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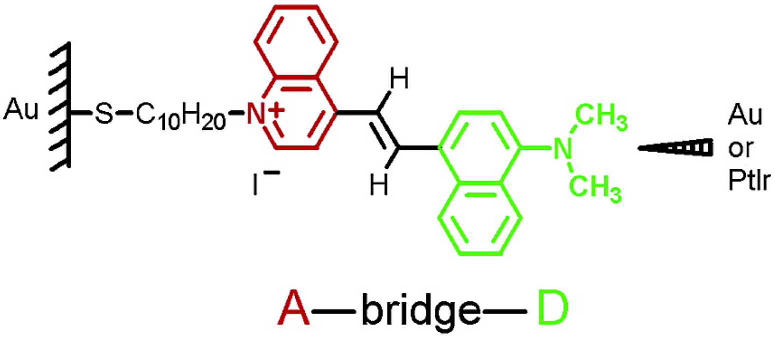

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Improved Molecular Rectification from Self-Assembled Monolayers of a Sterically Hindered Dye

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Abstract: Self-assembled monolayers (SAMs) formed from the reaction of 1-(10-acetylsulfanyldecyl)-4-{2-(4-dimethylaminonaphthalen-1-yl)-vinyl}-quinolinium iodide (**1a**) and gold-coated substrates exhibit asymmetric current−voltage (I−V) characteristics with a rectification ratio of 50−150 at ±1 V. It is the highest to date for a molecular diode, and the improved behavior may be assigned in part to the controlled alignment of the donor−(π-bridge)−acceptor moieties and in part to steric hindrance, which imposes a nonplanar structure and effectively isolates the molecular orbitals of the donor and acceptor end groups. The molecular origin of the rectification is verified by its suppression upon exposure to HCl vapor, which protonates the dimethylamino group and inhibits the electron-donating properties, with restoration upon exposure to NH_3. It is also established by a reduced rectification ratio of ca. 2 at ±1 V when the cationic $D-\pi-A^+$ moieties adopt an antiparallel arrangement in self-assembled films of the derivative, bis-[1-(10-decyl)-4-{2-(4-dimethylaminonaphthalen-1-yl)-vinyl}-quinolinium]-disulfide diiodide (**1b**), which adsorbs via one of its terminal donors without rupture of the sulfur−sulfur bond: $Au|D-\pi-A^+-C_{10}H_{20}-S-S-C_{10}H_{20}-{}^+A-\pi-D\ (I^-)_2$.

Introduction

Intrinsic rectification from organic materials arises when a donor/acceptor sequence is aligned between nonoxidizable electrodes, the devices being classified as rectifying junctions when separate layers of donors and acceptors are in physical contact[1−3] and as molecular diodes when the subunits are linked via an electron bridge.[4−11] There are few examples. Eight D−bridge−A materials are known to exhibit asymmetric I−V characteristics when aligned as Langmuir−Blodgett (LB) films[4−6,7a] or SAMs[7−11] and contacted by noble metal electrodes, while others show similar behavior when the contact is protected by a surface coating: for example, Pt/(LB film)/Mg/Ag[12,13] and Au/(LB film)/Hg−S−C_nH_{2n+1}.[14] There are also many reports of molecular rectification from films contacted by oxidizable electrodes, but such claims are ambiguous as the molecule-induced effects are probably overwhelmed by electrical asymmetry from oxide-induced Schottky barriers. Their influence is highlighted by the properties of magnesium phthalocyanine, which exhibits symmetrical I−V characteristics when sandwiched between gold and aluminum and investigated before breaking the vacuum but has a rectification ratio of ca. 1000 at ±2 V when exposed to air and reevacuated.[15] Similar charac-

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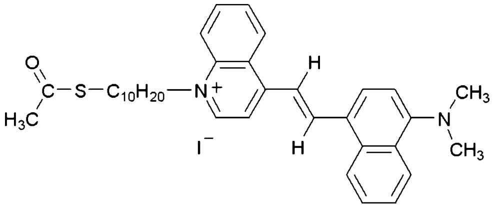

Figure 1. Molecular structure of the sterically hindered precursor, 1-(10-acetylsulfanyldecyl)-4-{2-(4-dimethylaminonaphthalen-1-yl)-vinyl}-quinolinium iodide (**1a**), for self-assembly on gold substrates.

teristics are also reported for organic films contacted by titanium, where the properties are dependent upon trace gases present during evaporation of the electrode.[16]

Claims of molecular rectification should be restricted to films contacted by nonoxidizable electrodes, and, to exclude electrode-induced effects, it is also advisable to corroborate the influence of the organic layer by chemically disrupting the rectifying moiety[7b,8,10] or by reversing the orientation of the molecular dipole.[4c,11] For example, LB monolayers of the isomers, *N*-hexadecyl-5-[4-(*N*,*N*-dimethylamino)-benzylidene]-5,6,7,8-tetrahydroisoquinolinium iodide [$C_{16}H_{33}{-}A^+{-}\pi{-}D\ I^-$] and *N*-methyl-5-[4-(*N*-methyl-*N*-hexadecylamino)-benzylidene]-5,6,7,8-tetrahydroiso-quinolinium iodide [$C_{16}H_{33}{-}D{-}\pi{-}A^+\ I^-$], where the hydrophobic tail is located on opposite sides of the chromophore, exhibit rectification in opposite quadrants of the I−V plot.[4c] The behavior is induced by reversed chromophore alignments, and, as predicted by the Aviram and Ratner model,[17] electron flow at forward bias is from the cathode to acceptor on one side of the device and from the donor to anode on the other side. It confirms that the behavior is intrinsic to the molecule and not induced by the contacts, this also being corroborated by symmetrical I−V characteristics from 1:1 mixed films of the isomers in which the molecular dipoles are randomly oriented.

