Dyes and Pigments 89 (2011) 188-192



Contents lists available at ScienceDirect

Dves and Pigments



journal homepage: www.elsevier.com/locate/dyepig

Short communication

Photoswitching of bisthienylethene using 2D- π -A type pyran-based fluorescent dye for rewritable optical storage

Sheng Wang^{a,*}, Qiaozhen Qi^{a,b}, Chengpeng Li^{a,b}, Guohua Ding^b, Sung-Hoon Kim^c

^a School of Chemistry Science & Technology, Zhanjiang Normal University, Development Center for New Materials Engineering & Technology in Universities of Guangdong, Zhanjiang 524048, PR China

^b College of Chemistry and Bioengineering, Guilin University of Technology, Guilin 541004, PR China ^c Department of Textile System Engineering, Kyungpook National University, Daegu 702-701, South Korea

ARTICLE INFO

Article history: Received 21 August 2010 Received in revised form 19 September 2010 Accepted 23 September 2010 Available online 1 October 2010

Keywords: Photochromism Bisthienvlethene Fluorescence Photoswitching Pyran-based dye Optical storage

1. Introduction

Organic photochromic materials have attracted extensive attention in reversible optical storage, where information can be written, read, and erased in binary states using different photons [1-3]. Among various types of photochromic compounds, bisthienylethene (BTE) derivatives are the most promising compounds because of their excellent fatigue resistance and thermal stability in both isomeric forms, picoseconds switching times, high photochemical quantum yields [4]. The BTE derivatives undergo reversible photocyclization reactions between colorless ring-open and colored ringclosed isomers when irradiated with the appropriate wavelength of light (Scheme 1). The open- and closed-ring isomers of the bisthienylethenes differ from each other not only in their absorption but also in various physical and chemical properties, such as luminescence, refractive indices, oxidation/reduction potentials, and chiral properties, magnetic interactions, and so on [5].

Different types of signal outputs can be utilized for memory and switching devices. Among the various photon-mode molecular

ABSTRACT

The photoswitching of photochromic bisthienylethene mixed electron donor- π -accepter (2D- π -A) type fluorescent dye with appropriate doping ratio was constructed, which showed excellent fluorescence switch "on" and "off" when the photochromic bisthienylethene undergoes ring-opening and ring-closed photoisomerization with UV and visible-light irradiation in solution and PMMA film. The erasable and rewritable photo-images on the photochromic bisthienylethene mixed $2D-\pi$ -A type fluorescent dye in PMMA were successfully demonstrated, which will provide a simple and viable method for optical data storage based photochromic fluorescent materials. These developments are crucial for fundamental research and eventual technical application for all-photo mode high-density optical data storage.

© 2010 Elsevier Ltd. All rights reserved.

memory systems, bistable photoswitching of fluorescence emission is considered to be a promising signaling mode, not only because the fluorescence signals can be readily and sensitively recognized. but also because the small number of photons required for their excitation induce few side effects to spoil the digitalized signals [6,7]. To this end, many groups have done much significant work on both fundamental and practical application with fluorescent changes as optical information storage [8–10]. However, these methods require complicated design and multistep synthetic procedures, which certainly limits their extensive applicability in optical storage devices. So, the demand to further develop the facile approach and new stable high-density optical storage material is necessary. The pyran-based fluorescent dyes with electron donor- π -accepter (D- π -A) molecular structure showed the interesting optical characteristics, which have been intensively developed for applications using as photo- (PL) and electroluminescent (EL) materials [11], fluorescent sensor and logic memory [12], and organic light-emitting device (OLED) [13,14]. Herein, we developed a simple approach to construct fluorescent photoswitching of photochromic bisthienylethene compound (BTE-Br) mixed a 2D- π -A pyran-based fluorescent dye (DPC) for rewritable optical storage (as shown in Scheme 2). The absorption of ringclosing isomer of BTE-Br can well match with the fluorescence

Corresponding author. Tel.: +86 759 318 2515; fax: +86 759 318 3510. E-mail address: wangsheng@zhjnc.edu.cn (S. Wang).

