

Polarized light spectroscopy of azobenzene or disperse red 1 with Mn_{12} single-molecule magnets in PMMA film hybrid materials

Invited Paper

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Abstract: A series of organic/inorganic hybrid materials containing the single-molecule magnet $[Mn_{12}(CH_3COO)_{16}(H_2O)_4O_{12}] \cdot 2CH_3COOH \cdot 4H_2O$ with the photochromic compounds azobenzene or disperse red 1 cast into polymethyl methacrylate films was prepared. To understand the photomodulation of analogous mixtures' AC susceptibility, we investigated the molecular alignment based on Weigert's effect accompanying cycles of cis-trans photoisomerization by alternate irradiations with polarized UV and visible light. Polarized electronic spectra of the hybrid materials demonstrated gradually increasing anisotropy. These features suggest interactions between photochromic compounds and the Mn_{12} complex in polymethyl methacrylate.

Keywords: Single-molecule magnets • Disperse red 1 • Organic/inorganic hybrid materials • Polarized spectroscopy • Weigert effect

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1. Introduction

In general azo compounds in the trans form are rodlike and more stable than the bent cis. The trans form can undergo trans-to-cis conversion followed by spontaneous relaxation to trans depending on the matrix. Both angular motion and dipole change (cis azobenzene has a dipole of ca. 3 Debye) during cis-trans isomerization cycles must be accommodated by the matrix.

The photochemical behavior of photochromic azobenzene derivatives including disperse red 1 (DR1), e.g. absorbance changes, reversible cis-trans photoisomerization, etc. has been investigated [1-4]. In particular, Weigert's effect (polarized light induced optical dichroism of azo compounds) has long been known for photochromic liquid crystalline materials [5].

Various photochromic organic/magnetic inorganic hybrids have been developed to obtain photochemically driven magnetic materials [6], for example: self-assembling vesicles [7-9], liquid crystals [10], LB thin

films [11,12], nano-wires of bridged metal complexes [13], and supramolecular composites in solution or a polymer matrix [14-18]. Although photofunctional polymers and liquid crystalline materials containing azobenzene groups have been widely studied [19-22], for most of these systems photomodulation of the inorganic species' electronic properties is not understood.

Recently, we have developed a new organic/inorganic hybrid material composed of the single-molecule magnet $[Mn_{12}(CH_3COO)_{16}(H_2O)_4O_{12}] \cdot 2CH_3COOH \cdot 4H_2O$ (Mn_{12} complex) and azobenzene (AZ) in a cast polymethyl methacrylate (PMMA) film (PMMA-AZ- Mn_{12}). This is the first example of in-phase AC susceptibility photomodulation by alternate irradiations with UV and visible light [23]. Comparing the magnetic properties of PMMA- Mn_{12} (without AZ) and PMMA-AZ- Mn_{12} (containing AZ) suggested the importance of interactions between species in PMMA films [24]; however, the role of AZ cis-trans photoisomerization in photocontrolling magnetic susceptibility is unclear.

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Optical dichroism after alternating UV and visible polarized light irradiation may be useful to examine interactions between AZ or DR1 and the Mn_{12} complex in the polymer matrix. This is neither the conventional experiment using polarized UV light to examine Weigert's effect nor the normal one for cis-trans isomerization using nonpolarized UV and visible light.

In this study we examined a series of hybrid materials, PMMA-AZ- Mn_{12} , PMMA-DR1- Mn_{12} , PMMA-AZ, and PMMA-DR1 to compare the interactions of the Mn_{12} complex with AZ and DR1 (Fig. 1). These show Weigert's effect. Using more dilute hybrid materials than in our previous work, we employed alternating irradiations with polarized UV and visible light to generate cis-trans photoisomerization cycles. We observed molecular rearrangement with polarized absorption spectroscopy at room temperature.

