Strongly Fluorescent Hydrogel as a Blue-Emitting Nanomaterial: An Approach toward Understanding Fluorescence−Structure Relationship

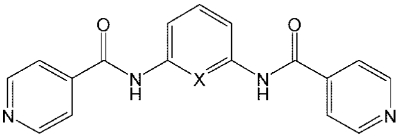
Tae Ho Kim, Joobeom Seo, Soo Jin Lee, Shim Sung Lee, Jineun Kim, and Jong Hwa Jung*

Department of Chemistry and Research Institute of Natural Science, Gyeongsang National University, Jinju 660-701, Korea

Received July 17, 2007
Revised Manuscript Received October 20, 2007

Low molecular mass organic gelators (LMOGs) have gained considerable interest because of the advantages of organogel networks for various optical applications including enhanced charge transport, fluorescence, and sensing abilities.[1–4] For these applications, long alkyl chains or steroidal groups have been incorporated into the gelator structure and have been necessary for the effective gelation process.[5–12] However, these structural elements are normally inactive and contribute little to the optical properties. In particular, luminescent organic materials are currently of great interest because of their various applications in photochemistry,[13–15] as organic light-emitting diodes (OLEDs),[16–21] and as chemical sensors for small molecules.[22–25] Among the materials with green, red, and blue color emissive materials, the development of blue fluorescence emissive materials is most important, because of the limitation of few examples of blue emitting fluorophors and unsatisfaction of physical properties such as photoluminescent (PL) efficiency and thermal stability.

In this communication, we report a new class of LMOGs with simple pyridine substituents instead of long alkyl chains or steroidal structures, endowing the gel system with greater potential for optical applications. Specifically, we demonstrate in this work a strongly enhanced blue fluorescence emission gated by the gelation process. Also, we examine the structural relationship of hydrogel **1** that affects the switching between self-assembled fluorescence and nonfluorescence emission. Compound **2** was prepared as a reference for **1**.



1; X = N
2; X = C

In the course of the syntheses of highly fluorescent organic chromophores in the solid state, we found that one of our newly synthesized fluorescent molecules, **1**, possesses a strong gelation capability in an aqueous system at room temperature. Compound **1** was dissolved in water (0.1 wt %) with gentle heating (Figure 1a, left vial). On cooling to room temperature, this solution exhibited no gravitational flow; it could be turned upside down safely (Figure 1a, right vial). It is noteworthy that compound **1** can gelate water regardless of pH. It was also found that this hydrogelation process is completely thermoreversible exhibiting the sol–gel transition temperature (T_{gel}) of ~72 °C at pH 7 as determined by differential scanning calorimetry (DSC) observation (Supporting Information, Figure S1). In contrast, it is revealed that compound **2** can not gelate water as well as any organic solvents such as methanol, chloroform, acetonitrile, and toluene.

To gain insights into the aggregation morphology of the hydrogel **1** at different pH values, a sample of dried gel was transferred onto a glass slide and subjected to scanning electron microscopy (SEM) observation. Micrographs of hydrogel **1** obtained at pH 2 and 7 showed entangled three-dimensional networks of bundles of fiber aggregates (Figure 1b,c), whereas the hydrogel **1** obtained at pH 13 showed a linear fiber structure 500–700 nm in width (Figure 1d). Surprisingly, Figure 1e shows a peculiar example of “gelation-induced fluorescence emission”: the hydrogel **1** obtained at pH 7 is the most strongly fluorescent (Figure 1e, center vial), while hydrogels of **1** obtained at pH 2 and 13 are weakly fluorescent (Figure 1e, left and right vials). In addition, the entangled fibrillar structure of hydrogel **1**

---

* Corresponding author. E-mail: jonghwa@gnu.ac.kr.

