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Structure-distortion-induced photomagnetic effect in azobenzene/polyoxometalate Langmuir–Blodgett films†

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We have prepared photomagnetic Langmuir–Blodgett films composed of an amphiphilic azobenzene and a magnetic polyoxometalate. The obtained film possesses a well-organized layered structure where polyoxometalate anions are sandwiched by azobenzene cations in a single-layered manner. Reversible photoisomerization of azobenzene was achieved even at low temperature, accompanying intensity changes in the d–d transition of polyoxometalate anions. The photomagnetic effect was observed reversibly upon alternate UV and visible light irradiation. Based on polarized spectroscopy, the observed photomagnetic effect is ascribed to the structure-distortion of polyoxometalate layers.

Introduction

Photomagnetism has been one of the most attractive topics for the molecule-based magnetism community.[1] In principle, the phenomenon is attributed to photoinduced electron transfer, leading to changes in the spin state. For example, in Co–Fe Prussian Blue, excitation of an intervalence charge transfer band results in trapping the metastable high-spin state.[2] The design of such photomagnetic materials is one of the main challenges of material science because of potential applications in optical memory and switching devices.[3–7] However, the number of successful examples is still small, and it is desirable to propose a possible concept in order to obtain an optically switchable magnetic material. On the other hand, organic photochromic molecules have been used as building blocks for fabricating a photoswitchable molecular system.[8] Along these lines, we have focused on integration of magnetic materials into organic photochromic molecules to facilitate phototuning of the magnetization.[9–15] This strategy has offered prospects for phototunable magnetic materials.

The air–liquid interface is often used to direct assembly processes.[16] Traditional Langmuir monolayers can form two-dimensional molecular crystals or can selectively bind molecules or ions from the subphase to produce multicomponent assemblies.[17] Langmuir–Blodgett (LB) films can be obtained by transferring the Langmuir monolayers onto the solid substrate. This method is called the LB method, in which the number of layers and their sequence can be controlled at the molecular level.[18] On the basis of these features, two-dimensional assemblies of magnetic materials have been fabricated as a part of LB films.[19–21] Confinement of reactants to the air–water interface directs lateral propagation of a two-dimensional network.

Polyoxometalates (POMs) are discrete anionic metal oxides that can be classified as useful building blocks for functional materials.[22–24] POMs have attracted much interest because of a wide variety of physical and chemical properties, ranging from conductivity, magnetism, catalysis, electrochromism, and so on.[25–28] POMs are advantageous for integrating with a broad range of molecules, which, in turn, are considered to be discrete building blocks for development of functional materials. Thus, POMs could be extended to organic–inorganic hybrids by using non-covalent and/or covalent interactions. For example, Coronado *et al.* have developed fascinating Langmuir–Blodgett films of POM.[29–31] They have demonstrated that the clever use of an air–liquid interface could be quite effective in fabricating anisotropic magnetic thin films. Moreover, they also show the possibility of designing a multi-functional molecular assembly using POMs.

Herein, we report on the photomagnetic Langmuir–Blodgett films composed of an amphiphilic azobenzene (AZ, a photochromic organic molecule) and a Co^{II}-ion-containing polyoxometalate anion (Co–POM, a ferromagnetic cluster) (Scheme 1). The film was characterized by X-ray diffraction (XRD), UV-Vis absorption spectroscopy (UV-Vis), and superconducting

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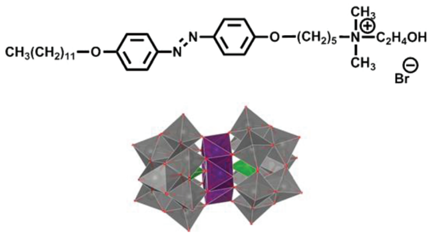
† Electronic supplementary information (ESI) available: Synthesis of materials; linear FT-IR dichroism spectroscopy; preparation and characterization of the model film. See DOI: 10.1039/c3dt51402a



