Fullerates: interaction of divalent metal ions with Langmuir monolayers and multilayers of mono-substituted C₆₀–malonic acid

Harish M. Patel,[a] Jon M. Didymus,[a] Kim K. W. Wong,[a] Andreas Hirsch,[b] Andreas Skiebe,[b] Iris Lamparth[b] and Stephen Mann*[a]

[a] *School of Chemistry, University of Bath, Bath, UK BA2 7AY*
[b] *Institut für Organische Chemie, Universität Erlangen, Henkestrasse 42, 91054, Erlangen, Germany*

Stable Langmuir monolayers of $C_{60}[C(CO_2H)_2]$ are formed on pure water and on solutions containing Ca^{2+} or Cd^{2+} ions; cation–headgroup interactions result in expanded monolayers and the transfer of Ca^{2+}–fullerene multilayers onto quartz substrates.

There is continuing interest in the chemistry of chemically modified C_{60}. Previous studies have shown that floating monolayers of unmodified C_{60} molecules can be produced at the air/water interface[1] but that the highly hydrophobic nature of the molecules often results in multilayer films.[2,3] Several chemically modified C_{60} derivatives have been described recently and some of these materials, such as an *N*-acetylfulleropyrrolidine derivative,[4] an aliphatic carboxylic acid adduct[5] and a fullerene cryptate,[6] have sufficient amphiphilic character to give stable monolayer films at the air/water interface.

In this paper we describe the surface active and metal-ion binding properties of a recently synthesized malonic acid derivative of C_{60}, $C_{60}[C(CO_2H)_2]$ **1**.[7] Compound **1** is a stereochemically specific monoadduct in which the dicarboxylic acid group is directly coupled to the C_{60} cage at a single equatorial site. The bifunctionality of the polar side group and the associated C_{2v} symmetry of the molecule suggest that **1** might be sufficiently amphiphilic to undergo self assembly when spread at the air/water interface. Furthermore, the malonic acid substituent offers potential for metal-ion binding and the formation of salt-like 'fullerates'. Together, these properties suggest that cations could be incorporated into organized multilayer assemblies of fullerenes derivatized with appropriate pendent groups.

The fullerene malonic acid **1** was prepared as described in the literature,[7] and dissolved in tetrahydrofuran to a concentration of 9.73×10^{-5} mol dm^{-3}. Langmuir monolayers of **1** were formed on pure water or aqueous solutions of $CaCl_2$ or $CdCl_2$, buffered to pH 8 by sodium hydroxide solution (2.0 mol dm^{-3}).† Fig. 1 shows isotherms for $C_{60}[C(CO_2H)_2]$ spread on pure water at 290 K. The method of spreading of the thf solution of **1** was critical to the formation of high quality monolayers. In initial experiments, two or three 50 µl drops of the solution were added in quick succession to the air/water interface. Under these conditions, isotherms were recorded but the limiting area per molecule varied between 5 and 25 $Å^2$ [Fig. 1(*a*)]. These values are clearly too small compared with the predicted value of *ca.* 86 $Å^2$ for hexagonally close-packed fullerene molecules with intermolecular distances of *ca.* 10 Å. Similar low limiting areas have been reported for underivatized C_{60}[2,3] and derivatized fullerenes,[6] and indicate multilayer formation. However, if a single drop of the thf solution was allowed to evaporate for at least 5 min prior to addition of the next drop, then stable monolayers of **1** could be routinely achieved [Fig. 1(*b*)]. The isotherms showed an initial increase in surface pressure at 200 $Å^2$, a well established liquid phase, and a distinct phase transition to the fully compressed solid domain. The limiting area per molecule was extrapolated to be 100 ± 4 $Å^2$. Assuming a close-packed hexagonal lattice, this value corresponds to an inter-headgroup spacing of 10.75 Å. Further

