Stereoselective Luminescence Quenching in the Complex of Excited Triplet State of Δ-Tris(2,2'-bipyridine)ruthenium(II) with Optically Active Viologens in an Aqueous Solution[1]

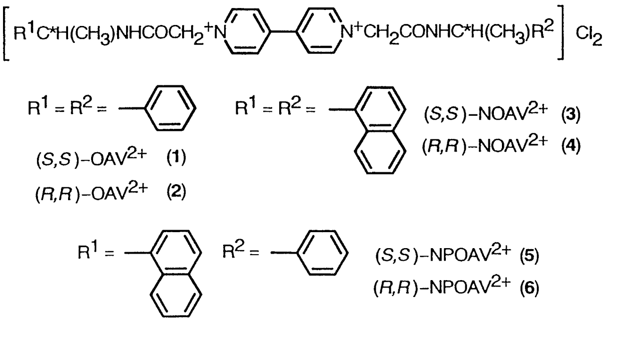
Keiichi Tsukahara,* Junko Kaneko, Tomoko Miyaji, Tomoko Hara, Masako Kato, and Masaru Kimura
Department of Chemistry, Faculty of Science, Nara Women's University, Nara 630

(Received January 30, 1997; CL-970078)

Stereoselectivity was found in the intracomplex quenching process between the excited triplet state of Δ-tris(2,2'-bipyridine)ruthenium(II) and optically active viologen containing naphthyl group(s), where the bipyridine ligand interacts with the naphthyl group of viologen.

Stereoselectivity in the electron-transfer (ET) reaction has been received considerable attention because of both theoretical basis and applications, for example, the regulation of the electron flow in biological systems in which the electron donor and acceptor are fixed in their orientation.[2] The best studied metal complex in the stereoselective photoinduced ET reactions is a tris(2,2'-bipyridine)ruthenium(II) ($[Ru(bpy)_3]^{2+}$) ion.[3,4] Homochiral preference in the photoinduced ET quenching of the excited triplet state of $[Ru(bpy)_3]^{2+}$ ($^3([Ru(bpy)_3]^{2+})^*$) by cobalt(III) complexes has been demonstrated.[2,3] Rau and Ratz have first reported the stereoselectivity in the luminescence quenching of $^3([Ru(bpy)_3]^{2+})^*$ by optically active viologen, 1-methyl-1'-[(3*S*)-(−)-3-pinanylmethyl]-4,4'-bipyridinium ion (*S*-PMV^{2+}).[5] The Λ-isomer is preferentially quenched by *S*-PMV^{2+}.

In this work we present the stereoselectivity in the intracomplex ET quenching process between $^3([Ru(bpy)_3]^{2+})^*$ and optically active viologens containing naphthyl and/or phenyl groups (**1**—**6**). Interestingly we found that $^3(\Delta\text{-}[Ru(bpy)_3]^{2+})^*$ was preferentially quenched by (*S*,*S*)-isomers in contrast to Rau's results.[5]



A Δ-$[Ru(bpy)_3]Cl_2\cdot 6H_2O$ complex was prepared by the previously reported method.[4] Viologens containing naphthyl and/or phenyl groups (**1** —**6**) were prepared by the same method reported previously.[6,7] Chloride salts were used for kinetic measurements. The luminescence decay was followed by a NAES-500 ns-fluorometer with an excitation at >420 nm (Toshiba Y44 cut-off filter) for an Ar-saturated aqueous solution.

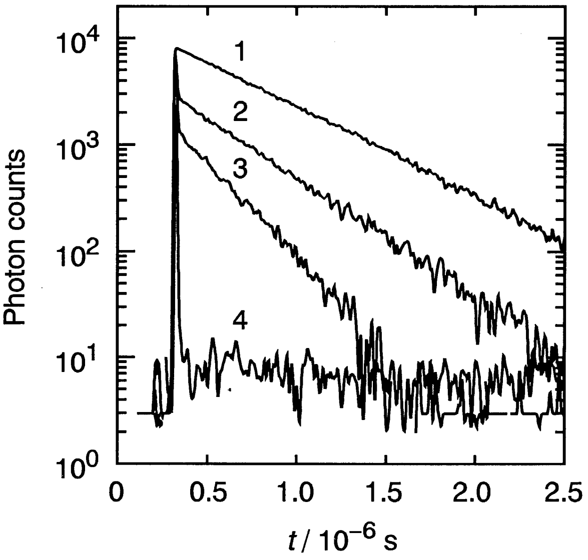
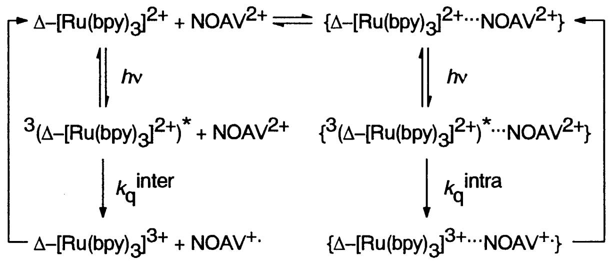


