

Synthesis and Properties of Multiply N-Confused Porphyrins

Evolution toward Totally N-Confused Porphyrins

Figure of object is one of the essential factors to determine the functionality. In the realm of chemistry, it is true that is fundamental the shape of the molecules for their properties such as optical, coordination, host-guest behavior, etc. Porphyrin is a widely studied functional pigment that can coordinate a variety of metals with four pyrrolic nitrogens in a square-planar arrangement in the core. In the biotic system, porphyrin plays an essential role as a reaction center like chlorophyll, photosynthetic reaction center in the plants, and hemoglobin, oxygen carrier in a red hemocyte of vertebrates. It also acts a useful biomimetic molecule in the artificial system.

From the structural resemblance to normal porphyrins, N-confused porphyrin (NCP), wherein one of the pyrrole rings has linkages with *meso* carbons at α and β' positions, can form complexes with a variety of metals in unique inner- and outer-coordination modes. The new properties of NCP as a novel functional dye and metal coordination ligand are going to be still more revealed and explored. Quite new features, however, would emerge for the NCP analogs including two or more *confused* pyrroles, that is, multiply N-confused porphyrins (N_x CP). The "evolution" of the confused porphyrin family is shown in Figure 1. At the time the author's research on such multiply N_x CP started, it could not be said whether such analogs were reality or not, and how the properties of these analogs were. The stability of N_x CP, estimated by DFT calculations, decreased at ca. 18 kcal/mol by increasing the number of *confused* pyrrole rings. The author, however, believes that the *evolution* as seen in the section title will be ongoing by the efforts to design and prepare the target molecules.

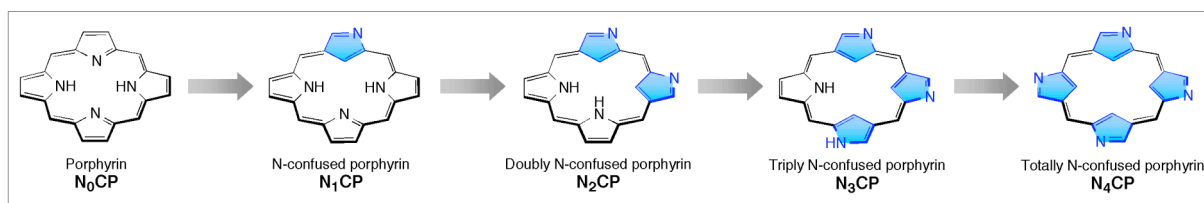


Figure 1 Evolution of N-confused porphyrin family.

Redox Control of N-Confused Porphyrins Metal Complexes Modulated by Anion at the Outer NH

N-Confused porphyrin bearing C_6F_5 groups at *meso* positions (NCP- F_5), which was obtained by stepwise reactions, can form paramagnetic Cu^{II} complex as well as diamagnetic Ag^{III} , Ni^{II} , and Pd^{II} complexes, whose square-planar structures were elucidated by X-ray single crystal analyses. NCP behaves as *chameleon-like* ligand, which act dianionic and trianionic ones to form neutral square-planar complex by attachment and detachment of the proton at the peripheral nitrogen. Actually, diamagnetic Cu^{III} complex of NCP- F_5 was obtained by oxidation and elucidated by X-ray diffraction analysis. The facile interconversion between Cu^{II} and Cu^{III} complexes was also achieved by the chemical oxidation/reduction (Figure 2).

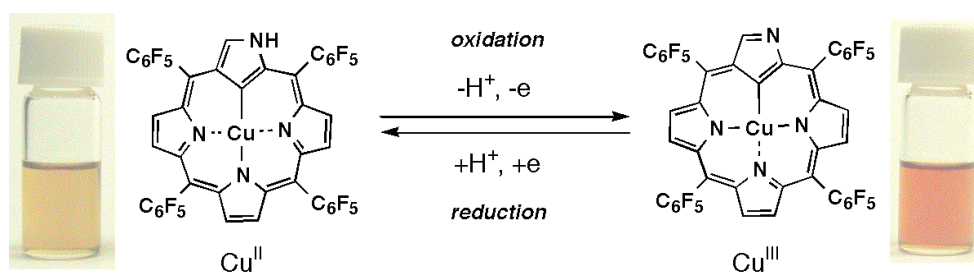


Figure 2 Conversion and color changes between Cu^{II} and Cu^{III} complexes of NCP- F_5 .

