A multiple switching bisthienylethene and its photochromic fluorescent organogelator†

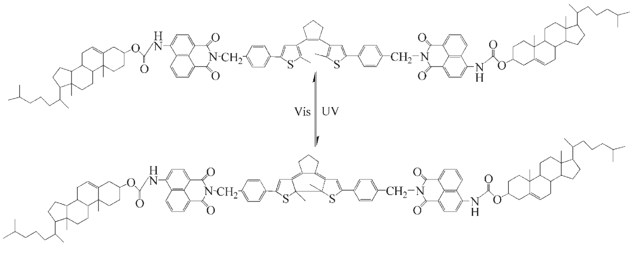
Sheng Wang, Wei Shen, Yanli Feng and He Tian*

Received (in Cambridge, UK) 1st November 2005, Accepted 3rd February 2006
First published as an Advance Article on the web 24th February 2006
DOI: 10.1039/b515412j

A multiple switching fluorescent photochromic bisthienylethene bridged naphthalimide bearing cholesteryl groups was synthesized and its organogelator showed excellent photo-responsive and thermal reversible performance by light, thermal.

Low-molecular-weight (LMW) gelators have attracted much attention in recent years.[1–3] Of particular interest for organogelator materials science are "smart gels", *i.e.* gels whose properties can be controlled reversibly or irreversibly in response to changes in external chemical, photochemical, thermal stimuli or sound.[4] Such responsive systems are highly desirable in thermo- and mechano-responsive sensor materials or in applications like drug delivery or catalysis, or in nano- and mesoscopic assemblies with interesting optical and electronic properties and so on.[5] Several groups exploited these features for the development of "smart" LMW organogelators.[1–8] However, it is a tremendous challenging task to design controllable gelation systems based on reversible changes of a gelator molecule induced by external stimuli.

Some organogelators with photochromic units including azobenzene or naphthopyran derivatives have been reported,[9,10] in which the gelation was controlled by heat, light, or acidity as external stimuli. Among various types of photochromic compounds, bisthienylethene (BTE) derivatives are the most promising because of their excellent fatigue resistance and thermal stability in both isomeric forms, picosecond switching rate, and high photochemical quantum yields.[11,12] More recently, BTE derivatives incorporating a chiral moiety have been shown to reversibly control supramolecular chirality switching between different chiral aggregates in the gel phase.[13] As an attempt to obtain a new functional organogelator with potential photonics applications, we have designed and synthesized a photochromic gelator containing bisthienylethene bridged fluorescent naphthalimide units bearing cholesteryl groups (shown in Scheme 1, BTE-NA-(chol)$_2$). This novel photochromic gelator exhibits excellent reversible photochromic behaviour in gel phase. Interestingly, it can fluoresce the in gel phase but it scarcely emits in solution. In addition, this system is sensitive to fluoride ions in solution, which is a promising fluorescent molecular switch by fluoride ions and protons.



Scheme 1 The structure and photochromic process of BTE-NA-(chol)$_2$.

Naphthalimide (NA) is an excellent fluorescent chromophore with high photostability and high fluorescent quantum yield.[14] Two naphthalimides are covalently attached to a photochromic dithienylcyclopentene unit[15] for the purpose of photoswitching fluorescence with high contrast. The cholesteryl groups are expected to assemble through van der Waals interaction and naphthalimides are connected with cholesteryl groups by amide bonding and are expected to behave as sites for hydrogen bonding. This novel naphthalimide dimer based on cholesteryls tethered by a photochromic bisthienylethene-bridge was synthesized by the Suzuki coupling method (shown in Scheme S1)†. All key intermediates and the final product are identified by ^{1}H NMR spectroscopy and MS or MALDI-TOF-MS.†

BTE-NA-(chol)$_2$ undergoes reversible photochromic reaction. Irradiation of a solution of BTE-NA-(chol)$_2$ with UV light at 365 nm led to the appearance of a new absorption band at round 540 nm and the light yellow solution of BTE-NA-(chol)$_2$ turned to red (Fig. 1), which is attributed to large π-electron delocalization

