Electronic Supplementary Material (ESI) for Soft Matter.

Electronic Supplementary Information

Acylhydrazone functionalized benzimidazole-based metallogel for efficient detection and separation of Cr^{3+}

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16. A part of the literatures about the detection limits of Cr^{3+} were provided in the followed table.	**Table S6**

1. Materials and physical methods

All other reagents and solvents were commercially available at analytical grade and were used without further purification. All metal ions were purchased from Alfa Aesar Chemical Reagent Co (Tianjin, China). All other reagents and solvents were commercially available at analytical grade and were used without further purification. Melting points were measured on an X-4 digital melting-point apparatus (uncorrected). ^{1}H NMR spectrum were recorded on a Mercury-400 BB spectrometer at 400 MHz and ^{13}C NMR spectrum were recorded on a Mercury-600 BB spectrometer at 151 MHz. ^{1}H chemical shifts are reported in ppm downfield from tetramethylsilane (TMS, TM scale with the solvent resonances as internal standards). Mass spectra were performed on a Bruker Esquire 3000 plus mass spectrometer (Bruker-FranzenAnalytik GmbH Bremen, Germany) equipped with ESI interface and ion trap analyzer. 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 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 infrared spectra were performed on a Digilab FTS-3000 Fourier transform-infrared spectrophotometer. Fluorescence spectra were recorded on a Shimadzu RF-5301PC spectrofluorophotometer.

2. Synthesis and characterization of gelator BM

1-*N*-methoxycarbonylmethyl-2-undecyl-*1H*-benzo[d]imidazole [S1] (1.49 g, 4.0 mmol) was mixed in 25 mL EtOH, hydrazine (2.17 g, 40 mmol) was mixed in 25 mL EtOH, strirred at room temperature for 30 min, and then the latter slowly dripped into the former. The solution was stirred under reflux for 10 h at 80 °C. After cooling to room temperature, the solid product that appeared in the flask was filtered and recrystallized with ethanol to get crystalline product **B11** (yield: 73.6 %; m. p. 98-102 °C). Then the compound (**B11**) (1.36 g, 4 mmol) was added into a solution of 2-hydroxy naphthalene formaldehyde (0.68 g, 4 mmol) in EtOH (30 mL), the mixture was heated at 80 °C for 8 h at acetic acid (2-3 drops). After reaction was finished, the mixture was cooled to room temperature to extract the yellow-green solid. The precipitate was collected by filtration, recrystallized with DMF and EtOH and then dried in vacuum; giving a yellow-green powder compound (*E*)-*N*′- (2-hydroxynaphthalen-1-yl) methylene) -2- (2-undecyl -*1H*- benzo[d]imidazole-1-yl) acylhydrazone **BM** (1.54 g). **BM**: yield: 78.2 %; m. p. >156-160 °C; ^{13}C NMR (DMSO-d_6, 150 MHz), δ/ppm: 167.78, 157.67, 147.26, 144.26, 133.95, 131.97, 129.3, 128.2, 123.95, 118.58, 110.61, 40.39, 31.79, 29.18, 27.23, 22.51, 14.38. Anal. Calcd. For $C_{31}H_{38}N_4O_2$: C, 74.67; H, 7.68; N, 11.24; O, 6.42. ^{1}H NMR (400 MHz, $CDCl_3$,): δ 13.2 (d, J = 8.0 Hz, 1H, O–H), δ 12.3 (s, 1H, N–H), δ 8.17 (d, J = 5.6 Hz, 1H, N=CH), 7.9 (d, J = 6.0 Hz, 1H) 7.62-7.89 (m, 1H, ArH). ESI-MS calcd for $[C_{31}H_{38}N_2O_2 + H]^+ = 499.30$; found: 499.33.

3. General procedure for ^{1}H NMR experiments

A serious of different concentrations **BM** was respectively added into DMSO-d_6. The concentrations dependent ^{1}H-NMR of **BM** was analyzed. For the ^{1}H-NMR titration, the solution of **BM** and the appropriate concentrated solution of guest ions were prepared in DMSO-d_6. Aliquots of the two solutions were mixed directly in NMR tubes.

4. General procedure for fluorescence spectra experiments

All the fluorescence spectroscopy was carried out in DMSO solution on a Shimadzu RF–5301 spectrometer. With different equivalents perchlorate salt of cations (Ba^{2+}, Tb^{3+}, Cd^{2+}, Ag^{+}, Co^{2+}, La^{3+}, Mg^{2+}, Cr^{3+}, Hg^{2+}, Ca^{2+}, Cu^{2+}, Eu^{3+}, Al^{3+}, Ni^{2+}, Zn^{2+}, Fe^{3+} and Pb^{2+}) were added into **BM** while keeping the host concentration constant (2.0×10^{-4} M) in all the experiments. The detection limits for guest ions were determined by fluorescent titrations and calculated on the basis of 3σ/s method. The addition and diffusion of appropriate equiv. of Cr^{3+} and Fe^{3+} to the **BMG** (0.5 %, in glycerol) generated the corresponding supramolecular metallogel **BMG-Fe**. Fluorescence properties of above supramolecular gels were tested at 420 nm.

