Supporting Information

Redox Sensitive Self-Assembling Dipeptide for Sustained Intracellular Drug Delivery

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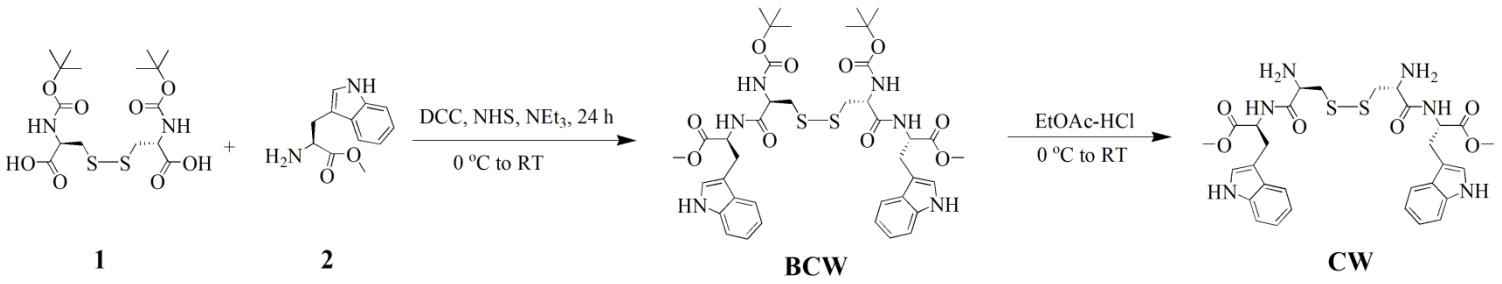


Scheme S1: Synthesis of dipeptide **BCW** and corresponding *N*-deprotected derivative **CW**.

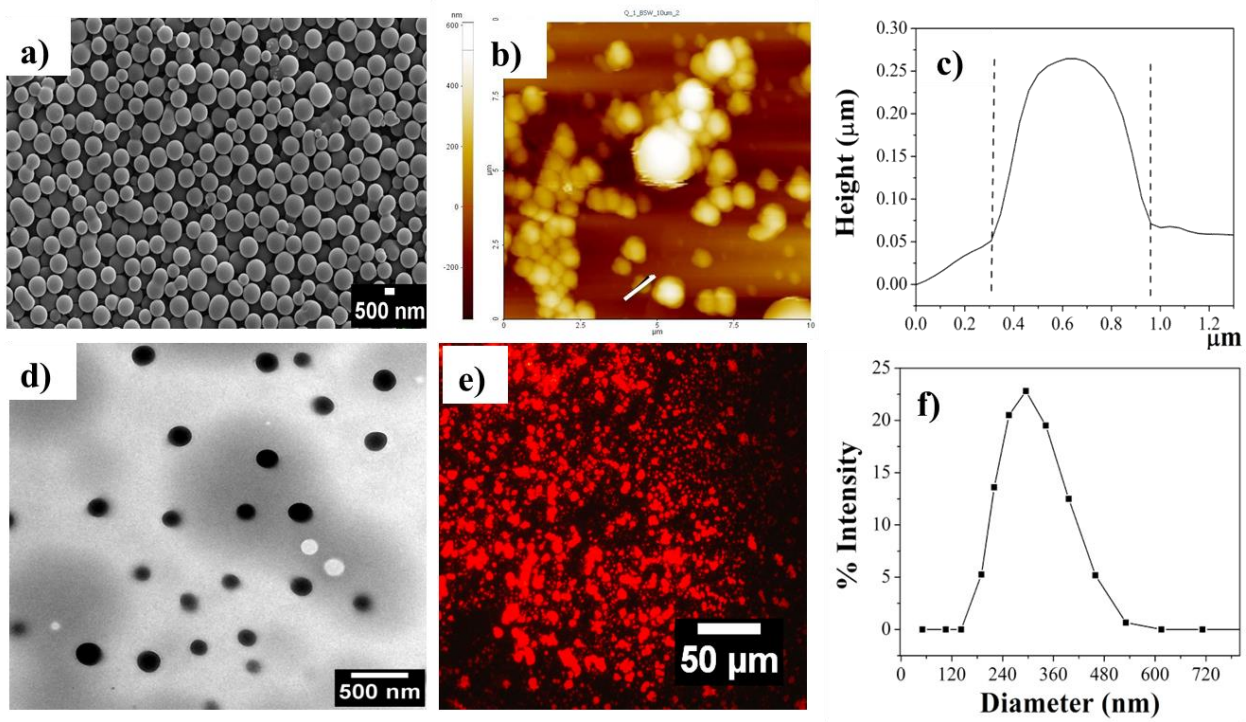


Figure S1: Microscopic and size distribution analyses of **BCW**. Compound **BCW** in MeOH (1 mg/ml) a) SEM, b) AFM, c) AFM cross-sectional analysis along the line, d) TEM, e) fluorescence microscopic images of **BCW**+0.02 equivalents of Rhodamine B (λ_{ex} = 510-560 nm), f) DLS of **BCW**.

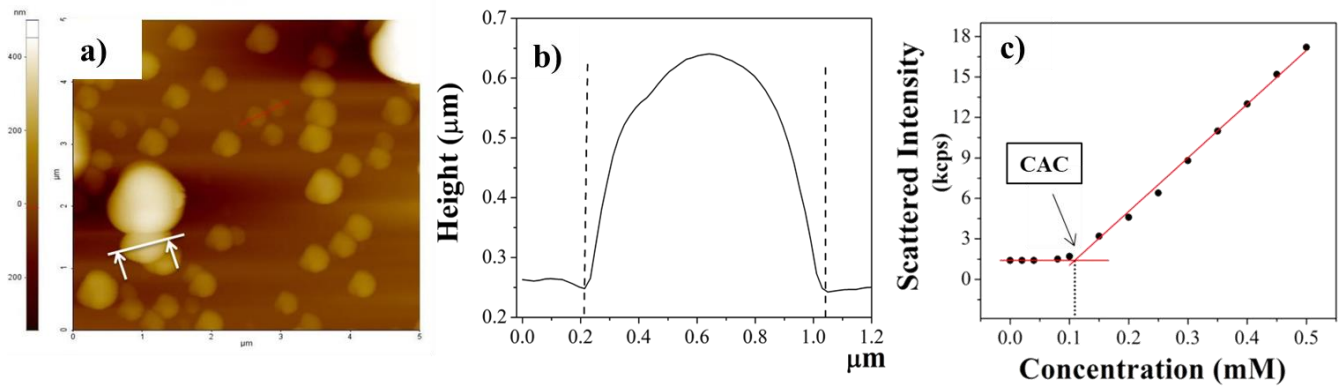


Figure S2: Morphological analysis of **CW** dissolved in water (1 mg/ml) a) AFM, b) AFM cross-sectional analysis along the line; c) Scattered intensities collected from the different concentration solutions of **CW** in water. The intersection point in the plot corresponds to CAC.

