

**Linearly, Circularly, or Non-Polarized Light
Induced Supramolecular Arrangement of
Diastereomer Schiff Base Ni (II), Cu (II),
and Zn (II) Complexes by Azobenzene
in PMMA Matrix**

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Abstract

Three pairs of diastereomers of Schiff base bis(*N*-2-hydroxy-1-isopropyl-3,5-di-bromosalicydenaminato)nickel(II), copper(II), and zinc(II) complexes and their organic/inorganic hybrid materials with azobenzene (**AZ**) in PMMA cast thin films have been investigated by means of polarized electronic and IR spectra and CD (circular dichroism) spectra. Due to Weigert effect for **AZ**, not only **AZ** but also metal complexes dispersed separately increased optical anisotropy after linearly polarized UV light irradiation, while supramolecular chirality after circularly polarized UV light irradiation. Besides control results by non-polarized light, optical anisotropy and supramolecular chirality were confirmed by polarized spectra (overlapped π - π^* and n - π^* bands and d-d bands for electronic or C=N bands for IR) and CD spectra, respectively. Degree of induced optical anisotropy mainly depends on flexibility of central metal ions (less depends on diastereomers about ligands), while degree of induced supramolecular chirality mainly depends on chirality of ligands. In other words, optical active complexes are easy to form chiral supramolecular arrangement after circularly polarized UV light irradiation.

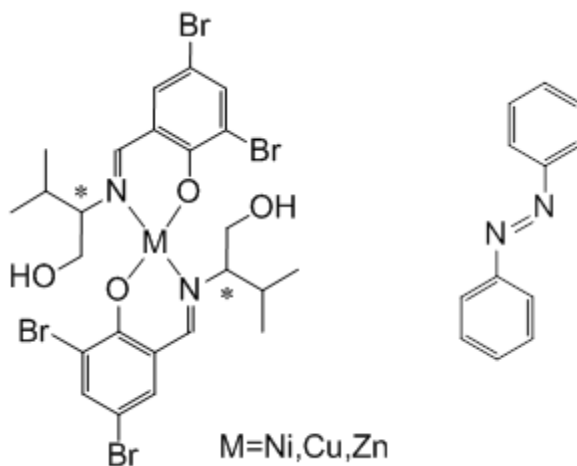
Keywords: Polarized light, Weigert effect, Azobenzene, Schiff base complexes

Introduction

Systematically we have investigated on preparation organic/inorganic hybrid materials in polymer matrix (combination of azo-dyes and metal complexes) and control as well as detection of photo-induced molecular arrangement [1-6] focused on dipole-dipole interactions, various photofunctions of azo-dyes [7-9], structures of Schiff base complexes [10-11]. A well-known phenomenon to enhance optical anisotropy of azo-dyes by linearly polarized UV light, namely Weigert effect, may be a quite useful reason of not only basic methodology but also application of these researches of soft-matters or organic/inorganic hybrid materials.

To measure molecular orientation [12-14] or supramolecular chirality [15-17], there are some problems about spectroscopy, namely artifact CD peaks in the solid state [18-21]. In previous paper [22], we have attempted to discuss its effect in view of viscosity of soft-matter matrix and separate real CD peaks. In this way, technical preparation for supramolecular (helical) molecular orientation induced by circularly polarized UV light has been established. Besides Weigert effect for linearly polarized light, supramolecular chirality after circularly polarized UV light irradiation should be expected in analogy with liquid crystals [23-25].

Herein, we have investigated three pairs of diastereomers of Schiff base bis(*N*-2-hydroxy-1-isopropyl-3,5-dibromosalicydenamino)nickel(II), copper(II), and zinc(II) complexes (optically active ones are abbreviated as **Ni**, **Cu**, **Zn**, respectively, while meso ones are abbreviated as **Ni'**, **Cu'**, **Zn'**, respectively) and their organic/inorganic hybrid materials with azobenzene (**AZ**) in PMMA cast thin films (Scheme 1). The main question in this present study is correlation between molecular factors (flexibility [2] or chirality [26]) of metal complexes and polarization (non-polarized, linearly-polarized, or circularly-polarized) of light in the supramolecular interactions.