Figure 1. Luminescence decay-profile for the $^3(\Delta\text{-}[Ru(bpy)_3]^{2+})^*/$ (*S*,*S*)-$NOAV^{2+}$ system at 25 °C and I = 0.01 mol dm^{-3}. (1) 1.0 × 10^{-5} mol dm^{-3} Δ-$[Ru(bpy)_3]^{2+}$, (2) in the presence of 1.00 × 10^{-3} mol dm^{-3} (*S*,*S*)-$NOAV^{2+}$, (3) in the presence of 2.00×10^{-3} mol dm^{-3} (*S*,*S*)-$NOAV^{2+}$, and (4) lamp.

Figure 1 shows the luminescence decay-profile for the $^3(\Delta\text{-}[Ru(bpy)_3]^{2+})^*/$ (*S*,*S*)-$NOAV^{2+}$ system. Although the spontaneous decay of $^3(\Delta\text{-}[Ru(bpy)_3]^{2+})^*$ was fitted with a single exponential function, the decay in the presence of $NOAV^{2+}$ or $NPOAV^{2+}$ has two exponential components. The fast component within 20 ns after excitation is a major decay process and dependent on the concentration of viologen (Figure 1). The amplitudes of the fast component were 0.34, 0.48, 0.67, 0.75, and 0.81 for $[NOAV^{2+}]_0$ = 2.5 × 10^{-4} mol dm^{-3}, 5.0 × 10^{-4} mol dm^{-3}, 1.0 × 10^{-3} mol dm^{-3}, 1.5 × 10^{-3} mol dm^{-3}, and 2.0 × 10^{-3} mol dm^{-3}, respectively. The quenching rate was independent of the concentrations of viologen above 5.0 × 10^{-4} mol dm^{-3} at 25 °C and an ionic strength (I) of 0.01 mol dm^{-3}: k_q^{intra} = (2.4 ± 0.2) × 10^9 s^{-1}, (1.8 ± 0.2) × 10^9 s^{-1}, (1.7 ± 0.1) × 10^9 s^{-1}, and (1.5 ± 0.1) × 10^9 s^{-1} for (*S*,*S*)-$NOAV^{2+}$, (*R*,*R*)-$NOAV^{2+}$, (*S*,*S*)-$NPOAV^{2+}$, and (*R*,*R*)-$NPOAV^{2+}$, respectively. Moreover, we have the evidence of red shift in the luminescence spectral maximum by 4 nm on adding 3.0 × 10^{-3} mol dm^{-3} $NOAV^{2+}$ with a decrease in its intensity. On the contrary, no appreciable fast decay component was observed for the OAV^{2+} systems. These results strongly suggest that the complex of $^3(\Delta\text{-}[Ru(bpy)_3]^{2+})^*$ with $NOAV^{2+}$ or $NPOAV^{2+}$ forms through an interaction between the bipyridine ligand and the naphthyl group, followed by an *intra*complex quenching of $^3(\Delta\text{-}[Ru\text{-}(bpy)_3]^{2+})^*$ by the bound viologen. The quenching mechanism can be represented as follows:[8]



The values of k_q^{intra} for (*S,S*)-isomers of NOAV^{2+} and NPOAV^{2+} are larger than those for the (*R,R*)-isomers (the ratios are 1.13—1.33). The electronic structure of $^3([Ru(bpy)_3]^{2+})^*$ is $[Ru^{III}(bpy^{-\cdot})(bpy)_2]^{2+}$. Therefore, the stereoselectivity may arise from the charge-transfer interaction between a bipyridine ligand (probably $bpy^{-\cdot}$) in $^3([Ru(bpy)_3]^{2+})^*$ and the naphthyl and/or phenyl group in viologen. In the case of the quenching of $^3([Ru(bpy)_3]^{2+})^*$ by metal complexes, homochiral preference in the stereoselectivity arises from the interaction along C_3 axis.[3] The charge-transfer interaction in our optically active viologens might not be achieved along C_3 axis. In the case of PMV^{2+} in Rau's work,[5] the opposite stereoselectivity may arise from the absence of the aromatic substituents, and thus, the interaction along C_3 axis of the Ru(II) complex might be assumed in the case of PMV^{2+}.

