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Intermolecular Electron Transfer from Photogenerated $Ru(bpy)_3^+$ to [2Fe2S] Model Complexes of the Iron-Only Hydrogenase Active Site

Yong Na,[†] Jingxi Pan,[†] Mei Wang,*[,†] and Licheng Sun*[,†,‡]

State Key Laboratory of Fine Chemicals, DUT-KTH Joint Education and Research Center on Molecular Devices, Dalian University of Technology (DUT), 116012 Dalian, China, and Department of Chemistry, Royal Institute of Technology (KTH), 10044 Stockholm, Sweden

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Visible light-driven intermolecular electron transfer was observed from a reduced species $Ru(bpy)_3^+$, photogenerated via a reductive quenching of the ruthenium photosensitizer by a diethyldithiocarbamate anion, to bioinspired [2Fe2S] model complexes of the iron-only hydrogenase active site. The results indicate that $Ru(bpy)_3^{2+}$ can act as a photoactive functional model of the [4Fe4S] cluster, playing the role of an electron-transfer relay. The photogenerated Fe^IFe^0 species, which is proposed to be a crucial intermediate for proton reduction catalyzed electrochemically by the [2Fe2S] complexes, gives promise in the light-driven dihydrogen evolution using diiron complexes as surrogates of noble platinum catalysts.

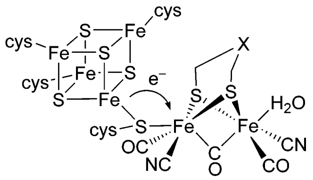

Figure 1. Structure of the hydrogen cluster in the iron-only hydrogenase active site.

The X-ray crystallographic studies reveal that the active site of iron-only hydrogenases, the so-called H-cluster, contains a [2Fe2S] subsite with one of the iron atoms connecting to a [4Fe4S] cluster via a cysteinyl bridge.[1,2] The [4Fe4S] cluster is assumed to function as an electron-transfer (ET) relay (Figure 1).[3] The remarkable catalytic activity of proton reduction by iron-only hydrogenases inspires scientists to create electrochemical and photochemical dihydrogen production systems based on iron complexes. Recently, a few synthetic [2Fe2S] model complexes of the iron-only hydrogenase active site have proven to be efficient catalysts for electrochemical hydrogen production.[4−7] In an attempt to develop light-driven hydrogen production systems, several biomimetic models of the iron-only hydrogenase active site covalently linked to ruthenium photosensitizers were synthesized and the possibility of ET from the photoexcited ruthenium complex to the dinuclear iron site was investigated.[8,9] Unfortunately, the excited states of ruthenium complexes were quenched either by energy transfer or by unwanted reverse ET,[9] and the desired forward ET did not occur. This is mainly because the reduction potential of the dinuclear iron complex is more negative than that of the excited state of the ruthenium complex, making the direct ET from the photosensitizer to the catalyst thermodynamically unfavorable. To overcome this problem, a stronger reductant $Ru(bpy)_3^+$, which can be generated via reductive quenching of the excited state of $Ru(bpy)_3^{2+}$,[10] might be a better candidate because it has a reduction potential close to that of all-carbonyl diiron dithiolate complexes. The $Ru(bpy)_3^+$ species has been successfully used in photochemical hydrogen generation in combination with the reduction catalysts of transition-metal complexes.[11−13] However, utilization of $Ru(bpy)_3^+$ is usually impeded by the back-ET reaction between $Ru(bpy)_3^+$ and the quencher.[14] Using a S-containing electron donor, the back-ET reaction can be

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* To whom correspondence should be addressed. E-mail: symbueno@dlut.edu.cn (M.W.), lichengs@kth.se (L.S.).

[†] Dalian University of Technology.

[‡] Royal Institute of Technology.

