

Self-assembling Dyes for Use as Molecular Rectifiers

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Monolayer films that comprise a donor-(π -bridge)-acceptor unit connected via a $-C_{10}H_{20}-S-$ bridge to gold-coated substrates have exhibited asymmetric current-voltage characteristics when investigated by scanning tunneling spectroscopy using $C_{10}H_{21}-S-$ coated gold tips. The experimental configuration locates the chromophore midway between the electrodes: [Au-S- $C_{10}H_{20}-D-\pi-A//C_{10}H_{21}-S-Au$ for dye 1; Au-S- $C_{10}H_{20}-A-\pi-D//C_{10}H_{21}-S-Au$ for dye 2]. It diminishes the likelihood of the properties being induced geometrical asymmetry. Instead, the diode-like characteristics are attributed to molecular rectification.

Keywords: Self-assembled monolayer, molecular rectifier, molecular electronics.

1. INTRODUCTION

Aviram and Ratner¹ provided the theoretical basis for molecular rectification in 1974. It was at first treated a curiosity but is now the subject of intense experimental²⁻⁸ and theoretical⁹⁻¹² activity. A donor-(electron-bridge)-acceptor sequence was proposed as the organic counterpart of the pn junction if sandwiched between metal contacts: $M_L/D\text{-bridge-}A/M_R$. When the electrode adjacent to the donor moiety is positively biased, electrons transfer from right to left in two steps. The first involves electron tunneling to and from the electrodes, from M_R to the LUMO of the acceptor and from the HOMO of the donor to M_L . This provides the D^+ -bridge- A^- excited state and electron transfer within the molecule then follows. Under conditions of reverse bias, D^- -bridge- A^+ is not readily accessible because the donor is a poor acceptor and vice versa. Thus, in this direction, the initial step probably involves intramolecular electron transfer, which is followed by tunneling from M_L to D^+ and A^- to M_R .

Experimental verification of the above model has proven difficult: early studies¹³⁻¹⁵ relied upon evaporated top electrodes and complications in contacting the ultra-thin films without shorting limited the choice to metals with low sublimation temperatures. But such electrodes readily oxidize. Consequently, any assignment of the electrical asymmetry is ambiguous: it may arise from the D-bridge-A unit or an oxide-induced Schottky barrier. A further complication arises from the need to align the chromophores: this was initially performed by the Langmuir-Blodgett technique, which by necessity utilizes molecules substituted by hydrophobic alkyl tail.¹⁶ It invariably results in the electrically nonlinear chromophore being adjacent to one electrode and separated from the other by the tail: e.g. $M/C_nH_{2n+1}-D\text{-bridge-}A/M$. This in itself can contribute to the electrical asymmetry^{12,17} and, for this reason, recent reports of rectification from LB films between gold

contacts³⁻⁸ also fail to verify the Aviram and Ratner model.¹

An alternative mechanism for rectification has been outlined by Kornilovitch *et al.*¹¹ It excludes the donor-acceptor moiety, referred to above, and is modeled on a π -conjugated unit with dissimilar alkylthiolate links to the electrodes. These act as asymmetric tunneling barriers: the voltage drop is different across each and numerical analysis has provided high current rectification ratios. But this has not been verified by experiment. Galperin *et al.*¹⁸ report a current ratio of only 2.0 at ± 1 V for Au-S- $C_mH_{2m+1}/C_nH_{2n+1}-S-Hg$ bilayer structures where the alkyl tails differ by seven methylenes. Our own experimental data^{2,19} indicate that the spatial contribution is small compared with the electrical asymmetry induced by a diode-like chromophore (see Fig. 1).

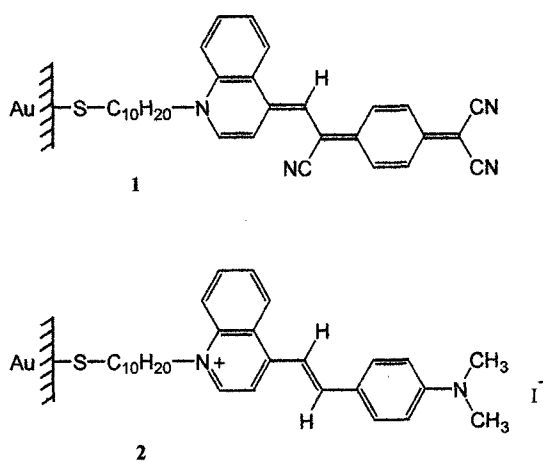


Fig. 1. Molecular structures of self-assembled D- π -A dyes on gold substrates: 1, the heterocycle is the donor and the $C(CN)_2$ group the acceptor; 2, the heterocyclic cation and $N(CH_3)_2$ group are the acceptor and donor respectively.

