

# Synthesis of a Fullerene[60] Cryptate and Systematic Langmuir–Blodgett and Thin-Film Investigations of Amphiphilic Fullerene Derivatives

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**Abstract:** The synthesis of the first fullerene cryptate **7** with a sodium ion bound to a benzo[2.2.2]cryptand covalently attached to a methanofullerene[60] is described. The amphiphilic properties of **7** as well as of a variety of other covalent fullerene derivatives with polar functional groups and the ability of these compounds to form Langmuir monolayers at the air–water interface were investigated in a systematic study. Among these derivatives are Diels–Alder adducts of

C<sub>60</sub> and methanofullerenes, four of which are fullerene C-glycosides. The films at the water surface were characterized by their surface pressure versus molecular area isotherms, compression and expansion

cycles, and optical light microscopy. UV/Vis spectroscopy and small-angle X-ray diffraction (SAXS) were employed for LB film characterization on solid substrates. Parameters influencing the spreading and monolayer character include a) polarity, b) balance of hydrophobicity to hydrophilicity, c) size and bulkiness of the polar groups attached to the fullerene, and d) presence of aromatic residues in these groups.

## Keywords

amphiphiles · C-glycosides · cryptates · fullerenes · ionophores · Langmuir–Blodgett films

## Introduction

Fullerenes, in particular the readily available C<sub>60</sub>, possess a wide range of physical and chemical properties that make them interesting building blocks for supramolecular assemblies and new materials. Among their prominent properties are the presence of an extended conjugated electron system with electrophilic character, the ability to exhibit varying conductivity upon doping with alkali metals,<sup>[1]</sup> and optical limiting when irradiated with laser light.<sup>[2]</sup> To exploit these properties it may be favorable to incorporate the fullerenes in layer structures, which can be obtained by self-assembly from solution<sup>[3]</sup> or by Langmuir–Blodgett (LB) technique.<sup>[2b,4]</sup> Possible applications of such thin ordered molecular films are surface coatings to provide bulk materials with the properties of the coating (e.g.,

color, conductivity) or to protect the bulk from its environment (e.g., oxidation, corrosion, mechanical stability). This has the advantage of employing only a small quantity of the surface coating material, which may be much more expensive than the bulk material. Further applications of layered fullerene-containing materials are active surface layers in microsenors<sup>[5]</sup> or new materials in optoelectronic devices<sup>[6]</sup> (hybrid electronics) that can be processed by classical lithographic techniques, known from microelectronics and chip manufacturing. In microsenors, specific interactions of the surface material with the ambient environment induce a change in the surface layer, which is transduced to the core of the sensor and transformed into a signal for further processing. First examples of such devices are a surface acoustic wave (SAW) resonator microsenor for organic solvent vapors<sup>[3a]</sup> and a glass fiber waveguide with optical limiting characteristics.<sup>[2b]</sup>

The large number of publications shows the strong interest in fullerene films,<sup>[2b,4,7]</sup> but so far all attempts to build up defined LB multilayers of bare fullerenes failed, and monolayers of pure C<sub>60</sub> or C<sub>70</sub> at the air–water interface are difficult to achieve.<sup>[4c–r,7b–d]</sup> The experiments point towards either modifying the fullerene core with a hydrophilic moiety (head group), thus introducing an amphiphilic character, or sufficiently embedding the unmodified fullerenes into a matrix monolayer. Good spreading results were obtained with matrix monolayers like azacrowns<sup>[4a]</sup> or amphiphilic polymers.<sup>[4b]</sup> Modifications of the fullerene core with hydrophilic addends lead to a significant improvement of the spreading behavior, as shown for addends such as a benzocrown derivative,<sup>[7a]</sup> a triethylene glycol chain,<sup>[7e]</sup> an *N*-acetyl pyrrolidine unit,<sup>[4c,4y]</sup> and dodecyl-

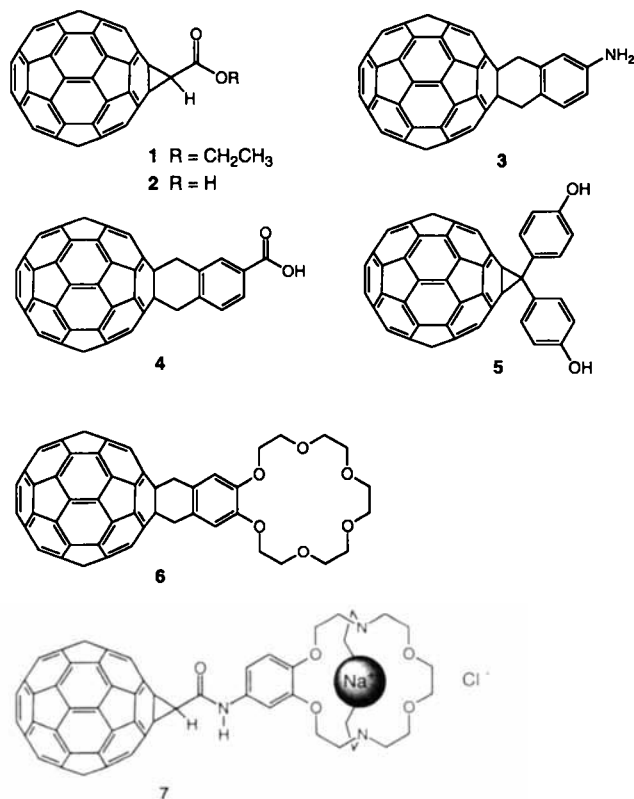
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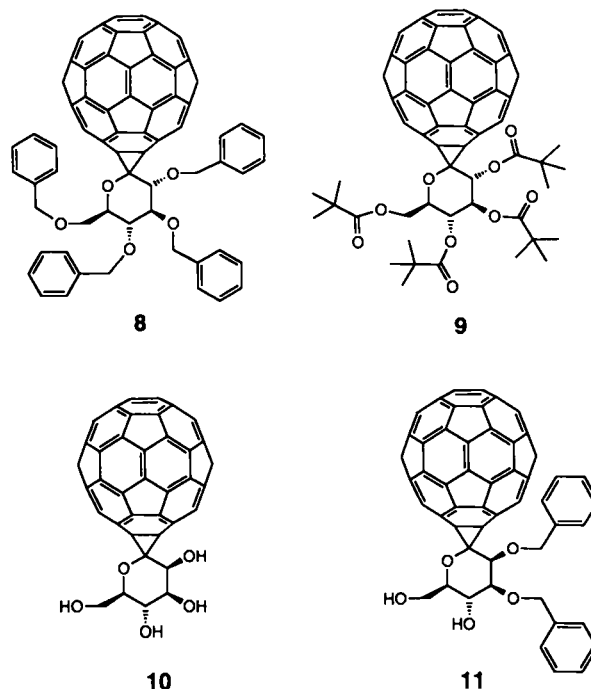
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amine.<sup>[7d]</sup> The disadvantage of covalently attaching a hydrophilic head group is the modification of the fullerene chromophore, which alters its physical and chemical properties. On the other hand, it could be shown that at low degree of functionalization the UV/Vis absorptions,<sup>[8]</sup> the redox characteristics,<sup>[9]</sup> and photophysical properties<sup>[10]</sup> of fullerenes do not change significantly. From these results and general considerations about the effect of head-group structure on the spreading behavior in classical amphiphiles, it became obvious that there was a need for a systematic study of the amphiphilic character in a variety of monofunctionalized buckminsterfullerenes.

Here we report on the amphiphilic character of fullerene monoadducts prepared by cyclopropanation of C<sub>60</sub> with diazo compounds (**1**,<sup>[8a]</sup> **2**,<sup>[11]</sup> **5**,<sup>[12]</sup> and **7**) or diazirines (**8–11**)<sup>[13]</sup> and by Diels–Alder addition of *ortho*-quinodimethane intermediates<sup>[14a]</sup> (**3**,<sup>[14b]</sup> **4**,<sup>[14c]</sup> and **6**<sup>[7a]</sup>). The advantages of these two synthetic approaches<sup>[15]</sup> are their general applicability and the production of defined and stable products in larger quantities. The synthesis of the first fullerene cryptate **7** with complexed Na<sup>+</sup> ion is described.



