Controlled alignment of molecular diodes *via* ionic assembly of cationic donor–(π-bridge)–acceptor molecules on anionic surfaces

Geoffrey J. Ashwell* and Anna Chwialkowska

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Alignment of cationic donor–(π-bridge)–acceptor molecules *via* metathesis with a self-assembled monolayer formed from sodium 3-mercapto-1-propanesulfonate results in ultra-thin rectifying Au–S–$(CH_2)_3SO_3^-$|A^+–π–D structures which exhibit optimum current ratios of 450 at ±1 V for *N*-methyl-5-(4-dibutylaminobenzylidene)-5,6,7,8-tetrahydroisoquinolinium.

Organic diodes are the smallest molecular electronic components obtained to date and comprise a donor–(electron bridge)–acceptor sequence.[1] There are few examples and, in the majority of reports, the rectification ratio is too small to have any real significance with characteristic values of 2–30 at ±1 V (refs. 2–13) and exceptionally 150 at ±1 V (ref. 14) when contacted by non-oxidisable electrodes. The molecules are aligned as monolayer films: self-assembly is preferable[8–14] as the criteria for controlled alignment at the air–water interface prior to Langmuir–Blodgett (LB) deposition locates the donor–acceptor moiety at one electrode and isolates it from the other by a hydrophobic alkyl tail.[6,7,15,16] In this work, we now report a novel method of alignment that results from self-organisation of cationic molecules on an anionic surface. This alleviates the need to substitute the active chromophore with either an alkyl tail or self-assembling groups and serendipitously, the technique has provided the highest reported rectification ratio to date from an ultra-thin molecular film.

Ionically coupled structures were obtained in two steps: (1) by immersing a gold-coated substrate in a methanol solution of sodium 3-mercapto-1-propanesulfonate† to obtain the anionic surface and (2) by metathesis with, for example, *N*-methyl-5-(4-dibutylaminobenzylidene)-5,6,7,8-tetrahydroisoquinolinium iodide in aqueous methanol to provide the required alignment of the donor–acceptor molecules. Following the second step, the film was rinsed with copious volumes of water to dissolve sodium iodide that may be trapped in the structure. Evidence of metathesis is provided by X-ray photoelectron spectroscopy (XPS). Significantly, peaks that correspond to the characteristic binding energies of the inorganic counterions, Na^+ and I^-, are either not found or are extremely weak. Instead, the spectrum shows peaks that are unique to the individual layers: peaks at 162 and 167 eV (S 2p) are distinctive of the binding energies of the two types of sulfur of the anionic layer, the former relating to the thiolate link and the latter, together with a peak at 533 eV (O 1s), corresponding to the negatively charged sulfonate group; a peak at 400 eV (N 1s) is characteristic of the binding energy of the nitrogens of the cationic A^+–π–D layer. Furthermore, areas under these peaks, corrected for atomic sensitivity factors of each, approximate to the ratios expected from the stoichiometry shown in Fig. 1.

Self-assembly (step 1) and ionic coupling (step 2) were each monitored from the frequency changes following deposition onto gold-coated 10 MHz quartz crystals, which were washed with acetone and water and then plasma cleaned prior to use. A Sauerbrey analysis[17] of the frequency data provided a mean area of 0.30 nm^2 $molecule^{-1}$ after *ca.* 2 h for the chemisorbed component [Au–S–C_3H_6–SO_3^- Na^+]. The D–π–A^+ cation was judiciously chosen to have a similar cross-section to favour close packing as well as an uncluttered positively-charged acceptor to couple with the anionic surface. A bulky dibutylamino donor was also employed to inhibit reversed orientations but further studies have demonstrated that the dimethylamino derivative also aligns. Metathesis occurs by immersing the anionically coated substrate in solutions of the cationic dye and the area of the latter saturates to 0.30 nm^2 $molecule^{-1}$ after immersion periods of 5 h (Fig. 2). The limiting area of the D–π–A^+ cation, which approximates to its van der Waals cross-section, is imposed by that of the anionic lattice and, as there is insufficient space for the molecules to penetrate, the data confirm that the anionic and cationic moieties form separate layers.

