Supporting information for:

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S1. Optical image of the hydrogel formed by 1

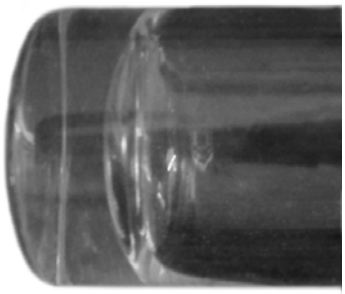

Figure S1. The hydrogel formed by 0.4 wt% of **1** in PBS buffer.

Hydrogelation of **1** demonstrates the ability of self-assembly of **1**.

S2. Characteristics of 1 at the concentration below the threshold concentration of self-assembly

S2.1 TEM image of 1 at 300 μM

Negative staining of TEM: Carbon coated grids were glow discharged just before using to increase their hydrophilicity. The sample solution (3 μL) was placed on the grid to cover the grid surface. After rinsing the grids for 10 s, a large drop of the ddH_2O was placed on parafilm and let the grid touch the water drop, with the sample-loaded surface facing the parafilm. The grid was tilted, and water was gently absorbed from the edge of the grid by using a filter paper for 3 times. The grid was stained immediately by letting the grid touch a drop of 2.0 % (w/v) uranyl acetate on the parafilm with the sample-loaded surface. The grid was tilted, and the stain solution was gently absorbed from the edge of the grid by using a filter paper for 3 times. The grid was allowed to dry in air for a few minutes and was examined immediately.

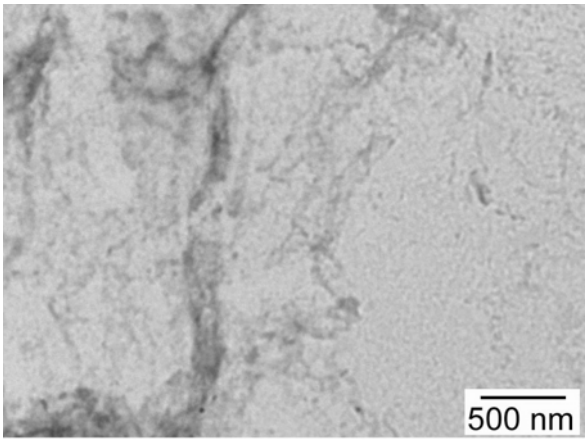

Figure S2. Negative-stained TEM images of the solution of **1** at 300 μM in PBS buffer.

