

Electronic Supplementary Information

Self-deformable gel system with asymmetric shape change based on gradient structure

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1. Materials and Methods

Ruthenium (III) chloride hydrate ($\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$, 99 %), 4,4'-dimethyl-2,2'-dipyridyl, ammonium hexafluorophosphate ($\text{NH}_4[\text{PF}_6]$), N-butyllithium (2.2 mol/L in hexane), sodium bromate (NaBrO_3), malonic acid (MA), N-isopropylacrylamide (NIPAAm), N,N',N',N'-tetramethylethylenediamine (TEMED), xylene were purchased from Aladdin Reagent (Shanghai, China). 2,2'-bipyridine, lithium chloride (LiCl), sodium dodecyl sulfate (SDS), methacrylic acid (MAA), diisopropylamine, dimethyl formamide (DMF), tetrahydrofuran (THF) were purchased from TCI reagent Co., Ltd (Shanghai, China). Cerium (III) sulfate and cerium (IV) sulfate were purchased from Sinopharm Chemical reagent Co., Ltd (Shanghai, China). Sodium bicarbonate (NaHCO_3), potassium persulfate (KPS), phosphorus pentoxide (P_2O_5), ether, acetone, dichloromethane (DCM), paraformaldehyde, nitric acid (HNO_3 , 68 %), methanol, dimethyl sulfoxide (DMSO) were purchased from Kelong Chemicals (Chengdu, China). N,N'-methylenebisacrylamide (MBA), 2,2-dimethoxy-2-phenylacetophenone (DMPA), were purchased from J&K Chemicals (Beijing, China) and recrystallized before use. The deionized water used in this study was lab made.

2. Characterizations

^1H NMR spectra were recorded on a 300MHz Bruker Avance-300 NMR spectrometer, and chemical shifts were reported in parts per million (ppm) in reference to the residual protons of the deuterated solvents. FTIR spectra were obtained on a FTIR spectrophotometer (Nicolet MX-1E) using KBr pellet pressing method. Particle size analyze was performed on a Malvern laser particle size analyzer (mastersizer 2000), and the dispersing agent was water. On-line observations of the

gel system were carried out on an Olympus stereomicroscope with image capture system. Image analysis was carried out by Olympus Cellsens standard software.

3. Synthesis of Ru(bpy)₃ monomer

The BZ active monomer ruthenium (4-vinyl-4'-methyl-2,2'-bipyridine)-bis-(2,2'-bipyridine)-bis-(hexafluorophosphate) (Ru(vmpy)(bpy)₂(PF₆)₂) was synthesized according to published literature^[1,2] with some improvements, The detailed procedure was as follow.

