6176 *Inorg. Chem.* **1998,** *37,* 6176−6180

Two-Electron Reduction of [{(bpy)$_2$Ru(dmbbbpy)}$_3$Ru]$^{8+}$ from (BNA)$_2$ via Photoinduced Electron Transfer [dmbbbpy = 2,2′-Bis(*N*-methylbenzimidazole-2-yl)-4,4′-bipyridine]

Md. Meser Ali,[†] Hiroyasu Sato,[‡] Masa-aki Haga,[†] Koji Tanaka,*,[†] Akio Yoshimura,[§] and Takeshi Ohno[§]

Coordination Chemistry Laboratories, Institute for Molecular Science, Myodaiji,
Okazaki 444-8585, Japan, Department of Chemistry for Materials, Faculty of Engineering,
Mie University, 1515 Kamihama Cho, Tsu 514, Japan, and Graduate School of Science,
Osaka University, Machikaneyama, Toyonaka, Osaka, 560, Japan

Received May 27, 1998

Photoirradiation (λ > 500 nm) of [{(bpy)$_2$Ru(dmbbbpy)}$_3$Ru]$^{8+}$ (**1**$^{8+}$) (dmbbbpy = 2,2′-bis(*N*-methylbenzimidazole-2-yl)-4,4′-bipyridine and bpy = 2,2′-bipyridine) in the presence of dimeric *N*-benzyldihydronicotinamide, (BNA)$_2$, produced stable two-electron reduced species (**1**$^{6+}$). Laser flash photolysis and emission spectroscopy were used to understand the reductive reaction pathways. The emission quenching k_q value (4.1×10^9 M^{-1} s^{-1}) obtained from Stern−Volmer plot is in excellent agreement with the electron-transfer rate constant, k_{et} (4.7×10^9 M^{-1} s^{-1}) determined from the decay kinetics of transient ^{3}**1**$^{8+}$ triplet−triplet absorption at 650 nm indicating that photoreduction of **1**$^{8+}$ proceeds via photoinduced electron transfer from (BNA)$_2$ to ^{3}**1**$^{8+*}$. After bimolecular electron-transfer process, **1**$^{8+}$ was reduced to **1**$^{7+}$ and the electron donor (BNA)$_2$ was oxidized. Oxidation of (BNA)$_2$ leads to the formation of highly reactive species, BNA$^•$ which then reduces **1**$^{7+}$ to **1**$^{6+}$. The quantum yield for the formation of the photoreduction product was 0.026.

Introduction

Redox reactions of excited states of transition-metal complexes have widely been investigated over the past decades.[1−18] The most widely investigated metal complex is [Ru(bpy)$_3$]$^{2+}$. Reductive and oxidative quenching of $*^3$[Ru(bpy)$_3$]$^{2+}$ in the presence of an electron donor (D) and acceptor (A) generate [Ru(bpy)$_3$]$^+$ and [Ru(bpy)$_3$]$^{3+}$, respectively, which work as strong reduction and oxidation reagents.[4] In most of the cases, however, accumulation of photochemically generated [Ru(bpy)$_3$]$^+$ or [Ru(bpy)$_3$]$^{3+}$ is prevented by the back electron-transfer reaction which regenerates the ground states of the systems (eqs 3 and 5).[2,4,5,8,9,11]

$$[\mathrm{Ru(bpy)_3}]^{2+} \xrightarrow{h\nu} [\mathrm{Ru(bpy)_3}]^{2+}* \qquad (1)$$

$$[\mathrm{Ru(bpy)_3}]^{2+}* + \mathrm{D} \rightarrow [\mathrm{Ru(bpy)_3}]^{+} + \mathrm{D}^{+} \qquad (2)$$

$$[\mathrm{Ru(bpy)_3}]^{+} + \mathrm{D}^{+} \rightarrow [\mathrm{Ru(bpy)_3}]^{2+} + \mathrm{D} \qquad (3)$$

$$[\mathrm{Ru(bpy)_3}]^{2+}* + \mathrm{A} \rightarrow [\mathrm{Ru(bpy)_3}]^{3+} + \mathrm{A}^{-} \qquad (4)$$

$$[\mathrm{Ru(bpy)_3}]^{3+} + \mathrm{A}^{-} \rightarrow [\mathrm{Ru(bpy)_3}]^{2+} + \mathrm{A} \qquad (5)$$

