

A Supramolecular Analog of the Photosynthetic Special Pair

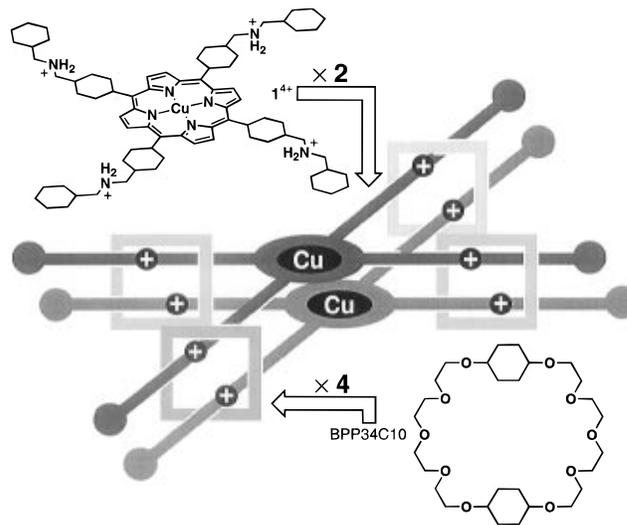
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On account of the porphyrin nucleus' extraordinary electronic and photocatalytic properties, a myriad of synthetic porphyrinoid oligomers have surfaced¹ in the recent chemical literature. One of the prime driving forces for the production of such porphyrinoid 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 tetrafurcated tetrakisammonium cation 1^{4+} —possessing a porphyrin core—would assemble with four molecules of the ditopic 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 Macrocycles with Two 1^{4+} Tetracations To Generate an Interwoven Supermolecule Possessing a Pair of Cofacially-Arranged Porphyrinoid Nuclei



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 $1 \cdot 4PF_6$ and a 4-fold excess of BPP34C10 was layered with *i*-Pr₂O—reveals a six-component superstructure that has self-assembled in accordance with our design criteria (Scheme 1). Pairs of C_i -related 1^{4+} tetracations have their dibenzylammonium sidearms threaded simultaneously through the cavities of four cyclically-disposed BPP34C10 macrocycles (Figure 1) in characteristic⁵ 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* $[N^+ \cdots H \cdots O]$ and $[C-H \cdots O]$ hydrogen bonding between the dibenzylammonium centers, attached to the porphyrin hub of 1^{4+} , and the oxygen atoms of BPP34C10's polyether linkages. The porphyrin core is non-planar and has an S_4 -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 \cdots Cu separation is 4.76 Å. Accompanying this offset is a skewing of each of the BPP34C10 macrorings' 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 \cdots Cu vector. A notable feature of the packing⁸ of the supermolecules is the ordered trapping of one of the PF_6^- 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 1^{4+} provides an axial EPR spectrum (Figure 2) with two distinct *g* values—*viz.*, $g_{||}$ and g_{\perp} . Both copper ($I = 3/2$) and nitrogen ($I = 1$) hyperfine splittings are well-resolved over the entire spectral range. The hyperfine splitting $A_{||}$ —due to the interaction of the unpaired electron with the Cu nucleus—is indicated in the figure. Moreover, there are