Surface pressure versus molecular area ( $\Pi/A$ ) isotherms of fullerene derivatives **1–7** were measured to study the relation between head-group structure and spreading behavior. To explore in more detail the influence of size and chemical nature of functional groups and aromatic residues in the head group, the four C-glycosides of C<sub>60</sub> **8–11** carrying differentially protected monosaccharide moieties were investigated. Optical microscopy investigations of the monolayers at the air–water interface and small-angle X-ray diffraction (SAXS) measurements on transferred multilayers helped to quantify the quality of the layer structures. Furthermore, LB transfer to substrate surfaces specifically modified with aliphatic and aromatic silanes was employed to test the concept of favorable interactions between the fullerene cores and aromatic rings.<sup>[7a,16]</sup>

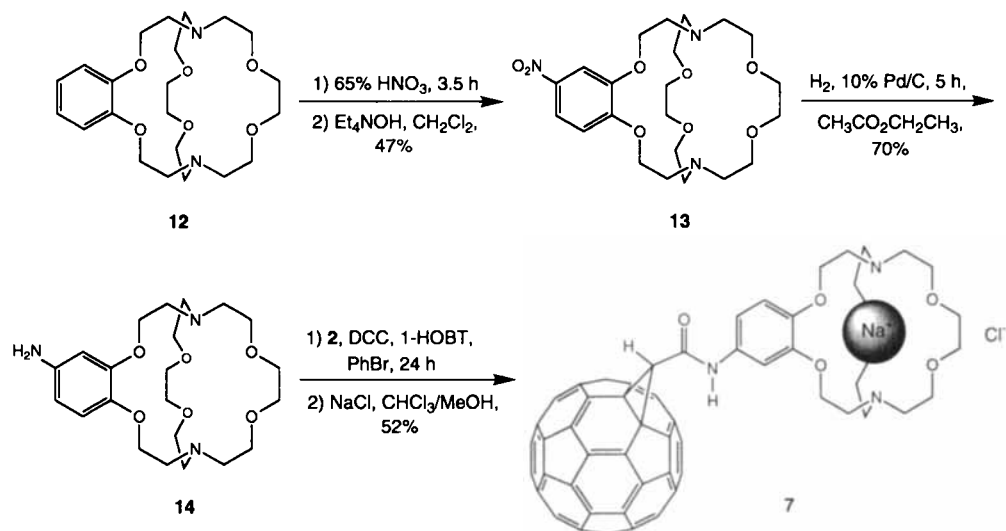


## Results and Discussion

**Synthesis of Fullerene[60] Cryptate 7:** The free crown ether **6** and its K<sup>+</sup> complex were the first functional fullerene derivatives to yield promising results in LB monolayer formation, in terms of the agreement between experimentally observed and calculated surface requirements for the carbon spheres in the monolayer.<sup>[7a]</sup> This encouraged us to prepare cryptate **7** with a larger, more hydrophilic head group. Alkali metal cryptates show higher thermodynamic stability and slower complexation kinetics than the corresponding crown ether complexes,<sup>[17]</sup> and this should enhance the stability of the complex when spread on the aqueous subphase. In addition, the fact that the size of the cationic cryptate moiety is comparable to that of the fullerene sphere should prevent aggregation of the latter in the absence of applied surface pressure.

For the preparation of **7** (Scheme 1), cryptand **12** was nitrated with 65% HNO<sub>3</sub> to give **13** in 47% yield. Catalytic hydrogenation (H<sub>2</sub>, 10% Pd/C)<sup>[18a]</sup> afforded the amino cryptand **14** as a pale yellow oil in 70% yield. The free amine **14** is sensitive to air and light and darkens upon standing,<sup>[18b]</sup> but it could be fully characterized, and storage under vacuum in the dark was possible for several months. Finally, fullerene cryptate **7** was obtained by reaction of amine **14** with the methanofullerene carboxylic acid **2**<sup>[11]</sup> under peptide coupling conditions followed by treatment of the product with NaCl.

The separation of the free precursor cryptands **13** and **14** from their alkali metal complexes, which are always formed as by-products during the reaction and the workup procedures, was readily achieved owing to the different solubilities of the oily free ionophores and the crystalline complexes in organic solvents. In contrast, the separation of pure free fullerene cryptand from traces of its alkali metal complexes was very difficult. The presence of sodium was confirmed analytically by atomic absorption spectroscopy (Na) as well as by <sup>23</sup>Na and <sup>1</sup>H NMR spectroscopy, and that of chlorine and sulfur by elemental analysis. The formation of the cryptates could not be prevented even when the Al<sub>2</sub>O<sub>3</sub>, required as stationary phase in the chromatographic workup of the amide coupling reaction, was first rinsed



Scheme 1. Synthesis of the fullerene cryptate **7**. DCC = 1,3-dicyclohexylcarbodiimide; 1-HOBT = 1-hydroxybenzotriazole.

with a solution of [2.2.2]cryptand to remove traces of alkali metal cations. Attempts to separate the fullerene cryptand from its complexes by chromatography or crystallization remained unsuccessful. A sample of the cryptand that was pure by  $^1\text{H}$  NMR could be obtained by statistical distribution of the alkali metal ions between a mixture of fullerene cryptand/cryptates and an excess of **12**, with subsequent removal of the mixture of **12** and its cryptates.

The  $^1\text{H}$  NMR spectra of cryptate **7** and the corresponding free cryptand differ strongly. The signal of the cyclopropane methine proton in **7** ( $\delta = 5.88$ ) is shifted downfield by 0.96 ppm relative to that in the spectrum of the free cryptand ( $\delta = 4.92$ ). Furthermore, the amide N–H resonance in **7** ( $\delta = 11.9$ ) is strongly shifted downfield from its position ( $\delta = 8.5$ ) in the free cryptand spectrum. These large differences in chemical shift cannot be rationalized by changes in conjugation across the benzene ring as a result of ion complexation. Possibly, the amide group adopts different orientations in the free and the complexed ionophore. This could influence the position of the methano bridge C–H resonance and bring the N–H proton into different orientations with regard to the strong paramagnetic ring currents present in the fullerene pentagons.<sup>[8a,19]</sup> Intermolecular hydrogen bonding provides another explanation for the observed spectral differences. Although hydrogen bonding between the amide groups of two fullerene ionophores does not seem highly probable owing to the sterically buried position of these groups between the bulky carbon sphere and the equally bulky ionophore head group, hydrogen bonding of the amide N–H to the  $\text{Cl}^-$  counterion is sterically possible. This effect could shift the N–H resonance downfield by several ppm and possibly also influence the location of the cyclopropane methine proton signal.

**$\Pi/A$  Isotherms of  $\text{C}_{60}$  and  $\text{C}_{70}$ :** All spreading and transfer experiments were carried out at a subphase temperature of  $20^\circ\text{C}$ . Pure  $\text{C}_{60}$  and  $\text{C}_{70}$ , respectively, spread from  $10^{-4}\text{M}$  solutions in toluene, show cross-sectional areas of less than  $30\text{ \AA}^2\text{ molecule}^{-1}$  in the  $\Pi/A$  isotherms at surface pressures above  $5\text{ mN m}^{-1}$  (Fig. 1) and a collapse pressure ( $\Pi_c$ ) around  $60\text{--}70\text{ mN m}^{-1}$  (Table 1, p. 249).

Extrapolating the linear part of the curve to  $\Pi = 0\text{ mN m}^{-1}$  yields a hypothetical cross-section per molecule at vanishing surface pressure,  $A_0$ .<sup>[4c]</sup> The expected molecular surface requirement in a  $\text{C}_{60}$  monolayer should be at least  $86.6\text{ \AA}^2$ , assuming a

tight hexagonal packing of the carbon spheres with a nearest center-to-center distance of  $10\text{ \AA}$ .<sup>[20]</sup> The measured values of  $A_0 \approx 28\text{ \AA}^2\text{ molecule}^{-1}$  for  $\text{C}_{60}$  and  $A_0 \approx 23\text{ \AA}^2\text{ molecule}^{-1}$  for  $\text{C}_{70}$  indicate formation of an undefined film of three-dimensional fullerene aggregates which have also been seen by other groups.<sup>[4c–h]</sup> Attempts to transfer such rigid films to solid substrates were difficult and did not result in defined multilayer structures.

