

Synthesis of Metal Complexes Aiming at Storage and Release of Chemical Energy

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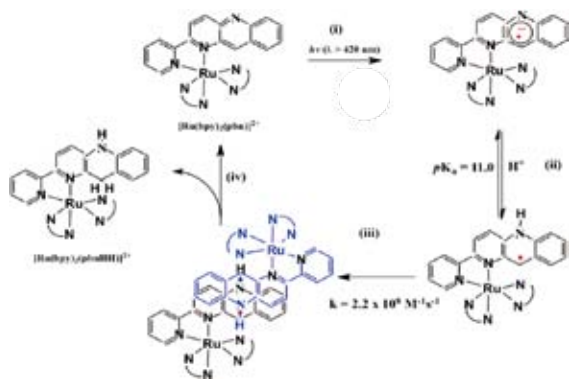
Artificial photosynthetic processes aimed at carbon dioxide reduction and water splitting are top research priorities for coping with the energy shortage that is anticipated in the near future to result from depletion of fossil fuels. Photoinduced one-electron transfer inevitably generates high-energy free radical intermediates that often trigger undesired side reactions, which is a serious issue that remains to be overcome. Proton coupled electron transfer is expected to substantially stabilize such radical intermediates, and could play a key role in multi-electron transfer to the relevant reaction sites involved in carbon dioxide reduction and water splitting.

Recently, we found that mono-nuclear $[\text{Ru}(\text{bpy})_2(\text{pbn})](\text{PF}_6)_2$ ($[\mathbf{1}]^{2+}$; bpy = 2,2'-bipyridine, pbn = 2-(2-pyridyl)-benzo[*b*]-1,5-naphthyridine) is smoothly reduced to $[\text{Ru}(\text{bpy})_2(\text{pbnH}_2)](\text{PF}_6)_2$ ($[\mathbf{1}\cdot\text{H}_2]^{2+}$; pbnH₂ = 5,10-dihydro-2-(2-pyridyl)benzo[*b*]-1,5-naphthyridine) by photoinduced two-electron reduction of pbn under irradiation with visible light in the presence of a sacrificial reagent. The reaction mechanism for the photoassisted two-electron reduction of $[\mathbf{1}]^{2+}$ (Scheme 1) is explained as follows; i) photoexcitation of $[\mathbf{1}]^{2+}$ and the subsequent reductive quenching of the photoexcited $[\mathbf{1}]^{2+*}$ by

a sacrificial donor produces $[\text{Ru}(\text{bpy})_2(\text{pbn}^{\bullet-})]^+$ ($[\mathbf{1}]^+$), ii) protonation of the non-coordinating nitrogen of the pbn^{•-} of $[\mathbf{1}]^+$ generates $[\text{Ru}(\text{bpy})_2(\text{pbnH}^{\bullet})]^{2+}$ ($[\mathbf{1}\cdot\text{H}]^{2+}$), iii) rapid dimerization of $[\mathbf{1}\cdot\text{H}]^{2+}$ through π - π interaction between two neutral pbnH[•] of $[\mathbf{1}\cdot\text{H}]^{2+}$ affords $\{[\mathbf{1}\cdot\text{H}]_2\}^{4+}$, and iv) intramolecular electron and proton transfer from one pbnH[•] to another one in $\{[\mathbf{1}\cdot\text{H}]_2\}^{4+}$ results in the disproportionation reaction to afford a 1:1 mixture of $[\mathbf{1}\cdot\text{H}_2]^{2+}$ (two-electron reduced form) and $[\mathbf{1}]^{2+}$ (the starting complex).

