Supporting Information

Periodic Auto-active Gel with Topologically "Polyrotaxane-interlocked" Structure

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1. Materials

4′-(4-hydroxyphenyl)-2,2′:6′,2″-terpyridine(*TpyPhOH*) and 4′-(4-methylphenyl)-2,2′:6′,2″-terpyridine-ruthenium(III) chloride (*[Ru(TpyPhMe)]Cl$_3$*) were synthesized and purified according to the previous method.[1] *N*-Isopropylacrylamide (*NIPAAm*) (Aldrich, A.R.) was purified by recrystallization from its toluene solution and dried under vacuum. 2,2′-Azobisisobutyronitrile (*AIBN*) (Aldrich, A.R.) was recrystallized from methanol prior to use. *N*-(3-Bromopropyl) phthalimide, acryloyl chloride, *N, N′*-methylene bis(2-acrylamide) (*BIS*) and 3,5-dimethylphenol were purchased form *J&K* chemicals. PEG (*Mn*=2000 g/mol) was extracted from water, dried overnight with anhydrous Na_2SO_4, concentrated and precipitated three times from diethyl ether. All the other reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. and used as received unless otherwise specified.

2. Synthesis of TpyNA (C4)

TpyNA (C4) was synthesized according to the route in Fig. S1. C3 was synthesized according the previous method.[2] The synthesis of C4 is as follows. A solution of acryloyl chloride (1.5 ml, 0.019 mol) in 20 ml dry CH_2Cl_2 was added drowise into a solution of C3 (4.5 g, 0.012 mol) and NEt_3 (1.6 ml, 0.012 mol) in 100 ml CH_2Cl_2 in a ice-water bath. The resulting mixture was stirred at room temperature for 12 h. After reaction, the mixture was throughly washed with $NaHCO_3$ (5 wt%), HCl (1 mol/l) and saturated NaCl. The organic phase was dried with anhydrous Na_2SO_4 over night and concentrated in vacuo. The pure product C4 was obtained by recrystalization from its ethanol solution. The ^{1}HNMR spectra is given in Fig. S2 and Fig. S3.

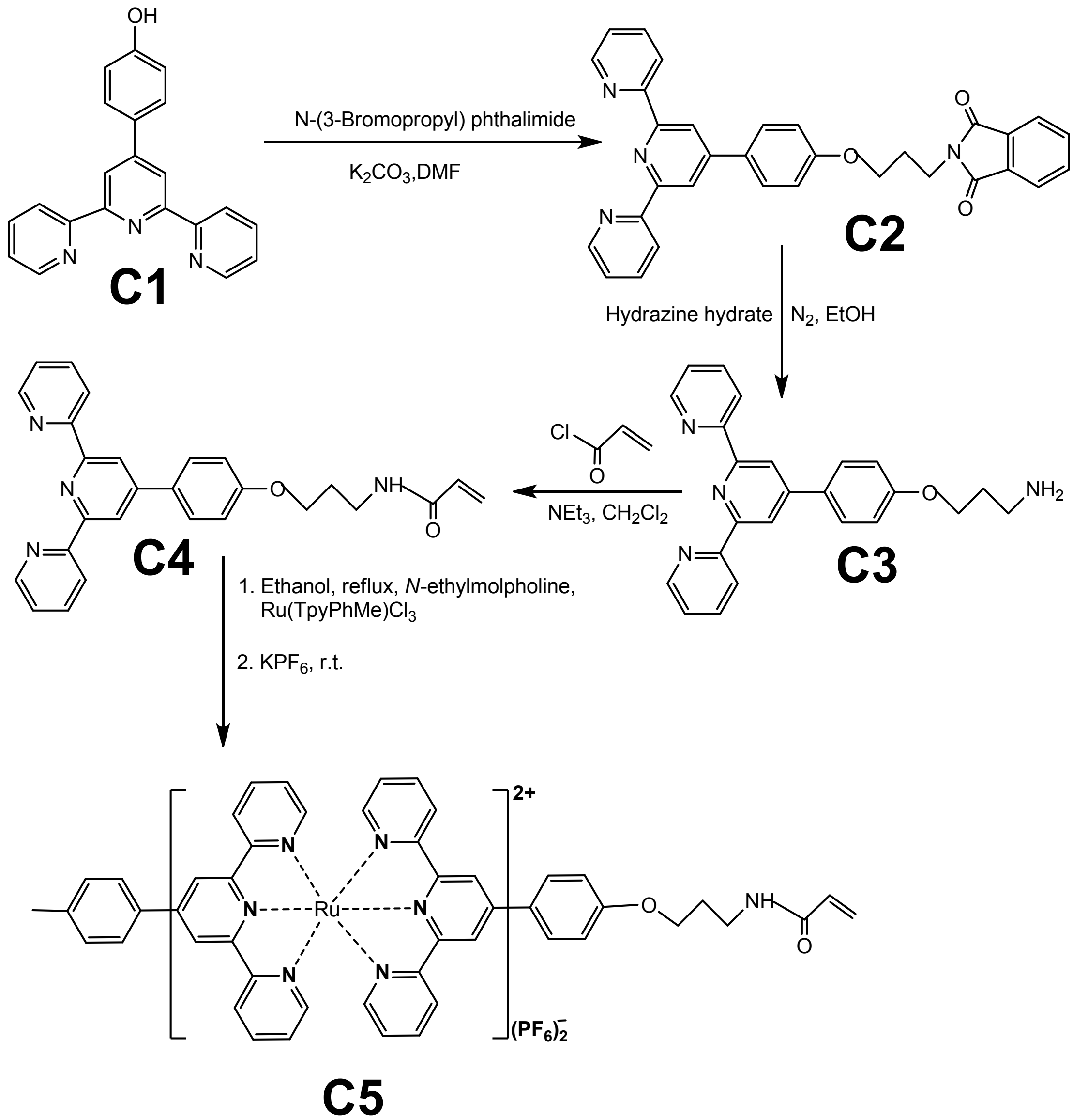


Fig. S1 The synthesis route for the ruthenium-terpyridine monomer (C5).

