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Uwe Hartnagel[a]; Andreas Hirsch[a]; Delphine Felder-Flesch[b]; Jean-Louis Gallani[b]; Cyril Bourgogne[b]
[a] Institut für Organische Chemie, Friedrich-Alexander-Universität Erlangen-Nürnberg, Erlangen, Germany [b] Institut de Physique et de Chimie des Matériaux de Strasbourg IPCMS, Strasbourg, France

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Spreading behaviour of a series of amphiphilic [3 : 3] [60]fullerene hexakisadducts: a systematic study

Uwe Hartnagel[a], Andreas Hirsch[a]*, Delphine Felder-Flesch[b]*,
Jean-Louis Gallani[b] and Cyril Bourgogne[b]

[a]*Institut für Organische Chemie, Friedrich-Alexander-Universität Erlangen-Nürnberg, Erlangen, Germany;* [b]*Institut de Physique et de Chimie des Matériaux de Strasbourg IPCMS, UMR CNRS/ULP 7504, Strasbourg, France*

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The spreading behaviour at the air–water interface of a series of [60]fullerene [3 : 3] hexakisadducts has been studied as a function of the hydrophobic–hydrophilic balance of the amphiphiles. More precisely, by changing both the nature and the size of the polar headgroup, by varying the nature of the chemical linker and/or spacer, by modifying the nature and/or the length of the spacer, it has been possible to perform a systematic study. The latter was carried out not only according to the pH of the aqueous subphase but also to its temperature highlighted various behaviours which in particular allowed to us to conclude that the optimal chemical design for this type of amphiphilic molecules is reached with the couples amine polar head/ester linker (**Hexa-4**) or carboxylic acid polar head/amide linker (**Hexa-5**).

Keywords: [60]fullerene; hexakisadducts; amphiphiles; thin films; Langmuir

1. Introduction

The preparation, characterisation and functionalisation of [60]fullerene thin films such as self-assembled monolayers (SAMs) [1–6], self-organised bilayers [7–10], or Langmuir–Blodgett films [11–15] are currently of great interest from both fundamental and practical viewpoints owing mainly to their unique electronic and/or structural characters. Both the SAM approach, achieved through junction moieties such as organosilane [16], organosulfur [17], or carboxylic acid [18], and the Langmuir technique allow control of the formation and the structure of the resulting film at a molecular level. In the latter field, working at the air–water interface, various [60]fullerene derivatives ranging from mono- [19–25], to *bis*- [26], up to hexa-adducts [27–30] have been studied in the past few years and showed encouraging results in terms of film quality and stability, roughness, reversibility, and transfer onto solid substrates. For example, Cardullo et al. [31] or more recently Hirano et al. [32] showed that fullerene mono-adducts bearing

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*Corresponding authors. Emails: andreas.hirsch@chemie.uni-erlangen.de; Delphine.Felder@ipcms.u-strasbg.fr

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dendritic branches display good spreading characterisitics and reversible compression/expansion behaviour has been described. Working on [60]fullerene *bis*-adducts, Nierengarten et al. have shown that encapsulation of the carbon sphere in a cyclic addend surrounded by either long alkyl chains [33,34] or cholesterol subunits [35] is a method of choice for obtaining stable and reversible monomolecular thin films, easily transferred onto solid substrates in order to prepare high-quality LB multilayers. Using an alternative approach to the previous studies, the same group highlighted that the fullerene can be attached into the branching shell of a dendritic [36] or diblock dendritic [37,38] structure. In this case, the C_{60} units are buried in the middle of the dendrimer which provides an insulating layer around them, thus preventing the irreversible three-dimensional aggregation resulting from fullerene–fullerene interactions [39,40]. Finally, various studies performed very recently on [60]fullerene hexakisadducts [27–30] showed that hexa-addition on the carbon sphere provided not only an ideal structure to prevent aggregation phenomenon but also an optimised hydrophilic–hydrophobic balance for preparing well-ordered supramolecular assemblies at the air–water interface.

With each key step related to the optimisation of such induced organisations relying on the chemical design, it becomes clear that carrying out systematic studies would be of great interest. If such studies have already been investigated for C_{60} *cis*-2 *bis*-adducts [33–35] with the aim of improving thin films quality for advanced materials applications [41–46], they remain to be done for amphiphilic [60]fullerene hexakisadducts, for which recent publications describe a promising future in biology more precisely as transmembrane anchor [47] or drug delivery systems [48]. Moreover, in contrast to mono- or *bis*-addition on [60]fullerene, hexa-addition allows a regioselective multifunctionalisation leading to versatile polyfunctional high added-value materials.

The synthesis, together with the aggregation properties of the amphiphilic [3 : 3] hexakisadducts **Hexa-1**–**7** (Figure 1) conducted by transmission electron microscopy (TEM) and pulse-gradient spin echo (PGSE) NMR spectroscopy, has been previously reported [49] and revealed the pH-dependent formation of aggregates.

