An ATP/ATPase responsive supramolecular fluorescent hydrogel constructed *via* electrostatic interactions between poly(sodium *p*-styrenesulfonate) and a tetraphenylethene derivative

Hu Wang,[a] Xiaofan Ji,*[a] Yang Li,[b] Zhengtao Li,[a] Guping Tang,[b] and Feihe Huang*[a]

[a] *State Key Laboratory of Chemical Engineering, Center for Chemistry of High-Performance & Novel Materials, Department of Chemistry, Zhejiang University, Hangzhou 310027, P. R. China; Fax and Tel: +86-571-8795-3189; Email: xiaofanji@zju.edu.cn; fhuang@zju.edu.cn*

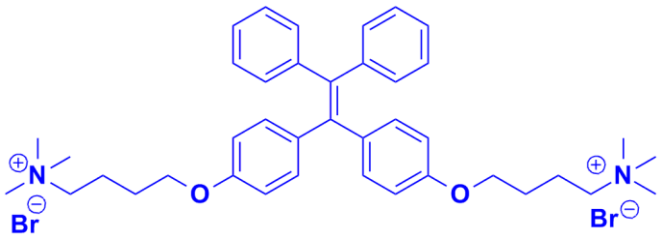
[b] *Department of Chemistry, Institute of Chemical Biology and Pharmaceutical Chemistry, Zhejiang University, Hangzhou 310027, P. R. China*

Supporting Information (11 pages)

1. Materials and methods

All reagents were commercially available and used as supplied without further purification. Compound **2** was prepared according to the published procedures.[S1] NMR spectra were recorded with a Bruker Avance DMX 500 spectrophotometer using the deuterated solvent as the lock and the residual solvent or TMS as the internal reference. The two-dimensional diffusion-ordered NMR spectra were recorded on a Bruker DRX 500 spectrometer. The fluorescence data were measured on an RF-5301 spectrofluorophotometer (Shimadzu Corporation). Rheological data were obtained using a Physica MCR302 rheometer (Anton Paar) with cone-plate geometry (diameter of 25 mm, 2 ° cone, truncation height of 0.3 mm). Oscillatory frequency sweep experiments were performed from 0.1 rad/s to 100 rad/s with a strain in the linear region at 25 ℃. Viscosity measurements were carried out with a Cannon-Ubbelohde semi-micro dilution viscometer at 25 ℃ in acetonitrile. Scanning electron microscopy investigations were carried out on a JEOL 6390LV instrument.

*2. ^{1}H NMR spectrum of **2***



The ^{1}H NMR spectrum of compound **2** is shown in Figure S1.

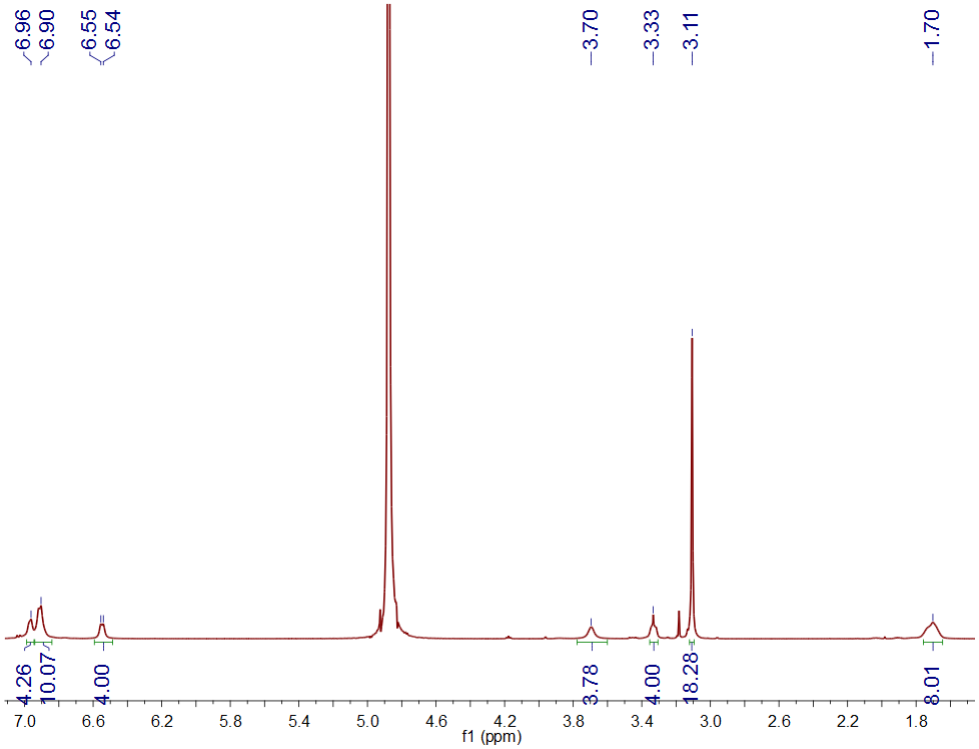


Figure S1. ^{1}H NMR spectrum (500 MHz, D_2O, 298 K) of **2**.

