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# Planar aromatic anchors control the electrical conductance of gold|molecule|graphene junctions†

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The synthesis of a family of alkanethiol molecules with planar aromatic head groups, designed to anchor molecules effectively to graphene electrodes, is reported. Characterisation of self-assembled monolayers of these molecules on a gold surface *via* conductive atomic force microscopy shows that when an aromatic head group is present, the conductance  $G_{\text{graphene}}$  obtained using a graphene coated probe is higher than the conductance  $G_{\text{Pt}}$  obtained using a platinum (Pt) probe. For Pt probe and graphene probe junctions, the tunnelling decay constant of benzyl ether derivatives with an alkanethiol molecular backbone is determined as  $\beta = 5.6 \text{ nm}^{-1}$  and  $3.5 \text{ nm}^{-1}$ , respectively. The conductance ratio  $G_{\text{graphene}}/G_{\text{Pt}}$  increases as the number of rings present in the aromatic head unit,  $n$ , increases. However, as the number of rings increases, the conductance path length increases because the planar head groups lie at an angle to the plane of the electrodes. This means that overall conductance decreases as  $n$  increases. Density functional theory-based charge transport calculations support these experimental findings. This study confirms that planar aromatic head groups can function as effective anchoring units for graphene electrodes in large area molecular junctions. However, the results also indicate that the size and geometry of these head groups must be considered in order to produce effective molecular designs.

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## Introduction

Molecular junctions, in which one or more molecules bridge the gap between a source and drain electrode, have been intensely studied during the past two decades.<sup>1–17</sup> A variety of methods for engineering the transport properties of molecules have been developed, based on manipulating conformation,<sup>18–22</sup> anchor groups,<sup>8,23–27</sup> electrodes,<sup>28–31</sup> quantum interference,<sup>32–42</sup> and heteroatom substitution,<sup>43–48</sup> both in single-molecule junctions and large-area junctions comprising self-assembled monolayers (SAMs) of organic molecules.<sup>29,49–51</sup> Typically in single-molecule experiments using mechanically controllable break junction (MCBJ)<sup>1</sup> or scanning tunnelling microscope (STM)<sup>2</sup> contacting methodologies, gold is the electrode material of choice. However, there is a growing interest in the study of molecular junctions

formed using graphene electrodes. For this purpose, planar aromatic moieties are desirable terminal groups for anchoring molecules to graphene electrodes owing to the strong  $\pi$ - $\pi$  interactions between their planar  $\pi$  systems and graphitic surfaces.<sup>25,28,30,52</sup> Methods used to determine the conductance of larger area junctions, such as conductive atomic force microscopy (cAFM), are well suited to investigations using different electrode materials.<sup>53,54</sup>

A major goal of molecular-scale electronics is the control of transport properties by systematically varying structural features of the molecule.<sup>55</sup> Studies of polycyclic aromatic hydrocarbons on graphene surfaces have shown an increase in the binding energy<sup>52</sup> as the number of fused rings increases. Additionally, in molecular junctions where a polycyclic aromatic hydrocarbon lies parallel to both electrodes, the “cross-plane conductance”<sup>56</sup> (*i.e.* the conductance perpendicular to the plane of the electrodes and substrate) increases with the number of fused rings. This present study investigates whether these trends persist when planar aromatics are used as the top contact groups in Au|SAM|Pt and Au|SAM|graphene junctions. Firstly, the synthesis of a family of alkanethiol molecules with planar aromatic head groups of differing sizes is presented. The preparation and characterisation of SAMs of these molecules on Au substrates is reported, followed by cAFM studies of the SAMs in which the effect on conductance of using either a Pt tip or graphene-coated Pt tip was investigated. The

