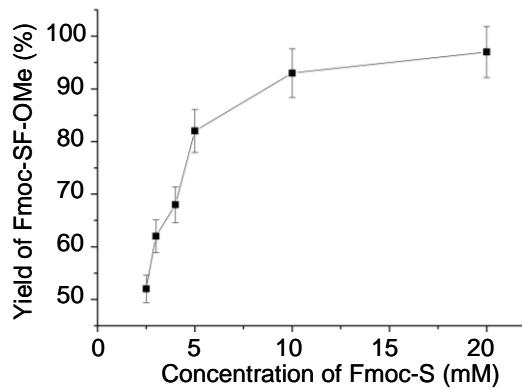


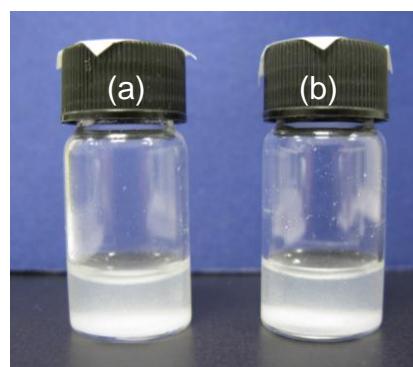
# Biocatalytic Self-Assembly of 2D Peptide-Based Nanostructures

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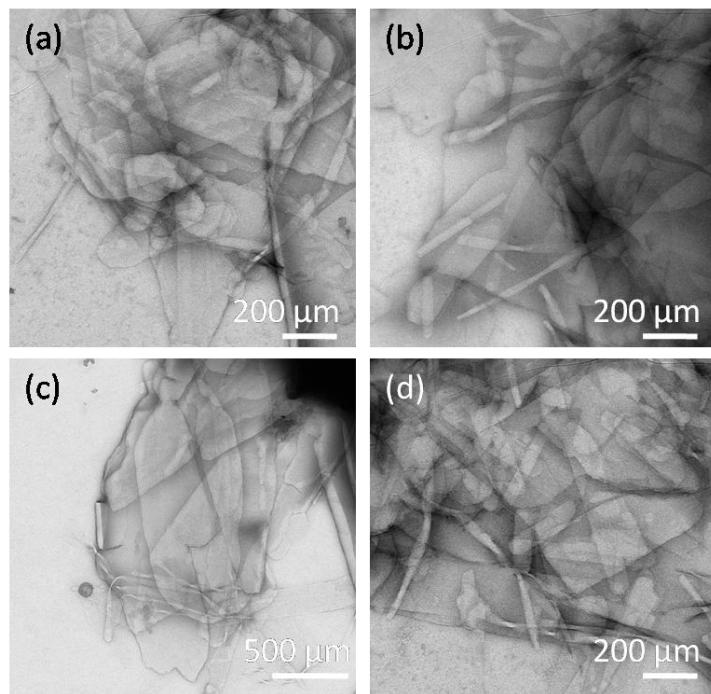
## Supplementary Information



