Supporting Information

Benzene Tricarboxamide Derivatives with Lipid and Ethylene Glycol Chains Self-Assemble into Distinct Nanostructures Driven by Molecular Packing

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Materials

Reagents and solvents were purchased from Sigma Aldrich and used without further purification, and m-dPEG$_R$-amine from Quanta Biodesign. Tetrahydrofuran (THF) was distilled under a nitrogen atmosphere from sodium and benzophenone. Dichloromethane was distilled under a nitrogen atmosphere from calcium hydride. Chloroform was distilled under a nitrogen atmosphere from calcium chloride.

Methods

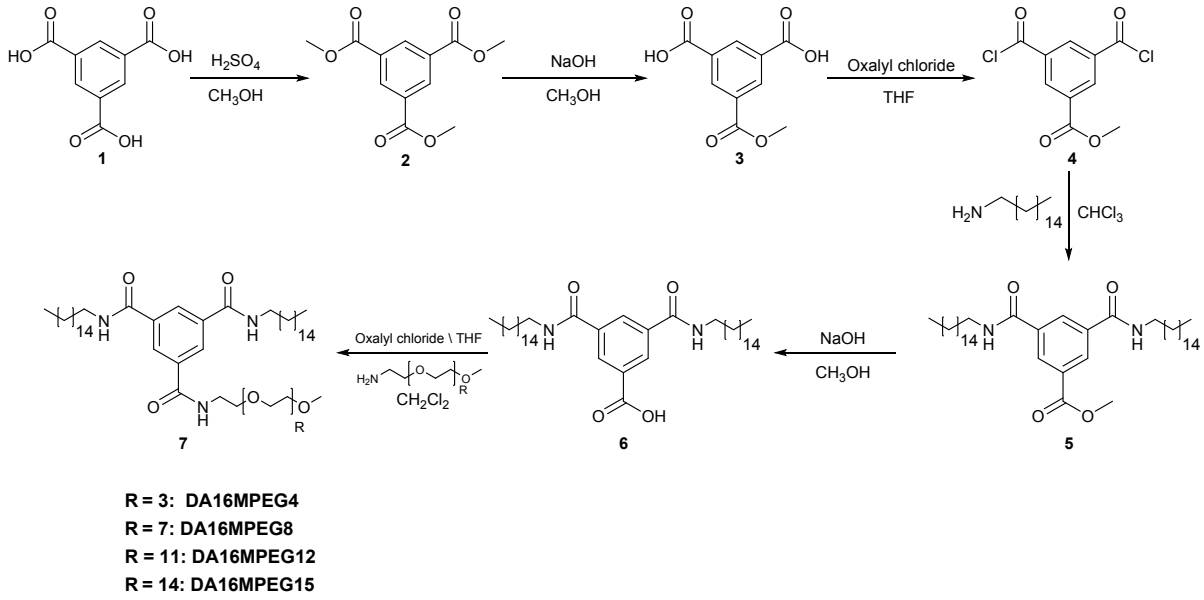
Thin layer chromatography (TLC) was performed on aluminium sheets coated with Merck silica gel 60 F_{24}. Spots were visualised under ultra-violet light (254 nm) with potassium permanganate as the visualising agent. Column chromatography was performed using Merck silica gel 60 (40–63 μm particle size) and a mobile phase as specified. Melting points were recorded using a Stuart SMP10 melting point apparatus. ^{1}H NMR and ^{13}C NMR spectra were recorded using either $CDCl_3$ or DMSO-d_6 as solvent on either a Bruker Nanobay 400 or Bruker DPX 400 operating at 400 MHz for ^{1}H NMR or at 100 MHz for ^{13}C NMR. Mass spectrometry analysis was carried out using a Thermo-Fisher Scientific Orbitrap XL LC-MS. Infrared (IR) spectroscopic analysis was carried out using a Perkin Elmer 100 FT-IR instrument with diamond-ATR sampling accessory and samples as sticky/ oily products. Spectra were scanned 32 times over the range 650−4000 cm^{-1}.

Cryogenic-Transmission Electron Microscopy (Cryo-TEM). Imaging was carried out using a field emission cryo-electron microscope (JEOL JEM-3200FSC), operating at 200 kV. Images were taken in bright field mode and using zero loss energy filtering (omega type) with a slit width of 20 eV. Micrographs were recorded using a Gatan Ultrascan 4000 CCD camera. The specimen temperature was maintained at -187 ^{o}C during the imaging. Vitrified specimens were prepared using an automated FEI Vitrobot device using Quantifoil 3.5/1 holey carbon copper

grids with a hole size of 3.5 μm. Just prior to use, grids were plasma cleaned using a Gatan Solarus 9500 plasma cleaner and then transferred into the environmental chamber of a FEI Vitrobot at room temperature and 100 % humidity. Thereafter 3 μl of sample solution was applied on the grid and it was blotted twice for 5 seconds and then vitrified in a 1/1 mixture of liquid ethane and propane at temperature of -180 °C. The grids with vitrified sample solution were maintained at liquid nitrogen temperature and then cryo-transferred to the microscope.

Small-Angle X-Ray Scattering (SAXS). Synchrotron SAXS experiments on solutions were performed using a BioSAXS robots on beamline BM29[1] at the ESRF European Synchrotron (Grenoble, France). Solutions were loaded into the 96 well plate of an EMBL BioSAXS robot, and then injected via an automated sample exchanger into a quartz capillary (1.0 mm internal diameter) in the X-ray beam. The quartz capillary was enclosed in a vacuum chamber, in order to avoid air scattering. After the sample was injected in the capillary and reached the X-ray beam, the flow was stopped during the SAXS data acquisition. BM29 operated with a fixed camera length (2.8 m) and fixed energy (12.5 keV). The images were captured using a Pilatus 2M detector. Data processing (background subtraction, radial averaging) was performed using the dedicated beamline software iSpyB.

Synthesis of DA16MPEG4, DA16MPEG8, DA16MPEG12 and DA16MPEG15



Scheme S1. Reaction scheme for DAmMPEGn compounds

Synthesis Details

Trimethyl benzene-1,3,5-tricarboxylate (2). Trimesic acid **1** (8.00 g, 38.07 mmol) was dissolved in a mixture of methanol (150 mL) and conc. H_2SO_4 (2 mL, 38.07 mmol) and the mixture stirred under reflux for 24 hours at 85 ˚C. Subsequently, the solvent was removed under vacuum and the residue dissolved in chloroform (150 mL) and washed with saturated sodium bicarbonate (200 mL). The organic layer was collected and the solvent was removed to obtain the desired product as a white powder (8.65g, 90%); IR (ATR) ν/cm^{-1}: 1724.7 (C = O, ester), 1237.7 (C - O, ester), 1445.7 (C = C, Aromatic); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 8.86 (3H, s, Aromatic), 3.98 (9H, s, -OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 165.41, 134.59, 131.20, 52.64; ESI-MS: *m/z* calculated for $[C_{12}H_{12}O_6 + H]^+$ = 253.22 Da Found = 253.07 Da.

Synthesis of 5-methoxycarbonyl-benzene-1,3-dicarboxylic acid (3). Trimethyl benzene-1,3,5-tricarboxylate **2** (5 g, 19 mmol) and 2.3 eq. NaOH (1.7 g, 44 mmol) were dissolved in MeOH (350 mL). The mixture was stirred for 24 hours under reflux at 85 °C, after which the mixture was allowed to cool down to room temperature. Thereafter, the mixture was concentrated to about 150 mL under vacuum, poured in 400 mL 1 M HCl in a separation funnel of 1 L and extracted with diethylether (3 x 300 mL). The organic layers were collected and the solvent was removed under vacuum. The crude product was recrystallized twice from ethyl

acetate and obtained as a white solid (2.86 g, 60%); IR (ATR) ν/cm^{-1}: 3248 (O-H, carboxylic acid), 1716 (C = O ester), 1187 (C - O ester), 1436 (C = C, Aromatic) ; ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm: 13.68 (1H, s, O*H*), 8.68 (3H, s, Aromatic), 3.95 (3H, s, O-C*H*$_3$); ^{13}C NMR(100 MHz, DMSO-d_6) δ ppm: 165.72 (O = *C* = OH), 164.85 (O = *C* - CH_3) 133.87 (C=*C*, Ar), 133.34 (C=*C*-COH) 130.68 (C=*C*-$COCH_3$), 52.68 (*C*H_3); ESI-MS: *m/z* calculated for $[C_{10}H_7O_6+H]^+$ = 239.05 Da Found = 239.20 Da.

Synthesis of methyl-3,5-bis-chlorocarbonyl-benzoate (4). 5-methoxycarbonylbenzene-1,3-dicarboxylic acid (1.0g, 4.46 mmol) was dissolved in 30 mL of dry THF under a nitrogen atmosphere and a catalytic amount of DMF (~ 2 droplets). To this solution was added dropwise a solution of 2.5 eq. oxalyl chloride (0.95 mL, 11.15 mmol) in 10 mL of dry THF. The reaction was stirred for 90 min at room temperature (completion checked with ^{1}H-NMR), after which the THF was removed *in vacuo* and the excess of oxalyl chloride was removed by co-evaporation with toluene (3 x 50 mL). The product was obtained as a yellow oil (1.12g, 97%). IR (ATR) ν/cm^{-1}: 1701 (C = O acyl chloride), 1698 (C = O ester), 1238 (C - O ester), 737 (C - Cl acyl chloride); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: ^{13}C NMR: δ =163.85 (O = *C* = Cl), 165.71 (O=*C*-CH_3), 133.86 (*C*=C-$COCH_3$, Aromatic), 133.36 (*C* = C-COCl), 132.07 (*C*-CCl), 129.83 (*C*-$COCH_3$), 52.70 (*C*H_3).

Synthesis of methyl-3,5-bis-n-hexadecylaminocarbonyl-benzoate (5). A solution of hexadecylamine (0.61 g, 2.53 mmol) and triethylamine (0.48 mL, 3.46 mmol) was dissolved in 30 mL dry $CHCl_3$ in ice bath under a nitrogen atmosphere. To this solution was added dropwise a solution of methyl-3,5-bis-chlorocarbonyl-benzoate **4** (0.3 g, 1.15 mmol) in 15 mL of dry $CHCl_3$. The reaction was stirred for 24 hours at room temperature under nitrogen atmosphere. Then, the solvent was removed under vacuum and the resulting crude product was purified with a short silica-gel (CH_2Cl2: MeOH; 100:2) obtained a white product (0.51 g, 66 %). IR (ATR) ν/cm^{-1}: 2921 (C – H alkyl), 1719 (C = O ester), 1662 (C = O amide), 1374 (C-N amide), 1165 (C - O ester) ; ^{1}H NMR (400 MHz/$CDCl_3$) δ ppm: δ 8.52 (2H, d, J=1.7 Hz, Ar-*H*), 8.41 (1H, t, J= 1.8 Hz), 6.33 (2H, t, J= 5.9, N-H) 3.97 (3H, s, O-C*H*$_3$), 3.48 (4H, m, N-C*H*$_2$-),1.63 (4H, m), 1.32(52H, m), 0.87 (6H, t, J= 6.8 Hz); ^{13}C NMR(100 MHz, $CDCl_3$) δ ppm: 165.8, 165.5, 135.5, 131.1, 129.7, 52.7, 40.4, 31.9, 29.7, 29.6, 29.5, 29.4, 29.3, 27.1, 22.7, 14.1; ESI-MS: *m/z* calculated for $[C_{42}H_{74}N_2O_4+H]^+$ = 671.06 Da Found = 671.57 Da.

Synthesis of 3,5-bis-n-hexadecylcarbamoyl benzoic acid (6). A solution of methyl-3,5-bis-*n*hexadecylaminocarbonylbenzoate (1.2 g, 1.79 mmol) and 2 eq. NaOH (0.14 g, 3.57 mmol) in 100 mL methanol and 2 mL water. The solution was stirred and reflux at 85 ˚C for 24h after which the solution was cooled and poured into 300 mL H2O that acidified with 1 M HCl. A white powder precipitated and was isolated by filtration. The product was dried under vacuum (0.73 g, 62 %). IR (ATR) ν/cm^{-1}: 2834 (O– H carboxylic acid), 1686 (C = O carboxylic acid), 1649 (C = O amide); ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm: 8.55 (s, 2H, Ar-*H*), 8.40 (s, 1H, Ar-*H*), 7.16 (t, 2H, N-*H*), 3.47 (m, 4H, NH-C*H2*), 1.66- 1.28 (m, 36H, C*H2*), 0.89 (m, 6H, C*H3*). ^{13}C NMR (100 MHz, DMSO-d_6) δ ppm: 167.6, 165.8, 165.5, 135.5, 131.1, 129.5, 52.7, 31.8, 29.7, 29.6, 29.5, 29.4, 29.3, 27.1, 22.7, 14.1; ESI-MS: *m/z* calculated for $[C_{42}H_{74}N_2O_4+H]^+$ = 657.04 Da Found = 657.55 Da.

General Synthesis for of 3,5-bis-n-hexadecylcarbamoyl-mono PEG (7). As a first step 3,5-bis-n-hexadecylcarbamoyl-benzoyl chloride was synthesised following the same procedure as described for **4**, 1 eq. of 3,5-bis-n-hexadecylcarbamoyl benzoic acid **6** (0.5 g,

0.76 mmol) and 1.5 eq. of oxalylchloride (97 µL, 1.14 mmol) yielding (0.5g, 98%). The resulted product was dissolved in dry CH_2Cl_2 and added slowly to a solution of m-PEG-$_R$ amine (R= 4, 8, 12, or 15) 1 eq. and triethylamine 2 eq. in dry CH_2Cl_2 in ice bath under a nitrogen atmosphere. The reaction was stirred overnight at room temperature under nitrogen atmosphere. Then, the solvent was removed under vacuum and the resulting crude product was purified with silica-gel.

Synthesis of DA16MPEG4. The synthesis of DA16MPEG4 was performed following the same procedure as described for **7,** was used m-PEG4 amine (50 mg, 0.21 mmol) and triethylamine (57 µl, 0.42 mmol) in 15 mL dry CH_2Cl_2 in 0 ˚C under a nitrogen atmosphere. To this solution, a solution of 3,5-bis-n-hexadecylaminocarbonyl-benzoyl chloride (162 mg, 0.21 mmol) in 5 mL of dry CH_2Cl_2. The reaction was stirred overnight at room temperature under nitrogen atmosphere. Then, the solvent was removed under vacuum and the resulted crude product was purified with silica-gel ($CHCl_3$: MeOH; 100:9) obtain a colourless product (85 mg, 48 %). %). IR (ATR) ν/cm^{-1}: 3454(N-H, amide), 2933 (C – H alkyl), 1645 (C = O amide), 1112 (C - O ester) ; ^{1}H NMR (400 MHz/$CDCl_3$) δ ppm: δ 8.38 (3H, t, J=1.7 Hz, Ar-*H*), 7.50 (1H, m, N-H), 6.77 (2H,m, N-H), 3.70 (2H, m), 3.65 (12H, m), 3.46 (4H, m, N-C*H*$_2$-), 3.23 (3H, s), 1.61 (4H, m), 1.26 (52 H, m), 0.88 (6H, t, J= 6.8 Hz); ^{13}C NMR(100 MHz, $CDCl_3$) δ ppm: 166.1, 165.9, 135.3,135.0, 128.7, 128.1, 71.9,70.6, 70.5, 70.4, 70.3, 69.7, 58.7, 53.4,50.8, 40.3, 31.9, 29.7, 29.6, 29.5, 29.4, 29.3, 27.0, 27.7, 14.1; ESI-MS: *m/z* calculated for $[C_{50}H_{91}N_3O_7+H]^+$ = 847.69 Da Found = 847.29 Da.

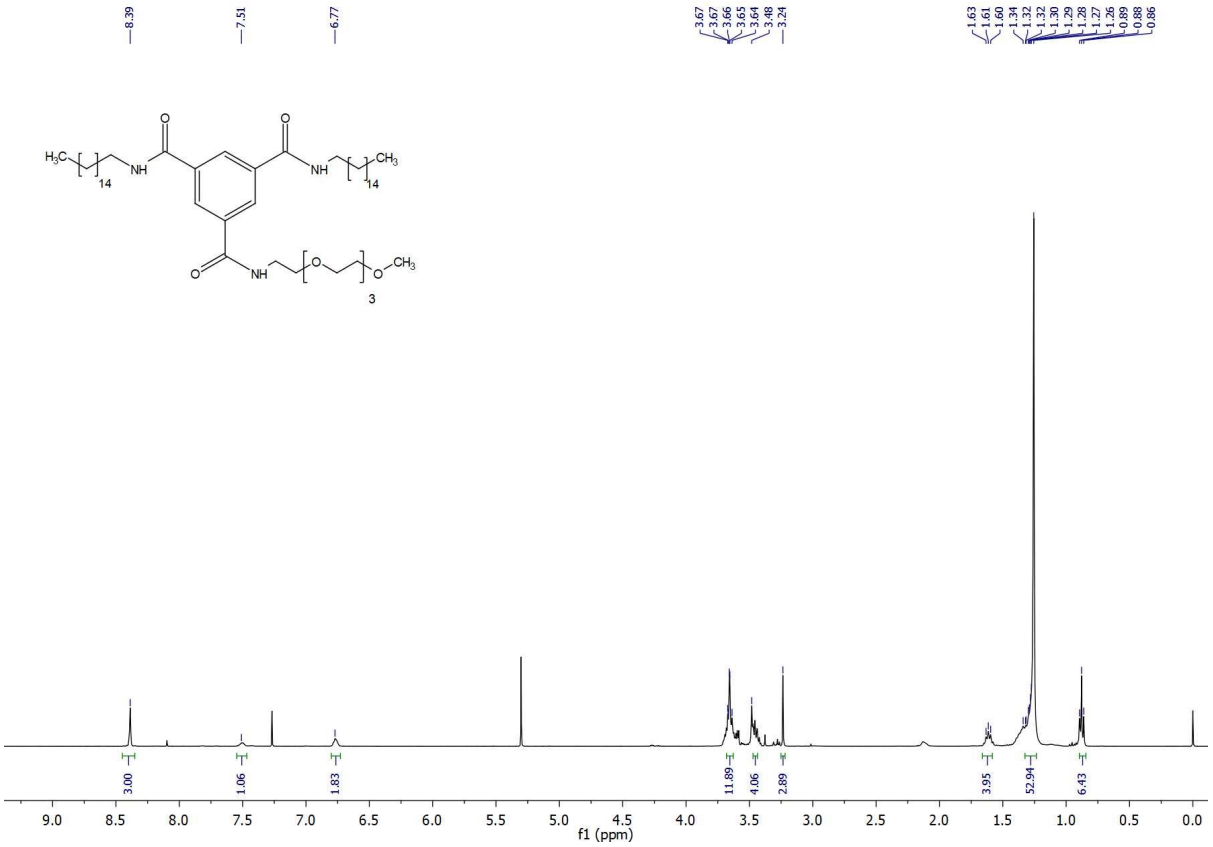


Figure S1: ^{1}H NMR spectrum of DA16MPEG4

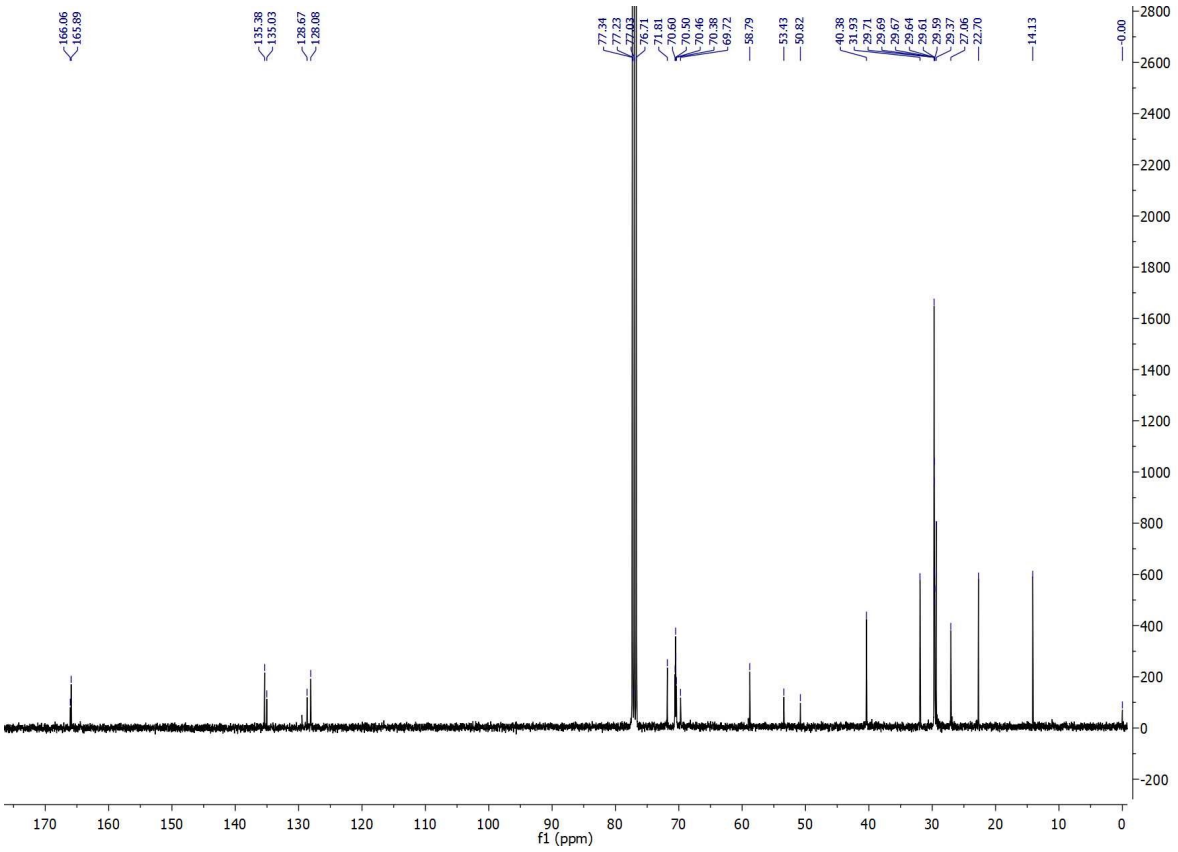


Figure S2: ^{13}C NMR spectrum of DA16MPEG4

Synthesis of DA16MPEG8. The synthesis of DA16MPEG8 was performed following the same procedure as described for **7,** was used m-PEG8 amine (90 mg, 0.23 mmol) and triethylamine (65 µl, 0.46 mmol) in 15 mL dry CH_2Cl_2 in 0 ˚C under a nitrogen atmosphere. To this solution, a solution of 3,5-bis-n-hexadecylaminocarbonyl-benzoyl chloride (158 mg, 0.23 mmol) in 5 mL of dry CH_2Cl_2. The reaction was stirred overnight at room temperature under nitrogen atmosphere. Then, the solvent was removed under vacuum and the resulting crude product was purified with silica-gel ($CHCl_3$: MeOH; 100:9) obtain a yellowish product (110 mg, 47 %). IR (ATR) ν/cm^{-1}: 3464 (N-H, amide), 2936 (C – H alkyl), 1675 (C = O amide), 1097 (C - O ester) ; ^1H NMR (400 MHz/$CDCl_3$) δ ppm: δ 8.44 (3H, t, J=1.7 Hz, Ar-*H*), 7.53 (1H, m, N-H), 6.93 (2H, m, N-H), 3.70 (2H, m), 3.60 (28H, m), 3.44 (4H, m, N-C*H*$_2$-), 3.32 (3H, s), 1.62 (4H, m), 1.26 (52 H, m), 0.88 (6H, t, J= 6.8 Hz); ^{13}C NMR(100 MHz, $CDCl_3$) δ ppm: 166.1, 165.9, 135.4,135.0, 128.7, 128.4, 71.8,70.6, 70.5, 70.4, 70.3, 58.7, 53.4, 40.4, 31.9, 29.7, 29.6, 29.5, 29.4, 29.3, 27.1, 27.7, 14.1; ESI-MS: *m/z* calculated for $[C_{58}H_{107}N_3O_{11}+H]^+$ = 1022.50 Da Found = 1022.79 Da.

