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Excitation Energy Transfer from Rhodamine 6G to Photochromic Fulgide

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In this work, a new fluorescence photoswitching system consisting of fulgide as a photochrome and rhodamine 6G as a fluorophor was designed and studied in methanol, dichloromethane and dioxane. The spectra of both the closed form of fulgide and rhodamine 6G were overlapped. Since the fulgide exhibited non-fluorescence, the emission spectra of blended system were attributed to rhodamine 6G only. The intensity of the fluorescence emission spectra of the rhodamine 6G was modified by the photochromism of fulgide upon irradiation with UV light at different time in methanol, dichloromethane and dioxane. The blended system exhibited quenching in fluorescence emission spectra in different solvents.

Keywords: Excitation energy, Transfer, Rhodamine 6G, Fulgide.

INTRODUCTION

Photochromic compounds which undergo a reversible photochromism reaction upon irradiation have widely been studied from fundamental academic research and the potential applications such as photo-responsive materials. The vast range of applications of photochromic materials was the subject of intensive studies in the past decade, such applications related to optical data storage and fluorescence switching devices[1-6]. Fulgides derivatives are one of the most important types of photochromic compounds. In 1905, fulgide was synthesized by Stobb as a derivative of 1,3-butadiene-2,3-dicarboxylic acid[7]. The phototransformation of fulgide from open form to closed form was reported by Becker *et al.*[8] Heller *et al.*[9,10] studied the photochromic and thermal irreversible reaction of fulgide. Indolylfulgide with trifluoroethylidene group were studied by Yokoyama *et al.*[11] and exhibited excellent photochromic irreversible transformation upon photo-irradiation in solution and in solid rigid matrices. One of the most important properties of fulgides their hydrolytic stability which make it promising material to used in memory devices and biological photo switches[12-14].

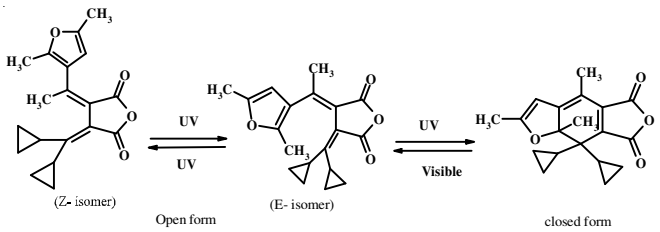
Upon irradiation with UV light, fulgide undergoes a reversible photo-transformation from the colourless open form to the deep colourd closed form (**Scheme-I**). The formation of the coloured form is accompanied by quenching of flourecence spectra of the closed form. Reversely, closed form returned to its initial open form upon irradition with visible light accompained by returning the emission intensity to the initial state[15].

The phototransformation of photochromic compounds upon irradiation with two different light which in conjunction with a change in flourecence is one of the important phenomina. So far, extensive studies reported in the fluorescence switching *via* reversible photoisomerization based on photochromic compounds[16-20].

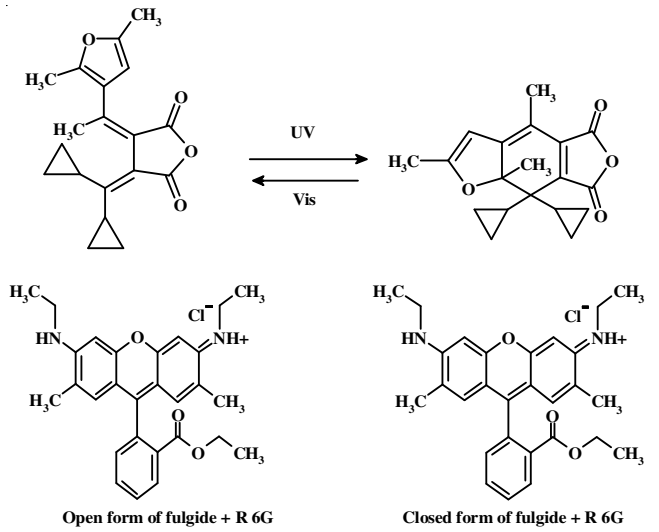
The modulation of fluorescence switching systems depends on the blended of fluorophore and photochromic compound into one molecule[21-24]. In this system, the modification of fluourescence spectra depends on electron transfer or energy transfer by photoisomerization process[25-30]. In this work we present a new fluorescence switching system based on fulgide as a photochromic compound (energy acceptor) and rhodamine 6G as a fluorescent dye (energy donor) in different solvents as shown in **Scheme-II**. The spectral overlap between the absorption spectra of the photochromic compound and emission spectra of fluorescent dye is important condition to modulat a fluorescence switching system[31-33].

