Photomagnetic Langmuir–Blodgett films consisting of azobenzene and Prussian Blue: Correlation between the film structure and the photomagnetic efficiency

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Abstract

A photomagnetic organized thin film consisting of an amphiphilic azobenzene, a smectite clay, and Prussian Blue has been prepared by utilizing the Langmuir–Blodgett (LB) method and an ion-exchange reaction. The magnetic LB films were revealed to possess an organized layered structure, and reversible photoisomerization of the azobenzene was observed even in the LB films. Upon photoillumination at 2 K, reversible changes in the magnetization were realized with the value of ca. 11%. This photoswitching in the magnetization is due to changes in the electrostatic field induced by photoisomerization of the azobenzene. A large photoinduced change in the magnetization would be owing to the highly ordered structure of the LB films. In order to verify the correlation between the film structure and photoswitching efficiency, the LB films have been fabricated in other condition. As results, it is confirmed that the packing state of the azobenzene plays an important and crucial role in accomplishment of the highly efficient photomagnetic switching.

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1. Introduction

In the field of the molecular magnetism, photocontrol on magnetic properties have been paid much attention, such as the photoinduced magnetization effect [1], the photoinduced magnetic pole inversion [2], the light-induced excited spin state trapping (LIESST) effect [3], the ligand-driven light-induced spin state change (LD-LISC) effect [4] and so on. However, in designing of such solid compounds, it is required to introduce an appropriate strength of the ligand field or the cooperative effect (i.e. π–π interaction, hydrogen bonds, and so on). Along this line, there remains limitation in the development of these compounds. In order to overcome these issues, we have focused on the incorporation of magnetic materials into photochromic assemblies to facilitate phototuning of the magnetization. Actually, we have reported on such composite magnetic materials: Prussian Blue intercalated into azobenzene bilayered vesicles [5] or Langmuir–Blodgett (LB) films [6], and iron oxide nanoparticles enclosed by spiropyran vesicles [7] or coordinated by azobenzene molecules [8]. This strategy has offered the new perspectives for the photocontrolable magnetic materials and a variety of hybrid photomagnets have been fabricated [9].

We have recently designed the photocontrollable magnetic LB films composed of an amphiphilic azobenzene, a clay mineral (montmorillonite), and Prussian Blue [6]. This magnetic LB films were found to possess a well-organized layered structure and, upon photoillumination at 2 K, reversible changes in the magnetization were realized with the value of ca. 11%. This value was much larger (ca. 10 times) than our previous work [5], which is originated from the highly ordered structure of the film. In this sense, the efficiency of photoinduced changes in the magnetization would be closely related to the film structure. Therefore, we report herein the correlation between the film structure and the photomagnetic efficiency, especially focused on the density of the azobenzene in the LB films.
2. Experimental section

An amphiphilic azobenzene (Scheme 1, abbreviated as C_{12}AzoC_{5}N\(^{+}\)) was synthesized according to a previous report [10]. The smectite clay mineral that we used was montmorillonite (Kunipia P) from Kunimine Co., Japan. A schematic illustration of the film preparation process is shown in Scheme 2. Briefly, the solution of C_{12}AzoC_{5}N\(^{+}\) was spread on the subphase of the clay suspension (50 ppm) at room temperature. A hybrid monolayer of C_{12}AzoC_{5}N\(^{+}\) and the clay single nanosheet was compressed with a desired surface pressure (i.e. 20, or 30 mN m\(^{-1}\)) and then, transferred onto hydrophobic substrates by a horizontal dipping technique. Followed by rinsing with pure water, the transferred film was immersed in an aqueous FeCl\(_2\) solution (1 mM) for 1 min. After rinsing, it was dipped in an aqueous K\(_3\)Fe(CN)\(_6\) solution (1 mM) for 1 min. The surface was rinsed and dried by blasting with N\(_2\). Hybrid LB films composed of C_{12}AzoC_{5}N\(^{+}\), clay single nanosheets, and Prussian Blue were fabricated by repeating this method.

3. Results and discussion

3.1. Characterization of floating monolayers and hybrid LB Films.

In this section, we describe the characterization of floating monolayers and hybrid LB films. It should be noted that results mentioned below are common in each film preparing condition.

