Supporting Information

Materials and general methods:

Chemicals: Fmoc-amino acids, trifluoro acetic acid (TFA), and O-(Benzotriazol-1-yl)-N,N,N',N'-tetramethyluroniumhexafluorophosphate (HBTU) were obtained from GL Biochem (Shanghai). 2-naphthalene acetic acid and 4-Nitrophenyl phosphate disodium salt hexahydrate were obtained from Alfa (China). The pbs buffer (20X) was obtained from sangon (Shanghai). Alkali phosphatase was obtained from Takara with the activity of 30 U/μL (Dalian, China). Chemical reagents and solvents were used as received from commercial sources.

General methods: ^{1}H NMR (Bruker ARX 400) was used to characterize the synthesized compounds. ESI-MS spectrometric analyses were performed at the Thermo Finnigan LCQ AD System. AFM was done on a Veeco multimode V system with the tip of Veeco RTESP. Emission spectra were detected on a Perkin-Elmer LS-55 luminance spectrometer at excitation wavelength of 272 nm. Rheology test was done on an AR 2000ex (TA instrument) system, 40 mm parallel plates was used during the experiment at the gap of 500 μm. Vortex were performed on a Vortex-5 system (V087EX-5 from Qi Lin Bei Er Co., Haimen, P. R. China).

Peptide synthesis. Nap-GFF was prepared by solid phase peptide synthesis (SPPS) using 2-chlorotrityl chloride resin and the corresponding N-Fmoc protected amino acids. The first amino acid (Fmoc-Phenylalanine) was loaded on the resin at the C-terminal with the loading efficiency about 0.8 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, the N-terminus of the peptides was

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coupled with 2-naphthalene acetic acid to attach the aromatic group on the tripeptide. 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 dichloromethane (DCM) for 2 min (5 ml per gram of resin). The peptide derivative was cleaved from the resin by ice-cold reagent B and the mixture was stirred at room temperature, concentrated by the rotary evaporator, and poured into ice-cold diethylether, successively. The resulting precipitate was centrifuged for 10 min at 2 ^{0}C at 10,000 rpm. Afterward the supernatant was decanted and the solid was dissolved in DMSO. The title compound was obtained by HPLC and lyophilization.

Characterizations of Nap-GFF (*1*):

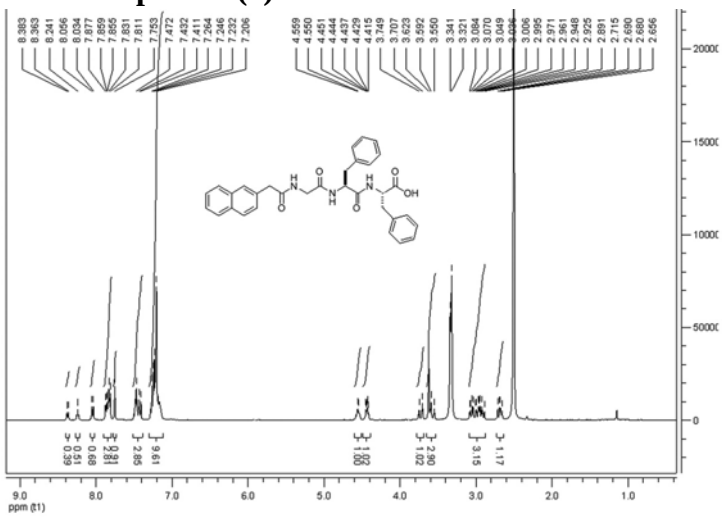

Figure S-1. ^{1}H NMR of compound ***1***

^{1}H NMR (400 MHz, DMSO-d_6): δ 8.37 (d=6.76 , 1H), 8.24 (m, 1H), 8.04 (d, 1H), 7.81-7.88 (m, 3H), 7.74 (s, 1H), 7.41-7.48 (m, 3H), 7.20-7.265 (m, 10H), 4.55-4.56 (m, 1H), 4.41-4.45 (m, 1H), 3.70-3.75 (m, 1H), 3.55-3.63 (m, 3H), 2.89-3.093 (m, 3H), 2.65-2.71 (m, 1H). MS: calc. M^+ = 538.23, obsvd. M^+ = 538.7.

