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Photo-driven molecular switch based on the photochromism and solvatochromism of diarylethene dialdehyde

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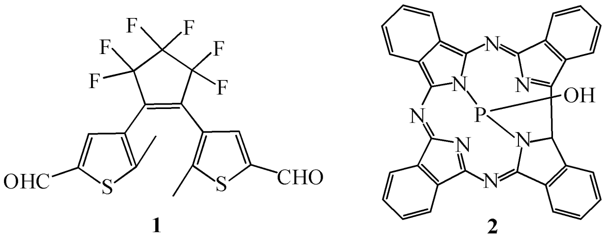
The two distinct characters of diarylethene dialdehyde derivative-photochromism and solvatochromism are displayed in particular circumstances. The fluorescence of phosphorus (III) tetrabenzotriazacorrole can be reversibly regulated by the three kinds of status of the diarylethene dialdehyde, colorless ring-opened form, red ring-closed form, and blue ring-closed form, which is gated by visible light, ultraviolet light and ethanol individually or jointly. Based on this effect, a novel molecular INH logic switch is proposed.

diarylethene, photochromism, solvatochromism, INH logic switch

Photochromic materials have attracted remarkable attention for their potential applications in optoelectronic devices such as optical memories and photoinduced switches[1]. Among these materials, diarylethene derivatives are the most promising candidates because of their notable thermal stability and outstanding fatigue resistance[2]. The conventional approaches have been used through controlling their conformations (parallel or antiparallel)[3], changing the acid strength[4], tuning the intramolecular proton transfer[5], and coordinating with ions[6]. In order to convert chemical, light, and thermal input signals into specific output signals, efficient strategies could be carried out by exploiting the mutual interaction between different kinds of state of diarylethene and a compatible molecule or molecular unit[7].

What is more, mimicking the functions of semiconductor logic gates used in modern computing is of particular interest. Using ions, molecules and light as inputs, the logic gate functions have been demonstrated, including the ID (or YES)[8], AND[9], OR[10], NOT[11], XOR[12] and the inhibiting (INH)[13] logic functions.

In this report, we present an example of a 1,2-dithienylalkene derivative that shows both photochromism and solvatochromism. Meanwhile, this report also provides a new example of energy transfer from the chromophore to the multistates of diarylethene components controlled by more than two types of external inputs. On the basis of this result, a novel photo-driven molecular INH logic switch is projected.



1 **2**

Scheme 1 The structure of diarylethene dialdehyde 1 and phosphorus tetrabenzotriazacorrole 2.

The photochromic diarylethene, 1,2-bis(2-methyl-5-formyl-thien-3-yl) perfluorocyclopentene 1 (BMFTP), was synthesized according to the previous ref. [14]. The

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phthalocyanine-like compound, phosphorus tetrabenzotriazacorrole 2 (TBC), was synthesized according to the ref. [15]. The products were detected by IR, MS and NMR analyses. BMFTP interconvert between colorless ring-open isomer BMFTP(O) and colored ring-closed isomer BMFTP(C) by alternating irradiation with UV and visible light, respectively. The UV-Vis absorption spectra of ring-open and ring-closed isomers for BMFTP are shown in Figure 1. Irradiated with 254 nm UV light, the colorless BMFTP(O) in THF was converted to blue, and the maximum absorption wavelength was 620 nm. The ring-closed isomer BMFTP(C) was the product of photocyclization.

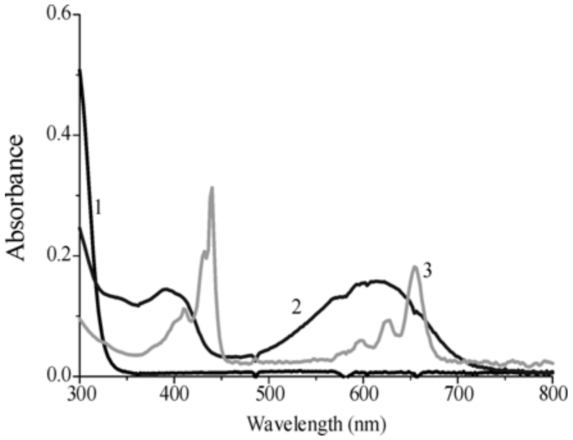


Figure 1 The UV-Vis absorption spectra of BMFTP(O) (curve 1), BMFTP(C) (curve 2) and TBC (curve 3) in THF.

It was found that the addition of alcohol to the BMFTP(C) solution could cause the blue-shift of the absorption spectrum. For instance, adding 20 equiv. ethanol to the THF solution of BMFTP(C) resulted in shifting the maximum absorption wavelength from 620 to 534 nm (Figure 2). The absorption wavelength was blue-shifted about 86 nm. During this process, the molecular system was stayed in dark. However, the solvatochromism could not be found with other diarylethene derivatives without aldehyde group. Although the color of the solution was different, the molecules were still the ring-closed isomers. If the solution was irradiated with 254 nm UV light again, the color would return back to blue. On the other hand, if the red-colored solution was irradiated by visible light, the solution would be colorless. It showed that the aldehyde groups might have generated strong H-bond with ethanol. The H-bond resulted in the blue-shift of the absorption spectrum and changed the color of solution from blue to red. When the red solution was irradiated by UV again, the H-bond could be broken, and then the colored ring-closed isomer appeared blue again. Under the irradiation of visible light, the red-colored ring-closed isomer BMFTP(C) was photoinduced to form colorless ring-open isomer BMFTP(O).

