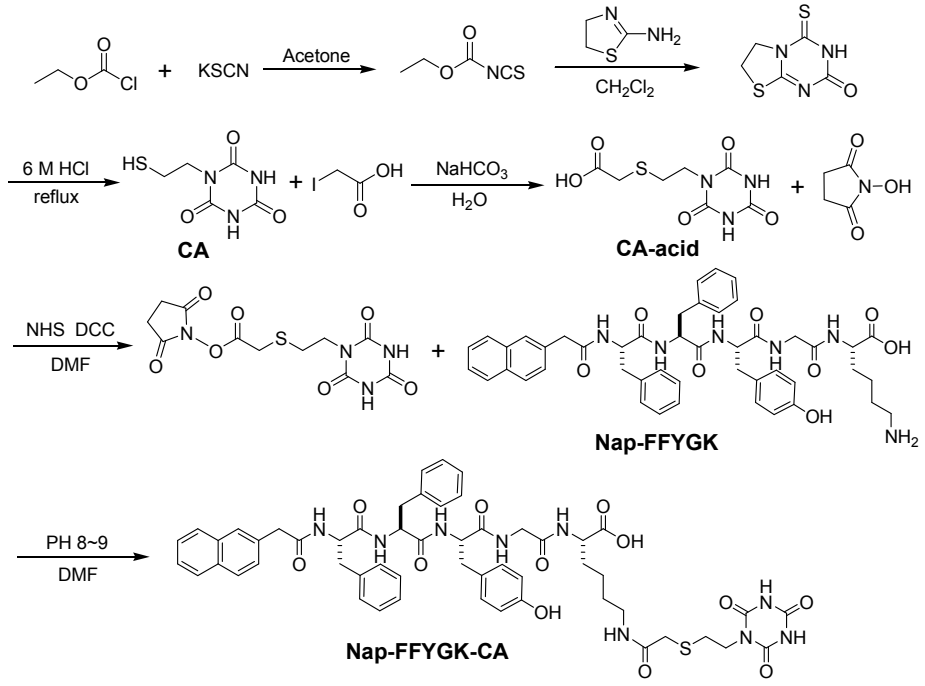
Supporting Information

Materials and methods:

Chemicals: Fmoc-amino acids were obtained from GL Biochem (Shanghai). Ethyl chloroformate, potassium thiocyanate, 2-amino-2-thiazoline and iodoacetic acid were purchased from Aladdin Chemistry CO. Ltd. Commercially available reagents were used without further purification, unless noted otherwise. Nanopure water was used for all experiments. All other chemicals were reagent grade or better.

General methods: The synthesized compounds were characterized by ^{1}H NMR (Bruker ARX 400) using DMSO-d_6 as the solvent and ESI-MS spectrometric analyses were performed at the Thermo Finnigan LCQ AD System. HPLC was conducted at LUMTECH HPLC (Germany) system using a C_{18} RP column with MeOH (0.1% of TFA) and water (0.1% of TFA) as the eluents, LC-MS was conducted at the LCMS-20AD (Shimadzu) system, and rheology was performed on an AR 2000ex (TA instrument) system using a parallel plates (40 mm) at the gap of 500 μm. TEM was done on a Tecnai G2 F20 system.



Scheme 1. The synthetic route to Nap-FFYGK-CA

Synthesis and characterization:

