

# Organic rectifying junctions fabricated by ionic coupling

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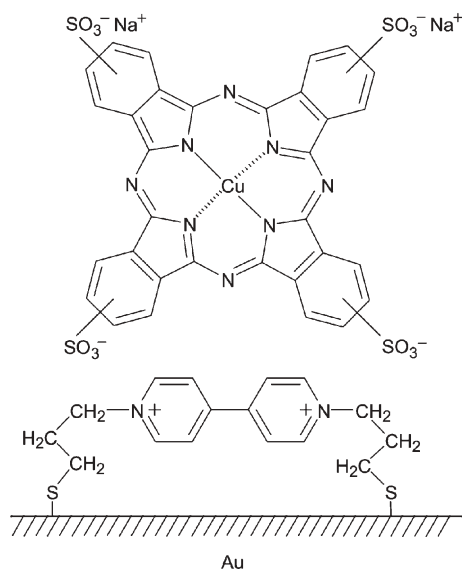
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**Ionically-assembled structures that comprise discrete layers of cationic acceptors (4,4'-bipyridinium) and anionic donors (copper phthalocyanine-3,4',4'',4'''-tetrasulfonate) exhibit asymmetric current-voltage (*I*-*V*) characteristics with high rectification ratios of 60–100 at  $\pm 1$  V.**

To mimic the functions of silicon-based devices it is necessary to design molecules that self-organise in an appropriate manner, the shortest active sequence being metal|donor–acceptor|metal. It is described as a molecular diode<sup>1</sup> when the organic moieties are linked *via* an electron bridge and as a rectifying junction when they are in physical contact. There are few examples and the rectification ratios are far too small to have any real significance, typically 2–30 at  $\pm 1$  V for Langmuir–Blodgett monolayers<sup>2–6a</sup> and self-assembled monolayers (SAMs),<sup>6–11</sup> the films in each case being contacted by non-oxidisable electrodes. In this work, we now report a novel method of self-organisation that yields an optimum ratio of 100 at  $\pm 1$  V for an organic rectifying junction where cationic acceptors and anionic donors couple as separate layers (Fig. 1). It is the first example where ionic assembly has been used to provide an ultra-thin donor–acceptor sequence for molecular rectification.

Films were fabricated in two steps: (i) by immersing gold-coated substrates in a methanol solution of

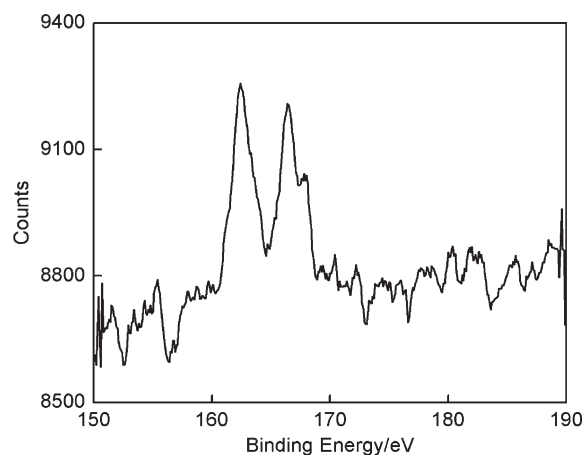


**Fig. 1** Rectifying junction: molecular structures of the self-assembled 4,4'-bipyridinium acceptor and ionically coupled copper phthalocyanine-3,4',4'',4'''-tetrasulfonate donor,  $\text{CuPc}(\text{SO}_3^-)_4(\text{Na}^+)_n$  where  $n = 2$  but experimental studies suggest  $1 \leq n \leq 2$ .

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*N,N'*-bis-(3-acetyl-sufanylpropyl)-4,4'-bipyridinium diiodide<sup>†</sup> [ $\text{BP}^{2+}(\text{I}^-)_2$ ] to which two drops of ammonia solution were added to remove the acetyl groups and then (ii) by metathesis with copper phthalocyanine-3,4',4'',4'''-tetrasulfonate tetrasodium salt [ $\text{CuPc}(\text{SO}_3^-)_4(\text{Na}^+)_4$ ] in aqueous methanol. The frequency change for deposition onto the gold electrodes of 10 MHz quartz crystals was used to monitor the process. A Sauerbrey analysis<sup>12</sup> of the data yielded an area of *ca.*  $0.75 \text{ nm}^2 \text{ molecule}^{-1}$  after the first step, which is consistent with the 4,4'-bipyridinium acceptor aligning parallel to the substrate and being anchored *via* both  $\text{Au-S}-(\text{CH}_2)_3$  links. The frequency change following metathesis suggests that the counterions are replaced by  $\text{CuPc}(\text{SO}_3^-)_4(\text{Na}^+)_n$  where  $1 \leq n \leq 2$ , the area being constrained by the underlying SAM and the calculated values being inappropriate outside this range.

