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Photochemical Stereospecific Hydrogenation of a Ru Complex with an NAD^+/NADH-Type Ligand

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A polypyridylruthenium complex with an NAD^+/NADH model ligand, $[Ru(bpy)_2(pbn)]^{2+}$ [bpy = 2,2′-bipyridine; pbn = 2-(2-pyridyl)-benzo[*b*]-1,5-naphthyridine] in a D_2O/CH_3CN/triethylamine solution, undergoes stereospecific hydrogenation to give Δ-(*S*)- and Λ-(*R*)-$[Ru(bpy)_2(pbnDD)]^{2+}$ [pbnDD = 5,10-dideutero-2-(2-pyridyl)benzo-[*b*]-1,5-naphthyridine] upon visible-light irradiation. This result clearly indicates the pathway via the π-stacked dimer of the deuterated one-electron-reduced species. The reduction of $[Ru(bpy)_2(pbn)]^{2+}$ with $Na_2S_2O_4$ in D_2O did not afford any stereospecific products. Furthermore, the more sterically crowded Ru complex, $[Ru(dmb)_2(pbn)]^{2+}$ (dmb = 6,6′-dimethyl-2,2′-bipyridine), did not produce the corresponding pbnDD species upon irradiation.

Highly stereoselective photochemical reactions can occur in size/shape-specific cages such as cyclodextrins and zeolites or because of differences in the reactivities of geometric isomers in solution.[1] We have explored the question of whether stereoselective reactions could occur in photoinduced hydrogenation reactions (involving two electrons and two protons) as a result of steric hindrance between monomeric species with bulky frameworks undergoing disproportionation via dimeric intermediates in such a way that all possible combinations of the monomers cannot be formed.

We have investigated a polypyridylruthenium complex with an NAD^+/NADH model ligand, $[Ru(bpy)_2(pbn)]^{2+}$ ($[\mathbf{1}]^{2+}$) in a wet CH_3CN/amine solution, that undergoes proton-coupled two-electron reduction to give $[Ru(bpy)_2(pbnHH)]^{2+}$ ($[\mathbf{1}\cdot HH]^{2+}$; pbnHH = 5,10-dihydro-2-(2-pyridyl)-benzo[*b*]-1,5-naphthyridine) upon irradiation of visible light ($\Phi_{355nm} = 0.21$).[2] Protonation of the noncoordinating N atom of the one-electron-reduced species takes place below pH 11 to form $[\mathbf{1}\cdot H]^{2+}$ (pK_a ~11) in water.[3] We postulated that species $[\mathbf{1}\cdot HH]^{2+}$ forms by disproportionation through a π-stacked dimer of two $[\mathbf{1}\cdot H]^{2+}$ below pH 11 and via a hydrogen-bonded dimer with $[\mathbf{1}]^+$ and $[\mathbf{1}\cdot H]^{2+}$ above pH 11.[3] Here we report clear evidence of the stereospecific photochemical formation of Δ-$[Ru(bpy)_2\{(S)\text{-pbnDD}\}]^{2+}$ (Δ-(*S*)-$[\mathbf{1}\cdot DD]^{2+}$) and Λ-$[Ru(bpy)_2\{(R)\text{-pbnDD}\}]^{2+}$ (Λ-(*R*)-$[\mathbf{1}\cdot DD]^{2+}$) in D_2O, indicating the pathway via the π-stacked dimer of the deutrated one-electron-reduced species in D_2O/CH_3CN. We also prepared $[Ru(dmb)_2(pbn)]^{2+}$ ($[\mathbf{2}]^{2+}$; dmb = 6,6′-dimethyl-2,2′-bipyridine), which may prevent π-stacked-dimer formation because of the bulky dmb group, and investigated its single-crystal X-ray structure and its proton-coupled reduction by photolysis and pulse radiolysis, as we did previously for $[\mathbf{1}]^{2+}$. Our results on $[\mathbf{2}]^{2+}$ clearly show a dramatic difference in the reactivity compared to those on $[\mathbf{1}]^{2+}$.

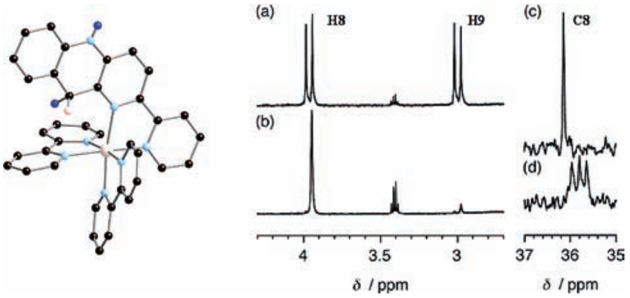

Figure 1. ^1H NMR spectra of $[\mathbf{1}\cdot HH]^{2+}$ (a) and $[\mathbf{1}\cdot DD]^{2+}$ (b) and ^{13}C NMR spectra of $[\mathbf{1}\cdot HH]^{2+}$ (c) and $[\mathbf{1}\cdot DD]^{2+}$ (d) in CD_3CN. H9 (a blue atom attached to C8) is located above the pyridine ring of bpy.

