Experimental section

Materials
All reagents were purchased from Aldrich or Acros Organics and used as received unless otherwise specified. All solvents were of AR quality and were purchased from Biosolve. Chloroform was dried over molecular sieves and dichloromethane was dried over an aluminium oxide column. CD and UV measurements were conducted in demineralized water. Deuterated solvents were purchased from Cambridge Isotopes Laboratories. All reactions were run in oven-dried glassware under an argon
atmosphere. 3,5-Bis-(3S)-(3,7-dimethyl-octylaminocarbonyl) benzoic acid 15 was synthesized according to literature procedures.\textsuperscript{1}

**Instrumentation and Analysis**

CD and UV spectra were recorded on a Jasco J-815 CD spectropolarimeter equipped with a Jasco PTC-348 WI temperature controller and a Jasco V-650 UV-vis spectrometer with a Jasco ETCT-762 temperature controller. Cells with an optical path length of 1.0 cm (for \( \sim 10^{-5} \) M solutions) or 0.2 mm (for \( \sim 10^{-3} \) M gels) were used. The molar ellipticity is calculated as: \( \Delta \varepsilon = \text{Cotton-effect}/(32980 \times c \times l) \) where \( c \) is the concentration in mol/L and \( l \) = the optical path length in cm. \( ^1\)H-NMR and \( ^{13}\)C-NMR spectra were recorded on a Varian Gemini 400 MHz NMR (400 MHz for \( ^1\)H-NMR and 100 MHz for \( ^{13}\)C-NMR). Proton chemical shifts are reported in ppm downfield from tetramethylsilane (TMS). Carbon chemical shifts are reported downfield from TMS using the resonance of the deuterated solvent as the internal standard. IR spectra were recorded on a Perkin Elmer 1600 FT-IR. GPC measurements were performed on a Resi Pore column with chloroform (at room temperature) as the eluent (flow = 1 mL/min) and employing a RI and PDA (\( \lambda = 254 \) nm) as the detector. The molecular weights were determined using the polystyrene calibration method. DSC measurements were performed on a TA Q2000 (third heating run, 40 K min\(^{-1}\)). Matrix assisted laser desorption/ionisation mass spectra were obtained on a PerSeptive Biosystems Voyager DE-PRO spectrometer or a Bruker autoflex speed spectrometer using \( \alpha \)-cyano-4-hydroxycinnamic acid (CHCA) and 2-[(2E)-3-(4-tert-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB) as matrices.

BTA concentration at CGC as shown in Table 1 was derived from the weight fraction converted to molarity corrected with a factor 2 for bifunctional 4a-c and 5.

**Cryogenic transmission electron microscopy**

The sample vitrification procedure was carried out using an automated vitrification robot (FEI Vitrobot\textsuperscript{TM} Mark III). Cryo-TEM grids, R2/2 Quantifoil Jena grids, were purchased from Quantifoil Micro Tools GmbH. Prior to the vitrification procedure (3 \( \mu \)L aliquots, blotting time varied from 8 s to 12 s, \(-4\) mm blotting offset, 100% relative humidity) the grids were surface plasma treated using a Cressington 208 carbon coater operating at 5 mA for 40 s. The cryo-TEM experiments were performed on a FEI Technai 20, type Sphera (www.cryotem.nl). The Technai 20 is equipped with a LaB6 filament operating at 200 kV and the images were recorded using a 1k x 1k Gatan CCD camera.

**Rheometry**

Shear controlled dynamic oscillatory rheology experiments were performed on an Anton Paar RheoplusV32 rheometer. Measurements were performed in a plate-plate geometry (tool PP25) with gaps of 0.3–0.7 mm and a diameter of 25 mm. Motor and plate-plate distance calibrations were performed before the experiment. All samples were measured at 10 wt% in H\(_2\)O after the gel had equilibrated overnight at 60°C to obtain a homogeneous gel. Samples were measured at 20°C and all
experiments were performed twice (with unique samples) to confirm reproducibility. All strain-dependent measurements were performed in the linear frequency regime along with the frequency-dependent measurements that were performed in the linear strain regime for each individual sample. Stability checks were performed by short measurements at constant strain and frequency until a stable value was obtained (< 10 min).

