Supporting Information

Unzipping the Role of Chirality in Nanoscale Self-Assembly of Tripeptide Hydrogels

Silvia Marchesan,[a] Lynne Waddington,[a] Christopher D. Easton,[a] David A. Winkler,[a, b] Liz Goodall,[a] John Forsythe,[c] and Patrick G. Hartley[a]*

a. CSIRO Materials Science and Engineering, Bayview Avenue, Clayton VIC 3168, Australia.

b. Monash Institute of Pharmaceutical Sciences, 384 Royal Pde. Parkville 3052, Australia.

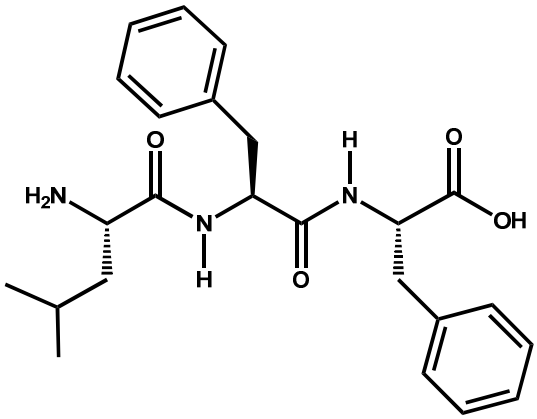
c. Monash University, Department of Materials Engineering, PO Box 69M, VIC 3800, Australia.

*Silvia.Marchesan@csiro.au

Supporting Information Table of Contents

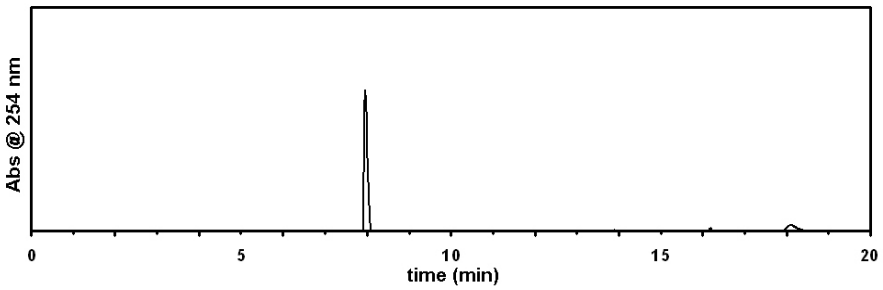
I – Analytical Characterization of Peptides

