In: Computational Chemistry
Editor: Daria Bove
ISBN: 978-1-63321-354-8
© 2014 Nova Science Publishers, Inc.

No part of this digital document may be reproduced, stored in a retrieval system or transmitted commercially in any form or by any means. The publisher has taken reasonable care in the preparation of this digital document, but makes no expressed or implied warranty of any kind and assumes no responsibility for any errors or omissions. No liability is assumed for incidental or consequential damages in connection with or arising out of information contained herein. This digital document is sold with the clear understanding that the publisher is not engaged in rendering legal, medical or any other professional services.

Chapter 5

INTERPRETATION OF CHIRAL ORDERING OF HYBRID SYSTEM OF SEVERAL AZO DYES AND CHIRAL SCHIFF BASE CO(II) COMPLEX INDUCED BY CIRCULARLY POLARIZED LIGHT

Nobumitsu Sunaga, Shohei Furuya, Maiko Ito, Chigusa Kominato and Takashiro Akitsu*

Department of Chemistry, Faculty of Science, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku Tokyo, Japan

ABSTRACT

It is well known that Weigert effect emerges optical anisotropy induced by linearly polarized light in the case of azo dyes, liquid crystals, and such polymers and its application for holography. We have reported on supramolecular interactions for controlling molecular arrangement of photo-inactive metal complexes between directly photo-functional azo dyes and photo-inactive metal complexes in flexible polymer films. In this work, we have prepared PMMA cast films of three azo dyes, such as azobenzene (**AZ**), disodium 6-hydroxy-5-((2-methoxy-5-methyl-4-sulfophenyl)azo)-2-naphthalenesulfonate (Allura Red), 4,4'-di-n-octyloxyazoxybenzene, and hybrid materials containing a new chiral Schiff base Co(II) complex ($C_{32}H_{32}CoN_2O_2$ showing IR band (C=N) at *c.a.* 1630 cm^{-1}) as a chiral dopant. After circularly polarized UV light

irradiation, we compared and found that the degree of chiral ordering (increasing of CD intensity) of **AZ** was the highest among three ones. 4,4'-Di-*n*-octyloxyazoxybenzene having long chain exhibited characteristic increasing of dichroism at π–π* band, which may affect on chiral ordering. With the aid of computational chemistry, we attempted to interpret interactions between transition dipole moments of azo dyes (especially **AZ** was effective) and Co(II) complexes as their light-induced helical arrangement. Theoretical treatment with ZINDO calculations of spectra about the angles of transition dipole moments suggested that supramolecular interactions induced by polarized light predominantly resulted from π–π* transition for **AZ**+PMMA, whereas n-π* transition for Co(II) complex+**AZ**+PMMA.

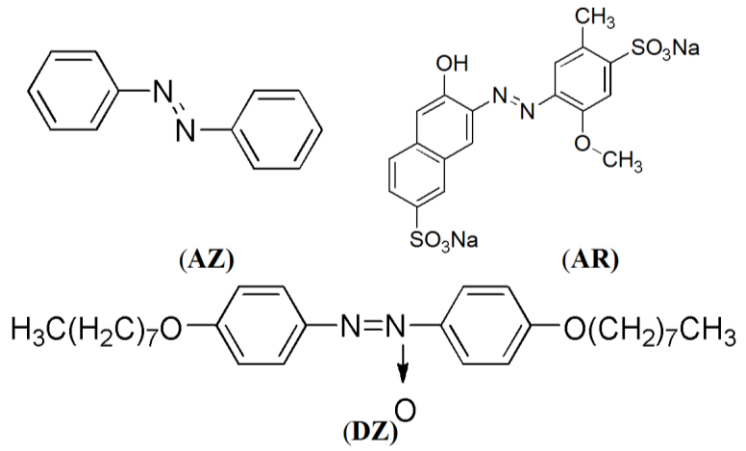
INTRODUCTION

One of the advantages of organic/inorganic hybrid materials may be easy design for supramolecular multifunctional materials, for example metal complexes incorporating azo-moiety with large dichromic ratios [1]. According to recent development of this field, reversible photo-switching magnetic materials composed of photochromic organic compounds and magnetic inorganic compounds driven by light have been reported [2]. Furthermore, since other molecular features of metal complexes can be used potentially, for example intermolecular fluorescence [3], molecular recognition by chirality [4], single-molecule magnets as well as molecule-based magnets [5], we have employed various metal complexes as the inorganic components of such organic/inorganic hybrid materials.

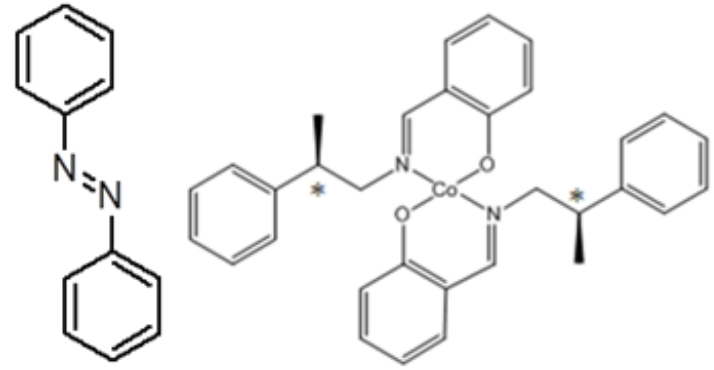
In this context, we have also focused on photo-tuning of optical anisotropy (molecular alighment) of azo-components by (linearly) polarized UV light irradiation (Weigert effect) [6] in contrast to conventional cis-trans photoisomerization of photocromic azo-compounds. On the other hand, circularly polarized UV light irradiation can induce or control chiral or helical molecular arrangement of such organic/inorganic hybrid materials. Combination of linearly or circularly polarized UV light irradiation and polarized spectroscopy or CD spectroscopy can control or be observed molecular orientation potentially, though intermolecular effects are unclear without chiral fillers or previous chiral filler + chiral complex + PMMA cast film systems [7].

