Supporting information to:

"Quantification of ready-made molecular bilayer junctions having large structural uncertainty"

XPS results for NH_2-$(CH_2)_{16}$- SH /Au

XPS measurements were done by a PHI, Quantum 2000 at a tilt angle, Θ of 20°, 45° or 90°, using monochromatic AlK_{α} radiation with a measuring spot of 100 μ, scanned over an area of about 1200 x 500 μ^2, at a pass energy of 47 eV. In order to avoid degradation of the samples during the measurements, the neutralising ion beam was switched off. Standard sensitivity factors were used to convert peak areas to atomic concentrations.

Table T1: Atomic concentration

Θ	Au4f	C1s			N1s[(a)]	O1s[(a)]		S2p	Thick. [(b)]	footprint
(°)		C-H	C-N / C-O	C=O		O=C	O-C	S-Au	(Å)	Å^2/molec
Energy [eV]		284.8	286.2	288.2 ± 0.2	399.9	531.5 ± 0.2	532.9 ± 0.3	162.2		
45°	24.6	52.4	5.1	3.8	4.8	5.9	1.3	2.1	22.6	23.26
90°	36.3	45.6	4.7	2.8	3.5	5.1	0.3	1.8	21.4	25.64

a) The binding energy of the nitrogen indicates for oxidation of the terminal amine into an amide. Such oxidation is inline with the presence of ~ 1.5 oxygen atoms per nitrogen. We assume that the flakes junctions are less oxidized because of immediate formation of the junction, and further protection by top layer.
b) The averaged thickness of the organic layer (22±0.9) is compatible with estimated thickness of amino thiol (1.26Å * 18 atoms = 22.7), indicating for a possible tilt angle (from normal) of 12°±7°.

Table T2. The net amount of junctions which were measured (#Junc); non-shorted (R>30Ω); used in tunneling ($G_0\rho$); used in field-emission (FN) analyses.

Label	# Junc.	R>30Ω	*G0, ρ*	FN
0/0	12	3	12	2
0/12	5	3	3	1
0/18	7	2	2	1
0/22	10	4	3	5
12/18	14	4	4	5
12/22	16	2	4	2
18/12	14	8	4	2
18/18	21	14	4	10
18/22	15	14	11	11
22/18	9	6	3	5
22/22	11	10	5	8
N/N	13	7	7	5
N/O	12	11	12	12