1. Photoinduced Four- and Six-Electron Reduction of Mononuclear Ruthenium Complexes Having NAD⁺ Analogous Ligands

Mono-nuclear complexes are generally easier to synthesize and analyze their reaction mechanisms compared with multi-nuclear metal complexes. Photoinduced multi-electron redox reaction under visible light irradiation using mono-nuclear metal complexes is a fascinating approach to harvesting solar energy. Successful photochemical two electron reduction of $[\mathbf{1}]^{2+}$ drove us to investigate the photoinduced four- and six-electron reduction of $[\text{Ru}(\text{bpy})(\text{pbn})_2](\text{PF}_6)_2$ ($[\mathbf{2}]^{2+}$) and $[\text{Ru}(\text{pbn})_3](\text{PF}_6)_2$ ($[\mathbf{3}]^{2+}$), respectively, under irradiation with visible light. Photoirradiation ($\lambda > 420$ nm) of $[\mathbf{2}]^{2+}$ and $[\mathbf{3}]^{2+}$ in $\text{CH}_3\text{CN}/\text{triethanolamine}$ (TEOA) brought about proton coupled four- and six-electron reduction of the complexes to produce $[\text{Ru}(\text{bpy})(\text{pbnH}_2)_2](\text{PF}_6)_2$ ($[\mathbf{2}\cdot\text{H}_4]^{2+}$) and $[\text{Ru}(\text{pbnH}_2)_3](\text{PF}_6)_2$ ($[\mathbf{3}\cdot\text{H}_6]^{2+}$), respectively. To elucidate the mechanism for the novel photoinduced multi-electron reduction, we examined redox and photophysical behavior of $[\mathbf{2}\cdot\text{H}_2]^{2+}$ having both pbn and pbnHH ligands. The complexes $[\mathbf{2}]^{2+}$ and $[\mathbf{2}\cdot\text{H}_2]^{2+}$ exhibit two ($E_{1/2} = -0.69$ and -0.82 V vs. SCE) and one ($E_{1/2} = -0.69$ V) reversible (pbn^{•-}/pbn) redox couples, respectively, and $[\mathbf{2}\cdot\text{H}_2]^{2+}$ and $[\mathbf{2}\cdot\text{H}_4]^{2+}$ displayed the pbnH₂



Scheme 1. Proposed mechanism for photochemical two-electron reduction of $[\mathbf{1}]^{2+}$.

localized irreversible anodic peak at 1.15 V. The metal centered Ru^{II}/Ru^{III} redox potentials of [2]²⁺, [2•H₂]²⁺ and [2•H₄]²⁺ are observed at $E_{1/2} = 1.44$ V, 1.70 V and 1.70 V, respectively. The MLCT ($d-\pi_{\text{pbn}^*}$) band of [2]²⁺ and [2•H₂]²⁺ is observed around 530 nm, and both complexes exhibit emissions from their lowest energy ³MLCT ($d-\pi_{\text{pbn}^*}$) excited states around 780 nm. The emission maximum of [2•H₂]²⁺ (786 nm) in *n*-C₄H₉CN at 77 K, and the 0–0 transition energy of the complex is determined as 1.58 eV. The excited state redox potential for the (Ru^{II*}/Ru^I) couple calculated from the equation of $E(\text{Ru}^{\text{II}*}/\text{Ru}^{\text{I}}) = E_{1/2}(\text{pbn}^{\bullet-}/\text{pbn}) + E_{\text{em}}(0-0)$ is 0.89 V. Thus, the redox potential of the (Ru^{II*}/Ru^I) couple is located at a more negative potential than that of the oxidation of pbnH₂. Photoirradiation of the MLCT ($d-\pi_{\text{pbn}^*}$) band of [2•H₂]²⁺ bearing both pbn and pbnH₂ ligands, therefore, accepts one electron through intermolecular electron transfer from TEOA to the ruthenium center without accompanying intramolecular electron transfer from pbnH₂. Indeed, the electronic absorption spectrum of [2•H₂]²⁺ in CH₃CN/TEOA (4:1, v/v) smoothly and completely changed to that of [2•H₄]²⁺ at the expense of the MLCT ($d-\pi_{\text{pbn}^*}$) absorption band at 530 nm of [2•H₂]²⁺ under irradiation with visible light ($\lambda > 420$ nm). The photoinduced four- and six-electron reduction of [2]²⁺ and [3]²⁺ in CH₃CN/TEOA, therefore, is achieved by the repeated two-electron reduction of the Ru–pbn framework as described in Scheme 1.

