Self-regulated Supramolecular Assembly Driven by a Chemical-Oscillating Reaction

Hongwei Zhou,[a,b] Enxiang Liang,[a,b] Xiaobin Ding,*[a] Zhaohui Zheng*[a] and Yuxing Peng[a]

[a]Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu 610041, P. R. China. E-mail: xbding@cioc.ac.cn; zhzheng@cioc.ac.cn.
[b]Graduate School of the Chinese Academy of Sciences, Beijing 100049, P. R. China

Part I Experimental details

Materials

4′-(4-hydroxyphenyl)-2,2′:6′,2″-terpyridine(*TpyPhOH*),4′-(4-methylphenyl)-2,2′:6′,2″-terpyridine(*TpyPhMe*) and 4′-(4-methylphenyl)-2,2′:6′,2″-terpyridine-ruthenium(III) chloride (*[Ru(TpyPhMe)]Cl₃*) were synthesized and purified according to a previously reported method.[1] *N*-Isopropylacrylamide (NIPAAm) (Aldrich, 98%) was purified by recrystallization from its toluene solution and dried in vacum. $RuCl_3 \cdot 3H_2O$ (Aldrich, A.R.) was used as received. 2,2′-Azobisisobutyronitrile (AIBN) (Aldrich, 98%) was recrystallized from methanol prior to use. All other reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. and used as received unless otherwise specified.

Characterizations

^{1}HNMR spectra were recorded at 25 ℃ on a Bruker AV300 NMR spectrometer at 300 MHz. Chemical shifts (δ) are reported in parts per million (ppm) with reference to the residual protons of the deuterated solvents.

Relative molecular weight and molecular weight distribution were determined by a gel permeation chromatography (GPC) system equipped with a waters model 1515

pump, a model 2410 refractive index detector, and an OH-pak KB-803 column operated at 25 ℃. THF was used as the mobile phase at a flow rate of 0.8 ml·min^{-1}.

Preparation of 4′-(4-allyloxyphenyl)-2,2′:6′,2″-terpyridine (TpyPhA)

Under N$_2$ atomsphere, TpyOH (1.57 g, 4.83 mmol) in 10 ml dry DMF was added to a suspension of K$_2$CO$_3$ (3.34 g, 21.4 mmol)/DMF (20 ml). A light yellow mixture was obtained and stirred at room temperature for 30 min. Then a 10 ml allyl bromide (1.17g, 9.67 mmol) /DMF solution was added dropwise within 30 min and then the system was immerged into preheated 50℃ thermostated oil bath. The complete reaction was detected by TCL technique and the hot reaction mixture was filtered to remove inorganic phase. The solvent was removed by rotary evaporator to get crude product as light brown solid and then recrystallized from DMF/ethanol to obtain target product as white needles (1.48 g, 4.05 mmol, 84%). ^{1}HNMR (300 MHz, DMSO, 25 °C, δ) 8.75 (d, J = 4.2 Hz, 2H), 8.65 (d, J = 7.4 Hz, 4H), 8.03 (t, J = 7.7 Hz, 2H), 7.88 (d, J = 8.7 Hz, 2H), 7.58–7.43 (m, 2H), 7.15 (d, J = 8.8 Hz,2H), 6.07 (m, 1H), 5.44 (d, J = 18.8 Hz, 1H), 5.30 (d, J = 9.1 Hz, 1H), 4.67 (s, 2H); UV−vis (acetonitrile): λmax (ε) = 285 (33600), 223 (16400); EIMS m/z (%): 366.11 (100), 388.07 (53).
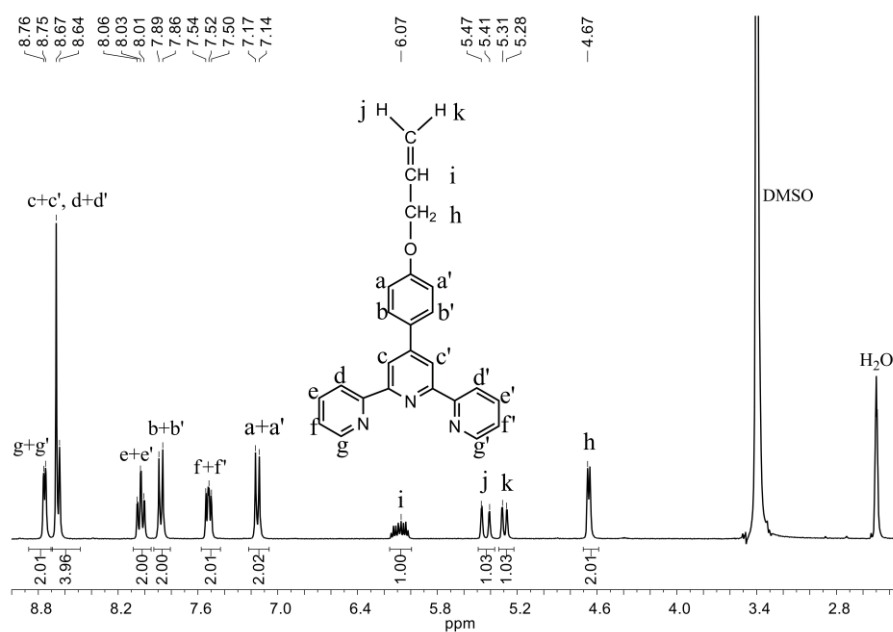
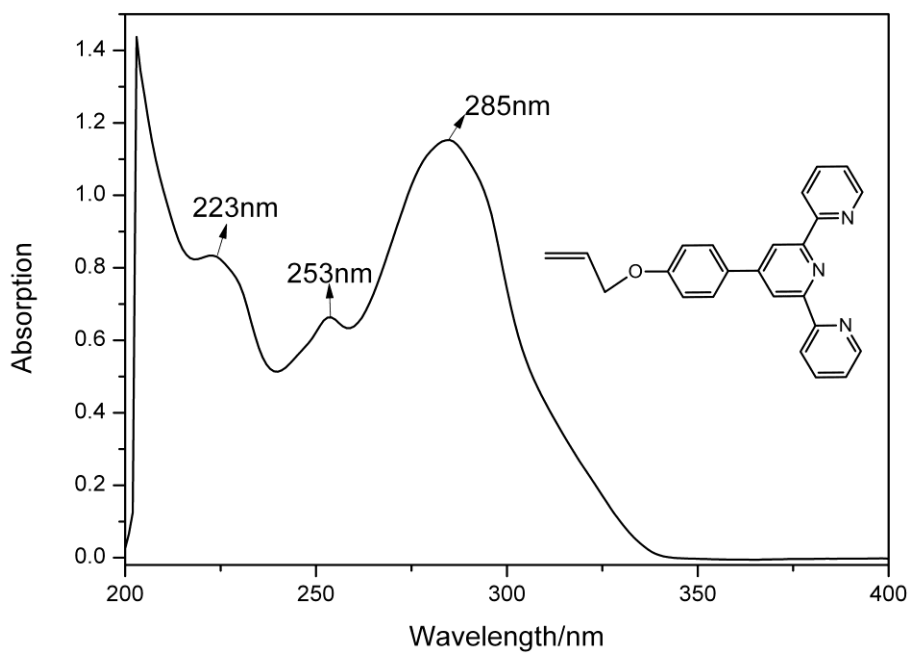**Figure S1** ^{1}HNMR (300 MHz) spectrum of TpyPhA in DMSO