Herein we have investigated three azo-dyes (azobenzene (**AZ**), Allura Red AC (**AR**), and 4,4'-di-n-octyloxyazoxybenzene (**DZ**)) (Figure 1(a)) to select

effective photoresponsive components and improved an **AZ** system with the assistance of chiral filler (a chiral Schiff base Co(II) complex (**Co**)) (Figure 1(b)). In this study, we attempted to interpret anisotropic parameters based on transition dipole moments evaluated by ZINDO calculations. In addition, we have assembled a model of interaction by using the dipole moment of the azo dyes calculated to discuss supramolarular chirality induced by polarized UV light.



(a)



(b)

Figure 1. Molecular structures of (a) azo-dyes (**AZ**, **AR**, and **DZ**) and (b) components of hybrid material **AZ+Co**.

EXPERIMENTAL SECTION

Materials

All reagents including three azo dyes (**AZ**, **AR**, and **DZ**) and solvents were commercially available (Wako, TCI, and Aldrich) and were used as purchased without further purification.

Preparations of Bis (N-*R*-2-Phenlypropyl-Salicydenaminato) Cobalt(II) (Co)

To a solution of benzaldehyde (0.610 g, 5.00 mmol) dissolved in methanol (50 mL) and *R*-(+)-β-methylphenythylamine (0.676 g, 5.00 mmol) was added and stirred at 313 K for 2 hr under nitrogen atmosphere to give rise to orange solution of ligand. Then cobalt(II) sulfate heptahydrate (0.703 g, 2.50 mmol) was added and stirred for 4 hr and the resulting green precipitate of product was filtered. Yield 0.2166 g (16.25 %). IR (Nujol mull): 1620 cm^{-1} (C=N).

Preparations of Hybrid Materials

0.5 mL of acetone solution (0.78 mol/L) of azobenzene (**AZ**), disodium 6-hydroxy-5-((2-methoxy-5-methyl-4-sulfophenyl)azo)-2-naphthalenesulfonate (Allura Red) (**AR**), 4,4'-di-n-octyloxyazoxybenzene (**DZ**), or **AZ**+**Co** (10 mmol) and 1.0 mL of acetone solution of poly(methyl methacrylate (PMMA) were cast onto a slide glass and dried for overnight at room temperature to give rise to **PMMA** film of hybrid **AZ+PMMA**, **AR+PMMA**, **DZ+PMMA**, and **AZ+Co+PMMA**, respectively.

Physical Measurements

Infrared spectra were recorded a JASCO FT-IR 4200 spectrophotometer equipped with a polarizer in the range of 4000-400 cm^{-1} at 298 K. Electronic spectra were measured on a JASCO V-570 spectrophotometer equipped with a

polarizer in the range of 900-200 nm at 298 K. Circular dichroism (CD) spectra were measured on a JASCO J-725 spectropolarimeter in the range of 800-200 nm at 298 K. UV and visible light source used was Hayashi LA-310UV and LA-251Xe, respectively with visible ($\lambda > 350$ nm) or UV ($\lambda < 350$ nm) cut filters and ($\lambda/4$-) polarizers.

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 ZINDO with B3LYP functional. The vertical excitation energy was calculated with the 6-31+G(d) basis set for H, C, N, and O based on the singlet ground state geometry.

RESULTS AND DISCUSSION

Computational Results

Figure 2 indicates calculated direction and magnitude of dipole moments for azo-dyes. Optimized structures were calculated under assuming cis-isomers which produced after UV light irradiation in a PMMA matrix. The evaluated dipole moments are 3.154 Debye, 21.26 Debye, and 5.983 Debye for AZ, **AR**, and **DZ**, respectively.

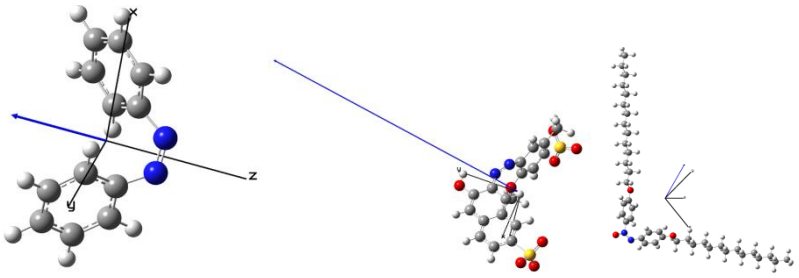


Figure 2. Optimized structures with calculated dipole moment for **AZ** [left], **AR** [middle], and **DZ** [right].

