Preparation and deposition of stable monolayers of fullerene derivatives

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Two new fullerene derivatives have been synthesized, which tend to form Langmuir monolayers. Robust monomolecular layers are formed at the air/water interface, that can be transferred onto hydrophilic substrates by Langmuir–Blodgett or Langmuir–Schaefer techniques. The measured areas per molecule (105 Å^2 for **1a** dropped from a deuteriochloroform solution at 20 °C) reach those expected for a true monolayer of C_{60} at the air/water interface.

Since fullerenes were first discovered,[1] and an efficient synthesis for them was developed,[2] the preparation of thin films containing fullerenes has become an important issue in the applications of these new forms of carbon.[3] In this connection, either self-assembled monolayer (SAM) or Langmuir–Blodgett (LB) deposition techniques may play a significant role.[3] A very nice example of molecular recognition applied to the formation of molecular monolayers has also been reported recently.[4] Whereas monomolecular layers of fullerenes and fullerene derivatives have already been obtained by several groups, their deposition has raised some difficulty, with very few successful results.[3] Both C_{60} and C_{70} form condensed layers at the air/water interface.[5–7] However, the layers of C_{60} are poorly behaved, and their transfer to solid substrates generally results in films of poor quality.[6,8] In fact, the non-amphiphilic C_{60} molecules tend to aggregate, and form layers several molecules thick at the air/water interface,[6] instead of true monolayers, unless very dilute spreading solutions are used.[9] For pure C_{60}, monolayers form only if the concentration of C_{60} solution is lower than 10^{-5} M,[9] and extreme care should be taken during the film compression, otherwise multilayers are obtained with an average typical cross-sectional area of *ca.* 22 Å^2 molecule^{-1}, which means that up to five molecules are crowded atop each other.[6]

Since then, two strategies have been used to overcome these problems and prepare stable C_{60} monolayers. One is to chemically modify a surface with a reagent that allows covalent bonding to C_{60};[3,7,10] another is to chemically modify C_{60} itself,[11–13] to produce a self-assembling derivative.[3,6,14–27] Here, we report results obtained by the second strategy.

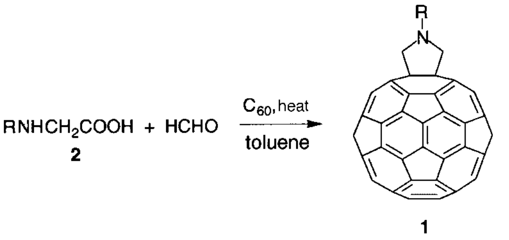
Results and Discussion

Compounds **1a,b** were prepared according to Scheme 1. Condensation of glycine derivatives **2a,b** with paraformaldehyde generates the reactive 1,3-dipole azomethine ylide, which readily adds to C_{60} across the junction between two six-membered rings.[28] Both products possess C_{2v} symmetry, due to fast nitrogen inversion, easily detectable by the reduced number of resonances in the ^{13}C NMR spectra and by the equivalence of the pyrrolidine methylene protons in the ^{1}H NMR spectra.

Compound **1a** was dissolved in deuteriochloroform or toluene, to form three solutions of concentrations 1.44×10^{-4} M, 1.03×10^{-3} M or 9.90×10^{-4} M, respectively. The surface pressure–area isotherms of **1a** are shown in Fig. 1. Both curves (*a*) and (*b*) of Fig. 1 show that the floating films are very rigid, and have a high collapse pressure (> 70 mN m^{-1}).

Fig. 1(*b*) shows, for **1a** dissolved in deuteriochloroform, a molecular area of $A_o = 105.4$ Å^2 (extrapolated to zero film pressure, $\Pi = 0$), in fair agreement with the theoretically expected value of 93 Å^2 molecule^{-1} (ref. 29) and the experimentally determined value of 96 Å^2 molecule^{-1} (ref. 17) for pure C_{60}. Obviously, the chemically modified **1a**, with deuteriochloroform as a spreading solvent, forms a stable and true monolayer on air/water interface, but also has a slightly increased area, when compared to the expected C_{60} area of 93 Å^2 molecule^{-1}. Using different spreading solution concentrations (1.44×10^{-4}–1.0×10^{-3} M) or different subphase temperatures (10–23 °C) had no effect on the isotherm; thus, monomolecular layers are formed much more easily for compound **1a** than for pure C_{60}, even with concentrated (10^{-3} M) spreading solutions.