Scheme 1. Structures of [left] optically active (asymmetric carbons are *R* and *R*-configurations) complexes (**Ni**, **Cu**, and **Zn**) and meso (asymmetric carbons are *R* and *S*-configurations) complexes (**Ni'**, **Cu'**, and **Zn'**) and [right] azobenzene (**AZ**).

Experimental Sections

General 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. Chiral (optically active; **Ni**, **Cu**, and **Zn**) and achiral (meso; **Ni'**, **Cu'**, and **Zn'**) Schiff base Ni(II), Cu(II), and Zn(II) complexes, respectively, served for hybrid materials were prepared.

Preparation of optically active bis(N-2-hydroxy-1-isopropyl-3,5-dibromosalicydenaminato) nickel(II) (Ni). To a solution of 3,5-dibromosalicylaldehyde (0.2798 g, 1 mmol) dissolved in methanol (50 mL), *D*-valinol (0.1269 g, 1 mmol) was added and stirred at 313 K for 2 h to give yellow solution of ligand. Nickel(II) acetate tetrahydrate (0.1244 g, 0.5 mmol) was added to the resulting solution to give green solution of the complex. After stirring for 4 h, this crude green compound was filtered and recrystallized from methanol. Yield 0.2665 g (67.7%). Anal. Found: C, 36.67; H, 3.94; N, 3.43%. Calc. for $C_{24}H_{28}NiBr_4N_2O_4 \cdot CH_3OH$: C, 36.64; H, 3.59; N, 3.56 %. IR (Nujol mull (cm^{-1})): 691(w), 720(m), 757(w), 864(w), 1060(w), 1140(w), 1212(w), 1306(w), 1377(m), 1462(m), 1500(w), 1574(w), 1633(w) (C=N), 2853(s), 2923(s), 2954(s). Electronic spectra (nm): 392, 607 (acetone); 236, 260, 389, 603 (methanol); 250, 344, 396 (chloroform).

Preparation of optically active bis(N-2-hydroxy-1-isopropyl-3,5-dibromosalicydenaminato) copper (II) (Cu). To a solution of 3,5-dibromosalicylaldehyde (0.2800 g, 1 mmol) dissolved in methanol (50 mL), *D*-valinol (0.1125 g, 1 mmol) was added and stirred at 313 K for 2 h to give yellow solution of ligand. Copper(II) acetate monohydrate (0.0998 g, 0.5 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 0.2735 g (69.1%). Anal. Found: C, 36.45; H, 3.92; N, 3.40%. Calc. for $C_{24}H_{28}CuBr_4N_2O_4 \cdot CH_3OH$: C, 36.41; H, 3.56; N, 3.54 %. IR (Nujol mull (cm^{-1})): 714(w), 737(w), 754(w), 864(w), 1047(w), 1148(m), 1211(w), 1315(w), 1377(m), 1405(w), 1443(m), 1462(m), 1502(w), 1580(w), 1629(m) (C=N), 2854(s), 2925(s), 2454(s). Electronic spectra (nm): 385, 608 (acetone); 250, 382, 633 (methanol); 250, 388, 603 (chloroform).

Preparation of optically active bis(N-2-hydroxy-1-isopropyl-3,5-dibromosalicydenaminato) zinc (II) (Zn). To a solution of 3,5-dibromosalicylaldehyde (0.2798 g, 1 mmol) dissolved in methanol (50 mL), *D*-valinol (0.1153 g, 1 mmol) was added and stirred at 313 K for 2 h to give yellow solution of ligand. Zinc(II) acetate dihydrate (0.1098 g, 0.5 mmol) was added to the resulting solution to give yellow solution of the complex. After stirring for 4 h, this crude yellow compound was filtered and recrystallized from methanol. Yield 0.2906 g (73.2%). Anal. Found: C,

36.37; H, 3.91; N, 3.29%. Calc. for $C_{24}H_{28}ZnBr_4N_2O_4 \cdot CH_3OH$: C, 36.33; H, 3.56; N, 3.53 %. IR (Nujol mull (cm^{-1})): 694(w), 718(m), 754(w), 866(w), 1064(m), 1146(m), 1210(m), 1301(m), 1377(s), 1409(m), 1456(s), 1504(w), 1576(w), 1615(m) (C=N), 2855(s), 2934(s). Electronic spectra (nm): 385 (acetone); 243, 382 (methanol); 249, 388 (chloroform).

