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Synthesis of reversible fluorescent organogel containing 2-(2′-hydroxyphenyl)benzoxazole: fluorescence enhancement upon gelation and detecting property for nerve gas simulant

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ABSTRACT

A new low molecular mass organogelator **1** containing 2-(2′-hydroxyphenyl)benzoxazole (HPB) group with long alkyl chain was synthesized by the reaction with 5-amino-2-(2′-hydroxy-4′-methylphenyl)benzoxazole and dodecyl isocyanate in THF at room temperature. The reversible gelation ability of **1** was investigated using a heating-cooling method in various organic solvents. The stable organogel was formed from carbon tetrachloride or from cyclohexane at the concentration as low as 0.9%. The self-assembled supramolecular gel structure formed by non-covalent bonding was confirmed with field emission-scanning electron microscope (FE-SEM) exhibiting fibril- or ribbon-shaped structure depending on the solvent used. Regarding the aggregation-induced emission enhancement (AIEE) phenomenon, the optical properties were investigated in its solution and gelled state. The detecting properties of resulting organogel toward nerve gas simulant were monitored by UV–vis and fluorescence spectroscopy. Both color change from colorless to greenish yellow and disruption of gel structure resulting from alteration in intermolecular forces were observed upon the exposure to nerve gas simulant.

1. Introduction

The supramolecular organogels composed of low molecular mass molecules in organic media have attracted much attention due to their unique characteristics and a wide range of potential applications in templates of nano-scale in organic materials,[1] organic soft materials,[2] optical sensors,[3] and optoelectronic materials.[4] The gelation process is an attractive phenomenon occurred by self-assembly of small molecules in aqueous or in organic solvents resulting from weak secondary interactions, leading to the formation of a 3-dimensional supramolecular structure of nanometer to micrometer dimension.[5] Such weak secondary intermolecular interactions include hydrogen bonding, π–π interaction between heterocyclic rings, van der Waals force between long alkyl chains, and electrostatic forces.[6] A number of reports on the gelation from small molecules have been made including development of gels with photo-responsive properties.[7]

Compounds containing 2-(2′-hydroxyphenyl)benzoxazole (HPB) have been studied extensively on account of their special photonic and structural features exhibiting two emissions by the mechanism of the excited-state intramolecular proton transfer (ESIPT).[8] The proton at hydroxyl group of HPB is transferred to the nitrogen atom and returns to the hydroxyl group at the ground state. HPB has two tautomers with two emission maxima corresponding to the enol and keto forms at short and long wavelengths, respectively (Scheme S1 in the supplementary data). In the case of enol tautomer, the phenol group can be internally rotated with respect to the plane of the benzoxazole ring with large spatial volume. In contrast, in the keto form, the plane of phenol group and benzoxazole ring coexist in the same plane due to intramolecular hydrogen bonding between the NH in protonated benzoxazole ring and carbonyl group in deprotonated phenol group resulting from ESIPT, which can provide planar π–π interaction of heterocyclic rings. It was verified that the presence of hydroxyl group in HPB moieties was essential for gelation because of enhanced planarity.[8a]

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It is known that the aggregation often quenches the emission, which has been a problem in the development of efficient environmental sensor, biological probes and light-emitting diodes. Recently, unusual phenomenon of aggregation-induced emission enhancement (AIEE) was observed.[9] AIEE is one of the interesting challenges for prevention of emission quenching by aggregation. It has been reported that the HPB-containing compound showed AIEE phenomenon upon gelation.[8a] It showed a weak emission intensity in fully soluble state, while the emission intensity was noticeably enhanced by gelation.

