

Strongly Fluorescent Organogel System Comprising Fibrillar Self-Assembly of a Trifluoromethyl-Based Cyanostilbene Derivative

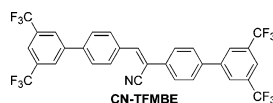
Byeong-Kwan An, Deug-Sang Lee,[†] Jong-Soon Lee,[†] Yil-Sung Park,[†] Hyung-Su Song,[†] and Soo Young Park*

School of Materials Science and Engineering, ENG445, Seoul National University,
San 56-1, Shillim-dong, Kwanak-ku, Seoul 151-744, Korea, and Central R&D center, Dongwoo FineChem Co., Ltd.,
1177, Pyungtaek-Si, Kyunggi-Do, 451-764, Korea

Received June 26, 2004; E-mail: parksy@plaza.snu.ac.kr

Recently, low-molecular-mass organic gelators (LMOGs) with π -conjugated molecular structure have gained much interest due to advantages of the specific nature of organogel networks for various optoelectronic applications such as enhanced charge transport, fluorescence, and sensing abilities.¹ Relevant to these applications, the incorporation of the long alkyl chains or steroidal groups into the gelator structure has been considered very necessary for the effective gelation process,² although these structural elements are normally inactive and undesirable for the optoelectronic properties. In this communication, we report a new class of LMOGs with simple trifluoromethyl (CF_3) substituents instead of the long alkyl chains or steroidal parts, endowing the gel system with better potential for optoelectronic applications. Specifically, we demonstrate in this work a strongly enhanced fluorescence emission gated by the gelation process.

In the course of the systematic syntheses of highly fluorescent organic chromophores in the solid state, we came to find that one of our newly synthesized fluorescent molecules, 1-cyano-*trans*-1,2-bis-(3',5'-bis-trifluoromethyl-biphenyl)ethylene (CN-TFMBE), possessed a strong gelation power at room temperature.



The powder of the CN-TFMBE was well dissolved in 1,2-dichloroethane (0.8 wt/vol %) by gentle heating (Figure 1a, left vial), which, after cooling to room temperature, exhibited no gravitational flow, as it could be turned upside down safely (Figure 1a, right vial). It was also found that this gelation process was completely thermoreversible with the gel melting temperature of about 51 °C as determined by the "dropping ball method". The gelation ability of CN-TFMBE was evaluated in various organic solvents under the same experimental condition as in 1,2-dichloroethane. Gelation of CN-TFMBE was similarly effected in toluene, chloroform, and *tert*-butyl alcohol. However, it was partially gelled in octane and showed no gelation in tetrahydrofuran.

To gain insight into the aggregation morphology of CN-TFMBE in the organogel, a dried gel sample was transferred onto a glass slide and subjected to the scanning electron microscopy (SEM) observation. The SEM images in Figure 1c suggest that CN-TFMBE gelator creates entangled three-dimensional networks consisting of the bundles of fibrous aggregates, which must be responsible for the observed gelation. Figure 1b shows a peculiar example of "gelation-induced fluorescence emission": CN-TFMBE gel is strongly fluorescent, while CN-TFMBE itself is totally nonfluorescent in 1,2-dichloroethane solution. Surprisingly, the fluorescence

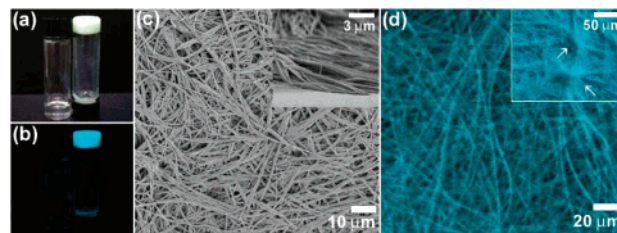
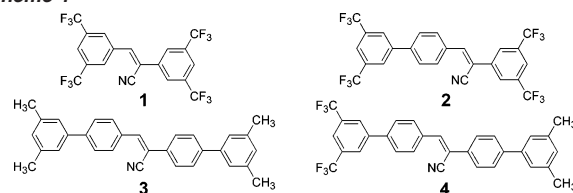


Figure 1. (a) Photo of CN-TFMBE (0.8 wt/vol %) dissolved in 1,2-dichloroethane at 60 °C (left vial) and the corresponding organogel at 20 °C (right vial). (b) Fluorescence emission of CN-TFMBE solution (left vial) and CN-TFMBE gel (right vial) under the UV light (365 nm), the same vials as in a. (c) SEM images of a dried gel of CN-TFMBE in 1,2-dichloroethane. (d) Fluorescence microscopy images of a CN-TFMBE organogel. The arrows in the inset photo indicate the node where the fibrous structures of CN-TFMBE are largely bundled and knotted.

