

**Polarized UV Light Induced Molecular  
Arrangement Depending on Flexibility of Chiral  
Schiff Base Ni(II), Cu(II), and Zn(II) Complexes by  
Azobenzene in PMMA Matrix**

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**Abstract**

Three chiral Schiff base (bis(*N-R*-2-phenylpropyl-3,5-dibromosalicydenaminato)) nickel(II), copper(II), and zinc(II) complexes and their hybrid materials with azobenzene (**AZ**) have been investigated by means of electronic and CD (circular dichroism) spectra in PMMA matrix. Due to Weigert effect, metal complexes as well as **AZ** increased their optical anisotropy after linearly polarized UV light, which was confirmed by with polarized electronic and IR spectra. Furthermore, we have measured CD spectra before and after circularly polarized UV light. We have found that supramolecular chirality resulting from molecular arrangement could be induced for rigid Zn(II) complex was larger than that of flexible Ni(II) or Cu(II) complexes.

**Keywords:** Polarized light, Weigert effect, Azobenzene, Schiff base complexes

**Introduction**

In recent years, we have systematically reported on preparation (combination

of azo-dyes and metal complexes) and control as well as detection of photo-induced molecular arrangement for organic/inorganic hybrid materials in polymer matrix [1-5]. Theoretical understanding about dipole-dipole interactions of polarized optical spectra [1, 2], effects of chiral azo-dyes [3] as well as chiral Schiff base complexes [4] have been investigated besides conventional cis-trans photoisomerization of azobenzene (**AZ**) [5] and Weigert effect, which induced optical anisotropy by (linearly) polarized UV light irradiation. In this way, positive applications of it may provide useful methodology for researches of softmatters or organic/inorganic hybrid materials.

When chiral materials are treated in the solid states or as softmatters keeping molecular orientation [6], so-called artifact due to solid-state CD spectra sometimes may make it impossible to carry out accurate measurements. Some instruments have been developed to overcome this problem [7, 8]. Recently, we have attempted to discuss its effect in view of viscosity of softmatter matrix [9, 10] and separate real CD peaks [11]. In this way, technical preparation for supramolecular (helical) molecular orientation induced by circularly polarized UV light has been established and ready at present.

Herein, we have investigated on organic/inorganic hybrid materials of **AZ** and chiral Schiff base (bis(*N-R*-2-phenylpropyl-3,5-dibromosalicydenaminato)) nickel(II) (**Ni**), copper(II) (**Cu**), and zinc(II) (**Zn**) complexes (Fig. 1) in PMMA matrix. These systems of hybrid materials potentially exhibit Weigert effect after polarized UV light irradiation. In addition, we investigate correlation between molecular flexibility of metal complexes and polarized light induced molecular arrangement by both linearly and circularly polarized UV light.

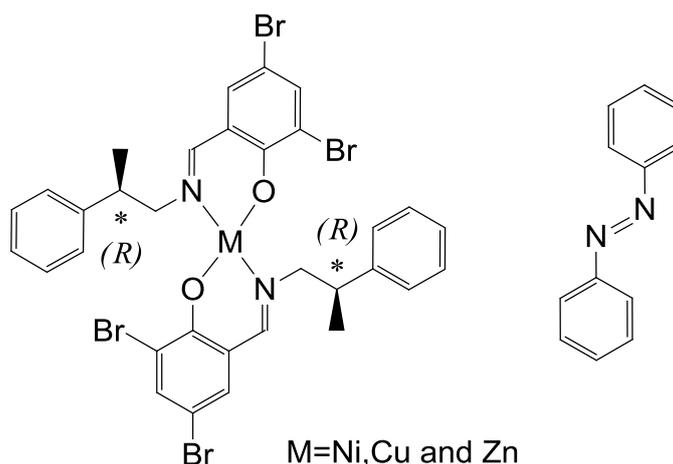


Fig. 1. Molecular structures of azobenzene [**AZ**] and bis(*N-R*-2-phenylpropyl-3,5-dibromosalicydenaminato) nickel(II) [**Ni**], copper(II) [**Cu**], and zinc(II) [**Zn**] (M = Ni, Cu, and Zn, respectively).

