

Supporting Information

Preparation of peptides: All peptides were prepared by standard solid phase peptide synthesis (SPPS) by using 2-chlorotrityl chloride resin and the corresponding N-Fmoc protected amino acids with side chains properly protected. Firstly the C-terminal of the first amino acid was conjugated on the resin. Anhydrous N,N'-dimethyl formamide (DMF) containing 20% piperidine was used to remove Fmoc protected group. To couple the next amino acid to the free amino group, O-Benzotriazol-1-yl-N,N,N',N'-tetramethyluronium hexafluorophosphate (HBTU) was used as coupling reagent. Peptides chain was extended according the standard SPPS protocol. NSAIDs were used at the final step. Lastly, 95% TFA containing 2.5% H₂O and 2.5% TIS was used to cleave peptides derivative from resin and the mixture was filtered. Ice cold diethylether was poured into filtrate concentrated by rotary evaporation. The precipitate was centrifuged for 5 min at 5000 rpm speed. The solid was dried by vacuum pump and then purified by HPLC to obtain the pure compounds.

Characterization of the gelators:

Compound Npx-G^DF^DF^DY: ¹H NMR (400 MHz, DMSO) δ 12.70 (s, 1H), 9.22 (s, 1H), 8.26 – 8.05 (m, 3H), 7.93 (d, *J* = 8.5 Hz, 1H), 7.80 – 7.66 (m, 3H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.13 (dt, *J* = 50.7, 13.7 Hz, 13H), 6.66 (d, *J* = 7.4 Hz, 2H), 4.57 – 4.34 (m, 3H), 3.85 (s, 2H), 3.60 (d, *J* = 3.7 Hz, 1H), 3.34 (s, 2H), 3.01 – 2.61 (m, 6H), 1.37 (d, *J* = 6.5 Hz, 3H). MS: calc. *M* = 744.83, obsvd. (*M* + H)⁺ = 745.3239, (*M* + Na)⁺ = 767.3042.

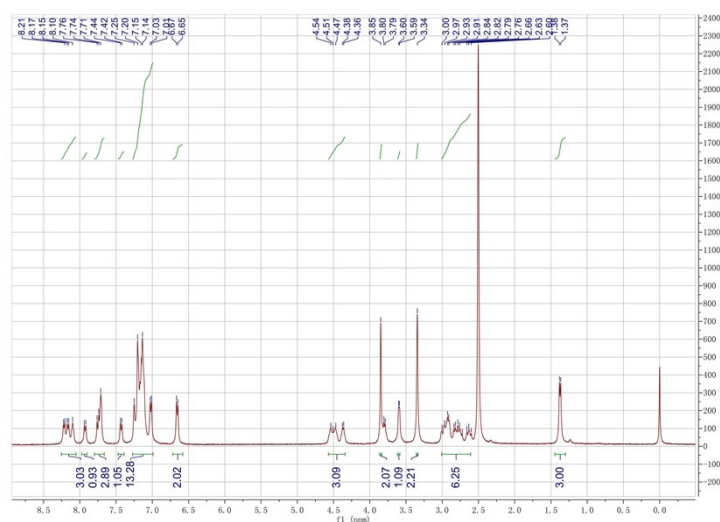


Fig. S1. ^1H NMR spectrum of Npx- $\text{G}^{\text{D}}\text{F}^{\text{D}}\text{F}^{\text{D}}\text{Y}$

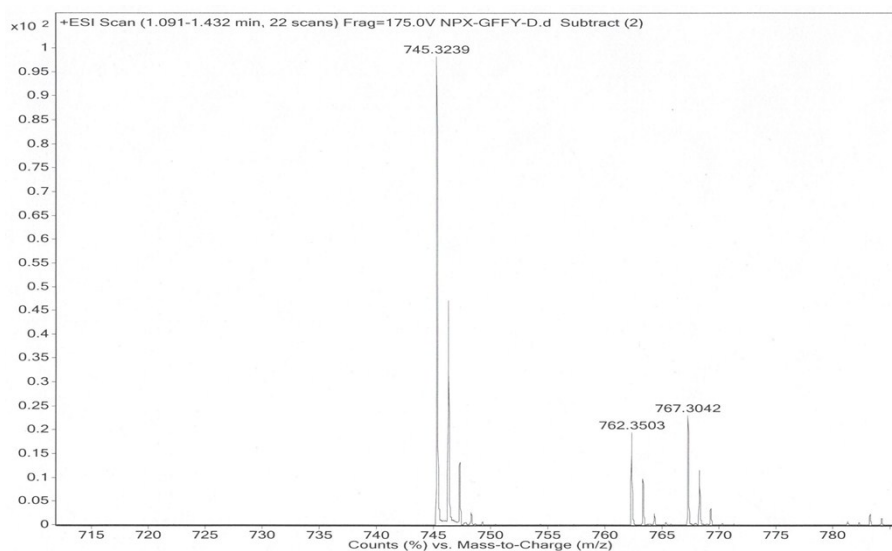


Fig. S2. HR-MS spectrum of Npx- $\text{G}^{\text{D}}\text{F}^{\text{D}}\text{F}^{\text{D}}\text{Y}$

Compound Fbp- $\text{G}^{\text{D}}\text{F}^{\text{D}}\text{F}^{\text{D}}\text{Y}$: ^1H NMR (400 MHz, DMSO) δ 9.22 (s, 1H), 8.32 – 7.90 (m, 4H), 7.25 (ddd, J = 79.3, 44.2, 8.3 Hz, 19H), 6.66 (d, J = 6.8 Hz, 2H), 4.61 – 4.33 (m, 3H), 3.82 – 3.54 (m, 3H), 3.05 – 2.63 (m, 6H), 1.33 (d, J = 6.3 Hz, 3H). MS: calc. M = 758.83, obsvd. $(M + \text{H})^+$ = 759.3194, $(M + \text{Na})^+$ = 781.3004.

