A Folded, Secondary Structure in Step-Growth Oligomers from Covalently Linked, Crowded Aromatics. Supporting Information

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General. Reagents employed were either commercially available or prepared according to a known procedure as noted below. Anhydrous and oxygen-free CH_2Cl_2 and Et_2O were obtained from a Schlenk manifold with purification columns packed with activated alumina and supported copper catalyst (Glass Contour, Irvine, CA).[1] Unless otherwise noted, all reactions were run in oven-dried glassware. Column chromatography was performed on a CombiFlash® Sg100c system using RediSep™ normal phase silica columns (ISCO, Inc., Lincoln, NE). ^{1}H NMR (300, 400 or 500 MHz) and ^{13}C NMR (75, 100 or 125 MHz) spectra were recorded on a Bruker DRX-300, 400 or 500 spectrometer. Infrared spectra were obtained using KBr pellets or NaCl plates on a Perkin-Elmer Paragon 1000 FT-IR spectrometer.

Mass spectroscopy. High- or low-resolution fast atom bombardment mass spectroscopy was performed using a JMS HX110A Tandem mass spectrometer (JEOL Ltd., Tokyo, Japan). Acceleration voltage: 10 kV; ionization beam: 6 kV Xe; matrix: 3-nitrobenzyl alcohol.

Low-resolution matrix-assisted laser desorption ionization mass spectroscopy were performed on a Voyager DE-PRO mass spectrometer (AB Biosystems, Framingham, MA). Acceleration voltage: 20 kV; matrix: dithranol-THF.

General procedure 1, alkylation. To a 50 ml dry flask outfitted with a magnetic stir bar was added anhydrous K_2CO_3 (2.76 g, 20.0 mmol), KI (332 mg, 2.00 mmol), *N*-Boc 3-bromopropylamine (4.76 g, 20.0 mmol) and the aromatic diol (5.00 mmol). The flask was then degassed and flushed with dry nitrogen. DMF (25 ml) was added through a syringe and the reaction mixture was stirred vigorously at 50 °C for 24 h. The resulting slurry, after cooled to room temperature, was poured into water (25 ml) and extracted with EtOAc (2 × 50 ml). The combined organic layers were successively washed with water (3 × 25 ml) and brine, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica gel chromatography or recrystallization.

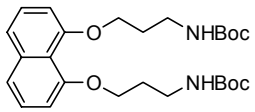
General procedure 2, Boc-deprotection. To a 10 ml dry flask outfitted with a magnetic stir bar and a drying tube was added the di-Boc-protected diamine (0.500 mmol) and hydrogen bromide in acetic acid (30%wt., 2.5 ml). The slurry was stirred vigorously at room temperature for 2 h. Anhydrous Et_2O (7 ml) was added to precipitate the product. Filtration and washing with anhydrous Et_2O yielded the desired diamine dihydrobromide.

General procedure 3, coupling through acid chloride. To a 50 ml dry flask outfitted with a magnetic stir bar and a condenser was added methyl 3,5-dicarboxyl-2,4,6-tris(dodecyloxy)benzoate **5** (1.55 g, 2.00 mmol), CH_2Cl_2 (10 ml) and $SOCl_2$ (0.87 ml, 12 mmol). The reaction mixture was stirred and refluxed under a nitrogen atmosphere for 2 h. Then volatiles were distilled off under reduced pressure. To the light-brown oily residue under nitrogen was added successively CH_2Cl_2 (10 ml) and a solution of Et_3N (0.83 ml, 6.0 mmol) and the primary amine (4.4-8.0 mmol) in CH_2Cl_2 (10 ml). After 3 h of stirring at room temperature the resulting solution was diluted with CH_2Cl_2 (25 ml) and poured into 30 ml of water. The separated aqueous layer was extracted with CH_2Cl_2 (2 × 40 ml) and the combined organic phases were washed with water and brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by silica gel chromatography.

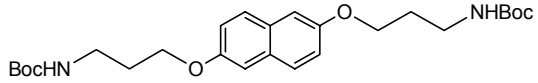
General procedure 4, double peptide coupling. To a 10 ml dry flask outfitted with a magnetic stir bar was added the carboxylic acid (50.0 μmol), diamine dihydrobromide (25.0 μmol), 1-hydroxy-7-azabenzotriazole (6.8 mg, 50 μmol), DMAP (16.5 mg, 135 μmol), CH_2Cl_2 (1.5 ml) and DMF (0.4 ml). Then, with stirring, a solution of EDC hydrochloride (10.6 mg, 55.0 μmol) in CH_2Cl_2 (0.6 ml) was added. The homogeneous or heterogeneous reaction mixture was stirred under a nitrogen atmosphere at room temperature overnight. As below, the residue was treated by the following methods.

(a) CH_2Cl_2 was evaporated off the heterogeneous reaction mixture under reduced pressure. Hot DMF was added to just dissolve the residue. The resulting solution was slowly cooled to room temperature and further to 0 °C. The precipitant was filtrated out and washed with ice-cold DMF.

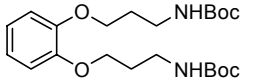
(b) The homogeneous reaction mixture was diluted with CH_2Cl_2 (8 ml) and poured into water (10 ml). The separated aqueous layer was extracted with CH_2Cl_2 (15 ml) and the combined organic layers were washed with water (3 × 10 ml) and brine (5 ml), dried over $MgSO_4$ and concentrated under reduced pressure. The residue was subject to silica gel chromatography.



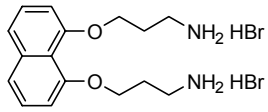
1,8-Bis(*N*-Boc-3-aminopropoxy)naphthalene was prepared according to general procedure 1 from 1,8-dihydroxynaphthalene[2] (800 mg, 5.00 mmol). Silica gel chromatography (EtOAc-CH_2Cl_2, 2% to 9%) yielded the title compound as pale yellow crystals (2.02 g, 85%). Rf 0.25 (9% EtOAc-CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40-7.31 (m, 4H), 6.81 (d, J = 7.2 Hz, 2H), 5.62 (br, 2H), 4.22 (t, J = 5.4 Hz, 4H), 3.38 (m, 4H), 2.12 (m, 4H), 1.39 (s, 18H) ppm.



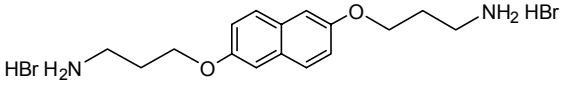
2,6-Bis(*N*-Boc-3-aminopropoxy)naphthalene was prepared from 2,6-dihydroxynaphthalene (800 mg, 5.00 mmol) through a method analogous to general procedure 1 except using CH_2Cl_2 instead of EtOAc upon extraction. Recrystallization form EtOAc yielded white crystals (1.78 g, 75%). ^{1}H NMR (300 MHz, $CDCl_3$) 7.61 (d, J = 8.7 Hz, 2H), 7.11 (m, 4H), 4.79 (br, 2H), 4.11 (t, J = 6.0 Hz, 4H), 3.36 (m, 4H), 2.03 (m, 4H), 1.45 (s, 18H).



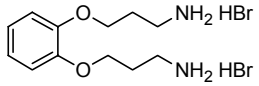
1,2-Bis(*N*-Boc-3-aminopropoxy)benzene was prepared according to general procedure 1 from catechol (550 mg, 5.00 mmol). Silica gel chromatography (13% to 33% EtOAc-hexanes) yielded white crystals (1.15 g, 54%). Rf 0.45 (43% EtOAc-hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) 6.90 (m, 4H), 5.24 (br, 2H), 4.08 (t, J = 5.8 Hz, 4H), 3.36 (m, 4H), 2.02 (m, 4H), 1.44 (s, 18H).



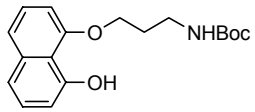
1,8-Bis(3-aminopropoxy)naphthalene dihydrobromide was prepared according to general procedure 2 from 1,8-bis(*N*-Boc-3-aminopropoxy)naphthalene as an off-white powder (201 mg, 92%). ^{1}H NMR (400 MHz, DMSO-d_6) 7.86 (br, 6H), 7.42 (m, 4H), 6.96 (dd, J = 1.1, 7.4 Hz, 2H), 4.18 (t, J = 6.2 Hz, 4H), 3.09 (m, 4H), 2.13 (m, 4H). ^{13}C NMR (75 MHz, DMSO-d_6) 157.3, 138.6, 128.3, 122.3, 118.8, 109.2, 67.6, 38.5, 29.0. IR (KBr) 3435, 3042, 2942, 1585, 1508, 1477, 1284 cm^{-1}. HRMS (FAB; M+H$^+$) calcd for $C_{16}H_{23}O_2N_2$ 275.1760; found 275.1739.



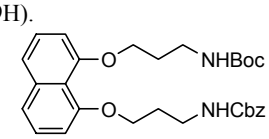
2,6-Bis(3-aminopropoxy)naphthalene dihydrobromide was prepared according to general procedure 2 from 2,6-bis(*N*-Boc-3-aminopropoxy)naphthalene as an off-white powder (210 mg, 96%). ^{1}H NMR (500 MHz, DMSO-d_6) 7.86 (br, 6H), 7.74 (d, J = 8.9 Hz, 2H), 7.29 (d, J = 1.7 Hz, 2H), 7.16 (d, J = 8.9 Hz, 2H), 4.16 (t, J = 5.9 Hz, 4H), 3.02 (m, 4H), 2.09 (m, 4H). ^{13}C NMR (75 MHz, DMSO-d_6) 155.5, 130.3, 129.0, 119.8, 108.0, 65.5, 37.2, 27.7. IR (KBr) 3431, 3002, 2929, 2878, 1604, 1508, 1466, 1233. HRMS (FAB; M+H$^+$) calcd for $C_{16}H_{23}O_2N_2$ 275.1760; found 275.1743.



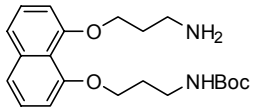
1,2-Bis(3-aminopropoxy)benzene dihydrobromide was prepared according to general procedure 2 from 1,2-bis(*N*-Boc-3-aminopropoxy)benzene dihydrobromide as a yellowish-grey solid (164 mg, 85%). ^{1}H NMR (500 MHz, DMSO-d_6) 7.84 (br, 6H), 7.01 (m, 2H), 6.93 (m, 2H), 4.07 (t, J = 6.1 Hz, 4H), 2.99 (m, 4H), 2.03 (m, 4H). ^{13}C NMR (75 MHz, DMSO-d_6) 149.8, 123.1, 116.0, 67.7, 38.5, 29.0. IR (KBr) 3369, 3108, 3009, 2932, 1595, 1512, 1472, 1261, 1120, 740. HRMS (FAB; M+H$^+$) calcd for $C_{12}H_{21}O_2N_2$ 225.1603; found 225.1619.



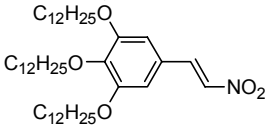
1-(*N*-Boc-3-aminopropoxy)-8-hydroxynaphthalene. To a 100 ml dry flask outfitted with a magnetic stir bar was added anhydrous K_2CO_3 (2.76 g, 20.0 mmol), KI (332 mg, 2.00 mmol), *N*-Boc-3-bromopropylamine (2.62 g, 11.0 mmol) and 1,8-dihydroxynaphthalene (1.60 g, 10.0 mmol). The flask was then degassed and flushed with dry nitrogen. DMF (50 ml) was added through a syringe and the reaction mixture was stirred vigorously at 50 °C for 24 h. The resulting slurry, after cooled to room temperature, was poured into water (50 ml) and extracted with EtOAc (2 × 100 ml). The combined organic layers were successively washed with water (3 × 50 ml) and brine, dried over $MgSO_4$ and concentrated under reduced pressure. Silica gel chromatography (EtOAc-CH_2Cl_2, 0% to 2%) yielded the title compound as a white solid (2.25 g, 71%). Rf 0.7 (9% EtOAc-CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$) 9.37 (s, 1H), 7.33 (m, 4H), 6.86 (dd, J = 1.5, 7.3 Hz, 1H), 6.75 (d, J = 7.6 Hz, 1H), 4.76 (br, 1H), 4.26 (t, J = 6.3 Hz, 2H), 3.34 (m, 2H), 2.12 (m, 2H), 1.43 (s, 9H).



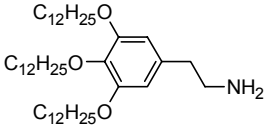
1-(*N*-Boc-3-aminopropoxy)-8-(*N*-Cbz-3-aminopropoxy) naphthalene. To a 25 ml dry flask outfitted with a magnetic stir bar was added anhydrous K_2CO_3 (697 mg, 5.05 mmol), KI (84 mg, 0.51 mmol), *N*-Cbz-3-bromopropylamine[3] (1.37 g, 5.05 mmol) and 1-(*N*-Boc-3-aminopropoxy)-8-hydroxynaphthalene (800 mg, 2.52 mmol). The flask was then degassed and flushed with dry nitrogen. DMF (13 ml) was added through a syringe and the reaction mixture was stirred vigorously at 55 °C for 36 h. The resulting slurry, after cooled to room temperature, was poured into water (15 ml) and extracted with EtOAc (2 × 30 ml). The combined organic layers were successively washed with water (3 × 15 ml) and brine, dried over $MgSO_4$ and concentrated under reduced pressure. Silica gel chromatography (28% EtOAc-hexanes) yielded the title compound as an off-white solid (1.08 g, 84%). Rf 0.3 (38% EtOAc-hexanes). ^{1}H NMR (500 MHz, CD_2Cl_2) 7.37 (m, 9H), 6.87 (d, J = 7.3 Hz, 1H), 6.78 (d, J = 7.4 Hz, 1H), 6.06 (br, 1H), 5.54 (br, 1H), 5.06 (s, 2H), 4.27 (t, J = 5.3 Hz, 2H), 4.12 (t, J = 5.4 Hz, 2H), 3.47 (m, 2H), 3.34 (m, 2H), 2.19 (m, 2H), 2.07 (m, 2H), 1.40 (s, 9H).