Self-assembly of the 4,4'-bipyridinium salt is apparent from the X-ray photoelectron spectrum, following the first step, which exhibits peaks at 162.4 eV (S 2p) and 619.6 eV (I 3d) that are characteristic of the binding energies of the gold thiolate link and iodide counterion. The latter is unobserved following metathesis and XPS studies reveal additional peaks at 166.4 eV (S 2p), 531.2 eV (O 1s), 936.5 eV (Cu 2p) and 1074 eV (Na 1s) that are unique to the counterion, the additional sulfur peak being characteristic of the sulfonate groups of the  $\text{CuPc}(\text{SO}_3^-)_4(\text{Na}^+)_n$  counterion. The areas of the two different types of sulfur peak, shown in Fig. 2, have a ratio of *ca.* 1 : 1 and are consistent with a stoichiometry of  $[\text{BP}^{2+}]_2\text{Cu}(\text{SO}_3^-)_4$ . These data suggest exclusion of  $\text{Na}^+$  ions but they are influenced by the different atomic depth profiles of sulfur atoms bound to the gold-coated substrate and at the surface of the ionically coupled film. Furthermore, the area of the sodium peak compared with those of copper and sulfur of the



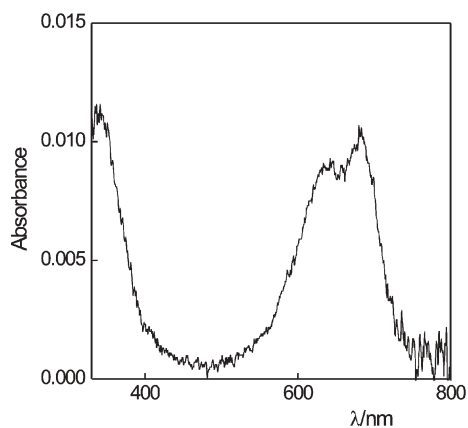
**Fig. 2** XPS data of the gold-thiolate (S 2p, 162.4 eV) and sulfonate groups (S 2p, 166.4 eV) of the organic rectifying junction where the peak heights and areas are probably influenced by the different atomic depth profiles of the two types of sulfur in the ionically coupled film.

anionic moiety, corrected for their atomic sensitivity factors, yields a ratio of  $\text{CuPc}(\text{SO}_3^-)_4$  to  $\text{Na}^+$  of *ca.* 1 : 1 to 1 : 2. The range probably arises from different atomic depth profiles and it is also assumed that this ratio is sample dependent. Nonetheless, the XPS derived data are consistent with the stoichiometric ratios indicated by the Sauerbrey analysis above.

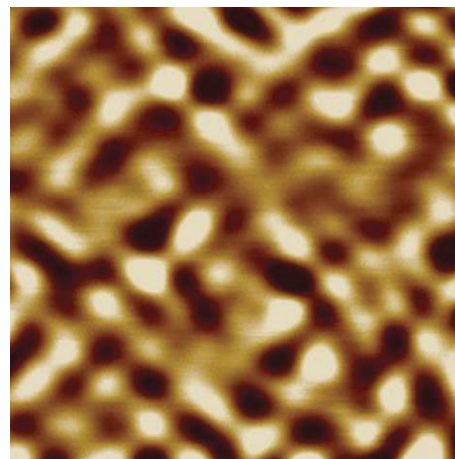
The UV/visible spectrum of the ionically coupled film exhibits maxima at 340, 640 and 675 nm. It was obtained in transmission for a film assembled on a 10 nm thick platinum overlay on a glass substrate, the platinum in this case being preferable to gold as it has an uncomplicated absorption profile that may be readily subtracted to yield the spectrum of the assembled organic layer. The low-energy transition, shown in Fig. 3, is characteristic of the Q band of the phthalocyanine moiety and, as established by XPS studies, also confirms metathesis.

A Nanoscope IV MultiMode scanning tunnelling microscope (Veeco Instruments, Cambridge) was used to investigate the surface of ionically coupled films on gold-coated highly oriented pyrolytic graphite as well as gold-coated mica, the former being amorphous and the latter Au(111). STM images from both types of substrate, obtained using a gold probe, a set point current of 0.2 nA and sample bias of  $-1$  V, exhibit *ca.* 2 nm long “streaks” that correspond to the van der Waals dimension of an edge of the phthalocyanine moiety (Fig. 4). The image is not as well defined as those reported for physisorbed phthalocyanine molecules that adopt face-down arrangements on planar Au(111) substrates.<sup>13</sup> However, disorder is probably induced in the ionically coupled films by a distance mismatch between the negatively charged sulfonate groups in the upper layer and positive charges on the bipyridinium cations in the lower layer.

