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Chapter 5

**WAVELENGTH DEPENDENCE OF POLARIZED
UV LIGHT INDUCED SUPRAMOLECULAR
ORIENTATION OF AZOBENZENE-
CONTAINING ORGANIC/INORGANIC HYBRID
MATERIALS OF CHIRAL SCHIFF BASE Ni(II),
Cu(II) AND Zn(II) COMPLEXES**

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ABSTRACT

We have synthesized nine organic/inorganic hybrid materials in polymethylmethacrylate (PMMA) cast films composed of azo-groups containing diastereomers of Schiff base Ni(II), Cu(II) and Zn(II) complexes and azobenzene and chiral Schiff base Ni(II), Cu(II) and Zn(II) complexes. Linearly or circularly polarized UV light-induced molecular orientation of the components was investigated as increasing

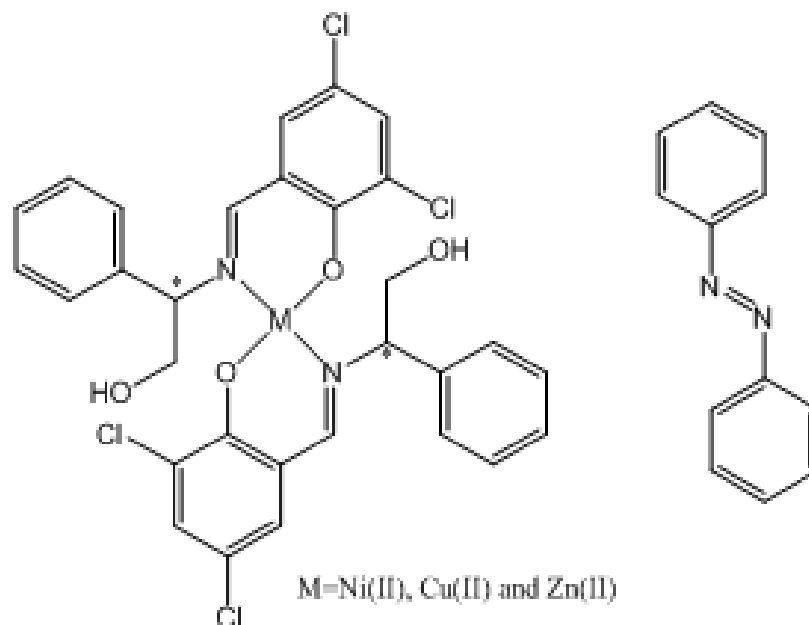
optical anisotropy with polarized UV-vis or IR spectroscopy or supramolecular chiral alignment with CD spectroscopy. By comparing experimental and simulated (TD-DFT) UV-vis spectra, reliable assignment of spectral bands was obtained to discuss effective light absorption for Weigert effect. Furthermore, differences of CD bands before and after circularly polarized light UV irradiation suggested chiral molecular ordering, which was induced differently by using continuous (below 350 nm) or selective wavelengths (260, 318, and 380 nm) UV light.

INTRODUCTION

Organic/inorganic hybrid materials composed of photochromic dyes such as azobenzene (**AZ**) and inorganic coordination complexes in polymers have been investigated as a key technology for controlling light or other functions. Such organic/inorganic hybrid materials may be facility of designing supramolecular materials, for example metal complexes incorporating azo-groups in ligands with large dichromic ratios [1-3]. Applications of such supramolecular materials can also be expected as photo-controlling hybrid magnets [4-9], fluorescence sensors [10, 11], (supra)molecular recognition of chirality [12-14], and nano-scaled magnetic materials [15-18].

It has been well known that quite large circular anisotropy could be induced for films of liquid crystalline polymers having azo-groups in side chains after illumination of circularly polarized light. Then, it became to be possible to form the light-induced supramolecular chiral [19-22] order by irradiation with circularly polarized light in the amorphous **AZ** polymers [23-25]. To date, the mechanism has been elucidated well [26], and circularly polarized light with opposite handedness produces enantiomeric structures potentially. By using this property, chiroptical switch was also reported [27]. Moreover, linear birefringence photoinduced in films of amorphous **AZ** polymers can be erased by irradiation with circularly polarized light. The explanation is that circularly polarized light activates the photoisomerization of all azo-groups in the plane of the films, restoring the preferred random arrangement of the chromophores [28-30].

We also focused on photo-tuning of optical anisotropy of **AZ**, namely polarized UV light-induced alignment caused by selected photoisomerization and molecular reorientation of **AZ** (so-called Weigert effect) [31-33], in contrast to conventional *cis-trans* photoisomerization of **AZ**. During a series of the related studies of such organic/inorganic hybrid materials and photo-



Scheme 2. Structures of hybrid materials of **AZ** and chiral (*R,R*-form) Schiff base Ni(II) (**7**), Cu(II) (**8**) and Zn(II) (**9**) complexes.

