

Cobaltocene as a spin filter

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In the context of investigating organic molecules for molecular electronics, doping molecular wires with transition metal atoms provides additional means of controlling their transport behavior. The incorporation of transition metal atoms may generate spin dependence because the conduction channels of only one spin component align with the chemical potential of the leads, resulting in a spin polarized electric current. The possibility to create such a spin polarized current is investigated here with the organometallic moiety cobaltocene. According to our calculations, cobaltocene contacted with gold electrodes acts as a robust spin filter: Applying a voltage less than 0.2 V causes the current of one spin component crossing the molecular bridge to be two orders of magnitude larger than the other. We address the key issue of sensitivity to molecule-lead geometry by showing that a weak barrier generated by CH₂ groups between the cobaltocene and the leads is crucial in reducing the sensitivity to the contact geometry while only reducing the current modestly. These results suggest cobaltocene as a robust basic building block for molecular spintronics. © 2007 American Institute of Physics. [DOI: 10.1063/1.2796151]

The demonstration of electronic functionality in single molecule structures has progressed tremendously in recent years.^{1–12} Meanwhile, the spin degree of freedom of the electron has attracted increasing attention because of its nonvolatile, power-saving, and fast-responding nature. Traditional spintronic devices are based on the fact that the current passing through a ferromagnetic layer becomes spin polarized.^{13,14} Then, giant magnetoresistance can be achieved because changing the direction of magnetization of one of a pair of ferromagnetic layers switches the device between aligned (on) and antialigned (off) states. The development of spin filters has, therefore, been the goal of many research programs over the last several years.^{15,16}

Spin dependent effects also offer opportunities in molecular conduction, with molecules being responsible for spin generation and detection. The ability to generate electron spin current in molecular systems is important for the field of spintronics and also for investigating basic properties of spin transport in molecular electronic systems. In a metal-molecule-metal junction, the most straightforward route to spin dependence is through a molecular magnet in which the conduction channels of only one spin component align with the chemical potential, resulting in a spin polarized electric current. Here we investigate spin dependent transport through a molecule containing a simple well-studied functional group—cobaltocene, a member of the metallocene

family¹⁷ bearing one free spin. We show that a simple molecule incorporating a cobaltocene moiety acts as a robust spin filter, and hence a basic building block in molecular spintronics.

Molecules containing the ferrocene moiety were first put forward as flexible and robust building blocks,¹⁸ and their unique transport properties were observed.⁸ Other molecules containing transition metal atoms have also been proposed as promising candidates for a variety of molecular electronic purposes.^{19–26} Cobaltocene is closely related to ferrocene but with one additional electron, yielding a spin 1/2 moiety favorable for spintronics.^{22,25}

The molecule that we study, shown in Fig. 1, has a cobaltocene moiety with each ring attached to a CH₂ spacer connected to a sulfur anchoring atom which then attaches chemically to a gold lead. We will refer to it as Co-1. (The purpose of adding a spacer will be discussed later.) We address the fully coherent transport through this molecule expected at low temperature. Density functional theory combined with Green function techniques is used for the electron transport calculations.^{27–31} The geometries of isolated molecules are fully relaxed with residual forces less than 0.01 eV/Å. Double-zeta plus polarization basis sets and optimized Troullier–Martins pseudopotentials³² are used for all calculations.³³ The PBE version of generalized gradient approximation³⁴ is adopted for exchange correlation (see Ref. 30 for computational details). A sufficiently large section of each lead (six or seven layers on each side) is

