

The Anomalous Effect of Quantum Interference in Organic Spin Filters

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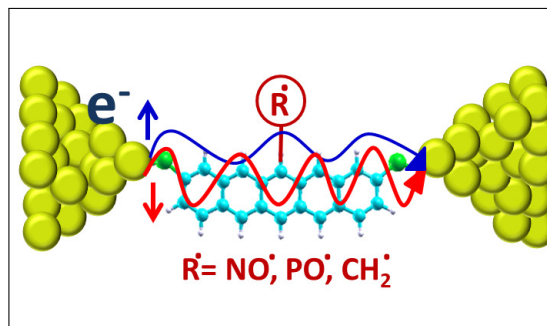
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Abstract

The molecular topology in the single-molecular nano-junctions through which the de Broglie wave propagates plays a crucial role in controlling the molecular conductance. The enhancement and reduction of the conductance due to constructive and destructive Quantum Interference (QI) in para and meta connected molecules respectively has already been well established. Herein, we investigated the influence of QI on spin transport in the molecular junctions containing organic radicals as magnetic centres. The role of the localized spins on the QI as well as on spin filtering capability is investigated employing density functional theory in combination with non-equilibrium Green's function (NEGF-DFT) techniques. Various organic radicals including nitroxide (NO), phenoxy (PO) and methyl (CH_2) radicals attached to the central benzene ring of pentacene with different terminal connections (para and meta) to gold electrodes are examined. Due to more obvious QI effects, para connected pentacene is found to be more conductive than meta one. Surprisingly, on incorporating a radical centre, along with spin filtering, a significant quenching of QI effects is observed which manifests itself in such a way that the conductance of meta coupled radicals is found to be more than para by two orders of magnitude. The decoherence induced by radical centre is analysed and discussed in terms of spin-spin coupling of radical's unpaired electron with the tunneling electrons.

Graphical TOC Entry



On a road towards miniaturization of electronic components, the community has expanded its roots to molecular electronics.^{1,2} Over the past decades, molecular electronics has allied with organic spintronics for various technological applications including high density memory storage, magnetic logic devices, magnetic sensors and so on.^{3,4} Various aspects of molecular spintronics which involves manipulation of electron spin, spin filtering, spin tunneling, spin transport across the interface has been an extensive area of research from the past many years.^{5,6} Among them, spin filters are the devices that enable to produce spin-polarized current by preferentially favoring the transport of electron of one spin orientation over the other. Organic molecules are the most appealing candidates for such components owing to the weak spin-orbit and hyperfine interactions. The use of organic radicals as components of spin filters was first reported by Herrmann and coworkers.^{7,8} The degeneracy splitting of α and β orbitals in organic radicals brings the MO level of one spin orientation closer to the Fermi level of electrodes and thus resulting in higher conductance of one spin type over the other.⁹ Followed by this, Smeu et al. investigated the spin filtering efficiency of various σ and π type radical systems.¹⁰ Shil et al. came up with the use of high spin organic diradical as a component of spin filter.¹¹

The capability to tailor the electron spin with an enhanced control over electron transport in organic molecular materials has become a biggest challenge for molecular spintronics.¹² Of the various quantum effects that can be exploited in phase coherent regime, Quantum Interference (QI) plays a fundamental role in controlling the current through single molecule devices.¹³ QI effects are associated with coherent superposition of de Broglie waves traversing along multiple paths¹⁴ or only frontier molecular orbitals through a molecule.^{15,16} The most striking feature of QI is the appearance of sharp valleyed dip in transmission close to Fermi energy which appears when the phases of the electron traversing along different pathways of the molecule exactly cancel each other, thus leading to destructive quantum interference (DQI) and an obvious decrease in conductance. On the other hand, interference manifests itself in a constructive (CQI) way when the electron waves traversing along different path-

ways are in-phase with each other. The presence/absence of QI-induced dips effects have been demonstrated extensively in recent years in various systems such as cross-conjugated molecules,^{17,18} π -conjugated molecules with different connectivities,¹⁹ effect of introduction of heteroatoms.²⁰ Recently, Tao and coworkers have experimentally probed the charge transport by tuning the QI in para and meta connected molecules with an electrochemical gate voltage.²¹

A single benzene molecule where the electrodes are attached meta with respect to each other is expected to exhibit low conductance due to destructive quantum interference, while para-coupled analog is predicted to be a better conductor.²² This switching from CQI to DQI on changing the connectivity has been established starting from a single benzene molecule to various polycyclic hydrocarbons.^{23,24} But only few reports have described QI effects in systems exhibiting spin polarization.²⁵⁻²⁷ Recently, Li et al. proposed a mechanism for tuning the spin filtering ratio based on QI effects in a nickel based junction.²⁸ Ratner and coworkers have demonstrated that how DQI features can be controlled by addition of a donor or acceptor group to the polyacetylene chain bridging graphene nanoribbons (ZGNR).²⁹ But the role of QI in tuning the overall conductance and the spin filtering efficiency of organic radical molecular junction, which are expected to be the most efficient spin filters has not been explored yet.

