Kinetic study of the photo-induced electron transfer reaction between ruthenium(II) complexes of 2,2′-bipyridine derivatives and methyl viologen. Effects of bulky substituents introduced onto 2,2′-bipyridine †

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Ruthenium(II) complexes of 2,2′-bipyridine derivatives, $[Ru(Rbpy)_3]^{2+}$ (Rbpy = 4,4′-di(alkylaminocarbonyl)-2,2′-bipyridine; alkyl = propyl, hexyl or adamantyl), have been newly synthesized and their photo-induced electron transfer (ET) reaction with methyl viologen (MV^{2+}) has been investigated. The rate constant of the ET reaction decreases in the order alkyl = propyl > hexyl > adamantyl, which is opposite to the increasing order of the size of the alkylaminocarbonyl substituent introduced onto 2,2′-bipyridine. After correction of the diffusion rate, the ET reaction in the exciplex, $[*Ru(Rbpy)_3^{2+} \cdots MV^{2+}] \longrightarrow [Ru(Rbpy)_3^{3+} \cdots MV^{\bullet+}]$, was analyzed on the basis of Marcus' theory. The electronic coupling matrix element (H_{rp}) decreases in the order propyl (2.28×10^{-3} eV) > hexyl (1.86×10^{-3} eV) > adamantyl (1.37×10^{-3} eV), while the reorganization energy (λ) depends little on the alkyl group of Rbpy; $\lambda = 0.772$ eV, 0.767 eV and 0.798 eV for R = propyl, hexyl and adamantyl, respectively. Thus, not the λ value but the H_{rp} value is responsible for the above-mentioned decreasing order of the rate constant. This means that the bulky substituent decreases the orbital overlap between donor and acceptor to suppress the ET reaction. The H_{rp} value exponentially decreases with increasing electron transfer distance (r_{AB}), as follows: $H_{rp} = H_{rp}° \exp[-\beta(r_{AB} - r_{AB}°)/2]$ with $\beta = 11$ nm^{-1}, where $H_{rp}°$ is the electronic coupling matrix element when r_{AB} is the closest distance ($r_{AB}°$) for effective contact between donor and acceptor. This β value is almost the same as the value (12 nm^{-1}) reported for the thermal ET reaction between aromatic compounds.

Introduction

Photo-induced electron transfer (ET) reactions form one of the important subjects of research over the last two decades.[1] Since ruthenium(II) tris(2,2′-bipyridine), $[Ru(bpy)_3]^{2+}$, was successfully utilized for H_2 evolution from water,[2–5] many studies have been carried out to elucidate the photochemical properties of $[Ru(bpy)_3]^{2+}$.[1a,b,6,7] This complex is still one of the best photosensitizers because of its long-lived photo-excited state and significantly negative reduction potential at the excited state. Detailed knowledge of the photo-induced ET reaction of this complex is necessary for making further developments of photochemical applications of this complex.

According to Marcus,[8] the rate constant for the ET reaction is represented as a function of the free energy change ($\Delta G°$), the electronic coupling matrix element (H_{rp}), and the reorganization energy (λ), as shown in eqn. 1.

$$k_{et} = \frac{2\pi}{h} \cdot \frac{H_{rp}^2}{\left(4\pi k_b T \lambda\right)^{1/2}} \exp\left\{ \frac{-\left(\Delta G° + \lambda\right)^2}{4 k_b T \lambda} \right\} \qquad (1)$$

The H_{rp} value is considered to decrease exponentially with increasing donor–acceptor separation (r_{AB}), as shown by the following eqn. 2.[8a]

$$H_{rp} = H_{rp}° \exp[-\beta(r_{AB} - r_{AB}°)/2] \qquad (2)$$

In this equation, $H_{rp}°$ is the electronic coupling matrix element when r_{AB} is the closest distance ($r_{AB}°$) for effective contact between donor and acceptor. The orbital parameter β is considered a measure of orbital expansion of the electron transfer reaction system; when β is small, the orbital overlap between donor and acceptor does not decrease very much as the donor–acceptor distance increases. In other words, when β is small, the orbitals participating in the ET reaction expand well and the H_{rp} value is not very sensitive to the distance. Thus, the β value is important for the ET reaction. Of these parameters, the $\Delta G°$ value can be experimentally evaluated with redox potentials at the ground state, quenching reaction rate, and absorption and emission spectra. However, it is not easy to evaluate experimentally the H_{rp}, λ and β values, although they are fundamental parameters in the ET reaction. Actually, only a few of these values have been experimentally presented; for instance, Hoffman and coworkers reported the λ value in the photo-induced ET reaction between $[Ru(bpy)_3]^{2+}$ and methyl viologen (MV^{2+}),[9] and also we evaluated the H_{rp} and λ values in the similar photo-induced ET reaction between $[Ru(bpy)_3]^{2+}$ and such viologens as MV^{2+} and 4,4′-bipyridyl-1,1′-di(propionic acid) and the reverse ET reaction between $[Ru(bpy)_3]^{3+}$ and one-electron reduced viologens.[10] Moreover, the β value has not been experimentally evaluated yet in the photo-induced ET reactions of ruthenium(II) complexes, to our best knowledge.

In the present work, we synthesized three Ru(II) complexes of 2,2′-bipyridine derivatives, namely $[Ru(prbpy)_3]Cl_2$ **1** (prbpy =

4,4′-di(*n*-propylaminocarbonyl)-2,2′-bipyridine), [Ru(chbpy)₃]-Cl₂ **2** (chbpy = 4,4′-di(cyclohexylaminocarbonyl)-2,2′-bipyridine) and [Ru(adbpy)₃]Cl₂ **3** (adbpy = 4,4′-di(adamantyl-aminocarbonyl)-2,2′-bipyridine), as shown in Scheme 1. We
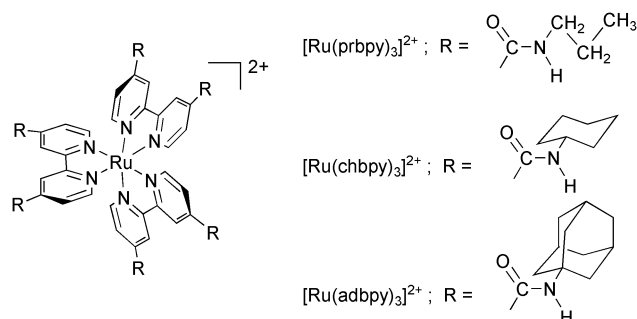
Scheme 1

investigated the photo-induced ET reaction between these Ru(II) complexes and MV²⁺, to clarify the dependence of ET reaction rate on the intermolecular distance, since these complexes have similar photochemical properties but different sizes. It is our intention here to evaluate experimentally the H_{rp}, λ and β values, to present a clear relationship between the H_{rp} value and the size of Ru(II) complexes and to report the β value.

