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Introduction

1.1 General Introduction

Biological systems have developed various kinds of photoactive organs to adapt themselves to environmental electromagnetic radiation, sunlight. In biological systems, light is used in two ways as shown in Figure 1.1. In plants, for example, photosynthetic systems have evolved to utilize light as an energy source. Carbohydrates are produced from water and carbon dioxide in plants by using light as an energy source. Another category is the use of light for information access and transmission. Light is used to seek out optimum conditions for their life. Photoresponsive biological systems for vision, phototaxis, and phototropism have evolved to recognize surrounding conditions and to access external information. In the former, photoinduced electron transfer is a key chemical reaction. On the other hand, photoisomerization plays a key role in the latter.

Photoisomerization is one of the fundamental reactions in photochemistry [1–3]. *Trans–cis* isomerization, sigmatropic rearrangements, and electrocyclic rearrangements are typical examples. Molecules capable of these reversible photoisomerization reactions are called photochromic molecules or molecular photoswitches [4–10]. The two isomers differ from each other not only in their absorption and fluorescence spectra but also in their geometrical structures, oxidation/reduction potentials, refractive indices, and dielectric constants.

Scheme 1.1 shows typical examples of photoswitchable molecules and when they were discovered. The three upper molecules, azobenzene [11], spirobenzopyran [12], and bridged imidazole dimer [13], belong to T-type (thermally reversible) molecular photoswitches, in which photogenerated right-side colored isomers are thermally unstable and spontaneously revert back to left-side colorless isomers in the dark. Azobenzene undergoes a large change in geometrical structure during the photoisomerization reaction from the *trans*- to the *cis*-form. The distance between 4 and 4' carbon atoms (the long axis of the molecule) decreases from 0.90 to 0.55 nm and the dipole moment increases from 0.5 to 3.1 D [14, 15]. A spirobenzopyran derivative, 6-nitro-1',3',3'-trimethylspiro[2*H*-1-benzopyran-2,2'-indoline], converts from a less polar spiro-form to a polar merocyanine-form upon irradiation with UV light. It is reported that the dipole moment of the spiro-form is 6.2 D, while it

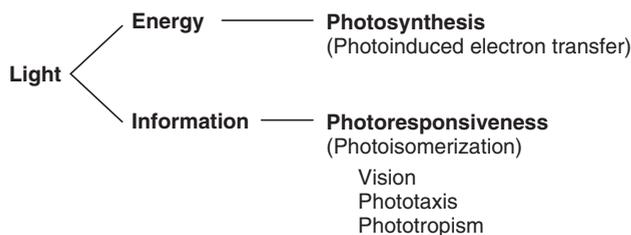


Figure 1.1 The use of light in biological systems.

increases to 13.9 D in the merocyanine form [16]. The blue color of the merocyanine form disappears in less than an hour even in high-*T_g* polymer matrices in the dark at room temperature [17]. A colorless bridged imidazole dimer, 1,8-TPID-naphthalene (TPID: dimer of triphenylimidazolyl radicals), turns green in toluene upon irradiation with UV light, and the green color disappears in less than a few seconds after switching off the UV light [18]. The imidazole dimer exhibits extremely quick response.

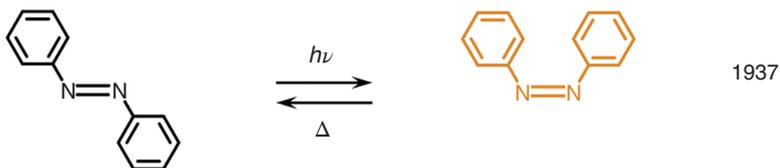
The two lower molecules, furylfulgide [19] and diarylethene [20–22], undergo P-type (thermally irreversible but photochemically reversible) photoswitching reactions. In the P-type molecular photoswitches, photogenerated right-side colored isomers are thermally stable and practically never return to the right-side colorless isomers in the dark at room temperature. Although many molecular photoswitches have been so far reported, P-type chromophores are very rare. The families, furylfulgides and diarylethenes, are two such rare examples exhibiting P-type reactivity. The primary difference between furylfulgides and diarylethenes is fatigue resistance. Photoinduced coloration/decouration cycles of well-designed diarylethene derivatives can be repeated more than 10^4 times maintaining adequate photoswitching ability (see Section 3.3), whereas in most cases the corresponding cycles of furylfulgides are limited to less than 10^2 times.

