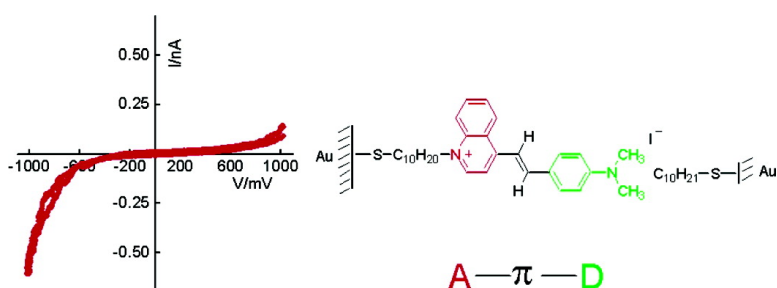


## Molecular Rectification: Self-Assembled Monolayers in Which Donor-( $\pi$ -Bridge)-Acceptor Moieties Are Centrally Located and Symmetrically Coupled to Both Gold Electrodes

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## Molecular Rectification: Self-Assembled Monolayers in Which Donor-( $\pi$ -Bridge)-Acceptor Moieties Are Centrally Located and Symmetrically Coupled to Both Gold Electrodes

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**Abstract:** Self-assembled monolayers (SAMs) obtained from 1-(10-acetylsulfanyldodecyl)-4-[2-(4-dimethylaminophenyl)vinyl]quinolinium iodide exhibit asymmetric current-voltage ( $I$ - $V$ ) characteristics. The rectification may be reversibly switched: it is suppressed when the film is exposed to HCl vapor, the intramolecular charge-transfer axis being inhibited by protonation, but restored when exposed to  $\text{NH}_3$ . The behavior is intrinsic to the donor-( $\pi$ -bridge)-acceptor moiety, and ambiguity in the assignment has been excluded by matching the alkyl tails on the substrate and contacting STM tip to locate the chromophore midway between the electrodes:  $\text{Au-S-C}_{10}\text{H}_{21}/\text{D}-\pi\text{-A-C}_{10}\text{H}_{20}\text{-S-Au}$ . Films contacted by gold tips exhibit rectification ratios of ca. 18 at  $\pm 1$  V, whereas those contacted by pentanethiolate ( $\text{Au-S-C}_5\text{H}_{11}$ )- and decanethiolate ( $\text{Au-S-C}_{10}\text{H}_{21}$ )-coated tips have corresponding ratios of ca. 11 and 5, respectively. The  $I$ - $V$  curves are different, but when adjusted for thickness the current versus electric field dependence is indistinguishable. Seven dyes are reported: SAMs with sterically hindered  $\text{D}-\pi\text{-A}$  moieties, in which the donor and acceptor are twisted out of plane, exhibit rectification, whereas those that are planar or have a weak donor-acceptor combination do not.

### Introduction

Molecular electronics represents the ultimate challenge in device miniaturization<sup>1,2</sup> where the molecular rectifier is a vital component and chemical substitution may be used to assign functionality. Aviram and Ratner<sup>3</sup> provided the theoretical basis in 1974. They defined a donor-( $\sigma$ -bridge)-acceptor sequence as the organic counterpart of the  $p$ - $n$  junction, which has since been modified<sup>4-6</sup> to include a sterically hindered  $\pi$ -bridge to enforce a nonplanar structure and disconnected through-molecule orbital overlap of the donor and acceptor. Yet experimental verification of molecular rectification has proven difficult: there is a need to align the polar molecules, make electrical contact across ultrathin films, and locate the  $\text{D}$ -bridge- $\text{A}$  unit midway between nonoxidizable gold electrodes. Geometrical asymmetry can give rise to rectifying characteristics,<sup>7</sup> albeit they are much weaker than those from the  $\text{D}$ -bridge- $\text{A}$  moiety,<sup>5,6</sup> and it is preferable to avoid

Langmuir-Blodgett (LB) films<sup>8-11</sup> that position the electrically nonlinear chromophore adjacent to one electrode and isolate it from the other by an extended aliphatic tail.

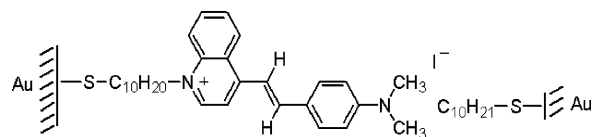
Noble metal electrodes are essential as oxide-induced electrical asymmetries overshadow the much weaker molecular effects. Relevant to this,  $\text{Au/MgPc/Al}$  structures exhibit symmetrical  $I$ - $V$  curves when measured before breaking the vacuum but have rectification ratios of ca.  $10^3$  at  $\pm 2$  V when exposed to air and reevacuated,<sup>12</sup> there being a blocking contact for hole injection at the aluminum electrode. Thus, claims of molecular rectification from films contacted by  $\text{Al/Al}_2\text{O}_3$  (refs 13-15) and more recently  $\text{Ti/TiO}_2$  (refs 16,17) are unconvincing. Further-

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more, to avoid ambiguity, the electrodes must be unreactive toward the organic layer: this rules out the report by Chabinyč et al.<sup>18</sup> of molecular rectification from an electron acceptor, a TCNQ derivative, chemisorbed via a decanethiolate link to silver and contacted by a mercury drop:  $\text{Ag-S-C}_{10}\text{H}_{20}\text{-TCNQ/C}_n\text{H}_{2n+1}\text{-S-Hg}$ . The authors infer that the electrical asymmetry arises from a conjugated component asymmetrically placed between the electrodes. However, TCNQ also self-assembles on silver and reacts to yield polycrystalline  $\text{Ag}^{\delta+}\text{TCNQ}^{\delta-}$  (ref 19), which is known to undergo field-induced transitions from a high to low impedance state.<sup>20</sup> It is therefore feasible that the molecule reported by Chabinyč et al.<sup>18</sup> adopts alternative orientations with the TCNQ moiety both adjacent and isolated from the electrode, the latter by chemisorption via the sulfur and the former involving physisorption and subsequent chemical reaction. This can explain the anomalous behavior.

Molecular rectification is once more the subject of intense theoretical interest,<sup>21–23</sup> and it has been mooted that asymmetric tunneling barriers are a contributory factor. Kornilovitch et al.<sup>23</sup> have excluded the D-bridge-A moiety and instead base their model on a conjugated unit that is linked to the electrodes by dissimilar alkanethiolate groups with the HOMO and LUMO positioned asymmetrically with respect to the Fermi level: metal/ $-\text{S-C}_m\text{H}_{2m}-\pi-\text{C}_n\text{H}_{2n}-\text{S}$ /metal. It is assumed that most of the applied voltage drops across the longer alkyl barrier and that resonant tunneling occurs at different voltages for the opposite polarities. Chang et al.<sup>14</sup> have attributed this model to films of 3-(2-tetradecoxynaphth-6-yl)-propanethiolate, self-assembled on platinum and contacted by titanium, which exhibit a rectification ratio of  $5 \times 10^5$  at  $\pm 2.3$  V. Yet the electrical asymmetry is ambiguous: the molecule is an unlikely candidate for such extreme diode-like behavior, and, as the top electrode readily oxidizes, the behavior is more likely to originate from a blocking contact. Other studies suggest that the effect is small: asymmetrically located squaraine chromophores exhibit symmetrical I-V characteristics;<sup>24</sup>  $\text{Au-S-C}_m\text{H}_{2m+1}/\text{C}_n\text{H}_{2n+1}\text{-S-Hg}$  bilayer structures have a rectification ratio of 2 at  $\pm 1$  V when the tails differ by seven methylenes;<sup>25</sup> and experimental data reported here suggest that the contribution from asymmetric tunneling barriers is negligible as compared with rectification



**Figure 1.** Bilayer device structure of a self-assembled film of a hemicyanine dye (1) probed by a decanethiolate-coated gold tip, which locates the donor-acceptor moiety midway between the electrodes.

induced by diode-like chromophores. The D-bridge-A unit is not dispensable.

