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New Photochromic Dithienylethene Based on Porphyrin for a Nondestructive Information Processing

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ABSTRACT

A new 1-[2-methyl-5-(4-tetraphenylporphyrinphenyl)-3-thienyl)-2-[2-methyl-3-thienyl]-cyclopentene (DTE-TPP) combined by 3,3'-(1-Cyclopentene-1,2-diyl) bis(5-chloro-2-methylthiophene) (DTE) and tetraphenyl porphyrin (TPP) can transform between the open isomer and the closed isomer upon the irradiation of UV or visible light. Herein, they can be used to write binary data. Furthermore, the open form can emit luminescence but the closed cannot while irradiated in another light that can't cause optical chemical reactions. Therefore, the data can be read out without damage.

Keywords: Photochromism; dithienylethene; Photochemistry; porphyrin; fluorescence and luminescence.

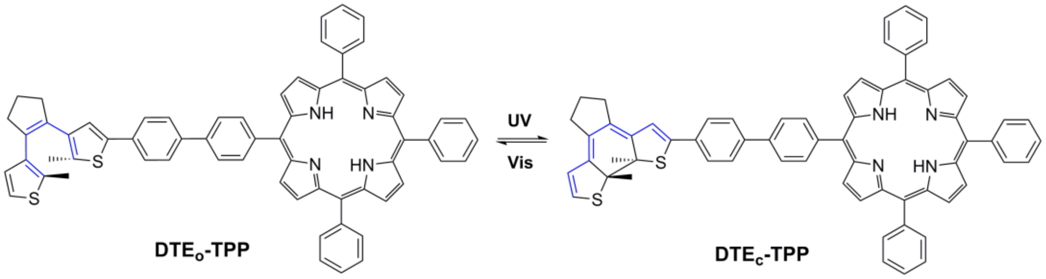
INTRODUCTION

Organic photochromic molecules have received increasing attention during the past decades because of their photo-reversibility [1]. They have shown a favorable potential in photonic applications of optical switch, photo-electronic devices and especially data storage [2]. Materials for fast and high density data storage are in a very high demand with the rapid development of current science and technology. With organic photochromic materials, writing and nondestructive reading [3] of information have been accomplished theoretically in all-photon mode at molecular or atomic scales within nanosecond or picosecond levels. And the fluorescent tuning [4] with fast response times and high sensitivity is now considered as the most convenient mean of modulating the variable properties for nondestructive data readout processing.

Photochromism is defined as light-induced reversible transformation of a molecule between two isomers having different absorption spectra. Several kinds of photochromic compounds have been reported, including diarylethenes [5], spiropyrans [6], fulgides [7], stilbenes [8], azobenzenes [9] etc. These compounds characteristically exhibit two different chemical forms (open-ring form and closed-ring form) which are transformed from one to the other upon irradiation with light of appropriate wavelengths. Among above, photochromic diarylethenes have attracted more attention owing to favorable thermal stability, high fatigue resistance and reliable photochromic reactivity in both solution and even solid state [10].

As an important application for photo-information storage, the photochromes can be used to store binary information by ultraviolet and visible light [11]. Two major problems [12] have been put forward for this application while reading the information. Firstly, the exciting light of readout device should not be absorbed by neither the open nor closed forms to avoid data corruption in reading process. Secondly, the readout is based on the emission fluorescence which should not cause the photo-chemical reactions to keep the data intact. A direct method to resolve the two problems is to separate the excitation and emission wavelengths from the absorption wavelength of both isomers. In this article, the method will be described in details.

Porphyrins [13] are known as natural molecules to absorb light strongly in the visible and near-UV, are often fluorescent with reasonably long excited singlet state lifetimes, and undergo reversible one-electron redox reactions. In the case that porphyrin is used as the luminescent center in combination with a dithienylethene and there is enough space with no overlap in energy and wave function between the two transitions. Hence, it would be apt to separate the excitation and luminescence from the two isomers. In this work, we will describe how a dithienylethene based on a porphyrin to constitute a photo-memory molecule with nondestructive readout capability. Porphyrins have been employed as fluorescent reporters in various photochromic molecular frame designed for the similar purposes [14]. In the clear majority of these cases, the bridges combine diarylethenes with porphyrins are always coordination bonds which are replaced by C-C bond in this article.



