

Supporting Information

Preparation of peptide: Peptides Ada-G^{DFDF}Y and Ada-G^{DFDF}pY were 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 by a tert-butyl group. The first amino acid (Fmoc-D-Tyr(OtBu)-OH or Fmoc-D-Tyr(H₂PO₃)-OH) was loaded on the resin at the C-terminal with the loading efficiency about 1.0 mmol/g. 20% piperidine in anhydrous N,N'-dimethylformamide (DMF) was used during the 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, Ada group was used to couple with the peptide. After the last coupling step, excessive reagents were removed by a single DMF wash for 5 min (5 ml per gram of resin), followed by five steps of washing using dichloromethane (DCM) for 2 min (5 ml per gram of resin). The peptide derivatives were cleaved from the resin by ice-cold reagent B (95% Trifluoroacetic acid, 2.5% Triisopropylsilane, 2.5% double-distilled water) and the mixture was stirred at room temperature for 30 min, filtered, and poured into ice-cold diethylether. The resulting precipitate was centrifuged for 10 min at 4°C at 10,000 rpm. Afterward the supernatant was decanted and dissolved in double-distilled (dd) water and lyophilized.

Characterization of Ada-G^{DFDF}Y: ¹H NMR (400 MHz, DMSO) δ 8.17 (dd, *J* = 7.5, 4.9 Hz, 2H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.84 (t, *J* = 5.8 Hz, 1H), 7.27 – 7.10 (m, 9H), 7.02 (d, *J* = 8.1 Hz, 2H), 6.66 (d, *J* = 8.0 Hz, 2H), 4.51 (m, 2H), 4.37 (dd, *J* = 13.4, 7.3 Hz, 1H), 4.10 (d, *J* = 4.4 Hz, 1H), 3.66 (dd, *J* = 16.5, 5.5 Hz, 1H), 3.50 (dd, *J* = 16.5, 5.3 Hz, 1H), 3.17 (d, *J* = 3.4 Hz, 2H), 3.05 – 2.90 (m, 3H), 2.86 – 2.74 (m, 2H), 2.67 (dd, *J* = 13.4, 9.4 Hz, 1H), 1.86 (d, *J* = 13.7 Hz, 5H), 1.59 (dd, *J* = 31.8, 11.5 Hz, 11H). MS: calc. M⁺ = 708.3523, obsvd. (M+H)⁺ = 709.3595.

