, 129.7, 136.1, 170.8, 171.0, 173.1. MALDI-TOF MS (α-cyano-4-hydroxycinnamic acid matrix): 2069.11 (M^+, calcd. 2069.35), 2092.89 $(M + Na)^+$, 2108.79 $(M + K)^+$. This procedure has already been reported in reference 19: (S. K. Mohanty, T. Shyamala, S. Baskaran and A. K. Mishra, *Macromolecules*, 2004, 37, 5364).

Synthesis of *N-Tris*[(2-{[(*tris*{[2carboxyethoxy]methyl}-ethyl)amino]- carbonyl} ethoxy) methyl] methyl }-4-pyren-1yl-butyramide (2GA) : The amide 2GB (140 mg,

0.07 mmol) was stirred in 10 mL of 96% formic acid for 24 h. Then the formic acid was removed at reduced pressure to produce the titled compound in quantitative yield. **IR** (neat): 3230, 2912, 1720, 1667, 1530, 1375, 1280 cm^{-1}; **^{1}H NMR** (CD_3COCD_3, 400 MHz): δ 2.20 - 2.44 (m, 28H), 3.57 - 3.75 (m, 52H), 6.35 (bs, 3H), 7.72 – 8.30 (m, 9H); **^{13}C NMR** (CD_3COCD_3, 100 MHz): δ 28.0, 36.0, 37.0, 60.0, 60.3, 67.0, 67.4, 69.0, 80.4, 123.4, 124.6, 124.7, 124.8, 124.9, 125.0, 125.6, 125.7, 126.4, 127.2, 127.3, 127.4, 128.6, 129.7, 136.1, 170.8, 171.0; **MS** (ESI): *m/z* 1565 $(M+1)^+$.

Synthesis of *N Tris*({2-{({tris[(2-{[(tris{[2-(*tert*-butoxy carbonyl)ethoxy]methyl}methyl)amino]carbonyl}-ethoxy) methyl]methyl}amino)carbonyl]ethoxy}methyl)methyl-}-4-pyren-1yl-butyramide (3GB): To a solution of 4-(1-Pyrene)butyric acid (35 mg, 0.12 mmol) in THF (5 mL) was added HOBt (17 mg, 0.12 mmol). The reaction mixture was stirred for 5 min. after which Et_3N (20 µL, 0.12 mmol) was added followed by EDCl (23 mg, 0.12 mmol). Tris({2-({[*tris{*[2-(*tert*-butoxycarbonyl) ethoxy] methyl}- ethylamino] carbonyl} ethoxy}methyl}amino} carbonyl} ethoxy }methyl) methylamine (700 mg, 0.12 mmol) was added drop wise to the reaction mixture. The reaction mixture was then allowed to stir at room temperature. After the completion of reaction the THF was removed under vacuum and the crude mass was diluted with ethyl acetate (10 mL). The organic layer was then washed successively with 0.5 M HCl (5 mL) and saturated brine solution (5 mL). The organic layer was separated, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to yield the crude compound which was purified over silica gel using first 100 % EtOAc and then 10 % MeOH in EtOAc to afford the pure compound (350 mg) in 48 % yield. **IR** (neat): 3392, 2998, 1721, 1657, 1257 cm^{-1}; **^{1}H NMR** (CDCl3, 400 MHz): δ 1.2 (s, 9H), 2.10 (bs, 4H), 3.27 (t, J = 6.9 Hz, 2H), 5.15 (s, 1H), 7.16-8.20 (m, 9H). **^{13}C NMR** (CDCl3, 100 MHz) δ 27.5, 28.3, 32.6, 36.8, 51.2, 123.4, 124.7, 124.9, 125.0, 125.1, 125.9, 126.7, 127.3, 127.4, 127.5, 128.8, 129.9, 130.9, 136.0, 172.0. MS (LRMS): 344 (M+1), 343 (M+).

Synthesis of *N Tris*({2-{({*tris*[(2-{[(*tris*{[2-(carboxyethoxy] methyl} methyl) amino] carbonyl} - ethoxy) methyl] methyl} amino) carbonyl]ethoxy}methyl)methyl -}-4-pyren-1yl-butyramide (3GA): The amide 3GB (400 mg, 0.067 mmol) was stirred in 10

mL of 96% formic acid for 48 h. Then the formic acid was removed at reduced pressure to produce the titled compound in quantitative yield. **IR** (neat): 3200, 2960, 1718, 1644, 1548, 1459, 1404, 1267 cm^{-1}**; ^{1}H NMR** (DMSO d_6, 400 MHz): δ 2.42 – 2.53 (m, 82H), 3.61 - 3.68 (m, 158H), 5.02 (m, 2H), 6.22 – 6.30 (m, 10H), 6.71 (bs, 3H), 7.72 – 8.30 (m, 9H); **^{13}C NMR** (DMSO d_6, 100 MHz): δ 30.6, 35.3, 54.9, 61.0, 61.1, 67.8, 69.8, 123.4, 124.6, 124.7, 124.8, 124.9, 125.0, 125.6, 125.7, 126.4, 127.2, 127.3, 127.4, 128.6, 129.7, 136.1, 162.5, 170.8, 171.0, 173.2; **MALDI-TOF MS** (α-cyano-4-hydroxycinnamic acid matrix): *m/z* 4442 $(M)^+$.

The synthesis of ***N-Tris*[(2-{[(*tris*{[2-(ethoxycarbonyl) ethoxy]methyl}-methyl) amino]- carbonyl }ethoxy) methyl] methyl }-4-pyre-1yl-butyramide (2GE)** has already been reported in reference 19: (S. K. Mohanty, T. Shyamala, S. Baskaran and A. K. Mishra, *Macromolecules*, 2004, **37**, 5364).