

Gelation-induced fluorescence enhancement of benzoxazole-based organogel and its naked-eye fluoride detection†

Tae Hyeon Kim,^a Moon Soo Choi,^a Byeong-Hyeok Sohn,^b Soo-Young Park,^c Won Seok Lyoo^d and Taek Seung Lee^{*a}

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The benzoxazole derivative gelator **1 forms a stable DMF/toluene cosolvent gel with dramatically enhanced fluorescence emission compared to its mother solution. The translucent colorless gel was changed to a solution with strong greenish fluorescence in the presence of fluoride anion with disruption of the gel structure.**

Supramolecular structures composed of low molecular mass molecules have attracted much interest due to their unique characteristics and wide range of potential applications as templates of nano-scale inorganic materials,¹ organic soft materials,² and optical sensors.³ Gelation is an intriguing phenomenon demonstrated by small molecules in aqueous or organic solvents resulting from weak secondary interactions, leading to the formation of three-dimensional supramolecular structures of nanometer to micrometer dimensions.⁴

Self-assembled gelation for supramolecular structure is organized by intermolecular physical interaction facilitated by hydrogen bonding and other subsequent weak interactions such as the π - π interaction of heterocyclic rings, van der Waals forces of long alkyl chains, and electrostatic forces.^{2a,5} Along with a number of reports on the gelation of small molecules, many efforts have been devoted to the development of gels with optical absorption or fluorescence.⁶

Fluorescent sensors for anions have been extensively studied since the sensing of fluoride anions is of special interest due to their importance in biological and industrial systems.⁷ Recently, Žinić and co-workers reported on fluoride sensing with a gel based on oxalamide-derived anthraquinone.⁸ The gel showed the color change and the gel-to-sol phase transition in the presence of fluoride anion, which may provide the basis for the development of the sensing of fluoride with the naked eye.

In this communication, we designed a low molecular mass molecule **1** composed of the 2-(2'-hydroxyphenyl)benzoxazole (HPB) unit, urea groups, and long alkyl chains, which could

function as π - π interactions, hydrogen bonding, and van der Waals interactions, respectively [Fig. 1(A)]. As already reported in detail, HPB has two tautomers with two emission maxima of the enol (weak fluorescence) and keto (strong fluorescence) forms by excited state intramolecular proton transfer (ESIPT) (see Scheme S2 in the ESI†).⁹ The intramolecular hydrogen bonding in HPB can be altered by the presence of fluoride anion regardless of its monomeric or polymeric form, which showed a visually noticeable color change as reported earlier.^{9b,c} Our interest is focused on the following: (1) gelator **1** adopts a flat conformation in the aggregation state originating from intramolecular hydrogen bonding in the HPB unit, which may induce a facilitated proton transfer between the hydroxyl proton of benzene ring and the nitrogen of the benzoxazole group; (2) the hydroxyl groups in HPB are able to selectively interact with fluoride anions, which may provide the color changes; (3) the urea moieties are able to bind with fluoride anions; therefore, intermolecular hydrogen bonding between neighboring urea moieties would be disrupted in the presence of fluoride anion, which may bring about the gel-to-sol transition.

Gelator **1** was synthesized from the reaction of 5-amino-2-(5'-amino-2'-hydroxyphenyl)benzoxazole and octyl isocyanate in THF at ambient conditions. Powdery **1** was dissolved completely in hot DMF, and cold toluene was added dropwise to the solution [0.5 wt%, DMF-toluene = 1 : 9 (v/v)] giving a stable and highly fluorescent gel as shown in Fig. 1(B). Gel formation

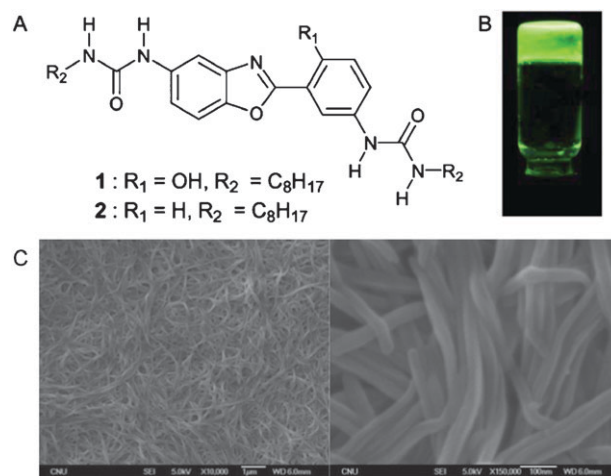


Fig. 1 (A) Structure of the benzoxazole derivatives **1** and **2**; (B) photograph of fluorescent gel, and (C) FE-SEM images of xerogel **1** (scale bar: left = 1 μ m; right = 100 nm).