To utilize [Ru(bpy)$_3$]$^+$ as a strong one-electron donor, several attempts have been taken to circumvent the back electron-transfer process. As for example, introduction of functional groups to bpy and modification of quencher reductants have been tried in order to build up [Ru(bpy)$_3$]$^+$ in solutions.[1,2,7,10] Photoinduced electron transfer is generally a one-electron transfer process. On the contrary, all the chemical reactions including artificial solar energy conversion schemes are multiple electron-transfer processes.[19] Thus, it is highly desired to construct a catalytic system which is able to store multiple electrons during visible light irradiation for multielectron redox processes. Multimetallic complexes which show multielectron redox reactions are therefore, promising candidates for the generation of stable two-electron reduction product in the presence of a quencher reductant under visible light irradiation. Only one example up to date is a mixed-metal trinuclear complex, [{(bpy)$_2$Ru(dpb)}$_2$IrCl$_2$]$^{5+}$ [20] (dpb = 2,3-bis{2-pyridyl}-benzoquinoxaline), which has ability to store two electrons in the presence of quencher reductant during visible light irradiation. However, the quantum yield for the two-electron transfer process was low (0.0015). Accordingly, an attempt has been made for the generation of stable two-electron reduction product

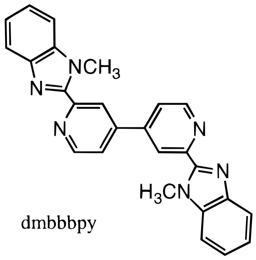
---

[†] Institute for Molecular Science.
[‡] Mie University.
[§] Osaka University.

(1) Mallouk, T. E.; Krueger, J. S.; Mayer, J. E.; Dymond, C. M. G. *Inorg. Chem.* **1989**, *28*, 3509.
(2) Sun, H.; Hoffman, M. Z. *J. Phys. Chem.* **1994**, *98*, 11721.
(3) Deronzier. A.; Meyer, T. J. *Inorg. Chem.* **1980**, *10*, 2916.
(4) Sutin, N. *J. Photochem.* **1979**, *10*, 19.
(5) Sutin, N.; Creutz, C. *Inorg. Chem.* **1976**, *15*, 498.
(6) Sutin, N.; Creutz, C. *J. Am. Chem. Soc.* **1976**, *98*, 6385.
(7) Nishida, S.; Harima, Y.; Yamashita, K. *Inorg. Chem.* **1989**, *28*, 4073.
(8) DeLaive, P. J.; Lee, J. T.; Sprintschnik, H. W.; Abruna, H.; Meyer, T. J.; Whitten, D. G. *J. Am. Chem. Soc.* **1977**, *99*, 7096.
(9) Lin, C.-T.; Bottcher, W.; Chou, M.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1976**, *98*, 6540.
(10) Delaive, P. J.; Foreman, T. K.; Giannotti, C.; Whitten, D. G. *J. Am. Chem. Soc.* **1980**, *102*, 5627.
(11) Garrera, H. A.; Cosa, J. J.; Previtali, C. *J. Photochem. Photobiol.* **1989**, *47*, 145.
(12) Nagale, J. K.; Bernstein, J. S.; Young, R. C.; Meyer, T. J. *Inorg. Chem.* **1981**, *20*, 1762.
(13) Kitamura, N.; Okano, S.; Tazuke, S. *Chem. Phys. Lett.* **1982**, *90*, 13.
(14) Baggott, J. E. *J. Phys. Chem.* **1983**, *87*, 5223.
(15) Westmoreland, T. D.; Schanze, K. S.; Neveux, P. E.; Danielson, E., Jr.; Sullivan, B. P.; Chen, P.; Meyer, T. J. *Inorg. Chem.* **1985**, *24*, 2596.
(16) Garrera, H. A.; Gsponer, H. E.; Garcia, N. A.; Cosa, J. J.; Previtali, C. M. *J. Photochem.* **1986**, *33*, 257.
(17) Kim, H.; Kitamura, N.; Kawanishi, Y.; Tazuke, S. *J. Phys. Chem.* **1989**, *93*, 5757.
(18) Kitamura, N.; Kim, H.; Okano, S.; Tazuke, S. *J. Phys. Chem.* **1989**, *93*, 5750.
(19) Balzani, V.; Juris, A.; Venturi, M.; Campagna, S.; Serroni, S. *Chem. Rev.* **1996**, *96*, 774.

10.1021/ic980586e CCC: $15.00

with relatively good quantum yield by the absorption of not only two photons but also one photon. Along this line, we examined photochemical behavior of a new tetranuclear ruthenium complex, $[\{(bpy)_2Ru(dmbbbpy)\}_3Ru]^{8+}$ (dmbbbpy = 2,2′-bis(*N*-methylbenzimidazol-2-yl)-4,4′-bipyridine) where reversible redox reactions take place in the bridging dmbbbpy ligands.



dmbbbpy

As a mild reductant, we have chosen dimeric *N*-benzyldihydronicotinamide, $(BNA)_2$ which is widely used as a two-electron donor.[23] In addition, the structure of $(BNA)_2$ is very close to the NAD dimer which is formed in biological one-electron reduction of NAD^+.[21,22] The tetranuclear complex, $[\{(bpy)_2Ru(dmbbbpy)\}_3Ru]^{8+}$ in the ground state cannot be reduced by $(BNA)_2$.