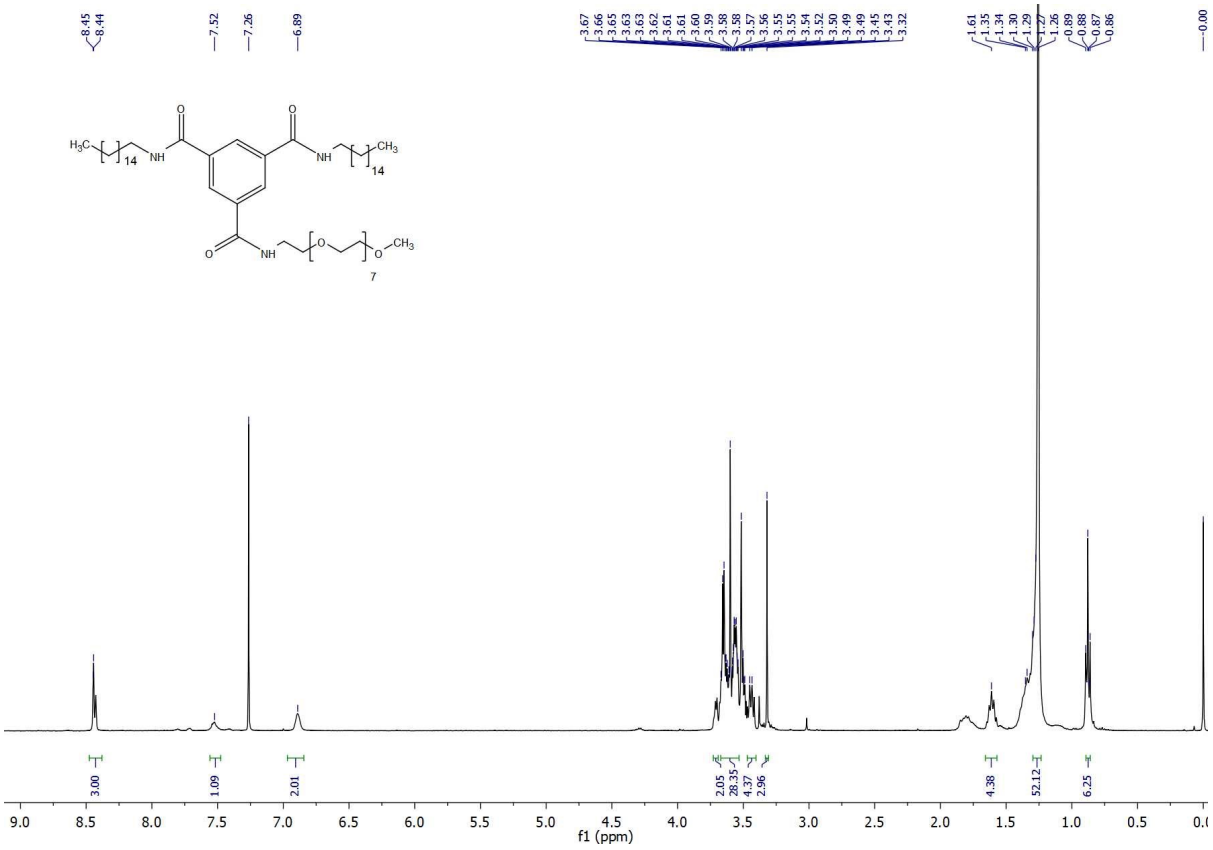


Figure S3: ^{1}H NMR spectrum of DA16MPEG8

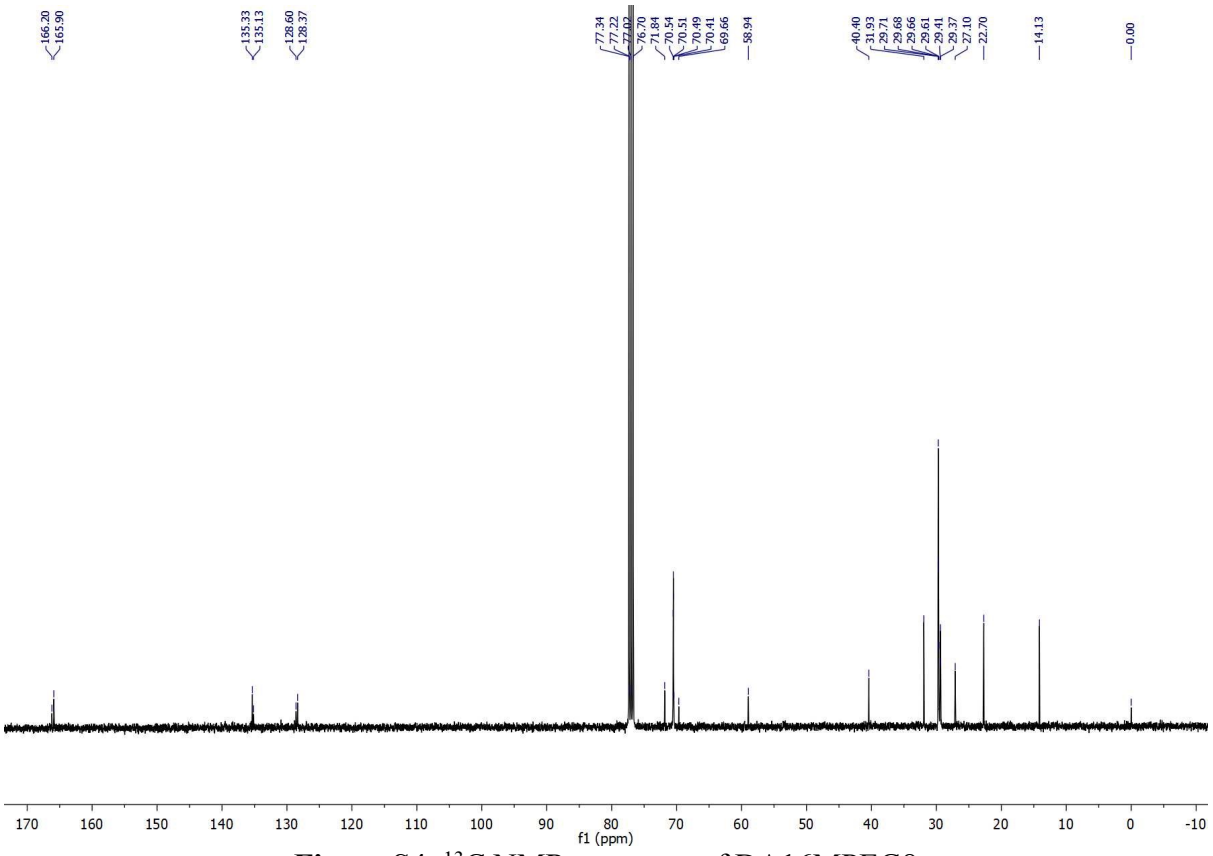


Figure S4: ^{13}C NMR spectrum of DA16MPEG8

Synthesis of DA16MPEG12. The synthesis of DA16MPEG12 was performed following the same procedure as described for **7,** was used m-PEG12 amine (23 mg, 0.04 mmol) and triethylamine (11.6 µl, 0.08 mmol) in 15 mL dry CH_2Cl_2 in 0 ˚C under a nitrogen atmosphere. To this solution, a solution of 3,5-bis-n-hexadecylaminocarbonyl-benzoyl chloride (29 mg, 0.04 mmol) in 5 mL of dry CH_2Cl_2. The reaction was stirred overnight at room temperature under nitrogen atmosphere. Then, the solvent was removed under vacuum and the resulting crude product was purified with silica-gel ($CHCl_3$: MeOH; 100:9) obtain a colourless product (35 mg, 50 %). IR (ATR) ν/cm^{-1}: 3436 (N-H, amide), 2936 (C – H alkyl), 1668 (C = O amide), 1079 (C - O ester) ; ^{1}H NMR (400 MHz/$CDCl_3$) δ ppm: δ 8.44 (3H, t, J=1.7 Hz, Ar-*H*), 7.54 (1H, m, N-H), 6.91 (2H,m, N-H), 3.70 (2H, m), 3.60 (44H, m), 3.44 (4H, m, N-C*H*$_2$-), 3.32 (3H, s), 1.62 (4H, m), 1.26 (52 H, m), 0.88 (6H, t, J= 6.8 Hz); ^{13}C NMR(100 MHz, $CDCl_3$) δ ppm: 166.1, 165.9, 135.4,135.1, 128.6, 128.4, 71.9, 70.6, 70.5, 70.4, 70.3, 58.7, 53.4, 40.4, 31.9, 29.7, 29.6, 29.5, 29.4, 29.3, 27.1, 27.7, 14.1; ESI-MS: *m/z* calculated for $[C_{66}H_{123}N_3O_{15}+Na]^+$ = 1220.70 Da Found = 1220.88 Da.

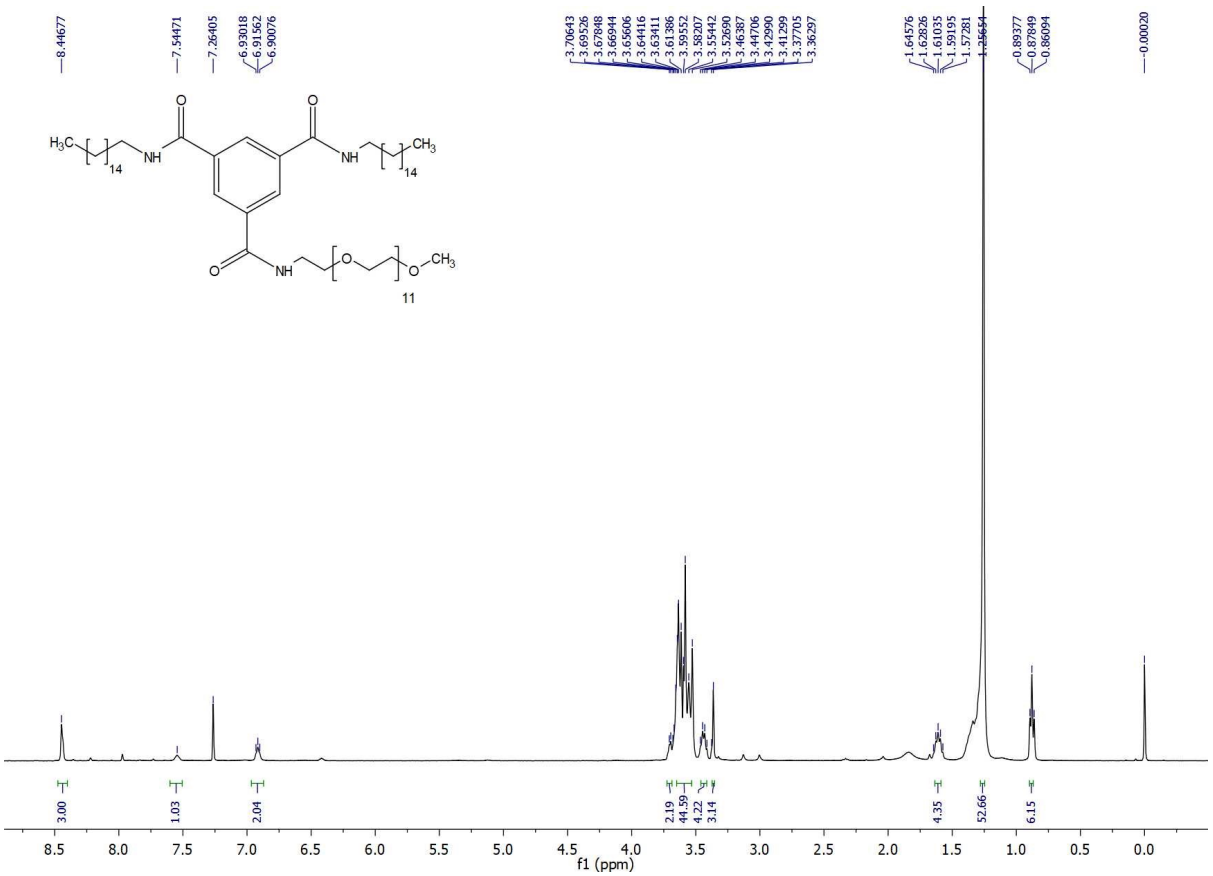


Figure S5: ^{1}H NMR spectrum of DA16MPEG12

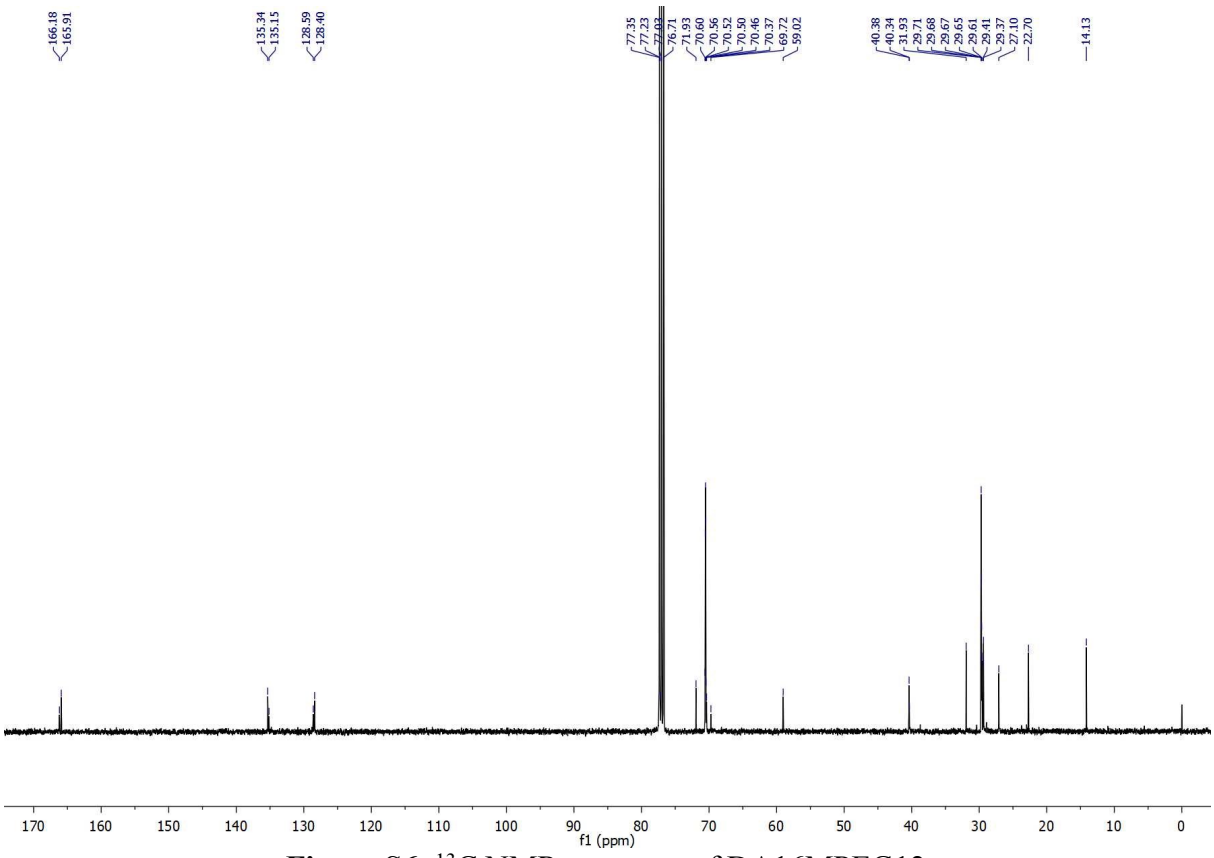


Figure S6: ^{13}C NMR spectrum of DA16MPEG12

Synthesis of DA16MPEG15. The synthesis of DA16MPEG15 was performed following the same procedure as described for **7,** was used m-PEG15 amine (37 mg, 0.05 mmol) and triethylamine (15 µl, 0.46 mmol) in 15 mL dry CH_2Cl_2 in 0 ˚C under a nitrogen atmosphere. To this solution, a solution of 3,5-bis-n-hexadecylaminocarbonyl-benzoyl chloride (36 mg, 0.05 mmol) in 5 mL of dry CH_2Cl_2. The mixture was stirred for overnight at room temperature under nitrogen atmosphere. Then, the solvent was removed under vacuum and the resulting crude product was purified with silica-gel ($CHCl_3$: MeOH; 100:9) obtain a colourless product (33 mg, 46 %). IR (ATR) ν/cm^{-1}: 3454 (N-H, amide), 2933 (C – H alkyl), 1662 (C = O amide), 1098 (C - O ester) ; ^1H NMR (400 MHz/$CDCl_3$) δ ppm: 8.44 (3H, t, J=1.7 Hz, Ar-*H*), 7.58 (1H, m, N-H), 6.93 (2H,m, N-H), 3.70 (2H, m), 3.60 (56H, m), 3.44 (4H, m, N-C*H*$_2$-), 3.32 (3H, s), 1.62 (4H, m), 1.26 (52 H, m), 0.88 (6H, t, J= 6.8 Hz); ^{13}C NMR(100 MHz, $CDCl_3$) δ ppm: 166.1, 165.9, 135.4,135.0, 128.7, 128.4, 71.8,70.6, 70.5, 70.4, 70.3, 58.7, 53.4, 40.4, 31.9, 29.7, 29.6, 29.5, 29.4, 29.3, 27.1, 27.7, 14.1; ESI-MS: *m/z* calculated for $[C_{72}H_{135}N_3O_{18}+H]^+$ = 1330.85 Da Found = 1330.79 Da.

