

Communication

The Viscosity and Intermolecular Interaction of Organic and Inorganic Hybrid Systems Composed of Chiral Schiff Base Ni(II), Cu(II), and Zn(II) Complexes with Long Ligands, Azobenzene, and PMMA

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Abstract: We have here synthesized new chiral Schiff base Ni(II), Cu(II), Zn(II) complexes (**Ni**, **Cu**, **Zn**) and hybrid materials with azobenzene (**AZ**) in polymethyl methacrylate (**PMMA**). Linearly polarized UV light irradiation of these hybrid materials slightly increased their optical anisotropy of **AZ** as well as the complexes, which were measured with polarized IR and UV-Vis spectra and discussed based on TD-DFT calculations. Non-linear concentration (viscosity) dependence of **PMMA** solutions about artifact peaks suggested weak intermolecular interactions due to the flexibility of complexes by inserted methylene chains. Molecular modeling indicated that large spaces around complexes in **PMMA** resulted in easy molecular orientation (**Ni** > **Cu** > **Zn**) as short-term saturation of the UV light irradiation.

Keywords: PMMA; azobenzene; Schiff base complexes; viscosity; polarized light; Weigert effect

1. Introduction

The study of organic–inorganic materials of Schiff base complexes and polymers is progressing to impart new features such as fluorescence properties [1]. Indeed, we have also systematically prepared organic/inorganic hybrid materials composed of chiral Schiff base mononuclear and dinuclear complexes including or mixing azo-moiety in synthetic polymer (e.g., polymethyl methacrylate (**PMMA**) and polyvinyl alcohol [2]) or biopolymer (albumin [3] or laccase [4]) matrices. In addition, optical alignment by the Weigert effect of azobenzene (**AZ**) has been widely used [5]. By the UV irradiation of polarized light to **PMMA** cast film containing **AZ** (azo-moieties) and chiral Schiff base complexes, an increase in optical anisotropy was observed in our previous studies [6–9]. After linearly or circularly polarized UV light irradiation, we have also measured polarized electronic (UV-Vis), infrared (IR), and circular dichroism (CD) spectra in order to elucidate light-induced molecular orientation of each component by the direct Weigert effect of **AZ** (azo-moiety) or supramolecular transmission to metal complexes. However, a detailed mechanism and intermolecular interaction is not reasonably understood. In other words, the mechanism has not been clarified; specifically, the interaction between **AZ** and metal complex in **PMMA** film is still unclear.

Previously, to elucidate intermolecular interactions, we designed metal complexes involving an electron-withdrawing (Br– or halogen) group, an UV absorbing and hydrophobic (Ph–) group, and a strong hydrogen-bonding (HO–) group to **PMMA** [10]. Here, we prepared new similar Ni(II), Cu(II), and Zn(II) complexes (abbreviated as **Ni**, **Cu**, and **Zn**, respectively) that enhance flexibility by inserting one more methylene chains between the Ph– group and the asymmetric carbon atom (Figure 1). We

focused on the polarized light-induced molecular orientation control of the present complexes. In order to examine intermolecular interactions further, we employed concentration (viscosity) dependence of PMMA solutions and molecular modeling.

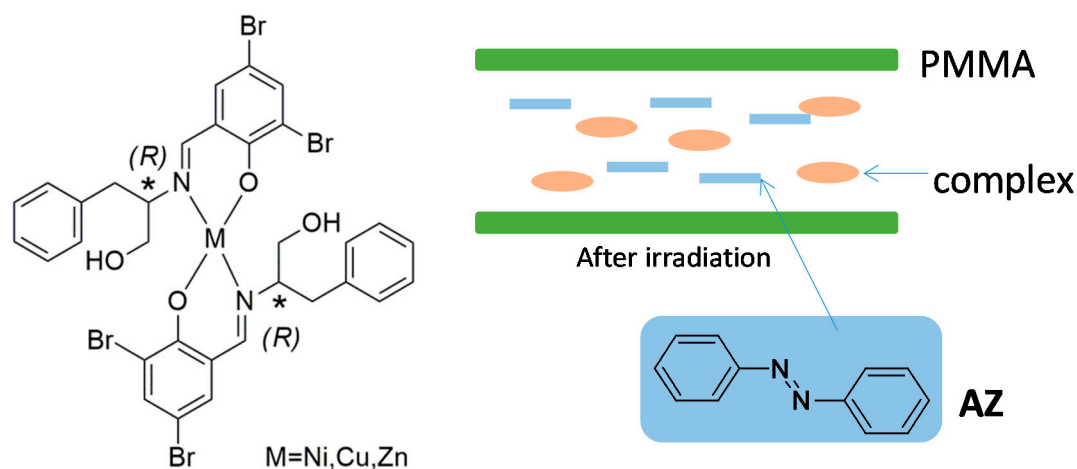


Figure 1. (Left) Molecular structures of Ni, Cu, and Zn; (Right) Schematic representation of organic/inorganic hybrid materials $M+AZ+PMMA$ showing anisotropic molecular orientation after linearly polarized UV light irradiation.

