

# Molecular rectification using a gold/(LB film)/gold structure

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Langmuir–Blodgett (LB) films of 5-(4-dibutylamino-benzylidene)-2-octadecyl-5,6,7,8-tetrahydroisoquinolinium octadecylsulfate, co-deposited in a 1:1 ratio with octadecanoic acid and sandwiched between gold electrodes, have shown asymmetric current–voltage characteristics with an optimum rectification ratio of 70 at  $\pm 1$  V; the use of noble metal electrodes provides unambiguous evidence of molecular rectification.

In their theoretical paper, Aviram and Ratner<sup>1</sup> suggested that donor–( $\sigma$ -bridge)–acceptor molecules are organic counterparts of the pn junction and, if suitably aligned, would rectify because  $D^+ - \sigma - A^-$  is relatively accessible whereas  $D^- - \sigma - A^+$  is not. However, although published as long ago as 1974, experimental verification of this concept has proven difficult.<sup>2–4</sup> The first report, by Sambles and co-workers<sup>2</sup> at Exeter University, has been corroborated by Metzger<sup>3</sup> at the University of Alabama with both groups using a zwitterionic dye: (Z)- $\beta$ -(N-hexadecyl-4-quinolinium)- $\alpha$ -cyano-4-styryldicyanomethanide. The dye was synthesised as part of Cranfield's nonlinear optics programme<sup>5</sup> and has a D– $\pi$ –A structure in which the donor and acceptor are rotated out-of-plane and resonance between the charge-transfer states is suppressed. It also forms non-centrosymmetric LB films and, when sandwiched as a monolayer between aluminium electrodes,<sup>3</sup> exhibits a current rectification ratio of *ca.* 30 at  $\pm 1.5$  V, the voltage corresponding to a field of 600 MV m<sup>-1</sup> across the 2.5 nm thick molecular layer.

Sambles *et al.*<sup>4</sup> have reported an improved rectification ratio of 130 at  $\pm 2.5$  V (*ca.* 200 MV m<sup>-1</sup>) for an Ag/(D– $\sigma$ –A)/Mg device comprising five LB layers of 3,5-dinitrobenzyl-7-(1-oxohexylamino)-pyren-2-ylcarbamate. However, as for the zwitterion,<sup>2,3</sup> the upper electrode was restricted to a metal with a low sublimation temperature and, consequently, to one which readily oxidises in air. Thus, although the current–voltage characteristics are probably a consequence of the molecular film, rather than an oxide layer, a risk of Schottky barrier formation makes any assignment of the rectification ambiguous. Nonetheless, rectifying molecules have prompted considerable theoretical interest<sup>6–8</sup> and renewed appeal for molecular electronic devices requires the problem of electrical contact to be addressed. Noble metals will short with the lower electrode when evaporated onto thin organic films but, by using thicker LB assemblies, Fischer *et al.*<sup>9</sup> have observed asymmetric current–voltage characteristics from the *heteromolecular* interface between a metallophthalocyanine and perylene-3,4,9,10-tetracarboxyldiimide sandwiched between gold electrodes. This is not rectification in the Aviram and Ratner<sup>1</sup> sense because the properties relate to the interface and not to the individual components. However, it provides supporting evidence for the materials outlined above.<sup>2–4</sup>

In this communication, we report rectification by an Au/(LB film)/Au device where the active organic layer is 5-(4-

dibutylaminobenzylidene)-2-octadecyl-5,6,7,8-tetrahydroisoquinolinium octadecylsulfate co-deposited in a 1:1 ratio with octadecanoic acid (Fig. 1). The iodide salt of the dye was synthesised using a procedure adapted from that previously described for the dimethylamino analogue<sup>10</sup> and subsequently, the octadecylsulfate salt was obtained by metathesis at the air–water interface. Dilute solutions of sodium octadecylsulfate in methanol and the iodide salt and octadecanoic acid in chloroform were spread in a 1:1:1 mole ratio onto the pure water subphase of a Nima Technology LB trough (model 622), left for 5 min and then compressed at 0.5 cm<sup>2</sup> s<sup>-1</sup> (*ca.* 0.1% s<sup>-1</sup> of the compartment area). The water-soluble ions, Na<sup>+</sup> and I<sup>-</sup>, dissolve into the aqueous subphase and are not incorporated in the deposited LB film.

