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Photoinduced Electron Transfer Affected by Electrical Potential Difference in LB Films

Toshihiro KONDO and Masamichi FUJIHIRA*
Department of Biomolecular Engineering, Tokyo Institute of Technology,
4259 Nagatsuta, Midori-ku, Yokohama 227

The comparison of the dependence of the electron transfer quenching rate on the signs in head group charge indicates that the inner potential difference of the electrical double layer (EDL) created between the sensitizer and the ferrocene monolayer, $\Delta\phi$, has to be taken into account for estimation of the effective standard free energy of the electron transfer quenching reaction, $\Delta G°$.

We have studied LB film molecular assemblies with spatial regularity and examined their properties for photoelectric conversion.[1)] In connection with this photoelectric conversion device, we have studied the photoinduced electron transfer kinetics in the LB films containing the sensitizer (S) and the electron donors (D) with different standard redox potentials, $E°$'s.[2)] However, contrary to our expectations, photoinduced electron transfer quenching was observed even in S/D LB systems in which the electron transfer seemed to be an up-hill reaction based on the energy levels determined by the halfwave potentials, $E_{1/2}$, in acetonitrile.

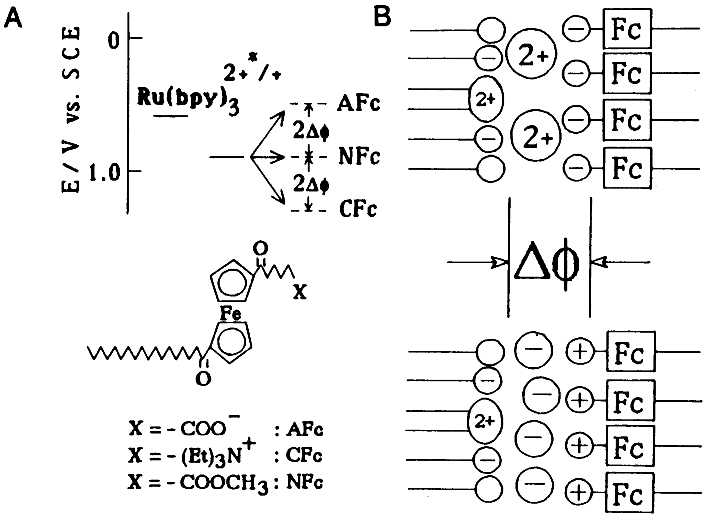
In the present work, for the purpose of interpreting this unexpected result, three kinds of amphiphilic ferrocene derivatives, i.e. AFc, CFc, and NFc in Fig. 1A, as donors with the same E°, the same alkyl chain spacer, and the different charges (+1, 0, −1) at the hydrophilic head groups were newly synthesized. As the sensitizer, a $Ru(bpy)_3^{2+}$ derivative with two nonadecyl chains (RuC19) was used as previously.[3)] For monolayers, RuC19 was mixed with arachidic acid (AA) and methyl arachidate (MA) with a molar ratio of 1:2:2, while the ferrocene derivatives were used by themselves. Each sample consisted of 5 layers of the S/D pair and 5 layers of the AA/AA spacer deposited alternatively upon 5 layers of the pure AA monolayer deposited in advance on a quartz plate for its surface pretreatment. All the film preparations were carried out in the dark to avoid photooxidation of the films.[4)] By using nanosecond laser photolysis, the luminescence decays were measured for these S/D systems at 20°C under a nitrogen atmosphere.

In Fig. 1A are also shown energy levels of the excited $Ru(bpy)_3^{2+}$ and the ferrocene derivatives in their ground states in terms of their standard redox potentials (full lines).[2,3)] Namely, in this energy diagram, the effect of the EDL between the D and S monolayers is not taken into account. All the redox potentials of three kinds of ferrocene derivatives were ca. 900 mV vs. SCE determined by cyclic voltammetry in acetonitrile. It was thought that the electron transfer quenching from all ferrocene derivatives to excited $Ru(bpy)_3^{2+}$ was up-hill reaction.

The luminescence decay curves for three types of S/D systems with AFc, CFc, and NFc are shown in curves b − d in Fig. 2, respectively, together with a reference decay curve a for an LB film in which the pure monolayer of AA was deposited in place of the ferrocene layer. It is noteworthy that among curves b − d only curve b clearly shows a fast decay component within ca. 1 μs (102.4 channels), while other two curves are very similar to the reference curve a and decay almost single exponentially without appreciable quenching.

The most important and intrinsic factor in the LB film affecting the relative energy levels between the donor and the sensitizer may be the electrical potential differences created between the monolayers inside the LB films. The region across which the present electron transfer is expected to occur is the EDL where the hydrophilic head-groups of the RuC19 and the ferrocene amphiphiles are facing each other. As shown in the schematic diagram of the LB film structures in Fig. 1B, it seems to be quite reasonable to assume that i) the positive charges of Ru(bpy)$_3^{2+}$ are neutralized by the carboxylate anions present in the same plane in the mixed monolayer, ii) the negative charges of the head-groups of AFc, -COO$^-$, are in contact with their counter Ca^{2+} cations, and iii) the positive charges of CFc, -(ethyl)$_3$N$^+$, in contact with their counter ClO$_4^-$ anions.

By comparing the luminescence decay characteristics for the S/D LB systems with three kinds of donor amphiphiles, whose oxidation potentials are the same but whose signs of the head groups are different, i.e. negative, neutral, and positive, it is concluded that electrical potential difference between the hydrophilic head groups in the LB films has to be taken into account for estimation of the effective energy gap $\Delta G°$ between the donor and the sensitizer. In other words, the absolute magnitude and the sign of the electrical potential difference between the layers in LB films can be varied by changing the hydrophilic head groups.



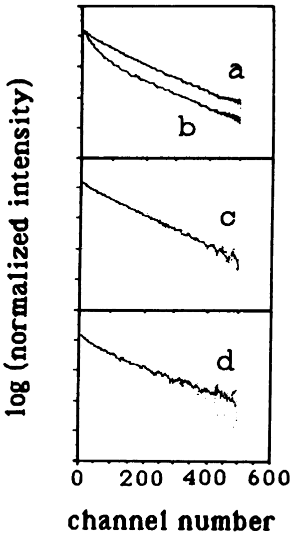


Fig. 1. A) Energy diagrams of excited Ru(bpy)$_3^{2+}$ and ferrocene derivatives in their ground states with (---) and without (———) the influence of the electrical double layer created inside the heterogeneous LB films. B) Schematic diagrams of EDL's created in the S/AFc pair and in the S/CFc pair.

Fig. 2. Luminescence decay curves of the S/D LB systems with various donor molecules. a) RuC19/AA, b) RuC19/AFc, c) RuC19/CFc, and d) RuC19/NFc. On the abscissa, 512 channels correspond to 5 μs.

References

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