Effects of the covalent linker groups on the spin transport properties of single nickelocene molecules attached to single-walled carbon nanotubes

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Citation: The Journal of Chemical Physics 136, 194707 (2012); doi: 10.1063/1.4721628

View online: http://dx.doi.org/10.1063/1.4721628

View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/136/19?ver=pdforcv

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I. INTRODUCTION

Following the continuous miniaturization of silicon-based microelectronic devices, molecular spintronics is winning growing attention as a platform for logic and memory devices.1,2 Sandwiching organic molecules between two ferromagnetic electrodes is one widely used experimental approach for constructing molecular spintronic devices. Another possibility is that of connecting magnetic molecules to non-magnetic leads.3–5 In this case, single-walled carbon nanotubes (SWCNTs) may be an interesting material set to explore. SWCNTs with nearly perfect structures are easily available in large quantities and since their diameters are about 1–2 nm, they are suitable for future circuit interconnects with ultrahigh integration density. More importantly for spintronics the spin-relaxation length in honeycomb carbon is very long thus that SWCNTs can be used as spin channels with ballistic transport characteristics.6 Finally it is important to note that in a SWCNT all the atoms reside on the surface, so that one expects that small surface modifications may produce large effects on the electron transmission.

For this reason grafting and coupling appropriate magnetic molecules on SWCNTs to construct supramolecular spintronic devices with specific functionality, good performance and high thermal stability appear as a tantalizing prospect for molecular spintronics.1,7 Note that grafting magnetic molecules on SWCNTs can also be considered as a sort of doping strategy for CNTs. Previous experimental and theoretical investigations have shown the possibility of inducing a spin polarization in SWCNTs by adsorbing 3d transition metal atoms,8–10 whereas organic molecules have been mainly used to tune the carrier type and concentration.11,12 Only rarely molecules have been employed as a source of spin.13–15 However, compared with the limited doping types of 3d transition metal atoms, both the atomic structure and the magnetic properties of organic molecules are more easily tuned to meet the required conditions for the production of spintronic devices.

Magnetic molecules have been already successfully grafted onto SWCNTs by using appropriate linker groups.14–17 In particular supramolecular spin valves consisting of bis(phthalocyaninato)terbium (III) complexes attached to a SWCNT have been recently assembled. These may display a magnetoresistance ratio in excess of 300% at temperatures below 1 K.15 The key question in such experiments is related to how the spin moment resident on the magnetic molecule transfers to the CNT, and thus modifies its transport properties. Clearly two ingredients are relevant for such transfer. On the one hand the magnetic ground state of the molecule produces a well-defined set of spin-polarized molecular orbitals, which may electronically couple to the conducting SWCNT channel. On the other hand the linker groups, as in conventional molecular electronic devices,18–23 control the strength and the efficiency of the electronic coupling between the magnetic molecules and the SWCNT, thus they ultimately control the spin interaction.24 In a recent paper we have explored how changing the magnetic molecule affects the spin-polarization of a SWCNT.25 Here we concentrate on the second ingredient, i.e., we investigate how the same magnetic molecule (nickelocene—NiCp2) (Refs. 25–28) may become an efficient source of spin transmission.
polarization depending on the specific linking group used to attach it to a SWCNT.

Our study is carried out by employing the non-equilibrium Green’s function formalism combined with spin density functional theory (i.e., the NEGF + DFT approach). 25–37 We consider here a (4,4) armchair SWCNT (Refs. 25 and 38–40) as transport channel and a number of linker groups, which all form a covalent bond with the nanotube. When compared to linker groups providing non-covalent interaction between the target molecule and the nanotube sidewall, the covalent linkers improve significantly the device stability. Furthermore, the covalent approach allows us some control in the degree of functionalization and therefore in the properties of the fabricated device. Thus, three different covalent linkers are considered here, namely, aziridine rings, pyrrolidine rings, and the amide group. These are often employed to wire a target molecule to the nanotube sidewall, as documented in recent reviews. 42, 43 Our calculations show that both pyrrolidine and amide cause a reduction in the transmission around the Fermi level ($E_F$) due to the $sp^2 \rightarrow sp^3$ transition occurring upon the bond formation. In contrast, aziridine attaches to the two carbon atoms perpendicular to the nanotube axis, it does not destroy the $sp^2$ character and the nanotube conductance is little affected. It is only in this last situation that the transfer of the molecule spin polarization to the nanotube is efficient. In fact our calculations show that only when NiCp$_2$ is bonded to the SWCNTs via aziridine the low-bias electron transport through the nanotube becomes spin-polarized. This demonstrates that the linking group, as well as the magnetic molecule itself, plays a crucial role in the formation of supramolecular devices capable of filtering spins.