5. Study of FT-IR spectroscopy

IR spectra were recorded on a Digilab FTS-3000 Fourier transform-infrared spectrophotometer. The xerogels of **BMG**, **BMG-Fe** and **BMG-FeCr** were prepared by drying a resulting gel on a glass slice for a long time. All the samples were mixed well-distributedly with KBr to create a compact pellet for the IR detection.

6. Study of scanning electron microscopy (SEM)

Determination of the SEM images was performed on a JSM-6701F FE-SEM microscope. A SEM sample was fabricated by spreading the resultant gel on a petri dish, and slow evaporated the solvent in a vacuum oven for one month. Then gold powder was sprayed on the sample after the detection system was vacuumized. The SEM image of the xerogel was determined with an accelerating voltage of 8 kV.

7. Study of X-ray diffraction analysis (XRD)

The XRD spectra of xerogels, which were fabricated by drying the resultant gels under vacuum, was performed on a Rigaku RINT2000 diffractometer equipped with graphite monochromated CuKa radiation (Cu Kα radiation, λ = 1.54073 Å). The obtained data were collected with 2θ ranging from 0 to 60° and treated by Origin 8.5 via curve smoothing processes. The *d* spacing values were calculated by Bragg's law ($n\lambda = 2d\sin\theta$, *d* is the distance between atomic layers in a crystal or a molecular aggregate; λ is the wavelength of the incident X-ray beam; n is an integer which is generally adopted as 1)

8. General procedure for MS spectra experiments

The operation of MS spectra was carefully described according to your advice. Firstly, the organogel **BMG** (0.5 %, in glycerol) was prepared in glycerol, and then adding 1.0 equiv. Fe^{3+} followed by 1.0 equiv. Cr^{3+} into **BMG** (according to the detection limit of **BMG** for Fe^{3+} and Cr^{3+}) formed metallogel **BMG-FeCr**. Thirdly, a xerogel sample was fabricated by spreading the resultant metallogel on a petri dish, and slow evaporated the solvent in a vacuum oven for a period of time. The MS spectra were operated by laboratory manager.

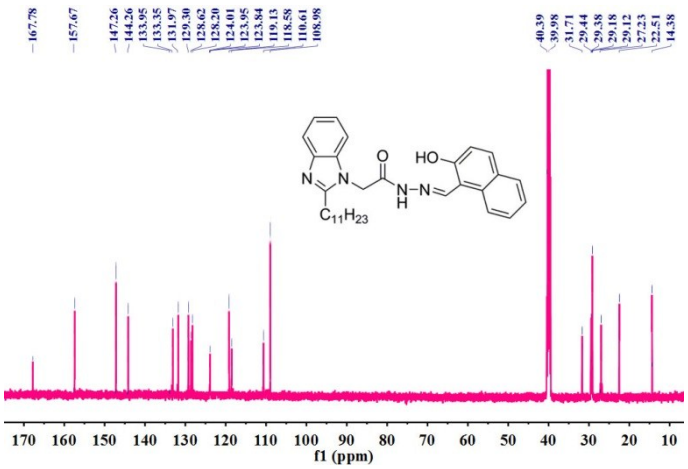


Fig. S1. ^{13}C NMR spectrum (150 MHz, 298 K) of **BM** in DMSO-d_6.

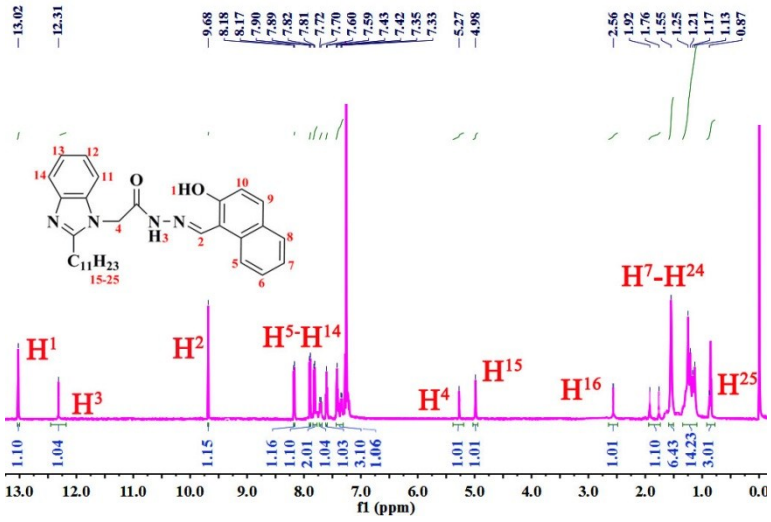


Fig. S2. ^{1}H NMR spectrum (600 MHz, 298 K) of **BM** in $CDCl_3$.

