Synthesis of Metal Complexes Aiming at Reversible Conversion between Chemical Energy and Electrical One

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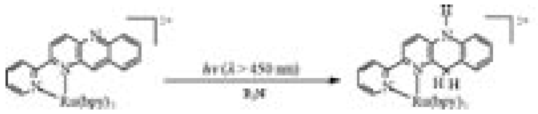
Metal ions involved in various metal proteins play key roles to generate metabolic energies through redox reactions of bio-organic molecules. Metal complexes that have an ability to oxidize organic molecules at potentials more negative than reduction of dioxygen are feasible molecular energy converters from chemical energy to electrical one. High valent Ru=O complexes are prepared by sequential proton and electron loss of the correspondent aqua-Ru complexes. Although some of them are active for the oxidation of organic molecules, the oxidation potentials required to convert from Ru-OH_2 to high valent Ru=O species are generally too positive for the purpose of the use as the energy converters. On the other hand, unusual Ru–oxyl radical complexes spontaneously are formed by deprotonation of aqua-Ru-dioxolene complexes due to intramolecular charge transfer from the negatively charged deprotonated aqua ligand to dioxolene (eq 1). Oxyl radical

$$\begin{aligned} &[\mathrm{Ru^{II}(dbQ)(trpy)(OH_2)}]^{2+} \underset{+\mathrm{H^+}}{\overset{-\mathrm{H^+}}{\rightleftharpoons}} [\mathrm{Ru^{II}(dbQ)(trpy)(OH^-)}]^{+} \\ &(\mathrm{dbQ} = \text{dibutylquinone}) \quad \underset{+\mathrm{H^+}}{\overset{-\mathrm{H^+}}{\rightleftharpoons}} [\mathrm{Ru^{II}(dbSQ)(trpy)(O^{\cdot -})}]^{0} \qquad (1) \end{aligned}$$

complexes formed in eq 1 are expected to have an ability to abstract hydrogen atom of C–H bonds of organic molecules, which would play the key role in the energy conversion from chemical energy to electrical one.

The difficulty in photochemical activation of small inorganic molecules such as N_2, O_2, CO_2, and H_2O results from the undesirable formation of high energy intermediates that are produced by stepwise one-electron transfer to the reaction centers. Recently, we showed that a mononuclear $[Ru^{II}(pbn)(bpy)_2]^{2+}$ (bpy = 2,2'-bipyridine, pbn = 2-(2-pyridyl)benzo[*b*]-1,5-naphthyridine) ($[\mathbf{1}]^{2+}$) is smoothly reduced to $[Ru(pbnH_2)(bpy)_2]^{2+}$ ($[\mathbf{1}H_2]^{2+}$) under visible light irradiation in the presence of sacrificial electron donors (eq 2). Furthermore, oxidation of $[\mathbf{1}H_2]^{2+}$ by appropriate oxidants smoothly regenerates $[\mathbf{1}]^{2+}$. Thus, the $[\mathbf{1}H_2]^{2+}/[\mathbf{1}]^{2+}$ redox couple is the first functional model of the nicotinamide adenine dinucleotide NAD^+/NADH redox reaction that works as a reservoir/source of two electrons and one proton in various biological energy transfer systems.



(2)

1. Synthesis and Electrochemical Reduction of Novel Ruthenium Complex Having *N*,*N*-Bis(benzo[*b*]-1,5-naphthyridin-2-ylmethyl)propane-2-amine Ligand as NAD^+/NADH Type Redox Site

Hydrogenation is one of the most important reactions in chemical transformations of a wide range of materials. A variety of metal-hydrides have been used in catalytic hydrogenation reactions under hydrogen gas, but those compounds are generally sensitive to water because of their high reactivity. Alternatively, electrocatalytic reduction without using hydrogen gas has several advantages such as clean, simple, safe, and easy regulation of reactivity of catalysts by choosing applied potentials. On the other hand, the nicotinamide adenine dinucleotide redox couple (NAD^+/NADH) functions as a reservoir/source of two electrons and one proton in various biological redox reactions. To mimic the efficiency and versatility of the NAD^+/NADH redox couple, a variety of model reactions have been conducted by using NADH model compounds. However, the reactions reported so far have been limited to stoichiometric ones. We, therefore, prepared $[Ru(bpy)_2(pbn)](PF_6)_2$ as a molecular electrocatalyst to simulate the function of the NAD^+/NADH redox couple. As mentioned above, the $[Ru(bpy)_2(pbn)]^{2+}/[Ru(bpy)_2(pbnH_2)]^{2+}$ redox couple well simulates the NAD^+/NADH couple. To improve the ability of

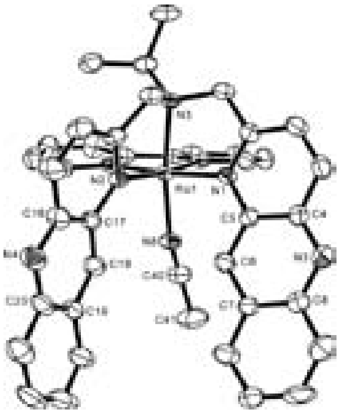


Figure 1. Crystal structure of [Ru(bbnma)(CH_3CN)]$^{2+}$.