Scheme 1: Photo-chemical transitions of isomeric forms of the DTE-TPP.

The photochromic isomerization of DTE-TPP induced by photo irradiation in CH_2Cl_2 was measured by spectroscopic method at room temperature. The solution of switches readily turned from light pink to kelly green upon irradiating it with the UV light. The color change implies that the photochromic isomerization of 1,2-dithienylethene moiety from the open to the closed form occurs efficiently in porphyrinic switches as shown in Scheme 1. The dithienylethenes underwent photo-chemical transformations between ring-opening isomers and ring-closed isomers upon the alternating irradiation of UV and visible light. Figure 1 illustrates the changes in the UV-Vis spectra of DTE-TPP in CH_2Cl_2 upon irradiation with 254 nm light. The open form of DTE-TPP has obvious absorption at wavelength (λ = 272 nm). And the Soret band of porphyrin exists at wavelength (λ = 418 nm). Upon irradiation with UV light (λ = 254 nm), a new broad absorption band appears around 674 nm ranging from 635 to 755 nm because of the formation of the closed isomer of the DTE ligand in the photochrome. The green solution is bleached in a large extent after irradiation with visible light, and a small protuberance arises at 272 nm.

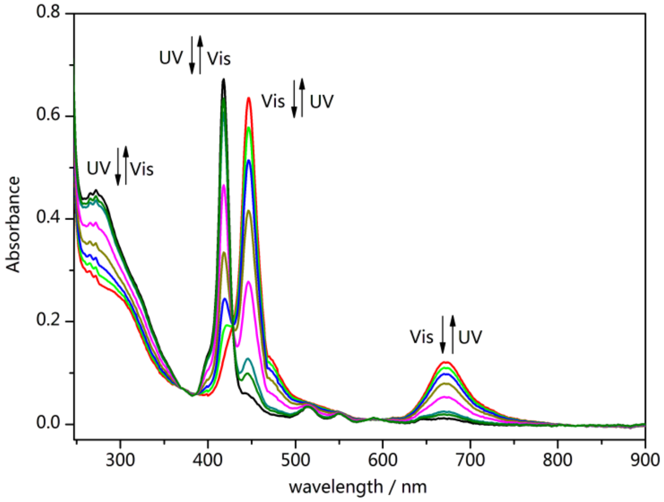


Figure 1: Changes in UV-Vis absorption spectra of a CH2Cl2 solution of the DTE-TPP upon irradiation with 254 nm light. Irradiation periods are 0, 10, 20, 40, 60, 80, 100 and 150 s. The irradiation intensity of UV light is 100 µW/cm^2 (λ=254 nm). The exciting light (λ=530 nm) comes from a Ultraviolet High Pressure Mercury Lamps （UV LAMP, 500 µW/cm^2） with a specific filter. The Visible light comes from the sunshine with a barrier filter and the intensity is ~320 µW/cm^2.

