CHEMISTRY LETTERS, pp. 1639-1642, 1993.

Single Exponential Decay for the Luminescence Intensity of $Ru(bpy)_3^{2+}$ Complex in Langmuir-Blodgett Films

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

The luminescence decay curves of $Ru(bpy)_3^{2+}$ in Langmuir-Blodgett (LB) films were often fitted by multiexponential functions whereas those in homogeneous solutions by a single exponential one. Responsible conditions in the LB film preparation for the luminescence decay kinetics were examined. The single exponential decay was observed when the film was prepared in a clean atmosphere and photooxidation of the LB films was avoided.

In connection with photosynthesis and molecular devices, Langmuir-Blodgett (LB) films containing redoxactive and photoactive amphiphiles have been used to study photochemical reactions and photoinduced electron and energy transfer in well organized molecular assemblies.[1-3] The transient state of the reaction has been discussed to describe the kinetics of photoinduced electron transfer reaction in organic molecules mimicking the natural system. The luminescent decay curves of the dye molecules without quenchers as a control experiment for the decay curves of the systems containing the quenchers, should be simple and preferably be presented by a single exponential curve. In last two decades since the first report by Demas and Adamson in 1971[4] on the possible use of $Ru(bpy)_3^{2+}$ as a photosensitizer, the ruthenium complex and its derivatives have established themselves as superior sensitizers for photoredox processes.[5] However, in the LB films of $Ru(bpy)_3^{2+}$ derivatives[6-9] or the adsorbed submonolayers of the complex on powders,[10] the luminescent decay curves have never been approximated by a single exponential function, while the complexes gave the single exponential decay curves in solutions.[5]

We have used a long alkylchain derivative of $Ru(bpy)_3^{2+}$ (RuC19) as a photosensitizer[6-9] for photoinduced electron transfer in LB films. However, we found that luminescence decay curves for LB films of $Ru(bpy)_3^{2+}$ without quenchers could be fitted well as a sum of two or three exponential functions, although the reason for the fast quenching component has not been clarified yet.[11,12] Other than our results, the most of decay curves of $Ru(bpy)_3^{2+}$ adsorbed on solids also could be rarely fitted as a single exponential function.[10] Although the concentration quenching,[13] the triplet-triplet annihilation,[14] and the photooxidation[11] have been considered as one of the mechanisms for the fast quenching, the final definite conclusion has not been obtained.

† Present address : Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060.

Previously, we reported that photooxidative products, which were formed during the monolayer preparation and/or during the luminescence decay measurement, acted as the quenchers.[11,12] In the present work, we studied other factors than the photooxidation that cause the fast decay component. Especially, the effect of cleanliness of the atmosphere for the film preparation was studied carefully to obtain the films giving a single exponential curve.

By using the LB technique, samples containing 1-4 layers of sensitizer/spacer heterogeneous structures on each side of a quartz plate were prepared in the dark as shown in Fig. 1, where the quartz plate was precoated with 5 layers of the pure arachidic acid (AA) monolayers on each side. The sensitizer layer was a 1: 2 mixed monolayer of RuC19 and AA or the same mixture with a methyl arachidate (MA) diluent with molar ratios of 1:2:2, 1:2:7, and 1:2:17. Dioctadecyldimethylammonium chloride (DODAC) and MA as well as AA were used as non-luminescent spacers. The luminescence decay curves for the LB films were recorded using the equipment as described previously.[11,12]

