Electronic Supplementary Information

Competitive Coordination Control the AIE and Micro States of Supramolecular Gel: an Efficient Approach for Reversible Dual-Channel Stimuli-Response Materials

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Materials and instruments

All reagents and starting materials were obtained from commercial suppliers and used as received unless otherwise noted. All anions water solution were obtained from their sodium salts or potassium salts respectively, while all cations solution were obtained from their perchlorate salts, which were purchased from Alfa Aesar and used as received. Fresh double distilled water was used throughout the experiment. Nuclear magnetic resonance (NMR) spectra were recorded on Varian Mercury 400 and Varian Inova 600 instruments. Mass spectra were recorded on a Bruker Esquire 6000 MS instrument. The X-ray diffraction analysis (XRD) was performed in a transmission mode with a Rigaku RINT2000 diffractometer equipped with graphite monochromated CuKa radiation (λ = 1.54073 Å). The morphologies and sizes of the xerogels were characterized using field emission scanning electron microscopy (FE-SEM, JSM-6701F) at an accelerating voltage of 8 kV. The infrared spectra were performed on a Digilab FTS-3000 Fourier transform-infrared spectrophotometer. Melting points were measured on an X-4 digital melting-point apparatus (uncorrected). Fluorescence spectra were recorded on a Shimadzu RF-5301PC spectrofluorophotometer. Elemental analyses were performed by Thermo Scientific Flash 2000 organic elemental analyzer.
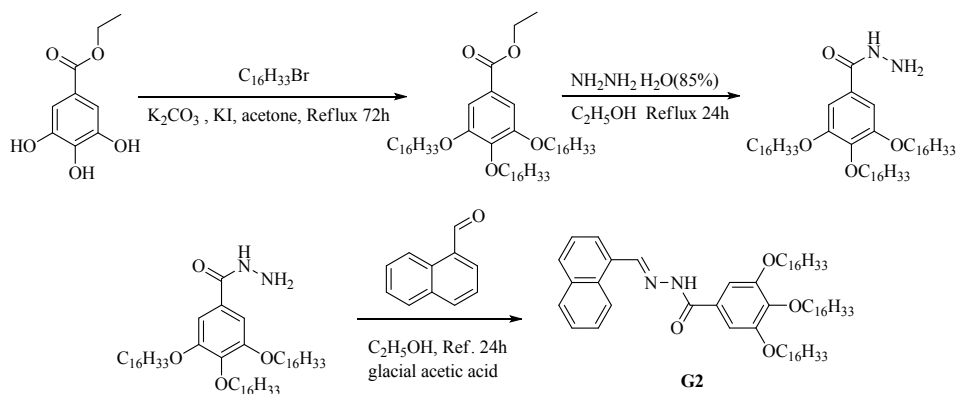
Scheme S1 The synthetic route of organogelator **G2**.

Synthesis of gelator G2

Compounds 3,4,5-tris(hexadecyloxy)benzo-hydrazide were synthesized according to literatures methods.[1] **G2** was synthesized as follow: 1-naphthaldehyde (1 mmol), 3,4,5-tris(hexadecyloxy)benzohydrazide (1 mmol) and acetic acid (0.1 mL, as a catalyst) were added to ethanol (20 mL). Then the reaction mixture was stirred under refluxed conditions for 24 hours, after removing the solvent, yielding the precipitate of **G2**. Recrystallized with $CHCl_3$-C_2H_5OH to get solid of **G2**.

Characterization of G2: Yield: 75%, m.p. 89-91℃ ^1H NMR (CDCl$_3$, 400 MHz): δ, 9.77 (s, 1H,-NH), 9.04 (s, 1H, -N=CH), 8.85 (d, J = 6.4 Hz, 1H, -ArH), 7.99 (s, 1H, ArH), 7.87 (t, J = 7.8 Hz, 2H, -ArH), 7.51-7.45 (m, 3H, -ArH), 7.11 (s, 2H, -ArH), 3.98 (t, J = 6.4 Hz, 6H, -OCH$_2$), 1.77 (t, J = 6.9 Hz, 6H, -OCH$_2$CH$_2$), 1.43~1.25 (m, 72H, -CH$_2$), 0.88 (t, J = 6.2 Hz, 9H, -CH$_3$). ^{13}C NMR (CDCl$_3$, 600 MHz): 166.95, 152.78, 142.26, 141.34, 107.87, 133.80, 131.10, 130.71, 129.06, 128.82, 127.74, 127.37, 127.00, 126.19, 125.26, 124.60, 107.87, 105.91, 105.12, 73.56, 73.45, 69.39, 69.11, 68.92, 31.93, 30.34, 30.23, 29.73, 29.67, 29.38, 29.28, 29.17, 26.09, 22.70, 14.13. IR (KBr, cm^{-1}) v: 3450 (N-H), 1717(C=O), 1649 (C=N); MS-ESI calcd for $C_{66}H_{111}N_2O_4$ [**G2** + H]$^+$: 995.8544; found: 995.8096.

