Electronic Supplementary Material (ESI) for Soft Matter.

Formation of peptide-based oligomers in dimethylsulfoxide: Identifying the precursor of fibril formation

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Supporting Information

To be submitted to: *Soft Matter*

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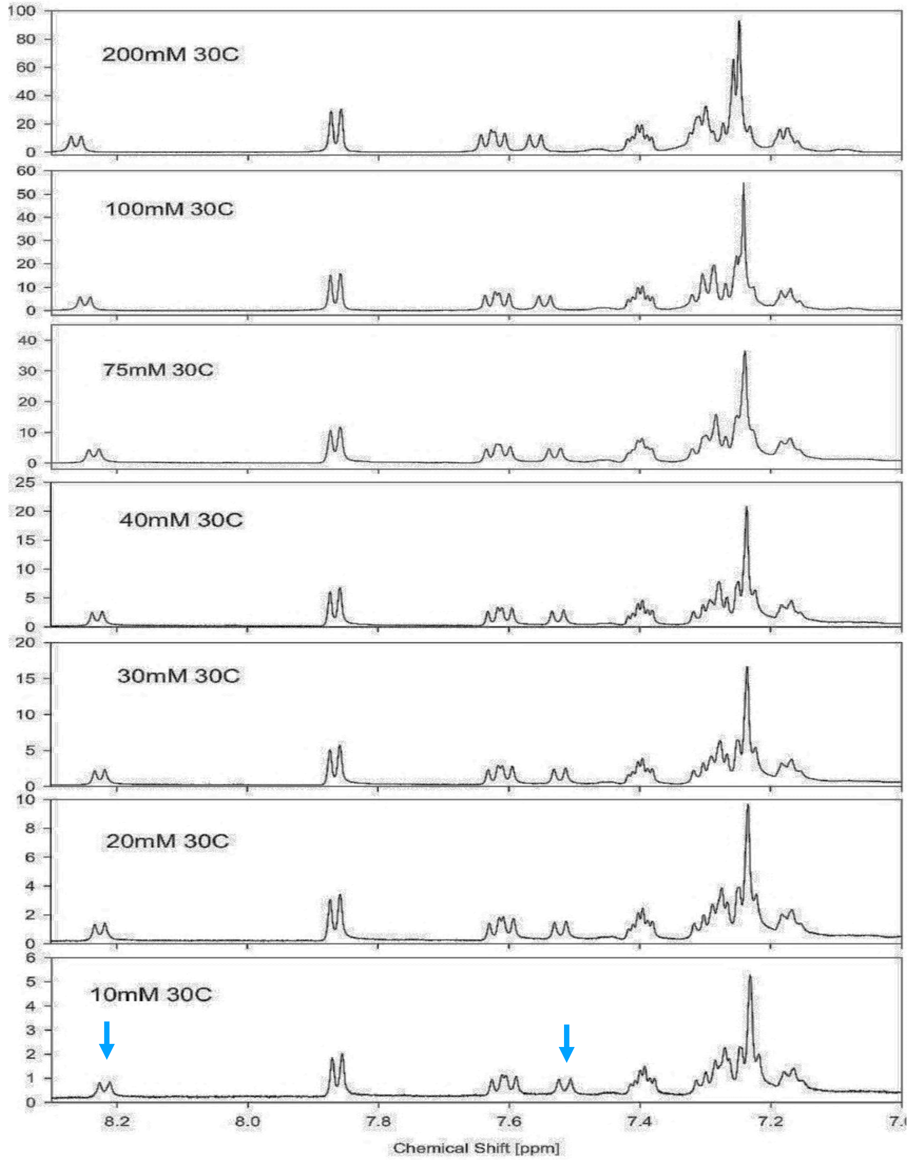


Figure S1: ^{1}H NMR spectrum of the indicated FmocFF concentrations in DMSO at 30° C. In the 10 mM spectrum, the position of the N- and C-terminal proton signals at 8.23 and 7.55 pm are marked by arrows.