Formation of hydrogels I: 20 mg compound ***1*** and 1 equiv. of Na_2CO_3 (to neutralize the carboxylic acid on ***1***) were firstly dispersed in 1.0 ml pbs buffer (pH=7.4), and then a sonication and a heating-cooling cycle were applied successively to produce hydrogels with 2 wt% of ***1***. Gel I was formed by mixing equal volume of pbs buffer and gels with 2 wt% of ***1*** by a votex for 30 seconds.

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Protein expression and purification.

Gene corresponding to the tandem L27 domain of mouse MPP6 (residues 1-106AA) and L27 domain of mouse Mals3 (residues 3-66AA) was PCR-amplified from a mouse testis cDNA library. The chimera gene $L27_{MPP6}$-3C-$L27_{Mals3}$ was constructed with individual genes connected with a sequence encoding a protease 3C cleavage site (Leu-Glu-Val-Leu-Phe-Gln-Gly-Pro) and cloned into a modified pET32a vector (Novagen), in which the trx-tag, S-tag, and the thrombin recognition site were replaced by GST-tag followed by a sequence encoding a protease TEV cleavage site (Glu-Asn-Leu-Tyr-Phe-Gln-Ser). The resulting protein contained a GST-tag in its N-terminus. Protein was expressed in BL21 (DE3) *Escherichia coil* cells at 16℃ for 16-18h. The GST-tagged protein was purified with Glutathione sepharose (GE Healthcare) affinity chromatography. After protease TEV digestion, the N-terminal GST-tag was removed by passing the digestion mixture through an ion-exhange column (GE Healthcare). The MPP6 complex protein was obtained by the SE-HPLC.

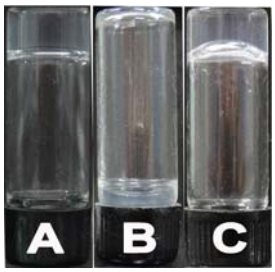

Figure S-2. Optical images of A) gel I with 1 wt% of ***1*** in pbs buffer, B) the solution formed by mixing the gel with 2 wt% of ***1*** and a pbs solution containing 0.1 mg/mL of the MPP6 complex protein (votex for 30 seconds), and C) gel II formed from solution of B (being kept at room temperature for 2 hours)

Protein degradation experiment.

A 0.1 mg/mL of protein solution in PBS buffer (pH 7.4) was mixed with the 2% gel with 1:1 proportion (v:v) by votex for 30 seconds and then the resulting gel (gel II) was incubated at room temperature. The degradation rate was terminated by adding

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sample loading dye buffer for SDS-PAGE at different time points. Samples were boiled at 100℃ for 5 min and electrophoresed on 15% sodium dodecyl sulfate polyacrylamide gel (SDS-PAGE). The protein degradation rate was analyzed by Adobe Photoshop CS4 software. The experiment was repeated for 3 times.

Analysis of CBB stained bands in SDS-PAGE

The coomassie brilliant blue (CBB) R-250 stained SDS-PAGE was scanned as grayscale image with a scanner of HP Scanjet G2410 and analyzed with Adobe Photoshop CS4. The protein bands were circled and estimated the integral grayscale pixel value minus background, which was selected at the blank area in the SDS-PAGE. The integral grayscale pixel value of control bands were normalized to 1, and the resulting ratios of sample bands were regarded as effective values.