(1) Peters, J. W.; Lanzilotta, W. N.; Lemon, B. J.; Seefeldt, L. C. *Science* **1998**, *282*, 1853.
(2) Nicolet, Y.; Piras, C.; Legrand, P.; Hatchikian, C. E.; Fontecilla-Camps, J. C. *Structure* **1999**, *7*, 13.
(3) Liu, X.; Ibrahim, S. K.; Tard, C.; Pickett, C. J. *Coord. Chem. Rev.* **2005**, *249*, 1641.
(4) Gloaguen, F.; Lawrence, J. D.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **2001**, *123*, 9476.
(5) Ott, S.; Kritikos, M.; Åkermark, B.; Sun, L.; Lomoth, R. *Angew. Chem., Int. Ed.* **2004**, *43*, 1006.
(6) Mejia-Rodriguez, R.; Chong, D.; Reibenspies, J. H.; Soriaga, M. P.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **2004**, *126*, 12004.
(7) Capon, J.-F.; Gloaguen, F.; Schollhammer, P.; Talarmin, J. *Coord. Chem. Rev.* **2005**, *249*, 1664.
(8) Sun, L.; Åkermark, B.; Ott, S. *Coord. Chem. Rev.* **2005**, *249*, 1653.
(9) Eksröm, J.; Abrahamsson, M.; Olson, C.; Bergquist, J.; Kaynak, F. B.; Eriksson, L.; Sun, L.; Becker, H.-C.; Åkermark, B.; Hammarström, L.; Ott, S. *Dalton Trans.* **2006**, 4599.
(10) Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1976**, *98*, 6384.
(11) Brown, G. M.; Brunschwig, B. S.; Creutz, C.; Endicott, J. F.; Sutin, N. *J. Am. Chem. Soc.* **1979**, *101*, 1298.
(12) Krishnan, C. V.; Sutin, N. *J. Am. Chem. Soc.* **1981**, *103*, 2141.
(13) Fisher, J. R.; Cole-Hamilton, D. J. *J. Chem. Soc., Dalton Trans.* **1984**, 809.
(14) Creutz, C.; Sutin, N. *Inorg. Chem.* **1976**, *15*, 496.

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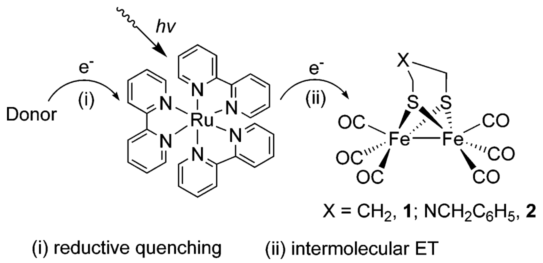

Figure 2. Bioinspired triad system for photoinduced ET.

suppressed by rapid dimerization of thiyl radicals, formed after ET from dithio anions to the excited state of Ru(bpy)$_3^{2+}$,[15] so that the lifetime of Ru(bpy)$_3^+$ can be prolonged and the expected ET reaction might readily take place.

On the basis of the aforementioned considerations, we designed a triad reaction system as shown in Figure 2, composed of Ru(bpy)$_3^{2+}$ as a photosensitizer, a diethyldithiocarbamate anion (dtc$^-$) as an electron donor, and {(μ-SCH$_2$)$_2$X}[Fe(CO)$_3$]$_2$ (X = CH$_2$, **1**; NCH$_2$C$_6$H$_5$, **2**) as a catalyst to mimic the diiron subsite. The working principle of the triad system is that the excited state of Ru(bpy)$_3^{2+}$ is quenched reductively by dtc$^-$, leading to the formation of Ru(bpy)$_3^+$. Consequently, one electron transfers from Ru(bpy)$_3^+$ to the diiron dithiolate complex **1** or **2**, resulting in the formation of Fe$^{\mathrm{I}}$Fe^0 species, which is proposed to be a crucial intermediate for the dihydrogen evolution catalyzed electrochemically by the [2Fe2S] complexes.[6,7] The designed ET processes were unambiguously corroborated by laser flash photolysis evidence. To the best of our knowledge, the observation of the light-driven ET from a photosensitizer to an iron-only hydrogenase active site model complex is unprecedented.

Photoactive complex Ru(bpy)$_3^{2+}$ and diiron complexes **1** and **2** were synthesized according to literature procedures.[16−18] As reported, Ru(bpy)$_3^{2+}$ displays three reversible reduction peaks for three bipyridyl ligands in the cyclic voltammogram, with the first reduction peak at -1.29 V ($E_{1/2}$) vs saturated calomel electrode (SCE).[19] Diiron complexes **1** and **2** each display a quasi-reversible reduction peak at -1.20 and -1.17 V vs SCE, respectively, assigned to the one-electron-reduction process of Fe$^{\mathrm{I}}$Fe$^{\mathrm{I}}$ to Fe$^{\mathrm{I}}$Fe^0. Evidently, the redox potential $E_{1/2}$ [Ru(bpy)$_3^{2+/+}$] is 90−120 mV more negative than E_{pc} (Fe$^{\mathrm{I}}$Fe$^{\mathrm{I}}$/Fe$^{\mathrm{I}}$Fe^0), so that the one-electron-reduction processes of complexes **1** and **2** by photogenerated Ru(bpy)$_3^+$ are thermodynamically feasible.