2. Results

2.1. Polarized IR Spectra

The angular dependence of polarized IR spectra after irradiation of linearly polarized UV light is exhibited in Figure 2. Linearly polarized UV light irradiation resulted in the induction of anisotropic molecular orientation, not only AZ directly but also the complexes through supramolecular transmission in the PMMA matrix. Polarized IR spectra of C=N bands can provide selective information about the molecular orientation of complexes only [11]. In order for a discussion of the Weigert effect, namely, the orientation of dyes in general and among many methods [12], we employed conventional polarized absorption spectra [13] (Tables S1–S3), and these two parameters (R and S) for the degree of photoinduced optical anisotropy (spectral dichroism):

$$R = \frac{A_0}{A_{90}};$$

$$S = \frac{A_0 - A_{90}}{A_0 + A_{90}},$$

where A_{90} and A_0 denote the absorbance measured with the measuring polarizer perpendicular and parallel, respectively, to the electric vector of irradiation polarized light. Ideal isotropic systems of $S = 0$ and $R = 1$ and both S and R parameters are changed as dichroism by molecular alignment increases.

As for $Ni+AZ+PMMA$, saturation of induced molecular orientation was observed at 0.5 min with $R = 1.29$ and $S = 0.0888$. Though induced anisotropy of Ni was also confirmed, the degree of orientation was considered to be the weakest among them.

As for $Cu+AZ+PMMA$, saturation of induced molecular orientation was observed at 10 min with $R = 1.32$ and $S = 0.0970$. The longest time for saturation of molecular orientation may be ascribed to the flexibility of the coordination environment of copper(II) complexes.

As for $Zn+AZ+PMMA$, saturation of induced molecular orientation was observed at 0.5 min with $R = 1.31$ and $S = 0.0927$. Transmission of molecular anisotropy was quickly observed for a zinc(II) complex because of their stiffness of compressed tetrahedral coordination environment. The order of

saturation time is **Ni** < **Cu** < **Zn**, which may be attributed to the difference in transmission of molecular orientation due to the molecular geometry and molecular flexibility of the complexes.

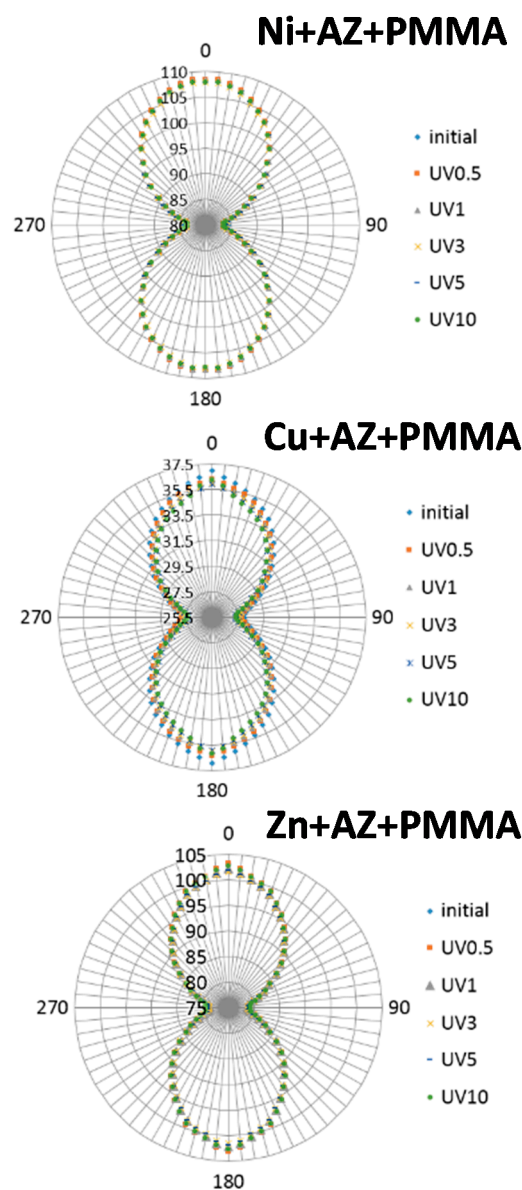


Figure 2. Angular dependence of polarized IR spectra (C=N bands at 1634, 1628, and 1617 cm^{-1}) after irradiation of linearly polarized UV light **Ni+AZ+PMMA**, **Cu+AZ+PMMA**, and **Zn+AZ+PMMA**, respectively.

