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Covalent Attachment of Various Substituents in Closest Proximity to the C_{60}-Core: A Broad Synthetic Approach to Stable Fullerene Derivatives

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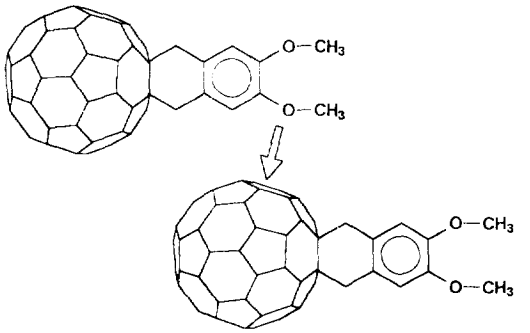
Abstract: α-Substituted *o*-quinodimethanes facilitate the covalent attachment of many attractive molecules in closest proximity to the C_{60}-core. Thermal isomerization of various (±)-hydroxybenzocyclobutene esters **4**, **8**, **10** and **13** in the presence of C_{60} provided the corresponding fullerene adducts **5(n)**, **7(n)**, **9(n)**, **11(n)** and **12(n)** in high yields. Using a dumbbell shaped bis-*o*-quinodimethane precursor **19**, accessible from (±)-7-hydroxybenzocyclobutene and dodecanedicarboxylic acid dichloride, a soluble C_{60}-containing polymer **20** was formed.

INTRODUCTION

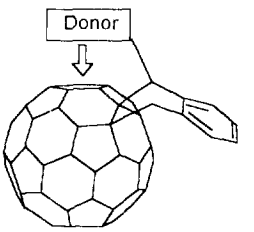
The [4+2] cycloaddition reaction of *o*-quinodimethanes with buckminsterfullerene (**1**) [1a-g] is well known for giving very stable adducts in excellent yields. The extremely reactive *o*-quinodimethane intermediates are formed *in-situ* either by thermal isomerization of benzocyclobutenes,[2a-e] thermal SO_2 extrusion from benzo[c]thiophene-2,2-dioxides [3a-c] or thermal CO_2 extrusion from 3-isochromanones.[4]

Functionalized fullerene derivatives are especially interesting target compounds because their reactivity enables the covalent attachment of attractive reaction partners (e.g. electron donors or polymers) to C_{60}. The reactive functional groups (e.g. amino, carboxyl, hydroxyl [5]) may be introduced either on the aromatic ring or at the benzylic position. Previously published results from our group showed that electron rich aromatic systems, which are covalently attached to C_{60}, exhibit an intermolecular interaction with C_{60} (scheme 1).[1c] This interaction leads to a significant reduction of the band gap, but due to the intermolecular nature of this it is only observed in the solid state.

To obtain C_{60}-adducts, which demonstrate new electronic properties even in solution (by intramolecular interactions), it is necessary to introduce the electron rich aromatic systems in close proximity to the C_{60}-core.



Scheme 1. Intermolecular interaction



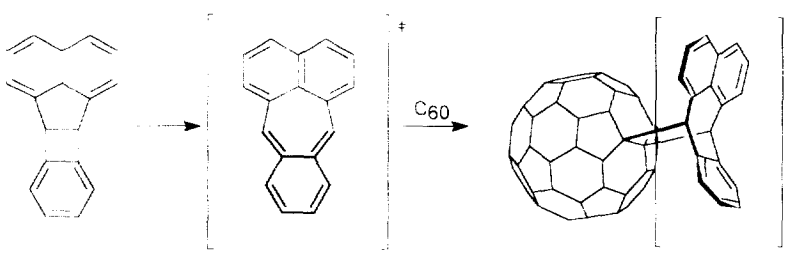
Scheme 2. Intramolecular interaction

The method of choice for this purpose is the introduction of the interacting compounds at the benzylic position (scheme 2). Besides this aspect, some *o*-quinodimethane precursors are especially well suited for the incorporation of fullerenes into polymers.[6a,b] In this publication we present a synthetic approach to benzylic substituted C_{60}-adducts as well as C_{60} containing polymers.

RESULTS AND DISCUSSION

Benzocyclobutenes are the best-suited *o*-quinodimethane precursors, because, on the one hand, benzocyclobutenes (substituted at the benzylic position) are easy to prepare and, on the other hand, the required temperature for ring opening and consequently the generation of *o*-quinodimethanes is very low as compared to other methods.[2a-e,3a-e,7]

Firstly, it was necessary to prove that the [4+2] cycloaddition of benzylic substituted *o*-quinodimethanes to C_{60} is not inhibited by steric hindrance. Towards this end, 6b,10b-dihydrobenzo[j]cyclobuta[a]-acenaphthylene **2**, which is easily accessible by the addition of benzyne to acenaphthylene,[2f] was treated with C_{60}. The reaction conditions and the work up for all C_{60}-adducts presented in this article are similar. Therefore, they are described only for the addition of **2** to C_{60} as a typical example (scheme 3).



2 **3(n)**

Scheme 3. Synthesis of compound **3(n)**

Refluxing C_{60} **1** in the presence of **2** (ratio 1 : 1.5) in 1,2,4-trichlorobenzene for five hours affords a mixture of the adducts **3(n)** (n: 1 and 2). The formation of by-products has not been observed. After the reaction the solvent is evaporated under vacuum and the residue is dissolved in chloroform. Due to the good solubility of the adducts, the raw material can be easily separated by chromatography on polystyrene gel with chloroform as the mobile phase.[9a,b,c] The reaction mixture consists of 11% of unchanged C_{60}, 57% of **3(n=1)** and 32% of **3(n=2)**. The structure of the adducts formed (scheme 3) is substantiated by FD mass spectrometry, ^{1}H NMR and ^{13}C NMR spectroscopy. The relative yields of the different multiadducts can be influenced by changing the ratio of C_{60} to 6b,10b-dihydrobenzo[j]cyclobuta[a]-acenaphthylene. The yields of all C_{60}-adducts are summarized in table 2 in the experimental part. The successful addition of **2** to **1** illustrates that bulky substituents at the benzylic position do not inhibit the cycloaddition reactions to C_{60}. This offers the possibility to prepare a variety of benzylic substituted C_{60}-adducts.

a.) Preparation of (±)-7-hydroxybenzocyclobutene derivatives and their cycloaddition reactions to C_{60}

Benzyne, which is formed in the conventional manner from anthranilic acid, reacts *in-situ* with vinyl acetate in a [2+2] cycloaddition reaction to furnish (±)-7-acetoxybenzocyclobutene (**4**) [2f]

The [4+2] cycloaddition of **4** to C_{60} affords the corresponding adducts **5(n)** (scheme 4). As for all the C_{60}-compounds described herein, the adducts **5(n)** are stable in air and well soluble in halogenated hydrocarbons and tetrahydrofuran. The cyclic voltammetric analysis of the adducts **5(n)** shows that a) they can be reversibly charged with up to four electrons and b) the reduction potentials of the adducts **5(n)** are significantly shifted to lower values as compared to C_{60} (table 1).