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(6) Crystal data for $C_{264}H_{296}N_{16}O_{40}Cu_2 \cdot 5PF_6 \cdot 3Cl \cdot MeCN \cdot MeOH$: $M = 5364.54$, triclinic, $a = 16.838(3)$ Å, $b = 21.226(4)$ Å, $c = 23.660(2)$ Å, $\alpha = 72.68(1)^\circ$, $\beta = 81.74(1)^\circ$, $\gamma = 71.70(2)^\circ$, $V = 7653(2)$ Å³, space group $P\bar{1}$, $Z = 1$ (the superstructure has crystallographic C_i symmetry), $D_c = 1.164$ g cm⁻³, $\mu(Cu K\alpha) = 1.354$ mm⁻¹, $\lambda = 1.54178$ Å, $F(000) = 2806$. Data for a red plate ($0.33 \times 0.17 \times 0.07$ mm) were measured on a Siemens P4/RA diffractometer with Cu $K\alpha$ radiation (graphite monochromated) with ω scans at 203 K. Of the 15256 independent reflections measured ($\theta \leq 50^\circ$), 7029 had $|I_0| > 2\sigma(I_0)$, and were considered to be observed. The structure was solved by direct methods. Only five PF_6^- anions were located, four in general positions and one on a special position. As observed in previous cases (Ashton, P. R.; Glink, P. T.; Stoddart, J. F.; Tasker, P. A.; White, A. J. P.; Williams, D. J. *Chem. Eur. J.* **1996**, *2*, 729–736), repeated recrystallization—in an attempt to produce crystals of a suitable size for data collection—can lead to partial anion exchange. The superstructure's three remaining charges are made up by Cl^- anions, disordered over 12 quarter occupied positions. Disorder was observed for one of the terminal benzyl groups, and in two sections of one of the macrocyclic polyethers. This disorder was resolved by splitting the respective atoms into two positions with partial occupancy. Hydrogen atoms were placed in idealized positions with $U_{eq}(H) = 1.2U_{eq}(C)$ and $U_{eq}(H) = 1.5U_{eq}(Me)$, respectively, and were allowed to ride on their parent atoms. Full-matrix least-squares refinement based on F^2 with the central porphyrin units and the disordered Cl^- anions and solvent molecules held isotropic (on account of a shortage of observed data), the remaining non-hydrogen atoms anisotropic, gave $R_1 = 0.1499$ and $wR_2 = 0.3822$. All computations were carried out with the SHELXTL 5.03 package.

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(8) See the Supporting Information for details.

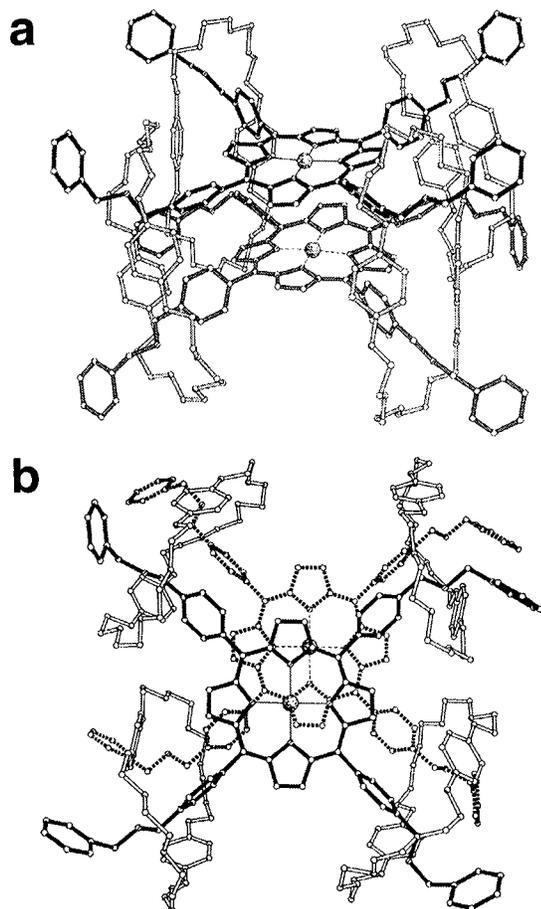


Figure 1. The crystal structure of the $[(\text{BPP34C10})_4 \cdot (\mathbf{1})_2]^{8+}$ supermolecule: (a) elevation; (b) plan view.