A Nanoscope IV MultiMode scanning tunnelling microscope (Veeco Instruments, Cambridge) was used to probe the surface of films on gold-coated highly oriented pyrolytic graphite (HOPG) but failed to provide clear images. This probably results from the ionically coupled films being inherently disordered. Nonetheless, reproducible *I–V* characteristics have been obtained by landing a PtIr probe at different locations across each of six films and by averaging the data from ten scans at each site to obtain relatively noise free plots. Films were normally investigated about a day after ionic assembly and nearly all *I–V* curves from 190 separate data sets collected in this way exhibit rectification ratios in excess of 100 at ±1 V (Fig. 3) with 20% in the range 400–450 at ±1 V. Higher ratios from ultra-thin organic films have only been reported from structures contacted by non-oxidisable electrodes where oxide-induced Schottky barrier effects tend to dominate the observed *I–V* characteristics. Thus, the rectification ratio is the highest to

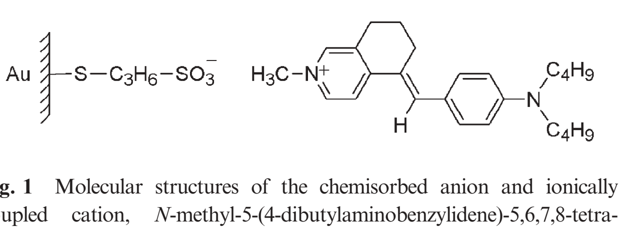

Fig. 1 Molecular structures of the chemisorbed anion and ionically coupled cation, *N*-methyl-5-(4-dibutylaminobenzylidene)-5,6,7,8-tetrahydroisoquinolinium.

The Nanomaterials Group, Cranfield University, Cranfield, UK MK43 0AL. E-mail: g.j.ashwell@cranfield.ac.uk; Fax: 44 01234 752452; Tel: 44 01234 754684

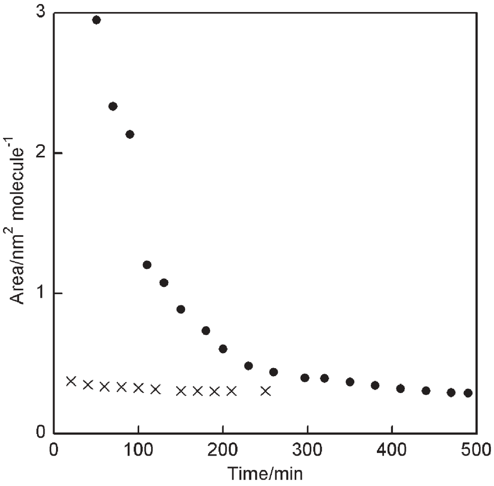

Fig. 2 Mean area *versus* the period of immersion of the substrates: (×) Au–S–(CH$_2$)$_3$SO$_3^-$Na$^+$ by immersion of a 10 MHz quartz crystal in a methanol solution of the thiol derivative (*ca.* 3 × 10^{-3} M); (•) the cationic A^+–π–D component by immersion of the anionically coated substrate in an aqueous methanol solution of *N*-methyl-5-(4-dibutylaminobenzylidene)-5,6,7,8-tetrahydroisoquinolinium iodide (*ca.* 3 × 10^{-4} M). The time denotes the sum of the periods of immersion.

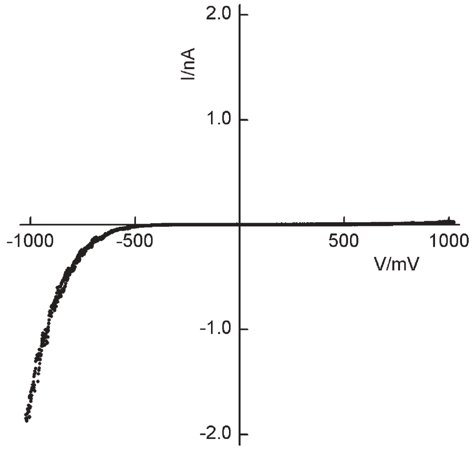

Fig. 3 *I–V* characteristics of an Au–S–(CH$_2$)$_3$SO$_3^-$|A^+–π–D structure contacted by a PtIr probe where the cation is *N*-methyl-5-(4-dibutylaminobenzylidene)-5,6,7,8-tetrahydroisoquinolinium. Data were obtained for a set point current of 0.1 nA and substrate voltage of –0.1 V and averaged for ten scans from the same site. The bias is designated by the sign of the substrate electrode.

