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This review documents the exceptional range of research avenues in supramolecular fullerene chemistry that have been pursued during the past decade. It illustrates how molecular complexation of pristine fullerenes developed from solid state enclathration by π -electron-rich compounds to inclusion complexation by designed macrocyclic receptors in the liquid phase. Progress in covalent fullerene functionalisation led to the development of spectacular supramolecular architectures including rotaxanes, catenanes, DNA complexes, diads and triads for photoinduced electron and energy transfer and ordered thin films. All of these molecular assemblies and supramolecular arrays feature distinct properties as a consequence of the presence of the fullerene components. Recent investigations hinting at potential technological applications of supramolecular fullerene, such as in sensorics, are highlighted.

1 Introduction

Contemporary chemistry is characterised by both the vigorous search for new efficient methods for covalent bond formation and the development of the 'chemistry beyond the molecule',¹ the formation of supramolecular complexes, assemblies and arrays held together by weak intermolecular interactions. It is

therefore not surprising that, with the availability of macroscopic quantities of buckminsterfullerene, C_{60} ,² in the nineties,³ scientists rapidly became interested in exploring both the molecular and supramolecular chemistry of the new carbon allotrope. While the covalent functionalisation of the carbon sphere has seen a rapid, dramatic development and several review articles, books and monographs have been published on this subject,⁴ supramolecular fullerene chemistry has not yet been explored to the same extent. Whereas early efforts were mainly directed at the molecular complexation of the pure carbon sphere in the solid state and in solution, the construction of novel supramolecular architectures bearing properly functionalised carbon spheres as structural motifs developed later, since it required that the covalent chemistry of C_{60} , and in particular its regio- and stereoselective multiple functionalisation, had first been vanquished.⁵ This article provides an overview on the various aspects of supramolecular fullerene chemistry that are currently attracting increasing interest.

One of the main challenges that scientists in general and supramolecular chemists in particular are faced with is the production of novel chemical systems supporting real-life device properties. The unique physical and chemical properties of C_{60} —such as electronic absorption bands expanding throughout the entire UV/Vis spectrum, efficient singlet oxygen sensitising ability, strong electron acceptor character, and superconductivity upon doping with alkali metals—make it an attractive component to be incorporated in functional molecular

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François Diederich, studying different aspects of fullerene chemistry, such as the incorporation of C_{60} into molecular assemblies and supramolecular arrays, the electrochemical properties of covalent fullerene adducts—in collaboration with Professor Luis Echegoyen—and the covalent modification of 6–5-open methanofullerenes. Since March 1999, he has been a research scientist at BASF Ludwigshafen.

assemblies and supramolecular arrays. This article illustrates how these properties are being exploited with several potential applications, even at this early stage, already being latent.⁶

2 Solid state complexes with π -electron rich compounds

To our knowledge, the first example of C_{60} involved in supramolecular phenomena was reported⁷ by Ermer in 1991. Hydroquinone (HQ) and C_{60} were dissolved in hot benzene—in a 3:1 (HQ: C_{60}) molar ratio—and the solvent was allowed to evaporate giving rise to black crystals suitable for X-ray crystallographic analysis. The X-ray crystal structure (Fig. 1)

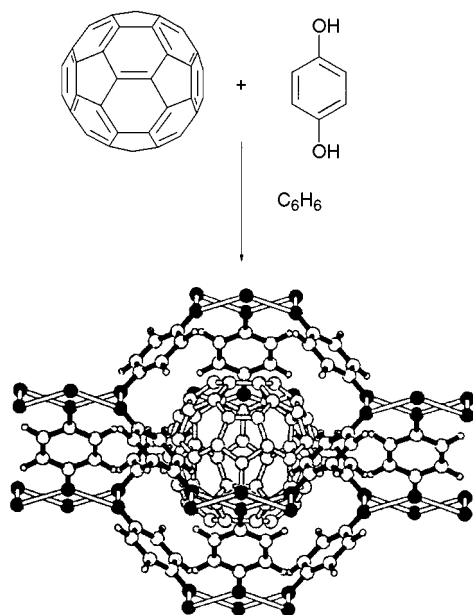


Fig. 1 Ball and stick representation of the super-polonium structure of $[HQ]_3C_{60}$.⁷ One H-bonded HQ supercube enclathrating the C_{60} molecule is shown. The hydrogen atoms of the OH groups are omitted for clarity and the O–H...O hydrogen bonds are represented as white bonds. Reproduced with permission from ref. 7.

revealed the formation of a 3:1 complex $[HQ]_3[C_{60}]$ in which the HQ host builds up a H-bonded three-dimensional so-called super-polonium network. These networks are constructed by large super-cubic cages with central cavities that accommodate the C_{60} guest molecules. The enclathration of C_{60} is rather tight, nevertheless the C_{60} molecules show a high degree of disorder and no individual bond lengths could be measured. The nature of this disorder was attributed to different orientations of the carbon sphere statistically distributed over the unit cell rather than to thermal motions of the C_{60} molecule. In contrast, the HQ network is well-defined. The distance between the HQ plane and the C-surface of C_{60} was found to be 3.1 Å.

Later on, C_{60} was co-crystallised from a CS_2 solution with two equivalents of bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF).⁸ The X-ray crystal analysis of the co-crystals at 150 K revealed (Fig. 2) that a C_{60} molecule is sandwiched by two concave BEDT-TTF molecules and that the rotational motion of C_{60} is halted completely at that temperature. Short intermolecular contacts ranging from 3.45 Å to 3.57 Å were observed between the carbon atoms of a pentagon of C_{60} and a TTF sulfur atom of a neighbouring BEDT-TTF molecule in the crystal. UV/Vis spectroscopic measurements on the complex in a KBr pellet showed a distinct absorption at $\lambda_{max} = 750$ nm, which was assigned to charge transfer interactions between the strong donor BEDT-TTF and the fullerene acceptor.

It was also found⁹ that co-crystallisation of C_{60} and ferrocene (Fc) molecules from a benzene solution produced black single

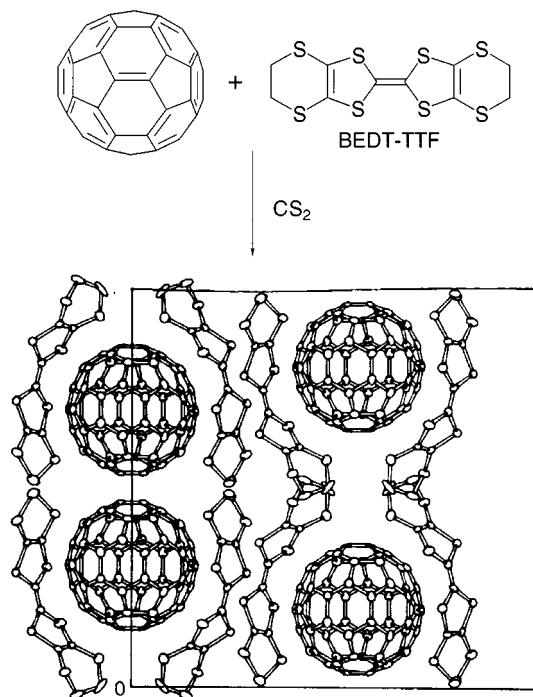


Fig. 2 Ball and stick representation of the $[BEDT-TTF]_2C_{60}$ X-ray crystal structure in a view along the c axis.⁸ Reproduced with permission from ref. 8.

crystals whose solid state structure showed the formation of $[C_{60}][Fc]_2$ complexes. These complexes consist of close-packed layers of C_{60} molecules stacked directly one above the other. The holes between the layers are filled by Fc molecules, as depicted in Fig. 3. One cyclopentadienyl (Cp) ring of a Fc

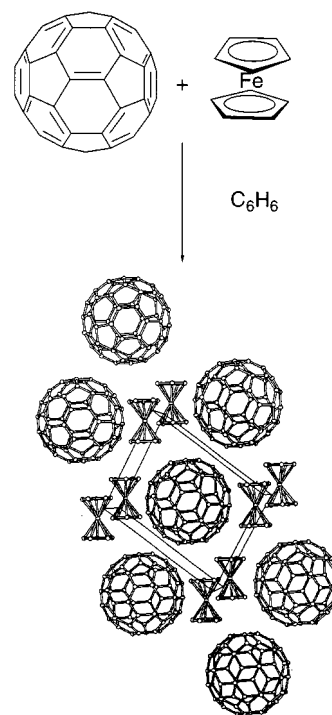


Fig. 3 Ball and stick representation of the packing diagram of the X-ray structure of $[Fc]_2C_{60}$ along the bc plane.⁹ Reproduced with permission from ref. 9.

molecule is situated in a plane parallel to one of the pentagons on the carbon sphere with an interplanar distance of 3.3 Å.

In all three cases, weak charge transfer interactions between the π -electron deficient C_{60} and the second, π -electron rich component were invoked as providing one of the driving forces

for complex formation, since short distance contacts are observed between the surface of the carbon sphere and the donor moieties HQ, BEDT-TTF, and Fc, respectively. However, there is little evidence for the existence of these interactions in solution. Presumably, the geometries and stoichiometries of the complexes in the solid state are largely determined by van der Waals interactions in conjunction with crystal packing forces in order to accommodate the convex surface of the C_{60} molecules and fill the voids between them. Nevertheless, these early solid state studies clearly revealed that the electron accepting fullerenes prefer being surrounded by electron rich rather than electron deficient π -systems. This provided an important design criterion in the construction of synthetic macrocyclic receptors for molecular complexation of the carbon sphere in both solid and liquid phases.

