Synthetic Control of Quantum Interference by Regulating Charge on a Single Atom in Heteroaromatic Molecular Junctions

Saman Naghibi,† Ali K. Ismael,§ Ali K. Ismael,† Andrea Vezzoli,§† Mohsin K. Al-Khaykanee,‡¶ Xijia Zheng,† Iain M. Grace,† Donald Benthell,§ Simon J. Higgins,§ Colin J. Lamberton,§‡ and Richard J. Nichols*§¶

†Department of Chemistry, University of Liverpool, Crown Street, Liverpool L69 7ZD, U.K.
‡Department of Physics, Lancaster University, Lancaster LA1 4YB, U.K.
§Department of Physics, College of Education for Pure Science, Tikrit University, Tikrit 34001, Iraq
¶Department of Physics, College of Science, University of Babylon, Babylon S1002, Iraq

Supporting Information

ABSTRACT: A key area of activity in contemporary molecular electronics is the chemical control of conductance of molecular junctions and devices. Here we study and modify a range of pyrrolodipyrindines (carbazole-like) molecular wires. We are able to change the electrical conductance and quantum interference patterns by chemically regulating the bridging nitrogen atom in the tricyclic ring system. A series of eight different N-substituted pyrrolodipyrindines has been synthesized and subjected to single-molecule electrical characterization using an STM break junction. Correlations of these experimental data with theoretical calculations underline the importance of the pyrrolic nitrogen in facilitating conductance across the molecular bridge and controlling quantum interference. The large chemical modulation for the meta-connected series is not apparent for the para-series, showing the competition between (i) meta-connectivity quantum interference phenomena and (ii) the ability of the pyrrolic nitrogen to facilitate conductance, that can be modulated by chemical substitution.

In recent years, quantum interference has been one of the most actively pursued topics in molecular electronics. Quantum interference (QI), which can be either destructive or constructive, results in molecules not following classic electrical circuit rules, and this offers new opportunities to exploit their electrical properties. QI has been demonstrated across a wide range of molecules either as multi- or monolayer films sandwiched between pairs of conductors or as single molecules bridging between nanoelectrode pairs. For example, in the former case, it has been shown through direct two-terminal electrical measurements across self-assembled monolayers that QI is sensitive to chemical changes and conjugation patterns. Conjugation has been used as one of the primary ways of controlling quantum interference, with a classic exemplar being para- versus meta-substitution in a central benzene ring in a molecular wire. An example of this recorded at the single molecule level with the break-junction technique is the switch between constructive interference apparent for para-connected oligo(3)-phenylenevinylene to destructive QI for the analogue with meta-connectivity at the central benzene ring. However, QI phenomena can be very sensitive to precise junction details, including even through space interactions, and it has been shown that meta-coupled benzene molecules can even exhibit higher conductance than their para-analogues. This high sensitivity of QI to chemical structure has been used to distinguish two structural isomers within single molecule break junctions. It has been demonstrated that QI can be electrochemically controlled, notably in the case of anthraquinone (AQ) containing molecular bridges and thin films, which can be switched between the cross-conjugated AQ and the linearly conjugated H2AQ state by electrochemical reduction. QI has also been demonstrated in thin films of AQs and tetracyanoethylene acceptors creates a new resonance in the transmission function near the metal contact Fermi energy. This signature of QI gives rise to significant conductance enhancement (constructive QI). Another example of the modulation of QI through changes in noncovalent interactions is the sliding of individual π-stacked dimers in mechanically controlled break junctions. Even simple protonation of a molecule can significantly change QI patterns, for example, protonation of azulene molecular junctions can alleviate destructive interference. It has also been shown that strain introduced into ring structures within
molecules impacts charge transport pathways. Changing atom types within aromatic rings is expected to be an effective way of modulating QI, and in fact it has been shown that meta-connected five-membered rings can be tuned by swapping between different heteroatoms within the ring. On the other hand, molecular bridges containing fused aromatic ring systems are a veritable playground for investigating QI phenomena since they offer, through chemical synthesis, diverse control of connectivity, aromaticity and conjugation, heteroaromaticity, and substitution. This provides the basis of the present study in which the nitrogen heteroatom within a fused aromatic framework (carbazole) is chemically controlled, with this shown to be an effective way of tuning quantum interference and molecular conductance.