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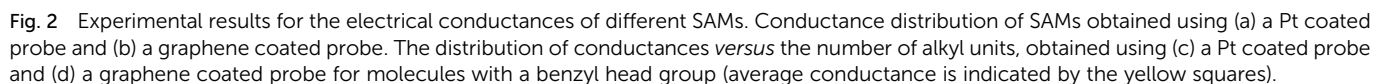
† Electronic supplementary information (ESI) available: Details of synthesis and characterisation of molecules; SAM formation and characterisation; computational studies. See DOI: <https://doi.org/10.1039/d2na00873d>

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**Table 1** The statistically most probable conductance values per molecule from SAMs measured using Pt and graphene coated AFM probes, derived from the histograms in Fig. 2a and b, and the ratio of the most probable conductance values measured using the two different probes

obtained from density functional theory (DFT) calculations, and  $\beta$  is the tunnelling decay constant of the molecular backbone. For the Pt probe junctions, we measure  $\beta = 5.6 \text{ nm}^{-1}$ , slightly below the typical range for alkanethiols and alkanedithiols in metallic junctions (*ca.*  $8\text{--}10 \text{ nm}^{-1}$ ).<sup>75,76</sup> In comparison, for the graphene probe junctions we measure  $\beta = 3.5 \text{ nm}^{-1}$  (Fig. 2d) which is consistent with recent studies that have shown that metal|molecule|graphene junction architectures afford lower  $\beta$  values than metal|molecule|metal junction architectures for alkane derivatives including alkanedithiols.<sup>76,77</sup>

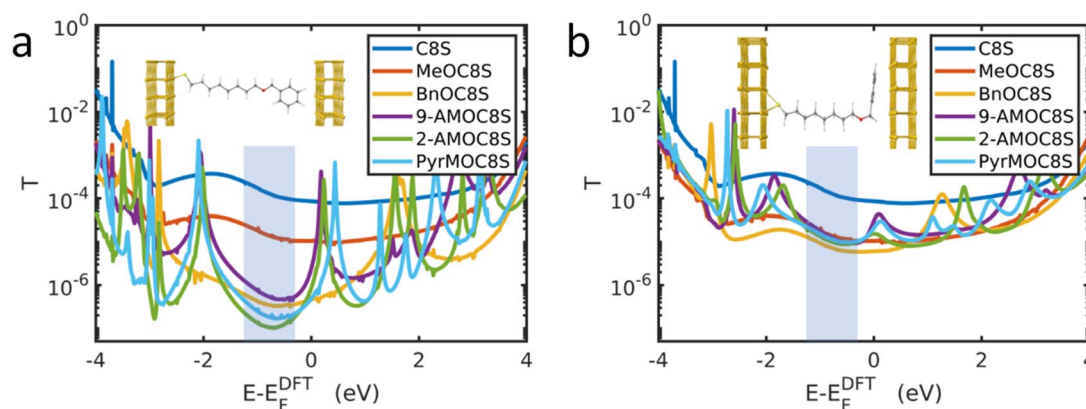
Charge transport simulations of molecular junctions were carried out using the SIESTA<sup>78</sup> density functional theory (DFT) code, combined with the Green's function transport code Gollum<sup>79</sup> (see Section S3 of ESI†). In the simulations, the thiol terminal group is bound to a Au bottom electrode and the other end of the molecule (usually an ether-linked head group) is in contact with a top Au electrode. Further details are provided in Section S3.1 of the ESI.† Where head groups are present, the angle  $\theta$  between the plane of the aromatic head group and the plane of the top electrode must be considered. The following discussion will use the formalism that  $\theta = 0^\circ$  when these planes are parallel and  $\theta = 90^\circ$  when these planes are perpendicular.



transmission. Fig. 3b shows that when an aromatic head group is present, near-parallel configurations ( $\theta \approx 0^\circ$ ) are more conductive than those in which the head group is perpendicular to the Au lead. In the parallel configuration, the transmission of all ether-functionalised species is similar in the HOMO–LUMO gap. The implication is that in the experimental system it is unlikely that the aromatic head groups lie perpendicular to the top electrode surface. Rather, as supported by the MD simulations discussed above, the head groups present in the experimental junctions may display a distribution of angles between the limits of parallel and perpendicular configurations. Realistic transmission curves are therefore expected to lie between those shown in Fig. 3a and b. However, the intensive calculations required to afford such data are beyond the scope of the present study.