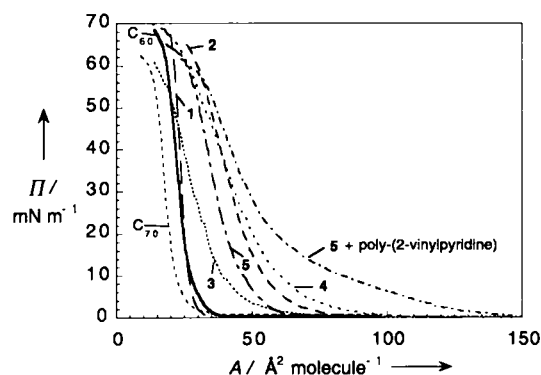


Fig. 1.  $\Pi/A$  isotherms ( $20^\circ\text{C}$ ) of  $\text{C}_{60}$ ,  $\text{C}_{70}$ , and fullerene compounds **1**, **2**, **3**, **4**, **5**, and **5** + poly(2-vinylpyridine).

Aggregates of  $\text{C}_{60}$  can easily be distinguished from individually dispersed fullerene molecules by their UV/Vis spectra (Fig. 2). The spectra were obtained by sonicating a saturated  $\text{C}_{60}$  solution in chloroform containing  $\text{C}_{60}$  crystals at the bottom of a cuvette. The supernatant liquid initially was clear violet and showed the normal absorption bands of the molecular-disperse solution of buckminsterfullerene.<sup>[21a]</sup> Upon sonication it turned into a turbid brown dispersion of  $\text{C}_{60}$  aggregates (from the sediment) with a broad band between  $400$  and  $480\text{ nm}$  in the UV/Vis spectrum, identical to that of solid  $\text{C}_{60}$ .<sup>[21b]</sup> Such suspensions were also observed in  $n$ -hexane; they are stable for several weeks. This new absorption band ( $400\text{--}480\text{ nm}$ ) of solid  $\text{C}_{60}$ , which is absent in the solution, might be due to a break of the  $I_h$  symmetry of the molecular electronic structure when the molecule is surrounded by its fullerene neighbors on their defined lattice sites in the crystal.<sup>[21c]</sup> By this symmetry reduction, electronic transitions become allowed which were forbidden by

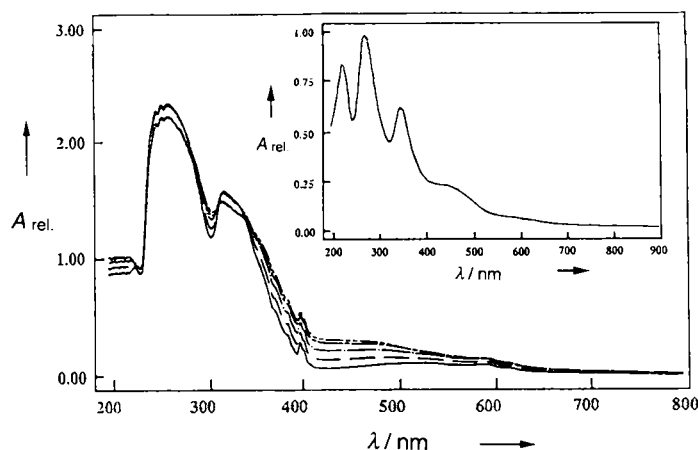


Fig. 2. UV/Vis spectra of pure  $C_{60}$  in a saturated  $CHCl_3$  solution after 5 s (—), 10 s (— · —), 30 s (---), and 60 s (····) sonication time. The solid line is the spectrum of the clear violet solution before sonication. The inset shows the spectrum of a thin solid  $C_{60}$  film.

symmetry in the solvated state with full  $I_h$  symmetry. Even though the individual  $C_{60}$  molecules rotate fast on their lattice sites at room temperature, electron polarization in the conjugated  $\pi$  system is much faster, and thus a single carbon sphere always "sees" and is influenced electronically by its  $C_{60}$  neighbors.

The fact that the experimentally observed surface requirements are too small by a factor of almost three and that the fullerenes form stable van der Waals crystals, which hardly dissolve in organic solvents, leads to the conclusion that the carbon molecules tend to aggregate at the air–water interface rather than forming a monomolecular layer. To overcome this aggregation tendency on the water surface and to provide the fullerene with an amphiphilic character,  $C_{60}$ -derivatives with polar addends seem suitable.

**$\Pi/A$  Isotherms of Fullerene Derivatives 1–7:** Parameters that determine the amphiphilic character and can be tuned by choosing different addends include a) polarity, b) balance between hydrophobicity and hydrophilicity, and c) size and bulkiness of the head group. In the course of the experiments, it was found that the aromatic or aliphatic character of head-group substituents also strongly influences the spreading behavior. A polar and hydrophilic head group is responsible for a strong interaction with the aqueous subphase, forcing the molecules towards the water surface into a two-dimensional arrangement. A sufficient in-plane size and bulkiness of the head group (larger than  $C_{60}$ ) parallel to the water surface should keep the fullerene cores apart and prevent aggregation and three-dimensional crystallization. Aliphatic substituents appear to be more suitable than aromatic ones since they cannot show attractive intermolecular  $\pi$ – $\pi$  interactions among themselves and with the fullerene chromophore.

Compounds 1–7, all monofunctionalized  $C_{60}$  derivatives, were spread from dilute solutions of about  $10^{-4}$  M concentration. The various derivatives required different solvents but, in order to exclude possible solvent effects, we studied the spreading behavior of palmitic acid as reference in all solvents considered:  $CHCl_3$ ,  $CH_2Cl_2$ , toluene, benzene, and THF. Also  $C_{60}$  and  $C_{70}$  were spread from toluene, benzene, and  $CHCl_3$ , and 1 from toluene and  $CHCl_3$ . No significant difference in spreading behavior was observed under these various experimental conditions.

In the following discussion, the experimental parameter  $A_0$  is evaluated as a measure for the ability of derivatives 1–7 to form a two-dimensional close-packed monolayer of the carbon spheres at the air–water interface with the addends ideally oriented perpendicularly into the water subphase. This arrangement is assumed to generate the most stable monolayer.

The head group of 1 is a small ethyl ester of rather low polarity. The resulting  $\Pi/A$  isotherm (Fig. 1) is very similar to that of pure  $C_{60}$ , leading to the same  $A_0 \approx 28 \text{ Å}^2 \text{ molecule}^{-1}$  and  $\Pi_c \approx 65 \text{ mN m}^{-1}$ . The weak polarity of the ester group is not sufficient to pull the molecule to the water surface and prevent 3D aggregation. The ester moiety seems to be small enough to fit into the interstitial sites between the fullerene molecules without significantly disturbing the crystal lattice. Hence the resulting aggregated films are as rigid and stable as observed with pure  $C_{60}$  and  $C_{70}$ .

In the free acid 2, the spreading behavior is dramatically improved compared to the ester 1. The surface requirement increases to  $A_0 = 54 \text{ Å}^2 \text{ molecule}^{-1}$ , which is almost twice the value of 1. This improvement can be easily explained by the higher polarity and hydrophilicity of the free carboxylic acid and its ability to be deprotonated or to form hydrogen bonds on contact with the water. However, the  $COOH$  group is even smaller than the  $COOCH_2CH_3$  moiety of 1 and should also fit into the interstices between the fullerene cores in the crystal. Therefore it does not seem to prevent the fullerene aggregation completely, as can be seen from the surface requirement which should be  $>86 \text{ Å}^2 \text{ molecule}^{-1}$  for a monomolecular layer.

Highly polar and hydrophilic head groups are also present in the amino derivative 3 and the carboxylic acid 4. These head groups possess the ability to form hydrogen bonds and can be protonated (in 3) or deprotonated (in 4) on contact with the aqueous subphase. In contrast to 1 and 2, derivatives 3 and 4 with their tetrahydronaphthalene moieties possess much bulkier head groups. The observed surface requirements,  $A_0 = 40 \text{ Å}^2 \text{ molecule}^{-1}$  for 3 and  $A_0 = 60 \text{ Å}^2 \text{ molecule}^{-1}$  for 4, do indeed provide better results compared to pure  $C_{60}$ , but these numbers are still far from a physically relevant value for a monolayer. Variations of the pH of the subphase between pH = 5 and 8 did not significantly change the measured isotherms.

