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A novel coumarin-derived acylhydrazone Schiff base gelator for Synthesis

of organogels and identification of Fe³⁺

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Abstract: A novel coumarin-derived acylhydrazone Schiff base fluorescent organogel (G₁) was designed and synthesized. Gelator G₁ can form stable organogels in isopropanol, tert-amyl alcohol, *n*-butanol and phenylamine. The organogel could be converted to solution by heating and the solution could be restored to gel state by cooling. The self-assemble mechanism of G1 was investigated by XRD, FT-IR and SEM techniques. The results indicated the intermolecular hydrogen bonding, *Van der* Waals interaction and π - π stacking are the forces for the self-assembly of the gelator to form the organogel. The optical properties of the compound was studied by UV-visible spectroscopy and fluorescence spectra. Further study presented that gelator G1 could selectively and sensitively response to Fe³⁺ only among tested cations. Beside the above functions, the organic gel factor G1 could also response to irradiation, heating and shaking, thus endowing the organogel with multi stimulus responsive properties.

Key Words: coumarin; acylhydrazone Schiff base; organogel; cation sensor.

1. Introduction

In the past few decades, low molecular weight organic gels(LMOGS) have been received extensive attention, which is an important kind of soft nanostructure material[1-5]. LMOGS are molecules that can self-assemble under specific conditions into structures that are able to immobilise the solvent to form organic gel by weak intermolecular forces such as hydrogen bond, $\pi - \pi$ stacking and van der Waals interaction. When the temperature, pH, different ions and irradiation change slightly, the gel phase transition can occur [6-12]. Many LMOGS have been designed and applied to bionic systems, drug delivery, tissue engineering, chemical sensors and optoelectronic equipment [13-23].

 Fe^{3+} is one of the essential elements of the human body and plays an important role in many biochemical reactions [24-25]. Fe^{3+} levels are associated with many diseases, including cancers and some organ dysfunctions [26-27]. At present, fluorescent probes have become powerful detection tools for chemical, biological and environmental applications, and can be used for real-time analysis with good

sensitivity and anti-interference [28-33]. Fe³⁺ analytical techniques such as electrothermal atomic absorption spectrometry [34], atomic absorption spectrometry [35], cold vapor atomic absorption spectrometry [36] and inductively coupled plasma mass spectroscopy [37] have many disadvantages, such as expensive instruments, well-controlled experimental conditions, complicated sample preparation processes and a lot of time.

Schiff base ligands have good metal binding affinity, and some of them will change the initial state of the target, the different metal ion concentration could effect the fluorescence intensity, so metal ions can be detected by a fluorescence spectrometer[38-43]. Some Schiff base metal complexes possess attractive electronic and photophysical properties [44], antitumor properties [45].

Coumarin is an important class of natural organic heterocyclic compounds. These compounds have good optical properties[46]. Substitution at different positions on the coumarin ring can give them different fluorescent properties. Coumarin Schiff base is a lactone ring compound with a chelating group such as C=N, C=O, which has good fluorescent characteristics, good sensitivity and selectivity for ion recognition[47].

Based on the above mentioned, here we report a novel coumarin-derived acylhydrazone Schiff base fluorescent organogel G1(**Scheme 1**), which shows highly selective colorimetric response to Fe^{3+} in EtOH/H₂O (1:1)mixed solution. Furthermore, G₁ can form a stable organogel in isopropanol, tert-amyl alcohol, *n*-butanol and phenylamine, which can response to heating, irradiation and vigorous agitation, thus endowing the organogel with multi stimulus responsive properties.



Scheme 1. Synthetic route of gelator G₁.

2. Experimental section

2.1 General instrumentations and reagents

All the reagents were purchased from Meryer Chemical Technology Co., Ltd. (Shanghai, China) and were of analytical grade. The aqueous solutions of metal ions were prepared from LiNO₃, NaNO₃, KNO₃, Ba(NO₃)₂, Ca(NO₃)₂, Mg(NO₃)₂, Cu(NO₃)₂, Fe(NO₃)₂, Fe(NO₃)₃, Fe₂(SO₄)₃, FeCl₃, AgNO₃, Al(NO₃)₃, Co(NO₃)₂, Ni(NO₃)₂, Pb(NO₃)₂, Zn(NO₃)₂, HgCl₂ and CdCl₂. Deionized water was prepared using a Milli Q[®] Direct 8 & 16 Ultrapure Water System (Billerica, MA, USA) for all experiments, and all the solution samples were prepared at room temperature, dissolved and allowed to stand for 12 h, and then subjected to spectrometry.

