Electronic Supplementary information for

Introducing Mesoscopic Charge Transfer Rates into Molecular Electronics

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ESI-1. ELECTROCHEMICAL GRAFTING OF AB MOLECULAR LAYER, DETERMINATION OF MOLECULAR LAYER THICKNESS BY AFM AND FABRICATION OF MOLECULAR JUNCTIONS.

Electrochemical grafting of the AB molecular layers was performed on a CHI (Model 420a) electrochemical workstation using standard 3 electrodes setup with a 0.1 M $TBABF_6$ electrolyte dissolved in acetonitrile. The eC bottom contact was used as working electrode (WE), a Pt wire as the counter electrode (CE) and an $Ag|Ag^+$ reference electrode (RE). Representative examples of grafting cyclic voltammograms (CVs) were provided in Figure ESI. 1. Large area "all carbon" molecular junctions were fabricated as reported previously.[1]

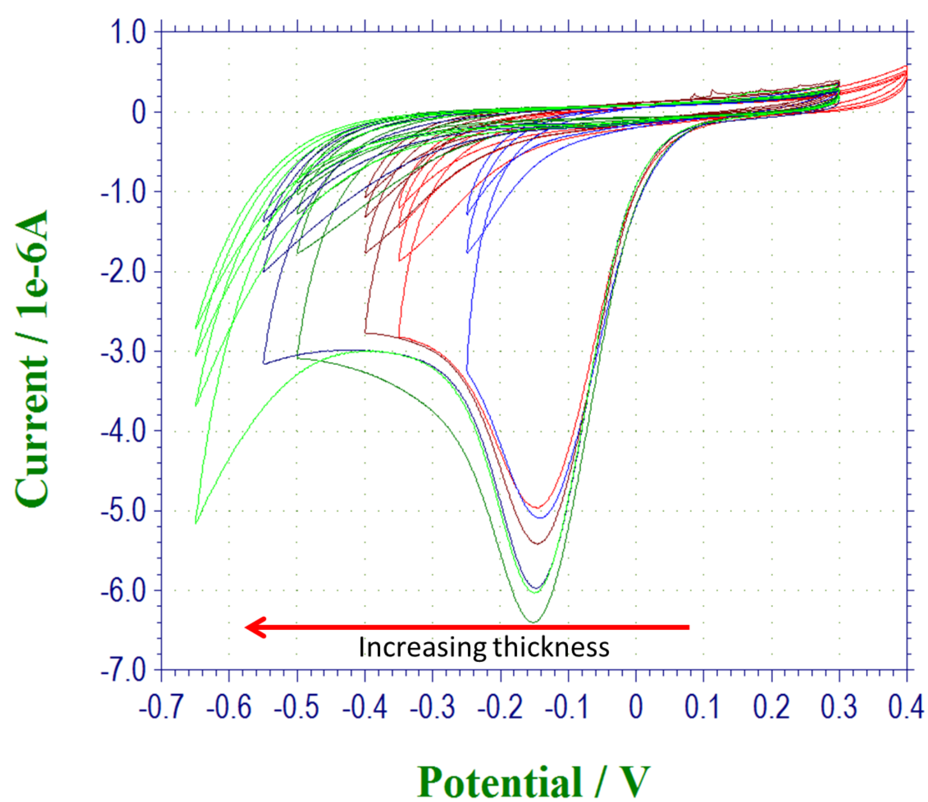

Figure ESI. 1. Examples of AB molecular grafting CVs on $Cr_4/Au_{30}/eC_{10}$.

Table ESI. 1. Electrochemical grafting parameters for AB on $Cr_4/Au_{30}/eC_{10}$: CV scan range, number of CV scans, sweep rate, AFM "scratch" thickness.

Molecules	CV scan range (V vs. Ag/Ag^+)	No. of CV scans	Scan rate (mV/s)	AFM "scratch" thickness (nm)
AB	0.3– (-0.40)	4	50	2.5 ± 0.14
	0.3 – (-0.45)	4	50	3.1 ± 0.34
	0.3 – (-0.50)	4	50	3.6 ± 0.39
	0.4 – (-0.55)	4	50	5.0*
	0.4 – (-0.60)	4	50	5.1*
	0.4 – (-0.60)	5	50	6.6*
	0.3 – (-0.65)	5	50	8.4 ± 0.59

*thickness estimated using the beta plot reported previously.[2]

