Chiral photochromism based on 6π-electrocyclization

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Photochromism involving chiral properties is important and interesting, particularly in the field of biological applications and liquid crystals. In this review, enantioselective and diastereoselective photochromic reactions based on thermally irreversible 6π-electrocyclizations are highlighted. Optical resolution of helical chirality of the hexatriene moiety can afford the enantiomers, however, racemization may occur. Diastereoselective photochromic reactions are more sophisticated and efforts to achieve high diastereoselectivity by us and others have been described.

Introduction

Photochromism is known as "a reversible transformation of a single chemical species being induced in one or both directions by electromagnetic radiation between two states having different distinguishable absorption spectra."[1] In general, photochromic reactions show reversible coloration/decoloration or reversible change in their colours upon photoirradiation (Fig. 1).

Photochromic compounds are categorized into two types. The compounds whose reversible change in absorption spectra occurs only when they are photoirradiated are called "P-type" photochromic compounds. On the other hand, when either or both transformation processes occur thermally as well as photochemically, they are called "T-type" photochromic compounds.

Upon photoirradiation, photochromic compounds change their structures. Therefore, all the physical/chemical properties such as refractive index, dielectric constant, electroconductivity, fluorescence, magnetism, supramolecular affinity, solubility, melting point, phase transition temperature, and so on, as well as the absorption spectra, may be changed by photochromic transformation. Recently, it has been reported that the shape of crystals of photochromic compounds and amorphous films containing photochromic moieties are also changed.[2] These motions are regarded as the direct conversion of light energy to mechanical energy.

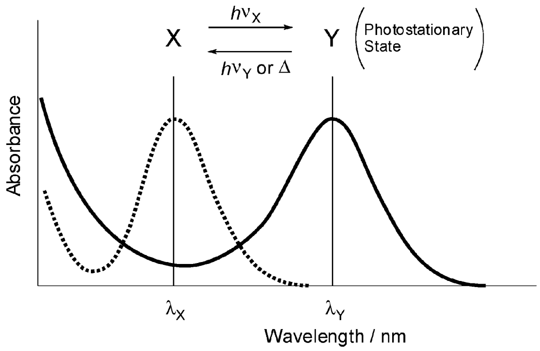

Fig. 1 Photochromism.

When a chiral unit is introduced in a photochromic system, a change in chiral properties can be induced by the photochromic reaction, in addition to the usual physical/chemical properties.[3] Because the chiral properties are important in the areas of biological activity, supramolecular interactions in biological molecules, and cholesteric liquid crystalline properties, control and change of them by light irradiation is of interest.

Introduction of a chiral unit into a photochromic system can be achieved by the following methods: (1) performing the photoirradiation in a chiral environment, (2) irradiation with circularly polarized light, (3) introduction of a chiral substituent to photochromic molecules. The first method includes photoreaction using chiral sensitizers.[4] The second method is exemplified by photochromic reactions to induce the cholesteric helical sense of liquid crystals.[5] In this review, the latter category will be described for P-type photochromic compounds based on 6π-electrocyclization reactions, such as fulgides and diarylethenes.

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Chirality in 6π-electrocyclization

The 6π-electrocyclization reaction occurs between 1,3,5-hexatriene and 1,3-cyclohexadiene. Most P-type photochromic compounds are categorized in this group, and one or two olefins of the hexatriene moiety are part of aromatic rings. Fulgides[6] and arylbutadienes[7] have one aromatic ring as the part of the hexatriene moiety, and diarylethenes have two aromatic rings.[8] Teraryls have three aromatic rings, but they usually belong to the T-type photochromic family because they lose aromatic stabilization energy of three aromatic rings when they cyclize.[9] On the contrary, the photogenerated cyclohexadiene isomers of most of the fulgides, arylbutadienes and diarylethenes are thermally stable. The photogenerated cyclohexadienes are usually deeply coloured and their absorption maximum wavelengths are located in a longer wavelength region than for the hexatriene isomers.