It is necessary for the models to take account of the D-bridge-A chromophore and its location between the electrodes. The relative contributions for LB films are unclear but rectification induced by geometrical asymmetry^{12,17} may be overstated. Evidence is sparse but four dyes, all π -bridged, have so far shown rectifying characteristics when sandwiched between non-oxidizable electrodes: three are cationic³⁻⁵ whereas the fourth is zwitterionic⁶⁻⁸ and has been extensively studied. It was synthesized as part of Canfield's nonlinear optics program²⁰ and was the first of the four to exhibit asymmetric current-voltage characteristics, albeit with a silver protected magnesium top contact.^{13,14} Rectification has since been reported for its Al/(LB monolayer)/Al device structures¹⁵ and more recently using gold electrodes.⁶⁻⁸

The rectifying behavior probably relates to the diode-like molecular structure but requires proof. The aim of this work is to provide experimental evidence of the Aviram and Ratner model,¹ albeit modified for a π rather than σ -bridge, by locating the D- π -A unit midway between the electrodes. It eliminates the asymmetric tunneling barriers and has been effectively realized by self-assembling the molecules on gold and using an alkanethiolate coated tip to probe the electrical properties.

2. MOLECULAR SELF-ASSEMBLY

Films were obtained by the immersion of gold-coated substrates in solutions of the thioacetate precursors (0.05 mg cm^{-3}), in acetonitrile for **1** and ethanol for **2**, to which ammonium hydroxide was added to displace the acetyl group. Substrates were then thoroughly rinsed with the solvent to remove any physisorbed material and dried in warm air. Determinations of the limiting molecular areas in contact with the substrate and the film thickness (Figs. 2 and 3) provided the optimum times for self-assembly.

Contact areas were derived from the observed frequency changes using the Sauerbrey analysis²¹ as dyes were chemisorbed by gold overlays on 10 MHz quartz crystals. The areas diminish to $0.36 \pm 0.03 \text{ nm}^2 \text{ molecule}^{-1}$ for **1** and $0.32 \pm 0.03 \text{ nm}^2 \text{ molecule}^{-1}$ for **2**, the limiting values in each case being close approximations of the van der Waals cross-sections of the broadest parts chromophores. There is no further change for immersion times in excess of ca. 80 min at which point the molecular areas converge.

The monolayer thickness was determined by analysis of the surface plasmon resonance, which was studied using a Kretschmann configuration²² and p-polarized monochromatic light for films on gold-coated BK7 glass prisms. For dye **1**, the real and imaginary components of the dielectric permittivity saturate to $\epsilon_r = 2.6 \pm 0.2$ and $\epsilon_i = 0.8 \pm 0.2$ at 532 nm and the thickness to $2.25 \pm 0.05 \text{ nm}$, the thickness being verified using a frequency doubled Nd:YAG and five wavelengths of a HeNe multiline laser. For dye **2**, the real and imaginary components of the dielectric permittivity saturate to 3.1 ± 0.1 and 0.5 ± 0.1

respectively at 532 nm and the thickness to $3.30 \pm 0.10 \text{ nm}$, the dimension being obtained for fourteen determinations using Nd:YAG and HeNe lasers. Again, there is no significant change in the data for immersion times greater than ca. 80 min.

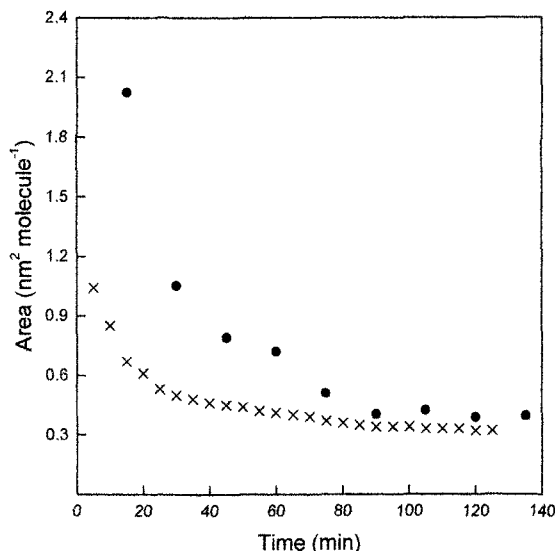


Fig. 2. Mean area occupied by the dye molecules versus the period of immersion of the gold-coated substrates: (●) dye 1; (x) dye 2.