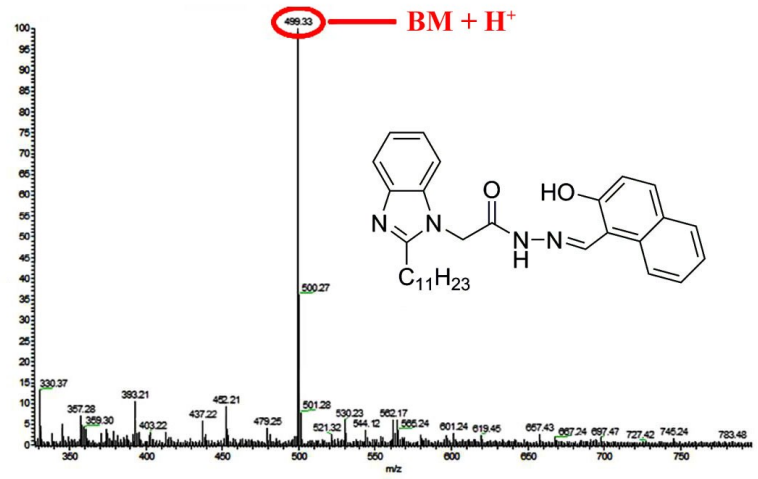


Fig. S3. Mass spectrum of **BM**.

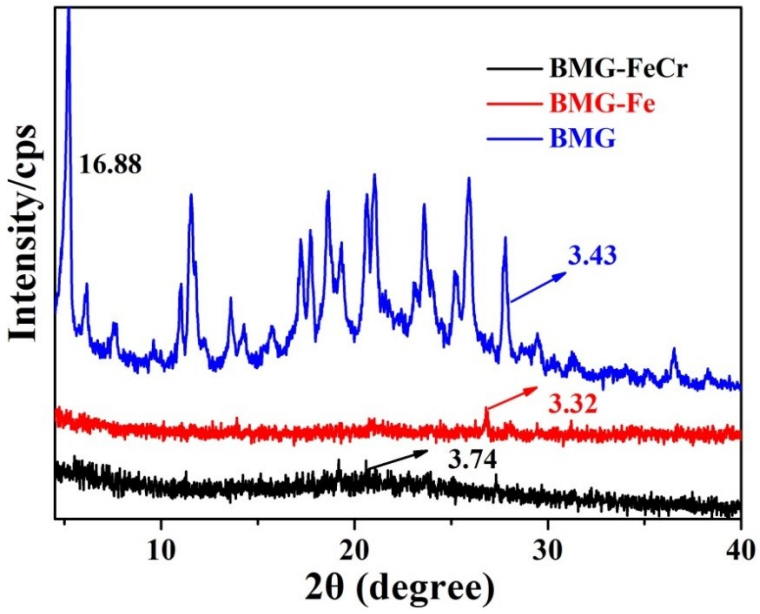


Fig. S4. Powder X-ray diffraction patterns of xerogel **BMG**, **BMG-Fe** and **BMG - FeCr**.

Table S1. Gelation Property of organogelator **BM**.

Solvent	Gelation behavior[a]	[b] T_{gel} (℃, wt %)	CGC (%)
MeOH	P	—	—
EtOH	P	—	—
n-PrOH	P	—	—
i-PrOH	S	—	—
n-BuOH	S	—	—
t-BuOH	SP	—	—
i-PeOH	S	—	—
Cyclohexanol	S	—	—
Acetone	S	—	—
Ethylene glycol	G	23°C (1 %)	—
Acetonitrile	P	—	—
Ethyl acetate	P	—	—
DMSO	S	—	—
Tert-butanol	S	—	—
DMF	S	—	—
Glycerol	**G**	**43°C (1 %)**	**0.5%**
Dichloromethane	S	—	—
Chloroform	S	—	—
Carbon tetrachloride	P	—	—

[a] G, gel ; S, solution ; SP, solution precipitate (wt %, w/v, 10 mg mL^{-1} = 1.0 %)

[b] T_{gel}: The gel-sol transition temperature (℃)

