

## Electrochemical Studies on Langmuir–Blodgett Films of 1-*tert*-Butyl-1,9-dihydrofullerene-60

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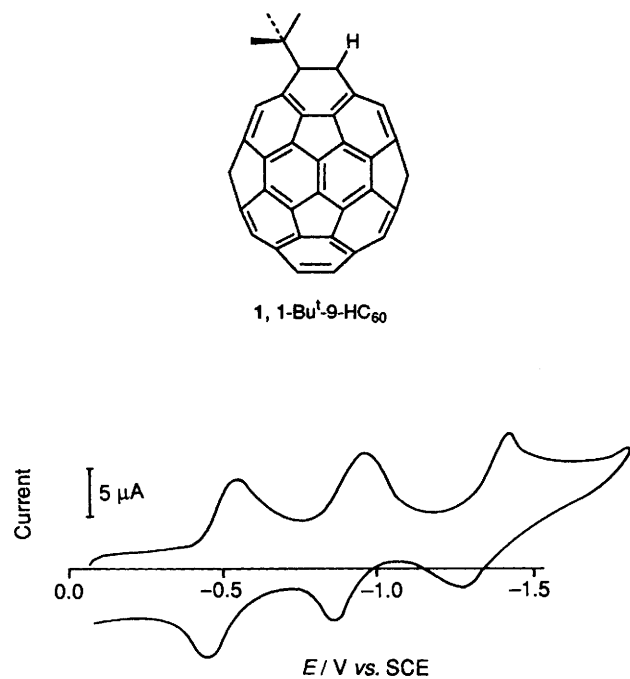
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Langmuir–Blodgett (LB) films of 1-*tert*-butyl-1,9-dihydrofullerene-60 are shown to undergo well defined multistage electrochemical reductions to yield the trianion species, with the first two redox waves stable to recycling; these data contrast with those for LB films of the parent system C<sub>60</sub>.

Studies on fullerenes C<sub>x</sub> ( $x = 60$  and  $70$ ) are currently at the forefront of research among a broad cross-section of the scientific community.<sup>1</sup> The majority of work has concerned C<sub>60</sub>, although higher homologues, notably C<sub>70</sub>, are receiving increased attention. The rich redox chemistry displayed by C<sub>60</sub> underscores many of the remarkable chemical and physical properties of this material, *e.g.* the formation of superconductors with alkali metals,<sup>2,3</sup> and ferromagnetic<sup>4,5</sup> and paramagnetic salts<sup>6</sup> with strong organic and organometallic electron donors. Recent reports from several laboratories<sup>7–12</sup> have demonstrated that C<sub>60</sub> can be reduced electrochemically, in a stepwise manner, leading to the penta-anion and the

hexa-anion species, the reduced species obtained and their relative stability being dependent upon the temperature, the solvent and the supporting electrolyte used.<sup>12</sup>

Thin films of fullerenes are of interest because they exhibit superconductivity upon reduction,<sup>2,3</sup> display interesting photoelectrochemical behaviour<sup>10</sup> and possess electrochemical characteristics that are different from those of the dissolved species.<sup>7,13</sup> For example, cyclic voltammetry studies of multilayer films of C<sub>60</sub> formed by dip coating show a large splitting between the reduction and oxidation waves for the first and second electron-transfer processes, which is considered indicative of considerable reorganisation of the film structure.<sup>10,14</sup>

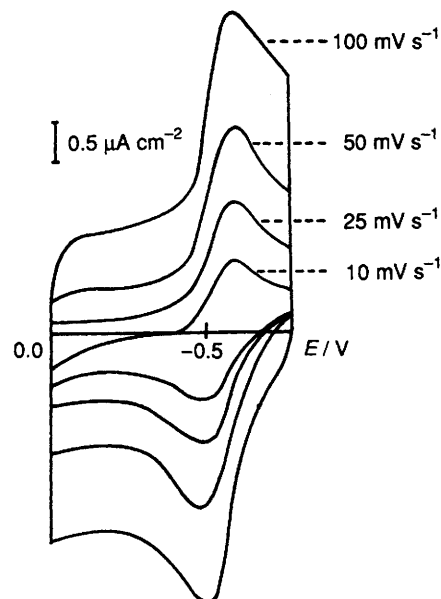


**Fig. 1** Cyclic voltammetry response of a monolayer film of 1-Bu<sup>t</sup>-9-HC<sub>60</sub> 1 on hydrophobic ITO glass, 0.1 mol l<sup>-1</sup> TBAPF<sub>6</sub>-acetonitrile solution at a scan rate of 10 mV s<sup>-1</sup>, vs. standard calomel electrode (SCE)

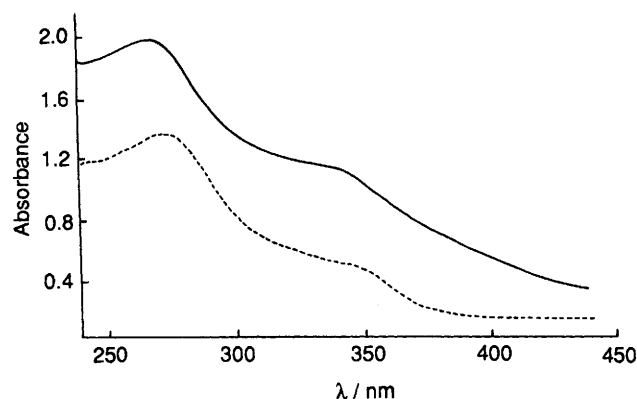
Several groups,<sup>15–20</sup> including ourselves,<sup>17,18</sup> have reported the formation of condensed layers of C<sub>60</sub> at the air–water interface. However, transfer to solid substrates using the Langmuir–Blodgett (LB) method generally results in poor-quality films exhibiting deposition ratios much less than unity. Improved transfer may be achieved by mixing C<sub>60</sub> with a long-chain fatty acid.

