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### Giant amplification of tunnel magnetoresistance in a molecular junction: Molecular spin-valve transistor

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Amplification of tunnel magnetoresistance by gate field in a molecular junction is the most important requirement for the development of a molecular spin valve transistor. Herein, we predict a giant amplification of tunnel magnetoresistance in a single molecular spin valve junction, which consists of Ru-bis-terpyridine molecule as a spacer between two ferromagnetic nickel contacts. Based on the first-principles quantum transport approach, we show that a modest change in the gate field that is experimentally accessible can lead to a substantial amplification (320%) of tunnel magnetoresistance. The origin of such large amplification is attributed to the spin dependent modification of orbitals at the molecule-lead interface and the resultant Stark effect induced shift in channel position with respect to the Fermi energy. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4873396]

When a thin semiconducting (or insulating) spacer acts as a tunnel barrier between two ferromagnetic contacts, the resistance in the circuit depends upon the relative orientation of the magnetization of the contact layers.<sup>1–3</sup> Usually, circuit resistance in this device changes from minimum resistance for the parallel spin configuration (PC) to maximum resistance for the antiparallel spin configuration (APC) between the contacts resulting in a spin-valve effect<sup>4</sup>—the foundation behind modern high density data storage device. The relative change in resistance between the PC and the APC in such a device is known as the tunnel magnetoresistance (TMR), which is much higher than the magnetoresistance observed in a spin-valve device with a metallic spacer. This has made the TMR device much more appealing as a read head sensor for the high density data storage. With the strong demand for downsizing the TMR device and the tremendous progress in nanotechnology in recent years, it has now been possible to demonstrate the TMR effect in a single molecular junction.<sup>5–10</sup> The advantages of low cost production, chemical flexibility, self-assembly process, tunable electronic structure, and long spin lifetime in organic molecules make them viable spacer candidates for a TMR device.

For example, using a spin-polarized scanning tunneling microscope, researchers have already demonstrated spin valve effect with a tunnel magnetoresistance as high as 60% in a hydrogen phthalocyanine molecule as a spacer between two ferromagnetic cobalt contacts.<sup>5</sup> In another instance, Bagrets et al. have demonstrated negative TMR of 50% in the same hydrogen phthalocyanine molecule using a combination of ferromagnetic and antiferromagnetic electrodes.<sup>6</sup> In a pioneering attempt, researchers have recently fabricated a Ni/1,4-benzenedithiol/Ni spin-valve junction using the break junction technique.<sup>7,8</sup> They reported a very high magnetoresistance as predicted from theory.<sup>11–13</sup> Until now, only two-terminal, molecular spin-valve (MSV) junctions have received major attention.<sup>5–15</sup> Achieving additional control of TMR in such a molecular junction by a gate field is the prerequisite for a spin-valve transistor.<sup>16</sup>

In this Letter, we predict giant amplification (320%) of TMR by gate field in a molecular spin valve junction, which consists of a Ru-bis-terpyridine (RBT) molecule as a spacer between two ferromagnetic nickel contacts. Our firstprinciples quantum transport calculations show a bias dependent variation in TMR with a peak value of 350% at 0.8 V in the absence of gate field. A modest change in the gate field from 0 V/A to 0.4 V/A, which is experimentally accessible, leads to a significant amplification in the peak value of TMR to 1470% at 0.3 V. We have unambiguously identified the root cause for such amplification, which is attributed to the gate field induced increase in majority spin current in the PC at low bias arising from the shift in participating frontier molecular orbitals (MOs) levels towards the Fermienergy; minority spin current does not exhibit appreciable change with gate field in the same bias range. In the case of APC, both majority and minority spin currents are not affected by gate field at low bias. Orbital analysis indicates that the hybridized orbitals at the interface play a key role in determining the spin dependent current in the device.

