

Fano-Resonance-Driven Spin-Valve Effect Using Single-Molecule Magnets**

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One of the distinctive features of waves is the interference phenomenon between waves that are propagating along different paths. Fano resonance, which occurs by the quantum mechanical interference between discrete and continuum states, is a manifestation of the wave-nature of electrons,^[1] which has been observed in various systems from atomic spectrum^[2] to conductance in nanoscale devices.^[3] Recently its fundamental importance in nanoscience has been discussed in an extensive Review article.^[4] For example, its usefulness for novel applications was addressed through theoretical studies showing that ultrafast DNA sequencing can be accomplished by deciphering the unique Fano-resonance patterns of each nucleotide.^[5]

On the other hand, single-molecule magnetism, which originates from unpaired electron spins with anisotropy, has attracted great attention because of its potential applications to molecular-scale spintronics, namely molecular spintronics.^[6] As a result, diverse magnetic molecules have been synthesized and characterized,^[7] stimulating new ideas for the development of novel spintronic devices.^[8] Typically a single-molecule magnet (SMM) is chemically attached to two metallic electrodes to form a metal-molecule-metal junction, and spin-dependent currents are driven across the junction.^[6a,b] Though the small size of these molecules provides a great advance toward the miniaturization of electronic devices, it also gives rise to a lack of reproducibility owing to highly sensitive electronic coupling in the atomic-level contact.^[9]

To circumvent such a contact problem, we propose using spin-dependent Fano resonance. When discrete spin states of an SMM are coupled to the continuum bands of a nano-

conductor, the conductance of the device exhibits a strong spin-dependent Fano-resonance pattern. As a proof of concept, we studied a carbon nanotube (CNT) decorated with magnetic molecules through π - π stacking, whose spin-dependent conductance can be controlled by means of an external magnetic field. We believe that this is the origin of the large magnetoresistance observed in recent experiments.^[10] Because such a device would not require direct metal-molecule contacts as well as ferromagnetic electrodes, it offers a practical way to realize true molecular spintronic devices, as demonstrated by Ruben, Wernsdorfer, and co-workers in Ref. [10].

Figure 1 shows a schematic drawing of the spin-valve device we studied, consisting of two SMMs and an armchair

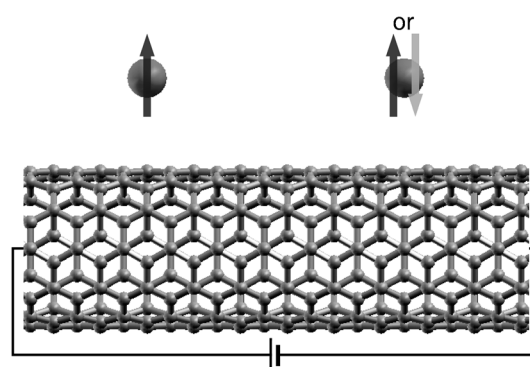


Figure 1. A schematic drawing of a spin-valve device based on a carbon nanotube decorated with single-molecule magnets. The relative spin-orientation of the molecules can be manipulated using an external magnetic field.

(6,6) CNT. Spin-dependent electrical currents are triggered as a finite bias voltage is applied across the CNT. Spin-polarized quantum transport through the device was calculated using the POSTRANS software package, incorporating the non-equilibrium Green function (NEGF) method and density functional theory (DFT).^[11] Methods for transmission calculations and transmission eigenchannel analysis are explained in the Supporting Information. Electron interaction were treated with the standard Perdew–Burke–Ernzerhof (PBE) functional. We adopted the Troullier–Martins-type pseudo-potentials^[12] and single-zeta polarization basis sets (if not mentioned explicitly). A mesh cutoff of 200 Ry was used. We note that the PBE functional is not appropriate to describe non-covalent interactions such as π - π stacking. Hence, we simply put molecules (optimized as isolated) on the CNT surface with a fixed distance (3.4 Å) without post-structural

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relaxations. Inclusion of the dispersion interaction may affect the local structure and the distance. However, it does not change our conclusion, which is drawn mainly from qualitative discussions.

