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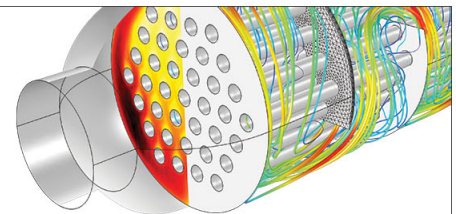
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## Robust reproducible large-area molecular rectifier junctions

Hui-Juan Che,<sup>1,2</sup> Perq-Jon Chia,<sup>1,a)</sup> Lay-Lay Chua,<sup>1</sup> Sankaran Sivaramakrishnan,<sup>1</sup> Jie-Cong Tang,<sup>2</sup> Andrew T. S. Wee,<sup>1</sup> Hardy S. O. Chan,<sup>2,b)</sup> and Peter K. H. Ho<sup>1,c)</sup>

<sup>1</sup>Department of Physics, National University of Singapore, Lower Kent Ridge Road, Singapore S117542, Singapore

<sup>2</sup>Department of Chemistry, National University of Singapore, Lower Kent Ridge Road, Singapore S117543, Singapore

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Stable rectifying molecular junctions have been obtained by sandwiching self-assembled monolayer films containing “push-pull” donor- $\pi$ -acceptor (D- $\pi$ -A) moieties between Au and poly(3,4-ethylenedioxythiophene) electrodes. These D- $\pi$ -A moieties possess moderate molecular dipoles, but assemble into films with nearly zero dipole moment due to adoption of high average tilt angles. Nevertheless reproducible and well-behaved rectifications (ratio up to 3.3) in the expected polarity were obtained. At low biases, the current-voltage characteristics follow Simmons’s tunneling theory with reasonable barrier heights and an effective tunnel mass of  $\sim 0.5m_e$ . This suggests that asymmetric tunneling, and not carrier injection, is the origin of the rectification. © 2008 American Institute of Physics. [DOI: 10.1063/1.2940592]

Molecular electronics present the ultimate challenge in device miniaturization where molecular rectifiers<sup>1–3</sup> may provide the basic components for memory and logic elements. Both donor-barrier-acceptor (D- $\sigma$ -A) molecules<sup>4–6</sup> and donor- $\pi$ -acceptor (D- $\pi$ -A) complexes<sup>7–11</sup> have been investigated as possible rectifier materials. The key challenge is the fabrication of reliable device structures and with sufficiently high yields. Although moderately rectifying junctions have been demonstrated using Langmuir–Blodgett (LB) films,<sup>5,6,8–10,12</sup> tunnel tips,<sup>11,13,14</sup> and mercury-drop contacts,<sup>6,15,16</sup> they have been plagued by sizeable hystereses and current-voltage instabilities. Recently, it was demonstrated that poly(3,4-ethylenedioxythiophene):poly(styrenesulfonic acid (PEDT:PSSH) films can be used as the top electrode for reproducible large-area tunnel junctions with alkyl dithiols.<sup>17,18</sup> Using a similar approach, we show here that reproducible and rectifying IV characteristics can be obtained from Au/thiol-tail-D- $\pi$ -A self-assembled monolayer (SAM)/PEDT:PSSH device structures in high yields.

The D- $\pi$ -A SAM molecules were synthesized in house and shown in Fig. 1. The D- $\pi$ -A moiety is either an asymmetrically substituted *p*-phenylene (Ia and Ib) or *p,p'*-asymmetrically substituted *trans*-stilbene (IIa and IIb) moiety [molecular models in Fig. 2(a)]. Ia and IIa have the positive end of the dipole oriented toward the alkyl spacer, while Ib and IIb have the reverse orientation. For comparison, we also fabricated C<sub>14</sub>H<sub>29</sub>SH (“C<sub>14</sub>SH”) SAM devices, which have a similar tunnel width (Table I).