In addition, we investigated them to irradiate with not only linearly but also circularly polarized UV light (selective wavelength (260, 318 (π - π^* band of **AZ**) and 380 nm) and continuous wavelength (below 350 nm)), and examined the dipole moments and different molecular orientation induced. Furthermore, we attempted to observe supramolecular chiral molecular arrangement for the system by means of CD spectra before and after circularly polarized UV light irradiation.

RESULTS AND DISCUSSION

Optimized Structures and Experimental or Simulated UV-Vis and CD Spectra

Figures 1 and 2 exhibit comparison between experimental and simulated UV-vis and CD spectra based on optimized structures for **1-3** and **6-9**, respectively.

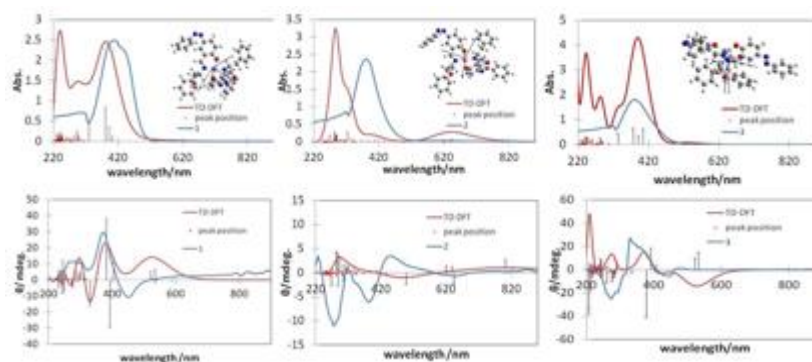


Figure 1. Experimental and simulated (TD-DFT) UV-vis and CD spectra for 1-3.

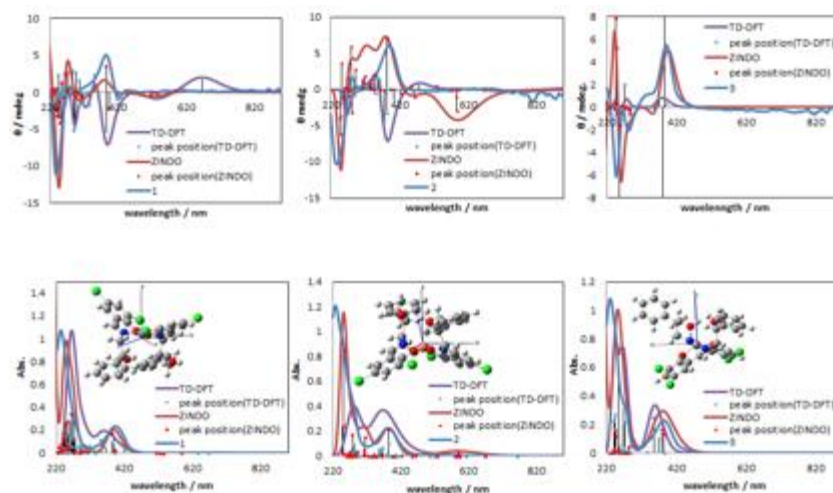


Figure 2. Experimental and simulated (TD-DFT and ZINDO) UV-vis and CD spectra for 7-9.

Generally optimized structures (in **PMMA** films) of these complexes differs from crystal structures, because predominant peaks of diffuse reflectance spectra appears at 606, 410, and 266 nm for **7**, 621, 426, and 265 nm for **8**, and 606, 408, and 298 nm for **9**. Experimental UV-vis spectra of azo-containing complexes could be assigned based on ground and excited molecular orbitals as follows: d-d bands are at 621 and 649 nm for **1** and **2**, n- π^* bands are 317, 323 and 317 nm for **1**, **2**, and **3**, and π - π^* bands are 410, 374, and 386 nm for **1**, **2**, and **3**, respectively. Diastereomers (**1-3** and **4-6**)

indicated similar UV-vis spectra. Complexes **4-6** exhibited no CD peaks, which suggested to be meso *R,S*-form. On the other hand, UV-vis spectra of without azo-group complexes could be assigned as follows: d-d bands at 572 and 603 nm for **7** and **8**, n- π^* bands are 232, 228, and 231 nm for **7**, **8**, and **9**, and π - π^* bands are 392, 383, and 386 nm for **7**, **8**, and **9**, respectively.

Selected predominant peaks for azo-containing complexes are assigned to be the following transitions between molecular orbitals: for **1**, 589 nm (d-d band)(HOMO (178) to LUMO (179)), 382 nm (π - π^* band)(HOMO-2 (176) to LUMO+1 (180)), and 243 nm (n- π^* band)(HOMO-7 (171) to LUMO+3 (182)); for **2**, 643 nm (d-d band)(HOMO-1 (181 β) to LUMO (183 β)), 396nm (π - π^* band)(HOMO-3 (179 β) to LUMO+1 (184 β)), and 249nm (n- π^* band)(HOMO-13 (169) to LUMO+3 (186 β)); for **3**, 386 nm (π - π^* band)(HOMO (175) to LUMO+1 (177)), 244 nm (n- π^* band) (HOMO-1 (174) to LUMO+3 (179)).