It should be noted that, for all molecules in Table 1, the area at film collapse (A_c) is much smaller than the extrapolated area at zero pressure (A_0): it appears that for the very robust films in this study, A_c, measured at very high film pressures, measures an incipient clustering of molecules, rather than the



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Scheme 1 (**a**, R = $CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_3$; **b**, R = *n*-$C_{12}H_{25}$)

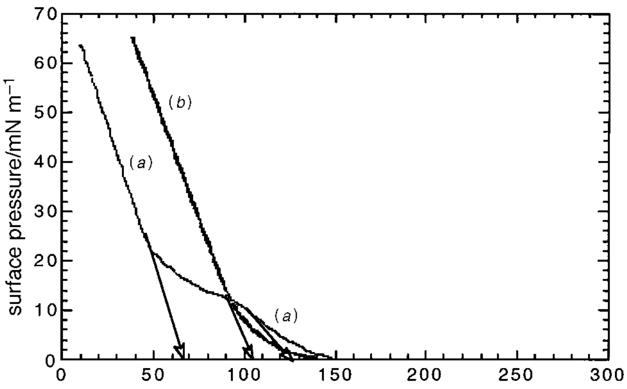

Fig. 1 Surface pressure–area isotherms of **1a** at 20 °C: (*a*) [**1a**] 1.03×10^{-3} M in toluene; (*b*) [**1a**] 9.9×10^{-4} M in deuteriochloroform

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Table 1 Molecular areas (Å^2 molecule^{-1}) A_{ons} (at first onset of non-zero film pressure), A_0 (linearly extrapolated from finite pressure to zero film pressure), A_c (at film collapse) and collapse pressures Π_c as a function of temperature T

		molecular areas/Å^2 molecule^{-1}			
compound	T/°C	A_{ons}	A_0	A_c	Π_c/mN m^{-1}
1a (in C_7H_9)	20	140	134.4±2	—	—
		68	67.8±2	≈40	>65
1a (in $CDCl_3$)	20	150	105±2	<40	>65
1b (in $CDCl_3$)	20	97	66	≈40	>70

ideal area for a 'relaxed' film with 'normal' intermolecular distances and with no clustering in the direction normal to the film plane.

When toluene is used as the spreading solvent, Fig. 1(*a*) shows a lower molecular area ($A_0 = 67.8$ Å^2), together with a shoulder at 134.4 Å^2. This shoulder appears only sometimes with toluene, even at different subphase temperatures, but never with deuteriochloroform: it may be due to some transient molecular association.[17] The smaller molecular area for **1a** spread from a toluene solution [Fig. 1(*a*)], compared with **1a** in deuteriochloroform [Fig. 1(*b*)] suggests that the molecules of **1a** 'dropped' from toluene are partially clustered.

Using either toluene or deuteriochloroform, the Langmuir films at the air/water interface were robust, and stable (no barrier movement) over a period of at least 48 h at an applied pressure of 25 mN m^{-1}. The water temperature showed very little influence on the air/water film properties within the range of 10–25 °C.

The Langmuir film of **1a** was transferred at 25 mN m^{-1} by the LB technique onto quartz at a dipping speed <3.5 mm min^{-1}, or carefully transferred onto highly oriented pyrolytic graphite (HOPG) by the Langmuir–Schaefer (quasi-horizontal transfer) technique. The film transfer was Y-type. It is found that good transfer conditions for the first layer were very important for the successful deposition of subsequent layers.

