

Photochromism of Diarylethenes and Fulgides: A brief review

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Abstract

A phenomenon known as photochromism occurs when two species experience reversible colour changes brought on by light. An intriguing feature is controlling the properties of molecules that react to external stimuli like H^+ , voltage, light, etc. by making small structural changes. The steric and electronic effects typically have a significant impact on the characteristics of photochromic materials. Specifically, there is ongoing research into the creation, synthesis, and testing of organic photochromic materials, which are used in high-tech display systems, eye-protective laser goggles, self-developing cameras, and other applications. Here in this brief review the synthesis and properties of diarylethenes and fulgides are consolidated.

Keywords: Photochromism, Diarylethenes, Fulgides.

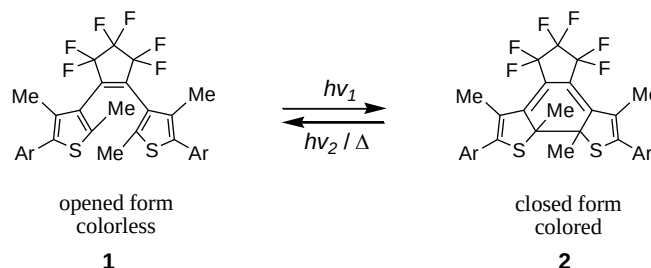
1. Introduction

A glance at the history of organic chemistry reveals that there has been a shift from the synthesis of complex organic systems towards more application-based simple molecules. The latter can be traced in almost every field that one can think of. Photochromism is a phenomenon where two species undergo reversible colour change induced by light. [1] Control of the properties of molecules that respond to external stimuli such as H^+ , voltage, light, etc. via subtle structural modifications is an exciting aspect. In the properties of organic photochromic compounds, the steric and electronic effect generally play a dramatic role. In particular, the quest for design, synthesis and demonstration of organic photochromic materials, [2] which find applications in sophisticated display systems, [3] eye-protective laser-goggles, [4] self-developing photography, [5] etc. continues unabated; photochromism is a photoinduced reversible phenomenon between two species with distinct absorption properties.[1] A variety of molecular systems have been shown in the literature to exhibit photochromism based on different kinds of chemical transformations. Among these diaryethenes, fulgides are two important classes of photochromic compounds. Here in this mini review, the synthesis and properties of these two systems are discussed.

2. Photochromism of Diarylethenes

Diarylethenes are an important class of photochromic compounds having heterocyclic aryl groups, [6a] cf. Scheme 1. Ever since their discovery, photoresponsive diarylethenes have gained widespread appeal as fundamental molecular systems for molecular-level devices. Remarkable facets such as high fatigue

resistance and thermal stability towards coloration-decoloration cycles bestow the class of dithienylethylene-based photochromes with unique opportunities for a gamut of applications in the field of optoelectronic materials.



Scheme 1.

In diarylethenes that contain aromatic rings with low aromatic stabilization energy such as furan, thiophene, selenophene, thiazole, etc., the closed-forms become more stable than the open-forms. On the other hand, when the aromatic rings with high stabilization energy like pyrrole, indole, benzene, etc. are present, closed-forms become comparatively less stable.

For application of photochromic materials in memory or data storage, it is important that the photochromic compounds show absorptions that are highly distinct, preferably one of the species absorbing in the region of 650-680 nm. In dithienylethenes, the absorption characteristics of the open-forms solely depend on the upper cycloalkene derivative and those for the closed-forms depend on the substitution of the thienyl moiety. It is noteworthy that the open-forms absorb in the shorter wavelength region, whereas the closed-forms with extended π -conjugation absorb in the longer wavelength region. The absorption characteristics of

the closed-forms of a variety of dithienylethylenes 3-8 along with their lifetimes are listed below in Chart 1.

