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A Single Molecular System Gating Electron Transfer by Ring Inversion of a Methylpyridylpyrimidine Ligand on Copper

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Molecular machines have received much attention recently because of their potential applications in molecular devices.[1] Many artificial molecular machines have been created using transition-metal complexes or organic compounds. These machines are driven by external stimuli such as heat, light, or electrons, giving rise to various motions at the molecular level,[2] including elastic and rotative motion in biosystems.[3] However, there are few reported examples of molecular motions that yield an effective output, such as an electrical signal.[4] In contrast, biomolecules, which are regarded as highly function-integrated molecular machines, utilize their motion very effectively in important biological processes. For example, electron transfer (ET) proteins comprising multiple redox centers mediate unidirectional ET events with high efficiency in processes such as photosynthesis[5] and respiration.[6] Recent studies have determined that conformational changes in proteins play a key role in the ET steps between redox components.[7] Conformational ET rate control was also observed in small artificial molecular systems using copper complexes with macrocyclic ligands designed as model compounds mimicking blue copper proteins.[8] However, there are no reports of the regulation of ET events by active control of ligand motion in copper complexes. In the present work, we succeeded in regulating ET to an electrode via copper complexes by controlled rotational motion of a methylpyridylpyrimidine ligand.

Structural interconversion was accomplished via pyrimidine ring inversion arising from the lability of d^{10} metal−nitrogen bonds. 4-Methyl-2-(2′-pyridyl)pyrimidine[9a] (**Mepypm**) was employed as a ligand in Cu^{I} complexes; in addition, 2,9-dianthracenylphenanthroline[9b] (**danphen**) was embedded in the complex to lock the ring inversion by means of the steric effects of two anthracene planes.

Reaction of [Cu(**danphen**)$(MeCN)_2$]BF_4 and 1 equiv of **Mepypm** in dry dichloromethane produced the ocher compound [Cu(**Mepypm**)(**danphen**)]BF_4 (**1·BF$_4$**). Because bulky groups at the 2- and 9-positions impede homoleptic complexation, the heteroleptic Cu^{I} complex was formed selectively.[10] Another heteroleptic Cu^{I} complex containing a macrocyclic ligand, **2·BF$_4$**, was synthesized as a reference with a different steric effect on ring inversion. X-ray structural analysis revealed that the methyl group is oriented toward the metal center, and no disorder was found in the crystal structure, suggesting that all **1·BF$_4$** species exist as the inner (***i***) isomer in the solid state (Figure S1).

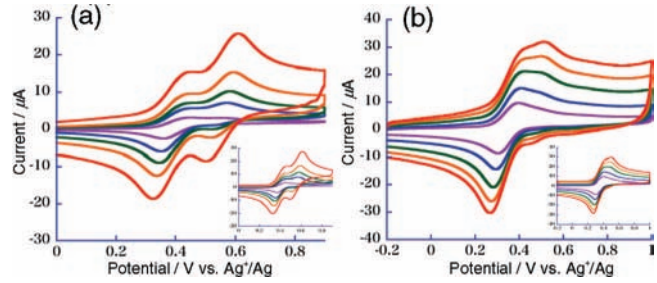

Figure 1. Cyclic voltammograms (vs Ag^+/Ag) in 0.1 M Bu_4NBF_4/CH_2Cl_2 at 296 K. Insets: simulated CVs. Scan rates, from inside to outside: (a) 0.01, 0.05, 0.1, 0.2, and 0.5 V s^{-1} for **1·BF$_4$**; (b) 0.1, 0.25, 0.5, 0.75, and 1.0 V s^{-1} for **2·BF$_4$**.

In the cyclic voltammogram (CV) of **1·BF$_4$** (Figure 1), two redox waves were observed at $E^{0\prime} = 0.38$ and 0.55 V vs Ag^+/Ag, indicating that $\mathbf{1}^+$ exists in solution as a mixture of two isomers, namely, the inner and outer (***o***) isomers. The redox couple with the more positive $E^{0\prime}$ can be assigned to the ***i*** isomer, because the presence of a methyl group adjacent to the coordinating N atom prevents the formation of a favorable square-planar structure in the Cu^{II} state.[8] As the scan rate increased, the anodic peak current for the second (***i*** isomer) wave, i_{ai}, increased relative to that of the first (***o*** isomer) wave, i_{ao}. In addition, the cathodic peak current, i_{ci}, grew with increasing scan rate.

