

Scale-up of room-temperature constructive quantum interference from single molecules to self-assembled molecular-electronic films

Xintai Wang^{a,e†}, Troy L. R. Bennett^{b,†}, Ali Ismael^{a,c,†}, Luke A. Wilkinson^b, Joseph Hamill^d, Andrew J. P. White^b, Iain M. Grace^a, Oleg V. Kolosov^a, Tim Albrecht^d, Benjamin J. Robinson^{a*}, Nicholas J. Long^{b*}, Lesley F. Cohen^{e*} and Colin J. Lambert^{a*}

^aPhysics Department, Lancaster University, Lancaster, LA1 4YB, UK.

^bDepartment of Chemistry, Imperial College London, MSRH, White City, London, W12 0BZ, UK.

^cDepartment of Physics, College of Education for Pure Science, Tikrit University, Tikrit, Iraq.

^dDepartment of Chemistry, Birmingham University, Edgbaston, Birmingham, B15 2TT, UK.

^eThe Blackett Laboratory, Imperial College London, South Kensington Campus, London, SW7 2AZ, UK.

ABSTRACT: The realization of self-assembled molecular-electronic films, whose room-temperature transport properties are controlled by quantum interference (QI), is an essential step in the scale-up QI effects from single molecules to parallel arrays of molecules. Recently, the effect of *destructive* QI (DQI) on the electrical conductance of self-assembled monolayers (SAMs) has been investigated. Here, through a combined experimental and theoretical investigation, we demonstrate chemical control of different forms of *constructive* QI (CQI) in cross-plane transport through SAMs and assess its influence on cross-plane thermoelectricity in SAMs. It is known that the electrical conductance of single molecules can be controlled in a deterministic manner, by chemically varying their connectivity to external electrodes. Here, by employing synthetic methodologies to vary the connectivity of terminal anchor groups around aromatic anthracene cores, and by forming SAMs of the resulting molecules, we clearly demonstrate that this signature of CQI can be translated into SAM-on-gold molecular films. We show that the conductance of vertical molecular junctions formed from anthracene-based molecules with two different connectivities differ by a factor of approximately 16, in agreement with theoretical predictions for their conductance ratio based on constructive QI effects within the core. We also demonstrate that for molecules with thioether anchor groups, the Seebeck coefficient of such films is connectivity dependent and with an appropriate choice of connectivity can be boosted by ~50%. This demonstration of QI and its influence on thermoelectricity in SAMs represents a critical step towards functional ultra-thin-film devices for future thermoelectric and molecular-scale electronics applications.

Molecular electronic devices have the potential to deliver logic gates, sensors, memories and thermoelectric energy harvesters with ultra-low power requirements and sub-10 nm device footprints.¹⁻⁴ Single-molecule electronic junctions⁵⁻¹² and self-assembled monolayers¹³⁻¹⁵ have been

investigated intensively over the past few years, because their room-temperature electrical conductance has been shown to be controlled by destructive quantum interference (DQI).¹⁶⁻²⁰ More recently the effect of quantum interference on the Seebeck coefficient of single molecules has also been studied²¹⁻²⁶. Figure 1(A) illustrates an example where a room-temperature constructive quantum interference (CQI) effect would be expected from an anthracene molecular core. Here, electrical current is injected into and collected from the core via the green arrows, or alternatively via the red arrows.

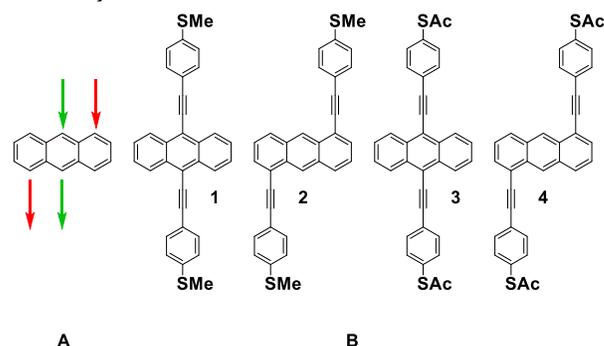


Fig. 1 | Structures of studied molecules. (A) A sketch of an anthracene core with connectivities 7,2' and 1,5'. (B) Chemical realisations of molecular wires with anthracene cores. 1 and 3 correspond to the 7,2' connectivity, while 2 and 4 correspond to the 1,5' connectivity.