In this work, we now report improved rectification from molecular diodes formed from the reaction of 1-(10-acetylsulfanyldecyl)-4-{2-(4-dimethylaminonaphthalen-1-yl)-vinyl}-quinolinium iodide (**1a**, Figure 1) and gold-coated substrates. They exhibit improved rectification ratios of 50−150 at ±1 V, which may be compared to 11−18 at ±1 V for SAMs of a less sterically hindered dimethylaminophenyl analogue[10] and ca. 1 at ±1 V for those formed from the *N*-(10-acetylsulfanyldecyl)-4-{2-(4-dimethylaminophenyl)-vinyl}-pyridinium derivative, which has an almost planar chromophore. The structure/property relationship highlights the dependence of the rectification upon steric hindrance, the $D{-}\pi{-}A^+$ moiety reported here having double-ring substituents on opposite sides of a CH═CH bridge, which induce the nonplanarity. MOPAC calculations show the electroactive ends to be rotated out-of-plane with a dihedral angle of 61° between the separate ring systems. Rectification arises from the broken conjugation. It effectively confines the orbitals of the donor and acceptor moieties to opposite sides of the bridge and, when contacted by nonoxizable electrodes, electrons move at forward bias from the substrate electrode (cathode) to acceptor on one side of the device and from the donor to probe (anode) on the other. The molecular and Fermi energies are mismatched at reverse bias, and improved rectification has been achieved from monolayer films.

The nonplanar $D{-}\pi{-}A^+$ moiety may be likened to the σ-bridged diode proposed by Aviram and Ratner.[17] The latter is preferable for rectification, but, as two of the three reported examples[12−14] exhibit rectification at bias opposite to that predicted by LB alignment, it is feasible that a σ-bridge permits a "scorpion-like" configuration with the donor located over the back of the acceptor. It is therefore necessary to consider the rigidity of the bridge, and, for this reason, the Cranfield study is restricted to sterically hindered π-bridged molecules where alignment is controlled by self-assembly.

Results and Discussion

Noncentrosymmetric SAMs. Films were obtained by immersing platinum and gold-coated substrates, for example, highly oriented pyrolytic graphite (HOPG), BK7 glass, and 10 MHz quartz crystals, in ethanol solutions of 1-(10-acetylsulfanyldecyl)-4-{2-(4-dimethylaminonaphthalen-1-yl)-vinyl}-quinolinium iodide (0.1 mg cm^{-3}) to which two drops of ammonia were added to displace the acetyl group. Substrates were repeatedly immersed for periods of 1 h and thoroughly rinsed each time with solvent to remove physisorbed material from the surface. Optimum conditions for chemisorption were obtained by monitoring the frequency of the gold-coated quartz crystals, which saturate to a constant value after a combined immersion period of ca. 8 h, and a Sauerbrey analysis[18] of the change provides a limiting area of 0.35 ± 0.03 nm^2 $molecule^{-1}$ (Figure 2). It approximates to the van der Waals cross-section of the wide-bodied chromophore, the quinolinium and naphthalene groups having cross-sections of 0.28 nm^2 each, and denotes close packing of the chromophores. The immersion time to achieve the limiting area is considerably longer than previously observed for related dyes, typically 1−2 h under similar conditions,[7−11] and it is feasible that physisorption via the $N(CH_3)_2$ group[1] competes with and temporarily blocks chemisorption via the sulfur atom. However, the latter is verified by X-ray photoelectron spectrometry (XPS), a peak at 162 eV being characteristic of the S 2p binding energy of the gold thiolate link.

Surface plasmon resonance (SPR) studies were performed on SAMs on gold-coated BK7 glass slides using an attenuated

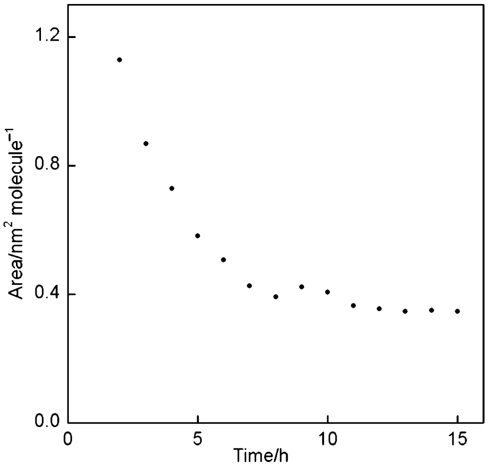

Figure 2. Variation of the mean molecular area versus the total period of immersion of a gold-coated 10 MHz quartz crystal in an ethanol solution of 1-(10-acetylsulfanyldecyl)-4-{2-(4-dimethylaminonaphthalen-1-yl)-vinyl}-quinolinium iodide (**1a**, 0.1 mg cm^{-3}) to which two drops of ammonia were added.

