Towards graphyne molecular electronics

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α-Graphyne, a carbon-expanded version of graphene (‘carbo-graphene’) that was recently evidenced as an alternative zero-gap semiconductor, remains a theoretical material. Nevertheless, using specific synthesis methods, molecular units of α-graphyne (‘carbo-benzene’ macrocycles) can be inserted between two anilinyl (4-NH2-C6H4)-anchoring groups that allow these fragments to form molecular junctions between gold electrodes. Here, electrical measurements by the scanning tunnelling microscopy (STM) break junction technique and electron transport calculations are carried out on such a carbo-benzene, providing unprecedented single molecule conductance values: 106 nS through a 1.94-nm N–N distance, essentially 10 times the conductance of a shorter nanographenic hexabenzocoronene analogue. Deleting a C4 edge of the rigid C18 carbo-benzene circuit results in a flexible ‘carbo-butadiene’ molecule that has a conductance 40 times lower. Furthermore, carbo-benzene junctions exhibit field-effect transistor behaviour when an electrochemical gate potential is applied, opening the way for device applications. All the results are interpreted on the basis of theoretical calculations.
The revolution in carbon materials can be illustrated by a series of breakthroughs, from the discovery of zero-dimensional carbon fullerenes (C_{60}, 1982)\(^1\) to that of one-dimensional (1D) carbon nanotubes (CNTs, 1991)\(^2\), and most recently of two-dimensional (2D) graphene sheets\(^3\). The interest they have attracted is largely due to their unique electrical properties. The extremely high conductivity of graphene is theoretically rationalized as a consequence of its band structure exhibiting a so-called Dirac cone, supposed to be one of the unique features of graphene allowing long-range ballistic transport\(^4\). Recently, however, first-principles calculations have shown that \(\alpha\)-graphyne, a theoretical carbon allotrope composed of ‘giant’ hexagonal units made of graphenic \(sp^2\) and nongraphenic \(sp\) carbon atoms in a 1/3 ratio (Fig. 1), also exhibits Dirac cones\(^5,6\), implying that structures containing \(\alpha\)-graphyne units could be key to the advent of another generation of carbon electrical materials\(^6,7\). \(\alpha\)-Graphyne\(^8\), whose appealing structure was first proposed by Baughman in 1987 for possible electronic, optical and mechanical properties\(^8,9\), is actually the total \(carbo\)-mers of graphene (‘carbo-graphene’): it indeed arises from the insertion of C\(_2\) units into each bond of graphene by formal \(carbo\)-merization. This process, defined in 1995 at the molecular level\(^9\), was also more recently theoretically applied to carbon allotropes of lower dimensionality such as CNTs\(^10–12\), or fullerenes\(^13\). Although such \(carbo\)-allo tropes remain unknown, \(\alpha\)-graphyne can be viewed as an assembly of fused \(carbo\)-benzene rings\(^14\). The highly symmetrical ‘carbon-and \(\pi\)-electron-enriched’ structure of these C\(_{18}\) macrocycles has naturally prompted much effort for their experimental synthesis\(^15\), and theoretical analysis of their fundamental electronic properties, in particular electron delocalization and aromaticity\(^16\).

Similarly to chemical analogy (that is, atom or group replacement, for example, replacing carbon with silicon), \(carbo\)-merization (by C\(_2\)k expansion) is a systematic means for creating molecular diversity, and therefore a natural tool for investigating structure–activity relationships. An emerging research gap in graphene science—going beyond graphene technology—is the need for structural generalization. This has been recently addressed at the experimental level by considering chemical analogues, for example, silicene\(^17\) and related composite inorganic 2D materials\(^18\), as well as partial \(carbo\)-mers, for example, \(\gamma\)-graphyne. Total \(carbo\)-mers of graphene such as \(\alpha\)-graphyne or \(\alpha\)-graphdiyne have been considered at the theoretical level only. Nevertheless, a variation of the graphene structure is currently more realistically addressed by restricting the infinite sheet to fragments of controlled size and shape: nanoribbons, flakes, functional nanographenes\(^19\), small polycyclic aromatic hydrocarbons, oligophenylene and ultimately the benzene molecule itself\(^20\). In their seminal paper ‘Electron Transport in Single Molecules: From Benzene to Graphene’, Chen and Tao\(^20\) justify the relevance of the continuity between the single molecule and the corresponding infinite material made of fused molecular units. The same principle may apply to \(carbo\)-benzenes, thus making the study of known single \(carbo\)-benzenic molecules relevant to gaining insight into the still to be realized \(carbo\)-graphene material.