All assembly steps were conducted in a Class 1000 cleanroom and Class 100 laminar flow hood. For the molecular tunnel junction devices, patterned 50 nm Au bottom electrodes were evaporated through a shadow mask onto 15 × 15 mm<sup>2</sup> SiO<sub>2</sub>/Si wafers. These were then O<sub>2</sub> plasma treated and annealed at 250–320 °C (critical for well-behaved ellipsometric data), and then immersed in a freshly prepared 2.5 mM cyclohexanone solution of the SAM for

>36 h. The substrates were then removed, washed with tetrahydrofuran, isopropanol (twice), and blown dry with N<sub>2</sub>. The top electrode of a 60-nm-thick 1:16 PEDT:PSSH was spin coated<sup>19,20</sup> over the SAM, and a 100 nm Al contact layer was then evaporated through a shadow mask to define 0.1 × 0.1 mm<sup>2</sup> molecular junctions.

The SAM adsorption kinetics was followed by spectroscopic ellipsometry [Fig. 2(b)]. The data showed the D- $\pi$ -A monolayers reached their final thicknesses after  $\sim 30$  h. The final ellipsometric thickness (Table I) of C<sub>14</sub>SH was consistent with published results.<sup>21,22</sup> However the final thicknesses of Ia, IIa, and IIb were considerably smaller than their extended lengths, but similar to the contracted conformations which disposed the D- $\pi$ -A moieties along (rather than perpendicular to) the film surfaces [Fig. 2(a)]. As a result, the effective dipole moments in these films can be expected to be small, which has been confirmed by Ultraviolet Photoelectron Spectroscopy (UPS) work function measurements [Fig. 2(c)]. The measured change in work function  $\Delta\phi$  is related to the net dipole moment  $\mu$  in the film by<sup>23,24</sup>  $\Delta\phi = (dq/\epsilon_r\epsilon_0\sigma) = (\mu/\epsilon_r\epsilon_0\sigma)$ , where  $d$  is distance between the charge planes,  $q$  is charge per molecule,  $\epsilon_r$  is relative dielectric constant ( $\approx 3$ ), and  $\sigma$  is the molecular cross section or footprint (estimated to be  $\approx 30$  Å<sup>2</sup>, larger than the 22 Å<sup>2</sup> for alkyl chains because of the bulky D- $\pi$ -A moieties). This gives  $\Delta\phi = 0.42\mu$ , with  $\mu$  in Debye and  $\Delta\phi$  in eV units. From the measured  $\Delta\phi$  of  $< 0.2$  eV, we obtained  $\mu < 0.5$  D, which is about one-tenth of the molecular  $\mu$  in model compounds or from quantum chemical calculations (Table I). Therefore the D- $\pi$ -A units here must be highly tilted, probably in order to reduce their mutual electrostatic energy. Nevertheless these SAM molecules cannot fully reverse their

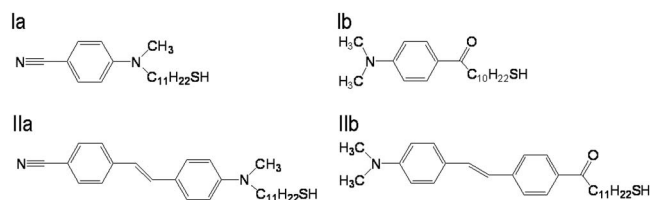


FIG. 1. Chemical structures of the Ia, IIa, Ib, and IIb SAMs.

<sup>a)</sup>Also at Electrical and Computer Engineering.

<sup>b)</sup>Electronic mail: chmcs@nus.edu.sg.

<sup>c)</sup>Electronic mail: phyhop@nus.edu.sg.