The cyclization of hexatriene can be induced either photochemically or thermally. Because the reaction is governed by the Woodward–Hoffmann rules, the stereochemistry of the substituents at the bond-forming carbon atoms depends on the reaction mode; light or heat. Light-mode reactions occur *via* conrotatory ring closure/opening, whereas heat-mode reactions occur *via* disrotatory ring closure/opening. When all the substituents on both carbon atoms on both ends are larger than hydrogen, the heat mode reactions are strongly inhibited because of the steric congestion. On the contrary, the light mode cyclization/opening is not restricted sterically.

As shown in Fig. 2, when no chiral perturbation to the system exists, a racemic mixture of cyclohexadienes is produced, because the two helical, energetically equivalent enantiomeric conformers cyclize with the same cyclization quantum yield. The conformer with (*P*)-helicity (right-handed screw) cyclizes to produce the left side enantiomer of cyclohexadiene (**A**), and that with (*M*)-helicity (left-handed screw) cyclizes to give the right side enantiomer (**B**). Although the enantiomers of cyclohexadienes cannot interconvert to each other directly, the enantiomeric conformers of hexatriene can be exchanged thermally in most cases.

If the ratio of the population of the helical hexatriene conformers is changed from 50: 50 in some way, the ratio of one of the isomers of cyclohexadienes would be changed. There are two ways to achieve this type of selectivity. One is to resolve the helically enantiomeric conformers of the hexatriene. The other is to introduce a chiral unit to the neighbor of the hexatriene moiety so that one of the helical conformers becomes more stable than the other. The two helical conformers are diastereomeric to each other. Upon photoirradiation, two diastereomeric cyclohexadienes in different amounts may be produced. It is important to make the ratio of *P*- and *M*-helicity conformers at the ground state highly biased. Details of both methods will be described in the following sections.

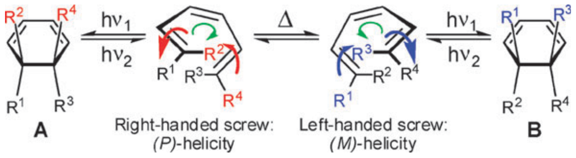


Fig. 2 Helical chirality and 6π-electrocyclizations of hexatriene.

Optical resolution of enantiomers

The first method is the optical resolution of helically enantiomeric conformers. It is a prerequisite that the helical structures are stable enough towards racemization to be separated. Yokoyama and co-workers have succeeded in separating the enantiomers of an indolylfulgide **1*E***.[10] Although the resolved enantiomers were stable in solution at room temperature, they racemized upon heating in solution or upon prolonged irradiation with 405 nm light which induced photocyclization. The photochemical racemization probably occurred *via* the *Z*-form (**1*Z***) where the steric barrier of racemization would be lower than for **1*E***, although the quantum yield of *E*-to-*Z* isomerization is almost zero (Fig. 3).

Takeshita and Yamato resolved a cyclophane-type diarylethene **2**.[11] Because of the steric congestion, no racemization occurred either with heat or light irradiation (Fig. 4).

When the compounds occur as single crystals, the molecular environment is highly restricted. If molecules of a photochromic compound adopt a helically chiral non-racemic conformation in the single crystal, then the occurrence of an enantioselective photocyclization in an ordered molecular alignment is expected when an individual single crystal was photoirradiated. Irie, Matsuda and co-workers showed that a diarylethene **3** crystallized with $P2_1$ space group. The helicity of the hexatriene moiety was the same for all the molecules in a single crystal. Upon photoirradiation of a single crystal, the molecules in it gave the same enantiomer of the closed form (Fig. 5).[12]

Feringa and co-workers reported the separation of three different conformers of a teraryl **4** by chiral HPLC. They occur as one parallel conformation which cannot cyclize upon photoirradiation and two enantiomeric antiparallel conformations which can cyclize upon photoirradiation (Fig. 6).[13] The separated isomers were conformationally stable

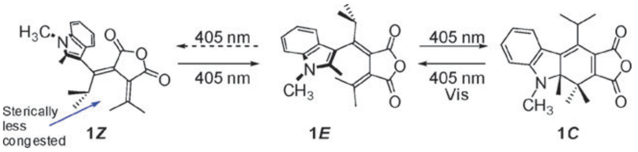


Fig. 3 Photochromism of optically resolved indolylfulgide.

