Supporting information

The intelligent writable material based on supramolecular self-assembly gel

Xinxian Ma[a*], Bo Qiao[a], Yingshan Lai[a], Yutao Geng[a], Jinlong Le[a], Enke Feng[a], Xinning Han[a], Minghua Liu[b*]

a.College of Chemistry and Chemical Engineering, Ningxia Normal University, Guyuan 756000, People's Republic of China.Fax: 86 954 2079637; Tel: 86 954 2079637; E-mail: maxinxian@163.com

b.CAS Key Laboratory of Colloid, Interface and Chemical Thermodynamics, Institute of Chemistry, Chinese Academy of Sciences, Beijing, P. R. China
E-mail: liumh@iccas.ac.cn; Tel: +86-10-82615803

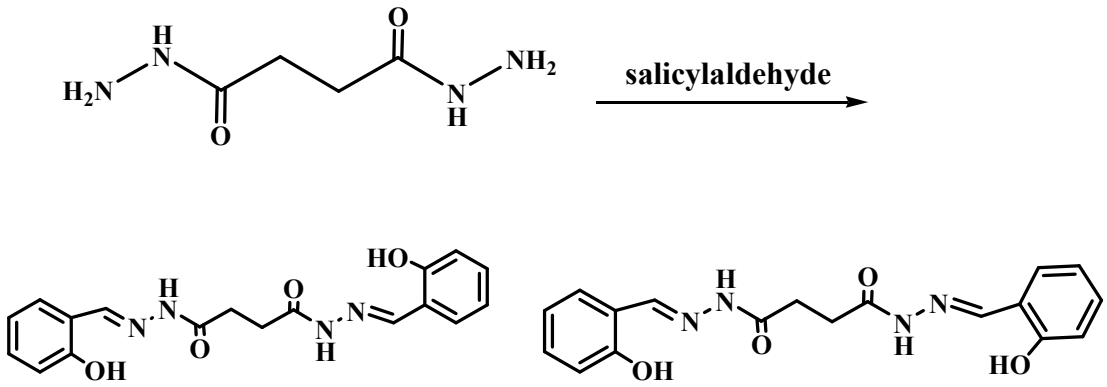
Materials

Butanedioyl dihydrazide was purchased from Shanghai Sinofluoro Scientific 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. FT-IR (Fourier transform infrared) spectra were conducted within the 4000–500cm^{-1} wavenumber range using a Nicolet 360 FT-IR spectrometer with the KBr pellet technique. The measurements of steady-state luminescence were performed with a spectrofluorimeter (HITACHI F-4500, Japan). The morphologies of the as-synthesized samples were characterized with a JSM-6701F SEM using an accelerating voltage of 5kV. All measurements were carried out at room temperature.

Synthesis of G1



Scheme S1 Synthesis of Gelator G1

Synthesis of gelator G1

The solution of Butanedioyl dihydrazide (8.00g, 0.05mol) in DMF (100mL) was mixed with Salicylaldehyde (12.21g, 0.10mol) 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 gelator G1. Yield: 17.78g (88%). Anal. calcd for $C_{18}H_{18}N_4O_4$: C 61.01, H 5.12, N 15.81. Found: C 60.99, H 5.08, N 15.77.

It is noteworthy that this G1 has two rotamers, so there are two sets of NMR signals.

Major product: ^{1}H NMR (400MHz, DMSO-D_6): δ (ppm) 11.71 (d, 1H, OH), 11.19 (d, 1H, NH), 8.35 (s, 1H, N=CH), 7.49 (d, *J* = 8.0 Hz, 1H, Ar-H), 7.26 (ddd, *J* = 16.6, 12.0, 4.5 Hz, 1H, Ar-H), 6.96-6.79 (m, 2H, Ar-H), 2.62-2.51 (m, 2H, -CH_2-).

Minor product: ^{1}H NMR (400 MHz, DMSO-D_6) of: δ (ppm) 11.29 (d, 1H, OH), 10.14 (d, 1H, NH), 8.28 (s, 1H, N=CH), 7.64(t, *J* = 7.9 Hz, 1H, Ar-H), 7.26 (ddd, *J* = 16.6, 12.0, 4.5 Hz, 1H, Ar-H), 6.96-6.79 (m, 2H, Ar-H), 2.93 (dd, *J* = 12.1, 5.2 Hz, 2H, -CH_2-).

