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Triply Stacked Heterogeneous Array of Porphyrins and Phthalocyanine through Stepwise Formation of a Fourfold Rotaxane and an Ionic Complex

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Supporting Information

ABSTRACT: We report the preparation and crystal structure of a triply stacked metal complex array in which a Cu−phthalocyanine is sandwiched between different Cu−porphyrins. The discrete heterogeneous assembly was prepared through formation of a fourfold rotaxane from a tetradactyl porphyrin with alkylammonium moieties and a phthalocyanine bearing four crown ethers and the subsequent formation of an ionic complex between the fourfold rotaxane and a tetraanionic porphyrin. The tetraanionic porphyrin, Cu−TPPS^{4-}, is selectively bound to the fourfold rotaxane through cooperative $\pi-\pi$ and ionic interactions. The crystal structure revealed the columnar stacked array of the three planar building components in a precise order and spatial arrangement that promote intermolecular electronic communication.

The emergence of chemical properties can arise from intermolecular communication among multiple molecular components that are assembled through accurate sequential and spatial arrangements.[1] In biological systems, the precise intermolecular communication occurs in and is regulated by proteins, for which covalent synthetic approaches are basically adopted. On the other hand, non-covalent self-assembly approaches are well-suited for generating flexible and switchable molecular organizations that are thermodynamically and/or kinetically controlled.[2] 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 through cooperation among multiple ionic interactions and/or other intermolecular forces. For example, some cationic planar molecules have been found to act as DNA intercalators that can bind to DNA through electrostatic and $\pi-\pi$ interactions.[3] Such cooperative molecular interactions have been employed for ionic complexation between a tetracationic porphyrin and a tetraanionic porphyrin.[4] Porphyrins and phthalocyanines are promising building blocks for molecular devices and materials, including photodevices,[5] actuators,[6] sensors,[7] molecular hosts,[8] catalysts,[9] therapeutic agents,[10] and so on. Since their potential uses are derived from their predictable and robust frameworks, remarkable stabilities, ability to be chemically modified, and photophysical and electrochemical properties, intermolecular electronic communication among porphyrins and phthalocyanines could be expanded to manifold applications in precisely organized systems.[11]

We recently reported $4\cdot4Cl^-$, a mechanically linked heterodimer of a Cu−porphyrin and a Cu−phthalocyanine obtained via formation of a fourfold rotaxane.[12] In the dinuclear Cu^{2+} complex of the fourfold rotaxane, the Cu^{2+}−porphyrin and Cu^{2+}−phthalocyanine were stacked efficiently on one another to afford reversibly switchable spin−spin communication. The heterogeneously stacked dimer consisting of a Cu−porphyrin and a Cu−phthalocyanine has four cations as crown ether-wrapped ammonium ions standing in a square around the highly conjugated system of the phthalocyanine core. The structure of the molecular assembly is clear-cut and would exhibit molecular complementarity with tetraanionic porphyrins. Herein we report the extension of this approach to afford a heterogeneous stacked porphyrin−phthalocyanine−porphyrin array with precisely controlled spatial arrangement through formation of the fourfold rotaxane and subsequent ionic complexation.

The metal complex array **5** was prepared in 69% yield in three steps (Scheme 1): (a) preparation of fourfold rotaxane **3** from a metal-free porphyrin with four alkylammonium chains, $[\mathbf{1}\cdot5H]^{5+}\cdot5BARF^-$ ($BARF^-$ = tetrakis[3,5-bis(trifluoromethyl)-phenyl]borate), and a metal-free phthalocyanine with peripheral crown ethers, **2**; (b) insertion of metal ions to give the dinuclear Cu^{2+} complex $4\cdot4Cl^-$ as reported previously;[12] and (c) subsequent formation of an ionic complex between $4\cdot4Cl^-$ and $4TBA^+\cdot Cu-TPPS^{4-}$ [TBA^+ = tetrabutylammonium; Cu−$TPPS^{4-}$ = 5,10,15,20-tetrakis(sulfonatophenyl)porphyrinato-copper(II)] to afford the triply stacked porphyrin−phthalocyanine−TPPS array **5**.

