Fabrication and Characterization of Novel Photomemory and Photoswitching System Using Functional Photochromic Compounds

木梨, 憲司

(Degree)
博士 (理学)

(Date of Degree)
2008-03-25

(Date of Publication)
2009-07-28

(Resource Type)
doctoral thesis

(Report Number)
甲4192

(URL)
https://hdl.handle.net/20.500.14094/D1004192

Doctoral Dissertation

Fabrication and Characterization of Novel Photomemory and Photoswitching System Using Functional Photochromic Compounds

（機能性フォトクロミック化合物を用いた新規光メモリ・スイッチングシステムの創製と評価）

Graduate School of Science and Technology
Kobe University

January, 2008

Kenji KINASHI

Contents

Preface

Preface

The present thesis is collection of the studies carried out under the direction of Professor Yasukiyo UEDA and Associate Professor Kenji ISHIDA at Kobe University. This thesis proposes several ideas about photomemory and photoswitches, and is estimating those ideas. In ***chapter 1-3***, synthesis and properties of the photochromic compounds such as spirobenzopyran, azobenzene, diarylethe and spirobenzopyran-azobenzene bi-functional photochromic compounds are described. An attempt to development of thermal stability of spirobenzopyran using silica matrix have been accomplished to avoid thermal unstability as described in ***chapter 1***. An achieved possibility of the recording and deletion using single UV light was suggested by fabrication the glass sandwiched three-layered structure as described in ***chapter 2***. A development of memory density have been established by bi-functional photochromic compound (SpAz) as described in ***chapter 3***.

General Introduction

-Motivation of This Thesis

Photochromism is referred to as a light-induced reversible transformation of a chemical species between two isomers having different absorption spectra [1,2]. The two isomers differ from one another not only in the absorption spectra but also in various physical and chemical properties such as refractive indices, dielectric constants, oxidation–reduction potentials and geometrical structures [3-6]. The instant property changes by photoirradiation without processing leads to their use in various optoelectronic devices, such as optical memory, optical switching, displays, and nonlinear optics [2,7,8]. The possibility of using photochromic compounds for optical data storage was first suggested in 1956 by Yehuda Hirshberg [9]. Since that time, there have been many investigations by various academic and commercial groups, particularly in the area of 3D optical data storage which promises discs that can hold a terabyte of data. Initially, issues with thermal back-reactions and destructive reading dogged these studies, but more recently more-stable systems have been developed. For the fabrication of actual optical memory and optical switching, it require to overcome several problems [10]: (1) the thermal stability under ambient conditions, (2) the fatigue resistant for a repeating of recording and deletion, (3) the sensitivity to the laser diode, (4) the non-destructive read-out capability, (5) the high sensitivity, (6) the high response, (7) the solubility to a polymer, and in addition to those problems, a decreasing of recording density by aggregation, two kinds of light source is necessary to use for record and delete in optical memory and optical switching using photochromic compound.

In this thesis, we tried to avoid those problems above mentioned, three types of attempts have been studied. The thermal stability (***chapter 1***), the increasing of recording density (***chapter 2***) and the problem of two kinds of light source (***chapter 3***).

In chapter 1: Three types of spiropyran derivatives (SP18, SPOH and SPCOOH) were synthesized. Silica matrix is forms polar moiety like as alcohol solvent. PMC-form of SPOH and SPCOOH in silica matrix is stabilized dramatically. Life-half times of SPOH and SPCOOH in silica matrix were estimated to be about $8x10^7$ and $3x10^7$ sec, respectively. It is concluded that PMC-form of SPOH in silica matrix has high thermal stability and thermal bleaching and the application potential for optical memory and photooptical switching.

In chapter 2: We have synthesized a novel bi-functional photochromic compound spirobenzopyran-azobenzene (SpAz) by coupling reaction with spirobenzopyran (Sp) and azobenzene (Az). In toluene solution, SpAz showed four kinds of photoisomers depending on the wavelength of the irradiated light at r.t.. Fluorescence lifetimes of SpAz were obtained to be 117 ps for *trans* and PMC-form and 115 ps for *cis* and PMC-form in toluene solution at -10 °C. These results indicate that photoisomerization depending on the irradiated wavelength is independently occurred regardless of the conformational change of *trans-cis* photoisomerization in Az moiety. In the PMMA films, the fluorescence lifetime was 1520 ps for SpAz (*cis* and PMC-form) at r.t.. The measured lifetime was about 10 times larger in PMMA matrix than in toluene solution.

In chapter 3: we fabricated a novel reversible photoswitching system using diarylethene/glass/bisazomethine three-layered structure. This three-layered structure can be carried out a reversible photoswitching by a single UV light. Upon UV light irradiation from the diarylethene side as recording in the three-layered structure, the color of diarylethene layer changed from colorless to colored. When UV light was irradiated from the bisazomethine side, on the other hand, the diarylethene layer was returned to colorless. It is suggested that a reversible photoswitching system is carried out by a three-layered structure consisted of diarylethene/glass/bisazomethine three-layered structure.

Photochemistry

-Determination of Amount of Light Absorbed

The photokinetic differential equations for the changes of the concentration of the reactant with time cannot be integrated in the given form. The reason is that the amount of the light absorbed I_i of a reactant A_i per time and volume unit depends on the volume element where the reaction takes place and on the time of irradiation t in a very complex manner. This is one of the essential difficulties in photokinetics. This I_i only can be calculated if the geometry of the light source and of the reactor is exactly defined. In principle the following statements are assumed.

The photoreaction takes place in a cell with planar and parallel windows. The radiation area is F [cm^2]. The exciting radiation is monochromic. Its incidence is perpendicular to the front window. The intensity of the incident radiation I_0 [mol•sec^{-1}•cm^{-2}] is constant with respect to time and over the total front area. The sample is not opaque; it can absorb light, but does not scatter. The exit window does not reflect light. All these statements are taken into consideration in **Fig. 1**. A small volume element parallel to the entrance window is considered according to the given assumptions. This volume element has a front area of F [cm^2] and a path-length Δz [cm]. It is assumed to be at a distance z [cm] from this entrance window. Its volume is given by

$$V = F\Delta z[cm^3] \qquad (1.1)$$

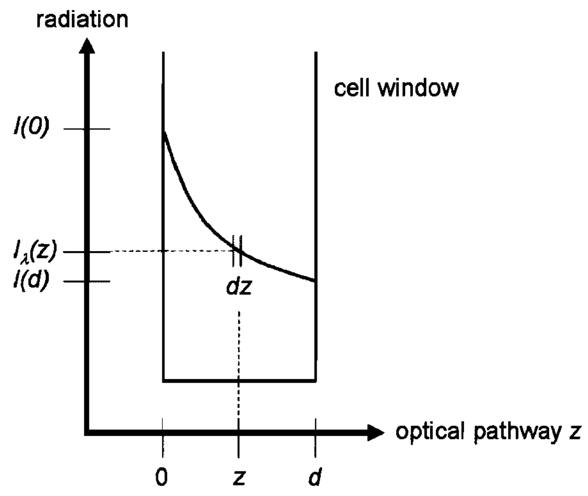


Figure. 1. Schematic drawing to understand the derivation of eq. 1.7. For calculation of the intensity of irradiation, Lambert-Beer's law is used for a wavelength λ. Decadic units are taken as used in practice.

I(z) [mol•sec^{-1}•cm^{-2}] is intensity of irradiation at a distance *z* from the entrance window per irradiation area. Therefore the amount of light absorbed by reactant *Ai* within the volume element *V* is (': wavelength of irradiation)

$$I_{abs}(A_i) = \kappa' a_i I(z) F \Delta z \qquad (1.2)$$

In this relationship κ' is named the Napierian (natural) molar absorption coefficient [1•mol^{-1}•sec^{-1}] of reactant *Ai* at wavelength of irradiation. In principle the derivation of the kinetic equations becomes easier if exponential function and Napierian units are used first. Derivation of relationship above by the volume of the chosen volume element results in

$$I_{abs}(A_i)/V = I_i = \kappa_i' a_i I(z) \qquad (1.3)$$

the amount of light absorbed in mole photons per volume and second. The use of the units mole per litre results in

$$I_i(z) = 1000\kappa_i' a_i I(z) \qquad (1.4)$$

where the factor 1000 corrects for the different units (litres, cm^3).

The change in the number of photons absorbed in the volume element depends on the path length of the radiation in this volume *dz*. Therefore the following differential equation is valid:

$$dI(z) = -I(z)\sum \kappa_i' a_i dz \qquad (1.5)$$

whereby the sum over all those reactants which absorb at the considered wavelength has to be taken.

The integration has to be take into account the fact that the concentration a_i are functions of the irradiation time as well as of the location z of the molecules irradiated. For this reason the intensity of irradiation has to be integrated starting at $I(0)=I_0$ at $z=0$

$$I(z) = I_0 \exp(-\int_0^z \sum(\kappa_i' a_i)dz) \qquad (1.6)$$

This is a generalized form of Bouguer-Lambert-Beer's law. Inserting eq.(1.5) in eq.(1.4) gives the moles of light quanta which are absorbed by reaction A_i at a distance z from the entrance window per second and litre:

$$I_i(z) = 1000\kappa_i' a_i I_0 \exp(-\int_0^z \sum(\kappa_i' a_i)dz) \qquad (1.7)$$

In this equation the factor 1000 takes care of the fact that the units of concentration (mole/litre) and irradiation I_0 [mol•sec^{-1}•cm^{-2}] are combined. Therefore the amount of light absorbed in some volume at a distance *z* has the dimension [mol •sec^{-1}].

In the course of this formal deduction of light absorbed, the Napierian molar absorption coefficient κ is used. Later in the experimental section and during the practical examples using absorbance measurements, ε symbolizes the decadic (molar) absorption coefficients obtained in calibration experiments using UV/Vis spectrometer.

A very simple derivation of the amount of light absorbed in possible using Lambert-Beer's law in solution given by

$$I(d)=I(0)\bullet 10^{-d\sum \varepsilon_i' a_i} \qquad (1.8)$$

using the decadic absorption coefficient and derived in **Fig. 1** at the wavelength of irradiation λ', which is symbolized by a superscript (') in the following. Using the decadic instead of the Napierian absorption coefficient is symbolized by writing ε instead of κ. This is advantageous in practical applications since normal instrumentation supplies data in decadic units. Because monochromic radiation is prerequisite to apply this law, only this type of irradiation can be used in photokinetics. This part of radiation lost within the reaction vessel can be determined as the difference between incident *I(0)* radiation per square area.

$$I_{abs}(d)=I(0)-I(d)=I(0)[1-10^{-d\sum \varepsilon_i' a_i}]$$

where

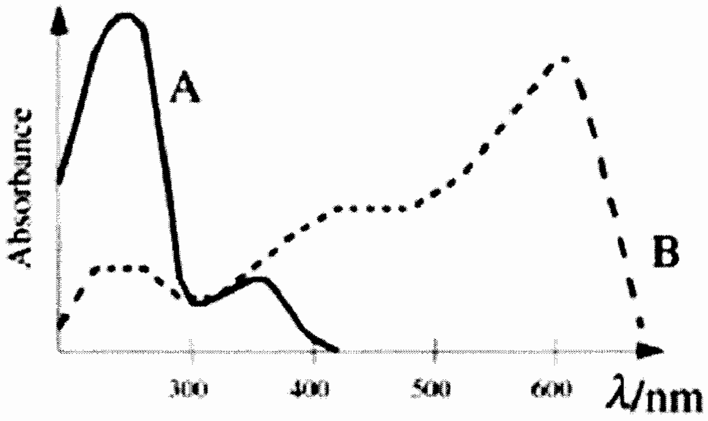
$$d\sum_{i=1}^{i=n}\varepsilon_i' a_i = E' \qquad (1.9)$$

represents the total absorbance of the solution at the wavelength of irradiation.

Photochromism

-Definition of Photochromism

"Photochromism is a reversible transformation of a chemical species induced in one or both directions by absorption of electromagnetic radiation between two forms, A and B, having differenta absorption spectra" [1], as shown in **Fig. 1**.



$$A \underset{h\nu', \Delta}{\overset{h\nu}{\rightleftharpoons}} B$$

Figure 1. Typically thermal irreversible and/or reversible photochromic reaction.

The thermodynamically stable form A is transformed by irradiation into form B. The back reaction can occur thermally (Photochromism of Thermal(T)-type) or photochemically (Photochromism of Photo(P)-type) [7]. The most prevalent organic photochromic systems involve unimolecular reactions: the most common photochromic molecules have a colorless or pale yellow form A and a colored form B (e.g., red or blue). This phenomenon is referred to as positive photochromism. Other systems are bimolecular, such as those involving photocycloaddition reactions. When λmax(A) > λmax(B), photochromism is negative or inverse. The unimolecular processes are encountered, for example, with spiropyrans, a family of molecules that has been studied extensively. Solid photochromic spiropyrans or solutions (in ethanol, toluene, ether, ketones, esters, etc.) are colorless or weakly colored. Upon UV irradiation, they become colored. The colored solutions fade thermally to their original state; in many cases, they can also be decolorized (bleached) by visible light. A few spiropyrans display negative photochromism. They are colored in the dark and bleached by UV light. Many spiropyrans are also thermochromic, and spectra of the colored forms are identical to those produced photochemically.

Families of organic photochromic compounds is shown in below; In all cases, hv' < hv.

Spirobenzopyrans, spironaphthooxazines, naphthopyrans, azobenzenes, dihydroindolizines, perimidinespirocyclohexadienones and quinones undergo thermally reversible photochromic reactions (T-type). Photogenerated isomers are thermally unstable and return to the initial isomers even in the dark. Thermally irreversible photochromic compounds are useful for applications such as optical memory, optical switching and display. Diarylethenes and furylfulgides exhibit thermally stable photochromic reactions (P-type).

In this review, we introduce P-type of photochromic compounds (**Fig. 2**) and T-type of photochromic compounds (**Fig. 3**).

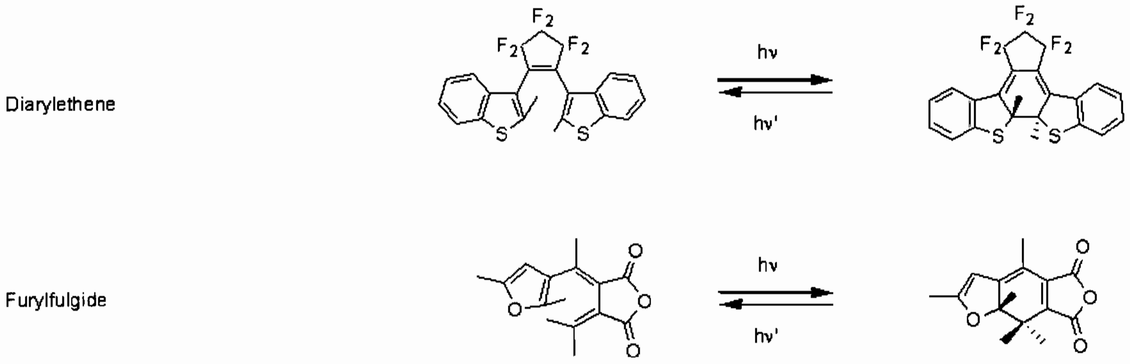


Figure 2. Typical P-type of photochromic compounds.

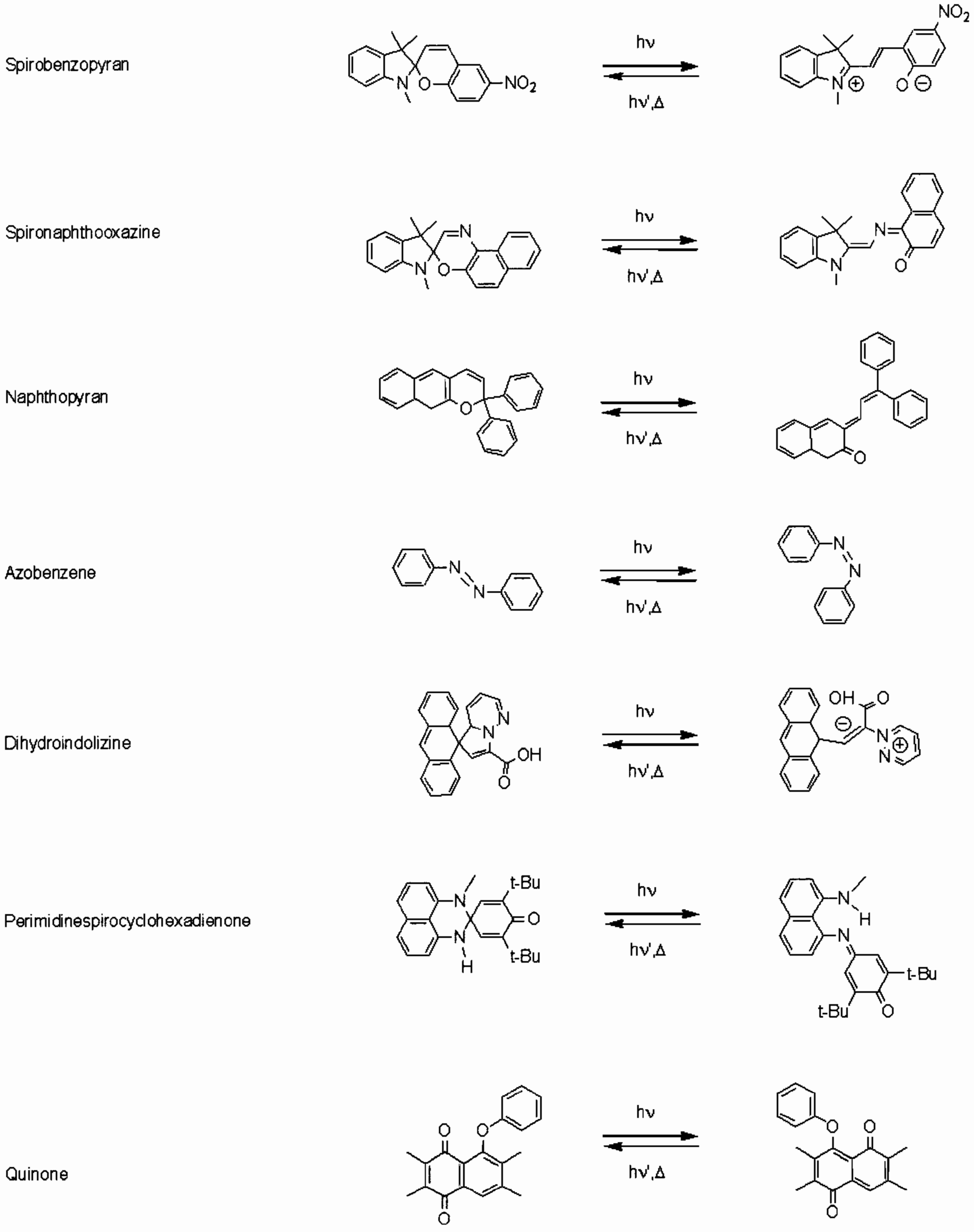


Figure 3. Typical T-type of photochromic compounds.