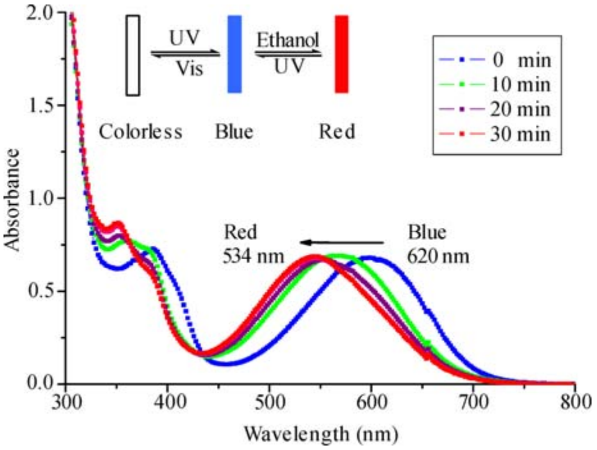


Figure 2 The absorption spectra movement of BMFTP(C) in THF with the addition of ethanol.

The blue-shift effect of diaryethene dialdehyde could be used as the shutter of the fluorescence. This assumption was confirmed with the mixture THF solution of diarylethene 1 and TBC 2 (Scheme 2). The BMFTP and TBC were dissolved in THF with the concentration of 1×10^{-4} mol/L, respectively. In this system, TBC displays the typical fluorescence with $\lambda_{\max}$=659 nm. The ring-open and ring-closed isomers of BMFTP have no fluorescence. The difference of two kinds of isomers of BMFTP is the absorption spectra. BMFTP(C) shows absorption at the wavelength range of 500—700 nm, while, BMFTP(O) has no absorption. Therefore, the initial mixture solution of 1 and 2 in THF showed a strong fluorescence emission with $\lambda_{\max}$=659 nm (curve 3 in Figure 3). Under the irradiation with ultraviolet light, the ring-open BMFTP(O) was photoisomerized to the ring-closed BMFTP(C), and the fluorescence intensity of the mixture solution was reduced to ca. 19.3% of the initial value at 659 nm (curve 2 in Figure 3). The fluorescence of TBC was greatly quenched. The effect was based on the fact that the BMFTP(C) had relatively strong absorption in the fluorescence emission wavelength range, and the energy transfer from TBC to BMFTP(C) could take place efficiently. The ring-open isomer BMFTP(O) had no such absorption band, so the fluorescence of TBC was stronger at the initial mixture state without UV irradiation.

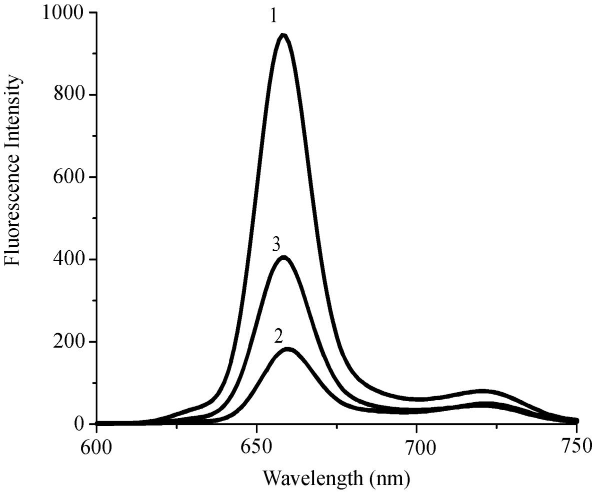
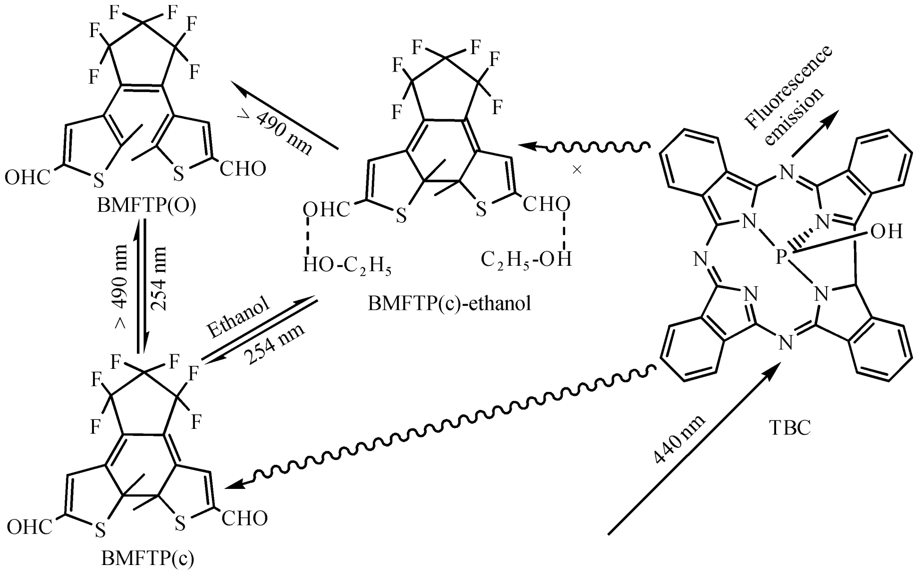


