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PAPER

Polarized spectroscopy and polarized UV light-induced molecular orientation of chiral diphenyl Schiff base Ni(II) and Cu(II) complexes and azobenzene in a PMMA film

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We have investigated polarized UV light-induced molecular orientation, namely increasing optical anisotropy of chiral diphenyl Schiff base Ni(II) and Cu(II) complexes (**diph(SS)Ni** and **diph(SS)Cu**) as well as azobenzene (**AZ**), as organic/inorganic hybrid materials in polymethylmethacrylate (**PMMA**) cast films. The driving force and reason for polarized UV light-induced molecular orientation of **AZ** are the so-called Weigert effect and accompanying molecular alignment of **diph(SS)Ni** or **diph(SS)Cu** is attributed to intermolecular interactions between two components dispersed in a flexible matrix environment of **PMMA**, which is confirmed with CD spectra. Gradual increase of the degree of dichroism was measured with polarized absorption electronic spectra. The anisotropic parameters were evaluated from them and were discussed based on interactions between electric transition dipole moments calculated by TD-DFT.

Introduction

One of the advantages of organic/inorganic hybrid materials may be facility of designing supramolecular multifunctional materials, for example metal complexes incorporating azo-ligands with large dichromic ratios.[1] Along recent development of this field, reversible photo-magnetic switching functional organic/inorganic hybrid materials composed of photochromic organic compounds and magnetic inorganic compounds have been reported as one example.[2] Furthermore, we have employed various types of metal complexes as inorganic components to use molecular functions of metal complexes such as fluorescence intermolecular interactions,[3] chiral recognitions[4] and molecular based magnetism.[5] In particular, we also focused on photo-tuning of optical anisotropy of **AZ**, namely polarized UV light-induced alignment caused by selected photoisomerization and molecular orientation of **AZ** (Weigert effect),[6] in contrast to conventional *cis-trans* photoisomerization of **AZ**. During a series of the related studies of such organic/inorganic hybrid materials and photo-induced dichroism observed with polarized spectroscopy,[7] it may have been possible to discuss the degree of molecular orientation of components in view of electric transition dipole moments for clear interpretation and deep understanding of angular dependence of absorbance of polarized spectra.

Herein, we prepared organic/inorganic hybrid materials as **PMMA** cast films containing chiral Schiff base Ni(II) and Cu(II) complexes (**diph(SS)Ni** and **diph(SS)Cu**, respectively) and **AZ** (Fig. 1). Investigation of anisotropic parameters taken from polarized spectra was carried out for some organic/inorganic hybrid materials (**AZ+diph(SS)Ni+PMMA**, **AZ+diph(SS)Cu+PMMA** and **AZ+PMMA** for comparison). In this study, we attempted to interpret anisotropic parameters based on transition dipole moments evaluated by TD-DFT.

Experimental

Materials

All reagents and solvents were analytically pure and were used as received without further purification.

Preparation of [(1*S*,2*S*)-*N*,*N*′-bis(3,5-dicholosalicylidene)-diphenyl-1,2-diamine-κ^4*O*,*N*,*N*′,*O*]nickel(II) (diph(SS)Ni)

To a solution of 3,5-dichlorosalicylaldehyde (0.3820 g, 2 mmol) dissolved in methanol (100 mL), (1*S*,2*S*)-(-)-1,2-diphenylethylenediamine (0.2123 g, 1 mmol), and copper(II) acetate hydrate

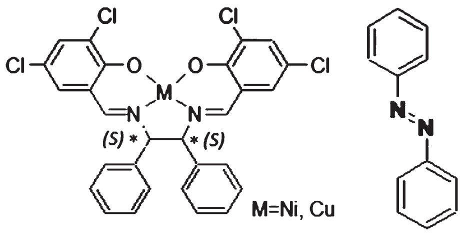

Fig. 1 Structures of chiral Schiff base Ni(II) complex (**diph(SS)Ni**) and Cu(II) complex (**diph(SS)Cu**) and the *trans* form of **AZ**.

