Supporting Information for:

Inelastic Electron Tunneling Spectroscopy of Alkane Monolayers with Dissimilar Attachment Chemistry to Gold

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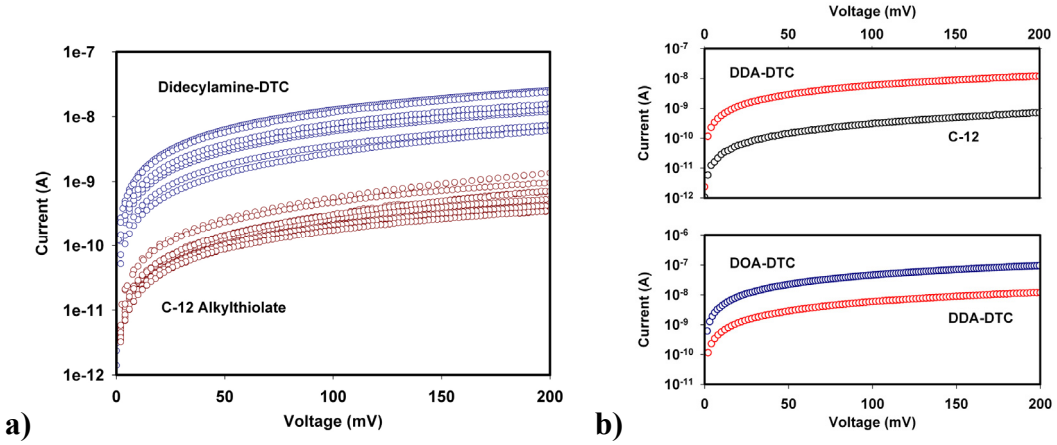

Figure 1. Qualitative comparison of alkanethiolate and alkyl-dithiocarbamate microsphere junction current densities. a) Plot showing measured current from 0 to 200 mV for several microsphere junctions incorporating DDA-DTC (blue) and C-12 alkanethiolate (red). DDA-DTC microsphere junctions are consistently more conductive than the analogous C-12 devices by approximately a factor of 20 (1.3 orders of magnitude) in good agreement with predicted values.[15] The observed spread in data for each monolayer system is attributed to variations in microsphere deposition during the assembly process. **b)** Electron transport data for alkyl-DTC microsphere junctions acquired at 5 K. Comparison of current density in devices used for IETS analysis, DDA-DTC and C-12 alkanethiolate (top) and DOA-DTC and DDA-DTC (bottom).

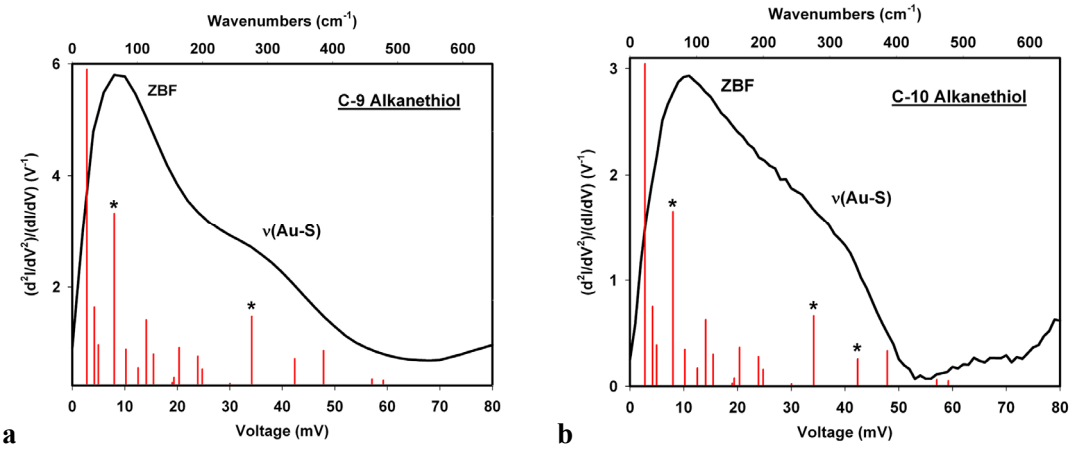

Figure 2. IETS analysis of C-9 and C-10 alkanethiolate monolayers from 0 to 80 mV bias. Low energy IETS spectra showing the zero bias features (ZBF) and single broad shoulder characteristic of alkane monothiolate SAMs. Calculated vibrational modes are shown in red and displayed in correspondence to their theoretical frequencies with heights proportional to the calculated intensity. Asterisks mark calculated modes which coincide with major peaks in the experimental spectra.

