

Induced rectification from self-assembled monolayers of sterically hindered π -bridged chromophores

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Self-assembled monolayers (SAMs) obtained *via* the chemisorption of bis-[1-(10-decyl)-4-{2-(4-methoxynaphthalen-1-yl)vinyl}quinolinium]disulfide diiodide (**1**) on gold-coated highly oriented pyrolytic graphite (HOPG) substrates exhibit asymmetric current–voltage characteristics with rectification ratios of *ca.* 30 at ± 1 V when contacted by PtIr or Au probes. The ratio decreases to *ca.* 10 at ± 1 V for pentanethiolate-coated gold probes, which locate the donor–(π -bridge)–acceptor moiety approximately midway between the electrodes: Au–S–C₅H₁₁//D– π –A–C₁₀H₂₀–S–Au. The I–V characteristics are different but the current *versus* electric field dependence is indistinguishable for both types of electrode, the field being calculated for a monolayer thickness of 2.4 ± 0.1 nm and an assumed bilayer thickness of 3.2 nm (*i.e.* 0.8 nm for pentanethiolate). SAMs obtained from bis-[1-(10-decyl)-4-{2-(4-methoxyphenyl)vinyl}pyridinium]disulfide diiodide (**2**) exhibit symmetrical I–V characteristics and, unlike the bulkier rectifying analogue above, its D– π –A chromophore is almost planar. This structure–property relationship highlights the significance of steric hindrance for rectification from π -bridged donor–acceptor molecules and consistent I–V characteristics have been obtained from SAMs investigated by scanning tunnelling spectroscopy (STS) as well as electrometer-based techniques with an alkanethiolate-coated mercury droplet electrode.

Introduction

Meinhard,¹ in 1964, reported organic rectifying junctions from bulk bilayers fabricated from n-type and p-type materials but the experimental study was flawed by the use of oxidisable lead electrodes. The concept has since been verified by reports of electrical asymmetry from Au/(bulk donor)/(bulk acceptor)/Au devices^{2,3} but these should be considered as rectifying junctions rather than rectifying molecules. Aviram and Ratner,⁴ in 1974, proposed a donor–(σ -bridge)–acceptor sequence as the organic counterpart of the p–n junction and then, 16 years later, Ashwell, Sambles and co-workers⁵ reported the first example of a molecular diode to stand the test of time. Asymmetric I–V characteristics were obtained from Langmuir–Blodgett films of a π -bridged dye, Z- β -[N-(hexadecyl)-4-quinolinium]- α -cyano-4-styryldicyanomethanide, C₁₆H₃₃–Q3CNQ, contacted by magnesium electrodes with a silver overlay to suppress oxidation. The discovery led Metzger *et al.* to ask “*Is Ashwell’s Zwitterion a Molecular Diode?*” as the title of his first paper on the dye⁶ and, although his views were initially negative, he has since published extensively and claimed molecular rectification for LB films sandwiched between aluminium electrodes.⁷ For such films, the behaviour is ambiguous as the electrical asymmetry cannot be decoupled from that of the oxide-induced Schottky barrier. However, recent studies have confirmed molecular rectification from LB films^{8,9} of C₁₆H₃₃–Q3CNQ contacted by non-oxidisable electrodes as well as self-assembled Au–S–C_nH_{2n}–Q3CNQ monolayers.^{9,10}

Metzger and co-workers^{7b,11} have argued that the rectifying behaviour is induced, at least in part, by the insulating tail but this conflicts with experimental evidence:^{9,10} *e.g.* a systematic lengthening of the alkyl tail provides no significant variation of the rectification ratio from Au–S–C_nH_{2n}–Q3CNQ structures where $3 \leq n \leq 12$; exposure to acid and then base causes the I–V characteristics of these analogues to reversibly alter between symmetrical and rectifying as the donor–acceptor combination is first disrupted and then restored. This has also been observed for the LB film and chemical switching of the rectifying behaviour, first off and then on, verifies that the donor–acceptor moiety is responsible for the electrical asymmetry.⁹ Rectification is also maintained when the chromophore is located midway between the two electrodes to suppress asymmetric coupling of the D– π –A moiety with each of the contacts. It has been demonstrated by scanning tunnelling spectroscopy (STS) with the SAM contacted by coated gold probes: Au–S–C₁₀H₂₀–Q3CNQ//C₁₀H₂₁–S–Au.¹⁰

LB and self-assembling derivatives of five different D– π –A chromophores^{8–10,12–15} and a conjugated oligomer with electron-donating bithiophene and electron-accepting bithiazole segments¹⁶ are known to exhibit electrical asymmetry when contacted by non-oxidisable electrodes. The polarity for rectification is dependent upon the dipole orientation and, thus, molecules connected *via* their acceptors (Au–S–C_nH_{2n}–A– π –D) and donors (Au–S–C_nH_{2n}–D– π –A) exhibit higher currents in opposite quadrants of the I–V plot. To exclude electrode-induced effects, electrical asymmetries from films of these dyes have been verified by a range of complementary techniques: *e.g.* (i) electrometer-based methods using evaporated gold pads;^{8,13c,14,15} (ii) STS studies using alkanethiolate-coated

