Cyclotriveratrylene polarisation assisted aggregation of C_{60}

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Excess cyclotriveratrylene (CTV) and C_{60} in toluene results in micelle-like aggregation of the fullerenes arising from CTV polarisation of the fullerene, leading to a one-dimensional zigzag polymeric array of fullerenes in the solid state, each in the cavity of a CTV molecule.

Supramolecular complexes of fullerenes have been prepared for C_{60} and C_{70} for a variety of host systems including calixarenes,[1–6] cyclotriveratrylene (CTV),[7] and γ-cyclodextrin.[8] Any complexation of C_{60} is predetermined in part by the dimensions and shape of the cavity and solvation effects, inherently thwarted by the spherical and non-polarised nature of the fullerene. Here we show that complexation by a saturated toluene solution of 'bowl shaped' CTV **1** (R = Me), Fig. 1, results in aggregation of the fullerenes leading to a polymeric zigzag array of fullerenes in the solid state, each in the cavity of a CTV molecule, with an overall composition $CTV·C_{60}$. The aggregation is a secondary process assisted by polarisation of the fullerene by the host molecule. These findings have implications for the complexation of C_{60} in general, notably that polarisation of the fullerene by complexation leads to fullerene aggregation, possibly in a micelle-like structure. We have also established this type of structure for [(p-Bu^t-calix[8]-arene)$_3$(C$_{60}$)$_3$] where each double cone calixarene spans two fullerenes which are in a triangular array at the limit of van der Waals contacts.[6]

Earlier studies on CTV showed that toluene solutions of CTV and C_{60} can afford the 'fullerene rich' complex $(CTV·1.5C_{60})$.[7] This has been structurally authenticated showing a similar 'ball and socket' nanostructure for the individual C_{60}–CTV units, but with the other fullerene component being part of an overall structure dominated by fullerene–fullerene interactions, the fullerenes collectively comprising a two-dimensional closed pack array.[6]
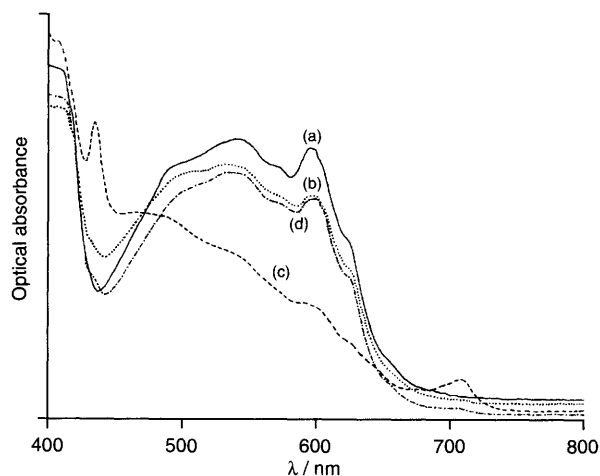
There is an immediate slight colour change from magenta to red–purple on mixing C_{60} and CTV solutions (10-fold excess) associated with a pronounced change in the visible spectrum near *ca.* 430 nm, Fig. 2. This is ascribed to the formation of
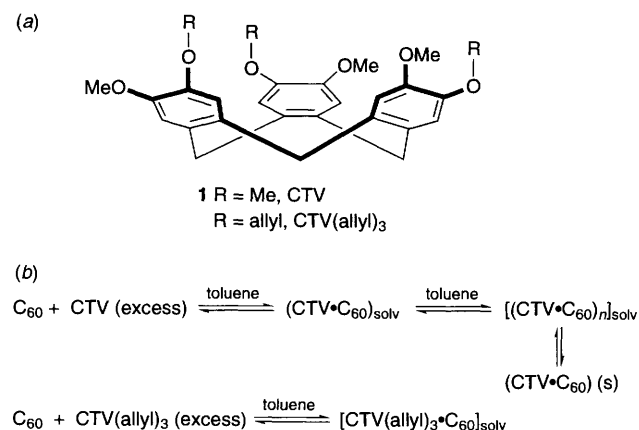
host–guest species in solution, $(CTV·C_{60})_{solv}$, Fig. 1(b). The resulting brown colour formed over several hours is associated with crystallisation of the 1:1 complex† and arises from aggregation of C_{60}, possibly as $[(CTV·C_{60})_n]_{solv}$, noting that C_{60} in toluene alone exists as a solvated monomer.[9] The allyl substituted analogue $CTV(allyl)_3$ [**1**, R = allyl, Fig. 1(a)] with C_{60} only shows solvated host–guest species, evident by a similar slight change in colour and visible spectrum, Fig. 2, but here there was no further colour change or precipitation of a host–guest complex even using an excess of $CTV(allyl)_3$. In fact the spectra are very similar with a shoulder at *ca.* 430 nm, and also a peak at *ca.* 708 nm, although this is more distinct in the $CTV(allyl)_3$ case. Presumably for $CTV(allyl)_3$ the extended allyl groups on the CTV and the deeper cavity disfavour aggregation of the host–guest complexes of the type for CTV; any fullerene–fullerene interaction is seemingly at the expense of host–guest interactions with pure C_{60} crystallising from toluene as the unsolvated cubic close packed modification.[10]

