Supporting Information

Chemodosimetric gelation system showing fluorescence and sol-to-gel transition by fluoride anion in aqueous media

Miae Park, Donghak Jang, Soon Young Kim and Jong-In Hong*

Department of Chemistry, College of Natural Sciences, Seoul National University, Seoul 151-747, Korea

jihong@snu.ac.kr

Material and synthesis: 7-Hydroxycoumarin-4-acetic acid (Aldrich), dodecylamine (Fluka), tert-butyldimethylchlorosilane (Acros), tert-butyldiphenylchlorosilane (Aldrich), N,N`-diisopropylcarbodiimide (Aldrich), 1-hydroxybenzotriazole (TCI), imidazole (Aldrich), and all solvent were used without further purification. 1H and 13C NMR spectra were measured on Bruker Advance 300 or 500 spectrometers. The XWINNMR program was used for the pulse program. GC-MS was performed with JEOL JMS-AX505WA and HP5890 Series II using the FAB method.

Gelation Procedure: Gelator in a 1:1 (v/v) mixture of MeOH and 10 mM HEPES buffer solution (pH 7.40) were heated until the solutions were clear. The clear solution turned immediately to turn precipitate or gel when cooled to room temperature. For the anion tests, an appropriate amount of NaX dissolved in a buffer solution was added to a suspension of **1** in MeOH .

Scanning electron microscope images: Gels were diluted with 500 μL of the cosolvent. The diluted suspensions were dropped onto glass slides, and then dried in air. The prepared specimens were coated with Au. SEM images were observed with a JEOL-JSM 5410LV.

Wide angle X-ray scattering analysis: Gels were dried in air, and then concentrated in vacuo to remove any remained solvent. The dried samples were analyzed with Bruker GADDS. The wave length of the X-ray was 1.5406 Å.

Photophysical properties measurement: The fluorescence emission spectra were obtained on a Jasco FP-7500 spectrophotometer. Fluorescence life time was obtained on a PTI`s QM-4/2005SE. The absorption spectra were obtained on BECKMAN DU-800.

Sample preparation of 1 + F^- for ^{1}H NMR analysis: N_2 gas was blown on the obtained gels to remove methanol. The concentrated gels were further dried using a freeze dryer (Labconco`s Freeze Dryer-18 and Sin`s FD5508). Obtained xerogels were dissolved in dichloromethane, and then washed twice with 1 N HCl to suppress any further reaction.

Gelation behavior

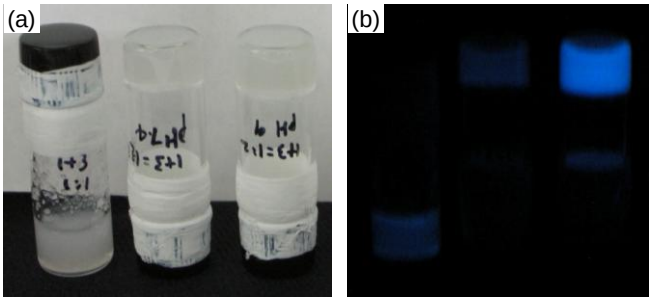

Fig. S1. (a) Gelation behavior of 1:1 (pH 7.4), 1:2 (pH 7.4), and 1:2 (pH 9.0) mixtures of **1** and **3**, and (b) corresponding fluorescence emission photographs (λ_{ex} = 365 nm) in 1:1 mixtures of MeOH and the corresponding buffer solution (10 mM HEPES buffer for pH 7.4; CHES buffer for pH 9.0).

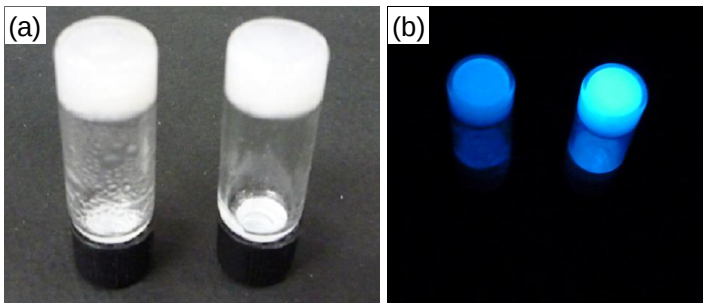

Fig. S2. (a) Gelation behavior of **1** when the TBDMS protecting groups were completely removed by F^- (left) or were partially removed by F^- by the general gelation procedure (right), and (b) the corresponding fluorescence emission photographs (λ_{ex} = 365 nm). The TBDMS protecting groups were completely removed when a solution of **1** + F^- (1.0 equiv. NaF) in a 1:1 mixture of MeOH and HEPES buffer was stored at 85 °C for 24 h. The completion of the cleavage of the TBDMS protecting groups was confirmed by TLC analysis.

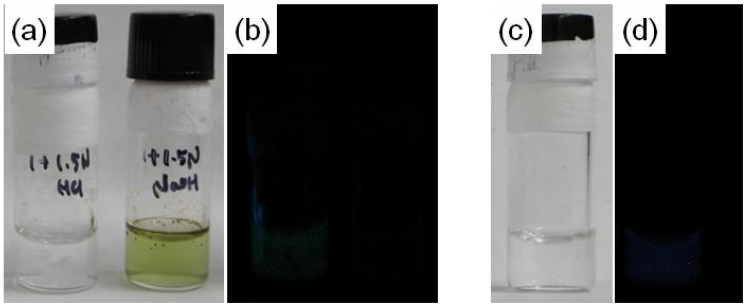

Fig. S3. (a) Photograph and (b) the corresponding fluorescence emission photographs (λ_{ex} = 365 nm) of **1** + HCl (aq) (1.5 N) (left) and 1 + NaOH (aq) (1.5 N) (right). (c) photograph and (d) the corresponding fluorescence photograph (λ_{ex} = 365 nm) of **1** + 1.0 eq. $NaHCO_3$ (aq).

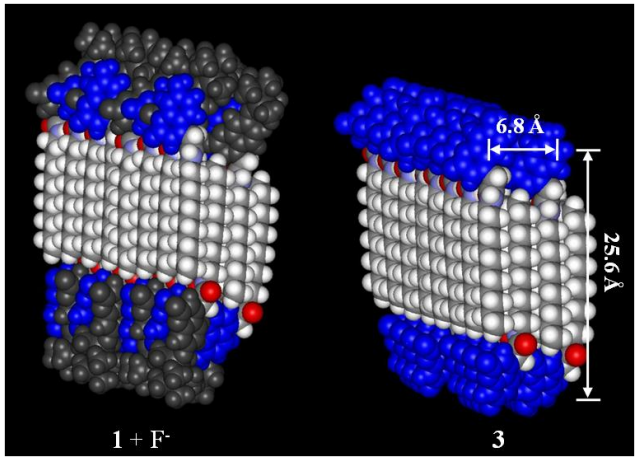

Fig. S4. Proposed model of the self-assembled **1** + F^- and **3**. Compound **1** is shown in dark grey and compound **3** is shown in blue. Compounds **1** and **3** alternate with each other and are arranged in an antiparallel fashion.