Scheme 1 Structure of (top) AZ and (bottom) Co–POM.‡

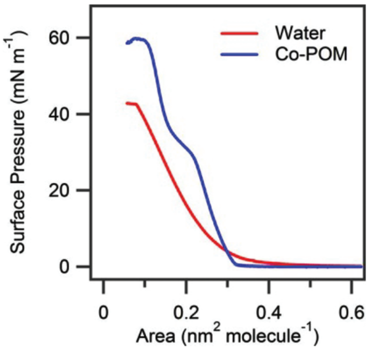


Fig. 1 Surface pressure–area (π–A) isotherms of AZ at the air–water interface: (red) on pure water and (blue) on Co–POM aqueous solution (1.0 μM).

quantum interference device (SQUID) magnetometry. As a result, we could prepare a highly organized film, which exhibits a photomagnetic effect derived from photoisomerization-induced structure-distortion.

Results and discussion

Film preparation

Fig. 1 shows π–A isotherms of hybrid monolayers when a solution of AZ was spread onto a surface of Co–POM aqueous solution (1.0 μM) and also onto pure water. The π–A isotherm on pure water (Fig. 1, red) shows that AZ by itself forms monolayers in an extended state at the air–water interface. When Co–POM aqueous solution was used as the subphase, the π–A isotherm was modified, shifting towards a smaller area per molecule compared with that on pure water (Fig. 1, blue). Moreover, the isotherm shows a steep increase in surface pressure, which corresponds to a dense packing of AZ. This tendency indicates that positively charged AZ monolayers could be electrostatically adsorbed onto Co–POM at the air–water interface.

Such dependence on isotherms has also been reported previously in the case of a dioctadecyldimethylammonium cation (DODA) and a polyoxometalate anion (POM).[32] Briefly, a shift in the lift-off area on isotherms corresponds to changes in the density of amphiphiles at the air–water interface. In the previously reported case, the lift-off area on isotherms shifted towards the smaller area when POM solution was used as the subphase, indicating hybridization of DODA and POM. As a result, the electrostatic repulsion between DODA head groups was compensated with a POM layer, which permits a higher molecular density for a given surface pressure.

As a densely packed hybrid monolayer was obtained, we proceeded to prepare Langmuir–Blodgett films. Transfer (Y-type) of the monolayer was carried out at a surface pressure of 30 mN m^{-1} by a vertical dipping method with a speed of 10 mm min^{-1}. The transfer ratio was found to be 0.9–1.0, indicating an ideal transfer.

Structure

In order to determine the structure of LB films, we performed XRD and linear dichroism spectroscopy.

First, we measured XRD patterns in a θ–2θ mode to confirm a layered structure of the film. Fig. 2 shows XRD patterns of the film and three diffraction peaks were given at 2θ = 1.40, 2.95, and 4.35°. These peaks are ascribed to the (001), (002), and (003) reflections from the Co–POM layer, respectively. Thus, LB films obviously possess the layered structure and, from the (001) diffraction peak, the basal spacing of the unit layer (AZ/Co–POM/AZ) is calculated to be 62.7 Å.

Next, we estimate a tilt angle of AZ in LB films using a linear UV-Vis dichroism measurement.[33] Fig. 3 shows UV-Vis

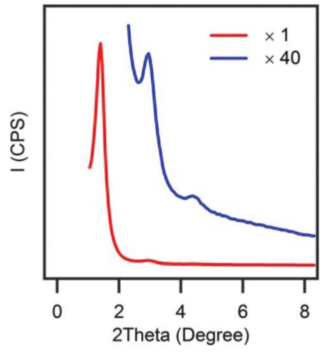


Fig. 2 XRD patterns for AZ/Co–POM films. 150 Co–POM layers were transferred onto each side of a glass substrate.

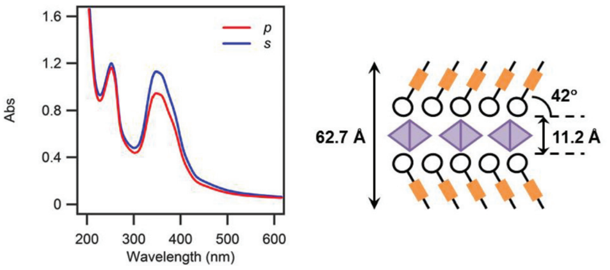


Fig. 3 (Left) Linear UV-Vis dichroism spectra for AZ/Co–POM films: (red) p-polarized and (blue) s-polarized spectra. 150 Co–POM layers were transferred onto each side of a quartz substrate. (Right) A schematic illustration of the film structure.