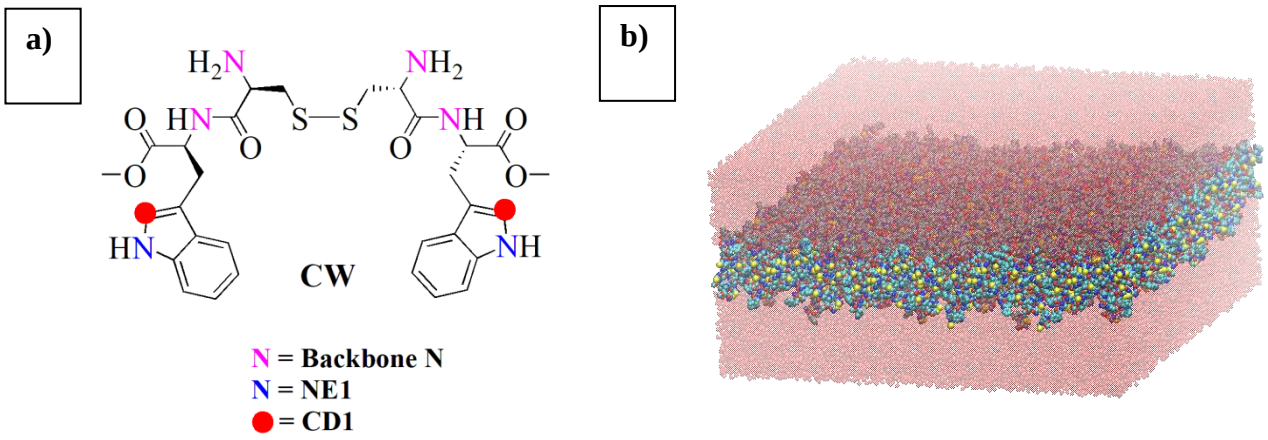


Figure S3: a) An initial labeled structure of **CW**, b) A snapshot of initial system configuration of flat dipeptide membrane.

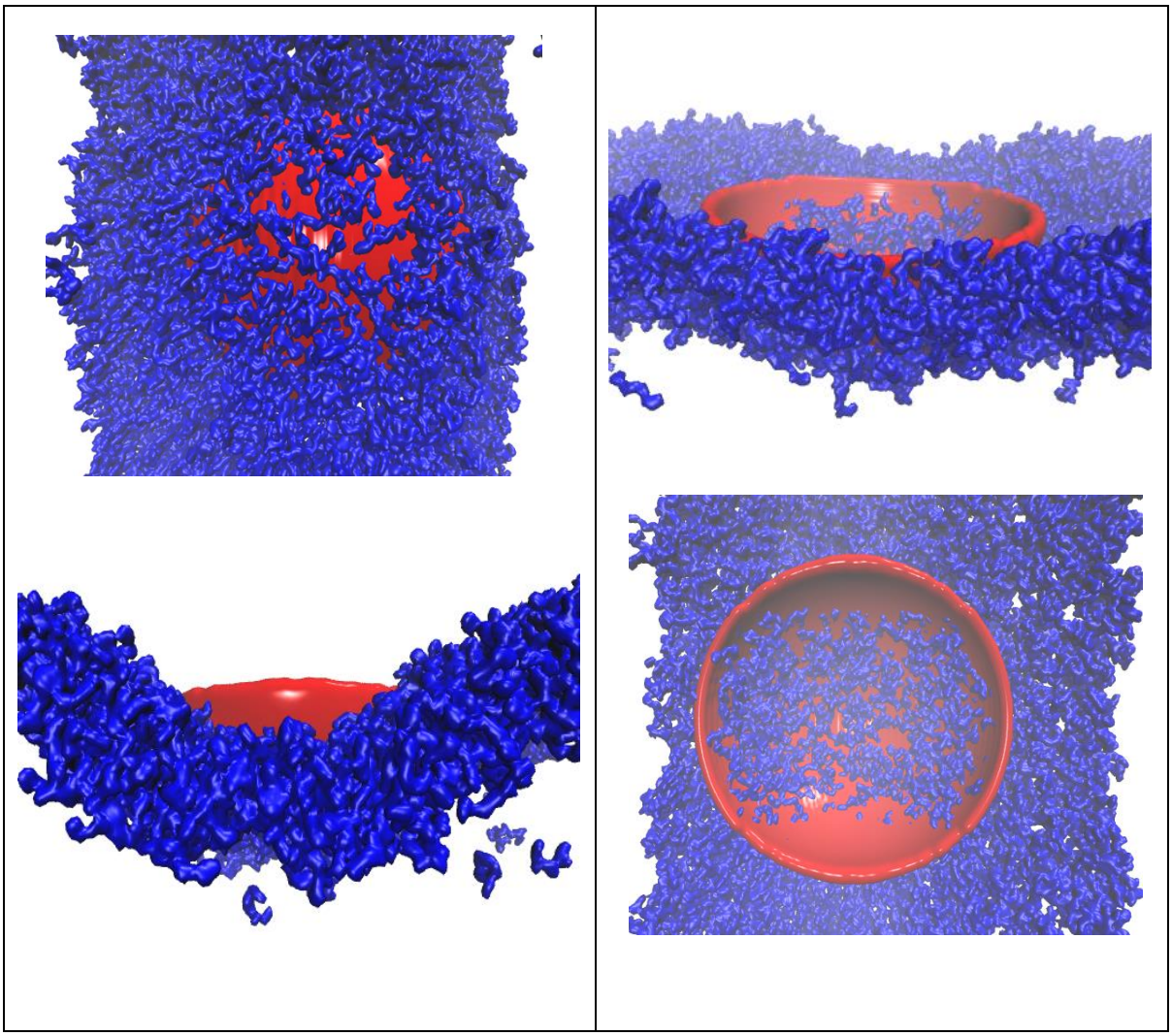


Figure S4: Snapshots of dipeptide membrane (blue) with a spherical fit (red).

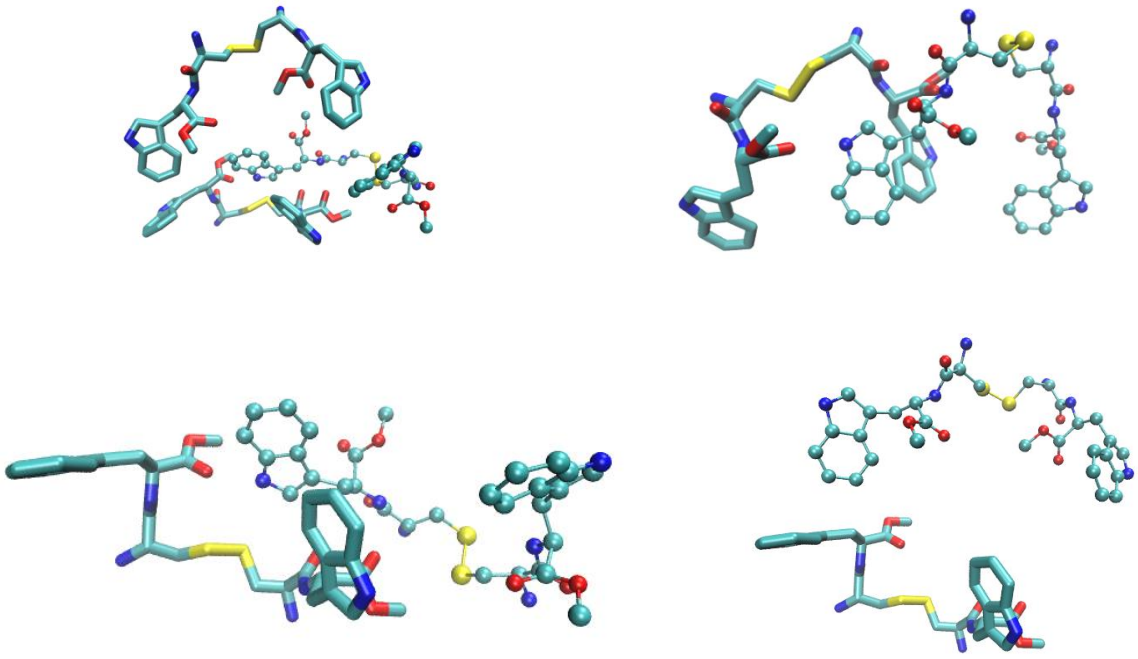
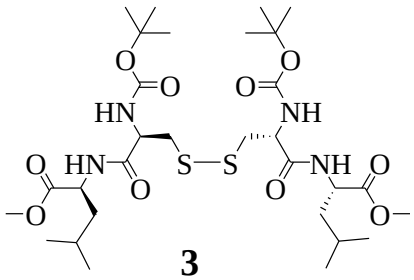


Figure S5: Different snapshots of the arrangement of two **CW** molecules exhibiting preferential attraction of the tryptophan groups.



