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Supramolecular Fullerene Materials

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Abstract. With its unique physical and chemical properties, buckminsterfullerene C_{60} is becoming an attractive functional component for incorporation into three-dimensional molecular assemblies and supramolecular arrays with potential applications as advanced materials. In this article, we discuss the self-organization of C_{60} derivatives into ordered fullerene thin films using *Langmuir* techniques. Subsequently, it is shown how metal ion complexation at a crown ether site in tight proximity to the fullerene surface perturbs the electronic structure of the carbon sphere. Covalently modified fullerenes are used for the construction of interlocked molecules, such as rotaxanes and catenanes, with fascinating topologies. Finally, the formation of a C_{60}-containing tetracationic cyclophane by Pt^{II}-directed self-assembly of two di(pyridyl)methanofullerene moieties is presented. These recent advances have become possible only through the development of a new synthetic methodology, which provides controlled, regioselective access to multiply functionalized fullerene derivatives.

Introduction

Our laboratory is actively involved in several projects exploring the design and preparation of advanced materials with unusual electronic, optical, or mechanical properties. In this article, we discuss in detail the development of supramolecular materials that rely on molecular fullerene components for displaying a specific function. All other efforts in our program at the materials interface have either been recently reviewed elsewhere or are not yet sufficiently advanced to be included in this brief account. In our most advanced projects, a diverse library of derivatives of tetraethynylethene (3,4-diethynylhex-3-ene-1,5-diyne, TEE) and 1,2-diethynylethene (hex-3-ene-1,5-diyne, DEE) are employed as versatile building blocks for carbon-rich molecular scaffolding [1]. These modular components have been applied to the synthesis of linear or cross-conjugated nanomaterials such as perethynylated dehydroannulenes, expanded radialenes, organometallic σ-acetylide species, poly(triacetylene)s, and donor-acceptor functionalized chromophores [1–3]. Poly(triacetylene)s [PTAs, $-(C{\equiv}C-CR{=}CR-C{\equiv}C)_n-$] are the third class of linearly conjugated polymers with a nonaromatic all-carbon backbone in the progression which starts with polyacetylene [PA, $-(CR{=}CR)_n-$] and poly(diacetylene) [PDA, $-(C{\equiv}C-CR{=}CR)_n-$], and ultimately leads to carbyne [$-(C{\equiv}C)_n-$] [4]. A comprehensive series of donor (D) and/or acceptor (A) substituted derivatives of DEEs and TEEs has been measured by third harmonic generation (THG) experiments, and the investigations on these one and two-dimensionally conjugated chromophores provided fundamental structure-property relationships which enhance substantially the predictability of third-order optical nonlinearities in organic materials [5].

In another avenue of research, the creation and modulation of functionality at the central core of dendrimers is explored. The dendritic shell can produce localized microenvironments analogous to those found at the active sites of enzymes and change profoundly the redox properties of electroactive cores such as porphyrins [6]. We also prepare dendritic rods with a PTA backbone, and recently, we demonstrated their properties as insulated molecular wires [7]. More recent work on templated advanced materials is situated at the organic/inorganic interface [8]. In a collaboration with *A. Baiker* (Laboratorium für Technische Chemie, ETHZ), aerogel materials are prepared around organic templates with catalytic, molecular recognition, and sensoric properties. In another collaboration with *R. Nesper* (Laboratorium für Anorganische Chemie, ETHZ), dendritic PTA molecular wires are developed as templates for the templated, size-selective growth of nanoporous transition-metal oxide materials such as the redox-active vanadium oxide nanotubes which have been recently discovered in the *Nesper* laboratories [9].

An important goal of supramolecular chemistry is the construction of large, but ordered molecular assemblies and supramolecular arrays with real-life device properties [10]. The unique physical and chemical properties of C_{60} – such as electronic absorption bands expanding throughout the entire UV/VIS wavelength region, efficient singlet-oxygen-sensitizing ability, strong electron-acceptor character, conductivity and low-temperature superconductivity of alkali-metal fullerides – make it an attractive component for molecular assemblies and supramolecular arrays [11]. Versatile synthetic methods are now available for the tailored multiple functionalization of C_{60} on the way to advanced materials [12][13].

