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for

Dynamic covalent bonding-triggered supramolecular gelation derived from tetrahydroxy-bisurea derivatives

Suansuan Wang, Kaiqiang Liu, Sheng Gao, Jinqiang Wang, Ravi Kumar Marella, and Yu Fang**

Key Laboratory of Applied Surface and Colloid Chemistry (Ministry of Education) School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an 710119, P. R. China. E-mail: kaiqiangliu@snnu.edu.cn, yfang@snnu.edu.cn.

Characterization of Compounds a-e

^{1}H NMR spectra were measured on Bruker AV 600 NMR spectrometers in DMSO-d_6 with tetramethylsilane (TMS) as an internal standard. Pressed KBr disks for the powder samples were used for the transmission infrared (FTIR) spectroscopy measurements, and their FTIR spectra were obtained with a Bio-Rad FTIR spectrometer. Mass spectrometry measurements were performed on an AXIMA-CFR in MALDI-TOF mode by using α-cyano-4-hydroxycinnamic acid (CCA) as the matrixes. Structural characterization data for all the resulting compounds are shown as follows:

Compound a: ^{1}H NMR (600 MHz, DMSO-d_6, TMS), δ = 2.17-2.28 (6H, s, 2-CH_3 (Ph)), δ = 3.40-3.46; 3.49-3.55 (8H, m, 4-CH_2-), δ = 3.59-3.66 (2H, m, 2-CH-), δ = 4.72-4.76 (4H, t, 4-OH), δ = 6.59-6.66 (2H, d, 2-NH-), δ = 7.32-7.36 (2H, d, 2-Ph), δ = 7.37-7.41 (2H, s, 2-Ph), δ = 7.83-7.88 (2H, s, 2-NH-), δ = 7.91-7.95 (2H, d, 2-Ph). FTIR (KBr): υ = 3312 cm^{-1} (O-H, stretch), υ = 3041 cm^{-1} (C-H, stretch, perylene core), υ = 2970 cm^{-1} (N-H, stretch), υ = 2883 cm^{-1} (C-H, stretch), υ = 1639 cm^{-1} (C=O, stretch), υ = 1593 cm^{-1} (C=C, stretch, perylene core).

Compound b: ^{1}H NMR (600 MHz, DMSO-d_6, TMS), δ = 3.37-3.42; 3.45-3.50 (8H, m, 4-CH_2-), δ = 3.55-3.61 (2H, m, 2-CH-), δ = 3.72-3.75 (2H, s, -CH-), δ = 4.69-4.73 (4H, t, 4-OH), δ = 5.79-6.01 (2H, d, 2-NH-), δ = 7.00-7.06 (4H, d, 2-Ph), δ = 7.23-7.29 (4H, s, 2-Ph), δ = 8.50-8.54 (4H, d, 2-NH-). FTIR (KBr): υ = 3380 cm^{-1} (O-H, stretch), υ = 3290 cm^{-1} (N-H, stretch), υ = 3100, 3031 cm^{-1} (C-H, stretch, perylene core), υ = 2876 cm^{-1} (C-H, stretch), υ = 1630 cm^{-1} (C=O, stretch), υ = 1572 cm^{-1} (C=C, stretch, perylene core).

Compound c: ^{1}H NMR (600 MHz, DMSO-d_6, TMS), δ = 3.37-3.42; 3.46-3.51 (8H, m, 4-CH_2-), δ = 3.55-3.61 (2H, m, 2-CH-), δ = 4.68-4.73 (4H, t, 4-OH), δ = 5.92-5.96 (2H, d, 2-NH-), δ = 7.18-

7.22 (4H, s, 2-Ph), δ = 8.37-8.43 (2H, s, 2-NH-). FTIR (KBr): υ = 3312 cm^{-1} (O-H, stretch), υ = 3041 cm^{-1} (C-H, stretch, perylene core), υ = 2974 cm^{-1} (N-H, stretch), υ = 2880 cm^{-1} (C-H, stretch), υ = 1639 cm^{-1} (C=O, stretch), υ = 1579 cm^{-1} (C=C, stretch, perylene core).

Compound d: ^{1}H NMR (600 MHz, DMSO-d_6, TMS), δ = 1.16-1.28 (4H, m, 4-CH$_2$-), δ = 1.30-1.40 (4H, m, 4-CH$_2$-), δ = 2.90-3.00 (4H, m, 4-CH$_2$-), δ = 3.35-3.44 (8H, m, 4-CH$_2$-), δ = 3.46-3.53 (2H, m, 2-CH-), δ = 4.57-4.69 (4H, t, 4-OH), δ = 5.60-5.71 (2H, d, 2-NH-), δ = 5.96-6.05 (2H, t, 2-NH-). FTIR (KBr): υ = 3334 cm^{-1} (O-H, stretch), υ = 2933 cm^{-1} (N-H, stretch), υ = 2864 cm^{-1} (C-H, stretch), υ = 1627cm^{-1} (C=O, stretch).

Compound e: ^{1}H NMR (600 MHz, DMSO-d_6, TMS), δ = 3.34-3.49 (8H, m, 4-CH$_2$-), δ = 3.51-3.58 (2H, m, 2-CH-), δ = 4.12-4.25 (4H, d, 2CH$_2$-), δ = 4.58-4.70 (4H, t, 4-OH), δ = 5.73-5.88 (2H, d, 2-NH-), δ = 6.42-6.58 (2H, t, 2-NH-), δ = 7.06-7.30 (4H, m, 4-Ph). FTIR (KBr): υ = 3321 cm^{-1} (O-H, stretch), υ = 3028 cm^{-1} (C-H, stretch, perylene core), υ = 2972 cm^{-1} (N-H, stretch), υ = 2885 cm^{-1} (C-H, stretch), υ = 1629 cm^{-1} (C=O, stretch), υ = 1577 cm^{-1} (C=C, stretch, perylene core).

Table S1 Gelation behaviours of compounds **a-e** at the concentration of 2.0% (w/v)

Solvents	**a**		**b**		**c**		**d**		**e**	
	S*	H-C	S*	H-C	S*	H-C	S*	H-C	S*	H-C
Water	TuS	TuS	TuS	TuS	TuS	TuS	TuS	TuS	TuS	TuS
Methanol	TuS	TuS	TuS	TuS	TuS	TuS	TuS	TuS	TuS	TuS
Ethanol	TuS	TuS	TuS	TuS	TuS	TuS	TuS	TuS	TuS	TuS
Isopropanol	TuS	TuS	TuS	TuS	TuS	TuS	TuS	TuS	TuS	TuS
Acetone	TuS	TuS	TuS	TuS	TuS	TuS	TuS	TuS	TuS	TuS
Acetonitrile	TuS	TuS	TuS	TuS	TuS	TuS	TuS	TuS	TuS	TuS
THF	TuS	TuS	TuS	TuS	TuS	TuS	TuS	TuS	TuS	TuS
Benzene	TuS	TuS	TuS	TuS	TuS	TuS	TuS	TuS	TuS	TuS
Toluene	TuS	TuS	TuS	TuS	TuS	TuS	TuS	TuS	TuS	TuS
m-Xylene	TuS	TuS	TuS	TuS	TuS	TuS	TuS	TuS	TuS	TuS
Hexane	TuS	TuS	TuS	TuS	TuS	TuS	TuS	TuS	TuS	TuS
Cyclohexane	TuS	TuS	VS	TuS	TuS	TuS	TuS	TuS	TuS	TuS
CH_2Cl_2	TuS	TuS	TuS	TuS	TuS	TuS	TuS	TuS	TuS	TuS
Chloroform	TuS	TuS	TuS	TuS	TuS	TuS	TuS	TuS	TuS	TuS
Ethyl Acetate	TuS	TuS	TuS	TuS	TuS	TuS	TuS	TuS	TuS	TuS
DMSO	S	S	S	S	S	S	S	S	S	S
DMF	TuS	TuS	TuS	P	TuS	TuS	TuS	TuS	TuS	TuS
TBMA	TuS	TuS	TuS	TuS	TuS	TuS	TuS	TuS	TuS	TuS
MTMS	TuS	TuS	TuS	TuS	TuS	TuS	TuS	TuS	TuS	TuS
MTES	TuS	TuS	TuS	TuS	TuS	TuS	TuS	TuS	TuS	TuS
PTMS	TuS	TuS	TuS	TuS	TuS	TuS	TuS	TuS	TuS	TuS
TEPS	TuS	TuS	TuS	TuS	TuS	TuS	TuS	TuS	TuS	TuS