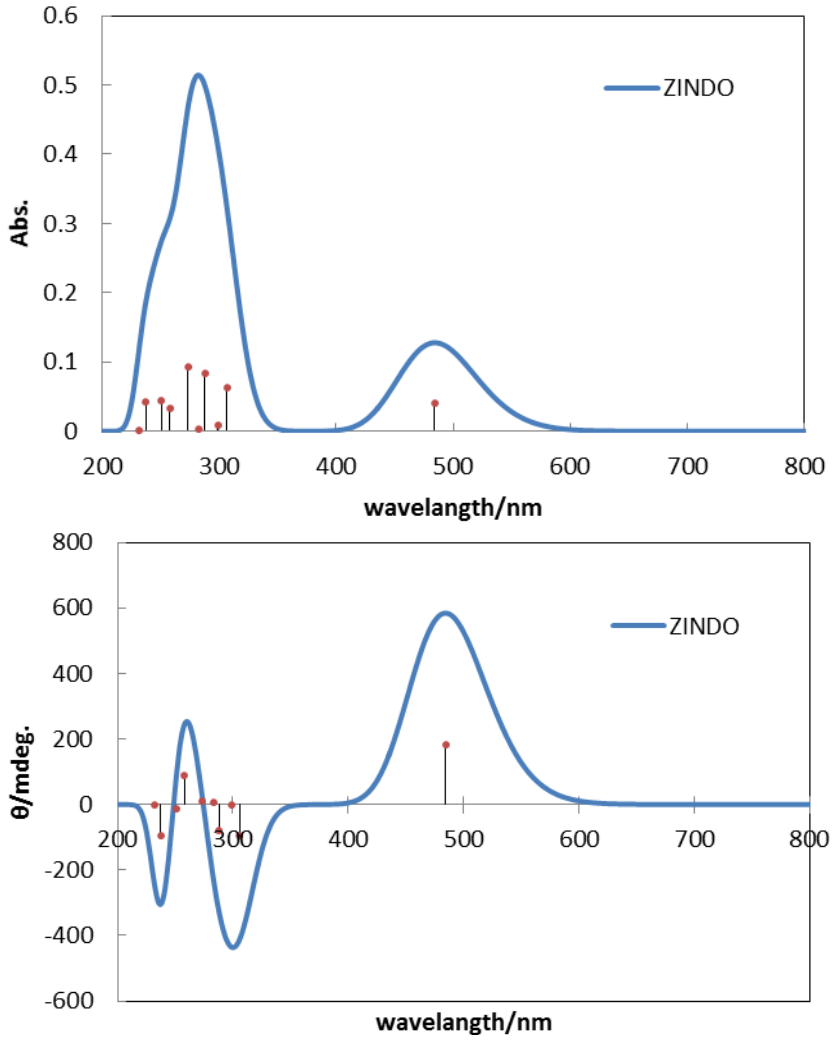


Figure 3. Simulated electronic spectra [above] and estimated (virtual) CD spectra [below] for **AZ**.

Figures 3-5 show simulated absorption spectra (transition energies and their intensity were calculated with ZINDO for the optimized structures and line width was added as Gaussian curves) and 'expected' simulated CD spectra (based on calculated transitions with sign of optical rotation by means of ZINDO and magnetic dipole transitions were assumed for CD) for achiral azo-dyes **AZ**, **AR**, and **DZ**, respectively. It should be noted that actual azo-

dyes, **AZ**, **AR**, and **DZ**, were achiral, in other word, did not appear the CD spectra, and (simulated) CD spectra were calculated to discuss assignment of CD bands due to supramolecular chirality in the later section. Because experimental CD spectra is impossible to determine, this is advantage of computational results essentially.

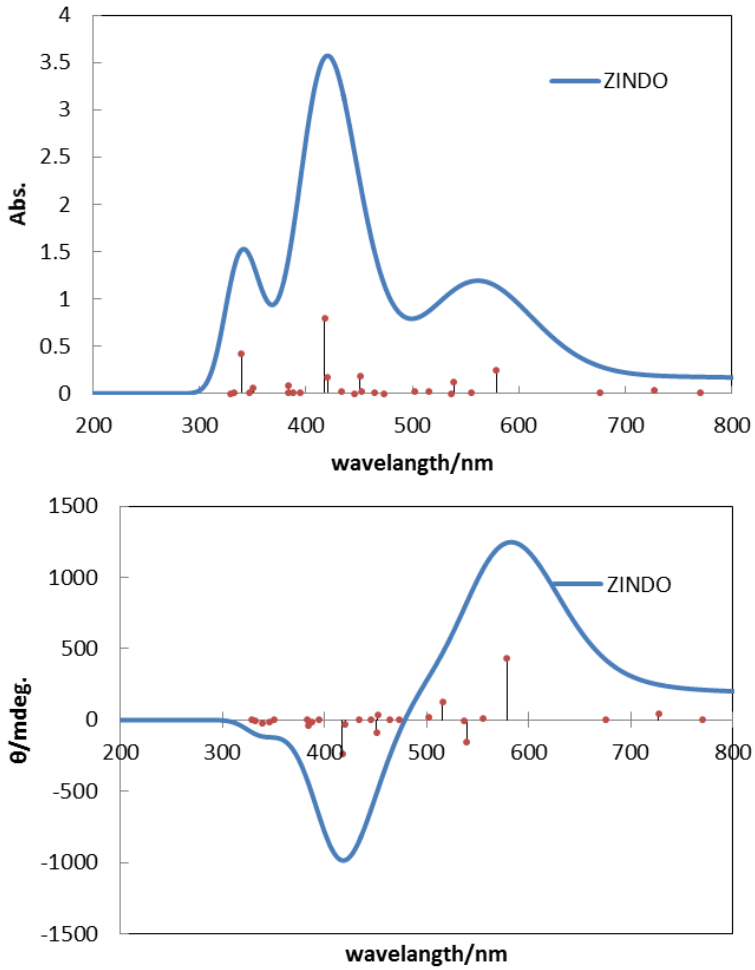


Figure 4. Simulated electronic spectra [above] and estimated (virtual) CD spectra [below] for **AR**.

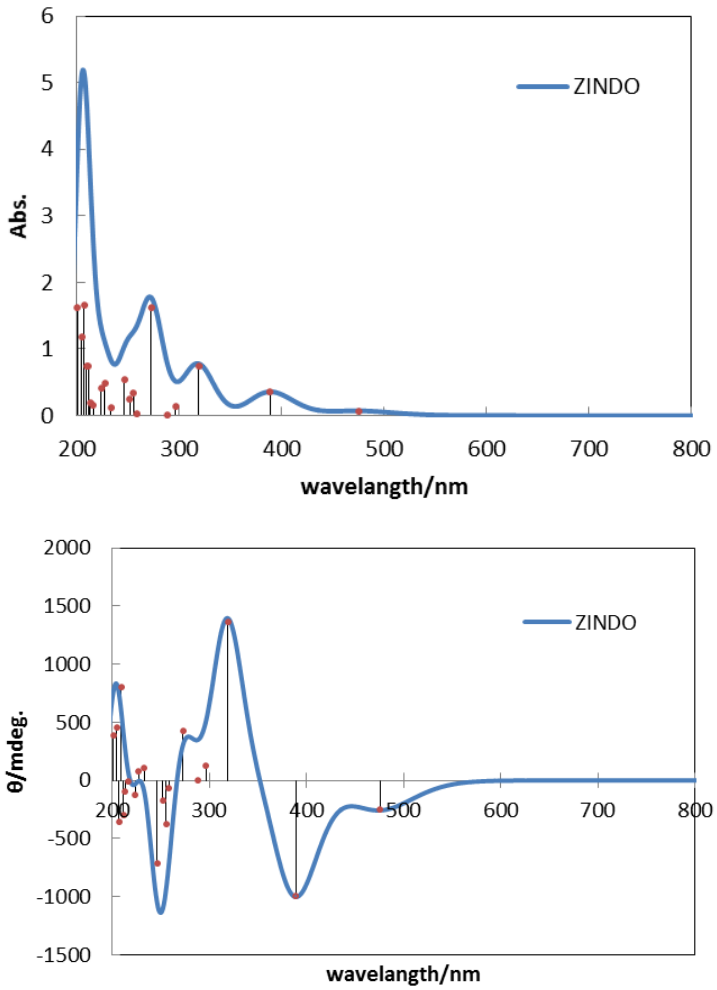


Figure 5. Simulated electronic spectra [above] and estimated (virtual) CD spectra [below] for **DZ**.

