Available online at www.sciencedirect.com

Dyes and Pigments 73 (2007) 118–120

www.elsevier.com/locate/dyepig

Effective non-destructive readout of photochromic bisthienylethene–phthalocyanine hybrid

Qianfu Luo [a,*], He Tian [b], Bingzhi Chen [b], Wei Huang [a,*]

[a] *Laboratory of Advanced Materials of Fudan University, Shanghai 200433, PR China*
[b] *Institute of Fine Chemicals, East China University of Science and Technology, Shanghai 200237, PR China*

Received 27 June 2005; received in revised form 11 July 2005; accepted 31 October 2005
Available online 5 January 2006

Abstract

The reversible changes of UV–vis absorbance (Q-band) during photochromic process were selected to achieve non-destructive readout in the paper. The light sources for "read" and "write" could be gotten easily from the light practical application at present. The photochromism in the net film was also observed, which would facilitate practical use of BTE–PC hybrid.

Keywords: Photochromic; Non-destructive readout; Bisthienylethene; Phthalocyanine; Absorption

1. Introduction

In order to meet the demand for high storage densities and fast data processing tares, future molecular memory systems will be required to operate exclusively on photon-mode effects, where binary data can be written, non-destructively read out, and erased using photons of different colors. Organic photochromic materials have been cited as promising candidates because each state of the photochromes displays unique spectroscopic properties and they can, therefore, represent each of the two binary states [1]. Among the photochromic compounds, bisthienylethenes (BTEs) are regarded as the best candidate, because of the thermal stability of both isomers and their fatigue resistance [2–10].

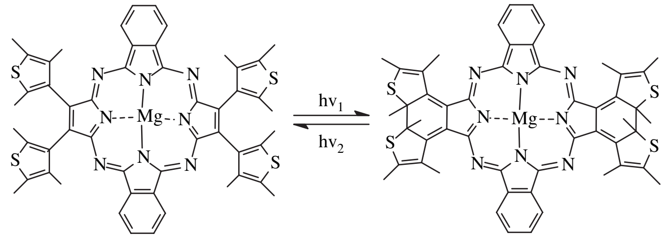
For practical applications to optical memory, non-destructive readout capability is indispensable. Usually, recording the differences in their UV–vis absorption spectra was not considered as a useful mechanism to read the stored information because the absorption bands of BTEs, which are unique to each isomer, are the same ones that induce the ring-opening and ring-closing reactions [11]. This problem can be circumvented by developing photochromic systems that employ gated mechanisms [12] or optical property changes which coincide with the photochromic transformation, such as, infrared light [13], refractive index [14], optical rotation [15], luminescence [11,16], etc. However, we could also resolve this problem by designing some new appropriate molecules, whose UV–vis absorption bands corresponding to the "write", "erase" and "read" processes are adequately distant from each other so that each state can avoid any interconversion when we monitor the changes in absorption for non-destructive readout. It is to say, if this compound produces one narrow absorption band for readout that does not overlap with the absorption bands where photochromic reaction is excited and the two isomers display varying absorption spectra in the readout region, we can directly use UV–vis absorption as a viable alternative for effective non-destructive readout. After all, UV–vis spectroscopy is by far the most common and convenient detection method used today.

We have designed and synthesized a novel family of photochromic BTE–phthalocyanines and phthalocyanine hybrids [9] in recent years. We found that there was an appropriate compound (**1**) which could be selected to achieve non-destructive readout capability by monitoring the changes (UV–vis absorbance) of Q-band during photochromic process. And the light

---

[*] Corresponding authors. Tel.: +86 21 556 64 184.
E-mail address: iamlqf@fudan.edu.cn (Q. Luo).

0143-7208/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2005.10.017



1a **1b**

Scheme 1. The photo-cyclization and back conversion process of compound **1**.

sources for "read" and "write" could be gotten easily from the light practical application at present (CD-ROM and DVD-ROM).