a. L-Leu-L-Phe-L-Phe

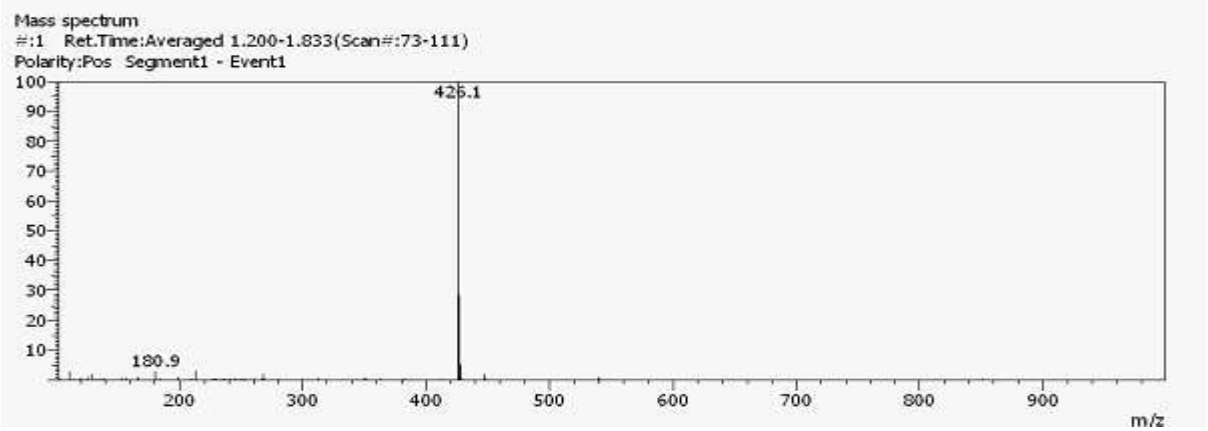


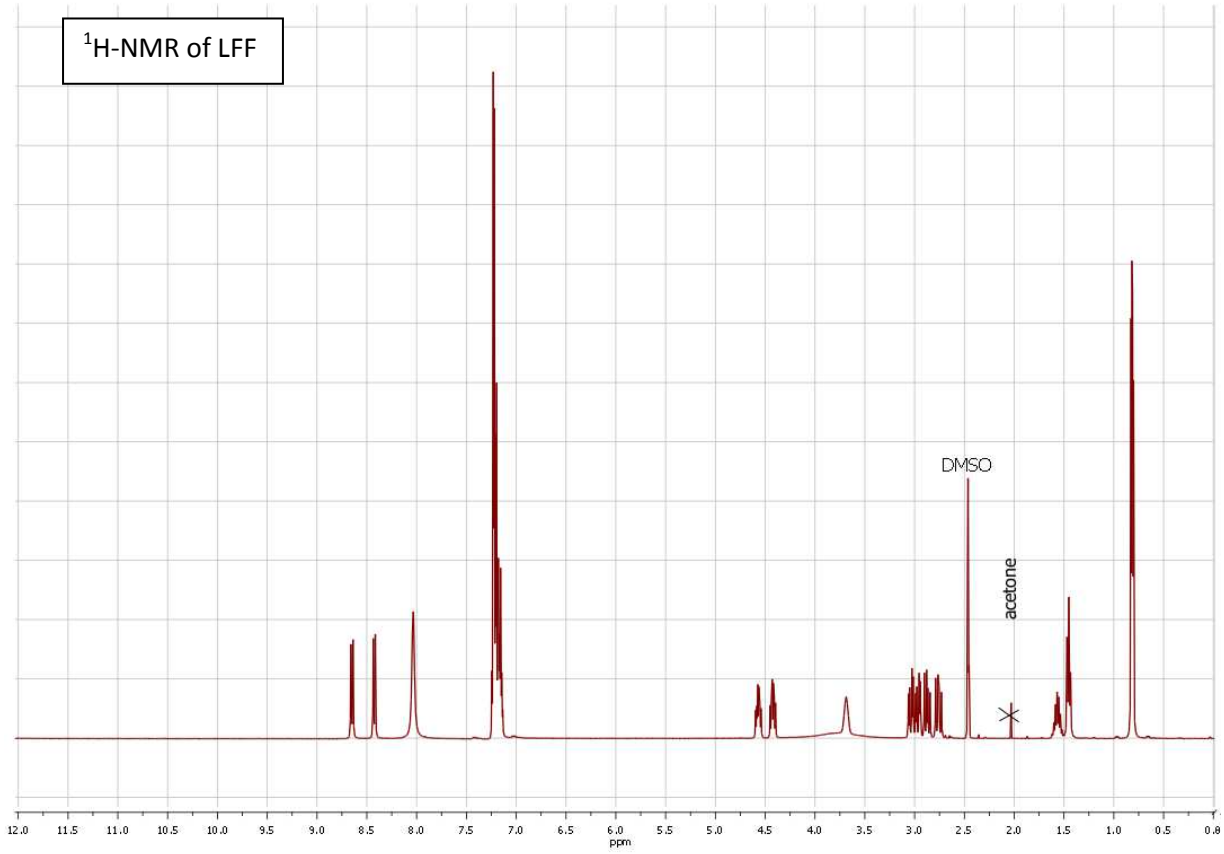
^{1}H-NMR (400 MHz, DMSO, TMS): δ 8.65 (d, *J* = 8 Hz, 1H, NH), 8.42 (d, *J* = 8 Hz, 1H, NH), 8.03 (s (br), 3H, NH_3^+), 7.23-7.14 (m, 10H, Ar), 4.55 (ddd, *J* = 4 Hz, 8 Hz, 8 Hz, 1H, αCH), 4.42 (ddd, *J* = 4 Hz, 8 Hz, 8 Hz, 1H, αCH), 3.69 (m, 1H, αCH), 3.04 (dd, *J* = 8 Hz, *Jgem* = - 14 Hz, 1H, βCH_2), 2.95 (dd, *J* = 8 Hz, *Jgem* = - 14 Hz, 1H, βCH_2), 2.88 (dd, *J* = 10 Hz, *Jgem* = - 14 Hz, 1H, βCH_2), 2.76 (dd, *J* = 10 Hz, *Jgem* = - 14 Hz, 1H, βCH_2), 1.57 (m, 1H, γCH), 1.45 (m, 2H, βCH_2), 0.83 (d, *J* = 4 Hz, 3H, CH_3), 0.81 (d, *J* = 4 Hz, 3H, CH_3). ^{13}C-NMR (100MHz, DMSO, TMS): δ (ppm) 173.1, 171.1, 169.4 (3 x CO); 137.8 (1C), 129.6 (2C), 129.5 (2C), 128.6 (2C), 128.5 (2C), 126.9 (1C), 126.8 (1C), (10 x Ar); 54.6, 53.9, 51.1 (3 x αC); 40.6 (1 x CH); 39.2, 37.1 (2 x βCH_2); 23.8, 23.3, 21.9 (γCH, 2 x CH_3). ESI-MS: m/z 426.1 $(M+H)^+$ $C_{24}H_{31}N_3O_4$ requires 426.2.

