

## Photo- and Proton-Dual-Responsive Fluorescence Switch Based on a Bisthiénylene-Bridged Naphthalimide Dimer and Its Application in Security Data Storage

Guiyuan Jiang,<sup>[a,b]</sup> Sheng Wang,<sup>[c]</sup> Wenfang Yuan,<sup>[a]</sup> Zhen Zhao,<sup>[b]</sup> Aijun Duan,<sup>[b]</sup> Chunming Xu,<sup>[b]</sup> Lei Jiang,<sup>[a]</sup> Yanlin Song,<sup>\*[a]</sup> and Daoben Zhu<sup>[a]</sup>

**Keywords:** Fluorescence / Photochromism / Dual-responsive / Security data storage

A photo- and proton-dual-responsive fluorescence switch based on a bisthiénylene-naphthalimide dimer was described. Security data storage based on this dual-responsive fluorescent molecular switch was proposed and demonstrated.

(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2007)

Efficient regulation of fluorescence in molecular systems has raised considerable interest in recent years because of its significant potential application in fluorescent probes,<sup>[1]</sup> sensors,<sup>[2]</sup> memory devices,<sup>[3]</sup> logic gates,<sup>[4]</sup> etc. A large number of fluorescent molecular switches with response to light,<sup>[5]</sup> temperature,<sup>[6]</sup> electrochemical potential,<sup>[7]</sup> pH,<sup>[2a,8]</sup> and metal ions<sup>[2b,9]</sup> have thus been investigated. However, most of these systems show on/off switching of fluorescence in only single-mode stimulus–response. For further practical applications, and also to enhance the multifunctionality of these systems, it is better to combine highly integrated modes into a single molecular unit that can exhibit multiresponsive modulation of luminescence.<sup>[10]</sup> As far as optoelectronic devices are concerned, a molecule that can undergo different types of transformations depending on the type of external stimulus is expected to play a significant role in multiple-mode and complex information processing.<sup>[11]</sup> For example, recent progress in information technologies has triggered an increased need for data protection and data security.<sup>[12]</sup> In the case of security needs, some very important or private information needs to be safely protected, that is, the recorded information can be firstly concealed and then secondly displayed in another mode when needed. However, with the use of traditional single-mode stimulus–response molecules as storage media, it is hard to achieve such a function. The development of multiresponsive fluo-

rescence molecules may provide a solution to this problem in which the whole process of writing, concealing, and displaying of the information can be effectively realized by comprehensively utilizing the different responsive modes of one molecule.

As a result of their good light stability, high fluorescent quantum yield, and facilely modified characteristics, naphthalimide derivatives have been widely exploited for studies related to molecular switches and light-emitting devices.<sup>[13]</sup> In our previous work, we reported a novel naphthalimide dimer tethered by a photochromic bisthiénylene bridge (BTE-NA), which was prepared by a Suzuki coupling method. On the basis of energy transfer, reversible high-degree fluorescence modulation of the naphthalimide chromophore was successfully realized by photoisomerization of the bisthiénylene subunit in polymer matrices.<sup>[14]</sup> Previous studies showed that fluorescence emission of 1,8-naphthalimide is strongly controlled by the electronic properties of the substitution group. Substitution at the 4-position of 1,8-naphthalimide with an electron-accepting group will quench the fluorescence, whereas an electron-donating group could cause strong fluorescence emission, which is a consequence of the push–pull conjugated electron system that exists over the whole molecule and leads to strong internal charge transfer.<sup>[15]</sup> Further studies showed that the push–pull electronic properties of the 4-position of 1,8-naphthalimide can be tuned by an external proton source. Thus, the molecule will show a tunable fluorescence response to both light and proton sources. In this communication, we intensively study the dual responsive property of BTE-NA and also demonstrate its application in security data storage. To the best of our knowledge, this is the first example of a security data storage device that uses a dual-responsive fluorescent molecular switch. The results will be

[a] Institute of Chemistry & Center for Molecular Science, Chinese Academy of Sciences, Beijing, 100080 China  
E-mail: ylsong@iccas.ac.cn

