

Photochemical Control of Cholesteric Molecular Arrangement and Its Reversibility

The Possibility of Full Color Rewritable Recording in the Photon Mode

If we change the molecular structures of photo-chromic compounds by means of light, we control information transmission among the liquid crystalline molecules whose photo properties of the liquid crystals change as a result of the change of the molecular arrangement. Such a method is the so-called vitrification of the liquid crystals. As for the new molecular structures in responding to light and temperature, it makes highly practical applications of photo-functionality possible.

Introduction

There has been a wide spread of research relating to the image formation and bit records using reversible photo-reactions. In utilizing the photo properties, not only can we anticipate high resolution images as well as non-contact record and read-out of these images, but it is quite possible to make multiple color and multiple value recording, multiple record exchange by skillfully manipulating the so-called properties of the light such as wavelength, polarization, phases and intensities. As for the photo chromic compounds, it is possible to take two states of different photo properties and make transitions between two states by means of photo-reaction. Although media reactions were proposed, (these methods were not satisfactory). Using these methods, the document that was recorded by light energy was already damaged during the process of reading out. This was the basic problem (with regarding to this technology). In order to rely on reversible chemical reactions for recording and or reading out, and if the record is damaged in the process of reading out, it has become the general issue for the reversible record of the photo-motor.

For nondestructive reading out process, it is possible to introduce gate function with photo-chromic compound reactions. As for the gate function, photo reaction would not occur upon the exposure to the ordinary light. When combine with another stimuli, photo reaction will proceed. Thus, by means of light intensity, chemical stimuli, and temperature, gate responds with either open or close in such a way when photo chromic compounds are synthesized. However, there are issues on the difficulty of synthetic chemistry that introduce both the domains of photo reaction and stimuli recognition.

On the other hand, there has been much research on combining photo chromic compounds and liquid crystal materials. As a minute amount of photo chromic compounds react in the matrix of liquid crystals, it is possible to read out with photo light that affects the molecular arrangements. In this article, we introduce how do we achieve information transmission for the gate function between the photo chromic compound and the cholesteric liquid crystal. When the gate is shut, there is no change of the molecular structure of photo chromic compounds in the matrix of liquid crystals. When this gate

From these results, new recording materials for recording and reading out applications based on visible color changes of cholesteric liquid crystals when recorded with the ultraviolet light are anticipated. However, when low molecular weight liquid crystals are used, there remains an issue of maintaining record from the state of this soft crystalline structure. In our case, we consider to solve this problem by using middle-range molecular weight liquid crystals.

The structures we used for the cholesteric compounds and the photo chromic compounds are shown in Fig.2. dichloesteryl ester (1) undergoes sufficiently rapid molecular rearrangement in the cholesteric liquid crystal phase. Besides, from this liquid phase, upon rapid cooling, the helical molecular arrangement in the cholesteric solid state is maintained at stable structures at room temperature. When molecular weights are higher than 1000, but not too high, the so-called mid-range molecular weight, they can have these two properties in combination. This is an important requirement. As for dialkyl azobenzenes 2a-e, they maintain good solubility in liquid crystalline materials (1). Moreover, these compounds indicate rapid isomerization when temperature is above 120°C; in which these compounds display isotropic properties of the liquid crystals.

Spread the blend of (1) and (2c) which contains 1~2 wt% of (2c) on a glass and sandwich the glass between quartz plates. When this (composite structure) is heated to 120° C then cool to 90° C, one obtains a liquid phase cholesteric thin film of thickness approximately 10 microns that can reflect light. Irradiate the mixture with the ultraviolet light of 366 nm while maintaining the liquid crystalline temperature. During the UV irradiation, the color of the thin film changes from red to green then to blue. If the sample is quickly cooled after UV irradiation by dipping the sample in a bath of ice water of 0° C, a solid thin-film that maintains the color before rapid cooling can be obtained. The color that was fixed according to the (remaining) photon energy from the original irradiating ultraviolet light photon energy changes. As for Fig.3, it shows the spectra of solid thin film as light of various irradiation energies pass through these thin films. The band with a transmittance of approximately 50% is the reflection band that arises from the helical arrangement of the molecule. One band already seen in the ultraviolet light region is the absorption band by means of $\pi \rightarrow \pi^*$ transition of azobenzene derivative.

