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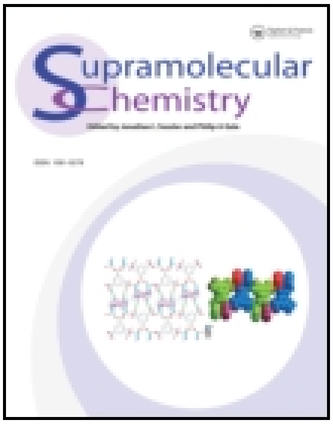

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Organogel of fluorescein-based derivative formation in the selected pH value

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Organogel of fluorescein-based derivative formation in the selected pH value

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In this work, film structure was obtained by self-assembly of fluorescein derivative via sol–gel process. The self-assembly structure and the formation mechanism had been studied and certified by scanning electron microscopy, IR, UV–vis, fluorescence and X-ray diffraction experiment data. The UV–vis absorption and emission spectra of the compound **1** were changed with the change of the pH value in the solution state. This gelator had certain selectivity for pH value and formed gels.

Keywords: organogel; self-assembly; fluorescein; pH value; film structure

1. Introduction

In recent years, supramolecular self-assembly has attracted abundant research interests because of its great application in many aspects of life science (*1–3*). As an important research topic in supramolecular chemistry, low molecular weight gels have seen a boom development due to their very smart nature and widely potential application (*4–6*). The low molecular weight gels can be obtained by the formation of a three-dimensional network structure through the weak intermolecular interactions, such as hydrogen bonds, electrostatic interactions, π–π stacking interactions, hydrophobic forces, non-specific vander Waals forces and chiral dipole–dipole interaction (*6*). At the same time, a plethora of exciting structures ranging from nanofibre, nanowhisker, nanotube, nanoball to monolayer, liquid crystal, vesicle and crystalline networks existed in these kinds of soft materials (*7–17*). An ongoing problem for the chemists constitutes how to get smart functional materials through controlling the molecular self-assembly process (*18–25*). A number of strategies have been developed to control and tune the molecular self-assembly of low-weight molecular gels. These smart low-weight molecular gels were responded to the changes in the environmental conditions including the value of pH, temperature, solvent polarity, light, catalytic action of enzymes and mechanical triggers (*26–29*). The pH value plays an important role in many vital moments, such as cell proliferation and apoptosis, multidrug resistance, ion transport, endocytosis and muscle contraction. On the other hand, the pH value can determine some kinds of molecular structure including rhodamine, fluorescein and so on (*30*). These kinds of compounds are used to be prepared for fluorescent chemosensors (*31*). The optical properties of these compounds will be changed with the molecular structure changing under different pH values. There are reports about various effects of pH on gel formation and the regulation on the formed nanostructures (*32–36*). Liu and coworkers have reported a kind of amphiphilic peptide dendron used as a hydrogelator that can form a hydrogel over a wide pH range (*37*). However, it is a challenge to prepare gels which can specially select a narrow pH range for gel formation conditions. Particularly, the effect of the pH value on the gel formation and morphology based on inconstant molecular derivative gelator has not been explored. In this paper, we report a new kind of organogel obtained via the self-assembly of fluorescein-based derivative. The organogel was only obtained from the mixed solvent DMF/H_2O under the pH value range of 8–11.

2. Results and discussion

The gelation ability of compound **1** was assessed by dissolving the compound with the concentration of 25 or 12.5 $mg\,ml^{-1}$ in a variety of solvents, as shown in Table 1. Compound **1** could form gels only in dichloromethane with the critical gelation concentration of 25 $mg\,ml^{-1}$. So the mixed solvent of DMF/H_2O was tried to prepare gel of compound **1**. It was taken into account that the molecular structure of compound **1** was changed with the pH value of solution. The solution with the pH value range from 1 to 14 was tested, respectively. The gels were obtained from solution with the pH value range of 8–12. To some extent, this organogel system could be potentially applied for pH sensor. The photograph of gel **1** in DMF/H_2O was shown

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Table 1. Gelation properties of compound **1** in various solvents.