3 Inclusion complexes of C_{60} by macrocyclic hosts

In an attempt to increase the water solubility of the C_{60} carbon allotrope, which can be of great importance for potential biological applications, it was discovered¹⁰ that a boiling aqueous solution of γ -cyclodextrin (γ -CD), but not β -CD, was able to extract C_{60} from a mixture of C_{60} and C_{70} . Since γ -CD—with the diameter of its cone-shaped cavity ranging from 7.5 to 8.3 Å and a cavity depth of *ca.* 8.0 Å—is too small to fully encapsulate a large hydrophobic molecule like C_{60} (with a van der Waals diameter of *ca.* 10 Å^{7,8}), a complex with 2:1 (CD: C_{60}) stoichiometry was proposed to be responsible for the selective extraction of C_{60} . Furthermore, a bicapped structure (Fig. 4) was deduced on the basis of ¹H and ¹³C NMR spectroscopic studies as well as elemental analysis.¹¹

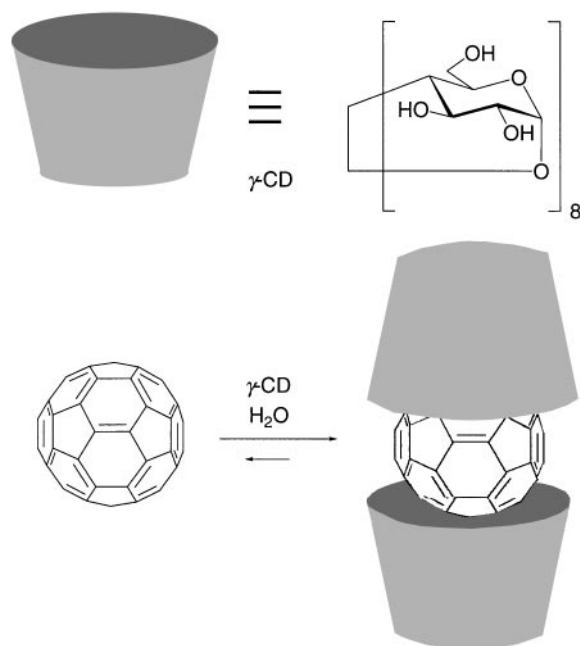


Fig. 4 Cartoon representation of the proposed bicapped geometry for the $[\gamma\text{-CD}]_2C_{60}$ complex in aqueous solution.¹⁰

Further evidence for complex formation was also derived from circular dichroism studies.¹¹ C_{60} is chromophoric but achiral whereas γ -CD is chiral but nonchromophoric. Medium intensity Cotton-effects ($\Delta\epsilon$ -values up to $12\text{ M}^{-1}\text{ cm}^{-1}$) were observed at $\lambda = 230$ and 258 nm which are believed to be induced by the chiral host γ -CD in the chromophoric C_{60} guest molecule. The authors suggested that n - π donor-acceptor interactions between the n -orbitals of the sugar O-atoms and the π -system of the fullerene contribute to the stability of the formed association.¹¹ It was also observed that upon laser

excitation (7 ns pulse, $\lambda_{\text{exc}} = 355\text{ nm}$) the quenching rate of the transient triplet fullerene state by dioxygen was slower than for pristine C_{60} by about a factor of 2, which indicates that γ -CD is covering a large portion of the carbon sphere in the complex.¹⁰

The electrochemical behaviour of the γ -CD inclusion complex was investigated¹² by cyclic voltammetry (CV) in aqueous solution (+ 0.2 M LiClO_4). First, it was shown that the UV/Vis spectrum of neutral C_{60} is practically unaffected by molecular inclusion. Subsequently, the $C_{60}^{\cdot-}$ monoradical anion was generated electrochemically and spectroelectrochemical investigations in the aqueous solution as well as electron paramagnetic resonance (EPR) measurements on frozen aqueous samples showed that the electronic structure of the monoradical anion in the complex in aqueous solution is similar to that of the $C_{60}^{\cdot-}$ monoradical anion in CH_2Cl_2 solution.

Another macrocyclic compound which has been studied with regard to its ability to form inclusion complexes with C_{60} is cyclotrimeratrylene (CTV).¹³ Crystals of $(C_{60})_{1.5}(\text{CTV})(\text{PhMe})_{0.5}$ were grown by slow evaporation of a CH_2Cl_2 -PhMe solution containing a 1:1 mixture of CTV and the carbon

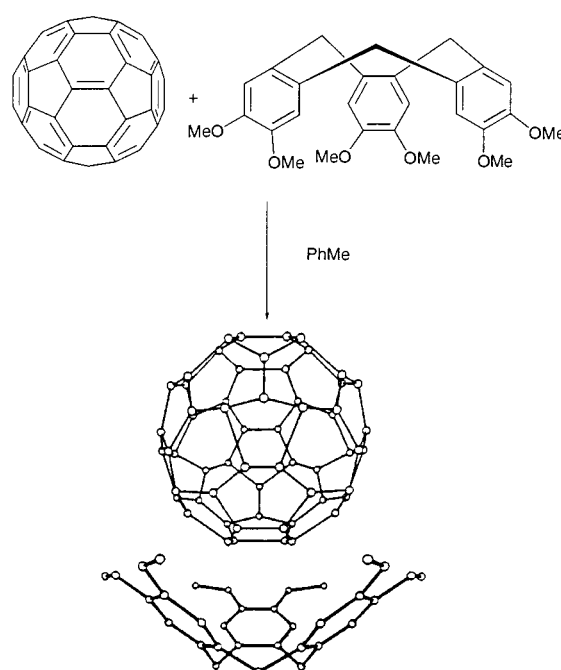


Fig. 5 Ball and stick representation of the X-ray structure of the $[\text{CTV}]C_{60}$ complex.¹³ Reproduced with permission from ref. 13.

sphere. The X-ray structure shows (Fig. 5) that C_{60} adopts a nesting position at van der Waals contact distance above the concave surface of the CTV macrocycle. The nine-membered ring in the CTV lines up with a six-membered ring in C_{60} compelling three adjacent five-membered rings of the fullerene to reside above the three electron rich aryl units in the CTV. Again, it can be assumed that weak π - π donor-acceptor interactions are contributing to the complex formation.

Recently, it was observed¹⁴ that, upon addition of CTV derivatives with acylated phenolic OH groups to C_{60} solutions in toluene and benzene, the UV/Vis spectrum of the carbon sphere underwent changes, with the intensity of the absorption in the 420–450 nm region slightly increasing upon addition of the host molecules. Isobestic points as well as Job plot analyses were indicative of a 1:1 host-guest interaction, and the association constants, K_a , for the formed 1:1 complexes were determined to be in the range of 4000 to 48000 M^{-1} in C_6H_6 and 5500 to 36300 M^{-1} in toluene (298 K, Benesi-Hildebrand method). Binding strength depends on the nature of the acyl groups in the CTV periphery with the highest K_a values being

measured for the tri-ester formed by *N*-methylpyrrole-2-carboxylic acid. Some CTV derivatives were also observed to bind C_{70} with K_a values ranging from 7700 to 16800 M^{-1} in the same solvents. The perturbation of the UV/Vis spectra of C_{60} upon complexation is indicative of donor–acceptor interactions between the π -electron rich aromatic rings in the CTV macrocycle and the π -electron deficient C_{60} sphere. Charge transfer interactions, however, usually do not make significant contributions to the stability of molecular complexes in the ground state. It must rather be assumed that van der Waals interactions between the large, stereoelectronically complementary surfaces of the two compounds are providing the major stabilisation for the solution complexes. The X-ray crystal structure of the 1:1 complex between CTV(OBz)₆ (OBz = OCOC₆H₅) and C_{60} that crystallised out of toluene depicted two different types of carbon balls, one nicely encapsulated by two host molecules and one bare one.

The complexation between calixarenes and fullerenes has been extensively studied. Calixarenes feature well-ordered macrocyclic arrays of aromatic rings but also possess the necessary flexibility which allows docking of large guest molecules such as fullerenes. The groups of Atwood¹⁵ and Shinkai¹⁶ discovered independently that toluene solutions of C_{60} and *p*-*t*Bu-calix[8]arene (**1**) form a sparingly soluble brown–yellow precipitate which was identified as the 1:1 complex [C_{60}]**1**. In this association, the fullerene most likely resides within the cavity of the macrocycle **1** presenting a structure which resembles that of a “ball and socket” (Fig. 6).

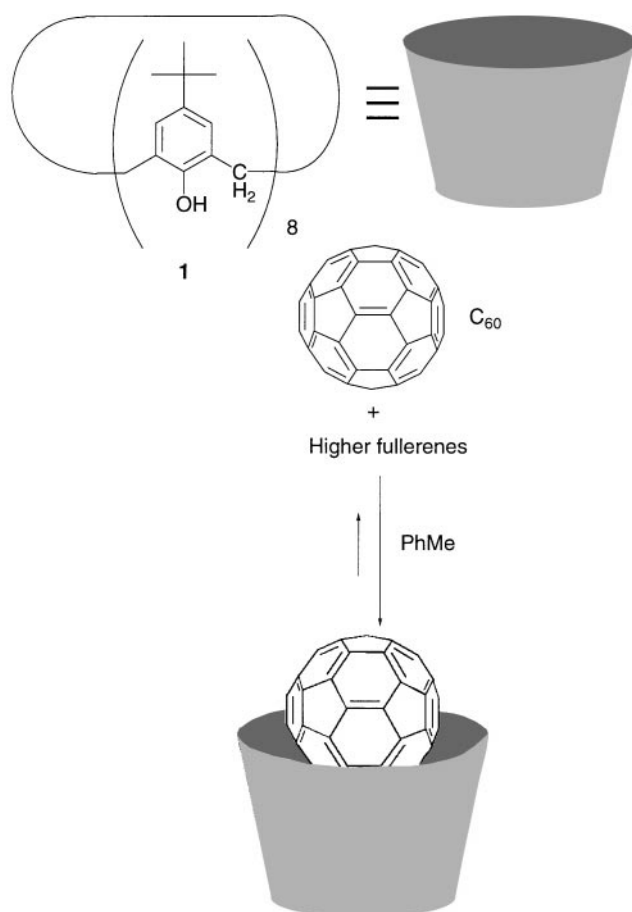


Fig. 6 C_{60} is readily separated from the higher fullerenes in toluene solution by specific inclusion complex formation with calix[8]arene **1**.^{15,16}

The circular H-bonding network between the OH-groups at the lower rim of the calixarene cone seems to be slightly weakened but retained as suggested by infrared (IR) spectroscopic studies. The complexation is highly selective for C_{60} over C_{70} and the

other higher fullerenes and provides the basis for a convenient and efficient isolation and purification of buckminsterfullerene from the soluble fullerene soot extract. By a protocol involving precipitation of the complex with **1** from toluene, followed by recrystallisation from $CHCl_3$, in which the calix[8]arene remains dissolved, high-purity C_{60} is readily obtained.

Verhoeven and co-workers¹⁷ carried out solid state ^{13}C NMR spectroscopic investigations to explore the nature of the intermolecular interactions in the complex between *p*-*t*Bu-calix[8]arene and C_{60} . The elemental analysis of the greenish microcrystalline material (from CS_2) they investigated was consistent with a 1:1 stoichiometry. They observed a significant upfield shift of 1.4 ppm of the C_{60} ^{13}C NMR resonance upon complexation providing indication for interactions between the carbon sphere and the aromatic rings of the macrocyclic receptor. This complexation-induced shift was accompanied by a sharpening of all calixarene signals and, in particular, by an increase in the number of aromatic resonances of the calixarene (as compared to free solid **1**). These data not only support the formation of a supramolecular complex but also suggest that a complexation-induced conformational change of the calixarene takes place. Such a conformational change is also indicated by the changes in the OH stretch observed in the IR spectrum of the bound macrocycle. The intricate pattern of the solid state ^{13}C NMR signals corresponding to the aryl rings of **1** is in agreement with the existence of two conformationally different phenolic rings in a 2:6 ratio; thus the calixarene host was proposed to possess an alternate cone conformation.

Calix[6]arene **2** was found¹⁸ to form solid state complexes with C_{60} and C_{70} from toluene solutions. Crystals suitable for X-ray analysis were obtained for both complexes, and X-ray analysis revealed that they both possessed a 1:2 stoichiometry ($[2][C_{60}]_2$ and $[2][C_{70}]_2$, respectively, see Fig. 7). The complexes turned out to be isostructural—despite the anisotropic shape of C_{70} —and they both crystallised in the same space group $P4_12_12$. The macrocyclic hosts show a double-cone conformation and each of the associated shallow cavities is occupied by a fullerene. It is worth noting that the lower rim H-bonding network between the OH-groups, which is present in the uncomplexed calixarene, is fully retained in the complexes. The authors described this arrangement as reminiscent of the jaws of a pincer acting on two adjacent spheres/ellipsoids.