We first used a paramagnetic vanadocene molecule, which has a spin of $3/2$. Although this molecule is not an SMM, it provides a simple model to investigate the concept of spin-dependent Fano resonance, once its spin orientation has purposely been fixed. Later, we applied the concept to a real SMM. The molecule stacked on the CNT surface provides localized and spin-polarized states, while the CNT acts as a conducting channel. When they are coupled, electron transmission through the CNT was influenced by the molecular states. As a result, the transmission values were significantly lower at the corresponding molecular energy levels, which is clearly shown in Figure 2A. The peaks in the upper panel represent energy levels of the highest occupied molecular orbital (HOMO), HOMO–1, and HOMO–2. Electron transmission as a function of energy (in the lower panel) also shows dips at the exact same energy with the peaks in the density of states (DOS). The transmission curve with multiple dips was well reproduced by the one-dimensional Fano–Anderson formula as shown in Figure 2A, indicating that the dips originate from Fano resonance.^[4,13] More details are explained in the Supporting Information. Interestingly, all the peaks and the corresponding dips in Figure 2A appear solely for spin-up electrons, because the vanadocene molecule has only spin-up states within the given energy range. Therefore, the transmission dips are evidently a consequence of spin-dependent Fano resonance.

The reason that the transmission drops from two to one can be understood as follows. Metallic pristine CNTs have two conducting channels in the vicinity of its Fermi energy, as the calculated transmission values at the region far from the resonance energies are two for each spin. The resonance, however, partially blocks both channels, yielding fractional transmission values. We analyzed the contribution of individual channels to the transmission dips using transmission eigenchannel analysis,^[14] details of which can be found in the Supporting Information. Interestingly, the sum of the two fractional values becomes one owing to the symmetry of the wave functions involved. In fact, it is consistent with a recent experiment showing that the Fano resonance induced by a defect in a metallic multiwall CNT caused the same amount of conductance drop as in this case (Figure 7 in Ref. [15]).

Further evidence of Fano resonance can be found from the interference pattern of wave functions of the CNT device. Eigenfunctions of the two transmission eigenchannels at the energy of the transmission dip by the HOMO–2 for spin-up electrons are shown in Figure 2B. One eigenchannel (upper panel) is strongly localized at the molecule, as well as at the left half of the CNT, resulting in zero transmission ($T=0$). On the contrary, the other channel (lower panel) at the same energy retains a delocalized feature of original CNT orbitals, leading to perfect transmission ($T=1$). For spin-down electrons, however, there is no molecular state in that energy range, so the transmission of the CNT is not changed. Thus, we confirmed that the spin-dependent Fano resonance causes the dips in the transmission curve.

