

**175. Synthesis of a Fullerene Derivative of Benzo[18]crown-6
by *Diels-Alder* Reaction:
Complexation Ability, Amphiphilic Properties, and X-Ray Crystal Structure
of a Dimethoxy-1,9-(methano[1,2]benzenomethano)fullerene[60]
Benzene Clathrate**

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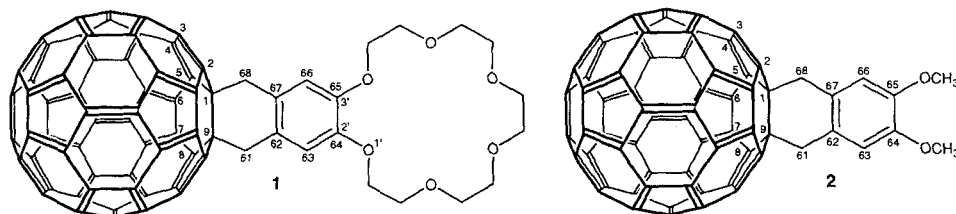
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A fullerene derivative **1** of benzo[18]crown-6 was obtained by *Diels-Alder* addition of fullerene[60](C₆₀) to the *ortho*-quinodimethane prepared *in situ* from 4,5-bis(bromomethyl)benzo[18]crown-6 (**3**) with Bu₄NI in toluene. Extraction experiments show that the complexation of K⁺ ions strongly increases the solubility of **1** in protic solvents like MeOH. Using *Langmuir-Blodgett* techniques, monolayers of the highly amphiphilic fullerene-derived crown ether **1** and its K⁺ ion complex were prepared. An X-ray crystal structure was obtained from a benzene clathrate of comparison compound **2**, synthesized by *Diels-Alder* reaction of C₆₀ with the *ortho*-quinodimethane derived from 1,2-bis(bromomethyl)-4,5-dimethoxybenzene (**4**). Both the fullerene molecule **2** and the benzene molecule are fully ordered in a crystal packing which is stabilized by intermolecular *van-der-Waals* contacts between the benzene ring and the C-spheres, intermolecular C···C contacts between the C₆₀ moieties, and intermolecular O···C contacts between the O-atoms of the veratrole moieties and fullerene C-atoms.

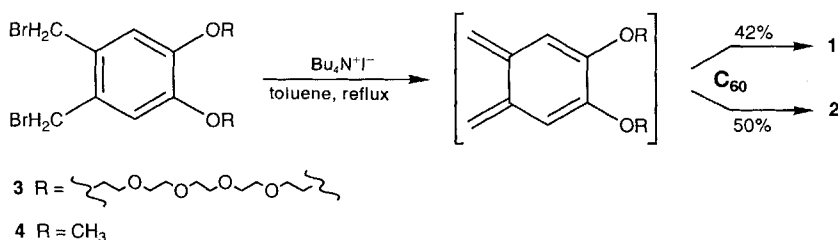
Introduction. – After the first period of the availability of fullerenes in macroscopic amounts [1] had been dedicated mainly to the investigation of physical properties of the C-spheres themselves as well as of the metal-doped phases of C₆₀ [2], the study of the chemical transformation of buckminsterfullerene to derivatives is now emerging as a rapidly expanding field [3]. As far as its chemical reactivity is concerned, C₆₀ behaves as an electron-deficient alkene, with its double bonds localized in a pentaradialene-type array, rather than as a fully delocalized aromatic system [4]. In a program aimed at the preparation of buckminsterfullerene derivatives with potentially interesting biological and materials properties [5], we now report the synthesis and properties of a crown-ether derivative of C₆₀ [6] obtained by *Diels-Alder* reaction [7]. The interest in a compound of this type arises from its metal-complexing abilities, its amphiphilic character [8], and from



its potential to form new conducting solid-state phases through doping with electropositive metals [2]. Of particular interest should be electrider-type structures [9] which **1** could form by dissolving K metal under complexation of K^+ in the crown moiety and delocalization of the electrons in the C-sphere and possibly over the entire lattice. In addition, we report the X-ray crystal structure of the benzene clathrate formed by comparison compound **2** which is also formed in a *Diels-Alder* reaction¹⁾.