**Figure S1.** Strain sweeps of compounds in the series $4$ (10 wt%, 20°C). Monitored at 30 rad/s ($4a$), 3 rad/s ($4b$), and 3 rad/s ($4c$).
Figure S2. Strain sweeps of compounds 1 (5 wt%, 1 rad/s, 20°C) and 5 (10 wt%, 2 rad/s, 20°C).

Figure S3. Frequency sweeps of compounds in series 4 (10 wt%, 20°C, 1% strain).
Figure S4. Frequency sweeps of compounds 1 (5 wt%, 20°C, 1% strain) and 5 (10 wt%, 20°C, 1% strain).

Synthesis

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Scheme S1. Synthetic route towards 1–5.

Synthetic procedures

26-Bromo-2,5,8,11,14-pentaoxahexacosane (6). A round bottom flask (25 ml) was charged with NaH (60% dispersion in mineral oil, 27.4 mmol, 1.10 g) and DMF (10 ml). The stirring solution was cooled to 0 °C and subsequently a solution of tetraethyleneglycol monomethyl ether (9.65 mmol, 2.01 g) in DMF (5 ml) was added dropwise. Another round bottom flask (100 ml) was charged with 1,12-dibromododecane (60.98 mmol, 20.01 g) and DMF (20 ml). After all solids dissolved the solution was placed in an ice bath. Under constant stirring the mixture of tetraethyleneglycol monomethyl ether and sodiumhydride in DMF was added dropwise in 15 minutes and the reaction mixture was stirred overnight at room temperature yielding a clear yellow solution. To this solution H2O (100 ml) was added producing a milky mixture which was extracted four times with hexane (100 ml). The organic layers were combined and concentrated before drying with MgSO4. Removal of the solvent in vacuo yielded a colorless oil which slowly crystallized upon standing. The material was purified by column chromatography (Hexane/dimethoxyethane 95/5-70/30) yielding the product as a colorless oil. Yield = 1.33 g, 32%. 1H-NMR (400 MHz, CDCl3, δ): 3.70 – 3.61 (mm, 12H, O-(CH2)2-O), 3.59 – 3.52 (mm, 4H, O-(CH2)2-O), 3.44 (t, 2H, CH2CH2CH2-O), 3.40 (t, 2H, BrCH2CH2), 3.37 (s, 3H, OCH3), 1.85 (quin, 2H, BrCH2CH2), 1.63 – 1.50 (m, 2H, CH2CH2CH2-O), 1.48 – 1.36 (m, 2H, CH2CH2CH2-O), 1.26 (mm, 16H, aliphatic). MALDI-TOF-MS: calculated MW = 454.23 g/mol, observed m/z = 455.06 [MH+]1, 477.07 [Na+ adduct].

2,5,8,11,14-Pentaoxahexacosan-26-phthalimide (7). A round bottom flask (50 ml) was equipped with a condenser and charged with 26-bromo-2,5,8,11,14-pentaoxahexacosane 6 (2.20 mmol, 1.003 g), potassium phthalimide (2.43 mmol, 0.450 g) and dry DMF (30 ml). The solvent was heated to 80 °C and subsequently stirred overnight at 50 °C. The solvent was removed in vacuo, and a slightly yellow paste was obtained. Deionized water (50 ml) was added and the mixture was extracted three times with diethylether (50 ml). The organic layers were combined, dried with MgSO4 and filtered after which the solvent was evaporated in vacuo yielding a slightly yellowish oil. Yield = 1.12 g, 97 %. 1H NMR (400 MHz, CDCl3 δ): 7.83 (dd, 2H, Ar), 7.71 (dd, 2H, Ar), 3.65 (mm, 15H, O-(CH2)2-O, NCH2CH2), 3.56 (mm, 4H, O-(CH2)2-O), 3.43 (t, 2H, CH2CH2CH2-O), 3.38 (s, 3H, OCH3), 1.73 – 1.61 (m, 2H, NCH2CH2), 1.61 – 1.50 (m, 2H, CH2CH2CH2-O), 1.27 (m, 16H, aliphatic).

