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Photoexcited states of dinuclear Ru complexes bridged by proton-dissociable benzimidazole derivatives

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Abstract

New dinuclear Ru complexes containing proton dissociable benzimidazole derivatives have been prepared, in which 2,2'-bis(2-benzimidazolyl)-4,4'-bipyridine(bbbpyH_2) is introduced as a new bridging ligand. New dinuclear Ru complexes can be classified into three types according to the number of the dissociable protons and redox activity of the central metal ions.
Three types of complexes exhibit different switching modes on the redox behaviors, emission, or metal-metal interaction. The proton dissociation in dinuclear Ru complexes leads to the changes of redox potentials and donor property of the ligand, which induces the switching of redox and photochemical properties in the complexes.

Introduction

The intramolecular electron transfer process between metal ions in ligand-bridged di- or oligonuclear complexes has paid much attention in order to understand the factors controlling the rate of electron transfer[1]. Several factors such as the donor-acceptor distance, the free-energy change of the reaction and the polarity of the solvent have been recognized to be responsible for the rate of electron transfer. In order to exploring the dependencies of the separation distance or the extent of the electronic interaction, various spacer groups have been used to connect the donor and acceptor groups[2]. Recently, dinuclear ruthenium complexes with polyene bridging ligands have been synthesized and proposed to have potential as a building block for synthesizing molecular level devices such as molecular size "wires"[3].

On the other hand, if a bridging ligand can respond to an external perturbation such as proton transfer or ion complexation, molecular switching in these supramolecular complexes can be achieved. The example of such a ligand-bridged di- or oligonuclear complex is relatively rare[4].

In the Ru complexes containing the proton dissociable LH, the thermodynamic relations between electron transfer, proton transfer and photoexcitation can be summarized by a three-dimensional cubic scheme(Fig. 1). This scheme is known as generalized Forster cycle[5], and the thermodynamic quantities in this scheme are correlated each other. This thermodynamic scheme inspires us to design the

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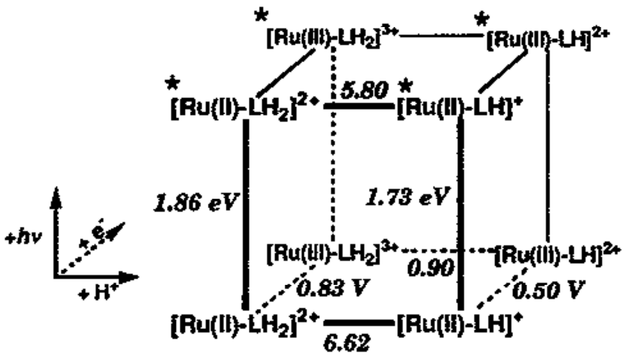

Fig. 1. Cubic Scheme involving one-electron transfer, one-proton transfer and photoexcitation for mononuclear $[Ru(bpy)_2(bbbpyH_2)]^{2+}$

supramolecular complexes which can possess a multi-mode activity for an external perturbation. The benzimidazole group has a σ/π-donor property and furthermore possesses a dissociative N-H proton. Once the benzimidazole unit is coordinated to the metal ion, the imino N-H proton becomes more acidic and can be easily dissociated. The deprotonation of the bridging ligand may induce the fairly large perturbation on the spectral and redox properties of dinuclear complexes. Recently, we have introduced a dinucleating ligand, 2,2'-bis(2-pyridyl)-bibenzimidazole($bpbimH_2$) in Fig. 2, and have elucidated that the dinuclear complexes exhibited the proton-induced switching of metal-metal interaction[6].

In order to generalize the proton-induced switching phenomena, several new bridging ligands containing benzimidazole moieties are introduced, and their dinuclear Ru and Os complexes are reported here. The influence of pH on the absorption spectra, oxidation potentials, and transient absorption spectra is investigated.