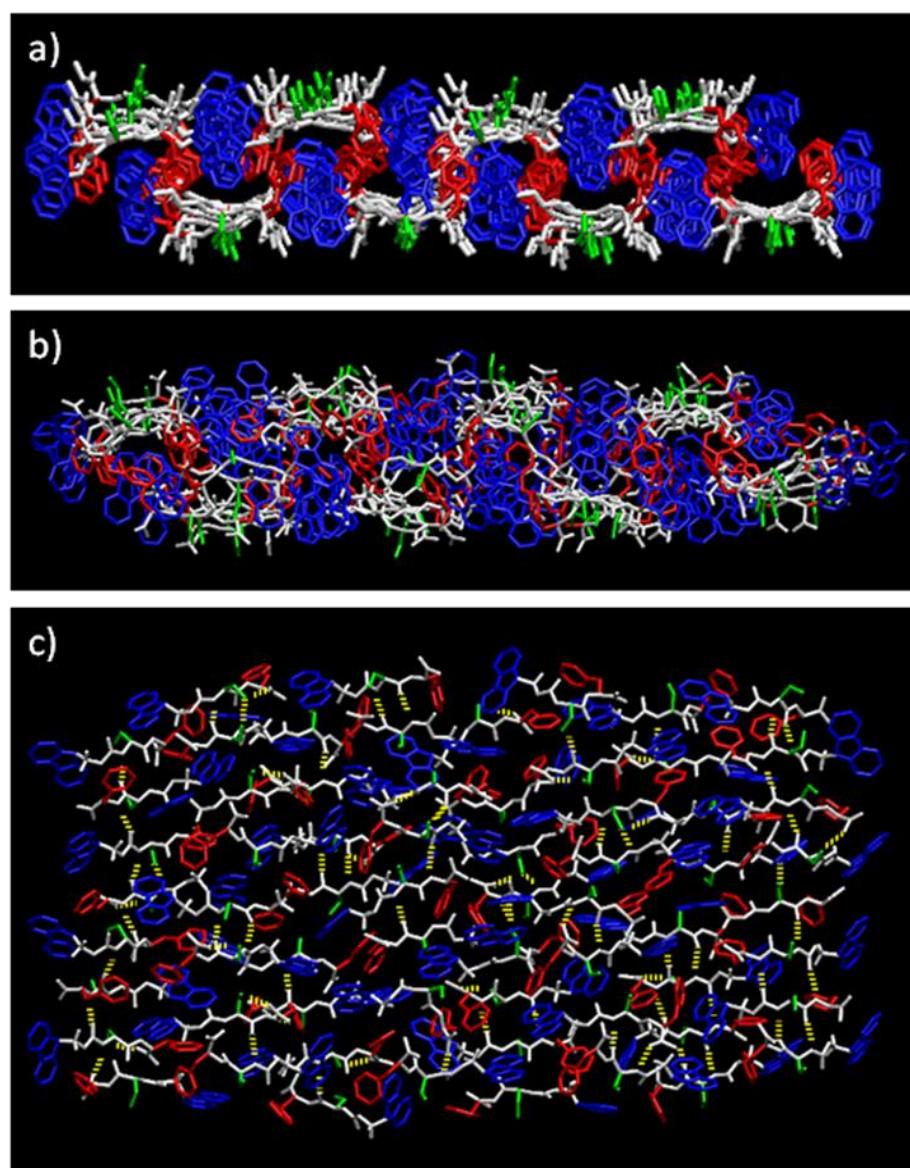
**Figure S1** – The relationship between concentration of Fmoc-S reactant used and the percentage yield of the desired aromatic peptide amphiphile Fmoc-SF-OMe; lower concentration of starting materials leads to lower product yields. Percentage yield calculated using HPLC method at 100 hours after the reaction was initiated.



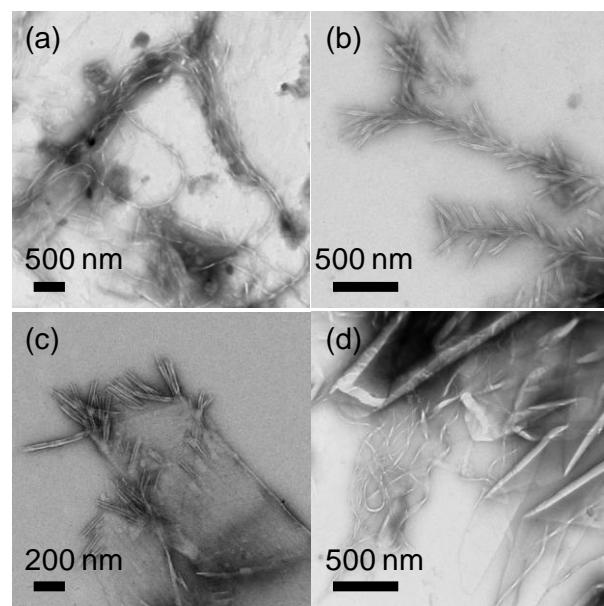
**Figure S2** – Synthesised Fmoc-SF-OMe (a), or a mixture of synthesised Fmoc-SF-OMe and F-OMe (b), forms a white precipitate in the aqueous buffer. Images taken after 24 hours.



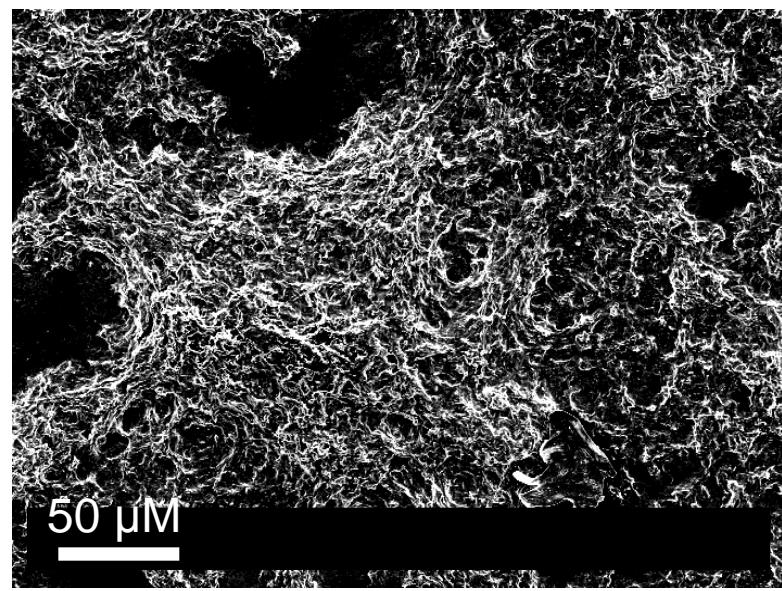
**Figure S3** – (a-d) Transmission Electron Microscopy (TEM) images of the nanoscale structure of Fmoc-SF-OMe after 72 hours.