2,5,8,11,14-Pentaoxahexacosan-26-amine (8). A round bottom flask (50 ml) was charged with ethanol (30 ml) and 2,5,8,11,14-pentaoxahexacosan-26-phthalimide 7 (1.005 g, 1.93 mmol) was added. Hydrazine monohydrate (2 ml) was added to the stirring solution and the mixture was heated to reflux overnight yielding a milky suspension. The solvent was removed in vacuo. Chloroform (25 ml) was added and the mixture was extracted three times with NaOH (1 M, 25ml). The organic layer was dried with MgSO4, filtered and concentrated in vacuo yielding a slightly yellow oil which
solidified upon standing. Yield = 0.711 g, 94%. $^1$H NMR (400 MHz, CDCl$_3$, $\delta$): 3.69 – 3.62 (mm, 12H, O-(CH$_2$)$_2$-O), 3.60 – 3.53 (mm, 4H, O-(CH$_2$)$_2$-O), 3.44 (t, 2H, CH$_2$CH$_2$CH$_2$O), 3.38 (s, 3H, OCH$_3$), 2.68 (t, 2H, NH$_2$CH$_2$CH$_2$), 1.65 – 1.51 (m, 2H, CH$_2$CH$_2$CH$_2$O), 1.42 (d, $J$ = 7.4 Hz, 2H, CH$_2$CH$_2$CH$_2$O), 1.26 (m, 16H, aliphatic). MALDI-TOF-MS: calculated MW = 391.33 g/mol, observed m/z = 392.17 [MH$^+$], 414.15 [Na$^+$ adduct].

$N^1,N^3,N^5$-Tri(2,5,8,11,14-pentaoxahexacosan-26-yl)benzene-1,3,5-tricarboxamide (1). To a stirring solution of 2,5,8,11,14-pentaoxahexacosan-26-amine (0.38 mmol, 0.153 g) in chloroform (2.5 ml) triethyl amine was added (0.76 mmol, 0.08 g). The reaction mixture was cooled to 0 °C and a solution of 1,3,5-benzenetricarbonyl trichloride (0.12 mmol, 31.9 mg) in chloroform (1 ml) was added dropwise. The reaction mixture was then allowed to reach room temperature and was stirred overnight. The solvent was removed in vacuo and the obtained white solid was purified by column chromatography (CHCl$_3$/methanol 95/5 v/v) obtaining the product as a slightly yellow oil which solidified upon standing. Yield = 0.111 g, 70%. $^1$H NMR (400 MHz, CDCl$_3$, $\delta$): 8.37 (s, 3H, Ar), 6.55 (t, $J$ = 26.0 Hz, 3H, CH$_2$NHC=O), 3.68 – 3.60 (mm, 36H, O-(CH$_2$)$_2$-O), 3.60 – 3.51 (mm, 12H, O-(CH$_2$)$_2$-O), 3.47 (t, 6H, C=ONH$_2$CH$_2$), 3.43 (t, $J$ = 6.8 Hz, 6H, CH$_2$CH$_2$CH$_2$O), 3.37 (s, 9H, CH$_2$OCH$_3$), 1.77 – 1.46 (m, 12H, CH$_2$CH$_2$CH$_2$O, CH$_2$CH$_2$CH$_2$O), 1.46 – 1.13 (m, 48H, aliphatic). $^{13}$C NMR (100 MHz, CDCl$_3$, $\delta$): 165.70, 135.21, 128.06, 76.68, 71.89, 71.52, 70.60, 70.57, 70.55, 70.49, 70.02, 59.01, 58.99, 40.36, 29.57, 29.52, 29.48, 29.44, 29.43, 29.41, 29.38, 29.21, 26.92, 26.03. MALDI-TOF-MS: calculated MW = 1329.97 g/mol, observed m/z = 1352.98 [Na$^+$ adduct]. FT-IR (ATR) ν (cm$^{-1}$): 3335, 3074, 2923, 2854, 1662, 1597, 1535, 1457, 1350, 1285, 1199, 1103, 1031, 944, 852, 728, 555.

Methyl 3,5-bis(chlorocarbonyl)benzoate (10). To a stirring solution of oxaly chloride (1.2 mmol, 0.1 ml) and DMF (catalytic amount) in chloroform (4 ml) at 0 °C 5-(methoxycarbonyl)isophthalic acid (0.406 mmol, 91.07 mg) was added as a white powder (0.406 mmol, 91.07 mg) and allowed to slowly dissolve. After 15 minutes the temperature was allowed to reach room temperature. After 1.5 hours the mixture became clear, the reaction mixture was concentrated in vacuo and oxalyl chloride was coevaporated with toluene two times (5 ml) after which the material was obtained as a yellow solid. $^1$H NMR (400 MHz, CDCl$_3$, $\delta$): 9.05 (d, 2H, Ar), 9.00 (t, $J$ = 1.6 Hz, 1H, Ar), 4.05 (s, 3H, OC=OCH$_3$).

