TICT Induced Fluorescence Color Change Actualized in an Organogel System

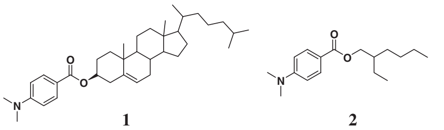
Yuya Iwashita, Kazunori Sugiyasu, Masato Ikeda, Norifumi Fujita, and Seiji Shinkai*
Department of Chemistry & Biochemisry, Graduate School of Engineering, Kyushu University,
6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581

(Received May 20, 2004; CL-040576)

A dimethylaminobenzoate group (TICT probe) was conjugated with a cholesterol group to assess the microenvironmental effect of the gel fibrils by a fluorescence method. It was found that the solvent-dependent dual fluorescence mode characteristic of TICT molecules in the sol phase almost disappears in the gel phase and only the shorter-wavelength fluorescence arising from the coplanar conformation is observed.

Recently, a low molecular-weight organogel system has offered a new methodology to assemble molecules into supramolecular nano-fibers using convenient and practical procedures.[1] Organogel system provides well-defined 1-D alignments of functional molecules, and responsiveness to stimuli (such as temperature, light, and redox) which are useful for the development of new functionality in soft materials.[2] The main research interest in the organogel system has been focused on a variety of supramolecular structures constructed in the gel system.[3] In addition, one can expect that they show the specific absorption and fluorescence spectroscopic properties depending on their difference in the aggregation mode and the sol-to-gel phase transition.[4] Taking their structural variety into consideration, the spectral characteristics would make it possible to utilize the gels as potential candidates for memory systems, devices, sensors, etc. For example, we previously reported phenanthroline-appended cholesterol-based gelators which change their fluorescence color in response to protonation and temperature.[5]

It is well known that the microenvironment around organogelator is very different between the gel phase and the sol phase.[4,6] In this communication, we report on a fluorescence color change based on the twisted intramolecular charge transfer (TICT) state in relation to the sol-to-gel phase transition phenomenon. One of the well-known TICT probes is a *p*-dimethylaminobenzoate (*p*-DMAB) group which shows a dual fluorescence property; one emission around 350 nm arises from a coplanar conformation of the torsional angle between dimethylamino group and benzoate plane and another around 500 nm arises from an orthogonal conformation (TICT state). The ratio of their fluorescence intensities depends on the solvent polarity, viscosity, and bulky substituents suppressing the rotation of the torsional angle.[7] Since organogels can be formed in various organic solvents and change their aggregation mode by thermal-stimulus, one can expect that combination of a TICT probe with an organogelator will lead to development of new soft materials featuring a function of thermo-reversible fluorescence color changes.


1 2

Scheme 1. Structures of compound **1** and reference **2**.

Our molecular design for the organogelator coupled with the TICT probe is shown in Scheme 1. Compound **1** has a cholesteryl moiety to impart the gel-forming ability as well as a *p*-DMAB group to report the microenvironmental effect. We also synthesized a non-gelling reference compound (**2**). These products were identified by ^{1}H NMR and MS spectral evidence (MALDI-TOF, CHCA matrix, *m*/*z* 534.45 ([**1** + H$^+$], calcd 534.43), *m*/*z* 278.22 ([**2** + H$^+$], calcd 278.21)) and elemental analyses. By the “stable-to-inversion of a test tube” method, we found that **1** forms an opaque gel with cyclohexane, 1,4-dioxane, *t*-butyl alcohol, 1-propanol, methanol, DMF, acetonitrile, and so on. Compound **1** showed the relatively low critical gelation concentration, 0.4 wt/vol % for acetone and acetonitrile, and 0.1 wt/vol % for methanol. These results indicate that **1** acts as an efficient and versatile gelator for various organic solvents.

The visual image of the superstructure constructed in this gel system can be obtained by scanning electron microscope (SEM). As shown in Figure 1, a plenty of fibrillar aggregates with 0.2–1.0-μm diameter were observed as often seen in organogel systems. This picture implies that **1** also forms a stacked 1-D aggregate as in the case of many other cholesterol-based gelators.[1]

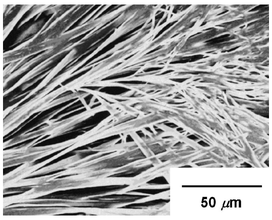


Figure 1. SEM image of xerogel of **1** prepared from cyclohexane.