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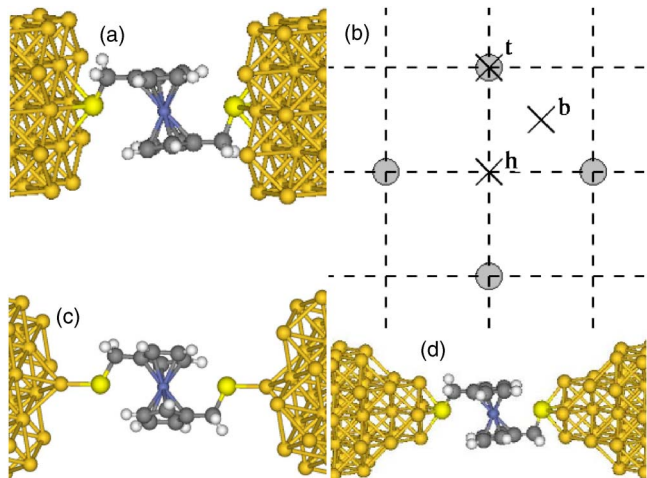


FIG. 1. (Color online) Adsorption sites of the Co-1 molecule on gold surfaces. (a) Adsorption between $8 \times 8 \text{ \AA}^2$ gold nanowires at hollow site. (b) Top view of gold 001 surface. Circles indicate gold atoms while crosses mark adsorption sites-hollow h , bridge b , and top t . (c) Adsorption on an apex Au atom. (d) A small island protruding out of both electrodes where Co-1 is adsorbed. Gray, white, dark gray, medium gray, and light gray denote carbon, hydrogen, cobalt, sulfur, and gold atoms, respectively.

included in our transport calculation to ensure that the spin polarization, which naturally extends from the cobaltocene moieties into the leads, has fully relaxed within the extended molecule. We can, therefore, use a spin independent self-energy³¹ to describe the unpolarized electrons in the semi-infinite leads.^{22–24} Note that the Fermi levels for spin up and down electrons converge in the reservoir (the difference is about 2 meV for the results presented here).

We perform spin polarized calculations^{22–24} assuming that the free spin residing in the cobaltocene points up. Physically this may come about through the magnetic anisotropy of the molecule together with the application of a magnetic field. In the fully quantum coherent, low-temperature regime, spin-flip scattering through sequential tunneling can be neglected.

A key issue in molecular electronics is that the effect of contact atomic structure on the conductance is usually strong.^{1,2,7,11,35–40} This is thought to be one of the main reasons affecting reproducibility in the experiments. For this reason, we consider several possible adsorption geometries.

Figure 2 shows transmission probabilities through the Co-1 molecule in eight circumstances. A resonance peak corresponding to the spin up component that peaks around 0.1 eV below the Fermi energy contributes to the equilibrium conductance. Note that the transmission spectra are basically unaltered upon various changes in either the contacts or the leads. Thus this system is a rare case in which the conductance is insensitive to the contact atomic structure. General knowledge of metallocenes¹⁷ suggests that this channel is provided by the highest occupied molecular orbital (HOMO) of cobaltocene, namely, the half-occupied antibonding molecular orbital (e_{2g}^{*1})¹ (with occupation number in the upper-right corner), which largely preserves the properties of the cobalt d states and so is higher in energy than the highest occupied level from the conjugated π bonding orbitals. When molecule and lead are connected, the strong coupling

