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Coherent Transport through Spin-Crossover Single Molecules

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Ⓢ *Supporting Information*

ABSTRACT: Coherent quantum transport calculations were performed for high- and low-spin states of a mononuclear Fe^{II} complex showing spin-crossover behavior using density functional theory methods combined with the non-equilibrium Green functions procedure. The high-spin state has a larger conductivity than the low-spin state; furthermore, it behaves as a spin filter, giving a β-polarized current.

Spin-crossover molecules are especially appealing because the spin of the molecule can be controlled by many external stimuli (e.g., temperature, pressure, light, and electric field).[1,2] Many mononuclear hexacoordinate Fe^{II} complexes show this property, with switching of the spin between the low-spin $S = 0$ state with a t_{2g}^6 electron configuration to the high-spin $S = 2$ ground state with $t_{2g}^4e_g^2$ configuration. These features as well as the small size and ease of manipulation of such molecules have been exploited in new electronic and spintronic devices, such as memories,[3] nanoparticle electronics,[4] and single-molecule devices.[5,6] Hence, they play an important role in molecular spintronics.[7] Although the spin-crossover behavior has been studied extensively,[1] electron transport through molecules of this kind is not yet fully understood. The results of recent experiments, such as those examining transport through spin-crossover Fe^{II} nanoparticles or single molecules, remain to be clarified.[4−6] For instance, it is not clear whether the differences in conductance found for the high- and low-spin states are attributable to the electronic structure or rather to the structural changes (and interaction with the electrodes) due to the increase in the size of the molecule associated with the spin transition. The goal of this work was to analyze the transport of a spin-crossover Fe^{II} complex using theoretical methods and to provide insight into the mechanisms involved.

To this end, we chose a *trans*-bis(isothiocyanato)iron(II) complex synthesized by Niel et al.[8] to facilitate the contacts with the gold electrodes through coordination of the S atoms located in threefold hollow sites of the Au(111) surface (Figure 1).[9,10] The calculations were carried out with the spin-crossover molecule sandwiched between five gold layers with a 4 × 3 surface unit cell using the Transiesta code[11,12] with the PBE functional,[13] a numerical single-ζ basis set, and a one-electron pseudopotential for the gold atoms,[14] while a double-ζ basis set was employed for the other atoms. The coherent transport properties were calculated using the nonequilibrium Green function procedure[15−17] combined with density functionl theory (DFT) calculations.

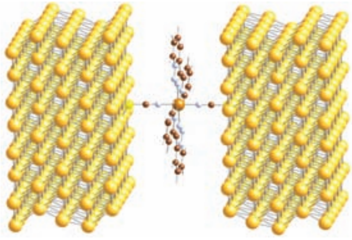

Figure 1. Structure of the device used in the calculations with the gold electrodes and the *trans*-bis(3-(2-pyridyl)[1,2,3]triazolo[1,5-*a*]-pyridine)bis(isothiocyanato)iron(II) complex.[8] Orange, blue, brown, and white spheres represent iron, nitrogen, carbon, and hydrogen atoms, respectively.

The calculation of the high-spin−low-spin (HS−LS) energy gap for the optimized isolated complex gave a value of 0.54 eV. It is well-known that generalized gradient approximation functionals, because of the presence of a large self-interaction error, usually overestimate the stability of the low-spin state.[18] Accordingly, we calculated the influence of an external electric field on such a HS−LS energy gap and found it to be relatively small. We found that an electric field of 0.05 V/Å, which could be induced by a probe microscope tip,[19] modifies this calculated HS−LS gap by only 0.005 eV. Hence, an electric field could induce the spin transition only at temperatures close to the transition temperature, where the high- and low-spin states are very close in free energy for the more stable high-spin entropic term. The different electric responses of the low- and high-spin states[20,21] or the thermal bistability of the dielectric constant due to the LS−HS transition[22] could be of great interest in detecting the nature of the state in electronic devices without employing magnetic fields. The calculated polarizability for the high-spin state is 14 au larger than the low-spin value when using optimized geometries for both spin states, and similar differences were previously found in other spin-crossover systems.[20]

To analyze the influence of the contact structure on the transport properties, we employed two different models. The first one fixing the Au−S distance at 2.5 Å for both states (mobile electrodes), and the other keeping the interelectrode distance at the value for the low-spin case (see the Supporting Information) in order to check the influence of a forced molecule−electrode interaction. The transmission spectra for the low- and high-spin states for the mobile electrode case are

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shown in Figure 2 (see Figure S1 in the Supporting Information for the fixed electrode case).