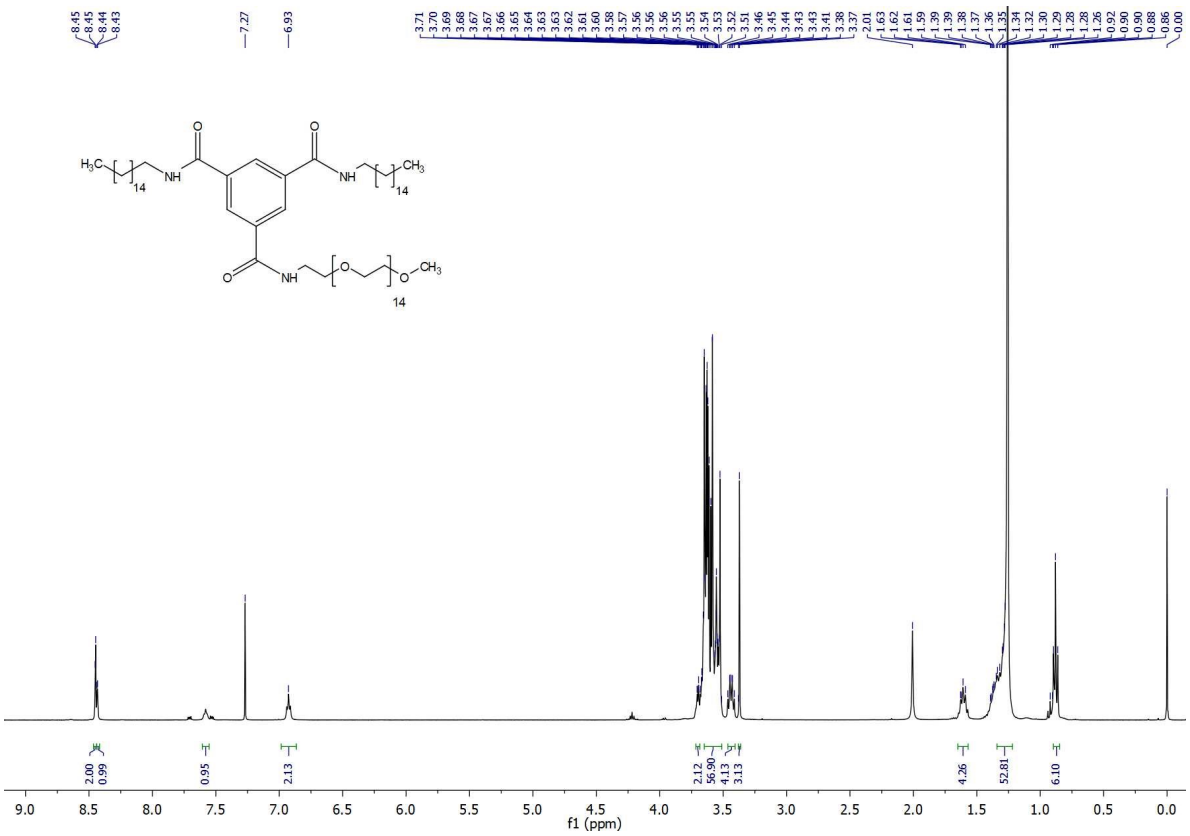
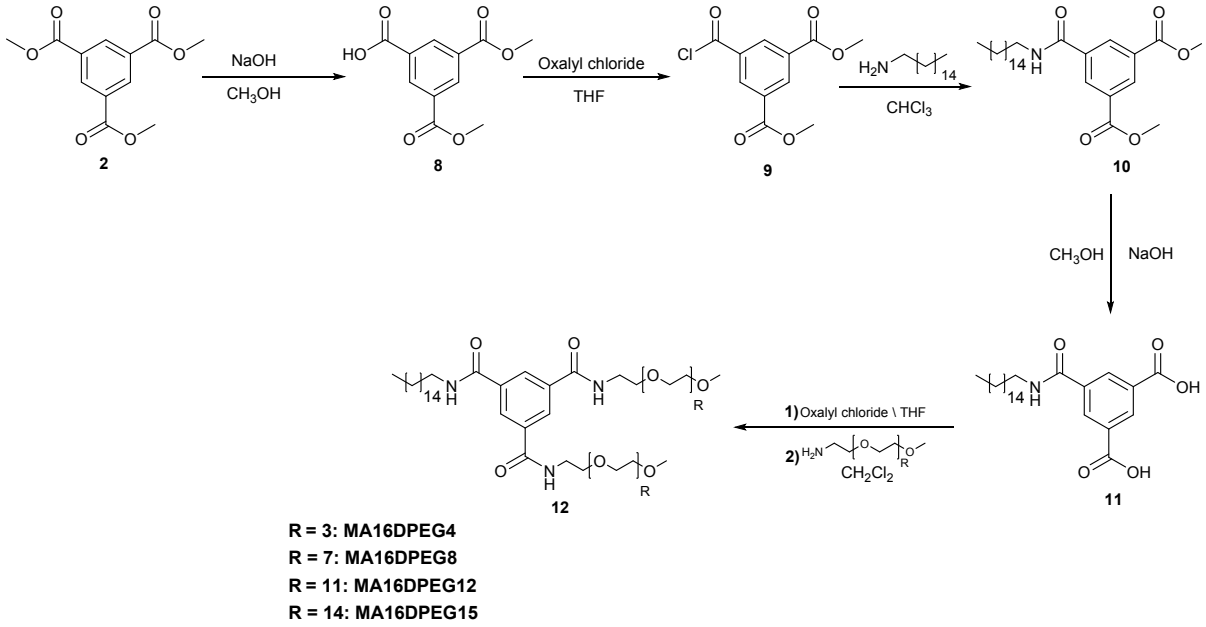


Figure S7: ^{1}H NMR spectrum of DA16MPEG15

Figure S8: ^{13}C NMR spectrum of DA16MPEG15

Synthesis of MA16DPEG4, MA16DPEG8, MA16DPEG12 and MA16DPEG15



Scheme S2. Reaction scheme for MA16DPEGn compounds

Synthesis of 1,3-dimethoxycarbonyl-benzene-5-carboxylic acid (8). Benzene-1,3,5-tricarboxylic acid trimethyl ester **2** (5.00 g, 19.82 mmol) and 4M NaOH (0.95 g, 23.78 mmol) were dissolved in methanol (150 mL) and refluxed for overnight at 85 ˚C. after which the solvent was removed under vacuum and dissolved in CH_2Cl_2 (300 mL) and extracted with saturated sodium bicarbonate solution (600 mL). The collected aqueous phase was washed with CH_2Cl_2 and acidified with 1M HCl resulting white precipitate that filtered and dried under vacuum giving white solid (3.30 g, 70%). IR (ATR) ν/cm^{-1}: 3248 (O-H, carboxylic acid), 1701 (C = O ester), 1215 (C - O ester), 1436 (C = C, Aromatic);^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 8.68 (3H, d, Ar–H), 3.96 (6H, s, –O*CH*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 165.62, 165.40, 133.09, 132.03, 52.65; M.P. = 192-195 ˚C**;** ESI-MS: *m/z* calculated for $[C_{11}H_{10}O_6+H]^+$ = 239.19 Da Found = 239.05 Da.

Synthesis of dimethyl 5-(chlorocarbonyl) isophthalate (9). 1,3-dimethoxycarbonyl-benzene-5-carboxylic acid **8** (0.5 g, 2.10 mmol) was dissolved in 25 mL dry chloroform. After addition of a catalytic amount DMF, oxalyl chloride (190 µL, 2.25 mmol) in 10 mL dry chloroform was added drop wise. After stirring for 90 minutes, the excess oxalyl chloride and chloroform were removed *in vacuo*. The remaining solid was co-evaporated twice with 50 mL toluene to ensure the removal of oxalyl chloride. The product was obtained as a yellow oil (0.52 g, 98%); IR (ATR) ν/cm^{-1}: 1722 (C = O acid chloride), 1436 (C = C, Aromatic), 1267 (C - O), 731 (C - Cl); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 167.62, 165.65,133.84, 133.32, 132.21, 129.47, 52.70.

Synthesis of dimethyl 5-(hexadecylcarbamoyl)isophthalate (10). A solution of hexadecylamine (1.12 g, 4.67 mmol) and TEA (0.79 g, 4.67 mmol) was dissolved in dry CH_2Cl_2 (50 mL) under nitrogen atmosphere at 0 ˚C. To this solution, a solution of dimethyl 5-(chlorocarbonyl) isophthalate **9** (1.00 g, 3.86 mmol) in dry CH_2Cl_2 (10 mL) was added drop wise to that and stirred for 24h at room temperature. Then, the solvent was removed under vacuum and the crude product was purified by column chromatography (CH_2Cl_2: MeOH, 100:1) yielding a white powder (1.12 g, 63%)**;** IR (ATR) ν/cm^{-1}: 2917 (N-H), 2849.4 (C-H), 1733.8 (C=O, ester), 1637.6 (C=O, amide), 1534.8 (N-H), 1443.23 (C=C, Aromatic), 1247 (C-O, ester), 1195.8 (C-N, amide), 742.8 (N-H); ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm: 8.79 (1H, s, Aromatic), 8.61 (2H, s, Aromatic), 6.22 (1H, t, N-*H*), 3.97 (6H, s, O-C*H*$_3$), 3.49 (2H, m, N-C*H*$_2$), 1.64 (2H, m, N-CH_2CH2), 1.35 (26H, m, alkyl), 0.87 (3H, t,-C*H*$_3$); ^{13}C NMR(100 MHz, $CDCl_3$) δ ppm: 165.62, 165.27, 133.09, 132.03, 131.18, 52.65, 40.43, 31.94, 29.58, 22.70, 14.14; ESI-MS: *m/z* calculated for $[C_{27}H_{43}NO_5+H]^+$ = 462.64 Da Found = 462.64 Da.

Synthesis of 5-(hexadecylcarbamoyl) isophthalic (11). Dimethyl 5-(hexadecylcarbamoyl)isophthalate **10** (0.78 g, 1.68 mmol) was dissolved in methanol (20 mL) with 4M NaOH (0.16 g, 3.86 mmol) that was stirred and reflux at 85 ˚C for 24 hours. the mixture was cooled to room temperature before being poured to 300 mL of 1M HCl. A white powder precipitate was formed and filtered. The precipitate was recrystallized from ethyl acetate (2 times), leading to a white product (0.30 g, 42%). IR (ATR) ν/cm^{-1}: 3358 (N – H amide), 2917 (O – H carboxylic acid), 1704 (C = O ester), 1630 (C = O amide), 1472 (C-N amide), 1158 (C - O ester); ^{1}H-NMR (400 MHz, DMSO-d_6) ppm δ: 13.52 (1H, OH), 8.89 (1H, t, N*H*), 8.63 (3H, d, Aromatic), 1.57 (2H, m, N-*CH*$_2$), 1.32 (26H, s, CH_2*CH*$_2$), 0.87 (3H, t, -*CH*$_3$); ^{13}C NMR (400 MHz, DMSO-d_6) ppm δ: 165.59, 164.72, 133.67, 133.09, 130.86, 40.43, 31.94, 29.19, 22.70, 14.14**;** ESI-MS: *m/z* calculated for $[C_{27}H_{43}NO_5+H]^+$ = 434.59 Da Found = 434.28 Da.

General Synthesis for of hexadecylcarbamoyl-3,5-bis-n- PEG (12). As a first step 5-(hexadecylcarbamoyl)isophthaloyl dichloride was synthesised following the same procedure as described for **9**, 1 eq. of 5-(hexadecylcarbamoyl) isophthalic **11** (0.2 g, 0.46 mmol) and 2.5 eq. of oxalylchloride (99 µL, 1.15 mmol) yielding (0.21g, 98%). The resulted product was dissolved in dry $CHCl_3$ and added slowly to a solution of m-PEG-$_R$ amine (R= 4, 8, 12, or 15) 2 eq. and triethylamine 3 eq. in dry CH_2Cl_2 in ice bath under a nitrogen atmosphere. The reaction was stirred overnight at room temperature under nitrogen atmosphere. Then, the solvent was removed under vacuum and the resulting crude product was purified by column chromatography.

Synthesis of MA16DPEG4 (12a). MA16DPEG4 was performed following the same procedure as described for **12,** was used m-PEG4 amine (300 mg, 0.66 mmol) and triethylamine (275 µl, 1.98 mmol) in 15 mL dry CH_2Cl_2 in 0 ˚C under a nitrogen atmosphere. To this solution, a solution of 5-(hexadecylcarbamoyl)isophthaloyl dichloride (270 mg, 1.32 mmol) in 5 mL of dry CH_2Cl_2. The reaction was stirred overnight at room temperature under nitrogen atmosphere. Then, the solvent was removed under vacuum and the resulting crude product was purified with silica-gel ($CHCl_3$: MeOH; 100:9.5) providing a colourless oil (266 mg, 50 %). IR (ATR) ν/cm^{-1}: 3448 (N-H, amide), 2927 (C – H alkyl), 1663 (C = O amide), 1108 (C - O ester) ; ^{1}H NMR (400 MHz/$CDCl_3$) δ ppm: δ 8.44 (1H, t, J=1.7 Hz, Ar-*H*), 8.42 (2H, d, J=1.6), 7.46 (2H, m, N-H), 6.88 (1H,m, N-H), 3.66 (24H, m), 3.49 (4H, m), 3.44 (2H, m, N-C*H*$_2$-), 3.28

(6H, s), 1.64 (2H, m), 1.26 (26 H, m), 0.88 (3H, t, J= 6.8 Hz); ^{13}C NMR(100 MHz, $CDCl_3$) δ ppm: 166.1, 165.9, 135.3,135.1, 128.4, 71.9, 70.6, 70.5, 70.4, 70.3,69.8, 58.7,40.3, 40.2, 31.9, 29.7, 29.6, 29.5, 29.4, 29.3, 27.1, 22.7, 14.1; ESI-MS: *m/z* calculated for $[C_{43}H_{77}N_3O_{11}+H]^+$ = 812.10 Da Found = 812.56 Da.

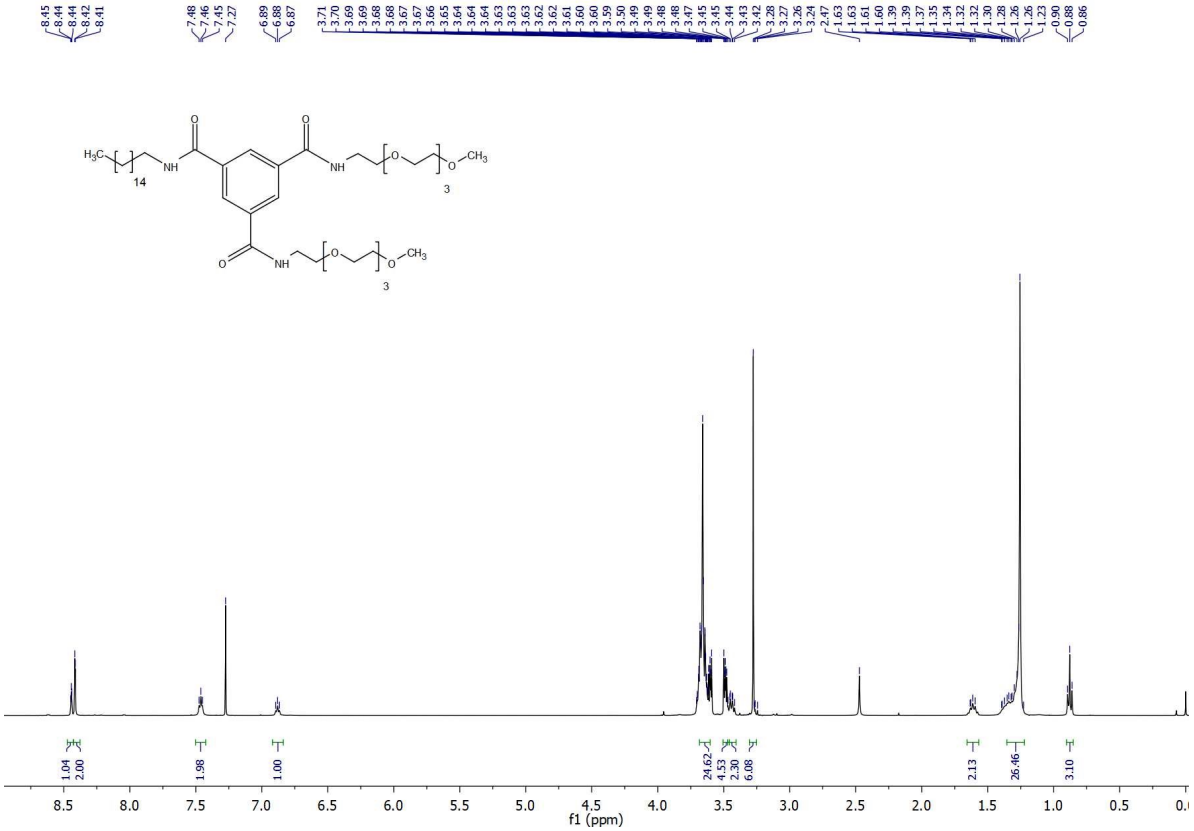


Figure S9: ^{1}H NMR spectrum of MA16DPEG4

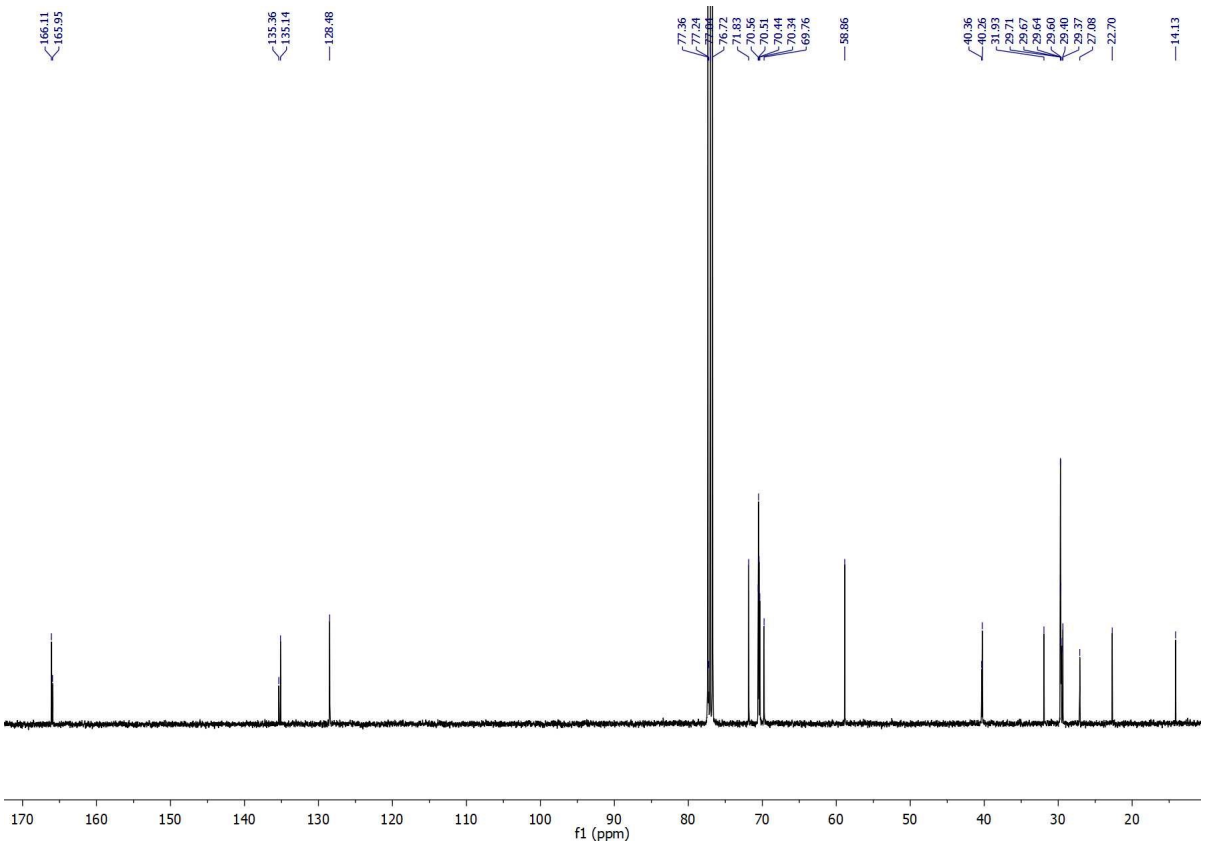


Figure S10: ^{13}C NMR spectrum of MA16DPEG4

Synthesis of MA16DPEG8 (12b). The synthesis of MA16DPEG8 was performed following the same procedure as described for **12,** was used m-PEG8 amine (78 mg, 0.20 mmol) and triethylamine (43 µl, 30 mmol) in 15 mL dry CH_2Cl_2 in 0 ˚C under a nitrogen atmosphere. To this solution, a solution of 3,5-bis-n-hexadecylaminocarbonyl-benzoyl chloride (47 mg, 0.10 mmol) in 5 mL of dry CH_2Cl_2. The reaction was stirred overnight at room temperature under nitrogen atmosphere. Then, the solvent was removed under vacuum and the resulting crude product was purified with silica-gel ($CHCl_3$: MeOH; 100:9.5) leading to a colourless oil (57 mg, 48 %). IR (ATR) ν/cm^{-1}: 3449 (N-H, amide), 2928 (C – H alkyl), 1663 (C = O amide), 1100 (C - O ester) ; ^1H NMR (400 MHz/$CDCl_3$) δ ppm: δ 8.48 (1H, t, J=1.7 Hz, Ar-*H*), 8.46 (2H, d, J=1.6), 7.46 (2H, t, J=5.18, N-H), 7.04 (1H, t, J= 5.68, N-H), 3.62 (56H, m), 3.53 (4H, m), 3.43 (2H, m, N-C*H*$_2$-), 3.34 (6H, s), 1.64 (2H, m), 1.26 (26 H, m), 0.88 (3H, t, J= 6.8 Hz); ^{13}C NMR(100 MHz, $CDCl_3$) δ ppm: 166.1, 165.9, 135.3,135.1, 128.7, 128.4, 71.9, 70.6, 70.5, 70.4, 70.3, 69.8, 58.7,40.3, 40.3, 31.9, 29.7, 29.6, 29.5, 29.4, 29.3, 27.1, 22.7, 14.1; ESI-MS: *m/z* calculated for $[C_{43}H_{77}N_3O_{11}+H]^+$ = 1164.51 Da Found = 1164.77 Da.