Table 1. Cyclic Voltammetric Analysis of **5(n=1)** and C_{60} 1 (THF/[TBA]PF_6, 0°C, Fc/Fc^+(internal standard): -0.310 V vs. SCE, working electrode: Au, counter electrode: Pt, scan rate: 100 mV/s)

	$E_0(1)$	$E_0(2)$	$E_0(3)$	$E_0(4)$
5(n=1)	- 0.68 V	- 1.23 V	- 1.83 V	- 2.28 V
C_{60}	- 0.33 V	- 0.92 V	- 1.49 V	- 1.99 V
Δ [5(n=1) - C_{60}]	- 0.35 V	- 0.31 V	- 0.34 V	- 0.29 V

The structure of the monoadduct **5(n=1)** is elucidated by spectroscopic measurements. The temperature-dependent ^{1}H NMR spectra of pure **5(n=1)** prove the existence of two different conformers at 28°C and show coalescence at a temperature of about 140°C [6c]. These two conformers, which are "frozen" at room temperature, differ in that the substituents of the benzocyclohexene unit can be located either in the pseudoaxial (conformer X) or the pseudoequatorial position (conformer Y). The ^{1}H NMR signals belonging to one conformer (X or Y) are arbitrarily assigned with **a** or **b** in the experimental part and fig. 1. The ratio of these conformers (1.06:1 in the case of **5(n=1)**) may be influenced by peri-interactions between the substituent and the *o*-phenyl proton and/or the C_{60}-unit (as observed in tetrahydronaphthalene compounds)[10] and by electronic interactions between the substituent and the C_{60}-core. The influence of the substituents is illustrated by the following examples. The adducts **7(n=1)** and **9(n=1)** (scheme 4) prefer different boat conformations (ratio 1.1.46 or 1.1.13, resp.) as compared to **11(n=1)** and **12(n=1)** (scheme 4) (ratio 1.38:1 or 1.66:1, resp.) (fig. 1). This is most probably due to the attractive interaction of electron-donating substituents (**7(n=1)** and **9(n=1)**) or repelling interaction of electron deficient substituents (**11(n=1)** and **12(n=1)**) with the electron deficient C_{60}-core.

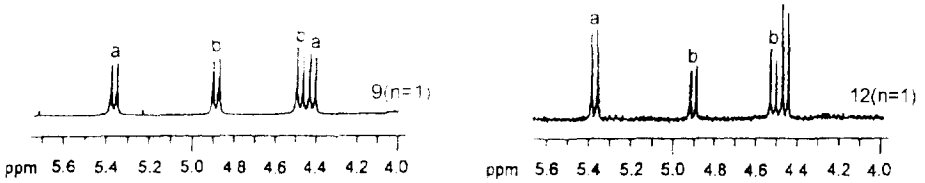
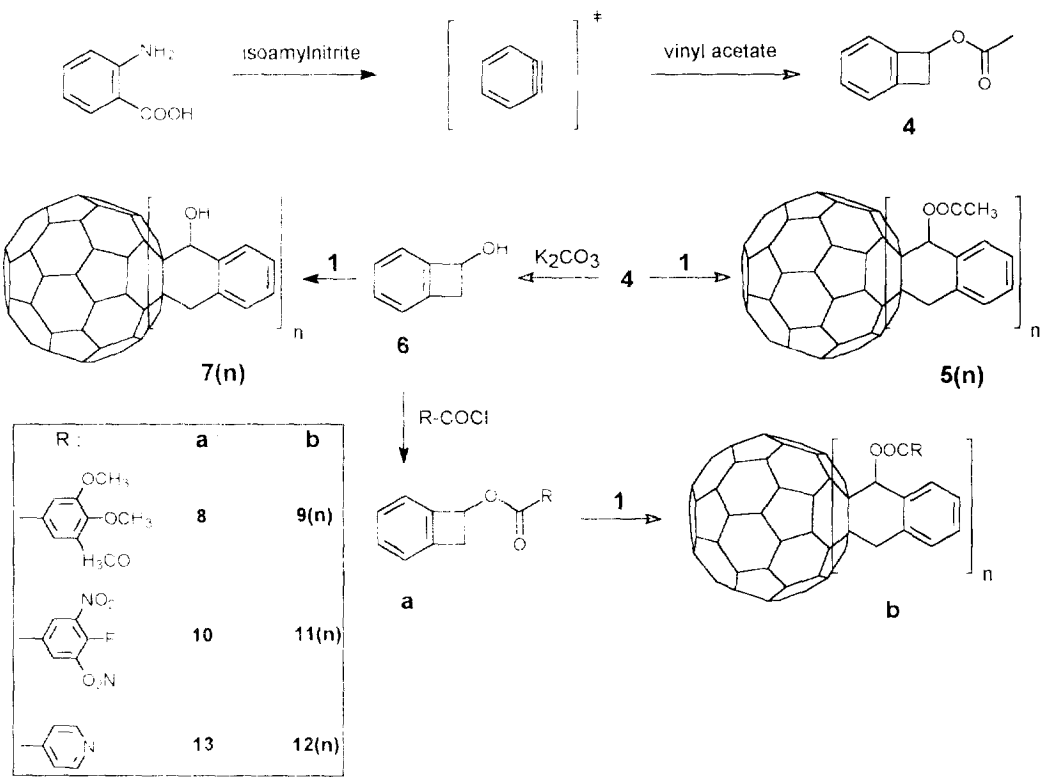


Fig. 1: ^{1}H NMR signals of the benzylic protons of the conformers **a** and **b**

By treatment with K_2CO_3, the ester **4** is easily cleaved to (±)-7-hydroxybenzocyclobutene **6** (scheme 4),[8] which is a key compound for the synthesis of fullerene adducts, substituted at the benzylic position. In principle, these adducts can be prepared by two different reaction sequences: 1) The addition of **6** to **1** affords

7(n), which may be further functionalized (C.F. Foote et al. [6c]). 2) In a first step, **6** is modified, followed by the addition of the resulting derivatives to **1**. For the covalent attachment of some reactants (e.g. nucleophiles or metal complexes) the first route is often impractical, because the direct addition of the reactant to the C_{60}-core may be preferred. Thus, the second route is more versatile for the preparation of a variety of fullerene compounds which are substituted at the benzylic position. This will be described in the following on the basis of some examples.