Methyl 3,5-bis(2,5,8,11,14-pentaoxahexacosan-26-ylcarbamoyl)benzoate (12). To a stirring solution of methyl 3,5-bis(chlorocarbonyl)benzoate (0.406 mmol, 106 mg) in chloroform (3 ml) triethylamine (1.62 mmol, 0.23 ml) was added. 2,5,8,11,14-pentaoxahexacosan-26-amine (0.89 mmol, 0.35 g) was dissolved in chloroform (1.5 ml) and added dropwise to the stirring reaction mixture at 0 °C. After addition the reaction mixture was stirred overnight at room temperature. The reaction mixture was concentrated in vacuo and the solids were dissolved in chloroform (10 ml) and extracted with HCl two times (1 M, 20 ml) and with brine (20 ml). The organic layer was dried with MgSO$_4$, filtered and
concentrated in vacuo. The material was purified by column chromatography (heptane/dimethoxyethane 60/40). Yield = 0.288 g, 73%. $^1$H NMR (400 MHz, CDCl$_3$ δ): 8.55 (d, $J = 1.7$ Hz, 2H, Ar), 8.45 (t, $J = 1.7$ Hz, 1H, Ar), 6.57 (t, $J = 5.6$ Hz, 2H, CH$_2$NHC=O), 3.97 (s, 3H, OC=OCH$_3$), 3.74 – 3.60 (mm, 24H, O-(CH$_2$)$_2$-O), 3.60 – 3.51 (mm, 8H, O-(CH$_2$)$_2$-O), 3.45 (m, 8H, C=ONH$_2$CH$_2$, CH$_2$CH$_2$CH$_2$O), 3.36 (s, 6H, CH$_2$OCH$_3$), 1.70 – 1.50 (mm, 8H, CH$_2$CH$_2$O, CH$_2$CH$_2$CH$_2$O), 1.49 – 1.13 (mm, 32H, aliphatic).

3,5-Bis(2,5,8,11,14-pentaoxahexacosan-26-ylcarbamoyl)benzoic acid (13). To a stirring solution of methyl 3,5-bis(2,5,8,11,14-pentaoxahexacosan-26-ylcarbamoyl)benzoate 12 in methanol (2 ml) lithium hydroxide monohydrate (0.83 mmol, 35 mg) and H$_2$O (0.05 ml) were added. The mixture was stirred overnight at room temperature, after which the solvent was removed in vacuo and H$_2$O (10 ml) was added. The solution was acidified with HCl (37 %) upon which the mixture became milky white. Subsequently, the reaction mixture was extracted three times with chloroform (10 ml). The organic layers were combined, dried with MgSO$_4$, filtered and concentrated in vacuo yielding the product as a colorless oil which solidified upon standing. Yield = 0.155 g, 77 %. $^1$H NMR (400 MHz, CDCl$_3$ δ): 8.55 (d, 2H, Ar), 8.45 (t, $J = 14.3$ Hz, 1H, Ar), 6.44 (bt, $J = 36.8$ Hz, 2H, C=ONH$_2$CH$_2$), 3.73 – 3.61 (mm, 24H, O-(CH$_2$)$_2$-O), 3.61 – 3.53 (mm, 8H, O-(CH$_2$)$_2$-O), 3.53 – 3.41 (dt, 8H, C=ONH$_2$CH$_2$, CH$_2$CH$_2$CH$_2$O), 3.38 (s, 6H, CH$_2$OCH$_3$), 1.73 – 1.48 (mm, 8H, CH$_2$CH$_2$O, CH$_2$CH$_2$O), 1.48 – 1.11 (mm, 32H, aliphatic).

