

STEREOCHEMISTRY AND MOLECULAR RECOGNITION ON THE SURFACE OF A SMECTITE CLAY MINERAL

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Abstract—Attempts at optical resolution and asymmetric syntheses using smectite clay minerals are described. Use of the method was prompted by the discovery that the saturated adsorption of a tris(chelated) metal complex, $[\text{Ru}(1,10\text{-phenanthroline})_3]^{2+}$, by Na-montmorillonite depended heavily on the stereochemical properties. The pure enantiomer was adsorbed by cation exchange at negative surface sites of the clay mineral, while the racemic mixture was adsorbed to two times excess of the cation exchange capacity. The chelate takes a uniform orientation on a clay mineral surface due to the matching between the molecular symmetry and the two-dimensional network of a phyllosilicate layer. On a clay mineral surface covered with the enantiomeric chelates, a vacant space capable of chiral discrimination was generated. Based on this, an ion-exchange adduct of smectite and the chiral chelate was used as an adsorbent for separating racemic mixtures or selectively producing either one of the optical isomers.

Key Words—Asymmetric Syntheses, Chiral Sensing, Circular Dichroism, Clay-modified Electrodes, Electric Dichroism, LB Films, Molecular Chirality, Optical Resolution, Stereoselectivity, Tris(1,10-phenanthroline)metal(II).

INTRODUCTION

‘Molecular recognition’ is one of the most extensively studied fields in chemistry today. A number of biomimetic systems such as crown ethers, cryptands, and cyclodextrins have been designed as artificial sites to activate an appropriate substrate in a specific way. In addition to the receptor model based on molecular units, the surface of a solid provides another possibility for molecular recognition. The clean surface of a single metal crystal, for example, provides information, at the atomic scale, about how bound molecules interact with other adsorbents on a surface.

The use of smectite clay minerals as a template for chemical reactions is of interest. In comparison to metals and bulk metal oxides, smectites are characterized by the following unique features from the view-point of molecular recognition: (1) two-dimensional network structures of a phyllosilicate layer; (2) large cation exchange capacity (CEC); and (3) exfoliation into inorganic nanolayers.

In the following, work on the use of smectites for optical resolution and asymmetric syntheses is reviewed. Attention is focused on how the features listed above are helpful in making the clay mineral surface a template for recognizing molecular chirality (Yamagishi, 1987).

Racemic adsorption of metal chelates by Na-montmorillonite

A study reporting the stereoselective adsorption of amino acids and glucoses by Na-montmorillonite (Bondy and Harrington, 1979) prompted the present authors to study the effect of molecular chirality on adsorption by clay minerals. Cationic tris(chelated)metal(II) complexes such as tris(1,10-phenanthroline)metal(II) ($[\text{M}(\text{phen})_3]^{2+}$) were used as an adsorbate. These chelates were chosen because their rigid and highly symmetric properties might be more helpful than flexible bioorganic molecules in detecting the subtle differences between adsorption structures (Yamagishi and Soma, 1981).

Tris(1,10-phenanthroline)metal(II) ($[\text{M}(\text{phen})_3]^{2+}$) has a chiral structure like a three-bladed propeller. Enantiomers are denoted as Δ - and Λ -isomers, depending on the direction of helical twisting (Figure 1). The adsorption of enantiomeric $[\text{Ru}(\text{phen})_3]^{2+}$ by the clay mineral was studied by measuring the electronic absorption spectrum. When a colloidal dispersion of Na-montmorillonite was added to an aqueous solution of Δ - $[\text{Ru}(\text{phen})_3]\text{Cl}_2$, the metal-to-ligand charge transfer (MLCT) transition band around 450 nm increased its intensity and shifted toward the longer wavelength with the simultaneous decrease of the π - π^* transition band localized in the ligands around 270 nm. These spectroscopic changes were caused by the adsorption of the chelate by a colloidal clay mineral. No effect of molecular chirality was detected when the spectral change was compared between the Δ - and Λ -enantiomers.

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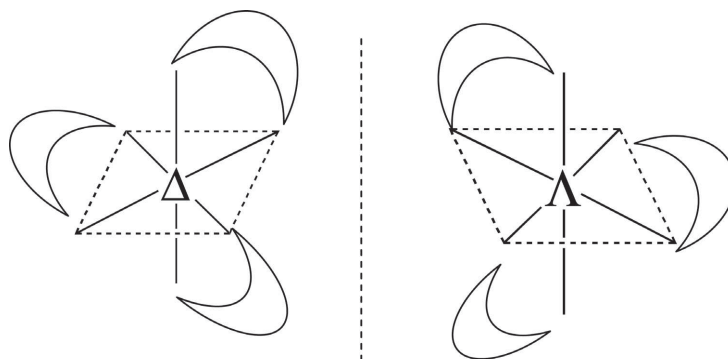


Figure 1. Chiral structures of a tris-chelated metal complex: (left) Δ -isomer and (right) Λ -isomer.

When the same experiments were performed using the racemic mixture of $[\text{Ru}(\text{phen})_3]^{2+}$, the change in the electronic spectra was distinctly different from the enantiomeric case. The bathochromic shift of the MLCT transition band was more pronounced and the π - π^* transition band split into two components. In addition to the spectroscopic differences, a remarkable difference was observed in the adsorption amounts. The chelates were adsorbed so strongly that the amount of adsorption increased linearly with increase in the amount of clay mineral added. In the case of the enantiomer, the adsorption was saturated when the ratio of clay mineral-to-metal chelate (denoted as $[\text{clay}]/[\text{chelate}]$) attained the value of 2, where $[\text{clay}]$ and $[\text{chelate}]$ were measured in terms of the CEC equivalent/L and mole/L, respectively. The results were reasonable as $[\text{Ru}(\text{phen})_3]^{2+}$ carried two positive charges and neutralized two negative charges on adsorption by a clay mineral surface. Contrary to this, in the case of the racemic mixture, the adsorption was already saturated at $[\text{clay}]/[\text{chelate}] = 1$. In other words, the chelate was adsorbed to two times excess over the CEC.

