Experimental Supporting Information

Materials: 2-Cl-trityl chloride resin (1.2 mmol/g) was obtain from Nankai University resin Co., Ltd. Fmoc-amino acids and o-benzotriazol-1-yl-N,N,N',N'-tetramehtyluronium hexafluorophosphate (HBTU) were bought from GL Biochem. (Shanghai). 2-naphthaleneacetic acid (Nap) is obtained from Aladdin (Shanghai). Chlorambucil (CRB) was obtained from J&K Chemical Technology (Beijing, China). Alkaline phosphatase (ALP) was acquired from TaKaRa biotechnology. Chemical regents and solvents were used as received from commercial sources. Commercially available reagents were used without further purification, unless noted otherwise. Dulbecco's modified Eagle's medium (DMEM), fetal bovine serum (FBS) and penicillin/streptomycin were purchased from Gibco Corporation.

General methods: ^{1}H NMR (Bruker ARS 400) and HR-MS(Agilent 6520 Q-TOF LC/MS) was used to character the compounds. LC-MS was conducted at the LCMS-2020 (Shimadzu) system. TEM (JEM100CXII) was performed at the Tecnai G2 F20 system, operating at 100 kV. Circular dichroism (CD) spectrum was obtained by a BioLogic (MOS-450) system.

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 entended according the standard SPPS protocol. After 2-caphthaleneacetic acid or chlorambucil coupling the third amino acid, 5 times DMF wash and following 5 times DCM wash were used to remove excessive reagents. Lastly, 95% trifluoroacetic acid (TFA) containing 2.5% H_2O and 2.5% TIS (trimethylsilane) was used to cleave peptides derivative from resin and the mixture was filtered. Ice-cold diethylether was poured into filtrate performed by rotary evaporation. The precipitate was centrifuged for 5 min at 5000 rpm speed. The solid was dried by vaccum pump to gain resulting compounds. The pure peptides were obtained by HPLC and lyophilization.

Characterization of the compounds:

Compound Nap-YYY: ^{1}H NMR (400 MHz, DMSO) δ 8.18 (dd, J = 21.5, 8.0 Hz, 2H), 7.98 (d, J = 8.3 Hz, 1H), 7.86 – 7.72 (m, 3H), 7.57 (s, 1H), 7.50 – 7.43 (m, 2H), 7.18 (dd, J = 28.7, 20.3 Hz, 2H), 6.99 (dd, J = 16.2, 8.5 Hz, 6H), 6.69 – 6.55 (m, 6H), 4.49 – 4.34 (m, 3H), 3.53 (dd, J = 44.9, 14.5 Hz, 3H), 3.17 (s, 1H), 2.97 – 2.78 (m, 4H), 2.70 – 2.53 (m, 3H). MS: calc. M = 675.73, obsvd. $(M + H)^+$ = 676.2652, $(M + Na)^+$ =

698.2470.