Scheme 1



intensity is enhanced over 170 times in the gel state (see Figure 1b). Therefore, the entangled fibrillar structure of the CN-TFMBE could be directly observed in the original nondried gel state by fluorescence optical microscopy (Figure 1d). The inset photo of Figure 1d shows that the fibrous structures of CN-TFMBE are largely bundled and knotted at the same node. The presence of this kind of nodes suggests that the CN-TFMBE gel constitutes a robust gel system with permanent solidlike networks.²

As mentioned earlier, the presence of long alkyl chains or steroidal groups has been considered to be essential for the stable LMOG assemblies.^{1,2} It is noted, however, that the simple CF_3 groups are equally effective as demonstrated for the CN-TFMBE organogel in this work. The origin of this unique gelation capability of CN-TFMBE is best explained in terms of the two structural features. First, the strong π - π stacking interactions exerted by rigid rodlike aromatic segments in CN-TFMBE must play an integral role in self-assembling of the gelator molecules. The second factor to be considered is the presence of CF_3 components in CN-TFMBE, which might induce and stabilize molecular assemblies with their strong secondary bonding forces.^{3,4} To evaluate how much these two factors affect the gel formation, we synthesized and investigated a series of CN-TFMBE analogues (1–4) shown in Scheme 1.

Compared to CN-TFMBE, the length of the rigid aromatic ring segments was intentionally reduced in **1** and **2** while retaining four CF_3 moieties to investigate the influence of π - π stacking interactions on the gel formation. The gelation tests revealed that neither

[†] Dongwoo FineChem Co., Ltd.

1 nor **2** showed gelation, probably due to the insufficient intermolecular interaction forces. It is noteworthy that the melting points increase with the number of aromatic phenyl rings in this series of molecules: **1** (101 °C) < **2** (204 °C) < CN-TFMBE (264 °C).⁵ This result implies that the elongated aromatic segments lead to the increased intermolecular interactions, which, in turn, reinforces the self-assembling process via strong π - π interactions. We further explored the issue of CF₃ contributions by examining the properties of **3** and **4**. These two molecules are identical in chemical composition and structure to CN-TFMBE with the exception of terminal methyl groups, i.e., **3** is fully methylated (four -CH₃), and **4** is partially methylated (two -CF₃ and two -CH₃) analogues. Different from the strong gel formation of CN-TFMBE, no gelation was again observed for **3** and **4**. It is again noted that the melting points increase with the numbers of CF₃ units: **3** (132 °C) < **4** (189 °C) < CN-TFMBE (264 °C),⁵ indicating the powerful role of CF₃ groups in reinforcing intermolecular interaction. Due to the insufficient intermolecular interactions, none of the CN-TFMBE derivatives **1**-**4** showed fibrous assembly structures that are generally in favor of the gel formation.⁶ Therefore, it is properly considered that the four CF₃ units in the CN-TFMBE gelator play the role of alternative forces to improve intermolecular interaction much like the long alkyl chain or steroidal group, given that the strong π - π stacking interactions between the rigid rodlike aromatic segments provide the essential driving force for gelation in conjugated LMOGs.

The remarkable fluorescence enhancement from CN-TFMBE gels can be unambiguously explained within the context of our previous report on the aggregation-induced enhanced emission (AIEE) phenomenon.^{7,8} Isolated CN-TFMBE molecules in dilute solution are considered to be significantly twisted by the steric interactions in biphenyl units as well as the bulky cyano groups attached into vinylene moiety, which generally suppresses the radiative decay channel. On the other hand, the more planar and conjugated conformation of CN-TFMBE is induced in the solid state due to the strong intermolecular forces, which tend to optimize close packing between molecules. This aggregation-induced planarization extends the effective π -conjugation length in the CN-TFMBE molecule. Furthermore, in the solid state, the bulky and polar cyano groups in CN-TFMBE play an important role of favoring *J*-type aggregation, which restricts the formation of the excimer complex.⁹ Consequently, CN-TFMBE molecules in the aggregated gel state are likely to show drastically enhanced fluorescence emission compared with those of isolated state due to the synergetic effect of intramolecular planarization and restricted excimer formation. This postulated AIEE phenomenon of CN-TFMBE is experimentally evidenced by the UV/vis absorption and photoluminescence (PL) studies of dilute solution (isolated state) and nanoparticle suspension (aggregated state) of CN-TFMBE (Figure 2). Nanoparticle suspension of CN-TFMBE (2×10^{-5} mol L⁻¹, average particle size of ca. 30 nm)¹⁰ was prepared by a simple precipitation method (80 vol % water addition in THF solution) for the quantitative comparison with the THF solution of CN-TFMBE (2×10^{-5} mol L⁻¹). The maximum peak in the absorption spectra of CN-TFMBE nanoparticle suspension in Figure 2a is clearly red-shifted compared with that of dilute solution due to the extension of the effective conjugation lengths caused by the planarization of twist molecular in nanoparticles. The new shoulder band (the arrow (↓) in Figure 2a), which is properly assigned to the *J*-aggregation band due to the specific arrangements by the cyano group, was observed around 420 nm in the absorption spectra of CN-TFMBE nanoparticle suspension. The process of the planarization and *J*-aggregate formation of CN-TFMBE in the condensed

