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Quantitative Photoswitching in Bis(dithiazole)ethene Enables Modulation of Light for Encoding Optical Signals**

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Abstract: *Using one ray of light to encode another ray of light is highly desirable because information in optical format can be directly transferred from one beam to another without converting back to the electronic format. One key medium to accomplish such an amazing task is photoswitchable molecules. Using bis(dithiazole)ethene that can be photoswitched between its ring-open and ring-closed states quantitatively with excellent fatigue resistance and high thermal stability, it is shown that quantitative photoreversibility allowed the photoswitching light to control other light travelling through the photoswitchable medium, a phenomenon of transferring information encoded in one light ray to others, thus imparting photo-optical modulation on the orthogonal light beam.*

Electro-optical modulators play the pivotal role in transferring electrical signals into optical signals, which can be transmitted in massive quantities over long distances in optical fibers. Typically, such devices are made of $LiNbO_3$ crystals and widely used in telecommunications. The inorganic $LiNbO_3$ crystal modulates light through a second-order nonlinear effect called electro-optic effect, $\chi^{(2)}$, which only exists in non-centrosymmetric materials.[1] This requirement of polar media limits many materials from such applications.[2] On the contrary, there has been little effort in developing optical materials to perform photo-optical modulation, or devices that convert optical signals at one wavelength to optical signals at other wavelengths. Here we show that quantitative photoswitching in bis(dithiazole)ethene (BTE, Figure 1) shows photo-optical modulation properties, successfully converting continuous waves into meaningful light pulses. The significance of this report is that it demonstrates a new concept to use linear optical photoswitching to achieve light modulation rather than the standard nonlinear optical phenomena, which require high laser powers to achieve nonlinear effects.

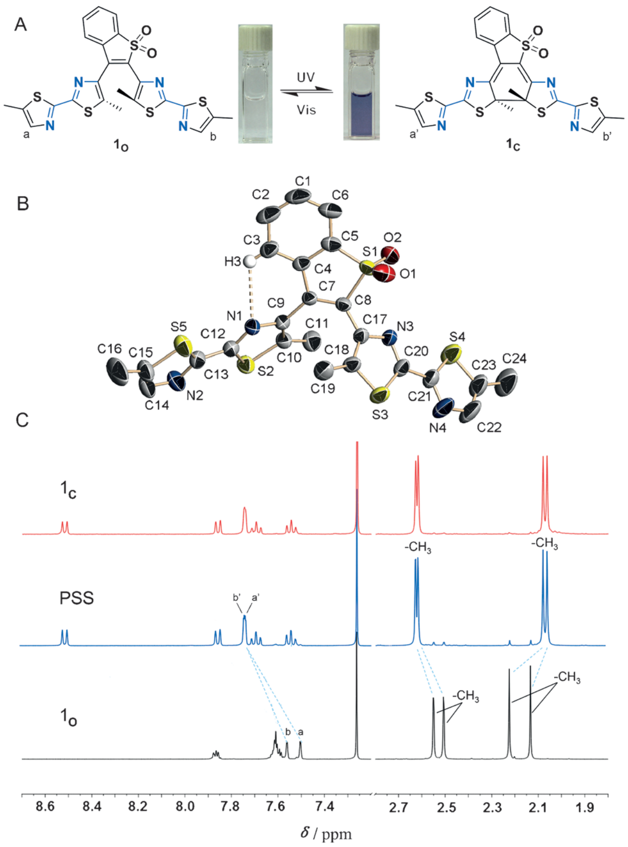

Figure 1. A) Reversible and quantitative UV and visible-light shuttle bis(dithiazole)ethene between its bistable states $\mathbf{1_O}$ and $\mathbf{1_C}$. B) ORTEP representation of the single-crystal structure of BTE in the $\mathbf{1_O}$ state (displacement ellipsoids: 50% probability). Selected interesting distances [Å]: C10⋯C18, 3.660(4); N1-H3, 2.560, C7-C8, 1.343(3); C7-C9, 1.519(3); C8-C17, 1.422(3). C) Comparing ^{1}H NMR spectra of $\mathbf{1_C}$, $\mathbf{1_O}$, and the irradiation-induced photostationary state (PSS) reveals that the PSS is essentially the ring-closed form ($\mathbf{1_C}$).