Compound 5 has two phenolic residues with the hydroxyl groups separated by approximately 9 Å. On a pure water subphase, the measured cross-sectional area is  $A_0 = 45 \text{ Å}^2 \text{ molecule}^{-1}$ , which can be increased to  $A_0 > 65 \text{ Å}^2 \text{ molecule}^{-1}$  (extrapolation of the steep part of the isotherm) by adding poly-(2-vinylpyridine) ( $10 \text{ mg L}^{-1}$ ) to the aqueous phase. The polymer is surface-active and presumably favors monolayer formation by hydrogen-bonding interactions between its pyridine N atoms and the phenolic OH groups of 5.

The first promising results were obtained with the crown ether 6, which gave an experimental molecular cross-sectional area of  $A_0 = 80 \text{ Å}^2 \text{ molecule}^{-1}$  on pure water (Fig. 3).<sup>[7a]</sup> When spread on a 1 M KCl subphase, 6 required an even larger area ( $A_0 > 90 \text{ Å}^2 \text{ molecule}^{-1}$ ) owing to complexation of potassium ions inside the crown and the resulting increase in hydrophilicity. The measured surface requirement points towards the existence of a real monolayer at low surface pressure, stabilized by the bulky and hydrophilic crown-ether head group, which can complex alkali metals.

The monolayer of free 6 on water was investigated by optical light microscopy before and after compression, and it was found that the film already existed in a condensed state even before any surface pressure was applied. In Figure 4a, the border between the uncompressed monolayer (upper bright half) and the plain

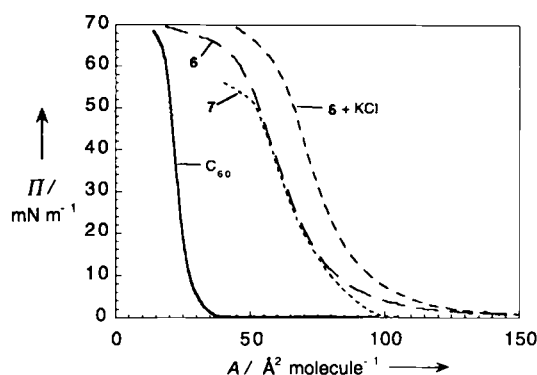


Fig. 3.  $\Pi/A$  isotherms (20 °C) of pure  $C_{60}$ , crown ether **6** on pure water and on a 1 M KCl solution, and of sodium cryptate **7**.

water surface (lower darker region) can be seen as a result of the strong self-aggregation of **6**. After one compression to 5 mN m<sup>-1</sup> and expansion, the film reveals severe damage, like cracks (dark regions) and wrinkles of collapsed film (white stripes) (Fig. 4b). Apparently the crown-ether moiety is not bulky enough to prevent contact between neighboring fullerenes in the plane when the film is compressed. Once the  $C_{60}$  cores are in contact with each other, they irreversibly aggregate and the monolayer does not expand any more.

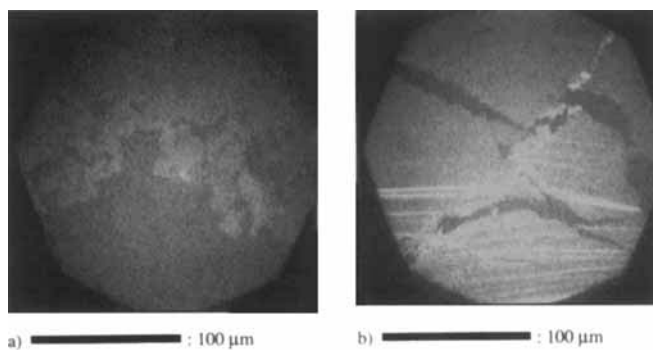


Fig. 4. Optical light microscopy pictures of a floating film of fullerene crown ether **6**. a) before and b) after compression to  $\Pi \approx 5$  mN m<sup>-1</sup> followed by expansion.

The sodium cryptate **7** shows the same course as **6** for the linear part of the isotherm ( $A_0 = 80$  Å<sup>2</sup> molecule<sup>-1</sup>), but a considerably sharper increase in the low surface pressure region. It forms a monomolecular layer with a molecular area of  $A = 95$  Å<sup>2</sup> molecule<sup>-1</sup> at the onset of surface pressure. The very hydrophilic cationic head group is similar in size to the  $C_{60}$  core, but it is still not able to prevent the aggregation, as can be seen by irreversible compression/expansion cycles and under the microscope where the same features as for **6** are found. Furthermore, the floating film is less stable than those formed by compounds **1–6**. This is indicated by the lower collapse pressure of  $\Pi_c = 50$  mN m<sup>-1</sup> compared to  $\Pi_c \geq 60$  mN m<sup>-1</sup> for the films of **1–6**.

Based on the results obtained in the studies of Langmuir films of buckminsterfullerene derivatives **1–7**, it becomes clear that the attachment of polar and hydrophilic head groups to the fullerene core yields compounds that become more similar to classical amphiphiles and give physically more relevant values for the measured surface requirements than pure  $C_{60}$  and  $C_{70}$ . The increase of these values seems to correlate with an enhanced degree of polarity and hydrophilicity of the addend as shown by

the comparison between **1** and **2** or between **3** and **4**. A second factor determining the observed cross-sectional area per molecule seems to be the size of the head group. Measurements of the  $\Pi/A$  isotherms of **2** and **4** indicate that the larger the head group, the greater is the molecular surface requirement. These observations apply for experiments under common spreading conditions (concentration  $\geq 10^{-4}$  M, compression ratio  $\geq 5$ ).

**$\Pi/A$  Isotherms of 8–11:** To explore in more detail the influence of the chemical nature of substituents at the head group on the spreading behavior, the four different fullerene C-glycosides **8–11** were investigated. These molecules are of potential biological interest due to their amphiphilic character (in **10** and **11**) and the combination of a sugar unit, ubiquitous in living systems, with the fullerene core, which provides its specific properties. Examples of biological activity reported in literature for buckminsterfullerene derivatives are inhibition of the HIV-1 protease<sup>[22a]</sup> and enhanced photoinduced cytotoxicity against HeLa S3 cells.<sup>[22b]</sup>

Compound **8** incorporates a fully benzyl-protected glucose moiety, providing a bulky head group with significant aromatic surface and rather low polarity. Owing to the absence of strong interactions with the aqueous phase, an amphiphilic behavior could not be expected. The small surface requirement of  $A_0 = 30$  Å<sup>2</sup> molecule<sup>-1</sup> (Fig. 5), which is identical to that mea-

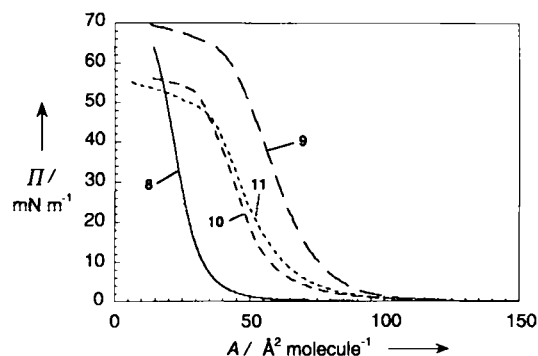


Fig. 5.  $\Pi/A$  isotherms (20 °C) of the fullerene sugar derivatives **8**, **9**, **10**, and **11**.

sured for pure  $C_{60}$ , is indeed clear proof for the lack of spreading ability. When the compressed film was reexpanded, patches became visible by observing the water surface under a flat angle, as macroscopic proof of the irreversible molecular aggregation. The large head group attached to  $C_{60}$  clearly does not prevent the fullerenes from forming three-dimensional aggregates at the air–water interface. Possibly, such aggregates are not only stabilized by fullerene–fullerene interactions, but also by attractive interactions between the benzene rings of the protecting groups or between these benzene rings and fullerene cores.