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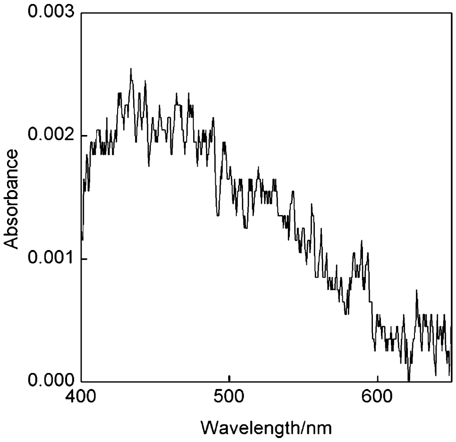

Figure 3. Visible spectrum of the SAM on platinum-coated glass substrates, the spectrum being corrected for absorption by the latter.

total reflection geometry in the Kretschmann configuration,[19] the gold coating being ca. 47 nm thick. Substrates were index matched to one face of a 60° BK7 crown glass prism, and reflectivity data were collected as the angle of incidence of a HeNe laser beam ($\lambda = 632.8$ nm, p-polarized) was varied. The data were corrected for reflections at the entrance and exit faces of the prism using Fresnel reflection formulas and then analyzed to provide thicknesses of the gold and SAM as well as the real (ϵ_r) and imaginary (ϵ_i) components of the dielectric permittivity of each. A two-layer analysis of the SPR data, with all six parameters unrestrained during fitting, provided the following for the organic layer: $d = 2.4 \pm 0.2$ nm; $\epsilon_r = 2.3 \pm 0.1$; and $\epsilon_i = 0.3 \pm 0.1$. The thickness is consistent with the cationic $D-\pi-A^+$ moieties being upright with the flexible linking groups tilting to fill the available space and is smaller than expected for the spherical counterions to reside at the surface, the ionic radius of iodide being 0.206 nm. It is feasible that they reside between molecules, and we note that the mean area of 0.35 ± 0.03 nm^2 molecule^{-1} derived from the frequency data is sufficient to locate the iodides in the region of the CH=CH bridging group.

Spectroscopic studies were performed in transmission but for the self-assembled dye on platinum-coated glass, the metal being preferable to gold as it has an uncomplicated absorption profile that may be subtracted to reveal the visible spectrum of the SAM. It exhibits a broad absorption centered about 450 nm (Figure 3), the maximum being shifted from 535 nm for the dye in chloroform. Such shifts are characteristic of the aggregate spectra of polar molecules and result from a parallel side-by-side alignment.

A cursory study of the surface structure of the SAM on gold-coated HOPG was performed using a Nanoscope IV scanning tunneling microscope (Figure 4), and characteristic I−V curves were then obtained at locations across each of three films (Figure 5). Surface features distant from grain boundaries were targeted, and, after successfully landing the probe, the data were averaged for typically 10−50 scans at each of the sites for set point currents of 0.2−0.5 nA and a substrate voltage of −0.2 V. Variation of these settings had minimal effect on the electrical asymmetry, and indistinguishable I−V curves were obtained using Au and PtIr probes. Extensive studies on other

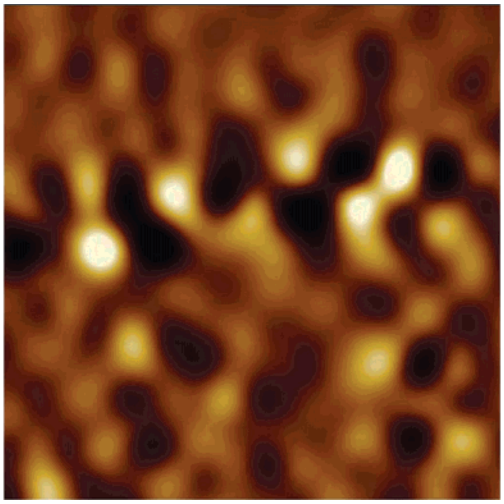

Figure 4. A 5 nm × 5 nm STM image of the rectifying monolayer, the data being obtained at a set point current of 0.2 nA and substrate bias of −1 V. The surface structure is different from that of the underlying gold layer, and there appear to be no features with dimensions that correspond to the iodide counterion.

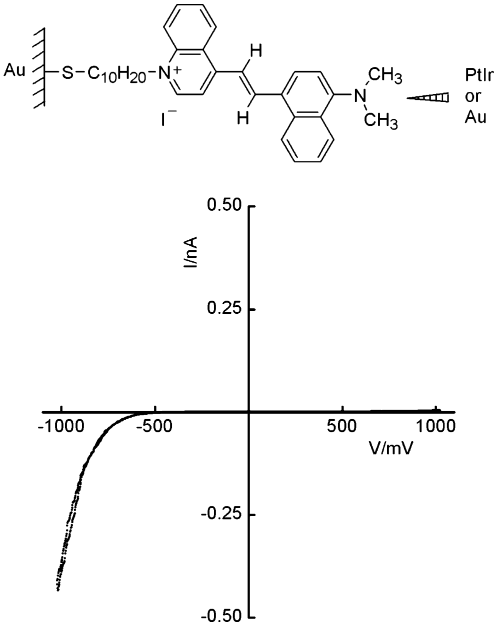

Figure 5. Device structure and I−V characteristics obtained by averaging 10 scans on the same site for a set point current of 0.35 nA and bias of −0.2 V, the behavior being indistinguishable when studied using Au and PtIr probes. The bias is defined by the sign of the substrate electrode, and the higher current in the negative quadrant corresponds to electron flow from the gold-coated substrate to the contacting tip. Similar behavior is obtained when the set point current and voltage are varied: they affect the magnitude of the current by influencing the distance between probe and surface but have no noticeable effect on the rectification ratio relative to the natural spread of values.