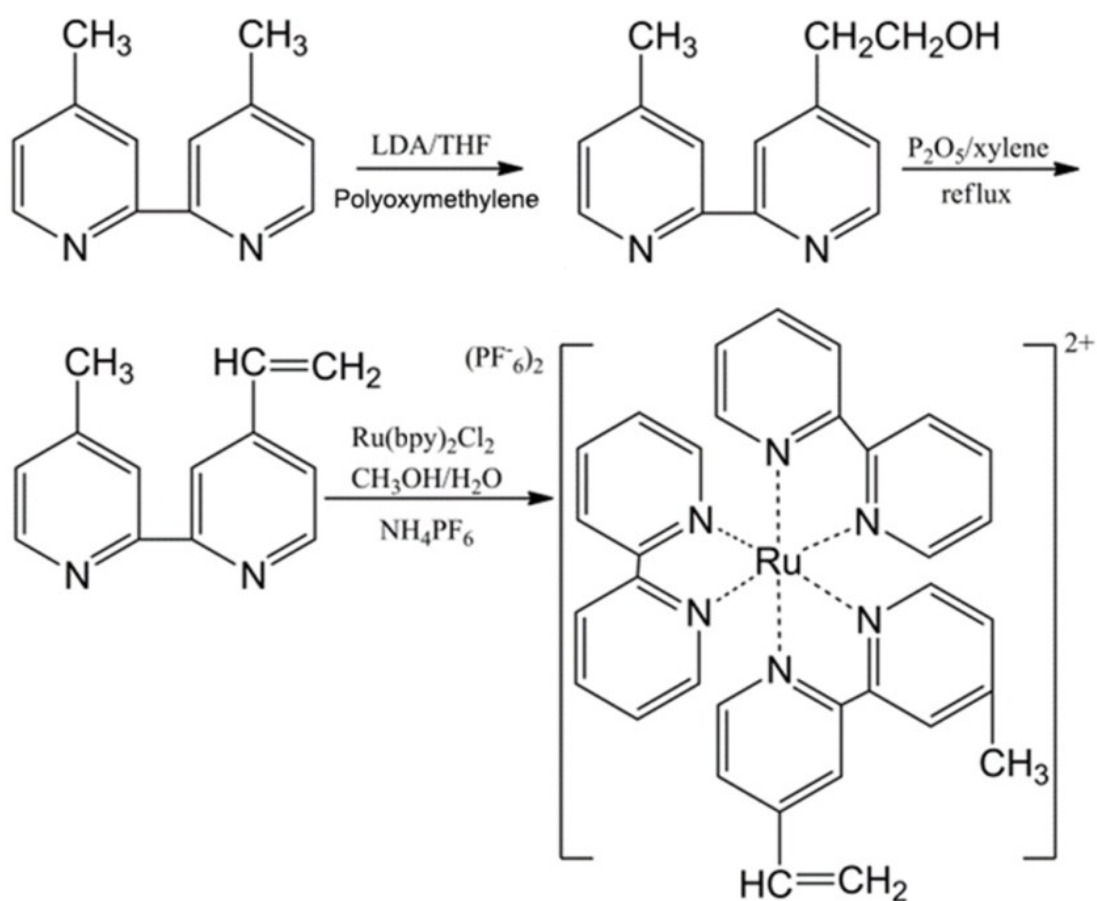


Figure S1 Synthetic route of Ru(vmpy)(bpy)₂(PF₆)₂

3.1 Synthesis of 4-hydroxyethyl-4'-methyl-2,2'-bipyridine

25.6 mL N-butyllithium and 8.0 mL diisopropylamine were added to 30 mL THF in a three-neck flask, the solution was thoroughly stirred. 10 g 4,4'-dimethyl-2,2'-dipyridyl in 250 mL THF was slowly added to the three-neck flask from a dropping funnel, and the color turned to brown. 2 h later, 1.7 g paraformaldehyde was added in, the reaction continued for over 24 h, the mixture gradually turned to green and opaque. The mixture was quenched with ice water and extracted with ether, then evaporated. The crude product was purified via column chromatography (DCM: MeOH=15:1) to get viscous liquid (7.63 g, yield: 65 %). $^1\text{H NMR}$ (300MHz, CDCl_3): δ 8.55-8.57 (d, 2 H), 8.20-8.25 (d, 2 H), 7.12-7.26 (q, 2 H), 3.93-3.97 (t, 2 H), 2.92-2.96 (t, 2 H), 2.43 (s, 3 H).