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‡Illustration of Co–POM drawn by using the software VESTA 3: K. Momma and F. Izumi, *J. Appl. Crystallogr.*, 2011, **44**, 1272.

absorption spectra recorded with polarized incident beams at an incident angle of 60° from the surface normal. Both spectra gave two intense absorption peaks at 252 nm and 350 nm. The peak at 250 nm is ascribed to the π–π* transition of *trans*-AZ (the short axis transition).[34] In addition, the peak at 350 nm is ascribed to the π–π* transition of *trans*-AZ (the long axis transition).[34] We chose an absorption peak at 350 nm for a linear dichroism investigation. Here, the dichroic ratio at 350 nm (D_{350}) is defined as the ratio of absorbance at 350 nm recorded with the p-polarized beam (A_p) to that with the s-polarized one (A_s): $D_{350} = A_\mathrm{p}/A_\mathrm{s}$. Theoretically, a relation between D_{350} and φ is provided as follows:

$$D_{350} = \frac{A_\mathrm{p}}{A_\mathrm{s}} = \frac{2(1-\sin^2\alpha) + (3\sin^2\alpha - 1)\sin^2\varphi}{2 - 3\sin^2\varphi}$$

where φ is a tilt angle from the surface normal for AZ, and α is an angle of the incident beam from the surface normal. From this equation, φ was estimated to be 48°. Additionally, a linear FT-IR dichroism measurement revealed that AZ tilts 46° from the surface normal (ESI†), which agrees well with the value obtained from UV-Vis measurements.

From these results and taking the molecular length of AZ into account, we could evaluate the thickness of the Co–POM layer within the film to be 11.2 Å. This value roughly corresponds to the diameter of the Keggin anions,[35] which indicates that Co–POM is arranged in a single layer as supposed for a Y-type transfer. The transfer during the upper stroke should involve large changes concerning Co–POM adsorbed along the last hybrid monolayer deposited onto a solid substrate. This reorganization could be explained by instability of double layer formation of the negatively charged Co–POM. Such a structure has been recently found in a single crystal of dioctadecyldimethylammonium cations (DODA) and Lindqvist hexamolybdate anions.[36]

Photochromic reaction

Photoisomerization of AZ in LB films was monitored by UV-Vis absorption spectra at room temperature and 10 K (Fig. 4). As already mentioned, the spectrum exhibits an intense peak at 350 nm, ascribed to the π–π* transition of *trans*-AZ (the long axis transition). At room temperature, before photo-irradiation, AZ in the film mainly exists as a *trans*-isomer, because it is thermodynamically more stable than a *cis*-isomer.[37] Upon UV light irradiation, *trans*-to-*cis* isomerization occurred as reflected by a decrease of absorbance at 350 nm. After reaching the photostationary state (*cis*-rich), the conversion efficiency was estimated to be *ca.* 65%, assuming that the conversion efficiency is 100% for a reaction in solution.[38] In addition, the reverse process (*i.e. cis*-to-*trans* isomerization) proceeded to a certain degree upon subsequent visible light irradiation, leading to the other photostationary state (*trans*-rich). The overall *trans*–*cis* isomerization cycle was repeated several times between two photostationary states (Fig. 4, top). Similar photochromic reactions have been reported in LB films containing azobenzene derivatives.[39]