Photolysis experiments with D_2O and H_2O solutions containing $[\mathbf{1}]^{2+}/CH_3CN$/triethylamine (TEA) produced $[\mathbf{1}\cdot DD]^{2+}$ ($m/z = 337.5838$) and $[\mathbf{1}\cdot HH]^{2+}$ ($m/z = 336.5725$), respectively. The ^1H and ^{13}C NMR spectra of $[\mathbf{1}\cdot HH]^{2+}$

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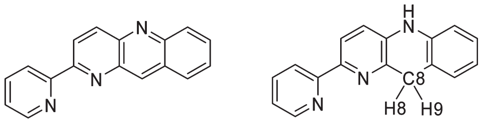
Scheme 1. Structures of pbn and pbnHH[a]



pbn pbnHH

[a] While the nomenclature for designating C8 is not standard, we adopted it to be consistent with X-ray structures in this paper and ref 3.

(Figure 1) show two doublet signals at 2.95 and 3.95 ppm ($J_{\mathrm{H-H}} = 21$ Hz) of the H atoms at C8 (Figure 1a and Scheme 1) and a singlet signal of C8 at 35.8 ppm (Figure 1c), respectively. H8 and H9 of the pbnHH ligand of $[\mathbf{1}\cdot\mathrm{HH}]^{2+}$ are magnetically inequivalent. Indeed, the crystal structure of $[\mathbf{1}\cdot\mathrm{HH}]^{2+}$ reported previously[3] shows that H9 and H8 are located above and outside the pyridine ring of bpy, respectively. The ^{1}H NMR signals at 3.95 and 2.95 ppm of $[\mathbf{1}\cdot\mathrm{HH}]^{2+}$ in Figure 1a, therefore, are attributable to H8 and H9, respectively, by considering the magnetic shielding effect of the aromatic ring currents. The ^{1}H and ^{13}C NMR spectra of $[\mathbf{1}\cdot\mathrm{DD}]^{2+}$ produced by photolysis show two broad singlet signals at 2.95 and 3.95 ppm of the H atoms at C8 with a peak intensity ratio of 0.06:0.94 (Figure 1b) and the appearance of a triplet signal ($J_{\mathrm{C-D}} = 20$ Hz) at 35.8 ppm, respectively, indicating selective deuteration at C8. However, the reduction of $[\mathbf{1}]^{2+}$ with $Na_2S_2O_4$ in D_2O shows singlet signals at 2.95 and 3.95 ppm with equal intensities, indicating that the formation pathway is quite different.

Proton-coupled two-electron reduction of $[\mathbf{1}]^{2+}$ in the presence of D_2O would produce four possible stereoisomers: Δ-(*R*)-$[\mathbf{1}\cdot\mathrm{DD}]^{2+}$, Δ-(*S*)-$[\mathbf{1}\cdot\mathrm{DD}]^{2+}$, Λ-(*R*)-$[\mathbf{1}\cdot\mathrm{DD}]^{2+}$, and Λ-(*S*)-$[\mathbf{1}\cdot\mathrm{DD}]^{2+}$ (Figure S1 in the Supporting Information). The pair of Δ-(*R*)-$[\mathbf{1}\cdot\mathrm{DD}]^{2+}$ and Λ-(*S*)-$[\mathbf{1}\cdot\mathrm{DD}]^{2+}$ and that of Δ-(*S*)-$[\mathbf{1}\cdot\mathrm{DD}]^{2+}$ and Λ-(*R*)-$[\mathbf{1}\cdot\mathrm{DD}]^{2+}$ are enantiomers that display the same NMR spectrum. Almost no signal at 2.95 ppm for $[\mathbf{1}\cdot\mathrm{DD}]^{2+}$ indicates that the highly selective deuteration at the H9 position of the C8 carbon takes place and leads to the formation of Δ-(*S*)-$[\mathbf{1}\cdot\mathrm{DD}]^{2+}$ and Λ-(*R*)-$[\mathbf{1}\cdot\mathrm{DD}]^{2+}$. While 12 combinations of $[\mathbf{1}\cdot\mathrm{D}]^{2+}$ for the π-stacked dimer $\{[\mathbf{1}\cdot\mathrm{D}]^{2+}\}_2$ are possible (shown in Figure S2 in the Supporting Information), only three conformers can form, avoiding close contacts of the H atoms of the pbn and bpy ligands. From these $\Lambda-\Lambda$, $\Delta-\Delta$, and $\Delta-\Lambda$ dimers (shown in Figure S3 in the Supporting Information), only Δ-(*S*)-$[\mathbf{1}\cdot\mathrm{DD}]^{2+}$ and Λ-(*R*)-$[\mathbf{1}\cdot\mathrm{DD}]^{2+}$ are formed.