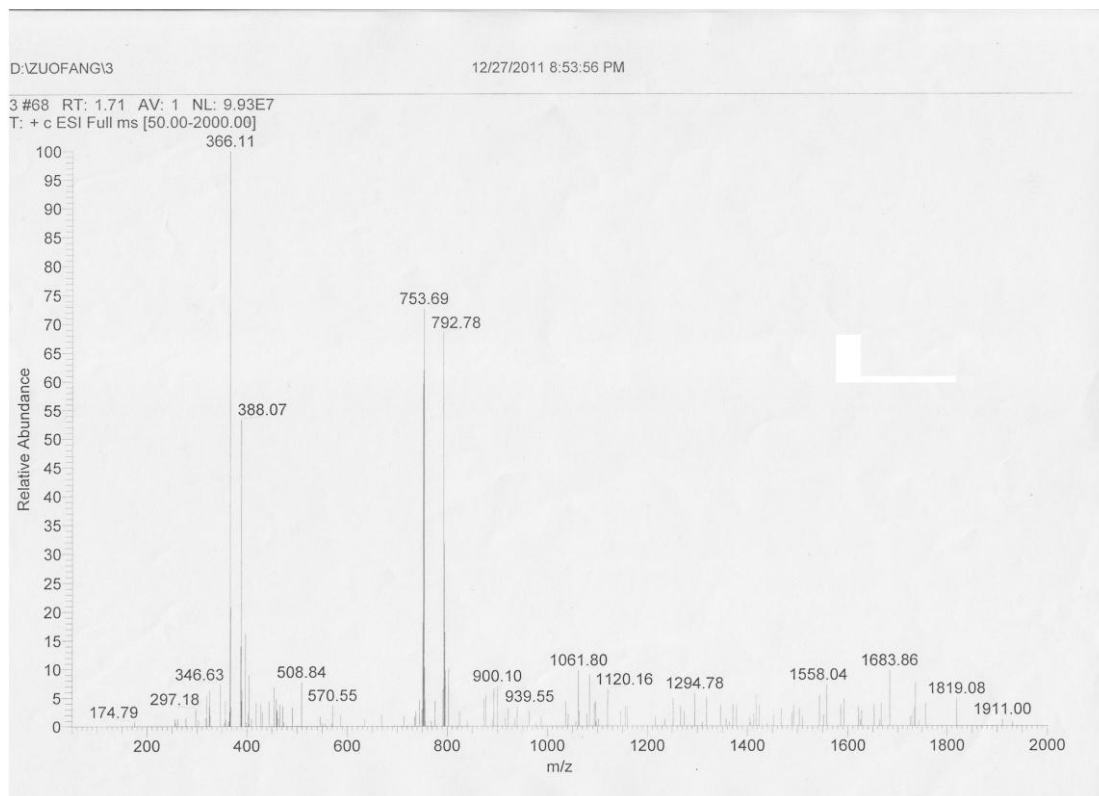**Figure S2** UV-vis spectra of TpyPhA in acetonitrile

3

Figure S3 MS spectrum of TpyPhA

Preparation of poly(NIPAAm-*co*-TpyPhA)

In a 100 ml ampule, a solution of NIPAAm (1.28 g, 11.33 mmol), TpyPhA (0.2580 g, 0.71 mmol), AIBN (0.0227 g, 0.14 mmol) in methanol (purged with N_2 before use) was prepared with assistance of ultrasound. Afterwards, the solution was treated with four freeze-evacuate-thaw cycles and sealed. The ampule was then immersed into preheated 60 ℃ thermostated oil bath and the polymerization proceeded for 72 h. The polymer solution was dialyzed against gradient methnol/water mixtures and freeze dried to get poly(NIPAAm-*co*-TpyPhA). GPC:

