PAPER

Direct Au–C contacts based on biphenylene for single molecule circuits†

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We propose a novel platform for stable and highly conducting single molecule electronics and characterize its mechanical, electronic and conducting properties using *ab initio* simulations. We study a biphenylene-based molecular architecture on gold and consider that the antiaromatic instability of biphenylene leads to the breaking of internal carbon–carbon bonds and subsequent formation of Au–C covalent bonds with the substrate. In the resulting conformation the conjugated rings have a large twist angle and stand almost upright on the surface. The top contact is realized by functionalizing one end of the biphenylene unit with a chemical linker group, which in the adsorbed geometry is positioned far from the surface. We consider several linker terminations for this top contact, which is approached in our simulations by a gold tip. Using Density-Functional Theory (DFT) and Non-Equilibrium Green's Function (NEGF) methods, we quantify the mechanical and electron transport properties of the molecular junction and discuss their relationship with the nature of the linker group. Our results show that this biphenylene-based platform is very stable and provides high electronic transparency to current flow, demonstrating its potential in single molecule conductance studies.

1. Introduction

Nanoscale circuits in which single molecules act as the active elements represent the ultimate step in electronic miniaturization. Molecules can be characterized and manipulated with sub-nanometer precision, placing them between two electrodes so that their conducting properties can be measured reliably. At the same time, atomistic simulation methods are able to provide a detailed picture of the main physical and chemical principles that govern electron transport across single molecules. Through chemical synthesis, molecular circuits with different properties and functionalities can be designed. Research has shown that, among these chemical properties, metal–molecule contacts play an essential role in electron transport.[1–4] They not only affect the geometry and mechanical properties at the junction but also often act as bottlenecks for electron flow. Thus, designing and realizing optimal metal–molecule contacts is essential for the development of efficient and reliable single molecule circuits.

Usually, each end of the molecule is functionalized with a chemical linker group, and each linker group binds to an electrode, bridging the nanogap. Recently, however, asymmetric molecules with more than one bond to the substrate electrode

have been investigated and reported to have many advantages for single molecule conductance studies. Thiol-terminated tripodal terminations were shown to provide strong electronic coupling to the substrate.[5] In another study, a molecular switch was realized in a molecule having a tripodal platform to the substrate and a cantilever arm protruding from the surface.[6] The electronic and transport properties of these molecules with tripodal wires were shown to depend on the orientation and conformation of the wires.[7] An ideal linker should be electronically transparent in order to result in high conductance, as well as mechanically stable and selective. Direct Au–C bonds were shown to be highly-conducting and reproducible metal–molecule contacts for single molecule transport. The conductance of alkanes or oligophenyls with Au–C bonds is much higher than with other terminations. Formation of Au–C bonds in single molecule transport was first demonstrated from trimethyltin end groups that cleave off *in situ*, resulting in covalent Au–C bonds between electrode tip atoms and the terminal Carbon atoms of the molecule.[8–10] Subsequently, other synthetic strategies were demonstrated, using trimethylsilyl groups[11] or the deprotonation of alkynyl groups, where an open bond is occupied by Au atom.[12] However, these approaches involve toxic precursors or residues, or rapid dimer formation.

In this paper we propose a bipodal molecular architecture for single molecule transport studies on gold having stable and highly-conducting metal–molecule links. From calculations based on Density-Functional Theory (DFT) and Non-Equilibrium Green's Functions (NEGF), we demonstrate the excellent mechanical, electronic and conducting properties of the proposed architecture.

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This molecular platform is based on biphenylene, a conjugated molecule consisting of two benzene rings connected by single bonds exhibiting an antiaromatic electronic structure. Aromaticity is a key concept describing the stability of conjugated systems. According to Hückel's rule, cyclic and planar conjugated systems are said to be aromatic if they have $4n + 2\pi$ electrons (where n is an integer), and antiaromatic if this number is $4n$. Antiaromatic molecules exhibit remarkable electronic properties[13–18] but are known to be very reactive and unstable. Antiaromatic instability makes these complexes likely to experience bending or rotation, or bond alternation and rearrangement leading to more stable structures.[13] As such, antiaromatic molecules are more prone to bond breaking and reformation than, for instance, aromatic counterparts. For instance, the breaking of the central C–C σ bonds in biphenylene was recently demonstrated,[19] where oxidative addition of biphenylene to Au resulted in stable organogold complexes.

