Proposal for all-electrical spin manipulation and detection for a single molecule on boron-substituted graphene

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All-electrical writing and reading of spin states attract considerable attention for their promising applications in energy-efficient spintronics devices. Here we show, based on rigorous first-principles calculations, that the spin properties can be manipulated and detected in molecular spintfaces, where an iron tetraphenyl porphyrin (FeTPP) molecule is deposited on boron-substituted graphene (B-G). Notably, a reversible spin switching between the $S = 1$ and $S = 3/2$ states is achieved by a gate electrode. We can trace the origin to a strong hybridization between the Fe-$d_z$ and B-$p_z$ orbitals. Combining density functional theory with nonequilibrium Green’s function formalism, we propose an experimentally feasible 3-terminal setup to probe the spin state. Furthermore, we show how the in-plane quantum transport for the B-G, which is non-spin polarized, can be modified by FeTPP, yielding a significant transport spin polarization near the Fermi energy (> 10% for typical coverage). Our work paves the way to realize all-electrical spintronics devices using molecular spintfaces.

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Achieving size-compact and energy-efficient control and detection of magnetism are paramount for the development of future spintronic devices. Using single molecules as quantum units opens a new pathway to reach the physical limits of miniaturization. Currently, spintronics devices are mainly operated via either an external magnetic field (e.g., polarization devices3,4 or electric currents (e.g., spin-transfer torque devices5,6), which are both highly power-consuming. More recently, electric-field manipulation of magnetism has been proposed7 and has been extensively studied in bulk and 2D materials8,9. However, the full-electrical programmable reading and writing of magnetism at the single-molecule level are still unsolved problems.

It is now well known that in molecular spintronics most of the phenomena are driven by the interface, which leads to the concept of spinferries10,11. Ideally, one aims at the control and detection12 at the individual molecule limit. Therefore, single molecules adsorbed on surfaces have become an ideal testbed to study the interaction of molecules with surfaces, the surrounding environment, and responses to external chemical stimuli. In particular, controlling molecular spin states by chemical functionalization of the surface allows for creating molecular devices with novel functionalities12. During the last decade, particular attention has been focused on the substitution of carbon atoms in the graphene lattice by heteroatoms leading to new physical and chemical properties13–16. In nitrogen-substituted graphene (N-G), scanning tunneling microscopy (STM)17 showed a dramatic change of the local electronic structure around the nitrogen depending on its surroundings. This suggests that the N-G may be used to tune the properties of adsorbed molecules, and indeed, the adsorption on top of the N site of N-G can modify the molecular levels by shifts18, charge transfer and level splitting19, or change of spin state20.

Alternatively, boron (B) is also suitable for direct incorporation into the graphene honeycomb lattice, resulting in at least an effective p-doping21,22. However, unlike N-G, the B-substituted graphene-based molecular interfaces have been much less investigated in both theory and experiment. Therefore, detailed insight into the interaction between molecule and B-graphene (B-G) at the atomic scale is currently lacking.

In this Letter, we propose the B-G substrate as an ideal spinfer for molecular magnets: We demonstrate, using density functional theory (DFT), the electrical tuning and probing of spin states in a single-molecule device adsorbed on B-G. We choose iron tetraphenyl porphyrin (FeTPP), which has different magnetic ground states on graphene and Au surfaces23,24. We find that a single FeTPP molecule on B-G allows for a reversible spin transition between $S = 1$ and $S = 3/2$ controlled by an external electrical gate. This effect is driven by a strong and tunable hybridization between FeTPP and B-G. Combining DFT with Keldysh Green’s function techniques, we further propose an experimentally feasible 3-terminal transport setup to probe the transport spin polarization (TSP). In contrast to pristine and N-G substrates, the in-plane spin transport for the B-G is significantly modified by the FeTPP with a TSP of more than 10% for a typical coverage. Our work shows a promising application to all-electrical writing and reading magnetization states in molecular spintronics devices.