4

Mn=6970 g·mol^{-1}, PDI=2.01; IR (KBr): v = 1650 (w), 1386 (m), 1367 (m); UV-vis

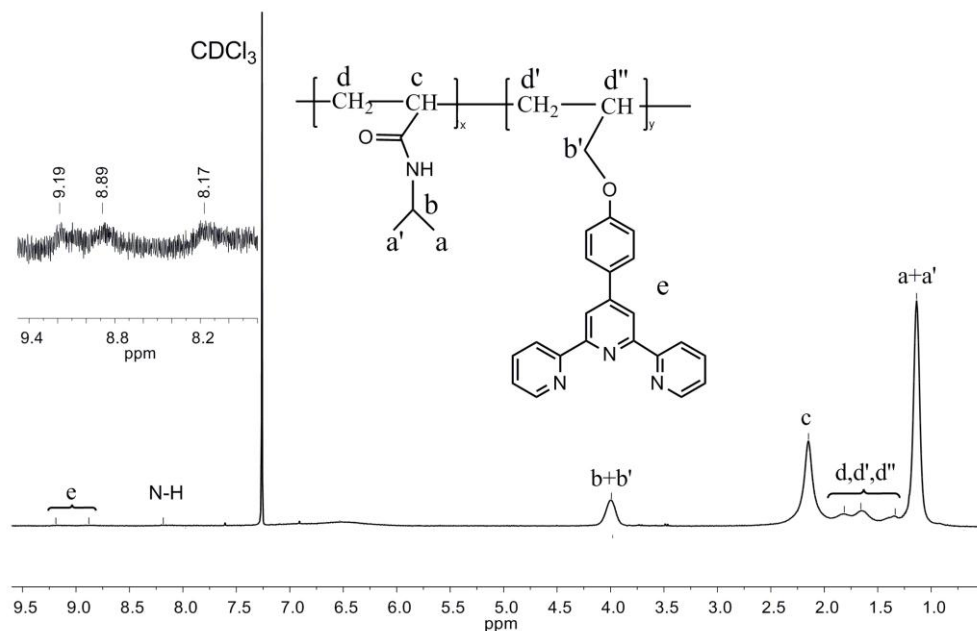(ethanol): λmax=286, 252 nm.

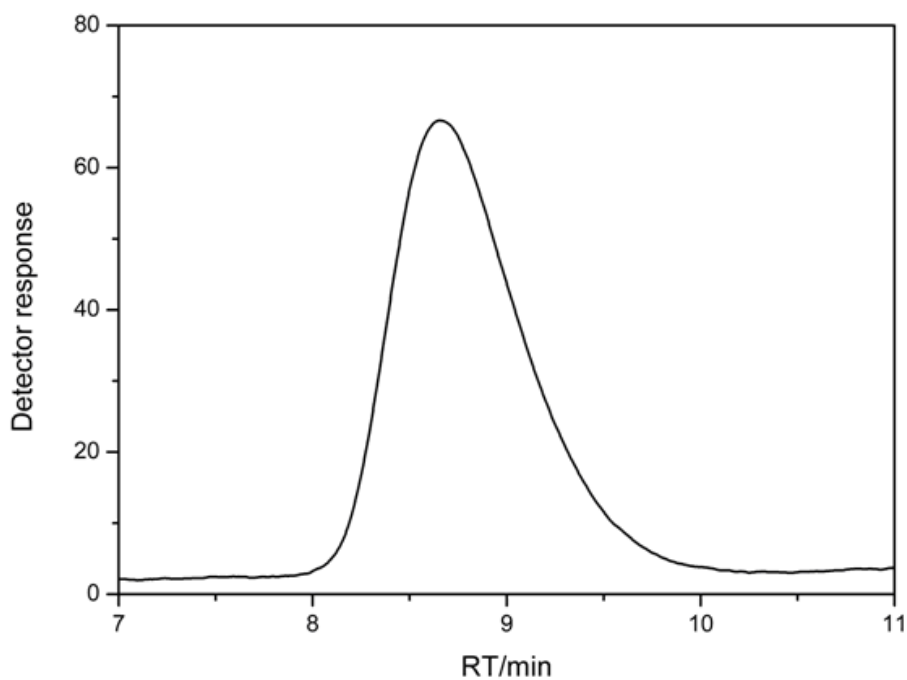**Figure S4** ^{1}HNMR spectrum of poly(NIPAAm-*co*-TpyPhA)

Figure S5 Gel permeation chromatographs of poly(NIPAAm-*co*-TpyPhA)