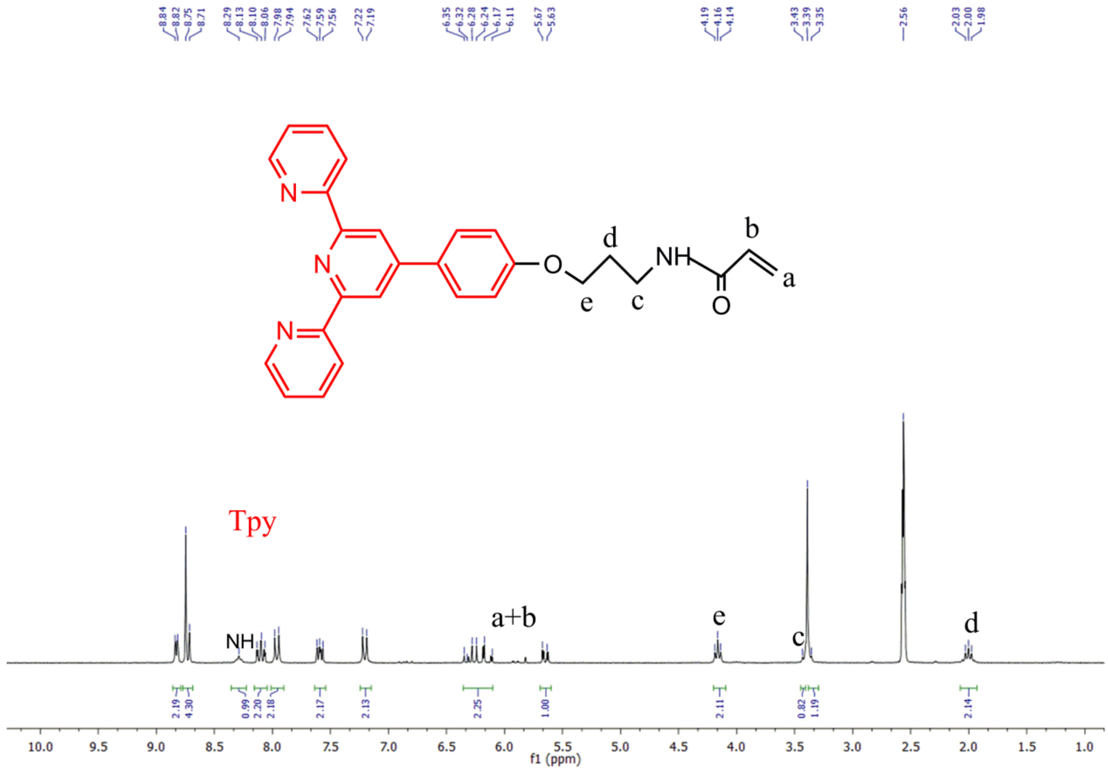


Fig. S2 ^{1}HNMR spectra of C4 in DMSO-d6.

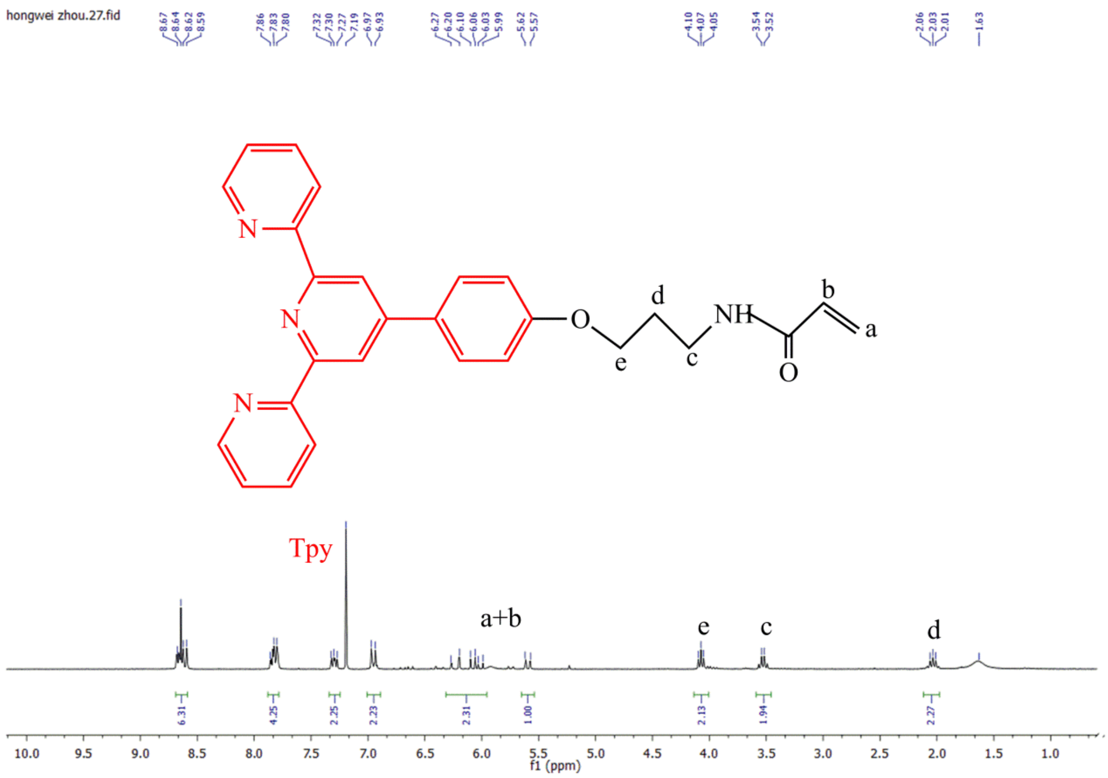


Fig. S3 ^{1}HNMR spectra of C4 in $CDCl_3$.

3. Synthesis of [Ru(II)(TpyNA)(TpyPhMe)]$(PF_6)_2$ (C5)

[Ru(II)(TpyNA)(TpyPhMe)]$(PF_6)_2$ was synthesized according to the route designed in **Fig. S1** by two steps. The detailed synthesis is as follows: [Ru(TpyPhMe)]Cl_3 (0.4119 g, 0.77 mmol) was disolved in 30 ml ethanol and then TpyPhA (0.3387 g, 0.77 mmol) and two drops of *N*-ethyl morpholine was added into the above solution. The resulting mixture was refluxed for 6 h. Afterwards, KPF_6 was added to replace the counter ions. The obtained precipitation was filtered and recrystallized to get **C5** as dark red solid. The ^{1}HNMR spectra is given in **Fig. S4** and the UV-VIS spectra is given in **Fig. S5**.

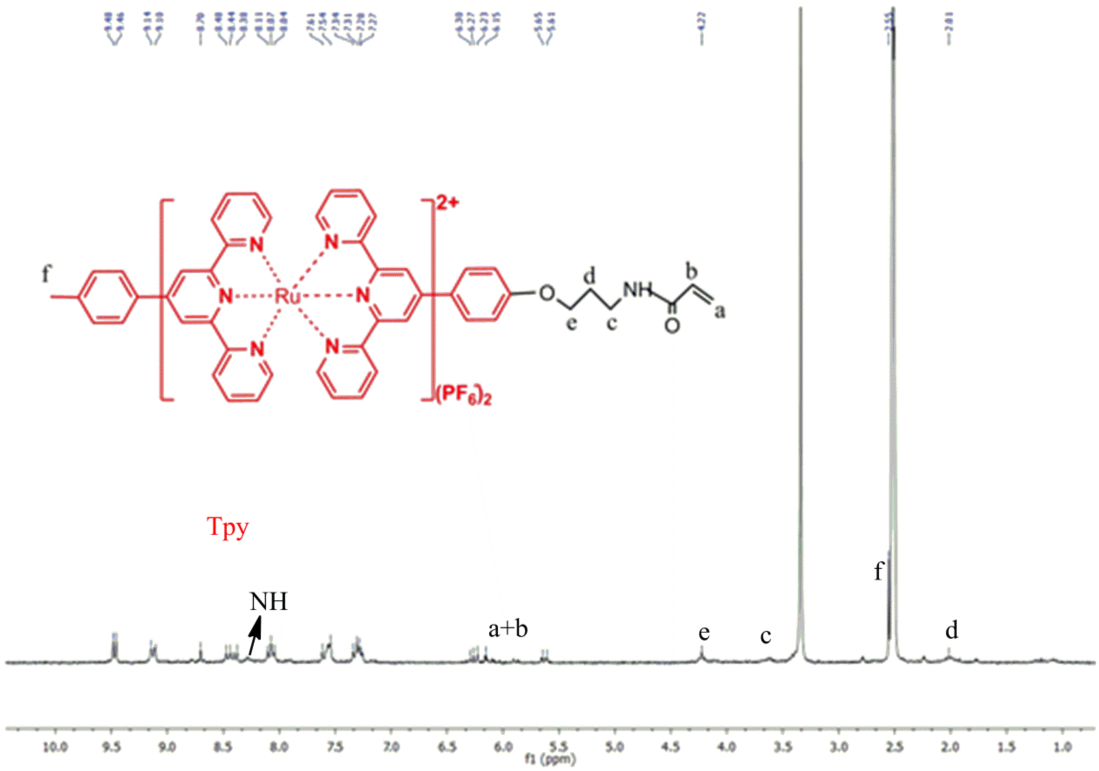


Fig. S4 ^{1}HNMR spectra of C5 in DMSO-d6.