In this study we probe the spin polarized transport using organic radicals as spin selective transmission source. Our aim is to investigate the dependence of conductance on the topological structure of the radicals, i.e., how combinations of para and meta couplings affects the spin polarized transport through the organic spin filters. We were prompted to use molecular bridges based on pentacene as the central unit as pentacene has been used as an active semiconducting material in electronic devices, such as organic field effect transistors (OFET).³⁰ The high charge carrier mobility and extended π electron system of pentacene facilitates electron transport and makes this system a promising candidate for single molecule devices. Further, in our preliminary calculations we found that QI effects dominate with

the increasing molecular length. The details can be found in SI where we have analyzed QI effects starting from benzene to pentacene. Here, we examine how the transition from CQI to DQI observed in parent pentacene on moving from para to meta connection is affected by attaching a radical across the pentacene core. Organic radicals including Nitroxide (NO), Phenoxy (PO) and Methyl (CH_2) are attached to central benzene ring of pentacene core, which is coupled to gold electrodes via thiol linkers as shown in Fig. 1.

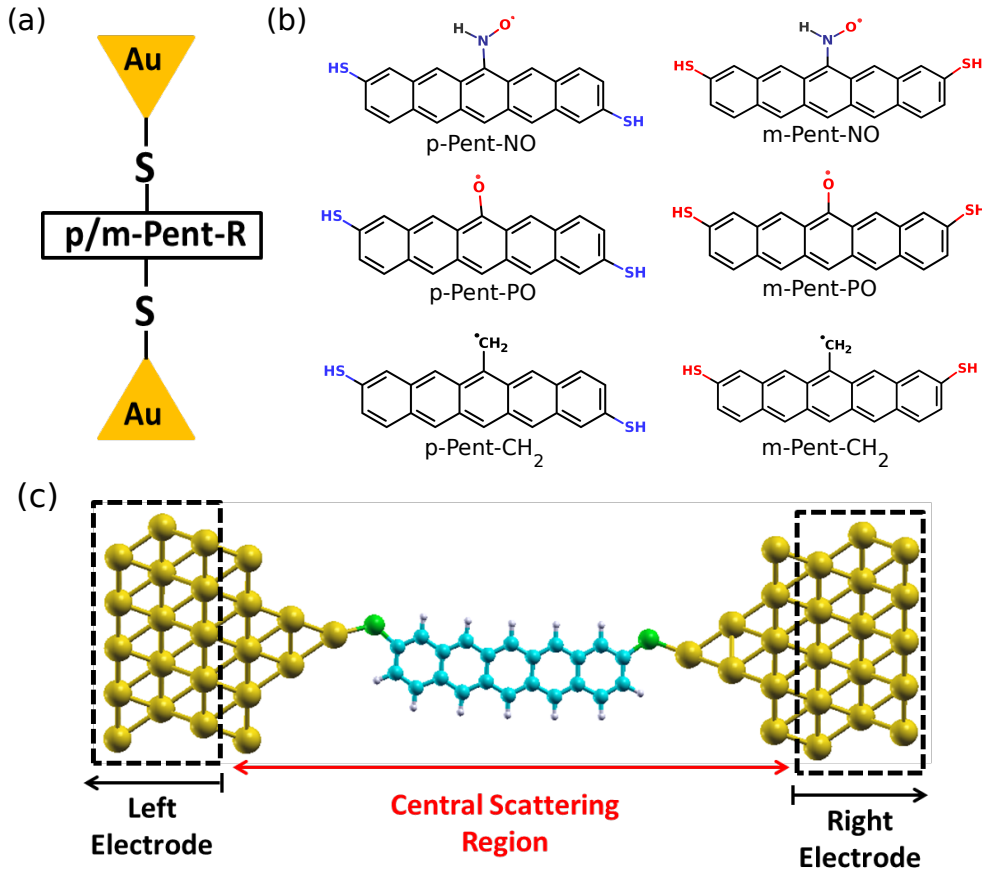


Figure 1: (a) Pentacene based radicals with para (p) and meta (m) coupling of terminal phenyl rings of pentacene to gold electrodes via thiol (S) anchoring group. (b) Molecular structures of investigated pentacene based radicals where Nitroxide (NO), Phenoxy (PO) and Methyl (CH_2) radicals are attached to central phenyl ring of pentacene core. (c) Device setup of Au-Molecule-Au junction with pentacene bridge coupled to Au(111) electrodes via sulphur atoms. The central scattering region consists of conical gold junction with an additional 5×5 layer of Au and central molecule. Semi-infinite left and right electrodes extend upto $z = \pm\infty$.

Experimentally such molecular junctions can be achieved with scanning tunneling microscopy (STM), wherein the target molecule is first adsorbed over the metallic surface of

the electrode and then a mettalic STM tip is brought in contact with it. During the approaching process of STM tip, various possible contacts could be formed, which increase the difficulty for the quantitative comparison between theory and experiments. For a theoretical description, the most common approach employs a combination of non-equilibrium Green's function (NEGF) technique with density functional theory (DFT) to obtain self-consistent Hamiltonian of the system.³¹ Within this DFT based approach, the electron transport through molecular junction is assumed to be coherent and elastic, where inelastic corrections due to electron-phonon interactions are not taken into account. Apart from this, the unavoidable self-interaction errors (SIEs) associated with exchange-correlation functionals of DFT results in small energy gaps between empty and occupied orbitals which causes unphysical large currents and overestimated conductance as compared to experimental values. Despite these limitations, this technique has shown successful applications in designing molecular electronic devices with reliable understandings.³² Here, in the first step, isolated molecules (shown in Fig. 1b) are optimized including the two S-H bonds at both the ends using B3LYP/def2-TZVP method in ORCA.³³ The optimized pentacene-radical systems are then placed between two gold electrodes in a two probe transport structure, consisting of three parts: left electrode, central scattering region and right electrode, as shown in Fig. 1c. The Au electrodes are modelled as Au(111) 5x5 surface with 3 layers in transport direction. The scattering region is composed of molecule connected to the conical gold junction containing four Au atoms on both sides and an additional 5x5 layer to replicate the bulk electrode. Geometry optimization is then performed for Au-Pentacene-Au junction with DFT as implemented in *SIESTA* code, with PBE exchange correlation functional.³⁴ During the optimization, all the gold atoms were fixed in their bulk lattice positions and only molecule is allowed to relax within the junction. In the relaxed junction Au-S distance is found to vary from 2.35 to 2.40 Å.