[b] State Key Laboratory of Heavy Oil Processing, University of Petroleum, Beijing, 102249 P. R. China

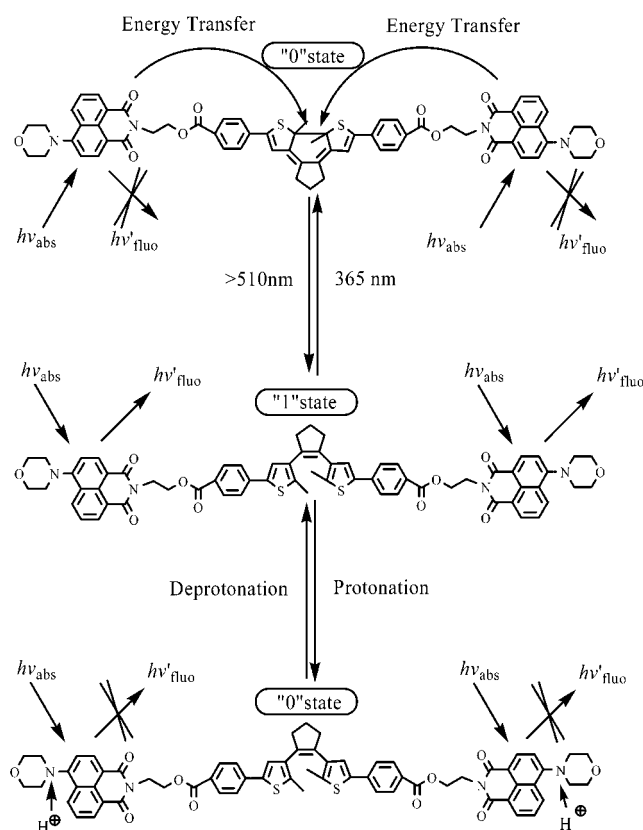
[c] Laboratory for Advanced Materials and Institute of Fine Chemicals, East China University of Science and Technology, Shanghai, 200237 P. R. China

of importance for the development of a strategy to realize security data storage by using sensitive fluorescence as a detection method.

Scheme 1 represents the structure and dual-mode fluorescence switching principles of BTE-NA. As can be seen, photochromic and proton-sensitive components coexist in the BTE-NA molecule and, in addition, the electron-donating morpholine group occupies the 4-position of the 1,8-naphthalimide functionality. With the 4-morpholine group as the donor and the naphthalimide moiety as the acceptor, this compound emits strong fluorescence that is due to the large push-pull conjugated electron system existing over the whole molecule.<sup>[15]</sup> Upon irradiation of the molecule at 365 nm, its fluorescence is efficiently quenched by energy transfer from naphthalimide to the bisthienylethene unit, and it can be recovered by visible light irradiation (Scheme 1). The fluorescence quantum yield, ring-opening, and ring-closing quantum yield of BTE-NA at the photo-stationary state were determined as 0.42 (Rhodamine B in tetrahydrofuran as a reference), 0.31, and 0.38, respectively. Meanwhile, the addition of external protons into the initial molecular system shields the unpaired electron of nitrogen in morpholine, which causes it to lose its electron-donating ability; thus, the fluorescence is quenched. Deprotonation of morpholine restores the fluorescence (Scheme 1). As different wavelengths of light can be alternately irradiated and

protonation and deprotonation can be reversibly carried out, such a dual-responsive fluorescence switch would be able to operate reversibly.

Figure 1 shows fluorescent spectra of BTE-NA in a  $\text{CH}_2\text{Cl}_2$  solution before and after irradiation. From Figure 1a, it can be seen that BTE-NA initially exhibits strong fluorescence emission. Upon irradiation with 365 nm light, the photochromic bisthienylethene unit is converted from the open- to closed-ring form and the fluorescence is efficiently quenched by intramolecular energy transfer. Back irradiation at wavelengths greater than 510 nm regenerated the open ring form and restored the original emission spectrum (Figure 1b). So, the intensity of naphthalimide fluorescence is conveniently regulated by alternate irradiation with UV and visible light. Such a photoswitch of fluorescence is dictated by the binary state, which means that the binary data stored in the two isomers can be transduced into the fluorescence signal and readout conveniently.