Absorption spectra of **2** are only slightly affected by the solvent polarity, giving its absorption maxima at 300–309 nm (data not shown here). As already known, fluorescence spectra of *p*-DMAB are significantly changed by the solvent polarity (polar solvent can stabilize the intramolecular charge transfer state).[7,8] We thus measured the fluorescence spectra of **1** gel and **2** solution in acetonitrile, 1-propanol, and cyclohexane, whose relative permittivities are 37.5, 20.3, and 2.0, respectively. The fluorescence maximum of **2** in acetonitrile solution appeared at 488 nm, which is attributed to emission from the TICT state, whereas that in cyclohexane solution appeared at 340 nm, which is attributed to emission from the coplanar conformation. In 1-propanol whose permittivity is between acetonitrile and cyclohexane, **2** showed the dual fluorescence property (Figure 2a). These results are all in line with those reported for the related TICT compounds.[7,8]

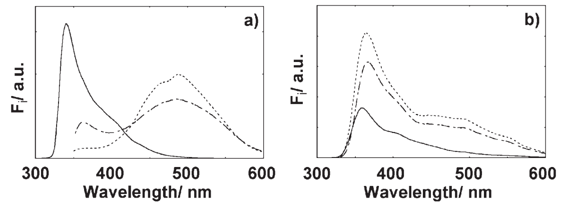


Figure 2. (a) Fluorescence spectra of **2** solution, and (b) fluorescence spectra of **1** gel in acetonitrile (dotted), 1-propanol (dashed), and cyclohexane (solid), $\lambda_{\rm ex} = 290\,\text{nm}$.

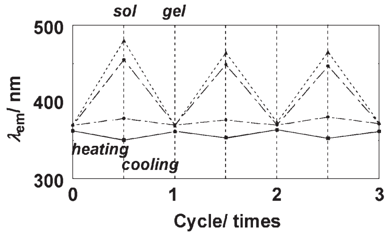


Figure 3. Reversibility in the fluorescence maximum change in **1** gel; aceonitrile (dotted), 1-propanol (dashed), and cyclohexane (solid).

Very interestingly, all **1** gels prepared from foregoing solvents gave only the shorter-wavelength fluorescence; that is, TICT emission was hardly observed even in the polar solvents such as acetonitrile and 1-propanol (Figure 2b). In order to confirm that these spectral differences are due to the self-assembly arising from gel-formation of **1**, we conducted the following two experiments. Firstly, the concentration of **1** was increased from 5.0×10^{-5} to 2.0×10^{-2} M, monitoring the fluorescence spectral change. In acetonitrile and 1-propanol, the fluorescence spectra drastically changed somewhat below their critical gelation concentrations (CGC; 7.5×10^{-3} M for acetonitrile, and 1.1×10^{-2} M for 1-propanol).[9] Secondly, the gel-formation process was monitored by a fluorescence spectroscopic method. The gel was first heated to obtain the sol phase, and then left in a thermostatic cell holder. The fluorescence spectra were measured as a function of the solvent temperature. In the first stage of the cooling process, the sol phase of **1** showed the same fluorescence spectrum as that of **2** solution. However, after further cooling and subsequent gel formation, fluorescence from the TICT state decreased with the increase in emission from the coplanar conformation. As a consequence, the fluorescence color changed from green to purple in acetonitrile, greenish blue to purple in 1-propanol, and did not change in cyclohexane (Table 1). These results indicate that the fluorescence spectral change is induced by the gel-formation; self-assembly of **1**.

Table 1. Fluorescence maxima of **1** in sol and gel phase

Solvent	$\lambda_{\rm em}$ of sol/nm	$T_{\rm gel}$/°C[10]	$\lambda_{\rm em}$ of gel/nm
acetonitrile	488 (green)	83	360 (purple)
1-propanol	485 362 (greenish blue)	57	366 (purple)
cyclohexane	340 (purple)	23	364 (purple)

From these spectral characteristics, one can propose that the microenvironment around the gel fibril and/or the molecular mobility of **1** are nearly the same, independent of the solvent polarity. These spectral changes can be repeated several times by heating-cooling recycle processes (Figure 3).

In conclusion, we have demonstrated that a cholesterol-appended *p*-DMAB derivative acts as an efficient gelator for various organic solvents. The gel showed only the shorter-wavelength fluorescence emission arising from the coplanar conformation independent of the solvent polarity, whereas the sol showed the conventional TICT fluorescence properties of *p*-DMAB. We believe that the present organogel system has unique potentials not only to assess the microenvironmental effect around organogel fibrils[4,6] but also to develop the new photochemical soft materials from organogels.

