Synthesis and Photoinduced Electron Transfer Processes in Ru(II)(bpy)$_2$/Os(III)(bpy)$_2$-Based Triad Complexes Containing Functionalized Diimide Ligands

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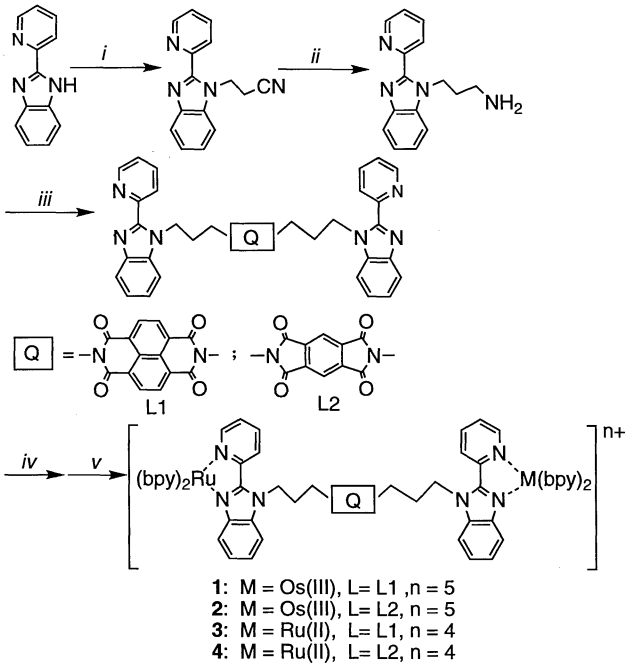
(Received March 13, 1997; CL-970184)

The charge separated(CS) state was efficiently formed as a result of stepwise electron transfer reactions in a novel Ru(II)(bpy)$_2$-diimide-Os(III)(bpy)$_2$ triad system (efficiency > 0.7); the rate of electron transfer and the charge separation yield were determined from picosecond time-resolved absorption spectra.

The successive electron transfer reactions occurring in the molecular arrays have attracted much attention toward mimicking the photosynthetic center in photosynthetic lipid membrane.[1] In order to achieve long-range charge separation with high efficiency the photosynthetic center uses a multi step sequence of electron transfer through an ensemble of donor and acceptor moieties. One of the simplest representative models for mimicking the photosynthetic center is a dyad or triad system which consists of electron donors(D) and/or acceptors(A) with different molecular sequences in the array such as D-A, D-D'-A, and D-A-A'.[2] In these array systems, the porphyrin or [Ru(bpy)$_3$]$^{2+}$ (bpy = 2,2'-bipyridine) as a chromophore of electron donor has been used, and quinone or methylviologen as an electron acceptor.[1,3] However, even in these model compounds, obtaining long-lived CS state with high efficiency is still difficult; only low efficiency (<0.6) has been achieved especially for the charge-separation in triads containing Ru(II) complexes.[4] Here, we report efficient charge separation in a novel molecular D-A-A' triad system involving M(bpy)$_2$ (M=Ru(II) and Os(III)) moieties with a diimide unit.[5]



Scheme 1. (*i*) CH_2=CHCN/Me_4NOH in dioxane,(*ii*) $NaBH_4$/$CoCl_2$•$6H_2O$ in MeOH, (*iii*) Dianhydride/Et_3N in toluene, (*iv*) M(bpy)$_2$Cl$_2$ in EtOH/H_2O, (*v*) Ru(bpy)$_2$Cl$_2$ in EtOH/H_2O.

The ligand, bis(2-pyridylbenzimidazolyl)-diimide (L1 or L2), was prepared from (2-pyridyl)benzimidazole as a starting compound (Scheme 1). The mixed-metal dinuclear complex, [Ru(bpy)$_2$(L)Os(bpy)$_2$](ClO$_4$)$_4$(L = L1(**1**) or L2 (**2**)), was prepared from the reaction of Ru(bpy)$_2$Cl$_2$ with mononuclear complex, [Os(bpy)$_2$(L)](ClO$_4$)$_2$(L=L1 or L2). For comparison, homodinuclear Ru complex, [Ru(bpy)$_2$(L)Ru(bpy)$_2$](ClO$_4$)$_4$ (L = L1 (**3**) or L2 (**4**)), was also synthesized according to the synthetic route as shown in Scheme 1. All new complexes **1**~**4** gave satisfactory ^{1}H NMR, MS, and elemental analyses. The Ru dinuclear complexes **3** and **4** exhibit a characteristic MLCT absorption band at 459 nm. The absorption spectra of mixed-metal RuOs dinuclear complexes **1** and **2** are essentially the sum of those of its components.