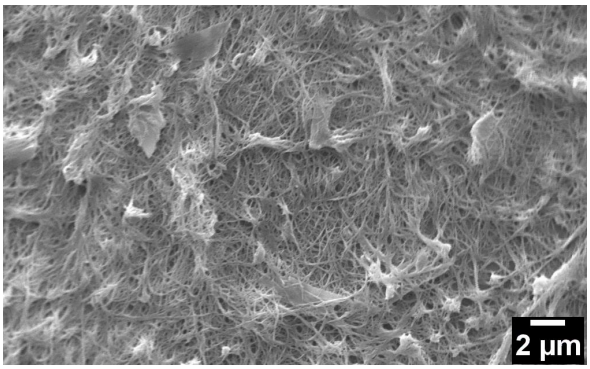


Figure S6: Chemical structure of leucine analogous of **BCW** and its fibrous self-assembly.

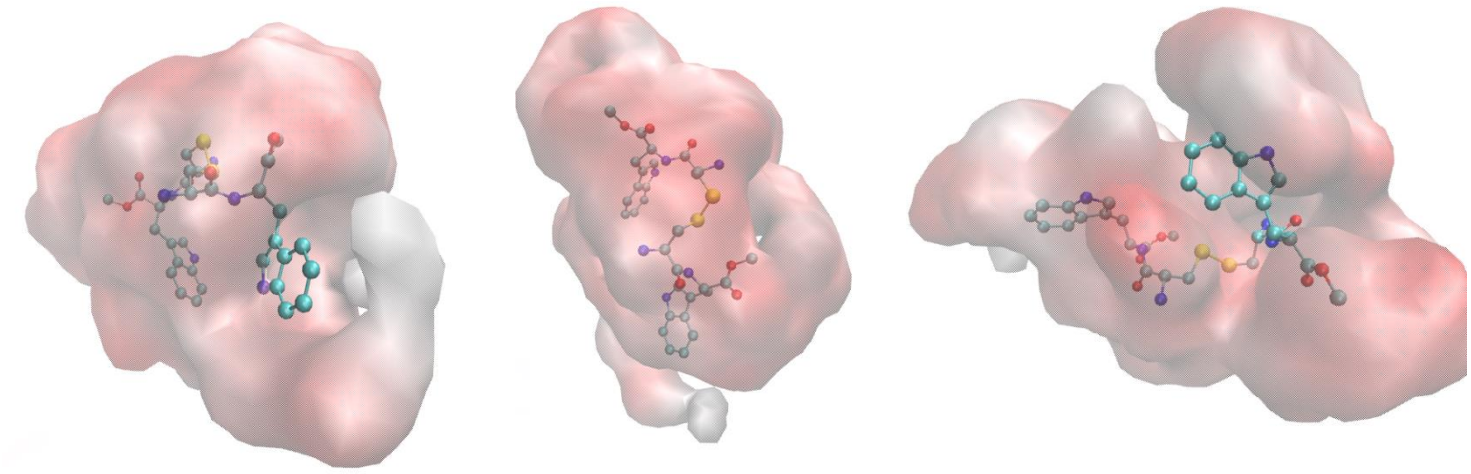


Figure S7: Snaphots of different orientation of **CW** molecule in water, showing the preferential attraction of water cloud (gradient shown from white to red) towards backbone than tryptophan residues. A cavity of water can be seen clearly around tryptophan.

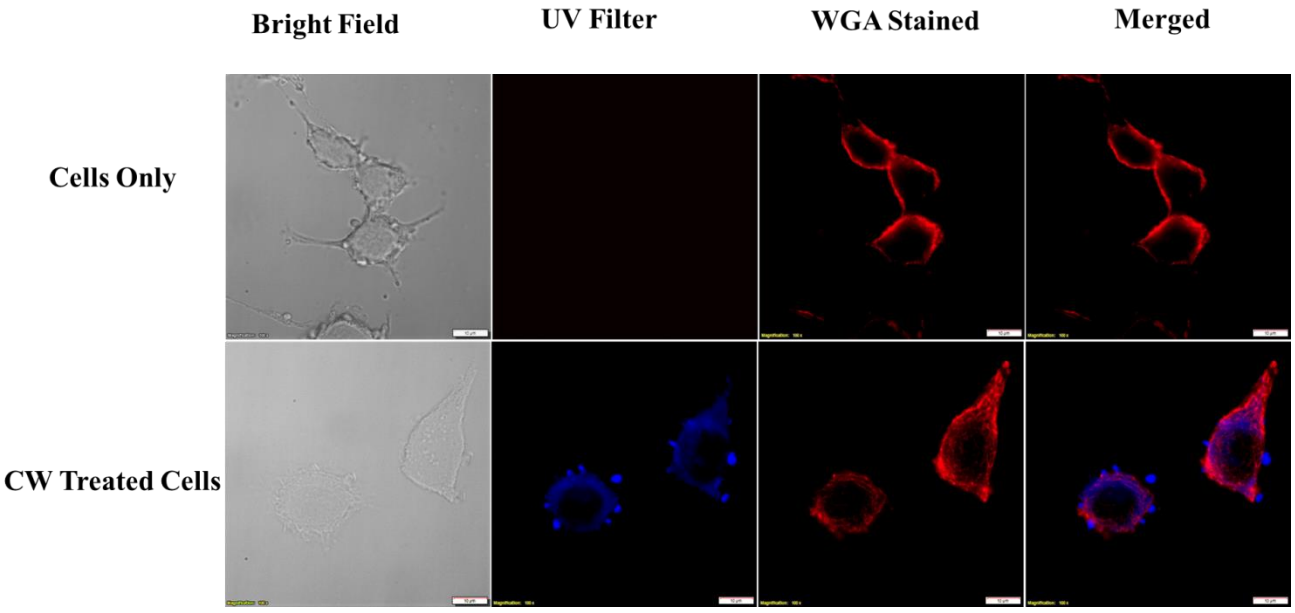


Figure S8: Cellular internalization of **CW** vesicles by CLSM in MDA-MB-231 cells. All images were captured at 100x magnification

