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Fluorescence enhancement upon gelation and thermally-driven fluorescence switches based on tetraphenylsilole-based organic gelators

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ABSTRACT

Two new organic gelators **1** and **2** based on the silole (silacyclopentadiene) framework were designed with the end to develop switchable fluorescent organogels, by making use of the aggregation-induced emission (AIE) feature of silole derivatives. As for other silole derivatives, compounds **1** and **2** exhibited AIE behavior as indicated by the significant fluorescence enhancement by introducing water to the THF solutions. Compounds **1** and **2** can gel hexane, methylcyclohexane and heptane. Large fluorescence enhancement was observed for compounds **1** and **2** after gelation. Moreover, their fluorescence intensities can be changed reversibly accompanying the gel–solution transition through alternating cooling and heating. Therefore, thermally-driven fluorescence switches can be achieved with organogels based on **1** and **2**.

1. Introduction

A number of organic gelators with various structures have been described recently [1–5] and various derivatives of urea [6–10], cholesterol [11,12], and amine acid [13] have been found to be efficient gelators. Among them chromophore-based gelators have received more attentions recently, since interesting spectral variation is observed in accompanying the corresponding gel–solution phase transition for these gelators. For instance, Ajayaghosh et al. reported the absorption spectral shifts and the tuning of the excitation energy transfer for oligo(*p*-phenylenevinylene) derived gelators after gelation [14,15] and gels with turnable emission [16–18]. By making use of the viscosity difference between gel and solution phases, we and others successfully achieved the thermal modulation of the pyrene monomer/excimer fluorescence and supramolecular exciplex formation after gelation [8,19]. In a few cases, gelation-induced-fluorescence-enhancement was observed. Such fluorescent organogels are especially interesting since organogels are thermally responsive and accordingly thermal fluorescence modulation can be realized. As a result, these fluorescent organogels may find potential applications in areas such as optical devices and sensors [20–26]. Park and co-workers reported the fluorescence increase after gelation with 1-cyano-*trans*-1,2-bis-(3′5′-bis-trifluoromethyl-biphenyl)ethylene(CN-TFMBE) [20,21]. Similar phenomena were described for gelators with oxadiazole [22], benzoxazole [23], naphthalene [24] and salicylideneaniline [25] moieties. A significant fluorescence enhancement was observed for gelation with a gelator containing anthracene and urea moieties as reported by us recently [26].

In this report, we report new examples of gelation-induced-fluorescence-enhancement with silole (silacyclopentadiene)-based gelators **1** and **2** (Scheme 1). The molecular design for the gelators is based on the Aggregation-Induced Emission (AIE) feature of silole [27,28], which was reported by Tang, Zhu and their coworkers. In fact, silole derivatives with AIE feature have attracted much more efforts and even interesting chemo-/biosensors have been developed based on silole molecules [29–31]. Besides, urea and cholesterol moieties are connected to the silole core in gelators **1** and **2**, respectively, to enhance the intermolecular interactions and thus facilitate the molecular assembly and gel formation as reported early [6–12]. The results show that (1) compounds **1** and **2** exhibit AIE behaviors; (2) compounds **1** and **2** can gel a few organic solvents; (3) gelation with compounds **1** and **2** is accompanied with fluorescence enhancement and as a result thermally-driven fluorescence switch is achieved.

2. Result and discussion

As shown in Fig. 1, both compounds **1** and **2** exhibited rather weak fluorescence in THF solution (1.0×10^{-5} M). But, their fluorescence intensities were significantly enhanced after addition of water. For instance, the emission intensity at 459 nm of compound **1** (1.0×10^{-5} M in THF) increased by nearly 66 times when water was added to the THF solution and the water content reached 95% (see Fig. 1 A); moreover, the emission maximum was shifted from 459 nm to 465 nm. Similarly, for compound **2** (1.0×10^{-5} M in THF) the fluorescence intensity at 480 nm was enhanced by