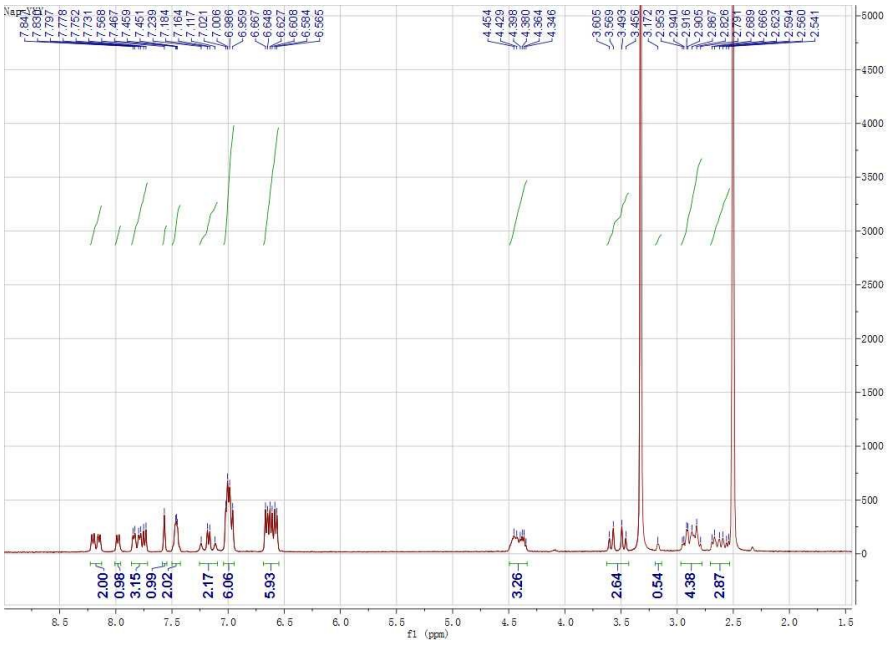

Fig. S-1. ^{1}H NMR spectrum of Nap-YYY

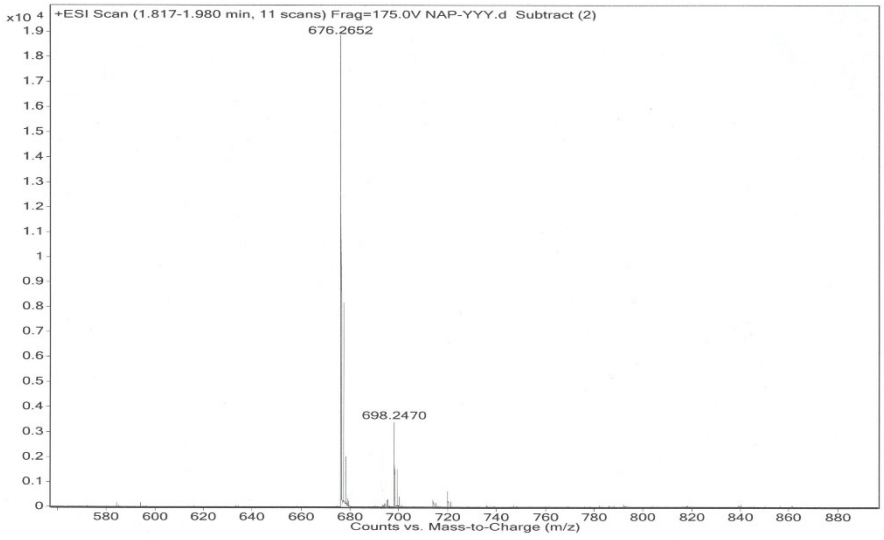

Fig. S-2. HR-MS spectrum of Nap-YYY

Compound Nap-pYYY: ^{1}H NMR (400 MHz, DMSO) δ 8.25 – 7.94 (m, 3H), 7.89 – 7.70 (m, 3H), 7.61 (s, 1H), 7.45 (dd, *J* = 10.9, 6.0 Hz, 2H), 7.28 – 6.87 (m, 9H), 6.64 (dd, *J* = 16.1, 8.4 Hz, 4H), 4.48 (dd, *J* = 9.3, 3.4 Hz, 2H), 4.40 – 4.34 (m, 1H), 3.60 (s, 1H), 2.97 – 2.78 (m, 5H), 2.72 – 2.62 (m, 2H). MS: calc. M = 755.71, obsvd. $(M + H)^+$ = 756.2312, $(M + Na)^+$ = 778.2122.