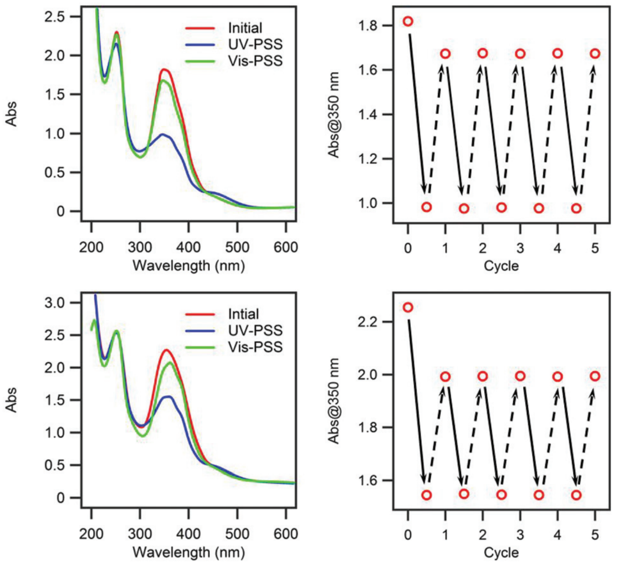

Fig. 4 Changes in UV-Vis absorption spectra for AZ/Co–POM films by photoisomerization: (top, left) at room temperature and (bottom, left) at 10 K. Changes in absorbance at 350 nm upon photoirradiation: (top, right) at room temperature and (bottom, right) at 10 K; (full arrow) UV irradiation and (broken arrow) visible light irradiation. In both spectra, the initial *trans* state (red) was first irradiated with UV light to achieve a *cis*-rich photostationary (blue) state. Then, it was subsequently irradiated with visible light to obtain a *trans*-rich photostationary state (green). The overall *trans*–*cis* isomerization cycle was repeated several times between two photostationary states. 300 Co–POM layers were transferred onto each side of a quartz substrate.

Subsequently, the photochromic reaction of AZ in the film was investigated at 10 K. Even at low temperature, the *cis*–*trans* isomerization of AZ was observed similar to that at room temperature. However, the fraction of *cis*-isomer after UV irradiation was calculated to be *ca.* 35%, which is much lower than that obtained at room temperature. This is because the photoisomerization of the azobenzene molecule, particularly *trans*-to-*cis* isomerization, accompanies the free volume change.[40] In other words, the *cis*-isomer is much more bulky than the *trans*-isomer. At low temperature, such molecular motion was significantly restricted, and therefore the photochemical transformation was inhibited to some extent. The overall *trans*–*cis* isomerization cycle was repeated several times between two photostationary states (Fig. 4, bottom).

It should be noted that, accompanied by the above photochromic reaction of AZ, we observed changes in UV-Vis absorption spectra in the visible region (Fig. 5). As Co–POM contains four $\mathrm{Co^{II}}$ ions, the d–d transition of $\mathrm{Co^{II}}$ ions was observed as a broad absorption peak between 500 and 900 nm. It should be considered that the d–d transition of $\mathrm{W^{V}}$ ions also appears in this region. However, it is unlikely that W ions possess the electronic state of +V, because the ground electronic state of W ions is +VI in Co–POM. In addition, reduction of Co–POM is also unlikely to occur under the conditions of film preparation. Therefore, the observed broad peak could be apparently assigned to the d–d transition of $\mathrm{Co^{II}}$ ions.

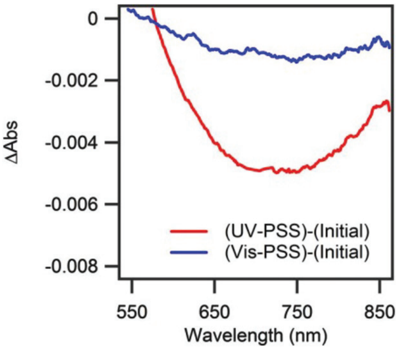

Fig. 5 Changes in UV-Vis absorption spectra for AZ/Co–POM films in the visible region at room temperature. For clarity, difference spectra are shown. A broad peak is ascribed to the d–d transition of Co^{II} ions (not to that of W^{V} ions), because the ground electronic state of W ions is +VI in Co–POM. As Co–POM was revealed not to exhibit photochromism (ESI†), the observed changes were apparently derived from photoisomerization of AZ. 300 Co–POM layers were transferred onto each side of a quartz substrate.