Thin-layer chromatography (TLC) was conducted on silica gel 60F₂₅₄ plates (Merck KGaA). The melting point was determined on an XRC-1u Melting Point Apparatus. FT-IR spectra of powder and xerogels were recorded on the Fourier Transform Infrared Spectrometer from Nicolet, USA. The UV-vis spectra were recorded on UV-2700 spectrophotometer. Fluorescent measurements were recorded on a Hitach F-7000 fluorescence spectrophotometer. ¹H NMR and ¹³C NMR spectrum were measured on the Bruker Avance 400 (400 MHz) spectrometer. The X-ray diffraction analysis (XRD) was performed on a Rigaku D/Max-2400 X-Ray Diffractometer. SEM images of the xerogels were obtained by using JSM-6701F instruments.

2.2 Synthesis of gelator G_1

The gelator G₁ synthesis as follows: compound (a) procured from commercial suppliers. Compound (c) wes prepared according to the literature procedures [48]. 1.25 g (6.64 mmol) of 3-acetyl coumarin and 1.54 g of 3,4,5-dodecyloxy benzoyl hydrazide (2.23 mmol) were dissolved in 30 mL of ethanol, added 1.0 mL of glacial acetic acid to the mixture. The reaction was refluxed at 85 °C for 30 h. After the reaction was completed, solvent was removed, Pure G1 powder was obtained after 3 times of recrystallization from anhydrous ethanol. Its yield was 75.3% (yellow powder). Mp: 161-163 °C The analysis data is as follows: ¹H NMR (400 MHz, CDCl₃): δ 8.50 (s, 1H, NH), 7.63-7.00 (m, 7H, Ar-H), 4.02-3.98 (m, 6H, OCH₂), 2.72 (s, 3H, -CH₃), 1.81-1.68 (m, 6H, OCH₂-CH₂-), 1.48-1.43 (m, 6H, -OCH₂-CH₂-), 1.34-1.29 (m, 48H, -CH₂-), 0.87 (t, 9H, -CH₃). ¹³C NMR (100MHz, CDCl₃): δ (ppm) 166.9, 155.3, 152.8, 152.8, 147.4(2C), 142.3, 134.3, 130.2, 128.7, 124.9, 124.6, 118.2, 116.7, 107.9 (2C), 73.5, 69.1 (2C), 31.9 (3C), 29.7 (3C), 29.7 (3C), 29.6 (3C), 29.4 (3C), 29.3 (3C), 29.3 (3C), 26.1 (3C), 26.0, 22.7 (3C), 14.1 (3C). HR-ESI-MS

calculated for [M+H₂O+H]⁺ 877.6652; found 877.7431.

2.3. Gelation test

A certain amount of gelator and solvents were put into a septum-capped test tube and heated until the solid was completely dissolved into the solvent. Then the cooled glass vial is turned over while observing whether the solution in the vial flows. If the solution does not flow, it means that the gelator forms a organogel. If the solution partially flows, it means that the solution and the solid can coexist, and the system has a partial gel formation. There are other situations, such as forming a solution, forming a precipitate or crystal *et.al*. After the completion of the organogel experiment, the critical gelator concentrations (CGC) were gained by the "stable to inversion of a test tube" method and the values of gel-sol transition temperature (T_{gel}) were tested by the "falling drop" method [49].

3. Results and discussion

3.1. Gelation properties of G_1

As shown in **Fig. 1**, the gelation propensity of G1 was tested in n-heptane, ethyl acetoacetate, acetone, n-butanol, DMSO, ethanol, tert-amyl alcohol, isopropanol, ethyl acetate, diethyl malonate, isooctane, methanol, DMF and phenylamine. G₁ can form stable gel in phenylamine, isopropanol, tert-amyl alcohol and n-butanol (The results are shown in **Table. 1**). The critical gel concentration (CGC) values of G₁ range from 4 mg/mL (isopropanol) to 8 mg/mL (n-butanol), while the gel-sol phase transition temperature (T_{gel}) values were within 42-90 °C, indicating that these gels are stable at room temperature. The T_{gel} of the isopropanol gel was 90 °C. Therefore, isopropanol is the best solvent for G₁ gel formation (see **Table. 2**).