The instant property changes of photoswitchable molecules by photoirradiation without any additional process lead to their use in various photoresponsive materials and photonic devices. When the bistable molecules are incorporated into materials, the electronic structure changes can be applied to optical memory media and conductance photoswitches, while the geometrical structure changes can be applied to light-driven actuators and others. Molecular photoswitches used in such applications are required to fulfill following properties.

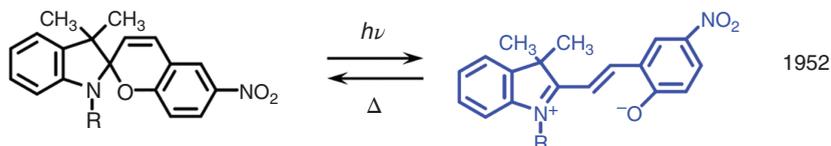
1. Thermal stability of both isomers
2. Fatigue-resistance
3. High sensitivity
4. Rapid response
5. Reactivity in the solid state.

Molecular photoswitches belonging to the diarylethene family fulfill the above requirements simultaneously. Diarylethenes are derivatives of stilbene. When the phenyl rings of stilbene are replaced with five-membered heterocyclic rings, such

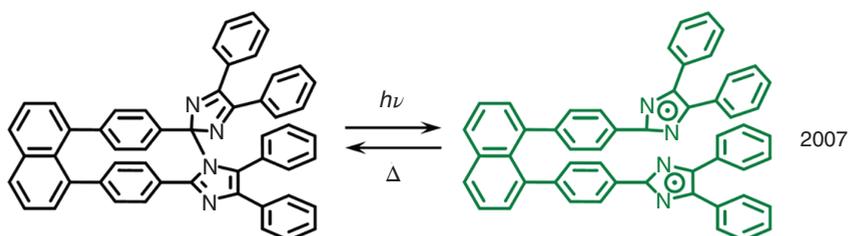
Azobenzene



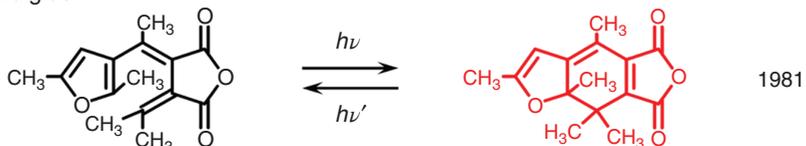
Spirobenzopyran



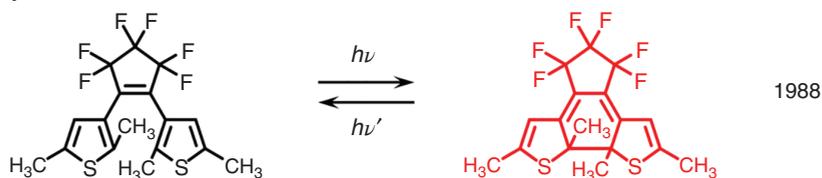
Bridged imidazole dimer



Furylfulgide



Diarylethene

**Scheme 1.1** Molecular photoswitches and years when they were discovered.

as thiophene or furan rings, both open- and closed-ring isomers become thermally stable and photoinduced coloration/decoloration cycles can be repeated many times. The best photoswitching performance of well-designed diarylethenes is summarized as follows.

1. Both isomers are thermally stable: half-life times at room temperature are as long as 470 000 years at 30 °C.
2. Photoinduced coloration/decoloration can be repeated for more than 10^4 cycles.

3. The quantum yield of cyclization (coloration) reaction is close to 1 (100%).
4. Response times of both coloration and decoloration reactions are less than 20 ps.
5. Many of diarylethene derivatives undergo photoswitching even in the single crystalline phase.

