Fast Naked-eye Detection of Zinc Ion by MolecularAssembly-assisted Polymerization of Diacetylene

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Supporting information

Peptide systhesis

The peptide derivative was prepared by solid phase peptide synthesis (SPPS) using 2-chlorotrityl chloride resin and the corresponding N-Fmoc protected amino acids with side chains properly protected. The first amino acid was loaded on the resin at the C-terminal with the loading efficiency about 1.1mmol/g. 20% piperidine in anhydrous N,N'-dimethylformamide (DMF) was used during deprotection of Fmoc group. Then the next Fmoc-protected amino acid was coupled to the free amino group using O-(Benzotriazol-1-yl)-N,N,N',N'-tetramethyluroniumhexafluorophosphate (HBTU) as the coupling reagent. The growth of the peptide chain was according to the established Fmoc SPPS protocol. At the final step, diacetylene (DA) was used to attach on the peptide. After the last coupling step, excessive reagents were removed by a single DMF wash for 5 minutes (5 mL per gram of resin), followed by five steps of washing using DCM for 1 min (5 mL per gram of resin). The peptide derivative was cleaved using 95% of trifluoroacetic acid with 2.5% of TMS and 2.5% of H_2O for 1 hours. 20 mL per gram of resin of ice-cold diethylether was then added to cleavage reagent. The resulting precipitate was centrifuged at 10,000 rpm and 4 ^oC for 10 min. Then the supernatant was decanted and the resulting solid were sent to HPLC purification, finally got about 66.2% yield.

Characterization of the peptides

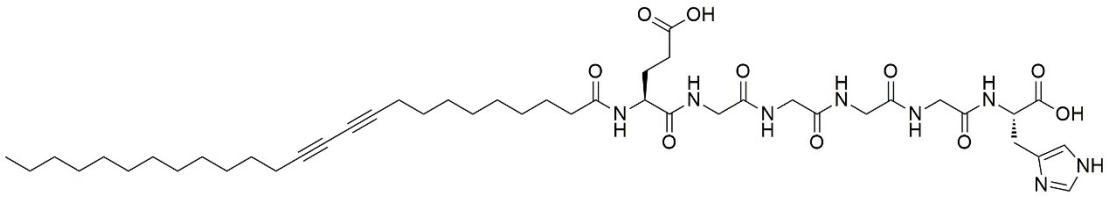

Figure S1. Chemical structure of DA-EGGGGH.

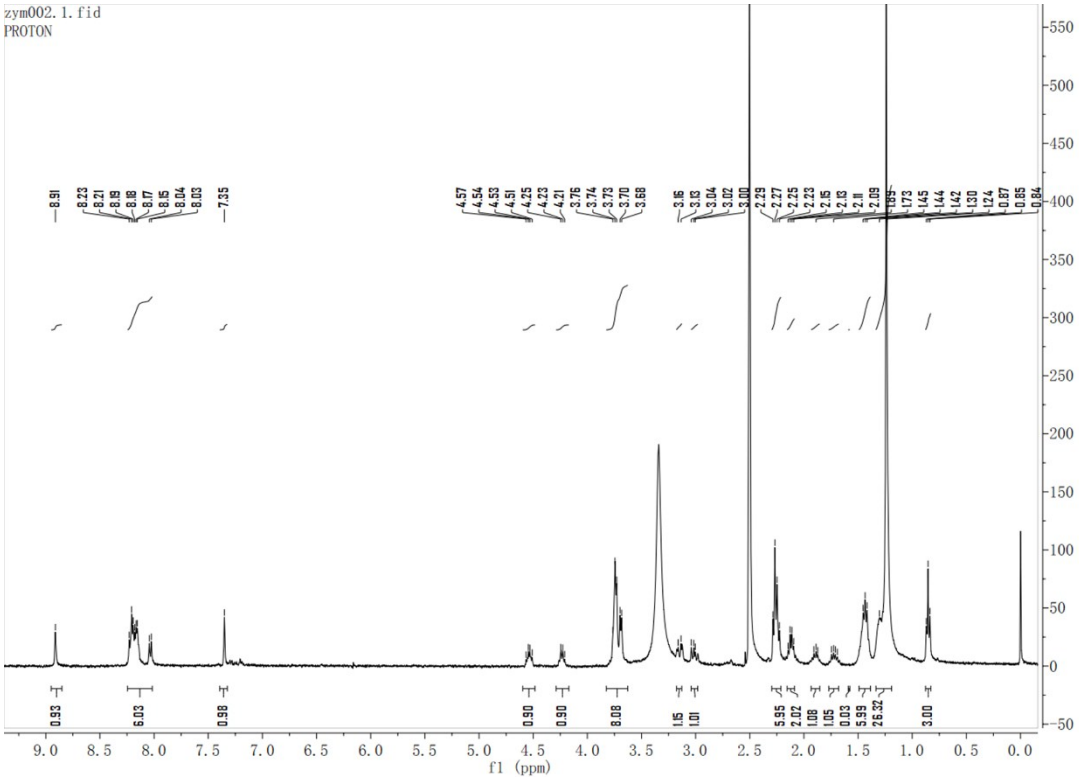

Figure S2. ^{1}H NMR spectrum of DA-EGGGGH.