As mentioned in the introduction, the emphasis is on fullerene materials which exhibit new electronic properties due to intramolecular interactions, even in solution. In order to promote these donor-acceptor interactions, the donor group should be introduced in close proximity (benzylic position) to the C_{60}-core. Based on the observation of a strong intermolecular interaction between oxygen and the C_{60}-core in the adduct of 4,5-dimethoxy-*o*-quinodimethane and C_{60} (scheme 1),[1a,c] the 3,4,5-trimethoxybenzoyl substituent

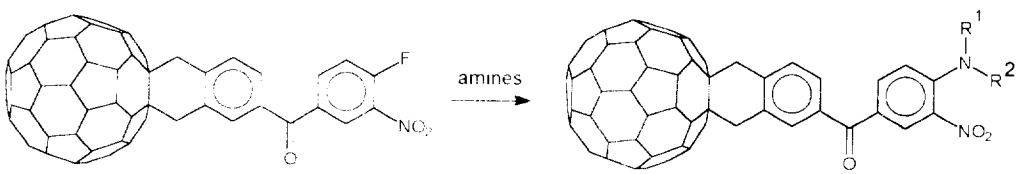


Scheme 4. Reaction sequence for the preparation of **5(n)**, **7(n)**, **9(n)**, **11(n)** and **12(n)**.

is introduced at the benzylic position. For this purpose, the ±-7-(3,4,5-trimethoxybenzoyl)-benzocyclobutenylester (**8**) is prepared by esterification of **6** with 3,4,5-trimethoxybenzoyl chloride. Reaction of **8** with C_{60} affords the corresponding adducts **9(n)** (scheme 4). However, **9(n=1)** does not show a charge-transfer band in the UV/VIS-spectrum. A weak intramolecular interaction is only indicated by ^{1}H NMR (fig. 1). In contrast to C_{60}-adducts with electron deficient aromatic substituents which prefer the formation of

conformer a (e.g. **11(n)** and **12(n)**, fig. 1), conformer b (fig. 1) is slightly preferred by **9(n)**. Obviously, the structure of the adduct is not flexible enough to permit an optimized arrangement of the substituent which would be necessary to achieve an intramolecular interaction. It appears more appropriate to attach the electron donating group via a more flexible spacer.

Previously published results from our group showed that activation of fluoro substituents by a nitro group enables C_{60}-adducts (scheme 5)[1b] to undergo nucleophilic aromatic substitution with aliphatic and aromatic amines. The major drawback of this approach has been the long reaction time required for the less nucleophilic aromatic amines (e.g. 4-aminoazobenzene). In order to counteract this handicap, a second nitro group must be introduced at ortho-position to the fluorine to increase the tendency toward nucleophilic substitutions. By nitration of 4-fluorobenzylic acid under drastic conditions, 4-fluoro-3,5-dinitrobenzylic acid is formed in nearly quantitative yield. The latter can be easily converted into the acid chloride by treatment with thionyl chloride.



Scheme 5. Nucleophilic substitution of a fluoro-nitro substituted fullerene adduct by amines

Esterification with **6** leads to 1-7-(4-fluoro-3,5-dinitrobenzoyl)benzocyclobutenylester (**10**) (scheme 4). The high reactivity of **10** is indicated by its reaction with cold methanol in the absence of any basic catalysts: The corresponding methoxy compound is formed in a few minutes. Thus, the derived C_{60}-adduct **11(n)** should be also well suited for further functionalization. Reaction of **10** with C_{60} in 1,2,4-trichlorobenzene leads to the adducts **11(n)** (scheme 4). Unexpectedly, these adducts are surprisingly resistant to nucleophilic substitutions, even in the presence of basic catalysts. This behavior may result from the extremely hydrophobic character of the neighboring C_{60}-core which makes the ionic transition state of the reaction unattractive.

An opposite reactivity to **11(n)** can be achieved by the introduction of a pyridyl unit. These adducts should be accessible to reactions with electrophiles such as alkyl halides to form stable pyridinium salts.

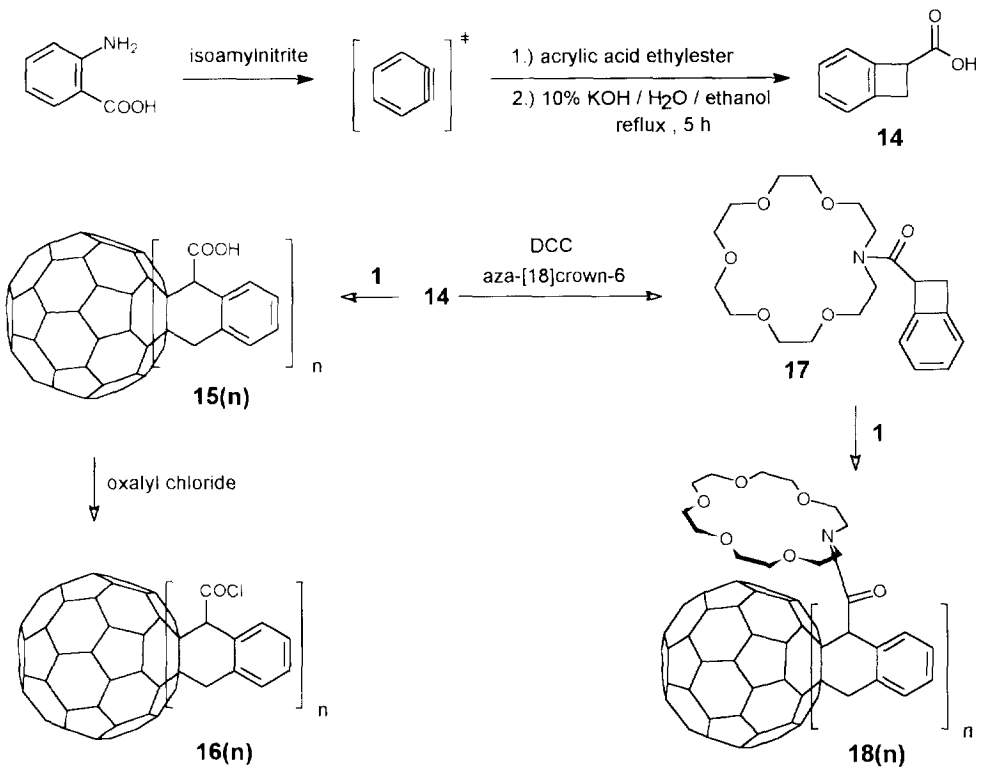
The pyridyl substituted adducts **12(n)** are synthesized from **13** according to the reaction sequence shown in scheme 4. These adducts can be alkylated at the nitrogen atom, for example by treatment with methyl iodide. Though the pyridinium salts derived from **12(n)** are only poorly soluble in halogenated hydrocarbon solvents, they are well suited for the incorporation of fullerenes into polymers which contain chloromethylene groups (e.g. chloromethylene functionalized polystyrene gel for chromatography). These C_{60}-containing resins may be promising due to their catalytic activity or suitability as stationary phases in chromatography.

b.) Preparation of (±)-7-benzocyclobutene carboxylic acid derivatives and their addition reactions to C_{60}

An extension of the applications of benzylic substituted benzocyclobutenes for the preparation of fullerene adducts is achieved by using (±)-7-benzocyclobutene carboxylic acid **14**. The cycloaddition of this compound to C_{60} furnishes C_{60}-carboxylic acid **15(n)** (scheme 6).

While the freshly prepared C_{60}-carboxylic acid **15(n)** is well soluble in halogenated hydrocarbons, the solubility decreases with aging. This behavior is probably caused by the slow formation of intermolecular

hydrogen bonds between the carboxylic groups. Thus, agglomeration occurs especially if multiadducts **15(n>1)** are present. The resulting low solubility of **15(n)** in chlorocarbon solvents prevents the separation of larger amounts of **15(n=1)**. To bring about a better solubility, **15(n)** is transformed into the carboxylic acid chloride **16(n)** by treatment with oxalyl chloride (scheme 6).