Experimental

Materials

2,2′-Bipyridyl-4,4′-dicarboxylic acid (dcbpy) was synthesized as reported.[11] Propylamine, cyclohexylamine, and adamantyl-amine were purchased from Nakarai Chemical Co. Ltd. (guaranteed grade) and used after distillation. Methyl viologen (1,1′-dimethyl-4,4′-bipyridinium dichloride) was purchased from Nakarai Chemical Co. Ltd. (guaranteed grade) and used without further purification. All the solvents were used after distillation.

Synthesis of 4,4′-di(propylaminocarbonyl)-2,2′-bipyridine (prbpy). Prbpy was prepared according to the synthesis of a similar compound,[12] as follows: dcbpy (480 mg) was reacted with thionyl chloride (10 ml) at 85 °C for 3 h to afford 2,2′-bi-pyridyl-4,4′-dicarbonyl chloride. After cooling to room temperature, the remaining thionyl chloride was removed from the solution by evaporation under reduced pressure. The residue was dissolved in benzene (40 ml) and *n*-propylamine (2 ml) was added. The solution was refluxed for 12 h. The crude solids separated by filtration were washed with acetone and then puri-fied by recrystallization from MeOH–chloroform (3 : 1 v/v). Yield 280 mg (44%). Found: C, 65.77; H, 6.87; N, 17.03%. $C_{18}H_{22}N_4O_2$ requires C, 66.24; H, 6.79; N, 17.17%. δ_H (CDCl₃, 400 MHz) 8.80 (d, 2H, 5-py), 8.60 (s, 2H, 3-py), 7.80 (d, 2H, 6-py), 6.40 (s, 2H, NH), 3.50 (q, 4H, CH₂), 1.70 (m, 4H, CH₂) and 1.00 (t, 6H, CH₃).

Synthesis of 4,4′-di(cyclohexylaminocarbonyl)-2,2′-bipyridine (chbpy). Chbpy was synthesized like prbpy, except that the solids were recrystallized from DMF. Yield 470 mg (28.3%). Found: C, 70.49; H, 7.35; N, 13.77%. $C_{24}H_{30}N_4O_2Cl_2$ requires C, 70.91; H, 7.44; N, 13.78%. δ_H (DMSO-d₆, 400 MHz) 8.90 (d, 62, 5-py), 8.80 (s, 2H, NH), 8.70 (s, 2H, 3-py), 7.80 (d, 2H, 6-py), 3.80 (m, 6H, ch) and ~1.50 (m, 20H, cyclohexyl).

Synthesis of 4,4′-di(adamantylaminocarbonyl)-2,2′-bipyridine (adbpy). Adbpy was synthesized like prbpy. Yield 510 mg (31.7%). Found: C, 74.40; H, 7.32; N, 10.94%. $C_{32}H_{38}N_4O_2$ requires C, 75.26; H, 7.50; N, 10.97%. δ_H (CDCl₃, 400 MHz) 8.80 (d, 2H, 5-py), 8.60 (s, 2H, 3-py), 7.80 (d, 2H, 6-py), 6.00 (s, 2H, NH) and ~2.00 (m, 30H, adamantyl).

Synthesis of [Ru(prbpy)₃]Cl₂ 1. Complex **1** was synthesized like [Ru(bpy)₃]Cl₂,[13] as follows: a solution of RuCl₃·3H₂O (52.5 mg) and prbpy (397 mg) in EtOH (10 ml) was kept at 80 °C for 10 days in a sealed glass tube. The crude products were separated by filtration and the purification was carried out by column chromatography (silica gel: eluent = methanol–chloroform (1 : 19 v/v)). Yield 113 mg (36.5%). The differential thermal analysis clearly indicated that four water molecules were included in the crystal. Found: C, 52.96; H, 5.90; N, 13.50%. RuC₅₄H₆₆N₁₂O₆Cl₂·4H₂O requies C, 53.02; H, 6.10; N, 13.74%. δ_H (CDCl₃, 400 MHz) 10.5 (s, 1H, NH), 8.95 (s, 1H, 6-py), 8.10 (s, 1H, 3-py), 7.70 (s, 1H, 5-py), 3.30 (d, 2H, >N–CH₂–), 1.75 (m, 2H, –CH₂–) and 0.95 (s, 3H, –CH₃).

Syntheses of [Ru(chbpy)₃]Cl₂ 2 and [Ru(adbpy)₃]Cl₂ 3. Complexes **2** and **3** were prepared similarly to **1**, except that DMF was used as the solvent for the synthesis of **2**. **2**: Yield 167 mg (46.6%). Found: C, 57.07; H, 6.62; N, 11.17%. RuC₇₂H₉₀-N₁₂O₆Cl₂·7H₂O requires C, 56.98; H, 6.91; N, 11.07%. δ_H (CDCl₃, 400 MHz) 9.60 (s, 6H, NH), 9.00 (s, 6H, 3-py), 7.90 (d, 6H, 5-py), 7.80 (d, 6H, 6-py), 3.80 (m, 6H, cyclohexyl) and ~1.50 (m, 60H, cyclohexyl). **3**: Yield 118 mg (26.3%). Found: C, 62.93; H, 6.60; N, 8.78%. RuC₉₆H₁₁₄N₁₂O₆Cl₂·7H₂O requires C, 63.00; H, 7.05; N, 9.18%. δ_H (DMSO-d₆, 400 MHz) 9.50 (d, 6H, 5-py), 8.60 (s, 6H, NH), 7.90 (s, 6H, 3-py), 7.80 (d, 6H, 6-py) and ~2.00 (m, 90H, adamantyl).

Electrochemical measurements

The cyclic voltammograms of the ruthenium(II) complexes were recorded at controlled temperature under nitrogen atmosphere with a combined system of potentiostat and function generator to which a glassy carbon electrode was attached as a working electrode (Toho technical research; model PS-06). A sample solution was prepared by dissolving the ruthenium(II) complex (1.0 mmol dm⁻³) in CH₂Cl₂ containing tetraethylammonium perchlorate (0.1 mol dm⁻³).

Quenching reaction

Solutions of the ruthenium(II) complexes (5.0 μmol dm⁻³) and methyl viologen (0.10–9.0 mmol dm⁻³) in EtOH–H₂O (4 ml; 9 : 1 v/v) were placed in a pyrex cell after five freeze–pump–thaw cycles. The ionic strength of the reaction solution was adjusted to 0.1 mol dm⁻³ by addition of tetraethylammonium chloride ((Et₄N)Cl). Then, the emission intensity and the lifetime of the Ru(II) complexes were measured at the controlled temperature (±0.1 °C), under visible light irradiation corresponding to the absorption maximum of these Ru(II) complexes. A Hitachi fluorometer F3010 was used for the measurements of emission intensity. The excited state lifetime was measured by laser flash photolysis, which was carried out with 355 nm laser pulses from a Continuum Surelite I-10 laser system. The emission spectra of the ruthenium(II) complexes were monitored with a photomultiplier (Hamamatsu R928) and a digital oscilloscope Tektronix TDS-380P.