The electronic charge transport properties are obtained using *TRANSIESTA* code, which employs NEGF technique in combination with DFT (NEGF-DFT).³⁵ This method has been

thoroughly described in literature.^{31,36} To briefly summarize, the retarded Green's function at energy E is obtained by inverting the Hamiltonian matrix as

$$G(E) = ((E + i\eta)S - H - \Sigma_L - \Sigma_R)^{-1} \quad (1)$$

where H and S are the Hamiltonian and the Overlap matrices for molecular region as determined by DFT. $i\eta$ is the infinitesimal imaginary part added in energy. $\Sigma_{L/R}$ are the self-energies that account for the effect of left and right electrode on central scattering region. Self energy is a complex quantity whose real part represents shift of energy levels and the imaginary part accounts for the level broadening matrix:

$$\Gamma_{L,R} = i(\Sigma_{L,R} - \Sigma_{L,R}^\dagger) \quad (2)$$

From these quantities, the electron density matrix is calculated as

$$\rho = \frac{1}{2\pi} \int (f(E, \mu_L) G \Gamma_L G^\dagger + f(E, \mu_R) G \Gamma_R G^\dagger) dE \quad (3)$$

where f is fermi distribution function given by

$$f(E, \mu) = \frac{1}{\exp((E - \mu)/KT) + 1} \quad (4)$$

and μ_L and μ_R are electrochemical potentials of left and right electrode. The quantity of interest here is electron transmission function, $T_\sigma(E)$, which represents the probability with which an electron of spin σ (up/down) and energy E can transmit from the left electrode to right electrode, through central scattering region. According to the Landauer-Büttiker formalism, the transmission function can be calculated as the trace of the product of coupling matrices $\Gamma_{L/R}$ and the Green's function of the central scattering region

$$T_\sigma(E) = \text{Tr}(\Gamma_R G \Gamma_L G^\dagger)_\sigma \quad (5)$$

The zero bias conductance is then obtained as

$$G = G_o T(E_F) \quad (6)$$

where $G_o = 2e^2/h$ is the quantum of conductance. The spin filtering efficiency (SFE) at the Fermi level is then given by

$$SFE = \frac{|T_\alpha(E_F) - T_\beta(E_F)|}{T_\alpha(E_F) + T_\beta(E_F)} \quad (7)$$

For NEGF-DFT calculation, norm-conserving pseudopotentials³⁷ are used to describe the core electrons, double- ζ polarized (DZP) basis set is used to describe the valence electrons of molecular atoms and SZ basis set is used for gold atoms. The generalized gradient approximation (GGA) is used for exchange correlation function. A mesh cutoff of 300 Ry is used with Brillouin zone sampling using 1x1x10 k-points.

The spin resolved transmission spectra obtained for parent pentacene and pentacene based radical systems under study is shown in Fig. 2. For parent pentacene, QI is encountered as dips (marked in Fig. 2) residing between HOMO and LUMO, where *p*-Pent shows a conductance of around 10^{-3} , while owing to DQI *m*-Pent gives a lower conductance of $\sim 10^{-5}$. Further, being a closed shell molecule bearing no magnetic centre, parent pentacene exhibits no spin polarization. However, for radical systems, the α and β transmission spectra differs significantly due to splitting of the degeneracy caused by an unpaired electron. For all the para connected radicals, the sharp dip (marked in Fig. 2), featuring QI of α spin channel appears at ~ 0.30 eV above Fermi level and gives a sharp minima of order of 10^{-7} . However, for meta connected radicals, the QI induced dip of α spin channel occurring at ~ 0.35 eV above Fermi level is of the order of 10^{-6} . The same is valid for QI dip of β spin channel appearing below Fermi level at around -0.40 eV. For both the spin channels, QI dips of meta connected radicals are one order of magnitude higher than their para analogues. The clear reduction of transmission for para connected radicals can also be seen at Fermi level. The zero bias