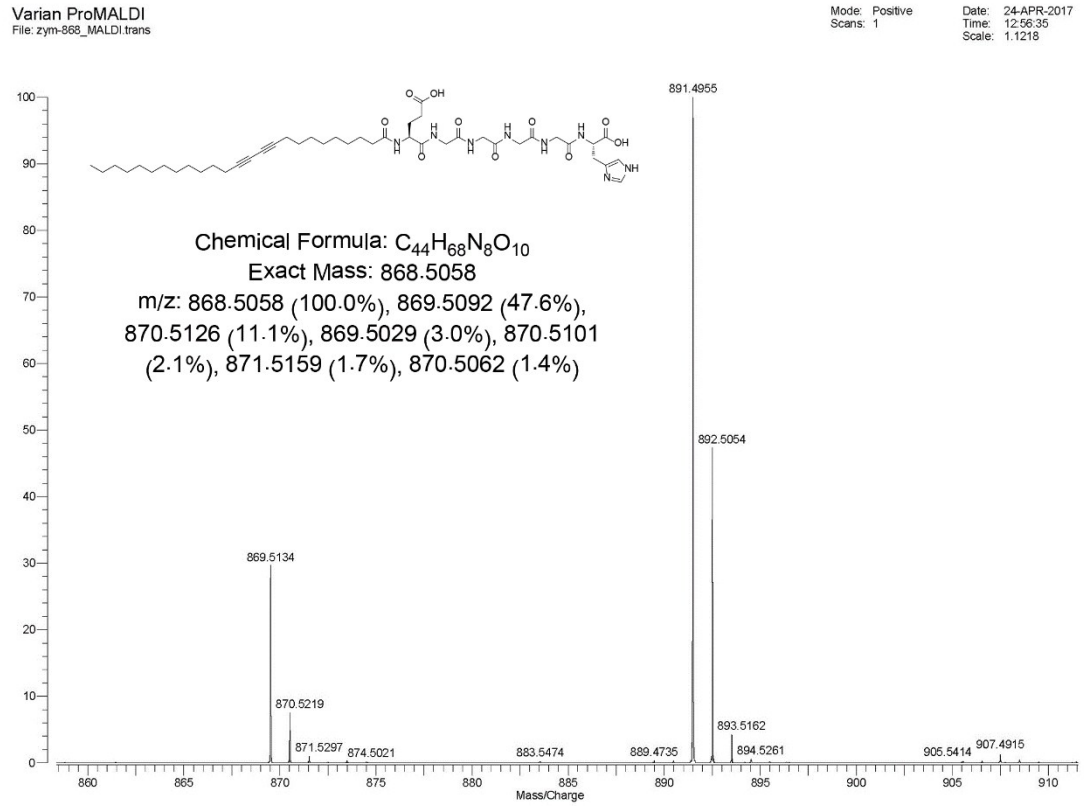

Figure S3. HR-MS spectrum of DA-EGGGGH.

^{1}H NMR (400 MHz, DMSO-d6) δ 8.91 (s, 1H), 8.25 – 8.02 (m, 6H), 7.35 (s, 1H), 4.54 (q, J = 8.1 Hz, 1H), 4.29 – 4.17 (m, 1H), 3.83 – 3.63 (m, 8H), 3.15 (d, J = 10.6 Hz, 1H), 3.04 – 2.98 (m, 1H), 2.26 (q, J = 8.9, 8.0 Hz, 6H), 2.12 (q, J = 6.9 Hz, 2H), 1.93 – 1.85 (m, 1H), 1.72 (dd, J = 14.0, 7.7 Hz, 1H), 1.49 – 1.39 (m, 6H), 1.34 – 1.19 (m, 26H), 0.85 (t, J = 6.6 Hz, 3H). HR-MS: calc. M = 868.5058, obsvd. $(M+H)^{+}$ = 869.5134, obsvd. $(M+Na)^{+}$ = 891.4955.

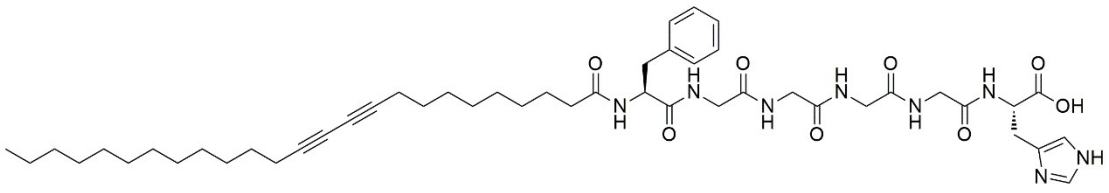

Figure S4. Chemical structure of DA-FGGGGH.

