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Novel fulleropyrrolidinium-based materials

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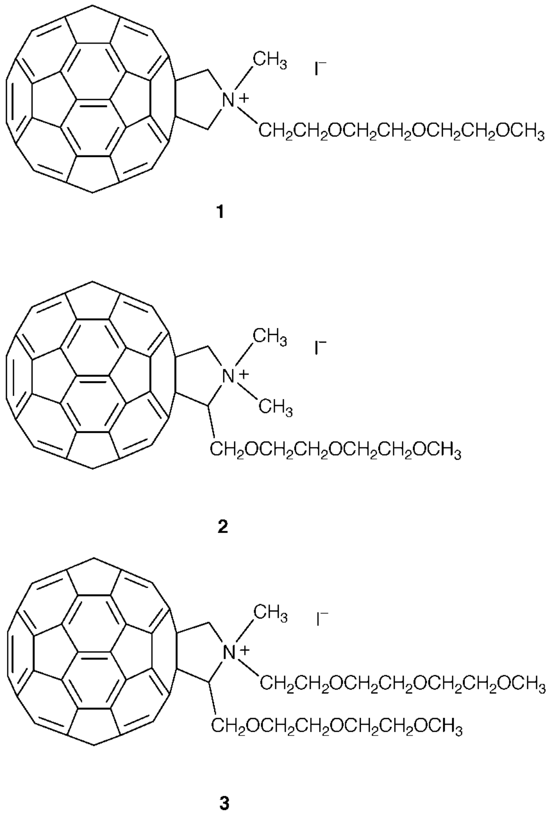
The cyclic voltammetry of a series of soluble *N*-methylfulleropyrrolidinium salts shows that these materials are better electron-acceptors than unmodified C_{60}. The stability of mono-reduced, zwitterionic, and doubly-reduced anionic species, produced either electrochemically or chemically, has been checked by absorption spectroscopy. Langmuir–Blodgett (LB) layers of the C_{60} derivatives mixed with tricosanoic acid have been built up on different substrates. The optical properties of the films have been characterized using absorption spectroscopy and their structure was investigated by X-ray diffraction.

Introduction

The fabrication of efficient artificial photosynthetic systems has been one of the major goals of chemistry over the last decades.[1–4] To mimic the highly elaborate natural systems, carefully organized assemblies of suitable molecular and supramolecular entities, realising the fundamental process of spatial charge separation, have to be obtained and the problem of their interfacing to the macroscopic world needs to be addressed. In this respect, lipid bilayer membranes,[5,6] self-assembly[7] and Langmuir–Blodgett (LB)[7–10] techniques have been studied, permitting the ordered arrangement of layers of photoactive molecules onto conducting and semiconducting surfaces.



Scheme 1

In the search for suitable candidates for stable and efficient photoconversion devices, fullerenes have attracted considerable interest. C_{60} is an excellent electron acceptor: in solution, where it is easily reduced and capable of accepting up to six electrons;[11–18] in alkali-metal intercalated complexes, which show superconductivity;[19,20] and in charge-transfer salts, which exhibit ferromagnetic properties.[21] Furthermore it has been proved to be an excellent moiety for light-induced inter- and intramolecular electron-transfer processes.[16,22–24] During the evolution of fullerene chemistry, several studies have addressed the modulation of the electronic properties of its derivatives (*cf.* TCNQ derivatives[25]). However, most C_{60} derivatives have decreased electronegativity,[26,27] and attempts to increase the electron-accepting properties of C_{60} have led to some success.[28–36] It is clear that an improvement of the accepting properties of C_{60}, coupled with the organic chemistry of fullerenes, may open up new and efficient charge-transfer processes. We reported recently the synthesis and electrochemical properties of a series of pyrrolidinium salt derivatives of C_{60} (**1**–**3** Scheme 1), which show enhanced electron-accepting properties with respect to both the parent pyrrolidine derivatives and C_{60}.[37] Moreover, cyclic voltammetry (CV) measurements performed at low temperatures and fast scan rates, using ultramicroelectrodes, allowed the observation, for the first time in fulleropyrrolidine derivatives, of six fullerene-centred reductions. If proven, the great stability of mono-reduced, zwitterionic, and doubly-reduced anionic species **1**–**3**, produced either electrochemically or chemically, might show

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that these novel compounds can be used as strong acceptors in a number of applications.