In this contribution, the charge transport properties, and in particular the single molecule conductance (SMC) of \(carbo\)-meric molecules (considered as the ‘basic units’ of infinite \(\alpha\)-graphyne), are explored both experimentally by scanning tunneling microscopy (STM) break junction techniques, and theoretically by NEGF-DFT (nonequilibrium Green’s function-density functional theory) calculations. Two \(carbo\)-meric molecules, differing by the nature of their conjugated bridge (macrocyclic in one case and acyclic in the other), are considered. In a step towards device applications, the electrochemical gating effect on the molecular junction conductance is also investigated.

**Results**

**Conductance of the \(carbo\)-benze ne A.** To measure molecular junction conductance, molecules have to be functionalized by anchoring groups to be wired into the metal junctions. It has been

![Figure 1 | Examples of carbon allotrope materials.](image_url)
reported that the amine (NH$_2$) functionality is a highly efficient anchoring group for SMC studies, as it can form molecular junctions with small fluctuations in conductance (because of its specific coupling with gold electrodes), and thus reduce the variability in binding geometries$^{21}$. Therefore, previously described diamino-functionalized carbo-meric molecules were selected for the present study$^{22}$, namely the ideally centrosymmetric (quadrupolar) para-dianilinyl-carbo-meric molecule A (Fig. 2a), and the di-anilinyl-dibutatrienylacetylene (DBA) B (Fig. 2b), in which the $\alpha$-graphenic macroaromatic C$_{18}$ circuit of A (which can also be regarded as a hexagonal carbocyclic alternative to the C$_{18}$N$_2$ heterocycle of square-shaped porphyrins)$^{23}$ is replaced by a linear (acyclic) $\pi$-conjugated C$_{10}$ chain, namely the carbo-mer of the $n$-butadiene core.

Measurements of charge transport through single carbo-meric molecular junctions were experimentally realized using the STM break junction technique, where an STM tip and a metal substrate function as two electrodes connecting to the two anchoring groups of the molecule$^{24-26}$. In STM break junction experiments, approaching and separating the tip and substrate electrodes allow the formation of an atomically thin metal junction$^{26,27}$. Electron transport through such an atomic wire can approach the ballistic transport limit manifested by the observation of a quantized conductance of value 1 $G_0$, ($G_0 = 2e^2/h = 77,500$ nS, where $e$ and $h$ are the electron charge and Planck’s constant, respectively)$^{28}$, which is revealed as steps in current-distance traces (Fig. 2c, inset, black) and a peak in the current histogram near 8,000 nA (Fig. 2c, black).

After the metal junction breaks, exponentially decaying traces are expected unless there are molecules trapped in the gap between the two electrodes. If conducting molecules are connected between the two electrodes by their anchoring groups, a molecular junction forms and current steps, which are usually orders of magnitude smaller than the $G_0$ value, are observed. These small current steps ($\approx 10$ nA) correspond to molecular junction conductance$^{26}$.

Some current-distance traces for the carbo-benzene A-mediated junction (Fig. 2c inset, red) clearly show characteristic current steps around 10 nA at a bias voltage of 0.1 V. In addition to quantum conductance current peak ($G_0$, $\approx 7,500$ nA) associated with Au atomic junctions$^{26}$, the histogram, generated using all traces without data selection, also shows a current maximum at 10 nA, corresponding to a SMC of ca 100 nS. The experimentally determined SMC value for the carbo-benzene A is $106 \pm 10$ nS, averaged from different experiments measured on different days. Similar results were obtained from two samples of A prepared by two different syntheses. This value represents the largest reported SMC of any amine-anchored molecule of similar length, such as a porphyrin or a highly conjugated oligophenylenylene-ethynylene (Supplementary Table 1). In particular, the SMC of the $\alpha$-graphene molecular fragment A studied here is much larger (106 nS through 1.94 nm) than that of the shorter, and therefore in principle more conductive, graphene molecular fragment hexabenzocoronene (HBC) measured with the same technique (14 nS through 1.4 nm)$^{29}$. The conductance of carbo-benzene can also be compared with another class of molecules previously studied by our group$^{27}$. The conductance of the dyes pararosaniline and malachite green depends on the pH of the solution they are found in. The highest conductance of the dyes was measured for pararosaniline at pH = 5.5 to be 71.6 nS. Not only is the conductance higher for carbo-benzene, but carbo-benzene has a N–N distance that is more than twice the N–N distance in pararosaniline (19.4 versus 9.6 Å, respectively).