^{0143-7208/\$ -} see front matter © 2010 Elsevier Ltd. All rights reserved. doi:10.1016/j.dyepig.2010.09.010



Scheme 1. Photochromism of bisthienylethene (BTE).

emission of DPC dye. The DPC fluorescent dye, as an excellent fluorescent dye, is selected to characterize a fluorescent signal. When these two components are mixed in a polymer film, the DPC fluorescent dye acts as an energy donor and the close-form BTE-Br is an energy acceptor. ON/OFF switching of fluorescence can be induced by intermolecular energy transfer from the fluorophore to the photochromic unit under light stimulation.

2. Experiment

2.1. Materials and instruments

Melting points were determined using a Beijing Tech X-4 with a digital thermometer and are uncorrected. UV-visible absorption spectra were measured on a Shimadzu UV-2550 spectrophotometer. Fluorescence spectra were measured on a PerkinElmer LS-55 Fluorescence spectrophotometer. Mass spectra were recorded on a Shimadzu OP1000 spectrometer using electron energy of 70 eV and the direct probe EI method. ¹H NMR spectra were recorded using a Varian Inova 400 MHz FT-NMR spectrometer with TMS as internal standard. Most of chemicals were purchased from Aldrich Chemical Co. and TCI. Solvents were purified by normal procedures and handled under moisture free atmosphere. The other materials were commercial products and were used without further purification. Polymethyl methacrylate (PMMA; $M_w = 10,000$) was used as the polymer matrix. 11.4 mg BTE-Br and 4.8 mg DPC dye were dissolved in a PMMA-cyclohexanone solution (10%, w/w). The BTE-Br/DPC/PMMA thin films were prepared by spin-coating (2000 rpm) the cyclohexanone solution onto a glass substrate



Scheme 2. The chemical structures and photoswitching behavior of photochromic BTE-Br and DPC fluorescent dye by irradiation with 254 nm and more than 540 nm, respectively (excitation: 405 nm).



Scheme 3. The synthetic process of photochromic BTE-Br and DPC fluorescent dye.

 $(7.5 \times 2.5 \text{ cm}, 1 \text{ mm thick})$. A UV (254 nm, 1.5 mW cm⁻²) lamp of was used as a UV-light source, and a xenon lamp ($\lambda > 540 \text{ nm}$, 300 W) was a visible-light source through a color filter.

2.2. Synthesis

The photochromic bisthienylethene compound and $2D-\pi$ -A pyran-based dye were 1,2-bis [5'-(4'-bromophenyl)-2'-methylthien-3'-yl] cyclopentene (BTE-Br) and allyl 2-(2,6-bis(-4-(dimethylamino) styryl)-4H-pyran-4-ylidene)-2-cyanoacetate (DPC). BTE-Br and DPC were synthesized according to previously reported method for BTE-Br [15] and DPC [16], and confirmed by ¹H NMR and MS The synthesis procedure for BTE-Br and DPC fluorescent dye is illustrated in Scheme 3.

2.3. Synthesis of 1,2-bis [5'-(4'-bromophenyl)-2'-methylthien-3'-yl] cyclopentene (BTE-Br)

1,2-Bis(5'-chloro-2'-methylthien-3'-yl)cyclopentene (1.00 g, 3.04 mmol) was dissolved in anhydrous THF (12 mL) and n-BuLi (5.0 mL of 1.6 M solution in hexane, 8 mmol) was added under nitrogen atmosphere at room temperature using a syringe. This solution was stirred for 30 min at room temperature, then B (n-BuO)₃ (2.3 mL, 8.3 mmol) was added and went on stirring for 1 h, then used in the Suzuki cross-coupling reaction (1). Then 1,4-dibromobenzene (3.40 g, 14.4 mmol) was dissolved in THF (12 mL) and [Pd(PPh_3)_4] (0.40 g, 0.3 mmol), aqueous K₂CO₃ (17 mL, 2 M) and 6 drops of ethylene glycol was added, the resulting solution



Fig. 1. Absorption spectral changes of BTE-Br in CH_2Cl_2 ($1.0 \times 10^{-5} \text{ mol } L^{-1}$) under different irradiation time by light of 365 nm at room temperature.