Formation of Stable *Langmuir* Films by Amphiphilic Fullerene Derivatives

The self-organization of C_{60} into structurally ordered thin films has attracted substantial attention since such films could find practical applications as active surface layers in microsensors and optoelectronic devices [14]. In a first attempt to prepare stable *Langmuir* monolayers of covalent C_{60} derivatives, we investigated

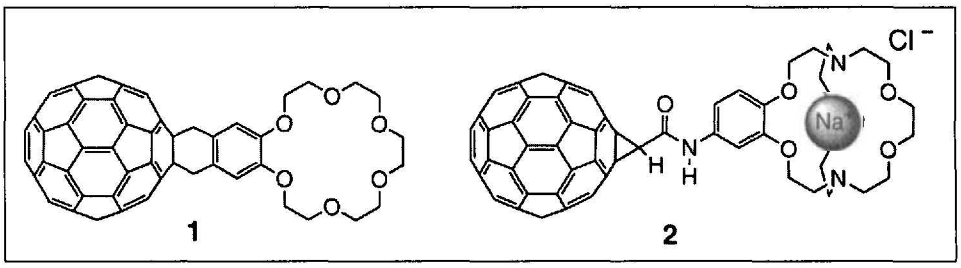

Fig. 1. *The crown-ether- and cryptate-containing amphiphilic derivatives of* C_{60} **1** *and* **2** *form* Langmuir *monolayers at the air-water interface, but also aggregate irreversibly in the absence of pressure*

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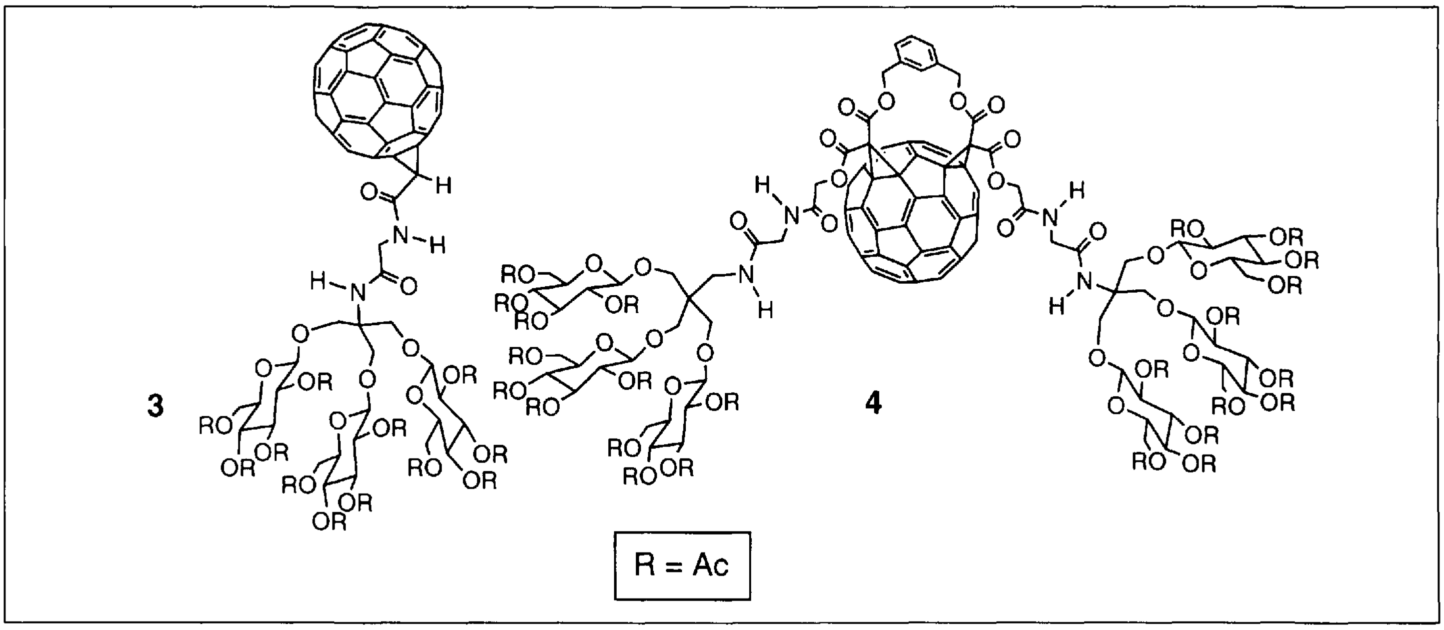