Here we explore the consequences of antiaromatic instability for single molecule transport contacts. We assume that these central C–C bonds in the biphenylene structure can be broken due to an external perturbation such as thermal annealing or a voltage pulse from an STM tip, and that the two C atoms form bonds with a Au(111) substrate. In this conformation, steric repulsion results in a large twist angle between the conjugated rings of biphenylene and the rings stand almost upright on the substrate. This constitutes the contact to one electrode. In order to address molecular transport, we functionalize one end of the biphenylene molecule, which in the adsorbed conformation points away from the surface, with an additional benzene ring which we functionalize with several linker groups (Fig. 1). This provides the contact to the other electrode (*e.g.* an STM tip). In our study, we consider several alternatives for the linker groups in this top contact so as to compare their mechanical and conducting properties with those of the bottom biphenylene-based contact. In particular, we analyze amine (–NH$_2$), methyl sulphide (–SCH$_3$), nitrile (–CN) and pyridine linkers, as well as direct Au–C bonds. Amine, nitrile, and pyridine groups form donor–acceptor bonds with Au, involving electron donation from N to Au. In amine bonds, the N lone pair is directed perpendicular to the molecular π system and, as a result, couples strongly with π orbitals. In single molecule transport, amine links have been shown to result in Highest Occupied Molecular Orbital (HOMO)-dominated transport.[20,21] Pyridine and nitrile groups have a σ (in-plane) lone pair which is poorly coupled to the π system. In molecular transport studies, these linkers have been shown to conduct *via* the Lowest Unoccupied Molecular Orbital (LUMO).[22–24] Methyl sulphide groups result in HOMO-dominated transport,[25] similar to amines. Au–C links are covalent metal–molecule bonds directed perpendicularly to the π system, resulting in very high conductance *via* occupied orbitals.[8] The mechanical properties of these linkers in Au junctions have also been investigated previously in symmetric molecules. Smaller rupture forces have been reported for alkanes with amine and methyl sulphide terminations than for bipyridine.[26–28]

Using DFT-based methods, we study the elastic and conducting properties of the biphenylene-based junction with five different
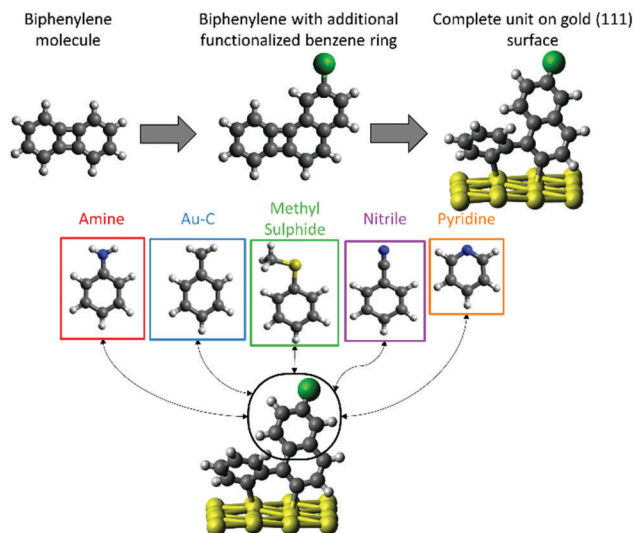

Fig. 1 Schematic illustration of the formation of a bipodal platform on Au(111) based on the antiaromatic instability of biphenylene and breaking of internal C–C bonds. An additional functionalized benzene ring is added to act as a top contact. Five different linker groups are considered.

chemical terminations in the top contact. From this analysis we show that the proposed bipodal platform presents very good mechanical and transport properties.