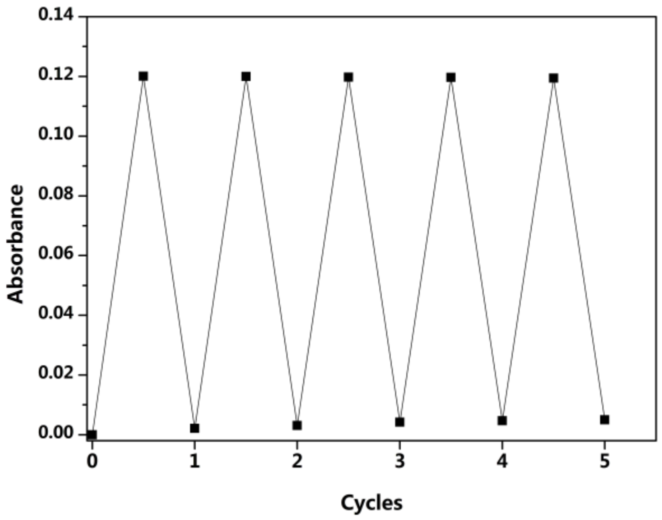


Figure 2: Cycling between the open and closed forms of the DTE-TPP by repetitive irradiation at λ = 254 nm for 3 min (high value) and visible light for 20 min (low value) at 20 °C in CH_2Cl_2. The ordinate shows the formation of the closed form as monitored by the absorbance at 674 nm.

A very important property of the optical switch is the fatigue resistance. Figure 2 shows the Photo cycling of DTE-TPP in solution of CH_2Cl_2 without degas. It indicates that the ring closed and open cycles of DTE-TPP are repeated at least 5 times with very little changes. Therefore, the porphyrinic dithienylethene DTE-TPP possesses feasible reversible photochromic property. Moreover, we have studied the influence of the molecular oxygen on the fatigue resistance as follows. We prepare two solutions of methanol of DTE-TPP in 1×10^{-6} M, degas by an ultrasound equipment (300 W) for 10 min, then the nitrogen and Oxygen are respectively bubbled into the two solutions for 20 min. Then, we measure the UV-Vis absorption of the two solution, after irradiation of the UV light (λ=254 nm) for 3 min, we measure the spectra again and no little distinction is observed. Then the two solutions are irradiated with the visible light (20 min) and the UV light (3 min) for 5 circles. There is no distinction in the UV-Vis spectra as before. The results indicate that the porphyrinc photochrome exhibits excellent fatigue resistance in even oxygen atmosphere.

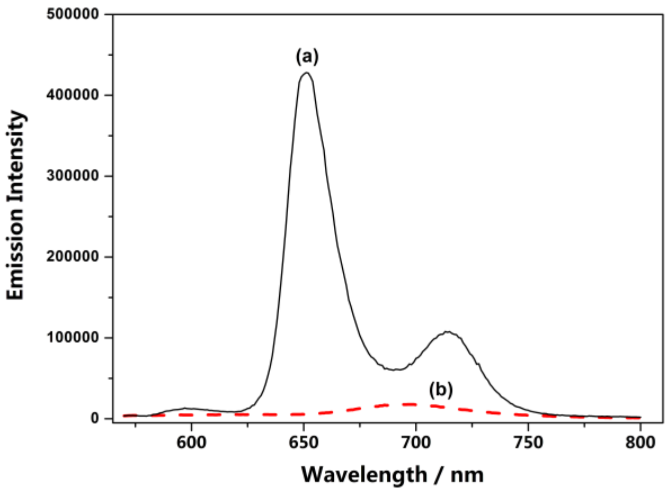


Figure 3: Emission spectra of DTE-TPP in solution of deoxygenated CH_2Cl_2 (a) the open form and (b) the closed form. λ_{ex} = 530 nm, λ_{em} = 651, 715 nm.

The open form of porphyrinic dithienylethene, DTEo-TPP, phosphoresces at 650-720 nm with slight varying intensities when excited throughout the UV-Vis region. Figure 3 illustrates that the open form of DTE-TPP emits high fluorescence intensity at 651 and 715 nm when induced at 530 nm. Irradiation of DTEo-TPP at 254 nm produced the ring-closed form DTEc-TPP. It exhibits strongly quenched porphyrin fluorescence. When DTEc-TPP is back irradiated at wavelengths greater than 550 nm, the DTEo-TPP is generated and the fluorescence restores at its original value. The fluorescence quenching in DTEc-TPP is attributed to the intramolecular energy transfer from the excited porphyrin to the closed dithienylethene units [11] because of the spectral overlapping in the range of 630-750 nm between the emission band from the pophyrin macrocycle and the enhanced absorption band of the closed dithienylethene ligand in switch DTE-TPP. Because of the energy transfer, the closed dithienylethene ligand absorbs the emitted light of the porphyrin range from 630 to 750 nm so that the fluorescence quenches. Moreover, the fluorescence emission intensity can be modulated by actinic reaction between the open and closed isomers. These results indicate that the fluorescence of the porphyrin macrocycles obviously depends on the state of the 1,2-dithienylethene ligand of the porphyrinic dithienylethene.