2.2. Polarized UV-Vis and CD Spectra with Theoretical Calculations

Figures 3–5 exhibit experimental (in acetone solution) and simulated (UB3LYP/6-31G(d)) CD and UV-Vis spectra of **Ni**, **Cu**, and **Zn**, respectively, based on optimized structures (Figures S1–S3). The π - π^* , n - π^* , and d-d bands could be reasonably assigned based on a theoretical simulation using Gaussian09 [14]. As the model structures in **PMMA**, the optimized structures of **Ni** and **Cu** afford a tetrahedrally distorted square planar geometry indicating dipole moment 3.2694 Debye with direction vector $(x, y, z) = (1.7223, 0.7499, -2.6759)$ and 5.2898 Debye with $(-1.5744, 4.2113, 2.7872)$, while that of **Zn** affords a compressed tetrahedral geometry indicating 8.2269 Debye with $(4.6534, -5.7037, 3.6736)$.

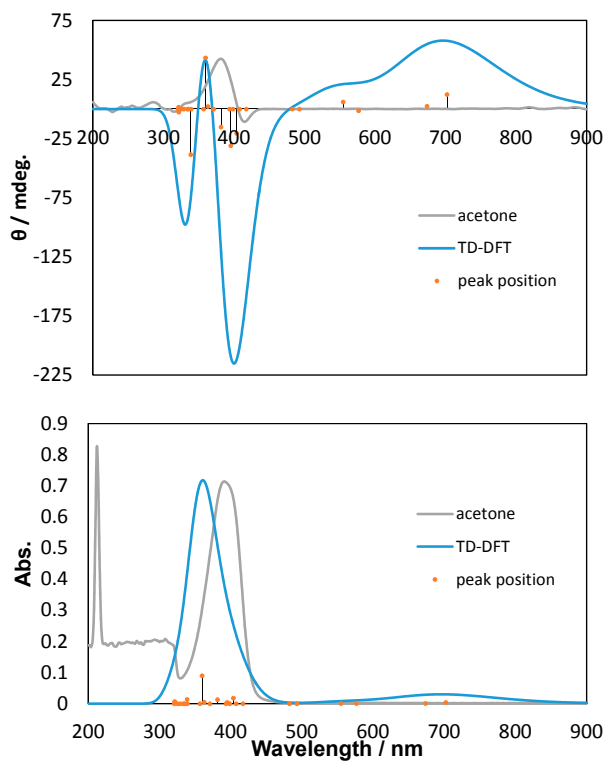


Figure 3. Experimental (in acetone solution) and simulated (UB3LYP/6-31G(d)) UV-Vis and CD spectra of Ni.

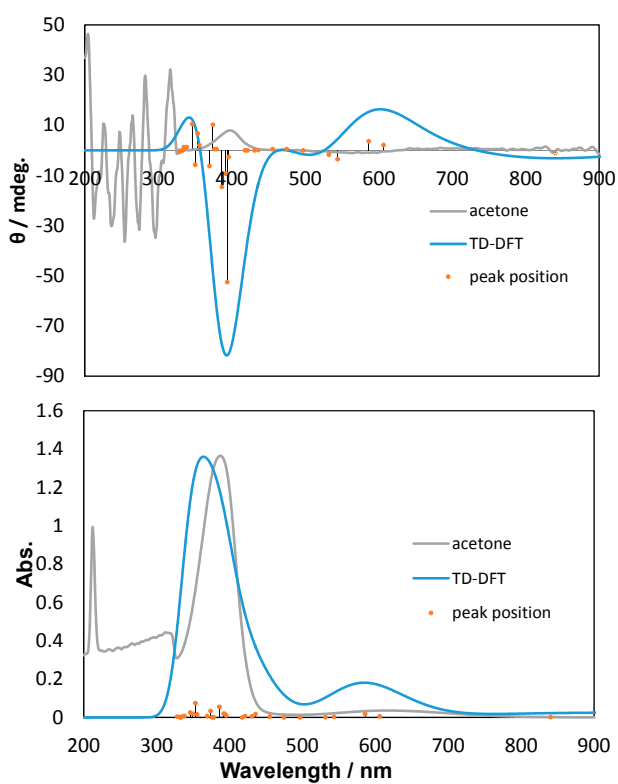


Figure 4. Experimental (in acetone solution) and simulated (UB3LYP/6-31G(d)) UV-Vis and CD spectra of Cu.

