

Chiral monolayer of self-assembled Δ -[Os(bpy)₂L(Cl)]⁺ [bpy = 2,2'-bipyridyl, L = 1,2-bis(4-pyridyl)ethane] on a platinum electrode

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A chiral osmium complex, Δ -(2,2'-bipyridyl) [1,2-bis(4-pyridyl)ethane] chloroosmium Δ -[Os(bpy)₂L(Cl)]⁺, is successfully self-assembled at a monolayer molecular level on a clean Pt electrode in non-aqueous solutions; the self-assembled Δ -[Os(bpy)₂L(Cl)]⁺ ions show a phenomenally repulsive interaction with each other on Pt in chiral-field formation and also in the Os^{II}-Os^{III} redox reaction, while racemic complexes interact less repulsively with each other.

Chiral monolayer creation at an electrode interface is a stimulating subject for atomic level surface design. Study of chiral electrode surfaces has been attempted with a cholesteric liquid crystal physically adsorbed on glassy carbon or Pt electrodes.¹ In other work, a chiral metal complex was inserted into a clay mineral by cation exchange leading to a chiral metal complex-modified clay electrode, where the chiral complex was Δ - or Λ -[Ru(phen)₃]²⁺ (phen = phenanthroline). Oxidation of racemic [Co(phen)₃]²⁺ to Λ -[Co(phen)₃]³⁺ on a Δ -[Ru(phen)₃]²⁺ modified clay electrode showed chiral performance in a 17% optical yield,² and the partial oxidation of phenylcyclohexylsulfide to chiral (*R*)-(+)-phenylcyclohexylsulfoxide on a Λ -[Ru(phen)₃]²⁺-modified clay electrode gave a 20% optical yield.² The properties of a chiral complex-modified clay in a dispersed colloid form were experimentally and theoretically clarified by Yamagishi *et al.*,³⁻⁵ but the electrochemical features of chiral [Ru(bpy)₃]²⁺ in a clay-modified electrode were reported to be different from those in a dispersed form by Villemure and Bard,⁶ showing that the electrochemical chirality determination of a metal complex-modified clay electrode is quite complicated and likely to arise from a small fraction of complex ions in defects of layer films of a laminal clay.

Metal electrode modification was carried out by application of a monolayer *via* a thiol RSH on Au in the form of RS-Au, where R contains an electroactive species.⁷⁻⁹ Recently, an organic thiol with asymmetric carbon, adsorbed on Hg in a self-

assembled manner, was reported to show an atomically two-dimensional chiral surface by Mandler and coworkers.¹⁰ As another metal electrode modification, osmium complexes [Os(bpy)₂L(Cl)]⁺ (L = 4,4'-bipyridine or derivatives) were self-assembled onto a Pt electrode through an N atom of bipyridine,¹¹ and the electrochemical behaviour was examined in aqueous and non-aqueous solutions.¹¹⁻¹⁵ The electron-transfer mechanism and the adsorption thermodynamics of the osmium complex self-assembled on Pt were discussed in detail since the electron-transfer reaction between the electrode and the complex bound to the electrode is a fairly straightforward system to be theoretically treated for elucidation of electron-transfer processes. An STM image of ordered self-assembled osmium complexes on Pt(111) was successfully observed by Hudson and Abruña,¹⁶ indicating that the self-assembled osmium complexes form a two-dimensional ordered phase on Pt(111). In these reports, the above osmium complexes were synthesized as racemic mixtures of chiral Δ - and Λ -complexes [Fig. 1(a), (b)], depicted by molecular modelling, and used as a racemic mixture in the following. These lead us to the study of the creation of a chiral electrode interface by self-assembled Δ - or Λ -metal complexes in a monolayer form.

The separation of chiral Δ -(2,2'-bipyridyl) [1,2-bis(4-pyridyl)ethane] chloroosmium hexafluorophosphate [Os(bpy)₂L(Cl)]PF₆ [L = 1,2-bis(4-pyridyl)ethane] was carried out from racemic [Os(bpy)₂L(Cl)]PF₆, which was prepared according to ref. 11. The latter was first purified by elution on a 300 mesh alumina column with acetone, and then subjected to anion exchange to give the water-soluble [Os(bpy)₂L(Cl)]Cl. Chiral separation from racemic [Os(bpy)₂L(Cl)]Cl was conducted at least three times by column treatment on CM Sephadex (Pharmacia) with a potassium antimony (+)-tartrate saturated aqueous solution as the eluting agent to yield the Δ -osmium

