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Proton-Coupled Electron Shuttling in a Covalently Linked Ruthenium−Copper Heterodinuclear Complex

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Supporting Information

ABSTRACT: A heterodinuclear complex based on a Ru^{II}−TPA [TPA = tris(2-pyridylmethyl)amine] complex having a peripheral $Cu^{II}(bpy)_2$ (bpy = 2,2′-bipyridine) group bonded through an amide linkage displayed reversible intramolecular electron transfer between the Ru and Cu complex units that can be controlled by protonation and deprotonation of the bridging amide moiety.

Molecular bistability between two states that can be switched clearly by external stimuli such as pH,[1] light,[2] heat,[3] or chemical[4] or redox processes[5] is essential for regulatation of molecular characteristics toward the development of promising functional molecules. Bistable molecules can exhibit detectable alterations of their structures and properties, including spin transitions ("spin crossover"),[6] molecular motions ("molecular machinery"),[7] or color changes ("chromism"),[8] as a result of the transition from one state to the other. However, most of bistable molecules reported to date have exhibited slow responses to external stimuli, which have hampered their practical use.[9] Quick and clear response is indispensable for realizing effective molecular functionality.

On the other hand, protonation and deprotonation of molecules are relatively fast and strongly affect the redox potentials of molecules. Thus, proton manipulation can be used as an external stimulus for rapid switching of molecular properties.[10] Among the class of compounds showing switching behavior in two phases, transition-metal complexes having polypyridyl ligands have been well-studied and shown to demonstrate clear changes in redox potential at the metal centers induced by protonation/deprotonation of the ligands.[11] Regulation of the redox potentials of metal centers has been achieved by deprotonation and protonation to control the oxidation states of the metal centers.[12] However, no example has been reported on molecular bistability involving the regulation of intramolecular localization of spin density in a binuclear transition-metal complex that exhibits clear magnetic responses in EPR measurements. In this process, the rapid protonation/deprotonation can be followed by much faster intramolecular electron transfer occurring on the submicrosecond time scale.

To achieve proton-coupled regulation of electronic bistability in binuclear transition-metal complexes, we designed a novel Ru^{II}−TPA [TPA = tris(2-pyridylmethyl)amine] complex connected to an electron-acceptor moiety via an amide linkage. We recently reported on the redox-potential control of Ru^{II} centers bearing TPA derivatives with amide moieties in which one of amide oxygen atoms coordinates to the Ru^{II} center, on the basis of protonation/deprotonation of the amide moiety.[13]

We report herein a unique intramolecular proton-coupled electron shuttling between a Ru^{II} center with a 2,2′-bipyridine (bpy)-appended TPA ligand and a Cu^{II} center bound to the appended bpy moiety. In this electron shuttling, the forward electron transfer (ET) from the Ru^{II} center to the Cu^{II} center is triggered by deprotonation of a coordinated amide moiety and the corresponding back-ET by its protonation. The key point in this molecular design to accomplish the fast and clear response to the external pH change is the distorted structure of the Cu^{II} moiety resulting from the presence of the 6-methyl group, which affords a small reorganization energy of electron transfer and thus allows a high ET rate to be attained.[14,15]

We first examined the regulation of intermolecular proton-coupled ET (PCET)[16] from the Ru^{II} complex $[RuCl((1\text{-}Naph)_2\text{-}TPA)]^+$ (**1**$^+$), which has two 1-naphthoylamide moieties at the 6-positions of two of the pyridine rings of TPA,[17] to $[Cu(Mebpy)_2]^{2+}$ (**2**$^{2+}$), a Cu^{II} complex with 6-methyl-2,2′-bipyridine (Mebpy),[18] by deprotonation of the N−*H* of the coordinated amide linkage of **1**$^+$ in CH_3CN (Scheme 1). The most important aspect of **2**$^{2+}$ as an electron acceptor is that the reduction potential of the Cu^{II} ion in **2**$^{2+}$ is between the redox potentials of the Ru^{II} ions for the protonated and deprotonated forms of **1** (**1**$^+$ and [**1**−**H**$^+$], respectively) (Table 1). This allows us to achieve directional control of the intermolecular ET between the Ru^{II} and Cu^{II} centers, as described in Scheme 1.