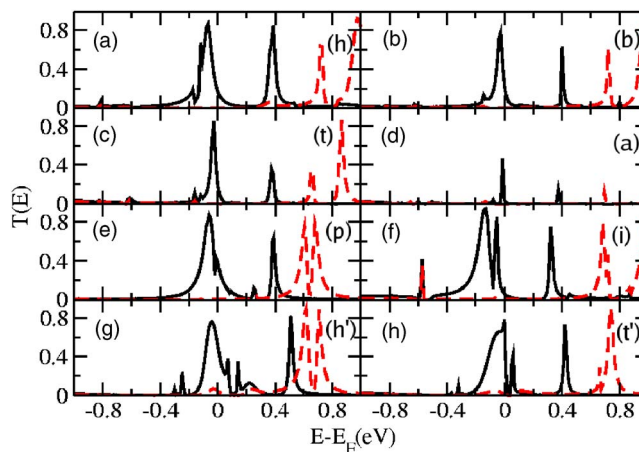


FIG. 2. (Color online) Transmission spectra of Co-1 with different adsorption geometries; solid and dashed lines denote the spin up and down components, respectively. [(a)–(c)] Hollow, bridge, and top sites of (001) oriented $8 \times 8 \text{ \AA}^2$ rodlike gold leads [as shown in Figs. 1(a) and 1(b)]. (d) Transmission for adsorption on top of an apex gold atom [Fig. 1(c)]. (e) The transmission function of Co-1 adsorbed at the hollow site of an infinite (001) surface. The surface is covered with a monolayer of Co-1 by repeating the structure shown in Fig. 1(a). (f) Transmission of Co-1 attached to a small island protruding from a (001) surface [Fig. 1(d)]. [(g)–(h)] Transmission for adsorption at the hollow and top sites of an infinite (111) surface. The surface is covered with a monolayer of Co-1 with a 4×4 unit cell.

broadens the states mentioned above. Consequently, cobaltocene moieties provide channels for low energy transport.

The polarized molecular orbital near the Fermi level can be visualized through the local density of states (LDOS): Figure 3 shows a surface of constant LDOS defined by $\rho(\mathbf{r}; E_F) = \text{const}$. We show here the spin up and down states of Co-1 when adsorbed at the hollow site [panels (a) and (b)] or on the top of apex gold atoms [panels (c) and (d)]. In both cases, the majority spin states are much more intense than those of the minority spin. The nonzero transmission probability of the minority spin component is caused by metal induced states^{41,42} localized on the sulfur atoms and the CH_2 spacers. Extreme differences in density of states imply, a highly polarized current.

The quality of spin filtering can be characterized by the ratio of the spin up and down transmission probabilities ($R = T^\uparrow/T^\downarrow$). The values both at the chemical potential (R_{E_F}) and on the resonant peak (R_{peak}) are shown in Table I. The ratio at E_F depends strongly on the broadening of the resonance (i.e., the coupling between the molecule and the leads) and on the alignment between the HOMO level and the chemical potential. Therefore, R_{E_F} values range from four to several hundreds. However, all the R_{peak} values are over 10, implying a robust spin filter.

In contrast to Co-1, the transport properties of a molecule lacking the CH_2 groups between the sulfur atoms and the cobaltocene moiety (Co-0) are found to be sensitive to the detailed atomic structure of the contacts. The transmission function of Co-0, shown in Fig. 4, has much broader features than that of Co-1 since the coupling between the cobaltocene and the gold leads is enhanced. More importantly, $T(E)$ is totally different in the case of hollow site adsorption from that for connection through apex gold atoms. Similar results were obtained in previous