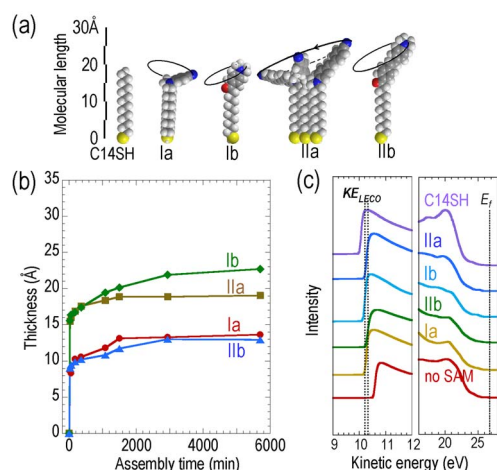


FIG. 2. (Color online) (a) Molecular model of the SAM molecules in the all-trans alkylene chain conformation. The loop denotes the orientation span of the D- $\pi$ -A moiety, are explicitly shown for IIa. (b) Ellipsometry SAM thickness on Au. (c) UPS spectra of (left) low-energy-cutoff (LECO) and (right)  $E_f$  regions.

orientation unlike in LB films<sup>10</sup> because they are tethered at one end to the Au surface. For Ib, the obtained thickness agrees well with the extended conformation. However for this molecule that the dominant contribution to  $\mu$  comes from the C=O group which lies nearly in the plane of the film, and hence also only a small dipole moment is expected across the film thickness.

Figure 3 shows that the molecular IV characteristics obtained from these tunnel junctions. It is clear that they are stable with repeated cycling and show little hystereses. Figures 3(b) and 3(d) give the IV characteristics for the IIa and

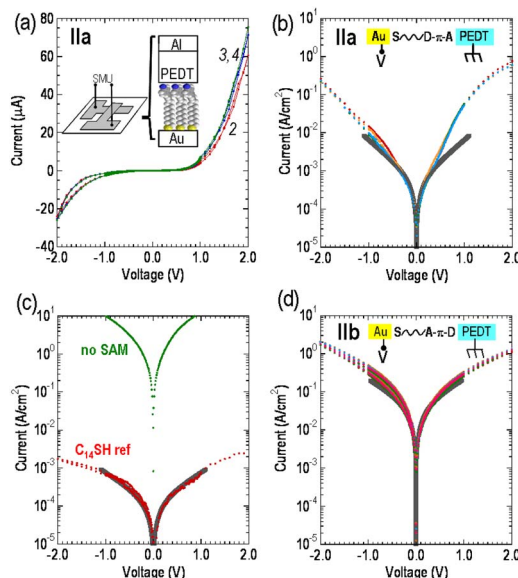


FIG. 3. (Color online) Electrical characteristics of the molecular tunnel junctions: Au/thiol tail-D- $\pi$ -A (and thiol tail-A- $\pi$ -D)/PEDT:PSSH/AI [see inset of (a)], device area 0.01 mm<sup>2</sup>, voltage applied on Au, in glovebox. Work function of PEDT:PSSH (5.1 eV) is similar to clean Au (5.0 eV). (a) Linear IV characteristics for IIa (repeated sweeps shown). (b) Log IV characteristics for IIa (five devices). Forward bias corresponds to donor end more positive. (c) IV characteristics of an insulating C<sub>14</sub>SH junction and of a “shorted” junction (no SAM) as references. (d) IV characteristics for IIb (five devices) showing rectification in the opposite direction. Symbols = data. Thick solid lines = Simmons’s tunnel model (parameters given in Table I).

IIb junctions, respectively. The typical device yield is 11 out of 12 (five of these data are shown explicitly). The small spread in the IV curves indicates excellent reproducibility of

TABLE I. Properties of the SAMs and their devices.

	C <sub>14</sub> SH	Ia	Ib	IIa	IIb
Tunnel width: theory ( $\text{\AA}$ ) <sup>a</sup>	21	18–22	19–23	19–27	20–29
Tunnel width ( $d$ ): expt ( $\text{\AA}$ ) <sup>b</sup>	20.2	17.8	23.5	22.5	17.6
Molecular conformation <sup>c</sup>	All-trans	Contracted	Extended	Contracted	Contracted
Dipole moment of D- $\pi$ -A: expt ( $D$ ) <sup>d</sup>	...	-5.9	5.1	-7.0	...
Dipole moment of D- $\pi$ -A: calc ( $D$ ) <sup>e</sup>	...	-5.7	4.3	-6.8	4.8
Work function $\phi$ (eV) <sup>f</sup>	4.45	4.65	4.6,4.4	4.65,4.75	4.75
Change in work function $\Delta\phi$ (eV) <sup>g</sup>	0.0	+0.2	+0.05	+0.25	+0.3
Effective tunnel barrier height $\Delta$ (eV) <sup>h</sup>	4.0	3.4	2.6	2.75	3.4
Rectification ratio <sup>i</sup>	1.4	2.2	1.4	3.3	2.0