Results and discussion

Photochemical properties of [Ru(prbpy)₃]²⁺ 1 (prbpy = 4,4′-di(propylaminocarbonyl)-2,2′-bipyridine), [Ru(chbpy)₃]²⁺ 2 (chbpy = 4,4′-di(propylaminocarbonyl)-2,2′-bipyridine) and [Ru(adbpy)₃]²⁺ 3 (adbpy = 4,4′-di(adamantylaminocarbonyl)-2,2′-bipyridine)

Photochemical properties of **1**, **2** and **3** are given in Table 1 with those of [Ru(bpy)₃]²⁺.[14] For **1**–**3** the metal to ligand charge transfer (MLCT) absorption band is observed at λ_{max} = 464–465 nm (ε = 21600–24500 mol⁻¹ dm³ cm⁻¹) and the emission spectrum is at λ_{max} = 614–616 nm in EtOH–H₂O (9 : 1 v/v), where uncorrected values of emission maxima are given. These

Table 1 Photochemical and electrochemical properties of [Ru(prbpy)₃]²⁺ **1** (prbpy = 4,4′-di(propylaminocarbonyl)-2,2′-bipyridine), [Ru(chbpy)₃]²⁺ **2** (chbpy = 4,4′-di(propylaminocarbonyl)-2,2′-bipyridine) and [Ru(adbpy)₃]²⁺ **3** (adbpy = 4,4′-di(adamantylaminocarbonyl)-2,2′-bipyridine) in EtOH–H₂O 9 : 1 (v/v) at 25 °C, compared with those of [Ru(bpy)₃]²⁺

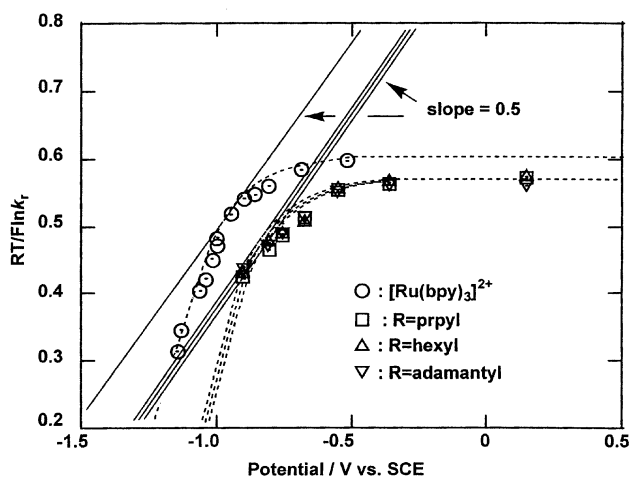|	Absorption		Emission			
	λ_{max}/nm	ε/mol⁻¹ dm³ cm⁻¹	λ_{max}/nm	τ/ns	$E(\mathrm{Ru}^{3+/2+})^{b}$/V $vs.$ SCE	$E(\mathrm{Ru}^{3+/2+}{}^{*})$/V $vs.$ SCE
[Ru(prbpy)₃]²⁺	464	24500	614	1400	+1.53	−0.61
[Ru(chbpy)₃]²⁺	464	21700	615	1420	+1.57	−0.60
[Ru(adbpy)₃]²⁺	465	21600	616	1290	+1.52	−0.62
[Ru(bpy)₃]²⁺	452	14900ᵃ	600	592ᵃ	+1.22ᶜ	−0.81ᵈ

ᵃ In a buffer solution of maleic acid/tris(hydroxymethyl)aminomethane/sodium hydroxide (pH 7.0), μ = 0.1 at 25 °C. ᵇ In dichloromethane. ᶜ This potential was measured in acetonitrile/tetrabutylammonium hexafluorophosphate (0.1 mol dm⁻³) with glassy carbon electrode. See ref. 14. ᵈ Ref. 20.

absorption and emission maxima are shifted to longer wavelengths relative to those of [Ru(bpy)₃]²⁺ by about 12 nm and 15 nm, respectively. The red-shift of absorption and emission spectra is easily interpreted in terms of the π* orbital of 2,2′-bipyridine becoming lower in energy upon the introduction of the electron-withdrawing alkylaminocarbonyl (CONHR) group. A similar observation was reported for [Ru(dmp)ₙ(decb)₃₋ₙ]²⁺ (dmp = 4,4′-dimethyl-2,2′-bipyridine; decb = 4,4′-di(ethoxycarbonyl)-2,2′-bipyridine; n = 1–3).[15] The decay of the emission spectra occurs in a single-exponential manner, which is ascertained by deconvolution. From the decay curve, the lifetime (τ) of the excited state was evaluated. The lifetimes of **1**, **2** and **3** are not sensitive to the alkyl group of CONHR, as expected (see Table 1). Interestingly, their lifetimes are about twice as long as that of [Ru(bpy)₃]²⁺, as was also found for similar ruthenium(II) complexes [Ru(decb)₃]²⁺ [15] and [Ru(menbpy)₃]²⁺ (menbpy = 4,4′-di{(1R,2S,5R)-(−)-menthoxycarbonyl}-2,2′-bipyridine).[16] Their longer lifetimes than that of [Ru(bpy)₃]²⁺ are understood by considering the following two factors: one is the energy separation between the ³MLCT and the ³MC (metal centered d–d) excited states. Since this energy separation increases upon the introduction of electron-withdrawing substituents (*vide supra*), the deactivation of the ³MLCT excited state through the ³MC excited state is suppressed, like that of [Ru(dmp)ₙ(decb)₃₋ₙ]²⁺.[15] On the other hand, the energy separation between ³MLCT and the ground states decreases upon the introduction of electron-withdrawing substituents. This would lead to acceleration of direct deactivation of the ³MLCT excited state to the ground state by the energy gap law.[17] There is another plausible factor, the protection of the excited *[Ru(Rbpy)₃]²⁺ by the bulky groups against solvent approach, as follows: the bulky groups introduced onto the Rbpy ligand do not allow solvent molecules to approach the core moiety of excited *[Ru(Rbpy)₃]²⁺, which suppresses the deactivation by the solvent. At this moment, it is difficult to decide which factor is more important and we need further experiments.

