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Prevalence of Coulomb blockade in electro-migrated junctions with conjugated and non-conjugated molecules

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Abstract

Conduction of electro-migration gap junctions coated with various organic molecules is studied to expose the prevalence of different transport processes. The principal comparison made here is between molecules with conjugated versus non-conjugated backbones. Coulomb blockade (CB) is observed in *all* junctions, including bare junctions and those with non-conjugated molecules, but at significantly lower prevalence than for conjugated molecules. Importantly, CB with high charging energy is seen almost exclusively on junctions with conjugated molecules. These results indicate that CB is ubiquitous in molecular electro-migration junction transport with prevalence that should be characterized using large numbers of samples.

1. Introduction

In recent years, various experimental schemes [1–3] have been proposed for constructing an appropriate metal–molecule–metal unit that can be used to examine electron transport through molecules. One of the most attractive methods for constructing such molecular junctions is through the use of electro-migration [4]. This method involves the production of a small gap in an otherwise continuous metal wire by applying an electric potential across the wire sufficient to induce metal atom migration due to momentum transfer from the conduction electrons. A major advantage of this method is that a gate can be placed in close proximity to the gap and to the molecules (e.g. figure 1(a)), and can then be used to vary the electronic properties of the molecules and the junction. Such an approach has been used to measure molecular species including C₆₀ [5, 6] and organic molecules containing metal ions [7, 8].

In spite of its advantages, electro-migration as a tool for producing molecular scale contacts suffers from a significant problem: the junction can be highly disordered. Because gap

formation is based on the migration of metal atoms, the final geometry of the gap varies from junction to junction. The most severe disorder complication is metal cluster formation during electro-migration. Metal clusters of varied sizes may form during the migration process and reside in and around the formed gap. Consequently an array of junction morphologies may form during electro-migration from the metal clusters, molecules and hybrids of these charge carrying geometries; models of such varied junction types are shown schematically in figure 1(c). This can lead to difficulties in measurement interpretation because electronic properties that are attributed to molecules can be consistent with the properties of metal clusters or hybrid structures populating the gap. For example, the presence of Coulomb blockade (CB) has been used commonly to indicate transport through single molecules [5–8]. CB is the result of single-electron charging of an island that is weakly coupled to the two metal electrodes, with consequent blockage of current flow over a finite bias range. Therefore CB is expected both for conjugated (i.e. charge carrying) molecules and for metal clusters. CB

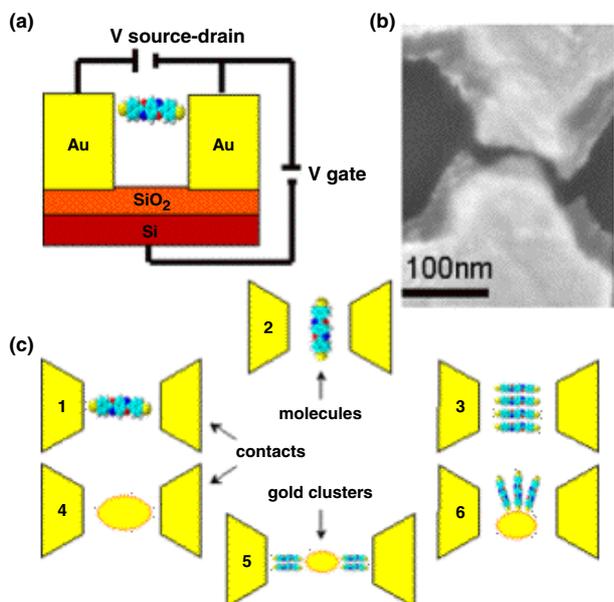


Figure 1. (a) Schematic diagram of electro-migration gap and measurement configuration. (b) Electron micrograph of typical electro-migration gap. (c) Six models describing possible geometries formed within the electro-migration gap by molecule(s) and contaminant gold particles.

is not expected (within reasonable potential limits) for non-conjugated molecules that cannot hold extra charge. Because electro-migration gaps are commonly employed for molecular conduction measurements, it is vital to understand empirically the difference in conduction through the various possible junction geometries, including formed metal clusters versus conduction through only molecules.