2. Experimental

The compound **1** [17] (BTE–PC) studied in this paper (shown in Scheme 1), namely, 2,3,14,15-tetra (2′,4′,5′-trimethyl-3′-thienyl) phthalocyanine Mg(II), was conveniently prepared by Mg(II) template-directed cyclization of maleonitrile [18] and 1,2-dicyanobenzene. The absorption spectra of **1** are shown in Fig. 1, and the data are listed in Table 1. Gouterman's highly simplified four-orbital model for porphyrin macrocycles provides a qualitative description of the optical spectra of compound **1**. The D_{2h} symmetric compound **1**'s splitting of the LUMO by the different substituents on the PC core leads to a large splitting of the Q-band (93 nm). Such a large splitting provides a very important narrow absorption band at around 609 nm which is far from the absorption bands which were used for erase (365 nm) and write (730 nm) to avoid any interconversion of the two photochromic states. So the higher-energy splitted Q-band, namely, 609 nm peak can be selectively used as readout region as long as changes in absorption coefficient at 609 nm coincide with the photochromic transformation.

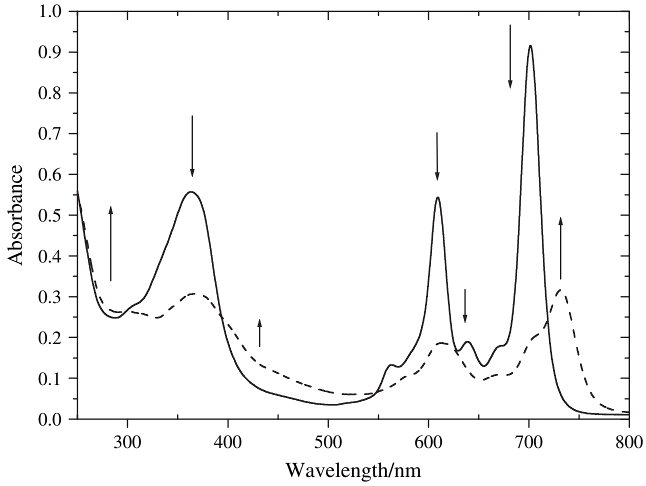


Fig. 1. Absorption spectra of compound **1** in $CHCl_3$ and the change in absorption of the compound under irradiation by light of 365 nm.

Table 1
The data of absorption (λ_{max}^{Ab}/nm) of the compounds **1** in $CHCl_3$ and in net film

Compound	**1** (In $CHCl_3$)	**1** (In net film)
λ_{max}^{Ab} (open)	702, 609, 564, 362	716, 619, 585, 386
λ_{max}^{Ab} (closed)	730, 612, 365	759, 621, 385

3. Results and discussion

The photochromic properties of compound **1** in $CHCl_3$ have been studied (shown in Fig. 1 and Scheme 1). Before irradiation with UV light, compound **1a** (open form) has the absorption band at splitting Q-band (702 nm and 609 nm) and B-band (362 nm). Upon irradiation to the solution of **1** with 365 nm light, the absorption bands, including 609 nm, gradually decreased and new absorption bands with a maximum at around 730 nm appeared due to the transformation of **1a** to the closed-form **1b** by photocyclization. The color of **1** in $CHCl_3$ was also changed from blue to green. The backward ring-opening reaction of **1b** regenerating compound **1a** took place on irradiation with the light of 730 nm.

The absorbance of **1a** at 609 nm in $CHCl_3$ is 5.4×10^{-1} before irradiation with UV light. When the solution of **1a** in $CHCl_3$ irradiated was by 365 nm light, the peak at 609 nm gradually decreased and finally measured less than 2×10^{-1} when the solution reached photo-stationary state. That means that the closed-form **1b** absorbs 609 nm light, relatively weakly. The back reaction irradiation at 730 nm light regenerates the open-form **1a** and restores the absorption coefficient at 609 nm. The significant difference (absorbance) between the open-form **1a** and closed-form **1b** matches the second condition that the two isomers display varying absorption spectra which represent each of the two binary states. Fig. 2 shows 30 cycles of write/erase by monitoring the absorbance at 609 nm, which proved that the absorbance at 609 nm could be conveniently regulated by 365 nm and 730 nm light.