Assuming the optimized structures, the magnitude (and direction vectors) of dipole moments are evaluated to be 5.008 D (-2.0207, -0.7877, 4.5137), 5.211 D (-3.8137, -3.5473, -0.1447), 8.044 D (2.3356, 1.4003, 7.5659), 2.642 D (-0.6419, -2.3950, -0.9123), 3.263 D (0.1369, -0.5262, 3.2178), and 5.740 D (0.2898, 0.0803, 5.7325) for **1-3** and **7-9** respectively. The present values for **1-3** are comparable to the analogous azo-containing ones which were considered as *cis-trans* photoisomerization.

Polarized UV-vis Spectra after Linearly Polarized UV Light Irradiation

Continuous wavelength of UV light below 350 nm (effective for not only photoisomerization but also Weigert effect consequently) was employed in this linearly polarized UV light irradiation experiment. At initial stage, considerable decreasing of π - π^* and n- π^* band is due to photoisomerization of *trans*-form to *cis*-form of azo-group by UV light irradiation. Weigert effect also causes dichroism with photochemical reaction. Due to Weigert effect by reorientation of azo-groups in complexes **1-6+PMMA** or **AZ** of **7-9+AZ+PMMA**, optical anisotropy, especially observed as decreasing intensity of π - π^* and n- π^* bands, increases as irradiation time proceeds (0.5, 1, 3, 5, 10, 30 min). Changes of π - π^* and n- π^* bands provide information of molecular orientation or conformation of ligands, while changes of d-d bands provide information of coordination geometry. Electric vector of polarized light and transition moment along the long molecular axis of azo-groups of complexes

or calculated with a TD-DFT method are parallel or perpendicular results in strong or weak intensity of absorption, respectively. Therefore, combination of Weigert effect and reorientation is associated with the resulting polarized spectral features.

As an example polarized UV-vis spectra of **7+AZ+PMMA** was shown in Figure 3. The degree of photoinduced optical anisotropy from polarized UV-vis spectra can be described by these two parameters:

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

$$R = A_{\text{perpendicular}} / A_{\text{parallel}}$$

where $A_{\text{perpendicular}}$ and A_{parallel} values denote absorbance measured with the measuring polarizers perpendicular or parallel to electric vector of irradiation polarized light. Ideal isotropic systems of $S = 0$ and $R = 1$ and both S and R parameters are changed as increasing dichroism by molecular alignment.

The degree of increasing optical anisotropy accompanying with Weigert effect depends on not steric shapes of ligands but central Ni(II), Cu(II) or Zn(II) metal ions. Because π - π^* absorption bands of all complexes cover the continuous wavelength of UV light, metal ions providing rigid coordination environment are effective to increase molecular orientation.^{43, 48-50} The order is as follows: in the case of chiral complexes, **1+PMMA** > **2+PMMA** > **3+PMMA** for π - π^* bands, **1+PMMA** > **2+PMMA** > **3+PMMA** for n - π^* bands, and **1+PMMA** > **2+PMMA** for d-d bands. Whereas, in the case of achiral ones, **4+PMMA** > **5+PMMA** > **6+PMMA** for π - π^* bands, **4+PMMA** > **5+PMMA** > **6+PMMA** for n - π^* bands, and **4+PMMA** > **5+PMMA** for d-d bands. In contrast to azo-containing hybrid systems, optical anisotropy of separated **AZ** hybrid materials depends on not only flexibility of coordination environment but also stable coordination geometries clearly.

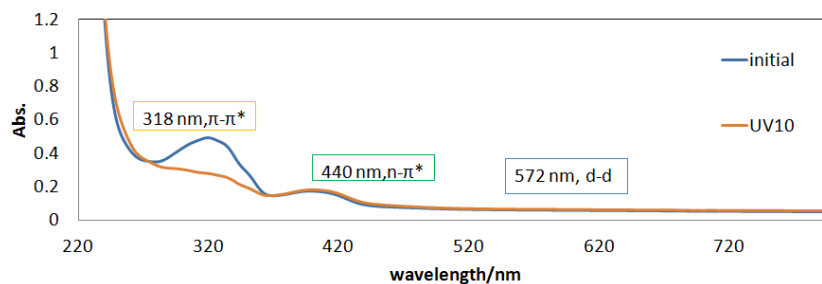


Figure 3. Polarized absorption spectra of **7+AZ+PMMA** with 0 degree showing predominant peaks before and after UV light irradiation for 10 min.

Supramolecular chiral arrangement of **AZ** induced by chiral complexes as chiral dopants and polarized UV light irradiation exhibiting Weigert effect may not result in remarkable changes of the parameters for optical anisotropy. We can derive the following information associated with molecular orientations with intermolecular interactions in these organic/inorganic hybrid materials. The order of the effect was **8+AZ+PMMA** > **7+AZ+PMMA** > **9+AZ+PMMA**. Reducing direct transmission of molecular alignment from **AZ** by rigidity of metal complexes due to Zn(II) ions is suggested. The degree of increasing optical anisotropy accompanying with Weigert effect of **AZ** depends not on whole molecular shapes of chiral ligands but on central Ni(II), Cu(II) or Zn(II) metal ions.