In order to distinguish between CB of organic molecules and CB of metal clusters in molecular electro-migrated junctions, we have studied metal junctions coated with various molecules. Comparisons are made principally between conjugated and non-conjugated molecules, where charge is dispersed over the conjugated structures, versus those localized in the non-conjugated species. In addition, comparisons are made between molecules with one versus two thiol end groups, and between molecules with and without large sterically significant side chains. The electron localization of the molecules affects the charge carrying capability (capacitance), and so the Coulomb blockade; the presence of thiol groups affects the adhesion of the molecules to the metals; and the presence of side chains affects the packing of the molecules, influencing the density and the placement of the molecule in the electro-migration gap.

In low temperature transport through the junctions, we find here that Coulomb blockade can be observed in all molecular species tested, including bare junctions and those coated with molecules with no electron-accepting properties, but at significantly lower prevalence than conjugated molecules. Besides this clear difference in prevalence, CB with large charging energy values is seen almost exclusively on junctions with molecules possessing the delocalized electrons. These results present typical incidence rates for CB due to both metal particle formation and molecular conduction, and show that CB

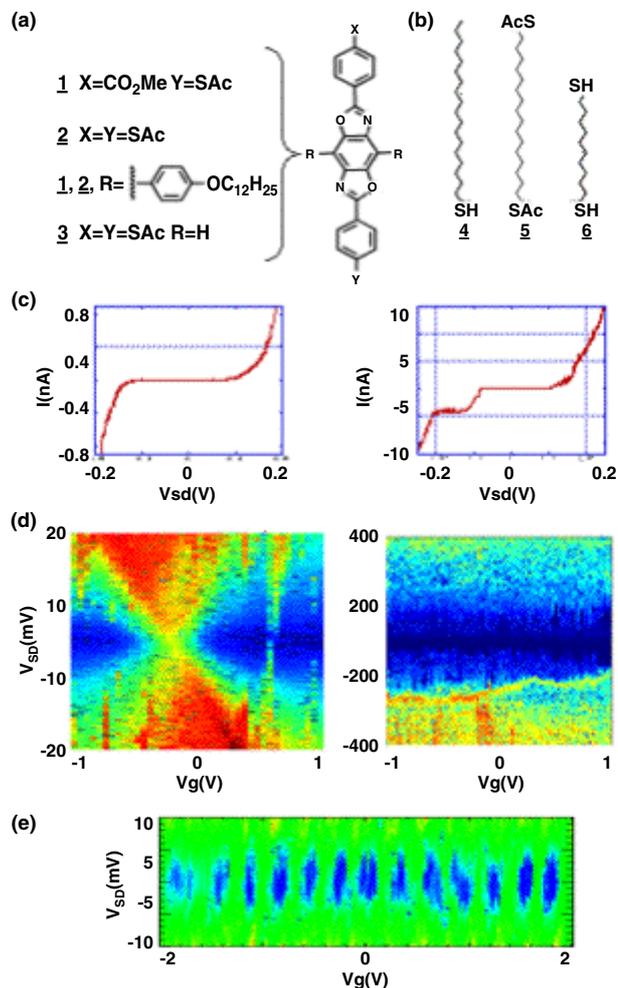


Figure 2. (a) Conjugated (1–3) and (b) non-conjugated (4–6) molecules used in electro-migrated junctions. Conjugated molecules include a monothiol with long side chains 1, a dithiol with long side chains 2 and a dithiol with no side chains 3. The non-conjugated molecules include a C_{18} monothiol 4, a C_{16} dithiol 5 and a C_{10} dithiol 6. (c) Tunneling I/V curve typical of junctions measured (left), and Coulomb blockade in an I/V trace as observed in measurements. (d) Left: dI/dV (colour) versus source–drain voltage versus gate voltage for a non-conjugated molecule showing low charging voltage Coulomb diamonds: the colour scale extends from 10^{-7} (blue) to 10^{-3} A (red). Right: dI/dV (colour) versus source–drain voltage versus gate voltage for bisoxazole: note the gate independence of the s–d gap and the large charging energy: the colour scale extends from 10^{-7} (blue) to 10^{-4} A (red). (e) Multiple charging states observed for a C_{10} coated junction suggesting gold cluster contamination: the colour scale extends from $10^{-6.5}$ (red) to 10^{-8} A (blue).

properties for any given molecular species should be derived with measurements of large numbers of junctions.