2. Methods and simulations

In this work we do not address the process of internal C–C bond breaking and formation of Au–C bonds. Instead, we assume this process can be stimulated *via*, *e.g.* thermal annealing or from voltage pulses using an STM tip, and study the geometry and electronic properties of the adsorbed biphenylene-based species on the Au surface.

The functionalized biphenylene-based molecule is shown adsorbed on the substrate in the bottom panel of Fig. 1. We considered the Au(111) surface. Each Au layer consist of 16 atoms. The adsorbed molecule is contacted by an STM tip modelled as a pyramidal structure. The electronic properties are carried out using the SIESTA code.[29] Norm-conserving non-local Kleinman–Bylander type pseudopotentials are used. Exchange–correlation is described using the semi-local generalised gradient approximation (GGA) in the PBE implementation. A local-orbital basis set is used in the calculations. Au atoms are described using a single-ζ polarized basis while a double-ζ polarized basis is used for molecular atoms.

Mechanical properties were investigated by approaching the tip to the molecule in steps of 0.2 Å and optimizing the geometry at each step for each linker considered. The position of molecular, tip and bottom surface atoms are relaxed at each displacement step until the forces fall below 0.02 eV Å^{-1}. A unit cell consisting of three Au layers is used and electronic properties are evaluated at the Γ point.

Transport calculations were performed using the DFT-NEGF formalism.[30] Additional Au layers were added to the optimized

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geometries to calculate the transport properties The unit cell for transmission calculations consists of 6 Au layers on each side (ESI,† Fig. S1). The junction electronic structure was calculated using a $5 \times 5 \times 1$ Monkhorst–Pack k-point grid. For transmission spectra, a $15 \times 15 \times 1$ k-point grid is used. Transmission eigenchannels are calculated at the center of the Brillouin zone using the method of by Paulsson and Brandbyge.[31,32]

3. Results and discussion

3.1 Mechanical properties

Fig. 2 shows the calculated mechanical properties of biphenylene-based junction with the five top linkers considered. The force is calculated as the derivative of the total energy with respect to the vertical displacement. Positive (negative) values mean that the tip-molecule interaction is attractive (repulsive). Because of the height of the molecule changes with the different linkers, we choose to shift the curves horizontally, as discussed below. Across the different functional groups in the top contact, we can distinguish four different regimes. (a) When the tip is far, there is little tip-molecule interaction the calculated forces are small. The exception to this is the Au–C link in the top contact. Being a covalent bond, the interaction is strong and the calculated force is not small at large distances. We therefore chose to restrict the simulations to within a certain tip height given the nontrivial experimental realization of this top Au–C contact. As the tip approaches, interaction with the top linker increases until this

attractive interaction reaches a maximum (b), signalling the formation of a metal–molecule bond. As the tip is further approached, the molecule relaxes by tilting and compressing until an equilibrium configuration with both contacts is established (c). At this distance the forces on the tip and substrate are minimized and the system is in equilibrium. At this equilibrium distance we carry out the transport calculations. In Fig. 2 we shift the calculated F vs. z curves horizontally so that relative displacement is defined with respect to this equilibrium distance. This allows us to unify the force analysis since the height of the molecule, and thus inter-electrode vertical distances, is different for each top termination. If the tip is approached further, the system enters in the repulsive regime, indicated by negative forces, and the junction is compressed (d). Snapshots of the calculated geometries illustrating these regimes are shown in Fig. 2 for the molecule with a pyridine top contact.