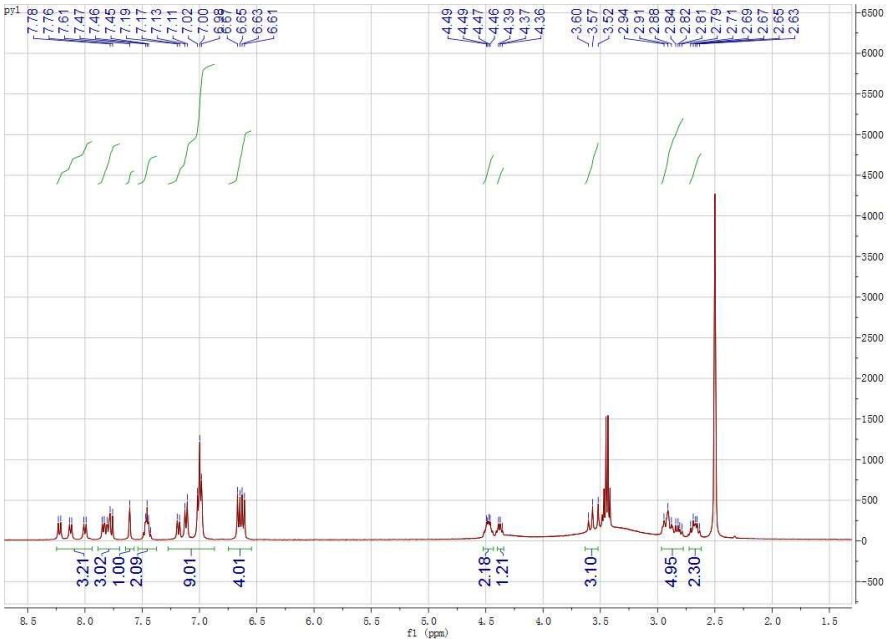

Fig. S-3. ^{1}H NMR spectrum of Nap-pYYY

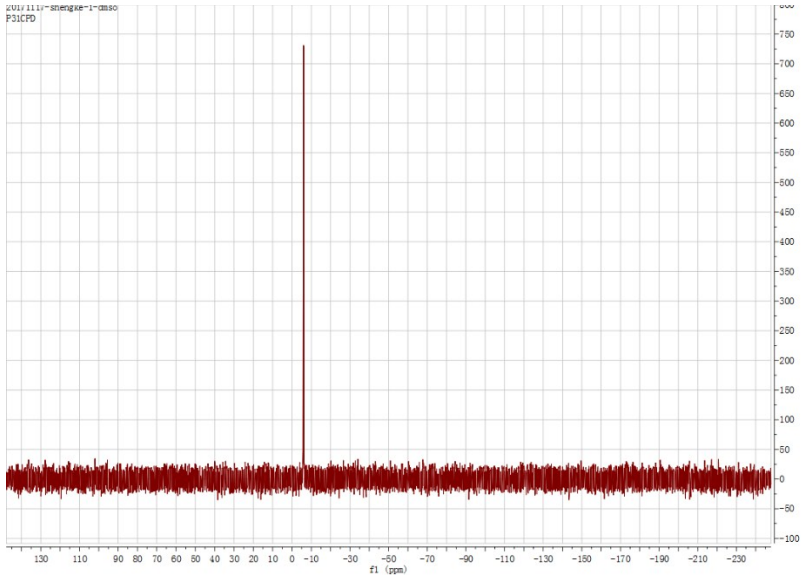

Fig. S-4. ^{31}P NMR spectrum of Nap-pYYY

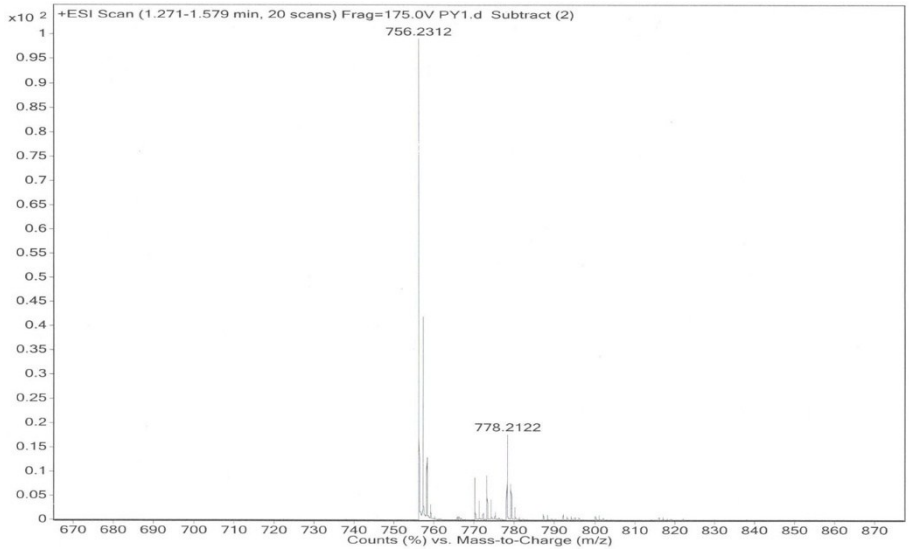

Fig. S-5. HR-MS spectrum of Nap-pYYY

Compound Nap-YpYY: ^{1}H NMR (400 MHz, DMSO) δ 8.18 (t, *J* = 9.0 Hz, 2H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.80 (dd, *J* = 27.7, 15.4 Hz, 3H), 7.58 (s, 1H), 7.45 (d, *J* = 3.3 Hz, 2H), 7.25 – 7.12 (m, 3H), 7.00 (dd, *J* = 15.1, 8.4 Hz, 6H), 6.62 (dd, *J* = 32.5, 8.3 Hz, 4H), 4.52 (d, *J* = 2.5 Hz, 1H), 4.38 (t, *J* = 10.6 Hz, 3H), 3.57 (t, *J* = 12.9 Hz, 2H), 2.98 – 2.71 (m, 6H), 2.65 – 2.56 (m, 1H). MS: calc. M = 755.71, obsvd. $(M + H)^+$ = 756.2314.

