

# Peptide anchored Langmuir–Blodgett films of a fullerene amphiphile

Pietro Tundo <sup>a,\*</sup>, Alvisè Perosa <sup>a</sup>, Maurizio Selva <sup>a</sup>, Ludovico Valli <sup>b</sup>,  
Cinzia Giannini <sup>c</sup>

<sup>a</sup> *Dipartimento di Scienze Ambientali, Università Ca' Foscari, Dorsoduro 2137, 30123, Venezia, Italy*

<sup>b</sup> *Dipartimento di Ingegneria dell'Innovazione, Università degli Studi di Lecce, Via Monteroni, 73100 Lecce, Italy*

<sup>c</sup> *PASTIS-CNRSM, S.C.p.A., SS7 per Mesagne Km 7 + 300, 72100, Brindisi, Italy*

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## Abstract

A new amphiphilic derivative of fullerene  $C_{60}$  bearing an oligoglycyl tail ( $C_{60}CHCOgly_2OEt$ , **2**) formed stable Langmuir floating films at the air–water interface. This occurred when the molecular assembly was stabilized by anchoring the amphiphilic  $C_{60}$ 's to the aqueous subphase, via hydrogen bonding interactions between a dipeptide (Gly–L–Leu) dissolved in the water subphase, and the oligoglycyl chain. The compression ( $\pi - A$ ) isotherm of the Langmuir floating film constructed in such a way showed no hysteresis, was steep, and evidenced that the monolayer collapsed at a surface pressure  $\pi \geq 65 \text{ mN m}^{-1}$ , thus confirming that the film was tightly packed, extremely stable, and rigid. A limiting area per molecule of  $89.1 \text{ \AA}^2$  was extrapolated, in agreement with the calculated cross-section area of the  $C_{60}$  fullerene. On the contrary, when the dipeptide was absent and pure water was used as the subphase, the  $\pi - A$  isotherm yielded a limiting area  $< 55 \text{ \AA}^2$  which indicated the formation of multiple layers; moreover it showed significant hysteresis, the film was fragile, and it collapsed at  $\pi \approx 50 \text{ mN m}^{-1}$ . Once anchored by the dipeptide, the floating monolayer of **2** could be transferred onto hydrophobic quartz, glass and silicon substrates, by successive vertical dipping cycles, each cycle made up of two down-strokes and two up-strokes, to yield the Langmuir–Blodgett film. Up to 200 down- and up-strokes could be repeated reproducibly, a noteworthy result for non-covalently assembled LB films of fullerenes. The transfer ratio was 1.0, except for the second down-stroke of each cycle that gave a transfer ratio of zero, making the sequence of successful transfers: *D, U, U*, (cleaning and spreading), *D, U, U*, (cleaning and spreading), and so on (*D* = down-stroke, *U* = up-stroke). The total number of deposited layers was therefore 150. X-ray diffraction spectra were registered and exhibited a peak, which was fitted by a Montecarlo method of simulation to obtain the distribution of the repeat unit responsible for scattering; such distribution, with thickness between 20 and 60 Å, was consistent with the size of the amphiphile and the transfer sequence. The UV–Vis spectra of the LB film exhibited the characteristic  $C_{60}$  bands, and the absorption peaks in the 200–400 nm range were proportional to the number of layers, indicating that the deposition was reproducible and that the molecular environment of  $C_{60}$  in each layer remained constant. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Fullerene; Amphiphilic; Langmuir–Blodgett film; Self assembly

\* Corresponding author. Tel.: +39-041-2578642; fax: +39-041-2578620.

E-mail addresses: tundop@unive.it (P. Tundo), alvisè@unive.it (A. Perosa).

