# Supporting information

## A thermal-responsive supramolecular organogel: dual luminescence property and luminescence conversion induced by $Cd^{2+}$

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### Materials

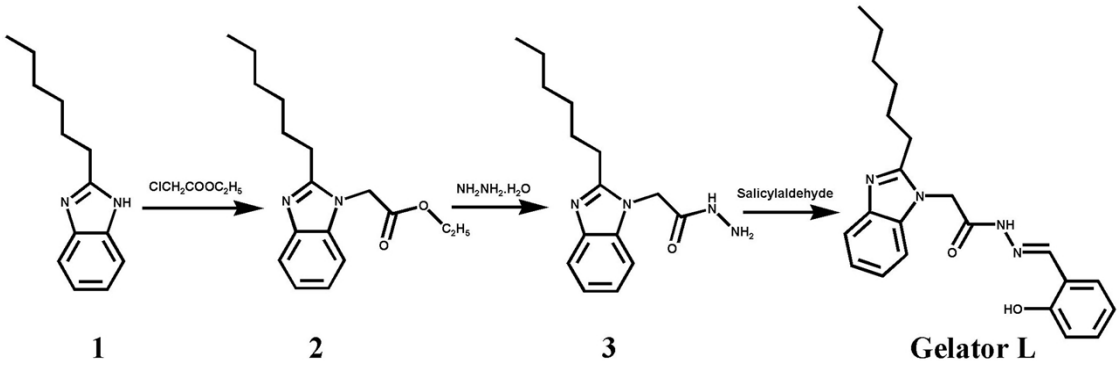
O-Phenylendiamine (≥98%) was purchased from Tianjin Guangfu Fine Chemical Research Institute, Heptanoic acid (≥98%) was purchased from Sinopharm Chemical Reagent Co., Ltd.. Ethyl chloroacetate and hydrazine hydrate (80%) were purchased from Alfa Aesar Chemical Co., Ltd.. Salicylaldehyde was purchased from Shanghai Bangcheng Chemical Co., Ltd.. All chemicals were used without further purification, unless otherwise noted.

### Measurements

$^1$H NMR spectra were recorded on a Bruker 400MHz spectrometer. Elemental analyses were performed with an Elementar VarioELcube. The morphologies of the as-synthesized samples were characterized with a JSM-6701F SEM using an accelerating voltage of 5kV. The measurements of steady-state luminescence were performed with a spectrofluorimeter (HITACHI F-4500, Japan). Fluorescence micrographs of the samples were imaged by fluorescent optical microscopy (Olympus BX53) by exciting the gel samples with an unfocused UV radiation (330−385nm). X-ray diffraction patterns (XRD) were determined with a Rigaku-Dmax 2400 diffractometer using Cu Kα radiation over the 2θ range of 4—90°. Fourier transform infrared (FT-IR) spectra were conducted within the 4000–500cm$^{-1}$

wavenumber range using a Nicolet 360 FT-IR spectrometer with the KBr pellet technique. All measurements were carried out at room temperature.

**Synthesis of 2-(2-hexyl-1H-benzimidazole-1-yl)-N'-(2-hydroxybenzylidene) acetohydrazide (gelator L)**




**Scheme S1**. Synthesis of Gelator L

**2-hexyl benzimidazole (1)** was prepared according to the literature method. [1,2]

**Synthesis of Ethyl-(2-hexyl-1H-benzimidazole-1-yl) acetate (2)**

Ethyl chloroacetate (0.12mol) and potassium carbonate (0.20mol) were added to a 60mL acetone solution of 2-hexyl benzimidazole (**1**) (0.1mol), then the solution was refluxed for 8h. After cooling to room temperature, the reaction mixture was filtered. Excess acetone was removed from the clear filtrate by distillation, and then was added to water. The residue was washed with water, and then was dried under air. Further purification was done by recrystallization from ethyl acetate to give Ethyl- (2-hexyl-1H-benzimidazole-1-yl) acetate (**2**). Yield: 23.10 g (80%).

