

Organometallic Spintronics: Dicobaltocene Switch

Rui Liu,[†] San-Huang Ke,^{†,‡} Harold U. Baranger,^{*,‡} and Weitao Yang^{*,†}

*Department of Chemistry, Duke University, Durham, North Carolina 27708-0354, and
Department of Physics, Duke University, Durham, North Carolina 27708-0305*

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ABSTRACT

A single-molecule spintronic switch and spin valve using two cobaltocene moieties is proposed. Spin-dependent transport through a lead–molecule–lead junction has been calculated using first-principles density functional and nonequilibrium Green function methods. We find that the antiparallel (singlet) configuration of the cobaltocene spins blocks electron transport near the Fermi energy, while the spin parallel (triplet) configuration enables much higher current. The energy difference between the antiparallel and parallel states depends on the insulating spacer separating the two cobaltocenes, allowing switching through the application of a moderate magnetic field.

The interesting phenomena that have come to light in the two fields of spintronics and single-molecule transport suggest that spintronic behavior in single molecules may be particularly rewarding. In molecular electronics, after investigations of self-assembled monolayers (SAMs),¹ various techniques for making single-molecule junctions, which avoid the problem of intermolecular interactions^{2,3} and dramatically reduce the size of junctions, have recently emerged.^{4–8} To improve these junctions, one would like to improve control over them and increase their response. Both of these point toward the difficult task of choosing molecules with intrinsic functionality. Here, we identify a class of molecules with strong intrinsic spintronic functionality.

Spintronics refers to the control of electrical current through manipulation of the spin of the electrons; it has been extensively investigated^{9–11} using layers of ferromagnetic material from both fundamental and device application points of view, as in, for example, the magnetic tunneling junction (MTJ). More recently, a spin-valve effect has been integrated into carbon nanotube and organic molecule/ferromagnetic lead structures,^{12,13} in which the valve mechanism is based on local magnetization fluctuations of individual magnetic domains in the contacts. Theoretical calculations, which include spin information by varying the relative orientation of the magnetization in the leads, are able to describe the polarized injection.^{14–17} This replacement of the insulating layer of a MTJ by molecules is a first step in combining single molecules and conventional spintronics. However, we pursue here a true molecular spintronics, emphasizing the functionality of the molecule and so leading to a completely

molecular scale device. The fine, reproducible control in a molecule makes dramatic effects possible.

By moving the active spins from the leads into the molecule, we form a switch through changing the alignment of these molecular spins. Candidate molecules should bear the following characteristics: two localized spin sites (or more) should be present, the spin configuration must be alterable, and the transport levels should have a clear spin character so as to ensure a high switch ratio. Cobaltocene, a chemically stable metallocene with one free spin,¹⁸ appears to be a good choice. In fact, ferrocene, a close cousin of cobaltocene in the metallocene family, has been proposed and tested previously in single-molecule structures,^{19–21} and near-perfect conduction has been experimentally obtained.²¹ Other organometallic molecules have been used to study the Kondo effect in single molecules.^{22–24} In this paper, we study two molecules, each containing two cobaltocene moieties but differing in the spacer between them.

Figure 1 shows the two dicobaltocene containing molecules, one without a spacer and one with the spacer group C₂H₄. Triple bonds are used as linkers for sulfur–cobaltocene, cobaltocene–cobaltocene, and cobaltocene–spacer connections. The molecules are assumed adsorbed at hollow sites of (001) direction semi-infinite 4 Å × 4 Å rodlike gold leads. The Au–S distance is set to 1.7 Å, the value yielding the lowest energy. We will refer to the two molecules from Figure 1a and b as DiCo and DiCo-2C, respectively.

Our main findings are the following: (1) The cobaltocene spins in DiCo and DiCo-2C can be in either a parallel or antiparallel state, with the antiparallel state having a lower energy. A magnetic field can switch either molecule from one state to the other; the field scale for DiCo is much higher. (2) The conductance in the parallel configuration is much larger than that for the antiparallel configuration, yielding

* To whom correspondence should be addressed. E-mail: baranger@phy.duke.edu (H.U.B.); yang@chem.duke.edu (W.Y.).

[†] Department of Chemistry.

[‡] Department of Physics.