The molecular spin valve device that we have investigated is shown in Fig. 1. The thiolate (-S) anchoring groups are used to attach the RBT molecule between two ferromagnetic nickel (111) electrodes. The choice of RBT molecule is prompted by experimental measurement of charge transport in the RBT molecular junction.<sup>17</sup> The molecular geometry is fully optimized within density functional theory that uses a posteriori B3LYP hybrid exchange-correlation functional.<sup>18</sup> The LANL2DZ effective core potential basis set,<sup>19</sup> which includes scalar relativistic effects, is used to describe the heavy atoms such as Ruthenium and Nickel; a triple valance zeta Gaussian basis function (6-311G\*) is used for the rest of the atoms in the device. A tight convergence criterion  $(10^{-8})$ a.u. for energy,  $10^{-6}$  a.u. for both maximum and root-mean square electron density) with ultra fine grid for numerical integration is used during our self consistent calculations. The interfacial distance between sulfur and the nearest nickel surface of the lead is 2.2 Å, which is obtained by minimizing the repulsive interaction within the spin unrestricted density functional theory.<sup>20</sup> This real space approach allows us to

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FIG. 1. Schematic diagram of a molecular spin-valve transistor.

construct the retarded spin polarized Green's function  $(G^{\sigma})$ of the open device  $^{21-24}$  by dividing it into two parts: (a) the active scattering region that consists of the molecular complex together with a finite number of nickel atoms from the lead giving the Hamiltonian matrix of dimension  $958 \times 958$ for each spin component, and (b) the rest of the electrode on each side that is assumed to retain its bulk (3D) property; 3D leads have been found<sup>23</sup> to better represent the experimental features. The  $G^{\sigma}$  is evaluated self-consistently for each applied bias point. To mimic the gate field, we have included a dipole interaction term  $(\vec{\epsilon_g} \cdot \sum_i \vec{r}(i))$  to the core Hamiltonian during self-consistent electronic structure calculation.<sup>25</sup> This permits us to include both first and higher order Stark effects. Then we recourse to a coherent spin conserved tunneling approach developed in Ref. 15 to calculate the spin dependent current of the device.

The results for bias dependent spin polarized current as a function of gate field for PC and APC are presented in Fig. 2; the APC is found to be energetically more stable (~0.03 eV in the absence of gate field) than the PC. Several interesting features are noticeable. First, irrespective of the applied  $\varepsilon_g$ , as in a typical spin-valve device, the current for the PC ( $I_{PC}$ ) is found to be higher than the current for the APC ( $I_{APC}$ ). In the absence of  $\varepsilon_g$  (Fig. 2(a)),  $I_{PC}$  increases steadily for a bias up to ~0.5 V beyond which it promptly transitions to a higher conductance state; however, the



FIG. 2. Current  $(I_{sd})$ -voltage  $(V_{sd})$  characteristics in a Ru-bis-terpyridine molecular tunnel junction for PC and APC at different gate fields: (a)  $\varepsilon_g = 0.0 \text{ V/Å}$ , (b)  $\varepsilon_g = 0.1 \text{ V/Å}$ , (c)  $\varepsilon_g = 0.3 \text{ V/Å}$ , (d)  $\varepsilon_g = 0.4 \text{ V/Å}$ .

transition in  $I_{APC}$  is much more gradual and occurs at a higher bias (~1.0 V). We term the bias value where  $I_{PC}$  suddenly changes to a higher value as the threshold voltage  $(V_{th})$ . As we increase  $\varepsilon_g$  (Fig. 2), we find that the  $V_{th}$  gets closer to 0 V. Unlike the  $I_{PC}$ , the  $I_{APC}$  does not change with  $\varepsilon_g$  at a small bias. But at a higher bias (>1.0 V), both the  $I_{PC}$ and  $I_{APC}$  decrease steadily with the increase in  $\varepsilon_g$ . Interestingly,  $I_{PC}$  shows a negative differential resistance (NDR) behavior at a higher bias, which is much more prominent for  $\varepsilon_g = 0.4 \text{ V/Å}$  (Fig. 2(d)). To understand the distinct features of  $I_{PC}$  and  $I_{APC}$  in Fig. 2, we analyze the  $\alpha$  and  $\beta$ components of the total spin currents ( $I_{\alpha}$  and  $I_{\beta}$ ) for PC and APC. In the case of PC, the major contribution to the total current comes from the  $\alpha$  states. For APC, as expected, both  $I_{\alpha}$  and  $I_{\beta}$  are almost same for bias up to ~0.25 V, beyond which  $\alpha$  current dominates the  $\beta$  current. To quantify this spin-selective resistive property of the device, we examine the spin-injection coefficient,  $\eta = (I_{\alpha} - I_{\beta})/(I_{\alpha} + I_{\beta})$ , for PC and APC at a small bias (0.1 V) with different gate field. In the case of APC,  $\eta = 0$  at a small bias as  $I_{\alpha} = I_{\beta}$ . For PC,  $\eta$ increases steadily with  $\varepsilon_g$  as shown in Fig. 3(a); a very high spin injection efficiency of 98% is achieved at low bias with  $\epsilon_g = 0.4 \, V/Å.$ 

