Controlling quantum interference by regulating charge on the bridging N atom of pyrrolodipyridine molecular junctions†

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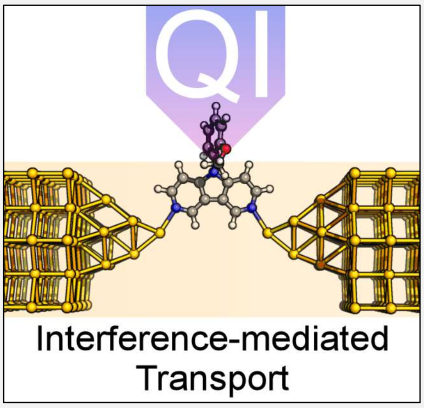
Phenomena unique to the quantum world arise in molecular electronic devices. For example, destructive interference phenomena have been used to fabricate single-molecule electrical switches, extremely efficient resistors and thermoelectric devices. However, there are few experimental reports so far on methods for controlling and tuning the magnitude and energy of such interference features. We synthesised both para- and meta-connected pyrrolodipyridines with different substituents on the pyrrolic N atom, and we measured their conductance as single-molecule junctions. We found that, in the meta compounds displaying destructive interference phenomena, the interference can in effect be turned off, by increasing electron density (charge) on this single N atom in the interference path, resulting in a conductance modulation of more than one order of magnitude. The overall results show the importance that small changes in the electronic structure of a molecular wire can have on its charge transport properties and demonstrate the fine control on molecular conductance of single-entity junctions that can be exerted by simple chemical design.



In molecular junctions, charge transport is affected by quantum phenomena with no classical equivalent.[1] For instance, the pattern of atomic connectivity in a molecular wire can significantly alter its electrical conductance, and it has been previously demonstrated that a phenyl ring can be an efficient conductor or an efficient insulator depending on the substitution pattern around the 6-membered ring.[2–4] When the conductance pathway is *via* the *para*- or *ortho*-related positions molecular conductance is high, while the pathway by way of *meta*-related positions gives rise to destructive quantum interference (DQI), a phenomenon that greatly reduces charge transport efficiency.[5–8] Such interference has been used to fabricate extremely efficient molecular insulators,[9] to design quantum electronic switches,[10–14] to study the fundamental phenomena governing molecular electronics,[15–18] and, more recently, to improve the performances of thermoelectric devices.[19]

Molecular wires incorporating a fluorene-like tricyclic scaffold (Figure 1) are an ideal platform to study the effect of heteroatom inclusion and electrode connectivity on the transport properties of the final junction, since it is relatively straightforward to prepare the desired compound. *Para*- and *meta*-connected fluorene derivatives, for instance, have been used to assess the effect of the heteroatom in the 9-position (X in Figure 1)[20] and the importance of the overall aromaticity of the tricyclic system[21] on molecular conductance. The main findings of these studies were

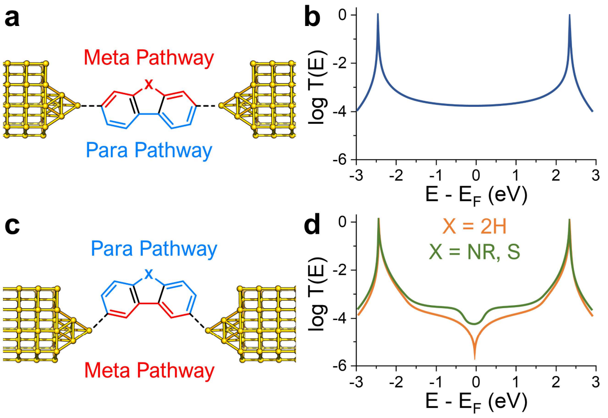


Figure 1: Structure of *para*-connected fluorene derivatives (a), with relative idealised transmission curve (b). Structure of meta-connected fluorene derivatives (c), with relative idealised transmission curves for X = 2H (biphenyl) and X = NR or S. The sharp dip in the *meta*-connected biphenyl (X = 2H) is due to the DQI, which is smoothed and reduced in magnitude when X = N or S as the *para* pathway is opened. The dotted line in (a) and (c) represents the molecular linker to the electrodes (*e.g.* $-SCH_3$, $-C{\equiv}C-C_5H_4N$, etc.)

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† Supporting Information available on chemrxiv.org.

