Chirality Effects on Energy Transfer from Polypyridyl Ru(II) to Os(II) Complexes in Langmuir-Blodgett Films

Kentaro Okamoto, Masayuki Takahashi, Masahiro Taniguchi, and Akihiko Yamagishi*
Division of Biological Sciences, Graduate School of Science, Hokkaido University, Sapporo 060-0810

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Energy transfer rate (k_2) from optically active tris(4,7-diphenyl-1,10-phenanthroline)ruthenium(II) (denoted by Ru(II)) to Os(II) has been studied in Langmuir–Blodgett (LB) films; k_2 is found to be larger for Λ-Ru(II)/Δ-Os(II) than for Λ-Ru(II)/Λ-Os(II) in a Y-type mixed film of Ru(II) and Os(II), while streoselectivity is reversed in an alternatively layered Y-type LB film of Ru(II) and Os(II).

Recently well-structured molecular films have been investigated extensively with a purpose of developing device materials.[1–4] In these attempts, the coordination compounds of transition metal ions are of potential value as a functional unit because of their unique electronic and magnetic properties.[5] In order to develop such a functional film as based on metal complexes, it will be important to know how they interact with each other dynamically in well-ordered films. In this communication, we present a study on energy transfer reactions between two kinds of metal complexes in a Langmuir–Blodgett (LB) film. A mixed LB film has been prepared, using tris(4,7-diphenyl-1,10-phenanthroline)ruthenium(II) (denoted by Ru(II)) and Os(II) complexes.[6] The energy transfer from excited Ru(II) (or Ru(II)*) to Os(II) has been studied with a focus on the effect of molecular chirality.

Ru(II) was prepared by reacting $K_2[RuCl_5(H_2O)]$ and 4,7-diphenyl-1,10-phenanthroline (dpp) and resolved into optical isomers as described previously.[6] The preparation and resolution of Os(II) were performed in a similar way by use of K_2OsCl_6 as a starting material. The measurements of surface pressure versus molecular area (π-A) isotherms were carried out by using a 0.1 M $NaClO_4$ aqueous solution as a subphase at 20 °C. A floating monolayer was transferred onto a hydrophobic quartz plate as a Y-type deposition film at a surface pressure of 20 mN m^{-1}. The transfer ratio was 1.0 ± 0.1.

The π-A isotherms are shown in Figure 1 when a chloroform solution of a mixture of stearic acid (SA) and either racemic (denoted by rac-) or Λ-Ru(II) was spread onto a subphase. The molar ratio of Ru(II) to SA was changed as Ru(II)/SA = 1:1, 1:2, 1:3 and 1:4. Repeated compression-expansion cycles below 40 mN m^{-1} caused no practical change in the isotherm curves, indicating the formation of stable monolayer in this surface pressure range. The surface pressure started to rise at about 1.5 nm^2 molecule^{-1} at Ru(II)/SA = 1 : 1 and 1 : 2 for both rac- and Λ-Ru(II). Since the lift-off area is nearly equal to the cross sectional area of Ru(II) (1.6 nm^2), the metal complex is concluded to form a monolayer at this surface pressure. As Ru(II)/SA increased to 3 and 4, the lift-off area increased to nearly 2.0 nm^2 molecule^{-1} for both rac- and Λ-Ru(II). When the π-A isotherm of Λ-Ru(II) is compared with that of rac-Ru(II) at the same Ru(II)/SA ratio, the former is always located at the smaller molecular area than the latter. The results implied that Λ-Ru(II) forms a more compact monolayer than rac-Ru(II). These differences are a direct evidence for the fact that the metal complexes interact stereoselectively with the nearest neighbors in the monolayer state.

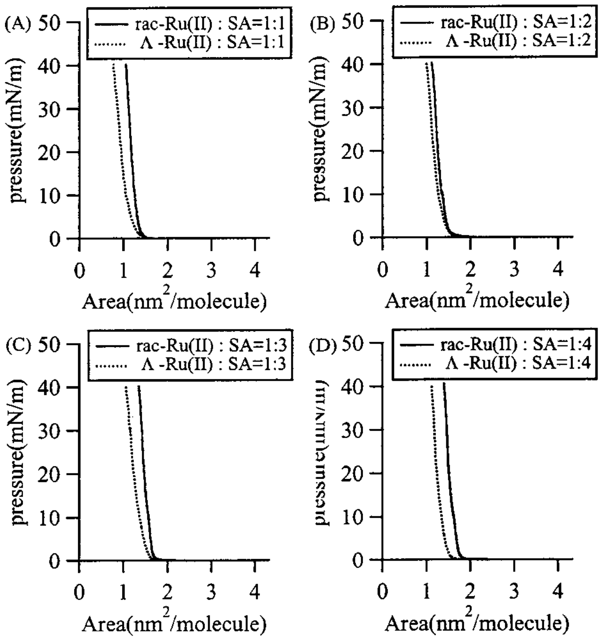


Figure 1. The π-A isotherms when a chloroform solution of a mixture of SA and either by rac- (solid) or Λ-Ru(II) (dotted) was spread onto an aqueous subphase of 0.1 M $NaClO_4$ at 20 ℃. The molar ratio of $[Ru(dpp)_3](ClO_4)_2$ to SA was changed as Ru(II)/SA = (A) 1:1, (B) 1:2, (C)1:3 and (D) 1:4.

