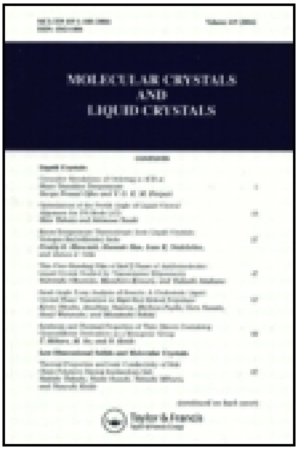


Molecular Crystals and Liquid Crystals

Photoresponsive Nanoassemblies of a Dithienylethene Organogelator

Jiaan Gan [a] , Jean-Luc Pozzo [a] & Fritz Vögtle [b]

[a] Photochemistry for Nanoscience, CNRS, UMR Bordeaux, Talence, France

[b] Kekulé Institute, Department of Chemistry and Biochemistry, University of Bonn, Germany

Version of record first published: 31 Aug 2006

To cite this article: Jiaan Gan, Jean-Luc Pozzo & Fritz Vögtle (2005): Photoresponsive Nanoassemblies of a Dithienylethene Organogelator, Molecular Crystals and Liquid Crystals, 430:1, 99-106

To link to this article: http://dx.doi.org/10.1080/15421400590946226

Mol. Cryst. Liq. Cryst., Vol. 430, pp. 99–106, 2005
Copyright © Taylor & Francis Inc.
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400590946226

Taylor & Francis
Taylor & Francis Group

Photoresponsive Nanoassemblies of a Dithienylethene Organogelator

Jiaan Gan
Jean-Luc Pozzo
Photochemistry for Nanoscience, CNRS, UMR Bordeaux,
Talence, France

Fritz Vögtle
Kekulé Institute, Department of Chemistry and Biochemistry,
University of Bonn, Germany

A 1,2-Bisdithienylperfluorocyclopentene covalently linked to aggregative gelling moieties based on a synthetic aminoacid unit have been synthesized. This rationnally designed molecular target lead to the spontaneous organisation of nanosized fibers which in turn form a 3D-network. The photoinduced ring-closure process involved in the photochromism of diarylethene suppresses the self-assembling properties. The system reversibly reverts back to the Gel state upon Visible irradiation.

Keywords: dithienylethene; gels; nanoassemblies; photochromism

INTRODUCTION

Recently, a wide variety of low molecular weight organogelators have emerged as a fascinating class of thermoreversible self-assembling materials [1]. Since there are many aspects of gelation remain unclear [2], it is still difficult to predict which molecular structures will act as an efficient gelator molecule. Low molecular mass organogelators (LMOGs) are able to self-associate to form fibre-like structures, entrapping solvent molecules within their void space driven by

The present research was finacially supported by CNRS and COST D-11 Supramolecular project D11/00015/99.

Address correspondence to Jean-Luc Pozzo, Photochemistry for Nanoscience, CNRS, UMR 5802 Bordeaux 1, 351 cours liberation, Talence, 33405, France. E-mail: jl.pozzo@lcoo.u-bordeaux1.fr

intermolecular interaction through hydrogen bonding, $\pi-\pi$ stacking and van der vaals interactions [3].