1-(3-Aminopropoxy)-8-(*N*-Boc-3-aminopropoxy) naphthalene. To a 50 ml dry flask outfitted with a magnetic stir bar was added palladium on activated carbon (10%wt., 200 mg, 0.188 mmol). The flask was then degassed and flushed with dry hydrogen. 1-(*N*-Boc-3-aminopropoxy)-8-(*N*-Cbz-3-aminopropoxy) naphthalene (958 mg, 1.88 mmol), dissolved in EtOAc (19 ml), was added through a syringe and the reaction mixture was stirred vigorously under a hydrogen atmosphere at room temperature for 6 h. The resulting mixture was filtered and concentrated under reduced pressure. Silica gel chromatography (100% EtOAc and then 50% MeOH-CH_2Cl_2) yielded the title compound as a thick, brownish-yellow semi-solid (472 mg, 67%). ^{1}H NMR (300 MHz, CD_2Cl_2) 7.38 (m, 4H), 6.86 (m, 2H), 6.26 (br, 1H), 4.19 (m, 4H), 3.40 (m, 2H), 3.02 (m, 2H), 2.10 (m, 4H), 1.60 (br, 2H), 1.42 (s, 9H). ^{13}C NMR (75 MHz, CD_2Cl_2) 157.0, 156.6, 156.5, 137.8, 126.8, 126.7, 120.8, 120.7, 117.8, 106.9, 106.6, 78.6, 67.9, 67.6, 40.0, 39.5, 33.1, 29.6, 28.6. IR (NaCl, neat) 3373, 3233, 3056, 2931, 2872, 1694, 1574, 1520, 1472, 1454, 1385, 1170. HRMS (FAB; M+H$^+$) calcd for $C_{21}H_{31}O_4N_2$ 357.2284; found 375.2308.

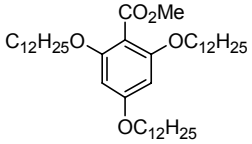


1-(2-Nitrovinyl)-3,4,5-tris(dodecyloxy)benzene. To a 250 ml dry flask outfitted with a magnetic stir bar and a condenser was added 3,4,5-tris(dodecyloxy)benzaldehyde[4] (18.2 g, 27.7 mmol), ammonium acetate (6.39 g, 83.0 mmol) and nitromethane (80 ml). The reaction mixture was stirred vigorously and refluxed overnight under a nitrogen atmosphere. The resulting mixture, after cooled to room temperature, was poured into water (200 ml) and extracted with Et_2O (3 × 250 ml). The combined organic layers were successively washed with water (2 × 150 ml) and brine, dried over $MgSO_4$, and concentrated under reduced pressure. Silica gel chromatography (4% Et_2O-hexanes) yielded the title compound as a bright-yellow solid (14.0 g, 72%). Rf 0.48 (13% Et_2O-hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) 7.90 (d, J = 13.6 Hz, 1H), 7.50 (d, J = 13.6 Hz, 1H), 6.72 (s, 2H), 4.01 (m, 6H), 1.78 (m, 6H), 1.47 (m, 6H), 1.27 (m, 48H), 0.88 (m, 9H).

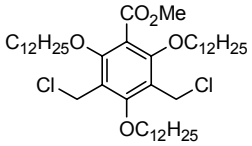


3,4,5-Tris(dodecyloxy)benzeneethanamine. To a 500 ml dry flask outfitted with a magnetic stir bar was added $LiAlH_4$ (1.95 g, 51.3 mmol). The flask was then degassed and flushed with dry nitrogen. Anhydrous Et_2O (80 ml) was added through a syringe.

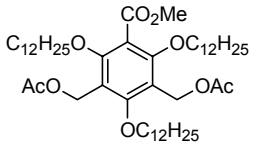
Then, with stirring, a solution of 1-(2-nitrovinyl)-3,4,5-tris(dodecyloxy)benzene (12.0 g, 17.1 mmol) in anhydrous Et_2O (190 ml) was added through a syringe at 0 °C. The reaction mixture was stirred vigorously at room temperature overnight. The resulting mixture was cooled to 0 °C and water (100 ml) was slowly added with extreme care. Then saturated aqueous NaOH (100 ml) was added. The two phases was separated and the aqueous layer was extracted with Et_2O (4 × 150 ml). The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. Silica gel chromatography (4% to 20% MeOH-CH_2Cl_2) yielded the title compound as an off-white waxy solid (7.4 g, 64%). ^{1}H NMR (400 MHz, $CDCl_3$) 6.38 (s, 2H), 3.93 (m, 6H), 2.94 (t, J = 6.8 Hz, 2H), 2.65 (t, J = 6.7 Hz, 2H), 1.76 (m, 6H), 1.26-1.46 (m, 56H), 0.88 (m, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) 152.7, 136.4, 134.3, 107.1, 73.3, 69.1, 43.3, 39.7, 32.0, 30.5, 29.8, 29.6, 29.5, 26.3, 22.8, 14.3. IR (KBr) 3350, 2921, 2852, 1589, 1507, 1468, 1380, 1238, 1121. HRMS (FAB; M+H$^+$) calcd for $C_{44}H_{84}O_3N$ 674.6451; found 674.6455.



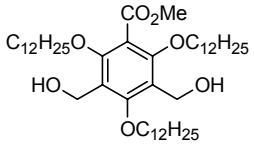
Methyl 2,4,6–tris(dodecyloxy)benzoate (2). 1-Bromododecane (46.0 ml, 192 mmol) was added to a stirred solution of methyl 2,4,6–trihydroxybenzoate (10.9 g, 60.0 mmol), potassium carbonate (53.0 g, 384 mmol) and DMF (60 ml) in a 300 ml dry round bottom flask. The suspension was stirred vigorously under a nitrogen atmosphere at 70º for 12 h. After the reaction mixture was cooled it was poured into 1000 ml diethyl ether, washed with water (3 × 200 ml) and brine (100 ml), dried over magnesium sulfate and concentrated under reduced pressure. Silica gel chromatography (3% diethyl ether-hexanes) yielded a colorless oil (32.7 g, 79%). Rf 0.5 (11% Et_2O-hexanes). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.06 (s, 2H), 3.92 (m, 6H), 3.84 (s, 3H), 1.73 (m, 6H), 1.26 (m, 54H), 0.88 (m, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) 167.4, 162.3, 158.4, 107.0, 92.5, 69.2, 68.9, 68.6, 52.3, 32.3, 30.9, 30.56, 30.0, 29.8, 29.6, 29.5, 26.4, 26.3, 23.1, 14.5. IR (NaCl, neat) 2924, 2854, 1733, 1610, 1497, 1467, 1436, 1385. HRMS (FAB; M+H$^+$) calcd for $C_{44}H_{81}O_5$ 689.6084; found 689.6060.



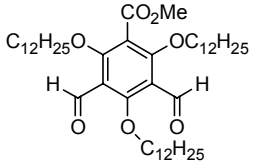
Methyl 3,5-bis(chloromethyl)-2,4,6–tris(dodecyloxy) benzoate (3). To methyl 2,4,6-tris(dodecyloxy)benzoate (17.7 g, 25.7 mmol) and anhydrous zinc chloride (6.98 g, 51.3mmol) in a 100 ml dry flask equipped with a stirrer was added chloromethyl methyl ether (27.0 ml, 356 mmol). The dark-red slurry, after stirred vigorously under a nitrogen atmosphere at room temperature overnight, was poured into 200 ml ice-water and the resulting mixture was stirred for 30 minutes to decompose unreacted chloromethyl methyl ether. That mixtrue was then extracted with diethyl ether (3 × 300 ml) and the combined organic layers were washed with water (2 × 200 ml) and brine (100 ml), dried over $MgSO_4$ and concentrated under reduced pressure. Silica gel chromatography (1.5% diethyl ether/hexanes) yielded a colorless oil (14.9 g, 74%). Rf 0.67 (9% Et_2O-hexanes). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.66 (s, 4H), 4.18 (t, J = 6.6 Hz, 2H), 4.06 (t, J = 6.5 Hz, 4H), 3.91 (s, 3H), 1.90 (m, 2H), 1.78 (m, 4H), 1.27 (m, 54H), 0.88 (m, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) 166.4, 159.9, 157.7, 121.8, 119.4, 76.3, 52.6, 35.7, 31.9, 30.2, 30.2, 29.6, 29.4, 25.8, 22.7. HRMS (FAB; M$^+$) calcd for $C_{46}H_{82}Cl_2O_5$ 784.5539; found 784.5547.



Methyl 3,5-bis(acetoxymethyl)-2,4,6–tris(dodecyloxy) benzoate (4). To a 500 ml dry flask equipped with a stir bar and a condenser was added methyl 3,5-bis(chloromethyl)-2,4,6–tris(dodecyloxy)benzoate (14.9 g, 19.0 mmol), sodium acetate (18.9 g, 230 mmol) and 170 ml of acetic acid. The suspension was stirred vigorously and refluxed overnight. After removing most of the acetic acid under reduced pressure the residue was diluted with water and extracted with ethyl ether (3 × 250 ml). The combined organic layers were washed with saturated Na_2CO_3 (3 × 200 ml), water (200 ml) and brine (100 ml), dried over $MgSO_4$ and concentrated. Silica gel chromatography (3% to 10% EtOAc-hexanes) yielded a colorless oil (13.9 g, 88%). Rf 0.47 (20% Et_2O-hexanes). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.11 (s, 4H), 3.91(m, 9H), 2.07 (s, 6H), 1.72 (m, 6H), 1.28 (m, 54H), 0.90 (m, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) 170.6, 166.5, 161.5, 158.5, 119.4, 119.1, 77.1, 76.6, 56.7, 52.5, 31.9, 30.1, 29.6, 29.4, 29.3, 25.9, 22.7, 20.9, 14.1. HRMS (FAB; M$^+$) calcd for $C_{50}H_{88}O_9$ 832.6428; found 832.6469.

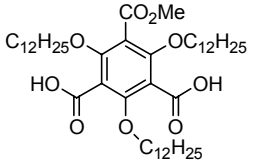


Methyl 3,5-bis(hydroxymethyl)-2,4,6–tris(dodecyloxy) benzoate. Potassium hydroxide (tech. 87%, 19.0 g, 295 mmol) dissolved in 20 ml of water was added to methyl 3,5-bis(acetoxymethyl)-2,4,6–tris(dodecyloxy)benzoate (3.60 g, 4.32 mmol) dissolved in isopropanol (40 ml). The biphasic mixture was stirred vigorously at room temperature for 8 h. *i*-PrOH was evaporated under reduced pressure and the resulting aqueous mixture was diluted with water and extracted with Et_2O (3 × 70 ml). The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated. Silica gel chromatography (9% EtOAc-hexanes) yielded a white solid (2.9 g, 90%). Rf 0.41 (22% EtOAc-hexanes). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.66 (d, J = 6.4 Hz, 4H), 3.96 (m, 6H), 3.91 (s, 3H), 2.35 (t, J = 6.4, 2H), 1.72 (m, 6H), 1.28 (m, 54H), 0.90 (m, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) 159.2, 156.3, 124.0, 119.2, 76.7, 76.4, 55.7, 52.5, 31.9, 30.3, 30.2, 29.6, 29.4, 25.9, 22.7, 14.1. HRMS (FAB; M$^+$) calcd for $C_{46}H_{84}O_7$ 748.6217; found 748.6191.

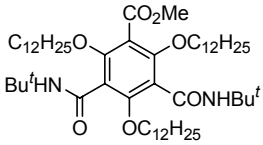


Methyl 3,5-diformyl-2,4,6–tris(dodecyloxy)benzoate. Tetrapropylammonium perruthenate (108 mg, 0.308 mmol) was added to a vigorously stirred mixture of methyl 3,5-bis(hydroxymethyl)-2,4,6–tris(dodecyloxy)benzoate (2.3 g, 3.07 mmol), 4-methylmorpholine *N*-oxide (1.08 g, 9.23 mmol) and powdered 4 Å molecular sieves (3.23 g) in CH_2Cl_2 (60 ml) at room temperature. The dark-green mixture was stirred vigorously under a nitrogen atmosphere at room temperature for 2 h and filtrated through a short silica pad, which was then washed with CH_2Cl_2 (4 × 40 ml). The colorless filtrate was evaporated to dryness under reduced pressure to yield a colorless oil (2.0 g, 87%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.27 (s, 2H), 4.05 (m, 6H), 3.91 (s, 3H), 1.77 (m, 6H), 1.27 (m, 54H), 0.89 (m, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) 187.1, 167.0, 165.3, 163.8, 162.4, 120.2, 119.2, 79.5, 77.5, 52.7, 31.9, 29.9, 29.8, 29.6, 29.3, 25.7, 22.7,

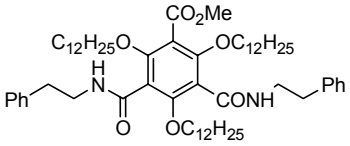
14.1. HRMS (FAB; M+H$^+$) calcd for $C_{46}H_{81}O_7$ 744.5982; found 744.5857.