multi-electron redox reaction of pbn, a new type of tridentate ligand, *N*,*N*-bis(benzo[*b*]-1,5-naphthyridin-2-ylmethyl) propane-2-amine (denoted as bbnma) possessing two benzo[*b*]-1,5-naphthyridines tethered to tertiary amine was designed and its ruthenium complex, [Ru(bbnma)(bpy)L](PF_6)$_2$, was synthesized. The conception of bbnma is to make a space not only to introduce substrates (*e.g.* ketones, imines, and related substrates) into the ruthenium center by a substitution reaction but also to place them forcibly at the vicinity of the two NADH type hydride sources generating on bbnam coordinated in a facial fashion (Figure 1). In fact, [Ru(bbnma)(bpy)(CO)]$^{2+}$ smoothly underwent four-electron reduction under the electrolysis at –0.95 V in the presence of pivalic acid, and [Ru(bbnmaH$_4$)(bpy)(CO)]$^{2+}$ was obtained in a high yield.

2. Photoinduced Four-, and Six-Electron Reduction of Mononuclear Ruthenium Complexes Bearing NAD$^+$ Analogous Ligands

The development of artificial photosynthetic processes aiming to generate high-energy molecules from low-energy ones (*e.g.* reduction of carbon dioxide or water splitting) is the top research priority to regulate consumption of non-renewable fossil fuels against the strong pressure of the energy demand that keeps increasing. Multi-electron reactions through stepwise one-electron transfer inevitably generate high-energy free radical intermaeiates, which often yield undesired products. Therefore construction of artificial photosynthetic systems that are able to mediate multi-electron transfer from photosensitizers to the reaction sites without accompanying high energy intermediates would open new era to achieve light-driven multi-electron carbon dioxide reduction and water splitting. Despite the large efforts devoted to the development of complex supramolecular assemblies for light harvesting and directional charge separation, photosynthetic systems designd for light-induced multi-electron transfer rarely generate reducing equivalents. As mentioned above, we have succeeded photochemical two-electron reduction of [Ru(bpy)$_2$(pbn)]$^{2+}$ ([**1**]$^{2+}$) affording [Ru(bpy)$_2$(pbnH$_2$)]$^{2+}$ in the presence of N(CH_2CH_2OH)$_3$ (eq 2). Photochemical two-electron reduction of [Ru(bpy)$_2$(pbn)]$^{2+}$ proceeds via (i) reductive quenching of photo-exited [Ru(bpy)$_2$(pbn)]$^{2+*}$ by N(CH_2CH_2OH)$_3$, (ii) subsequent protonation of free nitrogen of the anion radical pbn ligand of [Ru(bpy)$_2$(pbn$^{-\bullet}$)]$^+$, (iii) inter-molecular π–π adduct formation between two neutral pbnH$^\bullet$ of the resultant [Ru(bpy)$_2$(pbnH$^\bullet$)]$^+$, and (iv) disproportionation of {[Ru(bpy)$_2$(pbnH$^\bullet$)]$^+$}$_2$ affording an equimolar mixture of [Ru(bpy)$_2$(pbnHH)]$^{2+}$ and [Ru(bpy)$_2$(pbn)]$^{2+}$. The finding of the path for the two-electron reduction driven us to repeat the two-electron reduction of pbn of [Ru(bpy)(pbn)$_2$](PF_6)$_2$ ([**2**] (PF_6)$_2$) and [Ru(pbn)$_3$](PF_6)$_2$ ([**3**](PF_6)$_2$) to achieve the first photochemical four- and six-electron reductions of monomeric metal complexes.

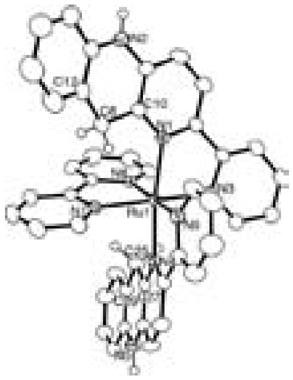


Figure 2. Crystal structure of [Ru(bpy)(pbnH$_2$)]$^{2+}$.

The molecular structure of [**2**](PF_6)$_2$ (Figure 2) has a C_2 symmetry. Although many attempts to grow single crystal of [**3**](PF_6)$_2$ for X-ray diffraction study were not succeeded, an appearance of 33 proton signals in the aromatic region in the ^{1}H NMR spectrum implied the formation of a single stereo isomer of [**3**]$^{2+}$. Low enrgy level of π* orbiatal of pbn of [**1**]$^{2+}$, [**2**]$^{2+}$ and, [**3**]$^{2+}$ reflects their redox potentilas; they showed one (–1.07 V vs Ag/AgNO$_3$), two (–1.01 and –1.14 V), and three (–0.94, –1.11, and –1.31 V) pbn localized reversible (pbn/pbn$^{-\bullet}$) redox couples in the cyclic voltammogram. Irradiation of visible light to [**2**](PF_6)$_2$ and [**3**](PF_6)$_2$ in CH_3CN/N(CH_2CH_2OH)$_3$ (4 : 1, v/v) smoothly produced [**2**·H$_4$]$^{2+}$ and [**3**·H$_6$]$^{2+}$ with time.

References

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