Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Understanding Interface (Odd-Even) Effects in Charge Tunneling using Polished EGaIn Electrode

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Background

Charge transport across metal-insulator-metal junctions has been performed across many different platforms using some reliable and some questionable or poorly understood systems. There are two main categories of junctions *viz;* i) Small area (or single molecule) junctions ($<1 \mu m^2$) that are time-consuming, require specialized techniques/instruments, and often give very low yields,[1] and ii) large-area junctions (> 100 μm^2) that conveniently generate statistically large data sets and are more convenient to form.

For small area junctions, conducting probe tips (STM, cpAFM) have been used to measure charge transport across SAMs.[2-8] Break junctions are the other major group of small area junctions.[9-13] Break junctions rely mechano-chemical trapping of a single molecule between two metal electrodes, which can only be used with few functional groups with metal electrodes and often give very low yields (< 5%) which makes it difficult to collect statistically significant data sets.[1]

The odd-even effect, which describes the oscillations in structure and resultant properties depending on the presence of either odd or even number of repeating units, has been widely observed across science and engineering fields. The odd-even effect in n-alkanethiolate self-assembled monolayers (SAMs) involves properties of wetting, charge transport, melting point and vibrational spectroscopy, which are dependent on presence of either odd or even number of C in the molecule. The odd-even effect is highly sensitive to substrate morphology or roughness,[14-16] chain length related molecular conformation[17-20] and also the test-bed.[21-23] Chemisorbed n-alkanethiol molecules on

silver (Ag) surface show different tilting angles for the terminal -CH_2-CH_3 group for odd or even number of carbons in the molecular chain. [14-15]

The nature of the electrode-SAM interface can change the interfacial dielectric constant and as such affect the potential drop across a junction.[24-25] In the case of a combined mechanism transport,[26] for example Schottky and tunneling,[26] or hopping and tunneling.[27-28]

In follow up studies we looked at effect of; i) having an asymmetrically positioned accessible HOMO[27, 29] or LUMO[(ref TCNQ)] on electrical rectification of a tunnel junction, ii) perturbation to the internal structure of the SAM by introducing amides capable of inter-chain hydrogen bonding,[30] iii) Effect of different terminal groups on charge transport across metal-SAM\metal junctions.[31]

The origin of the odd-even effect in [22]SAMs is either due to; i) variation in the tilting angle of the terminal group, either -CH_3 or -CH_2-CH_3, hence difference in potential point of contact or surface dipole. This has a major effect on interface properties and/or phenomena. ii) Effect of orientation on effective molecular dipole, for properties dependent on the bulk properties of the SAM.