*3. Partial NOESY NMR spectrum of a mixture of **1** and **2***

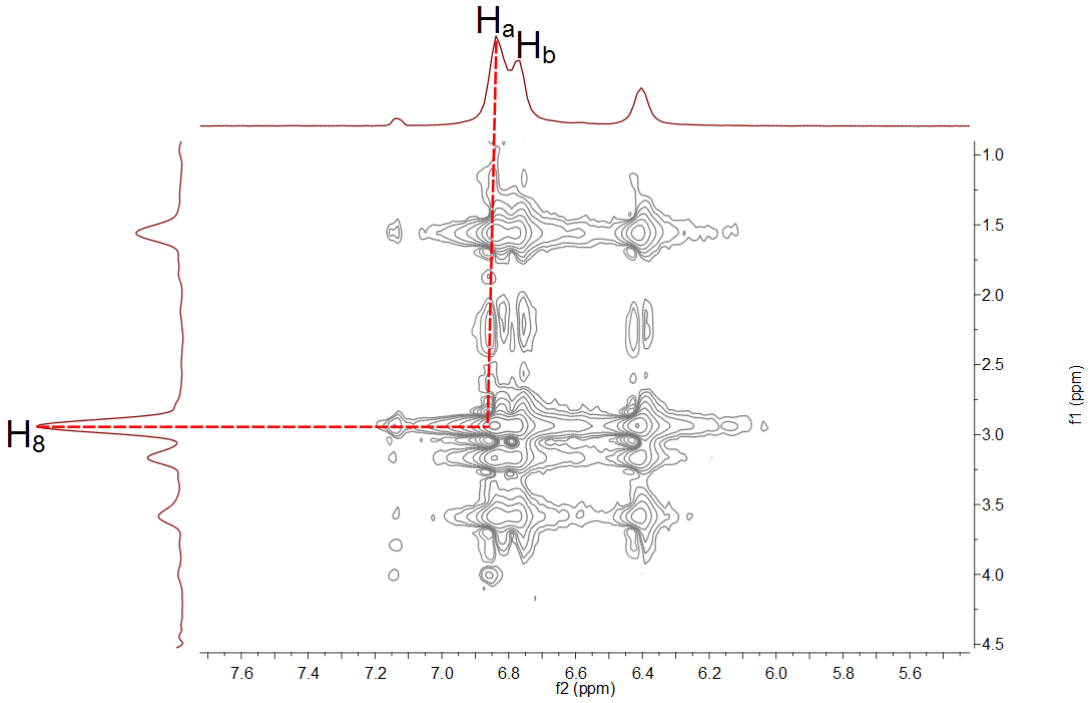


Figure S2. Partial NOESY NMR (500MHz, D_2O, 298 K) spectrum of a solution of 0.0290 mM **1** and 5.00 mM **2**.

*4. Rheological characterization of hydrogel **3** at different temperatures*

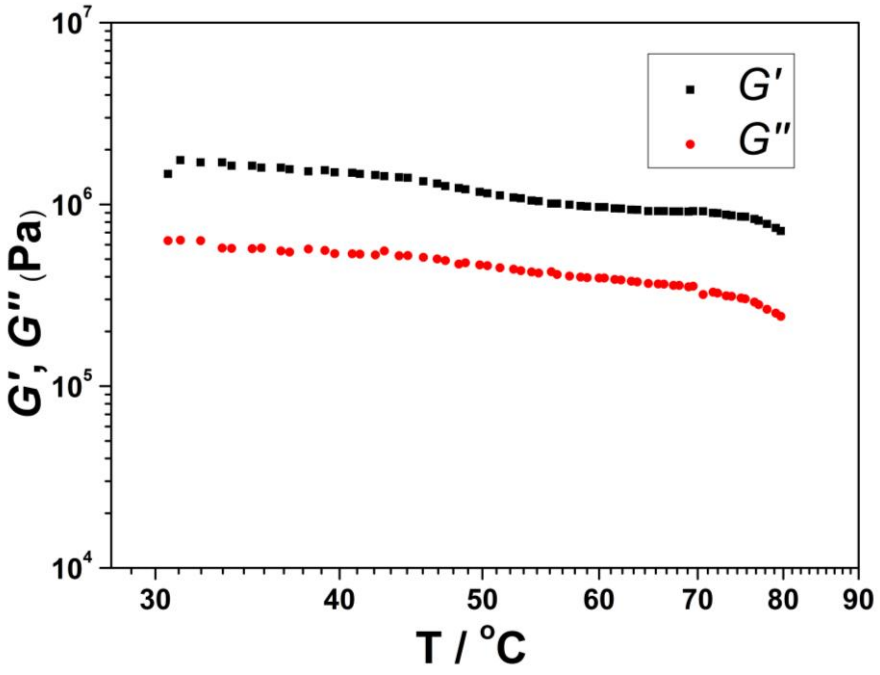


Figure S3. Rheological characterization of hydrogel **3** with the rise of temperature from 30 ℃ to 80 ℃.

