

## 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. Fmoc-FpY **1** was purchased from CS Bio Co. and the phosphatase (alkaline bovine) from Sigma – lot nr. 118K1394.

### Experimental procedures

#### Formation of gel

A 10 mM hydrogel was formed by dissolving **1** (12.6 mg) in 1 ml of 0.6 M phosphate buffer at pH 7.5 and the addition of 50 U of alkaline phosphatase produced a self-supporting gel of **2** after 90 minutes.

#### 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% acetonitrile in water at 4 min to 100% acetonitrile at 31 min using a flow rate of 0.7 ml/min and detection wavelength of 301 nm. Sample preparation involved mixing 20  $\mu$ l of gel with acetonitrile/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.

#### Determination of Critical Micelle Concentration

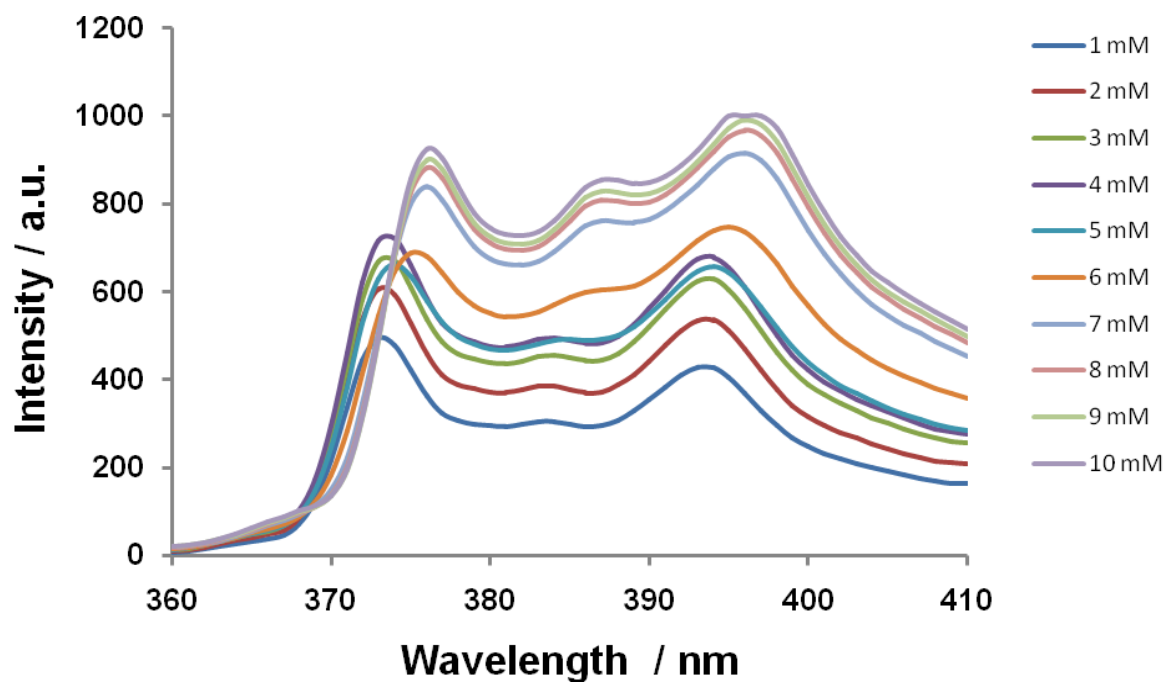
A stock solution of pyrene was prepared by dissolving 2.5 mg of pyrene in 5 ml of methanol; this was then used to prepare a solution 20 times more dilute (250  $\mu$ l in 5 ml of methanol). 50  $\mu$ l of the diluted pyrene solution was added to each of the ten different concentrations of **1**. These samples were excited at 334 nm in a fluorometer with slit widths set to 10 and 3 nm. The ratio of the first and third peak  $\lambda_{\text{max}}$  values was plotted against concentration to determine the critical micelle concentration.