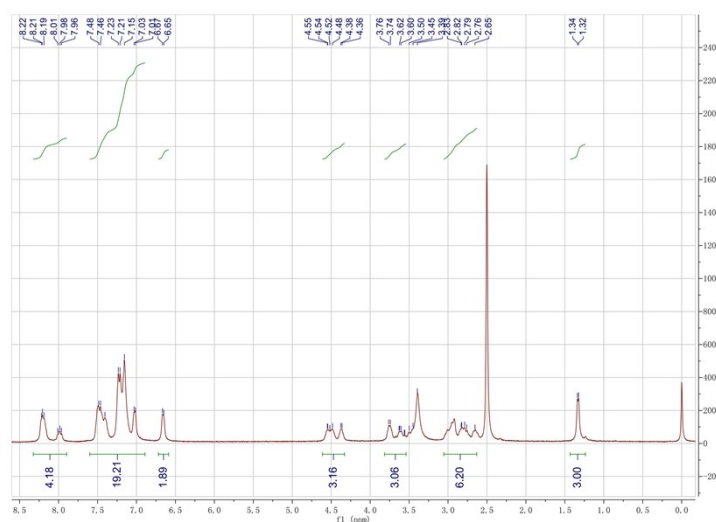


Fig. S3. ^1H NMR spectrum of Fbp-G^DF^DF^DY

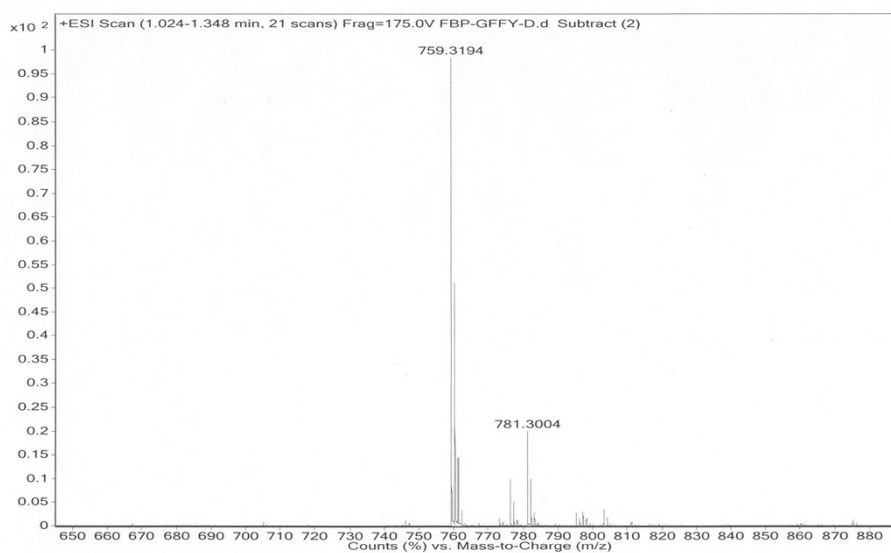


Fig. S4. HR-MS spectrum of Fbp-G^DF^DF^DY

Compound Car-G^DF^DF^DY: ^1H NMR (400 MHz, DMSO) δ 11.32 (s, 1H), 9.19 (s, 1H), 8.56 – 8.30 (m, 2H), 8.20 – 7.96 (m, 3H), 7.86 (d, J = 8.3 Hz, 1H), 7.51 – 7.30 (m, 3H), 7.26 – 7.01 (m, 11H), 6.89 (t, J = 6.3 Hz, 2H), 6.65 (d, J = 8.3 Hz, 2H), 4.62 – 4.35 (m, 3H), 3.83 – 3.41 (m, 4H), 2.98 (dd, J = 9.7, 4.0 Hz, 1H), 2.78 – 2.56 (m, 3H), 2.33 (t, J = 11.5 Hz, 1H), 1.35 (d, J = 5.8 Hz, 3H). MS: calc. M = 788.29, obsvd. M = 788.2830.