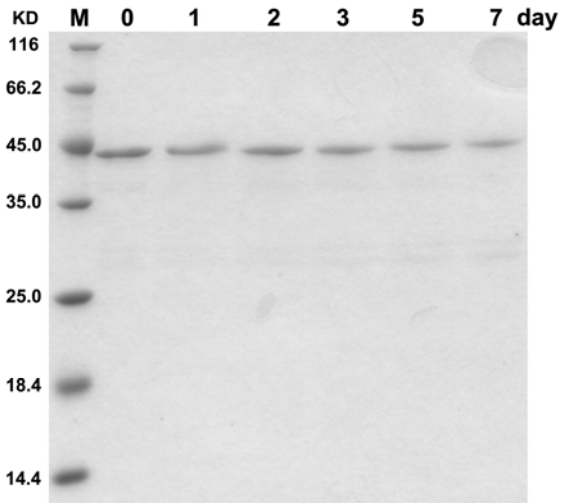

Figure S-3. The scanning image of SDS-PAGE gel electrophoresis of recombinant MPP6 complex protein in gel II at day 0-7

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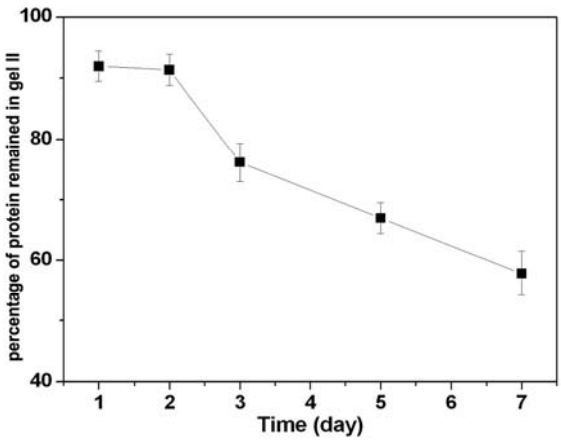

Figure S-4. The percentage of the MPP6 complex protein remained in gel II at different time points

Table S-1. The percentage of MPP6 complex protein remained in gel II at different time points

Time (day)	1	2	3	5	7
Protein remained (%)	91.9±2.4	91.4±2.5	76.2±3.1	66.9±2.5	57.8±3.6

Phosphatase activity assay.

A similar procedure for the encapsulation of the recombinant complex protein was used to incorporate phosphatase into the gel at a final concentration of 20 U/mL. 120 μL of the gel with the enzyme at different time points was taken and added to 2.0 mL of the substrate solution (concentration of 4-Nitrophenyl phosphate disodium salt hexahydrate = 5 mM in pbs buffer solutions) and then the UV intensity at 405 nm was measured after 3 minutes' incubation. The UV intensity obtained by adding 120 μL of PBS buffer solution containing 20 U/mL of the phosphatase to 2.0 mL of the substrate solution for 3 minutes was set to be 100% of activity.

Table S-2. The activity of phosphatase in the gel at different time points

Time (day)	1	2	3	5
Activity (%)	99.0±0.01	98.0±0.01	88.3±0.04	79.3±0.02

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The emission spectra of ***1*** in solution and in gels were used to study the aromatic interaction between naphthalene groups. Both gel I and gel II exhibited similar emission peaks. Similar to our previous observations,[1] the ^1L_b transition of naphthalene in solution phase at 335 nm showed a red-shift to 346 nm in the gels.[2] The stronger shoulder peaks at about 362 nm from the partial excimer of naphthalene in gels than that in the solution indicated the existence of more intense aggregations of ***1*** in the gel phases. The slightly stronger excimer peak of naphthalene at about 430 nm from gel II than that in gel I implied that the interaction between the protein and ***1*** facilitated the aromatic interaction between naphthalene groups on ***1***.