Scheme 1. Photo- and proton-controlled fluorescence switching principle of BTE-NA.

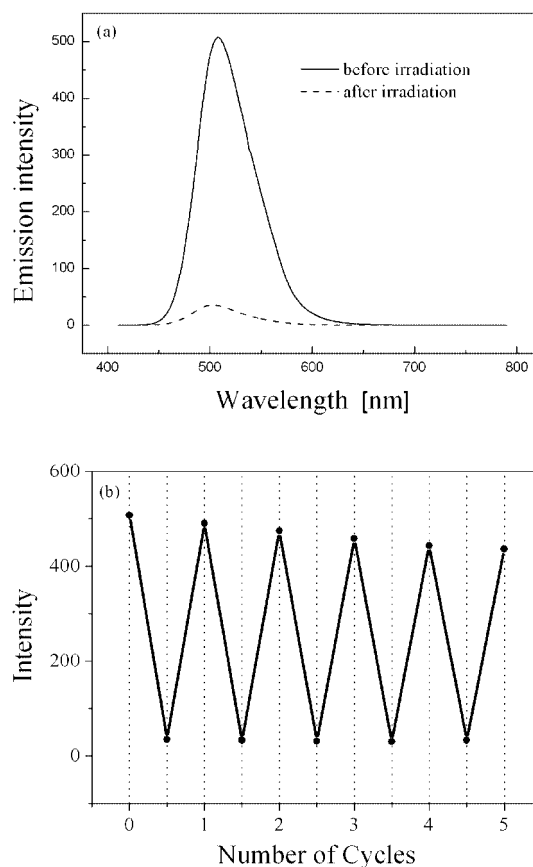


Figure 1. (a) Fluorescence spectra of BTE-NA ( $10^{-5}\text{mol L}^{-1}$ ) in  $\text{CH}_2\text{Cl}_2$  before (solid line) and after (dashed line) irradiation with 365 nm light for 5 min at room temperature. (b) The modulated emission peak intensity (excited at 400 nm) of BTE-NA ( $10^{-5}\text{mol L}^{-1}$ ) in  $\text{CH}_2\text{Cl}_2$  during alternating irradiation at 365 nm and  $>510\text{ nm}$ .

To investigate the proton-responsive properties, the emission spectra of BTE-NA by protonation/deprotonation were measured. Figure 2a shows the fluorescent spectral

change of BTE-NA with different acid concentrations. As can be seen, the addition of  $\text{CF}_3\text{COOH}$  to a solution of BTE-NA in  $\text{CH}_2\text{Cl}_2$  ( $10^{-5}\text{molL}^{-1}$ ) led to fluorescence reduction, and the fluorescent intensity decreased with increasing amounts of  $\text{CF}_3\text{COOH}$  added to the solution. When the acid concentration of the solution was increased to 131.0 mM, fluorescence was almost quenched. On this basis, treatment of the sample with an acid-equivalent amount of  $\text{NEt}_3$  can restore the initial fluorescent spectra, which is evidenced in Figure 2b. From Figure 2b, it can be seen that the initial (without acid addition) and the final spectrum (after  $\text{NEt}_3$  addition) of BTE-NA coincide, which indicates that the present system can be switched on or off in a totally reversible manner by protonation and deprotonation with  $\text{CF}_3\text{COOH}$  and  $\text{NEt}_3$ , respectively. Such a proton-controlled fluorescence emission coupled with a photochromic switch makes it possible to use BTE-NA as a security data storage device by using fluorescence as a readout method.