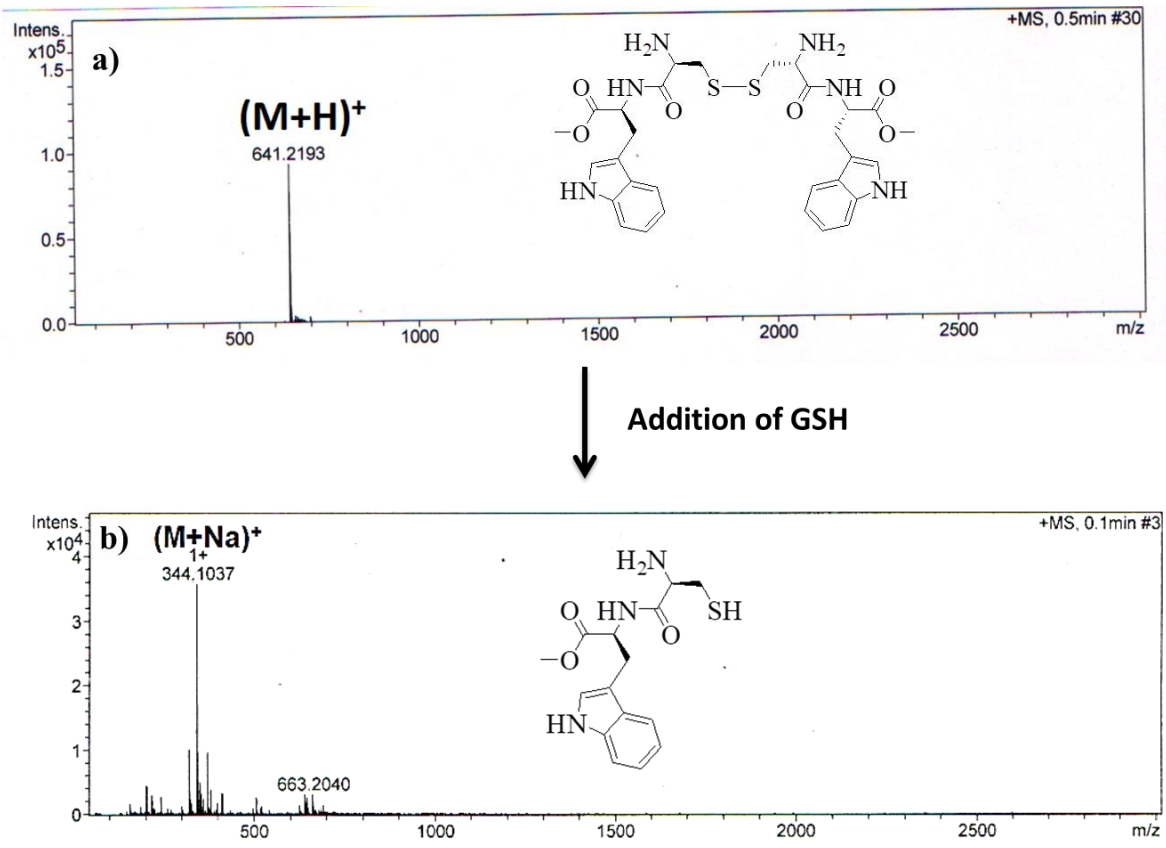


Figure S9: ESI-MS spectra of **CW** before and after the addition of GSH.

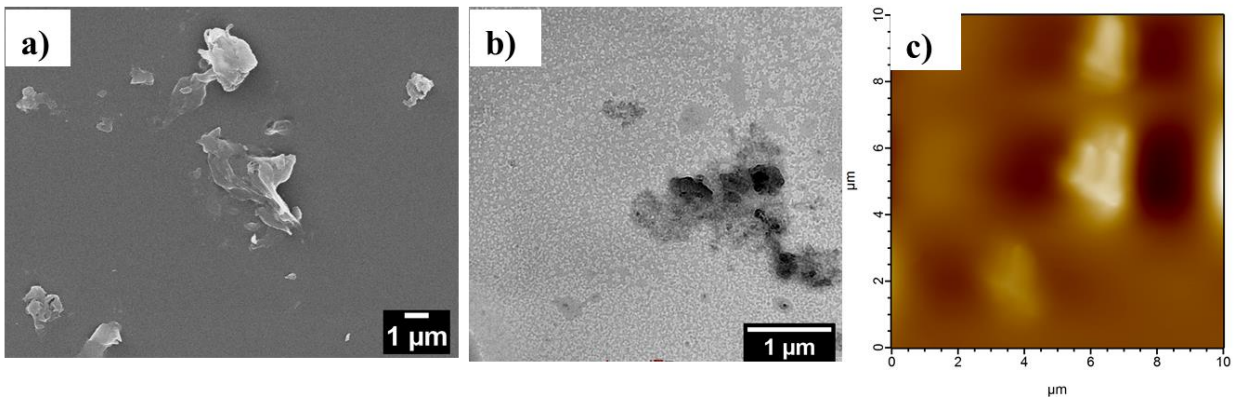


Figure S10: Morphological analysis of **CW** vesicles after the addition of GSH (10 mM) a) SEM, b) TEM, c) AFM.

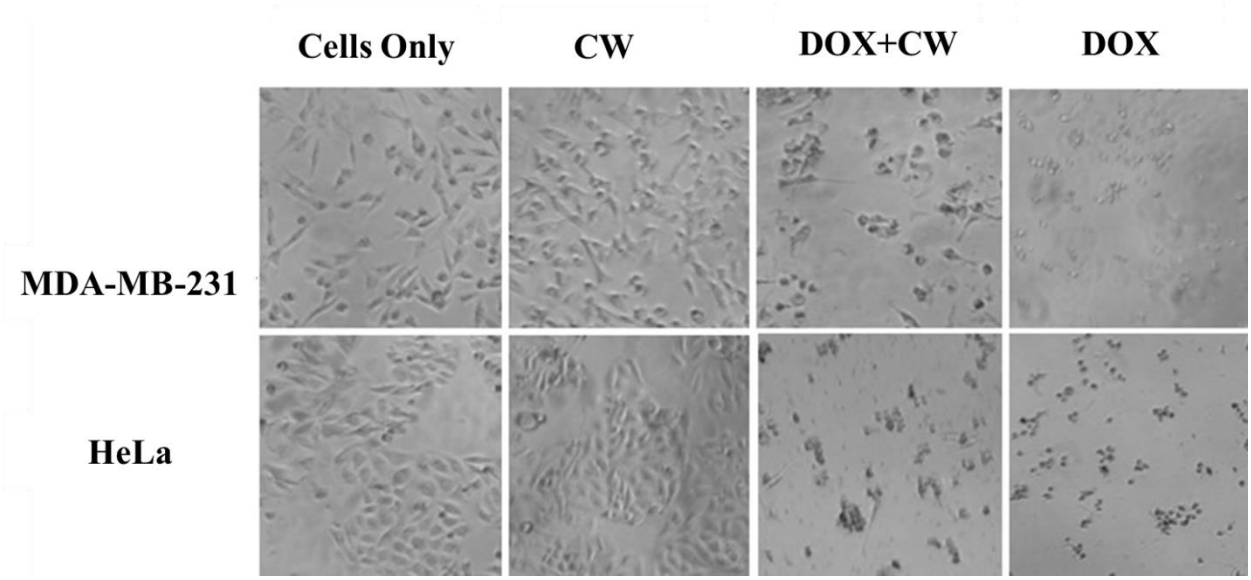


Figure S11: Optical microscopic images of treated cells after 72 h.