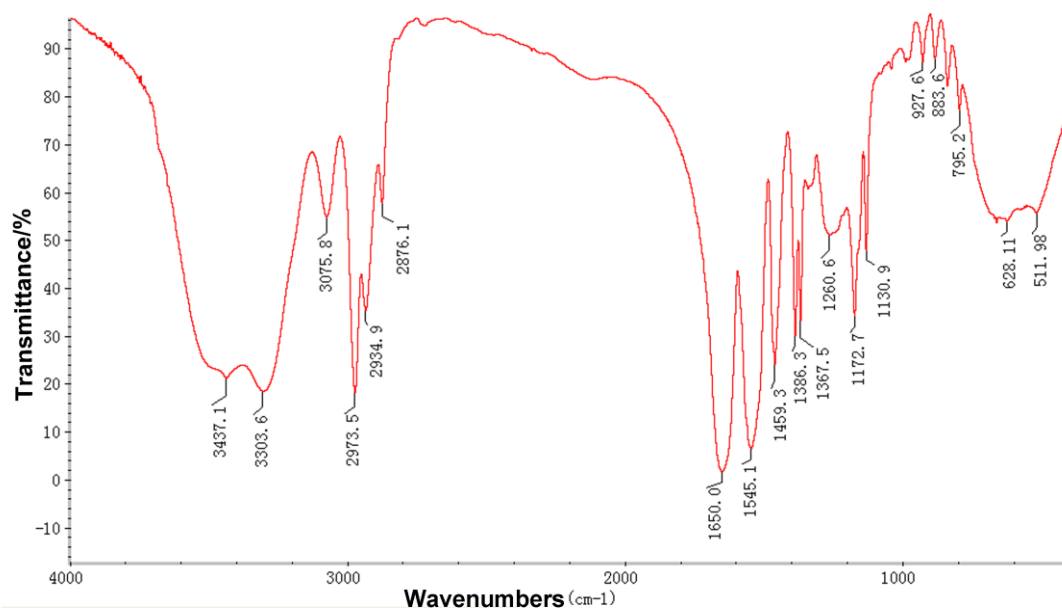**Figure S6** IR spectrum of poly(NIPAAm-*co*-TpyPhA) (KBr pellet method).
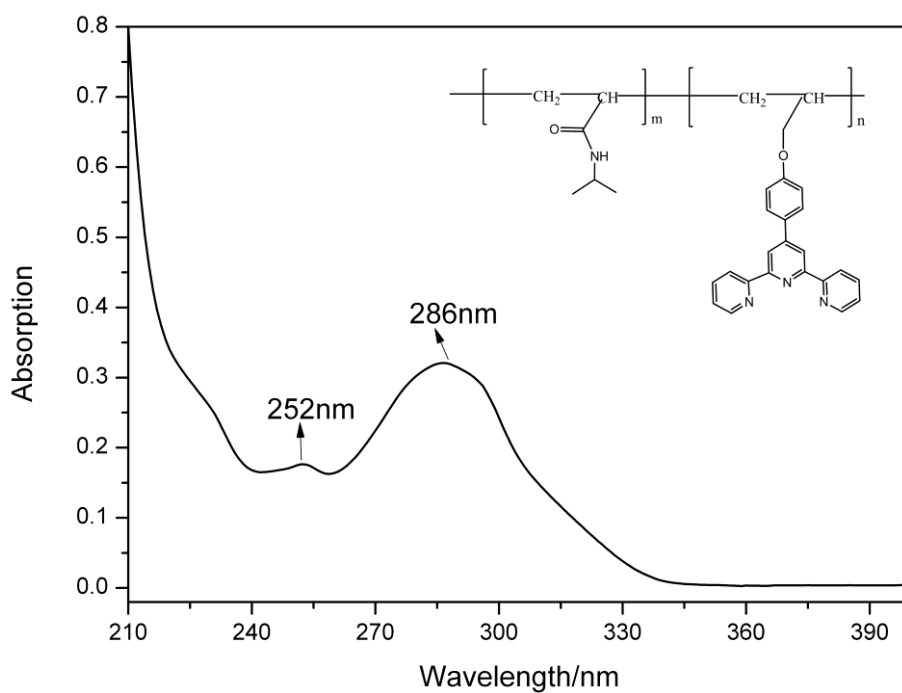

Figure S7 UV-vis spectra of poly(NIPAAm-*co*-TpyPhA) (0.17 mg ml^{-1} in ethanol).
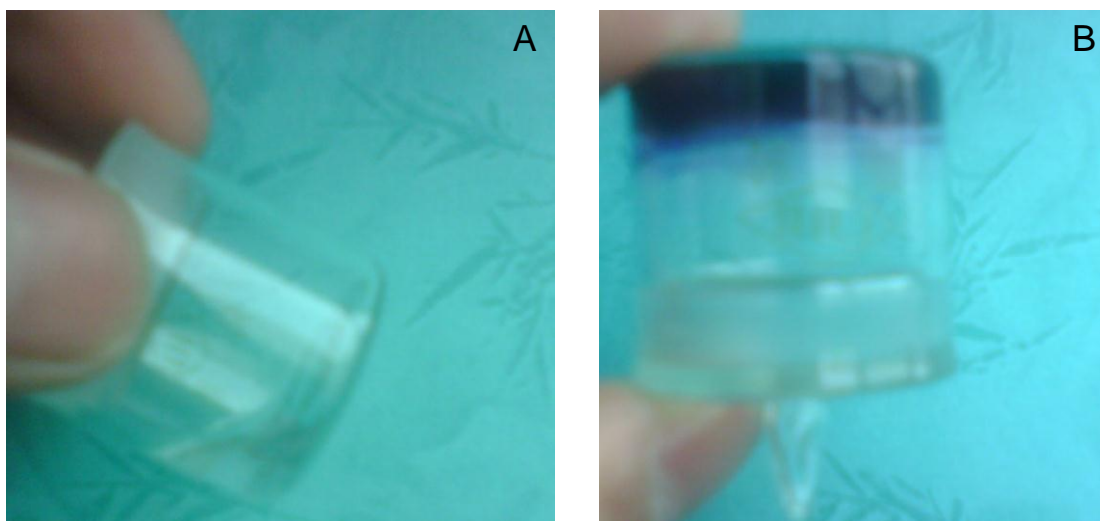
Figure S8 Photographs of poly(NIPAAm-*co*-TpyPhA) solution before (A) and after (B) addition of Fe^{2+} solution.