With this article, we would like to extend the study by reporting and explaining their spreading behaviour at the air–water interface by means of and according to chemical design. For this purpose, various structural parameters have been taken into account (Scheme 1) such as the nature, anionic for **Hexa-5** and **6** or cationic for **Hexa-1**–**4** and **Hexa-7**, and the size of the polar headgroup ($-(CO_2H)_{18}$ for **Hexa-6** compared to $-(CO_2H)_6$ for **Hexa-5**); the nature of the chemical linker: amide for **Hexa-1**–**3** and **Hexa-5** or ester for **Hexa-4**, **6**, and **7**; the nature and/or the length of the spacer: hydrophobic chain (**Hexa-1** and **Hexa-4**–**6**) or short (**Hexa-3**) or long (**Hexa-2**) hydrophilic chain or mixed alkyl-polyethyleneglycol chain (**Hexa-7**).

2. Experimental section

2.1. *Langmuir films*

Data were collected using a Teflon trough and symmetrical hydrophilic barriers. The trough was set in a Plexiglas enclosure so as to be protected from drafts and dust, and temperature was controlled to ±0.1°C. The ultrapure water ($\rho = 18.2\,\mathrm{M\Omega\,cm}$) used for the subphase was obtained from a Milli-RO3Plus/Milli-Q185 ultra purification system from Millipore. Surface pressure was measured by means of a platinum Wilhelmy plate.

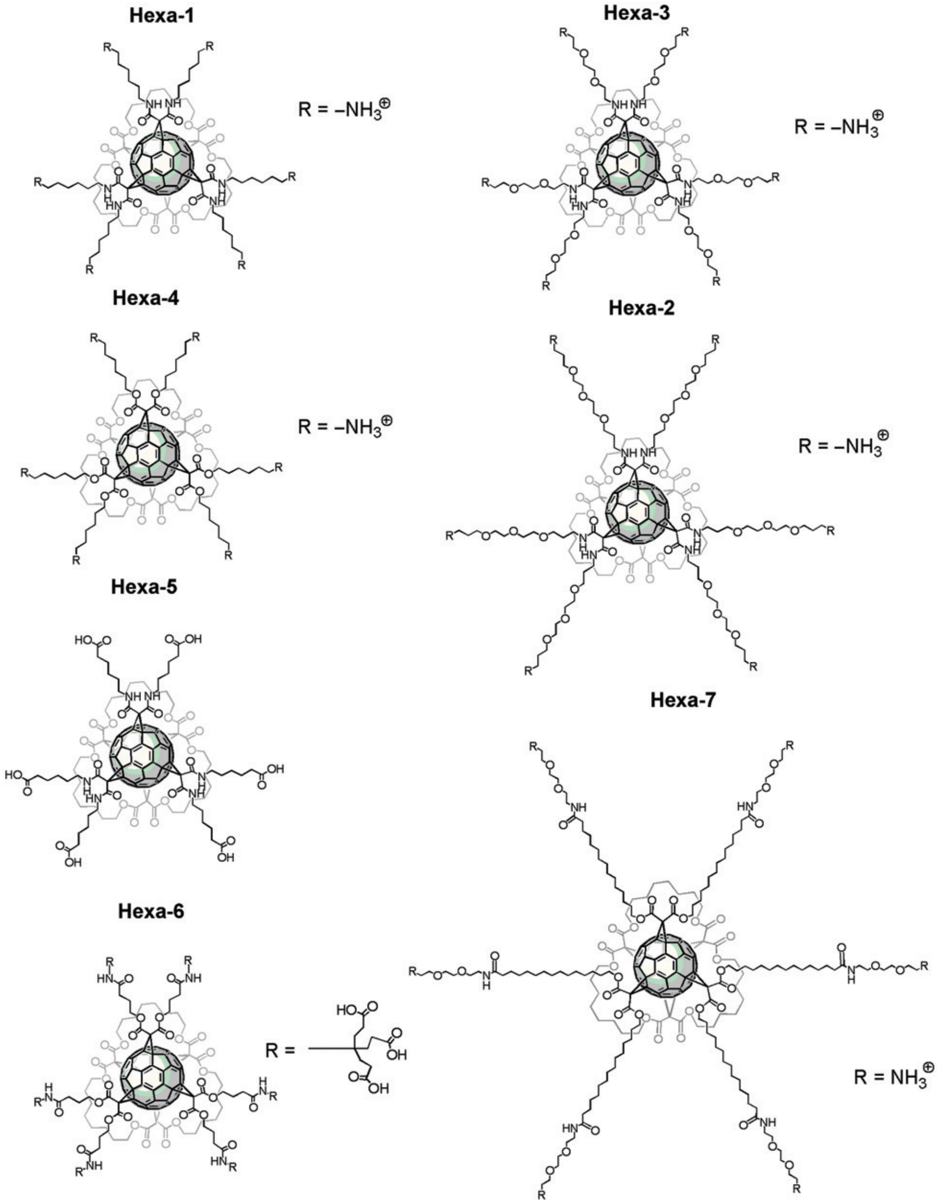
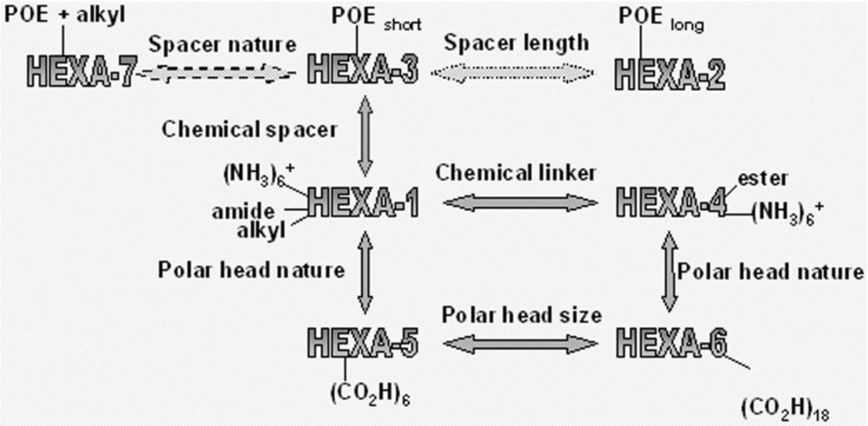