Results and Discussion. – *Synthesis.* Receptor **1** (Scheme) incorporates the benzo-[18]crown-6 structure, one of the prototypes of crown ethers, and its synthesis takes advantage of the recently developed *Diels-Alder* chemistry of C_{60} which reacts as dienophile with 1,3-dienes under formation of derivatives bridged across the 6–6 ring junction [7]. The conditions for the addition of C_{60} to *ortho*-quinodimethanes, generated

Scheme. Synthesis of the Fullerene[60] Derivatives **1** and **2**



in situ by 1,4-elimination of Br_2 from 1,2-bis(bromomethyl)benzene derivatives [7c], were optimized in the model reaction leading to **2**. Highest yields of **1** and **2** were obtained by refluxing C_{60} and the bis(bromomethyl) derivatives **3** and **4**, respectively, with Bu_4NI in toluene which, for solubility reasons, is the solvent of choice for fullerenes.

X-Ray Crystal Structure of a Benzene Clathrate of 2. When **2** was crystallized by vapor diffusion of pentane into its cognac-colored solution in benzene, black needles of a 2:1 **2**·benzene clathrate with a metallic luster, which were suitable for X-ray analysis, were obtained (Table 1)²⁾. The molecular structure of **2** confirms the expected bridging at the 6–6 ring junction of C_{60} (Fig. 1), and bond lengths and angles (Table 2) closely resemble those seen in the X-ray crystal structure of a previously reported *ortho*-xyleno-bridged fullerene [7a]. The cyclohexene ring adopts a boat conformation with an angle of $129.1(5)^\circ$ between the mean planes passing through $C(1')$, $C(1)$, $C(9)$, $C(4')$ and $C(1')$, $C(9')$, $C(10')$, $C(4')$ and torsional angles $C(1')-C(1)-C(9)-C(4')$ of $-0.4(5)^\circ$ and $C(1')-C(9)-C(10')-C(4')$ of $-2.9(5)^\circ$. The MeO groups, finally, are almost coplanar with the benzene ring (dihedral angles $C(8')-C(7')-O(13')-C(14')$ of $4.4(5)^\circ$ and $C(5')-C(6')-O(11')-C(12')$ of $-0.1(5)^\circ$), as is typically found for aromatic ether linkages [10].

¹⁾ Compound **2** as well as a crystal structure without included benzene were independently reported by Prof. K. Müllen and coworkers at the 'Hauptversammlung 1993, Deutsche Gesellschaft für Materialkunde', June 1–4, 1993, Friedrichshafen, where parts of our work were also presented for the first time.

²⁾ Atomic coordinates and equivalent isotropic displacement coefficients, bond lengths, bond angles, anisotropic displacement coefficients, and H-atom coordinates with isotropic displacement coefficients were deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB2 1EZ.

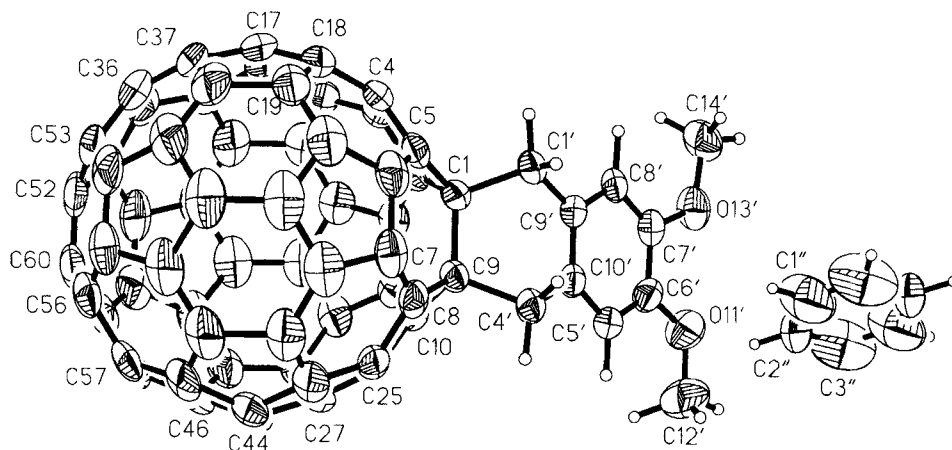


Fig. 1. *X-Ray crystal structure of 2·0.5 benzene*. Vibrational ellipsoids are shown at the 50% probability level. The numbering of the fullerene moiety was done according to: P.R. Birkett, P.B. Hitchcock, H.W. Kroto, R. Taylor, D.R.M. Walton, *Nature (London)* **1992**, 357, 479. For alternative numbering systems, see: R. Taylor, *J. Chem. Soc., Perkin Trans. 2* **1993**, 813.