S2.2 Fluorescent spectra of 1 at different concentration

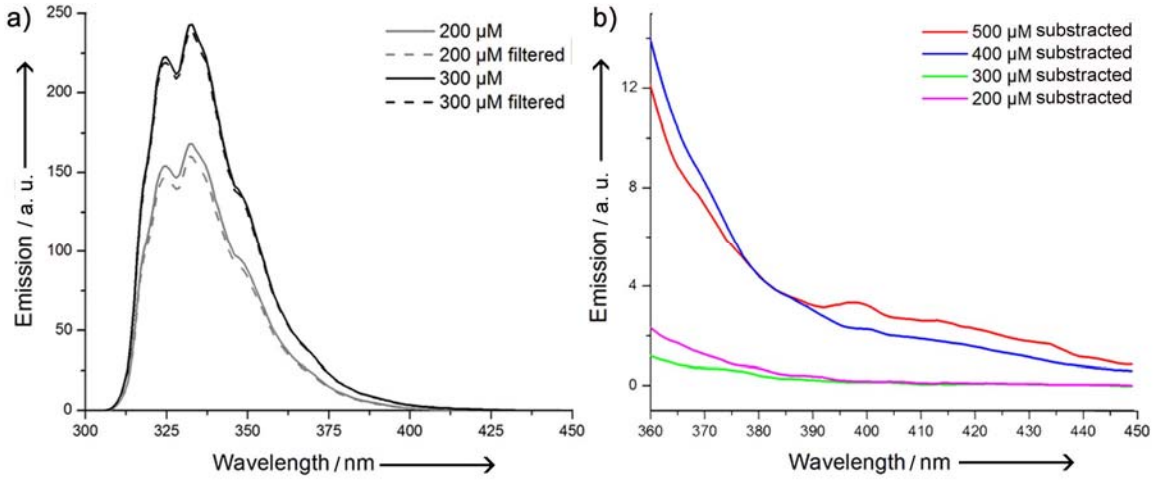

Figure S3. Fluorescence spectra of **1** in PBS buffer with increased concentration of **1** (λ_{ex} = 275 nm). a) Fluorescence spectra of **1** at 200 and 300 μM in PBS buffer with and without filtration. b) The excimer band of naphthalene group was obtained by subtraction of the fluorescence spectra of filtrated **1** from the spectra of as prepared **1** solution (λ_{ex} = 275 nm). Filtration of **1** induces little change in the emission intensity of **1** at 200 and 300 μM and there is little intensity for excimer of naphthalene at 200 and 300 μM.

S3. Long term cytotoxicity of 1 on PC12 cells

MTT cell viability test: Seed cells in a 96 well plate at a concentration of 50,000 cell/well. Allow attachment for 24 h at 37ºC, 5% CO_2, remove culture medium and place 100 µL new culture medium containing **1** into each well. After culturing at 37 ºC, 5 % CO_2 for desired time, add 10 µL of 5 mg/mL MTT ((3-(4,5-Dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide) to each well and incubate the plated at dark for 4 h. Add 100 µL 10 % SDS with 0.01 M HCl to each well to stop the reduction reaction and dissolve the purple. After incubation at 37 ºC for overnight, determine the viability by DTX 880 multimode detector.

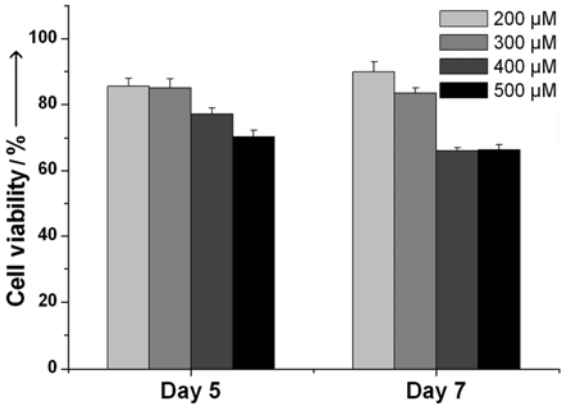

Figure S4. MTT cell viability tests of long-term cytotoxicity of **1** on PC12 cells.

S4. Time dependent cytotoxicity of 1 on HeLa cells

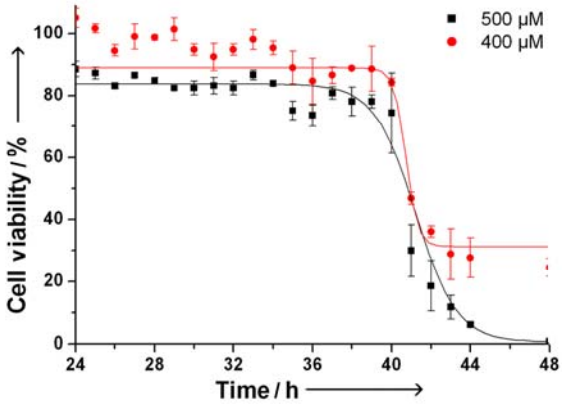

Figure S5. Time dependent cytotoxicity of the nanofibers of **1** towards HeLa cells.