When complex **2**$^{2+}$ was added to a CH_3CN solution of complex **1**$^+$, the absorption spectrum of the mixture consisted of a superposition of the spectra of **1**$^+$ and **2**$^{2+}$ [Figure S1 in the Supporting Information (SI)]. This indicates that the Ru^{II} center in the protonated complex **1**$^+$ does not undergo ET to the Cu^{II}

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Scheme 1. Intermolecular Proton-Coupled Electron Transfer between 1^+ and 2^{2+}

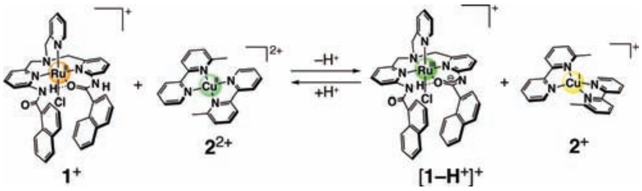


Table 1. Redox Potentials of Complexes 1^+, $[1-H^+]$, 2^{2+}, 4, and $4-H^+$ in CH_3CN[a]

complex	$E_{1/2}$ (Ru^{II}/Ru^{III}) (V)	$E_{1/2}$ (Cu^{I}/Cu^{II}) (V)
1^{+b}	+0.63	–
$[1-H^+]^b$	+0.13	–
2^{2+}	–	+0.41
4	+0.69	+0.39
$4-H^+$	+0.17	+0.40

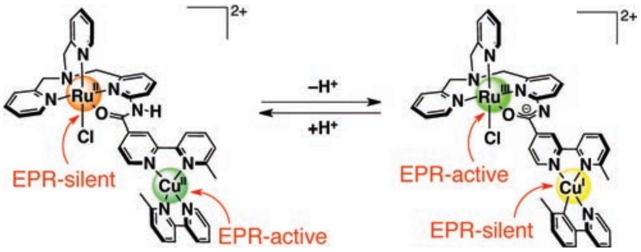
[a] Potentials were determined by cyclic voltammetry in the presence of 0.1 M $(n\text{-Bu})_4NPF_6$ as a supporting electrolyte under Ar at room temperature. The values are in V vs SCE. [b] Data from ref 13b.

complex because of uphill potential gaps. In sharp contrast, when complex 2^{2+} was added to the solution of 1^+ in the presence of NEt_3, forming $[1-H^+]$, a decrease in absorption at 472 nm [which is ascribed to the ligand-to-metal charge transfer (LMCT) transition of the Ru^{II} complex] was observed, and the decrease in absorbance was stopped by addition of 1 equiv of 2^{2+} (Figure S2).[19] The addition of $HClO_4$ to the basic solution allowed us to observe the recovery of the original indicating that the intermolecular ET between 1^+ and 2^{2+} is reversible upon addition of an acid and a base.[20]

For further confirmation of the intermolecular ET, electron paramagnetic resonance (EPR) spectroscopic measurements were performed. The frozen solution of mixture of 1^+ and 2^{2+} in CH_3CN at 98 K showed an intense EPR signal at $g = 2.09$ (Figure S5a), which is specific for Cu^{II} species in the $S = {}^1/_2$ spin state with tetrahedral distortion, as indicated by the small hyperfine coupling constant due to the Cu^{II} nuclei ($A_{Cu} = 92$ G). To this solution were added 1 equiv of NEt_3 in two aliquots, after which the EPR signal due to the Cu^{II} center disappeared and a new and relatively weak signal appeared at $g = 2.53$, 2.23, and 1.71 (Figure S5b), which is typical of Ru^{III} species in the low-spin state ($S = {}^1/_2$).[21] These results strongly support the occurrence of intermolecular ET from the Ru^{II} center of $[1-H^+]$ to the Cu^{II} center of 2^{2+}, resulting in the formation of low-spin Ru^{III} and diamagnetic Cu^{I} complexes. This EPR spectral change was also reversible, as in the case of the absorption spectral change.