## Experimental Sections

*Procedures.* Chemicals of the highest commercial grade available (solvents are from Kanto Chemical, organic compounds are from Tokyo Chemical Industry and metal sources from Wako) were used as received without further purification.

*Preparation of Ni.* To a solution of 3,5-dibromosalicylaldehyde (2.7991 g, 10 mmol) dissolved in methanol (50 mL), *R*-(+)- $\beta$ -methylphenethylamine (1.3612 g, 10 mmol) was added and stirred at 313 K for 2 h to give dark orange solution of ligand. Nickel(II) acetate tetrahydrate (1.2458 g, 5 mmol) was added to the resulting solution to give dark green solution of the complex. After stirring for 4 h, this crude dark green compound was filtered and recrystallized from methanol. Yield 3.9307 g (92.4%). Anal. Found: C, 45.17; H, 3.32; N, 3.29%. Calc. for  $C_{32}H_{28}NiBr_4N_2O_2$ : C, 44.83; H, 2.87; N, 3.15 %. IR (Nujol mull ( $cm^{-1}$ )): 665(w), 698(s), 720(s), 745(m), 761(m), 859(m), 959(w), 1011(w), 1023(w), 1168(s), 1215(m), 1293(w), 1315(s), 1375(w), 1385(w), 1411(m), 1436(s), 1494(w), 1515(w), 1580(w), 1612(s) (C=N). Electronic spectra (nm): 337, 412, 606 (acetone); 249, 384, 578 (methanol); 249, 263, 336, 423, 623 (chloroform).

*Preparation of Cu.* To a solution of 3,5-dibromosalicylaldehyde (0.8399 g, 3 mmol) dissolved in methanol (50 mL), *R*-(+)- $\beta$ -methylphenethylamine (0.4199 g, 3 mmol) was added and stirred at 313 K for 2 h to give orange solution of ligand. Copper(II) acetate monohydrate (0.2996 g, 1.5 mmol) was added to the resulting solution to give yellowish brown solution of the complex. After stirring for 4 h, this crude yellowish brown compound was filtered and recrystallized from methanol. Yield 1.2061 g (93.8 %). Anal. Found: C, 44.91; H, 3.30; N, 3.27 %. Calc. for  $C_{32}H_{28}CuBr_4N_2O_2$ : C, 44.84; H, 2.89; N, 3.07 %. IR (Nujol mull, ( $cm^{-1}$ )): 619(w), 627(w), 698(s), 752(m), 769(m), 849(m), 865(m), 971(w), 1157(s), 1212(m), 1318(m), 1387(m), 1411(m), 1439(s), 1493(w), 1510(m), 1578(m), 1615(s) (C=N). Electronic spectra (nm): 378, 587 (acetone); 258, 378, 587 (methanol); 251, 381, 610 (chloroform).

*Preparation of Zn.* To a solution of 3,5-dibromosalicylaldehyde (0.6997 g, 2.5 mmol) dissolved in methanol (50 mL), *R*-(+)- $\beta$ -methylphenethylamine (0.3529 g, 2.5 mmol) was added and stirred at 313 K for 2 h to give orange solution of ligand. Zinc(II) acetate dihydrate (0.2779 g, 1.25 mmol) was added to the resulting solution to give orange solution of the complex. After stirring for 4 h, this crude orange compound was filtered and recrystallized from methanol. Yield 0.7281 g (67.1%). Anal. Found: C, 44.82; H, 3.29; N, 3.27%. Calc. for  $C_{32}H_{28}ZnBr_4N_2O_2$ : C, 45.17; H, 3.11; N, 2.92%. IR (Nujol mull ( $cm^{-1}$ )): 612(w), 668(w), 702(s), 753(m), 760(s), 784(w), 837(w), 867(m), 874(m), 892(w), 915(w), 982(m), 1013(m), 1044(m), 1152(s), 1202(w), 1213(m), 1307(m), 1373(w), 1389(m), 1408(s), 1436(s), 1460(m), 1494(w), 1510(w), 1580(w), 1621(s) (C=N). Electronic spectra (nm): 385(acetone); 242, 381(methanol); 250, 389 (chloroform).