To shed light on the superior conducting properties of the carbo-benzene A, the electron transport was modelled with the NEGF technique in combination with DFT$^{30,31}$. The NEGF-DFT approach was previously employed to interpret STM experiments, and the details of the technique can be found in refs 27,32,33 and in the Methods section. To briefly summarize the method, a model was devised for a two-probe system consisting of a molecule bridging a gap between two semi-infinite metallic electrodes. This two-probe system is partitioned into the periodic left and right electrodes, and the nonperiodic molecular region (see Fig. 7). The NEGF-DFT formalism relies on a self-consistent electronic structure calculation from which can be extracted the transmission function—the probability that an electron with a given energy will pass from the left electrode, through the molecule and into the right electrode. Using a Landauer–Büttiker
Conductance of the carbo-n-flake. Conductance of the carbo-n-flake even though it is graphene flake. As rapidly with distance in the resonant transmission peaks, the transmission does not decay through the graphene flake. This means that, at energies between these levels, where resonant tunnelling can occur through the tails of the transmission peaks, the transmission does not decay as rapidly with distance in the carbo-n-flake as it does in the graphene flake. Carbo-n-flake is a more efficient molecular conductor even though it is ~40% longer than the graphene flake.

Conductance of the carbo-n-butadiene B. The SMC of the carbo-n-butadiene A was then compared with that of the carbo-butadiene (DBA) B. Topologically, these two molecules present the same type of π-conjugated chains between the two NH2 end groups, either in twin pathways inside the macroaromatic circuit of A, or as a single DBA chain in the acyclic wire of B. The STM break junction experiments were carried out under the same conditions, and sample individual current–distance traces and corresponding all-data histograms, constructed from 3,000 traces without selection, are illustrated in Fig. 2d. The SMC of DBA B was determined to be 2.7 nS from the current maximum of 0.27 nA in the histogram (Fig. 2d). The ability to control charge transport via an external perturbation is prerequisite for the design of useful molecular electronic devices38. This can be achieved by using an external potential, called electrochemical gating38–40, that shifts the frontier molecular orbitals (HOMO/LUMO) with respect to the Fermi level of the Au tip and substrate39,41. The resulting change in the energy separation (alignment) between the HOMO/LUMO and the Fermi level of the electrodes yields a field-effect transistor function39.

The electrochemical gating measurements are illustrated in Fig. 5. In an STM break junction configuration, a carbo-benzene molecule A was wired between the tip and substrate electrodes, acting as the ‘source’ and the ‘drain’ electrodes, respectively. The reference electrode, that is, the ‘gating electrode’, was used to tune the working electrode potentials and molecular orbital energies. When the frontier molecular orbitals of the molecule in the junction are modulated to approach the Fermi level of the source

Figure 3 | Structures and transmission spectra of carbo-benzene and graphene flake molecular junctions. (a.b) Two-probe structures for carbo-benzene A and a HBC graphene flake, respectively. (c) The transmission spectra corresponding to these systems: black for carbo-benzene, red for graphene flake. The carbo-benzene has a considerably smaller HOMO–LUMO gap, resulting in higher transmission over a wide energy range.

Gating for the carbo-benzene A. The ability to control charge transport via an external perturbation is prerequisite for the design of useful molecular electronic devices38. This can be achieved by using an external potential, called electrochemical gating38–40, that shifts the frontier molecular orbitals (HOMO/LUMO) with respect to the Fermi level of the Au tip and substrate39,41. The resulting change in the energy separation (alignment) between the HOMO/LUMO and the Fermi level of the electrodes yields a field-effect transistor function39.
and drain electrodes, an increase in the charge transport through the molecular junction is a priori expected. The gating effect was thus investigated by measuring the SMC of carbo-benzene junctions at different gating potentials, while keeping the bias voltage (the potential difference between the source and drain) constant. An ionic liquid of wide potential window (trihexyl tetradecyl-phosphonium-bis(2,4,4-trimethylphenyl)phosphinate) was used as the electrochemical gating electrolyte. A few sample current–distance traces, measured at a sample (drain) potential of $-0.1$, $-0.6$ and $-1.35$ V are shown in Fig. 5, along with all-data point current histograms, constructed from individual traces, without selection. The conductance is also plotted as a function of the gate (sample) potential, clearly showing a gating effect, that is, the increase in the SMC value as the gating potential becomes more negative, with an observed on/off ratio of an order of magnitude ($\approx 15$).

