Supporting Information

A novel supramolecular polymer gel based long-alkyl-chains

functionalized coumarin acylhydrazone for sequential

detection and separation of toxic ions

Jing-Han Hu,* Zhi-Yuan Yin, Kai Gui, Qing-Qing Fu, Ying Yao, Xu-Mei Fu and Hui-Xin Liu

College of Chemical and Biological Engineering, Lanzhou Jiaotong University, Lanzhou, gansu, 730070, P. R. China

Table of contents

Materials and physical methods

Experimental Section

Scheme 1 Detail synthesis of G2.

Fig S1. ¹H NMR spectra of gelator G2.

Fig S2. ¹³C NMR spectra of gelator G2.

Fig S3. HRMS of gelator G2.

Table S1. Gelation properties of gelator G2.

Fig S4. Fluorescence spectra of OGC (3.0%, n-BuOH/H₂O (v/v, 9:1)) in the presence of various anions (F⁻, Cl⁻, Br⁻, I⁻, H₂PO₄⁻, AcO⁻, ClO₄⁻, HSO₄⁻, SCN⁻, N³⁻, S²⁻and CN⁻, respectively, using their 0.1 mol L⁻¹ sodium or potassium salts water solution as the sources) at room temperature (λ_{ex} =340 nm).

Fig S5. The photo of drip plate test of OGC treated with different anions (F^- , CI^- , Br^- , I^- , $H_2PO_4^-$, AcO^- , CIO_4^- , HSO_4^- , SCN^- , N^{3-} , S^{2-} and CN^-) in the UV lamp (345nm) in the room temperature.

Fig S6. Fluorescence spectra of OGC-CN (3.0%, n-BuOH/H₂O (v/v, 9:1)) in the presence of various anions (Ca²⁺, Mg²⁺, Pb²⁺, Ni²⁺, Co²⁺, Hg²⁺, Zn²⁺, Cd²⁺, Ag⁺, Cr³⁺, Cu²⁺, Al³⁺, Fe³⁺, Ba²⁺, La³⁺, Eu³⁺and Tb³⁺), respectively, using their 0.1 mol L⁻¹ sodium or potassium salts water solution as the sources) at room temperature (λ_{ex} =340 nm).

Fig S7. Fluorescence spectra of supramolecular polymers (in gelated state) (a) OGC with increasing of CN⁻; (b) OGC with increasing of S²⁻. Insert: the color change of titration process (1: beginning; 2: middle; 3: end-point).

Fig S8. Fluorescence spectra of OGC-S (3.0%, n-BuOH/H₂O (v/v, 9:1)) in the presence of various anions (Ca²⁺, Mg²⁺, Pb²⁺, Ni²⁺, Co²⁺, Hg²⁺, Zn²⁺, Cd²⁺, Ag⁺, Cr³⁺, Cu²⁺, Al³⁺, Fe³⁺, Ba²⁺, La³⁺, Eu³⁺and Tb³⁺), respectively, using their 0.1 mol L⁻¹ sodium or potassium salts water solution as the sources) at room temperature (λ_{ex} =340 nm).

Fig S9. Fluorescence spectra of supramolecular polymers (in gelated state) (a) OGC and OGC+CN⁻; (b) OGC and OGC+S²⁻; (c) OGC-CN and OGC-CN+Fe³⁺; (d) OGC and OGC-S+Ag⁺.

Table S2 Calculation the detection line of OGC+CN⁻, OGC+S²⁻, OGC-CN+Fe³⁺ and OGC-S+Ag⁺.

Fig S10. Fluorescent linear fitting of titration curves for (a) OGC+CN⁻; (b) OGC+S²⁻; (c) OGC-CN+Fe³⁺ and (d) OGC-S+Ag⁺.

Fig S11. FT-IR spectra of (a) xerogel of OGC, OGC-CN and OGC-CN treated with Fe³⁺, (b) xerogel of OGC, OGC-S and OGC-S treated with Ag⁺.

Fig S12. SEM image of (a) OGC-CN xerogel; (b) OGC-CN xerogel treated with Fe³⁺; (c) OGC-S xerogel; (d) OGC-S xerogel treated with Ag⁺.