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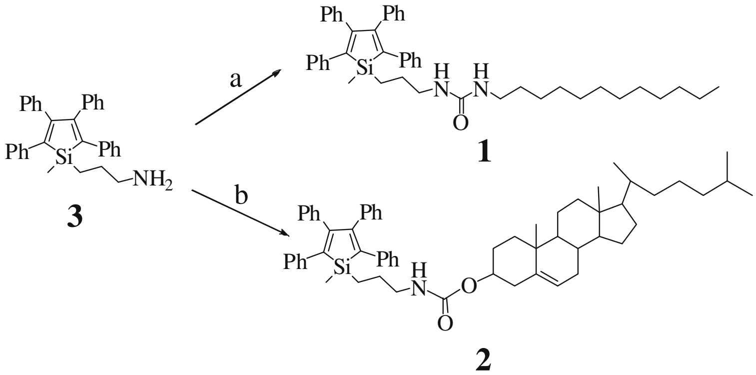

Scheme 1. Chemical structure of silole-based gelators and synthetic approach. (a) $C_{12}H_{25}NCO$, CH_2Cl_2, 40%. (b) Cholesteryl chloroformate/TEA, CH_2Cl_2, 46%.

190 times and the emission maximum was red-shifted by 3 nm when the volume ratio of THF *vs.* water reached 5:95 (see Fig. 1 B). As for other silole derivatives [27,28], the fluorescence quantum yields of compounds **1** and **2** in THF were rather low, being 5.85×10^{-4} and 2.3×10^{-3}, respectively, by reference to 9, 10-diphenylanthrance. After aggregation induced by addition of water to the THF solutions of **1** and **2**, their fluorescence quantum yields increased. For instance, the fluorescence quantum yields of **1** and **2** were measured to be 0.011 and 0.023, respectively, in the mixed solvent of THF/H_2O (v/v, 5/95). The fluorescence life-times of **1** and **2** were measured in THF and the mixed solvent of THF/H_2O. For the THF solution of compound **1** (1.0×10^{-5} M), the fluorescence life-time was estimated to be 161 ± 20 ps. But, when water was added to the THF solution (THF/H_2O, v/v, 5/95), the fluorescence exhibited a double-exponential decay, corresponding to $\tau_1 = 2.1 \pm 0.1$ ns and $\tau_2 = 5.8 \pm 0.07$ ns ($A_1/A_2 = 24:76$). For the THF solution of **2** (1.0×10^{-5} M), a double-exponential fluorescence decay was observed, corresponding $\tau_1 = 94 \pm 14$ ps and $\tau_2 = 3.0 \pm 0.2$ ns ($A_1/A_2 = 94:6$). After addition of water to the THF solution (THF/H_2O, v/v, 5/95), the fluorescence life times were prolonged to be 2.9 ± 0.2 ns (τ_1) and 6.7 ± 0.1 ns (τ_2) ($A_1/A_2 = 21:79$), respectively. The increase of the fluorescence life-times and fluorescence enhancement after addition of water were due to the aggregation of molecules of **1** and **2** as reported early [28,32].