## Discussion

When considering the C8 alkyl chain series, two trends are apparent in the experimental data as the number  $n$  of fused rings in the aromatic head group changes. The first trend is that the conductance tends to decrease as the size of the aromatic head group increases. This result is seemingly in contrast to previous studies. It has been reported that the electrical conductance of planar aromatic molecules adsorbed on planar electrodes increases with their size, when current flows perpendicular to the plane of the molecules.<sup>36</sup> Additionally, the binding energy between an aromatic head group and a planar electrode increases with the size of the head group.<sup>52,82</sup> However, these studies are concerned with aromatic systems that are coplanar to the electrode surface. The MD simulations, the agreement between experimental data and trends observed in Fig. 3a, and SAM thickness analysis (Fig. S41 and S42†) indicate that in the present work the aromatic head groups are tilted with respect to the probe. A consequence of this tilting is that the current pathway is longer for species with larger head groups. The observation that conductance falls with increasing head group size (and therefore molecular length) supports the



**Fig. 3** DFT-based transmission functions for Au|molecule|Au junctions. Where aromatic head groups are present (a) shows aromatic head groups approximately perpendicular to the top Au lead (*i.e.*,  $\theta \approx 90^\circ$ , see inset) and (b) shows aromatic head groups approximately parallel to the top Au lead (*i.e.*,  $\theta \approx 0^\circ$ , see inset).  $E_F^{\text{DFT}}$  is the DFT-predicted Fermi energy. In practice,  $E_F^{\text{DFT}}$  may not coincide with the experimental value  $E_F$ , which typically lies near the middle of the HOMO–LUMO gap, indicated by the shaded regions.



presence of tilted aromatic units. In contrast, **9-AMOC8S** has a similar (Pt probe) or lower (graphene probe) conductance than **BnOC8S**, despite its larger head group. In this case, the position of the additional fused rings in the former system is such that the effective length of the molecule remains similar to the latter. The head group of **9-AMOC8S** effectively becomes wider rather than longer and a reduction in conductance is not observed.

The second trend is the increase in the ratio between the conductance of Au|SAM|graphene junctions and the conductance of Au|SAM|Pt junctions (Table 1) as the number of fused rings in the ether-linked head group,  $n$ , increases. For **MeOC8S** ( $n = 0$ ), **BnOC8S** ( $n = 1$ ), **9-AMOC8S** ( $n = 3$ ) and **PyrMOC8S** ( $n = 4$ ), the ratio  $G_{\text{graphene}}/G_{\text{Pt}}$  is approximately equal to  $n + 1$ , indicating that the larger aromatics are more optimised to graphene contacts than Pt contacts. This observation can be attributed to  $\pi$ - $\pi$  interactions,<sup>52,82</sup> which are expected between aromatic species and graphene but not Pt. The presence of  $\pi$ - $\pi$  interactions when a graphene electrode is used would favour a smaller average value of  $\theta$  than for Pt, which the computational studies above indicate would result in increased conductance. For unsubstituted polyacenes adsorbed directly on graphene, the calculated binding energy increases linearly with the number of fused rings.<sup>82</sup> Therefore, in the present systems, the strength of  $\pi$ - $\pi$  interactions, and the concomitant reduction of  $\theta$ , would be expected to increase as  $n$  increases. This accounts for the observed trend in  $G_{\text{graphene}}/G_{\text{Pt}}$ . Additionally, the atomically smooth graphene surface may accommodate conformational changes in the SAM more readily than the sharper Pt probe.

