Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information for

Direct Au-C contacts based on biphenylene for single molecule circuits

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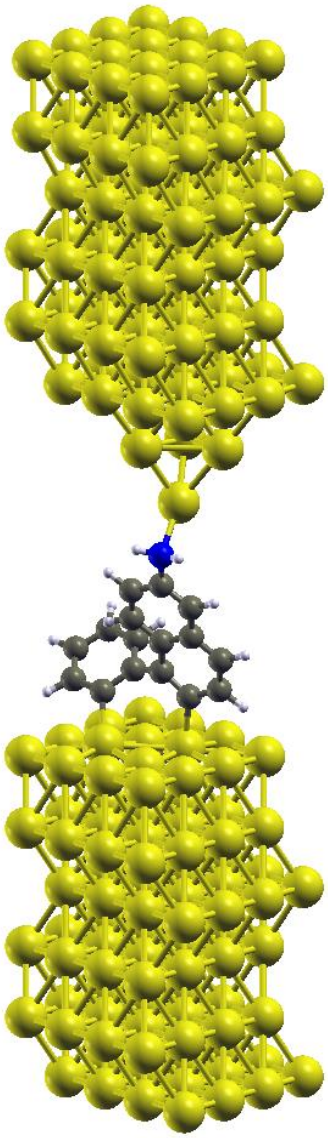
