Supporting Information

Anomalous length and voltage dependence of single molecule conductance

Wolfgang Haiss, Santiago Martin, Lisa E. Scullion, Laurent Bouffier, Simon J. Higgins and Richard J. Nichols

Centre for Nanoscale Science and Department of Chemistry, University of Liverpool, Crown Street, L69 7ZD, U.K.

SI-1. Synthesis of dodecane-1,12-dithiol[1]

A stirred solution of dodecane-1,12-diyl dibromide (0.317 g, 0.966 mmol) in THF (4 mL) was cooled at − 10 °C, and hexamethyldisilathiane (2.4 eq., Aldrich) and TBAF (2.2 eq., 1.0 M solution in THF with 5 % water, Aldrich) were added. The resulting reaction mixture was allowed to warm at room temperature while being stirred. After the disappearance of the bromide (about 30 minutes at ambient temperature, as monitored by thin-layer chromatography (TLC)), the reaction mixture was diluted with dichloromethane and washed with aqueous ammonium chloride, then twice with water. After evaporation of the organic solvent, the crude mixture was purified by flash column chromatography on silica gel (90 % cyclohexane/10 % diethyl ether). The dodecane-1,12-dithiol was thus obtained as a colourless oil that crystallized on standing (0.181 g, 80 %). HRMS (CI, $[M+NH_4]^+$) m/z calc. for $C_{12}H_{30}S_2N$ 252.18196, found 252.18215. ^{1}H NMR (200 MHz, $CDCl_3$) δ ppm = 2.50 (4H, quartet, 2 HS-$\underline{CH_2}$-), 1.59 (4H, quintet, 4H, 2 HS-CH_2-$\underline{CH_2}$-), 1.40-1.25 (broad multiplet, 18H, 2 HS- and 8 -CH_2-). The NMR data were in agreement with literature values.[2]

SI-2. Synthesis of 1,7 heptanedithioacetate

To a solution of dibromoheptane in acetone were added 2.5 equivalents of potassium thioacetate. The resulting mixture was stirred at reflux for approximately 12 hours under N_2. The mixture was then allowed to cool to room temperature at which point water was added followed by extraction with ethyl acetate. The combined organic extracts were washed with brine and then dried over $MgSO_4$ and filtered. After removal of the solvent, the dithioacetate was purified by column chromatography (hexane/ CH_2Cl_2 8/2) to provide the heptanedithioacetate (64% yield). The presence of the compound was confirmed by ^{1}H NMR (CDCl$_3$) δ 2.85 (t, 4H) 2.32 (s, 6H) 1.52-1.60 (m, 4H) 1.31-1.39 (m, 4H) 1.19-1.21 (m, 2H) ^{13}C NMR (CDCl$_3$) δ 196.3, 31.0, 30.1, 29.8, 29.4, 28.9.

SI-3. Exponential decay factors (β) of alkane chains determined with different methods

In Table SI-1 some theoretical and experimental values of the exponential decay factor (β) of oligo methylene (OM) chains are listed for comparison.