To achieve this reversible ET between Ru^{II} and Cu^{II} centers in one molecule as molecular bistability, we prepared a $Ru^{II}-$TPA complex having as a Cu^{II} binding site a Mebpy moiety bound at the 6-position of one of pyridine rings of TPA via an amide linkage. The Ru^{II} complex $[RuCl(TPA\text{-}Mebpy)]^+$ (**3**) bearing the *N*-[6-{2-(6′-methylpyridin-2′-yl)carbonylamide}pyridine-2-yl]-methyl-*N*-bis(2-pyridylmethyl)amine (TPA-Mebpy) ligand was synthesized using the procedure depicted in Scheme S1 in the SI. We first synthesized the complex $[RuCl(TPA\text{-}Clpy)]^+$ bearing the *N*-bis[{6-(2′-chloropyrid-4-yl)carbonylamide}pyrid-2-yl]methyl-*N*-(2-pyridylmethyl)amine (TPA-Clpy) ligand; this complex was crystallographically characterized to demonstrate the coordination of the amide oxygen to the Ru^{II} center (Figure S6). Complex **3** was then synthesized via Pd-catalyzed Stille coupling[22] of 2-trimethylstannyl-6-methylpyridine with $[RuCl(TPA\text{-}Clpy)]^+$. Formation of a $Cu^{II}-$Mebpy complex was accomplished via the reaction of **3** with $[Cu(NO_3)_2(6\text{-}Mebpy)]$ in EtOH containing NEt_3 to afford the deprotonated form $[RuCl\{TPA\text{-}(Cu\text{-}(Mebpy)_2) - H^+\}]^{3+}$ (**4−H⁺**).[23] After the condensation, an excess amount of NH_4PF_6 was added to the solution to obtain the precipitate of the protonated complex **4**. The formation of **4** was confirmed by electrospray ionization mass spectrometry (ESI-MS) and elemental analysis (Figure S8).

Scheme 2. Intramolecular Proton-Coupled Electron Shuttling in 4



The redox potentials of complex **4** were determined by cyclic voltammetry and differential pulse voltammetry in CH_3CN at room temperature in the presence of $(n\text{-Bu})_4NPF_6$ as a supporting electrolyte under an Ar atmosphere (Figure S9). The redox potentials (vs SCE) of $4-H^+$ were determined under basic conditions. The results are summarized in Table 1. Addition of 1 equiv of NEt_3 or 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) caused deprotonation of the amide bridge of **4**, affording $4-H^+$. As for the protonated form (**4**), the oxidation potential of the Ru^{II} center was determined to be +0.69 V, which is higher than the reduction potential of the Cu^{II} center (+0.39 V). Therefore, no ET from the Ru^{II} center to the Cu^{II} center occurred. In contrast, for the deprotonated form ($4-H^+$), the redox wave assigned to the Ru^{II}/Ru^{III} couple was negatively shifted to +0.17 V. This negative shift results from the deprotonation of the amide bridge, which induces an increase in the electron density at the Ru^{II} center, causing the Ru^{II} center to be more easily oxidized. As a result, the redox potential of the Ru center of $4-H^+$ was lowered to be more negative than that of the Cu center, providing the driving force for intramolecular ET ($-\Delta G_{et} = 0.23$ eV) to generate the Ru^{III}/Cu^{I} state. On the contrary, back-ET from the Cu^{I} center to the Ru^{III} center should be possible upon protonation of $4-H^+$, with $-\Delta G_{et} = 0.30$ eV. Thus, we can conclude that the oxidation states of the Ru and Cu centers in **4** should be Ru^{II} and Cu^{II} and those in $4-H^+$ should be Ru^{III} and Cu^{I} (Scheme 2).

Under acidic conditions in CH_3CN, **4** exhibited the LMCT absorption band of the Ru^{II}-complex moiety at 352 nm, and under basic conditions where $4-H^+$ should be formed, a red-shifted absorption was observed at 472 nm (Figure S10). In light of the oxidation states mentioned above, the absorption observed at 472 nm was ascribed to the MLCT transition of the Cu^{I}-$(6\text{-}Mebpy)_2$ moiety, and this assignment was confirmed by its consistency with that of authentic $[Cu(Mebpy)_2]^+$ in CH_3CN.[24] The spectrum of **4** was recovered by the addition of $HClO_4$. This spectral change was reversible and repeatable by alternate addition of acid and base in CH_3CN at room temperature (Figure 1).

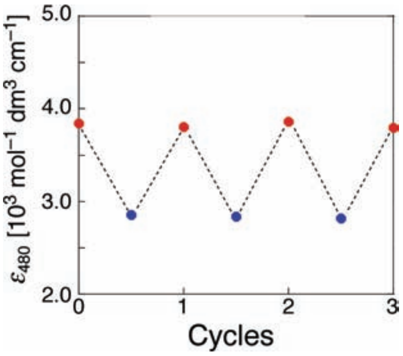


Figure 1. Repeatable response of complex **4** in CH_3CN by alternate addition of $HClO_4$ (red ●) and DBU (blue ●), as monitored by the absorption change at 480 nm.