Fig. 2. Absorption and fluorescence spectra of DPC dye in CH_2Cl_2 at room temperature (3 \times 10⁻⁵ mol L^{-1} , excitation: 405 nm).

was heated and reflux at a temperature of $60 \,^{\circ}$ C and then the solution of 1 was added dropwise via a syringe. Subsequently the mixture was refluxed for overnight and cooled to room temperature. And diethyl ether 50 mL and water 50 mL were added. The



Fig. 3. Absorption (a) and fluorescent emission (b) changes of BTE-Br blended with DPC dye with 254 nm light irradiation at different irradiation time in CH₂Cl₂ at room temperature (BTE: DPC dye = 2:1 equiv; 3×10^{-5} mol L⁻¹ excitation: 405 nm).

organic layer was separated and dried. After evaporation the compound was purified by column chromatography (SiO₂, hexane) gave a yellowish solid (1.30 g, 76%). mass (*m*/*z*) 567(M⁺); ¹H NMR (400 MHz, CDCl₃): δ = 1.97 (s, 6 H), 2.02–2.10 (m, 2H), 2.81 (t, *J* = 7.5 Hz, 4H), 6.98 (s, 2H), 7.32 (d, *J* = 8.4 Hz, 4H), 7.42 (d, *J* = 8.4 Hz, 4H).

2.4. Synthesis of allyl 2-(2,6-bis(-4-(dimethylamino) styryl)-4H-pyran-4-ylidene)-2-cyanoacetate (DPC)

A solution of allyl 2-cyano-2-(2,6-dimethyl-4H-pyran-4-ylidene) acetate (0.3 g, 1.35 mmol), 4-(dimethylamino) benzaldehyde (0.2 g, 2.7 mmol), and piperidine (0.14 mL) in n-propane (3 mL) was refluxed for 24 h using a Dean–Stark trap. The reaction solution was cooled to room temperature, and the solid product was isolated and washed well with n-propanol and dried. The crude product was recrystallized from methanol several times. Yield: 30%; mass (*m*/*z*) 493 (M⁺). ¹H NMR (400 MHz, CDCl₃): δ 3.04 (s, 12H), 4.70 (d, 2H), 5.26 (d, 1H), 5.43 (d, 1H), 5.99 (m, 1H), 6.52 (d, 1H), 6.54 (d, 1H), 6.65 (s, 1H), 6.71 (d, 4H), 7.38 (s, 2H), 7.42 (s, 4H), 7.97 (s, 1H).



Fig. 4. (a) Absorption and (b) fluorescent emission changes of BTE-Br blended with DPC dye in PMMA film with 254 nm light irradiation at initial state and photostability state (BTE: DPC dye = 1:2 equiv; excitation: 405 nm). The inset shows fluorescent emission monitoring of cyclical on and off (by alternative irradiation with UV and visible light) photoswitching of BTE-Br blended with DPC dye (at $\lambda_{em} = 605$ nm).

3. Results and discussion

3.1. Photochromic properties of BTE-Br in solution

The BTE-Br could readily dissolve in common organic solvents, such as chloroform, methylene chloride, THF toluene and cyclohexanone and showed typical absorption changes due to the photochromic reaction [17]. Fig. 1 shows the absorption spectral change of BTE in CH₂Cl₂ by irradiation with UV light. Upon irradiation with 254 nm light, the colorless solution of open-ring BTE-Br isomer turned to be purple, in which characteristic absorption maxima were observed at 366 nm and 550 nm arising from the closed ring form of bisthienylethene. Upon visible ($\lambda > 540$ nm) light irradiation, the purple color disappeared indicated returned to the initial open-ring isomer. The coloration and de coloration could be repeated more than 10 times.