Clearly the chelates interacted with each other on the clay mineral surface in a stereoselective manner. Here 'stereoselective manner' means that the situations are different depending on whether the interacting molecules are a Δ - Δ (or Λ - Λ) pair or a Δ - Λ pair. If the interaction was indifferent to such chirality effects, the question of whether the chelates were added as a pure enantiomer or as a racemic mixture would have made no difference. The fact that the racemic mixture was adsorbed to two times excess of the enantiomers suggested that the chelates preferred to form a racemic pair on the clay mineral surface. This type of adsorption is referred to as 'racemic adsorption by clays.'

The adsorption by Na-montmorillonite has been investigated over a wide range of chiral chelates (Yamagishi, 1982; Yamagishi and Fujita, 1984; Villemure, 1990). The classification of investigated chelates according to the stereochemical effects on adsorption behavior is listed in Table 1. The chelate that shows either racemic or enantiomeric adsorption is coordinated with two or three bulky planar ligands and

carries an electric charge of <2 . These facts are consistent with a view that the discrimination of chirality of an adsorbed molecule is performed by the stacking interaction between the adjacent molecules on a clay mineral surface. The stacking interaction between small ligands such as ethylenediamine is minimal. Electrostatic repulsion is too large to have chelates stacked if they are too positive, e.g. in the case of $[\text{Co}(\text{phen})_3]^{3+}$.

No stereochemical effect was observed when $[\text{M}(\text{phen})_3]^{2+}$ was adsorbed by other ion-exchangers such as cation-exchanging resins, zirconium phosphates, and layered niobates. Thus, the phenomena are specific to smectites. Note that the excess adsorption of $[\text{M}(\text{phen})_3]^{2+}$ over CEC was also reported by Loeppert *et al.* (1979). The significance of 'racemic adsorption' is that such excess adsorption was related to the stereochemical properties of adsorbed molecules.

Spectroscopic studies of the adsorption of metal complexes by Na-montmorillonite

The structural origin of racemic adsorption was investigated by applying a number of spectroscopic

Table 1. Classification of metal chelates according to the stereochemical effects on adsorption by a clay mineral.

Chelates showing racemic adsorption	
$[\text{M}(\text{phen})_3]^{2+}$	($M = \text{Ni, Fe, Ru, and Os}$)
$[\text{Fe}(\text{phen})_2(\text{CN})_2]$	
$[\text{Co}(\text{PAN})_2]^{2+}$	(PAN = pyridylazoresorcinol)
$[\text{Co}(\text{PAN})_2]^+$	
Chelates showing enantiomeric adsorption	
$[\text{Ru}(\text{bipy})_3]^{2+}$	
Chelates showing no stereochemical effect	
$[\text{Co}(\text{phen})_3]^{3+}$	
$[\text{Co}(\text{en})_3]^{3+}$	(en = ethylenediamine)
$\text{cis-}[\text{Co}(\text{en})_2\text{Cl}_2]^+$	
$[\text{Co}(\text{cyclohexylamine})_3]^{3+}$	
$[\text{Co}(\text{en})(\text{glyc})_2]^+$	(glyc = glycinate)
$[\text{Co}(\text{phen})(\text{glyc})_2]^+$	

methods such as X-ray diffraction (XRD) (Taniguchi *et al.*, 1991), electric dichroism (Yamagishi, 1982), electron spin resonance (ESR) (Yano *et al.*, 1992), photoelectron spectroscopy (Yamagishi *et al.*, 1982), and atomic force microscopy (AFM) (Takahashi *et al.* (2003)) together with theoretical calculations (Sato *et al.*, 1992). The basal spacing (d_{001}) was determined by XRD measurements for the adducts of Na-montmorillonite and $[M(\text{phen})_3]^{2+}$. The value of d_{001} was 1.78 nm when the chelate was adsorbed to the negative surface sites of a clay mineral. Subtracting the thickness of one layer (0.95 nm) from the basal spacing, the height of the interlayer space was estimated to be 0.83 nm. This height was nearly equal to that of $[M(\text{phen})_3]^{2+}$ along its C_3 axis. The basal spacing of a clay-chelate adduct was expanded to 2.90 nm when the chelate was adsorbed to two times excess of CEC. Accordingly the height of the interlayer space was estimated to be 1.95 nm. Fourier analyses for a sample of a 2:1 adduct of a clay mineral and racemic $[\text{Fe}(\text{phen})_3]^{2+}$ showed that the adsorbates formed a double molecular layer in the interlayer space. The peak of electron density in the middle of the space was ascribed to an anion, SO_4^{2-} , which was included to compensate the excess positive charge (Taniguchi *et al.*, 1991).

Electro-optical measurements were applied to determine the orientation of $[\text{Ru}(\text{phen})_3]^{2+}$ bound on the surface of a clay mineral layer. According to the method, an electric field pulse was applied to a dispersion containing a colloidal clay and the chelate. The anisotropy in optical absorption (dichroism) was induced by the alignment of a clay layer in the direction of electric field. The electric dichroism was monitored by linearly polarized light. The rise and decay of the signals corresponded to the orientation and de-orientation processes of clay particles in the presence and absence of electric field, respectively. The magnitude of the dichroism is related to the angle, θ , between the electric field and the polarization of the monitoring light: $\Delta A/A = (\rho/6)(1 + 3 \cos 2\theta)$

At the limit of complete orientation, ρ , the reduced linear dichroism, is expressed by: $\rho = (3/8)(1 - 3 \cos 2\phi)$ in which ϕ is the angle between the C_3 axis of the chelate and the direction normal to a clay mineral surface. The angle, ϕ , was obtained to be close to zero or the chelate was adsorbed with its C_3 axis perpendicular to the clay mineral surface (Figure 2).