(Z)- $\beta$ -(N-Hexadecyl-4-quinolinium)- $\alpha$ -cyano-4-styryldicyanomethanide ( $\text{C}_{16}\text{H}_{33}\text{-Q3CNQ}$ )<sup>26</sup> is the most extensively studied molecular rectifier and also the first to stand the test of time. Ashwell and Sambles<sup>4</sup> in 1990 reported rectifying characteristics from its LB films deposited on platinum and contacted by silver-coated magnesium, the protective overcoat being applied without breaking the vacuum, and Metzger et al.<sup>13</sup> later demonstrated similar behavior for films sandwiched between oxidizable aluminum electrodes. Rectification has since been confirmed at Cranfield,<sup>11a</sup> Exeter,<sup>11b</sup> and Tuscaloosa<sup>11c,d</sup> using gold contacts, but assignment of the data is ambiguous because the insulating  $\text{C}_{16}\text{H}_{33}$  tails, which isolate the chromophore from one of the electrodes, induce asymmetric coupling. The contribution is probably small, but, as a consequence of theoretical studies,<sup>7</sup> the I-V characteristics fail to provide proof of the Aviram and Ratner model.<sup>3</sup> However, evidence has been gained from self-assembled films of  $\text{Au-S-C}_{10}\text{H}_{20}\text{-Q3CNQ}$  contacted by decanethiolate-coated gold probes,<sup>5</sup> which locate the chromophores midway between the electrodes. The devices exhibit rectification ratios in the range 10–20 at  $\pm 1$  V, and, unlike LB-deposited films,<sup>4,11</sup> the chemisorbed species is not subject to field-induced changes.<sup>11b</sup>

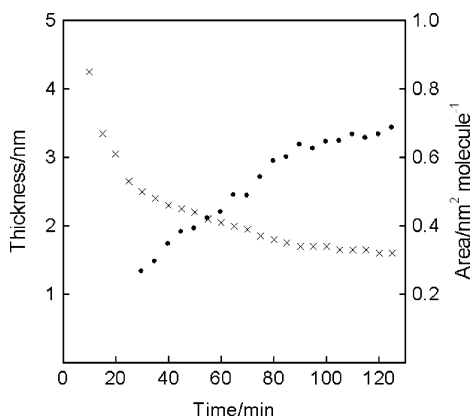
In this work, we report rectification from SAMs of some cationic D- $\pi$ -A dyes and, as above, position the molecules to steer clear of any effect induced by geometrical asymmetry (Figure 1). Under forward bias, the polarity for higher current is consistent with electrons tunneling from the electrode to the LUMO of the acceptor at one end of the device and from the HOMO of the donor to the electrode at the opposite end. Intramolecular electron transfer then follows to restore the molecular ground state. Under conditions of reverse bias, the donor and acceptor provide a higher barrier for tunneling between the molecule and electrodes, and, therefore, in this direction, the initial step is probably intramolecular. Significantly, protonation disrupts the charge-transfer axis and suppresses rectification, whereas exposure to base restores the electrical asymmetry. This is indicative of the behavior arising from the diode-like molecular structure rather than any extrinsic effect.

## Results and Discussion

**Quinolinium Hemicyanine (1).** Self-assembled films were obtained by immersing gold-coated substrates in an ethanol solution of the precursor, 1-(10-acetylsulfanyldodecyl)-4-[2-(4-dimethylaminophenyl)vinyl]quinolinium iodide ( $8 \times 10^{-5}$  M), to which a drop of ammonium hydroxide was added to displace

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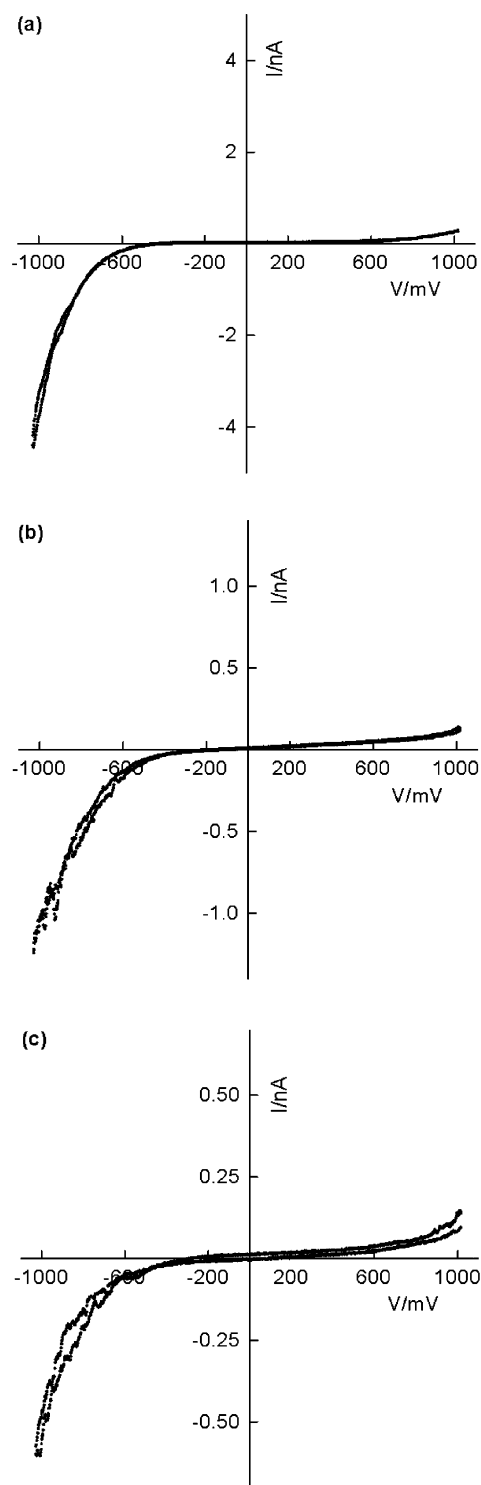
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**Figure 2.** Rate of molecular self-assembly of dye **1** on gold-coated substrates when immersed in an  $8 \times 10^{-5}$  M ethanol solution of the precursor containing ammonium hydroxide to remove the acetyl group: variation of the monolayer thickness (●) and molecular area (×) with time for the combined period of immersion.

the acetyl group. Optimum deposition was achieved by several short immersions of 5 min each, rather than a continuous period, the substrates being thoroughly rinsed each time with chloroform and ethanol to remove any physisorbed material. The process was monitored to obtain the film parameters (Figure 2): the monolayer thickness was determined by analysis of surface plasmon resonance (SPR) data, which were obtained using a Kretschmann geometry<sup>27</sup> for monolayers on gold-coated BK7 glass prisms, whereas the contact area was derived using the Sauerbrey equation<sup>28</sup> for monolayers on 10 MHz quartz crystals. Optimum deposition required a total immersion of ca. 90 min: the real and imaginary components of the dielectric permittivity saturate to  $\epsilon_r = 3.1 \pm 0.1$  and  $\epsilon_i = 0.5 \pm 0.1$  for  $\lambda = 532$  nm and the thickness and area to  $3.30 \pm 0.05$  nm and  $0.32 \pm 0.02$  nm<sup>2</sup> molecule<sup>-1</sup>, respectively, the SPR-derived values being consistent for 14 determinations on seven separate films. The area is consistent with the van der Waals cross-section of the quinolinium group, and thus it may be assumed that molecules are closely packed with insufficient space for the iodide counterions to be located between the chromophores. This is supported by the thickness, which is greater than the van der Waals molecular length of ca. 3.0 nm, indicating that the cationic dye molecules are upright with the iodide counterions located above, where they are shielded by the methyls of the donor group, rather than between. It is feasible that counterions may be replaced by  $\text{CH}_3\text{COO}^-$  generated by reaction of the 10-acetylthiodecyl group with the ammonium hydroxide solution or by  $\text{OH}^-$  from the latter. The film density is  $0.9 \pm 0.1$  Mg m<sup>-3</sup>.

I–V characteristics were obtained for self-assembled monolayers on gold-coated HOPG (highly oriented pyrolytic graphite) using a Nanoscope IV scanning tunneling microscope with the tip position initially set to provide a current of ca. 10 to 100 pA at 0.2 V. Rectification was observed for four types of tip: PtIr and Au where the active D– $\pi$ –A unit is asymmetrically located between the electrodes and isolated from the substrate by the insulating alkyl tail; and  $\text{C}_5\text{H}_{11}$ –S- and  $\text{C}_{10}\text{H}_{21}$ –S-coated gold tips where, for the latter, the chromophore is assumed to be centrally located. At forward bias, the data shown in Figure 3 correspond to electron flux from the gold-coated HOPG to

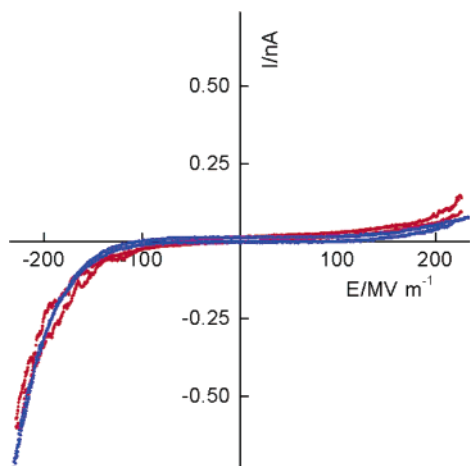


**Figure 3.** I–V characteristics of self-assembled monolayers of dye **1** on gold-coated HOPG investigated using three types of tip: (a) uncoated tip where the D– $\pi$ –A dye is asymmetrically coupled to one electrode; (b) a pentanethiolate-coated gold tip; and (c) a decanethiolate-coated gold tip where the chromophore is located midway between the electrodes,  $\text{Au-S-C}_{10}\text{H}_{21}/\text{D}-\pi-\text{A}-\text{C}_{10}\text{H}_{20}-\text{S-Au}$ . The polarity as shown corresponds to that of the gold-coated HOPG substrate.

