Naphthalimide-based fluorescent gelator for construction of both organogel and stimuli-responsive metallogel

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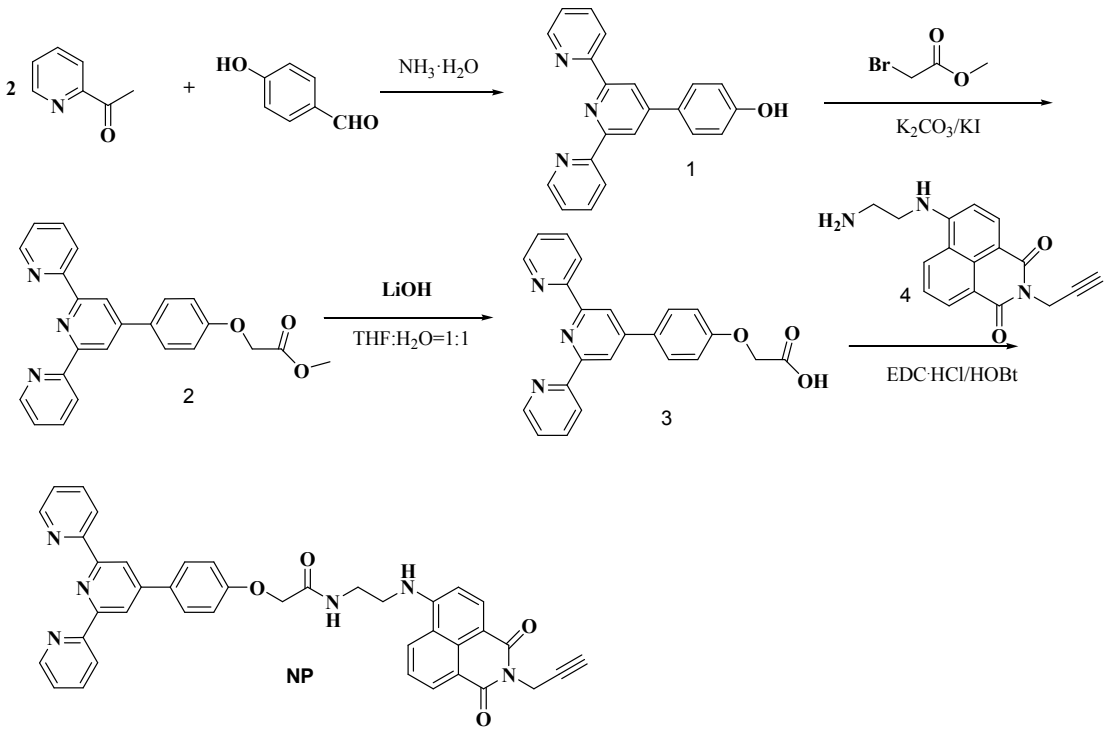

Scheme 1 the synthesis procedure of **NP**.

Synthesis of **1** (the synthesis of 1 was prepared from literature: Wang S X, Chu W H, Wang Y C, et al. Appl. Organometal. Chem. 2013，27，373-379).

Methyl 2-pyridyl ketone (4.48 g, 3.7 mmol) and KOH (4.2 g) were stirred for 30 min, then hydroxy benzaldehyde (2.44 g, 1.85 mmol) and 50 mL ammonium hydroxide were added. The reaction mixture was refluxed for 10 h, khaki solid (1.97g, yield: 16.35%) was obtained when the mixture was neutralized by HCl.

Synthesis of **2**

Compound **1** (1g, 3.1 mmol), methyl bromoacetate(0.47 g, 3.1 mmol), 0.85 g K_2CO_3(6.2 mmol) and 0.1 g KI were refluxed in acetone for 10 h. The reaction mixture was concentrated and purified by column chromatography (dichloromenthane/methanol, 10/1, v/v), white yellow solid was obtained (0.25 g, 22%). ^{1}H NMR (500M, $CDCl_3$, δ): 3.84 (s, 3H), 4.72 (s, 2H), 7.03-7.05(d, 2H, J=8.5 Hz), 7.34-7.36 (m, 2H), 7.87-7.89(d, 2H, J=8.5 Hz),8.66-8.72 (m, 6H).

Synthesis of **3**

Compound **2** (0.8 g, 2mmol) and LiOH (0.26 g, 10 mmol) were stirred in solvent mixture of THF and water (50 mL, v:v=1:1) for 72 h, the reaction mixture was concentrated and neutralized by HCl to pH=1-2, the filtrate was directly utilized without further purification (0.16g, yield: 20%).

^{1}H NMR (500M, $CDCl_3$, δ): 4.63(s, 2H), 7.08-7.09(d, 2H, J=8Hz), 7.51-7.54 (m, 2H), 7.87-7.88 (d, 2H, J=8.5 Hz), 8.02-8.05 (m, 2H), 8.66-8.67 (m, 4H), 8.76-8.77 (d, 2H, J=4 Hz).