The transport setup (see Fig. 1a.) consists of graphene with two contacts (L,R) and a charge-plane mimicking the back-gate underneath, and an Au tip electrode above the FeTPP. This setup allows for two possible current flows: The in-plane transport from left (L) to the right (R) graphene electrodes ($I_{\parallel}$), and the out-of-plane from L/R to Tip ($I_\perp$). This is feasible in state-of-the-art STM25,26, where the back-gate charge is capacitively controlled by a gate voltage. The gate charge enables “writing”, while the $I_{\parallel}$ or $I_\perp$ currents...
The proposed 3-terminal device allows an out-of-plane (perpendicular graphene with a model STM tip and a charge back-gate plane. The transport of the device enables studying the dependence of the spectroscopic state on the environment of the Fe atom that gives a ground state either in a low-spin state with \( S = 0 \), high-spin state with \( S = 2 \), or an intermediate spin state \( S = 1 \). In general, the ground states of the free FeTPP is \( S = 1 \) state with \( ^3A_{2g} \) having the occupancy of the 3d shell \( (d_{xy})^2(d_{xz})^2(d_{yz})^1 \), the last two orbitals being degenerate as a consequence of the molecular symmetry (Fig. 1). Figure 1 shows schematic sketches of spin-polarized projected densities of states (PDOS) of the FeTPP on doped graphene (without the STM tip). It has been demonstrated through combined STM experiments and DFT calculations that the molecule keeps the same electronic structure as in the gas phase after being deposited on pristine graphene due to weak molecule-substrate coupling, and the HOMO state originates essentially from the Fe \( d_{xz} \) spin-down orbital. In the case of N-G, the molecule remains \( S = 1 \) with the same spin configuration, while a clear downshift of the electronic spectrum is observed in good agreement with experiments. Surprisingly, a significant change happens when the molecule is attached to B-G: the total magnetic moment varies from 2 to 3 \( \mu_B \) with a change of oxidation state from Fe\( ^{2+} \) to Fe\( ^{3+} \). This variation is due to a chemical absorption nature as reflected in the calculated binding energy of 2.9 eV. On pristine graphene and N-G we tested different FeTPP orientations and positions, such as hollow and bridge site, showing little difference in electronic and magnetic properties. Meanwhile, the strong coupling between FeTPP and B-G leads to a clear preference for the Fe atom on top of the B atom at a distance \( d_{\text{Fe-Gr}} \) of 2.7 Å. The B-G leads to a redistribution of electron density, where the electron-deficient boron sites provide the enhanced binding capability. The Mulliken charge analysis shows that upon adsorption 0.7 electrons are transferred from Fe to B-G. In particular, the spin-down channel of Fe\( d_{xz} \), which was initially occupied, becomes an empty state just above \( E_F \) due to strong hybridization between Fe\( d_{xz} \) and B\( p_z \) by perfect orbital symmetry matching, as shown in Fig. 2. Such strong hybridization is also reflected in the charge density difference plotted in Fig. 2. Furthermore, the strong interaction also introduces a small spin-polarization of the B atom and the carbon atoms at the spinterface. For more details, see Sup-

**FIG. 1:** (a) Schematic view of a single FeTPP absorbed in substituted graphene with a model STM tip and a charge back-gate plane. The proposed 3-terminal device allows an out-of-plane (perpendicular graphene with a model STM tip and a charge back-gate plane. The transport of the device enables studying the dependence of the spectroscopic state on the environment of the Fe atom that gives a ground state either in a low-spin state with \( S = 0 \), high-spin state with \( S = 2 \), or an intermediate spin state \( S = 1 \). In general, the ground states of the free FeTPP is \( S = 1 \) state with \( ^3A_{2g} \) having the occupancy of the 3d shell \( (d_{xy})^2(d_{xz})^2(d_{yz})^1 \), the last two orbitals being degenerate as a consequence of the molecular symmetry (Fig. 1). Figure 1 shows schematic sketches of spin-polarized projected densities of states (PDOS) of the FeTPP on doped graphene (without the STM tip). It has been demonstrated through combined STM experiments and DFT calculations that the molecule keeps the same electronic structure as in the gas phase after being deposited on pristine graphene due to weak molecule-substrate coupling, and the HOMO state originates essentially from the Fe \( d_{xz} \) spin-down orbital. In the case of N-G, the molecule remains \( S = 1 \) with the same spin configuration, while a clear downshift of the electronic spectrum is observed in good agreement with experiments. Surprisingly, a significant change happens when the molecule is attached to B-G: the total magnetic moment varies from 2 to 3 \( \mu_B \) with a change of oxidation state from Fe\( ^{2+} \) to Fe\( ^{3+} \). This variation is due to a chemical absorption nature as reflected in the calculated binding energy of 2.9 eV. On pristine graphene and N-G we tested different FeTPP orientations and positions, such as hollow and bridge site, showing little difference in electronic and magnetic properties. Meanwhile, the strong coupling between FeTPP and B-G leads to a clear preference for the Fe atom on top of the B atom at a distance \( d_{\text{Fe-Gr}} \) of 2.7 Å. The B-G leads to a redistribution of electron density, where the electron-deficient boron sites provide the enhanced binding capability. The Mulliken charge analysis shows that upon adsorption 0.7 electrons are transferred from Fe to B-G. In particular, the spin-down channel of Fe\( d_{xz} \), which was initially occupied, becomes an empty state just above \( E_F \) due to strong hybridization between Fe\( d_{xz} \) and B\( p_z \) by perfect orbital symmetry matching, as shown in Fig. 2. Such strong hybridization is also reflected in the charge density difference plotted in Fig. 2. Furthermore, the strong interaction also introduces a small spin-polarization of the B atom and the carbon atoms at the spinterface. For more details, see Sup-