2. Experimental techniques

The molecular species tested are displayed in figure 2. Molecules 1–3 represent the conjugated moieties, 4–6 the non-conjugated ones. Molecules 1 and 2 (bisoxazole derivatives) were synthesized as described earlier [9]. Molecule 3 was

Table 1. Summary of transport results (I/V measurements) and film properties for junctions covered by the different molecules. The four possible results include Coulomb blockade, simple tunnelling, open junctions (no current) and finite conductivity ($dI/dV > 0$) at zero bias (labelled cond. (%)). The six molecular species tested are of similar length except the shorter C_{10} alkane-dithiol, **6**. Ellipsometry and contact angle (CA) measurements of molecular film properties on gold surfaces. The combination of very low measured ellipsometric thickness and high CA hysteresis indicates non-compact surface coverage.

Molecule	Conduction mechanism prevalence and film properties						Film properties	
	Coulomb blockade (%)		Tunnelling (%)	No current (%)	Cond. (%)	Total	Measured thickness (Å)	Contact angle hysteresis (deg)
1 Monothiol bisoxazole	27		27	45	1	85	19	10
2 Dithiol bisoxazole	30	29	24	44	2	124	13	23
3 No side bisoxazole	31		36	15	18	68	15–80	11
4 Alkane $C_{18}SH$	11		62	25	2	57	24	6
5 Alkane $C_{16}(SH)_2$	10	10	34	52	4	56	4	10
6 Alkane $C_{10}(SH)_2$	63	n/a	26	11	0	19	14	3
No molecules	11	11	32	51	6	69	n/a	n/a

synthesized as noted³ and molecule **5** was synthesized from the respective alkyl dibromide⁴. Molecules **4** and **6** are commercially available.

Junctions were prepared as previously described [4] and were cleaned in an $SC1^5$ solution for 5 min followed by 20 min of soaking in ethanol [12]. The clean samples were soaked in 1×10^{-4} M THF or ethanol solutions of the various molecules. Ammonium hydroxide (30 μ l, 0.5 M) was added to the molecule solution in order to cleave the thio-acetate protecting group of molecules **1–3** and **5**. The solutions containing the samples were kept for 2–4 h at 48 °C and then left overnight at room temperature, rinsed with THF and ethanol and N_2 dried. The adsorption time for the simple thiol molecules **4** and **6** was 2 h. The samples were then inserted into a probe station and cooled to 4 K. Both the electro-migration and the measurements were carried out at this temperature. We have chosen this low temperature to minimize instabilities coming from the mobility of gold and the molecules at the gold surface at higher temperatures. A semiconductor parameter analyser supplies voltages for source/drain and the gate and measures the current through the structures in a two-point geometry.

3. Results

Figure 2(c) shows typical I/V curves obtained for the molecules measured. Each junction tested shows one of the following four transport mechanisms: Coulomb blockade, tunnelling, non-tunnelling current at zero bias and no current. Table 1 summarizes the conduction results for each of the I/V profiles obtained for each molecule. We focus initially on the prevalence of CB features of junctions coated with different molecules. The most important result in table 1 is

³ Compound **3** was synthesized by double acylation of 2,5-diamino-1,4-benzoquinone with *p*-anisoyl chloride. Following reduction to the hydroquinone with $Na_2S_2O_4$, dehydration to the bis-benzoxazole was achieved following a known procedure (see Perry *et al* [10]). After demethylating with BBr_3 the phenols were transformed into thiol acetates (see Meier and Mayer [10]). The final step in the Meier procedure was altered by quenching the LAH reduction with acetyl chloride.

⁴ Compound **5** was synthesized from commercially available 1,16-dibromohexadecane by a known procedure [11].

⁵ 1:1:5 $H_2O_2:NH_4OH:H_2O$.

the appearance of CB in both conjugated and non-conjugated molecular junctions. Further, CB features are also seen at low incidence on bare gold samples. The prevalence of CB changes significantly when comparing conjugated to non-conjugated to no molecules (29% to 10% to 11%).

The data in table 1 comparing Coulomb blockade prevalence in conjugated versus non-conjugated molecules demonstrate a statistically significant difference as determined by a chi-squared analysis [13]. If the hypothesis tested is that the conjugated molecule Coulomb blockade prevalence measured (~29%) is different to the expected value of Coulomb blockade prevalence in the non-conjugated molecules as established by measurements (~11%), the data produce a chi-squared value of near 100. This chi-squared value results in a P -value of less than 0.001 for the parameter set tested, or there is less than 0.1% chance that the hypothesis is wrong. The large difference in prevalence and the large number of samples tested (>400) are the root of this small P -value, affirming that there is a significant difference in the blockade prevalence.

