Structural modulation of self-oscillating gels: Changing the proximity of the catalyst to the polymer backbone to tailor chemomechanical oscillation

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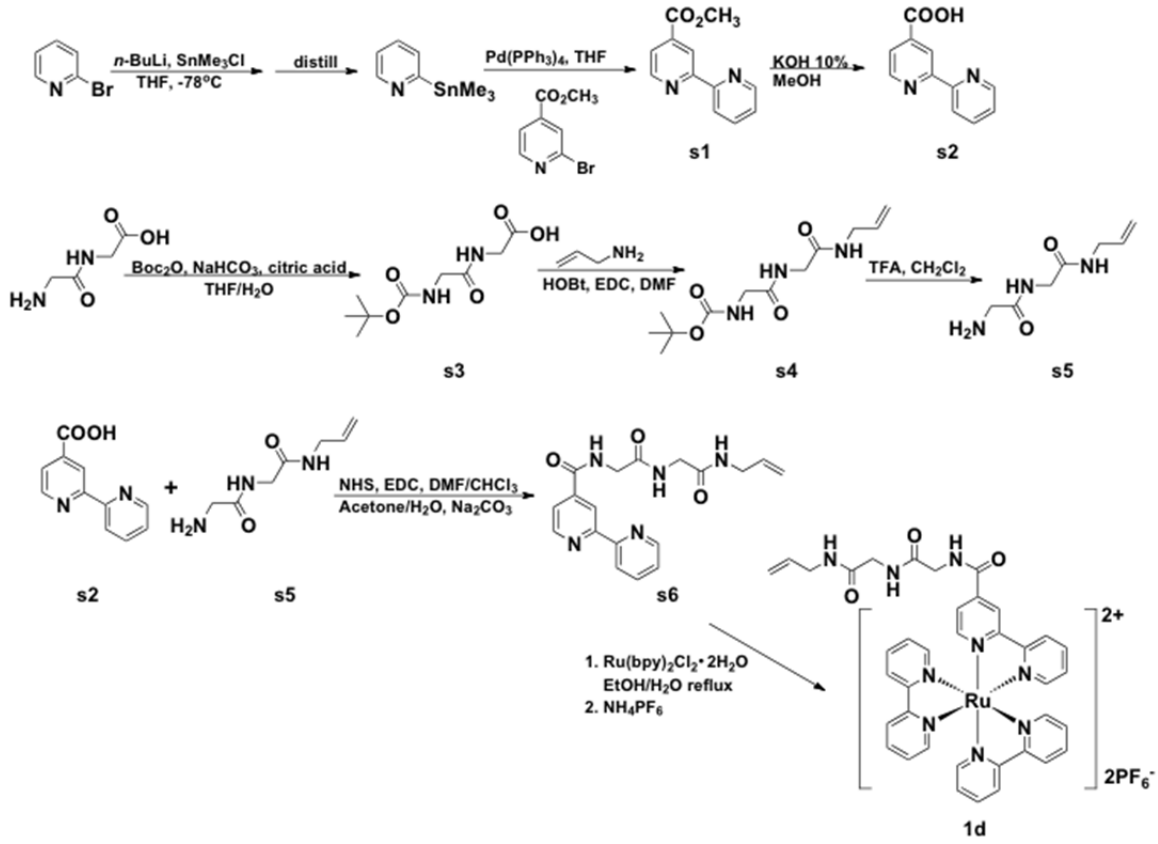
Supplementary Information

Synthesis



Methyl [2,2'-bipyridine]-4-carboxylate (s2)

Dry diethyl ether (25 mL) solution of 2-Bromopyridine (7.9 g, 50 mmol) was added dropwise into a 100 mL two-neck round bottom flask charged with dry diethyl ether (50 mL) solution of 1.6 M *n*-BuLi (31.25 mL, 50 mmol) at -78 °C under nitrogen. The reaction mixture was kept stirring at this low temperature for two hours. Then dry THF (10 mL) solution of chlorotrimethylstannane (9.95 g, 50 mmol) was added into the reaction mixture and the reaction temperature was slowly raised to room temperature. The reaction was stirred at room temperature for overnight. After that the solvent was removed and 2-(trimethylstannyl)pyridine (9.2 g) was distilled out as colorless liquid from the mixture under low pressure in a yield of 76%.

