Review

Induced CD on metal nanoclusters or other materials by chiral Schiff base metal complexes

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ABSTRACT

Induced circular dichroism (CD) band on plasmon region of metal nanoclusters by chiral metal complexes is described. The CD by chiral substances is also known to occur for metal nanoclusters, along with resonance plasmon absorption that shifts depending on the particle size. Some of the mechanisms of interactions between nanoparticles and plasmon have been clarified theoretically. Furthermore, applications such as the detection of biomolecules are expected for not only spectroscopic methods but also imaging methods. In addition to metal nanoclusters, chiral Schiff base metal complexes, such as azo-dyes, achiral metal complexes, metal dendrimers, metal oxide semiconductors, and proteins, exhibit unique optical absorption bands. It has been reported that an induced CD band is observed due to molecular alignment, e.g., in aggregates or dyes in crystal. This short review introduces the possibility of supramolecularly imparting chirality effects and functions to various materials such as colloidal gold by enumerating CDs induced by (azobenzene-containing) chiral Schiff base metal complexes. This review was compiled for the purpose of deepening the understanding of the induced CD phenomenon.

KEYWORDS: supramolecular chirality, induce circular dichroism, plasmon, transition moment, metal nanocluster, biomolecules.

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1. Introduction

1.1. Induced CD on metal nanoclusters by chiral species

In recent years, interest in chirality on the surface of nanostructures has increased rapidly [1]. We have shown that CD can be induced by the absorption lines of achiral molecules with which chiral molecules are closely interacting. Recently, it has been shown that chiral molecules bound to precious metal nanostructures can induce CD by surface plasmon resonance excitation. In the rapid progress of research on metal nanoclusters, experiments and theories on the induction of the chiral optical effect of CD in the plasmonic and exciton resonances of achiral inorganic nanocrystals capped and/or formed with chiral molecules have been reported. The main focus of this research is on metal and semiconductor nanoclusters with atomic cluster sizes up to 100 nm that interact with chiral molecules. On the other hand, the various factors associated with inorganic nanostructures that allow the possibility of obtaining CD by electron excitation are chiral shape, chiral composition of interacting achiral nanoparticles (NPs), essentially chiral crystals, and so on. These can be classified as achiral nanoparticles that interact closely with chiral molecules. The surface of the light may be distorted, while a super-helical light field may be used as the light [2, 3]. If the achiral NPs are arranged in a chiral arrangement with strong particle-to-particle interactions, the electronic excitation of the particles can cause chiral optical

activity naturally according to general principles. This is especially effective for plasmonic NPs, where particle-to-particle interactions (dipoles /multipoles) can extend to the nanometer scale. It should be emphasized here that it can be very difficult if the goal is to obtain substantial optical activity from the chiral assembly. This requires the formation of a relatively large number of assemblies with well-defined dominant-hand particle interactions. The CD signal from the chiral complex may also be lost in the dipole model. Clear experimental evidence of the near-field (dipole) mechanism is required. This is because when constructing a theoretical model, it is necessary to make assumptions about the orientation of chiral molecular dipoles with respect to the surface by the electrical transition dipole moment and the magnetic transition dipole moment of the molecule.

The transfer of chirality from biomolecules to plasmon resonance region is a collective phenomenon, and the large chiral plasmonic structure identifies a new electrodynamic mechanism for plasmonic CD [4, 5]. This is qualitatively different from the plasmonic chirality near-field dipole mechanism we described earlier. Nanostructures consisting of chiral and non-chiral elements can enhance or transfer chiral properties between elements such as molecules, semiconductor quantum dots, and metal nanocrystals. Interactions involved in the transmission or generation of chirality include orbital coupling of electron wavefunctions, dipole-dipole interactions, and electromagnetic interactions.

The coherently bound plasmons and excitons cause a new photoexcitation, or exciton, due to the strong coupling of these two oscillator systems. Time-resolved studies of the J-aggregate-Au nanoshell complex with degenerate nanoshell plasmons and J-aggregate exciton energies investigated the dynamic behavior of this binding system [6-8]. When metal nanoparticles are resonantly excited, they maintain collective electronic excitation known as localized surface plasmons. The ultrafast optical dynamics of the hybrid resonance plasmon-exciton system consisting of the J-aggregate-Au nanoshell complex are important there.