II. CALCULATION METHOD

Geometry optimization and electronic structure calculations have been performed by using the SIESTA package. 44 We use improved Troullier-Martins pseudopotentials to describe the core electrons and the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE) for the exchange and correlation energy. 35, 46 The wave functions for the valence electrons are expanded over a finite range numerical basis set, and a user-defined double zeta plus polarization (DZP) basis set is constructed for all elements including H, C, N, O, and Ni. 25, 38 Geometry optimization is performed by conjugate gradient relaxation until the forces are smaller than 0.03 eV Å$^{-1}$.

The spin-polarized transport calculations have been performed by using the SMEAGOL package. 36, 37 which is a practical implementation of the NEGF + DFT approach. Since SMEAGOL uses SIESTA as the DFT platform, we employ the same pseudopotentials, basis set and GGA functional, for both the geometry relaxation and the transport. Note that in this particular case the GGA functional seems quite adequate for the transport and we have checked that the inclusion of self-interaction corrections changes little the results. 47 The charge density is integrated over 70 energy points along the semi-circle, 25 energy points along the line in the complex plane, and 20 poles in the Fermi distribution (the electronic temperature is 25 meV). The zero-bias transmission functions for the spin-up and spin-down electrons ($\sigma = \uparrow/\downarrow$) are calculated from

$$T_\sigma(E) = Tr[\Gamma G_\sigma \Gamma G_\sigma^+(E)],$$

where $G_\sigma$ is the spin-dependent retarded Green’s function of the extended molecule and $\Gamma_{1,2}$ are the broadening functions of the left and right electrodes. It should be noted that the broadening functions $\Gamma_{1,2}$ are independent of spin since the semi-infinite SWCNT electrodes are not spin-polarized. More details about the numerical implementation can be found in the literature. 36, 37 The simulation cell consists of a 28.53 Å long (4,4) SWCNT which has absorbed the molecule of interest. This attaches to perfectly crystalline (4,4) SWCNTs, which act as the electrodes. As such, the transmission for a molecule-free nanotube is expected to be an integer ($T = 2$ at the Fermi level). In this case we do not consider the more realistic geometry where the leads are made of standard metals (for example, gold) as we wish to single out the scattering properties of the molecules.

III. RESULTS AND DISCUSSION

A. Effects of the linkers on the transport properties of a pristine (4,4) armchair SWCNT

Since the linker groups control both the atomic structure and the electronic coupling at the molecule-SWCNT interface, we first investigate the electronic transport properties of the (4,4) armchair SWCNT functionalized with the three covalent linkers only (i.e., without connecting NiCp$_2$). As shown in Fig. 1, there are two different binding configurations for aziridine and pyrrolidine depending on whether the reacted C-sites on the CNT are either perpendicular (type-O) or slanted (type-S) to the tube axis. Let us start our analysis from aziridine [Fig. 1(a)].

For the type-O configuration, the distance between the two reacted C atoms on the nanotube is optimized to be 2.147 Å, which is much larger than both the C–C bond length for the $sp^2$ bond of a pristine tube (of 1.438 Å) and the $sp^3$ one in ethane (1.54 Å). This means that the bond on the nanotube is broken and that a seven-membered ring with $sp^3$ character is actually formed. In contrast in the type-S configuration the C–C bond length at the reacted sites remains comparable to that of ethane (1.527 Å), suggesting an $sp^2 \rightarrow sp^3$ transition upon aziridine bonding. In this case a three-membered ring with relatively large strain energy is formed. This is supported by the fact that the binding energy of type-O (3.23 eV) is calculated to be about 1.3 eV higher than that of type-S (1.92 eV), in good agreement with previous plane-wave DFT calculations. 49