Scheme 6. Reaction sequence for the preparation of **15(n)**, **16(n)** and **18(n)**.

Due to its better solubility, **16(n)** is suitable for chromatographic separation on polystyrene gel with chloroform as the mobile phase.

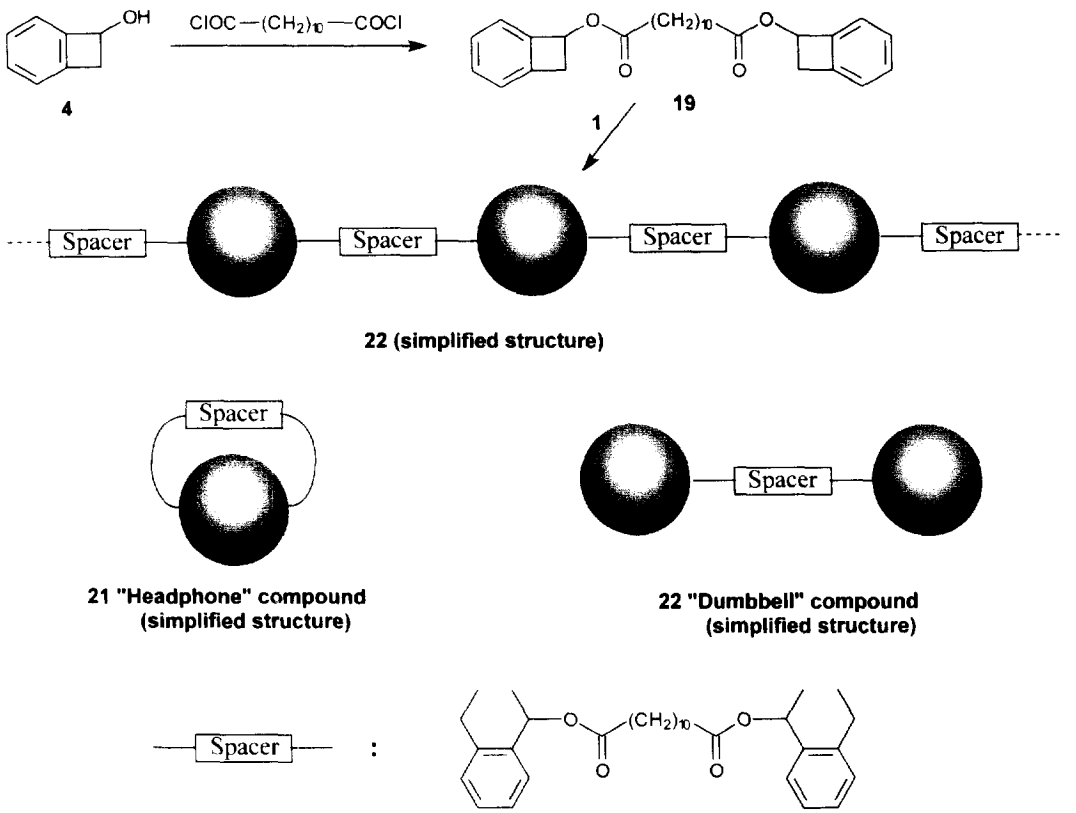
As described for the α-hydroxy-*o*-quinodimethane-C_{60}-adduct (**7(n)**) (chapter a)), again two different reaction pathways towards functionalized adducts are conceivable: 1) reaction of **16(n)** with amines or alcohols, and 2) transformation of **14** into esters or amides followed by addition to C_{60}. Via the second route it is possible to attach an ionophore covalently to C_{60}. For this purpose, **14** is condensed with aza-[18]-crown-6 in the presence of DCC (dicyclohexylcarbodiimide) to afford the amide **17**. Subsequent addition of **17** to C_{60} in 1,2,4-trichlorobenzene at 180°C provides the adducts **18(n)** in good yields (scheme 6). Owing to their capability for selective complexation of cations or the formation of electrides, these adducts possess a wide range of applications.[11] Complexation of cations may increase the amphiphilic character of these fullerene derivatives which could then be used for the preparation of LB-films.[11] Another aspect, the increased solubility in polar solvents,[11] is an important precondition for the physiological activity of fullerene adducts.

c.) Preparation of polymers with incorporated C_{60}-units

The application of fullerenes (e.g. as catalyst or stationary phase) often requires their immobilization. This can be attained by linking either C_{60} or C_{60} derivatives covalently with a carrier material. Therefore, the incorporation of fullerenes into polymers is an important aspect of fullerene chemistry. Several approaches directed towards the preparation of C_{60}-containing polymers have been published,[12a-c] but the great majority of the polymers were either poorly soluble (and hence not processible) or of a low molecular weight. In order to accomplish the synthesis of soluble, high molecular weight polymers, C_{60} is treated with bis-*o*-quinodimethane compounds in a repetitive Diels-Alder reaction. The diester compound **19** is accessible from ± -7-hydroxybenzo-cyclobutene (**6**) by reaction with 1,12-dodecanedicarboxylic acid dichloride (scheme 7). Six equivalents of this bis-*o*-quinodimethane precursor are heated up to 210°C in the presence of C_{60}, whereby the polymer **20** with C_{60} in the main-chain, a "headphone" compound **21** (which consists of several isomers) and a "dumbbell" compound **22** are formed (scheme 7, idealized structures).

A mixture of **21** and **22** has been separated from the higher molecular weight reaction products by careful chromatography on polystyrene gel with chloroform as a mobile phase. The isolation of pure **21** and **22** by SEC was not possible, thus their structures were not completely elucidated. FD-MS measurements of the mixture showed only the molecular ion peaks M/Z = 1154.2 (M^+ of **21**) and M/Z = 1874.3 (M^+ of **22**). Therefore, **21** and **22** are supposed to be formed by double addition of one molecule of **19** to one C_{60}-unit or by addition of one molecule of **19** to two C_{60}-units, respectively. Due to the flexible spacer and the large distance between the C_{60}-units, the polymer is extraordinary well soluble in chloroform, methylene chloride and THF.

By using preparative liquid chromatography with polystyrene gel as stationary phase, the adducts **21** and **22** and several polymer fractions are separated from the reaction mixture. For the highest molecular weight polymer fraction (~30% of the raw polymer material), analytic SEC reveals M_n = 9500, M_w = 10300, P_n = ~9 and D = 1,091. The UV/VIS spectra of all polymer fractions resemble that of C_{60}-adducts, but the absorption maximum at 435 nm, which is characteristic for monoadducts, is absent. This strange observation is only explainable on the assumption that the C_{60}-adducts are additionally functionalized by at least one *o*-quinodimethane. In our experience the "headphone" compound **21** is formed in large amounts even when using a six-fold excess of C_{60} (related to **19**). This suggests that the C_{60}-units in the polymer are additionally modified with loops ("headphone" structure). The existence of these "headphone" units in the polymer chain may avoid chain branching or cross-linking during the phase of chain growth, because chain branching at a "headphone" unit would require a five-fold addition to a C_{60}-unit, which is improbable as long as free C_{60} is present. Apart from the flexible spacer, the absence of cross-linking is another reason for the observed solubility of the polymer. Solutions of **20** in tetrachloroethane are processible into thin amorphous films (thickness: 245 nm) by spincoating at 1000 rpm. Insoluble films can be prepared by spincoating a mixture of **20** and a strong excess of **19** followed by heating to 250°C for 5 hours which causes cross-linking.