In the glucose derivative **9**, four pivaloyl protecting groups make the head group very voluminous and slightly more polar than that of **8**. In contrast to the latter, **9** exhibits a physically significant cross-section of  $A > 90$  Å<sup>2</sup> molecule<sup>-1</sup> at low surface pressure. The structure of the Langmuir films formed by **9** might well be different from those assumed to be favorable for the other compounds in this study. The fully aliphatic and highly branched substituents in **9** could presumably interact less favorably with the water surface than the highly polarizable fullerene core, and it may be possible that in this case the sugar moiety is pointing into the air and the fullerene core is in contact with the water. The aliphatic side chains must be very effective in suppressing fullerene aggregation in three dimensions, since **9** is

able to form a stable monolayer even without a strongly hydrophilic head group. The collapse pressure  $\Pi_c \approx 62 \text{ mN m}^{-1}$  is as high as that of pure  $\text{C}_{60}$ . Under the microscope, it is difficult to find any structural feature before surface pressure is applied and only a porous surface is faintly visible. After compression of the film to  $\Pi \approx 5 \text{ mN m}^{-1}$  and reexpansion, similar disorder as seen for fullerene crown **6** appears under the microscope. Cracks and white stripes of three-dimensionally aggregated molecules of **9** (due to film folding) indicate the irreversibility of any pressure-induced alteration of the film morphology. The same result is obtained in a hysteresis experiment where the floating film is repeatedly compressed and expanded (Fig. 6). For an ideal amphiphile like palmitic acid, the measured surface pressure follows the same curve in the  $\Pi/A$  isotherm upon compression and expansion. In the case of compound **9** the surface pressure increases slowly at  $A \approx 115 \text{ \AA}^2 \text{ molecule}^{-1}$  on initial compression to  $5 \text{ mN m}^{-1}$  according to the previously measured  $\Pi/A$  isotherm. When the film is reexpanded, the surface pressure drops sharply to  $0 \text{ mN m}^{-1}$  as a result of the irreversible fullerene aggregation. After leaving the film for more than 10 min in the expanded state to give it enough time for reorganization, a second compression cycle exhibits a shift in the onset of the surface pressure towards lower values ( $A = 95 \text{ \AA}^2 \text{ molecule}^{-1}$ ), and the isotherm commences with a steeper slope. At the point where the first compression ends ( $\Pi = 5 \text{ mN m}^{-1}$ ), the curves cross and the second compression now follows the common  $\Pi/A$  isotherm. This same behavior is observed when repeating the procedure for  $\Pi = 10, 15, 20$ , and  $30 \text{ mN m}^{-1}$  (Fig. 6).

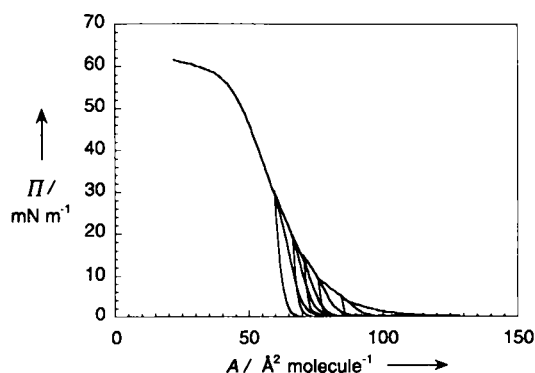


Fig. 6. Successive compression and expansion cycles (hysteresis) with a monolayer of **9** at  $20^\circ\text{C}$ , showing the irreversibility of the compression.

The mannose derivative **10** possesses four unprotected hydroxyl groups and is therefore the most hydrophilic compound in the fullerene sugar series **8–11**. The mannose is rather small compared to the size of the fullerene core, so the molecules partially aggregate in the film despite the tendency of the head groups to be in contact with the water subphase. Such three-dimensional aggregates can be seen in the microscopy pictures as white spots embedded in a condensed monolayer of **10** (Fig. 7). Other characteristics of the uncompressed film are cracks (dark regions) and double-layer rafts (brighter patches) that illustrate the rigidity of the monolayer as a result of the strong intermolecular attraction.

The  $\Pi/A$  isotherm of the partially deprotected mannose derivative **11** with two benzyl protecting groups at C(2) and C(3) of the sugar ring is similar to that of compound **10**. The two free hydrophilic hydroxyl groups undergo stabilizing interactions with the water subphase and balance the hydrophobic aggrega-

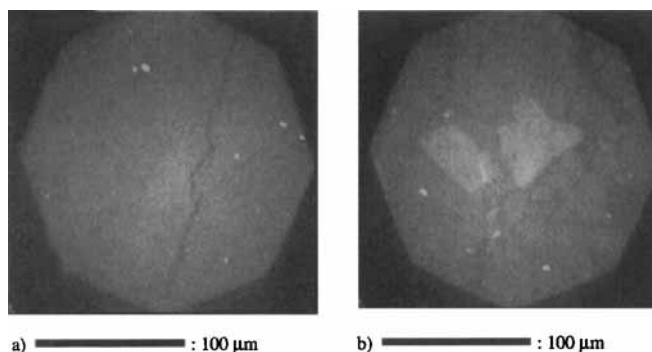


Fig. 7. Optical light microscopy pictures of a floating film of mannose derivative **10** before compression: a) aggregates (white spots) and cracks (dark line). b) double-layer rafts (bright regions).

tion tendency of the benzyl groups with the fullerene core. Thus the molecule is provided with an overall amphiphilic character. On the other hand, the collapse pressure of  $\Pi_c \approx 46 \text{ mN m}^{-1}$  is much lower than that of  $\text{C}_{60}$  indicating instability of the floating film.

**Langmuir–Blodgett Transfer:** The films of all four fullerene sugars **8–11** were transferred to solid substrates with different surface morphologies at surface pressures as low as  $5 \text{ mN m}^{-1}$  to minimize pressure-induced film damage. Hydrophilic materials like mica, glass, and quartz allowed only a single transfer on upstroke out of the aqueous phase. The transferred film adhered only weakly to the hydrophilic surface and subsequent submersion into water resulted in detachment of the film.

When the glass or quartz slides were exposed to a vapor of 1,1,1,3,3,3-hexamethyldisilazane  $((\text{CH}_3)_3\text{SiNHSi}(\text{CH}_3)_3)$ , a very hydrophobic aliphatic surface was obtained with trimethylsilyl groups pointing away from the substrate. The floating film of compound **9** showed no interaction with the substrate at  $\Pi \leq 5 \text{ mN m}^{-1}$ . None of the Langmuir films of the sugar derivatives **8–11** were transferred properly under these conditions, and only at surface pressures higher than  $10 \text{ mN m}^{-1}$  could the films of **11**, for example, be forced onto the alkylated substrate. Such Langmuir–Blodgett films formed by 15 to 30 Y-type transfers (up- and downstroke) did not reveal any layer structure in SAXS measurements.

When the glass and quartz were treated with benzylchlorodimethylsilane  $(\text{C}_6\text{H}_5\text{CH}_2(\text{CH}_3)_2\text{SiCl})$  in vacuum at about  $180^\circ\text{C}$ , hydrophobic surfaces with aromatic and aliphatic characteristics were obtained. The films of **9** and **10** could be transferred at  $\Pi \approx 5 \text{ mN m}^{-1}$  with transfer ratios of between 0.3 and 0.6 (Y-type), and a poor multilayer morphology (cracks and wrinkles) was observed by the naked eye. Pivaloyl derivative **9** was the only compound that could be transferred properly (Y-type), and the LB film of 20 double layers showed a Bragg peak in the SAXS diagram indicating a double-layer thickness of  $28.4 \text{ \AA}$ .

By immersing the glass or quartz slide overnight in *t*-butylchlorodiphenylsilane  $((\text{CH}_3)_3\text{C}(\text{C}_6\text{H}_5)_2\text{SiCl})$ , a highly aromatic surface was obtained allowing the transfer of films with transfer ratios of around 0.7–0.8. The SAXS diagram of LB multilayers obtained from the pivaloyl glucose derivative **9** displays a Bragg reflex, similar to the one in Figure 8, and Kiesig fringes. SAXS measurements on LB film samples of **10** and **11** show only Kiesig fringes from which the overall film thicknesses were calculated as  $\approx 320 \text{ \AA}$  (15 up- and downstrokes) for **10** and  $\approx 324 \text{ \AA}$  (8 up- and downstrokes) for **11**.

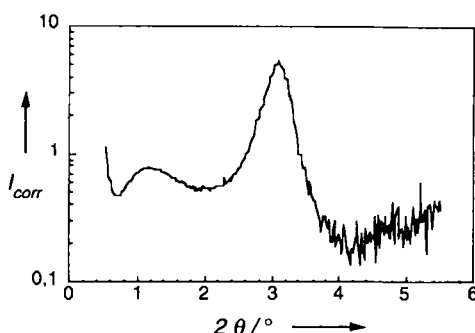


Fig. 8. SAXS diagram of an LB film of **9** on hydrophobized glass (benzyltrimethylchlorosilane): 20 double layers, Y-type, transferred at  $5 \text{ mNm}^{-1}$  and  $20^\circ\text{C}$ . Primary beam background subtracted by  $I_{\text{corr}} = I_0(4\pi\sin\theta/\lambda)^4$ , where  $\lambda = 1.5418 \text{ \AA}$ ,  $I_{\text{corr}}$  = corrected intensity and  $I_0$  = initial intensity of the reflected beam.