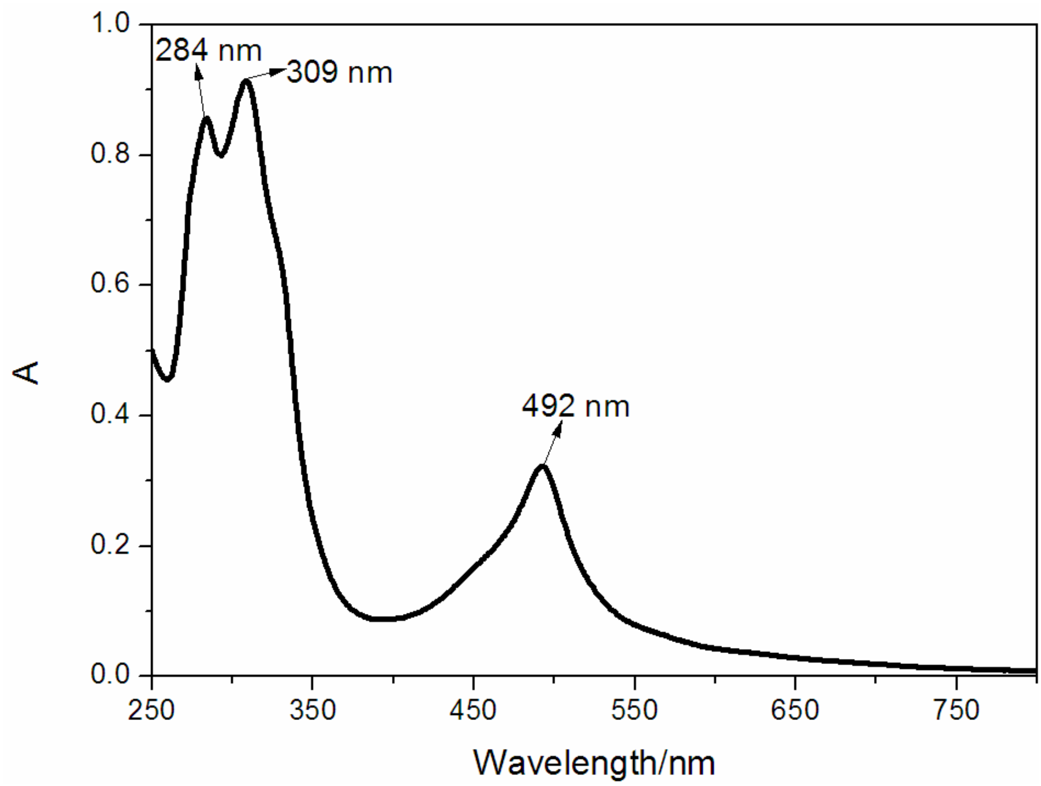


Fig. S5 UV-VIS spectra of C5 in MeCN.

4. Sythesis of PEG/α-CD polyrotaxane crosslinking agent

PEG/α-CD polyrotaxane crosslinking agent (MPR) was synthesized according to the route in Fig. S6 by an assembly process, a capping process and a modification process according to the previous literatures[3]. The ^{1}HNMR spectra of the key materials are given in Fig. S7. From the ^{1}HNMR spectra, the number of α-CD trapped on a individual PEG chain is estimated to be 7 and the coverage ratio is about 32%. The average degree of double bond substitution per α-CD unit is found to be 1.

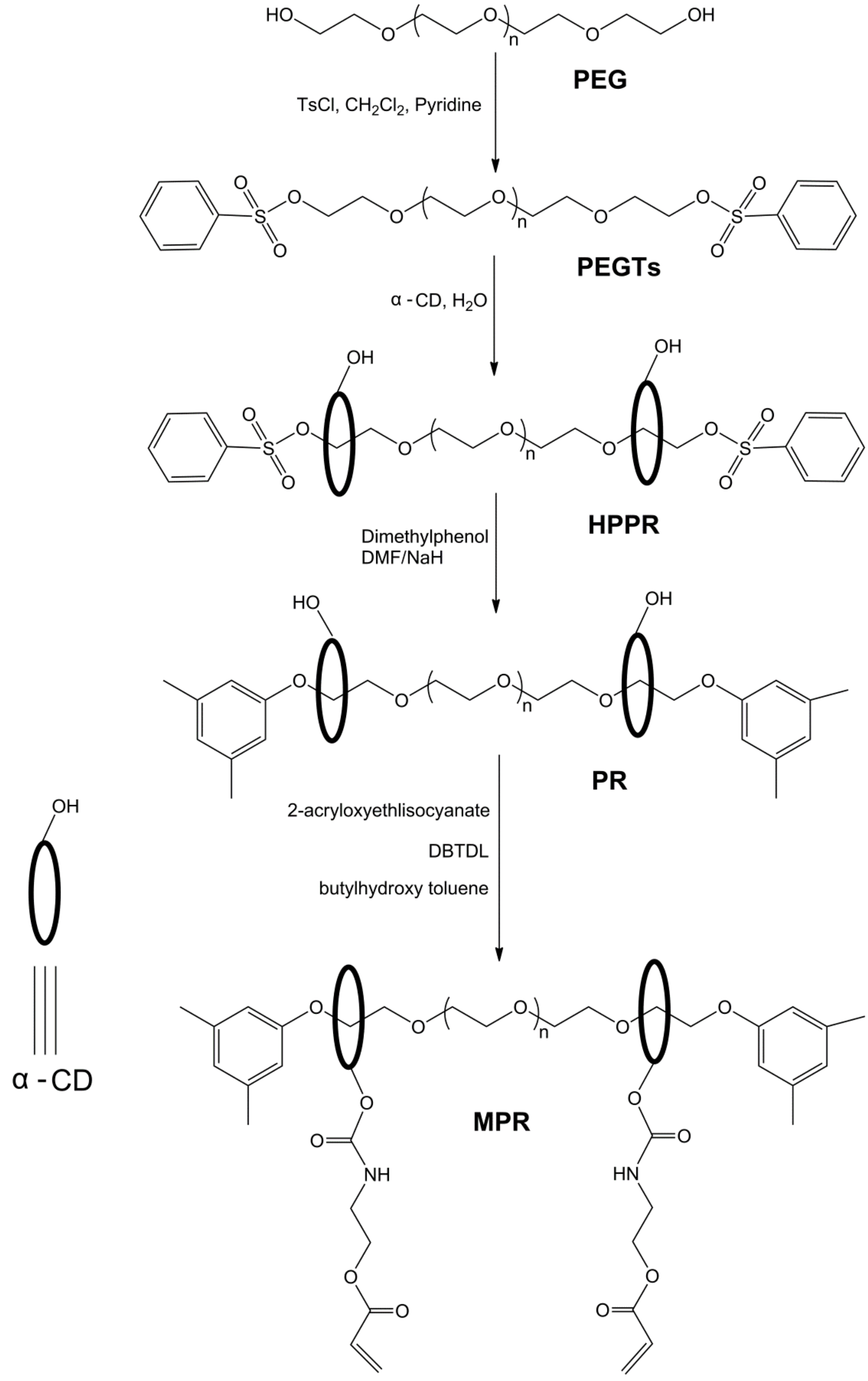


Fig. S6 Synthesis route for the PEG/α-CD polyrotaxane crosslinking agent.

