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Host-Guest Chemistry of Fullerenes; a Water-Soluble Complex between C_{70} and γ–Cyclodextrin

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Abstract: A water-soluble complex between C_{70} and γ–cyclodextrin has been prepared by boiling a conc. solution of γ-cyclodextrin (0.8M) in water with solid C_{70} suspended in water. The complex has been characterised by its UV/VIS spectrum and by photophysical methods.

We as well as others, have reported that C_{60} can be solubilized in water by complexation with γ-cyclodextrin (γ-CD),[1] a calixarene,[2] a water-soluble polymer,[3] or by using detergents.[4] However, the fullerenes often form aggregates. By using our method of boiling C_{60} in a γ-CD water solution (0.8M, 100°C) for 24 hours, a maximum concentration of *ca.* 10^{-3}M C_{60} in water can be obtained. On cooling, a precipitate is formed containing C_{60}-γ-CD complex and a large excess of γ-CD. Most but not all of the excess γ-CD can be removed by careful washing with cold water. No definite structural proof of the complex has yet been obtained. However, photophysical measurements provides indirect evidence for a structure with C_{60} enclosed by two γ-CD molecules has been obtained.[5] Furthermore, ^{1}H NMR and UV-data have revealed that the ratio of γ-CD to C_{60} in the complex depends on the excess of γ-CD. This ratio approaches two when a ten-fold excess of γ-CD is present.[6] Molecular modelling experiments also show that a 2:1 complex between γ-CD and C_{60} is a very reasonable structure and that C_{60} has just the right diameter to fit into the cavity generated by two head to head γ-CD:s. Such a structure has been suggested for a complex between α-CD and a carborane[7] and shown to be present in the crystals of γ-CD:12-crown 4: Li^+ (3:3:1).[8] Recently, we have also observed a 2:1 complex by mass spectrometry.[9]

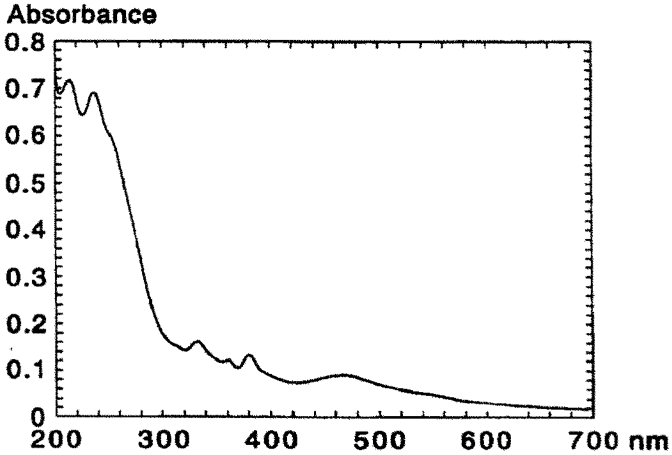

Fig. 1. Absorption spectrum of the complex between C_{70} and γ-cyclodextrin in water (conc. of C_{70} is $5x10^{-5}$ calculated from literature data[15]).

All our attempts to isolate the pure 2:1 complex have, however, failed. Instead we observe a slow decomposition of the complex in solution. On heating, the 2:1 complex decomposes rapidly giving a yellow solution of water-soluble aggregates containing C_{60} and γ-CD.[6] The same reaction can be induced at room temperature by adding DMSO (20%) to the aqueous-solution of the complex.

No host-guest complex of C_{70} has earlier been reported in the literature, although some unsuccessful attempts to prepare these complex have been made.[2,10] However, C_{70} has been shown to form a clathrate with hydroquinone and benzene.[11] We recently reported on the selectivity of γ-CD complexation with C_{60} over C_{70}.[6] No C_{70}-complex was observed (<5%) on boiling a fullerene mixture containing 93% C_{70} and 7% C_{60} with γ-CD (0.08M) in water. However, we have now found that if pure C_{70} (>99.5%) is boiled in a concentrated γ-CD-water solution (0.8M) for several hours a C_{70}-complex is indeed formed *albeit* in low concentration (*ca.* 5×10^{-5} M) as shown by its UV-spectrum (Fig. 1). Under these conditions the selectivity of complex formation between C_{60} and C_{70} has decreased. If a mixture of C_{60} and C_{70} (15:85) is refluxed in a conc. solution of γ-CD in water (0.8M) both fullerenes form γ-CD-complexes (C_{60}: C_{70} ca. 1:1) and the residue is slightly enriched in C_{70} (C_{60}:C_{70} is 6:94) which proves a small preference of γ-CD for the C_{60} molecule under these experimental conditions.