Though the reduction potential ($E^{\mathrm{Ru(III)/*Ru(II)}}$) of the Ru(II) complexes at the excited state was spectroscopically estimated by Navon and Sutin,[18] we could not adopt their method, because the redox potential of [Ru(bpy)₃]²⁺ in the ground state could not be measured in EtOH–H₂O. ‡ Therefore, we estimated the $E^{\mathrm{Ru(III)/*Ru(II)}}$ value with the method proposed by Meyer *et al.*[19] and Balzani *et al.*,[20] where the oxidative quenching reaction was carried out with such quenchers as nitrobenzene and p-quinone derivatives.§ In Fig. 1, the values of $(RT/F)\ln k_{\mathrm{r}}$ are plotted against the redox potential of the quencher. According to the method proposed,[19,20] the $\Delta G°$ value can be taken to be

Fig. 1 Relationships of quenching rate constant (k_{r}) and the redox potentials of quenchers (2,6-dichloro-p-benzoquinone, p-dinitrobenzene, o-dinitrobenzene, m-dinitrobenzene, methyl p-nitrobenzoate, methyl m-nitrobenzoate) in [Ru(bpy)₃]²⁺ (ref. 19) and [Ru(Rbpy)₃]²⁺ (Rbpy = 4,4′-di(alkylaminocarbonyl)-2,2′-bipyridine; alkyl = propyl, hexyl or adamantyl).

0 V at which the slope of the plot is 0.5. Such a potential giving $\Delta G° = 0$ is easily determined, as shown in Fig. 1. Comparing this potential of [Ru(bpy)₃]²⁺ with that of [Ru(Rbpy)₃]²⁺, we estimate that the $E^{\mathrm{Ru(III)/*Ru(II)}}$ value of [Ru(Rbpy)₃]²⁺ is different from that of [Ru(bpy)₃]²⁺ by about 0.2 V. On the basis of the reported $E^{\mathrm{Ru(III)/*Ru(II)}}$ value of [Ru(bpy)₃]²⁺ (−0.81 V (*vs.* SCE) in acetonitrile),¶ the $E^{\mathrm{Ru(III)/*Ru(II)}}$ values of **1**, **2** and **3** are evaluated to be −0.61, −0.60 and −0.62 V, respectively.∥

The reduction potentials ($E^{\mathrm{Ru(III)/Ru(II)}}$) of **1**, **2** and **3** at the ground state were measured with cyclic voltammetry to be +1.53, +1.57 and +1.52 V (*vs.* SCE), respectively, in dichloromethane. Their reduction potentials at the ground state are more positive (or less negative) than that of [Ru(bpy)₃]²⁺ by about 200 mV, like the reduction potential at the excited state. The shifts of reduction potential at both ground and excited states are interpreted in terms of the π and π* orbitals of 2,2′-bipyridine being stabilized in energy by introduction of the electron-withdrawing CONHR group to 2,2′-bipyridine. A similar explanation was previously presented for the reduction potentials of [Ru(dmp)ₙ(decb)₃₋ₙ]²⁺.[15]

The radii (r) of the Ru(II) complexes and MV²⁺ were estimated with the semiempirical equation $r = 1/2(d_x d_y d_z)^{1/3}$,[21] where

‡ In this method, the reduction potential, $E^{\mathrm{Ru(III)/Ru(II)}}$, at the ground state is necessary. However, we failed to measure the $E^{\mathrm{Ru(III)/Ru(II)}}$ values of **1**, **2** and **3** in EtOH–H₂O, because H₂ evolution occurred during the CV measurement.
§ 2,6-Dichloro-p-benzoquinone, p-dinitrobenzene, o-dinitrobenzene, m-dinitrobenzene, methyl p-nitrobenzoate, methyl m-nitrobenzoate were used here.

¶ The $E^{\mathrm{Ru(III)/*Ru(II)}}$ value of [Ru(bpy)₃]²⁺ was reported to be −0.81 V (*vs.* SCE) in acetonitrile.[19]
∥ To estimate the reduction potential at the excited state according to Meyer,[20] the value of $k_{\mathrm{q}}(\Delta G° = 0)$ is necessary. Though $k_{\mathrm{q}}(\Delta G° = 0)$ is not known for **1**, **2** and **3**, we could estimate correctly the reduction potentials of **1**, **2** and **3** at the excited state by comparing them with that of [Ru(bpy)₃]²⁺, since the reduction potential of [Ru(bpy)₃]²⁺ in the excited state is known.

d_x, d_y and d_z are the molecular sizes along the three axes of the CPK space-filling model. ** The estimated r values are 12.5, 12.9, 13.4 and 3.62 Å for **1**, **2**, **3** and MV^{2+}, respectively.

The above results indicate that the size of the Ru(II) complexes depends on the alkyl group of CONHR, as expected, while the redox potential and the lifetime of *[Ru(Rbpy)$_3$]$^{2+}$ are little influenced by the alkyl group. Thus, we can expect to investigate the dependences of electron transfer rate, H_{rp} and λ on the size of the donor without interference of the other factor.

Quenching reaction with MV^{2+}

The excited states of **1**, **2** and **3** were efficiently quenched by MV^{2+} in EtOH–H$_2$O (9 : 1 v/v). Fig. 2 shows the relation
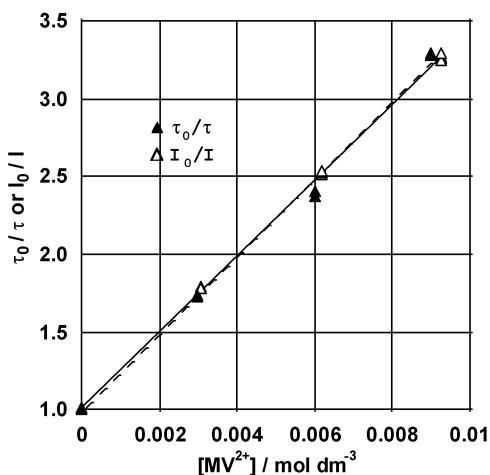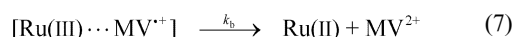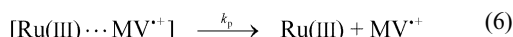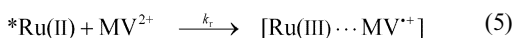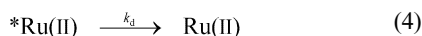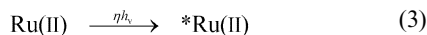

Fig. 2 The Stern–Volmer plot in the quenching reaction of [Ru(chbpy)$_3$]$^{2+}$ by MV^{2+} in EtOH–H$_2$O (9 : 1 v/v) at 25 °C.

between the τ_0/τ value and MV^{2+} concentration observed in the quenching reaction of [Ru(chbpy)$_3$]$^{2+}$ by MV^{2+} as an example, where τ_0 represents the lifetime in the absence of MV^{2+} (see ESI,† Fig. 4S and 5S for the relations observed in [Ru(prbpy)$_3$]$^{2+}$ and [Ru(adbpy)$_3$]$^{2+}$). The I_0/I value is almost the same as the τ_0/τ value, where I and I_0 are the emission intensities in the presence and the absence of quencher, respectively. This result clearly indicates that this quenching reaction proceeds not through a static quenching mechanism but through a dynamic quenching mechanism.

