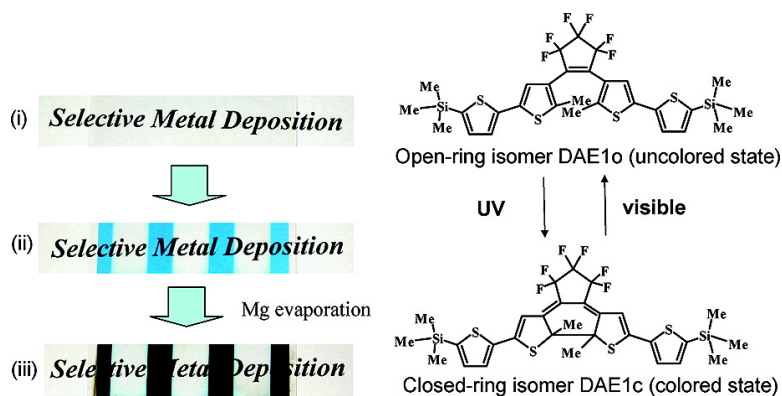


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## Selective Metal Deposition on Photoswitchable Molecular Surfaces

Tsuyoshi Tsujioka,<sup>\*,†,‡</sup> Yusuke Sesumi,<sup>†</sup> Rie Takagi,<sup>†</sup> Kyoko Masui,<sup>†</sup>  
Satoshi Yokojima,<sup>‡,§</sup> Kingo Uchida,<sup>‡,||</sup> and Shinichiro Nakamura<sup>‡,§</sup>

Department of Arts and Sciences, Faculty of Education, Osaka Kyoiku University,  
Asahigaoka 4-698-1, Kashiwara 582-8582, Japan, CREST Japan Science and Technology  
Agency, Mitsubishi Chemical Group Science and Technology Research Center Inc., Kamoshida  
1000, Aoba-ku, Yokohama 227-8502, Japan, and Department of Materials Chemistry, Faculty of  
Science and Technology, Ryukoku University, Seta, Otsu 520-2194, Japan

Received April 3, 2008; E-mail: tsujioka@cc.osaka-kyoiku.ac.jp

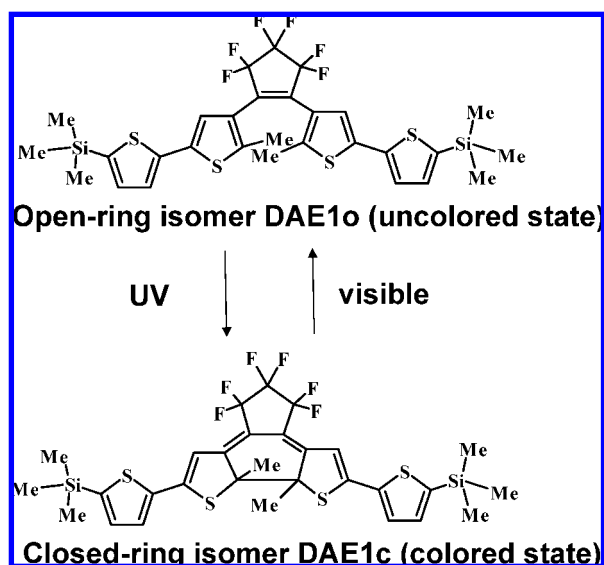
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**Abstract:** We report here a novel phenomenon: selective metal deposition on photoswitchable diarylethene (DAE) surfaces. Magnesium vapor was deposited by vacuum evaporation on the colored DAE but not on the uncolored surface. The selective deposition originates in the change of the glass transition temperature of the amorphous DAE film resulting from photoisomerization and therefore from changes of surface molecular motion. We clarified that Mg atoms on the uncolored surface actively migrated on the surface and were desorbed from the surface. The possibility of depositing other metals is also discussed. Light-controllable metal-integrated deposition was demonstrated as a new function of the photoswitchable molecular surfaces. This study reveals new features of the photoswitchable molecular surfaces, and their potential suggests bright prospects for future applications in organic electronics.

### Introduction

The quality of electronic and optical devices is primarily determined by surfaces and interfaces. To date, research on metal or semiconductor surfaces/interfaces in relation to catalysis and crystal growth has been well-documented, reflecting industrial demands.<sup>1–7</sup> Because of the increasing number of applications of organic materials, research has mainly concentrated on problems associated with carrier injection by electrodes.<sup>8–10</sup> To prepare metal thin films on organic layers, the vacuum evaporation method,<sup>11,12</sup> by which metals can be generally deposited on any organic or inorganic solid surface at room temperature,

### Scheme 1



<sup>†</sup> Osaka Kyoiku University.

<sup>‡</sup> CREST Japan Science and Technology Agency.

<sup>§</sup> Mitsubishi Chemical Group Science and Technology Research Center Inc.