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electrodes^{10,13a} and uncoated PtIr and Au probes;^{9,12,13a,13b,16} and (iii) characterisation using mercury droplet electrodes in the presence of a hexadecane solution of an alkanethiol,^{13a} where the self-assembled coating protects the mercury surface from oxidation. They provide effective control measures when used together to confirm the origin of the electrical asymmetry and, in addition, when combined with the chemical off/on switching of the rectifying behaviour, which has been observed for three of the D- π -A dyes.^{9,12,13a,13b}

Orientation-induced rectification has also been obtained from hybrid SAM/LB bilayer structures of squaraine dyes¹⁷ in which the donor-acceptor-donor chromophore is vertically aligned in the SAM and horizontally aligned in the LB film. Electrical asymmetry arises because the length of the D-A-D moiety is in contact with one electrode whereas only the donor is projected towards the other. Homomolecular films of squaraine dyes with self-assembling groups located at opposite ends of the D-A-D chromophore show similar behaviour because self-assembly *via* one and two anchoring groups provides vertical and horizontal alignments respectively with different arrangements at the substrate electrode and contact.¹⁸

In contrast to this and the π -bridged dyes, as detailed above, there are few unambiguous claims of molecular rectification from D- σ -A molecules. There are none for films contacted by non-oxidisable metals and three where the oxidisable electrodes have protective coatings: *viz.* LB films of a tetrathiafulvalene-trinitrofluorene¹⁹ derivative exhibit electrical asymmetry when contacted by alkanethiolate-coated mercury electrodes as do LB films of 3,5-dinitrobenzyl-7-(1-oxohexylamino)-pyren-2-ylcarbamate²⁰ and a dodecyloxyphenylurethane derivative of 2-bromo-5-(2-hydroxyethoxy)-TCNQ²¹ when contacted by silver-coated magnesium. There are also recent unsubstantiated claims of molecular rectification for films contacted by oxidisable electrodes, such as aluminium,^{22–24} and titanium,^{25,26} as well as electrodes that are known to react chemically with the molecular species.²⁷ The electrical asymmetry probably arises from Schottky barriers and, for example, this oxide-induced behaviour is clearly demonstrated by the I-V characteristics of Au/(magnesium phthalocyanine)/Al, which are symmetrical when investigated before breaking the vacuum but exhibit a rectification ratio of *ca.* 1000 at ± 2 V when exposed to air and re-evacuated.²⁸

In this paper, we report improved rectifying behaviour from SAMs of a sterically hindered cationic D- π -A dye (Fig. 1), which comprises a bulky 4-methoxynaphthyl donor that is linked *via* a -CH=CH- bridge to a bulky quinolinium acceptor. The steric hindrance is intended. It enforces the required non-planarity, which in turn provides an effective electron tunnelling barrier between the electroactive ends. Its SAMs exhibit rectification ratios of *ca.* 30 at ± 1 V and, significantly, electrical asymmetry is suppressed in SAMs of a less bulky analogue, which has an almost planar chromophore. No planar D- π -A moiety to date has shown rectifying behaviour.

Results and discussion

SAM 1: rectifying derivative

SAMs of **1** were obtained by immersing gold-coated substrates in a dilute chloroform solution of

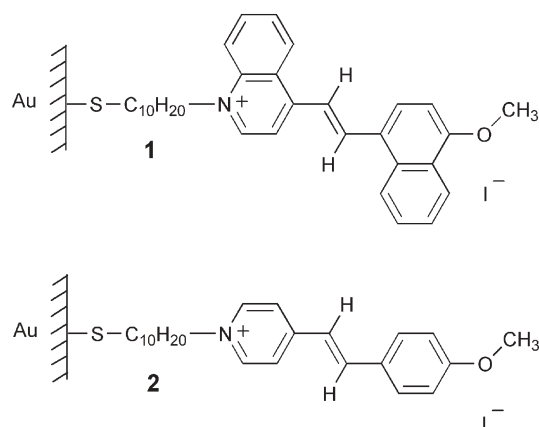


Fig. 1 Molecular structures of SAMs of rectifying (**1**) and non-rectifying (**2**) derivatives where the counterion in each case is iodide. A rectifying 7,7,8,8-tetracyano-*p*-quinodimethanide salt of **1** has also been formed by metathesis with Li⁺TCNQ⁻.

