

Circularly Polarized Luminescence of  $[\text{Ru}(\text{diimine})_3]^{2+}-\text{Ag}^+$  Exciplex System

Taro TSUBOMURA,\* Osamu IGARASHI, and Makoto MORITA

Department of Industrial Chemistry, Faculty of Engineering, Seikei University,  
Kichijoji-Kitamachi, Musashino, Tokyo 180

Circularly polarized luminescence of  $[\text{Ru}(\text{diimine})_3]^{2+}-\text{Ag}^+$  exciplexes in aqueous solution (diimine = 2,2'-bipyridine (bpy) and 1,10-phenanthroline (phen)) was studied. Remarkable enhancement of the emission dissymmetry factor  $g_{\text{em}}$  is observed for the exciplex.

Several exciplex systems involving inorganic complexes have been reported in recent years.<sup>1)</sup> The exciplex systems containing metal complexes are interesting as the intermediates of photocatalytic or photoredox reactions. The demonstration of the formation of exciplexes in metal complex system is often difficult in contrast to typical aromatic exciplex systems, since i) the life time of the exciplexes involving metal complexes is often similar to that of the complex monomer, and ii) the locations of the luminescence peak of the exciplex are not so much different from that of the complex monomer. Recently, Ayara, Demas, and DeGraff reported the exciplex-formation of  $[\text{Ru}(\text{bpy})_3]^{2+}$  with  $\text{Ag}(\text{I})$  ion.<sup>1a)</sup> They studied the luminescence "quenching" of the system thoroughly in detail. Although the apparent quenching had been attributed to oxidative electron transfer,<sup>2)</sup> they showed that the changes of the luminescence spectra, the luminescence intensities, and the life times are consistent with the formation of exciplexes.

We have been studying the circularly polarized luminescence (CPL) of several metal complexes.<sup>3)</sup> CPL spectra reveal the difference of the left- and right-handed circular polarization of luminescence emitted from chiral molecules. CPL spectra, therefore, offer us structural informations of the molecules in their excited-luminescent states. We now present that the exciplex formation of the Ru-Ag system is clearly shown by CPL technique.

The synthesis and optical resolution of  $[\text{Ru}(\text{bpy})_3]\text{I}_2$  and  $[\text{Ru}(\text{phen})_3](\text{ClO}_4)_2$  were done according to the usual method.<sup>4)</sup> The absorption and CD spectra were measured on commercially available instruments at room temperature. The CPL spectra were measured on an instrument constructed by us<sup>3a)</sup> at room temperature. The excitation source was 500 W super-high pressure mercury lamp with appropriate filters (365 nm). The emission was detected at  $180^\circ$  angle with respect to the excitation. The aqueous sample solutions of  $[\text{Ru}(\text{diimine})_3]^{2+}-\text{Ag}^+$  were prepared at different  $[\text{AgNO}_3]$  ( $0 - 1.5 \text{ M}$ ) and the total  $\text{NO}_3^-$  concentration was fixed at  $3.0 \text{ M}$  with  $\text{LiNO}_3$  ( $1 \text{ M} = 1 \text{ mol dm}^{-3}$ ). The concentration of the Ru complex was  $1.0 \times 10^{-4} \text{ M}$ . Each sample solution was deoxygenized by bubbling of nitrogen gas for 15 min before measurements. The luminescence and CPL spectra were measured four times for each sample and averaged.

Figure 1 shows the changes of the absorption and luminescence spectra of  $[\text{Ru}(\text{bpy})_3]^{2+}$  when the concentration of  $\text{Ag}^+$  ion is varied. The absorption spectrum of the solution with no  $\text{Ag}^+$  ion and that in  $1.5 \text{ M}$

$\text{Ag}^+$  are almost superimposable. However, the luminescence spectra show drastic change in proportion to the concentration of  $\text{Ag}^+$  ion. The well-known luminescence band emitted from  $^3\text{MLCT}$  states is located at  $16.3 \times 10^3 \text{ cm}^{-1}$  without  $\text{Ag}^+$  ion. Red shift and decrease in the emission intensity is observed as  $[\text{Ag}^+]$  increases. These observations coincide with the results of Ayara et al.<sup>1a)</sup>

Figure 2 illustrates the emission and absorption dissymmetry factors,  $g_{\text{em}}$  and  $g_{\text{abs}}$ . The dissymmetry factors are defined as follows.  $g_{\text{em}} = 2(I_L - I_R) / (I_L + I_R)$  and  $g_{\text{abs}} = (\epsilon_L - \epsilon_R) / (\epsilon_L + \epsilon_R)$ , where  $I_L$  and  $I_R$  are the intensities of left and right circularly polarized luminescence and  $\epsilon_L$  and  $\epsilon_R$  are the molar absorption coefficients for left and right circularly polarized light for each wavenumber of light, respectively. To begin with, we refer the  $g_{\text{em}}$  value of  $[\text{Ru}(\text{bpy})_3]^{2+}$  without  $\text{Ag}^+$  ion. The value become larger with increase of the wavenumber over the entire  $^3\text{MLCT}$  luminescence band. A remarkable increase of  $g_{\text{em}}$  of  $[\text{Ru}(\text{bpy})_3]^{2+}$  at the high energy side of the luminescence spectra is observed. The increase was already reported by Gafni et al.<sup>5)</sup> Although they attributed it to the contribution of the  $^1\text{MLCT}$  band, we thought that the increase is attributed to the contribution of another triplet MLCT state(s).