These drastically different atomic structures anticipate that their effects on the SWCNT transmission might be also radically different. As shown in Fig. 1(a) in the type-O configuration the attachment of the –NH group does not perturb the SWCNT transmission, $T(E)$, in a broad energy range near the Fermi level, except for the sharp transmission dip with value $T = 0.86$ appearing at $-1.66$ eV. In contrast, when aziridine binds in the type-S configuration it remarkably reduces the nanotube transmission around the Fermi level.
FIG. 1. Transmission coefficient as a function of energy for a (4,4) SWCNT functionalized with different linking groups: (a) aziridine ring, (b) pyrrolidine ring, and (c) amide. In the insets we report the geometry of the bonding structures investigated. For both aziridine and pyrrolidine we have considered two different bonding geometries, type-O (right) and type-S (left), depending on whether the reacted C sites are either perpendicular or slanted to the tube axis. For amide we have only considered the atop bonding site. In all the figures we also report the transmission coefficient for the pristine SWCNT (black dashed line).

Moving now to pyrrolidine we note that in this case the binding energy of the type-S configuration is about 0.28 eV larger than that of the type-O.56 Furthermore the distance between the two C atoms at the binding site in the type-O configuration is now only 1.678 Å. Since the C–C distances in the pyrrolidine rings of both configurations are close to the C–C bond length for sp3 hybridization, electron scattering occurs for both the π and π* bands and thus T(E) around the Fermi level are both decreased as compared with that of the pristine SWCNT [shown in Fig. 1(b)].

Finally the binding geometry for the amide group is much simpler, as this adsorbs at the atop site. Since an obvious sp2 → sp3 transition occurs for the connecting carbon atom,59 the adsorption of the amide group reduces the transmission around the Fermi level, especially at −0.32 eV where a full conducting channel is completely shut down [see Fig. 1(c)].

B. Effects of the linkers on the spin transport properties of the (4,4) armchair SWCNT grafted with one nickelocene molecule

We now move to investigate the spin transport properties of a single nickelocene molecule attached to the SWCNT. Note that for every linker we consider here only the most stable binding geometry. Since the electronic structure of NiCp2 in the staggered configuration is essentially identical to that of the eclipsed one,26,27 for the sake of brevity only the eclipsed configuration has been considered in our study. The ground-state electronic structure of an isolated nickelocene molecule is spin-polarized with a spin moment of 2 μB.26,27 This can be explained by charge-transfer. In fact although an isolated Ni atom has a [Ar]3d84s2 electronic configuration, in NiCp2 the bonding between Ni and the two Cp rings is dominated by the Ni 3d atomic orbitals and the Cp π-type ones. The strong Dsh crystalline field splits the d-shell into the A1 (dxy), the E2 (dxz, dyz, dz2−r2) and the E1 (dxy, dxz, dyz) doublets. Two of the 10 valence electrons are transferred from Ni to the Cp rings and six of them completely fill the lower lying molecular orbitals composed of the Ni 3d levels with A1 and E2 symmetry. The remaining two valence electrons can only partially occupy the doubly degenerate molecular orbitals composed of the Ni 3d levels with E1 symmetry and the Cp π-type ones resulting in a triplet ground state. Thus, the doubly degenerate doubly occupied molecular orbital mainly composed of Ni 3dxy and...
$3d_{xz}$ is the highest occupied molecular orbital (HOMO) for the spin-up electrons, while it is the lowest unoccupied molecular orbital (LUMO) for spin-down.

Let us start our analysis from NiCp$_2$ attached to the nanotube via aziridine ring (type-O configuration) [see Fig. 2(a)]. When NiCp$_2$ adsorbs on the nanotube the molecule original D$_{5h}$ symmetry is significantly lowered, although a reflection symmetry operation with respect to the mirror plane containing the CN bond and the Ni atom can still be applied (minor deviations are due to the relaxation of the Cp ring close to the binding site). Furthermore, due to the sp$^3$ hybridization occurring at the N site, the two Cp rings form an angle of 28.85° with the tube axis. As such, the shortest distances between the C atoms in the Cp ring and those in the SWCNT are calculated to be 2.422 Å, 2.796 Å, and 3.384 Å. Some of these are much shorter than twice the C van der Waals radius (1.70 Å). Note that in this case of rather strong covalent bonding van der Waals interactions are not expected to play a major role in determining the geometry of the molecules on the nanotube sidewall. This has been confirmed by additional calculations performed with van der Waals DFT functional, which show that the differences in any given bond length are never larger than 0.04 Å, causing no change in the transport properties.