bis-[1-(10-decyl)-4-{2-(4-methoxynaphthalen-1-yl)vinyl}quinolinium]disulfide diiodide (0.1 mg cm⁻³). The optimum conditions for chemisorption were found by monitoring the frequency change while depositing onto the gold electrodes of 10 MHz quartz crystals. The mean area, determined from a Sauerbrey²⁹ analysis of the frequency data, saturates to 0.40 ± 0.05 nm² molecule⁻¹ after *ca.* 2–3 h (Fig. 2). The thickness and real and imaginary components of the dielectric permittivity were derived from a two-layer analysis of the surface plasmon resonance (SPR) data, which were collected using a Kretschmann configuration.³⁰ Analysis yields a thickness of 2.4 ± 0.1 nm with $\epsilon_r = 2.4 \pm 0.1$ and $\epsilon_i = 0.2 \pm 0.1$ at 532 nm. The dimensions suggest that the chromophores adopt an almost upright orientation with the iodide residing at the surface, the thickness being greater than expected for the cationic dye alone and the area being insufficient to

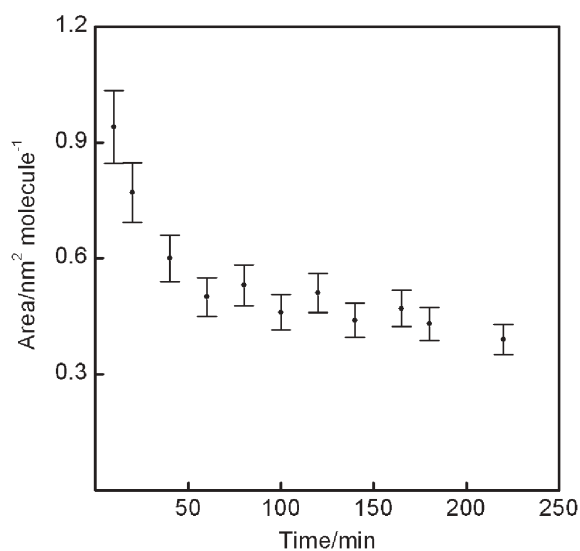


Fig. 2 Variation of the mean molecular area *versus* the total period of immersion of gold-coated 10 MHz quartz crystals in a chloroform solution of the precursor to SAM **1**, bis-[1-(10-decyl)-4-{2-(4-methoxynaphthalen-1-yl)vinyl}quinolinium]disulfide diiodide (0.1 mg cm⁻³).

readily locate the counterion between the sterically hindered molecules.

SAMs of the iodide salt of the dye were chemisorbed onto gold-coated highly oriented pyrolytic graphite (HOPG), the gold overlay being thermally evaporated to a thickness of *ca.* 50 nm using an Edwards 306 coating unit. Following a cursory study of the surface structure, using a Nanoscope IV scanning tunnelling microscope, the films were investigated at ambient temperature by STS and their I–V curves initially obtained with the tip set to provide a tunnelling current of *ca.* 100 pA at 0.2 V. The setting was then varied across a broad range of values to investigate tip-induced rectification, which was found to be small relative to the inherent properties of the films. The data are indistinguishable for PtIr and Au tips and exhibit rectification ratios of 30 at ± 1 V (Fig. 3), the ratio being averaged for data obtained on the same spot but which is also reproducible across the film. There is a distinct improvement in the electrical asymmetry relative to the ratio of 18 at ± 1 V obtained for the 4-dimethylaminophenyl analogue,^{13a} which has a stronger donor/acceptor combination but is far less sterically hindered than the D– π –A chromophore reported here. The higher forward bias current invariably occurs in the negative quadrant of the I–V plot (Figs. 4–7), the polarity being assigned to the substrate electrode and the data corresponding to electron flow from the substrate to tip. The polarity for rectification is as previously reported for other cationic dyes¹³ and is consistent with the quinolinium heterocycle and 4-methoxynaphthalene being the acceptor and donor respectively. It signifies electron tunnelling in a direction from the electrode to lowest unoccupied molecular orbital of the acceptor at one end of the device and from the highest occupied molecular orbital of the donor to adjacent electrode at the other end. Intramolecular electron transfer in

the same direction then follows to restore the ground state. The lower current at reverse bias results from a mismatch between the molecular and Fermi energy levels, which induces the observed electrical asymmetry.