tip: they signify electron tunneling from the electrode to the cationic acceptor at one end of the device ( $\text{A}^+ \rightarrow \text{A}^\circ$ ) and from the donor to the electrode at the opposite end ( $\text{D}^\circ \rightarrow \text{D}^+$ ), followed by intramolecular tunneling from  $\text{A}^\circ$  to  $\text{D}^+$ . In contrast, at reverse bias, the initial step probably involves electron transfer

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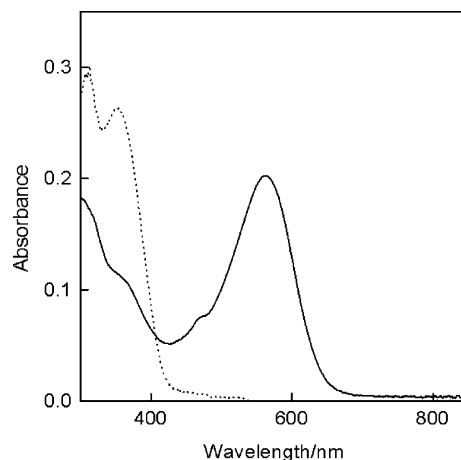
**Figure 4.** Current versus electric field characteristics of self-assembled films of dye **1** on gold-coated HOPG and investigated using two types of tip: uncoated where the organic layer has a thickness of 3.3 nm (blue); and decanethiolate-coated gold where the combined bilayer thickness is 4.5 nm (red). For clarity, data obtained for a pentanethiolate-coated tip have been omitted but exhibit almost indistinguishable field dependence.

from the dimethylamino donor to the heterocyclic acceptor followed by tunneling to and from the electrodes.

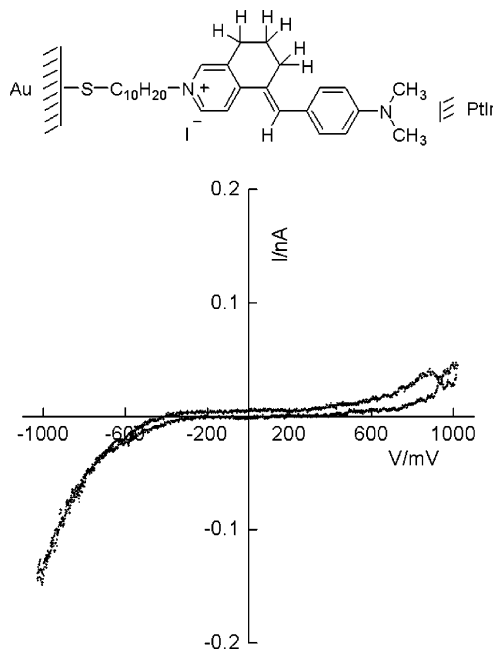
The I–V curves exhibit rectification ratios of ca. 18 for the PtIr and Au tips, ca. 11 for the C<sub>5</sub>H<sub>11</sub>–S–Au-coated tip, and ca. 5 for C<sub>10</sub>H<sub>21</sub>–S–Au, the values corresponding to the current ratios at –1 and +1 V. Yet the field dependence is almost indistinguishable. Data for the I–E plots, which are overlaid in Figure 4, were calculated using a bilayer thickness of 4.5 nm for Au–S–C<sub>10</sub>H<sub>20</sub>/D– $\pi$ –A–C<sub>10</sub>H<sub>20</sub>S–Au, the individual layer thicknesses being 3.3 nm for the dye and 1.2 nm for decanethiolate (cf. 0.8 nm for pentanethiolate), the dimensions being obtained by SPR analysis. The three different device configurations each exhibit rectification ratios of ca. 5 at ca. 220 MV m<sup>–1</sup>, which for the thickest structure corresponds to the highest field studied. This is significant as it has been reported<sup>7,23</sup> that asymmetric coupling can in itself lead to rectification and there has been discussion of the origin of electrical asymmetry in LB films where the chromophore is adjacent to one electrode and separated from the other by its aliphatic tail.<sup>7</sup> This does not apply here as the chromophore is centrally located when probed by the C<sub>10</sub>H<sub>21</sub>–S–Au tip, and the I–E data, shown in Figure 5, indicate that the D– $\pi$ –A moiety has a more significant effect than any other induced asymmetry.

**Chemical Switching of the Rectification.** Chemisorbed monolayers of dye **1** are stable in air, but the donor readily protonates [C<sub>6</sub>H<sub>4</sub>–N(CH<sub>3</sub>)<sub>2</sub> → C<sub>6</sub>H<sub>4</sub>–NH(CH<sub>3</sub>)<sub>2</sub>] in acidic media with disruption of the intramolecular charge-transfer axis (Figure 5). The process is reversible. Consequently, the rectification may be chemically switched, first off and then back on, the I–V curves being symmetrical when SAMs are briefly exposed to HCl vapor but showing restored asymmetry when exposed to NH<sub>3</sub>. We have recently reported<sup>6</sup> reversible switching of a dye analogous to **1** but with a truncated S–C<sub>3</sub>H<sub>6</sub> link between the chromophore and substrate. Other alkyl analogues in this series exhibit chemically switched I–V characteristics, and their reversibility clearly demonstrates that the rectification is intrinsic to the strong donor/acceptor combination.

**Other Hemicyanines (2 and 3).** SAMs of the isoquinolinium and pyridinium analogues, whose molecular structures are shown

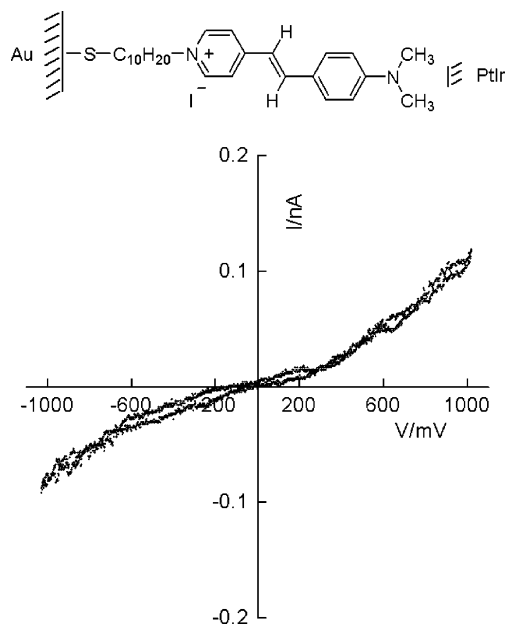


**Figure 5.** Absorption spectra of dye **1** (solid line) and its protonated form (broken line) in chloroform. Bleaching manifests protonation: the absorption maximum is shifted from 563 to 353 nm in chloroform, but the color is restored when the dye is exposed to base.



**Figure 6.** Molecular structure of a self-assembled isoquinolinium hemicyanine dye (**2**) and I–V characteristics probed using an uncoated PtIr tip. The polarity as shown corresponds to that of the gold-coated HOPG, and data were obtained with the tip position initially set to provide a tunneling current of ca. 100 pA at 0.2 V.

in Figures 6 and 7, exhibit indistinguishable thicknesses ( $1.9 \pm 0.1$  nm) and contact areas ( $0.48 \pm 0.05$  nm<sup>2</sup> molecule<sup>–1</sup>). They are significantly smaller than the van der Waals length and larger than the molecular cross-section, indicating a tilted arrangement with the iodide counterions probably located between chromophores. Previous studies on LB films have demonstrated dipole reversal<sup>8b</sup> as the counterion is shifted along the length of the D– $\pi$ –A chromophore, the molecular structure changing from aromatic to quinoid as the anion locates above the amino group.<sup>29</sup> Thus, unless structurally ordered, this self-assembled arrangement is less conducive to rectifying behavior because the iodides may polarize both forms of the cationic dye with the occurrence of opposing dipoles. Nonetheless, asymmetric I–V curves have been obtained for the isoquinolinium analogue, albeit with a rectification ratio of only 5 at  $\pm 1$  V when contacted

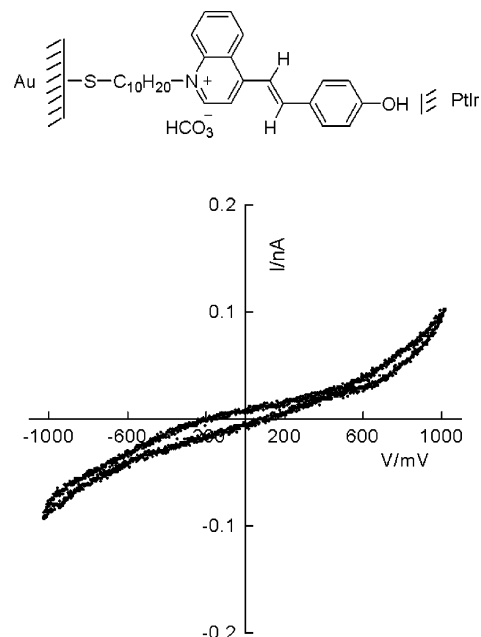


**Figure 7.** Molecular structure of a self-assembled pyridinium hemicyanine dye (**3**) and I–V characteristics probed using an uncoated PtIr tip. The polarity as shown corresponds to that of the gold-coated HOPG, and data were obtained with the tip position initially set to provide a tunneling current of ca. 100 pA at 0.2 V. Slight asymmetry may be induced by varying the initial conditions, but most films exhibit rectification ratios of less than 1.5  $\pm$  1 V with only one giving a ratio as high as ca. 3.