Compound **1** was also found to exhibit photochromism in solid state in net film, although the quantum yields are relatively low (less than 0.1). The open-form of **1** in net film

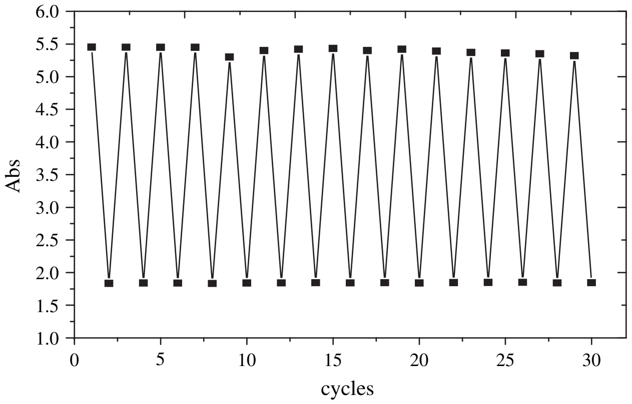


Fig. 2. The absorbance(×10) of compound **1** (in $CHCl_3$) at 609 nm modulated by the irradiation at 365 nm and 731 nm.

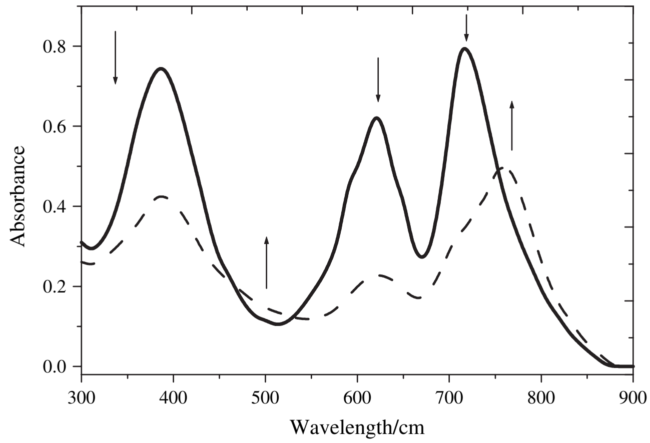


Fig. 3. Absorption spectra of compound **1** in net film (solid line) and the change in absorption under irradiation by light of 365 nm (broken line).

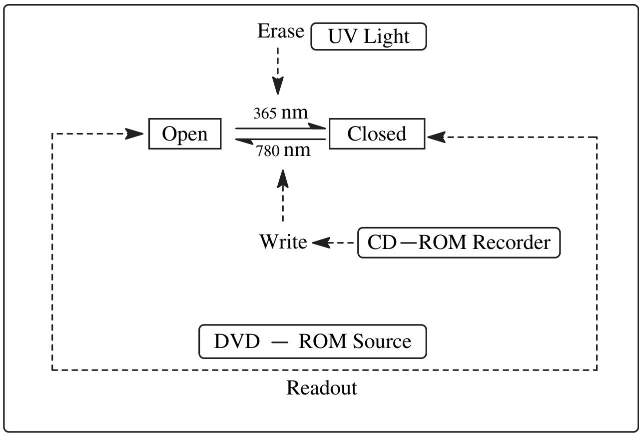


Fig. 4. The schematic diagram of the process for *write, read* and *erase*.

