

A Simple Molecule-Based Octastate Switch

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S Supporting Information

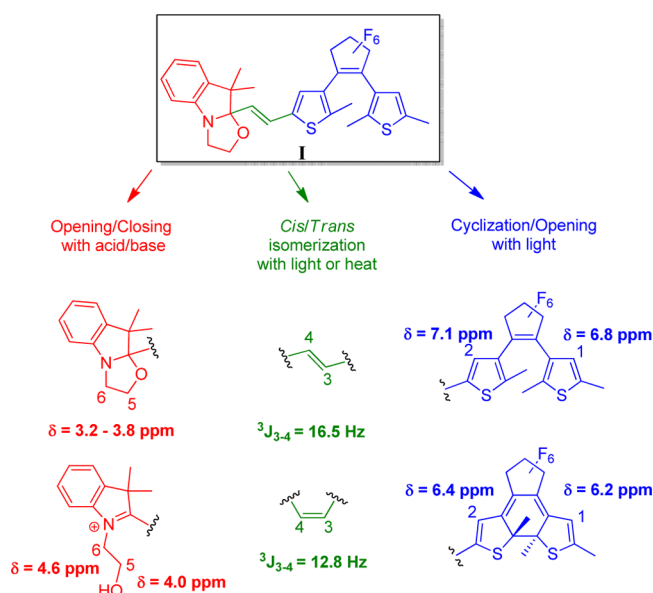
ABSTRACT: Dithienylethene oxazolidine hybrid system connected through an isomerizable double bond exists under eight molecular states on demand. Combinations of electrocyclization of dithienylethene, *Z/E* isomerization and acid–base oxazolidine change cause selective addressabilities. Two intricate gated photochromic performances allow the execution of an 8-step molecular switch, which renders this molecular system the most complex known up to date.

Over the past decade a great deal of effort has been focused on the synthesis, modification and application of molecular switches. The trend of miniaturization of electronic devices such as switches, transistors and logic gates has provided the main driving force in this area. The most rudimentary versions of these molecular systems (switches) can be the interconversion between two states, by an external stimulus such as light irradiation, change in the electric potential or pH.¹ These two isomeric forms exhibit different absorption spectra, geometries and physical properties such as hydrophobicity and redox chemistry, refractive index or dielectric constant.² Photochrome-based switches constitute a particularly popular family due to their fast response times, reversibility and ease of addressability. By taking another step forward, one can envisage a more complex system which can be addressed selectively and sequentially, which is one of the preconditions for successful applications in logic systems.³ Miniaturizing down to the molecular level embodies the integration of several switchable functions into a single molecule. In that regard, several multiphotochromes have been synthesized and studied during recent years. As the most successful members of the photochrome family, dithienylethenes (DTEs) were applied on numerous occasions,⁴ but the selective addressability proved to be the limiting factor.⁵ Several mixed examples of biphotochromes based on DTEs, dihydroazulenes,⁶ naphthopyrans,⁷ phenoxynaphthacenequinone,⁸ spiropyrans,⁹ coumarins,¹⁰ Schiff bases,¹¹ [1,10]-phenanthroline,¹² 8-hydroxy-2-methylquinolines,¹³ 4,4'-bithiazoles,¹⁴ naphthalimides,¹⁵ 5-methoxy-2-(2-pyridyl)thiazole,¹⁶ pyridyl,¹⁷ fulgimides,¹⁸ and benzo[*b*]thiophene-1,1-dioxide,¹⁹ have also been reported. Despite these efforts, there are still many hurdles to overcome, such as selective modulation of coexisting switches in a single molecule; higher thermal stability of their isomers; reversibility of the switching process; and exclusive use of photoaddressable units.