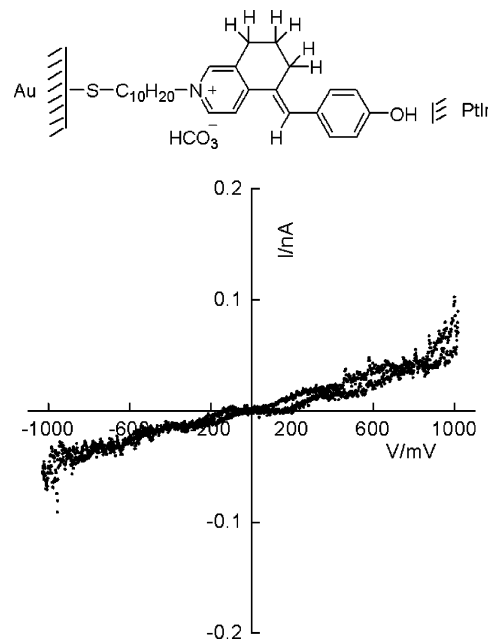
by an uncoated tip, the electric field being ca. 530 MV m<sup>-1</sup>.

Aviram and Ratner<sup>3</sup> proposed a D– $\sigma$ –A structure to provide an intramolecular tunneling barrier, whereas molecules reported here have  $\pi$ -conjugated bridges, which must be effectively broken by nonplanar structures. Significantly, geometries of the rectifying quinolinium and isoquinolinium analogues, which have been modeled, using the MOPAC programs of Cerius2 (Accelrys, Cambridge), exhibit dihedral angles of 31° and 48°, respectively, between the planes through the donor and acceptor moieties. In contrast, the pyridinium analogue is almost planar: its donor and acceptor groups are rotated out of the plane of the central CH=CH bridge by only ca. 5° each with a dihedral angle of 9.6° between their planes, defined here as the phenylene ring plus exocyclic nitrogen and heterocycle. X-ray crystallographic analysis<sup>30</sup> has similarly established a dihedral angle of 10.8° between the two six-membered rings. Therefore, in the absence of any significant out-of-plane rotation, it may be assumed that the D<sup>o</sup>– $\pi$ –A<sup>+</sup> ground state (aromatic) and D<sup>+</sup>= $\pi$ =A<sup>o</sup> excited state (quinoid) of the pyridinium dye are degenerate resonance forms.

Independent of the different types of packing, we note that dyes with significantly twisted D– $\pi$ –A structures (**1** and **2**) exhibit rectifying characteristics whereas the almost planar pyridinium analogue (**3**) does not. The I–V curves of the pyridinium dye, shown in Figure 7, demonstrate the need to



**Figure 8.** Molecular structure of the protonated form of the quinolinium merocyanine (**4**) and I–V characteristics when probed using an uncoated PtIr tip. The polarity as shown corresponds to that of the gold-coated HOPG, and data were obtained with the tip position initially set to provide a tunneling current of ca. 100 pA at 0.2 V.



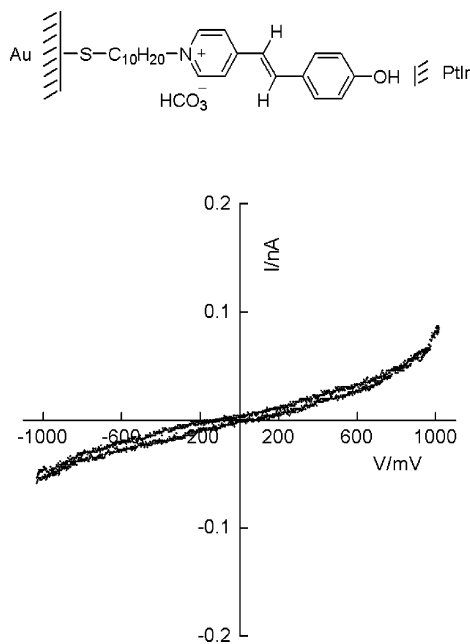
**Figure 9.** Molecular structure of the protonated form of the isoquinolinium merocyanine (**5**) and I–V characteristics when probed using an uncoated PtIr tip. The polarity as shown corresponds to that of the gold-coated HOPG, and data were obtained with the tip position initially set to provide a tunneling current of ca. 100 pA at 0.2 V.

sterically hinder the molecule to enforce a nonplanar arrangement and disconnect orbital overlap between donor and acceptor.

**Protonated Merocyanines (4–6).** Dyes were self-assembled in the presence of ammonium hydroxide to yield the colored merocyanine form, the monolayer thickness and contact area of the quinolinium, isoquinolinium, and pyridinium derivatives being  $1.7 \pm 0.2$  nm and  $0.40 \pm 0.05$  nm<sup>2</sup> molecule<sup>-1</sup> in each case. The merocyanine form is unstable and readily protonates [C<sub>6</sub>H<sub>4</sub>–O<sup>-</sup> → C<sub>6</sub>H<sub>4</sub>–OH], presumably by interaction with

(29) Anion-induced dipole reversal in LB films of (*E*)-4-[(*N*-alkyl-5,6,7,8-tetrahydro-5-isoquinolylidene)methyl]-*N,N*-dibutylaniline octadecyl sulfate has been demonstrated by experimental and theoretical methods: an altered polarity for rectification as the sulfate group is relocated; cancellation of the SHG in films when there is equivalent coexistence of the two forms; altered dimensions from MOPAC calculations consistent with a change from an aromatic to quinoid form as the counterion is moved along the long axis of the chromophore. Full details are provided in ref 8b.

(30) Coe, B. J.; Harris, J. A.; Asselberghs, I.; Clays, K.; Olbrechts, G.; Persoons, A.; Hupp, J. T.; Johnson, R. C.; Coles, S. J.; Hursthouse, M. B.; Nakatani, K. *Adv. Funct. Mater.* **2002**, *12*, 110–116.

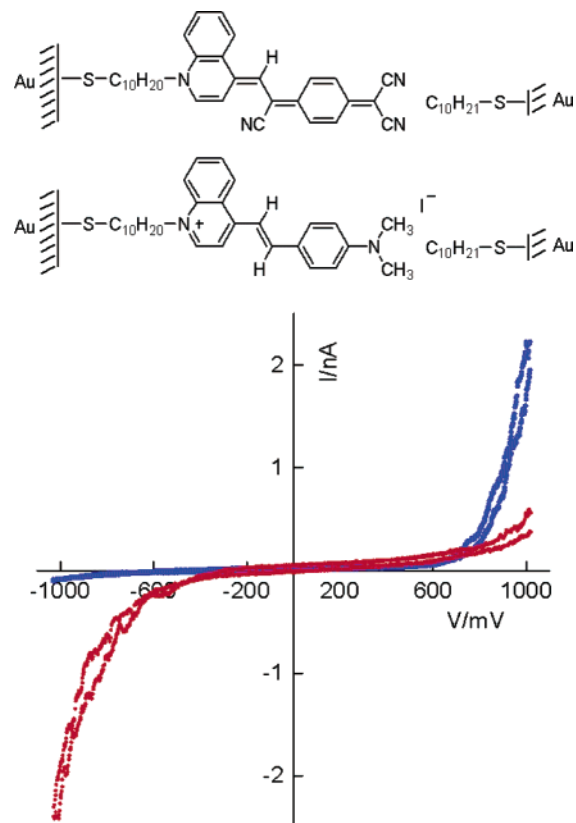


**Figure 10.** Molecular structure of the protonated form of the pyridinium merocyanine (**6**) and I–V characteristics when probed using an uncoated PtIr tip. The polarity as shown corresponds to that of the gold-coated HOPG, and data were obtained with the tip position initially set to provide a tunneling current of ca. 100 pA at 0.2 V.

atmospheric  $\text{H}_2\text{CO}_3$ . This disrupts the charge-transfer axis, the merocyanine having a strong donor–acceptor combination, which is weakened in the protonated form where OH is a weak donor. Consequences are loss of color and suppression of second-harmonic generation (SHG), but both may be fully restored upon exposure to  $\text{NH}_3$  vapor.

