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Magnetization Increase of Iron Oxide by Photoinduced Aggregation of Spiropyran

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Photoresponsive magnetic systems have attracted much attention in recent years.[1−4] The incorporation of organic photochromes into magnetic systems is one of the new strategies to realize such a system, which is one of the hottest topics at present.[2−7] A novel and complementary approach can be devised by combining the organic photochromes to induce structural changes into the sensitive nature of the magnetic properties. In our previous work, we have reported such a composite material comprising Prussian blue intercalated into photoresponsive organic molecules (azobenzene-containing multibilayer vesicles). Although this was the first known photocontrollable magnetic vesicles, the result was achieved at very low temperature (2 K). Therefore, we have focused our study on the iron oxide particles as magnetic materials and *photoinduced aggregation* of the spiropyran (SP1822) vesicles *at room temperature.*

Photofunctional magnetic vesicles of spiropyran (SP1822) contains iron oxide particles, which exhibits super-paramagnetic properties at room temperature.

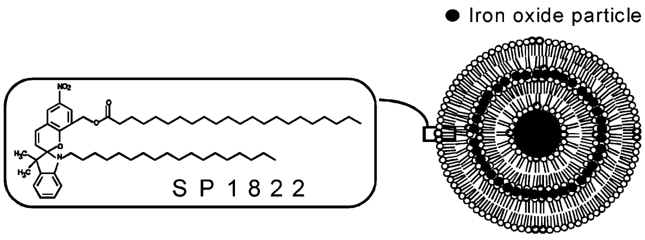

Photo-functional magnetic vesicle

They were designed to control the magnetic properties by photoillumination at room temperature. Photoinduced aggregation of the vesicles are of cylindrical structure-containing magnetic particles in a poly(vinyl alcohol) matrix. The incremental magnetization and the shifting of the blocking temperature were observed while the photoinduced aggregation of the vesicles occurred. These were shown from the changes of magnetic dipolar interactions between iron oxide particles. As a result, we were able to increase the magnetization value by photoillumination.

Spiropyran compounds are photochromic molecules that undergo interesting photochemical reaction: the transformation of a spiropyran molecule (SP) into photomerocyanine isomer (PMC) when illuminated by UV which brought about substantial structural changes of the photolyzed initial form. The conversion was suggested by photochromic effect and the enhancement of the dipole moment pertaining to a colored PMC.[8] Furthermore, it was reported that *J*-aggregations of amphiphilic PMC form when the mixed LB films of the spiropyran and alkane were illuminated by UV light at temperatures above 35 °C.[9,10]

The photofunctional magnetic vesicles were prepared as follows. A commercially available dye SP1822 (1′-octadecyl-3′,3′-dimethyl-6-nitro-8-[docosanoyl-oxymethyl]-spiro-[2H-1-benzopyran-2,2′-indoline]) was purchased from Hayashibara Biochem. Lab. Inc. Iron oxide (Fe_3O_4) particles were synthesized according to the literature.[11] The resulted colloid (hydrosol) solution was diluted to 300 times in deionized H_2O. The sonicated SP1822 and the iron oxide particles were prepared in deionized H_2O, and the dispersion was mixed with an aqueous solution of poly(vinyl alcohol) (PVA, MW 70 000; PVA, 200 mg; H_2O, 4 mL). PVA acts as a matrix (mixing volume ratio, SP1822:iron oxide colloid solution:PVA = 2:1:20). The composite film, hereafter designated film **1** (=SP1822 + iron oxide particles + PVA), was prepared by casting the above solution onto a clean glass plate (pretreated with concentrated sulfuric acid) at room temperature.

In Figure 1, photoinduced isomerization and aggregation of the vesicles in film **1** was monitored by UV−vis absorption spectroscopy. The film was almost transparent before illumination (absorption band of SP1822 was observed at ca. 240, 270, and 340 nm). In the initial regime of the UV illumination, the main photoreaction is the isomerization of SP1822 to photo-merocyanine isomer (PMC). It revealed the decrease in intensities of the absorption bands at ca. 240 and 270 nm as well as the concomitant increase in intensities of the bands at ca. 380 and 560 nm. On prolonged UV illumination, the formation of a *J*-aggregation was proposed by the presence of a shoulder band at ca. 620 nm.[9] Normally, the aggregation could only be observed in the special environments such as in Langmuir−Blodgett films of an amphiphilic spiropyran,[12] bilayer membrane,[13,14]

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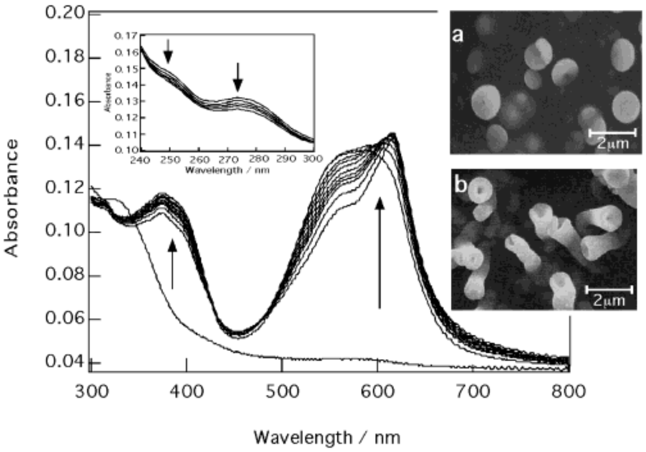