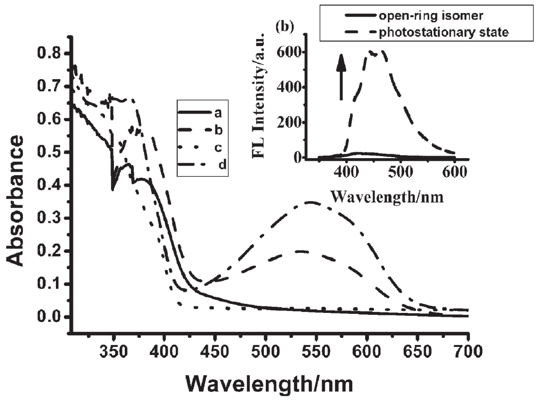


Fig. 1 Absorption spectra and fluorescent spectra (inset, excited at 355 nm) of the open-ring isomer BTE-NA-(chol)$_2$ (a: in gel; c: in solution) and the photostationary state (b: in gel; d: in solution) upon irradiation with 365 nm light at room temperature.

Labs for Advanced Materials and Institute of Fine Chemicals, East China University of Science & Technology, Shanghai, 200237, P.R. China. E-mail: tianhe@ecust.edu.cn; Fax: +86-21-64252288; Tel: +86-21-64252756

† Electronic supplementary information (ESI) available: procedure for the preparation of BTE-NA-(chol)$_2$ and the characterization, a brief description of analytical methods and the absorption and fluorescence spectra data of the system, SEM as well as sensing spectra for anions, (PDF). See DOI: 10.1039/b515412j

along the whole molecule. And after visible light ($\lambda > 510$ nm) irradiation the original absorption spectrum was converted back to that of the initial open-ring isomer of BTE-NA-(chol)$_2$. The cyclization and cycloreversion yield are 0.39 and 0.37, respectively.[19] The reversible spectral changes should be due to the reversible structural transformation between the closed-ring and open form of the bisthienylethene unit in BTE-NA-(chol)$_2$. Corresponding to the difference in absorption between the photochromic binary states, the luminescence spectra of BTE-NA-(chol)$_2$ is also indicated by binary status (the inset in Fig. 1). Interestingly, the very large enhanced luminescence (contrast ratio >50) of the closed-ring of BTE-NA-(chol)$_2$ at around 452 nm upon the irradiation with 365 nm light might be attributed to the formation of an extended π-conjugation system that results from the photocyclization as well as the self-assembled aggregates of BTE-NA-(chol)$_2$.[16] Regretfully, the enhanced fluorescence mechanism has still not been proved by reasonable proofs.

The gelation ability of BTE-NA-(chol)$_2$ was studied at a concentration of 0.5 w/v% in various solvents. We modified the solubility of BTE-NA-(chol)$_2$ in toluene by adding alcoholic solvents; as expected, most mixed solvents were finely gelated by BTE-NA-(chol)$_2$. We could also use benzene, *o*-xylene, and nitrobenzene for gelation instead of toluene. A very stable BTE-NA-(chol)$_2$ gel was formed above 0.5 w/v% and showed a high sol–gel phase-transition temperature.†

Hereafter, we used a mixed solvent of toluene and ethanol (1 : 3 v/v) as the standard medium. The visual images of the BTE-NA-(chol)$_2$ gel with a network structure composed of fibrous aggregates were observed with a scanning electronic microscope (SEM).† In addition, we measured the absorption and fluorescence spectra of BTE-NA-(chol)$_2$ gel in a 0.1 cm cell to obtain an insight into their photochromic properties in the gel phase, which retains photochromic performance as in solution. The yellow colour of BTE-NA-(chol)$_2$ gels turned to red and a new absorption band appeared at around 537 nm and gradually increased and reached a photo-stationary state (Fig. 1). Upon subsequent irradiation of the closed form of BTE-NA-(chol)$_2$ gel with visible light ($\lambda > 510$ nm), the system gradually returned to the initial status. This cycle could be repeated more than 10 times and the gel phase remained stable at room temperature. The cyclization and cycloreversion yield are 0.18 and 0.13, respectively.[19] There is also a difference in luminescence spectra between two photochromic states in the gel phase.† The fluorescent intensity of BTE-NA-(chol)$_2$ gel evidently increased and strong emission with λ_{max} at round 460 nm was observed upon irradiation with UV light (365 nm) and the original emission could also recovered by visible ($\lambda > 510$ nm) light irradiation.