The maximal absorption of **1** in CH$_3$CN is at 329 nm, with a low intense absorption at 458 nm. The UV/vis spectroelectrochemical (SEC) spectra of **1** has been reported by Pickett et al.[20] Intense absorption bands at 390, 580, and 700 nm, attributed to the one-electron-reduced Fe$^{\mathrm{I}}$Fe^0 species, were observed in UV/vis SEC spectra recorded during the reduction of **1** in *N*,*N'*-dimethylformamide under 0.7 MPa of CO. The clear distinction in UV/vis absorptions between Ru(bpy)$_3^+$ and Ru(bpy)$_3^{2+}$ and between Fe$^{\mathrm{I}}$Fe$^{\mathrm{I}}$ and Fe$^{\mathrm{I}}$Fe^0 species gave us the motivation to explore the related photoinduced ET process using time-resolved absorption spectroscopy, that is, the laser flash photolysis technique.

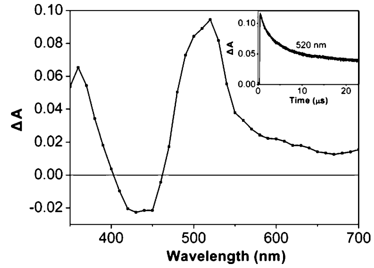

Figure 3. Transient absorption spectrum obtained at 2 μs following flash photolysis of a deoxygenated CH$_3$CN solution containing Ru(bpy)$_3^{2+}$ (5 × 10^{-5} M) and dtc$^-$ (10^{-3} M) under an argon atmosphere. Inset: kinetic trace at 520 nm.

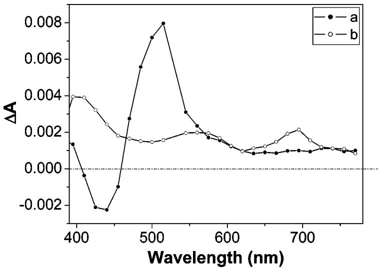

Figure 4. Transient absorption spectra obtained at 0.1 μs (a) and 10 μs (b) following laser flash photolysis of a deoxygenated CH$_3$CN solution containing Ru(bpy)$_3^{2+}$ (3 × 10^{-5} M), dtc$^-$ (10^{-3} M), and **1** (4 × 10^{-4} M) under an argon atmosphere.

In the absence of complex **1**, laser excitation (532 nm, pulse width 7 ns) of the deoxygenated solution of Ru(bpy)$_3^{2+}$ and dtc$^-$ resulted in the immediate formation of Ru(bpy)$_3^+$, which was characterized by an absorption band at around 520 nm (Figure 3).[15] The inset of Figure 3 shows the decay kinetics of Ru(bpy)$_3^+$ at 520 nm, which is a long-lived species and decays double exponentially with $\tau_1 = 2.3$ μs (14%) and $\tau_2 = 17.0$ μs (86%). When **1** was added to the solution in a concentration of 4 × 10^{-4} M, the transient absorption spectra obtained at 0.1 and 10 μs after laser excitation were totally different. As shown in Figure 4, the absorption spectrum of Ru(bpy)$_3^+$ can be clearly seen at 0.1 μs; however, at 10 μs, the absorption of Ru(bpy)$_3^+$ completely disappears, and synchronously the absorptions at ca. 400, 570, and 700 nm for a newly generated species in CH$_3$CN appear in the spectrum. These new absorptions are ascribed to the Fe$^{\mathrm{I}}$Fe^0 species of **1** by comparison to the UV/vis SEC spectrum reported by Pickett and co-workers.[20] The similar transient absorption spectra were obtained when flash photolysis of a deoxygenated CH$_3$CN solution of Ru(bpy)$_3^{2+}$, dtc$^-$, and **1** was made under an argon or CO atmosphere (Figure S1 in the Supporting Information), indicating that the photogenerated Fe$^{\mathrm{I}}$Fe^0 species did not lose CO ligand within the short measuring time scale. Flash photolysis of Ru(bpy)$_3^{2+}$, dtc$^-$, and **2** in the deoxygenated CH$_3$CN solution gave transient absorption spectra similar to those of complex

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(15) Deronzier, A.; Meyer, T. J. *Inorg. Chem.* **1980**, *19*, 2912.
(16) Thummel, R. P.; Lefoulon, F. *Inorg. Chem.* **1987**, *26*, 675.
(17) Bogan, L. E.; Lesch, D. A.; Rauchfuss, T. B. *J. Organomet. Chem.* **1983**, *250*, 429.
(18) Lawrence, J. D.; Li, H.; Rauchfuss, T. B. *Chem. Commun.* **2001**, 1482.
(19) Balzani, V.; Bergamini, G.; Marchioni, F.; Ceroni, P. *Coord. Chem. Rev.* **2006**, *250*, 1254.
(20) Borg, S. J.; Bergamini, T.; Best, S. P.; Razavet, M.; Liu, X.; Pickett, C. J. *J. Am. Chem. Soc.* **2004**, *126*, 16988.

