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Amphiphilic Cyclic Fullerene Bisadducts: Synthesis and Langmuir Films at the Air-Water Interface

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Abstract: Amphiphilic C_{60} bisadducts with a polar head-group located atop the carbon sphere and pendant long alkyl chains have been prepared. Preliminary investigations have shown their ability to form stable Langmuir films at the air-water interface.

In light of its unusual physical and chemical properties, C_{60} appears as an attractive group for supramolecular assemblies and new materials.[1] Incorporation of C_{60} in thin ordered films has become an important issue in the applications of this new carbon allotrope.[1-3] Whereas monolayers of pure C_{60} at the air-water interface are difficult to achieve,[2a, 3] modifications of the fullerene core with hydrophilic addends lead to significant improvements.[3] However, the synthesis of C_{60} derivatives with good spreading characteristics and reversible compression/expansion behaviour remains a challenge.[4] Here we report the synthesis and incorporation in Langmuir films of amphiphilic C_{60} bisadducts **1** and **2** (Figure 1).

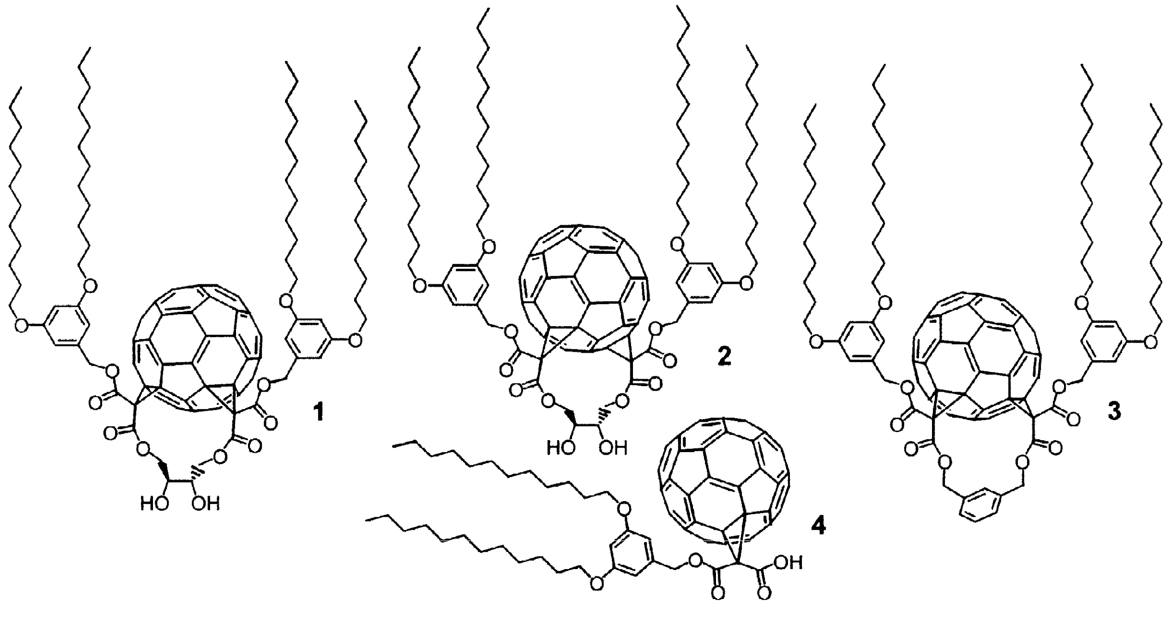

Figure 1. Amphiphilic cyclic C_{60} bisadducts **1**-**2**, and model compounds **3**-**4**.

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In a systematic study, their spreading behaviour has been compared to that of bisadduct **3**[5] with no polar head-group and of amphiphilic C_{60} monoadduct **4**.[6]

The preparation of compounds **1** and **2** is depicted in Figure 2. Esterification of diol (+)-**5** with the malonic mono-ester **6**[6] (DCC, DMAP, CH_2Cl_2, room temp.) yielded bismalonate (-)-**7** $\{[\alpha]_D^{30} = -4$ (c 4.61, CH_2Cl_2)$\}$. The functionalisation of C_{60} was based on the highly regio- and diastereoselective macrocyclisation reaction of the carbon sphere with optically pure bismalonate derivatives developed by Diederich and co-workers.[7] Treatment of C_{60} with (-)-**7**, I_2 and DBU in toluene at room temp. afforded the regioisomeric bisadducts **8** and **9** in 12 and 20% yield, respectively. Noteworthy is that the addition pattern in the cis-3 bisadduct **9** is chiral, therefore two diastereoisomeric bisadducts are possible; however, the very high asymmetric induction in the second intramolecular Bingel addition leads to the formation of **9** only.[8]