EXPERIMENTAL

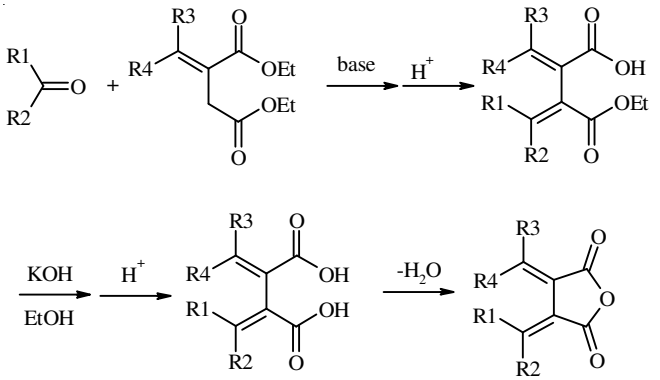
Fulgide was prepared according to reported method[34], as shown in **Scheme-III**. The solvents used for this studies were spectroscopic grade. Rhodamine R6G was obtained from Aldrich and used without further purification. The UV-visible electronic absorption spectra measurements were carried out



Scheme-I: Photo-transformation of fulgide from open to closed form



Scheme-II: Illustration of fluorescence switching system consisting of fulgide blended with rhodamine 6G



Scheme-III: Synthetic route of fulgide

by MultiSpec-1501 UV-visible Shimadzu spectrophotometer. fluorescence measurements were done using a Perkin-Elmer LS 55 fluorescence spectrometer. Photoirradiation was carried out with 3UVTM multi-wavelength UV lamp. Light intensity was measured using ferrioxalate actinometry[35]. The photochemical quantum Φ_c of phototransformation was calculated using the method described earlier[36].

RESULTS AND DISCUSSION

Fulgide can undergoes a reversible photochromism reaction when exposed to UV and visible light at different time in different solvents. Figs. 1-3 showed the absorption spectra of fulgide in methanol, dichloromethane and dioxane induced by photo-irradation at different time. Under irrradiation with UV light with 365 nm the colourless solution of fulgide became red due to the appearance of a new absorption band at (522, 530 and 508 nm) in methanol, dichloromethane and respectively, the new band attributed to the formation of closed ring of fulgide. The red solution of fulgide became colourless upon irradiation with visible light due to the transformation of closed ring to open ring. The photochemical quantum yield Φ_c of photo-transformation was calculated as 0.0083, 0.022, and 0.0135 in methanol, dichloromethane and dioxane, respectively.

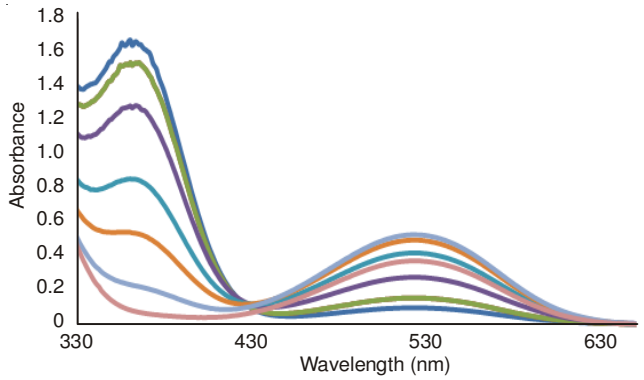


Fig. 1. Absorption spectra of fulgide by photo-irradiation at 0, 1, 2, 4, 9, 17 and 23 min in MeOH (C = 1 × 10^{-4} mol/L)