Such a change in connectivity in a classical resistor network would lead to only a small change in electrical conductance. In contrast, theory predicts and experiment confirms²⁷⁻²⁹ that the room temperature, single-molecule, low-bias electrical conductance G_1 for the green connectivity is approximately an order of magnitude greater than the conductance G_2 of the red connectivity. This is a clear signature of room-temperature phase-coherent transport and of the varying degrees of CQI for the two different

connectivities. The chemical realization of the green connectivity is molecule **1** of Fig. 1, in which the terminal groups attached to electrodes inject a current into the anthracene core via alkyne linkages. Similarly, molecule **2** is a realization of the red connectivity. **3** and **4** are alternative realisations of the red and green connectivities, in which the thioether terminal groups are replaced by thioacetate groups (which can be deprotected *in-situ* to grant terminal thiols for gold binding). These terminal anchor groups were chosen to demonstrate that further control over interfacial coupling and energy level alignment between molecules and electrodes could be achieved.³⁰⁻³¹ Our aim is to create self-assembled monolayers (SAMs) from these compounds, demonstrate that these single-molecule signatures of CQI can be translated into SAM-based devices and assess the effect of CQI on their Seebeck coefficients. We indeed find that the electrical conductances of SAMs formed from **1** and **3** are significantly higher than those of SAMs formed from **2** and **4**. We also measure and calculate the Seebeck coefficients of these SAMs and show that the sign and magnitude of their thermopower is determined by a combination of their connectivities and the nature of their (thiolate or thioether) anchor groups. It should be noted that whilst thiol groups generally lead to stronger binding and superior film stability than thioethers,³² the latter are preferential where intermolecular interactions within the SAM may result in monolayer reorganization during assembly.³³⁻³⁴

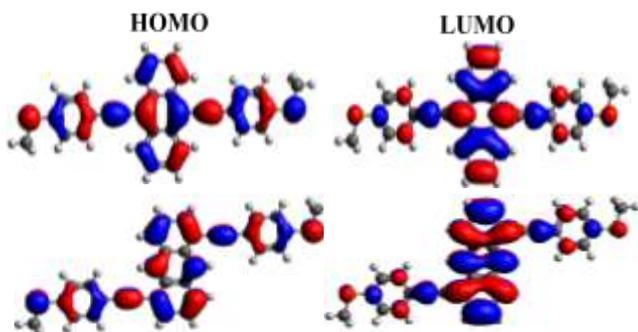
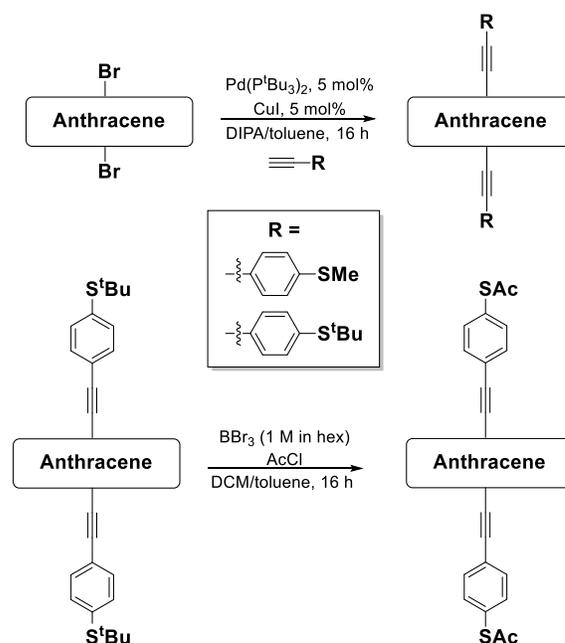


Fig. 2 | Frontier orbitals for 1 and 2: HOMO and LUMO orbitals for molecule 1 (top) and molecule 2 (bottom). (Orbitals for 3 and 4 are shown in the SI) Red (blue) corresponds to regions in space of positive (negative) orbital amplitude.

