

Photoswitchable Magnetic Langmuir-Blodgett Films

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A novel photo-controllable magnetic thin film consisting of amphiphilic azobenzene cations, a smectite clay, and Prussian Blue (also its analogue) has been designed and prepared by using the Langmuir-Blodgett method and an ion-exchange reaction. This magnetic thin film possesses a well-organized nanoscale layered structure. Reversible photoisomerization of the azobenzene chromophore realized photoswitching of the magnetization at low temperature. The changes in the magnetization values are due to the highly ordered structure of the hybrid multilayered films. Furthermore, the photoswitching was also realized at higher temperature (50 K) by using nickel-chromium Prussian Blue as magnetic materials.

Key words: Photo-control, LB film, Prussian Blue, Magnetic Properties

1. Introduction

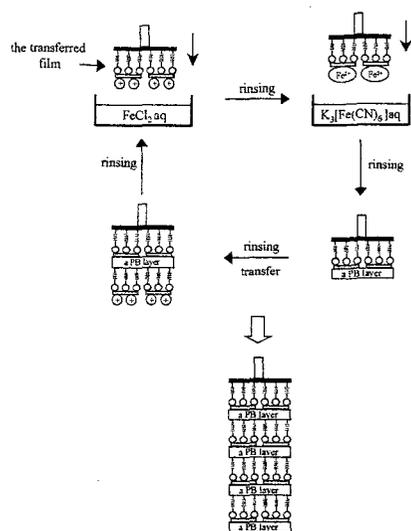
Recently, various kinds of photo-controllable materials have been reported in the field of magnetic materials.^[1] In order to achieve this issue, we have focused on the incorporation of photochromic compounds into magnetic systems to facilitate phototuning of the magnetization. This strategy has attracted much attention and several kinds of photo-controllable magnets have been reported by adopting this method.^[2] In our previous work, we have reported on composite magnetic materials containing Prussian Blue intercalated into azobenzene multi-bilayered vesicles.^[2a, b] However, the degree of photocontrol over the magnetization values was small in both cases. Therefore, it would be desirable to develop a novel photofunctional system that could achieve larger changes in the magnetization values by the use of photoillumination.

Represented by a Langmuir-Blodgett (LB) film, ultrathin films with highly ordered structures have many

applications in the field of optical devices, microelectronic devices, and sensors.^[3] Among various types of LB films, the clay hybrid LB film has remarkable features.^[4] In this work, we have designed a novel type of a hybrid multilayered film consisting of amphiphilic azobenzene cations, a smectite clay, and Prussian Blue (PB) (nickel-chromium Prussian Blue (Ni-Cr PB)). In this system, it is expected to realize larger photo-induced changes in the magnetization values due to the highly ordered molecular orientation of the LB film.

2. Experimental Section

An amphiphilic azobenzene derivative {5-[4-(4-dodecyloxy-phenylazo)-phenoxy]-pentyl}-(2-hydroxyethyl)-dimethyl-ammonium bromide (abbreviated as C₁₂AzoC₅N⁺) was synthesized according to a previous report.^[5] The smectite clay mineral was montmorillonite (*Kunipia P*). A preparation process of the hybrid multilayered films is shown in Scheme 1.



Scheme 1. Preparation methods of the hybrid multilayered films.

Briefly, the solution of $C_{12}AzoC_5N^+$ was spread on a subphase of the clay suspension (50 ppm) at room temperature. A floating hybrid monolayer of $C_{12}AzoC_5N^+$ and clay platelets was compressed with a surface pressure of 30 mN m^{-1} and then, transferred onto hydrophobic substrates by a horizontal dipping. Followed by rinsing with pure water (Millipore), the transferred film was immersed in an aqueous $FeCl_2$ (or $NiCl_2$) solution (1 mM) for 1 min. After rinsing, it was dipped in an aqueous $K_3[Fe(CN)_6]$ (or $K_3[Cr(CN)_6]$) solution (1 mM) for 1 min. The surface was rinsed and dried by blasting with N_2 . Hybrid multilayered films composed of $C_{12}AzoC_5N^+$, clay platelets, and PB (or Ni-Cr PB) were fabricated by repeating this method.

