

## Preparation and characterization of bisviologen-linked ruthenium(II) complexes

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### Abstract

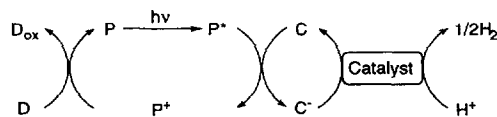
Bisviologen linked ruthenium(II) complexes with different methylene chain length between ruthenium complex and viologen,  $\text{Ru}(\text{bpy})_2(\text{dcbpy})\text{C}_m\text{V}_A\text{C}_n\text{V}_B$  ( $m=2, n=3; m=3, n=4$ ), were synthesized and characterized by using spectroscopic and electrochemical techniques. UV spectra of  $\text{Ru}(\text{bpy})_2(\text{dcbpy})\text{C}_m\text{V}_A\text{C}_n\text{V}_B$  are similar to that of  $\text{Ru}(\text{bpy})_2(\text{dcbpy})$ , indicating no interaction between ruthenium(II) complex moiety and binding bisviologen in the ground state. The photoexcited state of  $\text{Ru}(\text{bpy})_2(\text{dcbpy})$  moiety is oxidatively quenched by binding bisviologen and the intramolecular electron transfer occurs. Electrochemical properties of bisviologen linked ruthenium complexes show that photoinduced two step electron transfer from ruthenium complex moiety to bisviologen can occur to yield the long-lived charge separated states. Luminescence lifetime measurements show that the electron transfers from the photoexcited state of ruthenium(II) complex moiety to the binding bisviologen more rapidly than that of viologen free ruthenium(II) complexes, indicating the intramolecular electron transfer from photoexcited ruthenium(II) complex moiety to bisviologen. © 1998 Elsevier Science S.A. All rights reserved.

**Keywords:** Bisviologen-linked ruthenium(II) complex; Intramolecular electron transfer

### 1. Introduction

Photoinduced hydrogen evolution from water has been studied extensively using a system composed of four components: electron donor (D), photosensitizer (P), electron carrier (C) and catalyst as shown in Scheme 1 [1–4]. Among inorganic photosensitizers, ruthenium tris(2,2'-bipyridine) derivatives are the suitable compounds for photoinduced hydrogen evolution system, because ruthenium complexes possess following properties, such as photostability in water, high extinction coefficients in the visible region, and relatively long-lived excited states.

In this reaction, the reduction of electron carrier is one of the important steps. To improve this system the longer lifetimes of charge separated states between photosensitizer and electron carrier are desired. Charge separation processes have been extensively studied in acceptor-linked photosensitizer systems [5–15]. In these artificial systems, such as a viologen-linked ruthenium(II) complex, the intramolecular electron transfer from ruthenium complex moiety to binding viologen competes with the rapid back electron transfer from



Scheme 1. Photoinduced hydrogen evolution system.

acceptor to photosensitizer leading to the short-lived charge separated state [12–14]. To achieve the long-lived charge separated states in the model systems, the suppression of the back electron transfer is required. The charge separation is stabilized by a multistep electron transfer in a series of acceptors arranged in a fashion analogous to the electron transfer chain in photoreaction center. Among the viologen-linked ruthenium complexes, bisviologen linked ruthenium complexes, in which two viologens with different redox potentials are connected covalently, are suitable compounds to establish the effective photoinduced hydrogen evolution system, because photoinduced two-step electron transfer from photoexcited ruthenium complex moiety to acceptor can occur and back electron transfer is suppressed.

In this paper, we hope to describe the preparation and the photochemical and electrochemical characterization of bisviologen linked ruthenium(II) complexes,  $\text{Ru}(\text{bpy})_2(\text{dcbpy})\text{C}_m\text{V}_A\text{C}_n\text{V}_B$  ( $m=2, n=3; m=3, n=4$ ). These bis-

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viologen linked ruthenium(II) complexes were compared with  $\text{Ru}(\text{bpy})_2(\text{dcbpy})\text{C}_m\text{V}_A\text{C}_n$  and each energy level was represented. Two different viologen (1-ammoniopropyl-1'-butylviologen and 1-benzyl-1'-butylviologen, 1-ammonioethyl-1'-propylviologen and 1-benzyl-1'-propylviologen) are connected to the  $\text{Ru}(\text{bpy})_2(\text{dcbpy})$ , so that photoinduced electron transfer can occur to yield the long-lived charge separated states.

## 2. Experimental

### 2.1. Materials

All reagents were of analytical or of the highest grade available. 4,4'-Dimethyl-2,2'-bipyridine (dmbpy), 4,4'-dicarboxy-2,2'-bipyridine (dcbpy) and  $\text{Ru}(\text{bpy})_2\text{Cl}_2 \cdot n\text{H}_2\text{O}$  were prepared as previously described [16,13,17].  $\text{Ru}(\text{bpy})_2(\text{dcbpy})\text{C}_m\text{V}_A\text{C}_n$  was prepared analogously to the literature for the preparation of  $\text{Ru}(\text{bpy})_2(\text{dcbpy})\text{C}_n\text{VCH}_3$ , with the substitution of  $\text{C}_m\text{V}_A\text{C}_n$  [14]. The synthesis route of bisviologen linked ruthenium(II) complexes are shown in Scheme 2, and the structures of the compounds are shown in Fig. 1.