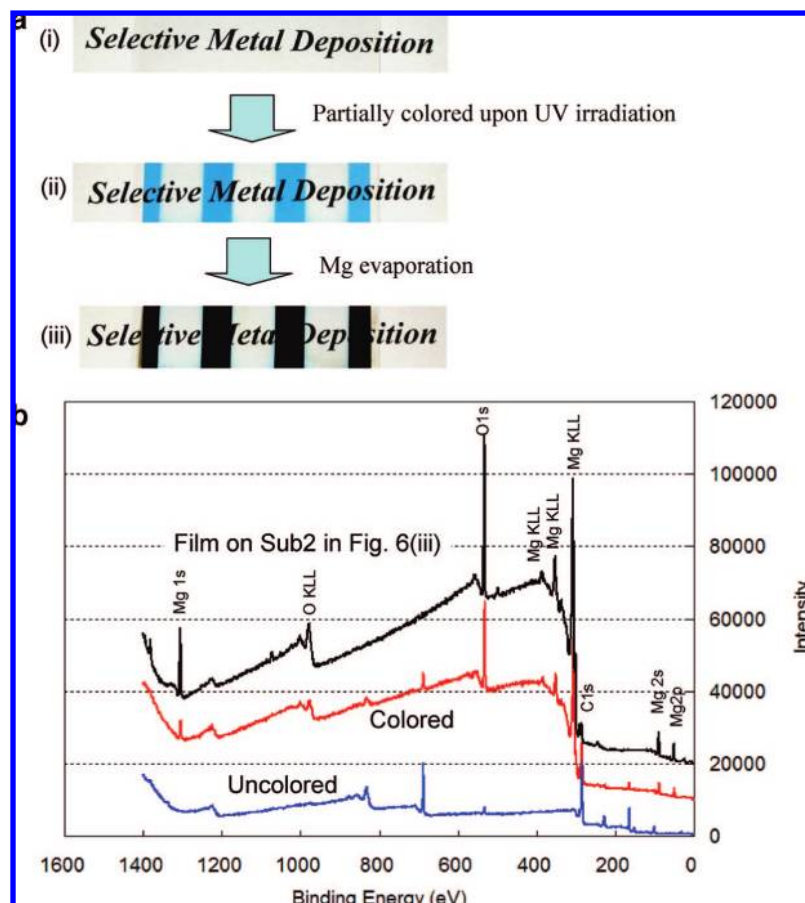
<sup>||</sup> Ryukoku University.

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is widely used. However, contrary to our expectations, we found that the ability of some organic materials to accept metal atoms is dependent upon the state of the materials. Detailed studies on the behaviors of metal-vapor atoms on polymer surfaces have been reported;<sup>13–17</sup> nevertheless, we found that the metal-

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**Figure 1.** (a) Selective metal deposition on a partially colored DAE1 film. (i) An uncolored DAE1 film. (ii) Upon UV irradiation using a photomask, parts of the film turned blue. (iii) After Mg metal deposition without masks, Mg (black) was deposited only on the colored surface. (b) XPS spectra of the surfaces of the colored and uncolored films and of the film on Sub2 in Figure 6(iii) after Mg evaporation.

deposition properties changed dramatically as the isomerization state of the organic materials was changed by the external application of light stimuli. Thus, a phenomenon apparently exists whereby selective metal deposition is possible. Here we report our findings with regard to photoswitchable (i.e., photochromic) molecules.<sup>18–26</sup> Our work has revealed that the selective metal deposition was correlated with the change of the glass transition temperature ( $T_g$ ) resulting from photoisomerization.

