Electronic Supplementary Information

All reagents were purchased from commercial sources at the highest purity and were used as supplied, unless stated otherwise in the experimental procedures.

Experimental procedures

Formation of gel in anaerobic conditions

Fmoc-cysteine **2** (0.0137 g, 0.04 mmol), phenylalanine methyl ester hydrochloride salt **1** (0.0345 g, 0.16 mmol), thermolysin (0.001 g) and ascorbic acid (0.007 g, 0.04 mmol) were dissolved in 2 ml of 0.1 M phosphate buffer (pH = 8). The solution was immediately degassed with nitrogen, by bubbling the gas through the solution in a sonicating bath. The solution was left to gel over a period of 16 h in nitrogen atmosphere.

The same reaction was repeated in oxidizing conditions without the addition of ascorbic acid and without the use of nitrogen.

HPLC

A Dionex P680 HPLC system equipped with a Macherey-Nagel C18 column of 250 mm length, 4.6 mm internal diameter and 5mm particle size was used to analyze the mixtures of peptide derivatives. The gradient used was a linear exchange between 40% methanol in water at 4 min to 100% methanol at 31 min using a flow rate of 0.7 ml/min. Sample preparation involved mixing 20µl of gel with methanol/water (1.5 ml, 50:50 v/v mixture) containing 0.1% trifluoroacetic acid.

Fluorescence spectroscopy

Fluorescence emission spectra were measured on a Jasco FP-6500 spectrofluorometer with light measured orthogonally to the excitation light, with excitation at 295 nm and emission data range between 300 and 600 nm.

Transmission electron microscopy

Carbon-coated copper grids (200 mesh) were glow discharged in air for 30 seconds. A small volume of the gel was transferred onto the support film and dried down using filter paper. 20 µl of the negative stain (1% aqueous methylamine vanadate was obtained from Nanovan; Nanoprobes) was applied and the mixture dried down again using filter paper to remove excess. The dried specimens were then imaged using a LEO 912 energy filtering transmission electron microscope operating at 120 kV fitted with 14bit/2K Proscan CCD camera.

Molecular modelling

Models were constructed using the HyperChem program. The Amber force field was used to energy minimize the structures formed in this program.

HPLC raw data

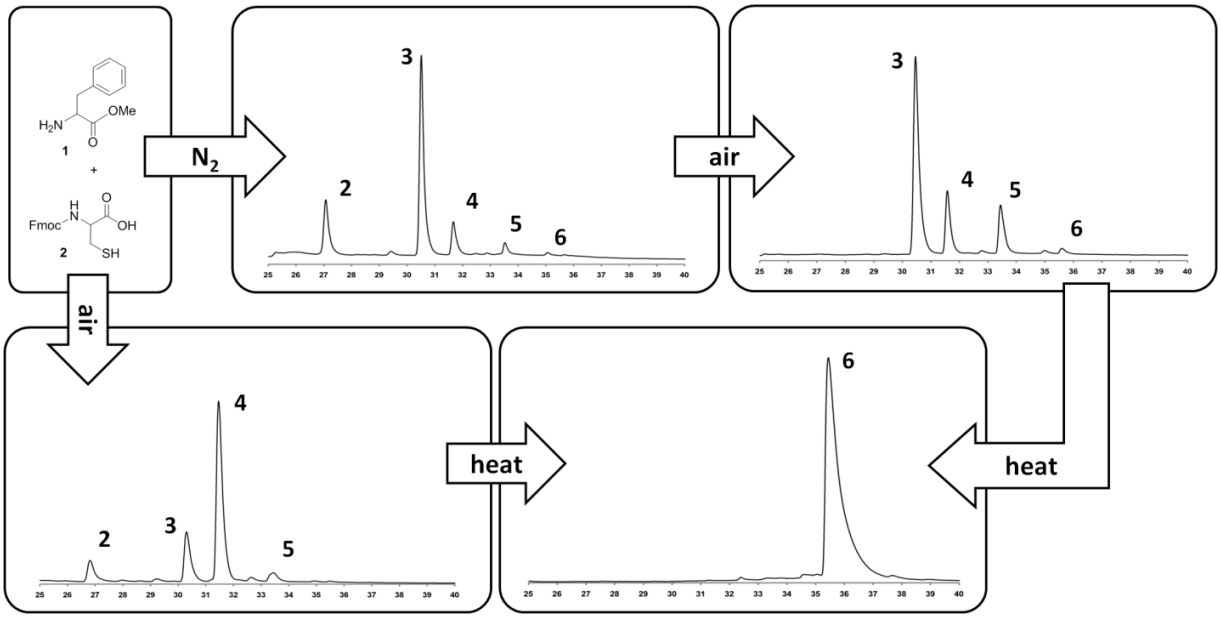

Figure S1. Figure 2 (in text) with the raw HPLC data presented.