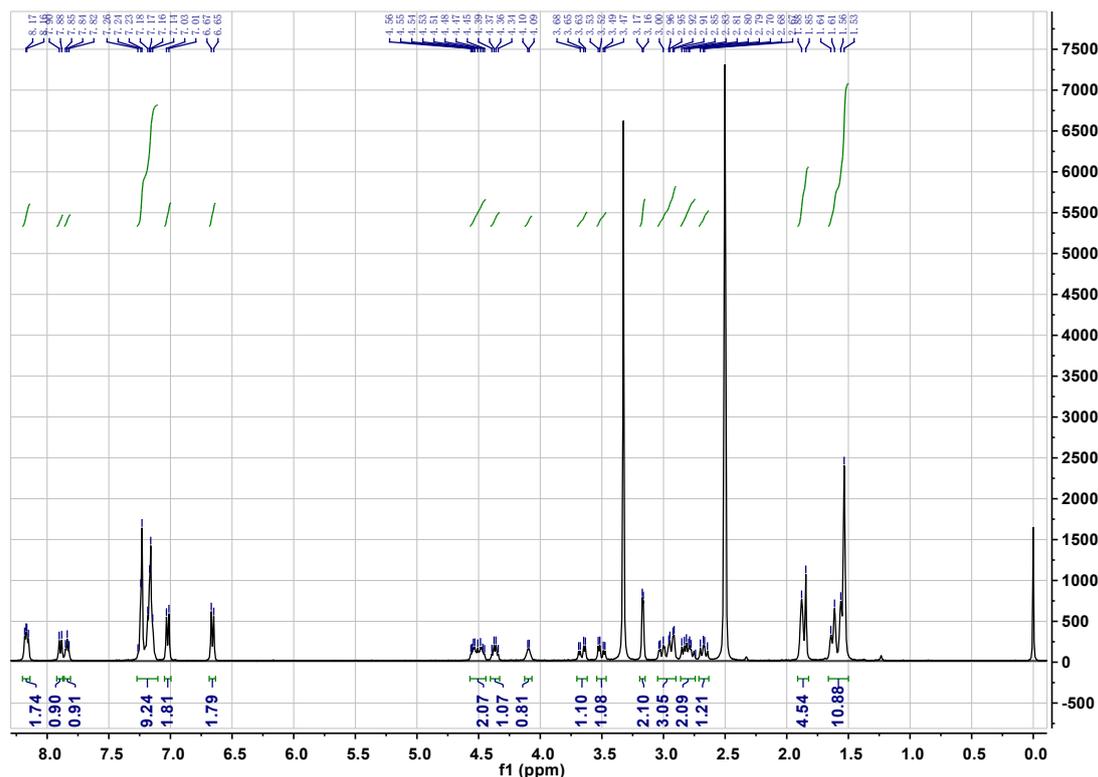


Figure S1. ^1H NMR of Ada-G^DF^DF^DY

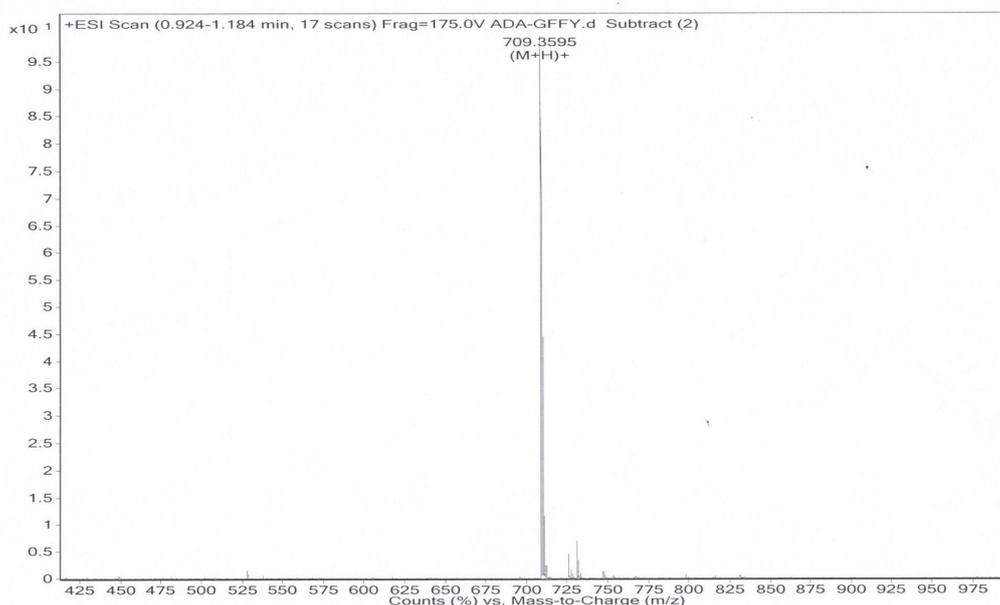


Figure S2. HR-MS of Ada-G^DF^DF^DY

Characterization of Ada-G^DF^DF^DpY: ^1H NMR (400 MHz, DMSO) δ 8.27 (d, J = 7.4 Hz, 1H), 8.18 (d, J = 8.2 Hz, 1H), 7.92 (d, J = 8.1 Hz, 1H), 7.84 (t, J = 5.0 Hz, 1H), 7.27 – 7.13 (m, 11H), 7.07 (d, J = 8.1 Hz, 2H), 4.59 – 4.39 (m, 3H), 3.66 (dd, J = 16.7, 5.7 Hz, 1H), 3.50 (dd, J = 16.6, 5.2 Hz, 2H), 3.03 (dd, J = 13.8, 4.1 Hz, 2H), 2.93 (m, 2H), 2.80 (dd, J = 13.8, 9.9 Hz, 1H), 2.67 (dd, J = 13.5, 9.7 Hz, 1H), 1.86 (d, J = 13.4 Hz, 5H), 1.59 (dd, J = 31.8, 11.1 Hz, 11H). MS: calc. M^+ = 788.3168, obsvd. $(M+H)^+$ = 789.3262.