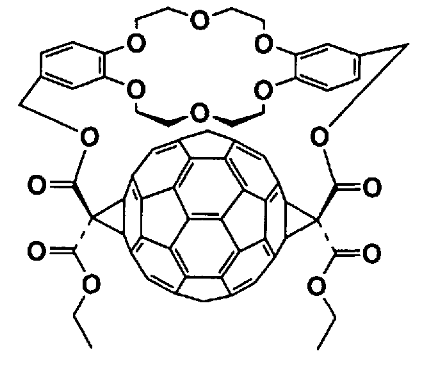
Fig. 2. *The fullerene-glycodendron conjugates* **3** *and* **4** *are the first amphiphilic fullerene derivatives which form* Langmuir *layers at the air-water interface that are* i) *monomolecular,* ii) *stable, and* iii) *form reversibly as evidenced by the lack of hysteresis in compression/expansion cycles*

the crown-ether fullerene conjugate **1** [15] in its free form and as K^+ complex, the cryptate-fullerene conjugate **2** [16], and an entire series of other amphiphilic fullerene derivatives. Compounds **1** and **2** (*Fig. 1*) both formed a monomolecular layer at the air-water interface, with a molecular area of A_0 around 80–90 Å² molecule⁻¹ which nicely corresponds to the expected molecular area in a C_{60} monolayer (86.6 Å² molecule⁻¹), assuming a tight hexagonal packing with a nearest center-to-center distance of 10 Å [17]. However, optical light microscopy before and after compression revealed that the films formed by free **1** and the cryptate **2** at the air-water interface already existed even before any pressure was applied, and irreversible compression/expansion cycles were observed. Most probably, the hydrophilic head group was not bulky enough to prevent the irreversible aggregation of the fullerene moieties in **1** or **2**, which is driven by the high cohesive energy of C_{60} (31 kcal mol⁻¹). We therefore targeted the synthesis of amphiphilic fullerene derivatives with head groups that are sufficiently bulky to keep the carbon spheres apart and prevent aggregation and three-dimensional crystallization in the absence of applied pressure.

To prevent fullerene aggregation, we attached carbohydrate-containing dendrons [18] as head groups to the carbon core and the resulting fullerene-glycodendron conjugates **3** and **4** (*Fig. 2*) were shown, in collaborative efforts, [19] to give layers at the air-water interface that are *i*) monomolecular, *ii*) stable, and *iii*) form reversibly as evidenced by the lack of hysteresis in compression and expansion cycles. The pressure/molecular area isotherms of **3** and **4** showed that the A_0 values are 96 and 220 Å² molecule⁻¹, respectively. Thus, the hydrophilic 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 fully reversible, stable monolayers of fullerene derivatives was observed at the air-water interface. The monolayers of **3** and **4** were both transferred onto quartz slides with the resulting films likely being of the X-type. In future work, transfer of these monomolecular layers to solid substrates could not only be used for the creation of ordered fullerene films (X-type LB transfer) with 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.

Modulation of Fullerene Redox Properties by Alkali-Metal Cation Complexation

In all previously known fullerene crown-ether conjugates, such as **1**, the ionophore component is located at a significant distance from the fullerene surface, and cation complexation does not induce changes in the reduction potentials of the carbon sphere [15][20]. In contrast, a significant perturbation of the electronic structure of the fullerene occurs when the bound cation is positioned closely and tightly on the fullerene surface such as seen in the recently prepared *trans-1* bis-adduct (±)-**5** (*Fig. 3*) [21]. This bis-adduct was obtained with high regioselectivity by the versatile, tether-directed *Bingel* macrocyclization [13] of C_{60} with a dibenzo[18]crown-6 derivative bearing two appended malonate groups.



(±)-**5** *trans-1*

Fig. 3. *In the* C_{60} *crown-ether conjugate* (±)-**5**, *the specific macrocyclic attachment places the dibenzo[18]crown-6 moiety in a close, tangential position with respect to the fullerene surface*

The ionophoric properties of (±)-**5** were investigated using a selective solvent polymeric membrane electrode, which revealed stable 1:1 complex formation with alkali-metal ions, in particular with K^+ ions. Cyclic voltammetric studies were performed in $MeCN/CH_2Cl_2$ 1:1 (+ 0.1M Bu_4NPF_6) in order to elucidate the effect of cation complexation on the redox properties of (±)-**5**. 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 excess KPF_6 to