NEGF-DFT simulations have been carried out to elucidate the gating mechanism. The calculations are similar to those performed to obtain the results displayed in Fig. 3; however, a gate effect was simulated by adding a gate-induced electrostatic boundary condition to the system (see Fig. 6a and Methods section). The result of the gate for carbo-benzene is that it shifts the LUMO (and other MOs) with respect to the Fermi level of the electrodes (Fig. 6b). Note that the sign convention for a field-effect transistor gate (in calculations) is the opposite of that adopted in an electrochemical gate (in experiment)\textsuperscript{39}; therefore, the sign of $V_G$ presented here has been reversed so that comparison with experiment can be made more easily. We can
see that the application of a negative gate voltage lowers the LUMO energy, bringing it closer to $E_F$, thereby increasing conductance. Figure 6c shows the calculated transmission at $E_F$ for different $V_{G\text{ theor}}$ values. Comparing the range of $V_{G\text{ theor}} = -5$ to $+5 \text{ V}$, there is good qualitative agreement with Fig. 5d. Note that the magnitude of the $V_{G\text{ theor}}$ values in Fig. 6c are arbitrary (the results indeed depend on the simulation box size, that is, the distance of the gate from the molecule); however, the theoretical trend does predict that, had it been possible to experimentally apply gate potential values of $V_G < -1.5 \text{ V}$ (in Fig. 5d), the conductance would go through a maximum as the LUMO would pass through the source-drain bias window, and decrease with more negative $V_G$. Although this was not achieved for carbo-benzene with this experimental set-up, it has been reported for other molecules.

**Discussion**

Single molecule charge transport properties are probed by STM break junction observations and NEGF-DFT calculations, demonstrating that the macrocyclic conjugation of the carbo-benzene core (the $\alpha$-graphyne unit) provides superior junction conductance. This effect is a priori compatible with the weak energetic aromaticity of the $C_8$ carbo-benzene macrocycle (a three time less aromatic, and thus less ‘insulating’, than the parent $C_6$ benzene ring). The small HOMO–LUMO gap of the carbo-benzene allows the gating of charge transport by shifting the alignment of molecular levels relative to the Fermi energy of the source and drain. Within the electrochemically accessible window, an order of magnitude increase in junction conductance is achieved. These remarkable electrical properties arise from the unique electronic structure of the carbo-benzene macrocycle, provided by the combination of $sp$ and $sp^2$ carbons, and make molecular fragments of $\alpha$-graphyne promising for the design of novel classes of carbon materials having potential for device applications.

**Methods**

**Preparation of the carbo-benzene A and carbo-butadiene B.** The carbo-meric conductors A and B were prepared according to previously described procedures, the last steps of which are described below (and in Supplementary Fig. 1).

Preparation of the $p$-bis(4-aminophenyl)tetraphenyl-carbo-benzene' A: 4-[10-(4-aminophenyl)-4,7,13,16-tetraphenylyclooctadeca-1,2,3,7,8,9,13,14,15-nonaen-5,11,17-trim-1-$p$]-aniline: A solution of p-bromo-$N,N'$-bis(trimethylsilyl)aniline (0.38 ml, 1.35 mmol) in tetrahydrofuran (THF) (1 ml) was added slowly at room temperature to a suspension of magnesium turnings (32 mg, 1.32 mmol) in THF (0.5 ml). After the Grignard reagent was formed, the mixture was added to a solution of the key [6]pericyclenedicarbonyl (0.5 ml). After the Grignard reagent was formed, the mixture was added to a solution of the key [6]pericyclenedicarbonyl. Addition of the key [6]pericyclenedicarbonyl was formed, the mixture was added to a solution of the key [6]pericyclenedicarbonyl. The stirring was maintained for $2 \text{ h}$ at $0 \text{ °C}$, and then overnight at room temperature. Addition of water, the aqueous layer was extracted with diethyl ether (Et$_2$O). The combined organic layers were washed with brine, dried over MgSO$_4$ and evaporated under reduced pressure. The obtained poorly stable [6]pericyclenedicarbonyl was purified using silica gel chromatography, eluting first with DCM:THF:acetone in ratios 8:1:1, 7:1.5:1.5, 6:2:2, and then subsequently with pentane to give pure A as a green solid (40 mg, 26% yield for the two steps).

**Preparation of the carbo-benzene A and carbo-butadiene B.** The carbo-meric conductors A and B were prepared according to previously described procedures, the last steps of which are described below (and in Supplementary Fig. 1).