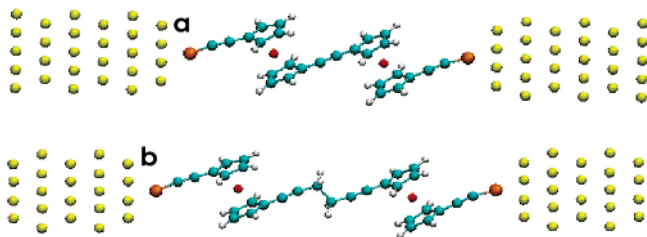


Figure 1. Structures of two molecules containing two cobaltocene moieties but having different spacers: (a) DiCo and (b) DiCo-2C adsorbed at hollow sites on Au(001) leads. Yellow, white, blue, red, and orange denote Au, H, C, Co, and S atoms, respectively.

the switch behavior. (3) DiCo-2C behaves not only as a switch but also as a spin valve.

The method that we use for calculating electron transport is first-principles density functional theory (DFT) combined with the nonequilibrium Green function technique (for the spin-unpolarized counterpart, see refs 25–29). We use the SIESTA package for the electronic structure.³⁰ The geometries of isolated molecules are fully relaxed, with residual forces less than 0.01 eV/Å. Double- ζ plus polarization (DZP) basis sets and optimized Troullier–Martins pseudopotentials³¹ are used for all calculations. The PBE version of generalized gradient approximation (GGA) functional³² is adopted for exchange correlation (see ref 29 for computational details).

In our transport calculations, we include a sufficiently large section of leads in the extended molecule (up to seven layers on each side) 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-energy²⁹ to describe the unpolarized electrons in the semi-infinite leads. Note that the Fermi levels for spin up and down electrons converge in the reservoir. The Landauer formalism³³ is used to study the spin coherent transport through the molecules. Since the effective potential depends on combined information of both spin components, the contributions to the total current are determined simultaneously in a self-consistent manner.

The energetics of the spin states is the first essential ingredient of the switch. The two separated spins localized in the cobaltocene moieties join to form a singlet or triplet state. The interaction between the spins is via the superexchange mechanism through the intervening electronic bonds. The superexchange naturally leads to the singlet (antiparallel) state having a lower energy. With the molecules attached to the leads, we find a singlet–triplet energy splitting of 12 meV for DiCo and 2 meV for DiCo-2C. As a check, the singlet–triplet splitting for the isolated molecule was found using Gaussian03 with the PBE functional and the LANL2DZ basis set; the results are consistent with those obtained from SIESTA. Insertion of the alkane spacer reduces the superexchange compared to the fully conjugated triple bond, hence lowering the energy difference. Likewise, the magnitude of magnetic field needed to overcome the splitting is significantly lowered, to about 20 T for DiCo-2C (assuming $g = 2$). According to our calculations, replacing the C_2H_4 spacer

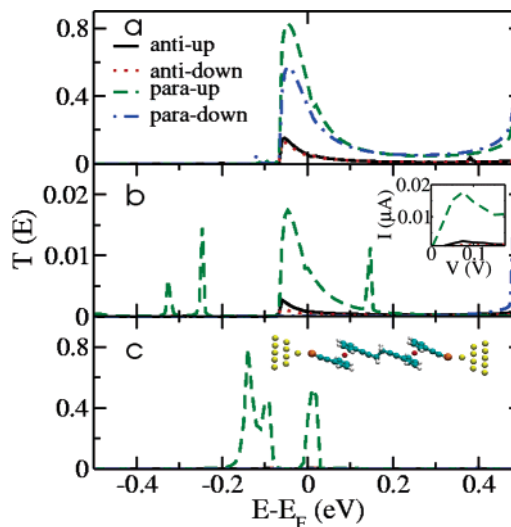


Figure 2. Transmission functions of (a) DiCo and (b) DiCo-2C (molecules shown in Figure 1). The I – V curve of DiCo-2C is shown in the inset of part b. (c) Transmission function of DiCo-2C with additional Au atoms between it and the leads, as indicated in the inset. The solid and dotted lines correspond to up and down conduction electron spins, respectively, in the antiparallel configuration of the localized cobaltocene spins, while the dashed and dashed–dotted lines show spin up and down contributions in the parallel configuration.

with C_4H_8 further lowers the energy difference by about an order of magnitude, extending beyond our ability to do a reliable quantitative calculation but being potentially interesting experimentally. Though DFT may not give accurate numbers at the several millielectronvolt level, or tens of teslas when translated into magnetic field, the trend of decreasing the singlet–triplet energy difference as the spacer increases is clear.