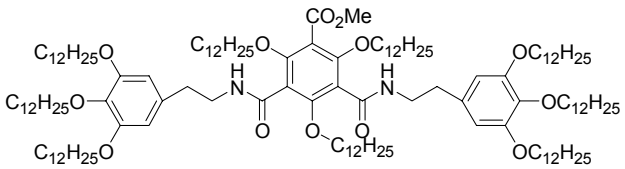
Methyl 3,5-dicarboxyl-2,4,6–tris(dodecyloxy)benzoate (5). A solution of $NaH_2PO_4{\cdot}2H_2O$ (3.14 g, 20.1 mmol), $NaClO_2$ (tech. 80%, 2.19 g, 19.4 mmol) and water (20 ml) was added to a stirred solution of methyl 3,5-diformyl-2,4,6–tris(dodecyloxy)benzoate (3.00 g, 4.03 mmol), *t*-butanol (60 ml) and 2-methyl-2-butene (20 ml). The biphasic solution was stirred vigorously at room temperature overnight. Organic solvents were evaporated under reduced pressure and the aqueous residue, after adding water (30 ml), was extracted with Et_2O (4 × 60 ml). The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated. Silica gel chromatography (3% MeOH-CH_2Cl_2) yielded a white solid (2.90 g, 93%). ^{1}H NMR (300 MHz, DMSO-d_6) δ 13.48 (br, 2H), 3.95 (m, 6H), 3.85 (s, 3H), 1.61 (m, 6H), 1.28 (m, 54H), 0.89 (m, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) 169.0, 165.3, 157.8, 119.3, 117.3, 76.8, 52.6, 31.9, 30.0, 29.6, 29.4, 25.7, 22.7, 14.1. HRMS (FAB; M+H$^+$) calcd for $C_{46}H_{81}O_9$ 776.5881; found 777.5837.



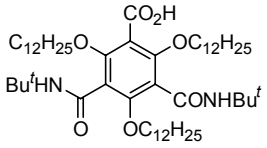
Methyl 3,5-bis[(*t*-butylamino)carbonyl]-2,4,6-tris (dodecyloxy)benzoate was prepared according to general procedure 3 from *t*-butylamine (0.63 ml, 6.0 mmol). Silica gel chromatography (5% to 10% EtOAc-hexanes) yielded an off-white solid (1.37 g, 77%). Rf 0.54 (20% EtOAc-hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) 5.63 (s, 2H), 4.06 (t, *J* = 6.8 Hz, 2H), 3.99 (t, *J* = 6.6 Hz, 4H), 3.88 (s, 3H), 1.67 (m, 6H), 1.43 (s, 18H), 1.26 (m, 54H), 0.88 (m, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) 165.6, 163.1, 155.8, 154.6, 123.2, 119.0, 76.3, 52.5, 52.0, 32.0, 30.3, 30.2, 29.7, 29.6, 29.5, 28.7, 26.0, 22.8, 14.3. IR (KBr) 3303, 2954, 2923, 2852, 1745, 1640, 1584, 1468, 1455, 1366, 1262, 1104. HRMS (FAB; M+H$^+$) calcd for $C_{54}H_{99}O_7N_2$ 887.7452; found 887.7473.



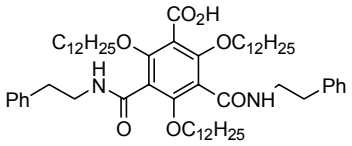
Methyl 3,5-bis[(β-phenethylamino)carbonyl]-2,4,6-tris(dodecyloxy)benzoate was prepared according to general procedure 3 from phenethylamine (1.00 ml, 8.00 mmol). Silica gel chromatography (3% Et_2O-CH_2Cl_2) yielded an off-white solid (1.51 g, 77%). Rf 0.47 (7% Et_2O -CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$) 7.25 (m, 10H), 5.97 (t, *J* = 5.9 Hz, 2H), 3.94 (m, 6H), 3.86 (s, 3H), 3.66 (m, 4H), 2.89 (t, *J* = 7.3 Hz, 4H), 1.62 (m, 6H), 1.25 (m, 54H), 0.88 (m, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) 165.3, 163.9, 156.1, 155.2, 138.3, 128.4, 126.3, 121.8, 119.0, 76.4, 76.1, 52.4, 41.3, 35.7, 32.0, 30.3, 30.2, 29.7, 29.5, 29.4, 25.9, 22.8, 14.3. IR (KBr) 3291, 3030, 2924, 2853, 1730, 1638, 1585, 1468, 1380, 1258, 698. HRMS (FAB; M+H$^+$) calcd for $C_{62}H_{99}O_7N_2$ 983.7452; found 983.7460.



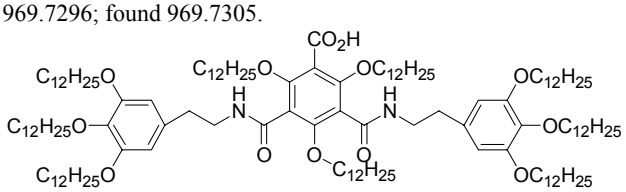
This methyl benzoate (**D21**) was prepared according to general procedure 3 from 3,4,5-tris(dodecyloxy)benzeneethanamine (2.97 g, 4.40 mmol). Silica gel chromatography (13% to 23% Et_2O-hexanes) yielded an off-white solid (3.01 g, 72%). Rf 0.5 (4% Et_2O -CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$) 6.39 (s, 4H), 5.90 (t, *J* = 5.9 Hz, 2H), 4.02-3.87 (m, 21H), 3.61 (m, 4H), 2.78 (t, *J* = 7.1 Hz, 4H), 1.83-1.64 (m, 18H), 1.47-1.25 (m, 162H), 0.88 (m, 27H). ^{13}C NMR (75 MHz, $CDCl_3$) 166.0, 164.6, 156.8, 155.9, 153.7, 137.4, 134.0, 122.7, 119.9, 107.5, 73.8, 69.6, 52.8, 41.7, 36.5, 32.3, 30.8, 30.5, 30.1, 29.9, 29.8, 29.3, 26.6, 26.3, 23.1, 14.5. IR (KBr) 3276, 3078, 2922, 2852, 1734, 1639, 1588, 1508, 1468, 1380, 1122. LRMS (MALDI; M+Na$^+$) calcd for $C_{134}H_{242}O_{13}N_2Na$ 2111; found 2113.



3,5-Bis[(*t*-butylamino)carbonyl]-2,4,6-tris(dodecyloxy) benzoic acid (6). To a 50 ml flask outfitted with a magnetic stir bar and a condenser was added methyl 3,5-bis[(*t*-butylamino)carbonyl]-2,4,6-tris(dodecyloxy)benzoate (887 mg, 1.00 mmol) and *i*-PrOH (11 ml). Then, with stirring, a solution of KOH (tech. 87%, 5.5 g, 86 mmol) in 5.5 ml water was added. The biphasic solution was stirred vigorously and refluxed overnight. *i*-PrOH was evaporated under reduced pressure and the resulting aqueous mixture was diluted with water (10 ml) and acidified with concentrated HCl to pH 2 and extracted with CH_2Cl_2 (4 × 20 ml). The combined organic layers were dried over $MgSO_4$ and evaporated to yield a white solid (864 mg, 99%). ^{1}H NMR (300MHz, $CDCl_3$) 5.73 (s, 2H), 4.06 (m, 6H), 1.70 (m, 6H), 1.44 (s, 18H), 1.25 (m, 54H), 0.88 (m, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) 169.2, 164.0, 156.9, 155.9, 123.8, 118.3, 77.3, 76.8, 52.4, 32.3, 30.6, 30.5, 30.1, 30.0, 29.9, 29.8, 29.0, 26.2, 23.1, 14.5. IR (KBr) 3326, 3067, 2925, 2854, 1743, 1642, 1583, 1457, 1367, 1222, 1110. HRMS (FAB; M+H$^+$) calcd for $C_{53}H_{97}O_7N_2$ 873.7296; found 873.7286.

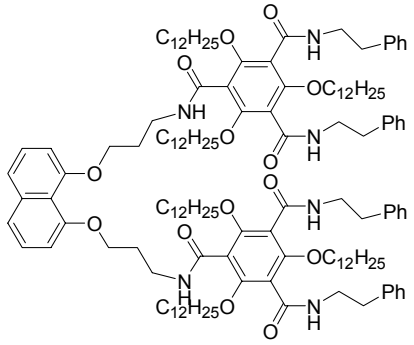


3,5-Bis[(β-phenethylamino)carbonyl]-2,4,6-tris(dodecyloxy) benzoic acid (7) was prepared in a manner analogous to **6** from methyl 3,5-bis[(β-phenethylamino)carbonyl]-2,4,6-tris(dodecyloxy)benzoate (983 mg, 1.00 mmol). Silica gel chromatography (2% MeOH-CH_2Cl_2) yielded an off-white solid (891 mg, 92%). Rf 0.4 (7% MeOH-CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) 7.29 (m, 4H), 7.21 (m, 6H), 6.06 (br, 2H), 3.96 (m, 6H), 3.66 (m, 4H), 2.90 (t, *J* = 7.2 Hz, 4H), 1.63 (m, 6H), 1.23 (m, 54H), 0.87 (m, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) 167.5, 164.7, 157.3, 156.6, 138.9, 129.1, 129.0, 127.0, 122.6, 118.1, 76.8, 41.7, 36.0, 32.3, 30.6, 30.5, 30.1, 29.9, 29.8, 26.2, 23.1, 14.5. IR (KBr) 3282, 3029, 2924, 2853, 1696, 1630, 1584, 1498, 1457, 1379, 1287, 1114, 698. HRMS (FAB; M+H$^+$) calcd for $C_{61}H_{97}O_7N_2$ 969.7296; found 969.7305.



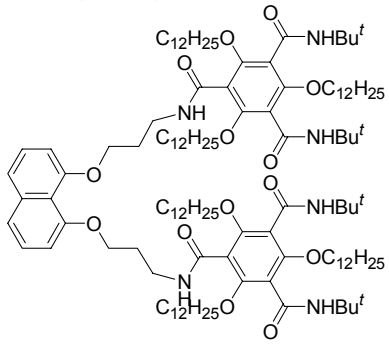
Benzoic acid **8** was prepared from methyl benzoate **D21** (2.09 g, 1.00 mmol) in a manner analogous to **6** except that a duel organic solvent of *i*-PrOH/THF (11:11 ml) was used instead of solely *i*-PrOH. Silica gel chromatography (1% MeOH-CH_2Cl_2) yielded an off-white solid (1.87 g, 90%). Rf 0.48 (7% MeOH-CH_2Cl_2). ^{1}H

NMR (300 MHz, $CDCl_3$) 10.62 (br, 1H), 6.42 (s, 4H), 6.12 (br, 2H), 4.04-3.89 (m, 18H), 3.60 (m, 4H), 2.79 (t, J = 7.1 Hz, 4H), 1.81-1.63 (m, 18H), 1.47-1.23 (m, 162H), 0.88 (m, 27H). ^{13}C NMR (75 MHz, $CDCl_3$) 167.1, 163.9, 156.5, 155.7, 152.9, 136.8, 133.4, 122.4, 117.8, 107.1, 73.4, 69.2, 41.6, 36.3, 32.1, 30.5, 30.4, 30.2, 29.8, 29.7, 29.5, 26.3, 25.9, 22.8, 14.3. IR (KBr) 3270, 3079, 2922, 2852, 1695, 1639, 1588, 1508, 1468, 1380, 1240, 1122. LRMS (MALDI; M+Na^+ and M+K^+) calcd for $C_{133}H_{240}O_{13}N_2Na$ 2097 and $C_{133}H_{240}O_{13}N_2K$ 2113; found 2099 and 2115.