UV/Vis measurements on LB films of all four fullerene sugars **8–11** transferred at  $\Pi \geq 10 \text{ mNm}^{-1}$  showed the three typical  $\text{C}_{60}$  absorption bands at  $\approx 220 \text{ nm}$ ,  $\approx 260 \text{ nm}$ , and  $\approx 330 \text{ nm}$ . Comparison of the relative absorption intensities per transferred layer in samples prepared from **9** and **10** clearly demonstrated that best monolayer transfer was obtained for highly aromatic substrate surfaces with *tert*-butyldiphenylsilyl groups facing out. This can be explained by the attractive interactions between the fullerene cores and the aromatic moieties at the substrate surface.<sup>[7a,16]</sup> For substrates modified with benzyltrimethylsilyl groups, the absorption intensities per “layer” were much lower owing to a less complete transfer of the floating film to the substrate. These intensities decreased further when alkylated or hydrophilic substrates were used. Visual observation of such transferred film fragments revealed a rather chaotic morphology with large holes and cracks.

The  $\Pi/A$  isotherm experiments with the C-glycosylated fullerene derivatives **8–11** yielded the same results with regard to the effects of hydrophilicity and bulkiness of the head group on the spreading behavior as was observed with compounds **1–7**. More hydrophilic head groups, like the ones in derivatives **10** or **11**, favor monolayer formation due to stabilizing interactions with the water surface. Very bulky head groups are effective in suppressing the fullerene aggregation as can be seen with compound **9**.

A new observation with the glycosylated fullerenes **8–11** was the influence of the attractive interaction between aromatic moieties and the fullerene core on the spreading and transfer behavior. This becomes clear when comparing the  $\Pi/A$  isotherms of **8** and **9**. In both molecules, the head group is of similar bulkiness and it is not very hydrophilic, but the molecular surface requirement is completely different. Compound **9** with its aliphatic substituents shows a reasonable value for the cross-sectional area, whereas the fully benzyl-protected derivative **8** behaves like pure  $\text{C}_{60}$  at the air–water interface, forming a collapsed film with only a third of the expected surface requirement. This behavior can be explained by strong attractive intermolecular interactions among the benzyl groups and between benzyl groups and fullerene cores leading to a three-dimensional aggregation of the molecules. Also, the preferred transfer of the floating films to substrates with highly aromatic surfaces mirrors the efficiency of such favorable fullerene–arene interactions.

Based on these results, further  $\text{C}_{60}$  derivatives will be synthesized with large and strongly hydrophilic head groups to achieve the goal of a fullerene amphiphile with good spreading characteristics and reversible compression and expansion behavior.

Table 1. Approximate values for collapse pressures  $\Pi_c$  and molecular surface requirements at vanishing surface pressure  $A_0$  evaluated from the  $\Pi/A$  isotherms of  $\text{C}_{60}$ ,  $\text{C}_{70}$  and compounds **1–11**.

Compound	$\Pi_c$ [mNm <sup>-1</sup> ]	$A_0$ [a]	Compound	$\Pi_c$ [mNm <sup>-1</sup> ]	$A_0$ [a]
$\text{C}_{60}$	64	28	<b>6</b>	60	80
$\text{C}_{70}$	60	23	<b>6</b> + 1 M KCl		
<b>1</b>	65	28	subphase	62	90
<b>2</b>	64	54	<b>7</b>	50	80
<b>3</b>	58	40	<b>8</b>	62	30
<b>4</b>	62	60	<b>9</b>	62	76
<b>5</b>	58	45	<b>10</b>	51	60
<b>5</b> + PVP [b]	56	65	<b>11</b>	46	65

[a]  $\text{\AA}^2 \text{ molecule}^{-1}$ . [b] PVP = poly(2-vinylpyridine).

## Experimental Procedure

**Materials:** All solvents for the film experiments were pure grade (p.a.) and used as purchased from Riedel–de Haën (D-30926 Seelze, Germany) or Fluka (CH-9470 Buchs, Switzerland). Reagents used for synthesis were reagent grade chemicals. The pure fullerenes were obtained by chromatography on charcoal/silica gel ( $\text{C}_{60}$ ) [**7a**] or alumina ( $\text{C}_{70}$ ) [**21a**]. The crude fullerene mixture was extracted from fullerene-containing soot (Polygon Enterprises, P. O. Box 5536, Waco, TX 76708, USA), and MER Corporation, 7960 South Kolb Road, Tucson, Arizona 85706, USA). Column chromatography: silica gel (70–270 mesh, 0.05–0.2 mm) from Macherey–Nagel; basic aluminium oxide 60 activity I (70–230 mesh, 0.06–0.2 mm) from E. Merck; Dowex ion-exchange resin (OH<sup>-</sup> form, 200–400 mesh, 1 × 8–400) from Aldrich; Dowex ion-exchange resin (H<sup>+</sup> form, 20–50 mesh, 50 × 8) from Fluka. Kryptofix 222 B and Kryptofix 222 were supplied by E. Merck.  $\text{H}_2\text{O}$  and aqueous solutions for treatment of the cryptands were obtained from in-line Barnstead and Skan Nanopure Cartridge Systems. Ethyl acetate was washed with 5% aqueous  $\text{Na}_2\text{CO}_3$  solution, with saturated aqueous NaCl solution, dried with  $\text{K}_2\text{CO}_3$ , and then distilled. Hydrogenation was carried out in a Büchiglas Uster hydrogenator.

Compounds **1** [**8a**], **2** [**11**], **5** [**12**], **6** [**7a**], **8** and **9** [**13a**], **10** and **11** [**13b**] were synthesized according to the reported procedures. The synthesis of **3** [**14b**] and **4** [**14c**] will be reported elsewhere.

The glass and quartz slides (Herafil 1,  $40 \times 15 \times 1 \text{ mm}^3$ , Heraeus, Germany) as well as the volumetric flasks for the spreading solutions were immersed for over 24 h in a solution of NoChromix (Godax Laboratories, USA) in concentrated  $\text{H}_2\text{SO}_4$ , rinsed with Milli Q water (resistivity ca. 18 M $\Omega\text{cm}$ ), and dried in a microwave oven prior to use. The Milli Q water was obtained by filtration of distilled water through a Milli-Q II system (Millipore Corp.).

**Surface hydrophobization:** The silanes for surface modifications were used as purchased from ABCR (Germany). Hydrophobic derivatization with 1,1,1,3,3,3-hexamethyldisilazane: The clean glass or quartz slides were exposed to saturated vapor of hexamethyldisilazane for 30 min at room temperature and then rinsed with dichloromethane. Hydrophobic derivatization with benzylchlorodimethylsilane: A container with the glass or quartz substrates and  $\approx 0.5 \text{ mL}$  of benzylchlorodimethylsilane was evacuated to  $< 0.2 \text{ Torr}$ , sealed, and then heated in an oil bath for 2 h at  $120^\circ\text{C}$ . After cooling to room temperature, the slides were rinsed with dichloromethane and water. Hydrophobic derivatization with *tert*-butylchlorodiphenylsilane: After immersion of the glass or quartz into *tert*-butylchlorodiphenylsilane for 24 h at room temperature, the substrates were washed with dichloromethane. The hydrophobicity of the surfaces was checked by contact angle measurements (G 1, Krüss, Germany), and the contact angle with water was always  $> 70^\circ$  (advancing mode).

**Equipment for product characterization:** Melting points were determined on a Büchi 510 apparatus and are uncorrected. UV/Vis spectra: Varian-CARY-5 spectrometer. IR spectra: Perkin-Elmer-FT 1600 spectrometer.  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{23}\text{Na}$  NMR Spectra: Bruker AMX-500 and Varian GEMINI-200 and -300 spectrometers; all NMR spectra were measured at 293 K. FAB-MS: VG-ZAB2-SEQ spectrometer; FAB mass spectra were determined in *m*-nitrobenzyl alcohol (3-NOBA) as the matrix. Elemental analyses were effected by the Mikrolabor des Laboratoriums für Organische Chemie at ETHZ.