Major product: ^{13}C NMR (100.5MHz, DMSO-D_6): δ (ppm) 172.83, 172.61, 167.72, 167.40, 157.10, 156.17, 146.34, 141.01, 130.92, 130.69, 129.32, 126.74, 119.76, 119.21, 118.36, 116.10, 28.52, 27.01.

Minor product: ^{13}C NMR (100.5MHz, DMSO-D_6): δ (ppm) 172.83, 172.61, 167.72, 167.40, 157.10, 156.17, 146.21, 140.92, 130.87, 130.63, 129.28, 126.68, 119.76, 119.03, 118.36, 115.92, 28.00, 26.33. ESI-MS: m/z $(L + H)^+$ 355.14.

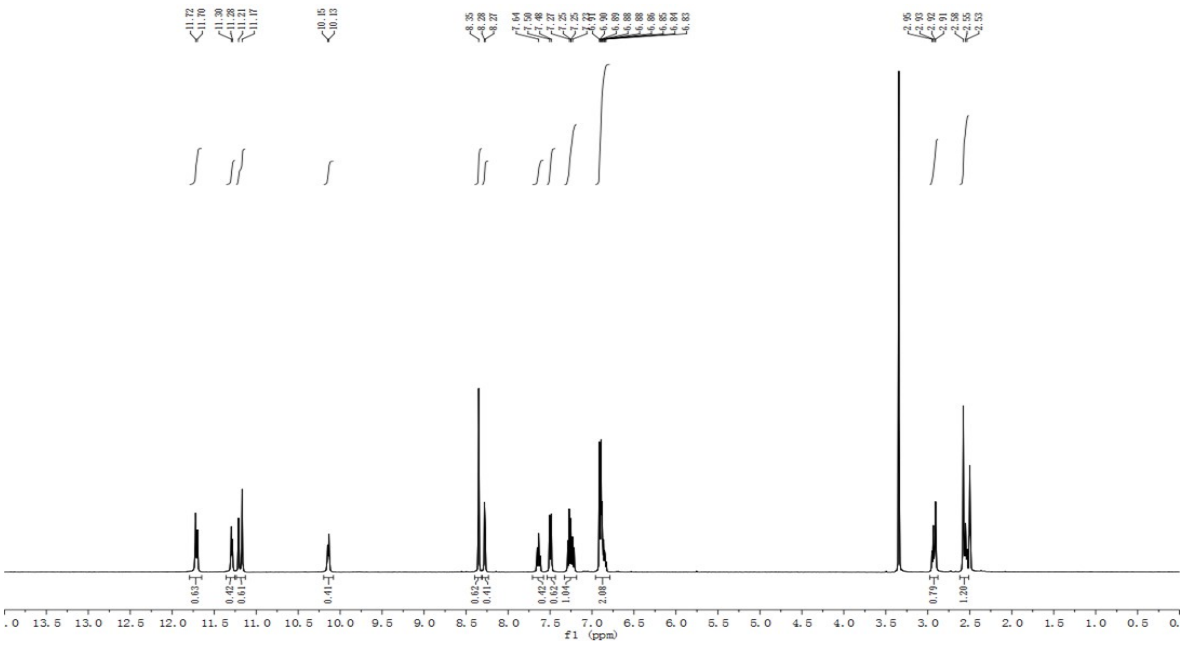


Fig. S1 ^1H NMR Spectrum of G1

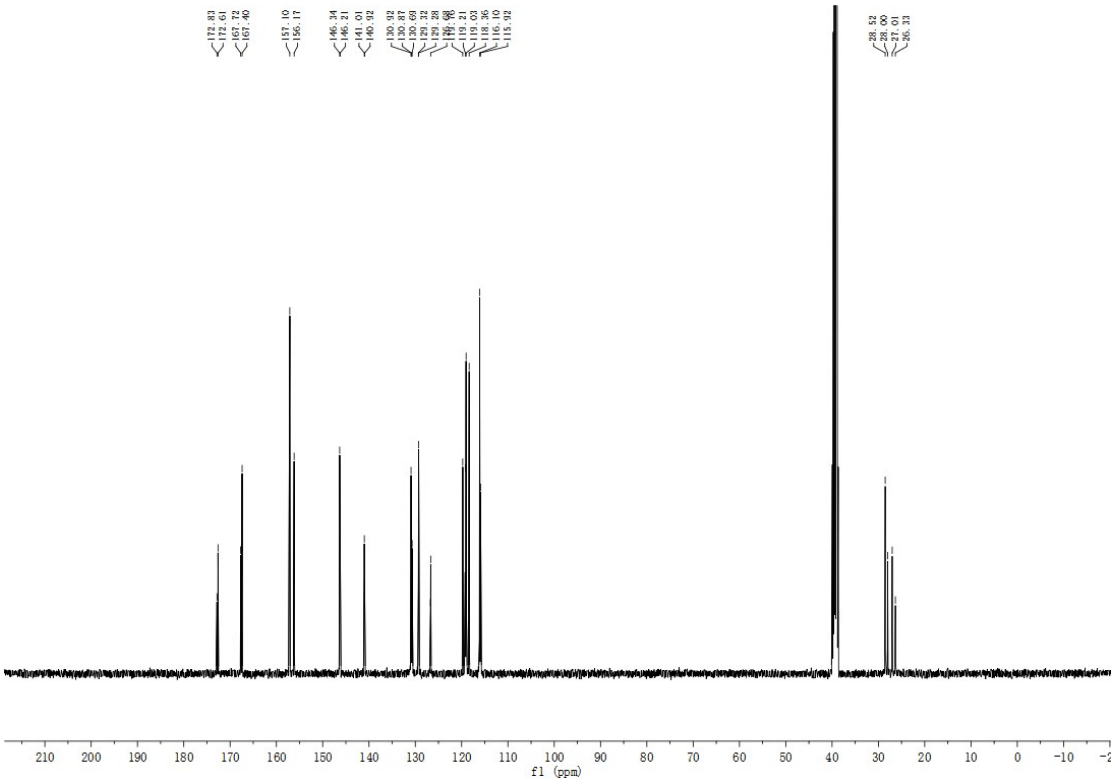


Fig. S2 ^{13}C NMR Spectrum of G1

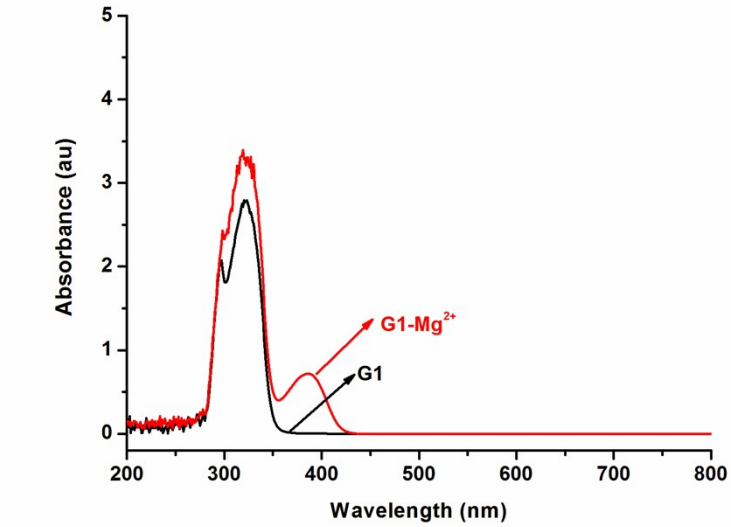