Year	Ref.	β / N	$\beta / Å^{-1}$	Error $/ Å^{-1}$	Length / N	Method	System	U / V
1999	3	*1.54*	1.20	-	9 - 11	STM height	Au-S-OM / Au	1
2001	4	*1.11*	0.87	0.1	24 – 32	Hg Drop	Hg-OM / OM-Ag	0.5
1999	5	0.89	*0.70*	0.1	18 - 36	Hg Drop	Hg-OM / OM-Hg	0 – 1.6
2000	6	1.29	*1.01*	-	18 - 24	Hg Drop	Hg-OM / OM-Hg	
2002	7	0.80	*0.63*	0.2	8 - 14	CP AFM	Au-S-OM / Au	
2000	8	1.45	*1.13*	-	6 - 10	CP AFM	Au-S-OM / Au	0 - 0.3
2001	9	1.19	*0.93*		4 - 12	CP AFM	Au-S-OM / Au	0 - 0.3
2002	10	*1.20*	0.94	0.06	6 – 14 Å	CP AFM	Au-S-OM / Au	0 - 0.3
2004	11	1.17	*0.91*		6 - 10	CP AFM	Au-S-OM / Au	0.3
2005	12	*1.08*	0.84	0.04	8 - 16	Micropore	Au-S-SAM / Au	0.1
2003	13	*1.01*	0.79	0.01	8 - 16	Micropore	Au-S-SAM / Au	0
2003	14	*1.20*	0.94	0.06	5 – 25 Å	Electrochemistry	Au-S-OM-Fc	
1995	15	1.21	0.94	0.06	5 - 9	Electrochemistry	Au-S-OM-Fc	
2006	16	*1.29*	1.01	0.03	5 – 30 Å	Electrochemistry	Au-S-OM-Fc	
2004	17	0.3	*0.23*	-	8 - 14	Theory	Au-S-OM-S-Au	1
2005	18	0.65	*0.51*	-	8 - 16	Theory	Au-S-OM-S-Au	0 – 1.5
2006	19	1.24	*0.97*	-	6 - 10	Theory	Au-S-OM-S-Au	0
2005	20	~ 1	*0.78*	-	4 - 12	Theory	Au-S-OMSAM / Au	
2006	21	~ 0.55	*0.43*	-	6 - 10	Theory	Au-S-OM-S-Au	
2006	22	~ 0.97	*0.76*		4 - 12	Theory	Au-S-OM-S-Au	
2005	23	0.97	0.76		4 - 12	Theory	Au-S-OM-S-Au	1
2005	12	*0.84*	0.66	0.02	8	Micropore	Au-S-SAM-S-Au	0
2004	11	0.99	*0.77*		6 - 10	CP AFM	Au-S-OM-S-Au	0.3
2006	24	0.83	*0.65*		8 - 11	I(s)	Au-S-OM-S-Au	
2009	25	0.90	*0.70*	0.05	8 - 12	I(s)	Au-S-OM-S-Au	0.6
2006	26	*0.96*	0.75	0.03	8 - 12	I(s)	Au-S-OM-S-Au	0.4
2007	27	1.03	*0.80*	0.03	6 - 12	I(s)	Au-S-OM-S-Au	0.1
2006	28	1.07	*0.84*	0.04	6 - 10	Break Junction	Au-S-OM-S-Au	0.1

2003	29	1.0	*0.78*	0.1	6 - 10	Break Junction	Au-S-OM-S-Au	0
2006	30	*0.77*	0.60		2 - 8	Break Junction	Au-OOC-OM-COO-Au	
2003	29	*1.04*	0.81	0.04	6 - 10	Break Junction	Au-S-OM-S-Au	0
2006	31	0.91	*0.71*	0.03	2 - 8	Break Junction	Au-NH2-OM-NH2-Au	0.025
2006	32	1.0	*0.78*		6 - 10	Break Junction	Au-S-OM-S-Au	0.1
2006	33	*0.84*	0.66	0.06	14 – 23 Å	Large Area SAM	Au-S-OM-S PEDOT Au	0.1
2006	33	*0.85*	0.57	0.05	14 – 23 Å	Large Area SAM	Au-S-OM-S PEDOT Au	0.5

Table SI-1: β factors of alkane chains determined with different methods. Values in italics are calculated from the originally quoted numbers assuming a C-C distance of 1.28 A. The Error relates to the originally quoted number.

SI-4: The two resistor model

In Figure SI-1 a model of the junction geometry (a) and the electrical equivalent circuit (b), which was used to fit the experimentally observed SMC values of alkanedithiols between gold contacts (dashed lines in Figure 2) is shown, where N represents the number of CH_2 groups in the oligo methylene chain.
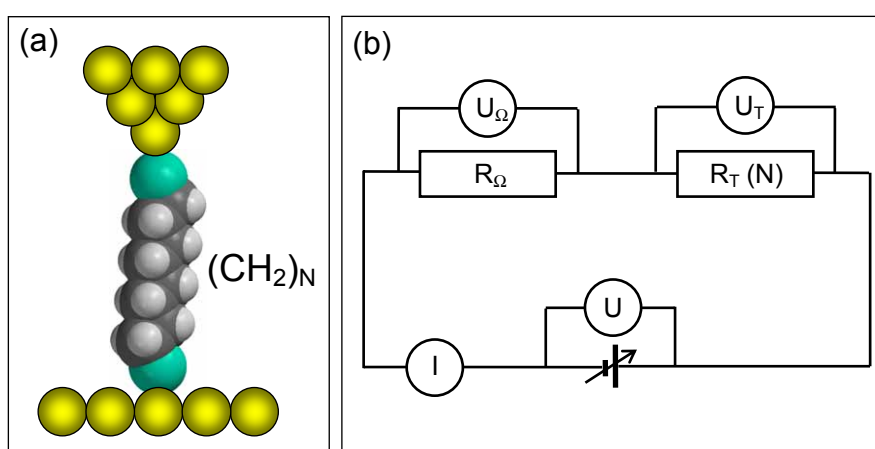