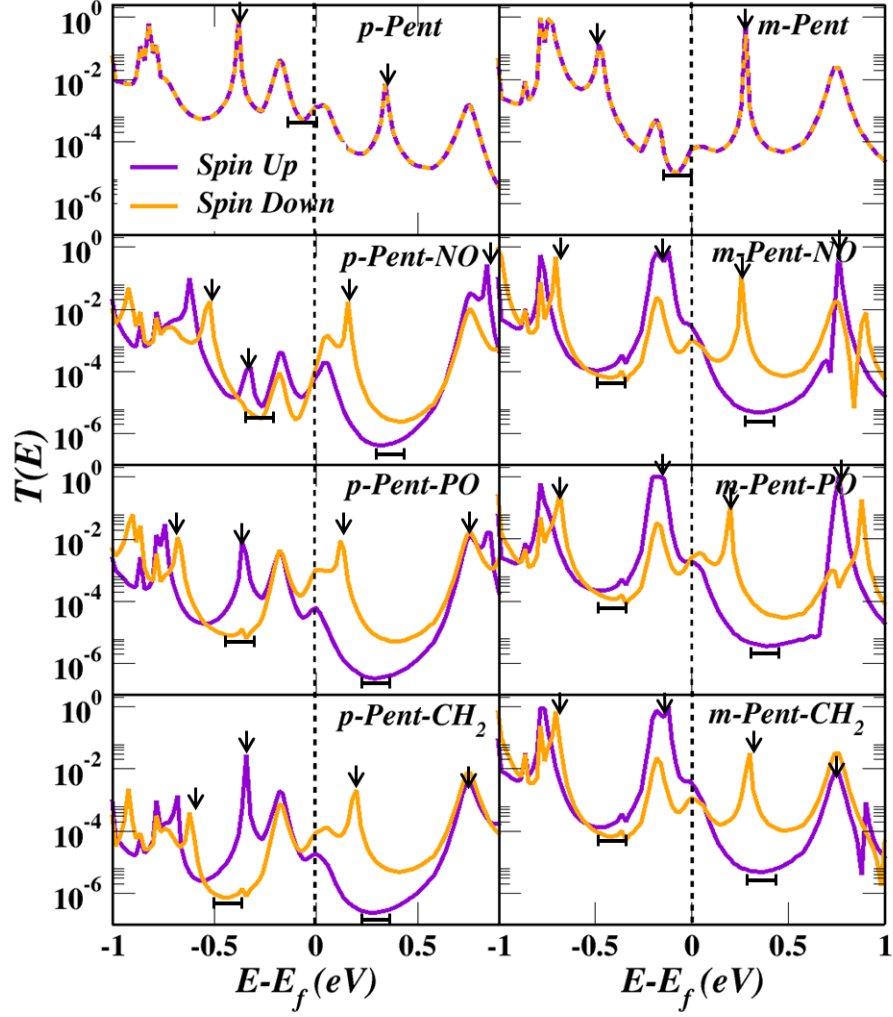


Figure 2: Spin resolved transmission spectra for para and meta connected pentacene (top panel) and pentacene based radicals (NO, PO, CH₂) where α and β spin transmission is denoted by purple and orange respectively. The vertical dotted lines denote the position of Fermi level. The arrows marked over the peaks below and above Fermi level denotes HOMO and LUMO resonance wherein the arrows pointing towards purple peaks denotes α resonance and those towards orange peaks is for β resonance. QI induced dips residing between HOMO and LUMO are also marked for both the spin channels.

conductance illustrated in Table 1 also reveals that switching from para to meta connectivity causes the conductance (G_α and G_β) to drop by two order of magnitude in parent pentacene core. In contrast, for all pentacene based radicals (NO, PO, CH_2), the same operation causes the conductance of both spin channels to increase by two orders of magnitude. Thus, indicating the strong quenching of QI effects observed in non-magnetic pentacene by attached radical moieties, thereby making meta connected radicals more conductive than para ones. This quenching of QI effects can also be seen clearly from sharp decrease in para/meta conductance ratio, which is of the order of 10^1 for parent pentacene, but has decreased to 10^{-2} for NO and CH_2 radicals and 10^{-1} for PO radical. The decrease in para/meta conductance ratio on introducing a radical group that participates in π electron system was also predicted by Herrmann et al.⁸

Table 1: Calculated conductance for α (G_α) and β (G_β) spin channels, total conductance (G_{total}) in units of G_0 and spin filtering efficiency (SFE) for para and meta connected pentacene based radicals.

Molecule	Anchoring	G (G_0)			SFE(%)	para/meta (G_{total})
		G_α	G_β	G_{total}		
Pent	para	1.26×10^{-3}	1.26×10^{-3}	2.52×10^{-3}	0	2.29×10^1
	meta	5.54×10^{-5}	5.38×10^{-5}	1.10×10^{-4}	0.01	
Pent-NO	para	6.19×10^{-5}	1.29×10^{-4}	1.90×10^{-4}	35.14	5.02×10^{-2}
	meta	2.80×10^{-3}	9.89×10^{-4}	3.78×10^{-3}	47.70	
Pent-PO	para	5.90×10^{-5}	9.84×10^{-4}	1.04×10^{-3}	88.60	2.41×10^{-1}
	meta	1.94×10^{-3}	2.36×10^{-3}	4.30×10^{-3}	9.70	
Pent- CH_2	para	1.81×10^{-5}	8.67×10^{-5}	1.04×10^{-4}	65.41	2.20×10^{-2}
	meta	3.56×10^{-3}	1.16×10^{-3}	4.72×10^{-3}	50.80	

Further, this picture is strongly supported by calculated zero-bias conductance corresponding to non-radical species i.e. the hydroxy or methyl derivatives of the radical systems shown in Fig. 1b. The obtained zero bias conductance of para and meta connected non-radical counterparts tabulated in Table 2 is found to be concordant with pentacene i.e. para is more conductive than meta. Thus, supporting our observation that radical unpaired electron is playing an anomalous role in tuning the conductance by introducing decoherence in de Broglie waves traversing along different pathways.

