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## Supramolecular Encapsulation of C<sub>60</sub> in a Water Soluble Calixarene; A Core-Shell Charge Transfer Complex.

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**Abstract.** A calix[8]arene derivative has been found to form a water soluble complex with fullerene-C<sub>60</sub>, but not with C<sub>70</sub>, which allows extraction of C<sub>60</sub> from e.g. toluene into the aqueous phase. Charge transfer character of the complex is evident from strong charge transfer absorption around 440 nm measured in water. Molecular modeling calculations indicate a core-shell structure for the complex.

### Introduction

Functionalising fullerenes<sup>1,2,3</sup> by using them as non-covalently bound building blocks in supramolecular constructs, leaving their extensive  $\pi$ -systems and remarkable redox properties essentially unimpaired, is a great challenge. Thus much effort is being directed to the construction of endohedral systems in which the nonpolar carbon-"shell" of the fullerenes encapsulates a smaller "core"-atom or perhaps even a molecule. We now report, however, a supramolecular system in which C<sub>60</sub> itself acts as a "core" embedded in the "shell" of a functionalised, water soluble calixarene leading to extensive electronic interaction of the charge transfer (CT) type between the  $\pi$ -systems of core and shell<sup>4</sup>.

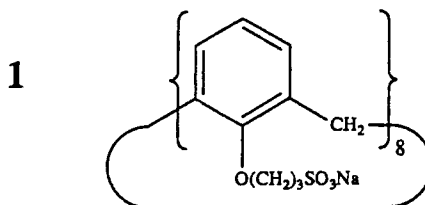
### Results and discussion

The electron deficient nature of the fullerenes C<sub>60</sub> and C<sub>70</sub> allows these to form CT-complexes with  $\pi$ -electron donors of the aniline type<sup>5-8</sup>. It has also been reported<sup>4c</sup> that whereas solutions of C<sub>60</sub> in solvents such as benzene and toluene are

purple, its solution in the neat 1,2-dimethoxybenzene (veratrole) are deep yellow. We now observed that solutions of C<sub>60</sub> in liquid,  $\pi$ -donating methoxy-substituted benzenes vary from light yellow via deep yellow to orange upon increasing substitution (mono-, 1,2-di- and 1,2,4 tri-MeO) and that the solubility of C<sub>60</sub> in such media appears to be enhanced. Comparison of the spectra of C<sub>60</sub> in toluene and in veratrole (see Fig. 1) revealed that in the latter a broad CT-absorption is readily detectable as a shoulder around 450 nm. (Note that the spectra in Figure 1 have been normalised on the strong 333-340 nm band,  $\epsilon = 51286 \text{ l.mol}^{-1}.\text{cm}^{-1}$  in toluene<sup>9,10</sup>). The apparent extinction coefficient of the CT-absorption at 450 nm amounts to  $\epsilon = 5000$ . This compares to  $\epsilon = 3700$  (600 nm) for the N,N-diethylaniline complex<sup>7</sup> and  $\epsilon = 10200$  (624 nm) for the N,N-dimethylaniline complex<sup>8</sup>, derived from Benesi-Hildebrand type analysis.

As the alkoxybenzene unit forms a basic building-block of many calixarene host-molecules, we decided to investigate the possibility to encapsulate C<sub>60</sub> in a water-soluble calixarene of suitable dimensions.

Molecular mechanics simulation via the Tripos Force Field<sup>11</sup> using Gasteiger-Hückel charges, indicated that from the available calixarenes especially calix[8]arene should be a suitable host for C<sub>60</sub>. Fig. 2 shows the predicted structure for such a complex involving the water soluble calix[8]aryloxy-49, 50, 51, 52, 53, 54, 55, 56 octakis-(propane-3-sulphonate) (1). Synthesis of 1 was achieved by reaction of calix[8]arene (Janssen Chimica) with 1,3-propanesultone, following literature procedures<sup>12</sup>.



In a typical solubilisation experiment 1 mg pure powdered C<sub>60</sub> was added to a colorless solution of 40 mg 1 in 10 ml of demineralized water and this mixture was refluxed. Dissolution was evident from yellowing of the mixture. Interestingly no solubilisation of C<sub>70</sub> occurs under these conditions. After 32