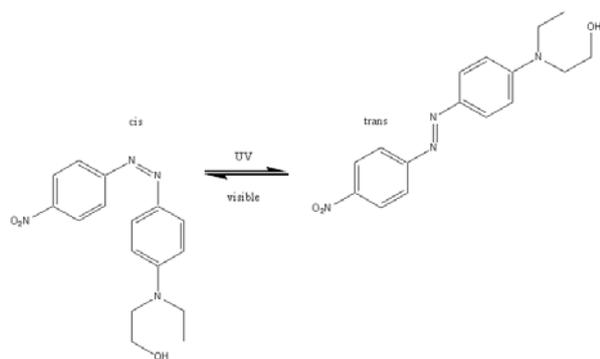


Figure 1. DR1 cis-trans photoisomerization.

2. Experimental

2.1. Materials

The polynuclear $[Mn_{12}(CH_3COO)_{16}(H_2O)_4O_{12}] \cdot 2CH_3COOH \cdot 4H_2O$ complex was prepared following the published procedure [25]. Azobenzene, direct red 1, and PMMA were obtained from WAKO or Aldrich and used as received.

2.2. Preparation of organic/inorganic hybrid materials

A series of solutions were prepared:

PMMA-AZ- Mn_{12} : An acetone solution (2 mL) of Mn_{12} complex (0.0303 g, 1.62×10^{-5} mol) containing AZ (0.0259 g, 1.42×10^{-4} mol);

PMMA-DR1- Mn_{12} : An acetone solution (2 mL) of Mn_{12} complex (0.0307 g, 1.64×10^{-5} mol) containing DR1 (0.0045 g, 1.43×10^{-4} mol);

PMMA-AZ: An acetone solution (2 mL) of AZ (0.0259 g, 1.42×10^{-4} mol);

PMMA-DR1: An acetone solution (2 mL) of DR1 (0.0045 g, 1.43×10^{-4} mol).

Each was separately added to 4 mL of an acetone solution of PMMA (ca. 10% w/w), cast on a glass plate, and allowed to evaporate at 298 K overnight.

2.3. Physical measurements

Absorption spectra were measured using a JASCO V-570 UV/VIS/NIR spectrophotometer equipped with a polarizer over 900-200 nm at 298 K. The DC magnetic susceptibility and hysteresis were measured at 2.0 and 5.0 K from -15000 to 15000 Oe using a Quantum Design MPMS-XL superconducting quantum interference device magnetometer (SQUID).

3. Results and discussion

3.1. Preparation and magnetic properties

The organic/inorganic hybrid materials PMMA-AZ- Mn_{12} and PMMA-DR1- Mn_{12} are cast polymer films containing brown solute derived from the black Mn_{12} complex and red or orange azo compounds (Fig. 2). Both Mn_{12} complex and AZ or DR1 are dissolved, not dispersed. Deterioration due to UV may lead to a heterogeneous appearance after several days of photoirradiation experiments.

Fig. 3 shows the M-H curves of these materials. Although the M-H curves of bulk $[Mn_{12}(CH_3COO)_{16}(H_2O)_4O_{12}] \cdot 2CH_3COOH \cdot 4H_2O$ exhibit large hysteresis widths below the blocking temperature, the present materials are paramagnetic. The preparation conditions may lead to exchange or loss of lattice solvent; this is one of the reasons for modulation of the magnetic properties [18,19].

3.2. Cis-trans photoisomerization

Concentrating on optical properties (azo groups' $\pi-\pi^*$ or $n-\pi^*$ absorbance) we measured cycles of cis-trans photoisomerization at room temperature to understand the environment flexibility in PMMA films.

Figs. 4 and 5 show absorption spectra of PMMA-AZ and PMMA-AZ- Mn_{12} , respectively. The polarizer measuring the absorption spectra was aligned at 45° to the irradiation electric vector E. The propagation direction was normal to the films.

After 3 min polarized UV or visible light irradiation, absorption measurements were carried out with polarizer settings every 10° from 0° to 90° to detect optically induced anisotropy. No isosbestic point (wavelength at which absorbance of cis and trans forms are equal) was found for any of the samples.