## 1. Introduction

Widespread attention has been paid to fullerene based materials, in view of its superconductivity in the interval of 18–30 K when doped, [1–4] and of its charge transfer, [5–7] and photochemical properties [8]. Incorporation of  $C_{60}$  into thin ordered films is an important goal for its application in new materials; but its successful inclusion into working devices requires that uniform, well ordered and relatively defect-free films be fabricated. A variety of techniques are known to produce fullerene thin films, such as vacuum sublimation, [9] solvent evaporation from a fine suspension, [10] self-assembly, [11] and Langmuir–Blodgett (LB) deposition [12]. The LB technique is particularly suited since it allows to build very regular multilayers, with a well-defined molecular orientation, and with good control over the film thickness, uniformity and architecture [13]. However, the production of Langmuir floating films of pure  $C_{60}$  does not yield an ideal close-packed monolayer of fullerene, [14–19] except for extremely low concentrations of the spreading solutions, [20–26] suggesting that floating films of  $C_{60}$  consist of more than a single layer in thickness. This behavior generates from the high cohesive energy ( $> 30 \text{ kcal mol}^{-1}$ ) between the buckyballs, [27–29] due to the strong intermolecular attractive  $\pi$ – $\pi$  interactions.

To overcome this drawback and to obtain organized fullerene monolayers,  $C_{60}$  derivatives obtained by the organic functionalization of fullerenes have been synthesized, and their thin films have been studied. Some have shown an interesting behavior due to their electrochemical behavior, [30,31] and some may conceivably provide access to interesting electronic devices [32]. An example reported by the groups of Diederich, Echegoyen, Leblanc, and Stoddart, describes ordered Langmuir films of  $C_{60}$ -dendrimer conjugates bearing acylated glucose groups [27]. While the floating film appeared stable, and showed reversible behavior in compression-decompression cycles, and the tendency of  $C_{60}$  to aggregate was suppressed; the monolayers could be transferred onto quartz slides (five up- and five down-strokes), with transfer ratios of 0.7 for the

up-stroke and about zero for the down-stroke. Huang and coworkers have investigated the photoelectric properties of  $C_{60}$  modified LB films, [33,34] and in particular of a  $C_{60}$ -aminocarboxylate derivative [35]. More recently, Nierengarten and co-workers have shown that fullerene-based amphiphilic dendrimers can form relatively stable Langmuir films, that can be transferred onto solid silanized substrates (13 layers) with transfer ratios between 0.8 and 1.0 [12].

The present approach to stable LB films of  $C_{60}$  involves self-assembly of an amphiphilic fullerene, through complementary hydrogen bonding interactions between oligopeptide units in the aqueous subphase. Analogous peptide binding has been used to form monolayers of amphiphilic poly(L-glutamic acid), [36] and of long chain fatty acids and amines [37,38]. And monomolecular Langmuir films of alkyl-oligopeptide amphiphiles have been fabricated by the spontaneous aggregation of their peptide chains, through hydrogen-bonding in the water subphase [36–43].

A new amphiphilic fullerene bearing an oligopeptidic tail, and able to form a stable floating film is here reported. This compound was expected to form a stabilized, regular, and homogeneous Langmuir film at the air–water interface by self-assembling in a hydrogen-bonded network, with a dipeptide dissolved in the aqueous phase. The reason for inserting the dipeptide was dual: (a) to bridge the gap between the oligopeptide chains and thereby anchor the amphiphilic  $C_{60}$ s; (b) to avoid the formation of clusters of  $C_{60}$  at the air–water interface, [27] caused by the tendency of  $C_{60}$  to form aggregates [27–29].

The result was foreseen as a stable (three-dimensional) self-assembled structure, such as the one represented pictorially in two dimensions, in Fig. 1.

Fig. 1 could also be represented as the use of screw-anchors (the dipeptides) to fasten the buckyballs through the oligopeptidic hydrophilic chain at the air–water interface.