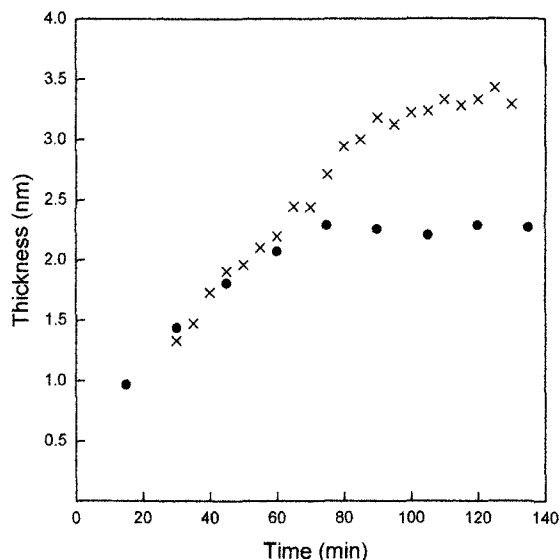


Fig. 3. Monolayer thickness versus the immersion time: (●) dye 1; (x) dye 2.

Densities derived from the molecular mass and film parameters are $1.0 \pm 0.1 \text{ Mg m}^{-3}$ for dye **1** and $0.9 \pm 0.1 \text{ Mg m}^{-3}$ for dye **2**. They are within the expected range for closely packed monolayers but the individual dimensions are unexpected. The cross-sections are similar with the areas of **1** and **2** differing by $0.04 \pm 0.06 \text{ nm}^2$ but the films have dissimilar thicknesses. They differ by $1.10 \pm 0.15 \text{ nm}$ whereas the van der Waals lengths are similar for both dyes and correspond to ca. 3 nm if the alkyl tails are fully stretched.

The film dimensions may be explained, in part, by slightly different packing arrangements and, in part, by the iodide counterion of **2** being located at the surface. The derived areas, which are almost indistinguishable, approximate to the van der Waals cross-sections of the chromophores and, thus, it is assumed that they are closely packed with insufficient space for the counterions of **2** to be located between. This is supported by the monolayer thickness of 3.3 nm, which is greater than the extended van der Waals molecular length. The film parameters suggest that the cationic molecules are upright with the counterions located above, rather than between, where they are shielded by the methyl groups of the donor. It is also feasible that the iodide counterions may be replaced by CH_3COO^- , which is generated from the reaction of the ammonia solution on the 10-acetylthiodecyl group, or even by OH^- .

Both thicknesses are consistent with the van der Waals molecular lengths if the narrower $(\text{CH}_2)_{10}$ tails are assumed to tilt to occupy the available volume.

3. MOLECULAR RECTIFICATION

Current-voltage curves from self-assembled films on gold-coated highly oriented pyrolytic graphite (HOPG) were investigated using a Nanoscope IV scanning tunneling microscope with the tip position initially set to provide a current of *ca.* 100 pA at 0.2 V.

Rectification was observed for two types of tip: (a) uncoated gold where the active D- π -A unit is asymmetrically located between the electrodes and isolated from the substrate by the insulating alkyl tail; (b) $\text{C}_{10}\text{H}_{21}\text{-S}$ coated gold tips where the chromophore is assumed to be centrally located. Dye **1** was also self-assembled on the tip and the current rectification investigated using uncoated and $\text{C}_{10}\text{H}_{21}\text{-S}$ coated gold substrates. In this case, reversal of the orientation causes the rectification to occur in the opposite quadrant of the current-voltage plot.

This work however focuses on the conventional configuration but using a coated tip to locate the chromophore midway between the electrodes. Slight asymmetry may arise from the interfacial gap and by the alkyl tails adopting different tilts, but the tunneling barriers are effectively the same. We note that Galperin *et al.*¹⁸ report only slight electrical asymmetry from junctions obtained by physical contact between dissimilar alkanethiols chemisorbed to mercury and gold electrodes, respectively. Thus, the more significant electrical asymmetries shown in Fig. 4 for the D- π -A units centrally located between the electrodes may be assigned to the intramolecular diode structure.

Extensive studies on monolayers of **1** probed by $\text{C}_{10}\text{H}_{21}\text{-S}$ -coated gold tips have yielded current rectification ratios in the range 11 to 18 at ± 1 V, the electric field being 250 MV m^{-1} for a combined bilayer thickness of *ca.* 4 nm. Films of **2** exhibit corresponding current ratios in the

range 5 to 9, the field across the bilayer in this case being reduced to 200 MV m^{-1} at ± 1 V by the thicker film structure.

