# Supporting Information

Self-Tunable Thermosensitive Behaviour by Reorganizable Architecture Variation in Belousov-Zhabotinsky Reaction

Hongwei Zhou, Enxiang Liang, Yi Pan, Xiaobin Ding,* Zhaohui Zheng,* Yuxing Peng

Materials

The terpyridine derivants[1,2] and poly(ethylene glycol monomethyl ether) p-toluenesulfonate (MPEGTs, Mn(MPEG)=2000 g·mol^{-1})[3] were synthesized and purified according to the previously reported methods. All other reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. and used as received unless otherwise specified. The structures of related polymers and compounds were confirmed by various techniques, 1HNMR, FT-IR, GPC, UV-vis, MS, some of which are given below.
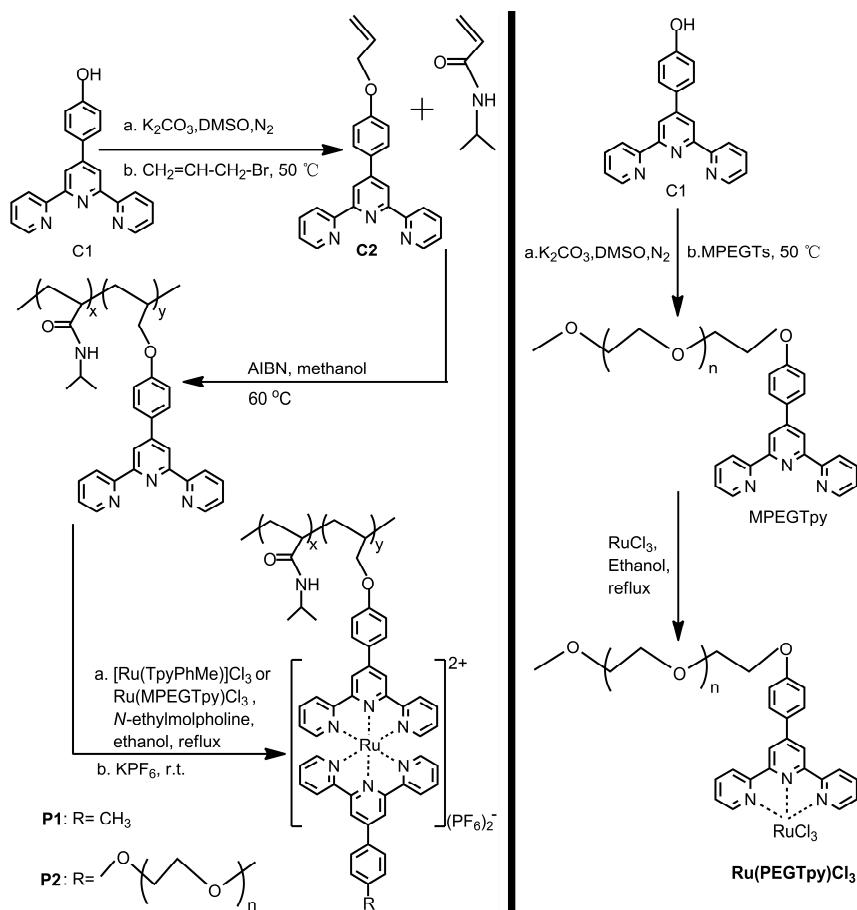
Scheme S1 Synthetic routes for the target polymers

Characterization and measurement

^{1}HNMR spectra were recorded at 25 °C on a NMR spectrometer (Bruker AV300) at 300 MHz. Chemical shifts (δ) are reported in parts per million (ppm) with reference to the residual protons of the deuterated solvents. FT-IR spectra were obtained on a FT-IR spectrophotometer (USA, Nicolet MX-1E) ranging from 400-4000 cm^{-1}. The average molecular weight and molecular weight distribution of the synthesized polymers were obtained in a gel permeation chromatography system equipped with a waters model 1515 pump, a model 2410 refractive index detector, and an OH-pak KB-803 column operated at 25 °C. THF was used as the mobile phase at a flow rate of 0.8 ml.min^{-1} and the column was calibrated using monodisperse polystyrene as standards.

LCST measurements were performed by recording the transmittance change against elevated temperature on a spectrophotometer (TU-1810 DPC, Purkinje General) equipped with a thermostatic controller with a heating rate of 1.0 °C·min^{-1}. Acidic Ce(IV) and Ce(III) solutions were utilized to keep the oxidized state and reduced state of Ru ions, respectively. For the reduction experiments, Na_2SO_3 solution was used as reducing agent. After addition of these stimuli, the solutions were efficiently stirred to ensure the complete responsiveness and homogeneity. Self-adapted thermosensitive behavior were studied by recording the transmittance change at 640 nm as a function of time on a spectrophotometer equipped with a thermostatic controller.