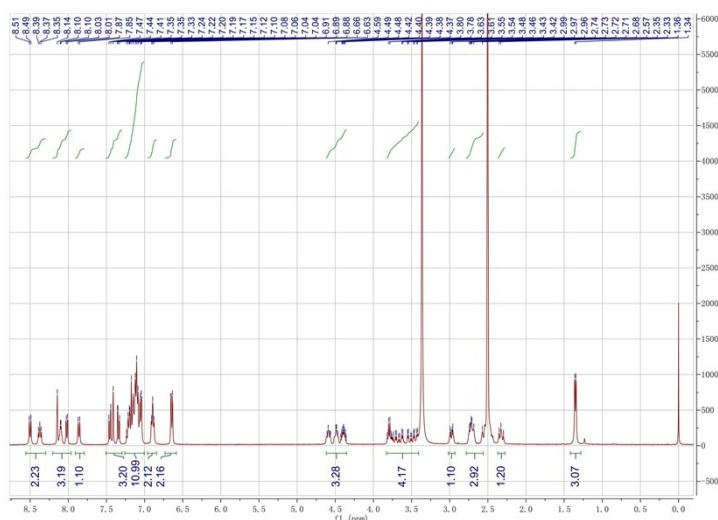


Fig. S5. ^1H NMR spectrum of Car-G^DF^DF^DY

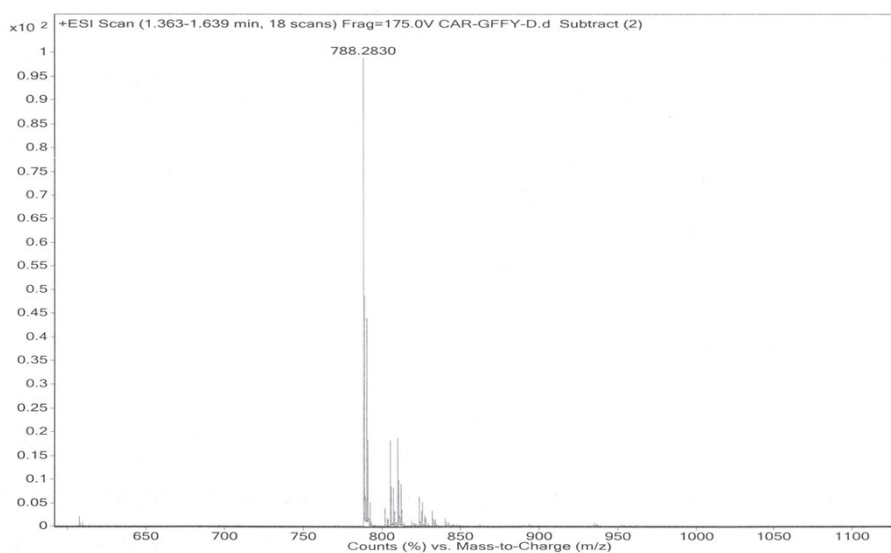


Fig. S6. HR-MS spectrum of Car-G^DF^DF^DY

Compound Kep-G^DF^DF^DY: ^1H NMR (400 MHz, DMSO) δ 9.23 (d, J = 1.6 Hz, 1H), 8.20 (ddd, J = 22.5, 10.2, 5.5 Hz, 3H), 7.98 (dd, J = 12.6, 8.5 Hz, 1H), 7.77 – 7.42 (m, 8H), 7.28 – 6.94 (m, 11H), 6.66 (dd, J = 8.5, 2.8 Hz, 2H), 4.59 – 4.32 (m, 3H), 3.85 – 3.53 (m, 3H), 3.03 – 2.61 (m, 6H), 1.32 (d, J = 7.0 Hz, 3H). MS: calc. M = 768.85, obsvd. $(M + H)^+ = 769.3224$.

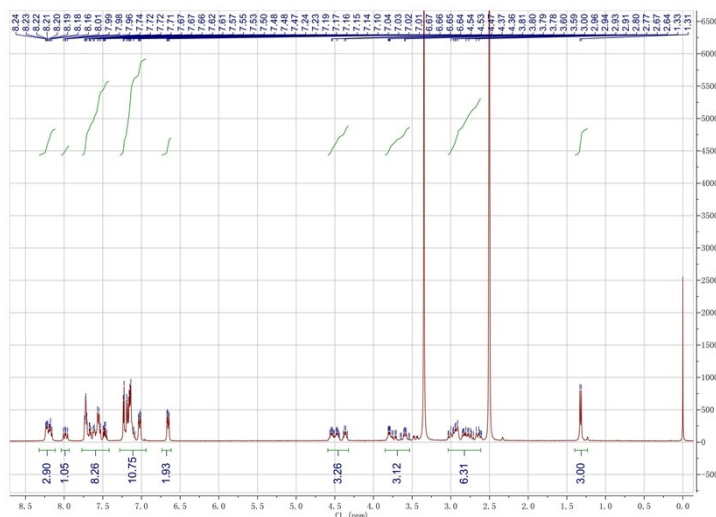


Fig. S7. ^1H NMR spectrum of Kep- $\text{G}^{\text{D}}\text{F}^{\text{D}}\text{F}^{\text{D}}\text{Y}$

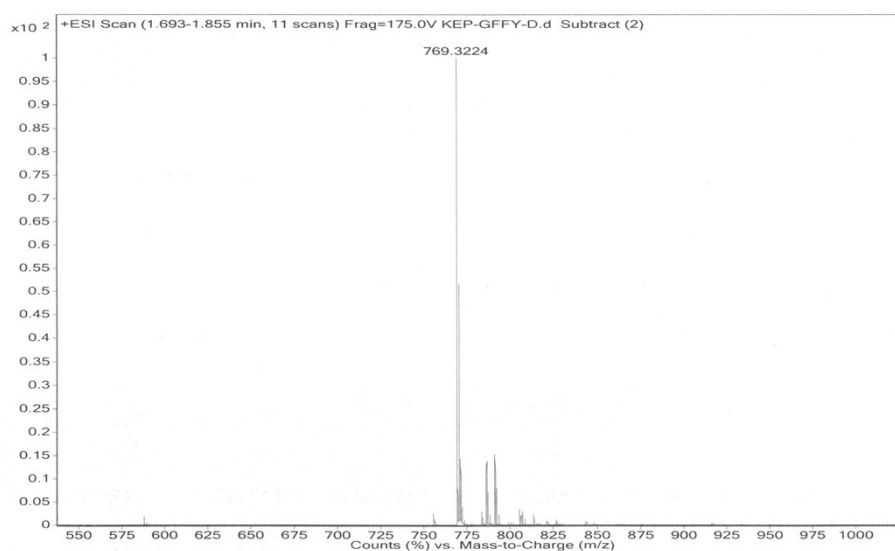


Fig. S8. HR-MS spectrum of Kep- $\text{G}^{\text{D}}\text{F}^{\text{D}}\text{F}^{\text{D}}\text{Y}$