Synthesis of **4**

The synthesis procedure of 4 could be seen from our previous literature 15 in the main context.

Synthesis of **NP**

Compound **3** (0.6 g, 1.6 mmol), EDC·HCl (920 mg, 4.8 mmol), HOBt (649 mg, 4.8 mmol), and 3mL Et_3N were stirred in $CHCl_3$ for 24 h, then the reaction mixture was concentrated and purified by column chromatography (dichloromenthane/methanol, 30/1, v/v), yellow solid was obtained (0.84 g, yield: 81%). Mp: 289-291°C. ^{1}H NMR (500M, DMSO-d_6, δ): 3.16-3.17 (2H, J=5.5 Hz), 3.51-3.54 (m, 2H), 4.07-4.10 (t, 1H), 4.62-4.63 (d, 2H, J=2 Hz), 4.64 (s, 2H), 6.80-6.90(1H, J=8.5 Hz), 7.13-7.15 (2H, J=8 Hz), 7.52-7.54 (t, 2H, J=5.5 Hz), 7.65-7.69 (t, 1H, J=8.5 Hz), 7.77-7.80(m, 3H), 8.03-8.06(t, 2H, J=7.5 Hz), 8.26-8.28 (d, 1H, J=8.5 Hz), 8.36-8.37(d, 1H, J=7.5 Hz), 8.54-8.57 (m, 2H), 8.66-8.67 (d, 2H, J=8 Hz),8.75-8.76 (2H, d, J=4.5 Hz). ^{13}CNMR (125 M, DMSO-d6): 30.7, 54.9, 115.5, 117.2, 120.9, 124.5, 128.1, 137.5, 142.0,149.3, 150.9, 155.0, 156.9, 155.5, 158.8, 161.9, 168.4, 206.6. MS calc. for $[C_{40}H_{31}N_6O_4+H]^+$: 659.2; Found: 659.3.

Table S1 The gelation properties of NP (25 mg/mL) in organic solvents.

Solvent	H-C	U
$CHCl_3$	I	I
methanol	I	I
ethanol	I	I
butanol	P	G
acetone	I	I
toluene	I	I
THF	P	G
DMSO	S	S
1,4-dioxane	P	G
2-methoxyethanol	P	G

Table S2 The gelation properties of **NP** (25 mg/mL) upon the addition of metal ions (with molecular ratio of 1:1) in 2-methoxyethanol.

ions	r.t.	H-C
$CaCl_2$	I	G
$MgCl_2$	I	S
$FeCl_2$	I	G
$Cd(OAc)_2$	G	G
$Cu(OAc)_2$	G	G
$HgCl_2$	I	I
$CuSO_4$	I	G
$ZnCl_2$	I	I

Note: P, precipitate; G, gel; S, solution; I: insoluble;

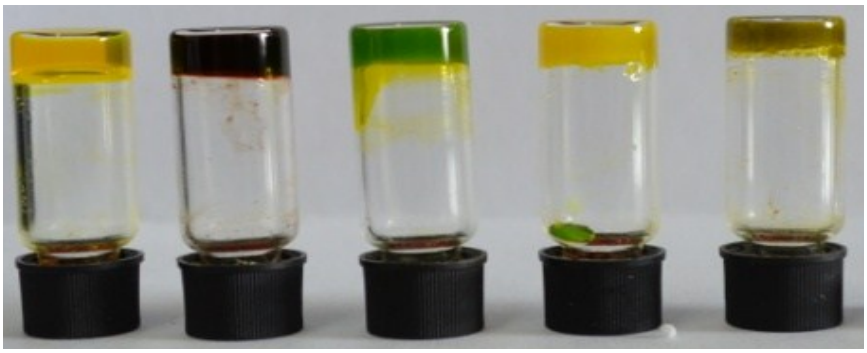

Fig. S1 Photos of the gels in 2-methoxyethanol, from left to right: **NP**/$Cd(OAc)_2$ metallogel; **NP**/$FeCl_2$ metallogel; **NP**/$Cu(OAc)_2$ metallogel; **NP** organogel; **NP**/$CuSO_4$ metallogel. Molecular ratios of **NP** and metal salts was 1:1.