Synthesis of terpyridine monomer 4′-(4-allyloxyphenyl)-2,2′:6′,2″-terpyridine (TpyPhA) (TpyPhA)[2]

Under N_2 atomsphere, TpyOH (1.57 g, 4.83 mmol) in 10 ml dry DMF was added to a suspension of K_2CO_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/DMF solution (allyl

bromide in excess amount) was added dropwise within 30 min and then the mixture was immerged into preheated 50 °C thermostated oil bath. The successful reaction was detected by silver nitrate solution through white AgBr precipitate and the complete conversion of TpyOH was detected by TCL technique. The hot reaction mixture was filtered to remove inorganic phase. The solvent and excess allyl bromide were removed by rotary evaporator to get crude product as light brown solid. The target product was obtained by recrystallization from DMF/ethanol (20/80, v/v) solution 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).

Preparation of poly(NIPAAm-*co*-TpyPhA)[2]

   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 purged methanol was prepared with assistance of ultrasound (In some cases, TpyPhA can not be completely dissolved when the amount of methanol is too small. However, the reaction mixture gradually became clear with the proceeding of polymerization). Afterwards, the solution was treated with four freeze-evacuate-thaw cycles and sealed. The ampule was then immersed into preheated 60 °C thermostated oil bath for 72 h and then the polymerization was stopped by exposing to air. The resulting polymer solution was concentrated, precipitated in large amount of cold diethyl ether, and filtered. To further remove the impurities such as the unreacted monomers and low-molecular-weight product, the crude product was dissolved, dialyzed against gradient methnol/water mixtures for 3 days and freeze dried to get poly(NIPAAm-*co*-TpyPhA). GPC: M_n=6970 g·mol^{-1}, PDI=2.01; IR (KBr): ν = 1650 (w), 1386 (m), 1367 (m); UV-vis (ethanol):

λmax=286, 252 nm.

Preparation of poly(NIPAAm-*co*-Ru(TpyPhMe-TpyPhA))(PF$_6$)$_2$ (P1)[2]

The procedure is as follows: 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 ethanol along with 50 μl 4-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 polymer P2. UV-vis (ethanol): λmax=494, 308 nm.

Preparation of terpyridine-terminated poly(ethylene glycol monomethyl ether) (MPEGTpy)

MPEGTpy was synthesized with a similar procedure to that used in synthesis of TpyPhA by replacing allyl bromide with MPEGTs. The product was purified by precipitation for four times from ice diethyl ether and dried in vacumme. ^{1}HNMR (300 MHz, DMSO, 25 °C, δ) 8.78 (d, J = 8.2 Hz, 2H), 8.66-8.69 (m, 4H), 8.01-8.06 (m, 2H), 7.88-7.97 (m, 2H), 7.45-7.55 (m, 2H), 7.10-7.17 (m, 2H), 4.20 (s, 2H), 3.36-3.79 (m), 3.26 (s, 3H). UV–vis (ethanol): λmax=286, 253, 223 nm.

Preparation of MPEGTpy mono-complex (Ru(MPEGTpy)Cl$_3$)

Ru(MPEGTpy)Cl3 was synthesized by a similar method in preparing [Ru(TpyPhMe)]Cl$_3$. The crude product was dissolved in water and extracted twice with CH$_2$Cl$_2$. The organic phase was volatilized and dried to get Ru(MPEGTpy)Cl$_3$ as brown powder. UV–vis (ethanol): λmax = 393, 311 nm.

Preparation of poly(NIPAAm-co-Ru(MPEGTpyMe-TpyPhA))(PF$_6$)$_2$ (P2)

A post-functionalization procedure similar to that used in preparation of P1 was carried out by simply replacing [Ru(TpyPhMe)]Cl$_3$ with Ru(MPEGTpy)Cl$_3$. UV-vis (ethanol): λmax =493, 308 nm. IR (KBr): ν = 1107 (s).