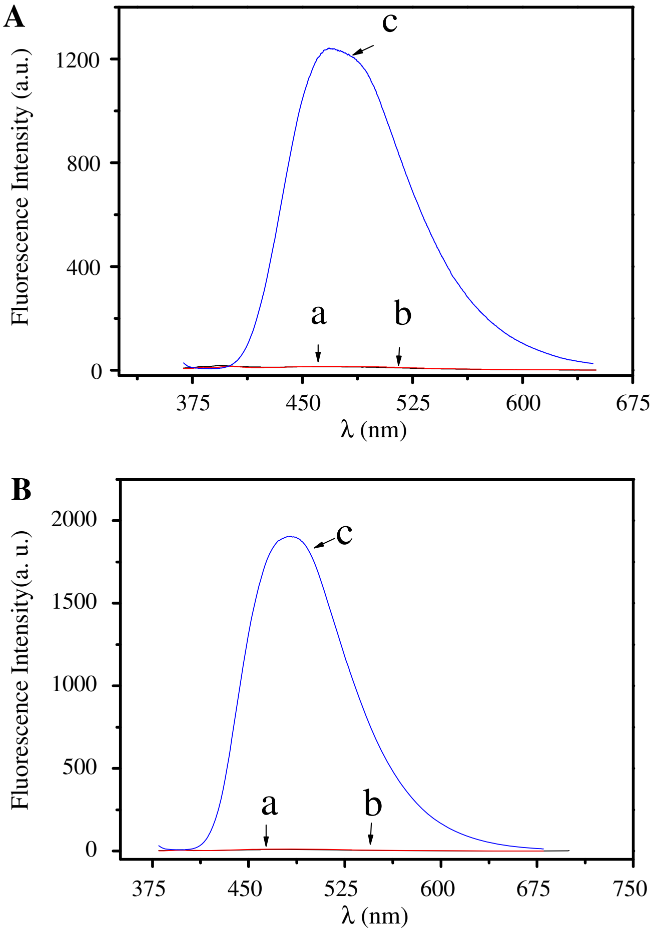

Fig. 1. The emission spectra of compounds **1** (10 μM) (**A**) and **2** (10 μM) (**B**) in the THF–water mixture with different volume percentages of water: (a) 0% H_2O; (b) 50% H_2O; (c) 95% H_2O.

After introducing water to the THF solutions of **1** and **2**, red-shifts were detected for their absorption spectra of **1** and **2** (see Fig. S1 in ESI). These results indicate that the enhanced-emission observed for compounds **1** and **2** can be ascribed to the formation of *J*-type aggregation of **1** and **2** after addition of water according to previous studies [28].

The gelation experiments were performed in a number of solvents for compounds **1** and **2**. The results indicated that the gelation abilities of compounds **1** and **2** were generally weak. Compound **1** can gel in hexane and methylcyclohexane. When the corresponding hot solutions of **1** in hexane (23 mg/mL) and in methylcyclohexane (25 mg/mL) were cooled down, opaque white gels were formed respectively (as shown in Fig. 2). As anticipated, a network of long fibers with widths about 100 nm was formed (see Fig. 3A for the SEM image of xerogel of **1**). Molecules of **1** in the gel phase were orderly arranged as indicated by XRD

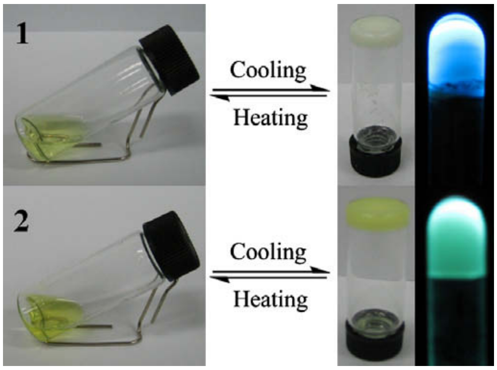

Fig. 2. Illustration of the gel formation with compounds **1** (23 mg/mL in hexane) and **2** (150 mg/mL in *n*-heptane), and the photos of the formed gels under the UV light (365 nm) illumination.

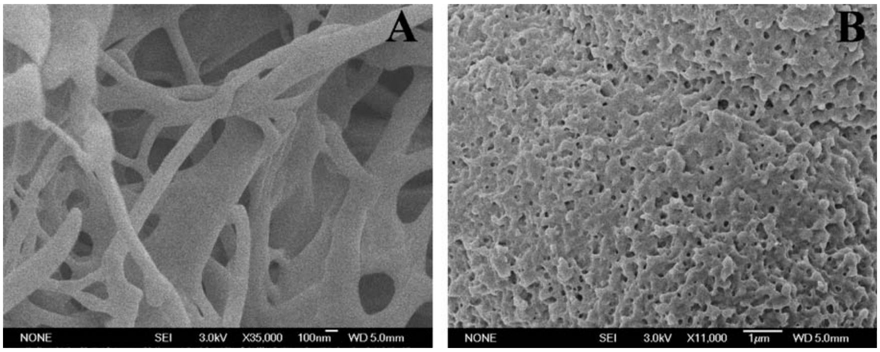

Fig. 3. SEM image of xerogel formed with **1** in hexane and that with **2** in *n*-heptane.