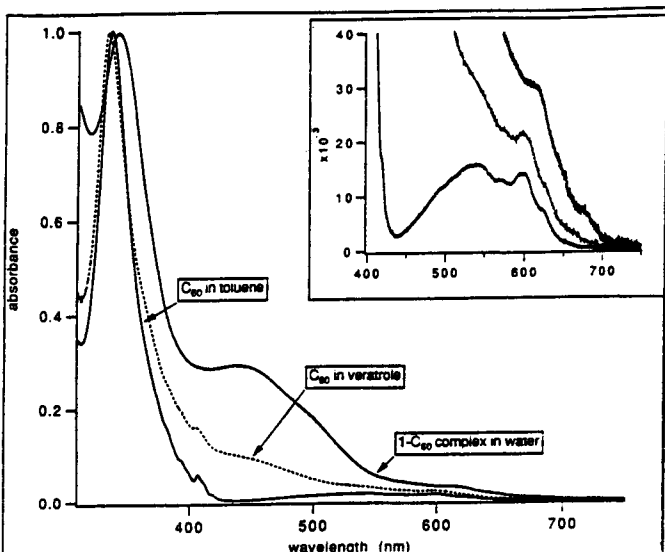


Fig. 1: Electronic absorption spectra of C<sub>60</sub> in neat toluene, in neat veratrole and solubilized in water by 1.

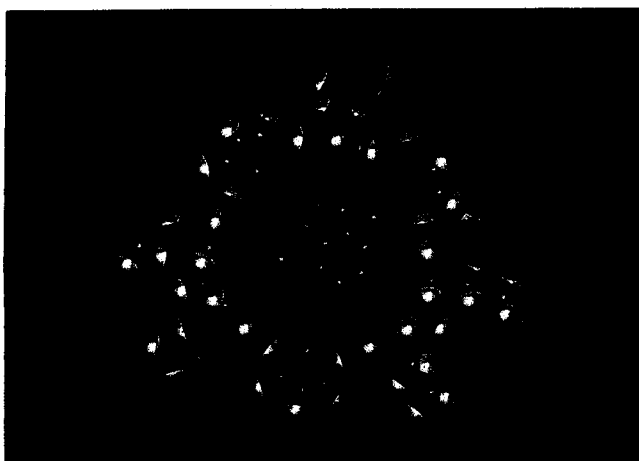


Fig.2: 'Top' and 'side' view of the 1- $C_{60}$  complex obtained by molecular modeling.

hours solid particles were removed by centrifugation and filtration resulting in a clear yellow solution.  $C_{60}$  cannot be extracted from this solution with either carbon disulfide or toluene. In fact, refluxing a solution of  $C_{60}$  in toluene with a solution of 1 in water allows one to extract  $C_{60}$  into the aqueous phase. At the other hand  $C_{60}$  can be extracted unchanged with toluene from the solid residue which remains after full evaporation of the aqueous solution. Together with the electronic absorption data (see, below) these experiments indicate that both hydrophobic interaction and CT-interaction play a role in the complex formation.

The absorption spectrum of the yellow aqueous solution of the complex between 1 and  $C_{60}$  displays absorption maxima at 340, 440, 620 and 680 (sh) nm (see Fig. 1). From comparison with the spectra of  $C_{60}$  in toluene and in veratrole the broad 440 nm band is attributed to a CT transition in which electron transfer from the calixarene shell to the fullerene core takes place. The extinction coefficient at 440 nm is ca. 15000 which indicates enhanced electronic interaction as compared to the intermolecular complexes of  $C_{60}$  with simple aromatic electron donors (see above)<sup>13</sup>. A stronger electronic interaction is also indicated by the shift (336  $\rightarrow$  340 nm) and broadening of the strong local  $C_{60}$  absorption and an apparent intensification of its weak long wavelength absorption in the 600-700 nm region (see inset of Fig. 1). The latter effect may tentatively be attributed<sup>8</sup> to a lowering of the local symmetry by complexation that reduces the forbidden character of these weak transitions compared to "isolated"  $C_{60}$ .

The molecular mechanics calculations (see Fig. 2) support the occurrence of strong  $\pi$ - $\pi$  overlap. Interestingly the complexed calixarene is predicted not to have a full cone conformation. Starting optimization of the complex with 1 in a cone conformation results in a structure for the complex with three aryl rings bending out of the cone (a sort of half cone/alternate cone conformation). While this sacrifices interaction with three aryl-rings of the calixarene it allows for optimal  $\pi$ - $\pi$  interaction of the other five rings with the fullerene.

It will clearly be of great interest to secure further the configuration of the present complex as well as to further explore the selectivity of 1 and related calixarenes in encapsulating various fullerenes. The water solubility and the Acceptor-core/ Donor-shell structure of such complexes open new possibilities to employ the strong photo-oxidative properties of the fullerene core in electron abstraction from reductants in aqueous media eventually mediated by the shell upon excitation in the CT absorption band. In this context the

present complex provides an interesting vehicle for transport of the hydrophobic fullerene unit via the aqueous phase which may allow its incorporation in bio-redox systems. These possibilities are presently under active investigation.

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