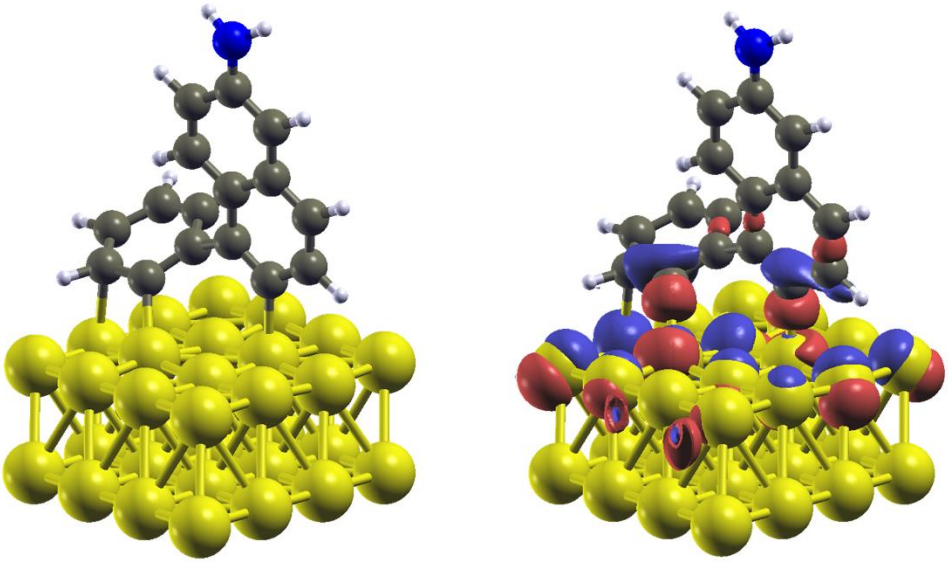
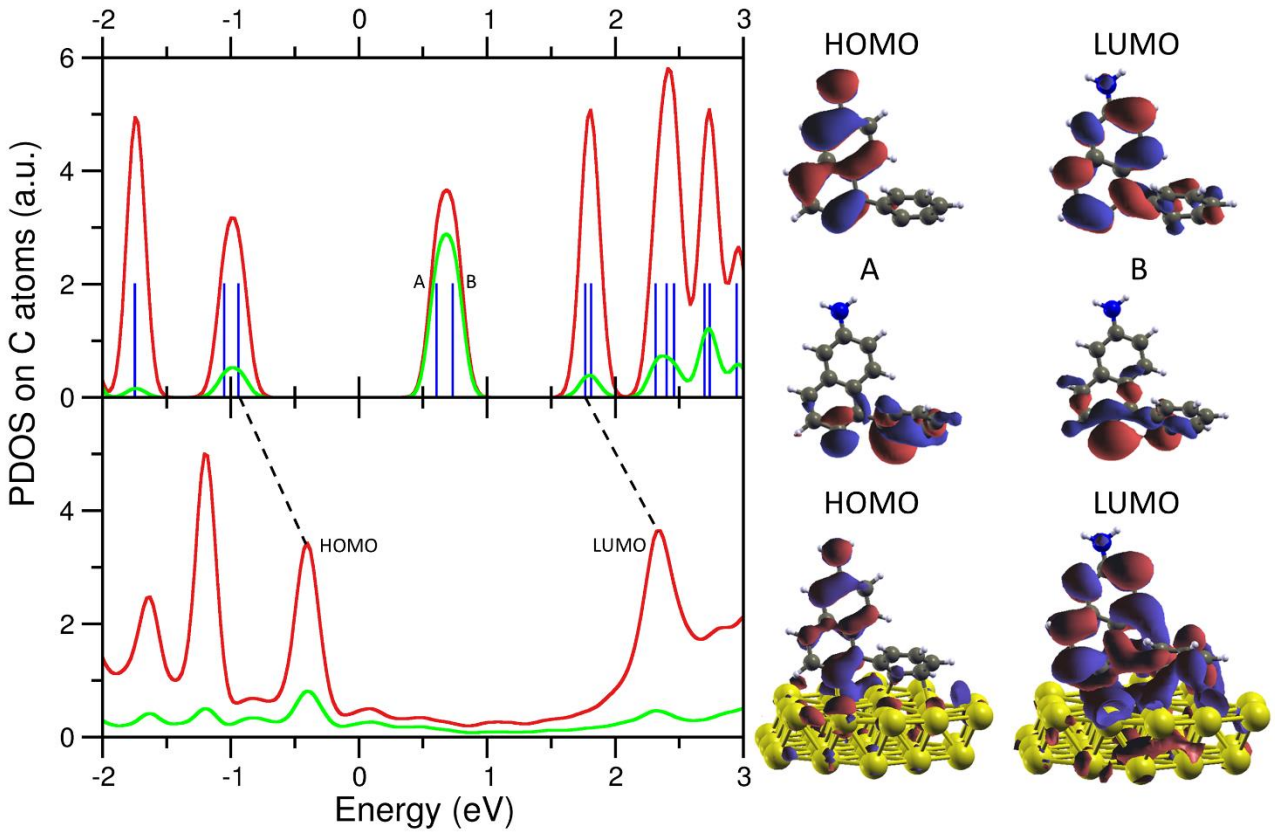


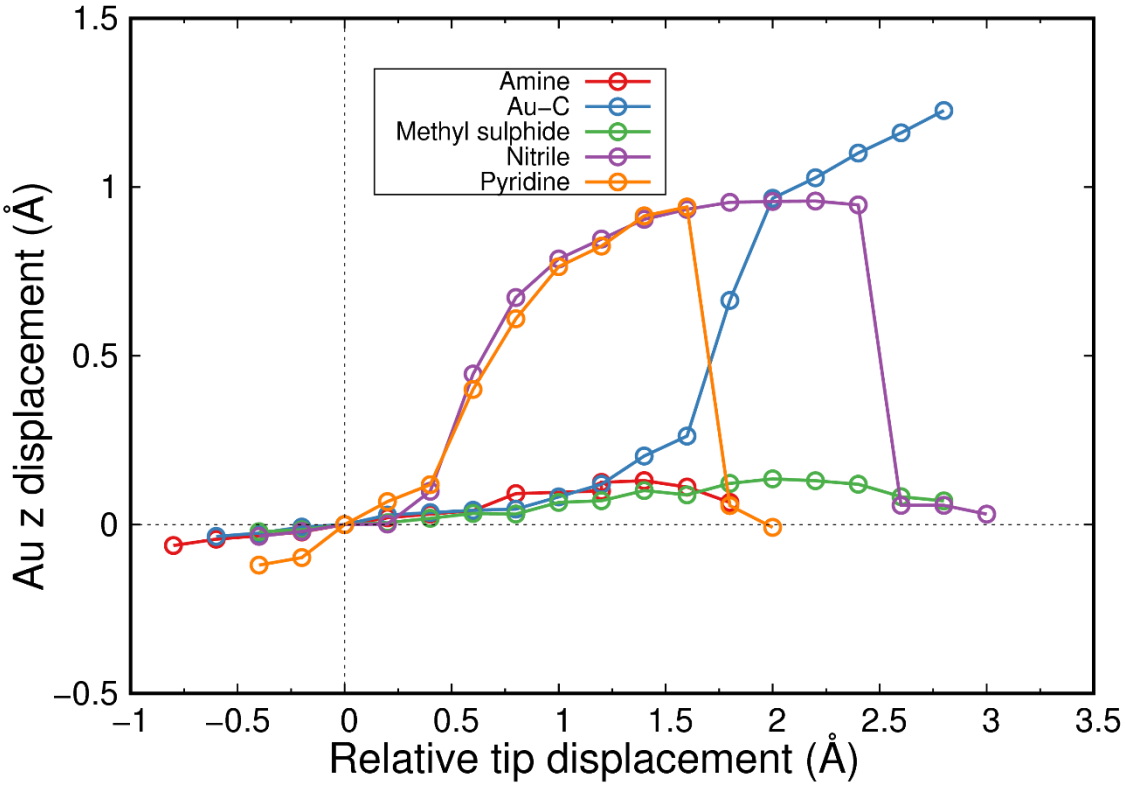
SI Fig.1 Unit cell used in transport calculations. Each Au layer consists of 16 atoms and there are six Au layers on each side.