For optical absorption measurements, 100 layers of the Y-type film of **1a** were deposited onto isopropyl alcohol-coated quartz (Spectrasil). The UV–VIS spectrum (Fig. 2) shows absorption maxima at 219.1, 267.9 and 341.3 nm, in a good agreement with those for C_{60} derivatives in cyclohexane.[28] To investigate the quality of the LB deposition, a stepped thickness structure was built up on a glass microscope slide pretreated with isopropyl alcohol. The variation of the absorbance with the number of film layers is shown in Fig. 3, indicating a good LB deposition up to about the first 20 layers.

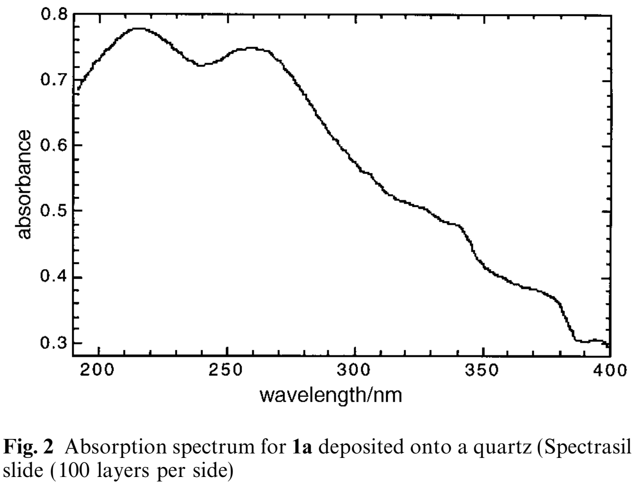

Fig. 2 Absorption spectrum for **1a** deposited onto a quartz (Spectrasil) slide (100 layers per side)

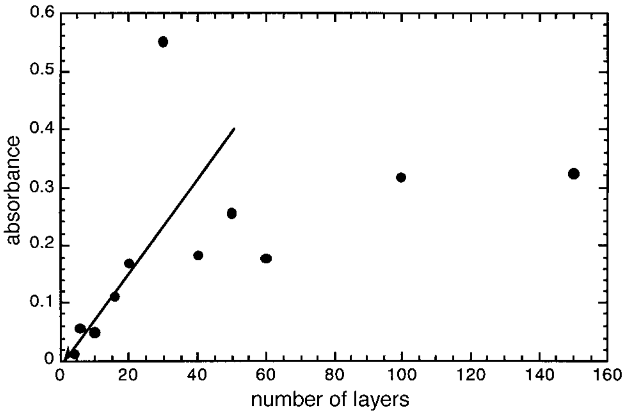

Fig. 3 Optical absorbance at 341.3 nm *vs.* number of LB layers of **1a** transferred onto a glass microscope slide

The orientation of the LB film for compound **1a** on HOPG was studied by STM, using bias voltages between 100 and 300 mV, the constant current mode, and set point currents between 2 and 5 nA. A typical well ordered region on the LB film of compound **1a** is shown in Fig. 4(*a*). A 7.9 Å separation in the horizontal axis, a 5.1 Å separation in the vertical axis and an angle of 85° were observed, which are very similar to our previous results obtained for pure C_{60}.[6] This indicates that compound **1a** can form a very well ordered region after transfer to a substrate. The image is not perfectly resolved, and the aliphatic chains are probably not seen clearly. Fig. 4(*b*) presents an approximate illustration of the presumed stacking, using the fcc lattice of pure C_{60}.

