C_{60}/Calixarene Complex

Controlling van der Waals Contacts in Complexes of Fullerene C_{60}**

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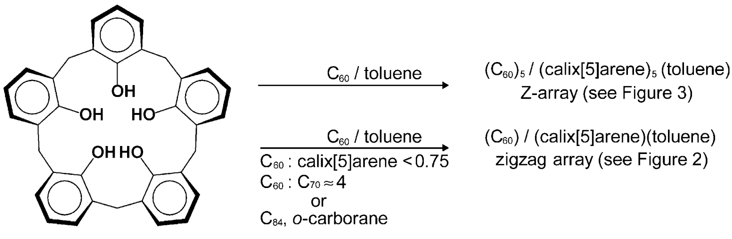
The most common method of generating fullerenes, using an electric arc between two graphite rods, yields C_{60} and C_{70} in a ratio of roughly 19:5. Consequently, the ubiquitous coexistence of C_{70} with C_{60} has been somewhat of a hindrance in the purification of the latter. Viable methods for the purification of fullerenes include supramolecular complexation with calix[*n*]arenes.[1] For example, we have shown that *p-tert*-butylcalix[8]arene binds C_{60} selectively, thus allowing C_{60} to be separated from fullerite with $>99.5\,\%$ purity.[2] Conceivably, the complex is a micellelike arrangement of three fullerenes surrounded by three double-cone calixarenes.[3] Calix[6]arene also forms a complex with either C_{60} or C_{70}, in which the fullerene is situated in each of the shallow cavities of the double-cone-shaped calixarene. This arrangement yields a 1:2 host–guest complex in which the fullerenes form an extended three-dimensional crisscrossed array of linear strands.[4]

Owing to the C_{5v} cone conformation of calix[5]arene (Scheme 1), its size and curvature are complementary to C_{60} and its principle axis extremities suit C_{70}.[5] Accordingly it has been a popular choice for host–guest studies with these fullerenes. Generally, 1:1 and 2:1 complexes result in which each fullerene is situated in the cavity of a calixarene. Various modified forms of calix[5]arene have also been used to probe the host–guest interaction, including substituted calix[5]arenes,[6,7] biscalix[5]arenes,[8–10] and calix[5]arenes self-assembled by means of noncovalent metal–ligand interactions.[11] Only recently has the solid-state structure of a C_{60} complex of the unmodified, shallow-cavity calix[5]arene been elucidated.[12] Here the fullerenes assemble in a Z-array, comprising five close-packed columns enshrouded by a sheath of calix[5]arene molecules. Some of the fullerenes are capped by two *trans*-calixarenes, while others are associated with the cavity of only one calixarene, or are not associated with any cavities at all.



Scheme 1. Crystallization of calix[5]arene with C_{60}, C_{70}, and other globular molecules.

In further exploring the chemistry of fullerenes and calix[5]arene, we have now encountered yet another complex with the same units but with the calixarene and fullerene in a simple 1:1 ratio (cf. 4:5 for the Z-array).[12] Initially this new complex formed in the presence of C_{70}, which is remarkable in that, far from being a hindrance, C_{70} actually facilitates the formation of a different complex of calix[5]arene and C_{60}. If the C_{60}:C_{70} molar ratio is varied while the total amount of calix[5]arene is kept constant (i.e. about 1.3:1 calixarene/fullerene) a progression of solid-state structures, from the Z-array to the new C_{60}/calix[5]arene structural motif **1**, and then to a C_{70}/calix[5]arene complex, is obtained.