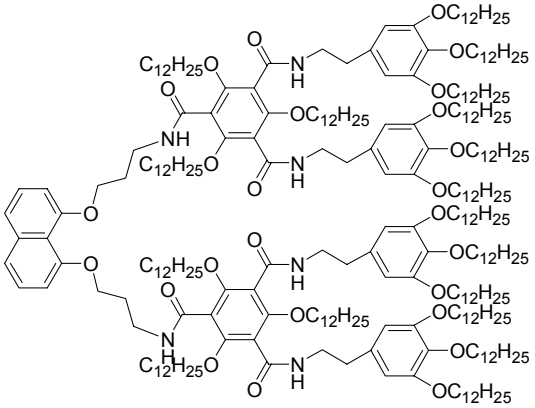
Dimer **9** was prepared according to general procedure 4 (purified by method (a)) from 3,5-bis[(β-phenethylamino)carbonyl]-2,4,6-tris(dodecyloxy)benzoic acid **7** (48.5 mg, 50.0 μmol) and 1,8-bis(3-aminopropoxy)naphthalene dihydrobromide (10.9 mg, 25.0 μmol) as a white solid (32 mg, 58%). ^{1}H NMR (500 MHz, CD_2Cl_2, 1 mM, 303 K) 7.64 (br, 2H), 7.39-7.24 (m, 24H), 7.00 (br, 4H), 6.80 (d, J = 7.5 Hz, 2H), 4.19 (t, J = 5.5 Hz, 4H), 3.92-3.86 (m, 12H), 3.68-3.63 (m, 12H), 2.98 (t, J = 8.0 Hz, 8H), 2.33 (m, 4H), 1.64-1.21 (m, 120H), 0.95-0.88 (m, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) 165.2, 165.2, 156.4, 155.0, 139.3, 137.6, 128.9, 128.9, 126.7, 123.4, 123.1, 121.0, 117.7, 106.8, 76.9, 68.4, 42.3, 39.9, 36.6, 32.5, 31.1, 30.6, 30.5, 30.4, 30.0, 29.4, 26.9, 26.8, 23.3, 14.8. IR (KBr) 3286, 3028, 2925, 2853, 1654, 1637, 1579, 1498, 1456, 1378, 1271, 1113, 697. LRMS (MALDI; M+Na^+) calcd for $C_{138}H_{210}O_{14}N_6Na$ 2199; found 2200.

^{1}H NMR (500 MHz, THF-d_8, 1 mM, 333 K) 8.21 (linker N*H*, br, 2H), 8.03 (non-linker N*H*, br, 4H), 7.36-7.23 (m, 20H), 7.20-7.18 (m, 4H), 6.88 (d, J = 7.8 Hz, 2H), 4.25 (br, 4H), 4.04 (m, 12H), 3.68 (m, overlapping with solvent peak), 3.04 (t, J = 8.5 Hz, 8H), 2.35 (m, overlapping with solvent peak), 1.68 (m, overlapping with solvent peak), 1.47 (br, 12 H), 1.34-1.22 (m), 0.93-0.87 (m, 18H).



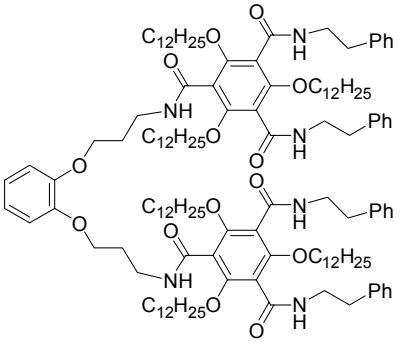
Dimer **10** was prepared according to general procedure 4 (treated by method (b)) from benzoic acid **6** (43.7 mg, 50.0 μmol) and 1,8-bis(3-aminopropoxy)naphthalene dihydrobromide (10.9 mg, 25.0 μmol). Silica gel chromatography (10% Et_2O-CH_2Cl_2) yielded an off-white solid (32 mg, 64%). Rf 0.35 (5% MeOH-CH_2Cl_2). ^{1}H NMR (500 MHz, CD_2Cl_2, 1 mM, 303 K) 7.43 (br, 2H), 7.34 (m, 2H), 7.28 (m, 2H), 6.68 (d, J = 7.6 Hz, 2H), 5.72 (s, 4H), 4.20 (t, J = 5.3 Hz, 4H), 4.02 (t, J = 6.7 Hz, 4H), 3.67 (t, J = 6.5 Hz, 8H), 3.63 (m, 4H), 2.26 (m, 4H), 1.76 (m, 4H), 1.51-1.18 (m, 152H), 0.94-0.91 (m, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) 165.3, 163.8, 155.3, 155.1, 155.0, 136.8, 126.8, 122.8, 122.5, 121.3, 117.3, 107.6, 76.8, 75.9, 70.5, 52.3, 41.1, 32.6, 31.0, 30.8, 30.3, 30.2, 30.1, 30.0, 29.3, 27.9, 26.6, 26.4, 23.4, 14.8. IR (KBr) 3306, 3058, 2926, 2854, 1641, 1579, 1458, 1381, 1222, 1108. LRMS (MALDI; M+Na^+) calcd for $C_{122}H_{210}O_{14}N_6Na$ 2007; found 2008.

^{1}H NMR (500 MHz, THF-d_8, 1 mM, 333 K) 7.63 (linker N*H*, t, J = 5.2 Hz, 2H), 7.34-7.27 (m, 4H), 6.86 (d, J = 7.5 Hz, 2H), 6.67 (non-linker N*H*, s, 4H), 4.23 (t, J = 5.4 Hz, 4H), 4.06 (t, J = 6.2 Hz, 4H), 3.97 (t, J = 6.5 Hz, 8H), 3.6 (m, overlapping with solvent peak), 2.3 (m, overlapping with solvent peak), 1.7-1.8 (m, overlapping with solvent peak), 1.65 (m, 10H), 1.46-1.30 (m), 0.93-0.90 (m, 18H).



Dimer **11** was prepared according to general procedure 4 (treated by method (b)) from benzoic acid **8** (104 mg, 50.0 μmol) and 1,8-bis(3-aminopropoxy)naphthalene dihydrobromide (10.9 mg, 25.0 μmol). Silica gel chromatography (5% Et_2O-CH_2Cl_2) yielded an off-white waxy solid (74 mg, 67%). Rf 0.6 (11% Et_2O-CH_2Cl_2). ^{1}H NMR (400 MHz, CD_2Cl_2, 1 mM, 303 K) 7.40-7.32 (m, 6H), 6.79 (d, J = 7.5 Hz, 2H), 6.63 (br, 4H), 6.44 (s, 8H), 4.19 (t, J = 5.3 Hz, 4H), 3.97-3.84 (m, 36H), 3.66-3.60 (m, 12H), 2.85 (t, J = 7.9 Hz, 8H), 2.31 (m, 4H), 1.82-1.71 (m, 26H), 1.66-1.22 (m, 334H), 0.94-0.88 (m, 54H). ^{13}C NMR (100 MHz, $CDCl_3$) 164.5, 164.1, 155.1, 154.8, 154.7, 153.0, 136.8, 136.6, 133.4, 126.4, 122.4, 121.6, 120.5, 116.7, 106.9, 106.4, 76.5, 75.8, 73.4, 69.2, 41.4, 40.3, 36.3, 32.0, 31.9, 30.5, 30.3, 29.8, 29.8, 29.7, 29.6, 29.5, 27.7, 26.3, 26.2, 26.0, 23.0, 22.8, 22.6, 14.2. IR (KBr) 3280, 3061, 2923, 2853, 1638, 1583, 1508, 1468, 1380, 1238, 1120. LRMS (MALDI; M+Na^+) calcd for $C_{282}H_{498}N_6O_{26}Na$ 4409; found 4415.

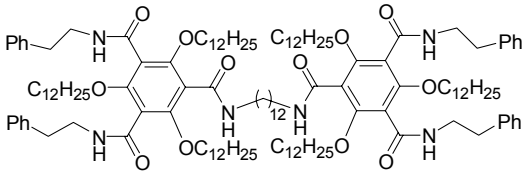
^{1}H NMR (400 MHz, THF-d_8, 1 mM, 333 K) 8.07 (linker N*H*, t, J = 5.5 Hz, 2H), 7.81 (non-linker N*H*, t, J = 5.6 Hz, 4H), 7.36-7.29 (m, 4H), 6.88 (d, J = 7.5 Hz, 2H), 6.51 (s, 8H), 4.25 (t, J = 5.7 Hz, 4H), 4.04 (t, J = 6.1 Hz, 12H), 3.99-3.90 (m, 24H), 3.6 (m, overlapping with solvent peak), 2.92 (t, J = 8.0 Hz, 8H), 2.3-2.4 (m, overlapping with solvent peak), 1.7 (m, overlapping with solvent peak), 1.54-1.23 (m), 0.95-0.87 (m, 54H).



Dimer **13** was prepared according to general procedure 4 (purified by method (a)) from 3,5-bis[(β-phenethylamino)carbonyl]-2,4,6-tris(dodecyloxy)benzoic acid **7** (48.5 mg, 50.0 μmol) and 1,2-bis(3-aminopropoxy)benzene dihydrobromide (9.7 mg, 25 μmol) as a white solid (34 mg, 64%).

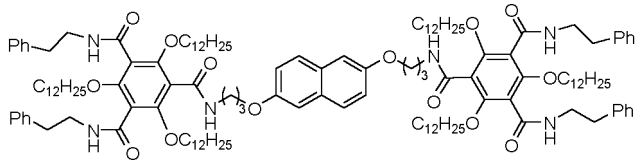
^{1}H NMR (500 MHz, CD_2Cl_2, 1 mM, 303 K) 7.49 (br, 2H), 7.31-7.23 (m, 24H), 6.92 (m, 4H), 4.07 (t, J = 5.3 Hz, 4H), 3.91 (t, J = 6.1 Hz, 12H), 3.69-3.65 (m, 12H), 3.00 (t, J = 8.0 Hz, 8H), 2.14 (br, 4H), 1.63-1.25 (m, 120H), 0.92 (m, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) 165.4, 154.9, 149.4, 139.5, 128.8, 126.5, 123.9, 123.6, 121.4, 113.6, 66.5, 42.4, 37.9, 36.8, 32.6, 31.2, 30.7, 30.5, 30.4, 30.0, 26.9, 23.4, 14.8. IR (KBr) 3292, 3030, 2925, 2853, 1638, 1583, 1498, 1468. 1455, 1378, 1256, 1113, 737, 698. LRMS (MALDI; M+Na$^+$) calcd for $C_{134}H_{208}O_{14}N_6Na$ 2149; found 2150.

^{1}H NMR (500 MHz, THF-d_8, 1 mM, 333 K) 8.08 (linker N*H*, br, 2H), 7.97 (non-linker N*H*, br, 4H), 7.27-7.23 (m, 16H), 7.18 (m, 4H), 6.91 (br, 2H), 6.86 (br, 2H), 4.08 (br, 4H), 4.01 (br, 12H), 3.6 (m, overlapping with solvent peak), 3.02 (t, J = 7.9 Hz, 8H), 2.17 (br, 4H), 1.64 (br, overlapping with solvent peak), 1.45 (br, 12 H), 1.34-1.26 (m), 0.92-0.90 (m, 18H).



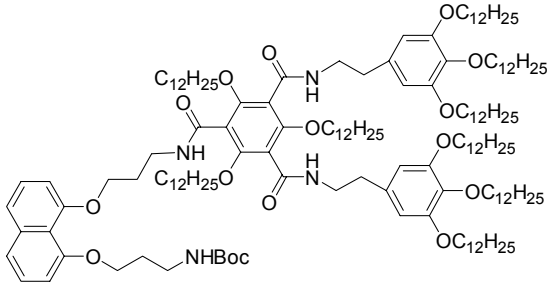
Dimer **14** was prepared according to general procedure 4 (purified by method (a)) from 3,5-bis[(β-phenethylamino)carbonyl]-2,4,6-tris(dodecyloxy)benzoic acid **7** (48.5 mg, 50.0 μmol) and 1,12-dodecanediamine (5.0 mg, 25 μmol) as a white solid (43 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$, 1 mM, 303 K) 7.31-7.21 (m, overlapping with $CHCl_3$), 5.92 (t, J = 5.8 Hz, 4H), 5.84 (br, 2H), 3.95-3.89 (m, 12H), 3.67 (m, 8H), 3.38 (m, 4H), 2.89 (t, J = 7.1 Hz, 8H), 1.64-1.55 (m, 16H), 1.26 (m, 124H), 0.88 (m, 18H). ^{1}H ^{13}C NMR (100 MHz, 5% CD_3OD-$CDCl_3$, 323 K) 165.4, 165.3, 155.7, 139.0, 128.8, 126.7, 122.0, 121.8, 76.5, 76.5, 41.8, 40.6, 36.1, 32.4, 30.7, 30.2, 30.0, 29.9, 27.7, 26.4, 23.2, 14.5. IR (KBr) 3292, 3030, 2924, 2853, 1638, 1582, 1497, 1468, 1378, 1297, 1112, 698. LRMS (MALDI; M+Na$^+$) calcd for $C_{134}H_{216}O_{12}N_6Na$ 2125; found 2126.

NMR (500 MHz, THF-d_8, 1 mM, 333 K) 7.31-7.28 (m, 20H), 7.19 (br, 6H), 4.03 (br, 12H), 3.6 (overlapping with solvent peak), 3.35 (m, 4H), 2.95 (br, 8H), 1.68-1.64 (m, overlapping with solvent peak), 1.43-1.30 (m), 0.92 (m, 18H). Overlapped amide resonances were assigned from the COSY spectrum: 7.19 (linker N*H*), 7.30 (non-linker N*H*).