^a Organic and Optoelectronic Materials Laboratory, Department of Advanced Organic Materials and Textile System Engineering, Chungnam National University, Daejeon 305-764, Korea. E-mail: tslee@cnu.ac.kr; Fax: +82 42 823 3736; Tel: +82 42 821 6615

^b School of Chemistry, NANO Systems Institute, Seoul National University, Seoul 151-747, Korea

^c Department of Polymer Science, Kyungpook National University, Daegu 702-701, Korea

^d School of Textiles, Yeungnam University, Gyeongsan, Gyeongbuk 712-749, Korea

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was not observed in other solvents or solvent mixtures such as aliphatic solvents, ethers, dioxanes, and tetrahydrofuran due to the poor solubility of **1**. The FE-SEM image reveals that the gelator **1** was self-assembled with three-dimensional networks composed of fibrous aggregates, which are approximately 30 nm in diameter and a few μm long [Fig. 1(C)].

In this organogel structure, the π - π stacking interactions among the HPB moieties, the hydrogen-bonding interactions between the urea moieties, and the van der Waals forces between the long alkyl chains cooperatively stabilized the aggregate structure; these are well-known interactions in gel systems.^{2a,5} Specifically to clarify the effect of the hydroxyl group in the HPB unit on gelation, we also designed and synthesized reference compound **2**, which does not contain an adjacent hydroxyl group and thereby cannot induce its planar keto tautomer upon excitation. As expected, **2** was not gelled but precipitated under such conditions that brought about the gelation of **1** because the molecular stacking between the HPB units was interfered with due to the lack of planarity. Therefore, it is presumed that the planarity of HPB from intramolecular hydrogen bonding is one of the driving forces for gelation.

Compound **1** is weakly luminescent in DMF solution [the absolute quantum yield measured in integrating sphere (Φ_F) was 1.4%, at 1.71×10^{-5} M]; however, it becomes highly fluorescent in the gel state ($\Phi_F = 34.7\%$) by aggregation-induced emission (AIE) as shown in Fig. 2(A).¹⁰ When **1** aggregated in the DMF/toluene mixture, its fluorescence increased significantly [Fig. 2(B)]. Interestingly, absorption of the aggregates (343 nm) in a such solution mixture was blue-shifted from that of the solution (360 nm). The blue-shift is unusual because aggregation usually induces a red-shift. In

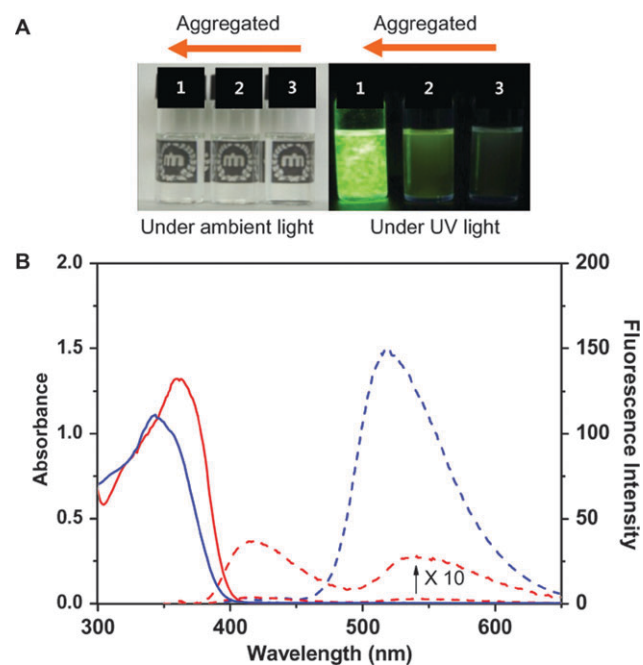


Fig. 2 (A) Photographs of the aggregation-induced gel formation of **1** (9.52×10^{-5} M); vial 1, DMF-toluene = 1 : 58 (v/v); vial 2, DMF-toluene = 1 : 10.8 (v/v); vial 3, DMF only; (B) UV-Vis (solid) and fluorescence (dashed) spectra of **1** (9.52×10^{-5} M); blue line (vial 1), DMF-toluene = 1 : 58 (v/v); and red line (vial 3), DMF.