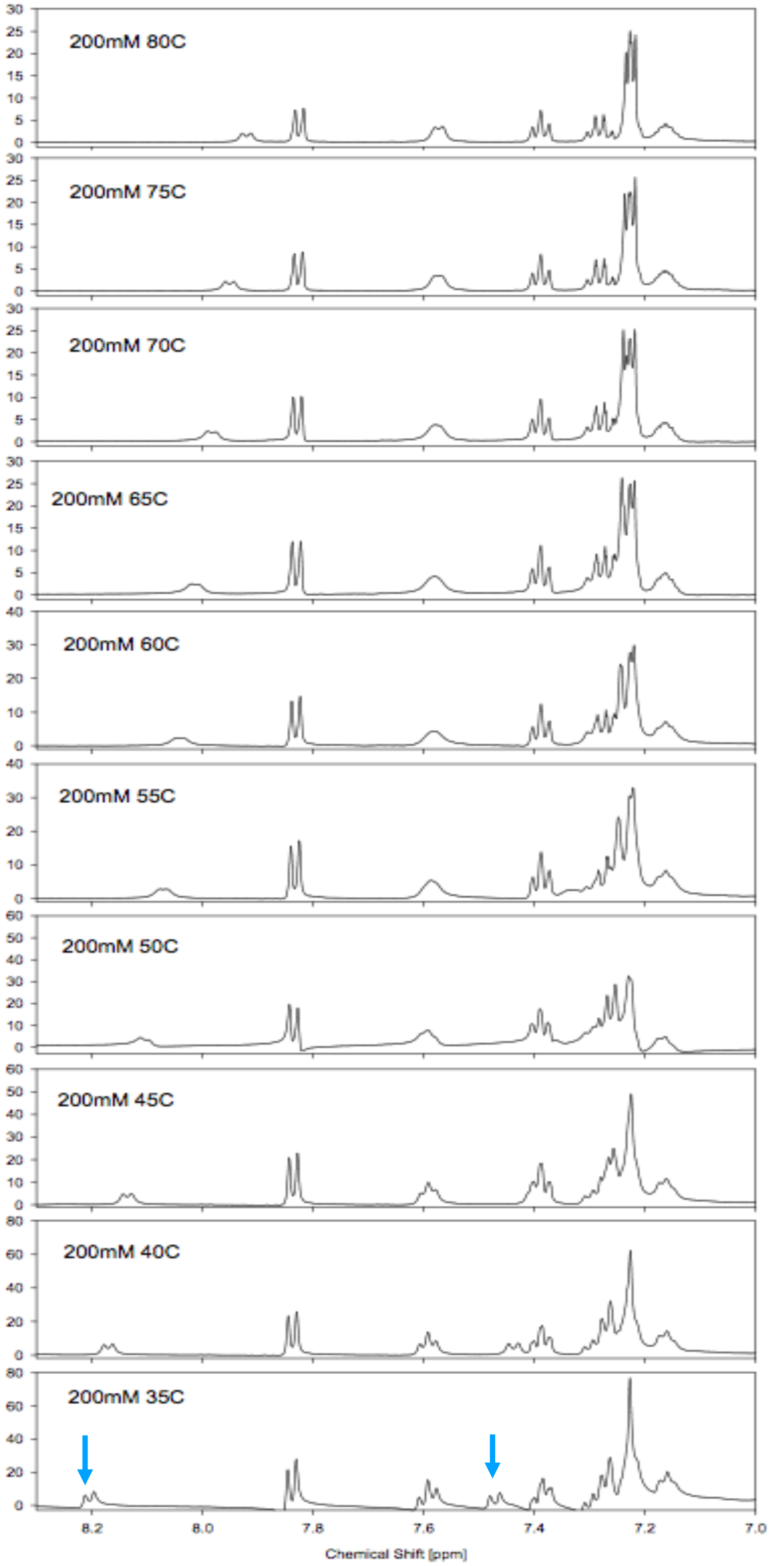


Figure S2: H-NMR spectrum of FmocFF in DMSO in the chemical shift region between 7.0 and 8. 3 ppm measured at the indicated temperatures. This spectral region exhibits the two doublets of the amide proton signal at 8.23 ppm (C-terminal) and 7.55 pm (N-terminal) which are indicated by arrows. The remaining signals are assignable to Fmoc hydrogens.