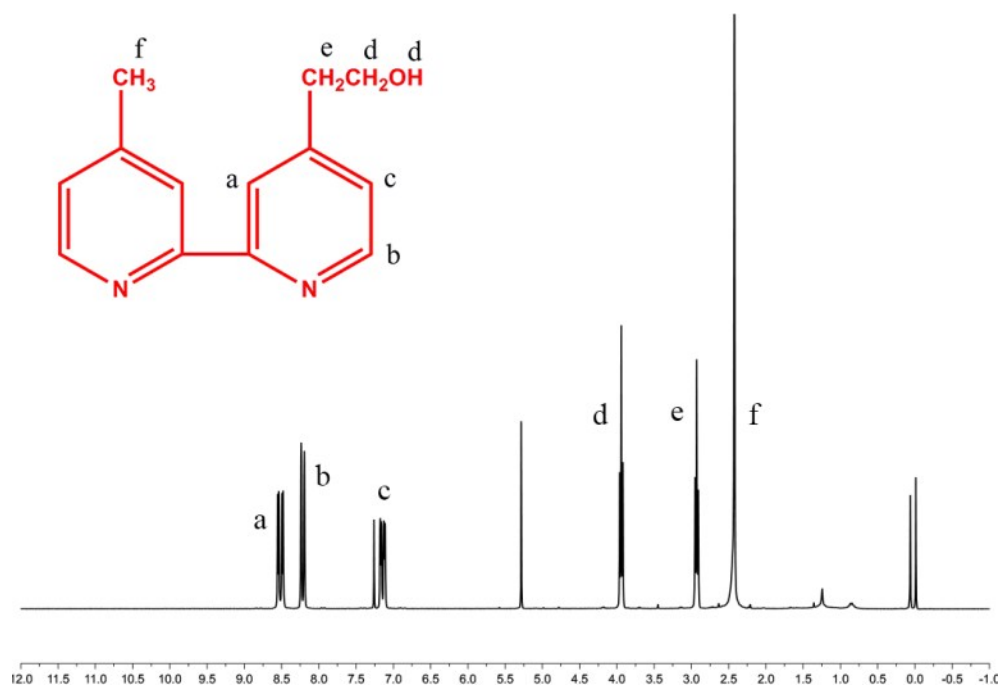


Figure S2 $^1\text{H NMR}$ spectrum of 4-hydroxyethyl-4'-methyl-2,2'-bipyridine

3.2 Synthesis of 4-Vinyl-4'-methyl-2,2'-bipyridine

7.5 g 4-hydroxyethyl-4'-methyl-2,2'-bipyridine in 200 mL of xylene was reflux with 30 g P_2O_5 for 2 h, then the mixture was cooled and ice cube was added to decompose the excess P_2O_5 . The aqueous layer was separated and the organic layer was extracted with DCM. By evaporation of DCM and purification via column chromatography (DCM: MeOH=15:1), a white solid was obtained (4.43g, yield: 60 %). 1H NMR (300MHz, $CDCl_3$): δ 8.61-8.63 (d, 1 H), 8.54-8.56 (d, 1 H), 8.41 (s, 1 H), 8.25 (s, 1 H), 7.30-7.32 (q, 1 H), 7.15-7.16(d, 1 H), 6.72-6.81 (q, 1 H), 6.07-6.13 (d, 1 H), 5.51-5.54 (d, 1 H), 2.45 (s, 3 H).

