# 1, 10–フェナントロリン誘導体のプロトン化により誘起された八面体構造と発光特性

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1,10-Phenanthroline-Based Octahedra Induced by Protonation of a Nitrogen Atom: Structures and Emission Properties

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Although a few metal-free octahedral compounds based on nitrogen-containing ligands are known, the realization of mixed ligand compounds remains difficult. To obtain an improved understanding of this class of compounds, two new octahedral compounds, [(tmphenH)(phen)]$PF_6$, and [(tmphenH)(tmphen)]$PF_6$ (where tmphen = 3,4,7,8-tetramethyl-1,10-phenanthroline and phen = 1,10-phenanthroline), were synthesized. The relationship between the emission properties, as evaluated using experimental measurements and theoretical calculations, and structures of the protonated compounds was studied. In addition, differences between the atomic charge distributions and geometries in the ground and singlet excited states were investigated using density functional theory calculations. Both complexes formed hydrogen-bonded octahedrons in acetonitrile solution, even in the excited state. Furthermore, in [(tmphenH)(tmphen)]$PF_6$, the addition of a methyl substituent suppressed thermal vibrations, resulting in a higher emission intensity.

*Keywords : Octahedral Compound; Phenanthroline; Planarity; Hydrogen Bond; Emission*

含窒素配位子に基づくメタルフリーな八面体化合物はいくつか知られているが、混合配位子化合物の実現は依然として困難である。このクラスの化合物の理解を深めるために、2 つの新しい八面体化合物、[(tmphenH)(phen)]$PF_6$ と[(tmphenH)(tmphen)]$PF_6$（tmphen = 3,4,7,8-テトラメチル-1,10-フェナントロリン、phen = 1,10-フェナントロリン）を合成した[1)]。本研究では、実験的測定と理論計算により、発光特性とプロトン化化合物の構造との関係を調べた。さらに、基底状態と一重項励起状態における原子電荷分布と形状の違いを密度汎関数理論(DFT)計算により調べた。

[(tmphenH)(phen)]$PF_6$ と[(tmphenH)(tmphen)]$PF_6$ はともにアセトニトリル溶液中では励起状態でも水素結合した八面体を形成していた。さらに、[(tmphenH)(tmphen)]$PF_6$ においては、メチル置換基を追加することによって、熱振動が抑制され発光強度が高くなることが明らかになった。

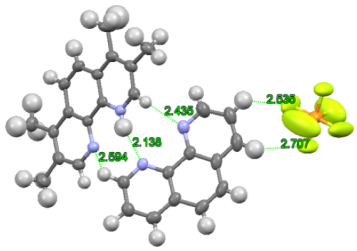


Figure. Crystal structure of [(tmphenH)(phen)]$PF_6$.

1) N. Yoshikawa, S. Yamazaki, A. Nakaoku, Y. Manabe, N. Tohnai, E. Nakata, H. Takashima, *ChemistrySelect*, **2023**, *8*, e202303561.