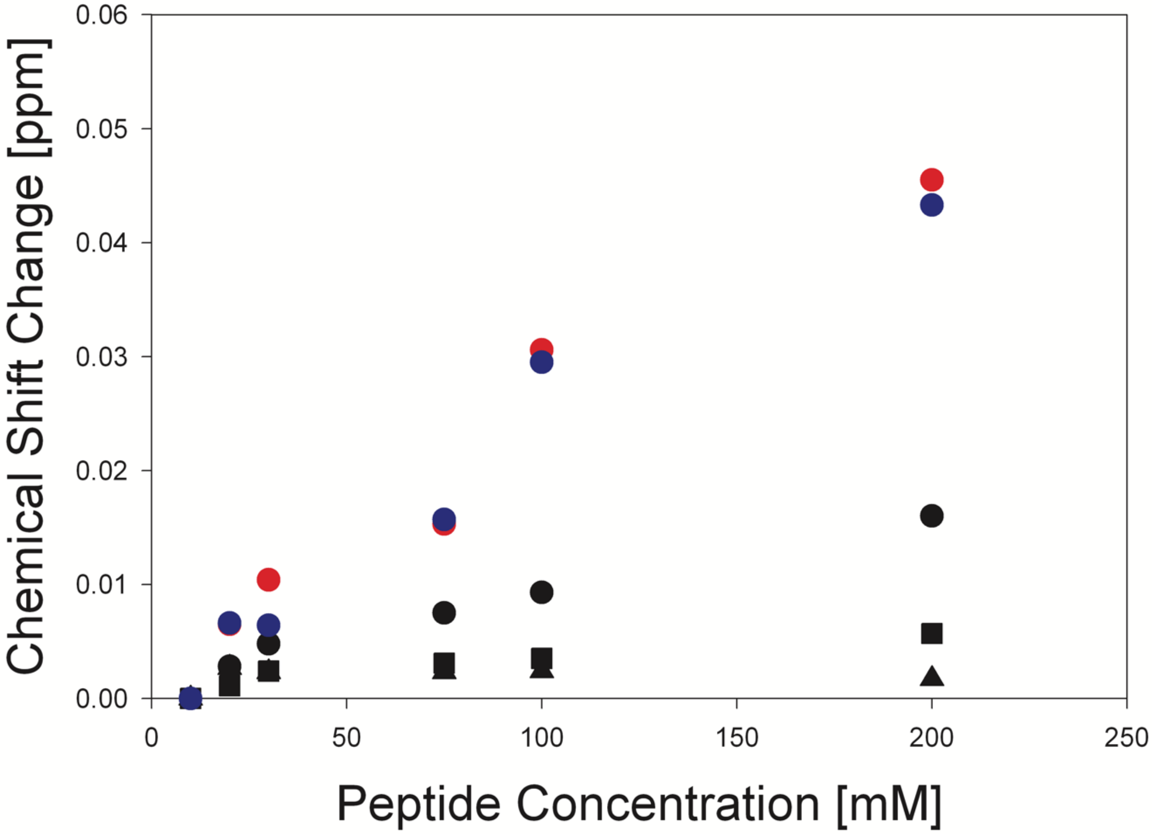
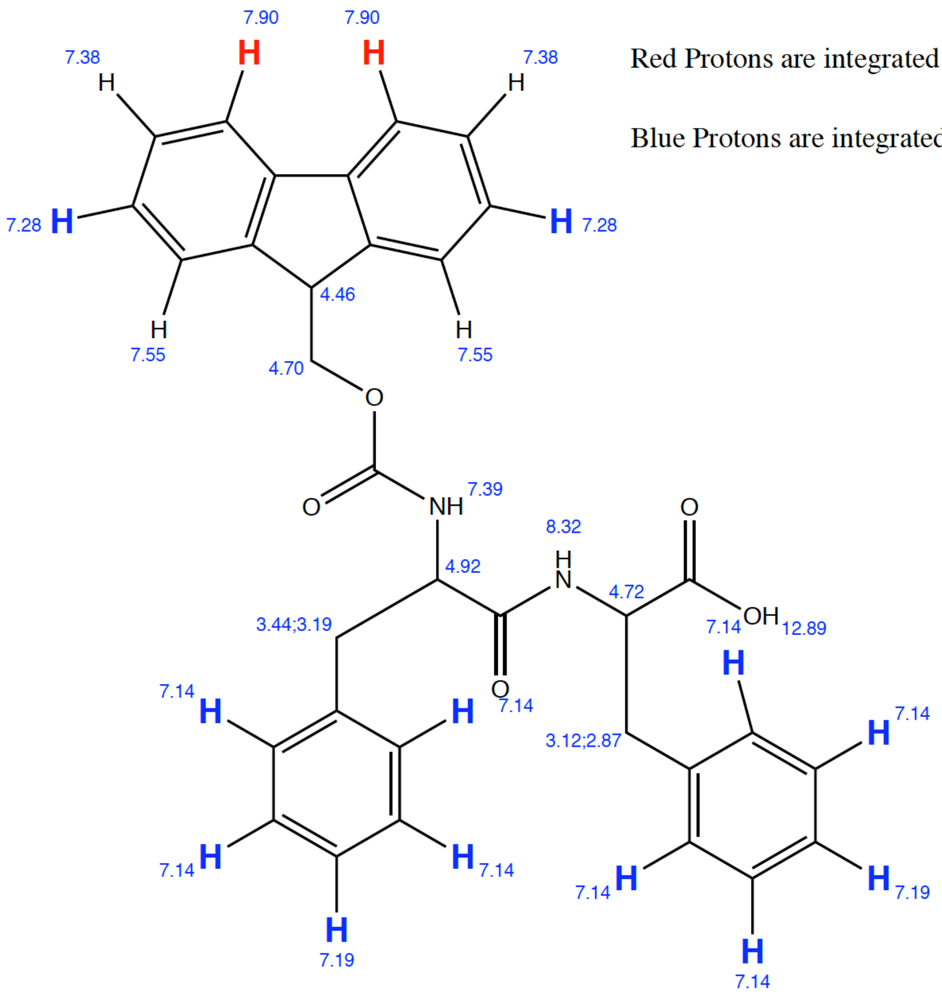