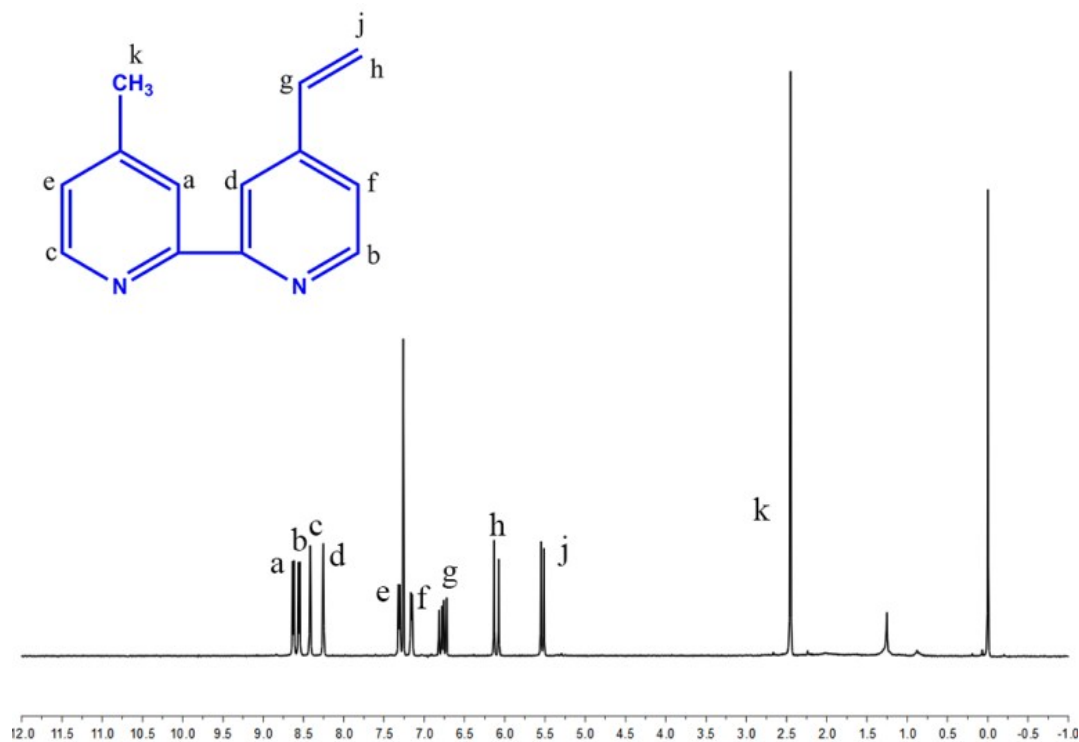


Figure S3 1H NMR spectrum of 4-vinyl-4'-methyl-2,2'-bipyridine

3.3 Synthesis of Ru(bpy)₂Cl₂

7.8 g RuCl₃·3H₂O, 9.36 g 2,2'-bipyridine and 8.4 g LiCl were added to 50 mL DMF, then the mixture was refluxed for 9 h. 250 mL acetone was poured into the mixture and kept overnight. After filtration, the solid was gently washed by deionized water until the filtrate turned to green then washed by ether for three times. Vacuum drying gave a white solid (6.62 g, yield: 53 %).

3.4 Synthesis of Ru(vmpy)(bpy)₂(PF₆)₂

1 g 4-Vinyl-4'-methyl-2,2'-bipyridine, 2.65 g Ru(bpy)₂Cl₂ and 1.52 g NaHCO₃ were refluxed together in 60 mL methanol-water (2:3 v/v) solution, until the mixture turned to blood red. 4 mL aqueous NH₄[PF₆] was added and a red solid precipitated out. The product (3.45 g, yield: 70 %) was obtained via recrystallization from acetone/DCM (1:1 v/v) solution. ¹H NMR (300MHz, acetone-*d*₆): δ 6.82-8.89 (aromatic moiety, 22 H), 6.41-6.47 (d, 1 H), 5.74-5.78 (d, 1 H), 2.49 (s, 3 H).