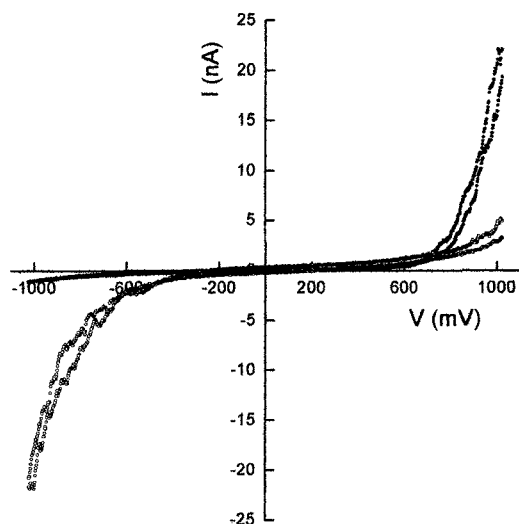


Fig. 4. Current-voltage curves using $\text{C}_{10}\text{H}_{21}\text{-S}$ coated tips, dye **1** exhibiting a higher current in the positive quadrant and dye **2** in the negative quadrant. The sign corresponds to the dye-coated substrate and, for clarity, the data have been normalized.

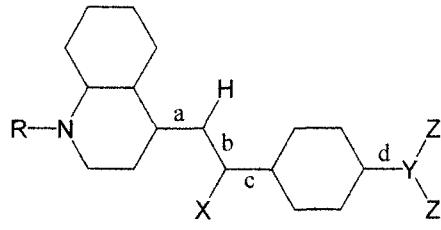
The current-voltage data in Fig. 4 indicate electron flux from the tip to dye-coated substrate for **1** under forward bias (positive quadrant) and in the opposite direction for **2** (negative quadrant). According to the Aviram and Ratner model,¹ they signify electron tunneling from the electrode to acceptor at one end of the device and from the donor to electrode at the opposite end. The data conform to the quinonoid form of **1**, whereby the $\text{C}(\text{CN})_2$ group is the acceptor and the heterocycle is the donor. The data further suggest that **2** adopts an aromatic form with a $\text{N}(\text{CH}_3)_2$ donor and heterocyclic acceptor.

The molecular structures shown in Fig. 1 are consistent with the two forms predicted from the current-voltage curves and have been verified by theoretical modeling. AM1 calculations provide dimensions for isolated molecules of **1** and **2** that conform to the quinonoid and aromatic forms respectively. The bond lengths of the central π -bridge are particularly sensitive to alternation and indicate a $=\text{CH}-\text{CH}=\text{}$ sequence for **1** and a $-\text{CH}=\text{CH}-$ sequence for **2**. Relevant dimensions are listed in Table I and a detailed discussion is included in ref. 2.

The current-voltage characteristics indicate that the electrical asymmetries are intrinsic to the molecule and the modeled dimensions conform to the altered bias for rectification. Proof that the behavior results from the diode-like structure has been obtained by protonating the $\text{C}(\text{CN})_2$ and $\text{N}(\text{CH}_3)_2$ groups, thereby effectively disrupting the charge-transfer axis. The dyes bleach and the absorption maxima in acetonitrile shift from 706

to 322 nm (**1**) and 530 to 360 nm (**2**). Exposure to acid suppresses the electrically nonlinear unit and the current-voltage curves become symmetric. This has been observed for the self-assembled films of **1** and **2** as well as LB films of analogues with long hydrophobic tails. The data indicate that the rectification is an intrinsic property of the strong donor-acceptor combination.

Table I. Theoretically modeled dimensions



Bond	Dye 1	Dye 2
a/nm	0.1361	0.1424
b/nm	0.1477	0.1368
c/nm	0.1370	0.1427
d/nm	0.1368	0.1374

X = CN or H; YZ₂ = C(CN)₂ or N(CH₃)₂

4. TRUNCATED LINKING GROUPS

As part of an ongoing investigation we are attempting to self-assemble dye molecules with truncated linking groups between the substrate and chromophore. C₃H₆ analogues of the dyes shown in Fig. 1 have been synthesized but only the cationic dye has been successfully deposited. The preliminary study has yielded rectifying characteristics and, in this case, we note that the number of alkyl carbons at opposite ends of the chromophore differs by only two. A rectification ratio of 12 at ±1 V is far in excess of what may be induced by any geometrical asymmetry.

5. CONCLUSION

Asymmetric current-voltage curves have been obtained for dissimilar D-π-A dyes fabricated as self-assembled monolayers with an Au-S-C₁₀H₂₀ connecting group bonded to the donor of one (**1**) and the acceptor of the other (**2**). Films probed by C₁₀H₂₁-S- coated gold tips, thereby locating the electrically nonlinear D-π-A midway between the electrodes, exhibit current rectification ratios of 11 to 18 at ±1 V for **1** and 5 to 9 for **2**. These dyes rectify in opposite quadrants of the current-voltage plots and the behavior is attributed to molecular rectification.

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