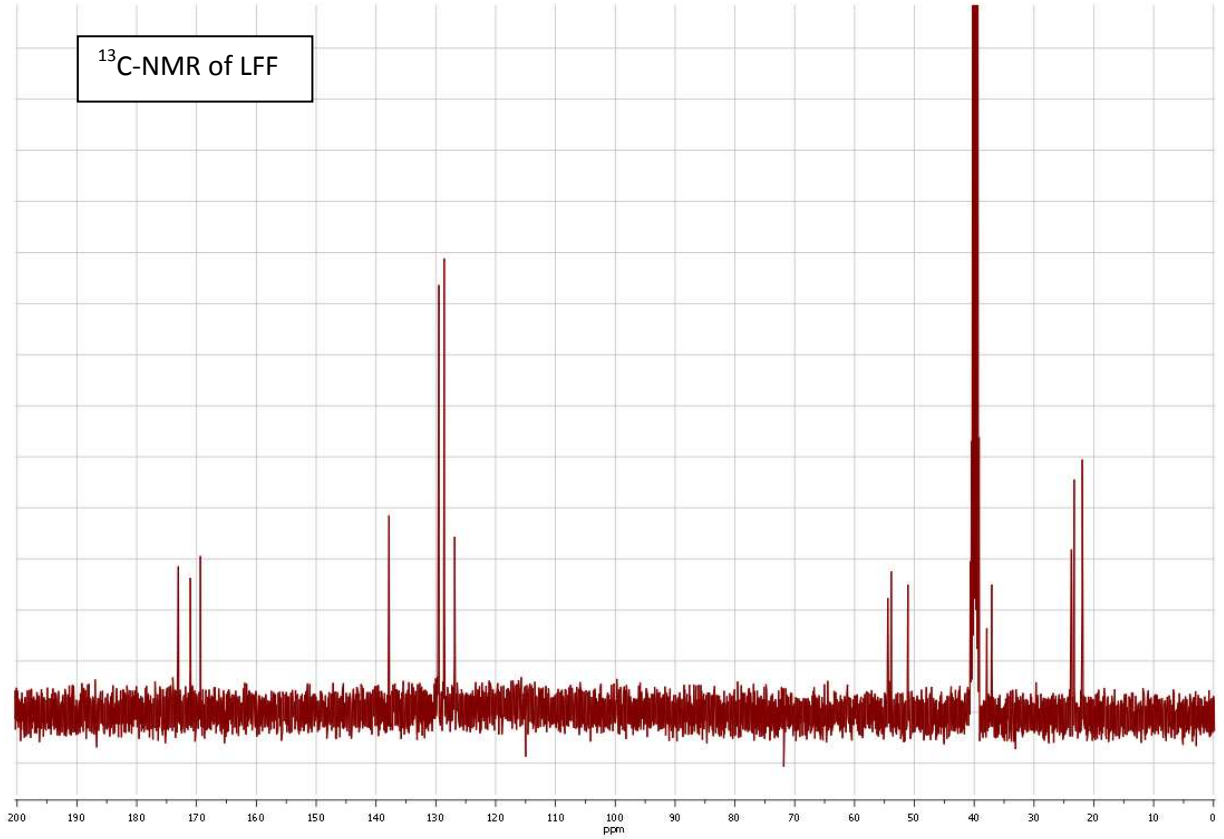
HPLC



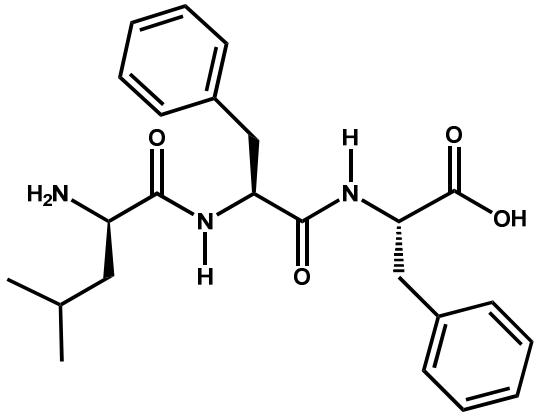
ESI-MS





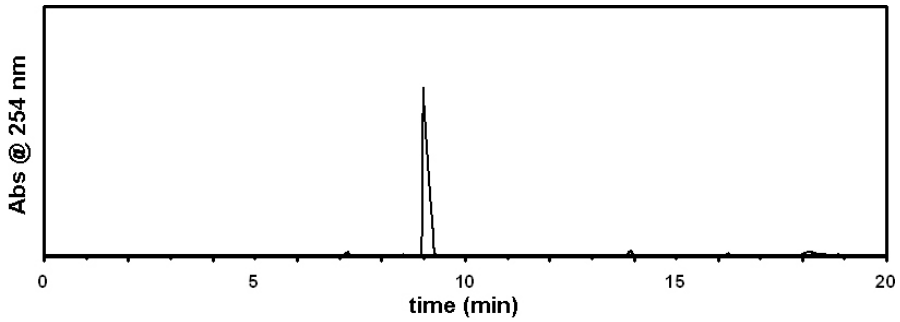


b. D-Leu-L-Phe-L-Phe

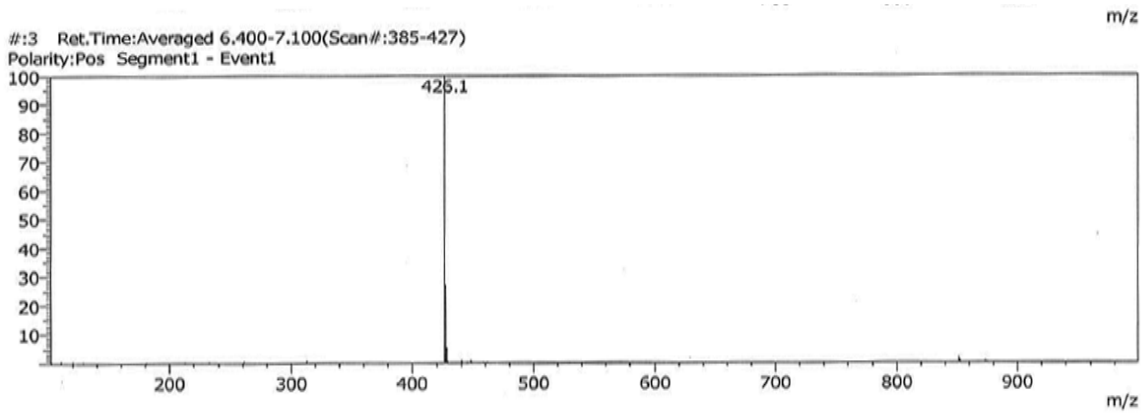


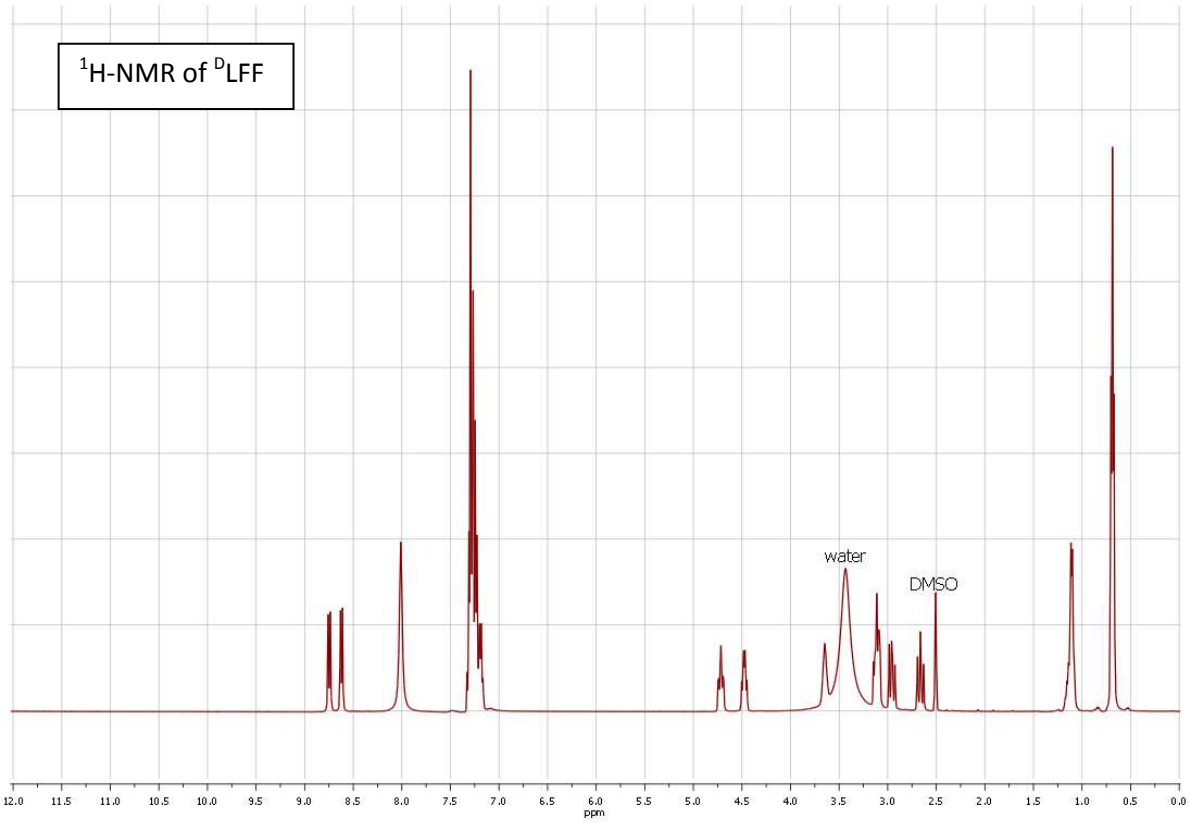
^{1}H-NMR (400 MHz, DMSO, TMS): δ (ppm) 8.69 (d, *J* = 8 Hz, 1H, NH), 8.56 (d, *J* = 8 Hz, 1H, NH) 7.95 (s (br), 3H, NH3+), 7.27-7.12(m, 10H, Ar), 4.66 (m, 1H, αCH), 4.42 (m, 1H, αCH), 3.59 (m, 1H, αCH), 3.08-3.03 (m, 2H, βCH_2), 2.90 (dd, *J* = 8 Hz, *Jgem* = -12 Hz, 1H, βCH_2), 2.60 (dd, *Jgem* = -12 Hz, 2H, βCH_2), 1.13-0.99 (m, 3H, γCH, βCH_2), 0.63 (d, *J* = 6 Hz, 3H, CH_3), 0.62 (d, *J* = 6 Hz, 3H, CH_3). ^{13}C-NMR (100MHz, DMSO, TMS): δ (ppm) 173.2, 171.6, 169.1 (3 x CO); 138.0 (1C), 129.8 (2C), 129.6 (2C), 128.7 (2C), 128.4 (2C), 127.0 (1C) (10 x Ar); 54.2, 54.1, 51.1 (3 x αC); 40.7 (1 x CH); 38.6, 37.0 (2 x βCH_2); 23.6, 22.9, 22.2 (γCH, 2 x CH_3). ESI-MS: m/z 426.1 $(M+H)^+$ $C_{24}H_{31}N_3O_4$ requires 426.2.