Fig.1. Gel testing in a variety of solvents

Table. 1. Gelation	n test results of	f compound G ₁
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Solvent	State	
<i>n</i> -Heptane	S	
Ethyl acetoacetate	PG	
Acetone	Ins	
Ethanol	PG	

DMSO	S
<i>n</i> -Butanol	G
Tert-amyl alcohol	G
Isopropanol	G
Ethyl acetate	S
Diethyl malonate	PG
Isooctane	S
Methanol	Ins
DMF	S
Phenylamine	G

S=solution; Ins=insoluble; G=gel; PG=partial gel.

Table. 2. The CGC and T_{gel} of the organic gel factor G1.

Solvent	CGC	$T_{gel}/^{o}C$
Phenylamine	5.5	42
Isopropanol	4	90
Tert-amyl alcohol	6	79
n-Butanol	8	82

As shown in **Fig. 2**, gelator G_1 can form a stable organogel in isopropyl alcohol solution, which can response to heating, irradiation and vigorous agitation, and the organogel can change to the solution state after being subjected to these stimuli. However, the solution can be restored to the gel state after being cooled for about 0.5 h, thus endowing the organogel with multi stimulus responsive properties.



Fig.2. multistimulus responsive propertie of G₁

3.2. Cation recognition properties

For the systematic study of the spectral properties of the gelator G_1 , the spectral experiments were carried out at room temperature. The UV-visible absorption spectrum and the fluorescence spectrum were tested using HEPES buffer (10 mM, pH=7.2, V _{ethanol}/V _{deionized water} = 1:1).

The UV-visible absorption spectrum of G_1 shows the typical coumarin-based absorption bands at 217 nm,300 nm and 350 nm, respectively(see **Fig. 3**). To evaluate the response properties of the G1, a series of recognition experiments were carried out at room temperature, In the aqueous solution of G1 (c=1.0µM), 10 eq various cations including K⁺, Na⁺, Li⁺, Ag⁺, Fe²⁺, Cu²⁺, Hg²⁺, Mg²⁺, Ba²⁺, Ca²⁺, Co²⁺, Zn²⁺, Cd²⁺, Al³⁺, Ni²⁺ and Pb²⁺were added, respectively. As shown in Fig. 4, when aqueous solution of Fe³⁺ was added, it was found that the maximum absorption wavelength was shifted to 228 nm (red shift). However, the other cations could not induce similar fluorescence changes.



Fig. 3. The UV-visible absorption spectrum of G_1 in HEPES buffer (10 mM, pH=7.2, V _{ethanol}/V _{deionized water} = 1:1)



Fig. 4. UV-vis spectral changes of probe G₁ upon additions of various metal ions.

The ethanol containing the G1was observed blue under the UV–vis lamp, When 5 times equivalent Fe^{3+} ion was added, the blue fluorescence decreases whereas it remains very much unchanged with the other ions (Fig. 5). It indicated that the G1 can selectively recognize Fe^{3+} . This phenomenon could also be confirmed by fluorescence spectroscopy. As shown in Fig. 6, the G1 showed a strong fluorescence emission at 378 nm upon excitation at 250 nm. This strong fluorescence of probe G1 may be due to the C=N-N isomerization with the acylhydrazone Schiff base fluorescence group. Upon addition of Fe^{3+} to the solution of gel factor G1, a obviously decreased in fluorescence intensity was observed. Whereas, upon the addition of various metal ions, including K⁺, Na⁺, Li⁺, Ag⁺, Hg²⁺, Mg²⁺, Ba²⁺, Ca²⁺, Cu²⁺, Fe²⁺, Co²⁺, Zn²⁺, Cd²⁺, Pb²⁺, Al³⁺, Ni²⁺ tested to the solution of the organic gel factor G1 did not induce significant fluorescence changes.



Fig. 5. Optical experiment under UV-vis lamp.



Fig. 6. Fluorescence spectra of G_1 in EtOH/water (1:1, v/v) containing HEPES buffer (0.02mM, pH=7.2) in the presence of different metal ions.



Fig. 7. Competitive experiments in the probe G_1 with Fe³⁺ system with interfering metal ions in EtOH/water (1:1, v/v) containing HEPES buffer (0.02 mM, pH= 7.2).