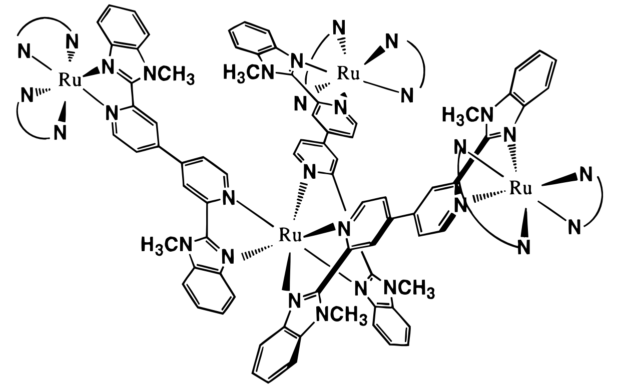
This paper describes the two-electron reduction of $[\{(bpy)_2Ru(dmbbbpy)\}_3Ru]^{8+}$ via photoinduced electron transfer from $(BNA)_2$ to triplet excited state of $[\{(bpy)_2Ru(dmbbbpy)\}_3Ru]^{8+}$. The precursor monomeric $[(bpy)_2Ru(dmbbbpy)]^{2+}$ and dimeric $[(bpy)_4Ru_2(dmbbbpy)]^{4+}$ ruthenium complexes of this family have been proven to function as electrocatalysts for the reduction of carbon dioxide to oxalate and formate.[24]

Experimental Section

Material. The ruthenium tetranuclear complex, $[\{(bpy)_2Ru(dmbbbpy)\}_3Ru](PF_6)_8$, was prepared and characterized as previously described elsewhere.[25] Acetonitrile was distilled twice over CaH_2. *N,N*-Dimethylformamide (Wako) was α pure grade and used without further purification. Tetra-*n*-butylammonium tetrafluoroborate (TBAB, Nacalai) was recrystalized from ethanol−petroleum ether and dried *in vacuo*. Dimeric *N*-benzyldihydronicotinamide, $(BNA)_2$ was synthesized according to the literature method.[26] All other supplied chemicals were of standard reagent grade quality.

Physical Measurements. Electronic absorption spectra were measured on a Shimadzu UV-3100 PC spectrophotometer from 200 to 850 nm. Electrochemical measurements were made at 20 °C with a BAS 100 B/W electrochemical workstation. The working and the auxiliary electrodes were a glassy carbon disk and a platinum wire, respectively. The reference electrode was $Ag/AgNO_3$ (0.01 M in 0.1 M TBAB CH_3CN), abbreviated as Ag/Ag^+. The $E_{1/2}$ values vs Ag/Ag^+ were found to be 0.34 V more negative than that vs SCE. Spectroelectrochemistry was performed by using a platinum minigrid (80 mesh) working electrode in a thin-layer cell (optical path length 0.5 mm). The cell was placed into the spectrophotometer, and the absorption change was monitored during the electrolysis. Transient absorption spectra of the solution were measured after exposure to the second harmonic pulse of a Q-switched Nd^{3+}:YAG laser by a procedure described elsewhere.[27]

Chart 1. Schematic View of $[\{Ru(bpy)_2(dmbbbpy)\}_3Ru]^{8+}$ ($\mathbf{1}^{8+}$)



Emission Quenching. A model MPF-2A Hitachi spectrofluorimeter was used to measure emission spectra at room temperature. Emission lifetime was measured by means of the single-photon-counting method on a Horiba NASE-550 nanosecond fluorimeter system. The sample was excited by 500 nm pulse from a hydrogen gas lamp through a Nikon G50 monochromator. The solution of $\mathbf{1}^{8+}$ (1×10^{-6} M) was degassed by bubbling with dry nitrogen for 15−20 min prior to the measurements. The emission maximum of $\mathbf{1}^{8+}$ is 760 nm in DMF at room temperature. No change was observed in the shape of the spectrum, and only intensity of the emission was decreased by the addition of a quencher. The Stern−Volmer plot (eq 6)

$$I_0/I = 1 + k_q[q] \qquad (6)$$

was obtained between the ratio of the emission intensities in the absence and the presence of a quencher (I_0/I) and the quencher concentration [q]. The observed rate constant k_{obsd} ($= k_q\tau^{-1}$) was determined from the Stern−Volmer constant k_q and the emission lifetime τ of $\mathbf{1}^{8+}$. The emission lifetime of $\mathbf{1}^{8+}$ is 30 ns in DMF at room temperature.