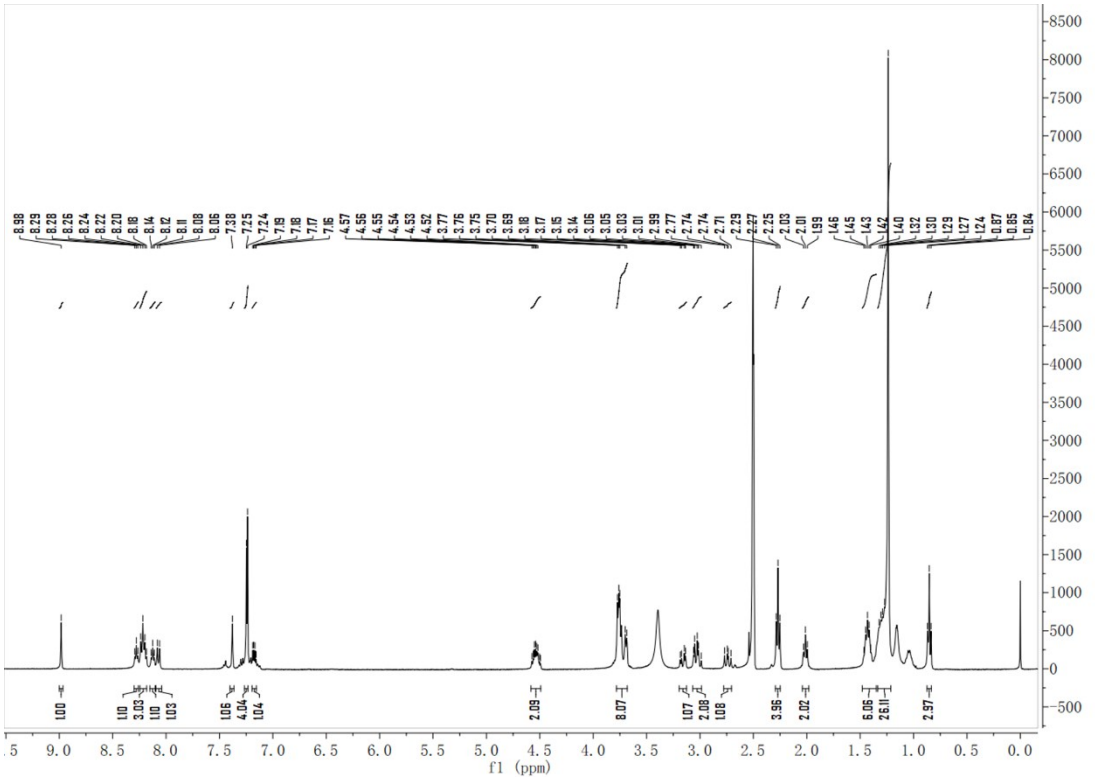

Figure S5. ^{1}H NMR spectrum of DA-FGGGGH.

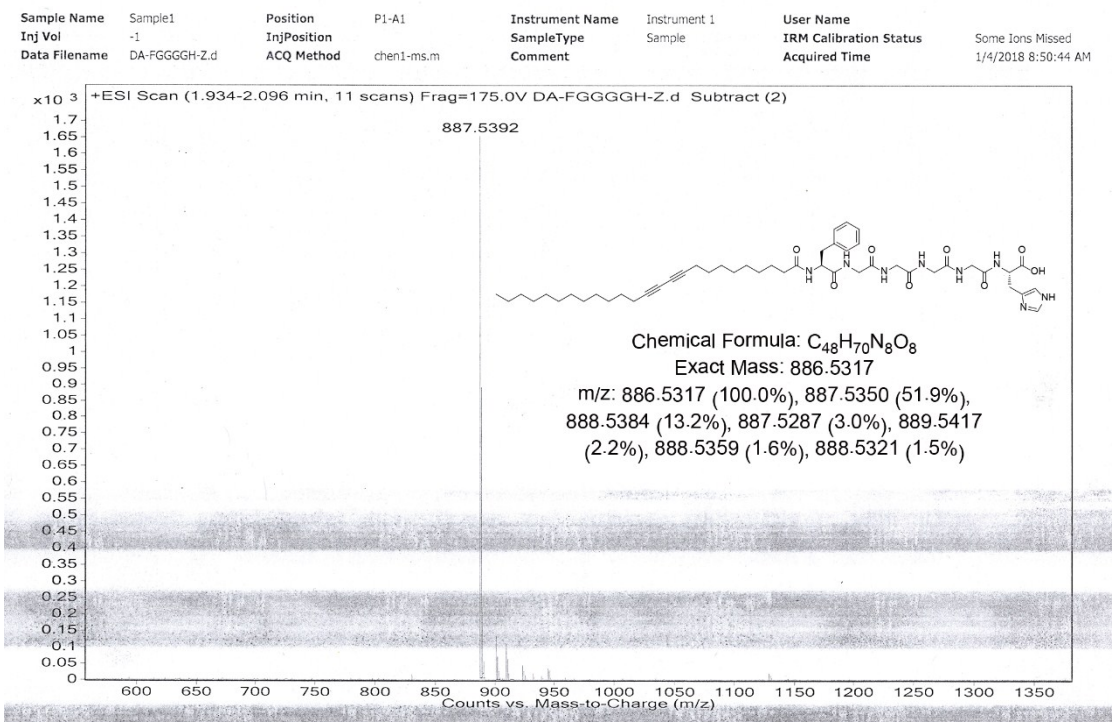

Figure S6. HR-MS spectrum of DA-FGGGGH.

^{1}H NMR (400 MHz, DMSO-d6) δ 8.98 (s, 1H), 8.28 (t, J = 5.5 Hz, 1H), 8.21 (q, J = 7.0, 5.9 Hz, 3H), 8.12 (t, J = 5.7 Hz, 1H), 8.07 (d, J = 8.3 Hz, 1H), 7.38 (s, 1H), 7.24 (d, J = 4.3 Hz, 4H), 7.17 (dd, J = 8.7, 4.3 Hz, 1H), 4.53 (tq, J = 9.8, 4.6 Hz, 2H), 3.78 – 3.68 (m, 8H), 3.16 (dd, J = 15.0, 4.7 Hz, 1H), 3.07 – 2.99 (m, 2H), 2.74 (dd, J = 13.7, 10.4 Hz, 1H), 2.27 (t, J = 6.8 Hz, 4H), 2.01 (t, J = 7.1 Hz, 2H), 1.43 (p, J = 5.9 Hz, 6H), 1.34 – 1.21 (m, 26H), 0.85 (t, J = 6.8 Hz, 3H).. HR-MS: calc. M = 886.5317, obsvd. $(M+H)^{+}$ = 887.5392.

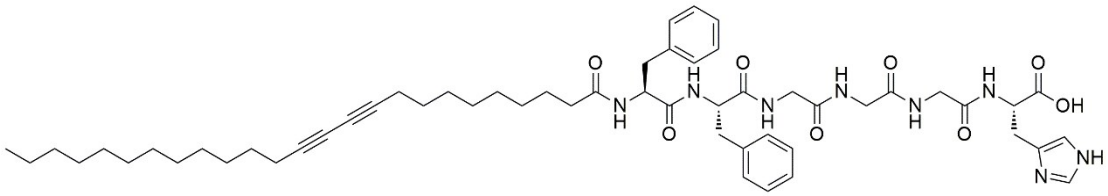

Figure S7. Chemical structure of DA-FFGGGH.