Next, we turn our focus to TMR, which is calculated using the common optimistic definition:  $^{11,12}$  TMR =  $(I_{PC} - I_{APC})/I_{APC}$ . Fig. 3(b) summarizes the bias and  $\varepsilon_{\varrho}$  dependent TMR values. In the absence of  $\varepsilon_g$ , TMR increases from 60% at 0.2 V to reach a peak value of 350% at 0.8 V and then gradually drops to 20% at 2.0 V. Since achieving atomic level control at the molecule-lead interface is a daunting challenge from the experimental perspective, we have varied the interfacial distance between the molecule and lead to gauge the junction dependent effect on TMR. For the two representative interfacial distances (1.9 Å and 2.5 Å), a similar bias dependent variation of TMR is noted. When we apply the gate field, the variation of TMR with  $V_{sd}$  follows a similar trend, but the magnitude of the peak value of TMR enhances significantly. For example, when we change the gate field from 0.0 V/Å to 0.4 V/Å, the peak value of TMR increases from 350% to 1470% (320% amplification), and the position of the peak shifts from 0.8 V to 0.3 V.

In order to gain a deeper understanding of the observed giant amplification in TMR, we examine the spin polarized transmission for PC and APC. First, we focus on the low bias transmission. In the case of PC (Fig. 4(a)), for  $\varepsilon_g = 0 \text{ V/Å}$ , the transmission peaks from  $\alpha$  states are closer



FIG. 3. (a) Spin-injection coefficient ( $\eta$ ) for the parallel spin configuration as a function of gate field ( $\varepsilon_g$ );  $\eta$  is zero for the antiparallel spin configuration at low bias. (b) Bias ( $V_{sd}$ ) dependent TMR as a function of gate field.



FIG. 4. Gate field dependent spin polarized transmission at  $V_{sd} \sim 0.3 \text{ V}$  for the parallel (PC) and the anti-parallel (APC) spin configuration. (a)  $\varepsilon_g = 0.0 \text{ V/Å}$ , (b)  $\varepsilon_g = 0.4 \text{ V/Å}$ , (c)  $\varepsilon_g = 0.0 \text{ V/Å}$ , (d)  $\varepsilon_g = 0.4 \text{ V/Å}$ . Notation:  $\alpha$  stands for spin up and  $\beta$  stands for spin down states.

to the Fermi energy than the beta states resulting in a higher current from the  $\alpha$  states than the  $\beta$  states. As we increase the gate field from 0 V/Å to 0.4 V/Å (Fig. 4(b)), the transmission peak position for the  $\alpha$  state at 0.26 eV is shifted to 0.12 eV bringing it much closer to the Fermi energy. In contrast, the  $\beta$  states do not show a strong response to  $\varepsilon_g$ . This explains why we see a much higher current from the  $\alpha$  state than the  $\beta$ state with the increase of  $\varepsilon_g$ , which is also reflected from the  $\varepsilon_{g}$  dependent  $\eta$  values (Fig. 3(a)). In the case of APC, at zero bias, both  $\alpha$  and  $\beta$  states transmissions are identical as expected. A small discrepancy between  $\alpha$  and  $\beta$  states in Fig. 4(c) is due to small bias induced asymmetry. When we increase the  $\varepsilon_{g}$  (Fig. 4(d)), though height of the transmission peak (at 0.48 eV) from the  $\beta$  state increases and the transmission peak height at 0.41 eV from the  $\alpha$  state decreases, no change in transmission values are found within the close vicinity of the Fermi-energy. This leads to no appreciable change in APC current at a low bias (Fig. 2). For higher bias (~1.8 V), at  $\varepsilon_g = 0.4 \text{ V/Å}$ , the transmission peaks position for PC and APC (Figs. 5(a) and 5(b)) move away from the Fermi energy for both  $\alpha$  and  $\beta$  states. A closer inspection of Fig. 5(a) reveals that the height of the transmission peaks for both  $\alpha$  and  $\beta$  states in PC decreases at  $V_{sd} = \sim 1.8$  V resulting in a NDR feature in current. However, in the case of APC (at  $V_{sd} = \sim 1.8 \text{ V}$ ), the transmission peak from  $\alpha$  state increases;  $\beta$  states are not affected. This leads to an increase in current for the APC with the increase of  $V_{sd}$ .