Synthesis of 1-(2-mercaptoethyl)-1,3,5-triazinane-2,4,6-trione (CA)[1]: The synthesis of CA was accordingly to ref. 1. Briefly, Ethyl chloroformate (4.34 g, 40 mmol) and 4.1 g (42 mmol) of potassium thiocyanate in 100 ml of acetone were heated for 15 min, and the precipitated KC1 was removed by filtration through celite. To the filtrate was added a solution of 10 mmol of the free base form of 2-amino-2-thiazoline in 200 ml of CH_2Cl_2, and the resulting mixture was heated for 0.5 h. The precipitate was collected, and the filtrate was concentrated to give a second crop product. The combined batches were washed with water to remove un-reacted KSCN and then re-crystallized from aqueous DMF to give compound 1 in 65% yield. A stirred suspension of compound 1 (2.0 g, 10.7 mmol) in 100 ml of 6 M HC1 was heated to reflux under an N_2 atmosphere for 8 h. Cooling gave, on filtration, 1.43 g of analytically pure compound CA. Evaporation of the filtrate and addition of 5 ml of H_2O gave an additional 0.37 g for a total yield of 90% of compound CA. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.47 (d, J = 10.2 Hz, 2H), 3.82–3.72 (m, 2H), 2.63 (tt, J = 9.1, 5.4 Hz, 3H).

Synthesis of CA-acid[1]: The synthesis of CA-acid was accordingly to ref. 1. Briefly, compound CA (208 mg, 1 mmol) was added to the solution of iodoacetic acid (205 mg, 1.1 mmol) in 2 mL saturated $NaHCO_3$ solution. After stirring for 1 h at room temperature, 1 M HCl was used to adjust pH to be around 1. Solution was cooled to 4℃. White precipitate was collected by filtration and washed by CH_2Cl_2 and cool water to give compound CA-acid. After dried under vacuum, 173 mg white powder was collected, giving a yield of 70%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.47 (s, 2H), 3.84 (t, J = 6.9 Hz, 2H), 3.30 (s, 2H), 2.75 (t, J = 7.0 Hz, 2H).