Photochromism does not have a rigorous definition, but is usually used to describe compounds that undergo a reversible photochemical reaction where an absorption band in the visible part of the electromagnetic spectrum changes dramatically in strength or wavelength. In many cases, an absorbance band is present in only one form. The degree of change required for a photochemical reaction to be dubbed "photochromic" is that which appears dramatic by eye, but in essence there is no dividing line between photochromic reactions and other photochemistry. Therefore, while the *trans-cis* photoisomerization of azobenzene is considered a photochromic reaction, the analogous reaction of stilbene is not. Since photochromism is just a special case of a photochemical reaction, almost any photochemical reaction type may be used to produce photochromism with appropriate molecular design. Some of the most common processes involved in photochromism are pericyclic reactions, *trans-cis* photoisomerizations, intramolecular hydrogen transfer, intramolecular group transfers, dissociation processes and electron transfers (oxidation-reduction).

-*Spiropyrans*

Spiropyrans are a very widely studied chemical class of compounds which exhibit photochromism [1,2]. They consist structurally of a pyran ring, usually a *2H*-1-benzopyran, linked via a common spiro group to another heterocyclic ring, e.g. colorless A. Irradiation of the colorless spiropyran A with UV light causes heterolytic cleavage of the carbon–oxygen bond forming the ring-opened colored species [11], often called the “photomerocyanine (PMC)” form, which can be either *cis*-(B) or *trans*-(C), or the ortho-quinoidal form represented by (D) in **Fig. 4** [12,13]. In fact the structure of the PMC form is probably best represented by a delocalized system with partial charges on nitrogen and oxygen atoms. For simplicity's sake we will use the equivalent of the *trans*-PMC structure (C) in this thesis.

A very large number of possibilities exist for varying the components of the spiropyran ring. The pyran ring is usually a substituted benzo or naphthopyran but the heterocyclic component can be chosen from a long list of ring systems, including indole, benzthiazole, benzoxazole, benzselenazole, quinoline, acridine, phenanthridine, benzopyran, naphthopyran, xanthene, pyrrolidine and thiazolidine. The thiopyran analogues have attracted much interest, as on ring opening they absorb at longer wavelengths than the corresponding pyrans [14,15].

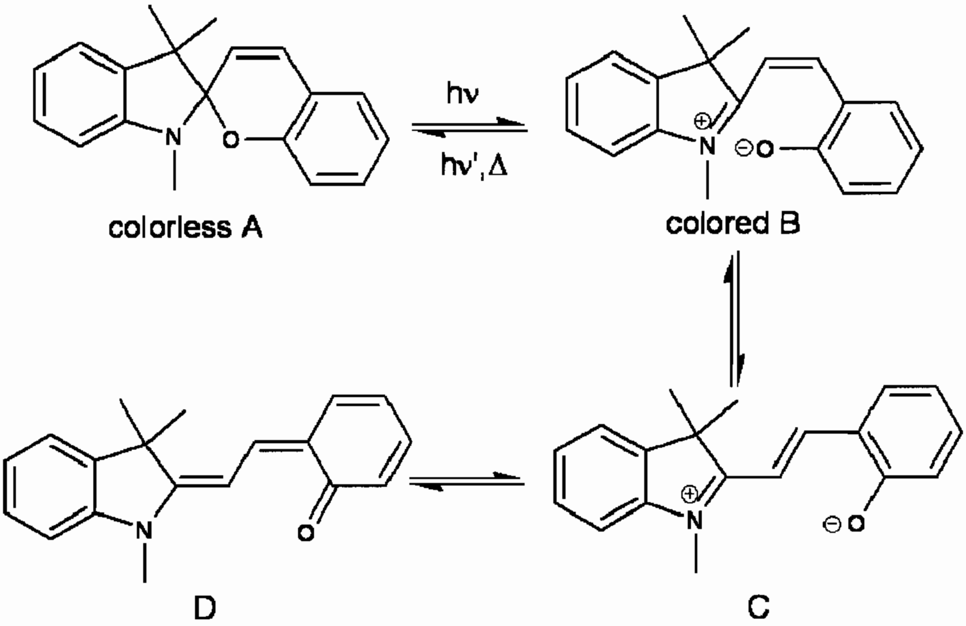


Figure 4. The structure of spiropyran, PMC and ortho-quinoidal form.

-Azobenzenes

Azobenzene is a chemical compound composed of two phenyl rings linked by a N=N double bond. The term "azobenzene" or simply "azo" is often used to refer to a wide class of molecules that share the core azobenzene structure, with different chemical functional groups extending from the phenyl rings. These compounds should be formally referred to as "diazenes". The diazines strongly absorb light and were historically used as dyes in a variety of industries.

One of the most intriguing properties of azobenzene (and derivatives) is the photoisomerization of *trans* and *cis* isomers, as shown in **Fig. 5**. The two isomers can be switched with particular wavelengths of light: UV light, which corresponds to the energy gap of the π-π* (S2 state) transition, for *trans*-to-*cis* conversion, and blue light, which is equivalent to that of the n-π* (S1 state) transition, for *cis*-to-*trans* photoisomerization [16-18]. For a variety of reasons, the *cis* isomer is less stable than the *trans* (for example, it has a distorted configuration and is less delocalized than the *trans* configuration). Thus, *cis*-azobenzene will thermally relax back to the *trans* via *cis*-to-*trans* isomerization. The *trans* isomer is more stable by approximately 50 kJ/mol, and the barrier to photoisomerization is approximately 200 kJ/mol [19].

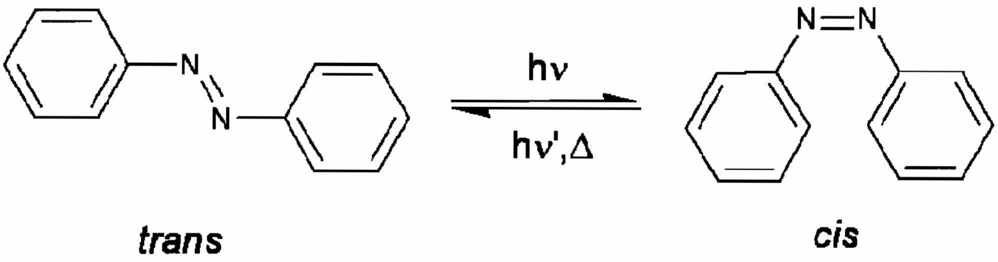


Figure 5. The structure of azobenzene, *trans* and *cis* form.

-Diarylehenes

In chemistry, diarylethene is the general name of a class of compounds that have aromatic groups bonded to each end of a carbon-carbon double bond. Ortho-substitution of the aromatic units results in a stabilization against oxidation [20], but the closed-ring form still has a low thermodynamic stability in most cases (e.g. 2,3-bis(1,2-dimethyl-3-indoly)maleic anhydride has a half-life of 3 h at 80°C) [21-24]. This problem can be addressed by lowering the aromaticity of the system. The most commonly used example are the dithienylethenes, i.e. alkenes with a thiophene ring on either side. The 2-position of the thiophenes is substituted with a methyl group, preventing oxidation of the closed-ring isomer. Often the two free α-positions on the double bond are connected in a 5 or 6-membered ring in order to lock the double bond into the *cis*-form [25]. This makes the dithienylethene undergo only open-closed ring photoisomerization, unconfused by E-Z isomerization.

The dithienylethenes are also of interest for the fact that their photoisomerization requires very little change of shape, as shown in **Fig. 6**. This means that their photoisomerization in a solid matrix can take place much more quickly than with most other photochromic molecules. In the case of some analogs, photochromic behavior can even be carried out in single crystals without disrupting the crystal structure.

One solution to the problem of oxidation is to replace the hydrogens ortho to the carbon-carbon double bond by groups that can not be removed during the oxidation. Following the Woodward-Hoffmann rules [26], the photochemical 6π cyclization takes place in a conrotatory fashion, leading to products with an anti configuration of the methyl substitutents. As both methyl groups are attached to a stereogenic center, two enantiomers (R,R and S,S) are formed, normally as a racemic mixture. This approach also has the advantage that the thermal (disrotatory) ring closure can not take place beacuse of steric hindrance between the substitution groups.

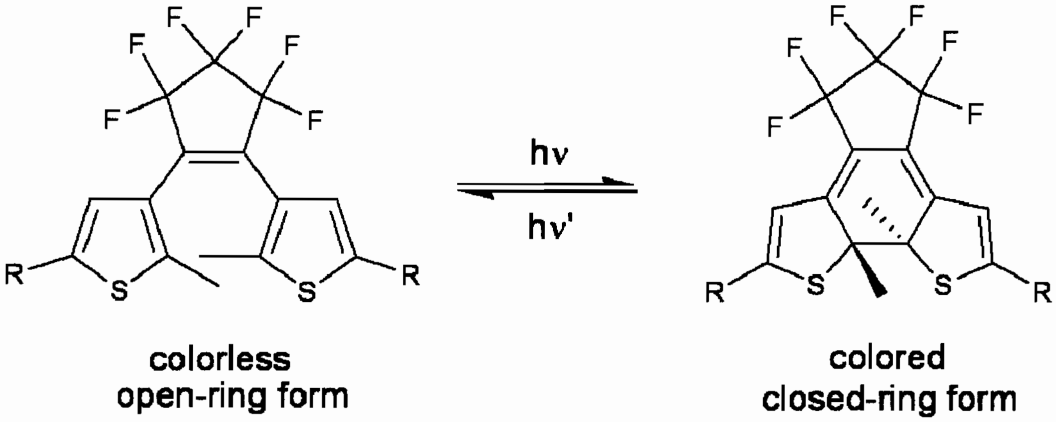


Figure 6. The structure of diarylethene, open-ring and closed-ring form.

References

[1] G. H. Brown, Techniques of Chemistry, Vol.III, Photochromism, Wiley-Interscience, New York, 1971.

[2] H. Durr, H. Bouas-Laurent, Photochromism Molecules and System, Elsevier, Amsterdam, 1990.

[3] M-S. Kim, H. Maruyama, T. Kawai, M. Irie, *Chem. Mater.* **15** (2003) 4539.

[4] E. Kim, Y. K. Choi, M. H. Lee, *Macromolecules* **32** (1999) 4855.

[5] K. Uchida, M. Saito, A. Murakami, S. Nakamura, M. Irie, *Adv. Mater.* **15** (2003) 121.

[6] F. Stellacci, C. Bertarelli, F. Toscano, M. C. Gallazzi, G. Zerbi, *Chem. Phys. Lett.* **302** (1999) 563.

[7] M. Irie, *Chem. Rev.* **100** (2000) 1685.

[8] H. Tian, S. Yang, *Chem. Soc. Rev.* **33** (2004) 85.

[9] Y. Hirshberg, *J. Am. Chem. Soc.* **78**(10) (1956) 2304.

[10] Y. Kubo, M. Kuwana, K. Yoshida, Y. Tomatake, T. Matsuzaki, S. Maeda, *J.*

Am. Chem. Soc. Commun. (1989) 35.

[11] J. Kolc, R.S. Becker, *J. Phys. Chem.*, **71** (1967) 4045.

[12] B. Nadolski, P. Uznanski, M. Kryszewski, *Makromol. Chem., Rapid Commum.*, **5** (1984) 327.

[13] S. M. Aldoshi, O. Atovmya, *Mol. Cryst. Liq. Cryst.*, **149** (1987) 251.

[14] M. Hirano, A. Miyashita, H. Nohira, *Chem. Lett.* (1991) 209.

[15] A. Miyashita, M. Hirano, S. Nakano, H. Nohira, *J. Mater. Chem.* **3**(2) (1993) 221.

[16] H. Rau, E. Lüddecke, *J. Am. Chem. Soc.* **104** (1982) 1616.

[17] I. K. Lednev, T. Q. Ye, R. E. Hester, J. N. Moore, *J. Phys. Chem.* **100** (1996) 13338.

[18] A. Cembran, F. Bernardi, M. Garavelli, L. Gagliardi, G. Orlandi, *J. Am. Chem. Soc.* **126** (2004) 3234.

[19] E. W-G. Diau, *J. Phys. Chem. A* **108** (2004) 950.

[20] M. Irie and W. Schnabol, *Europ. Polym. J.* **18** (1982) 15.

[21] S. Nakamura, M. Irie, *J. Org. Chem.* **53** (1988) 6136.

[22] Y. Nakayama, Y. Hayashi, K. Irie, *J. Org. Chem.* **55** (1990) 2592.

[23] K. Uchida, S. Nakamura, M. Irie, *Res. Chem. Intermed.* **21** (1995) 861.

[24] K. Uchida, T. Matsuoka, K. Sayo, M. Iwamoto, S. Hayashi, M. Irie, *Chem. Lett.* (1999) 835.

[25] M. Hanazawa, R. Sumiya, Y. Horikawa, M. Irie, *J. Chem. Soc., Chem. Commun.* (1992) 206

[26] The Conservation of Orbital Symmetry, R. B. Woodward, R. Hoffmann, Verlag Chemie: Weinheim, 1970.

Chapter 1

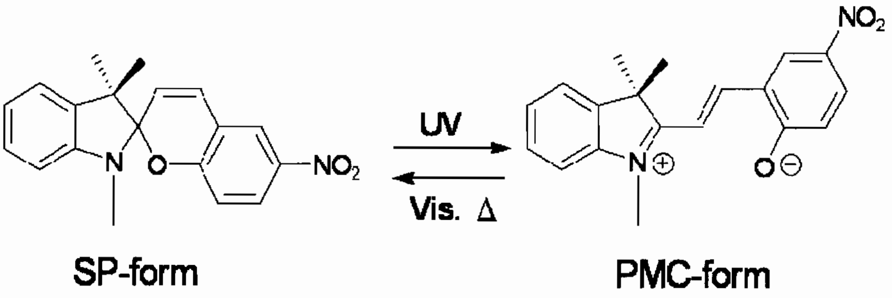
Thermal Stability of Merocyanine Form in Spiropyran/Silica composite Film Photochromism

1-1 Abstract

Three types of spiropyran derivatives introduced octadecyl group (SP18), hydroxyl group (SPOH) and carboxyl group (SPCOOH) were synthesized and were dispersed into various matrices such as chloroform solvent, polymethylmetacrylate (PMMA)/acetone solution and poly(perhydrosilazane) (PSz)/m-xylene solution. Thermal stability of photomerocyanine isomer (PMC-form) in spiropyran derivatives dispersed in silica composite film was studied. Intensity at λmax of PMC-form in silica composite film keeps at initial values in long time except for SP18. PMC-form of SPOH and SPCOOH forms intermolecular hydrogen bonding between hydroxyl or carboxyl group and oxygen atom in silica matrix. Therefore, PMC-form of SPOH and SPCOOH in silica composite film is stabilized dramatically.

1-2 Introduction

Light-induced reversible transformation between two isomers having different absorption spectra is referred to as photochromism [1-4]. Two isomers differ from one another not only in the absorption property but also in refractive indices, dielectric constants, oxidation-reduction potentials, and geometrical structures. Therefore, upon irradiation with an appropriate wavelength of light, these properties can be reversibly switched. One of the most widely studied features of photochromism is the intense absorption of the colored form in the visible region, which is of great importance for practical applications of photochromic compound in optical memory, photooptical switching and display, because photochromic compound can represent two digital codes “0” or “1” as different absorption spectra. Among many types of organic photochromic compounds, the chemistry of spiropyrans has been extensively investigated with special regards to their remarkable properties [5-8]. The photochromism of spiropyrans has a potential usefulness as optical memory and photooptical switching [9-14]. Upon UV irradiation, spirocarbon–oxygen (C–O) bond of the colorless spiro isomer (SP-form) is broken and the subsequent isomerization leads to colored opened isomers called photomerocyanine isomer (PMC-form), as shown in **Scheme 1-2-1**. However, in the last decades, the application of spiropyran in optical memory and optical switches has been hindered by the short half-life time of the colored PMC-form, which reverts thermally to the ring-closed colorless spiropyran. Various methods to stabilize the PMC-form have been developed [15-22].



Scheme 1-2-1. Structural change of spiropyran during photochromism.

In this study, three types of spiropyran derivatives introduced octadecyl group (SP18), hydroxyl group (SPOH) and carboxyl group (SPCOOH) were synthesized and were dispersed into various matrices such as chloroform solvent, polymethylmetacrylate (PMMA)/acetone solution and poly(perhydrosilazane) (PSz)/m-xylene solution. Thermal stability and thermal bleaching were investigated in the dark after UV irradiation. Especially, this work is focused on PSz/m-xylene solution, because PSz converts into colorless transparent silica film under the ambient condition [23,24].

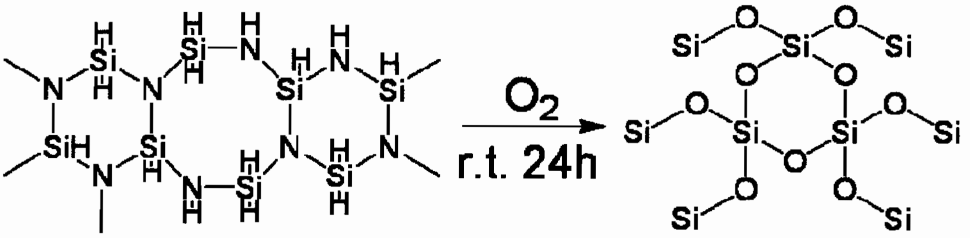
1-3 Experimental

-General

All reagents for synthesis and PSz/m-xylene solution were purchased from Tokyo Kasei Co., and Clariant Japan Co., and used without further purification. The chemical structure of synthesized compounds was characterized by 1H nuclear magnetic resonance spectrum (1H-NMR) and fast atom bombardment mass spectrum (FAB-MS). 1H-NMR spectra were recorded on a Brucker DPX400. FAB-MS were recorded on a JEOL JMS-GC mate IIR. The emission line (λ= 365nm) from Hg lamp was used to generate the PMC-form. UV-Vis. absorption spectroscopic study was performed with Shimadzu UV-2200 spectrophotometer.