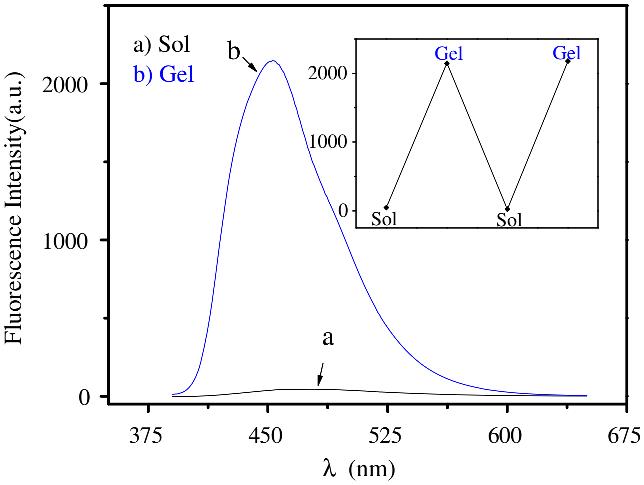

Fig. 4. The fluorescence spectra of compound **1** in *n*-hexane (23 mg/mL) before and after gel formation; inset shows the reversible variation of the emission intensity at 453 nm accompanying the solution–gel phase transition.

analysis. Three diffraction signals at 3.46°, 5.57° and 7.10° were observed as shown in Fig. S2A, corresponding to *d*-spacing of 2.55 nm, 1.57 nm and 1.25 nm, respectively. The molecular length of **1** was estimated to be 2.68 nm. Thus, the first diffraction peak may relate to the molecular length of **1**, and the other two diffraction signals may correspond to the intermolecular separations in different directions. Among the solvents tested, compound **2** can only lead to the gelation of *n*-heptane. As indicated in Fig. 2, a pale-yellow gel was formed by cooling the hot solution of **2** (150 mg/mL) in *n*-heptane. A worm-like structure was observed in the SEM image of xerogel of **2** as shown in Fig. 3B. As shown in Fig. S2B, one sharp and two broad diffraction signals at 2.05°, 3.14° and 6.99° were detected in the XRD spectrum of the xerogel, corresponding to *d*-spacing of 4.22 nm, 2.12 nm and 1.4 nm, respectively. They may correspond to the intermolecular separations in different directions. Interestingly, they are exactly in the ratio of 1:1/2:1/3, which implies a lamellar organization for molecules of **2** within the aggregates of the xerogel according to previous studies [25,33].

The ^{1}H NMR spectral results of **1** measured at different temperatures and concentrations (see Fig. S3 in ESI) indicated that the intermolecular H-bonds were formed between the urea moieties of neighboring molecules of **1** and these intermolecular H-bonds may be responsible for the gel formation of **1** [7,10]. The fact that gelation cannot occur for the methylcyclohexane solution of **1** containing tetrabutylammonium fluoride provides support for the above assumption (see Fig. S4 in ESI). It is probable that intermolecular H-bonds between the urea moieties would be disrupted in the presence of fluoride anion [34]. But, the corresponding π–π stacking and van der Waals interactions may also contribute to the gel formation with **1**.

As anticipated, the solution of compound **1** exhibited rather weak fluorescence (see Fig. 4). However, its fluorescence intensity increased largely after gel formation. For instance, the fluorescence intensity of **1** (23 mg/mL in hexane) at 470 nm was enhanced by 50 times and simultaneously the emission maximum was blue-shifted by 17 nm after gelation as shown in Fig. 4 [35]. Indeed, the fluorescence intensity enhancement after gelation can be easily distinguished by naked-eye (see photos under UV light illumination in Fig. 2). The xerogel formed with compound **1** exhibited strong emission as indicated by the fluorescence confocal microscopic image (see Fig. 5A). Such fluorescence intensity enhancement was likely due to the formation of self-assembly aggregates (see SEM images in Fig. 3) of **1** during the gelation process according to previous investigations [27,28]. Interestingly, the fluorescence intensity was reduced again after the transformation of the gel into the solution by heating. In this way, the fluorescence