Notes: S* = Sonication; H-C = Heating and Cooling Treatments; TuS = Turbid Solution; VS = Viscous Solution; S = Clear Solution; P = Precipitate;

TBMA = Tertiary-butyl methacrylate; MTMS = Methyltrimethoxysilane;

MTES = Methyltriethoxysilane; PTMS = Propyltrimethoxysilane; TEPS = Triethoxyphenylsilane.

Table S2 Gelation behaviours of compounds **a-e** at the concentration of 2.0% (w/v) in different volume ratio of DMSO and water

Compounds	**V_{DMSO} : V_{water}**						
	3 : 7	**4 : 6**	**5 : 5**	**6 : 4**	**7 : 3**	**8 : 2**	**9 : 1**
a	TuS	TuS	TuS	TuS	TuS	VS	VS
b	VS	VS	VS	P	S	S	S
c	TuS	TuS	TuS	TuS	P	S	S
d	VS	VS	VS	VS	P	P	S
e	TuS	TuS	TuS	TuS	VS	VS	S

Notes: TuS = Turbid Solution; VS = Viscous Solution; S = Clear Solution; P = Precipitate.

Table S3 Gelation behaviours of compounds **a-e** at the concentration of 4.0% (w/v) in different volume ratio of DMSO and water

Compounds	**V_{DMSO} : V_{water}**						
	3 : 7	**4 : 6**	**5 : 5**	**6 : 4**	**7 : 3**	**8 : 2**	**9 : 1**
a	TuS	TuS	TuS	TuS	TuS	TuS	TuS
b	VS	VS	VS	P	P	P	S
c	TuS	TuS	TuS	TuS	TuS	P	S
d	TuS	TuS	TuS	TuS	P	P	P
e	TuS	TuS	TuS	TuS	TuS	P	S

Notes: TuS = Turbid Solution; VS = Viscous Solution; S = Clear Solution; P = Precipiate.

Table S4 Gelation behaviours of compounds **a-e** at the concentration of 10.0% (w/v) in different volume ratio of DMSO and water

Compounds	$V_{DMSO} : V_{water}$						
	3 : 7	**4 : 6**	**5 : 5**	**6 : 4**	**7 : 3**	**8 : 2**	**9 : 1**
a	TuS	TuS	TuS	TuS	TuS	TuS	TuS
b	TuS	TuS	TuS	TuS	TuS	P	S
c	TuS	TuS	TuS	TuS	TuS	TuS	TuS
d	TuS	TuS	TuS	TuS	TuS	P	P
e	TuS	TuS	TuS	TuS	TuS	P	P

Notes: TuS = Turbid Solution; S = Clear Solution; P = Precipiate.

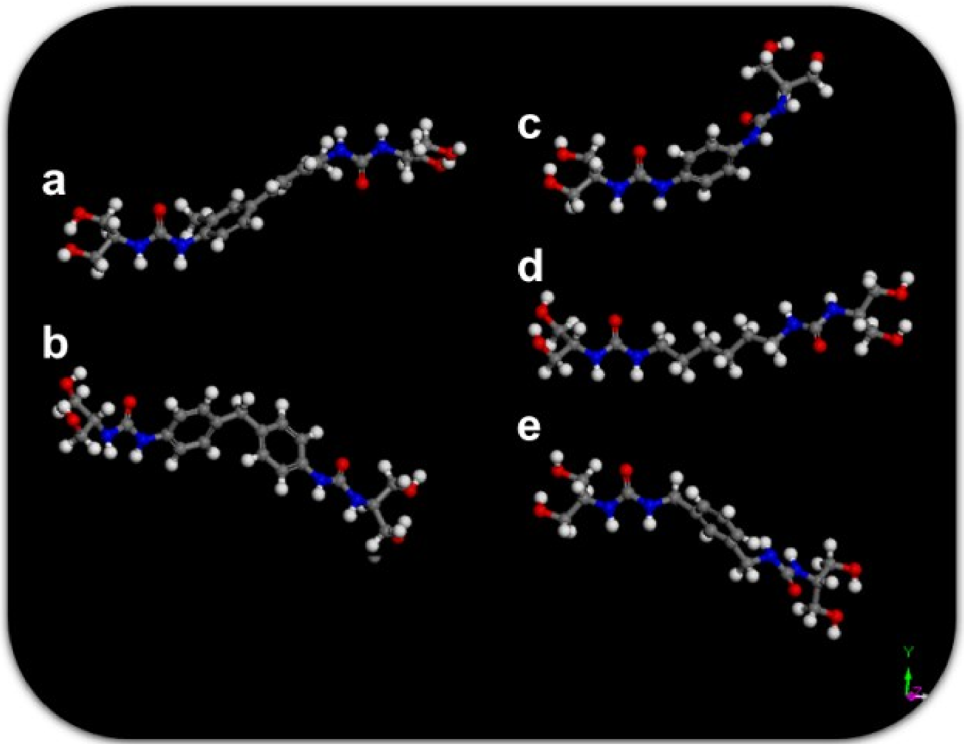

Fig. S1 Molecular structures of compounds **a**-**e** at energy-minimized state.

