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LETTER

A chemodosimetric gelation system showing fluorescence and sol-to-gel transition for fluoride anions in aqueous media†

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We developed a chemodosimetric gelation system which turns into a fluorescent gel in the presence of fluoride anions in aqueous media. The selective cleavage of a silyl ether protecting group on the gelator by a fluoride anion gives rise to an optical change (fluorescence turn-on) and a sol-to-gel transition in aqueous media.

Self-assembled supramolecular gels consist of low molecular weight gelators (LMWGs) and solvent molecules, in which noncovalent interactions, such as hydrogen bonding, van der Waals interactions, π–π stacking, electrostatic forces, and metal coordination, are crucial to forming three-dimensional networks.[1] Compared to gels derived from polymers or inorganic materials, self-assembled supramolecular gels made from LMWGs are relatively easy to modify to control their physical or optoelectronic properties.[2] Furthermore, the properties of gels derived from LMWGs can be tuned using the external stimuli that arise from reversible noncovalent interactions.[3]

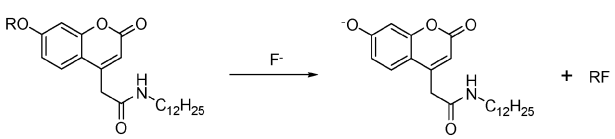
Recently, several gelation systems which induce fluorescence were reported. One can generally develop fluorescent gels by incorporating π-conjugated chromophores into LMWGs.[4] Spectral shift or turn-on of fluorescence was usually observed upon sol–gel transition, which triggers excimer (or exciplex) formation,[5] intermolecular exciton coupling,[6] conformation restriction,[7] and aggregation-induced enhanced emission.[8] Tuning of fluorescence emission wavelength through gelation has been utilized in light-emitting devices.[6a,b,7a,9] In addition, fluorescent gels doped with chromophores in a gel matrix were applied to light harvesting antennas[10] and fluorescent probes.[11] In particular, gelation systems which induced sol–gel transition and subsequently fluorescence change by external stimulus have been utilized as chemical probes for volatile solvents[12] and information storage devices.[13]

In recent years, many researchers have shown interest in the construction of anion-responsive supramolecular gels.[14] Among these, fluoride-responsive gels have received a great deal of attention because fluoride is involved in preventing dental caries and in medical treatment for osteoporosis.[15] Fluorides and protons were reported to trigger gel to sol transition and fluorescence emission after interaction with bisurea-functionalized naphthalene organogelators.[16] In addition, organogelators made with urea,[17] oxalamide,[18] or hydrazide[19] were also reported to induce gel to sol transitions and optical changes after the addition of fluoride anions, because the amidic NHs of these amide-containing organogelators could interact with the fluoride anions thus disturbing the effective hydrogen-bonding interactions between the gelators. However, because amidic NHs in the organogelators could also interact with other anions, the initiation of gel to sol transitions and optical changes would not necessarily be selective to fluoride.

Taking advantage of the selective cleavage of a Si–O bond by fluoride,[20] we developed chemodosimetric gelation systems, **1** and **2** (Scheme 1) having a silyl ether protecting group and a fluorescent signalling group,[21,22] that can selectively detect fluoride anions by the formation of fluorescent gels in aqueous media.

A simple silyl ether protection of a 7-hydroxycoumarin gelator (**3**) not only quenches its fluorescence emission but also prevents gelation. However, when the silyl ether protecting group is selectively cleaved by fluoride anions, the reaction triggers gelation and turns on the fluorescence emission. The effective aggregation between molecules of compound **1** or those of compound **2** is suppressed because the *tert*-butyldimethylsilyl (TBDMS) and *tert*-butyldiphenylsilyl (TBDPS) groups are relatively bulky. Therefore, removal of a bulky silyl ether protecting group by fluoride could induce gelation. At the same time, fluorescence emission increases upon release of phenolate in coumarin.[23]

Compound **1** was prepared by coupling 7-hydroxycoumarin-4-acetic acid with dodecylamine, after which a silyl ether moiety was attached by the reaction with *tert*-butyldimethylsilyl chloride.[24] We also prepared compound **3** without a silyl ether



1: R = *tert*-Butyldimethylsilyl (TBDMS)
2: R = *tert*-Butyldiphenylsilyl (TBDPS)
3: R = H

Scheme 1 Molecular structure of compounds **1**, **2**, and **3**, and Si–O bond cleavage by fluoride.