Preparation of meso bis(N-2-hydroxy-1-isopropyl-3,5-dibromosalicydenaminato) nickel(II) (Ni'). To a solution of 3,5-dibromosalicylaldehyde (0.2799 g, 1 mmol) dissolved in methanol (50 mL), *DL*-valinol (0.1512 g, 1 mmol) was added dropwise and stirred at 313 K for 2 h to give yellow solution of ligand. Nickel(II) acetate tetrahydrate (0.1244 g, 0.5 mmol) was added to the resulting solution to give greenish yellow solution of the complex. After stirring for 4 h, this crude greenish yellow compound was filtered and recrystallized from methanol. Yield 0.2675 g (68.0%). Anal. Found: C, 36.43; H, 3.93; N, 3.06%. Calc. for $C_{24}H_{28}NiBr_4N_2O_4$: C, 36.64; H, 3.59; N, 3.56 %. IR (KBr (cm^{-1})): 691(w), 721(w), 862(w), 1064(w), 1140(m), 1208(w), 1318(w), 1385(w), 1409(m), 1440(s), 1504(w), 1578(w), 1638(s) (C=N), 2964(m), 3292(m).

Preparation of meso bis(N-2-hydroxy-1-isopropyl-3,5-dibromosalicydenaminato) copper(II) (Cu'). To a solution of 3,5-dibromosalicylaldehyde (0.2799 g, 1 mmol) dissolved in methanol (50 mL), *DL*-valinol (0.1512 g, 1 mmol) was added dropwise and stirred at 313 K for 2 h to give yellow solution of ligand. Copper(II) acetate monohydrate (0.0998 g, 0.5 mmol) was added to the resulting solution to give dark green solution of the complex. After stirring for 4 h, this crude green compound was filtered and recrystallized from acetone/methanol. Yield 0.2918 g (73.7%). Anal. Found: C, 33.78; H, 2.96; N, 3.01 %. Calc. for $C_{24}H_{28}CuBr_4N_2O_4 \cdot 2(CH_3OH)$: C, 33.68; H, 3.29; N, 3.27 %. IR (KBr, (cm^{-1})): 708(w), 738(w), 866(w), 1049(w), 1148(m), 1206(w), 1315(w), 1407(w), 1442(s), 1503(w), 1581(w), 1631(s) (C=N), 2871(w), 2958(w), 3464(w).

Preparation of meso bis(N-2-hydroxy-1-isopropyl-3,5-dibromosalicydenaminato) zinc(II) (Zn'). To a solution of 3,5-dibromosalicylaldehyde (0.2799 g, 1 mmol) dissolved in methanol (50 mL), *DL*-valinol (0.1512 g, 1 mmol) was added dropwise and stirred at 313 K for 2 h to give yellow solution of ligand. Zinc(II) acetate dihydrate (0.1098 g, 0.5 mmol) was added to the resulting solution to give orange solution of the complex. After stirring for 4 h, this crude yellow compound was filtered and recrystallized from methanol. Yield 0.2137 g (53.5%). Anal. Found: C, 34.84; H, 3.22; N, 3.10%. Calc. for $C_{24}H_{28}ZnBr_4N_2O_4 \cdot (CH_3OH)$: C, 34.91; H, 3.42; N, 3.39%. IR (KBr (cm^{-1})): 693(w), 712(w), 869(w), 1062(w), 1146(m), 1214(w), 1318(w), 1388(m), 1416(m), 1444(s), 1508(w), 1580(m), 1620(s) (C=N), 2961(m), 3428(s).

Preparations of hybrid materials, Ni+AZ+PMMA, Cu+AZ+PMMA and Zn+AZ+PMMA. For UV-vis spectroscopy, acetone solutions **AZ** (1.83×10^{-3} g, 1.00×10^{-5} mol) and **PMMA** were mixed and acetone solutions of **Ni** (3.93×10^{-3} g, 5.0×10^{-6} mol) or **Cu** (3.95×10^{-3} g, 5.0×10^{-6} mol), or **Zn** (3.96×10^{-3} g, 5.0×10^{-6} mol) and acetone solutions **PMMA** were mixed and were cast on to a slide glass at room temperature. The corresponding *hybrid materials* of meso forms,

Ni'+AZ+PMMA, **Cu'+AZ+PMMA** and **Zn'+AZ+PMMA**, were also prepared in similar way.