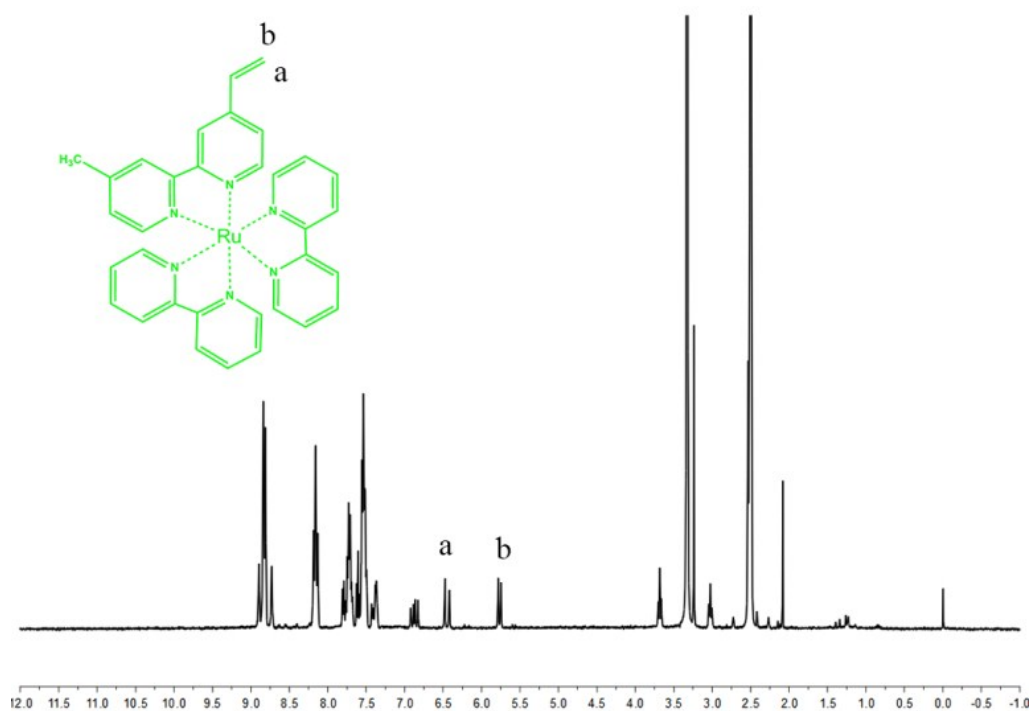


Figure S4 ¹H NMR spectrum of Ru(vmpy)(bpy)₂(PF₆)₂

4. Preparation of gradient Poly(Ru(bpy)₃-co-NIPAAm) gel

4.1 Polymerization of Poly(NIPAAm-co-MAA) micro-gel

50 mL of deionized water was added in a flask and bubbled with N₂ for 5 min. 0.99 g NIPAAm, 0.495 g MAA, 0.015 g MBA and 0.034 g KPS were added in the flask, and then the solution was thoroughly stirred. After that, 0.338 g SDS was added in, and the flask was sealed immediately. The polymerization was carried out for 5 h at 60 °C with mechanical stirring at 300 r.p.m. To remove SDS in the microgel dispersion, the dispersion was dialyzed against deionized water for 1 week with refreshing water every day. The surface area average particle size of the prepared micro-gel was 5.205 μm, and volume average particle size was 6.255 μm.

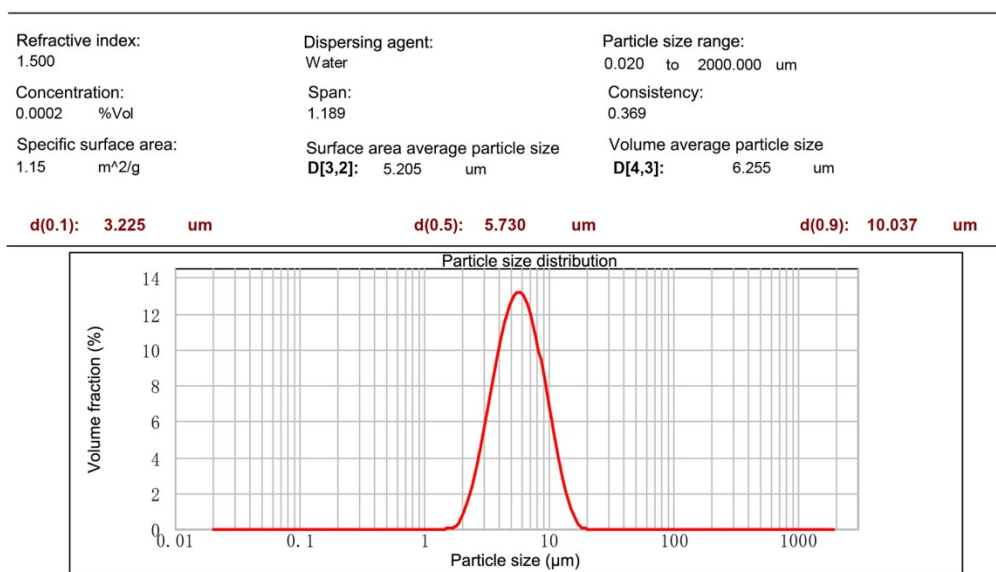


Figure S5 Particle size analyze report of the P(NIPAAm-co-MAA) micro-gel

4.2 Vinylation of Poly(NIPAAm-co-MAA) micro-gel

0.8 g GMA was added to 50 mL micro-gel dispersion, the mixture was heated to 50 °C and kept for 8 h with mechanical stirring (350 r.p.m). After that, the dispersion was dialyzed against ethanol for 1 week to remove unreacted GMA. Half of the micro-gel dispersion was then dialyzed against methanol for 4 days with changing methanol twice a day, and the obtained micro-gel/water

and micro-gel/methanol dispersion was stored at 4 °C for subsequent use. Stretching vibration of carbon-carbon double bond was found at 1690 cm^{-1} .