Figure 1. Molecular structures of the [60]fullerene hexakisadducts **Hexa-1**–**Hexa-7**. Counterion: TFA (trifluoroacetate).

Solutions at $1\,\mathrm{mg\,mL^{-1}}$ concentration were prepared using a chloroform solution for **Hexa-1**–**5** and **Hexa-7**, or a 1 : 4 mL mixture of ethanol and chloroform, respectively for **Hexa-6**. Usually, 50 μL of these solutions were spread on the water surface using a micro-syringe. Films were left to equilibrate for 30 min before any measurement started. The monolayers were compressed at typical barrier speeds of $10\,\mathrm{mm\,min^{-1}}$. Typical uncertainty on the collapse pressure is 2.5%.



Scheme 1. Comparison points allowing the systematic study.

2.2. *Brewster angle microscopy*

Brewster angle microscopy (BAM) was performed using a BAM2plus (Nanofilm Technologies GmbH) illuminated by an Ar laser. Images were recorded on a CCD camera, object field is 620 µm × 500 µm.

2.3. *Molecular modelling studies*

Molecular simulations were performed using Insight II and Discover 3 softwares from Accelrys (www.accelrys.com). Figure 3: snapshot of the arrangement of 4 Hexa-1 molecules after a 20 ps molecular dynamics simulation at 293 K. Figure 8: two previously optimised hexa-adducts were manually placed side by side using the interactive H-bond and bump monitors.

3. Results and discussion

It has been possible to record an isotherm for all of the compounds. In addition to those specifically discussed in the text, all other experiments are given as supporting information.

Isotherms of **Hexa-1** on pure water (pH 6.5) showed poor reproducibility, a rather small final molecular area, ca 130 Å^2 – still not unrealistic – and a rather low-collapse pressure, *ca* 5 mN m^{-1}. These observations are clearly consistent with the fact that the compound is essentially hydrophilic. Nevertheless, going to higher pH (10) for the subphase using potassium hydroxide yielded better results in terms of reproducibility, and collapse pressure reached 20 mN m^{-1} (Figure 2).

Furthermore, the molecular area, extrapolated to zero surface pressure was larger, *ca* 200 Å^2, a value in good agreement with molecular modelling study (Figure 3). However, the monomolecular film formed is slightly unstable, the surface pressure decreasing as soon as the compression is stopped, indicative of molecules dissolving into the aqueous subphase. This phenomenon was also confirmed by the BAM studies showing no modification of the film morphology at or beyond the collapse pressure. It is therefore probable that the

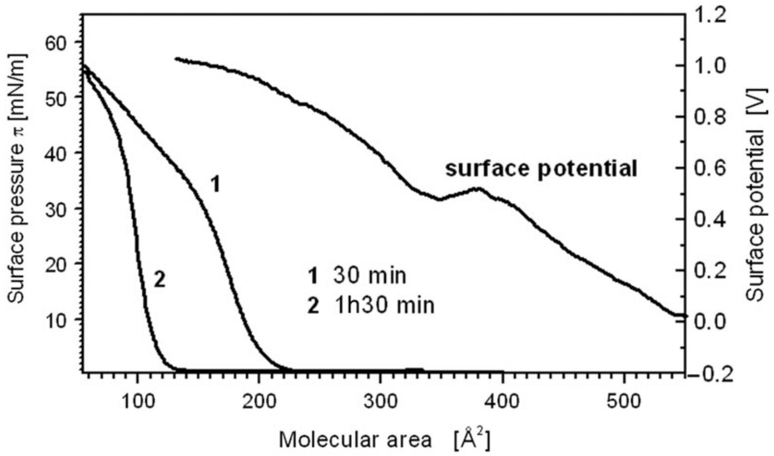


Figure 2. Pressure-area isotherm for **Hexa-1** at 20°C, pH 10 recorded after waiting time of 30 min (1) and 1 h 30 min (2) before compression and surface potential.