To a solution of poly(NIPAAm-*co*-TpyPhA), a solution of Fe^{2+} was added and a fast gelation process occurred within several seconds. The sol-gel transition provides additional supporting information for successful preparation of poly(NIPAAm-*co*-TpyPhA) because the strong Fe^{2+}-terpyrine complexation worked as crosslink points and promoted the formation of polymer networks.

Prefabrication of branch-like assembly poly(NIPAAm-*co*-Ru(TpyPhMe-TpyPhA))(PF$_6$)$_2$

Under an inert atmosphere, 0.1529 g poly(NIPAAm-*co*-TpyPhA) was added to [Ru(TpyPhMe)]Cl$_3$ (0.0110 g, 0.02 mmol) in methanol along with 50μl *N*-ethylmorpholine. Then the mixture was refluxed for 6 h. The resulting deep red solution was filtered and treated with three-fold excess of KPF$_6$. The resulting red precipitate was filtered off, dissolved, dialyzed against gradient methnol/water mixtures for one week and then freeze-dried to get the target branch-like assembly.
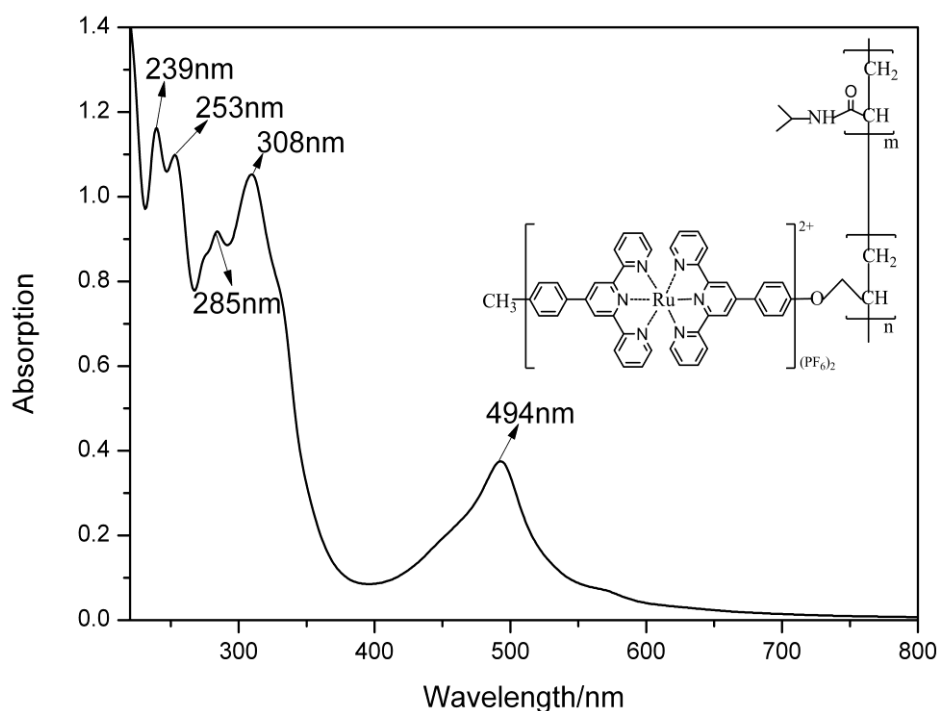
Figure S9 UV-vis spectra of poly(NIPAAm-*co*-Ru(TpyPhMe-TpyPhA))(PF$_6$)$_2$ (0.38 mg ml^{-1} in ethanol).

Absorption peak near 490 nm is a characteristic MLCT absorption for bis-complexed Ru-terpyridine complex and absorption peak near 308 nm represents the LMCT absorption for the bis-complex. This result indicates that the target branch-like assembly is successfully prefabricated.

On-line detection of self-regulated supramolecular assembly

On-line detections of optical transmittance change and measurement of UV-vis spectra were carried out using a spectrophotometer (TU-1810DPC, Purkinje General) equipped with a thermostatic controller. The SSA was studied by dissolving prefabricated assembly into an aqueous solution containing BZ reaction substrates. Detailed processes are as follows: appropriate volumes of BZ substrate solutions of known concentrations were transferred to a cuvette to make up the final volume to about 3 ml and the final concentrations of substrates to designed molar concentrations[2]. Solutions of H$_2$SO$_4$, MA, NaBrO$_3$, and prefabricated branch-like

assembly, were transferred sequently and separately. The optical transmittance changes as a function of time were recorded.