Au|monolayer structures show no obvious differences when contacted by these probes,[7b,9,10] the work function of the latter (PtIr, 5.5 eV)[20] being closely matched to that of substrate (Au, 5.2 eV),[21] but electrode-induced electrical asymmetry arises when the work functions are unmatched. Phthalocyanine LB films on HOPG exhibit rectification ratios of ca. 2.0 at ±2 V

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when contacted by PtIr.[22] The work function of the substrate electrode (HOPG, 4.6 eV)[23] is significantly lower, but the electrical asymmetry is trivial relative to the high rectification ratio obtained from the molecular diode shown in Figure 5.

I−V characteristics of the SAM were averaged for typically 10 scans on the same spot and investigated across 40 regions of three different films: ca. 80% provide rectification ratios in excess of 50 at ±1 V, of which 40% exhibit values in the range 100−150 at ±1 V (Figure 5) and may be compared to reported ratios of 4−30 at ±1 V for SAMs and LB monolayers contacted by nonoxidizable electrodes.[4−11] The improved behavior is attributed to controlled alignment of the sterically hindered chromophore, Au−$C_{10}H_{20}$−A^+−π−D. All scans exhibit higher forward bias currents in the negative quadrant of the I−V plot, designated here by the sign of the substrate electrode. It signifies electron tunneling from the cathode to lowest unoccupied molecular orbital (LUMO) of the heterocyclic acceptor on one side and from the highest occupied molecular orbital (HOMO) of the dimethylamino donor to anode on the other, with an energy mismatch between the molecular and Fermi levels at reverse bias.

Role of the Counterion. The location of the spherical counterions is ambiguous, but a film thickness of 2.4 nm and mean molecular area of 0.35 ± 0.03 nm^2 suggest that they probably reside in the region of the narrow CH═CH bridge that connects the donor and acceptor. They would then be trapped by surrounding molecules, and the I−V characteristics, which show minimal hysteresis and are stable for multiple scans, appear to confirm that the iodides are not shifted by the electric field. Any ambiguity is eliminated by tethering the counterions to the substrate, and, in this work, we report results from preliminary studies on SAMs obtained by metathesis of 1-methyl-4-{2-(4-dimethylaminonaphthalen-1-yl)-vinyl}-quinolinium iodide with an anionic surface, which acts as the counterion (Figure 6). Films were obtained by immersing gold-coated substrates in a methanol solution of sodium 3-mercapto-1-propanesulfonate for ca. 4 h and then in an aqueous methanol solution of the dye for ca. 2 h to yield Au−S−$(CH_2)_3SO_3^-$|A^+−π−D structures. A broad absorption band at 450 nm, characteristic of the cationic dye, confirms metathesis, and XPS studies provide data that are unique to the component species: 162 eV (S 2p, Au−S); 167 eV (S 2p, SO_3^-); 530 eV (O 1s); 400 eV (N 1s). These hybrid structures on gold-coated HOPG exhibit I−V curves that are similar to those of the conventional self-assembled structure shown in Figure 5: the rectification ratio is 100−200 at ±1 V, and the higher current results when the substrate electrode is negatively biased. It confirms that the dye molecule is aligned with the positively charged *N*-methyl-4-quinolinium group adjacent to the anionic surface, the direction of electron flow at forward bias being from substrate (cathode) to quinolinium acceptor on one side of the device and from the dimethylamino donor to contacting probe (anode) on the other.

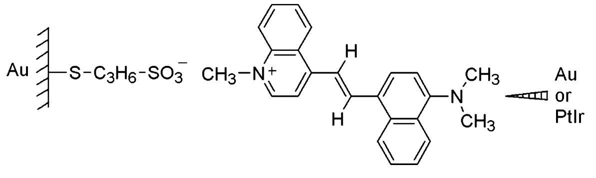

Figure 6. Molecular structure of Au−S−$(CH_2)_3SO_3^-$|A^+−π−D aligned films where the cationic dye is 1-methyl-4-{2-(4-dimethylaminonaphthalen-1-yl)-vinyl}-quinolinium iodide (**1c**). These hybrid structures exhibit I−V characteristics that are similar to those of **1a** but with slightly higher rectification ratios in the range 100−200 at ±1 V.

Disruption of the Donor−Acceptor Combination. The dye is susceptible to protonation and exhibits decoloration as the $N(CH_3)_2$ group converts to $^+NH(CH_3)_2$ with suppression of its electron-donating properties. The intramolecular charge-transfer band at 535 nm in ethanol diminishes with evolution of a transition at 400 nm when acid is added to solution (Figure 7). The original spectrum is restored upon addition of base, and the reversibility is also demonstrated by changes to the I−V characteristics. The SAM exhibits symmetrical I−V curves when briefly exposed to HCl vapor (Figure 8), the film this time being contacted by a PtIr probe that appears not to affect the shape of the I−V curve even though the work functions of the substrate and probe are slightly different. Rectification is restored when the SAM is exposed to NH_3 vapor and thoroughly rinsed with water to remove NH_4Cl from the surface. The reversibility verifies the molecular origin of the rectification as the donor/acceptor combination is disrupted and restored and permits us to exclude electrode-induced effects (e.g., different work functions) as well as asymmetric coupling of the

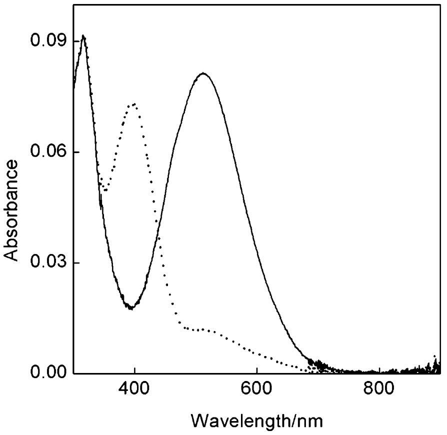

Figure 7. Visible spectrum of 1-(10-acetylsulfanyldecyl)-4-{2-(4-dimethylaminonaphthalen-1-yl)-vinyl}-quinolinium iodide in ethanol before (λ_{max} = 535 nm, solid line) and after (λ_{max} = 400 nm, broken line) the addition of one drop of concentrated HCl solution.