<sup>a</sup>Computed as the distance from the Au surface to the SAM surface for the range of disposition of the D- $\pi$ -A moieties shown in Fig. 2(a) assuming upright all-trans alkyl chains. This is estimated from  $d_{\text{Au-S}} + d_{\text{S-}\omega} + d_{\text{vdw}}$  where  $d_{\text{Au-S}}$  is the distance of S above the Au surface ( $\approx 1.2 \text{ \AA}$ ),  $d_{\text{S-}\omega}$  is the distance of the frontier atom/group above the S plane (AM1), and  $d_{\text{vdw}}$  is the van der Waals radius of that frontier atom/group (e.g.,  $\approx 2.0 \text{ \AA}$  for CH<sub>3</sub>).

<sup>b</sup>Obtained from the ellipsometric thicknesses ( $d_{\text{ellip}}$ ) after correction with  $+3.5 \text{ \AA}$ . This was given by the systematic error ( $-3.5 \text{ \AA}$ ) between  $d_{\text{ellip}}$  and theoretical thicknesses (taking into account the  $30^\circ$  tilt) for C<sub>8</sub>-C<sub>16</sub> alkyl thiols on Au. This correction probably accounts for the physisorption of ambient moisture that occurs on clean Au (which remained hydrophilic throughout the measurements) but not on the SAM-passivated Au surfaces. To obtain  $d_{\text{ellip}}$  we used refractive index  $n = A + B/\lambda^2$  (for D- $\pi$ -A:  $A = 1.46$ , and  $B = 0.01$ ; for C<sub>14</sub>SH:  $A = 1.42$ , and  $B = 0.01$ ) with  $\lambda$  in microns. The uncertainty is  $\pm 0.05$  units which gives a  $\pm 5\%$  error in the film thickness.

<sup>c</sup>“Contracted” is the nearly parallel orientation of the D- $\pi$ -A moiety on the film surface, while “extended” is the nearly perpendicular orientation of the D- $\pi$ -A moiety to the film surface. In addition, the alkyl chain could also be contracted due to lowered packing density.

<sup>d</sup>Literature dipole moments of selected D- $\pi$ -A model molecules Ref. 32. 1Debye ( $D$ ) =  $3.336 \times 10^{-28} \text{ C cm}$ .

<sup>e</sup>Theoretical dipole moment in the gas phase, computed as the mean of DFT (Gaussian 98, with B3LYP and STO-3G) and AM1 results. Satisfactory agreement was obtained (deviation  $< 15\%$ ) with experiment. Sign gives the polarity of the  $\omega$ -end of the molecules.

<sup>f</sup>Measured by UPS with He I ( $h\nu = 21.21 \text{ eV}$ ) excitation in an ESCALab MKII spectrometer from  $\phi = h\nu - (KE_{\text{Fermi}} - KE_{\text{LECO}})$ . For the clean Au surface exposed to ambient,  $\phi = 5.00 \text{ eV}$ . Instrumental precision,  $\pm 0.02 \text{ eV}$ , SAM reproducibility,  $\pm 0.2 \text{ eV}$ .

<sup>g</sup>Taken relative to the C<sub>14</sub>SH SAM layer to account for the Au-S dipolar contribution.

<sup>h</sup>Evaluated for  $V < |1 \text{ V}|$ , assuming electron tunneling, assuming  $m = 0.5m_e$ .