Fig S13. Partial ¹H NMR spectra of G2 (CHCl₃-d₆) with various equivalents of CN⁻.

Fig S14. (a) Fluorescent spectrum of OGC treated with OH⁻ and (b) fluorescent titrations spectra of

OGC with increasing of OH⁻.

Fig S15. UV-vis absorption and spectra of G2 (2.0×10^{-5} M) in the presence of different concentrations of S²⁻ in CHCl₃ solution.

Materials and physical methods

All reagents and starting materials were obtained from commercial suppliers and used as received unless otherwise noted. All anions were used as sodium or potassium salts while all cations were used as the 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 MR AVANCE NEO 500 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 RINT2000diffractometer equipped with graphite monochromated CuKa radiation (λ =1.54073 A). The morphologies and Sizes of the xerogels were characterized using field emission scanning electron microscopy (FE-SEM, JSM-6701F) at an accelerating voltage of 8kV. 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 а Shimadzu RF-5301PC spectrofluorophotometer.

Experimental Section

As shown in Scheme S1, the compound 3, 4, 5-tris (hexadecyloxy) benzohydrazide was synthesized according to the literature-reported methods. The G2 was synthesized as follow: 4-methyl-7-hydroxy8-2-oxo-2H-chromene -3-carbaldehyde (0.206g, 1mmol), 3, 4, 5-tris (hexadecyloxy)-benzohydrazide (1 mmol) and acetic acid (0.1 m L, as a catalyst) were added to ethanol (20 m L). Then the reaction mixture was stirred at 80°C for 24 h, after the solvent was removed, the precipitated G2 was yielded and recrystallized with CHCl₃–CH₂CH₃OH to get the pour solid G2.

(Yield: 50%). m.p.86-88°C. ¹H NMR (500 MHz, CDCl₃) δ 12.23, 10.63, 8.99, 7.49, 7.26, 7.23, 6.96, 6.09, 4.02, 2.44, 1.76, 1.45, 1.28, 1.26, 0.88. (Fig S1). ¹³C NMR (126 MHz, CDCl₃) δ 163.33, 162.25, 161.10, 154.23, 153.22, 152.79, 143.13, 141.87, 127.16, 126.74, 114.55, 111.90, 110.79, 106.21, 106.03, 76.77, 73.58, 69.34, 31.95, 29.63, 29.39, 26.12, 22.71, 18.94, 14.13. (Fig S2). ESI-MS m/z: calcd for C₆₆H₁₁₀N₂O₇ [G2+K] ⁺:1081.7945; found: 1081.7935 (Fig S3).





Fig S2. ¹³C NMR spectra of gelator G2.



Fig S3. HRMS of gelator G2.

i-PrOH	G	3min	4	38
i-PrOH-H ₂ O	SP	_	_	_
n-BuOH	G	1min	3	40
n-BuOH-H ₂ O(9:1)	G	1min	3	41
Acetone	SP	_	_	_
Acetonitrile	SP	_	_	_
DMSO	SP	_	_	_
DMF	SP	_	_	_
THF	S	_	_	_
Toluene	S	_	_	_
Chloroform	S	_	_	_
Methylene chloride	S	_	_	_
Carbon tetrachloride	S	_	_	_

^aG, gel; S, solution; SP, solution precipitate. ^bMGC is the minimum gelator concentration (w/v%,10 mg m L⁻¹= 1%). ^cMGT is the gelation temperature (°C) at the minimum gelator concentration

 Table S1. Gelation properties of gelator G2.



Fig S4. Fluorescence spectra of OGC (3.0%, n-BuOH-H₂O (v/v, 9:1)) in the presence of various anions (F⁻, Cl⁻, Br⁻, l⁻, H₂PO₄⁻, AcO⁻, ClO₄⁻, HSO₄⁻, SCN⁻, N³⁻, S²⁻and CN⁻, respectively, using their 0.1 mol L⁻¹ sodium or potassium salts water solution as the sources) at room temperature (λ_{ex} =340 nm).