Reference

1. A. Anthonysamy, S. Balasubramanian, V. Shanmugaiah and N. Mathivanan, *Dalton Transactions,* 2008, 2136.

2. J. Delgado, Y. Zhang, B. Xu and I.R. Epstein, *J. Phys. Chem. A*, 2011, **115**, 2208.

Part II Other supporting materials

Moive 1 This movie shows the reversible assembly/de-assembly/re-assembly process, as can be seen from the reversible color change when external stimuli are added. The first two drops of external stimuli are $Ce(SO_4)_2$ solutions (yellow). The following two drops are Na_2SO_3 solutions (colorless). Both the solutions are added in a large excess amount. In the initial solution, Ru ions are in the reduced state, the system is in its assembled state. Upon addition of $Ce(SO_4)_2$, the Ru ions are oxidized and a de-assembly process occurs. When Na_2SO_3 is added, the Ru ions are reduced again and a re-assembly process takes place.
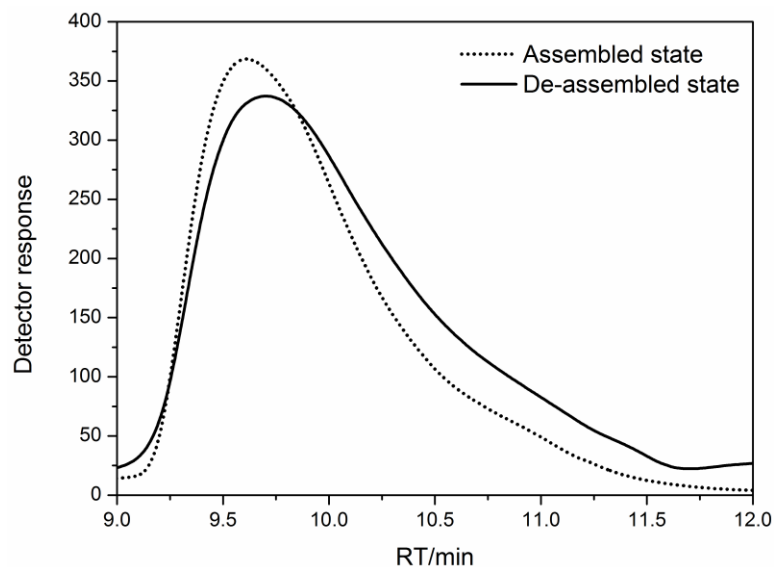
Figure S10 Gel permeation chromatographs of the assembly in the assembled state (dotted line) and the de-assembled state (solid line). In GPC system, a longer retention time (RT) indicates a smaller molecular weight. In the case of the assembled state, the RT is shorter and the average molecular weight is larger. In the case of the de-assembled state, the RT is longer and the average molecular weight is smaller. This result provides an additional demonstration for the de-assembly and assembly process.