addition to the blue-shift of the λ_{max} , the emission maximum was also blue-shifted (from 414 to 402 nm for the enol form and from 541 to 519 nm for the keto form) with remarkable emission enhancement of the keto tautomer upon aggregation.

Generally, in the heterocyclic compound, the aggregation-induced emission quenching is accompanied with a red-shift. A few reports have been published on the abnormal AIE arising from spectral blue-shifted aggregation, further study of which is needed for elucidation of the mechanism.¹¹ Intramolecular rotation of the benzoxazole group is more restricted by aggregation and thus ESIPT can be more easily developed in the solid gel state than in solution. Thus the planar conformation favored the increase in the fluorescence intensity of its keto form as well as in efficient π - π stacking for gel formation. Therefore, it is regarded that the planarity of HPB is one of the main driving forces for aggregation and the large increase in emission intensity.

Further evidence for enhanced proton transfer by aggregation was provided by time-resolved fluorescence spectroscopic analysis (see Fig. S1 in the ESI†). Compound **1** showed through the double-exponential decay that the long-lived excited state was a major contribution [$\tau_1 = 7.2$ ns (82.3%) and $\tau_2 = 0.5$ ns (17.7%) at 519 nm] in the wet-gel state, whereas a short-lived excited state was a major component ($\tau_1 = 0.2$ ns (89.1%) and $\tau_2 = 3.1$ ns (10.9%) at 541 nm) in the solution state, which demonstrated a delayed fluorescence decay due to facilitated proton transfer. Furthermore, the dried xerogel of **1** exhibited a much longer lifetime, such that the major contribution was composed of the long-lived excited state [$\tau_1 = 3.1$ ns (16.9%) and $\tau_2 = 7.9$ ns (83.1%) at 519 nm]. Considering these lifetime results, π - π stacking of the heterocyclic rings was occurred to form aggregates during the drying process as well as during gelation, which showed increased lifetime.

The UV-Vis and fluorescence spectral change of **1** was recorded in the presence of 100 equiv. of anions (F^- , Cl^- , Br^- , I^- , CH_3COO^- , H_2PO_4^-) in DMSO (Fig. 3 and see Fig. S2 in the ESI†). After the addition of fluoride anion, the absorption and emission maxima were increased and significantly shifted to longer wavelength (Fig. 3 and see Fig. S3 in the ESI†), while other anions did not show any shift. The anion-binding properties of **2** were also determined with the same target anions (see Fig. S4 in the ESI†). A noticeable spectral shift upon addition of

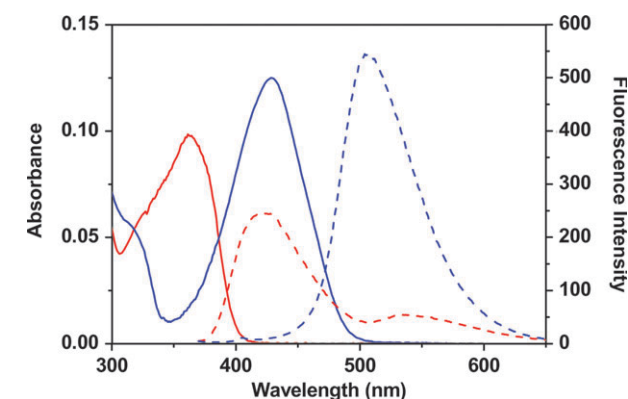


Fig. 3 UV-Vis (solid) and fluorescence (dashed) spectra of **1** (7.5×10^{-6} M) in DMSO before (red) and after (blue) addition of 100 equiv. of fluoride anion.

the target anions was not observed in the UV-Vis spectrum [see Fig. S4(A) in the ESI†], while the fluorescence intensity was quenched or increased upon exposure to anions. The amidic NH groups linked directly to the HPB unit can be responsible for the emission intensity change.⁸ Taking into account these results, absorption and emission maximum shifts are induced by interaction between the hydroxyl group in HPB and the target anion. Thus the presence of the hydroxyl group in HPB is crucial in gelation as well as in detecting anionic species.