Photoirradiation. The solution was photoirradiated from 100 HG Xenon arc lamp through a Toshiba Y-50 glass filter transmitting light ($\lambda > 500$ nm). The light was focused on a 1-cm cylindrical cell which contained the photolysis solution. The solution was thermostated at 20 °C and was degassed by bubbling with nitrogen for 30 min prior to photoirradiation. The progress of the photochemical reaction was monitored by absorption spectral changes. No spectral change was observed in the dark. Photoirradiation of the ruthenium tetranuclear complex in the absence of dimeric *N*-benzyldihydronicotinamide, $(BNA)_2$, did not cause any spectral changes. An observable spectral change was observed only when the complex was photoirradiated in the presence of $(BNA)_2$.

Quantum Yield. The commercially available ammonium salt of Reineck's salt was converted to potassium salt according to literature method.[28] The difference absorbance (ΔA) values at 600 nm were utilized to calculate the product of moles produced with the time course of photoirradiation. The ΔA value is related to the known ϵ values of $\mathbf{1}^{8+}$ and $\mathbf{1}^{6+}$ species. Thus, the quantum yield for the formation of photoproduct was determined by monitoring the absorption changes at 600 nm.

Results and Discussion

The tetranuclear ruthenium complex, $[\{(bpy)_2Ru(dmbbbpy)\}_3Ru](PF_6)_8$ ($\mathbf{1}^{8+}$), was synthesized by the reaction of $RuCl_3{\cdot}3H_2O$ with monomeric complex, $[(bpy)_2Ru(dmbbbpy)]^{2+}$ using the "complex-as-ligand" strategy.

The schematic view of $\mathbf{1}^{8+}$ is shown in Chart 1. The details of synthesis and characterization were described elsewhere.[25] In Chart 1, three $[Ru(bpy)_2]^{2+}$ units are linked to the central Ru metal through three bridging dmbbbpy ligands. Thus, the dendrimeric tetranuclear complex, $\mathbf{1}^{8+}$ contains a large number

---

(20) Molnar, S. M.; Nallas, G.; Bridgewater, J. S.; Brewer, K. J. *J. Am. Chem. Soc.* **1994**, *116*, 5208−5209.

(21) Ragg, E.; Scaglioni, L.; Mondeli, R.; Carela, V.; Carellia, I.; Casini, A.; Finazzi-Agro, A.; Liberatore, F.; Tortorella, S. *Biochim. Biophys. Acta* **1991**, *37*, 1076.

(22) Avigliano, L.; Carelli, V.; Casini, A.; Finazzi-Agro, A.; Liberatore, F. *J. Biochem.* **1985**, *391*, 226.

(23) Patz,M.; Kuwahara, Y.; Suenobu, T.; Fukuzumi, S. *Chem. Lett.* **1997**, 567−568.

(24) Ali, M. M.; Sato, H.; Mizukawa, T.; Tsuge, Y.; Haga. M.; Tanaka, K. *J. Chem. Soc., Chem. Commun.* **1998**, 249−250.

(25) Arakawa, R.; Matsuo, T.; Nozaki, K.; Ohno, T.; Haga, M. *Inorg. Chem.* **1995**, *34*, 2464−2467.

(26) Wallenfels, K.; Gellerich, M. *Chem. Ber.* **1959**, *92*, 1406.

(27) Ohno, T.; Yoshimura, A.; Mataga, N. *J. Phys. Chem.* **1990**, *94*, 4871−4876.

(28) Ernst, E. W.; Arthur W. A. *J. Am. Chem. Soc.* **1966**, *88*, 397−403.

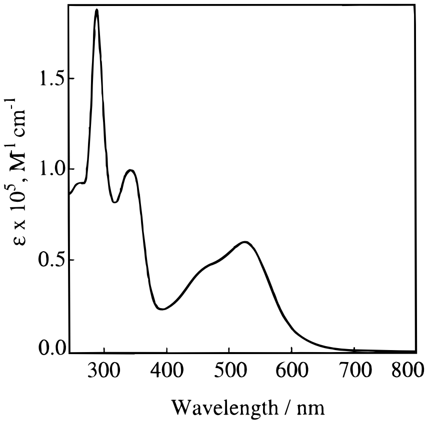


Figure 1. Absorption spectrum of $\mathbf{1}^{8+}$ (9.28×10^{-6} M) in DMF.