The pressure–area ( $\pi$ –*A*) isotherm exhibits a low-pressure expanded region, separated by a broad plateau from a steep high-pressure condensed phase (Fig. 2). A transition at *ca.* 35 mN m<sup>-1</sup> and 0.6 nm<sup>2</sup> molecule<sup>-1</sup> indicates the limiting conditions for a side-by-side arrangement of the three amphiphilic species. The area then reduces to *ca.* 0.4 nm<sup>2</sup> just prior to collapse and this suggests that the octadecanoic acid and octadecylsulfate moieties realign and pack one on top of the other in the high-pressure regime. In this study, the floating monolayer was deposited at the lower surface pressure of 30 mN m<sup>-1</sup> and a deposition rate of 80  $\mu$ m s<sup>-1</sup>, the films being transferred on the upstroke to maintain alignment. A Sauerbrey analysis<sup>11</sup> of the frequency change of an AT-cut 10 MHz quartz crystal, upon deposition of an LB monolayer, provided an area of  $0.62 \pm 0.03$  nm<sup>2</sup> molecule<sup>-1</sup> in contact with the substrate. Furthermore, analysis of the surface plasmon resonance at 532 nm gave a thickness of 3.15 nm layer<sup>-1</sup> and dielectric permittivities of  $\epsilon_r = 2.50$  and  $\epsilon_i = 0.01$ , the film being almost transparent at this wavelength. The dimensions conform to a density of 1.0 Mg m<sup>-3</sup>.

Our previous studies<sup>10</sup> have revealed that non-centrosymmetric structures of the dye may be obtained by repeated deposition on the upstroke, the LB multilayer having a second-order nonlinear optical susceptibility of  $\chi_{zzz}^{(2)} = 76$  pm V<sup>-1</sup> at 1.064  $\mu$ m and a chromophore tilt angle of  $\phi = 33^\circ$ , relative to the substrate normal. This uncommon Z-type arrangement arises from the fact that both ends of the molecule are

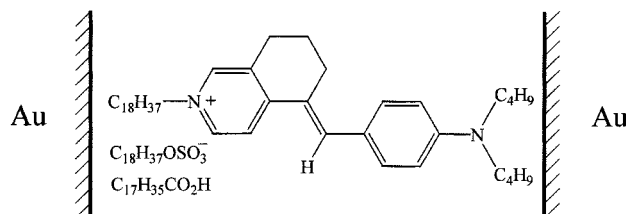
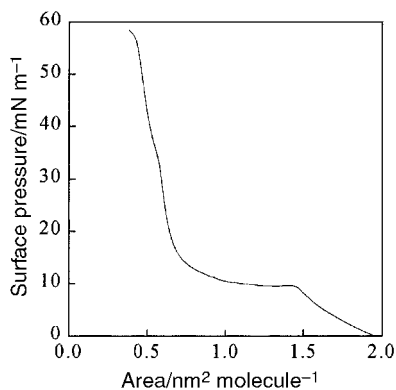


Fig. 1 Schematic representation of the Au/(LB film)/Au device showing the structures of the rectifying molecule and octadecanoic acid.



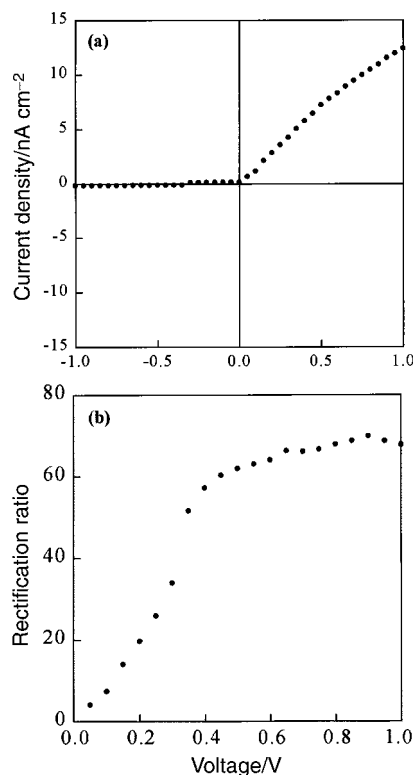
**Fig. 2** Surface pressure *versus* area isotherm of 5-(4-dibutylaminobenzylidene)-2-octadecyl-5,6,7,8-tetrahydroisoquinolinium octadecylsulfate and octadecanoic acid in a 1:1 mole ratio. The area corresponds to the combined molecular unit.

hydrophobic. Therefore, unlike conventional amphiphilic dyes which pack with compatible end groups at each interface, *i.e.* head-to-head and tail-to-tail, the molecule shown in Fig. 1 retains its orientation because the LB surface is invariably hydrophobic.<sup>10,12</sup> In this work, the non-centrosymmetric deposition provides an opportunity to investigate the nonlinear electrical characteristics of thick LB films and to simultaneously monitor the nonlinear optical behaviour to determine the degree of alignment.