*5. Specific viscosity of polymer **1**, compound **2**, and hydrogel **3***

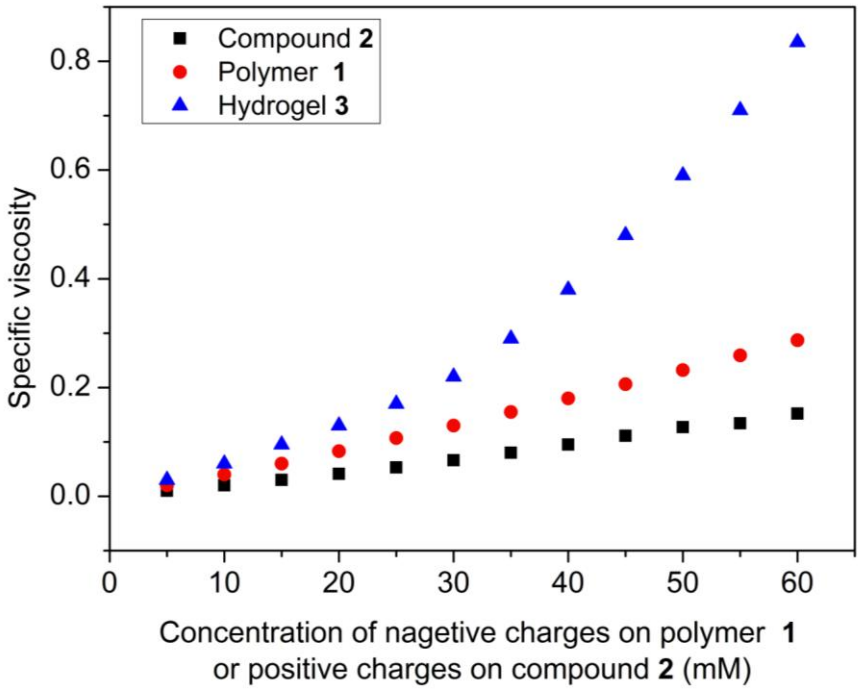
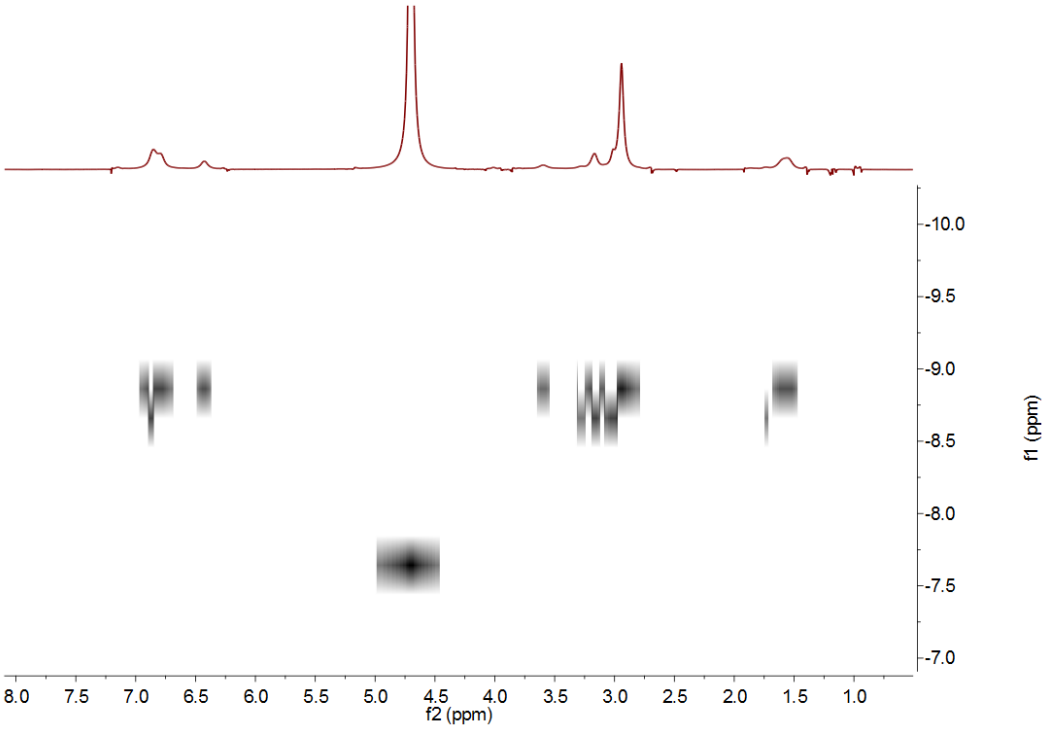
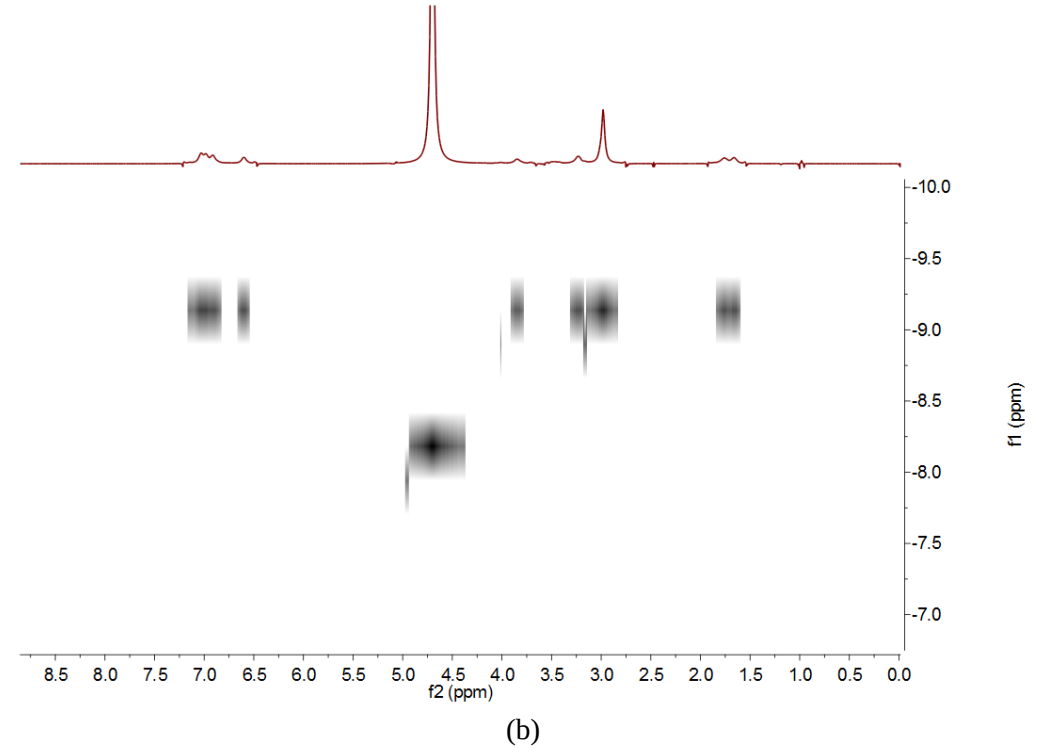