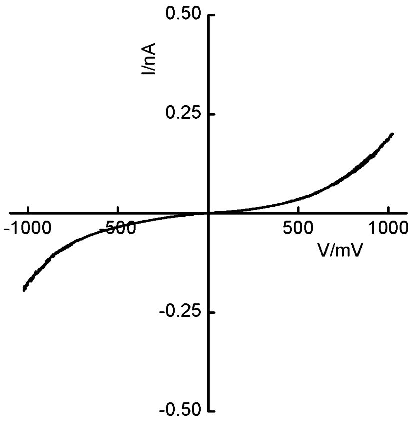

Figure 8. I−V characteristics of the SAM on gold-coated HOPG contacted by a PtIr probe following brief exposure to HCl vapor, which suppresses the electron donor properties at the upper interface. The curve was obtained using a set point current and voltage of 0.35 nA and −0.2 V, respectively, and the data were averaged for 10 scans on the same site. The magnitude of the current is dependent upon the set point conditions, which affect the contact distance between probe and surface, whereas the symmetrical shape of the curve is independent of the operating conditions.

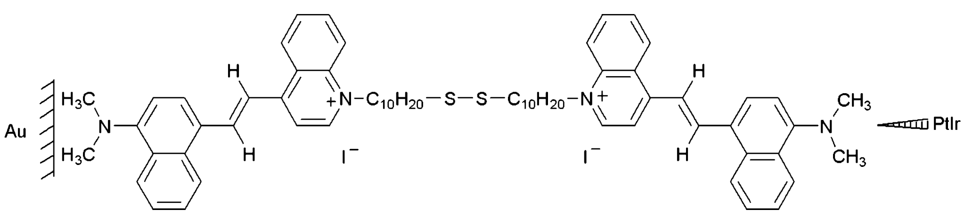

Figure 9. Molecular structure of bis-[1-(10-decyl)-4-{2-(4-dimethylaminonaphthalen-1-yl)-vinyl}-quinolinium]-disulfide diiodide (**1b**).

$D-\pi-A^+$ moiety with the electrodes as the cause of the behavior.

Symmetrical Bilayer Structures. SAMs formed from the thioacetate derivative self-assemble in a conventional manner via an $Au-S-C_{10}H_{20}$ link, whereas those formed from bis-[1-(10-decyl)-4-{2-(4-dimethylaminonaphthalen-1-yl)-vinyl}-quinolinium]-disulfide diiodide (**1b**, Figure 9) appear to assemble via physisorption of a terminal $N(CH_3)_2$ group without rupture of the central sulfur−sulfur bond. It is assumed that steric hindrance inhibits close contact between the gold substrate and center of the molecule, and this alternative arrangement provides an explanation of the anomalous rectification reported for the adsorption of $TCNQ-C_{10}H_{20}-S-S-C_{10}H_{20}-TCNQ$ on silver-coated substrates.[24] There is a precedent from this work for physisorption via one of the end groups, and, as TCNQ is also known to react to yield a surface layer of $Ag^{\delta+}TCNQ^{\delta-}$,[25] it is feasible that the electrical asymmetry arises from a chemically induced Schottky barrier rather than the molecule itself, which is simply an asymmetrically coupled electron acceptor when chemisorbed as $Ag-S-C_{10}H_{20}-TCNQ$.

Evidence of physisorption is provided by deposition studies on gold-coated 10 MHz quartz crystals as well as from XPS studies of the SAM. A Sauerbrey analysis[18] of the frequency data provides areas of 0.15−0.21 nm^2 molecule^{-1} from 16 separate studies for a molecular mass of 623, which corresponds to chemisorption via rupture of the central sulfur−sulfur bond. The frequency change is approximately twice that obtained for the thioacetate derivative and saturates in a quarter of the time. Furthermore, the areas are significantly smaller than the molecular cross-section but increase to meaningful values of 0.30−0.42 nm^2 molecule^{-1} for a molecular mass of 1246, which corresponds to the full molecule (Figure 10). The data are consistent with physisorption of the disulfide molecules via their terminal $N(CH_3)_2$ groups, and this is confirmed by XPS studies, which show an S 2p peak at 165 eV, characteristic of the binding energy of nonadsorbed sulfur (cf., 162 eV for Au−S). Chemisorption is not ruled out, but as interaction with the gold substrate is competitive it would appear that the bulky molecular structure limits access to rupture the sulfur−sulfur link.