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 KBr on a JASCO FT-IR 4200 plus spectrophotometer equipped with polarizer in the range of 4000-400 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 mW/cm^2) with optical filters (UV $\lambda = 200\text{-}400$ nm) leading to a sample by using optical fibers and polarizer through optical filters.

Results and Discussion

Linearly polarized UV light induced optical anisotropy. Assignment of spectral bands was done based on the analogous compounds [2]. However, **Zn** and **Zn'** did not exhibit d-d bands because of d^{10} configuration of Zn(II) ions (Fig. 1).

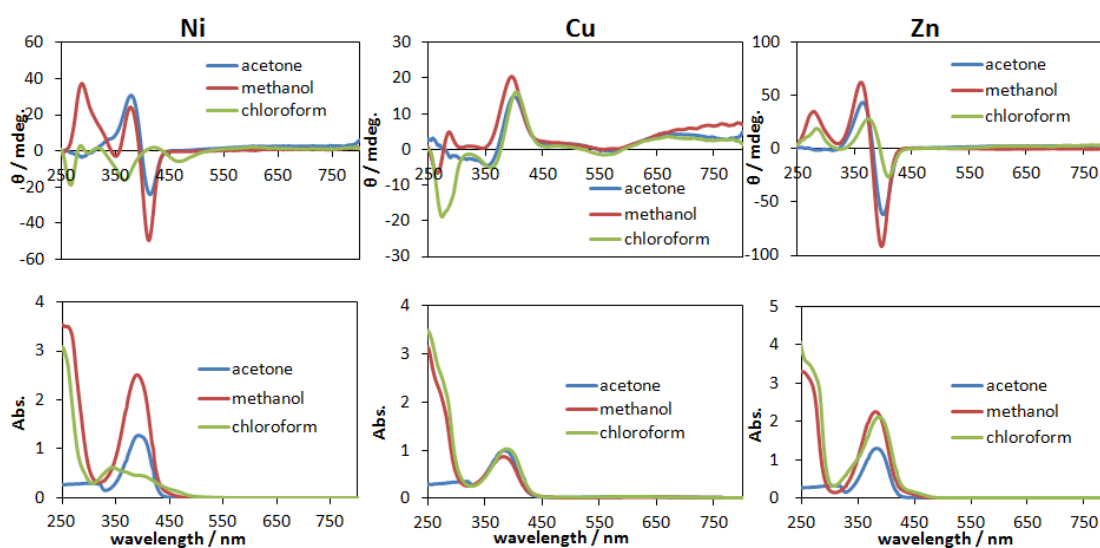


Fig. 1. Electronic and CD spectra of chiral **Ni**, **Cu**, and **Zn** complexes in acetone, methanol, and chloroform solutions.

Tables 1 and 2 summarized anisotropic parameters (R and S values) for polarized absorption spectra of hybrid materials **Ni+AZ+PMMA**, **Cu+AZ+PMMA**, **Zn+AZ+PMMA**, **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_{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. The π - π^* (318 nm) and n - π^* (440 nm) bands of **AZ** were directly changed by Weigert effect, while d-d bands of **Ni** (607 nm), **Cu** (608 nm), **Ni'** (606 nm) or **Cu'** (611 nm) were changed by supramolecular interaction in soft-matter PMMA matrix.

Initial large changes of π - π^* band intensity are attributed to cis-trans photoisomerization of **AZ**. Being focused on common π - π^* bands around 318 nm, the R values after linearly polarized UV light irradiation for 10 min are 0.9935, 0.9562, and 0.8673 for chiral materials **Cu+AZ+PMMA**, **Zn+AZ+PMMA**, and **Ni+AZ+PMMA**, respectively. As for the corresponding R values are 1.0051, 0.9466, and 0.9343 for achiral materials **Cu'+AZ+PMMA**, **Zn'+AZ+PMMA**, and **Ni'+AZ+PMMA**, respectively.

In this way, after linearly UV light irradiation, the order of the degree of (increasing of) optical anisotropy is **Ni(Ni')** > **Zn(Zn')** > **Cu(Cu')**, which suggests that flexibility of central metal ions is more important molecular factors than chirality of organic ligand moieties.

Table 1. The R values of anisotropic parameters polarized absorption spectra after liner polarized UV light irradiation.