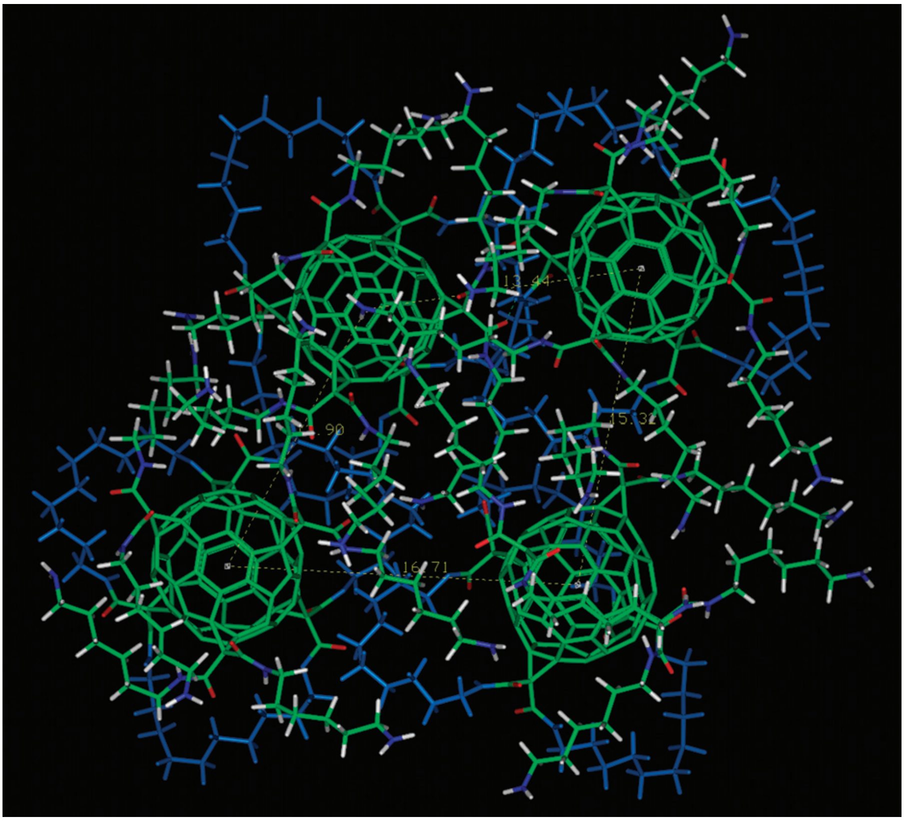


Figure 3. Molecular modelling of a tetramer of **Hexa-1** showing alignment of the C_{60} units and confirming a molecular area of 200 $Å^2$ at maximum compression.

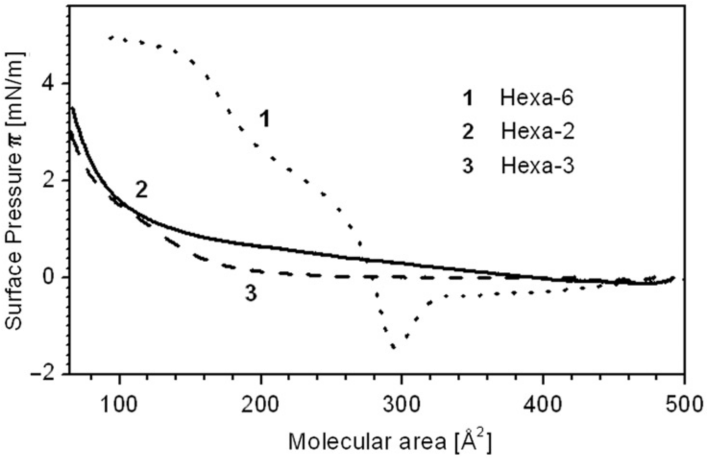


Figure 4. Isotherms of hexakisadducts **Hexa-2, -3**, and **-6** showing the hydrophilicity/solubility of the compounds. Recorded at 20°C and pH 10.

collapse intervenes via molecules dissolving into the water. Finally, it is worse noting that longer waiting time before compression (i.e., 1 h 30 min) gave a smaller molecular area indicative of molecules dissolved in the water subphase before compression. Measurement of the surface potential during the compression (blue curve in Figure 2) show that the intermolecular interactions already take place at large values of the molecular area A. The 'bump' around $A = 380\,Å^2$ is reproducible but unexplained so far, though it can certainly be ascribed to some molecular rearrangement. The surface potential reaches a rather high 1 V value at the end of the compression, even though the amine should be in their neutral form given the pH value, meaning that the molecules bear some dipole moment and that these moments are more or less aligned in the film (Figure 3).