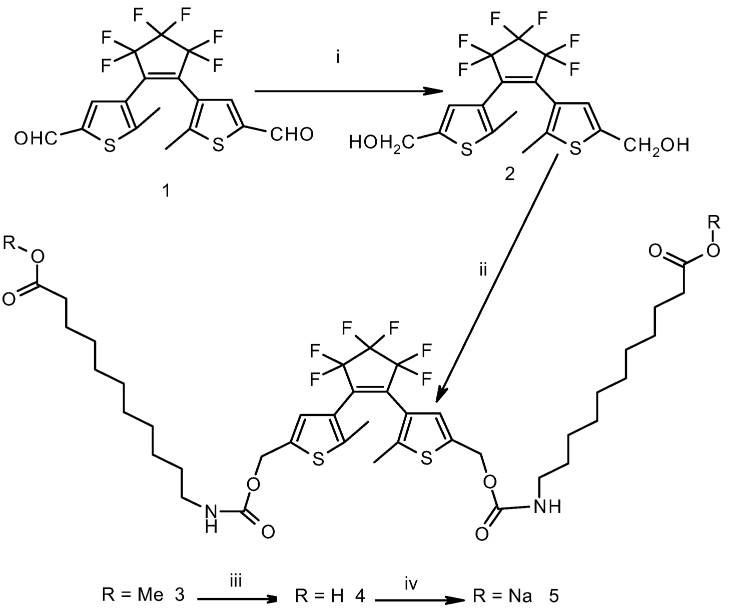
It is a tremendous challenging task to design controlled gelation systems based on isomerisation changes of a gelator molecule induced by external stimuli [4]. Introduction of a photoresponsive group onto the self-assembling unit is one of the promising approach toward such smart gels [5]. Microsphere-to-Gel fibre morphological transition can be induced by the photoisomerization of a malic acid amide to a fumaric acid amide [6]. Some organogelators with photochromic units have been reported for the design of special supramolecular materials [7,8]. Diarylethene derivatives are the most promising photochromic compounds because of their thermally irreversible and fatigue resistant photochromic performance [9]. Indeed, the photochromic reactions of 1,2-bis-thienylcyclopentenes functionalized with two amide groups have been reported to largely influence the medium viscosity [10]. More recently, these derivatives incorporating a chiral moiety have been shown to reversibly control supramolecular chirality switching between different chiral aggregates in the gel phase [11].

In this study, we designed and synthesized a photochromic dithienylethene derivative with two N-acyl-1,ω-amino acid moieties as side-arms (Scheme 1). The photochromic properties of this organogelator are kept and an efficient Gel-to-Sol phase transition process is observed upon irradiation with 254 nm UV light.

RESULTS AND DISCUSSION

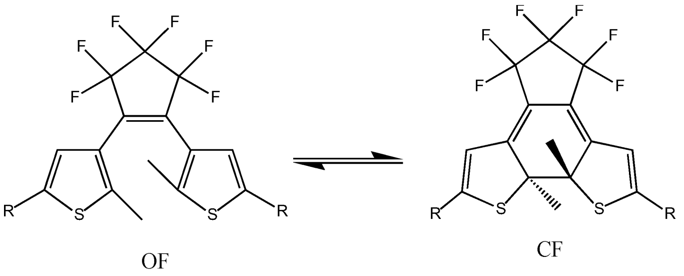
Molecular Design and Synthesis

Photochromic compounds based on diarylethene derivatives have attracted much attention for optoelectronic devices because both isomers of the compounds are stable and the coloration/decoloration cycles can be repeated as high as 10^4 times. Previously, we successfully prepared photochromic multiaddressable self-assembling naphthopyran gelators. Incorporation of the naphthopyran unit in the supramolecular system could lead to smart gels sensitive to light, temperature and acidity and this structural modification did not prevent gelation [12]. In this study, a simple 1,2-Bis(2-methylthien-3-yl) perfluorocyclopentene was selected as the photochromic core which has two different interconvertible isomers: the colorless open form (OF) and the colored closed form (CF) as depicted in Scheme 2. The photogenerated colored form are stable in the dark and can be converted back to the open form with a visible light. The photochromic urethane derivative was prepared through the condensation of the



SCHEME 1 (i) $NaBH_4$; (ii) $O{=}C{=}N{-}(CH_2)_{10}{-}COOMe$, TEA/THF; (iii) LiOH then 1 N HCl; (iv) NaOH 1N.

dithienylethene dialcohol **2** with an appropriate isocyanate. The diacid **4** was obtained by the saponification of the urethane ester with a mild lithium hydroxide base. One could expect that the gelling ability is retained when the 1,2-Bis(2-methylthien-3-yl) perfluorocyclopentene photochromic unit is introduced to the urethane derivatives.