In the ¹H NMR spectra of **1**, the hydroxyl proton in HPB showed peak splitting and the integral decreased by the addition of fluoride anions, which indicates the possible interaction between the hydroxyl proton in HPB and the fluoride anion (see Fig. S5 in the ESI†). The spectral shift and decreased integral of the proton signals from the urea moieties were due to the deprotonation of the urea groups by fluoride anions according to previous reports.¹² In the ¹H NMR spectra of **2**, all NH peaks disappeared upon addition of fluoride anion, which means that almost all NH was deprotonated by fluoride anion. Furthermore, the major decay time of the wet-gel state was decreased from 7.2 to 5.8 ns after the addition of 100 equiv. of fluoride anion [see Fig. S1(D) in the ESI†].

The naked-eye anion detection of **1** toward a number of selected target anions was examined in a DMF/toluene mixture as shown in Fig. 4(A). As expected, the color change was observed only in the presence of the fluoride anion. The presence of fluoride not only changes the color of the gel, but actively disrupts a preformed gel, as shown in Fig. 4(B). As discussed above, the urea moieties are able to bind with fluoride anions, thus, the intermolecular hydrogen bonding between neighboring urea moieties was disrupted in the presence of the fluoride anion.¹³ Placing fluoride anion on top of the DMF/toluene gel immediately produces a gel-to-sol transition with a color change from a translucent colorless gel to a solution with a strong greenish emission. Completion of the gel-to-sol transition occurred within 30 min. Though the disruption of the gel structure appeared in the presence of other anions, the dramatic color change and rapid gel-to-sol transition were observed only in the case of the fluoride anion. The acetate anion, because a high concentration was used, exhibited a weakly greenish yellow color with the gel-to-sol transition; however, the color was even weaker

than that with fluoride anion. Therefore, we believe that gel **1** can be used as a selective naked-eye sensor system for fluoride anion.

In conclusion, we have demonstrated the self-assembled gel formation which showed fluorescent properties of the gelator bearing HPB. As expected, the preferred planar conformation of the HPB core (caused by intramolecular proton transfer) played a crucial role in gel formation through its strong π - π interactions. We observed strong emission from gel **1**, but observed hardly any from the solution, which was induced by intramolecular proton transfer from the enol to the keto tautomer. Furthermore, we have described the naked-eye fluoride sensor which showed the gel-to-sol transition and a visibly noticeable color change, which were induced by the interaction between fluoride anion and amidic NH and hydroxyl proton in the HPB, respectively.