The switch operation comes from the fact that the triplet state (parallel cobaltocene spins) obtained by applying the external magnetic field conducts much better than the singlet state (antiparallel spins). Figure 2 shows transmission spectra, $T(E)$, of DiCo and DiCo-2C for both the spin up and spin down channels (up and down here refer to the spin of the incident lead electron). We see immediately that the aligned state of the molecule is indeed far more transparent. A standard quantitative figure of merit is the switch ratio, $S \equiv (G_{para}^{\uparrow} + G_{para}^{\downarrow}) / (G_{anti}^{\uparrow} + G_{anti}^{\downarrow})$. For DiCo, $S_{DiCo} = 8.1$. Though the absolute conductance of DiCo-2C is considerably smaller than that of DiCo because of the alkane barrier, the switch ratio is comparable, $S_{DiCo-2C} = 6.3$. Application of a magnetic field to switch the spin state of the molecule causes, then, a substantial change in the molecule’s conductance.

The polarization of the current in the conducting state is another important spintronics characteristic. When only one spin direction of the conducting electrons is transmitted, the system is called a spin valve. We see in Figure 2b that when the cobaltocene spins are parallel to each other (triplet state), DiCo-2C is, in addition to being a respectable switch, an excellent spin valve. Quantitatively, the spin-valve ratio $G_{para}^{\uparrow} / G_{para}^{\downarrow}$ is 264. The low bias I – V curve in the inset of Figure 2b shows clearly that DiCo-2C functions as both a switch and a spin valve.³⁴

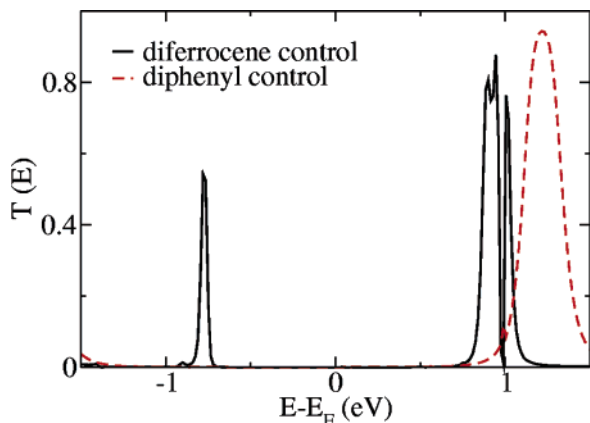


Figure 3. Transmission spectra of diferrocene (solid line) and diphenyl (dashed line) control molecules.

It is notable that the HOMO–LUMO gap (the gap between the “highest occupied molecular orbital” and the “lowest unoccupied molecular orbital”) on the isolated molecule commonly seen in measurements of organic molecules^{4,8,35,36} is absent here, as it is in certain other molecules containing metallocenes.²¹ For our molecules, general knowledge of metallocenes suggests that the absence of a HOMO–LUMO gap in conductance is due to the fully occupied nonbonding and half-occupied antibonding molecular orbitals (a'_{1g})²⁻ (e_{1g}^{*1})¹ of cobaltocene (with the occupation number in the upper right corner).¹⁸ These orbitals largely preserve the properties of the cobalt d states and thus are higher in energy than the highest level from the conjugated π bonding orbitals. In particular, we see in our calculations that the ionization potential of the occupied antibonding e_{1g}^{*1} orbital is close to the work function of the leads. When molecule and lead are connected, charge transfer takes place because of the strong coupling, and the states mentioned above broaden. Consequently, cobaltocene moieties provide channels for low energy transport.

We verify the above arguments by replacing the two cobaltocene functional groups of DiCo-2C by ferrocenes (see Figure 3). The e_{1g}^{*} state of ferrocene is not occupied, so the diferrocene control does not show significant density of states until 0.8 eV away from the Fermi level.³⁷ In a diphenyl analogue, which lacks any nonbonding d-related orbitals, the first significant density of states is even further from the Fermi level (about 1 eV). As expected, the transmission is very poor in both cases.

To clarify the switch mechanism, we look in detail at the local density of states (LDOS) at the Fermi energy, $\rho(\mathbf{r}; E_F)$, in DiCo-2C. Figure 4 shows surfaces of constant LDOS, defined by $\rho(\mathbf{r}; E_F) = \text{constant}$, for both the spin up and spin down conduction channels in both the singlet and triplet states of the molecule. When the cobaltocene spins are antiparallel (singlet), the localized unpaired electron occupying the e_{1g}^{*1} antibonding orbital has, for instance, its spin down on the left side of the molecule and up on the right side. On the left side of the molecule, then, the highest occupied spin up state is a a'_{1g} nonbonding orbital, which does not have a large weight at the Fermi energy. The unoccupied e_{1g}^{*1} orbital likewise does not have weight at E_F ,

