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Original article

A novel photochromic fulgide based on porphyrin for nondestructive information processing

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ABSTRACT

A fulgide connected to porphyrin (FUL-TPP) can transform its open isomer to closed isomer upon the irradiation with UV or visible light. Herein, they can be used to write binary data. Furthermore, the open form can emit luminescence but the closed cannot form while irradiated in another light that will not cause the optical chemical reaction. Therefore, the data can be read out without destruction.

1. Introduction

The photochromic molecules have attracted increasing attention during the past decades because of their photoreversibility [1–3]. Nondestructive readout is one of the most attractive aims [4] in optical materials for their applications in optic devices [5]. The fluorescent tuning has been a convenient mean of modulating the variable properties owing to the fast response times and high sensitivity [6,7].

Photochromism is defined as reversible chemical transition of a molecule with irradiation upon appropriate light. Two isomers show different structures and absorption spectra. Many kinds of photochromic compounds have been reported in the past decades, including diarylethenes [8], spiropyrans [9], fulguides [10], stilbenes [11], azobenzenes [12], etc. Among above, the fulgides always exhibit favorable thermal stability, high fatigue resistance and reliable phohochromic reactivity in both solution and even solid state. The fulgides could be used to store binary information by ultraviolet and visible light for the application for photo-information storage due to the excellent photochromic characteristics. However, two major problems should be resolved for the application while reading the stored data. Firstly, the exciting light of readout device would not be absorbed by either the open or the closed forms to avoid data damage in reading process. Secondly, the readout is based on the emissive luminescence which should not cause the photochemical reaction. Obviously, the direct method to resolve the dilemma is to separate the excitation and emission wavelengths from the absorption wavelengths of both isomers. In this article, the porphyrin was used as the luminescent center of fulgide and the method for nondestructive readout will be described in details.

Porphyrins [13] are known as natural molecules to exhibit characteristic Soret band in ultraviolet region and Q band in visible region and they will offer luminescence upon excitation. Therefore, they have been recognized as a class of popular luminescent materials that are applicable to bioassays, dyes, photosensitizer and other practical applications. In the case that porphyrin is used as the luminescent center in combination with a fulgide and there will be enough space with no overlap in energy and wave function between the two transitions. Hence, it would be apt to separate the excitation and luminescent from the two isomers. In this work, we will describe how a fulgide 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 frames designed for the similar purposes [14–19].

2. Experimental

To a stirred solution of isopropylidene diethyl succinate (3.0 g, 14.0 mmol) in tetrahydrofuran (50 mL) at 0 °C under nitrogen was

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added NaH (0.8 g, 20.0 mmol) rapidly. The resulting mixture was stirred for 30 min. The solution of 5-chloro-2-methyl-3-acetylthiophene (1.74 g, 10.0 mmol) in THF (20 mL) was added and the mixture was allowed to warm to room temperature. After 8 h, the solvent was removed. The resulting brown syrup was dissolved in ethyl acetate (50 mL) and acidified with conc. HCl (10 mL). The reaction mixture was extracted with ethyl acetate (2 × 20 mL). The combined organic layers were dried ($MgSO_4$) and filtered, and solvent was removed in vacuum. The semi-ester product was dissolved in 10% KOH-alcohol liquor (50 mL) and the solution refluxed for 2 h. Cold it to room temperature and acidified with conc. HCl (10 mL). The resulting mixture was extracted with ethyl acetate (2 × 20 mL). The combined organic layers were dried ($MgSO_4$) and filtered, and solvent was removed in vacuum. The residue was dissolved in anhydrous dichloromethane and acetylchloride (2 mL) was added at ice-cold bath. After 8 h, the solvent was removed and afforded the target compound. Purification by chromatography on silica gel with petroleum ether-EtOAc (1:10) to yield fulgide 1.98 g (66.9%) as yellow solid. To a stirred solution of anhydrous CH_2Cl_2 of fulgide (30 mg, 0.1 mmol) and NH_2-TPP (70 mg, 0.11 mmol), 1 mL of Et_3N was added dropwise and the mixture was refluxed for 5 h. Cool it down to room temperature, and 2 mol/L HCl was added to the pH 4∼5. The resulting mixture was extracted with CH_2Cl_2 (2 × 20 mL) and washed with water (3 × 20 mL) to the pH 7. The combined organic layers were dried ($MgSO_4$) and filtered, and solvent was removed in vacuum to yield 51 mg (59.2%) as amaranthine solid. The solid was dissolved in CH_2Cl_2 (15 mL) and 2 mL trifluoroacetic anhyride added. The solution turned red to green rapidly. The mixtures were stirred at room temperature for another 3 h. After reaction, the solution was removed in vacuum and the residue was washed with saturated $NaHCO_3$ aqueous solution, extracted with CH_2Cl_2, dried with $MgSO_4$ and filtered. The solution was removed in vacuum. Purification by chromatography on silica gel with petroleum ether: CH_2Cl_2 (5: 1) to yield 48 mg (51.6%) as violet solid. mp: > 250 °C. ^1H NMR ($CDCl_3$, 500 MHz): δ 9.04 (s, 2H), 8.78 (s, 6H), 8.41 (s, 2H), 7.92∼7.89 (m, 17H), 7.17 (s, 1H), 2.85 (s, 3H), 2.52 (s, 3H), 2.23 (s, 3H), 1.21 (s, 3H), -2.60 (s, 2H); ^{13}C NMR ($CDCl_3$, 127 MHz): δ 167.6, 166.6, 166.1, 159.5, 146.8, 142.3, 137.0, 135.6, 134.4, 133.7, 132.0, 131.9, 131.0, 129.1, 128.6, 128.1, 127.9, 125.9, 124.3, 120.1, 119.7, 22.0, 21.8, 14.6; IR (KBr) ν: 3455, 3369, 3315, 3052, 3023, 2918, 1812, 1616, 1596, 1510, 1470, 1440, 1349, 1279, 1176, 979, 796, 729, 698 cm^{-1}; MS(ESI, m/z): 908.24 $[M + H]^+$.