Despite the restricted solubility of previously reported ionic complexes between tetracationic and tetraanionic porphyrins,[4b] the obtained ternary array **5** shows good solubility in various organic solvents such as chloroform, dichloromethane, and methanol. Brown single crystals of **5** were obtained by slow

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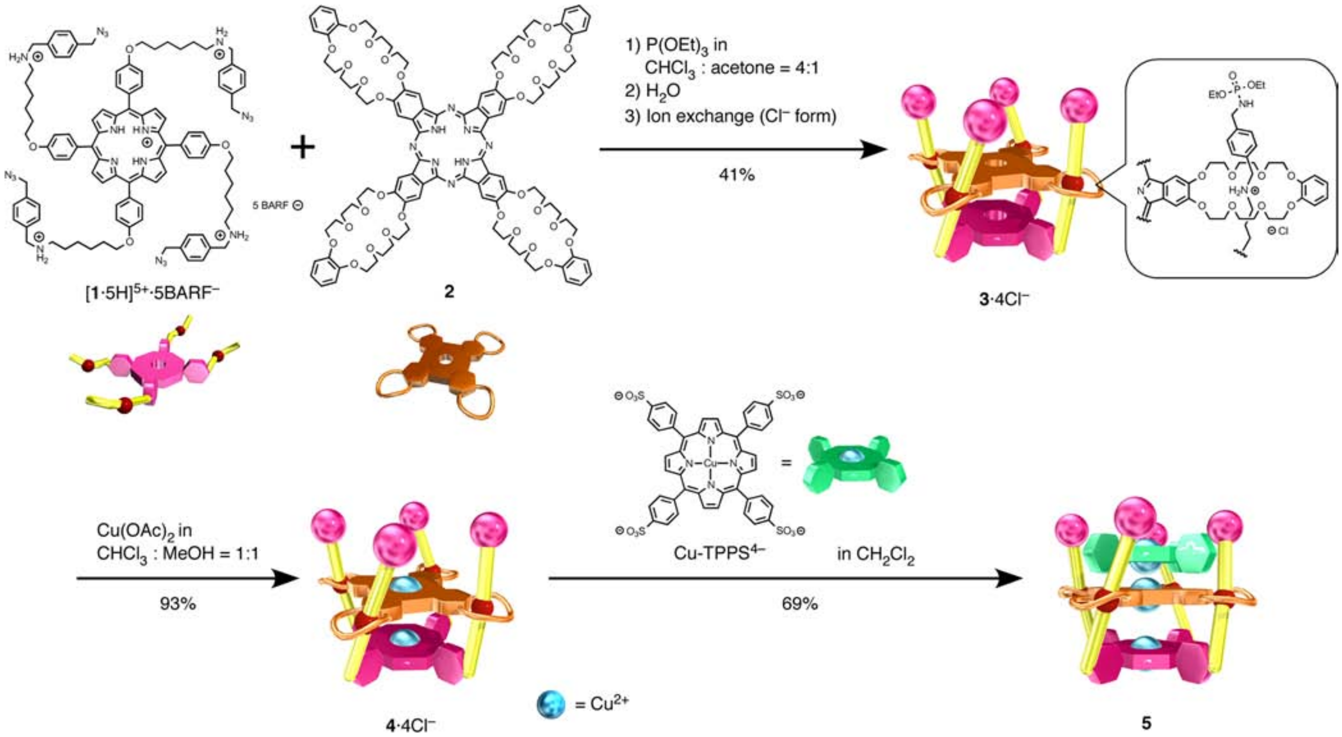
Scheme 1