#### Dynamic Light Scattering

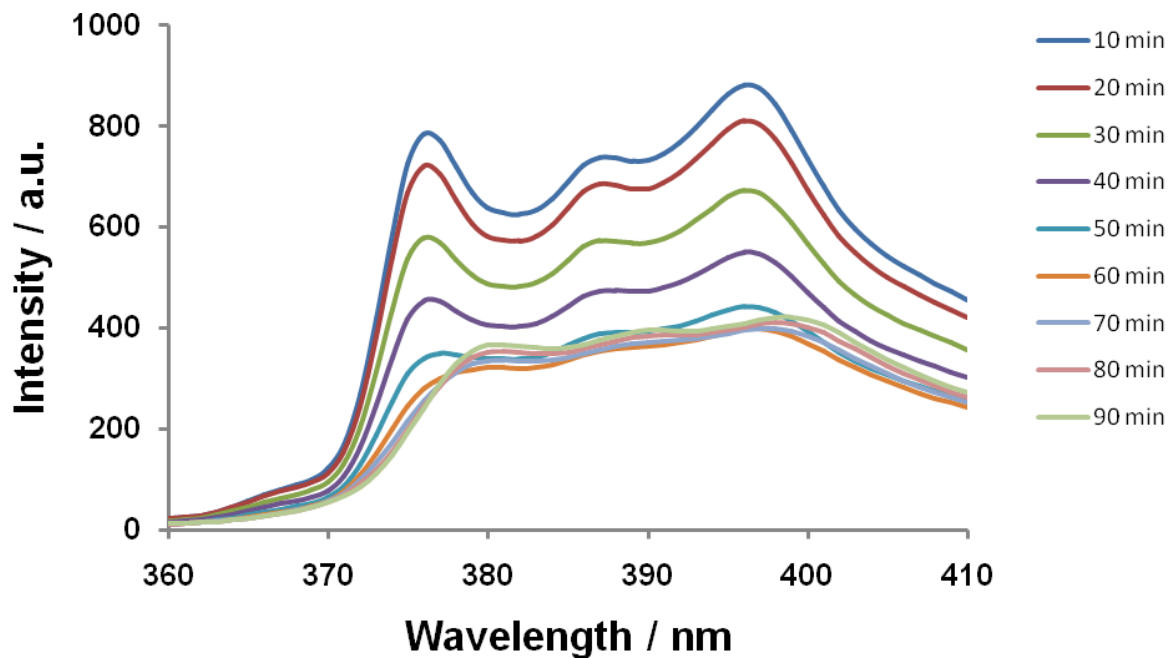
DLS was performed on an AVL/LSE-5004 light scattering electronics and multiple tau digital correlator. Solutions of 1, 5 and 10 mM concentrations of **1** were filtered, using a 0.2  $\mu$ m syringe filter, into glass tubes and analyzed using a DLS instrument at a temperature of 295 K, with an angle of 90° and wavelength of 632 nm.

#### Circular Dichroism

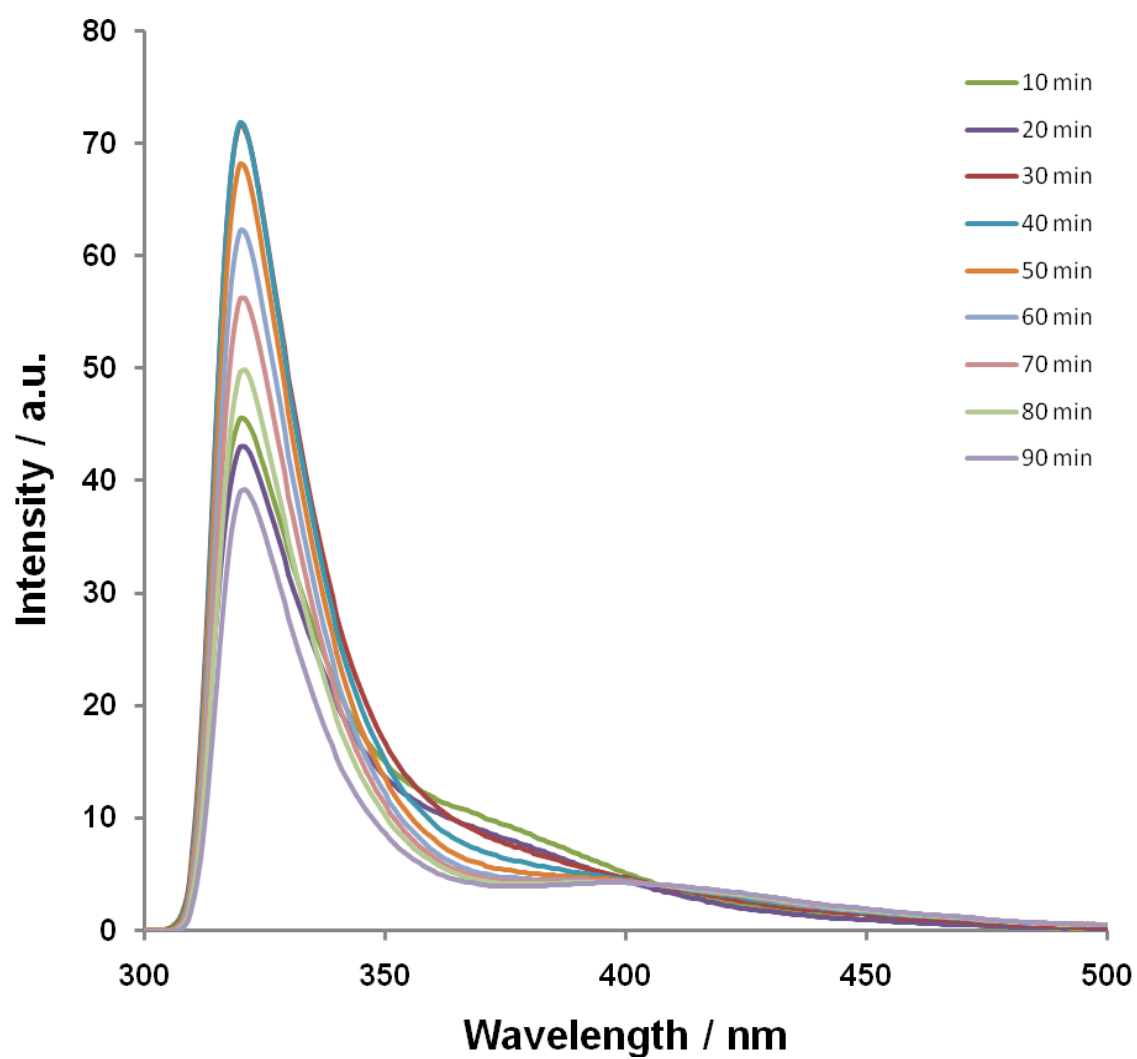
A 10 mM solution of **1** with phosphatase was placed in a 0.2 mm pathway quartz cuvette and the spectra were collected on a Jasco J-600 spectropolarimeter in a data range between 340 nm and 185 nm. Resolution and bandwidth were 1 nm with 50 mdeg sensitivity and 50 nm/min speed.