<sup>i</sup>Defined as absolute value of  $I_+/I_-$  where  $I_+$  is forward bias and  $I_-$  is reverse bias. Device structure: Au/tail-D- $\pi$ -A (Ia, IIa) or tail-A- $\pi$ -D (Ib, IIb)/PEDT:PSSH/AI.

these measurements. Figure 3(c) gives IV characteristics of the insulating C<sub>14</sub>SH junction and of the “shorted” junction (i.e., no SAM) for comparison. The current density is at least 1.5 orders of magnitude higher in the shorted junction (2–3 kΩ, due to depletion contact resistance<sup>20</sup>), but several orders of magnitude lower in the insulating junction. Therefore the results here are not compromised by pinhole defects through the films (estimated to be <10<sup>-2</sup>% of film area) or otherwise dominated by parasitic shunt conductance in the devices. This is a crucial validation of the measurements here. The devices can be repeatedly cycled to 2 V without electrical breakdown, which indicates a breakdown strength of >10 MV cm<sup>-1</sup>, slightly higher than that in mercury drop junctions.<sup>25</sup>

The IV characteristics at low biases (up to ±1 V) can be described by a simple form of Simmons’s tunneling theory:

$$j = \frac{e}{2\pi h d^2} \left[ \left( \Delta - \frac{eV_{\text{appl}}}{2} \right) \exp\left( -\frac{4\pi d\sqrt{2m}}{h} \sqrt{\Delta - \frac{eV_{\text{appl}}}{2}} \right) - \left( \Delta + \frac{eV_{\text{appl}}}{2} \right) \exp\left( -\frac{4\pi d\sqrt{2m}}{h} \sqrt{\Delta + \frac{eV_{\text{appl}}}{2}} \right) \right],$$

where V<sub>appl</sub> is applied bias, Δ is tunnel barrier height, d is tunnel width, h is Planck constant, e is electronic charge, and m is tunnel electron mass. This confirms tunneling and that the data are reliable. In order to extract Δ, we need to have an estimate of μ. Unfortunately the literature disagreed wildly on the tunnel mass (values assumed between 0.3–1.0 m<sub>e</sub>) primarily because widely differing β values [β = -(4π√2mΔ/h)] were obtained even for simple alkyl thiols.<sup>26,27</sup>

To determine the β value for alkyl chain tunneling across these well-behaved devices, we separately fabricated junctions with C<sub>8</sub>, C<sub>12</sub>, and C<sub>14</sub> alkyl thiol SAMs. We found β = 1.4 ± 0.1 Å<sup>-1</sup> at 1 V, which are among the highest reported,<sup>28,29</sup> higher than the 1.0 Å<sup>-1</sup> often seen in electrochemical experiments,<sup>26,27</sup> and considerably higher than the 0.6 Å<sup>-1</sup> obtained for alkyl dithiols<sup>17,18</sup> in similar Au/SAM/PEDT junctions. We think a larger β value suggests higher quality tunneling which is less compromised by the presence of shunt conduction through defects which typically have a weaker distance (and voltage) dependence. However for an alternative view, please see Ref. 30. We also do not yet understand the lower β values found in the alkyl dithiol junctions.<sup>17,18</sup> A possible explanation may be the presence of hairpin conformations that reduce the effective tunnel width, even though x-ray photoelectron spectroscopy suggests such conformations were minimized at the dithiol concentration used.<sup>18</sup>

For an assumed barrier height of 4.0 ± 0.5 eV (i.e., half of the σ-σ\* energy gap of 8.0 eV),<sup>31</sup> this β value suggests m = 0.5 ± 0.1 m<sub>e</sub>. Using this m value, we extracted the Δ values for the D-π-A SAMs (Table I) and found they were lowered by 0.6–1.4 eV, in broad agreement with the participation of π-π\* states (highest occupied molecular orbital-lowest unoccupied molecular orbital gap expected to be ~5–6 eV) in the tunnel path. The rectification direction (i.e., the polarity for forward bias) corresponds to the donor end more positive than the acceptor end. For a forward bias of >0.2–0.3 V, the current increases faster than theory, except

for Ib. This gives a rectification ratio (i.e., the ratio of current in forward bias to reverse bias) of up to 3.3 at ±2.0 V.

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