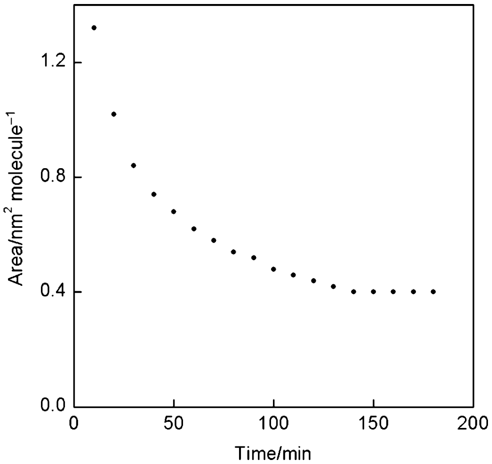

Figure 10. Variation of the mean molecular area versus the total period of immersion of a gold-coated 10 MHz quartz crystal in a solution of bis-[1-(10-decyl)-4-{2-(4-dimethylaminonaphthalen-1-yl)-vinyl}-quinolinium]-disulfide diiodide in ethanol (0.1 mg cm^{-3}). Limiting areas of 0.30−0.42 nm^2 molecule^{-1} from studies on 16 quartz crystals were calculated by assuming a molecular mass of 1246 for the adsorbed species, which corresponds to that of the full molecule without rupture of the S−S bond.

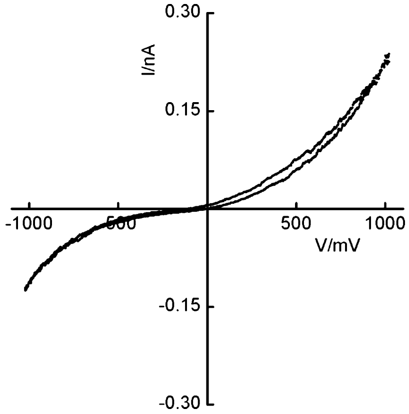

Figure 11. Typical I−V characteristics from a SAM of bis-[1-(10-decyl)-4-{2-(4-dimethylaminonaphthalen-1-yl)-vinyl}-quinolinium]-disulfide diiodide (**1b**) contacted by a PtIr probe, the data being averaged for 10 scans on the same site and obtained using a set point current and voltage of 0.2 nA and −0.2 V, respectively. The bias is defined by the sign of the substrate electrode, and the ratio of the current in the positive and negative quadrants is ca. 2 at ±1 V. The magnitude of the current is dependent upon the set point voltage and current, which influence the contact distance between probe and surface, whereas the general shape of the curve is independent of the operating conditions.

Such films exhibit almost symmetrical I−V characteristics with a tendency for the current to be slightly higher in the positive quadrant, where bias is defined as before, the behavior being reproducible for all films investigated as well as different regions of each (Figure 11). Rectification ratios of ca. 2 at ±1 V contrast with the much higher ratios of 50−150 at ±1 V of the chemisorbed film and may be explained by the donors locating at both interfaces: $Au|D-\pi-A^+-C_{10}H_{20}-S-S-C_{10}H_{20}-{}^+A-\pi-D\ (I^-)_2|PtIr$. The slight rectification is unlikely to arise from the different work functions (Au, 5.2 eV; PtIr, 5.5 eV),[20,21] as these should promote tunneling from substrate

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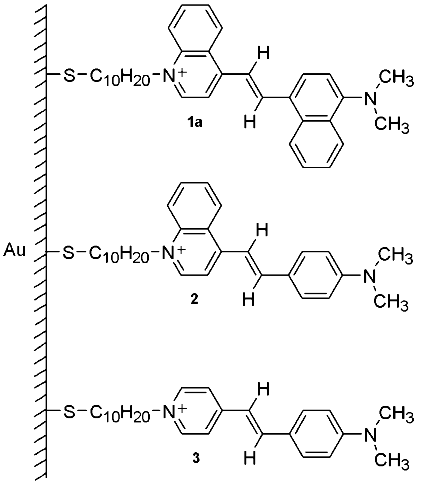

Figure 12. Molecular structures of self-assembling molecules that exhibit weaker steric hindrance as groups on opposite sides of the central CH═CH bridge are progressively changed from double-ring to single-ring substituents. For clarity, the counterions are omitted.

to tip and a higher current in the negative quadrant. It is also unlikely to be induced by the air gap between the PtIr probe and film, as this would also apply to I−V characteristics of the protonated form (Figure 8), which are symmetrical. It is feasible that the slight rectification arises from the D−π−A$^+$ moieties adopting different tilts at the two interfaces with significantly stronger coupling at the substrate electrode where the molecules are physisorbed and/or from polarization induced effects if the counterions locate differently on opposite sides on the film. However, whatever the mechanism, the partial suppression of the electrical asymmetry when the active moieties adopt an antiparallel arrangement corroborates the molecular origin of the rectifying behavior shown in Figure 5.

Structure/Property Relationship. The rectifying D−π−A$^+$ moiety is sterically hindered with double-ring substituents on opposite sides of a CH═CH bridge, and we note that the rectification ratio is dependent upon the size of the substituent groups. It decreases from an optimum of 150 at ±1 V for SAMs of **1a** to 18 at ±1 V when the double-ring naphthalene is substituted by benzene (**2**) to ca. 1 at ±1 V when the heterocycle is then substituted by pyridinium (**3**), the analogues being shown in Figure 12. Symmetrical I−V characteristics are also exhibited by SAMs of other sterically unhindered pyridinium dyes,[8,9] including neutral D−π−A chromophores, but rectification may be induced by appropriate substitution, for example, simply with a methyl to provide a sterically hindered nonplanar structure.[8] Intuitively, nonplanarity of the D−π−A$^+$ moiety should diminish with decreasing size of the substituent groups, and calculation of the dihedral angles between the planes of the component rings of the donor and acceptor moieties using the MOPAC/AM1 program of Cerius2 (Accelrys, Cambridge) provides confirmation. AM1 derived angles range from 61° for the sterically hindered dye (**1a**) to 10° for the nonrectifying 4-[2-(4-dimethylaminophenyl)-vinyl]-pyridinium analogue (**3**), the almost planar structure of the latter also being confirmed by X-ray structural studies.[26,27]