*Preparations of hybrid materials, Ni+AZ+PMMA, Cu+AZ+PMMA and Zn+AZ+PMMA.* Acetone solutions (1 mL) of **AZ** ( $1.7 \times 10^{-3}$  g in 10 mL acetone), acetone solutions (1 mL) of **Ni** ( $4.3 \times 10^{-3}$  g in 10 mL acetone) or **Cu** ( $4.2 \times 10^{-3}$  g in 10 mL acetone), or **Zn** ( $4.3 \times 10^{-3}$  g in 10 mL acetone) and acetone solution (2 mL) of **PMMA** (10%) were mixed and were cast on to a slide glass at room temperature.

*Physical Measurements.* Elemental analyses (C, H, N) were carried out with a Perkin-Elmer 2400II CHNS/O analyzer at Tokyo University of Science. Infrared spectra were recorded as Nujol mull on a JASCO FT-IR 4200 plus spectrophotometer equipped with polarizer in the range of 4000-400  $\text{cm}^{-1}$  at 298 K. Absorption spectra were measured on a JASCO V-570 UV/VIS/NIR spectrophotometer or a JASCO V-650 spectrophotometer equipped with polarizer in the range of 800-220 nm at 298 K. Photo-illumination were carried out using a lamp (1.0  $\text{mW}/\text{cm}^2$ ) with optical filters (UV  $\lambda = 200\text{-}400$  nm) (and  $\lambda/4$  filter for circularly polarized UV light) leading to a sample by using optical fibers and polarizer through optical filters.

## Results and Discussion

*Linearly polarized UV light induced optical anisotropy.* Tables 1 and 2 summarized optical anisotropic R and S values of hybrid materials **Ni+AZ+PMMA**, **Cu+AZ+PMMA** and **Zn+AZ+PMMA** after linearly UV light irradiation. In order for discussion of Weigert effect, the degree of photoinduced optical anisotropy (spectral dichroism) of absorption electronic spectra can be described commonly by these two parameters (R and S):

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

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

Where  $A_{\text{perpendicular}}$  and  $A_{\text{parallel}}$  values denote absorbance measured with the measuring polarizer 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.

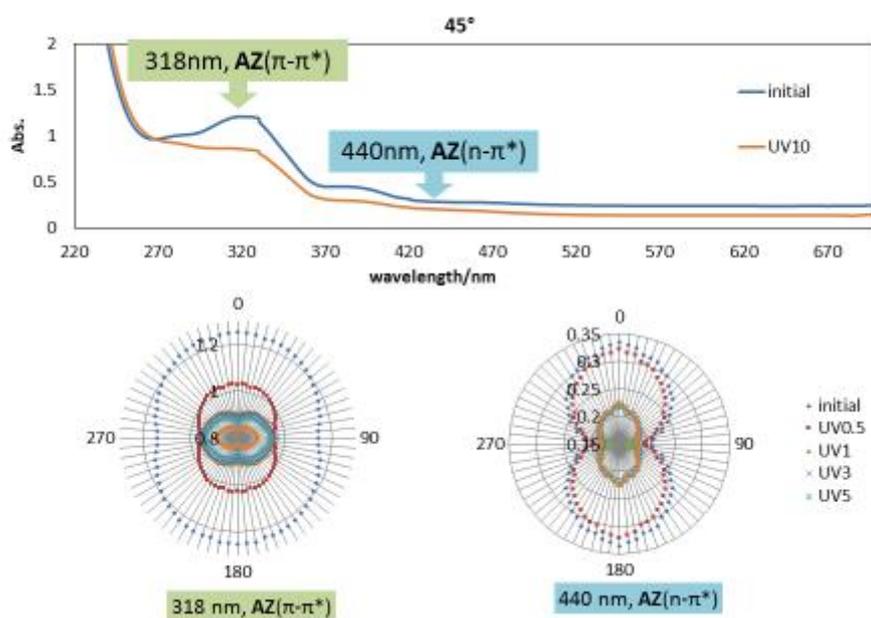
**Table 1.** The R values by UV-vis after linearly polarized UV light irradiation.