AZ photoisomerization reversibility was examined by the sequence: absorption spectrum measurement / 3 min UV irradiation / 3 min vis irradiation / absorption spectrum measurement. Reversibility is observed

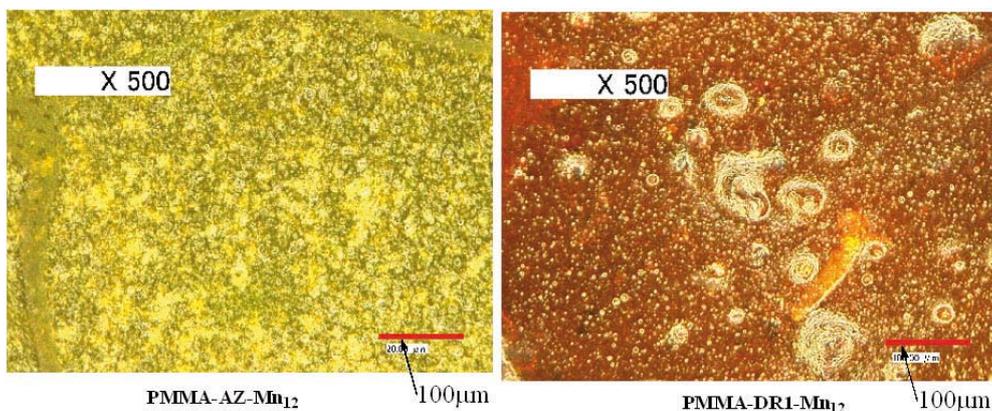


Figure 2. PMMA-AZ-Mn₁₂ and PMMA-DR1-Mn₁₂ films.

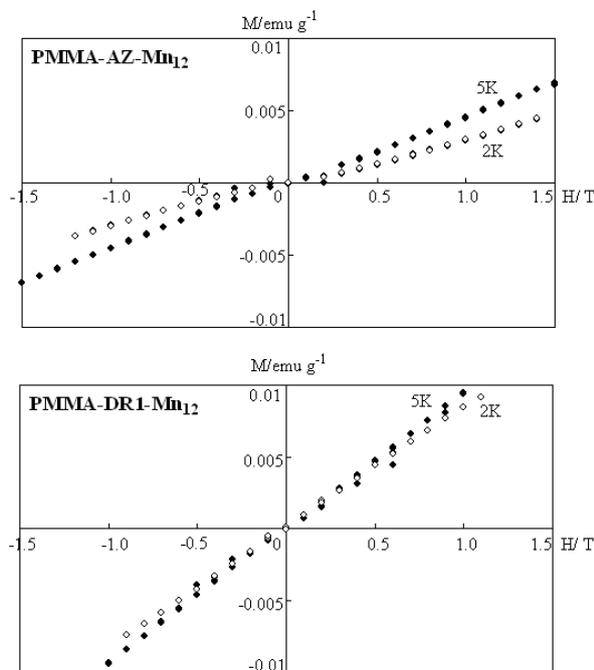


Figure 3. PMMA-AZ-Mn₁₂ and PMMA-DR1-Mn₁₂ magnetization field dependence (filled and empty circles for 5 and 2 K, respectively).

for 20 and 10 cycles for PMMA-AZ and PMMA-AZ-Mn₁₂, respectively. Thus, interaction with Mn₁₂ inhibits reversible cis-trans photoisomerization of AZ.

AZ shows π - π^* and n - π^* bands involving the azo groups around 316 and 436 nm. The intensity of the π - π^* band decreases with UV irradiation (conversion to cis form) and increases with visible light irradiation (to trans form). On the other hand, when the hybrid materials contain the dark brown Mn₁₂ complex, broad π - π^* and n - π^* bands occur around 320 and 410 nm because the components interact. In both samples the cis-trans absorbance difference is smaller for the n - π^* band than for the π - π^* .