## Results and Discussion

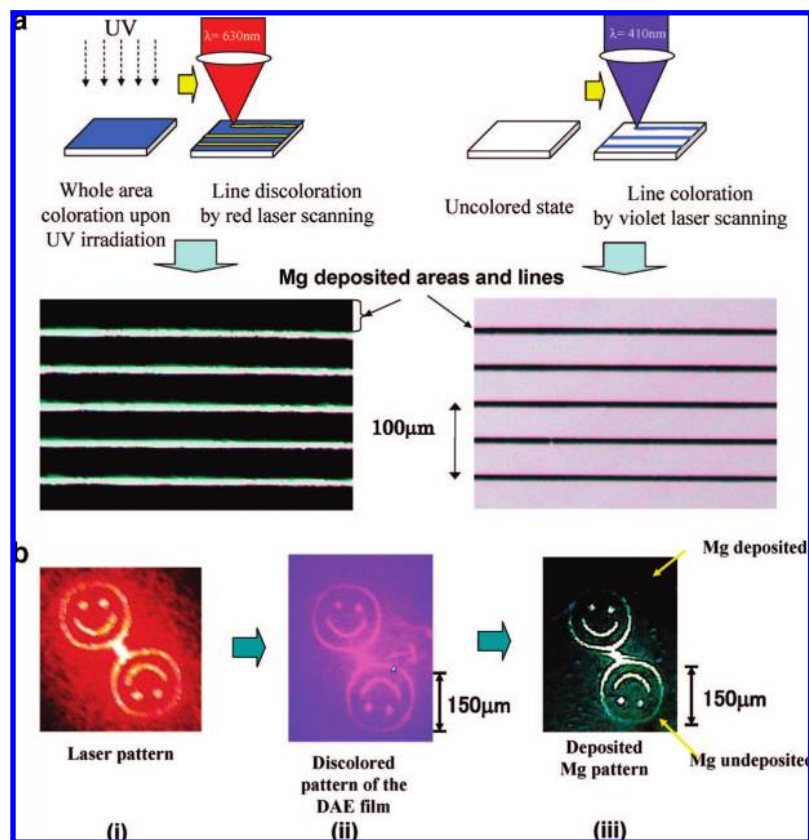
**Selective Metal Deposition.** We found that selective metal deposition occurs on the diarylethene (DAE) film DAE1. DAE1 is a photoswitchable molecule with two states: uncolored (DAE1o) and blue (DAE1c). After exposure to UV light, DAE1o switches to DAE1c, which then reverts to DAE1o after exposure to visible light (Scheme 1); both processes occur on a picosecond time scale. Unexpectedly, Mg metal vapor was deposited only on the colored-state film, as shown in Figure 1a, which depicts a film in a photostationary state containing 90% DAE1c molecules. The amorphous DAE1 film [Figure 1a(i)] was prepared on a glass substrate by a vacuum evaporation method (details for all of the experimental procedures in this work are described in the Supporting Information.). Then the film was partially exposed to UV light using a photomask,

forming blue-colored domains [Figure 1a(ii)]. This was followed by Mg deposition. Mg (black stripes) was deposited only on the colored domains, as shown in Figure 1a(iii). There was a clear threshold in the Mg deposition as the isomerization reaction proceeded (see Figure S2A,B in the Supporting Information) Using X-ray photoelectron spectroscopy (XPS), we verified that no Mg atoms or Mg-containing compounds were deposited on or penetrated into the uncolored domains, as shown in Figure 1b (see section 3 in the Supporting Information for details).

This patterning was also generated by applying a laser beam (Figure 2a). A focused beam of visible light ( $\lambda = 630$  nm) was applied to the blue surface generated by UV exposure, forming uncolored lines, after which Mg evaporation formed nondeposited lines whose line widths were less than  $10 \mu\text{m}$ . Conversely, lines were formed by Mg deposition on the colored-line surface generated by a focused violet laser ( $\lambda = 410$  nm) applied over the uncolored surface. Selective Mg deposition on cartoon-face images was also demonstrated, as shown in Figure 2b. The image size was  $\sim 150 \mu\text{m}$ . The smallest size of the metal patterns obtained by this method depends on the resolution limit of the light beam ( $\sim 1 \mu\text{m}$ ).

**Glass Transition Temperature and Selective Deposition.** Two obvious issues needed to be addressed. The first was the nature of the mechanism that caused the nondeposition phenomenon. The second was whether selective deposition is limited to the pairing of Mg atoms and DAE1 molecules. To understand the mechanism, we examined various factors associated with our hypothesis, such as surface charge and polarity, wettability,

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**Figure 2.** (a) Demonstrations of fine-pattern generation via maskless metal deposition using **DAE1** thin films (1 nm thick): (left) deposited Mg bands obtained after line discoloration of a colored film by scanning with a red laser ( $\lambda = 630$  nm); (right) deposited Mg lines obtained after line coloration of an uncolored film by scanning with a violet laser ( $\lambda = 410$  nm). (b) Cartoon-face laser patterns on a colored film compared with the Mg-free area after Mg deposition.

nanostructure, and sublimation, but none were found to be relevant (see the experimental results in section 4 in the Supporting Information). The relevant factors are presented below.

In an attempt to shed light on the dynamics and interactions which caused the selective deposition, we examined the effect of surface temperature on metal deposition using the Mg adsorbate and **DAE1** films. As shown in Figure 3a, no deposition was observed on the uncolored film at 20 °C, while deposition was observed on the colored film. However, as the temperature increased, the deposition was no longer observed even on the colored film. Furthermore, Mg deposition was observed on the uncolored surface at -15 °C. (The labels Y, N, and Y/N in Figure 3 denote Mg deposited, Mg undeposited, and the Mg deposition threshold, respectively.) These results show that there is a critical temperature above which Mg atoms can no longer adhere even on the colored film.