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moiety to examine whether or not **3** would form a gel. First, we tested the gelation behaviour of **3** using varying solvent conditions. A white opaque gel was formed, but with little fluorescence emission, in a 1 : 1 methanol/water cosolvent[25] after cooling a hot solution of **3**. The critical gelation concentration for **3** was 0.25 wt%, and was determined using the tube inversion method. We then tested self-assembling behaviour of **1** at 0.6 wt%. **1** was fully dissolved in methanol, but when an equal amount of water was added to the solution, a turbid solution formed. Although this turbid solution turned into a clear solution when heated, the clear solution turned turbid again after cooling to room temperature. As expected, the bulky TBDMS group prevented **1** from aggregating in an orderly way and forming gels. In the presence of 1.0 equivalent of F^-, however, an opaque gel was formed, similar to that formed with **3** (Fig. 1(a)). Interestingly, although the turbid solution of **1** and the gel **3** showed little fluorescence emission, upon the addition of F^- to suspension of **1**, the intensity of the fluorescence emission increased dramatically in the gel phase (Fig. 1(b)). Quantum yield of fluorogenic gels derived from **1** + F^- is 0.15 with a lifetime of 33 ns, although the quantum yield is lower than that of solution phase 7-hydroxycoumarin.[26]

This sol-to-gel transition induced by F^- occurs as a result of the effective aggregation of gelators, which is made possible by the cleavage of a silyl ether group. This cleavage also results in a large enhancement of fluorescence. Compound **2** behaved similarly, but was not as soluble as **1** in the same solvent system, and a higher concentration was necessary for gel formation.

SEM images of the xerogels of **3** and **1** + F^- exhibited bundles of fibrous structures of different sizes (Fig. 1(c) and (d)). To examine differences in the self-assembled structures and fluorescence properties, we performed wide-angle X-ray scattering (WAXS) and ^{1}H NMR analysis. The ^{1}H NMR spectra of the xerogels of **1** + F^- indicated that the silyl ether protecting groups were not completely cleaved by F^- (Fig. 2).

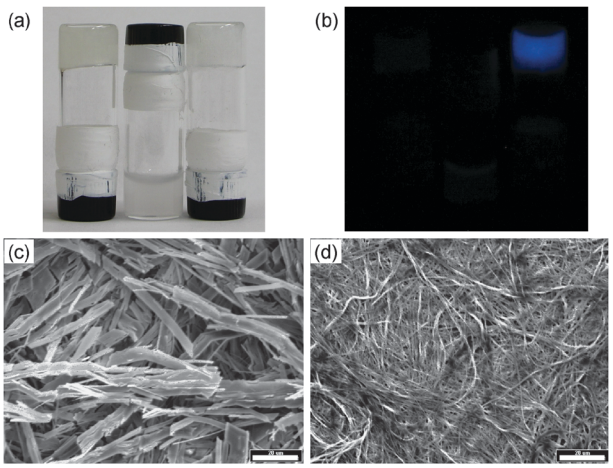

Fig. 1 (a) Visual photograph and (b) fluorescence photograph of **3** (0.6 wt%) (left), **1** + F^- (0.6 wt% of **1**, 1.0 equivalent NaF) in a 1 : 1 methanol/10 mM HEPES buffer (pH 7.40) cosolvent before the gelation process (middle), and after the gelation process (right). Fluorescence emission was observed upon excitation by UV irradiation (λ_{ex} = 365 nm). SEM images of xerogels of (c) **3** and (d) **1** + F^-. Scale bar = 20 μm.