Figure S4. Specific viscosity (H_2O, 25 ℃) of polymer **1** (●), compound **2** (■), and hydrogel **3** (▲) versus the concentration of charges.

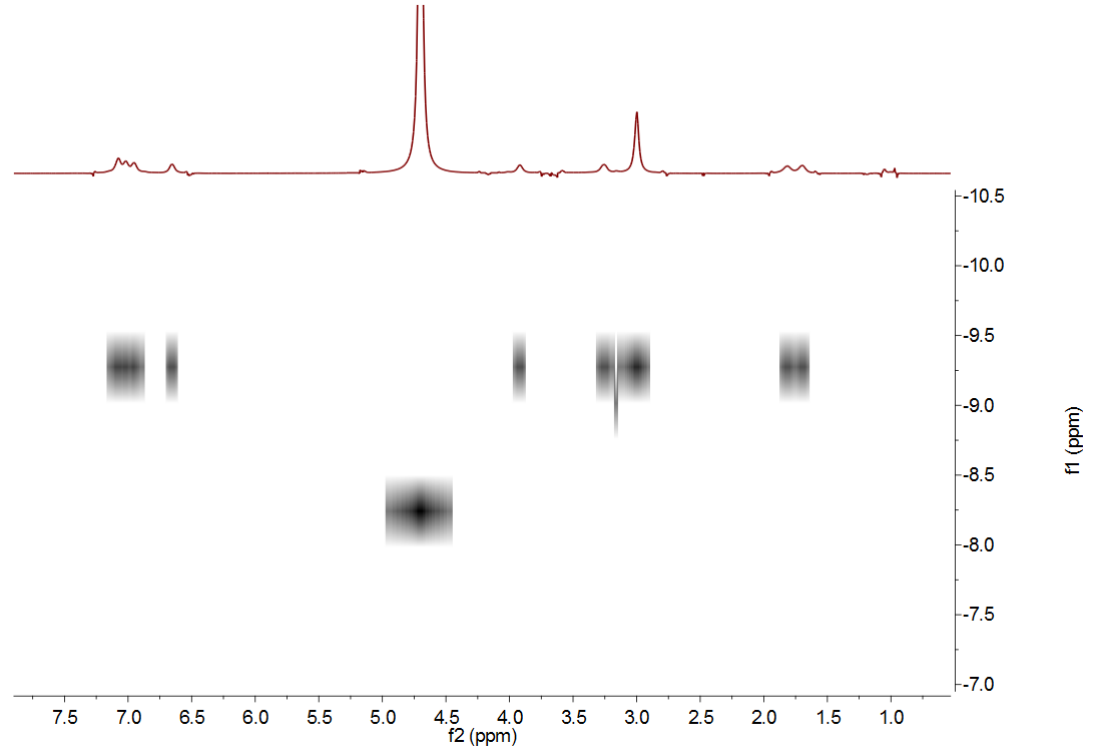
*6. Diffusion coefficient D (500 MHz, D_2O, 298 K) of mixture solutions of **1** with different concentrations of **2***