Table S1 Gelation Property of Organogelator **G2**.

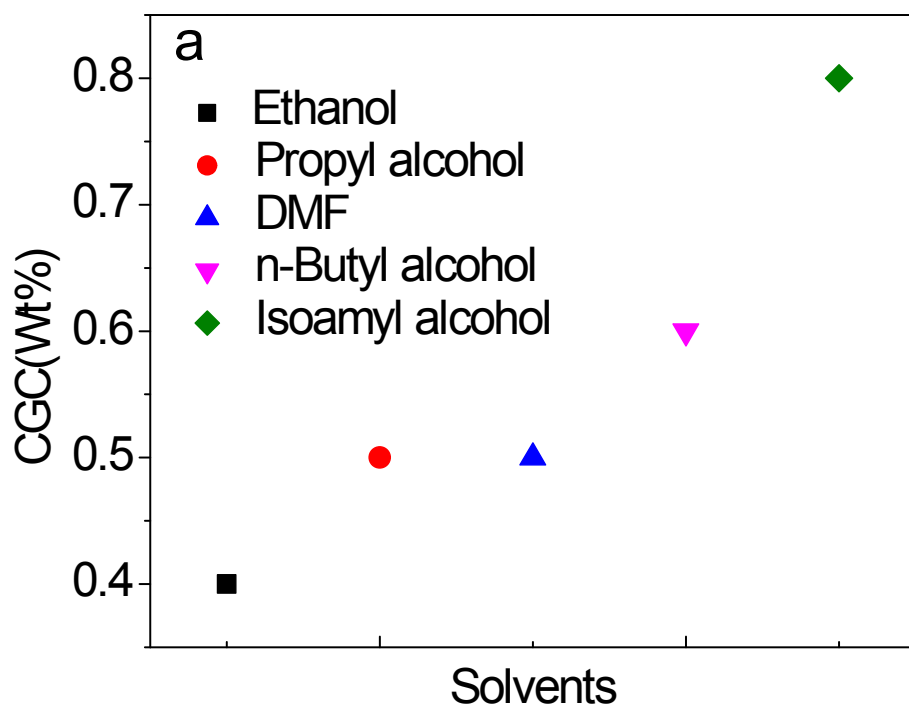| Entry	Solvent	State[a]	CGC[b]	T_{gel}[c] (℃, wt%)
1	Cyclohexane	S	\	\
2	Toluene	S	\	\
3	Petroleum ether	P	\	\
4	THF	S	\	\
5	Chloroform	S	\	\
6	Dichloromethae	F	\	\
7	Acetone	F	\	\
8	Acetonitrile	S	\	\
9	DMF	G	0.6	45(1%)
10	DMSO	P	\	\
11	Methanol	F	\	\
12	Ethanol	G	0.4	69(1%)
13	Ethanediol	F	\	\
14	Propyl alcohol	G	0.5	50(1%)
15	Isopropanol	F	\	\
16	n-Butyl alcohol	G	0.6	60(1%)
17	n-Amyl alcohol	PG	\	\
18	Isoamyl alcohol	G	0.8	52(1%)
19	Hexyl alcohol	PG	\	\