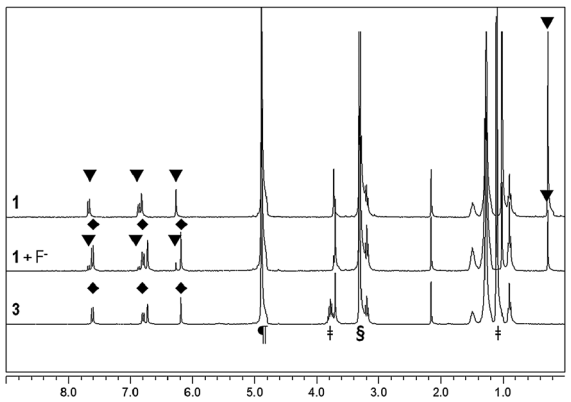

Fig. 2 ^{1}H NMR spectra of **1**, xerogel of **1** + F^-, and **3** in CD_3OD. Symbols under the bottom spectrum indicate chemical shifts of solvent residuals and impurity.¶: H_2O, §: MeOH, and ‡: diisopropylurea (impurity).

Residual signals representing **1** were still observed even after heating with F^-.

This partial removal of the silyl ether protecting groups seemed to influence the fluorescence and gelation behaviours of **1** + F^-. When **1** was treated with 1.0 equivalent of NaF, nonfluorogenic **1** (in which a TBDMS group remained intact) seemed to be intercalated between fluorogenic products formed by the removal of the silyl ethers on **1**. Therefore, the self-quenching effect, which arises from the complete aggregation of fluorescent molecules, was attenuated. This assumption was confirmed after investigating the self-assembled structures in a mixture of **1** and **3** in an appropriate ratio under the same gelation conditions. A 1 : 2 mixture of **1** and **3** formed gels that were fluorescent, but a 1 : 1 mixture of **1** and **3** did not form gels (Fig. S1, ESI†). In particular, gels derived from a 1 : 2 mixture of **1** and **3** at pH 9.00 demonstrated a stronger fluorescence emission than those formed at pH 7.40 because the phenolate form of gelators would strengthen ICT than the phenol form of gelators. Furthermore, gels formed after the complete removal of the TBDMS protecting groups on **1** by F^- showed relatively weak fluorescence, but the gels of **1** + F^- in which the TBDMS groups were not completely removed emitted a more intense fluorescence (Fig. S2, ESI†). Densely stacked coumarin moieties in gels formed after the complete removal of the TBDMS protecting groups would strengthen the self-quenching effect which induces a decrease of fluorescence.

According to WAXS data, gels derived from **3** and **1** + F^- are similarly self-assembled, leading to lamellar-type structures (Fig. 3). WAXS spectra revealed that depth and width of a unit cell are about 25.6 Å and 6.8 Å, respectively. Considering that the length of molecule **3** is about 22.5 Å[27] and the optimal distance for van der Waals interaction is 3.8 Å,[28] we could expect that gels derived from **3** and **1** + F^- are self-assembled into fibril structures with gelators interlocked with each other like a zipper (Fig. S4, ESI†). However, in the case of gels derived from **1** + F^-, interactions among fibrils were disturbed by projecting TBDMS moieties. Consequently, self-assembled fibrils in gels from **1** + F^- remained as thin fibrils unlike gels from **3**.

To confirm the selective response of **1** to F^-, gelation behaviour was investigated upon the addition of various other anions. In contrast to fluoride, Cl^-, Br^-, I^-, $H_2PO_4^-$, AcO^-,

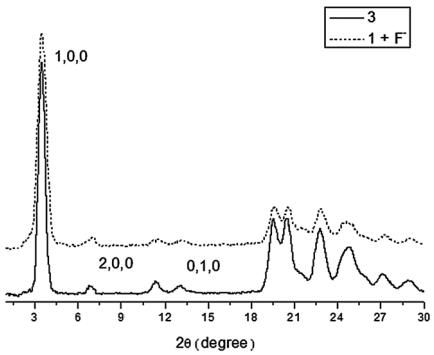

Fig. 3 Wide angle X-ray scattering spectra of gels from **3** and **1** + F^-.