In the dynamic quenching mechanism, the Ru(II) complex transforms to the excited state upon irradiation, independently of MV^{2+} (eqn. 3). The excited Ru(II) complex collides with MV^{2+} to form the encounter complex (eqn. 5), from which either charge separation (eqn. 6) or back-electron transfer (eqn. 7) occurs:

$$\text{Ru(II)} \xrightarrow{\eta h_\nu} \text{*Ru(II)} \quad (3)$$

$$\text{*Ru(II)} \xrightarrow{k_d} \text{Ru(II)} \quad (4)$$

$$\text{*Ru(II)} + \text{MV}^{2+} \xrightarrow{k_r} [\text{Ru(III)} \cdots \text{MV}^{\cdot+}] \quad (5)$$

$$[\text{Ru(III)} \cdots \text{MV}^{\cdot+}] \xrightarrow{k_p} \text{Ru(III)} + \text{MV}^{\cdot+} \quad (6)$$

$$[\text{Ru(III)} \cdots \text{MV}^{\cdot+}] \xrightarrow{k_b} \text{Ru(II)} + \text{MV}^{2+} \quad (7)$$

where Ru(II) represents [Ru(Rbpy)$_3$]$^{2+}$. In this mechanism, the Stern–Volmer relationship is given by eqn. 8.

$$\tau_0/\tau = I_0/I = 1 + k_r\tau_0[\text{MV}^{2+}] \quad (8)$$

The quenching rate constant (k_r) for each complex was evaluated from the slope of the Stern–Volmer plot and the obtained values are listed in Table 2, where τ_0 was measured in the absence of MV^{2+}. It is noted that the k_r value decreases as the size of the Ru(II) complex increases.

Correction of diffusion rate

Since these k_r values are considerably large, we must make a diffusion rate correction. The ET reaction (eqn. 5) is considered to consist of the diffusional formation of an exciplex (k_D in eqn. 9), the diffusional dissociation of the exciplex (k_{-D} in eqn. 9) and an ET reaction in the exciplex (k_r^{cor} in eqn. 10). Application of the usual steady-state approximation to the concentration of [*Ru(II)$^{2+}$ ··· MV^{2+}] leads to eqn. 11.[23]

$$\text{*[Ru(II)]}^{2+} + \text{MV}^{2+} \xrightleftharpoons[k_{-D}]{k_D} [\text{*Ru(II)}^{2+} \cdots \text{MV}^{2+}] \quad (9)$$

$$[\text{*Ru(II)}^{2+} \cdots \text{MV}^{2+}] \xrightarrow{k_r^{cor}} [\text{Ru(III)}^{3+} \cdots \text{MV}^{\cdot+}] \quad (10)$$

$$k_r^{cor} = k_r^{obs}k_{-D}/(k_D - k_r^{obs}) \quad (11)$$

The k_D and k_{-D} values were calculated according to Debye–Smoluchowski[24] and Eigen,[25] respectively, where the dielectric constant (ε_r) and viscosity (η) of the medium were taken from the reference †† and the radii (r) of the reactants estimated above were employed. The evaluated k_D, k_{-D}, and k_r^{cor} values are summarized in Table 2. The k_D value increases in the order **1** < **2** < **3** and the k_{-D} value decreases in the order **1** > **2** > **3**. Since these tendencies are not consistent with the order of k_r^{obs}, the diffusional formation and the diffusional dissociation of the exciplex are not responsible for the decreasing order of k_r^{obs}, **1** > **2** > **3**. ‡‡ On the other hand, the k_r^{cor} value decreases in the order **1** > **2** > **3**, which is consistent with the decreasing order of the k_r^{obs} value. Thus, it is concluded that the k_r^{cor} value is responsible for the decreasing order of k_r^{obs}; in other words, the ET reaction in the exciplex plays an important role in the overall ET reaction rate.

Analysis of ET reaction based on Marcus' theory:

We analyzed here the ET reaction in the exciplex with Marcus' theory. Eqn. 1 given by Marcus' theory is transformed to eqn. 12,

$$\ln\left(k_r^{cor}\, T^{1/2}\right) = \ln\frac{2}{h} \cdot \frac{H_{rp}^2}{(4\pi k_b\lambda)^{1/2}} - \frac{\left(\Delta G^\circ + \lambda\right)^2}{4\pi k_b T} \quad (12)$$

which apparently shows that a linear relationship exists between $\ln(k_r^{cor}\, T^{1/2})$ and $1/T$ if ΔG° is not sensitive to T. Actually, the ΔG° value varies little when the temperature changes from 10 °C to 40 °C,§§ and a linear relationship is obtained, as

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** Chem 3D was used for MM calculations with standard parameters. Chem 3D version 3.0 for Apple Macintosh, Cambridge Scientific Computing, Inc., Massachusetts. In the MM calculations, the Ru–N distance was assumed to be the same as the experimental bond distance (2.056 Å).[22]
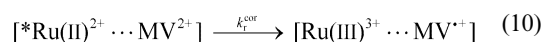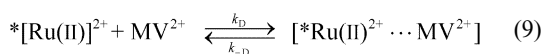
†† The dielectric constants (ε_r) used are 33.0, 31.2, 29.4, 27.7, 26.0 and 24.4 for 5, 15, 25, 35, 45 and 55 °C, respectively. The viscosity (η) values are 2.57, 1.96, 1.51, 1.19, 0.97 and 0.80 mPa s for 5, 15, 25, 35, 45 and 55 °C, respectively. These ε_r and η values were estimated from the reported values.[26a,b]

‡‡ The final results, such as H_{rp}, λ and β values, depend little on the estimated ε_r and η values (see ESI). Thus, the present conclusions are reliable in spite of the uncertainties of ε_r and η which arise from the use of mixed solvent.