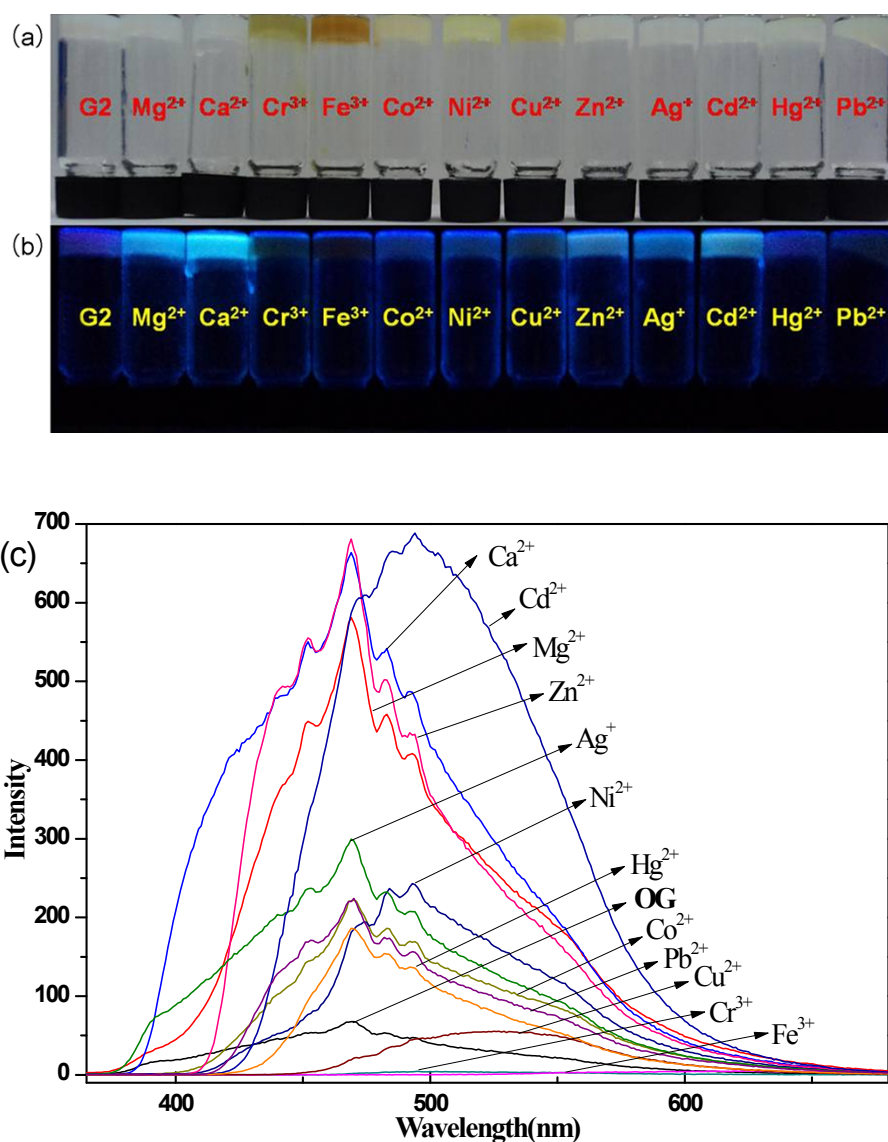**Fig. S1** Plots of CGCs of **G2** (1%) in the different solvents.

Fig. S2 (a) & (b) Photographs of organogel of **G2** in ethanol (1% w/v) and organogels of **G2** in the presence of various metal ions (in ethanol, 1%, w/v, using their perchlorate salts as the sources, **G2**: cation =1 : 1) under (a) room (b) UV light; (c) Fluorescence spectra of organogel of **G2** (**OG**) in ethanol (1%, w/v) and organogels of **G2** in the presence of various metal ions (in ethanol, 1%, w/v, using their perchlorate salts as the sources, **G2**: cation =1 : 1, λ_{ex} = 350 nm).