-Sample preparation

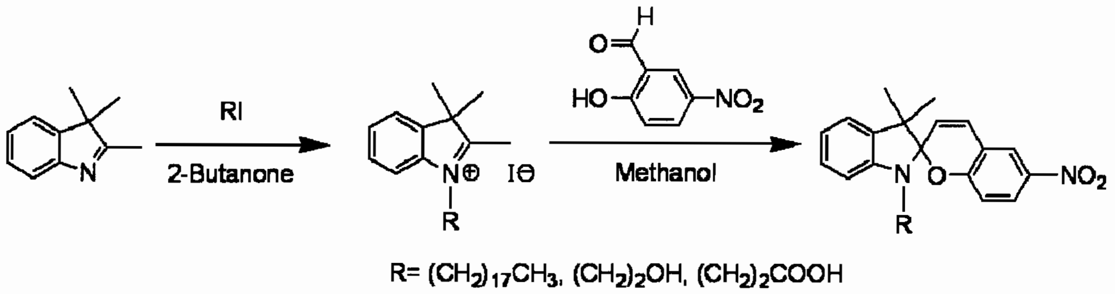
Three types of spiropyran derivatives were dissolved in chloroform, acetone solution with PMMA and m-xylene solution with PSz. Concentrations of spiropyran derivatives were 10^{-4} M in chloroform, 4 wt% in PMMA/acetone solution and $2x10^{-2}$ M in PSz/m-xylene solution, respectively. Thin films were prepared by spin-coating (4000 rpm) on a glass substrate. In the case of SP/PSz composite film, it had been carried out through a day at r.t. in order to convert from PSz to silica according to the reaction equation shown in **Scheme 1-3-1**.



Scheme 1-3-1. Interconversion between poly(perhydrosilazane) and silica

-Synthesis

General procedure for the synthesis of intermediates and spiropyran derivatives is illustrated in **Scheme 1-3-2**. Each spiropyran derivative was prepared by the method in the literatures [25,26].



Scheme 1-3-2. Synthetic procedure of spiropyran derivatives.

1-(2'-Hydroxyethyl)-2,3,3-trimethylindolenium iodide

To a solution of 2,3,3-trimethyl-3H-indole (1.30 g, 8.16 mmol) in 2-butanone 10 ml were added 1-iodoethanol (1.40 g, 8.16 mmol) with stirring. The mixture was heated at reflux for 48 h and cooled to precipitate a solid. The solid was separated by filtration, washed with cold acetone to give a white-red solid (2.43 g, 7.34 mmol) which was used without further purification. Yield 81.0%, mp 145.0-145.5 °C, FAB-MS (M+) 331.

1'-(2''-Hydroxyethyl)-3',3'-dimethyl-6-nitrospiro[2H-1-benzopyran-2,2'-indoline]

To a solution 1-(2'-hydroxyethyl)-2,3,3-trimethylindolenium iodide (1.00 g, 3.02 mmol) in 15 ml methanol were added piperidine (2,3 drops) and then 5-nitrosalicylaldehyde (0.50 g, 3.02 mmol) with stirring. The mixture was heated at reflux for 4 h and cooled. After evaporation of the solvent, the residue was purified by column chromatography (eluent chloroform) to give a white-red crystal (0.37 g, 1.06 mmol). Yield 35.0 %, mp 150.0-150.3 °C, FAB-MS (M+) 352, 1H NMR (400 MHz, $CDCl_3$) δ=1.15 (s, 3H), 1.24 (s, 3H), 3.34-3.42 (m, 1H), 3.52-3.56 (m, 1H), 3.67-3.72(m, 1H), 3.72-3.76 (m, 1H), 5.82 (d, *J*=10.2 Hz, 1H), 6.65 (d, *J*=7.5 Hz, 1H), 6.86 (d, *J*=10.2 Hz, 1H), 6.87 (t, *J*=7.5 Hz, 1H), 7.10 (d, *J*=7.5 Hz, 1H), 7.17 (t, *J*=7.5 Hz, 1H), 7.62 (d, *J*=2.7 Hz, 1H), 7.69 (d, *J*=2.7 Hz, 1H) ppm.

1-4 Results and Discussion

-Photochromic behavior in solution

Absorption spectra of SP-forms used here were quite similar independent of the kinds of substituent. Main absorption peaks of SP-form appeared around at

260 and 350 nm. These absorption bands were assigned to π–π* transitions of chlomene and of indoline rings, respectively. **Figure 1-4-1** shows UV-Vis. absorption spectra of spiropyran derivatives after UV light irradiation with 365 nm in chloroform solution. Upon UV light irradiation, the solution changed from colorless to deeply purple and a broad absorption peak assigned to PMC-form appeared around at 580 nm.

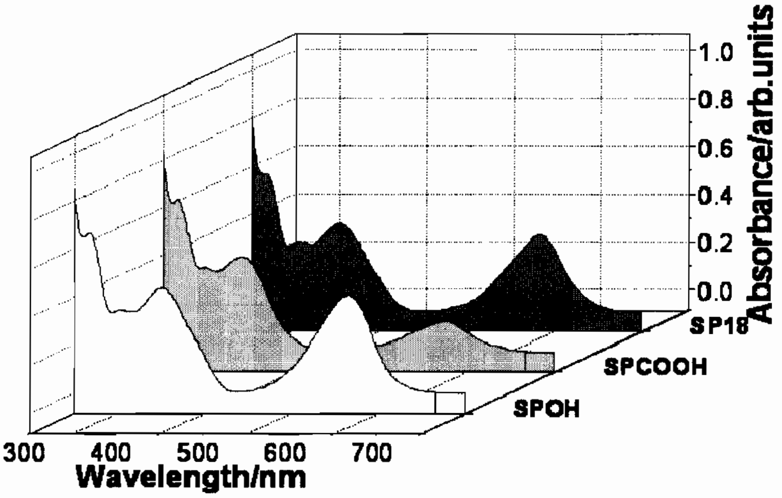


Figure 1-4-1. UV-Vis. Absorption spectra of PMC-form in chloroform solution.

The λmax of PMC-form of spiropyran derivatives in various matrices are shown in **Table 1-4-1**. In the case of silica matrix, the λmax of PMC-form of spiropyran derivatives showed the hypsochromic shift (blue shit) in the visible region. Nadolski et al has pointed out that in PMC-form, the ground state is more polar than the excited state and a polar solvent tends to stabilize the ground state, resulting to hypsochromic shift. In addition, they have also pointed out that the thermal stabilization rate slows down because the potential barrier of the isomerization reaction from PMC-form to SP-form becomes higher [27]. From the experimental results mentioned above, it seems that silica matrix is polar moiety comparing to other matrices. Richardt has introduced the transition energy expressed in kcal/mol in order to explain the solvent effect on □max of pyridium-*N*-phenoxide betain dye in various solvents. This parameter is referred as the E_T values, which are related with λmax by following equation [28].

$$E_T\,(\text{kcal/mol}) = 2.859 \times 10^4/\lambda\text{max(nm)}$$

Figure 1-4-2 shows linear plot of λmax of PMC-form versus E_T parameters of various solvent. E_T values of PMMA and silica matrices were estimated to 42 kcal/mol and 49 kcal/mol from λmax of PMC-form, respectively. Therefore, it is concluded that silica matrix forms polar moiety like as alcohol solvent.

Table 1-4-1. λmax of PMC-form spiropyran derivatives in various matrices

	λmax/nm		
	Chloroform	PMMA	Silica
SP18	580	575	550
SPOH	570	560	540
SPCOOH	580	570	545

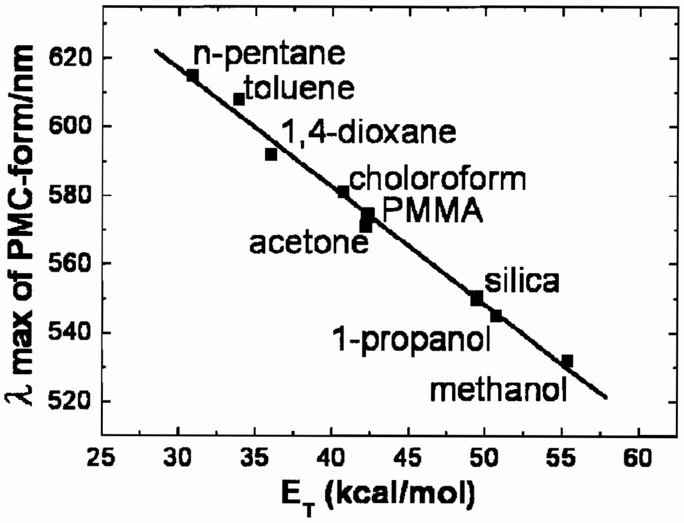


Figure 1-4-2. Plots of λmax/nm of PMC-form vs. E_T value for SP18 in various solution.

-Thermal stability

Figure 1-4-3 shows time dependence on absorption intensity at λmax of PMC-form in various matrices in the dark at 25 °C. In the case of chloroform solution and PMMA matrix, intensity at λmax of PMC-form decreases rapidly. Absorption intensity in silica matrix, on the other hand, keeps initial values for long period except for SP18. It is suggested that PMC-form molecules of SPOH and SPCOOH form intermolecular hydrogen bonding between a proton generated hydroxyl or carboxyl group and oxygen atom in silica matrix. Molecular vibration toward back reaction is inhibited by hydrogen bonding. Therefore, PMC-form of SPOH and SPCOOH in silica matrix is stabilized dramatically. Life-half times of intensity at λmax of various PMC-form molecules are summarized in **Tab. 1-4-2**. Life-half times of SPOH and SPCOOH in silica matrix were estimated to be about $8x10^7$ and $3x10^7$ sec, respectively. Thermal stability of PMC-form in this study is about 10^5 times higher than that of other photochromic compounds reported in the last few decades.

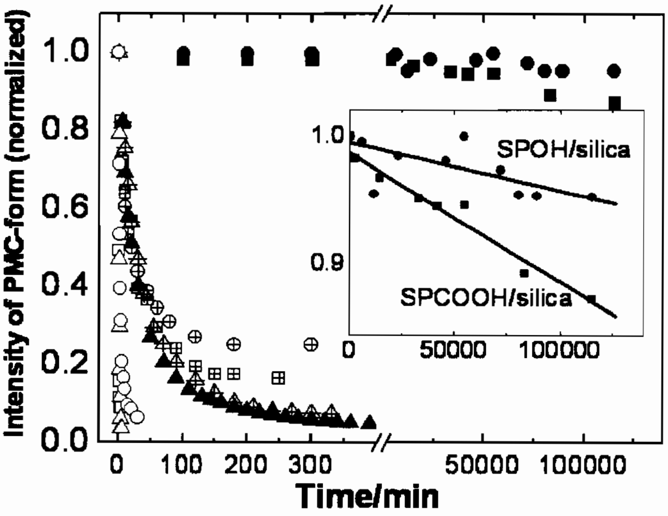


Figure 1-4-3. Time dependence on absorption intensity at lmax of PMC-form in various matrices in the dark at 25 ° C; Δ (open) SP18/chloroform, (cross) /PMMA, (filled) /silica, □ (open) SPCOOH/chloroform, (cross) /PMMA, (filled) /silica, ○ (open) SPOH/chloroform, (cross) /PMMA, (filled) /silica.

Table 1-4-2. Life-half time of PMC-form of spiropyran derivatives in various matrices

	$\tau_{1/2}$/sec		
	Chloroform	PMMA	Silica
SP18	84	1740	1900
SPOH	163	1260	8×10^7
SPCOOH	47	1529	3×10^7

-Thermal bleaching

Thermal bleaching of PMC form is evaluated with relative intensity (I/I_0) at λmax before and after heat treatment in the range between 30 and 130 °C for 1 min in the dark. **Figure 1-4-4** shows the thermal bleaching of PMC forms the thermal bleaching of SPCOOH and SPOH in silica matrix. Relative intensity of

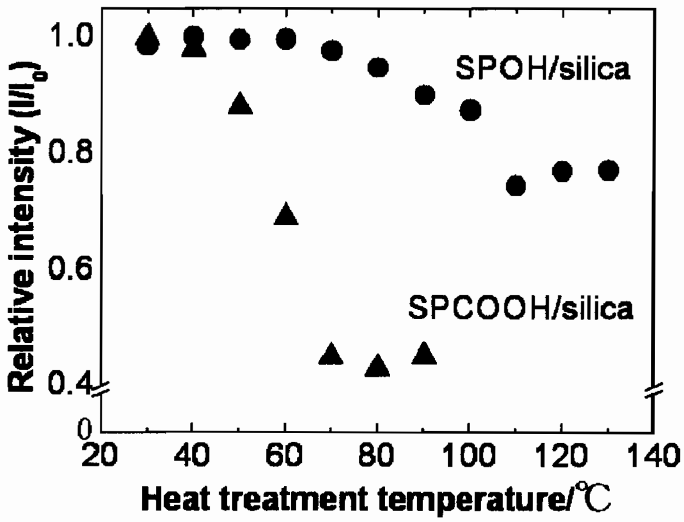


Figure 1-4-4. Thermal bleaching of PMC-form of SPOH and SPCOOH in silica matrix.

PMC form of SPCOOH was decreased rapidly by heat treatment above 40 °C. On the other hand, the degree of decreasing in that of SPOH is prevented remarkably under 100 °C. Thermal bleaching of PMC-form of SPOH around at 100 °C is about twice as high as that of SPCOOH. PMC-form of SPOH forms not only intermolecular hydrogen bonding between proton in OH group and oxygen in silica matrix but also intramolecular hydrogen bonding between proton in OH group and O^- generated by cleavage of spirocarbon–oxygen bond, as shown in

Fig. 1-4-5. On the other hand, only intermolecular hydrogen bonding forms because of steric hindrance of carboxyl group and structural vibration of resonance COO. Therefore, it is concluded that remarkable bleaching stability of PMC-form of SPOH in silica matrix is attributed by strong hydrogen bonding. Stabilized PMC-form of SPOH converts completely into SP-form upon visible light irradiation.

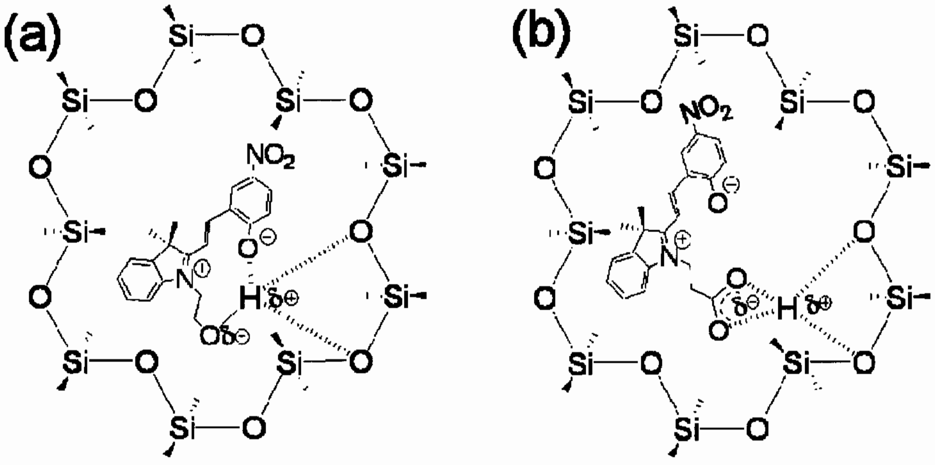


Figure 1-4-5. Schematic representation of PMC-form of SPOH and SPCOOH in silica matrix; (a) SPOH, (b) SPCOOH.

1-5 Conclusions

Three types of spiropyran derivatives (SP18, SPOH and SPCOOH) were synthesized. Silica matrix is forms polar moiety like as alcohol solvent. PMC-form of SPOH and SPCOOH in silica matrix is stabilized dramatically. Life-half times of SPOH and SPCOOH in silica matrix were estimated to be about $8x10^7$ and $3x10^7$ sec, respectively. PMC-form molecules of SPOH and SPCOOH form intermolecular hydrogen bonding between a proton generated hydroxyl or carboxyl group and oxygen atom in silica matrix. Thermal bleaching of PMC-form of SPOH is about twice as high as that of SPCOOH. Thermal bleaching of PMC-form hardly does not occur up to about 80 °C. It is concluded that PMC-form of SPOH in silica matrix has high thermal stability and thermal bleaching and the application potential for optical memory and photooptical switching.

1-6 References

[1] G. H. Brown, Techniques of Chemistry, Vol.III, Photochromism, Wiley-Interscience, New York, 1971.

[2] H. Durr, H. Bouas-Laurent, Photochromism Molecules and System, Elsevier, Amsterdam, 1990.

[3] M. Irie, *Chem. Rev.* **100** (2000) 1685.

[4] Andrew J. Myles, Tony J. Wigglesworth, Neil R. Branda, *Adv. Mater.* **15** (2003) 745.

[5] G. Berkoric, V. Krongauz, V. Weiss, *Chem. Rev.* **100** (2000) 1741.

[6] S. Hashimoto, A Shimojima, T. Yuzawa, H. Hiura, *J. Mol. Struct.* **1** (1991) 242.

[7] M. Suzuki, T. Asahi, H. Masuhara, *J. Photochem. Photobiol A: Chem.* **178** (2006) 170

[8] M.J. Cho, G.W. Kim, W.G. Jun, S.K. Lee, J. Jin, D.H. Choi, *Thin Solid Films* **500** (2006) 52

[9] K. Kinashi, K. Furuta, Y. Harada, Y. Ueda, *Chem. Lett.* **35** (2006) 298.

