Supplementary Information

Experimental

General
All starting materials were obtained from commercial suppliers and used as received. Thin layer chromatography was performed on Kieselgel F-254 pre-coated silica plates or RP-8 F-254s. Visualization was accomplished with TDM\(^1\). Column chromatography was carried out on Merck silica gel 60 (230-400 mesh ASTM). \(^1\)H-NMR spectra were recorded on a Varian Mercury, 400 MHz. Proton chemical shifts are reported in ppm downfield from tetramethylsilane (TMS). Matrix assisted laser desorption/ionization mass spectra were obtained using DHB (dihydroxybenzoic acid) as the matrix on a Bruker BIFLEX spectrometer. UV/Vis spectra were recorded on a VARIAN Cary 50 Conc spectrometer. CD spectra were recorded on a Jasco J-810 spectropolarimeter equipped with a Jasco PTC-423S/L Peltier type temperature control system. TEM images were obtained with a JEOL- JEM-1010 equipped with a CCD camera. SEM images were created with a Jeol JSM-6330F microscope.

Peptide synthesis
As mentioned in the main text the GANPNAAG peptide was easily prepared by standard solid-phase Fmoc protocols.\(^2\) To suppress side reactions, after introduction of the first asparagine in each deprotection step 0.1M HOBt was added to the 20% piperidine in DMF. The peptides were capped with either Ac\(_2\)O/DiPEA or the appropriate alkanoic acid dissolved in dichloromethane with diisopropylcarbodiimide as a coupling agent. The product was cleaved from the resin by treatment with TFA/H\(_2\)O (95:5) for two hours followed by precipitation in ether or removal of the volatiles. Column chromatography (eluent: CHCl\(_3\)/MeOH/H\(_2\)O 65:25:4) and subsequent lyophilization afforded pure compounds according to \(^1\)H-NMR, Maldi-TOF and TLC.

Data for C\(_{16}\)H\(_{31}\)C(O)-Gly-Ala-Asn-Pro-Asn-Ala-Ala-Gly-OH typical for all compounds prepared:
Yield: 76%, based on Fmoc-Gly loading (0.7 mmol/g) of initial resin.
TLC: R\(_f\) 0.33 (eluent: MeOH/CHCl\(_3\)/AcOH 25:65:10).

\(^1\)H-NMR [DMSO-d6]: \(\delta\) 0.85 (t, CH\(_3\) –alkyl chain, 3H), 1.12 (d, CH\(_3\) –Ala, 3H), 1.20 (m, -CH\(_2\)- alkyl chain; CH\(_3\) –Ala, 30H), 1.48 (m, CH\(_2\)-alkyl chain, 2H), 1.85 (m, CH\(_2\) Pro, 3H), 2.18 (m, CH\(_2\) Pro, \(\alpha\)-CH\(_2\)-alkylsttaart, 3H), 2.40 (m, CH\(_2\) Asn, 2H), 2.55 (dd, CH\(_2\) Asn, 1H), 2.65 (dd, CH\(_2\) Asn, 1H), 3.65 (m, \(\alpha\)-CH\(_2\) Gly; CH\(_2\) Pro, 3H), 3.75 (m, CH\(_2\) Pro; \(\alpha\)-CH\(_2\) Gly, 3H), 4.20 (m, CH\(_2\) Pro; \(\alpha\)-CH\(_2\) Ala, 4H), 4.40 (m, \(\alpha\)-CH\(_2\) Asn, 1H), 4.73 (q, \(\alpha\)-CH\(_2\) Asn, 1H), 6.92 (s, NH\(_2\) Asn, 1H), 7.10 (s, NH\(_2\) Asn, 1H), 7.20 (s, NH\(_2\) Asn, 1H), 7.52 (d, \(\alpha\)-NH Ala, 1H), 7.64 (s, NH\(_2\) Asn,1H), 7.72 (d, \(\alpha\)-NH Ala,1H), 7.88 (two d, \(\alpha\)-NH Asn; \(\alpha\)-NH Ala, 2H), 7.96 (broad s, \(\alpha\)-NH Gly, 2H), 8.27 (d, \(\alpha\)-NH Asn, 1H), 12.45 (broad s, OH, 1H).
Maldi-TOF: Calcd. for [C_{42}H_{72}N_{10}O_{12} + Na]^+ 931.5, found 931.2.

**TLC:**
From left to right: crude (i.e. obtained from resin after cleavage) product of C_6, C_{10}, C_{12}, C_{14} and C_{16}-GANPNAAG-OH on silica stained with TDM, eluent MeOH/CHCl_3/AcOH 25:65:10.

**Sample preparation:**
Aggregates were obtained by the addition of water to the appropriate peptide amphiphile to obtain a concentration of 1.0 mg/mL. These solutions were left hydrating at 50 °C for 45 minutes followed by 15 minutes of sonication at that temperature. After cooling to room temperature the samples were diluted to their final concentration of 0.2 mg/mL. These samples were found to be stable for at least four weeks as evidenced by the reproducibility of their CD spectra. In the dilution study, of which the graphs can be found in this supplementary material, the aggregates were sonicated after dilution to their final concentration and their CD spectra measured immediately.

**CD spectrometry:**
All samples were measured at a concentration of 0.2 mg/mL in a cell with a 1 mm light path. Spectra were recorded with the following settings: speed: 50 nm/min, response time: 2 sec, bandwidth: 1nm, data pitch: 0.5 nm, sensitivity: 1000 mdegrees. Temperature curves were measured at 196 nm at a speed of 1 or 3 K/min.

**Electron microscopy (EM):**
Samples for transmission EM were prepared by floating a carbon-coated copper grid on a drop of sample for 5 minutes followed by blotting off the remaining solvent with filter paper and drying in
vacuo. The dried grids were platinum shadowed at an angle of approximately 45 degrees. The microscope was set on an accelerating voltage of 60 kV.

Samples for cryo-SEM were prepared by fracturing at -140 °C a rapidly frozen solution containing peptide amphiphile, subsequent sublimation at -95 °C for 2-5 minutes followed by deposition of a thin layer of gold-palladium at -140 °C. The probe voltage was set at 3.0 kV.
Additional CD spectra of the Cₙ-GANPNAAG-OH compounds at various temperatures and their concentration dependence.

**Ac**: left: at 4 and 90 °C  
right: elipticity at 196 nm at different temperatures

**C₆**: left: at 4 and 90 °C  
right: elipticity at 196 nm at different temperatures

**C₁₂**: left at 4 and 90 °C  
right: elipticity at 196 nm at different temperatures

**C₁₄**: left at 4 and 90 °C  
right: elipticity at 196 nm at different temperatures
C_{16}: elipticity at 196 nm at different temperatures

C_{18}: left: at 4 and 90 °C
right: elipticity at 196 nm at different temperatures

C_{18}: left: initially formed aggregates
right: after heating to 90 °C and cooling to 20 °C.

C_{16}: left: initially formed aggregates
right: after heating to 90 °C and cooling to 20 °C.