Reference

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

2. H. W. Zhou, E. X. Liang, Z. H. Zheng, X. B. Ding, Y. X. Peng, Chem. Commun. 2012, 48, 10553.

3. I. Shenoy, W. Fu, J. Li, G. Jones, C. DiMarzio, S. Sridhar, M. Amiji, Int. J. Nanomedicine, 2006, 1, 51.
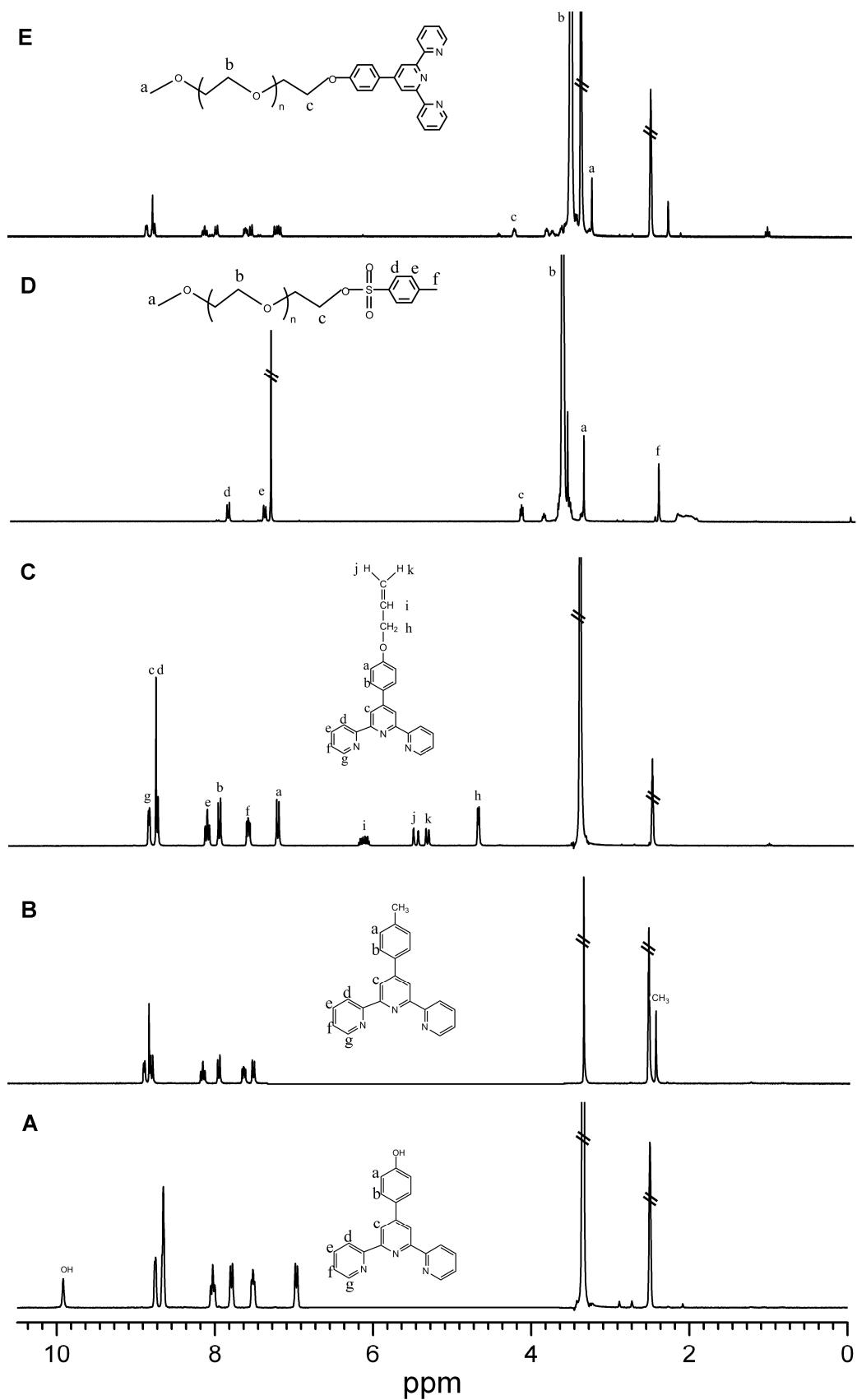
Figure S1 ^{1}HNMR spectra of the key polymers and terpyrine compounds.