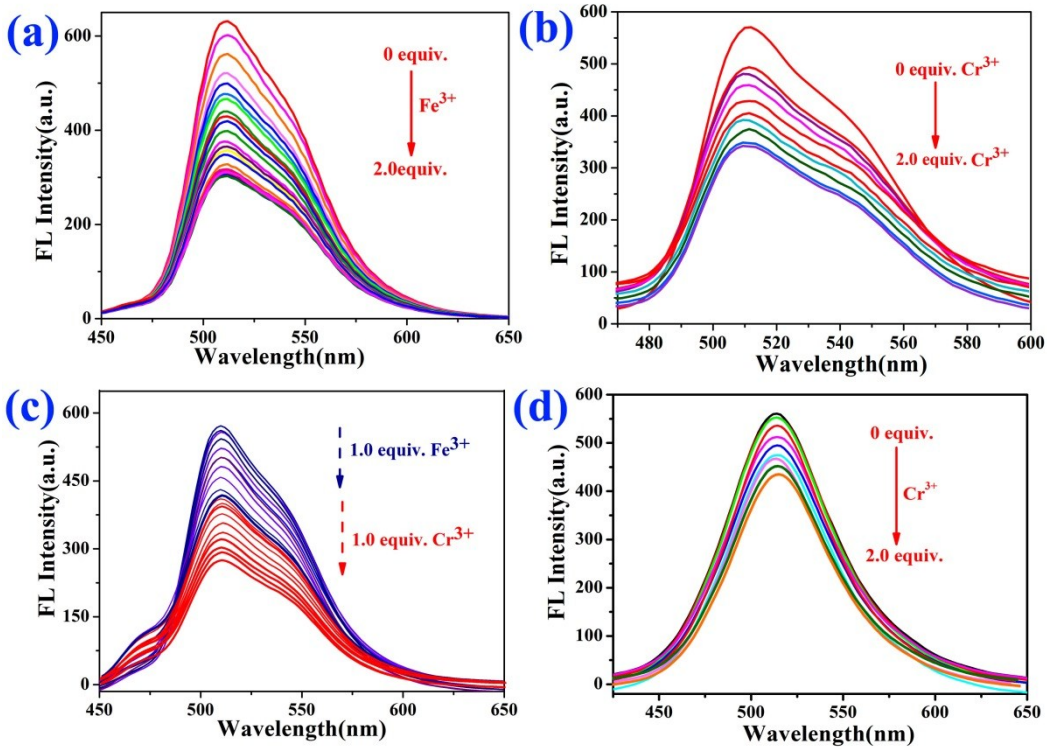


Fig. S5 Fluorescent titrations spectra (λ_{ex} = 425 nm) of **BM** (2 × 10^{-4} M) in the presence of different concentrations of (a) Fe^{3+}; (b) Cr^{3+}; (c) Fe^{3+} and Cr^{3+} in DMSO solution; (d) The fluorescent titrations (λ_{ex} = 420 nm) of **BMG** (0.5 %, in glycerol) for Cr^{3+} (The concentration of various cations is 0.1 M, in water).