SAMs contacted by alkanethiolate-coated gold tips exhibit rectification and permit the chromophores to be located midway between the two electrodes by attempting to match the thickness of the two alkane groups: Au–S–C_nH_{2n+1}//D– π –A–C₁₀H₂₀–S–Au. The area of 0.40 ± 0.05 nm², which may be compared with the 0.2 nm² cross-section of C₁₀H₂₀, suggests that the tail is highly tilted and, consequently, we estimate its thickness contribution to match that of pentanethiol when assembled on gold (*ca.* 0.8 nm). The I–V characteristics of **1**, contacted by the C₅H₁₁–S–Au-coated gold probe, exhibit a rectification ratio of 10 at ± 1 V (Fig. 4), which is significantly lower than obtained for the uncoated tips. However, the current *versus* electric field dependence is indistinguishable as shown in Fig. 5. Thus, it is assumed that geometrical asymmetry induced by the uncoated tips does not affect the electrical asymmetry. It is also consistent with a previous study on non-rectifying dyes where the length of the C_nH_{2n}–S–Au link has no profound effect.

There is some ambiguity in the precise mechanism as it is unclear whether the STM tip contacts the iodide counterion, which is probably located at the surface, or the methoxynaphthyl group. Both are electron donating but, as the iodide has a cross-section of 0.15 nm² (*r* = 0.216 nm) compared with 0.40 nm² occupied by the cationic chromophore, it is more likely that the latter is involved. Such ambiguity is removed by substituting the counterion by the TCNQ^{•–} radical anion, which is bulkier and occupies the entire surface. This may be achieved by immersing the aforementioned SAMs for *ca.* 30 min in ethanol solutions of Li⁺TCNQ^{•–}: 10 MHz quartz crystals exhibit a frequency change of *ca.* 20 Hz, which reflects replacement of the iodide by the radical anion. Furthermore, the monolayer thickness from SPR studies increases to 3.0 ± 0.1 nm for the radical anion salt, the 0.6 nm change approximating to the expected difference between the van der Waals length of the latter (1.1 nm) and diameter of the former (0.43 nm). The real and imaginary components of the dielectric permittivity are slightly altered with $\epsilon_r = 2.5 \pm 0.1$ and $\epsilon_i = 0.2 \pm 0.1$ at 532 nm.

SAMs of the TCNQ^{•–} salt also exhibit asymmetric I–V curves but with reduced rectification ratios of *ca.* 10 at ± 1 V for films contacted by PtIr probes (Fig. 6) and also by mercury droplet electrodes (Fig. 7) but the latter are qualified by the comments in the section below. The reduction is attributed, in part, to a 25% reduction of the electric field across the thicker monolayer of the TCNQ^{•–} salt, the monolayer thickness being 3.0 ± 0.1 nm compared with 2.4 ± 0.1 nm for the iodide salt. As before, the higher forward bias current is in the negative quadrant of the I–V plot, where the substrate electrode defines the polarity. It corresponds to electron transfer in a direction from substrate to tip in the PtIr//TCNQ^{•–} D– π –A⁺–C₁₀H₂₀–S–Au device, which corresponds to the quinolinium heterocycle being an electron acceptor. Significantly, the negatively charged counterion is an electron donor, as is the methoxy group, but the role of the former may be considered ambiguous. Neutral TCNQ undergoes a one-electron reduction to

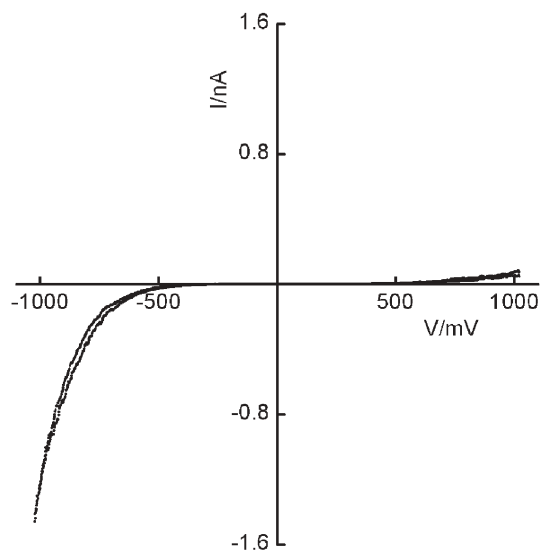


Fig. 3 I–V characteristics of the iodide salt of SAM **1**, the behaviour being indistinguishable for films contacted by PtIr or Au probes. The polarity relates to the substrate electrode and the higher forward bias current corresponds to electron flow from the gold-coated substrate to the contacting tip.

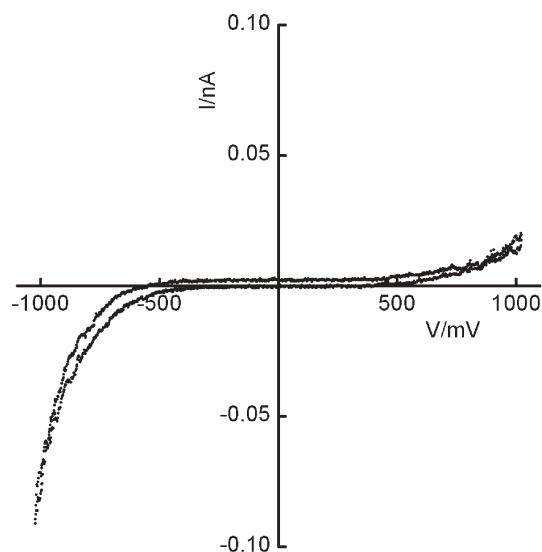


Fig. 4 I–V characteristics of the iodide salt of SAM **1** contacted by a C₅H₁₀–S–Au-coated tip. The polarity relates to the substrate electrode and at forward bias electrons tunnel from the substrate to the tip.