Table 1. *X-Ray Crystal Structure Data of 2*

Crystal data and data collection		Radiation	MoK _α
Empirical formula	C ₇₃ H ₁₅ O ₂	Temperature	293 K
<i>M_r</i>	923.9	Monochromator	highly oriented graphite crystal
Crystal size [mm]	0.4 × 0.3 × 0.2	Reflections collected	5290
Crystal system	monoclinic	Independent reflections	5037
Space group	<i>P</i> 2 ₁ / <i>n</i>	Observed reflections	2711 (<i>F</i> > 4.0 σ(<i>F</i>))
Unit cell dimensions	<i>a</i> = 13.201(4) Å	<i>Solution and refinement</i>	
	<i>b</i> = 18.091(4) Å		
	<i>c</i> = 16.585(10) Å		
	β = 104.29(4)°	System used	Siemens SHELXTL PLUS (VMS)
Volume	3838(3) Å ³	Solution	direct methods
<i>Z</i>	4	Refinement method	full-matrix least-squares
Density (calc.)	1.599 g cm ⁻³	C- and O-Atoms	anisotropic
Diffractometer	SYNTEX P21	H-Atoms	riding model, fixed isotropic <i>U</i>
		Number of parameters refined	725
		Final <i>R</i> indices	<i>R</i> = 3.77%, <i>wR</i> = 3.81 %

Table 2. *Selected Bond Lengths and Bond Angles in 2*. For numbering, see Fig. 1.

Bond length [Å]		Bond angle [°]	
C(1)–C(1')	1.573(6)	C(1')–C(1)–C(2)	110.0(3)
C(1)–C(2)	1.532(6)	C(1')–C(1)–C(9)	111.3(3)
C(1)–C(5)	1.522(5)	C(1')–C(1)–C(5)	108.6(3)
C(1)–C(9)	1.591(5)	C(2)–C(1)–C(5)	99.6(3)
C(9)–C(4')	1.574(6)	C(2)–C(1)–C(9)	113.1(3)
C(9)–C(8)	1.530(5)	C(5)–C(1)–C(9)	113.6(3)
C(9)–C(10)	1.520(6)	C(4')–C(9)–C(1)	110.8(3)
		C(4')–C(9)–C(8)	108.2(3)
		C(4')–C(9)–C(10)	108.9(3)
		C(1)–C(9)–C(8)	114.4(3)
		C(1)–C(9)–C(10)	114.4(3)
		C(8)–C(9)–C(10)	99.5(3)

In addition to 4 molecules of **2**, the unit cell comprises 2 molecules of benzene accommodated into interstices between the C-spheres (Fig. 2). Each benzene molecule shows near *van-der-Waals* contacts (C(2'')–C(45) 3.61(1) Å) to two neighboring fullerene moieties (Fig. 3a). The closest contact between an ether O-atom (O(13')) and a neighboring fullerene C-atom (C(7)) also equals approximately the sum of their *van-der-Waals* radii (3.07(1) Å) (Fig. 3b). Close intermolecular contacts are also observed between fullerene C-atoms, the shortest contact being 3.20(1) Å.

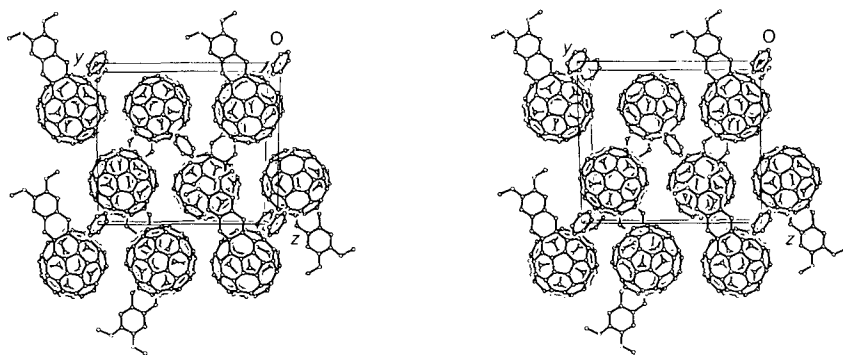


Fig. 2. Crystal packing of **2**·0.5 benzene as shown in the projection along the crystallographic *a*-axis

