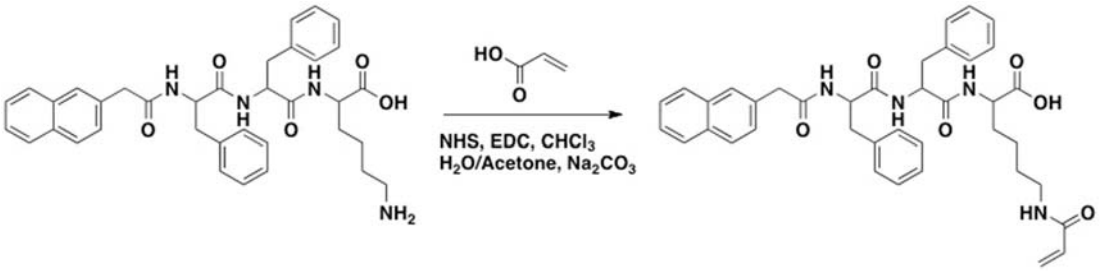
# Post-Self-Assembly Crosslinking of Molecular Nanofibers for Chemical Oscillatory Hydrogels

# SUPPORTING INFORMATION

## Experimental Section

### Synthesis of 6-acrylamido-2-(2-(2-(2-(naphthalen-2-yl)acetamido)-3-phenylpropanamido)-3-phenylpropanamido)hexanoic acid (1)




1-Ethyl-3-(3-dimethylaminopropyl) carbodiimine (EDC) (2.48 mmol, 385.0 mg) was added into chloroform (10 mL) solution of acrylic acid (1.24 mmol, 0.085 mL) and *N*-hydroxysuccinimide (NHS) (1.48 mmol, 170.3 mg). The mixture was stirred at room temperature for 2 hours. We then removed the solvent and dissolved the residue with 5 mL acetone. This acetone solution was added dropwise to a water/acetone solution (pH = 8 by addition of sodium carbonate) of 6-amino-2-(2-(2-(2-(naphthalen-2-yl)acetamido)-3-phenylpropanamido)-3-phenylpropanamido) hexanoic acid (NapFFK) (0.62 mmol, 376 mg). The mixture was stirred at room temperature for 4 h. We then removed the acetone and added concentrated hydrochloric acid into the residue until the mixture's pH was 2-3. We collected the white precipitate by filtering the mixture. The pure compound was obtained after column chromatography (silica gel, $CHCl_3$/MeOH) in 62.0% yield. $^1$H NMR (400 MHz, $d_6$-DMSO): $\delta$ 8.28 (d, 1H, $J$ = 8.4 Hz), 8.24 (d, 1H, $J$ = 6.4 Hz), 8.18 (d, 1H, $J$ = 8.0 Hz), 8.10 (t, 1H, $J$ = 5.2 Hz), 7.85 (d, 1H, $J$ = 8.4 Hz), 7.76 (dd, 2H, $J$ = 8.0, 16.0 Hz), 7.58 (s, 1H), 7.49-7.43 (m, 2H), 7.26-7.14 (m, 10H), 6.20 (dd, 1H, $J$ = 10.0, 17.2 Hz), 6.06 (dd, 1H, $J$ = 1.6, 16.8 Hz), 5.55 (dd, 1H, $J$ = 2.0, 10.0 Hz), 4.61-4.48 (m, 2H), 4.20-4.10 (m, 1H), 3.52 (dd, 2H, $J$ = 14.0, 38.4 Hz), 3.07-2.95 (m, 3H), 2.84-2.67 (m, 3H), 1.76-1.58 (m, 2H), 1.46-1.30 (m, 4H) ppm.

**Preparation of $Gel_{1+2}$**

**1** (6.6 mg) and **2** (1.2 mg) were mixed in 400 μL water, and the mixture was sonicated for thorough mixing. Meanwhile, 1N NaOH solution was added into the mixture to assist the dissolution of **1**. When the pH reached 10-12, the volume of the mixture was adjusted to 600 μL by adding water. Then the mixture was sonicated to mix thoroughly until it looked transparent. Finally, the gel solution was kept at room temperature for 2 h, and $Gel_{1+2}$ was formed.