The interaction of BTE-NA-(chol)$_2$ with fluoride anion was investigated in THF solution through spectrophotometer titration experiments. Upon addition of F^-, the band around 330 nm progressively increases, while a new band with a peak at round 495 nm forms (Fig. 2). The presence of two isosbestic points at 340 and 410 nm indicates that only two species coexist at the equilibrium, the solution of BTE-NA-(chol)$_2$ becoming an orange-red colour. The possible explanation for this phenomenon is the deprotonation of the amino moiety by F^-, which would result in a negatively charged density on the amide nitrogen, with associated enhancement in the push–pull effect of the ICT transition.[17]

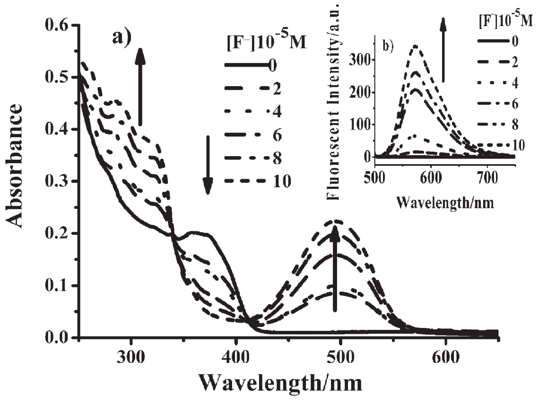


Fig. 2 The changes in absorption and the changes in fluorescence spectra (insert, excited at 495 nm) of the open form of BTE-NA-(chol)$_2$ (2.0×10^{-5} mol L^{-1} in THF) upon addition of TBAF (tetrabutylammonium fluoride salt) at room temperature.

The emission spectra of compound BTE-NA-(chol)$_2$ and its fluorescence titration with fluoride ions are shown as the inset in Fig. 2. The open form of BTE-NA-(chol)$_2$ displays no emission at 570 nm until F^- is added to the solution of BTE-NA-(chol)$_2$ in THF, when a significant emission at 570 nm is observed. The possible explanation for this phenomenon is that the change in electron density of the amide moiety upon fluoride addition influences the charge transfer between the amide group and the acceptor.[18]

Fig. 3 shows the whole multiple switching processes with photographic images of BTE-NA-(chol)$_2$ under the cooperative effects of light, thermal, fluoride ions and protons. The multiple switching could be repeated many times. Upon irradiation with 365 nm UV light and visible light ($\lambda > 510$ nm), the yellow colour open form of BTE-NA-(chol)$_2$ can be interconverted with the red colour closed-ring form in the gel or in solution, *i.e.* photochromic processes both in gel and in solution. The interconversion between the gel phase and solution could be easily achieved by thermal stimuli. The incorporation of cholesterol was presumably designed to induce chiral-sensitive selection, which is being measured for many different cases. In addition, the solutions of BTE-NA-(chol)$_2$ both in the open form and in the closed-ring form were sensitive to