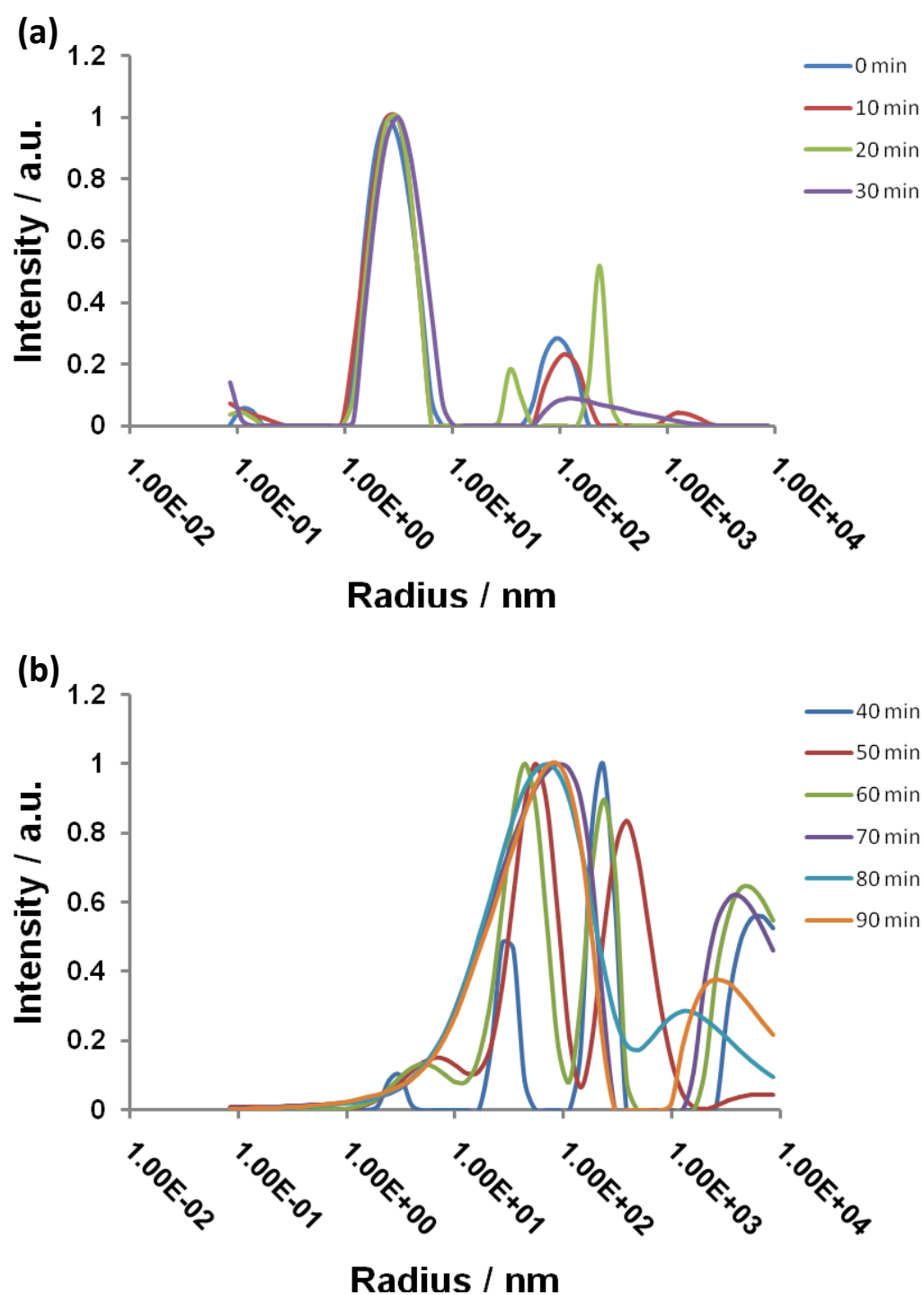
**Figure S1.** Pyrene fluorescence emission spectra (exc. wavelength = 334 nm) recorded for different concentrations of **1** in order to determine its critical micelle concentration.