(S)-N$_1$-(3,7-Dimethylotyl)-N$_3$N$_5$-di(2,5,8,11,14-pentaoxahexacosan-26-yl)benzene-1,3,5-tricarboxamide (2). To a stirring solution of 3,5-bis(2,5,8,11,14-pentaoxahexacosan-26-ylcarbamoyl)benzoic acid 13 (0.162 mmol, 0.155 g) in dry chloroform (2.5 ml) 1-chloro-N,N,2-trimethylpropenyl-1-amine (0.30 mmol, 0.04 ml) was added. After 3 hours the solvent and the excess 1-chloro-N,N,2-trimethylpropenyl-1-amine were removed in vacuo yielding 3,5-bis(2,5,8,11,14-pentaoxahexacosan-26-ylcarbamoyl)benzoyl chloride as a yellow paste which was used as such. To a stirring solution of 3,5-bis(2,5,8,11,14-pentaoxahexacosan-26-ylcarbamoyl)benzoyl chloride in dry chloroform (1.5 ml) (S)-3,7-dimethylotan-1-amine (0.20 mmol, 31.8 mg) and triethylamine (0.04 ml) were added, and the mixture was stirred overnight at room temperature. The solvent was removed in vacuo and the obtained material was purified by column chromatography (chloroform/methanol 100/0 – 90/10 v/v). Yield = 0.107 g, 60 %. $^1$H NMR (400 MHz, CDCl$_3$ δ): 8.38 (s, 3H, Ar), 7.07 – 6.77 (m, 3H, C=ONH$_2$CH$_2$), 3.82 – 3.59 (m, 24H, O-(CH$_2$)$_2$-O), 3.59 – 3.50 (m, 8H, O-(CH$_2$)$_2$-O), 3.50 – 3.38 (m, 10H, CH$_2$NHC=O, CH$_2$CH$_2$CH$_2$O), 3.35 (s, 6H, CH$_2$OCH$_3$), 1.72 – 1.06 (m, 50H, Aliphatic), 0.93 (d, $J = 6.5$ Hz, 3H, CH$_2$C(CH$_3$)$_2$CH$_2$), 0.86 (d, $J = 6.6$ Hz, 6H, CH$_2$(CH$_3$)$_2$). $^{13}$C NMR (100 MHz, CDCl$_3$ δ): 165.65, 165.63, 135.24, 127.97, 76.68, 71.89, 71.52, 70.61, 70.57, 70.55, 70.49, 70.03, 58.98, 40.36, 39.23, 38.50, 37.12, 36.63, 30.75, 29.57, 29.51, 29.47, 29.43, 29.41, 29.39, 29.38, 29.19, 27.93, 26.91, 26.02, 24.62, 22.68, 22.58, 19.48. MALDI-TOF-MS: calculated MW =
$1095.83 \text{ g/mol, observed } m/z = 1096.71 \text{ [MH}^+\text{], 1118.71 [Na}^+\text{ adduct], 1134.69 [K}^+\text{ adduct]}. \text{ FT-IR (ATR) } \nu (\text{cm}^{-1}) : 3310, 3074, 2923, 2854, 1643, 1594, 1531, 1466, 1435, 1365, 1350, 1328, 1289, 1200, 1107, 1031, 915, 852, 702, 645, 590.