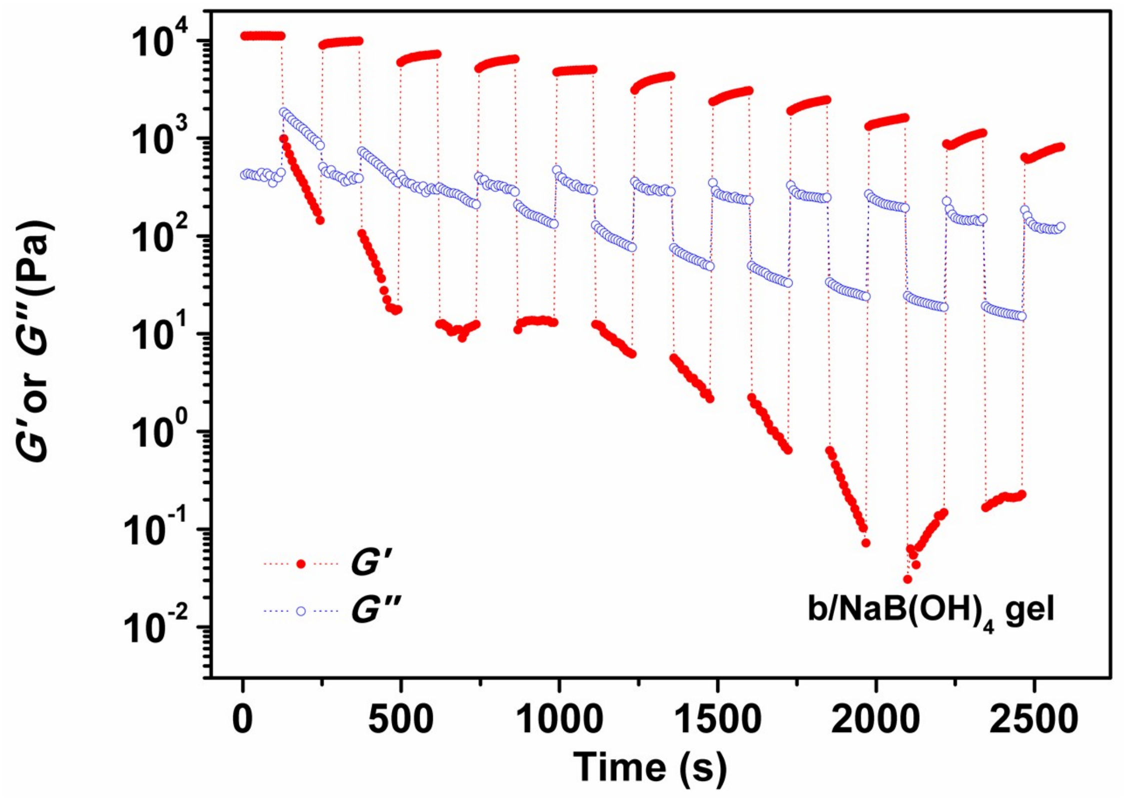

Fig. S2 Evolution of *G*′ and *G*″ as a function of time sweep for 10 cycles with the deformation and the recovery process. The sample is **b**/NaB(OH)$_4$ gel at the 4.0% (w/v) of compound **b** in DMSO : H_2O (9 : 1 v/v).

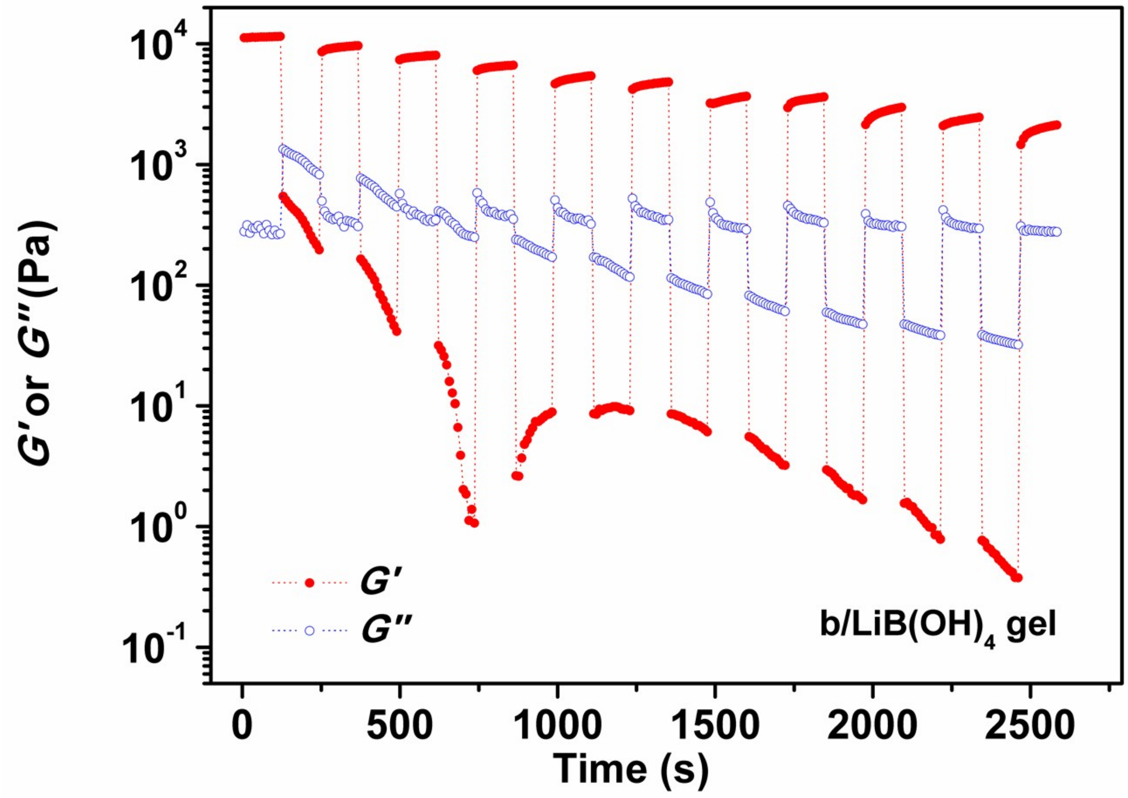

Fig. S3 Evolution of *G*′ and *G*″ as a function of time sweep for 10 cycles with the deformation and the recovery process. The sample is **b**/$LiB(OH)_4$ gel at the 4.0% (w/v) of compound **b** in DMSO : H_2O (9 : 1 v/v).

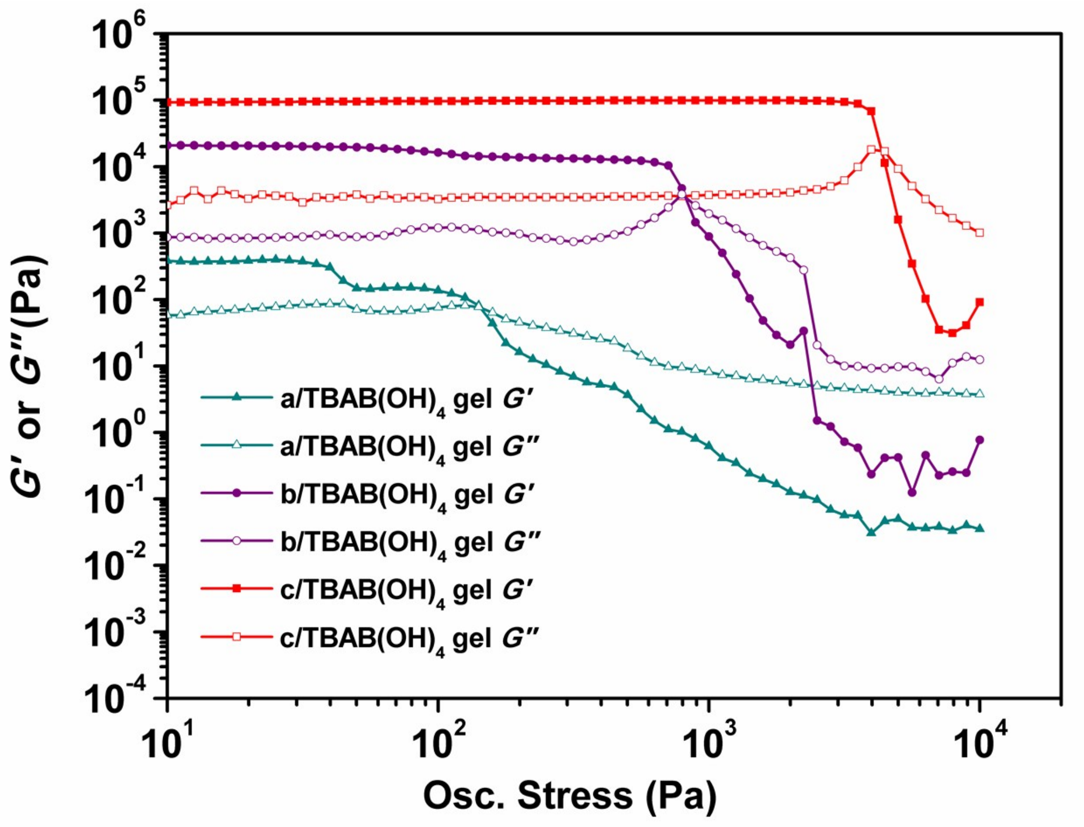

Fig. S4 Evolution of *G*′ and *G*″ as a function of the applied shear stress. The samples are **a**/TBAB(OH)$_4$ gel, **b**/TBAB(OH)$_4$ gel and **c**/TBAB(OH)$_4$ gel at 4.0% (w/v) in DMSO : H_2O (9 : 1 v/v).