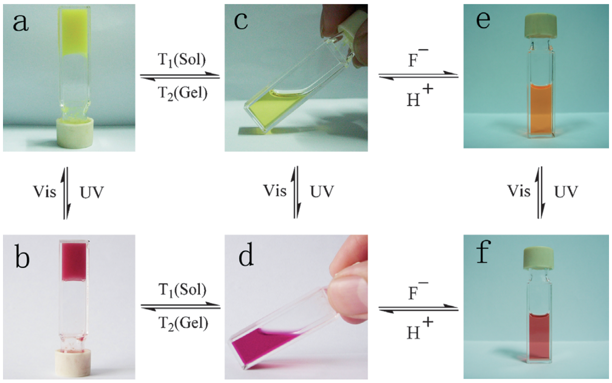


Fig. 3 Multiple switching images of BTE-NA-(chol)$_2$ under the cooperative effects of light, thermal, fluoride anions, protons. (a) Gel(open); (b) Gel(closed); (c) Sol(open); (d) Sol(closed); (e) Sol(open) + F^-; (f) Sol(closed) + F^-.

fluoride ion, which resulted in obvious changes in the absorption and fluorescence spectra. The reversible chemical switch could be obtained by proton stimuli.† Thus, this system constitutes a multi-mode complete reversible switch by light, thermal stimuli, fluoride ions as well as by protons.

In summary, we have succeeded in constructing a BTE-NA-(chol)$_2$ multiple switching system responding to light, thermal stimuli, fluoride anions, proton stimuli and a photochromic fluorescent organogel based on bisthienylethene bridged naphthalimides. It exhibits excellent photochromic properties and defined thermo reversible properties in an organogel system. At the same time, by taking advantage of the ability of F$^-$ and protons to induce obviously different absorption and fluorescence spectra of BTE-NA-(chol)$_2$ in solution under sequential alternating UV/Vis light irradiation, a multiple switch is realized, which makes it promising application in the fields of opto- and electronic smart materials, logic gate, fluorescence sensors and other molecular photonic devices.

This work was supported by NSFC/China (20476027; 90401026) and Scientific Committee of Shanghai.

Notes and references

1 J. H. van Esch and B. L. Feringa, *Angew. Chem., Int. Ed.*, 2000, **39**, 2263; D. J. Abdullah and R. G. Weiss, *Adv. Mater.*, 2000, **12**, 1237; O. Gronwald and S. Shinkai, *Chem.–Eur. J.*, 2001, **7**, 4328; A. Ajayaghosh, S. J. George and V. K. Praveen, *Angew. Chem., Int. Ed.*, 2003, **42**, 332; S. J. George, A. Ajayaghosh, P. Jonkheijm, A. P. H. J. Schenning and E. W. Meijer, *Angew. Chem., Int. Ed.*, 2004, **43**, 3422; Maaike de Loos, B. L. Feringa and J. H. van Esch, *Eur. J. Org. Chem.*, 2005, 3615; M. S. Neralagatta and M. Uday, *Chem. Soc. Rev.*, 2005, **34**, 821.

2 J. H. Jung, S. Shinkai and T. Shimizu, *Chem.–Eur. J.*, 2002, **8**, 2684; L. Frkanec, M. Jokic, J. Makarevic, K. Wolsperger and M. Zinic, *J. Am. Chem. Soc.*, 2002, **124**, 9716; M. George and R. G. Weiss, *Chem. Mater.*, 2003, **15**, 2879; M. George, S. L. Snyder, P. Terech, C. J. Glinka and R. G. Weiss, *J. Am. Chem. Soc.*, 2003, **125**, 10275; G. Wang and A. D. Hamilton, *Chem. Commun.*, 2003, 310; T. Sumiyoshi, K. Nishimura, M. Nakano, T. Handa, Y. Miwa and K. Tomioka, *J. Am. Chem. Soc.*, 2003, **125**, 12137.

3 R. Wang, C. Geiger, L. Chen, B. Swanson and D. G. Whitten, *J. Am. Chem. Soc.*, 2000, **122**, 2399; M. Ayabe, T. Kishida, N. Fujita, K. Sada and S. Shinkai, *Org. Biomol. Chem.*, 2003, **1**, 2744; P. Babu, N. M. Sangeetha, P. Vijaykumar, U. Maitra, K. Rissanen and A. R. Raju, *Chem.–Eur. J.*, 2003, **9**, 1922; K. Sugiyasu, N. Fujita and S. Shinkai, *Angew. Chem., Int. Ed.*, 2004, **43**, 1229.