NO_3^-, ClO_4^-, and N_3^- did not induce gelation or fluorescence enhancement using the same solvent conditions. These anions produced clear solutions upon heating, but only yielded turbid solutions after cooling. Only fluoride anions induced both gelation and fluorescence enhancement (Fig. 4). The other anions did not break the Si–O bond in the coumarin and, therefore, did not lead to gel formation or fluorescence emission. We also investigated whether pH influenced gelation behaviours of **1**. Although suspension of **1** in MeOH + 1.5 N aq. HCl (v/v, 1 : 1) was heated until forming a clear solution and subsequently cooled to room temperature, the acidic solution of **1** didn't show any changes such as gelation. In the case of strong basic condition (1.5 N aq. NaOH), heated solution of **1** formed greenish solution without fluorescence. In the case of mild basic condition (1 equiv. $NaHCO_3$), heated solution of **1** also didn't form gels, but exhibited very weak fluorescence emission (Fig. S3, ESI†).

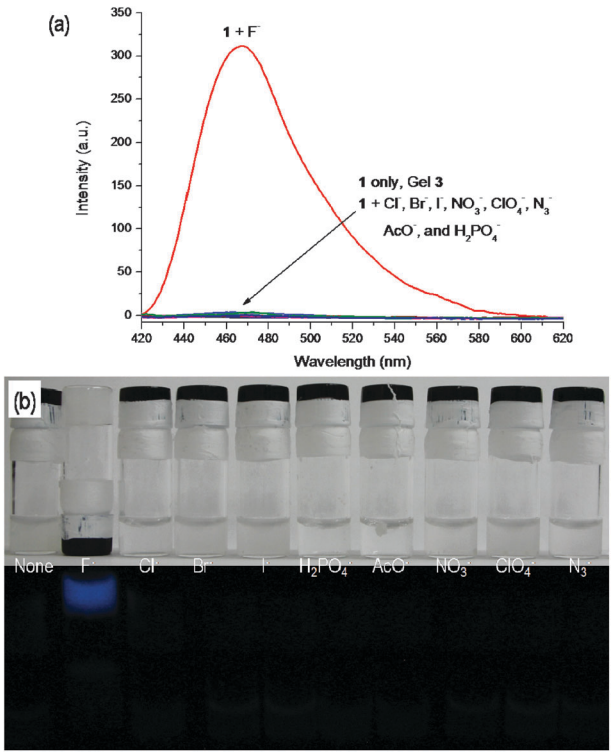

Fig. 4 (a) Fluorescence intensity (λ_{ex} = 405 nm) and (b) photographs and fluorescence photographs (λ_{ex} = 365 nm) of **1** in the presence of each anion (0.6 wt% of **1**, 1.0 equivalent NaX).

We developed chemodosimetric gelation systems which turn into fluorescent gels in aqueous solution when their silyl protecting groups are cleaved by F^-. The above-mentioned system is highly selective to F^- and exhibits both gelation and strong fluorescence as optical signals. This selectivity is a result of the affinity between F^- and silanol derivatives, which distinguishes this system from the amide-based F^- responsive gel systems previously reported.