3.2. Absorption and fluorescence properties of DPC fluorescent dye

The absorption and fluorescence emission properties of DPC fluorescent dye were also investigated by UV–Vis absorption and fluorescence emission spectrum method. DPC dye showed the typical intrinsic intramolecular charge transfer (ICT) character. Fig. 2 shows the absorption and fluorescent emission spectra of DPC dye in methylene chloride solution at room temperature. The absorption spectrum of DPC dye exhibited an absorption maximum at approximately 480 nm. The typical fluorescent emission peaks are observed at 610 nm by excitation with 405 nm light. In addition, the absorption and fluorescent emission spectra of DPC dye were not observed significant changes with UV or visible-light irradiation, which indicated that the DPC dye is photostable.

3.3. Fluorescence modulation switching of BTE-Br with DPC fluorescent dye

In generally, the fluorescent switch can be constructed by blending with fluorescent chromophore and photochromic compounds according to the appropriate ratio [18,19]. The absorption and fluorescent changes of BTE-Br blended with DPC fluorescent dye in the ration of 1:2 equivalent in CH₂Cl₂ were investigated with visible-light irradiation. Fig. 3a showed the absorption spectral changes of BTE-Br blended with DPC fluorescent dye in the ration of 1:2 equiv by irradiation with 254 nm light. The mixture solution showed the DPC fluorescent dve maximum absorption at 480 nm. Upon irradiation with 254 nm light, the orange solution turned to be purple, in which characteristic absorption maxima were observed at 366 nm and 530 nm arising from the closed ring form of bisthienylethene. Upon visible $(\lambda > 540 \text{ nm})$ light irradiation, the purple color returned to the initial orange solution. Corresponding to the absorption spectral changes, the fluorescent is also changed as shown in Fig. 3b. The mixture solution show the DPC fluorescent dye maximum fluorescent emission at 610 nm with 405 nm light excitation. Upon irradiation with 254 nm light, the fluorescent intensity at around 610 nm is gradually decreased and occurred red-shift and almost wholly quenched with UV irradiation light prolong. The possible explanation for the fluorescence quench and red-shift is due to an increase in intermolecular fluorescent energy transfer between the DPC fluorescent dye and the BTE-Br closed-ring isomers [20-22]. Upon visible (λ > 540 nm) light irradiation, the fluorescent intensity at 610 nm is recovered the initial state, which can be constructed the fluorescent switch by photochromic BTE-Br controlling the DPC fluorescent dye.

3.4. Photochromic BTE-Br with DPC fluorescent dye for rewritable optical storage

The photoswitching performances of photochromic BTE-Br with DPC fluorescent dye in PMMA film were also investigated. Fig. 4a showed the absorption spectra changes of photochromic BTE-Br with DPC fluorescent dye in initial state and photostability state in PMMA film, respectively. Upon irradiation with 254 nm light, the orange film turned to be purple, which maxima absorption shifted from 480 nm to 530 nm arising from the closed ring form of bisthienylethene. Upon visible ($\lambda > 540$ nm) light irradiation, the purple color returned to the initial orange. Corresponding to the



Fig. 5. (a) Principle scheme of the optical data recording on BTE-Br blended with DPC dye in PMMA film. (b) The process of optical storage images (right: optical; left: florescence) of BTE-Br blended with DPC dye in PMMA film. A and C: erasing; B and D: writing. Photo-rewritable imaging on BTE-Br blended with DPC dye in PMMA film by using UV light ($\lambda = 254$ nm) and visible light ($\lambda > 540$ nm). The purple regions represent the writing optical data parts irradiated with UV light.