Here described are some results towards the construction of a stabilized LB film containing fullerene, via hydrogen bond stabilization, in particular:

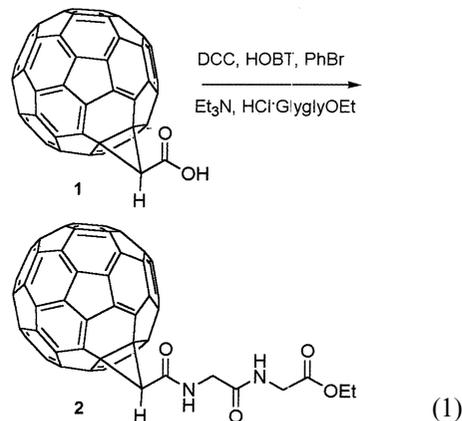
- the synthesis of new amphiphilic  $C_{60}$  functionalized by the oligoglycine fragment;
- the formation of the stabilized Langmuir floating monolayers of the amphiphilic  $C_{60}$ ;
- the transfer of the floating film on quartz slides to fabricate the corresponding LB film;
- the characterization of the LB film by X-ray diffraction (XRD) and UV–Vis spectroscopy.

## 2. Results and discussion

### 2.1. Synthesis of the amphiphilic fullerene

Diglycine ethyl ester  $-\text{[NHCH}_2\text{C(O)}\text{]}_2\text{OEt}$  ( $\text{Gly}_2\text{OEt}$ ), was used to functionalize the buckyball. (1,2-Methanofullerene  $C_{60}$ )-61-carboxylic acid **1**, prepared by the addition of (ethoxycarbonyl)-methyl diazoacetate to  $C_{60}$ , and successive hydrolysis, [44,45] was coupled with the oligopeptide by the traditional peptide coupling procedures [46]. The method used is analogous to the one previously reported for the synthesis of  $C_{60}$  linked to peptide *T* [4–8] (where a few milligrams were prepared and tested for biological activity) [47]. Accordingly, reaction of **1** with  $\text{Gly}_2\text{OEt}$  in the presence of DCC, HOBT, and bromobenzene as the solvent, proceeded at room temperature for 24 h and afforded amphiphilic fullerene **2** in a 42% yield, based on recovered  $C_{60}$ -carboxylic acid

**1** (Eq. (1)). The product appeared like a stable brown powder, which could be purified by silica gel column chromatography, by eluting with large volumes of a mixture of toluene and ethyl acetate (due to its low solubility in other solvents). It was fully characterized.



### 2.2. Langmuir experiments

The  $\pi$ -A isotherms of **2** (400  $\mu\text{l}$  of a  $1.1 \times 10^{-4}$  m chloroform solution) spread on pure water (curve 1, dotted line) and on a water subphase containing Gly-L-Leu (curve 2, solid line) are shown in Fig. 2. Chloroform was used as the spreading solvent, instead of aromatic solvents, since it is known that  $\pi$ -A isotherm interpretation of films containing  $C_{60}$  may be complicated by aromatics that remain trapped in the film, by complexation with the fullerenes [48]. The value of the limiting area per molecule,  $A_{\pi \rightarrow 0}$ , was extrapolated to zero pressure for each curve from the steepest portion of the Langmuir isotherm. In the presence of Gly-L-Leu in the water subphase (curve 2) a value in close agreement with that expected ( $86.6 \text{ \AA}^2$ ) [14–18] for a two-dimensional close-packed monolayer of the buckyball with the hydrophilic tail oriented toward the water phase, was obtained:  $89.1 \text{ \AA}^2$ , while in the presence of pure water (curve 1) the limiting area per molecule ( $< 55 \text{ \AA}^2$ ) indicated that fullerene interactions prevailed leading to the formation of multilayers. In addition, curve 2 of the floating

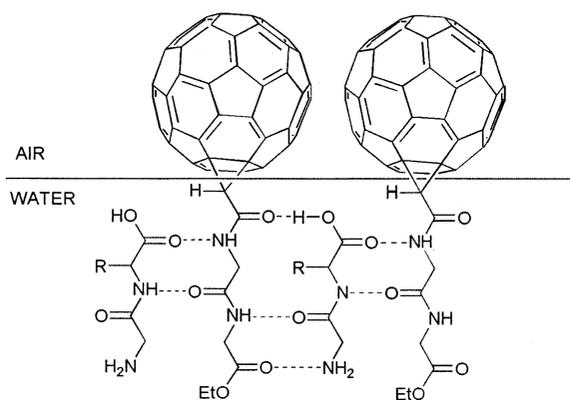


Fig. 1. Simplified pictorial representation of the plausible arrangement of the hydrogen bonded network in a stabilized Langmuir floating film of an oligoglycyl-functionalized fullerene.