#### 2.1.1. 1-Benzyl-4,4'-bipyridinium ( $\text{V}_B$ )

4,4'-Bipyridine (0.16 mol) and benzyl bromide (0.15 mol) were dissolved in 400 ml of acetone and stirred at room

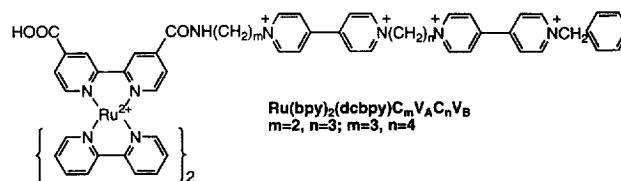
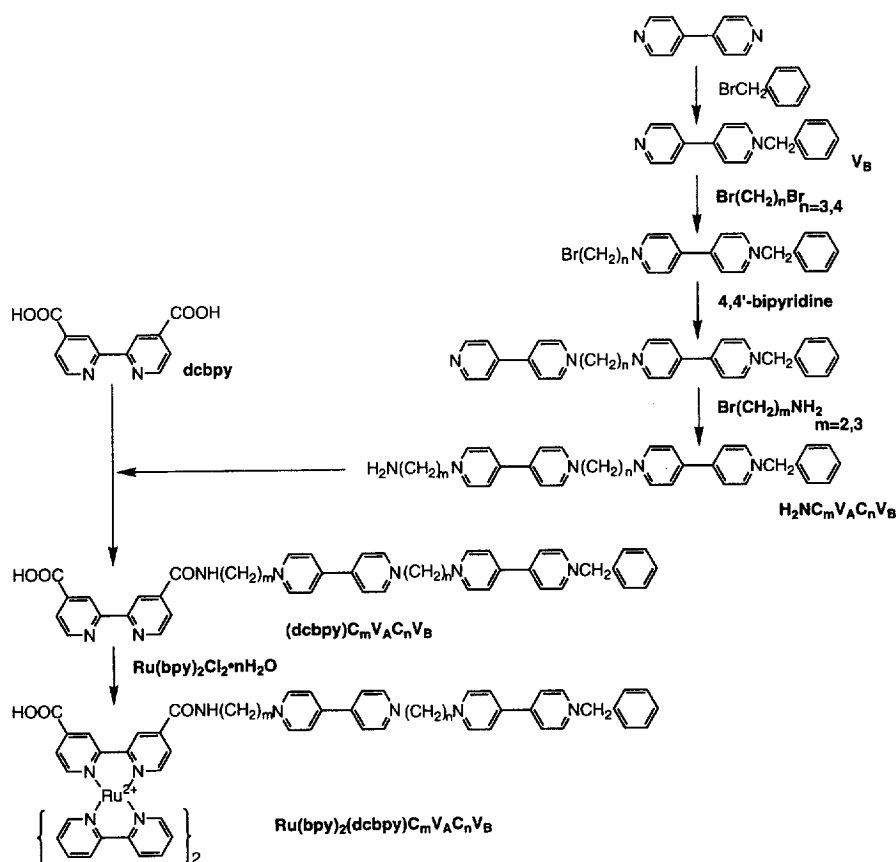


Fig. 1. Structures of  $\text{Ru}(\text{bpy})_2(\text{dcbpy})\text{C}_m\text{V}_A\text{C}_n\text{V}_B$ .

temperature for 24 h. A white precipitate was filtered and washed with acetone. The desired product was recrystallized from ethanol (EtOH) and water and dried under vacuum overnight.  $^1\text{H-NMR}$  in  $\text{D}_2\text{O}$ :  $\delta$  (ppm) 8.9–9.0 (d, 2H), 8.6–8.7 (dd, 2H), 8.2–8.4 (d, 2H), 7.7–7.9 (dd, 2H), 7.4–7.5 (multiplet, 5H), 5.7–5.8 (s, 2H).

#### 2.1.2. 1-Benzyl-1'-(n-4-bromobut-1-yl)-4,4'-bipyridinium ( $\text{BrC}_4\text{V}_B$ )

$\text{V}_B$  (15 mmol) was refluxed with excess 1,4-dibromobutane in 400 ml of acetonitrile (MeCN) for 24 h. A yellow precipitate was filtered, washed with MeCN and dried under vacuum overnight. The product was recrystallized from EtOH and water, and then reprecipitated from water by the addition of ammonium hexafluorophosphate ( $\text{NH}_4\text{PF}_6$ ). The white  $\text{PF}_6^-$  salt was filtered, washed with water and dried under vacuum overnight.  $^1\text{H-NMR}$  in dimethylsulfoxide- $d_6$  ( $\text{DMSO}-d_6$ ):  $\delta$  (ppm) 9.5–9.6 (d, 2H), 9.35–9.45 (d, 2H), 8.7–8.9 (multiplet, 4H), 7.45–7.7 (multiplet, 5H), 5.9–6.0



Scheme 2.

(s, 2H), 4.7–4.85 (t, 2H), 3.5–3.7 (t, 2H), 2.05–2.25 (quintet, 2H), 1.8–2.0 (quintet, 2H).

### 2.1.3. 1-Benzyl-1'-(n-3-bromoprop-1-yl)-4,4'-bipyridinium ( $\text{BrC}_3\text{V}_B$ )

$\text{BrC}_3\text{V}_B$  was prepared analogously to the procedure described above for the preparation of  $\text{BrC}_4\text{V}_B$ , with the substitution of 1,3-dibromopropane.  $^1\text{H-NMR}$  in  $\text{DMSO-}d_6$ :  $\delta$  (ppm) 9.45–9.6 (d, 2H), 9.3–9.45 (d, 2H), 8.7–8.85 (multiplet, 4H), 7.4–7.7 (multiplet, 5H), 5.8–5.85 (s, 2H), 4.7–4.9 (t, 2H), 3.55–3.7 (t, 2H), 2.5–2.7 (quintet, 2H).