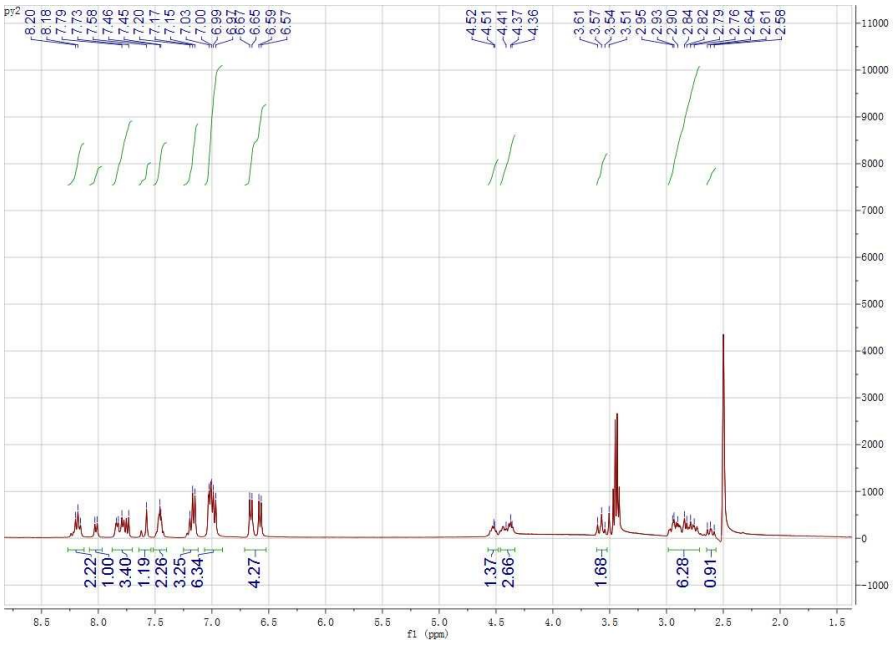

Fig. S-6. ^{1}H NMR spectrum of Nap-YpYY

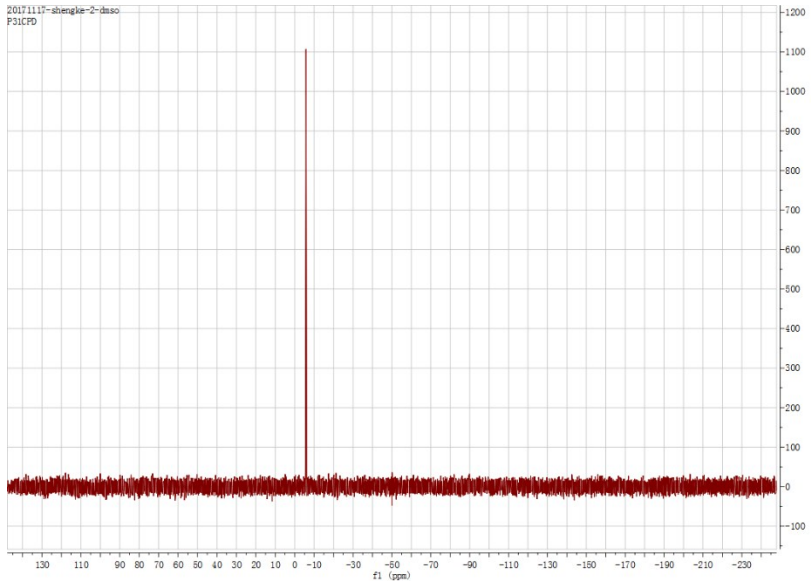

Fig. S-7. ^{31}P NMR spectrum of Nap-YpYY

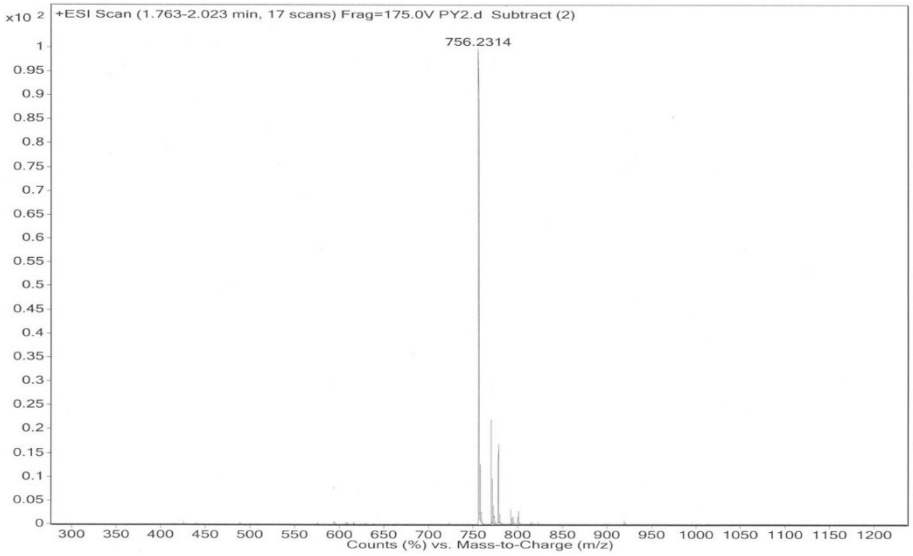

Fig. S-8. HR-MS spectrum of Nap-YpYY

Compound Nap-YYpY: ^{1}H NMR (400 MHz, DMSO) δ 8.18 (t, *J* = 9.0 Hz, 2H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.80 (dd, *J* = 27.7, 15.4 Hz, 3H), 7.58 (s, 1H), 7.45 (d, *J* = 3.3 Hz, 2H), 7.25 – 7.12 (m, 3H), 7.00 (dd, *J* = 15.1, 8.4 Hz, 6H), 6.62 (dd, *J* = 32.5, 8.3 Hz, 4H), 4.52 (d, *J* = 2.5 Hz, 1H), 4.38 (t, *J* = 10.6 Hz, 3H), 3.57 (t, *J* = 12.9 Hz, 2H), 2.98 – 2.71 (m, 6H), 2.65 – 2.56 (m, 1H). MS: calc. M = 755.71, obsvd. $(M + H)^+$ = 756.2312.

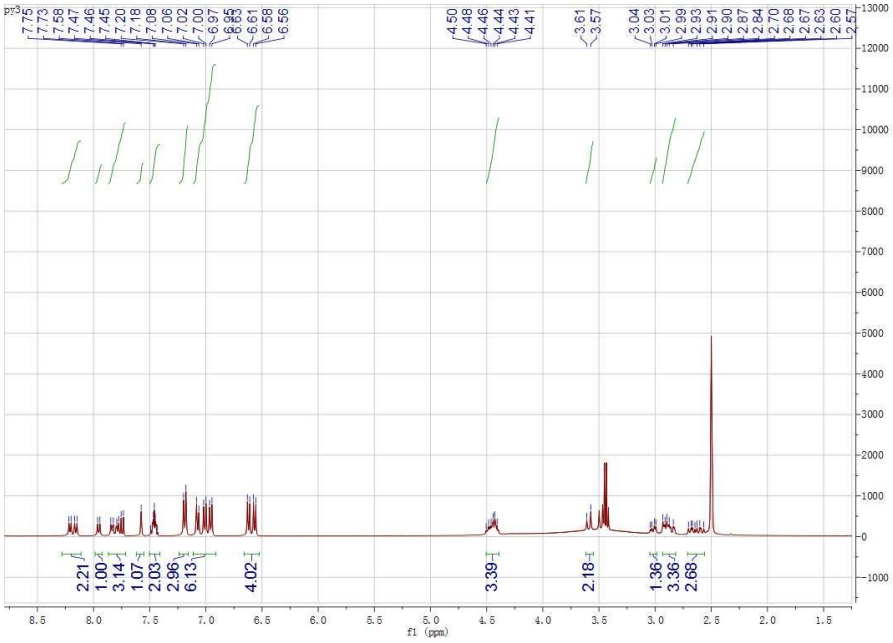

Fig. S-9. ^{1}H NMR spectrum of Nap-YYpY

Fig. S-10. ^{31}P NMR spectrum of Nap-YpYY

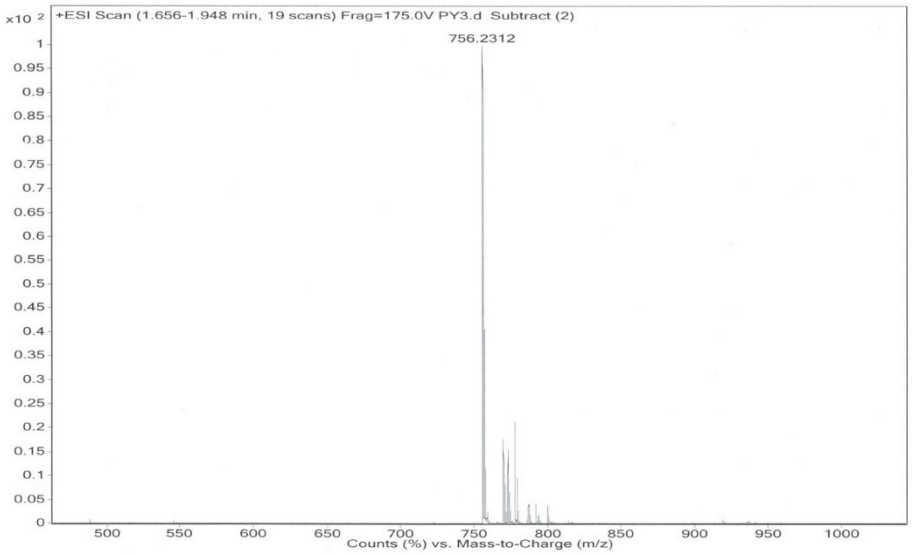

Fig. S-11. HR-MS spectrum of Nap-YYpY

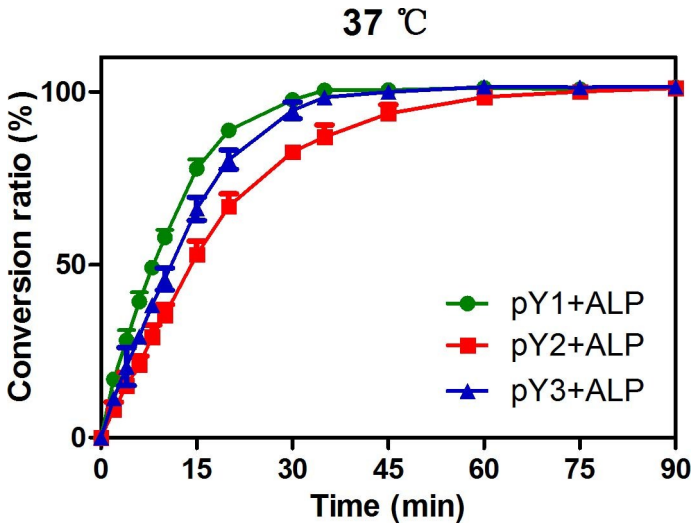

Fig. S-12. Conversion ratio from pY_1, pY_2 and pY_3 to Nap-YYY by adding ALP at 37℃

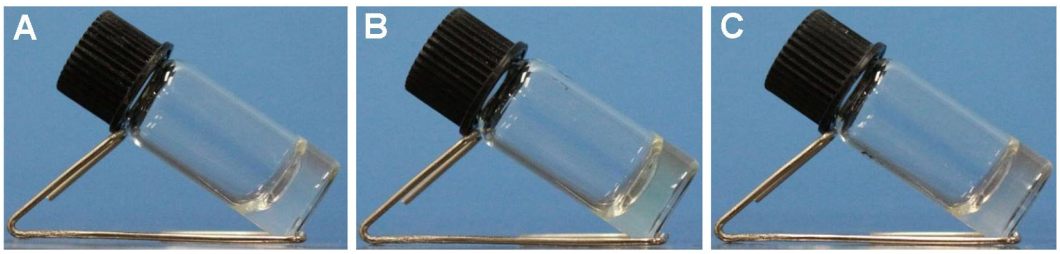

Fig. S-13. Optical images of hydrogels from A) pY_1, B) pY_2 and C) pY_3 treated with

ALP at 4 ℃ for 8h.