[10] F. M. Raymo, *Adv. Mater.* **14** (2002) 401.

[11] S.Giordani, M.A. Cejas, F.M. Raymo, *Tetrahedron* **60** (2004) 10973.

[12] Y. Zhou, D. Zhang, Y. Zhang, Y. Tang, D. Zhu, *J. Org. Chem.* **70** (2005) 6164.

[13] M.Q. Zhu, L. Zhu, J.J. Han, W. Wu, L.K. Hurst, A.D.Q. Li, *J. Am. Chem. Soc.* **128** (2006) 4303.

[14] D. Pisignano, E. Mele, L. Persano, A. Athanassiou, C. Fotakis, R. Cingolani, *J. Phys. Chem. B* **110** (2006) 4506.

[15] S.H. Kim, S.M. Lee, J.H. Park, J.H. Kim, S.W. Kang, *Dyes Pigm.* **45** (2000) 51.

[16] B.H. Lee, J.H. Kim, M.J. Cho, S.H. Lee, D.H. Choi, *Dyes Pigm.* **61** (2004) 235.

[17] Y. Kawanishi, K. Seki, T. Tamaki, M. Sakuragi, Y. Suzuki, *J. Photochem. Photobiol A: Chem.* **109** (1997) 237.

[18] X. Meng, W. Zhu, Z. Guo, J. Wang, H. Tian, *Tetrahedron* **62** (2006) 9840.

[19] Z. Liu, L. Jiang, Z. Liang, Y. Gao, *J. Mol. Struct.* **737** (2005) 267.

[20] A. Grofcsik, P. Baranyai, I. Bitter, A. Grün, É. Köszegi, M. Kubinyi, K. Pál, T. Vidóczy, *J. Mol. Struct.* **614** (2002) 69.

[21] A. Shumburo, M.C. Biewer, *Chem. Mater.* **14** (2002) 3745.

[22] S.H. Kim, S.Y. Park, C.J. Shin, N.S. Yoon, *Dyes Pigm.* **72** (2007) 299.

[23] H. Tagaya, T. Nagaoka, T. Kuwahara, M. Karasu, J. Kadokawa, K. Chiba, *Microporous Mater.* **21** (1998) 395.

[24] T. Hori, H. Tagaya, T. Nagaoka, J. Kadokawa, K. Chiba, *Appl. Surf. Sci.* **121/122** (1997) 530.

[25] X. Li, Y. Wang, T. Matsuura, *J. Meng, Heterocycles*, **51** (1999) 2639.

[26] X. Li, J. Li, Y. Wang, T. Matsuura, J. Meng, *J. Photochem. Photobiol A: Chem.* **161** (2004) 201.

[27] B. Nadolski, P. Uznanski, M. Kryszewski, *Makromol. Chem., Rapid Commun.* **5** (1984) 327.

[28] C. Richardt, *Chem. Rev.* **94** (1994) 2319.

Chapter2

Photoswitching of Photochromic Diarylethene Using Bisazomethine Dye

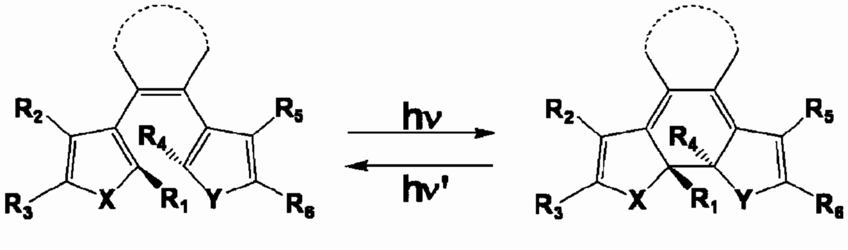
2-1 Abstract

Novel photoswitching system was fabricated of diarylethane/ glass/bisazomethine three-layered system. Diarylethene and bisazomethine used here are 1,2-bis(2,4-dimethyl-thiophene-3-yl)perfluorocyclopentene (DE) and *N,N'*-bis[(4-(*N,N*-diethylamino)benzylidene]diaminomaleonitrile (BAE). Bisazomethane is blue-violet compound and has an absorption in the wavelength region from 400 to 700 nm. Upon UV light irradiation on the DE layer in order to record optical information in the three-layered structure, the color of DE changed from colorless to colored (red). When UV light was irradiated on the BAE layer, on the other hand, DE was returned to colorless by the fluorescence from BAE. Upon visible light exposure on the BAE layer, the colored DE did not returned to colorless because visible light is absorbed with BAE. We prepared that photoswitching using single UV light is carried out by a sandwiched structure consisted of diarylethene/glass/bisazomethine three-layered structure.

2-2 Introduction

Light-induced reversible transformation between two isomers having different absorption spectra is referred to as photochromism [1]. The two isomers differ from one another not only in the absorption property but also in refractive indices, dielectric constants, oxidation-reduction potentials, and geometrical structures [2-5]. In practical, upon irradiation with an appropriate wavelength of light, these properties can be reversibly switched. Research on photochromic compounds has aroused much interest for their potential applications on photo memories and photoswitching devices [4-11], where each isomer of the photochromic compound can represent “0” or “1” of a digital code [12-14].

Therefore, for applications, thermal irreversibility of the photoswitching units is required in most cases. As a thermally irreversible system, diarylethenes may be the most promising compounds for these applications due to the good thermal stability and fatigue resistance of both isomers [15,16]. Typical diarylethenes undergo the following cyclization/cycloreversion photochromic reactions upon photoirradiation, as shown in **Scheme 2-2-1**. However, for applications in photoswitching using diarylethenes, two independent light sources are necessary to record and delete. However, two independent light sources are disadvantageous to application. In this study, we synthesized bisazomethine as a fluorescence material whose fluorescence spectrum has an overlap with the absorption spectrum of the closed-ring isomer of diarylethene. We have prepared photoswitching system consisted of diarylethene/glass/bisazomethine three-layered structure, which could be carried out by single UV light source.



Scheme 2-2-1. Photochromic reaction of typical diarylethene.

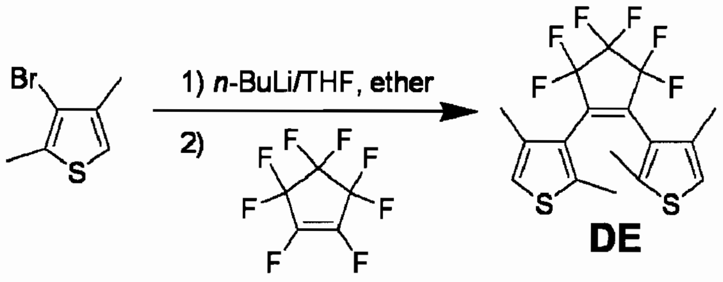
2-3 Experimental

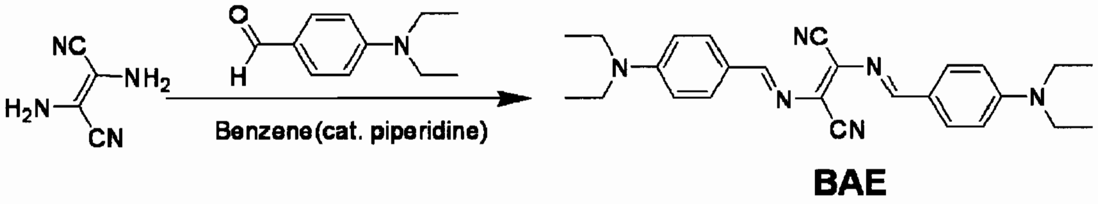
-General

All reagents for synthesis were purchased from Tokyo Kasei Co., and used without further purification. Poly(methyl methacylate) (PMMA) (*Mw*=10,000) was used as polymer matrix. The chemical structure of synthesized compounds was characterized by ^{1}H nuclear magnetic resonance spectrum (^{1}H-NMR) and fast atom bombardment mass spectrum (FAB-MS). ^{1}H-NMR spectrum was recorded on a Brucker DPX400 with $CDCl_3$ as the solvent and tetramethylsilane (TMS) as an initial standard. FAB-MS was recorded on a JEOL JMS-GC mate IIR. The emission lines (300 and 600 nm) from Xenon lamp (MAX-301, ASAHI SPECTRA) were used to generate the cyclized closed-ring isomer of DE (300 nm) and to return to the cycloreversed open-ring isomer of DE (600 nm). UV-Vis. absorption spectrum was measured with Shimadzu UV-2200 spectrophotometer. Photoluminescence (PL) spectrum was performed with HITACHI F-2500 Fluorescence Spectrophotometer.

-Synthesis

Synthetic procedure of diarylethene and bisazomethine dyes is illustrated in **Scheme 2-3-1**. 1,2-Bis(2,4-dimethylthiophene-3-yl)perfluorocyclopentene (DE) and *N,N'*-bis[(4-*(N,N*-diethylamino)benzylidene]diaminomaleonitrile (BAE) were synthesized according to literature method; [16,17] for DE, [18,19] for BAE and conformed by ^{1}H-NMR and FAB-MS.





Scheme 2-3-1. Synthetic procedure of DE and BAE.

1,2-bis(2,4-dimethylthiophene-3-yl)perfluorocyclopentene (DE)

To a stirring dry Et_2O (470 ml) and dry THF (30 ml) containing 3-bromo-2,4-dimethylthiophene (2.00 g, 10.47 mmol), 1.6 N *n*-BuLi hexane solution (6.7 ml, 10.47 mmol) was slowly added at −60 °C under an argon atmosphere. Then octafluorocyclopentene (0.7 ml, 5.24 mmol) was slowly added to the reaction mixture at −60 °C. The reaction was stopped by the addition of CH_3OH and extracted with Et_2O. The organic layer was dried with anhydrous $MgSO_4$, and evaporated in vacuo. The crude product was purified by column chromatography on silica gel using hexane to give 1,2-bis(2,4-dimethylthiophene-3-yl)perfluorocyclopentene (DE) 0.47 g (22.6%) as pale yellow crystal. m.p. 133.1-133.4, MS 386, ^{1}H-NMR (400 MHz, $CDCl_3$) δ=2.04 (s, 6H), 2.29 (s, 6H), 6.70 (s, 2H) ppm.

N,N'-bis[(4-(N,N- diethylamino)benzylidene]diaminomaleonitrile (BAE)

To a vigorously stirring solution containing diaminomaleonitrile (2.00 g, 18.50 mmol), *p-N,N*-diethylaminobenzaldehyde (3.28 g, 18.50 mmol) in benzene (100 ml), piperidine (2,3 drops) was added to the mixture, and the mixture stirred for 2h at refluxed temperature. Water was removed using a Dean-Stark trap. The reaction mixture was cooled to room temperature. The precipitated crude product was separated by filtration and washed with cold toluene. The crude product was purified by column chromatography on silica gel using hexane/chloroform (1/1) and recrystallized from chloroform to give *N,N'*-bis[(4-*(N,N*-diethylamino)benzylidene]diaminomaleonitrile (BAE) 5.87 g (74.4%) as blue-violet crystal. m.p. 282.5-284.8, MS 426, ^{1}H-NMR (400 MHz, CDCl$_3$) δ= 0.98 (t, 12H, *J*=7.2 Hz, -CH$_3$), 1.38 (sext, 8H, *J*=7.2 Hz, -CH$_2$-), 6.66 (d, 4H, *J*=8.8 Hz, 3Ph), 7.81 (d,4H, *J*=8.8 Hz, 2Ph), 8.54 (s, 2H, Ph-CH) ppm.

-Sample preparation

For the PMMA films, DE (or BAE) with the weight concentration of 4 wt% was mixed with 40 mg of PMMA and dissolved in 2 ml of acetone. Thin films were prepared by spin-coating with a spinning speed of 4000 rpm on a glass substrate (0.12-0.17 mm-thickness). **Figure 2-3-2** shows the schematic representation of the DE/glass/BAE. The preparing condition of the sandwich film was the same as the above method.

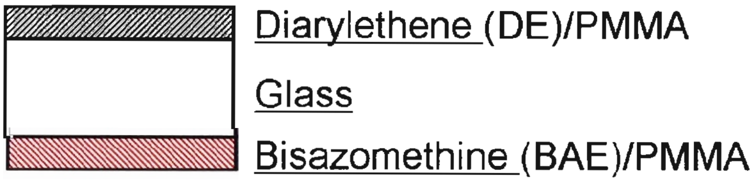


Figure 2-3-2. Schematic drawing of the diarylethene/glass/bisazomethine sandwiched film.

2-4 Results and Discussion

-Photochromic behavior of diarylethene

Photochromic compound DE underwent photochromism in solution at room temperature. The absorption spectral change of DE in hexane ($C=1.6\times10^{-4}$ M) by irradiation with 300 nm light using Xenon lamp was shown in **Fig. 2-4-1**. The absorption maximum of its colorless open-ring isomer was observed at 232 nm (ε, 1.4×10^{4} $M^{-1}cm^{-1}$). Upon irradiation with 300 nm UV light, the colorless solution turned to red with a new broad absorption band centered at 536 nm. The red color is due to the formation of the closed-ring isomer. The absorption coefficient of the closed-ring isomer at 358 and 536 nm were 2.9 $\times10^{3}$ and 2.2×10^{3} $M^{-1}cm^{-1}$, respectively. The isosbestic points 250, 280 and 290 nm were appeared under irradiation. The spectral shape and peak positions of DE in PMMA matrix were almost similar to the results of hexane solution. **Figure 2-4-2** represents the time-resolve photochromic reaction of DE in hexane (closed circle) and PMMA (open circle) by alternating UV and visible irradiation at room temperature. The absorption change was monitored at 536 nm which is absorption maximum of closed-ring isomer of DE. In hexane and

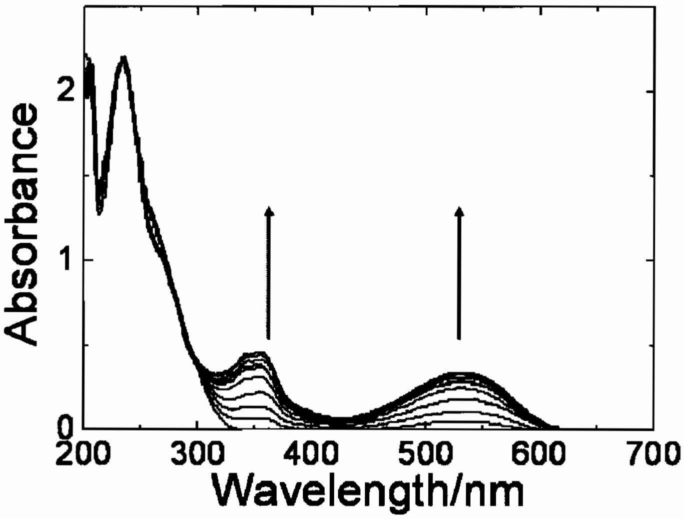


Figure 2-4-1. Absorption spectral change of DE in hexane (C=1.6x10^{-4} M) upon irradiation with 300 nm light.

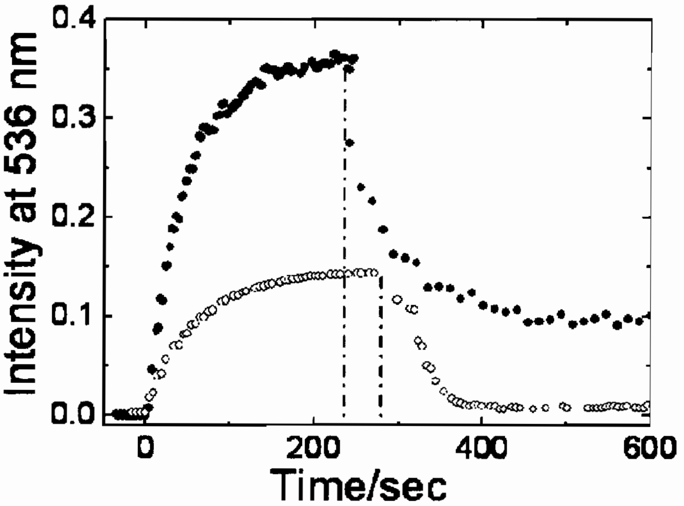


Figure 2-4-2. The time-resolve photochromic reaction of DE in hexane (closed circle) and PMMA (open circle) by alternating UV and visible irradiation as a function of time at room temperature

PMMA, the absorbance at 536 nm increased and DE reached the photostationaly state by 300 nm light irradiation for about 200-300 sec. Upon visible light (λ>430 nm) irradiation for about 100 sec, on the other hand, the absorbance at 536 nm decreased. The fatigue resistant property of DE in PMMA also exhibited a good reversibility, as shown in **Fig. 2-4-3**.

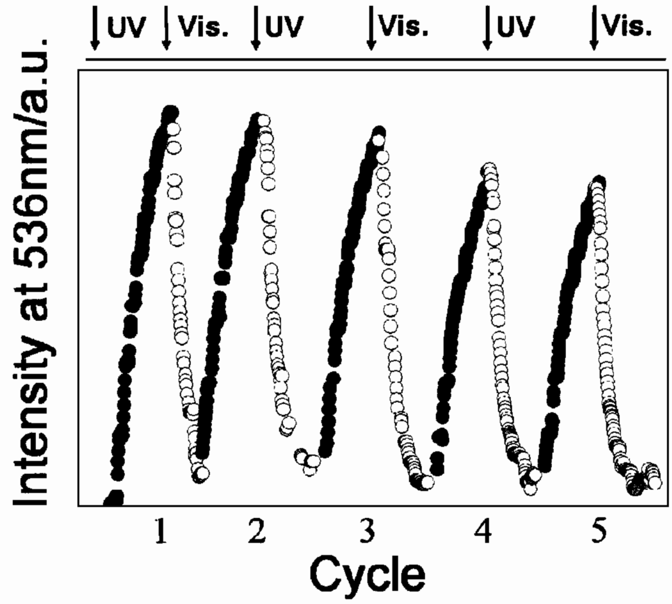


Figure 2-4-3. Absorbance change at 536 nm of DE in PMMA following periodic UV and Vis. irradiation.