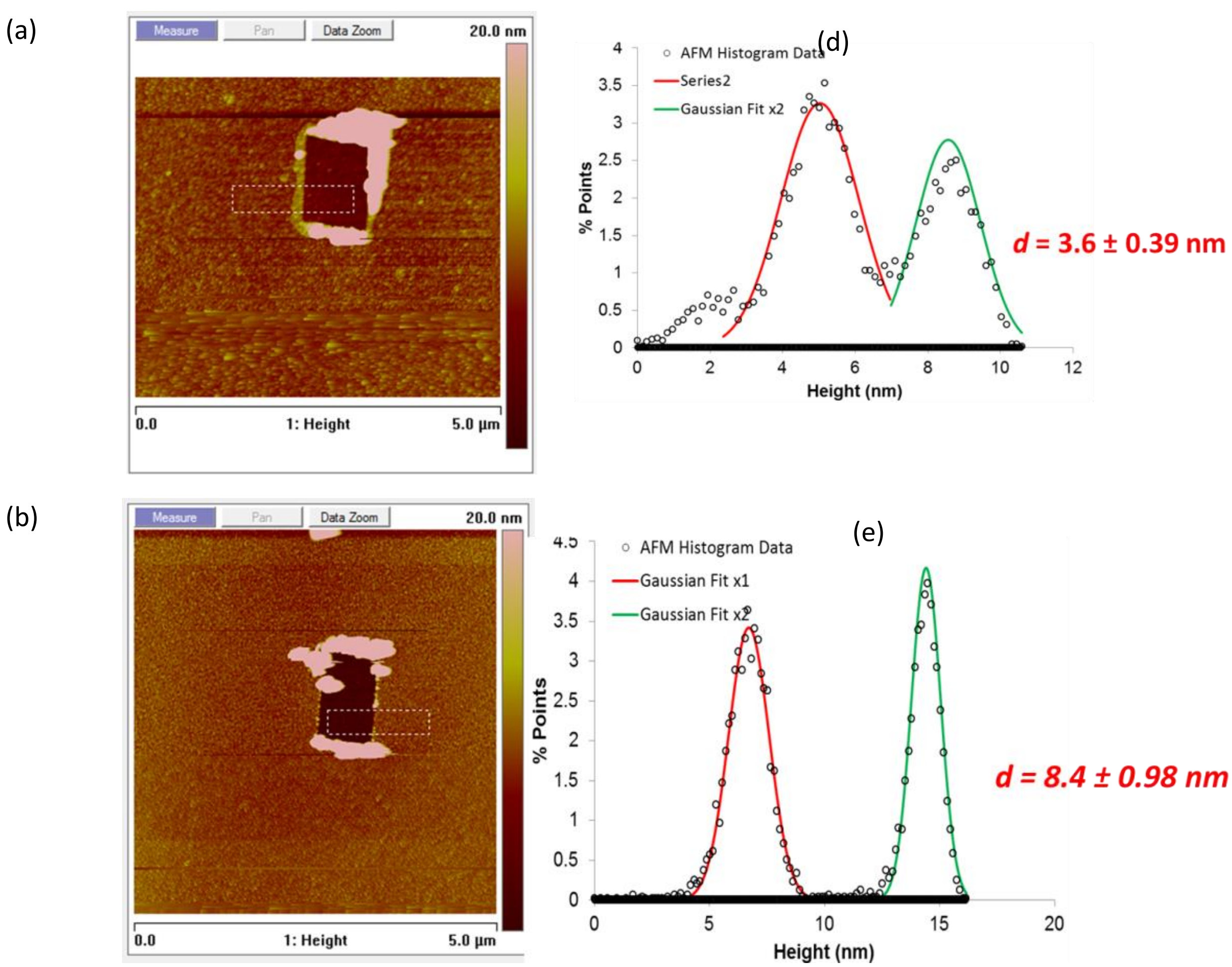

Figure ESI. 2. Examples of tapping mode AFM image of AB layer after scratching the molecular layer **(a and b)**, histogram of the height data and the corresponding fitted Gaussian distribution for thickness determination for AB layer **(c and d)**. Thickness of AB molecular layer shown with associated uncertainty.

ESI-2. EXAMPLES OF DATA FITTING AND PARAMETERS DETERMINATION

Table ESI. 1. Data fitting using the equivalent circuit shown in Figure 1b (main text) for 6.6 nm thickness film ($A = 0.00125\ cm^2$) at different bias potentials. R_c is the contact resistance (Ω), C_μ the capacitance (F), k the rate of electron transport (s^{-1}), G the conductance (S) and j the current density ($A.cm^{-2}$).