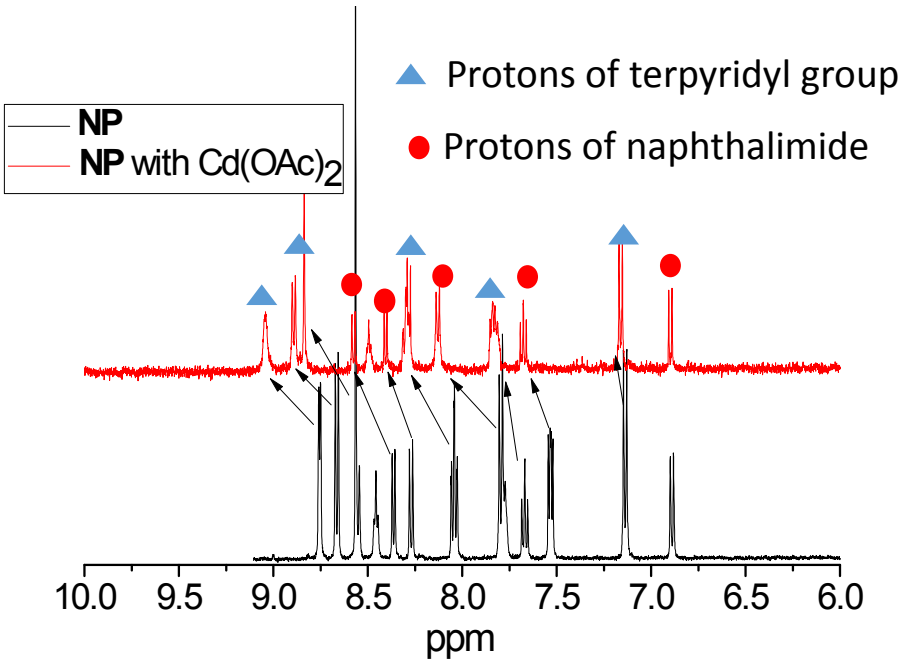

Fig. S2 ^{1}H NMR spectra of **NP** solution (8 mg/mL) and **NP** solution with the addition of $Cd(OAc)_2$. Upon the addition of $Cd(OAc)_2$, most Hs of the terpyridine and naphthalimide segment showed downfield shift, indicating the coordination interaction.

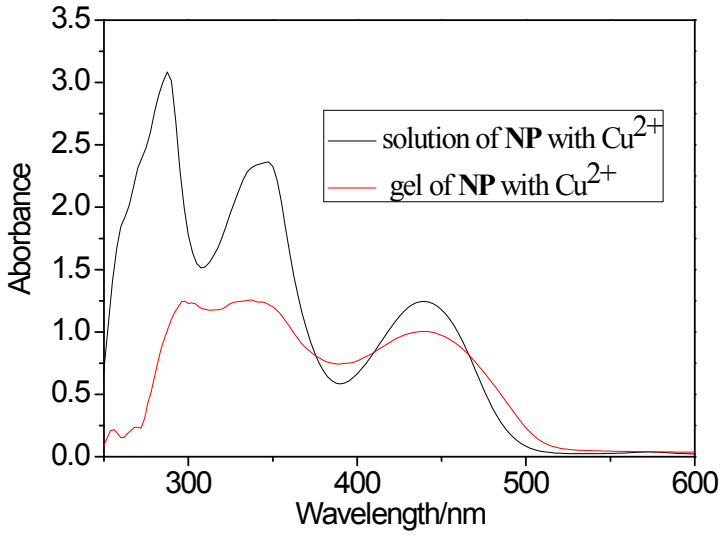

Fig. S3 UV-vis spectra of **NP**/Cu(OAc) gel (**NP**: 25 mg/mL, with molecular ratio of 1:1).

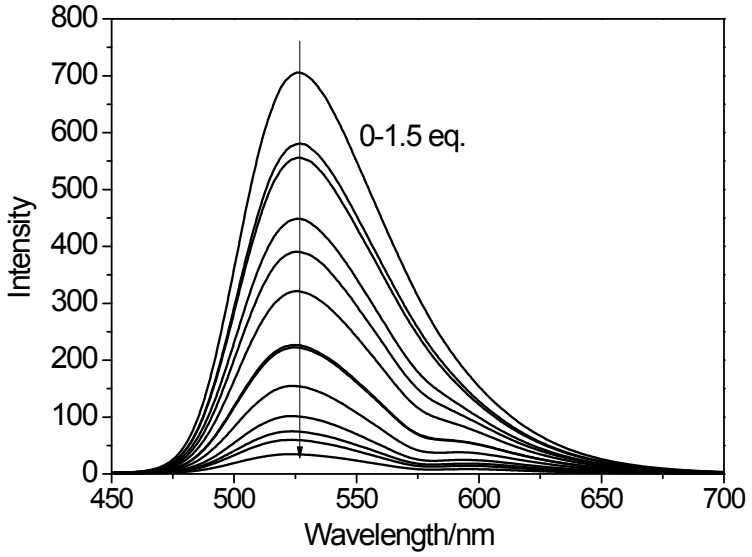

Fig. S4 Fluorescent titrations of **NP** (10^{-5} M) upon the addition of $FeCl_2$.