Preparation of the [6]pericyclenedicarbonyl 2a was directly used in the reduction step without further purification. The mixture was thus dissolved in dichloromethane (DCM), before addition of SnCl$_2$ (417 mg, 2.21 mmol), and then in HCl-Et$_2$O (2.0 ml, 4.40 mmol) at $-78 \text{ °C}$. The reaction mixture was allowed to warm up to room temperature, and then overnight at room temperature. After addition of water, the aqueous layer was extracted with diethyl ether (Et$_2$O). The combined organic layers were washed with brine, dried over MgSO$_4$ and evaporated under reduced pressure. The obtained poorly stable [6]pericyclenedicarbonyl was purified using silica gel chromatography, eluting first with DCM:THF:acetone in ratios 8:1:1, 7:1.5:1.5, 6:2:2, and then subsequently with pentane to give pure A as a green solid (40 mg, 26% yield for the two steps).

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The yellow arrow shows the C–C calcd for C54H32N2: 708.2565, found: 708.2635. UV–vis (CHCl3): crystal disk electrodes (10 mm diameter, 2.0 mm height, from MaTeck, Germany) were used for measurements. The STM tips were mechanically cut gold wires (wire (25,099), 379 (20,804) and m.p. (dec)

Electron and sample preparation. Before each experiment, Au[111] single crystal disk electrodes (10 mm diameter, 2.0 mm height, from MaTeck, Germany) were first cleaned with piranha solution in H2O (30%)+H2SO4 (concentrated, 96%) = 1:3; (CAUTION: ‘piranha’ solutions are very reactive mixtures! They must be handled with great care; use of protective equipment, such as gloves, goggles and lab coat, is necessary). The electrodes were rinsed with ultrasonic deionized water (Thermoscientific Barnstead Easypure II purification system equipped with a UV lamp providing water resistivity >18 MΩ cm). Immediately afterwards, the gold crystal was annealed in a hydrogen flame till it became red hot for 2 min followed by immediate quenching in hydrogen-saturated ultraclean water while it was still hot and dark red in colour. Finally, the crystal was dried under a stream of high-purity argon. The electrode was then immersed in THF solution containing 0.05 mM of carbo-n-butadiene (DBA) B. After the STM tip was engaged, the electrode surface was first imaged by STM in direct current (DCM) mode (Supplementary Fig. 2a), with a value of ~3.850 and 7.700 nA for a bias voltage of 0.05 V. These currents divided by the bias voltage give the conductance values of 77,000 and 154,000 nS, corresponding to quantized conductance one and two Ge, respectively, associated with Au atomic junctions (peaks in Supplementary Fig. 2b).

STM break junction experiments. STM break junction experiments were carried out with a Molecular Imaging Picoscan or Picoplus scanning tunnelling microscope (Agilent). Current preamplifiers with gains of 1, 10, and 1,000 nA were used for measurements. The STM tips were mechanically cut gold wires (wire diameter = 0.25 mm) and the substrate electrode was an Au[111] disk single crystal prepared as described above. The experimental procedure was to use the STM software to drive the tip to approach the molecule-modified electrode with preset parameters, typically a bias voltage of 0.1 V and a tunnelling setpoint of 0.1 nA. After the STM tip was engaged, the electrode surface was first imaged by STM in constant current mode, confirming a clean surface and a sharp tip. Before the measurement of single molecule conductance of the target molecules, the control experiment was typically performed using Au tips and Au substrate electrodes in pure solvent without adding molecules. What we observed is that there are current steps in individual current–distance traces (Supplementary Fig. 2a), with a value of ~3.850 and 7.700 nA for a bias voltage of 0.05 V. These currents divided by the bias voltage give the conductance values of 77,000 and 154,000 nS, corresponding to quantized conductance one and two Ge, respectively, associated with Au atomic junctions (peaks in Supplementary Fig. 2b).
carried out until the force on all atoms that were free to relax was less than 0.01 eV Å⁻¹ (VASP input files are provided in Supplementary Note 1).

For each structure that was relaxed (carbo-benzene, graphene flake, DBA having various dihedral angles) between Au electrodes, two-probe structures were constructed to calculate the electron transmission through each system. This was carried out by extending the electrodes by placing Au atoms at their appropriate crystal lattice positions resulting in a two-probe structure, as shown in Fig. 7. Atomic coordinates (xyz format) of all two-probe structures are available in the Supplementary Information. Note that bulk electrodes were used. The two-probe structure can be partitioned into three regions: the central region containing the molecule and parts of each electrode, and the right and left electrodes that extend to infinity in either direction. The electron transmission through such systems can be calculated with the NEGF formalism within the DFT (NEGF-DFT) framework. In this work, the Nanodcal implementation of NEGF-DFT was used (Nanoacademic Technologies http://nanoacademic.ca, accessed: 5 February 2014). Interested readers are directed to refs 30–33 where the technique has been extensively described.