Metal complexes of **NCP-F₅** exhibit the property of anion binding through the hydrogen bonding interaction at the peripheral NH of the confused pyrrole ring. **NCP-F₅** unfunctionalized at the outer nitrogen shows no affinity. The binding constants of the **M^{II}** complexes of **NCP-F₅** for halide anions in CH₂Cl₂ increase in the order of $F^- > Cl^- > Br^- > I^-$. The zwitterionic resonance form of the **M^{II}** complexes of **NCP** and interactions between X^- and C₆F₅ group are found essential for the efficient binding as judged by the small binding constants of metal complexes of phenyl-substituted **NCP** (**NCP-H₅**) for Cl^- ($< 10 M^{-1}$). The Cu^{III}/Cu^{II} red-ox potential of **NCP** was controlled by the addition of anions bound, whose association constants enhance the facility of the oxidation (Figure 3). The stimulus at the peripheral nitrogen is transferred to the center metal through the confused pyrrole.

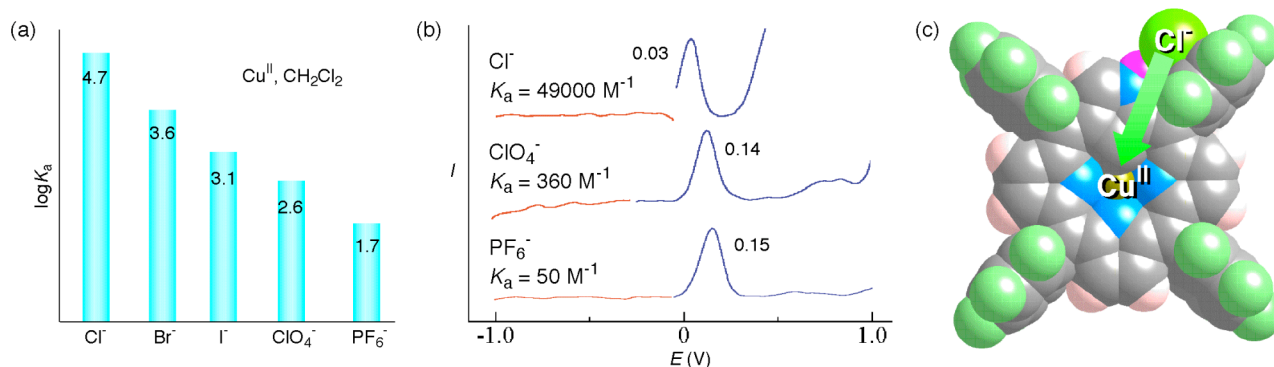


Figure 3 (a) Anion binding constants of Cu^{II} complex of **NCP-F₅** in CH₂Cl₂, (b) shifts of the red-ox potential (vs. Fe^{+/0}/Fc) coupled with Cu^{III}/Cu^{II} in the differential pulse voltammetry (DPV) of Cu^{II} complex of **NCP-F₅** (1 mM) in CH₂Cl₂ upon addition of Cl⁻, ClO₄⁻, and PF₆⁻ as tetrabutylammonium salts (0.1 M) (DPV with Br⁻ and I⁻ could not be determined due to the oxidation potentials of these halide anions), and (c) a possible anion binding mode of Cu^{II} complex.

***Cis*- and *Trans*-Doubly N-Confused Porphyrins (N₂CP): Efficient Anion Binding Receptors and Building Units for the Supramolecular 1-D Networks**

Cis-type of doubly N-confused porphyrins (***cis*-N₂CP**) was synthesized by step-wise after repeated trials. ¹H NMR and single crystal X-ray diffraction analyses have revealed the 3H's (2CH's and 1NH) arrangement in the core of ***cis*-N₂CP** both in solution and in the solid state, respectively. On the other hand, *trans*-isomer (***trans*-N₂CP**) was obtained via *fused* porphyrin derivative. Aromatic feature of ***trans*-N₂CP**, bearing four inner protons (2CH's and 2NH's), due to 18 π electronic system is contrasted to the weak aromaticity of *cis*-derivative. Both ***cis*-** and ***trans*-N₂CP**, trianionic and tetraanionic ligands as free bases, respectively, stabilize the higher oxidation states, Cu^{III} and Ag^{III}, in square-planar fashion. Moreover, an inner C-tolyl substituted Pd^{II} complex of ***cis*-N₂CP** was obtained using Pd(OAc)₂ in refluxing toluene.

Solid-state structure of Cu^{III} complex of ***trans*-N₂CP** shows 1-D rod-like hydrogen bonding supramolecular network comparable with zigzag one seen in *cis*-derivatives (Figure 4). Furthermore, hydrogen bonding donating NH at the periphery of both **N₂CP** exhibits the different affinities for anions; higher (*trans*) and lower (*cis*) than **NCP-F₅**. The different geometries, *cis* and *trans*, drastically affect the properties in solution as well as the self-assembled structures in the solid state.

