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Short communication

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

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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-π-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.

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 ring-closed 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 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 ring-closing isomer of BTE-Br can well match with the fluorescence

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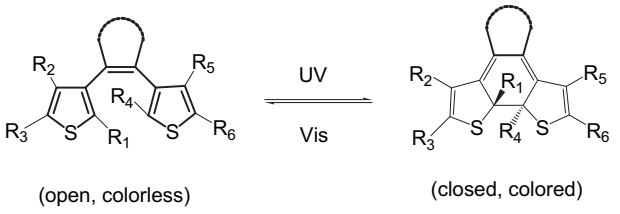


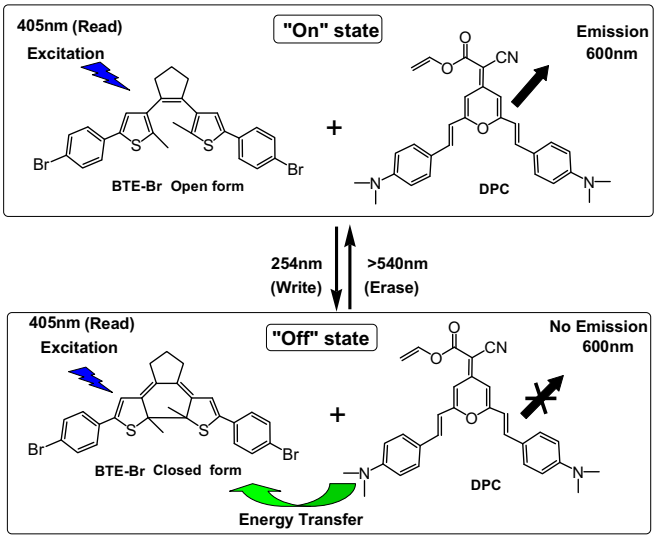
Scheme 1. Photochromism of bisthienylethene (BTE).

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.

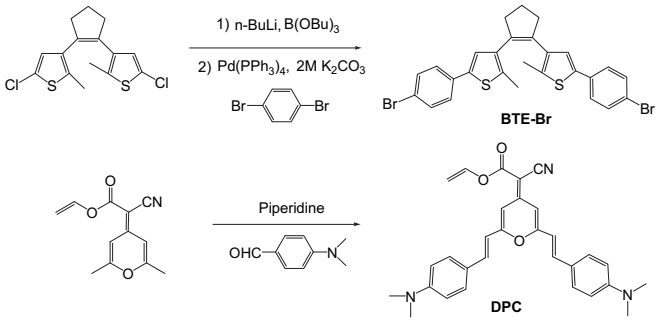
2. Experiment

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 QP1000 spectrometer using electron energy of 70 eV and the direct probe EI method. ^{1}H 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 × 2.5 cm, 1 mm thick). A UV (254 nm, 1.5 mW cm^{-2}) lamp of was used as a UV-light source, and a xenon lamp ($\lambda > 540$ nm, 300 W) was a visible-light source through a color filter.

2.2. Synthesis

The photochromic bisthienylethene compound and 2D-π-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 ^{1}H 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 K_2CO_3 (17 mL, 2 M) and 6 drops of ethylene glycol was added, the resulting solution

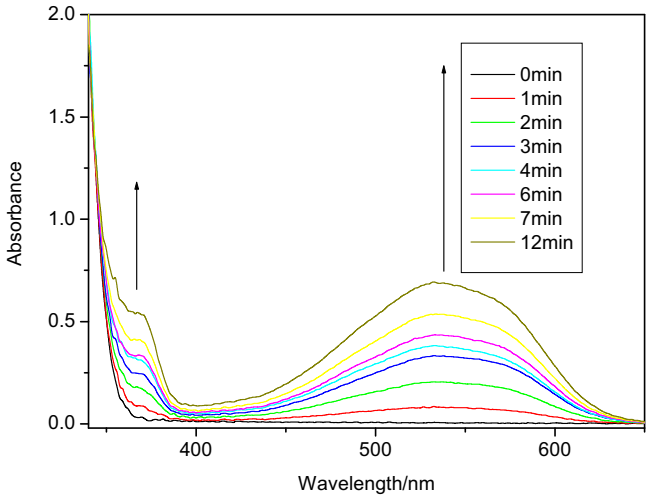


Fig. 1. Absorption spectral changes of BTE-Br in CH_2Cl_2 (1.0×10^{-5} mol L^{-1}) under different irradiation time by light of 365 nm at room temperature.