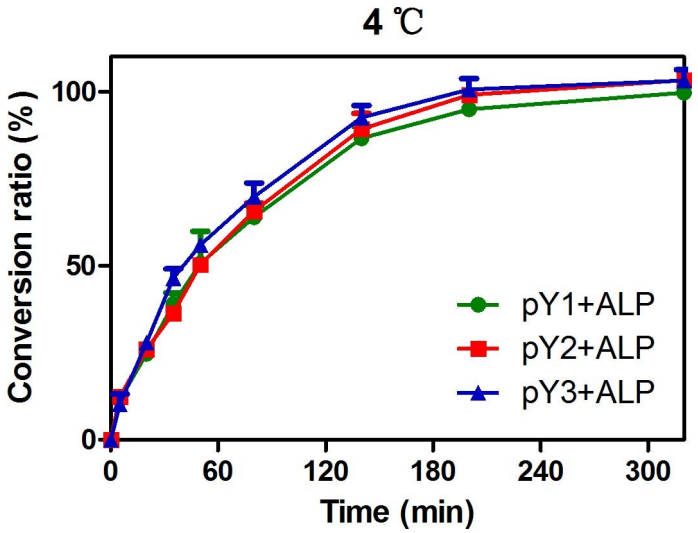

Fig. S-14. Conversion ratio from pY_1, pY_2 and pY_3 to Nap-YYY by adding ALP at 4℃

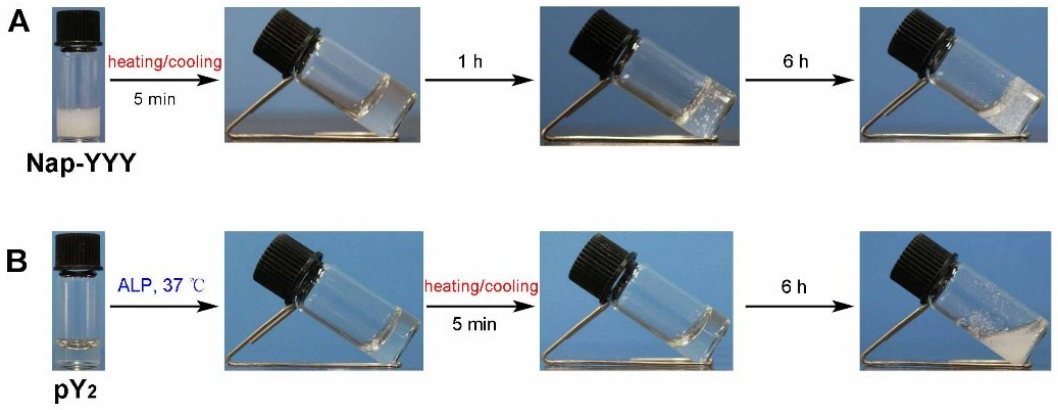

Fig. S-15. A) Change of hydrogel of Nap-YYY formed by heating-cooling process, B) Change of hydrogel of pY_2 with ALP after applying a heating-cooling process.

Assembly capacity of precursors and CMC value: The CMC values of Nap-pYYY, Nap-YpYY, Nap-YYpY was determined by dynamic light scattering (DLS). Solutions containing different concentration of compound were tested and the light scattering intensity was recorded for each concentration analyzed. The lower CMC values represent better assembly capacity.

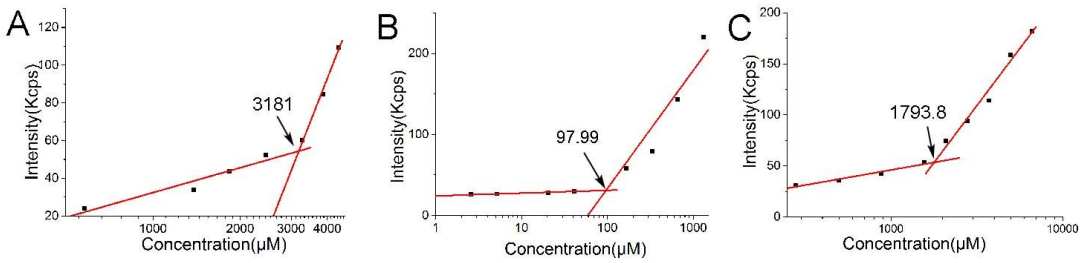

Fig. S-16. Critical micelle concentration (CMC) value of A) pY_1, B) pY_2 and C) pY_3 were determined by dynamic light scattering (DLS)