Since the unoccupied frontier MOs are found to provide the spatial path for transmission of spin polarized electrons from source to drain in all cases (Figs. 4 and 5), we analyze the lowest unoccupied molecular orbital (LUMO)



FIG. 5. Transmission plots for (a) PC and (b) APC at bias ~1.8 V and  $\varepsilon_g = 0.4 \text{ V/Å}$ . (c) Gate field dependent Stark shift associated with the LUMO for PC and APC. Notation:  $\alpha$  stands for spin up and  $\beta$  stands for spin down states.

for  $\alpha$  and  $\beta$  states in PC and APC for the active scattering region. In the case of PC, for the  $\alpha$  state, at  $\varepsilon_g = 0.0 \text{ V/Å}$ , in addition to the ruthenium d-state at the octahedral position, which mediates the coupling between the two perpendicular ter-pyridine complexes, the nickel d, s and sulfur p states contribute to the LUMO at a low bias; in contrast, for the  $\beta$ state, the LUMO has a very small d and s components of nickel lead. This explains why we see a much higher transmission from the  $\alpha$  state near the Fermi energy (Fig. 4(a)). In the case of APC, for both  $\alpha$  and  $\beta$  states, nickel d as well as s, and sulfur p states at one interface only contribute to the LUMO, resulting in a smaller transmission (Fig. 4(c)) near the Fermi energy. When we increase  $\varepsilon_g$  from 0.0 V/Å to 0.4 V/Å, in the case of PC, the electron distribution in the molecule for the  $\alpha$  state localizes along the direction of gate field resulting in a shift in energy level toward the Fermi energy. For  $\beta$  states, the response to  $\varepsilon_g$  is found to be much weaker. In the case of APC, for  $\varepsilon_g = 0.4 \text{ V/Å}$  (Fig. 4(d)), we find the electron distribution for both  $\alpha$  and  $\beta$  states to localize in the direction of  $\varepsilon_g$ . Increasing the  $V_{sd}$  for PC (Fig. 5(a)) leads to localization of electron distribution along the direction of current carrying axis causing the transmission peak heights to decrease. However, in the case of APC, interface states (p-component of sulfur and small d-component of nickel) contribute to the LUMO for the  $\alpha$ state with the increase of bias. To quantify the orbitals' response to the gate field, we examine the Stark shift  $(\epsilon(\varepsilon_g) - \epsilon(\varepsilon_g = 0))$  corresponding to  $\alpha$  and  $\beta$ -LUMO for PC and APC (Fig. 5(c)). Fig. 5(c) shows that  $\alpha$  state exhibits much stronger Stark shift with increase in gate field in comparison to  $\beta$  state for PC confirming the distinct spin dependent transmission; for APC, both the  $\alpha$  and  $\beta$  states show same Stark shift as expected.

In conclusion, we have demonstrated a molecular spin valve transistor by showing giant amplification of tunneling magnetoresistance in a single molecular junction via gate field. Our first-principles quantum transport calculations reveal that a modest change in the gate field from 0 to 0.4 V/Å, which is experimentally accessible,<sup>26</sup> can lead to a 320% change in TMR. Despite the challenges, the recent experimental demonstration of single molecular transistors<sup>26,27</sup> suggest that our prediction of a molecular spin valve transistor would open up experimental initiative toward its practical realization.

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