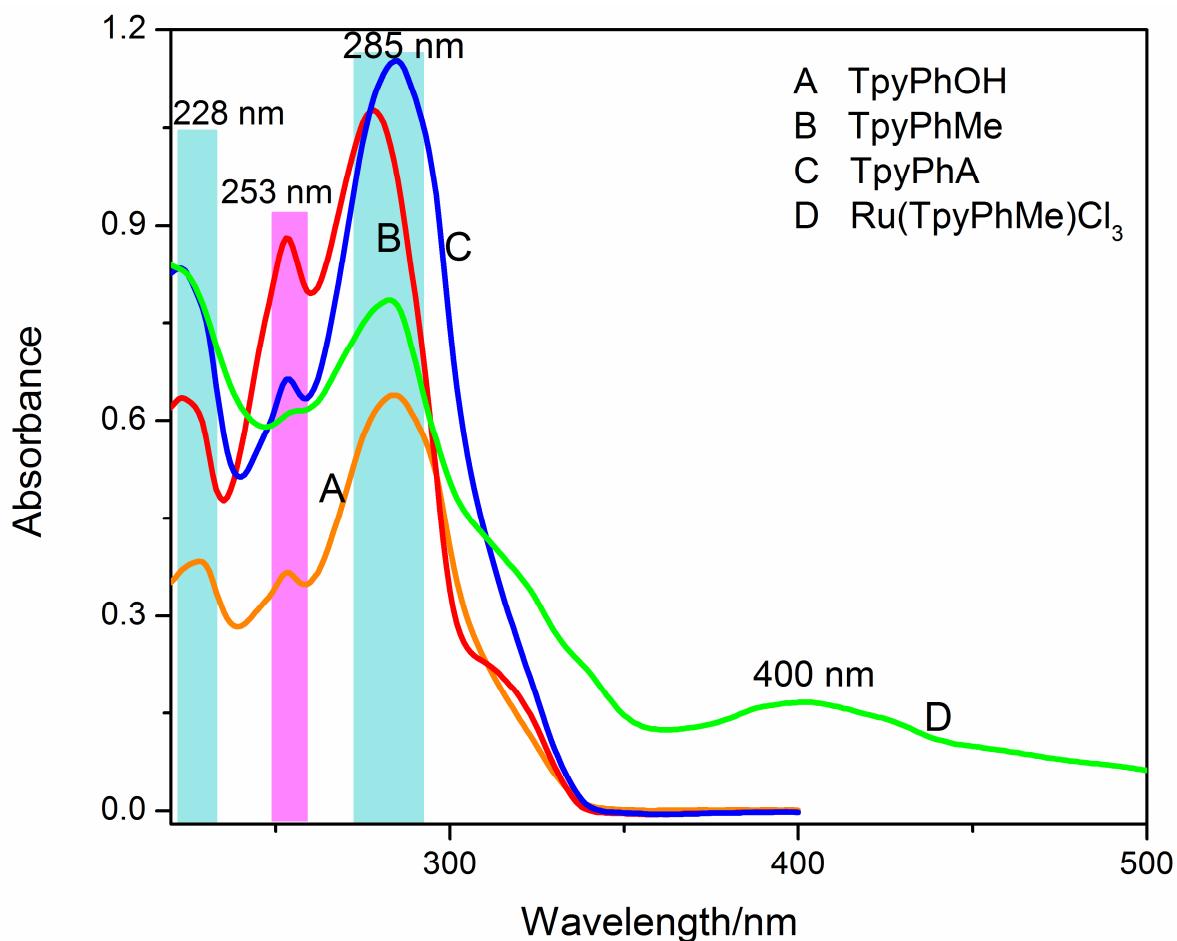
Figure S2 UV-vis spectra of the key terpyrine compounds.
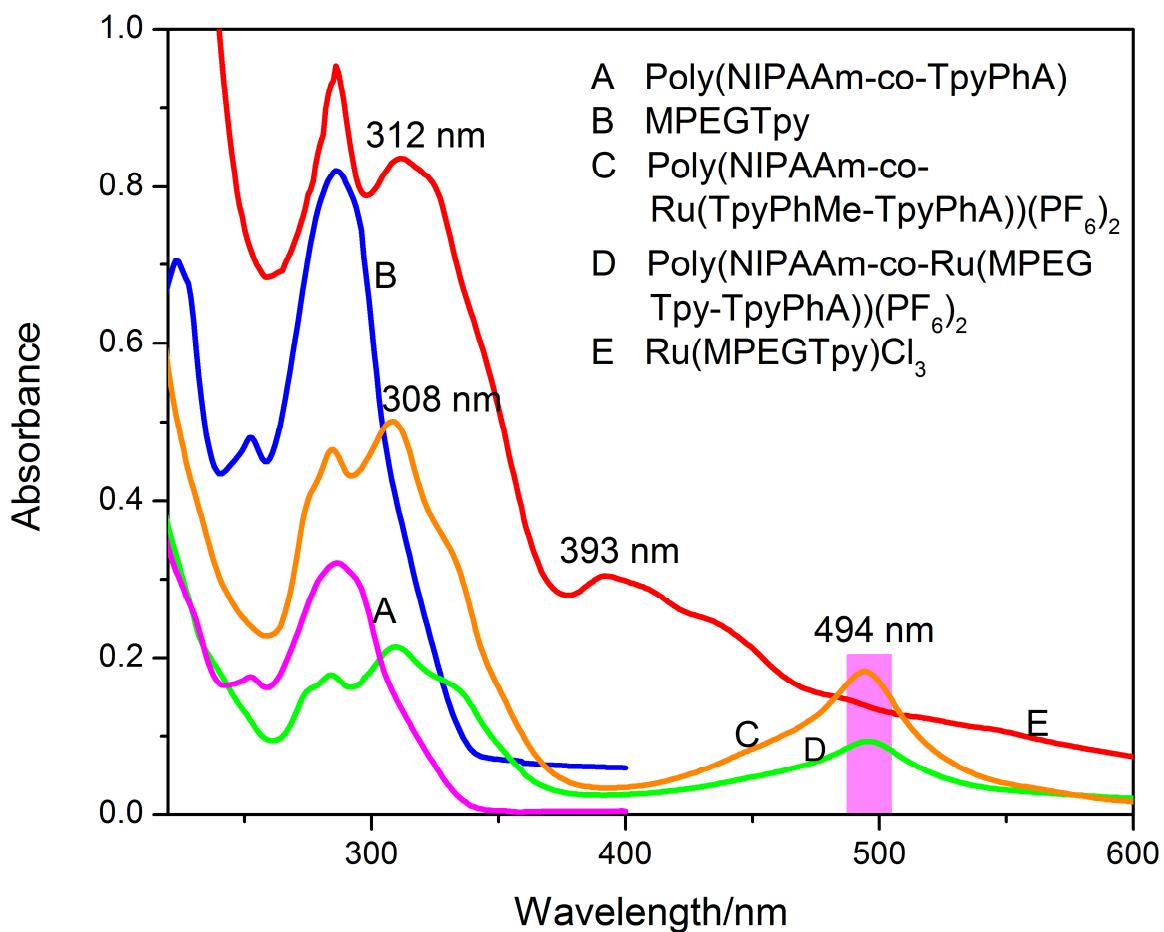
Figure S3 UV-vis spectra of the key polymers.