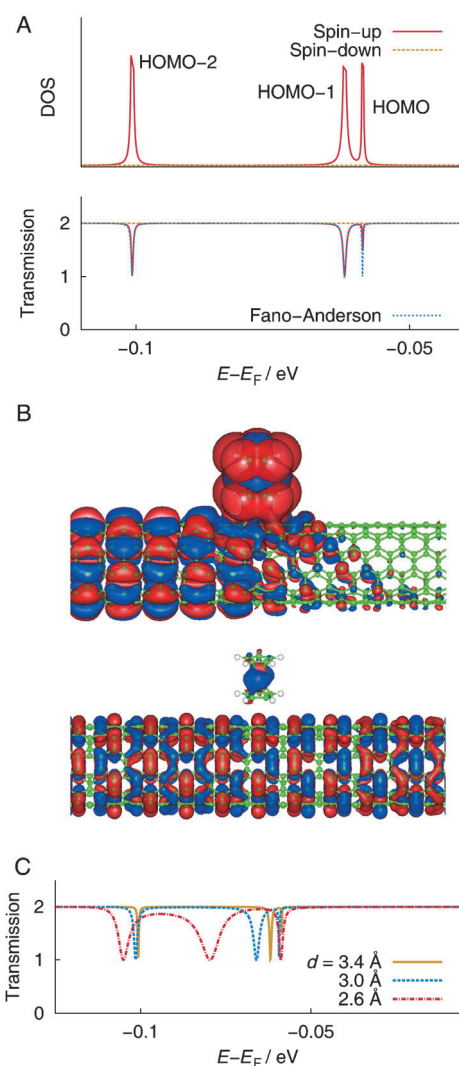


Figure 2. Evidence of the Fano resonance for the vanadocene-CNT system. A) DOS (top) and transmission (bottom). Transmission dips appear at the energies of the molecular states. The blue dotted line is produced by the Fano–Anderson formula. B) Eigenfunctions of two transmission eigenchannels at the energy of the transmission dip ($E-E_F = -0.1$ eV). The transmission values are 0 (top) and 1 (bottom). C) Transmission as a function of the distance (d) between the vanadocene and CNT.

We should mention that the transmission curves obtained from full NEGF calculations, including the electronic convergence, are almost identical to those from post-processed DFT calculations for the electronic convergence, but there is a slight shift of the energy of the dips (Supporting Information). Therefore, for the sake of computational efficiency, all the transmission curves discussed hereafter were calculated by the post-processing method.

The Fano resonance can be tuned by varying the coupling strength between the localized and conduction states. Several ways may be available to achieve it. For example, controlling the stacking distance between magnetic molecules and a CNT could increase or decrease the overlap between their wave functions. We have investigated the distance dependence of Fano resonance and found that the width of the dips was

drastically broadened as the distance decreases from 3.4 Å to 2.6 Å (Figure 2C), as a result of enhanced coupling. The shift of the peaks towards lower energy can be attributed to stabilization by the increased overlap of the wave functions.

In practice, the coupling strength can be tuned by changing the ligands of the metal complex. A covalent bond with the CNT would induce very broad peaks, as observed in the case of an atom added onto the CNT surface.^[16] However, it may destroy the magnetic state of molecules, and thus the spin-dependent Fano resonance would no longer be expected. Another way would be to use more delocalized ligands, allowing for coupling over a larger area. For the spin-dependent Fano resonance, the magnetic states should be delocalized over the ligand so as to mediate the coupling between the magnetic states of the metal atom in a molecular complex and the conduction channels.

Spin-dependent Fano resonance can be realized when the spin of a magnetic molecule is firmly oriented in the desirable direction. Paramagnetic molecules like vanadocene are not appropriate for real applications because of the random orientation of their spins. SMMs with strong anisotropic magnetic moments would be the best candidates to resolve this problem. A TbPc₂ molecule (Figure 3A) is an intriguing example of an SMM. The TbPc₂ molecule possesses not only a large magnetic moment, but also a relatively long relaxation rate.^[17] In addition, it has a large conjugated area provided by the double-decker phthalocyanine (Pc) ligands. To calculate the spin-dependent electron transmission for a TbPc₂-CNT device, double- and single-zeta polarization basis sets were used for the TbPc₂ and CNT, respectively. The magnetic moment of the SMM energetically prefers a perpendicular direction to the plane of the ligands, with a high energy barrier

(approximately 600 K) between the up and down directions ($\theta = 0^\circ$ and $\theta = 180^\circ$) because of a large spin-orbit coupling.^[10a,b] Moreover, the magnetic moment persists in its original direction until spin relaxation by quantum-mechanical tunneling has occurred, when thermal relaxation is suppressed under cryogenic conditions.^[10b,17] Hence, we investigated the spin-valve effect of the SMM device using spin-polarized calculations that only consider up and down spins. Figure 3B shows the result of spin-polarized transmission calculations and the corresponding DOS. Fano-resonance-driven patterns appear in the transmission curves of the system, which is essentially the same as with the non-collinear case (Supporting Information). Notably, the transmission drops from two to one at the resonance energies, as was observed in the vanadocene-CNT system. Although a spin-orbit coupling term has not been included in the calculations, it would only affect the energy levels of the molecule, while keeping the characteristic Fano-resonance patterns. Thus, our conclusion would not be altered.