Solvent	Compound **1**	Solvent	Compound **1**
Acetone	S	Toluene	P
DMF	S	Dichloromethane	G
H_2O	NI	Acetonitrile	P
Tetrahydrofuran	S	Chloroform	S
Petroleum ether	S	DMSO	S
Hexane	S	Dioxane	S
Ethyl acetate	S	Ethanol	S
Methanol	NI	Butanol	S
DMF/H_2O (1/1, v/v, pH 1.0)[a]	P	DMF/H_2O (1/1, v/v, pH 2.0)[a]	P
DMF/H_2O (1/1, v/v, pH 3.0)[a]	P	DMF/H_2O (1/1, v/v, pH 4.0)[a]	P
DMF/H_2O (1/1, v/v, pH 5.0)[a]	P	DMF/H_2O (1/1, v/v, pH 6.0)[a]	P
DMF/H_2O (1/1, v/v, pH 7.0)[a]	P	DMF/H_2O (1/1, v/v, pH 8.0)[a]	G
DMF/H_2O (1/1, v/v, pH 9.0)[a]	G	DMF/H_2O (1/1, v/v, pH 10.0)[a]	G
DMF/H_2O (1/1, v/v, pH 11.0)[a]	G	DMF/H_2O (1/1, v/v, pH 12.0)[a]	S
DMF/H_2O (1/1, v/v, pH 13.0)[a]	S	DMF/H_2O (1/1, v/v, pH 14.0)[a]	S

Notes: S, solution; P, precipitate; NI, not insoluble; G, gel. [**1**] = 25 mg ml^{-1}.
[a] [**1**] = 12.5 mg ml^{-1}.

in Figure 1. These gels were stable at room temperature for more than 1 week.

In order to understand the self-assembly process, the morphologies of the xerogels were analysed by field emission scanning electron microscopy (FE-SEM) after drying. The xerogels of **1** from DMF/H_2O (1/1, v/v) at the pH value of 8–11 had almost the same film framework. At the same time, there was irregular spherical particle with the diameter of about 1.0 μm. Through the observation of the SEM photograph, it could be seen that the self-assembly behaviour of **1** was not affected in the pH range of 8–11 (Figure 2).

To understand the finer details of the stacking process of **1** in gel state from the mixed solvent of DMF/H_2O (1/1, v/v), the UV–vis and fluorescence spectra of compound **1** in solution state were carried out in the pH range from 8 to 13, respectively. The UV–vis absorbance spectra of **1** showed two broad characteristic peaks at 460 and 490 nm for the $\pi-\pi*$ transitions (Figure 3) (*38*). The absorption intensity was gradually strengthened with the increasing pH value in the range of 8–11. Simultaneously the absorption peaks had a red shift. When the pH value increased to 13, the absorption intensity had a jump enlargement. At the same time, the absorption peaks had a bathochromic shift of 32 and 13 nm for 460 and 490 nm, respectively. It was interesting that the fluorescence emission of **1** was almost not the same as the UV–vis absorption experiment. The maximum fluorescence emission peak was at 525 nm at the pH value of 8 (Figure 4). The fluorescence emission was gradually weakened and had a red shift with the increasing pH value. The maximum fluorescence emission peak had a red shift of 12 nm when the pH value ranged from 8 to 13. These results displayed that $\pi-\pi$ stacking had happened after the pH value of the solution was increased (*39*). When pH > 7, the open-ring state was favourable to gelation in DMF/H_2O due to the formation of —COOH for hydrogen bonding and the planarity of the molecules for strong $\pi-\pi$ stacking.

Figure 1. Photograph of gel **1** in the DMF/H_2O (1/1, v/v) with the concentration of 12.5 mg ml^{-1} at the pH value of 10.