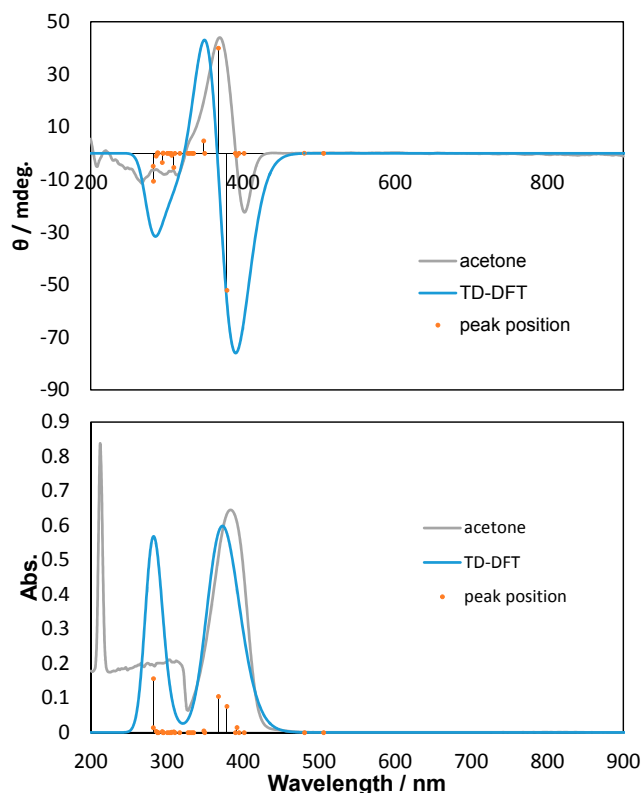


Figure 5. Experimental (in acetone solution) and simulated (UB3LYP/6-31G(d)) UV-Vis and CD spectra of Zn.

Contrary to IR spectra, UV-Vis spectra (Tables S4–S6) contain overlap of AZ and complexes with initially drastic spectral changes by *trans* to *cis* photoisomerization of AZ. Thus, polarized UV-Vis spectra contain information about molecular orientation of each component and their conformational (both ligands and coordination environment) changes—as expected, deviated from crystal structures [15].

As for **Ni+AZ+PMMA**, after 10 min, π - π^* (318 nm), n - π^* (440 nm), and d-d (610 nm) bands exhibited $R = 0.958$; $S = -0.0142$, $R = 1.02$; $S = 0.0078$, and $R = 1.08$; $S = 0.0269$, respectively.

As for **Cu+AZ+PMMA**, after 10 min, π - π^* (318 nm), n - π^* (440 nm), and d-d (614 nm) bands exhibited $R = 1.00$; $S = -0.0011$, $R = 0.954$; $S = -0.0055$, and $R = 0.998$; $S = -0.0007$, respectively.

As for **Zn+AZ+PMMA**, after 10 min, π - π^* (318 nm) and n - π^* (440 nm) bands exhibited $R = 0.969$; $S = -0.0105$ and $R = 1.05$; $S = -0.00152$, respectively.

In contrast to previous studies [15,16], however, supramolecular chirality resulting from helical orientation could not be observed as detectable changes of CD spectra (220–900 nm), even following circularly polarized UV light irradiation for 10 min (not shown). Long and flexible ligand conformation [17,18] exhibited a disadvantage in the supramolecular transmission of molecular orientation.

3. Discussion

Viscosity and CD Spectra with Molecular Modeling

In order to discuss intermolecular interaction in PMMA, Figure 6 shows a correlation between concentration of PMMA acetone solutions and the intensity of so-called artifact peak of solid-state CD spectra. Our previous studies [19,20] have successfully elucidated that there is a good correlation between viscosity (namely, concentration of PMMA acetone solutions of stiff chiral metal

complexes [21]) and intensity of artifact CD peaks, accompanying a gradual restriction of free rotation and losing isotropy of a chiral complex (Figure S4). In principle, isotropy of a chiral material reduces artifact peaks of CD spectra.