Herein we report the switching study of hybrid system I using light stimulus and/or chemicals (acid/base). We designed

a DTE covalently linked to an indolino[2,1-*b*]oxazolidine motif via a double bond (Chart 1), which all-photon switching mode

Chart 1. Structure of the Hybrid System I with Its Three Reactive Sites and Characteristic NMR Data Used As Probes



involving four trans isomers is restricted to chlorobenzene rich solutions.²⁰ Dithienylethenes are known to exist in two thermally stable states; therefore, they represent one of the most widely synthesized and studied (P-type) molecular switches nowadays.^{1a} As for the benzazolo-oxazolidine (BOX), its versatile nature ensures its photo-,²¹ acido-²² and electroaddressability²³ which have been exploited as organic molecular switches with large nonlinear optical contrast. With the ethylenic junction, the present system can exist in $2^3 = 8$ isomeric states. The fulfilment of a series of molecular design criteria, including incorporation of selectively and sequentially switchable subunits, is crucial to the unprecedented realization of an 8-step cycle which could be accomplished in a stepwise manner. We have investigated all possible interconversions, bearing in mind the achievement of a full cycle involving the eight different states. Stereoisomers may exist for some states but are not relevant for the current study. Each isomer is expected to have a unique spectral signature and their quantitative analyses have been followed by NMR in deuterated

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nondegassed acetonitrile. We selected thienylic, olefinic and oxazolidine protons as probes (Chart 1) to accurately quantify the consequences of irradiation, acid/base treatment or thermal evolution. Each possible conversion was then explored and characterized by its corresponding ^1H NMR (Figure 1) and UV–visible spectra (see Supporting Information (SI)) associated with its molecular structure (Scheme 1).

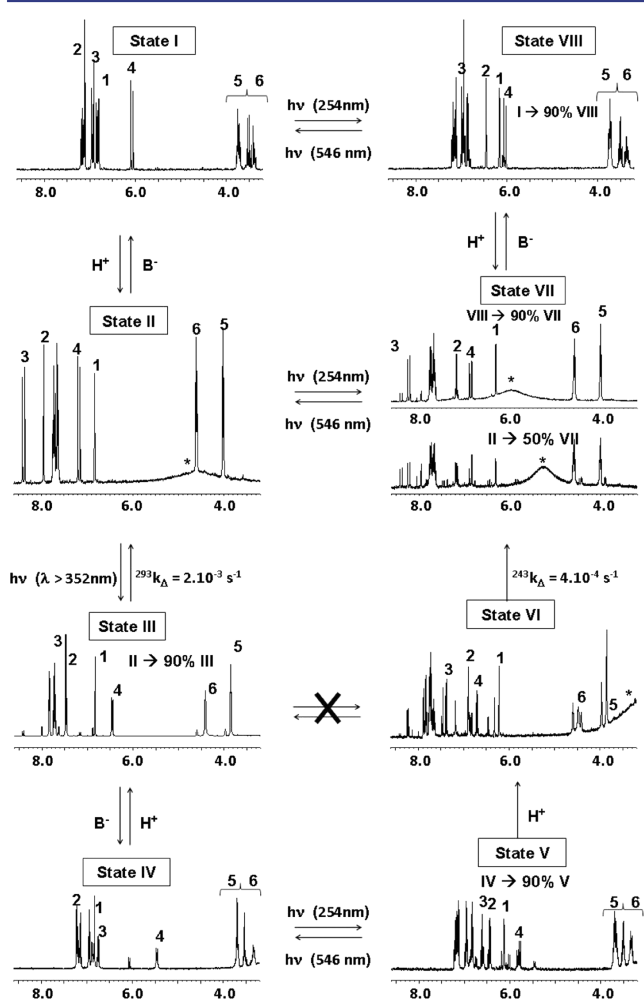
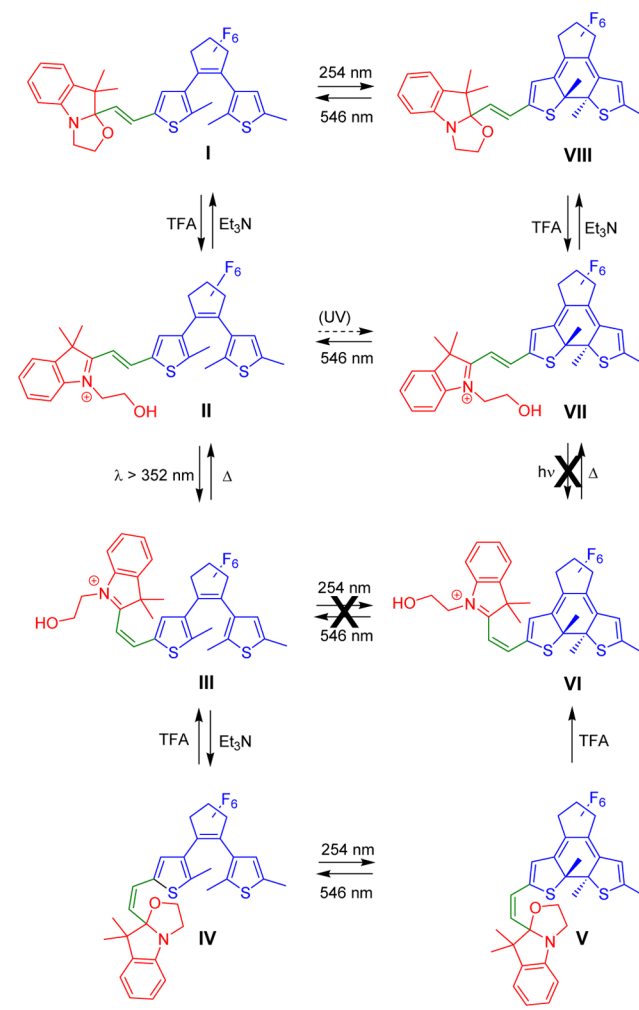