Recently, we have developed an alternative strategy to produce high quality multilayer films. The substituted fullerene, 1-*tert*-butyl-1,9-dihydrofullerene-60 (1-Bu<sup>t</sup>-9-HC<sub>60</sub>) 1 forms LB multilayers, without the need of added fatty acid, that are considerably better quality than those of unsubstituted fullerenes.<sup>21</sup> This provides an unprecedented opportunity to study the electrochemistry of LB films of a pure fullerene system. The results of this study are reported herein; the dramatically improved quality of the electrochemical data for 1-Bu<sup>t</sup>-9-HC<sub>60</sub>, relative to those of LB layers of C<sub>60</sub>, is a consequence of the more uniform monolayers obtained at the electrode with the substituted system.

LB films of compound 1 were built up on solid substrates by Y-type deposition, using methods reported previously.<sup>21</sup> Hydrophobic indium tin oxide (ITO) electrodes, using tetrabutylammonium hexafluorophosphate (TBA<sup>+</sup> PF<sub>6</sub><sup>-</sup>) as the supporting electrolyte in acetonitrile, were found to give the best quality electrochemical data: values of  $E_{1/2}$  for different TBA<sup>+</sup> X<sup>-</sup> salts (X<sup>-</sup> = PF<sub>6</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, BF<sub>4</sub><sup>-</sup>) vary by <50 mV. The optimum transfer pressure was found to be 25 mN m<sup>-1</sup>, and the electrochemical data varied only slightly with the conditions of film deposition, although at transfer pressures of <20 mN m<sup>-1</sup> the redox peaks were less well resolved, which could be due to the smaller amount of material transferred at lower pressures. This is in contrast to the marked sensitivity of the redox behaviour of C<sub>60</sub> to varying deposition conditions, reported by Bard *et al.*<sup>20</sup> The cyclic voltammogram of a monolayer LB film of compound 1 is shown in Fig. 1; three successive electron transfers are observed ( $E_{1/2}$  = -0.55, -0.94 and -1.37 V vs. SCE). This compares favourably with the data reported by Fagan *et al.* while our studies were in progress, for dissolved species of 1-Bu<sup>t</sup>-9-HC<sub>60</sub>.<sup>22</sup>



**Fig. 2** CV response of a monolayer film of compound 1 in TBAPF<sub>6</sub>-acetonitrile solution at different scan rates



**Fig. 3** UV-VIS spectrum of compound 1 in dichloromethane solution (TBAPF<sub>6</sub>) before (—) and 2 min after (---) controlled potential electrolysis at -0.7 V

The potential separation between the cathodic and anodic peaks for the first and second waves of the LB film samples of 1-Bu<sup>t</sup>-9-HC<sub>60</sub> is 65–70 mV, which is in good agreement with the characteristic value of 59 mV for a reversible one-electron transfer. The corresponding value for the third wave is significantly higher (120 mV) suggesting that reorganisation of the LB film structure takes place during the formation of the trianion species. Controlled potential coulometry confirmed that the first and second reductions were fully reversible one-electron transfers. Furthermore, it was possible to reduce and reoxidise the first two waves several times without loss of reversibility (as judged by constant charge transferred and the well defined cyclic voltammograms). The shape of the CV response for a monolayer film did not obey the theoretical 'surface wave' response even at a scan rate of 1.0 mV s<sup>-1</sup>. The shape of the wave (Fig. 2) is typical of a reversible diffusion controlled wave, with  $I_{pa}/I_{pc}$  = 1.0, and  $I_p$  proportional to the square root of the scan rate. This contrasts with the usual linear dependence on scan rate observed for solution-cast films of C<sub>60</sub>. A comparison of the CV response for different numbers of monolayers of 1-Bu<sup>t</sup>-9-HC<sub>60</sub> demonstrates that the CV shape becomes severely distorted when >3 layers have been deposited. These results show that ion transport into the films is effectively hindered as the film thickness increases.

We have performed spectroelectrochemistry on dichloromethane solutions of compound **1**. Fig. 3 displays the time-dependent spectra obtained between 240 and 450 nm before (full line) and after (dashed line) electrolysis of the neutral species to the monoanion radical. The prominent UV-VIS bands at 270 and 340 nm are replaced by bands of lower intensity at 275 and 350 nm upon electrolysis at  $-0.7$  V (vs. SCE). The original spectrum of **1** could be regenerated by reoxidation at  $0.0$  V. These data are entirely consistent with the reversible formation of  $1\text{-Bu}^t\text{-9-HC}_{60}^{\cdot-}$  in solution.

In conclusion, we have demonstrated that  $1\text{-Bu}^t\text{-9-HC}_{60}$  **1** produces high-quality Langmuir-Blodgett films which undergo multistage electrochemical reduction to the trianion species. The presence of the substituent group significantly improves the quality of the LB films, compared with the parent system  $\text{C}_{60}$ , and this gives rise to well defined, reversible redox behaviour.

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