Table 2: Calculated conductance for α (G_α) and β (G_β) spin channels, total conductance (G_{total}) in units of G_o for para and meta connected pentacene based non-radicals.

Molecule	Anchoring Position	G (G_o)			para/meta (G_{total})
		G_α	G_β	G_{total}	
Pent	para	1.26×10^{-3}	1.26×10^{-3}	2.52×10^{-3}	2.29×10^1
	meta	5.54×10^{-5}	5.38×10^{-5}	1.10×10^{-4}	
Pent-NOH	para	1.90×10^{-3}	1.90×10^{-3}	3.80×10^{-3}	4.30×10^1
	meta	4.43×10^{-5}	4.39×10^{-5}	8.82×10^{-5}	
Pent-POH	para	6.23×10^{-3}	6.25×10^{-3}	12.48×10^{-3}	6.21×10^1
	meta	9.79×10^{-5}	10.1×10^{-5}	19.69×10^{-5}	
Pent-CH ₃	para	1.19×10^{-3}	1.19×10^{-3}	2.38×10^{-3}	1.56×10^1
	meta	7.61×10^{-5}	7.62×10^{-5}	15.23×10^{-5}	

To elucidate the origin of the significant difference in para/meta conductance ratio in radical molecular junctions, we first compare the positions of the transmission peaks with the projected density of states (PDOS) peaks which includes density of states of the molecular part only. Fig. 3 reveals a good correspondence between the transmission peaks and molecular PDOS for both the spin channels of *p*-Pent-NO and *m*-Pent-NO, indicating that the former stems from resonating energy levels of the molecule. The dominant resonant peaks arises from HOMO-1, HOMO and LUMO of the molecule. Apart from the resonant peaks, the transmission is also driven by interface states (residing between HOMO and LUMO) which do not resemble to any of the electronic state of the molecule. PDOS projected on left and right electrode (shown in bottom panel of Fig. 3) reveals that these additional transport channels are induced by the coupling between the molecule and the metal electrodes. Such interface-induced states, known as metal-induced gap states (MIGS) have already been observed experimentally³⁸ as well as theoretically.^{39,40} The PDOS analysis of molecular region, left and right electrode for all the other radical systems is shown in SI.

Along with the MIGS, the coupling between the electrode and molecule will also modify the molecular orbitals (MOs) through rehybridization. To visualize these modified MOs and there energy levels, molecule projected self-consistent Hamiltonian (MPSH) eigenstates were calculated by projecting the self-consistent Hamiltonian onto the Hilbert space spanned by

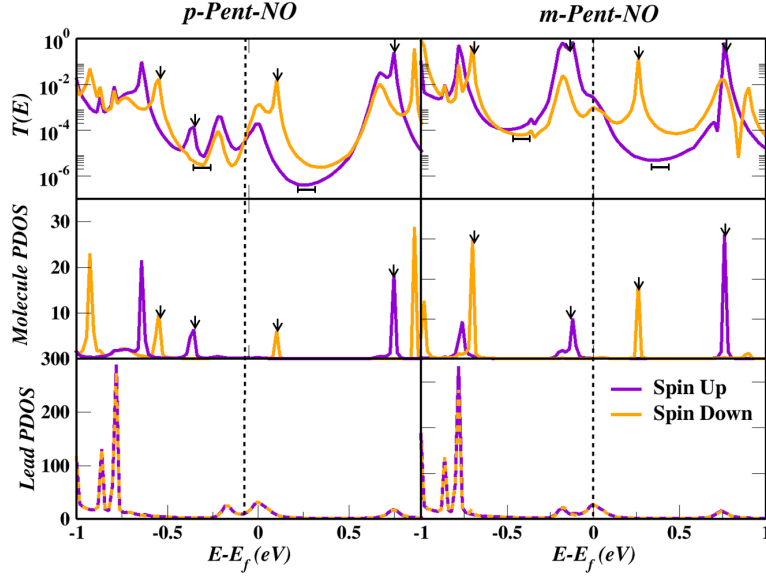


Figure 3: Calculated transmission spectra (top panel), Molecular PDOS (middle panel), DOS projected on Au electrode (bottom panel) for junction containing *p*-Pent-NO and *m*-Pent-NO. The α and β spin transmission is shown by purple and orange respectively. The arrows marked over the peaks denotes HOMO and LUMO resonance.

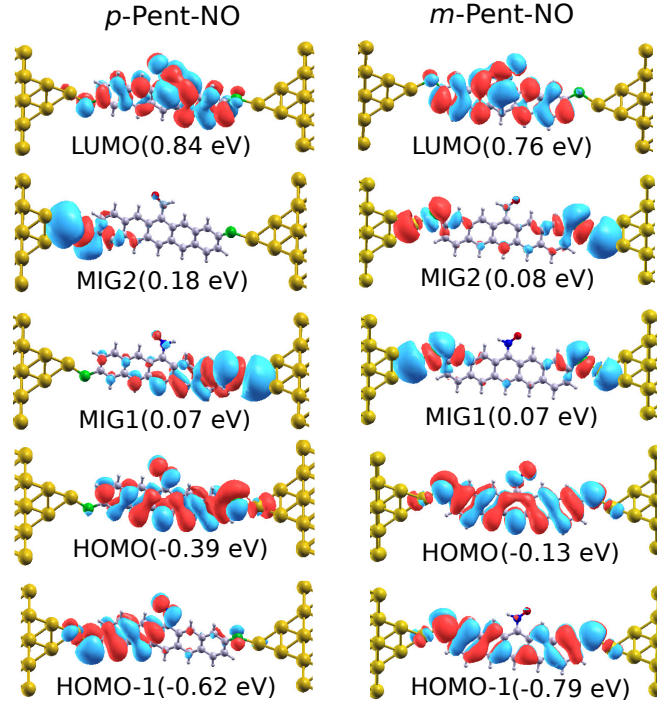


Figure 4: MPSH states, spatial distribution and energy eigenvalues of frontier MOs and metal-induced gap states (MIGS) located in the energy range of -1eV to +1 eV for α spin channel of *p*-Pent-NO and *m*-Pent-NO.