Figure 1. ^1H NMR spectra (500 MHz, CD_3CN) with characteristic signals of each state (*broad signal of water).

The opening of oxazolidine ring of **I** is produced instantaneously by adding TFA vapor, leading to the protonated open form **II**, being clearly identified by two well-resolved triplets at 4.02 and 4.61 ppm. The solution which was turned from colorless to yellow-orange is bleached quantitatively to **I** upon treatment with triethylamine ($\text{I} \leftrightarrow \text{II}$). When irradiation with light at $\lambda > 352$ nm is applied to state **II**, the *trans/cis* transformation to the state **III** is the only photo-induced reaction, as no ring closing of DTE to **VII** takes place. Coupling visible light and low temperature allows formation of the *cis*-isomer **III** with up to a 90% conversion yield. Its main reactivity concerns its thermal relaxation into **II** at ambient temperature ($^{293}k_{\Delta} = 2.10^{-3} \text{ s}^{-1}$; $\text{II} \leftrightarrow \text{III}$).

The ring closure of the BOX-unit in **III** is achieved upon triethylamine addition, and the isomer **IV** is formed ($\text{III} \leftrightarrow \text{IV}$). Subsequent irradiation of **IV** at 254 nm results in the formation of **V** with a photostationary state (PSS) composed of 90% of

Scheme 1. Modulability of the Octastate Switch



cyclized form. Total photobleaching of the state **V** is achieved by irradiating with visible light ($\text{IV} \leftrightarrow \text{V}$). Low temperature TFA treatment allowed conversion of **V** into **VI** ($\text{V} \rightarrow \text{VI}$). The hindered *cis*-form **VI** thermally evolves toward **VII** ($^{243}k_{\Delta} = 4.10^{-4} \text{ s}^{-1}$; $\text{VI} \rightarrow \text{VII}$), which is converted into **VIII** upon base addition. Finally, state **VIII** is decyclized upon visible light irradiation to give initial state **I**, leading then to a full eight-step cycle.