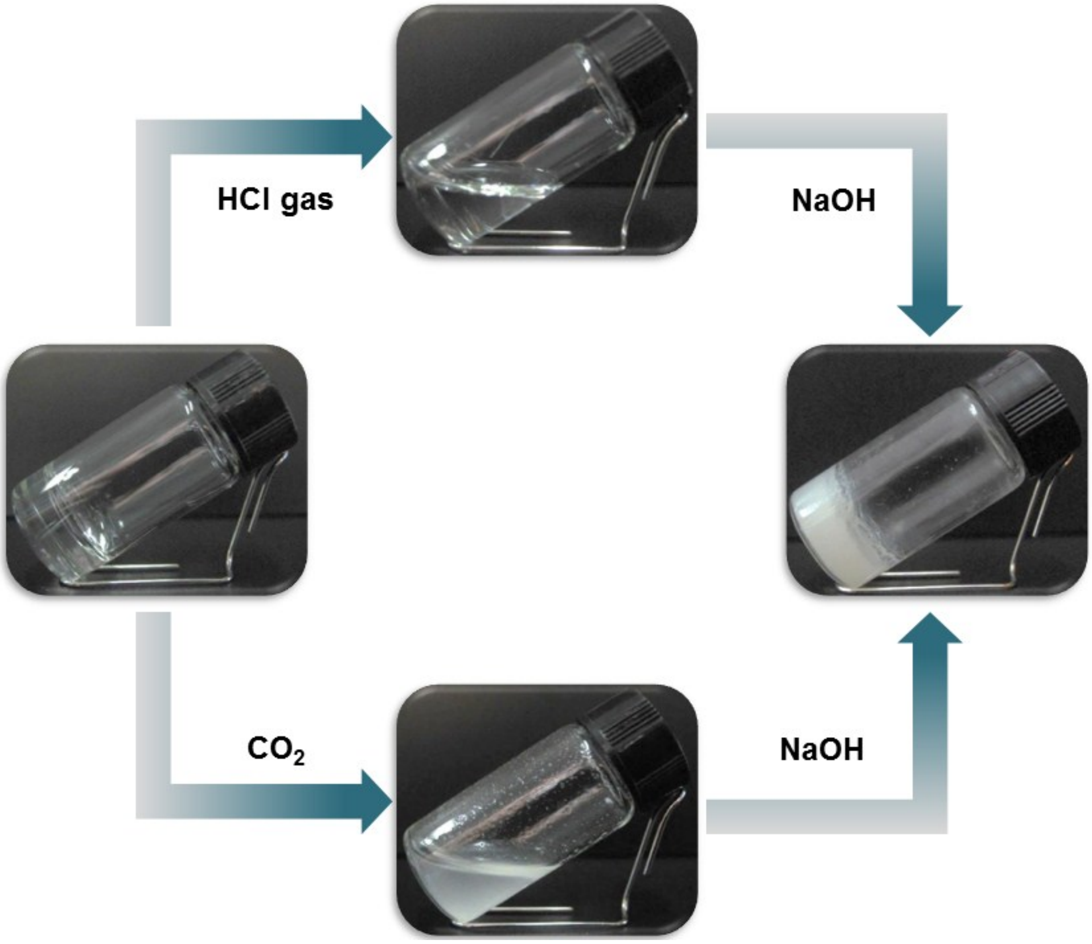

Fig. S5 The sol-gel phase transitions of the **b**/$NaB(OH)_4$ gel at the 4.0% (w/v) of compound **b** in DMSO : H_2O (9 : 1 v/v) at room temperature. The gel was changed rapidly into a sol when HCl gas or CO_2 was bubbled into the vial and the gel returned to its initial solid-like state when appropriate amount of NaOH was added.

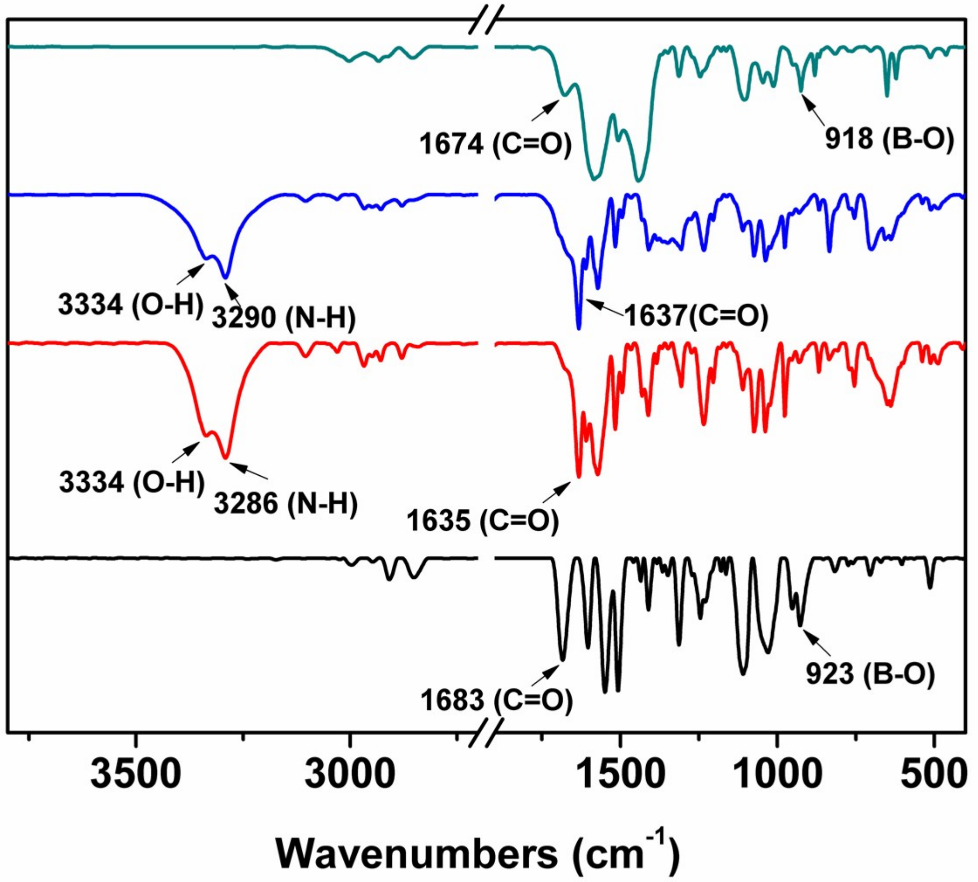

Fig. S6 FTIR spectra of (a) the freeze-dried **b**/NaB(OH)$_4$ gel at the 4.0% (w/v) of compound **b** in DMSO : H_2O (9 : 1 v/v), (b) **b**/NaB(OH)$_4$ gel destroyed by HCl gas, (c) **b**/NaB(OH)$_4$ gel destroyed by CO_2, (d) addition of appropriate amount of NaOH.