Scheme 7. Synthesis of polymers with incorporated C_{60} units in the main chain

CONCLUSIONS

The Diels-Alder cycloaddition of α-substituted benzocyclobutenes to C_{60} proves to be a versatile method for the generation of stable fullerene derivatives in very good yields. Thus, a multitude of compounds (specifically electron donors) can be introduced in close proximity to the C_{60}-core. The resulting intramolecular interactions of the attached compounds with the fullerene core open up a variety of potential new applications. Besides this aspect, it has been demonstrated that dumbbell shaped bis-benzocyclobutene compounds are especially well suited for the preparation of soluble C_{60}-containing main-chain polymers, which are also processible to thin films by spincoating. On the basis of these results the preparation of new stationary phases (e.g. for the separation of polynuclear aromatic hydrocarbons) or catalysts is conceivable.

EXPERIMENTAL

Compounds **8**, **10**, **13** and **19** were prepared by esterification of **6** with different carboxylic acid chlorides: ±-7-Benzocyclobutenol (**6**) (200 mg, 1.6 mmol, 1 eq.) triethylamine 1 eq. and 1 eq. of the carboxylic acid chloride (0.5 eq. of 1,12-dodecanedicarboxylic acid dichloride) were refluxed in 50 ml methylene chloride for 12 h. The formed triethylammonium-hydrochloride was removed by extracting the reaction mixture with 5%

HCl and 3 times with water. The crude product was purified by flash chromatography with methylene chloride as eluent. The yields of the pure esters are about 65%.

Compound **17** was formed by condensation of (±)-7-benzocyclobutene carboxylic acid (**14**) with aza-[18]-crown-6:[13]

(±)-7-Benzocyclobutene carboxylic acid **14** (200 mg, 1.35 mmol, 1 eq.), 355 mg (1.35 mmol, 1 eq.) of aza-[18]crown-6 and 304 mg (1.49 mmol, 1.1 eq.) of dicyclohexylcarbodiimide (DCC) were dissolved in 20 ml methylene chloride at -10°C and

stirred for 8 h. The white precipitate (dicyclohexylcarbamide) was removed by filtration. After removal of the solvent **17** was isolated in 81% yield

General conditions for the reaction of C_{60} with *o*-quinodimethanes, formed by thermal ring opening of benzocyclobutenes, to 3(n), 5(n), 7(n), 9(n), 11(n) and 12(n) [1a,b,6a]

C_{60} and the benzocyclobutene compound were dissolved in 1,2,4-trichlorobenzene (1 mg C_{60} / 1 ml) and refluxed for 5 h (the amounts of C_{60} and the benzocyclobutene derivative are listed in table 2). After ~30 min the color of the reaction mixture is observed to change from violet to dark brown. After removing the trichlorobenzene by vacuum evaporation, the brown solid was dissolved in trichloromethane and filtered through a 0.25 µm teflon-membrane filter. The different multiadducts were separated by chromatography on polystyrene gel with chloroform as mobile phase. The yields of all synthesized fullerene adducts (related to C_{60}) are given in table 2.

Table 2. Ratio of Starting Materials and Resulting Yields of C_{60}-Adducts

	Starting materials:			Separated products:			
Adduct No.	C_{60} [mmol]	BCB[a] [mmol]	ratio:	n = 1 [mg]	n = 2 [mg]	n ≥ 3 [mg]	unchanged C_{60} [mg]:
3(n)	0.139	**2** (0.21)	1:1.5	75.1 (57%)	53 (33%)	-	10.6 (10%)
5(n)	0.565	**4** (1.23)	1:2.2	85 (17%)	324 (55%)	187 (27%)	3.5 (1%)
7(n)	0.139	**6** (0.138)	1:1	85 (73%)	17 (13%)	-	14 (14%)
11(n)	0.414	**10** (0.621)	1:1.5	135 (31%)	92 (16%)	47.5 (7%)	137 (46%)
12(n)	0.69	**13** (0.35)	2:1	288 (44%)	26 (3%)	-	260 (53%)
9(n)	0.414	**8** (0.621)	1:1.5	132 (31%)	72 (13%)	44 (6%)	148 (50%)
15(n)	0.139	**14** (0.21)	1:1.5	10[b]	-	-	-
18(n)	0.12	**17** (0.1)	1.2:1	72.7 (54%)	26 (14%)	-	26 (32%)

[a] BCB = number of the corresponding benzocyclobutene derivative

[b] only a small amount was separated due the low solubility of **15(n)**

Characterization of the reaction products

3(n): MS(FD) of the crude material: M/Z = 948 ($[M]^+$ of **3(n=1)**, 100 %), 1176 ($[M]^+$ of **3(n=2)**, 67 %). Retention volume (600 x 20 mm column, polystyrene gel 100 Å / 5 µm, $CHCl_3$: 7 ml/min, injection: 2 ml): **3(n=1)**: 105.9 ml, **3(n=2)**: 93.0 ml, C_{60}: 130.62 ml

3(n=1): ^1H NMR (500 MHz, $C_2D_2Cl_4$, 28°C): δ = 5.91 (s, 2 H, CH), 7.51-7.57 (m, 4 H, CH), 7.71 (d, 2 H, CH, 7 Hz), 7.84 (dd, 2 H, CH, 5 Hz and 3 Hz), 8.02 ppm (d, 2 H, CH, 7 Hz); ^{13}C NMR (125 MHz, $C_2D_2Cl_4$, 28°C, J-modulated spin-echo): δ = 65.15 (CH, aliphatic C atoms), 72.06 (quaternary, aliphatic C atoms of C_{60}), 126.87, 127.19, 127.90, 128.76, 129.27 (CH, aromatic), 129.11, 136.06, 136.32, 136.78 (quaternary, aromatic C atoms), 139.37, 139.91, 140.20, 140.27, 141.71, 141.86, 142.16, 142.26, 142.38, 142.61, 142.72, 142.80, 143.27, 144.86, 144.90, 145.34, 145.38, 145.49, 145.55 (quaternary C_{60} atoms), 145.61, 145.64, 145.66 (quaternary C_{60} atoms, several signals overlapping) 145.88, 146.38, 146.41, 146.58, 146.65, 147.88 ppm (quaternary C_{60} atoms). UV/VIS ($CHCl_3$) similar to C_{60}, shows an absorption maximum at 435 nm. MS(FD): M/Z = 948 ($[M]^+$ of **3(n=1)**, 100 %)