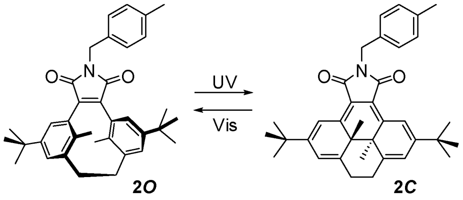


Fig. 4 Cyclophane-type enantiomerically stable diarylethene.

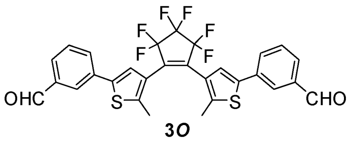


Fig. 5 Enantioselective photochromic diarylethene in a single crystal.

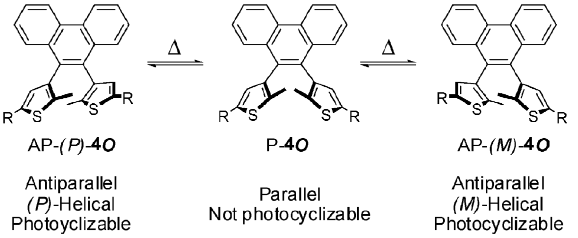


Fig. 6 Optically resolved photochromic teraryl.

at room temperature but racemized at elevated temperature. The activation energy values of the related compounds were around 110 kJ mol^{-1}.

Overall, except in certain circumstances, optical resolution is not a reliable method to obtain robust helical chirality.

Diastereoselective cyclization driven mainly by steric repulsion

The second method, the diastereoselective protocol, has been used for fulgides and diarylethenes. Although the helical chirality of the hexatriene moiety is usually interconverted between the *P*- and *M*-helical structures by thermal treatment, the ratio of helical structures can be biased when an intrinsic and non-racemizable chirality is introduced nearby the ring-closing carbon atoms to make the difference of the free energy of *P*- and *M*-helical conformations large. The ratio of the diastereomeric helical structures is determined by Boltzmann distribution through equilibrium. When the ratio of the conformational isomers at the ground state is maintained at the excited state and the spectroscopic properties and quantum yields of the diastereomeric closed forms are similar, the diastereomer ratio of the closed forms will be similar to the ratio of the diastereomeric conformers of the open forms at the ground state (Fig. 7).

Following the concept described above, Yokoyama and co-workers revealed the diastereoselective photochromism of fulgide derivatives possessing a C_2-symmetric chiral binaphthol as the helicity-controlling handle. The steric repulsion between one of the naphthalene groups of **5** and one of the methyl groups of the isopropylidenene group determined the major and minor helical conformations of the hexatriene moiety (Fig. 8).[14]

The ratio of the diastereomeric closed forms obtained by UV irradiation was 95 : 5 (90% diastereomer excess: de). When this compound was mixed in a nematic liquid crystal, it generated the cholesteric liquid crystalline phase. Iterative irradiation of UV and visible light changed the cholesteric pitch of the liquid crystal reversibly.[15]

Irie and co-workers reported the diastereoselective photocyclization of a diarylethene **6**, possessing a D- or L-menthyloxy group on one of the C–C bond forming carbon atoms (Fig. 9). The diastereoselectivity in solution depended greatly on the solvent polarity and the photoirradiation temperature. The diastereoselectivity was higher when the solvent polarity measured as $E_T(30)$ was higher, and the photoirradiation temperature was lower.[16] A 86.6% de was recorded in toluene at −40 °C.

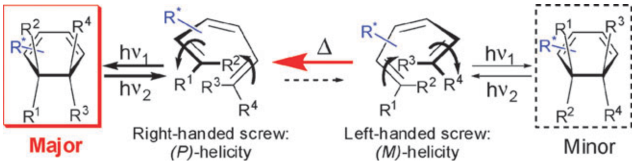


Fig. 7 Concept of diastereoselective photochromism.