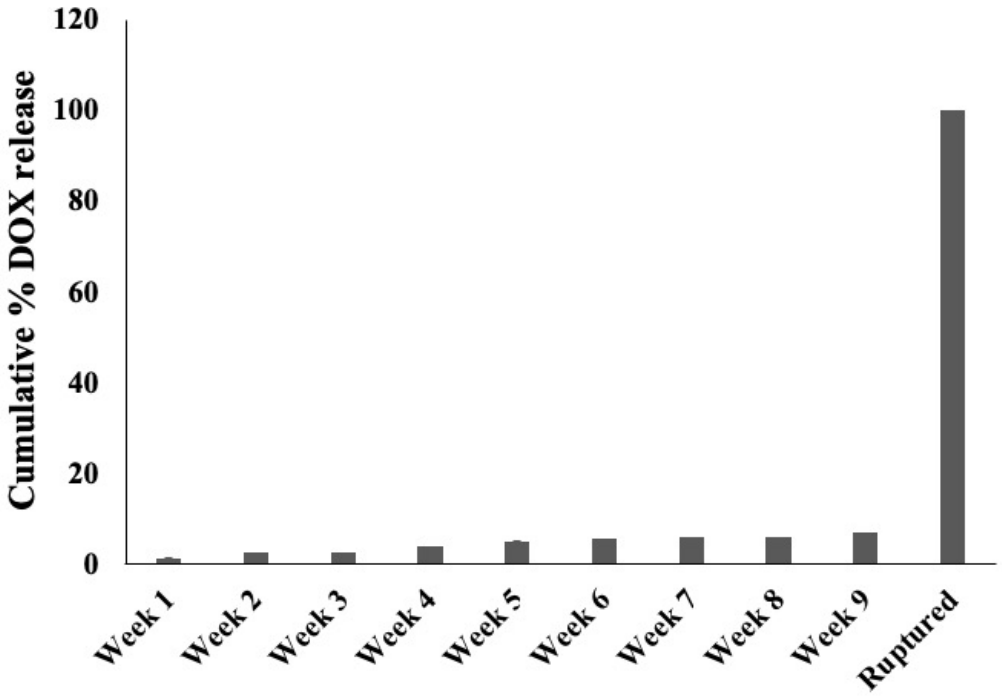


Figure S12: *In vitro* stability study of DOX-loaded **CW** vesicles stored in the dark at 4 ^{o}C.

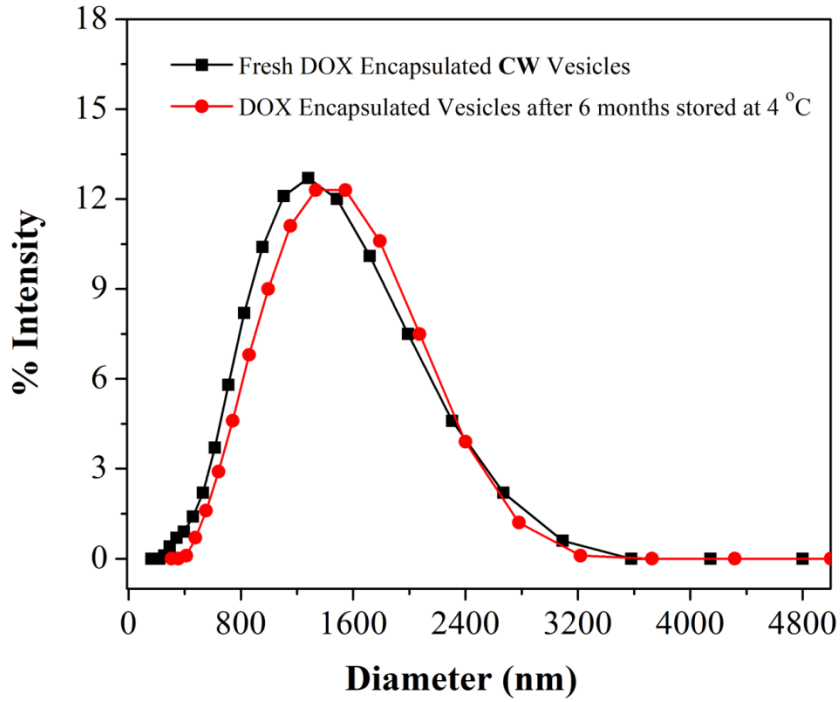


Figure S13: Aggregation study of DOX loaded **CW** vesicles stored in the dark at 4 ^{o}C using DLS data.

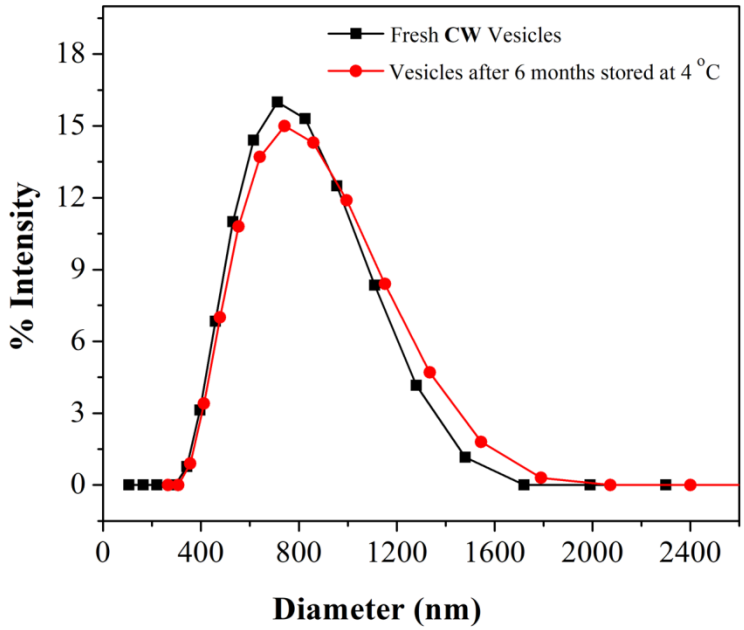


Figure S14: Aggregation study of empty **CW** vesicles stored at 4 ^{o}C using DLS data.

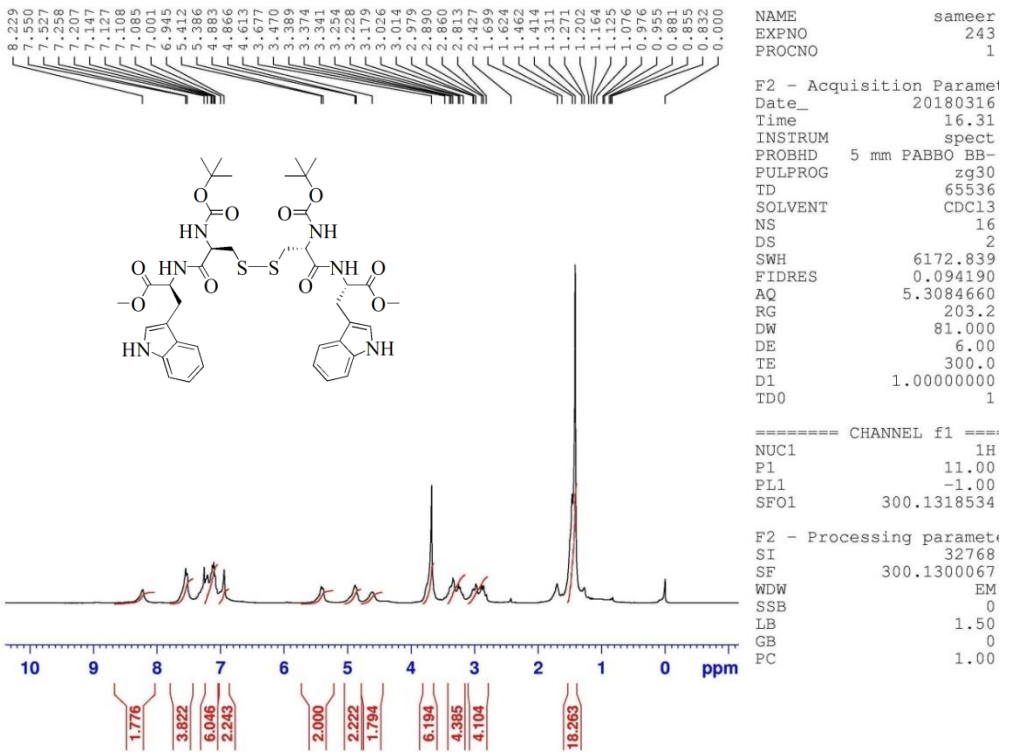


Figure S15: ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of tryptophan-based dipeptide **BCW**.