There are also several reports on chiral biomolecules such as chlorophylls [9], PS I [9], DNA [10], peptides [11], and proteins [12]. Using photosynthetic proteins such as Photosystem I as a model, there have been studies attempting to enhance the absorption band with a metal nanoparticle artificial antenna [13]. Photosystem I has a structure in which chlorophyll and carotenoid are embedded in a polypeptide chain, but no direct experimental demonstration of absorption enhancement has been reported. The synthesis of the Photosystem I metal colloid hybrid system showed that the binding of Photosystem I to metal nanoparticles clearly enhanced the absorption of light by Photosystem I. The discussion used a simple bipolar interaction model and assumed average chromophore-metal particle separation for all chlorophyll molecules.

Chiral molecules have been shown to induce CD by surface plasmon resonance of gold nanostructures when they approach the metal surface without directly binding to the metal. Although it is possible to detect minute changes in plasmon excitation as a result of molecular adsorption with high sensitivity, there is a lack of conformational information about the molecule, such as information about the chirality of the molecule [14, 15]. The nature of the interaction between the chiral molecule and the surface plasmon remains unresolved. One of the reasons for this is that there is no clear experimental evidence for the mechanism of CD induction. On the other hand, some systems do not include orbital hybridization in the CD mechanism in this case because there is no direct bond between the molecule and gold. Therefore, the CD spectrum calculated according to a simple bipolar interaction model is not perfect.

1.2. Important point of electromagnetic theory

Consider the interaction between nanoparticles and surface molecules and electromagnetic waves.

$$D = \varepsilon E + i\varphi B$$
$$H = B/\mu + i\varphi E \tag{1}$$

Above is a symmetric equation with the influence of chirality and the electric or magnetic field in the substance. ε is a function related to permittivity

and φ contains information about chirality. Since the material on the surface is a dielectric, the charge distribution with respect to the electric field differs depending on the molecule. Therefore, ε was introduced as a parameter. And in this model, the magnetic permeability is treated as almost eq. (1).

$$c^2 \nabla \times B = \frac{J}{\varepsilon_0} + \frac{\partial E}{\partial t}, \nabla \cdot E = \frac{\rho}{\varepsilon_0} \qquad (2)$$

where J : vector of current density, ρ : charge density, and c : velosity of light.

Next, Maxwell's equations for electric and magnetic fields are described. Since the system is extremely small, the time evolution during that period can be ignored. Also, consider an equation in which the current density and internal charge are set to 0. The above-mentioned eq. (1) and this are combined to make a problem analysis tool.

In a system in which the whole is spherical (a state in which molecules are thinly covered on metal nanoparticles), the shapes of electrostatic potential and vector potential are known and are shown below.

$$\emptyset_i = Q_i^1 \cdot (E \cdot r) + Q_i^2 \cdot (B \cdot r) + Q_i^3 \frac{(E \cdot r)}{r^3} + Q_i^4 \frac{(B \cdot r)}{r^3},$$

$$A_i = S_i^1 \cdot (E \times r) + S_i^2 \cdot (B \times r) + S_i^3 \frac{(E \times r)}{r^3} + S_i^4 \frac{(B \times r)}{r^3}$$

$$(3)$$

where ϕ : electrostatic potential, A : vector potential, i : index of minute parts, Q and S : each coefficient.

Each coefficient is obtained from the boundary conditions.

Here, let's interpret the system based on statistical mechanics. Many particles are linked to the electric field in the presence of nanoparticles. We thought that the canonical distribution in the equilibrium system could be applied. First, the polar coordinates are set from the center of the metal particle as the origin.

$$\mu_i = \mu(\sin\theta_i \cos\varphi_i, \sin\theta_i \sin\varphi_i, \cos\theta_i) \qquad (4)$$

All of the dipole moment of each coated molecule was set to μ. From eq. (4), the angle between the

electric field and the moment is θ. Based on these, Hamiltonian is written at below.

$$H = \sum_i \left[\frac{p_i^2}{2m} - E\mu\cos\theta_i\right] + \sum_{i<j} U_{ij} \qquad (5)$$

$$U_{ij} = -\frac{1}{4\pi\varepsilon_0 R^3}\{3(\mu_i \cdot e_R)(\mu_j \cdot e_R) - \mu_i \cdot \mu_j\} \qquad (6)$$

where U_{ij} : potential between moment. Adding up across all pairs, R: position vector between moment, and e_R: unit vector of R.