**7-Nitro-4,11,17,20,25,28-hexaoxa-1,14-diazatricyclo[12.8.8.0<sup>8,10</sup>]triaconta-5,7,9-triene (**13**):** A 65% aqueous  $\text{HNO}_3$  solution (3.5 mL) was added dropwise to **12** (1.047 g, 2.466 mmol) at  $0^\circ\text{C}$ . The ice bath was removed, and the yellow mixture was stirred at room temperature for 3.5 h, then cooled to  $0^\circ\text{C}$  and diluted with cold  $\text{H}_2\text{O}$  (100 mL). Addition of  $\text{CH}_2\text{Cl}_2$  (150 mL) was followed by dropwise addition of 40% aqueous  $\text{NET}_4\text{OH}$  solution to the stirred mixture until pH = 11. At pH = 10, the color of the mixture turned from bright yellow to orange-yellow. The aqueous phase was extracted with  $\text{CH}_2\text{Cl}_2$  (50 mL), and the collected organic extract washed with



H<sub>2</sub>O (2 × 100 mL) until neutral. The solvent was removed in vacuo to yield an orange paste that was triturated with PhCH<sub>3</sub> (5 mL) to give a precipitate (13·KNO<sub>3</sub>, see below). The mother liquor was decanted and the residue washed with PhCH<sub>3</sub> (2 × 5 mL). Mother liquor and organic extracts were collected and the solvent removed in vacuo to yield an oily product. The orange oil was dissolved in H<sub>2</sub>O/MeOH (95:5, 150 mL) and the solution obtained was passed through a short ion-exchange column (OH<sup>−</sup> form, prepared by washing the resin successively with 1% aqueous HCl solution, H<sub>2</sub>O, 2% aqueous NEt<sub>3</sub>/OH solution, H<sub>2</sub>O, and H<sub>2</sub>O/MeOH (95:5)). The product was eluted with H<sub>2</sub>O/MeOH (95:5, 1 L), and the solvent removed in vacuo to yield a yellow oil: 283 mg (24%) of 13. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ = 2.61–2.83 (m, 8H), 2.88–3.01 (m, 4H), 3.42–3.70 (m, 16H), 4.10–4.24 (m, 4H), 6.87 (d, *J* = 8.9 Hz, 1H), 7.71 (d, *J* = 2.6 Hz, 1H), 7.85 (dd, *J* = 8.9, 2.6 Hz, 1H); <sup>13</sup>C NMR (50.3 MHz, CDCl<sub>3</sub>): δ = 54.93, 55.10, 56.03, 56.11, 68.56, 68.86, 70.20, 71.05, 71.12, 110.10, 112.74, 118.37, 141.73, 149.05, 155.34; IR (neat): ν̄ = 3489 (w), 3078 (w), 2855 (s), 2355 (m), 2055 (w), 1583 (s), 1511 (s), 1461 (s), 1339 (s), 1272 (s), 1172 (m), 1128 (s), 1028 (s), 983 (s), 928 (s), 861 (m), 800 (m), 739 (s), 650 (m) cm<sup>−1</sup>; FAB-MS: *m/z* (%): 508 (14, [M + K]<sup>+</sup>), 492 (14, [M + Na]<sup>+</sup>), 470 (100, [M + H]<sup>+</sup>). C<sub>22</sub>H<sub>33</sub>N<sub>3</sub>O<sub>8</sub> (469.54): calcd C 56.28, H 7.51, N 8.95, O 27.26; found C 56.23, H 7.40, N 8.93, O 27.53. The crystalline yellow product obtained by trituration with PhCH<sub>3</sub> was characterized as 13·KNO<sub>3</sub> (830 mg, 59%). M.p. 230–232 °C; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ = 2.55–2.85 (m, 8H), 2.90–3.04 (m, 4H), 3.36–3.68 (m, 16H), 4.18–4.39 (m, 4H), 7.04 (d, *J* = 9.0 Hz, 1H), 7.75 (d, *J* = 2.6 Hz, 1H), 7.92 (dd, *J* = 9.0, 2.6 Hz, 1H); <sup>13</sup>C NMR (50.3 MHz, CDCl<sub>3</sub>): δ = 53.20, 54.78, 65.68, 66.12, 67.83, 70.01, 106.44, 110.55, 117.85, 141.19, 146.95, 152.55; IR (KBr): ν̄ = 3421 (w), 3094 (w), 3040 (m), 2876 (s), 2811 (s), 2375 (w), 2049 (w), 1741 (w), 1583 (s), 1507 (s), 1480 (s), 1343 (s), 1262 (s), 1224 (s), 1098 (s), 1022 (s), 946 (s), 875 (m), 832 (m), 804 (m), 750 (s), 657 (m) cm<sup>−1</sup>; FAB-MS: *m/z* (%): 508 (100, [M − NO<sub>3</sub>]<sup>+</sup>), 492 (12, [M − KNO<sub>3</sub> + Na]<sup>+</sup>), C<sub>22</sub>H<sub>33</sub>N<sub>3</sub>O<sub>8</sub>·K (570.64): calcd C 46.31, H 6.18, N 9.82, O 30.84; found C 46.34, H 6.09, N 9.75, O 30.65. 13·KNO<sub>3</sub> was submitted to the recovery process for cryptands [23] to yield 270 mg (23%) of 13. The overall yield of 13 was 553 mg (47%).

**7-Amino-4,11,17,20,25,28-hexaaza-1,14-diazatrypticlylo[12.8.8.0<sup>5,10</sup>]triacta-5,7,9-triene (14):** A solution of 13 (280 mg, 0.596 mmol) in oxygen-free ethyl acetate (10 mL) was added to a suspension of 10% Pd/C (650 mg) in oxygen-free ethyl acetate (50 mL), and the stirred mixture was hydrogenated at 4 bar/RT for 5 h. The reaction mixture was filtered through Celite, and the solvent removed in vacuo to give an off-white oil: 183 mg (70%) of 14. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 2.71–2.84 (m, 8H), 2.86–3.02 (m, 4H), 3.46–3.71 (m, 16H), 4.04–4.11 (m, 4H), 6.20 (dd, *J* = 8.4, 2.6 Hz, 1H), 6.29 (d, *J* = 2.6 Hz, 1H), 6.73 (d, *J* = 8.4 Hz, 1H); <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>): δ = 54.98, 55.39, 55.79, 56.11, 67.58, 69.90, 69.95, 70.13, 70.72, 70.97, 103.20, 107.25, 118.65, 141.55, 141.79, 150.64; IR (neat): ν̄ = 3422 (w), 3344 (m), 3222 (w), 2944 (s), 2855 (s), 1611 (m), 1589 (w), 1505 (s), 1444 (m), 1350 (w), 1294 (m), 1266 (m), 1222 (m), 1183 (m), 1122 (s), 978 (m), 933 (w), 828 (w), 722 (w) cm<sup>−1</sup>; FAB-MS: *m/z* (%): 462 (24, [M + Na]<sup>+</sup>), 440 (100, [M + H]<sup>+</sup>). HRMS [C<sub>22</sub>H<sub>33</sub>N<sub>3</sub>O<sub>6</sub> + H]<sup>+</sup>: calcd 440.2760; found 440.2746.