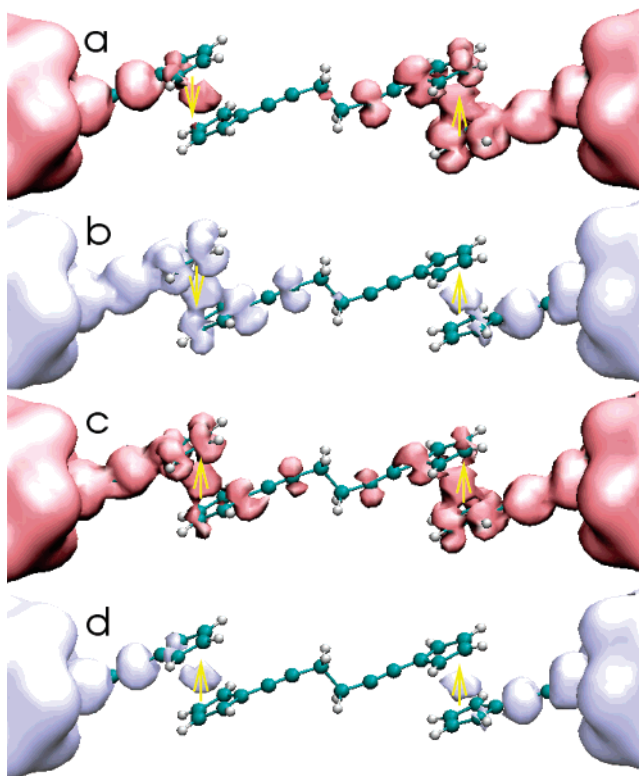


Figure 4. Surfaces of constant LDOS at the Fermi energy superposed on a model of DiCo-2C. (a/b) Spin up/down density of states in the singlet (antiparallel) configuration. The localized spin up/down electron occupies the antibonding orbital of right/left cobaltocene; both conduction channels are blocked. (c/d) Spin up/down density of states in the triplet (parallel) configuration. Both localized electrons are spin up, allowing good transmission of the spin up conduction electrons.

as it is too high in energy. This is, in fact, exactly what is seen in Figure 4: the spin up electron density at the Fermi energy is localized on the right where the e_{1g}^{*1} state is occupied (part a), and likewise, the spin down density is localized on the left (part b). Thus, for either spin, there is a large part of the molecule which is difficult to penetrate, and hence, the conductance is low.

When aligned parallel, the two unpaired spin up electrons both occupy e_{1g}^{*1} states; therefore, the spin up LDOS for the triplet DiCo-2C is intense on both sides. In contrast, spin down states are essentially absent around the Fermi level throughout the molecule. When bias is applied, spin up electrons traverse the molecule lead to lead while spin down electrons are blocked, thus producing both the switch and spin-valve effects.

Because spin-flip processes are not included in our calculations, these results set upper limits for both the switch ratio and spin-valve ratio. We anticipate, however, that spin-flip scattering in the 3 nm molecule is small: purely organic molecules are known to have a long spin coherence length^{17,38} because of very weak spin–orbit and hyperfine interactions, and the spin–orbit contribution of a single row 3 transition metal atom will not be large.

The DiCo molecule, though similar in many ways, differs from the above in that the stronger coupling between the

cobaltocenes causes a larger perturbation of their localized levels. The resulting level splittings bring minority spin states to the Fermi energy in the parallel state, thus explaining the lack of spin-valve behavior in DiCo.

Extreme sensitivity to contact geometry has proven to be a major problem in molecular electronic devices.^{39,40} To check the dependence of switching behavior on contact atomic structure, apex Au atoms were added between the sulfur anchoring groups of DiCo-2C and the leads (inset of Figure 2c). Figure 2c shows the transmission through DiCo-2C adsorbed on top of the added Au atoms. In the parallel state, the transmission of the majority spin component dominates as before. Its magnitude is, in fact, enhanced, leading to a switch ratio of 84—about an order of magnitude larger than without additional gold atoms. Thus, while the basic switch and spin-valve effects are robust upon this change in contact structure, a quantitative change takes place.

In conclusion, a dicobaltocene based molecular switch is proposed. The superexchange interaction can be controlled by the length of the spacer between the two cobaltocene moieties, allowing control of the on/off states with a magnetic field. The occupied antibonding state helps eliminate the gap seen in most molecular electronic devices, resulting in low bias operation. The on/off frequency depends on the spin relaxation time; we have not addressed that issue but rather leave it to be investigated experimentally.

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