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Dual Emission Caused by Ring Inversion Isomerization of a 4-Methyl-2-pyridyl-pyrimidine Copper(I) Complex

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Abstract: We developed a new convertible copper(I) complex using 2-pyridyl-4-methylpyrimidine and diphosphine as ligands. This complex exhibited mechanical bistability based on the inversion motion of the pyrimidine ring, leading to dual luminescence behavior. The inversion dynamics was strongly dependent on temperature and solvent. Variable-temperature ^{1}H NMR spectra revealed that the two isomers interconverted in solution via ring inversion, and the motion was frozen below 200 K. The complex exhibited characteristic CT absorption and emission bands in solution. Emission lifetime measurements demonstrated that the emission could be deconvoluted into two components. The fast and slow components were assigned to the two isomers, the excited states of which were characterized by different structural relaxation process and/or additional solvent coordination properties. The emission properties of the two isomers differed not only in lifetime and wavelength but also in heat sensitivity. The molar ratio of the two isomers varied with the polarity of the solvent via electrostatic interactions with the counteranion. The rate of inversion was affected by solvent, suggesting that inversion was promoted by solvent coordination.

The photoprocesses of transition metal complexes are of interest for their potential use in dye-sensitized solar cells,[1] light-emitting devices,[2] and photocatalysts[3] due to a combination of high thermal stability, reversible redox activity, intense visible absorption, and the formation of a long-lived charge transfer (CT) excited state. Recently, photofunctional molecules have been synthesized using simple metal complexes that exhibit dual phosphorescence as a result of the presence of two independent excited states.[4] Unfortunately, methods for selectively preparing one of the two states have thus far been limited. The state selection requires a system characterized by well-defined bistability via a reversible chemical process.

We have recently described novel molecular mechanical systems that operate as electron gates by exploiting the inversion motion of pyrimidine on copper to give inner (*i*-) or outer (*o*-) isomers in which a substituent on the pyrimidine is, respectively, proximal or distal to the copper center.[5] In the present work, we developed a new copper(I) complex using 4-methyl-2-(2′-pyridyl)pyrimidine (**Mepypm**) and bis[2-(diphenylphosphino)phenyl]ether (DPEphos) as ligands. This complex exhibited geometric bistability based on inversion of the pyrimidine, which led to dual luminescence behavior. The dynamics of inversion were sensitive to temperature and solvent, suggesting that the excitation process could be tuned using the inversion process.

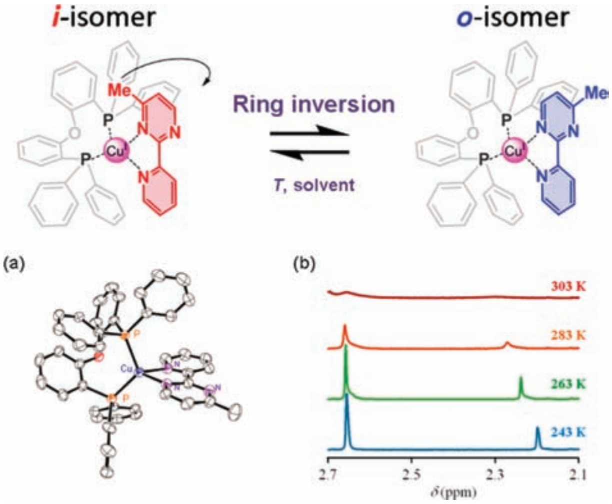

Figure 1. Ring inversion equilibrium between the *i*- and *o*-isomers of $\mathbf{1}^+$. (a) An ORTEP view of $\mathbf{1{\bullet}BF_4{\bullet}CHCl_3}$, showing 50% probability displacement ellipsoids. Hydrogen atoms, a counteranion, and a solvent molecule are omitted for clarity. (b) ^{1}H NMR spectra of $\mathbf{1}^+$ in acetone-d_6 at several temperatures in the methyl group region.

[Cu(**Mepypm**)(DPEphos)]BF_4 ($\mathbf{1{\bullet}BF_4}$) was newly synthesized by a reaction of [Cu(MeCN)$_4$]BF_4 with **Mepypm** and DPEphos in dichloromethane according to procedures described in the literature[6] (for synthetic details, see the Supporting Information).