### 2.1.4. 1-Benzyl-1'-(n-4-[1-(4,4'-bipyridinium)]but-1-yl]-4,4'-bipyridium ( $\text{BpyC}_4\text{V}_B$ )

$\text{BrC}_4\text{V}_B$  (2.0 mmol) and 4,4'-bipyridinium (excess) were dissolved in 150 ml of MeCN and heated to reflux for 12 h. The mixture was filtered to remove the precipitate and the product was precipitated by the addition of tetraethylammonium bromide ( $(\text{C}_2\text{H}_5)_4\text{NBr}$ ). The yellow precipitate was collected by the suction filtration, washed with MeCN and dried under vacuum. The  $\text{Br}^-$  salt was recrystallized from EtOH and MeOH, and dried under vacuum. The yellow  $\text{Br}^-$  salt was dissolved in water and  $\text{NH}_4\text{PF}_6$  was added to replace the counter-anion with  $\text{PF}_6^-$ . The white  $\text{PF}_6^-$  salt was filtered and dried under vacuum.  $^1\text{H-NMR}$  in  $\text{DMSO-}d_6$ :  $\delta$  (ppm) 9.45–9.55 (d, 2H), 9.3–9.4 (d, 2H), 9.15–9.25 (d, 2H), 8.85–8.95 (dd, 2H), 8.7–8.8 (multiplet, 4H), 8.6–8.7 (d, 2H), 8.0–8.1 (dd, 2H), 7.4–7.7 (multiplet, 5H), 5.9–6.0 (s, 2H), 4.6–4.8 (multiplet, 4H), 2.0–2.1 (multiplet, 4H).

### 2.1.5. 1-Benzyl-1'-(n-3-[1-(4,4'-bipyridinium)]prop-1-yl]-4,4'-bipyridium ( $\text{BpyC}_3\text{V}_B$ )

$\text{BpyC}_3\text{V}_B$  was prepared analogously to the procedure described above for the preparation of  $\text{BpyC}_4\text{V}_B$ , with the substitution of  $\text{BrC}_3\text{V}_B$ .  $^1\text{H-NMR}$  in  $\text{DMSO-}d_6$ :  $\delta$  (ppm) 9.45–9.6 (d, 2H), 9.3–9.45 (d, 2H), 8.7–8.85 (multiplet, 4H), 7.4–7.7 (multiplet, 5H), 5.8–5.85 (s, 2H), 4.7–4.9 (t, 2H), 3.55–3.7 (t, 2H), 2.5–2.7 (quintet, 2H).

### 2.1.6. 1-Benzyl-1'-(n-4-[1'-(n-3-ammonioprop-1-yl)-4,4'-bipyridinium]]but-1-yl]-4,4'-bipyridium ( $\text{H}_2\text{NC}_3\text{V}_A\text{C}_4\text{V}_B$ )

$\text{BpyC}_4\text{V}_B$  was dissolved in 400 ml of MeCN, treated with excess 3-bromopropylamine hydrobromide and heated to reflux for 24 h. A yellow precipitate was filtered, washed with MeCN and dried under vacuum overnight. The product was recrystallized from EtOH and water, and then dissolved in water and solution of  $\text{NH}_4\text{PF}_6$  was added to replace the counter-anion with  $\text{PF}_6^-$ . The  $\text{PF}_6^-$  salt was filtered, washed with water and dried under vacuum overnight.  $^1\text{H-NMR}$  in  $\text{DMSO-}d_6$ :  $\delta$  (ppm) 9.5–9.6 (d, 2H), 9.35–9.5 (multiplet, 6H), 8.75–8.9 (multiplet, 8H), 7.5–7.7 (multiplet, 5H), 5.95–6.05 (s, 2H), 4.7–4.9 (multiplet, 6H), 2.85–3.0 (t, 2H), 2.2–2.4 (quintet, 2H), 2.05–2.2 (multiplet, 4H).

### 2.1.7. 1-Benzyl-1'-(n-3-[1'-(n-2-ammonioeth-1-yl)-4,4'-bipyridinium]]prop-1-yl]-4,4'-bipyridium ( $\text{H}_2\text{NC}_2\text{V}_A\text{C}_3\text{V}_B$ )

$\text{H}_2\text{NC}_2\text{V}_A\text{C}_3\text{V}_B$  was prepared analogously to the procedure described above for the preparation of  $\text{H}_2\text{NC}_3\text{V}_A\text{C}_4\text{V}_B$ , with the substitution of  $\text{BpyC}_3\text{V}_B$  and 2-bromoethylamine hydrobromide.  $^1\text{H-NMR}$  in  $\text{DMSO-}d_6$ :  $\delta$  (ppm) 9.55–9.6 (d, 2H), 9.35–9.5 (multiplet, 6H), 8.8–9.0 (multiplet, 8H), 7.5–7.7 (multiplet, 5H), 5.95–6.05 (s, 2H), 4.8–5.0 (multiplet, 6H), 3.5–3.6 (t, 2H), 2.75–2.9 (quintet, 2H).