Table 1. AM1 Derived Dihedral Angles between Component Rings of the Donor and Acceptor Moieties, Rectification Ratios, and Absorption Maxima of the Dye When Self-Assembled and in Solution

			λ_{max}/nm	
dye	dihedral angle (deg)[a]	rectification ratio at ±1 V	SAM	$CHCl_3$
1a	61	50−150	450	535
2	31	11−18	540	563
3	10	1	460	495

[a] Calculations were performed on *N*-methyl derivatives.

There is correlation between the dihedral angle and rectification ratio but no obvious dependence of these properties on the charge-transfer spectra of these dyes (Table 1). Rectification requires the electrode Fermi levels at forward bias to align with the HOMO of the donor and LUMO of the acceptor, and there to be a significant energy mismatch at reverse bias. This in turn requires effectively isolating the donor and acceptor orbitals on opposite sides of the π-bridged molecule, and the high rectification ratio of 50−150 at ±1 V reported here suggests that the dihedral angle between the double-ring moieties is sufficient to break the conjugation to achieve this. It applies when the D−π−A$^+$ molecule is nonplanar, and the properties contrast with the nonrectifying behavior of the pyridinium derivative in which donor and acceptor are coupled via through-molecule orbital overlap.

Explanation of the rectifying behavior focuses upon the nonplanar D−π−A$^+$ moiety and pays no attention to electrical asymmetry induced by the Au−S−$C_{10}H_{20}$ linking group, which appears not to be relevant as it should also have effect when the donor−acceptor combination is disrupted by protonation (see Figure 8). Kornilovitch et al.[28] proposed rectification from a nonpolar conjugated unit when asymmetrically coupled to the electrodes via different alkanethiolate groups on opposite sides, Au−S−C_mH_{2m}−π−C_nH_{2n}−S−Au, and two experimental studies have since cited this model. The first involves contacting titanium electrodes,[29] but the intrinsic molecular properties are overwhelmed by a rectification ratio of 5×10^5 at ±2.3 V, which probably arises from an oxide-induced Ti/TiO_2 Schottky barrier. The second involves an elaborate Au|(Au nanoparticles)|$C_{17}H_{35}COO^-(Gd^{3+})_{1/3}$|$SiO_2$|Si structure,[30] where factors other than alkyl-induced spatial asymmetry come into play and its properties contrast with symmetrical I−V curves from an analogous device, studied at Cranfield, in which spatial symmetry is maintained by a $C_{18}H_{37}$−S−Au coated substrate electrode. There are also many nonrectifying examples where a conjugated unit is isolated from one of its electrodes by an alkyl or alkanethiolate tail, which suggests that the induced effect is negligible for characteristic tail lengths used in LB deposition and self-assembly. Furthermore, the rectifying behavior of Au|Au−S−C_nH_{2n}−Q3CNQ|PtIr,[7a] self-assembled from *Z*-β-[*N*-(ω-acetylsulfanylalkyl)-4-quinolinium]-α-cyano-4-styryldicyanomethanide, is independent of the length of the linking group: the rectification ratio is 30 at ±1 V for $3 \le n \le 12$, and the films exhibit symmetrical I−V curves when the donor group is inhibited by protonation. The same applies to analogues

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of SAM **2**, which exhibit rectification ratios of 11−18 at ±1 V with no apparent dependence upon length as the number of methylenes is increased from 3 to 10.[10] Thus, the linking group is unlikely to have any profound significance on the rectifying behavior of the sterically hindered dye reported here (Figure 5), and this is implied by the occurrence of symmetrical I−V characteristics when the electron-donating ability of the dimethylamino group is disrupted by protonation. The sterically hindered donor−acceptor combination is responsible for the observed molecular rectification.

Conclusion

Manipulation of the molecular structure and packing has resulted in improved electrical asymmetry from films of a sterically hindered chromophore, and rectification ratios of 50−150 at ±1 V for the SAM and 100−200 at ±1 V for the ionically coupled structure are the highest to date for a molecular diode. The properties relate at least in part to the increased nonplanarity of the chromophore, and there is correlation between the electrical asymmetry and the dihedral angle between the donor and acceptor moieties. Significantly, the molecular origin of the electrical asymmetry has been confirmed by chemically switching the chromophore to disrupt the donor−acceptor combination: exposure to HCl vapor protonates the molecules and they then exhibit symmetrical I−V characteristics, whereas exposure to NH_3 restores the original form as well as the rectifying behavior. Furthermore, antiparallel alignment of chromophores in physisorbed structures formed from the disulfide results in an expected suppression of the electrical asymmetry, which again corroborates our interpretation of the data.

Materials and Methods

Materials. Sodium 3-mercapto-1-propanesulfonate was supplied by Sigma Aldrich (Gillingham, UK) and chemisorbed to gold to provide the anionic surface. Precursors to SAMs **2** and **3** were available from a previous investigation,[10] and 1-(ω-acetylsufanyldecyl)-4-methylquinolinium iodide was synthesized as described[31] and used in the synthesis of the self-assembling dyes below.

