C_{60} Embedded in γ-Cyclodextrin: a Water-soluble Fullerene

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A water-soluble complex of C_{60} is formed on refluxing a solution of γ-cyclodextrin with solid C_{60}; the lifetime of the triplet excited state of C_{60} in the complex is 83 μs in an oxygen free solution.

The new carbon clusters[1] recently made available through Krätschmer's synthesis[2] are as intriguing as they are unexpected from a chemical point of view. It is now for the physicists and chemists to unravel the physical properties and chemistry of these new cluster molecules. The ease with which the carbon clusters are dissolved in hydrocarbon solvents such as toluene[2] is surprising and permits investigation with a large number of reactions and reagents. However, more methods and reactions and more applications would be possible if pure water could be used as a solvent for the clusters. The solubility in water for a carbon compound like C_{60} ought to be negligible, but water solubility could perhaps be achieved if the carbon clusters were embedded in a suitable water-soluble host molecule. The cyclodextrins (CDs) are interesting candidates for this purpose. It is known that spherical molecules such as carboranes form stable complexes with CDs.[3] The smaller CDs, α- and β-CD are too small to accommodate a large hydrophobic molecule like C_{60}. Even the diameter of the cavity in γ-CD is too small for C_{60}. However, the complex between an *o*-carborane and α-CD is suggested to contain two CD molecules.[3] There is also a paper on a bis-CD complex with a diphenylporphyrin.[4] Taken together these facts hint that γ-CD might be able to complex C_{60} as a 2:1 host–guest complex. Recently, C_{60} has been shown to form a clathrate with hydroquinone.[5]

To our delight we observed that a boiling aqueous solution of γ-CD, but not β-CD, was able to extract C_{60} from a mixture of C_{60} and C_{70}. The UV–VIS spectrum of the solution clearly showed the presence of carbon clusters in the water. We then purified C_{60} (>99%)[6] and treated it with an aqueous solution

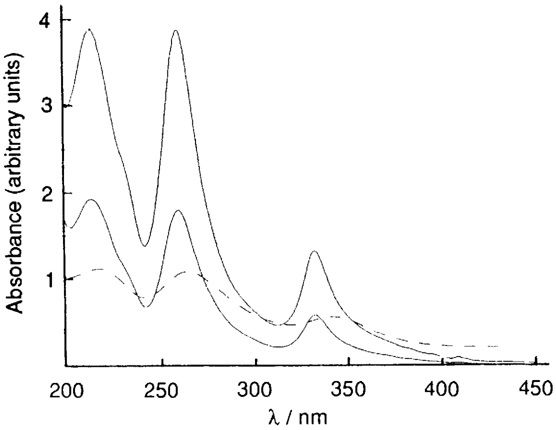

Fig. 1 UV-VIS spectrum of solution of C_{60} in γ-CD (0.02 mol dm^{-3}), —— after refluxing for 16 h and 48 h, – – – a solution of γ-CD-C_{60} precipitate dissolved in boiling water

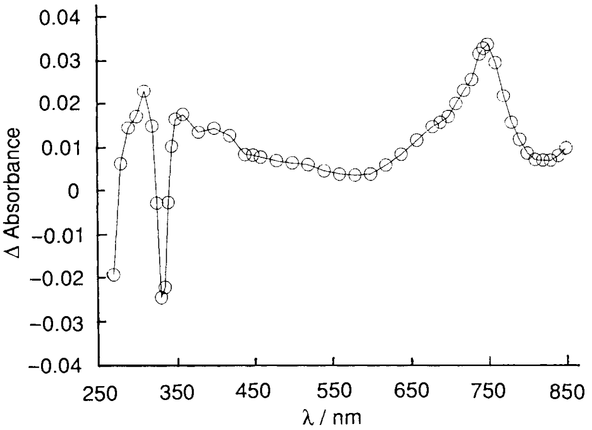

Fig. 2 Difference absorption spectrum obtained on laser excitation of a C_{60}–γ-CD complex dissolved in water. The spectrum was obtained by slicing traces at different wavelengths (indicated by ○), just after the laser pulse.