of redoxactive moieties, i.e., 4Ru, 3dmbbbpy, and 6bpy. As a result, $\mathbf{1}^{8+}$ undergoes multielectron redox reactions in a wide potential range: the cyclic voltammogram of $\mathbf{1}^{8+}$ showed four closely spaced reversible one-electron oxidation ($E°_1 = 0.392$ V, $E°_2 = 0.519$ V, $E°_3 = 0.548$ V, and $E°_4 = 0.588$ V {vs SCE}) processes in CH_3CN which were described in detail in our recent report.[29] In the reduction processes, the first reduction wave was observed at −0.90 V and an electrode absorption occurred after that in CH_3CN. On the other hand, a reversible redox wave appeared at −0.89 V in DMF. The number of electrons involved in the reduction wave at −0.89 V was confirmed to be 2 by controlled potential coulometry at −1.20 V (vs SCE) in DMF. In addition to the reduction wave at −0.89 V, four reversible redox waves were also observed at −1.32, −1.56, −1.74, and −1.91 V (vs SCE), respectively, in DMF solvent window. The cyclic voltammogram of the monomeric $[(bpy)_2Ru(dmbbbpy)]^{2+}$ [24] unit exhibited three reversible one-electron redox couples at $E_{1/2} = -1.10, -1.40$, and -1.64 V (vs SCE) in CH_3CN resulting from dmbbbpy and two bpy-based reductions, respectively. The dimeric $[(bpy)_2Ru(dmbbbpy)Ru(bpy)_2]^{4+}$ also showed three reversible reduction waves with a small positive shift (0.2 V) of the dmbbbpy-based reduction wave. Based on the reduction pattern of the monomeric, $[(bpy)_2Ru(dmbbbpy)]^{2+}$ and dimeric, $[(bpy)_2Ru(dmbbbpy)Ru(bpy)_2]^{4+}$ [24] complexes, the reduction wave at −0.89 V can be assigned as the two equivalent bridging ligand-based reductions. The assignment of the remaining redox waves at −1.32, −1.56, −1.74, and −1.91 V (vs SCE) is not straightforward due to considerable overlap of the reductive waves in the region.

The electronic absorption spectrum of $\mathbf{1}^{8+}$ in DMF is shown in Figure 1. The absorption band at 526 (63900) nm is assigned to Ru $d\pi-\pi^*$(dmbbbpy) metal-to-ligand charge-transfer (MLCT) transition. The bands at 346 (108 000) and 291 (206 100) nm are associated with $\pi-\pi^*$ transitions of dmbbbpy and bpy ligands respectively, from the analogy of the electronic absorption spectra of $[Ru(bpy)_2(bbbpyH_2)]^{2+}/[Ru_2(bpy)_4(bbbpyH_2)]^{4+}$.[30]

Figure 2 shows the electronic absorption spectrum of $\mathbf{1}^{6+}$ prepared by the controlled potential electrolysis of $\mathbf{1}^{8+}$ at −1.20 V (vs SCE) in the presence of 0.1 M Bu_4NBF_4 in DMF. The MLCT transition at 526 nm decreases in intensity and an absorption increasement is observed around the 580−800 nm region. The color of the solution changed from red to greenish blue after two-electron reduction. The two-electron reduced species $\mathbf{1}^{6+}$ is stable under N_2. Despite the occurrence of two-electron reduction of $\mathbf{1}^{8+}$, an absorption band assignable to the one-electron reduced form ($\mathbf{1}^{7+}$) was not detected during the electrolysis. Moreover, the electronic absorption spectrum of the equimolar mixture of the DMF solutions of $\mathbf{1}^{6+}$ and $\mathbf{1}^{8+}$ became the average of those of each species despite three species $\mathbf{1}^{8+}$, $\mathbf{1}^{6+}$, and $\mathbf{1}^{7+}$ exist as the equilibrium mixtures (eq 7) in the solution.

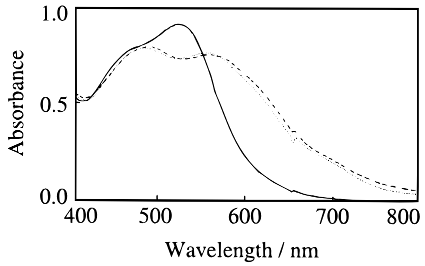
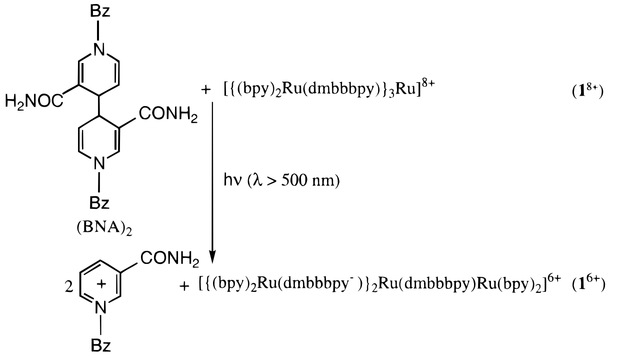


Figure 2. Absorption spectra of $\mathbf{1}^{8+}$ (—) (1.49×10^{-5} M) with 0.1 M Bu_4NBF_4 in DMF, (---) electrochemically generated two-electron reduced species, (···) after photoirradiation ($\lambda > 500$ nm) of $\mathbf{1}^{8+}$ (1.49×10^{-5} M) for 20 min in the presence of $(BNA)_2$ (10×10^{-3} M).