diffusion of diethyl ether into a solution of **5** in a mixed solvent of chloroform and methanol. The crystal structure revealed by synchrotron radiation is shown in Figure 1. We found a triply stacked structure involving the Cu–porphyrin and Cu–phthalocyanine of the fourfold rotaxane and the Cu–porphyrin of Cu–TPPS^{4-}. The crystal structure obviously indicates that each of the four alkylammonium chains of the tetracationic porphyrin is threaded into a crown ether attached peripherally on the phthalocyanine, forming the fourfold rotaxane structure. Moreover, the Cu–TPPS^{4-} moiety is perfectly stacked on the top of the phthalocyanine ring with a Cu–Cu distance of 3.6 Å to form an H-aggregate, whereas the porphyrin ring and the phthalocyanine ring of the fourfold rotaxane are stacked in a slightly slipped J-aggregate form with a Cu–Cu distance of 5.3 Å. All of the phenyl rings of Cu–TPPS^{4-} intervene between adjacent crown ethers to stabilize the ionic complex. To the best of our knowledge, this is the first example of an X-ray crystal structure of a facially stacked ionic complex between cyclic tetrapyrroles as well as the first crystal structure of a fourfold rotaxane.

The ionic complexation between the fourfold rotaxane and Cu–TPPS^{4-} was investigated by photometric titration experiments. The changes in the UV–vis spectrum of the fourfold rotaxane in the presence of increasing amounts of 4TBA$^+$·Cu–TPPS^{4-} are shown in Figure 2. The change in the Q band of the Cu–phthalocyanine upon stacking with Cu–TPPS^{4-} was used as a quantitative probe to verify the formation of the ionic complex. As the 4TBA$^+$·Cu–TPPS^{4-} concentration was increased ([Cu–TPPS^{4-}]/[**4**] ranging from 0.0 to 1.0), the absorbance at 683 nm gradually decreased while a new peak appeared at 708 nm, with an isosbestic point at 700 nm. This simultaneous change indicates the 1:1 complexation between **4** and Cu–TPPS^{4-} in the dilute solution in CH_2Cl_2 (2 μM). In contrast, no spectral change in the Q band was observed during the titration of nonionic Cu–tetraphenylporphyrin (Cu–TPP) under the same conditions (see the Figure 2 inset and Figure S1 in the Supporting Information). The specific molecular recognition was achieved through cooperative π–π and ionic interactions. The Soret band of the 1:1 complex was slightly blue-shifted and the Q band showed a significant red shift relative to the sum of the spectra of **4**·4Cl$^-$ and 4TBA$^+$·Cu–TPPS^{4-} (Figure S2). These spectral shifts are in good agreement with a theoretical description of a coherent interaction in an H-dimer consisting of heterochromophores.[13] This result strongly supports the existence of stacking interactions between the phthalocyanine and TPPS^{4-} in solution as well as in the crystal. In cyclic voltammetry of the trimer, the first oxidation peaks of the Cu–phthalocyanine and the Cu–TPPS^{4-} shifted to higher and lower potentials, respectively, from those of the corresponding monomers (Figure S3). These phenomena reflect the efficient π–π electronic interaction in the closely stacked system.

In summary, we have demonstrated the stepwise construction of a heterogeneous trinuclear metal complex based on supramolecular association and specific molecular recognition. As revealed by the crystal structure, three different components (Cu–porphyrin, Cu–phthalocyanine, and Cu–TPPS) stacked cofacially to form the discrete array in a well-defined orientation. We recently reported heterodinuclear complex formation in a fourfold rotaxane.[14] Since porphyrin and phthalocyanine macrocycles can form complexes with a variety of metal ions and can be functionalized through diverse substitutions, the strategy described here to array three different metal complexes in a discrete and predictable fashion should allow us to design emergent functions related to nanomagnetism, conductivity, and catalysis via intermolecular electronic communication among the stacked metal complexes.