CB is not expected for non-conjugated molecules in such a configuration and is definitely not expected for bare gold junctions. This result raises the possibility that many of the CB features seen in our junctions are due to isolated gold clusters located in the gap. This assumption is augmented by the charging energies evaluated from the Coulomb gaps. The charging energy is represented by the magnitude of the total voltage range over which current is blocked. The charging energies are plotted in figure 3 for all molecules measured. Excluding junctions with conjugated molecules, charging energies are predominantly distributed around 100 mV. Low charging energies from structures in the electro-migrated gap are the consequence of two properties: (a) a high capacitance to the leads and (b) accessible energy states for holding extra charge. Since both bare samples (no molecules) and non-conjugated molecules have no energy states to accommodate excess charge, these CB features are most likely to originate from contaminant gold clusters. Further evidence for the formation of gold clusters was observed in non-conjugated molecular junctions that display multiple Coulomb diamond periodicity (figure 2(e)); in these junctions, only a relatively

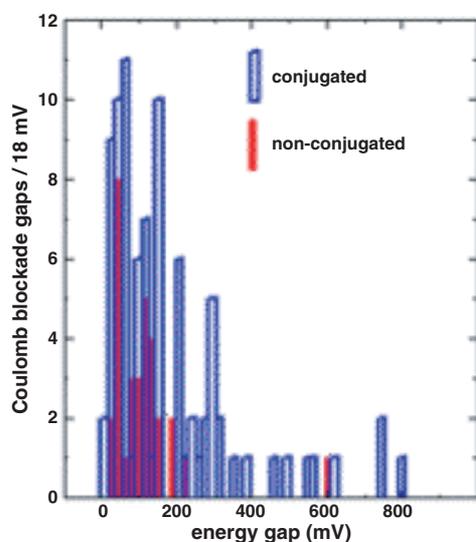


Figure 3. Histogram of the incidence of charging energies for all junctions showing Coulomb blockade, comparing conjugated coated to all other junctions (red/solid grey), including non-conjugated ones and ones with no molecules.

(This figure is in colour only in the electronic version)

large, multiple-charge-state system such as gold particles can produce such charging diamonds.

The distribution of the charging energies (figure 3) for the conjugated molecules shows properties consistent with the presence of both contaminant gold clusters and smaller capacitance charge carriers as expected for CB in the conjugated molecules. The CB distribution with lower than 300 mV gaps is similar for conjugated and non-conjugated molecular junctions. *However, CB with higher than 300 mV Coulomb gaps was found predominantly on samples coated with conjugated molecules.* From the histograms of figure 3 it is seen that CB gaps occur with charging energies higher than 300 mV and up to 800 mV, accounting for ~25% of the conjugated molecule junctions showing CB. The figure 3 data show a statistically significant difference in prevalence of Coulomb blockade between conjugated and non-conjugated molecules for charging energy greater than 200 mV, as determined by chi-squared analysis. The non-conjugated molecules showed only two samples with Coulomb blockade over 200 mV, representing about 11%, versus twenty with Coulomb blockade in the conjugated molecules corresponding to 25%. Given the total numbers tested, this difference results in a statistical difference with *P*-value less than 0.001, including a Yates correction [13].

4. Discussion

The large charging energy Coulomb blockade shown in figure 3 may be the result of only the respective molecular species bridging the gap, either as single molecules or in clumps in various orientations, corresponding to the schematic diagrams 1, 2 or 3 in figure 1(c). In the case of a single molecule the charging energies are expected to be higher both because of its small capacitance to the leads and because of the high energy separation between the molecular electronic levels. The size of