The kinetic formation of the adsorption layer of racemic chelates was studied by means of a stopped-flow electric dichroism apparatus (Taniguchi *et al.*, 1990). The rate was compared between the following two cases: (1) a dispersion of a Δ - $[\text{Ru}(\text{phen})_3]^{2+}$ /clay (denoting a clay particle adsorbing the chelate to cation-exchange sites) was mixed with a solution of Λ - $[\text{Ru}(\text{phen})_3]\text{Cl}_2$ and (2) a dispersion of a racemic $[\text{Ru}(\text{phen})_3]^{2+}$ /clay was mixed with a solution of racemic $[\text{Ru}(\text{phen})_3]\text{Cl}_2$ (Figure 3). In both cases, electric dichroism amplitude ($\Delta A/A$) and absorbance (A) increased on mixing,

indicating the occurrence of adsorption in excess of the CEC. The rates of increase were greater for (1) than for (2). The results were rationalized in terms of the mechanism that, in case of (1), the racemic layer was formed simply by pairing a preadsorbed Δ - $[\text{Ru}(\text{phen})_3]^{2+}$ with an incoming Λ - $[\text{Ru}(\text{phen})_3]^{2+}$, while, in case of (2), the process of molecular rearrangement was required among the preadsorbed racemic chelates before a racemic pair was formed.

Molecular model of racemic adsorption and its significance for chiral recognition

The phyllosilicate layer of a smectite clay mineral is composed of a two-dimensional network, in which a hexagonal hole exists in a unit cell with a size of $0.52 \text{ nm} \times 0.93 \text{ nm}$. When $[\text{Ru}(\text{phen})_3]^{2+}$ is placed on the silicate layer under the orientation as shown in Figure 2, one chelate molecule occupies three neighboring hexagonal holes with the bottom hydrogen atom located at the center of each hole. Under such a configuration, two racemic chelates might form a tightly stacking associate with their ligands in a key-and-lock arrangement. Such molecular stacking is impossible when pairing molecules have the same chirality (or enantiomeric chelates), because the facing ligands are sterically hindered with each other. Note that this stereoselectivity appears only when the pairing molecules take the orientation as in Figure 2. This is the reason that racemic adsorption is observed for smectites but not for the other ion-exchangers in which the chelates orient randomly (Sato *et al.*, 1992).

When the thin film of an ion-exchange adduct of racemic $[\text{Os}(\text{phen})_3]^{2+}$ /montmorillonite was analyzed by in-plane XRD measurements, the two-dimensional regularity existed with the periodicity of 0.95 nm

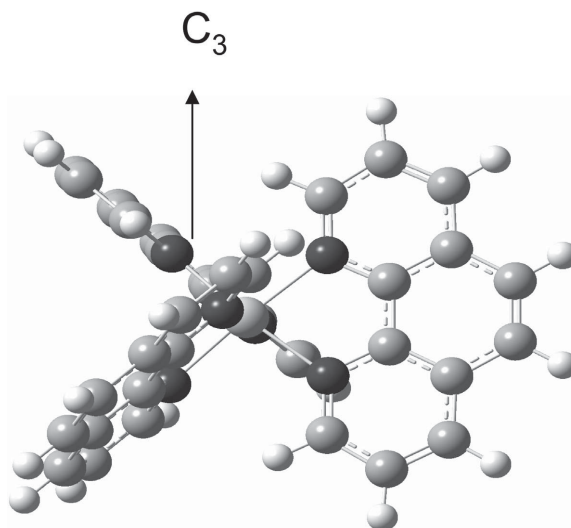


Figure 2. The orientation of $[M(\text{phen})_3]^{2+}$ adsorbed on a clay mineral surface.

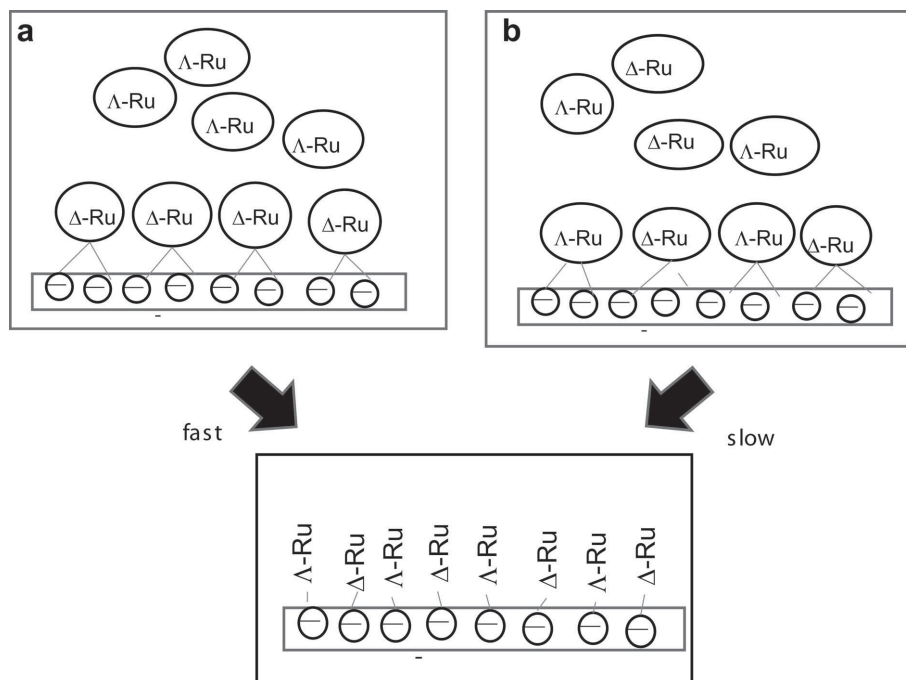


Figure 3. The kinetic formation of the racemic layer on a clay mineral surface: (a) clay/ Δ -[Ru(phen)₃]²⁺ + Λ -[Ru(phen)₃]Cl₂ and (b) clay/racemic [Ru(phen)₃]²⁺ + racemic [Ru(phen)₃]Cl₂.

(Umemura and Shinohara, 2004). No evidence for molecular arrangements on the surface of a smectite layer by means of AFM has been obtained thus far (Takahashi *et al.*, 2003). Scanning tunneling microscopy (STM) was successful only for highly crystalline clay minerals like hydroxalcite (Yao *et al.*, 1998a, 1998b).