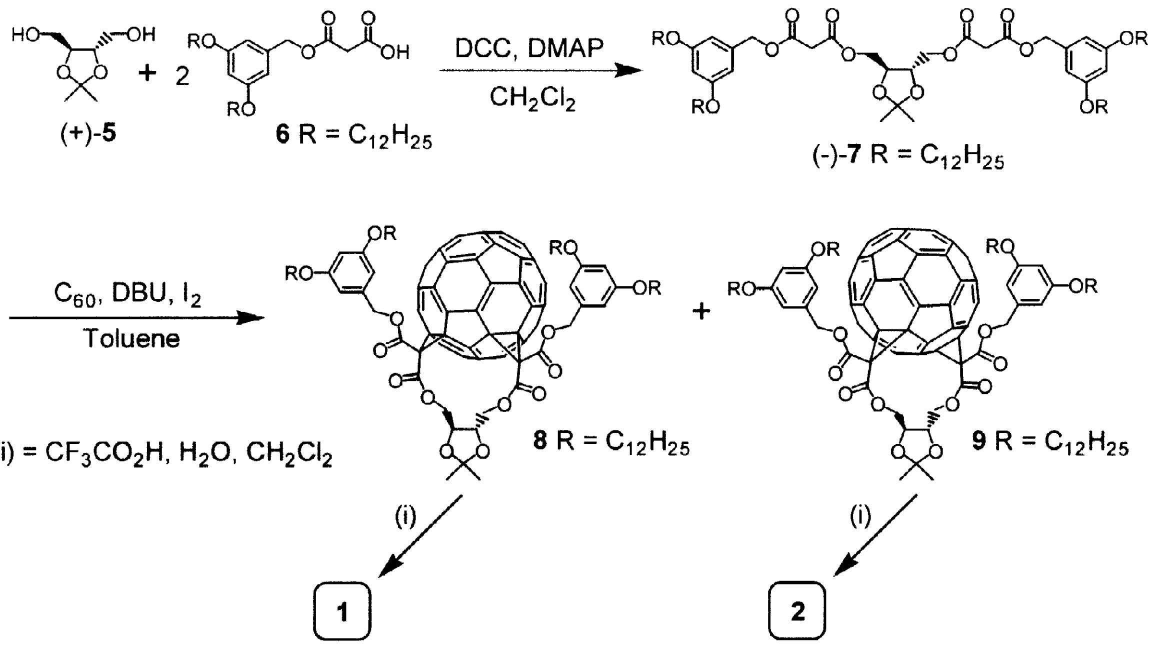

Figure 2. Preparation of the amphiphilic derivatives **1** and **2**.

Deprotection of **8** and **9** (CF_3CO_2H, CH_2Cl_2/H_2O 2:1, room temp., 3 days) gave **1** (89% yield) and **2** (64% yield), respectively. The relative position of the two cyclopropane rings in **1** and **2** on the C_{60} core was determined based on the molecular symmetry deduced from the ^1H- and ^{13}C-NMR spectra (C_1 for **1** and C_2 for **2**) as well as on the UV-VIS spectra.[9] It was previously shown[7, 10] that the absorption spectra of C_{60} bisadducts are highly dependent on the addition pattern and characteristic for each regioisomers; the UV-VIS spectra of **1** and **2** are fully consistent with those of previously reported analogous bisadducts.[7b] The fullerene derivatives **1**, **2**, **8** and **9** are all optically pure derivatives,[8] however due to the very dark color of their solutions, their optical rotations could not be determined.