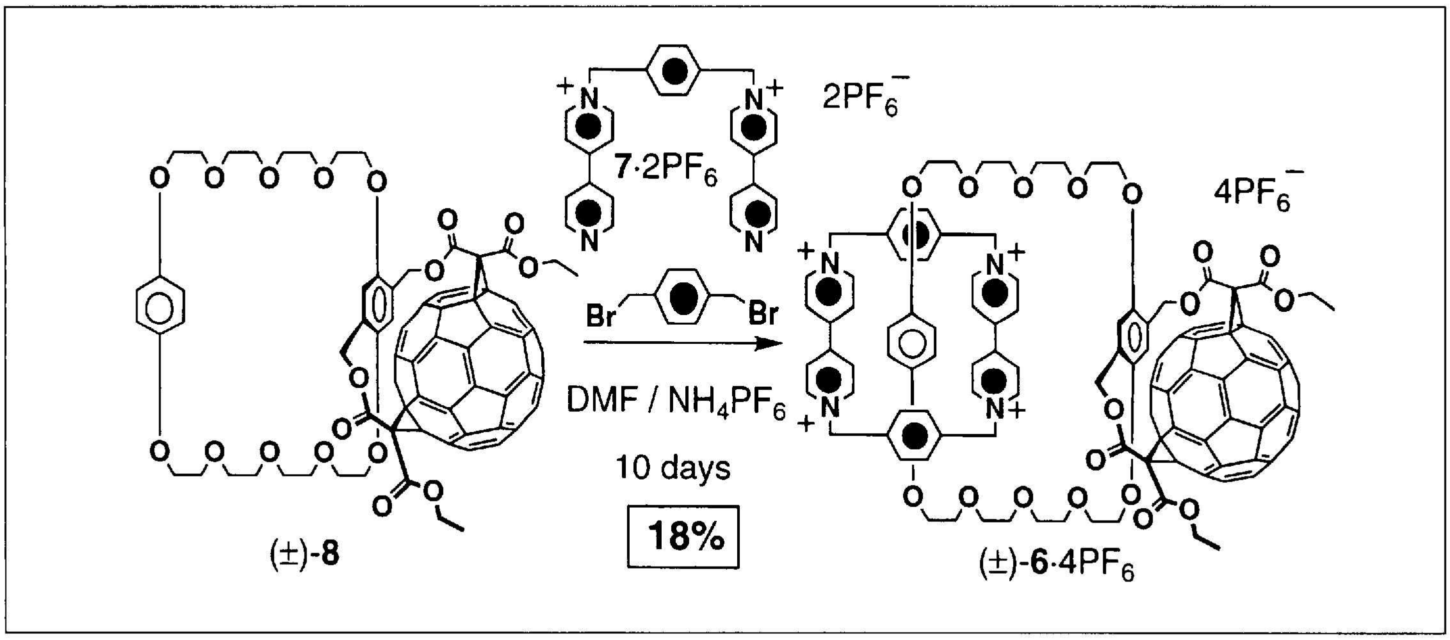


Fig. 4. *The self-assembly of the C_{60}-containing [2]catenane* (±)-**6**·*4PF*$_6$

a solution of (±)-**5** resulted in a large anodic shift (90 mV) of the fullerene-centered reduction processes, with the quasi reversible first one shifting from $E_{1/2} = -1.04$ V in free (±)-**5** to $E_{1/2} = -0.95$ V in the K^+ complex (*vs.* Fc/Fc^+ = ferrocene/ferricinium couple). This is the first ever observed effect of cation complexation on the redox properties of the carbon sphere in fullerene crown-ether conjugates. We are currently investigating whether the magnitude of the anodic shift depends significantly on the nature of the cation, which could provide access to interesting new generations of redox sensors. We expect that our *Bingel* macrocyclization reaction also represents a highly effective method for positioning other organic chromophores, such as porphyrins in sufficiently close proximity to the fullerene sphere to induce profound changes in the photophysical and redox properties of the carbon allotrope.

Interlocked Fullerene Structures: Catenanes and Rotaxanes

The modern construction of interlocked molecules such as rotaxanes and catenanes provides an outstanding example for template-directed synthesis [22]. These molecular assemblies are not only interesting because of their aesthetically appealing molecular architectures, but also due to their possible applications in molecular devices [10]. The introduction of fullerene components with interesting electronic and optical properties promises to further enhance the function and properties of such molecular assemblies.