Complexation Studies. In preliminary studies, the receptor behavior of **1** was analyzed in extraction experiments which were monitored by UV/VIS spectroscopy. The UV/VIS spectra of both **1** and **2** are virtually identical and typical of fullerenes bridged at a 6–6 junction with a closed transannular bond [5] (Fig. 4). Compared to the spectrum of C₆₀, the spectra of **1** and **2** are generally less structured and the long-wavelength absorptions between 450 and 650 nm are hypsochromically shifted. New features in the spectra are sharp absorption bands at 433 (**1**) and 434 nm (**2**) as well as a weak though clearly distinguishable absorption at 705 nm (for both **1** and **2**). These bands were observed in a variety of C₆₀ derivatives bridged at the 6–6 ring junction and having a closed transannular bond [5] [7a, d].

Solid-liquid saturation extractions were performed with **1** and **2** in pure MeOH and in 0.1M KBr in MeOH. Veratrole derivative **2** shows a very low solubility in pure MeOH and an even slightly lower one in the salt solution (Fig. 4). Crown ether **1**, however, is 21.5 times more soluble in the KBr solution than in the pure solvent (comparison of the optical densities at 432 nm). This solubility enhancement results from the incorporation of K⁺ ions into the crown-ether moiety: a nonspecific salt effect on the solubility of **1** can be excluded based on the control experiment with **2**. The absence of complexation-induced shifts of the electronic absorption bands of **1** suggests that the K⁺ ion bound in the crown moiety does not interact with the fullerene chromophore.

An independent qualitative indication for the complexation was also obtained by ¹H-NMR spectroscopy in CDCl₃/CD₃OD 7:3. Following solid/liquid saturation extrac-