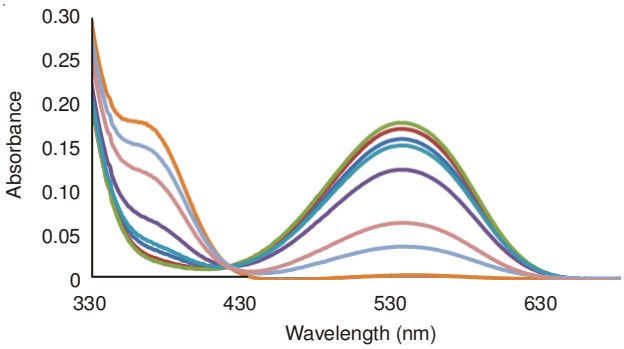


Fig. 2. Absorption spectra of fulgide by photo-irradiation at 0, 1, 2, 5, 8, 11, 16 and 26 min in dichloromethane (C = 1 × 10^{-4} mol/L)

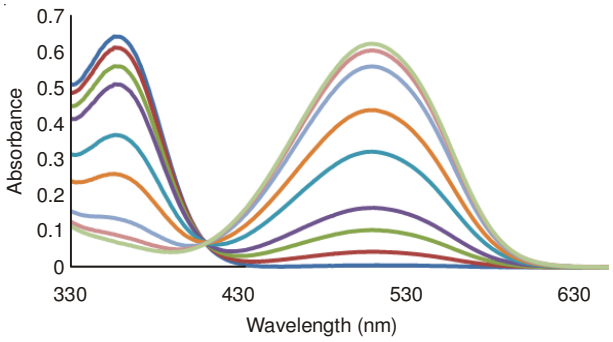


Fig. 3. Absorption spectra of fulgide by photo-irradiation at 0, 1, 2, 5, 8, 13, 18, 30 and 43 min in dioxane (C = 1 × 10^{-4} mol/L)

The absorption spectra of a system consisting of fulgide as a photochrome and rhodamine 6G as a fluorophor induced by photoirradiation at different time were measured in methanol, dichloromethane and dioxane, as shown in Figs. 4-6. In the absorption spectra of blended system, a sharp absorption bands at (545, 544 and 559 nm) in methanol, dichloromethane and dioxane, respectively were observed which attributed to the rhodamine 6G. By irradiation with UV light at different time the visible absorption band of the blended system became broader and stronger due to the overlap between the absorption

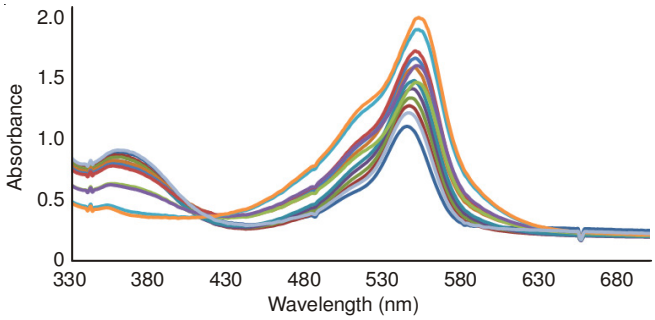


Fig. 4. Absorption of fulgide (C = 1 × 10^{-4} mol/L) blended with rhodamine 6G (C = 1 × 10^{-5} mol/L) by photo-irradiation at 0, 0.5, 1, 1.5, 2, 3, 3.5, 4, 5, 7, 9 and 11 min in MeOH

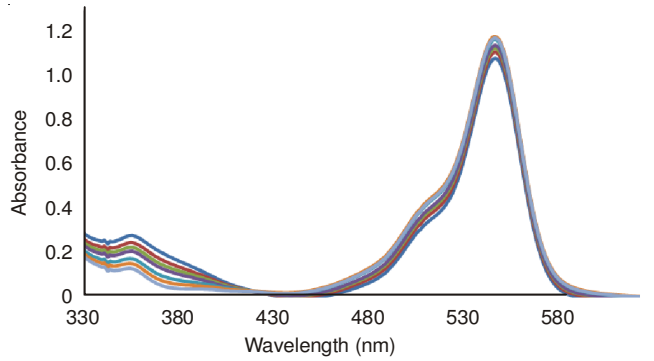


Fig. 5. Absorption of fulgide (C = 1 × 10^{-4} mol/L) blended with rhodamine 6G (C = 1 × 10^{-5} mol/L) by photo-irradiation at 0, 0.5, 1, 1.5, 2, 3, 3.5, 4, 5, 7, 9 and 11 min in dichloromethane