1.2 Discovery of Diarylethene Molecular Photoswitches

The diarylethene molecular photoswitches were serendipitously discovered during the course of a study on photoresponsive polymers [23]. Various polymers having molecular photoswitches, such as spirobenzopyran, azobenzene, or stilbene, in the side groups or main chains have been prepared in an attempt to modulate their conformations by photoirradiation. When azobenzene chromophores are incorporated into a polymer backbone, the solution viscosity was found to reversibly change upon alternate irradiation with UV and visible light [24]. Before UV light irradiation, the polymer has a rod-like extended conformation. Upon UV light irradiation, the azobenzene units convert from the *trans*- to the *cis*-form and the isomerization kinks the polymer chain, resulting in a compact conformation and a decrease in the viscosity, as shown in Figure 1.2. Not only viscosity but also other properties, such as pH, solubility, and sol-gel phase transition temperature, were successfully modulated upon photoirradiation [23–28].

Just like azobenzene, stilbene also undergoes the *trans*-*cis* photoisomerization reaction. The photoresponsive polymer research was extended to polymers having stilbene units. A polymer having stilbene units in the backbone can be prepared by 1,4-addition radical polymerization of 2,3-diphenylbutadiene, which is prepared from acetophenone, as shown in Figure 1.3 [29]. Upon irradiation with 313-nm light, the poly(2,3-diphenylbutadiene) efficiently underwent photocyclization reactions to produce a polymer having yellow colored dihydrophenanthrene units in a deaerated dichloromethane solution, instead of the *trans*-*cis* photoisomerization. The *trans*-*cis* photoisomerization of stilbene units in the backbone was strongly suppressed due to rigidity of the polymer chain. The dihydrophenanthrene units readily returned to the initial 2,3-diphenyl-2-butene units and the yellow color disappeared in less than 10 minutes at room temperature.

On the other hand, in the presence of air the dihydrophenanthrene units converted to phenanthrene units by hydrogen elimination and the reversibility was lost. To prevent hydrogen elimination and provide reversibility even under aerated conditions, 2,3-dimesitylbutadiene was designed (Figure 1.4A(a)). The synthesis of 2,3-dimesitylbutadiene was attempted by photoreduction of 2,4,6-trimethylacetophenone, as shown in Figure 1.4B(a). But, the synthesis of pinacol failed because of the bulky size of the mesityl group. To reduce steric hindrance, the mesitylene was replaced with 2,5-dimethylthiophene (Figure 1.4A(b)). According to the synthetic route shown in Figure 1.4B(b), 2,3-bis(2,5-dimethyl-3-thienyl)butadiene was successfully synthesized from 2,5-dimethyl-3-acetylthiophene. The butadiene was polymerized to poly(2,3-bis(2,5-dimethyl-3-thienyl)butadiene) by 1,4-addition radical polymerization.

Figure 1.2 Schematic illustration of the photoinduced conformational change of a polymer having azobenzene units in the backbone.

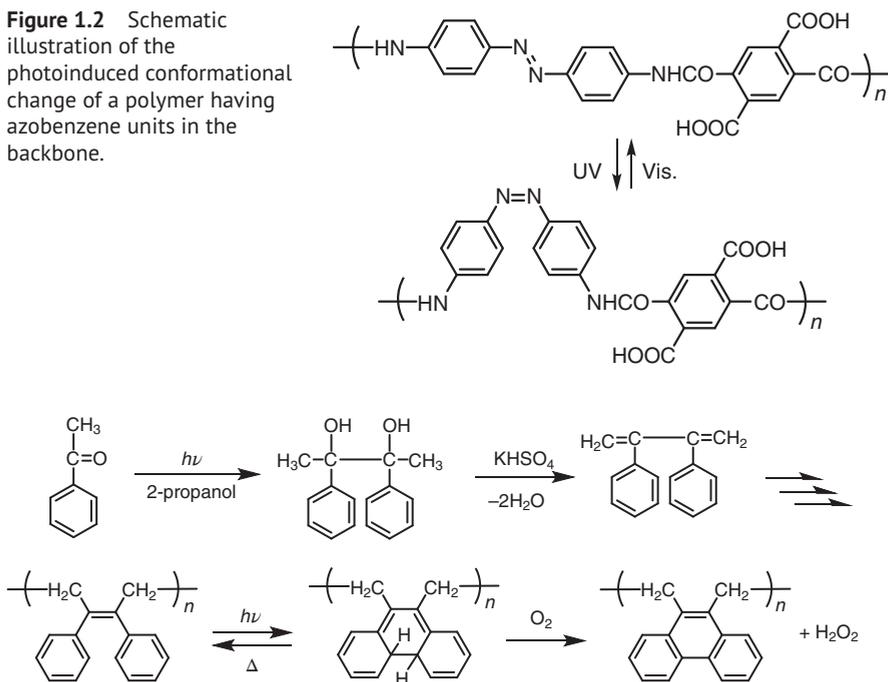


Figure 1.3 A synthesis route of poly(2,3-diphenylbutadiene) and its photochemical and thermal reactions.