Fukuzawa and co-workers^{19,20} reported comprehensive investigations of the complexation between calixarene receptors **3a–c** and C_{60} in organic solvents. Upon addition of calix[5]arene **3a–c** (Fig. 8) to C_{60} in several organic solvents (toluene, benzene, CS_2 , *o*-dichlorobenzene) they observed a change in colour from purple to pale yellow. This colour change was accompanied by an increase in the UV/Vis absorption of C_{60} in the 400 to 470 nm region. The stoichiometry of the complexes formed in solution was determined to be 1:1 by Job plot analysis; this stoichiometry was also confirmed by the observation of a clear isosbestic point at 478 nm. The association constants of the complexes were determined by UV/Vis titration experiments and found to be strongly solvent dependent. With receptor **3a**, the measured K_a values (at 298 K) increased from 308 M^{-1} in *o*-dichlorobenzene to 660 M^{-1} in CS_2 , to 1840 M^{-1} in benzene and to 2120 M^{-1} in toluene. Thus, association strength increases with decreasing solubility of C_{60} : the more weakly solvated guest is more strongly bound by the host. The K_a values were also found to be dependent on the substituents of the host molecule. Receptor **3a** with the highly polarisable iodide substituents formed the most stable complexes. Thus, association strength decreased in toluene from $K_a = 2120 M^{-1}$ (**3a**) to 1670 M^{-1} (**3b**) and to 590 M^{-1} (**3c**). This result underlines the important role of van der Waals interactions in the stabilisation of the fullerene complexes.

The authors were also successful in growing crystals of the complex between C_{60} and receptor **3a** which were suitable for

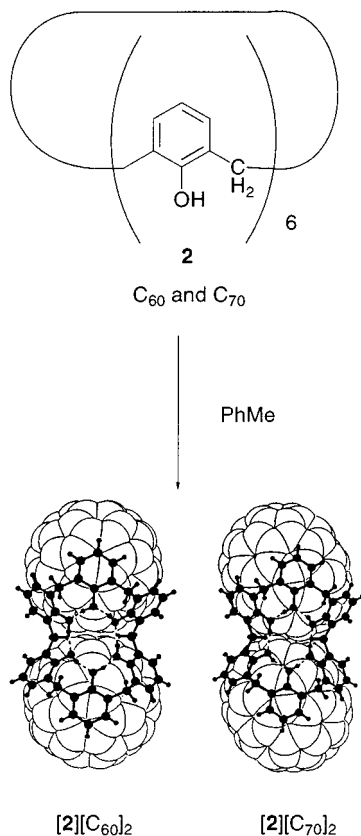


Fig. 7 X-ray structures of the complexes $[2][C_{60}]_2$ and $[2][C_{70}]_2$ viewed from below the calix[6]arene double cone. The atoms and bonds of the calixarene **2** are presented in a ball and stick representation and they are colored in black. Note that the H-bond network in the calixarene lower rim stays intact.¹⁸ Reproduced with permission from ref. 18.

X-ray structural analysis. Unlike in solution, the stoichiometry of the complex in the solid state was found to be 2 : 1 $[C_{60}][\mathbf{3a}]_2$. The fullerene is encapsulated within a cavity conformed by the two calixarene molecules, and the remarkably high number of 144 short intermolecular distances ($< 4.0 \text{ \AA}$) between carbon atoms of the fullerene and heavy atoms of the two encapsulating macrocyclic hosts was revealed.

This discovery of a complex with 2:1 stoichiometry in the solid state led Fukazawa and co-workers to covalently link two calix[5]arene macrocycles in order to produce shape-selective receptors, such as **4**, with well-defined cavity sizes.²⁰ With these bridged calix[5]arene receptors, they achieved a dramatic increase in the association constants for 1 : 1 complexes with C_{60} in solution. Thus, the K_a value for the complex formed with receptor **4** (Fig. 8) in toluene amounts to 76000 M^{-1} (298 K) and is to date the largest reported for any complex of C_{60} in an organic solvent. The solvent dependency of the association constant followed the same trend as had been observed with **3a–c**. The bridged receptor **4** binds C_{70} even better than C_{60} . Thus, the association constant of the 1 : 1 complex with C_{70} in toluene amounts to $K_a = 163000 \text{ M}^{-1}$. In other efficient double calix[5]arene receptors, the two receptor moieties are linked together by ethynediyl or buta-1,3-diynediyl bridges.

In most of the complexation studies presented to this point, convex fullerene surfaces, characterised by a large positive molecular electrostatic potential, interact with complementary concave aromatic receptor surfaces which, in return, are characterised by a very large negative molecular electrostatic potential.²¹ Van der Waals dispersion interactions greatly add to these electrostatic donor–acceptor interactions in providing stability to the associations formed in solution and in the solid state. To further increase the level of sophistication of supramolecular construction, it is necessary to covalently modify the carbon spheres so that they can be incorporated into

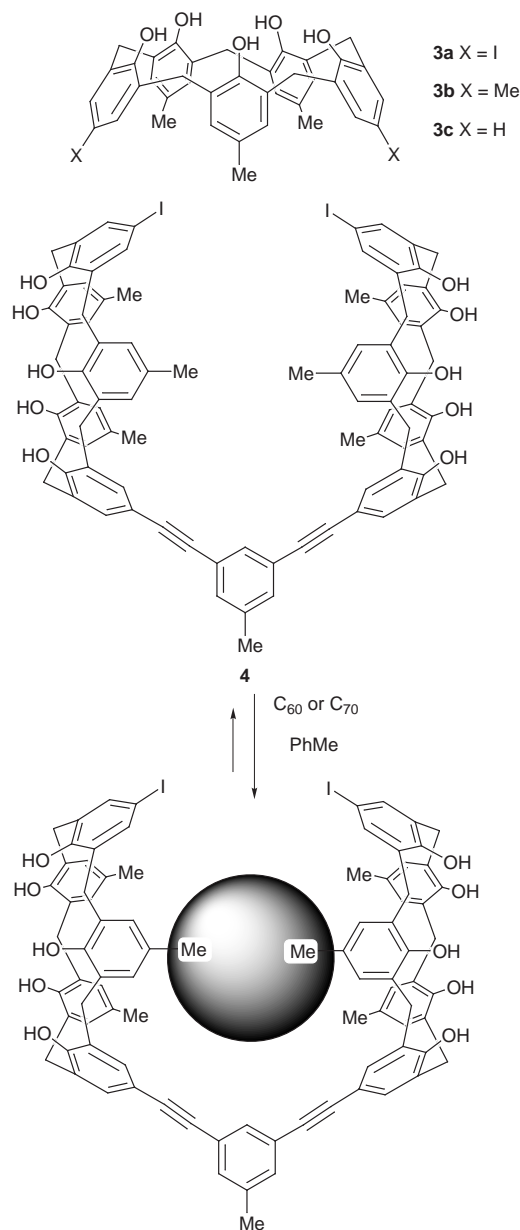


Fig. 8 Molecular structures of the calix[5]arenes **3a–c** and the bridged calixarene dimer **4** which are able to encapsulate both C_{60} and C_{70} in organic solvents.^{19,20}

more intricate molecular architectures which are ordered at the nanoscopic level by self-assembly techniques.

4 Molecular assemblies and supramolecular arrays incorporating C_{60}

Molecular self-assembly processes lead to the construction of large and ordered superstructures by the use of weak, reversible noncovalent bonding interactions between complementary molecular structures.²² The final superstructure formed represents, in most cases, a thermodynamic minimum for the system. Living systems utilise self-assembly for the formation of new functioning structures and superstructures and now chemists are increasingly transferring these concepts into the artificial domain of unnatural product syntheses in order to produce large multicomponent molecular structures with defined dimensions and functions. We describe in this section the efforts undertaken in order to merge functionalised fullerenes bearing the appropriate molecular recognition motifs with different complemen-

tary subunits giving rise to novel molecular assemblies and supramolecular arrays.

Tour and co-workers²³ sought to exploit the anionic phosphate groups along the DNA backbone in order to assemble cationic fullerene derivatives into the DNA double helix *via* Coulombic charge–charge interactions. With this goal in mind, they prepared the positively charged C₆₀-*N,N*-dimethylpyrrolidinium iodide **5** which undergoes complexation with double-stranded DNA (Fig. 9). Upon mixing an aqueous solution of

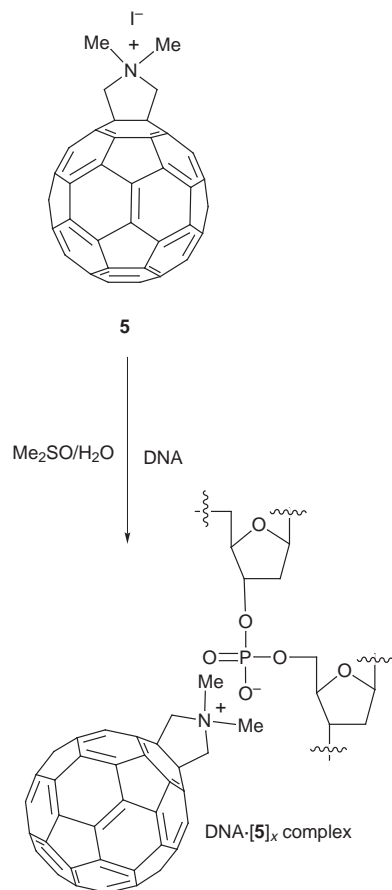
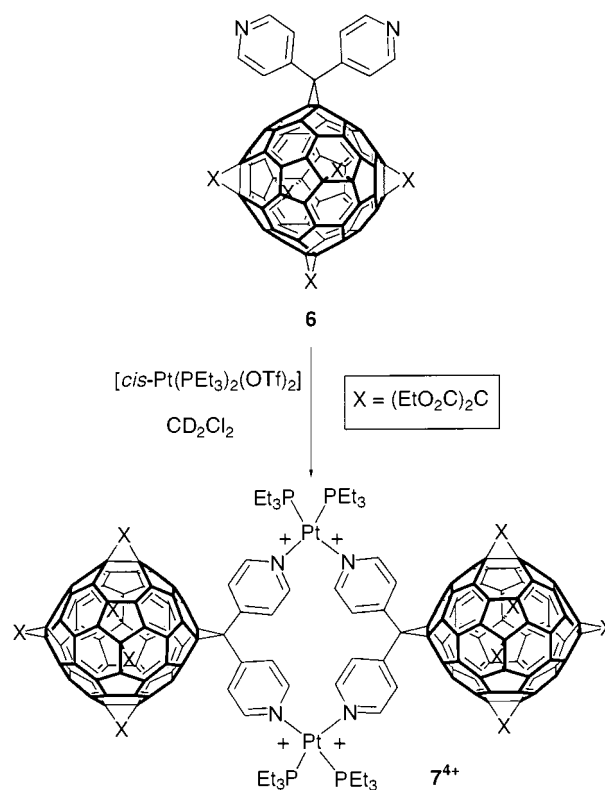


Fig. 9 The self-assembly of DNA with the positively charged C₆₀-*N,N*-dimethylpyrrolidinium cation **5**.²³

plasmid with a solution of **5** in Me₂SO, hybrid DNA–fullerene architectures were obtained which could be imaged by transmission electron microscopy (TEM) without the need for heavy metal coating or staining agents. Initially, a great deal of nonspecific aggregation was observed; this phenomenon was mainly attributed to the self-association between the hydrophobic fullerene units. In the presence of selected surfactants, however, which did not interfere with the ion pairing between **5** and DNA, the nonspecific aggregation between the formed complexes disappeared and the TEM images displayed associations in which the plasmids retained a circular shape. Whereas the diameters of the prerelaxed plasmid DNA amount to 580 nm, the diameters of the [DNA]_x[**5**]_x rings ranged between 100 and 150 nm. This dramatic condensation was explained by the packing of anionic DNA around aggregates of cationic **5** with the size of the formed nanostructures being controlled by the surfactants present. This condensation is reminiscent of DNA packing by histones in chromatin.