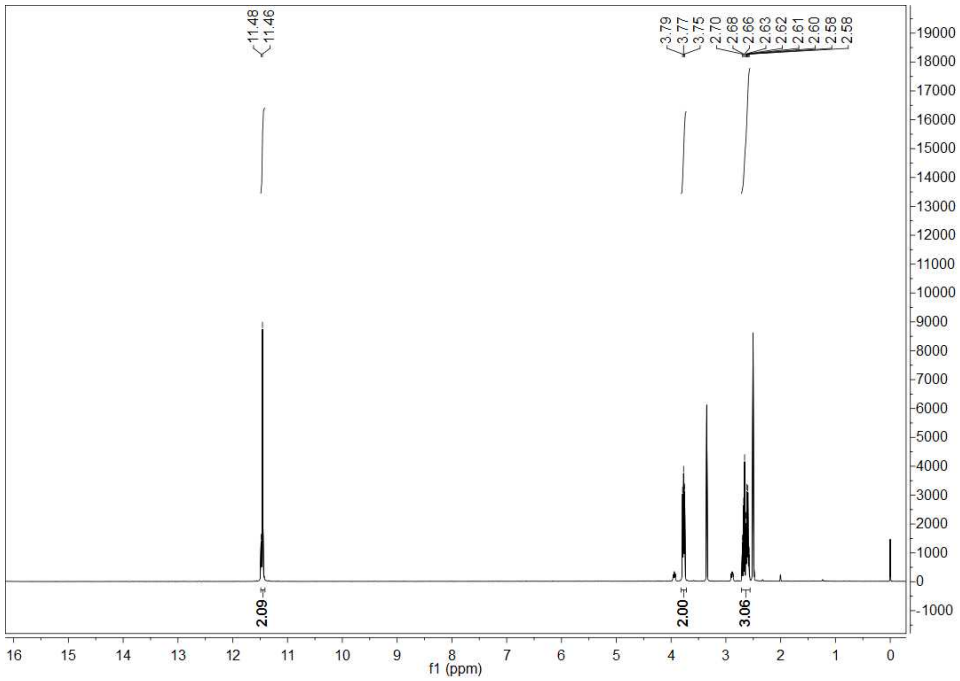


Fig. S-1. [1]H NMR of CA

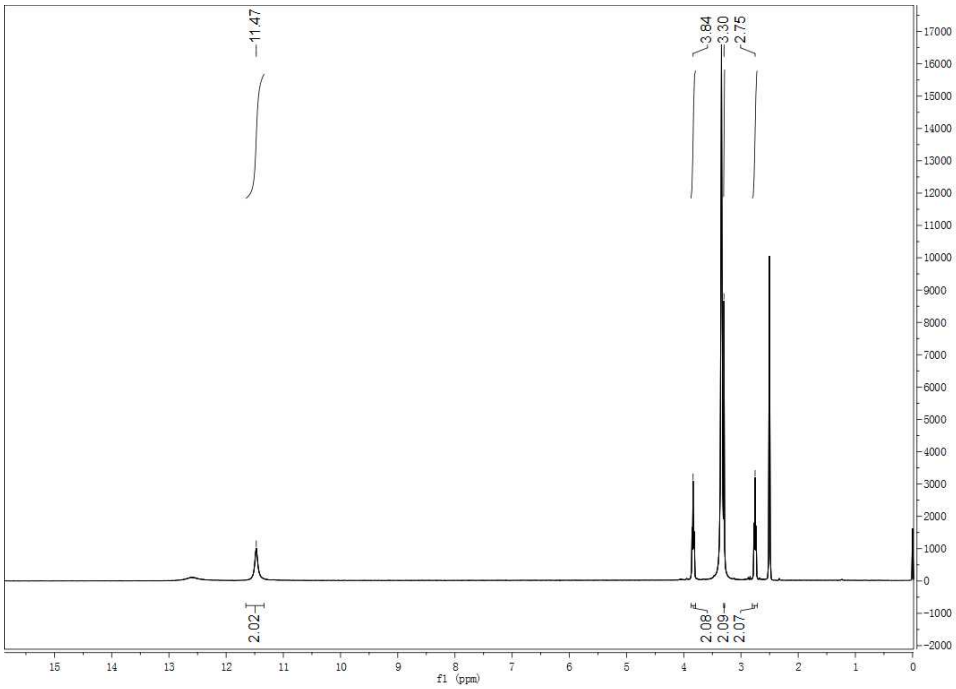


Fig. S-2. [1]H NMR of CA-acid

Synthesis of Nap-FFYGK: The peptide 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 by a tert-butyl group or

Pbf group or Boc group. After the first amino acid was loaded on the resin by its C-terminal, 20% piperidine in anhydrous N,N'-dimethylformamide (DMF) was used to 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 and diisopropylethylamine (DIEA) as catalysis reagent. The growth of the peptide chain was according to the established Fmoc SPPS protocol. After the last amino acid was coupled, excessive reagents were removed by a single DMF wash for 5 min (5 mL per gram of resin), followed by 5 times DCM wash for 2 min (5 mL per gram of resin). The peptide was cleaved using 95 % of trifluoroacetic acid (TFA) with 2.5 % of trimethylsilane (TMS) and 2.5 % of H_2O for 30 min. TFA was removed by rotary-evaporate process, then 20 mL per gram of resin of ice-cold diethylether was added. The resulting precipitate was filtrated and washed by ice-cold diethylether. The resulting solid was purified by HPLC and dried by lyophilizer.

Synthesis of Nap-FFYGK-CA: 1.1 mmol CA-acid was dissolved in DMF and 1.2 mmol DCC and NHS were added. After stirring for 2 h at room temperature, the resulting solution was filtrated to give the filtrate. 1 mmol Nap-FFYGK was then added in to the above filtrate. After 6 h reaction, the resulting solution was resorted to HPLC to purify the compound Nap-FFYGK-CA. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.48 (d, J = 13.4 Hz, 2H), 9.15 (s, 1H), 8.29 – 7.41 (m, 11H), 7.28 – 6.91 (m, 10H), 6.64 (d, J = 8.3 Hz, 2H), 4.52 (s, 3H), 4.18 (d, J = 4.7 Hz, 1H), 3.94 – 3.64 (m, 4H), 3.62 – 3.40 (m, 3H), 3.21 – 2.56 (m, 12H), 2.33 (s, 1H), 1.65 (d, J = 40.7 Hz, 2H), 1.43 – 1.21 (m, 4H). HR-MS: calc. M^+ = 1057.40, obsd. $[M+H]^+$ = 1058.4025.