In order to study the influence of subphase on LB film properties, the pure water subphase was replaced by a 2.59×10^{-2} M aqueous KCl solution. Typical surface pressure–area isotherms are shown in Fig. 5. For compound **1a**, the area per molecule on a dilute aqueous KCl surface is reduced by about 10% [Fig. 5(*b*)], relative to the isotherm on a pure water surface [Fig. 5(*a*)], and the pressure–area isotherm also shows a slight change. This may be due to the interaction between K^+ and the triethylene glycol chain, as if the triether ends of two **1a** molecules associated to form, roughly, one 18-crown-6, to coordinate to one K^+ ion.[22]

A deuteriochloroform solution of compound **1b** (1.32×10^{-4} M) was carefully spread on a purified water subphase. A typical surface area–pressure isotherm is shown in Fig. 6. The collapse pressure was >70 mN m^{-1}, but, despite many attempts, the area per molecule (extrapolated to zero pressure) did not exceed $A_0 = 66$ Å^2 (Table 1). This can be understood because in **1b**, unlike compound **1a**, both ends are hydrophobic, as is C_{60} itself, and this does not favor monolayer formation. However, compound **1b** forms a stable multilayer film on air/water interface, which did not show any noticeable area loss at a constant pressure (25 mN m^{-1}) at least for 48 h. The isotherm is reversible in the range 0–40 mN m^{-1}.

In conclusion, we report the synthesis of an amphiphilic and a hydrophobic fullerene derivative, prepared to improve monolayer formation at the air/water interface. Compound **1a** can be considered a model fullerene for LB film formation. It is prepared by a general synthetic route, the cycloaddition of azomethine ylides to C_{60}, that relies on the condensation between an α-amino acid and an aldehyde. The amino acid **2a** used here is of great potential value for monolayer studies. In principle it can be condensed with a variety of aldehydes (RCHO) for the preparation of an entire new class of compounds. This class is characterized by the presence of a triethylene glycol chain, introduced to ensure hydrophilicity and whatever R group (from the aldehyde) in position 2 of the pyrrolidine ring. By this approach, either donor or acceptor units can be attached to C_{60} and the resulting molecules should reasonably give stable monolayers. In fact, the model amphi-

