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

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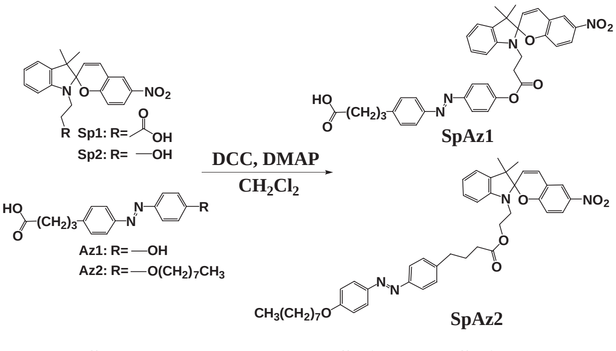
Two kinds of bi-functional photochromic compounds (**SpAz1** and **SpAz2**) were synthesized with spirobenzopyran and azobenzene derivatives by esterification. In chloroform solution, a novel photochromic compound (**SpAz2**) showed four kinds of isomers depending on the wavelength of the irradiated light. It is suggested that **SpAz2** has four digital codes for optical memory.

Light-induced reversible transformation between two isomers having different absorption spectra is referred to as photochromism.[1–4] 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. Therefore, upon irradiation with an appropriate wavelength of light, these properties can be reversibly switched. One of the most widely studied classes 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 molecular switching system, 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 and azobenzenes has been expensively investigated with special regards to their remarkable properties.[5–11] Particular attentions have been focused on spiropyrans and azobenzenes due to their potential applications to industrial fields.[2]

Here, we have prepared multi-changeable photochromic compounds in order to try realization of multi-addressable system. Two novel photochromic compounds (**SpAz1** and **SpAz2**) with spirobenzopyran and azobenzene moieties were synthesized by esterification using *N*,*N*′-dicyclohexylcarbodiimide and 4-dimethylaminopyridine as catalyst. The synthesis and molecular structures of **SpAz1** and **SpAz2** are shown in Scheme 1. **SpAz1** and **SpAz2** were consisted of **Sp1** and **Az1**, and **Sp2** and **Az2**, respectively.



Scheme 1. Synthesis of **SpAz1** and **SpAz2**.

The UV–vis absorption spectrum of **SpAz1** chloroform solution (7.0×10^{-5} M) showed two peaks at 330 and 430 nm, as indicated by solid line in Figure 1. The former is assigned to multiple peaks of π–π^* transition of benzopyran ring in spirobenzopyran moiety and π–π^* transition of *trans*-isomer of azobenzene moiety and the latter is assigned to n–π^* transition of *trans*-isomer of azobenzene moiety, respectively. When **SpAz1** chloroform solution is irradiated by UV light with the wavelength of 400 nm at rt, the absorption intensity at 350 nm decreased and the around at 450 nm increased, as shown in Figure 1a. The absorption peak around at 450 nm is assigned to the overlap of n-π^* transition of metastable *cis*-isomer of azobenzene moiety. **SpAz1** photoisomerized from *trans*-isomer to *cis*-one in azobenzene moiety. Moreover, weak absorption peak also appears around at 600 nm, as shown in Figure 1a′. This is assigned to photomerocyanine (PMC) form of spirobenzopyran moiety based on the heterolytic cleavage of C–O bond. It is noteworthy that **Sp1** dose not photoisomerize under the same irradiation condition. This indicates that photoisomerization in the spirobenzopyran moiety is induced by the photoisomerization in the azobenzene moiety. Upon light irradiation with 300 nm at rt, on the other hand, the broad absorption peak appears around at 600 nm in addition to initial absorption spectrum, as shown in Figures 1b and 1b′. Only photoisomerization from Sp form to PMC one occurs in this irradiation condition. After 360 nm irradiation, the spectral change is quite similar to 300 nm irradiation.

In the case of **SpAz2** chloroform solution with the same con-

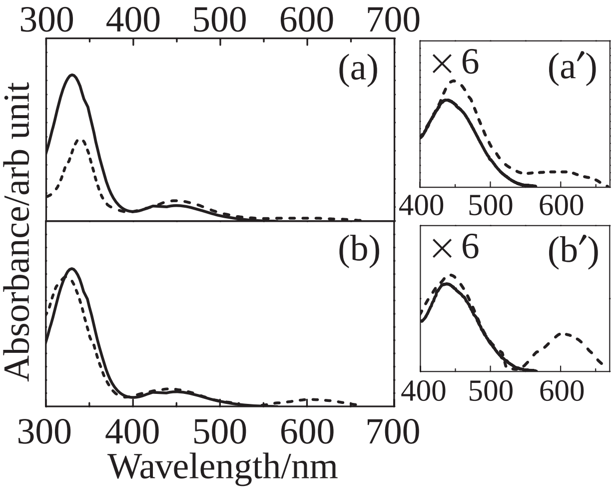


Figure 1. Absorption spectra of **SpAz1** chloroform solution at room temperature before (solid line) and after (dotted line) light irradiation with the wavelength of 400 nm (a and a′) and 300 nm (b and b′).

