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Supplementary Information: Interplay between quantum interference and conformational fluctuations in single-molecule break junctions

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Junction elongation data

In table 1 we show the range of separation between the gold tips used as initial condition in our calculations (first column) compared with the molecular lengths of the different molecules (second column) and the experimental measured step length.

Molecule	Displacement investigated in our calculations	Molecular length	Step-length
PP1	5.5-21 Å	1.31 Å	0.57 Å
PP2	9-21.5 Å	1.55 Å	0.73 Å
PP3	11-25.5 Å	1.79 Å	0.82 Å
PM1	5-20.5 Å	1.20 Å	0.56 Å
PM2	7-22.5 Å	1.45 Å	0.70 Å
PM3	10.5-25 Å	1.70 Å	0.87 Å
P1	4.5-19 Å	1.13 Å	0.61 Å
P2	8-22.5 Å	1.37 Å	0.75 Å
P3	10-24.5 Å	1.61 Å	0.86 Å
M1	4-18.5 Å	1.00 Å	n/a

Table 1. Range of separations used for each junction simulation (second column) and the calculated molecular length (third column) taken from Ref.[1].

Results for all molecules

Figure S1 shows the conductance traces for all the break junctions investigated in this study. The conductance traces calculated using bare DFT (green crosses) possess high-conductance plateaus until a few steps before the breaking of the junction. As in the specific cases in Figure 2, the PPn conductance traces show a rather flat plateau until the rupture of the junction while the PMn conductance traces rapidly decrease by two orders of magnitude. It is apparent that the qualitative behavior of the classes Pn (M1) is the same as the PPn (PMn) classes.

The effect of entropy is illustrated by the ensemble-averaged conductances plotted as red crosses. In this case, a transition from the higher pi-metal conductances occurs at the much smaller separations for both PPn and PMn, after which both molecules possess flat plateaus up to the rupture displacement. The plateau conductance of PMn is an order of magnitude lower than that of PPn, reflecting the significance of their meta versus para couplings and therefore we conclude that the signature of destructive versus constructive interference survives when entropy is included. The monofunctionalized molecules (Pn and M1) shows large variations in their conductances; in fact in these cases the metal-π bonds on the non-functionalized sides is easily broken by the fluctuations.

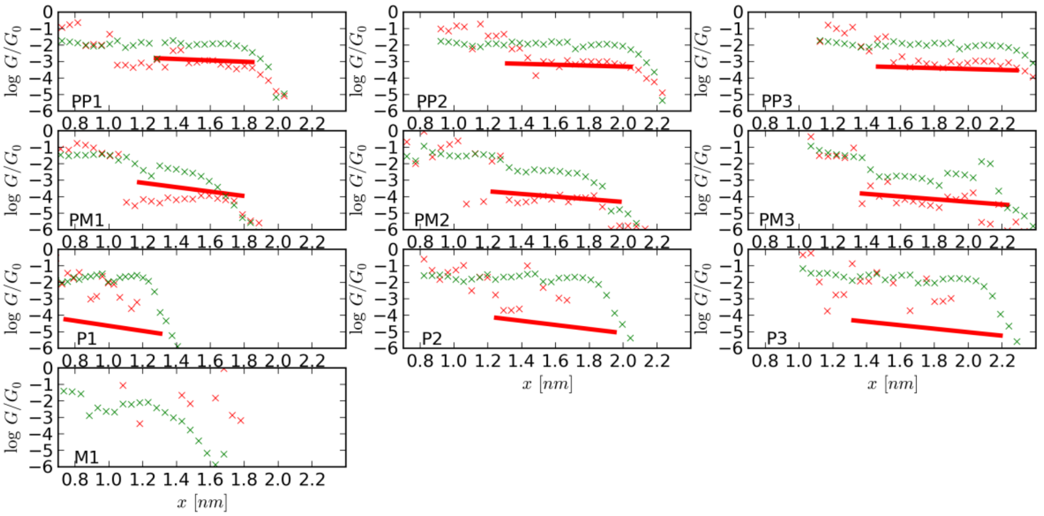

Figure S1 Conductance traces obtained with the data of the DFT and MD for all the break junctions investigated in this study. Green crosses are the conductances obtained from bare DFT based calculations. Red crosses are the ensemble-averaged conductances obtained with MD based calculations. The red lines are the averaged experimental traces from ref[1].