Our choice of connectivities in Fig. 1 was guided by ‘magic ratio theory’,²⁷ which predicts that the ratio $\frac{G_1}{G_2}$ of the low-bias, single-molecule conductances of **1** and **2** (**3** and **4**) should be $\frac{G_1}{G_2} = 16$ (ESI-Fig. S28). This simple theory illustrates how connectivity alone contributes to conductance ratios, without including chemical effects or Coulomb interactions. When the latter are included, recent studies³⁵ indicate that the qualitative trend in the ratio is preserved (*i.e.* that $\frac{G_1}{G_2} \gg 1$), but the precise value should be calculated using *ab initio* methods. Our aim is

to determine if this single-molecule signature of QI is preserved or modified in a SAM, where intermolecular interactions are also expected to play a role.

Fig. 2 shows the frontier orbitals of **1** and **2**, and in agreement with magic ratio theory, confirms the presence of CQI, which occurs when the HOMO has different colours (representing different amplitudes) at the ends of the molecule (*i.e.* blue at one end and red at the other) and the LUMO has the same colour (*i.e.* red at both ends)^{29, 36-38}



Scheme 1 | Synthesis of studied molecules. A representative synthetic pathway illustrating the construction of symmetric anthracenes through the use of Sonagashira (top) and *trans*-protection (bottom) reactions.

Molecules **1** and **2** bearing thioether termini could be synthesised from bromoanthracenes through the use of standard Sonagashira chemistry, however this same strategy could not be used to synthesise the thioacetate derivatives (**3** and **4**). This is due to a competing cyclo-oligomerisation reaction that occurs when reacting a thioacetate-terminated phenylacetylide moiety in the presence of a palladium catalyst.³⁹ As a result of this, a *trans*-protection strategy was employed utilising a *tert*-butyl protected thiol. Initially, dibromoanthracenes were reacted with the alkyne of choice (either 4-ethynyl-*tert*-butylthioether or 4-ethynylthioanisole) to generate symmetrically disubstituted products (**1**, **2**, **3A** and **4A**). All compounds could be purified via flash column chromatography and were obtained in good yields (>60%). Thioacetate substituted anthracenes (**3** and **4**) were then obtained through *trans*-protection reactions of **3A** and **4A** respectively. Molecule **4** could be purified through the use of flash chromatography alone, however recrystallization was required to isolate molecule **3**, resulting in a slightly reduced yield (see SI 1.3).

Deposited molecular films were characterized by atomic force microscopy (AFM), nano-scratching⁴⁰⁻⁴² and

polished Au-coated quartz crystal microbalance (QCM), which suggested the formation of high-uniformity SAMs with thicknesses in the range of 1.1-1.4 nm (ESI Table S5); corresponding to a monolayer of molecules in a perpendicular configuration with a tilt angle of 30°-50°.⁴³⁻⁴⁴ All molecular films were grown on freshly prepared template stripped Au substrates⁴⁵⁻⁴⁶ with a surface roughness of 80-150 pm (see Methods section). Molecular conductance was characterized by conductive AFM (cAFM), where the number of molecules under the probe is estimated from the contact area between probe and sample surface (obtained via Hertz Model⁴⁷⁻⁴⁹) and the single-molecule occupation area obtained from QCM and AFM.

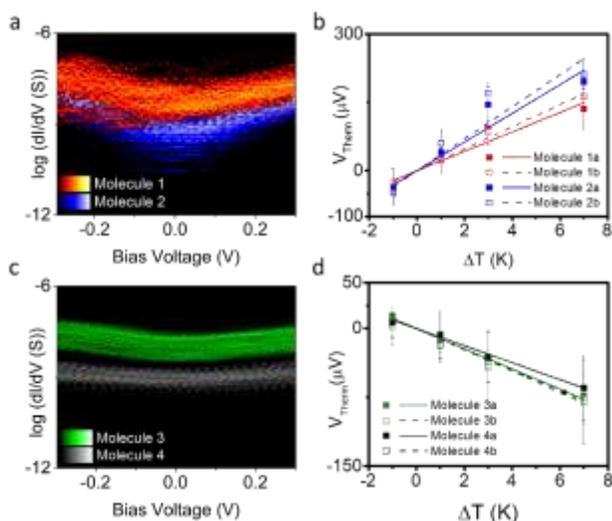


Fig. 3 | Electrical and thermoelectrical properties of SAMs. (a,c) Aggregate conductance vs voltage histogram of molecular conductance (molecule 1, 2 (a), and 3, 4 (c)), bias voltage between -0.3 V to -0.3 V. (b,d) Linear fit plot of Thermal Voltage vs. ΔT ($T_{\text{sample}} - T_{\text{probe}}$) for molecules 1,2 (b) and 3,4 (d), SAMs Xa and SAMs Xb indicate two measured samples.