3. Results and Discussion

3.1 $C_{12}AzoC_5N^+$ /Clay/PB LB Films

UV-vis absorption spectra of the hybrid multilayered films were measured every deposition cycle at room temperature. Each spectrum gave two intense absorption peaks at 370 nm and around 700 nm. The peak at 370 nm is ascribed to the $\pi-\pi^*$ transition of the trans isomer of $C_{12}AzoC_5N^+$ and the peak at around 700 nm is related to the inter-valence charge transfer (IVCT) band from Fe^{II} to Fe^{III} in the PB layer. Absorbance of each peak increased linearly with increasing numbers of hybrid layers and this indicates a reproducible transfer of the films. It is noteworthy that the IVCT band of PB was blue-shifted with increasing the number of hybrid layers. This spectral shift indicates the growth of PB domains in the hybrid

multilayered films.

Subsequently, photoisomerization of the hybrid multilayered films was monitored by UV-vis absorption spectroscopy. Before light illumination, the hybrid multilayered films only consisted of the trans form of $C_{12}AzoC_5N^+$ because it is thermodynamically more stable than the cis form.^[6] Both at room temperature and 10 K, UV illumination (365 nm) of the trans-isomer converted it to the cis-isomer resulting from decrease of the absorbance at 370 nm, which is ascribed to the $\pi-\pi^*$ transitions of the trans-isomer. After subsequent illumination with visible light (400-700 nm), the reverse process (i.e. cis-to-trans isomerization) also proceeded to a certain degree. The overall trans-cis isomerization cycle was repeated several times by alternative illumination with UV and visible light.

In order to get information on the orientation of the alkyl chains of $C_{12}AzoC_5N^+$ in the hybrid multilayered films, p-polarized IR-ER spectra were measured in the $-CH_2-$ stretching vibration region at various incident angles. These spectra gave two absorption peaks at 2914 and 2847 cm^{-1} , which are assigned to the antisymmetric and symmetric $-CH_2-$ stretching ($\nu_a(CH_2)$ and $\nu_s(CH_2)$) vibrations of $C_{12}AzoC_5N^+$, respectively. In the spectra, the peaks due to both bands appear as the negative absorbance with the incident angle below Brewster angle (θ_B ; 56° for a glass), while the same peaks appear as the positive one with the incident angle above θ_B . These spectral data indicate that the transition moments of the $\nu_a(CH_2)$ and $\nu_s(CH_2)$ band are estimated to be parallel to the film surface,^[7] that is, the alkyl chain of $C_{12}AzoC_5N^+$ in the hybrid multilayered films are almost perpendicular to the layers.

The XRD pattern for the hybrid multilayered films gave six diffraction peaks. This indicates that the hybrid film possesses a layered structure and, in addition, the thickness of one hybrid layer ($C_{12}AzoC_5N^+$ /clay/PB) is calculated to be 3.27 nm. Considering the thickness of a clay platelet (0.96 nm),^[8] the total thickness of the $C_{12}AzoC_5N^+$ and PB layers should therefore be 2.31 nm. Moreover, according to single-crystal X-ray structure analysis^[9] and the estimated orientation of $C_{12}AzoC_5N^+$, the molecular length of $C_{12}AzoC_5N^+$ has been determined to be 1.71 nm. From these estimations, the thickness of the adsorbed PB layers is calculated to be 0.60 nm. On

this occasion, we suggest that roughly one layer of the three-dimensional PB network is formed, even in the hybrid multilayered films.

The field-cooled magnetization curve at 10 G for the hybrid multilayered films exhibits ferromagnetic properties with a critical temperature (T_c) of 3.2 K. This lower T_c value than that of the bulk PB (5.6 K)^[10] indicates that the number of exchange pathways per magnetic ion is reduced due to lowering structural coherence or the dimensions. In addition, the presence of ferromagnetism at low temperature was supported by an observation of magnetic hysteresis loop at 2 K. This tendency also exhibits a ferromagnetic trend. Subsequently, we observed the influence of light illumination on magnetic properties of the hybrid multilayered films and also determined how the