Figure SI-1: Model of the junction geometry (a) and the electrical equivalent circuit (b).

The tunnelling resistor (R_T) is assumed to decay exponentially with decreasing molecular length where R_0 represents the contact resistance:

$$R_T \quad = \quad R_0 \exp(\beta N) \quad\quad\quad\quad (SI1)$$

The other resistor R_Ω is assumed to be independent of the molecular length. The bias voltage is divided between the two resistors according to:

$$U \quad = \quad U_{bias} \quad = \quad U_\Omega + U_T \quad\quad\quad\quad (SI2)$$

The voltage drop at R_T (U_T) and the voltage drop at R_Ω (U_Ω) is given by:

$$U_\Omega(N) \quad = \quad U(R_\Omega/(R_T + R_\Omega)) \quad\quad\quad\quad (SI3a)$$

$$U_T(N) \quad = \quad U(R_T/(R_T + R_\Omega)) \quad\quad\quad\quad (SI3b)$$

The current as a function of N can thus be expressed as:

$$I(N) \quad = \quad U/R \quad = \quad (U_\Omega(N) + U_T(N))/(R_\Omega + R_T) \quad\quad (SI4)$$

With Equations SI3a and SI3b the logarithm of the molecular conductance can thus be fitted with Equation SI5:

$$\ln(\sigma_M(N)) \quad = \quad \ln(1/(R_\Omega + R_0 \exp(\beta N)) \quad\quad\quad\quad (SI5)$$

The three parameters R_0, R_Ω and β resulting from a fit of the experimental data together with the fit quality (R^2 and Chi^2) are shown in Table SI-2 for comparison. Equation SI5 results in a rather perfect fit to the experimental data although there seems to exist no viable physical origin which can be attributed to this two resistor model and hence the lines in Figure 2 should be considered only as a guide to the eye. We never the less consider it worth to note in passing that this fitting procedure describes the experimental data perfectly for all conduction groups.

Conductance Group	R_0 /10^5 Ω	R_Ω /10^7 Ω	β /CH_2	R^2	Chi^2
A_1	3.8 ± 1.0	24.7 ± 1.3	0.95 ± 0.05	0.998	0.006
B_1	1.5 ± 0.4	1.3 ± 0.14	0.93 ± 0.05	0.999	0.010
C_1	0.3 ± 0.1	0.34 ± 0.06	0.95 ± 0.05	0.997	0.029

Table SI2: Parameter resulting from a fit of the experimental conductance data from Figure 2 to Equation SI5.

SI-5: Comparison of the experimental results obtained in air and under nitrogen

Since all the experiments were performed in air, it cannot be excluded that the presence of oxygen or water influences the obtained conduction values. For this reason we have performed experiments in a hermetically sealed chamber which was purged with nitrogen for up to 15 hours prior to the measurements. No systematic differences could be observed between the experiments performed in air and under nitrogen and hence the observed conductance values were consistent. Figure SI-2 shows the results of those experiments for pentanedithiol as an example.
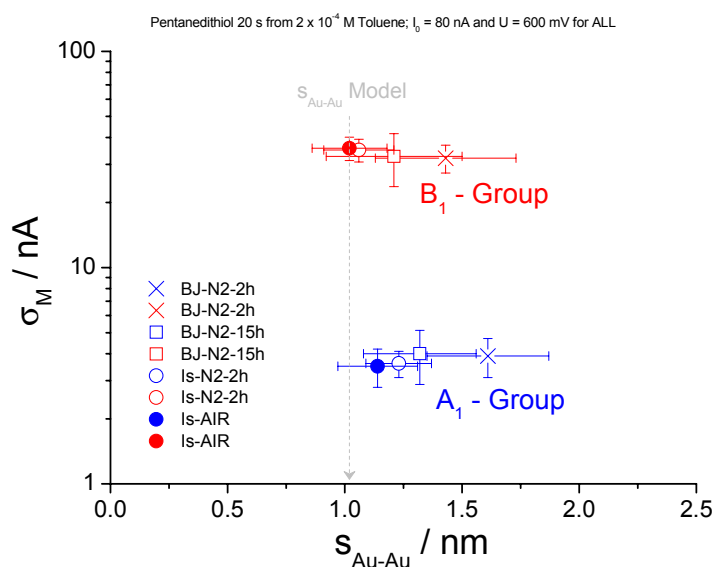