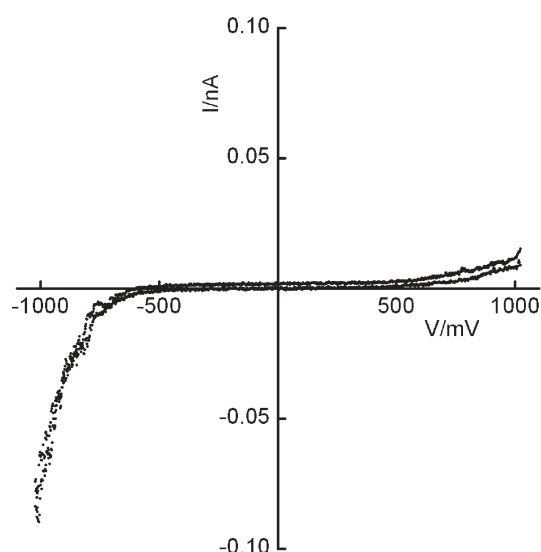


Fig. 6 I–V characteristics of the TCNQ[−] salt of SAM **1** contacted by a PtIr tip. The polarity relates to the substrate electrode and at forward bias electrons tunnel from the substrate to tip.

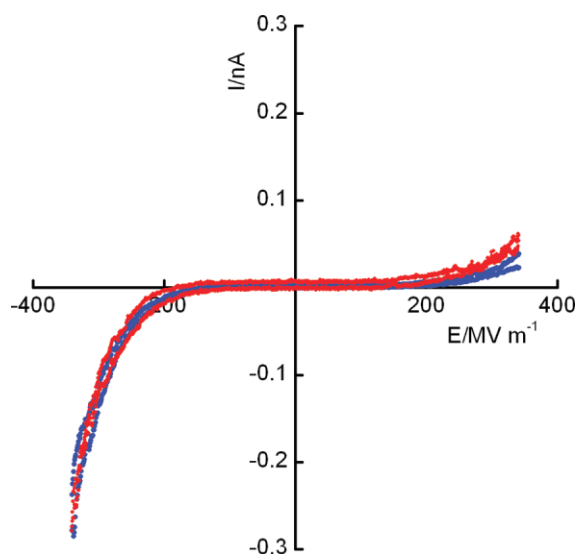


Fig. 5 Normalised current *versus* electric field dependence for films contacted by coated (red) and uncoated (blue) tips as in Figs. 3 and 4. The current for the coated tip is multiplied by a factor of three.

TCNQ[−] with a half-wave reduction potential of 0.19 V and, in addition, a two-electron reduction to TCNQ^{2−} with $E_{1/2} = -0.35$ V, both values *versus* the saturated calomel electrode.³¹ Thus, reduction of the counterion could contribute to the reduced rectification ratio of 10 at ± 1 V, as the device requires TCNQ[−] to be a strong donor (not an acceptor) with a reverse bias mismatch of the molecule's energy levels and the electrode's Fermi energy.

SAM **1**: mercury contacts

The I–V characteristics were also investigated by contacting the SAMs with octadecanethiolate-coated mercury electrodes, which were formed by adapting procedures that have been

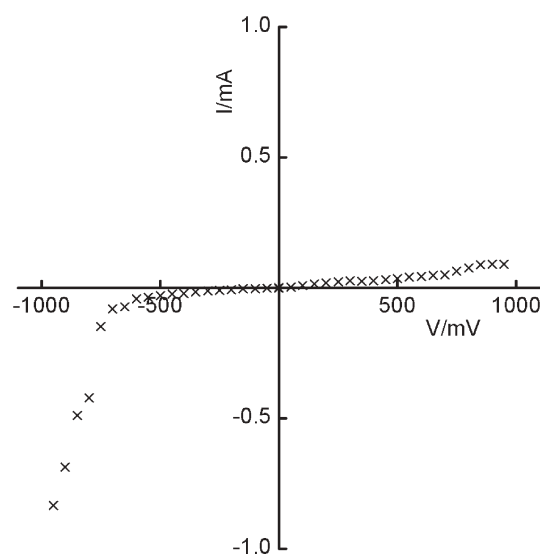


Fig. 7 I–V characteristics of the TCNQ[−] salt of SAM **1** contacted by a mercury droplet. The polarity relates to the substrate electrode and the data resemble those obtained using the PtIr tip.