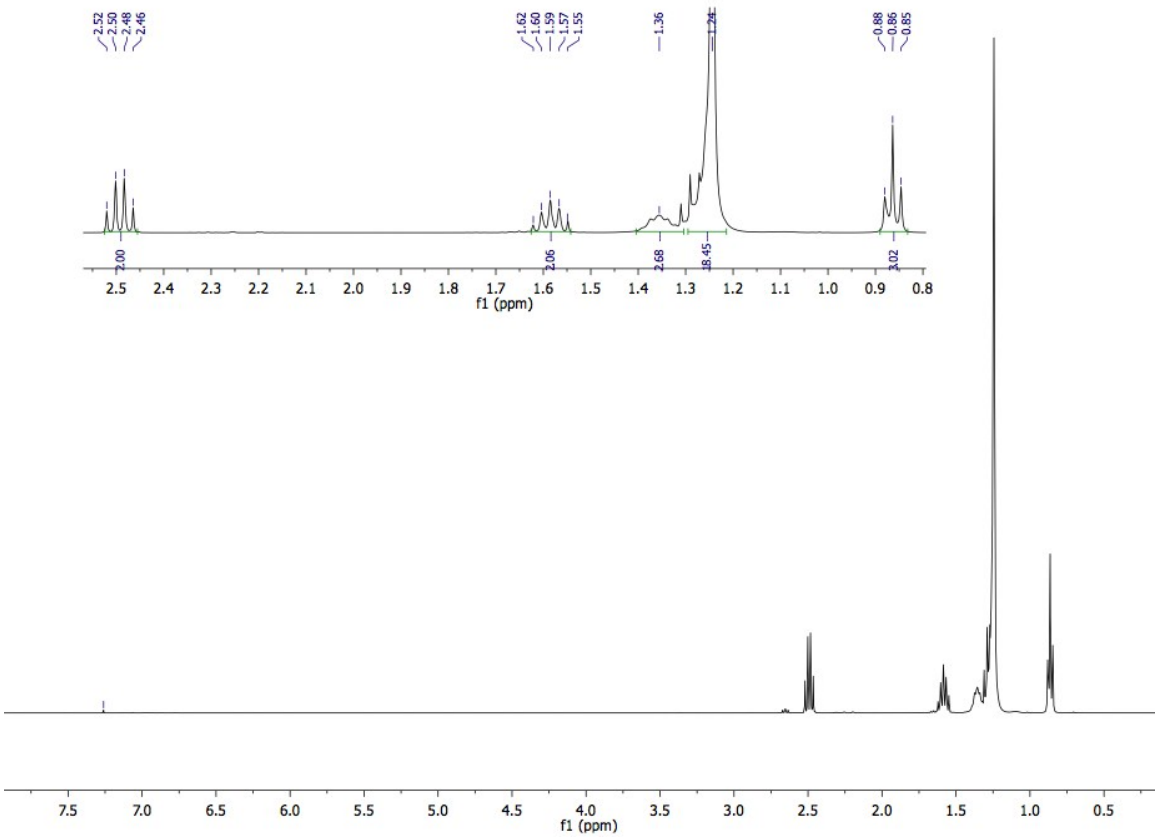

Figure S1. ^{1}H NMR spectrum of the synthesized C_{13}. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.29 (dd, *J*= *8* Hz, 2H), δ 1.59 (p, *J*= *8* Hz, 2H), δ 1.36 (m, 3H), δ 1.24 (m, 18 H), δ 0.86 (t, *J*= *8* Hz, 3H)