UV radiation minutes	initial	UV0.5	UV1	UV3	UV5	UV10	
Ni+AZ+PMMA	318 nm, π - π^* (AZ)	0.9679	0.9602	1.2730	0.9553	0.9414	0.8673
	440 nm, n - π^* (AZ)	1.0005	1.0404	3.5596	1.0316	1.0069	0.9614
	607 nm, d-d (Ni)	0.9856	1.0691	8.9349	1.0498	1.0001	0.9191
Cu+AZ+PMMA	318 nm, π - π^* (AZ)	1.0055	1.0155	0.9974	0.9971	1.0201	0.9935
	440 nm, n - π^* (AZ)	1.0370	1.0980	1.0215	1.0511	1.1153	1.0475
	608 nm, d-d (Cu)	1.0541	1.1299	1.0332	1.0707	1.1608	1.0668
Zn+AZ+PMMA	318 nm, π - π^* (AZ)	0.9954	0.9816	0.9711	0.9639	0.9714	0.9562
	440 nm, n - π^* (AZ)	1.1979	1.2108	1.1863	1.2166	1.3280	1.1996

Table 1. (Continued): The R values of anisotropic parameters polarized absorption spectra after liner polarized UV light irradiation.

Ni'+AZ+ PMMA	318 nm, $\pi-\pi^*$ (AZ)	0.9728	0.9205	0.9518	0.9220	0.9829	0.9343
	440 nm, $n-\pi^*$ (AZ)	0.9528	0.7752	0.9252	0.8824	1.0563	0.9438
	606 nm, d-d (Ni')	0.9487	0.7408	0.9027	0.8371	1.0967	0.9238
Cu'+AZ+ PMMA	318 nm, $\pi-\pi^*$ (AZ)	1.0189	1.0103	1.0189	1.0148	1.0120	1.0051
	440 nm, $n-\pi^*$ (AZ)	1.1060	1.1302	1.1579	1.1355	1.1373	1.1555
	611 nm, d-d (Cu')	1.1569	1.1872	1.2342	1.1982	1.2028	1.2226
Zn'+AZ+ PMMA	318 nm, $\pi-\pi^*$ (AZ)	1.0017	0.9883	0.9775	0.9543	0.9562	0.9466
	440 nm, $n-\pi^*$ (AZ)	1.1787	1.2377	1.2351	1.2546	1.2610	1.2161

Table 2. The S values of anisotropic parameters polarized absorption spectra after liner polarized UV light irradiation.

UV radiation minutes	initial	UV0.5	UV1	UV3	UV5	UV10	
Ni+AZ+ PMMA	318 nm, $\pi-\pi^*$ (AZ)	-0.0108	-0.0134	0.0834	-0.0151	-0.0199	-0.0463
	440 nm, $n-\pi^*$ (AZ)	0.0002	0.0133	0.4604	0.0104	0.0023	-0.0130
	607 nm, d-d (Ni)	-0.0048	0.0225	0.7256	0.0163	0.0002	-0.0277
Cu+AZ+ PMMA	318 nm, $\pi-\pi^*$ (AZ)	0.0018	0.0051	-0.0009	-0.0010	0.0067	-0.0022
	440 nm, $n-\pi^*$ (AZ)	0.0122	0.0316	0.0071	0.0167	0.0370	0.0156
	608 nm, d-d (Cu)	0.0171	0.0415	0.0110	0.0230	0.0509	0.0262
Zn+AZ+ PMMA	318 nm, $\pi-\pi^*$ (AZ)	-0.0015	-0.0062	-0.0097	-0.0122	-0.0096	-0.0148
	440 nm, $n-\pi^*$ (AZ)	0.0619	0.0657	0.0585	0.0673	0.0985	0.0624
Ni'+AZ+ PMMA	318 nm, $\pi-\pi^*$ (AZ)	-0.0092	-0.0272	-0.0163	-0.0267	-0.0057	-0.0224

Table 2. (Continued): The S values of anisotropic parameters polarized absorption spectra after liner polarized UV light irradiation.