The adsorption behavior was simulated theoretically by use of the Monte Carlo technique (Sato *et al.*, 1992). The predicted bound states of a pair of racemic and enantiomeric [M(phen)₃]²⁺ molecules at the minimum binding energy are shown in Figure 4 left and right, respectively. As was expected, a racemic pair forms an associate with their ligands interlocked closely, while an enantiomeric pair forms a loose association due to the steric repulsion between the facing ligands. When the free energy was calculated statistically using a

Metropolis algorithm, the racemic and enantiomeric pairs took the sharp minima of free energy at the intermolecular distances of 0.95 nm and 1.42 nm, respectively.

One important deduction of the model above is that a vacant space surrounded by the bound chelates exists when a clay surface is covered with enantiomeric [M(phen)₃]²⁺. Such a space is stereoselective toward further adsorption, as it accepts exclusively its optical antipode (Figure 5). Based on this hypothesis, an ion-exchange adduct of enantiomeric [M(phen)₃]²⁺ (M = Ni, Ru)/clay was used as a chiral adsorbent for optical resolution and asymmetric syntheses. A number of examples have been accumulated to demonstrate the capability of such a surface in discriminating molecular chirality.

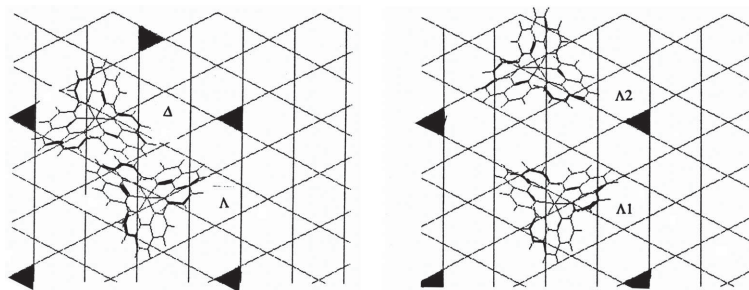


Figure 4. Calculated bound states of a pair of [M(phen)₃]²⁺ molecules on a phyllosilicate surface: (left) a racemic pair and (right) an enantiomeric pair.

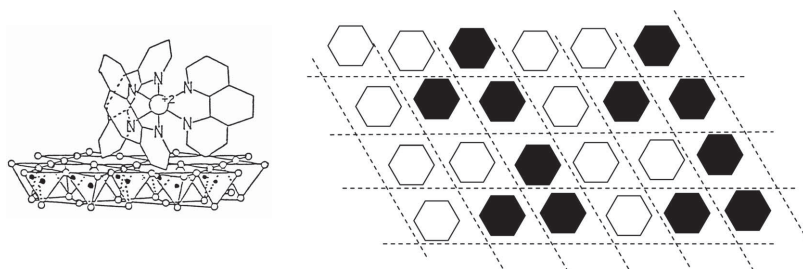


Figure 5. A model of a clay mineral surface covered with enantiomeric $[M(\text{phen})_3]^{2+}$ molecules: (left) one molecule occupies three neighboring tetragonal holes and (right) a vacant space (empty hexagonal) surrounded by bound chelates (filled hexagonals) is generated. Such a space accepts the antipodal enantiomer exclusively.

Examples of chiral discrimination on the surface of a smectite clay mineral

(1) *Anti-racemization of labile metal complexes on a smectite clay mineral surface.* The following example shows how chirality was recognized by the adsorbed molecules on the surface of the smectite (Yamagishi, 1985a). A labile complex, $[\text{Fe}(\text{phen})_3]^{2+}$, racemizes with a half-life ($t_{1/2}$) of 25 min in water at 25°C, while $[\text{Ni}(\text{phen})_3]^{2+}$ is less labile with $t_{1/2} = 3$ h under the same conditions. Racemic $[\text{Fe}(\text{phen})_3]\text{Cl}_2$ was added to an aqueous dispersion of a Δ - $[\text{Ni}(\text{phen})_3]^{2+}/\text{clay}$. The amount of $[\text{Fe}(\text{phen})_3]^{2+}$ added was less than the CEC. When the dispersion was monitored by means of the circular dichroism (CD) spectrum, no CD activity was observed initially in the wavelength region of 350–700 nm because Δ - $[\text{Ni}(\text{phen})_3]^{2+}$ was nearly transparent in this wavelength region. The CD band appeared after several minutes and developed over a period of hours until it nearly coincided with the CD spectrum of Λ - $[\text{Fe}(\text{phen})_3]^{2+}$. The results were rationalized in terms of the mechanism: (i) Λ - $[\text{Fe}(\text{phen})_3]^{2+}$, half of the $[\text{Fe}(\text{phen})_3]^{2+}$ added was adsorbed instantly by the Δ - $[\text{Ni}(\text{phen})_3]^{2+}/\text{clay}$; (ii) the remaining Δ - $[\text{Fe}(\text{phen})_3]^{2+}$ racemized gradually in water to Λ - $[\text{Fe}(\text{phen})_3]^{2+}$ and was adsorbed by the Δ - $[\text{Ni}(\text{phen})_3]^{2+}/\text{clay}$; and finally, (iii) all of the $[\text{Fe}(\text{phen})_3]^{2+}$ ions added were stabilized as the Λ -form by pairing with Δ - $[\text{Ni}(\text{phen})_3]^{2+}$ on the smectite surface.

(2) Clay-column chromatography for optical resolution.