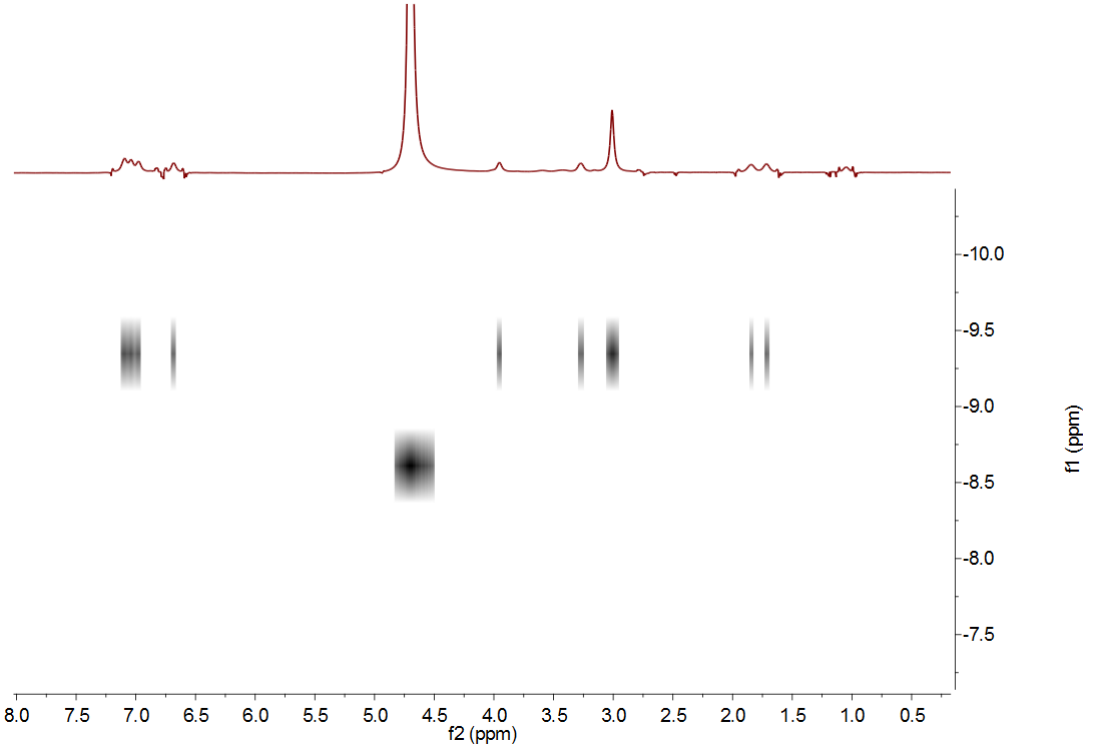
(a)



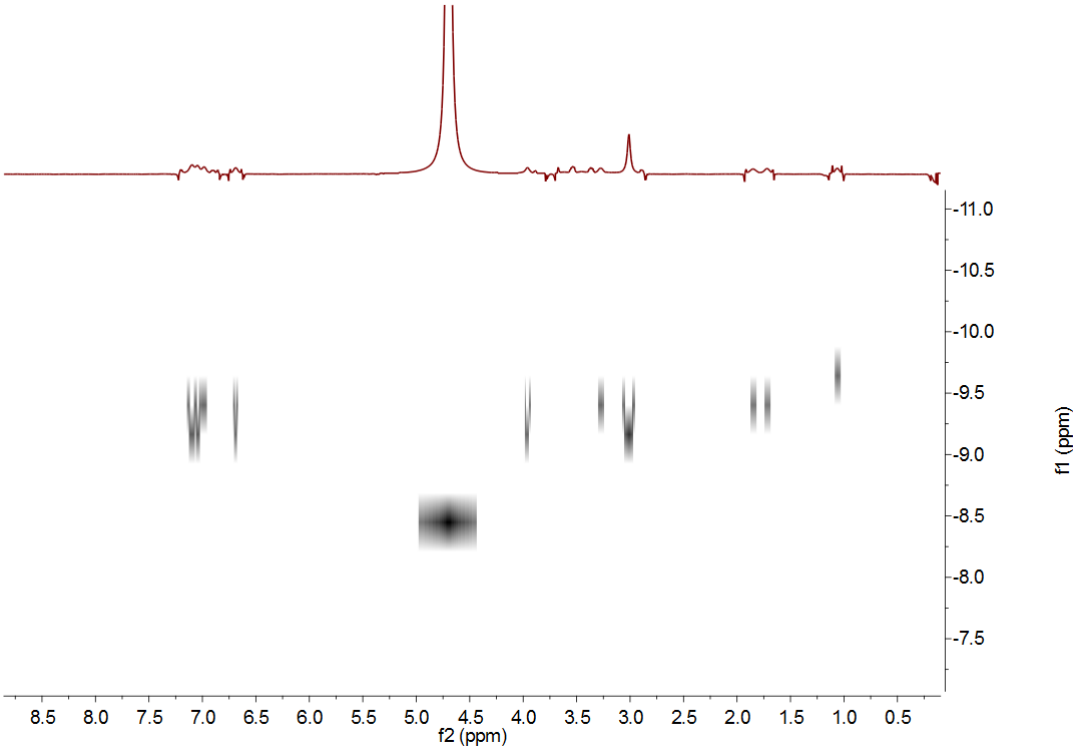
(b)


-10.5
-10.0
-9.5
-9.0
-8.5
-8.0
-7.5
-7.0
f1 (ppm)
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
f2 (ppm)

(c)


-10.0
-9.5
-9.0
-8.5
-8.0
-7.5
f1 (ppm)
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f2 (ppm)

(d)



(e)

Figure S5. Diffusion coefficient *D* (500 MHz, D_2O, 298 K) of mixture solution of **1** (2.94×10^{-3} mM) with different concentrations of **2**: (a) 0.250 mM; (b) 1.49 mM; (c) 2.84 mM; (d) 3.84 mM; (e) 5.21 mM.