$I$ - $V$  characteristics were investigated by targeting surface features, the 2 nm streaks, distant from grain boundaries. In excess of 100 curves were obtained at different locations across eight different films and the data each time were averaged for multiple scans on the same spot using contacting gold probes. Each of the films exhibits asymmetric  $I$ - $V$  curves and *ca.* 80% of the scans yield rectification ratios in the range 60–100 at  $\pm 1$  V (Fig. 5). The ratio is independent of the set point current and voltage, which were varied across a broad range: they affect the magnitude of the current by altering the distance between the probe and film surface but have minimal effect on the general



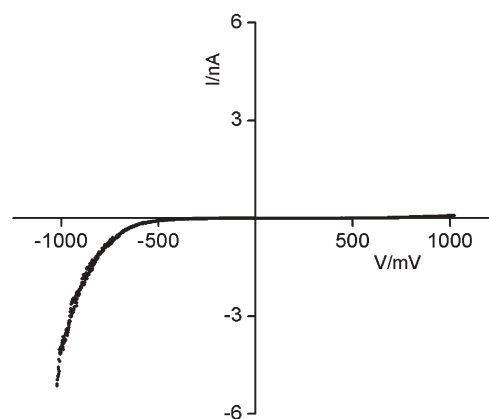
**Fig. 3** UV-visible spectrum of the  $\text{Au}|\text{BP}^{2+}|\text{CuPc}(\text{SO}_3^-)_4(\text{Na}^+)_n$  structure on platinum-coated glass, the data being corrected for absorption by the substrate.



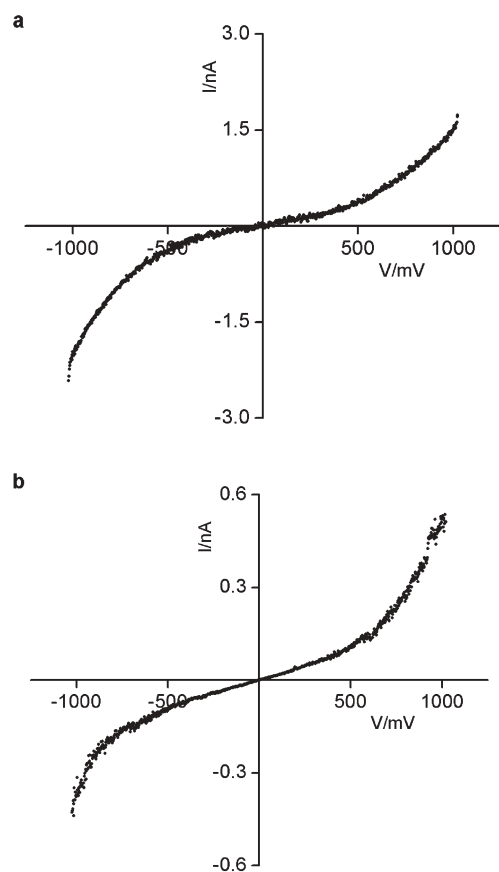
**Fig. 4** 10 nm  $\times$  10 nm STM image of an  $\text{Au}|\text{BP}^{2+}|\text{CuPc}(\text{SO}_3^-)_4(\text{Na}^+)_n$  structure obtained using an Au probe and a set point current and sample bias of 0.2 nA and  $-1$  V, respectively. The streaks correspond to an edge-on arrangement of phthalocyanine molecules at the surface.

shape of the  $I$ - $V$  curve. Almost indistinguishable data were obtained for PtIr probes and we note, for both types of contact, that the rectification ratio is higher than previously obtained from thick  $\text{Au}(\text{bulk donor})|(\text{bulk acceptor})|\text{Au}$  devices.<sup>14,15</sup> Furthermore, the structure represented by Fig. 1 is the first example of an ultra-thin organic rectifying junction that has been contacted by non-oxidisable electrodes.