Fig. S3 UV-vis of G1 and G1-Mg^{2+} (1×10^{-4} mol L^{-1}) in DMF

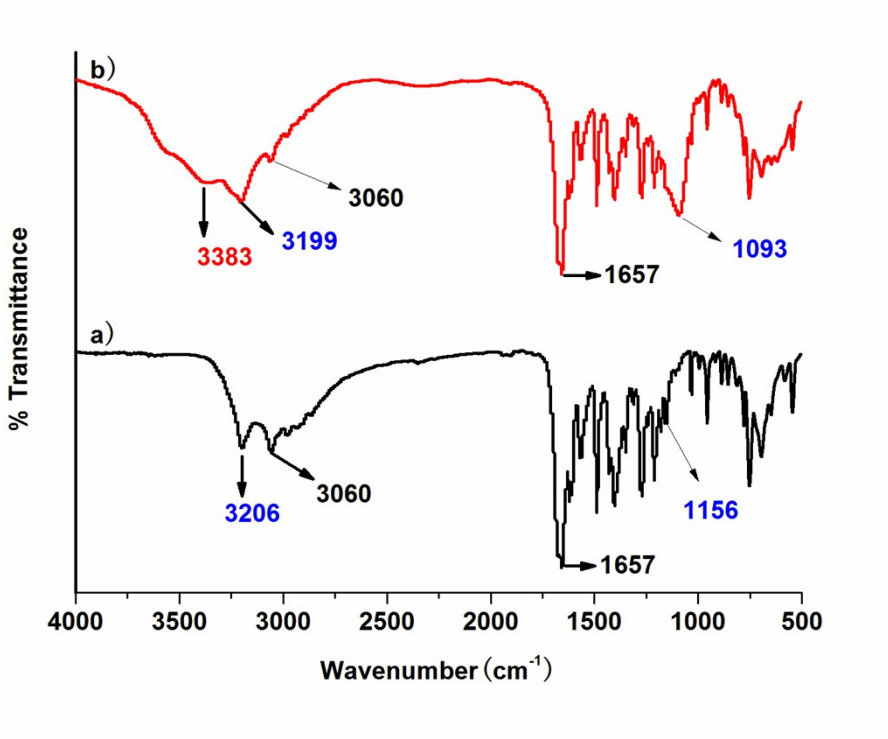


Fig. S4 FT-IR spectra of the gelator G1 (a) and G1–Mg^{2+} complex (b)

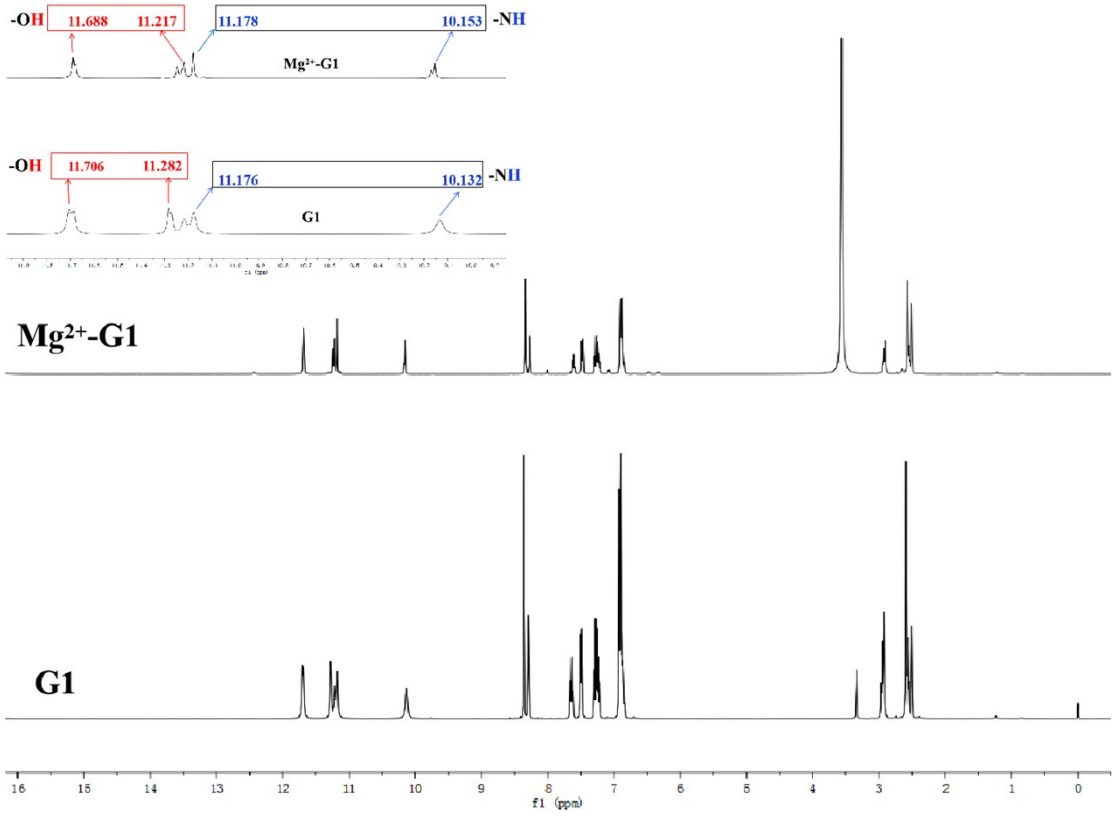


Fig. S5 ^{1}H NMR spectra of G1 and Mg^{2+}-G1 /[D_6]DMSO (60mg/mL). Inset: ^{1}H NMR spectra (O-H and N-H region) of G1 and Mg^{2+}-G1