The polymer having 2,3-dithienyl-2-butene units was dissolved in benzene and the solution was irradiated with 313-nm light. The colorless solution turned yellow ($\lambda_{\text{max}} \sim 430 \text{ nm}$) along with the formation of cyclized closed-ring isomers. The yellow color disappeared upon irradiation with visible light. In contrast to poly(2,3-diphenylbutadiene), the yellow color of the closed-ring isomer units was found to remain stable overnight in the dark. The yellow closed-ring units were stable even at 100°C and returned to the initial colorless open-ring isomer units with visible light. The dithienylethene unit in the polymer was unprecedentedly found to undergo a thermally irreversible photoswitching reaction. Poly(2,3-bis(2,5-dimethyl-3-furyl)butadiene) also underwent the thermally irreversible photoswitching reaction. The amazing result led us to study the photochemistry of the monomer unit, 2,3-di(2,5-dimethyl-3-thienyl)-2-butene and its derivatives in detail. This is the course of serendipitous discovery of diarylethene molecular photoswitches.

Since the discovery of thermally irreversible diarylethene molecular photoswitches in the middle of 1980s, various types of diarylethene derivatives have been synthesized to improve their photoswitching performance. Figure 1.5 shows a list of main diarylethene derivatives developed in Kyushu University and Rikkyo University until 2017. Upon irradiation with UV light, 2,3-di(2,5-dimethyl-3-thienyl)-2-butene underwent a *cis-trans* isomerization in addition to the cyclization reaction. To prevent the unfavorable

