

Programmed arraying of metal complexes in a supramolecular system: Stacked assembly of porphyrin and phthalocyanine

Molecular materials comprising of organized assemblies of functional molecules occasionally demonstrate chemical and physical phenomena that are unpredictable from the sum of their individual molecular components. These phenomena are caused by intermolecular communications defined by their electronic states and relative spatial orientations, i.e., angle and distance. Supramolecular systems have been used for building the interconnections between the molecular components to develop such functionalized molecular assemblies with a synergetic effect, because supramolecular linkages are well suited to flexible control of the interactions between them. Macrocyclic tetrapyrroles, such as porphyrins and phthalocyanines and their metal complexes, have been used as key building blocks for a wide range of molecular materials owing to their unique photophysical, electrochemical, magnetic, and catalytic properties. Organized porphyrin assemblies are also showing promise for the construction of higher functionalized systems, whilst the arraying of multiple porphyrins has been investigated by employing bio-inspired templates and regulated stacking interactions.

We have recently reported supramolecular stacked arrays of porphyrins and phthalocyanines connected by two- or fourfold rotaxanes [1-4]. A fourfold rotaxane, **3**, was prepared from tetradactyl porphyrin with four alkyl ammonium chains, **2**, and phthalocyanine with four peripheral crown ethers, **1** (Fig. 1). A rotaxane consisting of a secondary ammonium ion and a crown ether has been recognized as a versatile building block for supramolecular systems. This complexation occurred as a result of electrostatic stabilization and hydrogen bonds between the negatively charged interior of the dibenzo-24-crown-8 ethers and the cationic ammonium $R_2NH_2^+$ moieties. Since the terminuses of the alkylammonium chains were locked by large phosphoramidate moieties, the porphyrin and phthalocyanine are inseparable, but their interactions are flexibly convertible. The interaction between the two metal complexes was interconverted between the protonation state and deprotonation state of the secondary amines in the middle of the alkyl chains. In the dinuclear Cu^{2+} complex of the fourfold rotaxane, the Cu^{2+} -porphyrin and the Cu^{2+} -phthalocyanine were stacked efficiently on one another to afford spin-spin communication. Spin states of the dinuclear complex were reversibly switchable between the protonated (doublet) and deprotonated forms (singlet) (Fig. 1(b)) [1]. This switchable communication between two

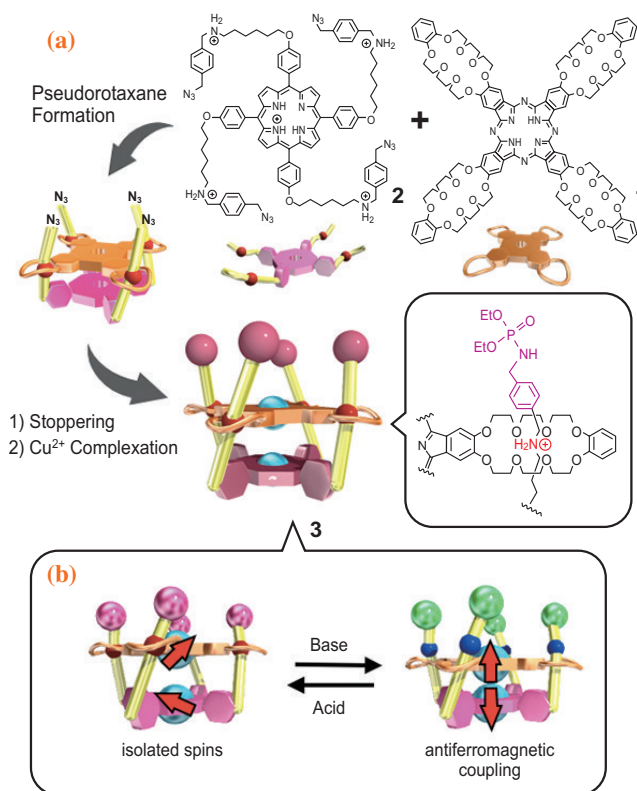


Fig. 1. (a) Synthesis of a dinuclear Cu^{2+} complex of the porphyrin/phthalocyanine fourfold rotaxane and (b) switchable spin-spin interaction between Cu^{2+} complexes in the fourfold rotaxane.

metal complexes demonstrated the obviously flexible character of the supramolecular rotaxane linkage. We also succeeded in the regioselective formation of the heterodinuclear complex in the fourfold rotaxane [2].

For the supramolecular architecture, ionic bonds as non-covalent interactions in molecular assemblies are usually categorized as relatively strong and nondirectional forces. However, they yield quite stable site- and configuration-specific molecular association by cooperation among multiple-ionic interactions and/or other intermolecular forces. For instance, there are many examples of intercalation phenomena of planar cationic dyes into polyanionic DNA duplexes through electrostatic and π - π interactions. From this viewpoint, the fourfold rotaxane would be a good platform for such a molecular association, because it has four cations as crown ether-wrapped ammonium ions standing in a square around the extended π -system of the phthalocyanine core. The structure of the molecular assembly is clear-cut and exhibits molecular

complementarity with tetraanionic porphyrins. The ionic complexation between the fourfold rotaxane and tetraanionic porphyrin ($\text{Cu}^{2+}\text{-TPPS}^{4-}$) was quite stable and stoichiometrically occurred even at a micromolar level in a solution, which was investigated by a photometric titration experiment (Fig. 2). However, without a crystallographic analysis, it is not possible to ascertain whether the $\text{Cu}^{2+}\text{-TPPS}^{4-}$ was stacked on top of the phthalocyanine ring or intercalated into the middle of the porphyrin and phthalocyanine.