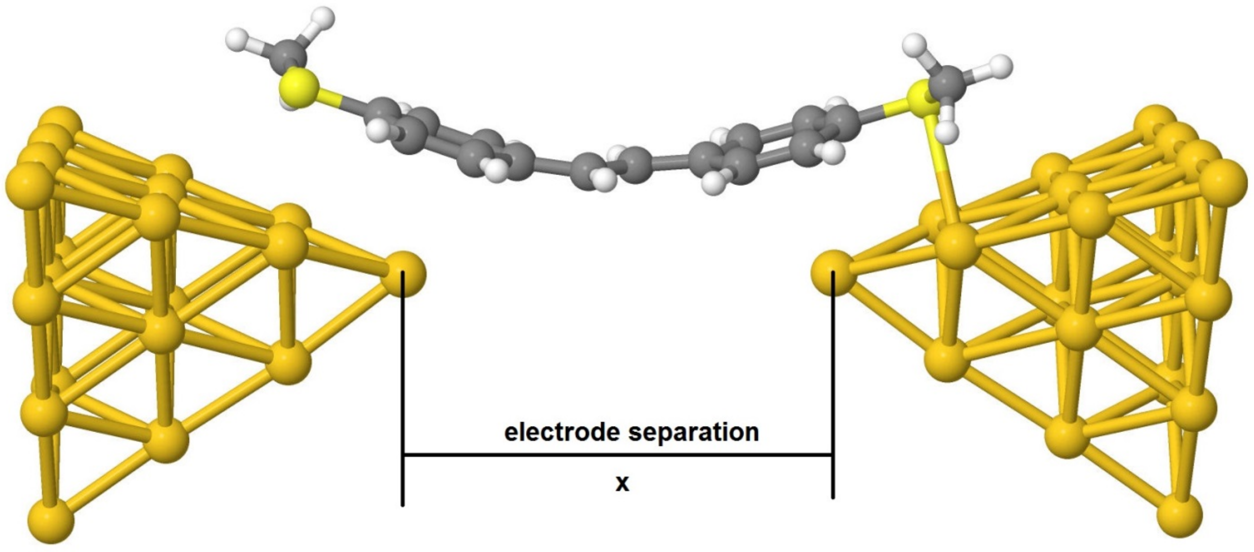

Figure S2. A typical optimized PP1 junction geometry, showing the molecule, two pyramidal electrode tips and the electrode separation x. During geometry optimization the two outermost left and right gold layers of the junction were kept fixed.

Comparison between non-equilibrium Green function method and wide band approximation.

To benchmark the wide-band approximation, we also calculated the transport with a full non-equilibrium Green function approach (NEGF) for the PP1 and PM1 frames. In order to perform the NEGF calculation we added several 111 directed gold bulk layers the junction geometries. The full geometry of the system is shown in Figure S3. The system is also treated as periodic in every direction and the transport calculation was performed with SMEAGOL[2, 3]. Figure S4 shows the comparison between the conductance trace curves obtained with WBA and NEGF calculation. Figure S5 also shows the transmission function of two junction geometries at different electrode separation.

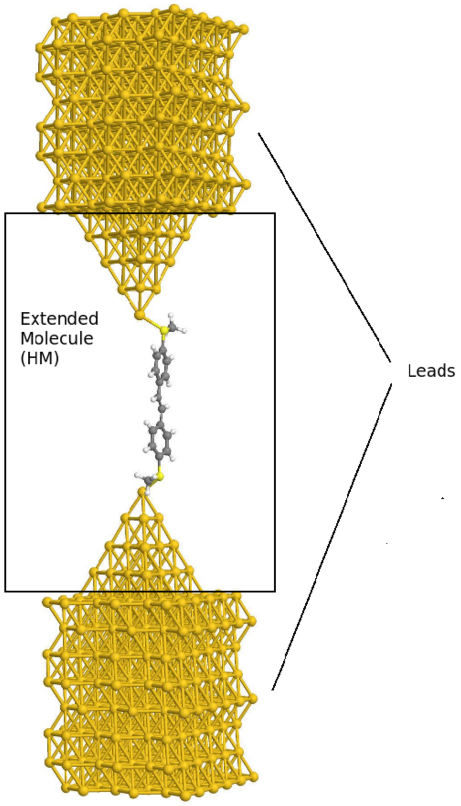

Figure S3. The structure of the system we used to perform the NEGF transport calculation. We attached to the ends of the extended molecules several layers of gold simulating the leads.

The wide band approximation with Γ=4eV (WBA) shows to be a reasonably acceptable approximation for calculating the conductance traces in comparison with the non-equilibrium Green function approach.