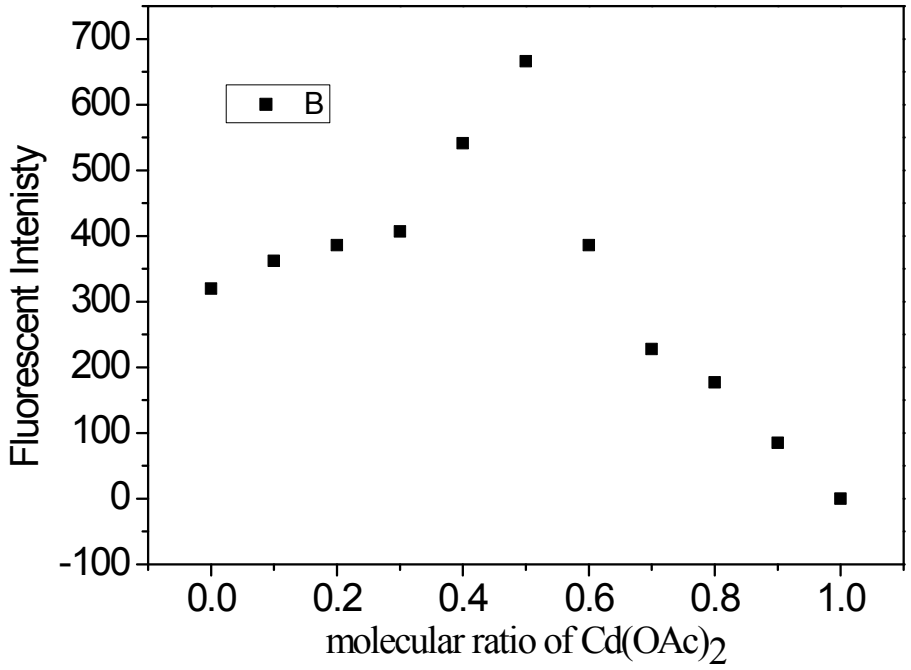

Fig. S5 Job plot experiments of NP with $Cd(OAc)_2$, the total concentration of NP and $Cd(OAc)_2$ was 10^{-4} M.

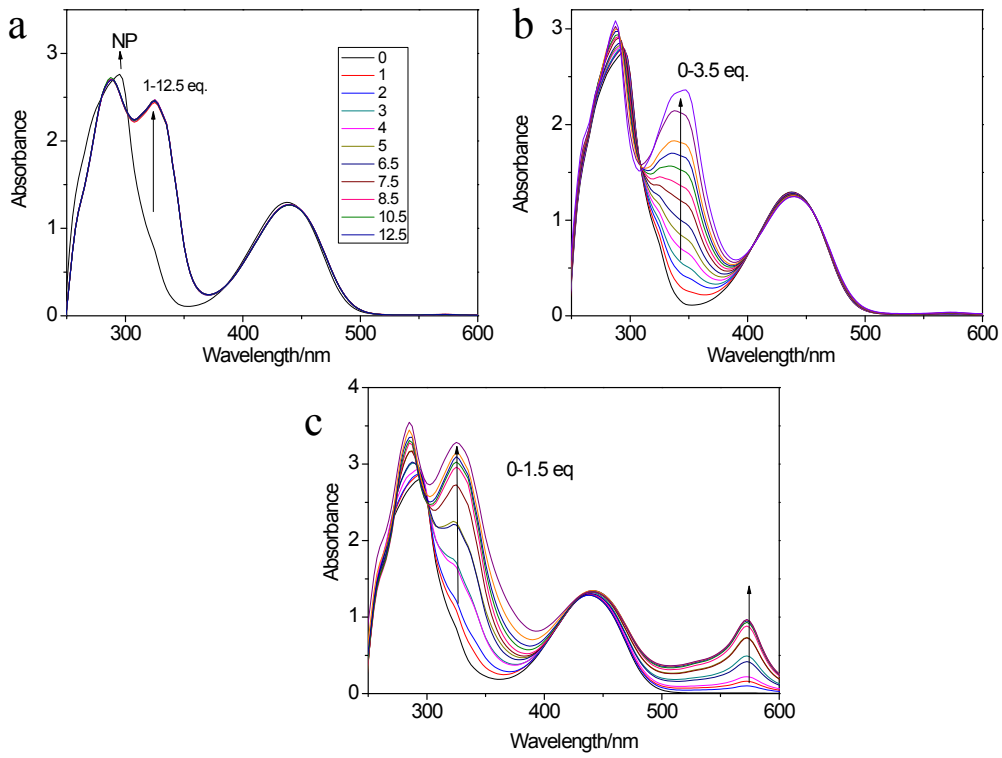

Fig. S6 UV-vis titration of **NP** upon the addition of metal ions. a) Upon the addition of $Cd(OAc)_2$ ion; b) Upon the addition of $Cu(OAc)_2$ ion; c) Upon the addition of $FeCl_2$ ion.