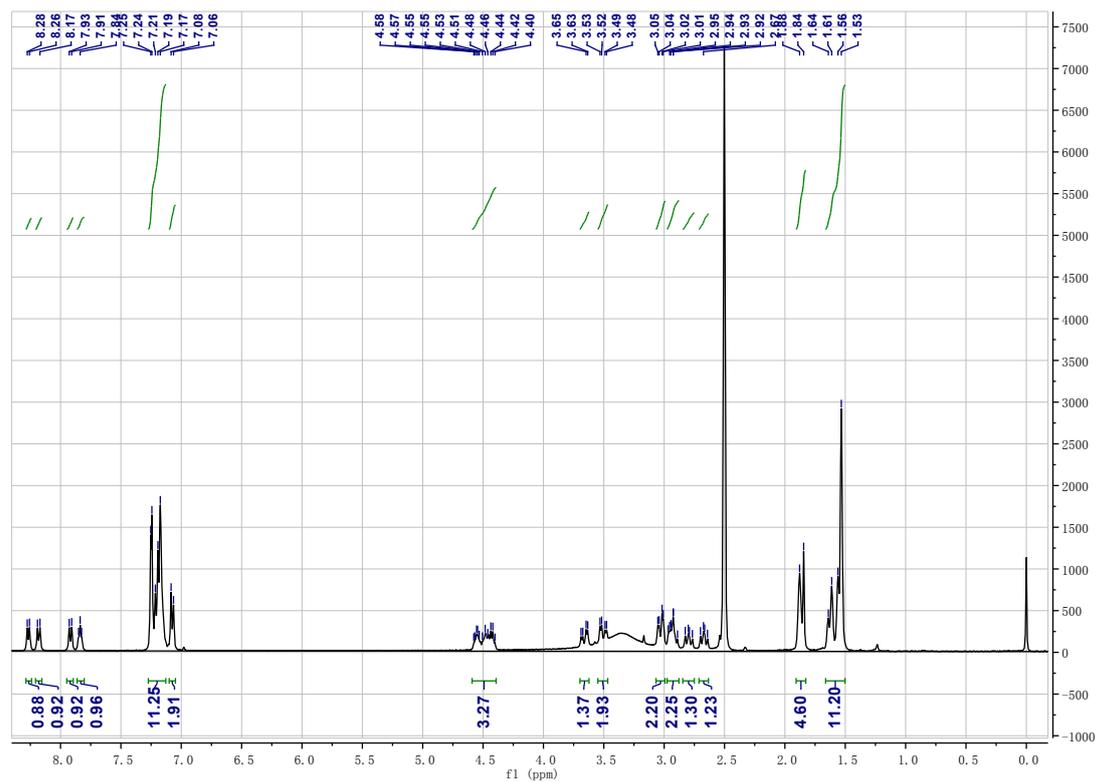


Figure S3. ^1H NMR of Ada-G^DF^DF^DpY

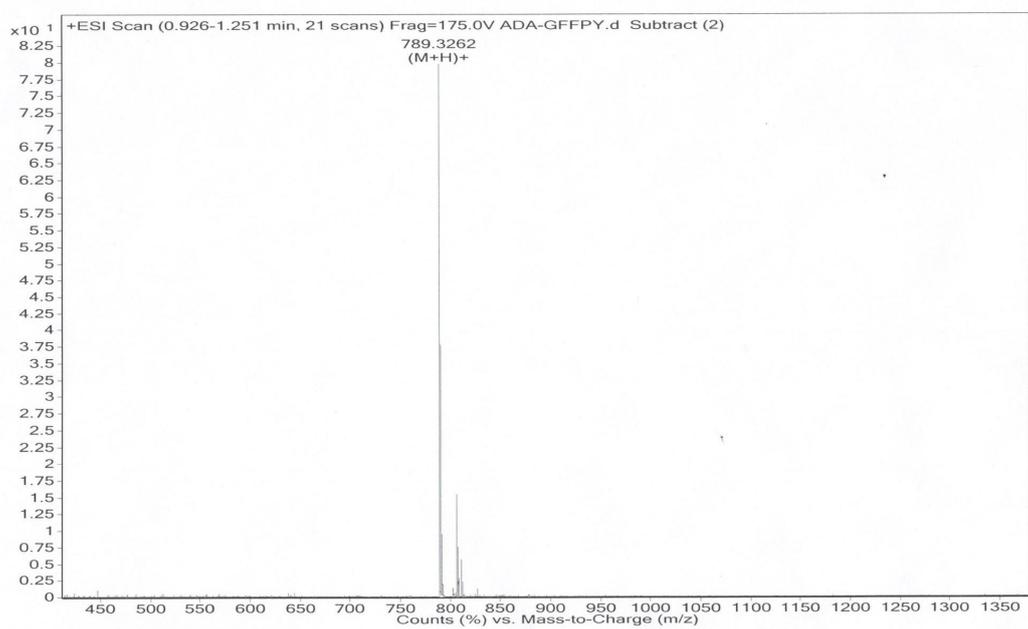


Figure S4. HR-MS of Ada-G^DF^DF^DpY

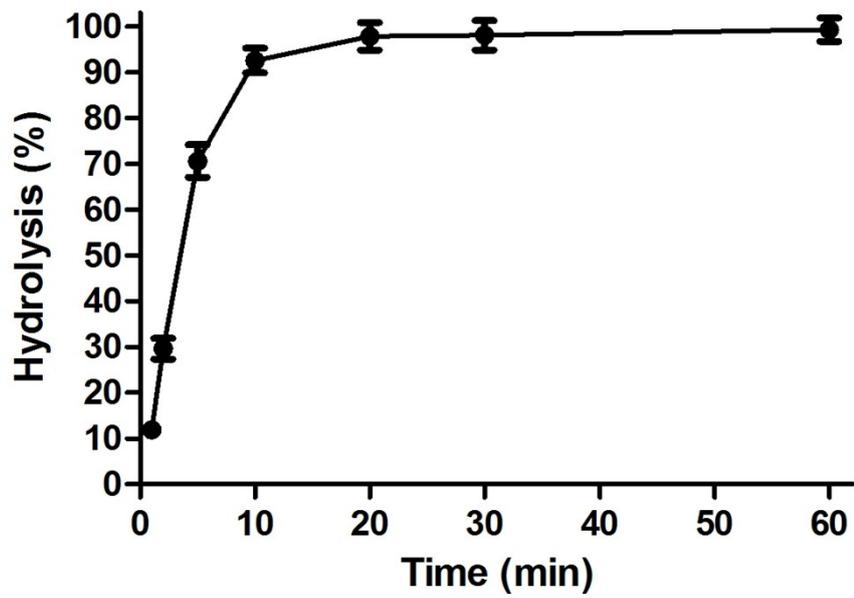


Figure S5. The hydrolysis rate of peptide Ada-G^DF^DF^DpY