UV radiation	minutes	initial	UV0.5	UV1	UV3	UV5	UV10
<b>Ni+AZ+PMMA</b>	318 nm, $\pi$ - $\pi^*$ ( <b>AZ</b> )	0.9887	0.9986	0.983	0.9699	0.9672	0.9699
	440 nm, $n$ - $\pi^*$ ( <b>AZ</b> )	0.9633	1.0131	0.9856	0.9957	0.9993	1.0092
	606 nm, d-d ( <b>Ni</b> )	0.8851	1.0115	0.9374	0.9705	0.9775	1.0063
<b>Cu+AZ+PMMA</b>	318 nm, $\pi$ - $\pi^*$ ( <b>AZ</b> )	1.0191	0.9978	0.9762	0.9708	0.9643	0.9716
	440 nm, $n$ - $\pi^*$ ( <b>AZ</b> )	1.0573	1.0629	1.0862	1.0905	1.0972	1.1052
	587 nm, d-d ( <b>Cu</b> )	1.1052	1.1155	1.1653	1.1811	1.1986	1.2246
<b>Zn+AZ+PMMA</b>	318 nm, $\pi$ - $\pi^*$ ( <b>AZ</b> )	1.0981	1.0763	0.9514	0.9219	0.9199	0.9302
	440 nm, $n$ - $\pi^*$ ( <b>AZ</b> )	1.7022	1.6521	1.3849	1.2392	1.2375	1.2337

**Table 2.** The S values by UV-vis after linearly polarized UV light irradiation.

UV	radiation minutes	initial	UV0.5	UV1	UV3	UV5	UV10
<b>Ni+AZ+PMMA</b>	318 nm, $\pi-\pi^*$ ( <b>AZ</b> )	-0.0038	-0.0005	-0.0057	-0.0101	-0.0111	-0.0101
	440 nm, $n-\pi^*$ ( <b>AZ</b> )	-0.0124	0.0043	-0.0048	-0.0014	-0.0002	0.0031
	606 nm, d-d ( <b>Ni</b> )	-0.0398	0.0038	-0.0213	-0.0099	-0.0076	0.0021
<b>Cu+AZ+PMMA</b>	318 nm, $\pi-\pi^*$ ( <b>AZ</b> )	0.0063	-0.0007	-0.008	-0.0098	-0.012	-0.0095
	440 nm, $n-\pi^*$ ( <b>AZ</b> )	0.0187	0.0205	0.0279	0.0293	0.0314	0.0339
	587 nm, d-d ( <b>Cu</b> )	0.0339	0.0371	0.0522	0.0569	0.0621	0.0696
<b>Zn+AZ+PMMA</b>	318 nm, $\pi-\pi^*$ ( <b>AZ</b> )	0.0317	0.0248	-0.016	-0.027	-0.027	-0.024
	440 nm, $n-\pi^*$ ( <b>AZ</b> )	0.1897	0.1786	0.1137	0.0738	0.0734	0.0723

Assignment of spectral peaks was in agreement with the analogous compounds [12]. As listed in Tables 1 and 2,  $\pi-\pi^*$  and  $n-\pi^*$  bands of **AZ** were directly changed by Weigert effect, while d-d bands of **Ni** or **Cu** were changed by supramolecular interaction in softmatter PMMA matrix. As shown in Fig. 2 for **Zn+AZ+PMMA** for example, **Zn** did not exhibit d-d bands because of  $d^{10}$  configuration of Zn(II) center.