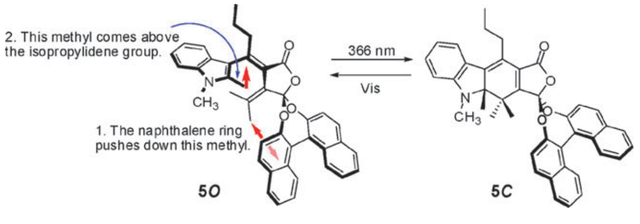


Fig. 8 (*R*)-binaphthol-condensed fulgide **5**.

This article was followed by a number of reports from the groups of Irie, Branda, Feringa and Yokoyama.

Irie, Matsuda and co-workers investigated the diastereoselective single crystalline photochromism of diarylethenes **7–9**[17] (Fig. 10). Although they showed no diastereoselectivity in solution, they were highly diastereoselective at the early stage of photoirradiation when the conversion to the closed form was low.

Irie, Yamaguchi and co-workers reported that the diester **10** with two chiral moieties on both ends of the molecule showed 25% de as its amorphous states (Fig. 10).[18]

Irie, Matsuda and co-workers revealed the self-aggregation behavior of the chiral PEG-containing diarylethene **11** in an aqueous solution. Judging from CD spectra, although the open form did not form a chiral aggregate, the closed form did. The lower critical solution temperature (LCST) was lower for the closed form.[19] Recently, they synthesized an amide version of the PEG-containing diarylethene **12**. Different from **11**, the open form of **12** formed a chiral aggregate in water. The LCST of the open form was 22 °C higher than that of the

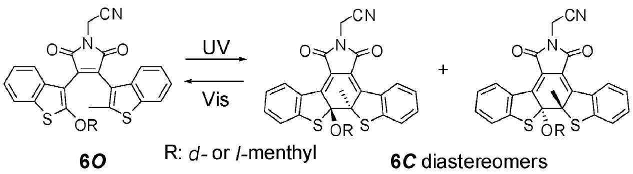


Fig. 9 Menthol-connected diarylethene **6**.

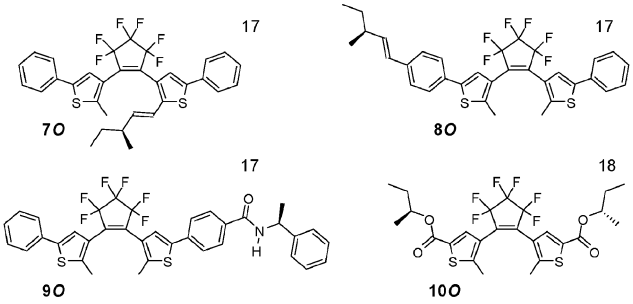
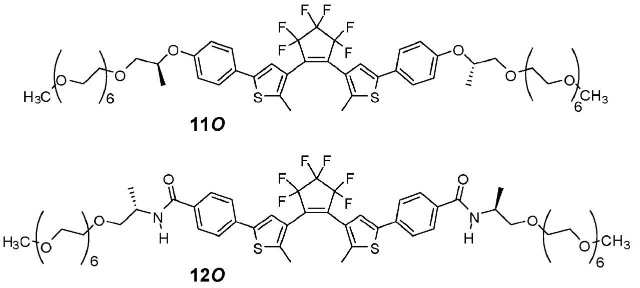


Fig. 10 Diastereoselective photochromic diarylethenes in single crystals and amorphous films.


11O

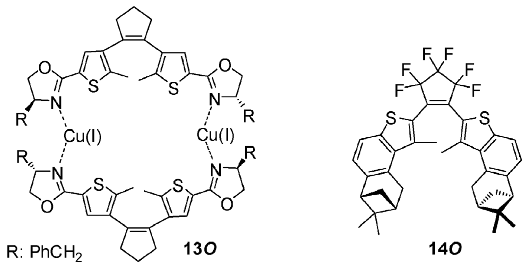
12O

Fig. 11 Diarylethenes with chiral PEG chains.

photostationary state (PSS). Therefore, the cloudiness of the solution was controlled by heat as well as light (Fig. 11).[20]