The retarded Green’s function at energy $E$ is $G(E) = [E - H - \Sigma_1 - \Sigma_2]^{-1}$, where $H$ and $\Sigma$ are the Hamiltonian and overlap matrices of the central region, and $\Sigma_1$, $\Sigma_2$ are the self-energies representing the influence of the two electrodes on the central region. The self-energies are complex quantities with the real part representing the influence of the two electrodes on the central region. The broadening effect of each electrode can be expressed as the broadening matrix, $\Gamma_1 = \Im (\Sigma_1 - \Sigma_2)$. The electronic density matrix for the central region is calculated as $ho = \frac{\Gamma}{\hbar} \int [f(E, \mu)G(E) + f(E, \mu)G(E)^*] d\mu$, with $\mu$ being the electrochemical potentials of the two electrodes and $f(E, \mu)$ is the Fermi-Dirac function. The density, $\rho$, is used to seed a subsequent DFT step, yielding a new $H$ to input into another Green’s function step, and the process is repeated until self-consistency is achieved.

The transmission function can then be obtained from the Green’s function as $T(E) = \text{Tr}(\Gamma G(E) G^*)$. This gives the probability of an electron with a given energy passing from electrode 1 through the molecule and into electrode 2. The low-bias conductance of the molecule can be approximated by the transmission at the Fermi level, $T_0$, of the electrodes multiplied by the quantum of conductance, $G_0 = (2e^2/h)$. The gate calculations are performed by setting up a system as shown in Fig. 6a. The gate is applied on one side of the central region simulation box by setting up a gate-induced electrostatic boundary condition for the Hartree potential when solving the Poisson equation. In Fig. 6a, the box dimension in the vertical dimension is 26 Å, and the molecule is near the middle. Therefore, the atoms of the molecule are ~13 Å from the gate (some are closer, some are farther).

For the numerical electron transport calculations, the valence electrons of Au were treated with double-$\zeta$ polarized basis sets and all other elements were treated with double-$\zeta$ polarized basis sets. The atomic cores were described with Trouiller–Martins norm-conserving pseudopotentials. The PBE-GGA was used for the exchange-correlation functional. A real-space grid with more than five points per Å was used to describe the basis. For the reciprocal space, the Brillouin zone was sampled with 2 Å was used to describe the basis. For the reciprocal space, the Brillouin zone was sampled with 2 Å points in the transverse dimension (perpendicular to the transport direction), which was sufficient since the cell had transverse vectors of 26.5 Å. We note here that some groups apply a shift to the energy of the Fermi level, $E_f$, of the electrodes multiplied by the quantum of conductance, $G_0 = (2e^2/h)$. The gate calculations are performed by setting up a system as shown in Fig. 6a.

Concluding Remarks

There are certainly other factors affecting the transmission. For example, the specific geometry at the anode–gold interface can have an important influence on the conductance/transmission.