The tricyclic scaffold of fluorene-like compounds (Figure 1) is an interesting candidate for substitution studies because (i) the two aryl units are locked in a coplanar geometry and therefore no variations in the inter-ring dihedral angle are expected, and (ii) multiple substitutions are possible, as various bridging atoms X, functional groups R, and para-/meta-(2,7-/3,6-) connectivity to the electrodes can be explored by appropriate choice of the synthetic process. A few studies have been performed to probe the effect of chemical substitution on the molecular conductance\(^{17–19}\) and thermoelectric properties\(^{20}\) of these tricyclic systems. The results to date suggest that, in the para-(2,7-) connectivity, the variations in conductance observed as X is changed are mostly due to modifications to the overall aromaticity of the tricyclic system,\(^{17}\) in agreement with previous studies showing an inverse correlation between aromaticity and conductance.\(^{21}\) However, when the fluorene scaffold is connected to the electrodes in a meta-pattern (3,6-), aromaticity and conductance are no longer correlated, with quantum interference effects\(^{17}\) and the individual atomic components of the molecular wire\(^{18}\) having the dominant effect on charge transport. This results, for instance, in meta-carbazoles (X = N) having a significantly higher conductance than the meta-dibenzofurans (X = O)\(^{19}\) or meta-silafuorenes (X = Si),\(^{18}\) in contrast with predictions based on the aromaticity of the central 5-membered ring. The peculiar behavior of carbazoles was attributed to a greater ability of the bridging N in facilitating electronic transmission as its lone pair couples the two aryl units, providing an alternative, high efficiency charge transport pathway. These results sparked our interest in studying the anomalous behavior of carbazoles by exploring their rich substitution chemistry, in the hope of shedding more light on the subtle interplay between quantum interference phenomena and chemical structure. We will demonstrate here that, in the series of meta-carbazoles we studied, the QI feature arising from meta-connectivity is shifted away from the Fermi energy of the electrodes and effectively switched off. Furthermore, when the electron density on the pyrrolic N in contacts to the electrodes embedded in the tricyclic system (pyridyl N), providing a constant high degree of coupling to the electrodes and ensuring relatively high conductance even in the presence of destructive interference phenomena. By focusing on a single class of tricyclic compounds, in this case N-based heterocycles, no significant changes in aromaticity or inter-ring dihedral angle are expected. The compounds were prepared by the sequence shown in Figure 2a, and full synthetic procedures and characterization are provided in the SI. In brief, we prepared 4,4′-dibromo-3,3′-dipyridine by

\[\begin{align*}
\text{Br} \quad \text{Br} \\
\text{N} \quad \text{N} \\
\text{O} \quad \text{O} \\
\text{N} \quad \text{N} \\
\text{N} \quad \text{N} \\
\text{N} \quad \text{N} \\
1M \quad 2M \quad 3M \\
4M \quad 5M
\end{align*}\]

Figure 2. (a) Synthetic pathway for the synthesis of the N-substituted pyrrolodipyrine, (b) structures of the meta-compounds used in this study, and (c) their para-analogues. Key in (a): (i) lithium disopropylamide (1 h, −94 °C, THF), CuCl\(_2\) (16 h, RT), 27%. (ii) Pd\(_2\)(dba)\(_3\)-CHCl\(_3\), Phos, KO\(_2\)Bu, RPhNH\(_2\) (overnight, 65−75 °C, toluene). Yield: 17−82%, depending on R (more details in the SI).
selective lithiation (lithium diisopropylamine in tetrahydrofuran) of 4-bromopyridine in the 3-position, followed by Ullmann-style coupling with CuCl₂. The dihalopyridine was then subjected to double Buchwald-Hartwig amination22–24 with an aniline derivative, using Pd(dba)₃·CHCl₃ as precatalyst and a bulky biaryl phosphine as ligand,25 to enforce cyclization to the desired compounds 1M–5M. The para-connected compounds 1P, 2P, and 5P were prepared in the same way, using 3,3′-dibromo-4,4′-dipyridine26 as starting material.