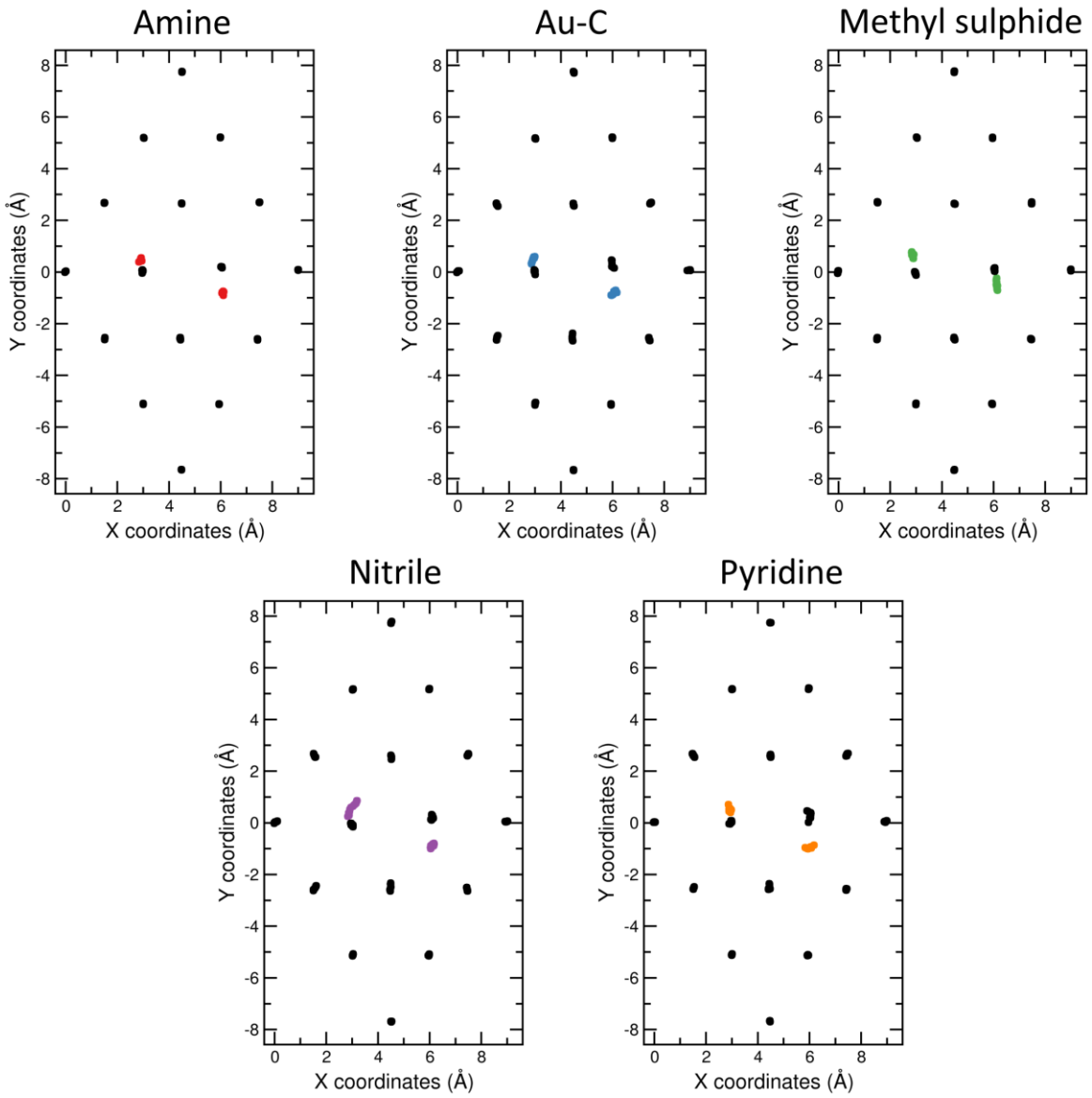
SI Fig.2 Electron density difference upon adsorption for an amine-terminated biphenylene-based molecule in a geometry similar to that of Fig. 2a (tip not visible). The structure is shown on the left for clarity. Electron density accumulation (depletion) is shown in red (blue) with respect to the isolated molecule plus Au surface. Electron density is displaced from the contact C atoms mainly towards the regions of the Au-C bonds. The nodal pattern of charge rearrangement upon adsorption has σ symmetry and is confined to the plane of the benzene rings.