	440 nm, n- π^* (AZ)	-0.0160	-0.0810	-0.0256	-0.0408	0.01843	-0.0191
	606 nm, d-d (Ni')	-0.0174	-0.0945	-0.0335	-0.0574	0.0313	-0.0261
	318 nm, π - π^* (AZ)	0.0063	0.0034	0.0063	0.0049	0.0040	0.0017
Cu'+AZ+ PMMA	440 nm, n- π^* (AZ)	0.0342	0.0426	0.0500	0.0432	0.0438	0.0493
	611 nm, d-d (Cu')	0.0497	0.0587	0.0724	0.0620	0.0633	0.0691
Zn'+AZ+ PMMA	318 nm, π - π^* (AZ)	0.0006	-0.0039	-0.0075	-0.0155	-0.0148	-0.0181
	440 nm, n- π^* (AZ)	0.0562	0.0734	0.0727	0.0782	0.0800	0.0672

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. Absorption frequencies of N=N band of AZ 1633 cm^{-1} and C=N bands depend on metal ions, Ni (1629 cm^{-1} for Cu, 1615 cm^{-1} for Zn, 1638 cm^{-1} for Ni', 1631 cm^{-1} for Cu', 1620 cm^{-1} for Zn'). For example, Fig. 2 depicts angular dependence of C=N band intensity during rotation of a polarizer. Tables 3 and 4 summarized optical anisotropic R and S values of polarized IR spectra of hybrid materials Ni-Zn+AZ+PMMA and Ni'-Zn'+AZ+PMMA after linearly UV light irradiation. Initial change of N=N band feature is attributed to cis-trans photoisomerization of free AZ. The circular diagrams suggest that reorientation of AZ effects on optical anisotropy observed by C=N bands. Moreover, the features of C=N band of complexes are also influenced by the effect of reorientation.

On the other hand, the R values after polarized UV light irradiation for 10 min are 1.2323, 1.2344, 1.2595, 1.1537, 1.2126, and 1.2499 for Ni+AZ+PMMA, Cu+AZ+PMMA, Zn+AZ+PMMA, Zn'+AZ+PMMA, Cu'+AZ+PMMA, and Ni'+AZ+PMMA, respectively. Neglecting the effect due to overlapping spectral bands, the results are in agreement with the results based on electronic spectra essentially.

Table 3. The R values of anisotropic parameters polarized IR spectra after liner polarized UV light irradiation.

UV radiation minutes	initial	UV0.5	UV1	UV3	UV5	UV10
Ni+AZ+ PMMA 1633 cm ⁻¹ , C=N(Ni)	1.2853	1.2634	1.2415	1.2364	1.2450	1.2323
Cu+AZ+ PMMA 1629 cm ⁻¹ , C=N(Cu)	1.2835	1.2558	1.2472	1.2403	1.2423	1.2344
Zn+AZ+ PMMA 1615 cm ⁻¹ , C=N(Zn)	1.2401	1.2404	1.2443	1.2225	1.2417	1.2595
Ni'+AZ+ PMMA 1638 cm ⁻¹ , C=N(Ni')	1.2415	1.2369	1.2615	1.2573	1.2500	1.2499
Cu'+AZ +PMMA 1631 cm ⁻¹ , C=N(Cu')	1.2156	1.1818	1.2284	1.2294	1.2226	1.2126
Zn'+AZ +PMMA 1620 cm ⁻¹ , C=N(Zn')	1.1668	1.1613	1.1761	1.1751	1.1559	1.1537

Table 4. The S values of anisotropic parameters polarized IR spectra after liner polarized UV light irradiation.

UV radiation minutes	initial	UV0.5	UV1	UV3	UV5	UV10
Ni+AZ+ PMMA 1633 cm ⁻¹ , C=N(Ni)	0.0868	0.0807	0.0745	0.0730	0.0755	0.0719
Cu+AZ+ PMMA 1629 cm ⁻¹ , C=N(Cu)	0.0888	0.0809	0.0781	0.0748	0.0771	0.0738
Zn+AZ+ PMMA 1615 cm ⁻¹ , C=N(Zn)	0.0741	0.0742	0.0753	0.0690	0.0746	0.0796
Ni'+AZ+ PMMA 1638 cm ⁻¹ , C=N(Ni')	0.0745	0.0732	0.0802	0.0790	0.0769	0.0769
Cu'+AZ +PMMA 1631 cm ⁻¹ , C=N(Cu')	0.0671	0.0572	0.0708	0.0710	0.0691	0.0662
Zn'+AZ +PMMA 1620 cm ⁻¹ , C=N(Zn')	0.0527	0.0511	0.0555	0.0551	0.0494	0.0487