If these energy eigenvalues are obtained, the partition function can be constructed. Let each eigenvalue be k, and the angle at k is θ_k.

$$\langle\theta\rangle = \frac{1}{Z(\beta)}\sum_k \theta_k e^{-\beta E_k} \qquad (7)$$

where $Z(\beta)$: partition function, and β : inverse temperature.

From the above, the expected value of the angle can be obtained. The temporal fluctuation of the electric field requires perturbation to solve the equation, but value of the electric field was considered to be almost constant because the system is minute (detailed treatment of partition function was omitted). The discussion of angles may be meaningful not only in terms of knowing the state of the system, because the optical rotation takes the inner product of two types of moments.

2. Nanoparticles and chiral materials

2.1. Additional chirality to metal nanoparticles

Let's start by looking at the elements of interaction one by one. Achiral metal nanoparticles are being actively researched in connection with biomolecules, though chiral nanoparticles can exhibit chiroptical properties by themselves [16, 17]. At first, chiral nanoparticles [18] should be excluded from the target of this story, except for establishing theoretical models or computational systems [19]. Surface adsorption of well-ordered molecules may sometimes induce chirality by itself, though induced CD in the plasmon region or fluorescence due to chiral molecules [20] should be restricted in this case. Using chirality for several reasons as a whole [21], we aim to use a detection method that can obtain further

information on chiral molecules using metal nanoparticles. In particular, the expression of chirality by the interaction between chiral molecules and nanomaterials is attracting attention for application to next-generation analytical methods. Such an expression of chirality also plays an important role in molecular recognition. There are CD, optical rotatory dispersion (ORD), or Surface-enhanced Raman Scattering (SERS) spectra to investigate such properties. What can be detected and the effects of intermolecular interactions will be summarized later.

2.2. Induced CD of metal nanoparticles by chiral (azo-)complexes

Chiral Schiff base zinc(II) complexes were synthesized, and induced CD was observed for gold nanoparticles [22] and CdSe [23]. The absorption and CD spectra of the mixed solution with three types of gold nanoparticles of different particle sizes were measured. The larger the particle size, the more difficult it is to observe the spectrum due to the influence of light scattering. In the UV-vis and CD spectra of the mixed solution, the smaller the particle size of the gold nanoparticles, the more the CD band of the zinc(II) complex disappeared and the fluorescence wavelength of the gold colloid and the complex shifted. Interaction was thus confirmed. In recent years, bio-sensing and imaging using plasmon resonance, fluorescence, refraction of light, etc., of colloidal gold have been actively used. We synthesized chiral shift base metal complexes with large dipole moments and attempted to observe induced CDs of CdSe nanoparticles, the absorption and fluorescence wavelengths of which shift depending on the particle size. We tried cis-trans photoisomerization of complexes containing azobenzene. In a solution containing only a complex, reversible isomerization is exhibited in the cis form by ultraviolet light irradiation and in the trans form by visible light irradiation, as in the case of ordinary azobenzenes. In the absorption spectrum, even large gold nanoparticles and high-concentration complexes are not affected by light scattering. The π–π* and n–π* bands of the CD spectrum disappeared, the plasmon band appeared positively, and there was a complex concentration dependence. Compared with the theory, the behavior when the electric dipole moment is

parallel to the surface of the gold colloid was shown. As described above, nano-inorganic substances and chiral metal complexes have "conditions" suitable for the induced CD phenomenon. Results show the possibility of supramolecularly imparting chirality effects to various functions of gold nanoparticles.

In any mixed solution of gold nanoparticles and a chiral Schiff base metal complex, the peak of induced CD appeared remarkably around 550 nm [24-26]. This is a band not found in the chiral metal complex and is a wavelength region corresponding to the plasmon peak of gold nanoparticles. It is considered that the angles of the dipole moments of the complex and gold nanoparticles are oriented in parallel. In this case, the molecular orientation of the chiral metal complex on the gold nanoparticle surface is important. Complex systems with metal nanoparticles have been studied for the purpose of synthesizing chiral Schiff base metal complexes showing induced CD and elucidating the adsorption structure on the gold nanoparticle surface. Theoretically, achiral gold nanoparticles exhibit a CD signal induced by the dipole-dipole interaction and dielectric effect of the adsorbed chiral molecule.

