Reversible phase change of new anthracene compounds triggered by the action of light and heat

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Abstract. We synthesized 2-anthroyl and 9-anthroyl ester compounds and investigated their bulk-phase changes associated with photodimerization under melting conditions (melt-photodimerization) and subsequent thermal back reactions. All the five anthroyl compounds exhibited melting points lower than ca. 160 °C, and they were nearly quantitatively converted to the corresponding photodimers by UV irradiation in their molten state. Among them, two 2-anthroyl compounds remained isotropic and lost fluidity during the melt-photodimerization. The obtained photodimers exhibited robust solid-state amorphous phases at room temperature. In contrast, the other three anthroyl compounds showed crystallization during the melt-photodimerization. It was also found that the photodimers returned to the corresponding monomers by heat. We successfully demonstrated rewritable photopatterning using the phase change of the anthracene compounds triggered by the action of light and heat.

1. Introduction
In these days, we treat with a lot amount of digital data at one time; therefore portable data storage media have become more and more important. Among these media, rewritable optical media such as CD-RW and DVD-RW have an advantage in resource saving and reduction of waste. Data recording layer of such media consists of inorganic compounds, such as Ge and Te, known as phase change materials. As long as the inorganic compounds are used as the recording layer, higher-energy-consuming processes, such as, sputtering and CVD are inevitably used for media manufacturing. However, if the recording layer is consisted of organic compounds, more simple processes, such as, spin coating and hot melting are applicable to the fabrication of the media.

It is well known that an anthracene is a typical organic compound that can undergo photodimerization reaction and the obtained photodimer reverts to the original anthracene by light or heat [1,2]. While the anthracene emits fluorescence, the photodimer does not. Using this difference, photopatterning, which can be read by fluorescence observation, was prepared by some researchers [3]. However, there is no example of photopatterning based on phase change associated with photodimerization and decomposition of anthracene compounds. If contrast of a photopatterning is based on phase difference between ordered and disordered phases, the photopattern will have advantage over that based on fluorescence, because the light of any wavelength can be used to read the photopattern based on the phase difference, in contrast, UV light which excites anthracene moiety must be used to read the fluorescence-based photopattern.
In this study, we synthesized five new anthroyl compounds, as shown in figure 1, and investigated their phase behaviour associated with photodimerization and thermal back reaction. It was found that some of the anthroyl compounds having an appropriate substituent showed reversible crystalline and solid-state amorphous phases at room temperature triggered by light and heat. Using this reversible phase change, we successfully demonstrated rewritable photopatterning whose images were visible by cross-polarized observation.

![Chemical structures of anthracene derivatives used in this study and their melting points (mp).](image)

**Figure 1.** Chemical structures of anthracene derivatives used in this study and their melting points (mp).

2. Experimental

All the anthroyl compounds were synthesized from 2-anthracene carboxylic acid or 9-anthracene carboxylic acid and bromo-terminated alkyl compounds having cyanobiphenyl, methoxybiphenyl, and so on, using 1,8-diazobicyclo[5.4.0]undec-7-ene (DBU) as a catalyst for esterification [4]. $^1$H NMR spectra were recorded on a JEOL JNM-ECX400. The thermal properties of the samples were evaluated by polarized optical microscopy (POM) using an Olympus BH2 equipped with a Mettler FP82HT hot stage and by differential scanning calorimetry (DSC) using a Seiko Instruments Inc. DSC 6200. Heating and cooling rates were 10 °C min$^{-1}$. Photoirradiation of the samples was carried out using monochromatic 365-nm UV light (5 mW cm$^{-2}$) from a 500-W high-pressure mercury lamp through optical filters. During the photoirradiation, the temperature of the samples was controlled by a Likam LK 600PH hot stage. Gel permeation chromatography (GPC) was conducted using a Shimadzu system (an LC-10ADvp pump unit, an SPD-10Avp UV detector (detection wavelength: 280 nm), a CTO-10Avp column oven and an SCL-10Avp controller) with Shodex KF800D and KF805L columns, using THF as the eluent. High-performance liquid chromatography (HPLC) was performed by a Tosoh system (a CCPM-II pump unit, a PD-8020 UV detector (detection wavelength: 290 nm), a CO-8020 column oven, and a PX-8020 controller) using a TSK silica-60 column. The mixed solution (toluene/dichloromethane/2-propanol = 90:10:0.2 v/v/v) was used as the eluent for the HPLC experiments.