3.1.1. \(\pi\)-\(\Lambda\) isotherms of floating monolayers

Fig. 1 shows the \(\pi\)-\(\Lambda\) isotherms of floating monolayers when a solution of C_{12}AzoC_{5}N\(^{+}\) was spread onto pure water and also onto the surface of the clay suspension at 50 ppm. The \(\pi\)-\(\Lambda\) isotherm of floating monolayers on pure water (Fig. 1a) lifted off at a lower molecular area than the estimated value for C_{12}AzoC_{5}N\(^{+}\), which indicates the slight dissolution of C_{12}AzoC_{5}N\(^{+}\) into the subphase. On the other hand, the \(\pi\)-\(\Lambda\) isotherm of floating monolayers on the clay suspension at 50 ppm (Fig. 1b) lifted off at around 0.4 nm\(^2\) molecule\(^{-1}\) and, as compressed, the surface pressure increased up to 50 mN m\(^{-1}\). Apparently, it is suggested the formation of stable hybrid monolayers at the air-suspension interface. This change in the isotherms indicates that charged C_{12}AzoC_{5}N\(^{+}\) monolayers could be electrostatically adsorbed onto the clay single nanosheet at the air-suspension interface [11]. Notably, the density of C_{12}AzoC_{5}N\(^{+}\) in hybrid LB films could be controlled by changing the transfer point that reflects the area per molecule.

3.1.2. UV–Vis absorption spectra for hybrid LB films.

The formation of hybrid LB films was monitored by UV–Vis absorption spectra measured in the process of the film preparation at room temperature. Each spectrum gave two characteristic absorption peaks at 370 nm and around 700 nm. The peak at 370 nm is ascribed to the \(\pi\)-\(\pi\)\(^*\) transition of C_{12}AzoC_{5}N\(^{+}\) (the trans isomer), and the broad peak at around 700 nm is related to the intervalence charge transfer (IVCT) band from Fe\(^{II}\) to Fe\(^{III}\) in the Prussian Blue. In order to confirm a reproducible transfer of floating monolayers, the absorbance of the \(\pi\)-\(\pi\)\(^*\) transition of C_{12}AzoC_{5}N\(^{+}\) was plotted as a function of the layer number. As a result, a linear increase in the absorbance could be seen, which indicates a reproducible transfer of floating monolayers in a layer-by-layer manner. Similarly, successive formation of Prussian Blue onto the clay
layer was monitored by plotting the absorbance of IVCT band versus layer number. Consequently, a linear increase in absorbance was seen and hence, the adsorption process of Prussian Blue was also reproducible.

3.1.3. Magnetic properties of hybrid LB films

The field-cooled magnetization against temperature plots obtained with an applied field of 10 G exhibit an abrupt rise in the magnetization below a critical temperature \( T_c \) of 3.2 K, attributed to the onset of long-range ferromagnetic order. The observed \( T_c \) value is lower than that of the bulk PB (5.6 K)\(^{12}\), which indicates that the number of exchange pathways per magnetic ion is reduced due to lowering structural coherence or the dimensions. The presence of a ferromagnetic state at low temperature is further supported by the presence of the hysteresis loop obtained by cycling the applied magnetic field at 2 K.

3.2. Photoresponse of hybrid LB films

In this section, we refer to photoresponse of hybrid LB films such as photoisomerization and photomagnetic property. The observed results are different in film preparing condition, and hence, the results would be shown in a separate manner.

3.2.1. Hybrid LB films prepared by transferring floating hybrid monolayers at 20 mN m\(^{-1}\)

Before light illumination, \( \text{C}_{12}\text{AzoC}_{5}\text{N}^+ \) in hybrid LB films are mainly consisted of the trans isomer, because it is thermodynamically more stable than the cis form (Fig. 2, spectrum a)\(^{13}\). Upon UV light illumination, trans–cis isomerization occurred as reflected by the decrease of absorbance at 370 nm (Fig. 2, spectrum b). In this photochemical process, it took about 20 min to reach the photostationary state. In addition, upon subsequent visible light illumination for 5 min, hybrid LB films underwent reverse process completely (i.e. cis–trans isomerization), and the spectrum was consistent with the initial one (Fig. 2, spectrum a). Thus, reversible photoisomerization was observed in hybrid LB films prepared by this condition.

The influence of photoillumination on the magnetization was examined at 2 K. Fig. 3 shows changes in the magnetization upon photoillumination. As can be seen in the figure, the magnetization decreased upon UV illumination and, on the contrary, visible light illumination led to recovery of the magnetization. However, in the third cycle (i.e. from step number 2 to 3), an abrupt decrease in the magnetization was observed, in which the change in the magnetization was about three times larger than that in the first cycle (i.e. from step number 0 to 1). This sudden drop in the magnetization might be concerned with the structure of the LB films. Except for this cycle, the switching behavior in the magnetization upon photoillumination is likely to be favorable.