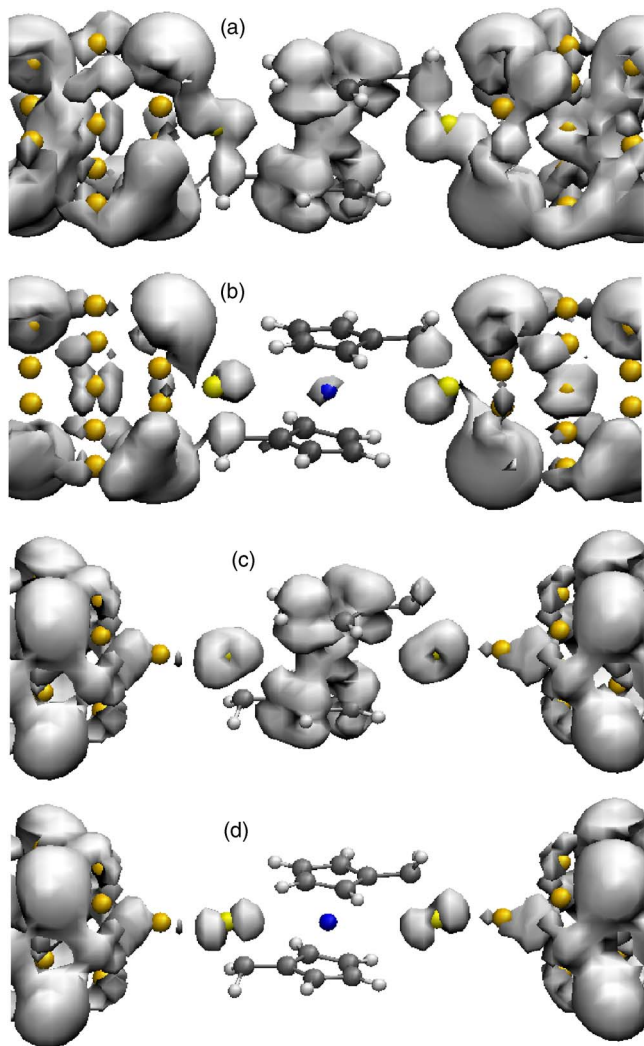


FIG. 3. (Color online) Surface of constant local density of states for Co-1 at the Fermi energy. [(a) and (b)] Spin up and down components, respectively, for (001) hollow site. [(c) and (d)] Spin up and down components, respectively, for Co-1 adsorbed on top of apex gold atoms.

calculations^{35,37} of a phenyldithiol molecule, with up to two orders of magnitude change in conductance when switching from hollow site adsorption to apex gold contacts.

A key aspect of the sensitivity of molecular electronic functionality to contact atomic structure is the dependence of lead-molecule charge transfer on that structure. To address this issue, we find the change in charge on the various parts of the molecules upon changing the adsorption site, reported in Table II. We find that the CH₂ groups in Co-1 act to screen out the dipole moment that develops between the cobaltocene moiety and the S atoms. For the case of apex gold

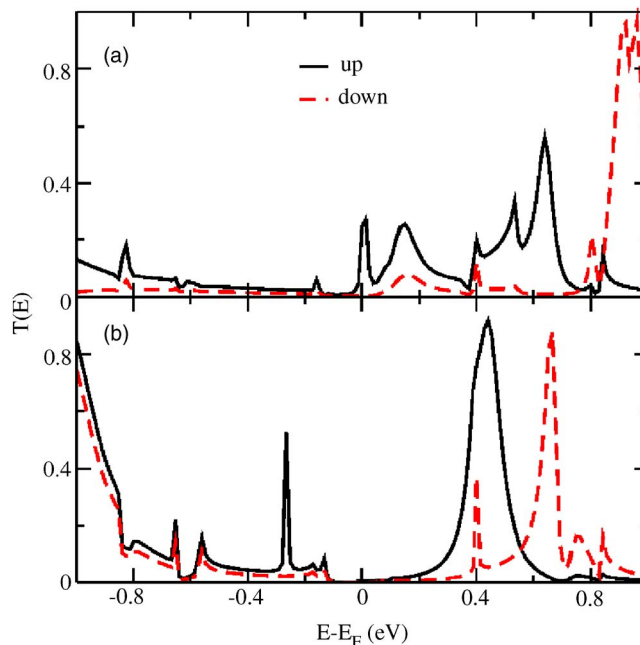


FIG. 4. (Color online) Transmission spectra of Co-0 adsorbed (a) at the (001) hollow site and (b) on top of apex gold atoms. Solid and dashed lines denote spin up and down components, respectively. Note the much greater sensitivity to contact geometry in this molecule than for Co-1 (compare to Fig. 2).