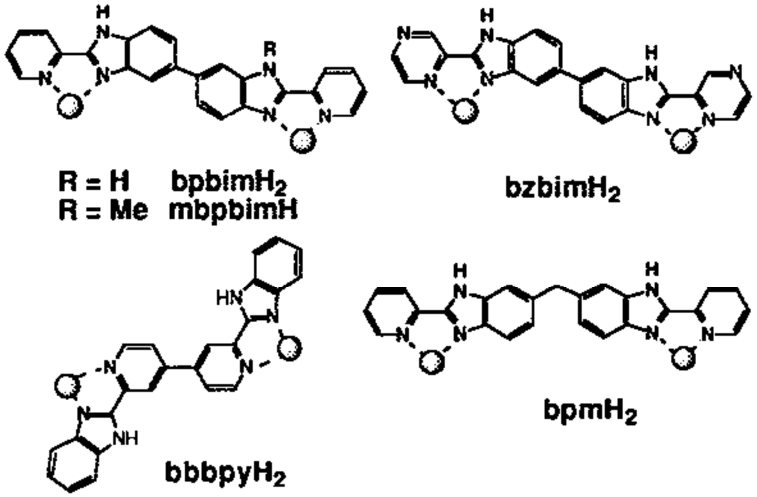

Fig. 2. Bridging ligands and their abbreviations

Three Different Types of Ru Dinuclear Complexes Containing Proton Dissociable Benzimidazole Derivatives

Several bridging ligands shown in Fig. 2 were used to bridge the M(bpy)$_2$ (M=Ru, Os, or Rh) moieties. These bridging ligands have different structural aspects such as separation distance and the number of dissociable protons. Among these ligands, 2,2'-bis(2-benzimidazolyl)-4,4'-bipyridine(bbbpyH$_2$) is one of structural isomers of bpbimH$_2$. The present dinuclear Ru complexes containing these bridging ligands can be classified into three types according to the number of the dissociable protons and redox activity of the central metal ions as shown in Fig. 3. Type 1 complex possesses two dissociable protons and two redox active metal ions. Type 2 complex has two dissociable protons and each different metal ion with respect to oxidation state or the kind; type 3 has one dissociable proton and two redox active centers. These three types behave quite differently.

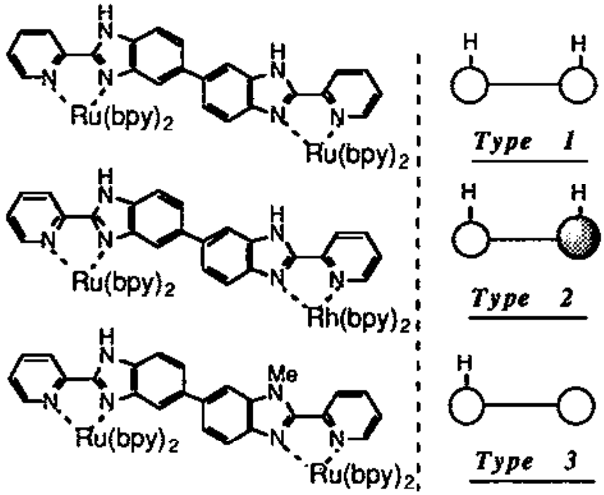

Fig. 3. Three Different Types of Dinuclear Complexes Bridged by Proton Dissociable Ligand ; The white and grey circles indicate the redox active and inactive(or different oxidation state) metal ions, respectively, and H on the circle stands for the dissociable proton.

Type 1 Dinuclear Complexes. The complex, [Ru(bpy)$_2$(L)Ru(bpy)$_2$]$^{4+}$ (L = bpbimH$_2$, bpmH$_2$, bzbimH$_2$ and bbbpyH$_2$), is the typical example of type 1 complexes. The bbbpyH$_2$ complex acts as a dibasic acid with pK_a values of 5.57 and 6.88 in CH$_3$CN/buffer(1:1 v/v). The redox potential of [Ru(bpy)$_2$(bbbpyH$_2$)Ru(bpy)$_2$]$^{4+}$ in CH$_3$CN shows two-electron oxidative process at +0.80 V , and three step-wise reduction processes at -1.32, -1.81, and -2.13 V vs Fc/Fc$^+$. The deprotonation on the bridging bbbpyH$_2$ results in the negative shift to +0.37 V for oxidation and -1.71 and -1.93 V for reduction. The proton-coupled redox reaction in CH$_3$CN/buffer(1:1 v/v) is proved by $E_{1/2}$ - pH plots (Pourbaix diagram)(Fig. 4). The $E_{1/2}$ - pH plots consists of four lines with slopes of -30 mV(pH 0.8 - 1.4), - 60 mV(pH 1.4 - 5.7), -30 mV(pH 5.7 - 7.2), and 0 mV/pH(pH>7.2). The break point of the two lines gives pK_a values. The MLCT absorption maxima of [Ru(bpy)$_2$(bbbpyH$_2$)Ru(bpy)$_2$](ClO$_4$)$_4$ is observed at 498 nm, and emission maxima