the basis functions of the molecule.⁴¹ Here, MPSH eigenstates represent the renormalized molecular energy levels in the presence of surrounding electrodes. From the spatial distribution of the MPSH states of α spin channel shown in Fig. 4, one can find that for *m*-Pent-NO, the delocalization of frontier MOs and MIGS covers well both the terminal sulphur atoms, indicating a strong terminal coupling. However, for *p*-Pent-NO, the terminal coupling is relatively weaker. Although, LUMO of *p*-Pent-NO is completely delocalized over the molecular backbone and the terminal sulphur atoms, but its contribution has been replaced by two MIGS states which appears close to the Fermi energy. The significance of orbital density on terminal atoms in determining the charge transport through a device was also proposed by Ernzerhof and Rocheleau.⁴² The low contribution of LUMO to electron transport is further assured by Transmission Eigenchannels (EC), shown in Fig. 5, which resembles closely to HOMO and MIGS and indicates that in case of *p*-Pent-NO the EC is either blocked by radical centre or is partially conductive due to weak terminal coupling. In contrast, *m*-Pent-NO exhibits fully conductive channels. The spatial distribution of MPSH states and ECs for β spin channel (shown in SI) also reveals higher conductance of *m*-Pent-NO than *p*-Pent-NO.

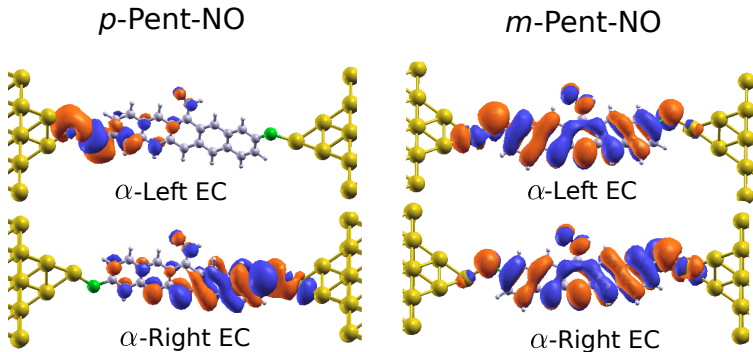


Figure 5: Transmission Eigenchannels (EC) for α spin channel of *p*-Pent-NO and *m*-Pent-NO. ECs of *p*-Pent-NO are either blocked by radical centre or by terminal thiol group.

Such breakdown of interference rules where the conductance of meta coupled molecules can be high is also witnessed in few other reports also.^{43,44} A recent report by Garner et al. hypothesized that if the σ system of the molecule is more strongly coupled to the electrodes than the π system, DQI effects can be masked by σ -conductance.^{45,46} But here for the radical

system, due to the presence of unpaired electron residing in π -orbital, σ -systems cannot be the dominant contributor to the transport. In addition, the quenching of QI effects has also been extensively discussed in terms of the dephasing introduced by electron-phonon interactions.⁴⁷ Here, in radical transport junctions, we speculate that it could be the elastic scattering of incoming electrons which might induces a phase breaking process and thus introduces decoherence/dephasing in pathways of de Broglie waves. Further, due to spin-spin coupling of unpaired electron with tunneling electrons, there may be instances where a single pathway containing radical moiety dominates instead of interfering multiple pathways, which results in quenching of QI effects.

In summary, we realized the anomalous behaviour of QI stemming from localized radical spins in molecular junctions. The anomaly is based on strong quenching of QI effects by radical centres yielding higher conductance for radicals in meta configuration which is in complete contrast to parent non-magnetic molecule. Along with the spin polarized current, the unpaired electron on radical site introduces decoherence in pathways of de Broglie waves, thereby quenching the QI effects. Although further investigations are required to reveal the mechanism underlying the quenching of QI effects on attaching a radical, our findings provide a potential approach to facilitate future design attempts of single localized spin molecular junctions.

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Supporting Information Available: Quantum interference in parent acenes, Molecular PDOS analysis, Energy level diagram and HOMO-LUMO gap for molecules in gas phase

and in junction, MPSH eigenstates and transmission eigenchannels.

