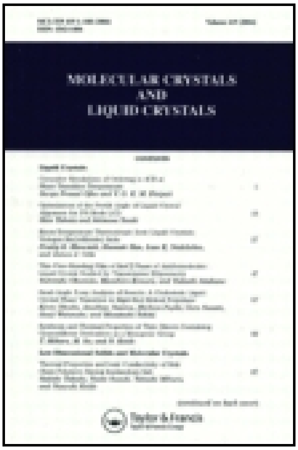

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STUDIES ON PHOTOCHROMIC MECHANISM AND APPLICATIONS OF PYRRYL SUBSTITUTED FULGIDES

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Abstract A series of pyrryl substituted fulgides have been designed and synthesized. Photochromic properties of fulgides have been investigated in various organic solvents. Photochromic mechanism of this kind of fulgides have been studied by means of nanosecond laser flash photolysis technique, both of excited singlet and excited triplet state are involved in the photocyclization process. A sample of optical disk was prepared by spin coating method. Photoinduced electron transfer between pyrryl fulgide and TCNQ has been found and studied by UV-Vis and EPR spectroscopic techniques.

1.INTRODUCTION

Photochromism has been known for a long time [1], a photochromic compound A can undergo a reversible color change on irradiation at an appropriate wavelength (λ_1) to form a more highly colored species B, which undergoes the reverse reaction either thermally or photochemically on irradiation at another wavelength(λ_2):

$$A \underset{\Delta \text{ or } \lambda_2}{\overset{\lambda_1}{\rightleftharpoons}} B$$

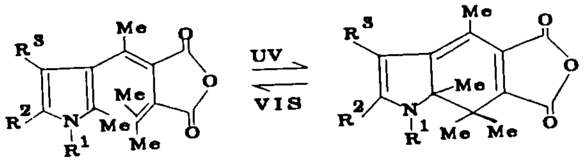
There are many kinds of organic photochromic systems [2], Fulgides are among the most promising candidates for the applications to erasable and rewritable organic optical memory media [3, 4]. The earlier scientific studies of fulgides were those of Heller et al [5] and Becker et al [6]. The synthesis, photochromic properties and the photochromic mechanism of some phenyl substituted fulgides have been clarified in their work. Recently, much attention have been paid to heterocyclic fulgides owing to their high performance of photochromism, many different types of fulgides such as furyl, thienyl, oxazoyl, indolyl substituted fulgides have been investigated [7-10]. To our knowledge, very few attempts have been made to study the synthesis and photochromic mechanism of pyrryl substituted fulgides [11-13]. In this paper, we put our emphasis on the photochromism of a series of pyrryl fulgides. The fatigue resistance and photochromic properties of fulgides can be modified by molecular tailoring, the fulgides continue to attract major interest both academically and commercialy, for example, Aberchrome -540 and Aberchrome -999 [2]have been used as chemical antinometers. It is of interest to modify the structure of photochromic fulgides so that their colored forms can absorb in the near IR reigon(780-830nm) which can match with the diode laser in optical information storage.

Three parts are comprised in the present studies (1), Molecular design and synthesis of pyrryl fulgides. (2), Investigation of photochromic properties and reaction mechanism. (3), Studies on applications of pyrryl fulgides in optical recording media.

2.Synthesis of pyrryl substituted fulgides.

Generally, fulgides are synthesized by Stobbe condensation from aryl ketone and dialkyl isopropylidene succinate.

The structures of pyrryl fulgides and their photocyclization products are shown in scheme 1 :



1 2

a.	$R^1=CH_3$	$R^2=CH_3$	$R^3=CH_3$
b.	$R^1=p\text{-}CH_3OC_6H_4$	$R^2=C_6H_5$	$R^3=H$
c.	$R^1=CH_3$	$R^2=C_6H_5$	$R^3=CH_3$
d.	$R^1=CH_3$	$R^2=C_6H_5$	$R^3=H$
e.	$R^1=C_6H_5$	$R^2=H$	$R^3=C_6H_5$
f.	$R^1=CH_3$	$R^2=CH_3$	R^3=C6H5
g.	$R^1=CH_3$	$R^2=p\text{-}CH_3O\text{-}C_6H_4$	$R^3=CH_3$
h.	$R^1=CH_3$	$R^2=CH_3$	$R^3=p\text{-}CH_3O\text{-}C_6H_4$
i.	$R^1=CH_3$	$R^2=C_6H_5$	$R^3=(CH_3)_2CH$
j.	$R^1=C_2H_5$	$R^2=C_6H_5$	$R^3=CH_3$
K.	$R^1=C_6H_5$	$R^2=C_6H_5$	$R^3=H$

The synthesis of a–e have been reported in our previous paper [14,15], other compounds were identified by MS, NMR and elemental analysis.

3. Photochromism of pyrryl fulgides

The solution of all synthesized fulgides 1a– 1k in common organic solvents was changed to deep blue or blue– green on irradiation by ultra-violet light. The coloured forms do not fade in the dark , It is attribute to the thermal stable 7,7a dihydroindole derivatives 2a–2k . The reaction can be reversed by exposure to visible light and the colour bleached , the typical absorption spectra change of pyrryl fulgide in the photochromic processes is shown in figure 1.