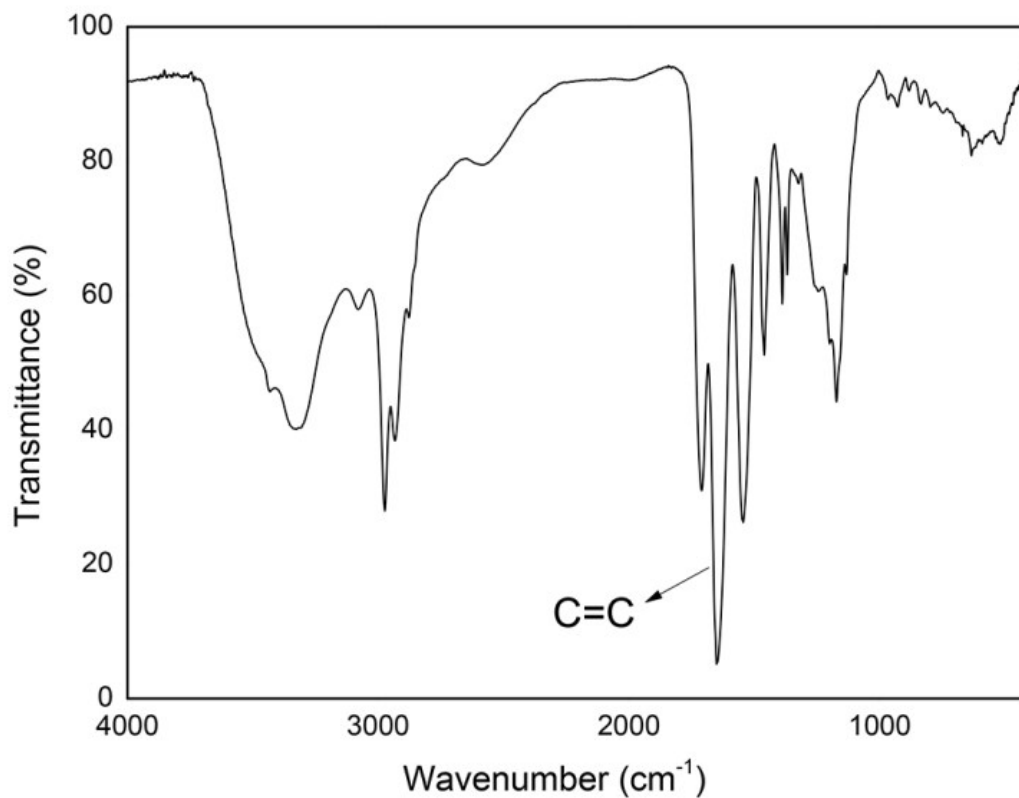


Figure S6 FTIR spectrum of vinyl-micro-gel

4.3 Polymerization of 1st network

1.1316 g NIPAAm and 22.6 mg KPS were dissolved in 10 mL micro-gel dispersion and the mixture was thoroughly stirred. Then 20 μL TEMED was added to the mixture as polymerization accelerator. The mixture was immediately injected into a self-made mold (two pieces of 10 cm \times 10 cm hydrophilic glass separated by a piece of 1 mm thick silicon rubber with a square hole), and the polymerization was carried out at 0 °C for 6 h.