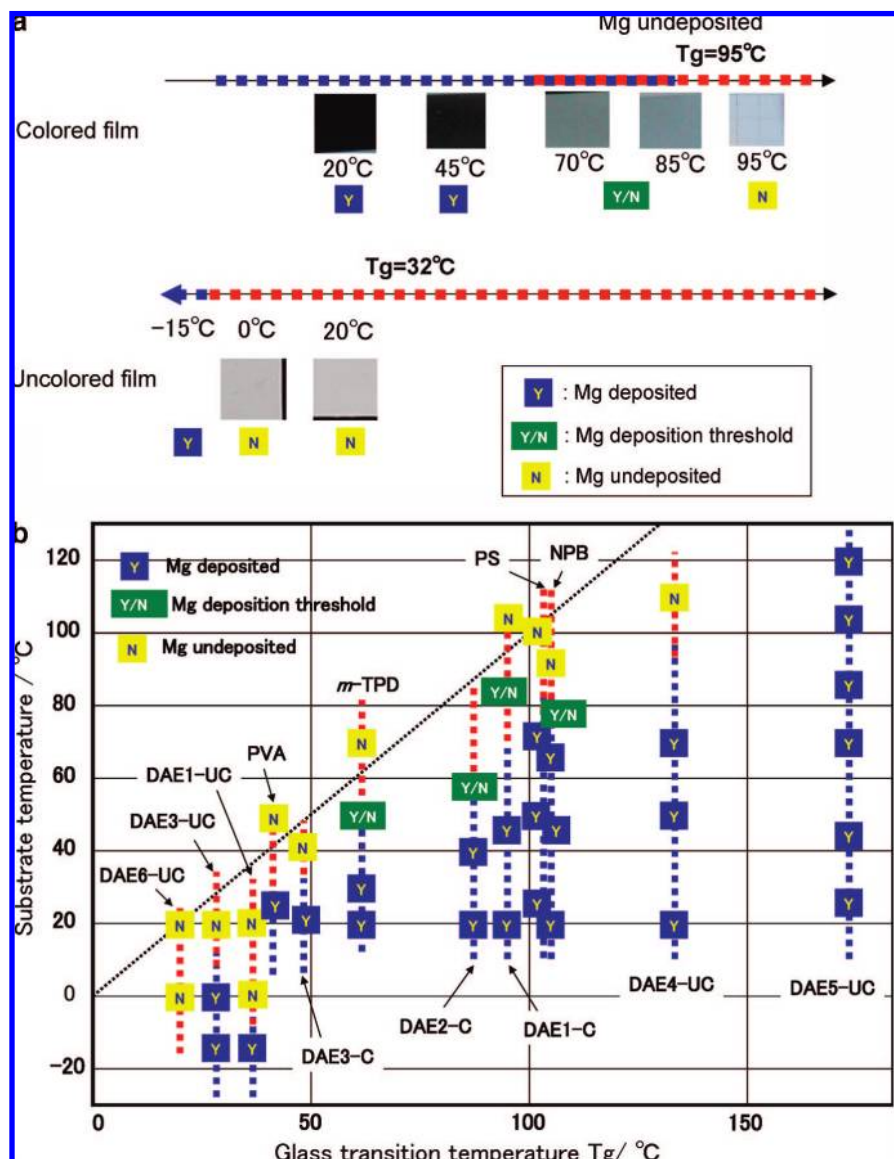
It was necessary to establish the dominant factors that determine the critical magnitude of surface molecular motion. We found that the  $T_g$  of the colored-state of **DAE1** is 95 °C, while that of uncolored-state is 32 °C. As shown in Figure 3a, when the temperature was close to or above  $T_g$ , no deposition was observed on either colored or uncolored states. It is therefore natural to infer that the critical magnitude of the molecular motion at the surface is determined by the surface property  $T_g$ .<sup>27–32</sup> This conclusion is consistent with the fact that several

DAEs with similar  $T_g$  values also show the selective deposition (see section 5 in the Supporting Information).

In an attempt to prove the hypothesis, we examined the Mg deposition capability by changing the substrate temperature on several photoswitchable molecular derivatives and other amorphous organic materials, including typical small molecules and polymers which have different values of  $T_g$ . The results are