$N_1,N_3$-Bis((S)-3,7-dimethyloctyl)-N5-(2,5,8,11,14-pentaoxahexacosan-26-yl)benzene-1,3,5-tricarboxamide (3). To a stirring solution of 3,5-bis((S)-3,7-dimethyloctyl)carbamoyl)benzoic acid 15 (0.201 mmol, 0.098 g) in dry chloroform (3 ml) 1-chloro-N,N,2-trimethylpropenyl-1-amine (0.46 mmol, 0.06 ml) was added. After 3 hours the solvent and the excess 1-chloro-N,N,2-trimethylpropenyl-1-amine were removed in vacuo yielding 3,5-bis((S)-3,7-dimethyloctyl)carbamoyl)benzoyl chloride as a yellow paste which was used as such. To a stirring solution of 3,5-bis((S)-3,7-dimethyloctyl)carbamoyl)benzoyl chloride (0.201 mmol) in dry chloroform (2 ml) was added 2,5,8,11,14-pentaoxahexacosan-26-amine (0.24 mmol, 94.5 mg) dissolved in chloroform (0.6 ml) followed by the addition of triethylamine (0.05 ml), and the mixture was stirred at room temperature for 4 hours. The solvent was removed in vacuo and the obtained material was purified by column chromatography (heptane/ethyl acetate 50/50 – 20/80 v/v). Yield = 0.107 g, 62 %. $^1$H NMR (400 MHz, CDCl$_3$, $\delta$): 8.35 (s, 3H, Ar), 6.55 – 6.34 (m, 3H, C=ONH$_2$CH$_2$), 3.68 – 3.59 (m, 12H, O-(CH$_2$)$_2$-O), 3.58 – 3.52 (m, 4H, O-(CH$_2$)$_2$-O), 3.52 – 3.45 (m, 6H, CH$_2$NHC=O), 3.43 (t, $J$ = 6.8 Hz, 2H, CH$_2$CH$_2$CH$_2$O), 3.36 (s, 3H, CH$_2$OCH$_3$), 1.71 – 1.09 (m, 40H, Aliphatic), 0.95 (d, $J$ = 6.5 Hz, 6H, CH$_3$C(CH$_3$)$_2$CH$_2$), 0.87 (d, $J$ = 6.6 Hz, 12H, CH$_2$(CH$_3$)$_2$). $^{13}$C NMR (100 MHz, CDCl$_3$, $\delta$): 165.55, 165.53, 135.26, 127.88, 76.67, 71.90, 71.52, 70.62, 70.59, 70.56, 70.51, 70.04, 58.99, 40.34, 39.23, 38.50, 37.11, 36.63, 30.73, 29.57, 29.49, 29.46, 29.41, 29.39, 29.36, 29.16, 27.93, 26.88, 26.02, 24.61, 22.68, 22.58, 19.48. MALDI-TOF-MS: calculated MW = 861.68 g/mol, observed m/z = 884.67 [Na$^+$ adduct], 900.64 [K$^+$ adduct]. FT-IR (ATR) $\nu$ (cm$^{-1}$): 3236, 3073, 2925, 2855, 1640, 1562, 1464, 1382, 1368, 1351, 1300, 1113, 906, 853, 804, 732, 692, 649.

$CDI$ activated pEG (16). Bishydroxy functionalized pEG (20 kg/mol) (2.5 mmol, 50 g) was dried at 100 °C for 3 hours in vacuo and subsequently dissolved in 190 mL of chloroform. Carbonyl diimidazole (4 mmol, 656 mg) in 10 mL chloroform was added to the solution. The reaction mixture was stirred for 24 hours at room temperature. After full conversion, the reaction mixture was concentrated to 50 mL by the removal of chloroform in vacuo. Diethyl ether (400 mL) was added to the mixture that resulted in precipitation of the product. The product was obtained as a white solid after filtration and an additional washing step with diethyl ether. Yield = 46 g, 95%. $^1$H-NMR (400 MHz, CDCl$_3$, $\delta$): 8.15 (s, 2H, Ar-H), 7.68 (s, 4H, Ar-H) 4.50 (t, 4H, CH$_2$OC=O), 3.7-3.4 (b, 18OH, O-(CH$_2$)$_2$-O).

General procedure for the synthesis of bisamino alkane functional pEG. The following procedure was used for all bisaminoalkane functional pEGs (17a-c) using the same reaction conditions as described for compound 4a.
**Bisamino octane functionalized pEG (17a).** Compound 16 (0.5 mmol, 10 g) was dried in vacuo at 60 °C for three hours and subsequently dissolved in 75 mL of chloroform. The solution was added dropwise to a solution of 1,8-diaminooctane (8 mmol, 1.15 g) in 25 mL of chloroform. The reaction mixture was stirred for 24 hours at room temperature. After full conversion, the reaction mixture was concentrated to 50 mL by the removal of chloroform in vacuo. Diethyl ether (350 mL) was added to the mixture that resulted in precipitation of the product. The product was obtained by filtration and subsequently redissolved in 50 mL of chloroform and precipitated from diethyl ether. Precipitation in diethyl ether was repeated till full removal of the excess of 1,8-diaminoctane was achieved. Yield = 8.1 g, 80%. 1H-NMR (400 MHz, CDCl₃, δ): 4.85 (s, 2H, NHC=O), 4.21 (t, 4H, CH₂O-C=O), 3.7 (b, 1800H, O-(CH₂)₂-O), 3.15 (q, 4H, CH₂NHC=O), 2.65 (t, 4H, CH₂NH₂), 1.9-1.2 (mm, 16H, aliphatic).