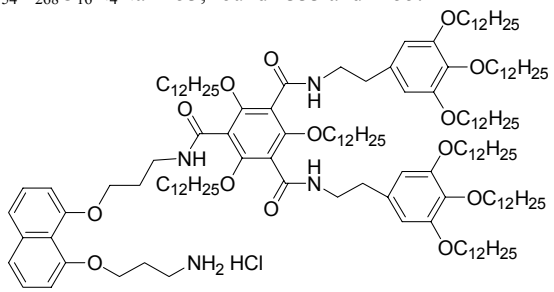


Dimer **15** was prepared according to general procedure 4 from 3,5-bis[(β-phenethylamino)carbonyl]-2,4,6-tris(dodecyloxy) benzoic acid **7** (48.5 mg, 50.0 μmol) and 2,6-bis(3-aminopropoxy)naphthalene dihydrobromide (10.9 mg, 25.0 μmol). CH_2Cl_2 was evaporated off the heterogeneous reaction mixture under reduced pressure and hot DMF (3 ml) was added to the residue. That heterogeneous mixture was slowly cooled to room temperature and further to 0 °C, filtrated and washed with ice-cold DMF. The filter cake was sonicated with 3 ml of MeOH, filtrated, washed with MeOH and collected as a white solid (13 mg, 24%). ^{1}H NMR (*vide infra*). A ^{13}C NMR spectrum for this compound couldn't be obtained due to its low solubility. IR (KBr) 3386, 3293, 2925, 2853, 1637, 1604, 1582, 1509, 1467, 1378, 1234, 1115, 698. LRMS (MALDI; M+Na$^+$) calcd for $C_{138}H_{210}O_{14}N_6Na$ 2199; found 2200.

^{1}H NMR (500 MHz, THF-d_8, 1 mM, 333 K) 7.63 (d, J = 8.5 Hz, 2H), 7.32 (linker N*H*, br, 2H), 7.28-7.25 (m, 16H), 7.21-7.16 (m, 10H; non-linker N*H*s reside at 7.20 ppm), 7.12 (d, J = 9.0 Hz, 2H), 4.21 (t, J = 6.3 Hz, 4H), 4.06-4.02 (m, 12H), 3.6 (m, overlapping with solvent peak), 2.93 (t, J = 7.5 Hz, 8H), 2.15 (m, 4H), 1.67 (m, 12H), 1.43-1.30 (m, 108H), 0.93-0.90 (m, 18H).

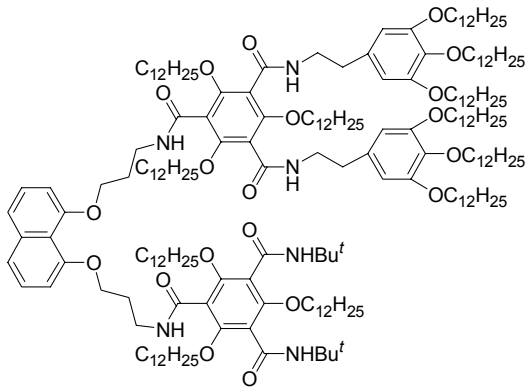


N-Boc amine **D41**. To a 25 ml dry flask outfitted with a magnetic stir bar was added benzoic acid **8** (415 mg, 0.200 mmol), 1-(3-aminopropoxy)-8-(*N*-Boc-3-aminopropoxy)naphthalene (79 mg, 0.21 mmol), 1-hydroxy-7-azabenzotriazole (27 mg, 0.20 mmol), DMAP (41 mg, 0.34 mmol), CH_2Cl_2 (4 ml) and DMF (1 ml). Then, with stirring, a solution of EDC hydrochloride (42 mg, 0.22 mmol) in CH_2Cl_2 (1 ml) was added. The reaction mixture was stirred under a nitrogen atmosphere at room temperature overnight, diluted with CH_2Cl_2 (15 ml) and poured into water (15 ml). The separated aqueous layer was extracted with CH_2Cl_2 (20 ml) and the combined organic layers were washed with water (3 × 15 ml) and brine (10 ml), dried over $MgSO_4$ and concentrated under reduced pressure. Silica gel chromatography (4% to 9% Et_2O-CH_2Cl_2) yielded an off-white solid (340 mg, 70%). Rf 0.50 (13% Et_2O-CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$) 7.64 (br, 1H), 7.34 (m, 3H), 7.20 (m, 1H), 6.79 (m, 1H), 6.58 (d, J = 7.8 Hz, 1H), 6.40 (s, 4H), 5.61 (br, 3H), 4.31 (br, 2H), 3.94 (m, 16H), 3.76-3.66 (m, 6H), 3.46 (m, 4H), 3.27 (m, 2H), 2.68 (t, J = 7.9 Hz, 4H), 2.24 (br, 2H), 2.04 (m, 2H), 1.77 (m, 16H), 1.26 (m, 164H), 0.88 (m, 27H). ^{13}C NMR (75 MHz, $CDCl_3$) 164.4, 163.9, 155.9, 155.5, 154.9, 152.9, 136.7, 133.5, 126.3, 126.2, 122.5, 121.5, 120.6, 120.4, 116.9, 106.9, 105.8, 78.8, 76.3, 75.9, 73.3, 69.2, 41.4, 40.5, 39.3, 36.2, 32.0, 30.5, 30.2, 29.8, 29.7, 29.6, 29.5, 28.5, 26.3, 25.8, 22.8, 14.2. IR (KBr) 3351, 3289, 3059, 2923, 2853, 1686, 1638, 1586, 1508, 1468, 1382, 1239, 1120. LRMS (MALDI; (M-Boc+2H)$^+$ and M+Na$^+$) calcd for $C_{149}H_{261}O_{14}N_4$ 2331 and $C_{154}H_{268}O_{16}N_4Na$ 2453; found 2333 and 2455.

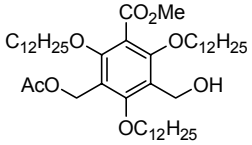


Amine hydrochloride (**D42**). To a 10 ml dry flask outfitted with a magnetic stir bar and a drying tube was added *N*-Boc amine **D41** (315 mg, 0.130 mmol) and ethereal HCl (2 M, 3.3 ml). The homogeneous solution was stirred at room temperature for 90 min. Volatiles were evaporated under reduced pressure and MeOH (5 ml) was added to the oily residue to precipitate the product. Filtration and washing with MeOH yielded an off-white powder (300 mg, 98%). ^{1}H NMR (500 MHz, $CDCl_3$) 8.43 (br, 1H), 8.16 (br, 3H), 7.43 (m, 2H), 7.35 (m, 2H), 6.98 (d, J = 7.5 Hz, 1H), 6.81 (d, J = 7.6 Hz, 1H), 6.66 (br, 2H), 6.39 (s, 4H), 4.41 (br, 2H), 4.20 (br, 2H), 3.93 (m, 18H), 3.57 (br, 6H), 3.23 (br, 2H), 2.77 (br, 4H), 2.37 (br, 2H), 2.17 (br, 2H), 1.75 (m, 12H), 1.44 (m, 12H), 1.30-1.11 (m, 156H), 0.88 (m, 27H). ^{13}C NMR (75 MHz, $CDCl_3$) 165.7, 165.2, 156.3, 155.9, 155.8, 155.3, 153.7, 137.8, 137.3, 133.9, 126.8, 126.6, 124.0, 122.1, 121.9, 121.5, 118.1, 109.1, 107.4, 73.8, 69.6, 68.1, 42.0, 32.4, 30.8, 30.1, 30.0, 29.8, 29.4, 26.6, 26.3, 23.1, 14.5. IR (KBr) 3290, 3058, 2924, 2853, 1638, 1585, 1508, 1468, 1382, 1238, 1120. LRMS (MALDI; M+H$^+$ and

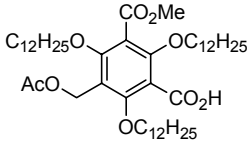
M+Na$^+$) calcd for $C_{149}H_{261}O_{14}N_4$ 2331 and $C_{149}H_{260}O_{14}N_4Na$ 2353; found 2333 and 2354.



Dimer **12** was prepared in a manner analogous to *N*-Boc amine **D41** from benzoic acid **6** (17 mg, 19 μmol) and the amine hydrochloride **D42** (46 mg, 19 μmol). Silica gel chromatography (17% EtOAc-hexanes) yielded an off-white waxy solid (40 mg, 66%). Rf 0.51 (5% MeOH-CH_2Cl_2). ^{1}H NMR (400 MHz, CD_2Cl_2, 1 mM, 303 K) 8.00 (br, 1H), 7.60 (br, 2H), 7.40-7.34 (m, 4H), 6.97 (br, 1H), 6.84 (m, 2H), 6.49 (s, 4H), 6.03 (s, 2H), 4.24 (br, 2H), 4.20 (br, 2H), 4.04-3.90 (m, 24H), 3.67-3.61 (m, 8H), 2.89 (t, J = 4.1 Hz, 4H), 2.38 (m, 2H), 2.30 (m, 2H), 1.84 (m, 8H), 1.81-1.21 (m, 250H), 0.94-0.88 (m, 36H). ^{13}C NMR (75 MHz, $CDCl_3$) 165.6, 165.0, 164.7, 156.3, 156.2, 155.6, 155.2, 155.1, 155.0, 153.6, 137.5, 137.3, 134.5, 126.9, 126.7, 123.3, 123.1, 123.0, 122.4, 121.2, 117.7, 107.5, 107.1, 106.9, 76.4, 76.3, 73.8, 69.6, 52.3, 42.1, 40.3, 39.4, 36.9, 32.3, 30.8, 30.1, 29.8, 29.3, 29.1, 28.9, 26.6, 26.4, 23.1, 14.5. IR (KBr) 3305, 3058, 2925, 2854, 1638, 1581, 1508, 1467, 1457, 1380, 1233, 1115. LRMS (MALDI; M+Na$^+$ and M+K$^+$) calcd for $C_{202}H_{354}O_{20}N_6Na$ 3208 and $C_{202}H_{354}O_{20}N_6K$ 3224; found 3213 and 3229.

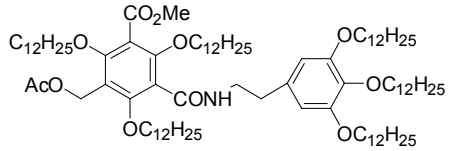


Methyl 3-(acetoxymethyl)-5-(hydroxymethyl)-2,4,6-tris(dodecyloxy)benzoate. To a 500 ml flask outfitted with a magnetic stir bar was added methyl 3,5-bis(acetoxymethyl)-2,4,6-tris(dodecyloxy)benzoate (13.1 g, 15.7 mmol) and *i*-PrOH (200 ml). Then, with stirring, a solution of KOH (tech. 87%, 881 mg, 13.7 mmol) in water (100 ml) was added. The biphasic solution was stirred vigorously at room temperature overnight. *i*-PrOH was evaporated under reduced pressure and the resulting aqueous mixture was extracted with Et_2O (3 × 200 ml). The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated. Silica gel chromatography (Et_2O-hexanes 6%, 11% and then 30%) eluted successively the starting material (6.7 g, 51%), the title compound (a colorless oil, 3.9 g, 31%, Rf 0.48 in 33% Et_2O-hexanes) and methyl 3,5-bis(hydroxymethyl)-2,4,6-tris(dodecyloxy)benzoate (1.04 g, 9%). ^{1}H NMR (300 MHz, $CDCl_3$) 5.08 (s, 2H), 4.65 (d, J = 6.6 Hz, 2H), 3.98-3.87 (m, 9H), 2.31 (t, J = 6.6 Hz, 1H), 2.05 (s, 3H), 1.74 (m, 6H), 1.26 (m, 54H), 0.88 (m, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) 170.3, 166.2, 160.0, 157.1, 157.0, 123.9, 119.1, 118.9, 76.9, 76.3, 56.7, 55.7, 52.6, 32.1, 30.4, 30.3, 29.8, 29.7, 29.6, 29.5, 26.1, 22.9, 21.2, 14.3. IR (NaCl, neat) 3524, 2925, 2854, 1742, 1589, 1466, 1442, 1380, 1204, 1121. HRMS (FAB; M+H$^+$) calcd for $C_{48}H_{87}O_8$ 791.6401; found 791.6385.

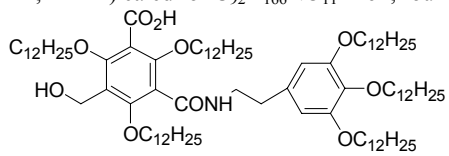


Methyl 3-(acetoxymethyl)-5-carboxyl-2,4,6-tris(dodecyloxy) benzoate (16). To a dry 250 ml flask outfitted with a magnetic stir bar was added methyl 3-(acetoxymethyl)-5-(hydroxymethyl)-2,4,6-tris(dodecyloxy)benzoate (5.70 g, 7.21 mmol), 4-methylmorpholine *N*-oxide (1.26 g, 10.8 mmol), 4Å molecular sieves (3.80 g), and CH_2Cl_2 (70 ml). Then, with stirring, tetrapropylammonium perruthenate (126 mg, 0.359 mmol) was added in one portion. The dark-green mixture was stirred vigorously under a nitrogen atmosphere at room temperature for 90 min and filtrated through a silica pad, which was then washed with CH_2Cl_2 (4 × 50 ml). The colorless filtrate was evaporated to dryness under reduced pressure to yield methyl 3-(acetoxymethyl)-5-formyl-2,4,6-tris(dodecyloxy)benzoate as a colorless oil (5.20 g, 91%). Rf 0.63 (17% EtOAc-hexanes).