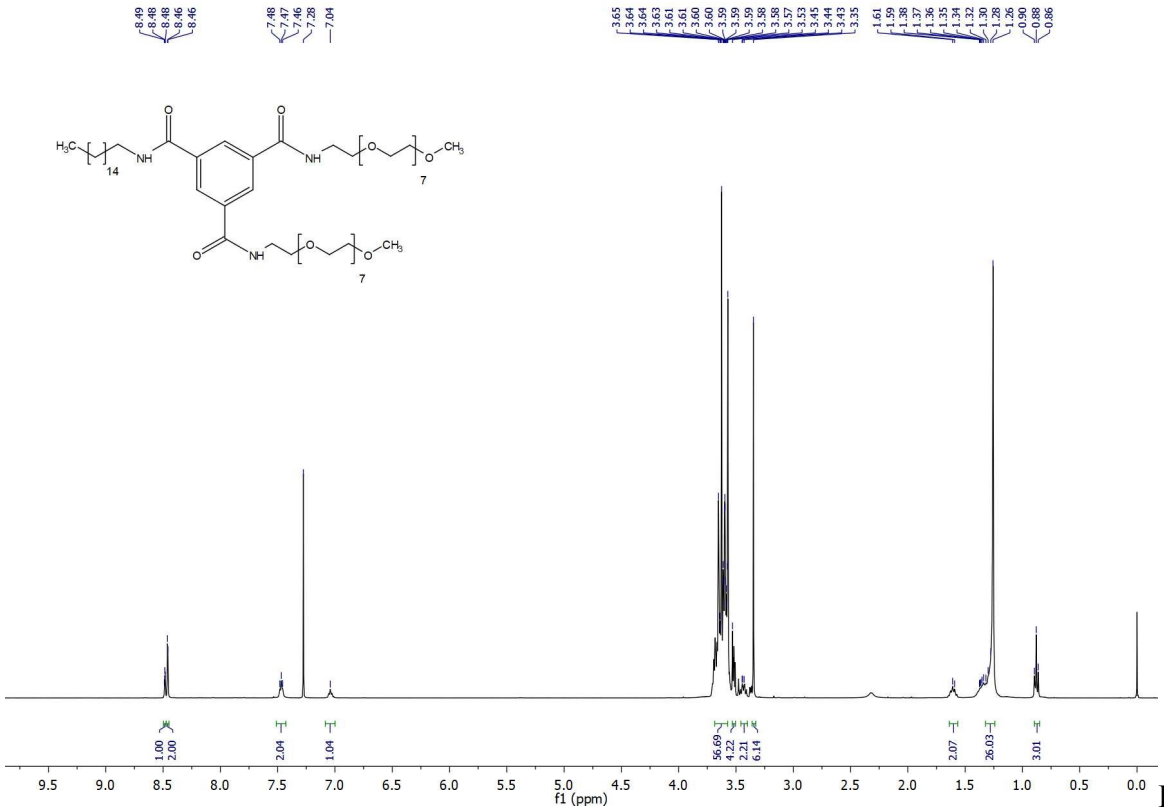


Figure S11: ^{1}H NMR spectrum of MA16DPEG8

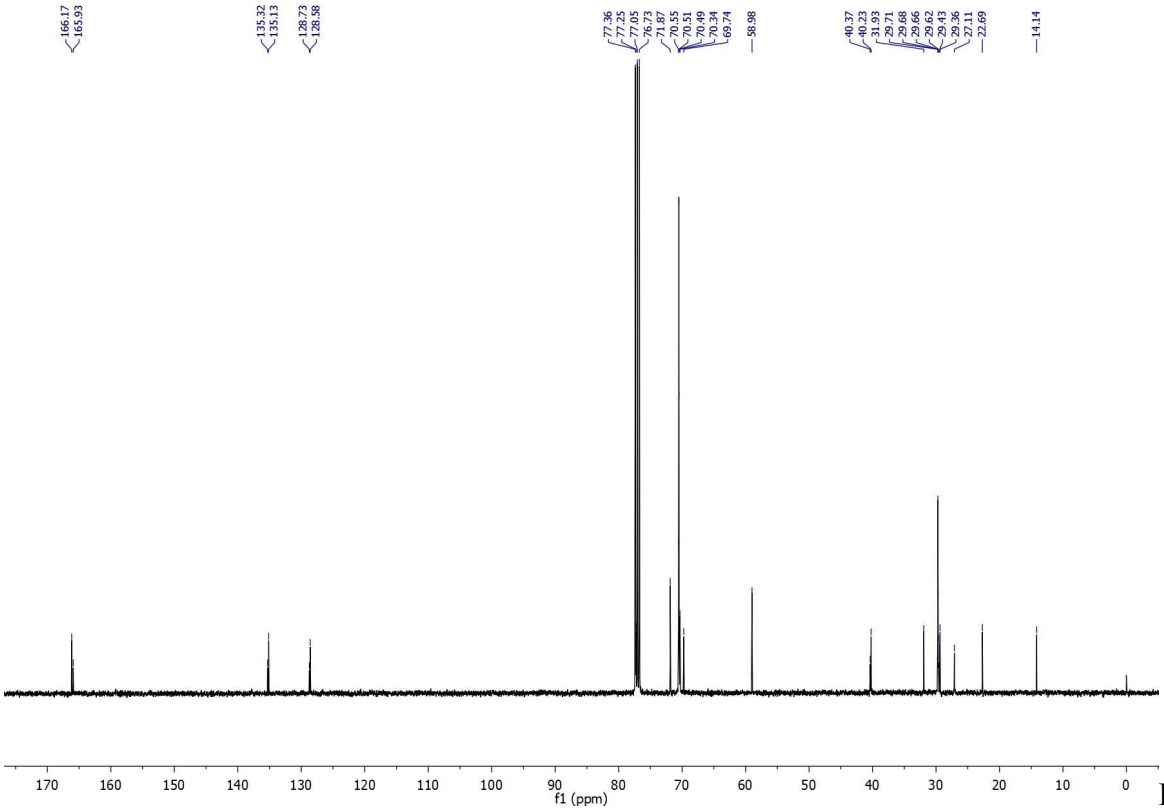


Figure S12: ^{13}C NMR spectrum of MA16DPEG8

Synthesis of MA16DPEG12 (12c). The synthesis of MA16DPEG12 was performed following the same procedure as described for **12,** was used m-PEG12 amine (52 mg, 0.09 mmol) and triethylamine (17.8 µl, 0.12 mmol) in 15 mL dry CH_2Cl_2 in 0 ˚C under a nitrogen atmosphere. To this solution, a solution of 3,5-bis-n-hexadecylaminocarbonyl-benzoyl chloride (26 mg, 0.04 mmol) in 5 mL of dry CH_2Cl_2. The reaction was stirred overnight at room temperature under nitrogen atmosphere. Then, the solvent was removed under vacuum and the resulting crude product was purified with silica-gel ($CHCl_3$: MeOH; 100:10) leading to a colourless oil (31mg, 48 %). IR (ATR) ν/cm^{-1}: 3449 (N-H, amide), 2925 (C – H alkyl), 1667 (C = O amide), 1064 (C - O ester) ; ^{1}H NMR (400 MHz/$CDCl_3$) δ ppm: δ 8.48 (1H, t, J=1.7 Hz, Ar-*H*), 8.46 (2H, d, J=1.6), 7.46 (2H, t, J=5.18, N-H), 7.04 (1H, t, J= 5.68, N-H), 3.62 (56H, m), 3.53 (4H, m), 3.43 (2H, m, N-C*H*$_2$-), 3.34 (6H, s), 1.64 (2H, m), 1.26 (88 H, m), 0.88 (3H, t, J= 6.8 Hz); ^{13}C NMR(100 MHz, $CDCl_3$) δ ppm: 166.1, 165.9, 135.3,135.1, 128.7, 128.4, 71.9, 70.6, 70.5, 70.4, 70.3, 69.8, 58.7,40.3, 40.3, 31.9, 29.7, 29.6, 29.5, 29.4, 29.3, 27.1, 22.7, 14.1; ESI-MS: *m/z* calculated for $[C_{75}H_{141}N_3O_{27}+Na]^+$ = 1538.93 Da Found = 1538.96 Da.

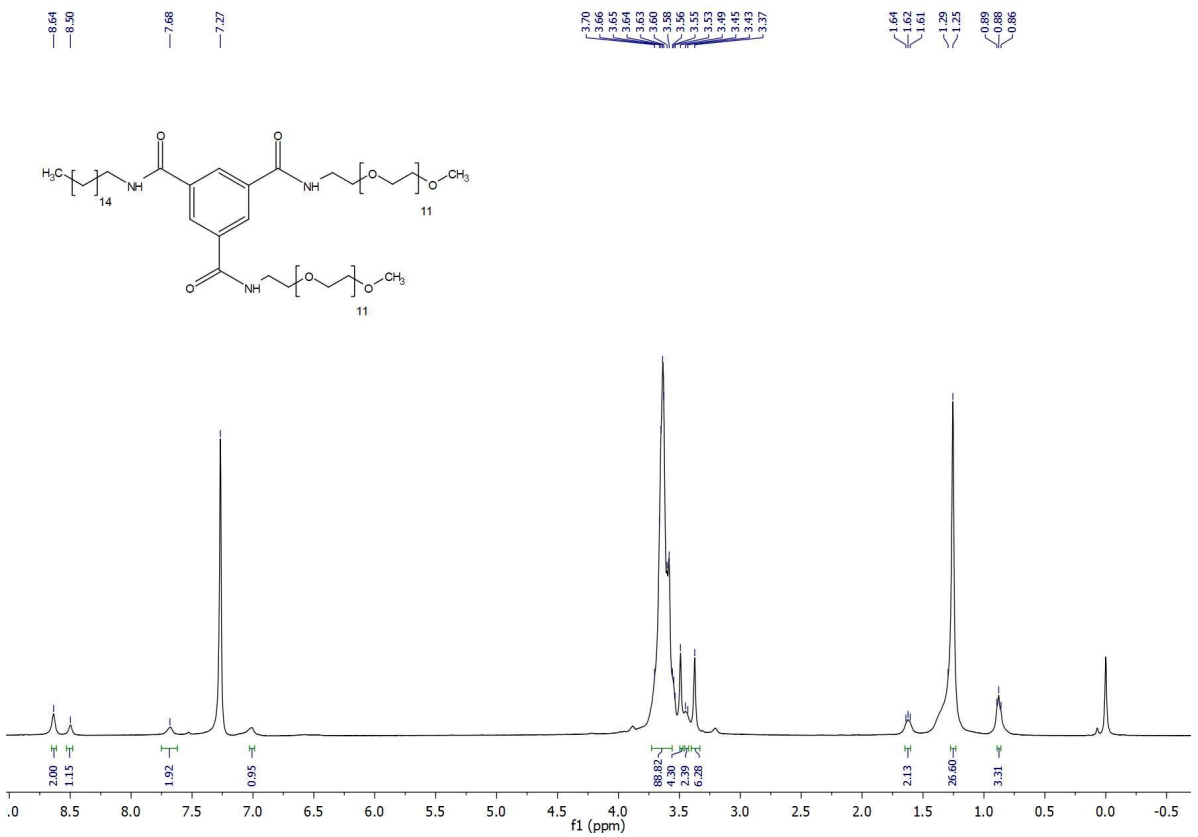


Figure S13: ^{1}H NMR spectrum of MA16DPEG12

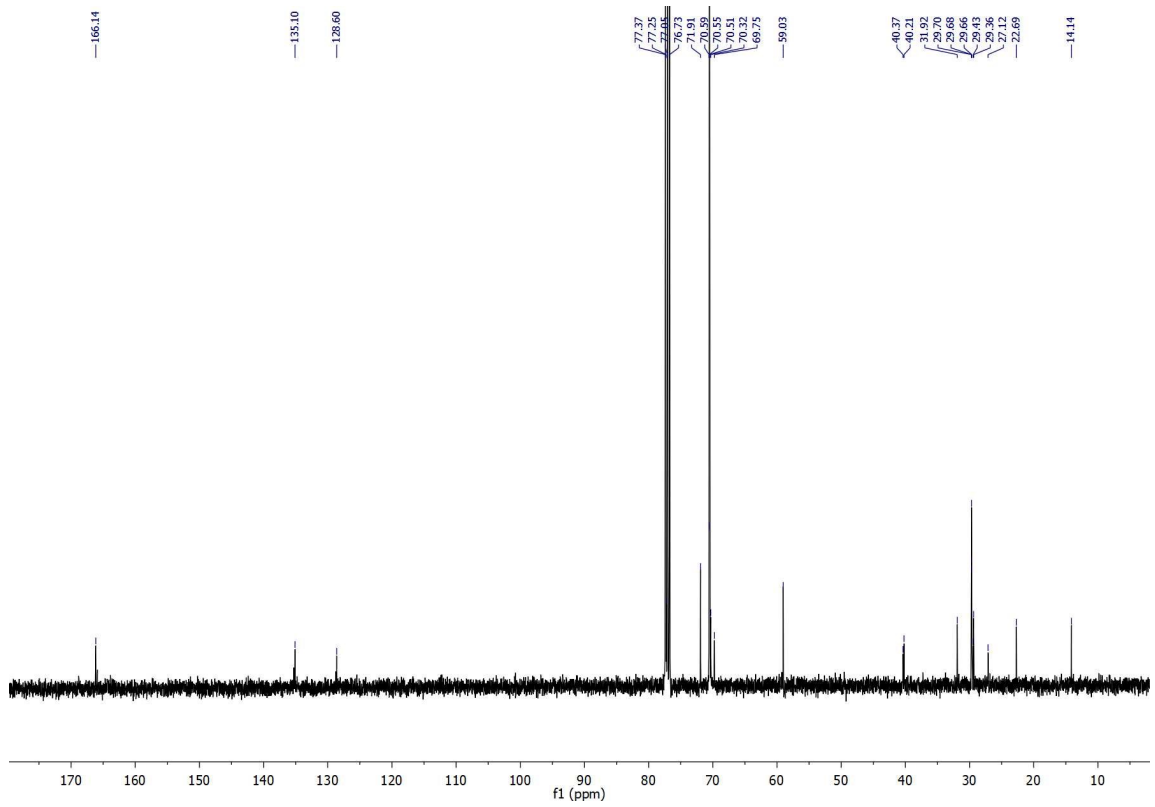


Figure S14: ^{13}C NMR spectrum of MA16DPEG12.

Synthesis of MA16DPEG15 (12d). The synthesis of MA16DPEG15 was performed following the same procedure as described for **12,** was used m-PEG15 amine (442 mg, 6.39 mmol) and triethylamine (133 µl, 9.59 mmol) in 15 mL dry CH_2Cl_2 in 0 ˚C under a nitrogen atmosphere. To this solution, a solution of 3,5-bis-n-hexadecylaminocarbonyl-benzoyl chloride (149 mg, 3.19 mmol) in 5 mL of dry CH_2Cl_2. The reaction was stirred overnight at room temperature under nitrogen atmosphere. Then, the solvent was removed under vacuum and the resulting crude product was purified with silica-gel ($CHCl_3$: MeOH; 100:10) proviting a colourless oil (267 mg, 47 %). IR (ATR) ν/cm^{-1}: 3449 (N-H, amide), 2924 (C – H alkyl), 1664 (C = O amide), 1097 (C - O ester) ; ^1H NMR (400 MHz/$CDCl_3$) δ ppm: δ 8.48 (1H, t, J=1.7 Hz, Ar-*H*), 8.46 (2H, d, J=1.6), 7.46 (2H, t, J=5.18, N-H), 7.04 (1H, t, J= 5.68, N-H), 3.62 (112H, m), 3.53 (4H, m), 3.43 (2H, m, N-C*H*$_2$-), 3.34 (6H, s), 1.64 (2H, m), 1.26 (26 H, m), 0.88 (3H, t, J= 6.8 Hz); ^{13}C NMR(100 MHz, $CDCl_3$) δ ppm: 166.1, 165.9, 135.3,135.1, 128.7, 128.4, 71.9, 70.6, 70.5, 70.4, 70.3, 69.8, 58.7,40.3, 40.3, 31.9, 29.7, 29.6, 29.5, 29.4, 29.3, 27.1, 22.7, 14.1; ESI-MS: *m/z* calculated for [$C_{75}H_{141}N_3O_{27}$+Na] = 1804.25 Da Found = 1803.11 Da.

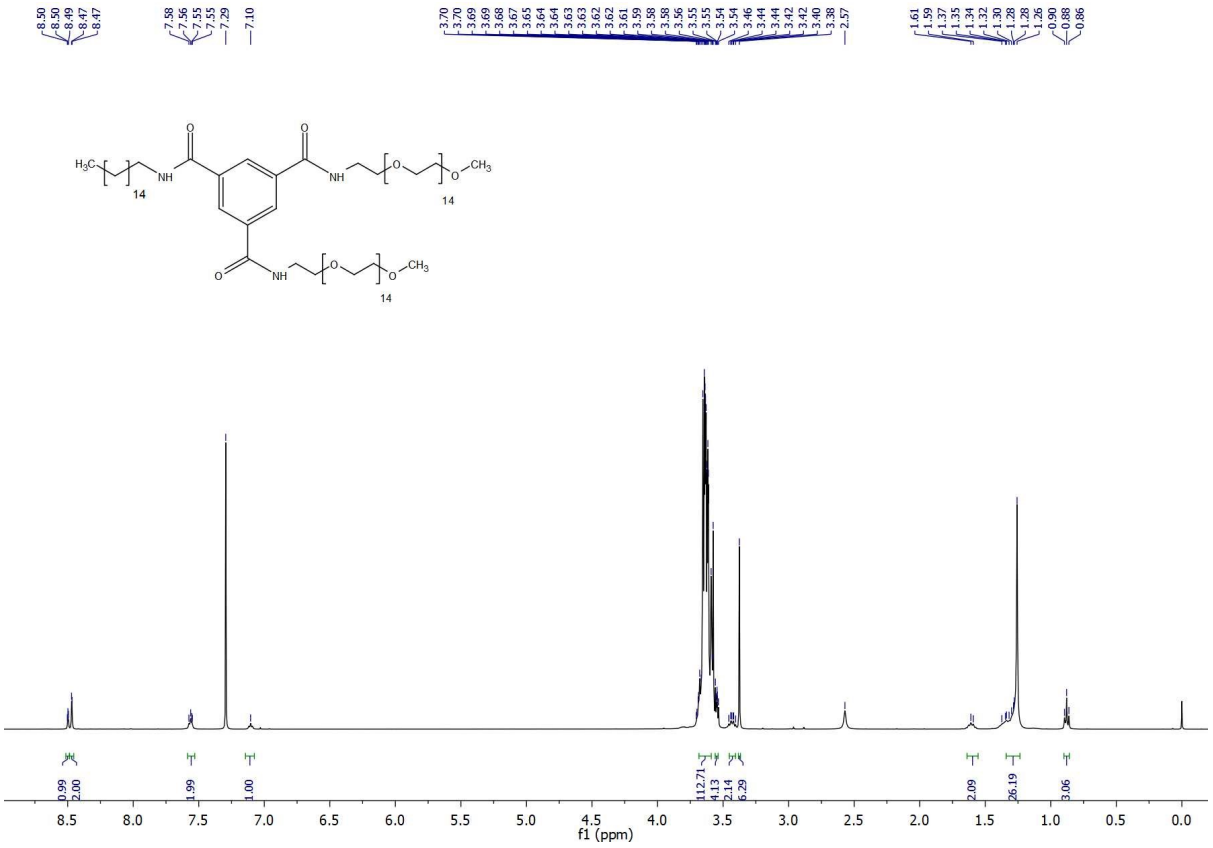
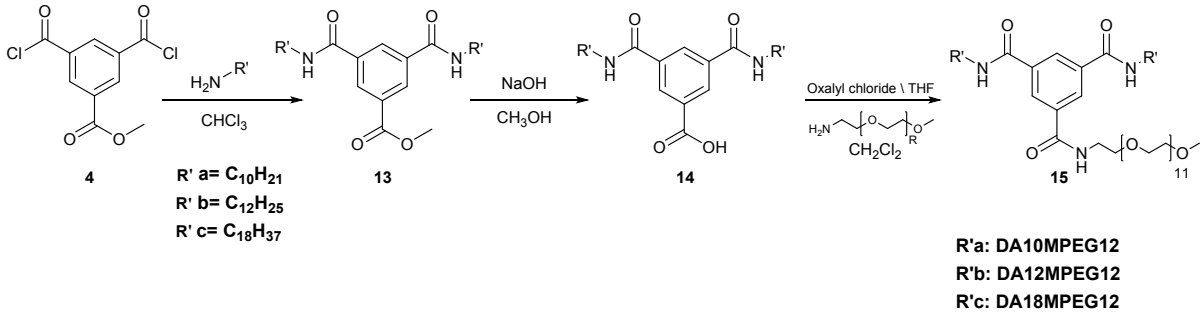


Figure S15: ^{1}H NMR spectrum of MA16DPEG15

Figure 16: ^{13}C NMR spectrum of MA16DPEG15

Synthesis of DA10MPEG12, DA12MPEG12, and DA18MPEG12



Scheme S3. Reaction schemes for DAmMPEG12 compounds

Synthesis of methyl-3,5-bis-n-decylaminocarbonyl-benzoate (13a). The same procedure was followed as described for **5**, A solution of decylamine (0.46 g, 2.97 mmol) and triethylamine (0.56 mL, 4.04 mmol) was dissolved in 30 mL dry CHCl3 in ice bath under a nitrogen atmosphere. To this solution was added dropwise a solution of methyl-3,5-bis-chlorocarbonyl-benzoate **4** (0.3 g, 1.35 mmol) in 15 mL of dry $CHCl_3$. The reaction was stirred for 24 hours at room temperature under nitrogen atmosphere. Then, the solvent was removed under vacuum and the resulting crude product was purified with a short silica-gel (CH_2Cl2: MeOH; 100:1) obtain a white product (0.41g, 70 %). IR (ATR) ν/cm^{-1}: 2936 (C – H alkyl), 1726 (C = O ester), 1665 (C = O amide), 1392 (C-N amide), 1187 (C - O ester) ; ^{1}H NMR (400 MHz/$CDCl_3$) δ ppm: δ 8.52 (2H, d, J=1.7 Hz, Ar-*H*), 8.41 (1H, t, J= 1.8 Hz) 3.97 (3H, s, O-C*H*$_3$), 3.48 (4H, m, N-C*H*$_2$-),1.63 (4H, m), 1.32(28H, m), 0.87(6H, t, J= 6.8 Hz); ^{13}C NMR(100 MHz, $CDCl_3$) δ ppm: 165.5, 165.1, 133.1, 130.2, 52.8, 38.4, 31.8, 29.2, 26.7, 23.2, 14.3; ESI-MS: *m/z* calculated for $[C_{30}H_{50}N_2O_4+H]^+$ = 503.74 Da Found = 503.38 Da.