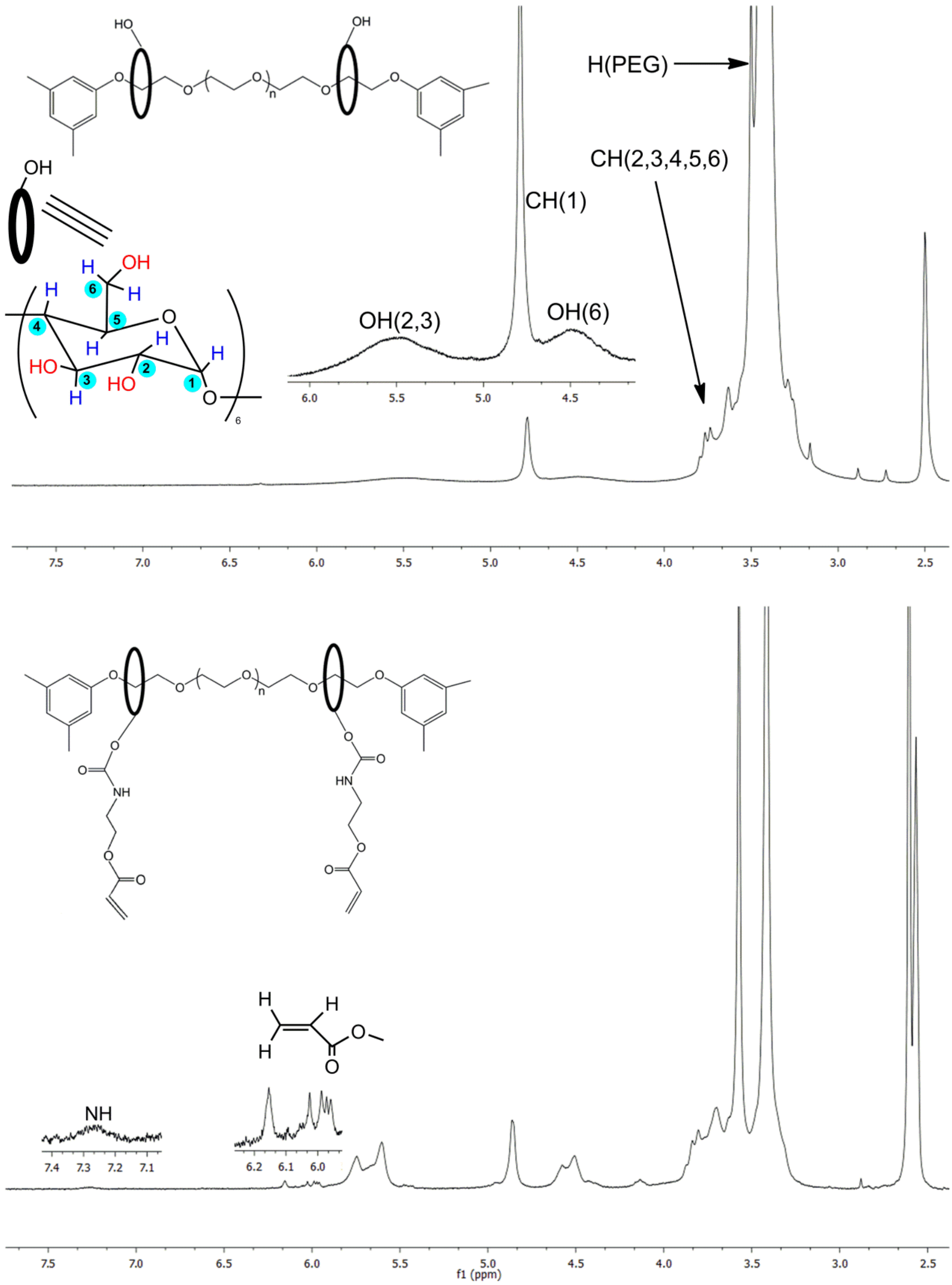


Fig. S7 ^{1}HNMR spectra of PR (upper) and MPR (lower) in DMSO-d6.

5. Preparation of the active gels.

The active gels were prepared by a free radical polymerization of NIPAAm and [Ru(II)(TpyNA)(TpyPhMe)]$(PF_6)_2$ in the presence of crosslinker. Take G1 as an example, a 1.0 ml solution of dry DMSO containing NIPAAm (0.5 g, 0.0044 mol)，C5 (0.025 g, 2.17 x 10^{-5} mol), BIS (0.0068 g, 4.39 x 10^{-5} mol)，AIBN (0.0089 g, 5.42 x 10^{-5} mol) was bubbled with neat N_2 for 30 min under ice-water bath. Afterwards, the pregel solution was injected into a mould of two Teflon slides separated by a 2 mm thickness silicone rubber sheet. After gelation at 60 ℃ for 24 h，the gel was thoroughly washed with DMSO and graded DMSO/H_2O to remove the unreacted monomers and residues. Other gels are prepared in a similar method (**Table S1**).

Table S1 Sample codes of BIS-crosslinked gels and topological gels.

Gels	NIPAAm (mol/l)	C5 (mol/l)	AIBN (mol/l)	BIS (mol%)	[a]MPR (mol%)	Solvent
G1	4.4	0.022	0.054	1		DMSO
G2	4.4	0.022	0.054	3	None	DMSO
G3	4.4	0.022	0.054	6		DMSO
TG1	4.4	0.022	0.054		2(α-CD)	DMSO
TG2	4.4	0.022	0.054	None	6(α-CD)	DMSO
TG3	4.4	0.022	0.054		12(α-CD)	DMSO

[a]For the preparation of topological gels, the MPR was first completely dissolved in dry DMSO with the assistance of ultrasound before adding the monomers and AIBN.