The protonated form is ever present, and self-assembled films of the three analogues exhibit I–V curves that are either symmetrical or at most have current ratios of ca. 2 at  $\pm 1$  V when contacted by uncoated tips (Figures 8–10). In this configuration, asymmetric barriers are created by alkyl tails,  $\text{Au-S-C}_{10}\text{H}_{20}$ -dye, which isolate the chromophores from the substrate electrode. The numerical analysis of Kornilovitch et al.<sup>23</sup> predicts a high rectification ratio for a relatively small difference in the number of methylenes in the tails that separate the electrodes from either side of the chromophore. Yet rectification is not observed or at best is very weak. The experimental data signify that the Kornilovitch model is not applicable to these films as well as for those of the protonated hemicyanines.

**Au-S-C<sub>10</sub>H<sub>20</sub>-Q3CNQ (7).** The dye depicted in Figure 11 is an analogue of the air-sensitive merocyanine in which the oxygen atom is substituted by  $\text{C}(\text{CN})_2$ , and, as a result, its films are far less susceptible to atmospheric protonation. For self-assembled films, we have reported<sup>5</sup> dimensions of  $2.25 \pm 0.05$  nm and  $0.36 \pm 0.03$  nm<sup>2</sup> molecule<sup>-1</sup>, respectively, and a rectification ratio of 11 at  $\pm 1$  V when contacted by a  $\text{C}_{10}\text{H}_{21}$ -S-Au-coated tip. The I–V characteristics, reinvestigated in this work, yield corresponding ratios of 10–20 at  $\pm 1$  V, which increase to ca. 30 when contacted by gold tips. The latter may be compared with ca. 4–8 for LB monolayers of  $\text{C}_{16}\text{H}_{33}$ -Q3CNQ, the weaker electrical asymmetry being explained by the coexistence of at least three LB phases,<sup>11a,26</sup> of which two are centrosymmetric and suppress the rectification.<sup>31</sup> Physisorbed LB-deposited molecules are also subject to field-induced



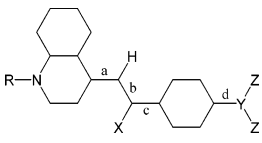
**Figure 11.** Molecular structures of self-assembled films of the Q3CNQ derivative (upper) and quinolinium hemicyanine (middle), contacted by  $\text{C}_{10}\text{H}_{21}$ -S-Au-coated gold tips, and their I–V characteristics (lower) where blue and red data points correspond to Q3CNQ and hemicyanine derivatives, respectively, and the current of the latter has been multiplied by a factor of 4. The dyes, respectively, exhibit higher currents in the positive and negative quadrants of the I–V plot, and the polarity corresponds to that of the substrate.

realignment with the I–V characteristics showing symmetrical behavior when the voltage is cycled.

The I–V characteristics are compared in Figure 11 with those of the quinolinium hemicyanine, in both cases for self-assembled films contacted by decanethiolate-coated gold tips, which attempt to locate the D– $\pi$ -A moiety midway between the electrodes. Any asymmetry arising from the interface between monolayers or the alkyl tails of each adopting slightly different tilts is unlikely to contribute to the electrical asymmetry. Therefore, the I–V characteristics may be attributed to chromophore-induced molecular rectification, and it is relevant that both exhibit symmetrical curves when exposed to HCl vapor, which disrupts the charge-transfer axes by protonating the  $\text{C}(\text{CN})_2$  swallowtail of **7** and the  $\text{N}(\text{CH}_3)_2$  group of **1**. Rectification is restored by exposure to  $\text{NH}_3$  vapor, but care must be taken as acid and base can dislodge the self-assembled molecules.

Current rectification ratios of SAMs contacted by  $\text{C}_{10}\text{H}_{21}$ -S-Au are typically 10–20 at  $\pm 1$  V for the Q3CNQ dye and 5–7 at  $\pm 1$  V for the hemicyanine, the bilayer device thicknesses being ca. 3.5 and 4.5 nm, respectively. The rectification ratios

(31)  $\text{C}_{16}\text{H}_{33}$ -Q3CNQ has at least three distinct LB forms: a noncentrosymmetric phase that exhibits a strong second-harmonic intensity and has a sharp J-aggregate band at 563 nm and two centrosymmetric phases that are either SHG-inactive or exhibit only a residual intensity and have absorption bands centred about 610 and 670 nm. A broad shoulder on the low-energy side of the J-aggregate band manifests phase coexistence.

**Table 1.** AM1-Derived Dimensions<sup>a</sup>


bond	Q3CNQ	hemicyanine
a/nm	0.1361	0.1424
b/nm	0.1477	0.1368
c/nm	0.1370	0.1427
d/nm	0.1368	0.1374

<sup>a</sup> X = CN or H; YZ<sub>2</sub> = C(CN)<sub>2</sub> or N(CH<sub>3</sub>)<sub>2</sub>.

are similar when electric field rather than voltage is considered, the hemicyanine exhibiting a ratio of 18 when contacted by an uncoated gold tip and having a monolayer thickness of 3.3 nm.

The I–V characteristics correspond to electron flux from the tip to dye-coated substrate for the Q3CNQ dye (positive quadrant) and in the opposite direction for the hemicyanine (negative quadrant). They signify tunneling from the electrode to the LUMO of the acceptor at one end of the device and from the HOMO of the donor to the electrode at the other end. By this mechanism, the data conform to the quinoid form of Q3CNQ and aromatic form of the hemicyanine, whereby the terminal C(CN)<sub>2</sub> and N(CH<sub>3</sub>)<sub>2</sub> groups are, respectively, the acceptor and donor. This has been verified by molecular modeling: relevant bond lengths are listed in Table 1, and a detailed discussion for the Q3CNQ analogue is included in ref 5. In this abbreviated version, we note that the central  $\pi$ -bridge is particularly sensitive to bond alternation and that the derived dimensions from AM1 calculations (Accelrys, Cambridge) indicate =CH–C(CN)= and –CH=CH– sequences for the Q3CNQ and hemicyanine, respectively. The exocyclic bond lengths that connect the ring to the terminal group are ca. 0.137 nm in each case: this dimension corresponds to double (C=C) and single (C–N) bonds, respectively, and to the quinoid and aromatic forms of the two dyes. The dimensions conform to the altered bias for rectification.

**Alternative Device Configurations.** I–V characteristics were also investigated by adapting the technique described by Chabinye et al.<sup>18</sup> SAMs **1** and **7** were immersed in 1 mM solutions of decanethiol in hexadecane, and mercury drops, suspended from syringes, were lowered onto the surface; prior to making physical contact, ca. 5 min was allowed for a monolayer to form on the mercury. The Au–S–C<sub>10</sub>H<sub>20</sub>–dye//C<sub>10</sub>H<sub>21</sub>–S–Hg bilayer devices were interrogated using a Keithley source/electrometer, and the I–V characteristics were found to be consistent with those previously obtained by scanning tunneling spectroscopy (STS). Both techniques showed rectification in opposite quadrants of the I–V plots. However, as reported by Chabinye et al.,<sup>18</sup> we also note that many device structures show evidence of shorting, as indicated by abrupt changes in the current as the voltage is cycled, and such films were discarded. Therefore, the STS technique is preferable.

**Confirmation of Molecular Rectification.** A series of control measures has been applied to exclude experimentally induced effects and to avoid ambiguity in the assignment of the I–V characteristics. The following observations for **1** and **7** demonstrate that the chromophore rather than asymmetric coupling or the metal/molecule interface induces the rectification:

(a) The dyes readily protonate with suppression of their intramolecular charge-transfer axes. Exposure to HCl followed by NH<sub>3</sub> demonstrates reversible off/on chemical switching of the rectifying characteristics and confirms that the D– $\pi$ –A moiety is responsible for the electrical asymmetry.

(b) Rectification is maintained when the chromophore is located midway between the electrodes, thereby indicating that asymmetric coupling is not responsible.

(c) The SAMs exhibit reproducible behavior with rectification in opposite quadrants of the I–V plots, which cannot be explained by tip-induced tunneling gaps. Assembling the dyes on the tip rather than the substrate alters the molecular orientation and reverses the polarity for rectification.

(d) The bias for rectification is consistent with the dipole alignment: Au–S–C<sub>10</sub>H<sub>21</sub>–A– $\pi$ –D for **1** where the N(CH<sub>3</sub>)<sub>2</sub> group is the donor and electrons tunnel via the molecule from substrate to tip under forward bias (negative quadrant); and Au–S–C<sub>10</sub>H<sub>21</sub>–D– $\pi$ –A for **7** where the C(CN)<sub>2</sub> group is the acceptor and electrons tunnel in the opposite direction under forward bias (positive quadrant).