The cycle was also investigated by starting with irradiation of **I**. Using 254 or 313 nm wavelengths to irradiate **I**, only the formation of **VIII** is observed, indicating the predominant photoreactivity of the DTE unit. It should be noted that the PSS, composed of 90% of DTE in its closed form, accompanied by a deep purple coloration of the solution, has been reached faster using 254 nm light (Figure S22 (SI)). Clearly, no typical signals for the open oxazolidine ring or for the *E/Z* isomerization of double bond can be found. Both DTE forms are thermally stable for weeks at ambient temperature. When treating **VIII** with TFA, the solution becomes deeply green due to the formation of the state **VII**, and reverse reaction can be achieved upon base treatment ($\text{VIII} \leftrightarrow \text{VII}$). When irradiated with 546 nm light, **VII** photobleached into **II**. On the contrary, even at 228 K, irradiations of **VII** at various wavelengths (313, 365 and 405 nm) were unsuccessful in achieving its *trans* to *cis* isomerization ($\text{VII} \rightarrow \text{VI}$). The state **II** is converted into **I** with base addition, or can lead to the cyclization of its DTE unit

upon irradiation with 254 or 313 nm light, somewhat inefficiently. Only 50% of the cyclized state VII is detected, while 90% were reached with I → VIII or IV → V. Thus, the system with all the four *trans*-isomers can be interconverted clockwise or anticlockwise. In contrast, such assumption was not checked with all the four *cis*-isomers, as no reaction was observed between the states III and VI, either thermally or photochemically, nor between VI and V.

Absorption spectra of each state in acetonitrile have been characterized along the different pathways (see SI) showing they are not simple linear combinations of the hybrid components, DTE and BOX. Comparison with the maxima absorption wavelength obtained for the free open BOX ($\lambda = 435$ nm), the opening of oxazolidine in the triad system is always characterized by a hypsochromic shift (up to 18 nm). For DTE, the wavelength of cyclization, evidenced by $\lambda = 580$ nm in free unit, is shortened (551 and 557 nm) in states V and VIII, but a strong bathochromic shift (+100 and 110 nm) is observed in states VI and VII. Their incorporation into the triad obviously induces a significant electronic coupling in the ground state.

As a whole, the acid-induced, photo- and thermochemical transformations between the eight isomeric forms of the dithienyl oxazolidine hybrid system can be summarized as depicted in Scheme 1. The pathways between the four *trans*-states are fully reversible: acid/base addition triggers the opening/closing of BOX, while UV-visible irradiation induces the cyclization/opening of the DTE-unit. It should however be noted that the open BOX diminished the reactivity of DTE as, at the PSS, 50 and 90% conversions were achieved from II and I, respectively. This much less efficient cyclization can be explained by change in electronic distribution upon deprotonation. In addition, photocyclization of IV into V being as efficient as from I to VIII, this clearly indicates that the status of BOX (closed or opened) allows for fully controlling the ability to photocyclize the DTE unit. Therefore, the photochromic DTE reactivity in the present hybrid system can be locked by controlling the nature of BOX, displaying a gated photochromism. Gated photochromism corresponds to a special form of photochromism in which one form is photochemically transformed into a nonphotochromic form, which becomes again photochromic upon reactivation with an external stimulus. Considering the *trans*-*cis* isomerization of the double bond, the state II appears then to act as keylocker as it could trigger the cycle toward the *cis* or the *trans*-isomer routes by simply selecting the appropriate wavelength, respectively (>352 or 254 nm). In fact, the reaction between the states II and III is the only open way toward the *cis*-isomer system, as none of the three other states (IV, V and VI) can be accessed from the *trans*-system. In addition, another approach of gated photochromism can be envisaged as states III and VI are not photoreactive, but only sensitive to change in temperature or pH which “unlock” them.

In conclusion, our hybrid system offers the unique opportunity of eight interconvertible isomers which represent the most complex multiaddressable molecule known to date. This attractive multistate photo- and acidochromic molecule describes a full eight-step cycle, which can be also shortcut on demand between the quartet of *trans*-isomers. The photoisomerization of the double bond connecting DTE and BOX subunits can be realized only under the acidic conditions. Concomitantly the ring-closure of DTE for charged species have been noticeably reduced. This double gated-photo-

chromism allows switching between isomers and control pathways that can provide a nondestructive readout capability.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures, NMR spectra, UV-visible spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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