

Modulation of Characteristics of a Ruthenium-Coordinated Flavin Analogue That Shows an Unusual Coordination Mode

KOJIMA Takahiko and FUKUZUMI Shunichi

(Graduate School of Engineering)

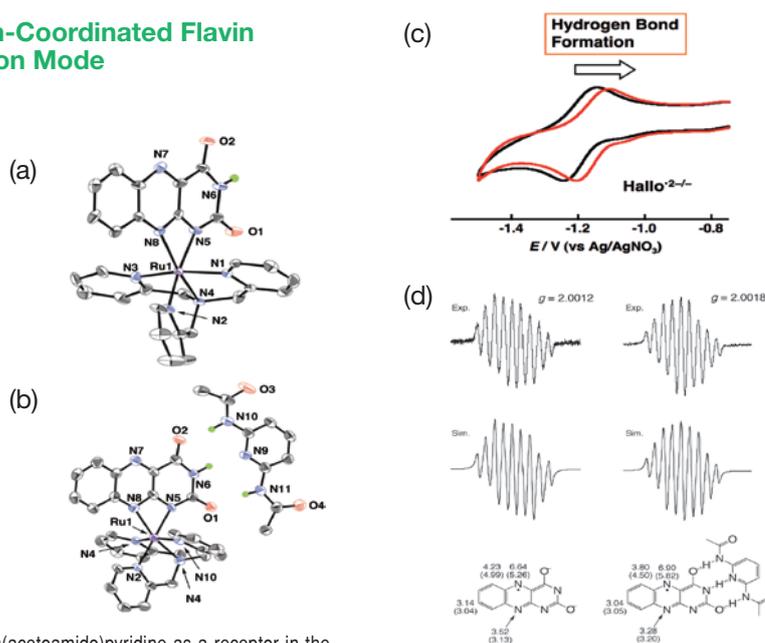
Angewandte Chemie International Edition, 46, 905-908 (2007)

▶ No. 51 in "100 Papers Selection" (p. 63)

Flavins are ubiquitous and redox-active heteroaromatic coenzymes, participating in many biological redox reactions, including oxidation of organic substrates and photoresponsive repair of damaged DNA. Their reactivity has been postulated to be regulated by non-covalent interactions with amino acid residues of apoproteins toward desired directions by controlling their redox properties. However, it is too complicated to evaluate the effects of non-covalent interactions on their redox potentials and electronic structures in proteins. On the other hand, flavins have been known to act as bidentate ligands through the 4-oxygen and 5-nitrogen atoms to form a five-membered chelate ring and those metal complexes have been demonstrated to show reversible redox processes of coordinated flavin ligands.

We synthesized a ruthenium complex of alloxazine (H_2Allo), which is a flavin analogue, with tris(2-pyridylmethyl)amine (TPA) as a tripodal tetradentate ligand. The complex, $[Ru(Hallo)(TPA)]ClO_4$ (**1**), was characterized by spectroscopic and electrochemical methods and X-ray crystallography. Crystallographic analysis of **1** revealed that **1** includes the deprotonated alloxazine ligand as a bidentate ligand in an unprecedented coordination mode to form a four-membered chelate ring through the 1- and 10-nitrogen atoms due to steric hindrance of the TPA ligand (Fig. (a)). A less-hindered environment around the $Hallo^-$ ligand in **1** allowed us to form a three-point hydrogen-bonded adduct of the ligand

with 2, 6-bis(acetoamido)pyridine as a receptor in the second coordination sphere of **1** and the structure of the adduct was also established by X-ray analysis (Fig. (b)). The hydrogen bonding caused a positive shift ($\Delta E_{1/2} = +43$ mV) of one-electron reduction potential of the $Hallo^-$ ligand to generate a stabilized ruthenium-bound alloxazine π -anion radical (Fig. (c)). The hydrogen bonding was revealed to exert considerable influence to control the electronic structure of the flavin analogue to alter the g value and the hyperfine coupling constants of the π -anion radical as observed in electron spin resonance spectra with or without the receptor (Fig. (d)). These



results indicate that such hydrogen bonding can regulate not only the redox potentials of flavins but also their electronic structures. Thus, a diverse reactivity of flavin coenzymes results from those noncovalent interactions in various environments in flavoproteins.