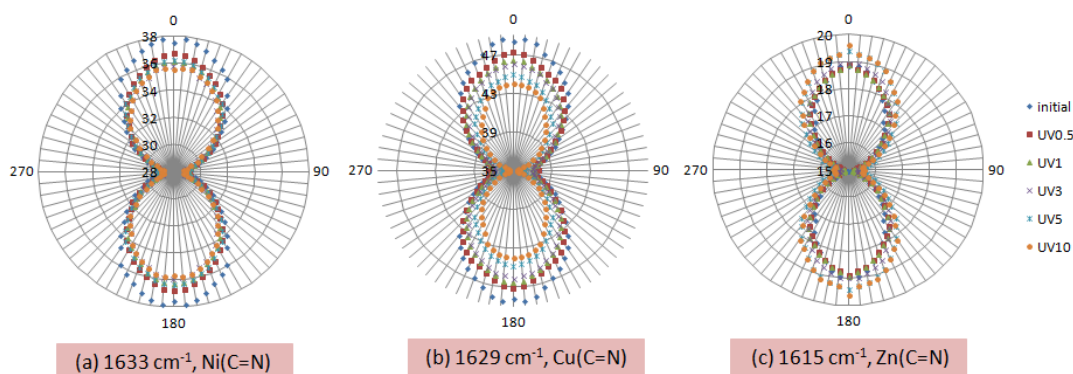


Fig. 2. Polarizer angle dependence of absorbance of C=N bands in IR spectra for **Ni+AZ+PMMA** [left], **Cu+AZ+PMMA** [middle], and **Zn+AZ+PMMA** [right] after linearly polarized UV light irradiation for 0, 0.5, 1, 3, 5, and 10 min.

Circularly polarized UV light induced chiral supramolecular arrangement. No change could be observed for CD spectra of **Ni'-Zn'+AZ+PMMA** before and after non-polarized UV light irradiation for 10 min (not shown), which suggested that, similar to liquid crystalline polymers [23-25], differences in CD bands by (linearly- or) circularly-polarized UV light irradiation could be attributed to chirality of the hybrid materials measured mainly.

Fig. 3 and 4 depicts CD spectra (and differences) of hybrid materials before and after circularly polarized 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 π - π^* region of the chiral metal complexes) are changed after circularly UV light irradiation for the hybrid materials. The data of achiral materials in Figs. 4 suggested the emerging CD bands of difference spectra are due to supramolecular chirality, not molecular chirality.

Optical active complexes are easy to form chiral supramolecular arrangement after circularly polarized UV light irradiation. The order of enhancing CD peaks is **Zn+AZ+PMMA** (320, little) < **Cu+AZ+PMMA** (321, -1.4716) < **Ni+AZ+PMMA** (322, 1.7407) [nm, θ /mdeg] in the chiral materials. On the other hand, the order of enhancing CD peaks is **Ni'+AZ+PMMA** (316, 0.3319) < **Cu'+AZ+PMMA** (320, 0.4539) < **Zn'+AZ+PMMA** (320, 0.7594) and (376, 0.7182) [nm, θ /mdeg] in the achiral ones. By the Weigert effect, the chiral complexes act as a chiral dopants for AZ, forming not a two dimensional order but a chiral (helical) molecular arrangement.