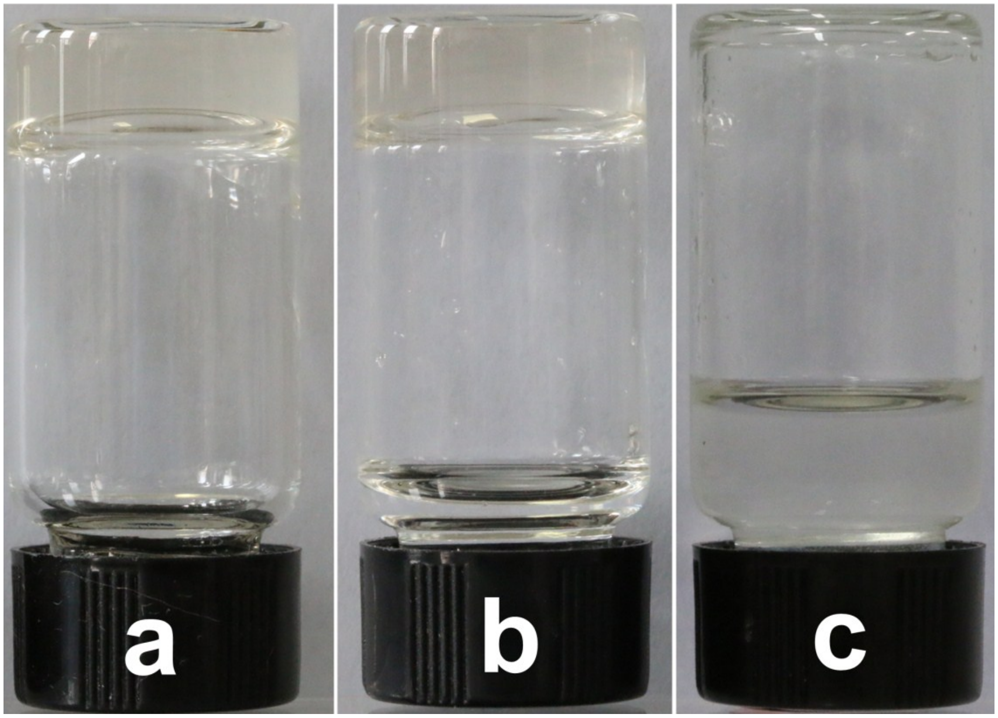

Fig. S7 Experiments to disrupt the urea hydrogen bonding in the gel state: (a) **b**/NaB(OH)$_4$ gel, (b) 250 μL of ethanol solution was injected into the vial and kept above the gel phase, (c) 250 μL of ethanol solution containing 1 equiv of tetrabutylammonium acetate was injected into the vial and kept above the gel phase. The photo was recorded in the concentration of compound **b** with 4.0% (w/v) in DMSO : H_2O (9 : 1 v/v). As a result, the presence of ethanol doesn't result in gel dissolution, but the gel turned into clear solution after addition of ethanol solution containing 1 equiv of tetrabutylammonium acetate. It shows that tetrabutylammonium acetate could disrupt urea-urea hydrogen bonding in the gel as proved NMR titration in Fig. 8.

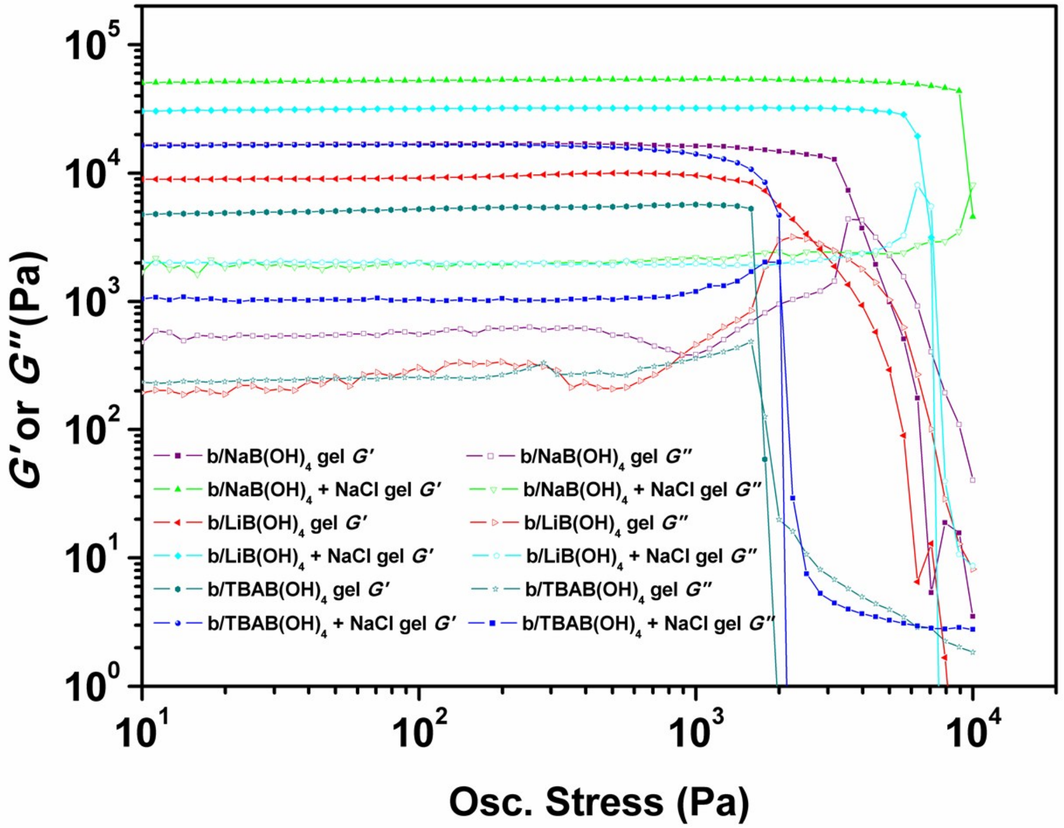

Fig. S8 Evolution of *G*′ and *G*″ as a function of the applied shear stress. The samples are **b**/XB(OH)$_4$ gel without NaCl and **b**/XB(OH)$_4$ gel upon addition of 1 equivalent of NaCl at 4.0% (w/v) of compound **b** in DMSO : H$_2$O (9 : 1 v/v). X = Na, Li, and TBA. The values of *G*′, *G*″ and yield stress (*Y*) are shown in Fig. S9.