the island taking part in the conduction can be estimated using simple geometrical arguments. The charging energy $e^2/2C$ for a molecule of approximately 1 nm length and width can be calculated by assuming that the capacitance of the molecule is given by $C = 4\pi\epsilon_0R$, where R is the length of the molecule. Thus a single molecule, which is charged, has a charging energy of about 1 eV. A charging energy of 200 meV and lower, as observed in the majority of the junctions, corresponds to islands of 3 nm diameter and larger. Therefore mechanisms other than conduction through molecules have to be taken into account. It cannot be excluded though that a combination of gold and molecules may yield a hybrid object that is likely to show such CB parameters (figure 1(c), schematic diagrams 5 and 6). We could not evaluate a distinct difference among the conjugated molecules between molecules with 1 versus 2 thiols and between molecules with and without side chains. The model of molecule/s or of a hybrid of gold and molecules has further support from the gating experiments: all junctions showing higher charging energies had no response to an applied gate voltage (see figure 2(d)). It may be expected that for any model involving only molecules migrating into or over the gap, the molecule will most probably be suspended between the two gap edges well above the dielectric (figure 1(a)). Such a location would screen the object from the gate field effect. However, an isolated gold cluster is expected to be bound directly to the dielectric surface and therefore easily field affected, as seen in figure 2(d).

We now focus on the surprising result of the significant prevalence of Coulomb blockade in non-conjugated and bare junctions. If it is assumed that contaminant gold cluster formation is responsible for this CB, then our results suggest that such gold cluster morphology occurs in electro-migrated gaps at about 10% incidence rate. It can be postulated that differences in the CB prevalence in general may be attributed to three parameters:

- (1) the amount of coverage by each molecule on the gold wire,
- (2) the number of thiol end groups (1 or 2) on each molecule and
- (3) electron delocalization in the molecular backbone, as shown above.

The coverage of the gold surface by each molecule was estimated from ellipsometry and contact angles (CA) measurements and is summarized in table 1. First, the CB prevalence rate for the C_{16} or C_{18} molecules is essentially that of the bare wires. However, the molecule that shows the highest CB% (63%) is a C_{10} dithiol molecule 6. This molecule does not have any charge carrying capacity (consists of sigma bonds only), but it does have two thiol end groups, and a very high density coverage. As shown in figure 2, it is substantially shorter than the conjugated molecule backbones, with the C_{16} or C_{18} molecules a closer match to the conjugated species. The ellipsometric thickness of 14 Å measured suggests that these C_{10} molecules are close packed with their long axis almost perpendicular to the surface. The small hysteresis (3°) verifies the close packing of these molecules on the gold surface, as opposed to the poorer coverage by both C_{16} and C_{18} molecules. This C_{10} result shows not only that charge carrying capability of the molecules is not essential for seeing CB, but also that a

well-packed molecular layer may be optimal for forming gold particles, able to produce CB in transport.

The lowest CB prevalence is found in long alkyl chain based thiols and dithiols and in clean junctions that have no molecules, all near 10%. In contrast to the C₁₀ molecules, the C₁₈ thiol and the C₁₆ dithiol form a poorly ordered layer on the gold surface (low ellipsometric thickness and high CA hysteresis), and consequently appear to not modify gold cluster formation beyond that observed with no molecular coverage. Similarly, for the conjugated molecules the influence of thiolation and the presence of side chains appear to have minimal differential impact on CB prevalence. This holds even though the film properties differ among these molecules. Molecule 1 covers the gold in a relatively close packed manner as is evident from the ellipsometric values, while molecule 2 forms a less compact layer. Molecule 3 forms an irregular and probably a multilayered structure. It is notable that the no-side-chain molecule 3 shows an excessive prevalence of non-CB, non-tunnelling conductivity near zero bias: this molecule most closely matches species tested in previous studies [7, 8].

5. Summary

In summary, the results of these measurements show that Coulomb blockade can be ubiquitous in electro-migration junctions generally, with molecular coatings of non-conjugated species or no molecules at all showing lower CB prevalence than those with conjugated molecules. The molecular conjugation is the most significant determinant of the prevalence of CB; thiolation and the presence of large side chains do not influence this prevalence as well as can be determined here. The distribution of charging energies differs significantly between conjugated and non-conjugated Coulomb blockade results, with the conjugated molecules showing substantial numbers of high charging energy junctions. These results are consistent with a model in which *all* junctions have a nominal probability of

contamination with gold clusters, which will generally support low charging energy CB; however, distinctive high charging energy CB can be discriminated in conjugated molecular junctions. These results show that with large sample numbers, the Coulomb blockade properties can be extracted from electro-migration gap experiments.

Acknowledgments

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