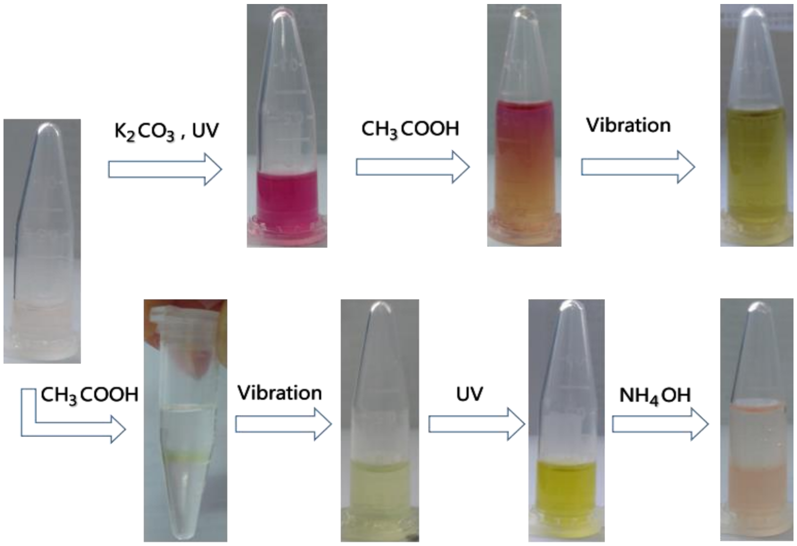
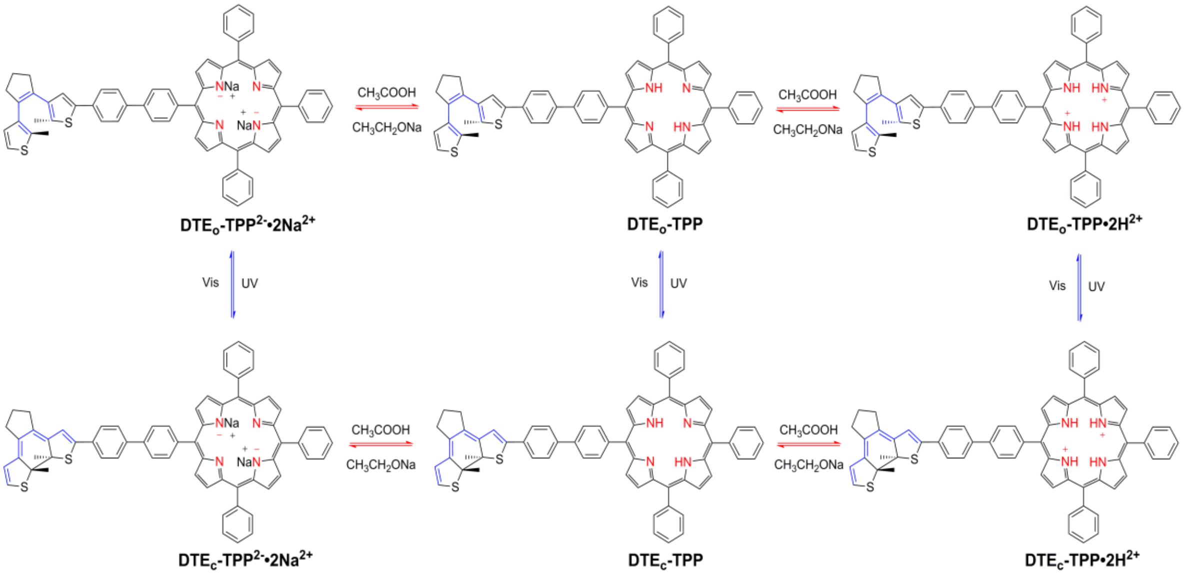


Figure 4: The color changes of the solution of CH_2Cl_2 of DTE-TPP.