Photoswitchable molecules such as spiropyrans and bistable bisarylethenes can be photo-interconverted between the ring-open and ring-closed forms, respectively.[3] Such molecular switches that can function as information storage,

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logic gates,[4,5] nondestructive readout,[6] and biological probes.[7] Using different wavelengths as optical outputs, we have demonstrated multi-addressable states based on molecular switches under photonic stimuli.[8] For device applications, however, the photoswitching molecule must exhibit excellent fatigue resistance, high thermal stability, and fast cyclization.[9] Rarely all these desired properties are found in a single molecule, but photoswitchable BTE is rather unusual and satisfies all these prerequisites.

BTE exists as one of the bistable states corresponding to the ring-open form of the bisarylethene system and here after named $\mathbf{1_O}$. It was synthesized from 2,3-dibromobenzo[*b*]thiophene-1,1-dioxide and the corresponding borate of 2-(4-bromo-5-methylthiazol-2-yl)-5-methylthiazole by Suzuki coupling (63.8% yield). X-ray crystallography, high-resolution mass spectroscopy (HRMS), ^{1}H and ^{13}C NMR spectroscopy confirmed its chemical structure (Figure 1 and the Supporting Informatin).

Important structural evidences originates from the single-crystal structure of $\mathbf{1_O}$, which was obtained by the diffusion method from a mixture of CH_2Cl_2 and hexane at room temperature.[10] The crystal structure reveals a typical anti-parallel conformation (Figure 1B), with a distance of 3.66 Å between two juxtaposed photoactive carbons (C10···C18), satisfying the prerequisites for bisarylethene photocyclization reactions.[11,12] In addition, the crystal structure also reveals that a weak CH···N hydrogen bond occurs with a N1···H3 distance of 2.56 Å, which is shorter than the sum of van der Waals radii of H (1.2 Å) and N (1.55 Å), consistent with the results reported by Kawai and co-workers.[9a] The weak CH···N hydrogen bonding in $\mathbf{1_O}$ can benefit quantitative photocyclization by rendering the two dithiazole units into favorable antiparallel conformation, a precursor for ring closure.

Interestingly, the ring-open form $\mathbf{1_O}$ undergoes photocyclization to form a ring-closed counterpart $\mathbf{1_C}$; this photochemical process can be monitored using ^{1}H NMR spectroscopy (Figure 1C). The unsymmetrical ethene bridge imparts chemical inequivalence among the four methyl groups (appearing at 2.13, 2.22, 2.51, and 2.55 ppm) and the two singlet hydrogen atoms (appearing at $H_a = 7.51$ and $H_b = 7.56$ ppm) on the two dithiazole units. Because the open form is more flexible and the closed form is more rigid, the difference between the inequivalent methyl groups and the two singlet protons becomes smaller as the photo-transformation from $\mathbf{1_O}$ to $\mathbf{1_C}$ takes place. As a result, the difference between the methyl groups changes from 0.09 and 0.04 ppm to 0.02 and 0.01 ppm, respectively. Similarly, the two singlet hydrogen peaks on the outside dithiazole hydrogen (H_a and H_b labeled with a and b on $\mathbf{1_O}$ and a′ and b′ on $\mathbf{1_C}$ in Figure 1 A) almost merge together upon photocyclization from the open to the closed form, shifting downfield from 7.51 and 7.56 ppm to 7.74 ppm. A couple of important conclusions can be drawn from the NMR studies. First, no other side products were observed during the photochemical conversion from $\mathbf{1_O}$ to $\mathbf{1_C}$. Second, the photostationary state (PSS) upon illuminating $\mathbf{1_O}$ was essentially the ring-closed $\mathbf{1_C}$, as evidenced by the comparison of the PSS to purified $\mathbf{1_C}$. Together, these results support a quantitative photochemical conversion from the ring-open form to the ring-closed form at the NMR sensitivity level.