The obtained 2-(trimethylstannyl)pyridine (9.2 g, 38 mmol), methyl 2-bromoisonicotinate (8.2 g, 38 mmol) and $Pd(PPh_3)_4$ (1.1g, 0.96 mmol) were mixed well in dry xylene (60 mL) under argon. The mixture was heated to 150 ^oC for 10 hours. The suspension was then filtered through celite and washed with dichloromethane. After evaporation of the solvents, the residue was purified by column chromatography to obtain **s1** as white powder (5.3 g) in a yield of 65%. **s1** (5.3 g) was dissolved in methanol (30 mL) and 10% potassium hydroxide (4 mL) was added into the solution. The mixture was stirred at room temperature for 2 hours. Diluted hydrochloric acid was added to the reaction mixture to adjust the pH till most precipitate was obtained. The mixture was filtered and the white suspension was collected and dried. **s2** was obtained as white powder in a yield of 98%.

***N*-Boc-diglycine (s3)**

A solution of di-*tert*-butyldicarbonate (3.20g, 14.7 mmol) in dioxane (14 mL) was added to an ice-cold, stirred solution of diglycine (1.80g, 13.6 mmol) in sodium hydroxide (1M, 40 mL). The biphasic suspension was stirred at 5 ^oC for 30 min and then allowed to warm to room temperature, after which time it was stirred fro 19 h under nitrogen. The solvent was removed in vacuo and sodium hydroxide (1 M, 25 mL) was added to the residue. Following acidification to pH 2 by addition of hydrochloric acid (1 M) the solution was extracted with ethyl acetate (5 x 90 mL). The organic washings were combined, dried over magnesium sulfate and filtered. The solvent was removed in vacuo to give the product (2.19 g, 69%) as a white power.

***Tert*-butyl (2-((2-(allylamino)-2-oxoethyl)amino)-2-oxoethyl)carbamate (s4)**

HOBt (703 mg, 5.2 mmol), EDC (1.29 g, 8.32 mmol) and **s3** (1.16g, 5 mmol) were added into a round bottom flask with dry DMF (20 mL). The mixture was stirred at room temperature for one hour. Then allylamine (0.4 mL, 5.2 mmol) was added into the mixture and the reaction was kept stirring overnight. After evaporation of the solvent, the residue was purified by column chromatography to obtain the product as white powder (1.06 g) in a yield of 78%.

***N*-Allyl-2-(2-aminoacetamido)acetamide (s5)**

Mixture of TFA (4 mL) and dichloromethane (4 mL) were added into a round bottom flask charged with **s4** (1.06 g). The mixture was stirred at room temperature for 2 hours. After the solvents were removed, dry ether was added into the residue and **s5** precipitated as white powder. The white precipitate was collected by filtration in a yield of 94%.

***N*-(2-((2-(LLYLmino)-2-oxoethyl)amino)-2-oxoethyl)-[2,2'-bipyridine]-4-carboxamide (s6)**

Dry DMF (5 mL) was added into a round bottom flask charged with NHS (172.6 mg, 1.5 mmol) and **s2** (200 mg, 1mmol). DMF (5 mL) solution of EDC (310.5 mg, 2 mmol) was added dropwise into the reaction mixture and the reaction mixture was kept stirring at room temperature for 4 hours. After removing the solvent, acetone was added into the residue. The residue's acetone solution was added dropwise into the water solution of **s5** (pH =7.5-8.0), and the mixture was kept stirring at room temperature for overnight. Part of the water was removed form the mixture and hydrochloric acid was used to adjust the pH of the solution till most white precipitate was formed. The white residue was purified by column chromatography to afford **s6** (155.2 mg) as white powder in a yield of 44%.