adsorption, for instance, despite comparable changes of approximately $-0.18e$ and $-0.16e$ on the cobaltocene in Co-1 and Co-O and $0.17e$ and $0.21e$ increases on the sulfur atoms, the CH₂ groups almost completely compensate the charge difference on the sulfur atoms of Co-1, leaving a $0.02e$ decrease. This results in weaker dipole moment change between the linker and the cobaltocene moiety, leaving the lineup of the molecular levels with the chemical potential closer to the original configuration. It is this change in the charge of the CH₂ groups in reaction to that of the sulfur and cobaltocene that we view as screening. However, if a substantial change happens in the surface structure or surface direction, as in the case of a protruding island or (111) adsorption, this screening behavior is not necessarily effective. In the island case, this is manifested by a small shift of the transmission peak to lower energy, which results in the smallest R_{E_F} value shown in Table I. Finally, note that though the charge varies on the cobaltocene moiety of Co-1, it does not seem to directly affect the overall transport. This may be because the HOMO level, which is responsible for the functionality of spin filter, is not fully occupied; thus small amounts of electron transfer or change in dipole moment may not shift its energy level appreciably.

TABLE I. Ratio of the spin up to spin down transmission for the eight cases shown in Fig. 2. R_{E_F} is the value at the chemical potential; R_{peak} is the largest value, occurring at an energy around -0.1 eV where the spin up transmission peaks. h , b , t , a , p , and i denote adsorption on a (001) lead in the case of a hollow site, bridge site, top site, apex gold, hollow site of an infinite surface, and hollow site of a protruding island, respectively. h' and t' denote adsorption on an infinite (111) surface at the hollow and top sites, respectively.

Contacts	h	b	t	a	p	i	h'	t'
R_{E_F}	367	768	130	293	99	4	11	83
R_{peak}	1810	1630	372	4700	334	127	12	83

TABLE II. Charge difference, with respect to a reference configuration, on the sulfur atoms (δQ_S), sulfur plus spacer atoms ($\delta Q_{SC_2H_4}$), and cobaltocene moiety (δQ_{Co}). The reference configuration is adsorption at the hollow site of (001) oriented nanowire leads. The subscripts b , t , and a refer to bridge, top, and apex adsorption sites; p and i refer to the infinite surface leads and islands on nanowires, respectively; h' and t' denote hollow and top adsorption sites on a (111) surface. Co-1 and Co-0 denote molecules with and without C_2H_4 spacers, respectively. The values are obtained via Mulliken population analysis. The minus sign denotes electron loss (transfer from the molecule to the lead).

	Co1 _b	Co1 _t	Co1 _a	Co1 _p	Co1 _i	Co1 _{h'}	Co1 _{t'}	Co0 _a
δQ_S	0.03	0.18	0.17	-0.01	0.17	0.00	-0.03	0.21
$\delta Q_{SC_2H_4}$	-0.02	0.04	-0.02	-0.02	0.26	0.24	-0.02	...
δQ_{Co}	-0.06	-0.14	-0.18	-0.08	0.00	-0.04	-0.09	-0.16

Our calculated results should be considered as an upper limit: Spin-flip, electron-phonon scattering, thermal broadening of the minority spin states, or other virtual processes could all result in a lower degree of spin polarization. Note, however, that our main results all have to do with the peaks in transmission at low temperature, for which our fully quantum coherent calculation is suitable (in contrast, say, to a sequential tunneling approach to the low conductance valleys). The spacer group CH_2 plays a particularly important role: it makes this molecular polarizer insensitive to various adsorption sites on the same surface. This screening is not sufficient, however, to make situations with very different contact structure equivalent, as we saw in the case of protruding island structure.

In conclusion, the cobaltocene containing molecules can generate a highly spin polarized current under a moderate bias and in a robust manner with respect to the contact structures with the gold leads. The spin polarization can approach 100%, making cobaltocene containing molecules an important basic building block for molecular spintronics.

Finally, we point out that the energy levels of the spin states, which should line up with the chemical potential, can be manipulated through chemical modification by attaching electron donors or acceptors.⁴³ Thus one should be able to use different materials as lead so as to realize efficient spin injection, and so we anticipate that cobaltocene could be used in a variety of contexts. Other metallocenes could also be considered. According to our preliminary calculations, nickelocene containing molecules can function similarly with Pb leads.

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