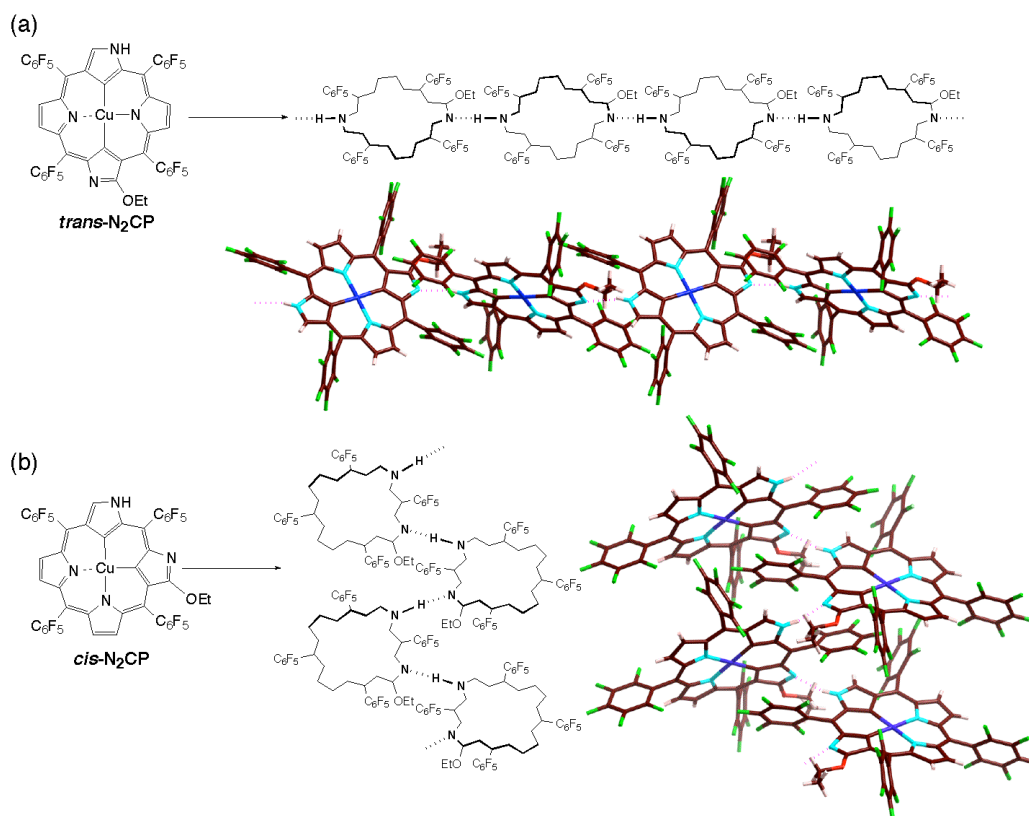


Figure 4 Hydrogen bonding 1-D chain in the solid state of Cu^{III} complexes of (a) *trans-N₂CP* and (b) *cis-N₂CP*. Solvent molecules are omitted for clarity in (a).

Creation of New Concepts from Confused Porphyrin Analogs

Transformation of NCP and N-confused corrole isomer to new compounds have been investigated (Figure 5). Cu^{II} complex of the first aryl-substituted *tripyrinone* derivative was obtained in the reaction of NCP-H₅ and Cu(OAc)₂ in refluxing toluene, and subsequent treatment with acid afforded a free tripyrrolic ligand that could bind a variety of transition metals. On the other hand, *oxyindolophyrin*, efficient fluorescent F⁻ sensor, is obtained from *corrordin*, a byproduct of the synthesis for *cis-N₂CP*, by the treatment with SnCl₂. At least it can be said safely the reactivity of the α -position of confused pyrroles played an important role for such transformations. Incorporation of *confusion* into oligopyrrolic macrocycles, therefore, can be interpreted, in some sense, to activate macrocycles for further mutation.

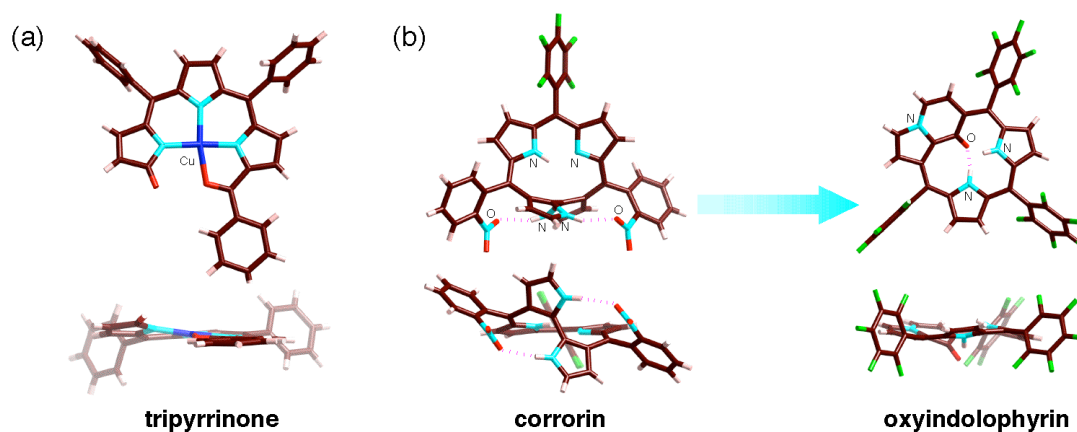


Figure 5 X-ray structures (top and side views) of (a) tripyrinone and (b) the transformation of corrordin to oxyindolophyrin.