§§ The ΔG° value changes little when the temperature increases from 10 °C to 40 °C in the similar reaction between [Ru(bpy)$_3$]$^{2+}$ and MV^{2+}.[10]

Table 2 The observed rate constants (k_r^{obs}) of the electron transfer reaction between methyl viologen (MV^{2+}) and the excited state of $[Ru(prbpy)_3]^{2+}$ **1** (prbpy = 4,4'-di(propylaminocarbonyl)-2,2'-bipyridine), $[Ru(chbpy)_3]^{2+}$ **2** (chbpy = 4,4'-di(propylaminocarbonyl)-2,2'-bipyridine) or $[Ru(adbpy)_3]^{2+}$ **3** (adbpy = 4,4'-di(adamantylaminocarbonyl)-2,2'-bipyridine), the diffusion rate constant (k_D) for the exciplex formation, the diffusional dissociation rate constant (k_{-D}) of the exciplex, and the electron transfer rate constant (k_r^{cor}) in the exciplex[a]

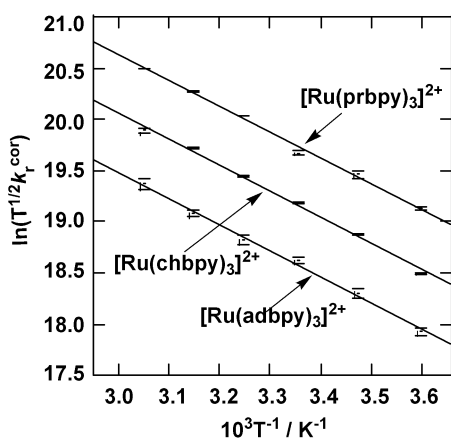| Ru(II)	$10^{-8} k_r^{obs\,a}$/mol^{-1} dm^3 s^{-1}	$10^{-9} k_D$/mol^{-1} dm^3 s^{-1}	$10^{-8} k_{-D}$/s^{-1}	$10^{-7} k_r^{cor}$/s^{-1}
$[Ru(prbpy)_3]^{2+}$	2.62 ± 0.01	6.09	4.52	2.03 ± 0.01
$[Ru(chbpy)_3]^{2+}$	1.72 ± 0.01	6.17	4.33	1.24 ± 0.01
$[Ru(adbpy)_3]^{2+}$	1.06 ± 0.03	6.27	4.12	0.707 ± 0.002

[a] In EtOH–H_2O (9 : 1 v/v; $\mu = 0.1$ ((Et_4N)Cl)) at 25 °C, [Ru(II)] = 5.0 μmol dm^{-3}, [MV^{2+}] = 0–9 mmol dm^{-3}.

Table 3 Rate constant (k_r^{cor}) of the electron transfer reaction in the exciplex, [*Ru(Rbpy)$_3$$^{2+}$ ··· MV^{2+}], electronic coupling matrix element (H_{rp}) and reorganization energy (λ)[a]

Ru(II)	$10^{-7} k_r^{cor}$/s^{-1}	$10^3 H_{rp}$/eV	λ/eV
$[Ru(prbpy)_3]^{2+}$	2.03	2.28	0.772
$[Ru(chbpy)_3]^{2+}$	1.24	1.86	0.767
$[Ru(adbpy)_3]^{2+}$	0.707	1.37	0.798

[a] In EtOH–H_2O (9 : 1 v/v, $\mu = 0.1$ mol dm^{-3}) at 25 °C.

Fig. 3 Plot of $\ln(T^{1/2}k_r^{cor})$ against T^{-1} in the quenching reactions of $[Ru(prbpy)_3]^{2+}$ **1** (prbpy = 4,4'-di(propylaminocarbonyl)-2,2'-bipyridine), $[Ru(chbpy)_3]^{2+}$ **2** (chbpy = 4,4'-di(propylaminocarbonyl)-2,2'-bipyridine) and $[Ru(adbpy)_3]^{2+}$ **3** (adbpy = 4,4'-di(adamantylaminocarbonyl)-2,2'-bipyridine) with methyl viologen (MV^{2+}).

shown in Fig. 3. From its slope, the λ value was evaluated with the independently measured $\Delta G°$ values; $\Delta G°$ is 0.05, 0.06 and 0.04 V for **1**, **2** and **3**, respectively.¶¶ From its intercept, the H_{rp} value was evaluated with the above-estimated λ value. Their values are listed in Table 3. The H_{rp} value decreases in the order **1 > 2 > 3**, while the λ value depends little on the size of the Ru(II) complex. The λ value is in general considered to be the sum of λ_{in} and λ_{out}; $\lambda = \lambda_{in} + \lambda_{out}$, where λ_{in} is the contribution from geometry changes of the reactant and the substrate and λ_{out} is the contribution from changes of solvent reorganization. The λ_{out} value is in general estimated with eqn. 13:[21,27]

$$\lambda_{out} = \{1/(2r_A) + 1/(2r_D) - 1/(r_{AD})\}(1/n^2 - 1/\varepsilon_r)\{e^2/(4\pi\varepsilon_0)\} \quad (13)$$

where r_A and r_D are the radii of methyl viologen and $[Ru(Rbpy)_3]^{2+}$, respectively, and r_{AD} is the distance between methyl viologen and $[Ru(Rbpy)_3]^{2+}$ in effective contact, the n

¶¶ The $\Delta G°$ value is evaluated as follows: $\Delta G° = E°(Ru(Rbpy)_3^{3+/2+*}) - E°(MV^{2+/+}) + (\omega_p - \omega_r)$, where $E°(MV^{2+/+}) = -0.66$ V (vs. SCE in EtOH–H_2O (9 : 1 v/v)), and ω_p and ω_r are the Coulombic work terms (~10^{-2} eV). Since the slope of the linear relationship in Fig. 3 is $-(\Delta G° + \lambda)^2/(4\pi k_b)$, the λ value is estimated with the $\Delta G°$ value which is measured electrochemically. Then, the H_{rp} value is estimated from the intercept with the estimated λ value.

and ε_r values are the refractive index and the dielectric constant of the medium, respectively, e is the charge of an electron and $4\pi\varepsilon_0$ is the dielectric constant in vacuum. The λ_{out} value calculated with this equation depends little on the nature of Rbpy; $\lambda_{out} = 0.846$ eV, 0.848 eV and 0.851 eV, for **1**, **2** and **3**, respectively.‖‖ In spite of the minimal dependence of λ_{out} on Rbpy, the λ value of **3** is much larger than those of **1** and **2** (see Table 3), which indicates that the λ_{in} value of **3** is larger than those of **1** and **2**. This is probably because bulky substituents such as the adamantyl group cause a marked change in steric repulsion with changes in the Ru–N distance induced by the ET reaction. However, the $(2\pi/h)\{1/(4\pi k_b\lambda^{1/2}\exp\{-(\Delta G° + \lambda)^2/(4k_bT\lambda)\}$ term which involves λ is calculated to be 3.80×10^{12}, 3.25×10^{12} and 3.57×10^{12} (eV^{-2} s^{-1}) for **1**, **2** and **3**, respectively, when the $\Delta G°$ and λ values evaluated here are used. These values are not consistent with the decreasing order of k_r^{cor}, **1 > 2 > 3**. On the other hand, the H_{rp}^2 value decreases in the order **1 > 2 > 3**. Thus, it is clearly concluded that not the λ value but the H_{rp} value is responsible for the decreasing order of k_r^{cor}, **1 > 2 > 3**.