Cyclic voltammogram of complex **1** shows two oxidation processes at +0.37 and +0.79 V and four reduction processes at -0.91, -1.28, -1.73, -1.95 V vs Fc$^+$/Fc in CH_3CN. The first and second oxidations correspond to Os(II/III) and Ru(II/III)-based processes, respectively.[6] Furthermore, the first and second reductions are L1$^{0/-}$ and L1$^{-/2-}$ based and the third and fourth ones are bpy based processes.[6] Complex **2** gave similar electrochemical behaviors except for reduction processes: only two waves were observed at -1.74 and -2.08 V vs Fc$^+$/Fc corresponding to succesive bpy reductions. The L2 imide reduction process of complex **2** has not been observed by electrochemical methods probably because of the steric hindrance around L2 moiety by two Ru(bpy)$_2$ groups, since the reduction process of L2 for mononuclear [Ru(bpy)$_2$(L2)]$^{2+}$ was observed at -1.18 V vs Fc$^+$/Fc under the same condition.

The homodinuclear Ru(II)-L1-Ru(II) complex **3** in CH_3CN (1.5×10^{-4} mol dm^{-3}) was irradiated using the second harmonics (532 nm, FWHM: 17 ps) of a Nd^{3+}:YAG mode-locked laser. The picosecond time-resolved absorption(TA) spectra observed at 15ps after excitation exhibits the bleaching of an MLCT band at 459 nm and the rise of absorption around 400 and 550 nm due to the anion radical of bpy ligand, indicating the formation of an MLCT triplet excited state of the Ru(II) moiety. In 200 ps, several absorption peaks appeared at 470, 610, 682, and 756 nm, which are characteristics of the L1 anion radical.[2a] These new TA peaks then disappeared with a single exponential decay (rate constant = 2.9×10^9 s^{-1}) through back electron transfer to reproduce the original form. The yield of formation of the CS state (Ru(III)-(L1$^-$)-Ru(II)) is calculated as 80-100% using the difference in extinction coefficients ($\Delta\varepsilon$) of the corresponding model complexes on the excitation of [Ru(bpy)$_2$(L3)]$^{2+}$ (-7800 dm^3 mol^{-1} cm^{-1} at 460 nm), and the redox process of [Ru(bpy)$_2$(L3)]$^{2+/3+}$(-12700 dm^3 mol^{-1} cm^{-1} at 470 nm) (where L3 = *N*-methyl-2-(2-pyridyl)benzimidazole),[7] and NIm$^{0/-}$(21500

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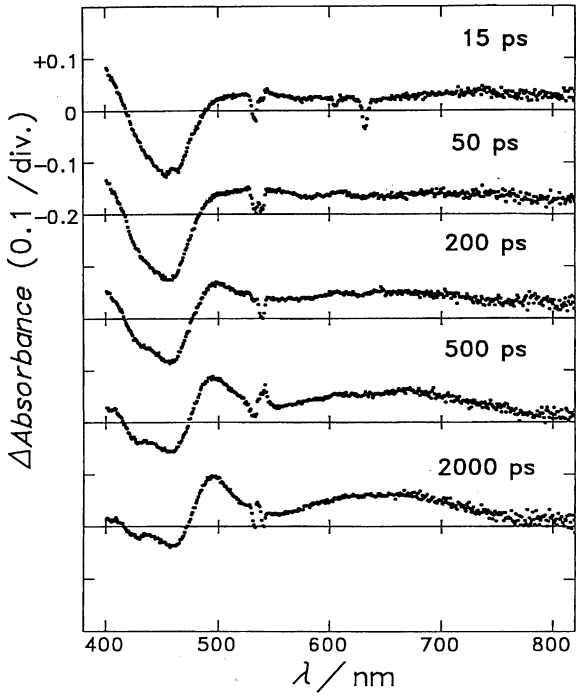
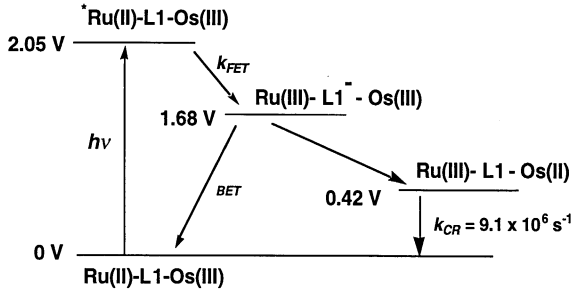