4 S.-I. Kawano, N. Fujita and S. Shinkai, *J. Am. Chem. Soc.*, 2004, **126**, 8592; S.-I. Kawano, N. Fujita and S. Shinkai, *Chem.–Eur. J.*, 2005, **11**, 4735 and the references cited therein.

5 Some examples recently: J. B. Beck and S. J. Rowan, *J. Am. Chem. Soc.*, 2003, **125**, 13922; N. Fujita, M. Asai, T. Yamashita and S. Shinkai, *J. Mater. Chem.*, 2004, **14**, 2106; M. Numata, K. Sugiyasu, T. Hasegawa and S. Shinkai, *Angew. Chem., Int. Ed.*, 2004, **43**, 3279.

6 A. Aggeli, M. Bell, N. Boden, J. N. Keen, P. F. Knowles, T. C. B. McLeish, M. Pitkeathly and S. E. Radford, *Nature*, 1997, **386**, 259; A. Aggeli, M. Bell, L. M. Carrick, C. W. G. Fishwick, R. Harding, P. J. Mawer, S. E. Radford, A. E. Strong and N. Boden, *J. Am. Chem. Soc.*, 2003, **125**, 9619; A. Aggeli, M. Bell, N. Boden, L. M. Carrick and A. E. Strong, *Angew. Chem., Int. Ed.*, 2003, **42**, 5603.

7 J. D. Hartgerink, E. Beniash and S. I. Stupp, *Science*, 2001, **294**, 1684; K. L. Niece, J. D. Hartgerink, J. J. J. M. Donners and S. I. Stupp, *J. Am. Chem. Soc.*, 2003, **125**, 7146; R. C. Claussen, B. M. Rabatic and S. I. Stupp, *J. Am. Chem. Soc.*, 2003, **125**, 12680.

8 F. S. Schoonbeek, J. H. van Esch, B. Wegewijs, D. B. Rep, M. P. de Haas, T. M. Klapwijk, R. M. Kellogg and B. L. Feringa, *Angew. Chem., Int. Ed.*, 1999, **38**, 1393.

9 S. van der Laan, B. L. Feringa, R. M. Kellogg and J. van Esch, *Langmuir*, 2002, **18**, 7136; S. A. Ahmed, X. Sallenave, F. Fages, G. Mieden-Gundert, W. M. Muller, U. Muller, F. Vogtle and J.-L. Pozzo, *Langmuir*, 2002, **18**, 7096; N. Koumura, M. Kudo and N. Tamaoki, *Langmuir*, 2004, **20**, 9897; S. Yagai, T. Nakajima, K. Kishikawa, S. Kohmoto, T. Karatsu and A. Kitamura, *J. Am. Chem. Soc.*, 2005, **127**, 11134.

10 M. De Loos, J. van Esch, R. M. Kellogg and B. L. Feringa, *Angew. Chem., Int. Ed.*, 2001, **40**, 613; J. J. D. de Jong, P. Ralph Hania, A. Pugžlys, L. N. Lucas, Maaike de Loos, M. Kellogg Richard, B. L. Feringa, K. Duppen and J. H. van Esch, *Angew. Chem., Int. Ed.*, 2005, **44**, 2373.

11 M. Irie, *Chem. Rev.*, 2000, **100**, 1685; B. L. Feringa ed., *Molecular Switches*, Wiley-VCH, Weinheim, 2001; V. Balzani, A. Credi and M. Venturi, *Molecular Devices and Machines: A Journey into the Nano World*, Wiley-VCH, Weinheim, 2003; H. Tian and S. J. Yang, *Chem. Soc. Rev.*, 2004, **33**, 85 and the references cited therein.