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(0.2488 g, 1 mmol) were added and stirred at 313 K for 4 h to yield brown the complex collected by filtration. Yield 0.5602 g (91%). Anal. Calc. for $C_{28}H_{18}Cl_4NiN_2O_2$: C, 54.69; H, 2.95; N, 4.56. Found: C, 54.58; H, 2.88; N, 4.40%. IR (Nujol mull):401, 406, 412, 422, 428, 440, 447, 455, 460, 465, 470, 481, 486, 509, 516, 522, 527, 543, 563, 570, 596, 617, 624, 631, 636, 645, 667, 693, 714, 721, 749, 763, 794, 845, 857, 866, 881, 918, 951, 956, 1001, 1076, 1103, 1121, 1160, 1175, 1216, 1274, 1322, 1331, 1347, 1360, 1366, 1377, 1412, 1450, 1588, 1600, 1620(C=N), 2671, 2728, 2855, 2905, 2911, 2939, 2957 cm^{-1}.

Preparation of [(1*S*,2*S*)-*N*,*N*'-bis(3,5-dicholosalicylidene)-diphenyl-1,2-diamine-κ^4*O*,*N*,*N*',*O*]copper(II) (diph(SS)Cu)

To a solution of 3,5-dichlorosalicylaldehyde (0.0955 g, 0.5 mmol) dissolved in methanol (50 mL), (1*S*,2*S*)-(-)-1,2-diphenylethylenediamine (0.0531 g, 0.25 mmol), and copper(II) acetate hydrate (0.0499 g, 0.25 mmol) were added and stirred at 313 K for 4 h to yield brown the complex collected by filtration. Yield 0.1288 g (83%). Anal. Calc. for $C_{28}H_{18}Cl_4CuN_2O_2$: C, 52.73; H, 3.16; N, 4.39. Found: C, 52.73; H, 2.92; N, 4.57%. IR (Nujol mull):401, 403, 406, 412, 417, 422, 425, 431, 438, 444, 447, 453, 455, 460, 465, 471, 480, 489, 495, 498, 509, 649, 666, 693, 721, 750, 763, 788, 851, 870, 889, 918, 972, 990, 1075, 1114, 1169, 1213, 1316, 1366, 1462, 1497, 1512, 1562, 1572, 1589, 1628(C=N), 1652, 2342, 2368, 2670, 2727, 2857, 2936 cm^{-1}.

Preparation of hybrid materials

Acetone solution (0.5 mL) of **AZ** (0.0018 g in 10 mL acetone), acetone solution (0.5 mL) of **diph(SS)Ni** or **diph(SS)Cu** and acetone solution (2 mL) of **PMMA** (10%) were cast onto a slide glass to give rise to PMMA film of hybrid materials **AZ+PMMA+diph(SS)Ni** or **AZ+PMMA+diph(SS)Cu**. Weight percentages are 0.036%, 0.021%, and 99.94% for **AZ**, **diph(SS)Ni** or **diph(SS)Cu** and **PMMA**, respectively. **AZ+PMMA+diph(SS)Ni**: CD spectrum in PMMA films (nm (θ/mdeg)): 586 (−1.95), 495 (−0.71), 482 (−1.13), 457 (+0.20), 420 (−3.34), 389 (−1.36), 367 (−2.04), 340 (−0.48), 276 (−4.90), 253 (+0.34), 245 (−0.73).

AZ+PMMA+diph(SS)Cu. CD spectrum in PMMA films (nm (θ/mdeg)): 617 (+1.24), 478 (+0.40), 460 (+0.66), 443 (+0.55), 406 (+1.42), 370 (−0.05), 342 (+0.55), 313 (+0.96), 252 (+3.43).

Physical measurements

Elemental analyses were carried out with a Perkin-Elmer 2400II 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 spectrophotometer equipped with a polarizer at 298 K. CD spectra were recorded on a JASCO J-820 spectrophotometer at 298 K. Fluorescence spectra were recorded on a JASCO FP-6200 spectrophotometer at 298 K. Photo-irradiation was carried out with D_2 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.

Computational methods

All calculations were performed using the Gaussian 09W software Revision A.02 (Gaussian, Inc.).[8] The gas phase geometry optimizations were carried out using TD-DFT with B3LYP functional. The vertical excitation energy was calculated with the Lanl2dz for Ni and Cu and with the $6-31+G(d)$ basis set for H, C, N, O, and Cl method based on doublet (for a Cu(II) complex) or singlet (for a Ni(II) complex) ground state geometry.