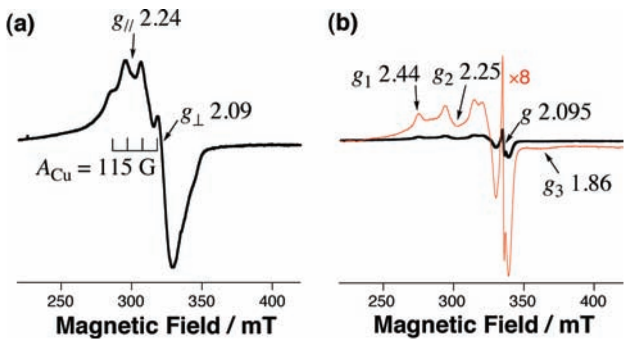


Figure 2. EPR spectra (CH_3CN, 98 K) of (a) **4** and (b) **4**−$\mathbf{H}^+$ obtained upon addition of 1 equiv of DBU to **4**.

To elucidate the oxidation states of the metal centers, EPR spectra of **4** and **4**−$\mathbf{H}^+$ were measured at 98 K in frozen CH_3CN solutions under acidic and basic conditions, respectively (Figure 2). The EPR spectrum of **4** under acidic conditions showed a clear signal at $g = 2.09$ with $A_{Cu} = 110$ G, corresponding to that of an $S = {}^1/_2$ Cu^{II} complex with a highly distorted coordination environment. This is consistent with the conclusion obtained from the redox potentials mentioned above. On the other hand, the EPR spectrum was drastically changed by addition of DBU. The EPR spectrum of **4**−$\mathbf{H}^+$ observed under basic conditions was revealed to include the Ru^{III} center ($S = {}^1/_2$) in the TPA coordination environment, which was observed at $g_1 = 2.44$, $g_2 = 2.25$, and $g_3 = 1.86$ with a large anisotropy.[25]

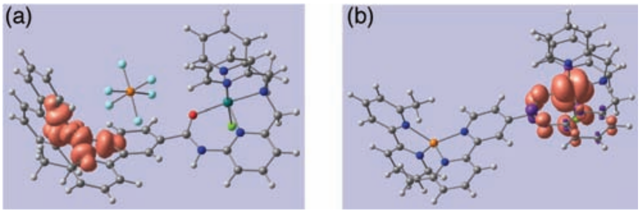


Figure 3. Spin density distributions of (a) $\mathbf{4}\cdot PF_6$ and (b) **4**−$\mathbf{H}^+$ obtained from DFT calculations at the B3LYP/SDD level of theory.

The spin densities of complexes **4** and **4**−$\mathbf{H}^+$ were investigated using density functional theory (DFT) calculations on the protonated and deprotonated species at the amide bridge.[26] The DFT calculations indicated that the protonated structure **4** exhibits localized spin density only on the Cu^{II} complex with the spin density ratio of the Cu^{II} center (0.66) and the two bpy ligands (0.34) as shown in Figure 3a, which is consistent with the EPR results in Figure 2a. In the optimized structure of **4**, the dihedral angle (θ) between the amide-linked Mebpy and the mean plane of the chelating amide moiety and the connected pyridine was estimated to be 38.4°, suggesting a distorted structure between the Ru−TPA moiety and the $Cu(Mebpy)_2$ moiety due to steric hindrance between the amide N−H and the 3-H of the linked pyridine of the amide-bonded Mebpy ligand (Figure S11a,b). In contrast to the case of the protonated form **4**, the spin density of the deprotonated structure **4**−$\mathbf{H}^+$ was mainly localized on the Ru^{III} complex moiety with the density ratio of the Ru^{III} center (0.82) and the ligands (0.18) as depicted in Figure 3b. The DFT calculations revealed that the spin density of the ligands mainly rides on the region of the pyridine−amide linkage. This part is coplanarized by the deprotonation, which reduces the steric hindrance (as represented by the smaller dihedral angle $\theta = 11.6°$) to extend π conjugation through the amide bridge (Figure S11c,d). This extension of π conjugation can elevate the energy level of the π orbital to make it easy for the unpaired electrons to delocalize into the bridging moiety made of one pyridine and the amide linkage.