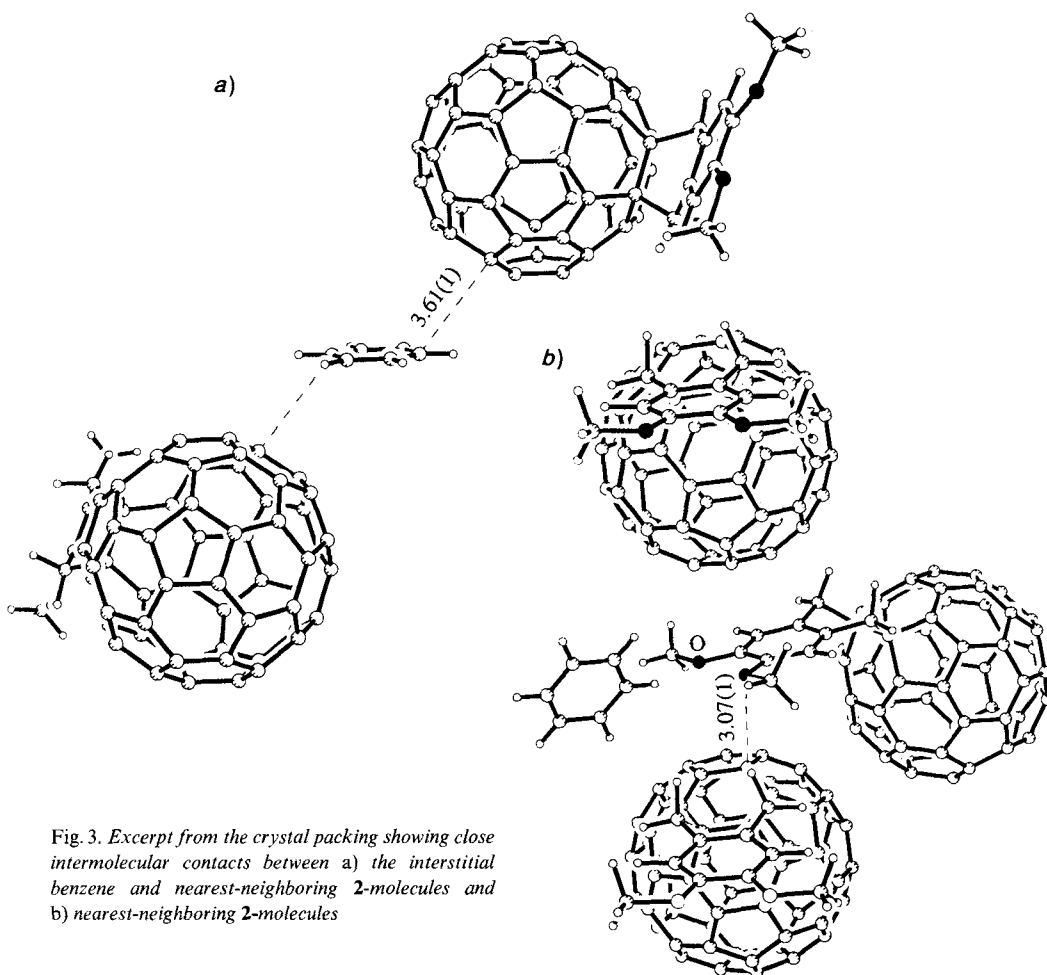


Fig. 3. Excerpt from the crystal packing showing close intermolecular contacts between a) the interstitial benzene and nearest-neighboring **2**-molecules and b) nearest-neighboring **2**-molecules

tion of KSCN with a solution of **1**, a small complexation-induced downfield shift (0.05 ppm) of the benzeno ^1H -resonance was observed. An identical complexation-induced shift can be measured under similar conditions for the corresponding protons of benzo[18]crown-6. Unfortunately, this shift is too small for a meaningful evaluation of the stability of the $\mathbf{1} \cdot \text{K}^+$ complex by ^1H -NMR binding titrations in homogeneous phase.

Amphiphilic Character of 1. As seen from Fig. 4, the crown ether **1** is much more soluble in MeOH (ca. 22 times) than the veratrole derivative **2**. This difference is due to the solubilizing effect of the crown moiety, which possesses six ether O-atoms to H-bond to the protic solvent molecules. Combined with the highly hydrophobic nature of the fullerene moiety, on the other hand, amphiphile **1** appeared as an ideal candidate for the formation of monolayers at a H_2O air interface [8].

Surface area *vs.* pressure measurements showed a pressure increase already at ca. $240 \text{ \AA}^2/\text{molecule}$. This points to an intensive interaction of the C_{60} derivative **1** with the H_2O surface (Fig. 5). Similar results were obtained with sugar and carboxylic-acid derivatives

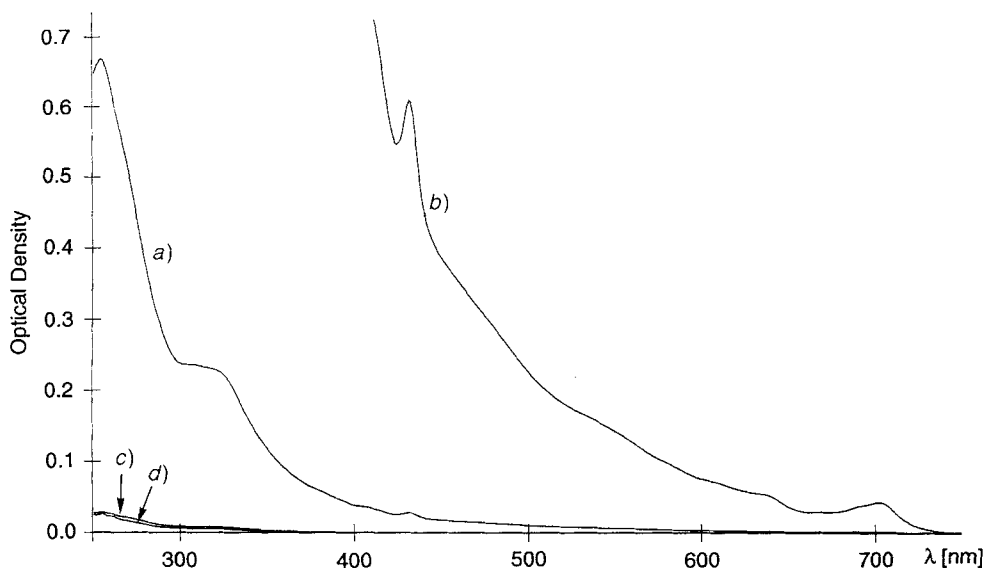


Fig. 4. UV/VIS Spectra of solutions prepared by solid-liquid extraction: a) **1** extracted with pure MeOH, b) **1** extracted with 0.1M KBr in MeOH, c) **2** extracted with pure MeOH, and d) **2** extracted with 0.1M KBr in MeOH. $T \approx 295$ K, $d = 1$ cm.