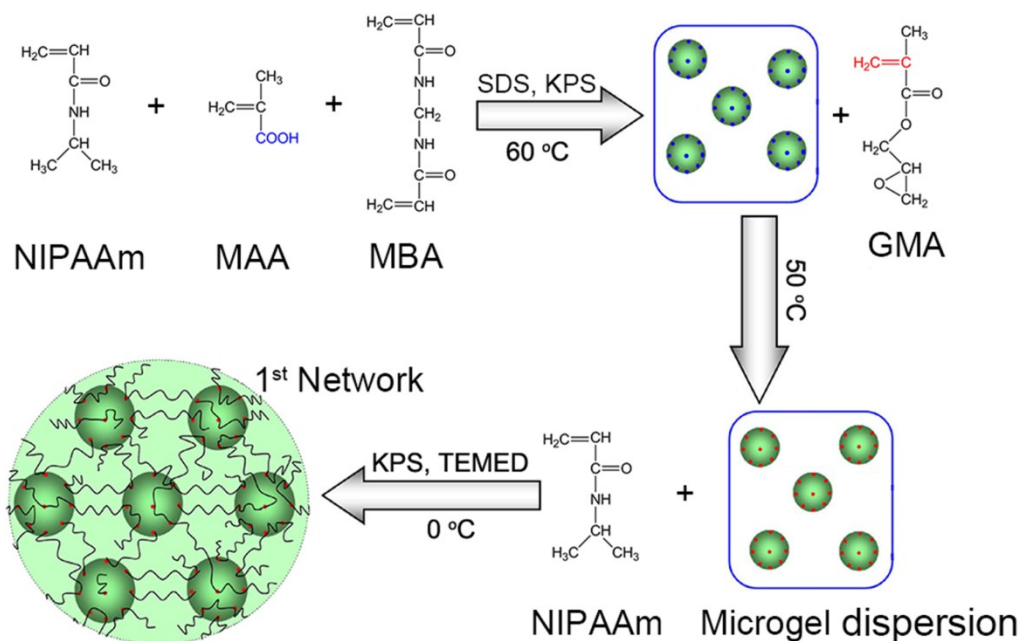


Figure S7 Preparation method of micro-gel crosslinked PNIPAAm 1st network

4.4 Polymerization of 2nd network

First, 0.4 g NIPAAm, 0.2 g Ru(bpy)₃, 30 mg DMPA and 1.5 mL DMSO were dissolved in 10 mL micro-gel/methanol dispersion (described in 4.2), the mixture was stirred for 5 min. Next, the freeze-dried 1st network was partially immersed into the solution for 15 min to form concentration gradient spontaneously. Crosslinking was performed under a 365 nm UV lamp (B100AP, Blak-Ray) for 30 min, a water tank was employed to reduce the heat effect. At last, the prepared gel was subjected to a solvent exchange process by being immersed in a series of graded water-methanol solutions (25, 50, 75 and 100 %) for two days, respectively.

5 Performance measurements

5.1 Static measurements

Equilibrium swelling ratios of the prepared Poly(Ru(bpy)₃-co-NIPAAm) gel under different condition (temperature or redox state) were investigated on an Olympus stereomicroscope with image capture system and thermostatic controller. In order to keep the gel in oxidized/reduced state, the gel was immersed in solution of 5 mM Ce(SO₄)₂ and 894 mM HNO₃ or Ce₂(SO₄)₃ and 894 mM HNO₃ for 20 min to reach equilibrium, then an image was recorded. The equilibrium swelling ratio was calculated by analyzing the recorded images.

5.2 Dynamic measurements

The self-deforming process of gradient Poly(Ru(bpy)₃-co-NIPAAm) gel was observed on an Olympus stereomicroscope with image capture system and thermostatic controller. The Poly(Ru(bpy)₃-co-NIPAAm) gel was put in a 24 well-plate, 2 mL of solution 1 ([HNO₃]=0.89M, [NaBrO₃]=0.168M) was added in, the gel totally turned to light green after 5 min. Then 2 mL of solution 2 ([HNO₃]=0.89M, [MA]=0.125M) was added, after 2 min of penetration and induction period, BZ reaction was initiated in the gel. The entire self-deforming process of the gel was recorded by image capture system. The image analysis was carried on with Cellsens standard software.

Video S1 shows the autonomous, reversible and periodic bending-stretching deformation of the gradient Poly(Ru(bpy)₃-co-NIPAAm) gel. Playback speed is 125×.

References

- [1] G. Sprintschnik, H. W. Sprintschnik, P. P. Kirsch and D. G. Whitten, *J. Am. Chem. Soc.*, 1977, **99**, 4947-4953.
- [2] P. K. Ghosh and T. G. Spiro, *J. Am. Chem. Soc.*, 1980, **102**, 5543-5549.