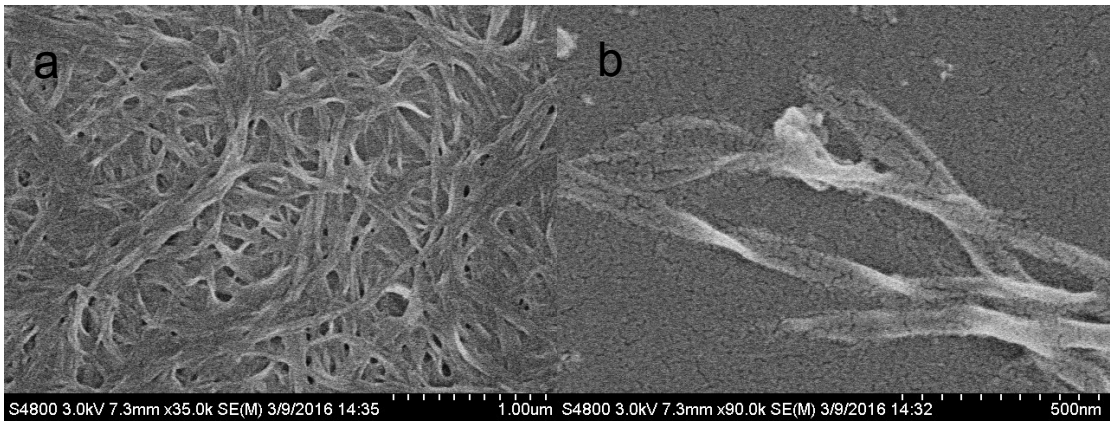

Fig. S7 SEM images of **NP** xerogel from 1, 4-dioxane. b) was the magnification picture of a).

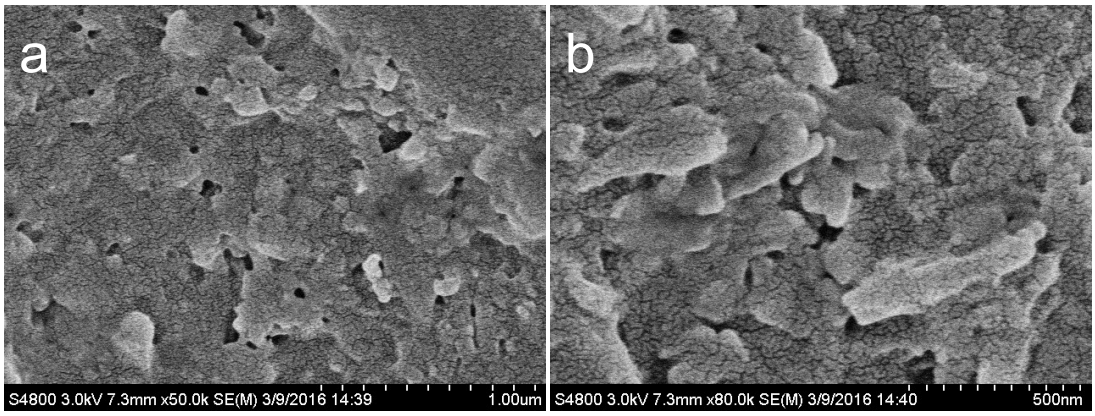

Fig. S8 SEM images of **NP** xerogel from butanol. b) was the magnification picture of a).

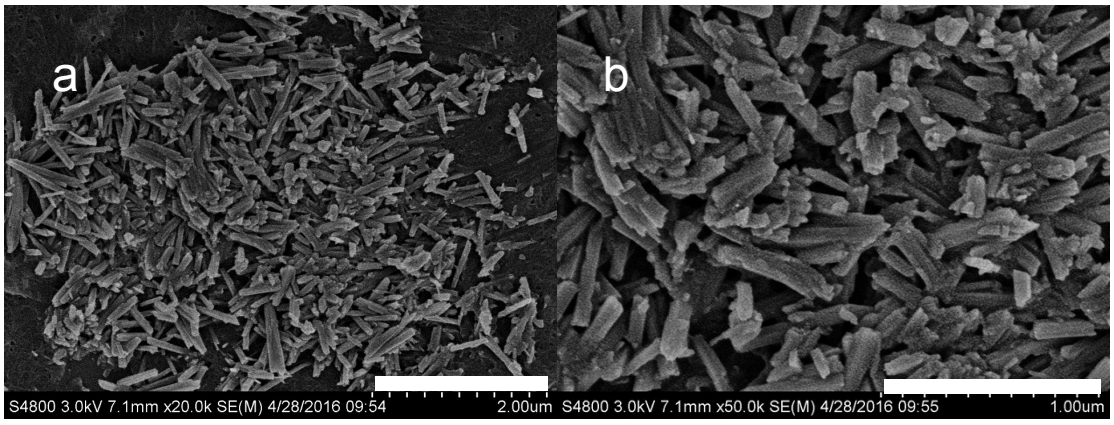

Fig. S9 SEM image of **NP**/$FeCl_2$ metallogel. b) was the magnification picture of a). Scale bar: 2 μm; 1 μm.