S5. Apoptosis assays on T98G cells

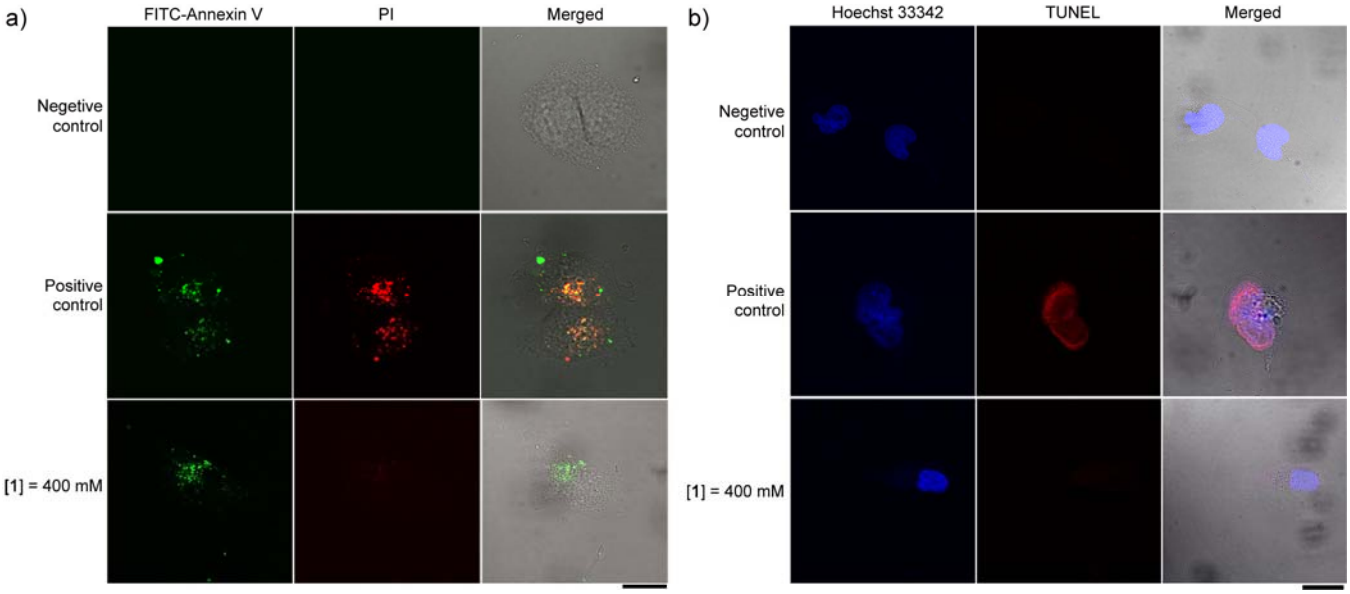

Figure S6. Apoptosis assays on T98G cells. a) FITC-annexin V and PI assays of T98G cells. Negative control is untreated T98G cells. Positive control induced by incubation of T98G cells with 10% DMSO for 24 h. T98G cells treated by 400 µM of **1** for 24 h shows positive FITC-annexin V stain but negative PI stain. b) TUNEL assays of T98G cells. Negative control is untreated T98G cells. Positive control induced by incubation of T98G cells with DNAase I for 30 min. Scale bar = 10 µm.

S6. Comparison of the intracellular concentrations of 1 in PC12 and T98G cells

*Intracellular concentration of **1***: Cells in exponential growth phase were seeded in 10 cm petri dish at 10,000 cell/mL. The cells were allowed for attachment for 24 h at 37 ºC, 5% CO_2. The culture medium was removed, and new culture medium containing **1** at 0 or 400 μM was added. After 12 h of incubation, cells were washed with PBS buffer for 3 times and collected by cell scraper with 1 mL of PBS buffer. Centrifuge the cell suspension at 600 g for 5 min to get cell pellet. Take 10 μL of cell pellet and lyse the cells in 200 μL of water and 200 μL of MeOH. Centrifuge at 12,000 g for 5 min to remove insoluble proteins and collect the lysate suspension. The concentration of **1** in the lysate was measured by LC-MS.

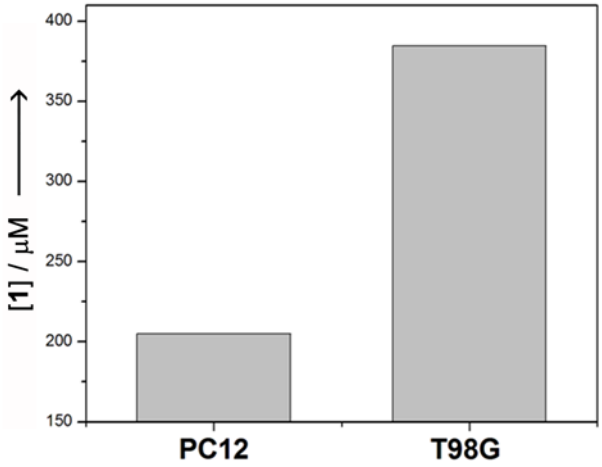

Figure S7. Intracellular concentration of **1** in PC12 and T98G cells after incubation with 400 μM of **1** for 12 h.