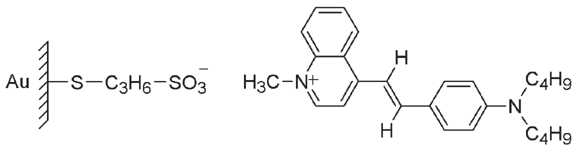

Fig. 4 Aligned molecular diode where the cation is *N*-methyl-4-{2-(4-dibutylaminophenyl)vinyl}quinolinium.

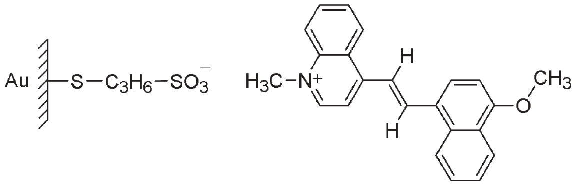

Fig. 5 Aligned molecular diode where the cation is *N*-methyl-4-{2-(4-methoxynaphthalen-1-yl)vinyl}quinolinium.

date from a molecular diode where the observed electrical asymmetry is intrinsic to the organic layer.

Interestingly, lower rectification ratios of 20–30 at ±1 V have been observed but, in each case, the data were obtained shortly after ionic coupling. Furthermore, with the PtIr probe located on the same site, the rectification continues to increase for several hours after deposition. Thus, the initial ratios may be explained by regions of less favourable alignment and the improved behaviour to self-ordering of the ionic lattice. Nonetheless, these rectification ratios are still higher than previously reported values of 8–22 at ±1 V from LB films of the iodide salts of amphiphilic derivatives of the dye molecule.[7] They are also higher than the ratio of *ca.* 5 at ±1 V from self-assembled monolayers (SAMs) where the D–π–A^+ moiety is connected *via* a decanethiolate link,[12a] the altered properties being attributed to the placement of the iodide counterion. There is sufficient space for it to reside between molecules and, with appropriate overlap, anion-induced polarization may cause the chromophore to transform to the quinoid D^+–π–A form as the iodide is displaced along its length.[15a] Thus, reduced rectification from LB monolayers and SAMs of this dye may be interpreted as arising from a mixed ground state and dipole reversal. Alignment on the anionic surface, as described here, rules out this problem.

It is important to establish the versatility of the method and we note that other cationic D–π–A^+ moieties exhibit asymmetric *I–V* characteristics when ionically coupled with the anionic surface. Films were fabricated as described above and, in each case, a Sauerbrey analysis of the frequency change following deposition on anionically coated quartz crystals yields areas at saturation of 0.30 ± 0.02 nm^2 molecule^{-1}. These data approximate to the molecular cross-sections but it is noted that values are limited by the area of the underlying Au–S–(CH$_2$)$_3$–SO$_3^-$ lattice structure. The rectifying cations include *N*-methyl-4-{2-(4-dibutylaminophenyl)vinyl}quinolinium (Fig. 4), which has a rectification ratio of *ca.* 14 at ±1 V when ionically coupled and 11–18 at ±1 V when the chromophore is self-assembled *via* an alkanethiolate link.[12] *N*-methyl-4-{2-(4-methoxynaphthalen-1-yl)vinyl}quinolinium (Fig. 5) yields a similar ratio of *ca.* 10 at ±1 V compared with 30 at ±1 V when conventionally assembled. There are also many other examples which are currently under investigation. They include linear D–π–A^+ and chevron-shaped D–π–A^+–π–D molecules and, in each case, the direction of electron flow at forward bias signifies that the positively charged heterocycle points towards the anionic substrate. Furthermore, rectification ratios from these ionically coupled structures are similar to those of conventional SAMs and the data confirm that the underlying anionic lattice effectively controls the alignment.