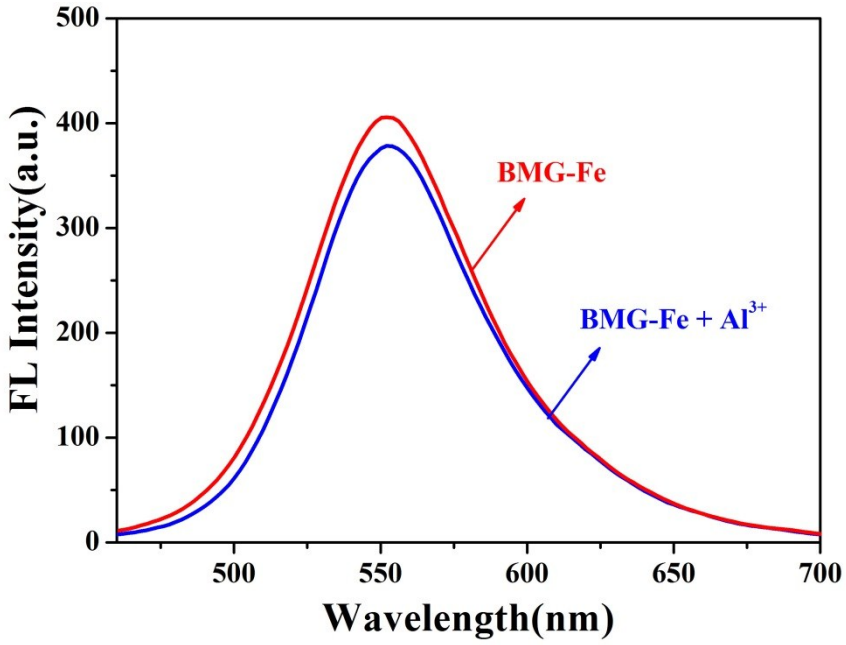
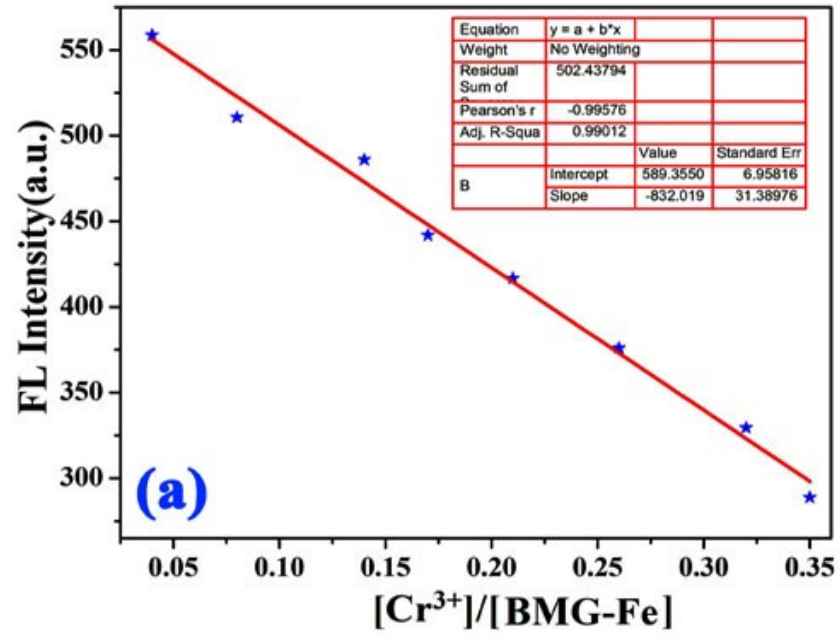
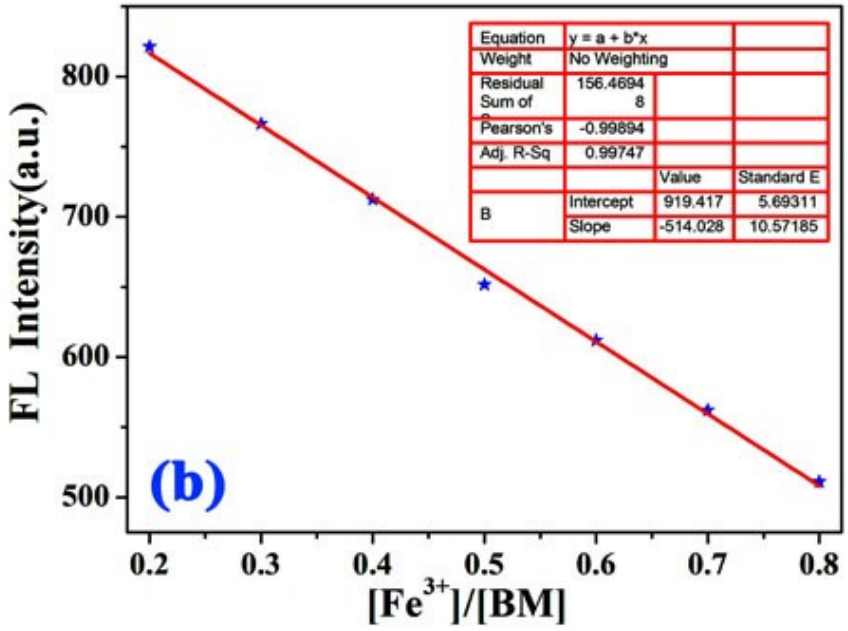


Fig. S6. The fluorescent spectra (λ_{ex} = 420 nm) of metallogel **BMG-Fe (BM**: Fe^{3+} = 1: 1, 0.5 %, in glycerol**)** in the presence of Al^{3+} (0.1 M, in water).


Equation y = a + b*x
Weight No Weighting
Residual Sum of 502.43794
Pearson's r -0.99576
Adj. R-Squa 0.99012
Value Standard Err
B Intercept 589.3550 6.95816
Slope -832.019 31.38976
FL Intensity(a.u.)
550
500
450
400
350
300
(a)
0.05 0.10 0.15 0.20 0.25 0.30 0.35
[Cr3+]/[BMG-Fe]


Equation y = a + b*x
Weight No Weighting
Residual Sum of 156.4694 8
Pearson's -0.99894
Adj. R-Sq 0.99747
Value Standard E
B Intercept 919.417 5.69311
Slope -514.028 10.57185
FL Intensity(a.u.)
800
700
600
500
(b)
0.2 0.3 0.4 0.5 0.6 0.7 0.8
[Fe3+]/[BM]