absorption spectral changes, the fluorescent is also changed as shown in Fig. 4b. The BTE-Br/DPC/PMMA thin film showed maximum fluorescent emission at 600 nm with 405 nm light excitation, which originate the maximum fluorescent emission of DPC dye. Upon irradiation with 254 nm light, the fluorescent intensity at 600 nm is gradually decreased and almost wholly quenched with irradiation light prolong. Upon visible ($\lambda > 540$ nm) light irradiation, the fluorescent intensity at 610 nm is recovered the initial state. This indicated the fluorescence emission of DPC dye can be also controlled by BTE-Br in PMMA solid film, which can be constructed the fluorescent photoswitching. The Fig. 4b inset showed the modulated fluorescent emission peak intensity at 600 nm of the film during alternating irradiation at 254 nm and more than 540 nm with 405 nm light excitation. The fluorescent "off" and "on" could be repeated more than 10 times.

The BTE-Br/DPC/PMMA film is suitable material for optical information recording. We demonstrated a possible procedure for data recording and erasing in Fig. 5a. Upon UV-light irradiation through the mask, the optical data were recorded on BTE-Br/DPC/ PMMA film irradiation region. When irradiation with visible-light on irradiation region, the optical data were erased. Fig. 5b showed the practical optical and fluorescent images of erasable and rewritable photoimaging on BTE-Br/DPC/PMMA film by patterned illumination with photomasks. When the A sate of BTE-Br/DPC/ PMMA was irradiated with 254 nm UV light for 1 min and arrived the photostable state, the word 'ZHJNU' (Zhanjiang Normal University abbreviated) was recorded as a first image in shown B state of Fig. 5b, which was subsequently erased with visible light. the recorded information is almost wholly disappeared for 5 min. which was followed by the recording of a second image, the dot in shown D state of Fig. 5b. The cycles of writing and erasing were repeated more than 10 times. We can find that the BTE-Br/DPC/ PMMA film was irradiated with 405 nm readout light for the fluorescence excitation of the DPC dye, strong fluorescence in the openring-form of BTE-Br state as well as the remarkably quenched fluorescence by the closed ring form of BTE-Br state under 254 nm irradiation condition could be bistably and nondestructively under repeated excitation. This successful demonstration of rewritable photoimage suggests the potential application of BTE-Br/DPC/ PMMA to rewritable optical memory media or imaging processes.

4. Conclusion

In conclusion, we construct a fluorescent switch which is consisted of photochromic BTE-Br blending with DPC fluorescent dye. It showed excellent fluorescence switching function in solution and doped in PMMA films with UV and visible-light irradiation, respectively. A facile approach to realizing erasable and rewritable optical storage was successfully demonstrated by using photochromic BTE-Br blending with DPC fluorescent dye in PMMA film. The fluorescence images of recording marks on BTE-Br/DPC/PMMA film exhibit both high brightness and contrast, which provides much better resolution and sensitivity. This result presents a feasible strategy for improving the ON/OFF ratio in readout of the stored information and will be of great significance for developing high-contrast optical storage devices.

Acknowledgements

This work was supported by National Natural Science Foundation of China (No. 20802065). The project sponsored by the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry (No. 2009-1001). This research was also supported by the Doctoral special funds of Zhanjiang Normal University (No. ZL0803).