On the other hand, ideally, these materials should be suitable for orderly covering of a surface. For achieving this, the Langmuir–Blodgett technique is a procedure of choice. However, the hydrophobic molecules of C_{60} tend to aggregate and form layers of several molecules thick at the air/water interface.[38] Therefore, it is important to modify C_{60} to obtain amphiphilic molecules.[39] We have previously shown that C_{60} can form a condensed layer on the water surface and that reproducible Y-type LB films (up to 50 layers in thickness) can be built up.[38,40,41] Here, we report a study of the behaviour of the new fullerene salts as LB films. The transferred layers were investigated using optical absorption measurements and X-ray diffraction.

Experimental

Tricosanoic acid (TA) was obtained from Sigma. Compounds **1**–**3** were prepared according to reported procedures.[37]

Electrochemical instrumentation and procedures

Materials and purification procedures used in the electrochemical experiments have been described elsewhere.[42] Potentials were measured with the ferrocene standard and are always *versus* SCE. $E_{1/2}$ values correspond to $(E_{pc}+E_{pa})/2$ from CV. Ferrocene was also used as an internal standard for checking the electrochemical reversibility of a redox couple. Voltammograms were recorded with an AMEL Model 552 instrument controlled either by an AMEL Model 568 or an ELCHEMA Model FG-206F function generator. Data acquisition was performed by a Nicolet Mod 3091 digital oscilloscope interfaced to a PC. Temperature control was accomplished within 0.1 °C with a Lauda Klein-Kryomat thermostat.

LB film preparation and characterisation

The LB film assemblies were built up using a constant perimeter trough located in a microelectronics clean room.

Approximately 300 µl of a solution containing $6.9 \cdot 10^{16}$ molecules of C_{60} derivative were dropped by microsyringe onto an ultra pure water subphase obtained by reverse osmosis, deionisation and UV sterilisation. The surface area was 600 cm^2. After evaporation of the solvent ($\sim$20 min), the floating monolayer was carefully compressed at a speed of approximately 10^{-2} nm^2 $molecule^{-1}$ s^{-1} to a surface pressure of about 45 mN m^{-1}.

Mixed fulleropyrrolidine and TA LB films for all derivatives of C_{60} were obtained. The molar ratio of derivatives of C_{60} : TA in mixed films was 1 : 4. The materials were dissolved separately in benzene. These solutions were mixed and the resulting solution was spread onto a water surface. After evaporation of the solvent ($\sim$20 min), the floating monolayer was carefully compressed at a speed of approximately 10^{-2} nm^2 $molecule^{-1}$ s^{-1} to a surface pressure of 27 mN m^{-1}. The C_{60}–TA layers were built up on quartz (Y-type deposition with a transfer ratio of 0.9 ± 0.1). Films of 40 monolayers on quartz were used for the absorption measurements. The films of both 20 and 40 monolayers thickness were deposited onto Si for X-ray measurements.

The absorption spectra of LB films were measured using a Perkin Elmer Lambda 19 spectrophotometer. Small scattering X-ray spectra were obtained with a Phillips X-ray energy Spectrometer with wavelength 1.3926×10^{-10}. All measurements were undertaken in air at room temperature.

Results and discussion

Electrochemical and chemical generation of reduced species

The synthesis and electrochemical characterisation of **1**–**3** have been recently reported.[37] For the CV study, carried out in THF solutions, ultramicroelectrodes were used for accessing low temperatures and high scan rates. The results revealed enhanced electron-acceptor behaviour for these species, providing a general anodic shift of the reduction processes, and demonstrating, for the first time for fullerene derivatives, the presence of a sixth fullerene-centred reduction process occurring at very negative potentials.