Anion Binding Chemistry using Oligopyrrolyl-Macrocycles

Investigation on other pyrrole-derivatives is also applicable to the porphyrin chemistry including NCP family. Major parts of the studies on acyclic and cyclic oligopyrrolyl anion receptors including quinoxaline moiety were performed when the author worked at the group of Prof. Jonathan L. Sessler, University of Texas at Austin, during the period from October to December 2001. Quinoxaline-bridged porphyrinoids (**QBP**), the first macrocycles containing dipyrrolylquinoxaline **DPQ** subunits, whose structures were confirmed by X-ray analyses, were synthesized from the condensation of the diformyl-substituted **DPQ** derivatives and 1,8-diaminoanthracene. The binding affinities for F^- and $H_2PO_4^-$ in CH_2Cl_2 were found to be enhanced relative to the simple **DPQ** “parent” system, presumably as the result of the combined effects of preorganization and cooperative binding permitted by the pyrrole NH donor groups. Furthermore, positive homotropic allosteric anion binding was observed and is ascribed to the structurally coupled nature of the two binding cavities present in the macrocycles (Figure 6).

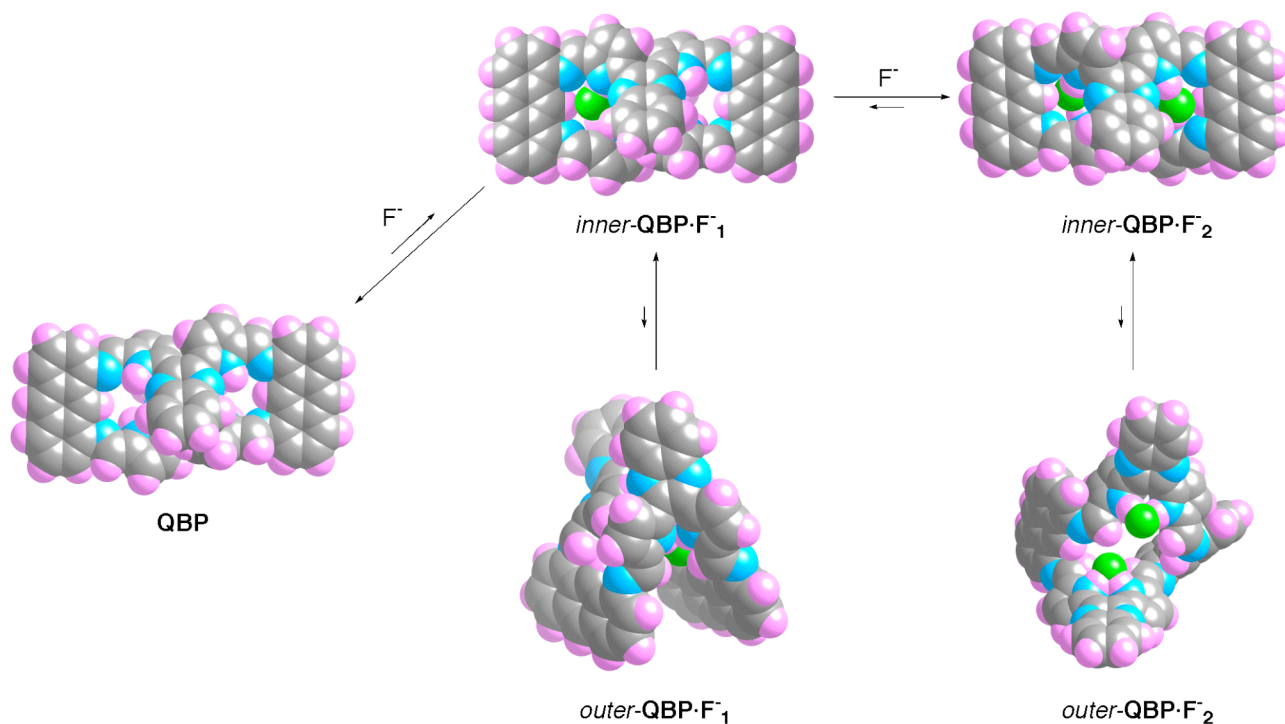


Figure 6 Optimized structures of quinoxaline-bridged porphyrinoid (**QBP**) and complexes with F^- based on ab initio calculations (HF/3-21G).

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