Redox-Induced Gating of the Exchange Interactions in a Single Organic Diradical

Rocco Gaudenzi,† Joeri de Bruijckere,† Daniel Reta,‡,¶ Ibério de P. R. Moreira,‡ Concepció Rovira,§ Jaume Veciana,§ Herre S. J. van der Zant,† and Enrique Burzurí*,†

†Kavli Institute of Nanoscience, Delft University of Technology, Lorentzweg 1, 2628 CJ Delft, The Netherlands
‡Departament de Ciència de Materials i Química Física & Institut de Química Teòrica i Computacional (IQTCUB), Universitat de Barcelona, C/Martí i Franquès 1, 08028 Barcelona, Spain
§Institut de Ciència de Materials de Barcelona (ICMAB-CSIC) and CIBER-BBN, Campus de la UAB, 08193, Bellaterra, Spain

*Supporting Information

ABSTRACT: Embedding a magnetic electroactive molecule in a three-terminal junction allows for the fast and local electric field control of magnetic properties desirable in spintronic devices and quantum gates. Here, we provide an example of this control through the reversible and stable charging of a single all-organic neutral diradical molecule. By means of inelastic electron tunnel spectroscopy we show that the added electron occupies a molecular orbital distinct from those containing the two radical electrons, forming a spin system with three antiferromagnetically coupled spins. Changing the redox state of the molecule therefore switches on and off a parallel exchange path between the two radical spins through the added electron. This electrically controlled gating of the intramolecular magnetic interactions constitutes an essential ingredient of a single-molecule \(\sqrt{\text{SWAP}}\) quantum gate.

KEYWORDS: molecular electronics, organic radicals, quantum information, spintronics, diradicals

Fast, reversible, and local control of magnetic properties of molecular systems is sought after as a potential path for molecule-based spintronic devices\(^1-3\) and quantum information processing.\(^4-6\) The control of the intramolecular exchange coupling could allow, for instance, for the realization of a single-molecule quantum gate.\(^7-10\) One way to achieve such control at the single-molecule level is to embed a magnetic electroactive molecule in a solid-state junction and use the gate electrode to change its magnetic properties through a form of spin-electric coupling.\(^7,11-17\) Traditional candidates are single-molecule magnets (SMMs), the magnetic parameters of which can be modulated with the addition of a charge\(^18-20\) or through magnetoelastic effects.\(^21\)

A promising alternative to SMMs is offered by all-organic radical molecules, where the magnetism arises from the unpaired spins of carbon atoms.\(^22,23\) The simplicity of their spin structure and the absence of metal centers have proven to yield robust molecular junctions\(^24-26\) and potentially allow overcoming the limitations inherent to SMMs owing to low spin–orbit coupling and hyperfine interaction. However, the existing experimental examples have shown either a relatively small electric control over the exchange coupling\(^26\) or a reduction of the molecule to a closed-shell system with no unpaired spins.\(^27\)

Here, we report the reversible and stable reduction of a neutral diradical molecule in a three-terminal device, by means of a gate electrode. Inelastic electron tunneling spectroscopy (IETS) in the two stable redox states shows that the added electron magnetically couples to the two radical spins, preserving their open-shell character, while changing the magnetic state of the molecule from a singlet to a doublet state with three unpaired electrons. This ability to reversibly switch on the exchange couplings between the added electron and the two radical spins could form the base for a \(\sqrt{\text{SWAP}}\) quantum gate.\(^7,28,29\)

RESULTS AND DISCUSSION

The molecule we use is a neutral 2,4,6-hexakis-(pentachlorophenyl)mesitylene diradical molecule,\(^30\) hereafter PTM-based diradical, schematically shown in Figure 1. It is made of three methyl carbon atoms connected via a central benzene ring. Two of these C atoms are methyl radicals with unpaired electrons, while the third binds a H that closes the
The resulting molecule is a two-spin magnetic system. Two chlorinated phenyl rings attach and surround each methyl carbon in a propeller-like conformation, as seen in Figure 1. The single-molecule junction is formed when a single molecule by measuring the dc current through the junction as a function of bias voltage \( V \), and extracting the differential conductance \( dI/dV \) at each step in the \( s \) value increases from 0 to 1/2. The value \( V_{\text{off}} \) marks the gate voltage at which the added spin stably resides (on) the molecule.

We probe the excitation spectrum of an individual diradical molecule by measuring the dc current \( I \) through the junction as a function of bias voltage \( V \) and extracting the differential conductance \( dI/dV \). Each step in the \( dI/dV \) spectrum signals the opening of an inelastic electron current channel via the excited state of the molecule with energy \( E \). Following the \( s \) value as a function of magnetic field \( B \) at fixed gate voltage \( V \), different step heights can be explained by a bias-dependent tuning of the magnetic couplings between the added electron and the redox center and, with that, switching on and off the magnetic couplings between the added electron and the two radial spins. For each state inelastic electron tunneling spectroscopy (IETS) is performed (yellow electron).