Comparison between the pressure-area isotherms of **Hexa-3** and **Hexa-1** revealed that going from an aliphatic to a hydrophilic spacer has a dramatic effect on the capacity of the compound to form a film on the water subphase. Indeed, **Hexa-3** hardly formed a film (Figure 4) and no significant surface pressure (π_{max} 2–3 $mN\,m^{-1}$) was observed at pH 10. Thus, it becomes obvious that hexakisadduct **Hexa-2**, having an even longer hydrophilic spacer, was unable to form a stable and high-quality film on water (π_{max} 2–3 $mN\,m^{-1}$). Pursuing the discussion on the derivatives for which the hydrophobic/hydrophilic balance leans clearly towards hydrosolubility, it is important to point out that **Hexa-6**, possessing a short aliphatic spacer and 18 carboxylate polar heads, displayed a spreading behaviour quite different than that of **Hexa-1** (long aliphatic spacer, six amine polar heads) and **Hexa-2** or **3** (hydrophilic spacer, six amine polar heads). Indeed, as shown in Figure 4, the surface pressure reached negative values, which is an indication that molecules dissolve into the water upon compression.

On pure water subphase **Hexa-4** formed a film (Figure 5(a)) but with a rather low-collapse pressure, *ca* π_{max} 6 $mN\,m^{-1}$. Going to higher pH yielded better results in terms of reproducibility and also gave a larger final molecular area of $190\,Å^2$ and a quite satisfactory collapse pressure of 40–45 $mN\,m^{-1}$. In addition, let us note that the collapse pressure varied almost linearly with the pH of the subphase as shown in Figure 5(b) (inset).

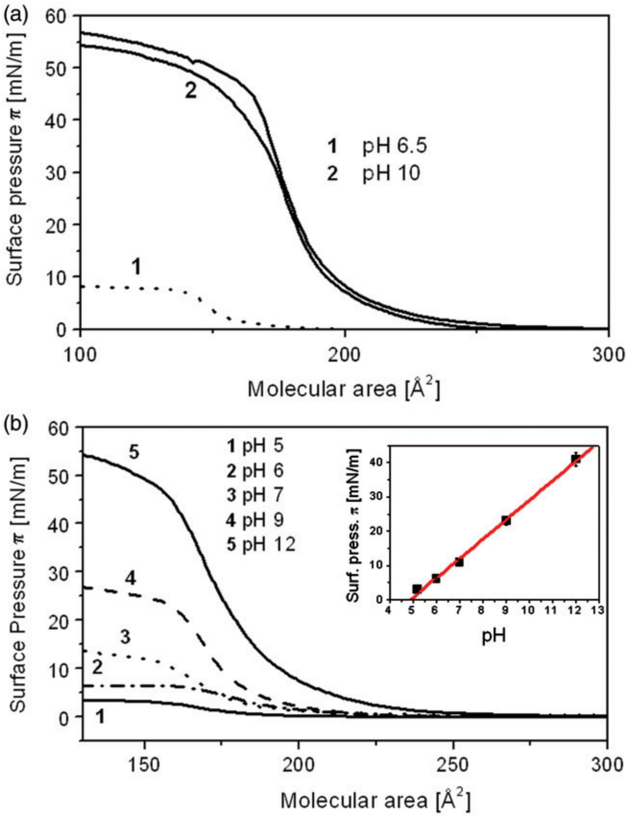
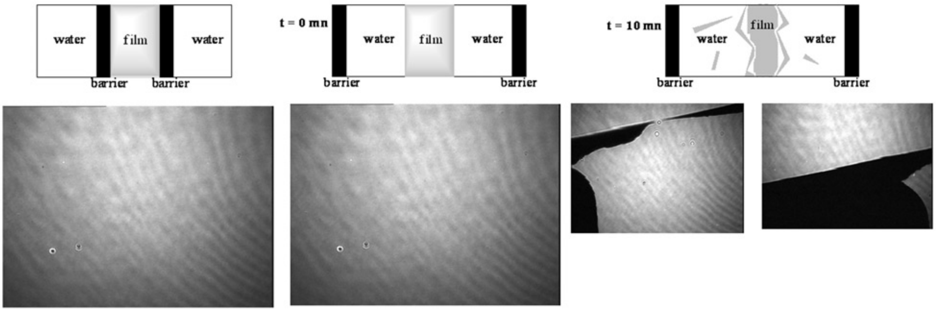


Figure 5. Isotherms of hexakisadduct **Hexa-4**. (a) On pure water (pH 6.5) and at pH 10 showing a good reproducibility. (b) As a function of pH. Inset is a plot of the collapse pressure π_c with a fit to a straight line, showing the almost linear correlation of π_c with the pH variation, error bars of 5%.