The slope of the calculated force vs. distance curves gives the junction stiffness. The values of the stiffness at equilibrium for the different functionalizations are shown in Table 1. In agreement with the trend previously reported[26] we find the pyridine-terminated molecule to have a high stiffness. In the biphenylene-based platform considered, the calculated stiffness decreases along the following series: pyridine, nitrile, Au–C, amine, and methyl sulphide. A similar trend is found in the calculated maximum force sustained by the junction. For pyridine, nitrile, amine and methyl sulphide terminations, it is 1.84, 1.19, 0.81 and 0.62 nN, respectively. This establishes pyridine and nitrile linkers as presenting a stronger interaction with the Au tip, while amine and methyl sulphide terminations are weakly interacting. A higher rupture force in bipyridine- than amine-terminated junctions was previously demonstrated.[24] However, in our case the binding to both electrodes in these biphenylene-based platforms is strongly asymmetric: the top contact is very different to the bipodal bonds to the substrate. Since rupture forces were shown to depend on the nature of the molecular backbone,[26,33] quantitative agreement should not be expected with symmetric molecules which have the same metal–molecule contact on both ends.

The trends observed in the calculated stiffness and maximum force sustained by the junction are consistent with the angle with respect to the π system at which the tip binds. Fig. 3 shows the evolution of the molecule-linker-tip angle along the approach trajectory. It is defined by the apical Au atom at the tip, the linker atom X (where X = N for pyridine, nitrile and amine links, S for methyl sulphide and C for Au–C bond), and the C atom in the top benzene ring. We see clear differences which match the trend observed in the calculated forces. For amine, methyl sulphide and Au–C links, the molecule gradually tilts to accommodate the increasing interaction with the tip. This is reflected in the
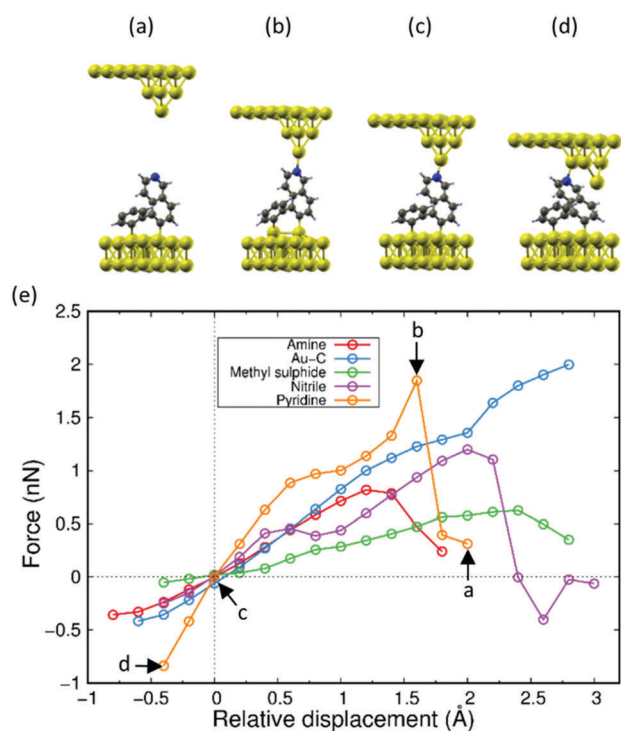

Fig. 2 (a–d) Snapshots of the tip approach trajectory for a pyridine-terminated top contact illustrating different interaction regimes. (e) Calculated forces as a function of tip displacement for the five linker terminations considered, measured from equilibria.

Table 1 Stiffness and conductance of the biphenylene-based junction with five different linkers

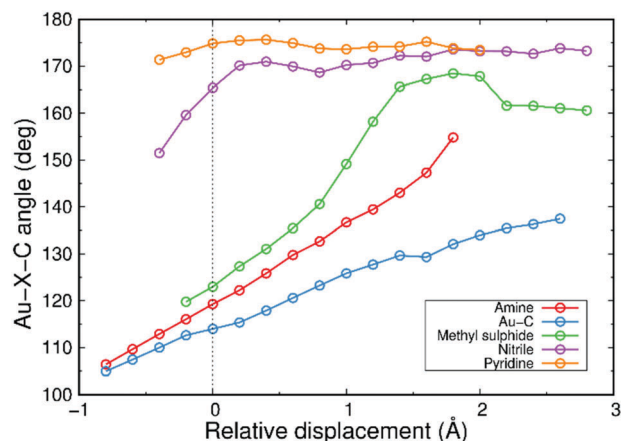| Linker	Amine	Au–C	Methyl sulphide	Nitrile	Pyridine
Stiffness nN Å^{-1}	0.61	0.77	0.18	0.84	1.31
$G(E_{\mathrm{F}})/G_0$ ($\times 10^{-2}$)	2.05	14.70	2.51	0.47	0.58