The value of $\ln H_{rp}^2$ is plotted against the radii of the Ru(II) complexes, as shown in Fig. 4. As expected from eqn. 2, a good
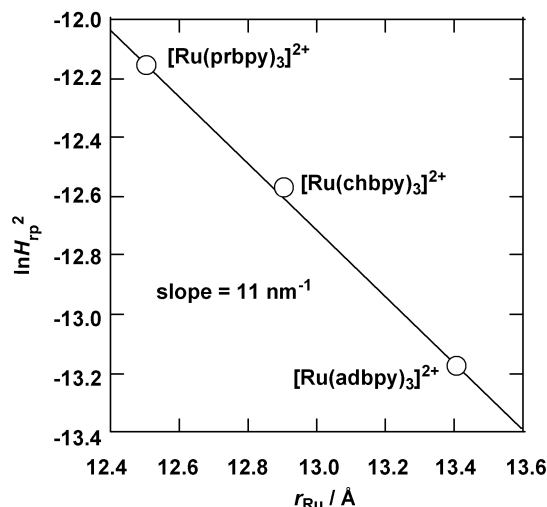
Fig. 4 Plot of $\ln H_{rp}^2$ against the radii of the Ru(II) complexes, r_{Ru}.

linear relationship was obtained, and the β value was estimated to be 11 nm^{-1} from the slope. This value is similar to the reported values which were estimated in nonbiological ET reactions;[8a] for instance, the β value was 12 nm^{-1} in the ET reaction of aromatic compounds.[29] Considering that the excited electron is in a diffuse orbital, one can expect that the β value could be

‖‖ We adopted here r_A and r_D evaluated with the semiempirical equation $1/2(d_xd_yd_z)^{1/3}$ (see text).[21] The r_{AD} value was assumed to be the sum of r_A and r_D, in the usual way. In the evaluation of λ_{out}, we adopted n and ε_r values for EtOH–H_2O (9 : 1 v/v) at 15 °C, because the n value has not been reported for EtOH–H_2O (9 : 1 v/v) at 25 °C; $n = 1.367$[28] and $\varepsilon_r = 31.19$.[26b] Though the experiments were carried out at 25 °C, the n value depends little on temperature as follows: for example, n of EtOH are 1.359 at 25 °C and 1.361 at 20 °C.[30] Thus, the present discussion is correct, at least semiquantitatively.

smaller in the photo-induced ET reaction than in the thermal ET reaction.[8a] The present β value is not consistent with this expectation, seemingly. However, the present result is reasonably interpreted in terms of orbitals participating in the ET reaction, as follows. In the ^{3}MLCT excited state of $[Ru(Rbpy)_3]^{2+}$, the excited electron is believed to exist in the π^* orbital of Rbpy. In the exciplex, $[*Ru(Rbpy)_3^{2+} \cdots MV^{2+}]$, the excited electron transfers from the π^* orbital of Rbpy to the LUMO of MV^{2+} which is also the π^* orbital. In the ET reactions of aromatic compounds investigated previously,[29] an odd electron in the π^* orbital of an aromatic anion radical transfers to the π^* orbital of a different aromatic compound. Thus, electron transfer occurs from the π^* orbital of one molecule to the π^* orbital of the other molecule in both the photo-induced ET reaction between $[Ru(Rbpy)_3]^{2+}$ and MV^{2+} and the thermal ET reaction between an aromatic anion radical and a neutral aromatic compound. From the above discussion, it is reasonably concluded that the π^* orbital of Rbpy expands similarly to that of aromatic compounds and the β value in the photo-induced ET reaction of the Ru(II) complexes of 2,2′-bipyridine derivatives is similar to that in the thermal ET reaction of aromatic anion radicals.

Strictly speaking, we need to consider not only the size but also the shape of the substituent, because a highly branched substituent such as the adamantyl group occupies the space around the bpy ligand to suppress the approach of methyl viologen to the $[Ru(bpy)_3]^{2+}$ core. In the present work, the highly branched adamantyl group gives a very small H_{rp} value, while the linear propyl group also gives a smaller H_{rp} value than expected; the H_{rp} value of **1** exists at a lower position than the linear relationship of Fig. 4. We need to perform more detailed studies with systematically synthesized $[Ru(Rbpy)_3]^{2+}$ to clarify how the size and the shape of substituent influence the ET reaction rate.

Conclusions

Ruthenium(II) complexes of 2,2′-bipyridine derivatives, $[Ru(Rbpy)_3]^{2+}$ (Rbpy = 4,4′-di(alkylaminocarbonyl)-2,2′-bipyridine; alkyl = propyl, hexyl or adamantyl), were newly synthesized here to investigate the distance dependence of their ET reactions with methyl viologen (MV^{2+}). These three Ru(II) complexes exhibit absorption and emission maxima at longer wavelength than those of $[Ru(bpy)_3]^{2+}$. They have more positive reduction potentials than that of $[Ru(bpy)_3]^{2+}$ by about 200 mV in both ground and excited states. All these results are interpreted in terms of the π and π^* orbitals of Rbpy becoming lower in energy because of the electron-withdrawing CONHR substituent introduced onto 2,2′-bipyridine, as previously discussed.[15] The ET reaction is slower in the order alkyl = propyl > hexyl > adamantyl, which is the opposite of the increasing order of the size of the substituent introduced onto 2,2′-bipyridine. Correction of diffusion rate was made and the rate constant (k_r^{cor}) of the ET reaction in the exciplex was evaluated. The k_r^{cor} value also decreases in the order alkyl = propyl > hexyl > adamantyl, while the diffusion rate for exciplex formation (k_D) increases in the order propyl < hexyl < adamantyl and the diffusional dissociation rate of the exciplex (k_{-D}) decreases in the order propyl > hexyl > adamantyl. Thus, the k_D and k_{-D} values are not responsible for the above-mentioned decreasing order of the rate constant but the k_r^{cor} value is responsible for the decreasing order of the overall ET reaction.

The ET reaction in the exciplex was analyzed on the basis of Marcus' theory. The electronic coupling matrix element (H_{rp}) and the reorganization energy (λ) were evaluated from the temperature dependence of the rate constant. The decreasing order of k_r^{cor}, **1 > 2 > 3**, is clearly interpreted in terms of the decreasing order of the H_{rp} value, **1 > 2 > 3**. This means that the bulky substituent decreases the orbital overlap between donor and

acceptor to suppress the photo-induced ET reaction of $[Ru(Rbpy)_3]^{2+}$. The λ value has little influence on the present ET reaction. Though these conclusions meet our expectations, they are experimentally presented for the first time in this work.