Results and discussion

Electronic and CD spectra of complexes

Fig. 2 shows comparison between simulated and experimental spectra of electronic and CD spectra in order to confirm reliable band assignment. As for metal complexes, d-d bands in simulated spectra appear at 563 nm and 556 nm and transition electric dipole moment is evaluated to be (0.0396, 0, 0.0127) and (−0.1315, 0, −0.0053) with oscillator strength of 0.0001 and 0.0009 for **diph(SS)Ni** and **diph(SS)Cu**, respectively. Moreover, n–π* and π–π* bands in simulated spectra appear at 477 nm and 339 nm and transition electric dipole moment is evaluated to be (0, 0, 0)

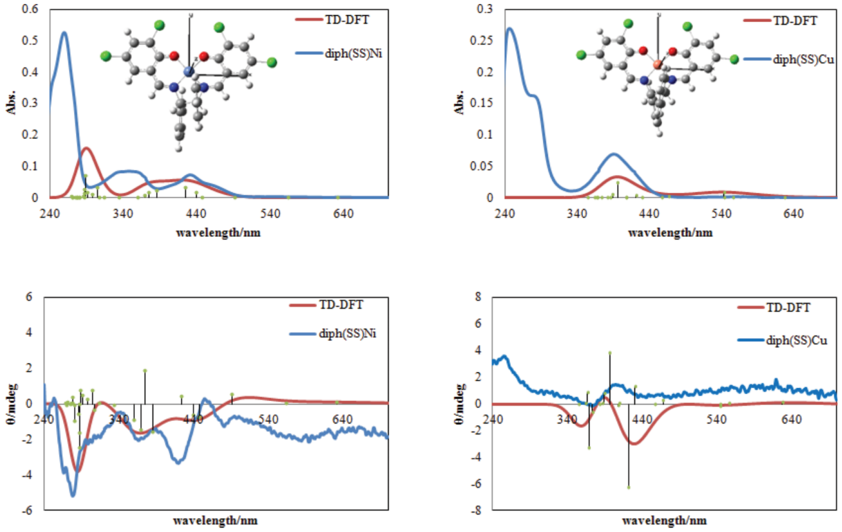


Fig. 2 Simulated (red) and experimental (blue) electronic spectra (above) and CD spectra (below) for **diph(SS)Ni** (left) and **diph(SS)Cu** (right) with optimized structures.

and (0.1445, −2.9027, 0) with oscillator strength of 0.0000 and 0.7558 for the *trans*-form of **AZ**. The corresponding n–π* and π–π* bands appear at 484 nm and 307 nm and transition electric dipole moment is evaluated to be (0.5511, −0.5741, 0) and (0.5471, −0.5755, 0) with oscillator strength of 0.0397 and 0.0625 for the *cis*-form of **AZ**. According to preceding studies on the related compounds,[9] the optimized structures and assignments of transitions for **diph(SS)Ni** and **diph(SS)Cu** are reasonable.

Polarized light-induced molecular orientation and optical anisotropy

After polarized UV light irradiation, intensity (absorbance as it measured) of some characteristic peaks of polarized absorption spectra gradually were measured. The spectra shown in Fig. 3–5 were obtained with polarizer aligned at 0 degrees before (0 min) and after polarized UV light irradiation for 60 min, and they were also measured for 0–90 degrees at every 5 degree before and after polarized UV light irradiation for 5, 10, 20, 30 and 60 min.

Fig. 3 shows polarized absorption spectra and circular diagrams of angular dependence of absorbance of π–π* and n–π* bands at 318 nm and 440 nm for **AZ+PMMA**. It should be noted that the large change of π–π* band at initial stage is attributed to photoisomerization from the *trans*-form of **AZ** to the *cis*-form of **AZ** by UV light irradiation. These circular diagrams about π–π* bands suggest clear optical anisotropy of **AZ**, which is similar to polymers containing azo-groups.[10]

Fig. 4 and 5 show polarized absorption spectra and circular diagrams of angular dependence of absorbance of π–π*, n–π*, and d–d bands at 318 nm, 440 nm, 563 and 556 nm for **AZ+PMMA+diph(SS)Ni** and **AZ+PMMA+diph(SS)Cu**, respectively. It should be noted that only **AZ** was influenced by Weigert effect directly among two components. Even weak d–d band at 563 and 556 nm is attributed to a **diph(SS)Ni** or **diph(SS)Cu** component, increasing optical anisotropy can be observed, which is obvious proof for supramolecular interactions between **AZ** and **diph(SS)Ni** or **diph(SS)Cu**.