Calix[5]arene and exclusively C_{70} form a complex isolated as clusters of slender dark-red needles (Figure 1 a), which have thus far been unsuitable for single-crystal X-ray analysis. These clusters form in the presence of C_{60} up to a C_{60}:C_{70} molar ratio of ca. 2.3:1 (with 1.4 mol equiv calix[5]arene) (Table 1). When the C_{60}:C_{70} molar ratio is close to ca. 4.5:1 (1.4 mol equiv calix[5]arene), the new complex **1** forms along with the C_{70}/calixarene complex (Figure 1 b and c). Complex **1** forms up to a 10:1 molar ratio of C_{60}:C_{70}, while at higher ratios the Z-array results (Figure 1 d).[12] The ability of C_{70} to influence the composition of a system in a crystal by mediating the crystallization process is unprecedented. In the absence of C_{70} and with excess calix[5]arene (1.3 mol-equiv) the C_{60}/calix[5]arene Z-array results (Figure 1 d).

X-ray diffraction analysis[13] of **1** reveals a simple 1:1:1 complex of C_{60}, calix[5]arene, and toluene (Figure 2). The C_{60} molecules form a slightly helical, zigzag, one-dimensional oligomeric array. It is not surprising that the *exo* cavity surface of two adjacent calix[5]arenes abut close to each C_{60}, considering the electron-deficient nature of the fullerene and the electron-rich oxygen atoms and arene rings of the calix[5]arenes.

To further investigate the role of C_{70} in the formation of **1** we seeded toluene solutions of fullerite (containing ca. 5:1 C_{60}:C_{70}) and calix[5]arene (close to the same molar ratios as above) with crystals of either the Z-array or the zigzag array. In all cases the only complex formed was the new C_{60}/calix[5]arene complex **1**. Moreover, addition of crystals of **1** to a 1:1 solution of C_{60} and calix[5]arene in toluene also results in the formation of **1**. Thus here the crystal is seeding the crystallization of **1** at the expense of the Z-array, as opposed to the C_{70} mediation in the previous experiments. Complex **1** can therefore be regarded as the thermodynamically favored product, at least when the ratio of C_{60} to calix[5]arene is 1:1. The Z-array seed crystals had no effect on the crystallization outcome for solutions of fullerite or C_{60} with calix[5]arene.

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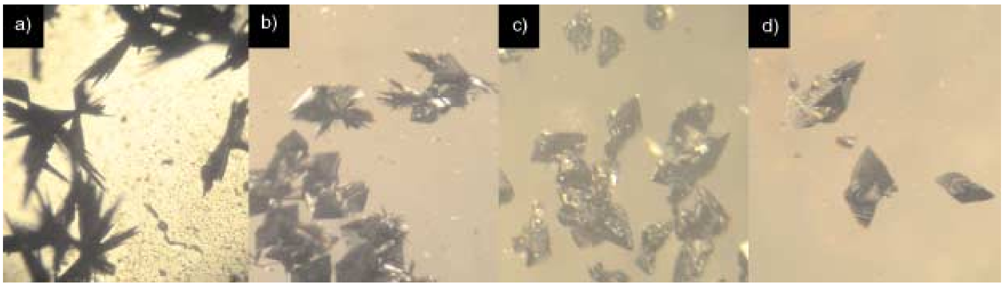

Figure 1. Photographs of crystals of a) C_{70}/calix[5]arene, b) **1** and C_{70}/calix[5]arene (2:1 C_{60}:C_{70} and calix[5]arene), c) **1** resulting from 4:1 C_{60}:C_{70} and calix[5]arene, and d) Z-array C_{60}/calix[5]arene (tenfold magnification)

Table 1: Crystallizations of calix[5]arene/C_{60}/C_{70} complexes from toluene (ca. 1 mg fullerene mL^{-1} toluene) and resulting complexes; yields ca. >75%.

C_{60}:C_{70}	C_{60}:Calix[5]arene	Crystal type
0–1.2:1	0–3.7:1	C_{70} complex[a]
2.3:1	0.49:1	zigzag array[b]/C_{70} complex
3.5–10.5:1	0.51–0.65:1	zigzag array
	0.07–0.7:1	zigzag array
	0.75–1.0:1	Z-array[c]

[a] C_{70}/calix[5]arene by comparison with X-ray powder diffraction data of C_{70}/calix[5]arene. [b] This paper. [c] Ref. [11].