The  $g_{\text{abs}}$  factors were calculated from CD and absorption data, and the factors reflect on the structure of the complex system in the ground-state. On the other hand,  $g_{\text{em}}$ , which is derived from CPL and luminescence data must reflect on the structure in their excited luminescent state. In Fig. 2,  $g_{\text{abs}}$  values do not change even in the most concentrated  $\text{Ag}^+$  solution. On the contrary, the values of  $g_{\text{em}}$  clearly increase in proportion to the concentration of  $\text{Ag}^+$  ion. The results show that the structure in the ground state is not changed even under high concentration of  $\text{Ag}^+$ , but the species in the excited state have different structure from the ground state. The CPL results show that the apparent decrease of the luminescence intensity is not due to the normal quenching process but due to the formation of exciplexes. Furthermore, Ayara et al. showed<sup>1a)</sup> that not only bimolecular exciplex,  $([\text{Ru}(\text{bpy})_3]^{2+}-\text{Ag}^+)^*$ , but also termolecular exciplex,  $([\text{Ru}(\text{bpy})_3]^{2+}-2\text{Ag}^+)^*$ , were formed in excite state. They reported the formation constants of the bimolecular and termolecular

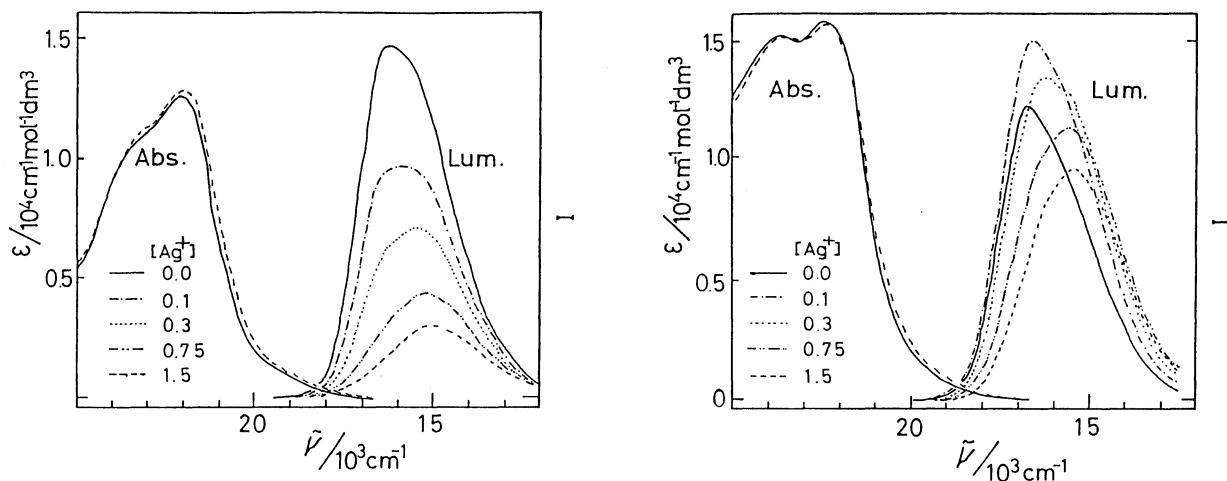


Fig. 1. Absorption and luminescence spectra of  $[\text{Ru}(\text{bpy})_3]^{2+}$  (left) and  $[\text{Ru}(\text{phen})_3]^{2+}$  (right) versus  $[\text{Ag}^+]$ .