Compound Oxp- $\text{G}^{\text{D}}\text{F}^{\text{D}}\text{F}^{\text{D}}\text{Y}$: ^1H NMR (400 MHz, DMSO) δ 8.27 – 7.97 (m, 3H), 7.60 – 7.00 (m, 19H), 6.67 (d, J = 8.4 Hz, 2H), 4.63 – 4.23 (m, 4H), 3.05 – 2.64 (m, 11H). MS: calc. M = 807.89, obsvd. $(M + H)^+$ = 808.3326.

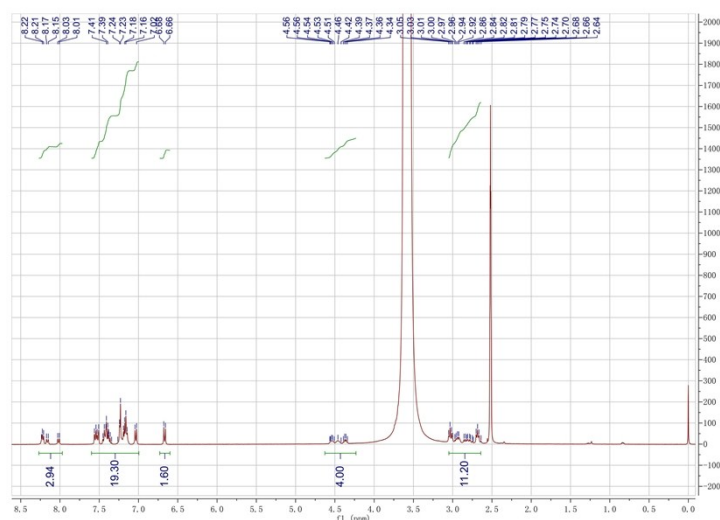


Fig. S9. ^1H NMR spectrum of Oxp-G^DF^DF^DY

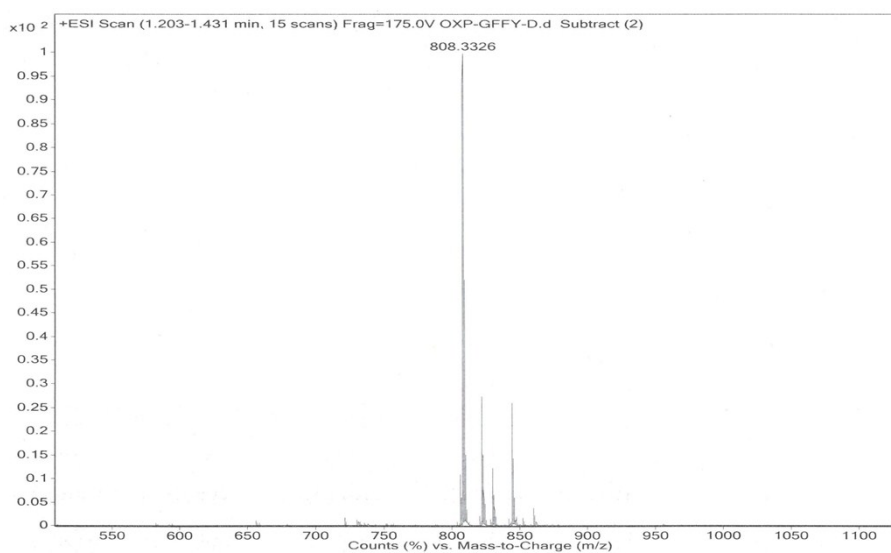


Fig. S10. HR-MS spectrum of Oxp-G^DF^DF^DY

Compound Fnp-G^DF^DF^DY: ^1H NMR (400 MHz, DMSO) δ 9.27 (s, 1H), 8.35 – 7.84 (m, 4H), 7.54 – 6.55 (m, 20H), 4.60 – 4.31 (m, 3H), 3.69 (ddd, J = 11.6, 9.9, 4.4 Hz, 3H), 3.05 – 2.60 (m, 6H), 1.26 (t, J = 8.8 Hz, 3H). MS: calc. M = 756.84, obsvd. $(M + H)^+ = 757.3221$.