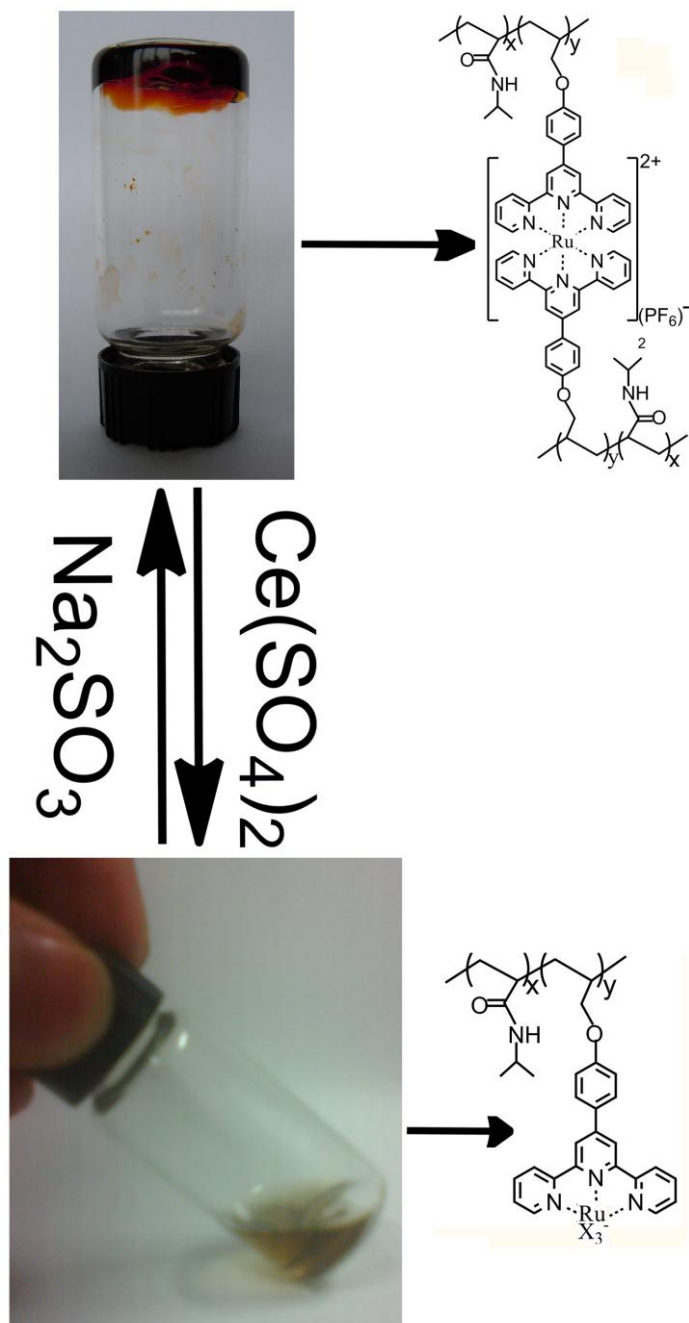
Figure S11 Reversible sol-gel transition under external stimuli. The system is composed of poly(NIPAAm-*co*-TpyPhA), Ru ions, H_2SO_4, and water. $Ce(SO_4)_2$ and Na_2SO_3 solutions are utilized as external stimuli. When the Ru ions are in the reduced state Ru(II), the system become jelly-like weak gel which is cross-linked by the bis-complex Ru(II)(tpy)$_2$. However, when $Ce(SO_4)_2$ is added, the gel is broken to form a solution.
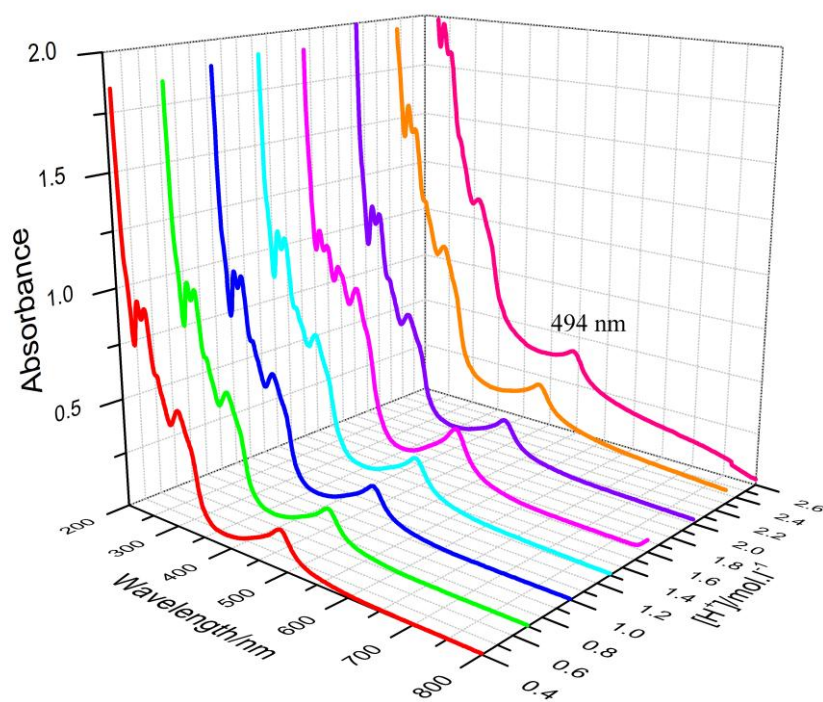
Figure S12 The re-assembly process of an already de-assembled system under different concentrations of [H$^+$].
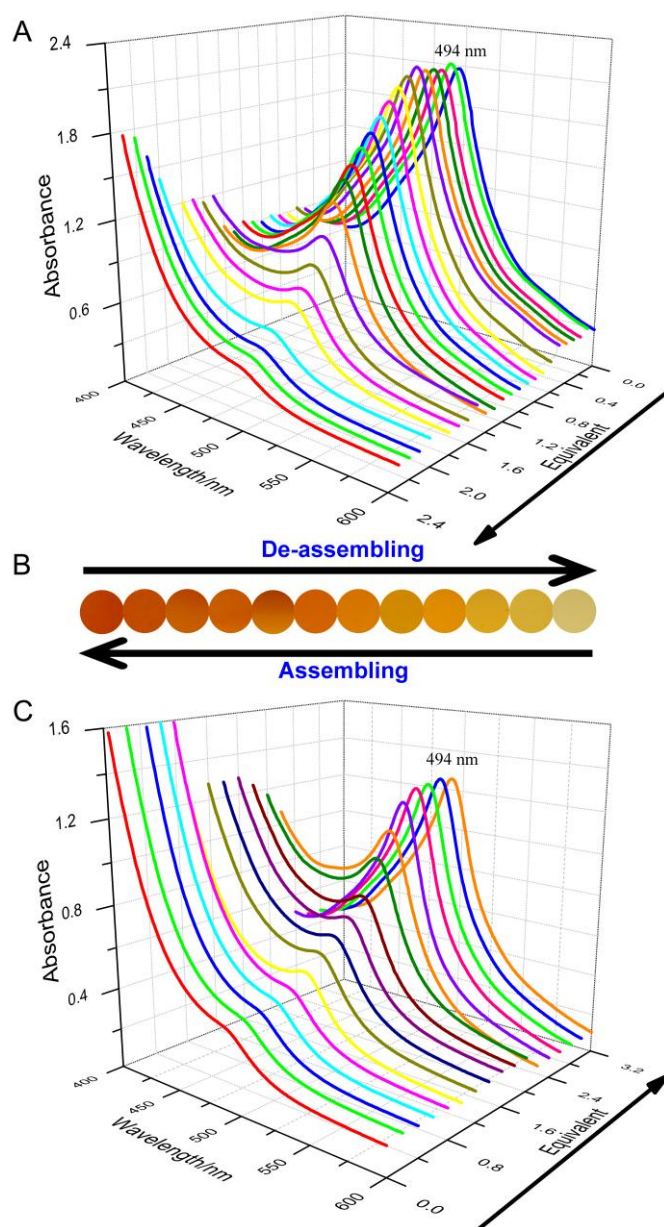
Figure S13. UV-vis spectras of the de-assembly process (A), re-assembly process (C), and the colour change of each state (B). Initial solution of A are composed of H_2SO_4 (0.2 mol·l^{-1}), [assembly]=2 mg·ml^{-1}. The mixture of A after complete de-assembly was used as the sample of C for studying the re-assembly process. Designed amount of $Ce(SO_4)_2$ and Na_2SO_3 were used as the oxidizing agent for A and the reducing agent for C, respectively.
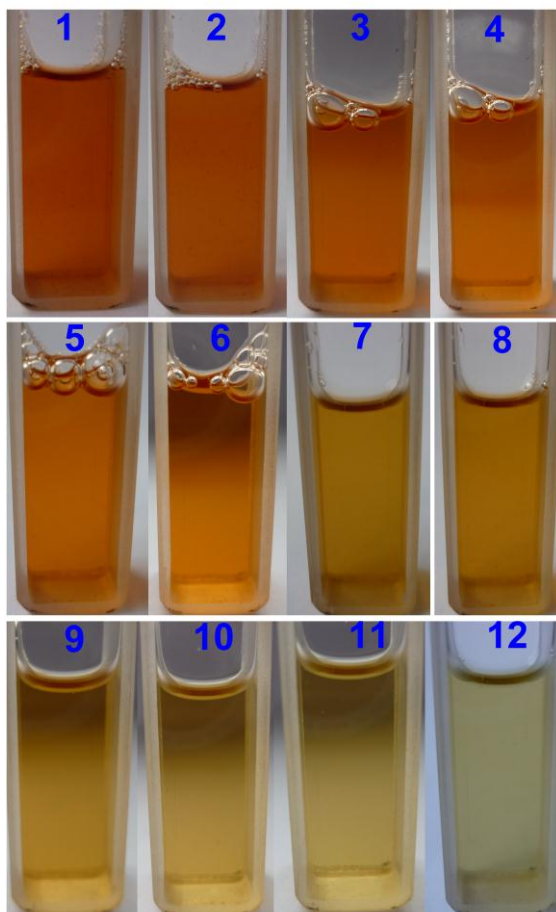
Figure S14 Representative pictures during the gradual de-assembly processs (from 1 to 12) and the re-assembly process (from 12 to 1). The condition is the same as that used in Figure S13.