The influence of solvent polarity on the absorption spectra of compound 1 and 2 have been investigated, the results are summarized in table 1 .

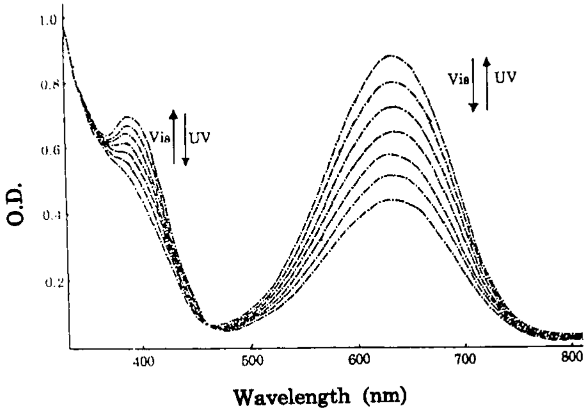


FIGURE 1 Typical absorption change of compound b in acetonitrile in photochromic processes

TABLE 1: UV-Visible spectroscopic characters of compounds 1 and 2

Solvent	λ max (nm) (1)					λ max (nm) (2)				
	1f	1g	1h	1i	1j	2f	2g	2h	2i	2j
Acetonitrile	371	390	380	390	391	699	720	695	700	710
Toluene	370	385	365	380	385	651	670	655	660	665
Cyclohexane	362	380	360	370	370	620	640	630	630	640

The solvent effect on the absorption spectra of compounds a- e have been discussed previously [10] , the coloured form (2) is markedly solvato-chromic and showns such large bathochromic shift but the solvent polarity showns little effect on the absorption spectra of fulgides. This can be rationalized by the formation of more polar species, after the photo - induced intramolecular electronic cyclization reaction occurred [10] .

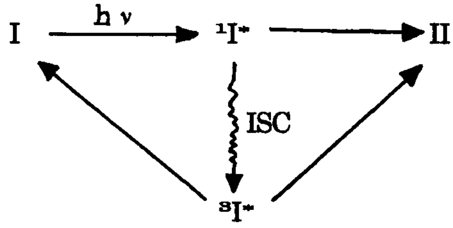
From table 1 we can seen that introducing the electron donating group in 5-position in pyrryl ring can shift the λ max of the coloured form to longer wavelength region , i. e. compound 2g pocesses λ max = 720nm in acetonotrile , which is the longest absorption among the known photochromic fulgides. The substituents in 4–position in pyrryl ring can also influence the photochromism of fulgides.Heller reported that (E) – 1, 2, 5–trimethyl–3–pyrryl fulgide and (Z)–2,5–dimethyl –1– phenyl –3– pyrryl fulgide undergo almost exclusively E→Z isomerization and only a trace of blue coloration, attributed to electrocyclic ring – closure which can be detected spectroscopically . Pyrryl fulgides lacking a substituent in 5–position degrade more rapidly,but a substituent group of phenyl in 4– or 5– position can stabilize the coloured form of pyrryl fulgides.

4. Studies on the mechanism of the photochromic reaction of pyrryl fulgides.

Becker et al [16] first gave convincing evidence that the phtochromism of phenyl fulgides was a molecular phenomenon resulting from the formation of a dihydronaphthalene derivative, and this was further confirmed by later studies of Heller and coworkers [17,18] . Lenoble and Becker [6] also belived that the photocyclization reaction of fulgide is caused by $\pi \rightarrow \pi^*$ excitation , i.e. a $\pi \rightarrow \pi^*$ excited singlet state is the decisive state for photochemical ring colsure reaction.

Recently, photochromic processes of some phenyl and furyl fulgides have been investigated by picosecond laser photolysis [19,20] It seems to be clear that in most case, cyclization takes place in accordance with Woodword – Hoffman rules, furthermore, the cyclization is an ultrafast process [21,22] . In our previous work, the photochromic process of compound 1a was examined by nanosecond laser flash photolysis techniques [14] , using the YAG laser (355nm) asexcitation wavelength, the quenching of the photo-cyclization processes by oxygen was observed, we supposed that one of the excited states of 1a is quenched by oxygen and also that some reaction intermediates of 1a probably is sensitive to oxygen

Laser flash photolysis experiments on compounds 1d, 1e [23, 24] lead to identical results with those described above for 1a, i.e. the oxygen quenching effect on the transient species were also observed. However,when the excitation wavelength was changed to 248nm (KrF laser), transient species were observed in nanosecond time scale and the transient species can severily be quenched by oxygen, we may assign the short-lived transient species to the excited triplet state of pyrryl fulgide, the photochromic mechanism of pyrryl fulgide can be sumarized in scheme 2 . Both of the excited singlet and the excited triplet state are involved in the photocyclization process.