This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Hirose, K.; Kobayashi, N. *Quantum transport calculations for nanosystems*; Jenny Stanford Publishing, 2014.
- (2) Tao, N. J. *Nanoscience And Technology: A Collection of Reviews from Nature Journals*; World Scientific, 2010.
- (3) Rocha, A. R.; Garcia-Suarez, V. M.; Bailey, S. W.; Lambert, C. J.; Ferrer, J.; Sanvito, S. Towards molecular spintronics. *Nat. Mater.* **2005**, *4*, 335–339.
- (4) Mannini, M.; Pineider, F.; Sainctavit, P.; Danieli, C.; Otero, E.; Sciancalepore, C.; Talarico, A. M.; Arrio, M.-A.; Cornia, A.; Gatteschi, D. et al. Magnetic memory of a single-molecule quantum magnet wired to a gold surface. *Nat. Mater.* **2009**, *8*, 194–197.
- (5) Dediu, V. A.; Hueso, L. E.; Bergenti, I.; Taliani, C. Spin routes in organic semiconductors. *Nat. Mater.* **2009**, *8*, 707–716.
- (6) Barraud, C.; Seneor, P.; Mattana, R.; Fusil, S.; Bouzehouane, K.; Deranlot, C.; Graziosi, P.; Hueso, L.; Bergenti, I.; Dediu, V. et al. Unravelling the role of the interface for spin injection into organic semiconductors. *Nat. Phys* **2010**, *6*, 615–620.
- (7) Herrmann, C.; Solomon, G. C.; Ratner, M. A. Organic radicals as spin filters. *J. Am. Chem. Soc.* **2010**, *132*, 3682–3684.
- (8) Herrmann, C.; Solomon, G. C.; Ratner, M. A. Designing organic spin filters in the coherent tunneling regime. *J. Chem. Phys.* **2011**, *134*, 224306.
- (9) Lach, S.; Altenhof, A.; Tarafder, K.; Schmitt, F.; Ali, M. E.; Vogel, M.; Sauther, J.; Oppeneer, P. M.; Ziegler, C. Metal–organic hybrid interface states of a ferromagnet/organic

- semiconductor hybrid junction as basis for engineering spin injection in organic spintronics. *Adv. Funct. Mater* **2012**, *22*, 989–997.
- (10) Smeu, M.; DiLabio, G. A. Calculations of Electron Transport through Simple π - and σ -Type Radicals. *J. Phys. Chem. C* **2010**, *114*, 17874–17879.
 - (11) Shil, S.; Bhattacharya, D.; Misra, A.; Klein, D. J. A high-spin organic diradical as a spin filter. *Phys. Chem. Chem. Phys.* **2015**, *17*, 23378–23383.
 - (12) Su, T. A.; Neupane, M.; Steigerwald, M. L.; Venkataraman, L.; Nuckolls, C. Chemical principles of single-molecule electronics. *Nat. Rev. Mater.* **2016**, *1*, 16002.
 - (13) Li, X.; Tan, Z.; Huang, X.; Bai, J.; Liu, J.; Hong, W. Experimental investigation of quantum interference in the charge transport through molecular architectures. *J. Mater. Chem. C* **2019**, *7*, 12790–12808.
 - (14) Hansen, T.; Solomon, G. C.; Andrews, D. Q.; Ratner, M. A. Interfering pathways in benzene: An analytical treatment. *J. Chem. Phys* **2009**, *131*, 194704.
 - (15) Taniguchi, M.; Tsutsui, M.; Mogi, R.; Sugawara, T.; Tsuji, Y.; Yoshizawa, K.; Kawai, T. Dependence of single-molecule conductance on molecule junction symmetry. *J. Am. Chem. Soc.* **2011**, *133*, 11426–11429.
 - (16) Lambert, C. Basic concepts of quantum interference and electron transport in single-molecule electronics. *Chem. Soc. Rev.* **2015**, *44*, 875–888.
 - (17) Alanazy, A. e. a. Cross-conjugation increases the conductance of meta-connected fluoronones. *Nanoscale* **2019**, *11*, 13720–13724.
 - (18) 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*, 305–309.

- (19) Manrique, D. Z.; Huang, C.; Baghernejad, M.; Zhao, X.; Al-Owaedi, O. A.; Sadeghi, H.; Kaliginedi, V.; Hong, W.; Gulcur, M.; Wandlowski, T. et al. A quantum circuit rule for interference effects in single-molecule electrical junctions. *Nat. Commun* **2015**, *6*, 1–8.
- (20) Sangtarash, S.; Sadeghi, H.; Lambert, C. J. Exploring quantum interference in heteroatom-substituted graphene-like molecules. *Nanoscale* **2016**, *8*, 13199–13205.
- (21) Li, Y.; Buerkle, M.; Li, G.; Rostamian, A.; Wang, H.; Wang, Z.; Bowler, D. R.; Miyazaki, T.; Xiang, L.; Asai, Y. et al. Gate controlling of quantum interference and direct observation of anti-resonances in single molecule charge transport. *Nat. Mater.* **2019**, *18*, 357–363.
- (22) Arroyo, C. R.; Tarkuc, S.; Frisenda, R.; Seldenthuis, J. S.; Woerde, C. H.; Eelkema, R.; Grozema, F. C.; Van Der Zant, H. S. Signatures of quantum interference effects on charge transport through a single benzene ring. *Angew. Chem* **2013**, *52*, 3152–3155.
- (23) Markussen, T.; Stadler, R.; Thygesen, K. S. The relation between structure and quantum interference in single molecule junctions. *Nano Lett.* **2010**, *10*, 4260–4265.
- (24) Berritta, M.; Manrique, D. Z.; Lambert, C. J. Interplay between quantum interference and conformational fluctuations in single-molecule break junctions. *Nanoscale* **2015**, *7*, 1096–1101.
- (25) Valli, A.; Amaricci, A.; Brosco, V.; Capone, M. Interplay between destructive quantum interference and symmetry-breaking phenomena in graphene quantum junctions. *Phys. Rev. B* **2019**, *100*, 075118.
- (26) Bergfield, J. P.; Solomon, G. C.; Stafford, C. A.; Ratner, M. A. Novel quantum interference effects in transport through molecular radicals. *Nano Lett.* **2011**, *11*, 2759–2764.
- (27) Pal, A. N.; Li, D.; Sarkar, S.; Chakrabarti, S.; Vilan, A.; Kronik, L.; Smogunov, A.;