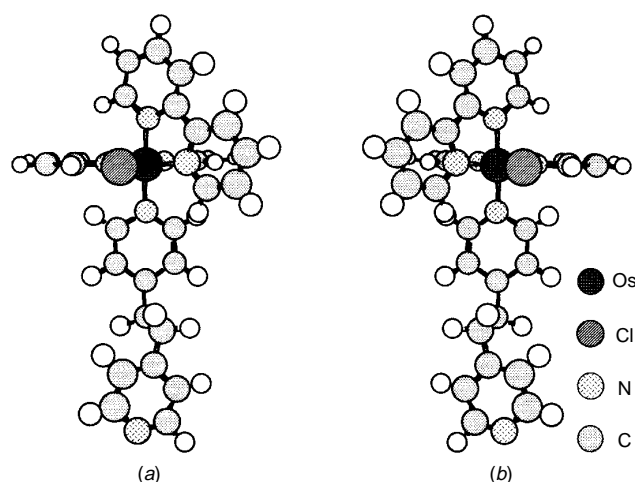


Fig. 1 Structures of (a) Δ - and (b) Λ -[Os^{II}(bpy)₂L(Cl)]⁺

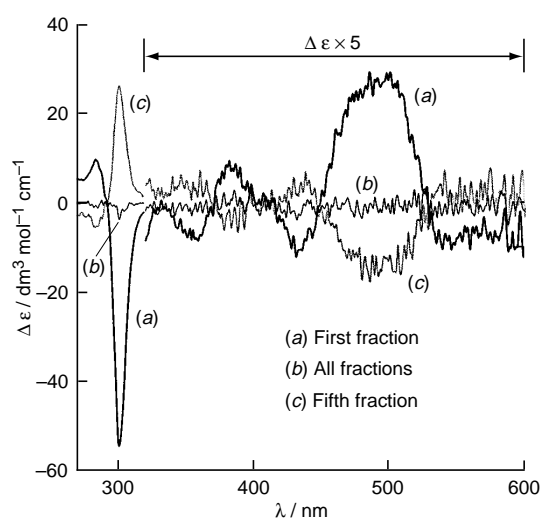


Fig. 2 Circular dichroism spectra of [Os^{II}(bpy)₂L(Cl)]⁺ after chiral separation. First fraction, fifth fraction and all fractions are assumed to be the Δ -, Λ -, and *rac*-species, respectively.

complex as the first of five fractions, since a clear column band separation was not observed. The last fraction containing the Λ -Os complex was also collected. This chiral column separation process also played the role of osmium complex purification. Thus, during the purification process of the racemic osmium complex, all fractions of the column band were collected. The circular dichroism spectra of Δ -, Λ -, and *rac*-complexes are shown in Fig. 2, where we find that the $\Delta\epsilon$ of the first fraction is $-55 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ at 299 nm, while there is a report that $\Delta\epsilon$ of Λ -[Os(bpy)₃]²⁺ is $400 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ at 300 nm.¹⁷ The osmium complexes prepared were stored in a dark cold dry-box before use.

For the monolayer self-assembling procedure, a polycrystalline Pt electrode was inserted into 0.5 mm of Δ - or *rac*-[Os(bpy)₂L(Cl)]Cl in CH₂Cl₂ solution for a given time, τ ; before this the Pt had been electrochemically polished by cyclic voltammetry (CV) up to 1.2 V (SCE) in perchloric acid solution.