**Synthesis of 2-(2-hexyl-1H-benzimidazole-1-yl) acethydrazide (3)**

The solution of ethyl (2-hexyl-1H-benzimidazole-1-yl) acetate (**2**) (0.07mol) in ethanol (40mL) was mixed with hydrazine hydrate (99%) (0.08mol).The solution was refluxed for 6h, then was evaporated under reduced pressure. The residue was washed with excess water. The solid separated was collected by filtration. The crude product was purified by recrystallization from ethanol to give 2-(2-hexyl -1H-benzimidazole -

1-yl) acethydrazide (**3**). Yield: 17.27 g (90%). Anal. calcd for $C_{15}H_{22}N_4O$: C 65.67, H 8.08, N 20.42. Found: C 65.83, H 8.29, N 20.67. $^1$H NMR (400MHz, $CDCl_3$): δ (ppm) 7.77-7.61 (m, 1H, -NH-),7.36 (s, 1H, Ar-H), 7.31-7.16 (m, 3H, Ar-H), 4.87-4.69 (m, 2H, -$CH_2$-), 3.78 (s, 2H, -$NH_2$-), 2.77-2.57 (m, 2H, -$CH_2$-), 1.85-1.70 (m, 2H, -$CH_2$-), 1.46-1.22(m, 6H, -$CH_2$-), 0.89 (t, *J* = 7.1 Hz, 3H, -$CH_3$); $^{13}$C NMR (100.5 MHz, DMSO-$D_6$): δ (ppm) 165.47, 154.79, 141.64, 135.10, 120.84, 120.66, 117.72, 109.10, 43.74, 30.54, 27.92, 26.12, 25.89, 21.56,13.42. ESI-MS: m/z $(L + H)^+$ 275.20.

**Synthesis of 2- (2-hexyl-1H-benzimidazole-1-yl) -N'- (2-hydroxybenzylidene) acetohydrazide (gelator L)**

The solution of 2-(2-hexyl-1H-benzimidazole-1-yl) acethydrazide (**3**) (0.05mol) in ethanol (100mL) was mixed with salicylaldehyde (0.06mol) and refluxed for 8h. Then the mixture was added to excess water. The solid separated was collected by filtration. The crude product was washed with ethanol three times to give 2-(2-hexyl-1H-benzimidazole-1-yl)-N'-(2-hydroxybenzylidene) acetohydrazide molecule (gelator **L**). Yield: 17.03 g (86%). This Gelator **L** has two rotamers.[3]

Major product: $^1$H NMR (400MHz, DMSO-$D_6$ ): δ (ppm) 11.72 (s, 1H, OH), 10.09 (s, 1H, NH), 8.36 (s, 1H, N=CH), 7.81 (d, *J* = 7.6 Hz, 1H, Ar-H), 7.54 (t, *J* = 6.9 Hz, 1H, Ar-H), 7.47-7.38 (m, 1H, Ar-H), 7.32-7.20 (m, 1H, Ar-H), 7.19-7.06 (m, 2H, Ar-H), 6.94-6.82 (m, 2H, Ar-H), 5.43 (s, 2H, N-$CH_2$-), 2.75 (t, J = 7.6 Hz, 2H, -$CH_2$-), 1.81-1.67 (m, 2H, -$CH_2$-), 1.25 (m, 6H, -$CH_2$-), 0.81 (t, *J* = 5.0 Hz, 3H, -$CH_3$).

Major product: $^{13}$C NMR (100.5MHz, DMSO-$D_6$): δ (ppm) 168.32, 163.64, 157.74, 156.89, 148.35, 142.70, 136.38, 131.64, 126.98, 121.73, 121.42, 119.72, 118.58, 116.57, 110.13, 44.28, 31.37, 28.76, 27.01, 26.81, 22.33, 14.21.