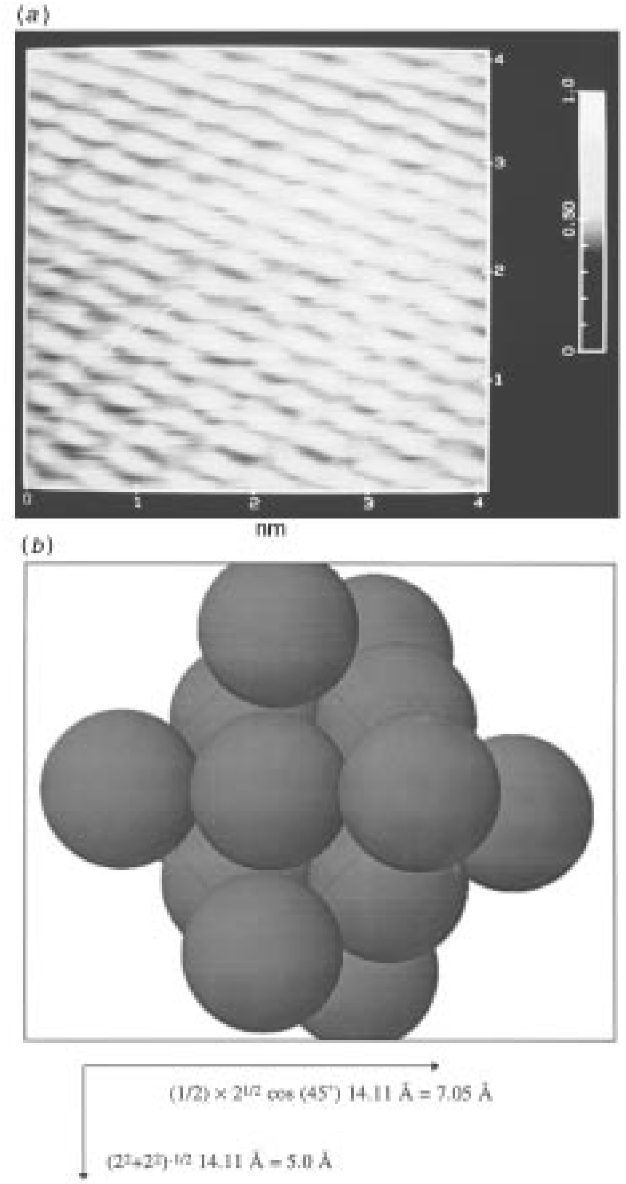

Fig. 4 (*a*) STM image of **1a** (20 layers deposited on HOPG by LS transfer). (*b*) Approximate computer model (CAChe Editor, on MacIntosh 8100AV), using the C_{60} fcc lattice ($a = 14.11$ Å) and touching van der Waals spheres of diameter 10 Å for the fullerene cores. The alkyl tails of **1a** are not shown. Repeat distances of 7.1 Å in the horizontal direction are seen assuming that the face diagonal [110] of the fcc lattice projects at an angle of 45° to the plane of projection. Repeat distances of 5.0 Å assume a [022] distance between the horizontal row of spheres seen in front, and the next horizontal row of spheres vertically below them, yet partially behind them.

philic fullerene derivative **1a** forms a stable 'true' monolayer at the air/water interface when 'dropped' from a deuteriochloroform solution (area per molecule at zero pressure of 105 Å^2, *vs.* calculated area of 93 Å^2 for pure C_{60}). This monolayer can be transferred onto a glass microscope slide or quartz slide by the LB method, or onto HOPG by the LS method. The same fullerene derivative **1a** has a very strong interaction with a KCl–water surface. Instead, the hydrophobic fullerene derivative **1b**, used for comparison, does not form a true monolayer film at the air/water interface.

Experimental

General

^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini 200 in $CDCl_3$ solutions. Chemical shifts are given in ppm (δ) relative to tetramethylsilane. UV–VIS absorption spectra were taken on a Jasco V550 UV–VIS spectrophotometer. MALDI (matrix-assisted laser desorption ionization) mass spectra were obtained in positive linear mode at 15 kV acceleration voltage on a Reflex™ time of flight mass spectrometer (Bruker) using 2,5-dihydroxybenzoic acid as matrix. Reactions were monitored by thin-layer chromatography using Merck precoated silica gel 60-F_{254} (0.25 mm thickness) plates. Flash column chromatography was performed employing 230–400 mesh silica gel (from Baker). Reaction yields were not optimized and refer to pure, isolated products.

C_{60} was purchased from Bucky USA (>99.5%). All other reagents were used as purchased from Fluka or Aldrich. The synthesis of *N*-(3,6,9-trioxadecyl)glycine **2a** has been described elsewhere.[30] All solvents were distilled prior to use. Cyclohexane, employed for UV–VIS measurements was a commercial spectrophotometric grade solvent.

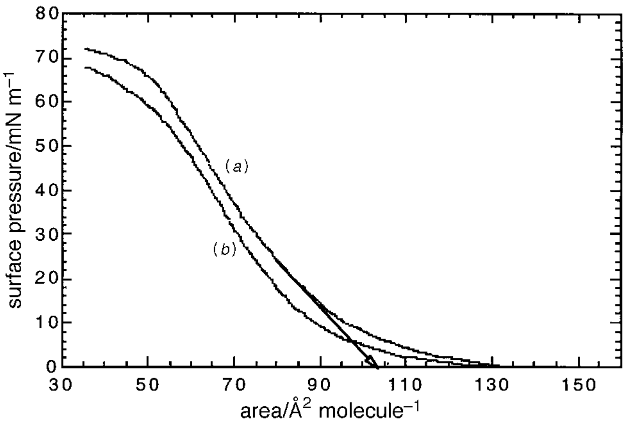

Fig. 5 Surface pressure–area isotherm of **1a** (*a*) on a pure Millipore Milli-Q water subphase and (*b*) on a Millipore Milli-Q water subphase made 2.59×10^{-2} M in KCl. Deuteriochloroform was used as the spreading solvent.