The colorless $\mathbf{1_O}$, which absorbs intensively at 340 nm, can be photoconverted to the purple ring-closed form $\mathbf{1_C}$ upon irradiation at 365 nm (Figures 1 A and 2 A). The resultant ring-closed form has an absorption band at 568 nm; this appearance of the purple-complement band is a characteristic indicator for a ring-open to ring-closed transformation. Impressively, the photostationary state (PSS) was reached within 20 s upon irradiation at 365 nm (1 mW; concentration: 20 μM), indicating a fast light response (Figure 2 A, inset).

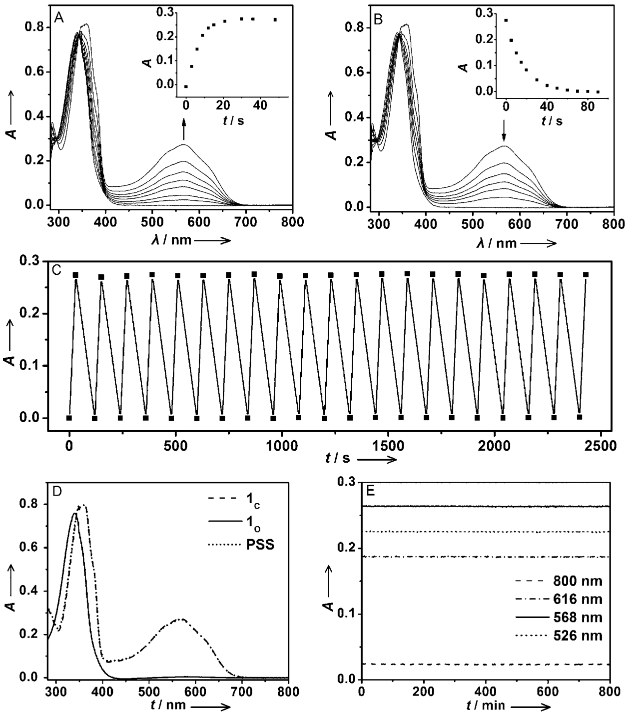

Figure 2. A) Quantitative photoswitching from $\mathbf{1_O}$ to $\mathbf{1_C}$ upon 365 nm irradiation (2.0×10^{-5} M, CH_3CN). B) Quantitatively reversible photoswitching from $\mathbf{1_C}$ to $\mathbf{1_O}$ (2.0×10^{-5} M, CH_3CN) upon > 510 nm light irradiation. Insets: absorbance changes at 568 nm as a function of irradiation time. The isosbestic points at 295 and 348 nm in both forward and backward photoswitching indicate 1:1 quantitative conversion. C) Reversible and quantitative alternating UV (365 nm) and visible (> 510 nm) light photoswitches between $\mathbf{1_C}$ and $\mathbf{1_O}$, demonstrating excellent fatigue resistance and reversibility. The returning to zero absorbance indicates quantitative formation of $\mathbf{1_O}$ after each photoswitching cycle. D) Pure $\mathbf{1_C}$ (dashed line) was irradiated with visible light to yield 100% pure $\mathbf{1_O}$ (solid line), which was then irradiated with UV light to return quantitatively back to the PSS (dotted line). E) Absorbance of $\mathbf{1_O}$ monitored at room temperature in CH_3CN after it reaches the PSS or 100% $\mathbf{1_C}$ under UV action; no reversal reaction was observed at 526, 568, and 616 nm after 800 minutes, indicating that $\mathbf{1_C}$, like $\mathbf{1_O}$, is thermally stable.