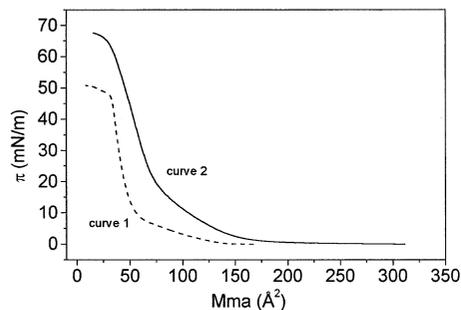


Fig. 2. Compression isotherms of **2** (400  $\mu\text{l}$  of  $1.1 \times 10^{-4}$  M solution in  $\text{CHCl}_3$ ) on a pure water subphase (dotted line), and on a water subphase containing Gly-L-Leu ( $1.0 \text{ g l}^{-1}$ , solid line).

monolayer in the presence of Gly-L-Leu showed a liquid expanded phase at  $\pi = 20 \text{ mN m}^{-1}$  and a condensed phase above that value; while curve 1 underwent the same transition at  $\pi < 10 \text{ mN m}^{-1}$ . Moreover, the collapse pressure was dramatically different: while the Langmuir film of **2** in the presence of Gly-L-Leu (curve 2) collapsed at  $\pi > 60 \text{ mN m}^{-1}$ , on pure water (curve 1) this occurred at a much lower pressure:  $\pi < 50 \text{ mN m}^{-1}$ . One can argue, in analogy to the formation of self-assembled monolayers of alkyl-oligopeptide amphiphiles, [39] and in analogy to the results obtained with amphiphilic fullerene containing dendrimers, [12] that this evidence indicates that the monolayer is formed only when it is stabilized by the anchoring effect of the dipeptide in the subphase through hydrogen bonding.

In addition, for curve 2, the extrapolated value of the limiting area per molecule was independent on the concentration of the spreading solution, as determined by depositing solutions of **2** with different concentrations. This implies that the monotone expansion of the  $A_{\pi \rightarrow 0}$  values upon lowering the concentration of the spreading solution, a general drawback typical of other fullerene derivatives, [49] does not occur for compound **2**.

Successive compression and expansion cycles were performed on the floating film of **2** with Gly-L-Leu in the subphase, in order to explore the reversibility of its formation. The response to such cycles was that compound **2** could be relaxed and recompressed without significant hysteresis,

provided Gly-L-Leu was present in the aqueous subphase: during the expansion following the first compression, the surface pressure described a curve close to the one registered while the floating layer was compressed. In addition, the floating film of compound **2** with Gly-L-Leu could be maintained overnight at a pressure of  $35 \text{ mN m}^{-1}$  with an area loss of just 1%. In the absence of the dipeptide (curve 1) on the other hand, the limiting area per molecule evidenced a large loss.

The high collapse pressure, the response to the compression/expansion cycles, and the resistance over time of the film all led to the conclusion that Gly-L-Leu inserted in the aqueous subphase has a strong anchoring effect on the film, rendering it rigid, organized, and stable.