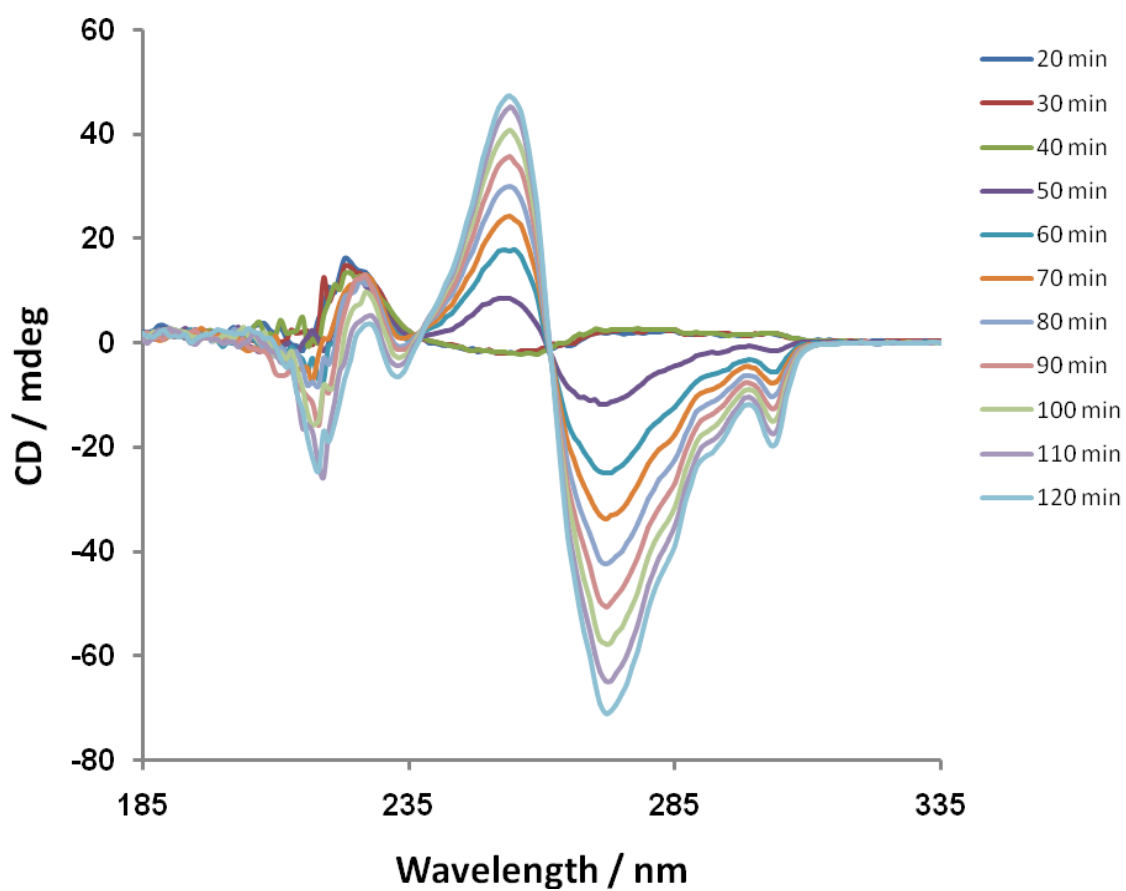
**Figure S2.** Pyrene fluorescence emission spectra (exc. wavelength = 334 nm) recorded at different time points of the reaction of **1** with alkaline phosphatase.



**Figure S3.** Fluorescence emission spectra (exc. wavelength = 295 nm) recorded at different time points of the reaction of **1** with alkaline phosphatase.



**Figure S4.** Dynamic light scattering data recorded at different time points of the reaction of **1** with alkaline phosphatase. For the first 30 min (a) a constant peak with a mean radius of 2.5-3 nm is observed. At 40 min (b) the data becomes erratic.



**Figure S5.** Circular dichroism data recorded at different time points of the reaction of **1** with alkaline phosphatase. An induction of chirality is observed at 50 min and beyond.