Adding other globular molecules such as *o*-carborane (1,2-$C_2B_{10}H_{12}$) or C_{84} in place of C_{70} to toluene solutions of C_{60} and calix[5]arene also results in the formation of **1**, even though the carborane itself is known to form complexes with the calixarene.[14] Thus these additives also mediate the crystallization of the new complex, although their role in the crystallization process is as yet unclear. However, in solutions of C_{60} and bowl-shaped molecules in a 1:1 ratio, aggregation of the fullerenes is proposed to occur by polarization effects,[15–17] and aggregation could then lead to the fullerene-rich Z-array. The other globular molecules could

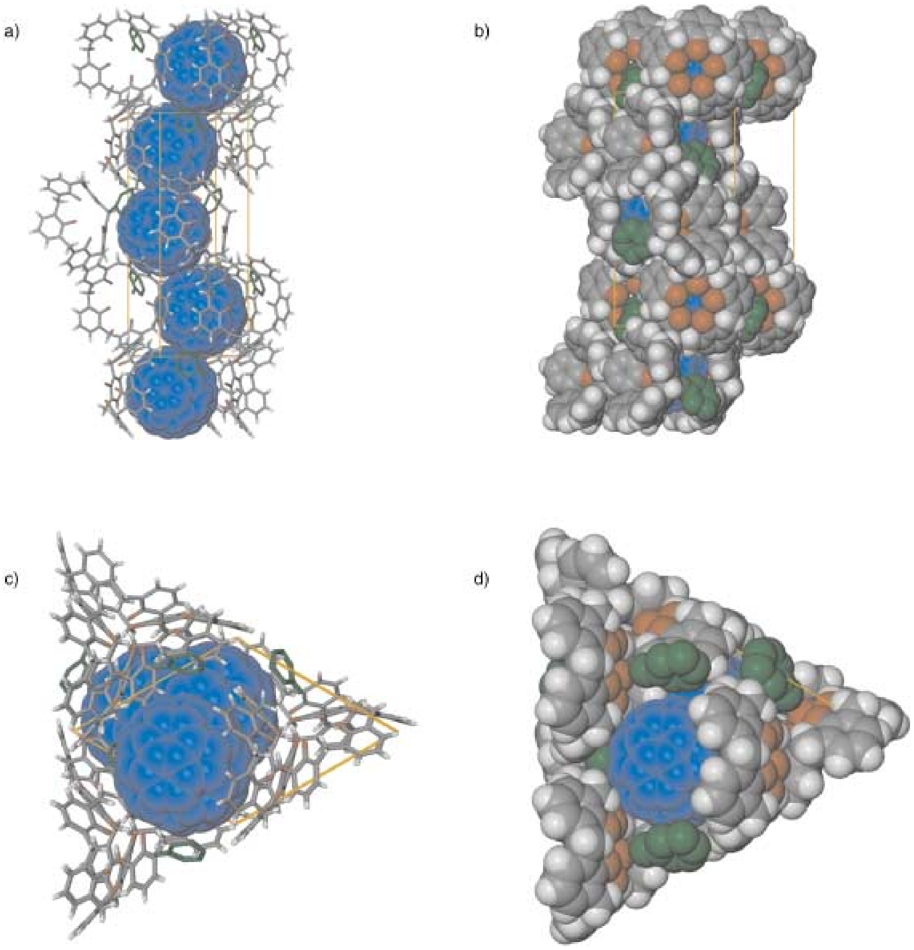

Figure 2. X-ray crystal structure of [(C_{60})(calix[5]arene)]·toluene (**1**) projected at right angles to the zigzag array of fullerenes (a and b), and almost along the array (c and d). Blue = C_{60}, dark and light gray = carbon and hydrogen atoms of the calixarene, red = oxygen atoms, dark green = toluene.

effectively disrupt the aggregation of C_{60} molecules. Moreover, the presence of an excess of calix[5]arene results in the new zigzag array, which can be rationalized by the dominance of the 1:1 supermolecule in solution, which possibly also minimizes aggregation of the fullerenes.