The weak complex between C_{70} and γ-CD has also been characterized by its photophysical properties. The difference absorption spectrum (Fig.2), composed of T_1-T_n absorption and ground state bleaching, obtained on pulsed laser excitation is similar to that of C_{70} in nonpolar organic solvents but different from that of C_{70} in ethanol.[12]

The rate of oxygen quenching by the C_{70}-triplet is not affected by γ-CD complexation. However, the rate of triplet-triplet annihilation (Fig. 3) is reduced to approximately 20 % on complexation,[13] similar to that observed for the corresponding C_{60}-complex.[6] Thus, we conclude that the C_{60} and C_{70} γ-CD complexes have similar structures.

Computer modelling (BIOGRAPH, BioDesign Inc.) of the 1:1 and 2:1-complexes between γ-CD and C_{70} reveals that in the minimum energy conformations, the C_8-axis of the host (γ-CD) coincides with the long axis (C_5) of the guest (C_{70}). In the hypothetical 1:1-complex a large part of the C_{70}-molecule is exposed to water whereas in the 2:1 complex C_{70} fills the cavity inside the two γ-CD:s even better than C_{60} in its corresponding complex (Fig. 4). The rotation of the C_{70}-molecule around the long axis should be fast but hindered around the short axis.

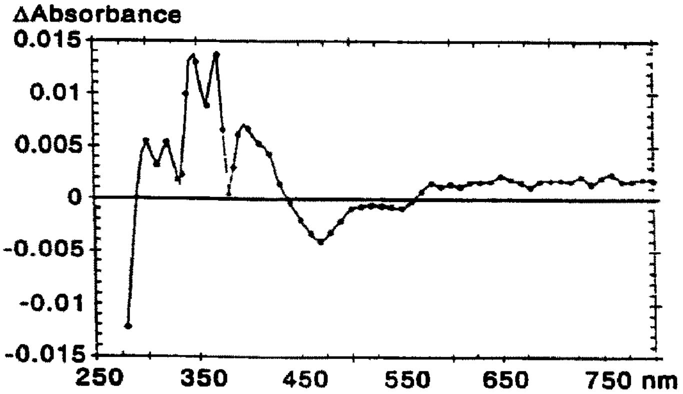

Fig. 2. Difference absorption spectrum obtained on laser excitation of a C_{70}-γ-CD complex dissolved in water. The spectrum was obtained by slicing traces at different wavelengths 1 μs after the laser pulse. The excitation wavelength was 532 nm (second harmonic from a Q-switched Nd:Yag laser, FWHM 7 ns).

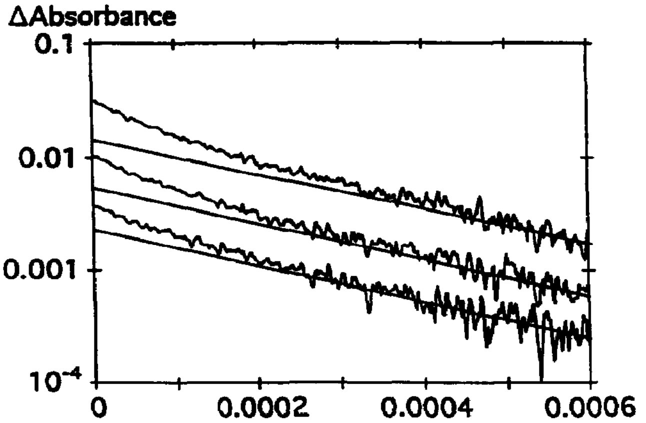

Fig. 3. Decay traces obtained at 400 nm, at different powers of the excitation laser pulse. The traces are shifted vertically for clarity. Absorbances at 0 s were 0.032, 0.0253, and 0.0185, respectively, from top to bottom. The straight lines, shown for comparison, correspond to a single exponential decay with a lifetime of 280 µs.