Aggregate conductance vs voltage histogram at low bias (-0.3 V to 0.3 V) for molecules 1-4 are shown in Figure 3a and c, while Figure 3 b and d shows the linear fit of thermal voltage vs. ΔT for different junction systems (see ESI Fig S36 for detailed comparison of molecules 1 and 2). The slope of the fit, $\frac{V_{\text{Thermal}}}{\Delta T}$, related with the Seebeck coefficient of the junction via equation: $S_{\text{junction}} = S_{\text{probe-Au}} - \frac{V_{\text{Thermal}}}{\Delta T}$ (the detailed number listed in Table 1). The Seebeck measurements of all SAMs were operated on two separate samples prepared with same recipe (labelled as SAMs Xa and SAMs Xb), and similar Seebeck coefficient values were obtained which confirmed the reliability of the measurement (Figure S37). The opposite slope of linear fit for $\frac{V_{\text{Thermal}}}{\Delta T}$ between 1,2 and 3,4 demonstrating that the exchange of anchor groups leads to a change in sign for Seebeck coefficient.

From the statistics of >200 different IV curves measured at different locations, the statistically-most-probable

zero-bias differential conductance for molecule 1 is 10.2 times larger than that for molecule 2, and 14.2 times larger than that of molecule 3.

To compute the electrical conductance of molecules 1-4, we use density functional theory combined with the quantum transport code Gollum⁵⁰ to obtain the transmission coefficient $T(E)$ describing electrons of energy E passing from the source to the drain electrodes, from which the room-temperature electrical conductance and Seebeck coefficient are determined.

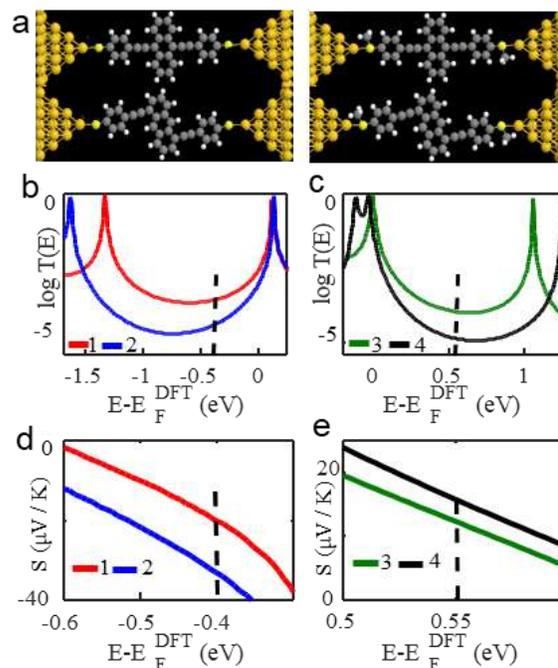


Fig. 4 | Charge transport in molecular junctions. (a) Schematic illustration of molecular junctions for 1, 2, 3 and 4. (b and c) Transmission functions $T(E)$ for 1 (red solid-line), 2 (blue solid-line), 3 (green solid-line) and 4 (black solid-line). (d and e) Plots of the room-temperature Seebeck coefficients of 1-4 as a function of the Fermi energy E_F .

Fig. 4a shows that after structural relaxation, when placed between gold electrodes, the molecules adopt an angle corresponding to the measured tilt angle of the SAM (for different views see Fig. S27). It has recently been demonstrated, by comparing $T(E)$ for a single molecule against SAMs consisting of 7 molecules,⁵¹ that the $T(E)$ for a SAM is approximately the same as for the single molecule. Fig. 4b shows the computed transmission coefficients for all four junctions, while Figs. 4d-e show the corresponding Seebeck coefficients as a function of the Fermi energy E_F . In agreement with previous studies,²⁷ we find that the closest agreement between theory and experiment is obtained for a Fermi energy near the mid-gap, indicated by the vertical dashed lines in Figs. 4b-c. The computed ratio of their transmission coefficients in gold-molecule-gold junctions (ESI-Fig. S28) for molecules 1 and 2 (similarly for 3 and 4) at $E = E_F^{\text{Gold}}$ is approximately 16. As described above, both molecules exhibit CQI near their gap centres and the conductance ratio arises from

the different degrees of constructive QI associated with their different connectivities.^{36-37, 52-57}