Brewster Angle Microscopy study showed that **Hexa-4** does not form islands on the water subphase but arranges into a homogeneous film immediately after deposition. Moreover, the film formation seems irreversible since nothing changes under the microscope immediately after decompression. The film is therefore rigid (Scheme 2): BAM images do not change while barriers are totally pushed away. Finally, after a few minutes (*ca* 10 min), images evolve, solid-type fractures appear and fragments of films are floating on the water surface.

For one moment let us now focus the discussion on the comparison between **Hexa-1** and **Hexa-4**. Indeed, these two derivatives both showing six amine polar heads together with aliphatic spacers differ from each other only by the nature of the chemical linker directly connected to the cyclopropane ring (Scheme 1). However, as shown in Figure 6, this simple change strongly influenced the stability of the monomolecular film. In fact, the maximum surface pressure (π_{max}) went from 20 mN m^{-1} for **Hexa-1** having amide connections to 45 mN m^{-1} for **Hexa-4** displaying ester linkers. In order to clarify such a phenomenon, we propose a model based on intra- or intermolecular hydrogen bonds (Figure 7).



Scheme 2. Scheme describing the rigidity of a monolayer of hexakisadduct Hexa-4 together with BAM pictures showing solid-type fractures. Pictures collected at 20°C, pH 10, barrier speed: 10 mm min^{-1}.

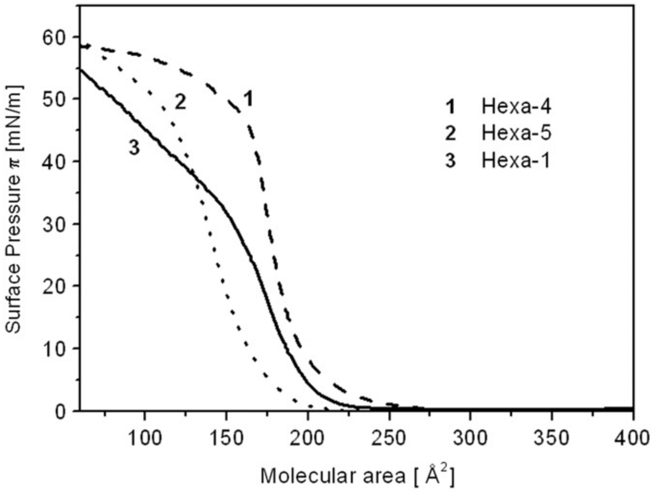


Figure 6. Isotherms of hexakisadducts **Hexa-1**, **-4**, and **-5** recorded at pH 10 (**Hexa-1** and **-4**) or pH 2 (**Hexa-5**).

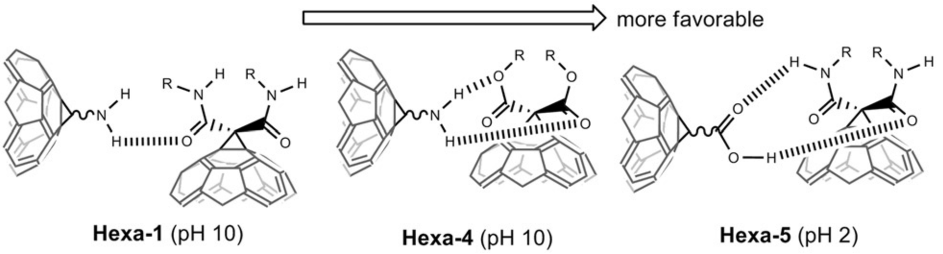


Figure 7. Proposed intermolecular H-bonding possibilities for **Hexa-4** and **Hexa-5** and less favourable for **Hexa-1** explaining films cohesion and/or rigidity.

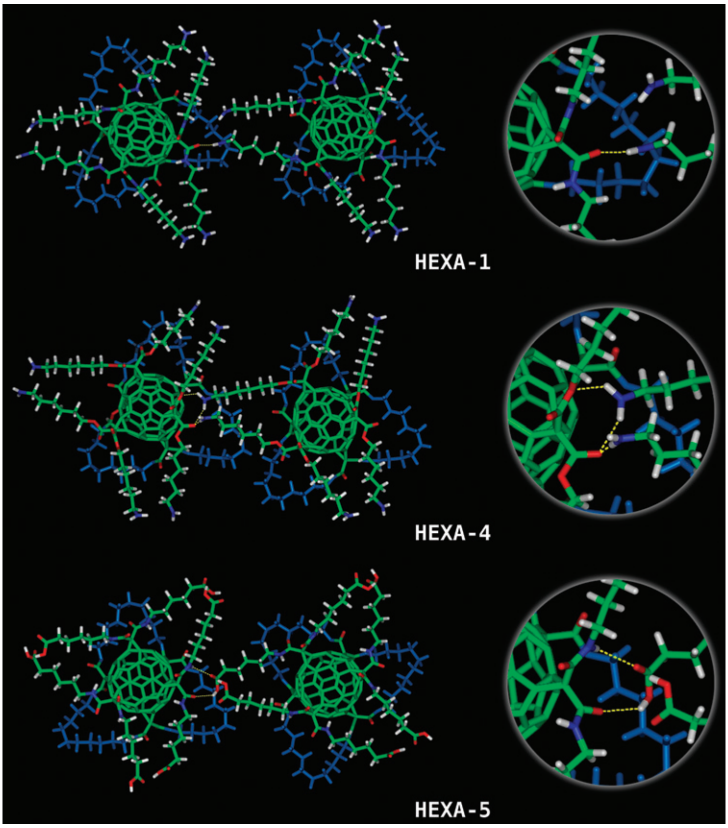


Figure 8. Molecular modelling studies showing the possibility of H-bonds between neighbours within monolayers of **Hexa-1**, **-4**, and **-5**.