6. Setup and online study of the AGs

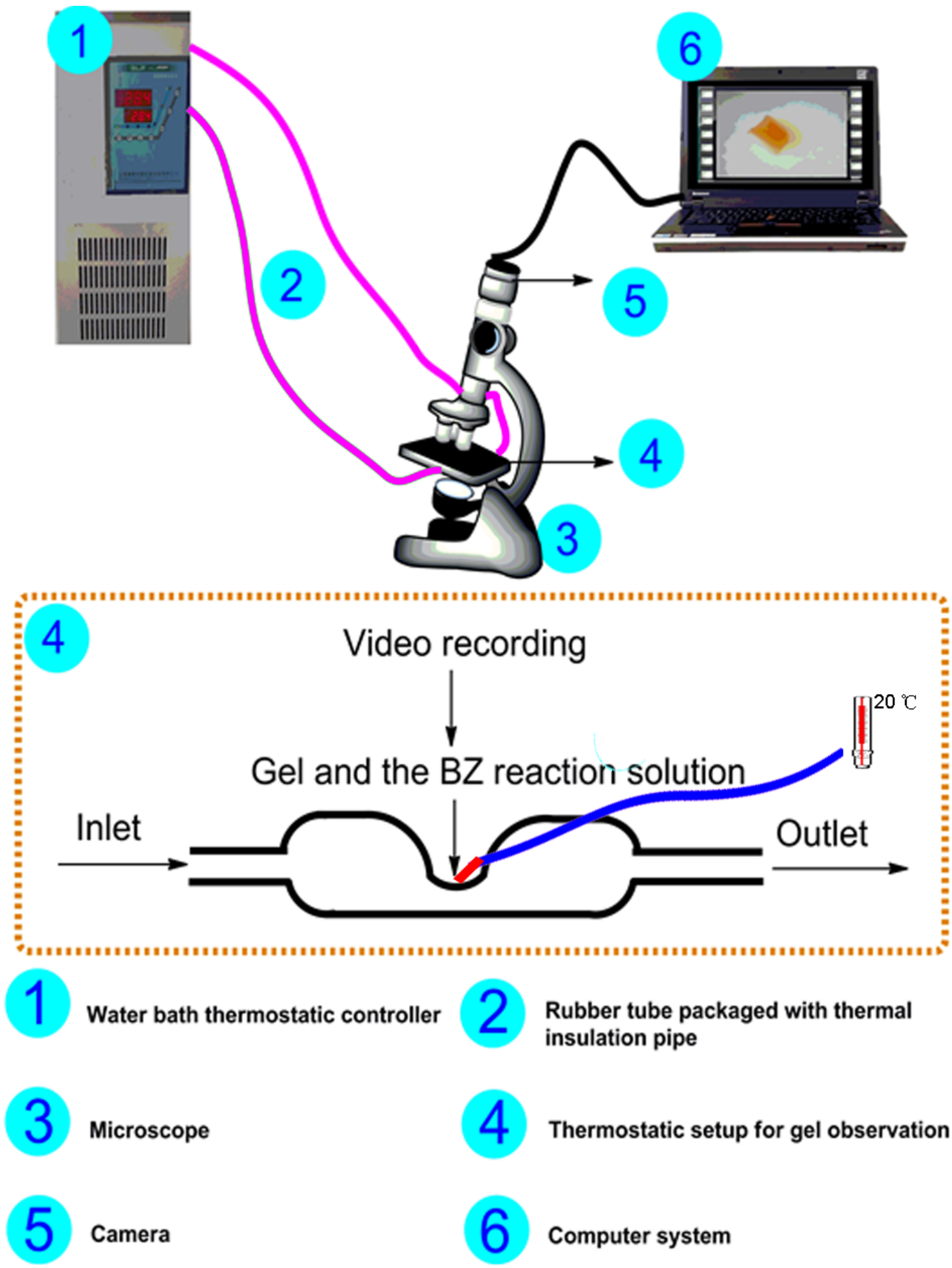


Fig. S8 The setup for online study of the AGs.

Most of the images were taken on the steup shown in Fig. S8. The temperature inside the small pool was controlled by a flowing water bath driven by a thermostatic circulator. The opitical images and videos of the AGs were recorded at different designed conditions. Analyzing the images gives the time and temperature-dependent responsive behaviors. To keep the AGs in the reduced and the oxidized state, the gel samples were first equilibrated in a solutions of 5 mM $Ce(SO_4)_2$ and 900 mM HNO_3 or 5 mM $Ce_2(SO_4)_3$ and 900 mM HNO_3.[4] The mechanical oscillation and the chemical wave propagation were also observed on the steup shown in Fig. S8. The concentration of BZ sustrates were fixed at: [$NaBrO_3$]=0.08 mol l^{-1}, [Malonic acid]=0.06 mol l^{-1}, [HNO_3] = 0.9 mol l^{-1}.

7. Other supporting materials

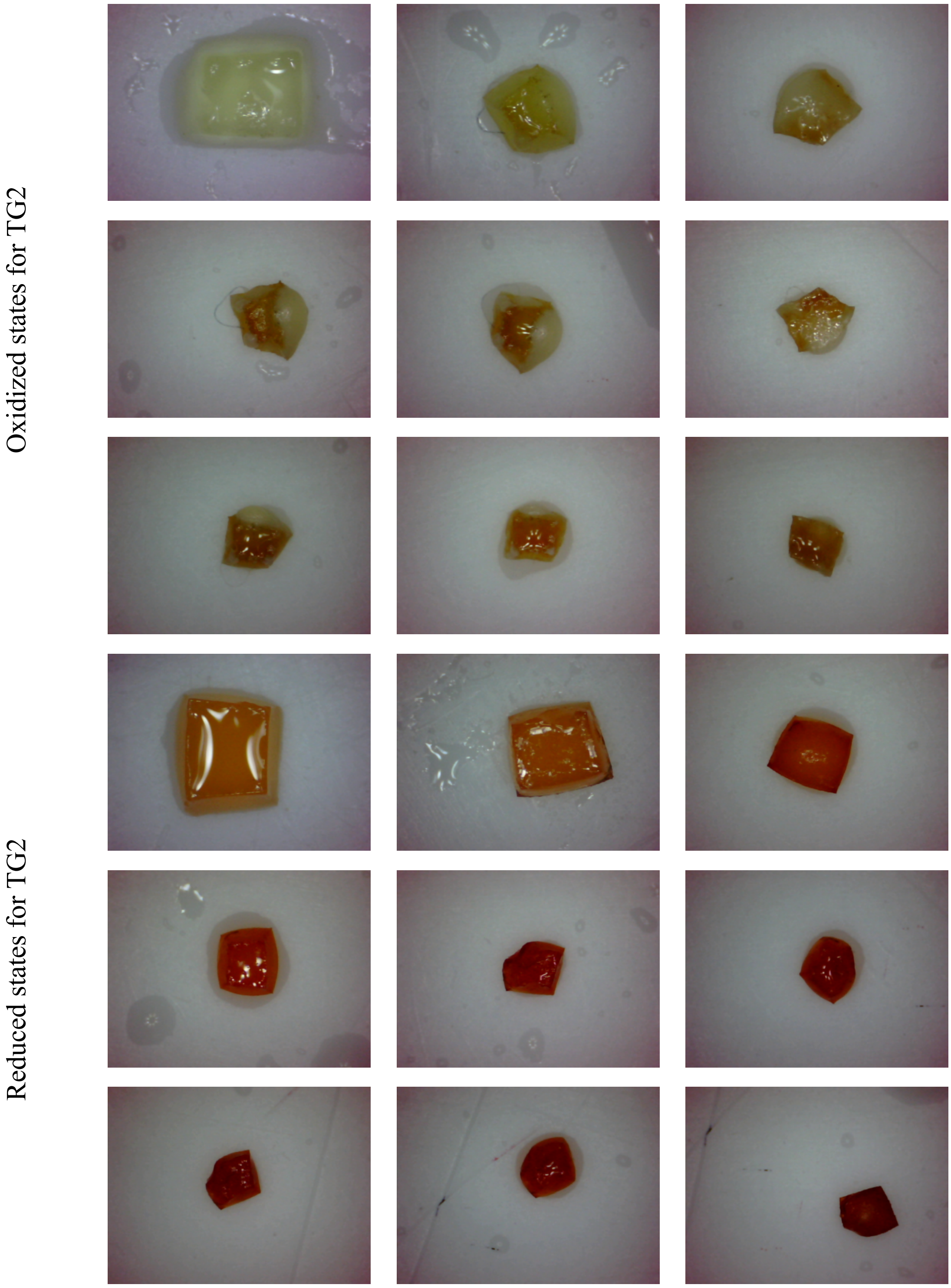


Fig. S9 Representitive optical images of the oxidized and reduced states of TG2 at different temperatures from 15 ℃ (the first image) to 50 ℃ (the last image). These images are related to Fig. 3.