### 2.3. Langmuir-Blodgett film deposition

The Langmuir floating film of **2** could be transferred at  $20^\circ\text{C}$  onto hydrophobic quartz, glass and silicon slides, at a surface pressure maintained at  $30 \text{ mN m}^{-1}$ , provided the dipeptide was present in the aqueous subphase. After each spreading, a series of two down- and two up-strokes was reproducibly carried out, and thereafter up to at least 200 strokes could be performed. For the first down-stroke ( $D$ ) and up-stroke ( $U$ ), the transfer ratios were 1.0, while it was 0 for the second downward passage, and 1.0 again for the second up-stroke. This pattern for the deposition ratio ( $D = 1.0$ ,  $U = 1.0$ ,  $D = 0$ ,  $U = 1.0$ ) was then constantly repeated reproducibly for each following series of four strokes, the repeat unit, yielding 150 effectively deposited layers. In this way, the global sequence of the successful transfer was  $D$ ,  $U$ ,  $U$ , (cleaning and spreading),  $D$ ,  $U$ ,  $U$ ,... and so on ( $D = \text{down}$  and  $U = \text{up}$ ), by moving the substrate:  $D$ ,  $U$ ,  $D$ ,  $U$ , (cleaning and spreading),  $D$ ,  $U$ ,... The necessity of interrupting the deposition after only four dippings arised from the fact that one of the two moving barriers of the trough became too close to the Wilhelmy plate, thus modifying the measurement of the surface pressure. The use of more concentrated spreading solutions or of larger volumes had always the effect of producing 3D aggregates of **2**.

## 2.4. X-ray diffraction

Fig. 3 shows the diffraction spectrum of the thin film obtained by 150 strokes through the monolayer of derivative **2**, in the presence of Gly–L–Leu, deposited onto a silicon substrate (curve a), in comparison with the XRD profile collected on the pure silicon substrate (curve b). The two diffraction profiles differ only for one peak at  $19.31^\circ$  (see arrow), which was attributed to the film structure. A Monte-Carlo method of simulation was applied to fit this peak [50]. In this way it was possible to obtain the distribution of the structure dimensions, which cause the scattering. This is depicted in Fig. 4. Throughout the bulk of the LB film, 80% of the repeat units have a thickness ranging from 20 to 60 Å, with an average of 40 Å. This is consistent with the deposition pattern and with the size of compound **2**: by considering that the length of the tail attached to the buckyball is roughly 10 Å, [51] and that the diameter of the  $C_{60}$  sphere is also about 10 Å, [52] the maximum thickness-per-monolayer of the LB film should therefore be of about 20 Å. In the ideal case of a perfect vertical stacking of the multilayer, the maximum thickness of the three layers deposited during each cycle (assumed as the repeat unit) is 60 Å. The smaller average thickness (40 Å) of layers with the same quality and the same transfer ratios, can be explained by the uncertainty on the orientation of **2** within the three layers respect to the plane of the silicon slide, by the possible interdigitation of the chains, and by the texture of the layers.

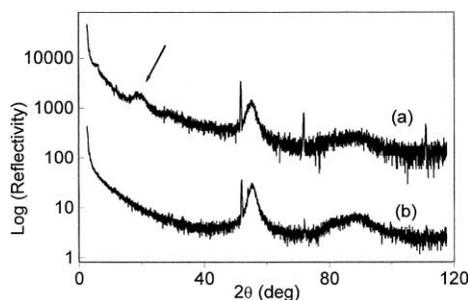


Fig. 3. XRD spectrum of the LB film obtained by 150 dipping cycles of derivative **2** deposited onto a silicon substrate (curve a) and XRD profile collected on the pure silicon substrate (curve b).

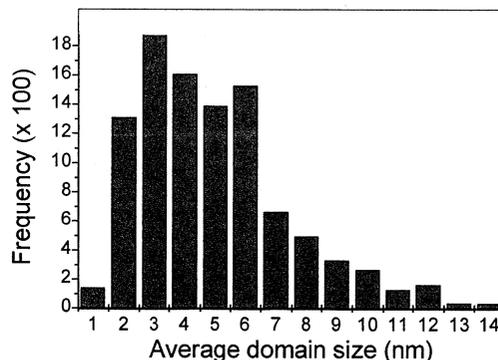


Fig. 4. Domain size distribution of the LB film obtained by 150 dipping cycles of derivative **2**.

## 2.5. LB film thickness

An average thickness of  $100 \pm 15$  nm was measured by a Tencor computerized surface profiler (Alpha-Step 200 Stylus Profilometer) for an LB film 25 repeat units (100 total strokes) thick, deposited onto hydrophobic Corning glass. This value is in agreement with the average domain size (4 nm) obtained by the diffraction spectrum (in fact:  $4 \text{ nm} \times 25 \text{ units} = 100 \text{ nm}$ ). The measurement was carried out after the deposition of a thin gold layer, of known thickness, both onto a clean region of the glass substrate and onto the LB film itself.