Single-molecule conductance was then determined using the scanning tunneling microscope break-junction (STM-BJ) technique,27 where gold point contacts are continuously formed and broken in a solution of the target molecule (here, in mesitylene/tetrahydrofuran 8:2 v:v), at room temperature and low DC bias (200 mV in this study), by driving a Au tip into contact with a Au substrate and then withdrawing it at constant speed (20 nm s⁻¹). 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, and the junction is then stretched until it ruptures. During the whole process, the current flow is recorded as a function of tip–substrate separation, and conductance (current/bias) is calculated in units of $G_0$ (quantum of conductance, $2e^2/h \approx 77.48$ μS). A typical break-junction trace shows a 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 times, and the corresponding conductance versus elongation traces are analyzed 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 summarized in Figure 3. The substituent on the pyrrolic N of the meta-family 1M–5M indeed has an effect on molecular conductance and modulates its value by more than one order of magnitude (Figure 3b), while it has almost no effect on the conductance of the para-analogues 1P, 2P, and 5P (Figure 3c), also in good agreement with our previous study on planarized 4,4′-dipyridines.28 It is worth mentioning that the bistable conductance behavior of 4,4′-dipyridine is retained in the para-series, which results in the well-resolved double peaks that can be observed in Figure 3c. Furthermore, compounds 5M and 5P have an additional possible binding mode through the pyridyl ring attached to the carbazolic N, which contribute to a low-conductance shoulder in both cases (more details in the SI). The overall results therefore suggest a relationship between charge transport efficiency and the electronic state of the bridging pyrrolic N. 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 characterize the effects of structural change. Examples of this are the correlation between molecular conductance and the Hammett parameter for substituted oligophenylethylene (OPE) molecular wires30 or the previously mentioned pyridinophane.31 Here, we expect a relationship between the charge density on the pyrrolic N atom and the electrical behavior of the pyrrolodipyridine junctions. A directly relevant measurable physical parameter that relates to the charge density on the nitrogen atom 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 versus their pKₐ (in water) shows a clear correlation (Figure 3d), with an apparent upper limit of conductance ($\sim 10^{−3.7}$ $G_0$) that can be attained with these molecular wires. This can be clearly observed in the histograms, where compounds 4M and 5M have very similar conductance, near to the limit.

The clear correlation between the charge residing on the pyrrolic N and molecular conductance allows us to introduce a simple conceptual model for the interpretation of the data. The lone pair on the pyrrolic N acts as a facilitator of charge transport,17,18 opening a nonconjugated but efficient alternative conductance pathway (green arrows in Figure 4c) that attenuates the interference phenomena introduced by the meta-pathway (orange arrows in Figure 4c) and grants relatively high conductance. The greater the electron density on the pyrrolic N, the larger the extent of aryl–aryl coupling provided by the lone pair and, therefore, the higher the molecular conductance, up to a limit of approximately $10^{−3.7}$ $G_0$.

While this simple model is enough for a qualitative interpretation of the data, molecular circuits do not behave like classic electrical networks, where the total conductance is the sum of the individual contributions. Multiple pathways in a
We then introduced a scissor operator to calculate the transmission coefficient $T(E)$ for electrons of energy $E$ passing from one electrode to the other via the molecule. We then introduced a scissor operator 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. 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 nanoevironment, which can change during an STM-BJ experiment. Therefore, molecular conductance cannot be exactly calculated, but information about it can be inferred from the behavior of $T(E)$ within the HOMO–LUMO bandgap, where $E_F$ generally lies. All the meta-compounds showed indeed signatures of destructive quantum interference in the calculated $T(E)$ profile, which result in a “dip” in the transmission curve (more details and $T(E)$ curves magnification in the SI). The DQI “dip” is however heavily shifted toward the nonconducting orbital and not as sharp as observed, for instance, in simple meta-connected aryls. These effects are due to the bridging N atom that couples the two pyrdyl rings and generates a strong asymmetry in the behavior of $T(E)$ in the HOMO–LUMO gap. Substituents on the pyrrolic N do not significantly change the energy position of the interference feature, but they control the value of the transmission coefficient at $E − E_F = 0$ (near the DFT-predicted Fermi level of the electrodes, Figure 4b). The same calculations were performed on the para-compounds 1P, 2P, and 5P, and the behavior 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 additional details). To provide further insights on the mechanisms of conductance modulation and to contribute to the theoretical framework that explains the correlation of molecular conductance with $p_Kr$, we calculated the net charge gain on the pyrrolic N in compounds 1M–5M by three different methods. Plotting these values against molecular conductance and $p_Kr$ shows a clear mutual dependence, with the implication that control of the charge on the bridging atom is the dominant mechanism. As can be observed in Table S1 and Figure S27, 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 demonstrated here that it is possible to chemically control the conductance of a molecular wire by appropriate choice of substituents and electrode connectivity pattern. The key phenomenon here is the competition between a quantum interference feature introduced by a meta-connectivity pattern, that suppresses conductance, and the presence of an alternative, high-conductance pathway through a single atom (the pyrrolic N), whose electron density can be modulated by appropriate chemical substitution. Control over the effect of quantum interference features at the $E_F$ of the metallic electrodes 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 by regulating the charge on just a single atomic component of the molecular wire. This represents an expansion of the portfolio of methods currently used to influence quantum interference phenomena, with a purely synthetic approach that complements the use of electrochemical/electrostatic potential to change the energy alignment with the electrodes $E_F$, or the use of light, potential, and acid–base interactions to trigger changes in the structure and degree of conjugation of the molecular wire.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.9b02319.