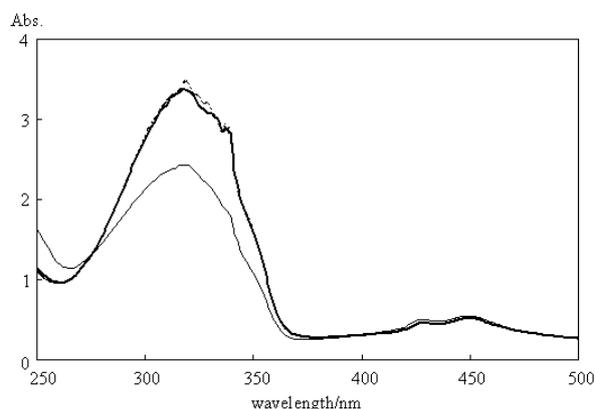


Figure 4. PMMA-AZ absorption spectra for alternating irradiations with polarized light at 298 K for 3 min (dotted line for initial, thin line for UV after 20 cycles, and bold line for visible after 20 cycles).

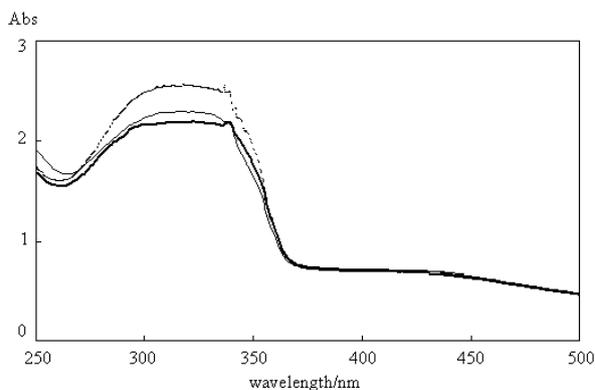


Figure 5. PMMA-AZ-Mn₁₂ absorption spectra. Conditions as in Fig. 4.

Figs. 6 and 7 show absorption spectra of PMMA-DR1 and PMMA-DR1-Mn₁₂. In a PMMA matrix, DR1 azo groups show a relatively weak π - π^* band around 280 nm and a stronger n - π^* band around 493 nm. The n - π^* intensity decreases upon formation of the cis form and increases with formation of the trans. On the

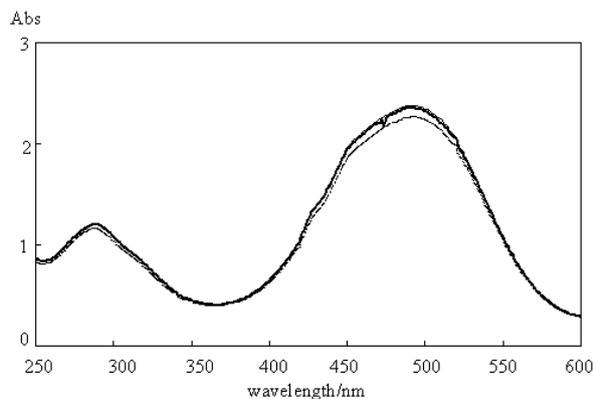


Figure 6. PMMA-DR1 absorption spectra. Conditions as in Fig. 4.

other hand, when the hybrid material contains the Mn_{12} complex, the absorbance of both peaks is enhanced and a broad $n-\pi^*$ band shifts up to around 485 nm. The presence of the Mn_{12} complex causes smaller $n-\pi^*$ absorbance changes upon isomerization for DR1 than it does for AZ. This difference between DR1 and AZ is attributed to both push-pull electronic effects and steric hindrance by substituents. Reversible cis-trans DR1 photoisomerization can be observed for 20 and 10 cycles for PMMA-DR1 and PMMA-DR1- Mn_{12} , respectively.

