Fullerates: interaction of divalent metal ions with Langmuir monolayers and multilayers of mono-substituted C_{60}–malonic acid

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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-

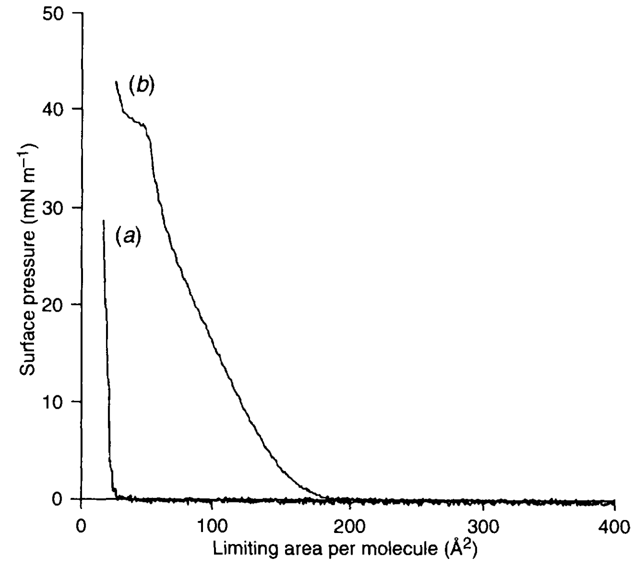

Fig. 1 Surface pressure–area isotherms for $C_{60}[C(CO_2H)_2]$ spread on pure water at 290 K, (*a*) from THF solution applied as a series of drops in quick succession, and (*b*) from THF as a series of single droplets but with solvent evaporation prior to addition of the next drop

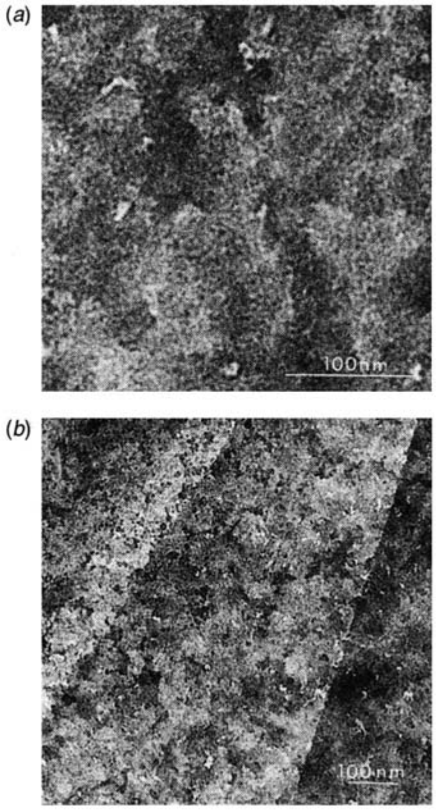

Fig. 2 TEM micrographs of (*a*) monolayer and (*b*) multilayer films of $C_{60}[C(CO_2H)_2]$. Scale bars = 100 nm.

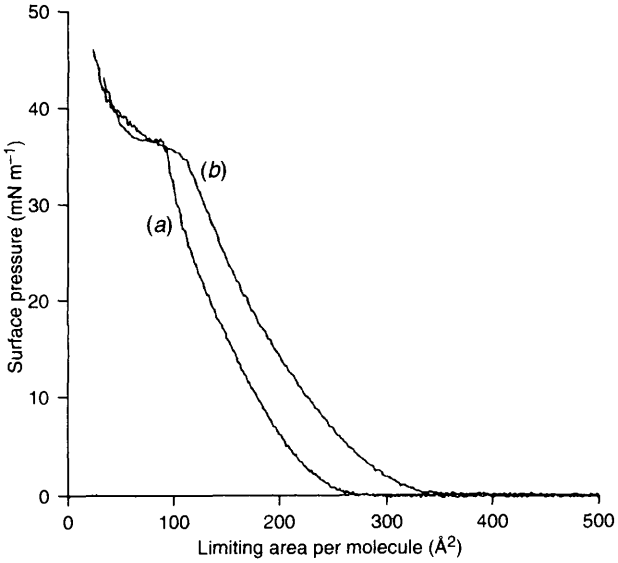

Fig. 3 Surface pressure–area isotherms at 290 K for $C_{60}[C(CO_2H)_2]$ spread on (*a*) 1 mmol dm^{-3} $CaCl_2$ subphase (pH 5.3) and (*b*) 1 mmol dm^{-3} $CdCl_2$ subphase (pH 6.3)

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 **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.

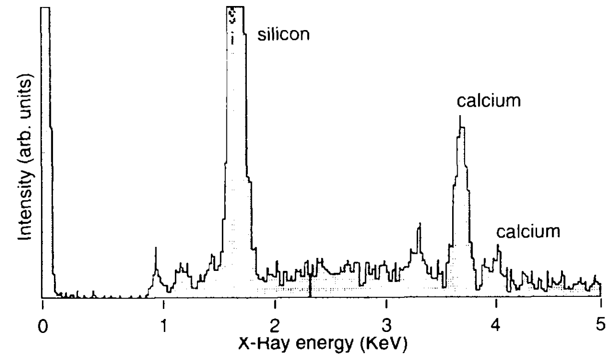

Fig. 4 EDXA spectrum of a multilayer thin film of $C_{60}[C(CO_2H)_2]$ transfered from a 1 mmol dm^{-3} $CaCl_2$ subphase onto an Si wafer, showing the presence of intercalated calcium

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.

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 hexamethyldisilazane, 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).

References

1 Y. S. Obeng and A. Bard, *J. Am. Chem. Soc.*, 1991, **113**, 6279.
2 T. Nakamura, H. Tachibana, M. Yumura, M. Matsumoto, R. Azumi, M. Tanaka and Y. Kawabata, *Langmuir*, 1992, **8**, 4.
3 C. Long, Y. Xu, F. Guo, Y. Li, D. Xu, Y. Xao and D. Zhu, *Solid State Commun.*, 1992, **82**, 381.
4 M. Maggini, A. Karlsson, L. Pasimeni, G. Scorrano, G. Prato and L. Valli, *Tetrahedron Lett.*, 1994, **35**, 18, 2985.
5 M. Matsumoto, H. Tachibana, R. Azumi, M. Tanaka, T. Nakamura, G. Yunome, M. Abe, S. Yamago and E. Nakamura, *Langmuir*, 1995, **11**, 660.
6 U. Jonas, F. Cardullo, P. Belik, F. Diederich, A. Gügel, E. Harth, A. Herrmann, L. Isaacs, K. Müllen, H. Ringsdorf, C. Thilgen, P. Uhlmann, A. Vasella, C. A. Waldraff and M. Walter, *Chem. Eur. J.*, 1995, **1**, 243.
7 I. Lamparth and A. Hirsch, *J. Chem. Soc., Chem. Commun.*, 1994, 1727.

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