(1) Seo, Y. J.; Bhuniya, S.; Kim, B. H. *Chem. Commun.* **2007**, 1804.
(2) Sugiyasu, K.; Fujita, N.; Shinkai, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 1229.
(3) Ryu, S. Y.; Kim, S.; Seo, J.; Kim, Y.-W.; Kwon, O.-H.; Jang, D.-J.; Park, S. Y. *Chem. Commun.* **2004**, 70.
(4) Engelkamp, H.; Middelbeek, S.; Nolte, R. J. M. *Science* **1999**, *284*, 785.
(5) Vemula, P. K.; Aslam, U.; Mallia, V. A.; John, G. *Chem. Mater.* **2007**, *19*, 138.
(6) John, G.; Zhu, G.; Li, J.; Dordick, J. S. *Angew. Chem., Int. Ed.* **2006**, *45*, 4772.
(7) Jung, J. H.; Do, Y.; Lee, Y.-A.; Shimizu, T. *Chem. Eur. J.* **2005**, *11*, 5538.
(8) Lee, S. J.; Lee, S. S.; Kim, J. S.; Lee, J. Y.; Jung, J. H. *Chem. Mater.* **2005**, *17*, 6517.
(9) Terech, P.; Weiss, R. G. *Chem. Rev.* **1997**, *97*, 3133.
(10) Jung, J. H.; John, G.; Masuda, M.; Yoshida, K.; Shinkai, S.; Shimizu, T. *Langmuir* **2001**, *17*, 7229.
(11) Jung, J. H.; Shinkai, S.; Shimizu, T. *Chem. Eur. J.* **2002**, *8*, 2684.
(12) Kiyonaka, S.; Shinkai, S.; Hamachi, I. *Chem. Eur. J.* **2003**, *9*, 976.
(13) Paw, W.; Cummings, S. D.; Mansour, M. A.; Connick, W. B.; Geiger, D. K.; Eisenberg, R. *Coord. Chem. Rev.* **1998**, *171*, 125.
(14) Cummings, S. D.; Eisenberg, R. *J. Am. Chem. Soc.* **1996**, *118*, 1949.
(15) Huertas, S.; Hissler, M.; McGarrah, J. E.; Lachicotte, R. J.; Eisenberg, R. *Inorg. Chem.* **2001**, *40*, 1183.
(16) Hissler, M.; Connick, W. B.; Geiger, D. K.; McGarrah, J. E.; Lipa, D.; Lachicotte, R. J.; Eisenberg, R. *Inorg. Chem.* **2000**, *39*, 447.
(17) Tang, C. W.; Vanslyke, S. A. *Appl. Phys. Lett.* **1987**, *51*, 913.
(18) Baldo, M. A.; O’Brien, D. F.; You, Y.; Shoustikov, A.; Sibley, S.; Thompson, M. E.; Forrest, S. R. *Nature* **1998**, *395*, 151.
(19) O’Brien, D. F.; Baldo, M. A.; Thompson, M. E.; Forrest, S. R. *Appl. Phys. Lett.* **1999**, *74*, 442.
(20) Kwong, R. C.; Laman, S.; Thompson, M. E. *Adv. Mater.* **2000**, *12*, 1134.
(21) Hu, N. X.; Esteghamatian, M.; Xie, S.; Popovic, Z.; Hor, A. M.; Ong, B.; Wang, S. *Adv. Mater.* **1999**, *11*, 173.
(22) Mansour, M. A.; Connick, W. B.; Lachicotte, R. J.; Gysling, H. J.; Eisenberg, R. *J. Am. Chem. Soc.* **1998**, *120*, 1329.
(23) Fung, E. Y.; Olmstead, M. M.; Vickery, J. C.; Balch, A. L. *Coord. Chem. Rev.* **1998**, *171*, 151.
(24) De Santis, G.; Fabbrizzi, L.; Licchelli, M.; Poggi, A.; Taglietti, A. *Angew. Chem., Int. Ed.* **1996**, *35*, 202.
(25) de Silva, A. P.; Gunaratne, H. Q. N.; Rice, T. E. *Angew. Chem., Int. Ed.* **1996**, *35*, 2116.

