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Photofunctionalization of Molecular Switch Based on Pyrimidine Ring Rotation in Copper Complexes

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Michihiro Nishikawa

Photofunctionalization of Molecular Switch Based on Pyrimidine Ring Rotation in Copper Complexes

Doctoral Thesis accepted by
The University of Tokyo, Tokyo, Japan

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3. Nishikawa M, Nomoto K, Kume S, Nishihara H (2013) Inorg Chem 52:369.

Supervisor's Foreword

Metal complexes bearing π-conjugated chelating ligands are fascinating not only in basic science focusing on their unique physical and chemical properties but also in application to molecular-based devices. For example, photophysical properties of metal complexes are valuable for fabrication of dye-sensitized solar cells and light-emitting devices, and redox-active metal complexes of their two oxidation states reversibly switchable by electronic stimuli are useful in application to nanotechnology such as molecular electronics. Our group has been constructing a single molecular system made of copper complexes bearing a bidentate ligand with a rotatable pyrimidine moiety. This system exhibits an electrochemical potential shift by the motion of the artificial molecular rotor.

Dr. Nishikawa has introduced photofunctions into the copper-pyrimidine molecular rotors in the course of his study for the Ph.D. Two of his remarkable achievements are development of a new class of luminescence, that is, dual emission caused by rotational isomerization, and construction of a new photoelectronic conversion system caused by the redox potential switching based on photoinduced-electron-transfer-driven rotation.

He started his Ph.D. research by investigating the rotational equilibrium in newly synthesized copper(I) complexes bearing two bidentate ligands, pyridylpyrimidine and bulky diphosphine, using NMR spectroscopy and single crystal X-ray structural analysis. He analyzed ion-pairing sensitivities of rotational bistability of the copper complexes from the viewpoint of both thermodynamics and kinetics, leading to discovery of evidence for the intramolecular process of interconversion and the suitability of a common organic solution state for the desired function. Next, he developed a molecular system that exhibits heat-sensitive dual luminescence behavior caused by the pyrimidine ring rotational isomerization in copper(I) complexes. This peculiar photochemical process was examined in detail by transient emission spectral measurement. Dr. Nishikawa's finding is valuable for designing a promising way to handle the photo-processes of transition metal complexes. Additionally, he created a novel process for conversion of light stimuli into electrochemical potential via reversibly working artificial molecular rotation. This was realized by two strategies, a redox mediator system and a partial oxidation system. In both systems, photoinduced electron transfer from the copper complex to the electron acceptor played a key role for the photo- and heat-driven rotation. In conclusion, his research provides novel electronic and photonic functions of copper-pyrimidine complexes based on repeatable conversion of external stimuli into redox potential signals.

Dr. Nishikawa's Ph.D. thesis comprises descriptions of his three research achievements noted above together with a general introduction and concluding remarks. The thesis demonstrates the excellence of his research concept, molecular design, experimental plan, and discussion of the results. I hope that the publishing of this thesis will stimulate researchers in the field of molecular science.

Tokyo, August 2013 Hiroshi Nishihara

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Contents

Chapter 1
General Introduction

Abstract I described general introduction for importance of metal complexes, well-established unique nature of copper complexes bearing diimines, and the previous research of our group on stimuli-responsive pyrimidine ring rotation in copper complexes. An advantage of our system is that we can extract useful electric responses from a simple multistable molecule. The aim of studies in my Ph.D course on development of new types of emission and photoresponsivity by photofunctionalization of the copper complex system is described.

Keywords: Metal complex · Molecular switch · Copper complex · Redox · Luminescence

1.1 Metal Complexes Bearing π-Conjugated Ligands

Metal complexes bearing π-conjugated ligands, such as chelating polypyridines, play an important role in both application and novel phenomena not only for their varieties of molecular structures and metal-ligand bond strengths but also their electrochemical, photophysical, magnetic, and other unique properties (Fig. 1.1). Ease of tuning for these functions by choosing metal and ligand components is one of the significant advantages for this class of materials. I described herein several examples to show the importance of the metal complexes.

1.1.1 Photophysics of Metal Complexes Bearing π-Conjugated Chelating Ligands

The photoprocesses of metal complexes bearing π-conjugated chelating ligands are of interest for their potential use in dye-sensitized solar cells [1–5], light-emitting devices [6–9], and photocatalysts [10–13] due to a combination of high