Spin-valve devices using SMMs coupled to a CNT have already been shown by recent experiments. Urdampilleta et al. have observed surprisingly large magnetoresistance for the TbPc₂-CNT device without ferromagnetic electrodes at a very low temperature.^[10a] This means that the magnetic moment of the SMM is a key factor for the large spin-valve effect. The same research group also found strong spin-dependent conductance for a graphene-based device decorated with the same molecules.^[10c]

To verify whether the large magnetoresistance can really be attributed to the Fano resonance, we have attached two vanadocene molecules to the CNT and examined the change in its transmission according to relative spin alignment between the two molecules, as depicted in Figure 1. For this calculation, we used vanadocene molecules instead of TbPc₂ to save computational costs, but the result can be transferred to the TbPc₂-CNT complex. Figure 4 shows the transmission curves calculated for both the spin-parallel and antiparallel cases. For SMMs like TbPc₂, the relative spin-orientation can be controlled using an external magnetic field to make it either parallel or antiparallel. For the parallel case, only the transmission of spin-up electrons has dips owing to the spin-dependent Fano resonance, while for the antiparallel case, the transmission of both spin-up and spin-down electrons has dips at the same resonance energies. In other words, for the parallel case, only spin-up electrons are influenced by the spin-up states of the SMMs, resulting in a partial block of the spin-up channel (inset in Figure 4A), whereas both spin-channels are simultaneously blocked by the spin-up state of one SMM and the spin-down state of the other (inset in Figure 4B). Therefore, conductance through the SMM-CNT device is regulated by the relative magnetic orientations of the two SMMs. One of the reasons why just two molecules are able to significantly change the conductance of the CNT device originates from the high surface-to-volume ratio of the CNT. For instance, the ultra-sensitivity of the CNT device has been used as a chemical sensor for single-molecule detection.^[18]

For a direct comparison between our model and the experiment, we estimated the number of SMMs required to

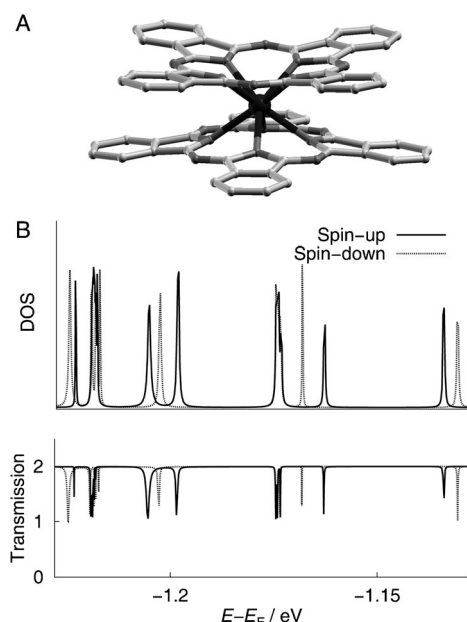


Figure 3. Spin-dependent transmission for a TbPc₂ molecule. A) Geometry of a TbPc₂ molecule. Hydrogen atoms attached to the Pc ligands are omitted for clarity. Central complexed metal is Tb, nitrogen is dark gray, and carbon is gray. B) Spin-polarized DOS (top) and transmission (bottom) for the TbPc₂-CNT system.

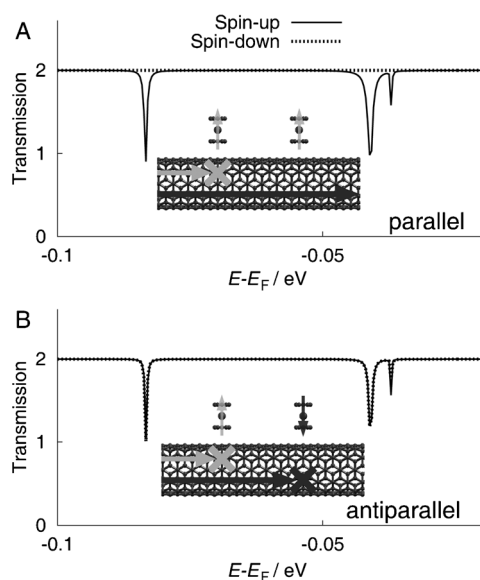


Figure 4. Transmission of the CNT with two vanadocene molecules. A) Parallel and B) antiparallel cases of relative spin alignment between the two molecules. Insets depict blocking of the spin channels of the CNT owing to the spin-dependent Fano resonance.

