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Theoretical investigation on the spectroscopy prosperities of four isomers of an encoder molecule FGDTE

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ABSTRACT

A molecule consisting of one dithienylethene covalently linked to two fulgimide photochromes has been designed as a 4-to-2 encoder. The combined molecule has four stable isomers, one may convert to another by particular irradiations. In this paper, we calculated the Gibbs free energies of the four isomers and got the order of their stabilities. Then the mechanisms of ring-opening and ring-closing of the monomers were explored in detail and the reaction conditions for structural conversion were also discussed. The corresponding absorption spectra of the combined molecules were researched and the new characters in the designed systems were predicted as well. Finally, we optimized their corresponding excited-state structures and analyzed the emission properties.

1. Introduction

Photochromism means a reversible transformation of a chemical species between two forms by the absorption of electromagnetic radiation, where the two forms have different absorption spectra [1,2]. Photochromic materials have attracted much attention because of their potential applications in optoelectronic devices, such as optical memories and optical switches [3–7]. Among photochromic systems, both dithienylethene (**DTE**) [8–13] and fulgimide (**FG**) [14–16] derivatives are the representatives based on their typical and regular reversible photo-cyclization and photocycloreversion reaction. Recently, a triad molecule **FGDTE** (Scheme 1) was reported by Professor Moore's group, it consists of one **DTE** photochrome covalently linked to two **FG** photochromes at one side [17,18]. Monomer molecules **FG** and **DTE** both have two stable isomers, each one bearing its own optical electronic properties, and they can undergo reversible ring-closing reactions when they exposed to UV and visible light (Scheme 2). Since the two **FG** chromophores share the same chemical environment, the combined molecule has four isomers: **FGoDTEo**, **FGoDTEc**, **FGcDTEo**, and **FGcDTEc** (the subscript o represents ring-open form, and c represents ring-closed form). Exposing **FGDTE** solution under different wavelength irradiations may result in different products containing distinct spectroscopic properties (Fig. 1). This phenomenon can be exploited as a 4-to-2 digital encoder, which converts 4 inputs of data into 2 outputs. Four lights (at 302 nm, 366 nm, 397 nm, and about 500 nm) as four different inputs irradiating the initial encoder can bring about two optical responses (absorb at 475 nm and 625 nm) as two outputs (Table 1). The truth table of the 4-to-2 encoder is shown in Table 2. Each input ($\mathbf{I_0}$–$\mathbf{I_3}$) can assume a value of either 0 or 1, and the two outputs ($\mathbf{O_0}$ and $\mathbf{O_1}$) comprise a 2-bit binary number.

The spectroscopy details of these molecules have been studied in experiment [17]. The absorption wavelengths are listed in Table 3. And the emission result indicates only **FGc** and **FGcDTEo** have measurable fluorescence at about 600 nm and 630 nm, respectively.

Several tentative theoretical studies about the frontier molecular orbitals and the absorption spectra of **FGDTE** have been done [12,19], and our calculations focus on the following important issues. First, what's the mechanism for ring-opening/closing of the two monomers and how can the 366 nm light excite the both **FGo** and **DTEo** into ring-closed forms? Second, what's the relationship between the absorptions and the reaction conditions for structural conversion and how can the combined molecules (**FGDTE**) entirely keep the absorption properties of their monomers? Third, why does

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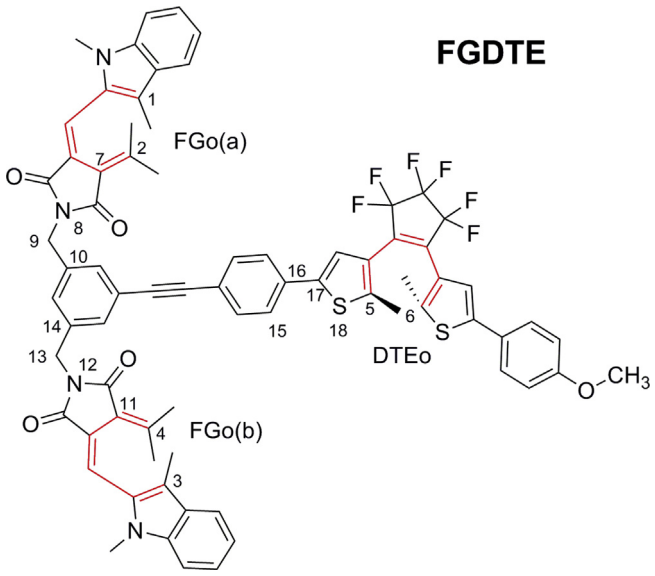


Scheme 1. The structure of **FGDTE** (in **FGoDTEo** form).