10.1021/cm701880e CCC: $37.00

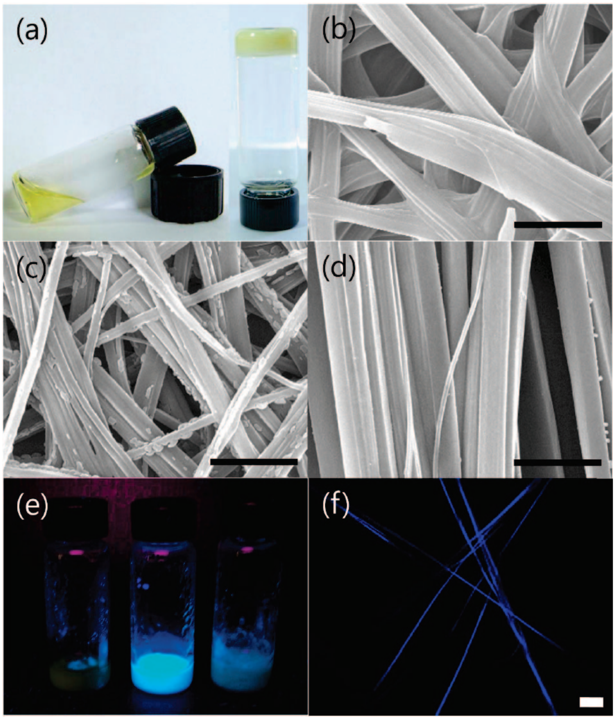


Figure 1. (a) Picture of hydrogel **1** at 90 °C (left) and 25 °C (right). SEM images of hydrogel **1** obtained at (b) pH 2, (c) pH 7, and (d) pH 13. (e) Picture of hydrogel **1** onbtained at pH 2 (left), pH 7 (center), and pH 13 (right). (f) Fluorescence image of hydrogel **1** obtained at pH 7. Scale bar: 2 μm.

obtained at pH 7 can be directly observed in the original nondried hydrogel state by fluorescence optical microscopy (Figure 1f). The fibrous structures of hydrogel **1** obtained at pH 7 are largely bundled and knotted at the same node, suggesting that hydrogel **1** constitutes a robust gel system with a permanent solid-like network.

The changes in the fluorescence for hydrogel **1** were investigated as a function of pH (Figure 2 and Supporting Information, Figure S2). Figure 2A shows the pH dependence of the blue fluorescence emission at 427 nm (excitation at 330 nm) that is the most intense at pH 7. The result indicates that the fluorescence of the hydrogel **1** is strongly pH dependent. On the other hand, **1** the in solution state was nonfluorescent (Figure 2A,d), suggesting that the strong fluorescence of hydrogel **1** at pH 7 originates from the self-assembled nanostructure.

Under acidic conditions, the fluorescence of hydrogel **1** gradually decreased (Figure 2B), suggesting that the fluorescence intensity of the hydrogel **1** is associated with protonation of the pyridine nitrogen. However, because the emission was not fully quenched at low pH, it may be anticipated that the emission is affected by either the partial deprotonation of the pyridine nitrogen or gelator **1** itself.

Under basic conditions, the fluorescence quenching of hydrogel **1** may be related to the thermal stabilization (T_{gel}) of the self-assembled gel, caused by the loss of an acidic proton. Therefore, we examined the effect of pH on the T_{gel} of hydrogel **1**. As expected, the T_{gel} of hydrogel **1** prepared at pH 13 (56 °C) was lower than that of hydrogel **1** prepared at pH 7 (72 °C; Supporting Information, Figure S1). These results suggest that the intense fluorescence emission of hydrogel **1** was produced by strong intermolecular interactions. Moreover, the fluorescence switching was fully reversible, because addition of strong acid (to pH 1) weakened the fluorescence intensity, which could be subsequently “switched on” again with large (up to a factor of 10) enhancements by addition of base. This topic is discussed in detail below with respect to single-crystal X-ray structures prepared under differing pH conditions.