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Notes and references

- (a) J. H. Jung, Y. Ono and S. Shinkai, *Langmuir*, 2000, **16**, 1643; (b) Y. Ono, K. Nakashima, M. Sano, J. Hojo and S. Shinkai, *J. Mater. Chem.*, 2001, **11**, 2412; (c) S. Shinkai and T. Shimizu, *Chem. Mater.*, 2002, **14**, 1445.
- (a) M. Suzuki, Y. Nakajima, M. Yumoto, M. Kimura, H. Shirai and K. Hanabusa, *Org. Biomol. Chem.*, 2004, **2**, 1155; (b) A. Ajayaghosh and V. K. Praveen, *Acc. Chem. Res.*, 2007, **40**, 644.
- (a) B. K. An, S. K. Kwon, S. D. Jung and S. Y. Park, *J. Am. Chem. Soc.*, 2002, **124**, 14410; (b) M. M. F. Choi and S. Shuang, *Analyst*, 2000, **125**, 301.
- (a) P. Terech and R. Weiss, *Chem. Rev.*, 1997, **97**, 3133; (b) J. H. van Esch and B. L. Feringa, *Angew. Chem., Int. Ed.*, 2000, **39**, 2263; (c) L. Estorff and A. Hamilton, *Chem. Rev.*, 2004, **104**, 1201.
- (a) M. Suzuki, Y. Nakajima, M. Yumoto, M. Kimura, S. J. Shirai and Hanabusa, *Langmuir*, 2003, **19**, 8622; (b) S. J. George and A. Ajayaghosh, *J. Am. Chem. Soc.*, 2001, **123**, 5148; (c) T. Ishi-i, T. Hirayama, K. Murakami, H. Tashiro, T. Thiemann, K. Kubo, A. Mori, S. Yamasaki, T. Akao, A. Tsuboyama, T. Mukaide, K. Ueno and S. Mataka, *Langmuir*, 2005, **21**, 1261; (d) J. J. van Gorp, J. A. J. M. Vekemans and E. W. Meijer, *J. Am. Chem. Soc.*, 2002, **124**, 14759; (e) M. P. Lightfoot, F. S. Mair, R. G. Pritchard and J. E. Warren, *Chem. Commun.*, 1999, 1945.
- (a) T. Ishi-i and S. Shinkai, in *Supramolecular Dye Chemistry*, ed. F. Würthner, Springer, Berlin, 2005 and refs cited therein; (b) F. Würthner, Z. Chen, V. Dehm and V. Stepanenko, *Chem. Commun.*, 2006, 1188.
- (a) C. B. Black, B. Andrioletti, A. C. Try, C. Ruiperez and J. L. Sessler, *J. Am. Chem. Soc.*, 1999, **121**, 10438 and refs cited therein; (b) R. Martínez-Mañez and F. Sancenón, *Chem. Rev.*, 2003, **103**, 4419; (c) C. Suksai and T. Tuntulani, *Chem. Soc. Rev.*, 2003, **32**, 192 and refs cited therein.
- Z. Džolić, M. Cametti, A. D. Cort, L. Mandolini and M. Žinić, *Chem. Commun.*, 2007, 3535.
- (a) J. K. Lee, H.-J. Kim, T. H. Kim, C.-S. Lee, W. H. Park, J. Kim and T. S. Lee, *Macromolecules*, 2005, **38**, 9427; (b) J. K. Lee, J. Na, W. H. Park, Y. K. Kwon and T. S. Lee, *Mol. Cryst. Liq. Cryst.*, 2004, **424**, 245; (c) J. K. Lee and T. S. Lee, *J. Polym. Sci., Part A: Polym. Chem.*, 2005, **43**, 1397.
- H. Tong, Y. Dong, M. Häußler, J. W. Y. Lam, Z. Li, Z. Guo, Z. Guo and B. Z. Tang, *Chem. Commun.*, 2006, 3705 and refs cited therein.
- (a) Z. Li, Y. Dong, B. Mi, Y. Tang, M. Häußler, H. Tong, Y. Dong, J. W. Y. Lam, Y. Ren, H. H. Y. Sung, K. S. Wong, P. Gao, I. D. Williams, H. S. Kwok and T. B. Tang, *J. Phys. Chem. B*, 2005, **109**, 10061; (b) C. J. Bhongale, C.-W. Chang, C.-S. Lee, E. W.-G. Diau and C.-S. Hsu, *J. Phys. Chem. B*, 2005, **109**, 13472.
- (a) H. Ren, Q. C. Wang, D. H. Qu and H. Tian, *Chem. Lett.*, 2004, **33**, 974; (b) B. Liu and H. Tian, *Chem. Lett.*, 2005, **34**, 686.
- R. Varghese, S. J. George and A. Ajayaghosh, *Chem. Commun.*, 2005, 593.

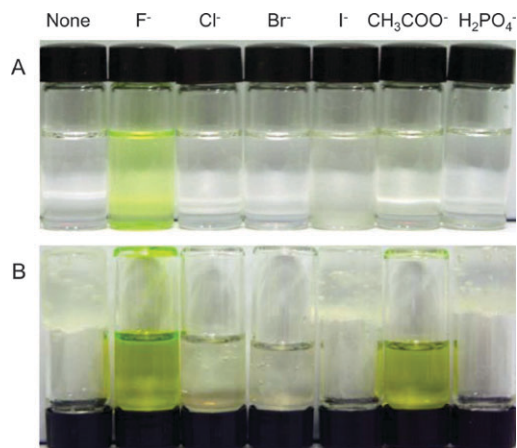


Fig. 4 Photographs of **1** (A) in DMF-toluene mixture (9.52×10^{-5} M, **1** : 58 (v/v)); and (B) gel upon addition of 100 equiv. of each anion.