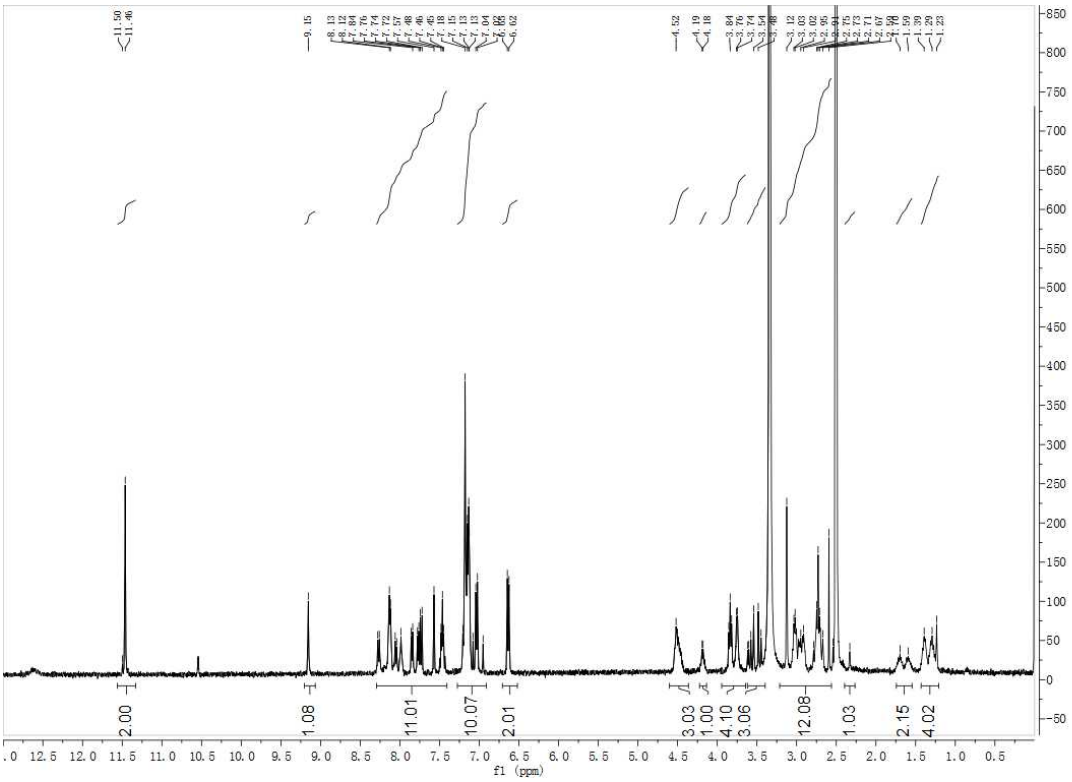


Fig. S-3. ^{1}H NMR of Nap-FFYGK-CA

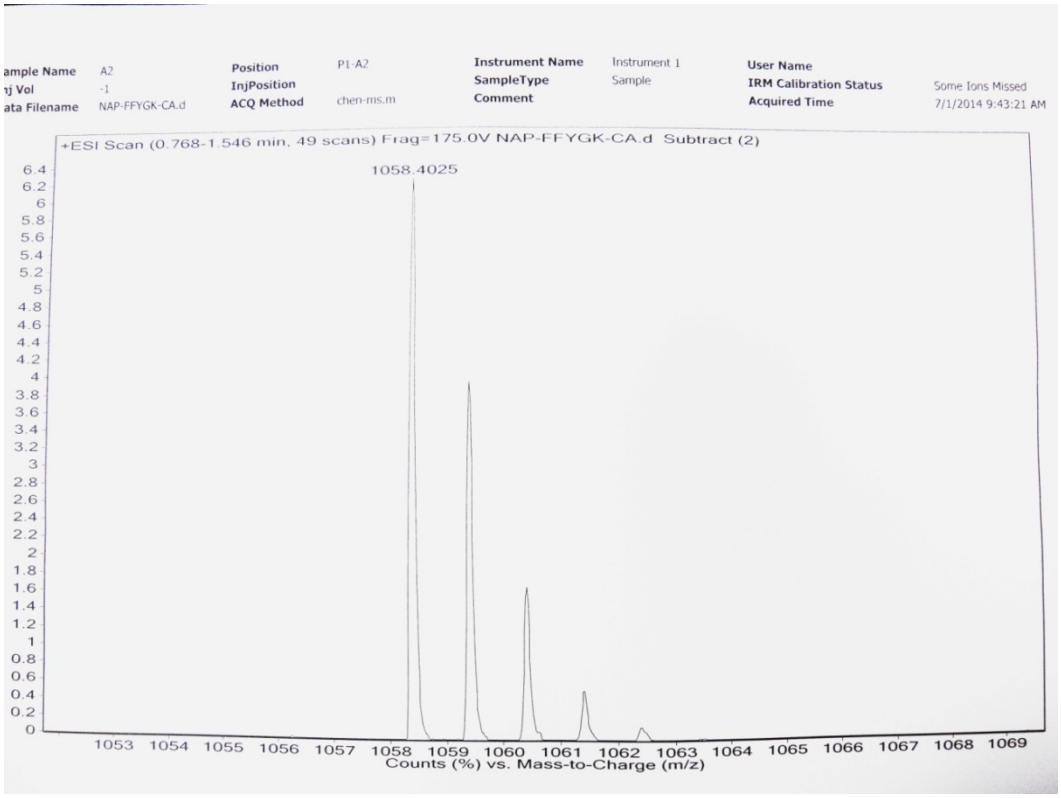


Fig. S-4. HR-MS of Nap-FFYGK-CA