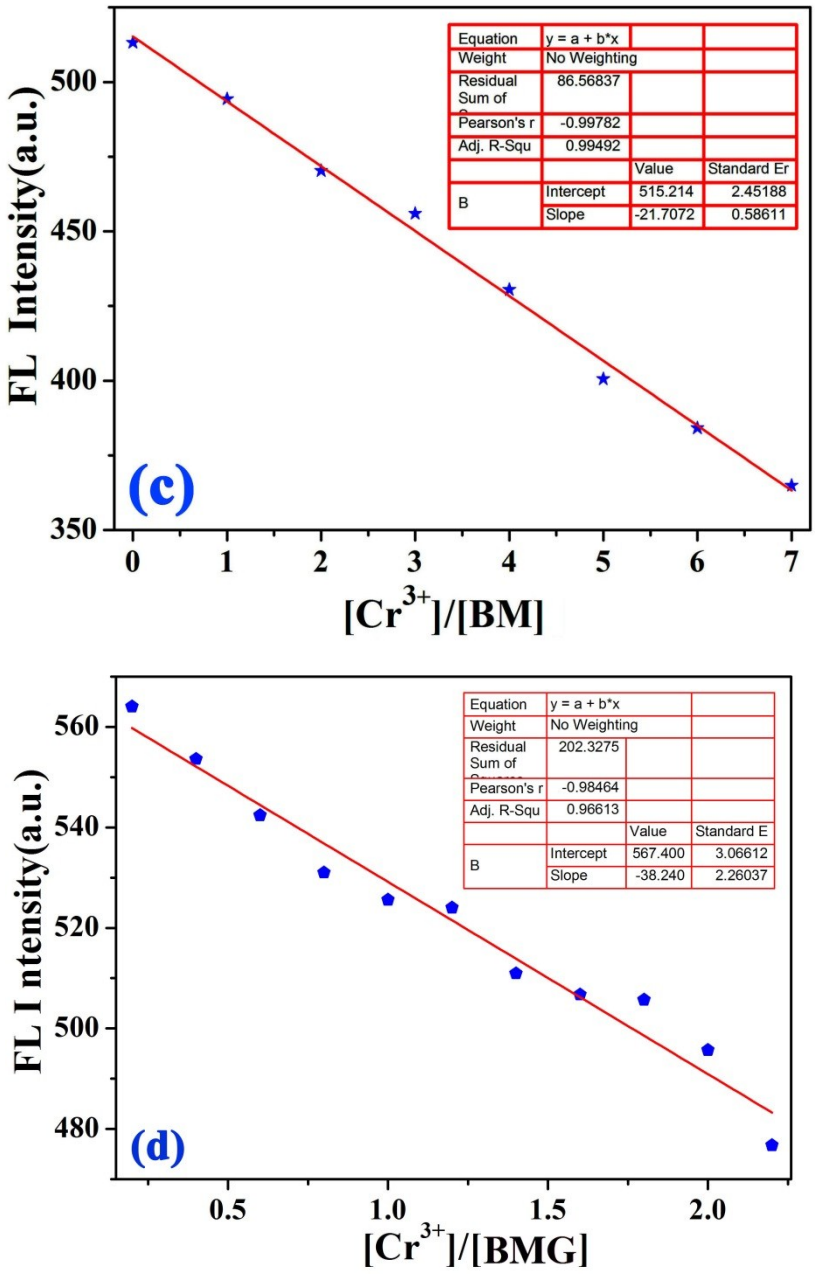


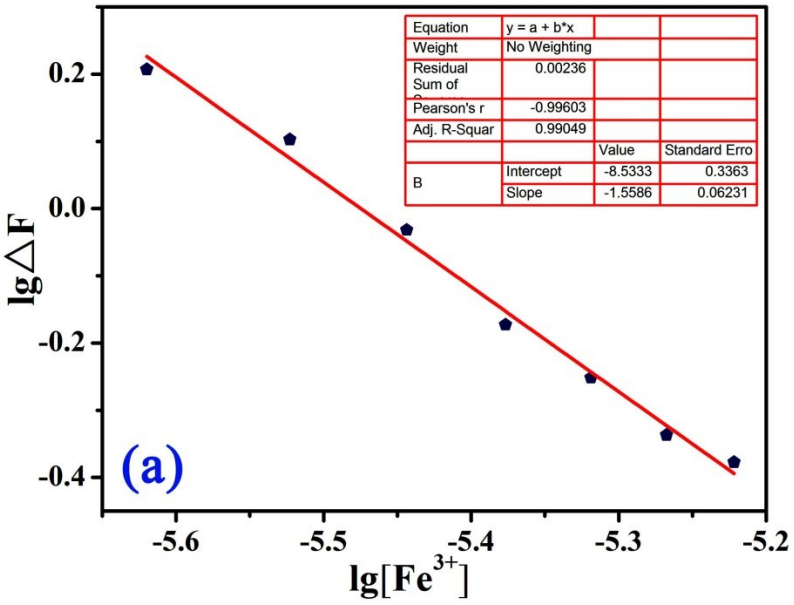
Fig. S7 The photograph of the fluorescent spectra linear range of (a) **BMG-Fe** (**BM**: Fe^{3+} = 1: 1, 0.5 %) for Cr^{3+}; (b) **BM** for Fe^{3+}; (c) **BM** for Cr^{3+}; (d) **BMG** (0.5 %) for Cr^{3+} (The concentration of various cations is 0.1 M, in water).

Table S2 (a) Detection limits of host gel/sol treated by metal ions.

Entry	Gel/Sol	Metal ions	Detection limits/M
1	**BMG-Fe**	Cr^{3+}	2.62×10^{-8}
2	**BM**	Cr^{3+}	5.57×10^{-7}
3	**BM**	Fe^{3+}	5.78×10^{-8}
4	**BMG**	Cr^{3+}	1.89×10^{-4}

Table S2 (b) Calculation formula and related date of the detection limits of **BMG-Fe**, BM and **BMG**.