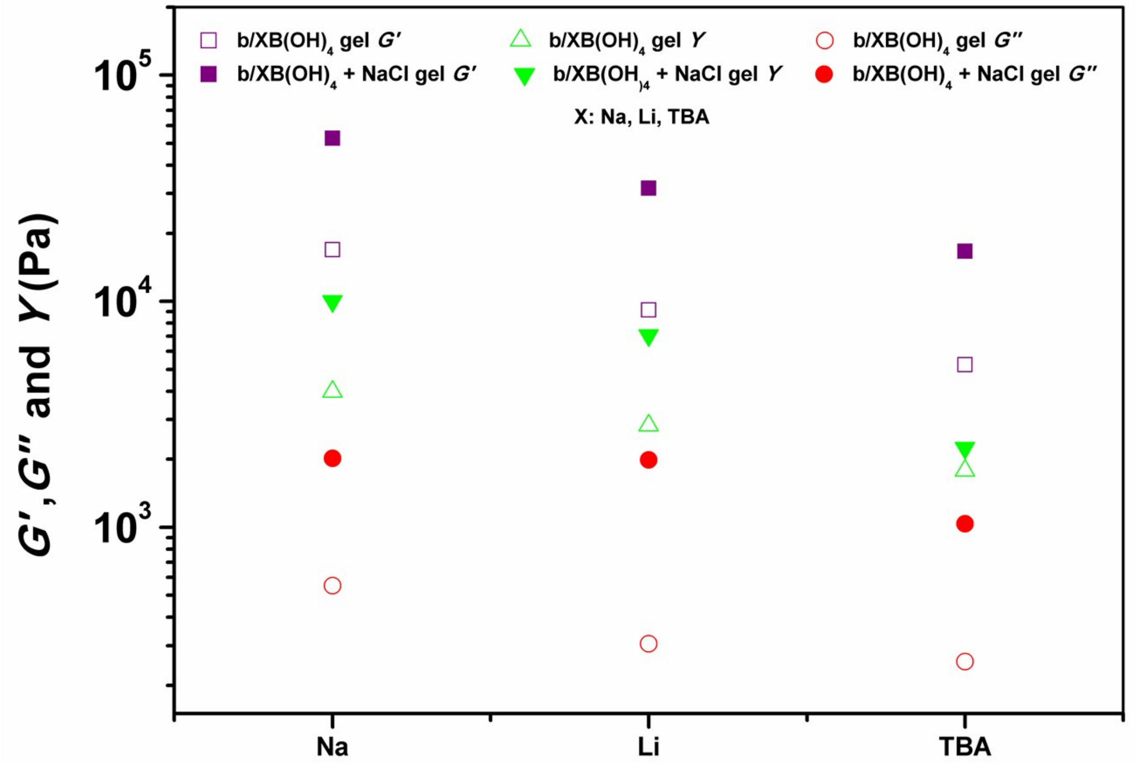

Fig. S9 The values of *G*′, *G*″ and yield stress (*Y*) of the the gels derived from compound **b** (4.0% w/v) with three different boric salts ($NaB(OH)_4$、$LiB(OH)_4$、$TBAB(OH)_4$) in DMSO : H_2O (9 : 1 v/v). As shown, all of rheological values were increased upon addition of 1 equivalent NaCl.

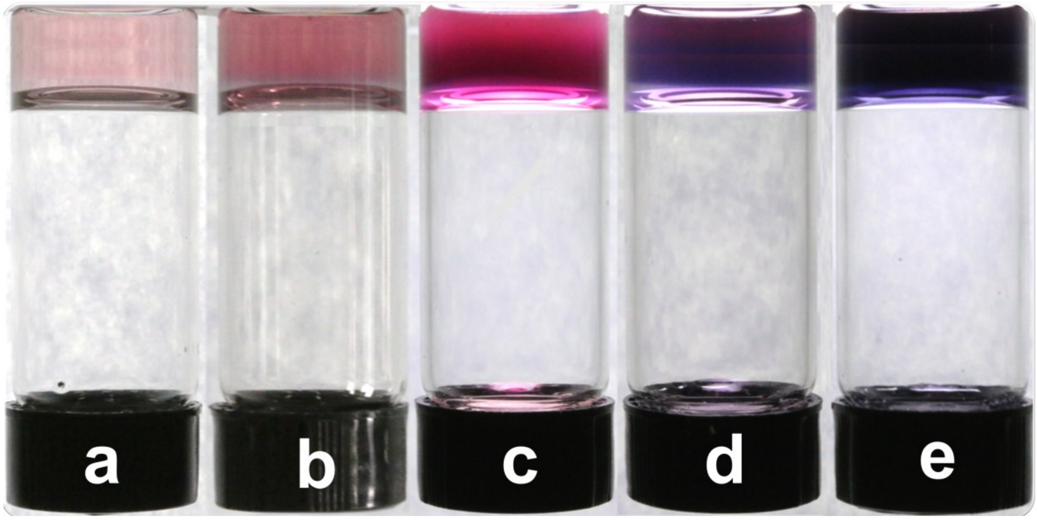

Fig. S10 Optical image of the gold nanoparticle/gel hybrids with the increase concentration of $HAuCl_4$: (a) 0.25 mM, (b) 0.50 mM, (c) 1.0 mM, (d) 1.5 mM, (e) 2.0 mM at the 4.0% (w/v) of compound **b** in DMSO : H_2O (9 : 1 v/v).

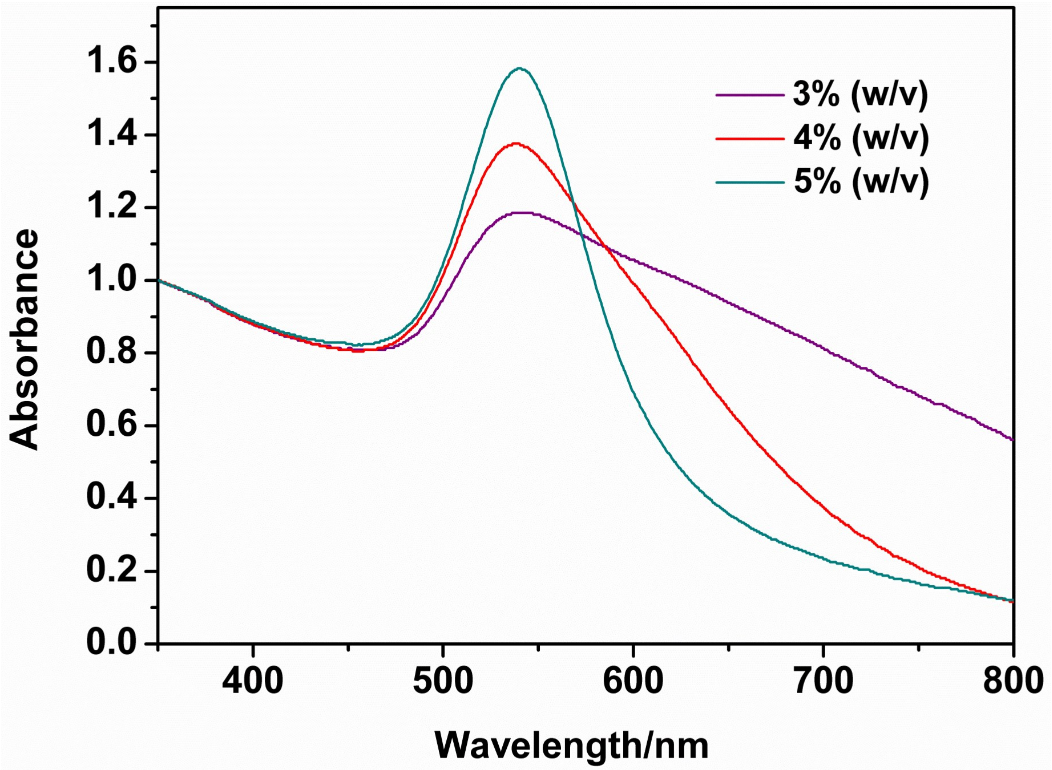

Fig. S11 UV-vis spectra of gold nanoparticle/gel hybrid solutions at various concentration of compound **b** (3.0%, 4.0%, 5.0%, w/v) in DMSO : H_2O (9 : 1 v/v) with the certain amount of $HAuCl_4$ (1.5 mM).