Relative to toluene-solvated C_{60}, the visible spectra of the brown solutions have new bands at 430, 475 and 708 nm, Fig. 2. The broad 475 nm band is assigned to a resonant inter-fullerene transition associated with the aggregates of C_{60}; similar bands have been observed for 3(p-Bu^t-calix-[8]arene)·3C$_{60}$,[6] (470 nm), films of pure C_{60} (450 nm)[11] and for C_{60} aggregates solubilised in aqueous solutions (450 nm).[5,9] The sharper bands at 430 and 708 nm most likely arise from symmetry-allowed transitions for highly polarised C_{60} in the aggregates. For the $CTV(allyl)_3$ two absorptions at the same wavelength are evident, albeit less resolved, as is the case for fresh solutions of excess CTV and C_{60}. This is consistent with an overall assignment of the two bands in all three spectra as symmetry-allowed transitions for polarised C_{60} in solvated 1:1 species for both CTV (intermediate) and $CTV(allyl)_3$, or as solvated aggregates of 1:1 species where the bands are more resolved. The assignment of these bands as arising from charge-transfer transitions between the host system and the electron-

(a)

1 R = Me, CTV
R = allyl, CTV(allyl)$_3$

(b)

$$C_{60} + CTV \text{ (excess)} \xrightarrow{\text{toluene}} (CTV·C_{60})_{solv} \xrightarrow{\text{toluene}} [(CTV·C_{60})_n]_{solv}$$

$$(CTV·C_{60}) \text{ (s)}$$

$$C_{60} + CTV(allyl)_3 \text{ (excess)} \xrightarrow{\text{toluene}} [CTV(allyl)_3·C_{60}]_{solv}$$

Fig. 1 (a) Complexing agents. (b) Equilibria involved in the formation of $CTV–C_{60}$ and $CTV(allyl)_3–C_{60}$ complexes.

Fig. 2 UV–VIS absorption spectra of toluene solutions of (a) C_{60}, (b) C_{60} with a excess of CTV (saturated), (c) (b) after *ca.* 24 h, and (d) C_{60} with excess $CTV(allyl)_3$

deficient fullerene has been ruled out in accordance with the recent findings that charge-transfer interactions are not responsible for colour variations for C_{60} in aromatic solvents.[12]

Saturated solutions of CTV are required to form the brown solutions and the resulting black precipitate of CTV·C_{60}. The findings are consistent with equilibria in solution involving complexation and aggregation, Fig. 1(*b*). For lower concentrations of CTV, ≤ *ca.* 5 equiv. for typically 5 mg of C_{60} in 5 ml of toluene, the fullerene rich compound CTV·1.5C_{60} crystallises from solution. Here there is no significant change in the UV–VIS spectrum compared to that of toluene solutions of C_{60} and therefore there is no clear evidence for micelle formation. However, the presence of aggregated species arising from polarisation of C_{60} in solvated CTV·C_{60} is implied, at least involving aggregation of CTV·C_{60} with solvated C_{60} since C_{60} is incorporated with the guest–host species in the solid.

The new 1:1 complex slowly decomposes in toluene at ambient temperature yielding magenta solutions [*cf.* decomposition of 3(*p*-Bu^t-calix[8]arene)·3C_{60} only above *ca.* 80 °C in toluene[1]] and on cooling and concentration *in vacuo* the fullerene rich complex is obtained, CTV·1.5C_{60}, along with uncomplexed C_{60}. Dichloromethane and chloroform degrade the complex to its constituents, as for the fullerene rich compound.[7]

Given that the complex crystallising from C_{60} containing toluene solutions saturated with CTV is the 1:1 complex, then the aggregates in solution must be small, most likely based on close packing of fullerenes yet without any of the fullerenes surrounded only by other fullerenes. However, molecular mechanics shows that for trigonal-planar, tetrahedral, and trigonal bipyramidal arrays of fullerenes, *exo*-cavity binding of CTV in the dimples of the triangular faces of the aggregates, as well as *endo*-cavity binding at the vertices, is possible and thus the aggregates in solution may have a ratio of CTV:C_{60} higher than 1:1. The binding of CTV in a dimple would be preferred with each of the aromatic rings residing over a fullerene. Interestingly this type of binding for CTV is consistent with the lack of formation of aggregates of C_{60} in the presence of CTV(allyl)$_3$ which is more sterically demanding than CTV.