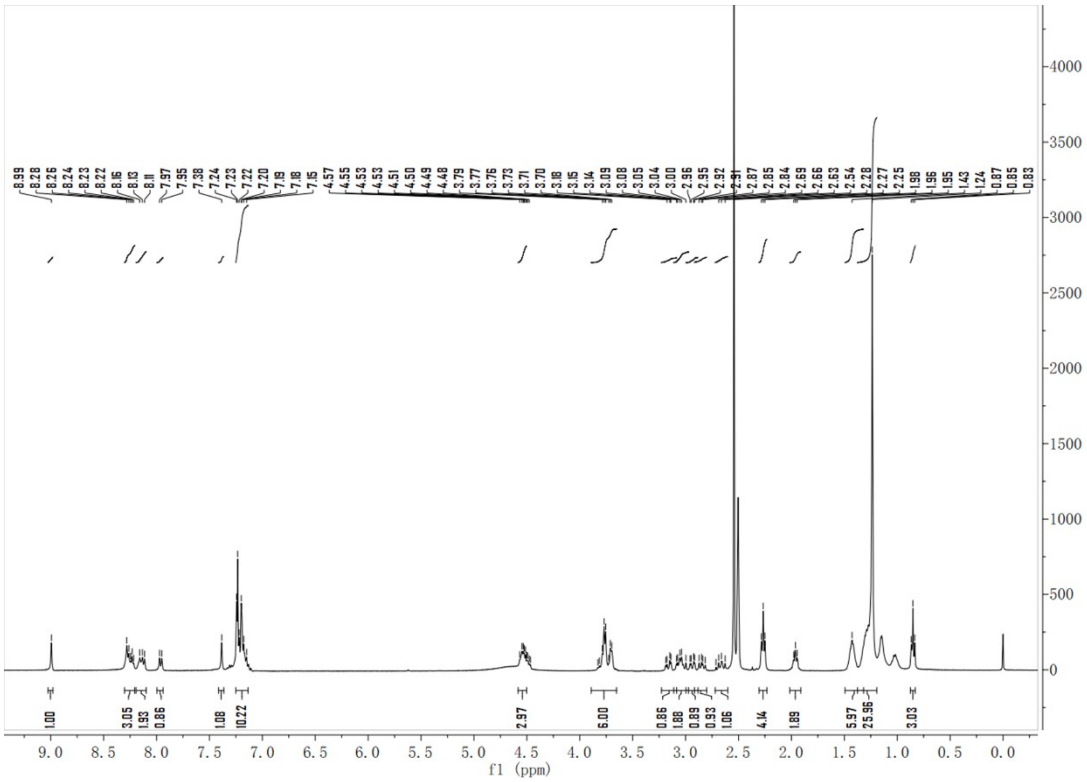

Figure S8. ^{1}H NMR spectrum of DA-FFGGGH.

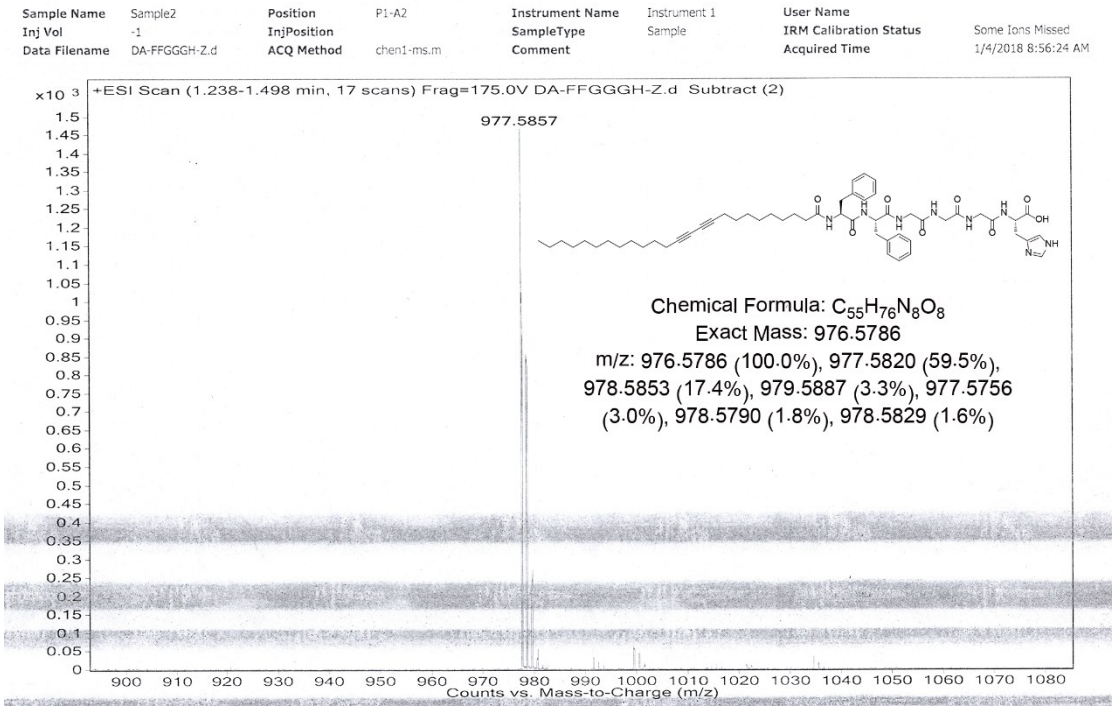

Figure S9. HR-MS spectrum of DA-FFGGGH.

