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Intramolecular Electron Arrangement with a Rotative Trigger

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The fabrication of molecular functionalities for a breakthrough in the size of devices is an intensively studied and discussed area of research. The clear extraction of a single molecule's response is vital, and the handling of valence electrons within a molecular system is the most promising way to cause an effective electronic response concerning a controlled transfer phenomenon such as electron conduction,[1] magnetic ordering,[2] or light energy transduction.[3]

Valence tautomerism[4] causes reversible energy conversion in electronic, magnetic, and optical systems accompanied by intramolecular electron transfer (ET). But most of their bistability and precipitous ET events depends on synergistic intermolecular interactions in a mesoscopic scale. Bond rearrangements and/or large structural conversions within a molecular structure, such as protonation[5] and photochromism,[6] are promising for a bistable ET handling in the isolated molecules.

Active control over molecular motion introduced a novel class of molecular machines in these two decades.[7] Unidirectional rotation or elastic motion has been achieved, but employing these motions functionally remains a task under development.

These research trends clearly point to the requirements for electron manipulation through geometrically defined molecular motion. In a recent paper, we reported the rotational motion of an asymmetric pyrimidine ring coordinated to copper, which causes a redox potential change of Cu(II/I), detectable as an electromotive force.[8] In the present study, we constructed a two-center intramolecular ET system using the above-mentioned copper complex component and ferrocene. Electron migration from the copper to the ferrocene was successfully regulated by inversion of the pyrimidine ring.

The compound 2-(2-(5-ferrocenyl)pyridyl)-4-methylpyrimidine (FcMpmpy) was prepared by Suzuki−Miyaura cross-coupling of ferrocenylboronic acid and the corresponding bromo compound. A heteroleptic copper(I) complex, $[Cu(FcMpmpy)(L_{Anth})]BF_4$ (L_{Anth} = 2,9-bis(9-anthryl)-1,10-phenanthroline, Figure 1), was readily formed in a one-pot reaction by mixing equimolar quantities of the ligands and $[Cu(MeCN)_4]BF_4$. No traces of the homoleptic complex, $[Cu(L_{Anth})_2]^+$, were found in the ^{1}H NMR spectrum, because its formation is sterically hindered.

Single crystals of $[Cu(FcMpmpy)(L_{Anth})]BF_4 \cdot p$-xylene (Figure S1) contain only the *i*-isomer (in which the methyl group is directed toward the copper center), with well-separated positioning of the complex cations. A single crystal of $[Cu(FcMpmpy)(L_{Anth})]BF_4 \cdot$benzene (Figure 1a) was found to contain ordered 1:1 arrays of *i*- and *o*-isomers, in which the alternate pyrimidine rings are proximal (Figure S2). These results demonstrate that the convertible nature of coordination isomers depends strongly on external structural conditions.

In the solution state, ^{1}H NMR signals of $[Cu(FcMpmpy)(L_{Anth})]^+$ in acetone-d_6 (Figure S3) were split into independent ones of the two isomers, with a ratio of ca. 3:2 at room temperature. These