The infrared spectra of **1** (Figure 5) in DMF/H_2O (1/1, v/v) confirmed that the hydrogen bonding plays an important role in the gelation and self-assembly process. It was observed that in the powder state of **1**, the C═O stretching frequency was at 1670 cm^{-1}. However, the same peak was shifted to a lower frequency at 1637 cm^{-1} in the xerogel **1**. Such a decrease in the amide stretching clearly indicates the presence of the strong intermolecular hydrogen bonding in gel **1**. The information of the long-range regulation to the molecular assembly could be deduced from the measurement of X-ray diffraction (XRD) data of the xerogel. The XRD pattern of xerogel of **1** prepared from DMF/H_2O (1/1, v/v) at a pH value of 10.0 showed that the structure was complicated (Figure 6). The obtained spacings for the xerogel were 21.5, 10.7 and 7.9 Å, with a ratio of 1:1/2:1/3, a character of lamellar packing of the molecules (*40*). The distance of 1.9 Å was

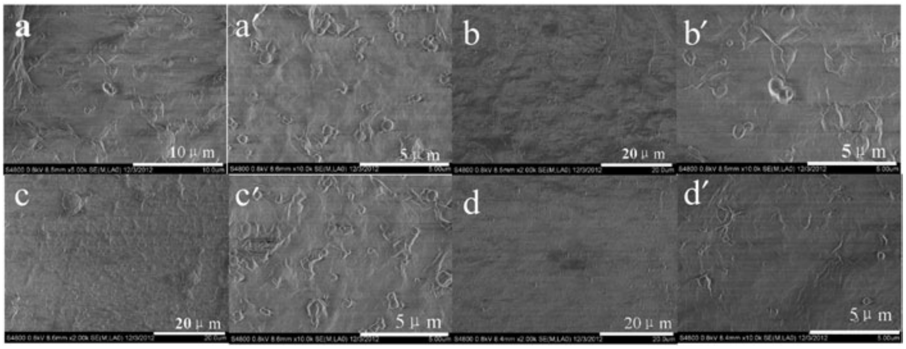


Figure 2. SEM images of the xerogels at room temperature (25°C); **1** in mixed solvent of DMF/H_2O (1/1, v/v) with the concentration of 12.5 mg ml^{-1} at different pH values; (a) and (a′), (b) and (b′), (c) and (c′), (d) and (d′) are at pH values of 8, 9, 10, 11, respectively; scale bars for a, a′, b, b′, c, c′, d and d′ are 10, 5, 20, 5, 20, 5, 20 and 5 μm, respectively.

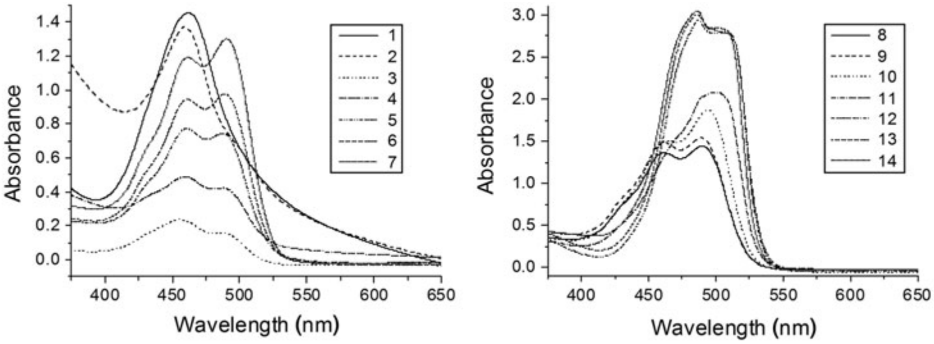


Figure 3. UV–vis spectra change of **1** in DMF/H_2O (1/1, v/v) solution ($C_1 = 10^{-4}$ M) with the change in pH value.