So far, we have tried to observe induced CDs of various complexes and various nanoparticles, and we have discussed the presence or absence of adsorption. For the complex on gold nanoparticles and the complex in which this induced CD was observed, X-ray photoelectron spectroscopy (XPS) and Scanning Tunneling Microscope (STM) measurements were carried out using the complex and a gold substrate as a model of the complex system for further analysis of the adsorption structure [24]. From the quantitative ratio, it was found by XPS measurement that the structure of the complex did not collapse and was adsorbed. It was also found by STM measurement that there is a high possibility that the complex is adsorbed almost vertically on the model substrate. Furthermore, when the dipole moment of the chiral molecule changed due to photoisomerization or photoorientation change of the ligand containing azobenzene, a corresponding change in the induced CD was also observed [25, 26].

2.3. Azobenzene as a ligand component of complexes and its photochemistry

Azobenzene dyes have a large transition dipole moment, and their molecular alignment will be stated again in later sections; here, we explain photoisomerization and photoorientation briefly [27, 28]. Besides azo-compounds on the surface of nanoparticles [29-33], the interaction between chiral complexes and azo-dyes will be introduced later in the paper. In the field of optical functional polymer organic materials such as liquid crystals, the Weigert effect has long been known, in which the dipole moment of the molecular major axis is oriented in the direction perpendicular to the electric vector of polarized light when irradiated with polarized ultraviolet light. Alternate irradiation of polarized ultraviolet and visible light causes cis–trans photoisomerization of azobenzene, which overcomes mitigation, increases anisotropic orientation due to linearly polarized light, and increases chiral molecular orientation due to circularly polarized light. The orientation of the metal complex dispersed in the medium as a composite material should also follow. Polarization spectroscopy has made it possible to discuss the effects of overlapping two components, changes in the optical anisotropy of the band unique to the components, and the effects on the coordination environment, ligand conformation, and molecular orientation. It should be noted that CD spectroscopy has a principal problem due to anisotropy. In any case, the ability to control chiral molecules from the outside is expected for molecular design, such as specific molecular recognition between chiral metal complexes.

2.4. Metal nanoparticles with metal complexes and optical device application

Regarding nanoparticles other than gold, spectroscopic measurements of silver nanoparticles and the plasmon effect are also being studied. Although it has been theoretically explained that plasmons and dipole moments increase in a composite system of nanoparticle chiral compounds, there have not been many experimental studies on chiral interactions and optical properties.

One of the reasons for this may be experimental difficulties. There is an example using the original

complex chiral azo-Schiff base complex as the dye in a dye-sensitized solar cell (DSSC) [34]. Since the first transition metal is used as the central metal, it is inexpensive and easy to synthesize. However, the conversion efficiency of the DSSC cell using this complex was not good. Therefore, we attempted to create a device with higher light collection ability by combining silver nanoparticles and applying a phenomenon called localized surface plasmon resonance [35, 36]. In the UV–vis spectrum of the complex, there is a maximum absorption peak near 400 nm, which is almost the same as the simulation result by time-dependent density-functional theory (TD-DFT) calculation. The CD spectrum did not give good data due to the problem of intensity [26].

2.5. Surface of semiconductor nanoparticles and dye-metal complexes

In the case of the Zn-porphyrin dye complex, it was observed that the maximum fluorescence wavelength of the fluorescence spectrum was larger than that of the carboxyl type in the salicylic acid type introduced at the para position, the spectrum width was widened, and the wavelength was shifted by a long wavelength due to adsorption onto titanium dioxide [37]. Electronic coupling with the dye complex was suggested, which was also shown to be advantageous for electron transfer. Not only the anchor part but also the adsorption orientation of the dye complex itself affects the factors that determine the performance, such as electron injection, reverse electron transfer, current density, release voltage (especially when there is a cosensitizer [38]), and the photoelectric conversion efficiency. This can be an important influencing factor. In the system in which quenching of the fluorescence spectrum was observed, it (spectrum) was explained as a phenomenon occurring due to a change in dye adsorption density due to intermolecular aggregation.

In this way, research focusing on various factors has been conducted in order to improve photoelectric conversion efficiency. Judging from the fact that NPs absorbs light, the situation is affected by the intermolecular interaction between dye molecules (or the dye–metal complex and titanium dioxide), and there is still much room for studies focusing on molecular orientation. Using the photosynthetic

antenna dye as a model, aligning the molecular orientation of the dye-metal complex to improve the light collection efficiency is considered to be an effective method [39].