References

- [1] Feringa BL, Molecular switches. Weinheim, Germany: Wiley-VCH; 2001.
- [2] Irie M. Photoreactive materials for ultrahigh-density optical memory. Amsterdam: Elsevier; 1994.
- [3] Tian H, Yang SJ. Recent progresses on diarylethene based photochromic switches. Chem Soc Rev 2004;33:85–97.
- [4] Tian H, Wang S. Photochromic bisthienylethene as multi-function switches. Chem Commun 2007;8:781–92.
- [5] Irie M. Diarylethenes for memories and switches. Chem Rev 2000;100 (5):1685-716.
- [6] Li H, Wang JX, Lin H, Xu L, Xu W, Wang RM, et al. Luminescence modulation of ordered upconversion nanopatterns by a photochromic diarylethene: rewritable optical storage with nondestructive readout. Adv Mater 2010;22:633–7.
- [7] Lim SJ, An BK, Jung SD, Chung MA, Park SY. Photoswitchable organic nanoparticles and a polymer film employing multifunctional molecules with enhanced fluorescence emission and bistable photochromism. Angew Chem Int Ed 2004;43(46):6346–50.
- [8] Jiang G, Wang S, Yuan W, Jiang L, Song Y, Tian H, et al. Highly fluorescent contrast for rewritable optical storage based on photochromic bisthienylethene-bridged naphthalimide dimer. Chem Mater 2006;18(2):235–7.
- [9] Tian H, Chen BZ, Tu HY, Müllen K. Novel bisthienylethene-based photochromic tetraazaporphyrin with photoregulating luminescence. Adv Mater 2002;14(12):918–23.
- [10] Berberich M, Krause AM, Orlandi M, Scandola F, Würthner F. Toward fluorescent memories with nondestructive readout: photoswitching of fluorescence by intramolecular electron transfer in a diaryl ethene–perylene bisimide photochromic system. Angew Chem Int Ed 2008;47(35):6616–9.
- [11] Moylan CR, Ermer S, Lovejoy SM, McComb IH, Leung DS, Wortmann R, et al. (Dicyanomethylene)pyran derivatives with C2v symmetry: an unusual class of nonlinear optical chromophores. J Am Chem Soc 1996;118:12950–5.
- [12] Guo ZQ, Zhu WH, Shen LJ, Tian H. A fluorophore capable of crossword puzzles and logic memory. Angew Chem Int Ed 2007;46:5549–649.
- [13] Kwak G, Wang S, Choi MS, Kim H, Choi KH, Han YS, et al. 2D-π-A type pyranbased dye derivatives: their syntheses and photophysical properties in various solvents. Dyes Pigments 2008;78:25–33.
- [14] Yao YS, Xiao J, Wang XS, Deng ZB, Zhang BW. Starburst DCM-type red-lightemitting materials for electroluminescence applications. Adv Funct Mater 2006;16:709–18.
- [15] de Jong JJD, Lucas LN, Hania R, Pugzlys A, Kellogg RM, Feringa BL, et al. Photochromic properties of perhydro- and perfluorodithienylcyclopentene molecular switches. Eur J Org Chem; 2003:1887–93.
- [16] Kwak G, Kim HY, Kang IK, Kim SH. Charge transfer dye in various polymers with different polarity: synthesis, photophysical properties, and unusual aggregation-induced fluorescence changes. Macromolecules 2009;42: 1733–8.
- [17] Lucas LN, Jong JJD, Van Esch JH, Kellog RM, Ferings BL. Synthesis of dithienylcyclopentene optical molecular switches. Eur J Org Chem 2003;1:155–66.
- [18] Chen Y, Xie N. Modulation of a fluorescent switch based on a controllable photochromic diarylethene shutter. J Mater Chem 2005;15:3229–32.
- [19] Corredor CC, Huang ZL, Belfield KD. Two-photon 3D optical data storage via fluorescence modulation of an efficient fluorene dye by a photochromic diarylethene. Adv Mater 2006;18:2910–4.
- [20] Li H, Wang JX, Lin H, Xu L, Xu W, Wang RM, et al. Amplification of fluorescent contrast by photonic crystals in optical storage. Adv Mater 2010;22:1237–41.
- [21] Zhang JJ, Tan WJ, Meng XL, Tian H. Soft mimic gear-shift with a multi-stimulus modified diarylethene. J Mater Chem 2009;19:5726–9.
- [22] Zhu WH, Meng XL, Yang YH, Zhang Q, Xie YS, Tian H. Bisthienylethene containing a benzothiadiazole unit as a bridge: photochromic performance dependence on substitution position. Chem Eur J 2010;16:899–906.