(e) STS and electrometer-based measurement techniques provide similar I–E characteristics and a consistent bias for rectification, which again suggests that the behavior is intrinsic to the D– $\pi$ –A chromophore.

## Conclusion

Asymmetric I–V characteristics have been obtained from self-assembled films of sterically hindered D– $\pi$ –A dyes but are suppressed when the chromophore is almost planar and the donor and acceptor are effectively coupled. Significantly, the bulky quinolinium and isoquinolinium hemicyanines exhibit rectification, whereas the pyridinium analogue does not. Furthermore, electrical asymmetry from chromophores **1** and **7** may be chemically switched, first off and then back on, by exposure to acid and base, respectively, which disrupts and then restores the intramolecular charge-transfer axis. None of the protonated forms exhibits any significant electrical asymmetry even when contacted by uncoated probes, the configuration locating the chromophores adjacent to the tip and isolating them from the substrate electrode by the S–C<sub>10</sub>H<sub>20</sub> tails. The experimental data demonstrate that the alkyl tunneling barrier has only a negligible effect on the shape of the I–V curves as compared with electrical asymmetries induced by the diode-like molecular structures of the unprotonated dyes.

We have provided evidence of Aviram and Ratner-type molecular rectification, albeit for sterically hindered D– $\pi$ –A molecules rather than the proposed D– $\sigma$ –A moiety, and have maintained electrical asymmetry when the chromophores are located midway between the electrodes.

## Experimental Section

**Materials.** Reactants and solvents were obtained from the Aldrich Chemical Co. (Gillingham, UK) and were used as supplied without further purification. Thioacetic acid S-(10-iododecyl) ester<sup>32,33</sup> and the

(32) Gittins, D. I.; Bethell, D.; Nicholls, R. J.; Schiffrin, D. J. *J. Mater. Chem.* **2000**, *10*, 79–83.

(33) Ashwell, G. J.; Paxton, G. A. N.; Whittam, A. J.; Tyrrell, W. D.; Berry, M.; Zhou, D. *J. Mater. Chem.* **2002**, *12*, 1631–1635.



precursor to SAM 7 (ref 5) were synthesized as previously described. Satisfactory analytical data were obtained.

**Precursor to SAM 1.** To a solution of lepidine (1.43 g, 10 mmol) in acetonitrile (100 cm<sup>3</sup>) was added thioacetic acid *S*-(10-iododecyl) ester (3.42 g, 10 mmol), the mixture being kept under nitrogen and heated at reflux for 2 days. The solvent was removed in vacuo at ambient temperature to give a crude yellow product of 1-(10-acetylsulfanyldodecyl)-4-methylquinolinium iodide, which was purified by column chromatography on silica gel, eluting with chloroform and then chloroform/methanol (10:1, v/v): yield, 53%; mp 97–99 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz, *J*/Hz): δ<sub>H</sub> 1.20–1.34 (m, 12H, CH<sub>2</sub>), 1.53 (quintet, *J* 7.0, 2H, SCH<sub>2</sub>CH<sub>2</sub>), 2.08 (quintet, *J* 7.0, 2H, CH<sub>2</sub>CH<sub>2</sub>N<sup>+</sup>), 2.30 (s, 3H, CH<sub>3</sub>CO), 2.83 (t, *J* 7.1, 2H, SCH<sub>2</sub>), 3.00 (s, 3H, Qn-CH<sub>3</sub>), 5.24 (t, *J* 7.0, 2H, CH<sub>2</sub>N<sup>+</sup>), 7.97 (t, *J* 7.8, 1H, Qn-H), 8.00 (d, *J* 7.0, 1H, Qn-H), 8.17 (t, *J* 8.4, 1H, Qn-H), 8.28 (d, *J* 8.7, 1H, Qn-H), 8.35 (d, *J* 8.7, 1H, Qn-H), 10.2 (d, *J* 5.8, 1H, Qn-H). MS (FAB): *m/z*, 358, 100% [M - I]<sup>+</sup>.

A solution of the above product (0.49 g, 1 mmol), 4-dimethylaminobenzaldehyde (0.15 g, 1 mmol), and piperidine (0.2 cm<sup>3</sup>) in acetonitrile (50 cm<sup>3</sup>) was heated at reflux for 24 h, following which a precipitate was collected by filtration from the cooled solution. The product was purified by column chromatography on silica gel, eluting initially with chloroform and then chloroform:methanol (95:5 and 75:25, v/v) to give purple crystals of 1-(10-acetylsulfanyldodecyl)-4-[2-(4-dimethylaminophenyl)vinyl]quinolinium iodide: yield, 40%; mp 146–148 °C. λ<sub>max</sub> (CHCl<sub>3</sub>): 563 nm. Found: C, 60.1; H, 6.4; N, 4.7. C<sub>31</sub>H<sub>41</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>I requires: C, 60.38; H, 6.70; N, 4.54. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz, *J*/Hz): δ<sub>H</sub> 1.26 (br s, 12H, CH<sub>2</sub>), 1.55 (quintet, *J* 7.1, 2H, SCH<sub>2</sub>CH<sub>2</sub>), 2.04 (quintet, *J* 6.7, 2H, CH<sub>2</sub>CH<sub>2</sub>N<sup>+</sup>), 2.32 (s, 3H, CH<sub>3</sub>-CO), 2.85 (t, *J* 7.2, 2H, SCH<sub>2</sub>), 3.12 (s, 6H, N(CH<sub>3</sub>)<sub>2</sub>), 4.98 (t, *J* 7.2, 2H, CH<sub>2</sub>N<sup>+</sup>), 6.75 (d, *J* 9.0, 2H, Ar-H), 7.62 (d, *J* 15.5, 1H, C=C-H), 7.69 (d, *J* 8.8, 2H, Ar-H), 7.84–7.96 (m, 2H, Qn-H and C=C-H), 8.05–8.18 (m, 2H, Qn-H), 8.23 (d, *J* 7.1, 1H, Qn-H), 8.61 (d, *J* 8.1, 1H, Qn-H), 9.81 (d, *J* 6.2, 1H, Qn-H). *m/z* (FAB): 489, 100% [M - I]<sup>+</sup>. HRMS (ES<sup>+</sup>): *m/z* calcd for C<sub>31</sub>H<sub>41</sub>N<sub>2</sub>O<sub>2</sub>S 489.2934, found 489.2931.

**Precursor to SAM 2.** To a solution of 5,6,7,8-tetrahydroisoquinoline (1.33 g, 10 mmol) in acetonitrile (100 cm<sup>3</sup>) was added thioacetic acid *S*-(10-iododecyl) ester (3.42 g, 10 mmol), the mixture being kept under nitrogen and heated at reflux for 2 days. The solvent was removed in vacuo at ambient temperature, and the crude product was purified by column chromatography on silica gel, eluting with chloroform:methanol (95:5 and 75:25 v/v) to yield 1-(10-acetylsulfanyldodecyl)-5,6,7,8-tetrahydroisoquinolinium iodide as an oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz, *J*/Hz): δ<sub>H</sub> 1.12–1.22 (m, 12H, CH<sub>2</sub>), 1.42 (quintet, *J* 7.0, 2H, SCH<sub>2</sub>CH<sub>2</sub>), 1.78 (br s, 4H, iQn-CH<sub>2</sub>), 1.90 (quintet, *J* 7.0, 2H, CH<sub>2</sub>-CH<sub>2</sub>N<sup>+</sup>), 2.19 (s, 3H, CH<sub>3</sub>CO), 2.72 (t, *J* 7.2, 2H, SCH<sub>2</sub>), 2.90 (br s, 4H, iQn-CH<sub>2</sub>), 4.64 (t, *J* 7.2, 2H, CH<sub>2</sub>N<sup>+</sup>), 7.68 (d, *J* 6.3, 1H, iQn-H), 8.76 (d, *J* 6.0, 1H, iQn-H), 9.08 (s, 1H, iQn-H). *m/z* (FAB): 348, 100% [M - I]<sup>+</sup>.