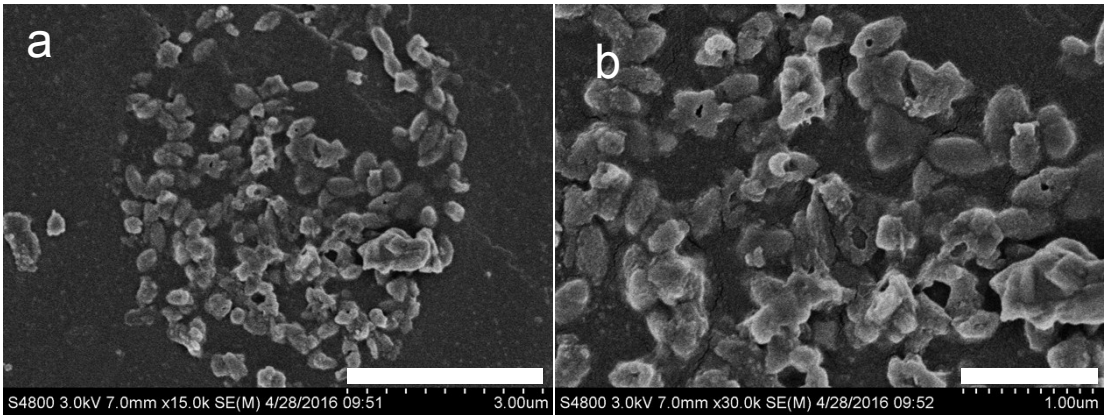

Fig. S10 SEM image of **NP**/$CaCl_2$ metallogel. b) was the magnification picture of a).

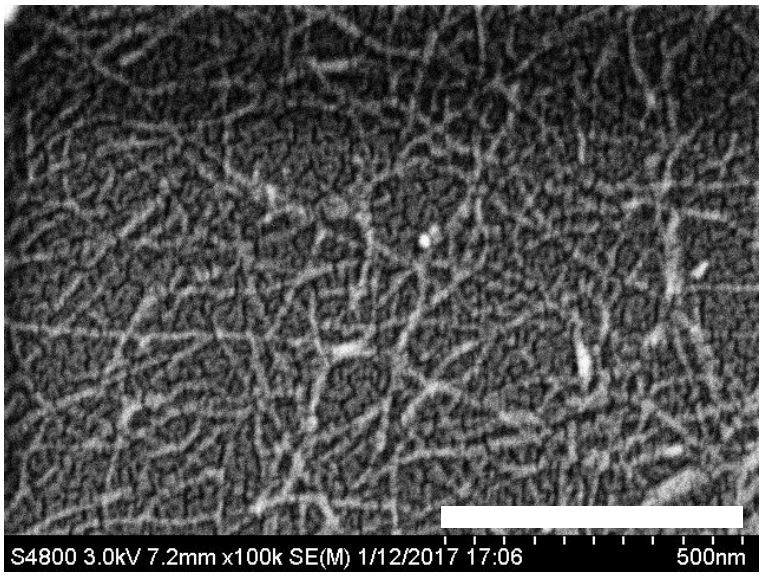

Fig. S11 SEM image of **NP**/$Cu(OAc)_2$ metallogel. Scale bar: 500 nm.

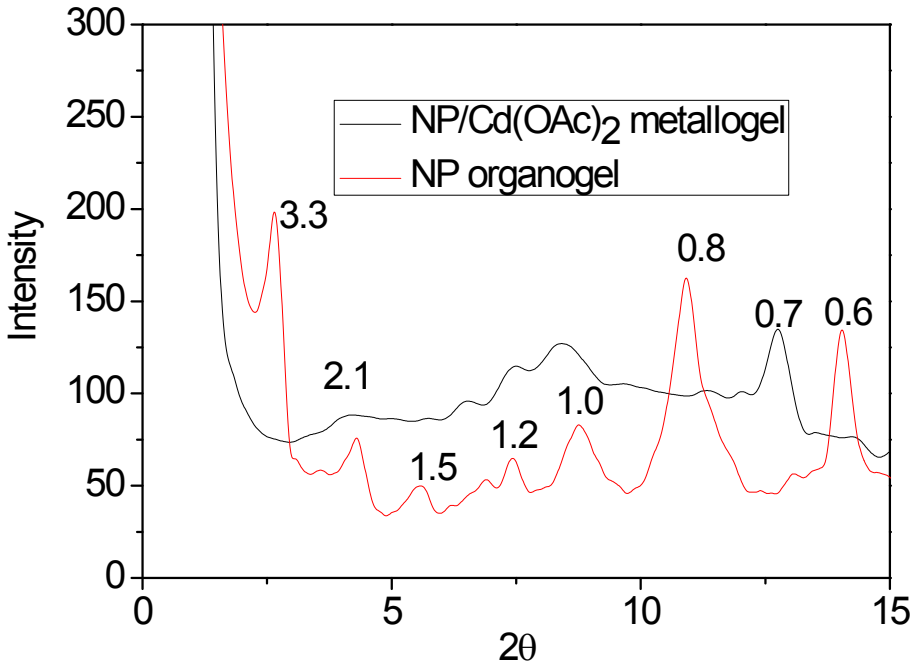

Fig. S12 XRD data of **NP** organogel and **NP**/$Cd(OAc)_2$ metallogel.