At the lower right corner of Fig.3, it is a plot showing the estimated trans-to-cis conversion of the azobenzene derivative taken from the light absorption change at 344 nm against irradiation energy.

In the plot of Fig.3, it also shows the peak wavelength of the reflective band against the irradiation energy. The peak wavelength of the reflected band with respect to of the solid membrane obtained from this process shifts to lower wavelength as the percentage of the cis isomer of azobenzene increases. The shifts of the reflection band (wavelength) in response to irradiation energy become larger as the initial concentration of the azobenzene derivative is increased (Fig.4).

function is utilized, it is possible to achieve recording reversible full-color document by means of photon mode mechanism.

The Color of the Cholesteric Liquid Crystals

Chemical compounds that behave as cholesteric liquid crystals display chromatic interference in the liquid crystal state. The color of the cholesteric liquid crystals is based on the molecular helical structures as shown in Fig.1 that respond with reflection light according to molecular arrangement. In the situation as the period of the molecular arrangement helix P , and the axis of the helix is parallel to the direction of the incident light with the wavelength $\lambda=nP$ (here, n is the average refractive index of the liquid crystals), the liquid crystal reflects only the light with the wavelengths in the neighborhood of $\Delta\lambda=P\Delta n$. Light with the wavelength outside of this range would just pass through.

Only, the light reflection of cholesteric liquid crystal through the helical structure is more complex in comparing to the simple thin film diffraction. The light that satisfies the wavelength condition (i.e. $\lambda=nP$) is decomposed into right polarization and left polarization. When the rotation of the electric field vector of the light in the traveling direction of the light is the same as the rotation of the long axis of the liquid crystal, the light will pass through. Conversely, the light will reflect. Reflection occurs for the light with the wavelengths such that when the incident angle makes an angle θ and the Bragg reflection condition $PCos\theta=\lambda/n$ is satisfied. On the other hand, the light observed has a shorter wavelength if it is looked upon at an angle.

The color interference of the cholesteric liquid crystal changes depending on the chemical structures of the liquid crystal, the compositions of the mixtures, the temperature, electric field and the external pressure, as well as the variety and the quantity of the impurities. In this way, it is possible to find the best helical pitch of the liquid crystal in a given environment.

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The research in controlling the helical pitches of the low molecular weight cholesteric in photo chemistry was conducted by Adams et al and by Sackmann. As for Adams et al, cholesteryl nonanoate is allowed to react with cholesteryl iodide. The ultraviolet light is irradiated on the reaction mixtures. As photo decomposition of the cholesteryl iodide occurs, the composition in the mixture also changes. The result according to the report is that the pitch of the cholesteric helix became shorter. As for Sackmann, he reported the change of the cholesteric helical pitch through the trans-cis reaction as azobenzene was added to cholesteric liquid crystal.

Also, in the plot of Fig.4, it shows that as the trans isomer of azobenzene is added, the wavelength of the reflective band is shifted to the longer wavelength. In contrast, it also shows that the wavelength is blue-shifted (to a shorter wavelength) as the cis isomer of azobenzene is added. Figure 5 plots the isomer transformation (the shifted $\Delta\lambda_{\max}$ of the reflective band after azobenzene addition) of azobenzene with respect to the number of carbons. Here, $\Delta\lambda_{\max}=\lambda_{\max}-\lambda_{\max(0)}$, λ_{\max} and $\lambda_{\max(0)}$ are the peak position of (**1**) with azobenzene and the peak position of pure (**1**) respectively. The curves of solid circle, ●, and the hollow circle, ○, show the solid films with respect to 2% and 1% trans-azobenzene addition. When the carbon numbers are 7 and 12, the shift, $\Delta\lambda_{\max}$, becomes the largest. On the other hand, as for the light-stable cis-isomer, the change $\Delta\lambda_{\max}$ is small with respect to the number of carbon atoms in the molecule.