In order to illustrate the anti-interference ability of the G1 to Fe^{3+} recognition, further study was carried out by adding other metal ions to a mixed solution of G₁ and Fe³⁺ in EtOH/water (1:1, v/v) containing HEPES buffer (0.02 mM, pH=7.2). As shown in **Fig. 7**, Fe³⁺ was added to the buffer containing the G1, and the curve showed that the fluorescence intensity was significantly reduced, and then an equal amount of other metal ions (K⁺, Na⁺, Li⁺, Ag⁺, Cu²⁺, Hg²⁺, Mg²⁺, Ba²⁺, Ca²⁺, Co²⁺, Zn²⁺, Cd²⁺, Al³⁺, Ni²⁺, Fe²⁺, Pb²⁺) were added, respectively. There was no significant change in the fluorescence intensity and the spectral curve shape. The results showed that the G1 had a strong anti-interference ability and high selectivity to Fe³⁺ in the presence of other metal ions.



Fig. 8. Fluorescence spectra of probe G_1 in EtOH/water (1:1, v/v) containing HEPES buffer (0.02 mM, pH= 7.2) in the presence of different iron salts.

Additionally, in order to explore the effect of anion on the recognition of Fe^{3+} by the G1. Aqueous solution of sulfate, nitrate and chloride in ethanol (0.02 mM HEPES, pH=7.2, V/V =1:1) was tested. As shown in **Fig. 8**, the equivalent equivalents of $Fe_2(SO_4)_3$, $FeCl_3$ or $Fe(NO_3)_3$ was added to the solution of G₁, and there were no significant differences in the fluorescence responses. The results showed that the anion does not affect the recognition of Fe^{3+} by G1.





Fig. 9. (a) Fluorescence emission spectra of the probe G_1 was titrated with Fe³⁺ in EtOH/water (1:1, v/v) containing HEPES buffer (0.02 mM, pH= 7.2). (b) Fluorescence spectrum of the probe G_1 was decreased with the increasing of Fe³⁺/G₁.(c)The complex constant curve of the titration of the organic gel factor G1 by the Fe³⁺

Quantitative off-on responses of the organic the organic gel factor G1 to Fe³⁺ were examined by fluorometric titrations. The emission spectra of the organic gel factor G1 reacted with different concentration Fe³⁺ in 2.0 mL of aqueous solution EtOH/water (1:1, v/v) containing HEPES buffer (0.02mM, pH=7.4 were recorded). As shown in **Fig. 9(a)**, during titration, the emission band of the organic gel factor G1 at 378 nm gradually decreased with the addition of increasing amount of Fe³⁺. As shown in **Fig. 9(b)**, with the addition of increasing Fe³⁺/G1, the fluorescence intensity of the the organic gel factor G1 decreased continuously, and the curve reached a steady state when 15 times of equivalent Fe³⁺ ions were added.

As shown in **Fig. 9(c)**, Benesi-Hildebrand (BH) diagram showed that the linear combination confirmed the stoichiometric complexation of Fe^{3+} with the G1 at 1:1. The binding constant of G1-Fe³⁺ complex was determined as Ka=7.306×10³M⁻¹. The detection line was calculated by recording the ten times fluorescence intensity of the G1 at 378nm. The minimum detection limit was 5.92×10^{-7} M (probe concentration 1×10^{-5} M) according to the formula LOD = $3\sigma/\text{Ka}(\sigma \text{ denotes the 10 relative standard deviation fluorescence intensity of G1})$. This indicates that the the G1can be used for quantitative detection of Fe³⁺ in a relatively wide range.

According to literatures [50-52], the fluorescence of Schiff base fluorescent probes varies, depending on the different functional groups of these probes, which are characterized by the combination of C=N and active carbonyl groups, which are complexed with Fe^{3+} on the molecular group playing an important role. Therefore, it is speculated that during the complexation of the factor G1-Fe³⁺, the Fe³⁺ may coordinate with the carbonyl group of the coumarin in the gelator G₁, the C=N and the carbonyl group of the hydrazide Schiff base, the electron or energy of factor G₁ is transferred from the excited state to Fe^{3+} , causing

fluorescence quenching (Fig. 10).



Fig. 10. G_1 - Fe³⁺ complexation mechanism

3.3. Self-assembly mechanism

During the formation of the G_1 organogel, the π - π stacking interactions among the coumarin moieties, the hydrogen bond interactions between the acylhydrazone/Schiff base moieties and the van der Waals forces between the long alkyl chain may cooperatively stabilize the aggregate structures.