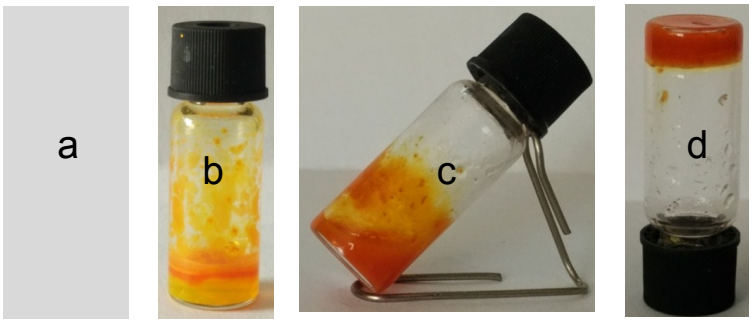

Fig. S13 the reversible phase changes of **NP**/$Cd(OAc)_2$ gel controlled by Na_2S and $AgNO_3$. a) **NP**/$Cd(OAc)_2$ gel; b) upon the addition of Na_2S for 10 min; c) upon the addition of Na_2S for 1 h; d)

upon further addition of $AgNO_3$.

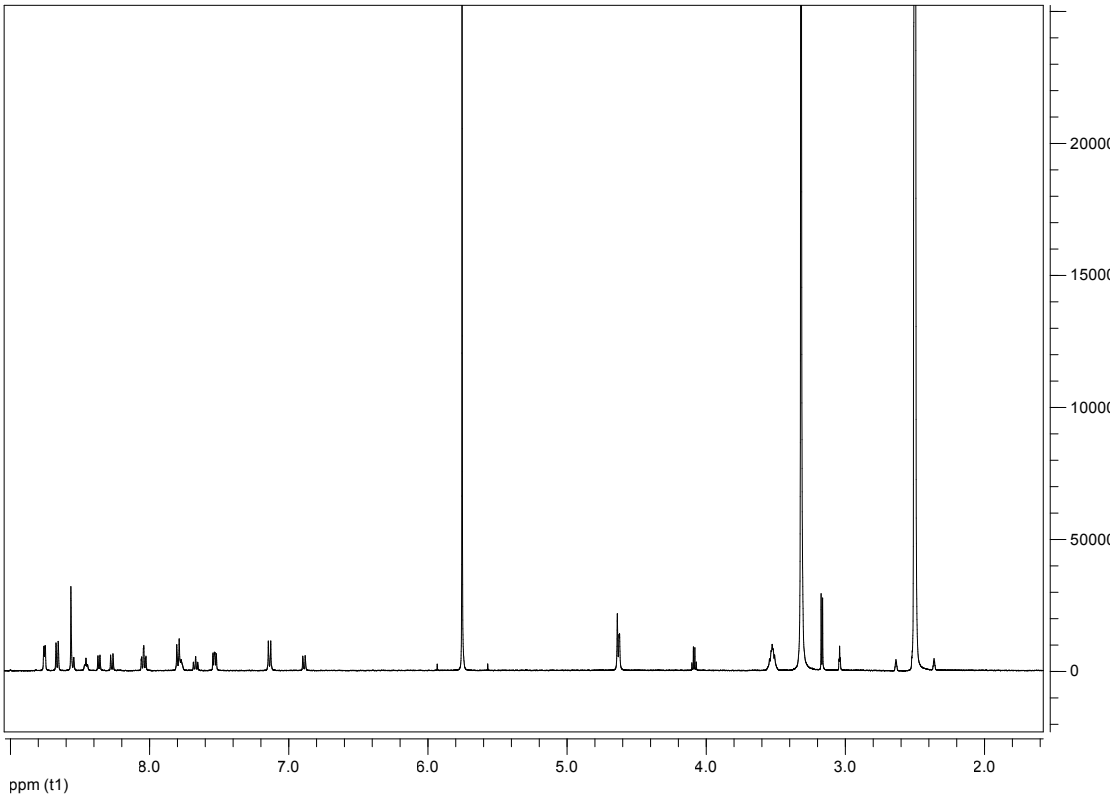

Fig. S14 ^{1}H NMR spectrum of **NP in DMSO-*d*$_6$**.