## 2.6. UV–Vis spectra

The refractive index  $n$  and the extinction coefficient  $k$  versus the wavelength  $\lambda$  have been calculated by a computer fit of reflectivity  $R(\lambda)$  and transmittivity  $T(\lambda)$  data.<sup>1</sup> The refractive index of

<sup>1</sup> The model takes into account a parallel-sided, isotropic film of refractive index  $n_1$  between media of indices  $n_0 = 1$  (air) and  $n_2$  (fused quartz substrate), the latter supposed to be very thick with respect to the wavelength. According to this model,  $R(\lambda)$  and  $T(\lambda)$  can be expressed by the following equations:

$$R(\lambda) = \frac{A \cosh \alpha + B \sinh \alpha - C \cos \beta + D \sin \beta}{E \cosh \alpha + F \sinh \alpha - G \cos \beta + H \sin \beta}, \quad T(\lambda) = \frac{8n_2 n_0 (n^2 + k^2)}{E \cosh \alpha + F \sinh \alpha - G \cos \beta + H \sin \beta}$$

Here,  $n$  and  $k$  are the refractive index and the extinction coefficient of the LB film, respectively [12]. If the reflectivity  $R$ , the transmittivity  $T$ , and the thickness of the film are known,  $n$  and  $k$  can be calculated.

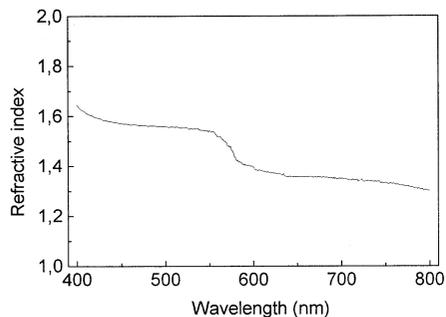


Fig. 5. Refractive index of the LB film obtained by 60 dippings of derivative **2** onto a quartz slide.

the film changes between 1.6 and 1.4 in the 400–800 nm spectral range. In the literature, to our knowledge, a refractive index of about 2 in the near-infrared and visible region for sublimated  $C_{60}$  films is reported [53]. The refractive index  $n$  and the extinction coefficient  $k$  are shown in Figs. 5 and 6, respectively. From the  $k$  measurements, we have determined the absorption coefficient  $\alpha = 4\pi k/\lambda$ , and the transmittance and reflectance of the multilayer are reported in Fig. 7.

Furthermore, the UV–Vis spectrum of the LB film of **2** (60 dipping cycles) exhibits three absorbance bands in the UV region at 339, 267 and 220 nm characteristic of  $C_{60}$ . Measurements carried out on samples having different thickness have shown that the absorption peaks in the 200–400 nm spectral range are proportional to the number of layers [12]. Fig. 8 illustrates the absorption at 257 nm as a function of the number of dippings. The straight line was drawn using a

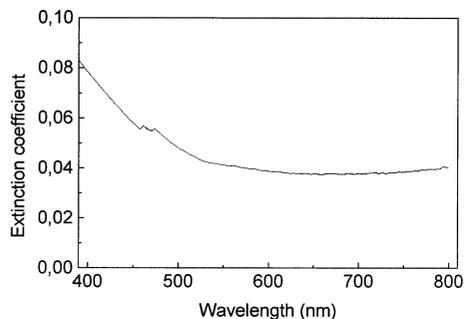


Fig. 6. Extinction coefficient of the LB film obtained by 60 dippings of derivative **2** onto a quartz slide.