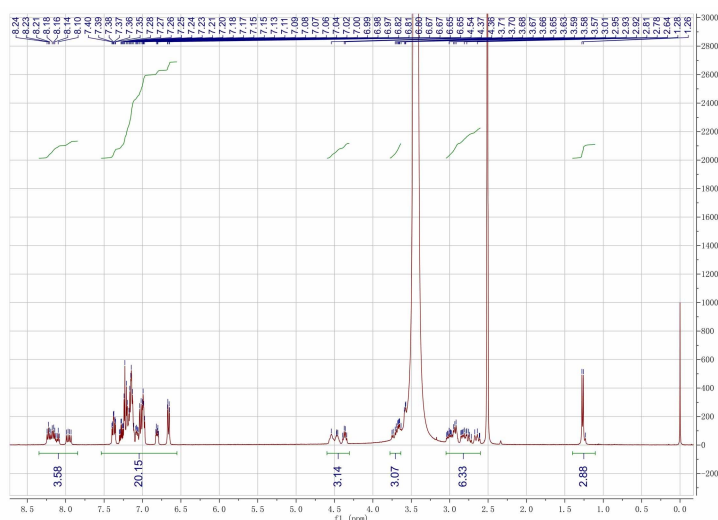


Fig. S11. ^1H NMR spectrum of Fnp-G^DF^DF^DY

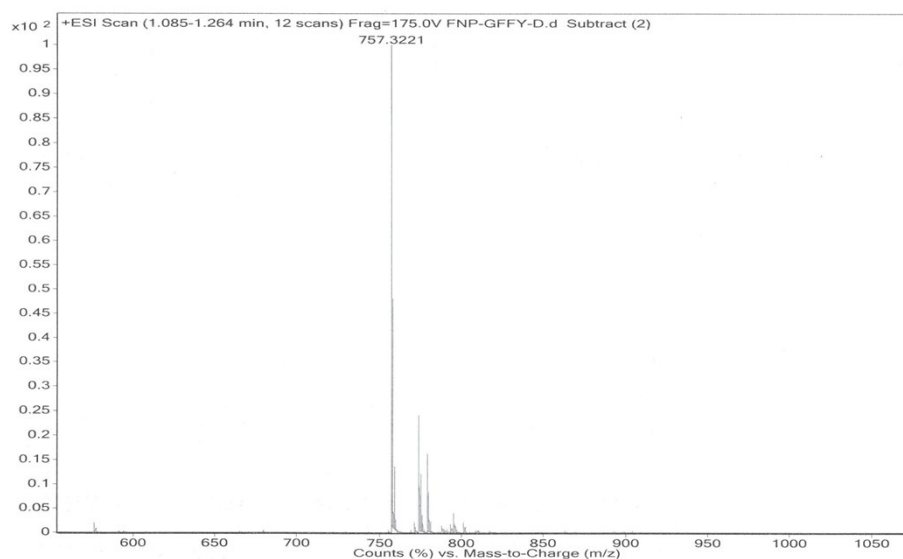


Fig. S12. HR-MS spectrum of Fnp-G^DF^DF^DY

Compound Ibp-G^DF^DF^DY: ^1H NMR (400 MHz, DMSO) δ 9.25 (s, 1H), 8.34 – 7.81 (m, 4H), 7.30 – 6.96 (m, 13H), 6.66 (dd, J = 8.5, 2.0 Hz, 2H), 4.67 – 4.29 (m, 3H), 3.79 – 3.52 (m, 3H), 3.03 – 2.59 (m, 6H), 2.37 (dt, J = 15.7, 7.9 Hz, 2H), 1.82 – 1.72 (m, 1H), 1.27 (d, J = 7.0 Hz, 3H), 1.05 – 0.75 (m, 6H). MS: calc. M = 720.85, obsvd. $(M + \text{H})^+ = 721.3585$.

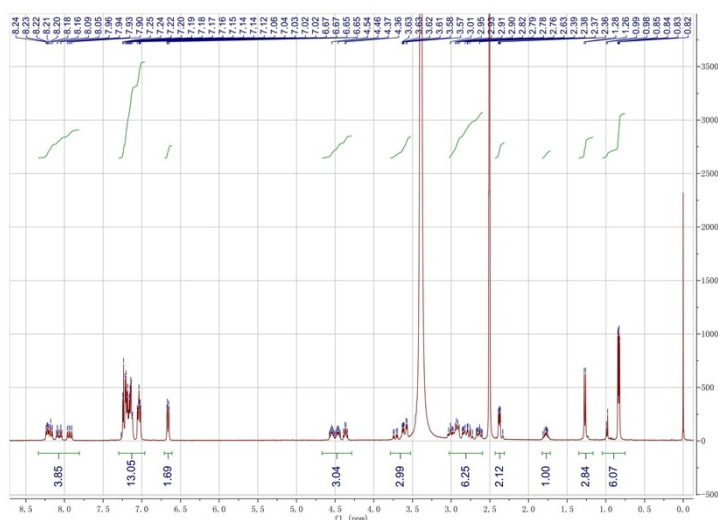


Fig. S13. ^1H NMR spectrum of Ibp-G $^{\text{D}}\text{F}^{\text{D}}\text{F}^{\text{D}}\text{Y}$

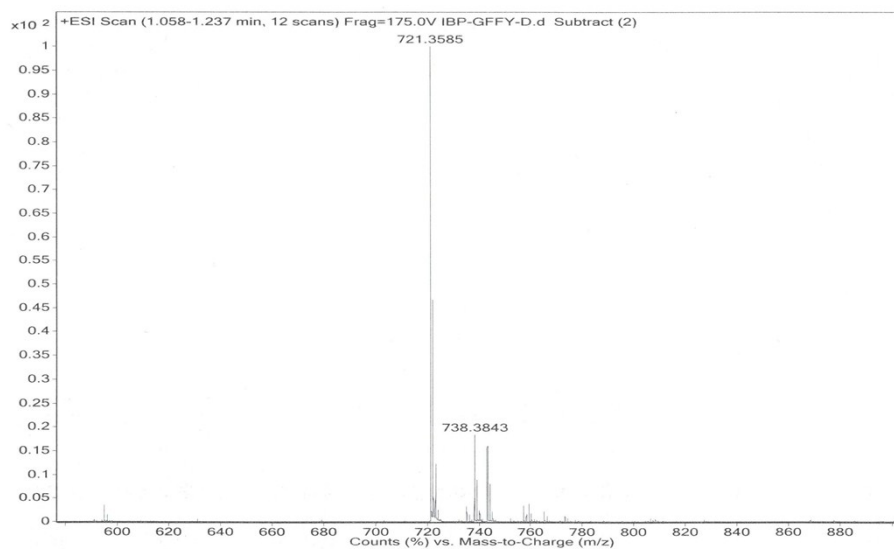


Fig. S14. HR-MS spectrum of Ibp-G $^{\text{D}}\text{F}^{\text{D}}\text{F}^{\text{D}}\text{Y}$