### 2.1.8. Bisviologen linked 4-carboxy-2,2'-bipyridine-4'-carbodiimide ((dcbpy) $\text{C}_m\text{V}_A\text{C}_n\text{V}_B$ )

$\text{H}_2\text{NC}_m\text{V}_A\text{C}_n\text{V}_B$  and dcbpy were stirred in the presence of 1-hydroxybenzotriazole (1.5 equiv.) and 1,3-diisopropylcarbodiimide (excess) in the dry DMF at 30°C for 16 h. The solvent was removed under vacuum, dissolved in a minimum amount of MeCN and tetraethylammonium bromide ( $(\text{C}_2\text{H}_5)_4\text{NBr}$ ) was added to obtain the  $\text{Br}^-$  salt. The  $\text{Br}^-$  salt was dissolved in water and  $\text{NH}_4\text{PF}_6$  was added to replace the counter-anion with  $\text{PF}_6^-$ . The  $\text{PF}_6^-$  salt was recrystallized from water and dried under vacuum.  $^1\text{H-NMR}$  ((dcbpy) $\text{C}_3\text{V}_A\text{C}_4\text{V}_B$ ) in  $\text{DMSO-}d_6$ :  $\delta$  (ppm) 9.35–9.6 (multiplet, 10H), 8.75–9.0 (multiplet, 12H), 7.5–7.7 (multiplet, 5H), 5.95–6.05 (s, 2H), 4.7–4.9 (multiplet, 8H), 2.2–2.4 (quintet, 2H), 2.05–2.2 (multiplet, 4H).  $^1\text{H-NMR}$  ((dcbpy) $\text{C}_2\text{V}_A\text{C}_3\text{V}_B$ ) in  $\text{DMSO-}d_6$ :  $\delta$  (ppm) 9.2–9.6 (multiplet, 10H), 8.7–8.9 (multiplet, 12H), 7.45–7.7 (multiplet, 5H), 5.95–6.05 (s, 2H), 4.7–5.0 (multiplet, 6H), 3.95–4.1 (quintet, 2H), 2.65–2.85 (multiplet, 4H).

### 2.1.9. $\text{Ru}(\text{bpy})_2(\text{dcbpy})\text{C}_m\text{V}_A\text{C}_n\text{V}_B$ ( $m = 2, n = 3; m = 3, n = 4$ )

The tris(bipyridyl)ruthenium(II) complexes were prepared by refluxing  $\text{Ru}(\text{bpy})_2\text{Cl}_2 \cdot n\text{H}_2\text{O}$  with either (dcbpy)- $\text{C}_3\text{V}_A\text{C}_4\text{V}_B$  or (dcbpy)- $\text{C}_2\text{V}_A\text{C}_3\text{V}_B$  in 1:1 EtOH:H<sub>2</sub>O under argon. The reaction was monitored by UV-vis spectroscopy. The Ru(II) complexes were applied to a neutral alumina column to remove the impurity and starting material (1:1 acetone:ethanol). The desired products were eluted with methanol.

## 2.2. Spectroscopic measurements

UV-vis absorption spectra were measured in 25 mmol  $\text{dm}^{-3}$  Tris-HCl buffer (pH7.4) using a Shimadzu Multi-Spec-1500 spectrometer.

$^1\text{H-NMR}$  spectra were recorded on a Varian GEMINI-200. The chemical shifts were referenced to the solvent peak calibrated against tetramethylsilane (TMS).

The luminescence spectra were measured in 25 mmol  $\text{dm}^{-3}$  Tris-HCl buffer (pH7.4) at room temperature using a Hitachi F-4000 spectrometer. The absorbance at the excitation wavelength was kept constant at 0.3 for all sample solutions in these experiments.

Luminescence lifetime measurements were carried out by using time-correlated single-photon-counting (Horiba NAES-500 spectrometer) under argon.

### 2.3. Electrochemical measurement

The one-electron-reduction potentials were measured by the technique of the cyclic voltammetry (Hokuto Denko Potentiostat/Galvanostat HA-301, Function Generation HB-111, Riken Denso X-Y recorder). All measurements were carried out under argon in the solution containing 0.1 mol dm<sup>-3</sup> of NaCl and 50 mmol dm<sup>-3</sup> phosphate buffer (pH 7.0) at a carbon working electrode. A Pt was used as the counter electrode. All potentials are relative to Ag/AgCl electrode as the reference.

## 3. Results and discussion

### 3.1. Photophysical properties of $\text{Ru}(\text{bpy})_2(\text{dcbpy})\text{C}_m\text{V}_A\text{C}_n\text{V}_B$ and $\text{Ru}(\text{bpy})_2(\text{dcbpy})\text{C}_m\text{V}_A\text{C}_n$

The absorption maxima of  $\text{Ru}(\text{bpy})_2(\text{dcbpy})\text{C}_m\text{V}_A\text{C}_n\text{V}_B$ ,  $\text{Ru}(\text{bpy})_2(\text{dcbpy})\text{C}_m\text{V}_A\text{C}_n$  and  $\text{Ru}(\text{bpy})_2(\text{dcbpy})$  are listed in Table 1. As an example, the absorption spectra of  $\text{Ru}(\text{bpy})_2(\text{dcbpy})\text{C}_3\text{V}_A\text{C}_4\text{V}_B$ ,  $\text{Ru}(\text{bpy})_2(\text{dcbpy})\text{C}_3\text{V}_A\text{C}_4$  and  $\text{Ru}(\text{bpy})_2(\text{dcbpy})$  are shown in Fig. 2. The absorption spectra of  $\text{Ru}(\text{bpy})_2(\text{dcbpy})\text{C}_m\text{V}_A\text{C}_n\text{V}_B$  and  $\text{Ru}(\text{bpy})_2(\text{dcbpy})\text{C}_m\text{V}_A\text{C}_n$  are similar to that of  $\text{Ru}(\text{bpy})_2(\text{dcbpy})$ , indicating no electronic interaction between the  $\text{Ru}(\text{bpy})_2(\text{dcbpy})$  site and the binding bisviologen in the ground state.