Figure 3 The fluorescence spectra of BMFTP-TBC system. Curve 1, The initial fluorescence spectra of the mixture solution of BMFTP and TBC in THF; curve 2, the fluorescence spectra of the mixture solution of BMFTP and TBC in THF irradiated by 254 nm UV light; curve 3, the fluorescence spectra of the above solution was added 20 equiv. of ethanol in dark after 30 min. The 440 nm light was used to excite the solution for the fluorescence detecting.

Further investigations of the mixture THF solution of BMFTP and TBC were carried out. Once the BMFTP(C) in solution was photocyclized by the irradiation of ultraviolet light, 20 equiv. of ethanol was added into the solution. The blue color of the mixture solution was gradually changed to red in 30 min in dark. The absorption spectrum movement would obviously decrease the spectral overlap of the fluorescence emission band of TBC and the absorption band of the BMFTP(C). As a result of the spectral blue-shift, the energy transfer from TBC to BMFTP(C) would have lower efficiency, and the fluorescence intensity of TBC was increased to ca. 42.9% of the initial value at 659nm (curve 3 in Figure 3). Thus, the addition of the ethanol led to an opening efficient pathway for the mutual interaction between TBC and BMFTP(C).

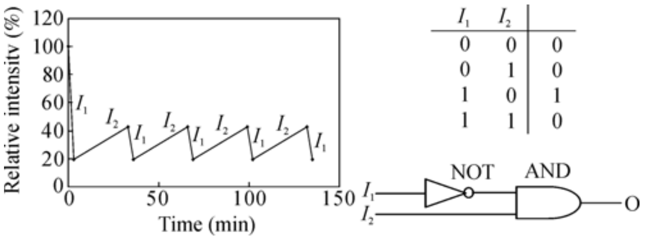
As expected, diarylethene 1 showed the corresponding photoswitching behavior as indicated in Scheme 2. In the mixture molecular system of BMFTP and TBC, the UV light acted as the shutter of the switch, and the ethanol acted as the shutter contact duration. Under the synergistical action of UV and ethanol, the fluorescence of TBC in the above mixture solution could be reversibly switched on (>ca. 20%) or off (<ca. 20%) consecutively by using UV to return the diarylethene dialdehyde used as BMFTP(C) individual units and ethanol to shift the absorption spectrum of BMFTP(C). The energy transfer used as the signal communication between TBC and the three kinds of status of BMFTP is gated by the visible light, ultraviolet light and ethanol.

The INH logic switch is the function which can be interpreted as a particular integration of an AND and a NOT logic functions, where the output signal is inhibited by one of the active inputs. Recently, the more complex two-input or three-input integrated INH logic gates were testified[16]. However, the fundamental photo-driven two-input INH gate has not been reported. Here, we demonstrate that the diarylethene dialdehyde based on TBC yields such an INH logic gate, which is derived by light and ethanol. The corresponding combinational



Scheme 2 Signal communication pattern between 1 and 2.

logic circuit incorporating two logic gates is illustrated in Scheme 3. The two inputs are UV I1 and ethanol I2.



I_1	I_2	
0	0	0
0	1	0
1	0	1
1	1	0

Scheme 3 Demonstration of the reversible fluorescence intensity alteration, the truth table and the corresponding INH logic circuit. I1 and I2 are UV and ethanol, respectively. The output signal (O) is 0 when the relative emission intensity at 659 nm is greater than ca. 20% of the initial value, otherwise it is 1.

The output signal is the fluorescence of the TBC. In order to comply with the truth table of INH logic function, the output value 0 indicates that the fluorescence intensity of the system is greater than ca. 20% of the initial value, and in other conditions, the output value is 1. UV and ethanol are both active inputs for the gating switch of fluorescence.

In summary, the present study is based on fluorescence quenching mechanism, which is dependent on a certain degree of overlap of the absorption bands of the molecular switch and the emission bands of the fluorescent molecule. The significant photochromism and solvatochromism effects could be used to regulate the fluorescence of phosphorus (III) tetrabenzotriazacorrole. A novel light-controlled molecular INH logic switch is constructed, whose two inputs are ultraviolet and ethanol, and output signal is the fluorescence of phosphorus (III) tetrabenzotriazacorrole.

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