Compound Fbf-G $^{\text{D}}\text{F}^{\text{D}}\text{F}^{\text{D}}\text{Y}$: ^1H NMR (400 MHz, DMSO) δ 9.23 (s, 1H), 8.31 – 8.10 (m, 3H), 8.10 – 7.30 (m, 10H), 7.28 – 6.95 (m, 11H), 6.66 (d, J = 8.4 Hz, 2H), 4.47 (dddd, J = 42.4, 21.3, 11.2, 6.2 Hz, 3H), 3.62 (ddd, J = 57.9, 16.6, 5.5 Hz, 2H), 3.26 (t, J = 6.8 Hz, 2H), 3.13 – 2.62 (m, 7H), 2.54 (s, 1H). MS: calc. M = 768.85, obsvd. $(M + \text{H})^+ = 769.3228$, $(M + \text{Na})^+ = 786.3491$, $(M + \text{K})^+ = 807.2723$.

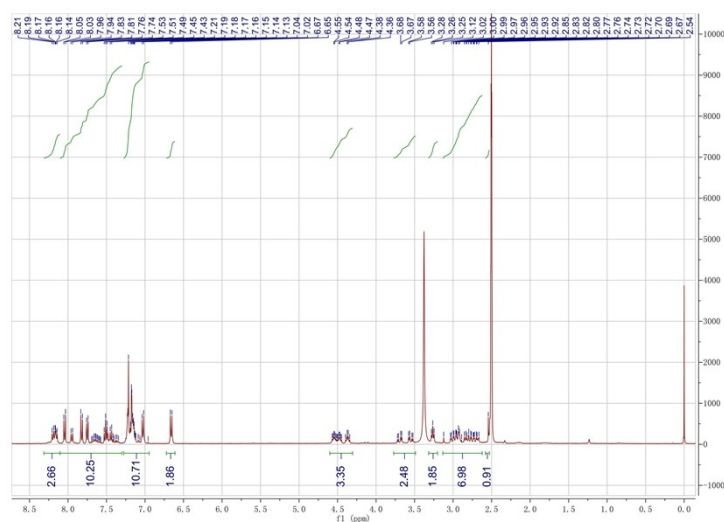


Fig. S15. ^1H NMR spectrum of Fbf-G^DF^DF^DY

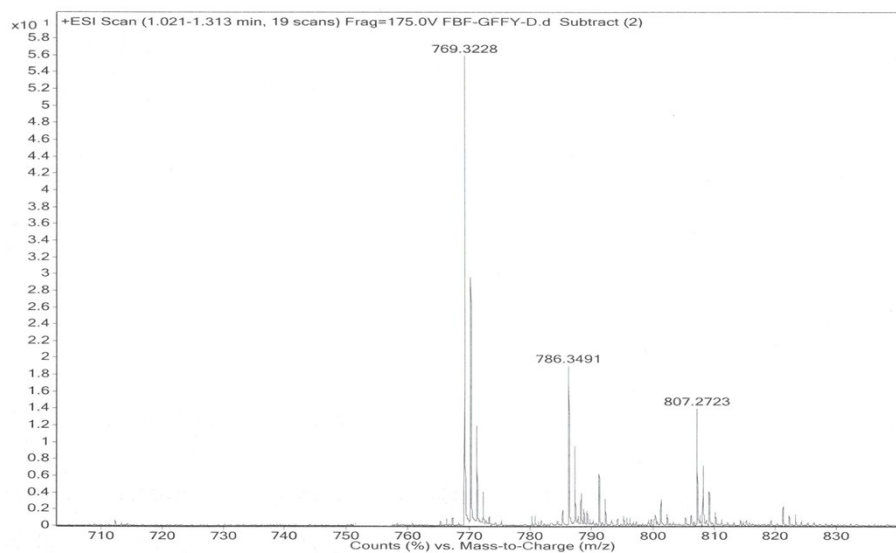


Fig. S16. HR-MS spectrum of Fbf-G^DF^DF^DY