5(n): MS(FD) of the crude material: M/Z = 882.2 ($[M]^+$ of **5(n=1)**, 66%), 1044.3 ($[M]^+$ of **5(n=2)**, 100%), 1206.3 ($[M]^+$ of **5(n=3)**, 68%), 1369.5 ($[M]^+$ of **5(n=4)**, 4%). Retention volume (600 x 20 mm column, polystyrene gel 100 Å / 5 µm, $CHCl_3$: 7 ml/min, injection: 2 ml): **5(n=1)**: 106.1 ml, **5(n=2)**: 95.9 ml, **5(n≥3)**: 90.5 ml, C_{60}: 130.6 ml

5(n=1) (Mixture of conformers a and b, ratio: 1.06 : 1): ^1H NMR (500 MHz, $C_2D_2Cl_4$, 28°C): δ = 2.28 (s, 3 H, CH_3, a), 2.28 (s, 3 H, CH_3, b), 4.33 (d, 1 H, CH_2, 14 Hz, a), 4.45 (d, 1 H, CH_2, 14 Hz, b), 4.83 (d, 1 H, CH_2, 14 Hz, a), 5.31 (d, 1 H, CH_2, 14 Hz, b), 7.49-7.64 ppm (m, 10 H, CH), ^{13}C NMR (125 MHz, $C_2D_2Cl_4$, 28°C, J-modulated spin-echo): δ = 44.20, 44.56 (secondary aliphatic C atoms), 64.31, 66.37, 69.51, 69.79 (quaternary aliphatic C atoms, conformers), 120.59, 121.58 (quaternary arene C atoms), 128.09, 128.53, 130.00, 131.22, 131.27, 132.37 (ternary arene C atoms), 134.22, 137.59, 137.65 (quaternary arene C atoms), 141.78, 141.87, 142.10, 142.27, 142.72, 142.78, 145.53, 145.59, 145.62, 145.77, 145.84, 146.38, 146.57, 146.64, 146.71 (C_{60}-C atoms), 152.55, 155.75, 156.97, 161.64 (quaternary arene C atoms), 170.57, 170.75 ppm (C=O). UV/VIS ($CHCl_3$) similar to C_{60}, shows an absorption maximum at 435 nm. MS(FD): M/Z = 882.2 ($[M]^+$ of **5(n=1)**, 100 %)

7(n): MS(FD) of the crude material: M/Z = 840 ($[M]^+$ of **7(n=1)**, 100%), 720 ($[M]^+$ of C_{60}, 35%). Retention volume (600 x 20 mm column, polystyrene gel 500 Å / 10 µm, $CHCl_3$: 7 ml/min, injection: 1.5 ml): **7(n=1)**: 156.17 ml, C_{60}: 147 ml

7(n=1) (Mixture of conformers a and b, ratio: 1 : 1.46): ^1H NMR (500 MHz, $C_2D_2Cl_4$ 28°C): δ = 2.84 (s, 1 H, OH, a), 2.90 (s, 1 H, OH, b), 4.29 (d, 1 H, CH_2, 13.8 Hz, a), 4.42 (d, 1 H, CH_2, 14 Hz, b), 4.73 d, 1 H, CH_2, 14 Hz, b), 5.52 (d, 1 H, CH_2, 13.8 Hz, a), 6.30 (s, 1 H, CHOH, a), 6.44 (s, 1 H, CHOH, b), 7.51-7.90 ppm (m, 8 H, CH, a and b); ^1H NMR (200 MHz, $C_2D_2Cl_4$ 140°C): δ = 2.98 (s, 1 H, OH), 4.66 (d, 1 H, CH_2, 13.8 Hz), 5.00 (d(br.), 1 H, CH_2), 6.48 (s, 1 H, CH), 7.16-7.90 ppm (m, 4 H, CH); ^{13}C NMR (125 MHz, $C_2D_2Cl_4$, 28°C, J-modulated spin-echo): δ = 44.91, 45.13 (secondary aliphatic C atoms), 65.54, 67.39 (quaternary aliphatic C atoms), 117.3, 120.70 (quaternary arene C atoms), 129.08, 129.24, 129.47, 129.75, 130.52, 130.55, 131.62 (ternary arene C atoms), 136.27, 136.57, 137.15, 137.19 (quaternary arene C atoms), 140.80-159.22 ppm (C_{60}-C atoms, several signals overlapping). UV/VIS ($CHCl_3$) similar to C_{60}, shows an absorption maximum at 435 nm. MS(FD): M/Z = 840 ($[M]^+$ of **7(n=1)**, 100 %)

8: MS(FD) M/Z = 314.0 ([M]$^+$ of **8**, 100%), 628.1 ([2M]$^+$ of **8**, 55%), 942.4 ([3M]$^+$ of **8**, 19%); ^{1}H NMR (200 MHz, $CDCl_3$, 30°C) δ = 3.39 (dd, CH_2, 1 H, 14.2 Hz and 1.8 Hz), 3.78 (dd, CH_2, 1 H, 14.2 Hz and 4.6 Hz), 6.16 (dd, CH_2, 4.6 Hz and 1.8 Hz), 7.18-7.41 ppm (m, CH, 6 H)

9(n): MS(FD) of the crude material M/Z = 1033.7 ([M]$^+$ of **9(n=1)**, 100%), 1346.8 ([M]$^+$ of **9(n=2)**, 48%). Retention volume (600 x 25 mm column, polystyrene gel 500 Å / 10 µm, $CHCl_3$, 7 ml/min, injection: 2 ml): **9(n=1)** 188.0 ml, **9(n=2)** 170.0 ml

9(n=1) (Mixture of conformers a and b, ratio 1 : 1.33) ^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 28°C): δ = 3.68 (s, 6 H, OCH_3, b), 3.78 (s, 3 H, OCH_3, a), 3.82 (s, 3 H, OCH_3, b), 3.88 (s, 6 H, OCH_3, a), 4.43 (d, 1 H, CH_2, 14 Hz, a), 4.50 (d, 1 H, CH_2, 14 Hz, b), 4.90 (d, 1 H, CH_2, 14 Hz, b), 5.38 (d, 1 H, CH_2, 14 Hz, a), 7.21-7.98 ppm (m, 10 H, CH); ^{1}H NMR (200 MHz, CD_2Cl_4, 140°C) δ = 3.93 (s, 6 H, OCH_3), 3.97 (s, 3 H, OCH_3), 4.8 (d(br.), 1 H, CH_2), 5.1 (br., 1 H, CH_2), 7.58-7.90 ppm (m, 5 H, CH). ^{13}C NMR (125 MHz, $C_2D_2Cl_4$, 28°C) δ = 44.27, 44.95 (secondary aliphatic C atoms), 56.41, 56.63, 61.28, 61.35 (primary aliphatic C atoms), 64.35, 66.37, 69.70 (two signals) (sp^3-C atoms of C_{60}), 75.77, 81.32 (secondary aliphatic C atoms) 107.42, 107.61, 123.58 (ternary C atoms), 124.02, 125.12, 128.2, 128.32, 129.07, 129.19, 130.49, 130.83 (quaternary aromatic C atoms), 134.95, 135.39, 136.56, 136.69, 137.09, 140.03, 142.01, 142.15, 142.26, 142.39, 142.45, 142.89, 143.34, 145.00, 145.02, 145.73, 145.86, 145.98, 146.04, 146.47, 146.50, 146.54, 146.76, 146.82, 146.86, 148.02 (C_{60}-C atoms, several signals overlapping), 151.84, 152.59, 153.41, 153.50, 154.56, 156.33, 156.37, 157.88 (quaternary arene C atoms), 165.34, 165.78 ppm (C=O). UV/VIS ($CHCl_3$) similar to C_{60}, shows an absorption maximum at 435 nm. MS(FD): M/Z = 1033.7 ([M]$^+$ of **9(n=1)**, 100 %)