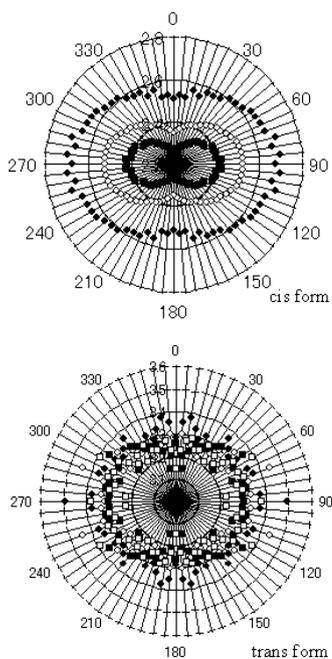


Figure 8. Circular diagram for PMMA-AZ $\pi-\pi^*$ at 318 nm for [above] *cis* form (filled circle for initial, empty circle for UV after 10 cycles, and filled square for UV after 20 cycles), [below] *trans* form (filled circle for initial, empty circle for visible after 1 cycle, filled square for visible after 10 cycles, and empty square for visible after 20 cycles).

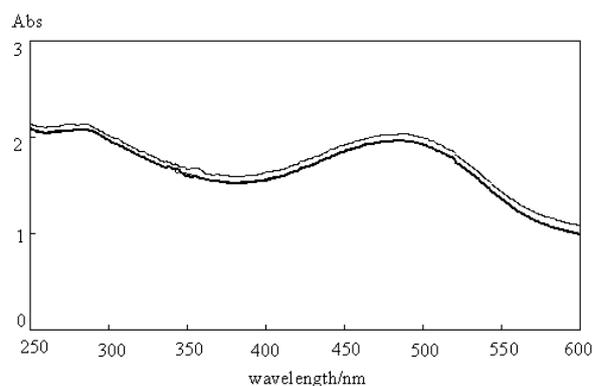


Figure 7. PMMA-DR1- Mn_{12} absorption spectra. Conditions as in Fig. 4 except that only 5 cycles were performed.

This suggests that interactions with the Mn_{12} complex prevent reversible cis-trans photoisomerization of DR1, as with AZ.

3.3. Photoinduced anisotropy

The azo $\pi-\pi^*$ transition is directed along the long molecular axis, while transitions of the aromatic rings exhibit no polarization dependence. Thus, polarized irradiation of polymers containing azo compounds may result in orientation of the azo groups perpendicular to

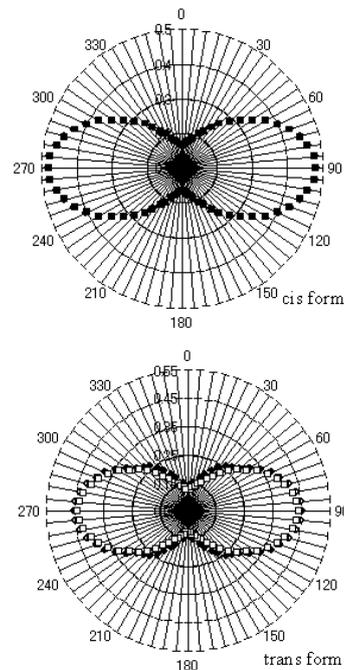


Figure 9. Circular diagram for PMMA-AZ $\pi-\pi^*$ at 436 nm for [above] *cis* form (filled circle for UV after 1 cycle, empty circle for UV after 10 cycles, and filled square for UV after 20 cycles), [below] *trans* form (filled circle for initial, empty circle for visible after 1 cycle, filled square for visible after 10 cycles, and empty square for visible after 20 cycles).