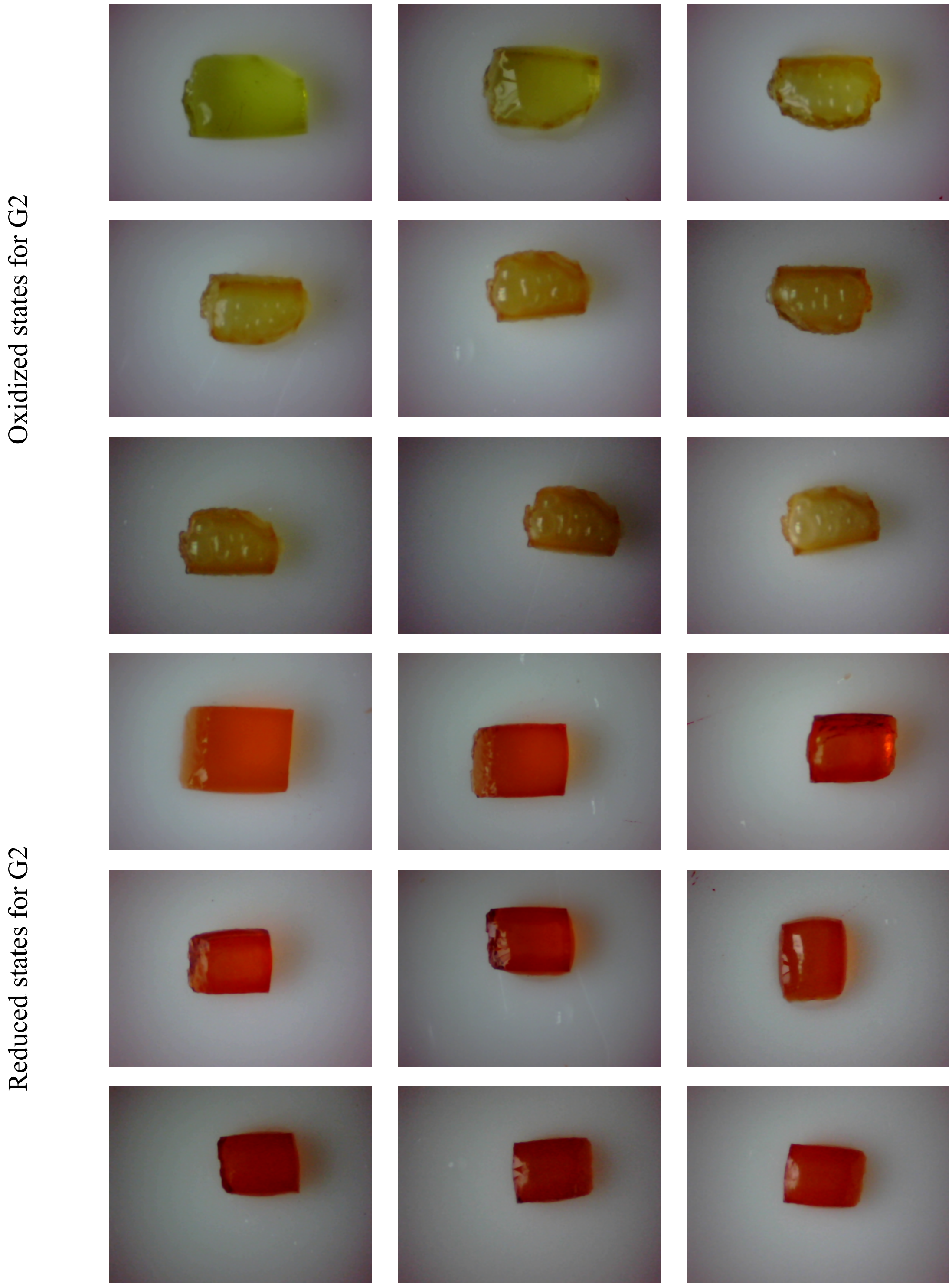


Fig. S10 Representitive optical images of the oxidized and reduced G2 at different temperatures from 15 ℃ (the first image) to 50 ℃ (the last image). These images are related to Fig. 3..

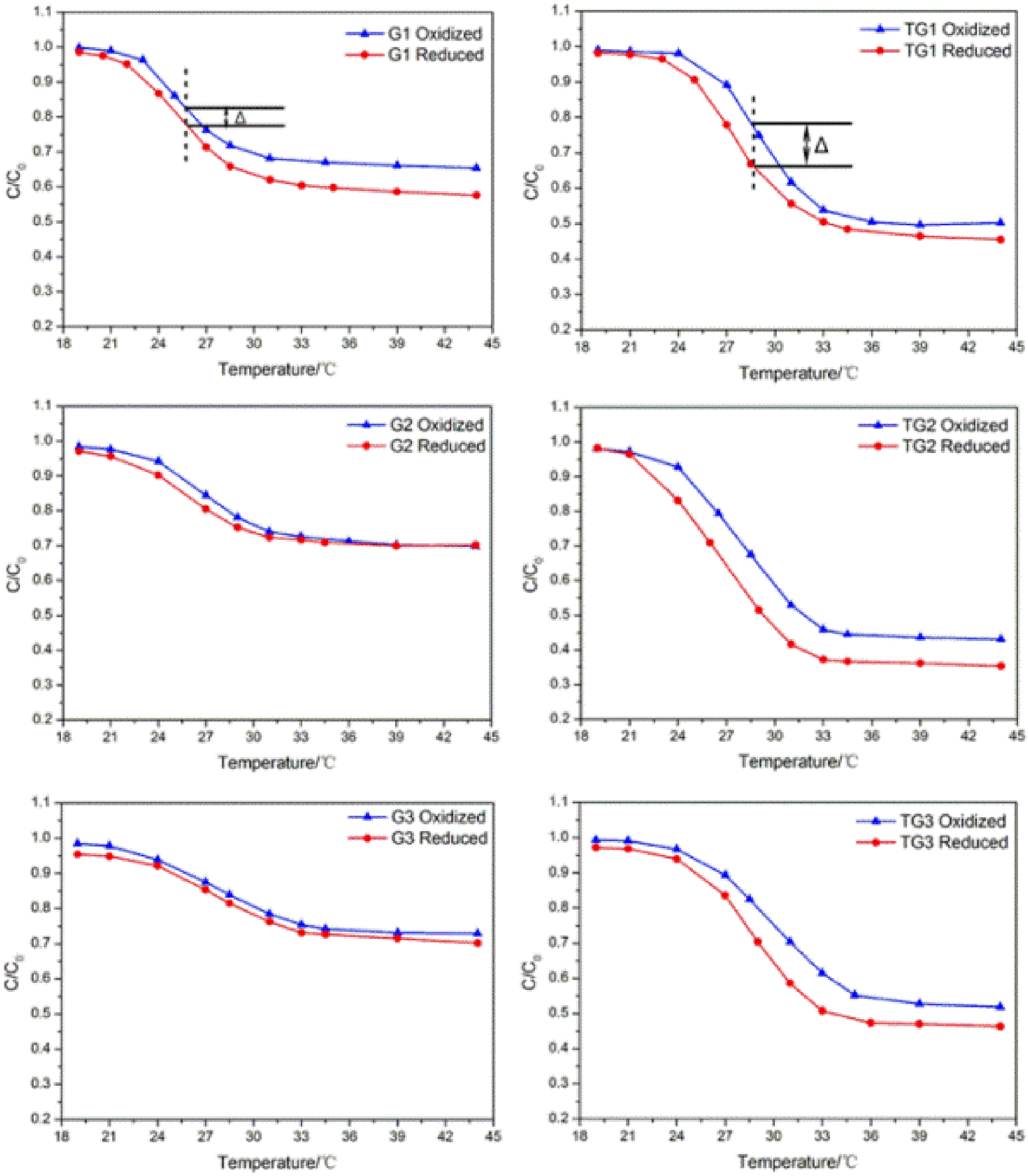


Fig. S11 Temperature-dependent circumference change of the AGs in both the oxidized states and the reduced states. C_0 is the equilibrated circumference of the gels in a solutions of 5 mM $Ce(SO_4)_2$ and 900 mM HNO_3 (oxidized state) or 5 mM $Ce_2(SO_4)_3$ and 900 mM HNO_3 (reduced state) at 18 ℃. C_i represents the equilibrated gel circumference at different temperatures.