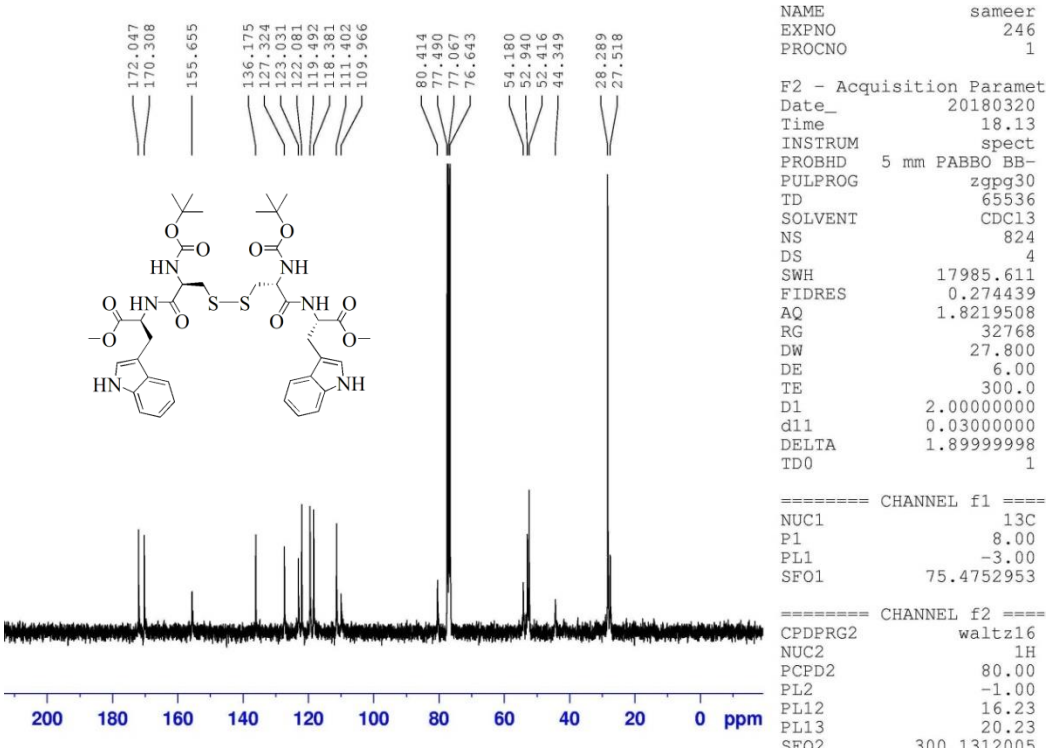


Figure S16: ^{13}C NMR spectrum ($CDCl_3$, 75 MHz) of tryptophan-based dipeptide **BCW**.

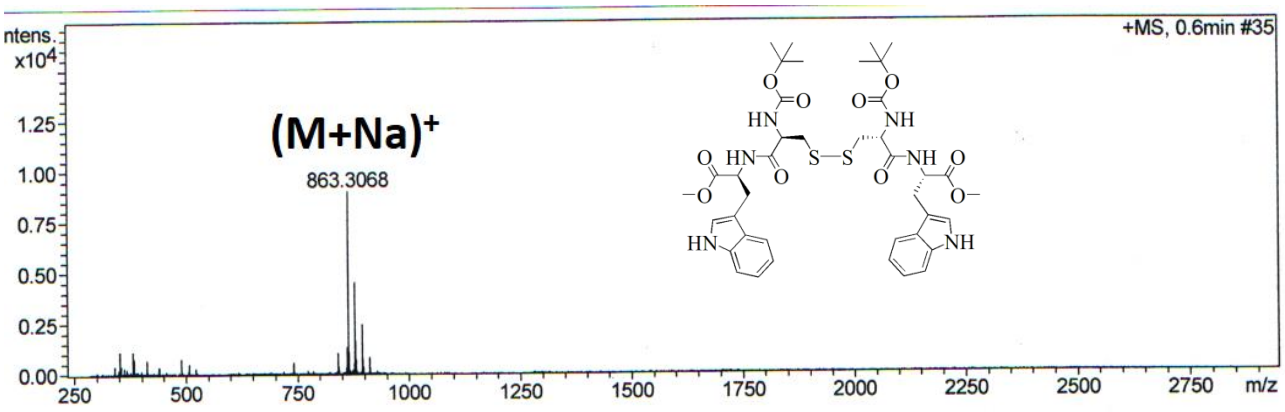


Figure S17: ESI-Mass spectrum of tryptophan-based dipeptide **BCW**.