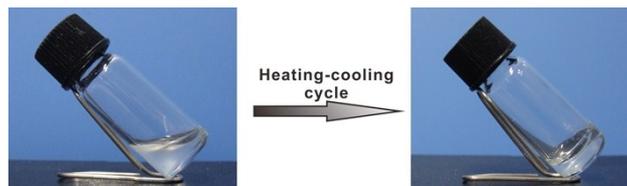


Figure S6. The optical picture of the turbid solution to transparent hydrogel

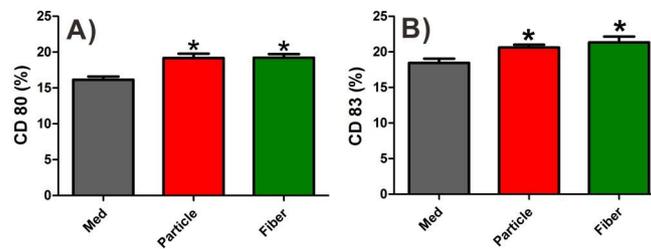


Figure S7. Flow cytometry of makers of DC maturation A) CD80 B) CD83

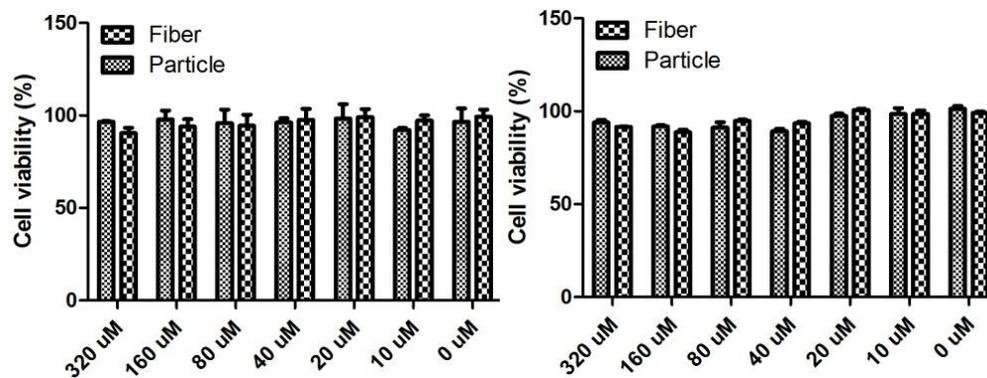