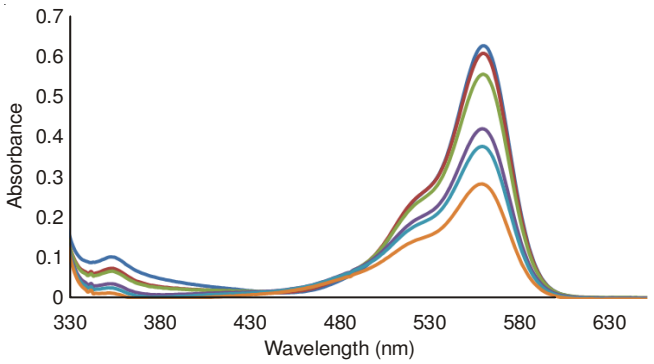


Fig. 6. Absorption of fulgide (C = 1 × 10^{-4} mol/L) blended with rhodamin 6G (C = 1 × 10^{-5} mol/L) by photo-irradiation at 0, 0.5, 1, 1.5, 2, 3 and 5 min in dioxan

spectra of fulgide in closed form and absorption spectra of rhodamine 6G.

Fig. 7 showed the emission spectra of fulgide and rhodamine 6G in different solvents. As observed, there is no fluorescence emission in fulgide in the region of 400-700 nm in different solvents. On the other hand rhodamine 6G exhibited emission peaks at (574, 583 and 576 nm) in methanol, dichloromethane and dioxane, respectively when excited at 520 nm. The results showed that the emission spectra of blended system was attributed to rhodamine 6G only.

The absorption spectra of fulgide and the emission spectra of rhodamine 6G were studied in different solvents (Fig. 8). The results exhibited no overlap between the absorption spectra of the open form of fulgide and the emission spectra of rhodamine 6G. Upon irradiation with UV light, a new absorption band was exhibited in the region 400-700 nm which was attributed

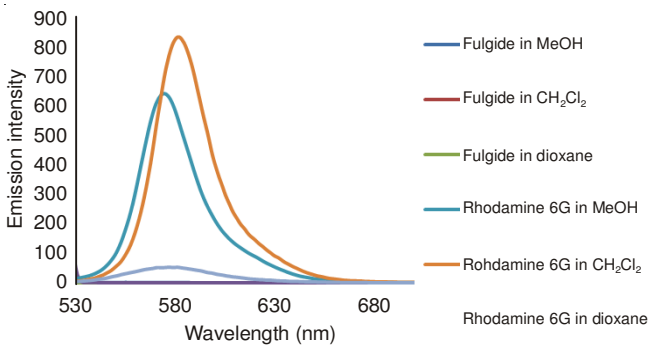


Fig. 7. Emission spectra of fulgide (C = 1 × 10^{-4} mol/L) and rhodamine 6G in MeOH, CH_2Cl_2 and dioxane (C = 1 × 10^{-5} mol /L), excited at 520 nm

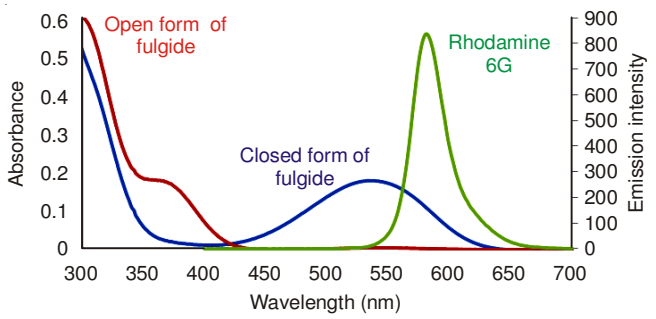


Fig. 8. Absorption spectra of fulgide and emission spectrum of rhodamine 6G in CH_2Cl_2

to the formation of closed form of fulgide. The new absorption band for the closed form of fulgide is overlapped with the emmesion band of rhodamine 6G. This spectral overlap resulted in energy transfer process between closed form of fulgide and rhodamine 6G.