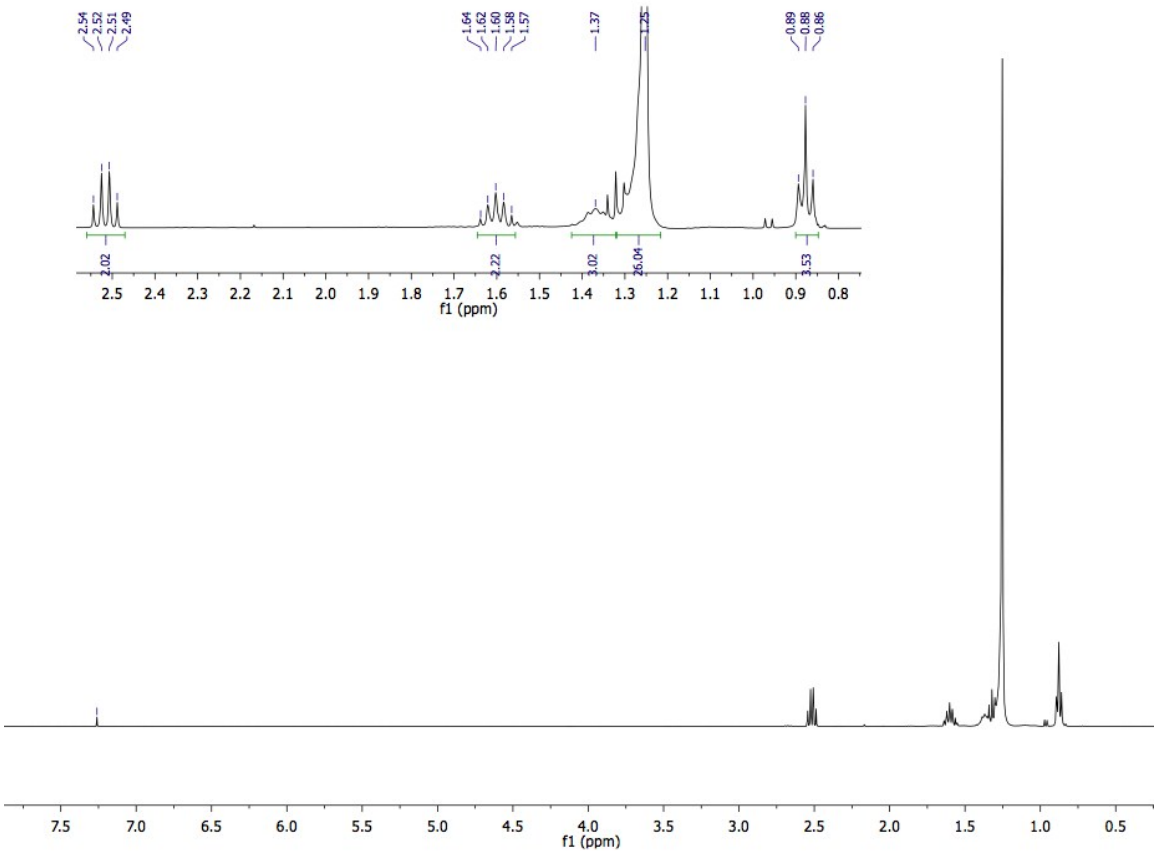

Figure S2. ^{1}H NMR spectrum of synthesized C_{17}. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.52 (dd, *J*= *8* Hz, 2H), δ 1.60 (p, *J*= *8* Hz, 2H), δ 1.37 (m, 3H), δ 1.25 (m, 26 H), δ 0.88 (t, *J*= *8* Hz, 3H)