The degree of photoinduced optical anisotropy (spectral dichroism) of polarized absorption electronic spectra can be described commonly by these two parameters:

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

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

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

According to Table 1, we can derive the following information associated with molecular orientations with intermolecular interactions in these organic/inorganic hybrid materials. The degree of increasing optical anisotropy accompanying with Weigert effect of **AZ** depends on not shapes of (identical) chiral ligands but central Ni(II) or Cu(II) metal ions; in other words, **AZ + PMMA** > **AZ + PMMA + diph(SS)Ni** > **AZ + PMMA + diph(SS)Cu** for π–π* bands, **AZ + PMMA + diph(SS)Cu** > **AZ + PMMA** > **AZ + PMMA + diph(SS)Cu** for n–π* bands, and **AZ + PMMA + diph(SS)Ni** > **AZ + PMMA + diph(SS)Cu** for d–d bands. Reducing direct transmission of molecular alignment from **AZ** by flexibility of metal complexes due to Ni(II) or Cu(II) ions is considered for Schiff base metal complexes,[11] discrepancy of tendency about molecular orientation between **AZ + PMMA + diph(SS)Ni** and **AZ + PMMA + diph(SS)Cu** cannot be explained reasonably. Therefore, to interpret dichroism of each component properly, dipole–dipole interactions (which could not be estimated from experimental data easily) between **AZ** and **diph(SS)Ni** or **diph(SS)Cu** should be treated appropriately.

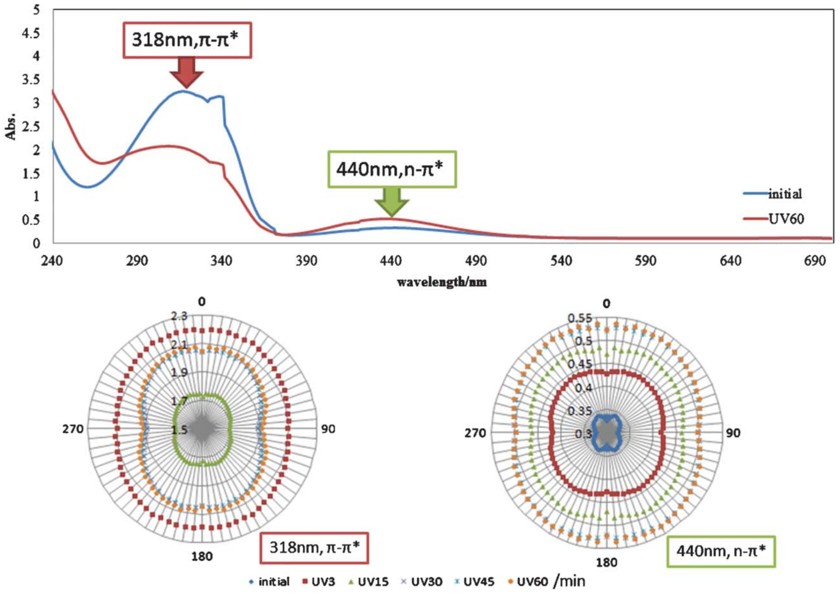


Fig. 3 Polarized absorption electronic spectra and angular dependence of a polarizer in absorbance at 318 and 440 nm for **AZ** after UV light irradiation for 0–60 min.

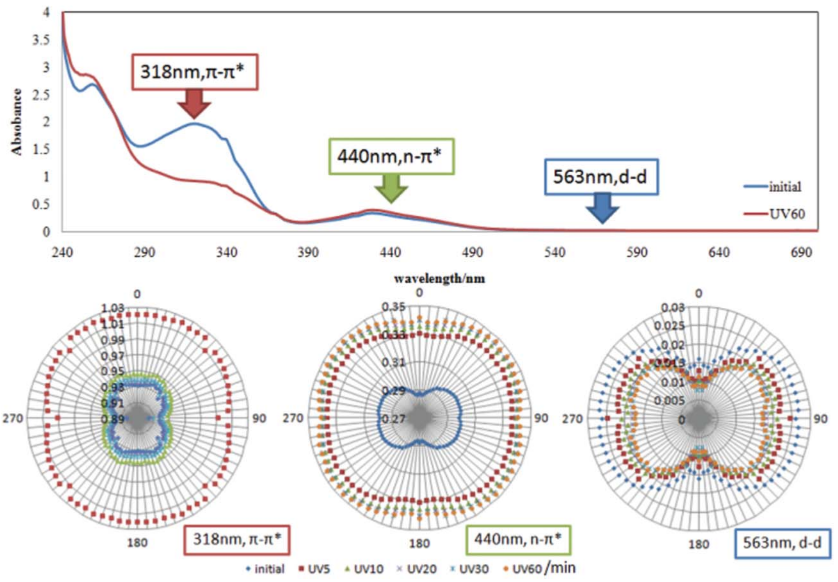


Fig. 4 Polarized absorption electronic spectra and angular dependence of a polarizer in absorbance at 318, 440 and 563 nm for **AZ+PMMA+diph(SS)Ni** after UV light irradiation for 0–60 min.