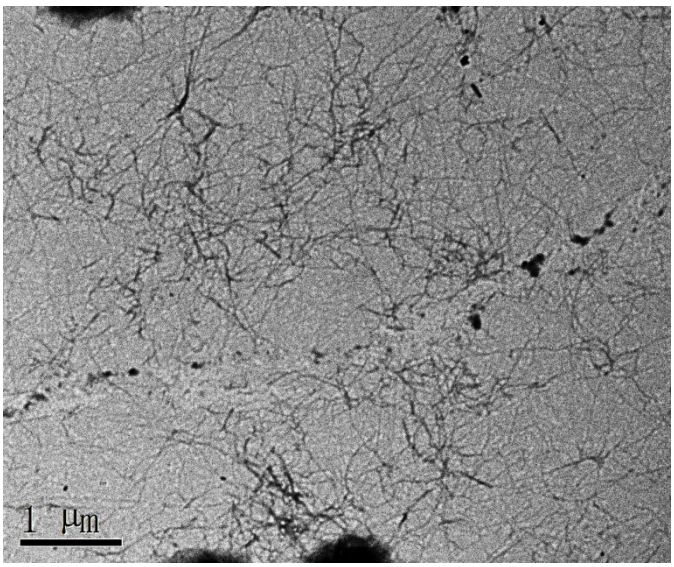


Fig. S-5. A representative TEM image of a gel of Nap-FFYGK-CA with 0.25 equivalent of melamine