Ionic coupling of the self-assembled 4,4'-bipyridinium cation with other anionic donors also yields rectifying junctions: films with methyl orange as donor exhibit a rectification ratio of 20 at  $\pm 1$  V and those with 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine-*p,p',p'',p'''*-tetrasulfonate provide a lower ratio of 10 at  $\pm 1$  V. The polarity for rectification is the same in each case and the direction of electron flow at forward bias may be explained by electron tunnelling from the substrate (cathode) to the lowest unoccupied molecular orbital of the bipyridinium acceptor on one side of the device and from the highest occupied molecular orbital of the



**Fig. 5**  $I$ - $V$  characteristics of an  $\text{Au}|\text{BP}^{2+}|\text{CuPc}(\text{SO}_3^-)_4(\text{Na}^+)_n$  structure contacted by an Au probe and obtained for a set point current of 0.7 nA and substrate voltage of  $-0.07$  V, the data being averaged for ten scans on the same spot. The bias is designated by the sign of the substrate electrode and the higher current in the negative quadrant relates to electron tunnelling from substrate to tip, *i.e.* from cathode to acceptor and from donor to anode.



**Fig. 6**  $I$ - $V$  characteristics: (a) Au|BP<sup>2+</sup>|CuPc(SO<sub>3</sub><sup>-</sup>)<sub>4</sub>|BP<sup>2+</sup>|Au trilayer, data obtained for a set point current of 0.2 nA and substrate voltage of -0.2 V; (b) Au|BP<sup>2+</sup> (I<sup>-</sup>)<sub>2</sub>|Au structure, data obtained for a set point current of 0.7 nA and substrate voltage of -0.07 V. The current is dependent upon set point conditions, which influence the contact distance between probe and surface, but the almost symmetrical shapes of the curves are unaffected.

copper phthalocyanine donor to probe (anode) on the other. Tunnelling is restricted in the opposite direction as a consequence of disparity between the molecular and Fermi levels when the input polarity is reversed.

It is important to corroborate molecule induced rectification and, in this case, evidence that it arises from the acceptor/donor sequence is provided by altered  $I$ - $V$  characteristics following deposition of a third layer: Au|BP<sup>2+</sup>|CuPc(SO<sub>3</sub><sup>-</sup>)<sub>4</sub>|BP<sup>2+</sup>|Au. Intuitively, rectifying behaviour is not expected from this almost symmetrical acceptor/donor/acceptor arrangement and the films exhibit almost symmetrical  $I$ - $V$  curves (Fig. 6a). Furthermore, studies on film structures without a donor-acceptor sequence invariably show non-rectifying behaviour and the self-assembled acceptor, Au|BP<sup>2+</sup> (I<sup>-</sup>)<sub>2</sub>|Au, also exhibits almost symmetrical  $I$ - $V$  curves (Fig. 6b). These induced changes suggest that the ionically coupled molecules are not brushed aside by the probe as we progress from a monolayer to bilayer (rectifying junction) to trilayer sequence and the  $I$ - $V$  characteristics are as expected. Furthermore, all three structures have been investigated using both Au and PtIr STM probes: their work functions are closely matched at 5.3 and 5.5 eV, respectively<sup>16,17</sup> and the  $I$ - $V$  curves are indistinguishable when contacted by each.

In conclusion, a rectifying junction with an optimum current ratio of 100 at  $\pm 1$  V has been obtained by ionically coupling a cationic acceptor layer and an anionic donor layer, the molecule-induced properties being verified by symmetrical  $I$ - $V$  curves from the acceptor layer alone and an acceptor-donor-acceptor trilayer structure. The rectification ratio is the highest to date from an organic rectifying junction and compares favourably with recently reported ratios of 50–150 at  $\pm 1$  V from SAMs of an optimised donor-( $\pi$ -bridge)-acceptor diode.<sup>18</sup> We note that it has been achieved without the need to synthesise complex molecules and the ionic sequencing of layers provides a relatively straightforward route to ultra-thin rectifying films.

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## Notes and references

<sup>†</sup> The viologen salt was obtained from the reaction of 4,4'-bipyridyl and thioacetic acid *S*-(3-iodopropyl) ester. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta_{\text{H}}$  2.26 (quintet, 4H,  $J$  7.1, CH<sub>2</sub>); 2.34 (s, 6H, CH<sub>3</sub>); 2.90 (t,  $J$  7.5, 4H, CH<sub>2</sub>); 4.74 (t,  $J$  7.2, 4H, CH<sub>2</sub>); 8.82 (d,  $J$  7.0, 4H, Py-H); 9.40 (d,  $J$  7.0, 4H, Py-H).  $m/z$  (ES<sup>-</sup>): 127, 100%, [I<sup>-</sup>].  $m/z$  (ES<sup>+</sup>): 195, 100% [M - 2I<sup>-</sup>]<sup>2+</sup>.

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