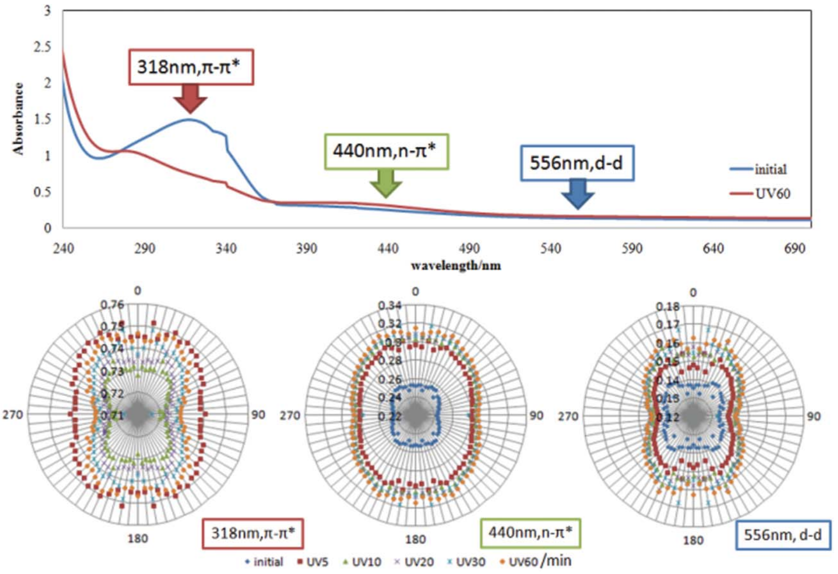


Fig. 5 Polarized absorption electronic spectra and angular dependence of a polarizer in absorbance at 318, 440 and 556 nm for **AZ+PMMA+diph(SS)Cu** after UV light irradiation for 0–60 min.

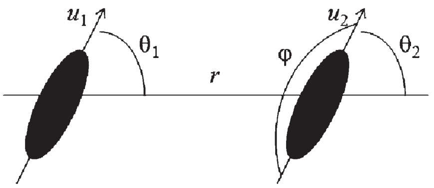
Comparison between calculated transition dipole moments and experimental parameters of optical anisotropy

Theoretical models and the resulting energy shown in Fig. 6 can be proposed to consider dipole–dipole interactions between metal complexes (**AZ + PMMA + diph(SS)Ni** and **AZ + PMMA + diph(SS)Cu**) and **AZ**. According to eqn (1), when two dipole moments are aligned in a line ($\theta_1 = \theta_2 = 0$) or parallel to each other ($\theta_1 = \theta_2 = \pi/2$), the energy w takes the maximum value ($-2\ u_1u_2/4\pi\varepsilon_0\varepsilon_r r^3$) or the minimum ($-u_1u_2/4\pi\varepsilon_0\varepsilon_r r^3$) value, respectively. For both cases, the distance between two dipoles' (r) dependence of energy (w) can be estimated that the w value takes the minimum value at $r = 0.01$ nm approximately, and the value of w will be convergent to 0 on increasing the r value.

In analogy of Boltzmann distribution, the mechanism of increasing optical anisotropy can be discussed, namely the number of N_i states of the in-line state with $E_\mathrm{i} = -2\ u_1u_2/4\pi\varepsilon_0\varepsilon_r r^3$ and the number of N_j states of the parallel state with $E_\mathrm{j} = -u_1u_2/4\pi\varepsilon_0\varepsilon_r r^3$. The change of optical anisotropy after polarized UV light irradiation corresponds to the change of the number of parallel dipoles. One of the anisotropy parameters (dichroism ratios, R) can be described by calculated transition electric dipole moments instead of experimental polarized absorbance ($A_0(A_\mathrm{parrallel})$ or $A_{90}(A_\mathrm{perpendicular})$). As shown in Fig. 7, the magnitude of A_0 (or A_{90}) can be derived as eqn (2), and the following two cases can be considered about optical anisotropy.