*7. Photographs of **2** under natural light and 365 nm UV light after addition of **1**, ATP, and alkaline phosphatase ATPase*

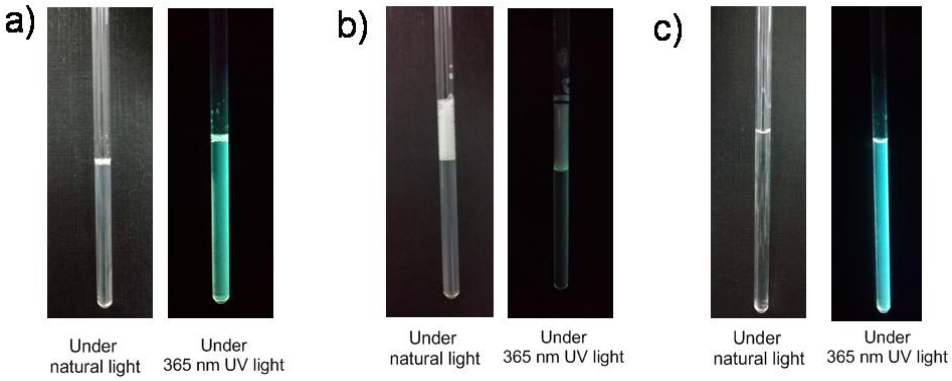


Figure S6. Photographs under natural light and 365 nm UV light: (a) a mixture solution of **1** (4.14×10^{-3} mM) and **2** (6.00 mM); (b) after addition of 12.0 mM of ATP to a; (c) after addition of 150 U L^{-1} alkaline phosphatase ATPase to b.

*8. Fluorescence spectra of **2**, hydrogel **3**, **3** after addition of ATP, and **3** after further addition of alkaline phosphatase ATPase*

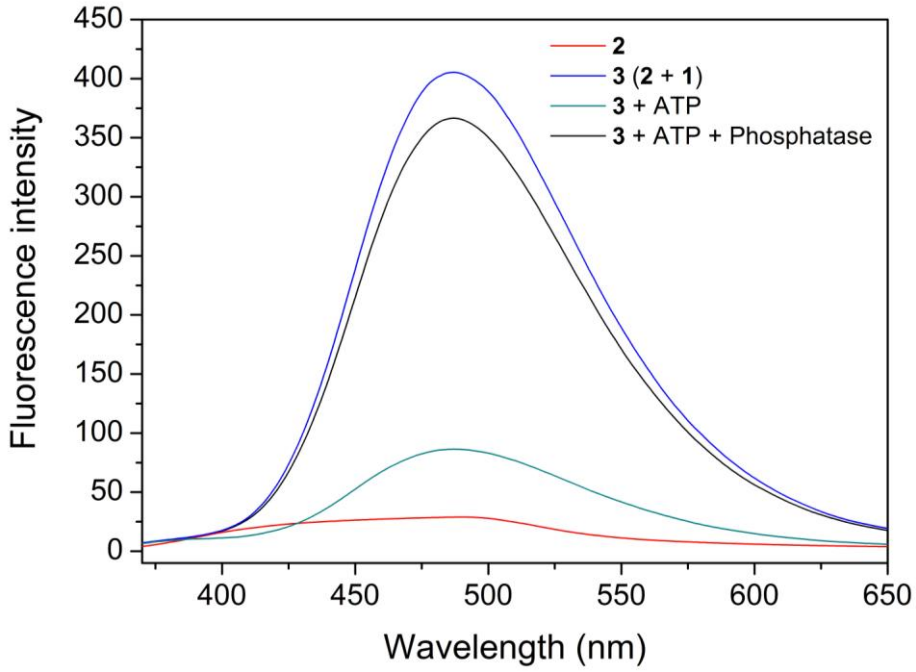


Figure S7. Fluorescence spectra of **2** (39.8 mM), hydrogel **3** (39.8 mM **2** + 0.234 mM **1**), hydrogel **3** (39.8 mM **2** + 0.234 mM **1**) after addition of ATP (79.6 mM), and hydrogel **3** (39.8 mM **2** + 0.234 mM **1**) after addition of ATP (79.6 mM) and alkaline phosphatase ATPase (150 U L^{-1}).