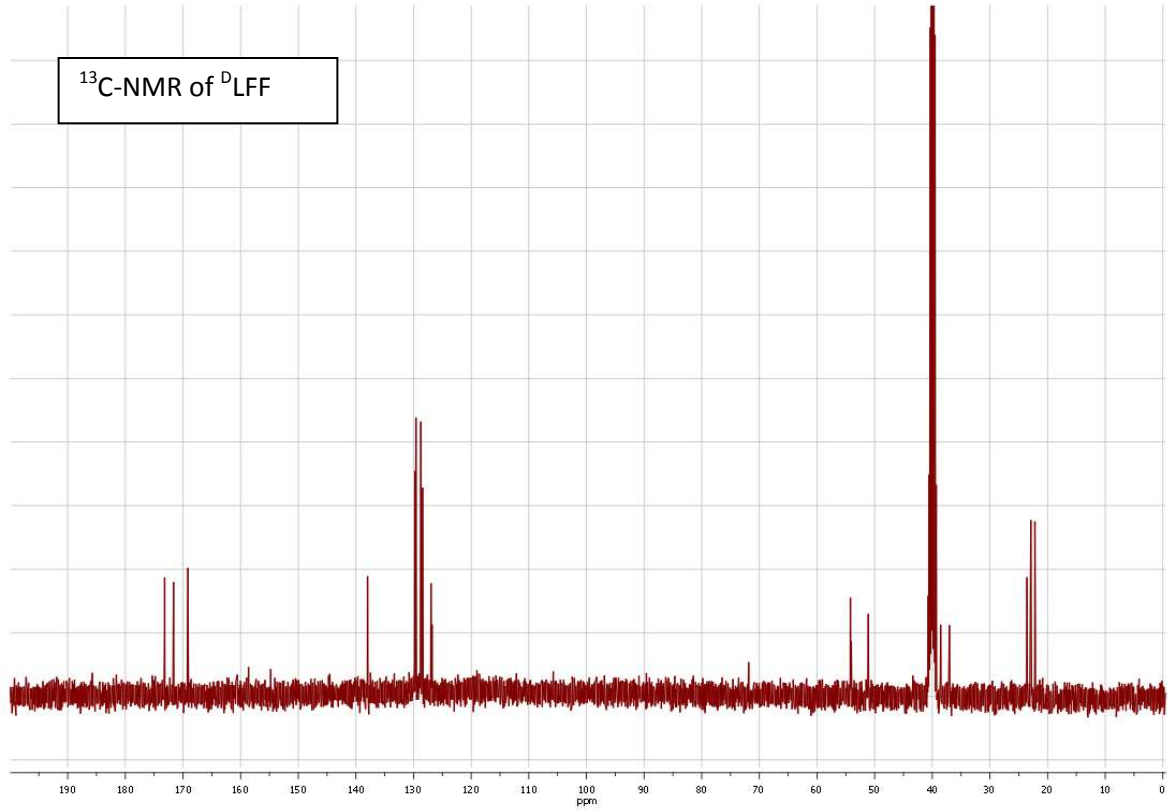
HPLC



ESI-MS

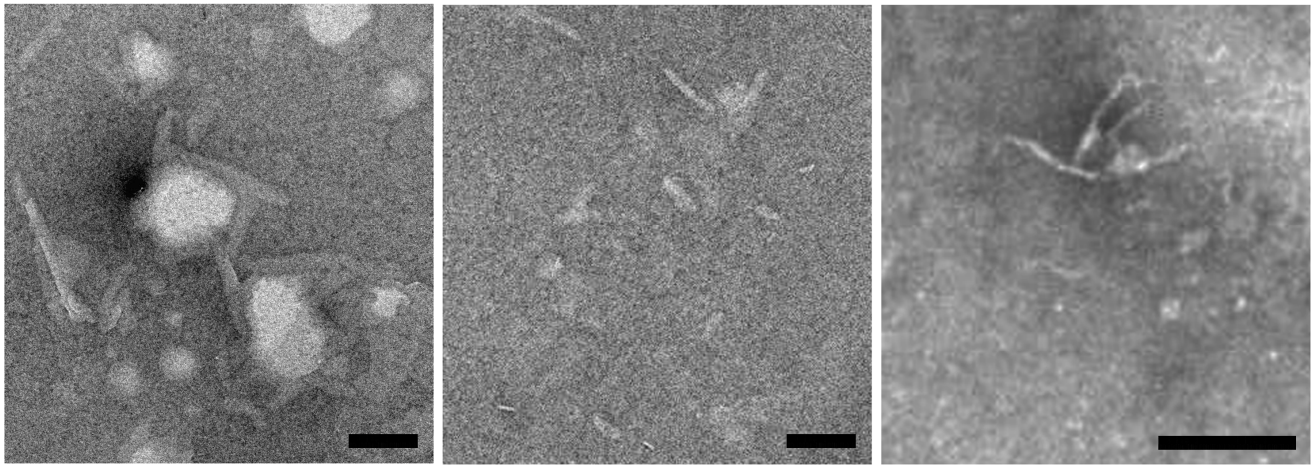






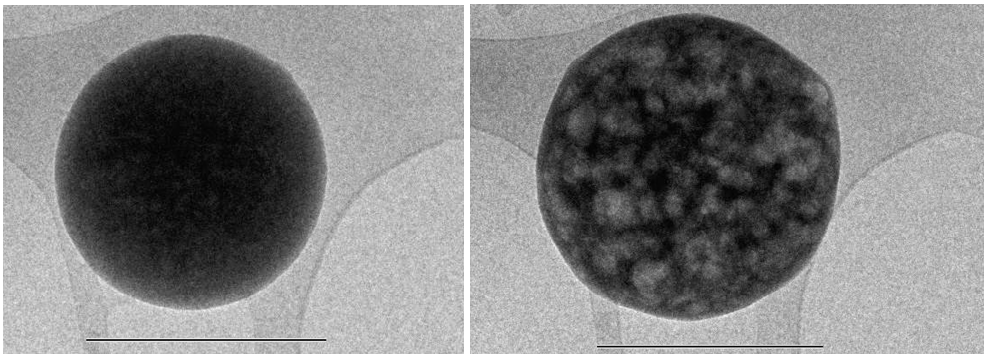
II- TEM images with negative staining displaying ^{D}LFF short fibers originating from globular structures.