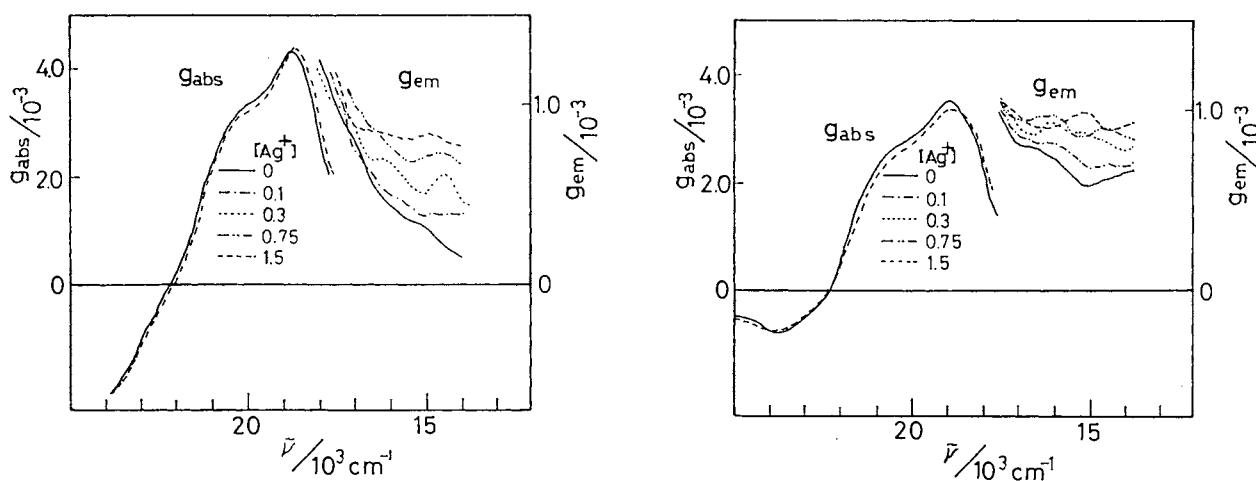


Fig. 2. Absorption and emission dissymmetry factors of  $[\text{Ru}(\text{bpy})_3]^{2+}-\text{Ag}^+$  (left) and  $[\text{Ru}(\text{phen})_3]^{2+}-\text{Ag}^+$  (right) exciplex system.

exciplexes. One can calculate the molar ratio of the emissive species,  $([\text{Ru}(\text{bpy})_3]^{2+})^* : ([\text{Ru}(\text{bpy})_3]^{2+}-\text{Ag}^+)^* : ([\text{Ru}(\text{bpy})_3]^{2+}-2\text{Ag}^+)^*$ , from the constants. Using the ratio, the  $g_{\text{em}}$  values of the two exciplexes were evaluated from the observed CPL data by least-squares method. Thus, the  $g_{\text{em}}$  values of the bimolecular and termolecular exciplexes were found to be 1.4 and 1.7 times as much as that of  $[\text{Ru}(\text{bpy})_3]^{2+}$  at  $14-15 \times 10^3 \text{ cm}^{-1}$ , although precise values could not be obtained because of the very weak observed CPL intensities ( $g_{\text{em}} < 10^{-3}$ ).

Besides the bpy complex, the exciplex formation of  $[\text{Ru}(\text{phen})_3]^{2+}-\text{Ag}^+$  system was also investigated. The absorption and luminescence spectra of the complex in  $0 - 1.5 \text{ M AgNO}_3$  solution are also shown in Fig. 1. The absorption spectrum does not change even in the presence of high  $[\text{Ag}^+]$ . The luminescence intensity of the solution does not decrease simply with proportion to the concentration of  $\text{Ag}^+$ . The intensity of the solution containing  $0.1 \text{ M Ag}^+$  is larger than that of  $[\text{Ru}(\text{phen})_3]^{2+}$  alone. When  $\text{Ag}^+$  is added furthermore, the intensity becomes smaller again. This result may also be interpreted as the formation of bimolecular and termolecular exciplexes. The bimolecular exciplex formed at low  $\text{Ag}^+$  concentration must emit more intense luminescence than the monomer. The luminescence intensity of termolecular exciplex, which exists under high concentration of  $\text{Ag}^+$  ion, should be small. The increase of  $g_{\text{em}}$  is also shown in Fig. 2 in proportion to the concentration of  $\text{Ag}^+$ . But, the change is less remarkable than that of  $[\text{Ru}(\text{bpy})_3]^{2+}-\text{Ag}^+$  system. It is very interesting that distinct differences are observed between the properties of the exciplexes of the bpy and phen complex.

The exciplex formation of  $[\text{Ru}(\text{diimine})_3]^{2+}-\text{Ag}^+$  system can be confirmed by CPL spectroscopy. CPL technique will become a powerful tool to investigate the nature of the species in the excited states as well as the exciplex formation.

## References

- 1) a) N. P. Ayara, J. N. Demas, and B. A. DeGraff, *J. Am. Chem. Soc.*, **110**, 1523 (1988); b) N. P. Ayara, J. N. Demas, and B. A. DeGraff, *J. Phys. Chem.*, **93**, 4104 (1989); c) A. B. P. Lever, P. Seymour, and P. R. Auburn, *Inorg. Chim. Acta.*, **145**, 43 (1988); d) N. P. Ayala, C. M. Flynn, Jr., L. Sacksteder, J. A. Demas, and B. A. DeGraff, *J. Am. Chem. Soc.*, **112**, 3837 (1990).
- 2) T. K. Foreman, J. B. S. Boniha, and D. G. Whitten, *J. Phys. Chem.*, **86**, 3436 (1982).
- 3) a) T. Tsubomura, I. Ohkouchi, and M. Morita, *Bull. Chem. Soc. Jpn.*, **64**, 2341 (1991) and the references cited there in; b) T. Tsubomura, K. Yasaku, T. Sato, and M. Morita, *Inorg. Chem.*, in press.
- 4) For synthesis, R. A. Palmer and T. S. Piper, *Inorg. Chem.*, **5**, 864 (1966); for optical resolution, F. P. Dwyer and E. C. Gyarfas, *J. Proc. Roy. Soc. N. S. Wales*, **83**, 174 (1949); F. P. Dwyer and E. C. Gyarfas, *ibid.*, **83**, 170 (1949).
- 5) A. Gafni and I. Z. Steinberg, *Israel J. Chem.*, **15**, 102 (1976).

( Received December 6, 1991 )