Organophosphonate compounds with high toxicity and volatile properties, such as Sarin, Soman, and Tabun, have rapid and fatal effects on mammals, and are applied in chemical weapons known as nerve gases.[10] The leading principle in nerve gas sensing is related to the reaction with a hydroxyl group and phosphate group to form a phosphate ester.[10] It is reported by us that fluorescence emission changes of 2,5-bis(5-aminobenzoxazol-2-yl)benzene-1,4-diol immobilized on silica particles were observed upon the addition of nerve gas simulant, which implied the facile interaction of hydroxyl groups with the phosphate group of nerve gases.[11]

In this study, we demonstrated reversible formation of 3-dimensional supramolecular architecture from the HPB-based organogel and its detection ability for a nerve agent using color change and disruption of gel structure. Our previous studied organogel showed irreversible sol–gel transition due to excessively strong hydrogen bonding force from two urea groups.[8a] That is, once the gel was heated to become solution, it never recovered its 3-dimensional structure. We conjectured introduction of one urea linkage to reduce the hydrogen bonding force between gelator molecules, expecting both facile and reversible gelation. We attempted to obtain improved portability with gel-state sensor compared to the solution-based sensory molecules. Following our interest in using supramolecular-inspired concept for the development of sensory protocol, we report herein the design of chromogenic and fluorogenic gel probe for nerve agent.

2. Results and discussion

As shown in Scheme 1, 5-amino-2-(2′-hydroxy-4′-methylphenyl)benzoxazole (**2**) was synthesized by the reaction of 2,4-diaminophenol dihydrochloride and 4-methylsalicylic acid in polyphosphoric acid (PPA) at 150 °C. Organogelator **1** was synthesized by the reaction of **2** with dodecyl isocyanate in THF at ambient condition. The amino group of **2** was reacted with dodecyl isocyanate so that the urea bond could be formed, which would provide intermolecular hydrogen bonding for gelation. The structure of **1** was confirmed with ^{1}H NMR, ^{13}C NMR spectroscopy, and elemental analysis.

It is noted that the planar keto tautomer of HPB can be used to facilitate π–π interaction. The planar keto form of HPB is dominant in the gel state, while the keto and enol forms coexist in solution state (not identical ratio). Therefore, tautomeric forms of the twisted enol form and the planar keto form could influence on the gelation. The planar keto form could offer strong π–π interaction, on the contrary, the twisted enol form prevent π–π interaction by internal rotation as reported. [8a]

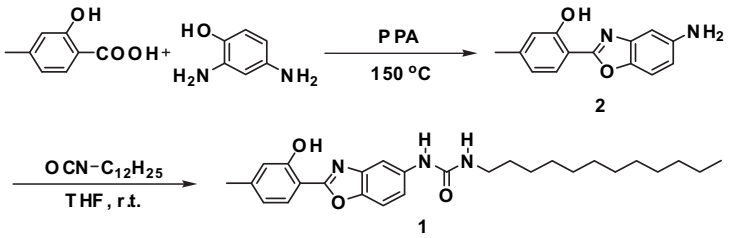
The length of alkyl chain, affecting van der Waals interaction in gel formation, was investigated with hexyl-, octyl-, dodecyl-, and octadecyl groups. Precipitate or fluidic aggregate instead of non-fluidic stable gel was observed when the alkyl chain length of the gelator was shorter than dodecyl group, such as hexyl or octyl group, suggesting suitable alkyl chain length should be employed enough to establish stable 3-dimensional structure by means of van der Waals force. However, precipitation was observed with much longer alkyl chain, such as octadecyl substituent, presumably due to excess interaction between chains.

The gelation ability of **1** was examined by dissolving in various organic solvents (Table S1 in the supplementary data). Gelation of **1** was carried out at a concentration of 1% (w/v) in carbon tetrachloride and cyclohexane using a heating–cooling method (Fig. 1). Compound **1** showed poor solubility in carbon tetrachloride and cyclohexane at room temperature but became completely soluble at elevated temperature. A transparent and weak fluorescent solution was turned to an opaque and strong green fluorescent gel when the temperature of **1** solution was cooled from boiling point to room temperature. The opaque gel returned to a transparent but weak fluorescent solution after *re*-heating. The cycles of gel-to-sol transition upon heating and the sol-to-gel transition upon cooling were reversible.