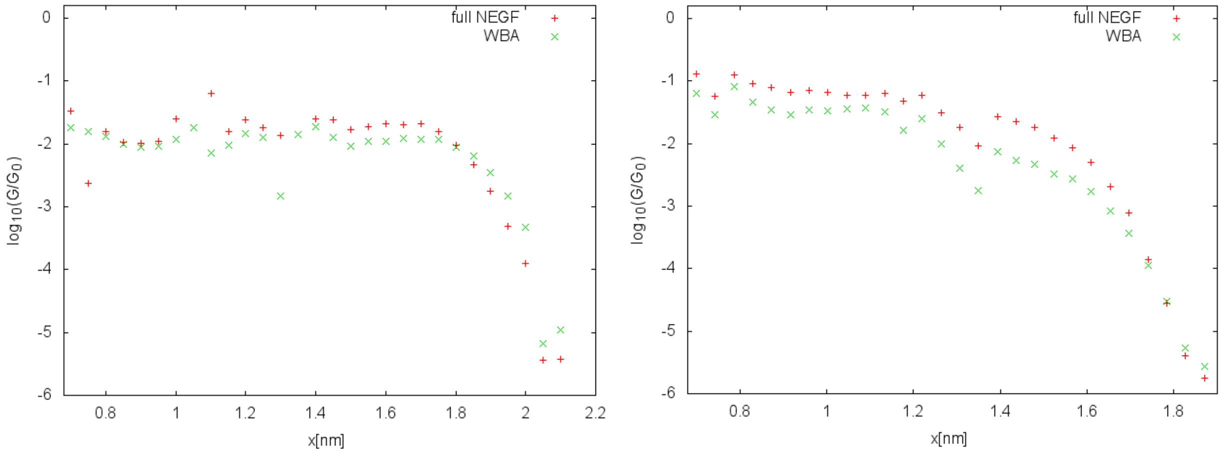

Figure S4 Here the comparison of the conductance curve for the PP1 molecule (left) obtained with the NEGF approach (red dots) and with the WBA (green dots). On the right we compare the trace obtained with NEGF approach (red dots) and WBA (green dots) for the PM1 molecule.

Comparison of conductance curves at zero and room temperature

Figure S5 shows the comparison of two transmission coefficient curves for two different electrode separation of the PP1 based junction. The conductance curves obtained with the full non-equilibrium Green function formalism (NEGF) are plotted with blue lines. The conductance curves obtained for the same junction geometry using the wide band approximation (WBA) are plotted using orange lines.

The red curve shows the transmission function of a junction geometry snapshot from the room temperature MD (labelled as MD). We can find a decrease of the conductance of two orders of magnitude.

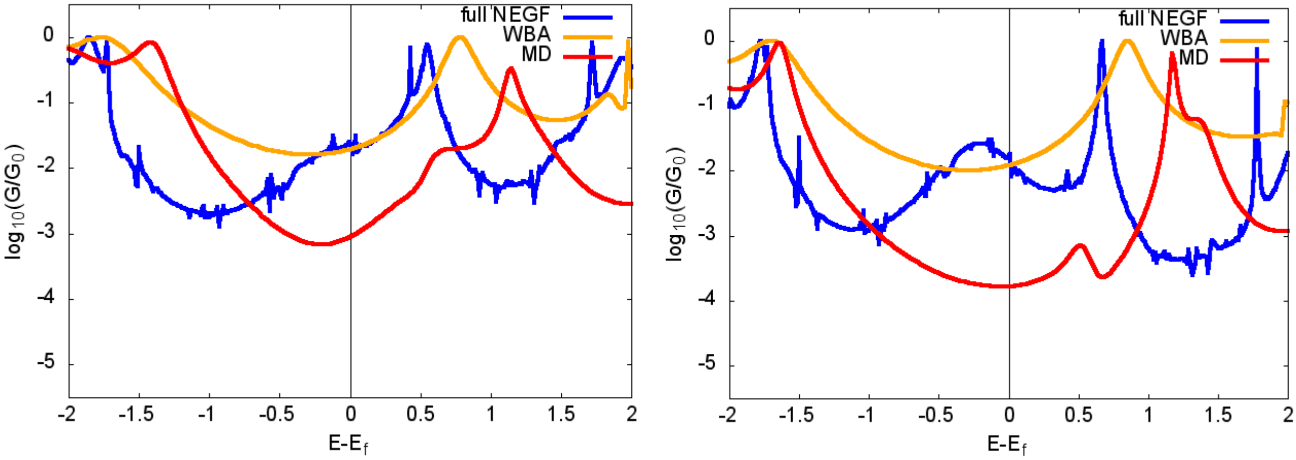

Figure S5 Conductance curves obtained for two different electrode separations for the PP1 based junctions. On the left the electrode separation is 13.8Å and on the right the electrode separation is 17.2Å. The blue and the orange curves show the transmission coefficient function for the DFT relaxed junction geometry with the full non-equilibrium Green function approach and with the wide band limit approximation, respectively. The red curve is the transmission coefficient function obtained with WBA for a snapshot of the MD conformational evolution.

References

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2. A. R. Rocha, V. M. García-Suárez, S. Bailey, C. Lambert, J. Ferrer and S. Sanvito, *Physical Review B*, 2006, **73**, 085414.
3. A. R. Rocha, V. M. Garcia-Suarez, S. W. Bailey, C. J. Lambert, J. Ferrer and S. Sanvito, *Nature materials*, 2005, **4**, 335-339.