References

1. Kroto, H. W., Heath, J. R., Obrien, S. C., Curl, R. F. & Smalley, R. E. C-60 - buckminsterfullerene. Nature 318, 162–163 (1985).
2. Iijima, S. Helical microtubules of graphitic carbon. Nature 354, 56–58 (1991).
3. Novoselov, K. S. et al. Electric field effect in atomically thin carbon films. Science 306, 666–668 (2004).
4. Malko, D., Neiss, C., Vines, F. & Gorling, A. Competition for graphene: graphene molecules with direction-dependent dirac cones. Phys. Rev. Lett. 108, 086804 (2012).
5. Kim, B. G. & Choi, H. J. Graphene: hexagonal network of carbon with versatile dirac cones. Phys. Rev. B 87, 115413 (2013).
6. Jalil, M., Lepetit, C. & Chauvin, R. Carbo-graphite: structural, mechanical, and electronic properties. J. Phys. Chem. C 117, 21671–21681 (2013).
7. Hirsch, A. The era of carbon allotropes. Nat. Mater. 9, 868–871 (2010).
8. Baughman, R. H., Eckhardt, H. & Kertesz, M. Structure-property predictions for new planar forms of carbon - layered phases containing sp² and sp atoms. J. Chem. Phys. 87, 6687–6699 (1987).
9. Chauvin, R. Carbonomers. I. A general concept of expanded molecules. J. Tetrahedron Lett. 36, 397–400 (1995).
10. Coluci, V. R., Braga, S. F., Legos, S. B., Galvao, D. S. & Baughman, R. H. Families of carbon nanotubes: Graphene-based nanotubes. Phys. Rev. B 68, 035430 (2003).
11. Lepetit, C., Zou, C. H. & Chauvin, R. Total carbo-mer of benzene, its carbo-silicene form, and the zigzag nanotube thereof. J. Org. Chem. 71, 6317–6324 (2006).
12. Liu, W., Li, Y. X. & Huang, Y. H. A computational prediction of total carbon-rich single-walled carbon nanotubes. J. Phys. Chem. Solids 72, 299–306 (2011).
13. Enyashin, A. N., Sofronov, A. A., Makurin, Y. N. & Ivanovskii, A. L. Structural and electronic properties of new alpha-carbon-based graphene fullerenes. Theor. Chem. J. Mol. Struct. 684, 29–33 (2004).
14. Maraval, V. & Chauvin, R. From macrocyclic oligo-acetylenes to aromatic ring-carbo-mers. Chem. Rev. 106, 5317–5343 (2006).
15. Leroyer, L., Maraval, V. & Chauvin, R. Synthesis of the butatriene C₄ function: methodology and applications. Chem. Rev. 112, 1310–1343 (2012).
16. Chauvin, R., Lepetit, C., Maraval, V. & Leroyer, L. Variation of aromaticity by twisting or expanding the conjugated double bond. Pure Appl. Chem. 82, 769–800 (2010).
17. Vogt, P. et al. Silicene: Compelling experimental evidence for graphene-like two-dimensional silicon. Phys. Rev. Lett. 108, 155501 (2012).
18. Rao, C. N. R., Matte, H. & Maitra, U. Graphene analogues of inorganic layered materials. Angew. Chem. Int. Ed. 52, 13162–13185 (2013).
19. Mullen, K. Evolution of graphene molecules: Structural and functional complexity as driving forces behind nanoscience. ACS Nano 8, 6531–6541 (2014).
20. Chen, F. & Tao, N. J. Electron transport in single molecules: From benzene to graphene. Accounts Chem. Res. 42, 429–438 (2009).
21. Venkataraman, L., Klare, J. E., Nuckolls, C., Hybertsen, M. S. & Steigerwald, M. L. Dependence of single-molecule junction conductance on molecular conformation. Nature 442, 904–907 (2006).
22. Rives, A. et al. Highly pi electron-rich macro-aro-matics: bis(p-aminophenyl)-carbo-benzenes and their DAA acyclic references. Chem. Commun. 48, 8763–8765 (2012).
23. Leroyer, L. et al. From hexacopy-[6]pericyclics to carbo-cyclohexadienes, carbo-benzenes, and dihydro-carbo-benzenes: synthesis, structure, and chromophoric and redox properties. Chem. Eur. J. 18, 3226–3240 (2012).
24. Z. & Borguet, E. Determining charge transport pathways through single porphyrin molecules using scanning tunneling microscopy break junctions. J. Am. Chem. Soc. 134, 63–66 (2012).
25. Li, Z., Park, T. H., Rawson, J., Therien, M. J. & Borguet, E. Quasi-ohmic single molecule charge transport through highly conjugated meso-meso ethyne-bridged porphyrin wire. Nano Lett. 12, 2722–2727 (2012).
26. Xu, B. Q. & Tao, N. J. Measurement of single-molecule resistance by repeated measurement of single-molecule junction conductance. Science 301, 1221–1223 (2003).
27. Li, Z. et al. Single-molecule sensing of environmental pH-an STM break junction and NEGF-DFT approach. Angew. Chem. Int. Ed. 53, 1098–1102 (2014).
28. Nitzan, A. & Ratner, M. A. Electron transport in molecular wire junctions. Interface 96, 1384–1389 (2003).
29. Diaz-Perez, J. et al. Gate-controlled electron transport in coronenes as a bottom-up approach towards graphene transistors. Nat. Commun. 1, 1–5 (2010).
30. Taylor, J., Guo, H. & Wang, J. Ab initio modeling of quantum transport properties of molecular electronic devices. Phys. Rev. B 63, 245407 (2001).