Table 1 The R and *S* (*italic*) values of anisotropic parameters of polarized absorption electronic spectra after polarized UV light irradiation (min)

AZ + PMMA			
UV time (min)	π–π* (318 nm)	n–π* (440 nm)	
0	1.0235 *0.0078*	1.0074 *0.0025*	
3	1.0463 *0.0152*	1.0249 *0.0082*	
15	1.0220 *0.0073*	1.0192 *0.0064*	
30	1.0838 *0.0272*	1.0534 *0.0175*	
45	1.0744 *0.0242*	1.0488 *0.0160*	
60	1.0659 *0.0215*	1.0516 *0.0169*	
AZ + PMMA + diph(SS)Ni			
UV time (min)	π–π* (318 nm)	n–π* (440 nm)	d–d (563 nm)
0	1.0221 *0.0073*	0.9658 *−0.0115*	0.6135 *−0.1479*
5	1.0290 *0.0152*	0.9825 *−0.0059*	0.5205 *−0.1902*
10	1.0291 *0.0073*	0.9890 *−0.0037*	0.4840 *−0.2077*
20	1.0305 *0.0272*	1.0007 *0.0002*	0.6328 *−0.1395*
30	1.0314 *0.0242*	1.0011 *0.0004*	0.6068 *−0.1508*
60	1.0320 *0.0215*	1.0030 *0.0010*	0.6504 *−0.1319*
AZ + PMMA + diph(SS)Cu			
UV time (min)	π–π* (318 nm)	n–π* (440 nm)	d–d (556 nm)
0	1.0064 *0.0021*	1.0332 *0.0110*	1.0145 *0.0048*
5	1.0063 *0.0021*	1.0580 *0.0190*	1.0681 *0.0222*
10	1.0079 *0.0026*	1.0591 *0.0193*	1.0723 *0.0235*
20	1.0167 *0.0055*	1.0758 *0.0246*	1.1016 *0.0327*
30	1.0290 *0.0096*	1.1042 *0.0336*	1.1612 *0.0510*
60	1.0239 *0.0079*	1.0926 *0.0299*	1.1358 *0.0433*



$$w(r,\theta_1,\theta_2,\phi)=-\frac{u_1u_2}{4\pi\varepsilon_0\varepsilon_r r^3}(2\cos\theta_1\cos\theta_2-\sin\theta_1\sin\theta_2\cos\phi) \quad (1)$$

Fig. 6 Theoretical model of dipole–dipole interactions and the description of its energy *w*, eqn (1).

$$R=\frac{A_0}{A_{90}}\propto\frac{\left|\langle f|\mu_0|i\rangle\right|^2 N_0}{\left|\langle f|\mu_{90}|i\rangle\right|^2 N_{90}}=\frac{\left|\langle f|\mu_0|i\rangle\right|^2}{\left|\langle f|\mu_{90}|i\rangle\right|^2}e^{-(E_0-E_{90})/kT} \quad (2)$$

Fig. 7 Description of dichroism ratios *R* with calculated parameters assuming Boltzmann distribution (2) and a model of energy levels dipole–dipole interactions with their energy interval kT. Blue highlight indicated expansion of equation the number of states (N_0 or N_{90} and green bands in pictures) of directed dipoles and their energy by Boltzmann distribution.

[case I] Interval of levels $< kT$: Because of small differences of energy levels and many levels, small differences between N_0 and N_{90} result in closing to $R = 1$, namely optical isotropy.

[case II] Interval of levels $> kT$: Because of large differences of energy levels and a few levels, large differences between N_0 and N_{90} result in closing to $R = 0$, namely optical anisotropy.

By Weigert effect after polarized UV light irradiation to the hybrid materials, **AZ** molecules change their molecular orientation (transition electric dipole moments) being perpendicular to electric vector of polarized UV light irradiated. According to the above consideration, discrepancy of tendency of increasing of optical anisotropy among π–π*, n–π*, and d–d bands should be attributed to the magnitude and the direction of transition electric dipole moments for π–π*, n–π*, and d–d transitions. In addition, dipoles can take various angles of orientation between 0 to π/2, which leads to various energy (*w*) and distribution of energy states.

Conclusions

In summary, we have compared increasing optical anisotropy of components of the hybrid materials of **AZ + PMMA + diph(SS)Ni** and **AZ + PMMA + diph(SS)Cu** and **AZ + PMMA** as a reference due to Weigert effect of **AZ** by irradiation of polarized UV light. The difference of the degree of optical dichroism between them has been discussed by assuming a qualitative model in analogy of theory of Boltzmann distribution with respect to calculated transition electric dipole moments with TD-DFT. Thus, dipole–dipole interactions can be influenced by molecular electronic structures which results in differences in apparent degree of optical anisotropy based on polarized absorption electronic spectra of both components.

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