The photoexcited states of  $\text{Ru}(\text{bpy})_2(\text{dcbpy})\text{C}_m\text{V}_A\text{C}_n\text{V}_B$  were studied using the luminescence emission spectra. As an example, the luminescence spectra of  $\text{Ru}(\text{bpy})_2(\text{dcbpy})\text{C}_3\text{V}_A\text{C}_4\text{V}_B$ ,  $\text{Ru}(\text{bpy})_2(\text{dcbpy})\text{C}_3\text{V}_A\text{C}_4$  and  $\text{Ru}(\text{bpy})_2(\text{dcbpy})$  are shown in Fig. 3. As an excitation wavelength, a peak wavelength of the MLCT band of ruthenium complexes was used. The absorbance at the excitation wavelength was kept constant to be 0.3 for all the sample solutions in these experiments. For  $\text{Ru}(\text{bpy})_2(\text{dcbpy})\text{C}_m\text{V}_A\text{C}_n\text{V}_B$  and  $\text{Ru}(\text{bpy})_2(\text{dcbpy})\text{C}_m\text{V}_A\text{C}_n$ , the shape of the luminescence spectra of  $\text{Ru}(\text{bpy})_2(\text{dcbpy})\text{C}_m\text{V}_A\text{C}_n\text{V}_B$  and  $\text{Ru}(\text{bpy})_2(\text{dcbpy})\text{C}_m\text{V}_A\text{C}_n$  are the same as that of  $\text{Ru}(\text{bpy})_2(\text{dcbpy})$ . However, the luminescence intensity of  $\text{Ru}(\text{bpy})_2(\text{dcbpy})\text{C}_m\text{V}_A\text{C}_n\text{V}_B$  and  $\text{Ru}(\text{bpy})_2(\text{dcbpy})\text{C}_m\text{V}_A\text{C}_n$  is lower than that of  $\text{Ru}(\text{bpy})_2(\text{dcbpy})$ . In addition, the photoexcited state of  $\text{Ru}(\text{bpy})_2(\text{dcbpy})\text{C}_m\text{V}_A\text{C}_n\text{V}_B$  was more effectively quenched than that of  $\text{Ru}(\text{bpy})_2(\text{dcbpy})\text{C}_m\text{V}_A\text{C}_n$  as shown in Fig. 3 (inset), indicating that two-step electron transfer may occur in the bisviologen linked ruthenium complex. These results indicate that the photoexcited state of  $\text{Ru}(\text{bpy})_2(\text{dcbpy})$  moiety is oxidatively quenched by the binding bisviologen due to an intramolecular electron transfer and no electronic interaction occurs between the  $\text{Ru}(\text{bpy})_2(\text{dcbpy})$  moiety and the binding bisviologen in the photoexcited state.

Table 1

Wavelength of absorption maxima of  $\text{Ru}(\text{bpy})_2(\text{dcbpy})\text{C}_m\text{V}_A\text{C}_n\text{V}_B$ ,  $\text{Ru}(\text{bpy})_2(\text{dcbpy})\text{C}_m\text{V}_A\text{C}_n$  and  $\text{Ru}(\text{bpy})_2(\text{dcbpy})$

Compound	Wavelength of absorption maxima (nm)		
$\text{Ru}(\text{bpy})_2(\text{dcbpy})$	244	287	458
$\text{Ru}(\text{bpy})_2(\text{dcbpy})\text{C}_2\text{V}_A\text{C}_3$	249	285	452
$\text{Ru}(\text{bpy})_2(\text{dcbpy})\text{C}_3\text{V}_A\text{C}_4$	254	285	454
$\text{Ru}(\text{bpy})_2(\text{dcbpy})\text{C}_2\text{V}_A\text{C}_3\text{V}_B$	255	284	454
$\text{Ru}(\text{bpy})_2(\text{dcbpy})\text{C}_3\text{V}_A\text{C}_4\text{V}_B$	255	283	455

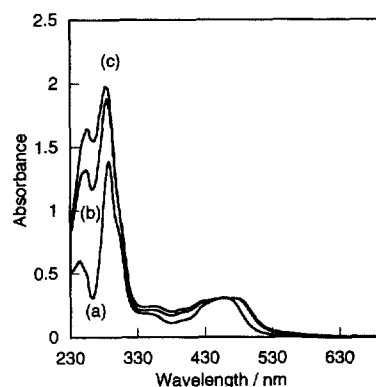


Fig. 2. Absorption spectra of  $\text{Ru}(\text{bpy})_2(\text{dcbpy})$  (a),  $\text{Ru}(\text{bpy})_2(\text{dcbpy})\text{C}_3\text{V}_A\text{C}_4$  (b) and  $\text{Ru}(\text{bpy})_2(\text{dcbpy})\text{C}_3\text{V}_A\text{C}_4\text{V}_B$  (c) in 25 mmol dm<sup>-3</sup> Tris-HCl buffer (pH 7.4).

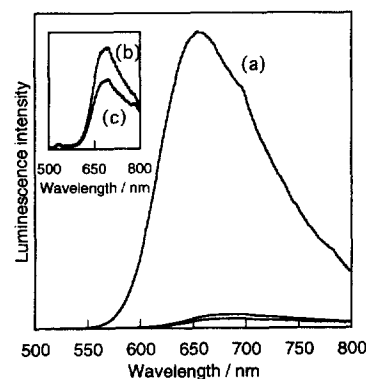


Fig. 3. Luminescence spectra of  $\text{Ru}(\text{bpy})_2(\text{dcbpy})$  (a),  $\text{Ru}(\text{bpy})_2(\text{dcbpy})\text{C}_3\text{V}_A\text{C}_4$  (b) and  $\text{Ru}(\text{bpy})_2(\text{dcbpy})\text{C}_3\text{V}_A\text{C}_4\text{V}_B$  (c) in 25 mmol dm<sup>-3</sup> Tris-HCl buffer (pH 7.4). The excitation wavelength was 450 nm. Inset shows the magnified Y-axis of the figure.