Synthetic procedures and characterization, further details and methods on STM-BJ experiments, UV–vis spectroscopy data, theoretical methods and additional calculations, proton NMR spectra (PDF).

**AUTHOR INFORMATION**

**Corresponding Authors**
*E-mail: nichols@liverpool.ac.uk.
*E-mail: c.lambert@lancaster.ac.uk.
*E-mail: andrea.vezzoli@liverpool.ac.uk.

**ORCID**

Simon J. Higgins: 0000-0003-3518-9061
Colin J. Lambert: 0000-0003-2332-9610
Richard J. Nichols: 0000-0002-1446-8275
Author Contributions

These authors contributed equally to this work.

Notes

The authors declare no competing financial interest.

NMR FIDs (Bruker format) for the compounds used in this study and their raw STM-Bj data can be found in the data catalogue in Liverpool at: https://datacat.liverpool.ac.uk/628 and alternatively at DOI: 10.17638/datacat.liverpool.ac.uk/628.

ACKNOWLEDGMENTS

We thank EPSRC for support (Grant Nos. EP/M005046/1, EP/M029522/1, EP/M014452/1, EP/M014169/1, EP/P027156/1, and EP/N03337X/1). This work was additionally supported by the European Commission through the FET Open project 767187 (QuLEt) and the EU project "Bac-to-Fuel". A.K.I. is grateful for financial assistance from Tikrit University (Iraq) and the Iraqi Ministry of Higher Education (SL-20).

REFERENCES

(1) Fracasso, D.; Valkenier, H.; Hummelen, J. C.; Solomon, G. C.; Chiuchi, R. C. Evidence for Quantum Interference in Sams of Arylethynylene Thiolates in Tunneling Junctions with Eutectic Ga-In (EGaIn) Top-Contacts. J. Am. Chem. Soc. 2011, 133 (24), 9556–9563.

(2) Guédon, C. M.; Valkenier, H.; Markussen, T.; Thygesen, K. S.; Hummelen, J. C.; van der Molen, S. J. Observation of Quantum Interference in Molecular Charge Transport. Nat. Nanotechnol. 2012, 7 (5), 305–309.

(3) Arroyo, C. R.; Frisenda, R.; Mouth-Poulus, K.; Seldenhuis, J. S.; Bjørnholm, T.; van der Zant, H. S. J. Quantum Interference Effects at Room Temperature in OPV-Based Single-Molecule Junctions. Nanoscale Res. Lett. 2013, 8 (1), 234.

(4) Borges, A.; Xia, J.; Liu, S. H.; Venkataraman, L.; Solomon, G. C. The Role of Through-Space Interactions in Modulating Constructive and Destructive Interference Effects in Benzene. Nano Lett. 2017, 17 (7), 4436–4442.

(5) Zhang, Y.-P.; Chen, L.; Zhang, Z.-Q.; Cao, J.; Tang, C.; Liu, J.; Duan, L.-L.; Huo, Y.; Shao, X.; Hong, W.; et al. Distinguishing Diketopyrrolopyrrole Isomers in Single-Molecule Junctions via Reversible Stimuli-Responsive Quantum Interference. J. Am. Chem. Soc. 2018, 140 (21), 6531–6535.

