

Dynamics and Aromatic Switching of Dimeric N-Confused Porphyrin Complexes

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論 文 名 : Dynamics and Aromatic Switching of Dimeric N-Confused Porphyrin Complexes (N-混乱ポルフィリン二量体金属錯体の動的ダイナミクスと芳香族性のスイッチングに関する研究)

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論 文 内 容 の 要 旨

Porphyrin is an 18π -electron conjugated and D_{2h} symmetric planer macrocyclic compound composed of four pyrrole rings interconnected at their α -position via methine bridges. In the N-confused porphyrin (NCP) skeleton, one of the four pyrrole units is connected to the *meso* carbons via an α and β' -linkage. Despite NCPs having stimulus-responsive sites in the porphyrin core, only a few papers on external stimulus responsiveness have been published. In the hope that NCPs with external stimulus-response moieties in their backbone can switch the function of the dimer and elicit new functions, the μ -oxo NCP dimers and fused ring NCP dimers were synthesized, and their switching behaviors and electronic structures were elucidated.

In Chapter 2, novel ruthenium(IV) NCP μ -oxo-bridged dimers (**Ru₂-2** and **Ru₂-3**) were reported as a porphyrin-based molecular rotor. The Ru- μ -oxo dimers showed distinct ring rotation in solution when probed the α -CH proton signals by NMR spectroscopy. To give further insight into the rotational barriers of the complexes, a line-shape analysis of the VT ^1H NMR spectra was conducted to estimate the rate constant for interconversion (k) in the specific temperature range. Moreover, symmetry-dependent rotation restriction was achieved by protonation at the peripheral imino-nitrogen moieties in **Ru₂-2** and **Ru₂-3** with trifluoroacetic acid. Strikingly, in the case of **Ru₂-2**, the ^1H NMR spectrum of the resulting dication species (i.e., **Ru₂-2H₂²⁺**) was well-resolved, demonstrating the interlocked single isomer at 298 K. The unsymmetrical spectral feature of **Ru₂-3** at 243 K indicates its lower basicity. The imino-nitrogen site is relatively crowded due to the *meso*-phenyl rings, and the double protonation is prevented.

In Chapter 3, novel dinuclear cobalt(III) NCP dimer complex (**Co₂-5**) was synthesized, and their redox properties were characterized by various spectroscopic means. For **Co₂-5**, two sets of oxidation and reduction waves were observed in the cyclic voltammetry. Such a split potential is also seen for typical porphyrin oligomer, indicating the delocalization of the SOMO of the one-electron oxidized and reduced species. These assignments were also supported by theoretical calculations. With these results in hand, application studies such as the development of near-infrared sensors and materials for nonlinear optics can be further investigated.

In Chapter 4, reflecting the NH tautomerism of NCP (2H vs. 3H forms in the core), the corresponding bis-metal complexes of the fused porphyrin dimer, **Ag₂-13** and **Ni₂-13**, have different electronic structures. The distinctive ring current effects were observed in the ^1H NMR spectra. The electronic structures of the

complexes can be changed by chemical reduction and oxidation. These properties will be applicable to molecular switches, which are important functions in molecular electronics. The NCP tape complexes can take various π -conjugated systems such as local/global aromaticity/antiaromaticity, and the systems can be interconverted by redox reactions.

In this thesis, the author investigated a novel aspect of NCP chemistry based on dimer structures. In particular, the unique rotation behaviors, external responsibilities, aromaticity/antiaromaticity, and peculiar optical and redox properties were elucidated in detail. The supramolecular study of NCP dimers in this thesis also showed the potential of NCP oligomers as molecular rotor material. This thesis also gives information about the interchromophore interactions of NCP dimers, which enables efficient electron transfer through the π -system in molecular wires. Antiaromatic compounds are recently gaining much attention in terms of their potential applications in organic electronics such as organic thin-film transistors and batteries as well as scientific interests. As discussed in Chapter 4, nickel triply linked NCP dimer **Ni₂-13**, which showed an extremely narrow HOMO-LUMO gap, will be an attractive material for NLO and organic bipolar semiconductors.