The chiral recognition by the modified smectite surface was applied to chromatographic resolution (Yamagishi, 1985b). A spherically shaped aggregate was prepared by spray-drying an aqueous dispersion of synthetic hectorite. Particles ~5 μm in size were soaked in a methanol solution containing Λ - $[\text{Ru}(\text{phen})_3]\text{Cl}_2$. The ion-exchanging of Λ - $[\text{Ru}(\text{phen})_3]^{2+}$ into the hectorite took place in seconds to produce a yellow-colored solid. The material was packed into a stainless steel tube and used as a column for high-performance liquid chromatography (HPLC) (Nakamura *et al.*, 1988a, 1998b). The chromatogram when a racemic mixture of 1,1'-bi-2-naphthol was eluted on the column (4 mm (i.d.) × 250 mm) with

methanol is shown in Figure 6. Two peaks with equal area were obtained on the base-line separation. From the CD spectra, the fewer and more retaining peaks contained the pure *R*- and *S*-enantiomers of 1,1'-bi-2-naphthol, respectively. The separation factor was calculated to be 1.78, which was quite large in comparison to the known chiral columns. The enthalpy change ($-\Delta H$) of adsorption was determined from the temperature dependence of the retention times: $-\Delta H = 3.1$ and 5.7 kJ mol⁻¹ for the *R*- and *S*-1,1'-bi-2-naphthol, respectively. Therefore, the high separation capability of the present column was ascribed to the large difference in adsorption enthalpy (~2.6 kJ mol⁻¹). From the XRD measurements, the basal spacings of ternary adducts of the clay mineral, Δ - $[\text{Ru}(\text{phen})_3]^{2+}$ and *R*- or *S*-1,1'-bi-2-naphthol were obtained as 2.78 nm and 2.45 nm, respectively. The more strongly adsorbed *S*-enantiomer gave the narrower spacing, or it was located closer to the clay mineral surface, probably forming a side-by-side association with Λ - $[\text{Ru}(\text{phen})_3]^{2+}$ (Yamagishi *et al.*, 1996).

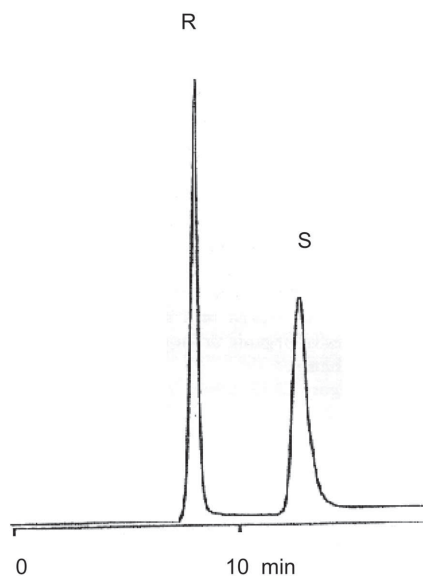


Figure 6. The chromatogram when a racemic mixture of 1,1'-bi-2-naphthol was eluted on a column packed with Λ - $[\text{Ru}(\text{phen})_3]^{2+}/\text{synthetic hectorite}$ with methanol.

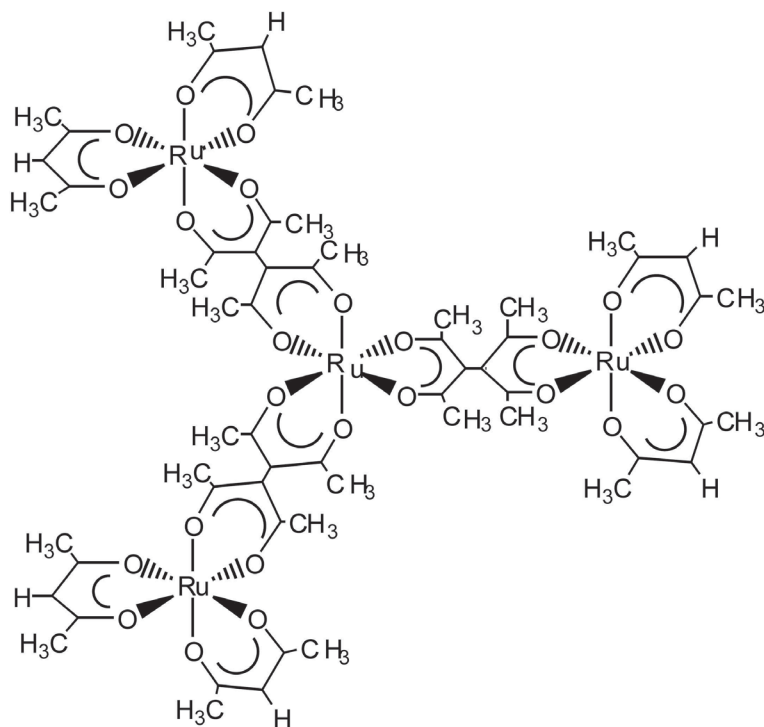


Figure 7. A star-burst type tetranuclear Ru(III) complex resolved successfully on a chiral-clay column.

The clay column possessed the following characteristics:

(1) Performance is stable and reproducible for a long time against the change of temperature or eluting solvents (except for water).

(2) The resolution capacity is high (e.g. 400 mg resolved for a single run on a 20 mm (i.d.) \times 250 mm column).

(3) Antipodal columns, or Δ -[Ru(phen)₃]²⁺/clay and Λ -[Ru(phen)₃]²⁺/clay, are both available. This is particularly useful in separating a mixture of diastereomeric species (Sato *et al.*, 2009).

(4) Systematic modification of a packing material is possible in order to tune resolution capability by changing the structure of a preadsorbed chelate (e.g. [Ru(bipy)₃]²⁺/clay) (Yamagishi *et al.*, 1996).

A column packed with Δ -[Ru(phen)₃]²⁺/synthetic hectorite is commercially available (Ceramosphere Ru-1, Shiseido, Japan) and is used for separating a wide range of organic and inorganic compounds. An example of a recent application was one where all of the four diastereomers of a star-burst type tetranuclear

ruthenium(III) complex were resolved (Figure 7). The diastereomers were differentiated by the parts connecting the core and periphery regions. Thus the column discriminated the local chirality within a large molecule (Fujimoto *et al.*, 2010; Sato *et al.*, 2012).

Asymmetric syntheses on a smectite surface modified with chiral chelates. Chirality recognition by a clay/chelate adduct was utilized to produce chiral molecules. The basic principle for this is shown in Figure 8. A prochiral molecule is adsorbed on a void space surrounded by chiral chelates. When the bound molecule undergoes a chemical change, it might transform to an optically active molecule under the steric control of the surrounding chelates.