(6) Darwish, N.; Díez-Pérez, I.; Da Silva, P.; Tao, N.; Gooding, J. J.; Paddan-Row, M. N. Observation of Electrochemically Controlled Quantum Interference in a Single Anthraquinone-Based Norbornyl-26-Stacked Dimers. Angew. Chem., Int. Ed. 2012, 51 (13), 3203–3206.

(7) Rabache, V.; Chaste, J.; Petit, P.; Della Rocca, M. L.; Martin, P.; Lacroix, J.-C.; McCreery, R. L.; Lafarge, P. Direct Observation of Large Quantum Interference Effect in Anthraquinone Solid-State Junctions. J. Am. Chem. Soc. 2013, 135 (28), 10218–10221.

(8) Li, Y.; Buerkle, M.; Li, G.; Rostamian, A.; Wang, H.; Wang, Z.; Bowler, D. R.; Miyazaki, T.; Xiang, L.; Asai, Y.; Zhou, G.; Tao, N. Gate Controlling of Quantum Interference and Direct Observation of Anti-Resonances in Single Molecular Charge Transport. Nat. Mater. 2019, 18 (4), 357–363.

(9) Bai, J.; Daoud, A.; Sangtarash, S.; Li, X.; Tang, Y.; Zou, Q.; Sadeghi, H.; Liu, S.; Huang, X.; Tan, Z.; et al. Anti-Resonance Features of Destructive Quantum Interference in Single-Molecule Thiophene Junctions Achieved by Electrochemical Gating. Nat. Mater. 2019, 18 (4), 364–369.

(10) Vezzoli, A.; Grace, I.; Brooke, C.; Wang, K.; Lambert, C. J.; Xu, B.; Nichols, R. J.; Higgins, S. J. Gating of Single Molecular Junction Conductance by Charge Transfer Complex Formation. Nanoscale 2015, 7 (45), 18949–18955.

(11) Wang, K.; Vezzoli, A.; Grace, I. M.; McLaughlin, M.; Nichols, R. J.; Xu, B.; Lambert, C. J.; Higgins, S. J. Charge Transfer Complexation Boosts Molecular Conductance through Fermi Level Pinning. Chem. Sci. 2019, 10, 2396.

(12) Frisenda, R.; Janssen, V. A. E. C.; Grozema, F. C.; van der Zant, H. S. J.; Renaud, N. Mechanically Controlled Quantum Interference in Individual α-Stacked Dimers. Nat. Chem. 2016, 8 (12), 1099–1102.

(13) Yang, G.; Sangtarash, S.; Liu, Z.; Li, X.; Sadeghi, H.; Tan, Z.; Li, R.; Zheng, J.; Dong, X.; Liu, J.-Y.; et al. Protonation Tuning of Quantum Interference in Azulene-Type Single-Molecule Junctions. Chem. Sci. 2017, 8 (11), 7505–7509.

(14) Tebikachew, B. E.; Li, H. B.; Pirrotta, A.; Börjesson, K.; Solomon, G. C.; Hihath, J.; Møth-Poulsen, K. Effect of Ring Strain on the Charge Transport of a Robust Norbornadiene-Quadricyclane-Based Molecular Photoswitch. J. Phys. Chem. C 2017, 121 (13), 7094–7110.

(15) Yang, Y.; Gantenbein, M.; Alqorashi, A.; Wei, J.; Sangtarash, S.; Hu, D.; Sadeghi, H.; Zhang, R.; Pi, J.; Chen, L.; et al. Heteroatom-Induced Molecular Asymmetry Tunes Quantum Interference in Charge Transport through Single-Molecule Junctions. J. Phys. Chem. C 2018, 122 (26), 14965–14970.

(16) González, M. T.; Zhao, X.; Manrique, D. Z.; Miguel, D.; Leary, E.; Gucur, M.; Batsanov, A. S.; Rubio-Bollinger, G.; Lambert, C. J.; Bryce, M. R.; et al. Structural versus Electrical Functionalization of Oligo(Phenylene Ethynylene) Diamine Molecular Junctions. J. Phys. Chem. C 2011, 118 (37), 21655–21662.

