http://dx.doi.org/10.5012/bkcs.2014.35.12.3668

Coumarin-Based Organogel Formed at Different Solvent Compositions and Their Luminescent Properties

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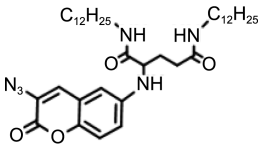
Received August 20, 2014, Accepted September 1, 2014

Key Words : Coumarin, Organogel, Luminescence properties, Fluorescence life times

Supramolecular gels based on low-weight molecules[1-4] have attracted considerable research interest due to their potential applications in fields such as molecular electronics,[5] light-energy conversion,[6] catalysis,[7,8] cosmetics[9] and drug delivery systems.[10,11] Although many researchers have reported various supramolecular gels in the literature,[12,13] but there is relatively little information regarding the photoluminescence properties of supramolecular gels, including changes of the emission colour, field emission, and light emitting properties. In particular, a few papers have reported the photoluminescence properties of supramolecular gels, including fluorescence intensity and lifetimes in different compositions of solvents.[14,15] Herein, we describe the formation of a coumarin-based supermolecular gel and its luminescence properties in various compositions of ethanol/DMSO, as determined by fluorimetry and time-resolved luminescence emission.



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Coumarin-based gelator **1** was synthesized in five steps (Scheme S1). The 2-acetamidoacetic acid (**4**) was reacted with 2-hydroxyl-5-bromo-benzaldehyde (**5**) to afford compound **3** in good yield. The introduction of an azide group in compound **2** was achieved by reaction with sodium nitrile and sodium azide. On the other hand, compound **6**, possessing double long alkyl chain groups, was prepared from glutamic acid as the starting material. Then, the coupling of compound **2** and compound **6** was performed in DMSO to produce desired product **1** in 50% yield, as confirmed by ^{1}H, ^{13}C NMR, mass spectroscopy and elemental analysis.

The organogel was prepared by dissolving 1.0 wt % of **1** in pure and mixed organic solvents and with one of the following solvents: DMF, DMSO, acetonitrile, acetone, ethyl acetate, ethanol, THF, *n*-hexane, toluene, xylene, benzene, cyclohexane, chloroform, methanol and water. As shown in Table S1 and Figure 1, **1** could be gelated in pure toluene, cyclohexane and ethanol. In addition, the gelation ability of **1** was tested in a mixture of ethanol/DMSO (10:0-0:10 v/v) and we observed that compound **1** could also gelate in mixed solvents containing ethanol/DMSO over the range of 10:0-5:5, v/v. On the other hand, **1** did not form a gel in more 50% of DMSO, due to its high solubility in DMSO.

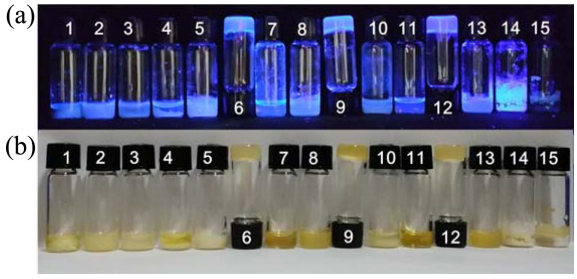

Figure 1. The photograph of organogel **1** (1 wt %) in different solvents (A) with and (B) without UV lamp irradiation. the following solvents: (1) DMF, (2) DMSO, (3) acetonitrile, (4) acetone, (5) ethyl acetate, (6) ethanol, (7) THF, (8) *n*-hexane, (9) toluene, (10) xylene, (11) benzene, (12) cyclohexane, (13) chloroform, (14) methanol and (15) water.

The morphologies of xerogel **1** prepared at different compositions of ethanol/DMSO were investigated by scanning electron microscopy (SEM). The SEM images of organogel **1** clearly displayed typical fiber structures with diameters of 75-125 nm (Figure 2), which were not dependent to the composition of the gelation solvents. Furthermore, fluorescence images of organogel **1** emitted a strong blue color under UV light with 350 nm (Figure 1(a)).

Since **1** could gelate a mixture of ethanol/DMSO (10:0, 7:3, and 5:5 v/v), quantitative luminescence properties of

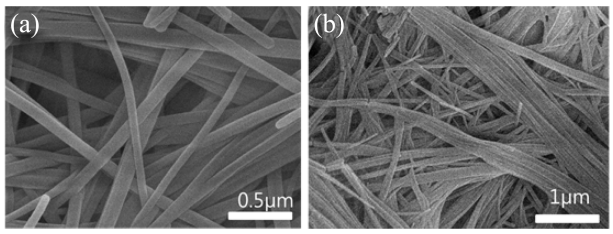

Figure 2. SEM images of xerogels **1** prepared from (A) pure ethanol and (B) a mixture of ethanol/DMSO (5:5 v/v).