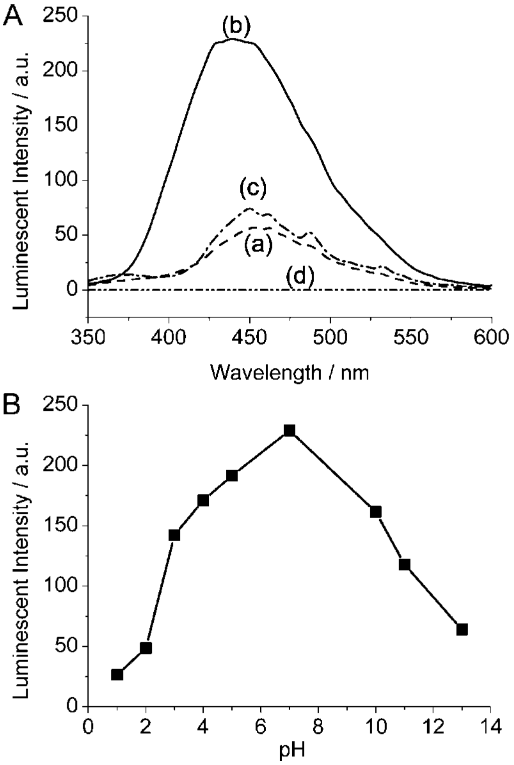


Figure 2. (A) Fluorescence spectra of the hydrogel **1** (0.1 wt %) prepared at different pH vlaues: (a) pH 2, (b) pH 7, and (c) pH 13 and (d) solution **1**. (B) pH dependence of the fluorescent intensity for gel **1** at 427 nm (λ_{ex} = 330 nm).

In general, long alkyl chains or steroidal groups have been considered essential for the stable LMOG assemblies.[26–29] However, the present study indicates that NH groups in the structures are equally effective, as demonstrated by the hydrogel **1**. The origin of the unique gelation capability of gelator **1** is best explained in terms of two structural features. First, the π−π stacking interactions exerted by rigid aromatic segments in gelator **1** play an integral role in self-assembling of the gelator molecules. Second, the presence of amide NH groups in gelator **1** induce and stabilize molecular assemblies by intermolecular hydrogen bonding.

To further elucidate the driving forces for gel formation and the mechanism of fluorescence of hydrogel **1** obtained at different pH conditions, we prepared single crystals, yellow in color, suitable for X-ray analysis from solutions of **1** at

---

(26) Suzuki, M.; Sato, T.; Shirai, H.; Hanabusa, K. *New J. Chem.* **2006**, *30*, 1184.

(27) Sugiyasu, K.; Fujita, N.; Shinkai, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 1229.

(28) Kawano, S.; Fujita, N.; Shinkai, S. *Chem. Commun.* **2003**, 1352.

(29) Murata, K.; Aoki, M.; Suzuki, T.; Harada, T.; Kawabata, H.; Komori, T.; Ohseto, F.; Ueda, K.; Shinkai, S. *J. Am. Chem. Soc.* **1994**, *116*, 6664.

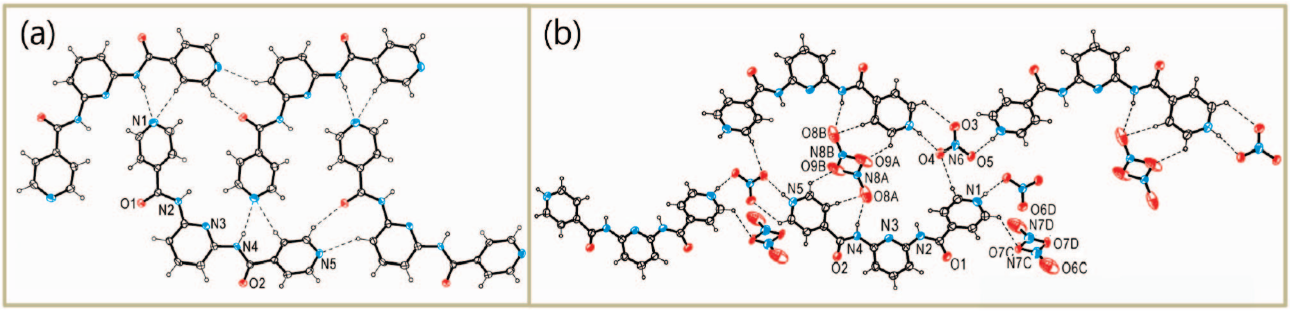


Figure 3. Crystal structures of **1** obtained at (a) pH 7 and 13 as a neutral form and (b) pH 2 as a nitric acid form (**1**·$2HNO_3$).

pH 2, 7, and 13, respectively. The single crystals of reference compound **2** were also prepared. The crystal structures are shown in Figure 3.