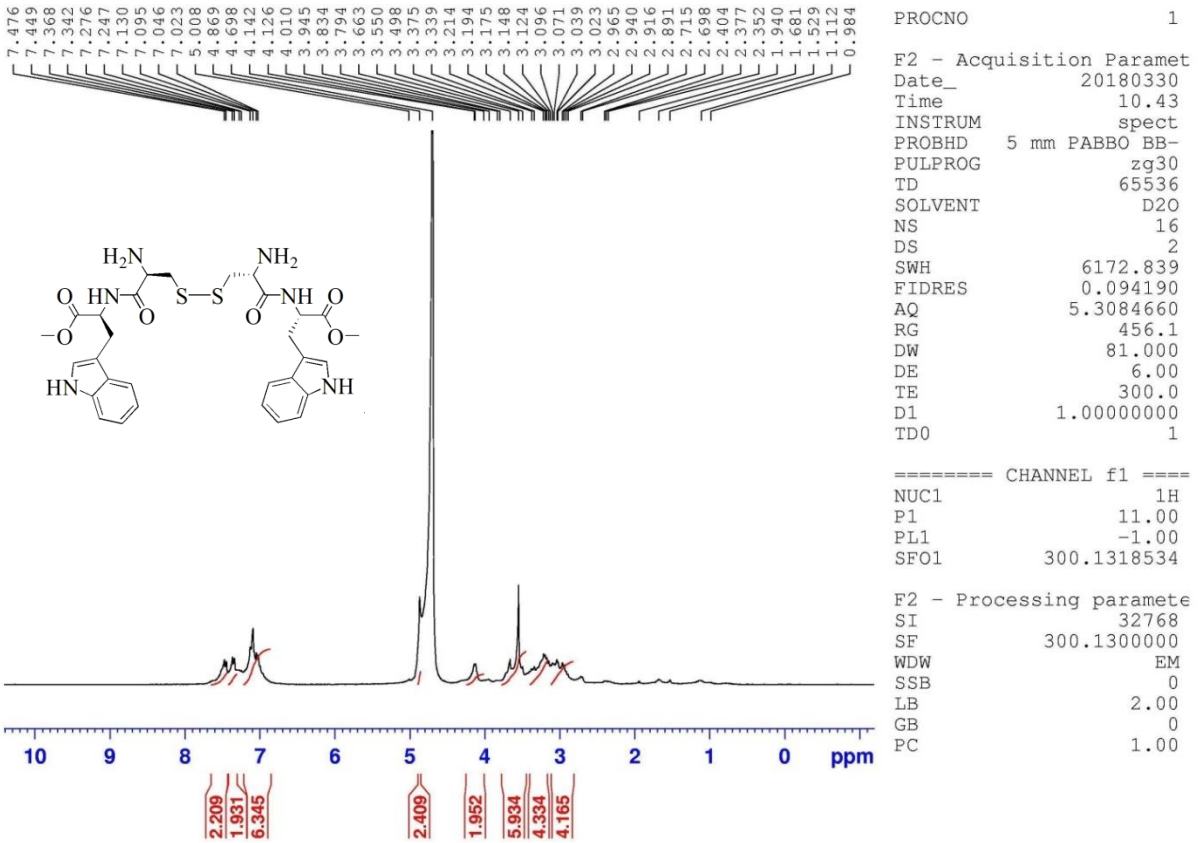


Figure S18: ^{1}H NMR spectrum (D_2O, 300 MHz) of diamine derivative **CW**.

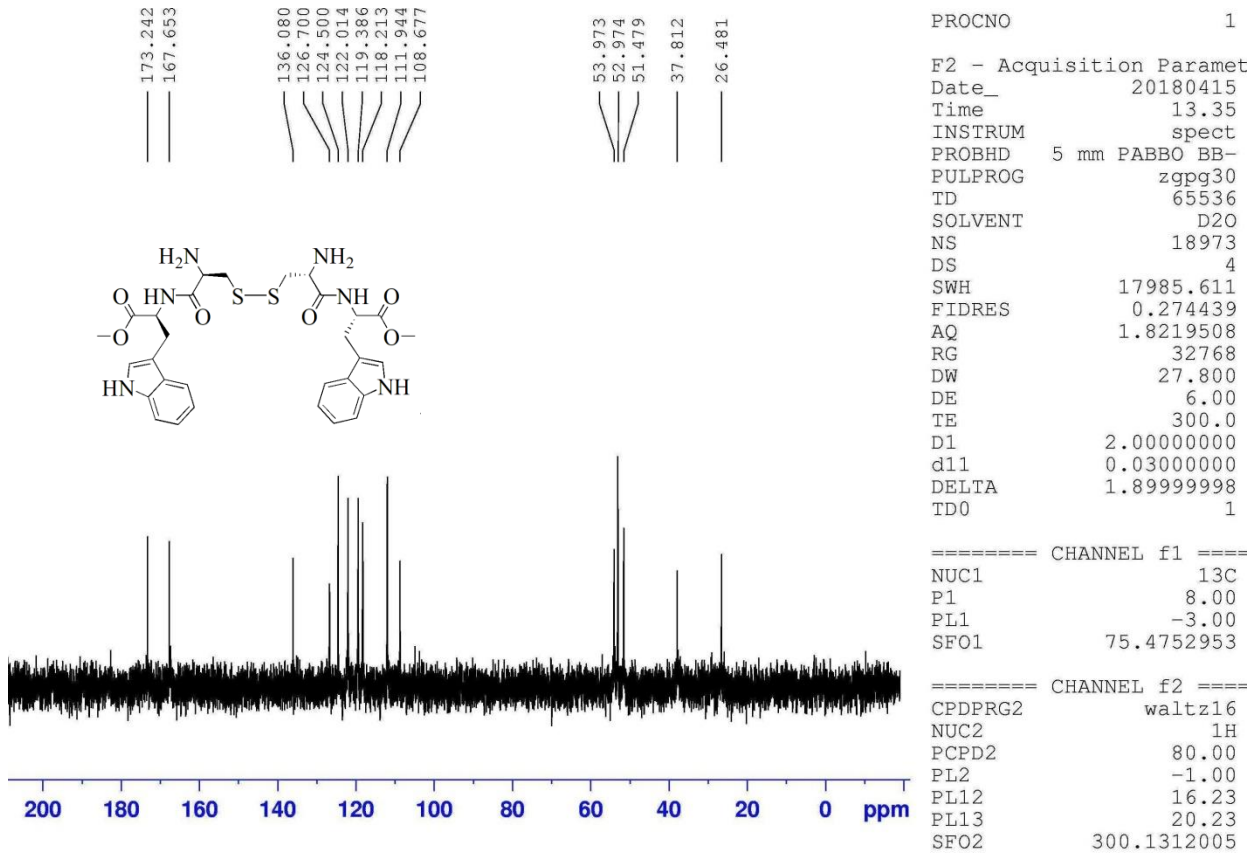


Figure S19: ^{13}C NMR spectrum (D_2O, 75 MHz) of diamine derivative **CW**.

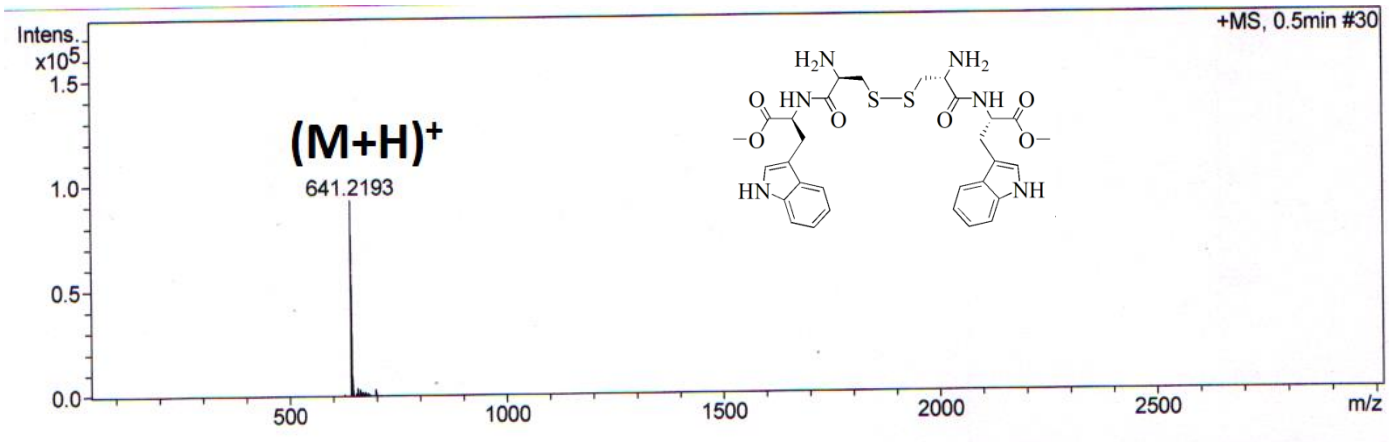


Figure S20: ESI-Mass spectrum of diamine derivative **CW**.