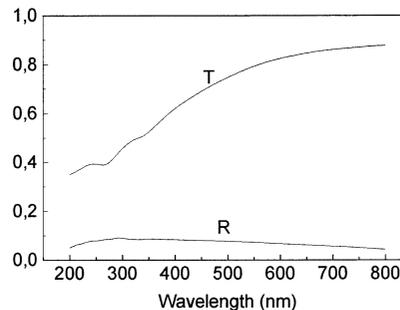


Fig. 7. Optical transmittance ( $T$ ) and reflectance ( $R$ ) of the LB film obtained by 60 dippings of derivative **2** onto a quartz slide.

least-squares fit. The linear behavior of the absorbance is apparent, and supports that a constant amount of fullerene was picked up at each cycle. This is also evidence for the successful transfer of at least 100 strokes. This indicates also that the deposition of the film was reproducible, that a constant amount of  $C_{60}$  derivative was picked up at each up- and down-stroke, and that the molecular environment of fullerene in each layer was practically constant during the deposition.

### 3. Conclusions

Compound **2** formed a stable and rigid Langmuir film at the air–water interface, only when a

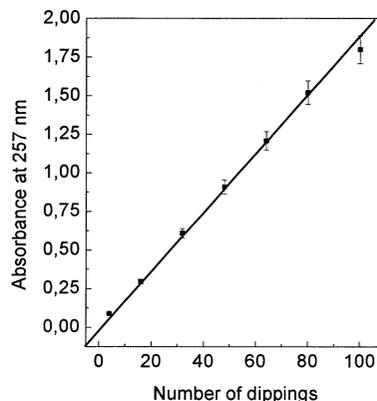


Fig. 8. Dependence of the absorbance of the LB film of **2** at 257 nm on the number of dippings.

dipeptide (Gly–L–Leu) was inserted in the aqueous subphase: Gly–L–Leu presumably stabilized the assembly by anchoring the amphiphilic C<sub>60</sub>'s via hydrogen-bonding interactions with the oligoglycyl chain at the air–water interface, and by suppressing fullerene aggregation.

This is the first time that a Langmuir–Blodgett film made of 150 layers is fabricated for non-covalently assembled LB films of fullerenes.

Although the structure of the LB film has been not defined yet at the molecular level (due to the uncertainty on the orientation of **2** within the three layers respect to the plane of the silicon slide, to the possible interdigitation of the chains, and to the arrangement of the H-bonds, which may affect the texture of the layers, and the distribution of the void and filled areas within the layers), all the experimental evidence (Langmuir isotherms, XRD, UV–Vis spectra) indicates that the global structure distribution and the molecular environment of the LB film of **2** remained constant. Ongoing work is aimed at clarifying the distribution of the amphiphiles in the LB film, by modifying the peptide chain attached to the fullerene, and by optimizing molecular recognition by the oligopeptide present in the aqueous subphase; and at developing suitable models for the interpretation of the results. The strong hydrogen-bonding interactions present in the aqueous subphase between the dissolved Gly–L–Leu and the diglycyl chain of **2** are the driving force for the spontaneous ordered aggregation, and lead to the observed stable and ordered LB film.

Depending on the nature of the solid substrate used for the LB transfer, the films may prove interesting for applications in optical technology [54,55].

## 4. Experimental

### 4.1. Synthesis of the amphiphilic fullerene *N*-(1,2-methanofullerene 60–61-carbonyl)-glycylglycyl ethyl ester **2**

A 50 ml flask was loaded with 20.0 mg (0.026 mmol) of (1,2-methanofullerene C<sub>60</sub>)-61-car-