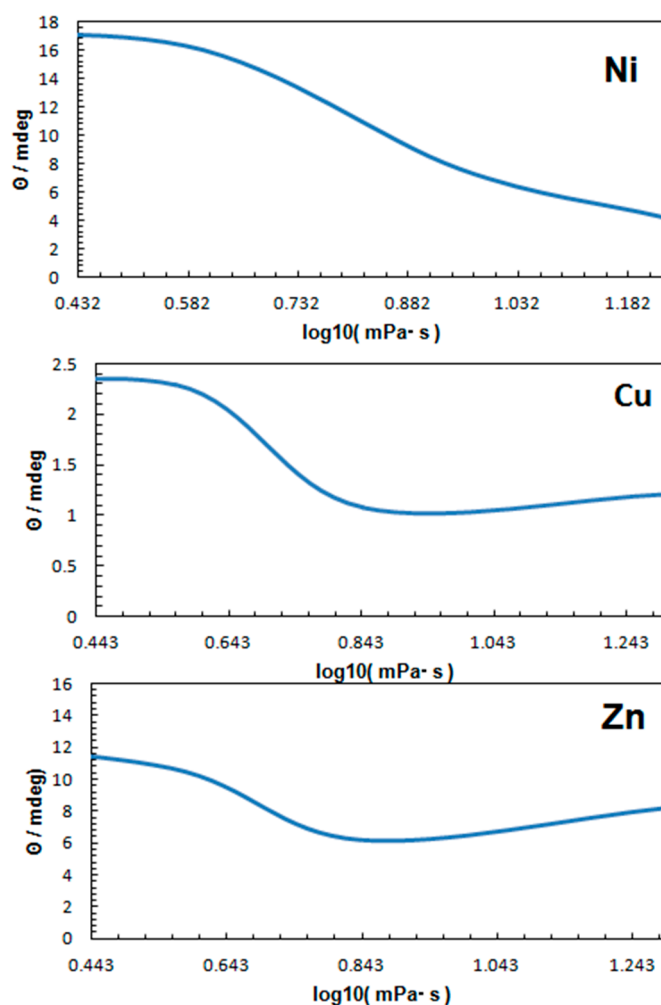


Figure 6. Correlation between concentration of **PMMA** acetone solutions **Ni**, **Cu**, or **Zn** and the intensity of artifact CD peaks.

In this study, we tested 1:2 mixtures of **PMMA** acetone solutions (2.5, 5, 10, 15, 20, 25 wt %) and 0.05 mM acetone solutions of complexes and **AZ**. The strongest artifact CD peaks could be observed at 10%, 15%, and 5% for **Ni**, **Cu**, and **Zn**, respectively. Contrary to other examples of relatively stiff complexes, a poor correlation between viscosity and intensity was found. Both the flexible conformation of ligands and the whole structure of the complexes resulted in a different fashion of intermolecular interaction between the complexes, **AZ**, and **PMMA**.

Molecular modeling (Figure 7) helps the visualization of intermolecular interaction fashion between complexes, **AZ**, and **PMMA** from the viewpoint of stereochemistry. In the **PMMA** matrix, free volume around **AZ** enables **AZ** to photoisomerize smoothly. Similar to the discussion of **AZ**, the order of free volume around complexes is **Ni** > **Cu** > **Zn**, which is in agreement with the easy-to-move complexes in **PMMA**.

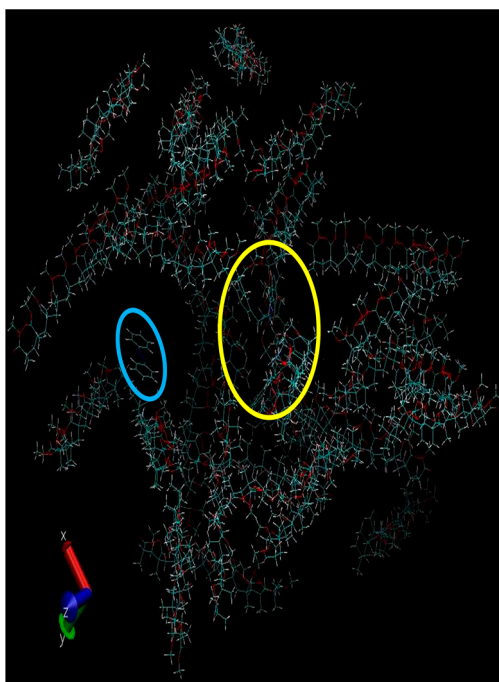


Figure 7. Molecular modeling of 2+AZ+PMMA. 2: yellow circle; AZ: blue circle.