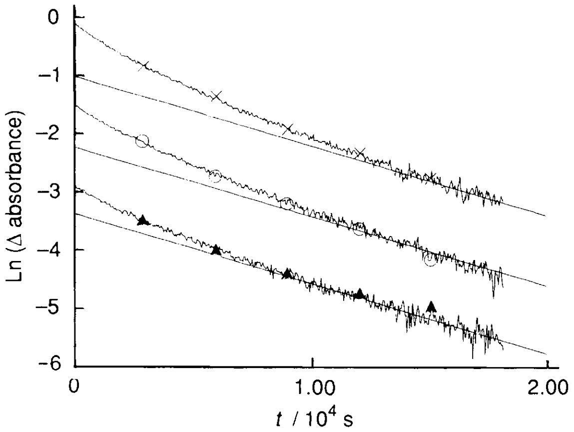

Fig. 3 Decay traces obtained at 750 nm, at different laser powers of the excitation pulse. The traces are shifted vertically for clarity, Δ absorbance values at 0 s were 0.40, 0.22 and 0.15 for ×, ○ and ▲, respectively. Straight lines corresponding to a first order lifetime of 83 μs are shown for comparison.

of γ-CD ($0.02\ \mathrm{mol\ dm^{-3}}$) under reflux and recorded the spectrum of the solution at intervals (Fig. 1). The rate of dissolution is quite slow and almost constant up to $10^{-5}\ \mathrm{mol\ dm^{-3}}$ C_{60} when a precipitate starts to form. The highest concentration of C_{60} in water which we have reached by this method is $8 \times 10^{-5}\ \mathrm{mol\ dm^{-3}}$. The UV–VIS spectrum of γ-CD–C_{60} in water, shown in Fig. 1, is slightly blue-shifted as compared to a toluene solution and slightly red-shifted as compared to a hexane solution.[7] On extraction of the aqueous solution with toluene C_{60} is completely transferred into the organic phase.

On attempted purification of the C_{60}–CD complex from excess γ-CD by gel filtration on Sephadex (G-25F) the complex was eluted before γ-CD but decomposed slowly.

By monitoring the rate of complex formation as a function of CD-concentration we found a non-linear relation consistent with the formation of a 2 : 1 complex. However, the appearance of light-scattering particles in water when low concentrations of γ-CD were used ($<0.005\ \mathrm{mol\ dm^{-3}}$) made the analysis more difficult. From these particles the γ-CD–C_{60} complex could be formed on addition of excess γ-CD and heating. When a high concentration of γ-CD was used to dissolve C_{60} a precipitate containing γ-CD and C_{60} formed. The precipitate was found to be insoluble in cold water but soluble in boiling water and gave a yellowish solution. The spectrum, shown in Fig. 1, is red-shifted compared to that of γ-CD–C_{60} and almost identical to that reported for a thin film of C_{60}.[2] This is an indication that clusters of C_{60} surrounded by γ-CDs can be formed under proper experimental conditions.