^{1}H NMR (400 MHz, DMSO-d6) δ 8.99 (s, 1H), 8.30 – 8.21 (m, 3H), 8.19 – 8.10 (m, 2H), 7.96 (d, J = 8.4 Hz, 1H), 7.38 (s, 1H), 7.25 – 7.13 (m, 10H), 4.58 – 4.50 (m, 3H), 3.74 (dt, J = 22.9, 6.0 Hz, 6H), 3.23 – 3.08 (m, 1H), 3.11 – 2.97 (m, 2H), 2.94 (dd, J = 13.7, 3.7 Hz, 1H), 2.84 (dd, J = 14.0, 9.2 Hz, 1H), 2.67 (q, J = 13.7, 11.8 Hz, 1H), 2.27 (t, J = 6.7 Hz, 4H), 1.96 (t, J = 6.6 Hz, 2H), 1.43 (s, 6H), 1.38 – 1.19 (m, 26H), 0.85 (t, J = 6.7 Hz, 3H). HR-MS：calc.M = 976.5786, obsvd. $(M+H)^{+}$ = 977.5857

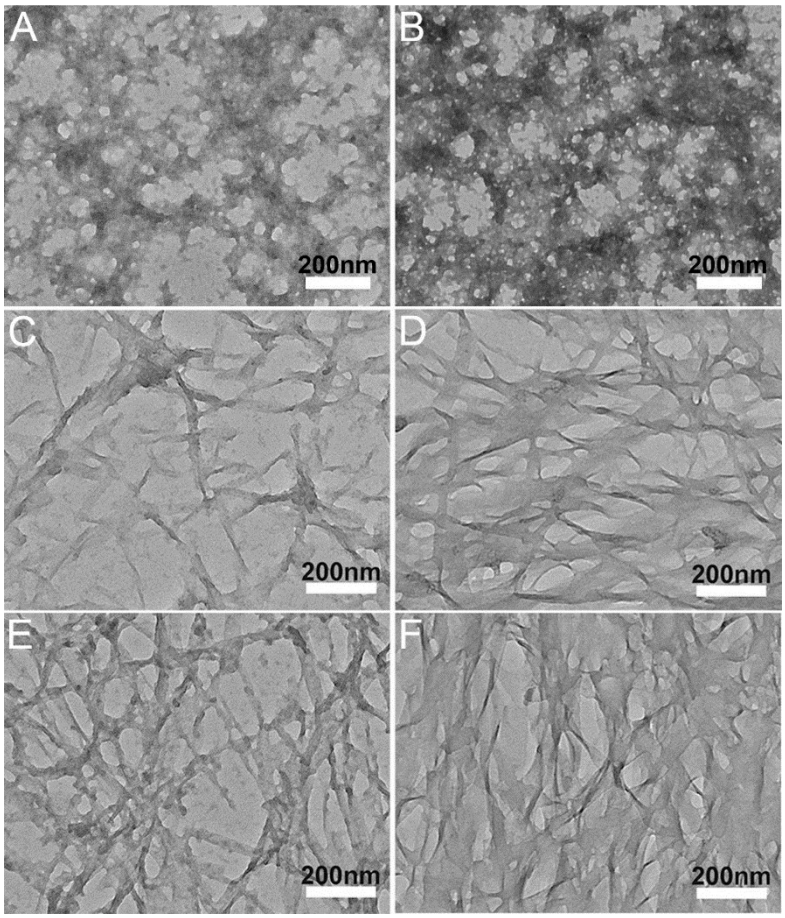

Figure S10. TEM of 0.5 wt% DA-EGGGGH A) before and B) after irradiation of UV. TEM images of 0.5 wt% DA-EGGGGH with 0.2 equiv. of zinc ions C) before and D) after irradiation of UV. TEM of 0.5 wt% DA-EGGGGH with 0.5 equiv. of zinc ions E) before and F) after irradiation of UV.

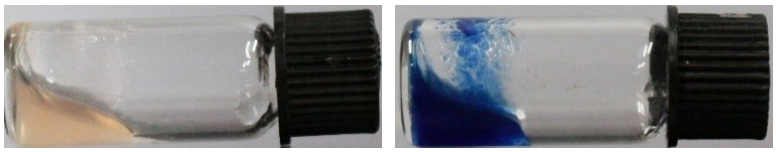

Figure S11. Optical images of 0.5 wt% DA-EGGGGH with 0.5 equiv. of zinc ions before and after UV.

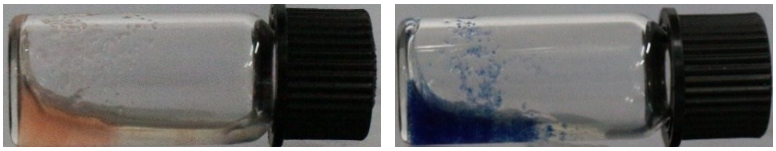

Figure S12. Optical images of 0.5 wt% DA-EGGGGH with 0.2 equiv. of zinc ions before and after UV.