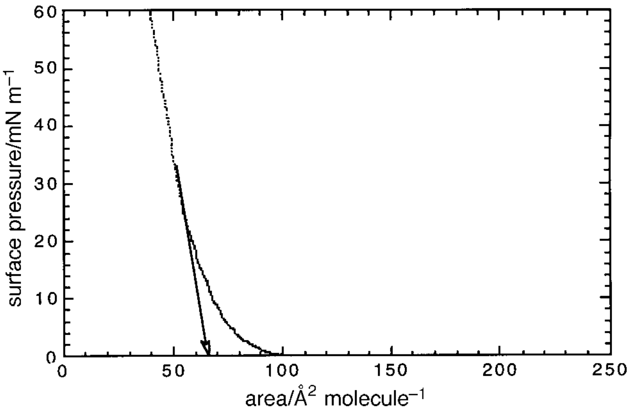

Fig. 6 Surface pressure–area isotherm of **1b** (concentration 1.32×10^{-4} M in deuteriochloroform)

N-(*n*-Dodecyl)glycine 2b

To a solution of *n*-dodecyl aldehyde (0.420 g, 2.28 mmol) and glycine ethyl ester hydrochloride (0.318 g, 2.28 mmol) in 12 ml of methanol–acetic acid (99 : 1), was added $NaBH_3CN$ (0.178 g, 2.84 mmol). The solution was stirred at room temperature for 2 h, then aqueous $NaHCO_3$ and ethyl acetate were added. The organic phase was separated and purified by column chromatography [eluent: light petroleum–ethyl acetate (9 : 1)] after which 0.180 g (0.663 mmol, 29%) of *N*-(*n*-dodecyl)glycine ethyl ester was obtained. ^{1}H NMR ($CDCl_3$): δ 4.18 (q, $J = 7.1$ Hz, 2H), 3.39 (s, 2H), 2.58 (t, $J = 7.1$ Hz, 3H), 1.96 (br s, 1H), 1.48 (t, $J = 6.7$ Hz, 2H), 1.26 (s, 20H), 0.87 (t, $J = 6.7$ Hz, 3H).

^{13}C NMR ($CDCl_3$): δ 172.59, 60.70, 51.06, 49.70, 31.94, 30.09, 29.64, 29.56, 29.37, 27.27, 22.71, 14.26, 14.13. IR (KCl): 2920, 2848, 2210, 1745, 1565, 1465, 1373, 1309, 1198, 1068, 900, 725, 593, 494 cm^{-1}. MS (EI): *m/z* 271 (M$^+$), 226, 212, 199, 198, 184, 116, 57. Anal. Calc. for $C_{16}H_{33}NO_2$: C, 70.8; H, 12.25; N, 5.16. Found: C, 71.7; H, 12.0; N, 5.17%.

To *N*-(*n*-dodecyl)glycine ethyl ester (0.100 g, 0.37 mmol) in 30 ml of methanol–water (1:1), was added sodium carbonate (0.400 g, 3.7 mmol) and the mixture was stirred for 72 h at room temperature. Then 0.5 ml of 12 M HCl was added and the resulting solution extracted with ethyl acetate. ^{1}H NMR [$CDCl_3$–CD_3OD (8:2)]: δ 3.31 (br s, 2H), 2.76 (br t, $J=7.3$ Hz, 2H), 1.59 (br s, 1H), 1.18 (s, 22 H), 0.81 (t, $J=6.4$ Hz, 3H). ^{13}C NMR [$CDCl_3$–CD_3OD (8:2)]: δ 168.9, 49.7, 49.3, 47.5, 47.3, 47.2, 31.6, 29.3, 29.2, 29.1, 28.8, 26.2, 25.9, 22.3, 13.7. IR (KCl): 3189, 2920, 2847, 1566, 1463, 1372, 1307, 1153, 1083, 873, 827, 798, 777, 726, 672, 529, 558, 507, 495, 466, 422, 405 cm^{-1}. MS (EI): *m/z* 243 (M$^+$), 199, 198, 89, 57.