4. Materials and Methods

Complexes (**Ni**, **Cu**, and **Zn**) were prepared according to literature methods [10,16,18] using the corresponding chiral amines and aldehydes having halogen. **Ni**: Yield: 52.5%. IR 1631 cm^{-1} (C=N). **Cu**: Yield: 46.2%. IR 1628 cm^{-1} (C=N). **Zn**: Yield: 71.8%. IR 1615 cm^{-1} (C=N). Hybrid materials of complexes (**Ni**, **Cu**, and **Zn**), AZ, and PMMA were prepared according to literature procedures [16,18].

Infrared (IR) spectra were recorded with Nujol mull on a JASCO FT-IR 4200 plus spectrophotometer (JASCO, Tokyo, Japan) equipped with a polarizer in the range of $4000\text{--}400\text{ cm}^{-1}$ at 298 K. Absorption electronic spectra were measured on a JASCO V-570 spectrophotometer equipped with a polarizer in the range of $900\text{--}200\text{ nm}$ at 298 K. Circular dichroism (CD) spectra were measured on a JASCO J-725 spectropolarimeter in the range of $800\text{--}200\text{ nm}$ at 298 K. Viscosity was measured on an A&D SV-10A type SV (A&D, Tokyo, Japan, 30 Hz frequency) at 298 K. Photo-illumination were carried out using a lamp (1.0 mW/cm^2) with optical filters (UV $\lambda = 200\text{--}400\text{ nm}$) and a polarizer.

All calculations were performed using the Gaussian 09W software Revision D.01 (Gaussian, Inc., Wallingford, CT, USA) [14]. The vertical excitation energy was calculated using the TD-DFT method based on the singlet ground state geometry. The exchange functional, the correlation functional, and the basis set were UB3LYP/6-31G8d.

5. Conclusions

In summary, we prepared organic/inorganic hybrid materials containing three new chiral complexes having Br-, Ph-, and -OH groups. Stereochemistry of ligands resulted in weakening propagation of optical anisotropy from azobenzene to chiral Schiff base metal complexes in PMMA polymer matrix. In contrast to previous analogous chiral Schiff base metal complexes without the methylene group (namely, connecting (*R*)-asymmetric carbon and the Ph- group directly), flexibility for **Ni**, **Cu**, and **Zn** was attributed to a methylene carbon between the (*R*)-asymmetric carbon and the Ph- group. Linearly polarized UV light irradiation induced anisotropic molecular orientation of AZ as well as complexes, and saturated irradiation time was **Ni** < **Cu** < **Zn**. Viscosity and CD intensity test suggested weak intermolecular interaction between flexible complexes and PMMA. This may be in agreement with the free volume of PMMA around complexes **Ni** > **Cu** > **Zn**.

Supplementary Materials: The following are available online at www.mdpi.com/2304-6740/4/3/20/s1. Figure S1: Optimized structure of Ni with dipole moment (arrow). Figure S2: Optimized structure of Cu with dipole moment (arrow). Figure S3: Optimized structure of Zn with dipole moment (arrow). Figure S4: PMMA concentration dependence of acetone solutions of Ni, Cu, and Zn. Table S1: The R and S values of polarized IR spectra for Ni+AZ+PMMA. Table S2: The R and S values of polarized IR spectra for Cu+AZ+PMMA. Table S3: The R and S values of polarized IR spectra for Zn+AZ+PMMA. Table S4: The R and S values of polarized UV-Vis spectra for Zn+AZ+PMMA. Table S5: The R and S values of polarized UV-Vis spectra for Ni+AZ+PMMA. Table S6: The R and S values of polarized UV-Vis spectra for Cu+AZ+PMMA.

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Author Contributions: Hiroshi Takano and Maiko Ito performed the experiments; Masahiro Takase performed computational chemistry; Nobumitsu Sunaga performed molecular modeling; Takashi Akitsu designed the study and wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

The following abbreviations are used in this manuscript:

AZ	azobenzene
CD	circular dichroism
IR	infrared
PMMA	polymethyl methacrylate
TD-DFT	time-dependent density functional theory
UV	ultraviolet
Vis	visible

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