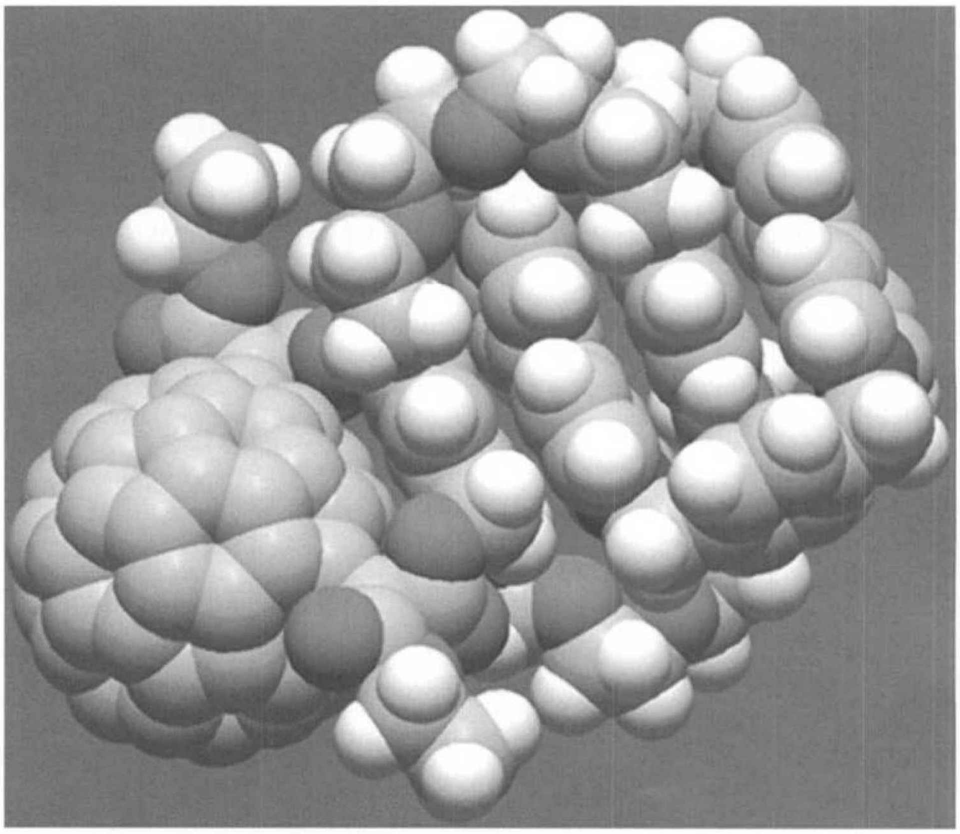


Fig. 5. *Molecular model of the [2]catenane* (±)-**6**$^{4+}$

The molecular recognition between π-electron-rich – *i.e.*, 1,4-dialkoxybenzene and 1,5-dialkoxynaphthalene – and π-electron-deficient – *i.e.*, paraquat – aromatic units has been exploited by *Stoddart* and coworkers for the self-assembly of a great variety of molecular assemblies and supramolecular arrays of unusual structure and function [10d] [22d,e]. In collaboration with this group, we prepared the C_{60}-containing [2]catenane (±)-**6**·$4PF_6$ in 18% yield by reaction of the bis(pyridylpyridinium) salt **7**·$2PF_6$ with 1,4-bis(bromomethyl)benzene in the presence of the crown ether (±)-**8** (*Fig. 4*) [23]. With the fullerene moiety acting as an electron acceptor, (±)-**6**·$4PF_6$ features an unprecedented intramolecular A-D-A-D-A stack (A = acceptor, D = donor), as portrayed by its space-filling model (*Fig. 5*).

The construction of a rotaxane with two fullerene stoppers provides an intriguing example of functional molecular fullerene components in interlocked molecules. *Sauvage* and coworkers have exploited the coordination geometry of 2,9-disubstituted 1,10-phenanthroline ligands around a Cu^I center to provide a number of supramolecular and molecular constructs with fascinating topologies, such as pseudorotaxanes, rotaxanes, [n]catenanes, and molecular knots [22a,b][24]. Oxidative coupling of the pseudorotaxane **9**·BF_4 with the di(alkynyl)methanofullerene **10** yielded the [2]rotaxane **11**·BF_4 in 15% yield (*Fig. 6*) [25].