Scheme 1. Photoirradiation ($\lambda > 500$ nm) of $\mathbf{1}^{8+}$ in the Presence of $(BNA)_2$ Produced Two-Electron Reduced Species, $\mathbf{1}^{6+}$



$$\mathbf{1}^{8+} + \mathbf{1}^{6+} \overset{k}{\rightleftarrows} 2(\mathbf{1}^{7+}) \qquad (7)$$

Similar behavior has been reported for the electronic spectra of a mixture of doubly and singly reduced forms of $[\{(bpy)_2Ru(dpb)\}_2IrCl_2]^{5+}$ by Brewer et al.[31] The spectrum of $\mathbf{1}^{7+}$ was, therefore, intermediate between those obtained for $\mathbf{1}^{6+}$ and $\mathbf{1}^{8+}$.

A deaerated solution of $\mathbf{1}^{8+}$ (1.49×10^{-5} M) is photoirradiated at $\lambda > 500$ nm in the presence of $(BNA)_2$ (0.01 M) for 20 min. A sharp color change from red to greenish blue was also observed during photoirradiation. The spectrum generated by photoirradiation is essentially same as that of electrochemically generated two-electron reduced species, $\mathbf{1}^{6+}$, as depicted in Figure 2. In addition, BNA^+ was detected by HPLC. Thus, photoirradiation of $\mathbf{1}^{8+}$ in DMF in the presence of $(BNA)_2$ produced stable two-electron reduced species, $\mathbf{1}^{6+}$ (Scheme 1).

The photochemically generated two-electron reduced species, $\mathbf{1}^{6+}$, was smoothly reoxidized to $\mathbf{1}^{8+}$ under the potential electrolysis at −0.50 V.

Molnar et al.[20] reported that photoirradiation of $[\{(bpy)Ru(dpb)\}_2IrCl_2]^{5+}$ in the presence of dimethylaniline or triphenylamine resulted in the formation of two-electron reduced species, $[\{(bpy)Ru(dpb)\}_2IrCl_2]^{3+}$ with a low quantum yield (0.0015). Any significant spectral changes, however, were not detected

---

(29) Haga, M.; Ali, M. M.; Sato, H.; Monjushiro, H.; Nozaki, K.; Kano, K. *Inorg. Chem.* **1998**, *37*, 2320−2324.

(30) Haga, M.; Ali, M. M.; Koseki, S.; Fujimoto, K.; Yoshimura, A.; Nozaki, K.; Ohno, T.; Nakajima, K.; Stufkens, D. J. *Inorg. Chem.* **1996**, *35*, 3336−3345.

(31) Bridgewater, J. S.; Vogler, L. M.; Molnar, S. M.; Brewer, K. J. *Inorg. Chem. Acta* **1993**, *208*, 179.

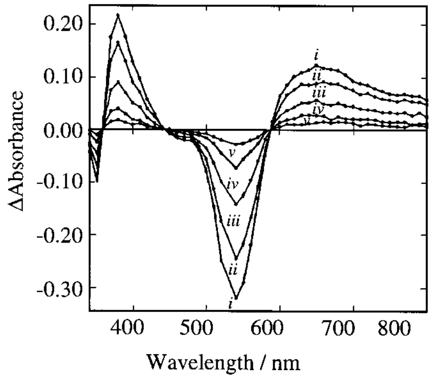


Figure 3. Transient difference absorption (TA) spectra of $\mathbf{1}^{8+}$ (1.70 × 10^{-5} M) in DMF recorded on a nanosecond time scale, 6 (i), 20 (ii), 40 (iii), 80 (iv), and 160 ns (v) after laser excitation.

during photoirradiation of $\mathbf{1}^{8+}$ in the presence of dimethylaniline or triphenylamine. Even using *N,N,N′,N″*-tetramethyl-1,4-benzenediamine as an electron donor whose oxidation potential[32] ($E° = 0.12$ V) is lower than that of $(BNA)_2$[23] ($E° = 0.26$ V) did not cause any spectral changes during visible light irradiation, indicating that the occurrence of the back electron-transfer reaction after formation of initial $\mathbf{1}^{7+}$ by quenching of $^3\mathbf{1}^{8+}$. The pathways for photochemical two-electron reduction of $\mathbf{1}^{8+}$, therefore, are apparently different from that of $[\{(bpy)Ru(dpb)\}_2IrCl_2]^{3+}$.[20] The fact that the stable two-electron reduced form is generated by photoirradiation of $\mathbf{1}^{8+}$ in the presence of $(BNA)_2$ is explained by depression of the back electron transfer from $\mathbf{1}^{7+}$ to $\{(BNA)_2\}^{\bullet+}$. The quantum yield for the formation of the photoproduct was 0.026 which is 17 times higher than that of the previously reported photochemical two-electron transfer process.[20]