boxylic acid **2**, 7.0 mg (0.052 mmol) of HOBT, 5.5 mg (0.026 mmol) of DCC, and 15 ml of a 1:6 mixture of DMSO and PhBr. The reaction was degassed by bubbling nitrogen, and cooled in an ice-water bath, with stirring, for 30 min. To this solution was added, via syringe, a solution made of 10.2 mg (0.052 mmol) of gly-gly ethyl ester and 5.3 mg (0.052 mmol) of triethyl amine in 10 ml of PhBr. The mixture was warmed to room temperature, and stirred under N<sub>2</sub> for 24 h. Formation of a brown precipitate was observed. PhBr was removed under reduced pressure, the product was adsorbed on a small portion of silica gel, and chromatographed over silica gel eluting first with toluene and then with a 1/1 mixture of toluene and ethyl acetate (*R<sub>f</sub>* = 0.27). Yield (based on recovered C<sub>60</sub>) = 30 mg (42%). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>/CS<sub>2</sub>/C<sub>6</sub>D<sub>6</sub>, 4:1:2) δ ppm 9.31 (t, 1H, *J* = 5.80 Hz), 8.47 (t, 1H, *J* = 5.80 Hz), 5.40 (s, 1H), 4.12 (q, 2H, *J* = 7.02 Hz), 4.03 (d, 2H, *J* = 5.80 Hz), 3.92 (d, 2H, *J* = 5.80 Hz), 1.20 (t, 3H, *J* = 7.02 Hz). λ<sub>max</sub> (*n*-hexane) nm<sup>-1</sup> 257, 328, 437. MALDI/MS, matrix: 2,5-hydroxybenzoic acid, 720 (C<sub>60</sub>), 921 (M + 1), 944 (M + 1 + Na), 960 (M + 1 + K).

### 4.2. Langmuir experiments

In the Langmuir experiments, compound **2** was dissolved in CHCl<sub>3</sub> (concentration: 1.1 × 10<sup>-4</sup> M). The resulting solution was uniformly spreaded over the subphase by adding small drops (≈ 5 μl) at different locations on the water surface (850 cm<sup>2</sup>, KSV5000 System 3 LB apparatus). After 15 min, the floating film was slowly compressed by the use of two mobile Teflon barriers at a rate of 2 × 10<sup>-2</sup> nm<sup>2</sup> s<sup>-1</sup> molecule<sup>-1</sup> and the surface pressure vs. area per molecule curve was recorded. The Wilhelmy plate was placed perpendicularly to the direction of motion of barriers; it was burnt to redness and quenched in methanol between runs. During a series of Langmuir film formation experiments, ultrapure water with resistivity greater than 18 MΩ cm and pH = 5.9 ca. was produced by a Millipore Milli Elix3-MilliQ system and used as the subphase after filtration through a 0.5 μm nylon disk. In a second series of experiments and during the multilayer deposi-

tions, a solution containing  $1.0 \text{ g l}^{-1}$  of glycyL-L-leucine was used as the subphase. The subphase was in both cases thermostated at  $20^\circ\text{C}$  by a Haake GH-D8 apparatus.

Depositions of compound **2** was carried out at a surface pressure of  $30 \text{ mN m}^{-1}$ , using various substrates, such as hydrophobized quartz, glass and silicon having a surface area of  $1.1 \text{ cm}^2$ . The LB film was successfully transferred onto various solid supports by up to 150 successive dipping/withdrawal cycles at a dipping speed of  $1\text{--}2 \text{ mm min}^{-1}$  for the downstrokes and  $6 \text{ mm min}^{-1}$  for the upstrokes.

### 4.3. Characterization of the LB film

#### 4.3.1. X-ray diffraction

XRD measurements were performed by using a Philips-1880 diffractometer equipped with a 3-kW generator. A Cu target was used as X-ray source ( $\text{CuK}\alpha$  radiation). The collimation system of slits was made of an entrance slit  $1/30^\circ$  wide to collimate the beam impinging onto the sample surface and, on the diffracted beam, a Soller slit followed by  $0.1 \text{ mm}$  scattered slit located at a distance of  $10 \text{ cm}$  from the sample. A flat graphite monochromator was located before the proportional counter in order to reduce the background noise in the detector. During the X-ray measurements the incident angle was kept fixed at  $0.5^\circ$  varying only the detector angle ( $2\theta$ ).

#### 4.3.2. UV–Vis spectra

Optical measurements at room temperature were made using a Varian Cary 5 double-beam spectrophotometer and unpolarized light at nearly normal incidence in the  $200\text{--}800 \text{ nm}$  spectral range. In particular, reflectivity measurements were carried out using an integrating sphere. The refractive index  $n$  and extinction coefficient  $k$  at normal incidence were determined from both transmission and reflection measurements for a  $60\text{-layer}$  thick LB film deposited onto quartz.

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