Polarized IR Spectra after Linearly Polarized UV Light Irradiation

Continuous Polarized IR spectra were also employed to observe components in hybrid materials separately. Figure 4 shows angular dependence of IR transmittance of N=N of **AZ** (1557, 1559, and 1558 cm^{-1}) and C=N (1633, 1636, and 1635 cm^{-1}) for **7-9+AZ+PMMA**, respectively. Initial considerable change is also attributed to photoisomerization of **AZ**. The circular diagrams suggest that reorientation of **AZ** effects on relatively large optical anisotropy observed.

CD Spectra after Circularly Polarized UV Light Irradiation of Continuous or Selective Wavelengths

Figure 5 shows the differences of CD spectra for **1-6+PMMA** before and after circularly polarized UV light irradiation of continuous wavelength (below 350 nm) or selective wavelengths (260, 318, and 380 nm) for 10 min. As well known for liquid crystalline azo-polymers, circularly polarized UV light of *continuous wavelengths* induces chiral (supra)molecular alignment of molecules containing azo-groups. Although **1-3** are chiral molecules appearing CD peaks mentioned in TD-DFT calculations, CD peaks due to chiral (supra)molecular alignment emerge at different wavelengths (around 400 nm) from that due to molecular chirality for hybrid materials composed of achiral molecules **4-6** as well as chiral molecules **1-3**. In addition, as acting as chiral dopants by themselves, effective emerging of the CD peaks for **1-3** may be reasonable even if solid-state artifact CD peaks emerged [67].

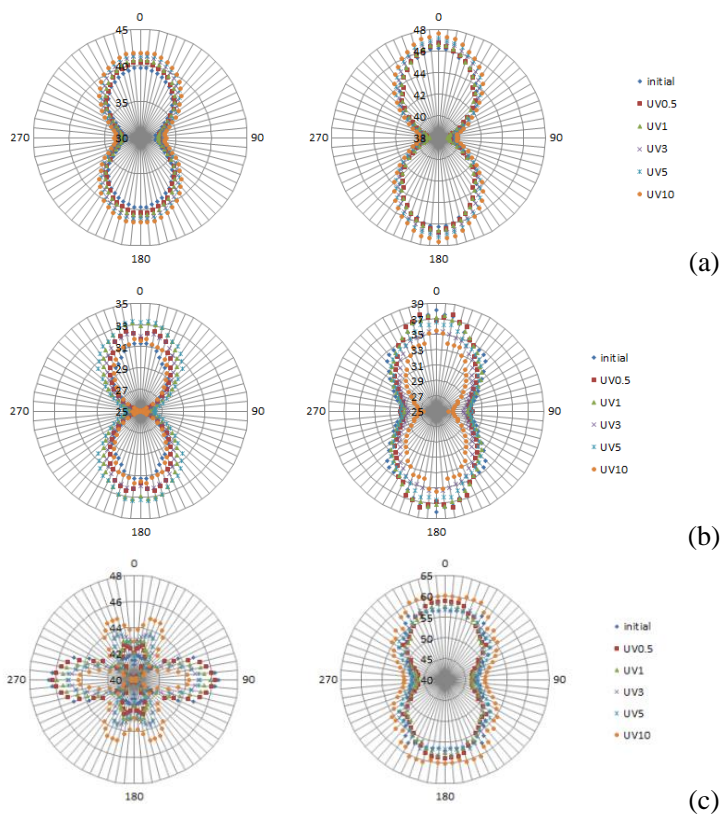


Figure 4. Circular diagram of angular dependence of transmission of the predominant peaks polarized IR spectra of (a) **7+AZ+PMMA**, (b) **8+AZ+PMMA**, and (c) **9+AZ+PMMA**, (left; C=N and right; N=N) after UV light irradiation for 0 (blue), 0.5 (red), 1 (green), 3 (violet), 5 (light blue) and 10 (orange) min.

In analogy with the mechanism of Weigert effect accompanying with *cis-trans* photoisomerization, circularly polarized UV light of *selective wavelengths* (260, 318, and 380 nm) was also irradiated to the hybrid materials. Among three wavelengths, 318 nm is equivalent to the energy of $\pi-\pi^*$ of band of azo-groups exhibiting intense absorption. The CD peaks due to supramolecular chirality appeared at 260, 350, and 420 nm for **1+PMMA**, 270, 360, and 400 nm for **2+PMMA**, 280, 360, and 420 nm for **3+PMMA**, 360, 400, and 460 nm for **4+PMMA**, 350, 360, and 460 nm for **5+PMMA**, 360, 390, and 400 nm for **6+PMMA**. For selective wavelengths, difference of CD peaks and intensity among irradiation wavelengths and the differences among complexes (metal and diastereomers) could be observed clearly.