3. Results and discussion

For the first time, the structure and isomerization of the FUL-TPP used in this work are shown in Scheme 1. The open form of FUL-TPP in CH_2Cl_2 has nearly no absorption band in the visible region. Upon irradiation with UV light (λ = 254 nm), the pink solution turned kelly and a new absorption band appeared around 667 nm ranging from 637 to 714 nm. Another interesting phenomenon shown in Fig. 1 is that the absorption in Soret band of porphyrin red shift from 418 to 448 nm of FUL-TPP due to the increasing electron density from the gradual formation of the closed isomer. The green solution was bleached in a large extent after irradiation with visible light, and a small protuberance arises at nearly 273 nm. These ring closing and opening cycles were repeated at least 10 times (Fig. 2). Therefore, the FUL-TPP showed feasible reversible photochromic reaction (Scheme 2).

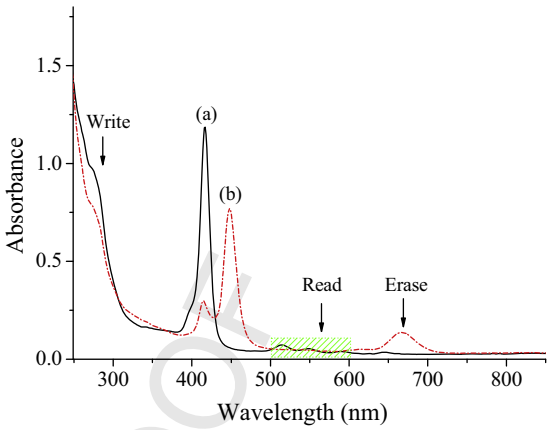


Fig. 1. UV–Vis absorption spectra of a CH_2Cl_2 solution of the FUL-TPP: (a) open form, (b) closed form.

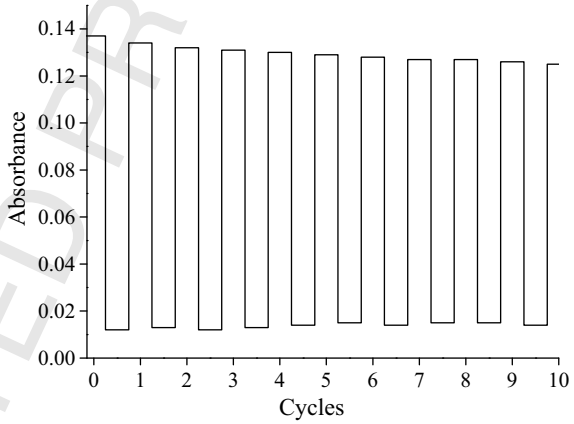
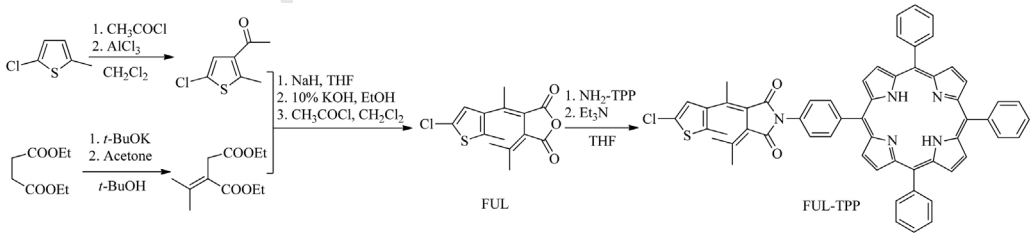


Fig. 2. Photocycling of the FUL-TPP in solution of CH_2Cl_2. The absorbance at λ = 667 nm measured for 5 s after each switching operation are shown: after UV irradiation for 2 min (high value) and after visible light irradiation for 20 min (low value).

The compound FUL-TPP-O can emit fluorescence at 627 nm when induced with the UV–Vis region (Fig. 3). The excitation wavelengths exist in a window from 500 to 600 nm. Accordingly, their closed isomeric forms luminescence quenched while excited at the corresponding light. Meanwhile, both FUL-TPP-O and FUL-TPP-C would not be converted to each other under irradiation with the light in this region. Hence, a nondestructive readout method would be achieved. Moreover, the emission intensity could be modulated by actinic reaction between the open and closed isomers.



Scheme 1. Synthetic route of the FUL-TPP.