Figure S3: Change of the chemical shift of the C-terminal amide proton (blue), the N-terminal amide proton (red), the Fmoc CH protons labeled blue (filled circles) and red (triangle) in Figure S4 and the F-proton at para positions of the phenyl rings.



Red Protons are integrated from 7.8 to 7.9

Blue Protons are integrated from 7.10 to 7.35

Figure S4: FmocFF structure displaying the chemical shifts of the CH and NH groups.

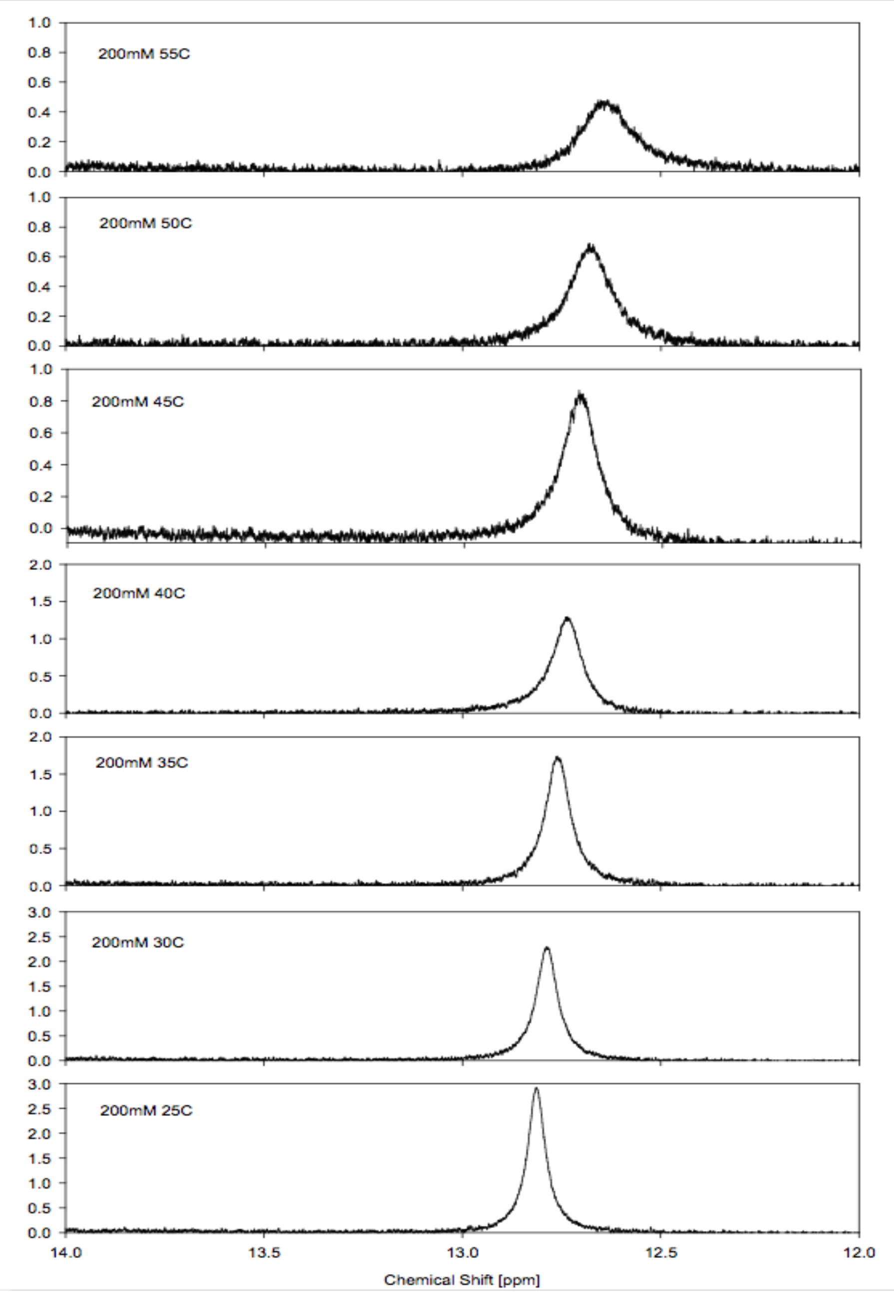


Figure S5: H-NMR spectrum of FmocFF in DMSO in the chemical shift region between 12 and 14 ppm measured at the indicated temperatures. This spectral region exhibits the proton signal assignable to the COOH group in carboxylate dimers.