Anal. calcd for $C_{22}H_{26}N_4O_2$: C 69.82, H 6.92, N 14.80. Found: C 69.77, H 6.79, N 14.44. ESI-MS: m/z $(L + H)^+$ 379.12.

Minor product: $^1$H NMR (400 MHz, DMSO-$D_6$) of: δ (ppm) 12.10 (s, 1H, OH), 10.88 (s, 1H, NH), 8.47 (s, 1H, N=CH), 7.81 (d, *J* = 7.6 Hz, 1H, Ar-H), 7.54 (t, *J* = 6.9 Hz, 1H, Ar-H), 7.47-7.38 (m, 1H, Ar-H), 7.32-7.20 (m, 1H, Ar-H), 7.19-7.06 (m, 2H, Ar-H), 6.94-6.82 (m, 2H, Ar-H), 5.01(s, 2H, N-$CH_2$-), 2.75 (t, J = 7.6 Hz, 2H, -$CH_2$-), 1.81-1.67 (m, 2H, -$CH_2$-), 1.25 (m, 6H, -$CH_2$-), 0.81 (t, *J* = 5.0 Hz, 3H, -$CH_3$).

Minor product: $^{13}C$ NMR (100.5MHz, DMSO-$D_6$): δ (ppm) 168.32, 163.64, 157.74, 156.19, 148.35, 142.32, 136.11, 131.92, 129.54, 121.91, 121.65, 120.52, 118.98, 116.74, 110.03, 45.10, 31.39, 28.79, 27.12, 26.81, 22.33, 14.21.

## Reference


1 W. O. Pool, H. J. Harwood, A. W. Ralston, *J. Am. Chem. Soc.* 1937, **59**, 178-179.

2 Y. M. Zhang, Q. Lin, T. B. Wei, X. P. Qin, Y. Li, *Chem Commun.*, 2009, 6074–6076.

3 J. F. Wang and Y. Pang, *RSC Adv.*, 2014, **4**, 5845-5848.

**Tsg (gel−sol transition temperature)**

Tube inversion method: the glass tubes (volume 5mL) containing the samples were immersed in an oil bath and the heat was increased at the rate of 1°/min. After each temperature step the test tubes were inverted in order to check whether the sample flowed or not. The temperature at which solvent ran from the sample was recorded as the Tsg value, which reflects the temperature of the gel-sol transition.