The pitch shift of the cholesteric (liquid crystal) by means of adding achiral compounds are reported by Sackmann, Kozawaguchi, Labes, and Solladie *et al.* Labes *et al* studied the induction of the chiral structures by means of the field of the cholesteric liquid crystal as oligo-phenylene compounds are added and the resulting effects on the cholesteric pitch of the liquid crystals. Moreover, Solladie *et al* shows the effects of such additions from the matching of the sizes and shapes of the host and the guest molecules. The results of this report such that a small difference in the length of the alkyl chains that are substituted in the trans-azobenzene results in huge change cannot be easily explained. It can be considered that only a certain length of the alkyl chain in trans-azobenzene for the size and the shape of the host to give rise to strong interaction, it cannot easily induce chiral structures.

In Figure 6, we shows the spectral changes at room temperature of the transmitted light passing through a solid (cholesteric) thin film that is made by rapidly cooling the film after ultraviolet light irradiation. For comparison purpose, when the ultraviolet light is not applied, the resulting spectrum is shown as the dotted line in the same figure. As for the recovery of the (absorption) band in the neighborhood of 340 nm after 70 hours, it is the thermal isomerization reaction of azobenzene from cis to trans isomer. In contrast to the absorption spectral changes in the ultraviolet region, there is completely no change of the reflection band near 500 nm which is indicative of the basic cholesteric structure. Furthermore, the color of the solid thin-film is totally unaffected, even if we irradiate the film with the ultraviolet light (366 nm) which gives rise to isomerization reaction of the azobenzene derivative or we irradiate the film with the visible light (>420 nm). Moreover, the reflected light of the solid thin film containing 1 wt% of azobenzene derivative was stable at least one year. However, once we heat (the film) to a temperature above 120° C to melt the cholesteric structure, azobenzene derivative returns from cis isomer to trans isomer.

Reversible Full-Color Recording of Photon Mode

According to the characteristics of the mixture of (**1**) and azobenzene derivative as described in previous sections, it is possible for the photon mode to the reversible full-color image recording. In Figure 7, we show the photo of solid thin-film obtained from rapid cooling of the film after ultraviolet light irradiation on the film when mask was

placed on (top) of the film. When irradiate the sample at 87°C, those parts which were black-masked are red, those parts which the UV light transmitted through are blue. At 93°C, the black-masked parts are green while the transmitted parts are green. In another set of experiment with the masks, even though a 150 micron thick glass plate is inserted between the mask plate and the liquid crystal plate, it shows the image resolution of 25 microns. Once the image is made and fixed, the image disappears when (the film) is heated to temperatures above 120°C; After that, as the liquid crystal is kept at a temperature, we can make images with UV irradiation by inserting a mask on top of the film. It is possible to repeat such operations infinitely. Moreover, the image once fixed through rapid cooling, neither the visible light nor the UV irradiation can affect the (quality) of the image.

Conclusions

In this paper, we introduce the function of new gate function that control the information transmission through temperature changes between the azobenzene derivative and the liquid crystal molecules. This made possible through two characteristics of cholesteric liquid crystals: 1) the rapid responsiveness of molecular rearrangements in liquid state and the stability of the resulting molecular arrangement in solid state of the cholesteric liquid crystals. By means of such gate function, it is possible to reliably read out record that was made through the photo-reaction of azobenzene derivative inside of a bright room environment. The reality of making a reversible full color recording by means of photon mode has come close.

Although we know many organic molecules that show interesting photochemical properties, the examples for using these materials for realistic applications are few. In order to develop these materials for specific functions, it is necessary to highly control the molecular interactions in these materials for their functionality similar to those seen in the biological bodies. In the future, we aim to build a molecular system in the synthetic molecules function with a (level of) cooperation that would be surprising, even for an organism..