Two of the studied molecules do not follow the observed  $G_{\text{graphene}}/G_{\text{Pt}} = n + 1$  pattern. **C8S** is shorter than the other species and does not contain an ether linker, limiting its possible conformations in a SAM. Therefore, it is not unreasonable that **C8S** behaves differently to the other molecules. **2-AMOC8S** shows a much smaller  $G_{\text{graphene}}/G_{\text{Pt}}$  ratio (1.32) than would be expected based on observations for the remainder of the ether-linked series (Table 1). This may relate to the connectivity of the anthracene unit in **2-AMOC8S** where in certain conformations the additional rings have a much larger effect on molecular length *versus* **BnOC8S** in comparison to **9-AMOC8S** or **PyrMOC8S**. This geometric difference could impact SAM packing and the energy barrier associated with deviating from  $\theta \approx 90^\circ$  in the presence of a top electrode. It is possible that related conformational effects are responsible for the relatively poor fit of the conductance data for **2-AMOC8S** to a Gaussian curve in comparison to that of the other molecules in Fig. 2a.

The above observations indicate that polycyclic aromatic anchoring units have potential as graphene contacts in Au|SAM|graphene molecular junctions. The model systems studied in this work serve as a proof of concept and will inform design strategies for future SAM based devices. In order to best utilise the favourable interactions between aromatic species and graphene, more complex molecular designs are necessary. Achieving high molecular conductance will require consideration of factors such as: (i) how best to include large aromatic systems without significantly increasing molecular length; (ii) how to minimise  $\theta$  while accounting for geometric

requirements at the Au electrode and the desirability of conjugated molecular backbones. To minimise  $\theta$ , it may prove important to reduce steric clash between neighbouring aromatic head groups. Methods to achieve this could include the use of large-footprint anchoring units<sup>54,83</sup> on the gold surface to increase head group spacing, or the use of mixed monolayers containing functional species bearing aromatic contact units alongside simple “spacer” molecules.<sup>84</sup>

## Conclusions

The self-assembly and conductance properties of a series of alkanethiol derivatives bearing ether-linked aromatic head groups, and reference compounds, were investigated using AFM imaging, QCM studies and cAFM experiments. DFT and MD studies support the experimental observations. A sub-series of species with increasing alkyl linker length were observed to show an expected exponential conductance decay with increasing molecular length, with a tunnelling decay constant of  $\beta = 5.6 \text{ nm}^{-1}$  in Au|SAM|Pt junctions and  $\beta = 3.5 \text{ nm}^{-1}$  in Au|SAM|graphene junctions. Using both Pt and graphene top electrodes, conductance was observed to decrease as the size of the aromatic head group increased. This was attributed to an increasing junction length caused by the head groups being tilted with respect to the planar electrode, as larger head groups have a greater impact on the length of an extended molecule. The ratio of the conductances measured using graphene and Pt top electrodes,  $G_{\text{graphene}}/G_{\text{Pt}}$ , generally increased with the number of aromatic rings in the head group. As  $\pi$ - $\pi$  interactions are known to increase in strength for progressively larger aromatic systems, this effect is attributed to an increasing tendency towards coplanarity with the graphene electrode as the size of the aromatic head group increases. These results indicate the effectiveness of aromatic head groups as contacts for graphene electrodes in asymmetric metal|SAM|graphene molecular junctions. Furthermore, they highlight some important considerations that must be made when designing optimised molecules for such junctions. The geometry of the head group is key; to maximise conductance it should lie near parallel to the graphene electrode in a molecular junction and have minimal impact on the length of the conductance pathway. These observations contribute to the design of the next generation of molecules for use in hybrid nanodevices.

## Author contributions

L. J. O. synthesised the molecules. X. W. and B. P.-J. performed device fabrication and measurements. M. J. carried out the calculations with assistance from H. S. The funding for this work was obtained by B. J. R., M. R. B. and C. J. L. who supervised the research and contributed to interpreting the results. L. J. O. and M. R. B. coordinated the writing of the manuscript, with contributions from all co-authors.

## Conflicts of interest

There are no conflicts to declare.



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