Since possible applications of these molecules will require stable reduced species, this stability, already assessed in the CV timescale, was checked on a much longer timescale after their either electrochemical or chemical generation. The one-electron reduced form of species **1**–**3** was successfully produced by performing bulk electrolysis of 0.2 mM, 0.05 M TBAH benzonitrile solutions. The electrolysis was performed at −0.6 V (for **1**, $E_{1/2}$ (I) = −0.38 V, in benzonitrile) and its progress was monitored *in situ* by recording periodically the UV–Vis–NIR spectra of the electrolysed solution and the corresponding steady-state voltammetry. The appearance of the typical absorption features in the Vis and NIR regions for the one-electron reduced fullerene is in excellent agreement with similar absorption spectra produced by time-resolved techniques in charge-transfer complexes of fullerene derivatives.[43] The first cathodic wave in the voltammetric curve gradually evolved into a cathanodic wave (for $<100\%$ electrolysis), becoming fully anodic when a charge corresponding to 100% electrolysis had passed.

The conservation of electroactive mass was established by the invariance of the overall height of the cathanodic wave and the final anodic one. The electrolysed solution was stable for several hours. Conversely, the rapid degradation of reduced **1** was observed when its further reduction was attempted by setting the electrolysis potential at −1.0 V (for **1**, $E_{1/2}$ (II) = −0.80 V in benzonitrile).

Stable two-electron (fullerene-centred) reduced species were, instead, obtained by chemical reduction of **1**–**3** benzonitrile solutions. Cobaltocene was used as the reducing agent and was added in increasing amounts to 0.5 mM **1**–**3** solutions. Cobaltocene was successfully used for preparing C_{60} salts.[44,45] However, in view of the better electron-acceptor character of **1**–**3** with respect to C_{60}, cobaltocene was expected to generate at least the corresponding two-electron reduced forms. The $E_{1/2}$ of cobaltocenium/cobaltocene redox couple is −0.84 V[46] *vs.* −0.80 for the second reduction of **1** in benzonitrile. The addition of sub-stoichiometric amounts of

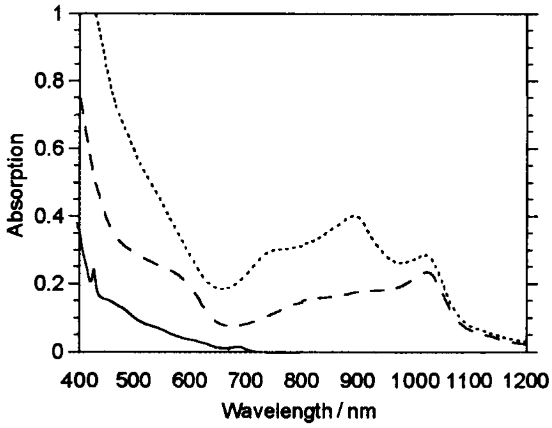

Fig. 1 Visible–NIR absorption spectra evolution during addition of cobaltocene to a 0.5 mM **1** benzonitrile solution. *T* = 25 °C. Spectra refer to 0 (full line), 50% (dashed line), and 150% (dotted line) (percentage relative to **1**) added cobaltocene amounts.

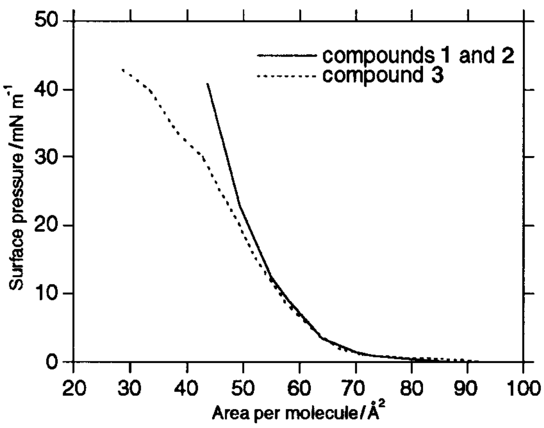

Fig. 2 Pressure *vs.* area isotherms of compounds **1** and **2** (full line) and **3** (dotted line).