We became interested in the incorporation of fullerenes into multicomponent molecular systems providing access to the construction of two- and three-dimensional supramolecular architectures with defined geometries. In order to achieve this objective, we exploited the Pt^{II}-directed self-assembly of multidentate ligands. By mixing (Scheme 1) an equimolar



Scheme 1 The self-assembly of the di(pyridyl)methano-containing C₆₀ hexakis-adduct **6** and [cis-Pt(PEt₃)₂(OTf)₂] to give the tetracationic cyclophane **7**⁴⁺ incorporating two fullerene substructures.²⁴

amount of the C₆₀ hexakis-adduct **6** and [cis-Pt(PEt₃)₂(OTf)₂], the tetracationic cyclophane **7**⁴⁺ was obtained in an amazing, quantitative yield as the tetrakis-triflate salt.²⁴ The highly symmetrical (D_{2h}) solution structure of **7**⁴⁺ was proven by ¹H, ¹⁹F and ³¹P NMR as well as IR spectroscopy. The X-ray crystal structure of **7**⁴⁺ revealed (Fig. 10) that the four vertex atoms of

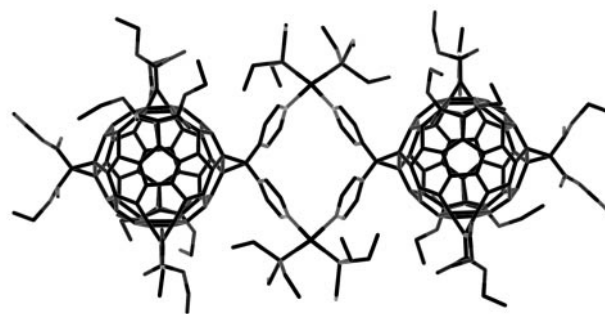


Fig. 10 X-Ray structure of the tetracationic cyclophane **7**⁴⁺. The counterions and solvent molecules are omitted for clarity.²⁴

the central cyclophane sub-structure, *i.e.* the two Pt^{II} centres and the two quaternary carbon atoms of the di(pyridyl)methano groups, form a perfectly planar parallelogram at the cost of angle strain. The sum of the internal angles in this parallelogram amounts to 390(5)°, whereas an angle sum of only 360° is required for a perfectly planar assembly. In view of the quantitative nature of the self-assembly process, we now envision utilising this strategy for selectively building up even more complex supramolecular fullerene arrays. Starting from a *trans*-1 bis[di(pyridyl)methano] derivative, in which the two multidentate ligands are attached to the two poles of the carbon sphere, linear oligomeric rods with alternating fullerene and cyclophane substructures in the backbone should become available. By replacement of two and more of the diethyl malonate addends in hexakis-adduct **6** by di(pyridyl)methano addends and mixed self-assembly, using additional multidentate

spacer components,²⁵ three-dimensional fullerene networks should become accessible.

A subcategory of self-assembly has been termed self-assembly with covalent modification. It refers to self-assembly processes in which the formation of covalent linkages within an assembly is irrevocable and irreversible. In the last few years, chemists have exploited this approach to self-assemble a number of interlocked molecules—mainly, catenanes and rotaxanes—in which two or more discrete chemical entities are bound together by a so-called mechanical bond, *i.e.* without the aid of valence forces.²² These molecular assemblies are not only interesting as a result of their undeniable aesthetic appeal, but also because of their possible applications in molecular devices. The introduction of fullerenes promises further enhancement of the functionality of such molecular assemblies.

Stoddart and co-workers^{22c} have capitalised on the molecular recognition between π -electron rich—such as 1,4-dialkoxybenzene and 1,5-dialkoxynaphthalene—and π -electron defi-

cient—such as paraquat (*N,N'*-dimethylbipyridinium)—aromatic units to self-assemble a variety of interlocked molecules. Utilising this strategy, a collaborative venture between the Stoddart and Diederich groups led to the preparation of the C₆₀-containing [2]catenane (\pm)-**8**-4PF₆ (Fig. 11).²⁶ This molecule holds a very intriguing architecture featuring three macrocycles, two of which are interlocked. In addition, it features an unprecedented intramolecular A–D–A–D–A stack (A = acceptor, D = donor), with the fullerene unit acting as an additional electron accepting moiety.

Sauvage and co-workers took advantage of the coordination geometry of 2,9-disubstituted 1,10-phenanthroline ligands around a Cu^I centre to construct a number of molecular and supramolecular architectures such as catenanes, rotaxanes and even molecular knots.^{22d} In an early collaboration with this group, the [2]rotaxane **9**-BF₄, possessing two fullerene stoppers at the termini of its thread-like component, was obtained by oxidative coupling of two mono-alkyne-deprotected di(alky-

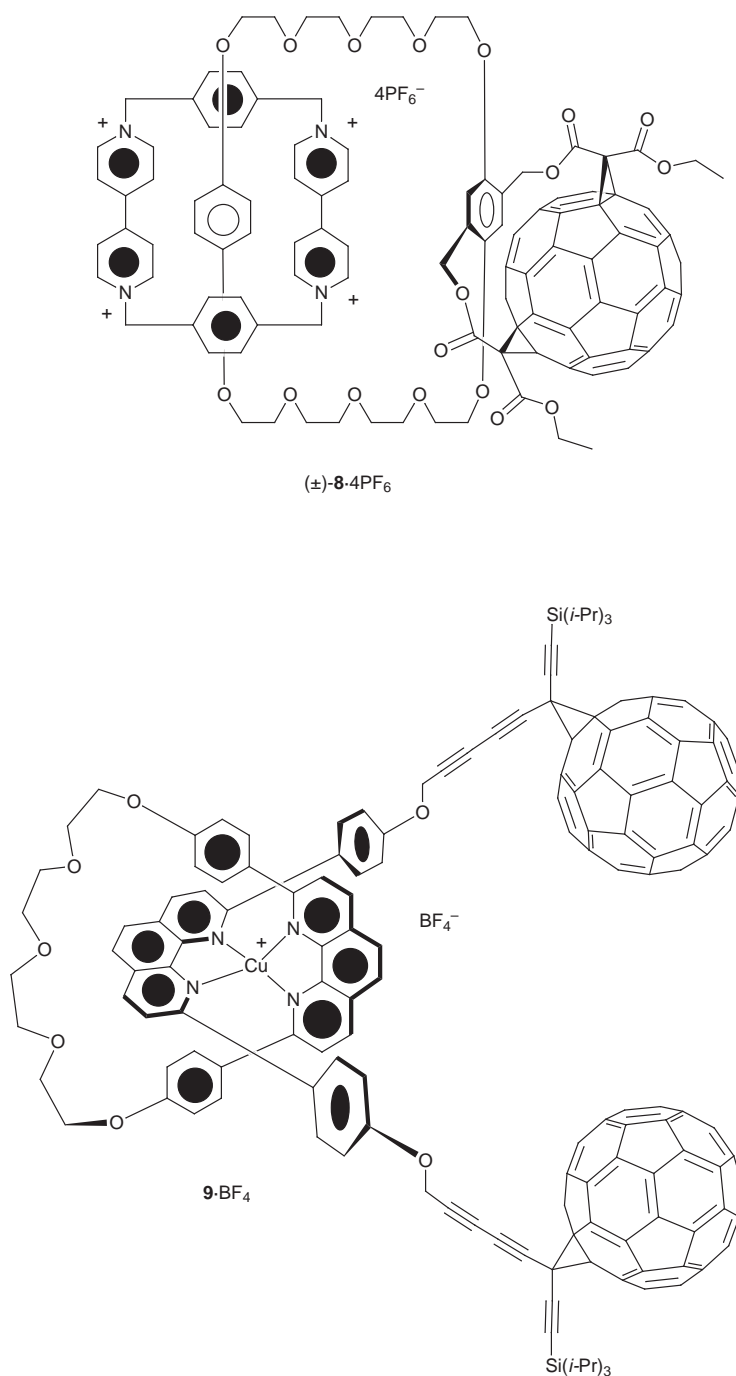


Fig. 11 Fullerene-containing interlocked molecules; the [2]catenane (\pm)-**8**-4PF₆²⁶ and the [2]rotaxane **9**-BF₄.²⁷

nyl)methanofullerenes with a terminally diethynylated [2]pseudorotaxane component (Fig. 11).²⁷ This interlocked molecule features interesting electrochemical properties. The presence of the Cu^I centre does not affect the redox properties of the fullerene stoppers, however, the redox potential of the Cu^I/Cu^{II} couple was significantly altered in **9**·BF₄ compared to other similar phenanthroline complexes lacking the fullerene moieties. The redox potential $E_{1/2}$ for the Cu^I/Cu^{II} couple was shifted anodically by *ca.* 300 mV to +0.865 V (*vs.* the standard calomel electrode, SCE). The origin of this shift still remains a matter of discussion. It is possible that the strong electron withdrawing character of the C₆₀ stoppers destabilises the Cu^{II} state. On the other hand, the presence of the bulky carbon spheres could induce changes in the solvation around the metal-ion centre which may be responsible for the observed potential change.

Furthermore, the molecular assembly **9**·BF₄ also displays very interesting photophysical properties as a consequence of the presence of the fullerene stoppers. These properties will be discussed in the next section.

5 Photoinduced electron transfer and energy transfer in C₆₀-containing donor–acceptor diads and triads

C₆₀ is capable of accepting reversibly up to six electrons. This property along with the fact that the energy levels of its first excited singlet and triplet states are comparable to those of large π -systems such as porphyrins—lower than those of other common small organic acceptor components—and that the carbon sphere possesses a rigid framework in ground and excited states suggested that C₆₀ might show peculiar photophysical properties different from those of previously studied acceptors. Accordingly, many investigations have been carried out on the photoinduced electron transfer between C₆₀ and a series of covalently linked electron donors.²⁸ The study of such processes is of substantial importance for many fundamental

and practical purposes such as gaining a better understanding of natural photosynthesis and the creation of photochemical molecular devices.

It can be argued that this research is not strictly supramolecular since in most cases the donor and acceptor are linked by covalent bonds. Nevertheless, we consider it appropriate to discuss this research here, since, similarly to noncovalent assemblies, the ultimate function expressed by these covalently linked multicomponent systems differs distinctively from the function of the individual subcomponents. Furthermore, in the most recent cases noncovalent bonding interactions play an important role, *vide infra*.