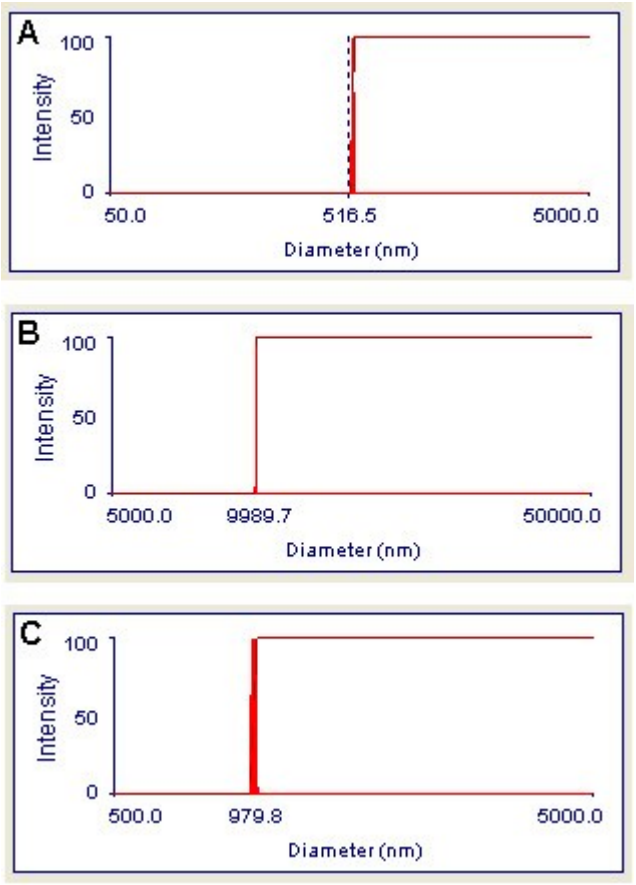

Fig. S-17. DLS results of precursors A) pY_1, B) pY_2 and C) pY_3 were determined by dynamic light scattering (DLS).