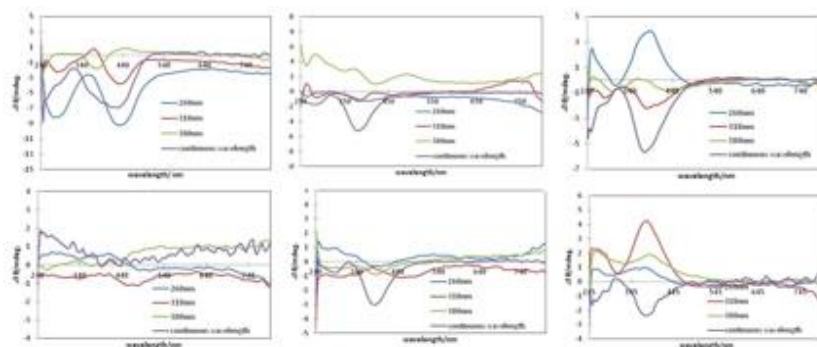


Figure 5. The differences of CD spectra for **1+PMMA** [left above], **2+PMMA** [center above], **3+PMMA** [right above], **4+PMMA** [left below], **5+PMMA** [center below] and **6+PMMA** [right below] before and after circularly polarized UV light irradiation of continuous wavelength (below 350 nm) or selective wavelengths (260, 318, and 380 nm) for 10 min.

The order of this effect is Ni complexes (**1** and **4**) > Cu ones (**2** and **5**) > Zn ones (**3** and **6**), and this results suggests that optical anisotropy depends not only on flexibility of coordination due to metal and molecular structures associated with chirality but also on electronic structures associated with light absorption. On the other hand, the intensity of CD spectra of **7-9+AZ+PMMA**, before and after circularly polarized UV light irradiation with UVSOR synchrotron facility for 3 min or up to 8 min, respectively. The irradiating wavelength effect on emerging CD peaks resulting from supramolecular chiral alignment has not been observed for the previous azo-group separated systems (**7-9+AZ+PMMA**) [65, 67]. By using a light source having a narrow wavelength width at UVSOR (wavelength selective (260, 318 (π - π^* of **AZ**) and 380 nm), induced chiral order is caused absorption wavelength selective. Changes in the observed shape of the CD spectra, the induction of supramolecular chirality or conformational change of the molecules can be considered. Changes in the CD spectra of this time, appeared only change in absorption intensity with increasing the irradiation time, which suggested that molecules of supramolecular chirality were induced by Weigert effect of **AZ** by circularly polarized light irradiation, rather than the changes in molecular structures. In addition, induced chiral order is caused absorption wavelength selective, which suggests that it is a new knowledge of the radiation source only. The order of this effect is **8** > **7** > **9**, and this results suggests that optical anisotropy depends not only on flexibility of coordination environment but also on coordination geometries.

Theoretical Interpretation of the Optical Rotation Strength Using Coupled Oscillator Model

In order for interpretation of supramolecular chirality, we attempt to discuss spatial relationship between **AZ** molecules assuming dipole-dipole interaction. For this reason, we will apply coupled oscillator model hereafter [59-62]. If only the Coulomb interaction of the chromospheres A between B two can be considered, we assume system dipole interactions between paired the two ones. Now, the Hamiltonian of the system is represented by the equation (1).

$$H = H_A(r_A) + H_B(r_B) + V_{AB} \quad (1)$$

where Hamiltonian $H_A(r_A)$ or $H_B(r_B)$ is of the chromophores A or B, V_{AB} is Coulomb interaction potential between the chromophore A and B. By the wave function of the ground states and excited states of the chromophores A or B, to introduce electric transition dipole moment, optical rotation strength of the formula is derived as the equation (2).

$$R_{0a} = - \left(\frac{2\pi\nu_a\nu_b}{\hbar c(\nu_a^2 - \nu_b^2)} \right) (\mu_{0a} \cdot T \cdot \mu_{0b}) (R_{AB} \times \mu_{0a} \cdot \mu_{0b}) \quad (2)$$

where ν_a or ν_b are absorption frequency, μ_{0a} or μ_{0b} is electric transition dipole moment, R_{AB} is a distance of A and B, T is parameter. To simplify this, consider that both chromospheres are identical, and hereafter assume connecting both two, is orthogonal (Figure 6). At this time, from equation (2), the optical rotation strength becomes the following equation (3).

$$R_{\pm} = \mp \left(\frac{\pi\nu_0}{2c} \right) R_{12} \mu_{0a}^2 \sin\theta_{12} \quad (3)$$

Furthermore, we considered as follows. The intensity of CD bands can be represented by optical rotation strength R. From the CD spectra measured, R is determined according to the following equation (4).