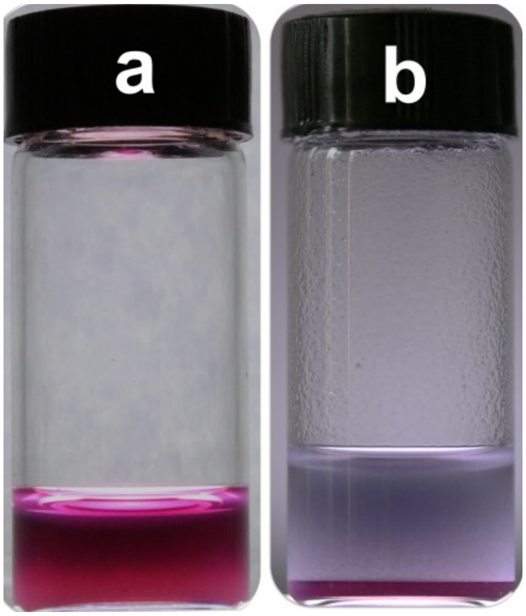

Fig. S12 Optical images of (a) the gold nanoparticle/gel, (b) 250 μL of ethanol solution containing 1 equiv of tetrabutylammonium acetate was injected into the vial and kept above the gold nanoparticle/gel phase. The photo was recorded in the concentration of compound **b** at 5.0% (w/v) with the certain amount of $HAuCl_4$ (1.5 mM). The upper part of the gel b was destroyed firstly result in Au particles to meet closer and the colors of the system were changed distinctly from red wine to purple.

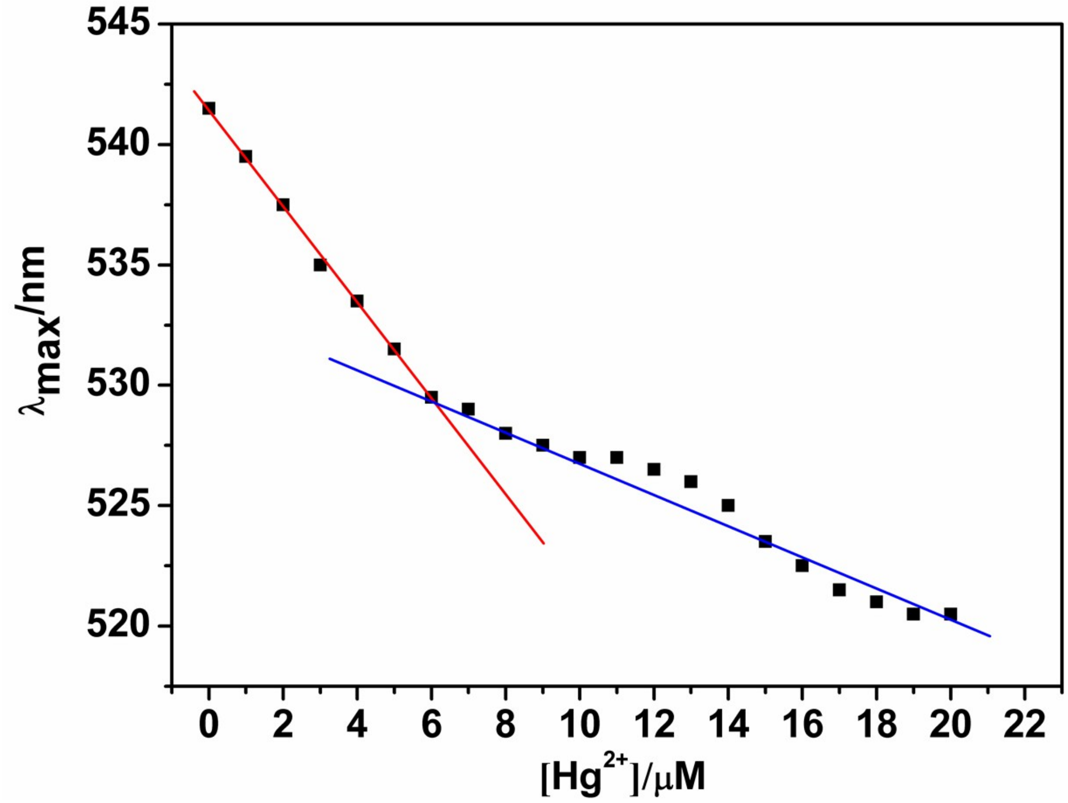

Fig. S13 Plot of absorption intensity maximum at λ_{LSPR} of for gelator-Au NPs composites against concentrations of Hg^{2+} ions.

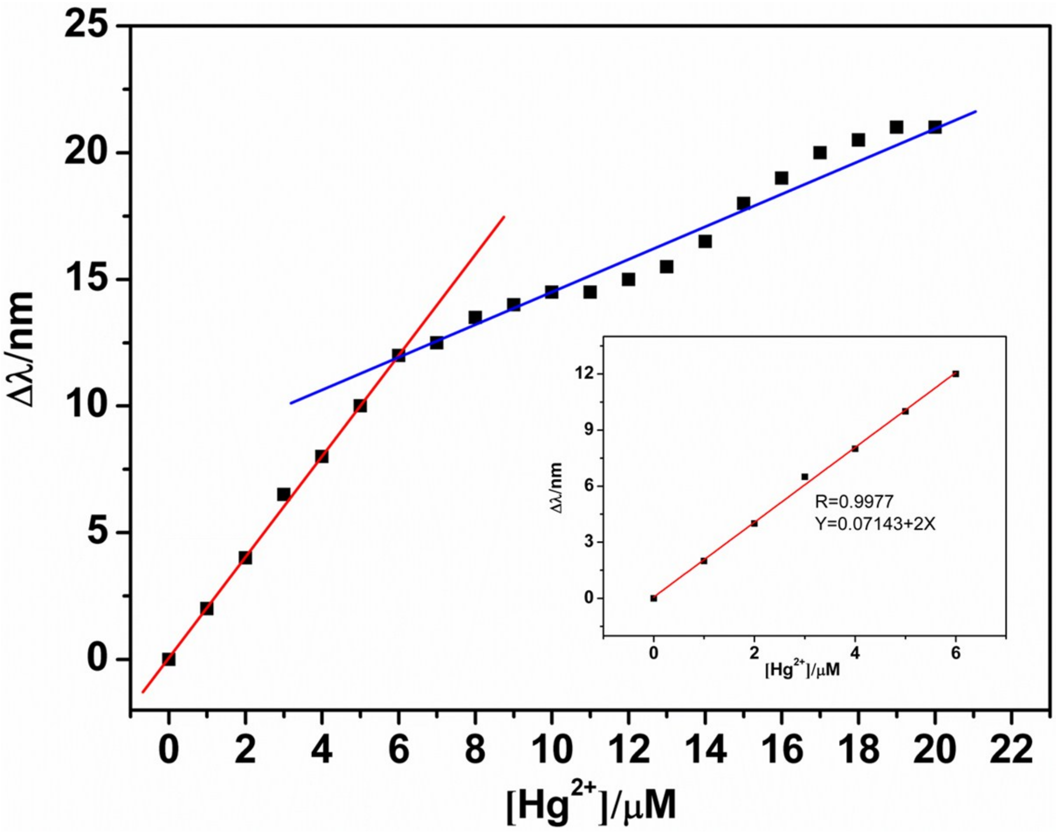

Fig. S14 Plot of shift in the LSPR band maximum ($\Delta\lambda_{LSPR}$) of gelator-Au NPs composites against concentrations of Hg^{2+} ions. The inset shows a plot of the wavelength shift versus the concentrations of Hg^{2+} (0-6 μM).