Figure 2 shows the decay curve of fluorescence at 700–750 nm when a mixed film (10 layers) of SA, Λ-Ru(II) and Δ-Os(II) (upper) (or Λ-Os(II) (lower)) at the ratio of 3 : 1 : 0.01 was irradiated at 460 nm. Both Ru(II) and Os(II) are excited by this light, while only Os(II) emits fluorescence in the range of 700–750 nm. According to the figure, the half-life time of Os(II)* is much longer than the intrinsic decay of Os(II)* (the half-life of 8 ± 2 ns), supporting the presence of a process generating Os(II)* by energy transfer from Ru(II)*. The apparent half-life time of Ru(II)* in a LB film of pure Ru(II) was about 150 nsec. The decay profiles are analyzed by assuming the following three processes:

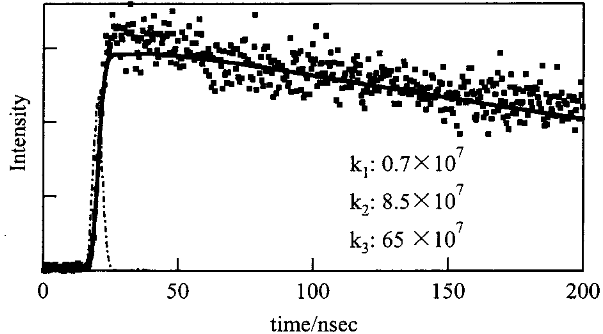
$$\mathrm{Os(II)} + h\upsilon \rightarrow \mathrm{Os(II)^*}\ \text{direct excitation};\ k_{di} \quad (3)$$
$$\mathrm{Ru(II)^*} + \mathrm{Os(II)} \rightarrow \mathrm{Ru(II)} + \mathrm{Os(II)^*}\ \text{(energy transfer)};\ \ k_{tr} \quad (4)$$
$$\mathrm{Os(II)^*} \rightarrow \mathrm{Os(II)} + h\upsilon\ \text{spontaneous decay)}\ ;\ k_{os} \quad (5)$$

The time change of fluorescence intensity (or the number of photons) at 700 nm–750 nm, I_{os}, is expressed by the following equation:

$$dI_{os}/dt=k_{os}k_{di}[\mathrm{Os(II)}]I_{in}+ (k_{os}k_{tr}[\mathrm{Os(II)}]/k_{ru})I_{ru}-k_{os}I_{os}, \quad (6)$$

in which I_{in} and I_{ru} are the time profile of excitation laser pulse

(A) Λ-Ru(II) + Δ-Os(II)



(B) Λ-Ru(II) + Λ-Os(II)

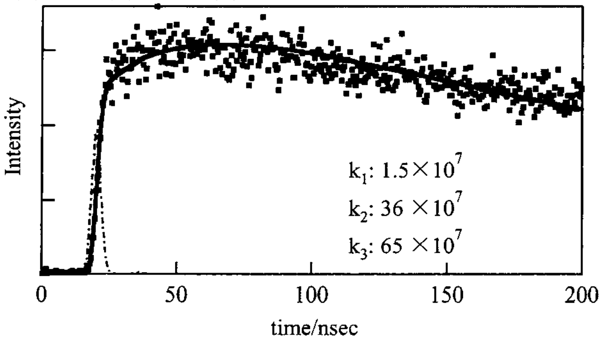
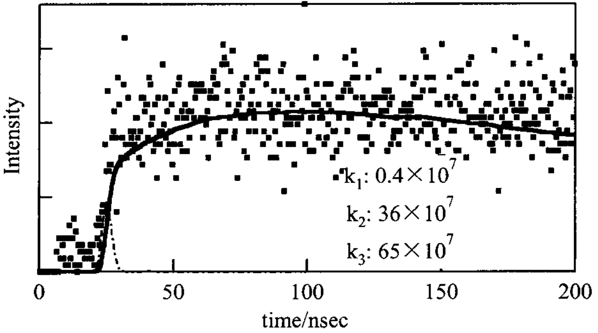


Figure 2. The decay profiles of fluorescence at 700-750 nm for the Y-type LB films (10 layers) of a 3:1:0.01 mixture of SA, Λ-Ru(II) and either Δ-Os(II) (upper) or Λ-Os(II) (lower), respectively. The solid curves are the simulated ones based on equation (6). The time profile of laser pulse is also shown by the dash-dotted line.