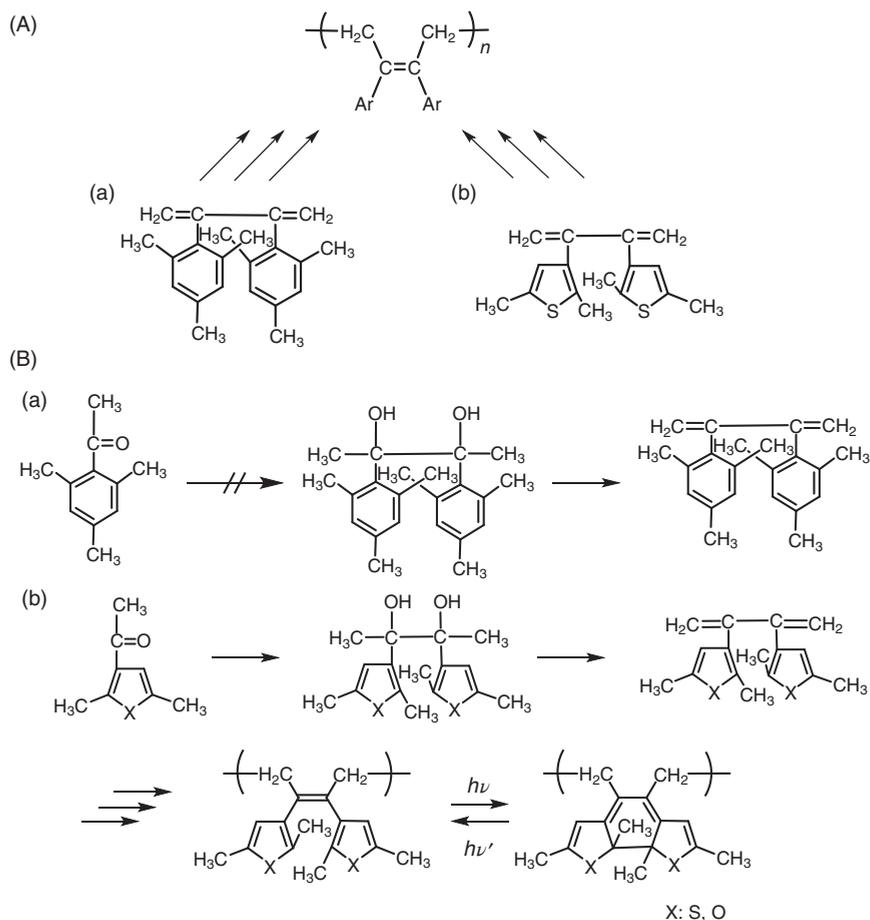


Figure 1.4 (A) Synthesis of polymers having (a) 2,3-dimesitylbutene units and (b) 2,3-di(2,5-dimethyl-3-thienyl)butene units in the backbone. (B) (a) A synthetic route to prepare 2,3-dimesitylbutadiene. (b) Synthetic routes and photochemical reactions of poly(2,3-di(2,5-dimethyl-3-thienyl)butadiene) and poly(2,3-di(2,5-dimethyl-3-furyl)butadiene).

cis-trans photoisomerization, a cyclic bridge, such as maleic anhydride or maleimide, was introduced. Although diarylethene derivatives with the maleic anhydride or maleimide bridge showed photocyclization reactivity in less polar solvents, the reactivity was strongly suppressed in polar solvents, such as methanol or acetonitrile. To provide photoswitching reactivity even in polar solvents, the ethene bridges were replaced with perfluorocycloalkenes with four-, five-, and six-membered rings [30]. The 1,2-bis(2-methyl-1-benzothiophen-3-yl)perfluorocycloalkenes underwent reversible photoinduced cyclization/cycloreversion reactions in polar methanol and acetonitrile. Among the three derivatives having four-, five-, and six-membered rings, five-membered 1,2-bis(2-methyl-1-benzothiophen-3-yl)perfluorocyclopentene was found to offer

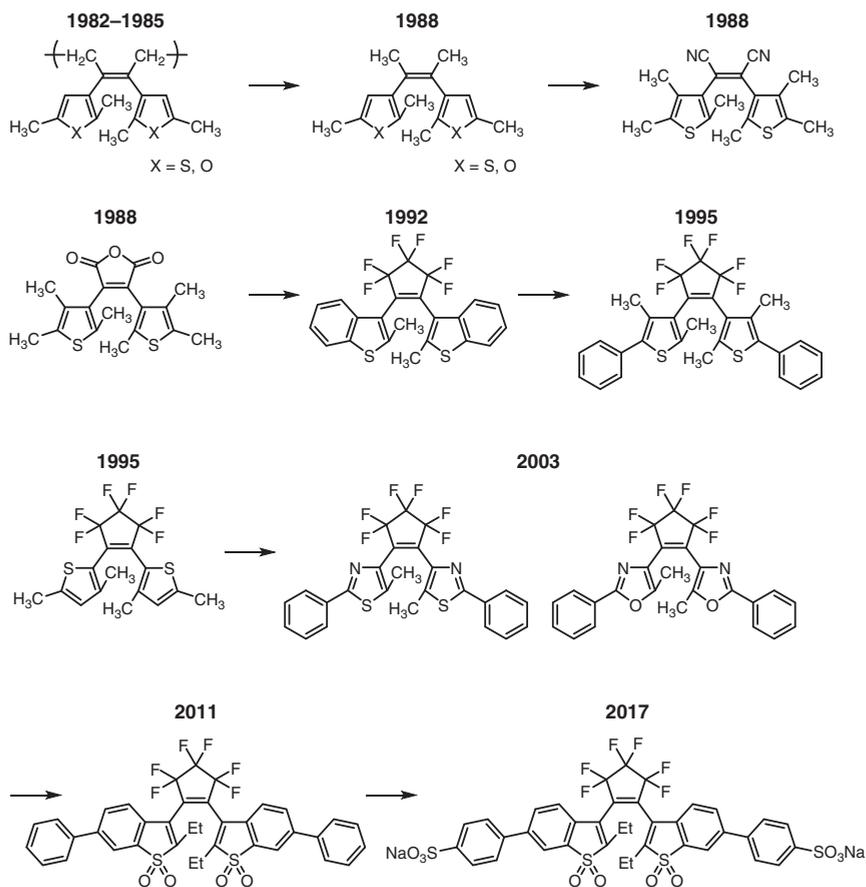


Figure 1.5 Development of diarylethene molecular photoswitches.

the highest resistance to photofatigue. Since then, perfluorocyclopentene derivatives have been mainly studied.