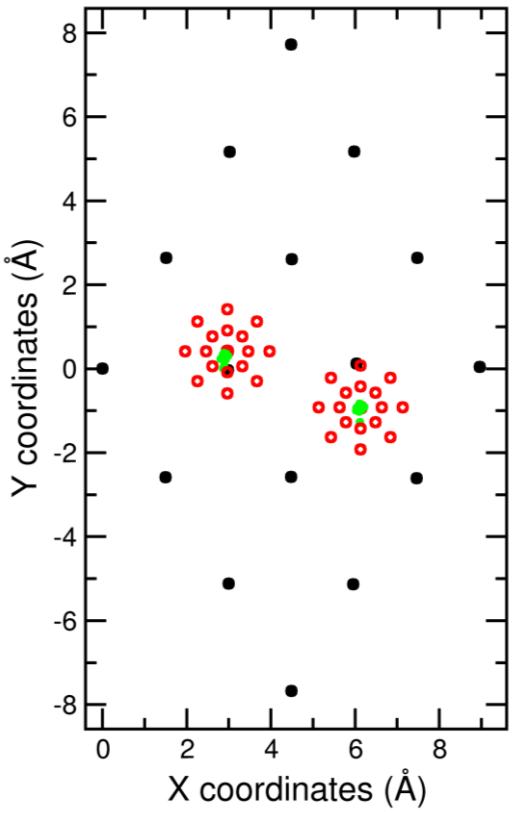
SI Fig.3 PDOS on the molecular C atoms (red) of the isolated molecule (top panel, spin polarised) and at the junction (bottom panel). The PDOS on the contact C atoms is shown in green. Contour plots to the right show relevant wave functions: C radicals (labelled A and B), HOMO and LUMO of the isolated molecule, and the latter two at the junction.



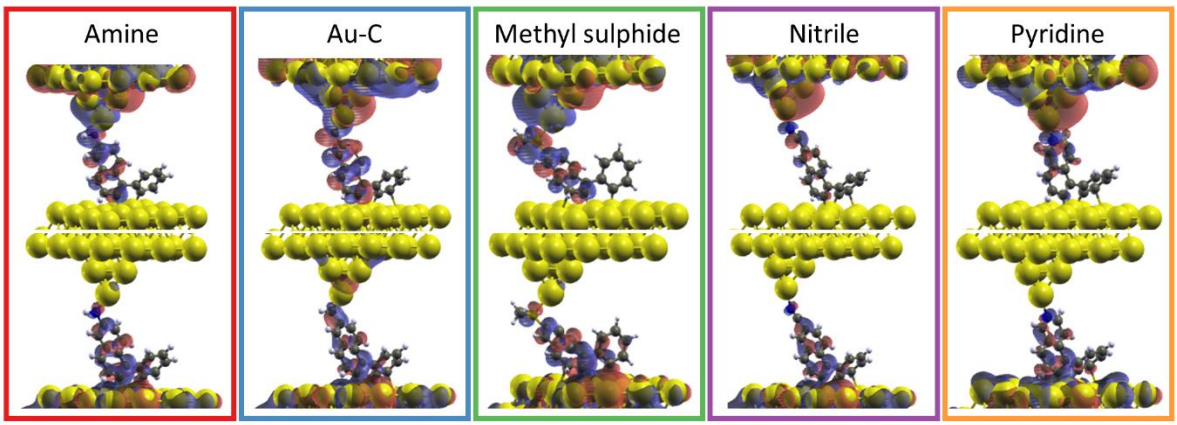
SI Fig.4 Height of the contact Au atom in the substrate measured from its position at equilibrium as a function of tip displacement. Since the height of the molecule changes with the top linker termination, the horizontal axis is measured with respect to the equilibrium distance for each linker. For nitrile, pyridine and Au-C links, the substrate Au atom is lifted from the surface.