12 For examples: J. M. Endtner, F. Effenberger, A. Hartschuh and H. Port, *J. Am. Chem. Soc.*, 2000, **122**, 3037; L. N. Lucas, J. van Esch, B. L. Feringa and R. M. Kellogg, *Chem. Commun.*, 2001, 759; T. B. Norsten and N. R. Branda, *J. Am. Chem. Soc.*, 2001, **123**, 1784; H. Tian, B. Z. Chen, H. Y. Tu and K. Müllen, *Adv. Mater.*, 2002, **14**, 918; T. J. Wigglesworth and N. R. Branda, *Adv. Mater.*, 2004, **16**, 123; C. Bertarelli, A. Bianco, F. D'Amore, M. C. Gallazzi and G. Zerbi, *Adv. Funct. Mater.*, 2004, **14**, 357; K. Higashiguchi, K. Matsuda, N. Tanifuji and M. Irie, *J. Am. Chem. Soc.*, 2005, **127**, 7272; T. J. Wigglesworth, D. Sud, T. B. Norsten, V. S. Lekhi and N. R. Branda, *J. Am. Chem. Soc.*, 2005, **127**, 7272; M. Frigoli and G. H. Mehl, *Angew. Chem., Int. Ed.*, 2005, **44**, 5048.

13 J. de Jong, L. N. Lucas, R. M. Kellogg, J. van Esch and B. L. Feringa, *Science*, 2004, **304**, 278; J. J. D. de Jong, T. D. Tiemersma-Wegman, J. H. van Esch and B. L. Feringa, *J. Am. Chem. Soc.*, 2005, **127**, 13804.

14 H. Tian, T. Xu, Y. B. Zhao and K. C. Chen, *J. Chem. Soc., Perkin Trans. 2*, 1999, 545; J. Gan, H. Tian, Z. H. Wang, K. Chen, J. Hill, P. A. Lane, M. D. Rahn, A. M. Fox and D. D. C. Bradley, *J. Organomet. Chem.*, 2002, **645**, 168.

15 L. N. Lucas, J. J. D. Jong, J. H. van Esch, R. M. Kellogg and B. L. Feringa, *Eur. J. Org. Chem.*, 2003, 155; B. Qin, R. Yao, X. Zhao and H. Tian, *Org. Biomol. Chem.*, 2003, **1**, 2187.

16 M. Han and M. Hara, *J. Am. Chem. Soc.*, 2005, **127**, 10951.

17 A. P. de Silva, H. Q. N. Gunaratne, T. Gunnlaugsson, A. J. M. Huxley, C. P. McCoy and J. E. Rice, *Chem. Rev.*, 1997, **97**, 1515; T. Gunnlaugsson, P. E. Kruger, T. Clive Lee, R. Parkesh, F. M. Pfeffer and G. M. Hussey, *Tetrahedron Lett.*, 2003, **35**, 6575; Q. Chen and C. Chen, *Tetrahedron Lett.*, 2004, **45**, 6493; S. Solé and F. P. Gabbaï, *Chem. Commun.*, 2004, 1284; G. Xu and M. A. Tarr, *Chem. Commun.*, 2004, 1050; M. Vázquez, L. Fabbrizzi, A. Taglietti, R. M. Pedrido, A. M. González-Noya and M. R. Bermejo, *Angew. Chem., Int. Ed.*, 2004, **43**, 1962; J. Ren, Q. Wang, D. Qu, X. Zhao and H. Tian, *Chem. Lett.*, 2004, **33**, 974.

18 M. Boiocchi, L. D. Boca, D. E. Gómez, L. Fabbrizzi, M. Licchelli and E. Monzani, *J. Am. Chem. Soc.*, 2004, **126**, 16507; B. Liu and H. Tian, *J. Mater. Chem.*, 2005, **15**, 2681; B. Liu and H. Tian, *Chem. Lett.*, 2005, **34**, 686.

19 A. Osuka, D. Fujikane, H. Shinmori, S. Kobatake and M. Irie, *J. Org. Chem.*, 2001, **66**, 3913; Y. Yokohama, T. Goto, T. Inoue, M. Yokoyama and Y. Kurita, *Chem. Lett.*, 1988, 1049; M. Irie, K. Sakemura, M. Okinaka and K. Uchida, *J. Org. Chem.*, 1995, 8305.