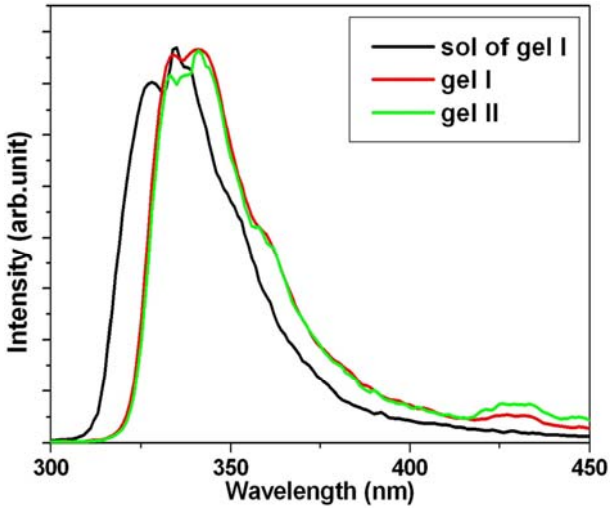

Figure S-5. Emission spectra of solution of gel I, gel I, and gel II (λ_{exc} = 272 nm)

Crystal growth.

The crystal of Nap-GFF was obtained from ethanol by a heating-cooling process: 50 mg of Nap-GFF obtained by HPLC was suspended in 3 mL of ethanol (95%). The suspension was heated by a hot water bath, and then the hot solution was filtered through a filter membrane (0.5 μm). The crystal of Nap-GFF was obtained after cooling back to room temperature in the water bath.

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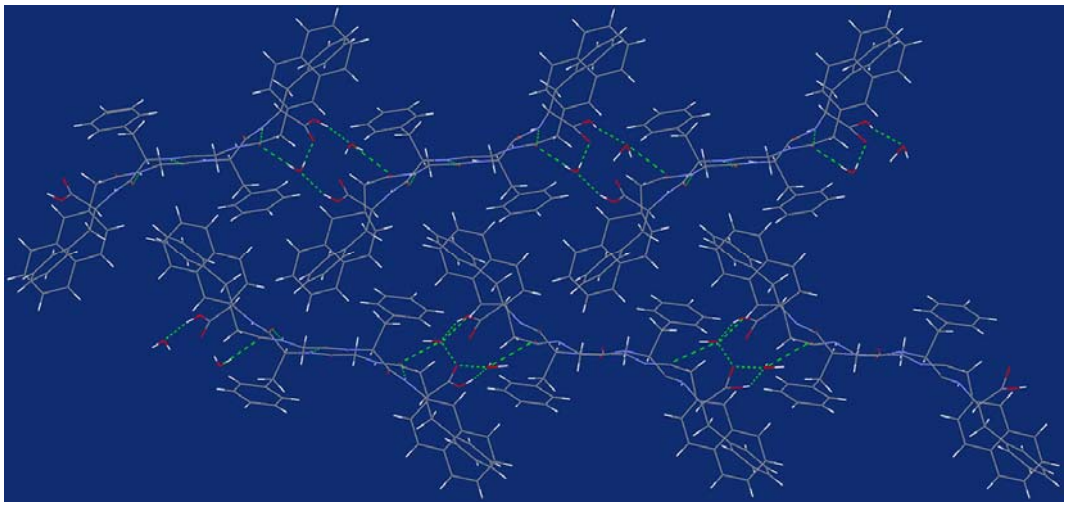

Figure S-6. The crystal structure of Nap-GFF (an enlarged image)