### 3.2. Electrochemical properties of $\text{Ru}(\text{bpy})_2(\text{dcbpy})\text{C}_m\text{V}_A\text{C}_n\text{V}_B$ and $\text{Ru}(\text{bpy})_2(\text{dcbpy})\text{C}_m\text{V}_A\text{C}_n$

The one-electron reduction potentials were measured by using the technique of cyclic voltammetry. The excitation energies of the  $\text{Ru}(\text{bpy})_2(\text{dcbpy})\text{C}_m\text{V}_A\text{C}_n\text{V}_B$  and  $\text{Ru}(\text{bpy})_2(\text{dcbpy})\text{C}_m\text{V}_A\text{C}_n$  were calculated from the average value of the frequencies of the longest wavelength of the absorption maxima and the shortest wavelength of luminescence emission maxima. From electrochemical and photophysical measurements, the estimates of the energy levels of  $\text{Ru}(\text{bpy})_2(\text{dcbpy})\text{C}_m\text{V}_A\text{C}_n\text{V}_B$  and  $\text{Ru}(\text{bpy})_2(\text{dcbpy})\text{C}_m\text{V}_A\text{C}_n$

Table 2

The first excited state energies of Ru(bpy)<sub>2</sub>(dcbpy) and redox potentials (vs. Ag/AgCl) for Ru(bpy)<sub>2</sub>(dcbpy), C<sub>m</sub>V<sub>A</sub>C<sub>n</sub> and C<sub>n</sub>V<sub>B</sub>

Compound	*P (eV) <sup>a</sup>	E <sub>o</sub> <sup>1</sup> (V) <sup>b</sup>	E <sub>r</sub> <sup>1</sup> (V) <sup>c</sup>
Ru(bpy) <sub>2</sub> (dcbpy)	2.23	1.14	
C <sub>2</sub> V <sub>A</sub> C <sub>3</sub>			-0.635
C <sub>3</sub> V <sub>A</sub> C <sub>4</sub>			-0.670
C <sub>3</sub> V <sub>B</sub>			-0.620
C <sub>4</sub> V <sub>B</sub>			-0.630

<sup>a</sup>\*P is the energy of the first excited state taken as the mean of the frequencies of the longest wavelength of the absorption maxima and the shortest wavelength of the emission maxima.

<sup>b</sup>E<sub>o</sub><sup>1</sup> is the first oxidation potential.

<sup>c</sup>E<sub>r</sub><sup>1</sup> is the first reduction potential.

C<sub>m</sub>V<sub>A</sub>C<sub>n</sub> are listed in Table 2. The energies of charge separated state of (Ru(bpy)<sub>2</sub>(dcbpy))<sup>+</sup>C<sub>m</sub>V<sub>A</sub><sup>-</sup>C<sub>n</sub>V<sub>B</sub>, (Ru(bpy)<sub>2</sub>(dcbpy))<sup>+</sup>C<sub>m</sub>V<sub>A</sub>C<sub>n</sub>V<sub>B</sub><sup>-</sup> and (Ru(bpy)<sub>2</sub>(dcbpy))<sup>+</sup>-C<sub>m</sub>V<sub>A</sub><sup>-</sup>C<sub>n</sub> were estimated from the first oxidation potential of Ru(bpy)<sub>2</sub>(dcbpy) and the first reduction potential of C<sub>m</sub>V<sub>A</sub>C<sub>n</sub> and C<sub>n</sub>V<sub>B</sub>. The results are listed in Table 3. No correction for Coulomb effects was attempted because of no interaction between each chromophore in the ground state.

For Ru(bpy)<sub>2</sub>(dcbpy)C<sub>m</sub>V<sub>A</sub>C<sub>n</sub>, the excited state of the ruthenium(II) complex lies at 2.23 eV above the ground state and the (Ru(bpy)<sub>2</sub>(dcbpy))<sup>+</sup>C<sub>m</sub>V<sub>A</sub><sup>-</sup>C<sub>n</sub> charge separated states lie at 1.78–1.81 eV. For Ru(bpy)<sub>2</sub>(dcbpy)C<sub>m</sub>V<sub>A</sub>C<sub>n</sub>V<sub>B</sub>, the excited state of the ruthenium(II) complex lies at

2.23 eV above the ground state. The charge separated states of (Ru(bpy)<sub>2</sub>(dcbpy))<sup>+</sup>C<sub>m</sub>V<sub>A</sub><sup>-</sup>C<sub>n</sub>V<sub>B</sub> and (Ru(bpy)<sub>2</sub>(dcbpy))<sup>+</sup>C<sub>m</sub>V<sub>A</sub>C<sub>n</sub>V<sub>B</sub><sup>-</sup> lie at 1.78–1.81 eV and 1.76–1.77 eV above ground state, respectively. This result indicates that the two-step electron transfer occurs and the back electron transfer is suppressed. Scheme 3 shows the energy levels of the transient states of Ru(bpy)<sub>2</sub>(dcbpy)C<sub>m</sub>V<sub>A</sub>C<sub>n</sub>V<sub>B</sub> estimated from Table 3. The electron transfer pathways are considered as shown in Scheme 3. Step 1 represents non-radiative and radiative processes. Step 2, 3 and 5 represent electron transfer processes and step 4 and 6 represent charge recombination processes. In the case of Ru(bpy)<sub>2</sub>(dcbpy)-C<sub>m</sub>V<sub>A</sub>C<sub>n</sub>V<sub>B</sub>, the energy difference between the excited state of ruthenium(II) complex and each charge separated state is 0.42–0.45 and 0.46–0.47 eV. From the luminescence and electrochemical measurements, the charge separated state between the ruthenium complex moiety and binding bisviologen may be much longer than that of Ru(bpy)<sub>2</sub>(dcbpy)-C<sub>m</sub>V<sub>A</sub>C<sub>n</sub>, because the effective two-step electron transfer from photoexcited ruthenium complex moiety to bisviologen can occur and the back electron transfer is suppressed in the bisviologen linked ruthenium complexes as shown in Scheme 3.