To a 250 ml flask outfitted with a magnetic stir bar was added methyl 3-(acetoxymethyl)-5-formyl-2,4,6-tris(dodecyloxy) benzoate (5.20 g, 6.59 mmol), *t*-BuOH (50 ml), and 2-methyl-2-butene (15 ml). Then, with stirring, a solution of $NaClO_2$ (tech. 80%, 1.79 g, 15.8 mmol) and $NaH_2PO_4 \cdot 2H_2O$ (2.57 g, 16.5 mmol) in water (18 ml) was added. The biphasic solution was stirred vigorously at room temperature overnight. Organic solvents were evaporated under reduced pressure and the aqueous residue, after adding water (40 ml), was extracted with Et_2O (4 × 70 ml). The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated. Silica gel chromatography (2% to 7% MeOH-CH_2Cl_2) yielded the benzoic acid **16** as a colorless oil (5.06 g, 87% for two steps). Rf 0.4 (7% MeOH-CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$) 10.74 (br, 1H), 5.11 (s, 2H), 4.06-3.91 (m, 9H), 2.07 (s, 3H), 1.71 (m, 6H), 1.25 (m, 54H), 0.88 (m, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) 170.7, 169.8, 165.9, 159.5, 159.4, 156.8, 119.2, 119.0, 117.3, 76.9, 76.4, 56.2, 52.6, 31.9, 30.0, 29.6, 29.3, 25.8, 22.6, 20.9, 14.1. IR (NaCl, neat) 3161, 2925, 2854, 1742, 1705, 1587, 1466, 1380, 1229, 1109. HRMS (FAB; M$^+$) calcd for $C_{48}H_{84}O_9$ 804.6115; found 804.6074.

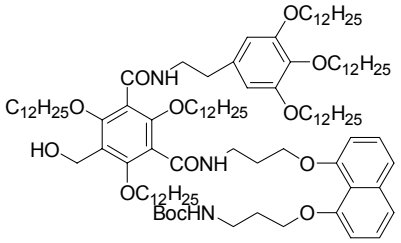


Benzamide **17** was prepared in a manner analogous to *N*-Boc amine **D41** from benzoic acid **16** (1.61 g, 2.00 mmol) and 3,4,5-tris(dodecyloxy)benzeneethanamine (1.48 g, 2.20 mmol). Silica gel chromatography (7% EtOAc-hexanes) yielded an off-white solid (2.30 g, 79%). Rf 0.47 (20% EtOAc-hexanes). ^{1}H NMR (300 MHz, $CDCl_3$) 6.40 (s, 2H), 5.93 (t, J = 6.0 Hz, 1H), 5.07 (s, 2H), 4.03-3.88 (m, 15H), 3.63 (m, 2H), 2.79 (t, J = 6.8 Hz, 2H), 2.04 (s, 3H), 1.80-1.63 (m, 12H), 1.47-1.25 (m, 108H), 0.88 (m, 18H). ^{13}C NMR (75 MHz, $CDCl_3$) 170.9, 166.4, 165.0, 159.1, 158.5, 156.2, 153.7, 137.3, 134.1, 122.7, 119.7, 119.4, 107.5, 77.2, 76.9, 73.7, 69.5, 56.7, 52.8, 41.7, 36.5, 32.3, 30.8, 30.6, 30.5, 30.1, 29.9, 29.8, 26.6, 26.3, 23.1, 21.3, 14.5. IR (KBr) 3272, 3079, 2922, 2851, 1737, 1641, 1589, 1509, 1468, 1383, 1240, 1122. LRMS (FAB; M+H$^+$) calcd for $C_{92}H_{166}NO_{11}$ 1461; found 1461.

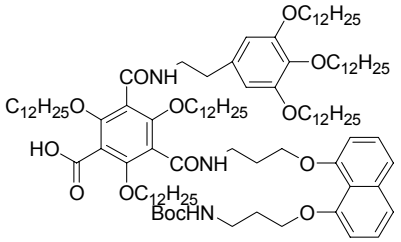


This compound (**D51**) was prepared from benzamide **17** (2.17g, 1.49 mmol) in a manner analogous to **6** except that a duel organic solvent of *i*-PrOH/THF (8:8 ml) was used instead of solely *i*-PrOH. Silica gel chromatography (3% EtOAc-CH_2Cl_2 and then 9% MeOH-CH_2Cl_2) yielded an off-white solid (1.88 g，90%). Rf 0.25 (4% MeOH-CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$) 6.43 (s, 2H), 6.09 (t, J = 5.9 Hz, 1H), 4.62 (s, 2H), 4.06-3.88 (m, 12H), 3.63 (m, 2H), 2.80 (t, J = 6.8 Hz, 2H), 1.80-1.71 (m, 12H), 1.44-1.23 (m, 108H), 0.88 (m, 18H). ^{13}C NMR (75 MHz, $CDCl_3$) 167.7,

164.4, 157.8, 157.2, 155.2, 152.9, 136.8, 133.5, 123.9, 122.3, 117.7, 107.2, 77.2, 73.4, 69.3, 55.3, 41.5, 36.2, 32.1, 30.5, 30.4, 30.3, 29.8, 29.7, 29.5, 26.4, 26.1, 26.0, 22.9, 14.3. IR (KBr) 3435, 3270, 3079, 2923, 2853, 1701, 1637, 1589, 1508, 1468, 1458, 1380, 1240, 1120. LRMS (FAB; $M+H^+$) calcd for $C_{89}H_{162}NO_{10}$ 1405; found 1405.

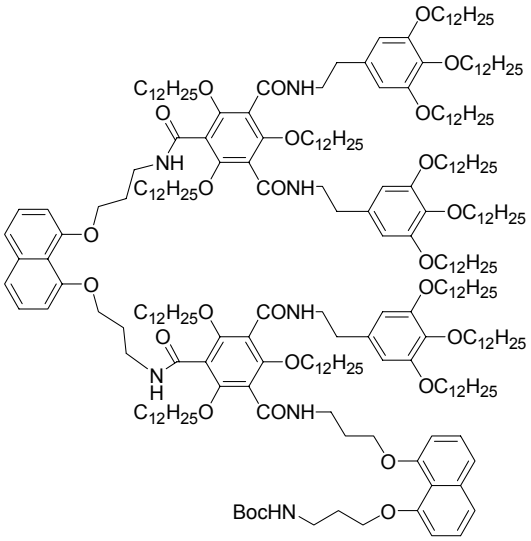


This compound (**D53**) was prepared in a manner analogous to *N*-Boc amine **D41** from benzoic acid **D51** (1.60 g, 1.14 mmol) and 1-(3-aminopropoxy)-8-(*N*-Boc-3-aminopropoxy)naphthalene (447 mg, 1.20 mmol). Silica gel chromatography (7% to 11% Et_2O-CH_2Cl_2) yielded an off-white solid (1.51 g, 75%). Rf 0.51 (17% Et_2O-CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) 7.64 (br, 1H), 7.36-7.29 (m, 3H), 7.14 (m, 1H), 6.78 (m, 1H), 6.47 (d, J = 7.8 Hz, 1H), 6.42 (s, 2H), 5.56 (br, 1H), 5.43 (t, J = 6.0 Hz, 1H), 4.50 (d, J = 6.1 Hz, 2H), 4.31 (br, 2H), 3.98-3.90 (m, 8H), 3.83-3.75 (m, 4H), 3.66 (m, 4H), 3.42 (m, 2H), 3.27 (m, 2H), 2.66 (t, J = 7.8 Hz, 2H), 2.33 (br, 1H), 2.25 (br, 2H), 2.02 (m, 2H), 1.84-1.70 (m, 8H), 1.48-1.10 (m, 112H), 0.88 (m, 18H). ^{13}C NMR (75 MHz, $CDCl_3$) 164.9, 164.4, 156.3, 156.1, 155.8, 155.4, 155.0, 154.0, 152.9, 136.8, 136.7, 133.8, 126.2, 126.1, 123.5, 122.5, 121.9, 120.7, 120.5, 116.9, 107.1, 106.8, 105.7, 78.9, 76.4, 76.2, 75.9, 73.4, 69.6, 69.2, 68.8, 55.3, 41.5, 40.8, 39.3, 32.1, 30.5, 30.3, 29.8, 29.5, 28.6, 26.4, 26.1, 25.9, 22.9, 14.3. IR (KBr) 3350, 3292, 3058, 2924, 2853, 1685, 1637, 1587, 1508, 1468, 1458, 1382, 1239, 1117. LRMS (MALDI; $(M\text{-}Boc+2H)^+$ and $M+Na^+$) calcd for $C_{105}H_{182}O_{11}N_3$ 1661 and $C_{110}H_{189}O_{13}N_3Na$ 1783; found 1661 and 1784.

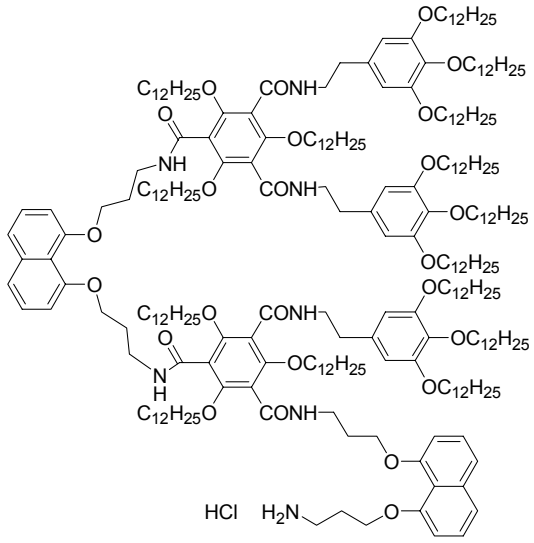


Benzoic acid **18** was prepared from the benzyl alcohol **D53** (1.42 g, 0.806 mmol). In a manner analogous to methyl 3-(acetoxymethyl)-5-formyl-2,4,6-tris(dodecyloxy)benzoate, the benzaldehyde moiety was obtained as an off-white solid (1.27 g, 0.722 mmol, 90%).

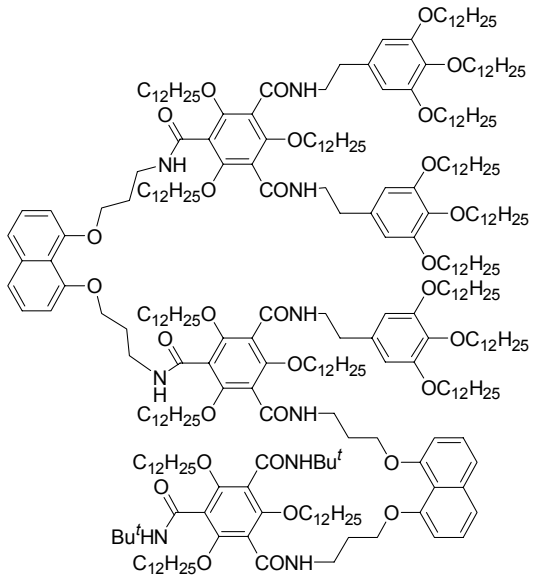
To that benzaldehyde in a 50 ml flask outfitted with a magnetic stir bar was added *t*-BuOH (4ml), 2-methyl-2-butene (2 ml) and THF (15 ml). Then, with stirring, a solution of $NaClO_2$ (tech. 80%, 197 mg, 1.74 mmol) and $NaH_2PO_4{\cdot}2H_2O$ (282 mg, 1.80 mmol) in water (2 ml) was added. The biphasic solution was stirred vigorously at room temperature overnight. Organic solvents were evaporated under reduced pressure and the aqueous residue, after adding water (15 ml), was extracted with CH_2Cl_2 (4 × 20 ml). The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated. Silica gel chromatography (7% Et_2O-CH_2Cl_2 and then 7% MeOH-CH_2Cl_2) yielded benzoic acid **18** as an off-white solid (979 mg, 68% for two steps). Rf 0.4 (7% MeOH-CH_2Cl_2). ^1H NMR (500 MHz, CD_2Cl_2) 7.57 (br, 1H), 7.37-7.32 (m, 3H), 7.18 (m, 1H), 6.82 (m, 1H), 6.61 (d, J =7.6 Hz, 1H), 6.45 (s, 2H), 5.62 (br, 1H), 5.51 (br, 1H), 4.32 (br, 2H), 4.02 (t, J = 6.6 Hz, 2H), 3.97 (t, J = 6.4 Hz, 4H), 3.89 (m, 6H), 3.66-3.61 (m, 4H), 3.45 (m, 2H), 3.27 (br, 2H), 2.71 (t, J = 7.3 Hz, 2H), 2.23 (br, 2H), 2.02 (br, 2H), 1.82 (m, 4H), 1.72 (m, 4H), 1.52-1.09 (m, 112H), 0.89 (m, 18H). ^{13}C NMR (75 MHz, $CDCl_3$) 167.4, 165.1, 164.5, 156.8, 156.3, 156.0, 155.8, 155.7, 153.7, 137.4, 137.3, 134.4, 126.9, 126.8, 123.0, 122.5, 121.4, 121.2, 119.0, 117.5, 107.6, 106.5, 79.6, 77.2, 76.1, 73.8, 69.6, 69.1, 63.9, 60.8, 41.9, 40.8,40.0, 36.5, 32.3, 30.8, 30.5, 30.1, 30.0, 29.9, 29.8, 28.8, 26.6, 26.2, 26.1, 23.1, 14.5. IR (KBr) 3350, 3288, 3059, 2924, 2853, 2673, 1695, 1639, 1586, 1508, 1468, 1457, 1382, 1238, 1120. LRMS (MALDI; $(M\text{-}Boc+2H)^+$, $M+Na^+$ and $M+K^+$) calcd for $C_{105}H_{180}O_{12}N_3$ 1675, $C_{110}H_{187}O_{14}N_3Na$ 1797 and $C_{110}H_{187}O_{14}N_3K$ 1813; found 1676, 1799 and 1815.