Conversely, visible-light irradiation (> 510 nm) on the photochemically generated $\mathbf{1_C}$ converts it back to its original colorless open form $\mathbf{1_O}$ (Figure 2B). The ring-open form $\mathbf{1_O}$ exhibits weak fluorescence while the corresponding closed form $\mathbf{1_C}$ has essentially no emission (Figure S1 in the Supporting Information).

Alternating irradiation with UV (365 nm) and visible light (> 510 nm) toggled the photoswitch repeatedly between the open $\mathbf{1_O}$ and closed $\mathbf{1_C}$ forms with remarkable fatigue resistance (Figure 2C). The absorption spectra of the repeatedly toggled $\mathbf{1_O}$ or $\mathbf{1_C}$ reproduce those absorbance values of their pure forms. Moreover, the absorption spectrum of PSS overlaps exactly with the corresponding pure closed form $\mathbf{1_C}$ (Figure 2D), confirming that the conversion from the ring-open form to the ring-closed form was achieved quantitatively (photocyclization yield $\geq 99\%$). The reverse photochemical reaction is also quantitative as evidenced by the quantitative disappearance of the absorption band at 568 nm. The optical absorption results reveal that the quantitative and reversible photoswitching between $\mathbf{1_C}$ and $\mathbf{1_O}$ operates even at the UV/Vis sensitivity level (about 10^{-5} M), without residue starting materials, nor reaction side products.

Unlike many known photochroms,[13,14] $\mathbf{1_C}$ has excellent thermal stability and does not thermally convert back to the reactant as demonstrated by the constant absorbance values at different wavelengths of 616, 568, and 526 nm (Figure 2E). As a result, the pure closed form $\mathbf{1_C}$ was easily obtained by traditional column chromatography. Together, these data reveal that both the open ($\mathbf{1_O}$) and the closed ($\mathbf{1_C}$) forms are thermally stable and their photochemical interconversions are quantitative, for both forward and backward reactions.

To demonstrate photoswitching in molecules such as $\mathbf{1_O}$ and $\mathbf{1_C}$ can be used for transmission of information, we carried out photo-optical modulation. In electro-optical modulation, an electric field applied perpendicular to the light beam travelling in a nonlinear medium imparts modulation of the output signals. Similarly, phase shifting in Mach–Zegnder devices using photochromic materials can also achieve output modulation.[15] In our photo-optical modulation, laser beams at individual wavelengths modulate orthogonal light beams at other wavelengths, turning them on and off by a photoswitching medium. In Figure 3A, two lasers, one at 561 nm and the other at 375 nm, induce photochemical conversions in the photoswitchable thin film containing 1.2% w/w of $\mathbf{1_O}$ and $\mathbf{1_C}$ in polylactide. Laser light of 375 nm switches the open form $\mathbf{1_O}$ to the closed form $\mathbf{1_C}$, whereas the 561 nm laser light switches the closed form back to the open form. Photochemical conversions between the bistable states are carried out reversibly and quantitatively. Unlike our previous spiropyran–merocyanine system, in which the merocyanine will automatically undergo thermal reaction to close the ring and yield spiropyran,[14] both of the bistable states, $\mathbf{1_O}$ and $\mathbf{1_C}$, are thermally stable as reported in Figure 2. This attribute is important because information transiently stored in such photoswitchable molecules is not vulnerable to thermal fluctuation. The photoswitchable thin film is placed such that it has a 45° incident angle with respect to the modulating laser beams and a 45° incident angle with respect to the nonmodulated and modulated white light beam (Figure 3A). Here the two lasers encode binary digital information into the photoswitchable $\mathbf{1_O} \leftrightarrow \mathbf{1_C}$ thin film. The photoswitching within the thin film in turn encodes orthogonal nonmodulated beams into digitally encoded modulation.