The critical gelation concentrations (CGC) in carbon tetrachloride and cyclohexane were found to be 0.9% (w/v). The lowest gelation temperature in carbon tetrachloride and cyclohexane were found to be 22 and 27 °C, respectively. Compound **1** was insoluble in *n*-hexane even at elevated temperature and partially gelled in aromatic solvents, such as benzene, toluene and *p*-xylene. On the other hand, **1** was precipitated in alcoholic and polar solvents, such as methanol, ethanol, isopropanol, *n*-butanol, THF, DMF, DMSO, acetone, and ethyl acetate.

FE-SEM images show that **1** in carbon tetrachloride (1% (w/v)) was self-assembled with 3-dimensional networks consisting of fibrous aggregates, which are of approximately 50 nm in diameter and a few μm length (Fig. 2(A) and (B)). Those fibers were composed of a bundle of a few fibrils of 5 nm diameter. On the other hand, a ribbon-shaped structure, approximately 100 nm in width, a few nm in thickness and in length was observed in cyclohexane-gel of **1** (Fig. 2(C) and (D)). It was reported that the difference in the nanostructure of CCl_4–gel and cyclohexane-gel lies in the affinity between the gelator and solvent molecules.[12]

The optical changes during the sol–gel transition of **1** were examined by UV–vis and fluorescence spectroscopy (Fig. 3). In the



Scheme 1. Synthetic route of **1**.

UV–vis spectra in carbon tetrachloride (5.0×10^{-5} M), the absorption maxima of **1** decreased and the bandwidth increased with long absorption tail beyond 400 nm upon cooling to room temperature, indicative of aggregation. It appears that the decrease in absorption

and the presence of long-tailed absorption resulted from the scattering of aggregate particles. In the fluorescence spectra, the emission maximum of **1** in carbon tetrachloride showed an emission of 490 nm from keto tautomer of HPB. Along with the long wavelength emission from keto tautomer, emission with considerably small intensity at short wavelength of 400 nm was also observed from enol tautomer. This implies that **1** existed dominantly as the keto form in carbon tetrachloride, which was influenced by solvent polarity.[8e]

3 min of cooling time, the non-fluorescent solution of **1** in hot carbon tetrachloride became highly fluorescent gel with green emission (Fig. S1 in the supplementary data).

Such enhanced emission was monitored as a function of cooling time as shown in Figure 4(A). The fluorescence intensity of the **1**-CCl_4 solution increased upon cooling to room temperature, which means the aggregated **1** exhibited stronger emission intensity than in solution. Compound **1** was weakly fluorescent in carbon tetrachloride solution (at lower concentration than CGC), which showed

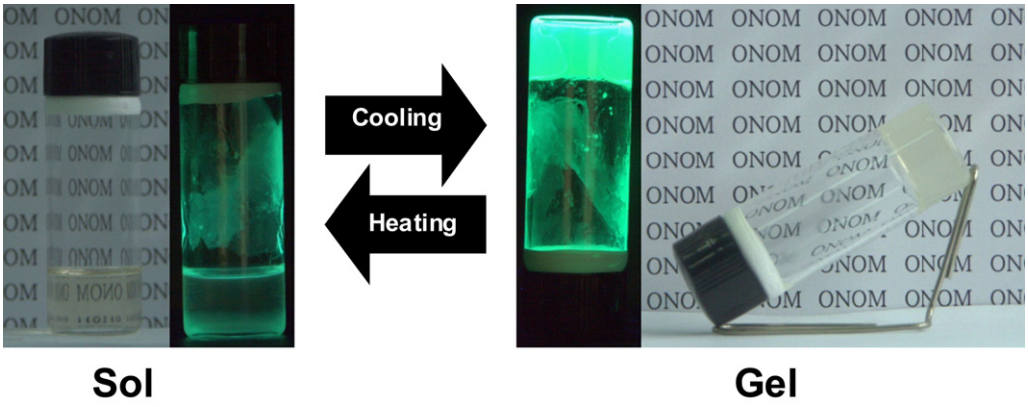


Figure 1. Photographs demonstrating sol–gel process of **1** in CCl_4 (1% (w/v)) using the heating–cooling method.