*9. Controlled formation of hydrogel **3** by addition of ATP and alkaline phosphatase ATPase*

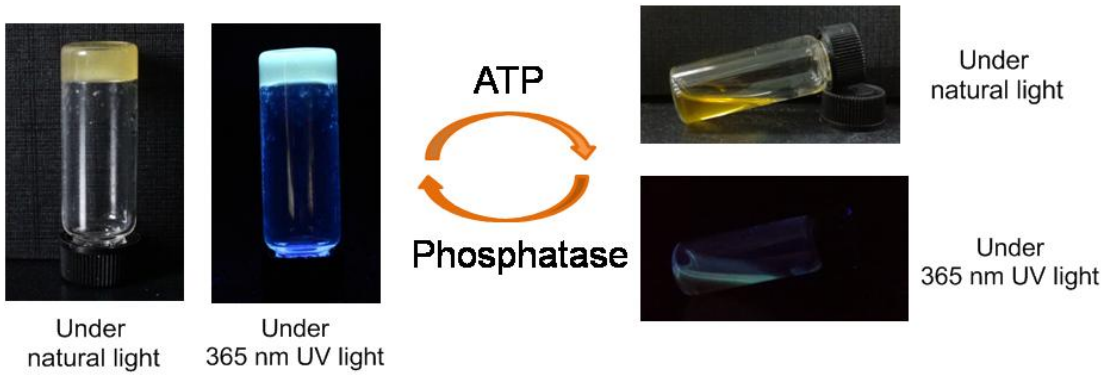


Figure S8. Controlled formation of hydrogel **3** (39.8 mM **2** + 0.234 mM **1**) by addition of ATP (79.6 mM) and alkaline phosphatase ATPase (150 U L^{-1}). Photographs of the hydrogel were taken under either natural light or 365 nm UV light.

*10. Response of a mixture of **1** and **2** toward ADP and pyrophosphate ($Na_4P_2O_7$)*

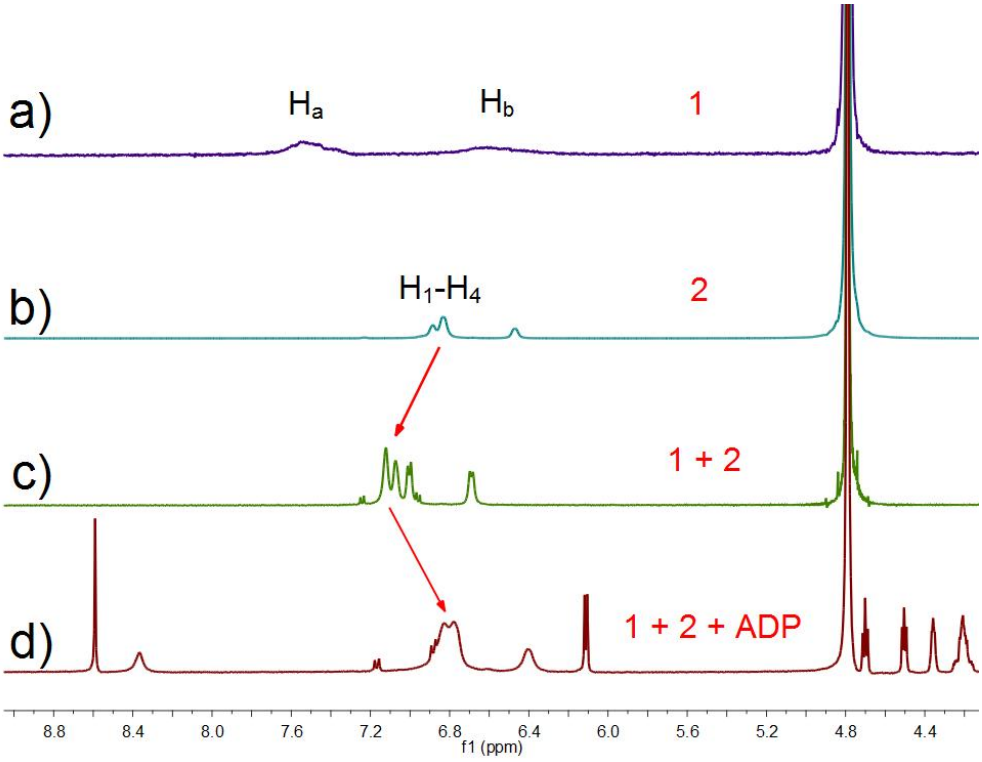


Figure S9. Partial ^{1}H NMR spectra (500 MHz, D_2O, 298 K): (a) 4.14×10^{-3} mM **1**; (b) 6.00 mM **2**; (c) a mixed solution of 4.14×10^{-3} mM **1** and 6.00 mM **2**; (d) a mixed solution of 4.14×10^{-3} mM **1**, 6.00 mM **2** and 12.0 mM ADP.