**Fabrication of x-$Gel_{1+2}$**

After the bottle containing $Gel_{1+2}$ was sealed with a rubber septum, $Gel_{1+2}$ was degassed with $N_2$. After 2 mg $V_{50}$ was dissolved in 20 μL of degassed water, 2 μL of the $V_{50}$ solution was added to $Gel_{1+2}$. The mixture was sonicated thoroughly. The gel was drawn into a syringe and injected into a sandwich mold made from two glass slides and a piece of silicon rubber sheet. The mold was sealed and placed under UV light for 20 min. After the mold was removed, the gel sheet was immersed in water for dialysis for 1 day. Thus, the x-$Gel_{1+2}$ was obtained.

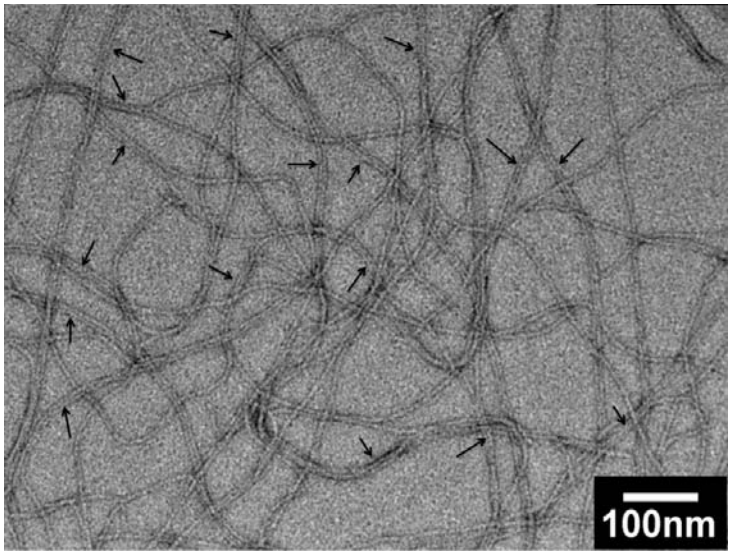



**Figure s1**. TEM image showing parallel nanofibers in $Gel_{1+2}$. Black arrows point to regions where two single fibers align with each other.

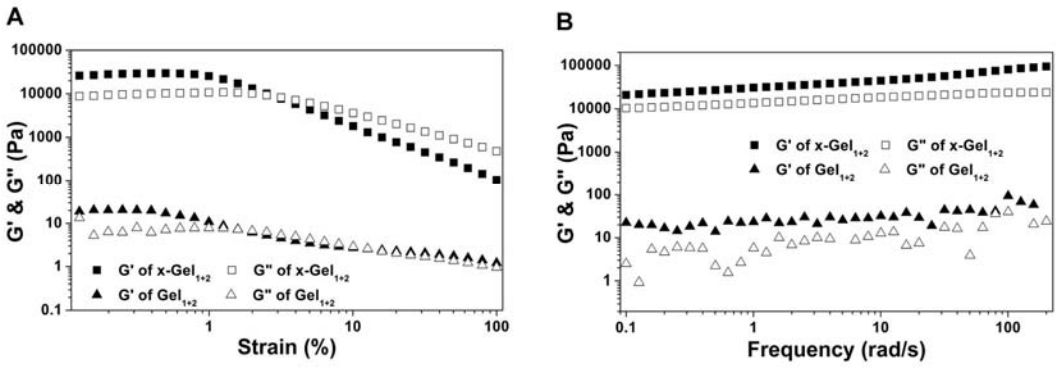



**Figure S2**. (A) Strain and (B) Frequency dependences of dynamic storage modulus ($G'$) and loss modulus ($G''$) of x-$Gel_{1+2}$ and $Gel_{1+2}$

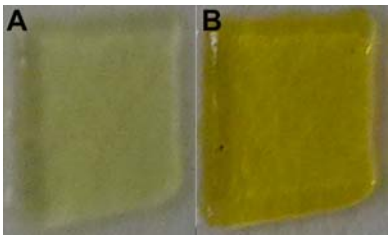



Figure s2. Optical images of oxidized x-$Gel_{1+2}$ (A) and x-$Gel_{1+2}$ (B).