(A) Λ-Ru(II) / Δ-Os(II) / Δ-Os(II) / Λ-Ru(II)



(B) Λ-Ru(II) / Λ-Os(II) / Λ-Os(II) / Λ-Ru(II)

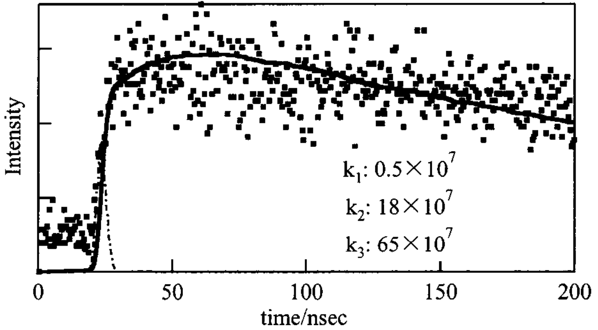


Figure 3. The decay profiles of fluorescence at 700-750 nm films the LB films in which the monolayer of 3:1 SA and Λ-Ru(II) was deposited alternatively with the monolayer of 1:0.01 SA and either Δ-Os(II) or Λ-Os(II) to form a Y-type film. The solid curves are the simulated ones based on equation (6). The time profile of laser pulse is also shown by the dash-dotted line.

(450 nm) and the fluorescence intensity from Ru(II)* (600–650 nm) (not shown), respectively. k_{os}, k_{di}, k_{tr} and k_{ru} are the rate constants of (5), (3), (4) and spontaneous emission rate from Ru(II)*, respectively. According to equation (6), the time course of I_{os} (t) can be constructed successively by using the observed time profiles of I_{ru}(t) and I_{in}(t) for a given set of three parameters, $k_1 = k_{os}k_{di}$, $k_2 = (k_{os}k_{tr}[\mathrm{Os(II)}]/k_{ru})$ and $k_3 = k_{os}$. We attempted to find the best values of these parameters by comparing the simulated and observed time courses of I_{os}. The dotted curves in Figure 2 are the examples of the simulation results for the time increment of 0.42 nsec. The values of k_1, k_2 and k_3 are given in each figure. Since k_2 for Λ-Ru(II)/Λ- Os(II)) (upper) is more than 4 times larger than that for Λ-Ru(II)/Δ-Os(II) (lower), it is certain that energy transfer takes place stereoselectively. From the chirality effect on the π-A curves (Figure 1), the pure enantiomers are deduced to attain closer stacking than the racemic unit in a mixed LB film. Based on this, the energy transfer is expected to be more favored for theΛ-Ru(II)*/Λ-Os(II) pair than for the Λ-Ru(II)*/Δ-Os(II) pair. The experimental observations coincide with this expectation.

When the experiments were performed for the Δ-Ru(II)*/Δ-Os(II) and Δ-Ru(II)*/Λ-Os(II) pairs, it was shown that the energy transfer was more favored for the Δ-Ru(II)*/Δ-Os(II) than for the Δ-Ru(II)*/Λ-Os(II) pair, confirming the same stereoselectivity.

The simular experiments were performed for another type of LB film in which the monolayer of 3:1 SA and Λ-Ru(II) was deposited alternatively with the monolayer of 1 : 0.01 SA and Δ-Os(II) (or Λ-Os(II)) to form a Y-type film. In this film, Os(II) is mixed with Ru(II) in an inter-layer way. This is contrasted with the previous film in which Os(II) is mixed with Ru(II) in an intra-layer way. The upper and lower parts in Figure 3 are the results for Λ-Ru(II)/Λ-Os(II) and Λ-Ru(II)/Δ-Os(II), respectively. k_2 for Λ-Ru(II)/Δ-Os(II) (upper) is 2 times larger than that for Λ-Ru(II)/Λ-Os(II) (lower), which is the reverse of the results in the intra-layer mixed films. The observed difference was beyond the error in estimating the rate constants (30 %). At the present stage, there is no structural evidence for the stacking interaction between Ru(II) and Os(II) complexes in the alternative films. Thus it is not possible to rationalize the results in terms of the difference of molecular association between the same and opposite enantiomers. At least, however, the present results have confirmed a fact that stereoselectivity in energy transfer is dependent on a layer structure drastically.[7]

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