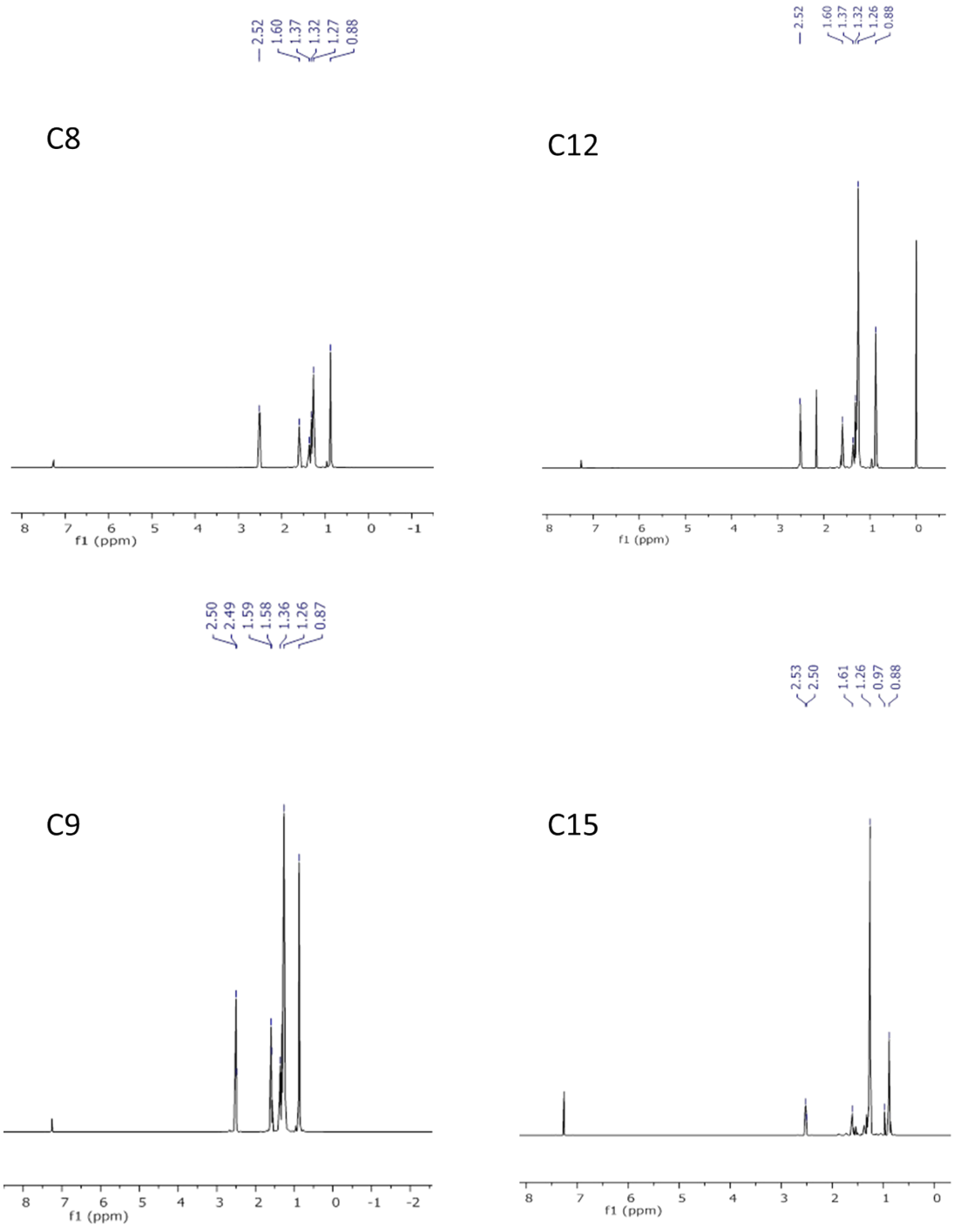

Figure S3. Sample ^{1}H NMR spectra of other purified n-alkanethiol compounds.

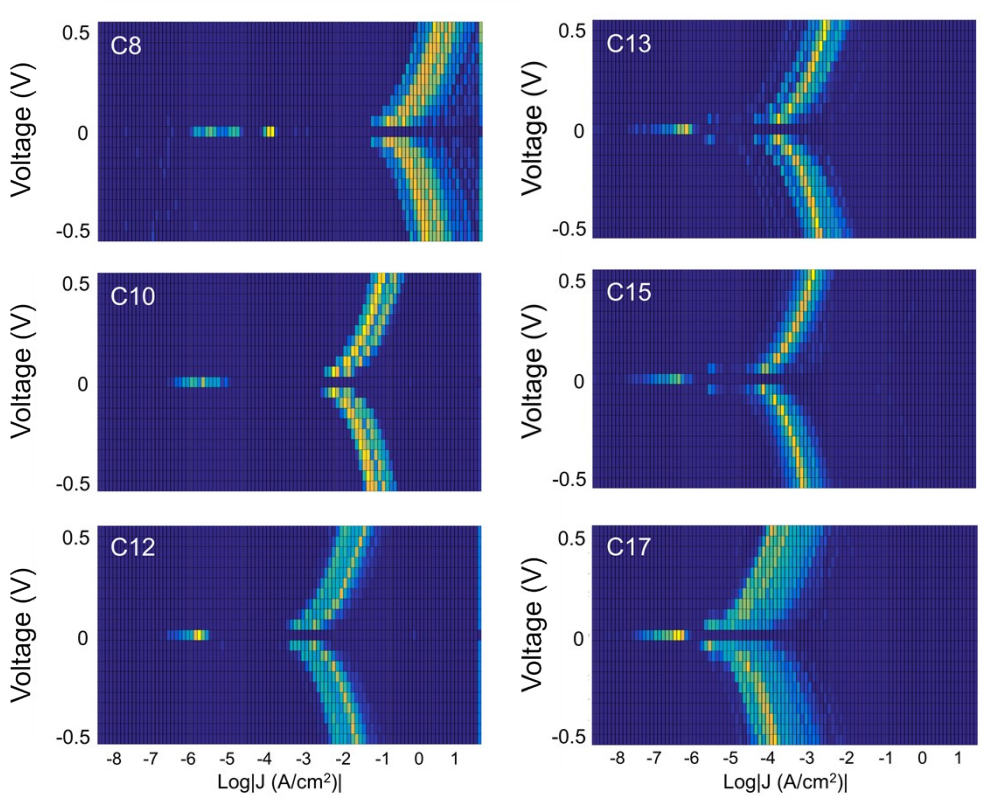

Figure S4. The charge tunneling results of some molecules are shown in heat-map forms, demonstrating the distribution of measurements.