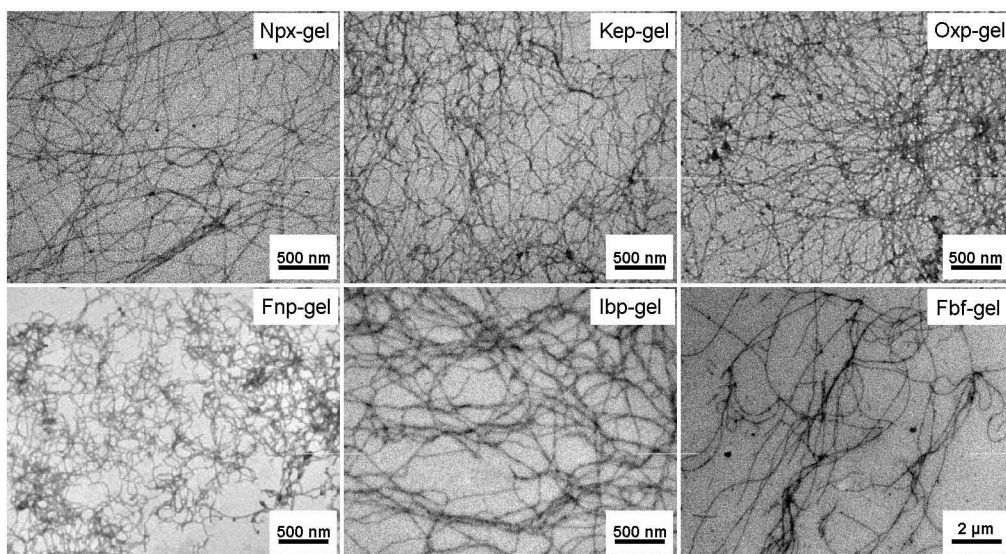


Fig. S17. TEM image of Npx-gel, Kep- gel, Oxp- gel, Fnp- gel, lbp- gel and Fbf- gel

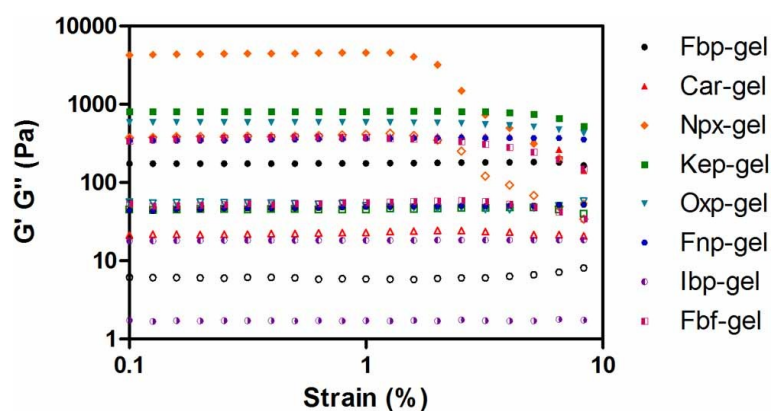


Fig. S18. Dynamic strain sweep at frequency of 1 rad/s at 37°C

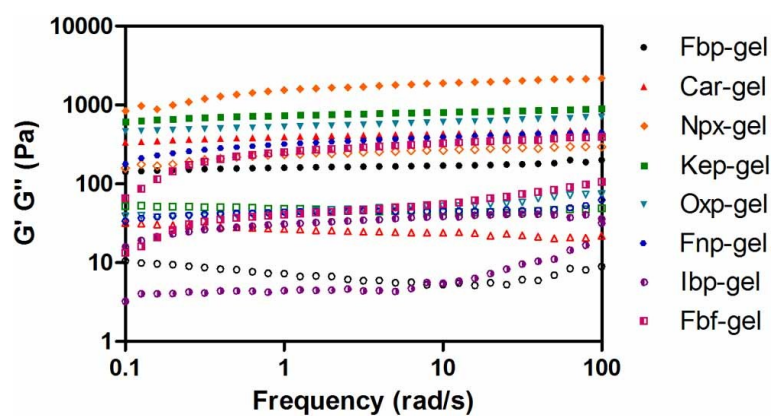


Fig. S19. Dynamic frequency sweep at strain of 1% at 37 °C

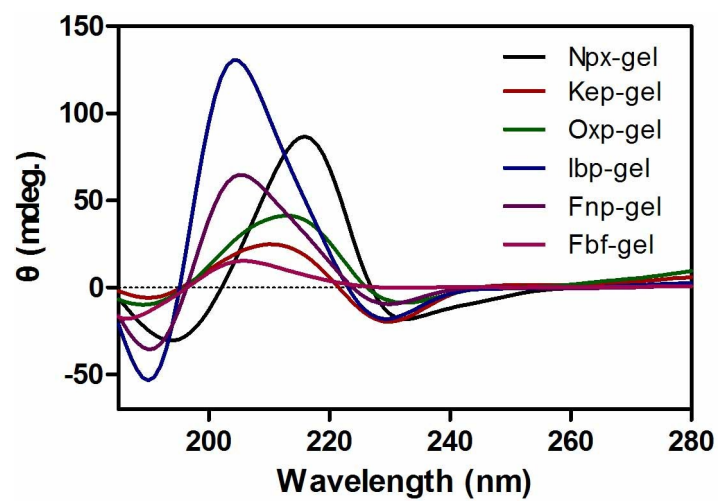


Fig. S20. CD spectra of Npx-gel, Kep-gel, Oxp-gel, Ibp-gel, Fnp-gel and Fbf-gel

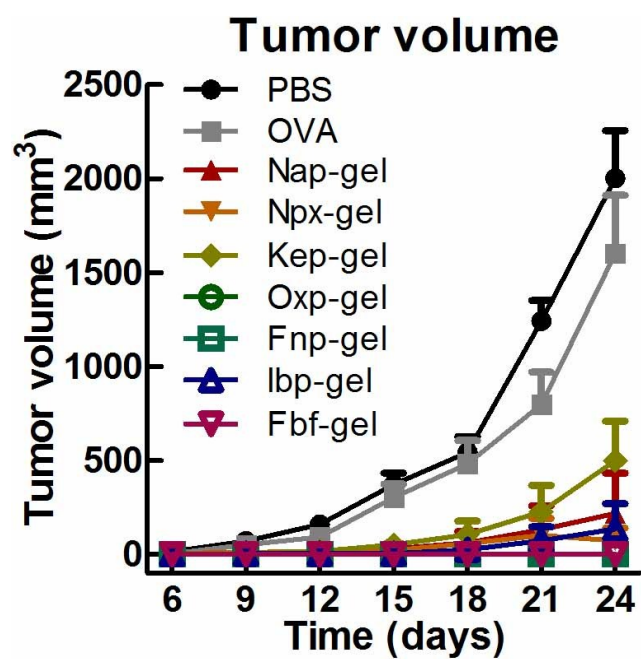


Fig. S21. Preventative immune effect of PBS, OVA, Nap-gel, Npx-gel, Kep-gel, Oxp-gel, Fnp-gel, Ibp-gel, and Fbf-gel to B16-OVA tumor