In Fig. 2(b) we present the spin-resolved transmission spectrum of the nanotube functionalized with aziridine/NiCp$_2$ (type-O structure). As one can see the most striking feature is that the adsorption of nickelocene makes $T(E)$ spin-polarized. The spin-up and spin-down electrons $T(E)$ can be described as composed of a smooth “baseline,” which resembles the transmission of the SWCNT functionalized by aziridine only [Fig. 1(a)], plus dips which are caused by the adsorbed nickelocene. To be more specific, for spin-up electrons two transmission dips approaching unity appear below the Fermi level, a narrow one at $-0.03$ eV and a broad one at $-0.25$ eV. Eigenchannel analysis shows that only one conducting channel remains open at these two energies, namely, $\pi$ $(\pi^*)$ at $-0.03$ eV $(0.25$ eV). In contrast, the transmission dips for spin-down electrons occur at $-1.58$ eV and 0.70 eV, i.e., they are far away from $E_F$. Since for efficient spin filtering the transmission of the two spin orientations must differ appreciably over a sufficiently broad energy range near the Fermi level, our results demonstrate that aziridine is a suitable linker for constructing supramolecular spin-devices.

A deeper insight into the conductance of NiCp$_2$/aziridine functionalized SWCNT can be obtained from the DOS of the N and Ni atoms, shown in Figs. 2(c) and 2(d), which unsurprisingly presents spin-polarization for both. Around $E_F$ there is a one-to-one correspondence between the Ni DOS and the transmission dips, indicating that electron scattering generated by the interaction between the NiCp$_2$ frontier molecular orbitals and the two low-energy SWCNT bands results in the reduced transmission. Although NiCp$_2$ remains spin polarization after adsorption on the nanotube, the degeneracy of the HOMO is lifted. This is now composed of the Ni $3d_{xz}$ atomic orbital only, which is even under the reflection symmetry operation with respect to the mirror plane containing the connecting CN bond. As such the NiCp$_2$ HOMO interacts mostly with the SWCNT $\pi$ state and thus induces the transmission dip at $-0.03$ eV. This is a typical through-bond interaction because the DOS of the connecting N atom shows a sharp resonance peak at the same energy. In contrast the HOMO-1, composed of the Ni $3d_{yz}$ atomic orbital and odd under the same reflection symmetry, interacts strongly with the SWCNT $\pi^*$ state and induces the transmission dip at $-0.25$ eV. The transmission dip at $-0.03$ eV is a typical through-bond interaction because the DOS of the connecting N atom shows a sharp resonance peak at the same energy. In contrast the HOMO-1, composed of the Ni $3d_{yz}$ atomic orbital and odd under the same reflection symmetry, interacts strongly with the SWCNT $\pi^*$ state and induces the transmission dip at $-0.25$ eV.
−0.25 eV. In this case the interaction is a through-space type due to the lack of the DOS peak of the N atom at the corresponding energy. It should be noted that the short distance between the binding Cp ring and the nanotube sidewall makes the interaction between the odd HOMO-1 of NiCp₂ and the SWCNT π* state much stronger, as evidenced by the much broader transmission dip at −0.25 eV. Finally, the NiCp₂ LUMO remains nearly degenerate, and the Ni 3d_{yz} and 3d_{xz} atomic orbitals contribute together to the DOS peak at 0.70 eV for spin-down electrons. As they interact, respectively, with the SWCNT π* and π bands, the transmission at 0.70 eV is depressed significantly.