Entry	A (Slope)	B (Intercept)	R^2	S
1	832.019	589.355	0.99012	8.3202×10^{8}
2	21.7072	515.214	0.99492	1.6836×10^{6}
3	514.028	919.417	0.99747	
	5.1403×10^{8}			
4	38.2400	567.400	0.99613	
	3.8240×10^{7}			
calculation formula	**Linear Equation: y=Ax + B** $\delta = \sqrt{\frac{\sum (F-\bar{F})^2}{(N-1)}}$ **(N = 20) K = 3** **LOD = K × δ/s** **S = A×10⁶**			



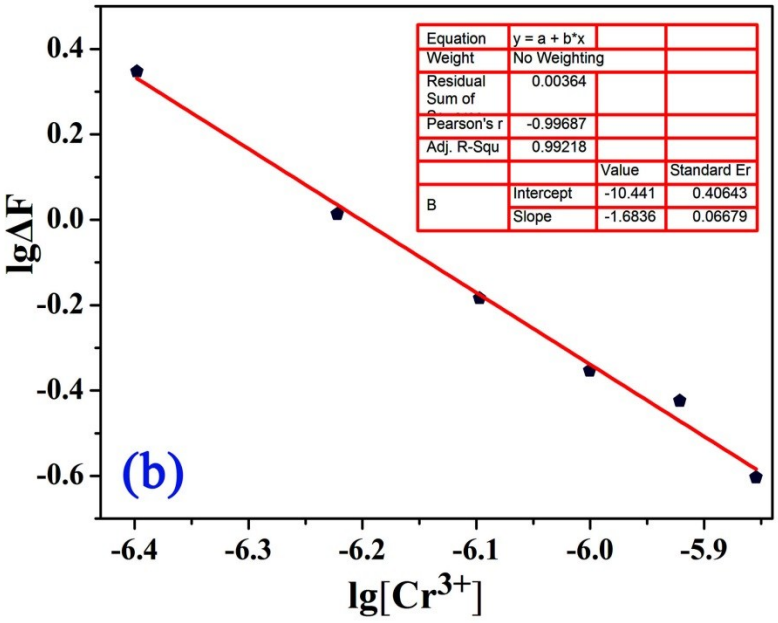


Fig. S8 The photograph of the linear range for **BM** (2×10^{-4} M) upon addition of different amounts of (a) Fe^{3+} and (b) Cr^{3+} (λ_{ex} = 425 nm).

Table S3. Association constants of the BM treated by metal ions, calculation formula and related date.

Entry	Metal ions	A (Slope)	B (Intercept)	R^2	Ka/ M^{-2}
1	Fe^3	1.5586	8.5333	0.99049	7.87×10^{11}
2	Cr^{3+}	1.6836	10.441	0.99218	2.96×10^{9}
calculation formula	**Linear Equation: y=Ax + B** $\log\frac{I-Imin}{Imax-I} = \log Ka + n\log\,[M^{3+}]$				