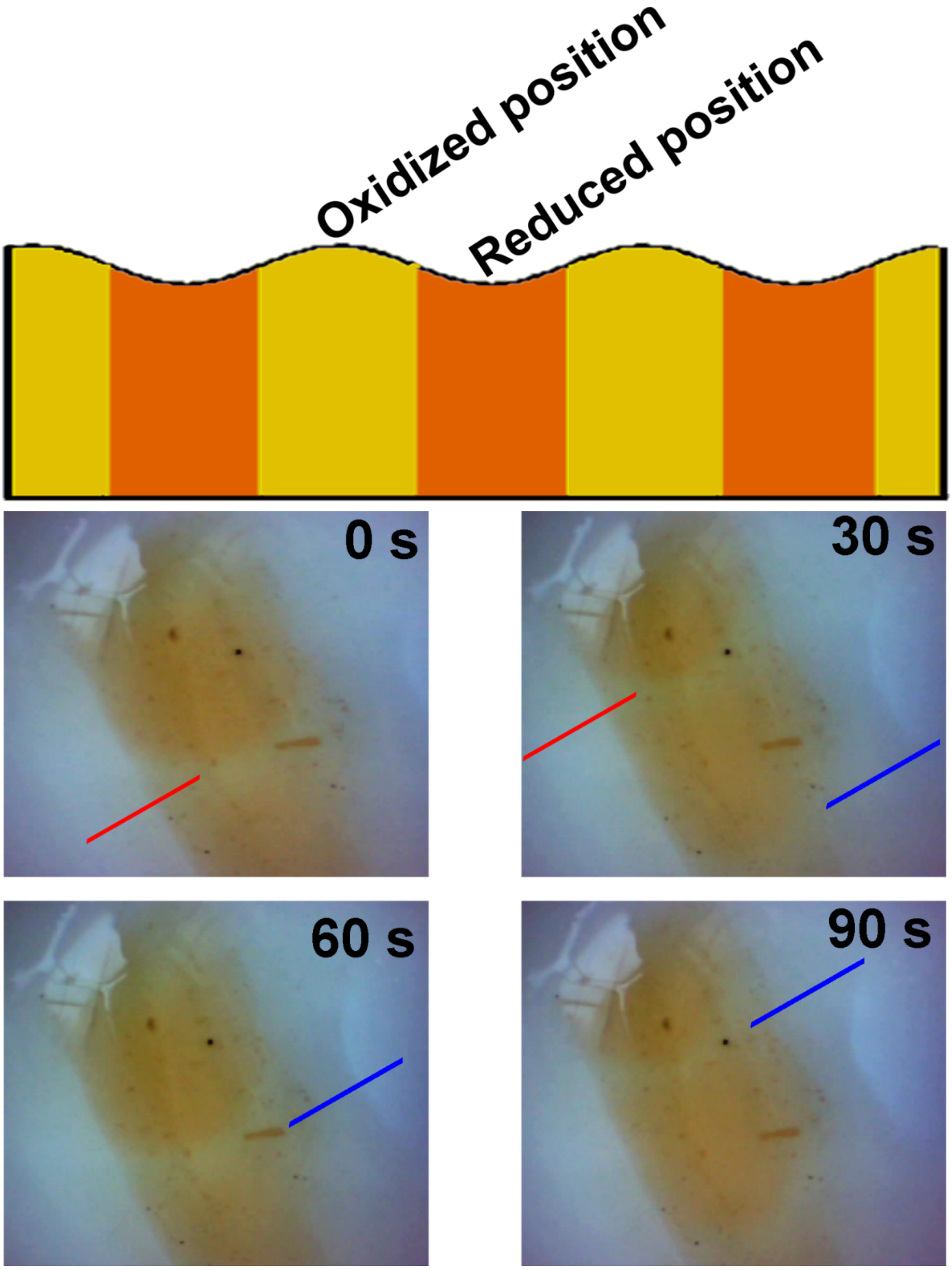
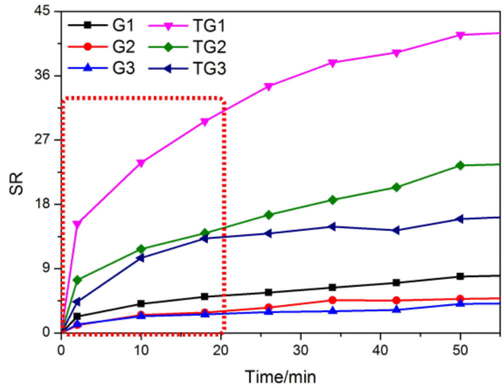
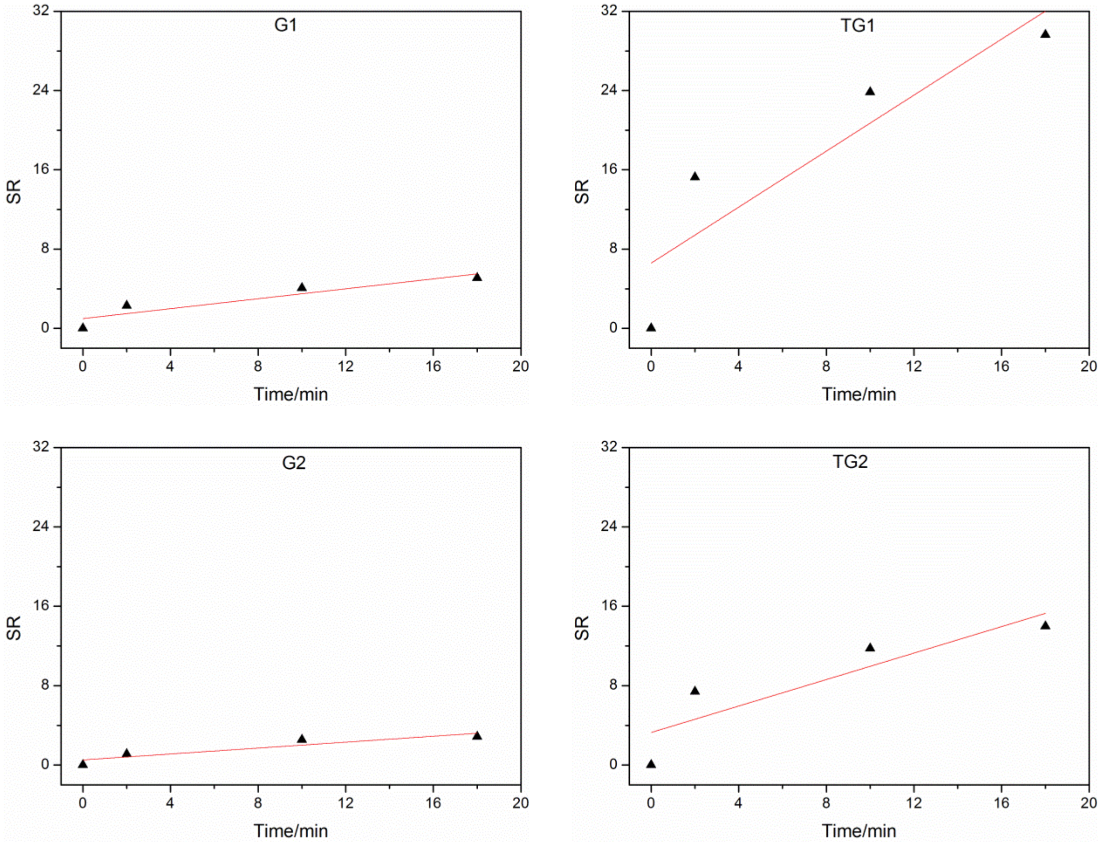


Fig. S12 Chemical wave and mechanical peristalsis in TG2.