Emission Quenching. When the absorption band of $\mathbf{1}^{8+}$ in DMF containing $(BNA)_2$ was excited at 525 nm where $(BNA)_2$ has no absorption band, the emission of $^3\mathbf{1}^{8+*}$ is quenched by the electron transfer from $(BNA)_2$ to $^3\mathbf{1}^{8+*}$ (eq 8). The observed rate constant k_{obs} in a deaerated DMF solution was determined to be 4.7 × 10^9 M^{-1} s^{-1} from the Stern−Volmer plot.

$$(BNA)_2 + {}^3\mathbf{1}^{8+}{*} \xrightarrow{k_{obsd}} (BNA)_2^{\bullet+} + \mathbf{1}^{7+} \qquad (8)$$

Transient Absorption Spectra. The transient difference absorption (TA) spectrum at ambient temperature was measured immediately after laser excitation of $\mathbf{1}^{8+}$ in DMF. The TA spectrum of $\mathbf{1}^{8+}$ exhibits a strong bleaching of the $\pi-\pi^*$ transition of dmbbbpy at 350 nm and of the MLCT band at 540 nm and an absorption enhancement at 380 and 650 nm (Figure 3). By comparison with reported spectra of other relevant complexes[30,33] the bands around 380 and 650 nm are assigned to the $\pi-\pi^*$ transition of reduced dmbbbpy$^-$. It is, therefore, concluded that the lowest excited state of $[\{(bpy)_2Ru(dmbbbpy)\}_3Ru]^{8+}$ is Ru(II) to dmbbbpy CT in character. The transient difference absorption spectrum of $\mathbf{1}^{8+}$ solution was also measured in the presence of electron donor $(BNA)_2$. The decay rate of $^3\mathbf{1}^{8+}{*}$ became faster with an increase of the concentration of $(BNA)_2$. The bimolecular quenching rate constant (k_q) of $^3\mathbf{1}^{8+}{*}$ by $(BNA)_2$ was determined to be 4.1 × 10^9 M^{-1s-1} from the decay kinetics of transient $^3\mathbf{1}^{8+*}$ triplet−triplet absorption at 650 nm following excitation at 532 nm.

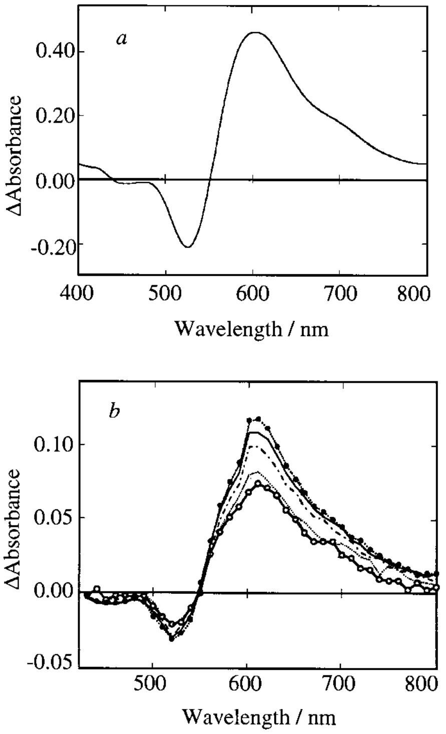


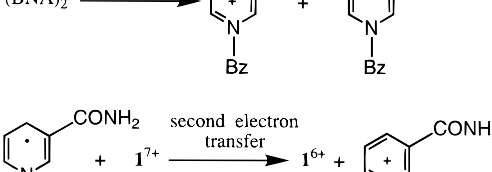
Figure 4. Difference absorption spectra of (a) electrochemically generated two-electron reduced species, $\mathbf{1}^{6+}$ (1.85 × 10^{-5} M) in DMF (0.1 M Bu_4NBF_4). (b) TA spectra of $\mathbf{1}^{8+}$ (1.70 × 10^{-5} M) in the presence of added $(BNA)_2$ (3.70 × 10^{-3} M) recorded on a microsecond time scale, 2 (−○−), 10 (···), 50 (−·−), 100 (−), and 400 μs (··●··) after laser excitation.