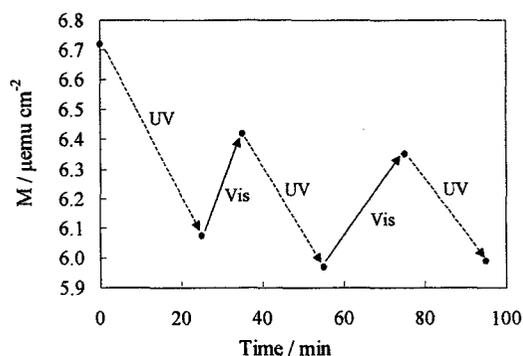


Fig. 1 Changes in the magnetization for hybrid multilayered films ($C_{12}AzoC_3N^+/Clay/PB$), by photoillumination at 2 K and 10 G.

magnetization changed by alternate illumination with UV and visible light at 2 K (Figure 1). During the UV light illumination, the magnetization value decreased and even after the light illumination was stopped, this decreased magnetization value was maintained for at least 2 hours. Then, we illuminated the films with visible light for a further 10 min and, as a result, the magnetization value recovered by ca. 50%. After this process, the photo-induced changes in the magnetization (totally ca. 11%) were repeated several times. This photoswitching of the magnetization is due to the changes in the electrostatic field of PB. Actually, λ_{max} of the IVCT band from Fe^{II} to Fe^{III} was changed reversibly by alternate illumination with UV and visible light and repeated several times. Reversible changes in λ_{max} are almost consistent with the changes in the magnetization. This means that changes in the electrostatic field driven by photoisomerization of the

azobenzene led to changes in the Coulombic energy. Moreover, they might affect the superexchange interaction between the spins in the PB magnet.

3.2 $C_{12}AzoC_3N^+/Clay/Ni-Cr$ PB LB Films

Among various PB analogues, the bulk Ni-Cr PB exhibits ferromagnetism with a relative high T_c of 72 K.^[11] Accordingly, we prepared similar films by using Ni-Cr PB instead of PB. In this system, it is expected to realize the photoswitching in the magnetization at higher temperature than in the case of PB. Characterizations for the hybrid multilayered films were carried out in the same manner as described above. Briefly, a reproducible transfer of the films and photoisomerization of the hybrid multilayered films were confirmed by UV-vis absorption spectroscopy. From X-ray diffraction measurement, it is supposed roughly one layer of the three-dimensional Ni-Cr PB network is formed. With regarding to magnetic measurements, the hybrid multilayered films exhibit ferromagnetic properties with T_c of 71 K (Figure 2) and moreover, photoswitching in the magnetization was observed at 50 K (Figure 3).

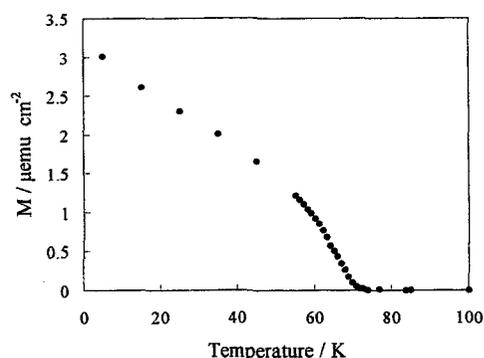


Fig. 2 Field-cooled magnetization curve for the hybrid multilayered films ($C_{12}AzoC_3N^+/Clay/Ni-Cr$ PB) at 10 G.

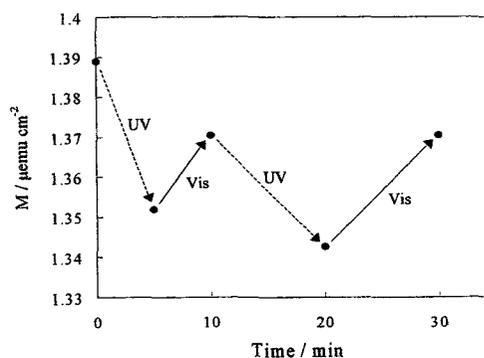


Fig. 3 Changes in the magnetization for hybrid multilayered films ($C_{12}AzoC_3N^+/Clay/PB$), by photoillumination at 50 K and 10 G.

4. Conclusion

We have designed a novel photofunctional LB film consisting of amphiphilic azobenzene cations, a smectite clay, and Prussian Blue, whose magnetic properties could be controlled by photoillumination. The present work demonstrates that an air-suspension interface can be quite effective for designing novel photofunctional systems due to its highly ordered structure. In addition, this strategy may offer new perspectives, not only for photofunctional materials but also for nanoscale composite materials.

5. Acknowledgement

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