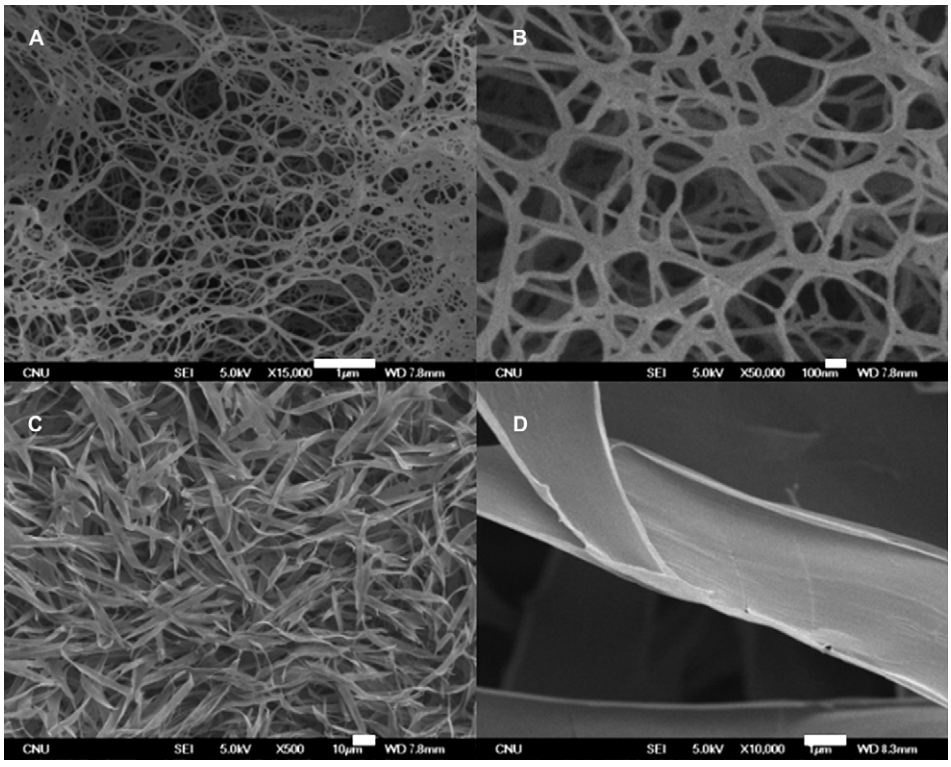


Figure 2. FE-SEM photographs of freeze-dried CCl_4–gel (1% (w/v), A and B) and cyclohexane-gel (1% (w/v), C and D) (Scale bars (A) 1 μm, (B) 100 nm, (C) 10 μm and (D) 1 μm).

As mentioned above, the planar keto form can strengthen π–π interaction between the HPB, which is considered to be one of the important driving forces for gelation. The emission intensity was enhanced dramatically in aggregate state at room temperature compared to that of the solution at 76 °C (bp of carbon tetrachloride). This enhanced fluorescence emission intensity can be confirmed by the photographs of gelation (Fig. 1). Within less than

absolute quantum yield (Φ_F) of 4.8% measured in integrating sphere (Φ_F 5.2% in THF), while it became highly luminescent in the gel state (Φ_F 32%). This behavior was attributed to the AIEE phenomenon. Further evidence of AIEE was observed from solvent-induced aggregation, which was performed in solvent mixtures of carbon tetrachloride (gelation media) and THF (good solvent) as shown in Figure 4(B).