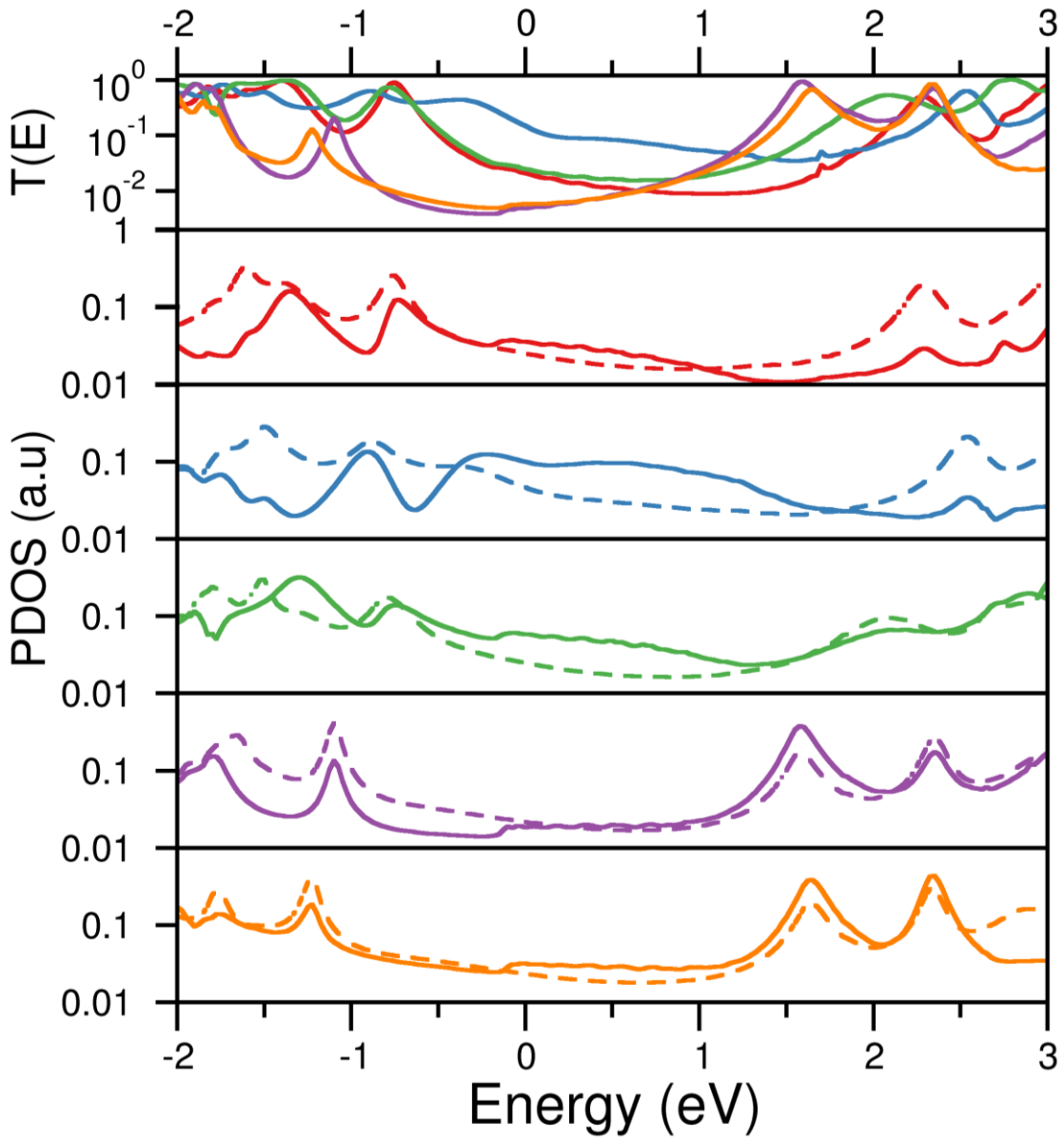
SI Fig.5 X and y coordinates of the surface Au atoms (black) and contact C atoms (color) during the tip approach simulations of Figs. 2 and 3 in the main text.