These results indicate that the ***i*** → ***o*** ring-inversion process occurs over a time scale similar to the scan rate in solution and that the change in relative isomer stability with oxidation promotes ring inversion to a different ***i/o*** molar ratio; the Cu^{II} derivatives generated during the oxidation process favor a square-planar configuration, which is more stable in the ***o*** configuration. In the case of **2·BF$_4$**, which does not have bulky groups on phenanthroline, higher scan rates or lower temperature[11] were required to observe two distinct waves corresponding to the ***o*** and ***i*** isomers, whose redox potentials were determined as $E^{0\prime} = 0.31$ and 0.46 V vs Ag^+/Ag at 293 K by simulation analysis of the CV (Table S3). These differences indicate that the inversion rate of $\mathbf{2}^+$ is higher than that of $\mathbf{1}^+$. This was evidenced by the difference in broadness of the methyl-group resonance in the ^{1}H NMR spectra at room temperature (Figure S3). Two sharp, clearly resolved methyl signals corresponding to the two isomers of $\mathbf{1}^+$ were observed, whereas the signal derived from the ***o*** configuration of $\mathbf{2}^+$ was broad, demonstrating that the interconversion between the ***i*** and ***o*** isomers in $\mathbf{2}^+$ is comparable with the ^{1}H NMR time scale and much faster than in $\mathbf{1}^+$. In the CVs of $\mathbf{1}^+$, the existence of $\mathbf{1}^{2+}$(***i***) is clearly discernible, indicating that the ***i*** configuration of a metastable $\mathbf{1}^{2+}$(***i***) state can be locked against ring inversion by the inversion barrier of two anthracene moieties.

These redox processes associated with the conformational interconversion can be interpreted by a dual-pathway square-scheme

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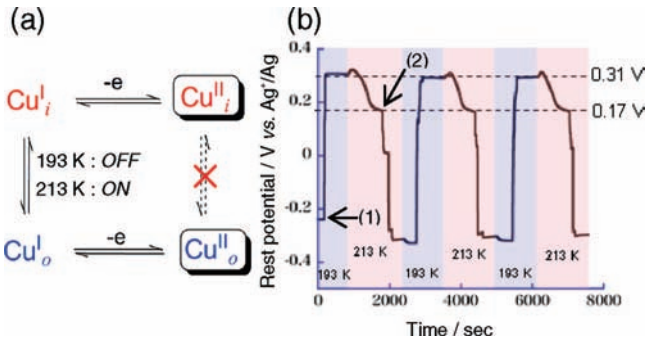

Figure 2. (a) Dual-pathway ET mechanism. (b) Time course of the change in E_{rest} (1) on addition of $(NH_4)_2[Ce^{IV}(NO_3)_6]$ and (2) on addition of $[Fe(\eta^5\text{-}C_5Me_5)_2]$. The negative shift in E_{rest} ($\Delta E = 0.14$ V) was observed over a time span of 900 s.