Fig. 3 Angle defined by the apical Au tip atom, the linker atom X, and a molecular backbone C atom in the benzene ring as a function of tip height, measured from equilibria.

continuous change in the C–X–Au angle to ~120 degrees at equilibrium (Fig. 3). On the other hand, for nitrile and pyridine contacts, this value remains more or less constant around 170 degrees, indicative of in-plane binding *via* the σ lone pair until a clearly repulsive interaction is established between tip and molecule.

Taken together, the calculated mechanical properties provide a picture of stiff and more reactive contacts to Au for nitrile and pyridine through the σ system and soft contacts to Au for amine, methyl sulphide and Au–C links, which are also less reactive for the first two.

So far we have discussed the mechanical properties of the metal-tip top contact but we now address the bottom Au–C bonds to the substrate. The binding energy of the biphenylene molecule to the Au surface, calculated by cleaving the bonds in an amine-functionalized molecule and keeping the molecular geometry fixed in a structure similar to that of Fig. 2a, where interaction with the top contact is small, is 1.2 eV per Au–C bond. In this geometry, analysis of charge rearrangement upon bond formation reveals it to be localized mostly at the biphenylene-substrate interface (ESI,† Fig. S2). C atoms closest to the surface are most affected by the formation of Au–C links. Electron density is displaced from the bonding C atoms towards the Au–C bond regions and, to a smaller extent, towards the benzene rings. Importantly, this charge rearrangement upon Au–C bond formation has a σ symmetry pattern since it takes place in the plane of the benzene rings. The biphenylene HOMO and LUMO experience minor changes from the isolated molecule to the adsorbed environment (ESI,† Fig. S3). The states at the cleaved C atoms hybridize with Au atoms at the surface and the spectral features of the contact C atoms are smoothened out when adsorbed.

As the tip is approached in the simulations, the surface Au contact atoms in the bottom contact can be lifted (ESI,† Fig. S4). This happens for the more reactive pyridine and nitrile linkers and corresponds to the sudden jumps in the calculated force displayed on Fig. 2. Amine- and methyl sulphide-terminated

junctions show no such jumps. The case of a Au–C bond in the top contact is special, since this breaking this covalent bond would result in a radical. Instead, when the tip is far, the molecule is lifted from the substrate. In all cases, the bond lengths of the bottom two Au–C bonds remain almost unaltered and no changes in the adsorption geometry of the bottom contact are seen (ESI,† Fig. S5). Additional structural relaxations of the adsorbed molecule where the initial geometry was shifted parallel to the surface resulted in similar final structures (ESI,† Fig. S6). These results highlight the stability and directionality of the Au–C bonds to the substrate.

3.2 Transmission properties

The calculated transmission spectra for the biphenylene-based molecule with are shown in Fig. 4 for the five different top linkers considered. First, we address zero bias conductance. The conductance is highest with a top Au–C bond. This is followed by amine and methyl sulphide linkers, whose conductance is similar to each other and ~6–7 × smaller than with the top Au–C bond. Nitrile and pyridine contacts provide the lowest conductance, a factor ~35–30 lower than for Au–C (Table 1).