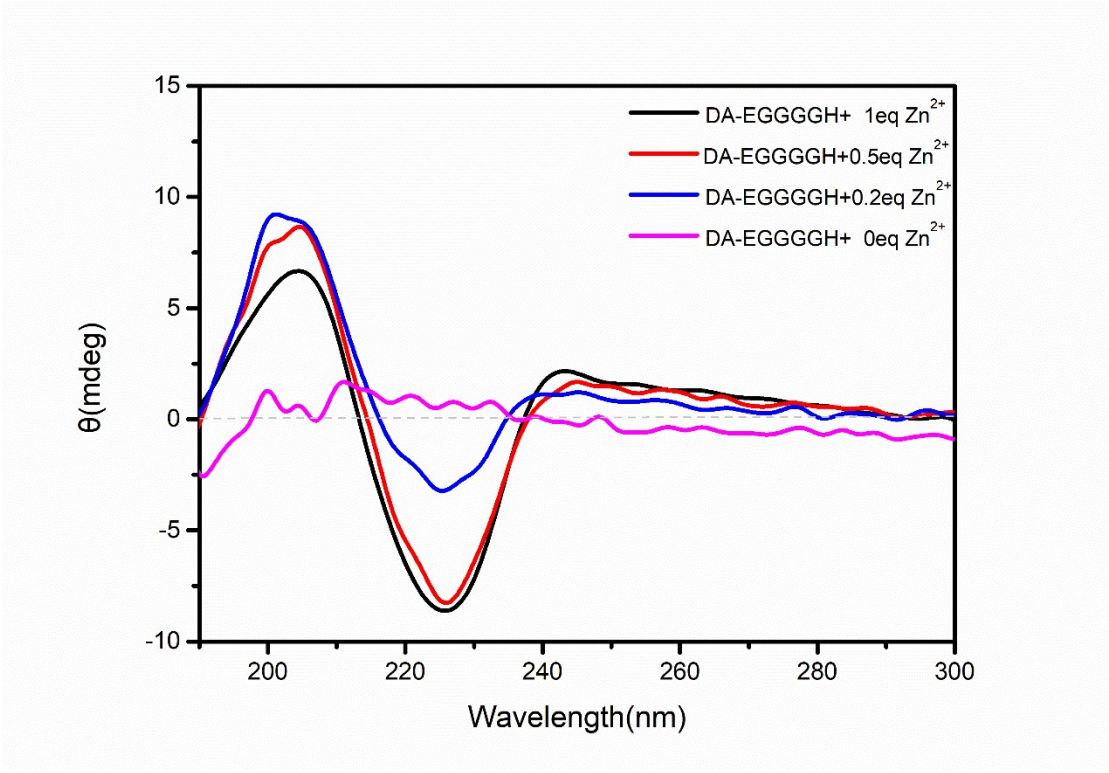

Figure S13. CD spectra of hydrogel of ***1*** with different concentration of Zn^{2+} before irradiation.

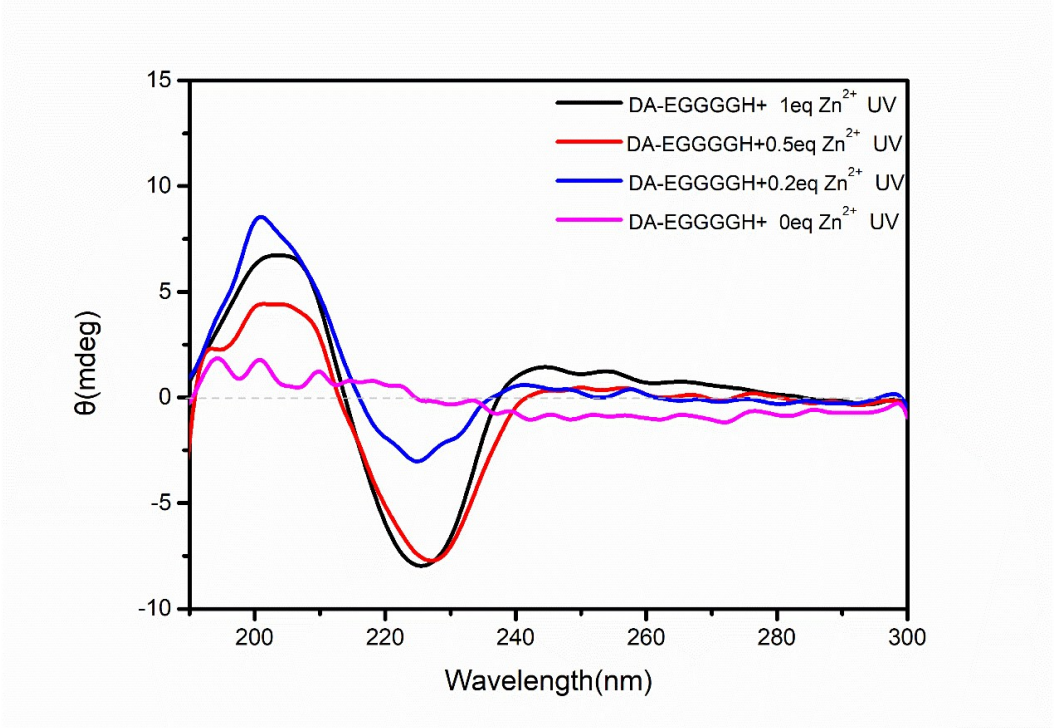

Figure S14. CD spectra of hydrogel of ***1*** with different concentration of Zn^{2+} after

irradiation.

