Electronic Supporting Information for

A dual thermal and photo-switchable shrinking-swelling supramolecular peptide dendron gel

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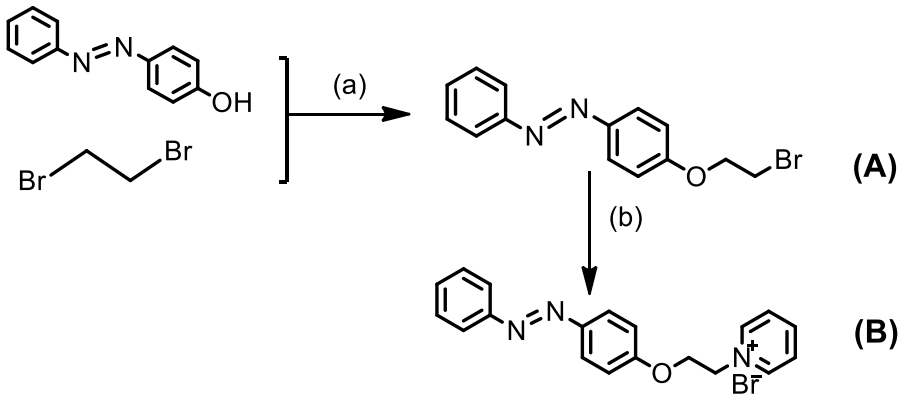
1.1 Materials

The gelator OGAc was synthesized according to our previous work (P. Duan, L.Qin, X. Zhu, M. Liu, *Chem. Eur. J.* 2011, 17, 6389-6395). All starting materials used in synthesis of $AZOC_2Py$ were obtained from commercial suppliers and used without any additional purification. Milli-Q water (18.2 MΩ cm) was used in all experiments. All the organic solvents were purified and dried according to standard methods.

1.2 Measurement

The UV/Vis and CD spectra were detected using JASCO UV-550 and JASCO J-810 spectrophotometers, respectively. Fourier transform infrared (FT-IR) spectra were recorded on a JASCO FT/IR-660 plus spectrophotometer with a wavenumber resolution of 4 cm^{-1}at room temperature. X-ray diffraction (XRD) was achieved on a Rigaku D/Max-2500 X-ray diffractometer (Japan) with Cu_{Ka} radiation(λ=1.5406Å), which was operated at 45 kV, 100 mA. AFM was performed by using Fastscan mode (Nanoscope IIIa, Digital Instruments) with a pyramidal Si_3N_4 tip. The HR-TEM images were obtained on a Tecnai G2 F20 U-TWIN operating at accelerating voltages of 200 kV. PH value was obtained on the METTLER TOLEDO/FE20 PH at a room temperature around 20℃. TLC was performed on silica gel HF254 flake and column chromatography was carried out with 230–400 mesh silica gel. ^1H NMR spectra and^{13}C NMR spectra were recorded with a Bruker Fourier 300 (300 MHz) spectrometer in $CDCl_3$ or DMSO-d_6 by using Me4Si as an internal standard. MS spectra were determined with BEFLEX III for the ESI mass spectrometer. Elemental analyses were performed on a Carlo–Erba-1106 instrument. All the photographs of the gel were taken by using a Canon EOS60D.