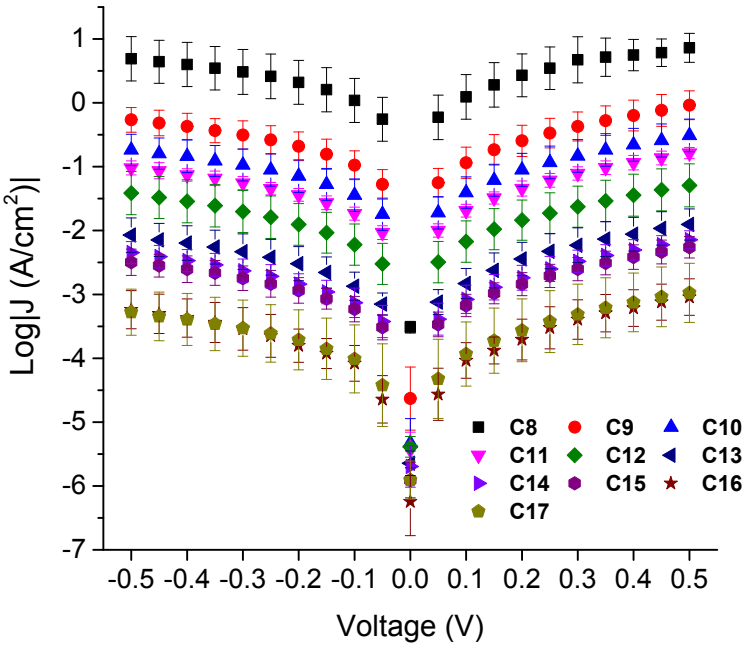

Figure S5. The charge tunneling rates across n-alkanethiolate molecular junctions on $Au^{Ti\text{-}TS}$ with regards to voltage.

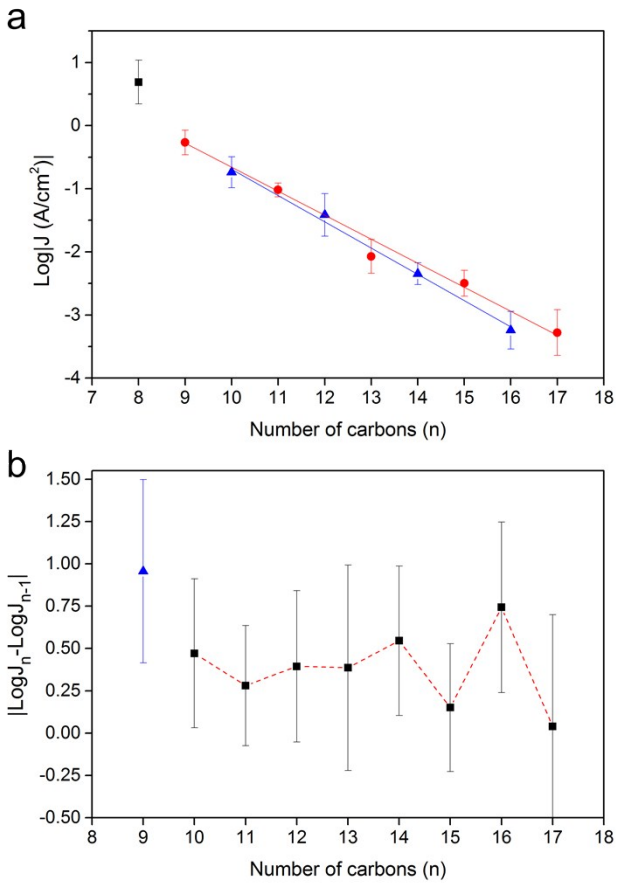

Figure S6. Odd-even effect in tunneling current across n-alkanethiolate SAMs with flattened bottom electrode and top electrode. a) The current density, *log*|*J*|, was linear fitted with chain length of the molecules. b) The magnitude of odd-even oscillation in tunneling current.

Table S1. Current density and deviation calculated from Gaussian fits of junctions on Au.

Molecule length	Log|J|	Deviation	Number of junctions	Number of trances
8	0.6894	0.3471	9	92
9	-0.2667	0.1942	10	159
10	-0.7383	0.2452	22	241
11	-1.0191	0.1103	20	226
12	-1.4137	0.3369	18	173
13	-2.071	0.2698	16	104
14	-2.3456	0.172	27	393
15	-2.4968	0.2054	27	301
16	-3.2401	0.2986	20	310
17	-3.2793	0.3612	12	305

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