As an example, a phenyl alkyl sulfide was adsorbed by an adduct of Na-montmorillonite ion-exchanged with chiral [Ru(phen)₃]²⁺ or [Ru(bipy)₃]²⁺ (bipy = 2,2'-bipyridine) and photo-oxidized to a sulfoxide under the illumination of visible light. The reaction was driven by the photosensitizing action of the ruthenium(II) complexes. As summarized



Figure 8. A schematic model for the transformation of a prochiral molecule to a chiral molecule under the steric control of chelates bound on a clay mineral surface.

Table 2. Stereoselectivities of ethylbenzyl phenyl sulfide under various heterogeneous oxidative conditions.

Heterogeneous catalyst	Condition	Enantiomer excess (%)		Diastereomer ratio (<i>SR</i> + <i>RS</i>):(<i>RR</i> + <i>SS</i>)*
		<i>SR-RR</i>	<i>RR-SS</i>	
Δ -[Ru(phen) ₃] ²⁺ /clay	at 25°C	-28	30	56:44
Δ -[Ru(phen) ₃] ²⁺ /clay	at 4°C	-33	-36	51:49
Δ -[Ru(phen) ₃] ²⁺ /clay	at 4°C (oxidized by NaIO ₄)	-12	58:42	
Δ -[Ru(phen) ₃] ²⁺ /clay	at 4°C (sodium-D(+)-tartrate added)	-30	-30	45:55
Δ -[Ru(phen) ₃] ²⁺ /clay	at 4°C (dibenzoyl-D(+)-tartaric acid added)	-43	66:34	

* *Sr*, *RS*, *RR*, and *SS* define the absolute configurations in sulfoxide and asymmetric carbon in a product molecule.

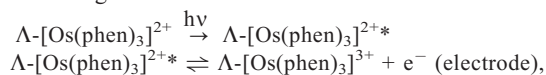
in Table 2, a chiral sulfoxide was produced at the enantioselectivity level (e.e.) of ~43% (Fujita *et al.*, 2006). The chirality of a sulfoxide molecule was determined by the absolute configuration of preadsorbed Ru(II) complexes. Note that no chiral induction was attained for the homogenous system (water/methanol) although the same chiral chelates were used as a photosensitizer. Thus, the steric control on the smectite surface was essential to chiral recognition.

The method was applied to the auto-catalytic systems. A prochiral aldehyde was transformed to chiral pyrimidyl alkanol by the catalytic reaction of bis(isopropyl)zinc(0) (*i*-Pr₂Zn). The reaction was performed in the presence of Δ -[Ru(phen)₃]²⁺/clay or Λ -[Ru(phen)₃]²⁺/clay. As shown in Table 3, the enantiomer excess of the product attained as high as ~80–90%. Again chiral selectivity was determined by the absolute configuration of the adsorbed chelates (Kawasaki *et al.*, 2009).

(4) *Chiral sensing on an electrode modified with a smectite film.* Chiral recognition by a smectite surface modified with chiral chelates was extended to the electrochemical sensing of chiral molecules. For this purpose, the film of a smectite clay mineral, just a few nm thick, was prepared and deposited on an electrode surface. The Langmuir-Blodgett (LB) method coupled with self-assembly was employed to prepare the films (Tamura *et al.*, 1999). A monolayer of a cationic

amphiphile (octadecylammonium) was formed on an aqueous dispersion of Na-montmorillonite. Exfoliated clay particles (clay nanosheets) were adsorbed by the monolayer due to the electrostatic interaction. The adsorption of nanosheets continued until the organic monolayer was fully covered with a single clay mineral layer (Shimada *et al.*, 2012). The floating film thus prepared was deposited onto an indium tin oxide-coated (ITO) glass by the LB method. The modified electrode was soaked in an aqueous solution of Λ -[Os(phen)₃]²⁺. Octadecylammonium cations in a film were removed through replacement by Λ -[Os(phen)₃]²⁺ ions in a solution (self-assembly). In this way, an ITO electrode modified with a thin film of Λ -[Os(phen)₃]²⁺/clay was prepared. The ultrathin film of a smectite clay mineral provided a sample for investigating the properties of a single layer (Sato *et al.*, 2001).

When UV light was irradiated onto the ITO electrode modified with a thin film of Λ -[Os(phen)₃]²⁺/clay, photocurrent was observed in the direction oxidizing the Os(II) complex in the film. The current was due to the following reaction:



in which e⁻ denotes an electron injected into an electrode.

The oxidation current was enhanced in the presence of *R*- (or *S*-1,1'-bi-2-naphthol) in an electrolyte solution.

Table 3. Heterogeneous enantioselective syntheses of chiral pyrimidyl alkanol by the reaction of *i*-Pr₂Zn with aldehyde in the presence of chiral [Ru(phen)₃]²⁺/synthetic hectorite.

Intercalator	Pyrimidyl alkanol		
	Yield (%)	Enantiomer excess (%)	Configuration
Δ -[Ru(phen) ₃] ²⁺ /clay	80	69	<i>S</i>
Λ -[Ru(phen) ₃] ²⁺ /clay	91	90	<i>R</i>
Δ -[Ru(phen) ₃] ²⁺ /clay	82	63	<i>S</i>
Λ -[Ru(phen) ₃] ²⁺ /clay	80	69	<i>R</i>
Δ -[Ru(phen) ₃] ²⁺ /clay	90	44	<i>S</i>
Λ -[Ru(phen) ₃] ²⁺ /clay	85	72	<i>R</i>

Table 4. Chiral selectivities of a modified electrode toward binaphthyl

Binaphthyl derivative	$i(S)/nA\text{ cm}^{-2*}$	$i(R)/nA\text{ cm}^{-2*}$	Photocurrent selectivity	Adsorption selectivity**
-NH ₂	71.8	53.3	1.35	1.23
-OH	146.1	78.5	1.86	1.78
-OCH ₂ CH ₂ Br	13.6	13.6	1.0	1.10
-OCH ₂ N(CH ₃) ₂	13.6	13.6	1.0	1.07

* The oxidation current when *S*- or *R*-binaphthyl derivative was oxidized in terms of nanoampere per square cm.

** The adsorption selectivity is the separation factor of a binaphthyl derivative on a column packed with Λ -[Ru(phen)₃]²⁺/synthetic hectorite.