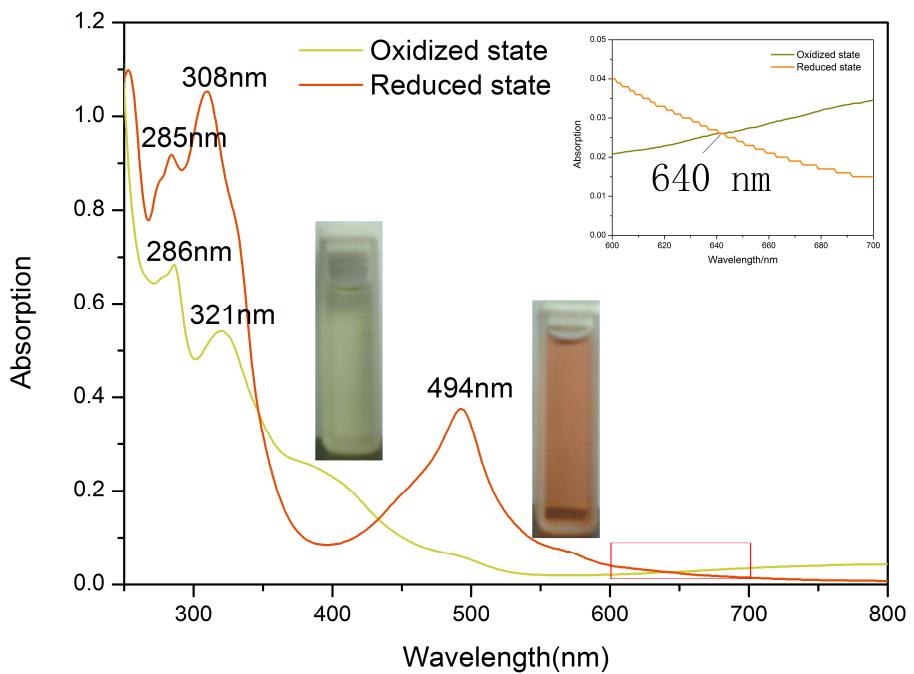
Figure S4 UV-vis spectrum of P1 in the reduced state and the oxidized state. An isosbestic point was found at 640 nm.
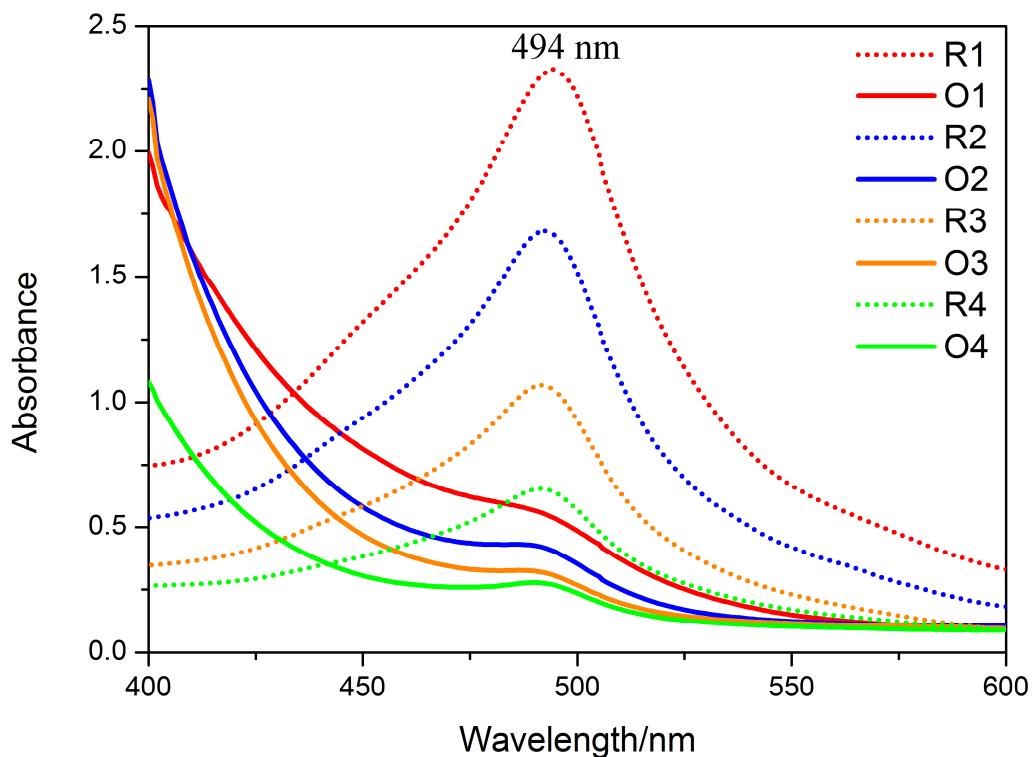