Linearly Polarized UV Light-Induced Molecular Arrangement

After linearly polarized UV light irradiation, intensity (absorbance as it measured) of some characteristic peaks of polarized absorption spectra gradually were measured. Figures 6-8 were obtained with polarizer aligned at 0 degree before (0 min) and after liner polarized UV light irradiation for 10

min for hybrid materials **AZ+PMMA**, **AR+PMMMA**, and **DZ+PMMA**, respectively. They were also measured for 0-90 degree at every 5 degree before and after linearly polarized UV light irradiation for 1, 3, 5 and 10 min.

Figure 6 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 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 [9].

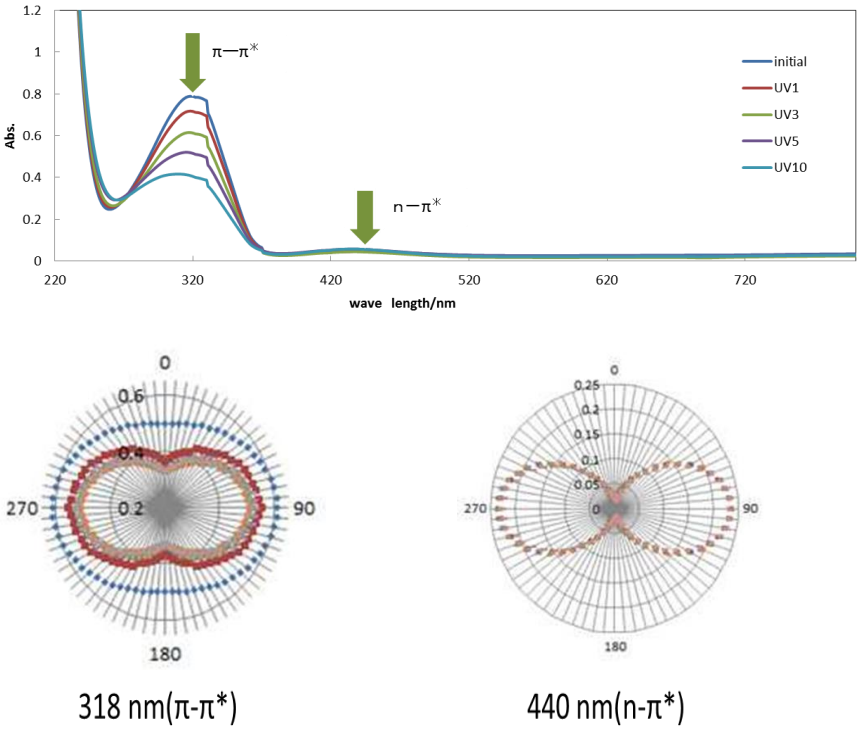


Figure 6. Polarized electronic spectra [above] and circular diagrams [below] for **AZ+PMMA**.

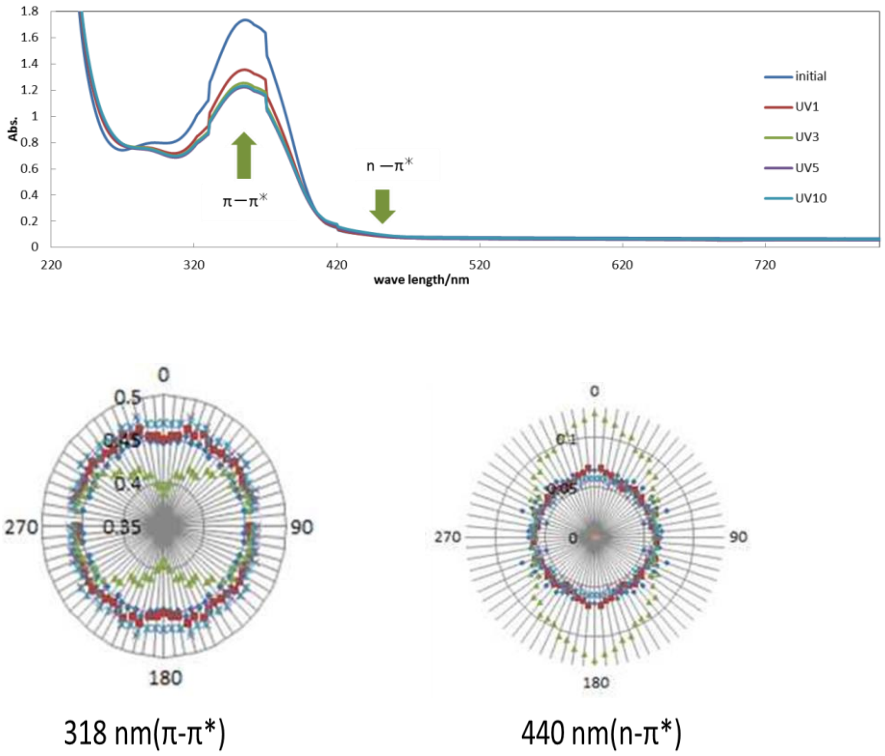


Figure 7. Polarized electronic spectra [above] and circular diagrams [below] for **DR+PMMA**.

Figures 7 and 8 show polarized electronic spectra and circular diagrams of angular dependence of absorbance of π–π* and n–π* at 318 nm, 440 nm, for **AR+PMMA** and **DZ+PMMA**, respectively. It should be noted that only **AZ+PMMA** was influenced clearly by Weigert effect directly among two components. Therefore, **AZ** is the most effectively photo responsible azo-dyes among three samples.

Comparing with π–π* and n–π* bands at 318 nm, 440 nm, respectively, in short-wavelength (UV) region of experimental spectra (Figures 6-8), calculated electronic spectra (Figures 2-4) were possible to reproduce qualitative features of the bands as well as the transitions.