Although diarylethene photoswitches exhibit brilliant color changes upon photoirradiation, most of them are nonfluorescent or very weakly fluorescent in both isomer forms. It was a long-standing ambition to prepare photoswitchable fluorescent diarylethenes without attaching fluorescent chromophores to the diarylethenes. In 2011, sulfone derivatives of 1,2-bis(2-ethyl-6-aryl-1-benzothiophen-3-yl)perfluorocyclopentene were found to exhibit very strong fluorescence (fluorescence quantum yield ~ 0.9) in the closed-ring isomers [31]. The turn-on mode fluorescent diarylethenes are now extensively applied to super-resolution fluorescence microscopy in materials science and biological systems. Diarylethenes are able to switch both absorption (color) and fluorescence emission upon photoirradiation.

At first sight, the most striking phenomenon observed in molecular photoswitches is a photoinduced instantaneous color change. Figure 1.6 shows photos of the color

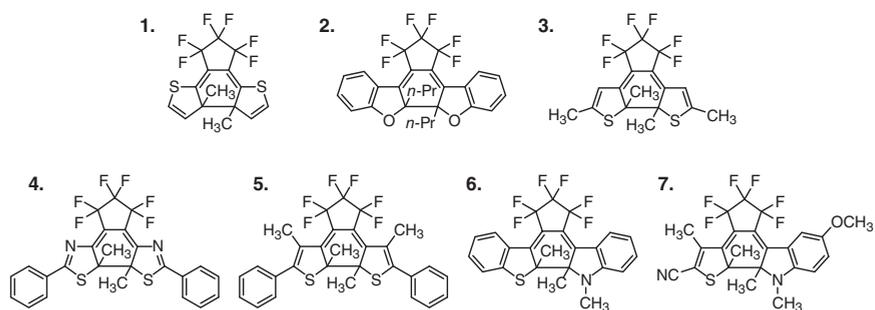
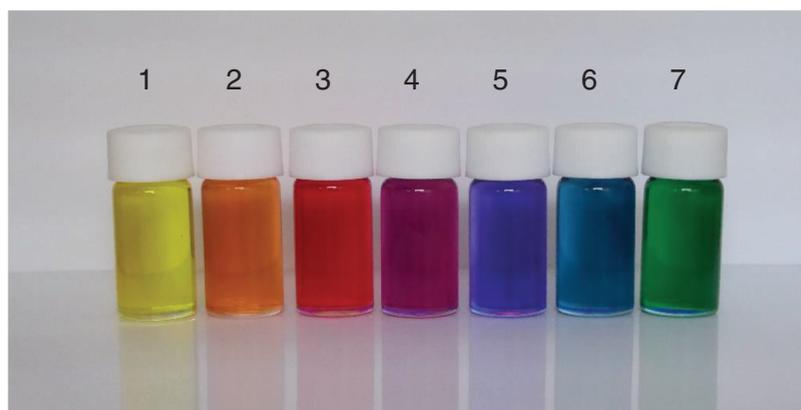
UV \downarrow \uparrow Vis.

Figure 1.6 Color changes of diarylethene derivatives 1–7 in toluene upon irradiation with UV and visible light.

changes of diarylethene derivatives in solution. When the toluene solutions of the derivatives are irradiated with UV light, the colorless solutions turn yellow, orange, red, violet, blue, cyan, and green. The chemical structures of the derivatives are shown below in the photos. These colors disappear upon irradiation with visible light. The photoinduced coloration/decoloration cycles upon alternate irradiation with UV and visible light can be repeated many times.

The color changes are ascribed to the electronic structure changes of the derivatives from the open- to the closed-ring isomers. Two typical examples of the electronic structure changes are shown in Figure 1.7. 1,2-Bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene (**3**) and 1,2-bis(3,5-dimethyl-2-thienyl)perfluorocyclopentene (**1**) undergo reversible electrocyclic rearrangements. The electrocyclic reactions involve rearrangements of positions of single and double bonds in a molecule. During the reactions, a new single bond is made between the central reactive carbon atoms by the cyclization reaction and the bond is broken as the ring is opened.