**Sodium chloride complex of N-(4,11,17,20,25,28-hexaaza-1,14-diazatrypticlylo[12.8.8.0<sup>5,10</sup>]triacta-5,7,9-trien-7-yl)-1,2-dihydro-1,2-methanofullerene[60]-61-carboxamide (7):** To a stirred solution of 2 [11] (75.5 mg, 0.097 mmol) and 1-HOBT (26.2 mg, 0.194 mmol) in PhBr (32 mL) was added, under N<sub>2</sub>, DCC (40 mg, 0.194 mmol) followed by a solution of 14 (51 mg, 0.116 mmol) in PhBr (3 mL). After stirring at RT for 24 h, the mixture was submitted to column chromatography (Al<sub>2</sub>O<sub>3</sub>, previously rinsed with a solution of [2.2.2]cryptand in CHCl<sub>3</sub>, using CHCl<sub>3</sub>/MeOH (95:5) for the elution of [2.2.2]cryptand/cryptates, then equilibrated with CH<sub>2</sub>Cl<sub>2</sub>). Elution of the reaction mixture with PhCH<sub>3</sub> gave PhBr; subsequent elution with CH<sub>2</sub>Cl<sub>2</sub> followed by CHCl<sub>3</sub>/MeOH (95:5) gave the fullerene cryptand/cryptates. A first brown fraction containing a mixture of free and complexed fullerene cryptand was collected followed by a second fraction containing only the alkali metal fullerene cryptates. The residue of the first fraction was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and resubmitted to column chromatography (see conditions above). Again, the first fraction was collected, and its residue submitted twice to the following procedure to remove alkali metals: To a solution of the brown solid (80 mg) in CHCl<sub>3</sub> (12 mL) and MeOH (6 mL), cryptand 12 (500 mg, 1.177 mmol) was added. The mixture was stirred at 40 °C for 5 d, and the solvents were removed in vacuo. MeOH (3 mL) was added, the suspension centrifuged, and the mother liquor decanted (× 3) in order to remove cryptand 12 and its cryptates. The residue was dried in vacuo to yield 61 mg (52%) of fullerene cryptand. M.p. > 270 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 2.65–2.82 (m, 8H), 2.88–3.05 (m, 4H), 3.45–3.73 (m, 16H), 4.05–4.24 (m, 4H), 4.92 (s, 1H), 6.87 (d, *J* = 8.6 Hz, 1H), 7.48 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.78 (d, *J* = 2.4 Hz, 1H), 8.49 (s, br, 1H); FAB-MS: *m/z* (%): 1239 (7, [M + K]<sup>+</sup>, <sup>12</sup>C<sub>83</sub><sup>13</sup>CH<sub>33</sub>N<sub>3</sub>O<sub>7</sub>K), 1238 (5, [M + K]<sup>+</sup>, <sup>12</sup>C<sub>84</sub>H<sub>33</sub>N<sub>3</sub>O<sub>7</sub>K), 1223 (24, [M + Na]<sup>+</sup>, <sup>12</sup>C<sub>83</sub><sup>13</sup>CH<sub>33</sub>N<sub>3</sub>O<sub>7</sub>Na), 1222 (26, [M + Na]<sup>+</sup>, <sup>12</sup>C<sub>84</sub>H<sub>33</sub>N<sub>3</sub>O<sub>7</sub>Na), 1201 (89, [M + H]<sup>+</sup>, <sup>12</sup>C<sub>83</sub><sup>13</sup>CH<sub>33</sub>N<sub>3</sub>O<sub>7</sub>), 1200 (99, [M + H]<sup>+</sup>, <sup>12</sup>C<sub>84</sub>H<sub>33</sub>N<sub>3</sub>O<sub>7</sub>), 721 (81, <sup>12</sup>C<sub>59</sub><sup>13</sup>C), 720 (100, <sup>12</sup>C<sub>60</sub>). To a solution of the free fullerene cryptand (61 mg) in CHCl<sub>3</sub> (10 mL) and MeOH (5 mL) was added an excess of NaCl. After stirring the mixture at 40 °C for 1 d and filtering off the excess of NaCl, the solvents were removed in vacuo and the dark solid was crystallized by vapor diffusion of Et<sub>2</sub>O into a CHCl<sub>3</sub> solution: 64 mg (52%) of 7. M.p. > 270 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 2.60–2.75 (m, 8H), 2.78–2.98 (m, 4H), 3.42–

3.75 (m, 16H), 4.1–4.38 (m, 4H), 5.88 (s, 1H), 6.82 (d, *J* = 8.9 Hz, 1H), 8.03 (dd, *J* = 8.9, 2.3 Hz, 1H), 8.10 (d, *J* = 2.3 Hz, 1H), 11.91 (s, 1H); <sup>13</sup>C NMR (125.7 MHz, CDCl<sub>3</sub>): δ = 42.61, 52.97, 53.10, 53.22, 53.51, 65.45, 65.78, 67.81, 67.88, 68.35, 68.52, 72.70, 106.93, 112.84, 113.42, 134.58, 136.77, 140.67, 140.80, 140.86, 141.76, 142.16, 142.18, 142.24, 142.74, 142.78, 142.80, 142.82, 142.88, 142.92, 143.13, 143.75, 143.95, 144.09, 144.28, 144.43, 144.50, 144.62, 144.91, 144.94, 144.96, 144.98, 145.02, 145.06, 145.67, 145.93, 146.33, 147.53, 149.69, 164.62; <sup>23</sup>Na NMR (132.3 MHz, CDCl<sub>3</sub>; external refer.: 2 M NaCl solution in D<sub>2</sub>O): δ = −9.45; IR (KBr): ν̄ = 3455 (w), 3322 (m), 2922 (s), 2855 (s), 1678 (m), 1622 (s), 1505 (s), 1461 (w), 1428 (m), 1350 (w), 1217 (m), 1128 (m), 1094 (s), 933 (m), 811 (w), 728 (w), 522 (s) cm<sup>−1</sup>; UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub> (ε) = 698 (380), 480 (1720), 428 (2810), 327 (29700), 260 (98300) nm; FAB-MS: *m/z* (%): 1239 (7, [M − NaCl + K]<sup>+</sup>, <sup>12</sup>C<sub>83</sub><sup>13</sup>CH<sub>33</sub>N<sub>3</sub>O<sub>7</sub>K), 1238 (8, [M − NaCl + K]<sup>+</sup>, <sup>12</sup>C<sub>84</sub>H<sub>33</sub>N<sub>3</sub>O<sub>7</sub>K), 1223 (40, [M − Cl]<sup>+</sup>, <sup>12</sup>C<sub>83</sub><sup>13</sup>CH<sub>33</sub>N<sub>3</sub>O<sub>7</sub>Na), 1222 (43, [M − Cl]<sup>+</sup>, <sup>12</sup>C<sub>84</sub>H<sub>33</sub>N<sub>3</sub>O<sub>7</sub>Na), 721 (83, <sup>12</sup>C<sub>59</sub><sup>13</sup>C), 720 (100, <sup>12</sup>C<sub>60</sub>).

**Π/A isotherm measurements:** The Π/A isotherms were measured at 20 °C either on a self-built, computer-controlled Teflon trough with a surface of 180 cm<sup>2</sup> or on a Lauda FW 2 film balance (Teflon, surface 930 cm<sup>2</sup>) with computer control, both equipped with a Langmuir pressure pickup system. The subphase was Milli Q water (resistivity ca. 18 MΩ cm). The molecular compression speed was between 1100 and 1800 m<sup>2</sup> s<sup>−1</sup> mol<sup>−1</sup>, and the spreading behavior did not change within these limits. The molecular compression speed was calculated from the surface area change divided by the measuring time and the sample quantity. The spreading solutions were all approximately 10<sup>−4</sup> M in concentration. The solvents used were toluene, benzene, or CHCl<sub>3</sub> for C<sub>60</sub> and C<sub>70</sub>; toluene for 1; CHCl<sub>3</sub> with ca. 1% DMSO for 2; CH<sub>2</sub>Cl<sub>2</sub> for 3; CHCl<sub>3</sub> with ca. 2% pyridine for 4; THF for 5; CH<sub>2</sub>Cl<sub>2</sub> for 6; CHCl<sub>3</sub> with < 1% CH<sub>3</sub>OH for 7; toluene for 8; toluene for 9; CH<sub>2</sub>Cl<sub>2</sub> with 13% (H<sub>3</sub>C)<sub>2</sub>SO for 10; toluene for 11.

**Microscopy measurements:** The microscopy pictures were taken on a self-built Teflon trough with a surface area of 12 cm<sup>2</sup> and a Wilhelmy pressure pickup system. The microscope (Olympus STM-MJS) was equipped with a video camera (Hamamatsu C2400), which was connected to an image processor (Hamamatsu Argus-10) and a video recorder (Blaupunkt RTV-915 HIFI). The pictures were digitized from the video recorder by a Macintosh Quadra 840 AV (Apple Computer). A volume of 20 μL was spread from 10<sup>−4</sup> M concentrated solutions in the single experiments.

**Multilayer experiments:** For the LB multilayer transfers, the substrates were dipped vertically with a speed of 0.2 mm s<sup>−1</sup> through the floating films at a surface pressure of Π = 5 mN m<sup>−1</sup>. SAXS measurements were performed on a θ–2θ goniometer (Siemens) with the Cu<sub>Kα</sub> line irradiation (λ = 1.5418 Å).

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