In order for quantitative discussion of optical anisotropy, the S and R parameters were employed. The degree of photoinduced optical anisotropy (spectral dichroism) of polarized absorption electronic spectra can be described commonly by these two parameters:

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

where $A_{perpendicular}$ and $A_{parrallel}$ 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.

Table 1 summarized these parameters and revealed that the order of optical anisotropy induced by linearly polarized UV light was **AZ+PMMA** > **AR+PMMA** > **DZ+PMMA**.

Table 1. The R and S values after linearly polarized UV light irradiation for AZ+PMMA, AR+PMMA, and DZ+PMMA

AZ+PMMA				
UV time(min)	**π-π*(318 nm)**		**n-π*(440 nm)**	
	R	**S**	**R**	**S**
0	0.81216	-0.0668	0.07549	-0.4454
1	0.66003	-0.1278	0.08517	-0.4387
3	0.62809	-0.1415	0.08501	-0.4388
5	0.62288	-0.1438	0.07592	-0.4451
10	0.64778	-0.1330	0.09538	-0.4317
AR+PMMA				
0	1.02075	0.00687	1.00839	0.00279
1	1.03382	0.01115	1.12017	0.03852
3	1.30258	0.09162	2.06155	0.26137
5	0.98848	-0.0039	0.98618	-0.0046
10	0.97111	-0.0097	0.9212	-0.0270
DZ+PMMA				
0	0.99626	-0.00125	0.97223	-0.00934
1	0.99055	-0.00316	1.19129	0.05994
3	0.95376	-0.01566	0.97950	-0.00688
5	0.95569	-0.01499	0.93995	-0.02042
10	0.94791	-0.01767	0.95967	-0.01362

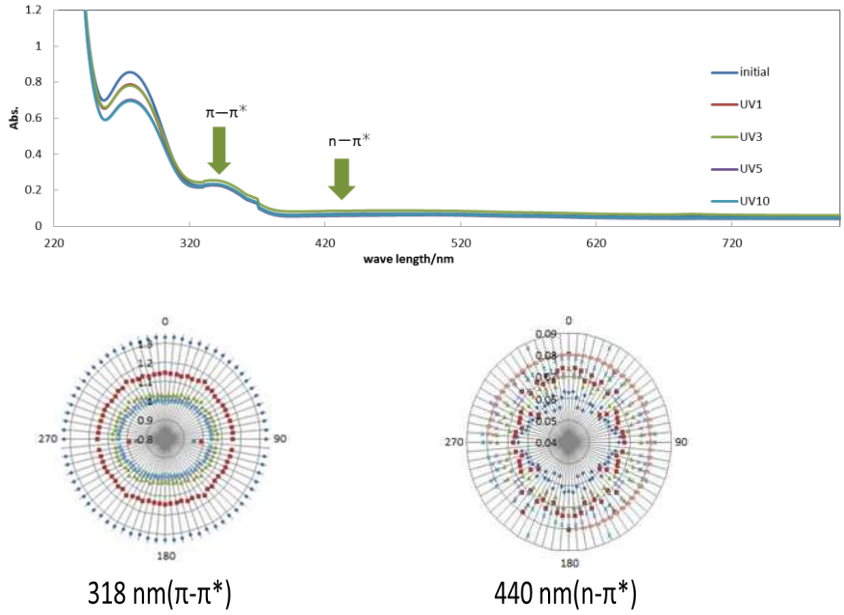


Figure 8. Polarized electronic spectra [above] and circular diagrams [below] for **DZ+PMMA**.

Linearly Polarized UV Light-Induced Molecular Arrangement for AZ+Co+PMMA

As for **AZ** only, the most effective azo-dye, the effect of photo-inactive chiral dopant (**Co**) was also investigated. After linearly polarized UV light irradiation, intensity (absorbance as it measured) of some characteristic peaks for not only **AZ** but also **Co** was measured. Figure 9 shows polarized electronic spectra and circular diagrams of angular dependence of absorbance of π-π* band, n-π* band, and d-d bands due to **Co** at 318 nm, 440 nm, and 520 nm for **AZ+Co+PMMA**. Table 2 summarized the corresponding R and S values. It should be noted that only **AZ** was influenced by Weigert effect directly among two components. Therefore, increasing optical anisotropy detected by the d-d band at 520 nm for **AZ+Co+PMMA** is attributed to **Co** which is also obvious proof of supramolecular interaction between **AZ** and **Co**.

Reducing direct transmission of molecular alignment from **AZ** by flexibility of metal complexes due to Co(II) ions is considered for Schiff base

metal complexes [10], discrepancy of tendency about molecular orientation between **AZ+Co+PMMA** cannot be explained reasonably. Therefore, to interpret dichroism of each component properly, dipole-dipole interactions (which could not be estimated from experimental data straightforwardly) between **AZ** and **Co** should be treated appropriately.

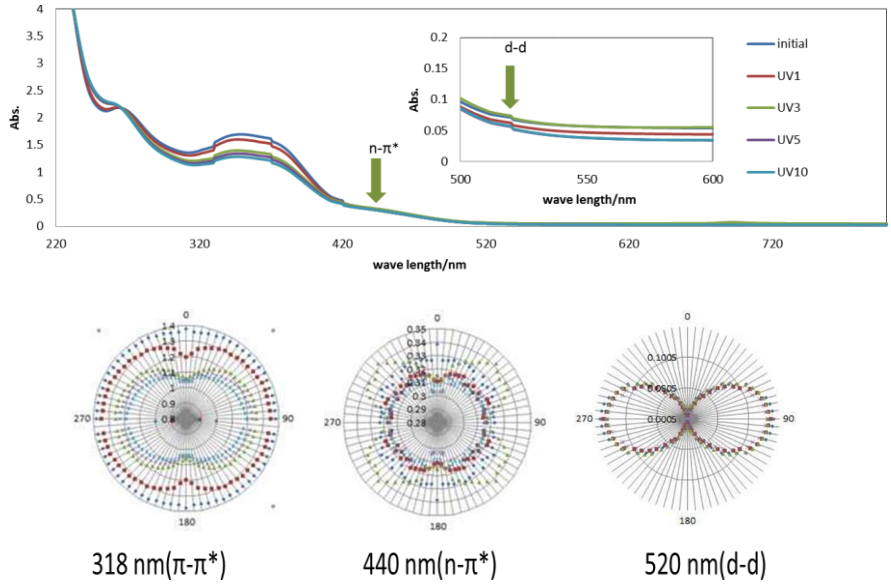


Figure 9. Polarized electronic spectra [above] and circular diagrams [below] for **AZ+Co+PMMA**.