Ruthenium complex 1d

Water (1 mL) and ethanol (9 mL) were added into a 50 mL two-neck round bottom flask charged with *cis*-dichlorobis(2,2'-bipyridine)ruthenium(II) dihydrate (260 mg, 0.5 mmol) and **s2** (155 mg, 0.44 mmol). The solution of the mixture was bubbled with nitrogen for 30 min. Then the mixture was refluxed under nitrogen for 3 days. After removing the solvent, NH_4PF_6 solution (0.6 M) was added into the residue and red precipitate was collected and washed by cold water. The ruthenium complex **1d** was obtained by purifying the red precipitate through column chromatography of Sephadex LH-20. Finnaly, **1d** was obtained as red solid in a yield of 95%.

General procedure for copolymer preparation

IPAAm (**2**), ruthenium catalyst, *N,N'*-methylenebisacrylamide (**3**) and *N,N'*-azobisisobutyronitrile (AIBN) (4 wt%) are dissolved in methanol in feed composition as shown in Table 1 under nitrogen. The solution is injected into a mode that is made by two glass sheets separated by a silicon rubber spacer (0.1 mm thickness). The mode is sealed with Epoxy. The solution was polymerized at 60 ^oC for 24 hours. The resulting copolymer sheet is washed by methanol to remove unreacted monomers and then stored in pure water for dialysis for three days.

Oscillation Profiles

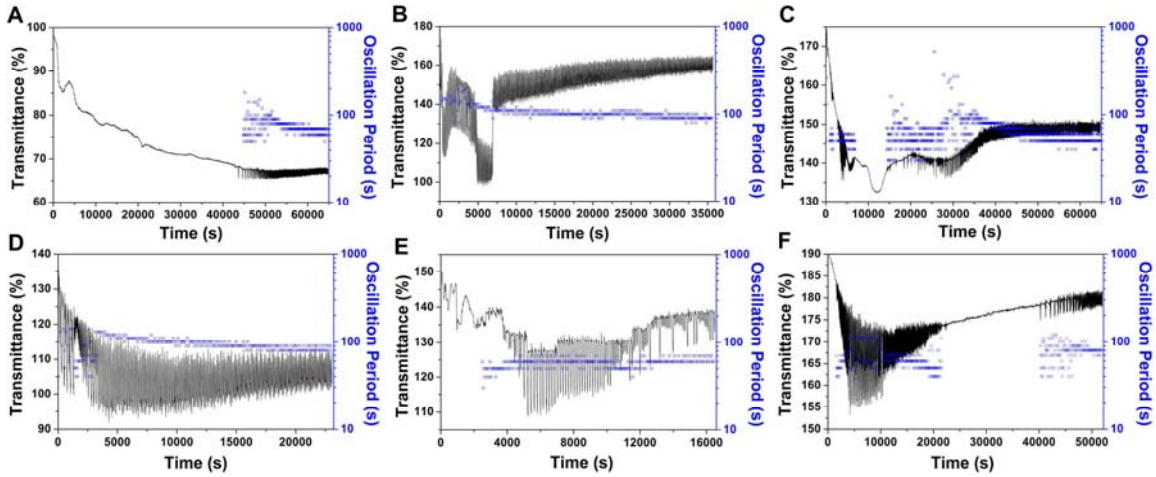


Figure S1. Oscillation profiles of gels (A) **4**, (B) **5-I**, (C) **5-II**, (D) **5-III**, (E) **6-II** and (F) **6-III** under condition A. The black solid line represents the change of transmittance, corresponding to the chemical oscillation of the gels the blue open circles show the oscillation periods.