We now focus upon *N*-methyl-4-{2-(4-dimethylaminonaphthalen-1-yl)vinyl}quinolinium whose ionically coupled films yield high rectification ratios (Fig. 6). When initially deposited, ratios of 30–60 at ±1 V are typical but, as already noted above, the electrical asymmetry tends to increase with time and this is attributed to self-ordering of the ionic lattice. Rectification ratios of 100–200 at

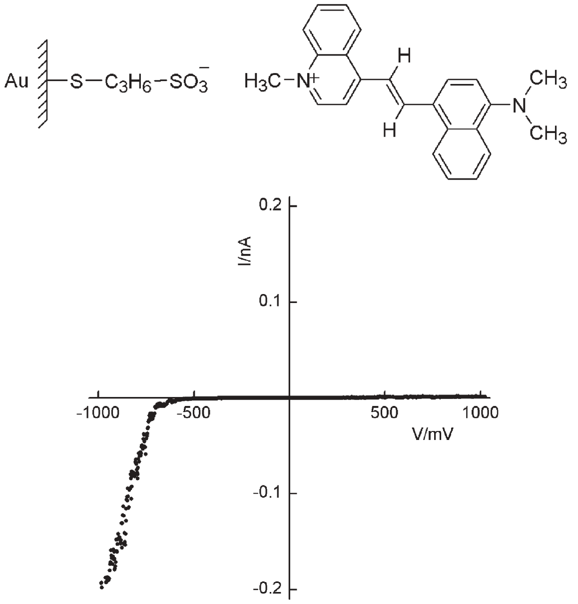

Fig. 6 Aligned molecular diode where the cation is *N*-methyl-4-{2-(4-dimethylaminonaphthalen-1-yl)vinyl}quinolinium and *I*–*V* characteristics of its $\mathrm{Au{-}S{-}(CH_2)_3SO_3^-|A^+{-}\pi{-}D}$ structure contacted by a PtIr probe. Data were obtained for a set point current of 0.1 nA and substrate voltage of –0.1 V and averaged for ten scans from the same site. The bias is designated by the sign of the substrate electrode.

±1 V are more typical of the aged films and these high values overlap the upper end of the reported range of 50–150 at ±1 V for conventional SAMs of this chromophore when connected by a decanethiolate link.[14] The set point current and voltage were varied for this dye and each of the other films: they affect the magnitude of the current by altering the distance between probe and surface but have minimal effect on the shape of the *I*–*V* curve. In addition, the probe and substrate are made from different metals but have closely matching work functions (Au, 5.1–5.3 eV; PtIr, 5.5 eV):[18,19] they provide symmetrical *I*–*V* characteristics when in contact with nonpolar molecules but exhibit electrical asymmetry when in contact with the ionically coupled films. The bias for molecular rectification in each case suggests that the cationic acceptor (heterocycle) points towards the anionic surface with electron tunnelling at forward bias from the cathode to acceptor on one side of the device and from the donor to anode on the other.

A comparison of the properties of the dyes indicates improved rectification for the stronger electron-donating group: ionically coupled films of the methoxy analogue of the naphthalene-1-yl dye exhibit rectification ratios of *ca.* 10 at ±1 V compared with an optimum of 200 at ±1 V for the dimethylamino analogue even though the packing is similar, as indicated by indistinguishable molecular areas from each. Furthermore, the rectification ratio is dependent upon steric hindrance, which induces the nonplanarity in a bulky chromophore and maintains the integrity of the donor and acceptor ends of these π-bridged molecules. Significantly, the least sterically hindered of the dyes with dialkylamino donors exhibits the weakest rectification with a ratio of *ca.* 14 at ±1 V whereas the bulkiest analogue, with a $\mathrm{CH_2CH_2CH_2}$ link between the conjugated part of the heterocycle and bridge, exhibits an optimum rectification ratio of 450 at ±1 V.

In conclusion, a novel method of alignment has been achieved for cationic $\mathrm{D{-}\pi{-}A^+}$ chromophores on an anionic surface and the rectification is either on a par or higher than when LB deposited or conventionally self-assembled. Furthermore, the rectification ratios from ionically coupled films of *N*-methyl-5-(4-dibutylaminobenzylidene)-5,6,7,8-tetrahydroisoquinolinium (Fig. 1) and *N*-methyl-4-{2-(4-dimethylaminonaphthalen-1-yl)-vinyl}quinolinium (Fig. 6) on $\mathrm{Au{-}S{-}C_3H_6{-}SO_3^-}$ substrates are higher than all other values reported for molecular diodes to date.[2–16] The data confirm the versatility of the technique and we note that alignment is achieved without the need to synthesise amphiphilic derivatives or molecules with self-assembling thiol groups. The anionic surface, provided by a commercially available material, yields an uncomplicated route to ultra-thin rectifying films.