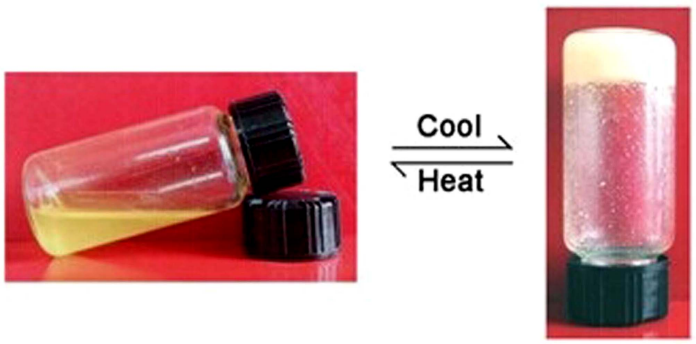



**Fig. S1** Sol–gel phase transitions of the B-gel induced by temperature.

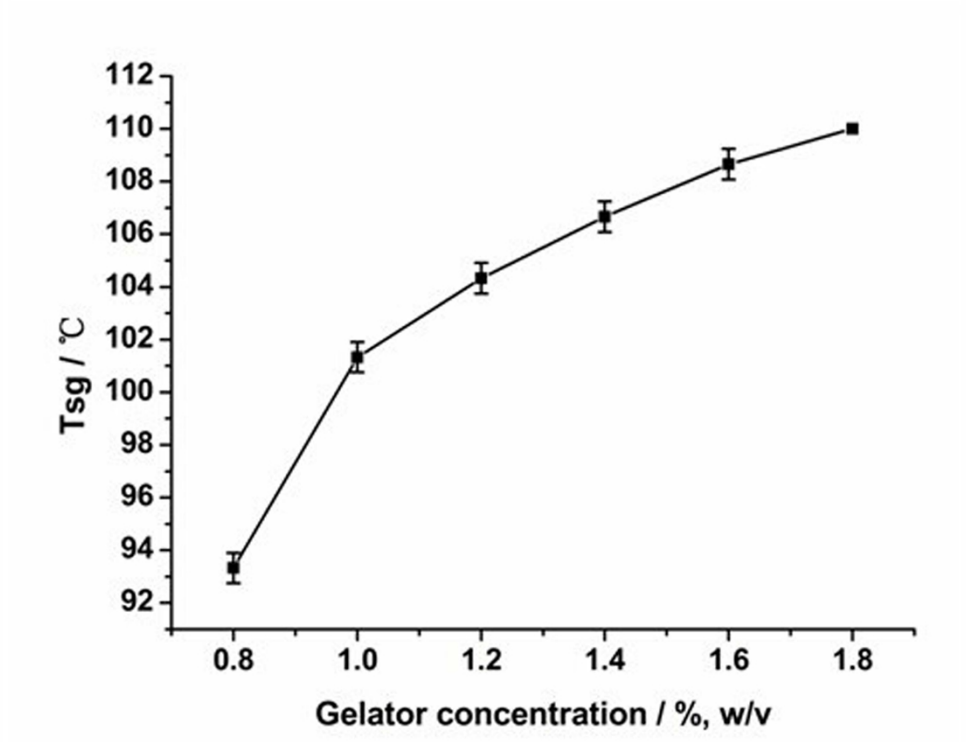



**Fig. S2** The change of Tsg in G-gel with respect to the gelator concentration.

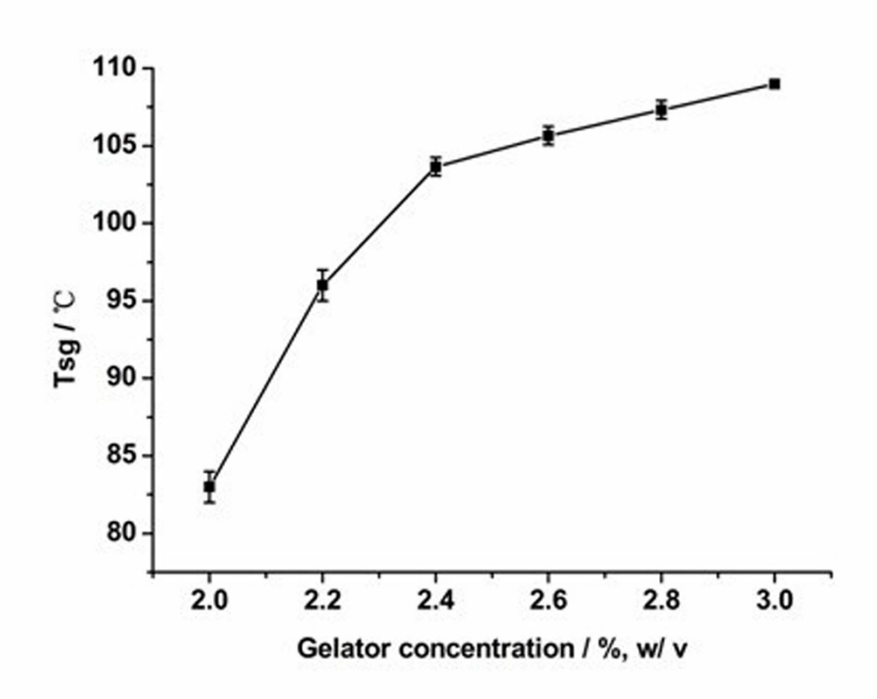



**Fig. S3** The change of Tsg in B-gel with respect to the gelator concentration

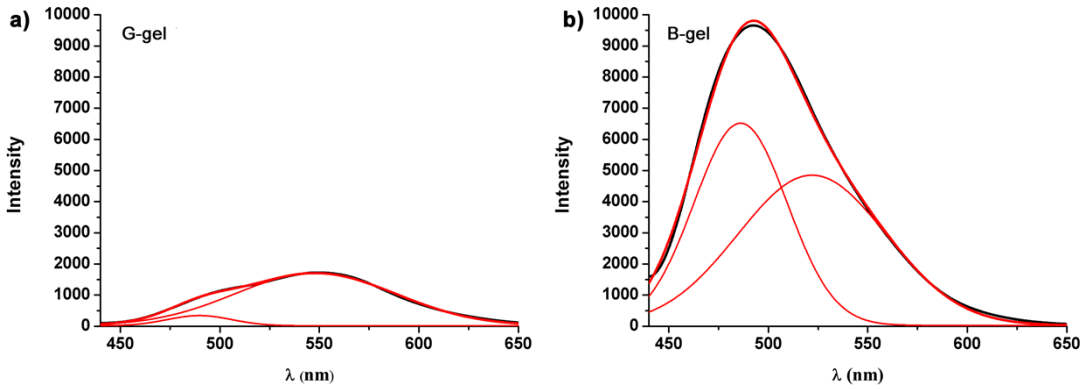