Table 2. The R and S values after linearly polarized UV light irradiation for AZ+Co+PMMA

AZ+Co+PMMA				
UV time(min)	**π-π*(318 nm)**		**n-π*(440 nm)**	
	R	**S**	**R**	**S**
0	0.99826	-0.00056	1.04761	0.01562
1	0.88750	-0.03896	0.98047	-0.00655
3	0.84688	-0.05378	0.99987	-0.000042
5	0.85647	-0.05025	0.99556	-0.00148
10	0.86792	-0.04605	0.97422	-0.00867

Circularly Polarized UV Light-Induced Molecular Arrangement

In order to induce chiral (or helical) molecular arrangement by means of circularly polarized UV light, we investigate increasing CD bands (actually difference in intensity of a certain CD peaks) for **AZ+PMMA**, **AR+PMMA**, **DZ+PMMA**, and **AZ+Co+PMMA** (Figures 10-13, respectively). Photo-responsibility may be effective for **AZ+PMMA**, and **AZ+Co+PMMA** should be compared to discuss the effect of chiral dopant. In the linearly polarized light irradiation, **AZ+Co+PMMA** was confirmed optical anisotropy of up to 3 minutes after irradiation. In addition, the circularly polarized light irradiation, **AZ+Co+PMMA** was confirmed after irradiation 10 minutes.

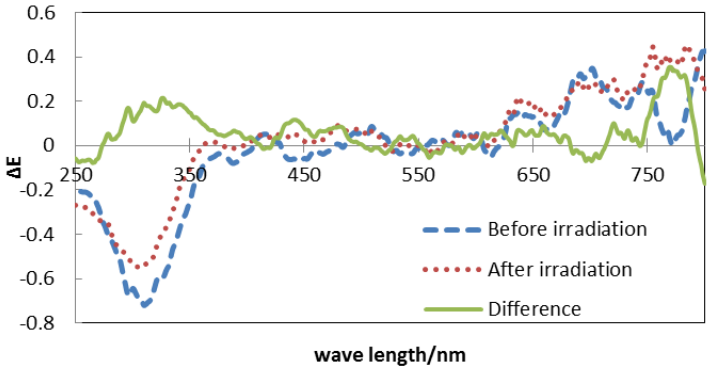


Figure 10. Difference of CD spectra after circularly polarized UV light for 3 min **AZ+PMMA**.

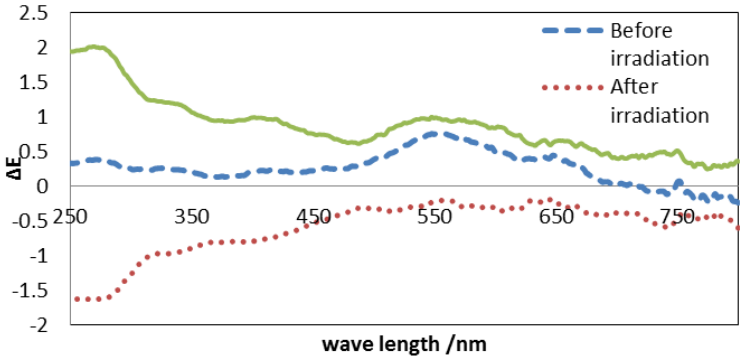


Figure 11. Difference of CD spectra after circularly polarized UV light for 3 min **DR+PMMA**.

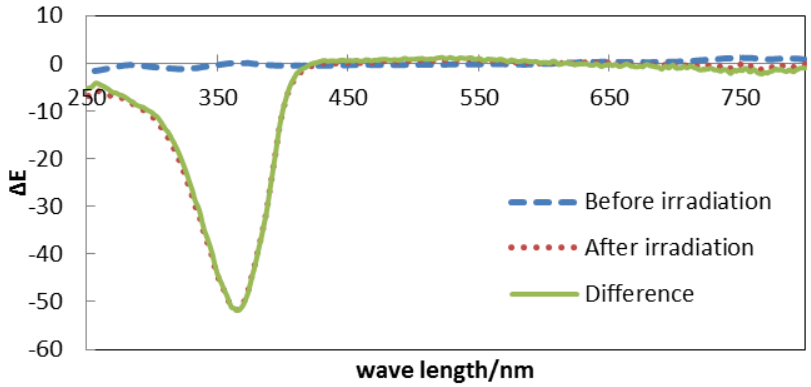


Figure 12. Difference of CD spectra after circularly polarized UV light for 3 min **DR+PMMA**.

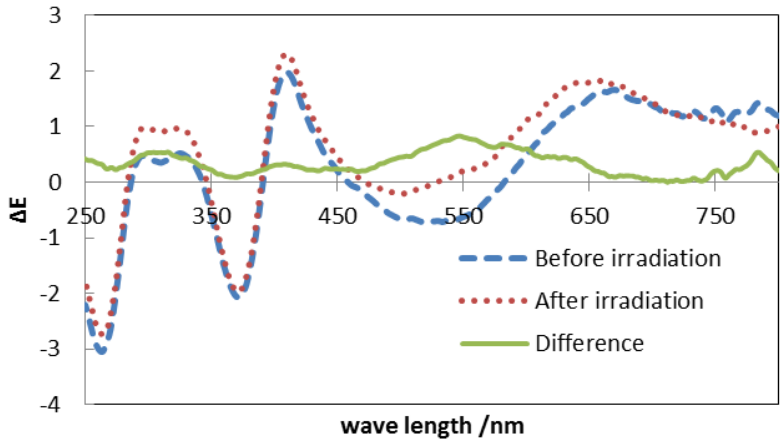


Figure 13. Difference of CD spectra after circularly polarized UV light for 10 min **AZ+Co+PMMA**.