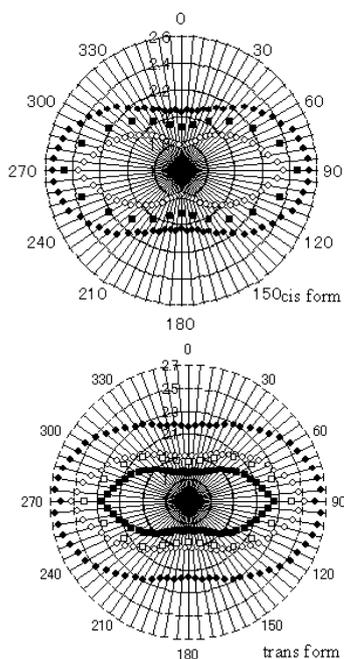


Figure 10. Circular diagram for PMMA-AZ-Mn₁₂ $\bar{n}-\bar{\sigma}^*$ at 320 nm for [above] cis form (filled circle for UV after 1 cycle, empty circle for UV after 5 cycles, and filled square for UV after 10 cycles), [below] trans form (filled circle for initial, empty circle for visible after 1 cycle, filled square for visible after 5 cycles, and empty square for visible after 10 cycles).

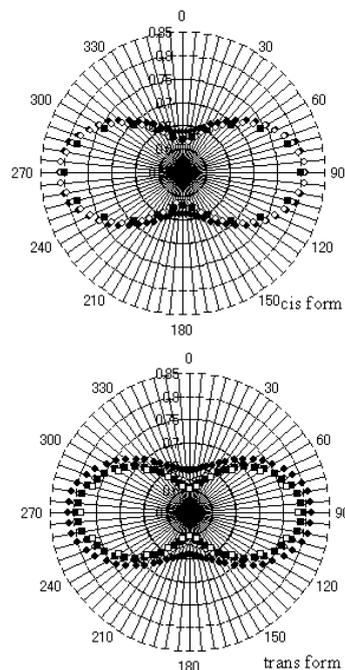


Figure 11. Circular diagram for PMMA-AZ-Mn₁₂ $\bar{n}-\bar{\sigma}^*$ at 436 nm for [above] cis form and [below] trans form (symbols as in Fig. 10).

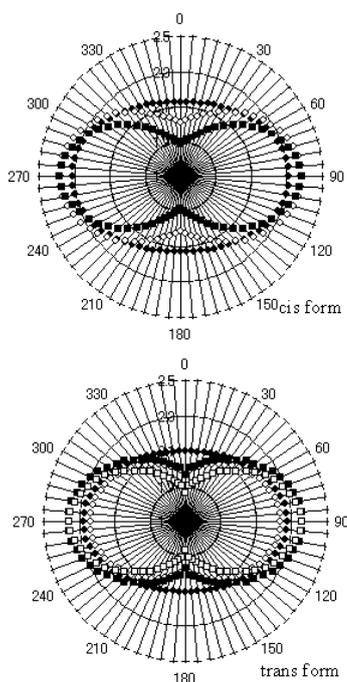


Figure 12. Circular diagram for PMMA-DR1 $\bar{n}-\bar{\sigma}^*$ at 493 nm for [above] cis form and [below] trans form (symbols as in Fig. 10).

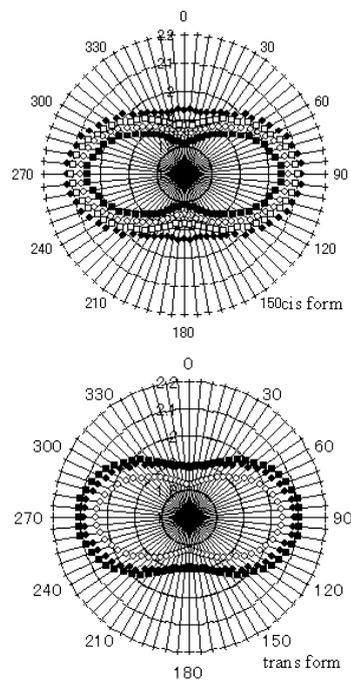


Figure 13. Circular diagram for PMMA-DR1-Mn₁₂ $\bar{n}-\bar{\sigma}^*$ at 485 nm for [above] cis form and [below] trans form (symbols as in Fig. 10).

Table 1. Photoanisotropy parameters S and R for cis solutes in PMMA film (number of photoisomerization cycles in parentheses).