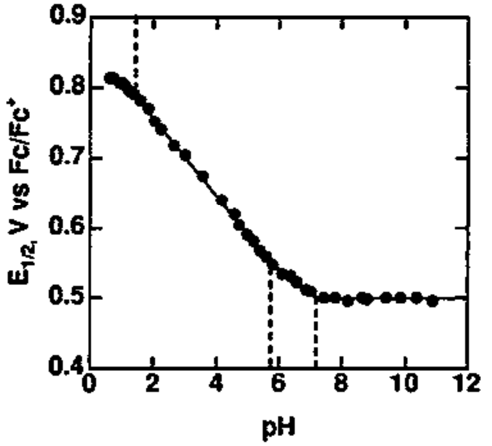

Fig. 4. The oxidation potentials $E_{1/2}$ - pH diagram for [Ru(bpy)$_2$(bbbpyH$_2$)Ru-(bpy)$_2$](ClO$_4$)$_4$ in CH$_3$CN - buffer(1:1 v/v)

at 719 nm with 202 ns. Recently, dinuclear complex bridged by 2,2':4',4'':2'',2'''-quaterpyridine(qpy) has been reported[7]. The dinuclear qpy complex showed MLCT absorption maxima at 471 nm and emitted at 685 nm with a surprisingly long lifetime of 2.0 μs, in sharp contrast to 202 ns for bbbpyH$_2$ complex.

The transient absorption(TA) spectrum of protonated [Ru(bpy)$_2$(bbbpyH$_2$)Ru(bpy)$_2$](ClO$_4$)$_4$ exhibits three bleached bands at 500, 430 and 343nm and three enhanced ones at 580, 380, and 310nm(Fig. 5a). Strong bleaching of π–π* transition of bbbpyH$_2$ at 343 nm indicates the reduction of bbbpyH$_2$. Comparing with the TA spectra of related Ru benzimidazole complexes[8], the appearance of the band at 580 nm is assigned to a π–π* band of bbbpyH$_2^-$. The deprotonation from the bridging ligand leads to the drastic change

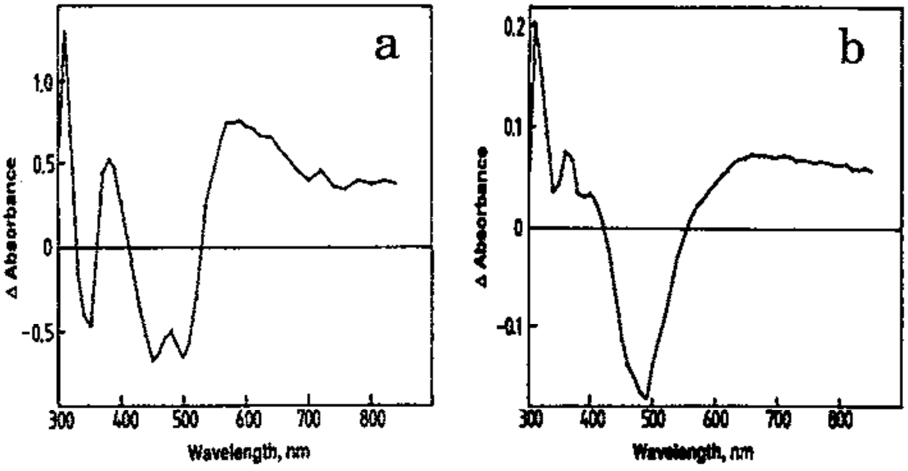

Fig. 5. TA spectra for protonated [Ru(bpy)$_2$(bbbpyH$_2$)Ru(bpy)$_2$](ClO$_4$)$_4$ (a) and its deprotonated form (b) in CH$_3$CN at room temperature.

in the TA spectrum; two bleached bands at 490nm and three enhanced ones at 675, 362, and 310 nm, and no bleaching is observed in the region for the π–π* transition of bbbpy(343nm) and no appreciable appearance of the band at 580 nm(Fig. 5b). These data indicates the deprotonation brings the change of the localized site of excited electron from bridging ligand to the peripheral bpy ligand.