3.2.2. Hybrid LB films prepared by transferring floating hybrid monolayers at 30 mN m\(^{-1}\)

As already mentioned above, before light illumination, \( \text{C}_{12}\text{AzoC}_{5}\text{N}^+ \) in hybrid LB films is mainly composed of the

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trans photoisomerization behavior of hybrid LB films, the reverse photochemical process (cis–trans isomerization) also proceeded, the spectrum of after visible light illumination (Fig. 4, spectrum c) was not agreement with that of initial state. Such a behavior in the spectra would be due to the change in the molecular orientation of C12AzoC5N+ in the LB films. After this process, reversible photoisomerization was observed between the spectrum b and c in Fig. 4.

With regard to photomagnetic property, photoswitching behavior in the magnetization was greatly improved (Fig. 5). Briefly, the UV-light-induced decrease and visible-light-induced increase of the magnetization was observed and repeated several times. It is noteworthy that the photoswitching efficiency, ca. 11%, is higher than our previous work (ca. 10 times) [5]. In addition, the photomagnetic switching behavior was quite reproducible, compared with the case of hybrid LB films mentioned above (i.e. performing the hybrid monolayers transfer at 20 mN m⁻¹).

### 3.2.3. Discussion about the difference in photoresponse

With respect to photoisomerization of C12AzoC5N+ in hybrid LB films, the reverse photochemical process (cis–trans isomerization) varied significantly in film preparing condition. Such a different photoisomerization behavior is deduced to be the change in the molecular orientation of C12AzoC5N+ in the LB films during photoisomerization. In fact, it has previously reported that the reorientation of the azobenzene, through the photoisomerization process, occurred in the LB films [14]. In our case, such a reorientation of the azobenzene molecule is assumed to proceed during photoisomerization process, due to the tightly packing of the C12AzoC5N+ in case of the LB films prepared by transferring floating monolayer at 30 mN m⁻¹. As a consequence, once the molecular orientation of C12AzoC5N+ in hybrid LB films was rearranged, it is likely to be maintained as supported by UV–Vis absorption spectra (Fig. 4).

Based on this assumption, the photomagnetic behaviors would also be related to the structure of hybrid LB films, especially the density of C12AzoC5N+ in the LB films. As already known, photoisomerization of the azobenzene molecule accompanies the free volume change, that is, the cis isomer is much more bulky than the trans one. Along this line, if the molecular packing of C12AzoC5N+ is loose, the structure of hybrid LB films might be changed via photoisomerization. The C12AzoC5N+ layers in the LB films prepared by transferring floating monolayers at 20 mN m⁻¹ are not so densely packed. Therefore, it is so flexible that their

### Table 1

Comparison of the photoresponse of hybrid LB films prepared at different conditions

| Step Number | Fraction of the cis isomer in photostationary state (%) | Photoisomerization behavior | FWHM value in XRD patterns (°) | Photomagnetic behavior |
|-------------|--------------------------------------------------------|----------------------------|--------------------------------|------------------------|
| 1           | 81.4                                                   | R                          | 1.38                           | PR                     |
| 2           | 45.3                                                   | PR                         | 0.83                           | R                      |

Fraction of the cis isomer in the photostationary state was estimated by using a calculation based on the difference spectra [15]. In this table ‘R’ and ‘PR’ denote ‘quite reversible’ and ‘partially reversible’, respectively. FWHM (full width at half maximum) value in XRD patterns is applied to the (001) reflection, and this value would be concerned with the rigidity of hybrid LB films.
arrangement is supposed to change easily through photoisomerization. In this sense, the LB films would become disordered to some extent and hence, the magnetization is affected by this structural alternation, resulting in the irregular change in the magnetization (Fig. 3). On the contrary, an improvement in the photoswitching efficiency of the magnetization would be observed when floating monolayers were transferred at 30 mN m\(^{-1}\). Such an improvement would be ascribed to the increase of the C\(_{12}\)Azo-C\(_5\)N\(^+\) density in hybrid LB films as confirmed by the \(\pi-A\) isotherm measurement. Therefore, it could be mentioned that the higher molecular orientation of C\(_{12}\)Azo-C\(_5\)N\(^+\) is, the larger changes in the magnetization upon photolllumination. This conclusion is supported by the comparison with our previous system (i.e. Prussian Blue intercalated into the C\(_{12}\)Azo-C\(_5\)N\(^+\) vesicle dispersed in the polymer matrix). Conclusively, in order to achieve the high photoswitching efficiency in the magnetization, it would be essential to construct the well-ordered structure with the high density of photochromic compounds. Finally, above results are summarized and depicted in Table 1.