Figure SI-2: Comparison of the experimental results obtained for pentanedithol using the *I*(*s*) technique in air (filled circles) and after purging the STM chamber for 2 hours (open circles) and 15 hours (open squares) with nitrogen. Results obtained with the break junction technique are shown for comparison (crosses).

SI-6: Comparison of the experimental data with the results of other research groups

The experimental results obtained for the low voltage conductance of alkanedithiols between gold contacts from Figure 2 (small filled circles) are compared with the results of some other research groups in Figure SI-3, where the open stars represent results obtained by Morita and Lindsay[34] using a conducting probe AFM, crosses were obtained by Li *et al* using STM[35] and the down triangles were obtained by Li *et al*[28] using the break junction method.
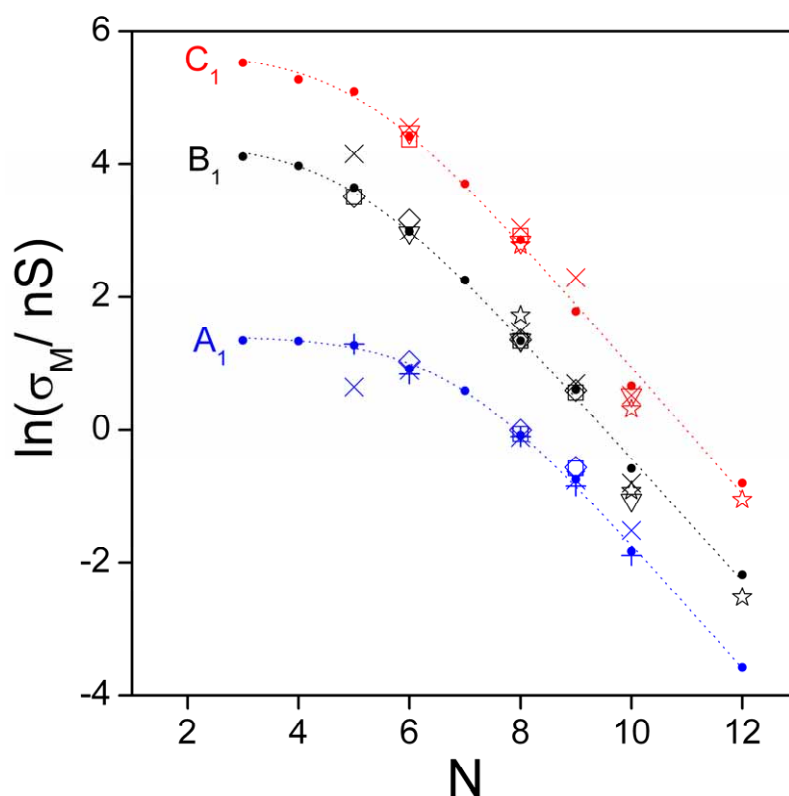

Figure SI-3: Comparison of the experimental data obtained with the *I(s)* technique (filled circles) and the *BJ* technique (black and red filled circles) with the results of other research groups; see text for details and references.

Also shown in Figure SI-3 are the results obtained by our own group using the $I(t)$ technique[36, 37] (crosses) the matrix isolation mix method[25] (open diamonds) and the matrix isolation replacement method[25] (open squares). The same colours have been used for the results of a particular conductance group to facilitate direct comparison (blue for A_1, black for B_1, and red for C_1). As it is evident from Figure SI-3 the results obtained by the various techniques are in good agreement.

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