1.3 Synthesis of 1-(2-(4-(phenyldiazenyl)phenoxy)ethyl))pyridinium bromide ($AZOC_2Py$)



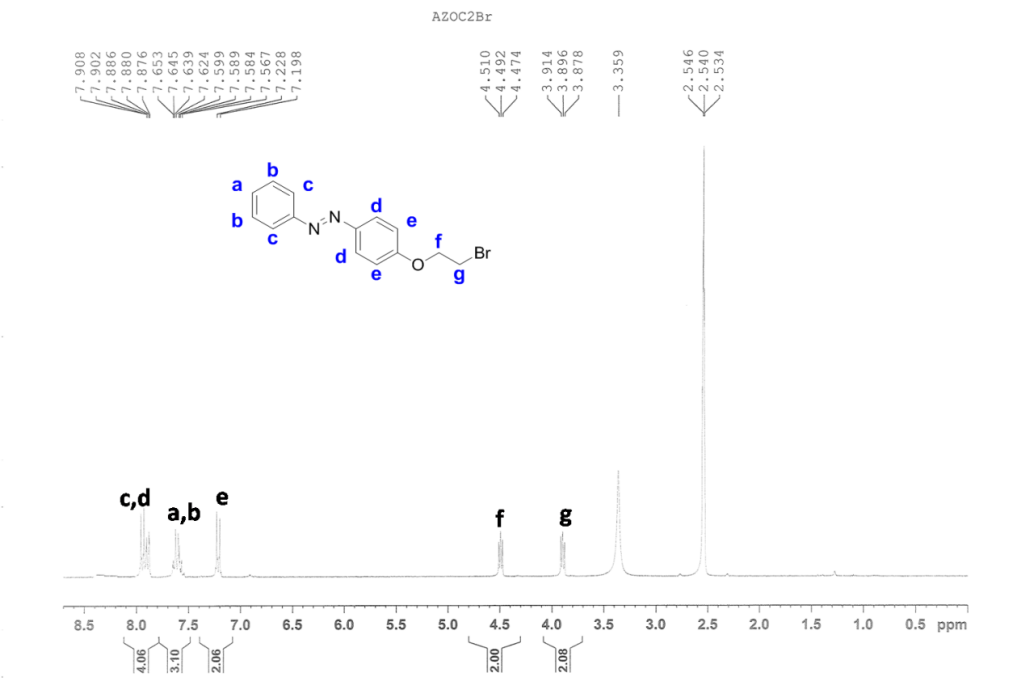
Scheme S1. The synthetic route of $AzoC_2Py$.

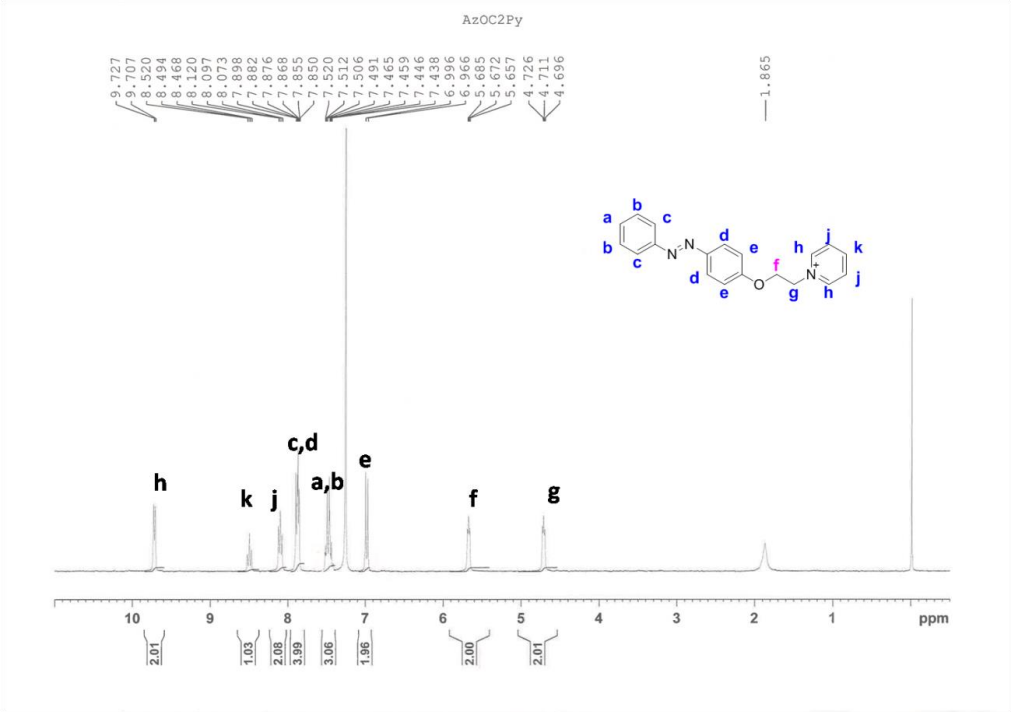
(a) Synthesis of 1-(4-(2-bromoethoxyphenyl)-2-phenyldiazene)($AZOC_2Br$)(A):