One of the first ‘active’ fullerene diads was reported by the groups of Williams and Verhoeven.²⁹ This diad **10** (C₆₀–An) is composed of a fulleropyrrolidine acceptor covalently attached to an *N,N*-dimethylaniline (An) donor component (Fig. 12). A sharp decrease in the fluorescence of **10** was observed upon increasing solvent polarity. Since the population of a charge separated state is energetically possible in polar solvents, the quenching was attributed to an intramolecular electron transfer pathway which deactivates the excited state to yield the charge separated state (C₆₀^{•−}–An^{•+}). A strong indication that the electron donating dimethylaniline substituent is involved in this quenching process came from the fact that addition of trifluoroacetic acid (TFA) to a CH₂Cl₂ solution of **10**, to protonate the aniline moiety, resulted in a recovery of the fluorescence intensity to the level of nonpolar solvents. *N*-Methylfulleropyrrolidine, a model compound lacking the aniline donor group, did exhibit fluorescence even in polar solvents, proving that the pyrrolidine moiety was not responsible for the quenching process. However, no transient state corresponding to the fullerene radical anion could be detected as a result of the fact that the charge separated state has a very short—less than nanoseconds—lifetime.

Approaches taken in order to augment the lifetime of the charge separated state include i) increasing the length of the linker between the donor and the acceptor moieties²⁸ and ii) constructing a molecular triad in which the charge recombina-

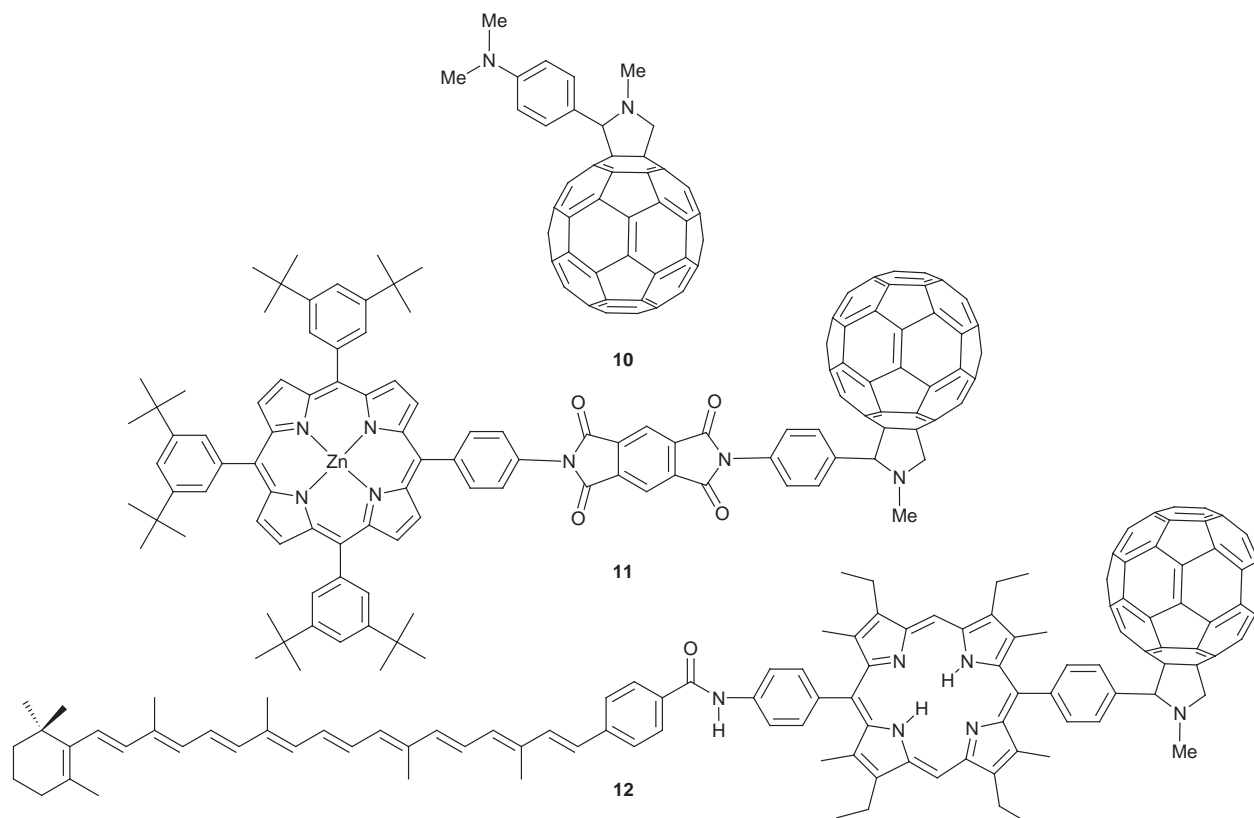


Fig. 12 Molecular structures of diad **10**²⁹ and triads **11**³⁰ and **12**³¹ all of them incorporating a fullerene moiety as an electron acceptor component.

tion step competes with a second intramolecular electron transfer process to yield a longer-lived charge separated state.

This second strategy was pursued by Sakata, Imahori and co-workers.³⁰ They synthesised the porphyrin–pyromellitimide–C₆₀ (P–Im–C₆₀) triad **11** (Fig. 12) designed to display a sequence of electron transfer processes. Irradiation of **11** with a laser pulse at $\lambda = 590$ nm in dioxane provided the corresponding porphyrin excited singlet state ¹P–Im–C₆₀ which, after intramolecular electron transfer, is converted into the charge separated state P⁺–Im⁻–C₆₀, with evidence for this state coming from transient spectroscopic studies. The final step is a charge shift to produce the charge separated state P⁺–Im–C₆₀⁻. The absorption corresponding to the porphyrin centered radical cation P⁺ was observed to decay with a time constant of 1.3 ns.

The groups of A. L. Moore, T. A. Moore and D. Gust³¹ prepared the carotene–porphyrin–fullerene (C–P–C₆₀) triad **12** (Fig. 12) and its physical properties were studied by time-resolved spectroscopic methods. When triad **12** is excited at $\lambda = 590$ nm in 2-methyltetrahydrofuran at ambient temperature, the porphyrin singlet excited state C–¹P–C₆₀ is formed and it decays by a combination of singlet–singlet energy transfer and intramolecular electron transfer pathways to the charge separated state C–P⁺–C₆₀⁻. This is followed by a second fast intramolecular electron transfer—competing with the charge recombination pathway—to afford the long-lived charge separated state C⁺–P–C₆₀⁻ which decays with a time constant of 170 ns *via* a charge recombination step to the carotenoid triplet state ³C–P–C₆₀ before returning to the ground state. The long-lived charge separated state could be detected by means of nanosecond transient absorption spectroscopy. By featuring a long-lived charge separated state generated by photoinduced charge transfer and formation of a triplet state by charge recombination, triad **12** displays phenomena previously observed mostly in photosynthetic reaction centers.

As mentioned in the previous section, the [2]rotaxane **9**·BF₄ with two fullerene stoppers presents interesting photophysical properties and it is—to our knowledge—the first supramolecular assembly containing fullerene subunits whose photophysical properties have been studied.³² These properties differ significantly from those observed in related rotaxanes lacking the fullerene components or in di(alkynyl)methanofullerenes since excited state intercomponent processes take place in **9**·BF₄. The singlet excited state localised in the fullerene and the metal-to-ligand charge transfer (MCLT) excited state confined on the Cu^I complex are both quenched. Deactivation of the fullerene singlet excited state occurs by means of energy transfer to the Cu^I complex moiety. This process competes with intersystem crossing to the fullerene triplet excited state. More interestingly, the quenching of the Cu^I-complex excited state takes place *via* an intramolecular electron transfer pathway which gives rise to the charge separated state (Cu^{II}–C₆₀⁻). No direct evidence for the charge separated state could be obtained, since the charge recombination is fast, thus making the lifetime of the charge separated state very short (<1 ns). Further evidence for the existence of such a charge separated state is derived from the fact that the ability of [2]rotaxane **9**·BF₄ to photosensitise the formation of singlet oxygen is greatly diminished since the fullerene triplet state in the rotaxane is also quenched by intramolecular electron transfer to the same charge separated state.

There was substantial interest in studying the photochemically induced intercomponent processes between a donor and a fullerene acceptor moiety which are brought together by noncovalent bonding interactions, *i.e.* in a truly *supramolecular* diad, rather than by covalent bonds. With this target in mind, the methanofullerene **13** bearing a pyridine residue at the methano bridge was synthesised in our laboratories.^{33a} Methanofullerene **13** forms a 1:1 complex with zinc *meso*-tetraphenylporphyrin (ZnTTP) through coordination of the pyridyl moiety to the Zn^{II}

ion, thus providing an example for the noncovalent assembly of a porphyrin–fullerene diad (Fig. 13).^{33b} The association con-

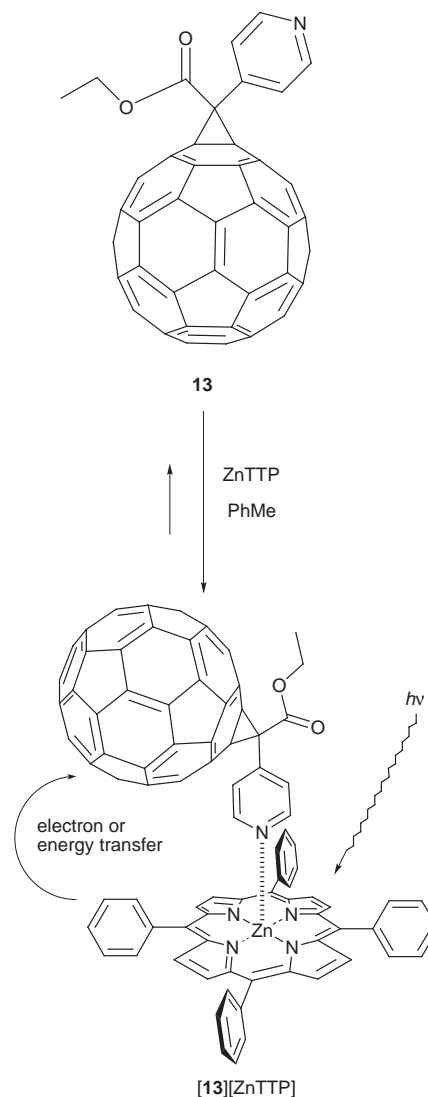


Fig. 13 A supramolecular fullerene-containing diad.^{33a} The donor-acceptor components are brought in close proximity by metal–ligand interactions.

stant for the complex was calculated from ¹H NMR and fluorescence titrations to be $K_a \sim 3000$ M⁻¹ (298 K) in benzene or toluene. Upon laser excitation of the 1:1 complex in toluene solution at $\lambda = 530$ nm, the intensity of the luminescence originating from the porphyrin singlet excited state (¹ZnTTP···C₆₀) decreases in comparison with that measured for free ZnTTP. This quenching can be attributed to an intercomponent process between the ZnTTP and the fullerene moieties within the complex. No experimental evidence could be found for either an electron transfer or an energy transfer mechanism. Since energy transfer has been shown to proceed quickly through noncovalent bonds, it was suggested that the quenching takes place *via* the latter mechanism giving rise to the ZnTTP···¹C₆₀ excited state.