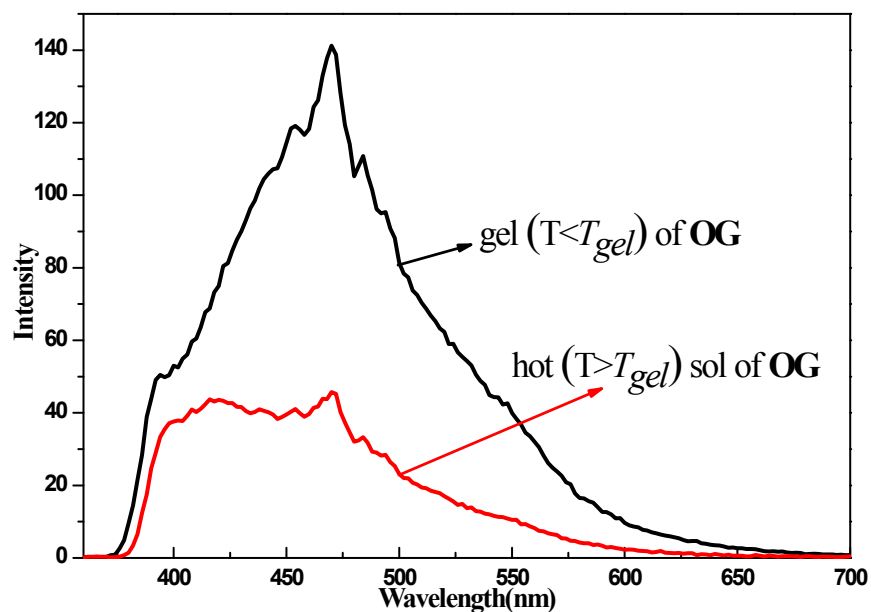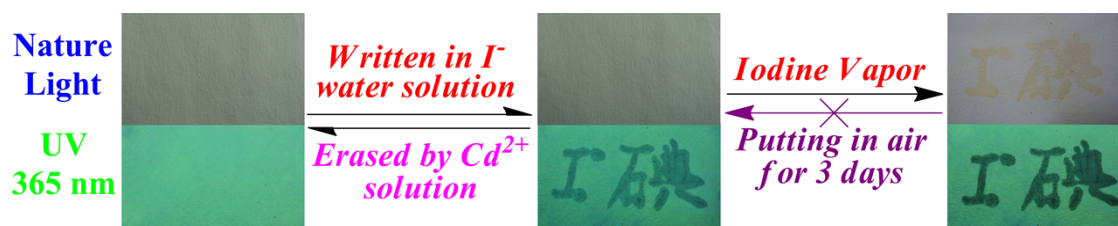**Fig. S3** Temperature-dependent fluorescent spectra of the **OG.**

Fig. S4 Writing, erasing and coloration of a nature light invisible image on a **CdG** supramolecular polymer based-paper (obtained by immerging filter paper in hot solution of 1% ethanol metallogel **CdG**, **G2** : Cd^{2+} = 1 : 1. Writing: written in I^- water solution; erasing: brushed *by* Cd^{2+} water solution; coloration: exposing the **CdG** film into the iodine vapour ca. 5 sec.) The photographs were taken at room temperature under room light and exposure to a 365-nm ultraviolet light.
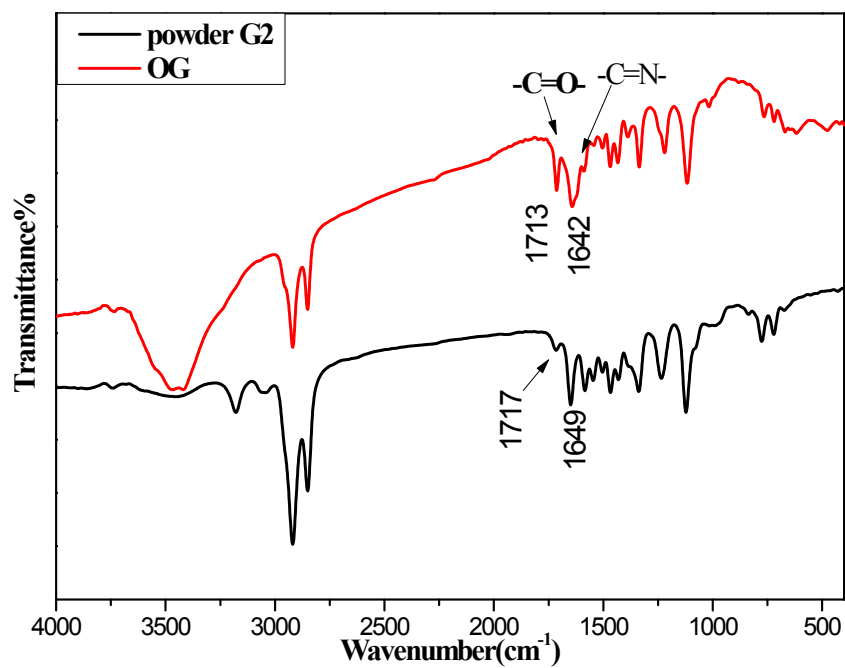
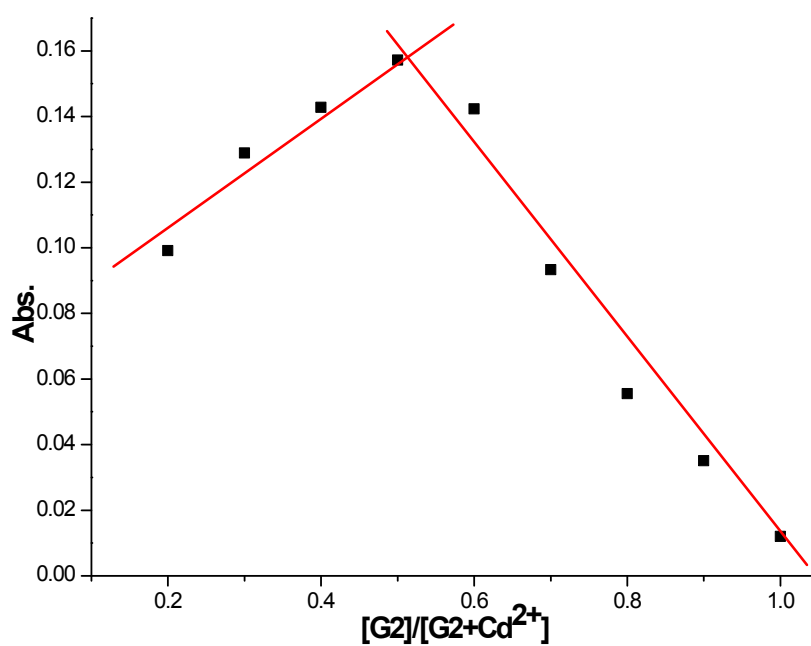**Fig. S5** FT-IR spectra of powdered **G2** and xerogel of organogel **OG**.