The **Fig. 11** displays the FT-IR spectra of G1 powder and the xerogels from isopropanol. In the xerogels, the stretching vibrational peak of N-H is located at 3425 cm⁻¹. The vibration peaks at 1635 and 1585 cm⁻¹ are assigned to the C=O and aromatic vibrational peaks, respectively[53]. These vibrational peaks indicate that all of the amide groups are involved in hydrogen bonding[54].



Fig.11. FT-IR spectra of G₁ powder and isopropanol xerogel.



Fig. 12. X-ray diffraction patterns of G₁ powder and isopropanol xerogel.

The organogel aggregation pattern can be further studied by comparing the X-ray diffraction patterns (XRD) of the organic gel factor G1 and its isopropanol xerogel (Fig. 12). Compared with the gel factor powder, the isopropanol xerogel shows a broader diffraction peak at $2\theta=22.52^{\circ}$, It showed that π - π stacking exists between the coumarin groups of the G1 isopropanol organogel[55].

In order to study the assembly structure of coumarin-appended acylhydrazone Schiff base G1, the organogel of critical gel concentration in isopropanol were prepared. After lyophilization, they were observed by SEM. As shown in **Fig. 13**, (a) is the morphology at a low magnification of the isopropanol gel, (b) is the morphology at 5000 times higher magnification of the isopropanol gel, and (c) is the morphology at 500 times higher magnification of the isopropanol gel, and (c) is the morphology at 500 times higher magnification of the isopropanol gel. It was observed at a low magnification that the isopropanol gel was formed by the globular structure, and it was observed at a high magnification that the globular structures were composed of reticular windings. (d) The morphology of 50000 times magnification after ultraviolet lamp irradiation, (e) Low magnification Morphology of isopropanol Gel after adding Fe³⁺, and (f) 20000 magnification morphology of isopropanol gel after adding Fe³⁺. Under low power microscope, it was observed that isopropanol gel collapsed into solution after adding Fe³⁺, which indicated that the organic gel could recognize Fe³⁺.



Fig. 13. Scanning electron micrograph of the isopropanol xerogel.

(a) is the morphology at a low magnification of the isopropanol gel, (b) is the morphology at 5000 times higher magnification of the isopropanol gel, and (c) is the morphology at 500 times higher magnification of the isopropanol gel. (d) The morphology of 50000 times magnification after ultraviolet lamp irradiation, (e) Low magnification Morphology of isopropanol Gel after adding Fe^{3+} , and (f) 20000 magnification morphology of isopropanol gel after adding Fe^{3+} .

4. Conclusions

In summary, we have designed and synthesized a new coumarin-derived acylhydrazone Schiff base fluorescent organogel (G₁). It has been found that gelator G1 can form stable organogels in isopropanol, tert-amyl alcohol, *n*-butanol and phenylamine. And G₁ can response to heating, irradiation and vigorous agitation, the solution can be reformed to the gel state after being cooled for about 0.5 h. The supramolecular aggregation in solution was studied through concentration depended UV-vis spectra and fluorescence spectroscopy, concentration depended XRD, FT-IR and SEM spectroscopic studies. All the results indicated that the hydrophobic interaction between alkyl chains, the π - π stacking interactions between the coumarin moieties, and the hydrogen-bonding between the acylhydrazone/schiff base moieties play important roles during the formation of ordered gels. More importantly, the organic gel factor G1 can recognize Fe³⁺. The G1 formed a 1:1 complex with Fe³⁺ which inhibits the C=N-N isomerization and generated complexation quenched fluorescence effect. Metal cation selectivity studies with the gel factor G1-Fe³⁺ complex in the fluorescence spectroscopy revealed that the complex is detected easily in the presence of the Fe³⁺. Therefore, the G1 has potential application value for rapid and real time detection of Fe³⁺.

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Declaration of interests

 $\sqrt{}$ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

□The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Solution

Author contributions

Yun-Shang Yang: Methodology, Investigation, Writing

Chuan Liang: Writing - Original Draft.

Chen Yang: Writing: Review & Editing

Ying-Peng Zhang: Methodology, Investigation, Writing: Review & Editing

Bao-Xu Wang: Review & Editing

Jie Liu: Writing: Review & Editing

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Graphical Abstract

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- A novel coumarin-derived hydrazide Schiff based fluorescent organogel was synthesized.
- The gelator G1 can form stable organogels in isopropanol, tert-amyl alcohol, *n*-butanol and phenylamine.
- The G_1 can response to heating, irradiation and shaking.
- The gel factor could selectively and sensitively response to Fe^{3+} only among common metal cations.