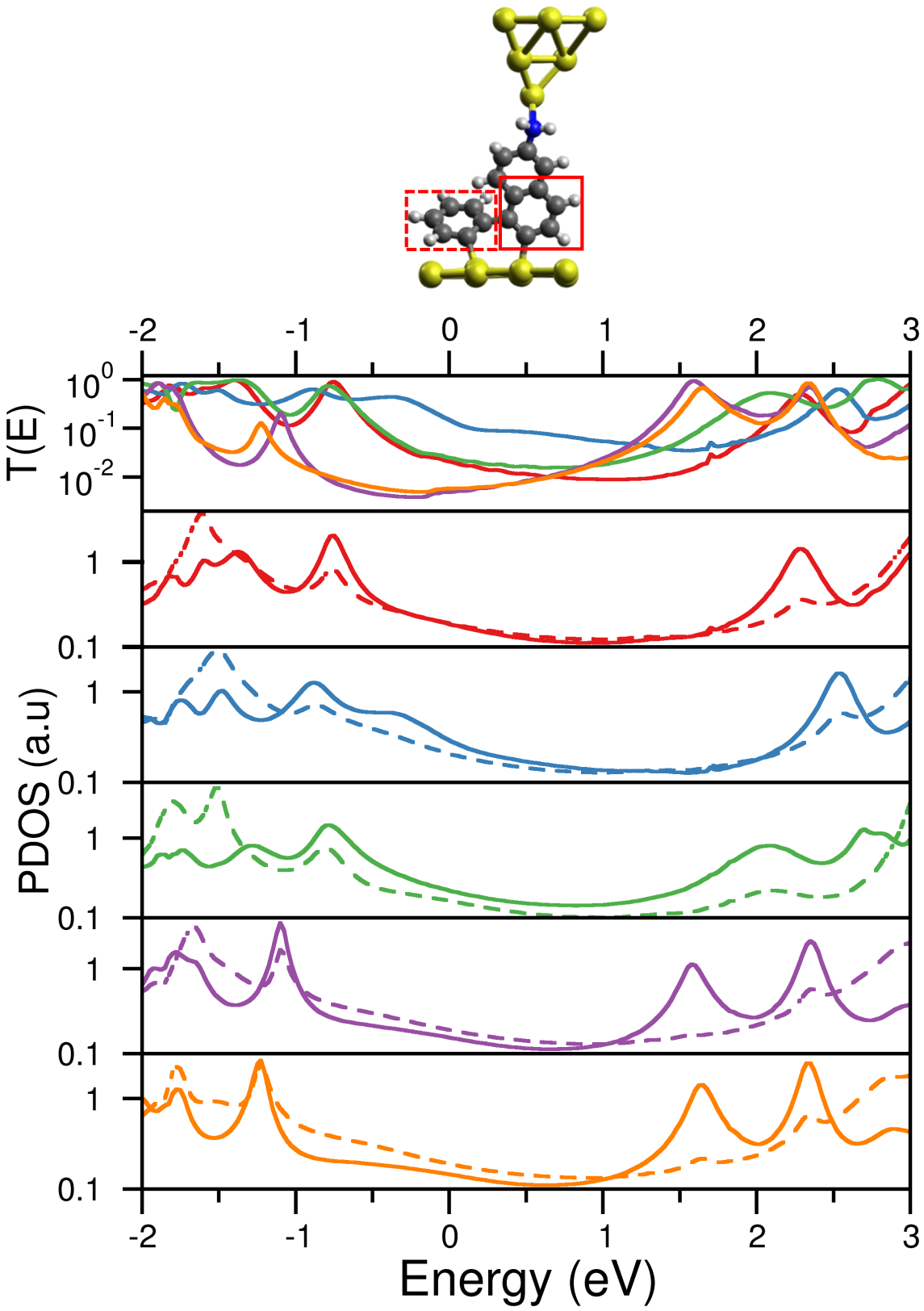
SI Fig.6 X and y coordinates of initial and final atomic positions during additional structural relaxations of an amine-terminated molecule where the initial molecular geometry was shifted laterally by 0.5Å or 1.0Å from the structure similar to that of Fig. 2a. In all cases, the contact C atoms relax to a final geometry close to that of the tip approach simulations. Black circles: Au surface atoms; open red circles: initial positions of the contact C atoms; filled red circle: (final) positions of the contact C atoms in Fig. 2 (tip far); filled green circles: final positions of the contact C atoms. All molecular and Au surface atoms were allowed to move.