Synthesis of methyl-3,5-bis-n-dodecylaminocarbonyl-benzoate (13b). This compound was synthesised by a similar procedure to methyl-3,5-bis-n-hexadecylaminocarbonyl-benzoate **5**, using dodecylamine (0.49 g, 2.62 mmol) and triethylamine (0.49 mL, 3.57 mmol) in 30 mL dry CHCl3 and 5-methoxycarbonyl-benzene-1,3-dicarboxylic acid (0.31 g, 1.19 mmol) in 15 mL of dry $CHCl_3$. purified with a short silica-gel (CH_2Cl2: MeOH; 100:1.5) providing a white product (0.42g, 64 %). IR (ATR) ν/cm^{-1}: 2924 (C – H alkyl), 1723 (C = O ester), 1665 (C = O amide), 1376 (C-N amide), 1169 (C - O ester) ; ^{1}H NMR (400 MHz/$CDCl_3$) δ ppm: δ 8.52 (2H, d, J=1.7 Hz, Ar-*H*), 8.41 (1H, t, J= 1.8 Hz), 6.33 (2H, t, J= 5.9, N-H) 3.97 (3H, s, O-C*H*$_3$), 3.48 (4H, m, N-C*H*$_2$-),1.63 (4H, m), 1.32(36H, m), 0.87 (6H, t, J= 6.8 Hz); ^{13}C NMR(100 MHz, $CDCl_3$) δ ppm: 165.8, 165.5, 135.5, 131.1, 129.7, 52.7, 40.4, 31.9, 29.7, 29.6, 29.5, 29.4, 29.3, 27.1, 22.7, 14.1; ESI-MS: *m/z* calculated for $[C_{34}H_{58}N_2O_4+H]^+$ = 559.85 Da Found = 559.38 Da.

Synthesis of methyl-3,5-bis-n-octadecylaminocarbonyl-benzoate (13c). Methyl-3,5-bis-n-octadecylaminocarbonyl-benzoate **13c** was synthesised by a similar procedure to methyl-3,5-bis-n-hexadecylaminocarbonyl-benzoate **5**, using octadecylamine (0.9 g, 3.34 mmol) and

triethylamine (0.63 mL, 4.55 mmol) in 30 mL dry CHCl3 and 5-methoxycarbonyl-benzene-1,3-dicarboxylic acid (0.39 g, 1.52 mmol) in 15 mL of dry $CHCl_3$. purified with a short silica-gel (CH_2Cl2: MeOH; 100:2.3) providing a white product (0.75 g, 68 %). IR (ATR) ν/cm^{-1}: 2927 (C – H alkyl), 1721 (C = O ester), 1662 (C = O amide), 1372 (C-N amide), 1167 (C - O ester) ; ^{1}H NMR (400 MHz/$CDCl_3$) δ ppm: δ 8.52 (2H, d, J=1.7 Hz, Ar-*H*), 8.41 (1H, t, J= 1.8 Hz), 6.28 (2H, t, J= 5.9, N-H) 3.97 (3H, s, O-C*H*$_3$), 3.48 (4H, m, N-C*H*$_2$-),1.63 (4H, m), 1.32(60 H, m), 0.87 (6H, t, J= 6.8 Hz); ^{13}C NMR(100 MHz, $CDCl_3$) δ ppm: 165.6, 165.3, 135.2, 131.1, 129.5, 52.4, 40.6, 31.9, 29.7, 29.6, 29.5, 29.4, 29.3, 27.0, 22.6, 14.1; ESI-MS: *m/z* calculated for $[C_{46}H_{82}N_2O_4+H]^+$ = 727.17 Da Found = 727.63Da.

Synthesis of 3,5-bis-n-decylcarbonyl-benzoic acid (14a). This compound was synthesised by similar procedure to 3,5-bis-n-hexadecylcarbamoyl benzoic acid **6**, using methyl-3,5-bis-n-decylaminocarbonyl-benzoate **13a** (0.45 g, 0.89 mmol) and 1.5 eq. of 4M NaOH (53 mg, 1.3 mmol) in methanol (60 mL). The solution was stirred and reflux at 85 ˚C for 24h. Then, the solution was cooled to room temperature before being poured into 400 mL H_2O (acidified with 1 M HCl). A white powder precipitated and was isolated by filtration and dried under vacuum leading to white product (0.29, 67%). IR (ATR) ν/cm^{-1}: 3358 (N-H amide), 2917 (O– H carboxylic acid), 1704 (C = O carboxylic acid), 1630 (C = O amide); ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm: 8.76 (2H, t, J= 5.6 MHz), 8.51 (3H, s, Ar-*H*), 8.40 (1H, s, Ar-*H*), 3.27 (4H, m, NH-C*H*$_2$), 1.25 (28H, m, C*H*$_2$), 0.85 (6H, m, C*H*$_3$); ^{13}C NMR (100 MHz, DMSO-d_6) δ ppm: 166.4, 165.5, 165.3, 135.2, 130.4, 129.5, 31.8, 29.7, 29.6, 29.5, 29.4, 29.3, 27.1, 22.7, 14.1; ESI-MS: *m/z* calculated for $[C_{29}H_{48}N_2O_4+H]^+$ = 489.71 Da Found = 489.36 Da.

Synthesis of 3,5-bis-n-dodecylcarbonyl-benzoic acid (14b). This compound was synthesised by a similar procedure to 3,5-bis-n-hexadecylcarbamoyl benzoic acid **6**, using methyl-3,5-bis-n-dodecylaminocarbonyl-benzoate **13b** (0.39 g, 0.69 mmol) and 1.5 eq. of 4M NaOH (40 mg, 1.05 mmol) in methanol (50 mL). The solution was stirred and reflux at 85 ˚C for 24h. Then, the solution was cooled to room temperature before being poured into 400 mL H_2O (acidified with 1 M HCl). A white powder precipitated and was isolated by filtration and dried under vacuum providing white product (0.25, 66%). IR (ATR) ν/cm^{-1}: 3291 (N-H amide), 2912 (O– H carboxylic acid), 1702 (C = O carboxylic acid), 1625 (C = O amide); ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm: 8.79 (2H, t, J= 5.6 MHz), 8.55 (1H, s, Ar-*H*), 8.51 (2H, s, Ar-*H*), 3.27 (4H, m, NH-C*H*$_2$),1.53 (4H, m) 1.25 (36H, m, C*H*$_2$), 0.85 (6H, m, C*H*$_3$); ^{13}C NMR (100 MHz, DMSO-d_6) δ ppm: 166.4, 165.5, 165.3, 135.2, 130.4, 129.5, 31.8, 29.7, 29.6, 29.5, 29.4, 29.3, 27.1, 22.7, 14.1; ESI-MS: *m/z* calculated for $[C_{33}H_{56}N_2O_4+H]^+$ = 545.42 Da Found = 545.82 Da.

Synthesis of 3,5-bis-n-octadecylcarbonyl-benzoic acid (14c). This compound was synthesised by a similar procedure to 3,5-bis-n-hexadecylcarbamoyl benzoic acid **6**, using methyl-3,5-bis-n-octadecylaminocarbonyl-benzoate **13c** (0.28 g, 0.39 mmol) and 1.5 eq. of 4M NaOH (23 mg, 0.58 mmol) in methanol (35 mL). The solution was stirred and reflux at 85 ˚C for 24h. Then, the solution was cooled to room temperature before being poured into 400 mL H_2O (acidified with 1 M HCl). A white powder precipitated and was isolated by filtration and dried under vacuum providing white product (0.18, 65 %). IR (ATR) ν/cm^{-1}: 3356(N-H amide), 2923 (O– H carboxylic acid), 1711 (C = O carboxylic acid), 1627 (C = O amide); ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm: 8.76 (2H, t, J= 5.6 MHz), 8.51 (2H, t, Ar-*H*), 8.40 (1H, d, Ar-*H*), 3.27 (4H, m, NH-C*H*$_2$), 1.25 (28H, m, C*H*$_2$), 0.85 (6H, m, C*H*$_3$); ^{13}C NMR (100 MHz, DMSO-d_6) δ ppm: 166.3, 165.4, 165.3, 135.4, 130.4, 129.5, 31.8, 29.7, 29.6, 29.5, 29.4, 29.3, 27.1, 22.7, 14.1; ESI-MS: *m/z* calculated for $[C_{33}H_{80}N_2O_4+H]^+$ = 713.15 Da Found = 713.61 Da.

Synthesis of DA10MPEG12 (15a). As a first step the 3,5-bis-n-decylaminocarbonyl-benzoyl chloride was formed following procedure **7** using (28 mg, 0.06 mmol) of 3,5-bis-n-decylcarbonyl-benzoic acid **14a** and oxalyl chloride (10µL, 0.09 mmol) providing (29 mg, 99%). Subsequently, the synthesis of DA10MPEG12 was performed following the same procedure as described for **7,** using m-PEG12 amine (23.2 mg, 0.04 mmol) and triethylamine (11.6 µl, 0.08 mmol) in15 mL dry CH_2Cl_2 in 0 ˚C under a nitrogen atmosphere. To this solution, a solution of 3,5-bis-n-decylaminocarbonyl-benzoyl chloride (28.7 mg, 0.04 mmol) in 5 mL of dry CH_2Cl_2. The reaction was stirred overnight at room temperature under nitrogen atmosphere. Then, the solvent was removed under vacuum and the resulting crude product was purified with silica-gel ($CHCl_3$: MeOH; 100:8.5) leading to a colourless product (83 mg, 51 %). IR (ATR) ν/cm^{-1}: 3464 (N-H, amide), 2935 (C – H alkyl), 1665 (C = O amide), 1102 (C - O ester) ; ^{1}H NMR (400 MHz/$CDCl_3$) δ ppm: δ 8.45 (2H, t, J=1.7 Hz, Ar-*H*), 8.43 (1H, d,), 7.54 (1H, m, N-H), 6.91 (2H,m, N-H), 3.70 (2H, m), 3.60 (44H, m), 3.43 (4H, m, N-C*H*$_2$-), 3.36 (3H, s), 1.62 (4H, m), 1.26 (28H, m), 0.88 (6H, t, J= 6.8 Hz); ^{13}C NMR(100 MHz, $CDCl_3$) δ ppm: 166.1, 165.9, 135.4,135.1, 128.6, 128.4, 71.9, 70.6, 70.5, 70.4, 70.3, 58.7, 53.4, 40.4, 31.9, 29.7, 29.6, 29.5, 29.4, 29.3, 27.1, 27.7, 14.1; ESI-MS: *m/z* calculated for $[C_{45}H_{99}N_3O_{15}+Na]^+$ = 1052.37 Da Found = 1052.69 Da.

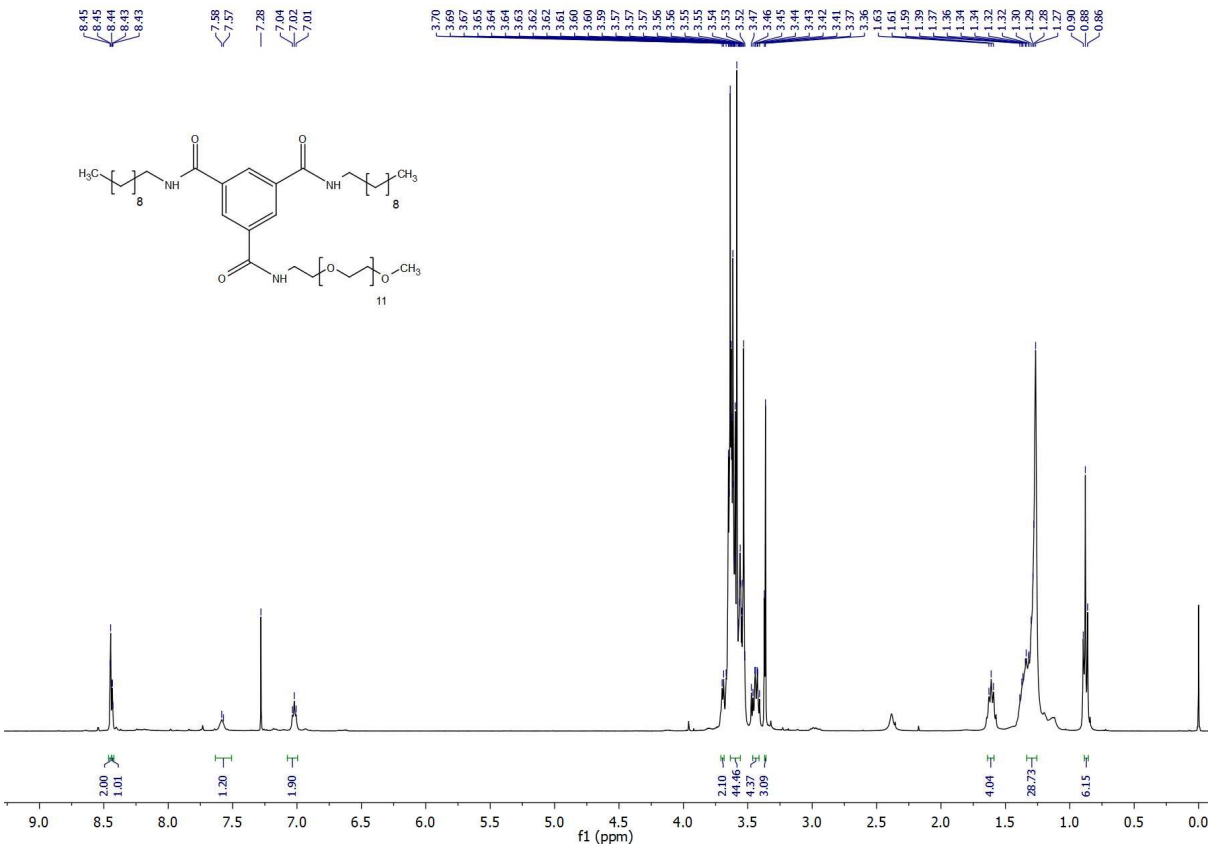


Figure S17: ^{1}H NMR spectrum of DA10MPEG12

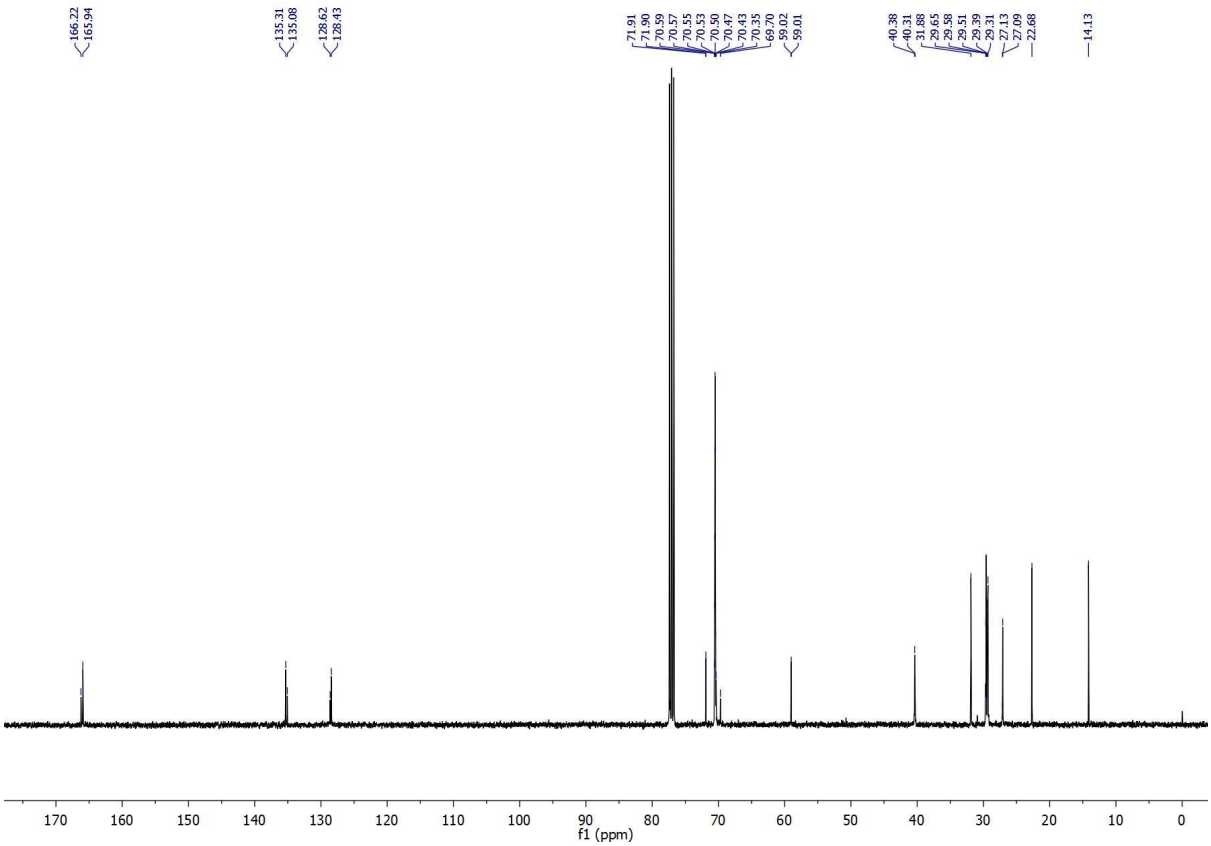


Figure S18: ^{13}C NMR spectrum of DA10MPEG12.

Synthesis of DA12MPEG12 (15b). As first step the 3,5-bis-n-dodecylaminocarbonyl-benzoyl chloride was formed following procedure **7** using (90 mg, 0.16 mmol) of 3,5-bis-n-dodecylcarbonyl-benzoic acid **14b** and oxalyl chloride (32 µL, 0.24 mmol) providing (91 mg, 99%). Then, the synthesis of DA12MPEG12 was performed following the same procedure as described for **7,** using m-PEG12 amine (90 mg, 0.16 mmol) and triethylamine (41.3 µl, 0.32 mmol) in 15 mL dry CH_2Cl_2 in 0 ˚C under a nitrogen atmosphere. To this solution, a solution of 3,5-bis-n-dodecylaminocarbonyl-benzoyl chloride (89 mg, 0.16 mmol) in 5 mL of dry CH_2Cl_2. The reaction was stirred overnight at room temperature under nitrogen atmosphere. Then, the solvent was removed under vacuum and the resulting crude product was purified with silica-gel ($CHCl_3$: MeOH; 100:8.7) leading to a colourless product (82.6 mg, 47 %). IR (ATR) ν/cm^{-1}: 3464 (N-H, amide), 2935 (C – H alkyl), 1665 (C = O amide), 1102 (C - O ester) ; ^1H NMR (400 MHz/$CDCl_3$) δ ppm: δ 8.46 (2H, t, J=1.7 Hz, Ar-*H*), 8.43 (1H, d,), 7.54 (1H, m, N-H), 6.91 (2H,m, N-H), 3.70 (2H, m), 3.60 (44H, m), 3.43 (4H, m, N-C*H*$_2$-), 3.36 (3H, s), 1.62 (4H, m), 1.26 (36 H, m), 0.88 (6H, t, J= 6.8 Hz); ^{13}C NMR(100 MHz, $CDCl_3$) δ ppm: 166.1, 165.9, 135.4,135.1, 128.6, 128.4, 71.9, 70.6, 70.5, 70.4, 70.3, 58.7, 53.4, 40.4, 31.9, 29.7, 29.6, 29.5, 29.4, 29.3, 27.1, 27.7, 14.1; ESI-MS: *m/z* calculated for $[C_{58}H_{107}N_3O_{15}+Na]^+$ = 1108.48 Da Found = 1108.75 Da.