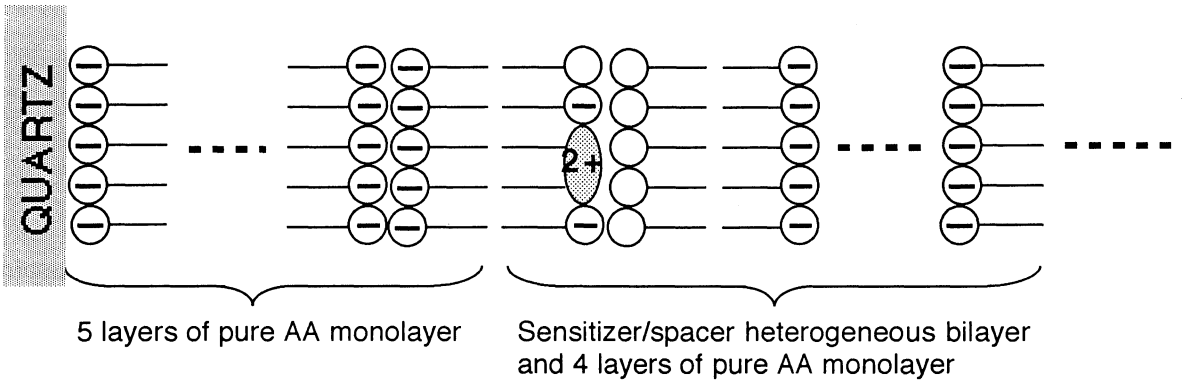

Fig. 1. The structure of the multilayered LB film consisting of an amphiphilic RuC19 used as the sensitizer and non-luminescent amphiphiles used as diluents and/or spacers.

We examined i) dilution ratios of non-luminescent molecules, ii) laser power used for irradiation of $Ru(bpy)_3^{2+}$ LB films, iii) atmosphere during the preparations and the decay measurements, iv) pH of the subphase, and v) counter ions added in the subphase as factors affecting the decay curves. Lifetimes (τ_0) and relative weights of pre-exponential factors (I_0) for the slow decay component observed for the LB films, which seems to be an inherent luminescence decay of $Ru(bpy)_3^{2+}$ without suffering from any quenching, increased with increasing dilution ratios. With an increase in the laser power, τ_0 and, in particular, I_0 decreased in atmospheres such as air, N_2, and N_2 + water vapor[12] and decreased slightly even *in vacuo*. The similar decrease in τ_0 and I_0 was also observed with an increase in time of irradiation. Both τ_0 and I_0 decreased with increasing pH in the pH range of 6.8 - 10.8. It seems that $Ru(bpy)_3^{2+}$ in excited state was quenched by OH^- incorporated into the LB films.[15] Although two anions of AA carboxylate were added in order to neutralize a divalent cation of the $Ru(bpy)_3^{2+}$ moiety in the sensitizer monolayer, the shape of surface pressure - area isotherms of the mixed monolayer was affected by the anions in the subphase. But, the luminescent characteristics were not changed by the anions. From these experiments, the above factors were found to affect somewhat the decay characteristics, none of them were the definite solution to obtain a single exponential decay curve. An example of the decay curves was shown in Fig. 2(a).

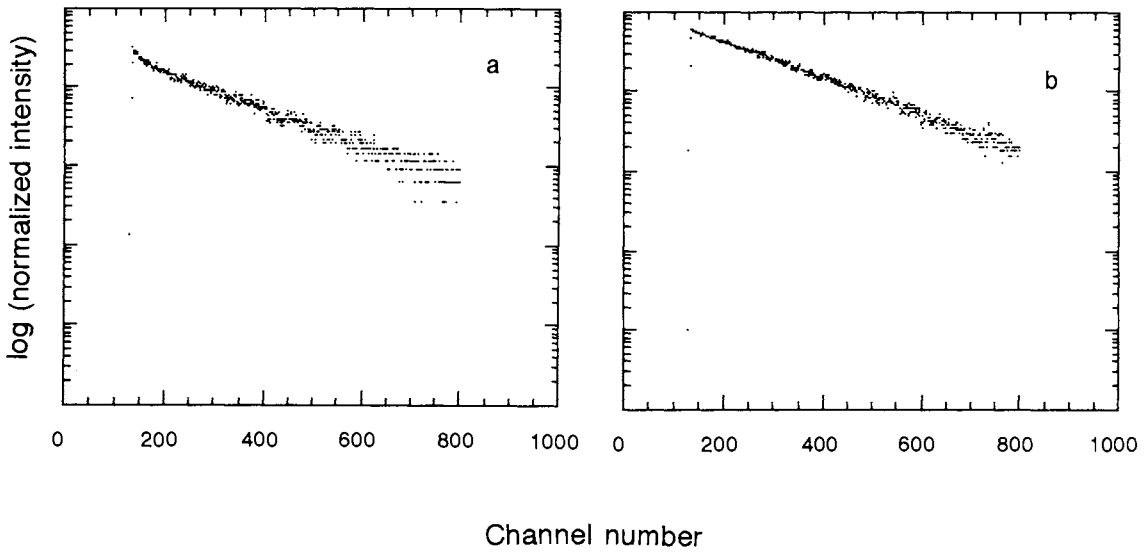

Fig. 2. Luminescence decay curves of the heterogeneous S/AA LB films. S = the mixed $Ru(bpy)_3^{2+}$ monolayer with AA molecules (1:2); (a) prepared in an open atmosphere, (b) prepared in the closed box in the clean room. On the abscissa, 1024 channels correspond to 5 μs.