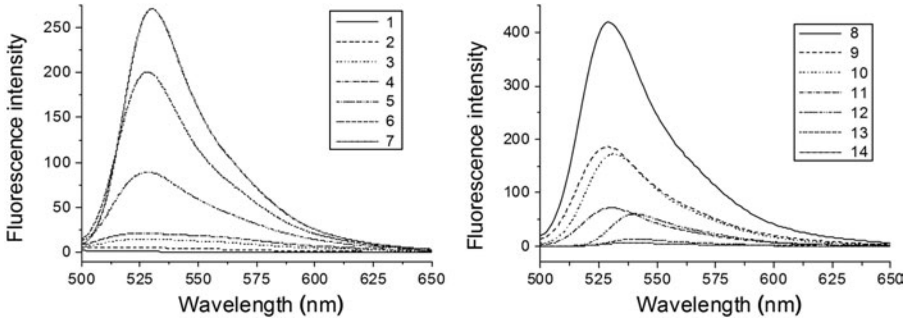


Figure 4. Fluorescence spectra change of **1** in DMF/H_2O (1/1, v/v) solution ($C_1 = 10^{-4}$ M) with the change in pH value ($\lambda_{ex} = 490$ nm).

close to the length of the molecular distance of **1**. The peaks at 4.5 and 4.0 Å were assigned to the length of the hydrogen bonding and π–π stacking, respectively (*41*).

3. Conclusion

In summary, a novel and simple fluorescein-based organogel has been designed and synthesised. It could form a film structure in a mixed solvent of DMF/H_2O at a suitable pH value. On the base of SEM, XRD, UV–vis, IR and fluorescence studies, it was indicated that the intermolecular non-covalent bond interaction of compound **1** was obviously strengthened in the gel state. Thus, this report may provide a new way for the preparation of organogel based on structure variable organic molecule.

4. Experimental

4.1 Materials

All starting materials were obtained from commercial supplies and used as received. Fluorescein isothiocyanate (99%) was obtained from Yacoo Chemical Reagent Co.,

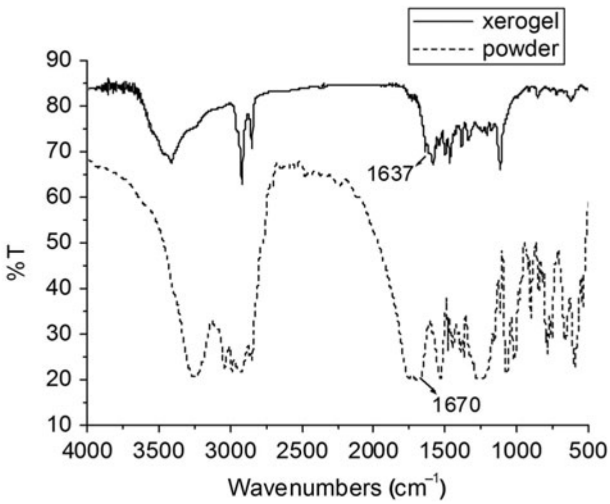


Figure 5. FT-IR spectra of **1** powder and the xerogel of **1** (12.5 mg ml^{-1}, pH 10.0) in DMF/H_2O (1/1, v/v) at room temperature (25°C).

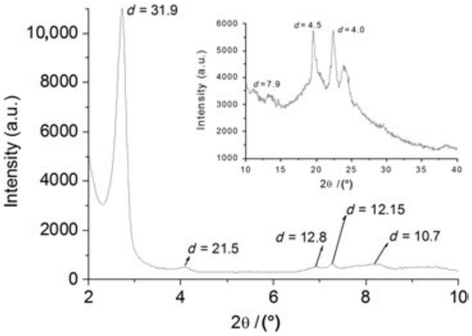


Figure 6. XRD profile of the xerogel of **1** (12.5 mg ml^{-1}, pH 10.0) in DMF/H_2O (1/1, v/v) at room temperature.

Ltd (Suzhou, P.R. China). Methyl gallate (99%), organic solvents, 1-bromododecane (98%) and ethylenediamine (95%) were supplied from Sinopharm Chemical Reagent Co., Ltd (Shanghai, P.R. China).

4.2 *Gelation test*

The gelation test on compound **1** was carried out with various single solvents and mixed solvents using a test tube inversion method (*35*). The gelators and solvents were put in a septum-capped test tube and heated (> 80°C) until the solid was dissolved. The sample vial was then cooled to 25°C (room temperature).