It is also noteworthy that polyoxometalates are known to exhibit photochromism in the presence of an electron donor.[41] Briefly, polyoxometalates exhibit a ligand-to-metal charge transfer (LMCT; oxygen to W^{VI} ion) band in the UV region. Upon excitation of this band, W^{VI} ions are reduced to form mixed-valence species, leading to an intervalence charge transfer (IVCT) band between 600 and 900 nm. That is, if Co–POM exhibits photochromism, absorbance should increase in the visible region. However, in our LB films, absorbance decreased upon UV light irradiation, concluding that the observed changes in the visible region are derived from the d–d transition of Co^{II} ions. In any case, as it is important to check whether Co–POM exhibits photochromism, we have prepared the model LB films by using a dioctadecyldimethylammonium cation (DODA) instead of AZ (structure characterization is given in ESI†). As a result, we could not observe any photochromic reaction in LB films of DODA and Co–POM (ESI†).

Magnetic properties

Co–POM contains the magnetic Co_4O_{16} cluster encapsulated between two polyoxotungstate moieties $[PW_9O_{34}]_9^-$. Co^{II} ions are ferromagnetically coupled in the magnetic cluster, giving rise to a highly magnetic ground state.[42] The temperature dependence of magnetization in LB films is plotted in Fig. 6. As can be seen, the magnetic behavior of the film is similar to that observed in the powdered sample of Co–POM, which indicates that the ferromagnetic clusters are maintained within the film. In detail, the χT product shows a sharp increase below 50 K upon cooling, and a maximum at *ca.* 6.5 K. Below this temperature, the χT product shows a decrease due to the magnetic anisotropy. However, the χT product of the film is relatively small compared with the powdered Co–POM, which might be because of a slight distortion of the Co–POM framework sandwiched by AZ layers. Such a distortion affects the symmetry of the magnetic cluster, leading to a reduction of the magnetic interaction.

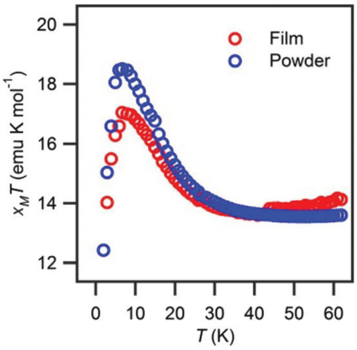

Fig. 6 Plots of χT *vs.* T under an applied field of 5000 Oe: (red) AZ/Co–POM films and (blue) Co–POM powders. χT values for AZ/Co–POM films were normalized to that for Co–POM powders. 300 Co–POM layers were transferred onto each side of a Mylar substrate.

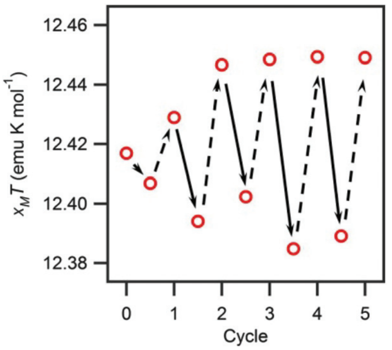

Fig. 7 Changes in normalized χT for AZ/Co–POM films upon photoirradiation at 2 K under an applied field of 5000 Oe: (full arrow) UV irradiation and (broken arrow) visible light irradiation. Upon UV irradiation, normalized χT values decreased and, on the other hand, normalized χT values recovered upon visible light irradiation. 300 Co–POM layers were transferred onto each side of a Mylar substrate.

Subsequently, we examined the influence of photoirradiation on the magnetic properties of the film at 2 K (Fig. 7). Upon UV irradiation (λ_{max} = 360 nm, 1.0 mW cm^{-2}, 15 min) the normalized χT value decreased from 12.43 to 12.39 emu K mol^{-1}. In contrast, visible light irradiation (λ = 400–700 nm, 1.0 mW cm^{-2}, 10 min) led to recovery of the χT value from 12.39 to 12.45 emu K mol^{-1}. After this process, reversible changes were repeated several times upon alternate irradiation with UV and visible light. It should be noted that the photomagnetic effect was maintained for at least 2 h, even after photoirradiation was stopped. As mentioned in the previous section, the observed photomagnetic effect would be related to changes in the d–d transition of Co^{II} ions, accompanied by the photochromism of AZ. Investigation of the mechanism is provided in the next section.