described elsewhere.^{32,33} The SAM was immersed in a dilute solution of octadecanethiol in hexadecane (1 mM) and a mercury droplet (*ca.* 1 mm diameter) was suspended from an airtight syringe below the surface. A 10 min period was allowed for a monolayer to form on the mercury, following which the electrode was lowered *via* a translation stage to make physical contact with the surface of the SAM. The Au–S–C₁₀H₂₀–dye//C₁₈H₃₇–S–Hg bilayer structure, which initially formed, was then interrogated using a Keithley source/electrometer and I–V curves obtained by sweeping the voltage at 0.05–0.2 V s^{−1}.

Three types of I–V characteristics have been observed, which we believe may be explained by the stabilities of the contacting electrode and resultant bilayer structure:

- for films contacted by pinhole-free $C_{18}H_{37}-S-Hg$ electrodes, which results in a thick bilayer structure, the dependence mimics the low electric field region obtained from the STS studies;

- when filamentary mercury penetrates the contacting octadecanethiolate-coated electrodes, as indicated by increased current, the I–V characteristics are similar to those obtained using uncoated Au or PtIr contacts;

- when mercury penetrates both layers, shorting occurs and the behaviour is erratic with abrupt changes in current as well as potential for recovery as the voltage is cycled.

Typical I–V characteristics from the TCNQ[−] salt of SAM **1**, contacted by the mercury electrode with probable filamentary penetration through the octadecanethiolate layer, are shown in Fig. 7. The voltage dependence is almost indistinguishable from the data obtained for films investigated by STS and contacted by uncoated probes (*e.g.* see Fig. 6). However, the current differs by about seven orders of magnitude and thus, if the STS data correspond to the current through a single molecule, it may be assumed that the penetrating mercury filaments have a combined cross-sectional area of *ca.* $1 \mu m^2$. It is noted that the direction of electron flow at forward bias is consistent for both types of electrode as well as for both types of counterion, iodide and TCNQ[−], and is from the electrode to acceptor on one side of the device and from the donor to electrode on the other side. The behaviour is expected, but nonetheless this commonality is constructive as it provides evidence that the observed properties are inherent to the molecule and not the contacts.

SAM 2: non-rectifying derivative

The rectifying molecule is sterically hindered and its behaviour has been attributed to the non-planar D– π –A moiety, which provides an electron tunnelling barrier between the electro-active ends. The analogue (**2**) with a methoxyphenyl donor and a pyridinium acceptor is sterically unhindered and X-ray structural studies³⁴ on related dyes indicate an almost planar chromophore. It was synthesised to highlight the structure–property relationship of these π -bridged molecules and its SAMs were chemisorbed from bis-[1-(10-decyl)-4-{2-(4-methoxyphenyl)vinyl}pyridinium]disulfide diiodide as described for the bulkier molecule. The area saturates to $0.28 \pm 0.03 \text{ nm}^2 \text{ molecule}^{-1}$ (Fig. 8), which is consistent with the smaller cross-section of the single-ring components and, as before, is indicative of molecular close packing. A thickness of $2.5 \pm 0.1 \text{ nm}$ (*cf.* 2.4 nm for **1**) from SPR studies suggests that the packing is similar in both films.

The I–V curves of SAM **2** are symmetrical (Fig. 9) and, as detailed above, may be attributed to the chromophore structure, which is probably almost planar for **2** but non-planar for **1**. Similar structure–property relationships have been observed for SAMs formed from a related cationic dye, 1-(10-acetylthiodecyl)-4-{2-(4-dimethylaminophenyl)vinyl}-quinolinium iodide (**3**), which exhibit modest rectification, and those formed from the pyridinium analogue, 1-(10-acetylthiodecyl)-4-{2-(4-dimethylaminophenyl)vinyl}quinolinium iodide (**4**), which do not.^{13a} The properties of these cationic dyes are contrasted in Table 1 with the data obtained here,

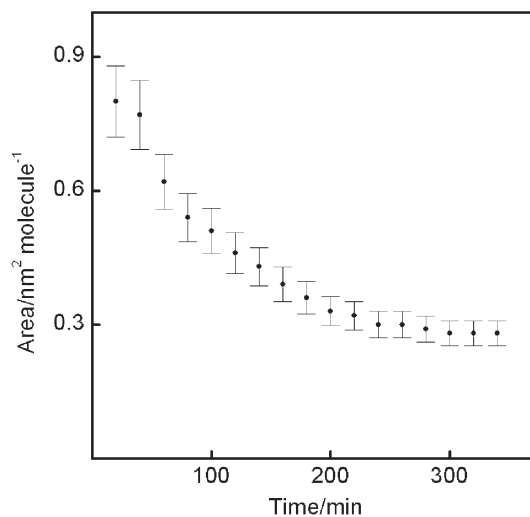


Fig. 8 Variation of the mean molecular area *versus* the total immersion time of a gold-coated 10 MHz quartz crystal in a chloroform solution of the precursor to SAM **2**, bis-[1-(10-decyl)-4-{2-(4-methoxyphenyl)vinyl}pyridinium]disulfide diiodide (0.1 mg cm^{-3}).