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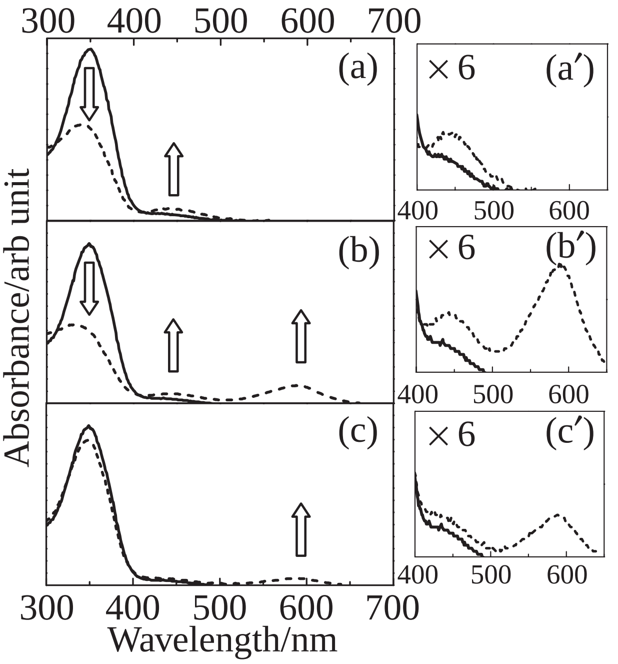

Figure 2. Absorption spectra of **SpAz2** chloroform solution at room temperature before (solid line) and after (dotted line) light irradiation with the wavelength of 400 nm (a and a′), 360 nm (b and b′), and 300 nm (c and c′).

centration, the absorption intensity at 350 nm decreased and that around at 450 nm increased by UV light irradiation with the wavelength of 400 nm at rt, as shown in Figure 2a. It is obvious that the azobenzene moiety in **SpAz2** is photoisomerized from *trans*-form to *cis*-one independently. Upon UV light irradiation with 360 nm, the broad absorption peak appears around at 590 nm in addition to similar spectral change observed under above visible light irradiation, as shown in Figure 2b. This indicates that the *trans–cis* photoisomerization in azobenzene moiety and the Sp-PMC photoisomerization in spirobenzopyran moiety occurred simultaneously. When the **SpAz2** chloroform solution was irradiated by the UV light shorter than 300 nm, on the other hand, the absorption intensity around at 590 nm increased but that at 350 nm scarcely changed, as shown in Figure 2c. Consequently, only spirobenzopyran moiety is photoisomerized under this condition. The photoisomerization of **SpAz2** was reversible. The photochromic behavior of **SpAz2** chloroform solution is summarized in Figure 3. The Sp form and *trans*-isomer of **SpAz2** is the most stable in four isomers under ambient condition.

SpAz2 exhibits four kinds of isomers depending on the wavelength of irradiation light. However, **SpAz1** dose not indicate such clear photochromic behavior. It is suggested that the distance between spirobenzopyran and azobenzene moieties is important for individual isomerization. Recently, Andrew and Barnes reported that dexter transfer based on wave-function overlap has an exponential distance dependence with a range of ca. 1 nm.[12] They pointed out that intramolecular energy migration is negligible in the case of intramolecular distance above 1 nm. The intramolecular distance between both photochromic moieties in **SpAz1** and **SpAz2** are estimated at 0.4 and 1.0 nm, respectively. **SpAz2** has sufficient intramolecular distance between spirobenzopyran and azobenzene moieties. Therefore, multi-photoisomerization is observed independently.

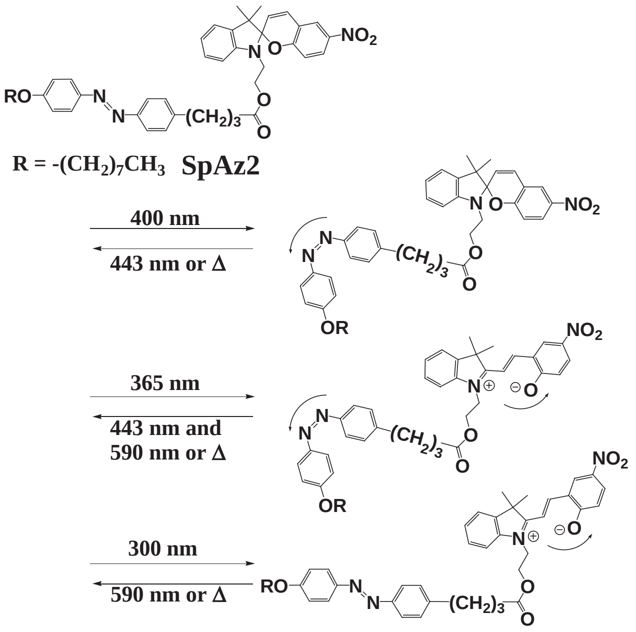

Figure 3. Photochromic behavior of **SpAz2** chloroform solution.

It is concluded that **SpAz2** has four digital codes and the application potential for multi-addressable system and molecular switching.

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