### 3.3. Photoexcited states of Ru(bpy)<sub>2</sub>(dcbpy)C<sub>m</sub>V<sub>A</sub>C<sub>n</sub>V<sub>B</sub>

The photoexcited state lifetime of Ru(bpy)<sub>2</sub>(dcbpy)-C<sub>m</sub>V<sub>A</sub>C<sub>n</sub>V<sub>B</sub> was measured by time-correlated single photon counting. The results are listed in Table 4. For Ru(bpy)<sub>2</sub>-

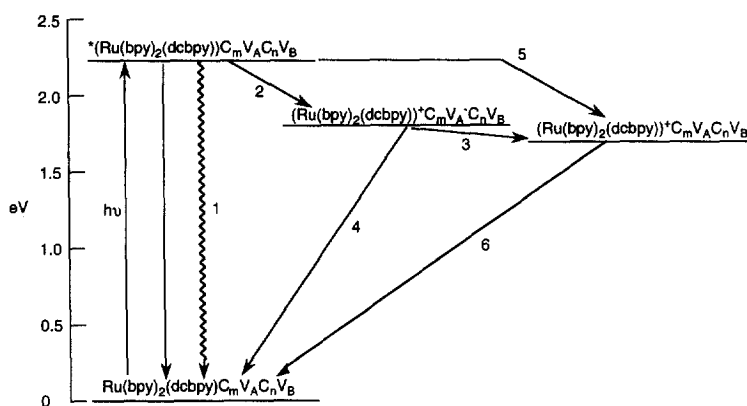
Table 3

Energies of the first excited state and the charge-separated state of Ru(bpy)<sub>2</sub>(dcbpy)C<sub>m</sub>V<sub>A</sub>C<sub>n</sub>V<sub>B</sub> and Ru(bpy)<sub>2</sub>(dcbpy)C<sub>m</sub>V<sub>A</sub>C<sub>n</sub>V<sub>B</sub>

Compound	*P (eV) <sup>a</sup>	E((Ru(bpy) <sub>2</sub> (dcbpy)) <sup>+</sup> C <sub>m</sub> V <sub>A</sub> <sup>-</sup> C <sub>n</sub> ) (eV) <sup>b</sup>	E((Ru(bpy) <sub>2</sub> (dcbpy)) <sup>+</sup> C <sub>m</sub> V <sub>A</sub> <sup>-</sup> C <sub>n</sub> V <sub>B</sub> ) (eV) <sup>b</sup>	E((Ru(bpy) <sub>2</sub> (dcbpy)) <sup>+</sup> C <sub>m</sub> V <sub>A</sub> C <sub>n</sub> V <sub>B</sub> <sup>-</sup> ) (eV) <sup>b</sup>
Ru(bpy) <sub>2</sub> (dcbpy)C <sub>2</sub> V <sub>A</sub> C <sub>3</sub> V <sub>B</sub>	2.23		1.78	1.76
Ru(bpy) <sub>2</sub> (dcbpy)C <sub>3</sub> V <sub>A</sub> C <sub>4</sub> V <sub>B</sub>	2.23		1.81	1.77
Ru(bpy) <sub>2</sub> (dcbpy)C <sub>2</sub> V <sub>A</sub> C <sub>3</sub>	2.23	1.78		
Ru(bpy) <sub>2</sub> (dcbpy)C <sub>3</sub> V <sub>A</sub> C <sub>4</sub>	2.23	1.81		

<sup>a</sup>\*P is the energy of the first excited state taken as the mean of the frequencies of the longest wavelength of the absorption maxima and the shortest wavelength of the emission maxima.

<sup>b</sup>Calculated from the results of cyclic voltammetric measurements.



Scheme 3.

Table 4

Luminescence lifetimes of Ru(bpy)<sub>2</sub>(dcbpy)C<sub>m</sub>V<sub>A</sub>C<sub>n</sub>V<sub>B</sub> and Ru(bpy)<sub>2</sub>(dcbpy)C<sub>m</sub>V<sub>A</sub>C<sub>n</sub>

Compound	$\tau_{\text{mono}}/10^{-9}$ s	$\tau_{\text{bis}}/10^{-9}$ s
Ru(bpy) <sub>2</sub> (dcbpy)C <sub>2</sub> V <sub>A</sub> C <sub>3</sub>	$\tau_s$ : 3.9 (86%), $\tau_l$ : 11.6 (14%)	
Ru(bpy) <sub>2</sub> (dcbpy)C <sub>3</sub> V <sub>A</sub> C <sub>4</sub>	$\tau_s$ : 3.7 (83%), $\tau_l$ : 18.6 (17%)	
Ru(bpy) <sub>2</sub> (dcbpy)C <sub>2</sub> V <sub>A</sub> C <sub>3</sub> V <sub>B</sub>		$\tau_s$ : 1.5 (86%), $\tau_l$ : 6.9 (14%)
Ru(bpy) <sub>2</sub> (dcbpy)C <sub>3</sub> V <sub>A</sub> C <sub>4</sub> V <sub>B</sub>		$\tau_s$ : 1.2 (76%), $\tau_l$ : 20.9 (24%)