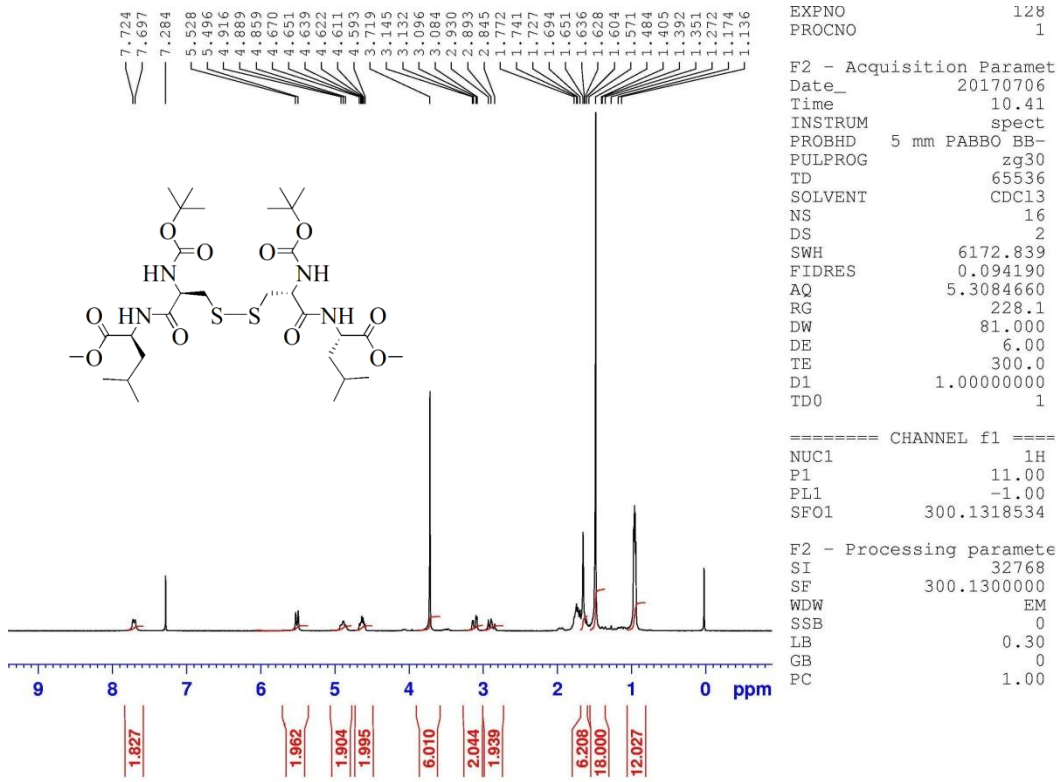


Figure S21: ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of leucine-based dipeptide **3**.

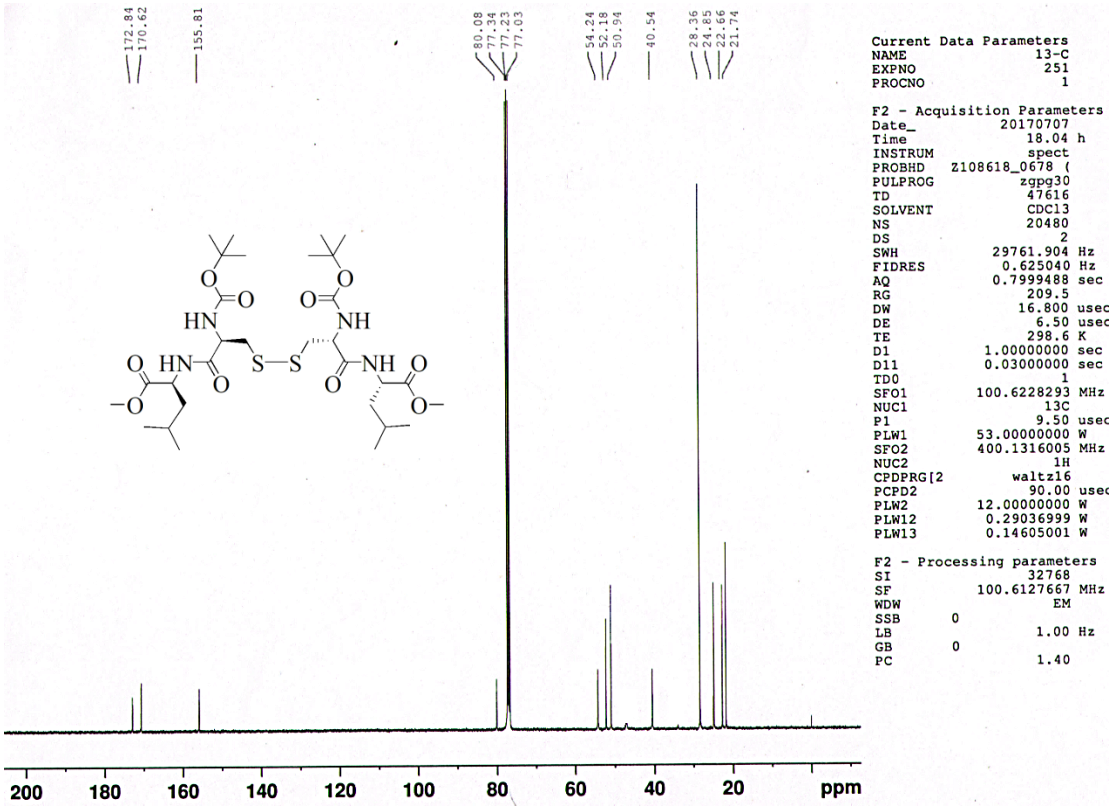


Figure S22: ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of leucine-based dipeptide **3**.

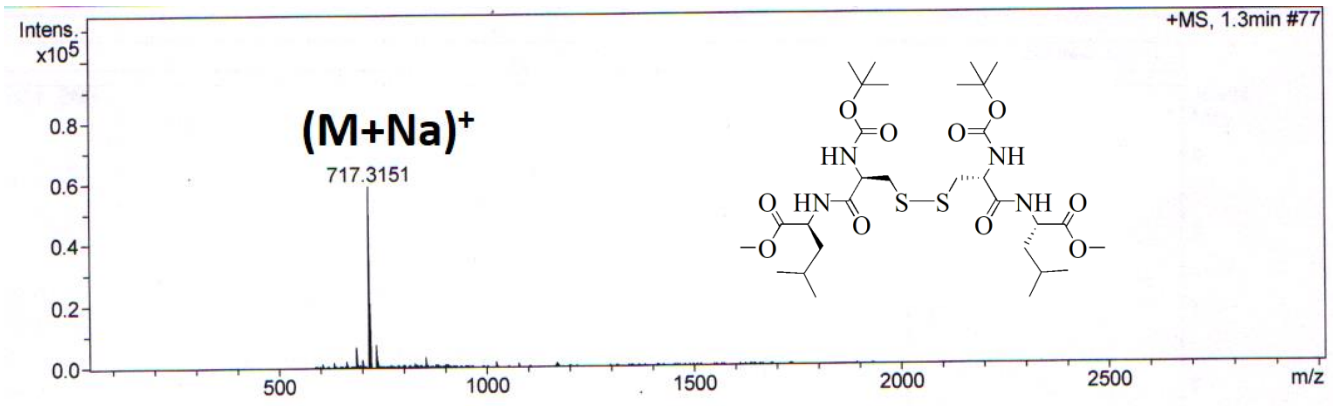


Figure S23: ESI-Mass spectrum of leucine-based dipeptide **3**.

References

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