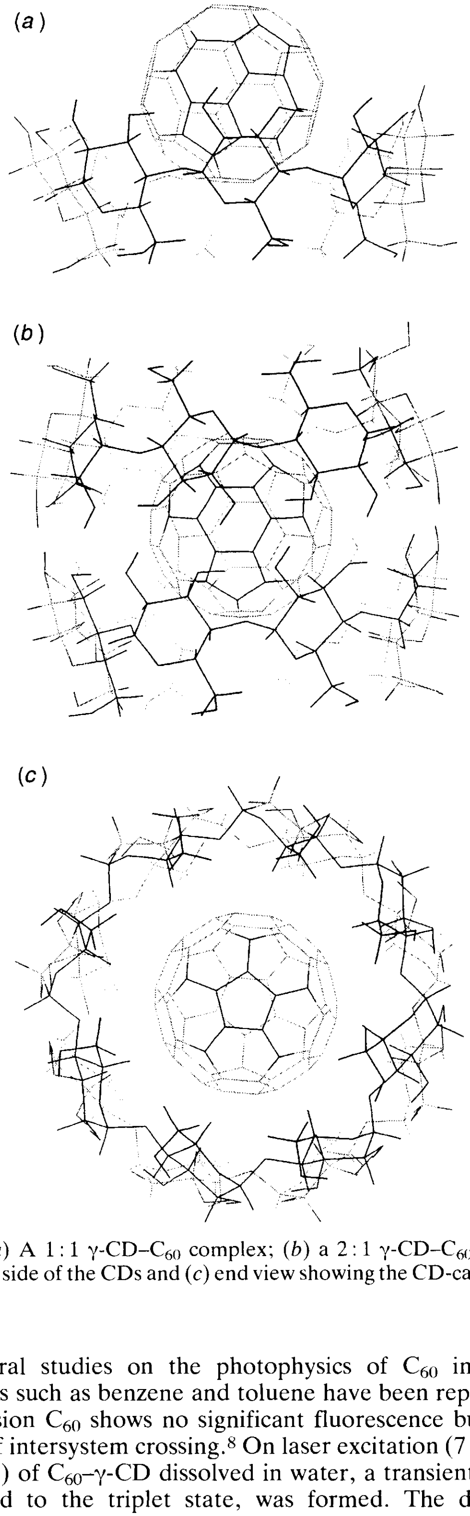

Fig. 4 (*a*) A 1 : 1 γ-CD–C_{60} complex; (*b*) a 2 : 1 γ-CD–C_{60} complex from the side of the CDs and (*c*) end view showing the CD-cavity filled with C_{60}

Several studies on the photophysics of C_{60} in organic solvents such as benzene and toluene have been reported. In conclusion C_{60} shows no significant fluorescence but a high yield of intersystem crossing.[8] On laser excitation (7 ns pulse, 355 nm) of C_{60}–γ-CD dissolved in water, a transient species, assigned to the triplet state, was formed. The difference absorption spectrum, belonging to this transient and to ground state bleaching, is shown in Fig. 2. The lifetime of the transient species was 83 μs in a nitrogen flushed solution (Fig. 3). The transient species was quenched with oxygen with a rate constant, $k = 6.4 \times 10^{8}\ \mathrm{dm^{3}\ mol^{-1}}$. The quenching rate is slower than expected for a 'free' C_{60} but only by a factor ~2.† This indicates that, for the excited triplet, ~50% of the

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† The factor was obtained by comparing the quenching rates in toluene and water, correcting for the different diffusion rates. The oxygen quenching rate constant was determined to $2.0 \times 10^{9}\ \mathrm{dm^{3}\ mol^{-1}\ s^{-1}}$ in toluene [*c.f.* ref. 8(*d*)] and the rate constants for diffusion are assumed to be (6.5 and 10) $\times 10^{9}\ \mathrm{dm^{3}\ mol^{-1}\ s^{-1}}$ for water and toluene, respectively.

C_{60} surface must be available for collision with oxygen. Furthermore, triplet–triplet annihilation is reduced by a factor ~4, when compared to a toluene solution.‡ In a γ-CD–C_{60} complex a large part of the C_{60} surface is covered, thus preventing collision of $^3C_{60}{}^*$ with oxygen and other $^3C_{60}{}^*$ molecules.

We have also performed simple molecular modelling to check the size of the CD-cavity in relation to that of C_{60} and C_{70} using the program BIOGRAPH (BioDesighn Inc.) Drelding II force field.[9] Docking of C_{60} and γ-CD gave the minimum energy for the structure shown in Fig. 4(*a*). Further docking with another γ-CD unit leads to the structure shown in Fig. 4(*b*) with considerable hydrogen bonding between the two CD units. The highest possible symmetry of such a 2:1, γ-CD–C_{60} complex is D_2. Removal of C_{60} leads to a small contraction of the dimeric γ-CD structure. A distortion of the position of C_{60} within the host–guest complex yielded the initial structure on energy minimization. As expected we found the preferred orientation of C_{70} within a γ-CD dimer to be the one with the long axis parallel to the symmetry axis of the CDs.

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‡ The factor was obtained by comparing the second-order decay rates in toluene and water, correcting for the different diffusion rates. The second-order rate constants determined assuming first plus second-order decay kinetics were (1.2 and 7.1) × 10^9 dm^3 mol^{-1} s^{-1}, for the water and toluene [*cf.* ref 8(*b*)] solutions, respectively. The molar absorbtivity for the triplet state, ε_T, at 750 nm was assumed to be 2 × 10^4 dm^3 mol^{-1} cm^{-1}.[8b]

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