**Fig. S4** Multi-peak fitting luminescence spectra of the G-gel (a) and B-gel (b) excited at 420nm. (The black line is experimental curve, the red lines are fitting curves.).

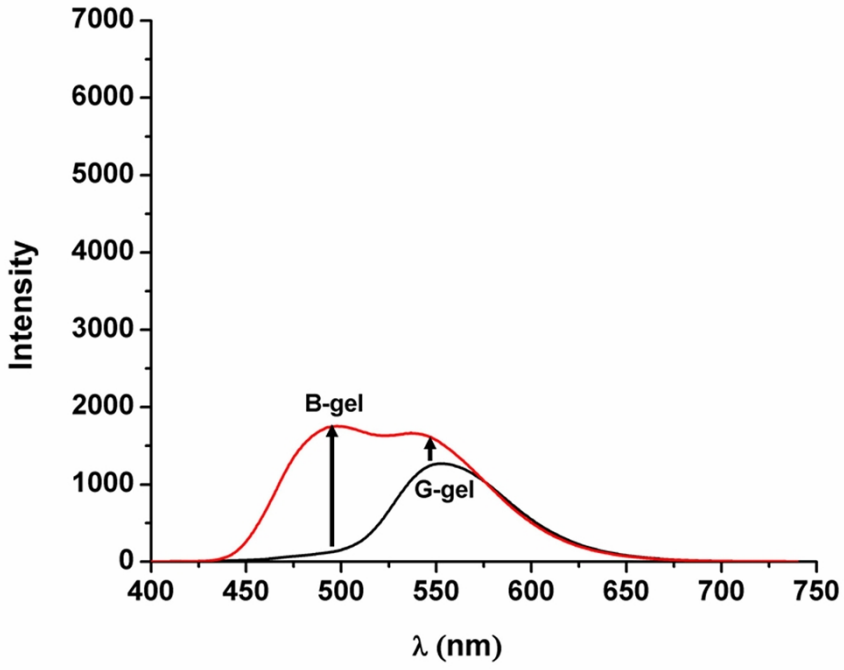



**Fig. S5** Luminescence spectra of G-gel (a), and B-gel (b) (having molar ratio L/$Cd^{2+}$ 1:1) excited at 380nm. In gels, the concentration of L in sample is 2 wt%.