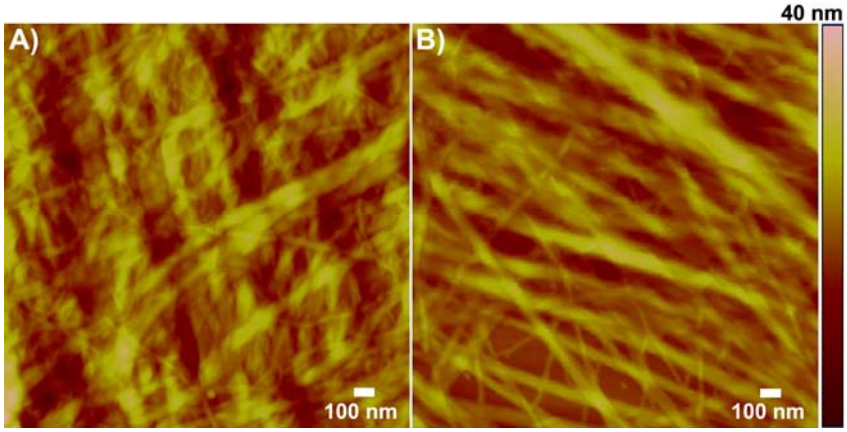

Figure S-7. AFM images of gel I before (A) and after (B) votex

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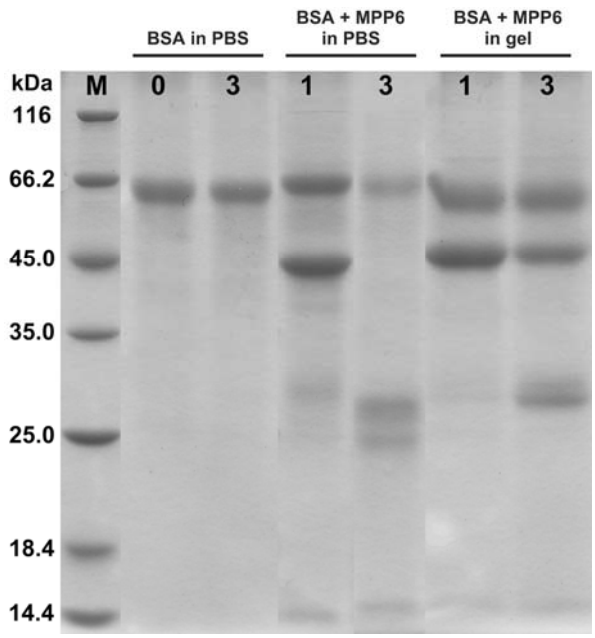

Figure S-8. The scanning image of SDS-PAGE gel electrophoresis of recombinant MPP6 complex protein and BSA in PBS buffer and in the gel at different time scales: lane 1) marker, lane 2) BSA in PBS at day 0, lane 3) BSA in PBS at day 3, lane 4) BSA and MPP6 in PBS at day 1, lane 5) BSA and MPP6 in PBS at day 3, lane 6) BSA and MPP6 in the gel at day 1, and lane 7) BSA and MPP6 in the gel at day 3

Table S-3. Crystallographic data and experimental details for Nap-GFF

Compound	**Nap-GFF**
formula	$C_{32}H_{33}N_3O_6$
Fw	555.61
a, Å	9.5455(6)
b, Å	14.7281(10)
c, Å	20.673(2)
α, °	90
β, °	90
γ, °	90

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V, Å^3	2906.3(4)
Z	4
Crystal system	Orthorhombic
space group	$P2_12_12_1$
d_{calc}, g cm^{-3}	1.270
T, K	173(2)
μ, mm^{-1}	0.721
F(000)	1176
Flack Para.	-0.1(2)
no. of refln	9229
no. of indep. refln.	5155
R_{int}	0.0410
$R1$, $wR2$ (I>2.0s(I))	0.0380, 0.0667
$R1$, $wR2$ (all data)	0.0613, 0.0711
Goodness of fit[a]	1.013
CCDC	784334

1. Y. H. Hu, H. M. Wang, J. Y. Wang, S. B. Wang, W. Liao, Y. G. Yang, Y. J. Zhang, D. L. Kong and Z. M. Yang, *Org. Biomol. Chem.*, 2010, **8**, 3267; H. M. Wang, C. H. Ren, Z. J. Song, L. Wang, X. M. Chen and Z. M. Yang, *Nanotechnology*, **21**, 225606.
2. T. Yamanaka, Y. Takahashi and K. Uchida, *Chem. Phys. Lett.*, 1990, **172**, 405.

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