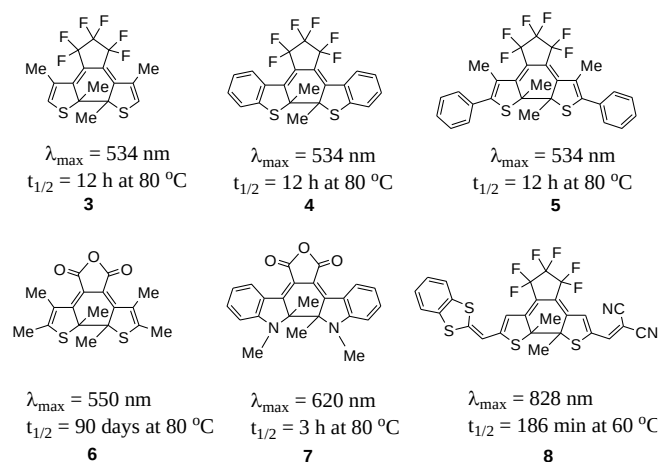
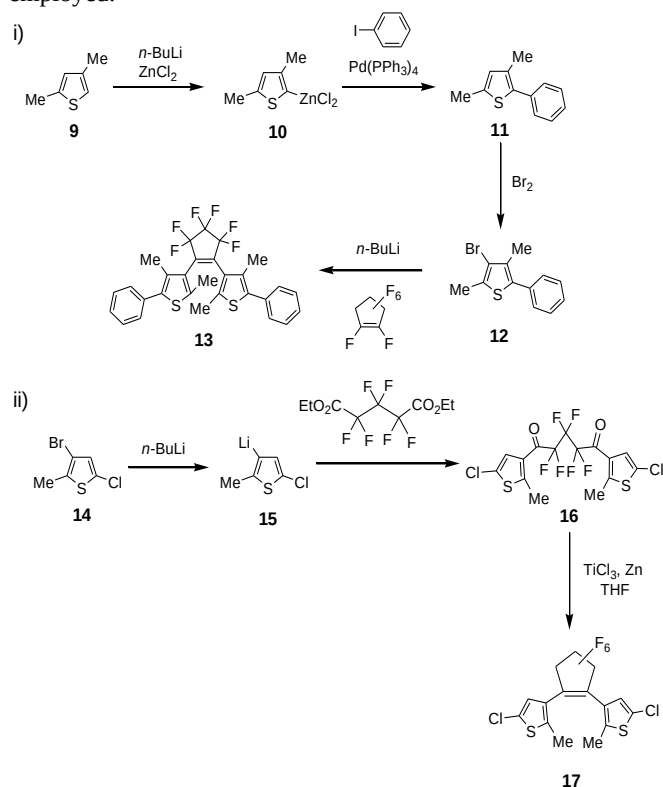


Chart 1.

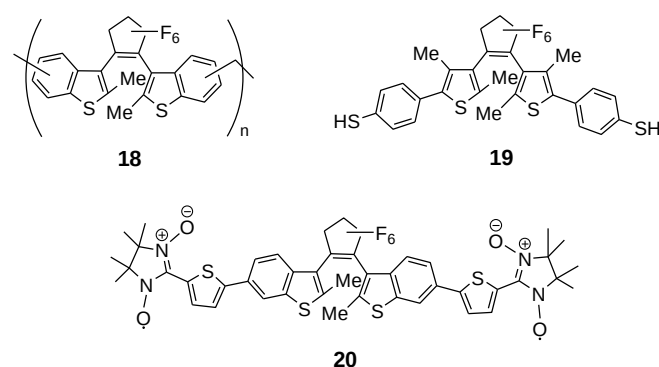
From the point of view of synthetic accessibility, a large number of synthetic protocols are available for dithienylethylenes. In Scheme 2 are shown two synthetic routes that are routinely employed.



Scheme 2

Dithienylethylenes have been exploited to modulate properties such as optical, electronic, magnetic, etc. For example, Jeong et al. reported that fluorescence of the polymeric dithienylethylene backbone in **18** is reversibly modulated in the solid state.[6b] Irie and co-workers designed the molecular system **19** for modulating conductivity in a bulk nanoparticle network in a reversible manner. [6c] They also reported the system **20** for modulating

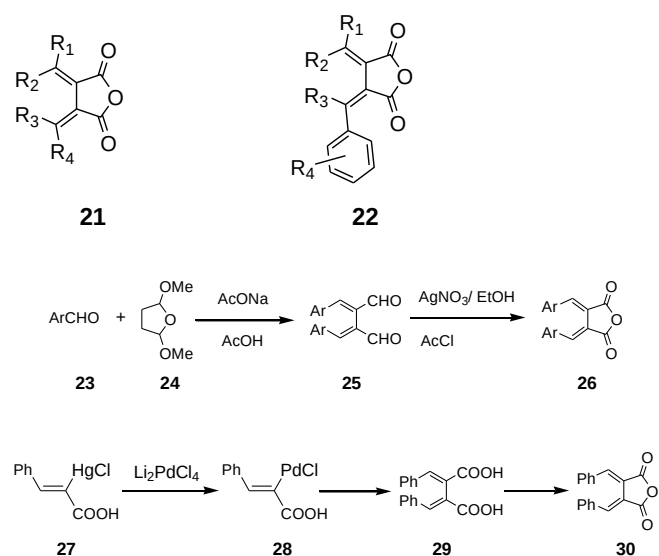
magnetism via interaction between the spin carriers at each end of DTE backbone. [6d]