Figure 1.7 shows the chemical structures of the open- and the closed-ring isomers and their absorption spectra. In both derivatives **3** and **1**, upon irradiation with appropriate wavelength of light (λ_1 or λ_3) a single bond is formed between the central reactive carbon atoms and the double bonds change the position. Upon irradiation with another wavelength of light (λ_2 or λ_4) the single bond is broken and the molecule returns to the initial structure. The color is controlled by the length of π -conjugation. In the open-ring isomers, two thiophene rings have no particular interaction and the spectra are comparable to substituted thiophenes. In the closed-ring isomers, the π -conjugation length depends on the attached position of thiophene rings to the ethene bridge. When the thiophene rings are attached to the ethene bridge at 3-position, such as derivative **3**, π -conjugation is delocalized throughout the molecule in the closed-ring isomer and the delocalization results in red color. The π -conjugation is further extended when phenyl groups are substituted at 5- and 5'-positions of the thiophene rings, such as **5**. The long π -conjugation shifts the absorption band to longer wavelengths, resulting in blue color. On the other hand, when the thiophene rings are attached to the ethene bridge at 2-position, such as derivative **1**, π -conjugation is localized in the central part. The short π -conjugation results in yellow color in the closed-ring isomer.

The photoswitching between two discrete states and thermal irreversibility of the two states are indispensable for applications to memory media and switching devices. The bistability is a basic characteristic of diarylethenes. Although the chemical structures of the two isomers suggest photoswitching between two discrete states, in general, the absorption and fluorescence spectra gradually change upon photoirradiation in ensemble systems. Figure 1.8b shows the photoswitching performance of 1,2-bis(2-ethyl-6-phenyl-1-benzothiophene-1,1-dioxide-3-yl)perfluorocyclopentene (**8**, Figure 1.8a) in the ensemble system in 1,4-dioxane. The gradual analog increase in the fluorescence intensity upon irradiation with UV light indicates a change in the concentrations of the two isomers. Upon UV irradiation

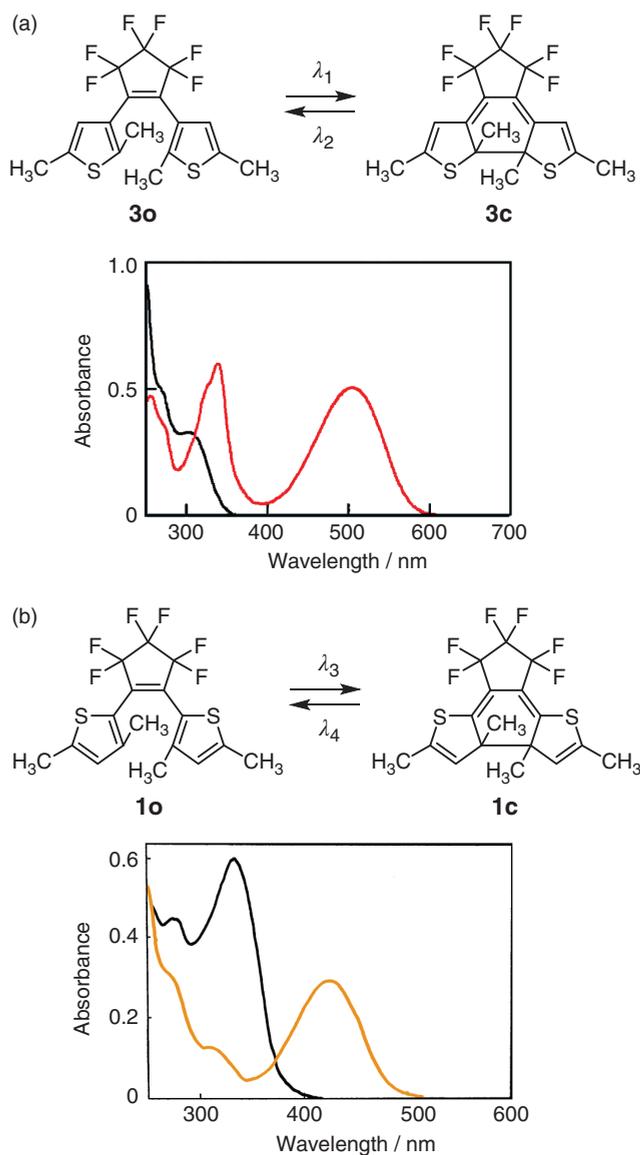


Figure 1.7 Chemical structures and absorption spectra of open- and closed-ring isomers of (a) **3** and (b) **1** in *n*-hexane.

the open-ring isomers convert to the fluorescent closed-ring isomers and the concentration ratio of the closed-ring isomers increases, causing the gradual increase in the fluorescence intensity. Subsequently, upon irradiation with visible light the ratio of the closed-ring isomers decreases, resulting in disappearance of the fluorescence. The switching between the two discrete states cannot be discerned from the photoswitching performance in the ensemble system.