4. Conclusions

We have designed the photocontrollable magnetic LB films composed of an amphiphilic azobenzene, montmorillonite, and Prussian Blue by means of the modified LB method and an ion-exchange reaction. In this hybrid LB films, photoswitching efficiency in the magnetization were reached to the maximum value of ca. 11%. When hybrid LB films were prepared in a certain condition that lowers the density of azobenzene molecules, the photoswitching behavior was found to be irregular due to the loosely packing of azobenzene molecules. Therefore, it would be concluded that it is necessary to construct the well-ordered structure with the high density of photochromic compounds for realizing the highly efficient photoswitching in the magnetization in an organic–inorganic hybrid system.

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References

[1] O. Sato, T. Iyoda, A. Fujishima, K. Hashimoto, Photoinduced magnetization of a cobalt–iron cyanide, Science 272 (1996) 704–705.
[2] S. Okoshi, K. Hashimoto, Design of a novel magnet exhibiting photoinduced magnetic pole inversion based on molecular field theory, J. Am. Chem. Soc. 121 (1999) 10591–10597.
[3] S. Decurtins, P. Gülich, C.P. Köhler, H. Spiering, A. Hauser, Light-induced excited spin state trapping in a transition-metal complex: the hexa-1-propyltetrazole-iron (II) tetrafluoroborate spin-crossover system, Chem. Phys. Lett. 105 (1984) 1–4.
[4] M.-L. Boillot, C. Roux, J.-P. Audiere, A. Dausse, J. Zarembowitch, Ligand-driven light-induced spin change in transition-metal complexes: selection of an appropriate system and first evidence of the effect, in Fe\(x\)(4-styrylpyridine\(_y\))(NCBP\(_z\))\(_{2}\), Inorg. Chem. 35 (1996) 3975–3980.
[5] Y. Einaga, O. Sato, T. Iyoda, A. Fujishima, K. Hashimoto, Photofunctional vesicles containing Prussian Blue and azobenzene, J. Am. Chem. Soc. 121 (1999) 3745–3780.
[6] T. Yamamoto, Y. Umemura, O. Sato, Y. Einaga, Photoswitchable magnetic films: Prussian Blue intercalated in Langmuir–Blodgett films consisting of an amphiphilic azobenzene and a clay mineral, Chem. Mater. 16 (2004) 1195–1201.
[7] M. Taguchi, G.-M. Li, Z.-Z. Gu, O. Sato, Y. Einaga, Magnetic vesicles of amphiphilic spiropyran containing iron oxide particles on a solid state substrate, Chem. Mater. 15 (2003) 4756–4760.
[8] R. Mikami, M. Taguchi, K. Yamada, K. Suzuki, O. Sato, Y. Einaga, Reversible photo-switching of the magnetization of iron oxide nanoparticles at room temperature, Angew. Chem. Int. Ed. 43 (2004) 6135–6139.
[9] S. Benard, E. Riviere, P. Yu, K. Nakatani, J.F. Delouis, A. photochromic molecule-based magnet, Chem. Mater. 13 (2001) 159–162.
[10] T. Kunitake, Y. Okahata, M. Shimomura, S. Yasumami, T. Takarabe, Formation of stable bilayer assemblies in water from single-chain amphiphiles. Relationship between the amphiphile structure and the aggregate morphology, J. Am. Chem. Soc. 103 (1981) 5401–5413.
[11] Y. Umemura, A. Yamagishi, R. Schoonheydt, A. Persoons, F. De Schryver, Formation of hybrid monolayers of alkylammonium cations and a clay mineral at an air–water interface: clay as an inorganic stabilizer for water-soluble amphiphiles, Thin Solid Films 388 (2001) 5–8.
[12] F. Herren, P. Fischer, A. Ludi, W. Haegl, Neutron diffraction study of Prussian Blue, Fe\(_x\)Fe(CN)\(_y\)\(_z\)\(_{2}\)\(_{2}\)\(_2\). Location of water molecules and long-range magnetic order, Inorg. Chem. 19 (1980) 956–959.
[13] A.W. Adamson, A. Vogler, H. Kunkely, R. Wachtler, Photocalorimetry. Enthalpies of photolysis of trans-azobenzene, ferrioxalate and cobaltioxalate ions, chromium hexacarbonyl, and dirhenium decarbonyl, J. Am. Chem. Soc. 100 (1978) 1298–1300.
[14] M. Schönhoff, M. Mertesdorf, M. Losche, Mechanism of photoreorientation of azobenzene dyes in molecular films, J. Phys. Chem. 100 (1996) 7558–7565.
[15] W.R. Brode, J.H. Gould, G.M. Wyman, The relation between the absorption spectra and the chemical constitution of dyes. XXV. Phototropism and cis-trans isomerism in aromatic azo compounds, J. Am. Chem. Soc. 74 (1952) 4641–4646.