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## Communications

### Highly Fluorescent Contrast for Rewritable Optical Storage Based on Photochromic Bisthienylethene-Bridged Naphthalimide Dimer

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Photonic devices that incorporate photochromic molecules represent the future of digital optical storage where the recording of information is all photon-mode recording method that allows the read, write, and erase functions to be controlled by light energy.<sup>1,2</sup> Different types of signal outputs by photoregulating physicochemical properties of photochromic compounds can be utilized for optical storage, including refractive index,<sup>3</sup> luminescence,<sup>4</sup> electric conductance,<sup>5</sup> optical rotation,<sup>6</sup> and magnetic interactions.<sup>7</sup> Among the various signal modes, bistable photoswitching of fluo-

rescence emission is considered to be a promising one, not only because the fluorescence signals can be readily and sensitively recognized but also because the small number of photons required for their excitation induces few side effects to spoil the digitalized signals.<sup>8</sup> To this end, many groups<sup>4</sup> including ours have done much significant work on both fundamental and practical application with fluorescent changes as nondestructive readout. However, restricted by the low emission contrast of the current photochromic system, the film for recording often needs a relatively large thickness to yield a sufficient optical difference for readout of the stored information. Castellano et al.<sup>9</sup> developed luminescent photoswitchable supramolecular systems to improve luminescence efficiency and signal-to-noise in optical storage, but regrettably, this molecular system was only applied in write-once read-many (WORM) optical

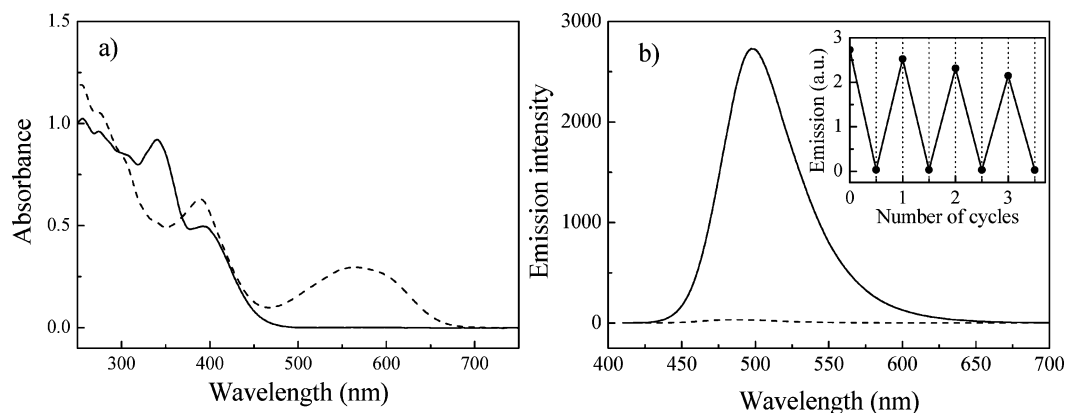
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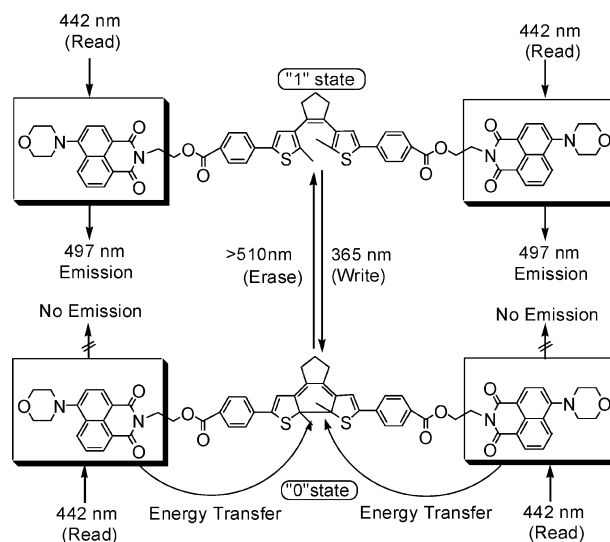
**Figure 1.** (a) Absorption and (b) fluorescence emission spectra change of BTE-NA doped in PMMA before (solid line) and after (dashed line) irradiation with 365 nm light for 5 min at room temperature. The inset shows the modulated emission peak intensity (excited at 400 nm) of the sample during alternating irradiation at 365 nm and  $>510$  nm.