**Fig. 2.** [Above] Polarized electronic spectra for **Zn+AZ+PMMA** after linearly polarized UV light irradiation. [Below] Polarizer angle dependence of absorbance of electronic spectra for **Zn+AZ+PMMA** after linearly polarized UV light irradiation.

In order for selective observation of component, in other words proof of supramolecular interaction from Weigert effect to optical anisotropy, polarized IR spectra were measured of which C=N bands of metal complexes used as a probe

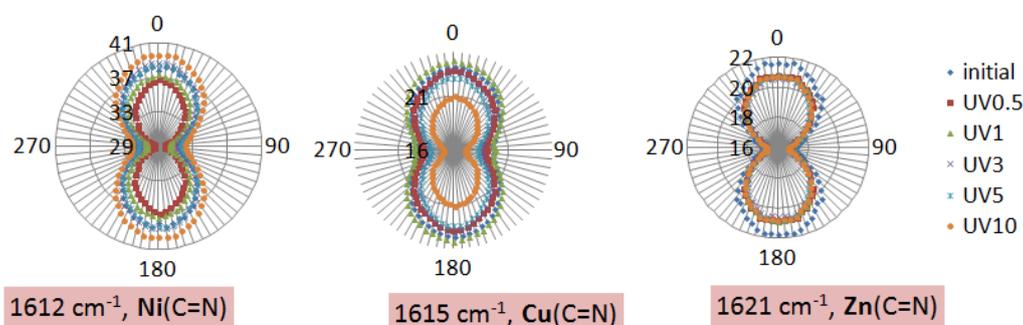
to detect each component separately [13]. Tables 3 and 4 summarized optical anisotropic R and S values from polarized IR spectra of hybrid materials **Ni+AZ+PMMA**, **Cu+AZ+PMMA** and **Zn+AZ+PMMA** after linearly UV light irradiation. Fig. 3 depicts angular dependence of C=N band intensity during rotation of a polarizer.

**Table 3.** The R values by IR after linearly polarized UV light irradiation.

UV radiation minutes	initial	UV0.5	UV1	UV3	UV5	UV10
<b>Ni+AZ+PMMA</b> 1612 cm <sup>-1</sup> , C=N(Ni)	1.1998	1.2396	1.2285	1.2377	1.2189	1.2279
<b>Cu+AZ+PMMA</b> 1615 cm <sup>-1</sup> , C=N(Cu)	1.2122	1.2261	1.231	1.2674	1.2468	1.2303
<b>Zn+AZ+PMMA</b> 1621 cm <sup>-1</sup> , C=N(Zn)	1.2632	1.2315	1.2309	1.2282	1.2259	1.2284