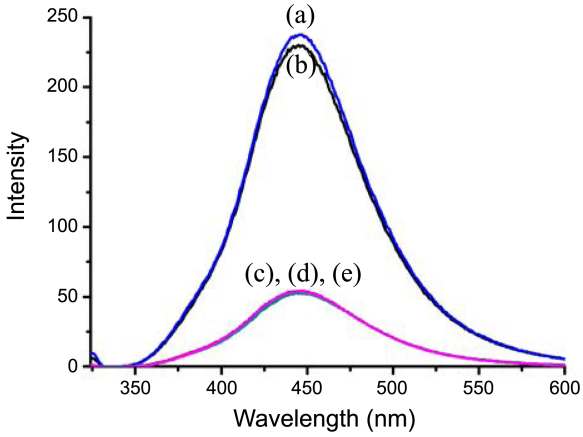

Figure 3. Fluorescence spectra of **1** at different composition of solvents; (a) DMSO, (b) ethanol/DMSO (3:7 v/v), (c) ethanol/DMSO (5:5), (d) ethanol/DMSO (7:3 v/v) and (e) ethanol.

organogel **1** were measured. In various ratios of ethanol/DMSO (10:0, 7:3, 5:5, 3:7 and 0:10 v/v), sol **1** prepared from ethanol/DMSO (3:7 and 0:10 v/v) exhibited a strong blue fluorescence under UV light, but upon gelation with ethanol/DMSO (10:0, 7:3 and 5:5 v/v), their fluorescence emissions were relatively weaker than that of sol **1**. The fluorescence emission properties as well as the absorption spectra of sol **1** and organogel **1** were observed. The absorption band of organogel **1** appeared at 336 nm (Figure S1), which was assigned as a $\pi \rightarrow \pi^*$ transition.[16] The emission spectra of organogel **1** with different ratios of ethanol/DMSO were observed with excitation at 334 nm (Figure 3). In the gel state, an emission band centered at 443 nm was observed. The band intensity decreased dramatically as the proportion of ethanol increased, which is attributed to aggregation-caused quenching (ACQ) effects[17,18] from π-π stacking between coumarin groups. On the other hand, the fluorescence intensities of sol **1** in different compositions of ethanol/DMSO (3:7 and 0:10 v/v) were relatively larger than that of gel **1**. These results indicate that molecule **1** exists the monomeric species without π-π stacking.

We observed the ^{1}H NMR spectra of organogel **1** prepared from pure ethanol under conditions in which the spectra were acquired at different temperature (Figure S2). As the temperature increased, the protons of the coumarin moieties were shifted to a higher magnetic field. In addition, the proton peaks of the coumarin moieties became sharper at increasing temperature. These results indicate that **1** formed a self-assembled structure by intermolecular interactions between the coumarin groups at low temperature, but became dissociated at high temperatures. To examine the driving force for gel formation, the FT IR spectra of both organogel **1** and sol **1** were also observed (Figure S3). The -NH and -C=O vibration bands of gel **1** appeared at 3305 cm^{-1} and 1654 cm^{-1}, respectively. In contrast, the -NH and -C=O vibration bands of sol **1** appeared at 3299 cm^{-1} and 1634 cm^{-1}, respectively. In comparison to sol **1**, -C=O vibration band of organogel **1** was shifted to the longer wavelength, due to the intermolecular hydrogen-bonding interactions.

Table 1. Fluorescence Life Times of **1** (1.0 wt %) at Different Composition of Solvents

Solvent Conditions	Life Times (τ)	State
EtOH (100%)	3.21 ns	Gel
EtOH/DMSO (7:3 v/v)	3.53 ns	Gel
EtOH/DMSO (5:5 v/v)	5.31 ns	Gel
EtOH/DMSO (3:7 v/v)	5.79 ns	Sol
DMSO (100%)	6.36 ns	Sol

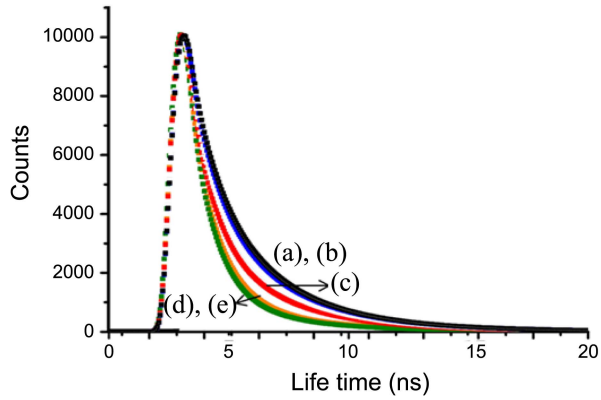

Figure 4. (a) Time resolved fluorescence decay of **1** (1.0 wt %) at different composition of solvents; (a) DMSO, (b) ethanol/DMSO (3:7 v/v), (c) ethanol/DMSO (5:5), (d) ethanol/DMSO (7:3 v/v) and (e) ethanol.