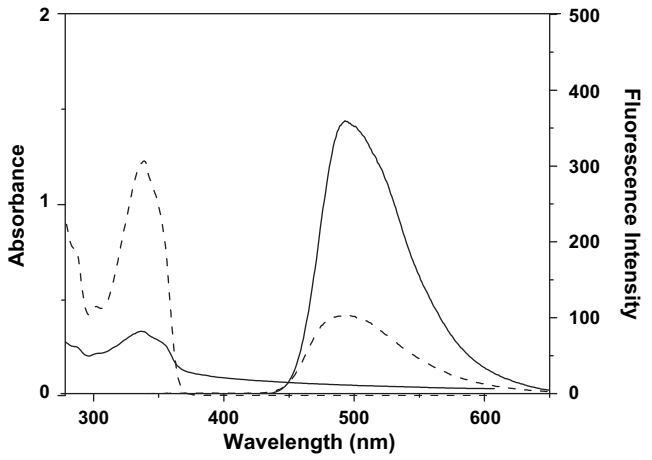


Figure 3. UV–vis and fluorescence spectra of **1** (5.0×10^{-5} M) in carbon tetrachloride at room temperature (aggregated state, solid line) and 76 °C (solution, dashed line); excitation wavelength 332 nm.

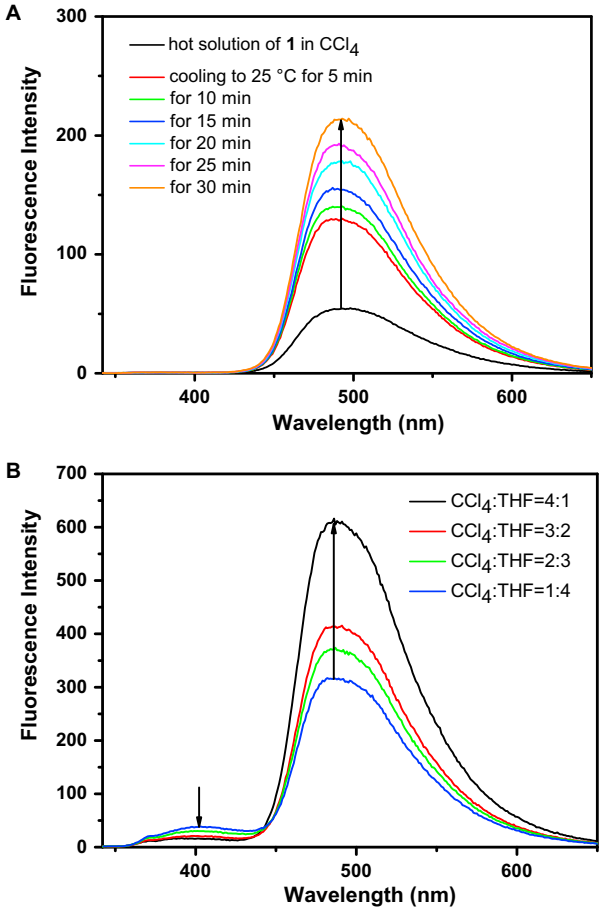


Figure 4. Fluorescence changes of (A) **1** in carbon tetrachloride (5.0×10^{-5} M) upon cooling to room temperature from 76 °C and (B) **1** in mixed solvents with different solvent ratios (1.0×10^{-5} M); excitation wavelength 332 nm.

The emission intensity at 485 nm resulting from the keto tautomer was observed to increase with increasing amount of carbon tetrachloride, while the emission intensity at 400 nm (enol tautomer) decreased, which means that the emission intensity of **1** was influenced considerably by aggregation (plus effect of solvent polarity). In the carbon tetrachloride solution, the ESIPT can develop more easily, which can restrict internal rotation between the benzoxazole and phenol group. Therefore, the resulting planar conformation facilitated the efficient π–π stacking for gel formation, thus exhibiting an increase in fluorescence intensity at a long wavelength emission in the gel state.