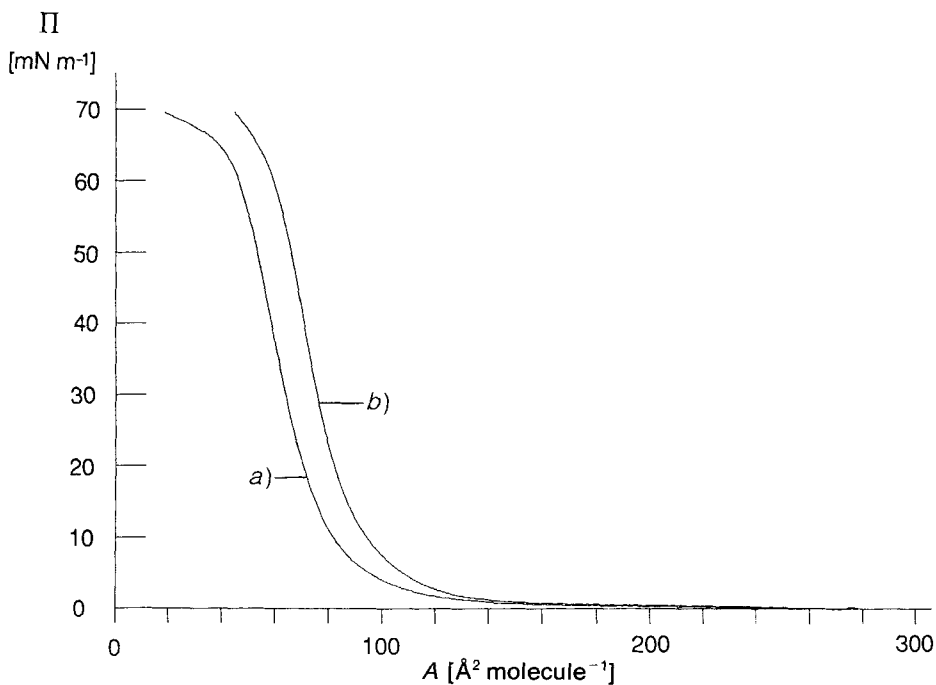


Fig. 5. Pressure area diagrams (Π/A isotherms) of **1** a) in pure H₂O and b) in 1.0M KCl

of fullerenes [11], but the crown compound **1** described here exhibits the best amphiphilic properties. In analogy to C_{60} , the curve continues as an isotherm with a steep pressure increase, however, showing a surface area of $80 \text{ \AA}^2/\text{molecule}$ corresponding to the theoretical value of C_{60} ($86.6 \text{ \AA}^2/\text{molecule}$). Succeeding expansion and compression experiments showed no hysteresis in pressure-area behavior, even at low surface pressures ($< 0.5 \text{ mNm}^{-1}$). This can be attributed to irreversible changes in the morphology of the rigid monolayer far away from any collapse, pointing to the fact that even an early domain formation of **1** is irreversible due to the high interaction of the fullerenes in the monolayer.

Attempts to transfer the film of **1** to mica at low pressure (1 mNm^{-1}) via the *Langmuir-Blodgett* technique were successful for the monolayer, but no multilayers could be obtained neither on hydrophilic nor on hydrophobic substrates.

Using a subphase containing K^+ ions with a concentration of 0.01 M and 0.1 M led only to a small but reproducible change in the isotherm of **1**. When the salt concentration was raised to 1 M , a significant increase in the surface area requirement was observed in the isotherm, leading to the ideal value as expected for C_{60} . Also a change in the spreading behavior was noticed since the solvent droplet flattened much stronger on contact with the K^+ subphase compared to pure H_2O .

The obvious stabilization of the monolayer upon complexation of K^+ ions is due to the increased hydrophilic character of the crown moiety, leading – as expected – to stronger interactions with the subphase. Studies of the complexation behavior with different metal ions as well as mono- and multilayer investigations on various solid supports are underway.