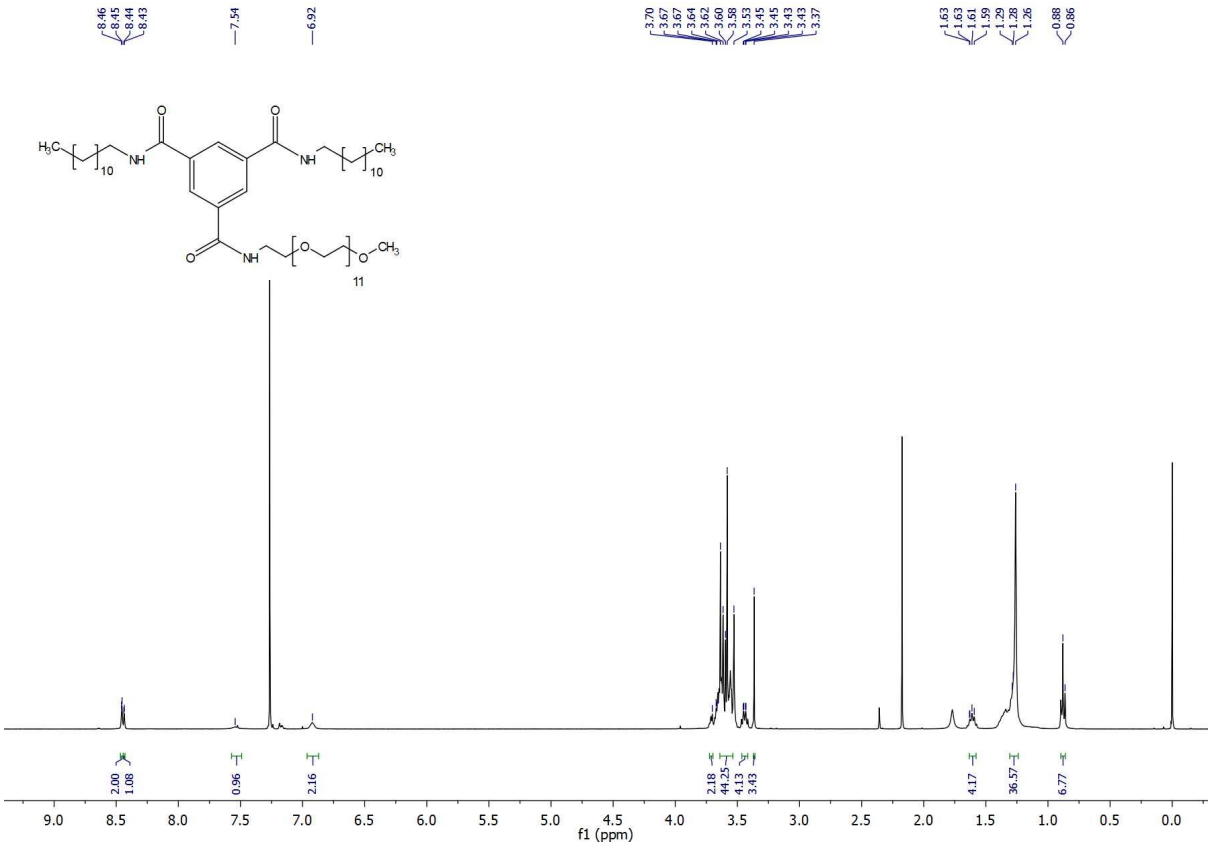


Figure S19: ^{1}H NMR spectrum of DA12MPEG12

Figure 20: ^{13}C NMR spectrum of DA12MPEG12.

Synthesis of DA18MPEG12 (15c). The 3,5-bis-n-octadecylaminocarbonyl-benzoyl chloride was formed following procedure **7** using (70 mg, 0.01 mmol) of 3,5-bis-n-octadecylcarbonyl-benzoic acid **14c** and oxalyl chloride (17 µl, 0.02 mmol) providing (70 mg, 98%). Subsequently, the synthesis of DA18MPEG12 was performed following the same procedure as described for **7,** was used m-PEG12 amine (50 mg, 0.09 mmol) and triethylamine (24.8 µl, 0.18 mmol) in 15 mL dry CH_2Cl_2 in 0 ˚C under a nitrogen atmosphere. To this solution, a solution of 3,5-bis-n-octadecylaminocarbonyl-benzoyl chloride (65 mg, 0.09 mmol) in 5 mL of dry CH_2Cl_2. The reaction was stirred overnight at room temperature under nitrogen atmosphere. Then, the solvent was removed under vacuum and the resulting crude product was purified with silica-gel ($CHCl_3$: MeOH; 100:8.7) leading to a colourless product (54 mg, 48 %). IR (ATR) ν/cm^{-1}: 3462 (N-H, amide), 2929 (C – H alkyl), 1663 (C = O amide), 1098 (C - O ester) ; ^{1}H NMR (400 MHz/$CDCl_3$) δ ppm: δ 8.46 (2H, t, J=1.7 Hz, Ar-*H*), 8.43 (1H, d,), 7.54 (1H, m, N-H), 6.91 (2H, m, N-H), 3.70 (2H, m), 3.60 (44H, m), 3.43 (4H, m, N-C*H*$_2$-), 3.36 (3H, s), 1.62 (4H, m), 1.26 (60 H, m), 0.88 (6H, t, J= 6.8 Hz); ^{13}C NMR(100 MHz, $CDCl_3$) δ ppm: 166.1, 165.9, 135.4,135.1, 128.6, 128.4, 71.9, 70.6, 70.5, 70.4, 70.3, 58.7, 53.4, 40.4, 31.9, 29.7, 29.6, 29.5, 29.4, 29.3, 27.1, 27.7, 14.1; ESI-MS: *m/z* calculated for $[C_{70}H_{131}N_3O_{15}+Na]^+$ = 1276.80 Da Found = 1276.94 Da.

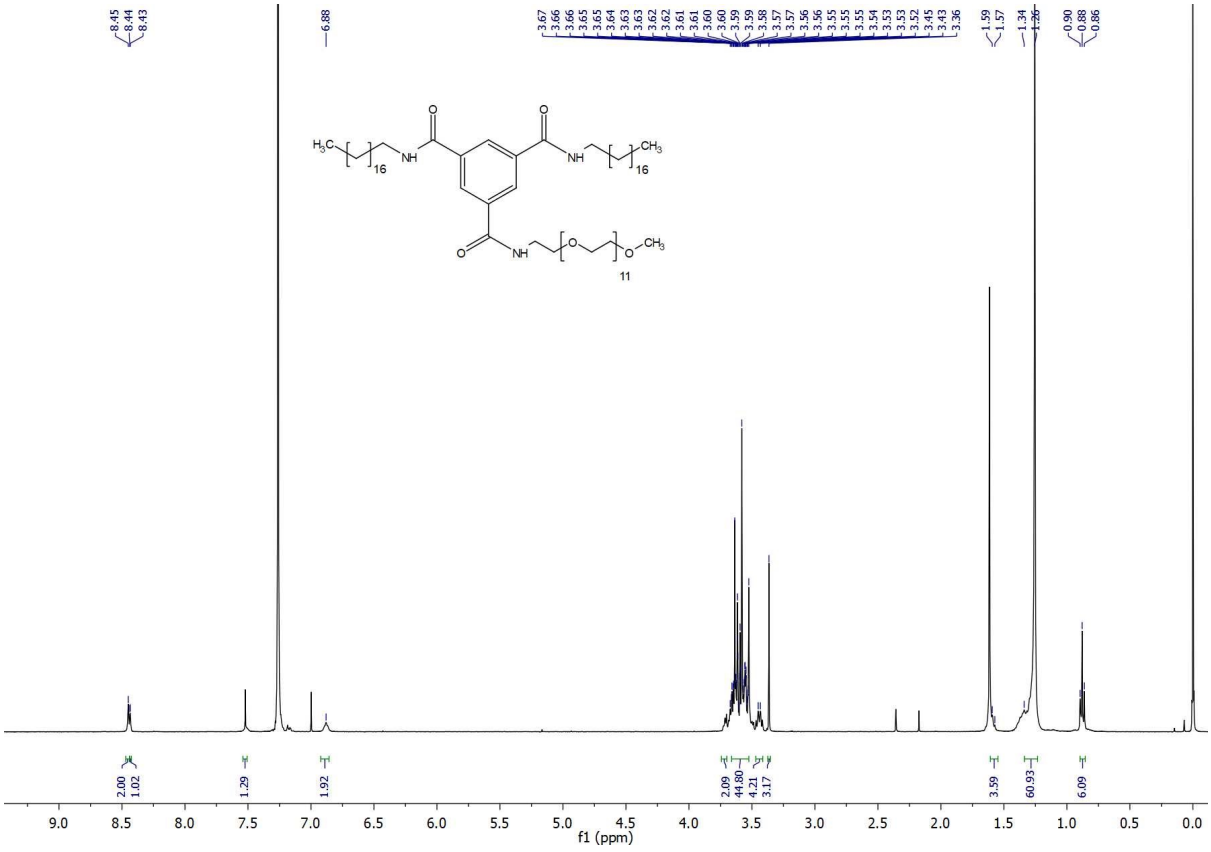
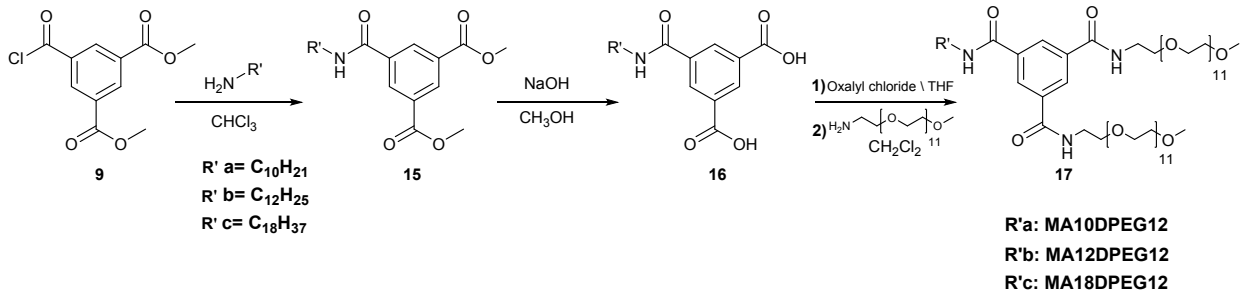


Figure S21: ^{1}H NMR spectrum of DA18MPEG12.

Figure S22:[13]C NMR spectrum of DA18MPEG12.

Synthesis of MA10DPEG12, MA12DPEG12, and MA18DPEG12



Scheme S4. Reaction schemes for MAmDPEG12 compounds

Synthesis of dimethyl 5-(decylcarbamoyl) isophthalate (15a). This compound **15a** was synthesised by a similar procedure to dimethyl 5-(hexadecylcarbamoyl) isophthalate **10,** a solution of decylamine (0.3 g, 1.9 mmol) and TEA (660 µl, 4.76 mmol) was dissolved in dry CH_2Cl_2 (40 mL) under nitrogen atmosphere at 0 ˚C. To this solution, a solution of dimethyl 5-(chlorocarbonyl) isophthalate **9** (0.4 g, 1.59 mmol) in dry CH_2Cl_2 (10 mL) was added drop wise to that and stirred for 24h at room temperature. Then, the solvent was removed under vacuum and the crude product was purified by column chromatography (CH_2Cl_2: MeOH, 100:1.2)

yielding a white powder (0.42 g, 71%); ; IR (ATR) ν/cm^{-1}: 2915 (N-H), 1731.2 (C=O, ester), 1629.4 (C=O, amide), 1559.8 (N-H), 1440.9 (C=C, Aromatic), 1267 (C-O, ester), 1178.7 (C-N, amide); ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm: 8.78 (1H, t, = 1.62 MHz), 8.60 (2H, d, J= 1.56 MHz), 6.30 (1H, t, N-*H*), 3.97 (6H, s, O-C*H*$_3$), 3.48 (2H, m, N-C*H*$_2$), 1.64 (2H, m, N-CH_2CH2), 1.26 (14H, m, alkyl), 0.87 (3H, t, J= 6.8 MHz, -C*H*$_3$); ^{13}C NMR(100 MHz, $CDCl_3$) δ ppm: 165.5, 165.4,135.6, 133.1, 132, 131.1, 52.6, 40.4, 31.9, 29.7, 29.6, 29.5, 29.4, 27.1, 22.6, 14.1; ESI-MS: *m/z* calculated for $[C_{21}H_{31}NO_5+H]^+$ = 378.48 Da Found = 378.22 Da.

Synthesis of dimethyl 5-(dodecylcarbamoyl) isophthalate (15b). This compound **15b** was synthesised by a similar procedure to dimethyl 5-(hexadecylcarbamoyl) isophthalate **10,** a solution of dodecylamine (0.3 g, 1.64 mmol) and TEA (550 µl, 4.11 mmol) was dissolved in dry CH_2Cl_2 (40 mL) under nitrogen atmosphere at 0 ˚C. To this solution, a solution of dimethyl 5-(chlorocarbonyl) isophthalate **9** (0.35 g, 1.37 mmol) in dry CH_2Cl_2 (10 mL) was added drop wise to that and stirred for 24h at room temperature. Then, the solvent was removed under vacuum and the crude product was purified by column chromatography (CH_2Cl_2: MeOH, 100:1) yielding a white powder (0.43 g, 76%); ; IR (ATR) ν/cm^{-1}: 2913 (N-H), 1736.1 (C=O, ester), 1625.9 (C=O, amide), 1556.2 (N-H), 1438.9 (C=C, Aromatic), 1264 (C-O, ester), 1172.9 (C-N, amide); ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm: 8.78 (1H, t, = 1.62 MHz), 8.60 (2H, d, J= 1.56 MHz), 6.30 (1H, t, N-*H*), 3.97 (6H, s, O-C*H*$_3$), 3.48 (2H, m, N-C*H*$_2$), 1.64 (2H, m, N-CH_2CH2), 1.26 (18H, m, alkyl), 0.87 (3H, t, J= 6.8 MHz, -C*H*$_3$); ^{13}C NMR(100 MHz, $CDCl_3$) δ ppm: 165.5, 165.4,135.6, 133.1, 132, 131.1, 52.6, 40.4, 31.9, 29.7, 29.6, 29.5, 29.4, 27.1, 22.6, 14.1; ESI-MS: *m/z* calculated for $[C_{23}H_{35}NO_5+H]^+$ = 406.48 Da Found = 406.25 Da.

Synthesis of dimethyl 5-(octadecylcarbamoyl) isophthalate (15c). This compound **15c** was synthesised by a similar procedure to dimethyl 5-(hexadecylcarbamoyl) isophthalate **10,** a solution of octadecylamine (0.5 g, 1.87 mmol) and TEA (450 µl, 3.12 mmol) was dissolved in dry CH_2Cl_2 (50 mL) under nitrogen atmosphere at 0 ˚C. To this solution, a solution of dimethyl 5-(chlorocarbonyl) isophthalate **9** (0.4 g, 1.56 mmol) in dry CH_2Cl_2 (10 mL) was added drop wise to that and stirred for 24h at room temperature. Then, the solvent was removed under vacuum and the crude product was purified by column chromatography (CH_2Cl_2: MeOH, 100:1) yielding a white powder (0.50 g, 67%); ; IR (ATR) ν/cm^{-1}: 2921 (N-H), 1729.8 (C=O, ester), 1628.2 (C=O, amide), 1549.9 (N-H), 1436.7 (C=C, Aromatic), 1261 (C-O, ester), 1175 (C-N, amide); ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm: 8.78 (1H, t, = 1.62 MHz), 8.60 (2H, d, J= 1.56 MHz), 6.30 (1H, t, N-*H*), 3.97 (6H, s, O-C*H*$_3$), 3.48 (2H, m, N-C*H*$_2$), 1.64 (2H, m, N-CH_2CH2), 1.26 (30 H, m, alkyl), 0.87 (3H, t, J= 6.8 MHz, -C*H*$_3$); ^{13}C NMR(100 MHz, $CDCl_3$) δ ppm: 165.5, 165.4,135.6, 133.1, 132, 131.1, 52.6, 40.4, 31.9, 29.7, 29.6, 29.5, 29.4, 27.1, 22.6, 14.1; ESI-MS: *m/z* calculated for $[C_{29}H_{47}NO_5+H]^+$ = 490.70 Da Found = 490.35 Da.

Synthesis of 5-(decylcarbamoyl) isophthalic (16a). Dimethyl 5-(decylcarbamoyl)isophthalate **15a** (0.3 g, 0.80 mmol) was dissolved in methanol (40 mL) with 4M NaOH (80 mg, 2.0 mmol) that was stirred and reflux at 85 ˚C for 24 hours. the mixture was cooled to room temperature before being poured to 300 mL of 1M HCl. A white powder precipitate was formed and filtered. The precipitate was recrystallized from ethyl acetate (2 times), providing a white product (0.12 g, 43%). IR (ATR) ν/cm^{-1}: 3329 (N – H amide), 2921 (O – H carboxylic acid), 1712 (C = O ester), 1628 (C = O amide), 1469 (C-N amide), 1152 (C - O ester); ^{1}H-NMR (400 MHz, DMSO-d_6) δ ppm: 8.87 (1H, t, = 1.62 MHz), 8.62 (2H, d, J= 1.68 MHz), 8.56 (1H, t, J= 1.66 MHz), 3.27 (2H, m), 1.50 (2H, m), 1.23 (14 H, m), 0.83 (3H, t, J= 6.8 MHz); ^{13}C NMR(100 MHz, DMSO-d_6) δ ppm: 165.5, 165.4,135.6, 133.1, 132, 131.1, 40.4, 31.9, 29.7, 29.6, 29.5, 29.4, 22.6, 14.1**;** ESI-MS: *m/z* calculated for $[C_{19}H_{27}NO_5+H]^+$ = 350.43 Da Found = 350.19 Da.

Synthesis of 5-(dodecylcarbamoyl) isophthalic (16b). Dimethyl 5-(dodecylcarbamoyl)isophthalate **15b** (0.38 g, 0.94 mmol) was dissolved in methanol (40 mL) with 4M NaOH (120 mg, 2.8 mmol) that was stirred and reflux at 85 ˚C for 24 hours. the mixture was cooled to room temperature before being poured to 300 mL of 1M HCl. A white powder precipitate was formed and filtered. The precipitate was recrystallized from ethyl acetate (2 times), providing a white product (0.17 g, 48%). IR (ATR) ν/cm^{-1}: 3323 (N – H amide), 2918 (O – H carboxylic acid), 1721 (C = O ester), 1632 (C = O amide), 1461 (C-N amide), 1160 (C - O ester); ^{1}H-NMR (400 MHz, DMSO-d_6) δ ppm: 8.87 (1H, t, = 1.62 MHz), 8.62 (2H, d, J= 1.68 MHz), 8.56 (1H, t, J= 1.66 MHz), 3.27 (2H, m), 1.50 (2H, m), 1.23 (18 H, m), 0.83 (3H, t, J= 6.8 MHz); ^{13}C NMR(100 MHz, DMSO-d_6) δ ppm: 165.5, 165.4,135.6, 133.1, 132, 131.1, 40.4, 31.9, 29.7, 29.6, 29.5, 29.4, 22.6, 14.1**;** ESI-MS: *m/z* calculated for $[C_{21}H_{31}NO_5+H]^+$ = 378.48 Da Found = 378.22 Da.

Synthesis of 5-(octadecylcarbamoyl) isophthalic (16c). Dimethyl 5-(octadecylcarbamoyl)isophthalate **15c** (0.47 g, 0.96 mmol) was dissolved in methanol (40 mL) with 4M NaOH (96 mg, 2.41 mmol) that was stirred and reflux at 85 ˚C for 24 hours. the mixture was cooled to room temperature before being poured to 300 mL of 1M HCl. A white powder precipitate was formed and filtered. The precipitate was recrystallized from ethyl acetate (2 times), providing a white product (0.25 g, 57%). IR (ATR) ν/cm^{-1}: 3326 (N – H amide), 2923 (O – H carboxylic acid), 1719 (C = O ester), 1629 (C = O amide), 1457 (C-N amide), 1164 (C - O ester); ^{1}H-NMR (400 MHz, DMSO-d_6) δ ppm: 8.87 (1H, t, = 1.62 MHz), 8.62 (2H, d, J= 1.68 MHz), 8.56 (1H, t, J= 1.66 MHz), 3.27 (2H, m), 1.50 (2H, m), 1.23 (30 H, m), 0.83 (3H, t, J= 6.8 MHz); ^{13}C NMR(100 MHz, DMSO-d_6) δ ppm: 165.5, 165.4,135.6, 133.1, 132, 131.1, 40.4, 31.9, 29.7, 29.6, 29.5, 29.4, 22.6, 14.1**;** ESI-MS: *m/z* calculated for $[C_{27}H_{43}NO_5+H]^+$ = 462.64 Da Found = 462.31 Da.

