A Supramolecular Analog of the Photosynthetic Special Pair

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On account of the porphyrin nucleus' extraordinary electronic and photocatalytic properties, a myriad of synthetic porphyrinoid oligomers have surfaced1 in the recent chemical literature. One of the prime driving forces for the production of such porphyrinoid assemblages has been the unraveling of the photosynthetic reaction center,2 where a "special pair" of two bacteriochlorophylls is held apart by ca. 3.2 Å with a slipped cofacial orientation.3 We conjectured that we should be able to self-assemble4 an interwoven analog of the photosynthetic special pair by exploiting our programmed approach for the noncovalent synthesis of interwoven supramolecular cages.5 In this procedure (Scheme 1), two units of the tetraturcated tetrakisammonium cation 4+—possessing a porphyrin core—would assemble with four molecules of the dibenzoic crown ether bis-p-phenylene-[34]crown-10 (BPP34C10) to generate a six-component interwoven aggregate where the four crown ether macrorings would

![Scheme 1. Schematic Representation Depicting the Anticipated Self-Assembly of Four BPP34C10 Macrocyles with Two 14+ Tetracations To Generate an Interverved Supermolecule Possessing a Pair of Cofacially-Arranged Porphyrinoid Nuclei](image)

tie two porphyrin subunits together in a cofacial orientation. Here, we report the noncovalent synthesis of the [BPP34C10]4+-(1)2]8+ supermolecule in the solid state, and in solution, as evidenced by X-ray crystallography and EPR spectroscopy, respectively.

The X-ray analysis6 of a single crystal—obtained when a MeCN solution containing 4PF6 and a 4-fold excess of BPP34C10 was layered with t-Pr3O—reveals a six-component superstructure that has self-assembled in accordance with our design criteria (Scheme 1). Pairs of C4-related 14+ tetracations have their dibenzoamyronium sidearms threaded simultaneously through the cavities of four cyclically-disposed BPP34C10 macrocycles (Figure 1) in characteristic7 fashion. In addition to conventional π—π stacking7 between the porphyrin nuclei (the mean interplanar separation is 3.65 Å), the supramolecular assemblage is stabilized via [N4—H···O] and [C—H···O] hydrogen bonding between the dibenzoamyronium centers, attached to the porphyrin hub of 14+, and the oxygen atoms of BPP34C10’s polyether linkages. The porphyrin core is non-planar and has an S4-type deformation, the angles subtended at Cu from the periphery being 166 and 172°. The pair of stacked porphyrin subunits adopt (Figure 1b) a sheared relationship, with the Cu atoms being offset by ca. 3.05 Å; the nonbonded Cu⋯Cu separation is 4.76 Å. Accompanying this offset is a skewing of each of the BPP34C10 macrocycles’ long axes to achieve a near-parallel alignment of the vectors linking the central oxygen atoms of each polyether linkage within each crown and the Cu⋯Cu vector. A notable feature of the packing8 of the supermolecules is the ordered trapping of one of the PF6− anions between the exo faces of lattice-translated BPP34C10 macrocycles and their associated pairs of benzyl groups (which are each involved in parallel π—π stacking interactions).

The Cu(II) ion (S = 1/2) of 14+ provides an axial EPR spectrum (Figure 2) with two distinct g values—gzz, gxx, and gyy. Both copper (l = 7/2) and nitrogen (l = 1) hyperfine splittings are well-resolved over the entire spectral range. The hyperfine splitting Azz—due to the interaction of the unpaired electron with the Cu nucleus—is indicated in the figure. Moreover, there are

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(7) See the Supporting Information for details.
These observations indicate that the porphyrin nuclei of $1^+$ are probably on account of charge repulsion. When magnetically dilute and thus are not aggregated in solution, supermolecule: (a) élévation: (b) plan view.

Figure 1. The crystal structure of the [(BPP34C10)$4^*(1)2^+$. Inset: half-field region showing the "porphyrin dimer's" transition.

Figure 2. EPR spectra (9.15 GHz, 40% MeCN/60% CH$_2$Cl$_2$, 60 K) of (a) 1·4PF$_6$ (5.6 mM, $g_\parallel = 2.195$, $g_\perp = 2.055$, $A_{C=O} = 200$ G) and (b) a solution of 1·4PF$_6$ and BPP34C10 (1:2:2), showing the formation of a "porphyrin dimer" with $S = 1$ ($A_{C=O} = 90$ G, $D_h = 0.023$ cm$^{-1}$). Inset: half-field region showing the "porphyrin dimer's" $\Delta m_s = 2$ transition.

no transitions in the half-field region around 0.16 T (not shown). These observations indicate that the porphyrin nuclei of $1^+$ are magnetically dilute and thus are not aggregated in solution, probably on account of charge repulsion. When BPP34C10 (2.2 mol equiv) is added to the solution of 1·4PF$_6$, a new spectrum results (Figure 2b) with transitions both in the region around $g = 2$ and in the half-field region (inset in Figure 2). This spectrum is indicative$^9$ of two Cu(II) ions with parallel electron spin coupling, which results in a triplet ($S = 1$) spin system. In this triplet system, the electron spin is delocalized over both Cu(II) centers, causing a decrease in the Cu and N hyperfine splitting. Furthermore, the interaction of the electron spin with two equivalent Cu nuclei results in a 7-line hyperfine pattern with relative intensities of 1:2:3:4:3:2:1. The dipolar interaction between the two electrons leads to an additional splitting of the EPR spectrum. The parallel component of this splitting, $D_h$, is estimated to be 0.023 cm$^{-1}$ (Figure 2b). The distance $r$ between the Cu(II) centers can be evaluated by using the relationship$^{10}$ $|D| = 0.65g^2r^3 (r$ in Å). If the (axial) dipolar interaction tensor is colinear with the $g$ tensor, i.e., if the Cu···Cu distance vector is more or less perpendicular to the complex's porphyrin macrorings, one can use $|D| = D_h$ and $g = g_\parallel$, which affords a value of $r = 5.1$ Å. This value represents an upper limit for the complex's Cu···Cu distance.$^{11}$

The noncovalent synthesis of the [(BPP34C10)$4^*(1)2^+$ supramolecular assembly—whose porphyrin subunits maintain a slipped cofacial orientation, thus resembling the photosynthetic reaction center—elegantly demonstrates the utility of self-assembly$^4$ for modern chemical synthesis. It shows that complex supramolecular architectures—analogous to those encountered in the natural world—may be generated efficiently from relatively elementary building blocks by using intermolecular interactions. Nevertheless, the spectacular feats of self-assembly witnessed in Nature can be rivaled only once the noncovalent bond has been completely understood and harnessed.

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Supporting Information Available: Synthetic scheme for the preparation of 1·4PF$_6$, and crystallographic data (18 pages). See any current masthead page for ordering and Internet access instructions.

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