In summary, we have synthesized a covalently linked Ru^{II}−TPA−$Cu^{II}(Mebpy)_2$ heterodinuclear complex using a Pd-catalyzed Stille coupling reaction followed by complexation of the appended 6-Mebpy moiety to form the $[Cu(Mebpy)_2]^{2+}$ part. The intramolecular ET reaction from the Ru^{II} center to the Cu^{II} complex and the back-ET in the opposite direction were reversibly switched by deprotonation and protonation, respectively, at the amide bridge of the complex. These phenomena are based on redox-potential control of the Ru center. Thus, we have achieved a novel bistability, *proton-coupled electron shuttling*, represented by reversible intramolecular PCET between two different metal centers in different coordination environments. In the case of the heterodinuclear complex **4**, the two electronic states Ru^{II}/Cu^{II} and Ru^{III}/Cu^{I} can be formed by additions of acid and base, respectively, which cause the intramolecular PCET reactions. Further application of this unique bistability, proton-coupled electron shuttling, to other phenomena is in progress in our laboratories.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Synthetic details, computational details, spectroscopic titrations, electrochemical data, complete ref 3c, and crystallographic data for $\mathbf{3}\cdot PF_6$ (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) The redox potential of the Ru^{II}/Ru^{III} couple of complex $\mathbf{1}^+$ was determined to be $E_{1/2}$ = +0.63 V (vs SCE) and shifted to +0.13 V upon deprotonation of the coordinated amide N—*H* (see ref 13b).

(18) Complex $\mathbf{2}^{2+}$ exhibited a reversible redox wave at $E_{1/2}$ = +0.41 V (vs SCE) due to the Cu^{II}/Cu^{I} couple. This redox process is expected to cause a structural conversion between a pseudo-square-planar structure of the Cu^{II} state and a tetrahedral structure of the Cu^{I} state. The redox potentials ($Cu^{I/II}$) for $[Cu(bpy)_2]^{2+}$ and $[Cu(6,6'\text{-}Me_2bpy)_2]^{2+}$ in CH_3CN at room temperature in the presence of 0.1 M $TBAPF_6$ as an electrolyte were also determined by cyclic voltammetry to be −0.17 and +0.72 V vs SCE. See: (a) Murali, M.; Palaniandavar, M. *Transition Met. Chem.* **1996**, *21*, 142. (b) Youiou, M.-T.; Ziessel, R.; Lehn, J.-M. *Inorg. Chem.* **1991**, *30*, 2144.

(19) The absorption spectrum after addition of 1 equiv of $\mathbf{2}^{2+}$ was comparable with the summation of the spectra of the one-electron-oxidized species $[Ru^{III}Cl((1\text{-Naph})_2\text{-TPA} - H^+)]^+$ ($[\mathbf{1}\text{—}\mathbf{H}^+]^+$), which was generated by the electrochemical oxidation, and the one-electron-reduced species $[Cu^{I}(Mebpy)_2]^+$ ($\mathbf{2}^+$), which was obtained by the chemical reduction with hydrazine (see Figure S3).

(20) When 1 equiv aliquots of NEt_3 and $HClO_4$ were added alternately to the mixture of $\mathbf{1}^+$ and $\mathbf{2}^{2+}$, the UV—vis absorption spectra varied back and forth between the one obtained by addition of NEt_3 and to the one obtained by addition of $HClO_4$. These spectral changes were observed repeatedly, indicating that ET from Ru^{II} to Cu^{II} and from Ru^{III} to Cu^{I} can be switched reversibly by addition of base and acid, respectively (see Figure S4).

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(23) The formation of the 1:1 heterodinuclear complex **4** was confirmed by a titration experiment, and the determination of the binding constant between **3** and $[Cu(NO_3)_2(6\text{-Mebpy})]$ is also included in the SI (see Figure S7).

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(25) An isotropic sharp signal due to an organic radical was also observed at g = 2.01, but the signal intensity was negligible (0.2%) relative to the signal due to the Ru^{III} center at 60 K.

(26) The DFT-optimized structures of **4** and $\mathbf{4}\text{—}\mathbf{H}^+$ are depicted in Figures S11a,b and S11c,d, respectively.