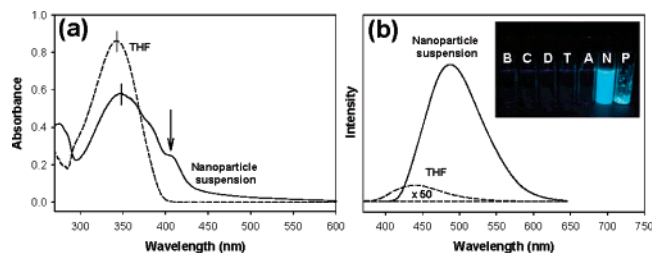


Figure 2. (a) UV/vis absorption spectra of CN-TFMBE (2×10^{-5} mol L⁻¹) in THF and its nanoparticle suspension (THF/water (1:4) mixture). (b) PL spectra of CN-TFMBE (2×10^{-5} mol L⁻¹) in THF and its nanoparticle suspension. The PL intensities were normalized by the corresponding UV absorbance. Inset photograph shows the fluorescence emission of CN-TFMBE (2×10^{-5} mol L⁻¹) in different solvents and in the solid state (B, benzene; C, chloroform; D, 1,2-dichloroethane; T, THF; A, acetonitrile; N, nanoparticle suspension; P, powder) under 365 nm UV light illumination.

phase is more dramatically evidenced by the PL studies (Figure 2b). The emission maximum peak of CN-TFMBE is again red-shifted by about 48 nm with the impressive increase in PL intensity from the dilute solution to the nanoparticles (over 460 times enhancement). The inset photograph of Figure 2b shows that aggregated CN-TFMBE (nanoparticle suspension (N) and powder (P), respectively) is strongly fluorescent, while isolated CN-TFMBE in any kind of solvent (benzene (B), chloroform (C), 1,2-dichloroethane (D), THF (T), and acetonitrile (A)) is virtually nonfluorescent. This result suggests that the strong fluorescence emission of CN-TFMBE in the nanoparticle and gel state is not caused by the special solvatochromic effect but by the unique AIEE phenomena.

In conclusion, we have demonstrated the first example of a simple conjugated LMOG (CN-TFMBE) without long alkyl chain or steroidal substituents. The unique gelation capability of CN-TFMBE is attributed to the cooperative effect of the strong π - π stacking interactions of rigid rodlike aromatic segments and supplementary intermolecular interactions induced by four CF₃ units. The remarkable fluorescence increase in the CN-TFMBE gel is attributed to the AIEE phenomenon.

Acknowledgment. This work has been supported in parts by Dongwoo FineChem Co., Ltd., and CRM-KOSEF.

Supporting Information Available: Synthetic and experimental details (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) (a) Sugiyasu, K.; Fujita, N.; Shinkai, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 1229–1233. (b) Ryu, S. Y.; Kim, S.; Seo, J.; Kim, Y.-W.; Kwon, O.-H.; Jang, D.-J.; Park, S. Y. *Chem. Commun.* **2004**, 70–71. (c) Engelkamp, H.; Middelbeek, S.; Nolte, R. J. M. *Science* **1999**, *284*, 785–788.
- (2) (a) Terech, P.; Weiss, R. G. *Chem. Rev.* **1997**, *97*, 3133–3160. (b) Abdallah, D. J.; Weiss, R. G. *Adv. Mater.* **2000**, *12*, 1237–1247.
- (3) (a) Krafft, M.-P.; Giulieri, F.; Riess, J. G. *Angew. Chem., Int. Ed.* **1993**, *32*, 741–743. (b) Giulieri, F.; Krafft, M.-P.; Riess, J. G. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1514–1515. (c) George, M.; Snyder, S. L.; Terech, P.; Glinka, C. J.; Weiss, R. G. *J. Am. Chem. Soc.* **2003**, *125*, 10275–10283.
- (4) Kim, H. I.; Koini, T.; Lee, T. R.; Perry, S. S. *Langmuir* **1997**, *13*, 7192–7196.
- (5) Melting points (mps) were obtained from the differential scanning calorimetry (DSC) thermogram.
- (6) See SEM images of microstructures of **1**–**4** (Figure S3) in Supporting Information.
- (7) An, B.-K.; Kwon, S.-K.; Jung, S.-D.; Park, S. Y. *J. Am. Chem. Soc.* **2002**, *124*, 14410–14415.
- (8) Similar phenomenon was also suggested by Tang et al.: Luo, J.; Xie, Z.; Lam, J. W. Y.; Cheng, L.; Chen, H.; Qiu, C.; Kwok, H. S.; Zhan, X.; Liu, Y.; Zhu, D.; Tang, B. Z. *Chem. Commun.* **2001**, 1740–1741.
- (9) Oelkrug, D.; Tompert, A.; Gierschner, J.; Egelhaaf, H.; Hanack, M.; Hohloch, M.; Steinhilber, E. *J. Phys. Chem. B* **1998**, *102*, 1902–1907.
- (10) See a SEM image (Figure S4) in Supporting Information. JA046215G