(dcbpy), the luminescence decay was first order kinetics and the excited lifetime was determined as 507 ns. For the mono- and bisviologen linked ruthenium complexes, the luminescence decays of Ru(bpy)<sub>2</sub>(dcbpy)C<sub>m</sub>V<sub>A</sub>C<sub>n</sub>V<sub>B</sub> and Ru(bpy)<sub>2</sub>(dcbpy)C<sub>m</sub>V<sub>A</sub>C<sub>n</sub> were much shorter than that of Ru(bpy)<sub>2</sub>(dcbpy) due to the quenching of photoexcited Ru(bpy)<sub>2</sub>(dcbpy) moiety by the binding viologen. This result also indicates that the oxidative quenching of photoexcited state of Ru(bpy)<sub>2</sub>(dcbpy) site is the major deactivation pathway of the photoexcited state. In the case of mono- and bisviologen linked ruthenium complexes, the decays obeyed double exponential kinetics. The reason of two components of lifetime is explained as follows. For the mono- and bisviologen linked ruthenium complexes, there may be two conformers. In quinone linked porphyrins, two conformers are proposed by Siemiarz et al. [18]. A shorter component ( $\tau_s$ ) is attributed to the intramolecular electron transfer reaction and a longer component ( $\tau_l$ ) is not attributed to the electron transfer.

The photoexcited lifetimes ( $\tau_s$ ) of Ru(bpy)<sub>2</sub>(dcbpy)-C<sub>m</sub>V<sub>A</sub>C<sub>n</sub>V<sub>B</sub> are shorter than that of Ru(bpy)<sub>2</sub>(dcbpy)-C<sub>m</sub>V<sub>A</sub>C<sub>n</sub>, indicating that the photoexcited ruthenium complex moiety in Ru(bpy)<sub>2</sub>(dcbpy)C<sub>m</sub>V<sub>A</sub>C<sub>n</sub>V<sub>B</sub> is quenched by V<sub>A</sub> and V<sub>B</sub> as shown in Scheme 4, where Ru<sup>2+</sup> represents Ru(bpy)<sub>2</sub>(dcbpy) moiety.

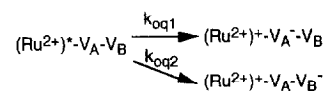
From Scheme 4, the intramolecular electron transfer rate constants ( $k_{\text{oq1}}$ ,  $k_{\text{oq2}}$ ) can be determined from the measured lifetime of photoexcited ruthenium complexes according to Eqs. (1) and (2).

$$k_{\text{bis}} = k_{\text{oq1}} + k_{\text{oq2}} = \frac{1}{\tau_{\text{bis},s}} - \frac{1}{\tau_d} \quad (1)$$

$$k_{\text{oq1}} = \frac{1}{\tau_{\text{mono},s}} - \frac{1}{\tau_d} \quad (2)$$

where  $\tau_d$  is the excited state lifetime of the viologen free ruthenium(II) complex.  $\tau_{\text{mono},s}$  and  $\tau_{\text{bis},s}$  are the shorter components of excited state lifetimes of the mono- and bisviologen linked ruthenium complexes, respectively. The apparent intramolecular electron transfer rate ( $k_{\text{bis}}$ ) in Ru(bpy)<sub>2</sub>(dcbpy)C<sub>m</sub>V<sub>A</sub>C<sub>n</sub>V<sub>B</sub> represents as follows,  $k_{\text{bis}} = k_{\text{oq1}} + k_{\text{oq2}}$ . As  $k_{\text{oq1}}$  value is the same as the intramolecular electron transfer rate in Ru(bpy)<sub>2</sub>(dcbpy)C<sub>m</sub>V<sub>A</sub>C<sub>n</sub>,  $k_{\text{oq1}}$  represents as shown in Eq. (2). The intramolecular electron transfer rate constants are given in Table 5.

The electrochemical measurements show that the two step electron transfer from the photoexcited state of ruthenium



Scheme 4.

Table 5

Intramolecular electron transfer rates of Ru(bpy)<sub>2</sub>(dcbpy)C<sub>m</sub>V<sub>A</sub>C<sub>n</sub>V<sub>B</sub> and Ru(bpy)<sub>2</sub>(dcbpy)C<sub>m</sub>V<sub>A</sub>C<sub>n</sub>

Compound	$k_{\text{oq1}}/10^8$ s <sup>-1</sup>	$k_{\text{oq2}}/10^8$ s <sup>-1</sup>
Ru(bpy) <sub>2</sub> (dcbpy)C <sub>2</sub> V <sub>A</sub> C <sub>3</sub>	2.54	
Ru(bpy) <sub>2</sub> (dcbpy)C <sub>3</sub> V <sub>A</sub> C <sub>4</sub>	2.68	
Ru(bpy) <sub>2</sub> (dcbpy)C <sub>2</sub> V <sub>A</sub> C <sub>3</sub> V <sub>B</sub>	2.54	4.10
Ru(bpy) <sub>2</sub> (dcbpy)C <sub>3</sub> V <sub>A</sub> C <sub>4</sub> V <sub>B</sub>	2.68	5.63

complex to bisviologen may occur. On the other hand, the luminescence lifetime measurements suggest that the electron transfers from the photoexcited ruthenium complex moiety to V<sub>A</sub> and V<sub>B</sub>. These results indicate that the two step electron transfer may occur with the concomitant electron transfer from the photoexcited state of ruthenium complex moiety to V<sub>A</sub> and V<sub>B</sub>.

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