Figure 1. UV−visible spectral changes of film **1** on illumination with UV light. The spectra were recorded during illumination from $t = 0$ min to $t = 180$ min. The inset (left) represents the magnification for the short wavelength region. The inset (right) shows SEM images of film **1** (a) before illumination and (b) after 180 min of UV illumination.

liquid crystal matrixes,[15] etc. In this system, however, the photoinduced aggregation of the vesicles, resulting from the presence of iron oxide particles, was observed even in a PVA matrix. Hence, irregular-shaped structures played a significant role in the initial formation and growth of aggregation. Furthermore, when we prepared a PVA film containing SP1822 without iron oxide particles, only reversible photoisomerization of SP1822 and PMC was observed, i.e., the aggregation could not be observed.

The scanning electron micrograph (SEM) image of the films before illumination indicated the presence of the ringlike and spheroidal vesicles with heterogeneous diameters (500−1000 nm) (inset (a) in Figure 1). Energy-dispersive X-ray spectrometer (EDX) analysis (not shown) has shown that the iron atom existed within the vesicles but not on the outside. On the other hand, the aggregated objects with cylindrical structure were observed after UV illumination for 180 min at room temperature (inset (b) in Figure 1). It suggested that the transition dipole moments of photoisomerized PMC should take in a *J*-aggregation order in the layer plane on iron oxide particles.

The magnetic properties of film **1** were studied by SQUID measurements. The magnetic curve was measured at room temperature (300 K) (inset in Figure 2). A typical characteristic of super-paramagnetic behavior, showing almost immeasurable coercivity and remanence, was observed. The influence of UV illumination on the magnetic properties of the film **1** at room temperature is shown in Figure 2. During the period of UV illumination for 240 min, the magnetization value at 10 G increased from 72.8 to 76.5 $\mathrm{cm^3\ mol^{-1}\ G}$.

To study the magnetic dipolar interactions among iron oxide particles before and after UV illumination, zero-field-cooled (ZFC) susceptibility measurements were conducted (Figure 3). Strong interparticle interaction such as aggregation, as it was known, would result in

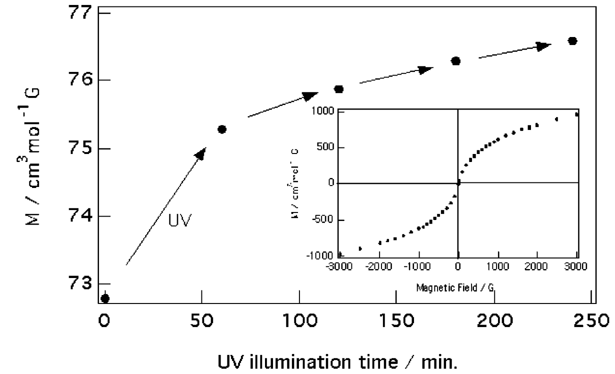

Figure 2. Changes in the magnetization for film **1** induced by UV light illumination at 300 K with an external magnetic field of 10 G. During each step, the illumination was continued for 60 min. The inset shows magnetization vs applied magnetic field at 300 K for film **1**.

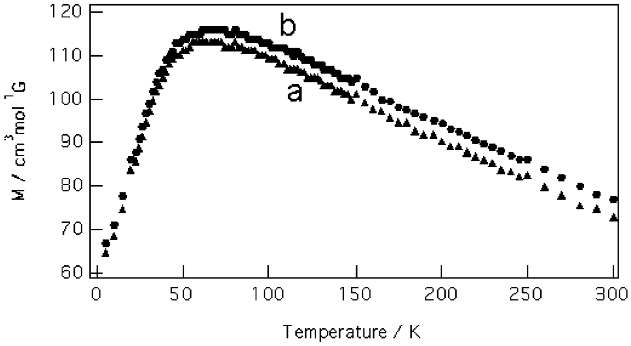

Figure 3. Magnetization vs temperature measured at 5 G in the zero-field-cooled states for film **1** (a) before illumination and (b) after 180 min of UV illumination.

the increase of the blocking temperature (T_b).[16−19] The temperature-dependent magnetization exhibits a cusp in the ZFC susceptibility. T_b's were estimated with 68 and 70 K before and after illumination, respectively. On the basis of common sense, super-paramagnetic particles become thermally unstable and the magnetization exponentially decrease when the temperature was above T_b. The general trend of the change is that T_b shifted toward higher temperature when the interactions between particles increased. When an iron oxide film (iron oxide particles + PVA) without spiropyran was prepared, photoillumination did not produce any changes in terms of magnetization. Although the photoinduced aggregation of vesicles was observed, the mechanisms of interparticle interaction were not clear at present. We concluded that magnetic dipolar interactions among adjacent iron oxide particles increased by the photoinduced aggregation of SP1822 in a PVA matrix.

In summary, we have succeeded in increasing the magnetization value of magnetic vesicles of spiropyran containing iron oxide particles by photoillumination, although our attempt to decrease the magnetization value, i.e., to realize a reversible control of the magnetic properties, were yet to be carried out. The results

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reported here showed that aggregation properties of spiropyran molecules were dominated by the matrix effect and chemical structure of the molecules, i.e., designing of ligand. Therefore, it is possible to realize the reversible photocontrol of magnetic properties even at room temperature by designing the appropriate composite materials.

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