We have carried out B3LYP/LANL2DZ hybrid density functional theory calculations on two of the three predicted sterically allowed dimers in a polarizable continuum model of an acetonitrile solution using the *Gaussian03* program package.[4] The $\Lambda-\Lambda$ dimer is the mirror-image structure of the calculated $\Delta-\Delta$ dimer. No other possible dimer orientations exhibited bound structures. The minimum energies for these dimers indicate that the $\Delta-\Lambda$ dimer (Figure 2) is roughly 5.0 kcal mol^{-1} more stable than the $\Delta-\Delta$ dimer, presumably because of the larger Ru−Ru distance (10.88 vs 9.23 Å; see Figure S4 in the Supporting Information) separating the positively charged metal centers. Because the calculational model did not include counterions to screen Coulombic repulsion, both $\Delta-\Lambda$ and $\Delta-\Delta$ dimer structures correspond to local minima, with the $\Delta-\Lambda$ minimum 17.7 kcal mol^{-1} higher than the energy of two isolated, solvated $[\mathbf{1}\cdot\mathrm{H}]^{2+}$ monomers.[5,6] This result is consistent with the fact that neither dimer structure exhibits a local minimum in the gas phase. Owing to these uncertainties, the calculated geometries and energetics are not quantitative but offer semiquantitative support for the existence and stereosepecificity of π-stacking dimer intermediates. This binding is further supported by localization of the highest occupied molecular orbital (HOMO) of the calculated dimer, as shown in Figure 2.

The influence of steric hindrance on the dimerization reaction in the proposed mechanism of photochemical two-electron reduction of $[\mathbf{1}]^{2+}$ in triethanolamine/CH_3CN was studied with the more sterically crowded Ru complex with dmb ligands ($[\mathbf{2}]^{2+}$). The single-crystal X-ray structure (Figure 3) indicates that long Ru−N bond lengths to the pbn and dmb ligands [2.064(3)−2.139(2) Å] of $[\mathbf{2}]^{2+}$ compared to the corresponding distances in $[\mathbf{1}]^{2+}$ [2.038(5)−2.116(5) Å]^{3} are associated with steric congestion around the Ru center. Furthermore, not only is the N1−Ru1−N7 bond angle of $[\mathbf{2}]^{2+}$ (77.2°) narrower than that of $[\mathbf{1}]^{2+}$ (86.4°) but also the π systems of the pbn ligand and one of the dmb ligands (i.e., trans to 2-pyridyl of pbn) are severely distorted from an orthogonal arrangement as a result of steric hindrance of the methyl groups (Figure 3b).

Titration of an aqueous solution containing $[\mathbf{2}]^{2+}$ by acid shows the disappearance of $[\mathbf{2}]^{2+}$ ($\lambda_{\max}$ = 353, 373, 390sh, 445, and 551 nm) and the formation of the protonated species ($\lambda_{\max}$ = 630 nm) with an isosbestic point at 583 nm. The pK_a = 1.1 is very similar to that of the protonated $[\mathbf{1}]^{2+}$ (pK_a = 1.7). The cyclic voltammogram of $[\mathbf{2}]^{2+}$ in *N*,*N*-dimethylformamide (DMF) shows reversible waves at −0.72, −1.37, and −1.66 V vs SCE, which can be assigned to pbn$^{\bullet-}$/pbn, (dmb, dmb$^{\bullet-}$)/(dmb)$_2$, and (dmb$^{\bullet-}$)$_2$/(dmb, dmb$^{\bullet-}$), respectively. $Na_2S_2O_4$ reduction of $[\mathbf{2}]^{2+}$ gives $[\mathbf{2}\cdot\mathrm{HH}]^{2+}$ (^{1}H NMR for protons of C8: 4.20 and 3.34 ppm, $J_{\mathrm{H-H}}$ = 19.5 Hz in acetone-d_6; m/z = 364.6121). However, irradiation of $[\mathbf{2}]^{2+}$ with visible light in DMF/TEA/H_2O did not produce $[\mathbf{2}\cdot\mathrm{HH}]^{2+}$.