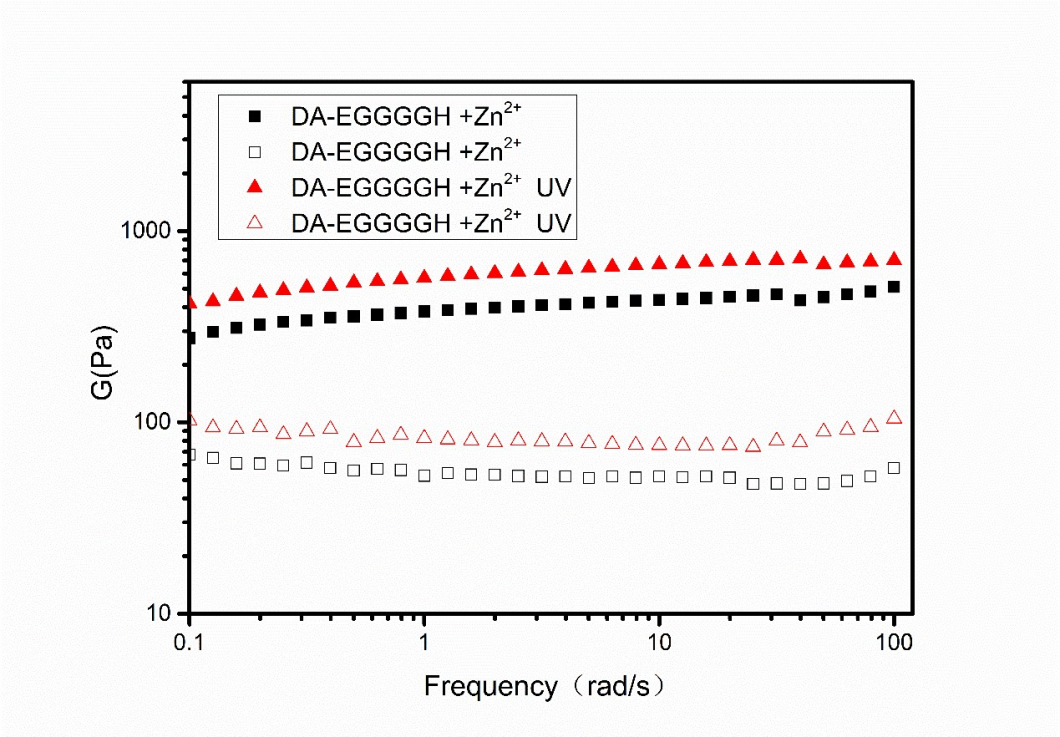

Figure S15. Oscillatory rheology dynamic frequency sweeps of hydrogel of ***1*** with 0.5 equiv. of Zn^{2+} before and after irradiation.

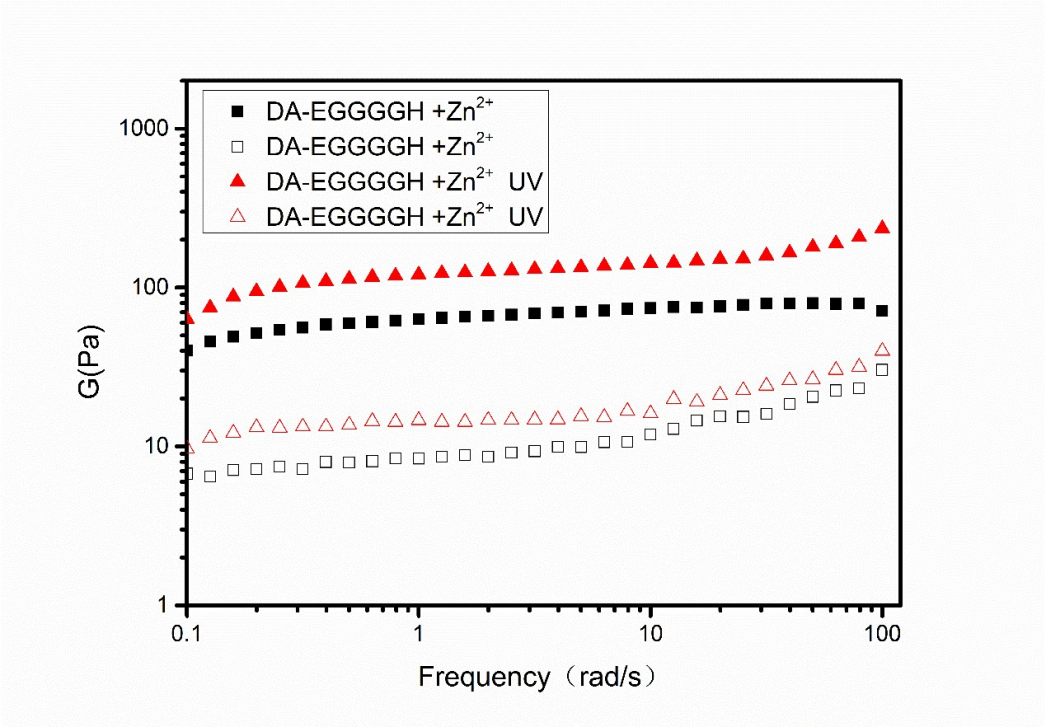

Figure S16. Oscillatory rheology dynamic frequency sweeps of hydrogel of ***1*** with 0.2

equiv. of Zn^{2+} before and after irradiation.