$R = \text{-}CH_2OCONH\text{-}(CH_2)_{10}COO^{-}\,Na^{+}$

SCHEME 2

Photochromic Properties

The comparison of the UV-vis absorption spectra of dialcohol **2** and disalt **5** in methanol at identical concentration were shown in Figure 1 and listed in Table 1. Upon irradiation with 254-nm light, the colorless solution of **2** and **5** gradually turned red. The absorption band at 296 nm for the open form of **2** decreased and two new absorption bands in the presence of an isosbestic point at 308 nm appeared. Similar spectral changes were observed for compound **5**. The isosbestic point has been measured at 306 nm and the two maxima absorption bands for the closed form of **5** were centered at 340 and 517 nm. These results including the appearance of an isosbestic point indicate that the incorporation of the gelation unit has not altered the photochromic properties of the 1,2-Bis(2-methylthien-3-yl) perfluorocyclopentene subunit. Both photostationary states for compounds **2** and **5** in methanol solution were attained at the same time, i.e. after 165 seconds irradiation. Upon visible light ($\lambda > 530$ nm) irradiation, the red color and the two absorption bands which was ascribed to the closed form of both **2** and **5** disappeared indicating that the designed LMOG reverts back to the initial open ring isomer.

Disalt **5** is an efficient gelator of polar organic solvents such as DMF and DMSO. The photochromism of dialcohol **2** and disalt **5** in DMF for comparison were investigated and the results were shown in Figure 2 and listed in Table 1. Upon irradiation with 254-nm light, dialcohol **2** in DMF exhibit the same photochromic behaviour as in methanolic solutions. The appearance of the isosbestic point and the two new

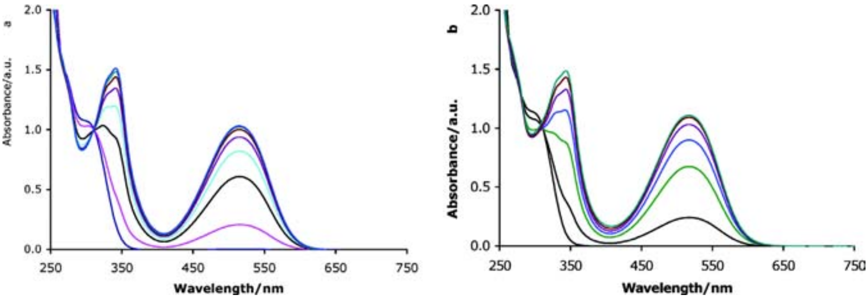


FIGURE 1 Changes in the UV-vis absorption spectra of dialcohol **2** (a) and disalt **5** (b) in methanol ($2{,}2 \times 10^{-4}$ M) when irradiated with 254 nm light. Irradiation periods for the solution studied are 0, 15, 45, 75, 105, 135, 165 s.

TABLE 1 UV-Vis Data and Photochemical Conversion of Compounds[a]

Compound	λ_{max}/nm ($\varepsilon \times 10^{-3}$ L mol^{-1}cm^{-1}) Open form	Closed form	Isosbestic point/nm
2 in MeOH	296^b (4.68)	339 (6.82) 513 (4.68)	308
5 in MeOH	298^b (4.89)	340 (6.68) 517 (5.03)	306
2 in DMF	301^b (4.44)	339 (5.36) 522 (3.21)	310
5 in DMF	309^b (5.59)	360 (5.17) 541 (1.51)	–

[a] UV/Vis spectroscopic data were obtained at ambient temperature. The photostationary state were obtained by irradiation of the solution of the open form with a hand-held 254 nm UV (470 μW/cm^2) lamp.

[b] shoulder.

absorption bands for the closed form were observed. The photostationary state of the dialcohol **2** in DMF was prolonged to 735 seconds and the isosbestic point was remained. The difference of the photochromic properties was assigned to solvent effect.

Under the same irradiation condition and at identical concentration as dialcohol **2** in DMF, no isosbestic point was observed for disalt **5** in DMF. Two new broad bands at 320–500 and 500–600 nm correspond to the closed form isomer. The photostationary state of the disalt in DMF attained at 375 seconds. Upon bleaching