The detection property of **1** for nerve gas was determined by UV–vis and fluorescence spectroscopy (Fig. 5). Diethylchlorophosphate (DCP), which has similar reactivity to nerve gases, such as Sarin, Soman, and Tabun, but lower toxicity than typical nerve agents, was used to test its sensitivity to organophosphonates (Scheme S2 in the supplementary data). Upon the addition of DCP to the **1** aggregates dispersed in carbon tetrachloride (5.0×10^{-5} M), the absorption maxima at both at 332 nm and at 390 nm increased. The long-tailed absorption beyond isosbestic point of 413 nm resulted from scattering of aggregates is clearly disappearing upon the addition of DCP, indicating aggregate structure was disrupted to become solution via the alteration in secondary intermolecular forces. Upon the addition of DCP, the emission spectra exhibited a small blue-shift and a small decrease in intensity was observed. It is presumed that the decrease in intensity resulted from the interruption of intermolecular hydrogen bonding leading to solution state with weaker fluorescence.

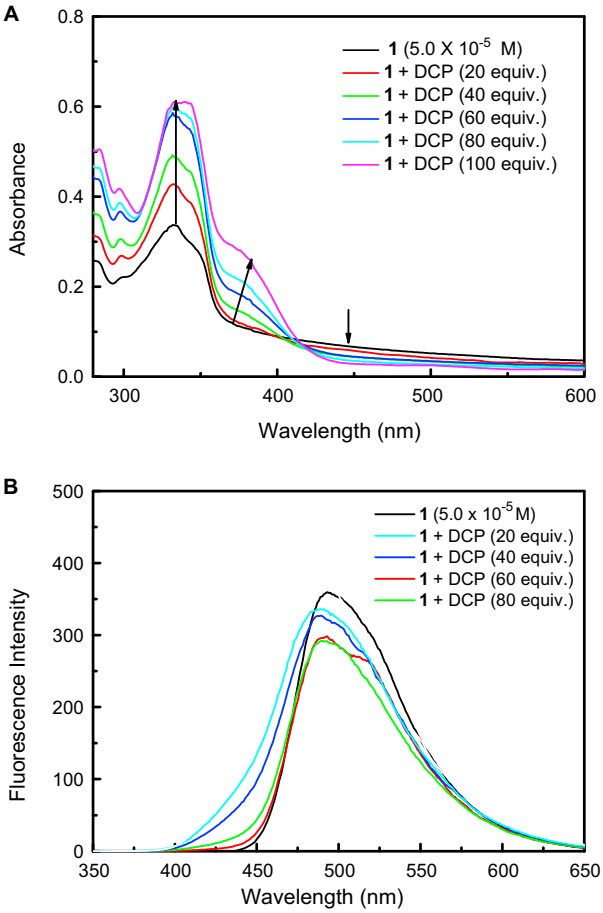


Figure 5. (A) UV–vis and (B) fluorescence changes of aggregated **1** in carbon tetrachloride upon the addition of DCP (from 20 to 100 equiv).

The mechanism to be employed in this system is based on the alteration in interaction with a hydroxyl group in phenol to form a phosphate ester.[10a] ^{1}H NMR spectra showed that the hydroxyl proton of HPB was chemically shifted to up-field and broadened upon the addition of DCP. Besides, there is a small shift of the urea peak to down-field, which means that both intramolecular (for HPB) and intermolecular (for urea) hydrogen bonding were

changed to interact with DCP molecules (Fig. S2 in the supplementary data).

As shown in Figure 6, the naked-eye observation for the selected target was examined in the CCl_4–gel. A drop of liquid DCP was placed on the top surface of the gel (1% (w/v)) and the sealed vial was left to stand for 1 h at room temperature (Fig. 6(A)). Both notable color change from colorless to yellow and 3-dimensional structure disruption were observed in the presence of DCP. Furthermore, upon addition of 0.1 equiv of DCP on the top surface of the gel, the color changes were observed at contact point instantaneously, which means the possibility to detect at very low concentration.