$^1I^*$, excited singlet state of fulgide. $^3I^*$, excited triplet state of fulgide, II, colored form of fulgide.ISC,intersystem crossing

Scheme 2: Photochromic mechanism of Pyrryl fulgides

5.Studies on the applications of pyrryl fulgides in optical storage

(1) An optical disk was prepared by spin-coating method, the fatigue resistance of the disk have been determined, the results shows that some pyrryl fulgides pocess high performance of fatigue resistance. A PMMA thin film doped with fulgide 1b is colored by ultra violet light and bleached by a Helium - Neon laser (632. 8nm) , no photo-decomposed products can be detected by spectroscopic methods over 500 cycles.

(2) Photoinduced electron transfer reaction between pyrryl fulgide and Tetracyanoquinodimethane (TCNQ)

When equal mole of compound 1b (F) and TCNQ (c=1.0x10^{-4}mol/l) were dissolved in acetronitrile, when the absorption spectra were measured immediately, there is not any new absorption band at longer than 400nm region to be observed. But the mixture was in stored for a period of time without exposure to the UV- visible light, a new absorption band at λmax=460nm, which is different from that of F(λmax=390nm, Fig.2, 1) and its coloured form (DID) (λmax= 640nm Fig. 2, 2) was observed (Fig. 2, 3). Apparently, the partialy electron transfer between F and TCNQ occured. The absorption band at λmax= 460nm could be assigned to the charge transfer complex (CTC, F$^{\delta+}$ TCNQ$^{\delta-}$).

When the CTC was irradiated with 460nm light, another new absorption band appeared at λmax =840nm, which might be attributed to the absorption of TCNQ$^{\cdot-}$ (Fig. 2, 4) . The TCNQ$^{\cdot-}$ results from the photoinduced electron transfer between F$^{\delta+}$ and TCNQ$^{\delta-}$, in CTC and the radical ion pair (RIP), F$^{\cdot+}$ TCNQ$^{\cdot-}$ was formed.

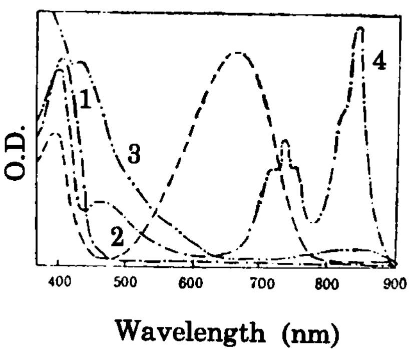


FIGURE 2 Absorption spectra of F (1), DID (2), CTC (3), and RIP (4), in acetonitrile

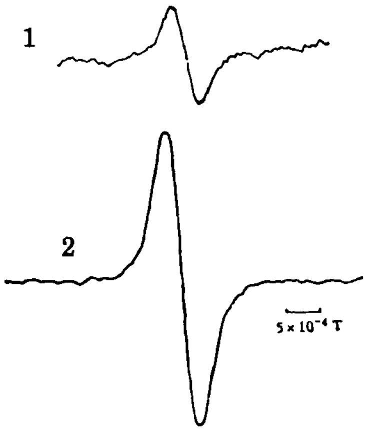
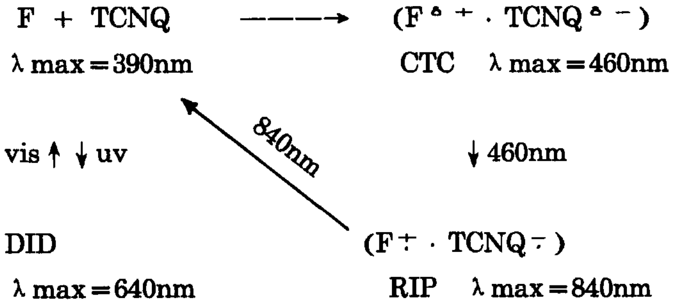


FIGURE 3 EPR spectra of RIP in acetonitrile. 1. At the begining of the irradiation with 460nm light. 2. After the irradiation with 460nm light.

In order to demonstrate the electron transfer between F and TCNQ, the ESR experiments were also conducted. Before the solution of F and TCNQ in acetonitrile was irradiated with 460nm light, no ESR signal was observed. After the irradiation, the ESR signal appeared as a single peak with g=2.0078, and was enhanced with the increasing irradiation time as shown in Fig3, 1 and 2 respectively. This observation provided the direct evidence for the formation of RIP, $F^{\cdot+}TCNQ^{\cdot-}$.

On the other hand,back electron transfer reaction between $F^{\cdot+}$ and $TCNQ^{\cdot-}$ occured when the Radical Ion Pair was irradiated with 840nm light, the absorption band at 840nm (RIP) decreased whilst absorption at 390nm (F and TCNQ) came up.

Sumarizing these facts, the mechanism of the electron transfer reaction between F and TCNQ can be depicted using the scheme 3:



Scheme 3

From the above results, we know that charge transfer complex was formed between F and TCNQ in the ground state, a longer absorption species (RIP) was obtained after the photoinduced electron transfer reaction was conducted on CTC. Back electron transfer reaction occured when the RIP was irradiated with the 840nm light , and this led to reappearance of F and TCNQ, a three angel cycle can be established.

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