The intervalence charge transfer(IT) bands are observed in the near infrared region for all the mixed-valence dinuclear complexes with the bridging ligands shown in Fig. 2. The bbbpyH_2 dinuclear complex exhibits the IT band at 8350 cm^{-1} (ε 170 $M^{-1}cm^{-1}$). The degree of the electronic coupling between the metal centers, H_{AB}, is calculated as 120 cm^{-1}. Upon the deprotonation of the bridging ligand, the IT band was unfortunately concealed beneath the strong LMCT band around 900 nm. In the case of bpbimH_2 bridged system, the proton induced switching of IT bands has been clearly observed[6].

Type 2 Dinuclear Complexes. Heterodinuclear $[Ru(bpy)_2(bpbimH_2)Rh(bpy)_2]^{5+}$ belongs to type 2 complex. The macroscopic pKa values for $[Ru(bpy)_2(bpbimH_2)Rh(bpy)_2]^{5+}$ is 2.25 and 6.27. In the Ru(II)-Rh(III) complex, the different oxidation states of both metal ions lead to larger pK_a difference, which leads to the selective proton transfer in the hetero-dinuclear complex. The diprotonated $[Ru(bpy)_2(bpbimH_2)Rh(bpy)_2]^{5+}$ is non-emissive due to the intramolecular electron transfer from excited Ru(II) site to Rh(III) one, however the emission was observed in monoprotonated state(Fig. 6). This observed emissive switching can be rationalized by the preferential deprotonation of the benzimidazole moiety on the Rh(III) site, accompanying the negative potential shift in the reduction potential on the Rh(III) site[9].

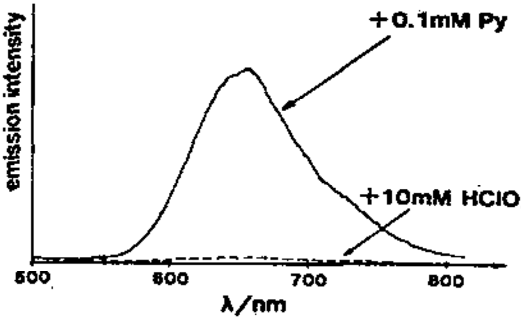

Fig. 6. Emission spectra of $[Ru(bpy)_2(bpbimH_{2-n})Rh(bpy)_2]^{(5-n)+}$ in CH_3CN containing 0.1mM pyridine(——) and 10mM $HClO_4$(----).

Type 3 Dinuclear Complexes. The complex, $[Ru(bpy)_2(mbpbimH)Ru(bpy)_2]^{4+}$, has an asymmetric structure with respect to the bridging ligand, and this Ru complex is classified to type 3. The mbpbimH complex acts as a monobasic acid with pK_a of 5.91. Cyclic voltammograms of protonated and deprotonated complexes are shown in Fig. 7. At the protonated state, only one two-electron wave at +0.78 V was observed. On the other hand, two well-separated one-electron waves at +0.32 and +0.78 V vs Fc/Fc$^+$ were observed when the deprotonation has occurred on the bridging ligand moieties. The switching from two-electron to two one-electron processes was observed.

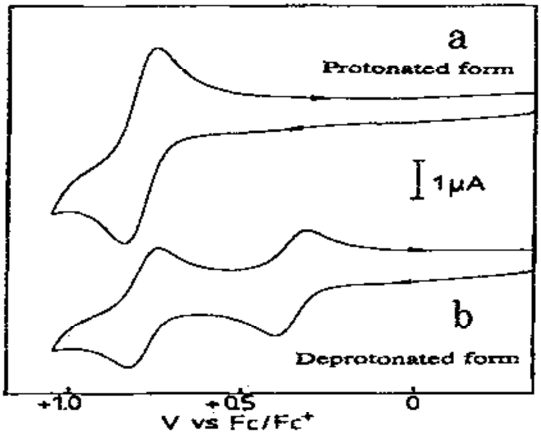

Fig. 7. Cyclic voltammograms of protonated [Ru(bpy)$_2$(mbpbimH)Ru(bpy)$_2$]$^{4+}$ (a) and its deprotonated form (b) in CH_3CN.

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