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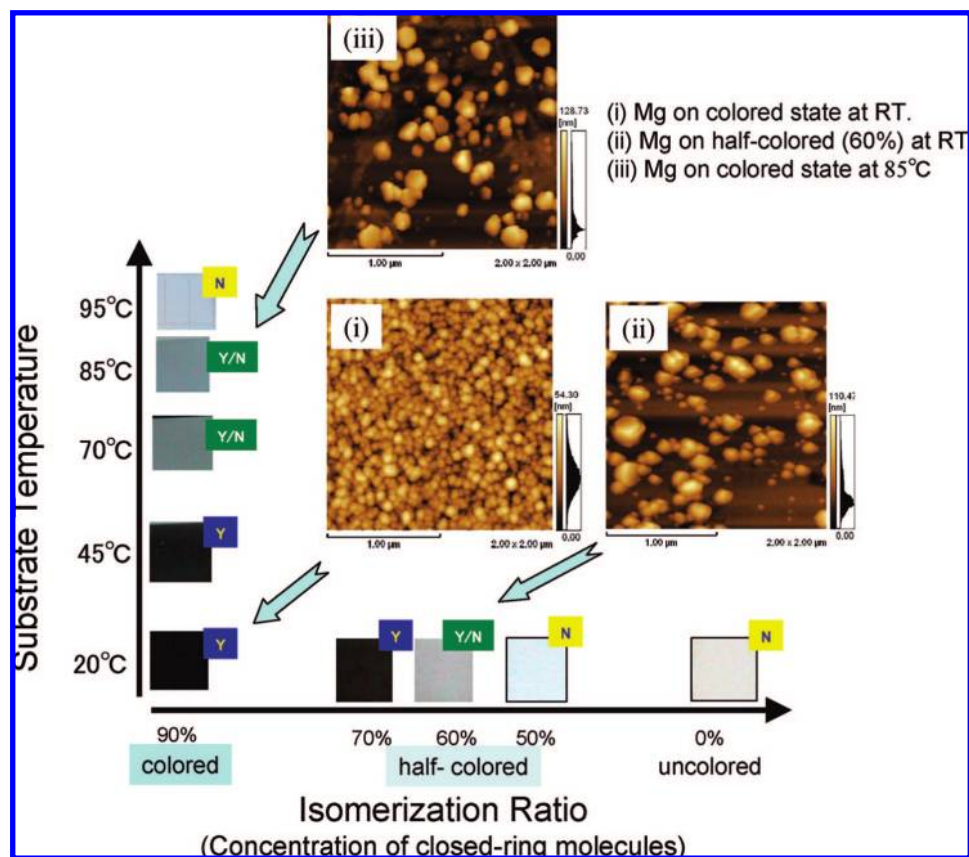


**Figure 3.** (a) Substrate-temperature dependence of Mg deposition for colored and uncolored DAE1 films. (b) Correlation of Mg deposition with  $T_g$ . The experiment was carried out for various organic materials, including photochromic derivatives (DAEs), other organic materials, and polymers (refer to section 6 and Figure S6 in the Supporting Information for the structures of the small molecules used).

summarized in Figure 3b. The horizontal and vertical axes denote  $T_g$  and the substrate temperature of the materials, respectively. The materials and corresponding  $T_g$  values shown in Figure 3b are listed in Table 1. The structures of the materials are presented in Figure S6 in the Supporting Information. For all of the materials in Figure 3b, it is clearly shown that the Mg deposition does occur (shown with letter Y) when the substrate temperature is far enough below the  $T_g$  of the material. The Mg deposition temperature is strongly correlated to the  $T_g$  of the material.

**Surface Molecular Motion and Atom Migration.** In order to understand the mechanism of this novel selectivity, we had to answer one important question: what happens to metal atoms on the surface at the threshold temperature of the adsorption? Three representative samples (Mg deposited on colored and half-colored surfaces and on a colored surface in which the substrate temperature was controlled) were prepared; with the first two samples, deposition was carried out at room temperature, while for the third, deposition was carried out at the threshold temperature of 85 °C. AFM images taken for the three cases

are shown in insets (i), (ii), and (iii), respectively, of Figure 4. Small Mg crystals with diameters of 10–100 nm filled the colored surface for the first sample [at room temperature; Figure 4, inset (i)]. In contrast, much larger Mg crystals, with diameters of >100 nm, were deposited only sparsely on the second and third samples [at threshold isomerization ratio and at threshold temperature, in insets (ii) and (iii), respectively, of Figure 4]. We found two features that commonly appeared at each threshold: (a) the crystal size was larger than that for the colored sample at room temperature; and (b) the number of crystals per unit area was significantly smaller. It is well-known that crystal size grows in proportion to increasing temperature.<sup>11</sup> Feature (a) indicates that enlargement of crystal size was also caused by the isomerization reaction. We have to consider feature (b), which is a consequence of the decrease of the nucleation rate relative to the desorption rate. At higher temperature and/or higher concentration of uncolored isomers, the motion of the molecules on the surface is greater. As the molecular motion on the surface increases, surface migration and interference of nucleation among the deposited Mg atoms also increase. The



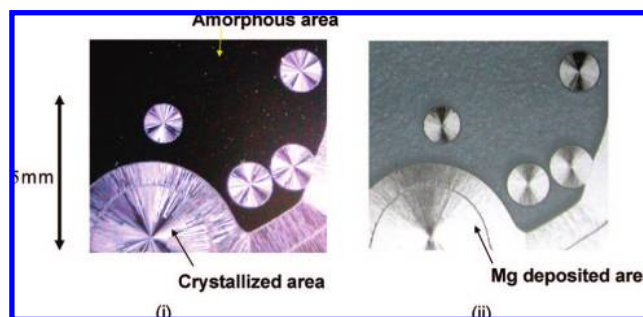
**Figure 4.** Substrate-temperature and isomerization-ratio dependences of Mg deposition. AFM images of Mg crystals on colored and half-colored DAE1 film surfaces after Mg evaporation are also displayed as insets.