FTIR spectroscopy

The instrument was a mains powered ML with ATR diamond press A2 technologies model with an instrumental footprint of 8 inches by 8 inches. No sample prep was required as the instrument was factory calibrated with NIST polystyrene. The sample was run at 128 background scans and at 128 sample scans at a resolution of 4 cm^{-1} which equates to a individual data point about every 2 cm^{-1} together with Happ Genzel apodisation and Mertz phase correction.

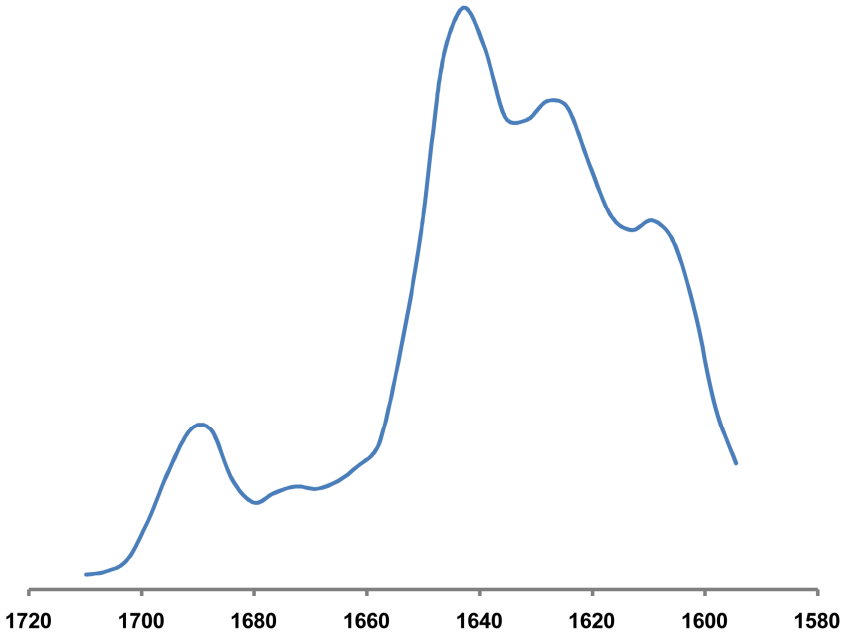

Figure S2. FTIR spectrum of the dried sample of the gel showing peaks at 1640 and 1690 cm^{-1} that are characteristic of the anti-parallel β-sheet arrangement.

Preparation of disulfide 6.

The hydrogel formed in anaerobic conditions from Fmoc-cysteine **2** (0.0137 g, 0.04 mmol), phenylalanine methyl ester hydrochloride salt **1** (0.0345 g, 0.16 mmol), thermolysin (0.001 g) and ascorbic acid (0.007 g, 0.04 mmol) dissolved in 2 ml of 0.1 M phosphate buffer (pH = 8) was heated to 105 °C for 24 h in an oil bath. The formed precipitate was filtered and washed with hot ethanol. The desired compound was obtained as a white powder (0.04 g, 99 %).

M.p. = decomposes at 280 °C; ^{1}H NMR (400.1 MHz, [D_6]DMSO, 25°C): = 7.87 (d, ^{3}J(H,H) = 7 Hz, 2H; ArH), 7.74-7.66 (m, 4H; ArH), 7.42-7.34 (m, 4H; ArH), 7.32-7.12 (m, 16H; ArH), 4.49-4.41 (m, 2H; CH), 4.36-4.15 (m, 4H; CH), 3.55 (s, 6H; CH_3), 3.18-2.92 (m, 8H; CH_2), 2.90-2.79 (m, 4H; CH_2); ^{13}C NMR (100.1 MHz, [D_6]DMSO, 25°C): = 174.4, 171.6, 170.3, 169.9, 155.9, 143.7, 140.6, 137.4, 136.9, 129.4, 129.3, 129.1, 128.3, 128.2, 128.0, 127.6, 127.1, 126.5, 126.4, 126.1, 125.3, 125.2, 120.1, 65.9, 60.5, 55.2, 53.7, 51.8, 46.5, 37.9, 36.7, 36.4; MS (ES+): *m*/*z* (%): 1030 (100) [M+Na^+]. HRMS (ES+): calculated for $C_{56}H_{55}O_{10}N_4S_2$ [M^+] 1007.3354, found 1007.3349.