(17) Gantenbein, M.; Wang, L.; Al-jobory, A. A.; Ismael, A. K.; Lambert, C. J.; Hong, W.; Bryce, M. R. Quantum Interference and Heteroaromaticity of Para- and Meta-Linked Bridged Biphiln Units in Single Molecular Conductance Measurements. Sci. Rep. 2017, 7 (1), 1794.

(18) Klausen, R. S.; Widawsky, J. R.; Su, T. a.; Li, H.; Chen, Q.; Steigerwald, M. L.; Venkataraman, L.; Nuckolls, C. Evaluating Atomic Components in Fluorene Wires. Chem. Sci. 2014, 5 (4), 1561.

(19) Alazary, A.; Leary, E.; Kobatake, T.; Sangtarash, S.; González, M. T.; Jiang, H.-W.; Bollinger, G. R.; Agrait, N.; Sadeghi, H.; Grace, I. Cross-Conjugation Increases the Conductance of Meta -Connected Fluorenones. Nanoscale 2019, 11, 13720.

(20) Yzambart, G.; Rincón-García, L.; Al-Jobory, A. A.; Ismael, A. K.; Rubio-Bollinger, G.; Lambert, C. J.; Agrait, N.; Bryce, M. R. Thermolectric Properties of 2,7-Dipryridylfluorene Derivatives in Single-Molecule Junctions. J. Phys. Chem. C 2018, 122, 27198.

(21) Chen, W.; Li, H.; Widawsky, J. R.; Appayee, C.; Venkataraman, L.; Breslow, R. Aromaticity Decreases Single-Molecule Conductance Junction. J. Am. Chem. Soc. 2014, 136 (3), 918–920.

(22) Guran, A. S.; Rennels, R. A.; Buchwald, S. L. A Simple Catalytic Method for the Conversion of Αryl Bromides to Arylamines. Angew. Chem., Int. Ed. Engl. 1995, 34 (12), 1348–1350.

(23) Louie, J.; Hartwig, J. F. Palladium-Catalyzed Synthesis of Arylamines from Aryl Halides. Mechanistic Studies Lead to Coupling in the Absence of Tin Reagents. Tetrahedron Lett. 1995, 36 (21), 3609–3612.

(24) Abboud, M.; Aubert, E.; Mamane, V. Double N-Arylation Reaction of Polyhalogenated 4,4′-Bipyrindines. Expeditious Synthesis of Functionalized 2,7-Diazacarbazoles. Beilstein J. Org. Chem. 2012, 8, 253–258.

(25) Strieter, E. R.; Buchwald, S. L. Evidence for the Formation and Structure of Palladacycles during Pd-Catalyzed C–N Bond Formation with Catalysts Derived from Bulky Monophosphinobisaryl Ligands. Angew. Chem., Int. Ed. 2006, 45 (6), 925–928.

(26) Durben, S.; Baumgartner, T.; 3,7-Diazadibenzophosphole Oxide: A Phosphorus-Bridged Viologen Analogue with Significantly Lowered Reduction Threshold. Angew. Chem. Int. Ed. 2011, 50 (34), 7948–7952.