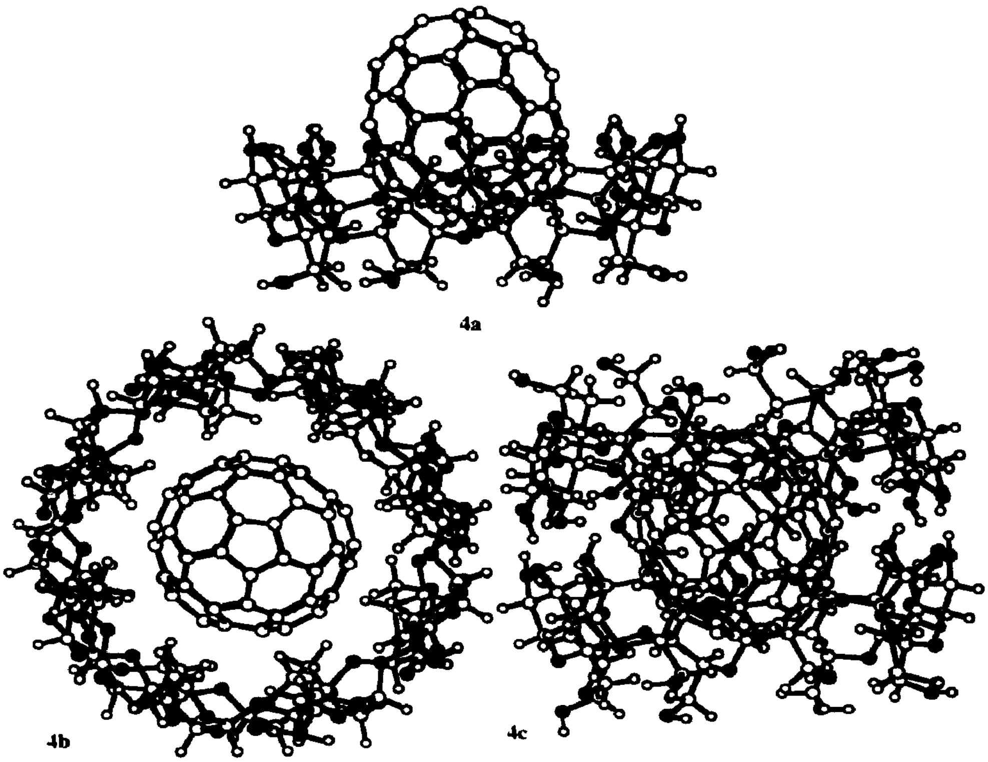

Fig. 4. Models (Biograph) of a) a 1:1 complex b) a 2:1 complex between γ-cyclodextrin and C_{70} seen along the C_8-symmetry axis of the cyclodextrin dimer c) seen perpendicular to the same axis.

The selectivity for γ-CD to form preferentially a complex with C_{60} under normal conditions can be understood as a kinetic selectivity determined by the relative rate of formation of the 1:1-complexes in the γ-CD-water solution. These 1:1 complexes then immediately react with another host molecule to form 2:1 complexes. The small selectivity in the very concentrated solutions (0.8M γ-CD in water) should reflect the thermodynamic selectivity. If so, this means that there exists a different route to the 2:1 complexes than *via* the 1:1-complexes.

In conclusion, γ-CD is capable of forming inclusion complexes with both C_{60} and C_{70} in water. There are relatively high barriers for the formation and decomposition of these complexes in water. The complexes are believed to contain a fullerene within two γ-CD's, hydrogen bonded to each other at the larger rim, containing sixteen secondary hydroxyl groups each, to form a spherical cavity with two small holes at the "poles" of the spherical host dimer (Fig.3).The openings are too small to allow the fullerene to escape easily. It remains to be tested if these water-soluble fullerene complexes also show biological activity similar to that of water-soluble fullerene derivatives.[14]

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