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Notes and references

† Sodium 3-mercapto-1-propanesulfonate is commercially available and the cationic molecules are either known or have been obtained by adapting reported procedures for amphiphilic and self-assembling derivatives of the series of dyes.[7,12–15]

1 A. Aviram and M. A. Ratner, *Chem. Phys. Lett.*, 1974, **29**, 277.
2 G. J. Ashwell, M. Sujka and A. Green, *Faraday Discuss.*, 2006, **131**, 23.
3 J. W. Baldwin, R. R. Amaresh, I. R. Peterson, W. J. Shumate, M. P. Cava, M. A. Amiri, R. Hamilton, G. J. Ashwell and R. M. Metzger, *J. Phys. Chem. B*, 2002, **106**, 12158.
4 A. Honciuc, A. Jaiswal, A. Gong, H. Ashworth, C. W. Spangler, I. R. Peterson, L. R. Dalton and R. M. Metzger, *J. Phys. Chem. B*, 2005, **109**, 857.
5 G. Ho, J. R. Heath, M. Kondratenko, D. F. Perepichta, K. Arsenault, M. Pézolet and M. R. Bryce, *Chem.–Eur. J*, 2005, **11**, 2914.
6 (*a*) R. M. Metzger, T. Xu and I. R. Peterson, *J. Phys. Chem. B*, 2001, **105**, 7280; (*b*) N. Okazaki, J. R. Sambles, M. J. Jory and G. J. Ashwell, *Appl. Phys. Lett.*, 2002, **81**, 2300.
7 G. J. Ashwell, B. J. Robinson, M. A. Amiri, D. Locatelli, S. Quici and D. Roberto, *J. Mater. Chem.*, 2005, **15**, 4203.
8 (*a*) P. Jiang, G. M. Morales, W. You and L. P. Yu, *Angew. Chem., Int. Ed.*, 2004, **43**, 4471; (*b*) M.-K. Ng, D.-C. Lee and L. P. Yu, *J. Am. Chem. Soc.*, 2002, **124**, 11862.
9 M. Elbing, R. Ochs, M. Koentopp, M. Fischer, C. von Hanisch, F. Weigend, F. Evers and H. B. Weber, *Proc. Natl. Acad. Sci. U. S. A.*, 2005, **102**, 8815.
10 (*a*) G. J. Ashwell, A. Chwialkowska and L. R. H. High, *J. Mater. Chem.*, 2004, **14**, 2389; (*b*) G. J. Ashwell, R. Hamilton and L. R. H. High, *J. Mater. Chem.*, 2003, **13**, 1501.
11 G. J. Ashwell, A. Chwialkowska and L. R. H. High, *J. Mater. Chem.*, 2004, **14**, 2848.
12 (*a*) G. J. Ashwell, W. D. Tyrrell and A. J. Whittam, *J. Am. Chem. Soc.*, 2004, **126**, 7102; (*b*) G. J. Ashwell, W. D. Tyrrell and A. J. Whittam, *J. Mater. Chem.*, 2003, **13**, 2855.
13 G. J. Ashwell, A. Mohib and J. R. Miller, *J. Mater. Chem.*, 2005, **15**, 1160.
14 G. J. Ashwell and A. Mohib, *J. Am. Chem. Soc.*, 2005, **127**, 16238.
15 (*a*) G. J. Ashwell and D. S. Gandolfo, *J. Mater. Chem.*, 2002, **12**, 411; (*b*) G. J. Ashwell and D. S. Gandolfo, *J. Mater. Chem.*, 2001, **11**, 246.
16 G. J. Ashwell and D. S. Gandolfo, *J. Mater. Chem.*, 2002, **12**, 417.
17 G. Sauerbrey, *Z. Phys.*, 1959, **155**, 206.
18 J. W. G. Wildöer, C. J. P. M. Harmans and H. van Kempen, *Phys. Rev. Lett.*, 1997, **55**, 16013.
19 D. R. Lide, *CRC Handbook of Physics and Chemistry*, 83rd edition, CRC Press, New York, 2003.