The slope of the compression isotherms is a measure of the film compressibility, a steeper slope meaning a larger rigidity. As can be seen in Figure 6, films of **Hexa-4** are more rigid than those of **Hexa-1**. This implies a more important cohesion between the molecules which we ascribe to the formation of a H-bond network between the molecules of **Hexa-4** through interactions between the amine polar heads of a molecule and the ester linker of its neighbour. Such interconnections are less favourable for **Hexa-1** because of the nature of its head and linker. The cohesion of the film is consequently lower, hence the weaker collapse pressure.

Those proposed H-bonding models were confirmed by molecular modelling studies (Figure 8) performed on dimers of **Hexa-1**, **-4** and **-5**.

We can thus conclude that the optimal chemical design for the preparation of Langmuir films made from this kind of [60]fullerene [3 : 3] hexakisadducts is obtained with the couple amine polar head/ester linker.

But let us extend the discussion to derivative **Hexa-5**. By comparing it to **Hexa-4** it was possible to study the influence of the nature of the polar head which, as seen in Figure 6, was also very pronounced. Indeed, if one considers an amide linker, going from six amine

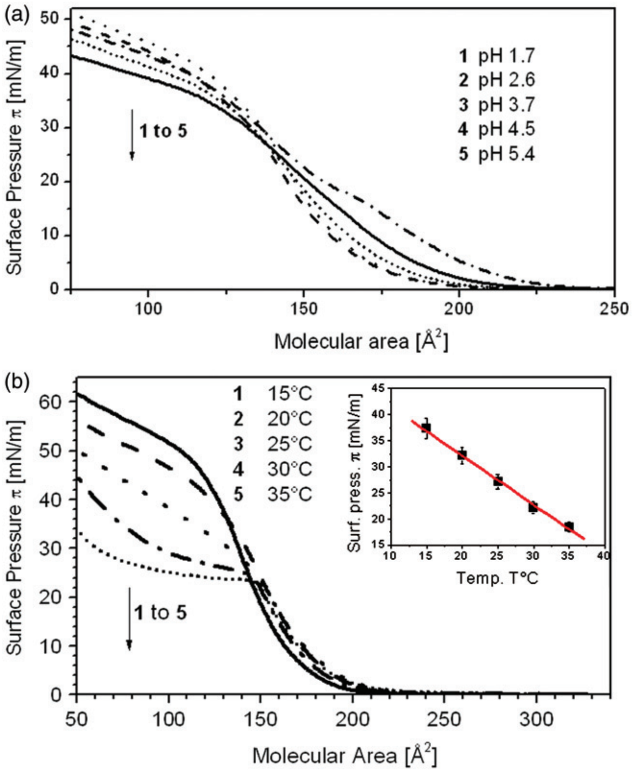


Figure 9. Isotherms of hexakisadduct **Hexa-5** as a function of (a) pH, (b) Variation of the temperature recorded at pH 2. Inset is a plot of the collapse pressure π_c with a fit to a straight line, showing the almost linear correlation of π_c with the T°C variation, error bars of 5%.

(**Hexa-1**) to six carboxylic acid polar heads (**Hexa-5**) almost doubled the maximum surface pressure withstanded by the monolayer which reached values of 40–45 $\mathrm{mN\,m^{-1}}$. It then seems obvious that a second optimal chemical design exists and is represented by the couple acid polar head/amide connection. Again, such an observation can be supported by the H-bonding model proposed previously and described in Figures 7 and 8. Indeed, the chemical design of compound **Hexa-5** allows intermolecular interactions between the carboxylic acid (pH 2) of a molecule and the amide linker of a close neighbour.

Dealing with the thorough study of the spreading behaviour of hexakisadduct **Hexa-5**, it has been possible to highlight a good reproducibility at pH 2 as well as a linear correlation between the pH and the maximum collapse pressure, the latter increasing to reach 35 $\mathrm{mN\,m^{-1}}$ when the aqueous subphase was acidified (pH 1.7) (Figure 9). In that, **Hexa-5** is the strict opposite of **Hexa-4** which is only logical when going from amine to acid polar heads.