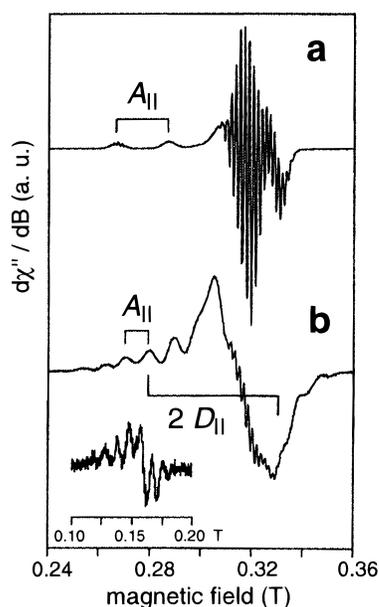


Figure 2. EPR spectra (9.15 GHz, 40% MeCN/60% CH_2Cl_2 , 60 K) of (a) $\mathbf{1} \cdot 4\text{PF}_6$ (5.6 mM, $g_{\parallel} = 2.195$, $g_{\perp} = 2.055$, $A_{\parallel\text{Cu}} = 200$ G) and (b) a solution of $\mathbf{1} \cdot 4\text{PF}_6$ and BPP34C10 (1:2.2), showing the formation of a "porphyrin dimer" with $S = 1$ ($A_{\parallel\text{Cu}} = 90$ G, $D_{\parallel} = 0.023$ 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 $\mathbf{1}^{4+}$ 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 $\mathbf{1} \cdot 4\text{PF}_6$, 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 indicative⁹ 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_{\parallel} , is estimated to be 0.023 cm^{-1} (Figure 2b). The distance r between the Cu(II) centers can be evaluated by using the relationship¹⁰ $|D| = 0.65g^2/r^3$ ($|D|$ in cm^{-1} , r in Å). If the (axial) dipolar interaction tensor is colinear with the \mathbf{g} tensor, *i.e.*, if the $\text{Cu} \cdots \text{Cu}$ distance vector is more or less perpendicular to the complex's porphyrin macrorings, one can use $|D| = D_{\parallel}$ and $g = g_{\parallel}$, which affords a value of $r = 5.1$ Å. This value represents an upper limit for the complex's $\text{Cu} \cdots \text{Cu}$ distance.¹¹ Hence, the triplet spectrum (Figure 2b) provides conclusive evidence that BPP34C10 induces the intermolecular aggregation of the $\mathbf{1}^{4+}$ tetracation's porphyrin subunits—by binding two secondary dialkylammonium moieties concurrently within its cavity—in solution, as well as in the solid state.¹²

The noncovalent synthesis of the $[(\text{BPP34C10})_4 \cdot (\mathbf{1})_2]^{8+}$ supramolecular assemblage—whose porphyrin subunits maintain a slipped cofacial orientation, thus resembling² the photosynthetic reaction center—elegantly demonstrates the utility of self-assembly⁴ for modern chemical synthesis. It shows that complex supramolecular architectures—analogueous 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 $\mathbf{1} \cdot 4\text{PF}_6$ and crystallographic data (18 pages). See any current masthead page for ordering and Internet access instructions.

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(11) Previous EPR studies on Cu–porphyrin dimers^{9a} have demonstrated that a geometry in which the $\text{Cu} \cdots \text{Cu}$ distance vector makes an angle with the normal to the porphyrin ring plane results in an (axial) \mathbf{D} tensor that is not colinear with the \mathbf{g} and \mathbf{A} tensors. In an extreme case, the \mathbf{D} and \mathbf{g} tensors could be considered to be perpendicular, which is, however, unlikely from a structural viewpoint, as well as from the appearance of the EPR spectrum. For this hypothetical case—using $|D| = 2D_{\parallel}$ and $g_{\text{eff}} = g_{\perp}$ —we calculated the lower limit for the $\text{Cu} \cdots \text{Cu}$ distance to be 3.9 Å.

(12) EPR spectra—recorded after $\mathbf{1} \cdot 4\text{PF}_6$ had been titrated against BPP34C10—revealed that the dimer is in dynamic equilibrium with the monomer. Indeed, the presence of N hyperfine splitting is an indication of monomer contribution. The relative contribution of this splitting was at a minimum when 2 mol equiv of BPP34C10 were present. This observation is consistent with the $[(\text{BPP34C10})_4 \cdot (\mathbf{1})_2]^{4+}$ supermolecule existing in solution.