Among the wavelengths of sunlight falling on the surface of the Earth, those with large energy are in the wavelength range of the so-called visible light region near 500 nm. In addition, it is known that titanium oxide alone absorbs up to around 400 nm, but it is considered necessary to further expand the wavelength range in order to improve the conversion efficiency and power generation efficiency of dye-sensitized solar cells (DSSCs). We have been developing and evaluating the physical properties of dye complexes to improve the performance of DSSCs using derivatives of the Schiff base metal complex, which is relatively easy to synthesize [40-42]. The aldehyde side of the Schiff base metal complex is azobenzene having an azo group, which is a chromophore, and the π-conjugated system is expanded with the aim of expanding the light absorption wavelength range (visible region by the azo-dyes) and improving the efficiency of electron transfer. Differences in light absorption wavelengths also occur due to differences in metals and ligands. We are thinking of using this to mix different light absorption regions and widen the wavelength region for absorption. Further studies have reported improving the conversion efficiency of DSSCs by combining chiral complex dyes exhibiting non-linear optical effects on the surface of titanium oxide [43].

3. Chiral complexes and materials - beyond nanoparticles

3.1. Exciton interaction of the transition dipole moment of dyes in a crystal

From now on, we will not necessarily target nanoclusters but will introduce related elements. We now discuss chiral metal complexes that can induce chirality in nanoclusters, other substances that interact with nanoclusters, and elements of optical interaction. Via interaction between the transition electric dipole and the transition electric dipole, the dye molecule forms a specific molecular sequence in the crystal and exhibits a color tone that is not seen in isolated molecules

(such as in solution). This can be considered an easy-to-understand example, and detailed research has been conducted on the exciton interaction of the electric dipole for several decades [44-49]. Such exciton interactions, along with plasmon interactions, are also important physical factors in discussing chiral optical effects on nanoclusters. Thus, we describe the prospects for these physical mechanisms to play an active role, conscious of their relationship with nanoclusters.

3.2. J- or H-aggregates

In addition to the conventional J- or H-aggregates between dyes [50], the dipole moments of chiral low molecules adsorbed on metal nanomaterials (gold nanoparticles, semiconductor quantum dots, etc.) that have a vertical dipole moment on the surface are arranged in parallel [51-53]. This is induced by the molecular orientation. Supramolecular phenomena, or, in other words, additional spectroscopic phenomena due to intermolecular molecular orientation, have been less studied than spectroscopic properties due to intramolecular three-dimensional and electronic structures. The current situation is that there is no such thing. By utilizing photoelectron transfer due to light absorption due to intermolecular orientation to improve the photoelectric conversion efficiency of dye-sensitized solar cells, but also by aiming to develop theoretical design guidelines, a much wider range of supramolecular chemistry can contribute to the basics and applications of energy materials.

In this context, synthesizing a new azo-complex with an extended π-conjugated system and large dipole moment in the ligands and extending the light absorption range to the long wavelength region using the formation of J-aggregates could be planed. It should be confirmed that the light absorption range is expanded to the long wavelength region even in a single dye; however, the wavelength range that could be covered is limited. In addition, in an attempt to widen the absorption wavelength, two kinds of dyes were adsorbed onto titanium oxide or metal nanoparticles to complement each other's weak absorption wavelengths. In order to make the cell easier to produce and to increase the light absorption wavelength region, we increased the

number of complexes to be used to two different kinds of complexes, a chiral azo-complex and zinc(II) phthalocyanine [54], and they were adsorbed onto the surface of titanium oxide or metal nanoparticles to develop a new photoelectric conversion mechanism using the aggregation interaction of these complexes.

3.3. Chiral azo-complexes in polymer films

An organic-inorganic composite material containing a metal complex and azobenzene in a polymer (polymethylmethacrylate) film was created, and this was alternately irradiated with linearly or circularly polarized ultraviolet and visible light, and then the polarization absorption spectrum was determined [55-61]. As a result of observation, it was confirmed that the optical anisotropy of the metal complex without a direct bond increased with increasing orientation of azobenzene due to the Weigert effect. Furthermore, an increase in optical anisotropy was also observed in the cis-type chiral Schiff base metal complex, which is expected to be more rigid. In each case, the increase in optical anisotropy depended on conditions such as the central metal of the complex, conformation, and chirality. Therefore, an organic-inorganic composite material containing azobenzene as a constituent element of a chiral metal complex having a diphenyl group is expected to have a larger steric effect and dipole moment.