A variety of interesting properties of this interlocked structure were discovered in collaborative work [26]. Whereas the presence of the Cu center did not affect the redox properties of the fullerene stoppers, the redox potential of the Cu^I/Cu^{II} couple in CH_2Cl_2 (+ 0.1M Bu_4NPF_6) was significantly altered in **11**·BF_4, as compared to other similar complexes lacking the fullerene units, shifting anodically by *ca.* 300 mV to +0.865 V (*vs.* the standard calomel electrode, SCE). The origin of this shift remains a matter of discussion. The strong electron-withdrawing effect of the fullerene stoppers could possibly destabilize the Cu^{II} state. More probably, however, the presence of the bulky carbon spheres alters significantly the solvation around the metal-ion center, which could induce the observed potential change. As previously observed for various bis(butadiynyl)methanofullerene derivatives [27], **11**·BF_4 undergoes reductive electrochemical polymerization during iterative cyclic voltammetry to give an insoluble, insulating film on the platinum cathode surface.

Detailed photophysical investigations showed that excited-state intercomponent processes take place in **11**·BF_4 [26]. The photophysical properties of rotaxane **11**·BF_4 differ significantly from those observed for related rotaxanes lacking fullerene components or for simple di(alkynyl)methanofullerenes. Thus, the excited singlet state localized on the fullerene and the metal-to-ligand charge-transfer (MLCT) excited state centered on the Cu^I complex are both quenched; correspondingly, both fullerene emission and the MLCT emission are missing in the rotaxane. Deactivation of the fullerene excited singlet state occurs by energy transfer to the Cu^I-complex moiety, which competes with intersystem crossing to the fullerene triplet state. The Cu^I-complex excited state is mainly quenched by electron transfer to form the charge-separated state consisting of the oxidized metal center $[Cu(phen)_2]^{2+}$ and the fullerene radical anion. The fullerene triplet state in the rotaxane is formed in reduced yield since it is also quenched by electron transfer to the same charge-separated state. In view of the weak population of the fullerene triplet, a dramatic decrease in the efficiency of the two fullerene stoppers to photosensitize the formation of singlet oxygen is measured, as compared to simple di(alkynyl)methanofullerenes. Direct evidence for the charge-separated state was not obtained, probably because it does not accumulate in solution as a result of the fact that the back electron-transfer reaction is faster than the forward reaction. However, clear indication of its existence came from the quenching of the triplet state of the fullerene stoppers and from the lack of singlet-oxygen sensitization.

The photophysical investigations of **11**·BF_4 revealed great promise of its molecular components for use in the construction of supermolecules capable of performing photoinduced electron transfer, especially since they are extremely stable under high-energy, long-duration laser irradiation. Their assembly in rigid supramolecular systems with longer, well-defined intercomponent distances is expected to promote long-lived charge separation, and this is currently under investigation [28].

Towards Large Supramolecular Fullerene Networks: Pt^{II}-Directed Self-Assembly of a Fullerene-Containing Cyclophane

The successful incorporation of fullerenes into multicomponent molecular systems such as the above-described rotaxanes and catenanes generated our interest in the construction of even more complex two- and three-dimensional systems. To achieve this objective, we exploited the Pt^{II}-directed self-assembly of multiden-