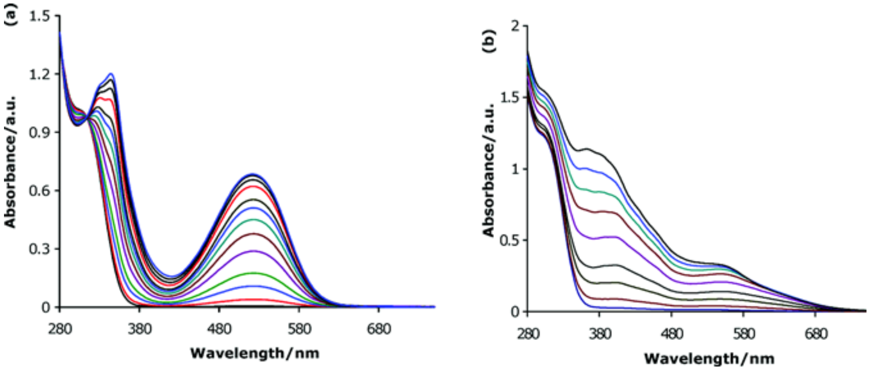


FIGURE 2 Changes in the UV-Vis absorption spectra of dialcohol **2** (a) and disalt **5** (b) in DMF (2,2 × 10^{-4} M) when irradiated with 254 nm light. Irradiation periods for (a) and (b) are 0, 15, 45, 75, 135, 195, 255, 315, 375, 495, 615, 735 s and 0, 15, 45, 75, 135, 195, 255, 315, 375 s respectively.

with visible light (>530 nm), the two absorption bands disappeared and returned to a colorless state. Though the reversal process was rather slow, the lowest cycloconversion from the closed form to the open form could be attributed to the aggregation state of the disalt organogelators driven by specific unknown noncolvalent intermolecular forces such as hydrogen bonding, hydrophobic interactions, dipole–dipole interactions, van der vaals interactions or metal coordination bond formation. Irie [13] has reported that the cycloreversion of a diarylethene derivative was strongly dependant on solvent viscosity. In the 3D gel network, the rotational freedom about the C−C bonds between the thiophene and cyclopentene rings may be decreased due to the aggregation state and one can expect that the ring-open process be suppressed.

Gelation Properties and Gel-to-Sol Phase Transition Process

The gelation behavior was investigated via the inverted test tube method and through rheological measurements. Disalt **5** has been found to be soluble in various alcoholic solvents and water, whereas it is insoluble in all of apolar solvents and most of the low polar solvents such as dichloromethane and chloroform etc., Remarkably corresponding diacid **4** was easily dissolved in such media. Disalt **5** is sparingly soluble in DMF and DMSO. Upon heating at 80–110°C, the fine powder of disalt **5** gradually dissolved. After cooling to the ambient temperature, gels were readily obtained which are then stable for months. Transition temperature (T_{gel}) of the gel in DMF as a function of organogelator concentration were shown in Figure 3. The Gel-to-Sol phase transition temperature of DMF in a concentration of 1% wt/vol (1.1×10^{-2} M) is as high as 120°C, which is close to a supergelator [14].

A strong gel of disalt **5** in DMF with a concentration of 3.7×10^{-3} M in an inverted cell ($T_{gel} = 96$°C), was irradiated using a hand-held 254 nm lamp. The colorless gel turned to brown red and then began to flow upon irradiation for 4 min as shown in Figure 4. The Gel-to-Sol process starting from the up part of the invert cell then to the whole cell can be observed clearly, because that the solution part was deeply colored and the gel part was still colorless.

The reversal bleaching process for the closed form of the gel (3.7×10^{-3} M) in DMF was rather low than that of the disalt **5** in DMF solution (2×10^{-4} M). Strong visible irradiation ($\lambda > 530$ nm) of the sol gave rise to the photocycloreversion to reform **5** in a gel phase. This represents the first example of a Gel-to-Sol phase transition that could be photoswitched in both directions using

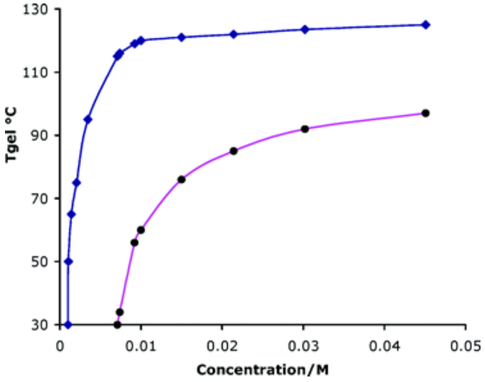


FIGURE 3 Gel-to-Sol phase transition temperatures as a function **5** concentration in DMF (◆) and DMSO (●).

appropriate wavelength. Different cycles have been realised showing that Tgel values decrease as a function of the number of UV/Vis. irradiation processes. In these conditions no photodegradation takes place as the initial Tgel value is recovered by simply heating and then cooling the uncoloured phase. The network structure is only partially reconstructed at 30°C and is totally regenerated using the thermal process.