A solution of the above product (0.48 g, 1 mmol), 4-dimethylaminobenzaldehyde (0.15 g, 1 mmol), and piperidine (0.2 cm<sup>3</sup>) in methanol (50 cm<sup>3</sup>) was heated at reflux for 24 h, following which the solvent was removed in vacuo at ambient temperature. The resultant oil was purified by column chromatography on silica gel, eluting with chloroform and then chloroform:methanol (75:25 v/v), to obtain bis-[1-(10-decyl)-5-(4-dimethylaminobenzylidene)-5,6,7,8-tetrahydroisoquinolinium iodide]disulfide as a red solid: yield 36%; mp 200 °C (dec). λ<sub>max</sub> (CHCl<sub>3</sub>): 477 nm. Found: C, 59.3; H, 6.9; N, 4.7. C<sub>56</sub>H<sub>80</sub>N<sub>4</sub>S<sub>2</sub>I<sub>2</sub> requires: C, 59.67; H, 7.15; N, 4.97. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz, *J*/Hz): δ<sub>H</sub> 1.28–1.38 (m, 24H, CH<sub>2</sub>), 1.64 (quintet, *J* 7.1, 4H, SCH<sub>2</sub>CH<sub>2</sub>), 1.89 (br m, 4H, CH<sub>2</sub>), 2.02 (br m, 4H, CH<sub>2</sub>CH<sub>2</sub>N<sup>+</sup>), 2.69 (t, *J* 7.2, 4H, SCH<sub>2</sub>), 2.91–2.98 (m, 8H, CH<sub>2</sub>), 3.05 (s, 12H, N(CH<sub>3</sub>)<sub>2</sub>), 4.70 (t, *J* 7.2, 4H, CH<sub>2</sub>N<sup>+</sup>), 6.72 (d, *J* 8.9, 4H, Ar-H), 7.44 (d, *J* 8.8, 4H, Ar-H), 7.46 (s, 2H, C=C-H), 8.10 (d, *J* 7.0, 2H, Qn-H), 8.81 (d, *J* 6.2, 2H, Qn-H), 9.00 (s, 2H, Qn-H). *m/z* (FAB): 436,

100% [M - 2I]<sup>2+</sup>; 999, 30% [M - I]<sup>+</sup>. HRMS (ES<sup>+</sup>): *m/z* calcd for C<sub>56</sub>H<sub>80</sub>N<sub>4</sub>S<sub>2</sub> 436.2907, found 436.2912; calcd for C<sub>56</sub>H<sub>80</sub>N<sub>4</sub>S<sub>2</sub>I 999.4864, found 999.4863.

**Precursor to SAM 3.** To a solution of 4-picoline (0.93 g, 10 mmol) in acetonitrile (100 cm<sup>3</sup>) was added thioacetic acid *S*-(10-iododecyl) ester (3.42 g, 10 mmol), the mixture being kept under nitrogen and heated at reflux for 2 days. The solvent was reduced in vacuo at ambient temperature, and the resultant oil was triturated with anhydrous diethyl ether to give 1-(10-acetylsulfanyldodecyl)-4-methylpyridinium iodide as a pale yellow solid: 89%, mp 67–69 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz, *J*/Hz): δ<sub>H</sub> 1.23–1.32 (m, 12H, CH<sub>2</sub>), 1.53 (quintet, *J* 7.1, 2H, SCH<sub>2</sub>CH<sub>2</sub>), 2.01 (p, *J* 6.7, 2H, CH<sub>2</sub>CH<sub>2</sub>N<sup>+</sup>), 2.31 (s, 3H, CH<sub>3</sub>CO), 2.68 (s, 3H, Py-CH<sub>3</sub>), 2.83 (t, *J* 7.3, 2H, SCH<sub>2</sub>), 4.85 (t, *J* 7.4, 2H, CH<sub>2</sub>N<sup>+</sup>), 7.90 (d, *J* 6.3, 2H, Py-H), 9.20 (d, *J* 6.5, 2H, Py-H). *m/z* (FAB): 308, 100% [M - I]<sup>+</sup>.

A solution of the above product (0.44 g, 1 mmol), 4-dimethylaminobenzaldehyde (0.15 g, 1 mmol), and piperidine (0.2 cm<sup>3</sup>) in methanol (50 cm<sup>3</sup>) was heated at reflux for 24 h, following which the solvent was removed in vacuo at ambient temperature. The resultant oil was purified by column chromatography on silica gel, eluting with chloroform and then chloroform-methanol (90:10 v/v) to obtain bis-[1-(10-decyl)-4-(2-(4-dimethylaminophenyl)vinyl)pyridinium iodide]disulfide as a red solid: yield 67%, mp 200–202 °C. λ<sub>max</sub> (CHCl<sub>3</sub>): 495 nm. Found: C, 57.4; H, 7.0; N, 5.1. C<sub>50</sub>H<sub>72</sub>N<sub>4</sub>S<sub>2</sub>I<sub>2</sub> requires: C, 57.35; H, 6.93; N, 5.35. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz, *J*/Hz): δ<sub>H</sub> 1.26 (br s, 24H, CH<sub>2</sub>), 1.66 (quintet, *J* 7.1, 4H, SCH<sub>2</sub>CH<sub>2</sub>), 1.97 (br s, 4H, CH<sub>2</sub>CH<sub>2</sub>N<sup>+</sup>), 2.68 (t, *J* 7.2, 4H, SCH<sub>2</sub>), 3.05 (s, 12H, N(CH<sub>3</sub>)<sub>2</sub>), 4.63 (t, *J* 7.4, 4H, CH<sub>2</sub>N<sup>+</sup>), 6.68 (d, *J* 8.1, 4H, Ar-H), 6.88 (d, *J* 15.9, 2H, C=C-H), 7.54 (d, *J* 8.4, 4H, Ar-H), 7.63 (d, *J* 16.1, 2H, C=C-H), 7.90 (d, *J* 6.5, 4H, Py-H), 8.90 (d, *J* 6.5, 4H, Py-H). *m/z* (FAB): 396, 100% [M - 2I]<sup>2+</sup>; 919, 15% [M - I]<sup>+</sup>. HRMS (ES<sup>+</sup>): *m/z* calcd for C<sub>50</sub>H<sub>72</sub>N<sub>4</sub>S<sub>2</sub> 396.2594, found 396.2587; calcd for C<sub>50</sub>H<sub>72</sub>N<sub>4</sub>S<sub>2</sub>I 919.4238, found 919.4248.

**Precursor to SAM 4.** To a solution of 1-(10-acetylsulfanyldodecyl)-4-methylquinolinium iodide (0.48 g, 1 mmol) and 4-hydroxybenzaldehyde (0.12 g, 1 mmol) in methanol (20 cm<sup>3</sup>) was added piperidine (0.2 cm<sup>3</sup>), and the resultant mixture was heated at reflux for 6 h. The solvent was removed in vacuo at ambient temperature, and the crude product was purified by column chromatography on silica gel, eluting with chloroform and chloroform-methanol (10:1 to 2:1, v/v). The resultant oil was dissolved in methanol and triturated with diethyl ether to yield bis-[1-(10-decyl)-4-(2-(4-hydroxyphenyl)vinyl)quinolinium iodide]disulfide as a yellow solid. <sup>1</sup>H NMR (CDCl<sub>3</sub> + CF<sub>3</sub>COOD, 250 MHz, *J*/Hz): δ<sub>H</sub> 1.27 (br s, 24H, CH<sub>2</sub>), 1.65 (quintet, *J* 7.2, 4H, SCH<sub>2</sub>CH<sub>2</sub>), 2.08 (quintet, *J* 7.4, 4H, CH<sub>2</sub>CH<sub>2</sub>N<sup>+</sup>), 2.70 (t, *J* 7.2, 4H, SCH<sub>2</sub>), 4.83 (t, *J* 7.2, 4H, CH<sub>2</sub>N<sup>+</sup>), 6.99 (d, *J* 8.7, 4H, Ar-H), 7.66 (d, *J* 8.8, 4H, Ar-H), 7.85 (d, *J* 15.5, 2H, C=C-H), 7.95 (d, *J* 8.7, 2H, Qn-H), 8.00 (br m, 4H, C=CH and Qn-H), 8.08 (t, *J* 8.0, 2H, Qn-H), 8.18 (d, *J* 7.7, 2H, Qn-H), 8.44 (d, *J* 8.5, 2H, Qn-H), 8.81 (d, *J* 6.3, 2H, Qn-H), 9.65 (s, 1H, OH). *m/z* (FAB): 419, 100% [M - 2I]<sup>2+</sup>; 837, 20% [M - HI - I]<sup>+</sup>; 965, 5% [M - I]<sup>+</sup>. HRMS (ES<sup>+</sup>): *m/z* calcd for C<sub>54</sub>H<sub>66</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub> 419.2272, found 419.2279; calcd for C<sub>54</sub>H<sub>65</sub>-N<sub>2</sub>O<sub>2</sub>S<sub>2</sub> 837.4482, found 837.4489; calcd for C<sub>54</sub>H<sub>66</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>I 965.3605, found 965.3613.