3. Results and discussion

Non-substituted anthracene and its photodimer have symmetric structure and thus have significantly high melting points at 216 [5] and 260 °C (accompanied by decomposition) [6], respectively. Such
high melting points prevent us from applying the non-substituted anthracene to phase change materials. Therefore, we synthesized new anthracene derivatives. As shown in figure 1, the melting points of the anthracene compounds have been effectively lowered by substitution.

Photoirradiation of the anthracene derivatives were carried out using Linkam hot stage and high pressure mercury lamp. 2 mg of the anthracene compounds were placed between glass plates and irradiated with UV light (365 nm, 5 mW cm\(^{-2}\)). If the molten sample of anthracene compound, 3 or 4, was cooled to room temperature without photoirradiation, it naturally returned to crystalline phase. However, when the sample was irradiated with UV light for more than 5 min in the molten state, it did not return to crystalline phase even if cooled to room temperature, instead solid-state amorphous phase was formed. This solid-state amorphous phase could be prepared by not only rapid cooling but also slow cooling after UV irradiation. This was the indication that the obtained amorphous phase was thermodynamically stable state. In contrast, UV irradiation in the molten state of the remaining anthracene compounds, 1, 2, and 5, resulted in the crystalline phase formation.

As above-mentioned, there were two kinds of phase behaviour in photoirradiation of the anthracene compounds in the molten state. One was solid-state amorphous phase formation and the other was crystalline phase formation. In both cases, we confirmed the dimer formation during UV irradiation in the molten state by means of GPC measurements. As the UV irradiation time increased, the peak associated with photodimers increased, instead the peak of anthracene monomers decreased. We found that the anthracene monomers converted to photodimers almost quantitatively in 20 min of UV irradiation. As a representative, GPC result obtained by melt-photoirradiation of 3 is shown in figure 2.

![Figure 2](image)

**Figure 2.** GPC charts of 3 obtained by UV irradiation in the molten state at 150 °C for various periods of time.

In addition, we found that the back reaction, namely, decomposition from dimer to monomer occurred by heating of the anthracene photodimers. We investigated the effect of heating temperature on the thermal back reaction by GPC analysis and found that the higher the heating temperature became, the sooner the back reaction from dimer to monomer proceeded. When the heating temperature exceeded to 200 °C, the photodimers reverted to the corresponding monomers almost quantitatively in 5 min. Interestingly, the reproduced monomers from amorphous-phased photodimers of 3 and 4 showed crystalline phase again at room temperature. NMR measurements also revealed the photodimerization in the molten state of the anthracene compounds and the subsequent thermal back reaction almost quantitatively occurred. Table 1 summarizes the phase change behaviour of the
anthracene compounds associated with photodimerization and thermal back reaction. The relationship between the structure of anthracene compounds and phase change behaviour have not been clarified yet, because the data obtained so far are too limited to explain.

| Anthracene derivatives | Phase of the photodimer at room temp. | Phase of the reproduced monomer at room temp. |
|------------------------|---------------------------------------|-----------------------------------------------|
| 1                      | Crystalline                           | Crystalline                                   |
| 2                      | Crystalline                           | Crystalline                                   |
| 3                      | Solid-state amorphous                 | Crystalline                                   |
| 4                      | Solid-state amorphous                 | Crystalline                                   |
| 5                      | Crystalline                           | Crystalline                                   |

*a Obtained by UV irradiation in the molten state.

*b Obtained by thermal back reaction.

Note that all the photodimers in table 1 were obtained by UV irradiation in the molten state. In fact, while UV irradiation of anthracene compound 3 in the crystalline phase also gave the photodimer, the phase of the obtained photodimer was crystalline phase. In order to investigate the difference between the two photodimerization conditions, we next carried out HPLC measurements. There is a possibility that asymmetric anthracene compound produces regio-isomers of photodimer in the dimerization reaction as shown in figure 3[7]. Unlike GPC analysis, HPLC measurement can detect the isomer formation under appropriate measuring condition. As shown in HPLC chart obtained by the UV irradiated sample of 3 (figure 4a), only one isomer was formed in the UV irradiation in the crystalline state, however, at least three isomers were produced in the UV irradiation in the molten state (figure 4b). From this result, it could be speculated that the presence of regio-isomers was a necessary condition for the formation of the solid-state amorphous phase for the photodimers. In addition, we found that the presence of regio-isomers is one of the necessary conditions but not sufficient condition from the next experimental results. HPLC analysis was also performed for the photodimerization reaction in the molten state of compounds 1 and 2. Although they formed crystalline phase during UV irradiation as already mentioned, we found that the obtained photodimers were mixtures of regio-isomers. This result indicated that the presence of the regio-isomers in the photodimer was necessary condition but not sufficient one for the formation of solid-state amorphous phase.