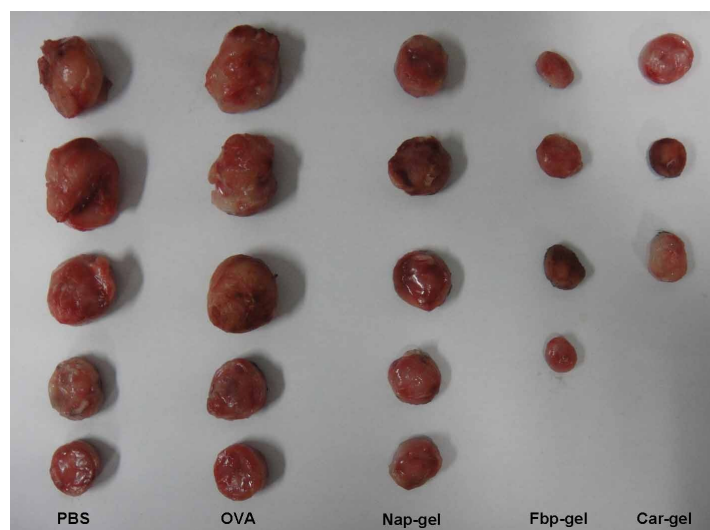


Fig. S22. Optical image of therapeutic immune effect of PBS, OVA, Nap-gel, Fbp-gel and Car-gel to EG7-OVA tumor

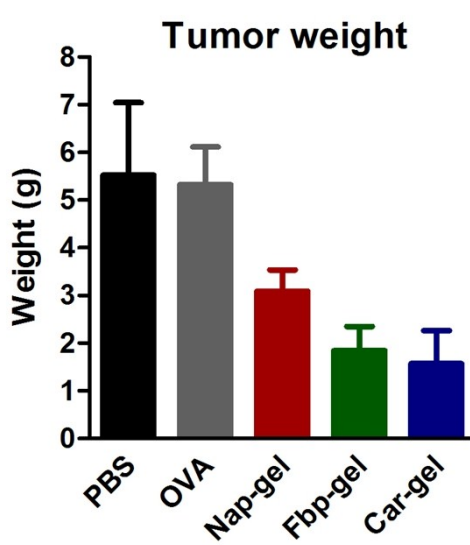


Fig. S23. Tumor weight of therapeutic immune effect of PBS, OVA, Nap-gel, Fbp-gel and Car-gel to EG7-OVA tumor

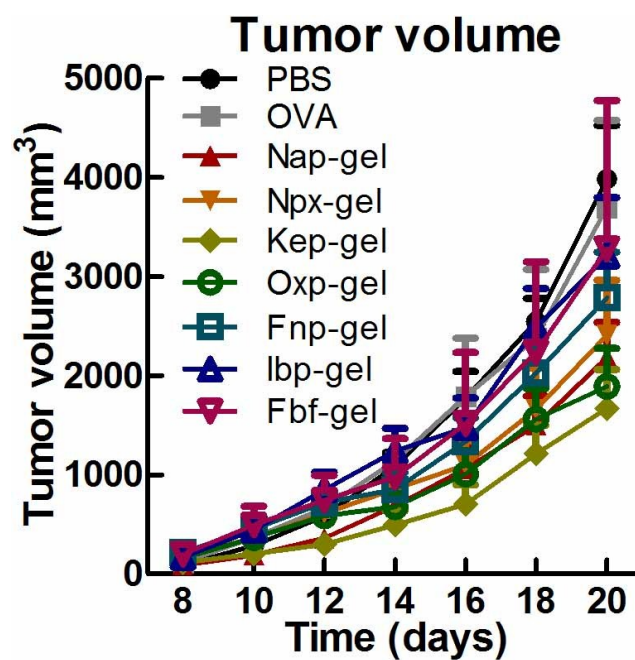


Fig. S24. Therapeutic immune effect of PBS, OVA, Nap-gel, Npx-gel, Kep-gel, Oxp-gel, Fnp-gel, Ibp-gel, and Fbf-gel to EG7-OVA tumor

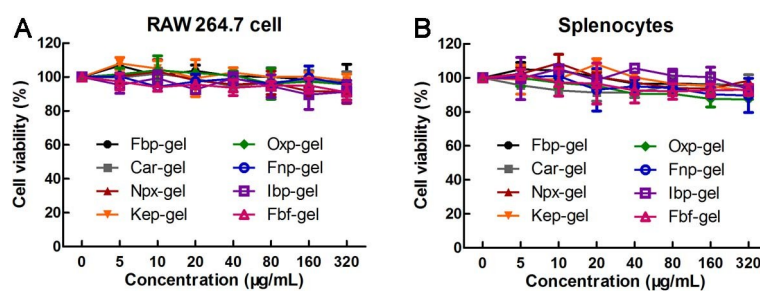


Fig. S25. The cytotoxicity evaluations of hydrogels on Raw 264.7 cells (A) and splenocytes (B).