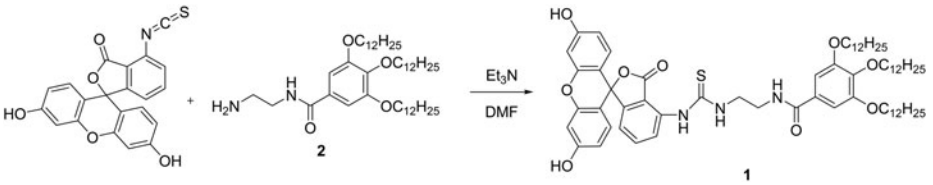
4.3 *Instrumentation conditions*

NMR and ^{13}C NMR spectra were recorded on a Mercury plus-Varian instrument (Varian, Ltd. Palo Alto, USA), at 400 and 100 Hz, respectively. Proton chemical shifts are reported in parts per million downfield from tetramethylsilane. HRMS was recorded on a LTQ-Orbitrap mass spectrometer (ThermoFisher, San Jose, CA, USA). Fourier transform infrared (FT-IR) spectra were collected by a Nexus 470 spectrometer (Nicolet Company, Madison, Wisconsin, USA), xerogel samples were prepared with KBr pellets. FE-SEM images were obtained using an FE-SEM S-4800 instrument (Hitachi, Ltd. Tokyo, Japan). Samples were prepared by spinning the samples on glass slices and coating with Au. Powdered XRDs were generated by using a Philips PW3830 X-ray generator (Cu target, $\lambda = 0.1542$ nm), with a power of 40 kV and 40 mA was used. UV–vis absorption spectra were recorded on a UV–vis 2550 spectroscope (Shimadzu, Ltd. Tokyo, Japan). Fluorescent spectra were recorded on Edinburgh Instruments FLS 900 (Edinburgh Instruments, Ltd. Livingston, UK).

4.4 *Synthesis*

The synthetic methodology for compound **1** is shown in Scheme 1. Compound **2** was prepared according to the previous reported method (*42*). The details of the synthesis are as follows.

Compound **2** (1.50 g, 2.1 mmol) and fluorescein isothiocyanate (0.81 g, 2.1 mmol) were placed in a flask, then anhydrous N,N-dimethylformamide (DMF) (40 ml) and Et_3N (5 ml) were added and then the slurry was stirred at room temperature for 10 h. A large amount of water was added to the solution, and the water phase was extracted three times with CH_2Cl_2. The organic phase was combined and dried by anhydrous $MgSO_4$. The solvent was removed under reduced pressure. Lastly, compound **1** (1.50 g, yield 65%) was obtained as an orange solid after purified by chromatography on silica gel with petroleum ether/ethyl acetate (4:1, v/v) as the eluent. ^{1}H NMR (400 MHz,



Scheme 1. Molecular structure of the self-assembly fluorescein derivatives of **1** and **1a**.

DMSO): δ 10.067 (s, 2H), 9.983 (s, 1H), 8.521 (s, 1H,), 8.126 (s, 2H,), 7.673 (s, 1H), 7.106 (s, 3H), 6.626 (s, 2H), 6.576 (d, 2H, $J = 8.4$ Hz), 6.505 (d, 2H, $J = 8.0$ Hz), 3.903 (m, 4H), 3.811 (t, 2H, $J = 6.0$ Hz), 3.666 (s, 2H), 3.447 (s, 2H), 1.645 (m, 4H), 1.572 (m, 2H), 1.371 (m, 6H), 1.189 (m, 48H), 0.801(t, 9H, $J = 6.0$ Hz). ^{13}C NMR (100 MHz, DMSO): 181.3, 168.9, 166.8, 163.6, 159.9, 152.6, 152.3, 147.7, 141.5, 140.4, 129.4, 129.1, 127.1, 124.4, 117.6, 113.0, 110.1, 106.6, 102.7, 83.6, 72.6, 68.7, 43.9, 40.5, 39.9, 31.9, 30.5, 29.7, 29.5, 29.4, 26.3, 22.6, 14.0, HRMS (ESI$^+$) calcd for $C_{66}H_{95}N_3NaO_9S$ [M + Na$^+$]: 1128.6687; found: 1128.6680.

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