Photoinduced structural changes in LB films

We have observed the photomagnetic effect in LB films, in which the d–d transition of Co^{II} ions changed upon photochromic reaction of AZ. As shown in Fig. 5, the d–d transition of Co^{II} ions changes in intensity, not absorption maxima wavelength. We have previously reported a photomagnetic effect in various systems where magnetic materials are hybridized with azobenzene molecules. Briefly, in the case of Prussian Blue intercalated into LB films of the amphiphilic azobenzene, we have observed reversible changes in an intervalence charge transfer (IVCT) band of Prussian Blue by photoisomerization of azobenzene molecules.[10] In other cases, reversible changes in the CN stretching vibration (bridge-mode: –Fe^{II}–CN–Fe^{III}–) by photoisomerization were observed in Prussian Blue/azobenzene reverse micelles and LB films, respectively.[11,13] It should be mentioned that the above spectral changes are the shift in wavelength and wavenumbers. Therefore, it is concluded that the photochromic reaction of azobenzene molecules affects the electronic states of Prussian Blue, leading to changes in magnetization values. However, in the present case, the d–d transition of Co^{II} ions changed reversibly in intensity. Therefore, it is unlikely that the electronic states of Co–POM were affected by photoisomerization.

For the above reason, we assume that the photomagnetic effect would be ascribed to orientational changes of Co–POM. Therefore, we performed XRD measurements before and after photoisomerization of AZ. As a result, the basal spacing (*d*) of LB films changes reversibly: an increase upon UV irradiation and a decrease upon visible light irradiation. Although reversible changes were achieved repeatedly, we observed only slight changes in the *d* value. This is because the efficiency of photoisomerization (*ca.* 65%) was relatively low in the film. In other words, the obtained *d* values in XRD measurements were averaged between the *trans*- and *cis*-rich states.

As the XRD measurement of LB films provides macroscopic information about the film structure, we examined linear UV-Vis dichroism spectra to obtain microscopic information. Fig. 8 shows changes in UV-Vis absorption spectra recorded with polarized incident beams at an incident angle of 60° from the surface normal. As the d–d transition of Co^{II} ions exhibits a broad peak, we provided difference polarized spectra in Fig. 8. Clearly, both p- and s-polarized spectra exhibited reversible changes in the d–d transition of Co^{II} ions: a decrease in intensity upon UV irradiation and recovery upon visible light irradiation. Again, as Co–POM lies flat along the AZ layer, the d–d transition of Co^{II} ions would direct to the almost same angle. In this situation, if we assume that an orientation of Co–POM changes by photoisomerization of AZ, the d–d transition of Co^{II} ions should change in polarized UV-Vis absorption spectra. Moreover, the observed changes were anisotropic with respect to incident polarized beams. Along these lines, we suggest that changes in the d–d transition of Co^{II} ions are reflected by a structure-distortion of LB films upon photochromic reaction. It should be noted that when we prepare the AZ/Co–POM hybrid in solution, so-called surfactant-encapsulated clusters, we observed neither a photomagnetic effect nor a structure-distortion despite reversible photoisomerization.