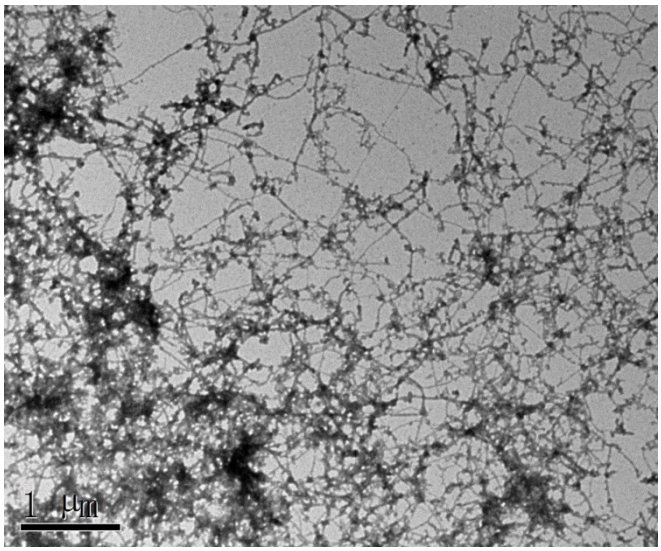


Fig. S-6. A representative TEM image of a gel of Nap-FFYGK-CA with 0.5 equivalent of melamine

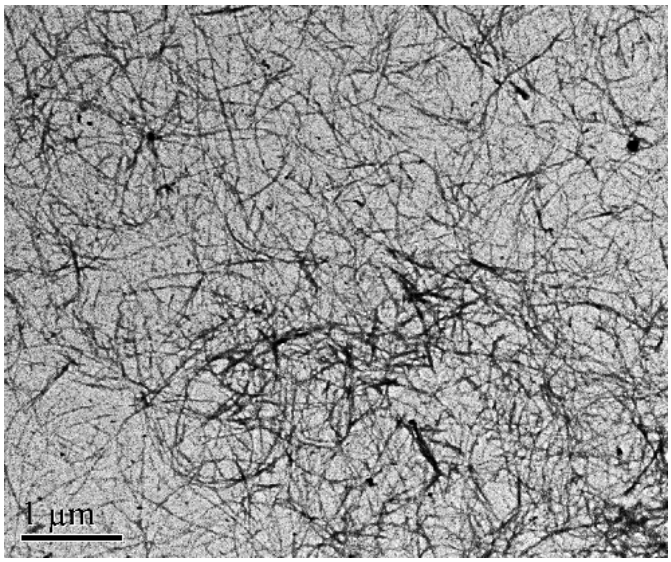


Fig. S-7. A representative TEM image of a gel of Nap-FFYGK-CA with 1 equivalent of melamine

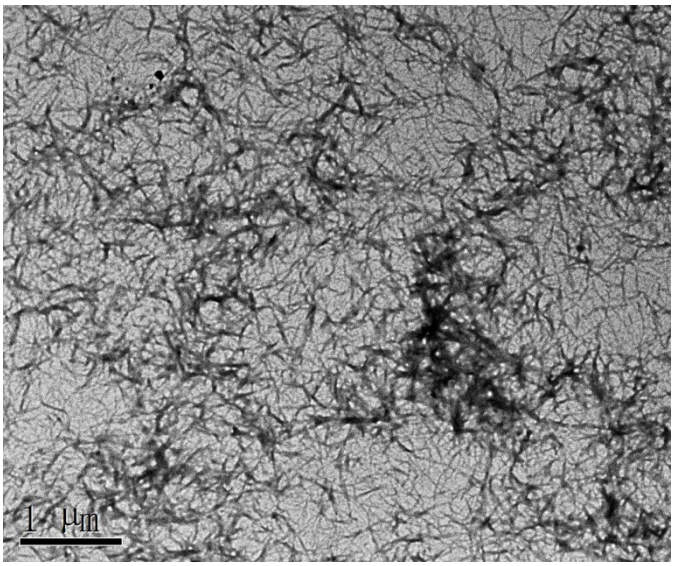


Fig. S-8. A representative TEM image of a gel of Nap-FFYGK-CA with 8 equivalent of melamine