The emission spectra of the blended system in different solvents were measured upon irradiation at different time with an excitation at 520 nm (Figs. 9-11). The blended system showed emission bands with λ_{max} at (574, 573 and 576 nm)

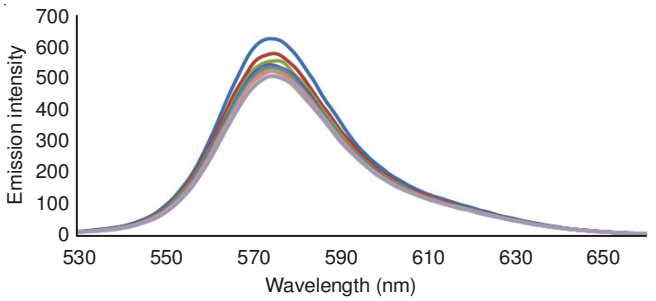


Fig. 9a. Emission spectra of fulgide blended with rhodamine 6G in MeOH upon irradiation with UV light at 0, 0.5, 1, 1.5, 2, 3, 3.5, 4, 6.5 and 8.5 min

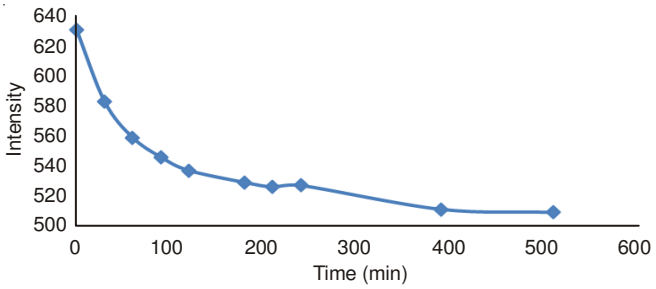


Fig. 9b. Plot of emission intensities for fulgide blended with rhodamine 6G *versus* radiation time in MeOH

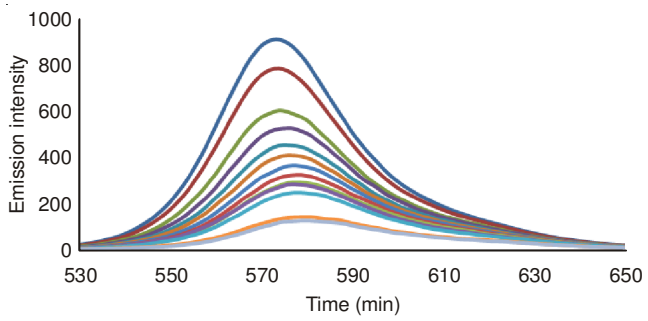


Fig. 10a. Emission spectra of fulgide blended with rhodamine 6G in CH_2Cl_2 upon irradiation with UV light at 0, 0.5, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5.5, 6.5, 13.5 and 23.5 min

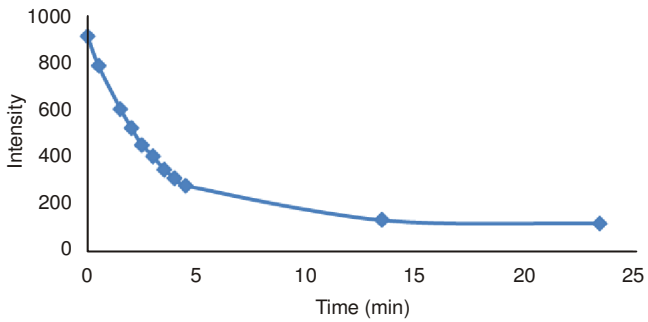


Fig.10b. Plot of emission intensities for fulgide blended with rhodamine 6G *versus* irradiation time in CH_2Cl_2

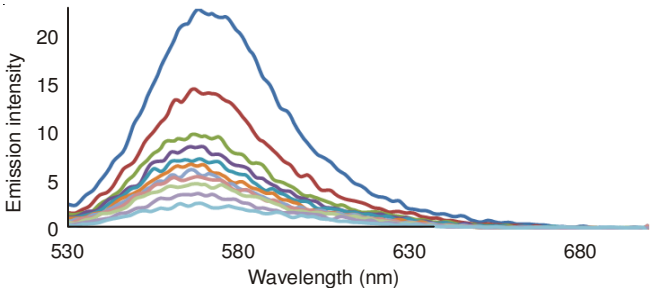


Fig. 11a. Emission spectra of fulgide blended with rhodamine 6G in dioxane upon irradiation with UV light at 0, 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 7 and 10 min