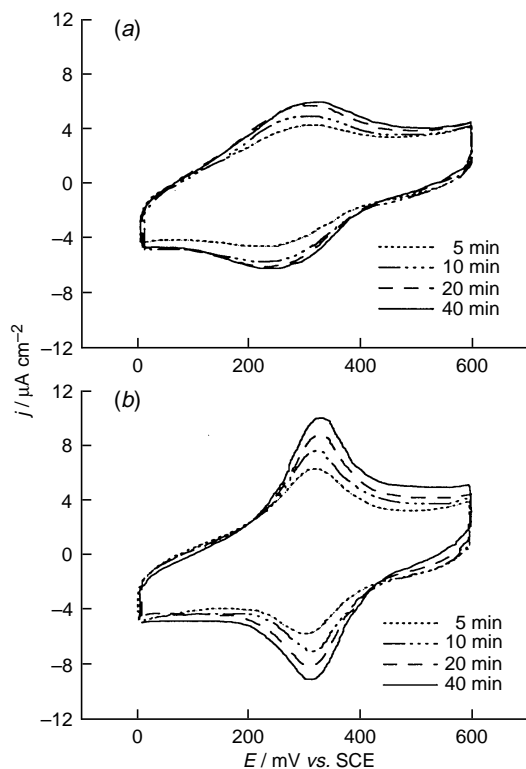


Fig. 3 CVs of (a) Δ - and (b) *rac*-[Os^{II}(bpy)₂L(Cl)]⁺ on a Pt electrode at 0.1 V s⁻¹ in 0.05 m TBAP-MeCN solution after Pt was inserted in 0.5 mm Δ - or *rac*-[Os^{II}(bpy)₂L(Cl)]⁺ for different self-assembling times τ

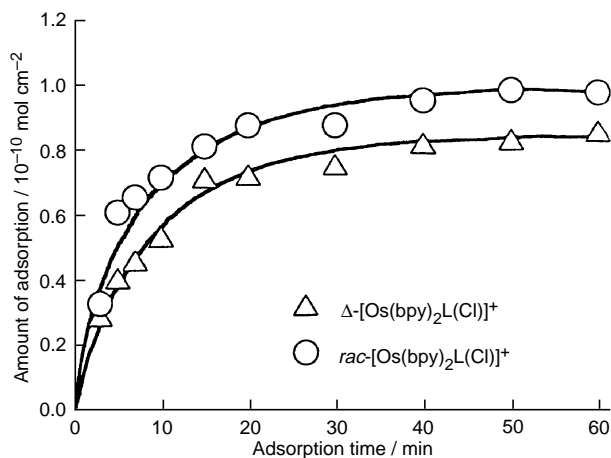
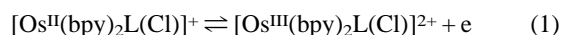


Fig. 4 Amount of charge of CV peaks of Fig. 3 vs. self-assembling adsorption time τ . Ordinate of the amount of the charge densities is expressed in mol cm^{-2} .

At each τ , the Pt was subjected to CV measurement at a sweep rate ν of 0.1 V s⁻¹ in 0.05 m tetrabutylammonium perchlorate (TBAP) in Me₂CN, as shown in Fig. 3, for the electrode reaction of eqn. (1).



Figs. 3(a) and (b) are for Δ - and *rac*-osmium complexes, respectively, with τ in the range 5–40 min. The sweep rate dependence of the CV current peak, j_p , showed a proportional relation vs. ν (at $\tau = 40$ min) when $\nu \leq 200 \text{ mV s}^{-1}$, irrespective of whether the electrode was modified by Δ - or *rac*-[Os(bpy)₂L(Cl)]⁺, as found for a racemic osmium complex in ref. 11. As in that work, the effect of the electron-transfer reaction kinetics on the CV was observed at sweep rates $> 100 \text{ V s}^{-1}$; the present data are indicative of a quasi-equilibrium state. Remarkable differences of CV characteristics, however, were observed between Δ - and *rac*-[Os(bpy)₂L(Cl)]⁺ modified Pt electrodes (Fig. 3). Various parameters for the *rac*-Os complex are in good agreement with those of Acevedo and Abruña.¹² Potential differences (ΔE) of anodic and cathodic current peaks are 70 and 30 mV for Δ - and *rac*-modified electrodes, respectively. The peak current height, j_p , of the Δ -osmium complex on Pt is roughly half that of the *rac*-osmium complex on Pt with half-height widths of 210 and 120 mV, respectively. The quantity of charge between anodic and cathodic reaction currents is plotted vs. τ in Fig. 4, where, at $\tau = 40$ min, the amounts of charge ΔQ appear to be saturated at 0.85×10^{-10} and $0.95 \times 10^{-10} \text{ mol cm}^{-2}$ for Δ - and *rac*-modified electrodes respectively, of which the latter amounts to a nearly complete monolayer assuming a cross-section of 1.54 nm² per molecule of the osmium complex.¹¹ These results show that a repulsive interaction energy is higher between chiral osmium complexes than between racemic osmium complexes or that a different ordered structure is suggested. The ordered STM structure has been observed for a self-assembled racemic osmium complex on Pt,¹⁶ and the above values suggest that the self-assembled ordered structure should be different for chiral and racemic complexes if chiral complexes also form an ordered monolayer structure.† STM measurements upon the chiral complex self-assembled on Pt are now under way.

Footnote

† The ordered molecule arrangement depicted in ref. 16 is for chiral complexes.

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