Figure S8. Biocompatibility of compounds

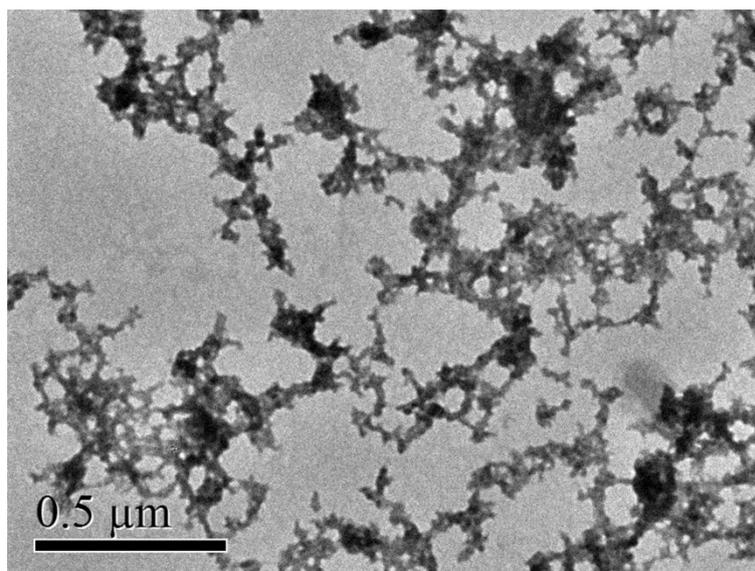


Figure S-9. The TEM image of the gel acquired from the nanoparticles after heating-cooling process

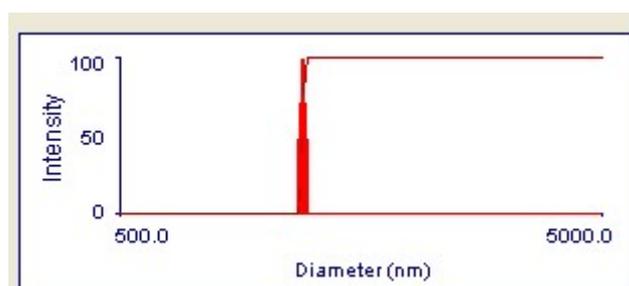


Figure S-10. The DLS of nanomaterials formed by enzyme catalytic