compression resulted in a collapse pressure of 40 mN m^{-1} followed by multilayer formation [Fig. 1(*b*)].
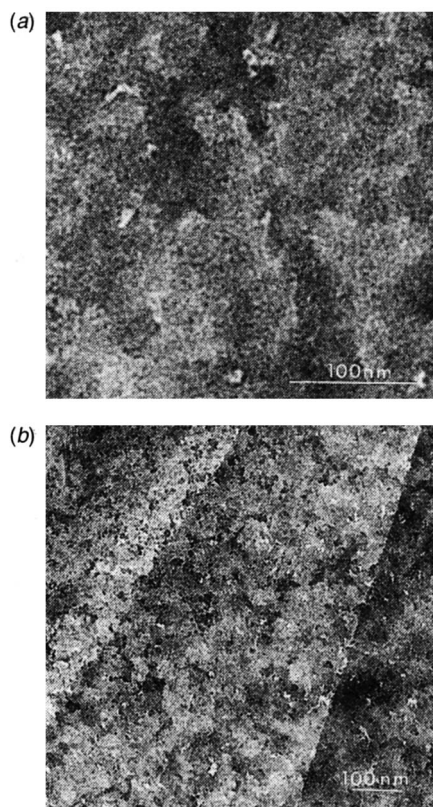
The UV–VIS spectrum of a multilayer film of **1** consisting of five monolayer transfers to a hydrophobic quartz wafer showed the characteristic bands at 220, 272, 330, 370 and 450 nm for the C_{60} moiety. TEM micrographs of either monolayers or multilayers showed inhomogeneous films possibly due to breakage during transfer to the electron microscope grids (Fig. 2).

Surface pressure–area isotherms for $C_{60}[C(CO_2H)_2]$ spread on aqueous subphases containing divalent cations showed well formed expanded monolayers (Fig. 3). At concentrations of 1 mmol dm^{-3} Ca^{2+} or Cd^{2+}, the onset of the liquid phase occurred at significantly higher areas (*ca.* 300 $Å^2$) than on pure water, suggesting that association of the metal cations with the carboxylate headgroups of **1** is established even in the apparently uncompressed state. Compression resulted in well defined liquid phases but only monolayers spread on Ca^{2+} solutions showed a distinct transition to the solid phase [Fig. 3(*a*)]. Areas per molecule of 160 and 230 $Å^2$ were determined for Ca^{2+} and Cd^{2+} subphases, respectively. In both cases, further compression resulted in a distinct phase change at a surface pressure of 35 mN m^{-1}, followed by an increase in pressure with a limiting area per molecule of 100 $Å^2$, similar to that for pure water.
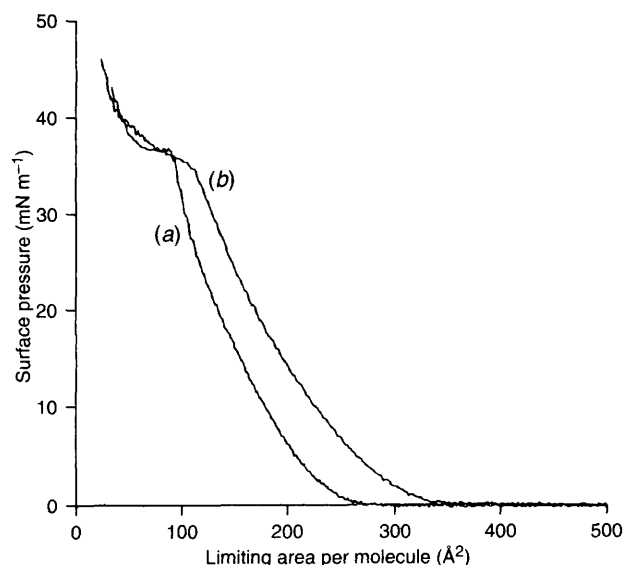
These results suggest that the divalent cations intercalate between the monolayer headgroups of $C_{60}[C(CO_2H)_2]$ to give expanded films that can be compressed to solid phases, but which on further compression revert to close-packed mono-
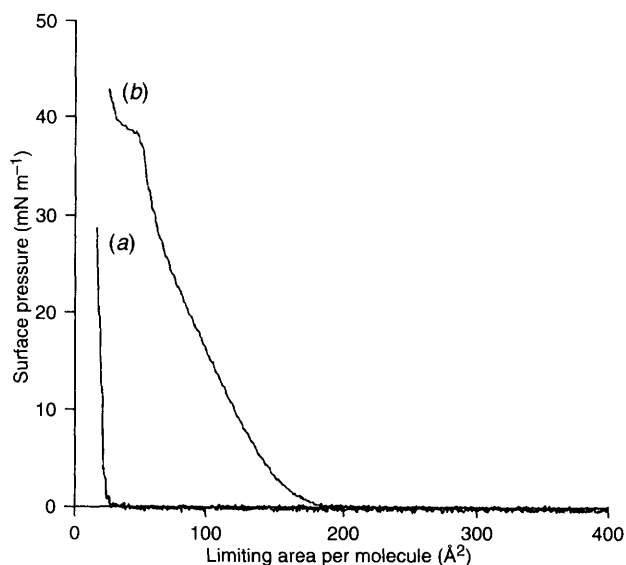
Fig. 1 Surface pressure–area isotherms for $C_{60}[C(CO_2H)_2]$ spread on pure water at 290 K, (*a*) from THF solution applied as a series of drops in quick succession, and (*b*) from THF as a series of single droplets but with solvent evaporation prior to addition of the next drop
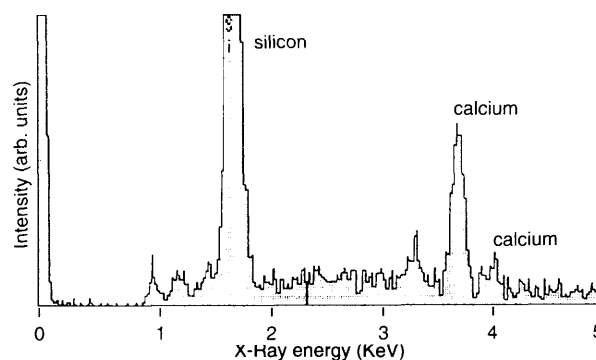
Fig. 2 TEM micrographs of (a) monolayer and (b) multilayer films of $C_{60}[C(CO_2H)_2]$. Scale bars = 100 nm.