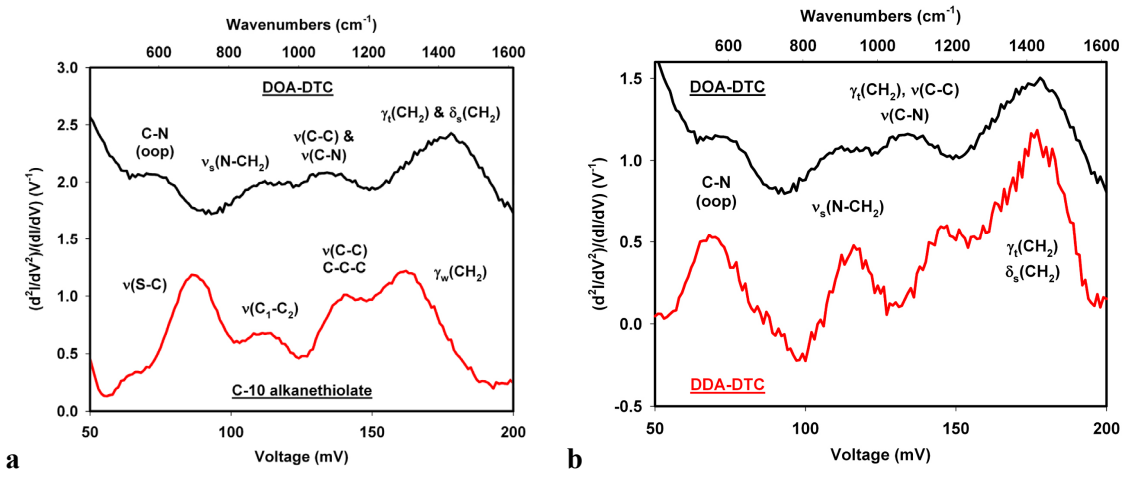

Figure 3. Comparison of alkanethiolate and dithiocarbamate "fingerprint regions". a) IETS analysis from 50 to 200 mV bias of a C-10 alkanethiolate microsphere junction (red) and a DOA-DTC junction (black). **b)** IETS analysis of a DDA-DTC (red) and a DOA-DTC junction (black). Dithiocarbamate monolayers display a characteristic peak at 71 mV arising from the DTC functional group ($C\text{-}N_{oop}$) while alkanethiolates are characterized by the intense ν(S-C) stretching mode at 87 mV bias.

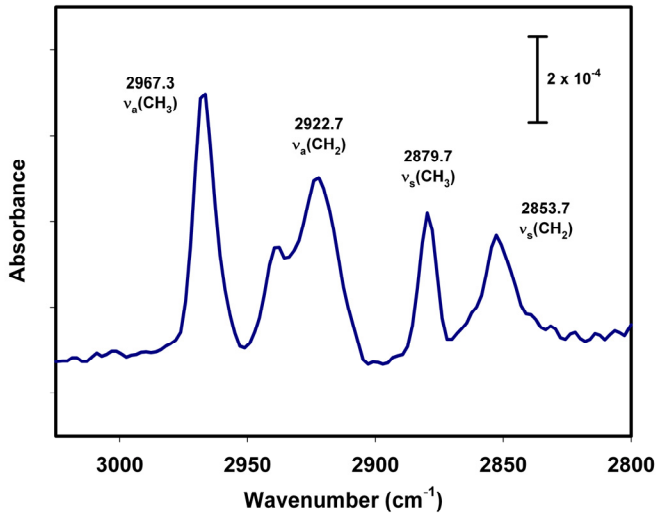

Figure 4. FT-IR specular reflectance spectrum for a DDA-DTC monolayer on gold. Spectrum acquired using a Varian 3100 FT-IR spectrophotometer equipped with a VeeMax II variable angle specular reflectance accessory and infrared polarizer with a liquid nitrogen cooled mercury-cadmium-telluride (MCT) detector. Source beam was set at 80° incident to the sample surface. A total of 5000 scans were collected using a resolution of 4 cm^{-1}. Measured frequency for the $\nu_a(CH_2)$ (2922.7 cm^{-1}) and $\nu_s(CH_2)$ (2853.7 cm^{-1}) stretching modes indicate a mixture of crystalline and liquid-like packing states in the monolayer which could account for the prominent methylene scissoring modes in IETS (177-181 mV).[40]