- Synthetic procedures and characterisation
- Further details and methods on the *STM-BJ* experiments
- UV/Vis spectroscopy data
- Theoretical methods and additional calculations

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that the atom bridging the two aryl units can induce small changes in conductance by acting on the aromaticity of the fluorene unit when *para*-connected to the electrodes,[22] and it can attenuate the DQI phenomena that suppress conductance in the *meta* case (Figure 1d).[21] The interference attenuation was found to be particularly strong in carbazoles (9-azafluorenes; X = NR), with conductance orders of magnitude higher than the corresponding 9-silafluorene (X = SiR_2),[20] dibenzofuran (X = O)[20,21] or dibenzothiophene (X = S).[21] This phenomenon was attributed to a greater ability of the N atom to couple the two aromatic rings using its lone pair of electrons, thus increasing charge transport efficiency. We reasoned that if the electron density on the pyrrolic N were to be altered by the presence of electron-donating or electron-withdrawing substituents, the attenuation of DQI effects should vary accordingly, thus providing an effective way to chemically gate conductance by acting on the magnitude of interference features. We therefore focussed our efforts on synthesising and measuring the conductance of two series of simple, fluorene-like pyrrolodipyridines: the *meta*-series **1-5** and the *para*-series **1P**, **2P** and **5P** (Figure 2). The main advantage of this model architecture is that the contacts are embedded in the biaryl system, therefore providing high coupling to the electrodes, and that by focussing on a single class of tricyclic compounds (N-based heterocycles) no significant changes in aromaticity are expected.

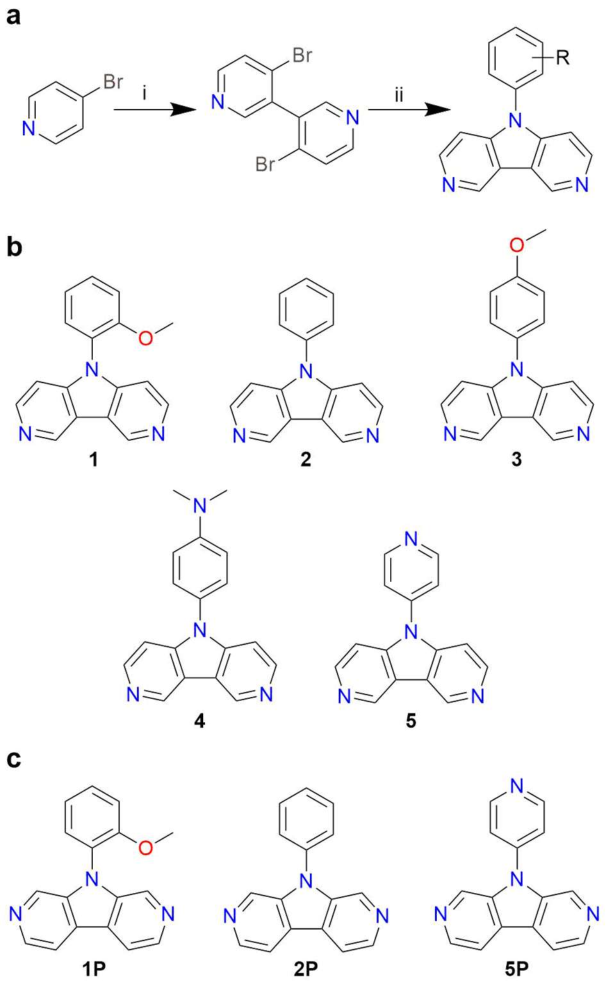

Figure 2: Synthetic pathway (a) for the synthesis of the *N*-substituted pyrrolodipyridine, and structures of the *meta* compounds used in this study (b) and their *para* analogues (c). Key: i) lithium diisopropylamide (1h, -94 ºC, THF), $CuCl_2$ (16 h, RT), 27 %. (ii) $Pd_2(dba)_3$•$CHCl_3$, SPhos, KO^tBu, $RPhNH_2$ (overnight, 65 - 75 ºC, Toluene), 17 – 82 %, depending on R.

The *meta*-connected compounds were prepared by the sequence shown in Figure 2, and full details and characterisation are provided in the SI. In brief, we prepared 4,4'-dibromo-3,3'-dipyridine by selective lithiation (lithium diisopropylamine in tetrahydrofuran) of 4-bromopyridine in the 3-position, followed by Ullmann-style coupling with $CuCl_2$. The dihalodipyridine was then subjected to catalytic double Buchwald-Hartwig amination[23–25] with a substituted aniline, using $Pd_2(dba)_3$•$CHCl_3$ as precatalyst and a bulky biaryl phosphine as ligand,[26] to enforce cyclisation to the desired compounds **1 - 5**. The *para*-connected compounds **1P**, **2P** and **5P** were prepared in the same way, using 3,3'-dibromo-4,4'-dipyridine[27] as starting material (procedures and characterisation in the SI). The single-molecule conductance was then determined using the scanning tunnelling microscope break-junction (*STM-BJ*) technique,[28] where gold point contacts are continuously formed and broken in a solution of the target molecule (here, in mesitylene:THF 8:2 v:v), at room temperature and low DC bias (200 mV in this study). When the point contact is broken, Au-molecule-Au junctions spontaneously form in the nanogap through interaction of the aurophilic pyridyl N termini with undercoordinated Au atoms. The junction is then stretched until its rupture, while recording the current flow as a function of tip-substrate separation, and conductance (current / bias) is calculated in units of G_0 (quantum of conductance, $2e^2/h \cong 77.48\,\mu S$). A typical break-junction trace shows series of plateaux at multiple integers of G_0, which are due to charge transport through a small number of (or just one) Au atoms, and molecule-dependent plateaux at much smaller conductance values. Junctions are fabricated and ruptured thousands of time, and the corresponding conductance *vs* elongation traces analysed statistically in frequency histograms and two-dimensional maps. Histograms give the most probable conductance value, while the maps correlate charge transport features to the evolution of the junctions from the atomic contact to its final rupture.