The diarylethylene family of photochromic compounds is highly promising from the point of view of application in the field of optoelectronics, molecular switches and optical memory storage devices. However, lack of efficient non-destructive readout capability limits their usage. Recently, this problem has been addressed by advanced technologies involving, e.g., the use of a reflection confocal microscope as a read out system, which has led to a great success in their practical applications.[7]

3. Photochromism of Fulgides

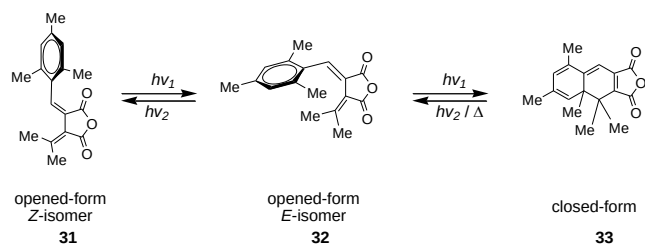
Fulgides—the famous thermally irreversible photochromic molecules—were first synthesized and characterized by Stobbe in the early twentieth century. Anhydrides of the derivatives of 1,3-butadiene-2,3-dicarboxylic acids, e.g., **21** and **22**, are generally called fulgides [8]. In Scheme 3 are shown the traditionally employed protocols for the synthesis of fulgides.



Scheme 3

For photochromism to be observed, the fulgide must contain at least one aromatic unit on the exo-methylene carbon atom to

make up a 1,3,5-hexatriene system, which may undergo a 6π -electrocyclic ring closure reversibly, cf. Scheme 4.



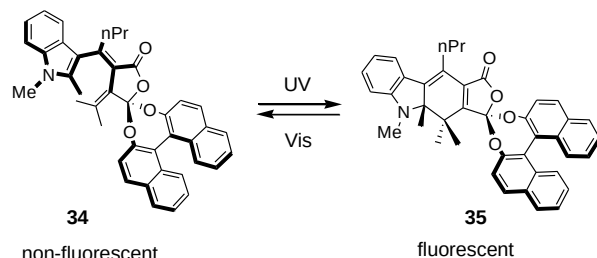
Scheme 4

Yokoyama et al. showed that quantum yield for the ring closure upon UV irradiation becomes larger and that for the E to Z isomerization becomes smaller in the presence of large alkyl groups. [9]

Photochromism of fulgides generally occurs between colorless open-forms and yellow-to-green closed-isomers. The absorption due to the colored species is attributed to π - π^* transition. That is the reason why an electron-donating group attached to the aryl ring of fulgides induces bathochromic shift in the absorption maximum for the closed-form.

Fulgides have been exploited to a great extent for generating nondestructive readout of fluorescence. Yokoyama et al. [8] found that the fluorescence property can be switched during the photochromism of fulgide 34, cf. Scheme 5.

A number of fulgides show photochromism when embedded in the polymeric matrix (PMMA film) or in the solid crystalline state. This property has been widely exploited for the development of ophthalmic lenses.



Scheme 5.

4. Applications of Photochromic Materials

Organic photochromic materials have been utilized to a great extent for the development of functional materials. Now a days, photochromic phenomenon is used in a numerous application. One of the principal uses of photochromic materials is in the development of eyewear technology. Preparation of commercially acceptable UV-protecting goggles necessitates high photocoloration, reasonable bleaching rate, thermal stability and good lifetimes. Photochromic compounds such as diarylethenes and fulgides, chromenes, spiropyrans, spirooxazines, etc., are also used in photoresponsive materials, chiroptical material, three-dimensional optical memory storage

devices, optical power-limiting substances, photoswitchable biomaterials, smart optics, etc.

5. Conclusions

The brief literature survey presented in the foregoing sections reveals that the photochromic systems are appealing from the point of view of applications in a variety of domains. Here in the synthesis and photochromic properties of diarylethenes and fulgides are discussed briefly. These photochromic materials have a wide range of applications as functional materials in numerous fields.

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