Scale bar = 200 nm.

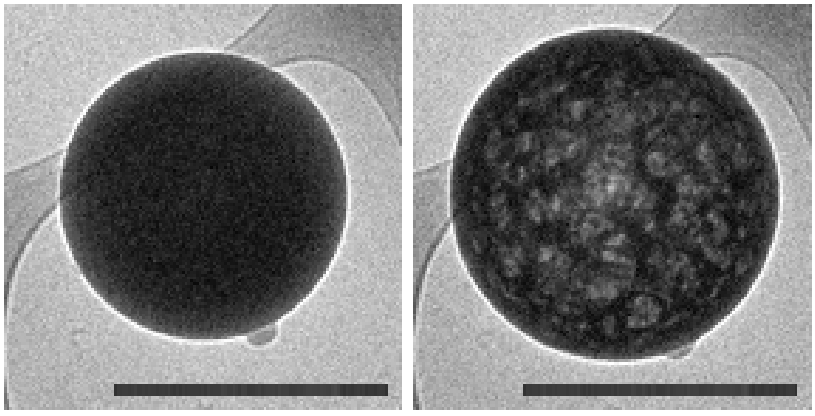


Cryo-TEM images of ^{D}LFF displaying how a globule responds to laser radiation damage just before disappearance.

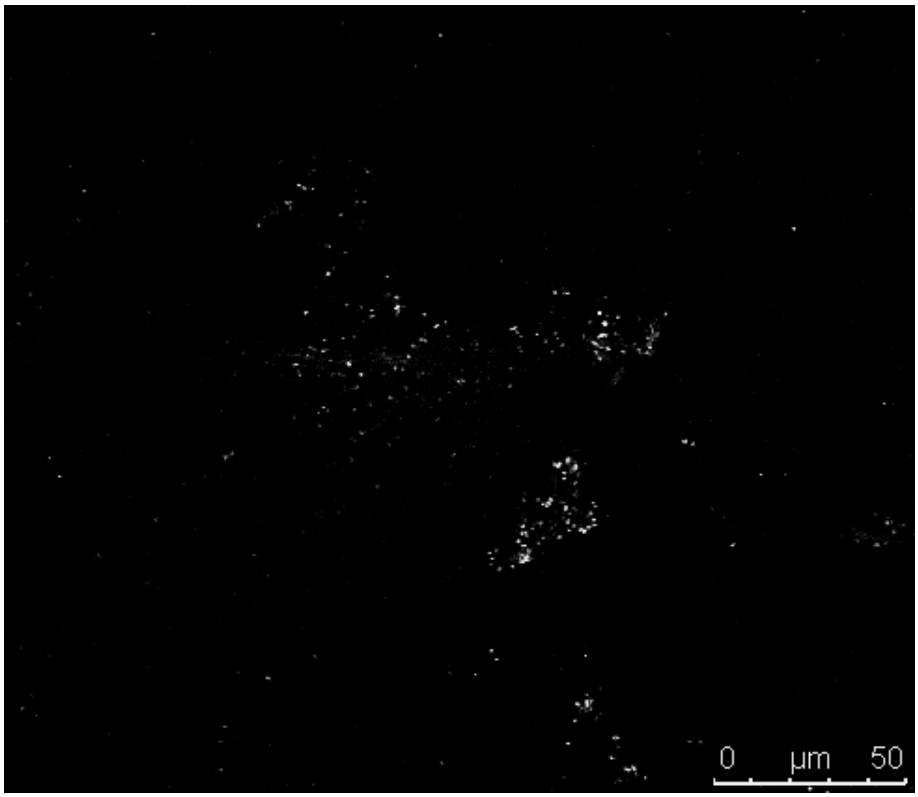
Scale bar = 500 nm.