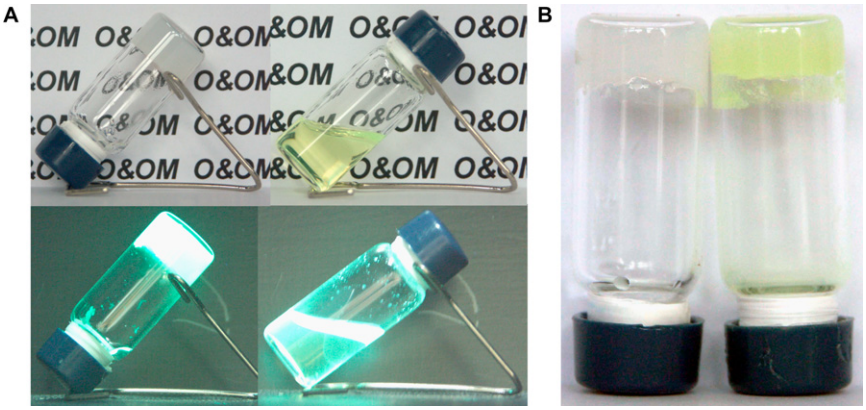


Figure 6. Photographs of CCl_4–gel of **1** (1% (w/v)) (A) before (left) and after (right) adding DCP liquid (100 equiv) under ambient (top) and UV (bottom) light and (B) before (left) and after (right) exposure to DCP vapor.

The sensing of **1** for the vapor DCP was also investigated at room temperature (Fig. 6(B)). The **1**-CCl_4 gel was placed in a 20 mL vial containing DCP under ambient conditions (Fig. S3 in the supplementary data). After sealing with parafilm, the vial was left to stand for 20 h. The color of the gel was changed from colorless to greenish yellow from the top within 10 min. It took 12 h for the entire color change to greenish yellow without disruption of gel structure. The **1**-cyclohexane gel also showed changes similar to **1**-CCl_4 gel. The gel structure was maintained in vapor-state detection because only a small amount of DCP was exposed to the **1** molecule. This behavior provides the possibility of a naked-eye chemosensor for nerve gases.

3. Conclusions

We demonstrated the thermo-reversible self-assembled gel formation, which showed unusual aggregation-induced emission enhancement property. The gelled **1** was 3-dimensionally organized with fibril structure in carbon tetrachloride and ribbon-shaped structure in cyclohexane. The gel exhibited reversible gel-to-sol and sol-to-gel transformation under repeated heating and cooling cycles. As expected, the preferred planar conformation of HPB core (caused by ESIPT) played a key role in gel formation through its strong π–π interactions showing noticeable strong emission from keto tautomer. We described the detection of nerve gas simulant through a visibly noticeable color change induced by an interaction between nerve gas simulant and HPB core. Overall, the presence of HPB in the gelator is essential both for gel formation and for nerve gas detection.

4. Experimental

4.1. Chemicals

All starting materials were obtained from commercial suppliers and used as received. 2,4-Diaminophenol dihydrochloride, dodecyl isocyanate, and DCP were purchased from Aldrich. 4-Methylsalicylic acid and PPA were supplied by TCI and Acros, respectively. The other chemicals were purchased from Duksan.

4.2. Instrumentation

The ^{1}H NMR spectra were recorded on Bruker Biospin DRX300 (Korea Basic Science Institute). The UV–vis spectra were recorded on Lambda 35 (PerkinElmer), and fluorescent spectra were measured on Cary Eclipse (Varian). FE-SEM images of the xerogels were obtained using a JEOL JSM-7000F with an accelerating voltage of 5.0 kV.