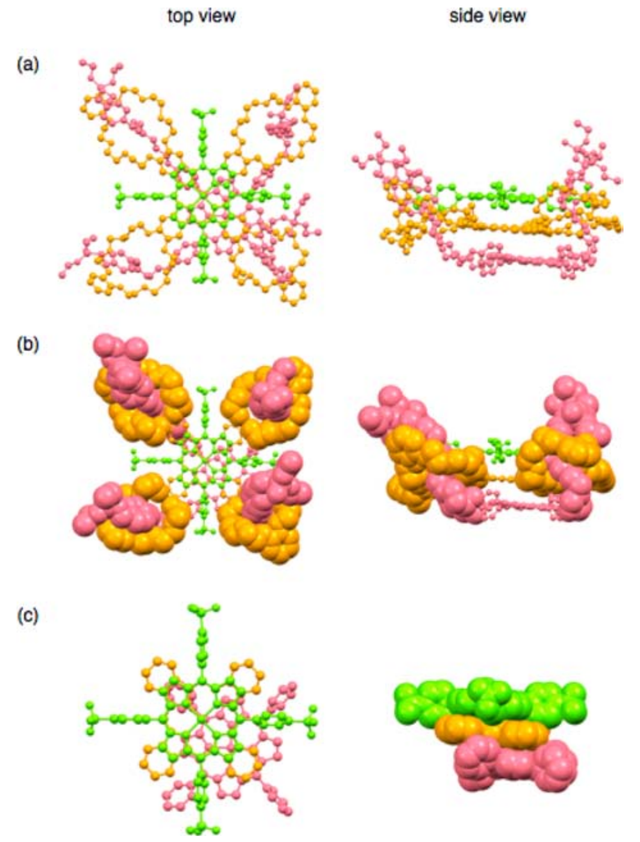


Figure 1. Crystal structure of the triply stacked assembly. (a) View of the entire structure of the assembly. (b) View in which the alkylammonium chains and crown ether rings have been emphasized as space-filling models to clarify the four rotaxane structures. (c) View of the extracted porphyrin and phthalocyanine rings to show the stacking structure. The rotaxane porphyrin, rotaxane phthalocyanine, and $TPPS^{4-}$ are shown in pink, orange, and green, respectively. Solvent molecules and hydrogen atoms have been omitted for clarity.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and crystallographic, photochemical, and electrochemical data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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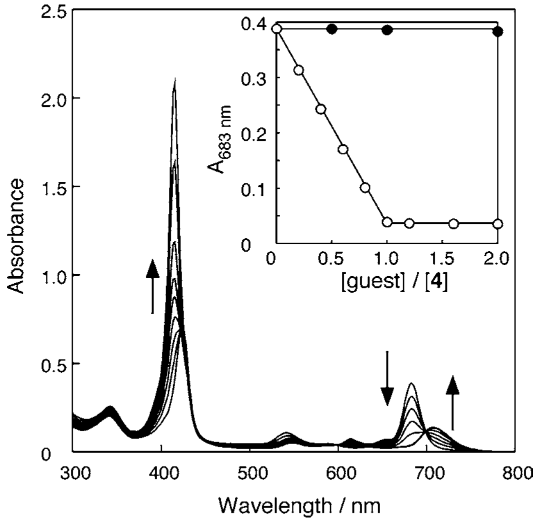

Figure 2. Photometric titration of the fourfold rotaxane $4{\cdot}4Cl^-$ with $4TBA^+{\cdot}Cu{-}TPPS^{4-}$. $4TBA^+{\cdot}Cu{-}TPPS^{4-}$ shows a strong Soret band at 416 nm but no significant peaks above 650 nm. The dinuclear copper complex $4{\cdot}4Cl^-$ was dissolved in CH_2Cl_2 at a concentration of 2.0×10^{-6} M at 293 K. The arrows indicate absorbance changes upon addition of 0−2 equiv of $4TBA^+{\cdot}Cu{-}TPPS^{4-}$. The inset shows plots of absorbance changes at 683 nm against the $Cu{-}TPPS^{4-}$/rotaxane ratio (○) and the Cu−TPP/rotaxane ratio (●).

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