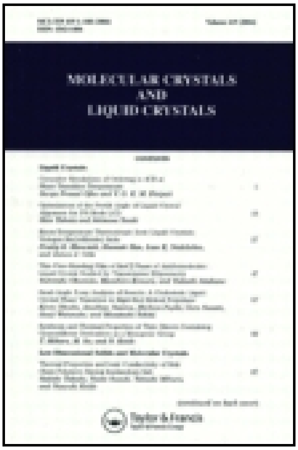

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Photochromism of Diarylethenes With Intralocking Arms

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PHOTOCHROMISM OF DIARYLETHENES WITH INTRALOCKING ARMS

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Abstract A new type of photochromic compounds, diarylethenes with heterocyclic rings, has been developed for optical data storage media. Attention was focused to design and synthesize photochromic compounds with sensitivity at diode laser wavelengths and gated photochemical reactivity.

INTRODUCTION

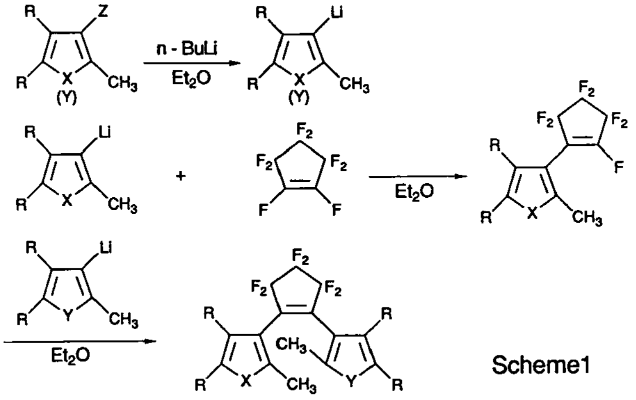
Although much efforts have been so far paid to utilize photochromic materials for optical data storage media, the materials still await the practical application. The limitation is due to the lack of suitable compounds which fulfill the requirements for the reversible recording media. The requirements for the use are follows:

1) Archival storage capability (thermal stability)
2) Low fatigue (can be cycled many times without of loss of performance)
3) High sensitivity at diode laser wavelengths and rapid response
4) Non-destructive readout capability.

We recently developed a new type of fatigue resistant and thermally irreversible photochromic compounds, diarylethenes with heterocyclic rings.[1-12] Besides fatigue resistance and thermal irreversibility, 3) and 4) are also equally required for the practical application. In this paper we report on our approach to gain access to compounds with sensitivity at longer wavelengths and reaction thresholds.

1,2-DIARYLPERFLUOROCYCLOPENTENES WITH SENSITIVITY AT LONGER WAVELENGTHS

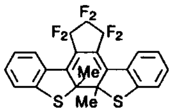
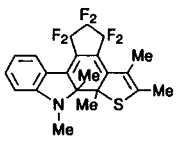
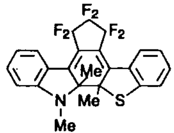
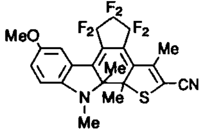
Symmetric and non-symmetric diarylethenes with various aryl groups were synthesized by elimination reactions of perfluorocyclopentene with organolithium compounds as shown in sheme 1.[7]



Scheme1

The mono- and di-substituted perfluorocyclopetene are selectively prepared by controlling the ratio of perfluorocyclopentene and organolithium compounds, and the mono-substituted compounds can be used for the synthesis of non-symmetric diarylethenes. Table 1 summarizes the absorption maxima of the closed-ring forms. A compound having an indole ring on one end and a benzothiophene ring on the other end underwent a photochromic reaction to produce a closed-ring form with absorption maximum at 572 nm. Replacing a benzothiophene ring of symmetric 1,2-bis(2-methylbenzo[b]thiophene-3-yl)perfluorocyclopentene caused a bathochromic shift of the closed-ring form as much as 46 nm. Non-symmetric substitution is effective to shift the absorption maximum to longer wavelengths. The maximum, however, was still shorter than 600 nm. To shift the maximum

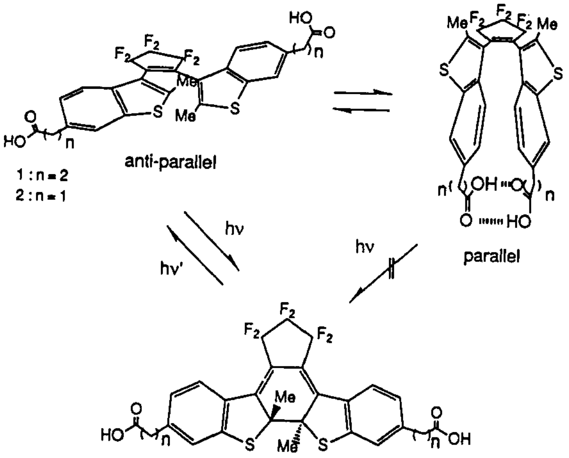
TABLE I Absorption Maxima of Closed-Ring Forms

Compd	λmax (nm)
	526
	568
	572
	665

further to longer wavelengths, we introduced an electron donating group into the indole ring and replaced the benzothiophene with 5-cyanothiophene. The absorption maximum of the closed ring form was observed at 665 nm in hexane and the edge was extended to 850 nm. The compound has sensitivity at the wavelenghts of conventional diode lasers.

NON-DESTRUCTIVE READOUT CAPABILITY

Photochromic media have not readout stability. Even very weak light can induce the reaction in proprtion to the number of photons absorbed by the media. Therefore, the memory is destroyed after many readout operations. A property that avoids the destructive readout is a gated photochemical reactivity. The gated reactivity means the property that irradition with any wavelength causes no reaction, while the photoreaction is induced in the presence of additional stimulation, such as chemicals, heat or another photon. We designed and synthesized chemical- and thermal-gated molecules by introducing substituents that have hydrogen-bonding ability into 1,2-diarylethenes.[11]



The molecules have two conformations, with the two rings in mirror and C_2 symmetries, and the conrotatory cyclization can proceed only from the conformation with C_2 symmetry. This means that the photocyclization is prohibited if the aryl groups are fixed to the mirror symmetry, or parallel orientation, while the reaction occurs when the conformation is in C_2 symmetry, or antiparallel orientaion.

Although photoreaction of 1 was observed in ethanol, it was completely prohibited in cylohexane. The addition of a very small amount of ethanol to the cyclohexane solution gained the photochemical reactivity. In the mixed solvents of cyclohexane and ethanol the cyclization quantum yield increased with increasing ethanol content and reached a plateau value of 0.51 in the solvent containing 15 vol% ethanol.

In order to confirm the conformation change by the addition of ethanol, ^{1}NMR spectra of the molecule were measured in cyclohexane-d_{12} and mixed solvents of cyclohexane-d_{12} and ethanol-d_{6}. The methyl protons at 2-position of the benzothienyl rings give information concerning the relative population of the two conformations.[6] In cyclohexane the upper field signal due to the antiparallel conformation was not observed, while it appeared upon the addition of ethanol. The NMR spectra clearly indicated that the molecule was in parallel conformation in cyclohexane, and it converted into antiparallel conformation upon the addition of small amount of ethanol. In cyclohexane the intra-locking groups fastened the molecule into parallel conformation and made the molecule photochemically inactive. Conversely, ethanol acted as a switch to unlock the system.

The hydrogen bonding can also be broken upon heating. In decalin the photocylization did not occur below 60°C, while it was clearly observed at temperature higher 100°C. The thermal-gated reactivity has potential for use in non-destructive readout.[12]

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