Title
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Permalink
https://escholarship.org/uc/item/5kt9b5kg

Journal
Journal of the American Chemical Society, 122(43)

ISSN
0002-7863

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Publication Date
2000-11-01

DOI
10.1021/ja002214m

Peer reviewed
Porphyryln—Fullerene Host—Guest Chemistry

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Received June 21, 2000

Fullerenes are spontaneously attracted to porphyrins and metalloporphyrins. This new supramolecular recognition element was first discovered in cocrystallates of C60 and C70 with tetraaarylporphyrins1,2 and octaethylmetalloporphyrins.3,4 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 \( \pi \) surface and a flat \( \pi \) surface (C-fullerene-to-porphyrin plane distance \( \approx 2.7 \) \( \AA \)) is largely van der Waals in origin.5

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 C60 (\( \approx 57 \) 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.6 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 \( \pi \) surface and a flat \( \pi \) surface (C-fullerene-to-porphyrin plane distance \( \approx 2.7 \) \( \AA \)) is largely van der Waals in origin.5

The palladium-linked\(^{6} \) 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 C60 or C70 to solutions of these bisporphyrins gave complexes that were chromatographically distinct and provide a basis for selectivity of fullerene binding and the chromatographic behavior of fullerenes on porphyrin-appended silica stationary phases.8

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=C)= 2.78, 2.85 and 2.86 Å.

Figure 2. Low temperature (\( \approx 90^\circ \)C) \(^1\)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 Pd2C\(_{60}\).

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. \(^1\)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.5 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

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 $-55^\circ$C for C$_{60}$:2 and $-30^\circ$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 $5.2 \times 10^3$ 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 “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.

**Acknowledgment.** Dedicated to Fred Wudl on the occasion of his 60th birthday. This work was supported by the Marsden Fund of New Zealand administered by the Royal Society of New Zealand, The University of Auckland Research Committee, the University of California, Riverside, and the National Institutes of Health (GM 23851).

**Supporting Information Available:** Synthesis and characterization data for 2, 2-C$_{60}$, and 2-C$_{70}$ including $^{1}$H 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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