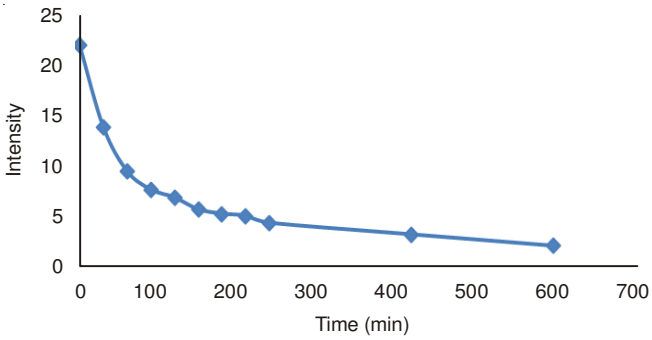
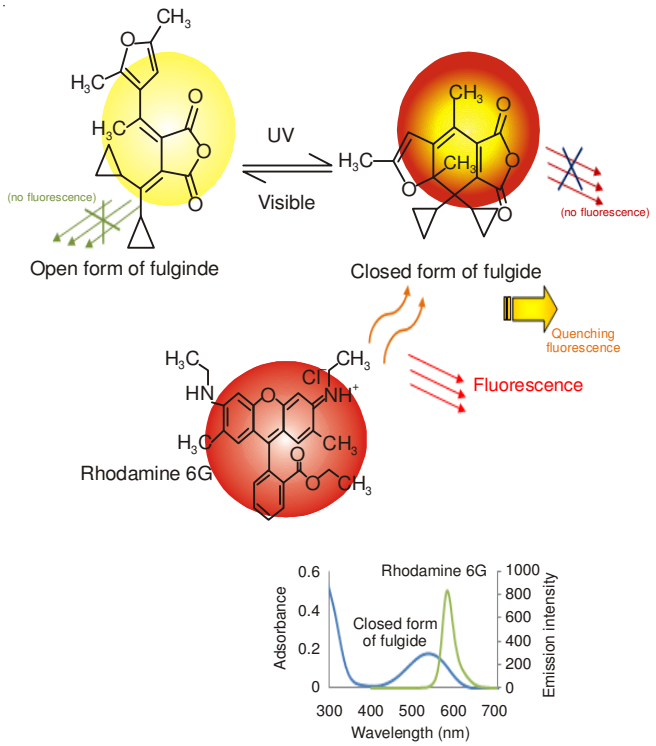


Fig. 11b. Plot of emission intensities for fulgide blended with rhodamine 6G *versus* radiation time in dioxane

in methanol, dichloromethane, dioxane, respectively, which attributed to rhodamine 6G only. The intensity of the emission band for blended system decrease by irradiation with UV light at different time.

In this study, the fluorescence emission of the system consisting of fulgide as a photochrome and rhodamine 6G as a fluorophor could be modified by photochromism of fulgide upon irradiation with UV and visible light in different solvents. Since the emission spectra of fluorophor rhodamine 6G overlapped with the absorption spectra of the closed form of fulgide, few photons absorbed by the fluorophor rhodamine 6G with increasing the concentration of the closed form of fulgide which led to quenching in emission spectra of blended system. The quenching in the fluorescence spectra was attributed to the intermolecular energy transfer between fulgide (energy acceptor) and rhodamine 6G (energy donor) as shown in **Scheme-IV**. The intensity of fluorescence emission of rhodamine 6G decreased by increasing the concentration of closed form of fulgide.



Scheme-IV: Intermolecular energy transfer between fulgide and rhodamine 6G

Conclusion

A new fluorescence switch system consisting a photochromic fulgide and rhodamine 6G as a fluorophor has been designed and studied. The fluorescence emission spectra of rhodamine 6G could be modulated by photoisomerization of fulgide by controlling the time of irradiation. The absorption spectra of closed form of fulgide overlapped with the emission spectra of rhodamine 6G. The emission spectra of the blended system attributed to of rhodamine 6G only. This system exhibited high quenching in the fluorescence spectra, which makes it one of the most important promising candidates as optical storage.

ACKNOWLEDGEMENTS

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