4.3. Synthesis of 5-amino-2-(2′-hydroxy-4′-methylphenyl)benzoxazole (2)

2,4-Diaminophenol dihydrochloride (6.43 g, 32.7 mmol) and 4.97 g (32.7 mmol) of 4-methylsalicylic acid were mixed with 150 ml of PPA. The reaction mixture was heated to 150 °C under ambient condition, and then stirred for 12 h. The resulting mixture was cooled to room temperature and poured into ice-water with vigorous stirring. The solution was neutralized by adding sodium bicarbonate. The crude product was collected by filtration, and recrystallized in ethanol. Further purification was carried out with column chromatography using an ethyl acetate–toluene mixture as a mobile phase. After evaporation, the product was dried in vacuo (yield: 2.03 g, 26%); ^{1}H NMR (300 MHz, DMSO-d_6): δ=11.31 (s, OH, 1H), 7.94 (s, 1H), 6.92 (d, Ar-H, 1H), 6.90 (d, Ar-H, 1H), 6.85 (d, Ar-H, 2H), 6.67 (d, Ar-H, 1H), 4.52 (s, NH, 2H), 2.35 (s, 3H).

4.4. Synthesis of 5-dodecylureyl-2-(2′-hydroxy-4′-methylphenyl)benzoxazole (1)

Compound **2** (0.17 g, 0.71 mmol) in 15 ml of THF was added into a mixture of 1.05 g (4.95 mmol) of dodecyl isocyanate and 15 ml of THF with constant stirring. The reaction mixture was stirred at room temperature for two days. The product was isolated by filtration, washed with THF several times, and then dried in vacuo (yield: 0.24 g, 74%); ^{1}H NMR (300 MHz, $CDCl_3$): δ=11.31 (s, OH, 1H), 7.92 (s, NH, 1H), 7.67 (d, Ar-H, 1H), 7.50 (d, Ar-H, 1H), 7.30 (d, Ar-H, 1H), 6.95 (s, Ar-H, 1H), 6.82 (d, Ar-H, 1H), 6.25 (s, Ar-H, 1H), 6.27 (t, NH, 1H), 3.22 (q, CH_2, 2H), 2.39 (s, CH_3, 3H), 1.55–1.18 (m, 23H). ^{13}C NMR (75 MHz, $CDCl_3$): δ=157.8, 155.6, 153.0, 145.9, 141.0, 139.9, 135.1, 129.0, 122.7, 119.8, 116.8, 116.3, 112.8, 111.0, 46.0, 32.8, 31.2, 30.5, 30.0, 23.8, 13.8 ppm. Found: C, 72.02; H, 8.27; N, 9.39. Calcd for $C_{27}H_{37}N_3O_3$: C, 71.81; H, 8.26; N, 9.30%.

4.5. Gelation test

A mixture of a weighed amount of **1** in carbon tetrachloride or cyclohexane in a screw-capped vial was heated to approximately boiling point until a clear solution appeared. And then, the mixture was cooled to room temperature at ambient conditions. Gelation was confirmed by the absence of solvent flow when the test vial was inverted. The critical gelation concentration (CGC) was determined by adding a measured amount of solvent until a stable gel was formed. The reversibility of the gel transition was tested by repeating the heating-cooling process several times.

4.6. Nerve gas simulant detection

Nerve gas detection was carried out in a 10 mm quartz cuvette. UV–vis and fluorescence spectral changes of **1** in carbon tetrachloride (5.0×10^{-5} M) in the presence and the absence of DCP were recorded. The amount of DCP added was increased ranging from 20 to 100 equiv. Two methods were adopted to confirm the naked-eye detection. In the first method, 100 equiv of DCP was added onto **1**-CCl_4 gel (1% (w/v)) in a 2 mL vial and kept under ambient conditions. With the second method, the **1**-CCl_4 gel (1% (w/v)) in a 2 mL vial was placed in a 20 mL vial containing DCP liquid (Fig. S3 in the supplementary data). The 20 mL vial was capped and kept in an ambient state.

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Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.tet.2010.01.006.

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