The results indicated that binaphthol acted as an electron acceptor to oxidize the Λ -Os(II) complex. Notably, the catalytic current was greater for *S*-1,1'-bi-2-naphthol than for *R*-1,1'-bi-2-naphthol (Table 4). In this way, the electrode sensed a chiral molecule electrochemically (He *et al.*, 2005). Sensing of a chiral molecule was also achieved by monitoring the emission from an adduct of a clay mineral and luminescent iridium(III) complex. The emission was stereoselectively quenched by a chiral quencher in a solution (Sato *et al.*, 2011a, 2011b).

(5) *Other applications of adducts of clay/chiral chelates.* An ion-exchanged adduct of clay-chiral chelates are also applied in the following examples:

(i) Non-linear optical materials: The self-standing film of chiral [Ru(phen)₃]²⁺/synthetic saponite exhibited high activity for second-harmonic generation (SHG). The results indicated that the film possessed a non-centrosymmetric structure due to the chirality of the intercalated chelates (Suzuki *et al.*, 2009). The SHG activity was also observed on a hybrid thin-film of a clay-chiral amphiphilic Ru(II) complex (Umemura *et al.*, 2002).

(ii) Microscopic barrier for energy transfer: the ultra-thin film of synthetic saponite was prepared such that an emitter/clay and a quencher/clay were deposited in an alternative manner. In such a film, a single clay mineral layer was revealed to act as a barrier for the transfer of photon energy (Inukai *et al.*, 2000).

(iii) Electron transmission through a clay mineral film: an electrode modified with a single layered clay film was prepared. Under normal conditions, the film was an electrical insulator. It transmitted electrons, however, when electrons were accumulated to high concentration at one side of the film through the catalytic redox reaction (Yoshida *et al.*, 2006).

CONCLUSIONS

Smectite clay minerals were used as an adsorbent for molecular recognition. A microscopic vacant space was generated on a smectite surface covered with an enantiomeric chelate, Δ - or Λ -[Ru(phen)₃]²⁺, to saturate

Such a space acted as a binding site with stereoselectivity. Clay minerals are ubiquitous and 'environmentally friendly.' The present method sheds light on the utility of such material for finely controlled chemical reactions. Previously, the main focus in this field has been on the use of chiral organic and bioorganic compounds.

An interesting problem which remains is the possibility of chirality present intrinsically in smectite clay minerals. Kaolinite is known to possess chiral structure (Kameda *et al.*, 2005). If structural chirality is discovered in smectites, it will be of huge practical value for the development of a chiral adsorbent.

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REFERENCES

- Bondy, S.C. and Harrington, M. (1979) L-amino acids and D-glucose bind stereospecifically to a colloidal clay. *Science*, **203**, 1243–1244.
- Fujimoto, N., Mori, Y., Yamagishi, A., and Sato, H. (2010) Molecular recognition of star-burst tetranuclear Ru(III) complexes on a chirally modified clay surface. *Chemical Communications*, **46**, 5473–5474.
- Fujita, S., Sato, H., Kakegawa, N., and Yamagishi, A. (2006) Enantioselective photooxidation of a sulfide by a chiral ruthenium(II) complex immobilized on a montmorillonite clay surface. *Journal of Physical Chemistry B*, **110**, 2533–2540.
- He, J.X., Sato, H., Umemura, Y., and Yamagishi, A. (2005) Sensing of molecular chirality on an electrode modified with a clay-metal complex hybrid film. *Journal of Physical Chemistry B*, **109**, 4679–4683.
- Inukai, K., Hotta, Y., Tomura, S., Takahashi, M., and Yamagishi, A. (2000) Preparation of the Langmuir-Blodgett film of a clay-alkylammonium adduct and its use