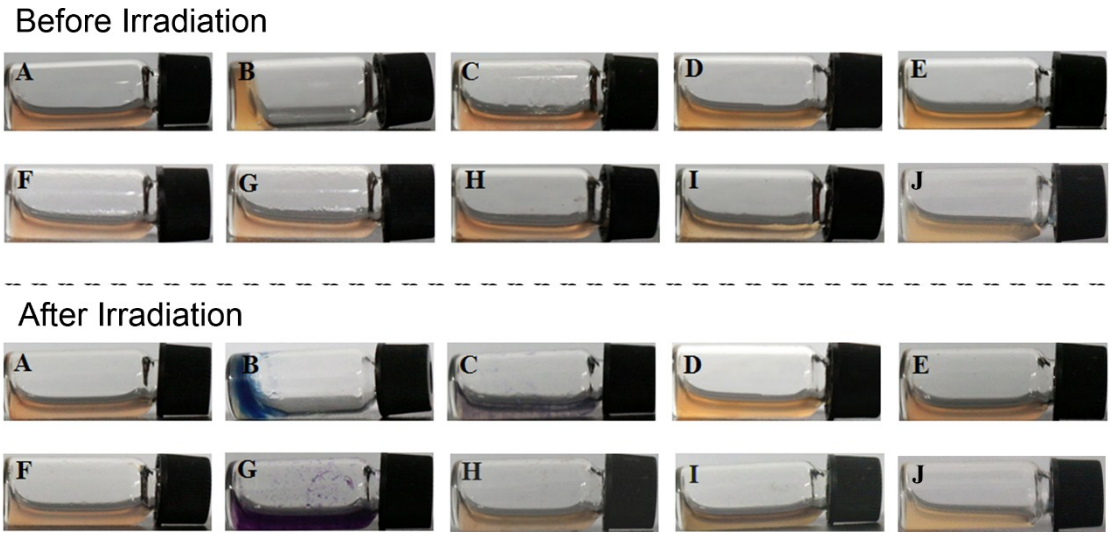

Figure S17. Optical images of solutions of 0.5 wt% DA-EGGGGH with the addition of 1.0 equiv. of A) Sr^{2+}, B) Zn^{2+}, C) Cu^{2+}, D) Ca^{2+}, E) Pb^{2+}, F) Ni^{2+}, G) Mn^{2+}, H) Fe^{2+}, I) Fe^{3+} and J) Cd^{2+} before and after UV.

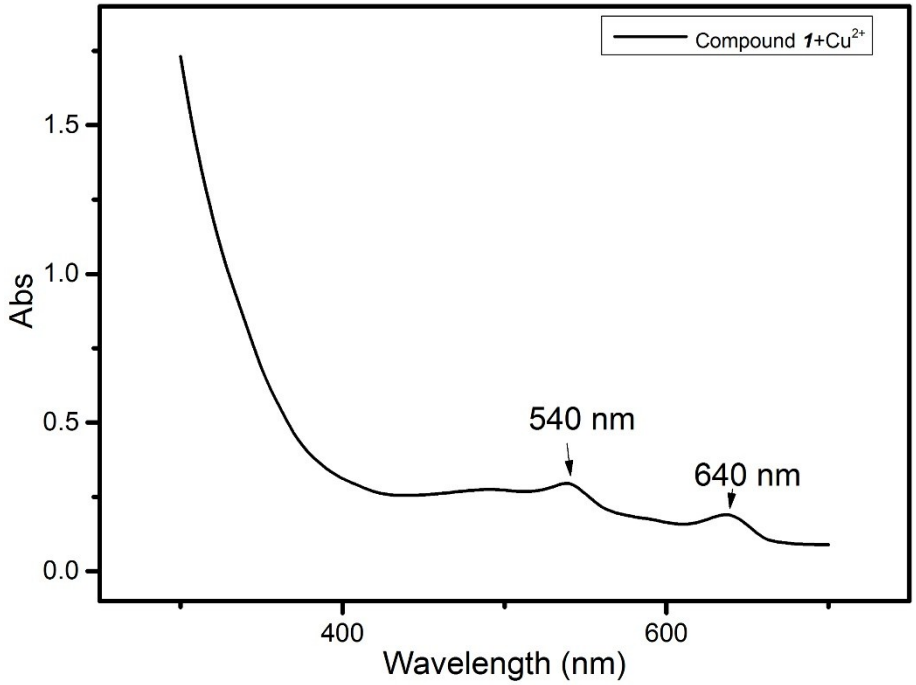

Figure S18. UV-Vis absorption spectrum of sol of ***1*** + Cu^{2+} after irradiation.

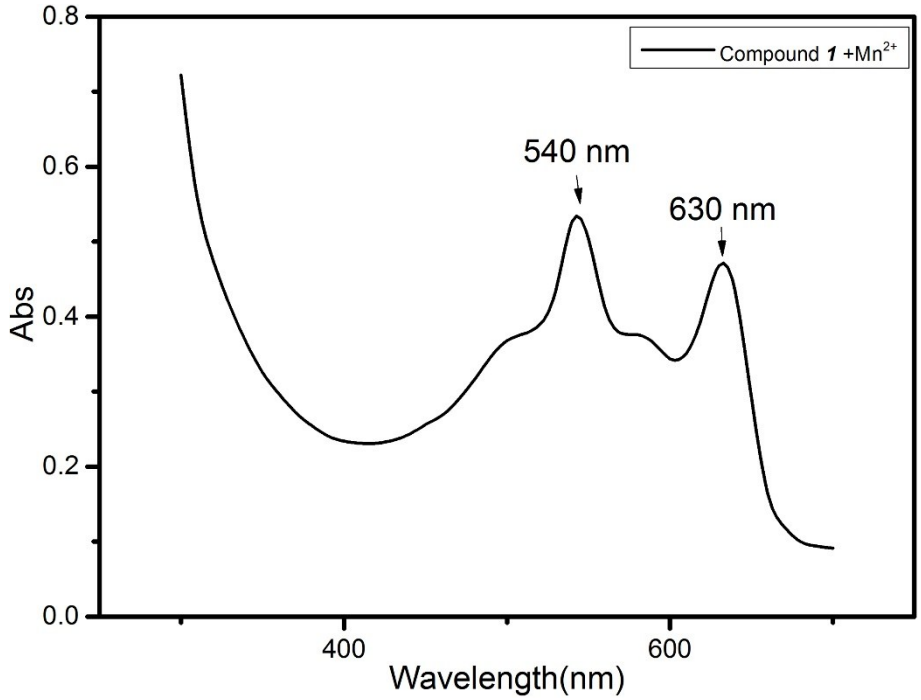

Figure S19. UV-Vis absorption spectrum of sol of ***1*** + Mn^{2+} after irradiation.