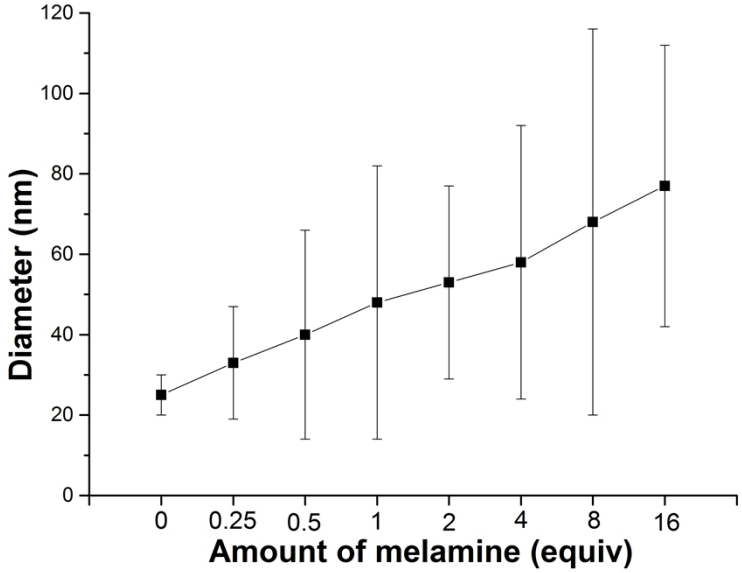


Fig. S-9. Diameter of the fibers in the gels of Nap-FFYGK-CA with different amount of melamine (more than 50 nanofibers in several TEM images were used and their diameter was calculated to obtain the mean diameter)

Rheology: Rheology test was carried out on an AR 2000ex (TA instrument) system, 40 mm parallel plate was used during the experiment at the gap of 500 μm. For the dynamic time sweep, the sample after heating was directly transferred to the rheometer and it was performed at the frequency of 1 rad/s and the strain of 0.1%. The gel was characterized for the dynamic frequency sweep in the frequency region of 0.1-100 rad/s at the strain of 0.1%. For dynamic strain sweep, it was characterized in the strain region of 0.1-10 % at the frequency of 1 rad/s.

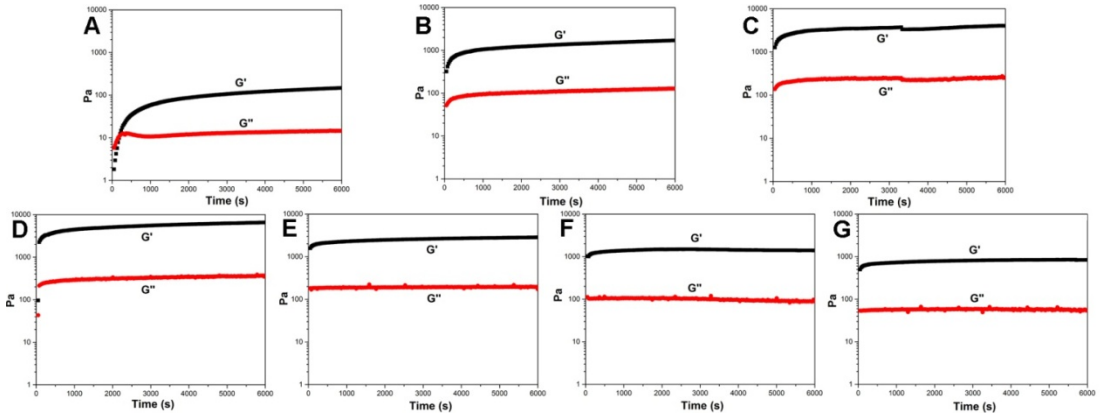


Fig. S-10. Rheological measurement with the mode of dynamic time sweep at the frequency of 1 rad/s and strain of 0.1% for the gels of Nap-FFYGK-CA with different equivalent of melamine: A (0.25 equiv), B (0.5 equiv), C (1 equiv), D (2 equiv), E (4 equiv), F (8 equiv), G (16 equiv)