For the slow decay component, plots of the first-order quenching rate constant vs. the concentrations of viologen became linear and the lifetimes are comparable with those for the quenching by OAV^{2+} and methylviologen. Therefore, the slow decay component must be due to the quenching of free $^3(\Delta\text{-}[Ru(bpy)_3]^{2+})^*$ by viologen through diffusive encounters. The stereoselectivity was also observed in these *inter*molecular quenching reactions: $k_q^{inter} = (6.5 \pm 0.5) \times 10^9$ dm^3 mol^{-1} s^{-1}, $(5.1 \pm 0.4) \times 10^9$ dm^3 mol^{-1} s^{-1}, $(9.0 \pm 0.5) \times 10^9$ dm^3 mol^{-1} s^{-1}, $(8.0 \pm 0.5) \times 10^9$ dm^3 mol^{-1} s^{-1}, $(1.20 \pm 0.05) \times 10^9$ dm^3 mol^{-1} s^{-1}, and $(1.10 \pm 0.05) \times 10^9$ dm^3 mol^{-1} s^{-1} for (*S,S*)-OAV^{2+}, (*R,R*)-OAV^{2+}, (*S,S*)-NOAV^{2+}, (*R,R*)-NOAV^{2+}, (*S,S*)-NPOAV^{2+}, and (*R,R*)-NPOAV^{2+}, respectively. The same stereoselectivity in the *inter*molecular quenching as that in the *intra*molecular quenching process may arise from that the chiral substituent of viologen interacts with the bpy ligand of the Ru(II) complex.

In conclusion we found the stereoselective *intra*complex ET quenching of $^3(\Delta\text{-}[Ru(bpy)_3]^{2+})^*$ with chiral viologen whose naphthyl group interacts with the bipyridine ligand of the ruthenium(II) complex.

This research was partly supported by Grants-in-Aid for Scientific Research Nos. 06640724, 07304076, and 08454209 from the Ministry of Education, Science, Sports and Culture. We thank Dr. S. Tachiyashiki, Kagawa Nutrition University, for discussions on the association between $[Ru(bpy)_3]^{2+}$ and viologens.

References and Notes

1 Dedicated to Professor Ralph G. Wilkins on the occasion of his 70th birthday.
2 K. Bernauer, "Electron-Transfer Reactions in Metalloproteins," Metal Ions in Biological Systems 27, ed by H. Sigel and A. Sigel, Marcel Dekker, New York (1991), p. 265.
3 G. B. Porter and R. H. Sparks, *J. Chem. Soc., Chem. Commun.*, **1979**, 1094; G. B. Porter and R. H. Sparks, *J. Photochem.*, **13**, 123 (1980); Y. Kaizu, T. Mori, and H. Kobayashi, *J. Phys. Chem.*, **89**, 332 (1985); D. H. Metcalf, S. W. Snyder, J. N. Demas, and F. S. Richardson, *J. Am. Chem. Soc.*, **112**, 5681 (1990).
4 M. Kato, T. Sasagawa, Y. Ishihara, S. Yamada, S. Fujitani, and M. Kimura, *J. Chem. Soc., Dalton Trans.*, **1994**, 583.
5 H. Rau and R. Ratz, *Angew. Chem., Int. Ed. Engl.*, **22**, 550 (1983).
6 K. Tsukahara, C. Kimura, J. Kaneko, and T. Hara, *Chem. Lett.*, **1994**, 2377.
7 K. Tsukahara, J. Kaneko, T. Miyaji, and K. Abe, *Tetrahedron Lett.*, **37**, 3149 (1996).
8 We could not determine the ground-state complexation constant between $[Ru(bpy)_3]^{2+}$ and NOAV^{2+}, because of a small absorption spectral change in aqueous solutions. Relatively small formation constants have been reported for the ion pairs between tris(1,10-phenanthroline)iron(II) and naphthalene-1-sulfonate or naphthalene-2-sulfonate ions (K = 5—8 dm^3 mol^{-1}).[9]
9 S. Tachiyashiki and H. Yamatera, *Inorg. Chem.*, **25**, 3209 (1986).