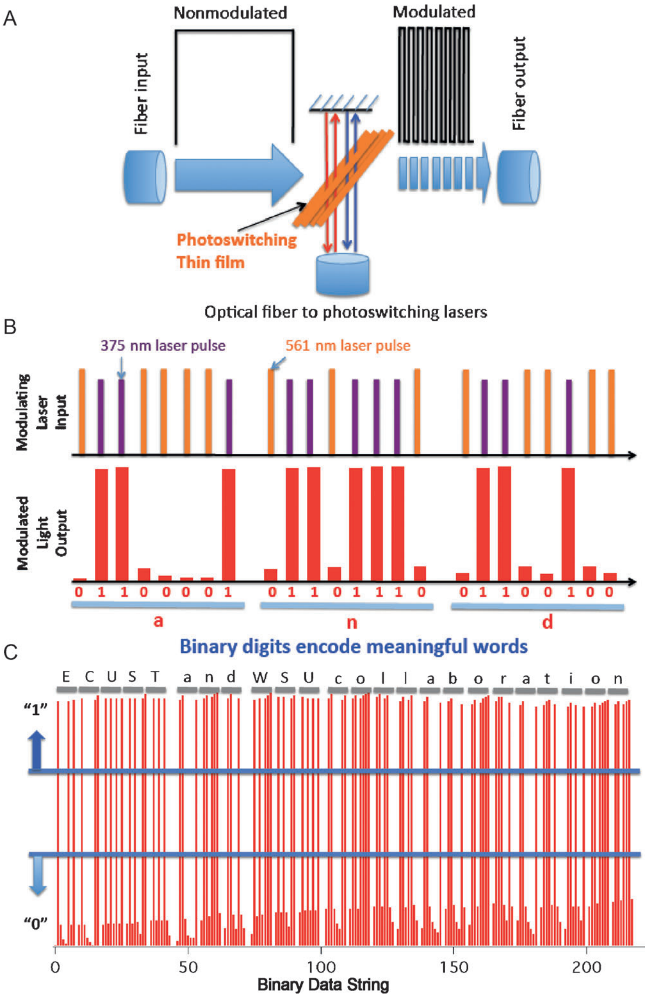

Figure 3. A) The photo-optical modulation system depicts that modulation beam (narrow arrows) and the input-output beam (wide arrows) are orthogonal; both have an incident angle of 45° with respect to the photoswitching thin film containing $\mathbf{1_O}$ and $\mathbf{1_C}$. B) Input white light is not modulated, but this multi-wavelength beam is modulated after passing through an active photoswitching thin film under the action of two encoding lasers. The 561 nm laser carries binary information of "0" and the 375 nm laser carries binary information of "1". Together, they impart meaningful information. The modulating lasers carry the information of the word "and"; this information is transmitted to the input white light through the photoswitching molecules, encoding meaningful output of the word "and" in binary digits. C) A phrase is encoded into the output optical fiber using the mechanism described above. Each letter has its corresponding 8-digit binary codes labeled by the gray bar above. The data stream shown here is multiplex output carrying the binary information faithfully from the encoding lasers.

To illustrate the principle, we transmitted alphabet letters using binary codes of standard 8-bit ASCII characters in optical fibers. Every letter in lower or capital case is assigned to an eight-digit binary code, that is, combinations of zeros and ones. For example, the small case letter "a" is "01100001" while the capital "W" is "01010111" in binary codes. In our experimental setting of measuring absorbance, the 375 nm laser beam encodes "1", whereas the 561 nm laser beam encodes "0", corresponding to the ring-closed ($\mathbf{1_C}$) and ring-open ($\mathbf{1_O}$) forms, respectively. The encoding beams (375 and 561 nm) emerged from an optical fiber and illuminated the photoswitchable film, and the transmitted laser beam was

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reflected back to enhance photoswitching. As shown in Figure 3, a white light beam fed from left without any encoded information serves as the input. After passing through this optically modulated medium, the region corresponding to the absorption of $\mathbf{1_C}$ (450–650 nm) is thus modulated. In principle, white light can also cause photoisomerization in the thin film, but under the strong influence of the lasers, the white-light-induced photoswitching is not noticeable. In other words, the information in the two laser beams is transferred into the orthogonal passing photons, the colors of which are defined by the photoswitching absorption band arranging from 450 nm to 650 nm.