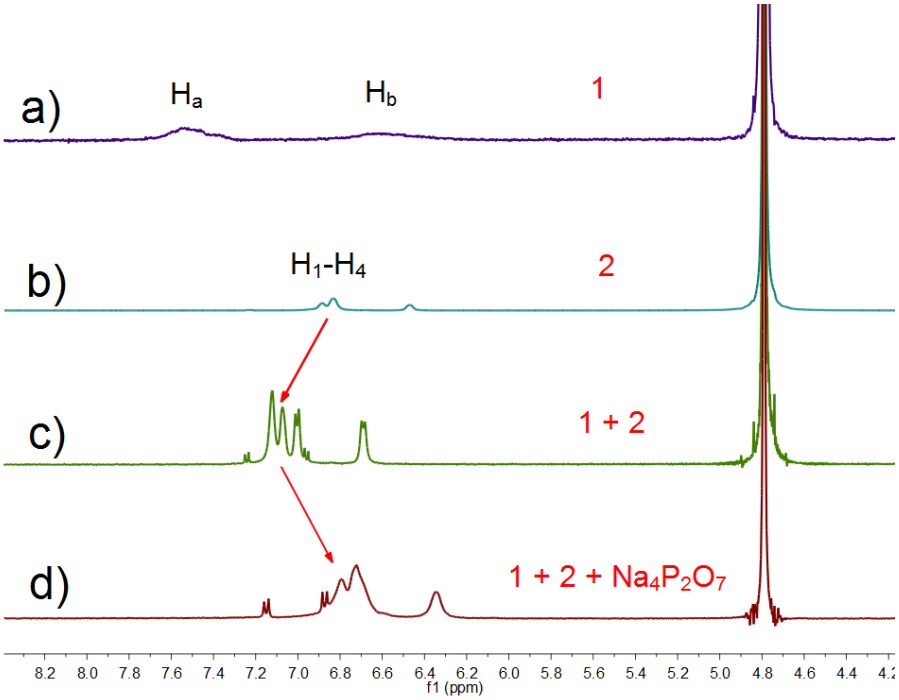


Figure S10. Partial ^{1}H NMR spectra (500 MHz, D_2O, 298 K): (a) 4.14 × 10^{-3} mM **1**; (b) 6.00 mM **2**; (c) a mixed solution of 4.14 × 10^{-3} mM **1** and 6.00 mM **2**; (d) a mixed solution of 4.14 × 10^{-3} mM **1**, 6.00 mM **2** and 12.0 mM $Na_4P_2O_7$.

From ^{1}H NMR spectra in Figure S9 and Figure S10, the peaks of protons H_1–H_4 on **2** shifted down field when 6.00 mM **2** and 4.14 × 10^{-3} mM **1** were mixed. Then, after 12.0 mM ADP or pyrophosphate was added into this mixture, these peaks shifted back to high field. These results demonstrate that the hydrogel **3** could response toward ADP and pyrophosphate.

*11. Response of hydrogel **3** toward ADP and $Na_4P_2O_7$*

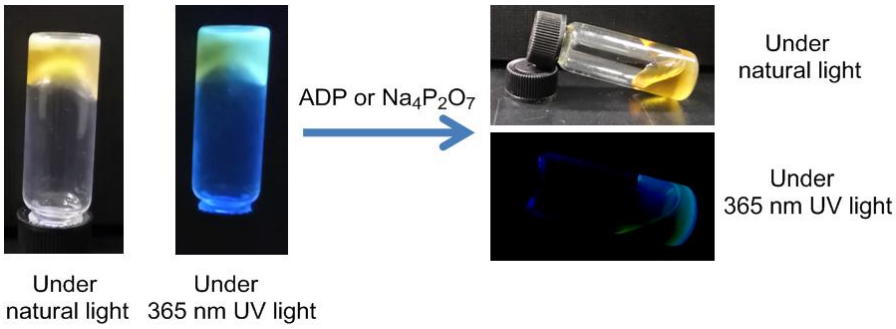


Figure S11. The gel-sol transformation of hydrogel **3** (39.8 mM **2** + 0.234 mM **1**) upon addition of ADP (79.6 mM) or $Na_4P_2O_7$ (79.6 mM).

*12. Dynamic color change photos during the gelation process of hydrogel **3***

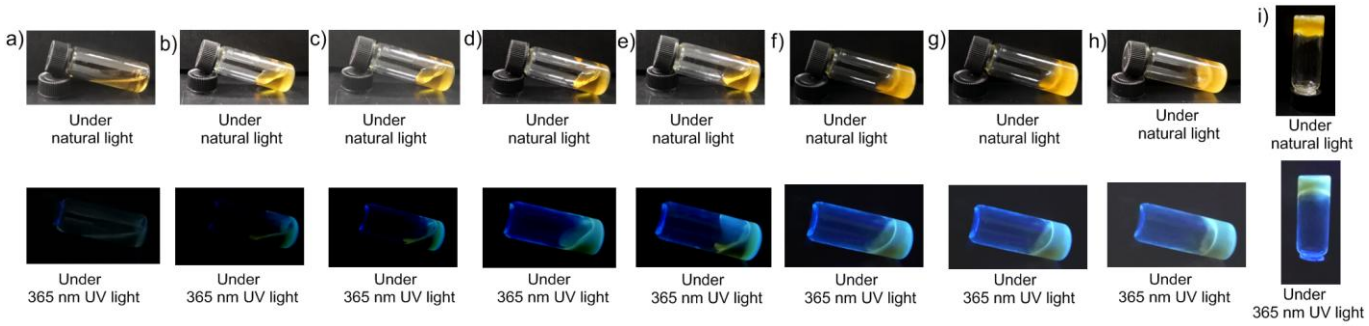


Figure S12. The dynamic color change photos during the gelation process of hydrogel **3** upon mixing a clear and free flowing aqueous solution of polymer **1** (0.234 mM) and **2** (39.8 mM) taken at different time points after mixing: a) 1 min; b) 2 min; c) 3 min; d) 4 min; e) 5 min; f) 6 min; g) 7 min; h) 8 min; i) 9 min.

Reference

S1. B.-P. Jiang, D.-S. Guo, Y.-C. Liu, K.-P. Wang and Y. Liu, *ACS Nano.*, 2014, **8**, 1609–1618.