Bias (mV)	R_c (Ω)	C_μ (nF)	R ($k\Omega$)	$k = 1/RC_\mu$ (s^{-1})	$G = 1/R$ (μS)	$j = GV/A$ ($mA.cm^{-2}$)
0	25.4	0.948	7,880	134	0.1269	-
100	25.8	0.925	3,960	273	0.2525	0.0202
-100	25.6	0.923	4,310	251	0.2320	-0.0186
200	26.0	0.924	1,400	773	0.7143	0.1143
-200	26.0	0.911	1,610	682	0.6211	-0.0994
300	26.0	0.923	558	1,942	1.79	0.4301
-300	26.1	0.910	603	1,822	1.65	-0.3980
350	27.0	0.919	354	3,074	2.82	0.7910
-350	26.2	0.911	381	2,881	2.62	-0.7349
400	27.3	0.919	230	4,731	4.34	1.3913
-400	26.2	0.913	248	4,416	4.03	-1.2903

Table ESI. 2. Data fitting using the equivalent circuit shown in Figure 1b (main text) for 5.1 nm thickness film ($A = 0.00125\ cm^2$) in different bias potentials. R_c is the contact resistance (Ω), C_μ the capacitance (F), k the rate of electron transport (s^{-1}), G the conductance (S) and j the current density ($A.cm^{-2}$).

Bias (mV)	R_c (Ω)	C_μ (nF)	R ($k\Omega$)	$k = 1/RC_\mu$ (s^{-1})	$G = 1/R$ (μS)	$j = GV/A$ ($mA.cm^{-2}$)
0	31.1	1.18	377	2,248	2.65	-
100	30.5	1.20	181	4,604	5.52	0.442
-100	30.8	1.19	181	4,643	5.52	-0.442
200	30.5	1.22	61.4	13,350	16.3	2.606
-200	30.0	1.22	61.0	13,350	16.3	-2.606
300	30.5	1.24	23.3	34,612	42.9	10.300
-300	29.6	1.25	22.8	35,088	43.9	-10.526
350	30.4	1.25	14.8	54,054	67.6	18.919
-350	29.5	1.26	14.4	55,115	69.4	-19.444
400	30.7	1.25	9.68	82,645	103.3	33.058
-400	29.4	1.26	9.31	85,247	107.4	-34.372

Table ESI. 3. Data fitting using the equivalent circuit shown in Figure 1b (main text) for 5.0 nm thickness film ($A = 0.00125\ cm^2$) in different bias potentials. R_c is the contact resistance (Ω), C_μ the capacitance (F), k the rate of electron transport (s^{-1}), G the conductance (S) and j the current density ($A.cm^{-2}$).

Bias (mV)	R_c (Ω)	C_μ (nF)	R ($k\Omega$)	$k = 1/RC_\mu$ (s^{-1})	$G = 1/R$ (μS)	$j = GV/A$ ($mA.cm^{-2}$)
0	24.9	1.40	164.0	4,355	6.10	-
100	24.9	1.40	80.2	8,906	12.47	0.998
-100	25.3	1.38	82.9	8,741	12.06	-0.965
200	25.3	1.39	27.7	25,972	36.10	5.776
-200	25.2	1.37	28.7	25,433	34.84	-5.575
300	25.8	1.37	10.8	67,586	92.59	22.222
-300	25.7	1.35	11.0	67,340	90.91	-21.818
350	25.3	1.37	6.94	105,177	144.09	40.346
-350	25.6	1.34	7.16	104,227	139.66	-39.106
400	25.9	1.35	4.58	161,734	218.34	69.869
-400	25.6	1.34	4.72	158,108	211.86	-67.797

ESI-3. COMPARISON BETWEEN CURRENT DENSITIES OBTAINED BY I-V AND IS.

Impedance spectroscopy (IS) was carried out using an AUTOLAB potentiostat equipped with a frequency response analysis (FRA) module and NOVA software from Metrohm. Conditions: frequency range from 5 MHz to 0.1 Hz (~170 frequencies logarithmically arranged), amplitude of 10 mV. Bias of 100 mV. Nyquist data was fitted using NOVA software with the circuit shown in Figure 1b in order to obtain circuit parameters. The conductance (G) and current densities (j) from IS were calculated as $G = 1/R$ and $j = GV/A$, where R is the resistance, V the bias potential and A the area, 0.00125 cm^2 (examples in ESI-2).