**Table 1.** Materials in Figure 3b and Their  $T_g$  Values

material	$T_g$ (°C)
DAE6-UC (uncolored state)	23
DAE3-UC (uncolored state)	28
DAE1-UC (uncolored state)	32
polyvinyl alcohol (PVA)	41
DAE3-C (colored state)	47
<i>N,N'</i> -diphenyl- <i>N,N'</i> -di-3-methylphenyl-1,1'-biphenyl-4,4'-diamine ( <i>m</i> -TPD)	63
DAE2-C (colored state)	87
DAE1-C (colored state)	95
styrene polymer (PS)	105
bis( <i>N</i> -naphthyl- <i>N</i> -phenyl)benzidine (NPB)	105
DAE4-UC (uncolored state)	132
DAE5 (uncolored state)	173

existence of a threshold temperature and/or threshold concentration, therefore, demonstrates that molecular motion on the surface is the dominant determining factor in the selectivity of Mg deposition.

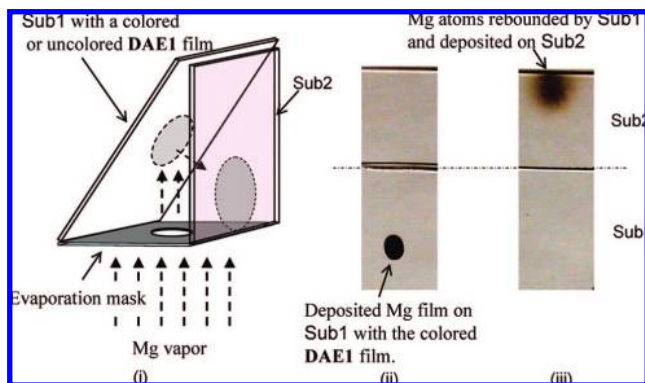
The difference in types of molecular motion on surfaces can also be illustrated by comparing Mg deposition on amorphous and crystalline uncolored films.<sup>31,32</sup> A partially crystallized uncolored film [Figure 5(i)] was observed under transmitted white light through crossed nicols. The bright circular patterns correspond to the crystalline phase, whereas the dark area is an amorphous phase. After Mg deposition at room temperature, only the crystallized area reflected light [Figure 5(ii)], indicating that Mg atoms were deposited only on the crystalline surface. Because the molecular motion on the crystalline surface is smaller than that on the amorphous film surface, even at the same ambient temperature and on same molecules, Mg atoms



**Figure 5.** Mg deposition on amorphous and crystallized uncolored films: (i) observed by transmitted light in crossed nicols before Mg deposition; (ii) observed by reflected white light after Mg deposition. White metallic areas correspond to the deposited Mg film.

on the crystalline surface are more tightly bound than those on the amorphous film surface. As a result, the magnitude of the Mg migration is not as large, and the nucleation rate is faster on the crystalline surface than on the amorphous one.

**Desorption from the Surface.** The next problem was to figure out the fate of the undeposited Mg atoms. Whether the atoms were incorporated into the film or rebounded from the surface still needed to be determined, since this characterizes the surface molecular motion and is closely associated with migration and the nucleation mechanism. The experiments shown in Figure 6 were then carried out. Two glass substrates, Sub1 and Sub2, were prepared at an acute angle in a vacuum, as shown in Figure 6(i). The 1 nm thick DAE1 film was formed on the Sub1 substrate. Mg vapor from the evaporation source was directed to Sub1 through a mask with a hole in the center. When the



**Figure 6.** Rebound of Mg atoms from a DAE1 film surface: (i) glass substrate arrangement of Sub1 with a DAE1 film and Sub2; (ii) results for the case of a colored DAE1 film on Sub1; (iii) results for the case of an uncolored DAE1 film on Sub1.

DAE1 was in the colored state, even though the DAE1 film was so thin that the blue color was not observed, the Mg vapor atoms were deposited on the colored surface on Sub1, as expected [Figure 6(ii)]. On the other hand, in the case of the uncolored DAE1 film on Sub1, the atoms rebounded and were deposited on Sub2 [Figure 6(iii)]. By XPS analysis, we verified the existence of Mg metal on the dark spot of Sub2 (Figure 1b). Thus, it was shown that the Mg atoms were not incorporated (did not penetrate) into the film but instead rebounded from the surface (see section 3 in the Supporting Information).