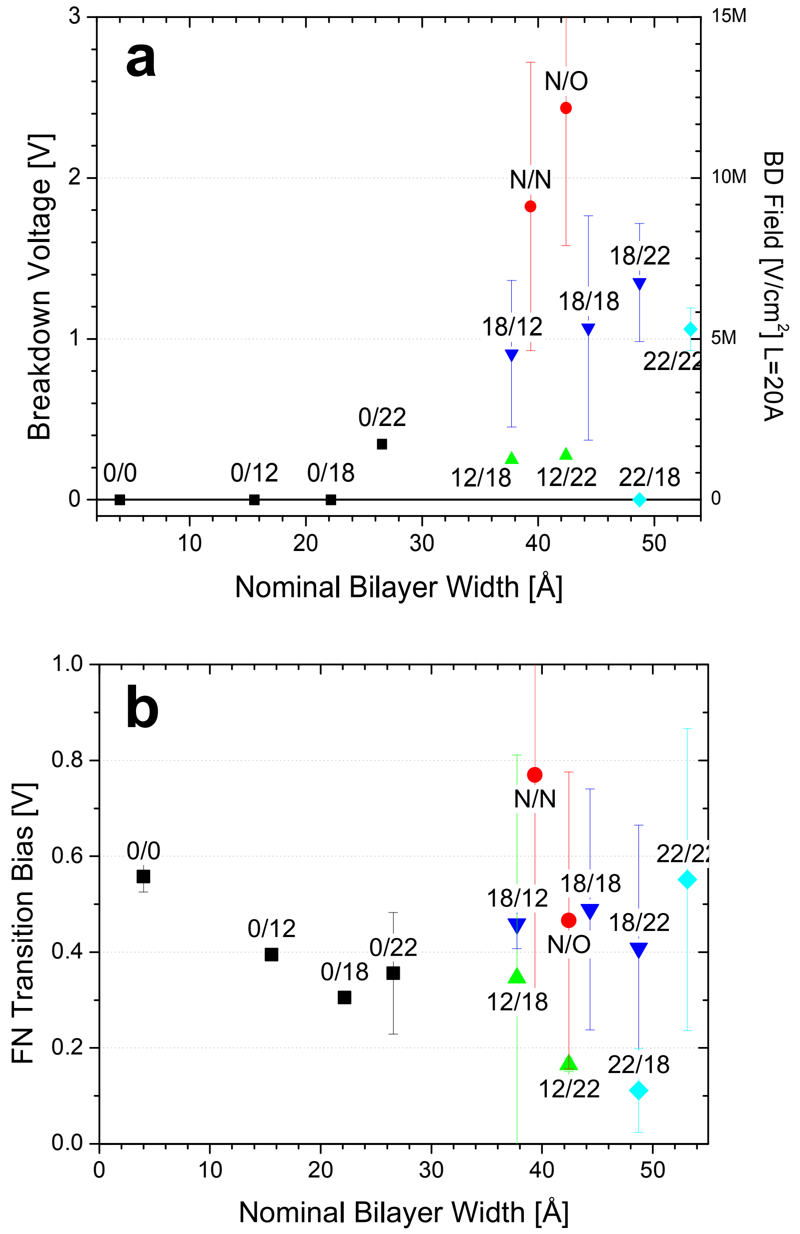

Figure S1. Limits of tunneling analysis, showing the breakdown voltage (**a**) and the transition bias into the Fowler-Nordheim transfer (**b**). The symbols are averages of all the measured junctions where breakdown or Fowler-Nordheim transition were observable. In (**a**), symbols on the X-axis indicate no observable breakdown for these junction types. The right Y-axis of (a) gives an approximate electric field value calculated for an approximate bilayer thickness of 20 Å. The symbols are specified in the legend to Figure 4 (main text).

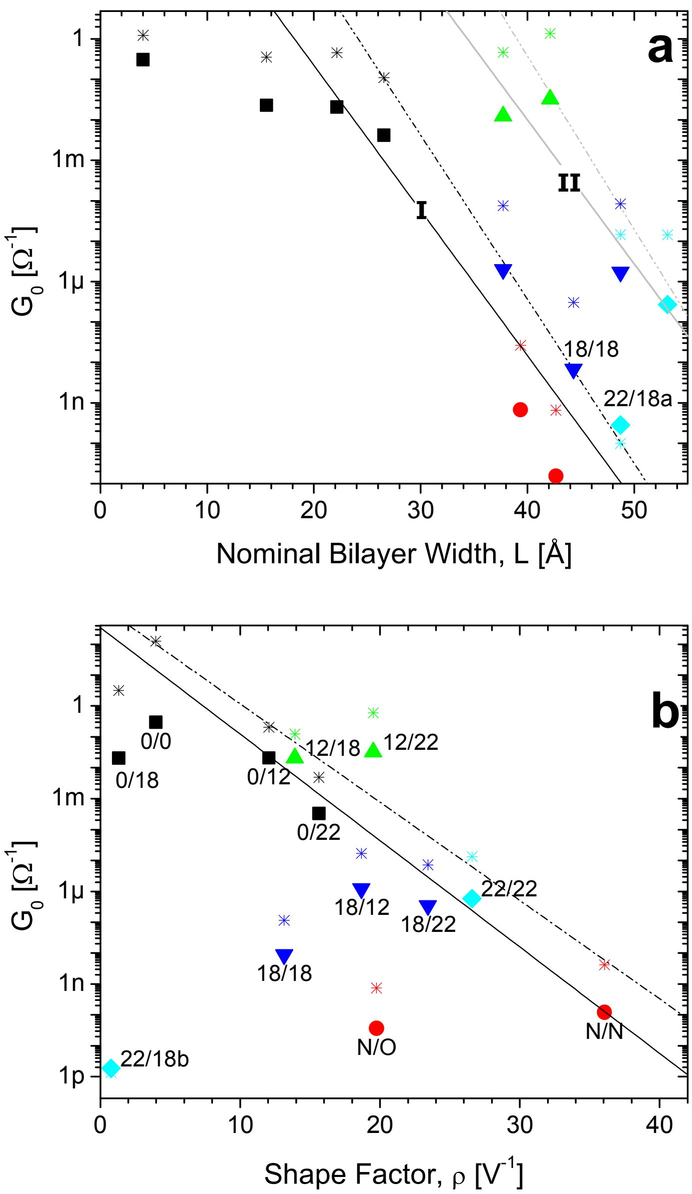

Figure S2. The Mujica-Ratner equivalent to Figure 4 (main text), namely semi-logarithmic plotting of equilibrium conductance (G_0) against nominal length (**a**) or shape factor (**b**) is shown by large, solid symbols. The Simmons alternative (*i.e.*, Figure 4, main text) plots the product G_0L (or $G_0\rho$) and is shown by asterisks. Solid lines are exponential fits within the Mujica-Ratner plot (solid symbols) and dashed lines are identical to the trend line of Figure 4 (*i.e.*, the Simmons variant).