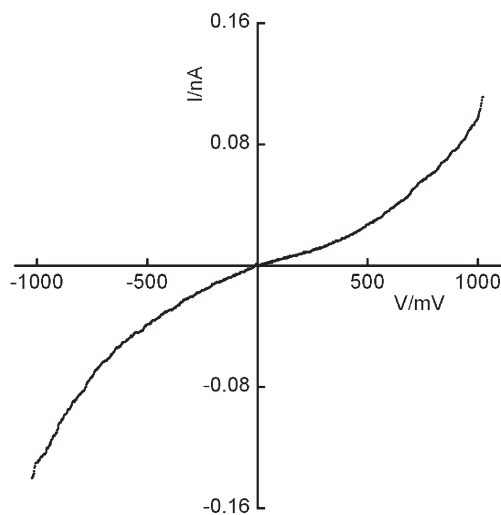


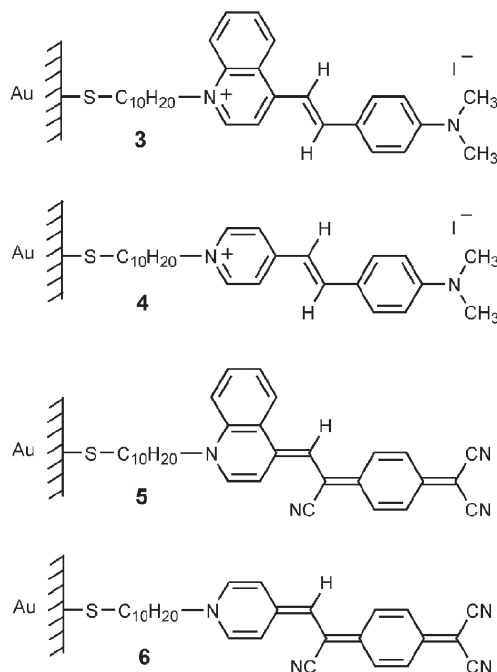
Fig. 9 Symmetrical I–V characteristics of the iodide salt of SAM **2**, the behaviour being indistinguishable for films contacted by PtIr or Au tips. The polarity relates to the substrate electrode and at forward bias electrons flow in a direction from the gold-coated HOPG substrate to the tip.

and structures of the self-assembled molecules are shown in Fig. 10.

The effect of steric hindrance is also clearly demonstrated by differences in the I–V characteristics of the extensively studied Au–S– C_nH_{2n} –Q3CNQ (**5**),⁹ as detailed in the introduction, and those of the pyridinium analogue, Au–S– $C_{10}H_{20}$ –P3CNQ (**6**).¹² Only the former exhibits electrical asymmetry but derivatives of the latter may be rendered rectifying by substituting an H by CH_3 on the $-CH=C(CN)-$ electron bridge or at the 3-position of the pyridinium ring. The bulkier methyl induces a non-planar arrangement, whereby the donor and acceptor are rotated out of plane, and provides the criteria for molecular rectification. Consequently, SAMs obtained

Table 1 Rectification ratios (RR) determined at ± 1 V

Dye	Electrodes		RR	Ref.
	Substrate	Top contact		
1 ^a	HOPG/Au	PtIr or Au	30	This work
1 ^b	HOPG/Au	PtIr or Hg	10	This work
2	HOPG/Au	PtIr	1	This work
3	HOPG/Au	PtIr or Au	18	13a
4	HOPG/Au	PtIr	1	13a
5	HOPG/Au	PtIr or Au	30	9
6	HOPG/Au	PtIr	1	12

^a Iodide salt. ^b TCNQ[−] salt.**Fig. 10** Structures of self-assembled D- π -A molecules with sterically hindered (**3** and **5**) and unhindered (**4** and **6**) forms. SAMs **5** and **6** are depicted as quinoid rather than zwitterionic, the molecular structures being consistent with the observed polarity for rectification where the C(CN)₂ group acts as the acceptor.

from *Z*- β -[*N*-(ω -acetylthioalkyl)-3-methyl-4-pyridinium]- α -cyano-4-styryldicyanomethanide act as molecular diodes¹² whereas those obtained from the unsubstituted analogue exhibit symmetrical I-V characteristics. The almost planar molecular structure removes the tunnelling barrier between the donor and acceptor ends of these π -bridged materials and the structure-property relationship clearly highlights the importance of steric hindrance.