Table 1 Area per molecule for compounds **1**–**3**

Compound	Area per molecule/Å^2
1	60±3
2	60±3
3	67±4

cobaltocene to a 0.2 mM deaerated benzonitrile solution of **1** resulted in the appearance of a NIR absorption peaked at 1027 nm typical of a fullerene-centred monoanion; while increasing the amount of cobaltocene resulted in novel absorption maxima at 762 and 892 nm appearing (Fig. 1). These data suggest the conversion of the fullerene-centred monoanion to the dianion.[47,48]

The solution was very stable, which contrasts with the results of the spectroelectrochemical experiment. Since the timescales are comparable for the two experiments, the reason for this is probably the different solution compositions in the two cases: in the electrochemical experiment a high concentration of supporting electrolyte (TBAH) is also present. A chemical reaction between doubly-reduced fullerene and TBAH might occur.

LB films

Fig. 2 shows the isotherms of derivatives **1**–**3**. The isotherms for compounds **1** and **2** were identical (within experimental error).

The areas per molecule for the different derivatives of C_{60}, obtained by extrapolating the steeply rising part to zero pressure, are shown in Table 1.

These results agree with previous studies on pure C_{60}, which found an area per molecule of approximately 60 Å^2.[38] These results suggest that the floating films of C_{60} derivatives are more than a single monolayer in thickness because the space-filling model of C_{60} molecule has a cross-sectional area of 80 Å^2. We attempted, unsuccessfully, to transfer the floating monolayers onto quartz, glass and Si substrates.

Table 2 Absorption maxima for compounds **1**–**3**

Compound	Positions of maxima/nm
1	257, 330
2	221, 261, 330
3	257

The isotherm for C_{60}:TA-**1**:4 was reminiscent of the isotherm for pure tricosanoic acid. The absorption spectrum of the LB films has a structure which is reminiscent of pure C_{60}. The positions of the maxima are summarized in Table 2. These were found to be dependent on the type of substitution, but independent of the number of monolayers. These maxima also correspond to those reported for pure C_{60} in LB film form (219, 266 and 340 nm).[38] However, clear structure of the absorption spectra was only observed for fulleropyrrolidinium ion **2**.

To study the reproducibility of the LB deposition, films with different thicknesses were built up on quartz substrates. Fig. 3 shows the dependence of the absorbance at 260 nm on the number of monolayers of TA–compound **1** and **2**. If we assume that absorption coefficients of all three derivatives of C_{60} are the same, then the change in absorbance indicates the difference in the number of fulleropyrrolidinium ions in the LB films. This number is larger for **2** than for **1** and **3**. The reproducibility of the LB films containing fulleropyrrolidinium

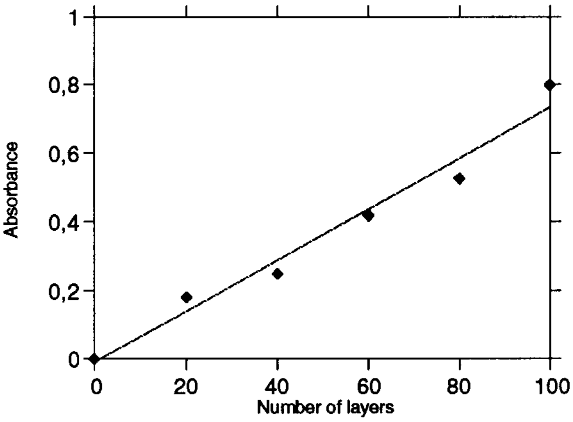

Fig. 3 Dependence of absorption at 260 nm on the number of deposed layers for compound **2** mixed with TA (1:4).

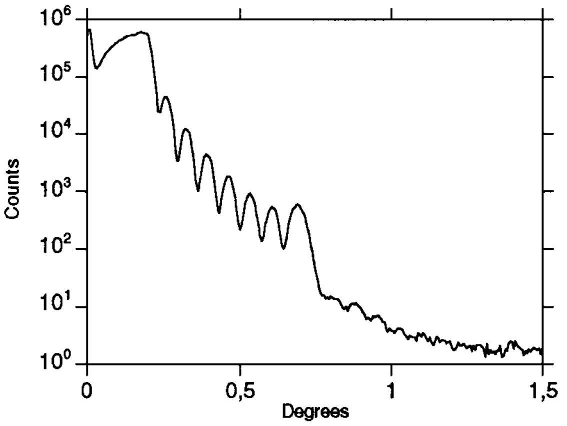

Fig. 4 X-ray diffraction, measured for compound **1** mixed with TA (1:4).