$$\begin{aligned} R &= 2.296 \times 10^{-39} \int_0^{\infty} \left\{ \frac{\Delta\varepsilon(\sigma)}{\sigma} \right\} d\sigma \\ &\approx \left(2.296 \times 10^{-39} / \sigma_0 \right) \int_0^{\infty} \Delta\varepsilon(\sigma) d\sigma \text{ (c.g.s)} \end{aligned} \quad (4)$$

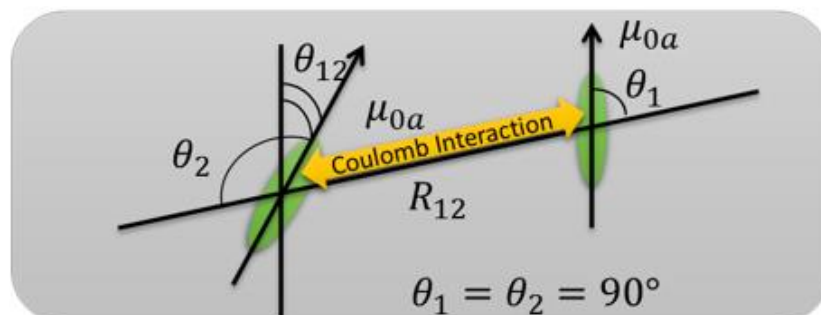


Figure 6. Coulomb interaction between the same chromospheres.

where σ is the wave number and is the σ_0 wavenumber of the peaks (the maximum) of the CD spectra.

As relational expressions, we calculated from equation (4) optical rotation strength of the induced CD spectra observed. Substituting equation (3), the degree of inclination (θ) of the dye molecules of interest was evaluated.

EXPERIMENTAL SECTION

General Procedures

Chemicals of the highest commercial grade available were purchased from Aldrich (St. Louis, USA), Wako (Osaka, Japan), and TCI (Tokyo, Japan) and used as received without further purification. PMMA (m.p. 378 K, density 1.188 g cm^{-3}) was purchased from Wako. 4-phenyldiazenylsalicylaldehyde was prepared according to the literature method [68, 69].

Preparations

Preparation of (R - 3 - phenyl - 2-aminopropane - 1 - ol - 4 - phenyldiazenylsalicydenaminato)nickel(II) (I)

To a solution of 4-phenyldiazenylsalicylaldehyde (0.4521 g, 2.000 mmol) dissolved in methanol (60 mL), D-(+)-phenylalaninol (0.3024 g, 2.000 mmol) was added dropwise and stirred at 340 K for 2h to give orange solution of ligand. Nickel(II) acetate tetrahydrate (0.2488 g, 1.000 mmol) was added to the resulting solution to give greenish brown solution of the complex. After

stirring for 2h, this crude greenish brown compound was filtered. Yield 0.4509 g (50.24%). Anal. Calc. for $C_{44}H_{40}NiN_6O_4$; C, 68.14; H, 5.20; N, 10.84. Found: C, 71.19; H, 5.30; N, 11.24%. IR (KBr (cm^{-1})): 690, 766, 1111, 1387, 1471, 1599 (N=N), 1635 (C=N), 2363, 2965, 3434.

Preparation of (R – 3 – phenyl – 2 – aminopropane – 1 – ol – 4 – phenyldiazenylsalicydenaminato)copper (II) (2)

To a solution of 4-phenyldiazenylsalicylaldehyde (0.4521 g, 2.000 mmol) dissolved in methanol (60 mL), D-(+)-phenylalaninol (0.3024 g, 2.000 mmol) was added dropwise and stirred at 340 K for 2h to give orange solution of ligand. Copper(II) acetate dihydrate (0.1997 g, 1.000 mmol) was added to the resulting solution to give green solution of the complex. After stirring for 2h, this crude green compound was filtered. Yield 0.2341 g (30.04%). Anal. Calc. for $C_{44}H_{40}CuN_6O_4$; C, 67.72; H, 5.17; N, 10.77. Found: C, 71.19; H, 5.30; N, 11.24%. IR (KBr (cm^{-1})): 691, 837, 1114, 1383, 1471, 1605 (N=N), 1631 (C=N), 2345, 2924, 3415.

Preparation of (R – 3 – phenyl – 2 – aminopropane – 1 – ol – 4 – phenyldiazenylsalicydenaminato)zinc (II) (3)

To a solution of 4-phenyldiazenylsalicylaldehyde (0.4521 g, 2.000 mmol) dissolved in methanol (60 mL), D-(+)-phenylalaninol (0.3024 g, 2.000 mmol) was added dropwise and stirred at 340 K for 2h to give orange solution of ligand. Zinc(II) acetate dihydrate (0.2195 g, 1.000 mmol) and sodium hydrogen carbonate were added to the resulting solution to give orange solution of the complex. After stirring for 2h, this crude orange compound was filtered. Yield 0.2341 g (30.04%). Anal. Calc. for $C_{44}H_{40}ZnN_6O_4$; C, 67.56; H, 5.15; N, 10.74. Found: C, 71.19; H, 5.30; N, 11.24%. IR (KBr (cm^{-1})): 691, 1113, 1394, 1474, 1606 (N=N), 1622 (C=N), 2360, 3444.