Conclusion

In conclusion, we report a molecular rectifier, only the sixth example to date that has been contacted by non-oxidisable metals. There are few examples to make a direct comparison but we note that the rectification ratio of 30 at ± 1 V is significantly higher than previously obtained for a related cationic D- π -A dye,^{13a} which had a less sterically hindered structure. It is likely that the improved rectification ratio relates, at least in part, to the increased non-planarity of the chromophore and,

significantly, analogues with sterically unhindered structures invariably show symmetrical I-V curves. The molecule with a single-ring pyridinium acceptor and a single-ring 4-methoxyphenyl donor, as reported here, is a prime example.

Experimental

Precursor to SAM 1

To a solution of *N*-(10-acetylthiodecyl)-4-methylquinolinium iodide (0.2 g, 0.4 mmol) and 4-methoxynaphthaldehyde (0.08 g, 0.4 mmol) in methanol (50 cm³) was added piperidine and the mixture heated at reflux for 3 h. The crude product, which was 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). Prior to use it was purified by preparative plate chromatography and yielded red microcrystals of bis-[1-(ω -decyl)-4-{2-(4-methoxynaphthalen-1-yl)vinyl}quinolinium]disulfide diiodide: yield, 16%; m.p. > 440 °C (decomp.). λ_{max} (CHCl₃): 485 nm. ¹H NMR (CDCl₃, 400 MHz, *J*/Hz): δ_{H} 1.26 (br, 24H, CH₂); 1.54 (br, 4H, SCH₂CH₂); 1.95–2.05 (m, 4H, CH₂CH₂N⁺); 2.68 (t, *J* 7.0, 4H, SCH₂); 3.42 (s, 6H, CH₃O); 4.98 (t, *J* 7.2, 4H, CH₂N⁺); 6.81 (d, *J* 7.8, 2H, Ar-H); 6.93 (t, *J* 7.5, 2H, Ar-H); 7.45–7.70 (m, 4H, Ar-H); 7.86–7.96 (m, 6H, Ar-H); 8.06–8.32 (m, 6H, Ar-H); 8.47 (d, *J* 7.3, 2H, Ar-H); 8.53 (d, *J* 16.0, 2H, C=C-H); 8.68 (d, *J* 8.8, 2H, Ar-H); 9.72 (d, *J* 6.2, 2H, Ar-H). *m/z* (ES⁺): 483, 100% [*M* - 2I]²⁺. *m/z* (ES[−]): 127, 100% [I[−]]. HRMS (ES⁺): *m/z* calc. for C₆₄H₇₄N₂O₂S₂, 483.2590; found 483.2585 [*M* - 2I]²⁺.

Precursor to SAM 2

To a solution of *N*-(10-acetylthiodecyl)-4-methylpyridinium iodide (0.22 g, 0.5 mmol) and 4-methoxybenzaldehyde (0.068 g, 0.5 mmol) in methanol (50 cm³) was added piperidine (0.4 cm³) and the mixture heated at reflux. The crude product, which was obtained by evaporation at ambient temperature, was purified by flash chromatography on silica gel, eluting sequentially with chloroform and chloroform-methanol mixtures (49 : 1 to 9 : 1, v/v). Prior to use, the product was purified by preparative plate chromatography to yield red crystals of bis-[1-(ω -decyl)-4-{2-(4-methoxyphenyl)vinyl}-pyridinium]disulfide diiodide: yield, 25%; m.p. > 304 °C (decomp.). λ_{max} (CHCl₃): 505 nm. ¹H NMR (CDCl₃, 400 MHz, *J*/Hz): δ_{H} 1.22 (br, 24H, CH₂); 1.63 (quintet, *J* 8.0, 4H, SCH₂CH₂); 1.88 (quintet, *J* 6.0, 4H, CH₂CH₂N⁺); 2.63 (t, *J* 7.5, 4H, SCH₂); 3.10 (s, 6H, CH₃O); 4.63 (t, *J* 7.2, 4H, CH₂N⁺); 6.86 (d, *J* 8.8, 4H, Ar-H); 6.94 (d, *J* 16.0, 2H, C=C-H); 7.54 (d, *J* 8.0, 4H, Ar-H); 7.64 (d, *J* 16.0, 2H, C=C-H); 7.97 (d, *J* 8.8, 4H, Ar-H); 8.91 (d, *J* 6.6, 4H, Ar-H). *m/z* (ES⁺): 383, 100% [*M* - 2I]²⁺. *m/z* (ES[−]): 127, 100% [I[−]]. HRMS (ES⁺): *m/z* calc. for C₄₈H₆₆N₂O₂S₂, 383.2277; found 383.2276 [*M* - 2I]²⁺.

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