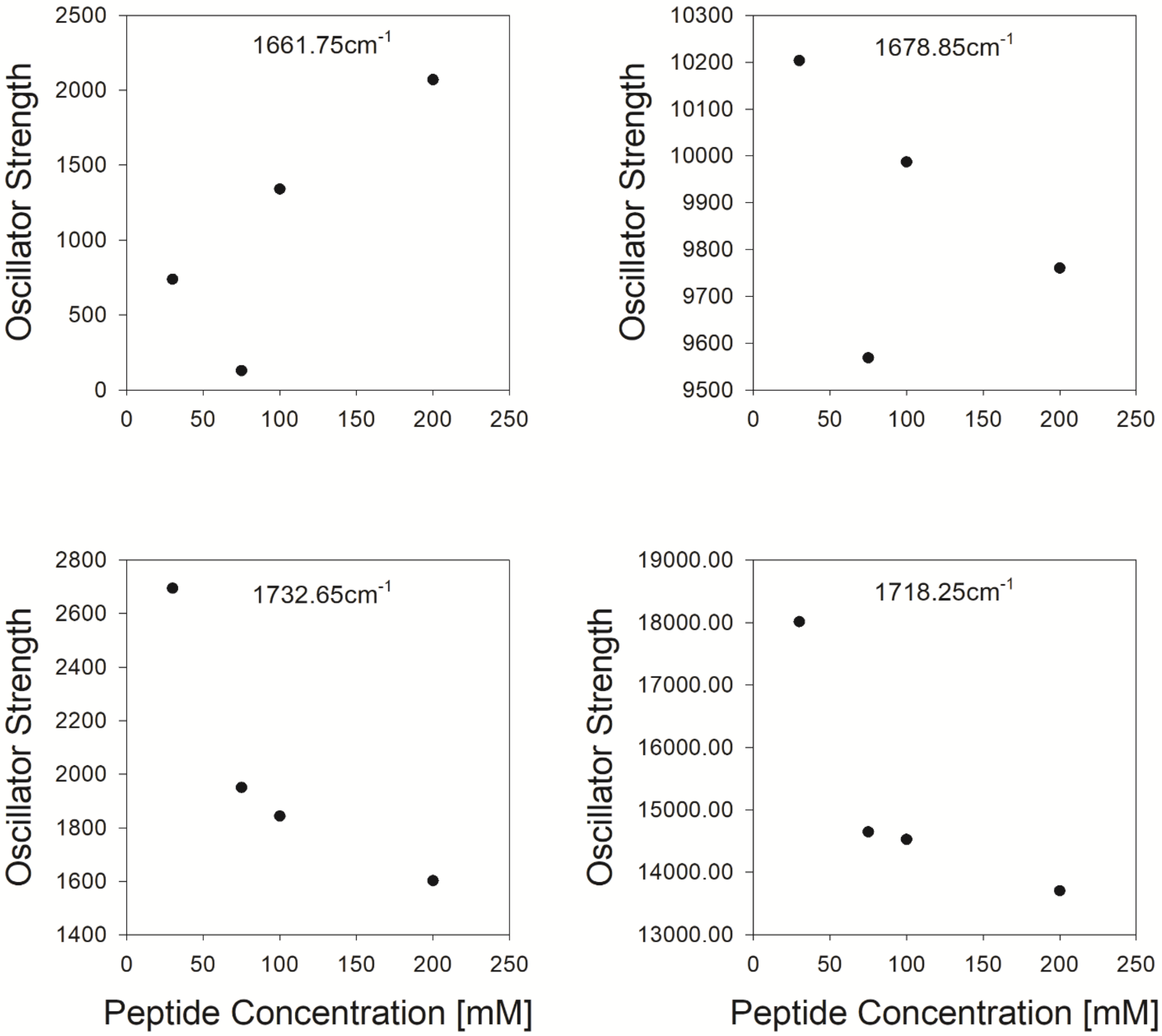


Figure S6: Integrated intensities (oscillator strength) of the indicated amide I sub-bands (1661.75 cm^{-1}, 1678.85 cm^{-1} and 1718.25 cm^{-1}) and the C=O band (1732.65 cm^{-1}) of FmocFF plotted as a function of peptide concentration. The sub-bands were obtained from a spectral decomposition described in the main text.

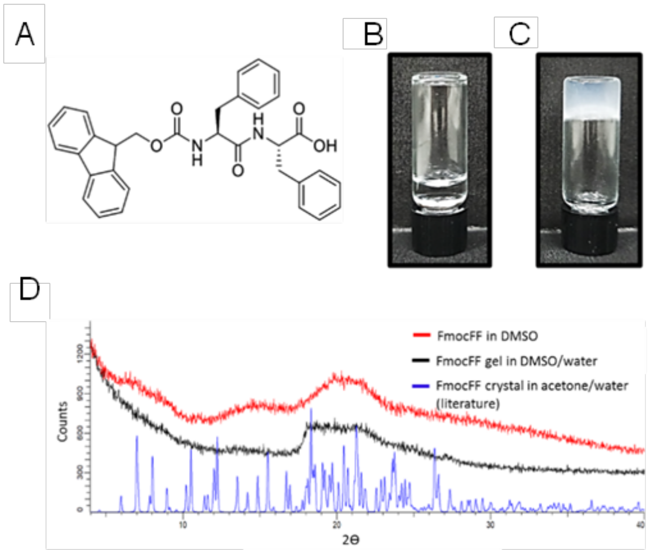


Figure S7: (A) Molecular structure of the FmocFF peptide. (B) Inverted vial of FmocFF solution in DMSO. (C) Inverted vial of FmocFF hydrogel in DMSO/water. (D) XRD characterization of FmocFF solution in DMSO (red), FmocFF hydrogel in DMSO/water (black) and simulated XRD curve of FmocFF crystal from acetone/water (blue).[1]