4-(phenyldiazenyl)phenol (1.078g, 5.4 mmol), 1,2-bromoethane (5ml, 54 mmol), potassium carbonate (1.5g, 10.8mmol) were dissolved in 60ml acetone. The mixture was refluxed for 24 h under an atmosphere of nitrogen. The residual salt was removed by filter and the filtrate was removed by rotary evaporation and crude product was obtained. After purification by silica column chromatography (petroleum ether /dichloromethane 5:1, Rf=0.23), the target product was obtained as a light orange crystalline solid. ^{1}H NMR (300 MHz, DMSO): δ=7.91-7.87 (m, 4H, ArH), 7.54-7.43 (m, 3 H, ArH), 7.05-7.02 (d, 2 H, ArH), 4.41–4.36 (t, 2H, CH_2), 3.71–3.67 (t, 2H, CH_2); ^{13}C NMR(300 MHz, $CDCl_3$): δ=160.5, 152.7, 147.5, 130.5, 129.1, 124.8, 122.6, 114.9, 68.1, 25.8; ESI-MS m/z: calcd for $C_{14}H_{13}BrN_2O$: 305.2;

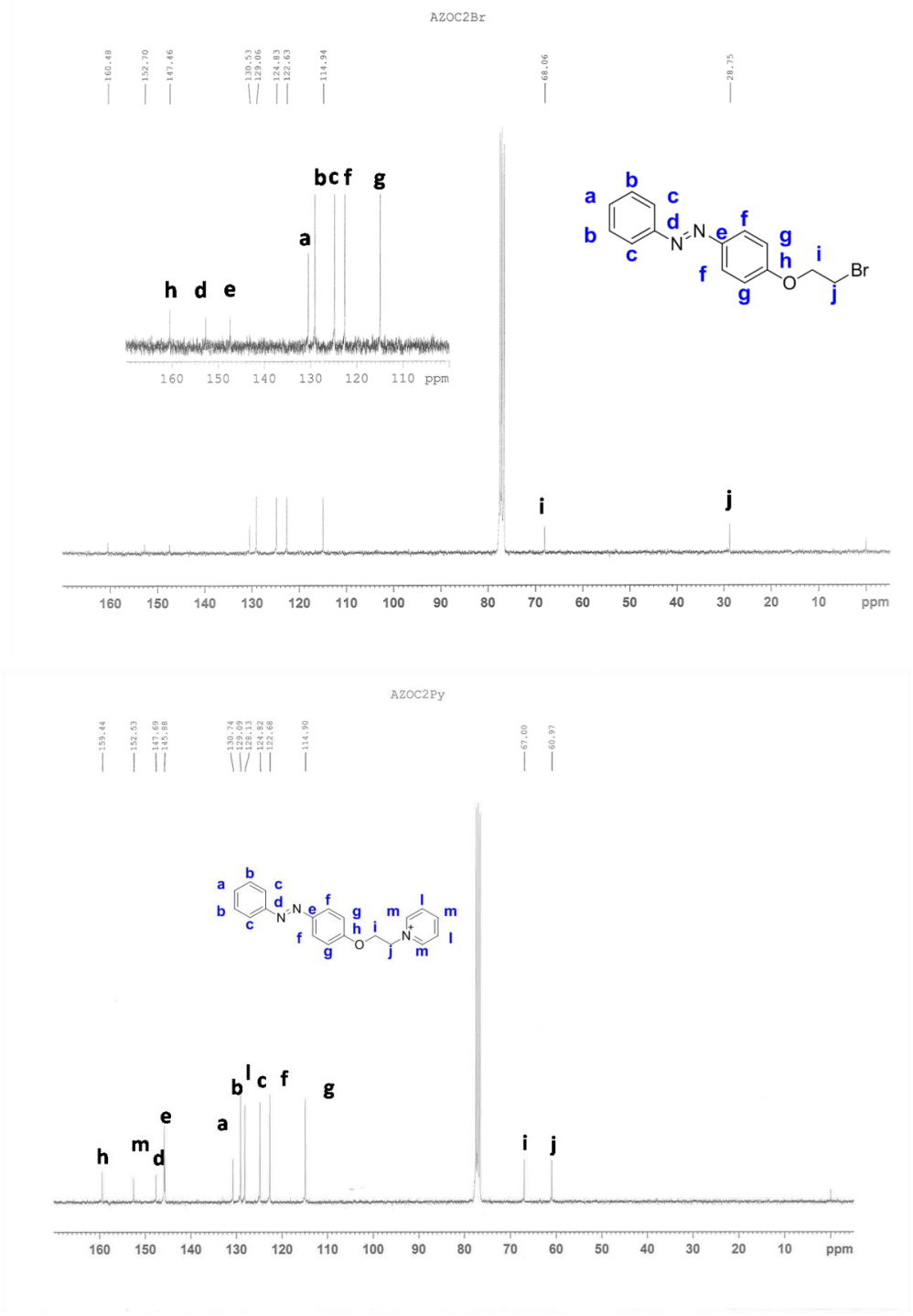
(b) 1-(2-(4-(phenyldiazenyl)phenoxy)ethyl))pyridinium bromide($AZOC_2Py$) (B) was prepared as follows:

The compound （ A ） (610.34mg ,2mmol) was dissolved in the dry pyridinium(40ml). The mixture was refluxed for 8h under an atmosphere of nitrogen. After the reaction, the solvent was removed by reduced pressure distillation and the obtained the crude orange product was recrystallized from methanol-diethyl ether solution. The final purified yellow precipitate was obtained by filtration. ^{1}H NMR (300 MHz, $CDCl_3$): δ=9.80-9.68 (d, 2H ,pyridine), 8.58-8.47 (t, 1 H, pyridine), 8.13-8.08 (t, 2 H, pyridine), 7.98–7.86 (m, 4H,ArH), 7.61-7.37 (m, 3H, ArH), 7.06-6.91 (m, 2H, ArH), 5.69-5.66 (t, 2H, CH_2),4.73-4.70 (t, 2H, CH_2); ^{13}C NMR(300 MHz, $CDCl_3$): δ=159.4, 152.3, 147.7, 145.9, 130.7, 129.0, 128.1, 124.8, 122.7, 114.9, 67.0, 61.0; ESI-MS m/z: calcd for $C_{19}H_{18}BrN_3O$: 383.06;





^{1}H NMR (300 MHz, $CDCl_3$ or DMSO-d_6) of **AZOC$_2$Br** and **AZOC$_2$Py**



^{13}C NMR (300 MHz, $CDCl_3$) of **AZOC$_2$Br** and **AZOC$_2$Py**

1.4 Preparation and characterize of hydrogel

The typical hydrogel was prepared by adding OGAc (1.34 mg, 0.002 mmol) and AZOC$_2$Py (2.7mM, 74 μL, 148 μL, 737 ul for **OGAc**/AZO mol ratio 10/1, 5/1, 1/1, respectively) aqueous solution to pure water (1 mL), which was slightly heated to a light yellow solution at 50 ℃ and then rest at room temperature for 12 h, the shrunken hydrogel with the OGAc/AZO mol ratio 5/1 was obtained. After that, the shrinkable sample was irradiated by UV light (150W UVA lamp, λ=365 nm, 20 cm away from the sample) at cool condition and further converted from shrinkage to

swelling. The co-assembled hydrogel obtained by the above methods were firstly diluted with water, cast on a freshly cleaved mica surface and then dried in a vacuum for AFM measurements. For the TEM measurements, a small amount of diluted hydrogel was placed onto carbon coated copper grid and dried in a vacuum or exposed to UV light. As for FT-IR spectra and XRD measurements, the samples of co-assemblies were cast onto silicon slices and dried as mentioned above. In the process of measuring the UV and CD spectra of hydrogels, a quartz cuvette with 1 mm width was used. All the samples for the characterizations were irradiated by UV (150 W UV lamp with main light at 365 nm) and visible light (40 W compact fluorescent lamp, >400 nm visible light) alternatively to see their changes.

1.5 The shrinkage ratio of the gel

The shrinking process was then monitored by measuring volume change($V_{expelled}$ / V_0) as a function of time(t) accompanied by the changes in UV-Vis spectra and photos were taken subsequently . Shrinking ratio (SR) is defined as follows:
$SR(t) = (V_0 - V_t) / V_0 \approx V_{expelled} / V_0$. According to Lambert beer's law *:* $A = \varepsilon bc$ & $A \propto 1 / V$, thus $SR(t) \approx 1 - A_0 / A_t$ (V_o / A_0, V_t / A_t, V_m / A_m is the volume or absorption value of Gel 1 phase state, gel shrinking for t hours ,equilibrium-shrinkage time respectively) , the relevant parameters listed in Table 1.

The reversible Gel 1 to S-gel or S-gel to Gel 2 transition process was characterized by recording the UV-Vis and CD spectra under Resting/Heating or alternative UV/Vis irradiation.