storage media. Enlightened by this thought, we expected to develop new photochromic compounds with high luminescence efficiency, high signal-to-noise, high sensitivity, and high activity in solid film to satisfy the requirements for rewritable optical devices.

In our strategy, a novel naphthalimide dimer tethered by a photochromic bisthiénylene bridge with very high-contrast fluorescence switching was synthesized by the Suzuki coupling method. This design incorporates several important principles that are vital to the success of molecular optical storage technologies. First, perhydrobisthiénylcylopentene was chosen as the photochromic unit because it represents the most prominent switching material so far. The synthesis can be performed on a large scale, and the starting materials are easily accessible.<sup>10</sup> Second, naphthalimide derivatives are excellent fluorescent chromophores because of the high photostability, high fluorescent quantum yield, and desirable spectroscopic properties.<sup>11</sup> Two naphthalimides are covalently attached to a photochromic bisthiénylene for the purpose of photoswitching fluorescence with high contrast by energy transfer. Third, the write, read, and erase cycles are independently addressed with photons of different wavelengths, thus alleviating the problems associated with destructive readout.

Scheme 1 presents the structures and optical switching function of bisthiénylene-bridged naphthalimide dimer (BTE-NA). The open and closed isomers of BTE-NA represent “1” and “0” binary digital code. It exhibits good photoregulating luminescence with very high contrast (85:1) in poly(methyl methacrylate) (PMMA) doped films. According to our experimental results, such a strong fluorescence emission with high-contrast switching in solid film could well solve the long-existing problem resulted from low fluorescence contrast in readout of the stored information. We also demonstrate its use in two-dimensional recording

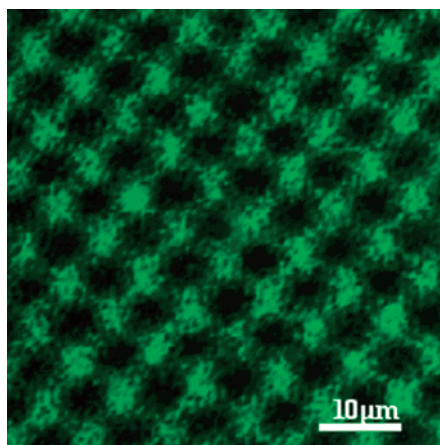
### Scheme 1. Structures and Photoswitching Behavior of BTE-NA



and that it is a suitable material for rewritable optical information storage.

Thin films of BTE-NA dispersed in PMMA were prepared by spin coating from tetrahydrofuran (THF) solution. During the course of our studies, we observed that BTE-NA undergoes the fast photochromism even in the polymer matrix, and their spectral changes are similar to those observed in THF solution, suggesting the polymer matrix does not significantly perturb the desired photochemical reactions of the current system, which ensures its photoactivity in the solid state and further application in memory devices. Figure 1 illustrates the absorbance and fluorescence spectra of the BTE-NA thin film before and after UV irradiation. The fluorescence spectrum of the naphthalimide unit at 497 nm matches the absorption spectrum of the closed-ring form of the bisthiénylene unit, so the fluorescence is efficiently quenched by the intramolecular energy transfer when the photochromic unit is converted from the open- to the closed-ring form upon irradiation with 365 nm. Back irradiation at a wavelength greater than 510 nm regenerated the open form and restored the original emission spectrum. The inset in Figure 1b shows a cycling experiment in which the emission of BTE-NA is monitored upon alternate irradiation with UV (365 nm) and visible ( $>510$