- as a barrier for interlayer photo-induced electron transfer. *Langmuir*, **16**, 7679–7684.
- Kameda, J., Yamagishi, A., and Kogure, T. (2005) Morphological characteristics of ordered kaolinite investigation using electron backscattered diffusion (EBSD). *American Mineralogist*, **90** 1462–1465.
- Kawasaki, T., Omine, T., Suzuki, K., Sato, H., Yamagishi, A., and Soai, K. (2009) Highly enantioselective asymmetric autocatalysis using chiral ruthenium complex-ion-exchanged synthetic saponite as chiral initiator. *Organic & Biomolecular Chemistry*, **7**, 1073–1075.
- Loeppert, R.H., Mortland, M.M., and Pinnavaia, T.J. (1979) Synthesis and properties of heat stable expanded smectite and vermiculite. *Clays and Clay Minerals*, **27**, 201–208.
- Nakamura, Y., Yamagishi, A., Matsumoto, A., Tohkubo, K., and Ohtsu, Y. (1988b) High performance liquid column chromatography on a column of spherically shaped synthetic hectorite. *Journal of Chromatography*, **482**, 165–167.
- Nakamura, Y., Yamagishi, A., Iwamoto, T., and Koga, M. (1988b) Adsorption properties of montmorillonite and synthetic saponite as packing materials in liquid column chromatography. *Clays and Clay Minerals*, **36**, 530–536.
- Sato, H., Yamagishi, A., and Kato, S. (1992) Monte Carlo simulations of the interactions of metal complexes with the silicate sheets of a clay. *Journal of the American Chemical Society*, **114**, 10933–10940.
- Sato, H., Yamagishi, A., and Kawamura, T. (2001) Molecular simulation for flexibility of a single clay layer. *Journal of Physical Chemistry B*, **105**, 7990–7997.
- Sato, H., Mori, Y., Fukuda, Y., and Yamagishi, A. (2009) Syntheses and vibrational circular dichroism spectra of the complete series of $[\text{Ru}(-) \text{ or } (+)\text{-tfac}]n(\text{acac})_n$ ($n = 0 \sim 3$, $\text{tfac} = 3\text{-trifluoroacetylcamphoraro}$ and $\text{acac} = \text{acetylacetonato}$). *Inorganic Chemistry*, **48**, 4353–4361.
- Sato, H., Tamura, K., Ohara, K., Nagaoka, S.-I., and Yamagishi, A. (2011a) Hybridization of clay minerals with the floating film of a cationic Ir(III) complex at an air–water interface. *New Journal of Chemistry*, **35**, 394–399.
- Sato, H., Tamura, K., Aoki, R., Kato, M., and Yamagishi, A. (2011b) Enantioselective sensing by luminescence from cyclometalated iridium(III) complexes adsorbed on a colloidal saponite. *Chemistry Letters*, **40**, 65–67.
- Sato, H., Sato, F., Taniguchi, M., and Yamagishi, A. (2012) Chirality effects on core-periphery connection in a star-burst type tetranuclear complex: Application of vibrational circular dichroism spectroscopy. *Dalton Transactions*, **41**, 1709–1712.
- Shimada, T., Yamada, H., and Umemura, Y. (2012) Surface potential studies on adsorption processes of a clay nanosheet onto a floating monolayer film of an amphiphilic ammonium cation. *Journal of Physical Chemistry B*, **116**, 4484–4491.
- Suzuki, Y., Matsunaga, R., Sato, H., Kogure, T., Akihiko, A., and Kawamata, J. (2009) Non-centrosymmetric behavior of a clay film ion-exchanged with chiral metal complexes. *Chemical Communications*, **45**, 6964–6966.
- Takahashi, S., Tanaka, R., Wakabayashi, N., Taniguchi, M., and Yamagishi, A. (2003) Design of a chiral surface by modifying an anionically charged single-layered inorganic compound with metal complexes. *Langmuir*, **19**, 6122–6125.
- Tamura, K., Setstuda, H., Taniguchi, M., and Yamagishi, A. (1999) Application of the Langmuir-Blodgett technique to prepare a clay-metal complex hybrid film. *Langmuir*, **15**, 6915–6920.
- Taniguchi, M., Kaneyoshi, M., Nakamura, Y., Yamagishi, A., and Iwamoto, T. (1990) A stopped-flow electric dichroism study on adsorption of metal chelates by a colloidal clay. *Journal Physical Chemistry*, **94**, 5896–5900.
- Taniguchi, M., Yamagishi, A., and Iwamoto, T. (1991) X-ray diffraction and electric dichroism studies on the adsorption of metal complexes by a clay. *Journal of Physical Chemistry*, **30**, 2462–2467.
- Umemura, Y. and Shinohara, E. (2004) Two-dimensional molecular ordering of Os(II) complexes in organo-clay hybrid ultrathin film. *Chemical Communications*, **42**, 1110–1111.
- Umemura, Y., Yamagishi, A., Schoonhedyt, R., Persoons, A., and De Schryver, F. (2002) Langmuir-Blodgett Films of a clay mineral and ruthenium(II) complexes with a noncentrosymmetric structure. *Journal of the American Chemical Society*, **124**, 992–997.
- Villemure, G. (1990) Effects of negative charge densities of smectite clays on the adsorption isotherms of racemic and enantiomeric tris(2,2'-bipyridyl)ruthenium(II) chloride. *Clays and Clay Minerals*, **38**, 622–630.
- Yamagishi, A. (1982) Racemic adsorption of tris(1,10-phenanthroline)iron(II) on a colloidal dispersed sodium montmorillonite. *Journal of Physical Chemistry*, **86**, 2474–2479.
- Yamagishi, A. (1985a) Chromatographic resolution of enantiomers having aromatic groups by an optically active clay-chelate adduct. *Journal of the American Chemical Society*, **107**, 732–733.
- Yamagishi, A. (1985b) Racemic adsorption, anti-racemization and induction of optical activity of metal chelate in the presence of a colloidal clay. *Inorganic Chemistry*, **24**, 1689–1695.
- Yamagishi, A. (1987) Optical resolution and asymmetric synthesis of use of adsorption on clay minerals. *Review of Coordination Chemistry*, **16**, 131–211.
- Yamagishi, A. and Fujita, N. (1984) Racemic adsorption of a bis(chelated)cobalt(III) complex by colloidal dispersed sodium montmorillonite. *Journal of Colloid and Interface Science*, **100**, 136–142.
- Yamagishi, A. and Soma, M. (1981) Optical resolution of metal chelates by use of adsorption on a colloidal clay. *Journal of the American Chemical Society*, **103**, 4640.
- Yamagishi, A., Tanaka, K., and Toyoshima, I. (1982) Auger electron spectroscopic evidence for racemic adsorption of tris(1,10-phenanthroline)iron(II) on sodium montmorillonite. *Chemical Communications*, 343–345.
- Yamagishi, A., Taniguchi, M., Imamura, Y., and Sato, H. (1996) Clay column chromatography for optical resolution: selectivities of $\Lambda\text{-}[\text{Ru}(\text{phen})_3]^{2+}$ and $\Lambda\text{-}[\text{Ru}(\text{bpy})_3]^{2+}$ laponite columns towards 1,1'-binaphthol. *Applied Clay Science*, **11**, 1–10.
- Yano, Y., Watanabe, T., Taniguchi, M., and Yamagishi, A. (1992) Electron spin resonance studies on tris(1,10-phenanthroline)copper(II) adsorbed by hectorite and saponite. *Clay Science*, **8**, 381–391.
- Yao, Y., Taniguchi, M., Nakata, M., Takahashi, M., and Yamagishi, A. (1998a) Nanoscale imaging of molecular adsorption of metal complexes on the surface of a hydrocalcite crystal. *Langmuir*, **14**, 2410–2414.
- Yao, Y., Taniguchi, M., Nakata, M., Takahashi, M., and Yamagishi, A. (1998b) Electrochemical scanning tunneling microscopy observation of ordered surface layers on an anionic clay-modified electrode. *Langmuir*, **14**, 2890–2895.
- Yoshida, J., Saruwatari, K., Kameda, J., Sato, H., Yamagishi, A., Sun, L., Corriea, M., and Villemure, G. (2006) Electron transfer through clay monolayer films fabricated by the Langmuir-Blodgett technique. *Langmuir*, **22**, 9591–9597.

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