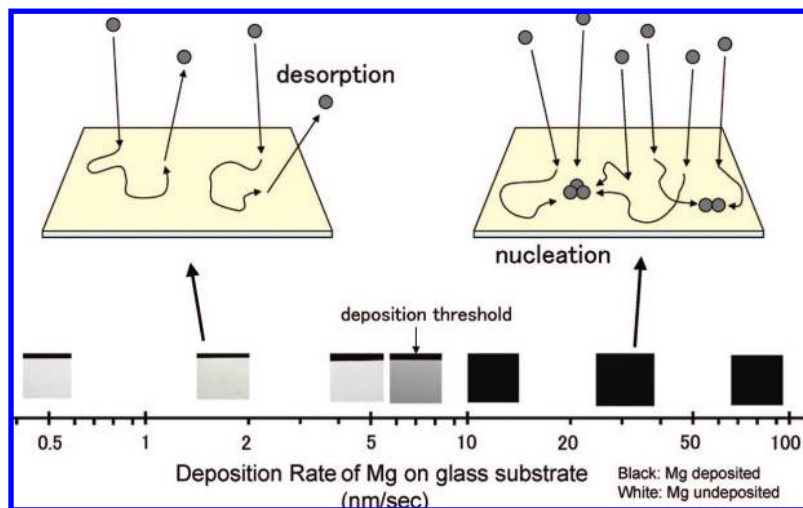
We now discuss whether the rebound is elastic or not. The deposition area of Mg on Sub2 did not correspond to the area of elastic rebound; instead, it seems to be a result of Mg vapor nonelastically rebounded in the direction normal to Sub1. This suggests that the rebound is not elastic. For this purpose, we investigated the deposition-rate dependence of Mg atoms on the uncolored surface (bottom panel of Figure 7). The Mg atoms were evaporated on the uncolored surface at room temperature. The deposition rate was defined by the rate on a glass substrate. When the deposition rate was increased to  $>7$  nm/s, a Mg film was formed even on the uncolored surface. This result means that Mg atoms did not rebound elastically, because elastic rebound is not directly dependent on the deposition rate: the Mg atoms are adsorbed once on the surface, migrate, and then

are desorbed from the surface at a low deposition rate. The mechanism is analogous to that for Ag atom desorption from some polymer (polyimide and polycarbonate) surfaces at high temperatures near their  $T_g$  values.<sup>14</sup> This result also indicates that the surface adsorption energy for Mg atoms on the uncolored surface is small compared with that on the colored surface, and therefore, Mg atoms are easily desorbed by thermal energy at room temperature.

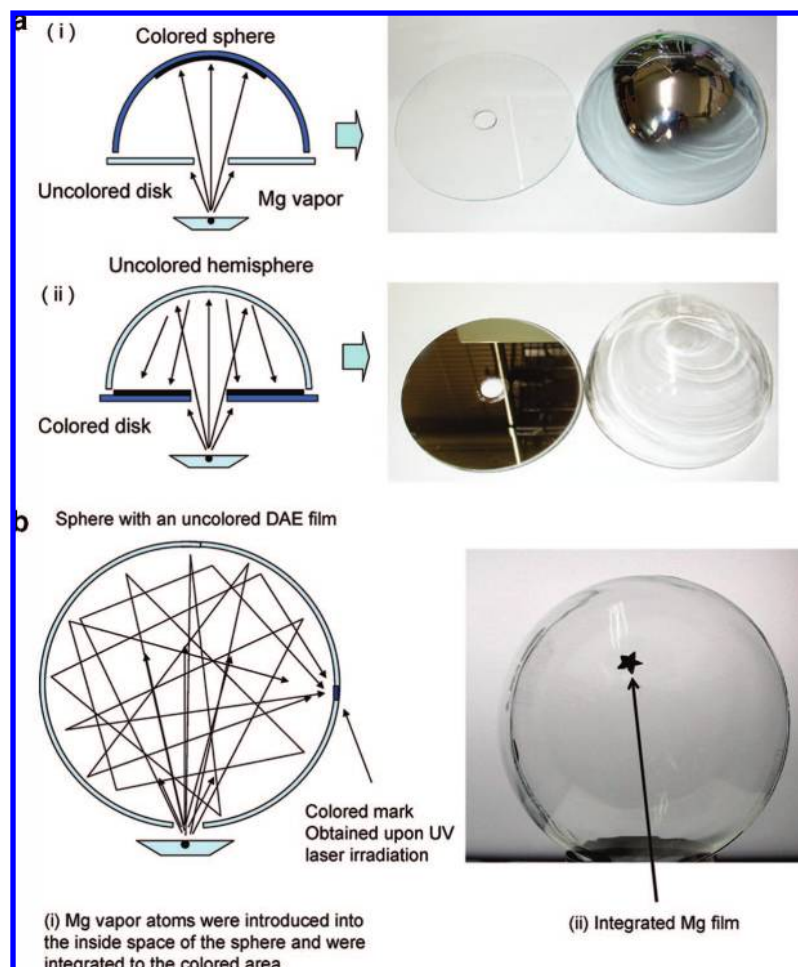
Very low sticking coefficients associated with Mg atoms on chemically terminated self-assembled monolayers (SAMs) have been reported by Walker et al.<sup>17</sup> They indicated very low sticking coefficients for Mg atoms on SAMs but high coefficients for Ca atoms. They also described that the sticking coefficient was affected by the interaction of the metal with the chemical termination of the SAM. We also found very low sticking coefficients for Mg atoms. Unexpectedly, these low values were found on many organic surfaces, depending on their  $T_g$  (photoisomerization state) and on the substrate temperature. Furthermore, the effective Mg sticking coefficients varied from zero (on the uncolored film) to unity (on the colored film) at a deposition rate of 1 nm/s (Figures 1a,b; 6; and 8a) and were not constant but depended on the deposition rate (Figure 7). We also found that the selective deposition was responsive for the property of the Mg atom but not for that of the Mg oxides (see section 3 in the Supporting Information).