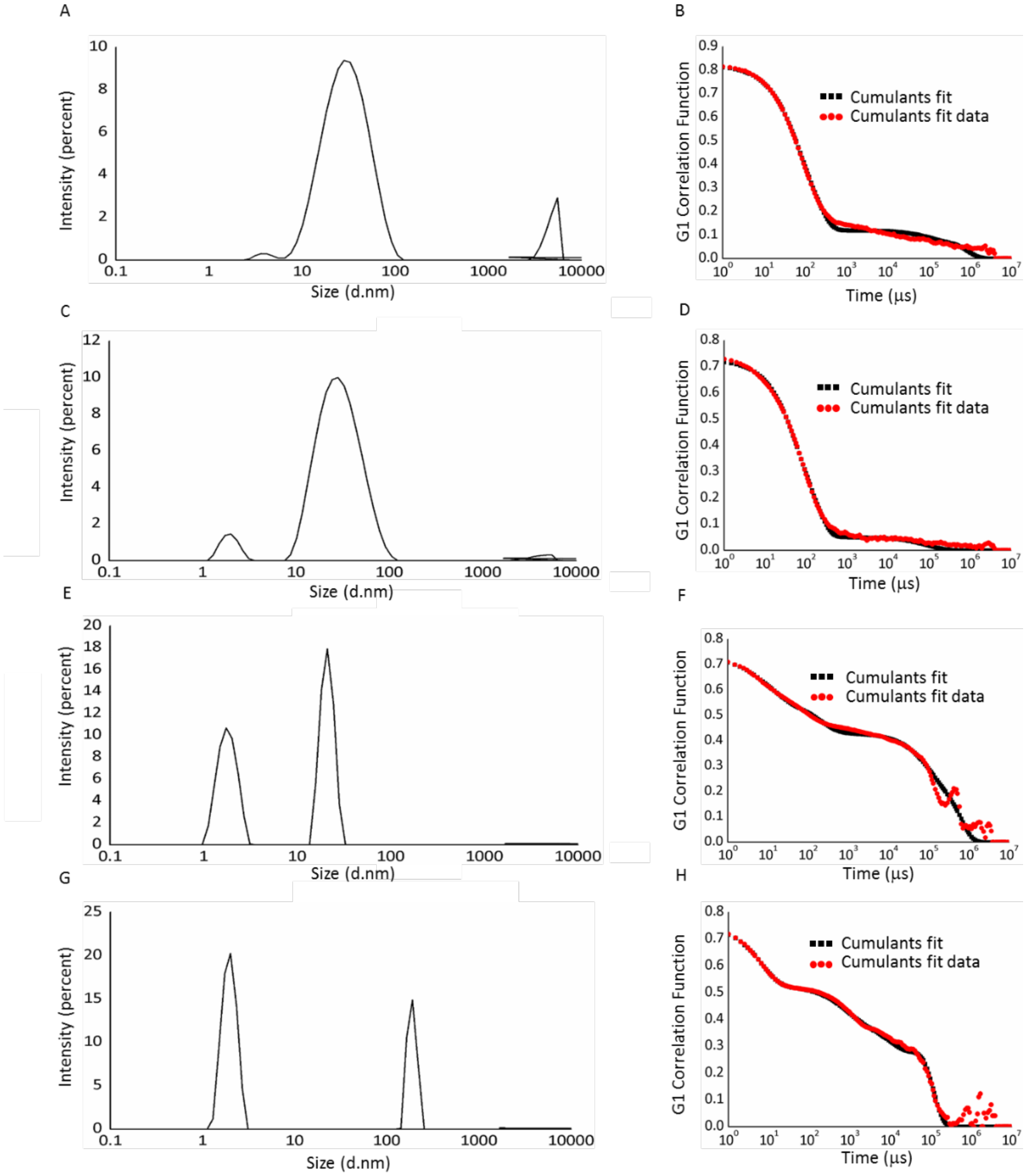


Figure S8: Concentration dependent DLS measurement of FmocFF solution in DMSO and their corresponding correlation plots (A-B) 10 mM, (C-D) 30 mM, (E-F) 70 mM, (G-H) 200 mM.