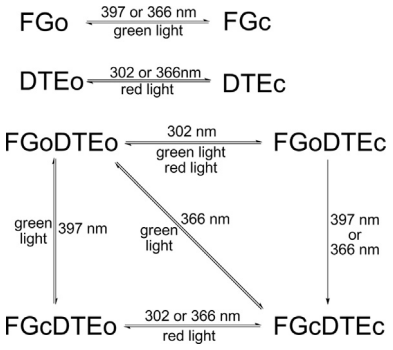


Fig. 1. Reaction conditions for isomerizations of **FG**, **DTE**, and **FGDTE**.

Table 1
Inputs and outputs for encoder function [17].

Inputs (λ)	Main components	Optical signals (absorption)	Outputs
I_0 (460–590 nm)	**FGoDTEo**		
I_1 (397 nm)	**FGcDTEo**	At 475 nm	O_0
I_2 (302 nm)	**FGoDTEc**	At 625 nm	O_1
I_3 (366 nm)	**FGcDTEc**	At 475 & 625 nm	O_0&O_1

Table 2
Truth table for this 4-to-2 encoder.

Input I_0	Input I_1	Input I_2	Input I_3	Output O_0	Output O_1
1	0	0	0	0	0
0	1	0	0	1	0
0	0	1	0	0	1
0	0	0	1	1	1

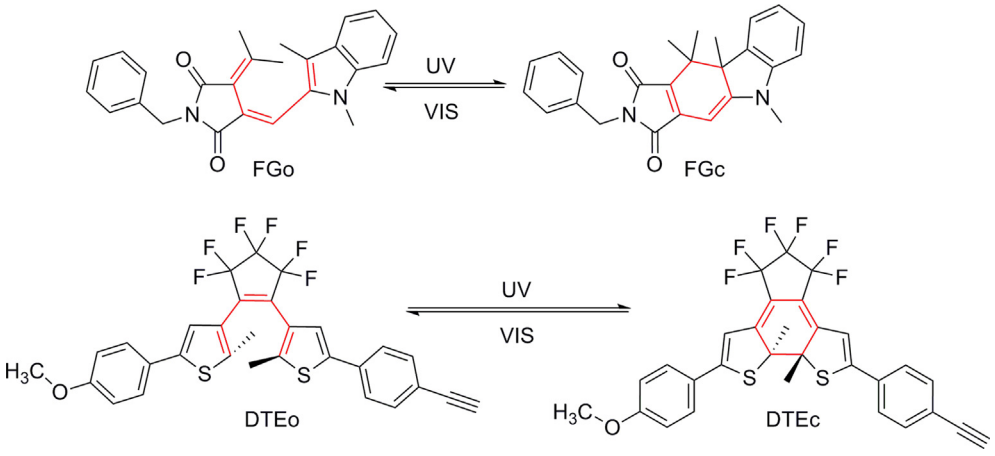
Table 3
Experimental absorption data of every molecule [17].

Molecule	Absorption/nm	Molecule	Absorption/nm
FGo	380	**FGoDTEo**	387,331,286
FGc	510,295,262	**FGoDTEc**	604,362
DTEo	306	**FGcDTEo**	511,324,270
DTEc	600,335,274	**FGcDTEc**	598,535,357,266

FGcDTEo (but not **FGcDTEc**) display measurable fluorescence emission? In addition, further molecular design should be explored and potential applications of the special emission properties need to be discussed.

2. Computational details

All the calculations were performed with the Gaussian09 program [20]. The ground-state structures of all isomers of **FG**, **DTE**, and **FGDTE** were optimized at CAM-B3LYP [21,22]/6-311G(d) level, without any symmetry constraint. And the harmonic vibrational spectrum of each species was determined analytically and it was checked that all structures correspond to true minima of the potential energy surface. To get a suitable TD-DFT [23–25] (time-dependent density functional theory) approach in absorption simulation, four popular functionals (CAM-B3LYP, B3LYP [26], M06 [27], and PBE0 [28]) for such organic switchable system [29] were tested. The calculated values are summed up in Table 4 together with the experimental data. As a result, the B3LYP calculations are in the best agreement with the experimental values, so the following researches of frontier molecular orbitals and absorption spectra are both in dependence on B3LYP method. After that, the excited-state geometry optimizations were performed by TD-CAM-B3LYP, and then the emission properties were calculated with TD-B3LYP. To be consistent with the experimental measurements, the calculations of absorption and emission were both performed in



Scheme 2. Conformation conversion of **FG** and **DTE**.