**Light-Controllable Metal Deposition.** Several demonstrations of Mg atom rebound are presented below. When Mg vapor was introduced into a hemispherical space whose inner surface was coated with uncolored and colored DAE1 molecules, it was deposited only on the colored area. Especially when DAE1 on the hemisphere was in the uncolored state, Mg was rebounded and deposited only on the disk with colored DAE1, as evidenced by the metallic surface of the disk shown in Figure 8a(ii).

When introduced into a sphere whose inner surface was coated with uncolored DAE1 except for a small, star-shaped colored area obtained by UV laser irradiation, Mg was integrated and deposited only on the star-shaped colored area, as shown in Figure 8b and the associated video (also see section 7 in the Supporting Information). These results show the accumulated deposition process after rebound of Mg atoms and indicate that we can control the metal Mg deposition area simply and



**Figure 7.** (top) Illustration of the migration, nucleation, and desorption of Mg atoms on the surface. (bottom) Rate dependence of Mg deposition on the uncolored surface.



**Figure 8.** (a) Demonstration of area-selective Mg deposition. Mg vapor was introduced into the space made by a combination of a hemisphere and a disk coated with DAEI film. (i) Results when the hemisphere was in the colored state and the disk was in the uncolored state. (ii) Results when the hemisphere was in the uncolored state and the disk was in the colored state. (b) Selective Mg vapor deposition in the “integrating sphere”. Uncolored DAEI was coated on the inner surface of the glass sphere, except for the star-shaped area of colored DAEI generated by UV irradiation.

Ⓜ A video showing deposition of the star-shaped area in the integrating sphere is available.

arbitrarily by light irradiation. This suggests a potential application of the photoswitchable molecular surface.

**Possibility of Selective Deposition of Other Metals.** Finally, we discuss whether the selective deposition is limited to the pairing of Mg atoms and DAEI molecules. We conducted experiments to ascertain the importance of the specific combination of films and adsorbent. First, attempts to produce selective metal deposition using metals other than Mg (Ca, Al, Li, Ag, and Au) on surfaces bearing DAEI molecules were unsuccessful.<sup>16,17</sup> We then investigated other possible combinations using various organic films and metal adsorbents. Since surface molecular motion plays an important role in Mg nondeposition, we tested vacuum grease or oil, which has more active molecular motion states than organic solid films but a vapor pressure still low enough for use in vacuum. Mg, Al, and Ca vapor atoms were not deposited on the surface of the vacuum grease film, but Ag atoms were deposited on this surface (see Figure S8 in the Supporting Information). These results show that the selective deposition is not limited to the pairing of Mg metal with DAEI. This suggests that there is a new area of chemical physics involving the relationship between metals and organic

surfaces and that the deposition selectivity is determined by a subtle balance between repulsive and attractive forces.

## Conclusion

We have reported a novel phenomenon, namely, selective metal deposition on a photoswitchable diarylethene film surface. Mg atoms were deposited on the colored surface but not on the uncolored surface. Our work revealed that the selective metal deposition was correlated with changes in the glass transition temperature ( $T_g$ ) and therefore with surface molecular motion associated with photoisomerization. We have also demonstrated light-controllable metal deposition using the selective deposition process. The present study illustrates some new features of photoswitchable molecular surfaces, and their potential suggests bright prospects for future applications in organic electronics, including preparation of fine electrodes and wiring.<sup>33–37</sup>

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**Supporting Information Available:** Experimental details and materials used in our experiments, XPS characterization of the Mg films and DAE surfaces, results of investigations of various mechanisms for the selective deposition,  $T_g$  values and selective deposition of other DAEs, and the investigation of the possibility of selective deposition of other metals. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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