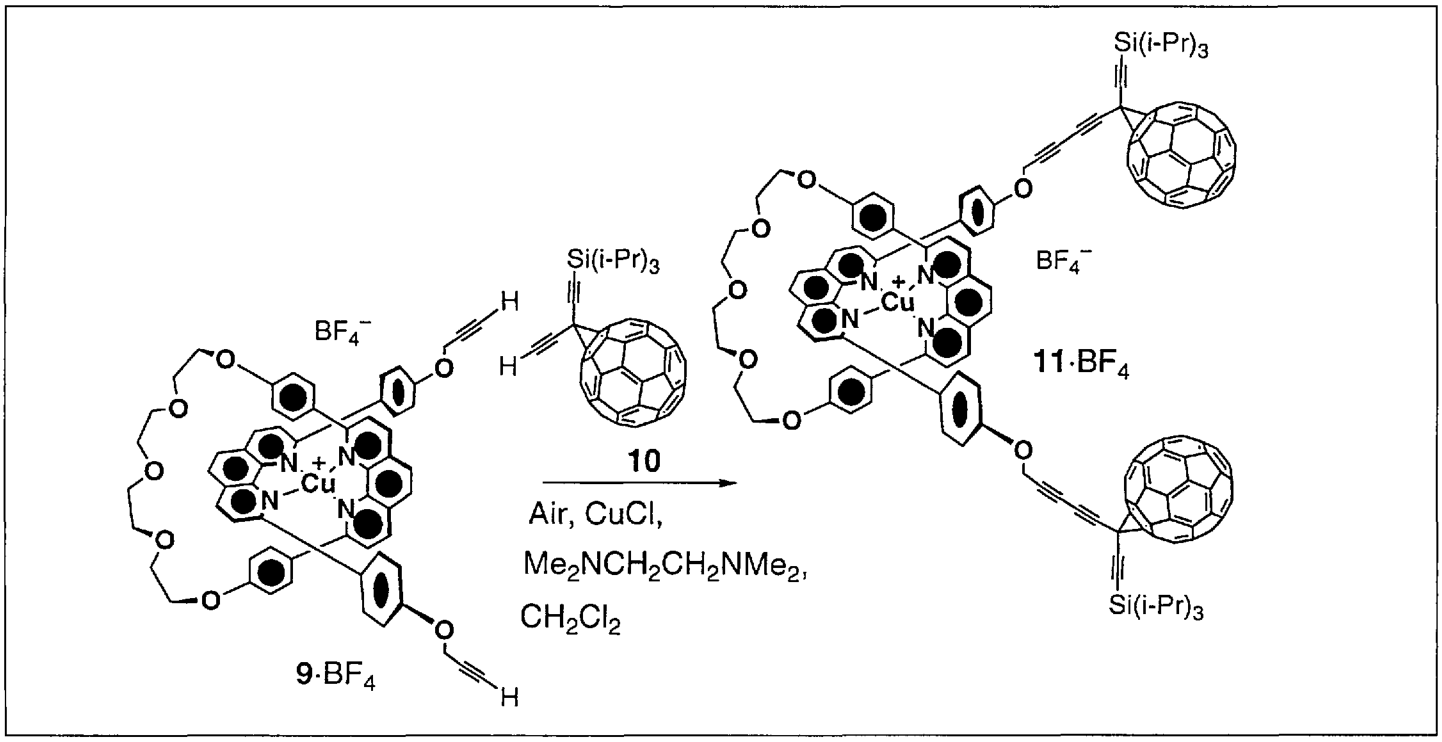


Fig. 6. *Synthesis of the C_{60}-stoppered [2]rotaxane* **11**·BF_4

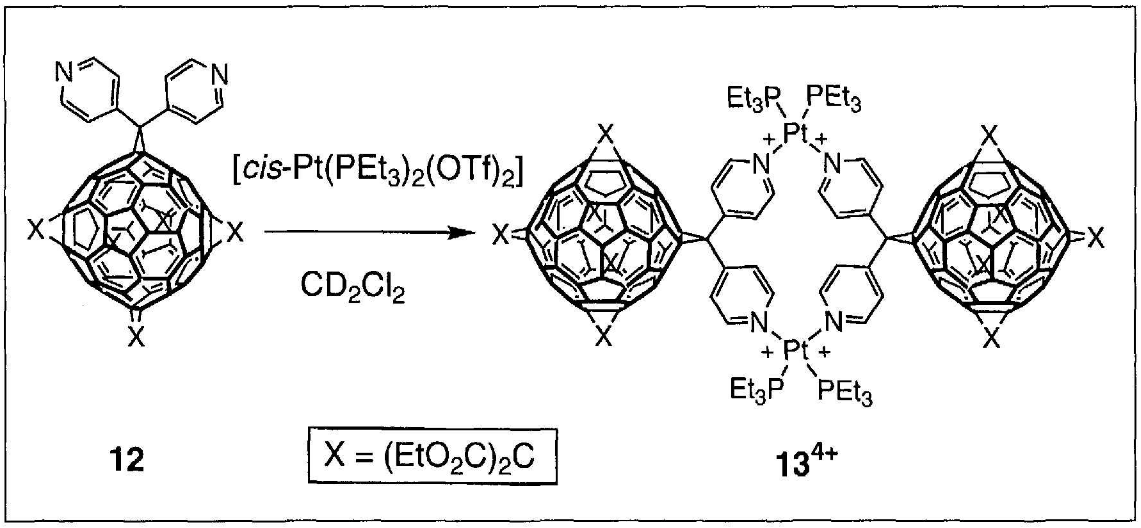


Fig. 7. *Self-assembly of the* C_{60} *hexakis-adduct* **12** *and* [cis-*Pt(PEt*$_3$*)*$_2$*(OTf)*$_2$*] to give the fullerene-containing cyclophane* $\mathbf{13}^{4+}$ *as triflate salt*

