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Communications to the Editor

Porphyrin−Fullerene Host−Guest Chemistry

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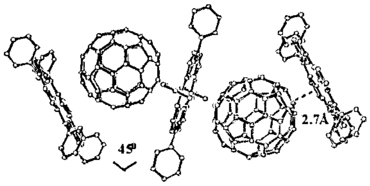
Fullerenes are spontaneously attracted to porphyrins and metalloporphyrins. This new supramolecular recognition element was first discovered in cocrystallates of C_{60} and C_{70} with tetraarylporphyrins[1−3] and octaethylmetalloporphyrins.[4,5] A natural feature of these structures is the zigzag arrangement of porphyrins with fullerenes sandwiched in the clefts. It is reproduced in calculations, and the unexpectedly strong interaction between a curved π surface and a flat π surface ($C_{\text{fullerene}}$-to-porphyrin plane distance ∼2.7 Å) is largely van der Waals in origin.[2]



With this knowledge we have used molecular modeling to design a jaw-like bis-porphyrin with a similar fullerene-sized bite. The palladium-linked *m*-pyridyl dimer shown in Figure 1 has a high calculated "gas phase" binding enthalpy for C_{60} (∼57 kcal·mol^{-1}) suggestive of tight fullerene binding in solution. A "chelate" effect from bidentate complexation should also contribute. While this work was in progress, a doubly strapped bis-porphyrin was reported to form a 1:1 complex with C_{60}.[6] Notably, the binding constant (7 × 10^{5} M^{-1}) exceeds those of traditional concave hosts such as calixarenes, cyclotriveratralenes, and resorcarenes.[7]

The palladium-linked[8] bis-porphyrins **1** and **2** were prepared according to Scheme 1 and characterized by ^{1}H NMR spectroscopy and FAB/MALDI mass spectrometry (see Supporting Information). Addition of C_{60} or C_{70} to solutions of these bis-porphyrins gave complexes that were chromatographically distinct from their individual components on thin layers or gravity columns. This indication of tight binding was also seen in MALDI mass spectra where substantial abundances of positive ions corresponding to **1**:C_{60}, **1**:C_{70}, **2**:C_{60}, and **2**:C_{70} were observed.

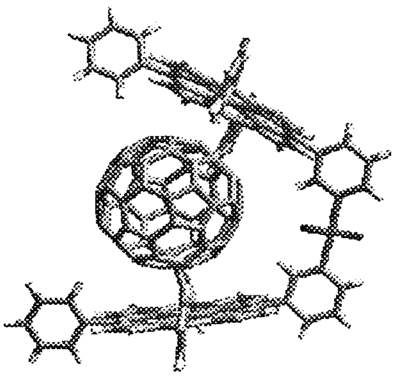


Figure 1. Calculated minimum energy structure of $PdCl_2$-linked mono-3-pyridyltriphenylporphyrinPd(II) bis complex of C_{60} (Universal Force Field, ver. 1.02). The porphyrin planes subtend an angle of 41.5° and Pd···C = 2.78, 2.85 and 2.86 Å.

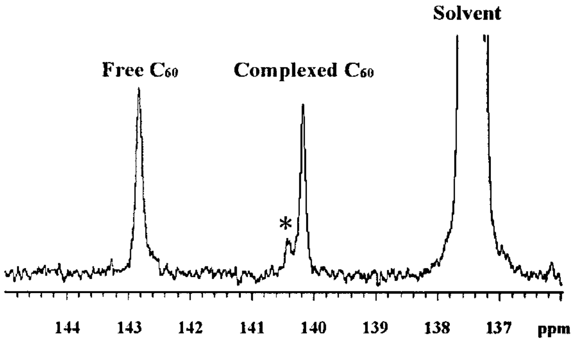


Figure 2. Low temperature (−90 °C) ^{13}C NMR spectrum of toluene solution of 2:1 mixture of C_{60} and **2**. The peak marked * is due to a small amount of Pd**2**·C_{60}.

^{1}H NMR spectroscopy of the porphyrin components and ^{13}C NMR spectroscopy of the fullerenes are very useful for revealing the structural details and the dynamics of complexation. When fullerenes are added to porphyrins **1** and **2**, ring current effects from the fullerenes cause upfield shifts in the central N−H protons (up to 0.34 ppm). Conversely, ring current effects of the porphyrins cause upfield shifts in the ^{13}C NMR of the fullerenes. For C_{60}, the shift is 2.7 ppm for complexation by **2** (see Figure 2). This is consistent with a prediction of 2.8 ppm based on a 2.7 Å approach of a fullerene 6:6 ring junction to the center of the porphyrin.[2] For C_{70}, the five different ^{13}C signals are shifted by 1.2−2.9 ppm. The details reveal orientation. The largest shift is found for the C_e carbon atoms of the equatorial belt, decreasing systematically toward the poles (see Figure 3). This is compelling evidence for "side-on" rather than "end-on" binding of C_{70} and can be understood in terms of maximizing van der Waals attraction. It is also consistent with the observation that C_{70} displaces C_{60} from **2** and provides a basis for selectivity of fullerene binding and the chromatographic behavior of fullerenes on porphyrin-appended silica stationary phases.[9]