Synthesis of MA10DPEG12 (17a). 5-(decylcarbamoyl)isophthaloyl dichloride was synthesised following procedure **12** using (70 mg, 0.20 mmol) of 5-(decylcarbamoyl)isophthalic acid **16a** and oxalyl chloride (45µL, 0.50 mmol) providing (76 mg, 99%). Subsequently, MA10DPEG12 was performed following the same procedure as described for **12,** m-PEG12 amine (130 mg, 0.23 mmol) and triethylamine (62 µl, 0.44 mmol) were dissolved in 15 mL dry CH_2Cl_2 in 0 ˚C under a nitrogen atmosphere. To this solution, a solution of 5-(decylcarbamoyl)isophthaloyl dichloride (45 mg, 0.11 mmol) in 5 mL of dry CH_2Cl_2 was added drop wise. The reaction was stirred overnight at room temperature under nitrogen atmosphere. Then, the solvent was removed under vacuum and the resulting crude product was purified with silica-gel ($CHCl_3$: MeOH; 100:10) leading to a colourless oil (78 mg, 47 %). IR (ATR) ν/cm^{-1}: 3464 (N-H, amide), 2927 (C – H alkyl), 1661 (C = O amide), 1099 (C - O ester) ; ^{1}H NMR (400 MHz/$CDCl_3$) δ ppm: δ 8.48 (1H, t, J=1.7 Hz, Ar-*H*), 8.46 (2H, d, J=1.6), 7.58 (2H, t, J=5.18, N-H), 7.06 (1H, t, J= 5.68, N-H), 3.62 (88H, m), 3.53 (4H, m), 3.43 (2H, m, N-C*H*$_2$-), 3.37 (6H, s), 1.64 (2H, m), 1.26 (14H, m), 0.88 (3H, t, J= 6.8 Hz); ^{13}C NMR(100 MHz, $CDCl_3$) δ ppm: 166.1, 165.9, 135.3,135.1, 128.7, 128.4, 71.9, 70.6, 70.5, 70.4, 70.3, 69.8, 58.7,40.3, 40.3, 31.9, 29.7, 29.6, 29.5, 29.4, 29.3, 27.1, 22.7, 14.1; ESI-MS: *m/z* calculated for $[C_{69}H_{129}N_3O_{27}+Na]^+$= 1454.7 Da Found = 1454.87 Da.

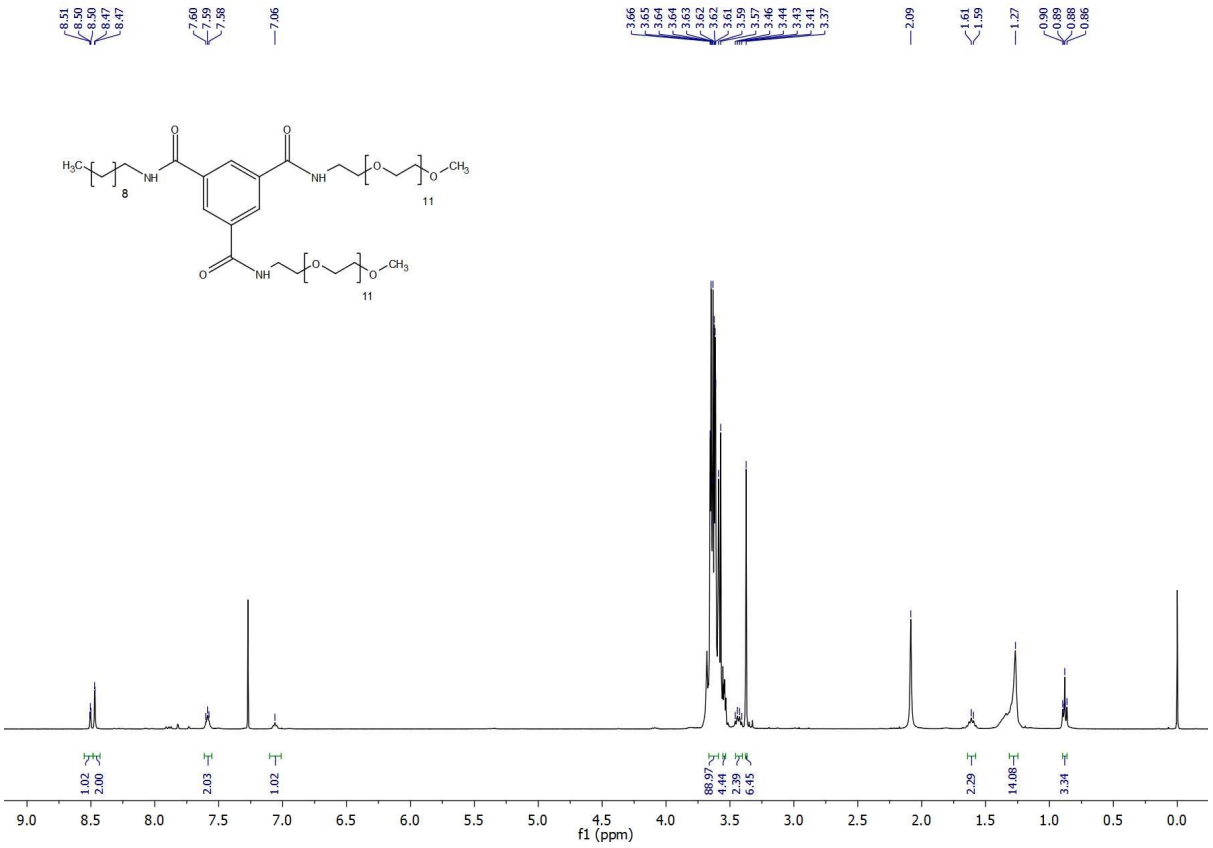


Figure S23: ^{1}H NMR spectrum of MA10DPEG12.

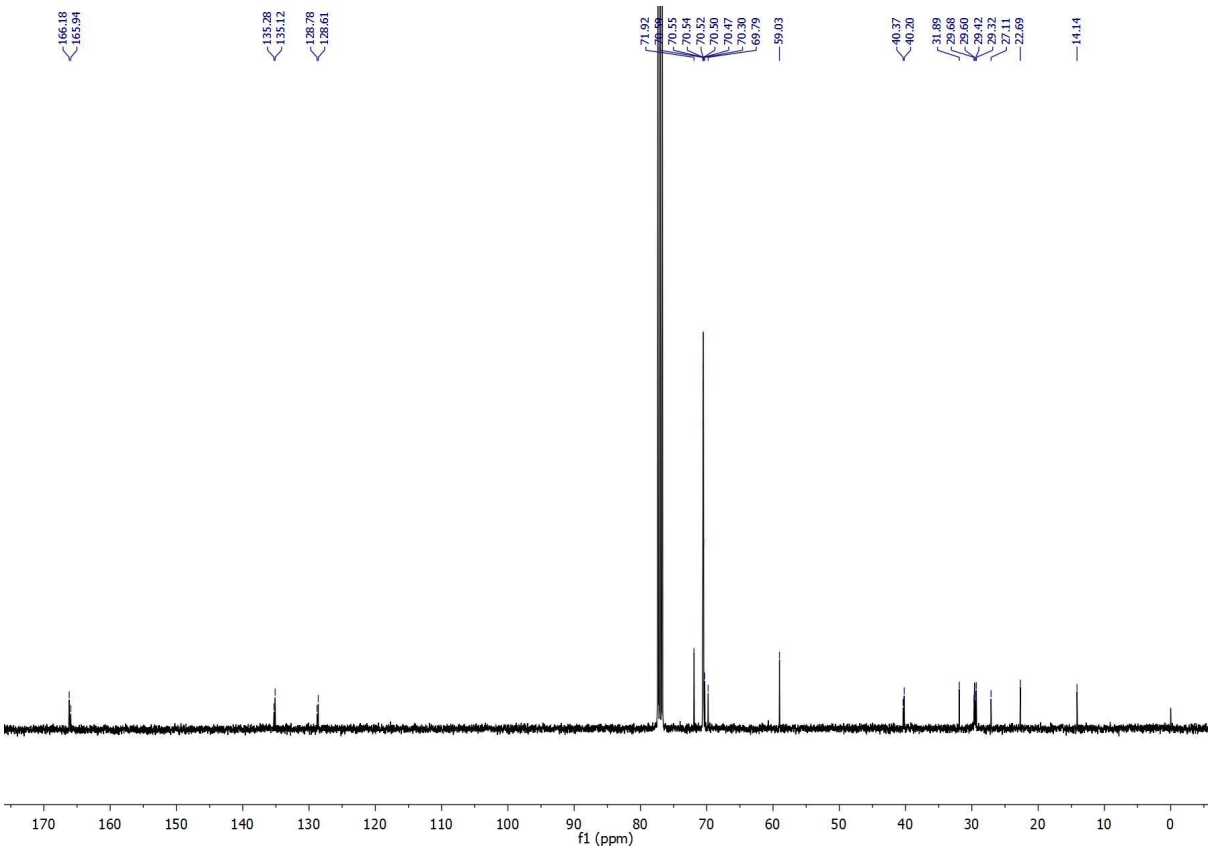


Figure S24: ^{13}C NMR spectrum of MA10DPEG12.

Synthesis of MA12DPEG12 (17b). 5-(dodecylcarbamoyl)isophthaloyl dichloride was synthesised following procedure **12** using (85 mg, 0.23 mmol) of 5-(dodecylcarbamoyl)isophthalic acid **16b** and oxalyl chloride (50 µl, 0.57 mmol) providing (92 mg, 99%). Then, MA12DPEG12 was performed following the same procedure as described for **12,** was used m-PEG12 amine (150 mg, 0.27 mmol) and triethylamine (56 µl, 0. 39 mmol) in 15 mL dry CH_2Cl_2 in 0 ˚C under a nitrogen atmosphere. a solution of 5-(dodecylcarbamoyl)isophthaloyl dichloride (55 mg, 0.13 mmol) in 5 mL of dry CH_2Cl_2 was added to the mixture drop wise. The reaction was stirred overnight at room temperature under nitrogen atmosphere. Then, the solvent was removed under vacuum and the resulting crude product was purified with silica-gel ($CHCl_3$: MeOH; 100:10) leading to a colourless oil (96 mg, 49 %). IR (ATR) ν/cm^{-1}: 3464 (N-H, amide), 2928 (C – H alkyl), 1667 (C = O amide), 1097 (C - O ester) ; ^{1}H NMR (400 MHz/$CDCl_3$) δ ppm: δ 8.48 (1H, t, J=1.7 Hz, Ar-*H*), 8.46 (2H, d, J=1.6), 7.58 (2H, t, J=5.18, N-H), 7.06 (1H, t, J= 5.68, N-H), 3.62 (88H, m), 3.53 (4H, m), 3.43 (2H, m, N-C*H*$_2$-), 3.37 (6H, s), 1.64 (2H, m), 1.26 (18H, m), 0.88 (3H, t, J= 6.8 Hz); ^{13}C NMR(100 MHz, $CDCl_3$) δ ppm: 166.1, 165.9, 135.3,135.1, 128.7, 128.4, 71.9, 70.6, 70.5, 70.4, 70.3, 69.8, 58.7,40.3, 40.3, 31.9, 29.7, 29.6, 29.5, 29.4, 29.3, 27.1, 22.7, 14.1; ESI-MS: *m/z* calculated for $[C_{69}H_{129}N_3O_{27}+Na]^+$ = 1482.82 Da Found = 1482.90 Da.

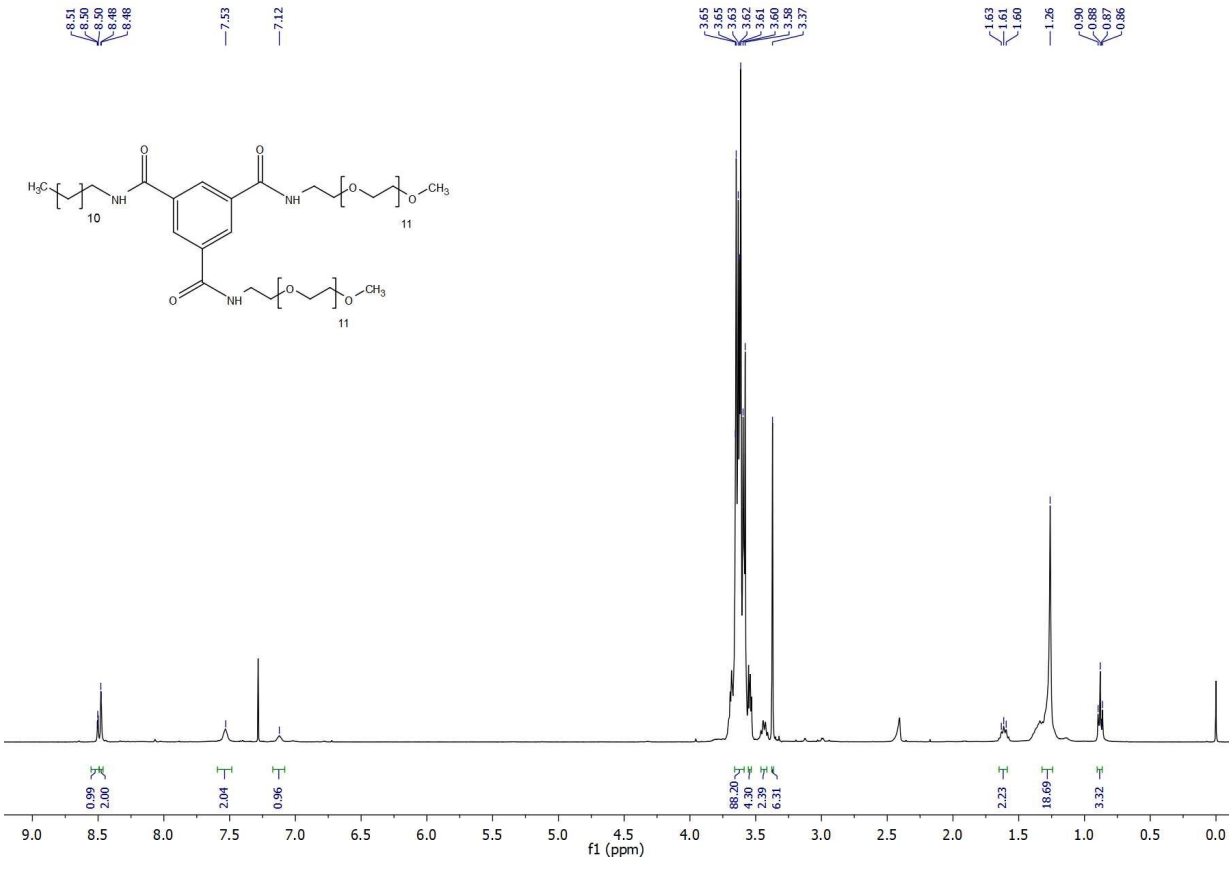


Figure S25:^{1}H NMR spectrum of MA12DPEG12.

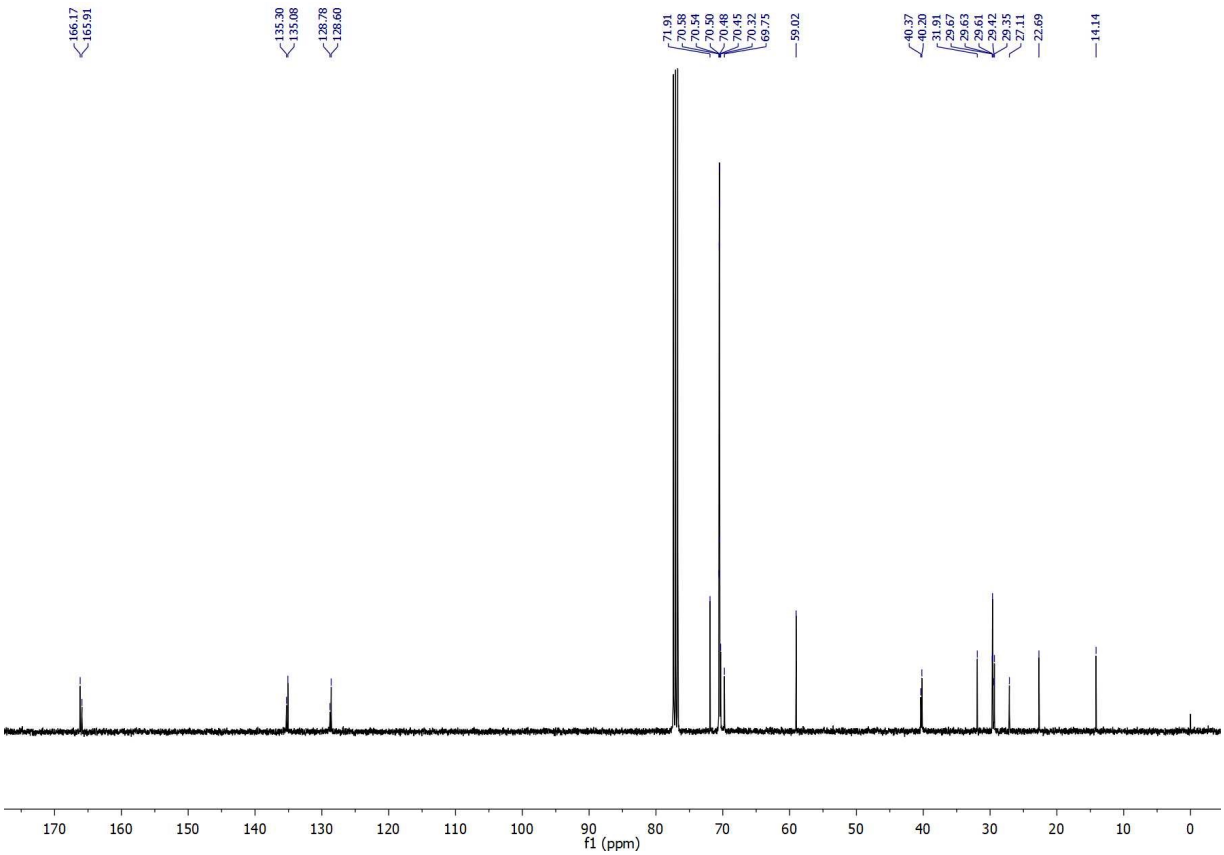


Figure S26: ^{13}C NMR spectrum of MA12DPEG12.

Synthesis of MA18DPEG12 (17c). 5-(octadecylcarbamoyl)isophthaloyl dichloride was synthesised following procedure **12** at the beginning using (40 mg, 0.09 mmol) of 5-(octadecylcarbamoyl)isophthalic acid **16c** and oxalyl chloride (20 µl, 0.23 mmol) providing (43 mg, 99%). Then, MA18DPEG12 was performed following the same procedure as described for **12,** m-PEG12 amine (90 mg, 0.16 mmol) and triethylamine (34 µl, 0.24 mmol) were dissolved in 15 mL dry CH_2Cl_2 in 0 ˚C under a nitrogen atmosphere. To this solution, 5-(octadecylcarbamoyl)isophthaloyl dichloride (40 mg, 0.08 mmol) in 5 mL of dry CH_2Cl_2 was added drop wise. The reaction was stirred overnight at room temperature under nitrogen atmosphere. Then, the solvent was removed under vacuum and the resulting crude product was purified with silica-gel ($CHCl_3$: MeOH; 100:10) leading to a colourless oil (58 mg, 46 %). IR (ATR) ν/cm^{-1}: 3449 (N-H, amide), 2925 (C – H alkyl), 1662 (C = O amide), 1097 (C - O ester) ; ^1H NMR (400 MHz/$CDCl_3$) δ ppm: δ 8.51 (1H, t, J=1.7 Hz, Ar-*H*), 8.48 (2H, d, J=1.6), 7.61 (2H, t, J=5.18, N-H), 7.10 (1H, t, J= 5.68, N-H), 3.62 (88H, m), 3.53 (4H, m), 3.43 (2H, m, N-C*H*$_2$-), 3.37 (6H, s), 1.64 (2H, m), 1.26 (30H, m), 0.88 (3H, t, J= 6.8 Hz); ^{13}C NMR(100 MHz, $CDCl_3$) δ ppm: 166.1, 165.9, 135.3,135.1, 128.7, 128.4, 71.9, 70.6, 70.5, 70.4, 70.3, 69.8, 58.7,40.3, 40.3, 31.9, 29.7, 29.6, 29.5, 29.4, 29.3, 27.1, 22.7, 14.1; ESI-MS: *m/z* calculated for $[C_{77}H_{145}N_3O_{27}+Na]^+$ = 1566.98 Da Found = 1556.99 Da.

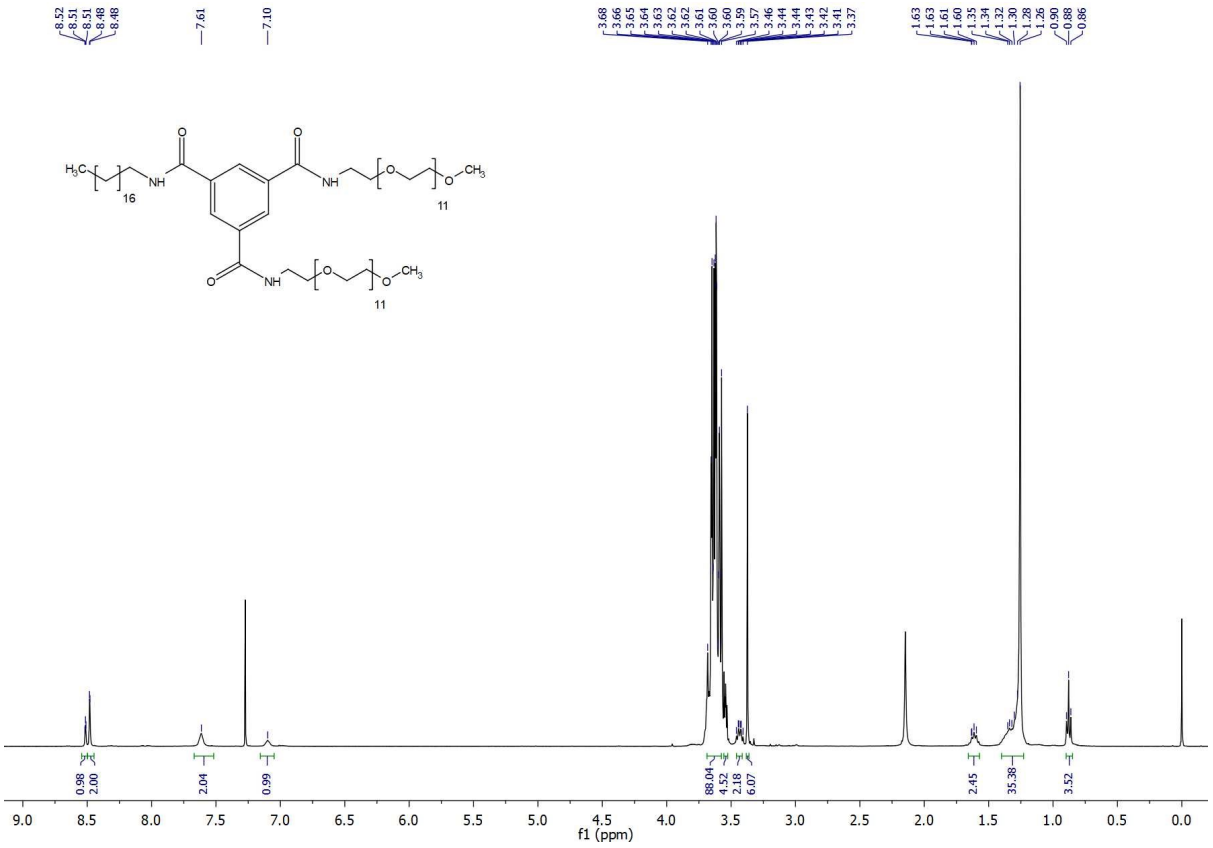


Figure S27:[1]H NMR spectrum of MA18DPEG12.