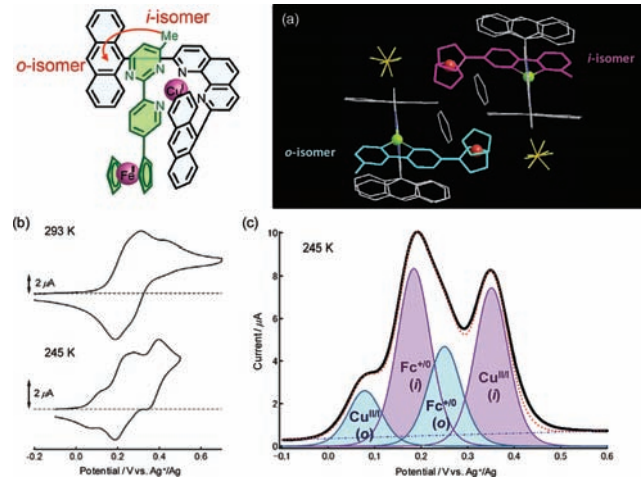

Figure 1. (a) Crystal structure of $[Cu(FcMpmpy)(L_{Anth})]BF_4 \cdot$benzene. (b) Cyclic voltammograms of $[Cu(FcMpmpy)(L_{Anth})]BF_4$ in 0.1 M Bu_4NBF_4−acetone at 293 K (upper) and 243 K (lower) at a scan rate of 25 mV s^{-1}. (c) Differential pulse voltammogram of $[Cu(FcMpmpy)(L_{Anth})]BF_4$ in 0.1 M Bu_4NBF_4−acetone at 243 K (black solid line). Deconvoluted peaks are overlaid and summed to yield simulative data (red dotted line).

isomers were assigned as *i*- (major) and *o*- (minor) isomers, respectively, based on their chemical shifts and considering the shielding effects of the copper and anthracene moieties. The molar ratio of the isomers was temperature-dependent, suggesting that *i*-/*o*-isomers interconvert through pyrimidine ring inversion to attain an equilibrated state. At temperatures below 233 K, the ring inversion appears to be thermally blocked, as van't Hoff plots of the inversion equilibrium did not follow the linearity (Figure S4).

Electrochemical measurements have revealed that the redox behavior of $[Cu(FcMpmpy)(L_{Anth})]^+$ significantly differs between two inversion isomers. A cyclic voltammogram of the complex at 243 K (Figure 1b) showed multiple redox waves that converged to a simple two-step wave at higher temperatures. The convergence can be interpreted as a rapid interconversion of the two isomers relative to the potential scan rate. A differential pulse voltammogram at 245 K (Figure 1c) can be deconvoluted into four redox peaks, and it is reasonable to assign them to two species, *i*- (major) and *o*- (minor) isomers with two redox centers (Cu(II/I) and ferrocenium/ferrocene). The simulative cyclic voltammogram analysis (Figure S5) also suggests the existence of two species with double redox processes. Relative *i*-/*o*- stability in each oxidation state can also be determined from these redox potentials: the *o*-isomer is highly favored in the divalent and trivalent states (K_{io} = [*o*-isomer]/[*i*-isomer] = 63 and 1.7 × 10^4, respectively) but not in the monovalent state (K_{io} = 0.44).

The potential order of redox centers in each isomer was determined by EPR and UV−vis absorption spectroscopy upon chemical oxidation. First, the potential order of the *o*-isomer was

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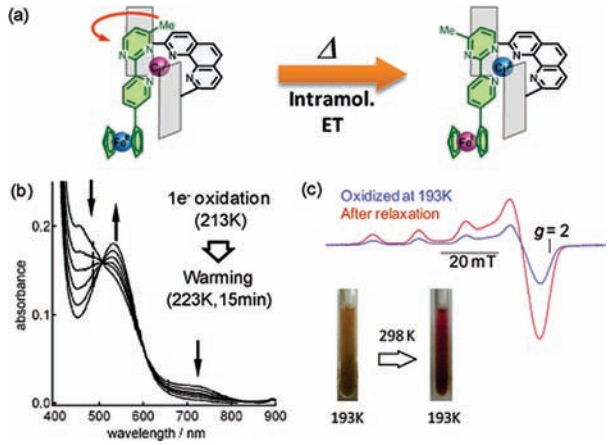

Figure 2. (a) Conceptual illustration of the rotation-triggered intramolecular ET process. (b) Time-course UV−vis absorption spectral changes of $[Cu(FcMpmpy)(L_{Anth})]^{2+}$ in acetone formed by the addition of $(NH_4)_2[Ce(NO_3)_6]$ to a solution of $[Cu(FcMpmpy)(L_{Anth})]BF_4$ at 213 K and upon warming to 223 K. (c) EPR spectra of $[Cu(FcMpmpy)(L_{Anth})]^{2+}$ measured in acetone after addition of $(NH_4)_2[Ce(NO_3)_6]$ to a solution of $[Cu(FcMpmpy)(L_{Anth})]BF_4$ at 193 K, followed by cooling to 100 K (blue), and after the subsequent warming to 298 K followed by cooling to 100 K via 193 K (red). The appearance of the sample at 193 K in each step is shown in the inset photographs.