$$[\mathrm{RuL_2(pbnH^{\bullet})}]^{2+} \overset{K_a}{\rightleftharpoons} [\mathrm{RuL_2(pbn^{\bullet-})}]^{+} + \mathrm{H}^{+} \qquad (1)$$

$$\begin{aligned} 2[\mathrm{RuL_2(pbnH^{\bullet})}]^{2+} &\rightarrow [\mathrm{RuL_2(pbnH^{\bullet})}]_2{}^{4+} \\ &\rightarrow [\mathrm{RuL_2(pbn)}]^{2+} + [\mathrm{RuL_2(pbnHH)}]^{2+} \quad k_2 \end{aligned} \qquad (2)$$

$$\begin{aligned} &[\mathrm{RuL_2(pbnH^{\bullet})}]^{2+} + [\mathrm{RuL_2(pbn^{\bullet-})}]^{+} + \mathrm{HA} \\ &\rightarrow [\mathrm{RuL_2(pbn)}]^{2+} + [\mathrm{RuL_2(pbnHH)}]^{2+} + \mathrm{A}^{-} \quad k_3 \end{aligned} \qquad (3)$$

$$\begin{aligned} 2[\mathrm{RuL_2(pbn^{\bullet-})}]^{+} + 2\mathrm{HA} &\rightarrow [\mathrm{RuL_2(pbn)}]^{2+} \\ &+ [\mathrm{RuL_2(pbnHH)}]^{2+} + 2\mathrm{A}^{-} \quad k_4 \end{aligned} \qquad (4)$$

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(4) Frisch, M. J.; et al. *Gaussian03*, revision C.02; see the Supporting Information.

(5) The Coulombic repulsion between two 2+ charges 11 Å apart in the gas phase is over 120 kcal mol^{-1}.

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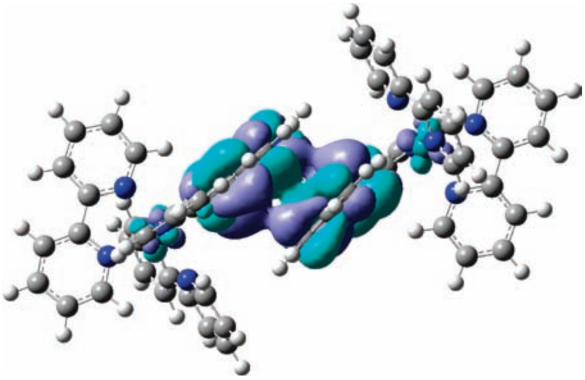

Figure 2. HOMO of π-stacking Δ,Λ-$\{[\mathbf{1}\cdot\mathrm{H}]^{2+}\}_2$ showing localization of the electrons in a bonding orbital between the π systems of the monomers.

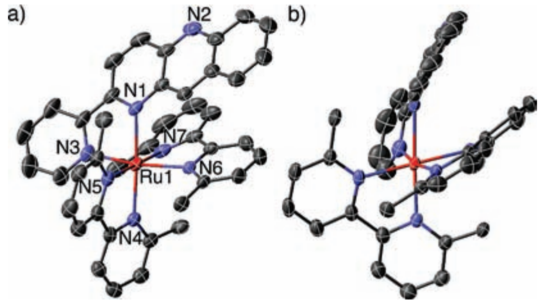

Figure 3. ORTEP drawing of the structure of $[\mathbf{2}]^{2+}$ with 50% thermal ellipsoids: front view (a) and side view (b). H atoms are omitted for simplicity.

$$k_{obs} = \frac{2\left[k_2 + \frac{k_3 K_a}{[\mathrm{H}^+]} + k_4\left(\frac{K_a}{[\mathrm{H}^+]}\right)^2\right]}{\left(1+\frac{K_a}{[\mathrm{H}^+]}\right)^2} \quad (5)$$