The β value was estimated to be about 11 nm^{-1}, which is similar to that of the thermal ET reaction between an aromatic anion radical and an aromatic compound. This is because the electron transfer occurs from the π^* orbital of aromatic system in both the photo-induced ET reaction of $[Ru(Rbpy)_3]^{2+}$ and the thermal ET reaction of the aromatic anion radical.

References

1 For instance, (*a*) K. Kalyanasundaram, *Coord. Chem. Rev.*, 1982, **46**, 46; (*b*) A. Juris, V. Balzani, F. Barigelleti, S. Campagna, P. Belser and A. von Zelewsky, *Coord. Chem. Rev.*, 1988, **84**, 85; (*c*) *Electron Transfer in Inorganic, Organic, and Biological Systems*, ed. J. R. Bolton, N. Mataga and G. McLendon, Adv. Chem. Ser. 228, ACS, Washington DC, Canadian Society for Chemistry, Ottawa, Canada, 1991.
2 (*a*) C. Creutz and N. Sutin, *Proc. Natl. Acad. Sci. USA*, 1975, **72**, 2858; (*b*) G. M. Brown, B. S. Brunschwig, C. Creutz, J. F. Endicott and N. Sutin, *J. Am. Chem. Soc.*, 1979, **101**, 1298; (*c*) N. Sutin and C. Creutz, *Pure Appl. Chem.*, 1980, **52**, 2717; (*d*) C. V. Krishnan, B. S. Brunschwig, C. Creutz and N. Sutin, *J. Am. Chem. Soc.*, 1985, **107**, 2005.
3 K. Kalyanasundaram, J. Kiwi and M. Grätzel, *Helv. Chim. Acta*, 1978, **61**, 2720.
4 M. Kirch, J.-M. Lehn and J.-P. Sauvage, *Helv. Chim. Acta*, 1979, **62**, 1345.
5 (*a*) P. J. DeLaive, B. P. Sullivan, T. J. Meyer and D. G. Whitten, *J. Am. Chem. Soc.*, 1979, **101**, 4007; (*b*) W. J. Dressick, T. J. Meyer, B. Durham and D. P. Rillena, *Inorg. Chem.*, 1982, **21**, 3451.
6 H. Yersin, W. Humbs and J. Straser, *Coord. Chem. Rev.*, 1997, **159**, 325 and references therein.
7 C. D. Clark and M. Z. Hoffman, *Coord. Chem. Rev.*, 1997, **159**, 359 and references therein.
8 (*a*) R. A. Marcus and N. Sutin, *Biochim. Biophys. Acta*, 1985, **811**, 265; (*b*) M. D. Newton and N. Sutin, *Annu. Rev. Phys. Chem.*, 1984, **35**, 437.
9 (*a*) C. D. Clark and M. Z. Hoffman, *J. Phys. Chem.*, 1996, **106**, 7526; (*b*) C. E. Crowley, C. D. Clark and M. Z. Hoffman, *Inorg. Chem.*, 1998, **37**, 5704.
10 T. Hamada, M. Tsukamoto, H. Ohtsuka and S. Sakaki, *Bull. Chem. Soc. Jpn.*, 1998, **71**, 2281.
11 G. Sprintschnik, H. W. Sprintnik, P. P. Kirsch and D. G. Whitten, *J. Am. Chem. Soc.*, 1977, **99**, 4947.
12 K. Ohkubo, T. Hamada, T. Inaoka and H. Ishida, *Inorg. Chem.*, 1989, **28**, 2021.
13 I. Fujita and H. Kobayashi, *Ber. Bunsen-Ges. Phys. Chem.*, 1972, **76**, 115; R. A. Palmer and T. S. Piper, *Inorg. Chem.*, 1966, **5**, 864.
14 C. M. Elliott, R. A. Freitag and D. D. Blaney, *J. Am. Chem. Soc.*, 1985, **107**, 4647.
15 W. F. Wacholtz, R. A. Auerbach and R. H. Schmell, *Inorg. Chem.*, 1986, **25**, 227.
16 K. Ohkubo, T. Hamada and H. Ishida, *J. Chem. Soc., Chem. Commun.*, 1993, 1423.
17 N. J. Turro, *Modern Molecular Photochemistry*, The Benjamin/Cummings Publishing Co., Menlo Park, CA, 1978, p. 183.
18 G. Navon and N. Sutin, *Inorg. Chem.*, 1974, **13**, 2159.
19 C. R. Bock, J. A. Connor, A. R. Gutierrez, T. J. Meyer, D. G. Whitten, B. P. Sullivan and J. K. Nagle, *J. Am. Chem. Soc.*, 1979, **101**, 4815.
20 V. Balzani, F. Scandra, G. Orlandi, N. Sabbatini and M. T. Indelli, *J. Am. Chem. Soc.*, 1981, **103**, 3370.
21 B. S. Brunschwig, S. Ehrenson and N. Sutin, *J. Phys. Chem.*, 1986, **90**, 3657.
22 D. P. Rillema and D. S. Jones, *J. Chem. Soc., Chem. Commun.*, 1979, 849.
23 M. Eigen, W. Kruse, G. Maass and L. De Maeyer, *Prog. React. Kinet.*, 1964, **2**, 287.

24 P. Debye, *Trans. Electrochem. Soc.*, 1942, **82**, 265; M. Z. Smoluchowski, *Phys. Chem.*, 1917, **92**, 129.

25 M. Eigen, *Z. Phys. Chem. (Munich)*, 1954, **1**, 176.

26 (*a*) *KagakuBinran*, 4th edn., Maruzen, Tokyo, 1993, ch. 13, p. II-501; (*b*) *Lange's Handbook of Chemistry*, J. A. Dean, Ed., 11th edn., McGraw-Hill, New York, 1973, pp. 10–148 and pp. 10–287.

27 (*a*) R. A. Marcus, *J. Chem. Phys.*, 1956, **24**, 966; (*b*) R. A. Marcus, *J. Chem. Phys.*, 1965, **43**, 679; (*c*) R. A. Marcus and N. Sutin, *Inorg. Chem.*, 1975, **14**, 213.

28 *Landolt-Börnstein Tabellen*, 5 Aufl., Springer-Verlag, Berlin, 1923.

29 J. R. Miller, J. V. Beitz and R. K. Huddleston, *J. Am. Chem. Soc.*, 1984, **106**, 5057.

30 *Organic Solvents*, J. A. Riddick and W. B. Bunger, Eds., 3rd edn, Wiley-Interscience, New York, 1970, p. 146.