Fig S5. The photo of drip plate test of OGC treated with different anions (F^- , Cl^- , Br^- , l^- , $H_2PO_4^-$, AcO^- , ClO_4^- , HSO_4^- , SCN^- , N^{3-} , S^{2-} and CN^-) in the UV lamp (345nm) in the room temperature.



Fig S6. Fluorescence spectra of OGC-CN (3.0%, n-BuOH-H₂O (v/v, 9:1)) in the presence of various anions (Ca²⁺, Mg²⁺, Pb²⁺, Ni²⁺, Co²⁺, Hg²⁺, Zn²⁺, Cd²⁺, Ag⁺, Cr³⁺, Cu²⁺, Al³⁺, Fe³⁺, Ba²⁺, La³⁺, Eu³⁺and Tb³⁺), respectively, using their 0.1 mol L⁻¹ sodium or potassium salts water solution as the sources) at room temperature (λ ex =340 nm).



Fig S7. Fluorescence spectra of supramolecular polymers (in gelated state) (a) OGC with increasing of CN⁻; (b) OGC with increasing of S²⁻. Insert: the color change of titration process (1: beginning; 2: middle; 3: end-point).



Fig S8. Fluorescence spectra of OGC-S (3.0%, n-BuOH-H₂O (v/v, 9:1)) in the presence of various anions (Ca²⁺, Mg²⁺, Pb²⁺, Ni²⁺, Co²⁺, Hg²⁺, Zn²⁺, Cd²⁺, Ag⁺, Cr³⁺, Cu²⁺, Al³⁺, Fe³⁺, Ba²⁺, La³⁺, Eu³⁺ and Tb³⁺), respectively, using their 0.1 mol L⁻¹ sodium or potassium salts water solution as the sources) at room temperature (λ_{ex} =340 nm).



Fig S9. Fluorescence spectra of supramolecular polymers (in gelated state) (a) OGC and OGC+CN⁻; (b) OGC and OGC+S²⁻; (c) OGC-CN and OGC-CN+Fe³⁺; (d) OGC and OGC-S+Ag⁺.

Calculation formula of LOD Linear Equation: y=Ax + B

$$LOD = K \times \frac{\delta}{s} (K = 3)$$
$$\delta = \sqrt{\frac{\sum (F_i - F_0)^2}{N - 1}} (N = 20)$$

$$S = A \times 10^6$$

State, F_i : the fluorescence intensity of OGV at λ_{ex} =340 nm; F_0 : the average of 20 times fluorescence intensity of OGV at λ_{ex} =340nm; A: scope of linear fitting of fluorescence titration; B: intercept of linear fitting of fluorescence titration.

	δ	А	S	LOD
OGC+CN ⁻		713.790	713.790×10 ⁶	1.64×10 ⁻⁸
OGC+S ²⁻	2.00	308.724	308.724×10 ⁶	3.88×10 ⁻⁸
OGC-CN+Fe ³⁺	3.90	-811.0296	811.0296×10 ⁶	1.44×10 ⁻⁸
OGC-S+Ag ⁺		-498.4043	498.4043×10 ⁶	2.35×10 ⁻⁸





Fig S10. Fluorescent linear fitting of titration curves for (a) OGC+CN⁻; (b) OGC+S²⁻; (c) OGC-CN+Fe³⁺ and (d) OGC-S+Ag⁺.



Fig S11. FT-IR spectra of (a) xerogel of OGC, OGC-CN and OGC-CN treated with Fe³⁺, (b) xerogel of OGC, OGC-S and OGC-S treated with Ag⁺.



Fig S12. SEM image of (a) OGC-CN xerogel; (b) OGC-CN xerogel treated with Fe³⁺; (c) OGC-S xerogel; (d) OGC-S xerogel treated with Ag⁺.



Fig S13. Partial ¹H NMR spectra of G2 (CHCl₃-d₆) with various equivalents of CN^{-} .



Fig S14. (a) Fluorescent spectrum of OGC treated with OH⁻ and (b) fluorescent titrations spectra of OGC with increasing of OH⁻.



Fig S15. UV-vis absorption and spectra of G2 (2.0×10^{-5} M) in the presence of different concentrations of S²⁻ in CHCl₃ solution.