In the study of photoinduced electron transfer in a dithienylethene-porphyrin-fulleren (DTE-P-C_{60}) published in J Am Chem Soc, D. Gust [15] has pointed that some ^{1}DTEc-P-C_{60} formed by energy will be converted to DTEo-P-C_{60} with the fraction converted depending on the quantum yield of isomerization. If this theory is also suitable for the DTE-TPP, it will bring a fatal blow on the nondestructive readout processing. To confirm it, we leave the solution of two isomers of DTE-TPP exposed under the light (λ = 530 nm, 500 μW/cm^2) for 20 min. No obvious distinction of UV-Vis absorption and luminescence spectra from that before irradiation are observed. This clearly demonstrates that this system is nondestructive under these conditions which is in accordance with axially coordinated porphyrinic photochromes [16].

In a general way, the solutions of the open form of great majority of diarylethenes are colorless, and the closed forms are usually dark colored. In this work, the open form of the solution of CH_2Cl_2 of DTE-TPP is light red that is because the porphyrinic derivatives are generally close to red. However, the color of the closed-ring form is green that different from us predict. To investigate the reason of the distinction, we designed the procedures as follows. First, we prepared a series of solutions of CH_2Cl_2, THF, EtOAc and DMSO of DTE-TPP in about 10^{-7} M. They are all nearly colorless but with a bit red. After irradiation with light at 254 nm for 20 mins, they all turned dark red except the solution of CH_2Cl_2. We predict that the reason may be the generation of acid by the irradiation upon UV light on CH_2Cl_2. To confirm our prediction, double solutions of CH_2Cl_2 was prepared and one of them was irradiated upon the UV light followed the addition of K_2CO_3 powder. To the other one, equal quantity of acetic acid was added carefully and the interface of the two solutions turned green. After vibration, the solutions blend to one phase and show green, then were moved to the UV light. After irradiation for 20 mins, the first one with K_2CO_3 turned deep red and the second one with CH_3COOH turned deep green. To the first one, the equal quality of glacial acetic acid was added, after vibration, the solution turned green. The second solution turned red after addition of ammonium hydroxide. These results indicate that the solution of CH_2Cl_2 of DTE-TPP shows red in acid and green in basic condition. The irradiation of UV light makes it turned from light to dark (Figure 4).



Scheme 2: Schematic of DTE-TPP in alcoholic solution.

To figure out the structure changes of DTE-TPP on each stage, we measured their UV-Vis spectra and ^{1}H-NMR Spectra. Scheme 2 exhibits the schematic of a DTE-TPP molecule in an alcoholic environment illustrating the closed states, the open states before and after irradiation with appropriate light, and the structures of porphyrin after protonation and alkalization. The protonation of porphyrin molecule with acetic acid will increase the Hydrogens based on nitrogen at $\delta = -2.76$ ppm. And inversely, the alkalization will make the Hydrogens disappear. No matter the porphyrin chromophore exist as a neutral, acerbic, or alkaline group, the dithienylethene will converted from the light-color open form to the deep-color closed form upon the irradiation of UV light ($\lambda = 254$ nm) and will bleach in visible light.

In summary, this work has shown that each of the two isomers of DTE-TPP exhibit the distinctions on structure and spectroscopy. The nondestructive readout method is clearly demonstrated when appropriate light is handled followed by detection of the responding emission after writing binary data for the application in optical information storage and any more photoelectricity-control devices.

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