Fig. S6 Job's plot of **G2** and Cd^{2+}, which indicated the stoichiometry of **G2**–Cd^{2+} Complex is 1:1.
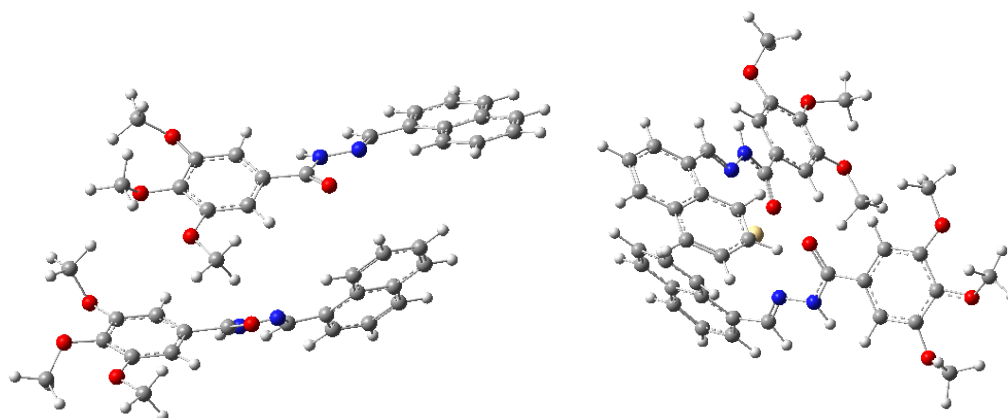
Fig. S7 Optimized self-assembly model of **OG** and **CdG** obtained by DFT calculations (the 3,4,5-tris(hexadecyloxy) group was replaced by 3,4,5-tris(methyloxy) group for clarity), the distance of π-π stacking between the naphthyl are 3.90 Å for **OG,** and 3.81 Å for **CdG**, respectively.

Computational Methods

All calculations were carried out with the Gaussian 09 programs.[2] The geometries

of all the species were calculated by the DFT[3] method with the B3LYP functional[4]

in conjunction with the LANL2DZ[5] basis set for Cd and the 6-31G* basis set for the

other element.

Reference

[1] Fu, Y.-P.; Lin, Q.; Wei, T.-B.; Chen, P.; Zhu, X.; Liu, X.; Zhang, Y.-M. Synthesis of 3,4,5-tris(hexadecyloxy) benzoylhydrazine. *Chem. Reagents*, **2013**, *35*, 367-368.

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[4] (a) Lee, C. T.; Yang, W. T.; Parr, R. G. Phys. Rev. B 1988, 37, 785−789. (b)

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[5] (a) Dunning, T. H., Jr.; Hay, P. J. In Modern TheoreticalChemistry; Schaefer, H. F., III, Ed.; Plenum: New York, 1976; Vol. 3, pp 1−28. (b) Hay, P. J.; Wadt, W. R. J. Chem. Phys. 1985, 82, 270−283. (c) Wadt, W. R.; Hay, P. J. J. Chem. Phys. 1985, 82, 284−298. (d) Hay, P. J.; Wadt, W. R. J. Chem. Phys. 1985, 82, 299−310

Complete List of Authors for References with more than 10 Authors

[2] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A.; Jr., Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, Revision A.01; Gaussian, Inc., Wallingford CT, 2009.