

Redox and Magnetic Properties of Cyclobutadienecobalt Complexes Having Two Ferrocenes and Two Anthraquinones

Toshiyuki NAKAYA, Masashi KURASHINA, Kosuke NAMIKI, Takako FUJITA, Masaki MURATA, Hiroshi NISHIHARA

Department of Chemistry, School of Science, The University of Tokyo
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

π -Conjugated redox-active complexes are expected to show unique physical and chemical properties due to strong electronic communication through π -conjugated chain. We have reported the electron transfer mechanism of one-dimensional π -conjugated D-A molecules in which D is an electron donor, ferrocene and A is an electron acceptor, anthraquinone. Intramolecular electron transfer of these complexes can be controlled by protonation because the acceptor ability of quinone increases by protonation. We have also reported that these protonated molecules in the solid state show valence tautomeric behavior at 50-300 K.

In this study, we are interested in two-dimensional π -conjugated molecules with D and A moieties, and employs cyclobutadienecobalt complexes with two ferrocenes and two anthraquinones. Two geometrical isomers were synthesized and formation of mixed-valence states caused by ferrocene-ferrocene (D-D) electronic interaction and anthraquinone-anthraquinone (A-A) electronic interaction, and electron transfer from ferrocene to anthraquinone by protonation (D-A electronic interaction) were investigated.

Synthesis of **1** and **2** (Figure 1a) was carried out by stirring a mixture of $\text{CpCo}(\text{PPh}_3)_2$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) and 1-ferrocenylethynylantraquinone ($\text{C}_{26}\text{H}_{16}\text{O}_2\text{Fe}$) in toluene for 36 h at 80 °C. Figure 1b shows X-ray structures of **1** and **2**.

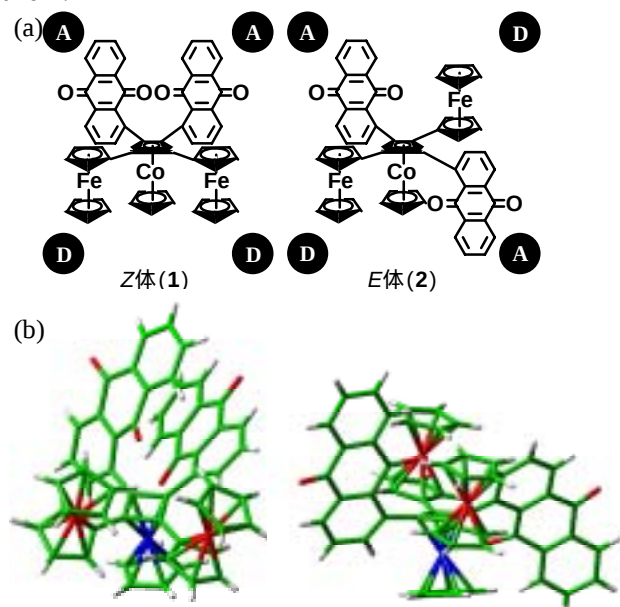


Fig. 1 The geometrical isomers (**1** and **2**) (a) and their X-ray structures (b)

Figure 2 shows cyclic voltammograms of **1** and **2**. Two reversible oxidation waves of ferrocene moieties, indicating a formation of $\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}$ mixed-valence state, and two reversible reduction waves of anthraquinone moieties, indicating a formation of AQ^0AQ^- mixed-valence state were observed.

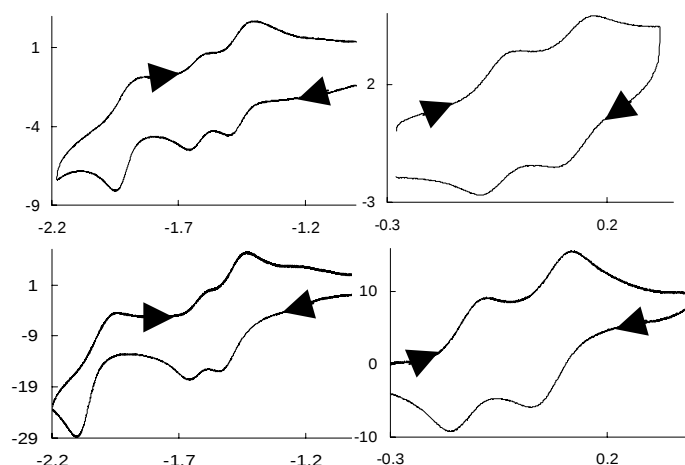


Fig. 2 Cyclic voltammograms of **1** and **2**.

Figure 3 shows results of molecular orbital calculation of **1**. The HOMO and next HOMO (HOMO-1) orbitals are delocalized around one ferrocene moiety and the cyclobutadienecobalt unit. The LUMO and next LUMO (LUMO+1) orbitals are localized at one anthraquinone moiety.

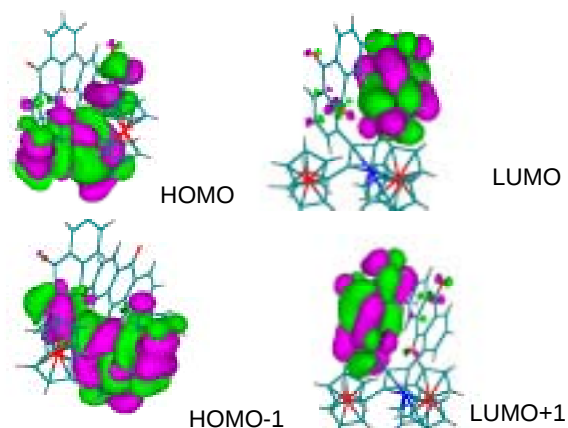


Fig. 3 Molecular orbitals of **1**

These results indicate that the ferrocene-ferrocene electronic interaction is caused through cyclobutadiene ring (π -orbital) and cobalt (d -orbital), whereas the anthraquinone-anthraquinone electronic interaction occurs through space.

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References

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