S7. Characteristics and cytotoxicity of a structure analog of 1

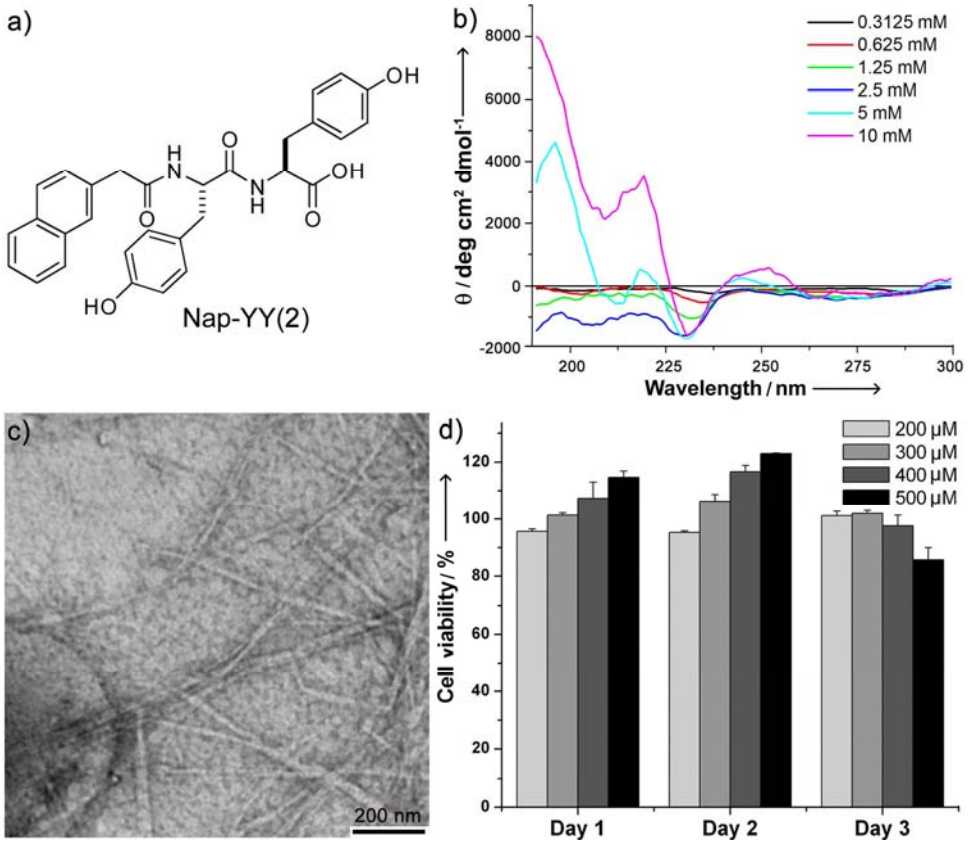

Figure S8. Replacement of phenylalanine in **1** to tyrosine gives rise to Nap-YY (**2**) that has poorer gelation ability and lower cytotoxicity than **1**. a) Chemical structure of **2**. b) Circular dichroism spectra of **2** at different concentrations in PBS buffer. c) TEM image of **2** at 5 mM shows the self-assembled structures of **2**. d) MTT assay of HeLa cells incubated with **2**.

S8. Quantification of concentration of 1 after filtration

Table S1. Concentrations of **1** after filtration.

Initial concentration (μM)	**Concentration after filtration(μM)**[a]
200	190
300	251
400	336
500	329

[a] Following filtration, the solutions of **1** were diluted three folds by MeOH to ensure complete dissolution of **1**. The concentration of **1** was calculated from the absorbance of the solution at 260 nm.