Langmuir monolayers of **1**, **2** and **4** were formed on pure water by spreading in the order of 50 µl drops of a 0.005 M solution of the corresponding compound in $CHCl_3$ with a gas-chromatography syringe. The isotherms were recorded at room temp. with the KSV5000 system, by using a constant barrier speed of 1 or 2 mm/min (the trough being 500 mm long). The Langmuir films were observed by using a Brewster angle microscope (BAM) (from Nanotechnology Thin Films). Compared to **3** for which no Langmuir film could be obtained, the polar head group in **1**, **2** and **4** is responsible for a strong interaction with the aqueous subphase, forcing the molecules towards the water surface into a two-dimensional arrangement. The isotherms obtained with **1** and **2** are similar (Figure 3A). Until 170 Å^2, the compression induces no significant (smaller than 0.1 mN/m) increase of the pressure and the BAM texture is constituted by nearly circular water domains ("uncovered regions") dispersed in a continuous film. These water domains disappear completely around 160 Å^2, as the pressure also begins to increase and the film stays homogeneous until a pressure of about 17mN/m is reached. It is important to note that the observed area of 160 Å^2 is in good agreement with the value which can be estimated for the molecular area of **1** or **2** (*ca.* 155 Å^2 based on molecular modeling). This indicates clearly the formation of an homogeneous monomolecular layer. This observed molecular area also suggests that the fullerene sphere should be at least partially surrounded by its alkyl chains thus preventing the embedding of the film. The collapse value (17 mN/m) is indeed smaller than the values found in the literature (about 30-50 mN/m) for other fullerene derivatives,[3] but similar to that obtained with mesogenic compounds for which stable monolayer films could be prepared.[11] The surface topography observed by BAM when compression of the film is continued after the collapse shows clearly the formation of a partial monolayer mixed with a partial bi- or multi-layer. Successive compression/decompression cycles with a monolayer of **1** are depicted in Figure 3B and show the reversibility of the process. The small shift observed for the further compression/decompression cycles seems to be the result of a film migration on the trough border and on the barrier at high pressure (the deposit on the Teflon could be observed because of the compound's deep red colour). Contrary to monoadduct **4**, the separation of the collapsed aggregates onto the water surface is observed for **1** and **2**, as shown by the reproducibility of the transition from the gaseous to the condensed phase after several compression/decompression cycles. For mono-adduct **4**, the substituent is not bulky enough to prevent contact between neighboring fullerenes when the film is compressed, three-dimensional aggregation occurs and formation of a monolayer appears difficult. Furthermore, once the fullerene cores are in contact with each other, they irreversibly aggregate and the layer does not expand any more. In contrast, the C_{60} core in **1** and **2** is somehow encapsulated in its addend, thus preventing irreversible aggregation and the compression/expansion process is perfectly reversible. We however believe that monolayers of **1** and **2** should be stabilized due to the presence of the aromatic groups by intermolecular π-π interactions among themselves and/or with the fullerene chromophore in the two-dimensional network, the aliphatic chains preventing aggregation and three dimensional crystallisation.

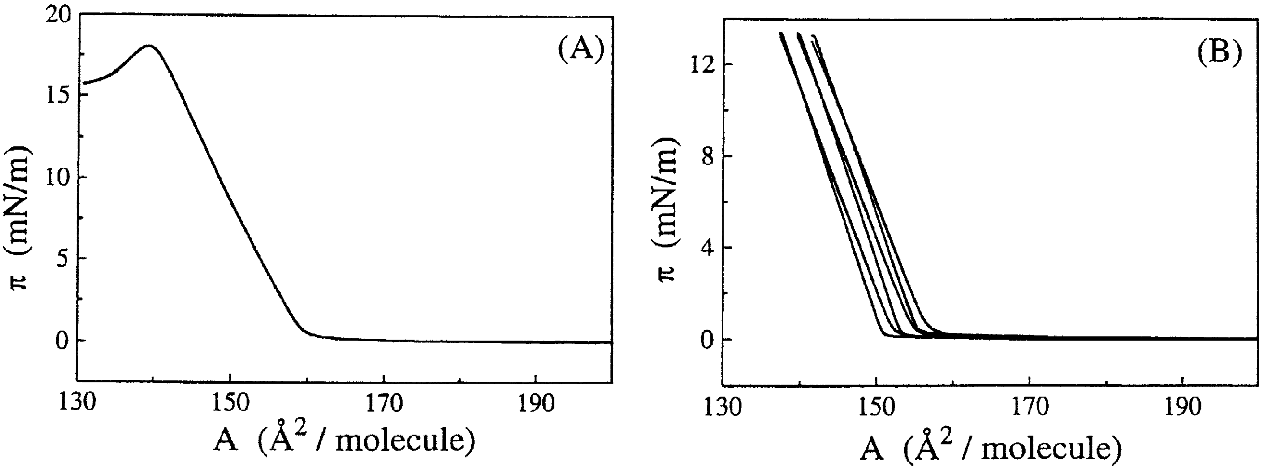

Figure 3. (A) Surface pressure-area isotherm of compound **2**. (B) Successive compression/ expansion cycles with a monolayer of **1**, showing the reversibility of the process.