Comparing with experimental results of CD spectra and "theoretical" CD spectra, the increasing bands of CD after circularly polarized UV light irradiation is not attributed to transitions due to molecular transitions because of absence of the corresponding transition. Therefore, emerging CD bands may be attributed to supramolecular chirality due to helical molecular arrangement induced by circularly polarized UV light irradiation. Assistance of the chiral dopant (**Co**) for **AZ** is agreement with this interpretation.

Examination of the Optical Rotation Strength by Coupled Oscillator Model

In order for qualitative interpretation of supramolecular chirality, we attempt to discuss spatial relationship between azo-dye molecules assuming dipole-dipole interaction. For this reason, we will apply coupled oscillator model [11].

If only the Coulomb interaction of the chromospheres A between B two can be considered, we assume system dipole interactions paired the two occurs. Now, the Hamiltonian of the system you are thinking is represented by the equation (1).

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

Where Hamiltonian $H_A(r_A)$ or $H_B(r_B)$ is of the chromophore *A* or *B*, V_{AB} is Coulomb interaction potential between the chromophore *A* and *B*. By the wave function of the ground states (${\Phi_0}^A$or ${\Phi_0}^B$) and excited states (Φ_a or Φ_b) of the chromophore *A* or *B*, to introduce electric transition dipole moment, optical rotation strength of the formula is derived as the equation (2).

$$R_{0a} = -\left(\frac{2\pi v_a v_b}{hc({v_a}^2 - {v_b}^2)}\right)(\mu_{0a} \cdot T \cdot \mu_{0b})(R_{AB} \times \mu_{0a} \cdot \mu_{0b}) \tag{2}$$

Where v_a or v_b is absorption frequency, μ_{0a} or μ_{0b} is electric transition dipole moment, R_{AB} is a distance of *A* and *B*, *T* is parameters.

To simplify this, consider that both chromospheres are identical, and hereafter assume R_{AB} connecting both two μ_{0a}, μ_{0b} is orthogonal (Figure14).

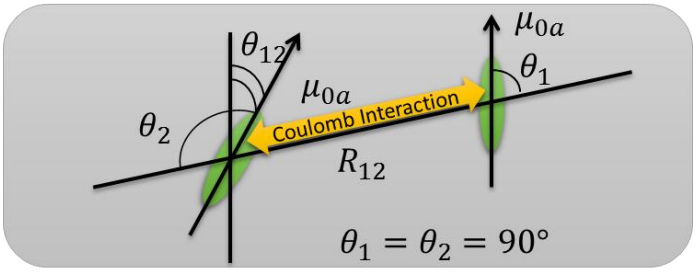


Figure14. Coulomb interaction between the same chromospheres.

At this time, from equation (2), the optical rotation strength $R_{\pm}$ becomes the following equation (3).

$$R_{\pm} = \mp\left(\pi v_0 / 2_c\right) R_{12} {\mu_{0a}}^2 \sin\theta_{12} \tag{3}$$

Further, we considered $R_{\pm}$ 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).

$$R = 2.296 \text{ x } 10^{-39} \int_0^{\infty} \left\{\Delta\, \varepsilon(\sigma) / \sigma\right\} d\sigma$$
$$\approx \left(2.296 \text{ x } 10^{-39} / \sigma_0\right) \int_0^{\infty} \Delta\varepsilon(\sigma) d\sigma \text{ (c.g.s)} \tag{4}$$

where σ is the wavenumber and σ_0 is the 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 (see Figures 10-13). Substituting equation (3), the degree of inclination (θ) of the dye molecules of interest was evaluated. The transition dipole moment at this time is based on the results of ZINDO. As a result, the angle of optical rotation and strength to transition electric dipole moment of each dye in the π-π* or n-π* transition state of each systems was summarized in Table 3.

Table 3. The angle of optical rotation and strength to transition electric dipole moment of each dye in the π-π* or n-π* transition states. For simplicity, R_{12} was assumed to be 0.5 nm all. In AZ+Co+PMMA, Co is considered as a chiral dopant

	AZ+Co+ PMMA	**AZ+ PMMA**	**AR+ PMMA**	**DZ+ PMMA**
R (n-π*)/c.g.s	6.25529×10^{-34}	1.03224×10^{-34}	1.69077×10^{-34}	4.20159×10^{-33}
θ / deg	3.490030×10^{-29}	5.75921×10^{-30}	9.59665×10^{-35}	4.22290×10^{-36}
μ_{0a}*(n-π*)/Debye*	0.795802	0.795803	0.023932	0.587770
R (π-π*)/c.g.s	3.95981×10^{-34}	6.53445×10^{-35}	1.24778×10^{-34}	2.81683×10^{-33}
θ/deg	1.40474×10^{-29}	2.31809×10^{-30}	1.95930×10^{-34}	2.69171×10^{-37}
μ_{0a}*(π-π*)/Debye*	0.794052	0.794052	0.012360	1.560796

The calculated results indicated that transition dipoles of **AZ** resulting in large electric dipole transition of n-π* and π-π* transitions are significantly inclined each other, which was attributed to mutual molecular orientation induced by circularly polarized UV light irradiation. In addition, comparison between A**Z+Co+PMMA** and **AZ+PMMA** suggested that chiral dopant (**Co**) strongly assisted to chiral molecular orientation of **AZ** induced because of the Coulomb interaction between **Co** and **AZ**.

CONCLUSION

Consequently, similar to linearly polarized UV light exhibited Weigert effect, circulary polarized UV light could induce chiral supramolecular arrangement of azo-dyes, **AZ**, **DR**, and **DZ**, and **AZ** is the most effective photosensitive azo-dye among them due to suitable to flexibility in PMMA environment. Additionally, chiral dopant (**Co**) could gain the effect to form chiral supramolecular arrangement of **AZ** after circulary polarized UV light radation, which was led by model discussion of dipole-dipole interaction to interpret n-π* and π-π* transitions.

ACKNOWLEDGMENT

This work was supported by the Research Foundation for Opto-Science and Technology.

REFERENCES

[1] Blackburn, O. A., Coe, B. J., Fielden, J., Helliwell, M., McDounall, J. J. W. & Hutchings, M. G. (2010). *Inorg. Chem*., *49*, 9136 and references therein; A. A. Khandar and Z. Revani, Polyhedron, 1998, 18, 129.