The film was deposited onto a rectangular glass substrate, coated at one end with a 10 nm thick gold electrode, the number of LB layers being 110. The second-harmonic intensity obtained from the region without a gold overlay increased quadratically with the number of layers, the susceptibility being as previously reported<sup>10</sup> and thus, confirming optimum non-centrosymmetric alignment. Gold electrodes, ranging in size from  $20 \times 5$  mm strips to 1 mm diameter pads, were thermally evaporated onto the LB film, to a thickness of 10 nm, using an Edwards 306 coating unit. This was performed at  $10^{-4}$  Pa with a deposition rate of  $0.1 \text{ nm s}^{-1}$  and a distance of 0.2 m between source and substrate. When corrected for the semi-transparent electrodes, the absorbance of the LB film indicated a loss of about ten LB layers during the evaporation process, the active organic component being approximately 100 layers or  $0.3 \mu\text{m}$  thick.

Electrical characterisation of the Au/(LB film)/Au structures was performed in air with a scan rate of  $30 \text{ mV s}^{-1}$ . They showed a range of behaviour with the inevitable heating during the evaporation of the top electrodes causing some films to exhibit a reduced second-harmonic intensity and ohmic characteristics. Consistent with this, studies on films without electrode assemblies revealed a rapid deterioration of the second-order behaviour when heated to  $80^\circ\text{C}$ , this being indicative of molecular reorientation with centric alignment either within or between layers. However, the majority of films showed some degree of rectification and, when optimally aligned, a current rectification ratio of *ca.* 70 at  $\pm 1$  V was achieved (Fig. 3). The voltage corresponds to an electric field of *ca.*  $3 \text{ MV m}^{-1}$  but its calculation is only valid in the absence of filamentary gold protruding into the fragile organic layer. The localised electric field which gives rise to the observed current-voltage characteristics is probably higher.

Compared with the previously reported studies,<sup>2,3</sup> there is little hysteresis but this may be expected when dealing with a multilayer structure rather than a monolayer. The individual current-voltage scans showed minimal variation when cycled in the negative or positive directions but, throughout a period of a few days, the current density decreased by *ca.* 30%. Furthermore, repetitive cycling resulted in the onset of ohmic characteristics for the Au/(LB film)/Au device, this being



**Fig. 3** Electrical characteristics of the Au/(LB multilayer)/Au device: (a) asymmetric current-voltage characteristics; (b) voltage dependence of the current rectification ratio. The LB film is nominally 100 layers thick but, as with all related structures, the magnitude of the current density is probably affected by filamentary gold. The current, when normalised for the number of layers, is similar to that obtained for the zwitterion.<sup>2,3</sup>

attributed to a random field-induced reorientation of the molecular dipoles.

The results compare favourably with the data of Sambles<sup>2</sup> using asymmetric electrode arrangements, *e.g.* Ag/(LB film)/Mg, and with the rectifying behaviour reported by Metzger<sup>3</sup> for LB monolayers sandwiched between oxidisable aluminium electrodes. The current density, normalised for the number of LB layers, is similar to values reported for structures of the rectifying zwitterion<sup>2,3</sup> and, for both dyes, is limited by the insulating alkyl barriers. However, there are significant differences. The shape of the current-voltage curve is unusual when compared with the previously reported power law dependence,  $I \propto aV + bV^3$ , of the zwitterion<sup>2</sup> and the rectification ratio appears to saturate at *ca.* 0.4 V, albeit with a moderately high value of 70. This behaviour may be explained by field-induced realignment and, relevant to this, Han *et al.*<sup>13</sup> have reported a significant enhancement of the second-harmonic intensity from LB films of a hemicyanine derivative when poled at  $1.3 \text{ MV m}^{-1}$  (*cf.*  $E = 3 \text{ MV m}^{-1}$  at 1 V in this work). Such realignment may relate to the molecular orientation or, alternatively, to a relative shift of the cationic dye with respect to its counterion. The sulfate group of the latter is likely to be adjacent to the positively charged isoquinolinium acceptor in the unpoled films (Fig. 1) and any field-induced shift towards the dibutylamino donor could result in a relocation of charge within the D- $\pi$ -A chromophore.

In conclusion, asymmetric current-voltage characteristics have been obtained for aligned molecular layers of a D- $\pi$ -A dye sandwiched between symmetrical gold electrodes. It is the first example where the behaviour may be unambiguously assigned to molecular rectification rather than to a possibility of the properties being induced by electrode asymmetry or a metal oxide layer. In this work, as in previous studies,<sup>2,3</sup> the through-plane conductivity is limited by the hydrophobic

octadecyl groups which separate the D- $\pi$ -A layers. However, an altered molecular structure in which the hydrophobic group is conjugated, rather than aliphatic, and forms part of an extended  $\pi$ -electron bridge may eliminate these insulating barriers. Preliminary examples have been synthesised and second-harmonic generation studies have confirmed non-centrosymmetric alignment when deposited as LB films.<sup>14</sup> They will be studied as part of our future molecular rectification programme.

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