-Absorption and fluorescence properties of bisazomethine

Figure 2-4-4 shows the absorption and photoluminescence (PL) spectra of BAE in chloroform (C=3.5x10^{-5} M). BAE exhibits the absorption maximum around at 545 nm (ε, 6.5x10^{4} M^{-1}cm^{-1}) in chloroform solution. The PL spectrum shows that the emission of BAE lies in the red region with peaks at 421 and 602 nm. BAE showed bright red PL when irradiated with 300 nm light. The FWHM of PL spectrum was about 50 nm, which is one of the narrowest FWHM of red-light-emitting materials so far. The reason for FWHM of bisanil dye was attributed to the symmetrical donor-accepter conjugated structure of the dye molecule [20].

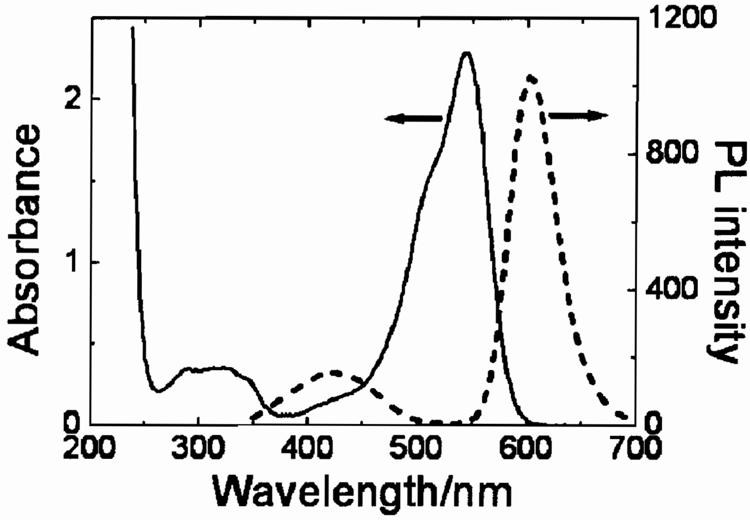


Figure 2-4-4. The absorption and PL spectra of BAE in chloroform solution (C=3.5x10^{-5} M).

In PMMA matrix as a solid state, absorption and PL properties of BAE exhibited the absorption and PL maximum at around 540 and 581 nm, respectively. The FWHM of PL maximum was about 59 nm. The PL intensity showed that the emission of BAE lies in the red region with a peak at 581 nm. The main absorption and PL properties at photostationary state of DE (the closed-ring isomer) and BAE are summarized in **Table 2-4-1**.

Table 2-4-1. The main absorption and PL properties of DE and BAE.

	Absorption, λ (nm)/ ε (10^3 M^{-1}cm^{-1})		PL, λ (nm)	
	Solution	PMMA	Solution	PMMA
DE	358/2.9 536/2.2	359 537	No Fluorescence	
BAE	545/65	575	602	581

-Photoswitching function of diarylethene/glass/bisazomethine three-layered structure

Upon UV light irradiation with 300 nm light on the BAE layer side in the three-layered structure, fluorescence with 581 nm light was induced form BAE, on the other hand, when irradiated 300 nm light from DE layer side, the fluorescence wasn't confirmed because DE didn't emit any fluorescence whether its formation was open- or closed-ring isomer, as shown in **Fig. 2-4-5**.

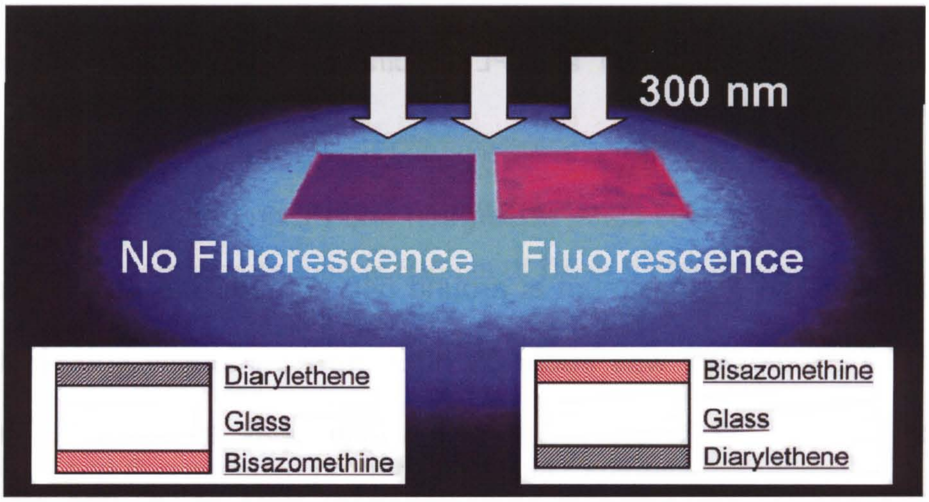


Figure 2-4-5. Photograph of two types of state which indicates no fluorescence and fluorescence of the three-layered structure upon irradiation with 300 nm light.

The photoswitching performance of the three-layered system was examined. **Figure 2-4-6** shows an absorption spectral change of the three-layered system upon irradiation with 300 nm light. The absorption spectrum is the summation of three absorption spectra of DE, BAE and glass substrate which has a wavelength region in less than about 330 nm. Upon irradiation with 300 nm light on the DE layer side in the three-layered structure, the color turned from red to deeply red. Main absorption peak around at 540 nm was assigned to π–π* transition of BAE, and the increasing absorption peaks at 359 and 537 nm were assigned to π–π* transition of closed-ring isomer of DE. A change in color can explain that the absorption spectrum of DE has an overlap with that of BAE. When 300 nm light was irradiated from BAE layer side, on the other hand, the deeply colored red was returned to red by the fluorescence with 581 nm from BAE.

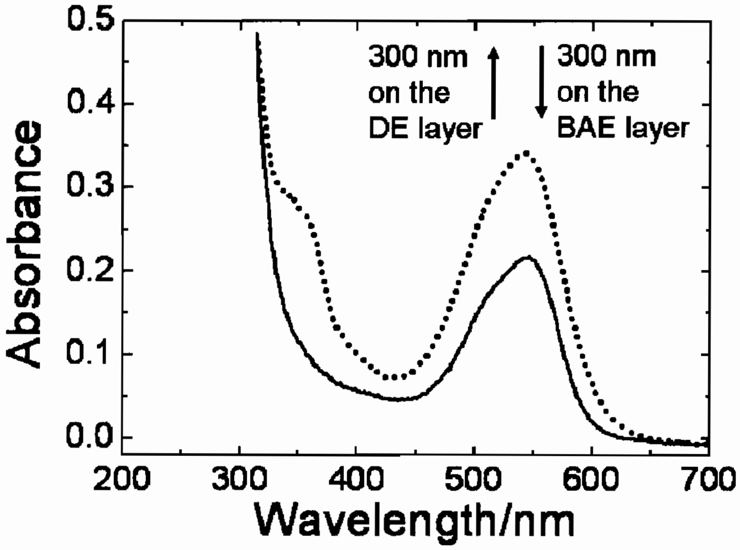


Figure 2-4-6. Absorption spectral change of diarylethene/glass/bisazomethine three-layered structure upon irradiation with 300 nm light; the open-ring isomer of DE and BAE with glass (solid line), the closed-ring isomer of DE and BAE with glass (dotted line).

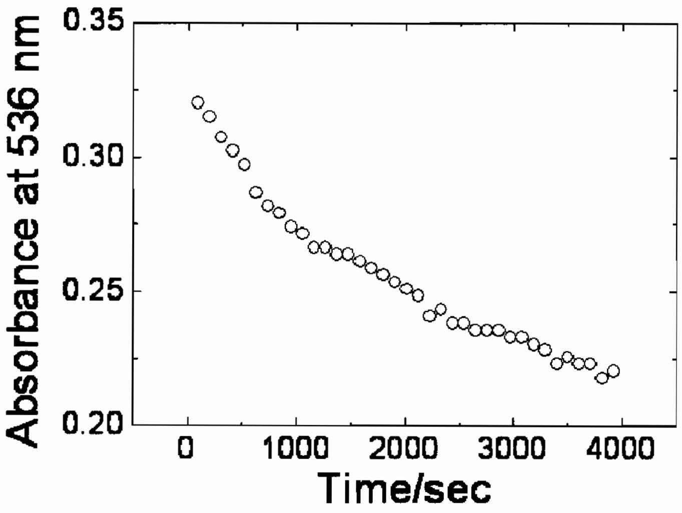


Figure 2-4-7. The evolution of absorbance at 536 nm in the three-layered structure after illumination with the fluorescence of 581nm from BAE.

It required about 3000 sec to make the closed-ring isomer faded, because the fluorescence intensity was so weak with this concentration. Kinetics of the cycloreversion process has linearly-decreasing character, as shown in **Fig. 2-4-7**. When the concentration of BAE was high, the fluorescence intensity of BAE was decreased remarkably by aggregation. Noteworthy performance in this system is that the colored DE did not returned to colorless upon visible light exposure on the BAE layer because visible light is absorbed by BAE. The closed-ring isomer of DE has a basic property which the open-ring isomer never returns in the dark for more than 12 h at 80 °C [16]. As a result, BAE in the three-layered structure inhibits the cycloreversion of DE and also assumes the role as a filter against deleting, simultaneously. Therefore, if only we should prepared an environment that DE layer side isn't exposed to visible light, it is possible that photoswitching system using single UV light is carried out by a sandwiched structure consisted of the three-layered structure. The photoswithing system using single UV light of the three-layered structure is summarized in **Fig. 2-4-8**.

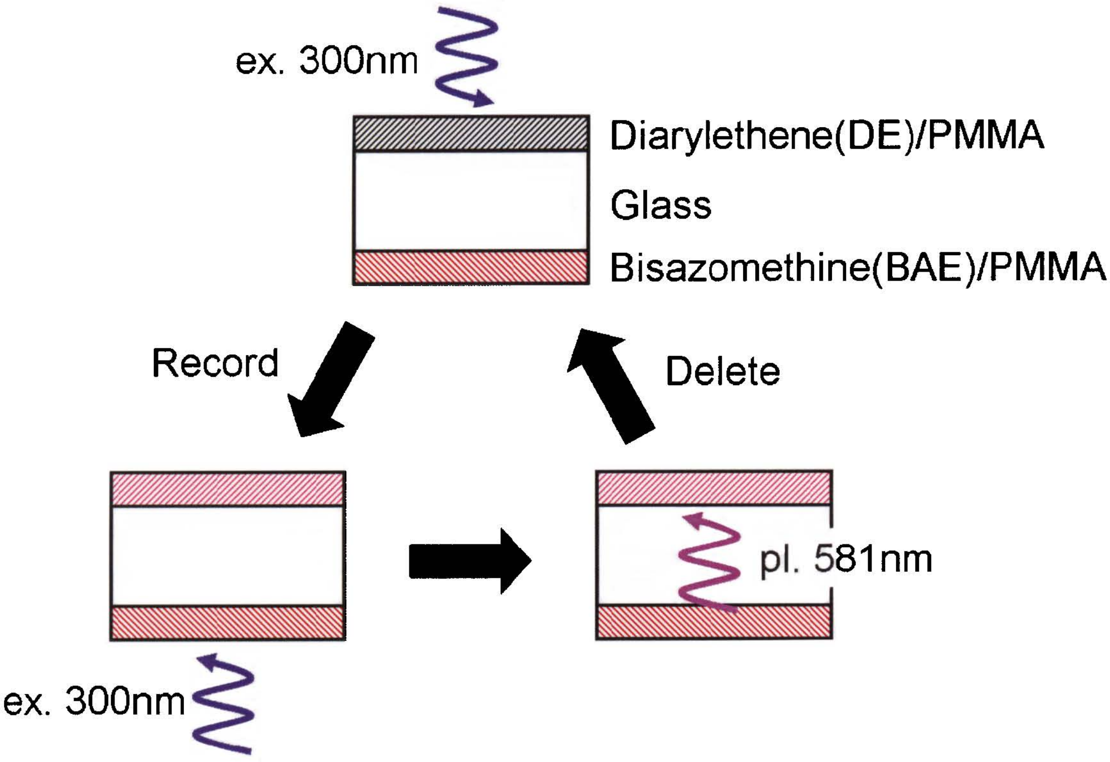


Figure 2-4-8. Schematic illustration of the photoswitching function by single UV light in the three-layered structure

A photograph of the change in the actual color is shown in **Fig. 2-4-9**. The deeply red area has DE (the closed-ring isomer) and BAE, on the other hand, the red area has DE (the open-ring isomer) and BAE. The practical capability of photoswitching on the three-layered structure was investigated by patterned irradiation through photomask. The word “Kobe Univ.” was recorded as image on the red area. The black area of a monochrome image in the lower left on **Fig. 2-4-9** emphasized only the color of a deeply red area. Therefore, it is suggested that prepared novel photoswitching using single UV light was established by diarylethane/glass/bisazomethine three-layered structure.

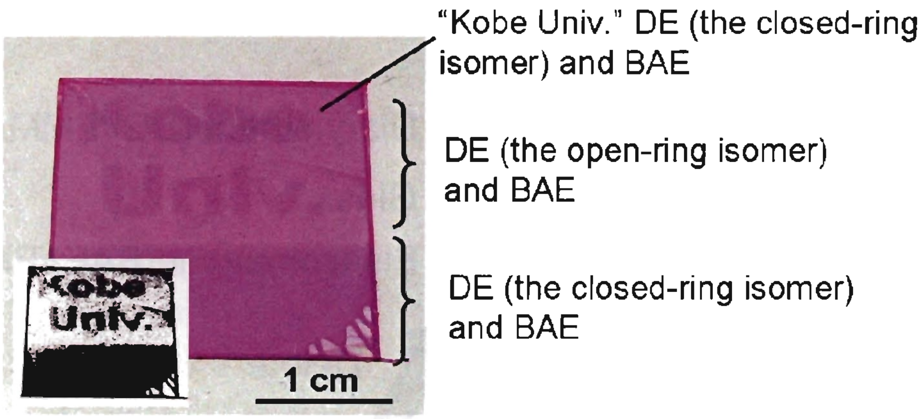


Figure 2-4-9. Photograph of the three-layered structure when irradiation with 300 nm light. The in set shows a monochrome image by which the deeply red area is emphasized.

2-5 Conclusions

Diarylethene and bisazomethine used here are 1,2-bis(2,4-dimethyl-thiophene-3-yl)perfluorocyclopentene (DE) and *N,N'*-bis[(4-(*N,N*-diethylamino)-benzylidene]diaminomaleonitrile (BAE). We prepared glass sandwiched three-layered structure with the thin film of DE and BAE. Upon UV light irradiation from DE layer side as recording in the three-layered structure, the color changed from red to deeply red. When UV light was irradiated from BAE layer side, on the other hand, the color was returned to initial state by fluorescence with 581 nm from BAE. Upon visible light exposure from BAE layer side, the color of the three-layered structure did not returned to initial state because visible light is absorbed by BAE, because absorption spectral region of

DE has an overlap with that of BAE. Therefore, it is concluded that novel photoswitching system using single UV light was established by diarylethane/glass/bisazomethine three-layered structure.

2-6 References

[1] G. H. Brown, Techniques of Chemistry, Vol.III, Photochromism, Wiley-Interscience, New York, 1971.
[2] M-S. Kim, H. Maruyama, T. Kawai, M. Irie, *Chem. Mater.* **15** (2003) 4539.
[3] E. Kim, Y. K. Choi, M. H. Lee, *Macromolecules* **32** (1999) 4855.
[4] K. Uchida, M. Saito, A. Murakami, S. Nakamura, M. Irie, *Adv. Mater.* **15** (2003) 121.
[5] F. Stellacci, C. Bertarelli, F. Toscano, M. C. Gallazzi, G. Zerbi, *Chem. Phys. Lett.* **302** (1999) 563.
[6] M. Irie, T. Fukaminato, T. Sasaki, N. Tamai, T. Kawai, *Nature* **420** (2002) 754.
[7] T. Kawai, T. Sasaki, M. Irie, *Chem. Commun.* (2001) 711.
[8] S. Kobatake, K. Shibata, K. Uchida, M. Irie, *J. Am. Chem. Soc.* **122** (2000) 12135.
[9] T. Yamada, S. Kobatake, K. Muto, M. Irie, *J. Am. Chem. Soc.* **122** (2000) 1589.
[10] M. Irie, O. Miyatake, K. Uchida, *J. Am. Chem. Soc.* **114** (1994) 8715.
[11] M. Irie, O. Miyatake, K. Uchida, T. Eriguchi, *J. Am. Chem. Soc.* **116** (1992) 9894.
[12] Z. Liu, A. A. Yasseri, J. S. Lindsey, D. F. Bocian, *Science* **302** (2003) 1543.
[13] A. J. Myles, T. J. Wigglesworth, N. R. Branda, *Adv. Mater.* **15** (2003) 745.
[14] J. P. Malval, I. Gosse, J.P. Morand, R. Lapouyade, *J. Am. Chem. Soc.* **124** (2002) 904.
[15] M. Hanazawa, R. Sumiya, Y. Horikawa, M. Irie, *J. Chem. Soc., Chem. Commun.* (1992) 206
[16] M. Irie, *Chem. Rev.* **100** (2000) 1685.
[17] S. Pu, G. Liu, G. Li, R. Wang, T. Yang, *J. Mol. Struct.* **833** (2007) 23.
[18] C. Zheng. S. Pu. J. Xu, M. Luo, D. Huang, L. Shen, *Tetrahedron* **63** (2007) 5437.
[19] K. Shirai, M. Matsuoka, K. Fukunishi, *Dyes Pigm.* **47** (2000) 107.
[20] S. H. Kim, S. H. Yoon, S.H. Kim, E. M. Han, *Dyes Pigm.* **64** (2005) 45.

[21] S. Miyata, J. Yu, Y. Sakuratani, Japanese Patent, Appl. No. 2000-143527.