In conclusion, we have prepared a novel low molecular mass organogelator using dithienylethene unit as photochromic core. This compound showed typical photochromic behavior of a diarylethene

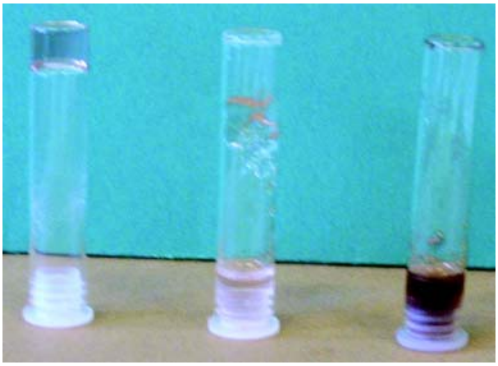


FIGURE 4 Photocontrolled Gel-to-Sol phase transition process. Left: gel before irradiation, Middle: photoregenerated gel with visible light >530 nm and Right: solution after irradiation.

derivative in solutions and acted as an efficient gelator for polar organic fluid. Photocontrolled Gel-to-Sol transition process of a DMF gel was undoubtedly observed. This dithienylethene organogelator showed great potential for the application of advanced optical materials and device using sol-gel technology.

REFERENCES

[1] Terech, P. & Weiss, R. G. (1997). *Chem. Rew.*, *97*, 3133.

[2] Oda, R., Huc, I., & Candau, S. J. (1998). *Angew. Chem. Int. Ed.*, *37*, 2689.

[3] Shumburo, A. & Biewer, M. C. (2002). *Chem. Mater.*, *14*, 3745.

[4] van Esch, J., Schoonbeek, F., De Loos, M., Veen, E. M., Kellogg, R. M., & Feringa, B. L. (1999). *Supramolecular science: where it is and where it is going*; Nato ASI Series C, Mathematical and physical sciences, Kluwer Academic: Dordrecht, Vol. 527, p 233.

[5] Pozzo, J. L., Clavier, G., & Desvergne, J. P. (1998). *J. Mater. Chem.*, *8*, 2575.

[6] Frkanec, L., Jokic, M., Makarevic, J., Wolsperger, K., & Zinic, M. (2002). *J. Am. Chem. Soc.*, *124*, 9716.

[7] Pozzo, J. L., Clavier, G., Rustmeyer, F., & Bouas-Laurent, H. (2000). *Mol. Cryst. Liq. Cryst.*, *344*, 101.

[8] De Loos, M., van Esch, J., Kellogg, R. M., & Feringa, B. L. (2001). *Angew. Chem. Int. Ed.*, *40*, 613.

[9] Irie, M. (2000). *Chem. Rev.*, *100*, 1685.

[10] Lucas, L. N., van Esch, J., Feringa, B. L., & Kellogg, R. M. (2001). *Chem. Comm.*, 759.

[11] de Jong, J., Lucas, L. N., Kellogg, R. M., van Esch, J., & Feringa, B. L. (2004). *Science*, *304*, 278.

[12] Ahmed, S., Sallenave, X., Fages, F., Mieden-Gundert, G., Müller, W. M., Müller, U., Vögtle, F., & Pozzo, J. L. (2002). *Langmuir*, *18*, 7096.

[13] Miyasaka, H., Nobuto, T., Murakami, M., Itaya, A., Tamai, N., & Irie, M. (2002). *J. Phys. Chem. A*, *106*, 8096.

[14] Gronwald, O. & Shinkai, S. (2001). *Chem. Eur. J.*, *7*, 4329.