I-V curves were obtained using an AUTOLAB potentiostat controlled by Nova software from Metrohm. Conditions: bias potentials ranging from -0.4 V to 0.4 V, at 100 $mV.s^{-1}$. Only data obtained at 100 mV bias are shown.

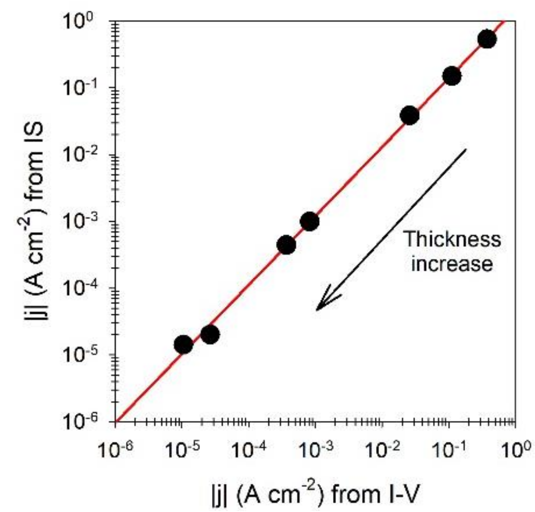

Figure ESI.3. Example of modulus of current density $|j|$ calculated from impedance spectroscopy (IS) plotted versus |j| obtained from current-voltage measurements (I-V). The results present a high correlation, with r^2=99.8%.

The natural logarithm dependence of the current density signal obtained by I-V with the molecular junction thickness L, as given by $ln|j| \propto -\beta L$ (attenuation plot), is in concordance with previous work for 100 mV bias ($\beta = \sim 2.6\, nm^{-1}$, Figure ESI.4).[2] As comparison between I-V and IS approaches, β value obtained by IS has presented a similar value of $\beta = \sim 2.6\, nm^{-1}$, Figure ESI.4.

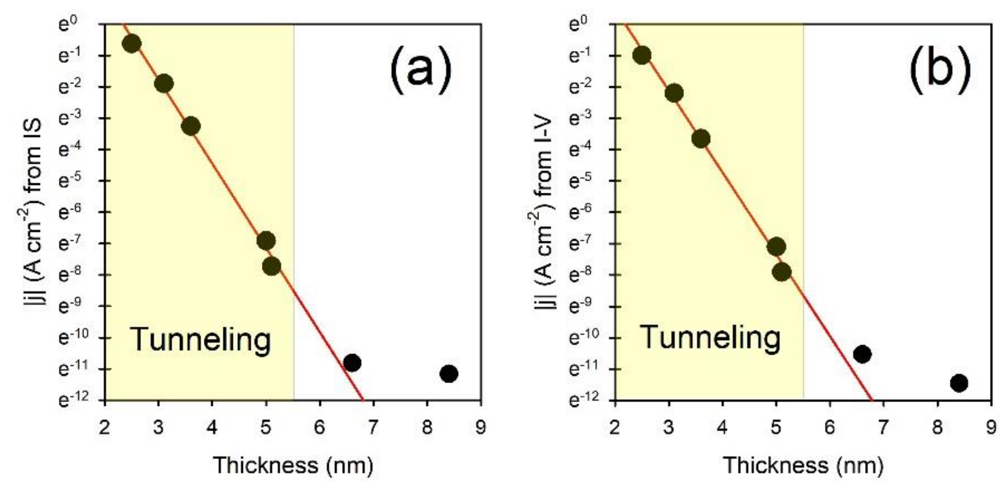

Figure ESI.4. Modulus of natural logarithm of current density ($|j|$) versus molecular junction thickness (L), obtained for both (a) IS and (b) I-V approaches at 100 mV bias. The fittings were performed from thickness from 2.6 to 5.1 nm, where quantum mechanical tunneling is operative[2] (r^2 > 99%).

References

1. A. Morteza Najarian, B. Szeto, U. M. Tefashe and R. L. McCreery, *ACS Nano*, 2016, **10**, 8918-8928.
2. S. Y. Sayed, J. A. Fereiro, H. Yan, R. L. McCreery and A. J. Bergren, *Proceedings of the National Academy of Sciences*, 2012, **109**, 11498.