Preparation of (R,S – 3 – phenyl – 2 – aminopropane – 1 – ol – 4 – phenyldiazenylsalicydenaminato)nickel(II) (4)

To a solution of 4-phenyldiazenylsalicylaldehyde (0.4521 g, 2.000 mmol) dissolved in methanol (60 mL), DL-phenylalaninol (0.3024 g, 2.000 mmol) was added dropwise and stirred at 340 K for 2h to give orange solution of ligand. Nickel(II) acetate tetrahydrate (0.2488 g, 1.000 mmol) was added to the resulting solution to give greenish brown solution of the complex. After stirring for 2h, this crude greenish brown compound was filtered. Yield 0.3663g (47.31%). Anal. Calc. for $C_{44}H_{40}NiN_6O_4$; C, 68.14; H, 5.20; N, 10.84.

Found: C, 71.19; H, 5.30; N, 11.24%. IR (KBr (cm⁻¹)): 703, 749, 1111, 1388, 1471, 1602 (N=N), 1638 (C=N), 2363, 2965, 3434.

Preparation of (R,S - 3 - phenyl - 2 - aminopropane - 1 - ol - 4 - phenyldiazenylsalicydenaminato)copper (II) (5)

To a solution of 4-phenyldiazenylsalicylaldehyde (0.4521 g, 2.000 mmol) dissolved in methanol (60 mL), *DL*-phenylalaninol (0.3024 g, 2.000 mmol) was added dropwise and stirred at 340 K for 2h to give orange solution of ligand. Copper(II) acetate dihydrate (0.1997 g, 1.000 mmol) was added to the resulting solution to give green solution of the complex. After stirring for 2h, this crude green compound was filtered. Yield 0.3067 g (39.35%). Anal. Calc. for C₄₄H₄₀NiN₆O₄; C, 67.72; H, 5.17; N, 10.77. Found: C, 71.19; H, 5.30; N, 11.24%. IR (KBr (cm⁻¹)): 687, 830, 1115, 1383, 1471, 1606 (N=N), 1632 (C=N), 2361, 2926, 3416.

Preparation of (R,S - 3 - phenyl - 2 - aminopropane - 1 - ol - 4 - phenyldiazenylsalicydenaminato)zinc (II) (6)

To a solution of 4-phenyldiazenylsalicylaldehyde (0.4521 g, 2.000 mmol) dissolved in methanol (60 mL), *DL*-phenylalaninol (0.3024 g, 2.000 mmol) was added dropwise and stirred at 340 K for 2h to give orange solution of ligand. Zinc(II) acetate dihydrate (0.2195 g 1.000 mmol) and sodium hydrogen carbonate were added to the resulting solution to give orange solution of the complex. After stirring for 2h, this crude orange compound was filtered. Yield 0.2521 g (32.31%). Anal. Calc. for C₄₄H₄₀NiN₆O₄; C, 67.56; H, 5.15; N, 10.74. Found: C, 71.19; H, 5.30; N, 11.24%. IR (KBr (cm⁻¹)): 691, 1111, 1398 1476, 1593 (N=N), 1635 (C=N), 2360, 3438.

Preparation of bis(R - 2 - phenylglycianol - 3,5 - dichlorosalicydenaminato)nickel(II) (7)

To a solution of 3,5-dichlorosalicylaldehyde (0.1911 g, 1.00 mmol) dissolved in methanol (50 mL), *R*-(-)-2-phenylglycianol (0.1372 g, 1.00 mmol) was added dropwise and stirred at 313 K for 2 h to give orange solution of ligand.

Nickel(II) acetate tetrahydrate (0.1244 g, 0.500 mmol) was added to the resulting solution to give greenish brown solution of the complex. After stirring for 2 h, this crude greenish brown compound was filtered to give green powder. Yield 0.2663 g (78.7%). Anal. Found: C, 52.3; H, 3.74; N, 3.85%. Calc. for C₃₀H₂₄Cl₄NiN₂O₄: C, 52.5; H, 3.98; N, 3.95%. IR (Nujol (cm⁻¹)): 757, 1156, 1377, 1458, 1516, 1585, 1632 (C=N), 2835, 2924, 2955.

Preparation of bis(R – 2 – phenylglycianol - 3,5 - dichlorosalicydenaminato)copper(II) (8)

To a solution of 3,5-dichlorosalicylaldehyde (0.1911 g, 1.00 mmol) dissolved in methanol (50 mL), *R*-(-)-2-phenylglycianol (0.1372 g, 1.00 mmol) was added dropwise and stirred at 313 K for 2 h to give orange solution of ligand. Copper(II) acetate monohydrate (0.0998 g, 0.500 mmol) was added to the resulting solution to give black solution of the complex. After stirring for 2 h, this crude green compound was filtered to give green powder. Yield 0.2657 g (78.0%). Anal. Found: C, 52.9; H, 3.63; N, 4.01%. Calc. for $C_{30}H_{24}Cl_4CuN_2O_4$: C, 52.8; H, 3.55; N, 4.11%. IR (Nujol (cm^{-1})): 722, 1166, 1377, 1462, 1514, 1592, 1631 (C=N), 2854, 2924, 2954.