**Precursor to SAM 5.** To a solution of 1-(10-acetylsulfanyldodecyl)-5,6,7,8-tetrahydroisoquinolinium iodide (0.48 g, 1 mmol) and 4-hydroxybenzaldehyde (0.12 g, 1 mmol) in methanol (20 cm<sup>3</sup>) was added piperidine (0.2 cm<sup>3</sup>), and the resultant mixture was heated at reflux for 6 h. The solvent was removed in vacuo at ambient temperature, and the crude product was purified by column chromatography on silica gel, eluting with ethyl acetate and then methanol. The resultant oil was dissolved in methanol and triturated with diethyl ether to precipitate bis-[1-(10-decyl)-5-(4-hydroxybenzylidene)-5,6,7,8-tetrahydroisoquinolinium iodide]disulfide as a yellow solid. <sup>1</sup>H NMR (CDCl<sub>3</sub> + CF<sub>3</sub>-COOD, 250 MHz, *J*/Hz): δ<sub>H</sub> 1.28 (br s, 24H, CH<sub>2</sub>), 1.64 (quintet, *J* 7.1, 4H, SCH<sub>2</sub>CH<sub>2</sub>), 1.89 (br s, 4H, CH<sub>2</sub>), 2.00 (br s, 4H, CH<sub>2</sub>CH<sub>2</sub>N<sup>+</sup>),

**Table 2.** Absorption Maxima of the Dyes and Their Protonated Forms

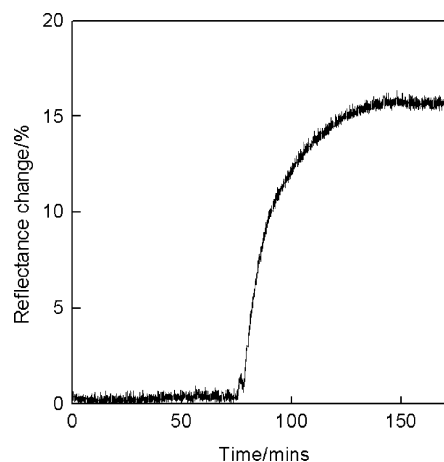
dye	$\lambda_{\max}(\text{CHCl}_3)/\text{nm}$	
	unprotonated	protonated
<b>1</b>	563	353
<b>2</b>	477	336
<b>3</b>	495	340
<b>4</b>	670	388
<b>5</b>	490	388
<b>6</b>	490	394
<b>7</b>	706 <sup>a</sup>	322 <sup>a</sup>

<sup>a</sup> Limited solubility necessitated study in  $\text{CH}_3\text{CN}$ .

2.70 (t,  $J$  7.2, 4H,  $\text{SCH}_2$ ), 2.91–2.97 (m, 8H,  $\text{CH}_2$ ), 4.41 (t,  $J$  7.5, 4H,  $\text{CH}_2\text{N}^+$ ), 6.95 (d,  $J$  8.7, 4H, Ar–H), 7.42 (d,  $J$  8.3, 4H, Ar–H), 7.51 (s, 2H, C=C–H), 7.90 (d,  $J$  6.7, 2H, Qn–H), 8.11 (d,  $J$  6.7, 2H, Qn–H), 8.21 (s, 1H, Qn–H), 9.73 (s, 1H, OH).  $m/z$  (FAB): 409, 100% [ $\text{M} - 2\text{I}^-$ ]<sup>+</sup>; 817, 10% [ $\text{M} - \text{HI} - \text{I}^-$ ]<sup>+</sup>; 945, 5% [ $\text{M} - \text{I}^-$ ]<sup>+</sup>. HRMS (ES<sup>+</sup>):  $m/z$  calcd for  $\text{C}_{52}\text{H}_{70}\text{N}_2\text{O}_2\text{S}_2$  409.2434, found 409.2432; calcd for  $\text{C}_{52}\text{H}_{69}\text{N}_2\text{O}_2\text{S}_2$  817.4795, found 817.4801; calcd for  $\text{C}_{52}\text{H}_{70}\text{N}_2\text{O}_2\text{S}_2\text{I}$  945.3918, found 945.3921.

**Precursor to SAM 6.** To a solution of 1-(10-acetylsulfanyldecyl)-4-methylpyridinium iodide (0.44 g, 1 mmol) and 4-hydroxybenzaldehyde (0.12 g, 1 mmol) in methanol (20  $\text{cm}^3$ ) was added piperidine (0.2  $\text{cm}^3$ ), and the resultant mixture was heated at reflux for 6 h. The solvent was removed in vacuo at ambient temperature, and the crude product was purified by column chromatography on silica gel, eluting with ethyl acetate and then methanol. The resultant oil was dissolved in methanol and triturated with diethyl ether to precipitate bis-[1-(10-decyl)-4-(2-(4-hydroxyphenyl)vinyl)pyridinium iodide]disulfide as a yellow solid. <sup>1</sup>H NMR ( $\text{CDCl}_3$  and  $\text{CF}_3\text{COOD}$ , 250 MHz,  $J/\text{Hz}$ ):  $\delta_{\text{H}}$  1.28 (br s, 24H,  $\text{CH}_2$ ), 1.64 (quintet,  $J$  7.1, 4H,  $\text{SCH}_2\text{CH}_2$ ), 2.00 (br s, 4H,  $\text{CH}_2\text{CH}_2\text{N}^+$ ), 2.64 (t,  $J$  7.2, 4H,  $\text{SCH}_2$ ), 4.46 (t,  $J$  7.5, 4H,  $\text{CH}_2\text{N}^+$ ), 6.50 (d,  $J$  8.0, 4H, Ar–H), 7.14 (d,  $J$  16.0, 2H, C=C–H), 7.58 (d,  $J$  8.4, 4H, Ar–H), 7.81 (d,  $J$  16.0, 2H, C=C–H), 8.05 (d,  $J$  6.7, 4H, Py–H), 8.67 (d,  $J$  6.5, 4H, Py–H).  $m/z$  (FAB): 369, 100% [ $\text{M} - 2\text{I}^-$ ]<sup>+</sup>; 737, 20% [ $\text{M} - \text{HI} - \text{I}^-$ ]<sup>+</sup>; 865, 5% [ $\text{M} - \text{I}^-$ ]<sup>+</sup>. HRMS (ES<sup>+</sup>):  $m/z$  calcd for  $\text{C}_{46}\text{H}_{62}\text{N}_2\text{O}_2\text{S}_2$  369.2121, found 369.2118; calcd for  $\text{C}_{46}\text{H}_{61}\text{N}_2\text{O}_2\text{S}_2$  737.4169, found 737.4179; calcd for  $\text{C}_{46}\text{H}_{62}\text{N}_2\text{O}_2\text{S}_2\text{I}$  865.3292, found 865.3300.

**Protonation.** The dyes exhibit a characteristic blue-shifted absorption when exposed to acid, but the charge-transfer band is restored when exposed to base (Table 2). Such changes also influence the SPR spectrum with the resonant angle in each case shifting to lower values when the dye is protonated. Glass/Au/SAM structures of the protonated forms of **1** to **7**, at an excitatory wavelength of 632.8 nm, exhibit optimum reflectance changes of 2–15% when exposed to 100 ppm of  $\text{NH}_3$  in a carrier gas, this being induced by the altered dielectric permittivities and absorption characteristics of the two forms. SAM **1** exhibits the largest reflectance change (Figure 12), the protonated form being transparent at the excitatory wavelength and the dye absorbing.



**Figure 12.** Variation of the reflectance from a glass/Au/SAM structure of the protonated form of **1** when exposed to 100 ppm  $\text{NH}_3$  in nitrogen and investigated at  $-0.2^\circ$  from the resonant angle. Reversal occurs when exposed to an acidified carrier gas. At the excitatory wavelength of 632.8 nm, the dielectric permittivities are  $\epsilon_r = 3.4 \pm 0.1$  and  $\epsilon_i \approx 0.7 \pm 0.1$  (dye) and  $\epsilon_r \approx 2.0$  and  $\epsilon_i \approx 0$  (protonated).

The films may be suitable for use as acid/base sensors with concentration monitored by utilizing changes in the SPR reflectance at a fixed angle of incidence. However, in this work, the switching has simply been used to disrupt the charge-transfer axis and to investigate its effect on the I–V characteristics.

**Monolayer Preparation.** The 10 MHz quartz crystals, which were gold-coated prior to purchase, were washed sequentially with chloroform, acetone, and water and then primed by plasma cleaning using a PlasmaPrep 2 (Gala Instrumente). BK7 glass and HOPG substrates were coated just prior to use, and the dyes self-assembled without further processing. SAMs were obtained by immersion of the substrates in ethanol solutions of the precursors (0.05  $\text{mg cm}^{-3}$ ), and the layer thickness and mean molecular area were determined by SPR and quartz crystal microbalance studies, respectively. Film dimensions were monitored as a function of the immersion time to determine the optimum conditions for chemisorption, the substrates being immersed for several short periods and thoroughly rinsed each time with chloroform and ethanol to remove any physisorbed material. A few drops of ammonium hydroxide were added to displace the acetyl groups from precursor **1** and **7** and to obtain the merocyanine rather than the protonated forms of **4** to **6**.

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