(27) Xu, B.; Tao, N. Measurement of Single-Molecule Resistance by Repeated Formation of Molecular Junctions. Science 2003, 301 (5637), 1221–1223.
(28) CRC Handbook of Chemistry and Physics, 91st ed.; Haynes, W. M., Ed.; CRC Press: Boca Raton, FL, 2010.
(29) Ismael, A. K.; Wang, K.; Vezzoli, A.; Al-Khaykanee, M. K.; Gallagher, H. E.; Grace, I. M.; Lambert, C. J.; Xu, B.; Nichols, R. J.; Higgins, S. J. Side-Group-Mediated Mechanical Conductance Switching in Molecular Junc-
tions. Angew. Chem., Int. Ed. 2017, 56 (48), 15378−15382.
(30) Li, X.; Xu, B.; Xiao, X.; Yang, X.; Zang, L.; Tao, N. Controlling Charge Transport in Single Molecules Using Electrochemical Gate. Faraday Discuss. 2006, 131, 111−120.
(31) Lo, W.-Y.; Bi, W.; Li, L.; Jung, I. H.; Yu, L. Edge-on Gating Effect in Molecular Wires. Nano Lett. 2015, 15, 958.
(32) Ferrer, J.; Lambert, C. J.; García-Suárez, V. M.; Manrique, D. Z.; Visontai, D.; Orozaganye, L.; Rodríguez-Ferradas, R.; Grace, I.; Bailey, S. W. D.; Gillemot, K.; et al. GOLLUM: A next-Generation Simulation Tool for Electron, Thermal and Spin Transport. New J. Phys. 2014, 16 (9), No. 093029.
(33) Neaton, J. B.; Hybertsen, M. S.; Louie, S. G. Renormalization of Molecular Electronic Levels at Metal-Molecule Interfaces. Phys. Rev. Lett. 2006, 97 (21), 1−4.
(34) Fiorentini, V.; Baldereschi, A. Dielectric Scaling of the Self-Energy Scissor Operator in Semiconductors and Insulators. Phys. Rev. B: Condens. Matter Mater. Phys. 1995, 51 (23), 17196−17198.
(35) Godby, R. W.; Schlüter, M.; Sham, L. J. Self-Energy Operators and Exchange-Correlation Potentials in Semiconductors. Phys. Rev. B: Condens. Matter Mater. Phys. 1988, 37 (17), 10159−10175.
(36) Loi, F. W.; van Veenendaal, M. A.; Jonkman, H. T.; Sawatzky, G. A. Band Gap, Excitons and Coulomb Interactions of Solid C60. J. Electron Spectrosc. Relat. Phenom. 1995, 72, 83−87.
(37) Hung, Y.; Jiang, J.; Chao, C.; Su, W.; Lin, S. Theoretical Study on the Correlation between Band Gap, Bandwidth, and Oscillator Strength in Fluorene-Based Donor−Acceptor Conjugated Copolymers. J. Phys. Chem. B 2009, 113 (24), 8268−8277.
(38) Garner, M. H.; Li, H.; Chen, Y.; Su, T. A.; Shangguan, Z.; Paley, D. W.; Liu, T.; Ng, F.; Li, H.; Xiao, S.; et al. Comprehensive Suppression of Single-Molecule Conductance Using Destructive σ-Interference. Nature 2018, 558 (7710), 415−419.
(39) Miao, R.; Xu, H.; Skripnik, M.; Cui, L.; Wang, K.; Pedersen, K. G. L.; Leijnse, M.; Pauly, F.; Wärnmark, K.; Meyhofer, E.; et al. Influence of Quantum Interference on the Thermoelectric Properties of Molecular Junctions. Nano Lett. 2018, 18 (9), 5666−5672.
(40) Huang, B.; Liu, X.; Yuan, Y.; Hong, Z.-W.; Zheng, J.-F.; Pei, L.-Q.; Shao, Y.; Li, J.-F.; Zhou, X.-S.; Chen, J.-Z.; et al. Controlling and Observing Sharp-Valleyed Quantum Interference Effect in Single Molecular Junctions. J. Am. Chem. Soc. 2018, 140 (50), 17685−17690.
(41) Roldan, D.; Kaliginedi, V.; Cobis, S.; Kolivska, V.; Bucher, C.; Hong, W.; Ralas, G.; Sandowski, T. Charge Transport in Photoswitchable Dimethylidyrypyrene-Type Single-Molecule Junctions. J. Am. Chem. Soc. 2013, 135 (16), 5974−5977.
(42) Carlotti, M.; Soni, S.; Kumar, S.; Ai, Y.; Sauter, E.; Zharnikov, M.; Chiechi, R. C. Two-Terminal Molecular Memory through Reversible Switching of Quantum Interference Features in Tunneling Junctions. Angew. Chem., Int. Ed. 2018, 57 (48), 15681−15685.
(43) van der Zant, H. S. J.; Valkenier, H.; Hummelen, J. C.; Koole, M.; Thijsen, J. M. Electric-Field Control of Interfering Transport Pathways in a Single-Molecule Anthraquinone Transistor. Nano Lett. 2015, 15 (8), 5569−5573.
(44) Schwarz, F.; Koch, M.; Kastlunger, G.; Berke, H.; Stadler, R.; Venkatesan, K.; Lörtscher, E. Charge Transport and Conductance Switching of Redox-Active Azulene Derivatives. Angew. Chem., Int. Ed. 2016, 55 (39), 11781−11786.