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31. Waldron, D., Haney, P., Larade, B., MacDonald, A. & Guo, H. Nonlinear spin current and magnetoresistance of molecular tunnel junctions. Phys. Rev. Lett. 96, 166801 (2006).
32. Li, Z., Smeu, M., Ratner, M. A. & Borguet, E. Effect of anchoring groups on single molecule charge transport through porphyrins. J. Phys. Chem. C 117, 14890–14898 (2013).
33. Li, Z. et al. Hapticity-dependent charge transport through carboxidithioate-terminated [5, 15− Bis (phenylethyl) porphato] zinc (II) complexes in metal−molecule−metal junctions. Nano Lett. 14, 5493−5499 (2014).
34. Cuevas, J. C. & Scheer, E. Molecular Electronics: An Introduction to Theory and Experiment, World Scientific Series in Nanotechnology and Nanoscience (World Scientific Publishing Company, 2010).
35. Buttiker, M., Imry, Y., Landauer, R. & Pinhas, S. Generalized many-channel conductance formula with application to small rings. Phys. Rev. B 31, 6207−6215 (1985).
36. Mayou, D., Zhou, Y. X. & Ernzerhof, M. The zero-voltage conductance of nanographenes: Simple rules and quantitative estimates. J. Phys. Chem. C 117, 7870−7884 (2013).
37. Mishchenko, A. et al. Single-molecule junctions based on nitrile-terminated biphenyl: a promising new anchoring group. J. Am. Chem. Soc. 133, 184−187 (2011).
38. Haiss, W. et al. Redox state dependence of single molecule conductivity. J. Am. Chem. Soc. 125, 15294−15295 (2003).
39. Xu, B. Q., Xiao, X. Y., Yang, X. M., Zang, L. & Tao, N. J. Large gate modulation in the current of a room temperature single molecule transistor. J. Am. Chem. Soc. 127, 2386−2387 (2005).
40. Li, Z. et al. Regulating a benzo[1,2-c:4,5-c′]difuran single molecule redox switch via electrochemical gating and optimization of molecule/electrode coupling. J. Am. Chem. Soc. 136, 8867−8870 (2014).
41. Tao, N. J. Electron transport in molecular junctions. Nat. Nanotechnol. 1, 173−181 (2006).
42. Kay, N. J. et al. Single-molecule electrochemical gating in ionic liquids. J. Am. Chem. Soc. 134, 16817−16826 (2012).
43. Leroyer, L., Zhou, C., Maraval, V. & Chauvin, R. Synthesis and stereoelectronic resolution of a [6]pericyclonediene: versatile access to pericyclonediol precursors of carbo-benzenes. C. R. Chim. 12, 412−429 (2009).
44. Afsari, S., Li, Z. & Borguet, E. Orientation-controlled single molecule junctions. Angew. Chem. Int. Ed. 53, 9771−9774 (2014).
45. Kresse, G. & Hafner, J. Ab initio molecular-dynamics for liquid-metals. Phys. Rev. B 47, 558−561 (1993).
46. Kresse, G. & Furthmuller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. Phys. Rev. B 54, 11169−11186 (1996).
47. Kresse, G. & Furthmuller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. Phys. Rev. B 54, 11169−11186 (1996).
48. Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized gradient approximation made simple. Phys. Rev. Lett. 77, 3865−3868 (1996).
49. Troullier, N. & Martins, J. L. Efficient pseudopotentials for plane-wave calculations. Phys. Rev. B 43, 1993−2006 (1991).
50. Guedon, C. M. et al. Observation of quantum interference in molecular charge transport. Nat. Nanotechnol. 7, 305−309 (2012).
51. Guedon, C. M., Choi, H. J., Louie, S. G. & Neaton, J. B. Length dependence of conductance in aromatic single-molecule junctions. Nano Lett. 9, 3949−3953 (2009).
52. Aguílara-Granja, F., Balbas, L. C. & Vega, A. Study of the structural and electronic properties of Rh-N and Ru-N clusters (N<20) within the density functional theory. J. Phys. Chem. A 113, 13483–13491 (2009).
53. Denis, P. A. & Iriarte, F. On the hydrogen addition to graphene. Theochem. J. Mol. Struct. 907, 93−103 (2009).
54. Rogan, J. et al. The structure and properties of small Pd clusters. Nanotechnology 19, 205701 (2008).
55. Martin-Samos, L. et al. Oxygen neutral defects in silica: origin of the distribution of the formation energies. Europhys. Lett. 66, 680−686 (2004).
56. Kamenetska, M. et al. Formation and evolution of single-molecule junctions. Phys. Rev. Lett. 102, 126803 (2009).

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Author contributions
The synthesis of graphyne molecules was achieved by A.B., V.M. and R.C. STM break junction measurements were performed by Z.L. and data analysis was carried out by Z.L. and E.B. Calculations were performed by M.S. and M.A.R. All authors discussed the results, co-wrote the paper and commented on the manuscripts.

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