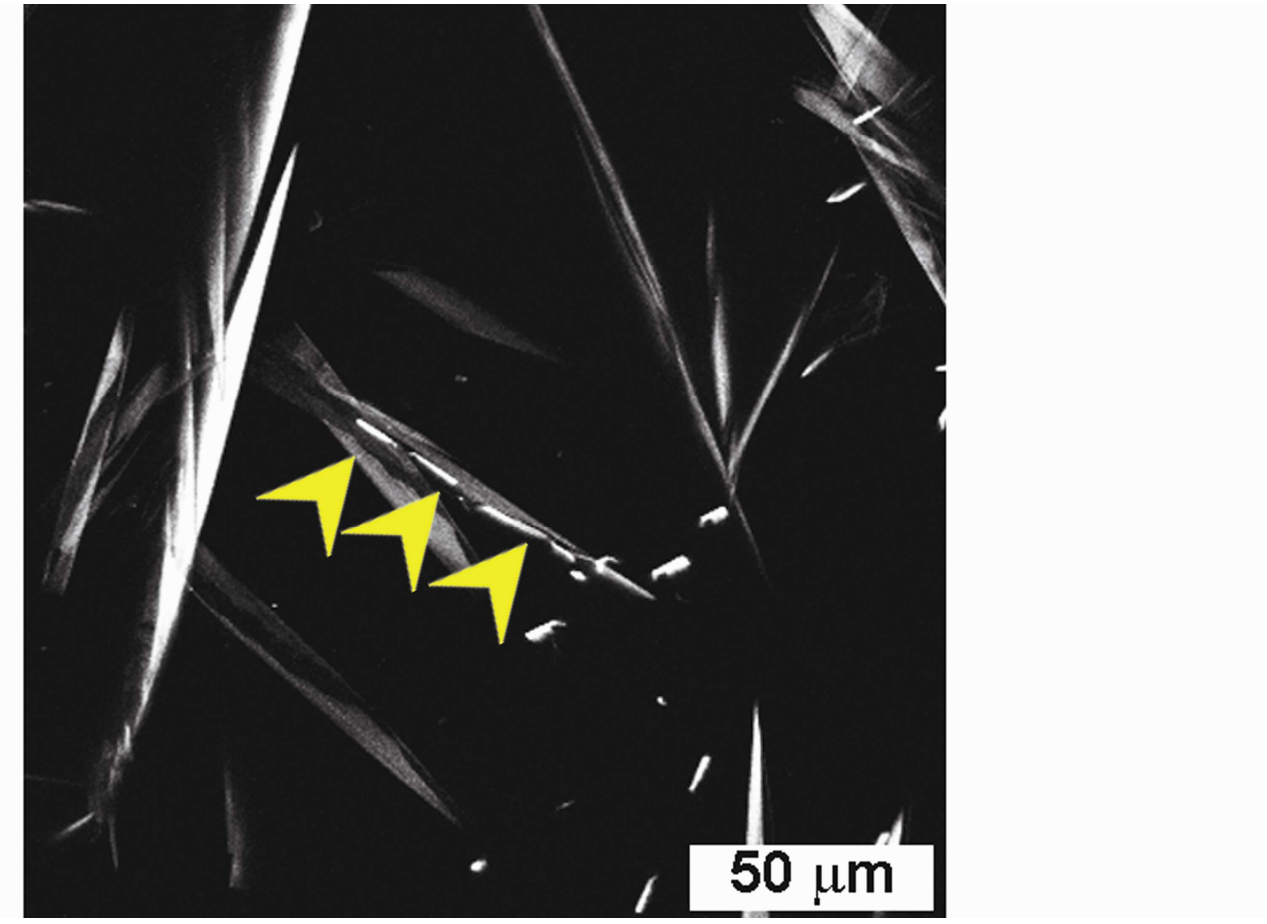
III- Cryo-TEM images showing how globular nuclei of LFF respond to laser radiation damage before disappearance. Scale bar = 500 nm.



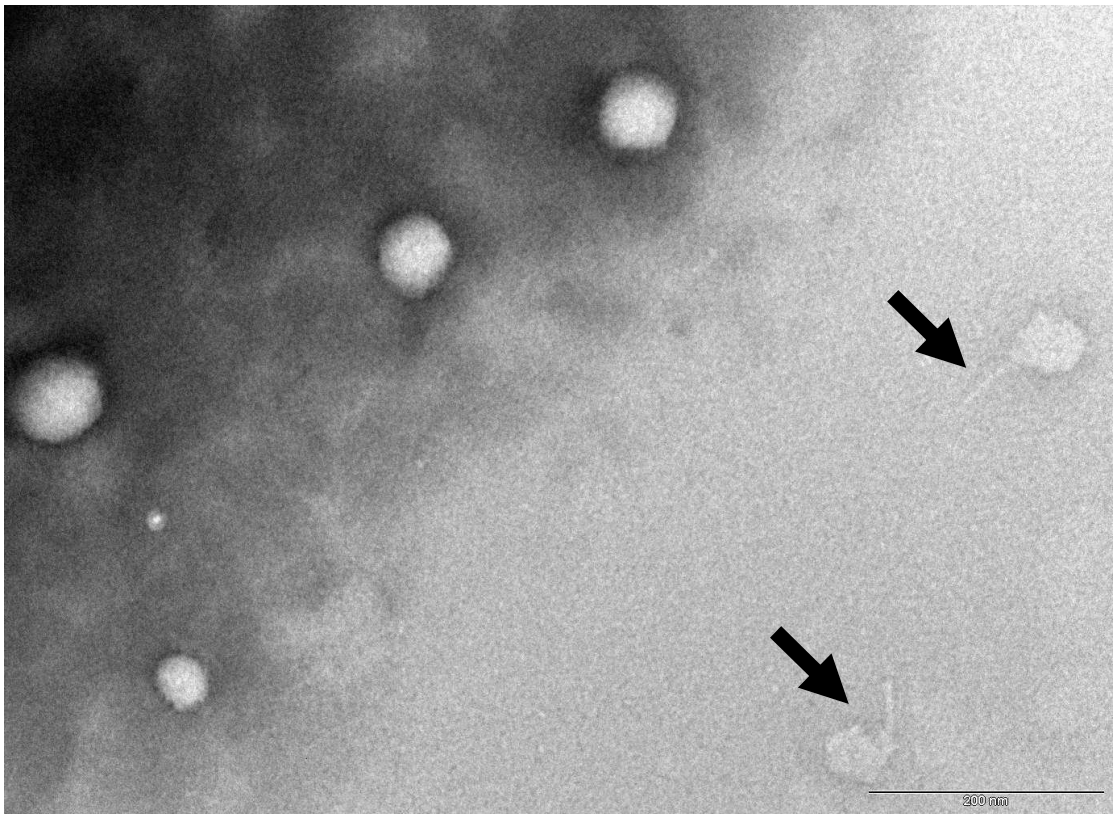
IV- Confocal images for Thioflavin T-stained samples of LFF after 7 days. Scale bar = 50 microns.