Branda and co-workers prepared several diarylethenes possessing natural product-derived substituents, which show diastereoselective photochromism. Diarylethene **13** has phenylalanine-derived oxazolines as the chelating agents to copper(I) atoms. When two diarylethene molecules form a cyclic dimeric complex, the steric repulsion between the benzyl groups was transmitted to the core hexatriene moiety to make one of the helical conformations more stable than the other. The electronic repulsion between the lone pairs of the confronting sulfur atoms might be assisting to raise the selectivity. Indeed, the diastereoselectivity was 86–89% de at 10^{-4} mol dm^{-3}, and 98% de at 10^{-3} mol dm^{-3}, though the latter was accompanied by the destruction of the compound by photoirradiation.[21] They also used pinene to make use of the difference of the steric repulsion between two methylene groups and two isopropylidene groups at the ends of the helical structure of **14**. Because they detected only one diastereomer, they assumed that the selectivity was 100%, with the aid of molecular orbital calculations (Fig. 12).[22]

Feringa used (*R*)-1-phenylethylamine for the synthesis of **15**. In toluene within the concentration range of 1–4 × 10^{-3} mol dm^{-3}, a solution of **15** formed a gel by a hydrogen bond network between the molecules. As the stereogenic carbon atoms worked to form a chiral aggregate, UV irradiation resulted in the production of chiral closed form with 96% de. Interestingly, the helical sense of the stable aggregate structure of the gel can be switched reversibly (Fig. 13).[23]



13O

14O

Fig. 12 Diarylethenes containing natural product-derived units.

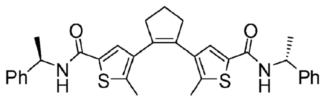

15O

Fig. 13 Diastereoselective photochromic diarylethene in gel.

Diastereoselective cyclization driven by steric as well as electronic repulsion

Allylic 1,3-strain and its application to diarylethenes

After the early success of diastereoselective photochromism of fulgide **5**, we envisioned to attain high diastereoselectivity for the photocyclization of diarylethenes. In order to achieve high diastereoselectivity, the chiral perturbation introduced to the neighboring groups of the hexatriene should work to bias the ratio of the conformational isomers effectively, with the aid of electronic as well as steric interactions. We employed allylic 1,3-strain[24] as the steric controller. Allylic 1,3-strain works around a double bond to restrict the rotation of a single bond bearing a stereogenic carbon atom at the allylic position. When R is larger than hydrogen, the steric repulsion between R and R^1–R^3 on the allylic carbon is so large that the smallest substituent R^1 such as hydrogen will come closest to R. If other substituents are larger than R^1, then the conformation around the allylic carbon atom is almost fixed. When the substituents R^2 and R^3 are not the same, then the space around the double bond is not symmetrical (Fig. 14).

We applied the concept of allylic strain to 1,2-bis(2-methyl-3-benzothienyl)hexafluorocyclopentene. When a methyl group is replaced by a stereogenic carbon atom bearing a hydrogen atom, a methyl group, and a mehoxymethoxy (MOMO) group, the smallest hydrogen atom should come inside of the hexatriene moiety to face the hexafluorocyclopentene. Then the conformation around the stereogenic center is practically fixed, and the second benzothiophene ring is located closer to the methyl group rather than the MOMO group, avoiding the steric repulsion with the MOMO group. Later, it was revealed that the electronic repulsion between the lone pairs of MOMO group and the lone pair of the sulfur atom plays a decisive role. In this situation, irradiation of UV light to the open form **16*O*** will generate one of the two possible diastereomers predominantly (Fig. 15).

When a toluene solution of **16*O*** was irradiated with 313-nm light, 85% of **16*O*** was converted to the closed form, and the selectivity was 88% de.[25]

Because the alignment of the atoms O–C–O worked very well as the electronic repulsive controller, we looked for better

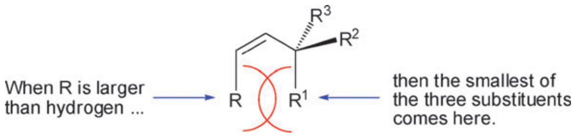
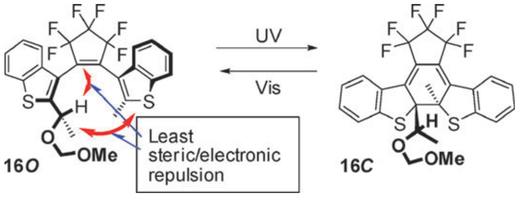


Fig. 14 Allylic 1,3-strain.