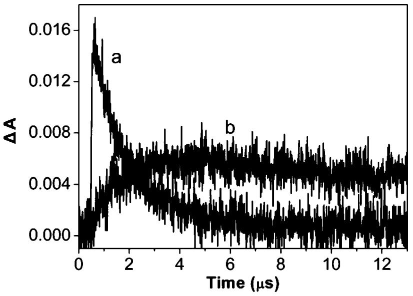
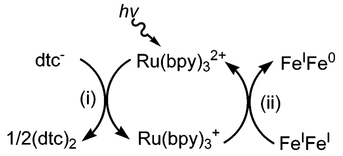


Figure 5. Kinetic traces at 520 nm (a) and 400 nm (b) obtained following flash photolysis of a deoxygenated CH_3CN solution containing $Ru(bpy)_3^{2+}$ (3×10^{-5} M), dtc^- (10^{-3} M), and **1** (2×10^{-4} M).

1 (Figure S2 in the Supporting Information). Moreover, control experiments showed that there was no direct interaction between **1** and the excited state of $Ru(bpy)_3^{2+}$. All of this evidence indicates that one electron has transferred from photogenerated $Ru(bpy)_3^+$ to [2Fe2S] complexes **1** and **2**.

The kinetic traces (Figure 5) were measured at a lower concentration of **1** (2×10^{-4} M) because the absorption of the ground state of **1** at ca. 450 nm could affect the data acquisition. In the presence of **1**, the lifetime of $Ru(bpy)_3^+$ was dramatically shortened to 1.4 μs (Figure 5a). The concomitant kinetics for the decay of $Ru(bpy)_3^+$ and the buildup of the Fe^IFe^0 species further support the conclusion that one-electron transfer from $Ru(bpy)_3^+$ to **1** occurs in the triad system. In addition, a similar result was obtained when **1** was replaced by $\{(\mu\text{-}SCH_2)_2NCH_2C_6H_5\}[Fe(CO)_3]_2$ (**2**; Figure S3 in the Supporting Information). By variation of the concentration of **1** from 0.06 to 0.2 mM, the rate constant of the ET reaction from $Ru(bpy)_3^+$ to Fe^IFe^I is determined to be 3.9×10^9 M^{-1} s^{-1} (Figure S4 in the Supporting Information), which is 1 order of magnitude faster than the previously reported rate constants for ET from $Ru(bpy)_3^+$ to Co^{II} [$(1.8-4.0) \times 10^8$ M^{-1} s^{-1}].[11,12] The photoinduced ET processes in the designed triad system is summarized in Scheme 1.

Scheme 1. Proposed Light-Driven ET Process of the Triad System



In conclusion, light-driven ET was successfully observed from a reduced species of the ruthenium photosensitizer to [2Fe2S] model complexes of the iron-only hydrogenase active site. The results indicate that $Ru(bpy)_3^{2+}$ may act as a photoactive functional model of the [4Fe4S] cluster, playing the role of an ET relay. $Ru(bpy)_3^+$, photogenerated via a reductive quenching, can be used as an effective reductant for activation of diiron precatalysts. Furthermore, in terms of light-driven hydrogen production, it could be more practical to employ an intermolecular system because it is more easily obtained and the unwanted energy-transfer or reverse-ET reactions can be avoided. The photogenerated Fe^IFe^0 species can, in principle, interact with protons to form an active $Fe^IFe^{II}-H$ species,[6,7] which is a very important intermediate for the H−H bond formation. The results show promise in the light-driven proton reduction to molecular hydrogen using diiron model complexes as surrogates of noble metal based catalysts. Studies on photochemical hydrogen production catalyzed by [2Fe2S] complexes are in progress.

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Supporting Information Available: Experimental details, transient absorption spectra of **1** and **2**, and kinetic traces of the triad system. This material is available free of charge via the Internet at http://pubs.acs.org.

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