The crystals of **1** grown at pH 7 and 13 were revealed to have the same molecular structure as a neutral form (Figure 3a and Supporting Information, Figures S3−S5). At pH 2, however, the crystals of **1** were grown as an acidic form **1**·$2HNO_3$ (Figure 3b andSupporting Information, Figures S6 and S7). Indeed, the hydrogen bonding arrangements found in each structure are noteworthy. As shown in Figure 3a, compound **1** in neutral form (grown at pH 7) is alternately arranged along the *b* axis to form a herringbone-type array. The molecular conformation and the array are stabilized by formation of several intermolecular hydrogen bonds such as C−H···O, C−H···N(pyridine), and N−H(amide)···N(pyridine) types, which have bond lengths of approximately 2.3–2.6 Å. The intermolecular hydrogen bond between amide NH and CO was not observed. Instead, the offset face-to-face type weak $\pi-\pi$ stacking interaction between pyridine moieties in neighboring arrays (centroid-to-centroid distance 3.4 Å) was observed (Supporting Information, Figure S4). These results indicate that the driving force in hydrogel formation of **1** at neutral conditions is mainly the intermolecular hydrogen bonding.

On the other hand, the crystalline compound **1** obtained at pH 2 is diprotonated via pyridine nitrogen atoms as shown in Figure 3b. The observed fluorescence quenching of **1** at lower pH is due to the protonation of the pyridine. Compound **1** in acidic form is arranged along the *b* axis forming a looped chain. In the extending structure, each diprotonated molecule is linked by nitrate ions (one nitrate ion is disordered) via C−H···O(nitrate) and N(pyridine)−H···O(nitrate) type hydrogen bonds, which have a bond length of approximately 1.95–2.57 Å. The amide NH was not involved in the hydrogen bonding.

Obviously, the molecular arrangement under acidic conditions is quite different from that in crystals obtained under neutral conditions even though the formation of hydrogels by gelator **1** occurs at any pH value. As described, the crystal structure **1** obtained in basic conditions was the same as that obtained under neutral conditions (Supporting Information, Figure S4), indicating that the large decrease of fluorescence of hydrogel **1** in basic conditions was attributed to the T_{gel} as mentioned above but not to the structural differences noted in acidic conditions.

In the case of **2**, which showed no fluorescence emission, the amide NH was bound only to the CH protons of the benzene group by intermolecular hydrogen bonds (Supporting Information, Figures S8−S10). Furthermore, the benzene moiety of **2** forms strong $\pi-\pi$ stacking with adjacent molecules, which would induce a quenching effect.

In conclusion, we have demonstrated the first example of a strongly fluorescent hydrogel, a nanomaterial with intense blue emission in a specified pH region. The unique gelation capability of **1** is attributed to the cooperative effects of the $\pi-\pi$ stacking and the intermolecular hydrogen bonding interactions. The remarkable fluorescence enhancement in the hydrogel **1** is induced by the self-assembled supramolecular nanostructure at pH 7. Such blue colored emissive nanomaterials could be of considerable importance in photochemistry and OLED fields.

Acknowledgment. This work was supported by Korea Research Foundation Grant (KRF-2005-070-C00068), KOSEF (R01-2005-000-10229-0), and Korea Ministry of Environment as “The Eco-technopia 21 Project”.

Supporting Information Available: Synthesis method, gelation test, pH dependence of fluorescence gel, preparation of single crystal, DSC data, crystal structures, and packing structures of **1** and **2** (PDF and CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

CM701880E