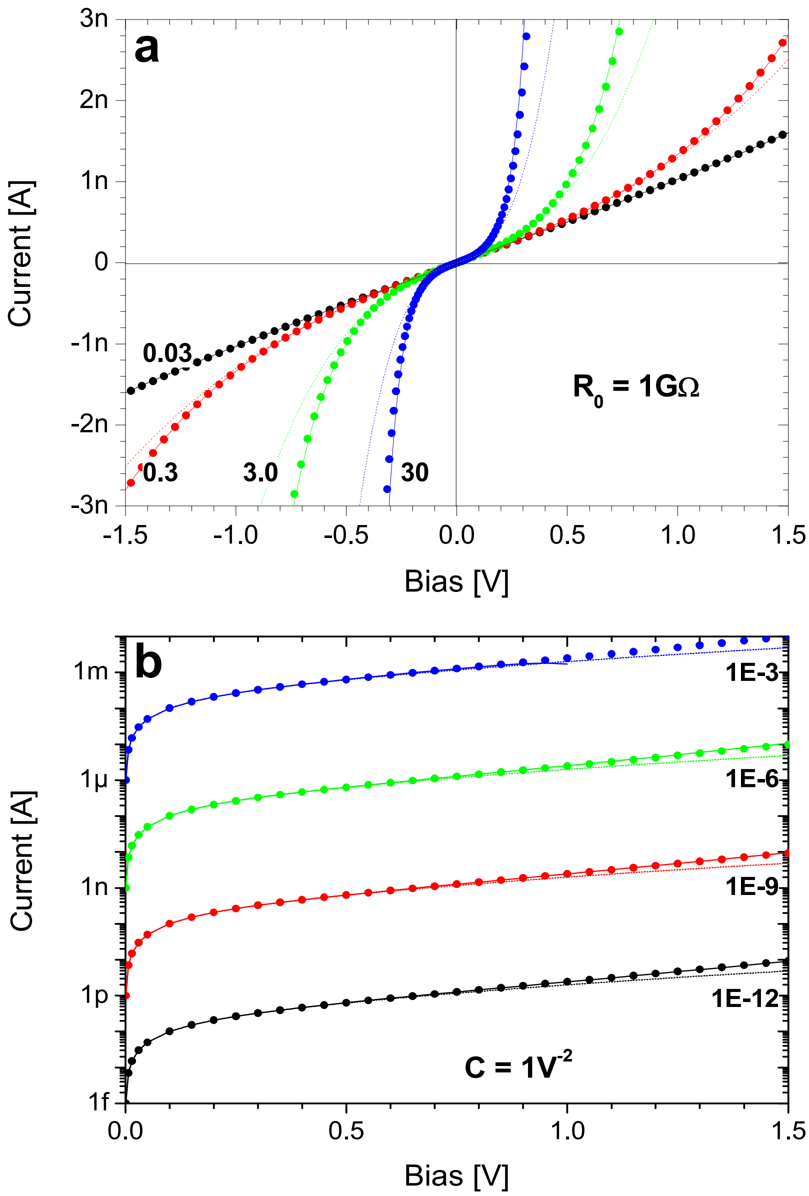

Figure S3. Comparison between simulated *I-V* curves calculated using the Simmons model (Equation A1, solid line), the Mujica-Ratner model (Equation B10, dots) and cubic relations (Equation 1, dashed line) for a constant equilibrium conductance (G_0= 10^{-9} Ω^{-1}, top panel, C is stated next to each curve) or for a constant cubic coefficient (C=1 V^{-2}, bottom panel, G_0 is stated next to each curve). Note that these seemingly identical curves translate into rather different barrier heights and lengths when using the two different models (see Table T2 below).

Table T2. Extracted junction parameters for the simulated curves of Figure S3

Top panel	C	G_0	φ [V]		L [Å]		β [1/Å]		ρ [1/V]	
			S[a]	MR[b]	S[a]	MR[b]	S[a]	MR[b]	S[a]	MR[b]
Blue	0.03	1E-9	12.10	12.36	13.3	6.3	1.59	4.45	1.75	1.62
Green	0.3	1E-9	3.62	6.15	23.0	10.0	0.87	2.70	5.55	5.21
Red	3	1E-9	1.08	3.12	39.9	16.3	0.48	1.67	17.58	16.65
Cian	30	1E-9	0.32	1.81	68.9	30.1	0.26	0.91	55.76	53.12
Bottom Panel										
Blue	1	1E-12	2.61	4.59	35.4	13.8	0.74	2.49	10.03	9.58
Green	1	1E-9	1.92	4.18	30.7	12.5	0.64	2.17	10.14	9.56
Red	1	1.E-6	1.24	3.37	25.3	10.0	0.51	2.05	10.40	9.51
Cian	1	1.E-3	0.53	2.96	19.1	8.8	0.33	1.51	12.04	9.47

a) a) Under ‘S’ appear values which were extracted according to the Simmons model from the corresponding C and G0 values, namely d was calculated from Equation A6 using A=1μm^2; then ρ from Equation A5; φ from their ratio; L from Equation A7 using arbitrary m^*=0.2; and finally β is the ratio d/L.

b) b) Under ‘MR’ appear values which were extracted according to the Mujica-Ratner model from the corresponding C and G0 values, namely N was calculated from Equation B13 using A=1μm^2 and A_0 = 20Å^2, and t=Δ=1. The extracted N was then rounded and a new t value was extracted using same Equation B13; then φ was calculated from Equation B12 and L=Na using a=1.255 (C-C distance); ρ was calculated using Equation 5; and finally β is the exponential slope of Equation 7a ($\beta = 2/a \cdot \ln(\varphi/t)$).