[2] Einaga, Y., Taguchi, M., Li, G., Akitsu, T., Sugai, T. & Sato, O. (2003). *Chem. Mater*., *15*, 8, R. Mikami, M. Taguchi, K. Yamada, K. Suzuki, O. Sato and Y. Einaga, Angew. *Chem. Int.* Ed., *43*, 6135, M. Taguchi, K. Yamada, K. Suzuki, O. Sato and Y. Einaga, *Chem. Mater*., 2003, *17*, 4554., T. Yamamoto, Y. Umemura, O. Sato and Y. Einaga, *J. Am. Chem. Soc*., 2005, *127*, 16065, T. Yamamoto, Y. Umemura, O. Sato and

Y. Einaga, *Chem. Mater*., 2004, *16*, 1195, Y. Einaga, R. Mikami, T. Akitsu and G. Li, *Thin Solid Films*, 2005, 493, 230.

[3] Akitsu, T. & Yoshida, A. (2011). *Curr. Phys. Chem*., *1*, 76, T. Akitsu and S. Yamamoto, *Asian Chem. Lett*., 2010, 14, 255.

[4] Akitsu, T. & Einaga, Y. (2005). *Polyhedron, 24*, 1869, Akitsu, T. & Y. Einaga, Polyhedron, 2005, 24, 2933, T. Akitsu, Polyhedron, 2007, 26, 2527.

[5] Akitsu, T. & Einaga, Y. (2006). *Inorg. Chem. Commun*., *9*, 1108, Akitsu, T. & J. Nishijo, J. Magn. Magn. Matter., 2008, 320, 1586, Akitsu, T. & J. Nishijo, J. Magn. Magn. Matter., 2007, 315, 95, T. Akitsu, J. Magn. Magn. Matter., 2009, 321, 207.

[6] Weigert, F. (1921). *Naturwissenschaften, 29*, 583, K. Ichimura, Chem. Rev., 2000, 100, 1847 and references therein.

[7] Akitsu, T., Ishioka, C. & Itoh, T. (2009). *Cent. Euro. J. Chem*., *7*, 690, Akitsu, T. & C. Ishioka, Asian Chem. Lett., 2010, 14, 37, Akitsu, T. & T. Itoh, Polyhedron, 2010, 29, 477, Akitsu, T. & R. Tanaka, Curr. Phys. Chem., 2011, 1, 82, Akitsu, T. & Y. Miura, J. Chem. Chem Eng.,2011, 5, 443, Y. Aritake, T. Takanashi, A. Yamazaki and T. Akitsu Polyhedron, 2011, 30, 886.

[8] Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M.A., Cheeseman, J. R., Scalmani, G., Barone, V., Mennucci, B., Petersson, G. A., Nakatsuji, H., Caricato, M., Li, X., Hratchian, H. P., Izmaylov, A. F., Bloino, J., Zheng, G., Sonnenberg, J. L., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Vreven, T., Montgomery, J. A. Jr., Peralta, J. E., Ogliaro, F., Bearpark, M., Heyd, J. J., Brothers, E., Kudin, K. N., Staroverov, V. N., Kobayashi, R., Normand, J., Raghavachari, K., Rendell, A., Burant, J. C., Iyengar, S. S., Tomasi, J., Cossi, M., Rega, N., Millam, J. M., Klene, M., Knox, J. E., Cross, J. B., Bakken, V., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R. E., Yazyev, O., Austin, A. J., Cammi, R., Pomelli, C., Ochterski, J., Martin, R. L., Morokuma, K., Zakrzewski, V. G., Voth, G. A., Salvador, P., Dannenberg, J. J., Dapprich, S., Daniels, A. D., Farkas, O., Foresman, J. B., Ortiz, J. V., Cioslowski, J. & Fox, D. J. (2009). GAUSSIAN 09 (Revision A.1), Gaussian, Inc., Wallingford, CT.

[9] Li, X., Lu, X., Lu, Q. & Yan, D. (2007). *Macromolecules, 40*, 3306, B. Sapich, A. B. E. Vix, J. P. Rabe and J. Stumpe, Macromolecules, 2005, 38, 10480, R. Advincula, M.-K. Park, A. Baba and F. Kaneko, Langmuir, 2003, 19, 654, T. Geue, A. Ziegler and J. Stumpe,

Macromolecules, 1997, 30, 5729, N. Bohm, A. Materny, W. Kiefer, H. Steins, M. M. Muller and G. Schottner, Macromolecules, 1996, 29, 2599, N. Bohm, A. Materny, H. Steins, M. M. Muller and G. Schottner, Macromolecules, 1998, 31, 4265, L. De Boni, C. Toro, A. E. Masunov and F. E. Hernandez, J. Phys. Chem. A, 2008, 112, 3886.

[10] Sakiyama, H., Okawa, H., Matsumoto, N., Kida, S. J. (1990). *Chem. Soc., Dalton Trans*., 2935, B. Bosnich, J. Am. Chem. Soc., 1968, 90, 627. H. Okawa, M. Nakamura and S. Kida, Inorg. Chim. Acta, 1986, 120, 185, Y. Nishida and S. Kida, Bull. Chem. Soc. Jpn., 1970, 43, 3814, H. Sakiyama, H. Okawa, N. Matsumoto and S. Kida, Bull. Chem. Soc. Jpn. 1991, 64, 2644. M. Ulusoy, H. Karabiyik, R. Kilincarslan, M. Aygun, B. Cetinkaya and S. Garcia-Granda, Struct. Chem., 2008, 19, 749, Akitsu, T. & Y. Einaga, Polyhedron, 2006, 25, 1089.

[11] Kanbara, S. & Nanzyo, M. (1984). "Spectroscopy in the polymer", Kyorotsu Publication, Japan, C. L. Cech, W. Hug, I. Tinoco Jr., Biopolymers, 15, 131(1976)., D.J. Caldwell, H.Eyring, "Theory of Optical Activity", Wiley-Interscience, New York (1971)., I. Tinoco, Jr., *Advan. Chem. Phys*., *4*, 113(1962).