**Measurement of Oscillations**

After the gel was cut into a square of edge 1 cm, it was put into an optical cell with a temperature-controlled water bath. The gel was immersed with BZ reaction solution prepared and mixed in advance. A microscope adapted with a CCD took images every few seconds. All images were analyzed by IDL software. We wrote a program for IDL to take spots along a line across the whole gel piece to obtain the time-space plot. Finally, image J was used to analyze the time-space plot to obtain the oscillation profile in Figure 3.

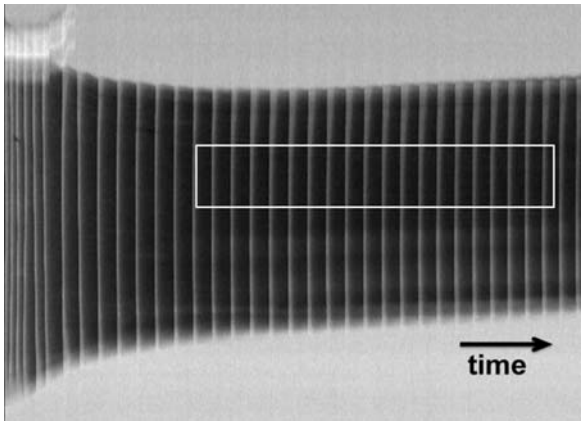


**Figure s3**. Time-space plot of poly(NIPAAm-Ru) at 20 °C in aqueous solution with the same initial conditions as Figure 3. The rectangular area was selected for analysis by image J to obtain the oscillation profile in Figure s4.

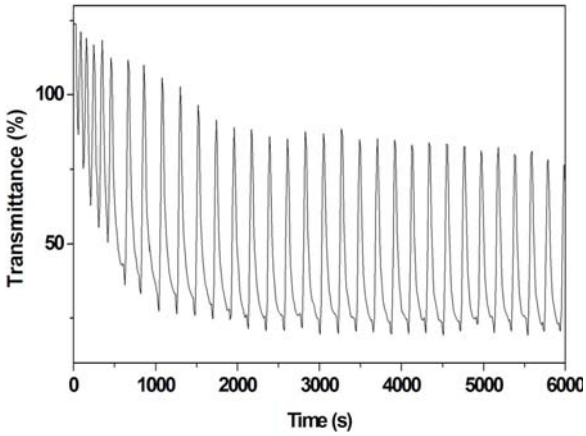



**Figure s4**. Oscillation profile of optical transmittance for poly(NIPAAm-Ru) at 20 °C in aqueous solution with the same initial conditions as Figure 3. The average oscillation period of the gel is 212 s after 1000s when the oscillation is stable.


**Figure s5**. Time-space plot of $Gel_{1+2}$ at 20 °C in aqueous solution with the same initial conditions as Figure 3. The rectangular area was selected for analysis by image J to obtain the oscillation profile in Figure 3A.

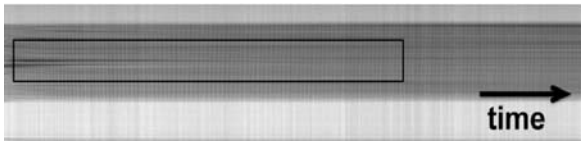



**Figure s6**. Time-space plot of x-$Gel_{1+2}$ at 20 °C in aqueous solution with the same initial conditions as Figure 3. The rectangular area was selected for analysis by image J to obtain the oscillation profile in Figure 3B.