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Molecular rectification: experimental and theoretical confirmation of anion-induced dipole reversal in cationic dyes $\stackrel{\wedge}{\sim}$

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Abstract

E-4-[(*N*-alkyl-5,6,7,8-tetrahydro-5-isoquinolylidene)methyl]-*N*,*N*-dibutylaniline octadecylsulfate is a molecular rectifier. Its Langmuir– Blodgett (LB) films exhibit asymmetric current–voltage characteristics but with rectification occurring in opposite quadrants of the *I/V* plot for the dodecyl and octadecyl analogues. This is attributed to an anion-induced reversal of the molecular dipole, the aromatic form of the dye being stabilized when the counterion is adjacent to the heterocyclic group and the quinonoid form when close to the anilino end. Such changes have been modeled theoretically using MNDO, AM1 and PM3 calculations, which show a dependence of the bond alternation on the location of the probe charge.

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1. Introduction

Bridged donor-acceptor molecules may be considered as organic counterparts of the pn junction because D⁺-(bridge)- A^- is relatively accessible, whereas D^- -(bridge)- A^+ is not [1]. However, there have been few examples of molecular rectification: (i) the zwitterion, Z- β -(N-hexadecyl-4-quinolinium)- α -cyano-4-styryldicyanomethanide [2,3], which has a rectification ratio of ca. 20 at ± 2 V when sandwiched as a monolayer between gold electrodes; (ii) an Ag/(LB multilayer)/Mg device of 3,5-dinitrobenzyl-7-(1-oxohexylamino)pyren-2-ylcarbamate which has an improved ratio of 130 at ± 2.5 V [4]; (iii) Au/(LB multilayer)/Au devices of the octadecyl analogue of the cationic dye shown in Fig. 1a [5]. In this work we report the properties of LB films of the dodecyl analogue, which also exhibit rectification but with reversed polarity. This is attributed to the proximity of the negatively charged group of the octadecylsulfate counterion to the anilino end of the dye and consequently, to the stabilization of the quinonoid form as shown in Fig. 1b.

2. Experiment

The dyes were spread from chloroform/methanol solution onto the pure water subphase of a Nima Technology LB trough (model 622), left for 10 min and compressed to 30 mN m^{-1} . Non-centrosymmetric structures were fabricated by depositing the floating monolayers onto goldcoated substrates and by repeating the process, on the upstroke, to obtain multilayer films. Gold pads were then thermally evaporated onto the organic overlay, this being performed using an Edwards 306 coating unit operating at 10^{-4} Pa, a deposition rate of 0.1 nm s⁻¹, and a distance of 0.2 m between source and substrate. Electrical characterization was performed with a scan rate of 30 mV s⁻¹.

3. Results and discussion

Asymmetric I-V curves have been reported for Au/(LB multilayer)/Au device structures of the octadecyl analogue [5] whereby, using non-oxidizable electrodes, the behavior may be unambiguously assigned to molecular rectification. The data are shown in Fig. 2 together with corresponding results obtained for films of the dodecyl analogue. Its I-V characteristics are reproducibly asymmetric but rectification occurs in the opposite quadrant of the plot: at +I/+V for the dodecyl analogue and -I/-V for the octadecyl analogue. This implies that the dipoles are reversed although, from the

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Fig. 1. Anion-induced dipole reversal: (a) octadecyl analogue; (b) dodecyl analogue.

initial alignment at the air-water interface, the molecular orientation should be consistent. Thus, we suggest that the dipole is independent of the orientation and that reversal may be explained by an altered location of the negatively charged counterion, relative to the isoquinolinium and anilino groups of the dye. This induces a change in the chargetransfer state, from the aromatic form to quinonoid form, as shown in Fig. 1.

Evidence is also provided by the second harmonic intensity, which increases quadratically with the number of layers but is partially cancelled when the dodecyl analogue is deposited onto monolayer films of the octadecyl analogue, and vice versa. Furthermore, in the absence of phase separation, the intensity is totally quenched when the dyes are



Fig. 2. *I–V* characteristics of the dodecyl (\bullet) and octadecyl (\times) analogues.



Fig. 3. Theoretically modeled bond lengths. Anion left: a, 1.375 Å; b, 1.399 Å; c, 1.412 Å; d, 1.478 Å; e, 1.354 Å; f, 1.462 Å; g, 1.405 Å; h, 1.394 Å; i, 1.416 Å; j, 1.416 Å. Anion right: a, 1.403 Å; b, 1.365 Å; c, 1.462 Å; d, 1.365 Å; e, 1.464 Å; f, 1.357 Å; g, 1.457 Å; h, 1.360 Å; i, 1.464 Å; j, 1.358 Å.

mixed in a 1:1 ratio. The structure is non-centrosymmetric and, therefore, the molecular dipoles must be opposed.

The hypothesis of dipole reversal has also been verified by theoretical modeling using the MOPAC package, MNDO, AM1 and PM3, of Cerius² (Accelrys, Cambridge). Using a simplified molecule where CH₃ replaces the alkyl groups and the anion is CH₃COO⁻, the calculations corroborate the proposed model of dipole reversal and demonstrate a dependence of the molecular dimensions on the location of a probe charge (Fig. 3). They indicate a transition from an aromatic to quinonoid form, normally attributed to the excited state for the isolated molecule, as the counterion is moved from the isoquinolinium end to the anilino group. Differences in the derived bond lengths of the two forms are very pronounced for the central bridging unit (ca. 0.1 Å), whose dimensions are susceptible to change and exhibit strong bond alternation. Thus, the hypothesis of dipole reversal is supported by both experiment and theory.

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