X-ray structural analysis of $\mathbf{1{\bullet}BF_4}$ revealed that the methyl group in **Mepypm** was oriented away from the metal center, and no disorder was found in the coordination mode (Figures 1a and S1). This result suggested that all $\mathbf{1{\bullet}BF_4}$ species exist as the *o*-isomer in a single crystal, in contrast with the existence of the *i*-isomer in a single crystal of the previous complex formed from **Mepypm** and a phenanthroline derivative.[5] The bulky diphosphine appeared to repel the methyl group of the *i*-isomer away from the metal center.

The ^{1}H NMR peaks of $\mathbf{1{\bullet}BF_4}$ in acetone-d_6 at 243 K could be clearly assigned to either the *i*- or *o*-isomer without evidence for other coordination species (Figures 1b and S2). The chemical shifts of these peaks were affected by the shielding effects of the copper and the phenyl group of DPEphos, and the major and minor peaks were assigned, respectively, to *o*- and *i*-isomers.[5] These signals broadened upon heating, indicating that the *i*- and *o*-isomers interconverted in solution by ring inversion, which occurred on the time scale of the ^{1}H NMR experiment (Figures 1b and S3).

The rates of interconversion were sufficiently high that the system reached equilibrium. The equilibrium constant was determined from the integral of the signals as a function of temperature. The molar

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10.1021/ja103718e

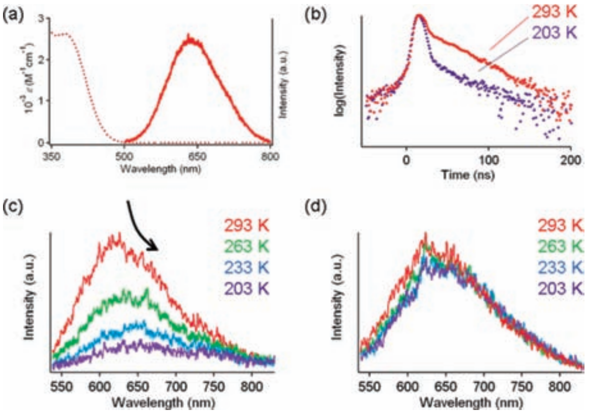

Figure 2. Photochemical properties of **1•BF$_4$**. (a) UV−vis absorption spectrum (dotted line) and the steady-state emission spectra using 400 nm excitation (solid line) of **1**$^+$ in acetone at room temperature. (b) Experimental 630 nm emission decay of **1**$^+$ in acetone at room temperature (red) and 203 K (purple) excited at 425 nm. Time-resolved emission spectra of **1**$^+$ in acetone at several temperatures for the slower ($\tau = 40$ ns) component (c) and the faster ($\tau = 2$ ns) component (d).

ratio of the *i*- and *o*-isomers in acetone remained 3:7 over the temperature range from 203 to 293 K (Figure S4).

The UV−vis absorption spectrum of **1**$^+$ in acetone showed the characteristic CT absorption bond ($\lambda_{\text{abs}} = 378$ nm, $\epsilon = 2.7 \times 10^3$ M^{-1} cm^{-1}) of the [Cu(diimine)(diphosphine)]$^+$ family (Figure 2a). The absence of an absorption around 450 nm and the independence of the absorption profile on the concentration of **1**$^+$ suggested that the formation of other species, such as [Cu(**Mepypm**)$_2$]$^+$, was negligible.[6] The steady-state emission spectrum of **1**$^+$ in acetone (Figure 2a) exhibited emission at $\lambda_{\text{em}} = 635$ nm from the CT state.[6] These results indicate that the wavelengths of maximum absorption and the emission energies of the *i*- and *o*-isomers were comparable.