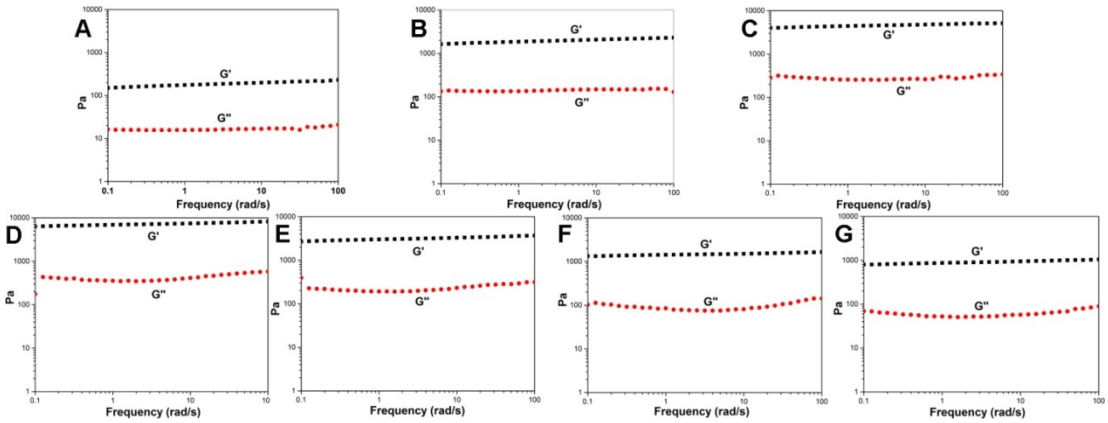


Fig. S-11. Rheological measurement with the mode of dynamic frequency sweep at the frequency of 1 rad/s and strain of 0.1% for the gel of Nap-FFYGK-CA with different equivalent of melamine: A (0.25 equiv), B (0.5 equiv), C(1 equiv), D(2 equiv), E(4 equiv), F(8 equiv), G(16 equiv)

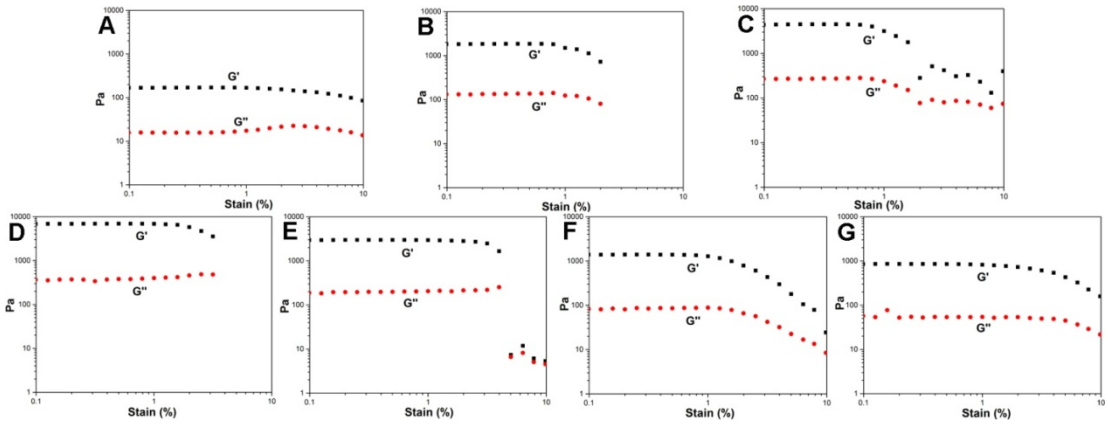


Fig. S-12. Rheological measurement with the mode of dynamic strain sweep at the frequency of 1 rad/s and strain of 0.1% for the gel of Nap-FFYGK-CA with different equivalent of melamine: A (0.25 equiv), B (0.5 equiv), C(1 equiv), D(2 equiv), E(4 equiv), F(8 equiv), G(16 equiv).

1 M. M. Ma, A. Paredes and D. Bong, *J. Am. Chem. Soc.*, 2008, **130**, 14456.