As published previously,[3] we monitored the disappearance of the one-electron-reduced species $[\mathbf{2}]^+$ and $[\mathbf{2}\cdot\mathrm{H}]^{2+}$ (see the detailed description in the Supporting Information). The decay kinetics via reactions (2)−(4) are, however, distinctly different for bpy and dmb derivatives, as shown in Figure 4. The disappearance of the one-electron-reduction product of the bpy and dmb complexes follows eqs 2−5 with the kinetic parameters $\mathrm{p}K_a = 11.0$, $k_2 = 2.2 \times 10^8\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$, $k_3 = 1.2 \times 10^8\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$, $k_4 \ll k_2, k_3$ (the bpy complex); $\mathrm{p}K_a = 10.9$, $k_3 = 3.8 \times 10^7\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$, $k_4 = 5 \times 10^4\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$, $k_2 \ll k_3, k_4$ (the dmb complex). The formation of the π-stacked dimer (eq 2) was suppressed for the dmb complex. The cross reaction (eq 3) between $[\mathbf{2}]^+$ and $[\mathbf{2}\cdot\mathrm{H}]^{2+}$ through a N−H···N hydrogen-bonding interaction, which should be less affected by steric hindrance created by the bulky dmb ligands (see Figure S5 in the Supporting Information), is only approximately three times slower than that of the bpy derivative. These pulse radiolysis observations agree with the photochemical results.

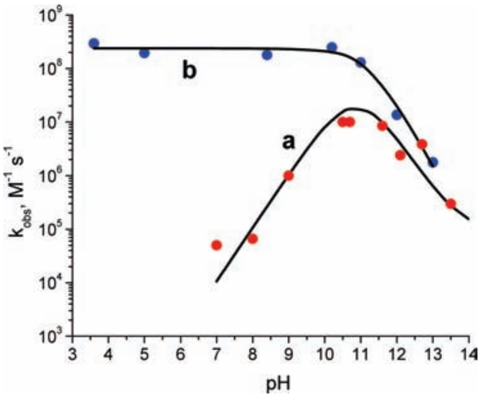

Figure 4. pH dependence of the observed second-order rate constants for the disappearance of (a) red dots, $[\mathbf{2}]^+$ and $[\mathbf{2}\cdot\mathrm{H}]^{2+}$ and the fit (line) with eq 5, and (b) blue dots, $[\mathbf{1}]^+$ and $[\mathbf{1}\cdot\mathrm{H}]^{2+}$ and the fit (line). See the text for the fit parameters. There is a 10% error margin for parameters obtained from the fit.

In summary, the stereoselective formation of Δ-(*S*)-$[\mathbf{1}\cdot\mathrm{DD}]^{2+}$ and Λ-(*R*)-$[\mathbf{1}\cdot\mathrm{DD}]^{2+}$ in the photoreduction of $[\mathbf{1}]^{2+}$ clearly rules out the possibility of pathways such as eqs 3 and 4. Unlike the radiation-induced reaction in water, our current photochemical experiments unambiguously show that *only disproportionation through the π-stacking dimer* can afford the formation of Δ-(*S*)-$[\mathbf{1}\cdot\mathrm{DD}]^{2+}$ and Λ-(*R*)-$[\mathbf{1}\cdot\mathrm{DD}]^{2+}$ (eq 2). A slow second-order decay of the reduced species was observed via the cross reaction (eq 3) in the pulse radiolysis experiments on $[\mathbf{2}]^{2+}$; however, no photoproduced $[\mathbf{2}\cdot\mathrm{HH}]^{2+}$ was observed. The trace intensity at 2.95 ppm in the ^{1}H NMR of $[\mathbf{1}\cdot\mathrm{DD}]^{2+}$ indicates that a minor pathway via cross reaction may still exist. The cross-reaction pathway would likely be completely suppressed in the photochemical reaction of $[\mathbf{1}]^{2+}$ under slightly more acidic conditions. The stereoselective formation of Δ-(*S*)-$[\mathbf{1}\cdot\mathrm{DD}]^{2+}$ and Λ-(*R*)-$[\mathbf{1}\cdot\mathrm{DD}]^{2+}$ via dimerization of a racemic mixture of monomers, followed by dispropotionation, is intriguing and may open new directions for photoinduced stereospecific hydride- and deuteride-transfer reactions from Δ-(*S*)-$[\mathbf{1}\cdot\mathrm{DD}]^{2+}$ and Λ-(*R*)-$[\mathbf{1}\cdot\mathrm{DD}]^{2+}$.

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Supporting Information Available: Experimental procedure, crystallographic data of $[\mathbf{2}]^{2+}$, chemical and photochemical reduction of $[\mathbf{2}]^{2+}$, mechanistic and kinetic studies by pulse radiolysis, possible conformations of π-stacking $\{[\mathbf{1}\cdot\mathrm{D}]^{2+}\}_2$, disproportionation schemes of π-stacking dimers, and Cartesian coordinates for the optimized B3LYP/LANL2DZ geometry of two kinds of π-stacking dimers. This material is available free of charge via the Internet at http://pubs.acs.org.