Chapter 3

Multi-photochromic Behavior of Hybrid Material with Spirobenzopyran and Azobenzene Moieties

3-1 Abstract

We have synthesized a novel bi-functional photochromic compound spirobenzopyran-azobenzene (SpAz) by coupling reaction with spirobenzopyran (Sp) and azobenzene (Az) derivatives. The absorption and fluorescence spectral properties of SpAz have been studied. In toluene solution ($3.5\text{x}10^{-5}$ M), SpAz showed four kinds of photoisomers depending on the wavelength of the irradiated light at r.t.. When SpAz toluene solution is irradiated by UV light with the wavelength of 400 nm light, Az moiety in SpAz was photoisomerized from *trans*-form to *cis*-form independently. Upon 360 nm light irradiation at r.t., Sp moiety in SpAz was photoisomerized from spiro (SP)-form to photomerocyanine (PMC)-form in addition to spectral change of *trans-cis* photoisomerization. Upon 300 nm light irradiation at r.t., on the other hand, Sp moiety in SpAz was photoisomerized from SP-form to PMC-form independently in addition to initial state. Fluorescence lifetimes of SpAz were obtained to be 69 ps for *trans* and PMC-form and 67 ps for *cis* and PMC-form in toluene solution at -10 °C. These results indicate that photoisomerization depending on the irradiated wavelength is independently occurred regardless of the conformational change of *trans-cis* photoisomerization in Az moiety. In the PMMA films, on the other hand, the fluorescence lifetime was 1520 ps for SpAz (*cis* and PMC-form) at room temperature. The measured lifetime was about 10 times larger in PMMA matrix

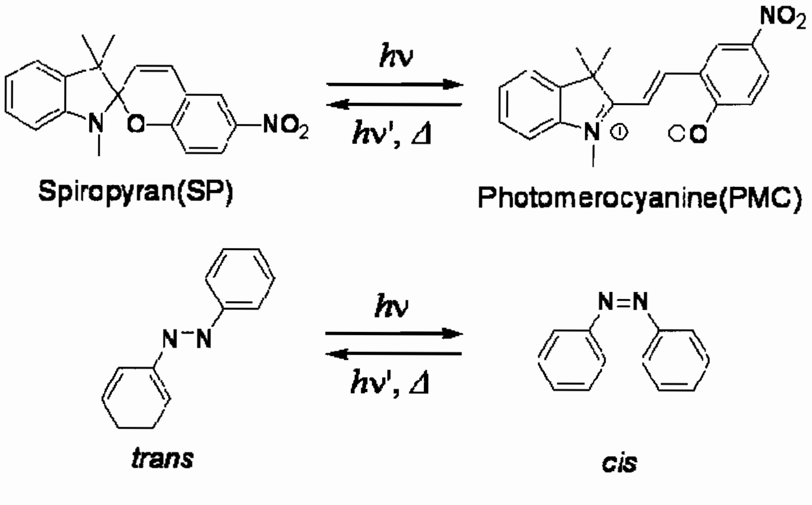
than in toluene solution. The difference of fluorescence lifetimes between in solution and in PMMA matrix should also be remarked. The fluorescence lifetime in PMMA film is 1 order of magnitude grater than that of in toluene solution. The very short lifetime in non-viscous solvents suggests the existence of a very fast radiationless transition process of $S_0 \leftarrow S_1$. This radiationless internal conversion is much influenced by the viscosity of the medium, resulting in 1 order of magnitude grater lifetimes in PMMA matrix.

3-2 Introduction

Photochromic compound is characterized by the ability to undergo a reversible transformation between two different chemical forms having different absorption spectra in response to light of appropriate wavelength [1-4]. Two isomers differ from one another not only in the absorption property but also in refractive indices, dielectric constants, oxidation-reduction potentials and geometrical structures. Therefore, upon irradiation with an appropriate wavelength of light, these properties can be reversibly switched. This indicates that photochromic compounds are of interest for potential application to erasable photomemory system. Photochromic compounds can represent "0(light off)" or "1(light on)" of two digital codes corresponding to each isomer. If two photochromic moieties can be introduced into certain molecule, the digital codes will be increased to 2x2=4. Among many types of organic photochromic compounds, the chemistry of spiropyrans (Sp) and azobenzenes (Az) has been extensively investigated with special regards to their remarkable properties [5-11].

Upon 360 nm light irradiation, spirocarbon–oxygen (C–O) bond of the colorless spiro isomer (SP-form) is broken and the subsequent photoisomerization leads to colored opened isomers called photomerocyanine isomer (PMC-form). Az molecule can undergo *trans-cis* photoisomerization with UV light irradiation [12-14]. The photoreaction of these kinds of photochromic compounds is shown in **Scheme 3-2-1**.

Recently, several bi-functional photochromic compounds have been reported [15-22]. In this study, bi-functional photochromic compound spirobenzopyran-azobenzene (SpAz) was synthesized with spirobenzopyran (Sp) and azobenzene (Az) and the photochromic behavior was investigated. Fluorescence lifetimes measured by picosecond time scale both in toluene solution and in PMMA matrix were also investigated.



Scheme 3-2-1. Structural changes of Sp and Az during photochromism.

3-3 Experimental

-General

The chemical structure of synthesized compounds was characterized by 1H nuclear magnetic resonance spectrum (1H-NMR) and fast atom bombardment mass spectrum (FAB-MS). 1H-NMR spectra were recorded on a Brucker DPX400 and FAB-MS were recorded on a JEOL JMS-GC mate IIR. Absorption spectroscopic study, measured in toluene solution (conc. 3.5×10^{-5} M) at room temperature, was performed with a Shimadzu UV-2200 UV-Vis. recording spectrophotometer. Fluorescence spectrum was measured with a Hitachi F-2500 fluorescence spectrophotometer. The irradiation of solution sample (1 cm path cell, 1 cm^3) was carried out in the spectrophotometer holder at a right angle to the analysis light. Fluorescence lifetimes in solution and in PMMA were measured with a following setup in **Fig. 3-3-2**. SpAz in toluene solution (conc. 3.5×10^{-4} M) were measured in a 1 mm optical length flow cell connected to a PTFE diaphragm pump (Cole-Parmer Instrument Co.) A regeneratively amplified Ti:sapphire laser system (Spectra Physics Hurricane) provided 100 fs, 1 mJ/pulse at 800 nm and a 1 kHz repetition rate. Excitation pulses were obtained using an optical parametric amplifier (OPA-800c). The fluorescence was dispersed by a monochromator (ARC SpectraPro-150), and detected by a picosecond streak camera (Hamamatsu C4334). The irradiation source, use to produce the photoisomer, was a Xe lamp (Asahi spectra MAX-301).

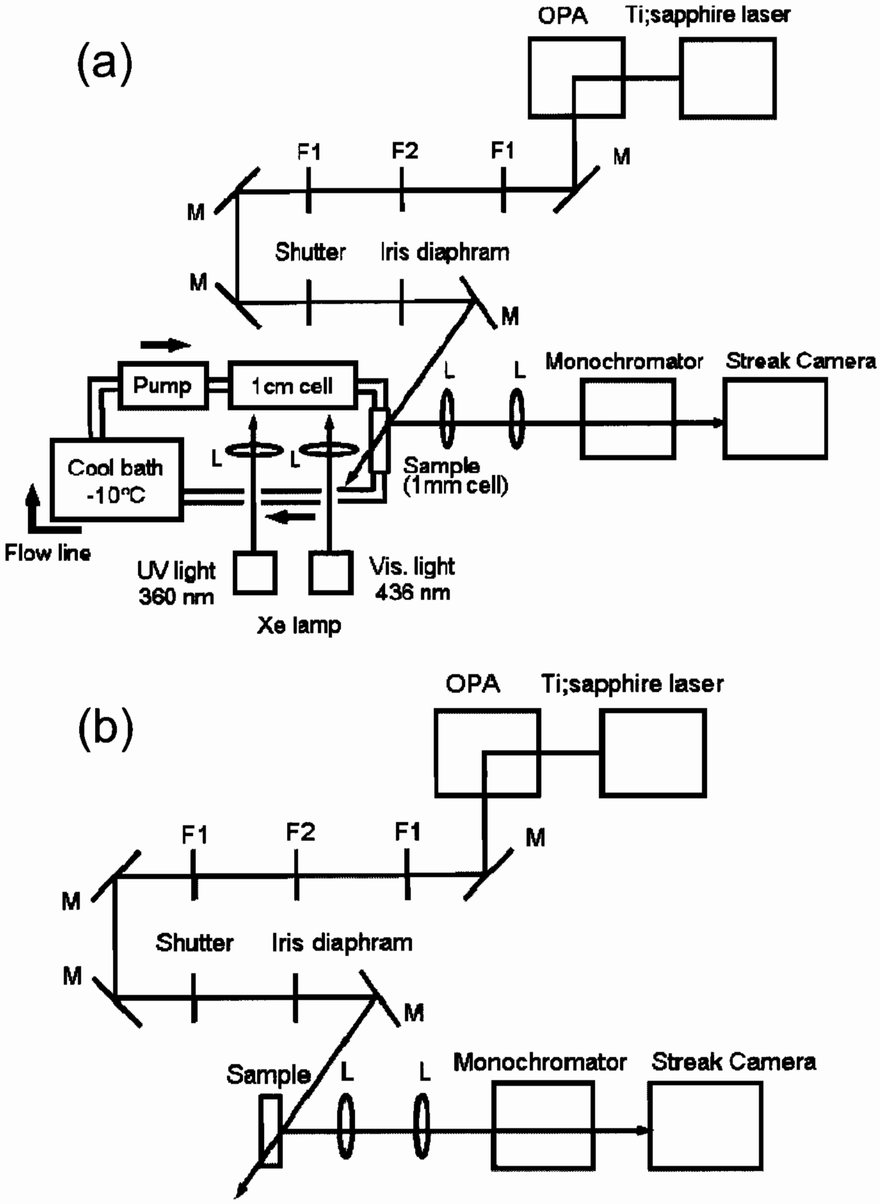


Figure 3-3-2. Schematic diagram of the fluorescence lifetime setup for in solution (a) and in PMMA (b): OPA (Optical parametric amplifier), F1 (Interference filter), F2 (ND filter), M (mirror), L (optical lens).

-Sample preparation

Synthesized photochromic compounds (Sp, Az and SpAz) were dissolved in toluene solution (conc. 3.5×10^{-5} M) and in PMMA/acetone solution (conc. 4 wt%).

Thin films were prepared by spin-coating (4000 rpm) on a quartz substrate. The thin films were dried overnight at room temperature under vacuum.

-Synthesis

General procedure for the synthesis of intermediates (Sp and Az) and SpAz is illustrated in **Scheme 3-3-1**. Each intermediates were prepared by the method in the literatures [23-26].

1-(2'-Hydroxyethyl)-2,3,3-trimethylindolenium iodide(1)

To a solution of 2,3,3-trimethyl-3H-indole (1.30 g, 8.16 mmol) in 2-butanone 10 ml were added 1-iodoethanol (1.40 g, 8.16 mmol) with stirring. The mixture was heated at reflux for 48 h and cooled to precipitate a solid. The solid was separated by filtration, washed with cold acetone to give a white-red solid (2.43 g, 7.34 mmol) which was used without further purification. Yield 81.0%, mp 145.0-145.5 °C, FAB-MS (M+) 331.

1'-(2''-Hydroxyethyl)-3',3'-dimethyl-6-nitrospiro[2H-1-benzopyran-2,2'-indoline] (Sp)

To a solution 1-(2'-hydroxyethyl)-2,3,3-trimethylindolenium iodide (1.00 g, 3.02 mmol) in 15 ml methanol were added piperidine (2,3 drops) and then 5-nitrosalicylaldehyde (0.50 g, 3.02 mmol) with stirring. The mixture was heated at reflux for 4 h and cooled. After evaporation of the solvent, the residue was purified by column chromatography (eluent chloroform) to give a white-red crystal (0.37 g, 1.06 mmol). Yield 35.0 %, mp 150.0-150.3 °C, FAB-MS (M+) 352, 1H NMR (400 MHz, $CDCl_3$) δ=1.15 (s, 3H), 1.24 (s, 3H), 3.34-3.42 (m, 1H), 3.52-3.56 (m, 1H), 3.67-3.72(m, 1H), 3.72-3.76 (m, 1H), 5.82 (d, J=10.2 Hz, 1H), 6.65 (d, *J*=7.5 Hz, 1H), 6.86 (d, *J*=10.2 Hz, 1H), 6.87 (t, *J*=7.5 Hz, 1H), 7.10 (d, *J*=7.5 Hz, 1H), 7.17 (t, *J*=7.5 Hz, 1H), 7.62 (d, *J*=2.7 Hz, 1H), 7.69 (d, *J*=2.7 Hz, 1H) ppm.

4-[4-(4-Hydroxyphenyldiazenyl)phenyl]butylic acid (2)

To a solution of 4-(4-aminophenyl)butylic acid (4.00 g, 26.5 mmol) in 600 ml of HCl (0.1 N), $NaNO_2$ (1.54 g, 22.3 mmol), $NH_4SO_3NH_2$ (2.56 g, 22.3 mmol) and then a solution of phenol (2.32 g 24.6 mmol) in 1000 ml of NaOH (0.1 N) were added with stirring at 5 °C. After getting the mixture's pH 3 by adding HCl (2.0 N), the precipitate was separated by filtration, washed with pure water to give an orange solid (5.20 g, 20.3 mmol) which was used without further purification. Yield 91.0 %, mp 165.7-168.8 °C, FAB-MS (M+) 284.

Octyl 4-[4-(4-octanoxyphenyldiazenyl)phenyl]butylate (3)

To a solution of 2 (0.50 g, 1.75 mmol) in 150 ml of dried DMF, K_2CO_3 (2.42 g, 17.5 mmol) and then 1-bromooctane (0.68 g, 3.50 mmol) were added with stirring. The mixture was refluxed for 6 hours under Ar atmosphere. Then the reaction mixture was cooled to 5 °C in ice bath and extracted using diethylether. After evaporation of the solvent, the residue was purified by silica gel column chromatography (eluent chloroform) to give an orange solid (0.76 g, 1.49 mmol). Yield 85.1 %, mp 51.6-52.3 °C, FAB-MS (M+) 508, 1H NMR (400 MHz, $CDCl_3$) δ=0.88 (brt, *J*=6.6 Hz, 6H, $PhO(CH_2)_8\underline{CH_3}$, $COO(CH_2)_8\underline{CH_3}$), 1.12-1.64 (m, 22H,

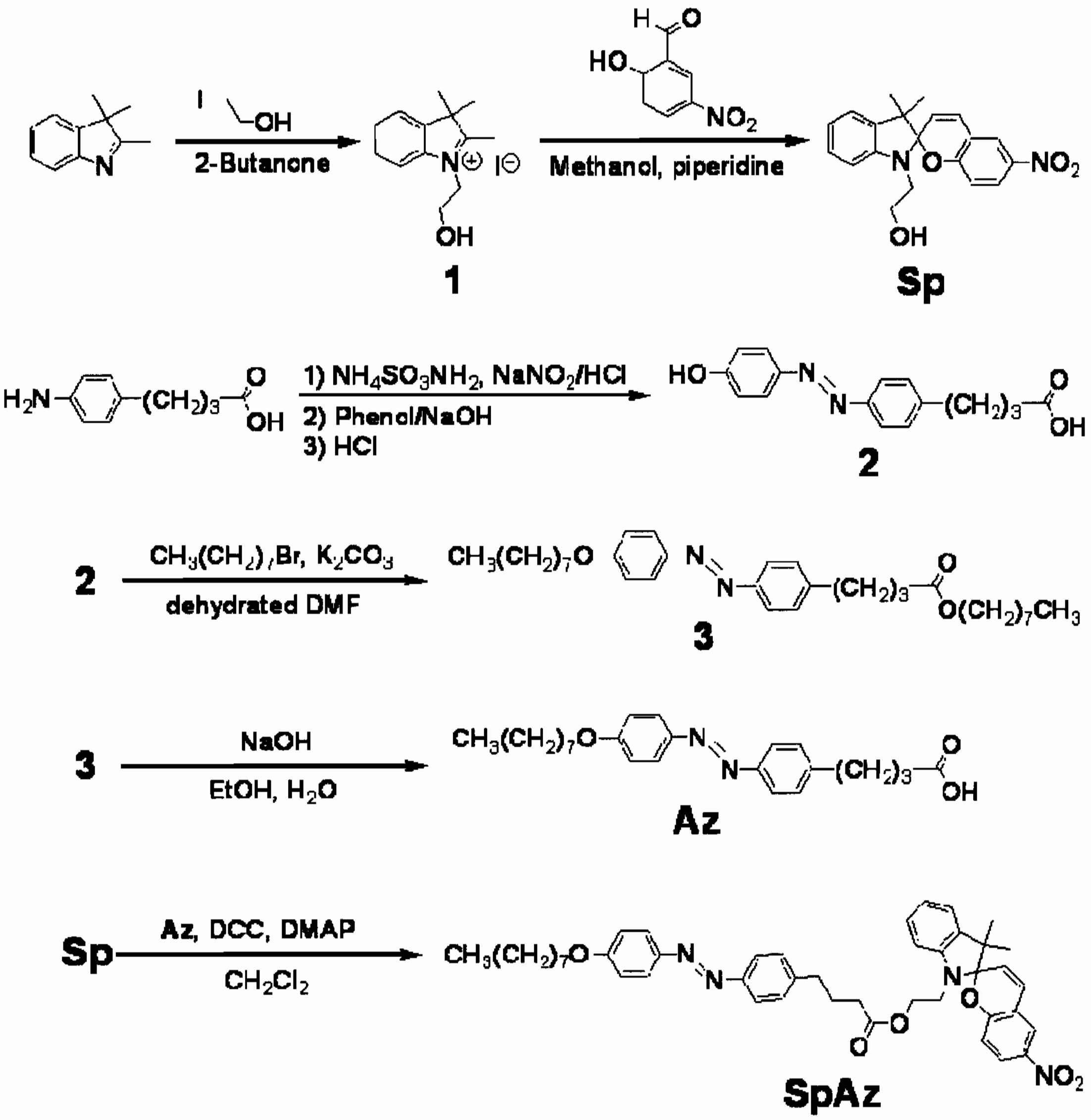
$PhOCH_2CH_2\underline{(CH_2)_5}$, $COOCH_2\underline{(CH_2)_6}$), 1.82 (quin, *J*=6.5 Hz, 2H, $PhOCH_2\underline{CH_2}$), 2.02 (quin, *J*=7.5 Hz, 2H, $PhCH_2\underline{CH_2}$), 2.35 (t, *J*=7.5 Hz, 2H, $PhCH_2CH_2\underline{CH_2}$), 2.73 (t, *J*=7.5 Hz, 2H, $Ph\underline{CH_2}$), 4.04 (t, *J*=6.5 Hz, 2, $PhO\underline{CH_2}$), 4.07 (t, *J*=6.7 Hz, 2H, $COO\underline{CH_2}$), 6.99 (d, *J*=8.9 Hz, 2H, 3',5'-H ar), 7.30 (d, *J*=8.3 Hz, 2H, 2,6-H ar), 7.80 (d, *J*=8.3 Hz, 2H, 3,5-H ar), 7.89 (d, *J*=8.9 Hz, 2H, 2',6'-H ar) ppm.