N-Boc amine **19** was prepared in a manner analogous to *N*-Boc amine **D41** from benzoic acid **18** (214 mg, 0.120 mmol) and the amine hydrochloride **D42** (300 mg, 0.127 mmol). Silica gel chromatography (6% Et_2O-CH_2Cl_2) yielded an off-white solid (325 mg, 66%). Rf 0.48 (5% MeOH-CH_2Cl_2). ^1H NMR (500 MHz, $CDCl_3$) 7.56 (br, 1H), 7.48 (br, 1H), 7.32-7.29 (m, 5H), 7.20 (m, 3H), 7.03 (br, 1H), 6.75 (br, 1H), 6.60 (m, 3H), 6.42 (s, 2H), 6.38 (s, 4H), 6.00 (br, 2H), 5.61 (br, 2H), 4.26 (br, 2H), 4.13-4.10 (m, 4H), 3.96-3.89 (m, 22 H), 3.76-3.73 (m, 4H), 3.66 (br, 4H), 3.58-3.51 (m, 10H), 3.38 (br, 2H), 3.25 (m, 2H), 3.13 (br, 2H), 2.71 (br, 4H), 2.64 (br, 2H), 2.21 (m, 6H), 2.00 (br, 2H), 1.79-1.72 (m, 18H), 1.67-1.06 (m, 282H), 0.89-0.85 (m, 45H). ^{13}C NMR (125 MHz, $CDCl_3$) 165.3, 165.2, 164.9, 156.6, 156.3, 155.9, 155.8, 155.5, 155.4, 155.1, 154.9, 153.7, 137.4, 137.3, 134.3, 134.2, 127.2, 126.9, 126.7, 123.0, 122.8, 122.6, 122.2, 121.9, 121.0, 117.5, 117.4, 108.1, 107.6, 107.5, 107.2, 106.9, 106.3, 79.1, 76.6, 76.4, 76.2, 76.0, 73.8, 69.6, 68.9, 41.9, 41.8, 40.7, 40.3, 39.8, 36.6, 32.3, 30.8, 30.6, 30.5, 30.1, 30.0, 29.8, 29.1, 28.9, 26.6, 26.4, 26.3, 26.2, 26.1, 23.1, 14.5. IR (KBr) 3283, 3059, 2924, 2854, 1719, 1638, 1581, 1507, 1468, 1381, 1236, 1118. LRMS (MALDI; $(M\text{-}Boc+2H)^+$, $M+Na^+$ and $M+K^+$) calcd for $C_{254}H_{438}N_7O_{25}$ 3987, $C_{259}H_{445}N_7O_{27}Na$ 4109 and $C_{259}H_{445}N_7O_{27}K$ 4125; found 3992, 4113 and 4129.



This amine hydrochloride (**D58**) was prepared in a manner analogous to the amine hydrochloride **D42** from *N*-Boc amine **19** (190 mg, 46.5 μmol) as a white powder (181 mg, 98%). ^{1}H MNR (400 MHz, CD_2Cl_2) 8.21 (br, 4H), 7.40-7.33 (m, 9H), 6.85-6.83 (m, 5H), 6.43 (s, 2H), 6.41 (s, 4H), 4.30-4.15 (br, 8H), 3.88 (m, 30H), 3.58 (br, 12H), 3.15 (br, 2H), 2.82 (br, 6H), 2.29-2.17 (br, 8H), 1.76-1.71 (m, 20H), 1.47-1.12 (m, 280H), 0.93-0.87 (m, 45H). ^{13}C NMR (75 MHz, $CDCl_3$) 166.1, 165.6, 165.3, 165.1, 155.9, 155.6, 155.3, 154.7, 153.6, 137.8, 137.3, 137.2, 134.3, 134.1, 126.8, 123.7, 123.2, 122.2, 121.9, 121.1, 118.2, 117.4, 109.1, 107.4, 106.8, 76.2, 73.8, 69.5, 36.5, 33.2, 32.7, 32.4, 31.6, 30.8, 30.1, 30.0, 29.8, 29.4, 28.9, 26.6, 26.5, 26.3, 23.1, 14.5. IR (KBr) 3292, 3058, 2924, 2853, 1639, 1582, 1508, 1468, 1383, 1238, 1118. LRMS (MALDI; M+H$^+$ and M+Na$^+$) calcd for $C_{254}H_{438}N_7O_{25}$ 3987 and $C_{254}H_{437}N_7O_{25}Na$ 4009; found 3992 and 4014.



Trimer **20** was prepared in a manner analogous to *N*-Boc amine **D41** from benzoic acid **6** (17.5 mg, 20.0 μmol) and the amine hydrochloride **D58** (80.5 mg, 20.0 μmol). Silica gel chromatography (4% Et_2O-CH_2Cl_2) yielded an off-white waxy solid (65 mg, 67%). Rf 0.59 (5% MeOH-CH_2Cl_2). ^{1}H NMR (400 MHz, CD_2Cl_2, 1 mM, 303 K) 8.60-8.54 (br, 6H), 7.41-7.36 (m, 8H), 7.22 (br, 1H), 6.88-6.85 (m, 3H), 6.77 (d, J = 7.3 Hz, 1H), 6.42 (s, 4H), 6.39 (s, 2H), 6.06 (br, 2H), 4.27 (br, 4H), 4.20 (br, 2H), 4.14 (br, 2H), 4.01-3.64 (m, 50H), 2.90-2.87 (m, 6H), 2.46 (br, 4H), 2.33 (br, 4H), 1.76-1.19 (m, 378H), 0.94-0.86 (m, 54H). ^{13}C NMR (75 MHz, $CDCl_3$) 165.6, 165.3, 164.9, 156.6, 156.6, 156.4, 155.4, 155.1, 155.0, 154.6, 154.5, 153.7, 153.6, 137.7, 137.4, 137.3, 134.4, 134.1, 127.0, 126.7, 123.8, 123.6, 123.4, 123.2, 122.6, 121.1, 117.8, 107.3, 106.9, 106.5, 77.6, 76.4, 73.8, 69.5, 69.4, 52.3, 41.9, 40.0, 36.7, 32.3, 30.9, 30.3, 30.1, 30.0, 29.8, 29.0, 26.6, 26.4, 23.1, 14.5. IR (KBr) 3293, 3059, 2925, 2854, 1638, 1580, 1507, 1467, 1458, 1380, 1233, 1116. LRMS (MALDI; M+H$^+$, M+Na$^+$ and M+K$^+$) calcd for $C_{307}H_{532}N_9O_{31}$ 4842, $C_{307}H_{531}N_9O_{31}Na$ 4864 and $C_{307}H_{531}N_9O_{31}K$ 4880; found 4848, 4870 and 4886.

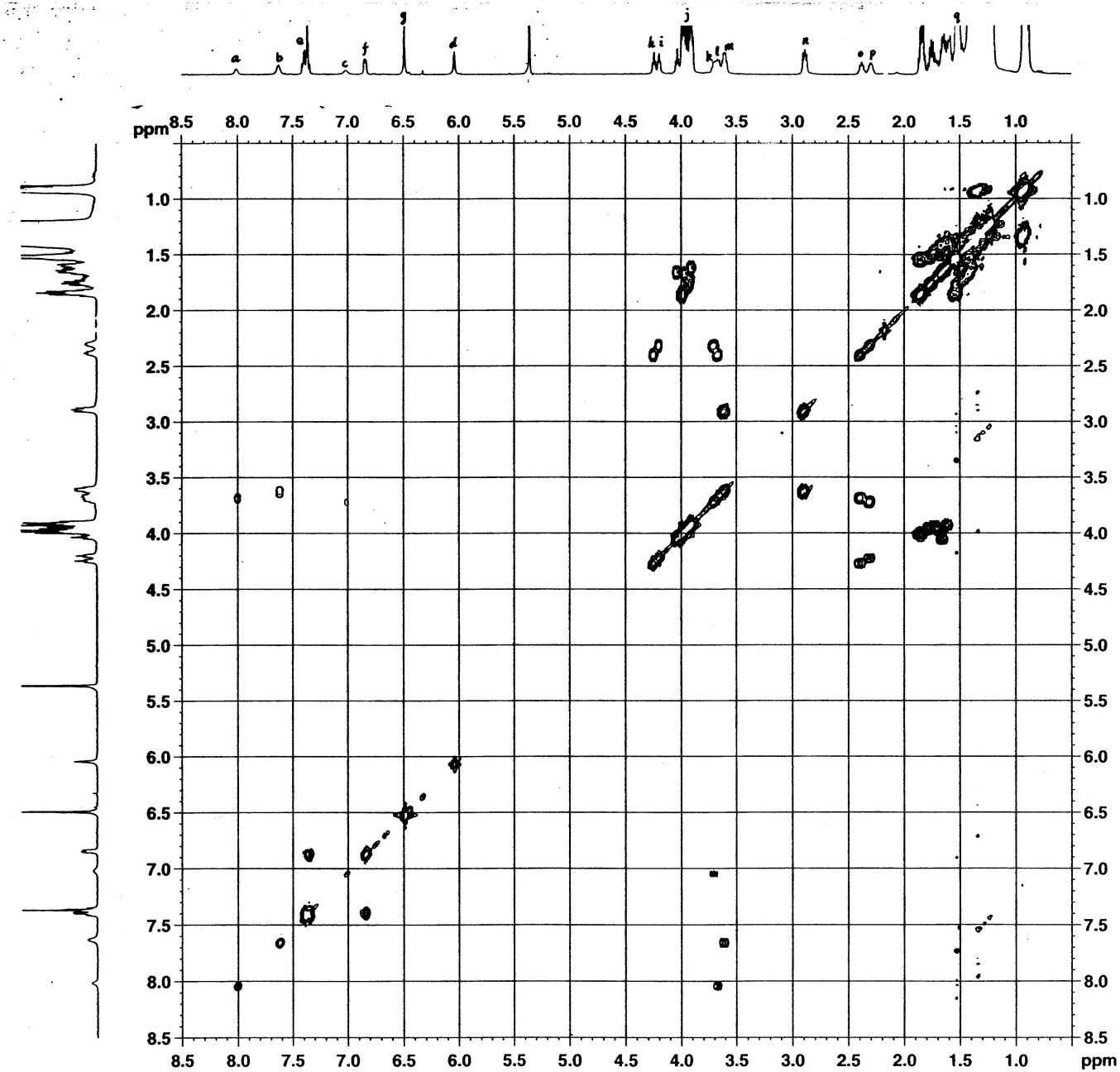
References

(1) Pangborn, A.B.; Giardello, M.A.; Grubbs, R.H.; Rosen, R.K.; Timmers, F.J. *Organometallics* **1996,** *15,* 1518-1520.

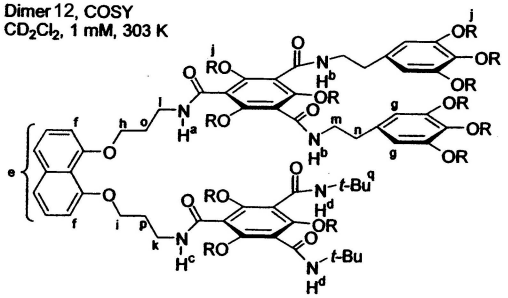
(2) Ragot, J.P.; Steeneck, C.; Alcaraz, M.L.; Taylor, R.J.K; *J. Chem. Soc., Perkin Trans.* **1999**, *1*, 1073-1082.

(3) Wei, W.H.; Tomohiro, T.; Kodaka, M.; Okuno, H.; *J. Org. Chem.* **2000,** *65,* 8979-8987.

(4) Meier, H.; Prass, E.; Zerban, G.; Kosteyn, F.; *Z. Naturforsch. B* **1988**, *43*, 889-896.