**Figure S4** - Fmoc-SF-OMe 64mer model: Blue: fluorenyl groups. White: peptide backbone. Red: phenylalanine side chains. Green: serine side chains. Hydrogens not shown for clarity. (a) Side view of starting structure. (b) Side view of structure minimized for 50000 steps. (c) Top view of minimized structure. Dotted yellow lines indicate hydrogen bonds with  $d < 3.4 \text{ \AA}$  and donor-acceptor angle  $< 25^\circ$ .



**Figure S5** - Transmission Electron Microscopy (TEM) images of the polymorphic nanoscale structure of Fmoc-SF-OMe. Twisted ribbons, branched twisted ribbons, frayed sheets, and developed nanosheets can be observed from (a-d) respectively. (a) 1 hour, (b,c) 24 hours, (d) 72 hours.

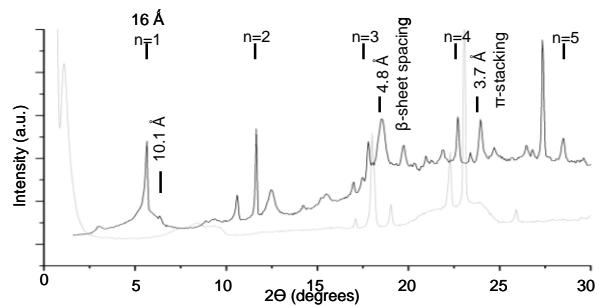


**Figure S6** – SEM image of self-assembled Fmoc-SF-OMe formed in the presence of 0.1 mg/mL *thermolysin*. At this low enzyme concentration only lamellar structures can be seen.



**Figure S7** – schematic of synthesis of Fmoc-SF-OMe. 98 % purity and 21 % yield.

**Characterisation of Fmoc-SF-OMe** – MS (ES+);  $m/z$  488.93  $[M + H]^+$ . Elemental analysis for C<sub>28</sub>H<sub>28</sub>N<sub>2</sub>O<sub>6</sub>: expected C: 68.8 %, H: 5.8 %, N: 5.7 %; found C: 67.3 %, H: 5.8 %, N: 6.4 %.



**Figure S8** - WAXS data of dried sample (black spectrum), peaks arising from *thermolysin* and buffer are shown on the grey spectrum. A full list of the peaks obtained from the sample is listed in Table S1.

Pos. [°2Th.]	Height [cts]	d-spacing [Å]	Rel. Int. [%]
5.5062	9775.04	16.05037	56.35
6.3251	1373.21	13.97411	7.92
8.787	1643.19	10.06366	9.47
9.2575	1351.81	9.55325	7.79
10.4535	4897.91	8.4628	28.23
11.5015	12757.21	7.69388	73.54
12.2759	3561.21	7.21025	20.53
14.0998	2740.14	6.28138	15.8
14.6678	4452.38	6.03941	25.67
15.0995	3424.75	5.8677	19.74
15.3937	3619.05	5.75618	20.86
16.8641	6225.87	5.25749	35.89
17.3514	5812.7	5.11091	33.51
17.7115	10334.59	5.0078	59.58
18.5026	11496.66	4.79543	66.27
19.6172	10429.08	4.52541	60.12
20.2073	7085.78	4.39457	40.85
20.8544	7385.07	4.25965	42.57
21.2134	8268.76	4.18836	47.67
21.7761	9409.22	4.08139	54.24
22.6011	17346.95	3.93424	100
23.278	8637.41	3.82135	49.79
23.8425	13521.52	3.73213	77.95
24.5952	9923.61	3.6196	57.21
25.6305	7435.01	3.47569	42.86
26.05	8696.26	3.42067	50.13
26.368	10846.1	3.38014	62.52
26.6832	9078.57	3.34091	52.34
27.2791	10518.58	3.26928	60.64
27.5877	8336.17	3.23339	48.06
28.388	11527.59	3.14405	66.45
29.4886	7993.81	3.02915	46.08

Table S1 – full list of peaks obtained for WAXS of dried sample.