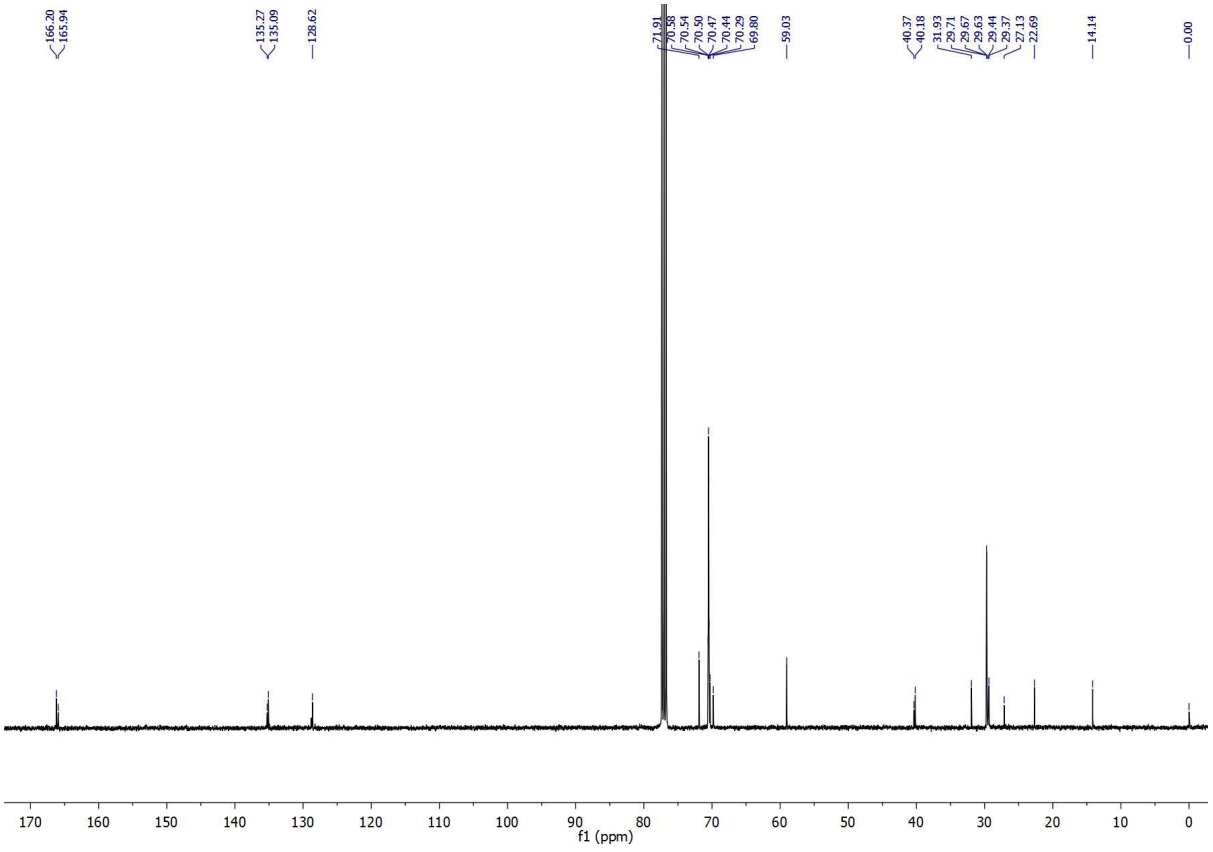


Figure S28: [13]C NMR spectrum of MA18DPEG12.

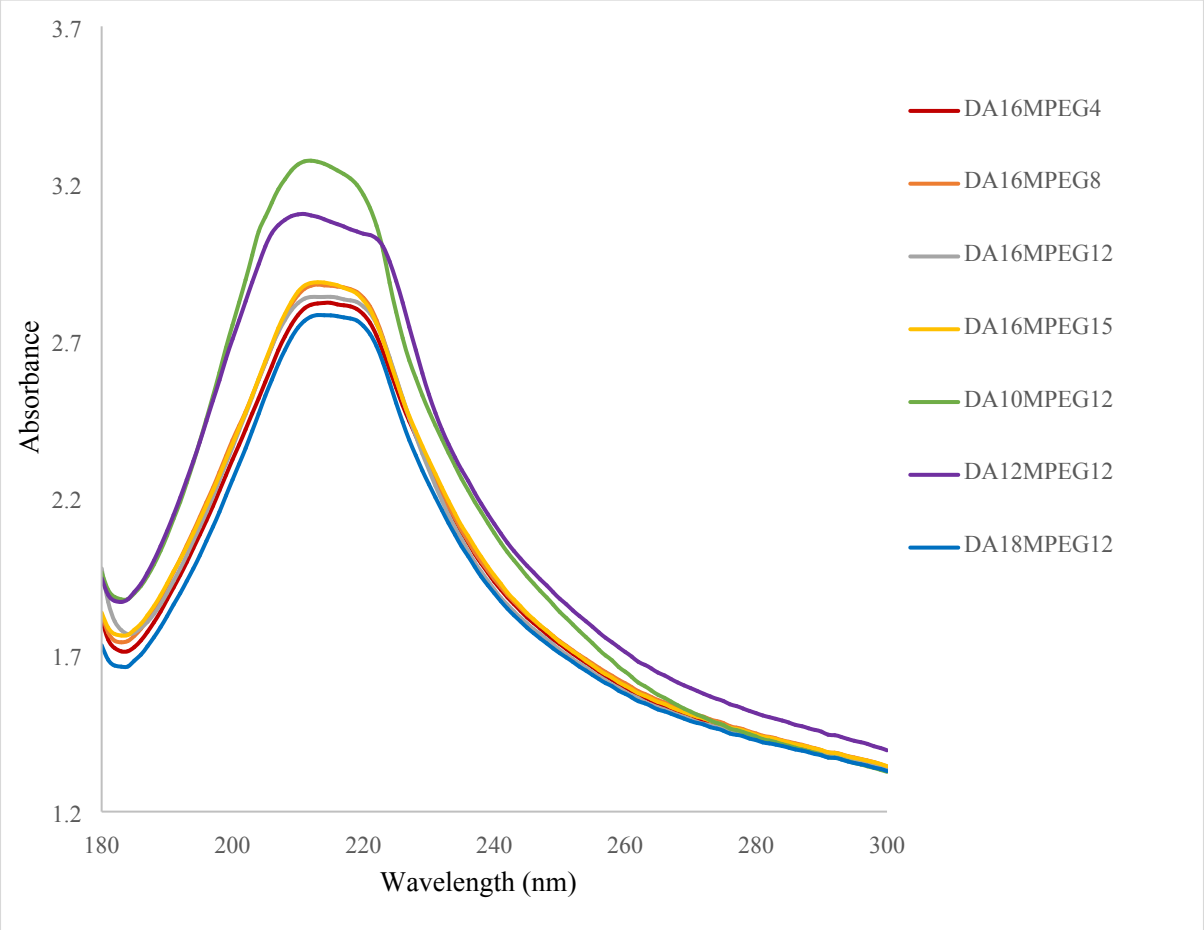


Figure S29: UV spectra for DA_mMPEG_n series

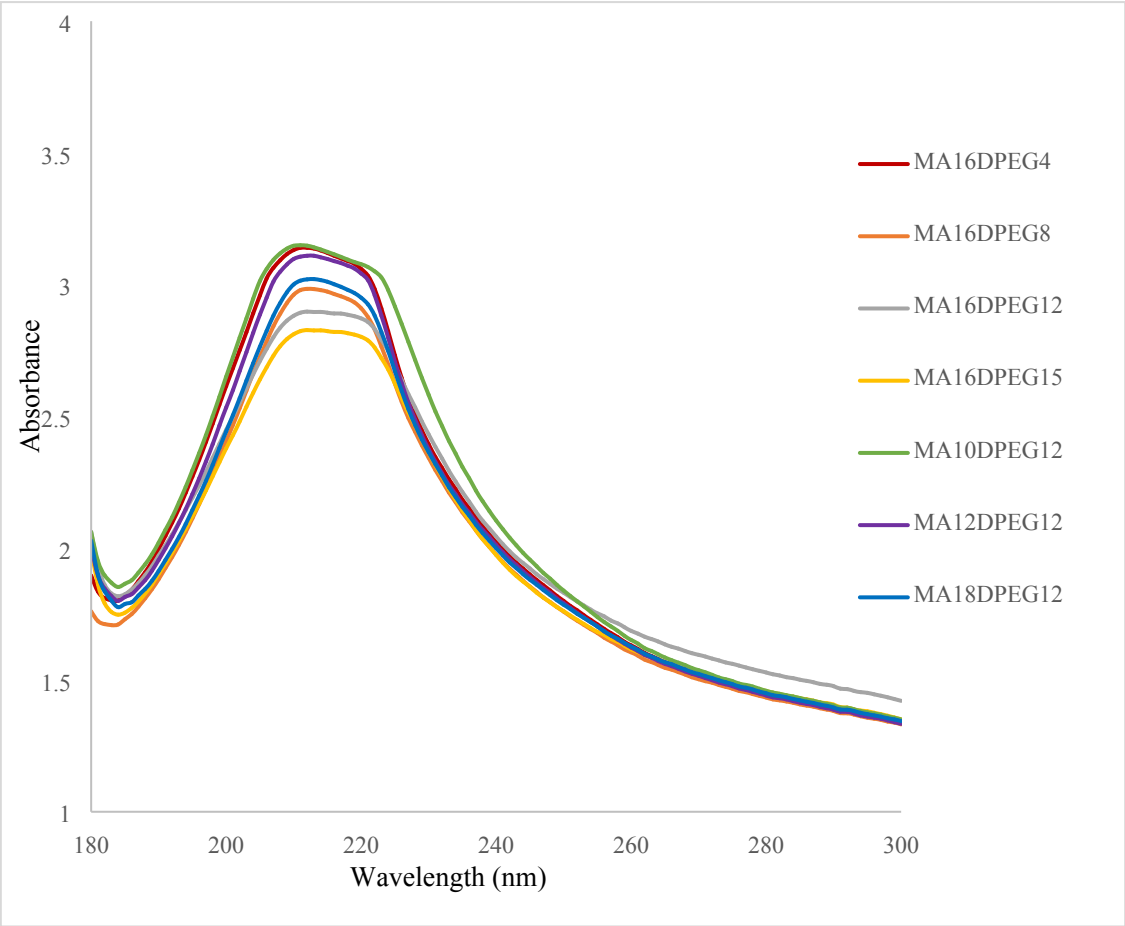


Figure S30: UV spectra for MA_mDPEG_n series

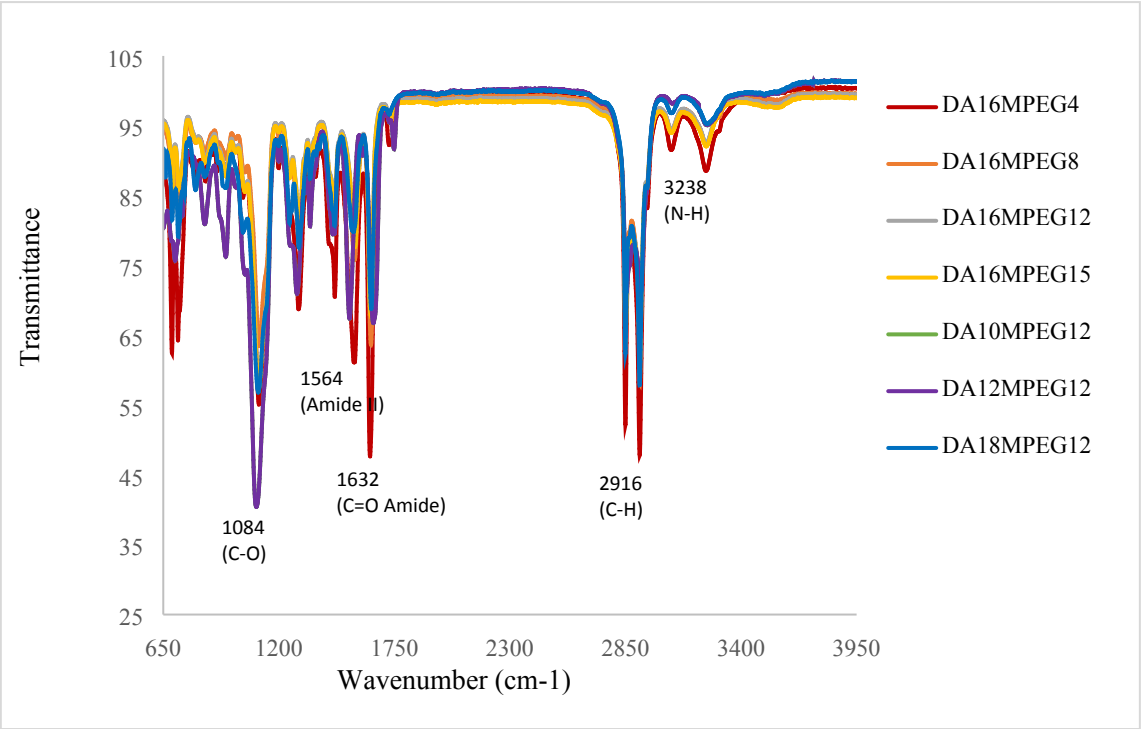


Figure S31: FT-IR spectra for DA_mMPEG_n series

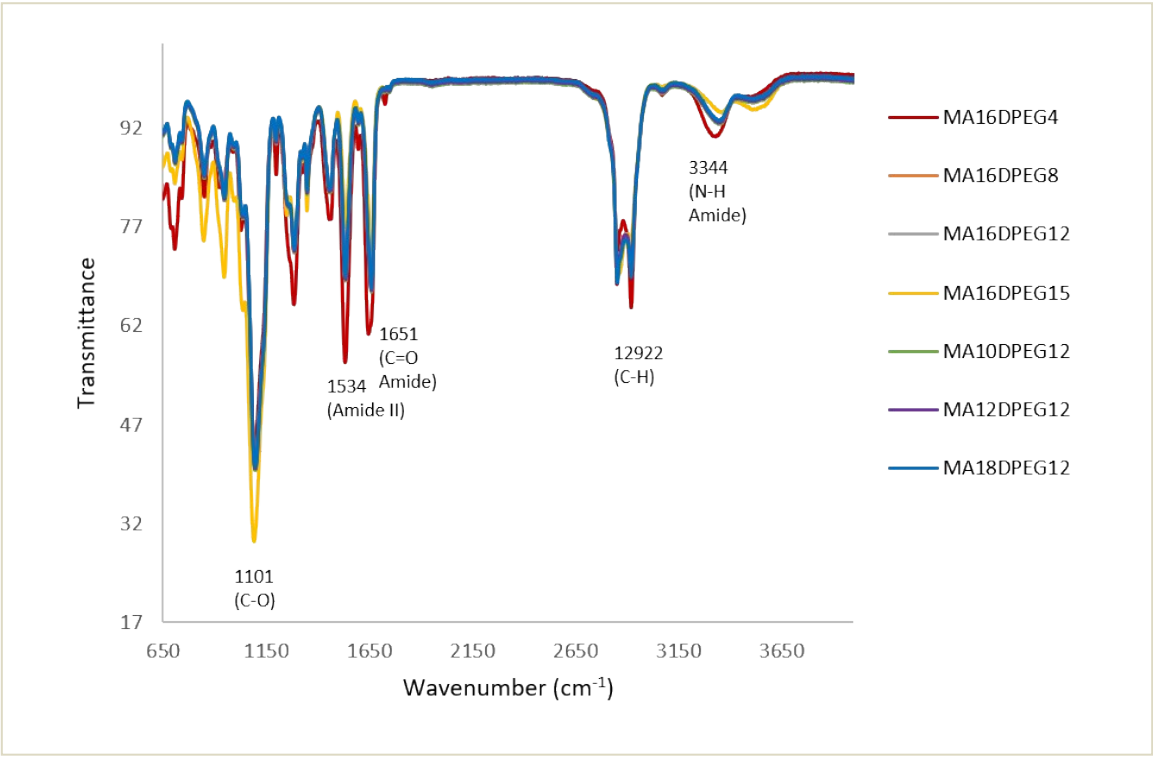


Figure S32: FT-IR spectra for MA_mDPEG_n series

Table S1. Parameters extracted from the fitting of the SAXS data[a] for MAmDPEGn samples.

All samples 1 wt% aqueous solutions.

	MA10-DPEG12	MA12-DPEG12	MA16-DPEG4	MA16-DPEG8	MA16-DPEG12	MA16-DPEG15	MA18-DPEG12
R_g [nm]	2.74						
ν	0.247						
I_0 [kDa][b]	2.81						
$R_c \pm \Delta R_c$ [nm]	--	1.03 ± 0.28	1.78 ± 0.02	1.45 ± 0.05	1.25 ± 0.19	1.18 ± 0.02	1.48 ± 0.02
R_s [nm]	--	3.12	3.76	3.38	3.10	3.60	3.79
η_s [b]	--	0.019	0.016	0.017	0.013	0.017	0.019
μ [b,c]	--	-2.76	-2.76	-2.76	-2.76	-2.76	-2.76
C	0.164	0.104	0.070	0.090	0.075	0.149	0.075

[a] Data fitted using form factors Generalized Gaussian Coil model for monomers (MA10DPEG12) or a Spherical Shell (model i) (all other samples) using the software SASfit.[2]

[b] Intensity data is in kDa, and can be converted to cm^{-1} using a conversion factor 0.000802551 which also puts the scattering contrast into units of cm^{-2}.

[c] Fixed parameter

Key: Generalized Gaussian Coil: radius of gyration R_g, Flory exponent ν, intensity at q = 0 I_0. **Spherical Shell:** core radius, R_c (Gaussian polydispersity ΔR_c), outer radius (including shell), R_s, scattering contrast of shell η_s, and core $\eta_c = \mu\eta_s$.. **Background:** constant background, C.

Table S2. Parameters extracted from the fitting of the SAXS data[a] for DAmMPEGn samples.

All samples 1 wt% aqueous solutions

	DA10-MPEG12	DA12-MPEG12	DA16-MPEG4	DA16-MPEG8	DA16-MPEG12	DA16-MPEG15	DA18-MPEG12
$t \pm \Delta t$ [nm]	2.24± 0.4	2.27± 0.002	2.23± 0.17	2.23[c]± 0.12	2.23[c]± 0.12[c]	2.12± 0.26	2.47± 0.02
η_{out} [b]	0.0541	0.0029	0.0094	0.0121	0.0143	0.0102	0.0183
σ_{out} [nm]	1.25	1.23	0.93	0.97	0.98	1.31	1.23
η_{in} [b]	-0.2449	-0.0058	-0.0117	-0.0150	-0.0180	-0.0159	-0.0243
σ_{in} [nm]	0.20	0.69	1.20	1.32	1.39	1.53	1.78
D [nm]	4.7	22.9	22.9[c]	22.9[c]	22.9[c]	14.9	22.9[c]
C	0.10	0.45	0.35	0.80	0.22	0.09	0.14

[a] Data fitted using Gaussian bilayer form factor[3] using the software SASfit.[2]

[b] Intensity data is in kDa, and can be converted to cm^{-1} using a conversion factor 0.000802551 which also puts the scattering contrast into units of cm^{-2}.

[c] Fixed parameter

Key: Gaussian bilayer: layer thickness t (Gaussian polydispersity Δt), scattering contrast of outer layers η_{out}, and inner layer η_{in}, Gaussian widths σ_{in} and 3.71_{out} of inner and outer layers respectively, D diameter (width) of layer system. **Background:** constant background, C.

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(2) Bressler, I.; Kohlbrecher, J.; Thünemann, A. F., SASfit: a tool for small-angle scattering data analysis using a library of analytical expressions. *J. Appl. Crystallogr.* **2015,** *48*, 1587-1598.

(3) Pabst, G.; Rappolt, M.; Amenitsch, H.; Laggner, P., Structural information from multilamellar liposomes at full hydration: Full q-range fitting with high quality x-ray data. *Phys. Rev. E* **2000,** *62* (3), 4000-4009.