Paddle-wheel 型ロジウム(II)二核錯体をコーナー素子とする超分子四角形の自己集合過程

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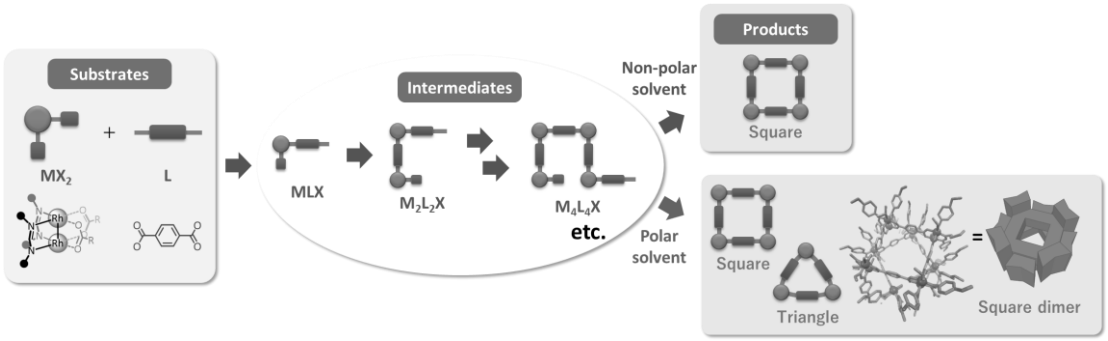
Self-assembly process of a supramolecular square built in paddle-wheel-type dinuclear rhodium(II) complex as a corner unit ([1]*Nihon University School of Medicine*, [2]*Graduate School of Arts and Sciences, The University of Tokyo*) ○Atsushi Okazawa,[1] Satoshi Takahashi,[2] Shuichi Hiraoka[2]

Paddle-wheel-type coordination geometry is a dinuclear coordination motif found in various transition-metal ions, and useful as building blocks for forming metal−organic frameworks and molecular self-assembly systems. Among such dinuclear compounds, Rh_2(II, II) complexes have been attracted as catalysts, photosensitizers, and dyes for solar cells. Cotton *et al*. have reported the self-assembly of supramolecules built in paddle-wheel-type *cis*-protected dinuclear rhodium(II) complexes as a corner unit.[1)] However, their self-assembly processes have been unclear. In this work, we revealed the self-assembly process of a supramolecular square by quantitative analysis based on ^{1}H NMR measurement (QASAP) and numerical analysis based on reaction models (NASAP). Solvent effect on the formation process was also investigated and it was found that the supramolecular square dimerizes in polar solvent.

Keywords : Molecular Self-Assembly; Rh(II) Complex; Reaction Mechanism; Quantitative NMR

Paddle-wheel 型構造は多くの遷移金属イオンに見られる二核配位様式で、金属有機構造体(MOF)や自己組織化分子システムのビルディングブロックとして利用される。特に、Rh_2(II, II)錯体は触媒、光増感剤、太陽電池用色素として着目されている。シス位を保護した paddle-wheel 型ロジウム(II)二核錯体をコーナー素子とした超分子構造は Cotton らによって精力的に研究されてきたが、その自己集合過程の詳細は明らかになっていない[1)]。そこで我々は、[Rh_2]コーナー素子と架橋配位子からなる自己集合四角形分子の形成過程を ^{1}H NMR 測定による定量解析(QASAP)[2)]および反応モデルを用いた数値解析(NASAP)[2)]により明らかにした。形成過程に及ぼす溶媒効果も調べ、極性溶媒中で超分子四角形が二量化することも見出した。



1) F. A. Cotton, C. Lin, C. A. Murillo, *Acc. Chem. Res.* **2001**, *34*, 759.
2) S. Hiraoka, S. Takahashi, H. Sato, *Chem. Rec.* **2020**, *21*, 443.