4-[4-(4-Octanoxyphenyldiazenyl)phenyl]butylic acid (Az)

To a solution of 3 (0.50 g, 0.98 mmol) in 200 ml of ethanol heated to 40 °C, 20 ml of NaOH (10 wt%) and then 20 ml of water were added and the mixture was stirred for 1.5 hours and cooled to 5 °C in an ice bath. The mixture was extracted using water by adding 100 ml of ethyl acetate, 100 ml of water and 50 ml of hexane. After adding 100 ml of chloroform to the extracted solution and getting its pH 3 by adding HCl (2.0 N), the solution was extracted using chloroform. The extracted solution was evaporated and the obtained solid was washed with water and hexane and then dried under reduced pressure at room temperature to give an orange solid (0.25 g, 0.62 mmol). Yield 63.3 %, mp 50.3-51.6 °C, FAB-MS (M+) 396, 1H NMR (400 MHz, $CDCl_3$) δ=0.88 (t, *J*=6.6 Hz, 3H, $PhO(CH_2)_7\underline{CH_3}$), 1.12-1.64 (m, 22H, $PhOCH_2CH_2\underline{(CH_2)_5}$, $COOCH_2\underline{(CH_2)_6}$), 1.82 (tt, *J*=6.5, 6.5 Hz, 2H, $PhOCH_2\underline{CH_2}$), 2.02 (tt, *J*=7.5, 7.5 Hz, 2H, $PhCH_2\underline{CH_2}$), 2.35 (t, *J*=7.5 Hz, 2H, $PhCH_2CH_2\underline{CH_2}$), 2.73 (t, *J*=7.5 Hz, 2H, $Ph\underline{CH_2}$), 4.04 (t, *J*=6.5 Hz, 2H, $PhO\underline{CH_2}$), 6.99 (d, *J*=8.9 Hz, 2H, 3',5'-H ar), 7.30 (d, *J*=8.3 Hz, 2H, 2,6-H ar), 7.80 (d, *J*=8.3 Hz, 2H, 3,5-H ar), 7.89 (d, *J*=8.9 Hz, H, 2',6'-H ar) ppm.

1-(2'-Ethyl-4-[4-(4-octanoxyphenyldiazenyl)phenyl]butirate)-3,3-dimethyl-6'-nitro spiro(indoline-2,2'-[2H-1])benzopyran (SpAz)

A solution of Sp (148 mg, 0.42 mmol), Az (167 mg, 0.42 mmol), 4-dimethylaminopyridine (DMAP) (6.10 mg, 0.05 mmol) and *N, N'*-dicyclohexylcarbodiimide (DCC) (81.6 mg, 0.42 mmol) in 50 ml of dried dichloromethane was stirred for 36 hours under Ar atmosphere in the dark at room temperature. After evaporation of the solvent, the residue was purified by column chromatography on silica gel (eluent chloroform) to obtain an orange crude product. Then the crude product was recrystallized from hexane to give an orange powder (SpAz) (83.2 mg, 0.11 mmol). Yield 27.1 %, mp 110.9-112.0 °C, FAB-MS (M+) 731. 1H NMR (400 MHz, CDCl3) δ=0.88 (s, 3H, $\mathrm{CH_3}$), 0.88 (t, *J*=6.6 Hz, 3H, $\mathrm{PhO(CH_2)_7\underline{CH_3}}$), 1.27-1.55 (m, 10H, $\mathrm{PhOCH_2CH_2\underline{(CH_2)_5}}$), 1.15 (s, 3H, $\mathrm{CH_3}$), 1.82 (tt, *J*=6.5, 6.5 Hz, 2H, $\mathrm{PhOCH_2\underline{CH_2}}$), 1.94 (tt, *J*=7.5, 7.5 Hz, 2H, $\mathrm{PhCH_2\underline{CH_2}}$), 2.27 (t, *J*=7.5 Hz, 2H, $\mathrm{PhCH_2CH_2\underline{CH_2}}$), 2.29 (t, *J*=6.3 Hz, 2H, $\mathrm{N\underline{CH_2}}$), 2.86 (t, *J*=7.5 Hz, 2H, $\mathrm{Ph\underline{CH_2}}$), 3.47 (t, *J*=6.3, 2H, $\mathrm{\underline{CH_2}O}$), 4.04 (t, *J*=6.5 Hz, 2, $\mathrm{PhO\underline{CH_2}}$), 4.23 (t, *J*=6.7 Hz, 2H, $\mathrm{COO\underline{CH_2}}$), 5.86 (d, *J*=10.8 Hz, 1H, -CH=), 6.66-7.21 (m, 6H, 5H ar and 1-CH=), 6.99 (d, *J*=8.9 Hz, 2H, 3',5'-H ar), 7.24 (d, *J*=8.3 Hz, 2H, 2,6-H ar), 7.77 (d, *J*=8.3 Hz, 2H, 3,5-H ar), 7.89 (d, *J*=8.9 Hz, H, 2',6'-H ar), 7.98-8.03 (m, 2H, 5-H ar and 7-H ar) ppm.



Scheme 3-3-1. The synthetic procedure of SpAz.

3-4 Results and Discussion

- Absorption and Fluorescence Behavior in Solution

Figure 3-4-1a shows UV-Vis. absorption spectral change of Sp in toluene solution (conc. 3.5×10^{-5} M) before and after 360 nm light irradiation. Main absorption peak of Sp appeared around at 285 and 335 nm. These absorption bands were assigned to $\pi-\pi^*$ transitions of chromene and of indoline rings, respectively. Upon 360 nm light irradiation, the solution changed from colorless to deeply blue and a broad absorption band with the maximum at 585 nm appeared. This band is assigned to PMC-form which is photoisomerized from SP-form based on the heterolytic cleavage of C–O bond. After being kept in the dark at room temperature or visible light irradiation, the photoisomer (PMC-form) returned to the initial colorless one (SP-form). The fluorescence spectrum with excitation at 360 nm light of Sp in toluene solution is shown in **Fig. 3-4-1b**. It is assigned to be the fluorescence from its PMC-form, which has a maximum at 625 nm. There is strong Stokes shift between absorption and emission spectra.

Figure 3-4-1c shows UV-Vis. absorption spectral change of Az in toluene solution (conc. 3.5×10^{-5} M). The absorption peak assigned to $\pi-\pi^*$ transition of *trans*-form of azobenzene appeared around at 350 nm. Upon 360 nm light irradiation, the absorption intensity at 350 nm decreased and a weak absorption peak appeared around at 450 nm due to the overlap of the $n-\pi^*$ transition of the metastable *cis*-form of azobenzene [27,28]. After being kept in the dark at room temperature or visible light irradiation, the photoisomer (*cis*-form) returned to the initial one (*trans*-form). No fluorescence was observed at around λ>500 nm with the excitation at 360 nm.

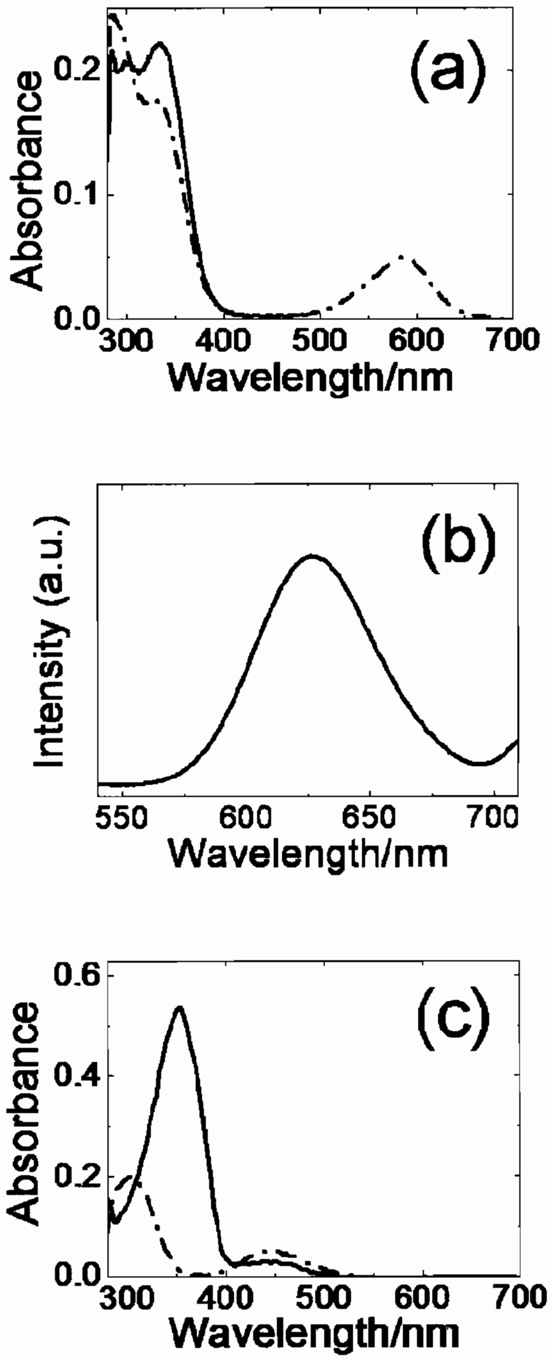


Figure 3-4-1. (a) Absorption spectral change of Sp in toluene solution before (solid line) and after (broken line) UV light irradiation at r.t.. (b) Fluorescence spectrum of Sp with excitation at 360 nm in toluene solution at r.t.. (c) Absorption spectral change of Az in toluene solution before (solid line) and after (broken line) UV light irradiation at r.t..

The UV-Vis. absorption spectrum of SpAz in toluene solution (conc. $3.5\text{x}10^{-5}$ M) showed two peaks around at 345 and 445 nm, as shown in **Fig. 3-4-2** (solid line). The former is assigned to multiple peaks of $\pi-\pi^*$ transition of chlomene, indoline rings in Sp moiety and of *trans*-form of Az moiety, and the latter is assigned to $n-\pi^*$ transition of *trans*-form of Az moiety, respectively. It is noticeable that the spectrum of SpAz is almost equal to the sum of Sp and Az spectra. Based on the absorption spectra of Sp and Az (**Fig. 3-4-1a** and **3-4-1c**), the irradiation wavelength of 300 nm light which is absorbed by Sp moiety preferentially, 360 nm light absorbed by Sp and Az moieties, and 400 nm light absorbed by Az moiety preferentially were selected to induce different three types of photochromism. When SpAz toluene solution was irradiated by 400 nm light, the absorption intensity at 345 nm decreased and that at 445 nm increased, as shown in **Fig. 3-4-2a**. This is assigned to that *trans-cis* photoisomerization in Az moiety occurred independently. When irradiated by 300 nm light, the broad absorption band with the maximum at 610 nm appeared, as shown in **Fig. 3-4-2c**. It is obvious that SP-PMC photoisomerization in Sp moiety of SpAz occurred independently. Moreover, irradiated by 360 nm light, the broad absorption band with the maximum at 610 nm appeared in addition to similar spectral change under the irradiation with 400 nm UV light (**Fig. 3-4-2b**). This indicates that the SP-PMC photoisomerization in Sp moiety and *trans-cis* photoisomerization in Az moiety occurred simultaneously. The photoisomerization of SpAz in toluene solution was reversible. SpAz showed four types of photoisomers depending on the wavelength of the light irradiated. Therefore, it is suggested that SpAz has four digital codes and the application potential for optical memory and/or optical switching system. The fluorescence spectrum with excitation at 360 nm of SpAz in toluene solution is shown in **Fig. 3-4-3**. It is assigned to be the fluorescence from its PMC-form of Sp moiety, which has a maximum at 645 nm. There is strong Stokes shift between absorption and emission spectra. The photochromic behaviors of SpAz in toluene solution are summarized in **Fig. 3-4-4**.

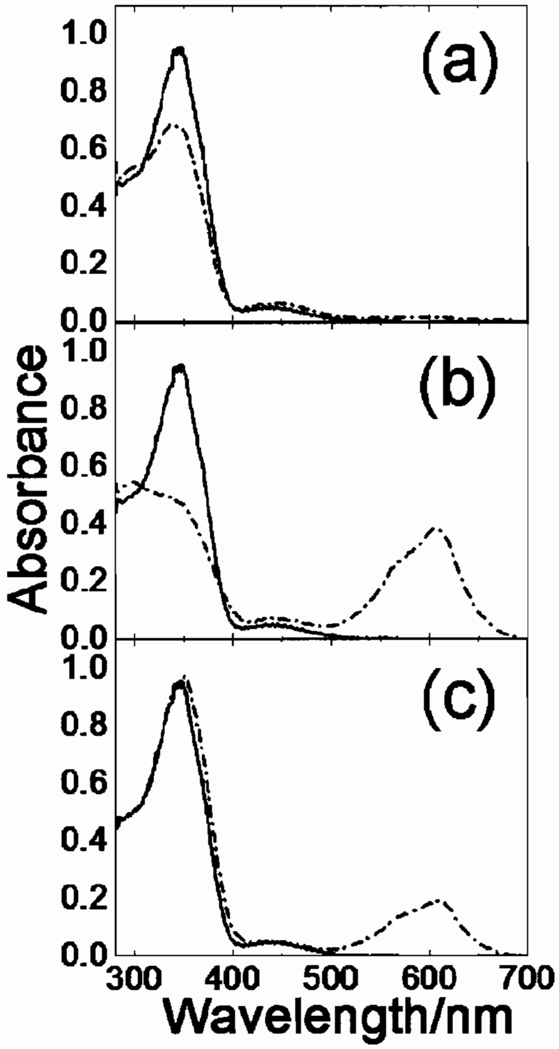


Figure 3-4-2. Absorption spectra of SpAz in toluene solution before (solid line) and after (broken line) light irradiation with the wavelength of (a) 400nm, (b) 360nm and (c) 300nm at r.t..

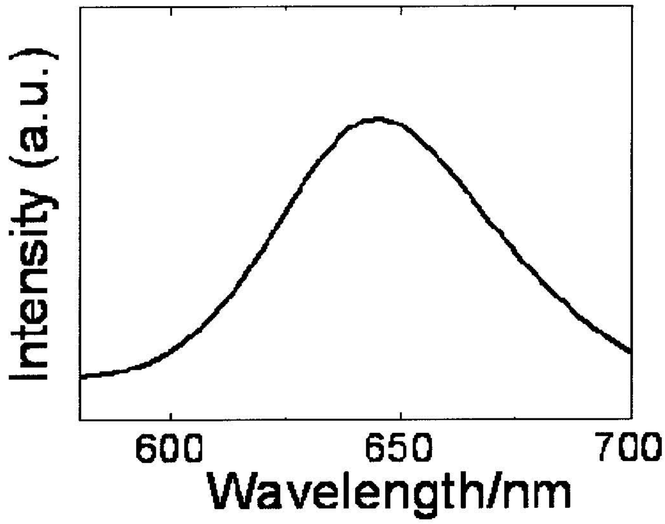


Figure 3-4-3. Fluorescence spectrum of SpAz with excitation at 360 nm in toluene solution at r.t..

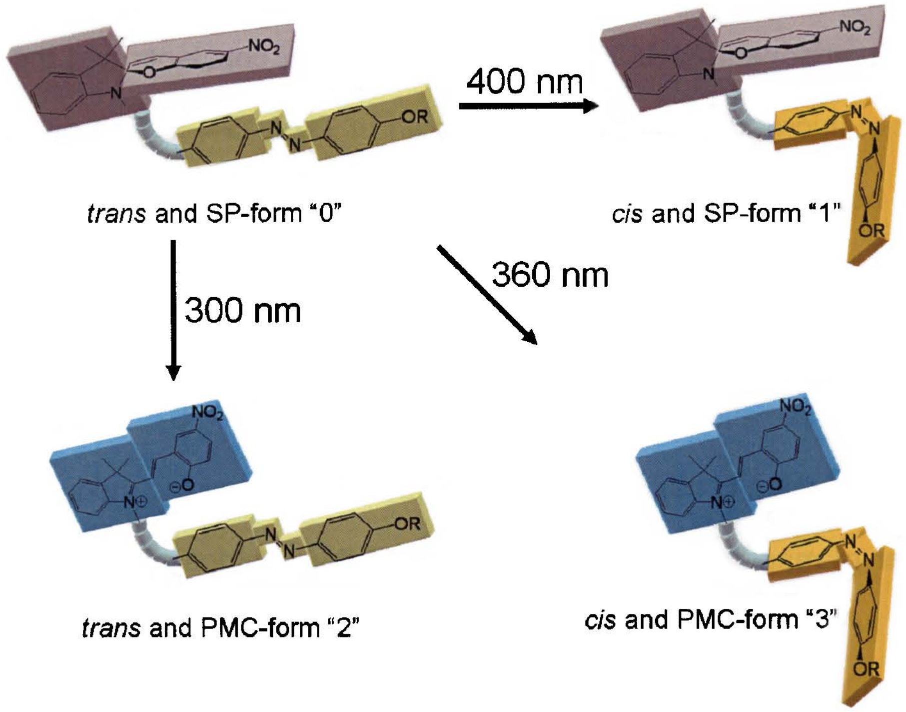


Figure 3-4-4. Schematic illustration for structural changes of SpAz.