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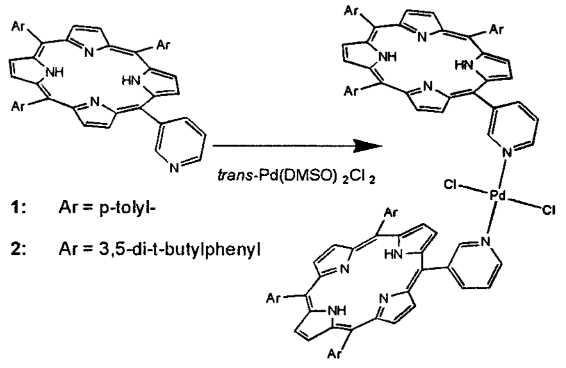
Scheme 1



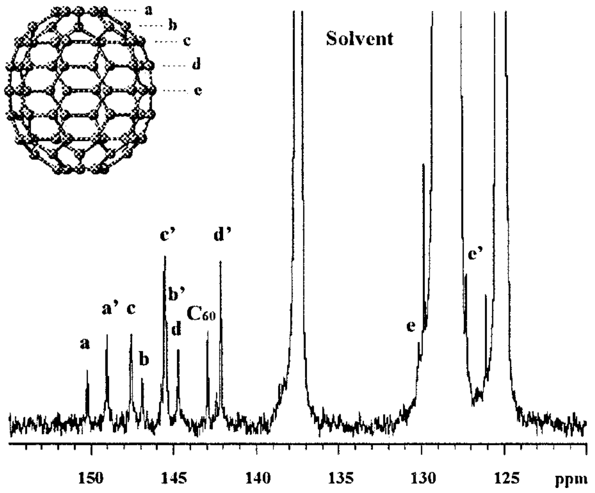


Figure 3. Low temperature (−60 °C) ^{13}C NMR spectrum of toluene solution of 1.5:1 mixture of C_{70} and **2**. Resonances a′−e′ are from complexed C_{70}.

In toluene solution at low temperatures, separate ^{13}C signals due to complexed and free fullerenes are observed (see Figures 2 and 3). Since the complexed and uncomplexed peak intensities are equal when 2 equiv of fullerene are present, 1:1 binding stoichiometry is established. At room temperature, however, signal averaging occurs due to rapid exchange of complexed and free fullerenes on the 500 MHz NMR time scale. Coalescence temperatures are −55° C for C_{60}:**2** and −30 °C for C_{70}:**2**. The binding constant for C_{60} to **2** at room temperature has been determined by ^{13}C NMR titrations[10] to be 5.2×10^3 M^{-1}. This tight-but-labile binding contrasts sharply with weak (54 M^{-1}) but slow binding of C_{60} to a calixarene cage.[11]

The use of excess $PdCl_2(DMSO)_2$ in Scheme 1 leads to partial metalation of the porphyrin. Treatment of this mixture of **2**, Pd**2**, and Pd_2**2** with C_{60} yields crystals suitable for X-ray diffraction (see Figure 4 and Supporting Information). Structural analysis shows that the expectations from modeling and NMR are realized (Figure 2). The porphyrin planes subtend an angle of 42°, and C_{60} is symmetrically centered over the porphyrins with a closest Pd···C distance of 2.856 (10) Å. These dimensions are consistent with those seen in untethered cocrystallates and are remarkably similar to those calculated (see Figure 1 caption).

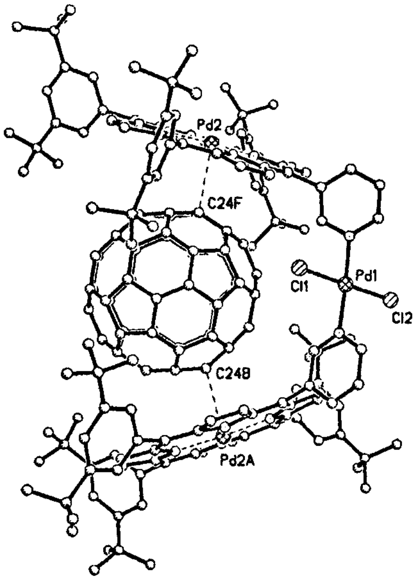


Figure 4. X-ray crystal structure of $Pd_{1.5}$**2**·C_{60}. The Pd2···C24F distance is 2.856(10) Å.

The combination of thermodynamic stability and kinetic lability seen in this work is a desirable feature in supramolecular systems, and applications of these chromophores to photoactive donor−acceptor systems can be anticipated. In this regard, when **2** is titrated with C_{60} in toluene, isosbestic points are observed in the visible spectrum at 413 and 430 nm (Supporting Information Figure S5). In addition, the porphyrin fluorescence emission at 655 nm decreases rapidly upon addition of C_{60}. This reflects the intimate contact of the porphyrin/fullerene chromophores and suggests a full investigation of the photophysics is warranted. To date, such investigations have been restricted to covalently or coordinatively linked fullerene/porphyrin conjugates.[12] The “jaws porphyrin” approach solves the problem of assembling discrete van der Waals complexes of donors and acceptors. Supramolecularly assembled chromophores are likely to behave differently from covalently linked ones. They also bear a closer resemblance to the natural photosystem.

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Supporting Information Available: Synthesis and characterization data for **2**, **2**·C_{60}, and **2**·C_{70} including ^1H NMR, UV−vis, MALDI mass spec. and X-ray data for $Pd_{1.5}$**2**·C_{60} (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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