

Synthesis and Redox Behavior of Dinuclear Ruthenium Complex Bridged by Bis(terpyridyl)xanthene

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【Introduction】 Dinuclear complex can provide unique reactivity since dinuclear complex have multi-reaction sites and multi-redox sites in one molecule. We have prepared mononuclear (Ru-dioxolene) complex $[\text{Ru}(\text{OH})(3,6\text{-}t\text{Bu}_2\text{qui})(\text{trpy})](\text{SbF}_6)$ ($\text{trpy} = 2,2':6'2''$ - terpyridine) and the dinuclear complex bridged by bis(terpyridyl)anthracene $[\text{Ru}_2(\text{OH})_2(3,6\text{-}t\text{Bu}_2\text{qui})_2(\text{btpyan})](\text{SbF}_6)_2$. Only the dinuclear complex enables catalytic electrochemical four-electron oxidation of water.¹⁾ In this study, we prepared dinuclear ruthenium complex bridged by 4,5-bis(terpyridyl)-2,7-di-*tert*-butyl-9,9'-dimethylxanthene (btpyxa) $[\text{Ru}_2(\text{bpy})_2(\text{btpyxa})\text{Cl}_2](\text{PF}_6)_2$ **[1]**(PF_6)₂ ($\text{bpy} = 2,2'$ -bipyridine) (Figure 1). And redox property of **1** was compared with that of $[\text{Ru}(\text{bpy})(\text{trpy})\text{Cl}](\text{Cl})$ **[2]**(Cl).

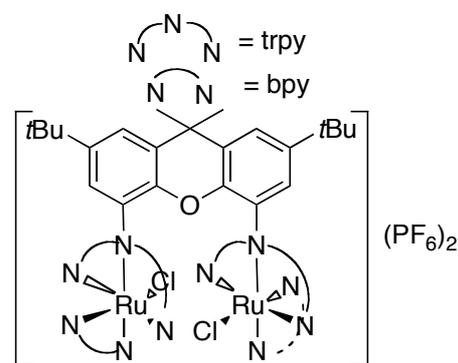


Figure 1.

$[\text{Ru}_2(\text{bpy})_2(\text{btpyxa})\text{Cl}_2](\text{PF}_6)_2$ **[1]**(PF_6)₂.

【Result and Discussion】Synthesis. $[\text{Ru}_2(\text{btpyxa})\text{Cl}_6]$, prepared as described^[2], was treated with bipyridine in ethanol/water in the present of triethylamine at 80 °C for 3 hours, and then addition of NH_4PF_6 gave **[1]**(PF_6)₂. **[1]**²⁺ was characterized by ESI-MS ($m/z = 685$ **[1]**²⁺) and ¹H NMR spectrum.

Redox Behavior. The cyclic voltammogram (CV) of **[1]**(PF_6)₂ in acetonitrile exhibits four reversible-like redox waves at $E_{1/2} = -1.68, -1.77, -2.00,$ and -2.09 V versus Ag/Ag^+ (Figure 2). According to CV of **[2]**⁺, redox waves at $E_{1/2} = -1.68$ and -1.77 and $E_{1/2} = -2.00$ and -2.09 V were assigned to $\text{bpy}/\text{bpy}^{\bullet-}$ and $\text{trpy}/\text{trpy}^{\bullet-}$, respectively. Each redox waves of $\text{bpy}/\text{bpy}^{\bullet-}$ and $\text{trpy}/\text{trpy}^{\bullet-}$ was observed for two steps redox waves, which was attribute to electrochemical interaction of the dinuclear **[1]**²⁺ between two $\{\text{Ru}(\text{bpy})(\text{trpy})\text{Cl}\}$ frameworks. CV of **[1]**(PF_6)₂ under CO_2 atmosphere reveals irreversible reduction wave at around -1.6 V, which means a reductive product of **[1]**²⁺ interacts with CO_2 .

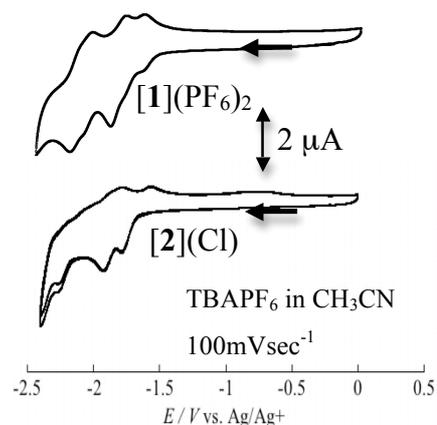


Figure 2. CV of **[1]**(PF_6)₂ and **[2]**(Cl).

1) T. Wada, K. Tsuge, K. Tanaka, *Angew. Chem. Int. Ed.* **2000**, 39, 1479.

2) T. Wada, K. Tanaka, *Eur. J. Inorg. Chem.* **2005**, 3832.