16O

16C

Fig. 15 Allyic strain-controlled diastereoselective photochromic diarylethene.

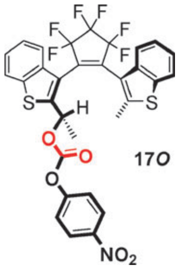


Fig. 16 Improved diastereoselective photochromic diarylethene with 4-nitrophenylcarbonate **17**.

substituents having O–C=O alignment. We thus synthesized benzoates, *N*-phenylurethanes and phenyl carbonates, with a 4-nitro, 4-methoxy or unsubstituted phenyl group on the side chain. Among the nine compounds, a diarylethene **17** with 4-nitrophenylcarbonate showed the best result, 94% de with 91% conversion (Fig. 16).[26]

Helicenoid diarylethenes

Helicene is the name of a group of polyannulated aromatic compounds having helical structures so as to avoid the collision between both ends of the molecule.[27] As the optically resolved helicenes have extremely high specific optical rotation values, generation and destruction of the helicene-like structure upon photoirradiation is very interesting, because the optical rotation can be measured at a wavelength where the compound does not have an absorption band. If the photochromic compound is irradiated on its absorption band, it would show photochromic reaction.

Branda and co-workers synthesized **18** where each wing has three aromatic rings. Upon photoirradiation, each three-ring group was connected by a new cyclohexadiene to form a helicenoid structure with seven rings in a helical arrangement; a dihydrohelicene (Fig. 17).[28] Later they reported the chiral helicenoid diarylethene **14**.[22]

We applied the allylic strain-controlled diastereoselective ring closure to the construction of helicenoid structures. First we tried to extend the aromatic rings of **16*O*** towards the upper directions. However, the steric repulsion between the helicene wings and the hexafluorocyclopentene ring prevented the synthetic reactions of the corresponding *O*-form. Therefore we prepared **19** (Fig. 17). The difference of the specific optical rotation of **19*O*** and its PSS was more than 1300° in ethyl acetate.[29] However, the drawback of this system is that the diastereoselectivity was only 47% de. Apparently the electronic repulsion between the lone pairs of MOMO group and the sulfur atom played an important role in the system of **16*O***. Indeed, when the MOMO group of **16*O*** was replaced by a *t*-BuO group, it showed only 30% de.[25]

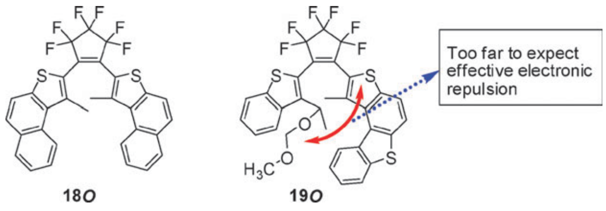


Fig. 17 Helicene-mimic diarylethenes.

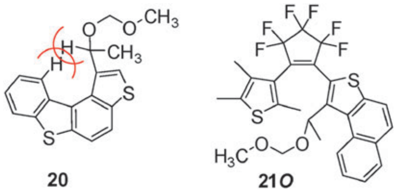


Fig. 18 Improved diastereoselective photochromic helicene-like diarylethene **21**.

In order to improve the diastereoselectivity of the helicenoid diarylethene, the MOMO group and the sulfur atom on the other heteroaromatic ring should come close. Therefore the chiral substituent should be located on the C-3 of the condensed heteroaromatic ring system, and the other heteroaromatic ring should be connected to the perfluorocyclopentene with C-3. However, when the number of condensed aromatic rings is four as shown in **20**, the steric congestion between the chiral substituent and the aromatic ring at the other end became large. Therefore the number of the condensed rings cannot exceed three. Accordingly, we synthesized **21*O*** (Fig. 18).