Table 1. The relevant parameters of the shrinking process in **OGAc-AZOC$_2$Py** co-assembly. The total gelator **OGAc** is 1.34 mg/ml , the original volume(V_0) was 1ml. OGAc/AZOC$_2$Py mol ratio was 5/1.

	$V^c_{expelled}$ / ml	**SR^e ($V_{expelled}$ / V_0) / %**	**A^d_t (344nm)**	**$^f[1-A_0 / A_t]$/%**
Sol[a] (0h)	-	-	0.78136	-
Gel 1[b] (Resting 2 h)	-	-	0.6058	-
Resting 4h	0.22	22	0.8055	24.7
Resting 6h	0.31	31	0.89072	32
Resting 8h	0.46	46	1.0897	44.4
Resting 12h	0.6	60	1.59584	62
Resting 24h	0.61	61	1.63523	63
Resting One week	0.66	66	1.7734	65.8

[a]the yellow solution (sol) was obtained at 50 ℃.
[b]Gel 1 was formed after resting 2h at a room temperature at 20 ℃.

[c]$V_{expelled}$ was the expelled water at the resting time(t).
[d]A_t was the absorption value of the sample from UV-Vis spectra at the resting time(t).
[e]Shrinking ratio (SR) is defined as follows: $SR(t) = (V_0 - V_t) / V_0 \approx V_{expelled} / V_0$.
[f]According to Lambert beer's law : $A = \varepsilon bc$ & $A \propto 1 / V$, thus $SR(t) \approx 1 - A_0 / A_t$ (V_o / A_0, V_t / A_t is the volume or absorption value of Gel 1 phase state, gel shrinking for t hours, V_o=1ml).

1.6 Morphological analysis of the co-assembly of OGAc with $AZOC_2Py$ exposed to external thermal or photo-stimuli

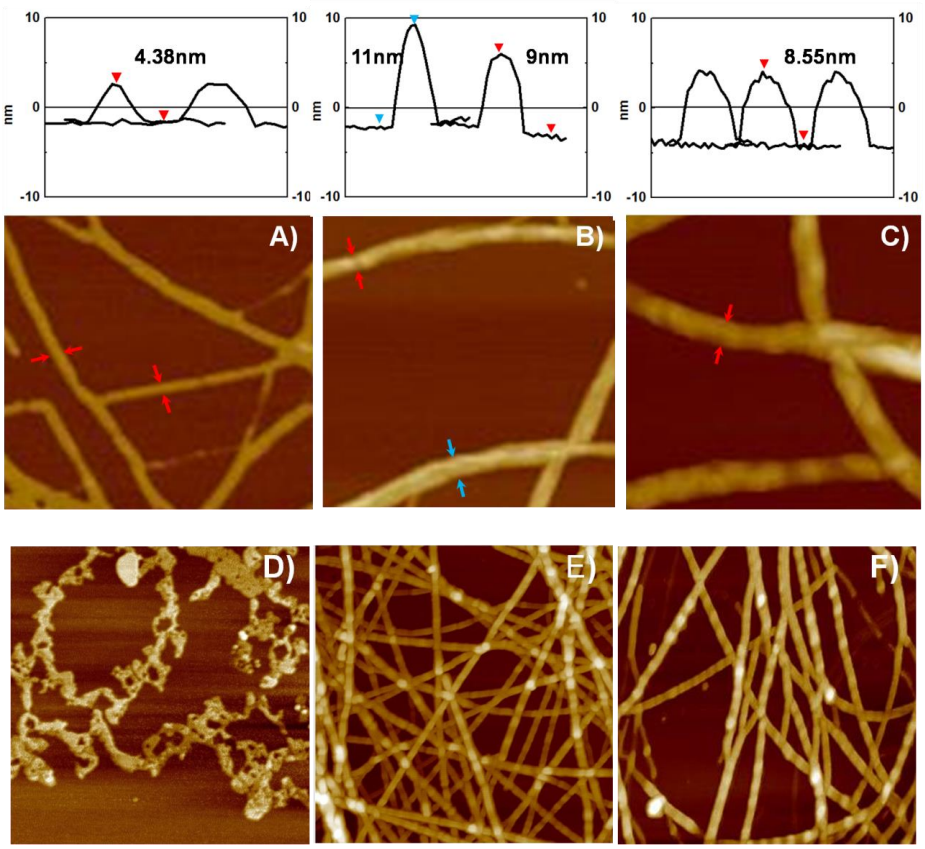


Fig S1. AFM Section analysis of co-assembly of OGAc with $AZOC_2Py$ (A) Gel 1 (B) S-gel (C) Gel 2 (exposed to UV lamp for 15 min). All of the images are 500 nm × 500 nm. The number list below each curve is average diameter. AFM images of the co-assembled hydrogel (D) Sol (E) Gel transition state before shrunk (F) Gel 1 after exposed to UV lamp for 15 min. Scar bar: 2.2μm×μm.