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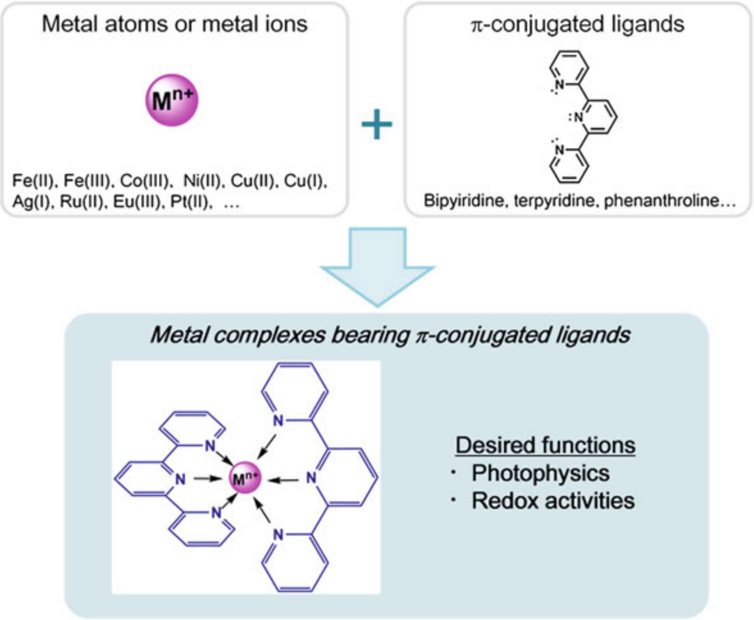
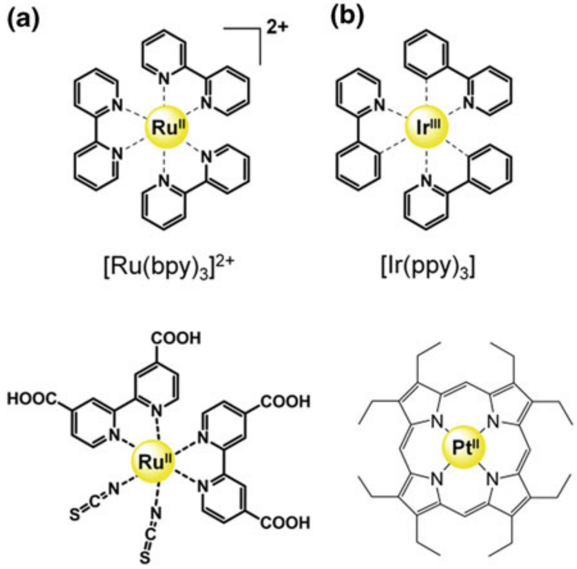


Fig. 1.1 Metal complexes bearing π-conjugated chelating polypyridine ligands

thermal stability, reversible redox activity, intense visible absorption, and the formation of a long-lived charge transfer (CT) excited state. Investigation of luminescence is important not only for luminescence itself but also properties related to photoexcited state.

For example, tris(bipyridine)ruthenium(II) complex ($[Ru(bpy)_3]^{2+}$, bpy = 2,2′-bipyridine) and their derivatives such as **A** have significant advantages for dye-sensitized solar cells (Fig. 1.2). Efficient injection of an electron into the conduction bond of the titanium oxide is achieved, because the lowest electronic excited state of them is of a metal-to-ligand-charge-transfer (MLCT) nature, involving the electronic transitions from a metal *d* orbital to a π^* antibonding orbital centered on the diimine ligand [5]. For another example, hydrogen production using light energy through photocatalytic ability of the complexes has been investigated [11].

The photophysics of metal complexes with other metals and ligands such as platinum(II) and iridium(III) have been well-studied. The emissive excited state of these complexes can be either MLCT or ligand centered (LC) depending on the ligand environment. Whatever the electronic nature, it is invariably triplet states, because of a consequence of the high spin-orbit coupling of the second and third row transition metal atom. Utilization of the triplet state has advantages for light-emitting devices. Unlike fluorescence dyes, an emission of materials doped with platinum(II) porphyrin (**B**) [5] results from both singlet and triplet excited states. It was also reported that nearly a maximum internal efficiency 100 % was achieved



$[Ru(bpy)_3]^{2+}$ $[Ir(ppy)_3]$

Fig. 1.2 Well-employed metal complexes for promising photofunctions

by employing the host organic materials doped with *fac*-tris(2-phenylpyridine)iridium(III) ($Ir(ppy)_3$ in Fig. 1.2) [6].

A single, dominant and lowest-energy-emissive excited state in ruthenium(II) complexes and most other chromophores is observed in a fluid solutions at room-temperature, due to a breakdown of the standard nonradiative decay pathways. One of the recent topics in photo-functional molecules is to build simple metal complexes, which exhibit dual phosphorescence derived from the two independent excited states [14–16].

Tor et al. have reported that a family of heteroleptic ruthenium(II) coordination complexes containing substituted 1,10-phenanthroline (phen) ligands with extended conjugation [15]. They found that ruthenium(II) complexes containing 4-substituted phen ligands exhibit two simultaneously emissive excited states at room-temperature in a fluid solution. The short-lived, short wavelength component is essentially bipyridine-based, while the long-lived, long wavelength component is localized predominantly on the more conjugated phen ligand. They concluded that an asymmetry in the phen facilitates the production of these two nonequilibrated emissive states.

Dual emission of cyclometalated iridium(III) polypyridine complexes was reported by Tang et al. [14]. The complexes showed dual emission in a fluid solution at room temperature. They assigned the higher energy band to a triplet intraligand ^{3}IL excited state, and the low energy feature to an excited state with high ^{3}MLCT/^{3}LLCT character. The latter should also possess substantial amine to a ligand charge transfer ^{3}NLCT. They showed an environmental-sensitivity of the emission, and concluded that the use of these compounds led to a new luminescent probe.