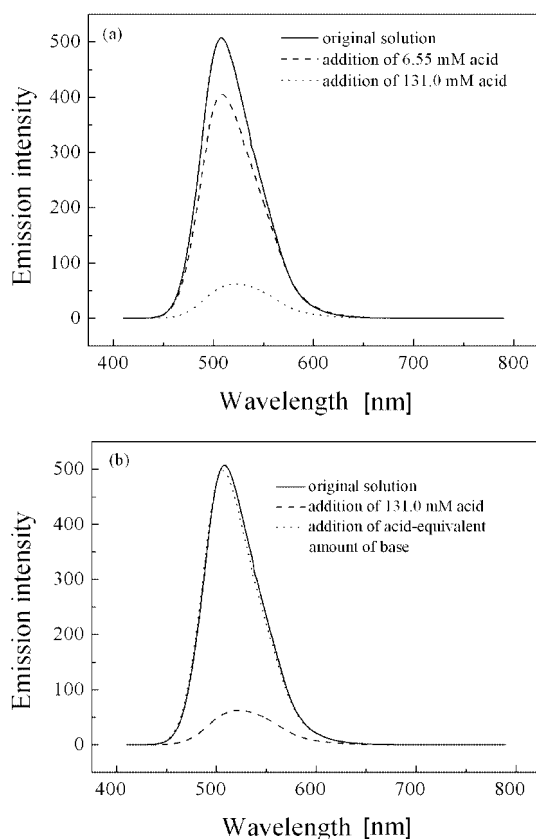


Figure 2. (a) Fluorescence spectra of BTE-NA ( $10^{-5}\text{molL}^{-1}$ ) with different acid concentrations (0–131.0 mM) in  $\text{CH}_2\text{Cl}_2$ . The acid is trifluoroacetic acid ( $\text{CF}_3\text{COOH}$ ). (b) Fluorescence spectra of BTE-NA ( $10^{-5}\text{molL}^{-1}$ ) in  $\text{CH}_2\text{Cl}_2$ . First, spectra without acid addition were measured (solid line), second,  $\text{CF}_3\text{COOH}$  (131.0 mM) was added (dashed line), and third, the acid-equivalent amount of  $\text{NEt}_3$  was added for deprotonation (dotted line).

To demonstrate the possibility of using BTE-NA for security data storage, a recording experiment was performed by utilizing a BTE-NA doped PMMA film (BTE-NA/PMMA, 1:50, by weight). The film was coated onto quartz

substrates under ambient conditions. The fluorescent image of the film was observed with a digital camera, with excitation at 440 nm. The initial fluorescent image of the film is shown in Figure 3a. A “Beijing map” photomask was then placed on the film, and the sample was irradiated with 365 nm light. After this, the mask was removed and the image was successfully transferred to the polymer film as a fluorescence pattern. Figure 3b illustrates a representative image generated by these experiments, in which the areas exposed to 365 nm light are dark and the masked areas appear luminescent. Subsequent exposure of the film to a vapor of  $\text{CF}_3\text{COOH}$  will cause the fluorescence image to disappear (Figure 3c). On treating the film with  $\text{NEt}_3$  vapor, the fluorescent information can be restored and the image reappears. Thus, the stored data can be concealed by acid treatment and recovered by deprotonation if needed. On the basis of fluorescence with the use of light and proton sources, the overall write–conceal–display process of information in security data storage was successfully demonstrated.

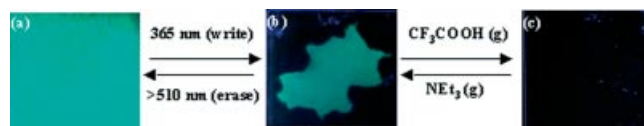


Figure 3. Fluorescence image of BTE-NA-PMMA film deposited on quartz ( $\lambda_{\text{ex}} = 440\text{ nm}$ ). (a) Fluorescence image of the film before irradiation. (b) Fluorescence image generated from 365 nm irradiation (5 min) of the film through a contact mask of Beijing map. The light regions indicate luminescence and the dark regions are nonluminescent. Back irradiation at a wavelength greater than 510 nm will erase the pattern. (c) After adding  $\text{CF}_3\text{COOH}$  vapors, the pattern disappears. The reversible process could be realized by adding  $\text{NEt}_3$  vapors, that is, the pattern reappears after  $\text{NEt}_3$  vapors are added.