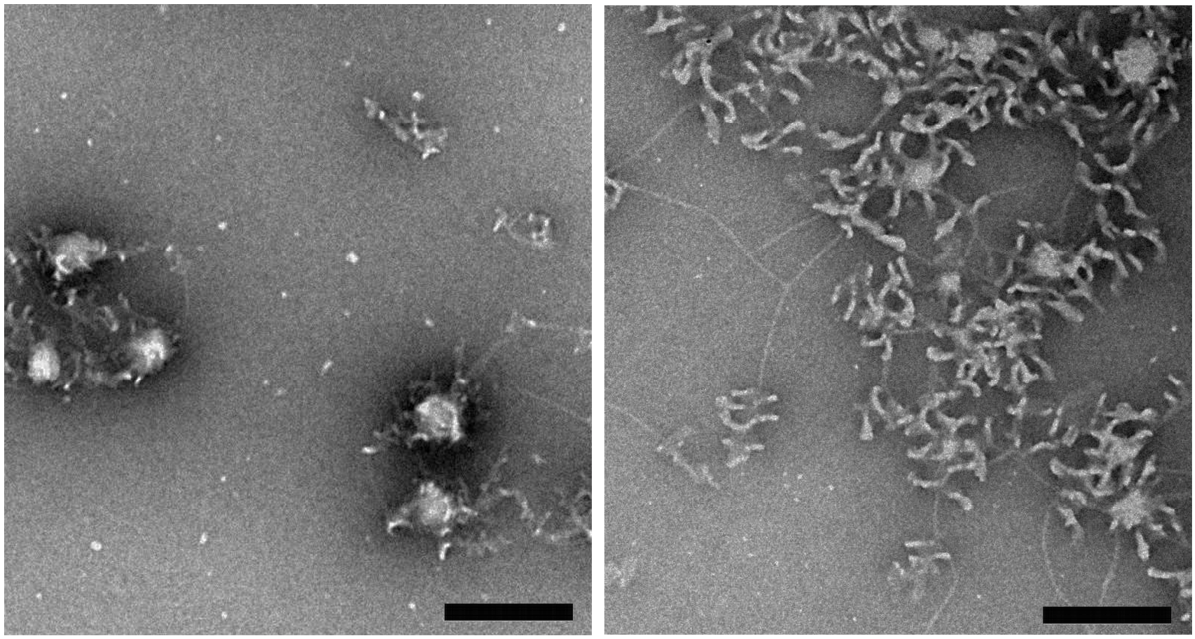


V- Confocal images for Thioflavin T-stained samples of LFF showing crystal needles aligning into plates. Scale bar = 50 microns.

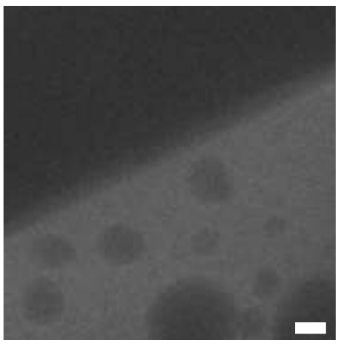


VI - TEM image with negative staining for LFF on fresh samples. Scale bar = 200 nm.





VII- Cryo-TEM image detail showing globules for LFF superimposed on a crystal plate. Scale bar = 200 nm.



VIII- *d* spacings from XRD diffraction analysis

d spacings (Å)	
^{D}LFF	LFF
19.5	16.7
9.8	9.5
-	8.4
6.5	6.3
4.9	4.6
3.9	3.8
2.9	2.9
2.8	2.7
2.7	2.6
2.4	-

IX -Theoretical average distances from molecular modelling

^{D}LFF

molecular length ~ 17.4Å
central Phe π-π stack distance ~ 4.2 Å
beta-strand distance ~4.9 Å
antiparallel distance ~10.3-10.5 Å

LFF

molecular length ~13.5Å
central Phe π-π stack distance ~4.3 Å
beta-strand distance ~4.2 Å
antiparallel distance ~8.8 Å