Linearly polarized light properly aligns the dipole moments of the two dyes to extend the available light absorption wavelengths through interaction (between excitons known as J- or H- aggregates, etc.) and addivability. We designed materials with the expectation of continuous generation of photoexcitation and photoelectron transfer reactions. By comparing the theoretical optical rotation intensity in relation to linearly and circularly polarized ultraviolet light irradiation, the angle comparison with respect to the optical rotation intensity of the π–π * and n–π * transition states and the transition of the complex in each transition state can be used to compare the electric dipole strengths.

3.4. Chiral transfer or induced CD of metal complexes

Dispersion-induced circular dichroism (DICD) and chiral metal complexes have been vigorously investigated for several decades [62-71]. Supramolecular and molecular assembled systems are being actively researched in order to realize functionality that cannot be achieved in single-component substances or single molecules. Therefore, when the properties related to structural-physical properties of chiral metal complexes, which have been discussed in the past as a single molecule, are extended to a complex system, the system can act as a probe in the same way, or a new phenomenon peculiar to the complex system is expected, or a physical property evaluation method is required. It may be done now, or research based on a new concept may be needed in the future. "Supramolecular chirality" is a property of probes peculiar to such a complex system. In recent years, research on chirality targeting nano/supramolecular materials such as chiral metal nanoparticles and liquid crystals showing chiral transfer, which are aimed at applications as asymmetric catalysts, has been actively conducted. Thus, chirality has been extensively studied in the field of metal complexes for a long time, in addition to the properties such as steric chemistry, asymmetric catalysis, and physical properties of biomolecules such as proteins and functional molecules such as liquid crystals.

Induced CD between metal complexes in solutions has also been investigated [72-75]. A system containing a chiral Schiff base Ni(II) complex and another (a)chiral Schiff base Cu(II) complex having the same ligand, or a Cu(II) ion coordinated PAMAM dendrimer, exhibited induced CD in the absorption region of achiral ones. Furthermore, we observed induced CD in the wavelength region corresponding to the surface plasmon peak for the first time. Thus, we would like to deepen our understanding by making it possible to discuss the dipole moment in detail as a phenomenon focused on interaction with light.

3.5. Chiral biomolecules and metal complexes

In a composite material comprising a metal complex and a protein, which is a biopolymer, since it is possible to design a ligand of the complex, it is possible to have high-selectivity and high-yield characteristics, and it is

environmentally friendly. As high-yield bio-hybrid materials, such composites are attracting attention in the fields of pharmaceuticals and biochemistry. To date, many examples of complex-protein complexes have been reported, and the artificial metal enzymes created are used as catalysts in Diels-Alder reactions and redox reactions. We also conducted research on the above-mentioned organic-inorganic composite materials in a system compatible with proteins that are biopolymers, and we succeeded in controlling the molecular orientation in protein systems as well as in organic polymer membranes. In these studies, we aim to create a new complex system by complexing a metal complex with a protein (artificial metalloproteins) as a functional material [76-81], evaluate the intermolecular interaction between the metal complex and the protein, and examine the optical properties of the complex system. The additional purpose is to examine the possibility of using it in a new spectroscopic evaluation method for life sciences, of course.

4. Conclusions

Based on the above, the combined chiral azo metal complex-gold nanoparticle systems were interesting. We now understand this experimentally and theoretically. Furthermore, metal NPs with chiral compounds may be chiral catalysts potentially.

In recent years, our laboratory has created an organic-inorganic composite material in which a chiral Schiff basic metal complex and photoresponsive organic molecules such as azobenzene are dispersed in a polymer membrane. In addition to this, along with the phenomenon wherein the molecular orientation of azobenzene is aligned by irradiation with polarized ultraviolet light (Weigert effect), the molecular orientation of the chiral Schiff base metal complex that undergoes supramolecular interaction such as π–π stacking is also aligned. This was clarified by measuring means using optical methods such as ultraviolet-visible spectroscopy and infrared spectroscopy in which a linear polarizer was installed. In organic-inorganic composite materials, a spectrum in which multiple components are superimposed is observed. Therefore, for the purpose of increasing selectivity, fluorescence spectroscopy that can select the excitation light/emission wavelength and achiral components is irrelevant. We are continuing our efforts to obtain detailed spectroscopic information on organic-inorganic composite materials via CD spectroscopy, which can observe only chiral metal complexes.

AUTHOR CONTRIBUTIONS

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CONFLICT OF INTEREST STATEMENT

The authors declare no conflict of interest.

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