Support was partially provided by the 21st Century COE Project, Functional Innovation of Molecular Informatics and a Grant-in-Aid for Scientific Research (S) (No. 15105004) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

References and Notes

1 For reviews, see; P. Terech and R. G. Weiss, *Chem. Rev.*, **97**, 3133 (1997); S. Shinkai and K. Murata, *J. Mater. Chem.*, **8**, 485 (1998); J. H. van Esch and B. L. Feringa, *Angew. Chem., Int. Ed.*, **39**, 2263 (2000).

2 K. Murata, M. Aoki, T. Suzuki, T. Hanada, H. Kawabata, T. Komori, F. Oseto, K. Ueda, and S. Shinkai, *J. Am. Chem. Soc.*, **116**, 6664 (1994); M. Moriyama, N. Mizoshita, T. Yokota, K. Kishimoto, and T. Kato, *Adv. Mater.*, **15**, 1335 (2003); J. J. D. de Jong, L. N. Lucas, R. M. Kellogg, J. H. van Esch, and B. L. Feringa, *Science*, **304**, 278 (2004); S.-i. Kawano, N. Fujita, and S. Shinkai, *J. Am. Chem. Soc.*, **126**, 8592 (2004).

3 K. Hanabusa, M. Yamada, M. Kimura, and H. Shirai, *Angew. Chem., Int. Ed.*, **35**, 2086 (1996); R. Oda, I. Huc, and S. J. Candau, *Angew. Chem., Int. Ed.*, **37**, 2689 (1998); M. de Loos, J. van Esch, R. M. Kellogg, and B. L. Feringa, *Angew. Chem., Int. Ed.*, **40**, 613 (2001); H. Ihara, T. Sakurai, T. Yamada, T. Hashimoto, M. Takafuji, T. Sagawa, and H. Hachisako, *Langmuir*, **18**, 7120 (2002); T. Kato, T. Kutsuna, K. Yabuuchi, and N. Mizoshita, *Langmuir*, **18**, 7086 (2002); M. Shirakawa, S.-i. Kawano, N. Fujita, K. Sada, and S. Shinkai, *J. Org. Chem.*, **68**, 5037 (2003).

4 U. Maitra, S. Mukhopadhyay, A. Sarkar, P. Rao, and S. S. Ind, *Angew. Chem., Int. Ed.*, **40**, 2281 (2001); A. Ajayaghosh and S. J. George, *J. Am. Chem. Soc.*, **123**, 5148 (2001); T. Sagawa, S. Fukugawa, T. Yamada, and H. Ihara, *Langmuir*, **18**, 7223 (2002); M. Ikeda, M. Takeuchi, and S. Shinkai, *Chem. Commun.*, **2003**, 1354; T. Yi, K. Sada, K. Sugiyasu, T. Hatano, and S. Shinkai, *Chem. Commun.*, **2003**, 344; S. Y. Ryu, S. Kim, J. Seo, Y.-W. Kim, O.-H. Kwon, D.-J. Jang, and S. Y. Park, *Chem. Commun.*, **2004**, 70; K. Sugiyasu, N. Fujita, and S. Shinkai, *Angew. Chem., Int. Ed.*, **43**, 1229 (2004).

5 K. Sugiyasu, N. Fujita, M. Takeuchi, S. Yamada, and S. Shinkai, *Org. Biomol. Chem.*, **1**, 895 (2003).

6 M. Suzuki, M. Yumoto, M. Kimura, H. Shirai, and K. Hanabusa, *Chem.—Eur. J.*, **9**, 348 (2003).

7 For comprehensive review, see; Z. R. Grabowski, K. Rotkiewicz, and W. Rettig, *Chem. Rev.*, **103**, 3899 (2003).

8 Y.-B. Jiang, *Spectrochim. Acta, Part A*, **55**, 833 (1999).

9 We confirmed that **1** forms fibrillar aggregates below its CGCs by SEM observation. Above these concentrations (critical aggregation concentrations: CACs), the fluorescence spectra drastically changed.

10 Sol-to-gel phase transition temperature ($T_{\rm gel}$) was determined by the turbidity change at 650 nm of the mixture using temperature dependent transmittance spectra.

Published on the web (Advance View) August 7, 2004; DOI 10.1246/cl.2004.1124