Brown single crystals of **4** were obtained and the crystal structure revealed by synchrotron radiation at beamline **BL02B1** in collaboration with Dr. Kunihisa Sugimoto (JASRI) is shown in Fig. 3. We found a triply stacked structure of $\text{Cu}^{2+}\text{-TPPS}^{4-}$ on Cu^{2+} -porphyrin and Cu^{2+} -phthalocyanine in the fourfold rotaxane. The crystal structure clearly indicated that four alkylammonium chains of the porphyrin threaded into each crown ring attached to the phthalocyanine to form the fourfold rotaxane structure. Moreover, the $\text{Cu}^{2+}\text{-TPPS}^{4-}$ moiety was perfectly stacked on top of the phthalocyanine ring with a Cu–Cu distance of 3.6 Å as an *H*-aggregate, whereas the porphyrin ring and phthalocyanine ring of the fourfold rotaxane were stacked in a slightly slipped *J*-aggregation form. All phenyl rings of $\text{Cu}^{2+}\text{-TPPS}^{4-}$ intervened between adjacent crown ethers to stabilize the ionic complex. To our best knowledge, this is the first example of an X-ray crystal structure of a facially stacked ionic complex between cyclic tetrapyrroles as well as that of a fourfold rotaxane. Recently, we found that $\text{Cu}^{2+}\text{-TPPS}^{4-}$ directly affects the electronic state of the phthalocyanine in the supramolecular assembly.

Since the electronic properties of porphyrin and phthalocyanine are tunable by complexation with metal ions and functionalization through diverse substitutions, this should allow the potential development of emergent functions related to nanomagnetism, conductivity, or catalysis via intermolecular electronic communications among the stacked metal complexes.

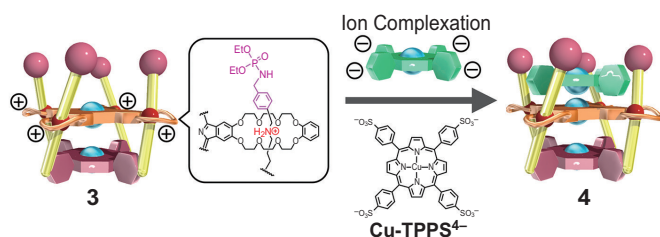


Fig. 2. Triply stacked array of Cu^{2+} -porphyrins, Cu^{2+} -phthalocyanine, and $\text{Cu}^{2+}\text{-TPPS}^{4-}$ formed via ionic complexation.

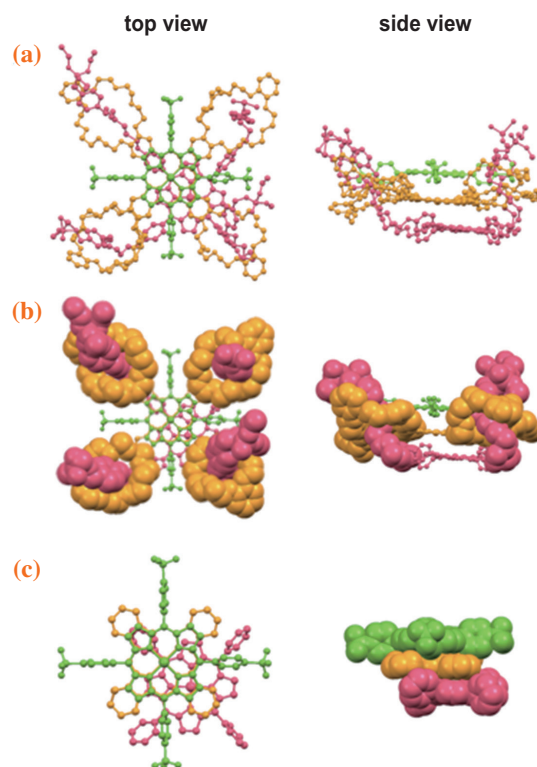


Fig. 3. Crystal structure of the triply stacked assembly: (a) the whole figure of the assembly, (b) the emphatic alkyl ammonium chains and the crown ether rings as a space-filling model to clarify the four rotaxane structures, and (c) the extracted porphyrin and phthalocyanine rings to show the stacking structure. Porphyrin and phthalocyanine of the fourfold rotaxane and $\text{Cu}^{2+}\text{-TPPS}^{4-}$ are represented in pink, orange, and green, respectively. Solvent molecules and hydrogen atoms have been omitted for clarity. [3]

Kentaro Tanaka^{a,*} and Yasuyuki Yamada^{a,b}

^a Department of Chemistry, Nagoya University

^b Research Center for Materials Science, Nagoya University

*E-mail: kentaro@chem.nagoya-u.ac.jp

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