10: m.p. 129°C, MS(FD): M/Z = 332 ([M]$^+$ of **10** 100%), ^{1}H NMR (200 MHz, $CDCl_3$, 30°C): δ = 3.43 (d, 1 H, CH_2, 14.6 Hz), 3.80 (dd, 1 H, CH_2, 4.4 Hz and 14.6 Hz), 6.20 (dd, 1 H, CHOR, 1.2 Hz and 4.0 Hz), 7.17-7.39 (m, 4 H, CH), 8.95 ppm (d, 2 H, CH, 6.3 Hz)

11(n): MS(FD) of the crude material: M/Z = 1052 ([M]$^+$ of **11(n=1)**, 78%), 1384 ([M]$^+$ of **11(n=2)**, 100%), 1716 ([M]$^+$ of **11(n=3)**, 16%). Retention volume (600 x 20 mm column, polystyrene gel 100 Å / 5 µm, $CHCl_3$, 7 ml/min, injection: 1 ml): **11(n=1)** 104.8 ml, **11(n=2)** 93.2 ml, **11(n≥3)** 84.6 ml, C_{60} 131.4 ml.

11(n=1) (Mixture of conformers a and b, ratio 1.38 : 1): ^{1}H NMR (500 MHz, CD_2Cl_4, 28°C): δ = 4.58 (d, 1 H, CH_2, 14 Hz, a), 4.64 (d, 1 H, CH_2, 16 Hz, b), 4.99 (d, 1 H, CH_2, 14 Hz, b), 5.4 (d, 1 H, CH_2, 14 Hz, a), 7.55-7.85 (m, 8 H, CH, a and b), 8.01 (s, 1 H, CHOR, a), 8.03 (s, 1 H, CHOR, b), 9.12 (s, 2 H, CH, a), 9.25 ppm (s, 2 H, CH, b). ^{1}H NMR (200 MHz, CD_2Cl_4, 140°C) δ = 4.79 (d, 1 H, CH_2, 14 Hz), 5.13 (d(br.), 1 H, CH_2), 7.67-7.92 (m, 4 H, CH), 9.16 ppm (s, 1 H, CH). ^{13}C NMR (125 MHz, CD_2Cl_4, 28°C, J-modulated spin-echo) δ = 44.02, 44.82 (aliphatic, secondary C atoms), 63.84, 66.14, 68.17, 69.22 (aliphatic, quarterary C_{60} atoms), 120.59, 121.58 (quaternary aromatic C atoms), 128.09, 128.53, 130.00, 131.22, 131.27, 132.37 (ternary aromatic C atoms), 134.22, 137.59, 137.65 (quaternary aromatic C atoms), 141.78, 141.87, 142.10, 142.27, 142.72, 142.78, 145.53, 145.59, 145.62, 145.77, 145.84, 146.38, 146.57, 146.64, 146.71 (quaternary C_{60}-C atoms, several signals overlapping), 152.55, 155.75, 156.97 (quaternary arene C atoms), 161.64 ppm (C=O, two signals). UV/VIS ($CHCl_3$) similar to C_{60}, shows an absorption maximum at 435 nm. MS(FD): M/Z = 1052 ([M]$^+$ of **11(n=1)** 100 %)

12(n): MS(FD) of the crude material: M/Z = 945.1 ([M]$^+$ of **12(n=1)**, 100%), 1170.2 ([M]$^+$ of **12(n=2)**, 20%), 1395.3 ([M]$^+$ of **12(n=3)**, 2%). Retention volume (600 x 20 mm column, polystyrene gel 100 Å / 5 µm, $CHCl_3$, 7 ml/min, injection: 2 ml): **12(n=1)** 103.9 ml, **12(n=2)** 93.9 ml, **12(n≥3)** 88.4 ml, C_{60} 130.6 ml.

12(n=1) (Mixture of conformers a and b, ratio: 1.66 / 1): ^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 28°C): δ = 4.52 (d, 1 H, CH_2, 14 Hz, a), 4.58 (d, 1 H, CH_2, 14 Hz, b), 4.97 (d, 1 H, CH_2, 14 Hz, b), 5.44 (d, 1 H, CH_2, 14 Hz, a), 7.60-7.67 (m, 8 H, CH, a and b), 7.72 (s, 1 H, CHOR, a), 7.74 (s, 1 H, CHOR, b), 8.00 (d, 2 H, CH, 6 Hz, b), 8.12 (d, 2 H, CH, 6 Hz, a), 8.81 (d, 2 H, CH, 5 Hz, a), 8.89 ppm (d, 2 H, CH, 6 Hz, b), ^{13}C NMR (125 MHz, $C_2D_2Cl_4$, 28°C, J-modulated spin-echo): δ = 44.5 (aliphatic, secondary C atoms), 64.23 (aliphatic, quaternary C_{60} atoms), 123.43, 129.35, 128.34, 130.40, 131.13 (CH, aromatic C atoms), 134.78, 137.98, 140.23, 140.40, 140.61, 140.65, 141.76, 141.82, 141.92, 142.08, 142.28 (several signals overlapping), 142.82 (several signals overlapping), 142.88, 142.93 (several signals overlapping), 143.34, 143.38, 144.96 (several signals overlapping), 145.01 (several signals overlapping), 145.40 (several signals overlapping), 145.64, 145.72, 145.76, 145.82, 145.89, 145.91, 145.96, 146.81 (several signals overlapping), 148.05 (several signals overlapping, quaternary C_{60} atoms), 151.10 (ternary aromatic C atoms in neighborhood to the nitrogen), 151.25, 153.18, 153.76, 157.19, 157.27 (quaternary arene C atoms), 163.5 ppm (C=O). UV/VIS ($CHCl_3$) similar to C_{60}, shows an absorption maximum at 435 nm. MS(FD): M/Z = 945.1 ([M]$^+$ of **12(n=1)**, 100 %).

13: m.p.: 63°C, MS(FD): M/Z = 225 ([M]$^+$ of **13**, 100%), ^{1}H NMR (200 MHz, $CDCl_3$, 30°C): δ = 3.36 (d, 1 H, CH_2, 14.6 Hz), 3.75 (dd, 1 H, CH_2, 4.5 Hz and 14.6 Hz), 6.14 (dd, 1 H, CHOR, 14.6 Hz and 4.5 Hz), 7.141-7.852 (m, 4 H, CH), 8.72 (d, 2 H, CH, 1.5 Hz), 8.75 ppm (d, 2 H, CH, 1.6 Hz).