tate ligands which in the hands of *Fujita* [29] and *Stang* [30] has led to the formation of some spectacular molecular architectures consisting of multinanometer-sized polynuclear molecular squares and three-dimensional molecular objects. By mixing an equimolar amount of the C_{60} hexakis-adduct **12** and [*cis*-Pt(PEt$_3$)$_2$(OTf)$_2$], the tetracationic cyclophane $\mathbf{13}^{4+}$ was obtained quantitatively as the tetrakis-triflate salt (*Fig. 7*) [31]. The highly symmetrical (D_{2h}) solution structure of $\mathbf{13}^{4+}$ was determined by ^{1}H, ^{19}F, and ^{31}P-NMR as well as by IR spectroscopy. The X-ray crystal-structure analysis (*Fig. 8*) revealed that the four vertex atoms of the cyclophane, *i.e.*, the two Pt$^{\text{II}}$ centers and the two quaternary C-atoms of the di(pyridyl)methano groups, form a perfectly planar parallelogram at the cost of substantial angle strain. The quantitative yield of formation of $\mathbf{13}^{4+}$ underlines the potential of this powerful metal-directed self-assembly process [32] to selectively build up complex supermolecular fullerene arrays: upon replacing one or more of the diethyl-malonate addends in $\mathbf{13}^{4+}$ with di(pyridyl)methano groups, larger assemblies such as rods or two- and three-dimensional fullerene networks should become accessible.

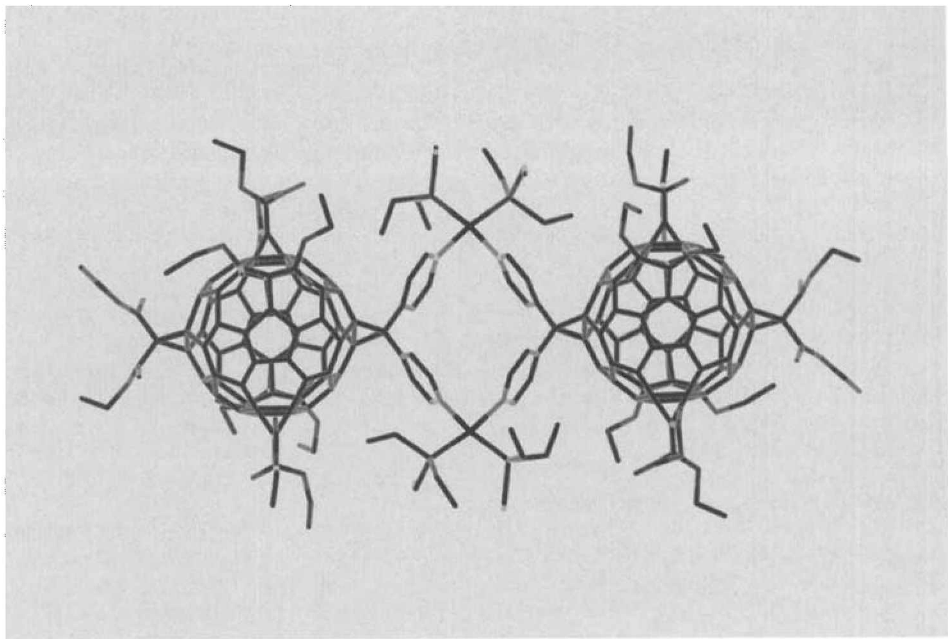


Fig. 8. *X-Ray crystal structure of the tetracationic cyclophane* $\mathbf{13}^{4+}$. The counterions and included solvent molecules are omitted for clarity.

Conclusions

When the first experimental evidence for the stability of buckminsterfullerene was obtained in 1985 [33], and, in particular, after the discovery of the bulk fullerene production process in 1990 [34], great hopes were raised that the new molecular carbon allotropes would rapidly find widespread applications as advanced materials in diverse technologies. These early hopes did not substantiate. At that time, it became clear that the covalent chemistry of fullerenes needed first to be developed [35] in a systematic way in order to provide efficient access to three-dimensional building blocks for potential subsequent materials applications. In the following, we worked out various routes to the regio- and stereoselective multiple functionalization of C_{60} [12][13], and these efforts paved the way to a rich diversity of complex and highly functional fullerene building blocks for three-dimensional molecular scaffolding. With these compounds in hands, focus on advanced fullerene materials and technologies became worthwhile again and the work described here can be viewed as a first step in this direction. Photochemical devices for conversion of solar energy into fuels and electricity, chemical and electrochemical sensors, storage and manipulation of information at the molecular level, microfabrication of processable polymeric fullerene films with insulating or conducting properties are some of the technological applications of covalent fullerene derivatives that we foresee being successfully developed in the coming years.

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