![Figure 3. Chemical structures of possible photodimer region-isomers obtained from 2-anthroyl compounds.](image-url)
Figure 4. HPLC charts of 3 measured after UV irradiation for 10 min in the crystalline phase (a) and in the molten phase (b).

In this stage, we think the fluidity of the photodimer is another one of the necessary conditions for the formation of the solid-state amorphous phase. A schematic illustration in figure 5 shows our speculation. When anthracene monomer was irradiated with UV light in the molten state, the obtained photodimer showed amorphous phase for a while after its formation. And then if the photodimer has enough fluidity at the irradiation temperature, it will organize into crystalline phase because the melting point of the photodimer is higher than the irradiation temperature. In fact, we confirmed the crystalline photodimers had the melting points at temperature higher than 200 °C. In contrast, if the photodimer does not have enough fluidity at the irradiation temperature, it cannot change to ordered phase and the amorphous phase will be immobilized. In order to clarify the mechanism of the solid-state amorphous phase formation, we are now doing computer simulation.

Figure 5. Schematic illustration for plausible mechanism of crystalline (a) or solid-state amorphous (b) phase formation in melt-photodimerization of the anthracene compounds.
As mentioned so far, we found that the some anthracene compounds can be converted to the photodimer which shows solid-state amorphous phase by light and heat, moreover, the photodimer can be returned to the crystalline monomer by heat. Therefore, next we tried to realize rewritable photopatterning based on the phase contrast using our anthracene compound 3. In order to record a photopattern, the compound 3 was melted to amorphous phase and irradiated with UV light through the photomask, and then the sample was cooled to room temperature. When the obtained sample was observed through crossed polarized light, we could see a pattern faithfully reflecting the photomask (figure 6a). With the careful observation of the photopattern, it was found that the dark part corresponded to the UV-irradiated part, and the bright part to the unirradiated part. Generally, in the cross polarized light observation, the light can penetrate through the ordered-phased region but not the amorphous-phased region. Therefore, the fact that the UV-irradiated parts composed the dark areas of the photopattern was consistent with the phase change from crystalline to solid-state amorphous phase. The photopattern can also be seen by fluorescence observation (figure 7). Compared to the two observations, cross polarized light observation is superior because the light of any wavelength can be used, in contrast, UV light which can excite anthracene moiety should be used in the fluorescence observation and such UV light gradually damages the photopattern.

![Figure 6](image)

**Figure 6.** (a) Cross-polarized-light image written in 3 and a photomask used for photopatterning. (b) Cross-polarized-light image of the erased sample. (c) Cross-polarized image written in the reproduced sample and a photomask used for rewriting another photopattern.

![Figure 7](image)

**Figure 7.** Fluorescence image of the same sample in figure 6a.

We also found that it could be possible to erase the photopattern by heating the sample at about 200 °C. The photodimer in the dark areas revered to the anthracene monomer by thermal back reaction, and the obtained monomer showed crystalline phase, consequently the whole sample became bright in
cross polarized light observation (figure 6b). In addition, it was confirmed that rewriting the photopattern in the erased sample was possible (figure 6c). Unfortunately, this rewriting process can be repeated in several times because thermal decomposition gradually occurred.

4. Conclusion
We synthesized new anthracene compounds and found that if the anthracene had an appropriate substituent, its photodimer obtained by UV-irradiation in the molten state showed solid-state amorphous phase. The obtained solid-state amorphous phase was very robust at room temperature, however, the photodimer reverted to the original monomer when heated at about 200 °C and the reproduced monomer showed crystalline phase. Using the reversible phase change of the anthracene compounds, we successfully demonstrated rewritable photopatterning by the action of light and heat.

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