- Tal, O. Nonmagnetic single-molecule spin-filter based on quantum interference. *Nat. Commun* **2019**, *10*, 1–8.
- (28) Li, D.; Banerjee, R.; Mondal, S.; Maliyov, I.; Romanova, M.; Dappe, Y. J.; Smogunov, A. Symmetry aspects of spin filtering in molecular junctions: Hybridization and quantum interference effects. *Phys. Rev. B* **2019**, *99*, 115403.
- (29) Saraiva-Souza, A.; Smeu, M.; Zhang, L.; Souza Filho, A. G.; Guo, H.; Ratner, M. A. Molecular spintronics: Destructive quantum interference controlled by a gate. *J. Am. Chem. Soc.* **2014**, *136*, 15065–15071.
- (30) Lee, S.; Jo, G.; Kang, S.-J.; Wang, G.; Choe, M.; Park, W.; Kim, D.-Y.; Kahng, Y. H.; Lee, T. Enhanced Charge Injection in Pentacene Field-Effect Transistors with Graphene Electrodes. *Adv. Mater* **2011**, *23*, 100–105.
- (31) Taylor, J.; Guo, H.; Wang, J. Ab initio modeling of quantum transport properties of molecular electronic devices. *Phys. Rev. B* **2001**, *63*, 245407.
- (32) Kim, W. Y.; Choi, Y. C.; Min, S. K.; Cho, Y.; Kim, K. S. Application of quantum chemistry to nanotechnology: electron and spin transport in molecular devices. *Chem. Soc. Rev* **2009**, *38*, 2319–2333.
- (33) Neese, F. The ORCA program system. *Wiley Interdiscip. Rev. Comput. Mol. Sci* **2012**, *2*, 73–78.
- (34) Soler, J. M.; Artacho, E.; Gale, J. D.; García, A.; Junquera, J.; Ordejón, P.; Sánchez-Portal, D. The SIESTA method for ab initio order-N materials simulation. *J. Phys. Condens. Matter* **2002**, *14*, 2745.
- (35) Stokbro, K.; Taylor, J.; Brandbyge, M.; Ordejon, P. TranSIESTA: a spice for molecular electronics. *Ann. N. Y. Acad. Sci* **2003**, *1006*, 212–226.

- (36) Datta, S. Nanoscale device modeling: the Green’s function method. *Superlattices Microstruct* **2000**, *28*, 253–278.
- (37) Troullier, N.; Martins, J. L. Efficient pseudopotentials for plane-wave calculations. *Phys. Rev. B* **1991**, *43*, 1993.
- (38) Zeng, C.; Li, B.; Wang, B.; Wang, H.; Wang, K.; Yang, J.; Hou, J.; Zhu, Q. What can a scanning tunneling microscope image do for the insulating alkanethiol molecules on Au (111) substrates? *J. Chem. Phys* **2002**, *117*, 851–856.
- (39) Crljen, Ž.; Grigoriev, A.; Wendin, G.; Stokbro, K. Nonlinear conductance in molecular devices: molecular length dependence. *Phys. Rev. B* **2005**, *71*, 165316.
- (40) Malen, J. A.; Doak, P.; Baheti, K.; Tilley, T. D.; Segalman, R. A.; Majumdar, A. Identifying the length dependence of orbital alignment and contact coupling in molecular heterojunctions. *Nano Lett.* **2009**, *9*, 1164–1169.
- (41) Stokbro, K.; Taylor, J.; Brandbyge, M.; Mozos, J.-L.; Ordejon, P. Theoretical study of the nonlinear conductance of Di-thiol benzene coupled to Au (1 1 1) surfaces via thiol and thiolate bonds. *Comput. Mater. Sci* **2003**, *27*, 151–160.
- (42) Rocheleau, P.; Ernzerhof, M. Molecular conductance obtained in terms of orbital densities and response functions. *J. Chem. Phys* **2009**, *130*, 184704.
- (43) Xia, J.; Capozzi, B.; Wei, S.; Strange, M.; Batra, A.; Moreno, J. R.; Amir, R. J.; Amir, E.; Solomon, G. C.; Venkataraman, L. et al. Breakdown of interference rules in azulene, a nonalternant hydrocarbon. *Nano Lett.* **2014**, *14*, 2941–2945.
- (44) Li, S.; Yu, H.; Schwieter, K.; Chen, K.; Li, B.; Liu, Y.; Moore, J. S.; Schroeder, C. M. Charge Transport and Quantum Interference Effects in Oxazole-Terminated Conjugated Oligomers. *J. Am. Chem. Soc.* **2019**, *141*, 16079–16084.

- (45) 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*, 415–419.
- (46) 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*, 4436–4442.
- (47) Maassen, J.; Zahid, F.; Guo, H. Effects of dephasing in molecular transport junctions using atomistic first principles. *Phys. Rev. B* **2009**, *80*, 125423.