In all cases discussed in this section, the electron acceptor component is a functionalised fullerene. By introducing addends at bonds between two six-membered rings (a 6–6 bond), the conjugated π -electron chromophore of the fullerene and its electron accepting ability usually are reduced.³⁴ Thus, most C₆₀ adducts are less suited as acceptor components in photoinduced electron transfer systems than pristine C₆₀. Therefore, it would be interesting to engage the pure, unfunctionalised carbon allotrope as a molecular acceptor component into supramolecular diads by complexation to calixarenes or cyclodextrins

bearing strong electron donor components. Such a proposal had already been advanced by Williams *et al.* in their first report on a fullerene-containing donor–acceptor diad.²⁹

6 Self-organisation of fullerenes into ordered films

Molecules in solution behave in a fairly incoherent manner. For fullerene materials to be able to support device-like properties at the macroscopic level, their organisation into structurally ordered films will be required. One of the most pursued approaches towards ordered fullerene films has been the formation of Langmuir monolayers at the air–water interface and their subsequent transfer as Langmuir–Blodgett films onto solid supports. The challenge in the reversible formation of stable Langmuir monolayers of fullerenes and their derivatives lies in overcoming the high aggregation tendency of the carbon sphere. With its high cohesive energy of $\sim 31 \text{ kcal mol}^{-1}$, C_{60}

prefers to undergo formation of scattered three-dimensional fullerene aggregates rather than monolayer formation.³⁵

In order to solve this problem, a series of amphiphilic covalent C_{60} derivatives, such as the fullerene–crown ether conjugate **14** and the fullerene–cryptate conjugate **15**, were prepared (Fig. 14).³⁶ In principle, both compounds formed a monomolecular layer at the air–water interface with a molecular area A_0 of approximately $80\text{--}90 \text{ \AA}^2 \text{ molecule}^{-1}$. This number corresponds nicely to the calculated molecular area in a C_{60} monolayer ($86.6 \text{ \AA}^2 \text{ molecule}^{-1}$) assuming a tight hexagonal packing with a nearest centre-to-centre distance of 10 \AA . However, optical light microscopy revealed that the films formed by free **14** and cryptate **15** were already present before any pressure had been applied, and irreversible compression–expansion cycles were observed. It is likely that the hydrophilic head groups in **14** and **15** were not bulky enough to prevent the aggregation of the carbon spheres. Therefore, the syntheses of amphiphilic fullerene derivatives with hydrophilic head groups large enough to keep the fullerene units apart in absence of pressure were targeted.

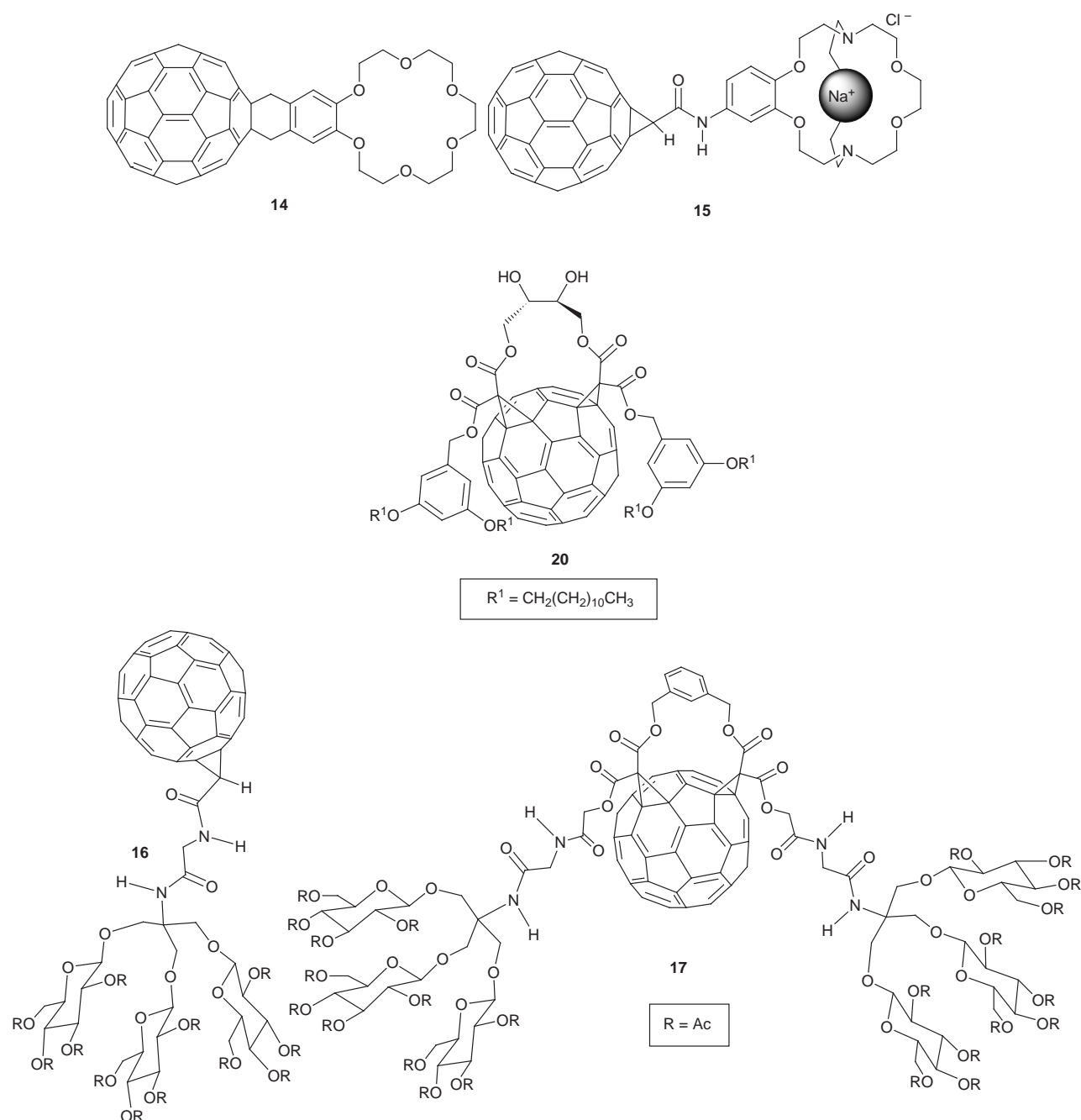


Fig. 14 Amphiphilic C_{60} derivatives **14–17**^{36,37} and **20**.³⁹

In order to prevent fullerene aggregation, carbohydrate-containing dendrons as bulky hydrophilic head groups were attached to the carbon cores and the resulting fullerene-glycodendron conjugates **16** and **17** (Fig. 14) were shown to give layers at the air–water interface that are i) monomolecular, ii) stable and iii) form reversibly as proven by the lack of hysteresis in compression–expansion cycles.³⁷ The pressure–area isotherms of **16** and **17** showed that the A_o values are 96 and 220 Å² molecule⁻¹, respectively. It can be concluded that the dendritic wedges limit the packing and keep the fullerenes at a distance that is larger than that corresponding to their closest contact. This was the first time, to our knowledge, that the formation of truly reversible, stable monolayers of fullerene derivatives had been observed at the air–water interface. The monolayers were transferred onto quartz slides by Langmuir–Blodgett (LB) techniques³⁵ with the resulting films being likely of the X-type. In future work, transfer of these monomolecular layers onto solid supports could not only be used for the creation of ordered fullerene films (X-type LB transfer) with potential applications in optical technology but also for the formation of ordered chiral sugar films (Z-type LB transfer on hydrophobic substrates) with applications as biosensors for carbohydrate binding proteins.

Another possible approach to avoid the aggregation of the fullerene moieties at the air–water interface is to surround the carbon spheres by a hydrophobic environment which will impede a close contact among the fullerene spheres. In this direction, mono- and multilayers of 1 : 1 mixtures of C₆₀ and C₇₀ and the amphiphilic azacrown derivatives **18** and **19** were spread at the air–water interface. These azacrown derivatives contain a hydrophobic cavity created by the substituents on the nitrogen atoms which behave like lipophilic ‘arms’ wrapping around the fullerene spheres as if they were ‘balls in a basket’ (Fig. 15).³⁸ The pressure–area isotherms for the hexaazacrown derivative **18** in the presence of C₆₀ and C₇₀ gave A_o values of 141 and 137 Å² molecule⁻¹, respectively. For the octaazacrown derivative **19** co-spread with C₆₀ and C₇₀, the corresponding observed A_o values were 263 and 269 Å² molecule⁻¹, respectively. All the curves were reproducible and repeated compression–expansion cycles (hysteresis curves) gave identical plots. The proposed structure for these films is the one with each fullerene molecule located inside an azacrown derivative as depicted in Fig. 15. Some support for this hypothesis was obtained from atomic force microscopy (AFM) measurements of the monolayers. Furthermore, these monolayers could be transferred onto solid supports by LB-techniques. Both **18** and the fullerenes were unable to form LB-films alone. In contrast, the 1 : 1 mixtures of **18** with C₆₀ or C₇₀ yielded homogenous LB-multilayers (Y-type on both hydrophilic and hydrophobic substrates) with an average bilayer thickness of ~47 Å. LB-multilayers of 1:1 mixtures of **19** and C₆₀ and C₇₀ were also obtained both with a bilayer thickness of ~37 Å.

Employing a similar, yet covalent strategy, Nierengarten and co-workers³⁹ prepared the fullerene amphiphile **20** possessing a small polar head-group and pendant long alkyl chains which can wrap around the carbon sphere, thus sheltering it from possible interactions with neighbouring fullerenes (Fig. 14). The pressure–area isotherms for **20** gave a molecular area $A_o = 160$ Å² molecule⁻¹ which is in good agreement with the estimated value for **20**. Furthermore, successive compression–expansion cycles took place indicating the reversibility of the process. It is proposed that the C₆₀ cores in **20** are encapsulated in a hydrophobic microenvironment created by the aryl rings and the long alkyl chains, thereby preventing their aggregation.