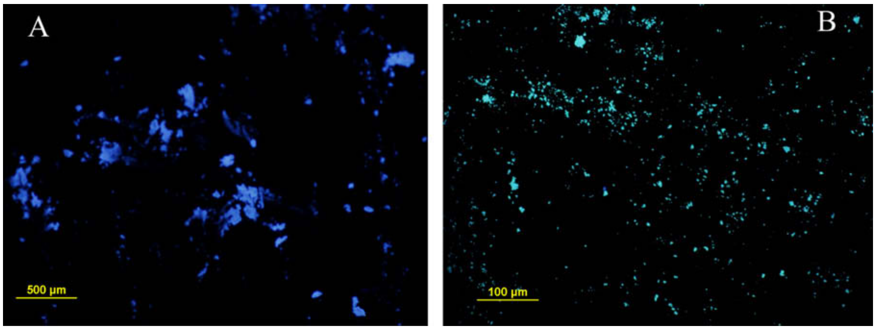

Fig. 5. Fluorescence confocal microscopic images of the xerogels based on **1** and **2**.

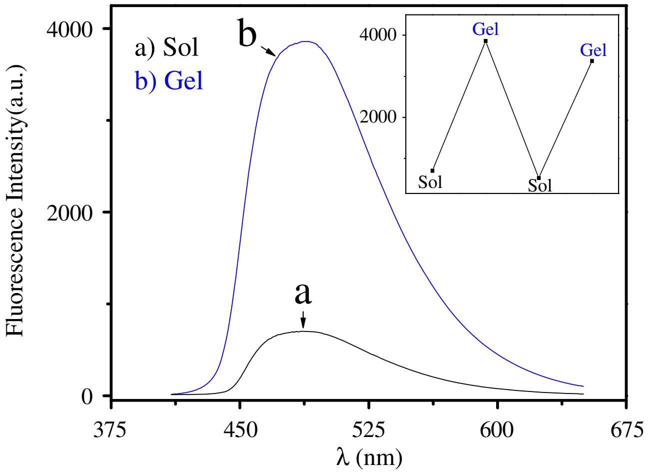

Fig. 6. The emission spectra of compound **2** in *n*-heptane (150 mg/mL) before and after gel formation; inset shows the reversible variation of the emission intensity at 490 nm accompanying the solution–gel phase transition.

intensity of **1** can be reversibly modulated accompanying the gel–solution transition through alternating cooling and heating (see inset of Fig. 3). Similar emission variation was observed for the ensemble of **1** in methylcyclohexane. Accordingly, a thermally-driven fluorescence switch can be established with organic gels based on compound **1**.

The gelation-induced-fluorescence-enhancement was also observed for the ensemble of **2** in heptane as shown in Fig. 6. The fluorescence intensity at 480 nm increased by more than six times after gel formation, and simultaneously the emission maximum was shifted from 480 nm to 483 nm after gelation. Also, the photo of the gel under UV light illumination (see Fig. 2) and fluorescence confocal microscopic measurement (see Fig. 5B) indicated the fluorescence enhancement after gelation with compound **2**. Moreover, the fluorescence intensity of **2** can be reversibly tuned by alternating heating and cooling as shown in the inset of Fig. 4.

In summary, we describe new examples of gelation-induced fluorescence enhancement with gelators **1** and **2** by making use of the aggregation-induced emission (AIE) feature of silole derivatives. As for other silole derivatives, compounds **1** and **2** exhibit AIE behavior as indicated by the significant fluorescence enhancement by introducing water to the THF solutions. Although the gelation abilities of **1** and **2** are weak, compounds **1** and **2** do gel a few solvents including hexane, methylcyclohexane and heptane. Of particular interest is the observation of large fluorescence enhancement for compounds **1** and **2** after gelation. Moreover, their fluorescence intensities can be changed reversibly accompanying the gel–solution transition through alternating cooling and heating. Therefore, thermally-driven fluorescence switches can be achieved with organogels based on **1** and **2**. These switchable fluorescent organogels may found potential applications in information storage and optical devices.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cplett.2009.05.029.

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[35] However, small red-shift was observed for the emission maximum of **1** after addition water to the THF solution. This may be due to the different molecular arrangements of **1** in the aggregates induced by addition of water and in the gel phase.