Preparation of bis(R – 2 – phenylglycianol - 3,5 - dichlorosalicydenaminato)zinc(II) (9)

To a solution of 3,5-dichlorosalicylaldehyde (0.1911 g, 1.00 mmol) dissolved in methanol (50 mL), *R*-(-)-2-phenylglycianol (0.1372 g, 1.00 mmol) was added dropwise and stirred at 313 K for 2 h to give orange solution of ligand. Zinc(II) acetate tetrahydrate (0.1098 g, 0.500 mmol) was added to the resulting solution to give orange solution of the complex. After stirring for 2 h, this crude orange compound was filtered to give orange powder. Yield 0.3114 g (91.1%). Anal. Found: C, 52.1; H, 3.60; N, 3.84%. Calc. for $C_{30}H_{24}Cl_4ZnN_2O_4$: C, 52.7; H, 3.54; N, 4.10%. IR (Nujol (cm^{-1})): 722, 1161, 1305, 1377, 1461, 1519, 1626 (C=N), 2360, 2854, 2924, 2955.

Preparation of Hybrid Materials as PMMA Films

Acetone solution (1 mL) of **1-6** and (2 mL) of PMMA (10%) were cast onto a slide glass overnight to give rise to PMMA film of hybrid materials **1+PMMA** - **6+PMMA**, respectively. While, acetone solution (1 mL) of **AZ** (0.0018 g in 10 mL acetone), acetone solution (1 mL) of **7-9** (0.0017 g in 5 mL acetone) and acetone solution (2 mL) of **PMMA** (10%) were cast onto a slide glass to give rise to **PMMA** film of hybrid materials **7+AZ+PMMA** - **9+AZ+PMMA**, respectively.

Physical Measurements

Elemental analyses were carried out with a Perkin-Elmer 2400 II CHNS/O analyzer at Tokyo University of Science. IR spectra were recorded on a JASCO FT-IR 4200 plus spectrophotometer. UV-vis absorption spectra were recorded

on a JASCO V-570 or V-650 UV/VIS/(NIR) spectrophotometer equipped with a polarizer at 298K. CD spectra were recorded on a JASCO J-820 or J-720WI spectrophotometer at 298K. Photo-irradiation was carried out with D₂ light source for 200-350 nm (with a visible cut filter) and Xe light source 350-800 nm (with a UV cut filter) with a polarizer. Photo-illumination were carried out using a lamp with optical filters (UV $\lambda = 200 - 400$ nm) leading to a sample by using optical fibres, quarter wave plate (Sigma Koki) and polarizer through optical filters. UV light at 260, 318, and 380 nm was carried out using linear polarized undulator radiation with quarter wave plate at UVSOR BL-1U [44].

Computational Methods

All calculations were performed using the Gaussian 09W software Revision A.02 (Gaussian, Inc.) [45]. The gas phase geometry optimizations were carried out using TD-DFT with B3LYP functional. The vertical excitation energy was calculated with ZINDO and Lanl2dz (TD-DFT) for Ni, Cu and Zn and with the 6-31+G(d) basis set for H, C, N, O, and Cl method based on the singlet ground state geometry.

CONCLUSION

In summary, we have prepared several organic/inorganic hybrid materials of **AZ** and Schiff base Ni(II), Cu(II), and Zn(II) complexes as **PMMA** cast films.

Linearly polarized UV light irradiation resulted in increasing optical anisotropy, which was observed not only polarized UV-vis spectra (overlapped bands) but also polarized IR spectra (separated bands, N = N of **AZ** and C = N of complexes). The order of this effect (**Cu** > **Ni** > **Zn**) is attributed to the arrangement (not magnitude) of transition electric dipole moments. According to preferred coordination geometries, [44-53] it suggests less susceptible to orientation by **AZ**. From this fact, optical anisotropy differences in the flexibility of coordination environment of the metal centre of the complex give rise to differences in the interaction with **AZ**.

Circularly polarized UV light irradiation resulted in increasing intensity of CD bands around 320 nm, which suggested induced chiral molecular orientation. Continuous wavelength circularly polarized UV light irradiation resulted in increasing intensity of CD bands, which suggested induced chiral

molecular orientation according to calculated dipole moment. On the other hand, using a light source having a narrow wavelength width in UVSOR (wavelength selective (260, 318(π - π^* of **AZ**) and 380 nm), induced chiral order is caused absorption wavelength selective, which suggests that it is a new information of the radiated light only.

We discussed the assignment and the origin of CD bands of hybrid materials of chiral metal complexes and **AZ** after polarized light irradiation by TD-DFT calculations and coupled oscillator model respectably.

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