has two Q absorption bands appearing at 716 nm and 619 nm (red shift than in $CHCl_3$). Upon irradiation with 365 nm light, the absorption of two Q-bands gradually decreased, and a new absorption band with a maximum at around 759 nm appeared (shown in Fig. 3). The backconversion occurs on irradiation of **1b** at 759 nm. From this, we can see that, in solid film, the absorption band of 619 nm (used as non-destructive readout) is farther from the absorption bands which were used for erase (365 nm) and write (759 nm) than that in $CHCl_3$. So, it is more effective to achieve non-destructive readout in net film than in $CHCl_3$ by detecting UV−vis absorption of this compound. Moreover, the light of 759 nm is close to the excitation source of CD-ROM, and the 619 nm light can use the DVD-ROM source, which approximate to practicality (as delineated in Fig. 4).

To confirm that the band around 619 nm is inactive for any direction of photochromic reaction, the prolonged irradiation (2 h) of solution **1a** and the photo-stationary **1b** in net film with 619 nm light results in no observable spectral changes as monitored by absorption. Both open-form **1a** and closed-form **1b** are, conveniently, photochemically inactive in this spectral region and irradiation with light at this wavelength has little effect on the photochemical interconversion of **1a** and **1b** in either direction. This clearly demonstrates that this system is non-destructive under these conditions and matches the necessary requirements to function as a non-destructive read/write/erase system.

In summary, upon alternative irradiation with 365 nm and 759 nm light, compound **1** was found to exhibit a remarkable change at around 619 nm, which confirmed that it is photochromic reaction inactive for both open form and closed form of compound **1**. To this kind of compound (**1a**), detecting the ultraviolet−visible (UV−vis) spectral change (in a spectral region where both the open and closed forms of the photochrome are transparent) was an effective and convenient approach to achieve non-destructive readout capability.

References

[1] Feringa BL. Molecular switches. Weinheim: Wiley-VCH; 2001.
[2] Irie M. Chem Rev 2000;100:1685.
[3] Tian H, Yang SJ. Chem Soc Rev 2004;32(2):85−97.
[4] Kobatake S, Mastsumoto Y, Irie M. Angew Chem 2005;117:2−4.
[5] Kim E, Choi YK, Lee MH. Macromolecules 1998;32:4855−60.
[6] Pu SZ, Zhang FS, Sun F, Wang RJ, Zhou XH, Chan SK. Tetrahedron Lett 2003;44:1011−4.
[7] Chen Y, Zeng DX. J Org Chem 2004;69:5037−40.
[8] Lucas LN, Esch J, Kellogg RM, Feringa BL. Chem Commun 2001:2313−4.
[9] Zhang P, Buncel E, Lemiexu RP. Adv Mater 2005;17:567−71.
[10] Hossain MK, Takeshita M, Yamato T. Tetrahedron Lett 2005;46:431−3.
[11] Norsten TB, Branda NR. Adv Mater 2001;13:347.
[12] (a) Irie M, Eriguchi T, Takata T, Uchida K. Tetrahedron 1997;53:214;
(b) Kawai SH, Glate SL, Lehn JM. Chem Eur J 1995;1:285.
[13] Uchida K, Saito M, Murakami A, Kobayashi T, Nakamura S, Irie M. Chem Eur J 2005;11:534.
[14] Tanio N, Irie M. Jpn J Appl Phys 1994;33:1550.
[15] (a) Feringa BL, Delden RA, Koumura N, Geertsema EM. Chem Rev 2000;100:1789;
(b) Agati G, McDonagh AF. J Am Chem Soc 1995;117:4425.
[16] (a) Norsten TB, Branda NR. J Am Chem Soc 2001;123:1784;
(b) Fernandez-Acebes A, Lehn JM. Chem Eur J 1999;5:3285.
[17] (a) Tian H, Chen BZ, Tu HY, Müllen K. Adv Mater 2002;14:918;
(b) Luo QF, Chen BZ, Wang MZ, Tian H. Adv Funct Mater 2003;13:233.
[18] Irie M, Mohri M. J Org Chem 1988;53:803.