When the terminal groups of molecules are changed from thioethers to thioacetates, the transmission coefficients for molecules **3** and **4** show the same trend as those associated with molecules **1** and **2** (see Table 1). The change in sign of the thermopower between terminal groups is due to the position of the frontier orbital energies relative to the Fermi energy of gold (Fig. 4); for the thioether-terminated molecules (**1** and **2**) the Fermi energy lies close to the LUMO, giving a positive slope and a negative Seebeck, whereas for the thiolate- (from thioacetate) terminated molecules (**3** and **4**) the HOMO is closer to the Fermi energy, giving a negative slope and a positive Seebeck.

Table 1 | Experimental measurements and standard uncertainty (std), and theoretical calculations ($E_F-E_F^{\text{DFT}} = -0.4$ eV for (1** and **2**), $E_F-E_F^{\text{DFT}} = +0.55$ eV for (**3** and **4**), average, yellow-lines in Fig S28 in the ESI)**

M	Exp. (G/Go)	std	Theo. (G/Go)	Exp. S ($\mu\text{V/K}$)	std	Theo. S ($\mu\text{V/K}$)
1	7.01E-5	9E-6	1.66E-4	-23.4	4.6	-20.0
2	6.88E-6	1E-6	1.05E-5	-31.8	6.1	-33.0
3	1.28E-4	5E-6	1.59E-4	+12.1	3.0	+12.5
4	9.0E-6	3E-6	1.00E-5	+10.4	1.1	+16.3

In summary, through the rational design, synthesis and implementation of a new family of molecules, we have demonstrated that unequivocal signatures of single-molecule room-temperature CQI, contained in the connectivity-dependent conductance ratio of **1** and **2** (**3** and **4**), can be translated into self-assembled molecular films. In contrast to previous work contrasting DQI with CQI effects in the Seebeck coefficient of a single molecule,¹⁴ here we have examined how different degrees of CQI can be used to control the thermopower of SAMs. Utilising CQI to control thermoelectricity is useful, since CQI allows the desirable possibility of high conductance, whereas DQI always leads to low conductance. With two different connectivities to the anthracene core, CQI effects lead to measured conductance ratios of $\left(\frac{G_1}{G_2}\right)_{\text{Exp.}} = 10.2$, $\left(\frac{G_3}{G_4}\right)_{\text{Exp.}} = 14.3$, for SAMs formed from **1** compared to **2** (**3** and **4**), which is comparable with the magic ratio of 16 and the single-molecule DFT values of $\left(\frac{G_1}{G_2}\right)_{\text{Theo.}} = 15.8$, $\left(\frac{G_3}{G_4}\right)_{\text{Theo.}} = 16.0$. Furthermore, we show that the thermoelectrical performance of anthracene-based molecular films can be boosted by a judicious choice of connectivity to electrodes, combined with an optimal choice of terminal groups. Although the effect of CQI on the electrical conductance of SAMs

was reported only recently⁵⁸, the above demonstration of CQI-controlled molecular films is the first report of CQI-boosted thermoelectricity. It opens the way to new design strategies for functional ultra-thin-film thermoelectric materials and electronic building blocks for future integrated circuits.

ASSOCIATED CONTENT

Supporting Information is provided which contains all experimental details including information about the synthesis of the molecules, device fabrication and characterisation and the theoretical demonstration of molecular orbitals as well as the calculated transmission coefficient of gold/molecule/gold systems for all molecules. The Supporting Information is available free of charge on the ACS Publications website at DOI: ****

AUTHOR INFORMATION

Correspondence and requests for materials should be addressed to Professor Colin Lambert (c.lambert@lancaster.ac.uk), Professor Lesley Cohen (l.cohen@imperial.ac.uk), Professor Nicholas Long (n.long@imperial.ac.uk) or Dr. Benjamin Robinson (b.j.robinson@lancaster.ac.uk)

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