Fig. S13 The analysis of the mechanical oscillation for TG2.


G1
G2
G3
TG1
TG2
TG3
SR
Time/min


G1
TG1
G2
TG2
SR
Time/min

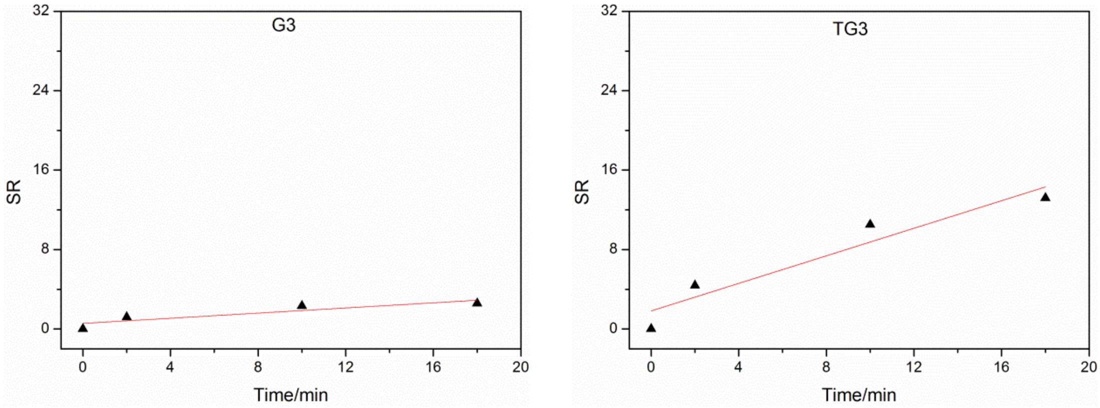


Fig. S14 Linear fitting curves of the marked position of Fig. 1c.

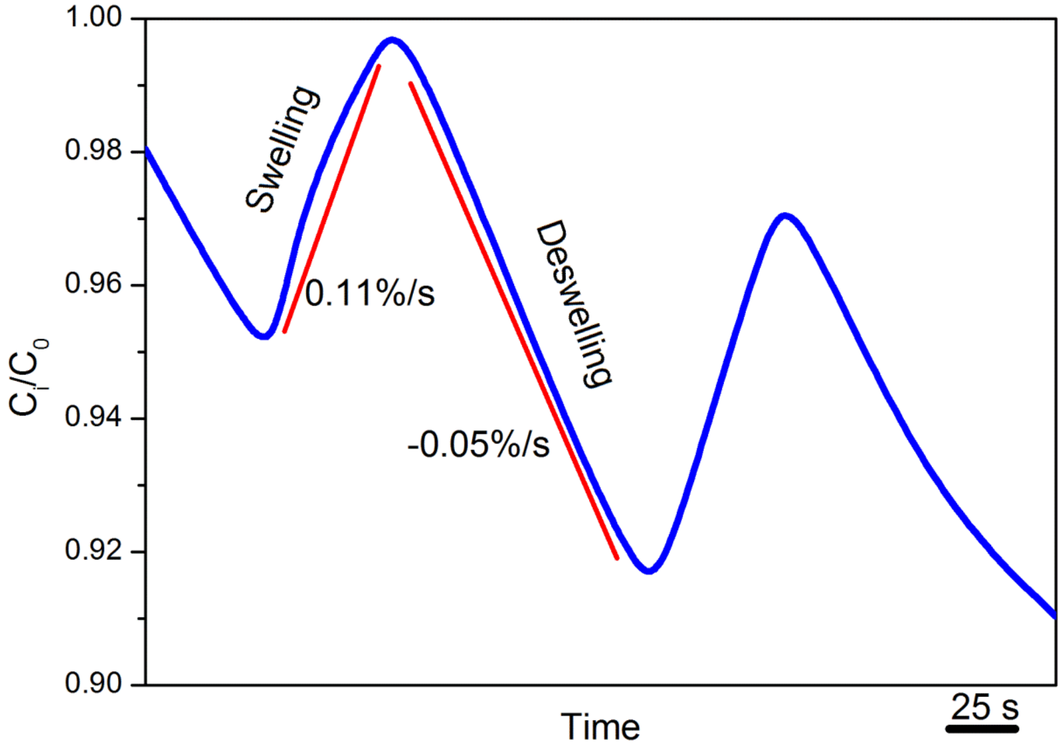


Fig. S15 The swelling and deswelling rates during the mechanical oscillation of TG2.

Table S2 Performances of the topological AGs

Structure	Performances	Ref.
"Polyrotaxane-interlocked" Structure	The amplitude is more than 8% as calculated from the circumference variation. The swelling/deswelling is on a scale of 20~40 um.	Present work
Microphase-separated structure	Swelling-deswelling amplitude of more than 10% of the gel thickness.	Ref5
	Gel cube is oscillating between 100 and 220 micrometers.	Ref6
Hierarchical structure	The swelling/deswelling is on a scale form 0.8~0.95 (L/L_0).	Ref7
Comb-type BZ-gel	The BZ-gel oscillates between	Ref4

	390 and 420 micrometers.	

Video TG-a and TG-b: Chemical waves and peristalsis in TG2.

Speed up: 100 X.

$[NaBrO_3]$=0.08 mol l^{-1}, [Malonic acid]=0.06 mol l^{-1}, $[HNO_3]$ = 0.9 mol l^{-1}, T=20 ℃.

Video TG-c: Mechanical oscillation of TG2.

Speed up: 100 X.

$[NaBrO_3]$=0.08 mol l^{-1}, [Malonic acid]=0.06 mol l^{-1}, $[HNO_3]$ = 0.9 mol l^{-1}, T=20 ℃.

Video TG-d: Mechanical oscillation of TG2.

Speed up: 100 X.

$[NaBrO_3]$=0.08 mol l^{-1}, [Malonic acid]=0.06 mol l^{-1}, $[HNO_3]$ = 0.9 mol l^{-1}, T=22 ℃.

Video G-a: Chemical waves in G2.

Speed up: 100 X.

$[NaBrO_3]$=0.08 mol l^{-1}, [Malonic acid]=0.06 mol l^{-1}, $[HNO_3]$ = 0.9 mol l^{-1}, T=19 ℃.

Video G-b: Mechanical oscillation of G2.

Speed up: 100 X.

$[NaBrO_3]$=0.08 mol l^{-1}, [Malonic acid]=0.06 mol l^{-1}, $[HNO_3]$ = 0.9 mol l^{-1}, *T*=19 ℃.

References

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