Figure S5 UV-vis spectrums of P1 under cyclic oxidation (O1-O4) and reduction (R1-R4) condition. The figure is related to Figure 2.
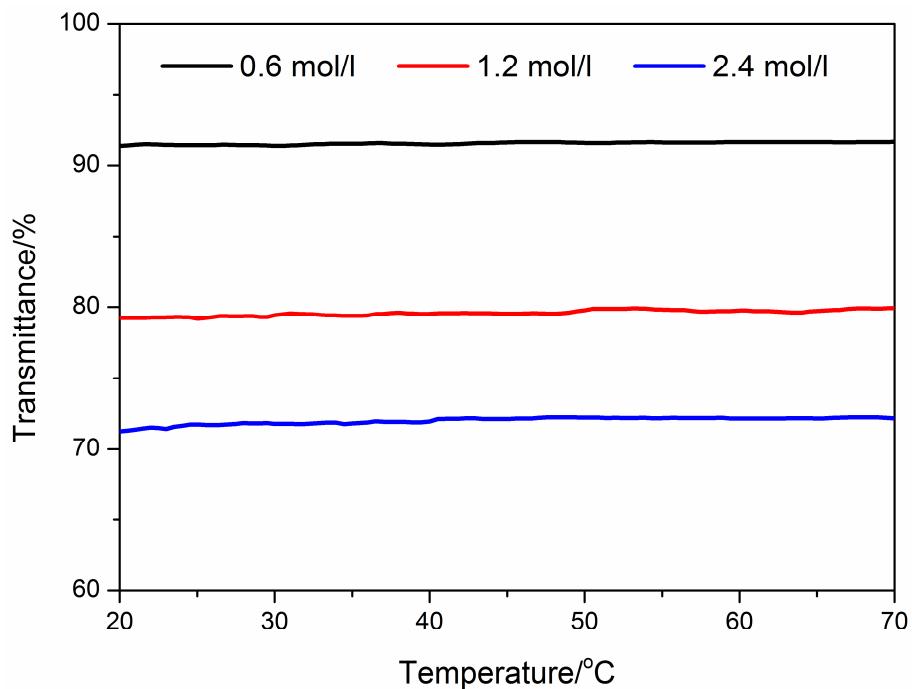
**Figure S6** Temperature dependent transmittance of P2 in different concentrations of KCl.
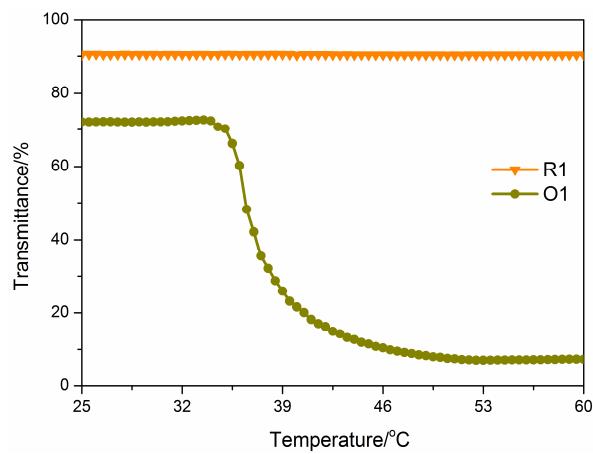
Figure S7 Temperature dependent transmittance of P2 in the reduced state R1 and the oxidized state O1.
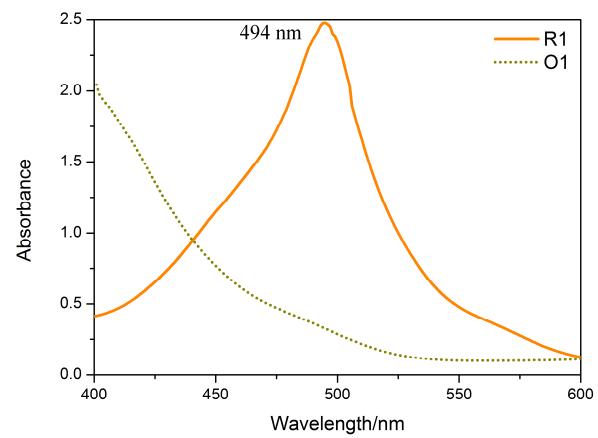