To confirm that either the Z-shaped or zigzag array **1** were representative of bulk samples, X-ray powder diffraction studies were undertaken. Distinct diffraction patterns were obtained, as was also the case for the C_{70}/calix[5]arene complex; we found no evidence for the presence of mixtures of two or three of the complexes. UV/Vis studies on toluene or chloroform solutions prepared from single crystals of the C_{60} Z-shaped and zigzag arrays, and the ill-defined C_{70} complex were undertaken. Spectra were recorded after a single crystal had been dissolved slowly over a period of one week in either solvent. Complex **1**, crystallized in the presence of C_{70}, showed only traces of the higher fullerene according to HPLC analysis. Both the electronic spectrum and single-crystal data show that the higher fullerene is not an integral part of the solid-state structure.[18,19]

The use of C_{70} as a mediator in crystallizing a new structural motif of C_{60} with calix[5]arene is interesting, since calix[5]arene is one of the few known hosts to complex C_{60} in solution.[1] We believe that the influence of globular additives on the resulting structure can be rationalized by considering how spherical molecules generally prefer to pack. In the fullerene-rich Z-array structure, the C_{60} molecules aggregate into several linear strands that make van der Waals contact with one another. Adjacent strands are staggered with respect to one another such that each C_{60} molecule is in close contact with four to six of its like neighbors. Careful consideration of the individual C_{60} molecules shows that each is in a two-dimensional, pseudohexagonal-close-packed environment. Indeed, each of the molecules of the central strand is surrounded by six nearest neighbors, and this is the preferred arrangement for close-packed spheres. The C_{70}, carborane, or C_{84} molecules are similar in size and shape to C_{60}. However, we postulate that these molecules are sufficiently different that they disrupt the formation of the pseudohexagonal-close-packed arrangement. This allows the C_{60} molecules to adopt the alternative low-energy structure **1**, in which hexagonal packing does not play a role. It is likely that during crystal growth C_{60} molecules in this less constrained structure can be replaced by the globular additives. However, the growth of crystals from solution is a dynamic and reversible process in which the molecules can be deposited as well as removed from the growth boundary of the material. In most cases, this mechanism allows the crystal to "repair" itself by rejecting molecules that might fit but that do not conform to the minimum-energy packing mode.

It is appropriate to summarize the types of structurally authenticated arrays of C_{60} involving large calixarenes and related molecules, and molecules with curved surfaces (Figure 3). Aggregates have been identified and characterized.[3] There are the one-dimensional arrays (linear,[20] zigzag,[15,16] linear double strands,[1] and a linear Z-array of five strands[12]), two-dimensional arrays (hexagonal-close-packed[16] and corrugated sheets[1]), and three-dimensional arrays.[4] Controlling the assembly of fullerenes into zigzag or Z-arrays, depending on the presence of a third component which itself does not form part of the assembly, is an important development in the materials science of fullerenes and promises to expand the structural types possible for C_{60} as well as for C_{70} and higher fullerenes. These results are particular timely with regard to constructing fullerene arrays (at the van der Waals limit or covalently linked) for polymerization.