Table S5 Control experiments

Number	**Compound b** (mol/L)	**$B(OH)_3$** (mol/L)	**NaOH** (mol/L)	**$HAuCl_4$** (mMol/L)	**$N_2H_4 \cdot H_2O$ in 250 μL of ethanol solution** (uL)
1	0	0	0	1.5×10^{-3}	30
2	0	0	9.2×10^{-2}	1.5×10^{-3}	30
3	0	9.2×10^{-2}	9.2×10^{-2}	1.5×10^{-3}	30
4	0	9.2×10^{-2}	0	1.5×10^{-3}	30
5	9.2×10^{-2}	0	0	1.5×10^{-3}	30
6	9.2×10^{-2}	9.2×10^{-2}	0	1.5×10^{-3}	30
7	9.2×10^{-2}	0	9.2×10^{-2}	1.5×10^{-3}	30

Notes: All of the above experiments were carried out in DMSO : H_2O (9 : 1 v/v). **1-7** couldn't form gels because of the lack of components. Then 250 μL of ethanol solution containing 30 μL of hydrazine hydrate as the reducing agent was injected into the system of **1-7**. After the complete formation of Au NPs, 6 μM Hg^{2+} ions was added into the system of **1-7.** The experimental results are displayed in Fig. S15.

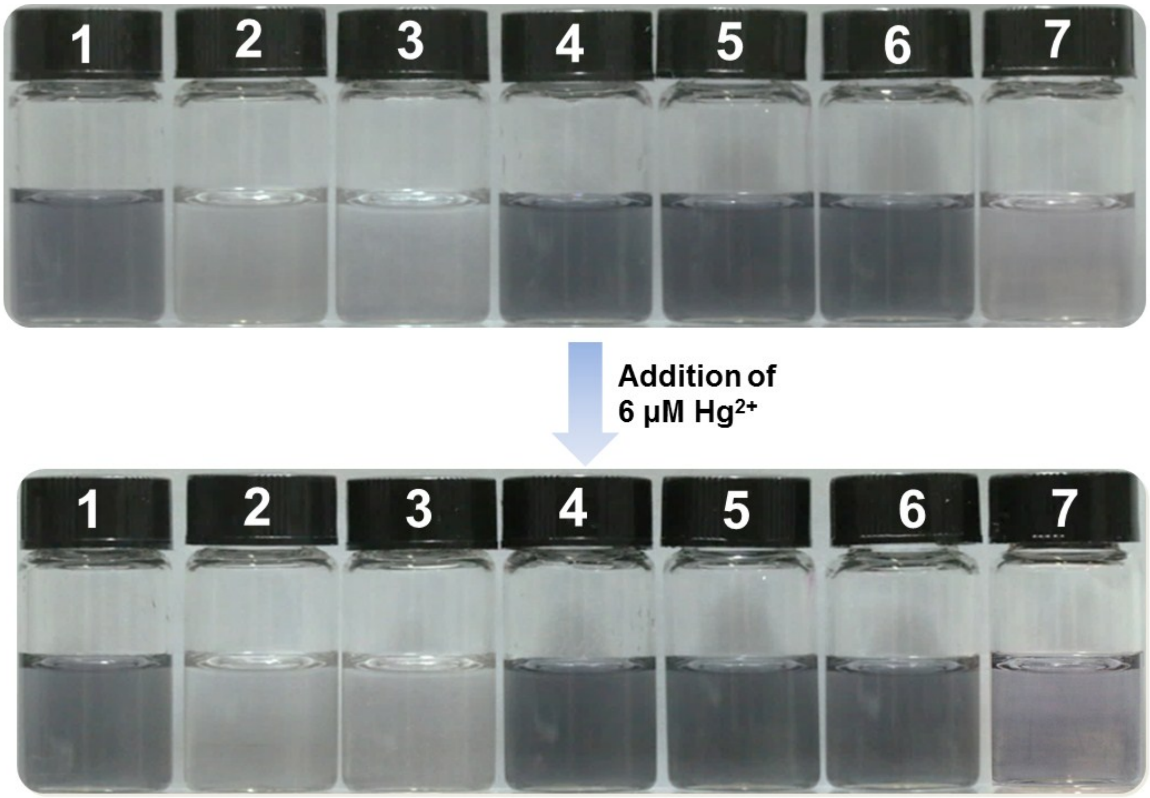

Fig. S15 Optical images of No.1- No.7 in **Table S5** before and after addition of 6 μM Hg^{2+} ions. There is no significant color changes was observed in the system of 1-7 upon addition of 6 μM Hg^{2+} ions which demonstrate that only the presence of the polymeric gelator derived from the urea compound and boric salts could be functioned as selective detection for Hg^{2+} ions.

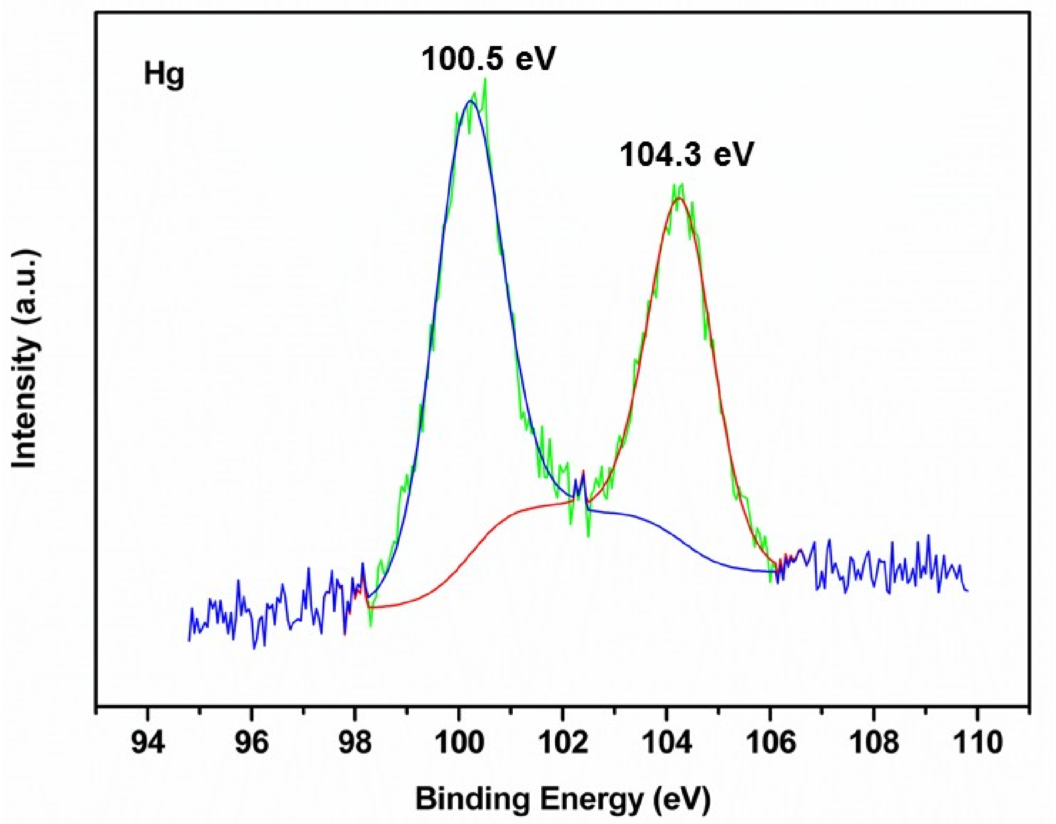

Fig. S16 XPS spectrum of the Hg 4f region (left peak: $4f_{7/2}$; right peak: $4f_{5/2}$) upon addition of Hg^{2+} in the Au-gel hybrid system.