Therefore, meaningful information was encoded into the blue, green, and red regions of visible light. Random alphabet soups rarely impart meaning. However, when these letters are encoded at a specific sequence, meaningful information is launched into the output fiber. For example, the word "and" consists of three letters arranged in a specific sequence and each letter is represented by an eight-digit binary code (Figure 3B). Thus the word "and" consists of the data string of 011000010, 01101110, and 01100100 in binary numbers. The definition of "0" is that the signal (absorbance in this case) is below 1/3 of the 100 % response; whereas "1" is defined when the response is greater than 2/3 of the 100 % value.

To demonstrate the proof-of-concept, we sent a data stream using 375 nm (binary 1) and 561 nm (binary 0) laser pulses carrying information of "ECUST and WSU collaboration" (Figure 3C). In this data stream taken from absorbance at 568 nm, each letter corresponds to eight binary digits that are grouped together with a grey bar and their corresponding letter above the data. A space is added between letters so that they can be easily recognized. Figure 3C depicts the read out of the data stream from the passing light orthogonal to the encoding lasers. The results prove that information encode by the lasers are faithfully transferred to the white light beam without a single error.

The above data stream was repeated twice; there are total of ≥ 348 codes imparted by photoswitching that correspond to the information transmitted. This experiment demonstrates that nonmodulated light was encoded by another orthogonal light beam, a photo-optical modulation similar to the known electro-optical modulation. Excellent fatigue resistance was observed in the photoswitching molecules $\mathbf{1_O}$ or $\mathbf{1_C}$. The photochemical conversion to the ring-closed state is nearly quantitative, while the reverse photochemical conversion to the ring-open form is high ($\geq 80\,\%$) because of limited time exposure to the photoswitching beam. Although the current photoswitching rate is rather limited, spiropyran–merocyanine photoswitching has been reported to be as fast as 40 ps.[16] At this speed, the photo-optical modulation can reach as high as 50 GHz, which is fast enough for potential applications in information communication.

In summary, we have developed a novel photoswitching system based on bis(dithiazole)ethene ($\mathbf{1_O}$ and $\mathbf{1_C}$) that have several advantages. Both bistable states are thermally stable and quantitative photoswitching of the full cycle (open to closed and then to open again) can be realized using light illumination with excellent fatigue resistance and reversibility. This collection of desired properties, such as quantitative photoswitching and fatigue resistance, enables the proof-of-concept on photo-optical modulation using $\mathbf{1_O}$ and $\mathbf{1_C}$ as the bistable counterparts, thus transmitting information in the lasers to other orthogonally passing light waves and launching it into the output optical fiber. Thus a new strategy to modulate light with encoded information emerges, using fundamental properties in molecular photoswitches.

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[10] Crystallographic data for BTE or $\mathbf{1_O}$: $C_{24}H_{18}N_4O_2S_5$, $M = 554.72$, monoclinic, space group $C2/C$, $a = 30.783(5)$, $b = 12.614(2)$, $c = 22.865(7)$ Å, $F(000) = 2288$, $\beta = 129.682(2)^\circ$, $V = 6833(3)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.078\ g\,cm^{-3}$, $T = 293(2)$ K, 13456 reflections measured, 5942 unique ($R_{int} = 0.0265$) which were used in all calculations. R_1 ($I > 2\sigma(I)$) = 0.0570, wR_2 (all data) = 0.1817, GOF = 1.065. CCDC 922682 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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