Figure 1. Picosecond time-resolved transient absorption spectra of complex **1**, $[Ru(bpy)_2(L1)Os(bpy)_2](ClO_4)_5$, in CH_3CN (3×10^{-4} mol dm^{-3}) at room temperature.

$dm^3mol^{-1}cm^{-1}$ at 470 nm)(NIm =*N,N'*-dihexyl-1,4,5,8-naphthalenediimide).[2a] Thus, the rate constants of the photoinduced electron transfer between the $Ru(bpy)_2$ and L1 for complex **3** are determined as $(1.1 \pm 0.1) \times 10^{10}$ s^{-1} and 2.9×10^9 s^{-1} from the excited state decay and the charge separation yield. The decay of the Ru(II)-MLCT excited state for complex **4** was found multi-exponential (rate constant = 2×10^{10} s^{-1}, $<10^7$ s^{-1}) as a result of the presence of conformational isomers arising from the propane groups.

The Ru(II)-L1-Os(III) mixed-valent complex **1** was selectively formed by one-electron oxidative electrolysis of Ru(II)-L1-Os(II) complex (3×10^{-4} mol dm^{-3}) at +0.5V in CH_3CN containing a supporting electrolyte (0.1 mol dm^{-3} *n*-Bu_4NClO_4).[6b] The TA spectrum of complex **1** immediately after the excitation shows the formation of Ru(II)-MLCT excited state as shown in Figure 1. A tiny tip at 610 nm appeared in 50 ps, followed by the appearance of absorption bands at 500 and 650 nm due to an Os(II)-MLCT. The tiny absorption at 610 nm appeared only in the earliest stage could indicate the formation of L1 anion radical. The fast electron transfer from $L1^-$ anion to Os(III) site gave a CS Ru(III)-L1-Os(II) state, which is the redox isomer state of the starting complex. The back electron transfer from $L1^-$ anion to Ru(III) site would reduce the production yield of the CS state that was estimated 75% from the transient absorption at 650 nm using the difference in extinction coefficients of the model complexes.[7] By considering the similarity of TA spectra for the early stage in both homodinuclear Ru complex **3** and mixed-valence complex **1**, the electron transfer occurred from Ru(II) to L1 at first, followed by rapid electron transfer from L1 anion radical to Os(III). The rate of charge recombination(CR) from Os(II) to Ru(III) is calculated as 9.1×10^6 s^{-1} (τ =110 ns). This slow CR rate implies the diimide unit keeps the Ru(III) and Os(II)



Scheme 2. Energy diagram for photoinduced electron transfer reaction in complex **1** in CH_3CN.

moieties apart from each other even though three donor or acceptor units are connected by a somewhat flexible propane linker. The direct photoinduced electron transfer process from Ru(II)-MLCT excited state to Os(III) is much slower compared to the stepwise electron transfer, which was confirmed by the comparative TA measurement of analogous Ru(II)-L2-Os(III) complex **2**; little detectable CS state of complex **2** was observed within the same time domain.

M. H. thanks the Iketani Science and Technology Foundation for the financial support. M. D. H also acknowledges the Ministry of Education, Science, Sports and Culture for a Japanese Government(Monbusho) Scholarship.

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