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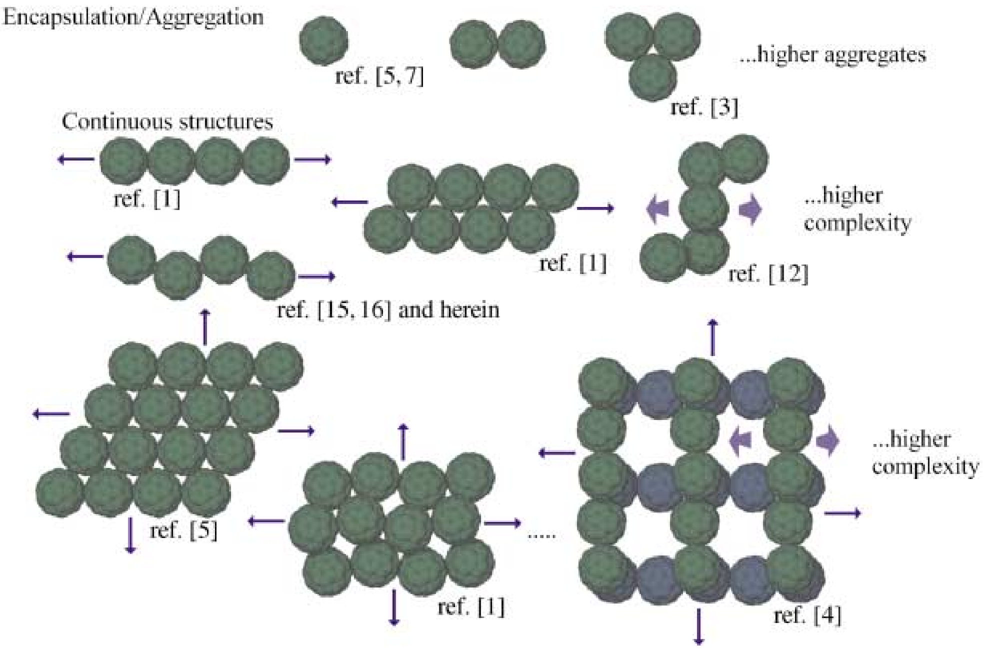

Figure 3. Encapsulation/aggregation and ordering of C_{60} molecules into 1D, 2D, and 3D arrays (host molecules not shown).

Keywords: aggregation · calixarenes · crystal growth · fullerenes · host–guest systems

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[13] Crystal data for [(C_{60})(calix[5]arene)]·toluene (**1**): $C_{102}H_{38}O_5$, $M_r = 1343.32$, dark red prism, $0.20 \times 0.20 \times 0.15$ mm^3, trigonal, space group $P3_2$ (No. 145), $a = b = 13.7630(1)$, $c = 26.9435(3)$ Å, $V = 4419.88(7)$ Å^3, $Z = 3$, $\rho_{\text{calcd}} = 1.514$ g cm^{-3}, $F_{000} = 2070$, Nonius KappaCCD area-detector (ω scan mode, $\text{Mo}_{K\alpha}$ radiation, $\lambda = 0.71073$ Å), $T = 173(2)$ K, $2\theta_{max} = 55.7°$, 21952 reflections collected, 10980 unique ($R_{\text{int}} = 0.0304$). The structure was solved and refined using the SHELX-97 software package and the X-Seed[21] interface. Direct methods yielded all non-hydrogen atoms of the calixarene and toluene molecules of the asymmetric unit. While none of the C_{60} atoms could be located unequivocally, the position of the rotationally disordered fullerene was indicated by a spheroid of difference electron density. Two idealized C_{60} molecules were placed on this position in two different orientations, and each molecule was assigned a site occupancy factor of 50%. This procedure allowed adequate refinement of a rotationally disordered model for C_{60} of known location. The calixarene atoms were refined anisotropically (full-matrix least squares method on F^2). Hydrogen atoms were placed in calculated positions with their isotropic thermal parameters riding on those of their parent atoms. Final GOF = 3.393, $R1 = 0.2557$, $wR2 = 0.6101$, R indices based on 9974 reflections with $I > 2\sigma(I)$ (refinement on F^2), 375 parameters, 626 restraints. Lorentz, polarization, and absorption corrections applied, $\mu = 0.092$ mm^{-1}. All X-ray structure figures were prepared with X-Seed.[21] CCDC-202602 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).
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