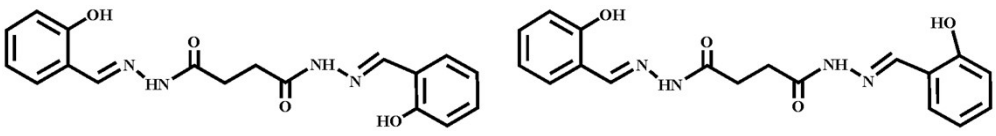


Fig. S6 Two rotamers of gelator G1

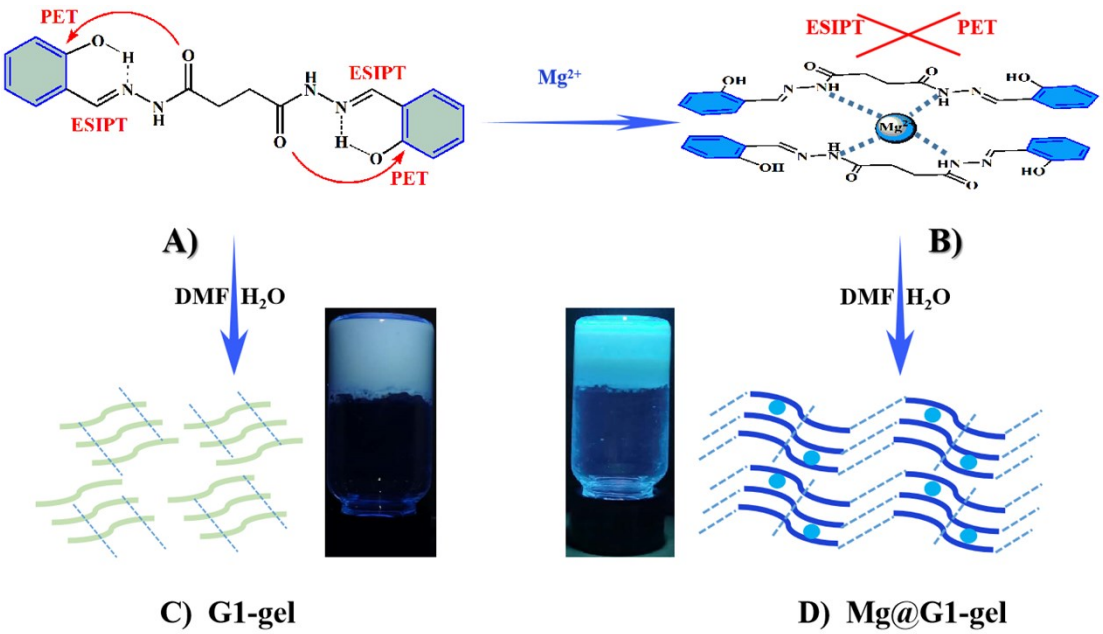


Fig. S7 The possible luminescence mechanism of the Mg@G1-gel

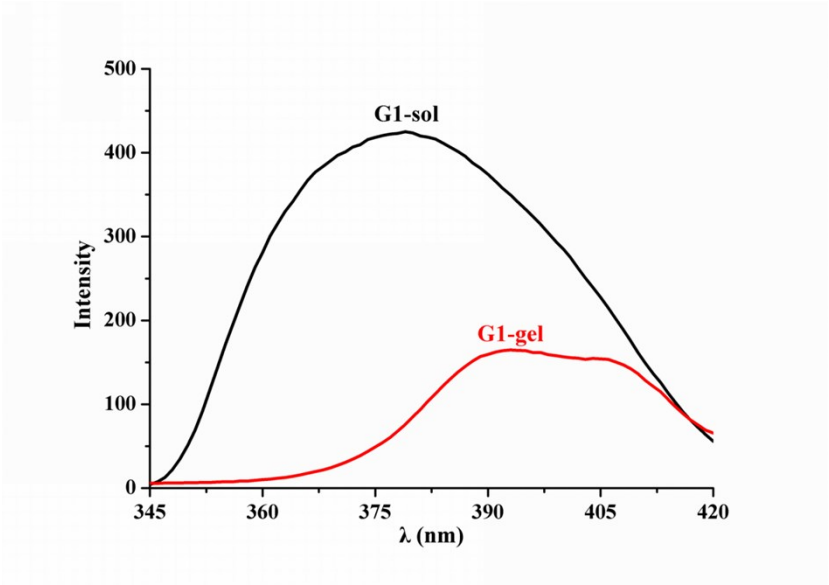


Fig. S8 Excitation spectra of G1-gel and G1-sol