obtain the experimentally observed magnetoresistance ratio ($MR \approx 300\%$) under the experimental condition. It has been shown that the velocity of electrons traveling through a metallic CNT is about $0.8 \times 10^6 \text{ ms}^{-1}$,^[19] which means that it takes approximately 375 femtoseconds for an electron to pass through a CNT that is approximately 300 nm long (this value has been used in the spin-valve measurement^[10a]). Because the relaxation time of the magnetic moment in TbPc_2 molecules is over microseconds,^[17] it is reasonable to assume that the molecular magnetic moments are fixed along the easy axis during conductance measurements. Moreover, the fastest bandwidth of the conductance measurements is on the order of MHz, meaning that a number of electrons may pass through the CNT during the measurements. Therefore, the conductance value should be averaged over many electrons. In addition, spin orientations of incoming electrons from nonmagnetic electrodes are unlikely to be determined, but once a spin enters the CNT, it keeps the original direction while traveling over a few micrometers.^[20] As stated above, we assume that the magnetic polarization of the SMMs remains either up ($\theta = 0^\circ$) or down ($\theta = 180^\circ$) during the conductance measurements so that we consider it a spin probe, which selectively hinders electron transport depending on the spin direction. In other words, an incoming electron with an arbitrary spin, as a linear combination of up and down states, can pass through the spin probes with a certain probability that is proportional to spin-dependent transmission values. Under these circumstances, we deduced an expected value of the conductance (G_{obs} ; Equation (1)) and MR (Equation (2)) when $N(=N_{\uparrow}+N_{\downarrow})$ numbers of SMMs are attached to the CNT, where the relative number of SMMs with up and down magnetic polarizations is given by the Boltzmann factor at low temperature (40 mK) in the presence

of a magnetic field (on: $B = 1 \text{ T}$, off: $B = 0 \text{ T}$). For details of the derivation, see the Supporting Information.

$$G_{\text{obs}}(\mu_{\text{res}}) = \frac{G_{\text{contact}} G_o}{2} [T^{N_{\uparrow}}(\mu_{\text{res}}) + T^{N_{\downarrow}}(\mu_{\text{res}})] \quad (1)$$

where $G_o = 2e^2/h$ (e : charge of an electron, h : Planck constant), G_{contact} is the conductance coming from the contact resistance between a CNT and the metal electrodes, $T(\mu_{\text{res}})$ is the mean transmission value of each conduction channel as a function of the chemical potential, and μ_{res} is the chemical potential as the Fermi energy is shifted to one resonance energy by means of an external gate. When the total number of SMMs N is an even number, the MR becomes a simple function of N as follows.

$$MR = \left(\frac{T^N(\mu_{\text{res}}) + 1}{2T^{N/2}(\mu_{\text{res}})} - 1 \right) \times 100\% \quad (2)$$

The MR is very sensitive to the number of SMMs. The mean transmission value for each conduction channel of a metallic CNT at the Fano resonance is $T = 0.5$, regardless of the type of SMMs (Supporting Information). Therefore, to be $MR = 300\%$, N should be six, according to our calculation. This number is surprisingly close to that estimated by the experiment (which was four).

Finally, we should mention that in real experiments the situation is much more complex. The magnetic orientation of the probing molecules is no longer fixed even at very low temperature because of the quantum tunneling of magnetization. The spin dynamics of SMMs should be considered for a quantitative description. In addition, there might be coupling effects between adjacent probing molecules, resulting in more complicated Fano-resonance patterns. However, we believe that the simple model in this study gives a qualitative explanation of the large spin-valve effect observed in the recent experiments.

In conclusion, we have shown that the coupling between discrete spin-states of a magnetic molecule and continuum bands of a carbon nanotube induces spin-dependent Fano resonance, which significantly changes the conductance of the carbon nanotube owing to its high surface-to-volume ratio. This effect can be used to design novel molecular-spintronic devices, as already demonstrated previously.^[10]

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