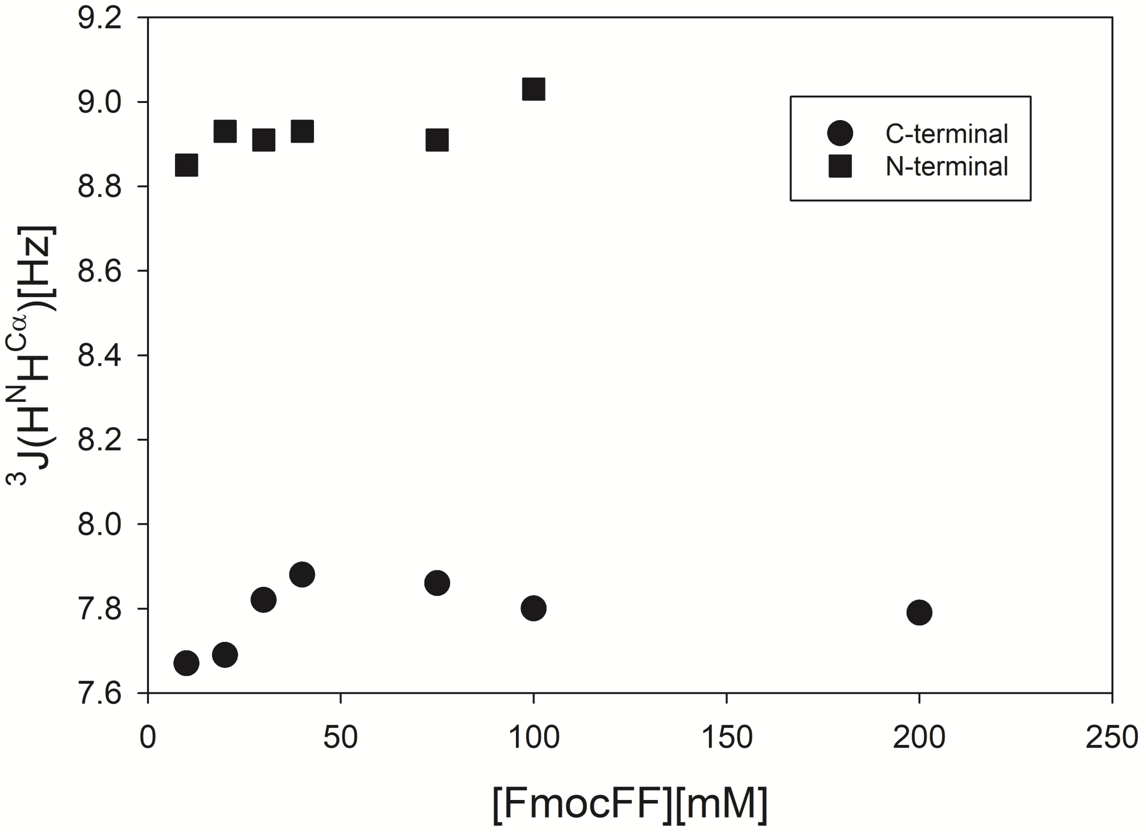


Figure S9: Concentration dependence of the $^3J(H^NH^{C\alpha})$ coupling constants of the indicated amide proton. The experimental uncertainty of the plotted values is ca. ±0.1 Hz .

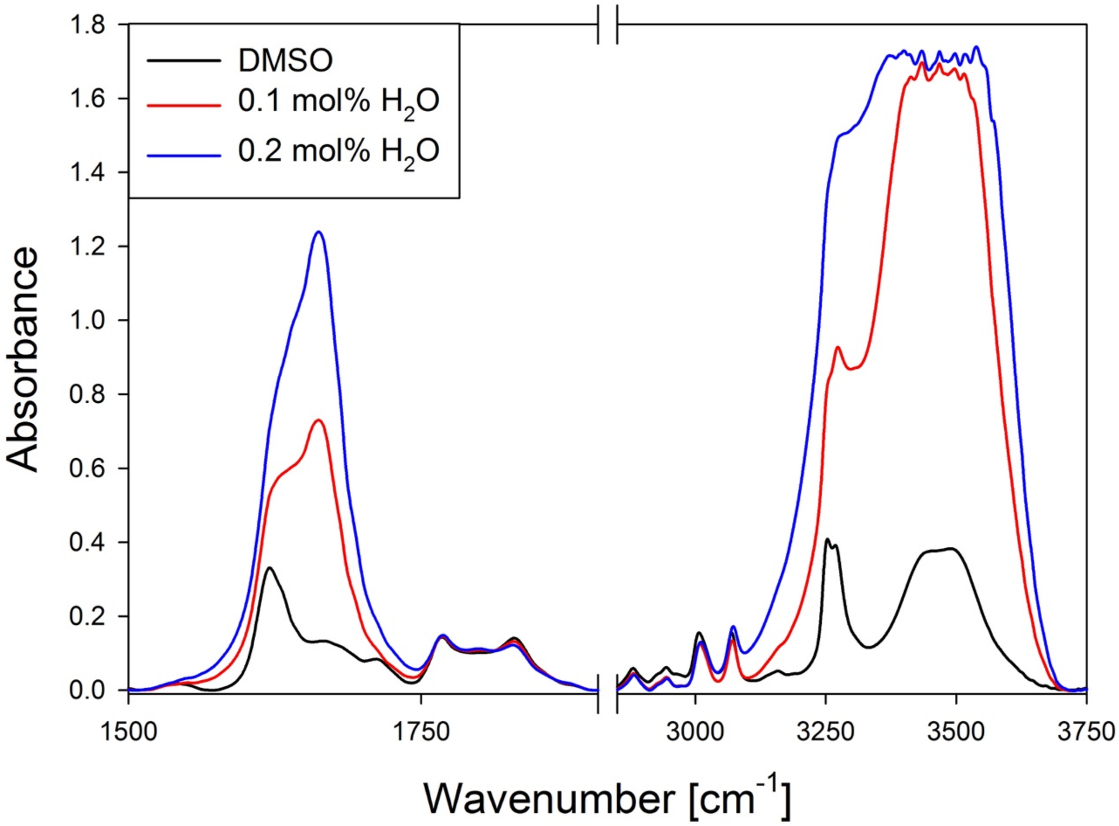


Figure S10: IR spectra of pure DMSO and mixtures of H_2O and DMSO, as indicated.

References

1. J. Raeburn, C. Mendoza-Cuenca, B. N. Cattoz, M. A. Little, A. E. Terry, A. Z. Cardoso, P. C. Griffiths and D. J. Adams, *Soft Matter*, 2015, **11**, 927–935.