Precursor to SAM 1a. To a solution of 1-(10-acetylsufanyldecyl)-4-methylquinolinium iodide (0.2 g, 0.4 mmol) and 4-dimethylaminonaphthaldehyde (0.08 g, 0.4 mmol) in methanol (50 cm^3) was added piperidine (0.4 cm^3), and the mixture was heated at reflux 5 h. The crude product, obtained by evaporation at ambient temperature, was purified by flash chromatography on silica gel, eluting initially with chloroform and then chloroform−methanol (9:1, v/v). Subsequent purification by preparative plate chromatography yielded purple microcrystals of 1-(10-acetysulfanyldecyl)-4-[2-(4-dimethylaminonaphthalen-1-yl)-vinyl]-quinolinium iodide (**1a**): yield, 20%; mp > 250 °C (dec). λ_{max} ($CHCl_3$): 535 nm. Anal. Calcd for $C_{35}H_{43}N_2OSI$: C, 63.05; H, 6.50; N, 4.20%. Found: C, 62.4; H, 6.4; N, 4.0%. ^{1}H NMR (C_2D_5OD/$CDCl_3$, 250 MHz, *J*/Hz): δ_H 1.20−1.35 (br m, 12H, CH_2); 1.53 (quintet, *J* 7.0, 2H, $SCH_2\mathit{CH_2}$); 2.04 (quintet, *J* 7.1, 2H, $\mathit{CH_2}CH_2N^+$); 2.29 (s, 3H, CH_3CO); 2.80 (t, *J* 7.3, 2H, SCH_2); 3.10 (s, 6H, CH_3); 5.05 (t, *J* 7.6, 2H, CH_2N^+); 7.45−7.51 (m, 3H, Ar−H); 7.61−7.76 (m, 3H, Ar−H); 7.89−7.98 (m, 2H, Ar−H); 8.09 (d, *J* 9.3, 1H, Ar−H); 8.17−8.24 (m, 2H, Ar−H); 8.39−8.52 (m, 2H, Ar−H); 9.85 (d, *J* 6.6, 1H, Ar−H). *m*/*z* (ES^+): 539, 100% $[M - I^-]^+$. *m*/*z* (ES^-): 127, 100% $[I^-]$. HRMS (ES^+): *m*/*z* calcd for $C_{35}H_{43}N_2OS$, 539.3091; found 539.3096 $[M - I^-]^+$.

Dye 1b. The dye was also obtained as the disulfide, bis-[1-(10-decyl)-4-{2-(4-dimethylaminonaphthalen-1-yl)-vinyl}-quinolinium]-disulfide diiodide, using the procedure described above: yield, 11%; mp > 290 °C (dec). λ_{max} ($CHCl_3$): 535 nm. ^{1}H NMR (C_2D_5OD/$CDCl_3$, 250 MHz, *J*/Hz): δ_H 1.2−1.3 (br m, 24H, CH_2); 1.52 (br, 4H, $SCH_2\mathit{CH_2}$); 1.80 (br, 4H, $\mathit{CH_2}CH_2N^+$); 2.69 (t, *J* 7.3, 4H, SCH_2); 3.12 (s, 12H, CH_3); 4.70 (t, *J* 7.2, 4H, CH_2N^+); 7.45−7.50 (m, 6H, Ar−H); 7.63 (d, *J* 8.2, 2H, Ar−H); 7.69−7.76 (m, 4H, Ar−H); 7.88−8.00 (m, 4H, Ar−H); 8.09 (d, *J* 8.9, 2H, Ar−H); 8.16−8.24 (m, 4H, Ar−H); 8.43 (d, *J* 15.7, 2H, $C{=}CH$); 8.51 (d, *J* 8.4, 2H, Ar−H); 9.02 (d, *J* 6.4, 2H, Ar−H). *m*/*z* (ES^+): 496, 100% $[M - 2I^-]^{2+}$. *m*/*z* (ES^-): 127, 100% $[I^-]$. HRMS (ES^+): *m*/*z* calcd for $C_{66}H_{80}N_4S_2$, 496.2907; found 496.2904 $[M - 2I^-]^{2+}$.

Dye 1c. 1-Methyl-4-[2-(4-dimethylaminonaphthalen-1-yl)-vinyl]-quinolinium iodide was obtained from 1,4-dimethylquinolinium iodide (0.2 g, 0.4 mmol) and 4-dimethylaminonaphthaldehyde by adapting the procedure for **1a**: yield, 80%; mp > 250 °C (dec). λ_{max} ($CHCl_3$): 590 nm. Anal. Calcd for $C_{24}H_{23}N_2I$: C, 61.81; H, 4.97; N, 6.01%. Found: C, 61.5; H, 5.1; N, 5.9%. *m*/*z* (ES^+): 339, 100% $[M - I^-]^+$. *m*/*z* (ES^-): 127, 100% $[I^-]$.

Substrate Preparation. The 10 MHz quartz crystals were coated on each side with gold electrodes as supplied and then washed with chloroform, propan-2-ol, and water and plasma cleaned just prior to use (PlasmaPrep 2, Gala Instrumente). BK7 glass and HOPG substrates were coated with gold overlays using a BOC Edwards 306A evaporator, the former to an optimum thickness of 47 nm for SPR studies. They were stored in the solvent used for self-assembly and plasma cleaned prior to use.

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