In summary, a photo- and proton-dual-responsive fluorescence switch based on a bisthiénylene-naphthalimide dimer was described. Reversible dual-switch of the fluorescence emission in BTE-NA by light and proton sources was successfully realized. The dual-switch mechanism involves the photoinduced energy transfer and proton-controlled electronic properties of the compounds. On this basis, security data storage based on such a dual-responsive fluorescent molecular switch was proposed and demonstrated. This study suggests that BTE-NA and other similar fluorescent molecular switches with dual-responsive properties may have promising applications in solid-state sensors, bioanalysis, and multifunctional optoelectronic devices, and it will throw new light on the design of multifunctional materials for security recording.

## Experimental Section

Fluorescence emission spectra were recorded with a Hitachi F-4500 Fluorescence Spectrophotometer. UV irradiation was performed by using a 100 W mercury lamp (B-100AP, UVP, Inc.) operating at  $12.5\text{ mWcm}^{-2}$  for 365 nm. For visible irradiation, light from a solar simulator (CMH-250, Aodite photoelectronic Technology Ltd., Beijing) was passed through a 510 nm cutoff filter. To prepare the

BTE-NA doped PMMA film for data storage, the BTE-NA and PMMA were mixed together with a weight ratio about 1:50 in tetrahydrofuran (THF) (the concentration of BTE-NA is  $10^{-3}$  mol L $^{-1}$ ), and the thin film was coated onto quartz substrates in the ambient condition at room temperature. The fluorescent image of the film was observed with a digital camera by using appropriate filters for blue-light excitation (440 nm). To treat the film for fluorescent image by protonation/deprotonation, the vapor of CF $_3$ COOH/NEt $_3$  was fluxed for several seconds into a cell, which contained the thin film deposit on one face. Dried air was used to purge excess CF $_3$ COOH or NEt $_3$  from the system before the other was introduced. The process was monitored by watching whether the recorded fluorescence pattern disappeared/reappeared with excitation at 440 nm.

## Acknowledgments

The project is supported by the NSFC (Grant Nos. 50625312, 60601027, U0634004 and 20421101) and 973 Program (Nos. 2006CB806200, 2006CB932100). The authors thank Prof. He Tian for helpful discussion and critical reading of the manuscript.