1.7 Spectral analysis of this co-assembly in different phase state

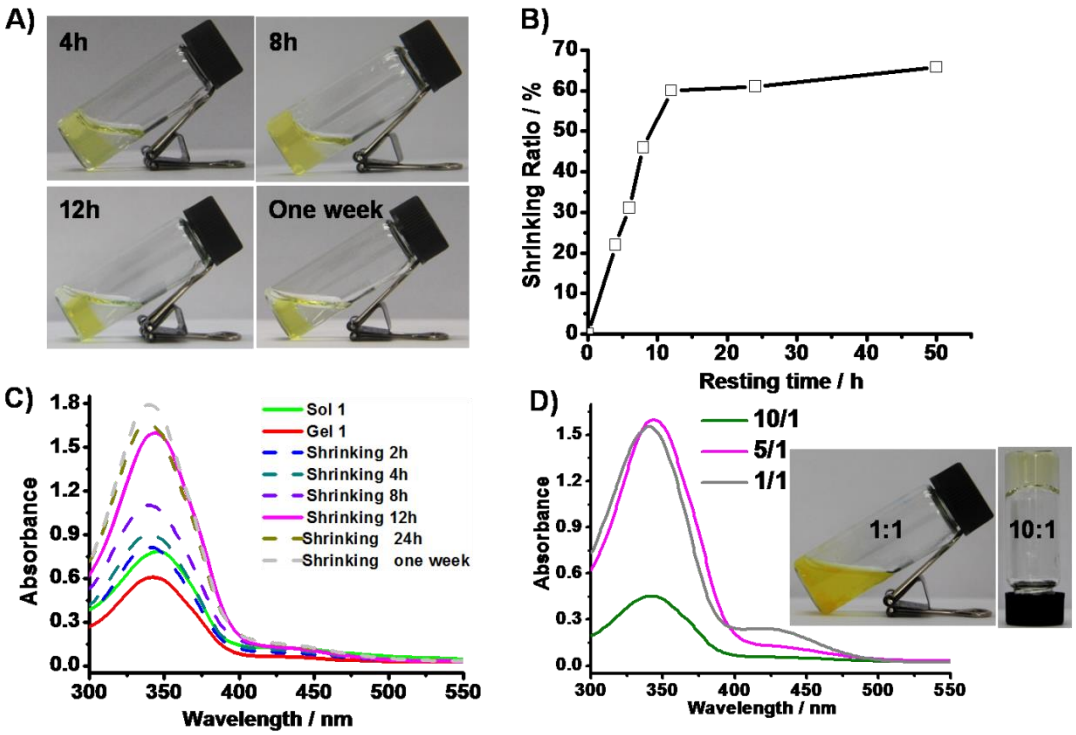


Fig S2. (A) Photographs demonstrating the shrinking process with varied resting time(t) (B) The plots of shrinking ratio($V_{expelled}$ / V_0) as a function of time(t), $V_{expelled}$ was the expelled water Of OGAc-AZOC_2Py hydrogel at the resting time(t) (C) UV spectra of OGAc-AZOC_2Py coassembly with different resting time(t), t(0 h) was the beginning time since the solution Sol 1 was obtained, OGAc/AZOC_2Py mol ratio was 5/1.(D) UV spectra Of OGAc-AZOC2Py with different mol ratio(10/1, 5/1, 1/1) and the photographs were taken after resting 12h approached to equilibrium-shrinkage state in this coassembly (5/1 mol ratio). The total gelator OGAc is 1.34 mg / ml in all cases, V_0 was the original volume, V_0=1ml.