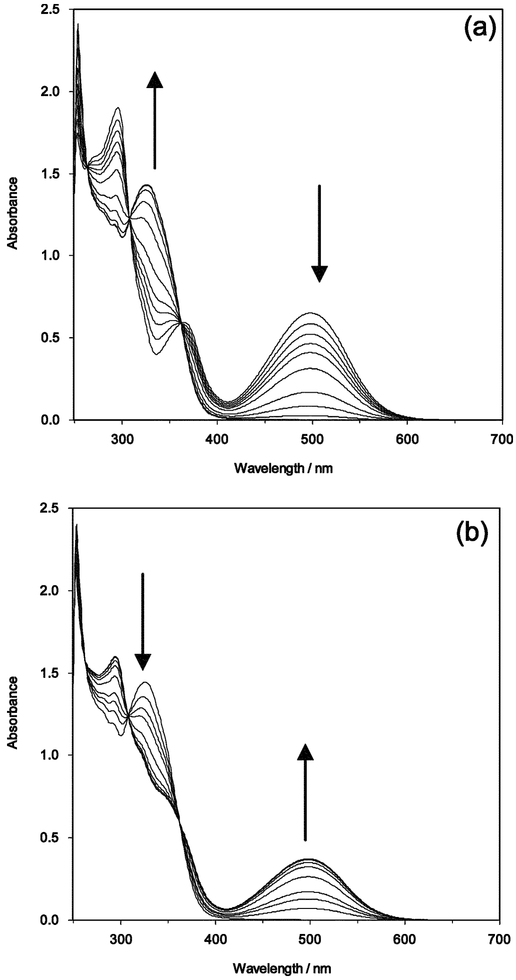


Fig. 19 Spectral change of **21** in ethyl acetate. Concentration: 1.35 × 10^{-4} mol dm^{-3}. (a) From **21*C*** to **21*O***; irradiation at 506 nm. (b) From **21*O*** to PSS; irradiation at 366 nm. (Reprinted from ref. 30 with modification. Copyright 2007, American Chemical Society.)

Upon UV irradiation, **21*O*** in ethyl acetate showed 90% de with 53% conversion. This improvement of the diastereoselectivity was achieved by using electronic repulsion. The change in specific optical rotation of **21** was, however, somewhat smaller than we had expected (950°), owing to the lower number of the condensed aromatic rings.[30] The change in absorption spectra upon photoirradiation is shown in Fig. 19.

Closing remarks

The methods to induce high diastereoselectivity can be classified by three ways. First classification is based on the position of the newly introduced chirality. The chiral position is usually far from the hexatriene, however, in our systems they are always close. According to the description of Branda in his microreview on diarylethene polymers, the carbon atoms on the aromatic rings at the both ends of conjugation are best not used for the position to construct the main chain polymer because those positions should be used to connect functional substituents.[31] Therefore, introduction of chirality to the periphery of the hexatriene, rather than at both ends of conjugation on the aromatic rings, should be preferable.

Another way of classification is that whether the molecule is C_2 symmetric or not. In most reported work, the molecules are C_2 symmetric whereas our systems are not, so far.

A third factor is how to control the ground-state molecular conformation—by intermolecular or intramolecular means. The former method is the environmental restriction of the conformation that Irie's group (single crystals) and Feringa's group (self aggregation) used. The latter method provides a more direct regulation of molecular conformation by the intramolecular interaction that Branda's group (natural product-related) and our group (allylic strain and steric/electronic repulsion) have adopted.

Among the combinations of the three classifications described above, we chose the following combination as the next strategy to construct chiral systems; (1) to introduce chiral units to the periphery of the hexatriene, (2) use of C_2 symmetry for the first time, (3) to control the ground state conformation directly and intramolecularly.

The compounds prepared with this system work quite well. Preliminary results have been presented on the JSPS-CNRS Seminar "New Horizons of Photochromism—From Design of Molecules to Applications, October 2008, Arras, France. The protocol presented represents the best and most versatile method to achieve near 100% diastereoselectivity for any type of benzothiophene-related diarylethenes,[32] results for which will be published in due course.

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