Let us also note that, contrary to **Hexa-4**, isotherms of hexakisadduct **Hexa-5** showed a temperature dependence, in the form of a fall of the maximum surface pressure withstood by the film when the temperature of the water subphase increases (Figure 9(b)).

Lastly, another difference between **Hexa-4** and **Hexa-5** came from the Brewster Angle microscope observations (Figure 10), showing many white spots corresponding to small

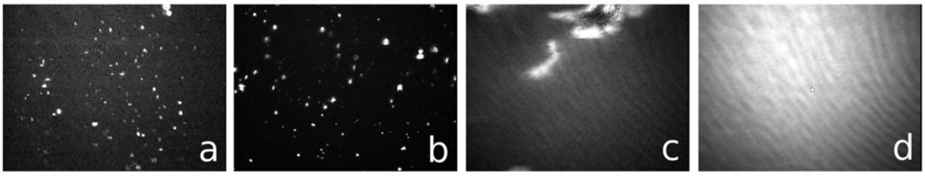


Figure 10. BAM pictures of hexakisadduct **Hexa-5** taken at 420 Å^2 (a), 320 Å^2 (b), 230 Å^2 (c) and 170 Å^2 (d).

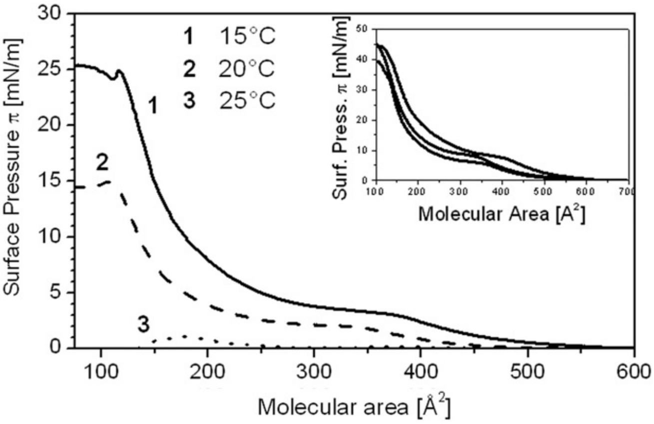


Figure 11. Isotherms of hexakisadduct **Hexa-7** as a function of T°C recorded at pH 10. Inset is a plot showing the poor reproducibility of the recorded isotherms at 15°C.

islands of compound appearing once **Hexa-5** was spread on the water. Their number decreased upon compression while their size increased. A transition seemed to occur around 230 Å^2 and an homogeneous film was seen around 170 Å^2.

Finally, **Hexa 7** also formed a thin film on water (Figure 11), this time showing a plateau probably indicative of first-order transitions. In terms of collapse pressure, best results were observed at 15°C; and above 25°C no more film formation was observed. This is consistent with the fact that dissolution of **Hexa 7** in the subphase, if it occurs, is weaker at lower temperatures. It can also be noted that isotherms recorded at 15°C showed poor reproducibility. Moreover, films were unstable, the surface pressure decreasing as soon as the compression was stopped, indicative of molecules dissolving into the water.

4. Conclusion

We have prepared and studied monolayers of a series of amphiphilic [3 : 3] hexakisadducts of C_{60} in which various structural parameters have been selectively varied. In conclusion, we have been able to establish a new relationship between the chemical design of these molecules and their ability to form a monolayer of the Langmuir-type (Table 1). We highlighted that the optimal balance is reached with the couples amine polar head/ester linker or carboxylic acid polar head/amide linker, the possible formation of

Table 1. Parameters of the Langmuir isotherms related to the chemical structure of the hexakisadducts 1–7.

Compound	Nature and number of polar head	Nature of the chemical linker[a]	Nature of the spacer[b]	pH	Collapse pressure π_c^c	Comments
Hexa-1	$-(NH_3)_6^+$	Amide	Alkyl	10	20	Reproducible[d]
Hexa-2	$-(NH_3)_6^+$	Amide	POE long	–	–	Hardly forms a film on a water surface
Hexa-3	$-(NH_3)_6^+$	Amide	POE short	–	–	Hardly forms a film on a water surface
Hexa-4	$-(NH_3)_6^+$	Ester	Alkyl	10	40	Reproducible[d]
Hexa-5	$-(CO_2H)_6$	Amide	Alkyl	2	35	Reproducible[d]
Hexa-6	$-(CO_2H)_{18}$	Ester	Alkyl	–	–	Polar head too large
Hexa-7	$-(NH_3)_6^+$	Ester	Alkyl + POE	10	20	Poorly reproducible[d]

Note: [a] Chemical group directly connected to the cyclopropane ring. [b] Bridge between the cyclopropane ring and the polar head. [c] In $mN\,m^{-1}$. [d] Recorded at 20°C.

inter-molecular H-bonds greatly enhancing the film cohesion and/or rigidity. We believe that these informations will be useful when aiming at elaborating new supramolecular assemblies of C_{60} multiadducts at surfaces and interfaces with specific functionalisation for biological applications [50,51].

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