In order to further confirm the above analysis, we insert a methylene (−CH₂−) group between NiCp₂ and aziridine. The optimized atomic structure and the corresponding spin-resolved transmission spectra of this new system are shown in Fig. 3. When compared to the case where the methylene group is absent [Fig. 2(b)], the most obvious difference is that the spin-up transmission dip at −0.25 eV below E_F and the spin-down one at 0.70 eV both disappear (although a transmission dip at −0.04 eV still exists for spin-up). As one can see from the Ni DOS [Fig. 3(c)], for spin-up electrons two well-separated peaks originating from the Ni 3d_{yz} and 3d_{xz} atomic orbitals are just below E_F with the corresponding spin-down peaks appearing at 0.90 eV and 0.95 eV. Therefore, the changes in the transmission spectra can be attributed to the inserted methylene group. On the one hand, the methylene group greatly increases the distance between NiCp₂ and the nanotube and thus the NiCp₂ odd HOMO-1 cannot any longer affect the SWCNT π* state and reduce the transmission. On the other hand, the methylene group shifts the NiCp₂
FIG. 5. (a) The optimized geometry structure of one nickelocene molecule attached to the (4,4) SWCNT sidewall through the amide group. (b) The spin-resolved zero-bias transmission spectra, the blue dot line for the spin-up electrons and the red solid line for the spin-down electrons. The transmission spectrum for the pristine SWCNT (dash line) is also given for comparison; (c) the DOS of the Ni center.

LUMO to higher energies and thus the transmission dip for spin-down electrons shifts from 0.70 eV to 0.92 eV.

Next we connect NiCp₂ to the nanotube through the pyrrolidine ring in the type-S configuration (see Fig. 4). Although the transmission is still spin-polarized, $T(E)$ for the two spins differ marginally: the dips are considerably narrow and the two baselines coincide over a broad energy range. Since the current is obtained by integrating the transmission over a finite energy range, we conclude that NiCp₂/pyrrolidine does not effectively act as a spin filter. In general the very narrow transmission dips appearing around $E_F$ simply indicate that pyrrolidine makes NiCp₂ interacting weakly with the nanotube, so that there is no transfer of spin-polarization.

The reasons for the weak electronic coupling provided by the pyrrolidine ring lie in two facts: (1) the C–C and C–N bonds in the pyrrolidine ring are all $\sigma$-type, which are not efficient spin channels; (2) the distance between NiCp₂ and the SWCNT is very large thus through-space interactions cannot occur.

Finally we investigate the spin transport properties of NiCp₂ connected to the SWCNT through the amide group (Fig. 5). In contrast to the cases of aziridine and pyrrolidine, where the interaction induces simple transmission dips around the Fermi level, this time a sharp transmission peak approaching two appears at $-0.07$ eV for spin-up electrons (note that the “baseline” transmission is around 1 at that particular energy). Since such transmission peak is accompanied by a small dip, it is more accurately described as a Fano resonance. When one looks at the spin-resolved DOS of the Ni center, this resonance originates from the NiCp₂ HOMO dominated by the Ni 3$d_{xz}$ atomic orbital. Since there are only sharp peaks in the spin-resolved DOS of the Ni center around the Fermi level, the transmission curves for the spin-up and spin-down electrons are almost identical except for the Fano resonance around $-0.07$ eV. This indicates that the spin filtering efficiency of NiCp₂/amide functionalized SWCNT is not very high.

IV. CONCLUSION

When a magnetic molecule is attached to a conducting channel it can transfer spin-polarization to it so to modify the channel electron transmission. The magnitude and efficiency of such transfer depend on the magnetic ground state of the molecule and on the way that is bonded to the channel. Expanding on our recent work, where we explored how the molecule spin-state affects the electron transport of a SWCNT, here we investigate how the efficiency of the spin-transfer depends on the linking group between the molecule, NiCp₂, and the nanotube. We find that the pyrrolidine ring and the amide group, which both produce a $sp^2$ to $sp^3$ bond reconfiguration at the reacted SWCNT site, reduce the electron transmission but fail in transferring spin-polarization. In contrast an aziridine ring perturbs less the nanotube transmission but couples the spin efficiently so that the low-bias conductance becomes spin-polarized. Our results demonstrate how subtle is bond engineering for spin transfer and how the choice of linking groups is crucial for constructing supramolecular spin-devices.

ACKNOWLEDGMENTS

This project was supported by the National Natural Science Foundation of China (Grant No. 61071012) and the MOST of China (Grant No. 2011CB933001). The SMEAGOL project (S.S.) is sponsored by Science Foundation of Ireland (07/IN.1/I945) and by CRANN.