- Fluorescence Lifetime Measurements

The fluorescence decay curves by the laser-pulse-induced photon-counting system are shown in **Fig. 3-4-5**. The decay for SpAz (circle; Az moiety is *cis*-form, square; Az moiety is *trans*-form) in toluene solution at -10 °C. The fluorescence signal from S_1 state rises within the instrument response function. The decay curves were well fitted to the bi-exponential functions and the time profiles are consisted of one main decaying component (circle; τ=67 ps, delta; τ=69 ps). It is noticeable that the lifetime for SpAz (*trans* and PMC-form) is almost the same as that for SpAz (*cis* and PMC-form), as shown in **Fig. 3-4-5a**. The fluorescence decay curves for SpAz in PMMA matrix at r.t is shown in **Fig. 3-4-5b**. It was well fitted to the mono-exponential functions and the time profile is consisted of one decaying component (τ=1520 ps). The best-fit time constants and the average lifetimes of fluorescence signals are shown in **Table 3-4-1**. The differences of lifetimes between in solution and in PMMA matrix should be remarked. The lifetimes in PMMA films are 1 order of magnitude grater than that of in toluene solution. The very short lifetimes in non-viscous solvents suggest the existence of a very fast radiationless transition process from $S_0 \leftarrow S_1$. This radiationless internal conversion is much influenced by the viscosity of the medium, resulting in 1 order of magnitude grater lifetimes in PMMA matrices [29]. These results indicated that if the energy transfer from Sp moiety to Az moiety could be occurred, the fluorescence lifetime from Sp moiety is guenched for *trans-cis* photoisomerization of Az moiety, however the fluorescence lifetime for *trans* and PMC-form is considered to be shorter than that of *cis* and PMC-form. Therefore, the results suggest that the energy transfer from Sp moiety to Az moiety isn't occurred. The fluorescence lifetime mechanisms of SpAz in toluene solution are summarized in **Fig. 3-4-6**.

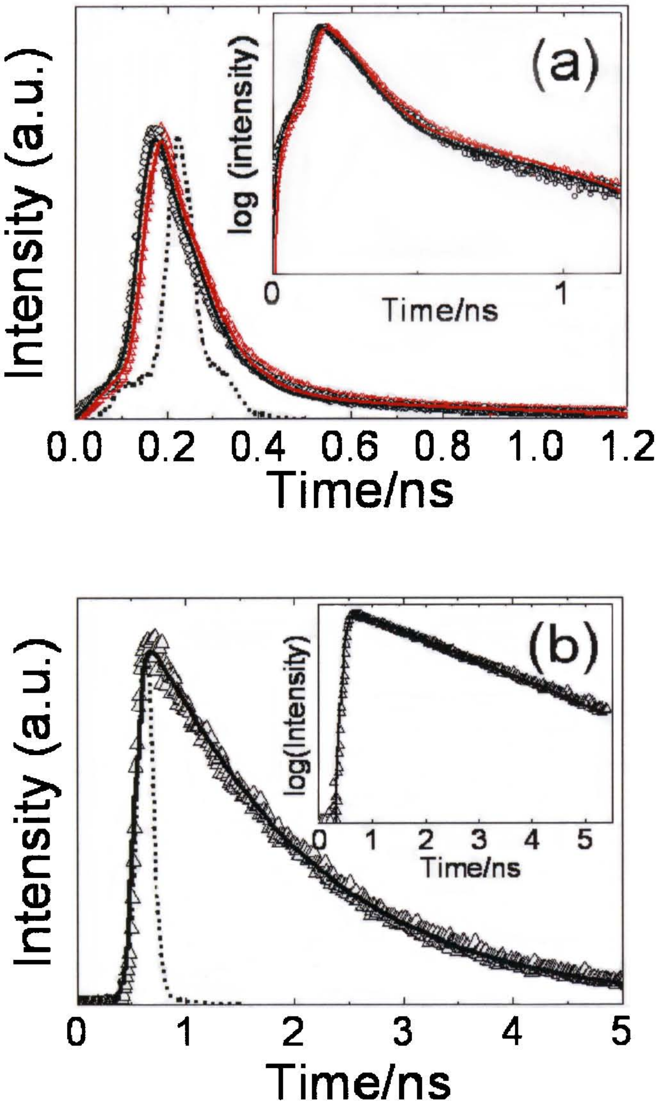


Figure 3-4-5. Time profiles of the S_1 state fluorescence signal for SpAz in toluene solution at -10 °C (a) and in PMMA matrix at r.t (b); circle; Az moiety is *cis*-form, square; Az moiety is *trans*-form, along with the instrument response functions. The insets show the logarithm for Y axis. The solid lines represent the best fits to the data by convolution of the instrument response function with a bi-exponential (a) and mono-exponential (b) function.

Table 3-4-1. Best-fit time constants and the average lifetimes of fluorescence signals of SpAz in toluene solution at -10°C and in PMMA matrix at r.t..

	τ_1 (ps)	τ_2 (ps)	<τ> (ps)
In toluene solution			
SpAz (*trans*)	69 (94.8%)	992 (5.2%)	117
SpAz (*cis*)	67 (93.9%)	850 (6.1%)	115
In PMMA films			
SpAz (*trans*)		N.D.	
SpAz (*cis*)	1520 (100%)	-	-

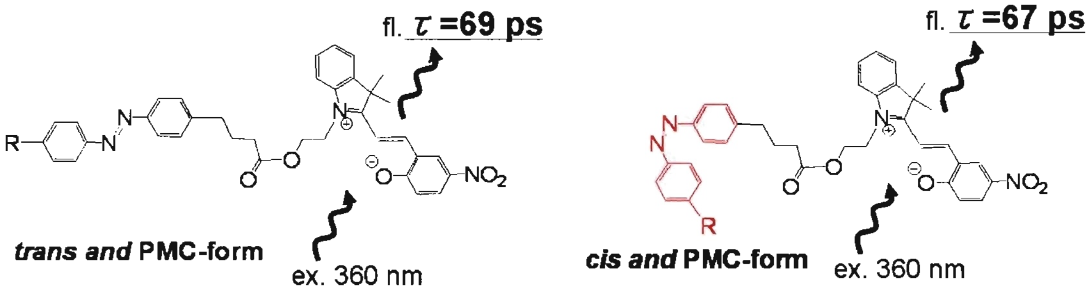


Figure 3-4-6. Schematic representation of the fluorescence lifetimes for SpAz in toluene solution at -10 °C; the left is *trans* and PMC-form and the right is *cis* and PMC-form.

3-5 Conclusions

In this study, bi-functional photochromic compound (SpAz) was synthesized with Sp and Az and its photochromic behavior was investigated. In toluene solution, SpAz showed four kinds of photoisomers depending on the wavelength of the irradiated light at r.t.. Fluorescence lifetime for SpAz (*trans* and PMC-form) was almost the same as that for SpAz (*cis* and PMC-form). This indicats that the excited energy transfer from Sp moiety to Az moiety isn't occurred. Therefore, multi-photoisimerization could be observed independently.

It is concluded that SpAz has four digital codes and the potential of fabrication of multi-addressable system and molecular switching for optical memory.

3-6 References

[1] G. H. Brown, Techniques of Chemistry, Vol.III, Photochromism, Wiley-Interscience, New York, 1971.

[2] H. Durr, H. Bouas-Laurent, Photochromism Molecules and System, Elsevier, Amsterdam, 1990.

[3] M. Irie, *Chem. Rev.* **100** (2000) 1685.

[4] Andrew J. Myles, Tony J. Wigglesworth, Neil R. Branda, *Adv. Mater.* **15** (2003) 745.

[5] G. Berkoric, V. Krongauz, V. Weiss, *Chem. Rev.* **100** (2000) 1741.

[6] S. Hashimoto, A Shimojima, T. Yuzawa, H. Hiura, *J. Mol. Struct.* **1** (1991) 242.

[7] M. Suzuki, T. Asahi, H. Masuhara, *J. Photochem. Photobiol A: Chem.* **178** (2006) 170.

[8] M. J. Cho, G. W. Kim, W. G. Jun, S. K. Lee, J. Jin, D. H. Choi, *Thin Solid Films* **500** (2006) 52.

[9] M. Querol, B. Bozic, N. Salluce, P. Balser, *Polyhedron* **22** (2003) 655.

[10] A. Y. Bobrovsky, N. I. Boiko, V. P. Shibaev. *Adv. Mater.* **11** (1999) 1025.

[11] S. Bénard, P. Yu. *Adv. Mater.* **12** (2000) 48.

[12] G.S. Hartley, *Nature* **140** (1937) 281.

[13] G.S. Hartley, *J. Chem. Soc.* (1938) 633.

[14] N. Tamai, H. Miyasaka, *Chem. Rev.* **100** (2000) 1875.

[15] F. Ortica, D. Levi, P. Brun, R. Guglielmetti, U. Mazzucato, G. Favaro, *J. Photochem. Photobiol. A: Chem.* **138** (2001) 123.

[16] F. Ortica, D. Levi, P. Brun, R. Guglielmetti, U. Mazzucato, G. Favaro, *J. Photochem. Photobiol. A: Chem.* **139** (2001) 133.

[17] G. Favaro, D. Levib, F. Ortica, A. Samat, R. Guglielmetti, U. Mazzucato, *J. Photochem. Photobiol. A: Chem.* **149** (2002) 91.

[18] F.M. Rayno, *Adv. Mater.* **14** (2002) 401.

[19] A. J. Myles, T. J. Wigglesworth, N. R. Branda, *Adv. Mater.* **15** (2003) 745.

[20] H. Choi, B. S. Ku, S. R. Keum, S. O. Kang, J. Ko, *Tetrahedron* **61** (2005) 3719.

[21] K. Kinashi and Y. Ueda, *Mol.Cryst.Liq.Cryst.* **445** (2006) 223.

[22] K. Kinashi, K. Furuta, Y. Harada, Y. Ueda, *Chem. Lett.* **35** (2006) 298.

[23] X. Li, Y. Wang, T. Matsuura, *J. Meng, Heterocycles*, **51** (1999) 2639.

[24] X. Li, J. Li, Y. Wang, T. Matsuura, J. Meng, *J. Photochem. Photobiol A: Chem.* **161** (2004) 201.

[25] T. D. Kim, K. S. Lee, G. U. Lee, O. K. Kim, *Polymer* **41** (2000) 5237.

[26] X. Zhao, X. Hu, C. Y. Yue, X. Xia, L. H. Gan, *Thin Solid Films* **417** (2002) 95.

[27] G. Zimmerman, *J. Chem. Phys.* **33** (1994)1550.

[28] Y. Wu, Y. Demachi, O. Tsutsumi, A. Kanazawa, T. Ikeda, *Macromolecules*, **31** (1998) 4457.

[29] K. Horie, K. Hirao, I. Mita, Y. Yakubo, T. Okamoto, M. Washio, S. Tagawa, Y. Tabata, *Chem. Phys. Lett.* **119** (1985) 499.

Chapter 4

Summary

Several ideas described by this thesis can be expected for application to optoelectronic devices, such as photomemory and photoswitches. For practical applications, however, several additional characteristics or technologies are required. For photomemory, for example, nondestructive readout capability and thermal stability are indispensable. And building of a recording and deletion system by single UV light is needed to accomplish the photoswitches. Moreover, improvement of a memory density in the area which could be limited is needed.

An attempt to development of thermal stability of spirobenzopyran using silica matrix have been accomplished to avoid thermal unstability as described in ***chapter 1***; Photoisomer of PMC-form in SPOH in silica matrix is stabilized dramatically. Life-half time of SPOH in silica matrix was estimated to be about $8x10^7$ sec. Because PMC-form of SPOH forms intermolecular hydrogen bonding between a proton generated hydroxyl or carboxyl group and oxygen atom in silica matrix. Therefore, it is suggested that PMC-form of SPOH in silica matrix has high thermal stability and the application potential for photomemory and photoswitches.

An achieved possibility of the recording and deleting using single UV light was suggested by fabrication the glass sandwiched three-layered structure with the thin film of diarylethene and bisazomethine as described in ***chapter 2;*** Upon UV light irradiation from diarylethene layer side as recording in the three-layered structure, the color changed from red to deeply red. When UV light was irradiated from biazomethine layer side, on the other hand, the color was returned to initial state by fluorescence with 581 nm from bisazomethine. Upon visible light exposure from bisazomethine layer side, the color of the three-layered structure did not returned to initial state because visible light is absorbed by bisazomethine, because absorption spectral region of diarylethene has an overlap with that of bisazomethine. Therefore, it is suggested that prepared novel photoswitching using single UV light was established by diarylethane/glass/bisazomethine three-layered structure.

An attempt to development of memory density have been established by bi-functional photochromic compound (SpAz) as described in ***chapter 3***; Synthesized SpAz showed four kinds of photoisomers depending on the wavelength of the irradiated light at r.t. Fluorescence lifetime for SpAz (*trans* and PMC-form) was almost the same as that for SpAz (*cis* and PMC-form). This indicats that the excited energy transfer from Sp moiety to Az moiety isn't occurred. Therefore, it is concluded that SpAz has four digital codes and the potential of fabrication of multi-addressable system photomemory.

This is one of the practical approaches to photomemory and photoswitches using photochromic compounds. Photochromic compounds are great promises in potential applications to photomemory and photoswitches.

Achievements

-List of Publications

Chapter 1

[1] K. Kinashi, Y. Harada, Y. Ueda "Thermal Stability of Merocyanine Form in Spiropyran/Silica composite Film" *Thin Solid Films* (2007) *in press.*

Chapter 2

[2] K. Kinashi, Y. Ono, T. Kotake, K. Ishida, Y. Ueda "Photoswitching of Photochromic Diarylethene Using Bisazomethine Dye" *to be prepared*

Chapter 3

[3] K. Kinashi Y. Ueda "Synthesis and Photochromic Behavior of Bi-functional Photochromic Compound" *Molecular Crystals and Liquid Crystals*, **445** (2006) 223-230.

[4] K. Kinashi, K. Furuta, Y. Harada, Y. Ueda "Multi-photochromic Behavior of Hybrid Material with Spirobenzopyran and Azobenzene Moieties" *Chemistry Letters* **35** (2006) 298-299.

[5] K. Kinashi, Y. Ono, Y. Koshiba, K. Ishida, Y. Naitoh, A. Ohtomo, Y. Ueda "Synthesis and Optical Properties of Novel Bi-functional Photochromic Compounds" *J. Photochem. Photobiol. A: Chem. to be prepared*

-Conference presentation

[1] “Photochromism of spirobenzopyran-azobenzene derivatives”
(The 51st Spring Meeting, 2004); The Japan Society of Applied Physics and Related Societies @ Tokyo University of Technology

[2] “Control of photoisomerization of spirobenzopyran-azobenzene derivatives”
(The 52nd Spring Meeting, 2005); The Japan Society of Applied Physics and Related Societies @ Saitama University

[3] “Selective Photoswitching of Functional Dye with Spirobenzopyran and Azobenzene Moieties”
(The 66th Autumn Meeting, 2005); The Japan Society of Applied Physics @ Tokushima University

[4] “Thermal Stability of Merocyanine Form in Spiropyran/Silica Hybrid Film”
(The 53rd Spring Meeting, 2006); The Japan Society of Applied Physics and Related Societies @ Musashi Institute of Technology

[5] “Photoswitching of Diarylethene/Glass/Bisazomethine Structure”
(The 53rd Spring Meeting, 2006); The Japan Society of Applied Physics and Related Societies @ Musashi Institute of Technology

[6] “Fabrication and Evaluation of Novel Spiropyran Derivatives with J-aggregate Formation Ability”
(The 67th Autumn Meeting, 2006); The Japan Society of Applied Physics @ Ritsumeikan University

[7] “Thermal Stability of Spiropyran Photoisomer”
(The 54th Spring Meeting, 2007); The Japan Society of Applied Physics and Related Societies @ Aoyama Gakuin University

[8] “Synthesis and Optical Properties of Novel Bi-functional Photochromic Compounds (II)”
(The 68th Autumn Meeting, 2007); The Japan Society of Applied Physics @ Hokkaido Institute of Technology

-International conference presentation

[1] “Fabrication of Multi-Addressable System using Photochromic Spirobenzopyran-Azobenzene Derivative”
KOEAR-JAPAN JOINT FORUM 2004 Organic Materials for Electronics and Photonics @ Okinawa, Japan.

[2] “Control of photoisomerization of novel spirobenzopyran-azobenzene derivatives”
The 2005 International Chemical Congress of Pacific Basin Societies (Pacifichem) @ Honolulu, Hawaii, USA

[3] “Photoswitching of Diaryethene/Glass/Bisazomethine System”
The Seventh International Symposium on Functional π-Electron Systems @ Osaka International Convention Center (Grand Cube Osaka), Osaka, Japan

[4] “Optical Storage of Diarylethene/Glass/Bisazomethine System”
KOEAR-JAPAN JOINT FORUM 2006 Organic Materials for Electronics and Photonics @ Toki Messe, Niigata, Japan

[5] “Thermal Stability of Merocyanine Form in Spiropyran/Silica Composite Film”
The 7th International Conference on Nano-Molecular Electronics @ International Conference Center Kobe, Kobe, Japan

[6] “Reversible Photoswitching by Single UV Light in Diarylethene/ Bisazomethine System”
The 3rd East Asia Symposium On Functional Dyes and Advanced Materials @ Lotte Hotel, Ulsan, S. Korea

Acknowledgements

First of all, I wish to express my sincere gratitude to Professor Yasukiyo UEDA for his affectionate encouragement and constant guidance. I have grate respect for him and feel privileged to have work under the direction to him.

I also express my deep gratitude to Associate Professor Kenji ISHIDA and Research Assistant Yasuko KOSHIBA for giving much advice and helpful discussion.

Grateful acknowledgement is also made to Senior Research Scientist Akira OHTOMO and Research Fellow Yukito NAITOH at Kobe Advanced ICT Research Center (KARC) for useful discussion and fluorescent lifetime measurements.

I deeply thank to Mr. Kenichiro FURUTA, Mr. Tomokazu KOTAKE, Mr. Yasuhisa HARADA, Mr. Masayoshi YAMAMOTO, Mr. Takashi HORIGUCHI, Ms. Yoko ONO, Mr. Satoshi NAKAMURA and Mr. Hiroyuki KITA for their help in Ueda laboratory.

Lastly, I would like to express my deep thanks to my family for their devoted support. I would like to dedicate this thesis to my family.

March, 2008

Kenji KINASHI