The k_q value is very close to k_{obs} (4.7 × 10^9 M^{-1} s^{-1}) indicating that the photoreduction of $\mathbf{1}^{8+}$ proceeds via the triplet excited state. One-electron reduction potential of $^3\mathbf{1}^{8+}{*}$ ($E° =$ 0.74 V) is higher than the one-electron oxidation of $(BNA)_2$ ($E° = 0.26$ V). The free energy change of the photoinduced electron transfer from $(BNA)_2$ to $^3\mathbf{1}^{8+}{*}$ is negative ($\Delta G°_{et} = -$0.48 eV). Accordingly, the electron-transfer rate constant (k_{et}) would approach the diffusion-limited value[34] which is consistent with both the k_{obs} and k_q values (vide supra). Thus, the photoreduction of $\mathbf{1}^{8+}$ by $(BNA)_2$ proceeds via photoinduced electron transfer from $(BNA)_2$ to $^3\mathbf{1}^{8+}{*}$ as represented in the eqs 9−12.

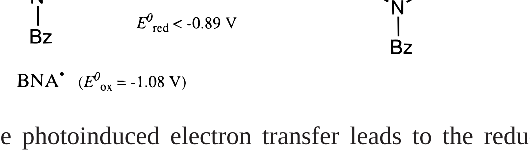
$$\mathbf{1}^{8+} \xrightarrow{h\nu} {}^3\mathbf{1}^{8+*} \qquad (9)$$

$$(BNA)_2 + {}^3\mathbf{1}^{8+*} \xrightarrow[k_{et}]{\text{electron transfer}} (BNA)_2^{\bullet+} + \mathbf{1}^{7+} \qquad (10)$$

$E^0_{ox} = 0.26$ V $E^0_{red} = 0.74$ V



(11)



(12)

BNA• ($E^0_{ox} = -1.08$ V)

The photoinduced electron transfer leads to the reduction of

---

(32) Bock, C. R.; Conor, J. A.; Gutierrez, A. R.; Meyer, T. J.; Whitten, D. G.; Sullivan, B. P.; Nagle, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 4816.
(33) Ohno, T.; Yoshimura, A.; Prasad, D. R.; Hoffman, M. Z. *J. Phys. Chem.* **1991**, *95*, 4723−4727.

1^{8+} and oxidation of (BNA)$_2$ (eqs 9 and 10). The resultant (BNA)$_2^{\bullet+}$ undergoes a fast C−C bond cleavage[23] and produces BNA$^+$ and BNA$^\bullet$ (eq 11). Since BNA$^\bullet$ is expected to be extremely reactive, the second electron transfer from BNA$^\bullet$ [35]($E° = -1.08$ V) to reductively quenched product, **1**$^{7+}$ ($E° < -0.89$ V), takes place easily. The possibility of three-electron reduction of **1**$^{8+}$ by BNA$^\bullet$ is reasonably excluded, since **1**$^{8+}$ can store only two-electron at potential more positive than the oxidation potential of BNA$^\bullet$ ($E° = -1.08$ V).

The transient difference absorption spectrum of the **1**$^{8+}$ solution in the presence of electron donor (BNA)$_2$ resulted in appearance of a new absorption band around 600 nm instead of the triple−triplet absorption band at 650 nm and the band slightly decrease in the time range of 50−400 ns. On the other hand, a slow rise of the absorbance was observed at 600 nm in the time range of 2−400 μs indicating the existence of the intermediate **1**$^{7+}$ (eq 10). There is a good agreement between the difference absorption spectrum of **1**$^{6+}$ obtained in the reductive electrochemical experiment (Figure 4a) and the difference absorption spectrum obtained by flash photolysis (Figure 4b). The yield of the formation of **1**$^{6+}$ for the latter was 13% on the basis of amount formed in the former.

Conclusion

The results indicate that photoirradiation of **1**$^{8+}$ in the presence of (BNA)$_2$ in dry DMF gives a stable reversible two-electron reduced species, **1**$^{6+}$. The triplet ^{3}**1**$^{8+*}$ is reductively quenched by electron transfer from (BNA)$_2$. The quenching process involves the reduction of **1**$^{8+}$ to **1**$^{7+}$and concomitant oxidation of (BNA)$_2$ to BNA$^+$ and BNA$^\bullet$. Then, the second electron transfer occurs easily from highly reactive species BNA$^\bullet$ to intermediate **1**$^{7+}$, leading to the formation of **1**$^{6+}$. The quantum yield for the formation of photoreduction product was 0.026. Our aim is the utilization of the stored two electrons in **1**$^{8+}$ for the reduction of organic substrate.

Acknowledgment. The authors thank Prof. Shunichi Fukuzumi (Osaka University) for his kind advice on the synthesis of (BNA)$_2$.

IC980586E

---

(34) Arbogast, W. J.; Foote, C. S.; Kao, M. *J. Am. Chem. Soc.* **1992**, *114*, 2278.

(35) Fukuzumi, S.; Koumitsu, S.; Hironaka, K.; Tanaka, T. *J. Am. Chem. Soc.* **1987**, *109*, 313.