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A method to achieve full-electrical writing of the magnetization states at the single-molecule level is attractive and promising, corresponding to a reversible spin manipulation. The coupling between FeTPP and B-G at the interface leads to an empty $d_{z^2}$ orbital very close to the Fermi energy. It turns out that external stimuli may easily tune it: We apply a gate due to the tunability of the interaction between FeTPP and B-G. Increasing the gate charge to $g = -2$ yields a difference compared to $g = -1$, while the spin state is not tunable with $g > 0$ where it remains $S = 3/2$. Although the case of FeTPP may seem specific for B-G, the proposed mechanism is quite generic, and a similar approach should be possible when the frontier molecular orbital is close to $E_F$.

For the electrical read-out of the single molecular spin states, we first consider the out-of-plane spin transport from the L/R graphene electrode to the Au tip electrode. Figure [S1] and b show the spin-dependent transmission functions with $g = 0$ and $g = -1$. We observe the transmissions exhibit a dip near the Fermi level due to the vanishing DOS in graphene at $g = 0$, and it shifts to below $E_F$ when $g = -1$. We find almost fully spin-polarized current near $E_F$ for both $g = 0$ and $g = -1$, as shown in Fig. [S2] and d. The scanning tunneling spectroscopy ($dI/dV$ curve), probing the energy dependence of $T_{\perp}$, should easily distinguish the two different spin states at $g = 0$ and $g = -1$, while shot noise measurements yielding $T_{\perp}$ would not. The STM tip may furthermore be used actively to manipulate the molecules and control their spin.

Next, we consider the in-plane transport where the electrical current runs through the graphene $xy$ plane (from L to R). Since we use pristine graphene as L/R-electrodes, the Fermi energy is positioned at the Dirac point for $g = 0$. Without FeTPP, the N-G and B-G systems retain the pristine sp² hybridization and conjugated planar structure, leading to a non-spin-polarized behavior. This is in contrast to the spin-polarized current reported in the case of B-substituted graphene nanoribbons[32]. To understand how the transport properties of the substrates are modified through the molecular interfacial hybridization effects, we plot in Fig. [S2]-f the corresponding transmission functions with FeTPP adsorbed
on B-G at $g = 0$ and $g = -1$. Interestingly, our calculations show that when $g = 0$, the spin-up and spin-down molecular orbitals hybridize very differently with the substrate, resulting in clear spin-dependent transport behavior (Fig. 3). For the spin-down channel (red lines), the transmission becomes almost linear at $E < E_F$ (similar to pristine B-G), which is significantly different from the rather broadened feature without FeTPP. On the other hand, the transmission for the spin-up (black lines) resembles B-G transport without molecule. As a result, we get a large transport spin polarization (TSP $\parallel$), defined as $TSP \parallel = (T_{\uparrow} - T_{\downarrow})/(T_{\uparrow} + T_{\downarrow})$, effect near the Fermi energy where it furthermore changes sign. For the applied $g$-periodic transport cell the TSP $\parallel$ reach values beyond 10% which is significant when we consider the corresponding inter-molecular distance of $\sim 16$ Å, below typical coverages.

On the other hand, the spin-up and spin-down transmission functions are almost degenerate when $g = -1$, resulting in the absence of TSP $\parallel$ (Fig. 3b). Such an on-off TSP via gating could be probed, e.g., in shot noise experiments. These results open an attractive route for the design of full-electrical writing and reading techniques in molecule/2D materials heterostructures.

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