In very elegant work, the groups of Echegoyen, Kaifer and Wilson described an alternative methodology to prepare thin film assemblies of fullerene derivatives by combining a defined intrafacial molecular recognition event, the complexation between primary ammonium salts and 18-crown-6 derivatives *via* a tripod array of H-bonds in conjunction with ion–dipole

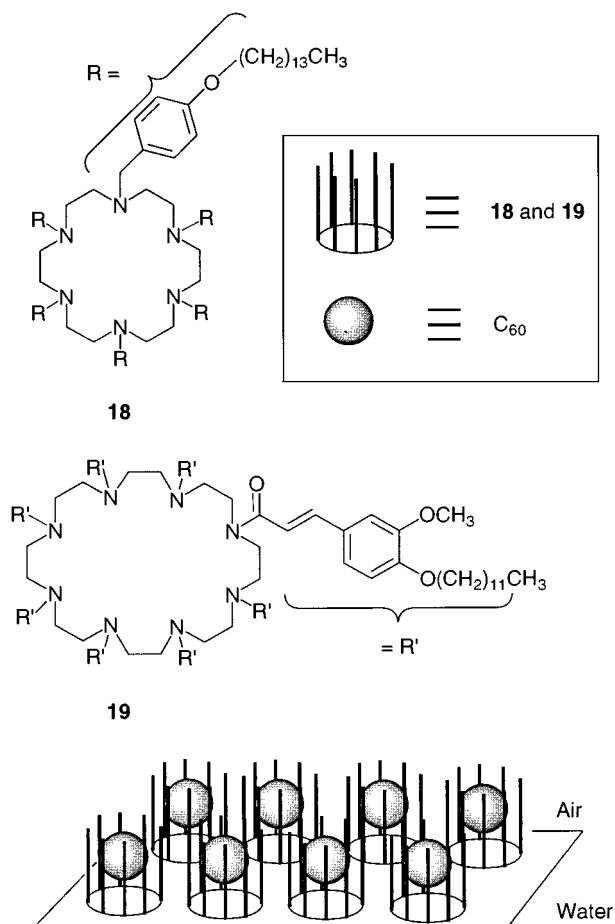


Fig. 15 Amphiphilic azacrown derivatives **18** and **19**.³⁸ Cartoon representation of the proposed structure for the molecular monolayer being formed at the air–water interface with the fullerenes positioned inside the hydrophobic cavity of the azacrown molecules.

interactions, with the formation of a self-assembled monolayer (SAM).⁴⁰ For that purpose, they synthesised the fullerene–crown ether adduct **21** which incorporates a monobenzo-18-crown-6 moiety pendant to the carbon sphere (Fig. 16). A gold electrode surface was chemically modified to support a thiolated SAM, formed of Cl⁻ H₃N⁺(CH₂)₂SS(CH₂)₂NH₃⁺Cl⁻ molecules, which displays a surface of primary ammonium groups. Subsequently, conjugate **21** was bound *via* ammonium ion–crown ether complexation, thereby forming a novel fullerene monolayer on the surface of the supramolecularly modified electrode. In order to obtain a quantitative assessment of the surface coverage, Osteryoung square wave voltammetry (OSWV) measurements were carried out. In these experiments, the difference between the Faradaic currents resulting from the reduction of the fullerene moiety of **21** self-assembled on the modified electrode and those obtained from simple diffusion of molecules of **21** on the bare gold surface, was determined. The measurements yielded for the difference in OSWV response in the two experiments a value of 1.4×10^{-10} mol cm⁻² which is in agreement with the calculated values for a compact C₆₀ monolayer assuming a face-centered cubic (fcc) packing ($\sim 1.9 \times 10^{-10}$ mol cm⁻²), thus demonstrating the close packing of the layer of **21** on the surface of the supramolecularly modified electrode.

7 Towards potential applications

So far we have shown how noncovalent bonding interactions are utilised to incorporate fullerenes and fullerene derivatives into molecular assemblies and supramolecular arrays, which, in

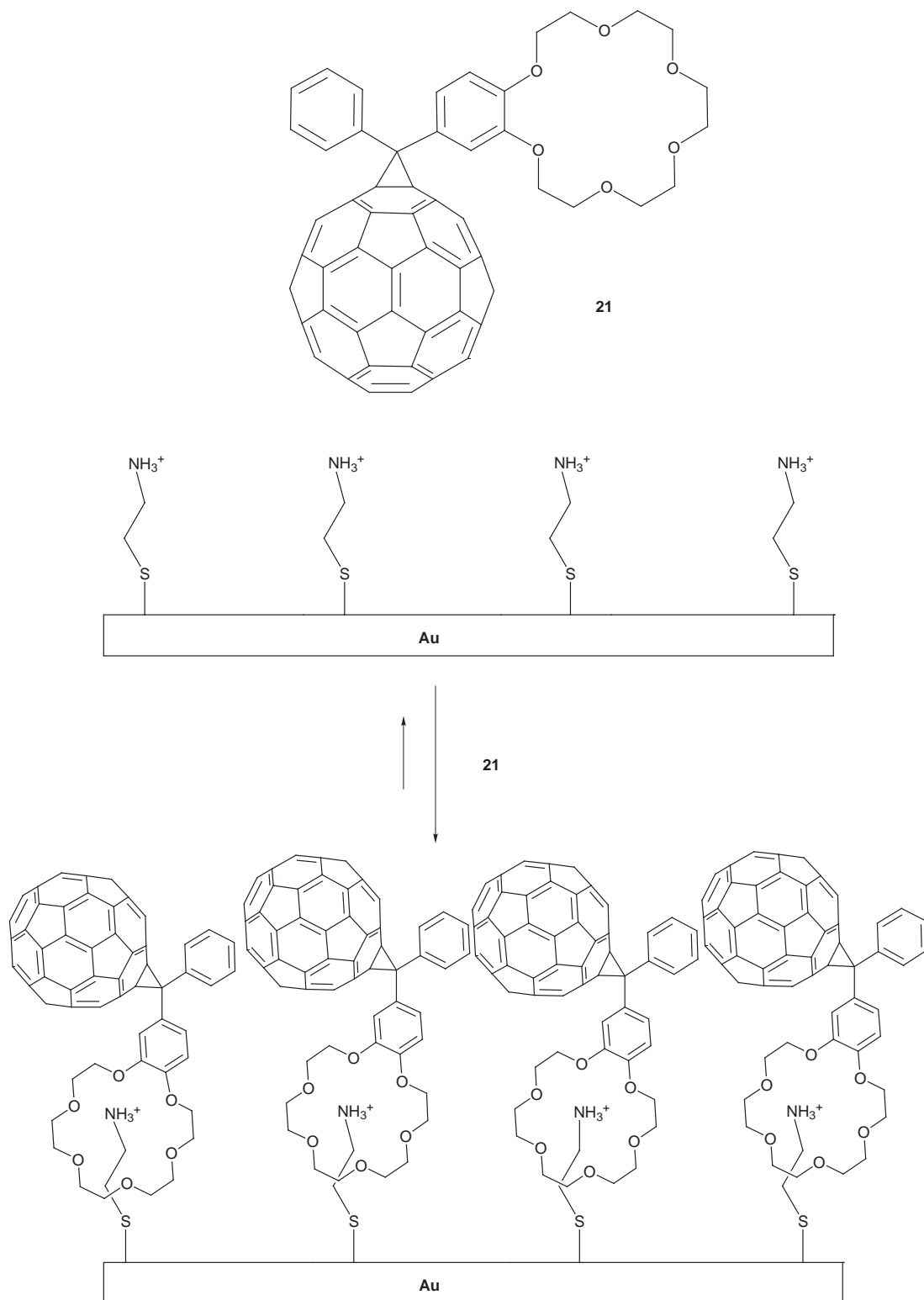


Fig. 16 The self-assembly of the crown ether- C_{60} conjugate **21** on a gold surface takes advantage of a unique combination of molecular ammonium ion recognition and formation of a self-assembled monolayer (SAM).⁴⁰

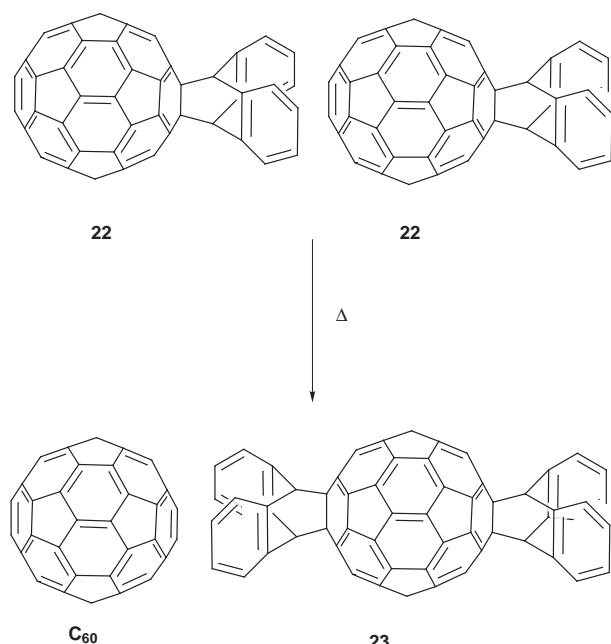
many cases display unique physical and chemical properties different from those of the individual molecular components. We would like to end this short account by illustrating how supramolecular concepts can be employed to achieve potential technological applications in fullerene chemistry.

There is an increasing demand for custom synthetic methodologies which generate highly functionalised C_{60} derivatives in a regio- and stereoselective manner. Such three-dimensional building blocks, in return, are needed for the construction of functional molecular and supramolecular fullerene-based materials. Template-directed synthesis has been recently shown to

provide selective access to fullerene derivatives featuring specific addition patterns, which are either not formed at all by stepwise, nontemplated conversions or are only obtained as a minor component in complex product mixtures.⁵

A fascinating example for such a template-directed synthesis was reported by Kräutler *et al.* who discovered a topochemically controlled regiospecific bis-functionalisation of C_{60} in the solid state.⁴¹ The crystalline monoadduct **22**, obtained by Diels–Alder addition of anthracene to C_{60} undergoes a regiospecific thermal transformation in the solid state to yield a 1 : 1 mixture of C_{60} and the *trans*-1 bis-anthracene adduct **23**. This reaction is

suggested to proceed by intermolecular anthracene transfer controlled by the crystal packing which provides the molding effect characteristic of a template (Scheme 2). In the crystal, the



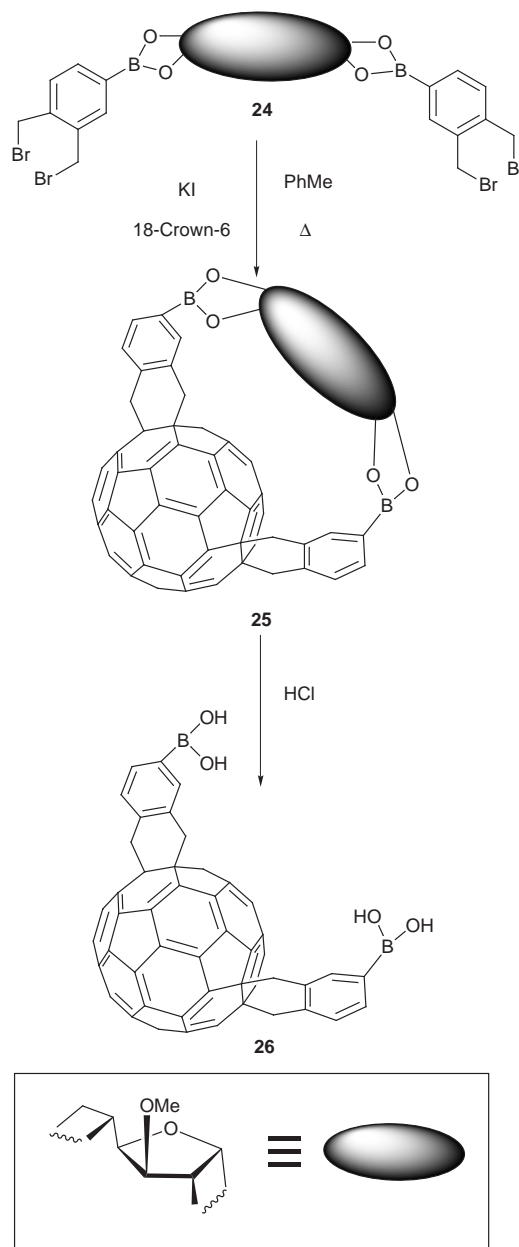
Scheme 2 Topochemically controlled reaction in the solid state between two molecules of the C_{60} -anthracene mono-adduct **22** to yield the *trans*-1 bis-anthracene adduct **23** and pristine C_{60} .⁴¹

two aryl rings in one molecule of **22** offer a cradle-like concave, electron-rich environment which accommodates part of the sterically and electronically complementary convex surface²¹ of the fullerene portion in a neighbouring molecule generating a perfect alignment of 6–6 bonds for intermolecular anthracene transfer. This protocol was the first reported regioselective synthesis of a C_{60} bis-adduct with a *trans*-1 substitution pattern.