The designed amphiphilic derivatives **1** and **2** reported in this paper show good spreading characteristics and a reversible compression/expansion behavior. The encapsulation of the fullerene core in its addend resulting from the cyclic structure of **1** or **2** prevents the aggregation usually observed for amphiphilic fullerene derivatives. Transfer experiments of molecular monolayers of **1** or **2** onto solid substrates and preparation of Langmuir-Blodgett films are still under investigation in our laboratory.

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4) During the preparation of this manuscript, the synthesis of amphiphilic fullerene-dendrimer conjugates with a reversible compression/expansion behavior has been reported, see: Cardullo, F.; Diederich, F.; Echegoyen, L.; Habicher, T.; Jayaraman, N.; Leblanc, R.M.; Stoddart, J.F.; Wang, S.; *Langmuir* **1998**, *14*, 1955-1959.
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8) For a detailed discussion on the regio- and diastereoselectivity of the macrocyclisation reaction on the fullerene core, see ref. 7b.
9) Selected spectroscopic data for **1**: UV-VIS λ_{max} (CH_2Cl_2)/nm 258 (149670), 318 (sh, 45810), 376 (sh, 16620), 436 (4370), 467 (3590); ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.89 (m, 12 H), 1.28 (m, 72 H), 1.75 (m, 8 H), 2.83 (d, J = 6, 1 H), 3.29 (d, J = 7.5, 1 H), 3.80 (m, 1 H), 3.89 (t, J = 6.5, 4 H), 3.90 (t, J = 6.5, 4 H), 4.04 (m, 1 H), 4.14 (m, 1 H), 4.71 (m, 1 H), 5.22 (d, J = 12, 2 H), 5.39 (d, J = 12, 2 H), 6.40 (t, J = 2, 1 H), 6.41 (t, J = 2, 1 H), 6.50 (m, 4 H); ^{13}C-NMR ($CDCl_3$, 50 MHz): 14.12, 22.70, 26.06, 29.22, 29.38, 29.44, 29.64, 29.69, 31.93, 45.82, 49.11, 66.29, 67.36, 68.21, 68.29, 68.61, 68.70, 69.91, 70.23, 70.33, 101.47, 106.74, 106.97, 134.45, 136.40, 136.61, 137.01, 137.58, 137.73, 138.16, 138.31, 138.67, 139.08, 140.90, 141.05, 141.20, 141.76, 142.08, 142.30, 143.13, 143.58, 143.64, 143.80, 143.93, 144.09, 144.24, 144.35, 144.61, 144.73, 145.05, 145.14, 145.28, 145.46, 145.69, 145.89, 145.94, 146.10, 146.16, 147.31, 147.40, 147.47, 148.85, 149.90, 160.37, 162.16, 162.55, 162.70; Anal. calc. for $C_{132}H_{118}O_{14}$: C 82.22, H 6.17; found: C 81.94, H 6.16. Selected spectroscopic data for **2**: UV-VIS λ_{max} (CH_2Cl_2)/nm 255 (117050), 316 (39610), 406 (5090), 451 (2420), 628 (570), 695 (290); ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.89 (t, J = 6, 12 H), 1.27 (m, 72 H), 1.76 (m, 8 H), 2.43 (d, J = 7, 2 H), 3.91 (t, J = 6.5, 8 H), 4.02 (m, 2 H), 4.25 (t, J = 10.5, 2 H), 4.71 (dd, J = 10.5 and 5, 2 H), 5.33 (d, J = 12, 2 H), 5.42 (d, J = 12, 2 H), 6.42 (t, J = 2, 2 H), 6.54 (d, J = 2, 4 H); ^{13}C-NMR ($CDCl_3$, 50 MHz): 14.12, 22.68, 26.09, 29.25, 29.35, 29.44, 29.63, 31.91, 49.55, 64.50, 66.17, 68.16, 68.99, 71.61, 101.61, 106.94, 129.76, 136.05, 136.39, 138.47, 138.91, 140.64, 140.93, 141.07, 141.44, 141.73, 142.17, 142.38, 143.52, 143.61, 144.22, 144.28, 144.41, 144.64, 144.72, 144.95, 145.24, 145.34, 145.43, 145.62, 146.30, 146.61, 160.49, 162.63, 162.96; Anal. calc. for $C_{132}H_{118}O_{14}$: C 82.22, H 6.17; found: C 82.15, H 6.37.
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