

ルテニウム二核錯体における架橋配位子に導入された多環芳香族炭化水素によるフロンティア軌道の変化に関する理論研究

(阪大基礎工¹・阪大院基礎工²・島根大理工³・台北科技大⁴・阪大 CSRN⁵・阪大 QIQB⁶・阪大 RCSEC⁷・阪大 ICS⁸) ○佐々木啓介¹・甘水君佳²・片岡祐介³・陳秀慧⁴・許益瑞⁴・岸亮平^{2,6,7}・北河康隆^{2,5,6,7}・中野雅由^{2,6,7,8}

Theoretical study on change in frontier orbitals by polycyclic aromatic hydrocarbons introduced to bridging ligands in dinuclear ruthenium complexes (¹Faculty of Engineering Science, Osaka University, ²Graduate School of Engineering Science, Osaka University, ³Graduate School of Natural Science and Technology, Shimane University, ⁴Department of Molecular Science and Engineering, National Taipei University of Technology, ⁵Center for Spintronics Research Network, Osaka University, ⁶Center for Quantum Information and Quantum Biology, Osaka University, ⁷Research Center for Solar Energy Chemistry, Graduate School of Engineering Science, Osaka University, ⁸Innovative Catalysis Science Division, OTRI, Osaka University) ○Keisuke Sasaki,¹ Naoka Amamizu,² Yusuke Kataoka,³ Hsiu-Hui Chen,⁴ I-Jui Hsu,⁴ Ryohei Kishi,^{2,6,7} Yasutaka Kitagawa^{2,5,6,7} and Masayoshi Nakano^{2,6,7,8}

[Ru₂(O₂CR)₄] complex (Fig. 1) that two Ru(II) ions are bridged by four acetate ligands to form a paddle-wheel structure is a well-known molecular unit with its rich redox and magnetic properties. For the above reason, it attracts much attention as the functional material for catalysts and magnetic compounds and so on. It has been suggested that the π -conjugated systems introduced to the ligands are related to the electronic state of the diruthenium unit,¹⁾ however a relationship between its functionality, electronic structures and substituents (R) has not been studied systematically. In this study, therefore we examine a change in the molecular structure and frontier orbital energy in detail when various polycyclic aromatic hydrocarbons are introduced into the acetate ligands.

Keywords : dinuclear ruthenium complex; paddle-wheel structure; polycyclic aromatic hydrocarbon; frontier orbital; density functional theory (DFT)

2つの Ru(II)イオンに4つのアセタト配位子がパドルホイール型に架橋した [Ru₂(O₂CR)₄]錯体(Fig.1)は、豊かな酸化還元特性や磁気的性質を持った分子単位であり、触媒や磁性化合物など機能性材料として注目されている。これまでに架橋配位子に導入された π 共役化合物が、ルテニウム2核部位の電子状態と関係していることが示唆されているが¹⁾、錯体の構造、電子状態そして導入置換基(R)の関係についての系統的な研究はなされていない。そこで本研究ではアセタト配位子の置換基(R)として π 共役系に着目し、種々の多環芳香族炭化水素を導入した際の分子構造やフロンティア軌道エネルギー変化などを詳しく調べた。計算結果の詳細は当日報告する。

1) S. Furukawa, S. Kitagawa, *Inorg. Chem.* **2004**, *43*, 6464-6472.

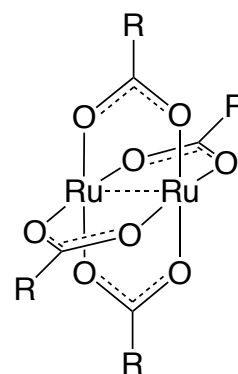


Fig.1 Structural formula of [Ru₂(O₂CR)₄]