Fig. 4 EDXA spectrum of a multilayer thin film of $C_{60}[C(CO_2H)_2]$ transfered from a 1 mmol dm^{-3} $CaCl_2$ subphase onto an Si wafer, showing the presence of intercalated calcium

1 on pure water is commensurate with the intercalation of Ca^{2+} ions between carboxylates of adjacent malonate headgroups such that a metal-ion bridged network is established at the monolayer/solution interface.

Multilayers consisting of up to ten monolayers were formed by transfer on to hydrophobic quartz or silicon substrates of solid-phase monolayers of 1 spread on Ca^{2+} or Cd^{2+} subphases. TEM micrographs showed inhomogeneous films that contained calcium by EDXA (Fig. 4) but not cadmium. The results suggest that calcium can be readily intercalated with close-packed molecules of 1 and co-assembled in organized arrays. Further experiments are underway to investigate the structure and properties of these metal fullerate thin films.

Fig. 3 Surface pressure–area isotherms at 290 K for $C_{60}[C(CO_2H)_2]$ spread on (a) 1 mmol dm^{-3} $CaCl_2$ subphase (pH 5.3) and (b) 1 mmol dm^{-3} $CdCl_2$ subphase (pH 6.3)

Footnote

† Isotherm measurements were made using a NIMA Technology System 2001 trough with computer interface control. Purified water (0.8 dm^3) was employed as the subphase, and surface-cleaned twice with suction via a Pasteur pipette. 200 µl of a 0.08 mg cm^{-3} solution of 1 in thf was spread at the air/water interface and the solvent allowed to evaporate for at least 15 min prior to compression. Surface pressure versus area per molecule isotherms were measured at a compression speed of 50 cm^2 min^{-1}. In separate experiments, 1–5 mmol dm^{-3} aqueous solutions of $CdCl_2$ and $CaCl_2$ were employed as the subphase. Control isotherms were carried out on each subphase, in the absence of a spread monolayer. Checks were also made for any surface activity due to contamination in the thf solvent.

Silicon wafers, rendered hydrophobic by treatment with hexa-methyldisilazane, were used for UV–VIS spectroscopy measurements of the LB multilayer films. The prepared films were transferred using a horizontal lifting method onto hydrophobic Si or quartz surfaces, or formvar-coated copper electron microscope grids, and studied by transmission electron microscopy (TEM) and energy dispersive X-ray analysis (EDXA).

layers depleted of the metal ions. In this regard, EDXA showed the presence of Ca in an expanded monolayer transferred onto a formvar substrate (data not shown), but no Cd was detected in the corresponding monolayer formed on a $CdCl_2$ solution. The data suggest that there is a stronger interaction between Ca^{2+} and the ionised carboxylate headgroups of the C_{60} malonic acid derivative than for Cd^{2+}, which is presumably lost from the expanded monolayer on transfer. The limiting area per molecule of 160 $Å^2$ for the Ca^{2+}-bound monolayer corresponds to an inter-headgroup spacing of 13.5 Å, assuming a hexagonal lattice. This increase of 2.75 Å compared with the monolayer of

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