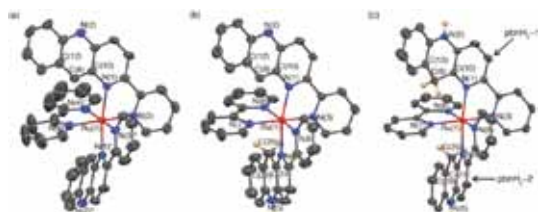


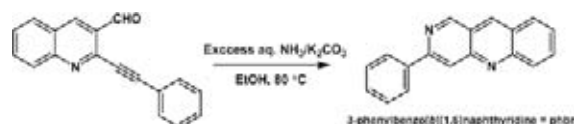
Figure 1. Crystal structures of [2]²⁺, [2•H₂]²⁺, and [2•H₄]²⁺.

2. Photochemical and Electrochemical Redox Behavior of Cyclometallated Ru(II) Complexes with NAD⁺/NADH Function

The world highly demands the renewable energy resources such as to capture and the storage of solar energy. One of the key issues for environmental science is to find out the alternative sources for the utilization of light driven energy in the form of chemical energy. In the realm of coordination chemistry ruthenium-poly-pyridyl complexes have been paid superior attention for molecular light-to-chemical energy conversion because of their unique photophysical properties and chemical stabilities. The photoinduced proton coupled “multielectronic reservoirs” of ruthenium complexes are far less common. A few research groups have reported the storage of more than one photo-excited electrons into the π^* orbital of

the poly-pyridyl ligands in the presence of sacrificial electron donors upon irradiation of visible light. Our group has developed two, four and six reversibly electron storing ability of [Ru(bpy)₂(pbn)](PF₆)₂, [Ru(bpy)(pbn)₂](PF₆)₂ and [Ru(pbn)₃](PF₆)₂ respectively, described above. We also found that [Ru(phbn)(bpy)₂](PF₆)₂ ([1]PF₆; phbn = 3-phenylbenzo[*b*][1,6]naphthyridine) undergoes photochemical proton coupled two electron reduction.

Treatment of 3-phenylbenzo[*b*][1,6]naphthyridine (phbn) obtained by Scheme 2 with [$\eta^6\text{-C}_6\text{H}_6$]RuCl₂]₂, NaPF₆ and NaOH in acetonitrile provides [Ru(phbn)(CH₃CN)₄]⁺PF₆.



Scheme 2. Synthesis of phbn.

Further addition of two equivalents of 2, 2'-bipyridyl with [Ru(phbn)(CH₃CN)₄]⁺ in 2-methoxyethanol medium gives [Ru(phbn)(bpy)₂]⁺ ([4]⁺). The complex [4]PF₆ was reduced to [Ru(phbnH₂)(bpy)₂]⁺ ([4•HH]PF₆) by chemical, electrochemical as well as photochemical methods (Scheme 3). The reaction of [4]PF₆ with NaBH₄ in methanol/H₂O mixture (9:1 v/v) gave [4•HH]PF₆ in a very good yield. Electrolysis of [4]PF₆ at –1.15 V (vs. SCE) in CH₃CN/H₂O (9:1 v/v) also produced [4•HH]PF₆ after two equivalent of electrons were consumed in the electrolysis. The continuous photolysis at ($\lambda \geq 420$ nm) of a 0.1 mM solution of [4]PF₆ in CH₃CN/Et₃N or CH₃CN/triethanolamine (CH₃CN/TEOA) (4:1, v/v) causes a decrease in the absorption band of [4]⁺ ($\lambda_{\text{max}} = 550$ nm) and the appearance of a new species with band ($\lambda_{\text{max}} = 425$ nm) with a gradual change in color of [4]PF₆ purple to brownish red. The HR-ESI mass spectra, cyclic voltammogram as well as the UV-vis spectra of the resultant product are consistent with those of [4•HH]PF₆ obtained by the chemical reduction method. The ¹H NMR spectrum of [4•HH]PF₆ in CD₃CN displayed 17 different signals with a total intensity of 29 protons, out of which 27 are in the aromatic region generating from two bpy and phbnH₂ ligand. An AB patterned doublet observed at 3.36 (¹H, d, $J = 19.53$), 3.52 (¹H, d, $J = 18.93$) ppm due to the germinal coupling of the methylene protons.



Scheme 3. Chemical, photo, and electrical reduction of [4]⁺.