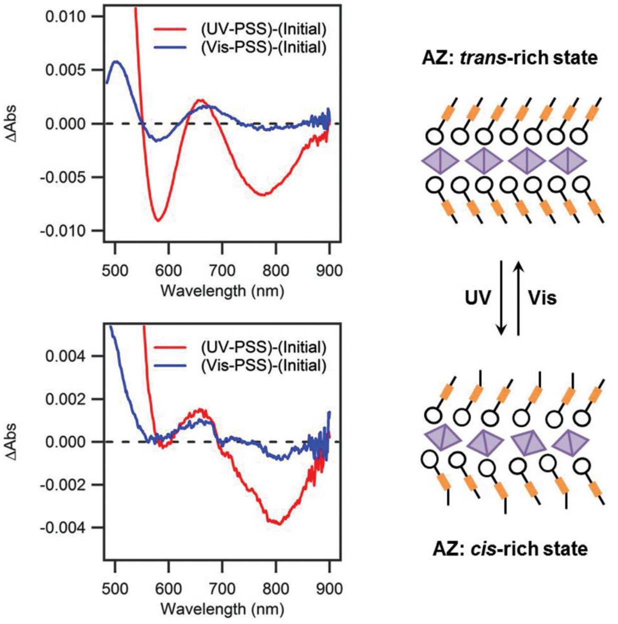

Fig. 8 Changes in linear UV-Vis dichroism spectra for AZ/Co–POM films in the visible region at room temperature: (top, left) p-polarized and (bottom, left) s-polarized spectra. For clarity, difference spectra are shown. In both polarized spectra, we observed reversible changes in absorption peaks ascribed to the d–d transition of Co^{II} ions. As Co–POM was revealed not to exhibit photochromism (ESI†), the observed changes were apparently derived from photoisomerization of AZ. 300 Co–POM layers were transferred onto each side of a quartz substrate. (Right) A schematic illustration of photochromism-induced orientational distortion in a Co–POM single layer.

Conclusions

We have prepared photomagnetic Langmuir–Blodgett films composed of an amphiphilic azobenzene and a magnetic polyoxometalate. From XRD and linear dichroism spectroscopy, it was confirmed that the film possesses the well-organized layered structure where polyoxometalate anions are sandwiched by azobenzene cations in a monolayered manner. Reversible photoisomerization of azobenzene molecules was achieved even at low temperature, accompanying intensity changes in the d–d transition of cobalt(II) ions in a polyoxometalate. Moreover, at 2 K, the photomagnetic effect was observed reversibly upon alternate UV and visible light irradiation. Based on investigation using polarized spectroscopy, the observed photomagnetic effect is ascribed to the structure-distortion of polyoxometalate layers. The present work demonstrates that confinement of functional materials could create a novel function (the photomagnetic effect in the present case). Furthermore, combination with other polyoxometalates enables the design of a multifunctional heterostructured film.

Experimental

Synthesis of materials

An amphiphilic azobenzene compound (AZ) was synthesized according to previous reports.[43,44] A polyoxometalate with a

Co_4O_{16} ferromagnetic cluster (Co–POM) was synthesized according to a previous report.[45] Detailed procedures are given in ESI.†

Langmuir–Blodgett film preparation

AZ was dissolved in a 9 : 1 mixture (by volume) of dichloromethane and ethanol to prepare a solution at 2.0 mM. The solution was spread on a subphase of Co–POM aqueous solution (1.0 μM) at room temperature. A floating monolayer of AZ was hybridized with Co–POM at the air–water interface. Fifteen minutes later, the floating hybrid monolayers were compressed up to a surface pressure of 30 mN m^{-1}. After 30 min, the floating hybrid monolayers were transferred onto a hydrophilic substrate by a vertical dipping method with a speed of 10 mm min^{-1}. Langmuir–Blodgett films composed of AZ and Co–POM were prepared by repeating this cycle.

Instruments

Preparation of the floating hybrid monolayer and measurements of the surface pressure–molecular area (π–A) isotherms were carried out using a computer-controlled film balance system (FSD-50, USI System, Japan). X-ray diffraction (XRD) patterns were recorded on a Philips X'Pert MRD high-resolution X-ray diffractometer using Ni-filtered Cu Kα radiation. UV-Vis absorption spectra were recorded on a V-560 spectrophotometer (JASCO). UV-Vis measurements at low temperature were performed using a closed-cycle helium refrigerator (Iwatani Co., Ltd). FT-IR absorption spectra were recorded on an FT-IR 660Plus spectrometer (JASCO, Japan). UV irradiation (filtered light, λ_{max} = 360 nm, 1.0 mW cm^{-2}) was carried out using an ultrahigh-pressure mercury lamp (Spot Cure SP-7, USHIO, Japan), and visible light irradiation (λ = 400–700 nm, 1.0 mW cm^{-2}) was carried out using a xenon lamp (Optical Modulex X 500, USHIO, Japan). The magnetic properties were investigated using a superconducting quantum interference device (SQUID) magnetometer (model MPMS-XL, Quantum Design).

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