Fullerene derivatives 1a and 1b

To C_{60} (50 mg, 0.07 mmol) in 30 ml of toluene, were added 0.07 mmol of amino acid (**2a** or **2b**) and 10.4 mg (0.35 mmol) of paraformaldehyde. The solution was heated to reflux for 1 h, the solvent evaporated and the crude product was purified by chromatography. The products were recrystallized from dichloromethane–methanol.

1a: $C_{69}H_{19}NO_3$, 38%; ^{1}H NMR δ 4.51 (s, 4H), 4.06 (t, $J=5.6$ Hz, 2H), 3.90–3.70 (m, 6H), 3.60–3.54 (m, 2H), 3.37 (s, 3H), 3.36 (t, $J=5.6$ Hz, 2H). ^{13}C NMR δ 155.15, 147.32, 146.26, 146.13, 146.08, 145.73, 145.42, 145.32, 144.59, 143.13, 142.65, 142.28, 142.10, 141.91, 140.17, 136.24, 72.07, 70.90, 70.81, 70.71, 70.55, 68.55, 59.13, 54.28. IR (KCl): 2865, 1427, 1340, 1185, 1113, 767, 704, 597, 575, 553, 526 cm^{-1}. MALDI-MS: *m/z* 909 (M$^+$), 932 (M+Na)$^+$. UV–VIS (cyclohexane) λ_{max}/nm: 702, 430, 323, 304, 255, 212. Anal. Calc. for $C_{16}H_{33}NO_2$: C, 91.08; H, 2.11; N, 1.54. Found: C, 90.0; H, 2.07; N, 1.51%.

1b: $C_{74}H_{29}N$, 41%; ^{1}H NMR δ 4.36 (s, 4H), 3.04 (t, $J=7.4$ Hz, 2H), 1.90 (qnt, $J=7.4$ Hz, 2H), 1.59 (m, 2H), 1.15–1.50 (m, 16H), 0.85 (m, 3H). ^{13}C NMR δ 153.98, 152.67, 146.19, 145.15, 144.98, 144.60, 144.35, 144.18, 143.48, 142.02, 141.55, 141.17, 141.00, 140.82, 139.11, 135.20, 69.57, 66.98, 54.14, 31.15, 28.95, 28.91, 28.62, 28.07, 26.91, 22.02, 13.35. IR (KCl): 2924, 2849, 1510, 1461, 1182, 526. MALDI-MS: *m/z* 931 (M$^+$). UV–VIS (cyclohexane) λ_{max}/nm: 702, 430, 323, 305, 255, 212. Anal. Calc. for $C_{74}H_{29}N$: C, 95.36; H, 3.14; N, 1.50. Found: C, 95.6; H, 3.24; N, 1.50%.

Monolayer and multilayer methodology

Solutions of compounds **1a** and **1b** in deuteriochloroform or toluene were carefully spread onto a purified water subphase (Millipore Milli-Q, resistivity 16 MΩ cm) in a vibration-isolated Lauda film balance at room temperature and also at thermostatically controlled lower water temperatures of 10, 15, and 20 °C. The spread solutions were left for periods ranging from 20 min to 12 h, after which they were compressed at a barrier speed of 26 mm min^{-1}.

The monolayer film at the air/water interface (also known as a Langmuir, or Pockels–Langmuir film) was transferred onto quartz (Spectrasil or Suprasil) slides by the Langmuir–Blodgett (LB, or vertical transfer) technique, or transferred onto highly oriented pyrolytic graphite (HOPG, Union Carbide ZYA grade) by the Langmuir–Schaefer (LS, or quasi-horizontal transfer) technique. The quartz slides were pretreated in isopropyl alcohol for 2 h, to make their surface hydrophobic.

UV–VIS spectra of LB multilayers were measured on a Perkin-Elmer Lambda 4B spectrophotometer. The LB films on a HOPG substrate were studied by scanning tunnelling microscopy (STM) in air at room temperature, using a Digital Instruments Nanoscope II equipped with a type A head, and a Pt/Ir tip, using bias voltages between 100 and 300 mV, the constant current mode, and set point currents between 2 and 5 nA.

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