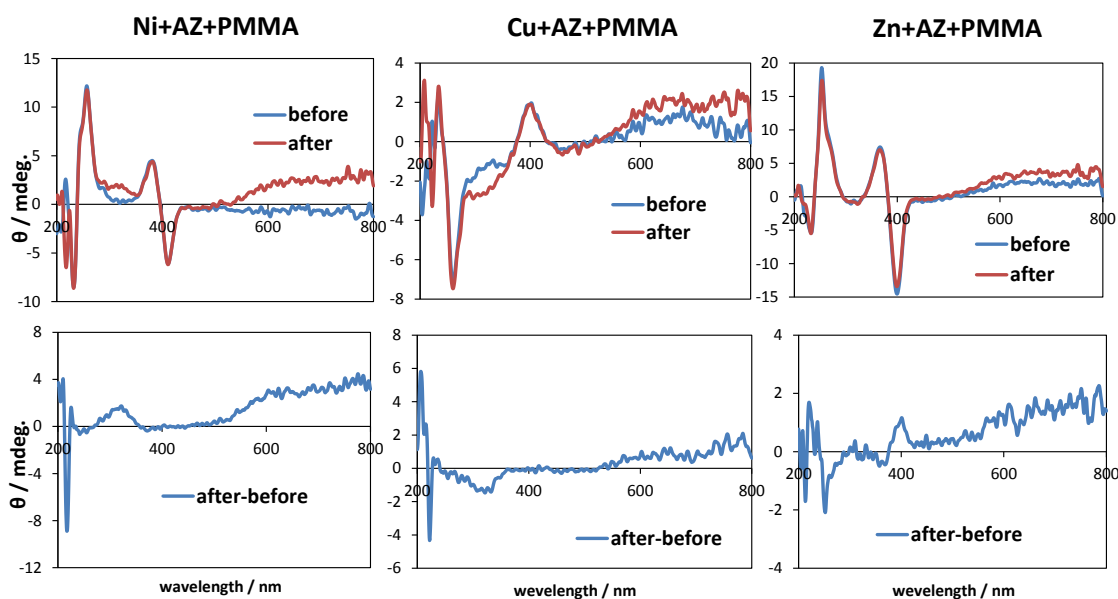


Fig. 3. [above] CD spectra and [below] their difference for **Ni+AZ+PMMA** [left], **Cu+AZ+PMMA** [middle], and **Zn+AZ+PMMA** [right] after circularly polarized UV light irradiation for 10 min.

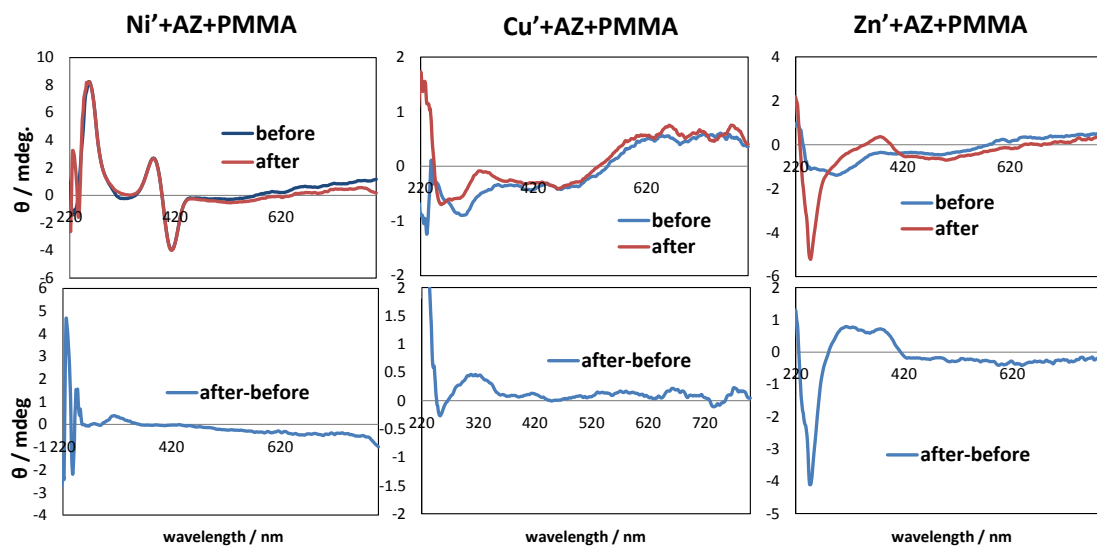


Fig. 4. [above] CD spectra and [below] their difference for **Ni'+AZ+PMMA** [left], **Cu'+AZ+PMMA** [middle], and **Zn'+AZ+PMMA** [right] after circularly polarized UV light irradiation for 10 min.

Conclusions

In summary, the correlation between molecular factors of metal complexes and polarization of light in the supramolecular interactions have been elucidated by

comparing appropriate systems associate with chirality of compounds and field. The magnitude of induced optical anisotropy mainly does not depend on diastereomers about ligands but depends on flexibility of central metal ions, while degree of induced supramolecular chirality mainly depends on chirality of ligands. Consequently, optical active complexes are easy to form chiral supramolecular arrangement after circularly polarized UV light irradiation.

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