Experimental Part

General. Reagents used were reagent-grade commercial products. The crude fullerene-enriched soot, containing ca. 5% of soluble fullerenes, was purchased from *Polygon Enterprises*, P.O. Box 5536, Waco, TX 76708, USA. Charcoal (activated) was acid-washed *Darco G60* from *Fluka*. The toluene used for *Diels-Alder* reactions was dried over molecular sieves ($4 \text{ \AA}$). Column chromatography: silica gel (230–400 mesh, $0.04\text{--}0.063 \text{ mm}$) from *E. Merck* and from *Macherey-Nagel*; C_{18} reversed-phase silica gel *100* from *Fluka*; FC = flash chromatography. UV/VIS Spectra: *Varian-CARY-5* spectrometer. IR Spectra: *Perkin-Elmer-FT1600* spectrometer. 1H - and ^{13}C -NMR Spectra: *Bruker-AMX-500* and *Varian-GEMINI-200* and -300 spectrometers. MS: MALDI-TOF spectra with reflectron detection were recorded in the negative-ion mode, acceleration voltage 10 kV ; *Bruker REFLEX* spectrometer; 2,5-dihydroxybenzoic acid (0.1 M in $MeCN/EtOH/H_2O$ 50:45:5) as a matrix.

Purification of Fullerene[60] (C_{60}). C_{60} was purified on activated charcoal according to [5b], with the exception of an increase in the ratio of crude fullerene mixture to stationary phase which makes the procedure even more efficient. In fact, the activity of the charcoal was high enough for the separation of 5.6 g of crude fullerene extract on a mixture of 57 g of activated charcoal and 125 g of silica gel (230–400 mesh, $0.04\text{--}0.063 \text{ mm}$) yielding 4.0 g (71% based on crude fullerene soot extract containing ca. 75% of C_{60}) of C_{60} , contaminated with 3–5% of $C_{60}O$, corresponding to the initial amount of this oxide present in the crude extract.

4,5-Bis(bromomethyl)benzo[18]crown-6 (3**)** was prepared according to [12], except for a change in reaction temp. ($30\text{--}35^\circ$ instead of 5°).

1,2-Bis(bromomethyl)-4,5-dimethoxybenzene [13] (4**).** A total of 31 ml of 33% HBr in $AcOH$ was added to a soln. of 10 g (72 mmol) of 1,2-dimethoxybenzene and 4.325 g (144 mmol) of paraformaldehyde in 43 ml of $AcOH$, while the temp. was kept at ca. 17° . After stirring at r.t. for 20 h, the mixture was heated to 65° for 1 h, then cooled to r.t., and the formed colorless precipitate filtered off. Concentration of the mother liquor afforded more product, which was further purified by FC (silica gel, CH_2Cl_2 ; R_f 0.48). The pure fractions were dried at $20^\circ/0.1 \text{ Torr}$ over

KOH: 20.3 g (87%) of **4**. M.p. 108–110°. ¹H-NMR (300 MHz, CDCl₃): 6.84 (s, 2H); 4.63 (s, 4H); 3.90 (s, 6H). ¹³C-NMR (75.5 MHz, CDCl₃): 149.48 (C(OMe)); 128.06 (C(CH₂Br)); 113.6 (CH); 56.08 (MeO); 30.66 (CH₂Br). EI-MS: 324.0 (*M*⁺), 243.0 ([*M* – HBr]⁺), 164.1 ([*M* – Br]⁺).