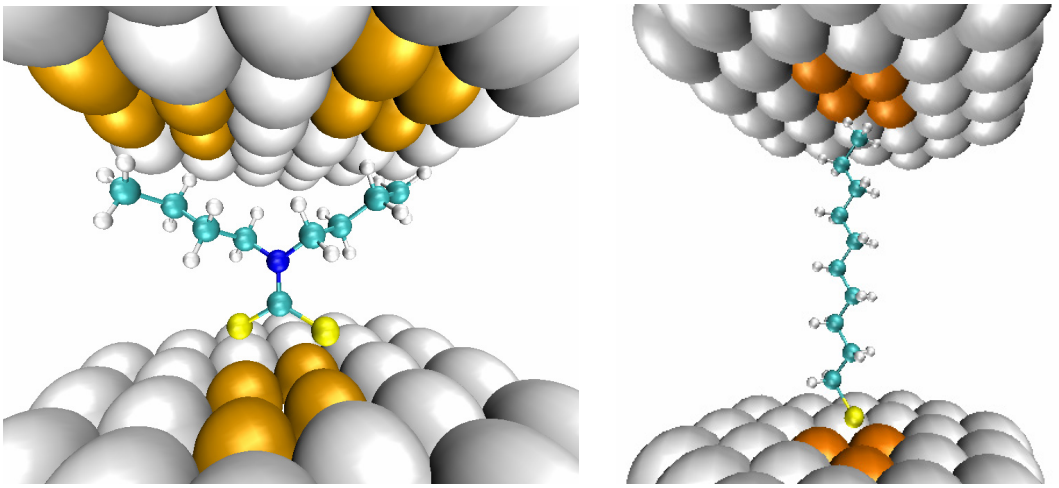

Figure 5. **Adsorption geometry used for the IETS simulation of DTC (left) and C10 (right)**. The cluster used to simulate the molecule-gold interaction included the molecule and the gold atoms in darker color. The effect of the remaining electrode atoms is incorporated in the model via a self-energy term that effectively introduced a broadening to the molecular levels.

Table 1. Computed frequencies and IETS intensities for dibutyl-DTC.[†]

Freq. (cm^{-1})	Int. x1000	Freq. (cm^{-1})	Int. x1000	Freq. (cm^{-1})	Int. x1000
32.9	3.5	865.8	3.0	1385.2	4.1
49.5	19.9	876.8	7.2	1425.0	6.5
49.8	3.9	893.6	8.8	1455.9	5.4
61.9	9.2	907.1	6.8	1456.6	8.3
74.5	94.8	925.2	3.5	1465.5	3.3
78.4	131.5	958.7	3.6	1465.6	3.0
130.6	4.3	983.6	8.3	1480.2	3.6
153.5	13.7	984.2	9.4	1480.2	4.6
216.1	3.0	1024.4	3.0	2889.8	7.3
242.7	4.3	1088.9	19.8	2892.2	11.3
299.8	2.9	1093.9	34.8	2899.2	3.8
308.1	9.3	1096.1	18.0	2901.4	7.9
337.3	5.9	1196.3	5.2	2930.9	5.0
417.8	4.3	1243.2	9.7	2930.9	5.1
422.7	23.4	1264.1	6.2	2968.8	17.8
528.9	16.0	1310.0	16.2	2968.8	16.4
575.6	28.8	1342.4	3.4	2973.2	5.0
586.9	5.3	1346.6	3.3	2973.4	3.8
763.1	16.0	1352.6	11.6	2982.5	3.0
770.4	20.3	1369.3	6.4	2995.6	3.1
				2995.8	3.9

Table 2. Computed frequencies and IETS intensities for C10 alkane monothiolate.[†]

Freq. (cm^{-1})	Int. x1000	Freq. (cm^{-1})	Int. x1000	Freq. (cm^{-1})	Int. x1000
22.6	18.7	710.2	15.4	1256.02	3.6
33.96	4.6	735.3	0.9	1290.05	1.3
40.05	2.4	838.4	5.6	1322.35	4.9
64.49	10.1	870.5	1	1348.61	2.8
82.46	2.1	958.5	1.5	1364.11	0.9
101.28	1	974.9	4.5	1369.26	1.5
113.58	3.9	1017.8	10.1	1387.13	6.5
124.85	1.8	1028.4	1.2	1455.9	2.6
164.35	2.2	1038.4	1.5	1471.76	0.7
192.9	1.7	1061.4	1.7	2897.17	0.9
199.74	1	1062.4	2.8	2902.87	1.4
275.81	4.1	1107.0	20.3	2923.33	4.8
341.71	1.6	1193.6	3.2	2989.4	32.5
386.11	2.1	1224.0	1.1		

[†]The (adimensional) intensities are for a plot of $(dI^2/dV^2)/(dI/dV)$ versus V. To shorten the table only the modes with meaningful intensity have been shown (defined as the ones with intensity larger than 1/50 of the most intense IETS mode)