From Fig. 4 a pattern is immediately apparent, since the linkers for which conductance is HOMO-dominated result also in higher conductance values. Nitrile and pyridine terminated molecules yield LUMO-derived transport and low conductance values. This relation of linker termination and dominant conducting state (empty or occupied) agrees with previous reports.[3] The Au–X–C contact angle of ~120 degrees for Au–C, amine and methyl sulphide is indicative of out of plane bonding and concomitant strong electronic coupling. These linkers result in high calculated conductance values. On the other hand, the in-plane tip binding by nitrile and pyridine contacts results is driven by the σ system and consequently the degree of electronic coupling provided by
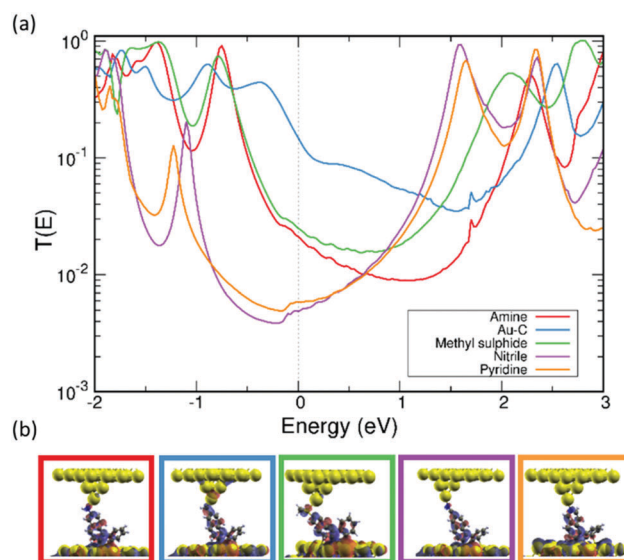

Fig. 4 (a) Calculated transmission spectra of biphenylene-based junction with the five linker terminations considered in for the top contact. (b) Real-space representation of the most conducting scattering states at the Fermi energy.

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these links is rather low since the tip is poorly coupled to the π system. The degree of electronic coupling provided by the different top terminations is reflected transmission eigenchannels at the Fermi energy shown in Fig. 4 and ESI,† Fig. S7.

We also note that the strong dependence of the transport properties with the top metal–molecule contact highlights its role as bottleneck for electron transport. The bottom bipodal Au–C bonds to the substrate provide strong electronic coupling, and the conducting molecular state is strongly determined by the top contact (ESI,† Fig. S8).

Finally, we comment on the role played by each of the bottom benzene rings derived from the biphenylene unit that are forming bonds with the substrate. An analysis of the Projected Density of States (PDOS) of each ring shows (ESI,† Fig. S9) that only the ring connected to the top contact is in the conducting pathway. The spectral features of the other benzene ring play a smaller role near the Fermi energy, especially in the conducting frontier orbital. This is reflected in the transmission eigenchannels involving mostly only one of the bottom benzene rings (Fig. 4 and ESI,† Fig. S7).

To quantify the role in conductance of the 'side' benzene ring not bonded to the top contact, we removed this ring and saturated the C atom it was bonded to, and fixed the positions of all other atoms in the junction. This allows us to calculate the contribution of the second benzene ring while excluding any possible effects of geometrical changes in conductance. We find that the calculated transmission spectrum is almost unchanged (ESI,† Fig. S10), demonstrating that conducting properties derive from the benzene ring in the tunnelling pathway alone. Thus, while both rings provide mechanical stability to the molecule through the two Au–C bonds to the substrate, only one of them (the one bonded to the top contact) plays a role in electron transport.

4. Conclusions

In this work, we proposed a new bipodal platform based on biphenylene for single molecule transport. The molecule has two covalent Au–C bonds to the Au substrate. We considered five different possibilities for the other contact to the electrodes and calculated the junction mechanical and conducting properties.

Our results show that the biphenylene-based structure provides a strong attachment to the substrate, which remained stable in all cases when a Au tip was approached to the molecule. We observed trends in the mechanical properties with the top linker termination consistent with previous results. We then calculated the conducting properties of the junctions with the different functionalizations. The observed trend in transport properties with the nature of the top contact was related to the calculated force and stiffness in terms of the electronic states (π or σ) of the tip-linker bond, which determines the electronic coupling of this top metal–molecule contact. We also showed that electron transport was limited by the chemical characteristics of the top contact. This makes the proposed biphenylene-based platform a mechanically robust and electronically transparent molecular architecture.

Our work paves the way for the development of new strategies for stable and highly conducting metal–molecule platforms for single molecule transport.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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