mechanism (Figure 2a).[12] According to this mechanism, we simulated the CVs at various scan rates (see the insets in Figure 1).[13] The simulated CVs are consistent with the experimental CVs. The thermodynamic and kinetic parameters for ring inversion were estimated by CV simulation at various temperatures (Table 1). Consistent with the NMR data above, the rate constant $k_{i\rightarrow o}$ for $\mathbf{2}^+$ at 293 K is ~150 times larger than that of $\mathbf{1}^+$. The most remarkable difference was found in the $\Delta S^{\ddagger}$ values: both are negative, but the value for $\mathbf{1}^+$ (-124 J K^{-1} mol^{-1}) is almost four times larger in magnitude than that for $\mathbf{2}^+$ (-33 J K^{-1} mol^{-1}). A lack of open space for the pyrimidine ring in the transition state of $\mathbf{1}^+$ accounts for the large negative activation entropy, indicating that the anthracene moieties function as "stoppers" for the rotational motion. Inversion is also influenced by the valence of the copper ion: the rate constant $k_{i\rightarrow o}$ in the Cu^{II} state is smaller than that in the Cu^{I} state. Slower inversion in the Cu^{II} complex arises because of stronger binding between the copper center and the coordinating N atoms, which is caused by crystal-field splitting and enhancement of electrostatic interactions. At low temperatures, not only are the two redox reactions reversible, but their peak current ratio is independent of the scan rate (Figure S4), indicating that on/off switching of ring inversion is controllable by temperature and that the inversion process in $\mathbf{1}^+$ can be frozen.

As ring inversion induces a change in the Cu^{II}/Cu^{I} redox potential, it is plausible that temperature-dependent on/off switching of the inversion motion can gate ET events between $\mathbf{1}^+$ and the surrounding environment. This gating of ET between $\mathbf{1}^+$ and an electrode was demonstrated by monitoring the shift in the electrode potential upon inversion. When 0.7 equiv of the oxidant $(NH_4)_2[Ce^{IV}(NO_3)_6]$ was added to a solution of $\mathbf{1}^+$ in 0.1 M $Bu_4NBF_4/CH_2Cl_2-CH_3COCH_3$ at 193 K, the rest potential (E_{rest}) shifted to +0.31 V vs Ag^+/Ag and then remained constant, indicating that nearly all of the ***o*** isomer was oxidized and that the rest potential was dominated by the $\mathbf{1}^{2+}(\boldsymbol{i})/\mathbf{1}^{+}(\boldsymbol{i})$ ratio ($E^{0\prime} = 0.34$ V at 193 K). Subsequent warming of the system to 213 K caused a negative shift in E_{rest} to +0.17 V without electron injection from outside. The E_{rest} value after warming suggests that the ET equilibrium is dominated by the $\mathbf{1}^{2+}(\boldsymbol{o})/\mathbf{1}^{+}(\boldsymbol{o})$ ratio ($E^{0\prime} = 0.14$ V at 213 K); thus, the observed potential shift appears to be mediated by the $\boldsymbol{i} \rightarrow \boldsymbol{o}$ ring-inversion process. The observed potential shift was identical to the calculated values (0.35 V at 193 K and 0.18 V at 213 K) according to the thermodynamic parameters of the inversion equilibrium (Table S4). Moreover, the 900 s interval required for the potential relaxation is reasonable for the time scale of the time course of the potential change simulated on the basis of the gated scheme (Figure S8), where the ring-inversion process in the Cu^{II} state is assumed to be frozen at 213 K. These results demonstrate that ET via $\mathbf{1}^+$ is gated by the ring inversion. Furthermore, the electron gating can be driven repeatedly, as the pyrimidine ring can be reset to the inner position by reduction of the copper center from Cu^{II} to Cu^{I}. The initial state was restored by reducing the Cu^{II} species with decamethylferrocene, and reproducible potential changes were obtained by repeating the sequence of procedures, as shown in Figure 2b.

Table 1. Kinetic Parameters for the Ring Inversion Process in Copper Complexes at 293 K[a]

complex	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})	$\Delta G^{\ddagger}$ (kJ mol^{-1})	$k_{i\rightarrow o}$ (s^{-1})
$\mathbf{1}^+$	36	−124	73	1
$\mathbf{2}^+$	50	−33	60	148

[a] Coexisting in 0.1 M Bu_4NBF_4 in CH_2Cl_2.

In conclusion, we constructed an ET gating system in a copper complex by ring inversion of a pyrimidine ligand, whose motion can be controlled by a steric approach. In comparison with the conformationally gated ET phenomena reported to date,[14] our approach provides a new single molecular system that extracts electric energy from controlled motion.

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Supporting Information Available: Materials and methods, crystal structure data (CIF), and electrochemical and spectral data. This material is available free of charge via the Internet at http://pubs.acs.org.

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