**Fig. S6** The possible luminescence mechanism of G-gel and B-gel

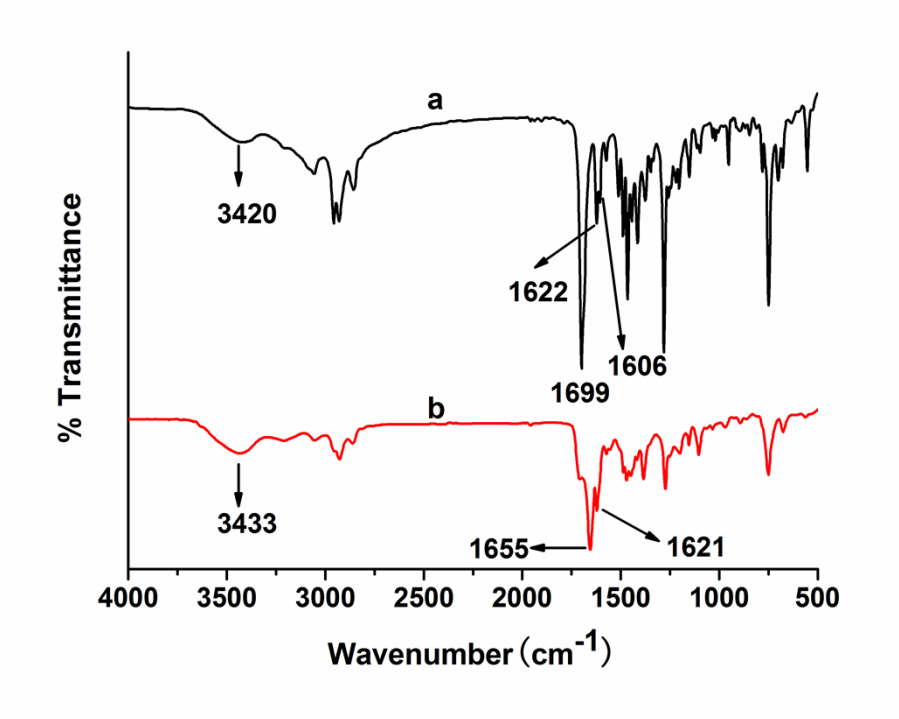



**Fig.S7** FT-IR spectra of the L (a) and xerogel (b) of the B-gel

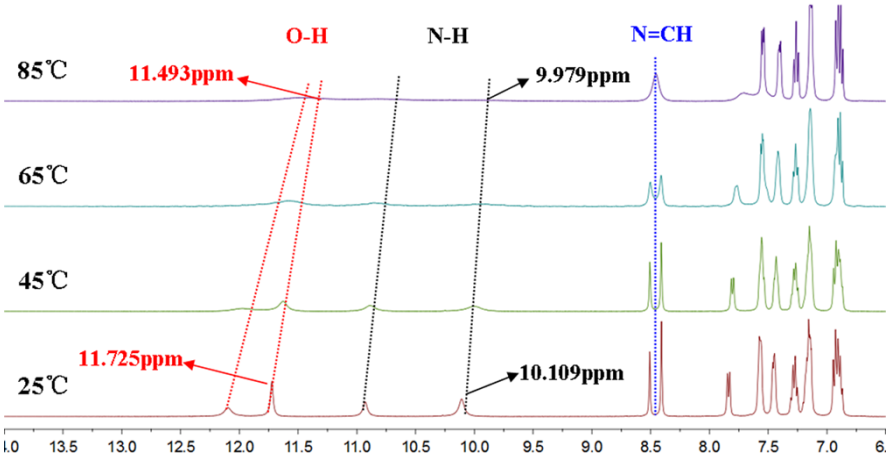



**Fig. S8** Temperature-dependent $^{1}$H NMR spectra (O-H and N-H region) of gelator L/[$D_6$] DMSO (60mg/mL)

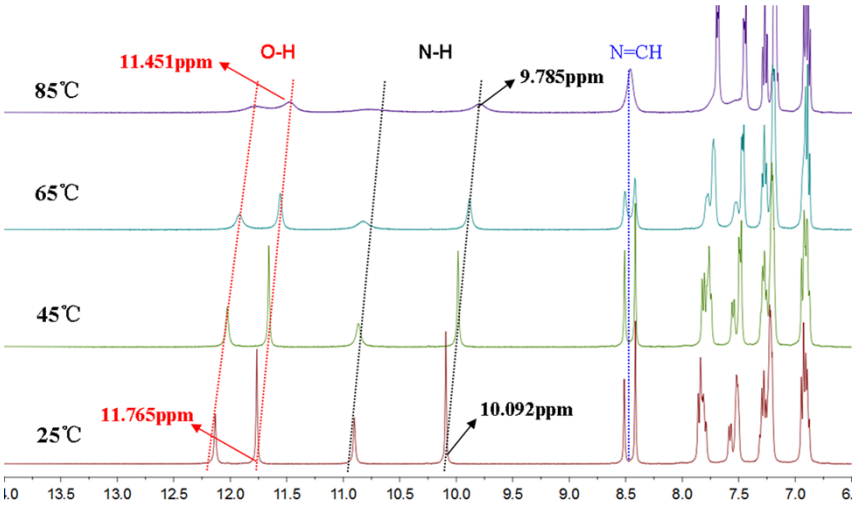