The main results are summarised in Figure 3. The substituent on the pyrrolic N of the *meta* family **1-5** has indeed an effect on molecular conductance and gates its value by more than 1 order of magnitude. Interpreting the data with the simple model explained in the introduction, the alternative pathway introduced by the bridging pyrrolic N attenuates the DQI arising from the *meta* pathway. The phenomenon can therefore be considered as similar to an electrostatic gate, where the charge residing on the bridging N atom modulates the charge transport efficiency of the alternative pathway and therefore its interference attenuation factor.

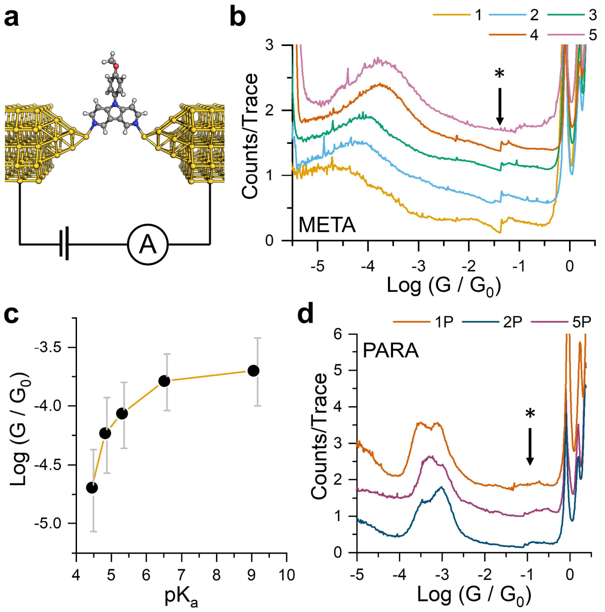

Figure 3: Structure of **3** as a single-molecule junction (a) and conductance histograms of compounds **1 – 6** (b). Logarithmic conductance *vs* pK$_a$ plot (c) with yellow connecting line as guide to eyes. We used the pK$_a$ of the anilinium ion corresponding to the aniline used in the synthesis of the compound by Buchwald-Hartwig amination. pK$_a$ data from the CRC Handbook of Chemistry and Physics.[37] Conductance histogram of **1P**, **2P** and **5P** (d); the asterisk in the conductance histograms marks a small artefact introduced by our 4-channel preamplifier transimpedance switch. Conductance data acquired at 200 mV bias and at 10 kSa/s, vertically shifted for clarity in (a) and (d) and normalised as counts/trace (all plots >3000 traces, with no data selection). Key in (a): C = grey, N = blue, O = red, Au = yellow. The error in (c) is 2σ of the conductance histogram gaussian fitting.

Chemical insight into molecular conductance can be gained by looking for correlations between molecular conductance and certain parameters classically used by physical organic chemists to characterise the effects of structural change. An example of this is the correlation between molecular conductance and the Hammett parameter for substituted oligophenylethylene (OPE) molecular wires.[29] Here we expect a correlation between the charge density on the pyrrolic N atom and the electrical behaviour of the pyrrolodipyridine junctions. In this case there is a directly relevant measurable physical parameter which relates to the charge density on the nitrogen atom and this is the acidity of the protons of the anilinium ions corresponding to the aniline building block used in the synthesis of these pyrrolodipyridines. Plotting the logarithm of conductance *vs* the pK$_a$ (in water) shows a clear correlation, with an apparent upper limit of conductance ($\sim 10^{-3.7}$ G_0) and therefore of interference attenuation, that can be attained with these molecular wires. This can be clearly observed in the histograms, where compound **4** and **5** have very similar conductance, near to the limit. To test the assumption of DQI effects discussed in the introduction, we measured the single-molecule conductance of the *para* analogues **1P**, **2P**, and **5P** (Figure 3d-e). In good agreement with other studies on bridged dipyridines,[30] the substituents on the bridging N which gated conductance by almost one order of magnitude in the *meta* connectivity had very little effect on the conductance of the *para* system (Figure 3d).