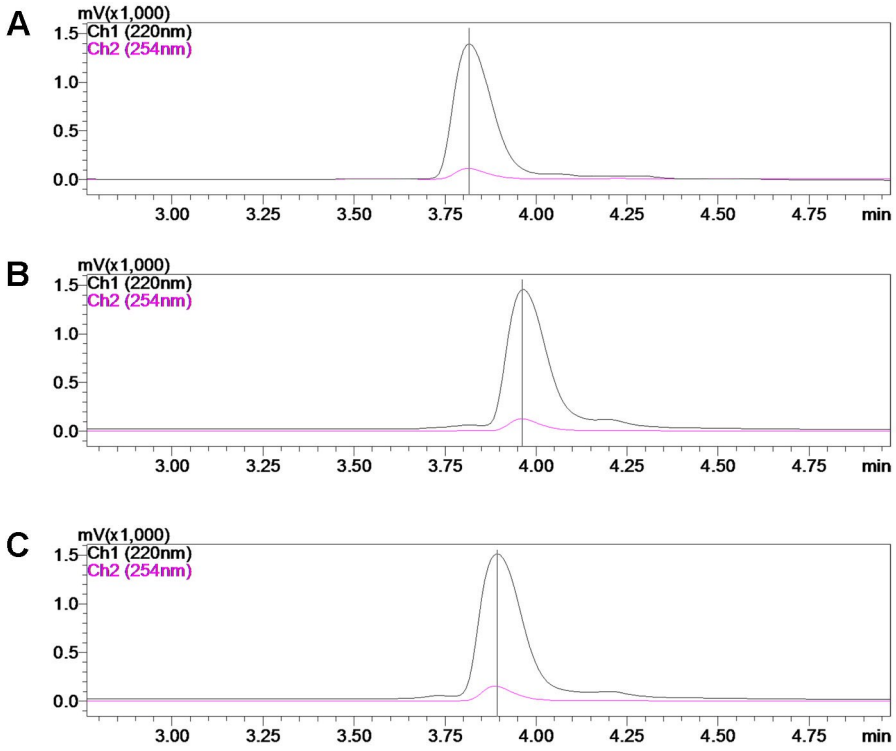

Fig. S-18. Liquid chromatogram of A) pY_1, B) pY_2 and C) pY_3

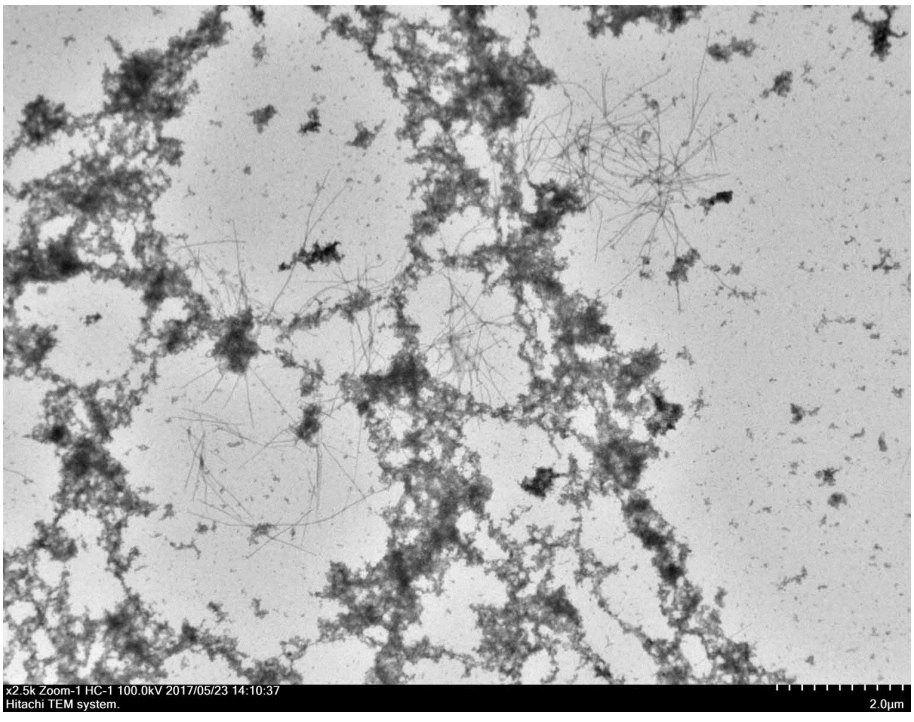

Fig. S-19. TEM image of Nap-YYY converted from pY_1 by adding ALP

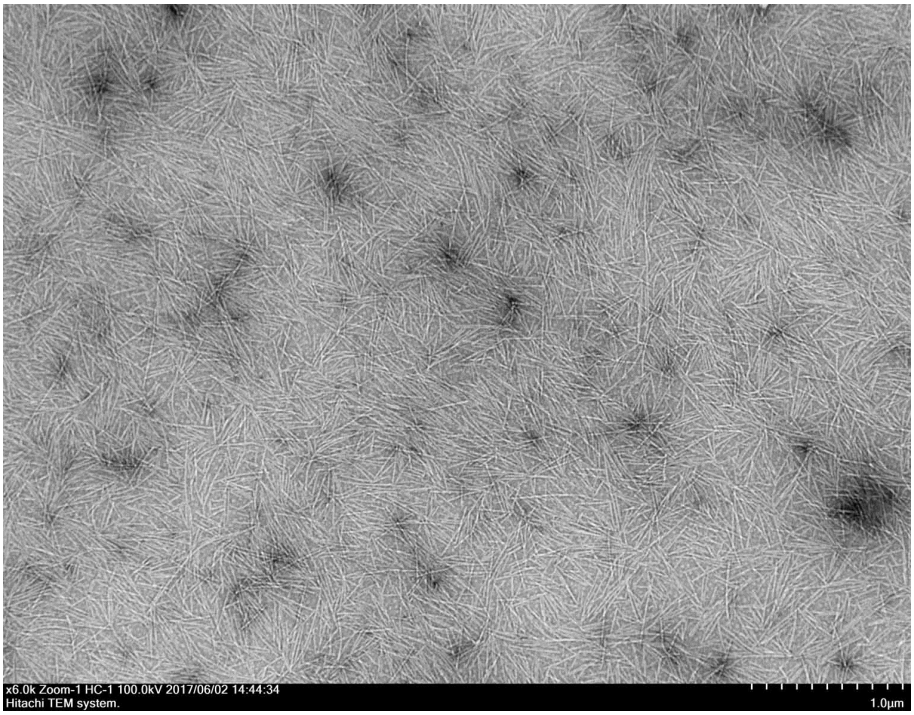

Fig. S-20. TEM image of Nap-YYY converted from pY_2 and by adding ALP

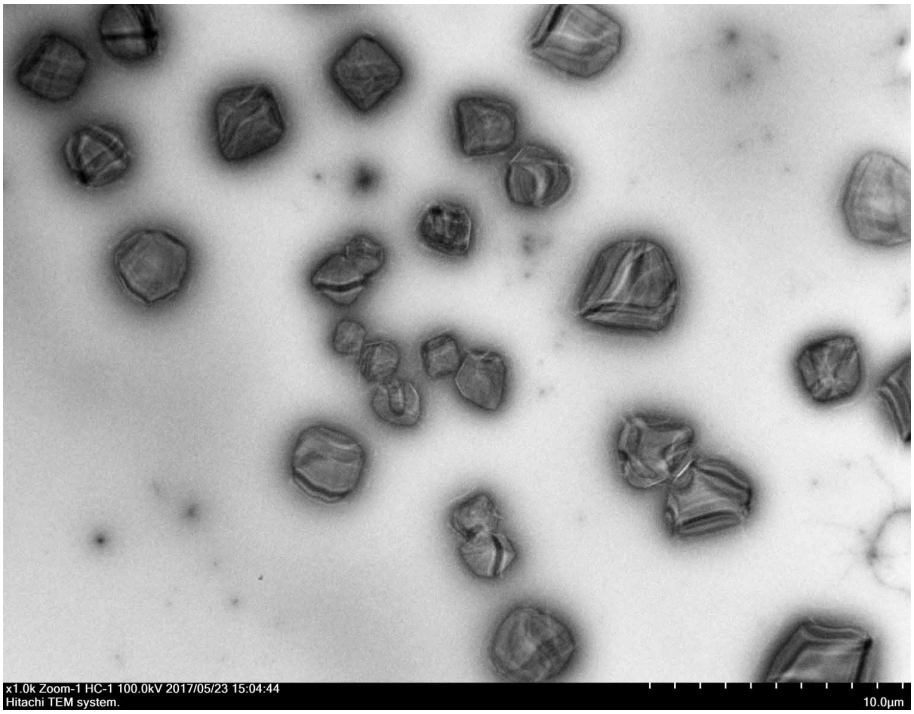

Fig. S-21. TEM image to show large precipitates of Nap-YYY converted from pY_3 by adding ALP

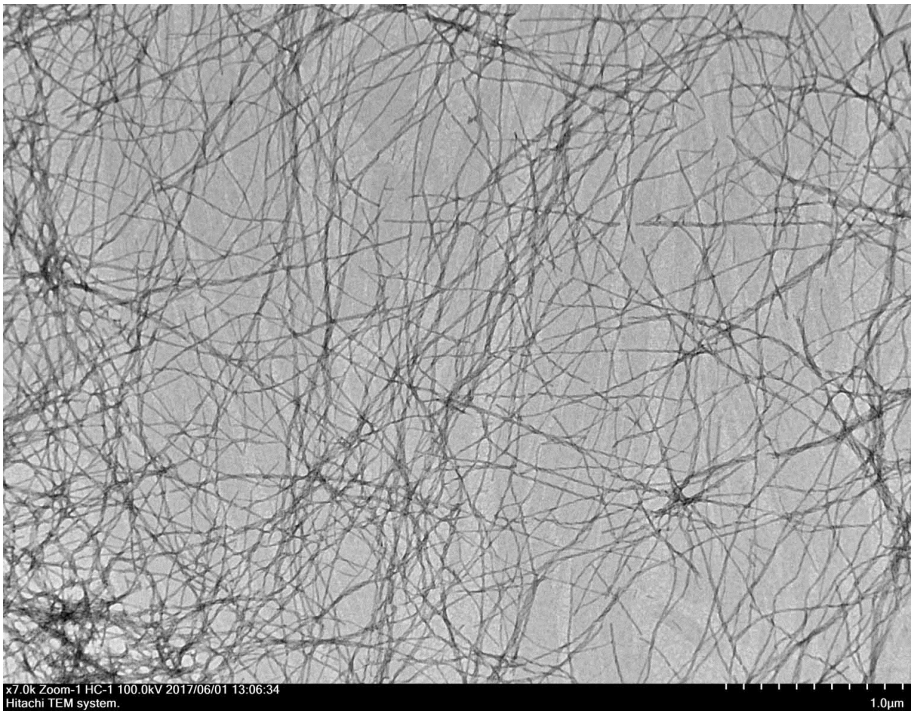

Fig. S-22. TEM image to show large fibers of Nap-YYY converted from pY_3 by adding ALP