Figure 1. Organic diradical spin system. (a) Scanning electron microscope (SEM) false color image of a Au nanowire on top of an Al2O3/AuPd gate. (b) Structure and magnetism schematics of the neutral diradical and reduced form of the diradical. The red dots and the dashed lines mark the radicals and the exchange interactions, respectively. A gate voltage allows reversibly adding a spin (blue dot) onto the redox center and, with that, switching on and off the magnetic couplings between the added electron and the two radial spins. For each state inelastic electron tunneling spectroscopy (IETS) is performed (yellow electron). (c) Differential conductance (red) and corresponding redox center spin (blue) as a function of \( V \).

Figure 2. Magnetic spectrum of the neutral diradical. (a) Differential conductance \( (dI/dV) \) spectra of the neutral diradical molecular junction at different magnetic fields and at a fixed gate voltage \( V = -2.3 \) V. An excitation step at \( -4.65 \) mV splits into three substeps under applied magnetic field. The superimposed dashed lines are fits using the model in ref 33. (b) \( d^2I/dV^2 \) color map showing the splitting as a function of \( V \) and \( B \). (c) Schematics of a two-spin system with exchange coupling \( J_{12} \), confined between two gold electrodes. (d) Spin spectrum and allowed transitions for a two-spin system with antiferromagnetic \( J_{12} \).
The excitations at +20 and +25 mV correspond therefore to the transitions |D(+1/2)⟩ → |D(−1/2)⟩. Figure 3c shows this magnetic field evolution. From this set of excitations we deduce that the magnetic spectrum consists of a doublet ground-state multiplet |D(−1)⟩, giving rise to the observed Kondo effect. A doublet excited multiplet |D(1)⟩ and a quartet excited multiplet |Q⟩, as shown in Figure 3d (see Supporting Information Section 1 for more details). The excitations at +20 and +25 mV correspond therefore to the transitions |D(−1)⟩ → |D(1)⟩ and |D(−1)⟩ → |Q⟩, respectively.

The spectrum we obtain at this gate voltage can be hosted by a system like the one depicted in Figure 3c, where the two unpaired spins couple via exchange interactions. A single molecule in a three-terminal device allows for the exchange of electrons between the redox center and the electrodes. The redox center turns on two of the three magnetic couplings, J13 and J23, which, in turn, influence the time evolution of the two-spin system. This fast, electrically controlled switching of the intramolecular magnetic interactions constitutes the essential ingredient of the quantum SWAP gate detailed in refs 9, 10, and 28, where two alternative read-out mechanisms are also proposed.

CONCLUSIONS

In summary, we show that incorporating an organic neutral diradical molecule in a three-terminal device allows for...
reversible and stable charging from the neutral state to its reduced state by means of a gate voltage. By performing IETS on both redox states, we find that the electron added onto the redox center magnetically couples to the radical spins, thereby driving the two-spin singlet into a three-spin doublet ground state (with three exchange couplings). In this way, by controlling the occupation of the redox center, the exchange interactions between the two radical spins and the added electron are switched on and off. Due to the large coupling to the leads, this switching takes place within subpicosecond time scales.

METHODS

Details on the Molecule. The studied molecule is a neutral 2,4,6-trichloro-α,α,α’,α’’,α’’,α’’’-hexakis(pentachlorophenyl)mesitylene diradical prepared as previously reported.10 Electron spin resonance spectroscopy in frozen solutions containing the molecules shows an S = 1 high-spin ground state, indicative of ferromagnetic exchange interactions between the two radical carbons in the molecule.

Junction Preparation. The molecular solution is prepared in a water-free glovebox environment. A small amount of molecular powder is dissolved in nitrogen-saturated dichlorobenzene to a concentration of approximately 0.5 mM.

Experimental Conditions. All the measurements reported here are performed in a high-vacuum chamber (P < 5 × 10⁻⁶ mbar) of a dilution refrigerator (~70 mK). A built-in superconducting magnet can be used to apply magnetic fields up to 9 T.

Electrical current I measurements are performed applying a dc bias voltage V to the source and drain gold electrodes and/or a dc gate voltage V_g while recording I. The differential conductance dI/dV is obtained by taking the numerical derivative of I.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.7b01578.

Additional details about the fits of the magnetic excitation spectra and the DFT calculations (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: E.BurzuriLinares@tudelft.nl.

ORCID

Daniel Reta: 0000-0003-0000-9892
Jaume Veciana: 0000-0003-1023-9923
Enrique Burzuri: 0000-0001-7906-7192

Present Address

School of Chemistry, The University of Manchester, Oxford Road, Manchester, M13 9PL United Kingdom.

Notes

The authors declare no competing financial interest.

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REFERENCES