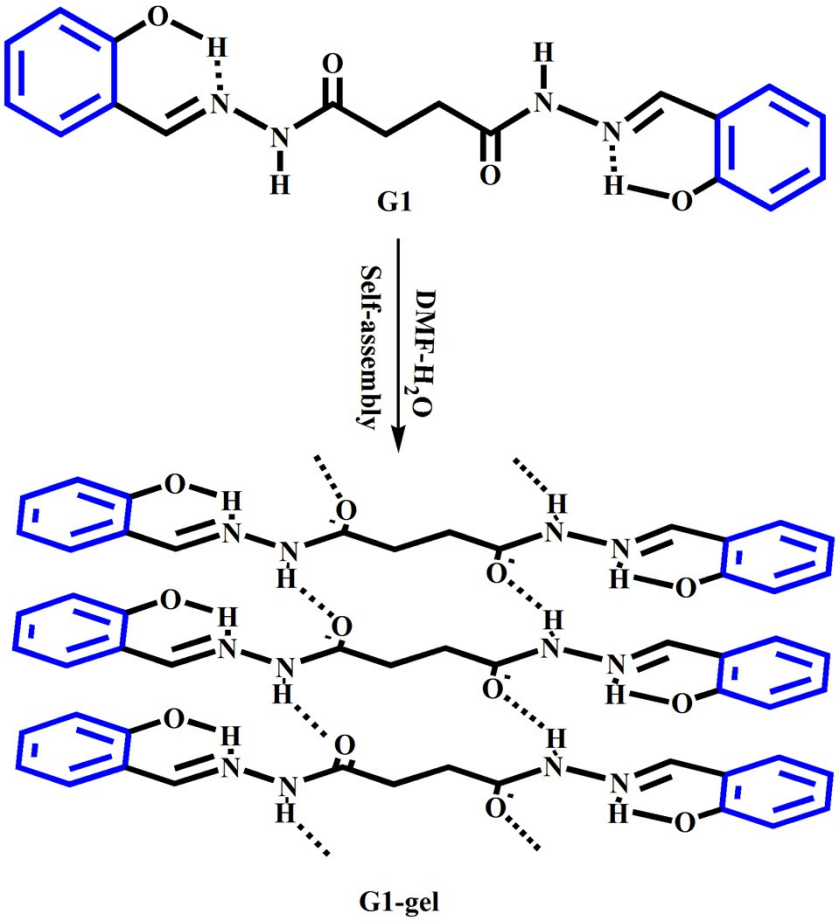


Fig. S9 Possible self-assembly mechanisms of G1-gel

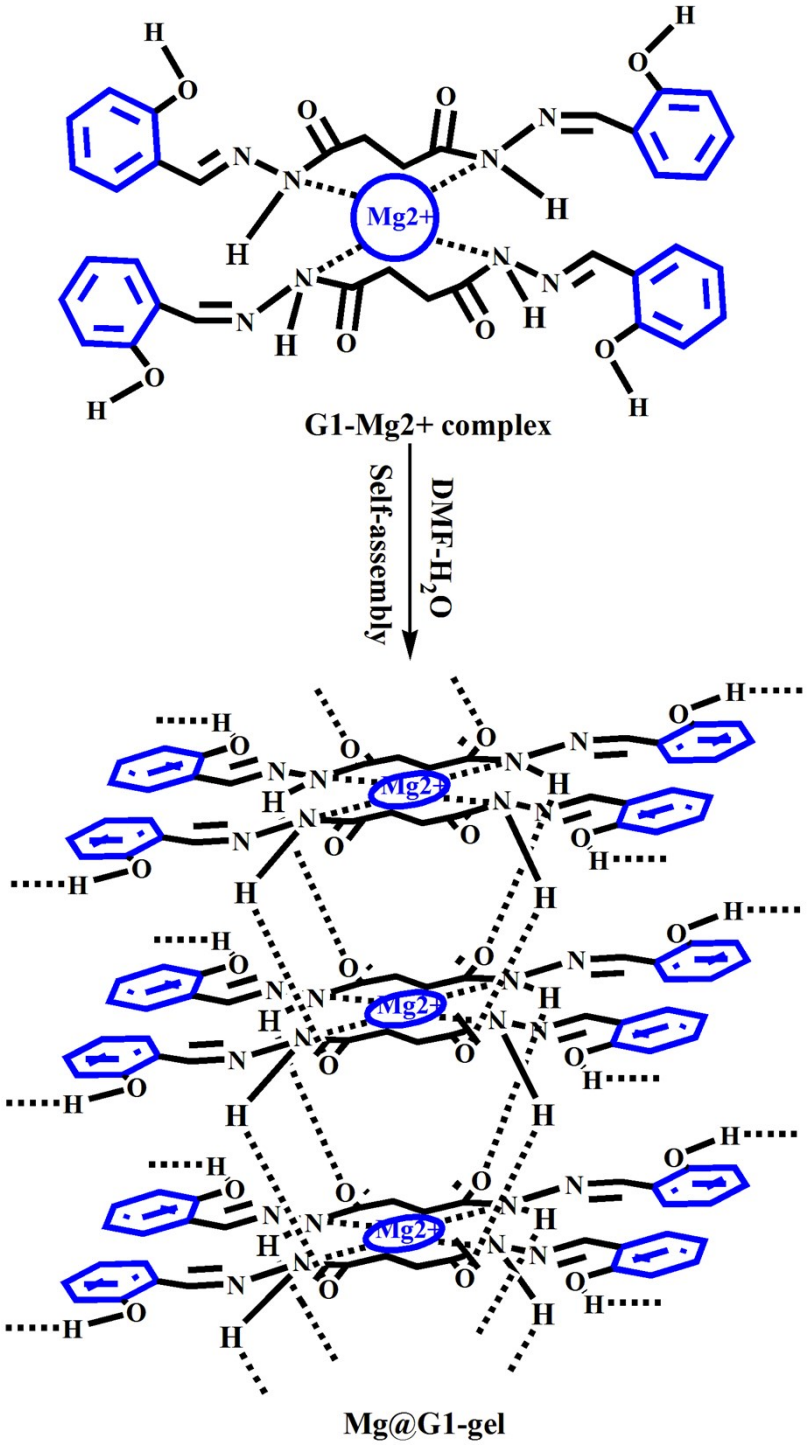


Fig. S10 Possible self-assembly mechanisms of Mg@G1-gel

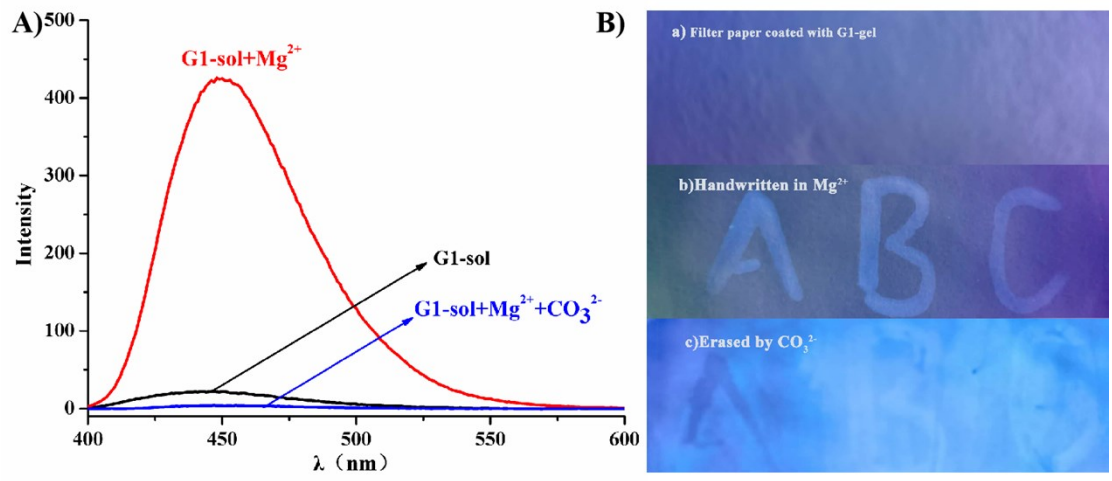


Fig. S11 (A) Fluorescence spectras of G1-sol, G1-sol+Mg^{2+} and G1-sol+Mg^{2+}+CO_3^{2-} (The concentration of G1 in the sample is 1×10^{-4} mol L^{-1}); (B)Photos of filter paper strip coated with G1-gel (a), handwriting with Mg^{2+} (b), handwriting of Mg^{2+} is erased by CO_3^{2-} (c)