•From *Angewandte Chemie International Edition*, 46, Miyazaki, S. et al., Modulation of Characteristics of a Ruthenium-Coordinated Flavin Analogue That Shows an Unusual Coordination Mode, 905-908, 2007. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

Visualization of Photo-assisted Polarization Switching in Multiferroic BiFeO₃ Thin Films

RANA Dhanvir Singh and TONOUCI Masayoshi

(Institute of Laser Engineering)

Applied Physics Letters, 91, 031909 (2007)

▶ No. 61 in "100 Papers Selection" (p. 64)

In the room temperature multiferroic $BiFeO_3$, the ferroelectric order is oriented along (111) crystallographic axis [Fig. 1(a)]. Upon illumination by band-gap ultrafast laser pulses, the electric-field polarized $BiFeO_3$ thin films emit terahertz radiation as a result of ultrafast depolarization of the ferroelectric order. The sign and the amplitude of THz-emission from $BiFeO_3$ depend on the polarity of ferroelectric domains. The emission is followed by ultrafast non-destructive retrieval of the spontaneous polarization of ferroelectric order, which suggests it to be a non-destructive optical technique for read-out of the electric data stored in its ferroelectric polarized state.

In this paper, we have acquired high resolution THz-emission images of ferroelectric domain, by combining two effects, namely; i) the electric-field dependence of THz-emission amplitude translates to hysteretic loops which resemble the ferroelectric behavior [Fig. 1(b)], and ii) a phenomenon called photo-assisted polarization switching; i.e., the coercive electric field for ferroelectric switching reduces to 70-100 kV/cm when poling by electric-field is performed simultaneous with the illumination by band-gap laser pulses. This coercive field is four-five factors less than that when switching is obtained by electric-field alone. This has enabled us to acquire the high resolution images of the ferroelectric domains and understand their photo-assisted switching dynamics. The images in Fig. 1(c) were acquired by performing a raster-scan for THz-emission at the Au dipole-type opti-

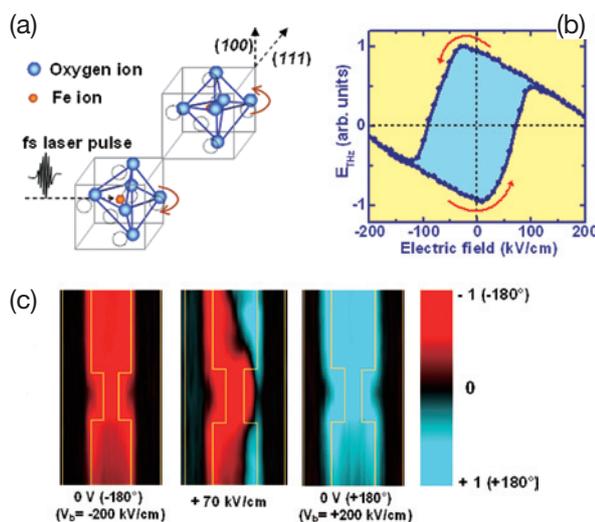


Fig. 1 (a) Ferroelectric distortion in $BiFeO_3$: The displacement of FeO_6 octahedra from their centro-symmetric positions (as indicated by dotted circles) along (111) orientation results in ferroelectric polarization. The skewed arrows indicate the tilting of alternate FeO_6 octahedra in opposite directions. **(b) THz-emission memory effect:** Ferroelectric like THz-emission versus electric-field hysteresis loop. **(c) Imaging of ferroelectric domains:** Left panel shows the THz-emission images of -180° switched ferroelectric domains without applied bias after poling in $V_b = -200$ kV/cm; middle panel: images obtained at the coercive electric-field bias of -70 kV/cm; and right panel: THz-emission images of $+180^\circ$ switched ferroelectric domains without applied bias after poling in $V_b = +200$ kV/cm. The yellow lines in these images indicate the position of Au-dipole antenna.

cal switch fabricated on the film. The switching dynamics can be understood by biasing the optical switch with different electric-field values. For instance, image obtained at the saturation electric-field bias of 200kV/cm and the coercive electric-field bias of ~ 70 kV/cm, respectively, depict the homogeneously aligned ferroelectric-domains and the coexisting domains of opposite polarities. These emission images with a few microns resolution are valuable for visualizing the ferroelectric domains, the critical understanding of the polarization switching

dynamics and exploring the possible consequences of photo-assisted effect on the long-term stability of ferroelectric memory in $BiFeO_3$. This technique could be equally promising for imaging the ferroelectric domains of other multiferroic/ ferroelectric memory materials. Once a smaller laser spot size of less than a micron is achieved, the THz-emission imaging in addition to its non-contact and non-destructive advantage will have as good resolution as any existing imaging technique.