determined, because the *o*-isomer is thermally dominant in both divalent and trivalent states. Upon 1e$^-$ oxidation at 293 K, an anisotropic EPR signal characteristic to Cu(II) with a spin density of 1.0 was observed (Figure S6).

Thus, it is concluded that an electron is extracted first from copper, then by ferrocene in the *o*-isomer form. The UV−vis spectra of each oxidized form could subsequently be assigned. A charge-transfer (CT) band from ferrocene to Cu(II) appears at 530 nm in the divalent state, and a typical ligand-to-metal charge transfer (LMCT) band of ferrocenium is found at ∼700 nm in the trivalent state (Figure S7).

The 1e$^-$ oxidation at 213 K, when ring inversion was thermally prohibited, afforded different spectral changes of two successive processes (Figure S8). The first spectral change (0−0.4 equiv) was characterized by a new absorption peak at 530 nm, which strongly suggests the formation of Cu(II) in the *o*-isomer form. In the second change (0.4−1.0 equiv), a new broad absorption peak at ∼700 nm appeared, whose energy and molar extinction coefficient are characteristic of ferrocenium LMCT. Thus, the oxidation can be attributed to the ferrocene moiety in the *i*-isomer form. The possibility of a second oxidation of the *o*-isomer can be excluded, because the disappearance of the CT band at 530 nm was not accompanied with ferrocenium LMCT emergence (Figure S7). These assignments are supported by the EPR spectrum of the sample oxidized with 1e$^-$ at 193 K, which shows a Cu(II) pattern with a smaller spin density (0.38) than the spectrum at 293 K.

The above results suggest that the 1e$^-$-oxidation center is reversed with the ring inversion, and the structural isomers (*i*- and *o*-) directly relate to the valence isomer (Cu(I)-ferrocenium and Cu(II)-ferrocene) in the divalent state. This means that the motions of pyrimidine inversion can induce directional electron transfer from copper to the ferrocene moiety (Figure 2a). This was experimentally demonstrated by monitoring the *i*- to *o*- isomerization by elevating the temperature to unlock the pyrimidine inversion.

The unequilibrated (*i*-rich) divalent state was prepared by oxidation of $[Cu(FcMpmpy)(L_{Anth})]^+$ at 213 K. Then, the sample was warmed to 223 K to monitor the *i*- to *o*-inversion. Upon warming, the absorption spectrum gradually evolved with an isosbestic point (Figure 2b). The spectral change could be described as breaching at 450 nm (metal-to-ligand CT (MLCT) on Cu(I)) and 700 nm (LMCT on ferrocenium), with a rise at 533 nm (CT from Cu(II) to ferrocene) signifying valence electron rearrangement. EPR also confirmed that warming the sample to room temperature after 1e$^-$ oxidation at 193 K increased the spin density from 0.36 to 0.86, with a significant change in the sample color (Figure 2c).

At present, we propose that the difference in stability of the Cu(II) coordination structure is the major factor for the reversed ET behavior of isomers. The Cu(II) state is likely to exist in a pentacoordinated form, and weak coordination of another species (anion or solvent) seems to be strongly hindered by the methyl substituent in the *i*-isomer form, destabilizing the Cu(II) state.

In conclusion, we have constructed a novel intramolecular electron gating system that converts the rotative motion of a coordinative pyrimidine ring into directional electron transfer between two redox centers. The rotational equilibrium in the monovalent state appears to be controllable by application of a weak interaction. We are currently developing molecular structures in which rotational motion can be driven by light-induced structural rearrangement.

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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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