1,9-Dihydro-64,65-dimethoxy-1,9-(methano[1,2]benzenomethano)fullerene[60] (= *1,9-Dihydro-64,65-dimethoxy-1,9-(benzo[1'',2'';2',3']but[2]eno)fullerene[60]*; **2**). A total of 100 mg (0.14 mmol) of **C**₆₀ and 167 mg (0.45 mmol) of Bu₄NI was mixed in 50 ml of dry toluene, sonicated, and purged with N₂. Subsequently, 67 mg (0.21 mmol) of **4** were added, and the mixture was refluxed in the dark for 27 h (purple→brown). After cooling down to r.t. and washing with H₂O, the mixture was submitted to FC (silica gel, toluene/hexane 3:1), yielding unreacted **C**₆₀ (20 mg) contaminated with I₂ and then the cognac-colored product (*R*_f 0.12). After evaporation, the product was redissolved in benzene and crystallized by vapor diffusion of pentane: 62 mg (50%) of **2**. Needle-shaped dark crystals with a metallic luster. UV/VIS (CH₂Cl₂): 705 (360), 636 (sh, 412), 434 (3630), 405 (sh, 4680), 318 (sh, 32920), 309 (33240), 256 (97340). ¹H-NMR (200 MHz, CS₂ with C₆D₆ as an internal lock, 300 K): 6.97 (s, 2H); 4.57 (br. s, 2H); 4.22 (br. s, 2H); 3.77 (s, 6H). ¹³C-NMR (125.8 MHz, C₂D₂Cl₄, 318 K): 157.18 (br.); 149.18; 147.92; 146.72; 146.48; 146.08; 145.70 (2 ×); 145.61; 144.97; 143.36; 142.81; 142.54; 142.32; 141.84; 140.35; 136.07 (br.); 130.68; 112.56 (CH); 66.49 (fullerene sp³-C); 56.78 (MeO); 45.21 (CH₂). MS (MALDI-TOF): 884.6 (*M*⁺), 720.2 (*C*₆₀⁺).

1,9-Dihydro-1,9-{[1',4',7',10',13',16']hexaoxacyclooctadecano[2',3':64,65](methano[1,2]benzenomethano)}-fullerene[60] (= *1,9,66,67,69,70,72,73,75,76,78,79-Dodecahydro-1,9-{[1''',4''',7''',10''',13''',16''']hexaoxacyclooctadeca[2''',3'''':4'',5'']benzo[1'',2'':2',3']but[2']eno}fullerene[60]*; **1**). A mixture of 500 mg (0.69 mmol) of **C**₆₀ and 830 mg (2.26 mmol) of Bu₄NI was reacted with 520 mg (1.04 mmol) of **3** in 250 ml of dry toluene as described above. After cooling down to r.t., the mixture was washed with H₂O, evaporated, and submitted to FC (50 g of *C*18 reversed-phase silica gel). Toluene eluted **C**₆₀ (186 mg) and a small amount of I₂ and toluene/MeOH 3:1 the functionalized fullerenes. Minor amounts of presumably higher adducts were separated from **1** by chromatography (short silica-gel column, benzene/MeOH 3:1, *R*_f 0.38). Vapor diffusion of pentane into the concentrated cognac-colored product fraction afforded 311 mg (42%) of **1**. Dark red-brown powder. UV/VIS (CH₂Cl₂): 705 (270), 636 (sh, 358), 433 (3900), 404 (sh, 5370), 317 (sh, 31740), 307 (32450), 256 (90110). ¹H-NMR (500 MHz, C₂D₂Cl₂, 353 K): 7.18 (s, 2H); 4.50 (br. s, 4H); 4.27–4.29 (*m*, 4H); 3.93–3.95 (*m*, 4H); 3.75–3.77 (*m*, 4H); 3.68–3.70 (*m*, 4H); 3.64 (s, 4H). ¹³C-NMR (125.8 MHz, C₂D₂Cl₄, 353 K): 157.17; 149.36; 147.97; 146.75; 146.52; 146.11; 145.74 (2 ×); 145.64; 145.01; 143.39; 142.84; 142.60; 142.36; 141.88; 140.41; 136.07; 131.50; 115.67 (CH); 71.16 (crown); 71.11 (crown); 71.07 (crown); 70.32 (crown); 70.16 (crown); 66.53 (fullerene sp³-C); 45.26 (benzylic CH₂). MS (MALDI-TOF): 1059.0 (*M*⁺), 720.0 (*C*₆₀⁺).

Area-Pressure Measurements with 1. A 0.1 mm soln. of **1** in CH₂Cl₂ (100 μl) was spread on a film balance with a surface area of 180 cm² at 20°. The compression rate was 12 cm² min⁻¹, and the surface pressure was measured with a *Langmuir* pressure pickup system. Pure H₂O (distilled and millipore-filtered, conductivity *ca.* 18 MΩ · cm) or 1.0M KCl in H₂O were used (*Fig. 5a* and *5b*, resp.).

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