The simple model we discussed in the introduction is enough for a qualitative interpretation of the data, but molecular circuits do not behave like classic electrical networks, where the total conductance is the sum of the individual contributions. Multiple pathways in a single-molecule contribute additional quantum interference effects, and therefore a rigorous DFT analysis is needed to better characterise the observed chemical gating of the DQI feature. We used the transport code Gollum[31] to calculate the transmission coefficient $T(E)$, for electrons of energy E passing from one electrode to the other *via* the molecule. We introduced a scissor operator[32–34] using the optical bandgap of the compounds to account for the inability of DFT-LDA accurately to predict the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies.[35,36] The conductance can be calculated from the transmission curves as $G = G_0 T(E_F)$, where $T(E_F)$ is the value of the transmission coefficient at the DFT-predicted Fermi energy of the metallic electrodes. The absolute position of the Fermi level of the electrodes cannot be predicted with full accuracy as it is dependent on the local shape of the electrodes and the surrounding nano-environment, which constantly change during an *STM-BJ* experiment. Therefore, molecular conductance cannot be exactly calculated, but information about it can be inferred from the behaviour of $T(E)$ within the HOMO-LUMO bandgap, where E_F generally lies. All the *meta* compounds showed signatures of DQI in the calculated $T(E)$ profile, which result in a "dip" in the transmission curve (Figure 4a). Substituents on the pyrrolic N do not change the energy position of the DQI feature, but they

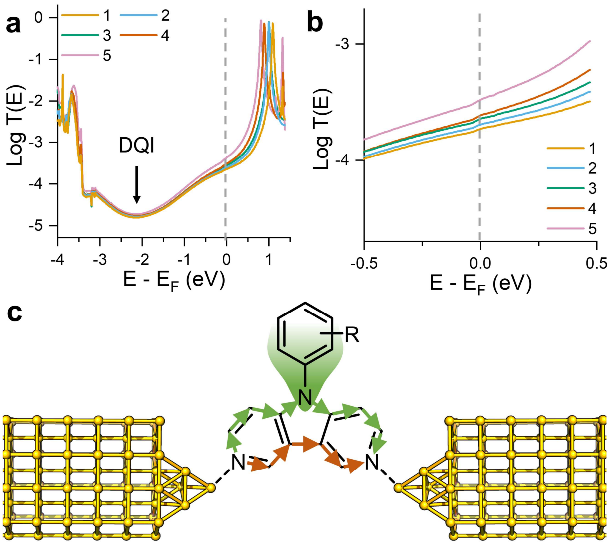

Figure 4: Transmission curves for compound **1-5** (a) and magnification of the area between -0.5 and 0.5 eV (b). The DFT-predicted Fermi energy is represented as a dotted grey line in (a). The destructive quantum interference (DQI) feature marked in (a) arises from the *meta* connectivity, highlighted in (c) in brown shade. The alternative (green) pathway efficiency is modulated by the electron density on the pyrrolic N (green shade).

control its magnitude, with an effect visibly significant at $E - E_F = 0$ (near the DFT-predicted Fermi level of the electrodes, Figure 4b). As discussed in the introduction, this can be understood as an attenuation of the interference phenomena arising from the presence of an alternative charge transport pathway (green arrows in Figure 4c), whose efficiency can be significantly modulated by the *N*-substituent in **1-5**. The same calculations were performed on the *para* compound **1P**, **2P** and **5P**, and the behaviour of $T(E)$ in the HOMO-LUMO gap was found to be insensitive to the nature of the substituent on the pyrrolic N (see SI for addition details). In order to provide further insights on the mechanism of DQI gating and to contribute to the theoretical framework which explains the correlation of molecular conductance with pK_a, we calculated the net charge gain on the pyrrolic N in compounds **1-5** by three different methods. Plotting these values against molecular conductance and pK_a shows a clear mutual dependence, with the implication that the DQI feature modulation (gating) by the charge on the bridging atom is the dominant mechanism. As can be observed in Table S1 and in Figure S27 (see SI), the changes in net electron gain are only minute (<10 %), but they contribute to a substantial change in the charge transport properties of the molecular junction.

In conclusion, we have shown here that destructive quantum interference features can be chemically gated to fine-tune their magnitude, and therefore, their effect on the conductance of a single-molecule junction. We used a model pyrrolodipyridine system, which can be prepared with a variety of substituents on the N atom bridging two pyridyl rings, and we showed that the phenomenon depends on the electron density on the pyrrolic nitrogen. Harnessing quantum interference features is important for the development of functional molecular devices such as efficient insulators and thermoelectric converters, and our results demonstrate an effective way to exert control on their magnitude by regulating the charge on just a single atomic component of the interference path.

Data Availability

NMR spectra (Bruker format) for compounds **1 – 4** and raw *STM-BJ* data can be found in the data catalogue in Liverpool at: https://datacat.liverpool.ac.uk/628.

Acknowledgements

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