We also investigated the time-resolved emission of organogel **1** with different ratios of H_2O/DMSO (Table 1 and Figure 4). The luminescence lifetime of the organogel obtained with pure ethanol was 3.21 ns. We observed the shortest luminescence lifetime of organogel **1** prepared at pure ethanol. The shortening luminescence life time from gels prepared in pure ethanol may be attributed to strong intermolecular interactions such as π-π stacking and intermolecular hydrogen bonding. On the other hand, the sol **1** in DMSO exhibited strong fluorescence emission with the lifetime of sol **1** being 6.36 ns.

To gain additional insights into the thermally promoted stability of organogel **1** prepared in pure ethanol, we performed sol-gel transition temperature (T_{gel}) by differential scanning calorimetry (DSC). Organogel **1** showed a phase transition at 87 °C (Figure S4). In contrast, when organogel **1** was prepared with a mixture of ethanol/DMSO (5:5 v/v%), we observed a phase transition at 66 °C. These results suggest that gel stability of the organogel prepared from pure ethanol was much higher than that prepared from a mixture of ethanol/DMSO (5:5 v/v).

In conclusion, we have demonstrated that a coumarin-based gelator could be gelated both pure solvents and in mixtures of organic solvents. In particular, **1** formed a gel in various ratios of ethanol/DMSO (10:0-5:5 v/v). Photophysical studies confirmed that the organogel exhibited typical π-π stacking interactions which gave rise to weak luminescence behavior. The luminescence lifetimes of the organogel were also dependent on solvent composition. In pure ethanol, the

organogel exhibited the shortest lifetime due to the stronger interaction such as π-π stacking and intermolecular hydrogen bonds. In contrast, the sol **1** prepared at pure DMSO showed the longest lifetime. The results of this work emphasize the validity of a gelator design that makes use of fluorescence moieties with versatile properties.

Experimental

Instruments. The NMR spectra for ^{1}H and ^{13}C NMR were measured using a Bruker ARX 300 apparatus. For the IR spectra, KBr pellets were formed and the IR spectra were observed over the range of 400–4000 cm^{-1}, using a Shimadzu FT-IR 8400S instrument. In addition, the mass spectra were observed using a JEOL JMS-700 mass spectrometer. A UV-vis spectrophotometer (Thermo Evolution 600) was used to obtain the absorption spectra. Gels were measured using a 0.50 mm path length quartz cuvette as well as a 4-mm path length quartz cuvette for emission measurements. The thermodynamic parameters were determined by a literature method reported previously.

Electron Microscopy. A field emission scanning electron microscope (FE-SEM, Philips XL30 S FEG) was used to observe the samples in which an accelerating voltage of 5–15 kV with an emission current of 10 μA was used. Prior to SEM visualization the organogel also freeze-dried under vacuum at −30 °C.

Fluorescence Lifetime Measurements. Using a conventional laser system, the emission lifetimes were measured upon generation with an excitation source (350 nm output of a Spectra-Physics Quanta-Ray Q-switched GCR-150-10 pulsed Nd:YAG laser). The signals for the luminescence decay were obtained using a Hamamatsu R928 PMT and the data were recorded on a Tektronix model TDS-620A (500 MHz, 2 GS/s) digital oscilloscope; these data were then analyzed by using fitting the data points to an exponential equation.

Typical Experimental Procedure for the Formation of a Supramolecular Gel: Compound **1** (4 mg, 1.0 wt %) was dissolved in pure ethanol or a mixture of ethanol/DMSO (0.4 mL) by heating. Then, the samples were maintained at room temperature to form the gel.

Acknowledgments. This work was supported by a grant from NRF (2014M2B2A9030338 and 2012R1A4A1027750), and Korea Ministry of Environment as "GAIA Project" (2012000550026). In addition, this work was partially supported by a grant from the Next-Generation BioGreen 21 Program (SSAC, grant#: PJ009041022012), Rural development Administration, Korea.

Supporting Information. Gelation test, VT ^{1}H NMR, DSC thermograms, FT IR spectra and synthetic experiment data.

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