Table 3 The monolayer thickness in mixed fullerene–TA films determined by Bragg's law and Kiessig fringes

Compound (1:4 derivative of C_{60}:TA)	Number of dipping cycles	*d* spacing/nm Bragg's law	Total thickness, *t*/nm Kiessig fringes
1	10	5.7±0.1	58±4
2	10	6.5±0.1	70±3
2	20	6.4±0.1	147±15
3	10	5.5±0.2	57±3

ion **2** was also much better than that of compounds **1** and **3**. The reason for this different behavior is not clear.

Fig. 4 shows an X-ray diffraction pattern. X-ray diffraction measurements were performed on a 20 monolayer structure of C_{60} derivative **1** and TA for both the specularly reflected X-ray beam and the off-specularity one for all three fulleropyrrolidinium ions.

For LB films containing compound **2** the X-ray diffraction was carried out on both 20 and 40 monolayer structures. One Bragg peak was observed for all films. A *d*-spacing (*i.e.* the thickness for one bilayer) was calculated using the condition for maxima according to Bragg's law,

$$n\lambda = 2d\sin\theta \qquad (1)$$

where λ is the X-ray wavelength, θ is the angle of incidence, d is the interplanar spacing and the integer n is known as the order of the reflection. Table 3 shows the data for all compounds.

The film thicknesses were also determined using Kiessig fringes at specular scan

$$t = n\lambda/2\theta \qquad (2)$$

where t is the total thickness, θ is the angle distance between nearest fringe maxima. These results are also reported in Table 3.

The thicknesses of all the LB films determined from specular and off-specular scans agree reasonably well with each other. X-ray diffraction studies show that all the LB films have structures which are characteristic of a crystalline material (Table 3). There is good agreement between the results obtained from Bragg's law and those from Kiessig fringes for samples. However, the structure of LB films containing derivative **3** is less ordered than the others.

To determine the orientation of the chains with respect to the substrate, the length of the TA molecule (32 Å) and the *d*-spacing should be compared. If *d* is less than 64 Å, then the molecule chains deviate slightly from the perpendicular to the surface of the bilayer. The tilt angle could be calculated by the formula,

$$\cos\alpha = d/(2l) \qquad (3)$$

where α is the tilt angle and l is the length of the molecule.

The pure TA LB film has *d*-spacing 55 Å and the molecule chain deviated slightly from the perpendicular to the substrate normal (the tilt angle is 28°).[49] Table 3 shows that *d*-spacings of LB films containing **3** coincide well with the *d*-spacing of pure TA LB film. However *d*-spacings of LB films containing **1** and **2** are different from that of pure TA LB film, particularly for **2**. This may mean that molecules of the C_{60} derivative either lie on the surface of the fatty acid or compress the fatty acid molecules. This results in a *d*-spacing for the LB films containing compounds **1**–**2** which is higher than that of pure TA. If we assume that the C_{60} derivative is located inside the LB films, the tilt angle of the fatty acid molecules would be less than 28°. For compound **2** the angle is equal to 0°. The C_{60} derivative **3** has a *d*-spacing for LB films which coincides with that of pure TA because there are only a few ions inside the LB films.

Conclusion

The stability of mono-reduced, zwitterionic, and doubly-reduced anionic **1**–**3**, produced either electrochemically or chemically, has been monitored by absorption spectroscopy. Mixed LB films containing new fulleropyrrolidinium ions were built up. It was found that all materials formed stable floating multilayer films on a water surface. The absorbance and X-ray measurements show that only two of the new fulleropyrrolidine derivatives form good quality mixed films.

Acknowledgements

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