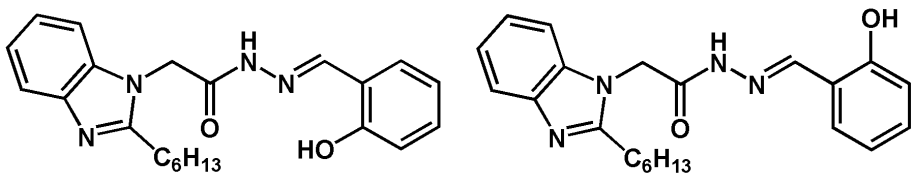



**Fig. S9** Temperature-dependent $^{1}$H NMR spectra (O-H and N-H region) of gelator L with 1 equivalent $Cd^{2+}$/[$D_6$] DMSO (gelator L 60mg/mL)




**La** **Lb**

**Fig. S10** Two rotamers of gelator L

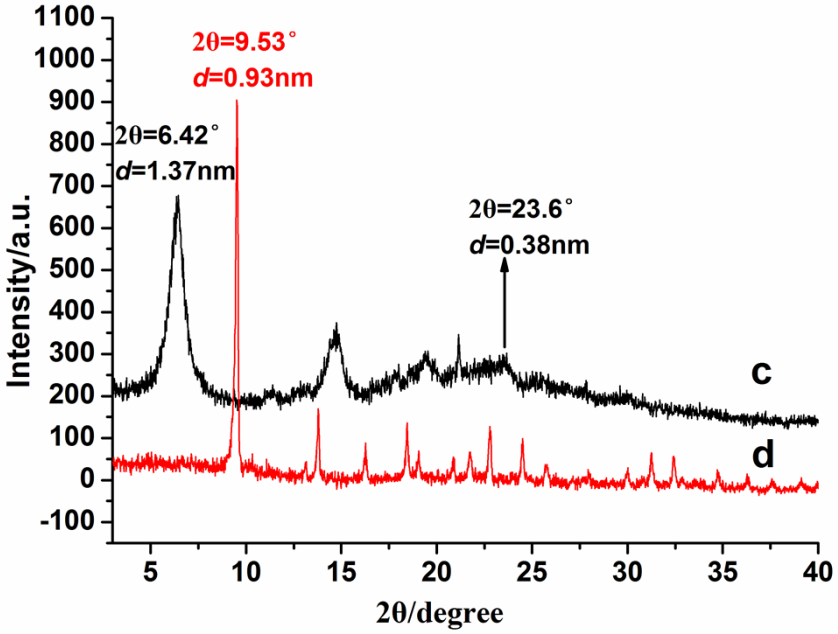



**Fig. S11** XRD pattern of the L (a) and xerogel of the B-gel (b).