Experimental

Synthesis of 1

To a mixture of **3** (201 mg, 0.52 mmol) and imidazole (114 mg, 1.68 mmol) in 2 mL DMF, *tert*-butyldimethylchlorosilane (97 mg, 0.65 mmol) was added and the reaction mixture was stirred at rt for 6 h. A white turbid solution was formed after the addition of about 50 mL of water. The addition of ethyl acetate was followed by washing with a large volume of water several times to give a solution, which was dried over anhydrous Na_2SO_4 and concentrated. After silica-column chromatography (CH_2Cl_2 to CH_2Cl_2 : MeOH = 100 : 1), the light yellowish solid **1** was obtained (191 mg, 73.4% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.27 (s, 6H), 0.89 (t, J = 6.8 Hz, 3H), 1.00 (s, 9H), 1.23–1.31 (m, 18H), 1.45 (t, J = 6.2 Hz, 2H), 3.24 (q, J = 6.7 Hz, 2H), 3.66 (s, 2H), 5.56 (t, 1H), 6.24 (s, 1H), 6.79 (d, J = 2.4 Hz, 1H), 6.82 (s, 1H), 7.56 (d, J = 9.4 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ −4.4, 14.1, 18.3, 22.7, 25.6, 26.8, 29.2, 29.4, 29.5, 29.6, 29.6, 31.9, 40.0, 41.0, 107.9, 113.0, 113.7, 117.6, 126.0, 149.7, 155.3, 159.7, 161.0, 167.3. HRMS (FAB+): m/z calcd for $C_{29}H_{48}NO_4Si$ $[M + H]^+$: 502.3353, found: 502.3342.

Synthesis of 2

The synthetic procedure for the production of **2** was identical to that of **1**, except that *tert*-butyldiphenylchlorosilane was used instead of *tert*-butyldimethylchlorosilane, to give **2** as a yellow liquid (333 mg, 77.7% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.89 (t, J = 6.7 Hz, 3H), 1.12 (s, 9H), 1.24–1.26 (m, 18H), 1.42 (t, J = 6.4 Hz, 2H), 3.21 (q, J = 6.6 Hz, 2H), 3.59 (s, 2H), 5.49 (t, 1H), 6.69 (s, 1H), 6.76 (d, J = 6.4 Hz, 1H), 7.38–7.47 (m, 7H), 7.71 (d, J = 7.1 Hz, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.2, 19.5, 22.7, 26.8, 29.2, 29.3, 29.5, 29.6, 29.7, 31.9, 40.0, 40.9, 107.9, 112.8, 113.6,117.4, 125.8, 128.1, 130.4, 131.6, 135.4, 149.5, 155.0, 159.5, 160.9, 167.2. HRMS (FAB+): m/z calcd for $C_{39}H_{52}NO_4Si$ $[M + H]^+$: 626.3666, found: 626.3657.

Synthesis of 3

To a solution of 7-hydroxycoumarin-4-acetic acid (619 mg, 2.81 mmol) and 1.0 equiv. of 1-hydroxybenzotriazole (382 mg, 2.83 mmol) in 20 mL THF, 1.1 equiv. of *N*,*N*′-diisopropylcarbodiimide (0.48 mL, 3.1 mmol) were added, followed by the addition of 1.0 equiv. of dodecylamine (530 mg, 2.86 mmol). After the yellowish reaction mixture was stirred at room temperature overnight, the mixture was concentrated. The residue was dissolved in ethyl acetate and washed with 1 N HCl and brine. The solution was dried over Na_2SO_4 and concentrated *in vacuo*. Purification by silica-column

chromatography (CH_2Cl_2 to CH_2Cl_2 : MeOH = 50 : 1) was conducted to give **3** as a white solid (553 mg, 41.2% yield). ^{1}H NMR (300 MHz, DMSO-d_6): δ 0.85 (t, J = 6.9 Hz, 3H), 1.21–1.23 (m, 18H), 1.38 (t, 2H), 3.04 (q, J = 5.9 Hz, 2H), 3.59 (s, 2H), 6.09 (s, 1H), 6.64 (s, 1H), 6.71 (d, J = 8.6 Hz, 1H), 7.56 (d, J = 8.7 Hz, 1H), 8.16 (t, J = 5.3 Hz, 1H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 13.9, 22.1, 23.3, 26.3, 28.7, 28.9, 28.9, 29.0, 31.3, 38.7, 38.9, 39.8, 102.3, 111.4, 111.6, 112.8, 126.6, 151.3, 155.0, 160.2, 161.3, 167.4. HRMS (FAB+): m/z calcd for $C_{23}H_{34}NO_4$ $[M + H]^+$: 388.2488, found: 388.2488.

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24 See the experimental section for details on the preparation and characterization of new compounds.

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