In the solid state‡ the 1:1 complex has a polymeric structure, Fig. 3, with each of the van der Waals 'ball and socket' moieties
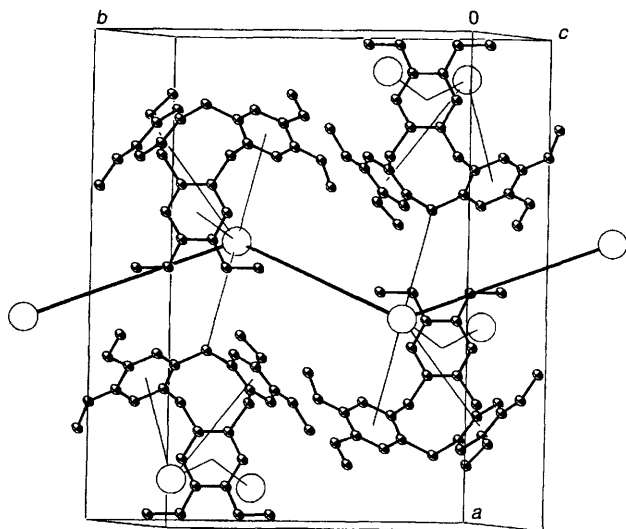
residing on a mirror plane, albeit with disorder associated with the C_{60} moieties; the closest C_{60}(centroid)···C,O$_{CTV}$ contacts are 6.52 Å, with the centroid of the CTV aromatic ring to the C_{60} centroid distances at 6.77 Å. Each fullerene has a very short contact to two other symmetry-related fullerenes, centroid–centroid distances being 9.87 Å, subtending an angle of 120.2°. These short contacts compare with the contacts in cubic close packed C_{60},[11] and in the fullerene rich complex CTV·1.5C_{60}. Such fullerene–fullerene interactions are likely to be prevalent in related fullerene rich complexes calix[6]arene·2C_{60}[1] and Bu^t-calix[6]arene·2C_{60}.[6] Other significant aspects of the structure are (*i*) an *exo*-CTV cavity–fullerene interaction (see above), the aromatic ring centroid-C_{60}–centroid distance at 6.62 Å, being similar to the above mentioned *endo*-CTV–C_{60} distances, and (*ii*) fullerene···H contacts associated with a methylene linkage of CTV ($C_{methylene}$–C_{60} centroid distance 6.78 Å).

Footnotes

† *Experimental*: Synthesis of CTV·C_{60}. In a typical experiment a solution of C_{60} (5.0 mg) in toluene (2.5 ml) was added to a solution of CTV (35.0 mg) in toluene (2.5 ml). After *ca.* 2 d the fine brown–black precipitate was collected and washed with acetonitrile (to remove any uncomplexed CTV which had precipitated) and hexane (6.0 mg, 74% yield. Anal. Found: C, 89.14 H, 2.55. Calc. C, 89.22; H, 2.58%).

‡ CTV·C_{60}: $C_{87}H_{30}O_3$, orthorhombic, space group *Pnma* (no. 62), *a* = 21.630(3), *b* = 17.122(4), *c* = 13.200(2) Å, *U* = 4888(2) Å^3, *Z* = 4, D_c = 1.526 g cm^{-3}, μ(Mo-Kα) = 0.91 cm^{-1} (no correction), Rigaku AFC7r diffractometer, Mo-Kα radiation, *T* = 183 K, 3606 unique reflections [1103 observed, *I* > 3.0σ(*I*)], refinement on *F*, 293 parameters, *R* = 0.123, R_w = 0.126 (σ weights). Solution by direct methods. The CTV and a disordered C_{60} lie across a mirror plane, *x*, 0.25, *y*; the six-membered ring of the C_{60} coplanar with the mirror and the adjoining six carbons atoms are not disordered, the remaining carbon atoms of the C_{60} molecule being disordered with populations sets at 0.5. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/91.

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Fig. 3 Three-dimensional solid-state structure of (CTV·C_{60})$_\infty$; for simplicity a small arbitrary radius of C_{60} with lines representing nearest contacts are shown