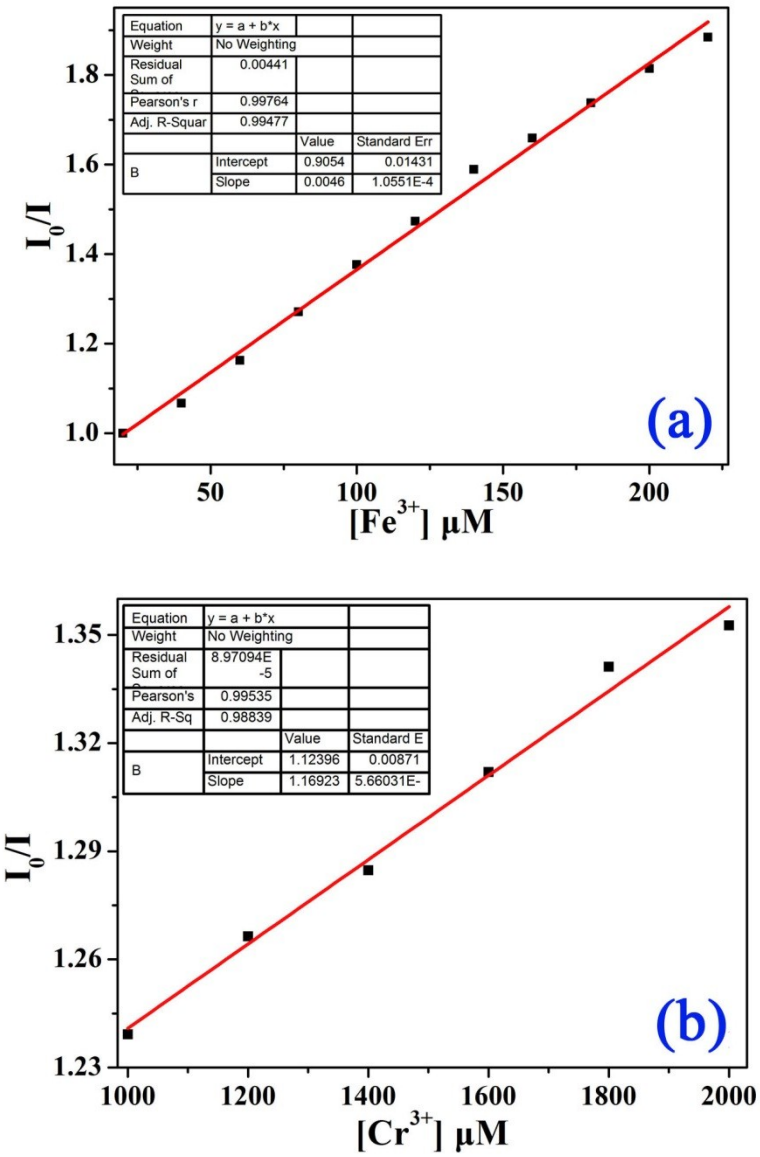


Fig. S9 The titration curves of **BM** (2×10^{-4} M, in DMSO) with the concentration range of (a) Fe^{3+} and (b) Cr^{3+}.

Table S4. Stern–Volmer constants of the BM treated by metal ions, calculation formula and related date.

Entry	Metal ions	A (Slope)	B (Intercept)	R^2	Ksv / M^{-1}
1	Fe^3	0.0046	0.9054	0.99477	4.60 ☒ 10^3
2	Cr^{3+}	1.6923	1.1240	0.98839	1.16 ☒ 10^6
calculation formula	**Linear Equation: y=Ax + B** $I_0/I = 1 + K_{SV}[Q]$				

The Stern–Volmer quenching equation:

$$I_0/I = 1 + K_{SV}[Q]$$

Where, I_0 represents the initial fluorescence intensity of **BM** prior to the addition of analyte;

I represents fluorescence intensity after addition of analyte;

[Q] represents the molar concentration of analytes, and K_{SV} represents the Stern–Volmer constant.

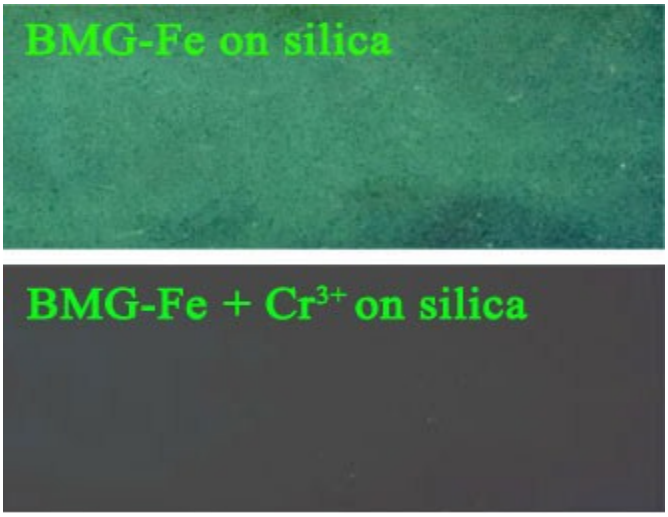


Fig. S10 Photographs of **BMG-Fe** (2×10^{-4} M) and the response of Cr^{3+}on the silica gel plate under irradiation at 365 nm by a UV lamp.

Table S5 Adsorption percentage of **BMG** and **BMG-Fe** for Cr^{3+}.

substance	Ions	Initial concentration (M)	Residual concentration (M)	Adsorption percentage %
BMG-Fe	Cr^{3+}	1×10^{-4}	3.64×10^{-6}	96.36%
BMG	Cr^{3+}	1×10^{-4}	1.64×10^{-5}	83.60%
	Calculation method of adsorption percentage: $Adsorption\ percentage(\%) = \left(1 - \frac{C_R \times V_R}{C_I \times V_I}\right) \times 100\%$ (state: C_R is the residual concentration of Cr^{3+}, C_I is the initial concentration of Cr^{3+}, V_R=V_I)			

Table S6 A part of the literatures about the uptake of Cr^{3+} were provided in the followed table.

Author	Journal and Year. Volume. Page	Adsorption percentage for Cr^{3+}
Kai-Feng Du. etc	Ind. Eng. Chem. Res. 2013, 52, 6502-6512	95.61%
Kai-Feng Du. etc	Ind. Eng. Chem. Res. 2011, 50, 10784–10791	82.4% (PH=6.42) 87.6% (PH=5.03)
Qi Lin etc	Chem. Eur. J. 2017, 23, 1–8	95.99%
	This work	96.36%

S1 H. Yao, H. P. Wu, J. Chang, Q.Lin, T. B. Wei and Y. M. Zhang, *New J. Chem.,* 2016, **40**, 4940-4944.