**Bisamino decane functionalized pEG (17b).** Yield = 8 g, 78%. 1H-NMR (400 MHz, CDCl₃, δ): 4.83 (s, 2H, NH(C=O)), 4.22 (t, 4H, CH₂O-C=O), 3.7 (b, 1800H, O-(CH₂)₂-O), 3.16 (q, 4H, CH₂NHC=O), 2.65 (t, 4H, CH₂NH₂), 1.9-1.2 (mm, 20H, aliphatic).

**Bisamino dodecane functionalized pEG (17c).** Yield = 7.5 g, 73%. 1H-NMR (400 MHz, CDCl₃, δ): 4.87 (s, 2H, NH(C=O)), 4.21 (t, 4H, CH₂O-C=O), 3.7 (b, 1800H, O-(CH₂)₂-O), 3.18 (q, 4H, CH₂NHC=O), 2.64 (t, 4H, CH₂NH₂), 1.9-1.2 (mm, 24H, aliphatic).

**General procedure for the synthesis of bisBTA alkane functional pEG.** The following procedure was used for all bisBTA alkane functional pEGs (4a-c and 5) using the same reaction conditions as described for compound 4a.

**BisBTA octane functionalized pEG (4a).** Compound 17a (0.05 mmol, 1 g), 3,5-bis-(3S)-(3,7-dimethyl-octylaminocarbonyl)-benzoic acid (0.12 mmol, 59 mg) were dissolved in 10 mL dry dichloromethane. Benzotriazol-1-yl-oxytripyrrolidinophosphonium hexafluorophosphate (PyBOP) (126 mg, 0.24 mmol) and N,N-diisopropylethylamine (DIPEA) (31 mg, 0.24 mmol) were added to the solution. The solution was stirred for 24 hours at room temperature. Dichloromethane was removed in vacuo. Subsequently, 50 mL of chloroform was added. The precipitates were removed by filtration. Chloroform was removed in vacuo and the product was dissolved in 10 mL of methanol and subsequently purified by dialysis. Yield = 0.72 g, 70%. 1H-NMR (400 MHz, CDCl₃, δ): 8.41 (s, 6H, Ar), 6.9-6.6 (t, 6H, NH(C=O)), 4.85 (s, 2H, NH(C=O)O), 4.21 (t, 4H, CH₂O-C=O), 3.7 (b, 1800H, O-(CH₂)₂-O), 3.48 (t, 12H, CH₂NH(C=O)), 3.15 (q, 4H, CH₂NH(C=O)O), 1.9-0.9 (mm, 58H, aliphatic). 13C-NMR (100 MHz, CDCl₃, δ): 165.7, 135.3, 128.1, 69.7, 69.2, 67.7, 63.7, 63.2, 61.3, 60.9, 39.2, 38.4, 37.1, 36.7, 30.8, 29.2, 24.6, 22.7, 22.6, 19.5. GPC (chboroform, polystyrene standards): $M_n = 18.6$ kg/mol, $PDI = 1.43$. DSC (40 °C/min, third heating run): $T_g = -60$ °C, $T_m = 57$ °C with ΔH 136 J/g.
**BisBTA decane functionalized pEG (4b)** Yield = 0.65 g, 63%. $^1$H-NMR (400 MHz, CDCl$_3$, δ): 8.40 (s, 6H, Ar), 6.9-6.6 (t, 6H, NH(C=O)), 4.95 (s, 2H, NH(C=O)O), 4.20 (t, 4H, CH$_2$O-C=O), 3.7 (b, 1800H, O-(CH$_2$)$_2$-O), 3.50 (t, 12H, CH$_2$NH(C=O)), 3.14 (q, 4H, CH$_2$NH(C=O)O), 1.7-0.9 (mm, 66H, aliphatic). $^{13}$C-NMR (100 MHz, CDCl$_3$, δ): 165.7, 135.4, 128.2, 67.7, 63.7, 39.2, 28.5, 37.1, 36.7, 30.8, 27.9, 24.5, 22.6, 19.5. GPC (chloroform, polystyrene standards): $M_n = 16.1$ kg/mol, $PDI = 1.52$. DSC (40 °C/min, third heating run): $T_g = -60$ °C, $T_m = 56$ °C with $\Delta H = 136$ J/g.