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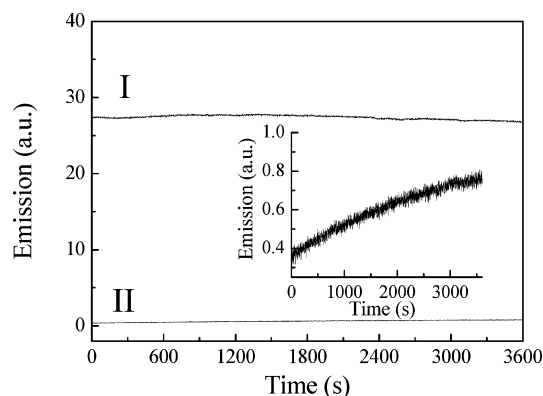


**Figure 2.** Fluorescence image generated from 365 nm irradiation (5 min) of the BTE-NA doped PMMA film through a dot-patterned contact mask. The light regions indicate luminescence, and the dark regions are non-luminescent ( $\lambda_{\text{ex}} = 442$  nm).

nm) light. It is noteworthy that the fluorescence on/off ratio is as high as 85:1. Such a high-contrast switching in the solid film presents a good strategy for solving the long-existing problem resulted from low fluorescence contrast in readout of the stored information. This is further verified by the following data-reading experiments.

As a method for readout of the stored information, the fluorescent change of BTE-NA is the most attractive alternative for its high resolution and high sensitivity. A two-dimensional recording pattern was demonstrated. Thin films for recording were prepared by spin coating a THF solution of a BTE-NA–PMMA mixture onto a glass substrate. Then, a mask pattern with periodically micrometer-size features was placed on the film and 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 with fine resolution. Figure 2 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.

Concerning the photostability of the written information, further fluorescence experiments were performed in the PMMA matrix by monitoring the emission peak intensity with 442 nm light illumination. As shown in Figure 3 (curve I), no discernible change to the initial emission intensity of the film was observed. However, prolonged irradiation of the film of the closed isomer at 442 nm results in an increase in emission, and the trend could be seen from the Figure 3 inset. This could be understood and interpreted as follows. In our case, the reading wavelength is at 442 nm (Scheme 1), where the BTE unit has no absorption. That is, the reading light successfully resides outside the spectral regions where the photochromic reactions are induced. But in the reading



**Figure 3.** Fluorescence peak intensity vs time curves of the BTE-NA doped in PMMA thin film, during 1 h of continuous irradiation by  $6 \mu\text{W}/\text{cm}^2$  at 442 nm. Reading signals of (I) open isomer and (II) closed isomer, and the inset shows the magnified reading curve of the closed isomer.

process, NA units fluoresce with a peak at 497 nm, which overlap with the absorption spectrum of the closed ring and could induce the ring-open photoreaction. Thus, the emission intensity was increased as shown in the Figure 3 inset. Even so, in contrast with the strong emission of the initial open form, the fluorescence of the closed isomer is so weak that the film could still keep a relatively high contrast ( $>35:1$ ) during 1 h of continuous reading, which accounts for the high stability of the recording. This could be clearly seen from Figure 3, where two reading curves were plotted together. In this sense, BTE-NA still can yet be regarded as a promising and competitive medium for erasable recording at the current stage.

In summary, we have described a novel fluorescent photochromic BTE-NA. Reversible, high-degree fluorescence modulation of naphthalimide chromophore was realized by photoisomerization of the bisthiénylene subunit in polymer matrixes, and photoinduced energy transfer is attributed to the mechanism. On this basis, two-dimensional recording employing fluorescence as the readout method is demonstrated. Considering its high-contrast photoswitchable fluorescence feature and the inherent characteristics of pristine bisthiénylene, BTE-NA can be suggested as a promising candidate for erasable optical data storage.

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**Supporting Information Available:** Synthetic details,  $^1\text{H}$  NMR and MS spectra, experimental details, and selected spectroscopic data (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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