**Table 4.** The S values by IR after linearly polarized UV light irradiation.

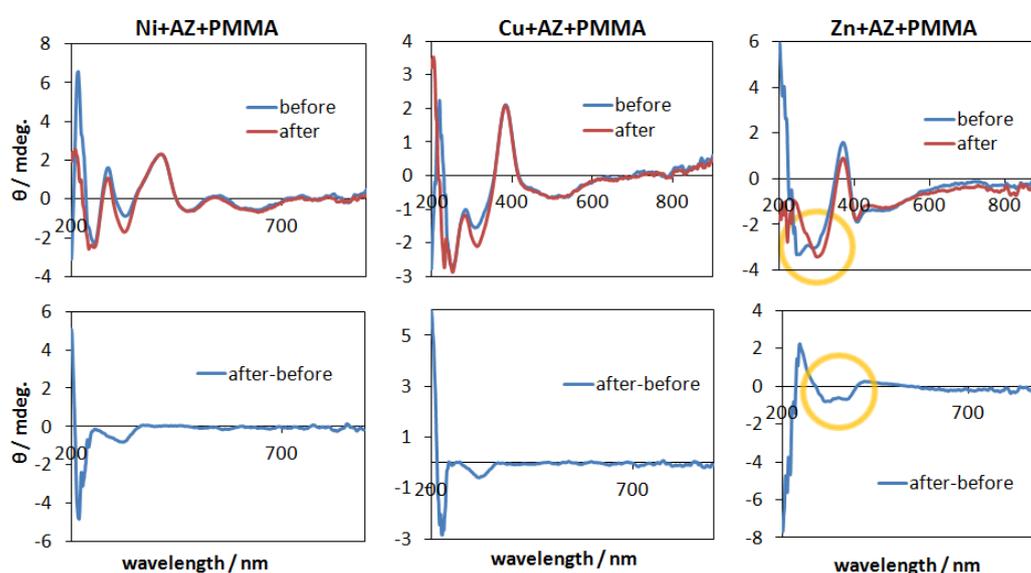
UV radiation minutes	initial	UV0.5	UV1	UV3	UV5	UV10
<b>Ni+AZ+PMMA</b> 1612 cm <sup>-1</sup> , C=N(Ni)	0.0624	0.0739	0.0708	0.0734	0.068	0.0706
<b>Cu+AZ+PMMA</b> 1615 cm <sup>-1</sup> , C=N(Cu)	0.0661	0.0701	0.0715	0.0818	0.076	0.0713
<b>Zn+AZ+PMMA</b> 1621 cm <sup>-1</sup> , C=N(Zn)	0.0807	0.0716	0.0715	0.0707	0.07	0.0708



**Fig. 3.** Polarizer angle dependence of absorbance of C=N bands in IR spectra for **Ni+AZ+PMMA** [left], **Cu+AZ+PMMA** [middle], and **Zn+AZ+PMMA** [right] after linearly polarized UV light irradiation for 0, 0.5, 1, 3, 5, and 10 min.

*Circularly polarized UV light induced optical anisotropy.* Fig. 3 depicts CD spectra of hybrid materials **Ni+AZ+PMMA**, **Cu+AZ+PMMA** and **Zn+AZ+PMMA** before and after circularly UV light irradiation. Because of helical molecular arrangement **AZ** directly induced by UV light irradiation, supramolecular chiral arrangement was also induced for the hybrid materials.

Therefore, CD bands (especially intensity in  $\pi$ - $\pi^*$  region of the chiral metal complexes) are changed after circularly UV light irradiation for three hybrid materials. It should be noted that characteristic CD peak shift around 250-350 nm could be observed only for **Zn+AZ+PMMA** (highlighted by circles in Fig. 4). To our knowledge, this is the first observation of CD spectral changes attributed to light induced supramolecular chiral arrangement of not azo-dyes mainly [14] but metal complexes clearly. In contrast to flexible **Ni** or **Cu**, rigid **Zn** containing electron-withdrawing Br-groups can be effectively communicated supramolecular chiral arrangement from directly photo-responsive component **AZ**.



**Fig. 4.** [Above] CD spectra for **Ni+AZ+PMMA**, **Cu+AZ+PMMA**, and **Zn+AZ+PMMA** before and after circularly polarized UV light irradiation. [Below] Difference CD spectra for **Ni+AZ+PMMA**, **Cu+AZ+PMMA**, and **Zn+AZ+PMMA** before and after circularly polarized UV light irradiation.

## Conclusions

In summary, we have prepared organic/inorganic hybrid materials (**Ni+AZ+PMMA**, **Cu+AZ+PMMA**, and **Zn+AZ+PMMA**) and not only linearly but also circularly polarized UV light irradiation induced increasing optical anisotropy due to Weigert effect of **AZ** and supramolecular chiral arrangement, respectively. As for the effects of circularly polarized UV light irradiation, rigid **Zn** more effectively communicates the changes of molecular arrangement than flexible **Ni** or **Cu**. This was confirmed by characteristic shift of the difference CD peaks.

## Acknowledgements

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