Moive 2 This movie shows the macroscopical colour change of SSA system. The initial condition was [MA]=50 mmol·l^{-1}, [NaBrO$_3$]=300 mmol·l^{-1}, [H$_2$SO$_4$]=1 mol·l^{-1}, and [assembly]=1.0 wt.%. The experiment was carried out at room temperature.

Moive 3 This movie shows the SSA behavior in a homogeneous condition. The initial substrate concentrations were fixed to [MA]=50 mmol·l^{-1}, [NaBrO$_3$]=300 mmol·l^{-1}, [H$_2$SO$_4$]=1 mol·l^{-1}, and [assembly]=0.5 wt.%.

Moive 4 This movie shows the SSA behavior in a heterogeneous condition. The initial substrate concentrations were fixed to [MA]=50 mmol·l^{-1}, [NaBrO$_3$]=300 mmol·l^{-1}, [H$_2$SO$_4$]=1 mol·l^{-1}, and [assembly]=0.5 wt.%.

A

T(℃/K)	14/287.15	16/289.15	18/291.15	19/292.15	21/294.15	23/296.15
P(s)	28.3	26.5	22.5	20.3	17.5	15.0

B

$Ea = (52.1 \pm 3.5)\,\mathrm{kJ \cdot mol^{-1}}$

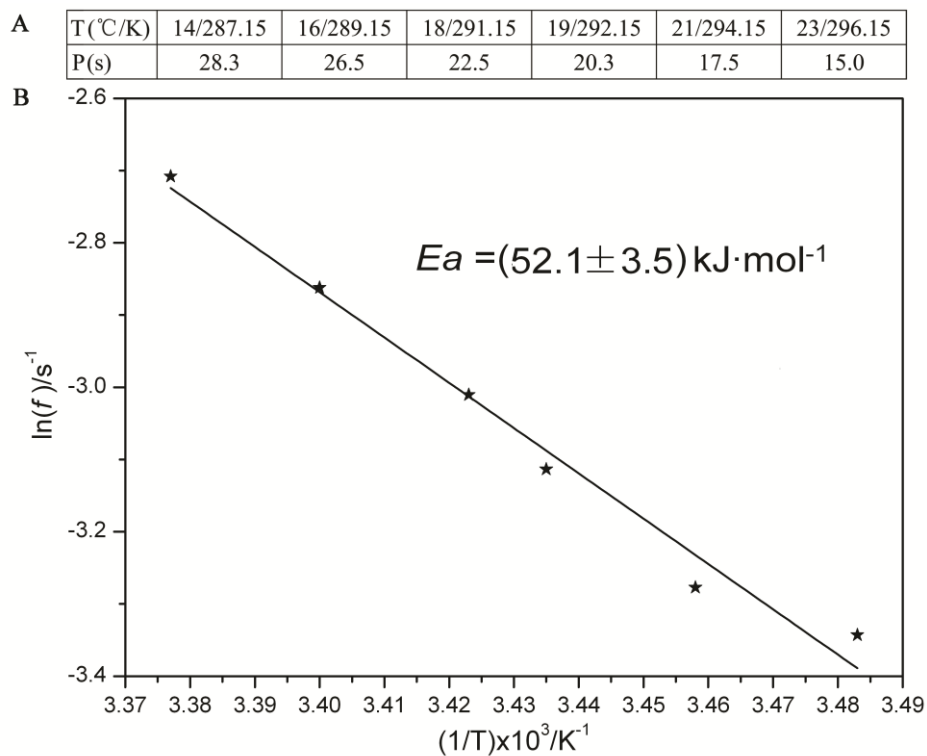(y-axis: $\ln(f)/\mathrm{s^{-1}}$, x-axis: $(1/T) \times 10^{3}/\mathrm{K^{-1}}$)

Figure S15. SSA period under different constant temperatures (A) and the Arrhenius linear fitting plot (B). The initial condition is the same as that used in Figure 3. *P*-period of SSA, *T*-Temperature of SSA system, *Ea* is the effective activation energy. Because the frequency of SSA here determines the speed of transformation from a assembled state to a de-sassembled state or vice versa, *Ea* here could also be regared as energy barrier needed to promote the assembly state transformation.

19