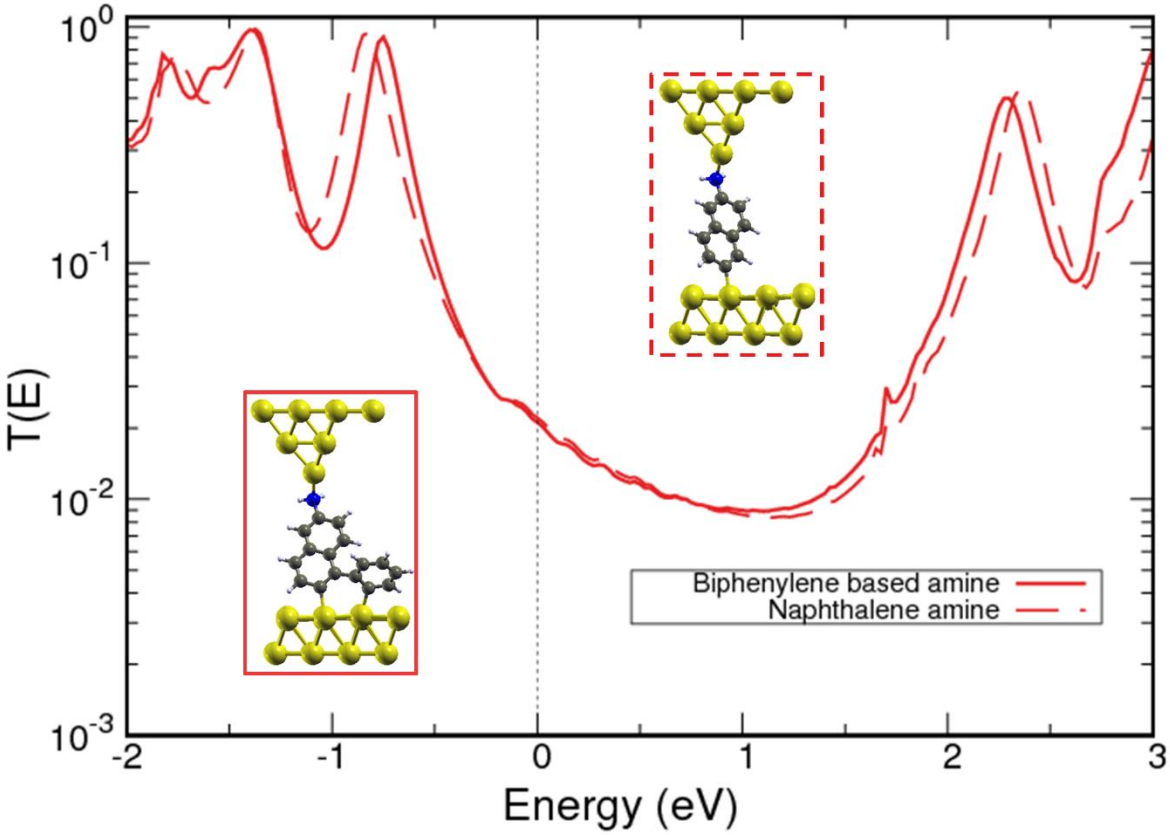
SI Fig.7 Calculated transmission eigenchannels at the Fermi energy incident from above (top panels) or below (bottom panels). In the bottom biphenylene-derived contacts, the side benzene ring is not in the tunnelling pathway.



SI Fig. 8 Calculated transmission spectra (top panel) and PDOS over the top contact atom X (dashed lines) and bottom contact C atom (solid lines) for the five linker terminations considered for the top contact. The top linker acts as the bottleneck for conductance.



SI Fig. 9 Calculated transmission spectra (top panel) and PDOS over both biphenylene-derived benzene rings in the bottom contact for the five linker terminations considered. The benzene ring bonded to the top contact determines the transport properties and is the main tunneling pathway.



SI Fig.10 Calculated transmission spectra for the amine-terminated junction and for a molecule in the same geometry but missing the side benzene ring in the bottom contact. The contribution to conductance of this side ring is small.