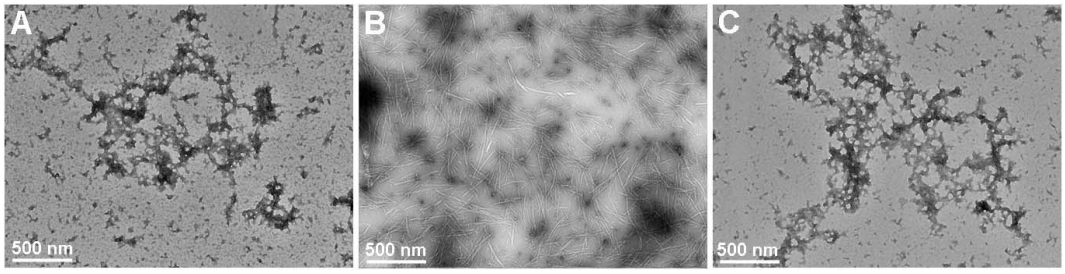

Fig. S-23. TEM images of PBS solution containing 0.5 wt% precusors A) pY_1, B) pY_2 and C) pY_3

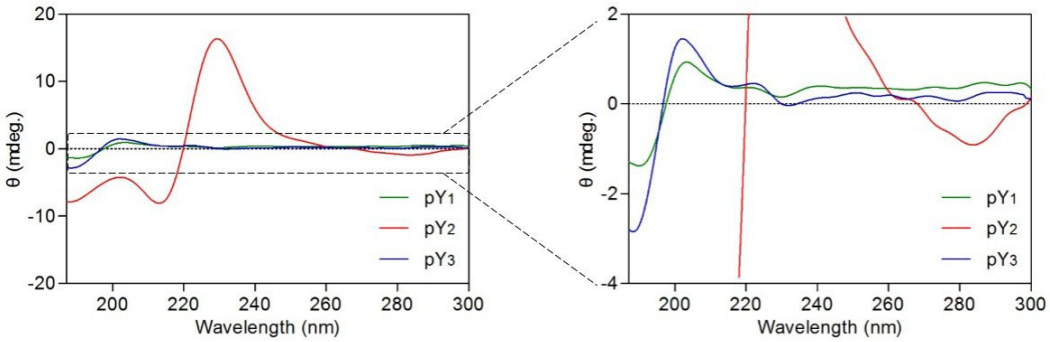

Fig. S-24. Enlarged CD spectrum of precursors in Fig. 3A

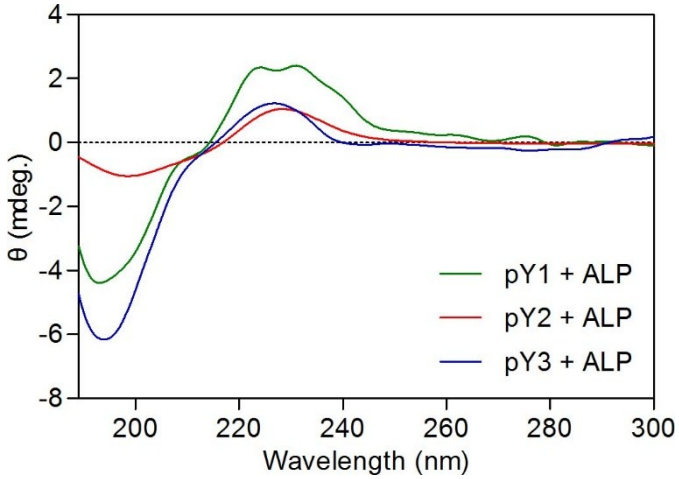

Fig. S-25. CD spectra of pY_1, pY_2 and pY_3 with ALP at concentration upon trespassing the critical aggregation concentration (3181, 98 and 1794 μM, respectively) at 37℃ after 4 h.

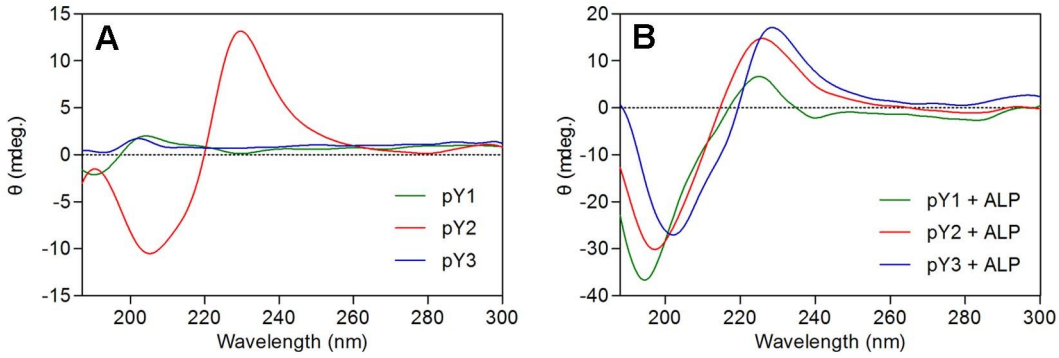

Fig. S-26. CD spectra of three precursors at the concentration of 0.5 wt% at 4 ℃ A) before and B) after adding ALP for 8h.

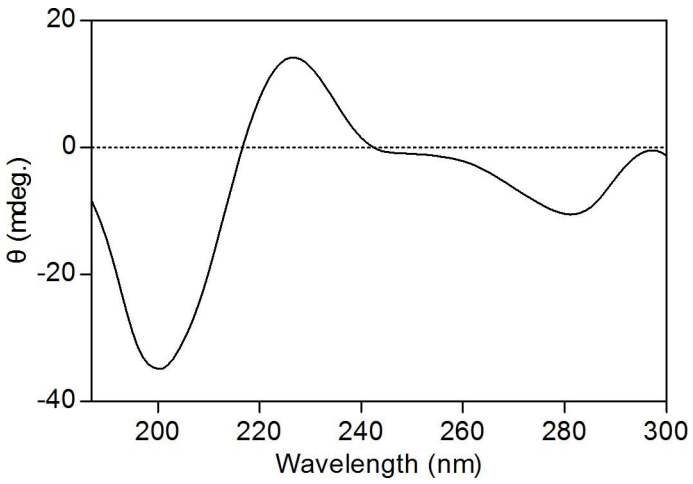

Fig. S-27. CD spectrum of Nap-YYY by heating-cooling process.