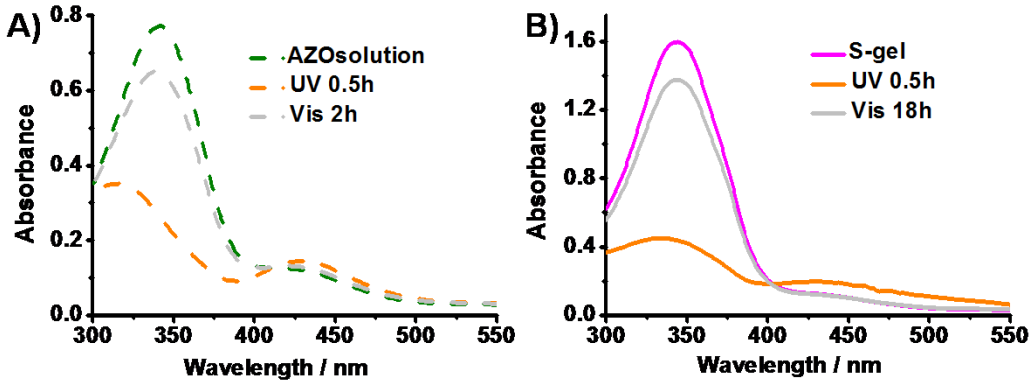


Fig S3. UV Spectra of **OGAc-AZOC$_2$Py** co-assembly (A) **AZOC$_2$Py** solution (B) **S-gel** at the equilibrium-shrinkage state (12h). OGAc/AZOC$_2$Py mol ratio was 5/1. UV irradiation (150W UV lamp) kept on 30 minutes and visible light (40 W compact fluorescent lamp) was proceed with 2h (AZO solution) or 18h (S-gel).

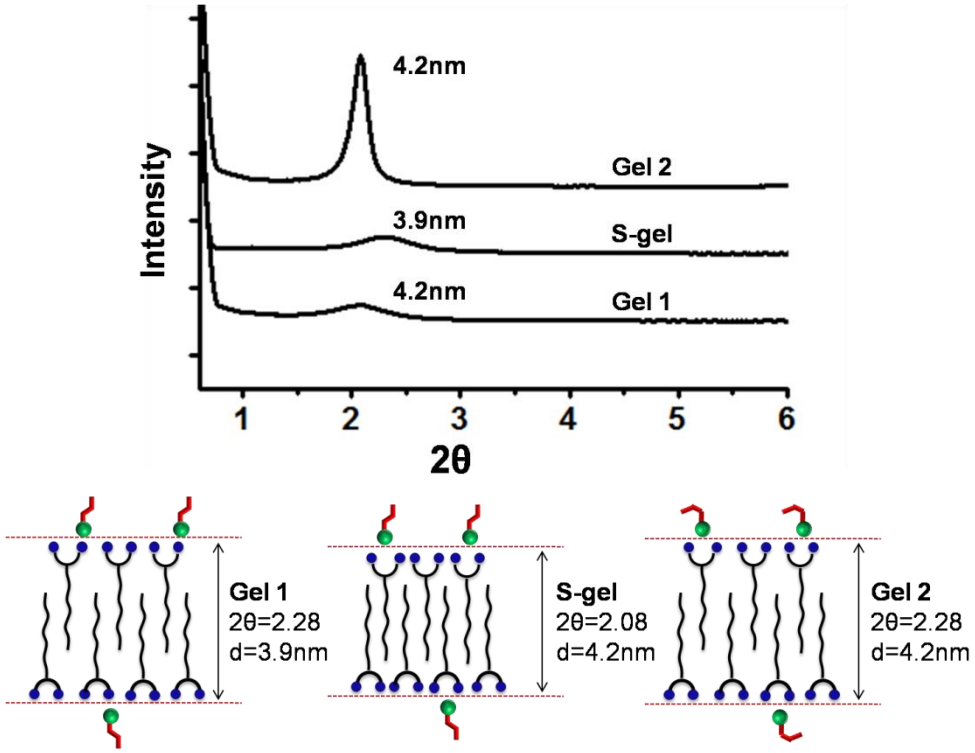


Fig S4. XRD profiles of the xerogels obtained from the co-assembled hydrogel in different phase state.

Table 2. Summary of XRD peaks and d-spacing values of the co-assembly of **OGAc/ AZOC$_2$Py**.