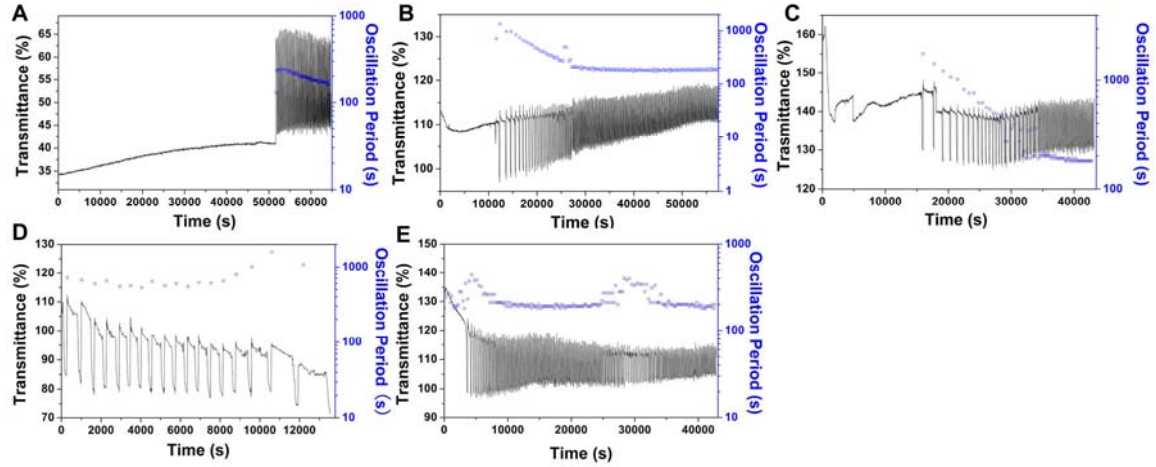


Figure S2. Oscillation profiles of gels (A) **4**, (B) **5-I**, (C) **5-III**, (D) **6-II** and (E) **6-III** under condition B. The black solid line represents the change of transmittance corresponding to the chemical oscillation of the gels, the blue open circles show the oscillation periods.

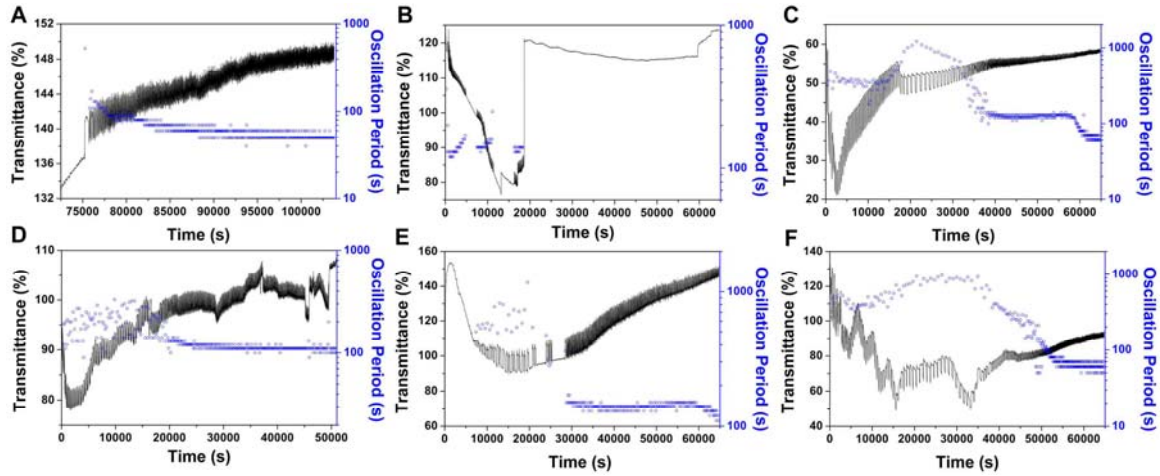


Figure S3. Oscillation profiles of gels **4** (A), **5-I** (B), **5-II** (C), **5-III** (D), **6-II** (E) and **6-III** (F) under condition C.

Video S1. Chemomechanical oscillation behaviour of gel **6-II** under BZ condition B.