	PMMA-AZ		PMMA-AZ - Mn ₁₂			PMMA-DR1		PMMA-DR-Mn ₁₂	
	π - π^*	n - π^*	π - π^*	n - π^*	n - π^*	n - π^*	n - π^*		
S(1)	0.0213	0.390	S(1)	-0.0729	-0.076	S(1)	-0.0270	S(1)	-0.0314
S(10)	0.0240	0.394	S(5)	-0.0879	-0.086	S(10)	-0.0544	S(10)	-0.0373
S(20)	0.0243	0.390	S(10)	-0.0788	-0.084	S(20)	-0.0755	S(20)	-0.0361
R(1)	1.066	2.915	R(1)	0.797	0.788	R(1)	0.921	R(1)	0.908
R(10)	1.074	2.958	R(5)	0.758	0.762	R(10)	0.845	R(10)	0.892
R(20)	1.075	2.915	R(20)	0.781	0.767	R(20)	0.789	R(20)	0.896

the electric vector E, as these cannot absorb the incident radiation. The resulting absorption spectrum anisotropy (dichroism) is commonly measured by two parameters:

$$S = (A_{\text{parallel}} - A_{\text{perpendicular}}) / (2A_{\text{perpendicular}} + A_{\text{parallel}}) \quad (1)$$

$$R = A_{\text{perpendicular}} / A_{\text{parallel}} \quad (2)$$

where $A_{\text{perpendicular}}$ and A_{parallel} denote absorbance measured with the measuring polarizers perpendicular or parallel to the irradiation electric vector. Ideal isotropic systems exhibit $S = 0$ and $R = 1$, and both S and R change with increasing optical anisotropy. The degree of photoinduced dichroism was calculated at the azo π - π^* absorbance maximum.

Figs. 8 and 9 show the PMMA-AZ circular diagrams (radial expression of absorbance as a function of angle between the irradiation electric vector and the spectrometer polarizer) of the azo π - π^* and n - π^* bands after 20 cis-trans photoisomerizations. Figs. 10 and 11 show corresponding diagrams for PMMA-AZ-Mn₁₂ after 10 cycles. Fig. 12 shows the circular diagram for the azo n - π^* bands of PMMA-DR1 after 20 photoisomerizations, and Fig. 13 shows the PMMA-DR1-Mn₁₂ diagram after 10.

Table 1 gives the corresponding values for R and S.

For both AZ and DR1 the presence of the Mn₁₂ complex decreases the number of cis-trans photoisomerizations and changes the degree of anisotropy induced.

4. Conclusions

The aim of this study was to understand the environment flexibility in PMMA films to determine the magnetic properties' photocontrol mechanism. We prepared cast PMMA films containing photochromic molecules (AZ or DR1) and Mn₁₂ complex. Using polarized absorption spectroscopy, we then examined their photoinduced anisotropy under repeated alternating irradiation with polarized UV and visible light.

In the series PMMA-AZ-Mn₁₂, PMMA-DR1-Mn₁₂, PMMA-AZ, and PMMA-DR1, the Mn₁₂ complex inhibits reversible cis-trans photoisomerization and reduces the photoinduced anisotropy of AZ or DR1. The fact that AZ can more easily undergo cis-trans photoisomerization and photoinduced anisotropy than DR1 is ascribed to a substituent effect.

In addition to absorbance, the molecular shape, polarity, and the direction of the transition moment may be changed by interactions among the azo compounds, Mn₁₂ complex, and the surrounding PMMA matrix. Moreover, the cis-trans photoisomerization results in a higher molecular mobility. This results in decreased order and aggregation in the polymer films.

We conclude that not only the azo compounds' photochemistry but also interactions between Mn₁₂ complexes are strongly influenced by the surrounding polymer matrix, and that interaction between azo compounds and the Mn₁₂ complex causes the photomodulation of AC susceptibility.

Acknowledgements

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