

VIII-E Development of Metal-Conjugated Multi-Electron Redox Systems in Metal-Dioxolene Complexes

Dioxolenes act as a versatile electron-acceptor or -donor through the reversible two-electron redox reactions among the three oxidation states of catechol (Cat), semiquinone (SQ), and quinone (Q). The dioxolene ligands offer a wide range of the metal complexes with a unique metal-conjugated intramolecular electron transfer, which is a fascinating nature to design electrocatalysts and electronic molecular devices. The ruthenium-terpyridine-dioxolene complexes exhibit the reversible two-electron redox behavior and each oxidation state has been recognized as a resonance hybrid on account of the accessible redox potentials between the metal center and the dioxolene ligand. Ferrocene-attached dioxolenes through π -conjugation provide a three-electron redox system, in which a new redox state of the ferrocenyl moiety is combined with the general two-electron redox reaction of the dioxolene moiety. The new oxidation state would be noninnocent, because the redox potentials of both moieties are close. Here we report the syntheses of a new ferrocene-attached dioxolene ligand and its ruthenium-terpyridine complex, and the metal-conjugated three reversible redox behavior.

VIII-E- 1 Syntheses of Ferrocenylcatechol and Its Ruthenium-Terpyridine Complex and the Metal-Conjugated Redox Behavior

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A ferrocene-attached dioxolene, 4-ferrocenylcatechol (Fc-CatH₂), and its ruthenium-acetato-terpyridine complex, [Ru^{II}(OAc)(SQ-Fc)(ph-terpy)] (**1**), were synthesized (Figure 1), where ph-terpy and SQ-Fc are 4'-phenyl-2,2':6',2''-terpyridine and 4-ferrocenyl-1,2-benzosemiquinone, respectively. The cyclic voltammogram of **1** shows three reversible redox waves at $E_{1/2} = -0.95, -0.15,$ and 0.40 V vs. Ag/Ag⁺, and the three redox couples correspond to (**1**⁻/**1**), (**1**/**1**⁺), and (**1**⁺/**1**²⁺), respectively, based on the rest potential (-0.22 V) of **1**. The UV-Vis-NIR absorption spectra of **1**⁻, **1**, **1**⁺, and **1**²⁺ were investigated by controlled potential electrolyses at $-1.30, -0.33, 0,$ and 0.50 V, respectively. The specific absorption of **1** in near-IR region was derived from superposition of two bands at 862 and 1015 nm. The higher energy band is similar to that of [Ru^{II}(OAc)(SQ)(terpy)] (**2**) (SQ = 1,2-benzosemiquinone and terpy = 2,2':6',2''-terpyridine) at 878 nm, which is assigned to a metal-to-ligand charge transfer (MLCT) band (Ru(II) to SQ). This fact suggests that **1** has a similar structure, [Ru^{II}(OAc)(SQ-Fc)(ph-terpy)], to **2**. The additional near-IR band is ascribable to another MLCT band (Fe(II) of the ferrocenyl group to SQ). In the absorption spectrum of **1**⁺, an intense band at 674 nm appeared and the maximal wavelength is shifted to a lower energy region than that of the MLCT band (Ru(III) to SQ) in [Ru^{III}(OAc)(SQ)(terpy)]⁺ (**2**⁺) at 556 nm. On the other hand, the absorption maximum at 1280 nm of a MLCT band in **1**⁺ is also shifted to a lower energy region compared with that (Fe(II) to SQ) of **1**. The significant lower energy shift of the MLCT bands is understandable by consideration of the metal-conjugated resonance between Ru(III)-SQ-Fc \rightleftharpoons Ru(II)-Q-Fc \rightleftharpoons Ru(II)-SQ-Fc⁺ (Q = 1,2-benzoquinone and Fc⁺ = Fe(III) form). The contribution of Ru(II)-SQ-Fc⁺ and Ru(II)-Q-Fc structures in **1**⁺ is responsible for the lower energy shift of the former and the latter MLCT bands, respectively.

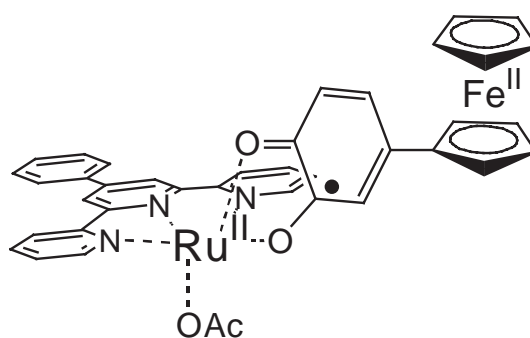


Figure 1. The structure of **1**.