Emission lifetime measurements of **1**$^+$ revealed that the decay curve could be deconvoluted into two components (Figures 2b and S5). The [Cu(diimine)(diphosphine)]$^+$ family is known to show a single decay.[6,7] Therefore, the two components could be reasonably assigned to the *i*- and *o*-isomers. The faster ($\tau = 2$ ns) and the slower ($\tau = 40$ ns) components were attributed to emission from the *o*- and *i*-isomers, respectively (Figure S5), because introduction of a bulky substituent into the coordination sphere is known to elongate the lifetime of the excited state of copper(I) complexes by inhibiting structural relaxation and/or preventing additional solvent coordination.[6,7] This assignment was further supported by the similarities between the emission lifetimes of the *o*-isomer and [Cu(bpy)(DPEphos)]$^+$ (bpy =2,2′-bipyridine), which does not contain bulky groups near the metal center (Figure S6). The emission spectra of two isomers were deconvoluted using time-dependent spectral measurements. The faster component was slightly red-shifted relative to the slower component, implying that the long-lived excited state of the *i*-isomer has the higher energy (Figure S7).

The differences between emission behaviors of these isomers were clearly reflected in the heat sensitivity. The emission decay profile showed that the relative intensity of the slower component decreased upon cooling and became almost negligible at 203 K (Figure S8). The lifetimes of the two components were almost temperature-independent, as demonstrated by the best fits of the decay profiles at each temperature (203−293 K). The deconvoluted emission spectra of the slower component were blue-shifted and showed an increase in the emission intensity upon heating (Figure 2c). The emission spectra of the faster component were relatively insensitive to temperature (Figure 2d). We deduce that the thermally enhanced emission of *i*-isomer was derived from thermal activation between close levels in fast equilibrium, which is discussed as ^{1}CT and low-lying ^{3}CT excited states.[6,7]

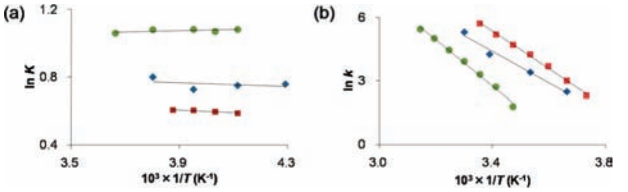

Figure 3. van’t Hoff plots (a) and Arrhenius plots (b) for the *i*- → *o*-inversion process of **1**$^+$ in $CDCl_3$ (green), acetone-d_6 (blue), and CD_3CN (red).

We conclude that the photoprocesses of the two isomers are different in the identity of the excited state. Control over the inversion dynamics is important for the development of a photoelectron transfer system composed of this complex family.

As for the dynamics of inversion, a lower population of the *o*-isomer was found in the polar solvent (Figures 3a, S9, and S10). The molar ratio of the *o*-isomer at 253 K was 74% in $CDCl_3$, 68% in acetone-d_6, and 65% in CD_3CN. This trend was observed across the full temperature range tested, and the equilibrium constant was almost temperature-invariant. Because the *i*- and *o*-isomers were similar with respect to the coordination skeleton, the polarity differences between the complex cations of the two isomers were expected to be small. Therefore, the isomer ratio was influenced by the electrostatic effects of the solvated contact ion pair. In less polar solvents, the *i*-isomer was destabilized by the approach of the counteranion to the copper center due to steric effects of the proximal methyl group. These results suggest that the ratio of the inversion isomers could be tuned by electrostatic interactions.

The kinetics of the inversion motion was evaluated by simulating the temperature-dependent ^{1}H NMR spectra in $CDCl_3$, acetone-d_6, and CD_3CN (Figures 3b, S11, and S12). The rate constant for the *i*- → *o*- inversion, *k*, at 293 K was 20 s^{-1} in $CDCl_3$, 70 s^{-1} in acetone-d_6, and 120 s^{-1} in CD_3CN. The *k* value at room temperature in CD_3CN was 1 order of magnitude larger than that in $CDCl_3$, suggesting that a coordinated solvent molecule promoted ring inversion by assisting dissociation of the pyrimidine N atoms from the copper center. The *k* value varied from 10^{-6} s^{-1} (frozen motion) to 10^3 s^{-1} as the temperature and solvent were varied.

In conclusion, a novel two-state conformational isomer system with an excitation process that was sensitive to the ligand ring inversion on the copper(I) center was synthesized. The inversion dynamics largely depended on the temperature and solvent, suggesting that it may be possible to control the ring inversion motions. This strategy may be useful in the construction of a single molecular system for light-energy processing.

Acknowledgment. This work was supported by Grants-in-Aid from MEXT of Japan (20750044, 20245013, and 21108002, area 2107) and the Global COE Program for Chemistry Innovation.

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

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JA103718E