Shinkai and co-workers⁴² elegantly applied the reversible formation of cyclic boronate esters between boronic acids and saccharides to achieve the regioselective template-directed multiple functionalisation of fullerenes. They reacted bis-boronate ester **24** in a Diels–Alder addition with C_{60} to afford regioselectively the *trans*-4 bis-adduct **25** (Scheme 3). The saccharide template was subsequently removed by treatment with aqueous HCl to produce the fullerene–boronic acid conjugate **26** which was found to retain the memory for the initial saccharide template.

Intermolecular interactions play an important role in HPLC separations of fullerenes and derivatives on designer stationary phases. Thus, Meyerhoff and co-workers described a stationary phase consisting of *meso*-(*p*-carboxyphenyl)-*meso*-triphenylporphyrin covalently attached to a silica gel support which has been used to separate C_{60} and C_{70} with straight toluene, a solvent in which the carbon spheres are reasonably soluble.⁴³ Furthermore, the same stationary phase, metallated with Zn^{II} or unmetallated, could be employed to separate the endohedral metallofullerenes $La@C_{82}$ and $Y@C_{82}$ from the mixture of empty fullerenes. The high selectivity obtained with this stationary phase is likely a result of van der Waals and electrostatic interactions between the spatially defined concave π -electron rich *meso*-tetraphenylporphyrin surface and the π -electron deficient fullerene spheres.⁴⁴

The photophysical properties of C_{60} are of great appeal for potential applications in biology and medicine. The fullerene–oligonucleotide conjugate **27** with a 14-meric oligodeoxynucleotide side chain was synthesised with the objective to exploit the efficient, fullerene-mediated photosensitisation of



Scheme 3 Regioselective functionalisation of C_{60} by double Diels–Alder addition of cyclic bis-boronate ester **24** and elimination of the saccharide template from *trans*-4 bis-adduct **25** under formation of bis-boronic acid **26**.⁴²

singlet oxygen for the sequence-specific cleavage of DNA strands.⁴⁵ The pendant oligonucleotide chain has the ability to bind either to complementary single stranded DNA *via* Watson–Crick base pairing under duplex formation or to complementary double stranded DNA *via* Hoogsteen base-pairing under triple helix formation. Similarly, triple helix formation occurs with complementary DNA possessing a hairpin structure (Fig. 17). Thus, three different complementary DNA fragments were used to test the photosensitising abilities of **27**: a single-stranded 20-mer; a duplex with 26 base-pairs and a 41-mer hairpin structure with 18 base pairs and a loop containing the remaining 5 bases. The bulky carbon sphere did not hamper complex formation and the associations formed with **27** were irradiated with a 1000 W xenon lamp at $\lambda \geq 310$ nm. Product analysis by gel electrophoresis showed that in all three cases photoinduced DNA cleavage took place only at selected sites. The cleavage sites were all located in those regions of the complexes which were expected from the known binding orientation of the fullerene–oligonucleotide conjugate to be close to the carbon sphere. Furthermore, cleavage nearly exclusively took place at

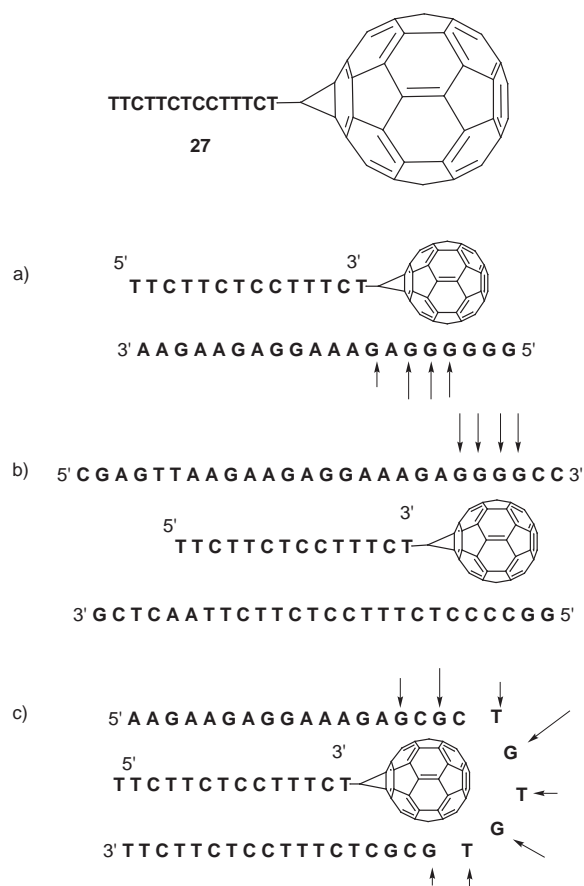


Fig. 17 Cartoon representation of the C_{60} -oligonucleotide conjugate **27** and its complexes with a) single stranded DNA, b) double helical DNA and c) DNA double helix with hairpin structure.⁴⁵ The arrows indicate the sites of cleavage upon irradiation and the length of the arrows represents the intensity of cleavage.

guanine bases, which is consistent with the involvement of singlet oxygen. In contrast, DNA cleavage by a fullerene derivative lacking the oligonucleotide strand did not show any side selectivity. Therefore, all findings are consistent with DNA strand cleavage following attack by singlet oxygen whose formation is photosensitized by the carbon sphere. However, an alternative pathway involving direct electron transfer from the guanine bases to the fullerene excited triplet state, followed by DNA cleavage could also be operating. The arrows in Fig. 17 indicate the sites of cleavage and the length of the arrows represents the intensity of the cleavage. These investigations suggested that well-designed fullerene derivatives could find application in the field of medicinal chemistry in general and photodynamic therapy in particular.

Finally, we would like to relate our efforts in the search of a new generation of redox sensors incorporating fullerene units. In all previously known fullerene-crown ether conjugates, such as **14**, the ionophore component is localised at a significant distance from the fullerene surface and cation complexation does not induce changes in the reduction potential of the carbon sphere. In contrast, a significant perturbation of the electronic structure of the C_{60} moiety was observed when a potassium ion was bound closely and tightly on the fullerene surface by ionophore (\pm)-**28** (Fig. 18).⁴⁶ This *trans*-1 bis-adduct was prepared by tether-directed Bingel macrocyclisation of C_{60} with a dibenzo-18-crown-6 bearing two appended malonate units. This reaction took place with high regioselectivity to yield the *trans*-1 bis-adduct (\pm)-**28**; in the presence of K^+ ions, which rigidify the 18-crown-6 tether by complexation, yields of isolated (\pm)-**28** reached up to 50%. The ionophoric properties of (\pm)-**28** were investigated using an ion-selective electrode membrane which revealed 1:1 complex formation with alkali

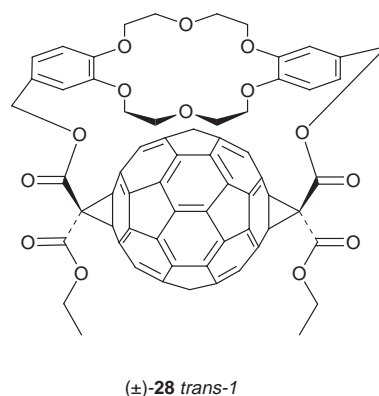


Fig. 18 The C_{60} crown ether conjugate (\pm)-**28** features a *trans*-1 bis-addition pattern.⁴⁶

metal ions, the most stable association occurring with K^+ ions. Cyclic voltammetric studies in $MeCN-CH_2Cl_2$ 1:1 (+0.1 M Bu_4NPF_6) were performed in order to elucidate the effect of cation complexation on the redox properties of (\pm)-**28**. Control studies with the free receptor were carried out in the presence of one equivalent of [2.2.2]cryptand to ensure that the crown ether was in its unbound state. Addition of an excess of KPF_6 to a solution of (\pm)-**28** resulted in a large anodic shift (90 mV) (from $E_{1/2} = -1.04$ V to $E_{1/2} = -0.95$ V vs. the ferrocene/ferricinium couple) of the first one-electron reduction potential associated with the fullerene core. This was the first ever observed effect of cation complexation on the redox properties of a fullerene core. The close proximity of a bound K^+ ion to the fullerene surface in (\pm)-**28** has in the meantime been confirmed by an X-ray crystal structure analysis. Further investigations are currently taking place in order to determine if the magnitude of the anodic shift depends substantially on the chemical nature of the cation; this issue is of great importance for the preparation of fullerene based sensors.

8 Conclusions

In this article, we have attempted to highlight the developments in fullerene supramolecular chemistry during the last decade.⁴⁷ Initially, unfunctionalised fullerenes were co-crystallised with a series of π -electron rich compounds leading to the formation of supramolecular complexes in the solid state. In the following, a diversity of inclusion complexes between pristine C_{60} or C_{70} and macrocyclic receptors such as γ -cyclodextrin or calixarenes—with 1:1 or 2:1 host-fullerene stoichiometries—were prepared in solution and in the solid state. The major driving force in all of these molecular recognition events is undoubtedly the van der Waals interactions between the large complementary surfaces of the binding partners. In addition with aromatic receptors such as calixarenes, electron donor-acceptor-type interactions are contributing to the stability of the formed inclusion complexes. A recent analysis of molecular electrostatic potentials²¹ revealed that these receptors have very negative molecular electrostatic potentials on their concave surfaces which should undergo favourable electrostatic donor-acceptor interactions with the convex fullerene surfaces which feature a large positive molecular electrostatic potential.

Research in supramolecular fullerene chemistry became greatly diversified with the advent of methods first for the mono and subsequently the regio- and stereoselective multiple functionalisation of the carbon spheres. This progress in covalent fullerene chemistry led to the development of spectacular functional supramolecular architectures. Examples are rotaxanes, catenanes, or molecular and supramolecular diads and triads modelling the photoinduced electron transfer processes at the photosynthetic reaction centres. All of these

molecular assemblies feature distinct properties as a consequence of the presence of the fullerene components. Thin films of fullerene materials have great promise to boast future real-life applications in sensorics and an increasing number of studies are hinting at potential technological applications of supramolecular fullerene science. It is clear that the examples discussed in this review represent nothing more than the first steps towards the design and preparation of fullerene molecular assemblies and supramolecular arrays which can display functionality at the macroscopic level. Nevertheless, they illustrate how carrying out innovative and imaginative research in fullerene chemistry—thanks to the spectacular properties that these carbon spheres possess—can prove to be of great utility in both material and biological sciences.

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