15(n): MS(FD) of the crude material: M/Z = 850.5 ([M-OH]$^+$ of **15(n=1)**, 100%), 867.8 ([M]$^+$ of **15(n=1)**, 35%), 1016.4 ([M]$^+$ of **15(n=2)**, 26%). Retention volume (600 x 20 mm column, polystyrene gel 100 Å / 5 µm, $CHCl_3$: 7 ml/min, injection: 1 ml): **15(n=1)**: 315 ml, C_{60}: 131.6 ml.

15(n=1) (exists in one preferred conformation): ^{1}H NMR (200 MHz, DMSO-d_6, 30°C): δ = 4.52 (d, 1 H, CH_2, 14 Hz), 5.37 (d, 1 H, CH_2, 14 Hz), 5.79 (s, 1 H, CH), 7.6-7.87 ppm (m, 4 H, CH).

16(n): MS(FD) of the crude material: M/Z = 850.3 ([M-Cl]$^+$ of **16(n=1)**, 100%), 886.2 ([M]$^+$ of **16(n=1)**, 88%), 720 ([M]$^+$ of C_{60}, 12%). Retention volume (600 x 20 mm column, polystyrene gel 100 Å / 5 µm, $CHCl_3$: 7 ml/min, injection: 1.5 ml): **16(n=1)**: 109.8 ml, **16(n=2)**: 99.6 ml, **16(n≥3)**: ~94 ml, C_{60}: 130.65 ml.

16(n=1) (exists in one preferred conformation): ^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 28°C): δ = 4.40 (d, 1 H, CH_2, 15 Hz), 5.06 (d, 1 H, CH_2, 15 Hz), 5.90 (s, 1 H, CH), 7.16-7.9 ppm (m, 4 H, CH).

17: colorless oil, MS(FD): M/Z = 393 ([M]$^+$ of **17**, 100%). ^{1}H NMR (200 MHz, $CDCl_3$, 30°C): δ = 3.10 (dd, 1 H, CH_2, 14.5 Hz and 4.8 Hz), 3.56 (dd, 1 H, CH_2, 14.5 Hz and 3 Hz), 3.8 (m, 4 H, CH_2), 3.6-3.75 (m, 20 H, CH_2), 4.57 (dd, CH, 1 H, 4.8 Hz and 3 Hz), 7.03-7.3 ppm (m, 4 H, CH).

18(n): MS(FD): M/Z = 1113.7 ([M]$^+$ of **18(n=1)**, 100 %), 1507.3 ([M]$^+$ of **18(n=2)**, 25%), 720.2 ([M]$^+$ of C_{60}, 16%). Retention volume (600 x 25 mm column, polystyrene gel 500 Å / 10 µm, $CHCl_3$: 10 ml/min, injection: 2 ml): **18(n=1)**: 184.1 ml, **18(n=2)**: 167.2 ml.

18(n=1) (exists in several conformations): ^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 28°C): δ = *protons of the aza-[18]crown-6*: 3.42- 3.52 (m (br.),17.6 H), 3.63- 3.66 (m (br.), 2 H), 3.71- 3.73 (m (br.), 1.6 H), 3.80- 3.85 (m (br.), 2.7 H) ⇒Σ = 24 protons; *benzylic protons*: 4.19 (d, 1.1 H, 14 Hz), 4.45 (d, 0.27 H, 14 Hz), 4.79 (d, 0.25 H, 14 Hz), 6.06 (m, 1.4 H) ⇒Σ = 3 protons; *aromatic protons*: 7.48 (m, 1.9 H), 7.59 (m, 1.25 H), 7.73 ppm (m, 0.84 H) ⇒Σ = 4 protons. ^{13}C NMR (125 MHz, $C_2D_2Cl_4$, 28°C): δ = 45.54 (two signals), 48.20 (two signals), 50.00 , 53.62 (secondary aliphatic C atoms) 69.5-70.95 (sp^3- C atoms of C_{60} and C atoms of the aza-crown), 113.96, 127.65, 127.90 (two signals), 128.62 (two signals),129.57 (two signals), 129.89, 129.95, 130.5, 131.0, 132.2 (ternary arene C atoms and ternary benzylic C atoms), 134.35, 135.11, 135.70,

136.59, 138.5, 139.12, 139.26, 139.84, 140.05, 141.29, 141.62, 141.79, 141.93, 142.06, 142.13, 142.18, 142.38, 144.38, 144.57, 144.72, 144.75, 144.78, 145.07, 145.15, 145.78, 145.83, 145.94, 146.03, 146.14, 146.21, 146.28, 147.42, 147.57, 148.30, 152.25, 153.10, 154.20, 155.08, 156.15, 157.08, 157.68, 159.54 (C_{60}-C atoms, several signals overlapping) 169.1, 171.01, 175.00 ppm (C=O). UV/VIS ($CHCl_3$): similar to C_{60}, shows an absorption maximum at 435 nm. MS(FD): M/Z = 1113.7 ($[M]^+$of **18(n=1)**, 100%)

19: m.p.: 76°- 78°C, MS(FD): M/Z = 434 (M^+ of **19**, 100 %); ^{1}H NMR (200 MHz, $CDCl_3$, 30°C): δ = 1.27 (s (br.), 6 H, CH_2), 1.63 (m, 2 H, CH_2), 2.33 (m, 2 H, CH_2), 3.20 (d, 1 H, benzylic CH_2, 14.3 Hz), 3.64 (dd, 1 H, benzylic CH_2, 14.3 Hz and 4.5 Hz), 5.92 (dd, 1 H, benzylic CH, 4.5 Hz and 1.9 Hz), 7.12-7.32 ppm (m, 4 H, CH).

20: Retention volume (600 x 25 mm column, polystyrene gel 500 Å / 10 µm, $CHCl_3$: 10 ml/min, injection: 2 ml) highest molecular weight fraction: 150 ml, lowest molecular weight fraction: 210 ml.

^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 28°C): δ = 1.25 (s (br.), 10 H, CH_2), 1.59 (s (br.), 4 H, CH_2), 2.25-2.75 (m (br.), 2 H, CH_2), 7.02-7.84 (m (br.), 4 H, CH) ppm, ^{13}C NMR (125 MHz, $C_2D_2Cl_4$, 28°C, J-modulated spin-echo): δ = 24.76, 24.96, 24.97, 24.99, 29.04, 29.06, 29.14, 29.15, 29.19, 29.22, 29.23, 29.26, 29.34, 29.37, 29.41, 29.72, 29.76, 33.9, 34.1, 34.41 (secondary aliphatic C atoms, several signals overlapping), 65.70, 69.87 (sp^3-C atoms of C_{60}), 127.51, 127.79, 128.15, 128.45, 128.85, 128.94, 129.53, 129.61, 129.65, 130.31, 130.38, 131.02, 131.07, 131.20, 132.63, 133.04, 133.31, 134.5-137.0 (quaternary arene C atoms, broadened signal), 137.5-160 (C_{60}-C atoms, broadened signal), 172.3-173.7 ppm (C=O, broadened signal).

21 and **22:** MS(FD) of the crude material: M/Z = 1154.2 ($[M]^+$ of **21** (headphone compound), 100%), 1874.3 ($[M^+]$ of **22** (dumbbell compound), 5%)

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