Sample	**Gel 1**	**S-gel**	**Gel 2**
2θ	2.08	2.28	2.08
d(nm)	4.2	3.9	4.2

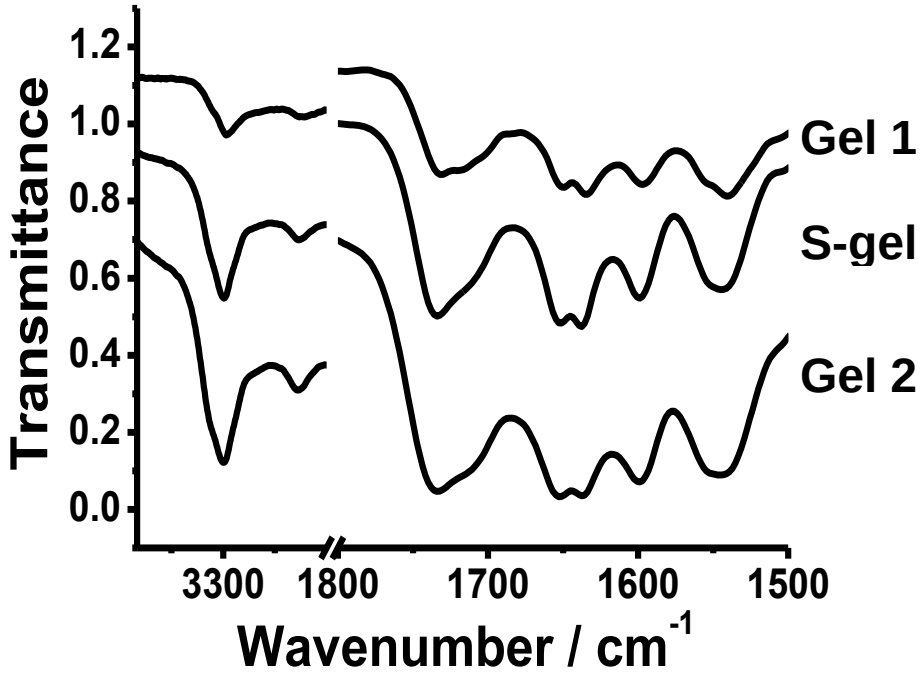


Fig S5. FT-IR Spectra of **OGAc-AZOC$_2$Py** co-assembly in different phase state.

Table 3. Characteristic Vibrations (cm^{-1}) in FT-IR of **OGAc-AZOC$_2$Py** co-assembled xerogels.

Gelling phase	ν (N-H) /cm^{-1}	ν-C=O/cm^{-1}	ν(C=O) /cm^{-1}	δ(N-H) /cm^{-1}	ν(COO$^-$) /cm^{-1}
Gel 1	3290.80	1730.97	1634.47	1540.35	1599.28
S-gel	3297.39	1733.82	1637.84	1544.44	1599.1
Gel 2	3298.84	1733.45	1651.95	1545.84	1599.25

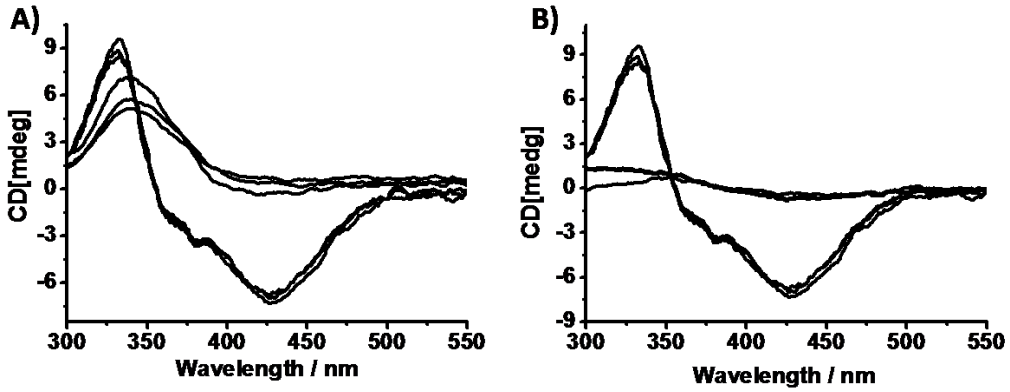


Fig S6.CD spectra of the reversible phase transition in **OGAc-AZOC$_2$Py** (A) Gel 1 to S-gel upon repeated Heating-Resting cycle (B) S-gel to Gel 2 upon repeated UV-Vis cycle.