**BisBTA dodecane functionalized pEG (4c)** Yield = 0.25 g, 75%. $^1$H-NMR (400 MHz, CDCl$_3$, δ): 8.40 (s, 6H, Ar), 6.9-6.6 (t, 6H, NH(C=O)), 4.84 (s, 2H, NH(C=O)O), 4.26 (t, 4H, CH$_2$O-C=O), 3.7 (b, 1800H, O-(CH$_2$)$_2$-O), 3.48 (t, 12H, CH$_2$NH(C=O)), 3.15 (q, 4H, CH$_2$NH(C=O)O), 1.9-0.9 (mm, 74H, aliphatic). $^{13}$C-NMR (100 MHz, CDCl$_3$, δ): 165.7, 135.2, 128.1, 69.8, 69.1, 67.6, 63.7, 63.2, 61.2, 60.8, 39.2, 38.4, 37.1, 36.7, 30.8, 29.2, 27.0, 26.9, 24.6, 22.7, 22.6, 19.3. GPC (chloroform, polystyrene standards): $M_n = 17.5$ kg/mol, $PDI = 1.38$. DSC (40 °C/min, third heating run): $T_g = -61$ °C, $T_m = 57$ °C with $\Delta H = 144$ J/g.

**BisBTA dodecyltetraethyleneglycol methyl ether functionalized pEG (5)** To a stirring solution of 3,5-bis(2,5,8,11,14-pentaoxahexacosan-26-ylcarbamoyl)benzoic acid $^{13}$ (0.087 mmol, 83 mg) and bisamine endfunctionalized PEG $^{17}$a in dry chloroform (10 ml) Benzotriazol-1-yl-oxytripyrrolidinophosphonium hexafluorophosphate (PyBOP) (0.05 g, 0.10 mmol) and N,N-diisopropylethylamine (DIPEA) (30 mg, 0.23 mmol) were added and the mixture was stirred for 24 hours at room temperature. The chloroform was removed in vacuo, the material was dissolved in methanol (10 ml) and purifed by dialysis. Yield = 0.472 g, 56%. $^1$H NMR (399 MHz, CDCl$_3$, δ): 8.39 (s, 3H, Ar), 6.88 – 6.65 (b, 3H, C=ONHCH$_2$), 4.82 (d, $J = 44.6$ Hz, 2H, OC=ONHCH$_2$), 4.26 – 4.13 (m, 4H, CH$_2$O-C=O), 3.64 (m, 1800H, O-(CH$_2$)$_2$-O), 3.14 (q, 4H, CH$_2$NH(C=O)O), 1.67 – 1.09 (m, 66H, aliphatic). $^{13}$C-NMR (100 MHz, CDCl$_3$, δ): 165.9, 156.5, 135.3, 128.4, 73.5, 72.0-69.1, 67.7, 63.8, 61.7, 59.1, 41.1, 40.4, 29.9, 29.8-29.1, 27.0, 26.8, 26.1.
Supporting information

**Table S1.** Summary of the GPC, DSC and IR data of compounds 4–5.

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<th>Compound</th>
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<th>( M_n^b ) [kg/mol]</th>
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<th>( T_g^c ) [°C]</th>
<th>( T_m^c ) [°C]</th>
<th>( \Delta H ) [J/g]</th>
<th>( \nu(\text{N-H}) ) [cm(^{-1})]</th>
<th>( \nu(\text{amide I}) ) [cm(^{-1})]</th>
<th>( \nu(\text{amide II}) ) [cm(^{-1})]</th>
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\(^a\) Theoretical molecular weight. \(^b\) Determined by GPC in chloroform. \(^c\) Derived from the third heating run (40 K min\(^{-1}\)).

**Figure S5.** UV-Vis absorption spectrum of 1 in water at 20 °C (\( c = 5 \times 10^{-5}\)M, \( l = 1\)cm).
Figure S6. UV-Vis absorption of 4c in water at 20 °C (c_BTA = 5.1 x 10^{-5}M, l = 1cm).

Figure S7. Molar circular dichroism of 4a-c in water as a function of temperature (c_BTA for 4a = 9.6 x 10^{-5}M, 4b = 9.6 x 10^{-5}M, 4c = 6.6 x 10^{-5}M, l = 1cm, λ = 223 nm).