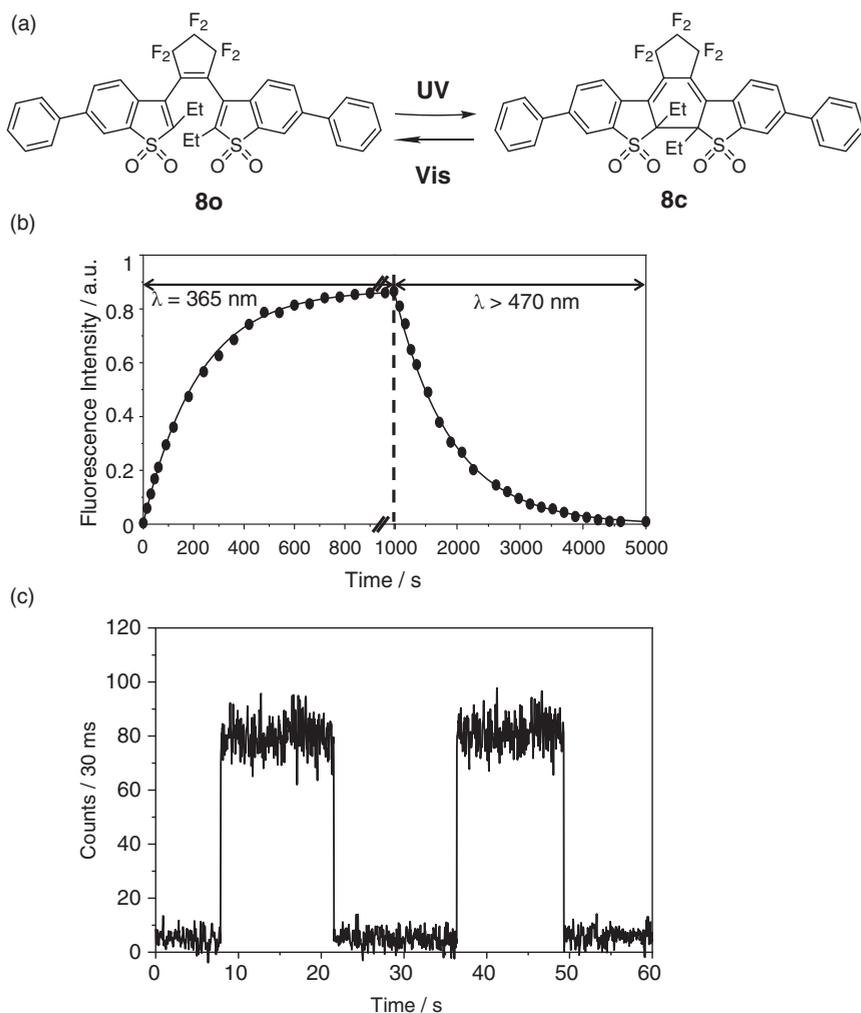


Figure 1.8 (a) Chemical structures of open- and closed-ring isomers of **8**. (b) Fluorescence photoswitching of **8** upon irradiation with UV and visible light in the ensemble system in 1,4-dioxane. (c) Fluorescence photoswitching of **8** at the single-molecule level in a Zeonex polyolefin film.

Digital *on/off* photoswitching between two discrete states was confirmed by measuring the switching response at a single-molecule level. Figure 1.8c shows the fluorescence photoswitching of a single molecule of derivative **8** upon alternate irradiation with UV and visible light. Upon irradiation with UV light, the fluorescence abruptly switches from the *off*-state to the *on*-state, while upon irradiation with visible light the *on*-state abruptly returns to the *off*-state. The digital photoswitching response definitely indicates that diarylethene photoswitch **8** has bistable states. The photoisomerization between two discrete isomer states expressed by the two chemical structures is experimentally evidenced.

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