Molecular design, confinement, and potential control of redox-active transition-metal complexes with π-conjugation

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Transition-metal complexes and clusters are eminent building blocks for constructing molecule-based assembly with a variety of structures and chemical characteristics. In redox-active transition-metal complexes,[1)] ligand-substitution lability may be significantly changed by controlling oxidation state of the central metal, allowing precise control of assembly and integration of metal complexes through coordination bonds. Here, we show our molecular design of redox-active transition-metal complexes with significant π-conjugation and their assembly on electrode surfaces (Figure 1). By use of trinuclear $\{Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6\}$ complexes, we have successfully observed electrochemically-[2)] and light-triggered[3)] CO dissociation, reversible trap/release behavior of CO and NO,[4,5)] and sequential layering of the cluster components.[2)] With dinuclear $\{Ru_2(\mu\text{-}O)(\mu\text{-}CH_3COO)_2\}$ complexes, proton-coupled electron transfer reactions have been observed in an aqueous media,[6)] and this behavior can be utilized for controlling potential gradient of hetero-molecules in a reversible manner. We also discuss a "dimerized" trinuclear complex in a mixed valent state, which was examined by cyclic voltammetry and in situ scanning tunneling microscopy techniques.

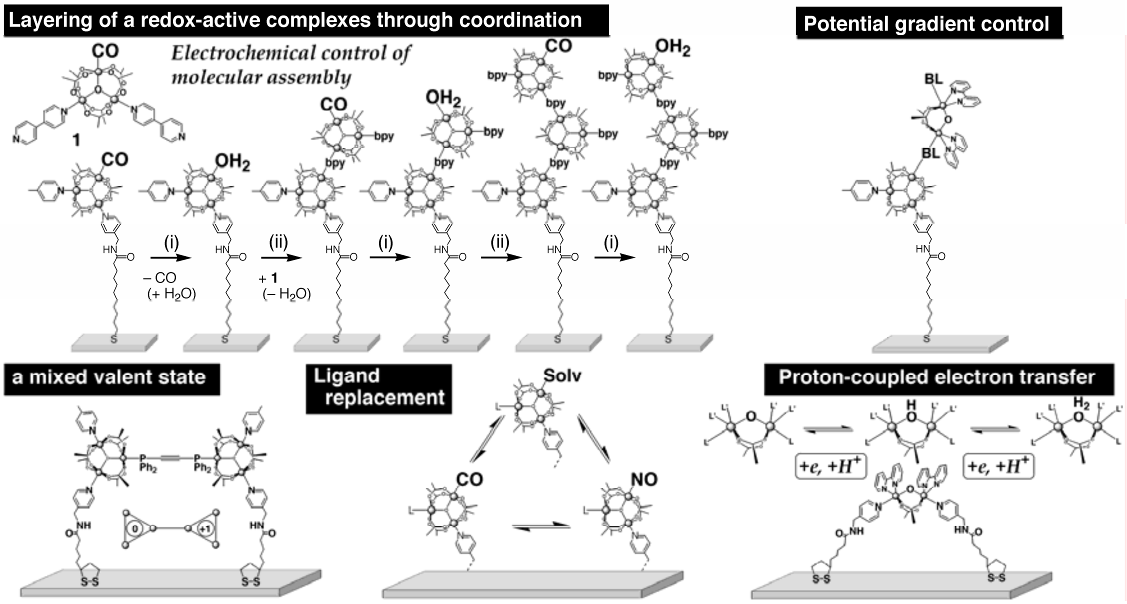

Figure 1: Surface assembly and chemical functions of redox-active Ru complexes

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