**Figure S8** UV-vis spectrums of P2 in the reduced state (R1) and oxidized state (O1).
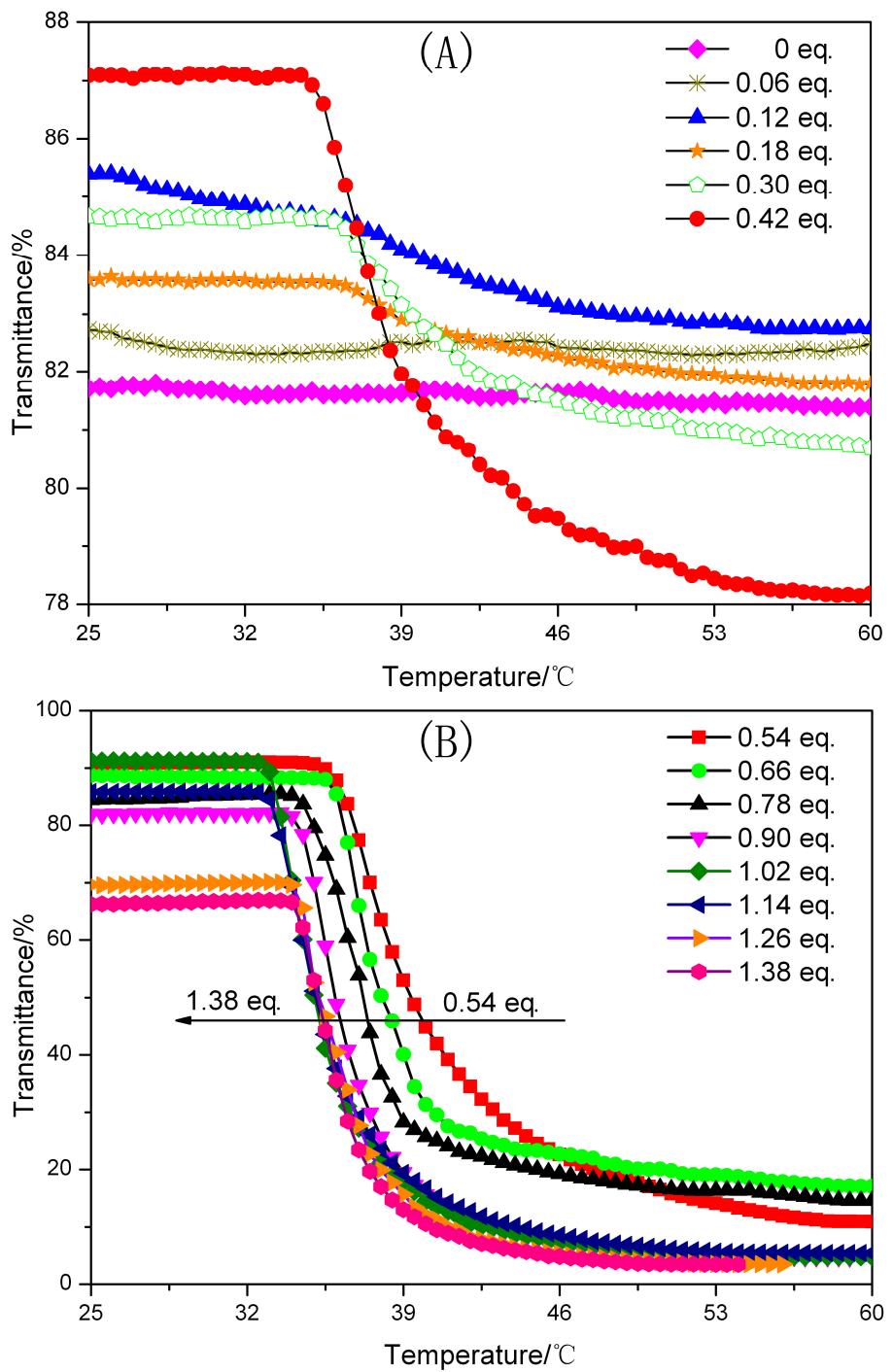
Figure S9 Temperature dependent transmittance of of P2 (1 mg·ml^{-1}) under gradual oxidizing condition. (A) The amount of Ce(IV) is changed from 0 to 0.42 eq.. (B) The amount of Ce(IV) is changed from 0.54-1.38 eq. The figure is related to Figure 4.
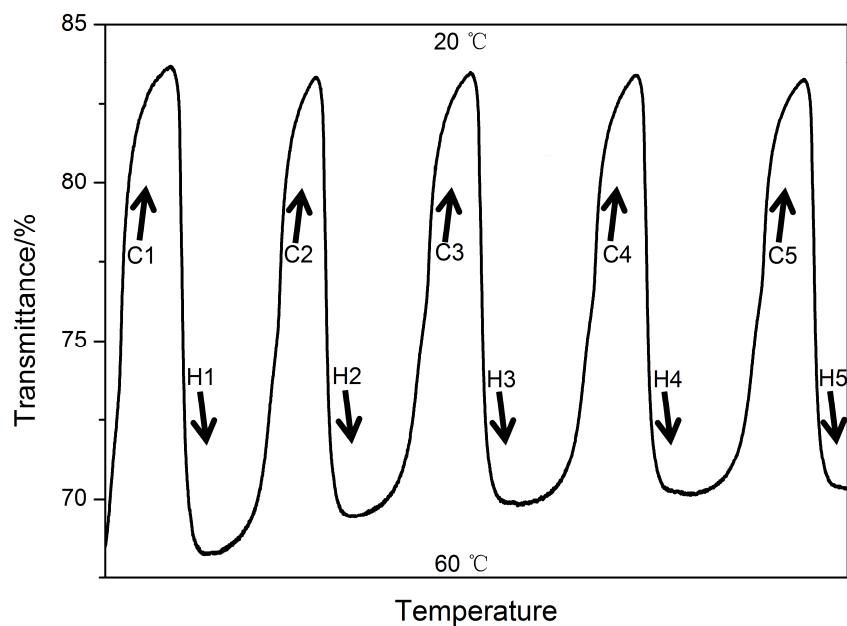
Figure S10 Temperature dependent transmittance of P1 under alternatively programmed cooling (C1-C5) and heating (H1-H5) condition. The stable thermosensitive behavior prevents the polymers from irreversible precipitation in the cyclic thermosensitivity test or in BZ reaction systems.