Dimer 12, COSY
CD_2Cl_2, 1 mM, 303 K

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PROCNO                      1

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D1                1.00000000 sec
d13               0.00000300 sec
D16               0.00050000 sec
IN0               0.00024994 sec

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P1                    6.60 usec
PL1                    0.00 dB
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====== GRADIENT CHANNEL =====
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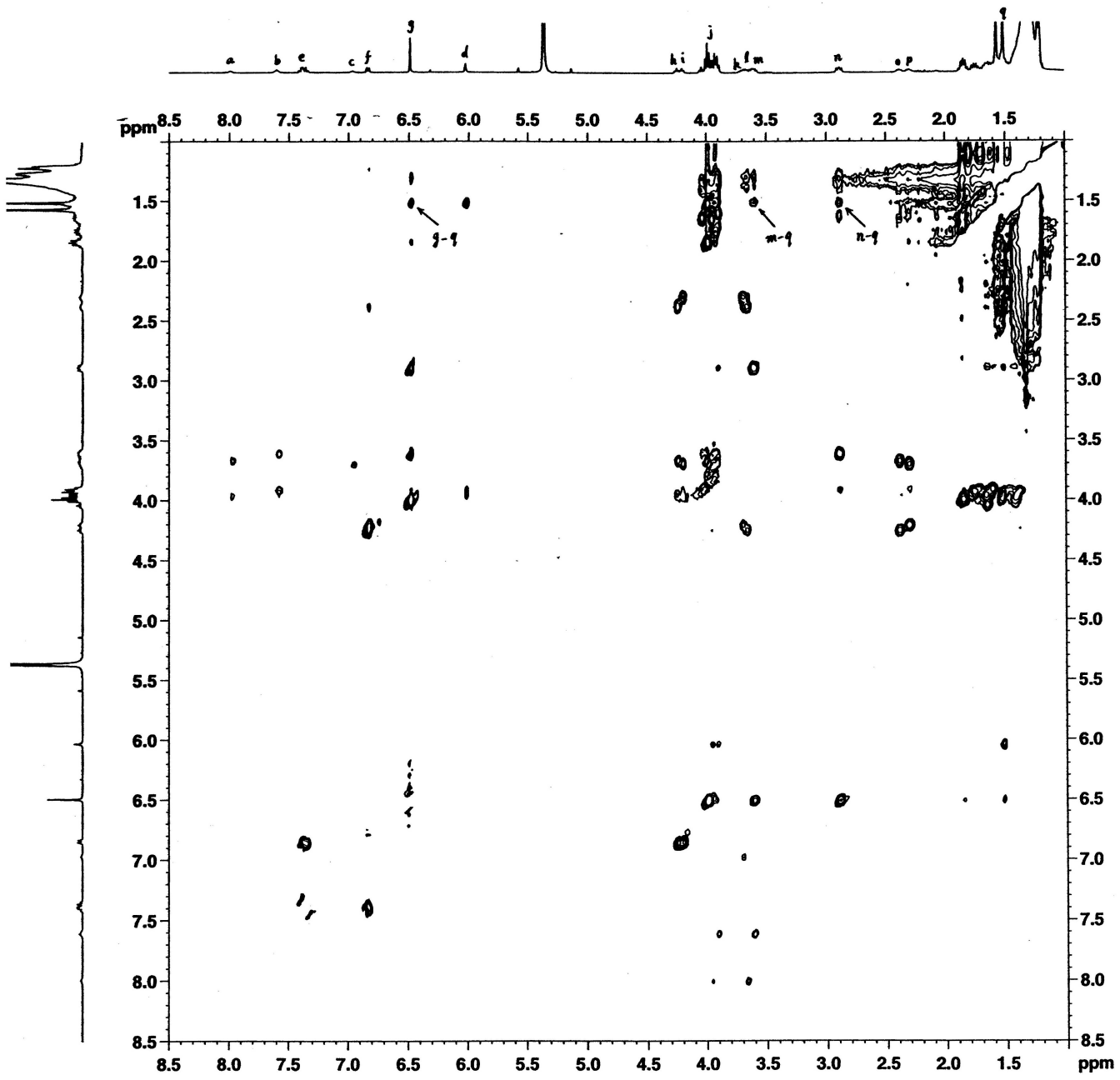
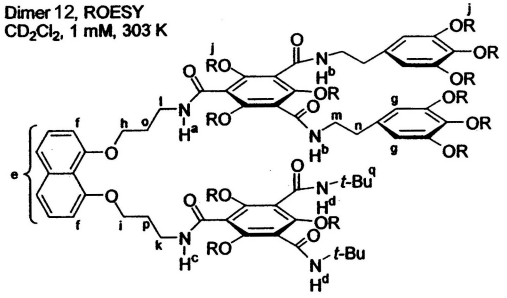


Dimer 12, ROESY
CD_2Cl_2, 1 mM, 303 K

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======== CHANNEL f1 ========
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PL1                 0.00 dB
PL11               22.00 dB
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F1 - Processing parameters
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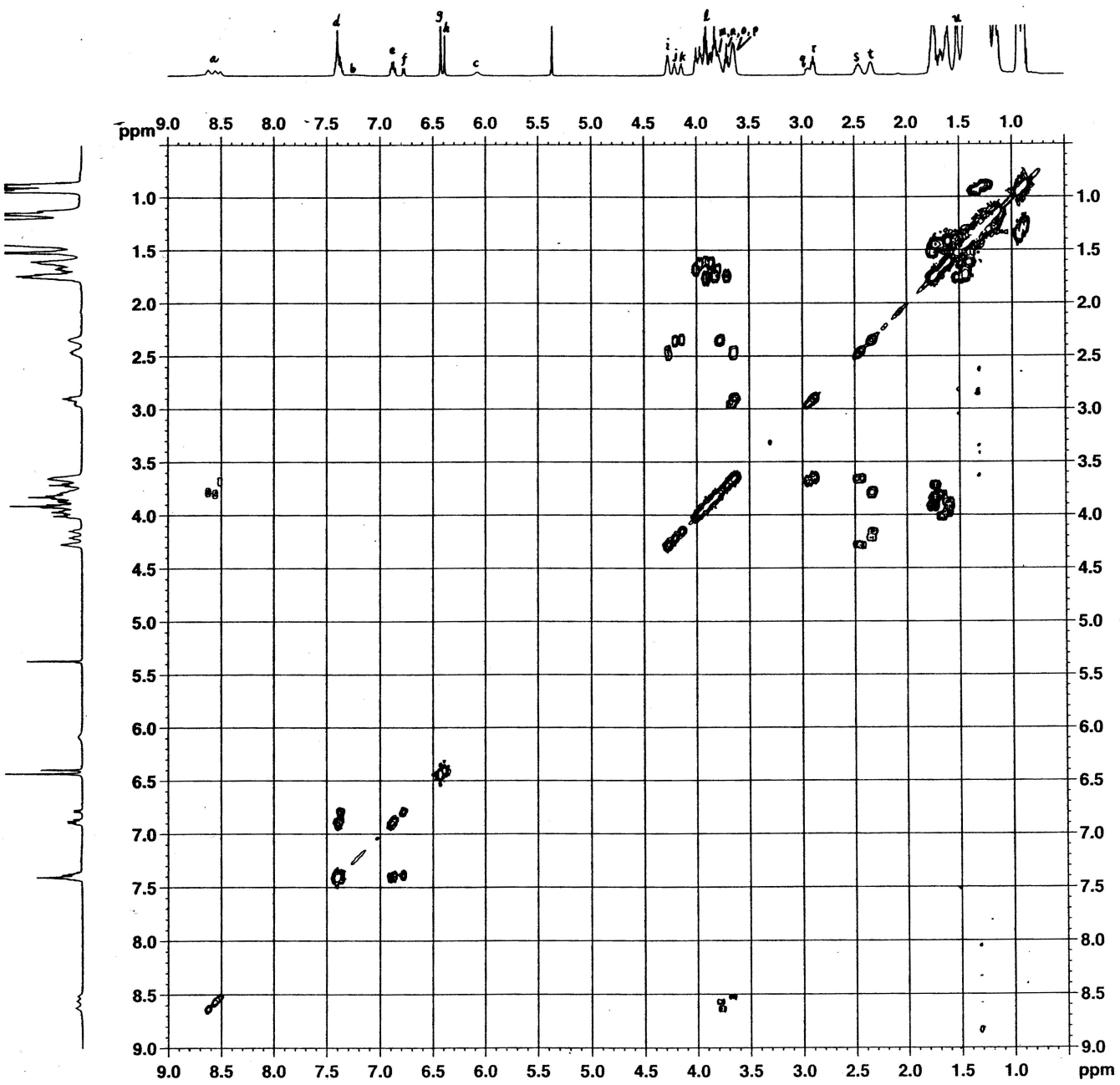
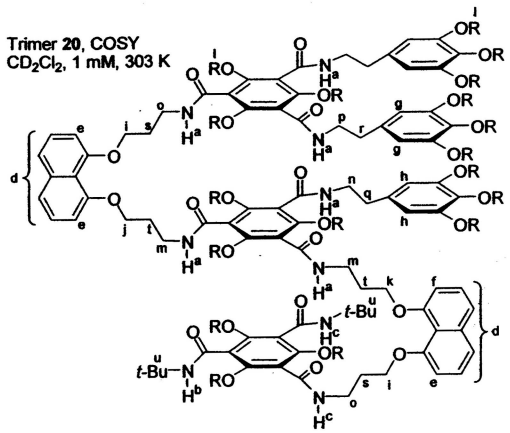


Trimer **20**, COSY
CD_2Cl_2, 1 mM, 303 K



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PROCNO                      1

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D1                  1.00000000 sec
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D16                 0.00050000 sec
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PL1                    0.00 dB
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====== GRADIENT CHANNEL =====
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FnMODE             undefined

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GB                           0
PC                        1.00

F1 - Processing parameters
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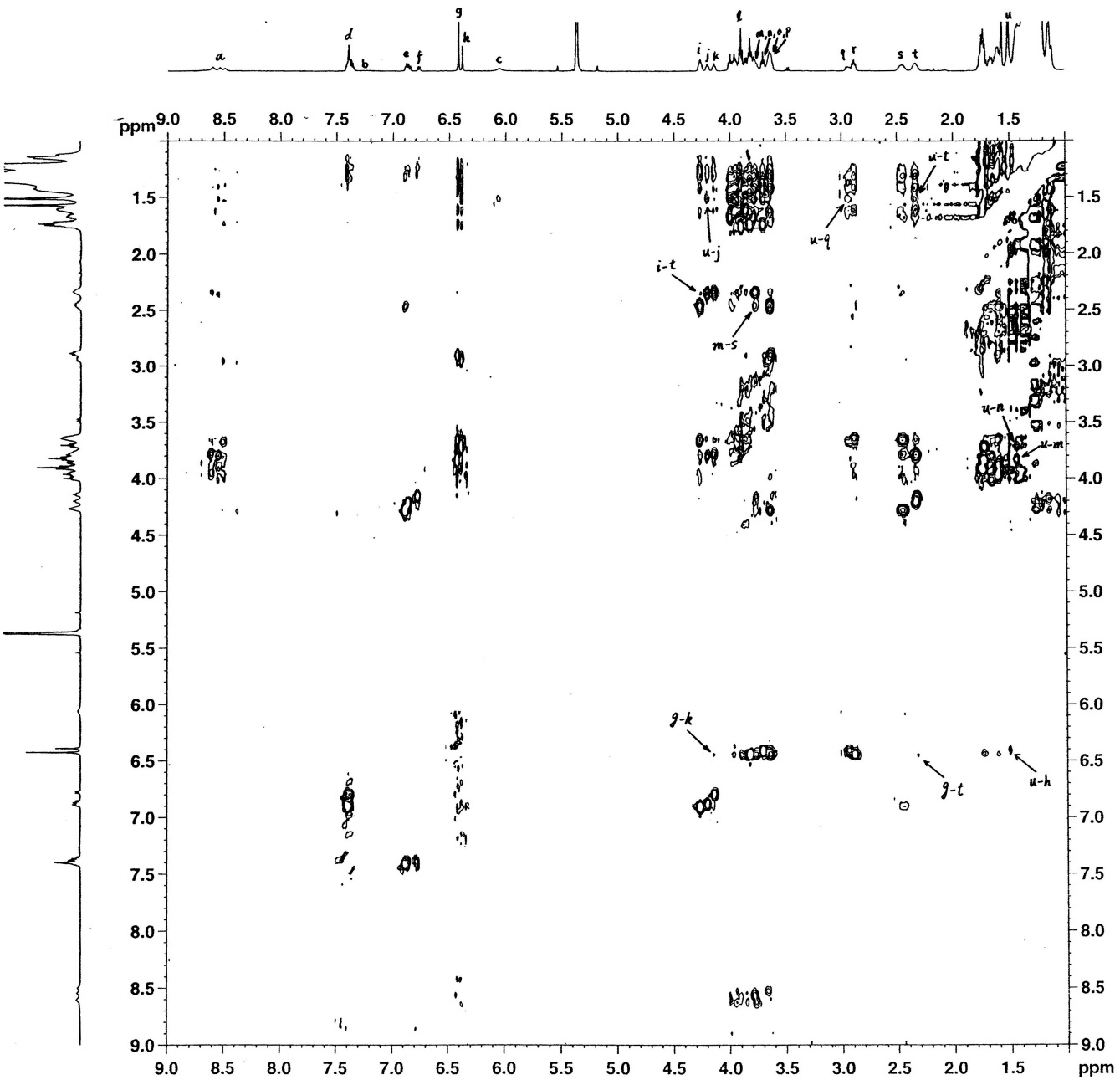
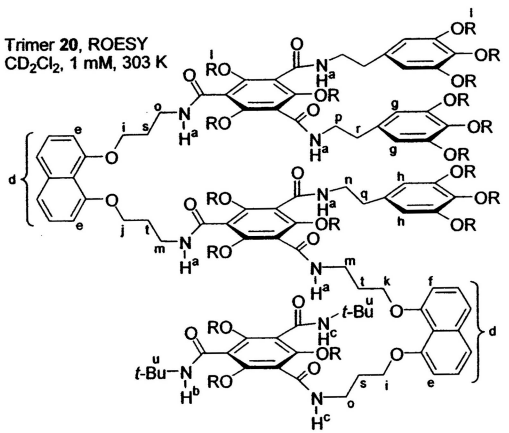


Trimer **20**, ROESY
CD_2Cl_2, 1 mM, 303 K

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PROCNO                       1

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D1                2.00000000 sec
d12               0.00002000 sec
IN0               0.00011109 sec

======== CHANNEL f1 ========
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F1 - Processing parameters
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