Therefore, we studied finally the effect of cleanliness of the atmosphere for the monolayer preparation as another possible factor. For this purpose, the trough was placed inside a closed box made of aluminum and the box was used in a clean room of class 10^5. In addition, to avoid the dust from our clothes, clothes specialized for a clean room were also used. A typical decay curve observed for the LB films thus prepared is shown in Fig. 2(b). Surprisingly, all curves for the RuC19 LB films without quenchers and with the various inactive spacers described above became a single exponential one and their τ_0 and I_0 were found to be ca. 1 μs and 1.0, respectively, when the photooxidation of the LB films was avoided by the use of appropriate atmosphere and irradiation conditions. It is a very trivial solution for the present problem, but it was found that the dust from the atmosphere was the main factor which gave the multiexponential decay. It has not been clarified yet what kinds of chemical species in the dust act as the quenchers, but it is very likely that some redox active compounds and some colored materials included in the dust act as the electron transfer and the energy transfer quenchers, respectively. Previously, we reported τ_0 and I_0 increased with increasing dilution ratios.[12] However, since τ_0 for 1:2 mixed films with AA, prepared in the clean atmosphere, was consistent with that for the mixed films with the high dilution ratios, prepared in the open atmosphere, it is concluded that the values of τ_0 in the previous 1:2 mixed films were made shorter by the dust.

In conclusion, we first reported here the single exponential decay curve of $Ru(bpy)_3^{2+}$ LB films by the careful preparation of the LB films in a clean atmosphere and by taking precautions against the photooxidation during the decay measurement.

References

1) H. Kuhn, *J. Photochem.*, **10**, 111 (1979); *Thin Solid Films*, **99**, 1 (1983).
2) D. Möbius, *Ber. Bunsenges. Phys. Chem.*, **82**, 848 (1978); *Acc. Chem. Res.*, **14**, 63 (1981).
3) M. Fujihira, *Mol. Cryst. Liq. Cryst.*, **183**, 59 (1990).
4) J. N. Demas and A. W. Adamson, *J. Am. Chem. Soc.*, **93**, 1800 (1971).
5) K. Kalyanasundaram, *Coord. Chem. Rev.*, **46**, 159 (1982).
6) T. Kajiwara, K. Hashimoto, T. Kawai, and T. Sakata, *J. Phys. Chem.*, **86**, 4516 (1982); K. Hashimoto, M. Hiramoto, T. Sakata, H. Muraki, H. Takemura, and M. Fujihira, *J. Phys. Chem.*, **91**, 6189 (1987).
7) M. Fujihira, K. Nishiyama, and K. Aoki, *Thin Solid Films*, **160**, 317 (1988).
8) T. Kondo, H. Yamada, K. Nishiyama, K. Suga, and M. Fujihira, *Thin Solid Films*, **179**, 463 (1989).
9) T. Kondo and M. Fujihira, *Chem. Lett.*, **1991**, 191.
10) T. Kondo, M. Yanagisawa, and M. Fujihira, *Electrochim. Acta*, **36**, 1793 (1991).
11) T. Kondo and M. Fujihira, *Kobunshi Ronbunshu*, **47**, 921 (1990).
12) M. Fujihira, M. Yanagisawa, T. Kondo, and K. Suga, *Thin Solid Films*, **210/211**, 265 (1992).
13) J. H. Baxendale and M. A. J. Rodgers, *Chem. Phys. Lett.*, **72**, 424 (1980); J.-C. Chambron and J.-P. Sauvage, *Chem. Phys. Lett.*, **182**, 603 (1991).
14) J. H. Baxendale and M. A. J. Rodgers, *J. Phys. Chem.*, **86**, 4906 (1982).
15) E. D. Goddard and J. A. Ackilli, *J. Colloid Sci.*, **18**, 585 (1963).

(Received May 31, 1993)