- [1] a) B. L. Feringa, *Molecular Switches*, Wiley-VCH, Weinheim, **2001**; b) M. Irie, *Chem. Rev.* **2000**, *100*, 1685–1716; c) H. Tian, S. J. Yang, *Chem. Soc. Rev.* **2004**, *33*, 85–97.
- [2] a) G. D. Luca, G. Pollicina, A. Romeo, L. M. Scolaro, *Chem. Mater.* **2006**, *18*, 2005–2007; b) J.-S. Yang, C.-S. Lin, C.-Y. Hwang, *Org. Lett.* **2001**, *3*, 889–892.
- [3] a) G. M. Tsiygoulis, J.-M. Lehn, *Angew. Chem. Int. Engl.* **1995**, *34*, 1119–1122; b) T. B. Norsten, N. R. Branda, *J. Am. Chem. Soc.* **2001**, *123*, 1784–1785; c) H. Tian, B. Chen, H. Tu, K. Müllen, *Adv. Mater.* **2002**, *14*, 918–923; d) M. Irie, T. Fukaminato, T. Sasaki, N. Tamai, T. Kawai, *Nature* **2002**, *420*, 759–760; e) T. Fukaminato, T. Sasaki, T. Kawai, N. Tamai, M. Irie, *J. Am. Chem. Soc.* **2004**, *126*, 14843–14849; f) W. F. Yuan, L. Sun, H. H. Tang, Y. Q. Wen, G. Y. Jiang, W. H. Huang, L. Jiang, Y. L. Song, H. Tian, D. B. Zhu, *Adv. Mater.* **2005**, *17*, 156–160.
- [4] a) D. H. Qu, Q. C. Wang, H. Tian, *Angew. Chem. Int. Ed.* **2005**, *44*, 5296–5299; b) G. X. Zhang, D. Q. Zhang, Y. C. Zhou, D. B. Zhu, *J. Org. Chem.* **2006**, *71*, 3970–3972.
- [5] a) S.-J. Lim, B.-K. An, S. D. Jung, M.-A. Chung, S. Y. Park, *Angew. Chem. Int. Ed.* **2004**, *43*, 6346–6350; b) F. M. Raymo, M. Tomasulo, *Chem. Soc. Rev.* **2005**, *34*, 327–336.
- [6] S. Uchiyama, N. Kawai, A. P. de Silva, K. Iwai, *J. Am. Chem. Soc.* **2004**, *126*, 3032–3033.
- [7] a) G. X. Zhang, D. Q. Zhang, X. F. Guo, D. B. Zhu, *Org. Lett.* **2004**, *6*, 1209–1212; b) G. De Santis, L. Fabbri, M. Licchelli, N. Sardone, A. H. Velders, *Chem. Eur. J.* **1996**, *2*, 1243–1250.
- [8] a) Y. Shiraishi, Y. Tokitoh, G. Nishimura, T. Hirai, *Org. Lett.* **2005**, *7*, 2611–2614; b) S. Abad, M. Kluciar, M. A. Miranda, U. Pischel, *J. Org. Chem.* **2005**, *70*, 10565–10568; c) F. Pina, M. J. Melo, A. J. Parola, M. Maestri, V. Balzani, *Chem. Eur. J.* **1998**, *4*, 2001–2007.
- [9] a) X. R. He, H. B. Liu, Y. L. Li, S. Wang, Y. J. Li, N. Wang, J. C. Xiao, X. H. Xu, D. B. Zhu, *Adv. Mater.* **2005**, *17*, 2811–2815; b) A. P. de Silva, H. Q. N. Gunaratne, C. P. McCoy, *J. Am. Chem. Soc.* **1997**, *119*, 7891–7892.
- [10] a) F. M. Raymo, *Adv. Mater.* **2002**, *14*, 401–414; b) X. F. Guo, D. Q. Zhang, D. B. Zhu, *Adv. Mater.* **2004**, *16*, 125–130; c) W. R. Browne, M. M. Pollard, B. de Lange, A. Meetsma, B. L. Feringa, *J. Am. Chem. Soc.* **2006**, *128*, 12412–12413.
- [11] a) J. F. Zhi, R. Baba, K. Hashimoto, A. Fujishima, *J. Photochem. Photobiol., A* **1995**, *92*, 91–97; b) L. Gobbi, P. Seiler, F. Diederich, *Angew. Chem. Int. Ed.* **1999**, *38*, 674–678; c) F. Pina, A. Roque, M. J. Melo, M. Maestri, L. Belladelli, V. Balzani, *Chem. Eur. J.* **1998**, *4*, 1184–1191; d) F. Pina, M. J. Melo, P. Passaniti, M. Maestri, V. Balzani, *Eur. J. Org. Chem.* **1999**, 3199–3207.
- [12] H. H. Pham, I. Gourevich, J. K. Oh, J. E. N. Jonkman, E. Kumacheva, *Adv. Mater.* **2004**, *16*, 516–520.
- [13] a) F. Cacialli, R. H. Friend, C. M. Bouche, P. Le Barny, H. Facchetti, F. Soyer, P. J. Robin, *J. Appl. Phys.* **1998**, *83*, 2343–2356; b) H. Tian, T. Xu, Y. B. Zhao, K. C. Chen, *J. Chem. Soc., Perkin Trans. 2* **1999**, *2*, 545–549; c) J. Gan, H. Tian, Z. H. Wang, K. Chen, J. Hill, P. A. Lane, M. D. Rahn, A. M. Fox, D. D. C. Bradley, *J. Organomet. Chem.* **2002**, *645*, 168–175.
- [14] G. Y. Jiang, S. Wang, W. F. Yuan, L. Jiang, Y. L. Song, H. Tian, D. B. Zhu, *Chem. Mater.* **2006**, *18*, 235–237.
- [15] a) M. S. Alexiou, V. Tychopoulos, S. Ghorbanian, J. H. P. Tynman, R. G. Brown, P. T. Brittain, *J. Chem. Soc., Perkin Trans. 2* **1990**, 837–842; b) H. Tian, J. Gan, K. C. Chen, J. He, Q. L. Song, X. Y. Hou, *J. Mater. Chem.* **2002**, *12*, 1262–1267.

Received: December 24, 2006

Published Online: March 20, 2007