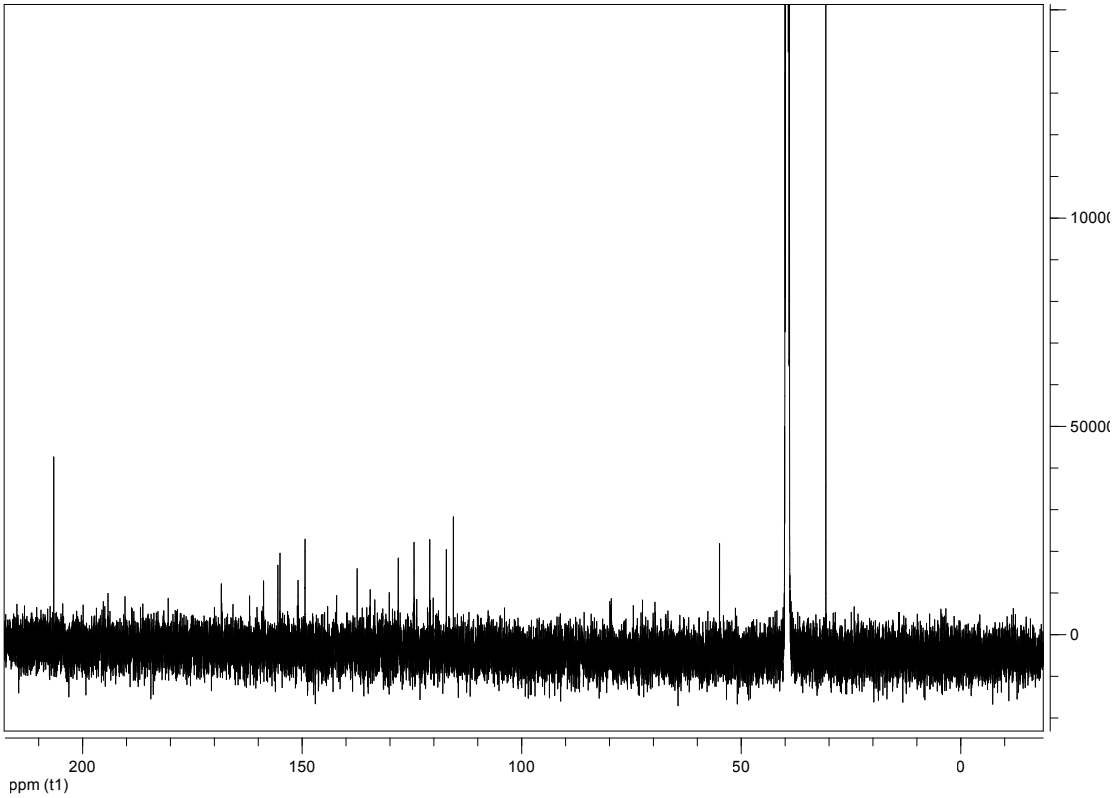

Fig. S15 ^{13}C NMR spectra of **NP**.

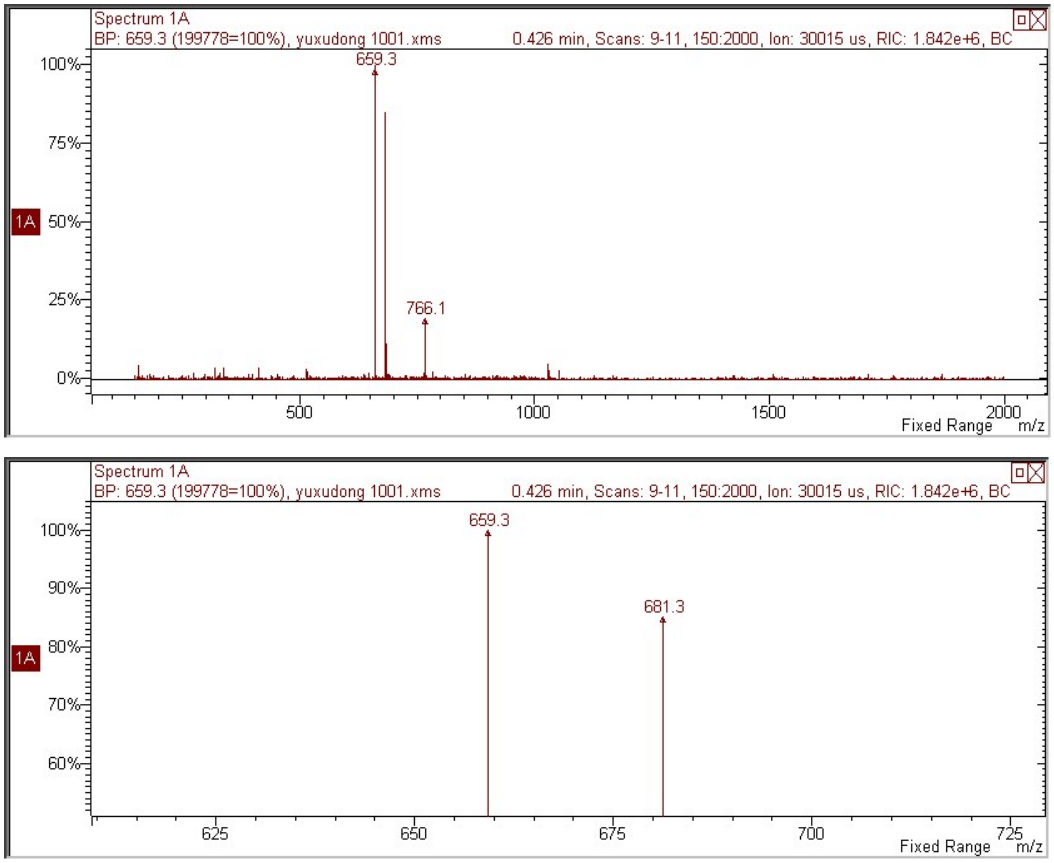

Fig. S16 MS spectrum of **NP**.