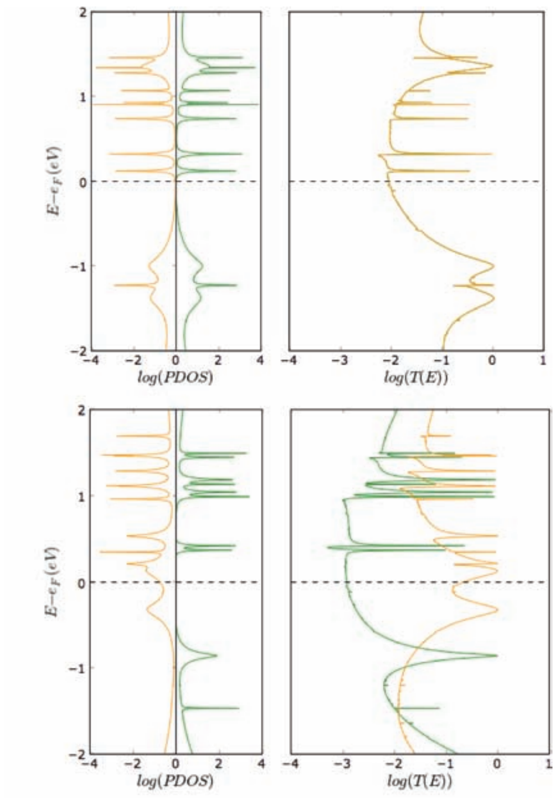
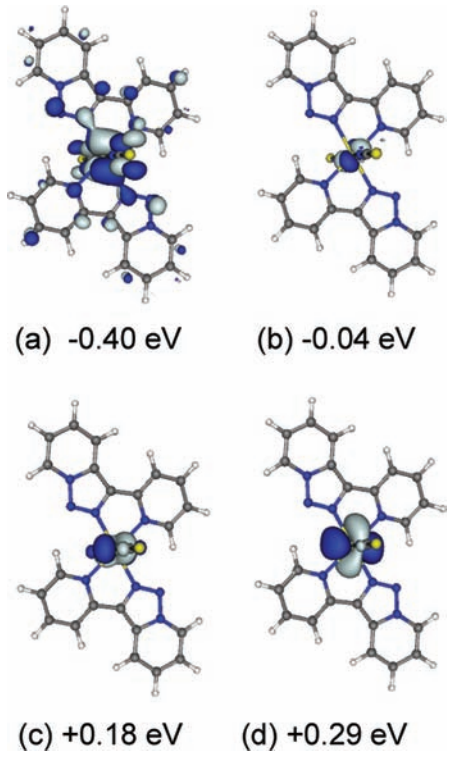


Figure 2. Logarithm of the calculated spin-resolved projected density of states of the Fe^{II} complex (left) and transmission spectra (right) when the Au−S bond distance was kept constant at 2.5 Å: low spin (top); high spin (bottom). Green and orange colors correspond to the α and β contributions, respectively.

Figure 2 and Figure S1 show large differences between high- and low-spin cases: (i) There are more levels close to the Fermi level for the high-spin system, most of them associated with β electrons. The β-occupied bands close to the Fermi level have contributions from the t_{2g} orbital (Figure 3a,b) bearing the unique β electron of the high-spin configuration ($t_{2g}{}^4e_g{}^2$). In the case of the low-spin state ($t_{2g}{}^6$), there are no occupied bands associated with the complex close to the Fermi level, and the higher-energy t_{2g} bands are below −1 eV. (ii) Also, the empty bands show a larger contribution close to the Fermi level for the high-spin state than for the low-spin state, mainly as a result of the presence of empty β t_{2g} bands (Figure 3c,d).

The projected density of states for the Fe^{II} complex and the transmission spectra for the mobile and fixed electrodes (see Figure 2 and Figure S1) are almost identical. We also repeated the calculation, this time using a new value of 1.9 Å for the Au−S bond distance and other Au−S coordination modes (see Figures S2 and S4), but there were still no important differences between the transmission spectra. Thus, the larger transmission of the high-spin state is due to the differences in the electronic configuration of the two states, while the size of the high-spin complex and consequently the stronger interaction with a system of fixed electrodes do not play a significant role.

Such differences in the transmission spectra for the high- and low-spin states are reflected in large differences in the calculated dependence of the current with an applied bias V (Figure 4; see Figure S3 for transmission spectra at different applied biases).[23]



(a) -0.40 eV (b) -0.04 eV

(c) +0.18 eV (d) +0.29 eV

Figure 3. High-spin β orbitals (and their energies) close to the Fermi level that make large contributions to the transmission.

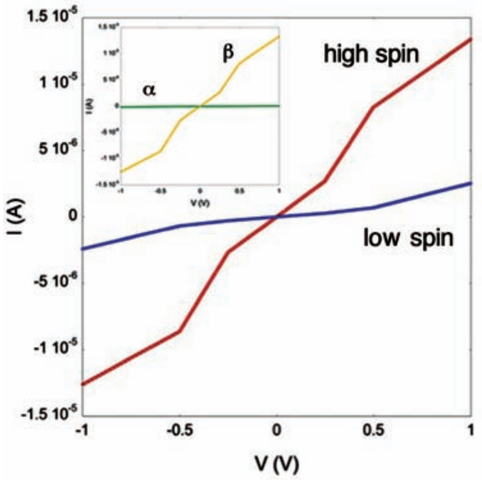


Figure 4. $I-V$ characteristics for the high-spin (red) and low-spin (blue) states. The inset shows the α (green) and β (orange) contributions to the current in the high-spin system.

The Fe^{II} complex in the high-spin state shows a larger current than the low-spin one, in agreement with the experimental data found on nanoparticles with a break-junction device.[4] Because of the electronic nature of the differences in transport for the low- and high-spin states, similar behavior could be found independently if the device is built up with either a single molecule or a nanoparticle. Analysis of the α and β components of the current of the high-spin system showed that practically all of the transport is due to β electrons. This finding was expected after the analysis of the spin-resolved transmission spectra because of the presence of β Fe^{II} t_{2g} orbital contributions close to the Fermi level. Thus, this high-spin Fe^{II} complex acts as a spin filter, exhibiting a higher transmission of β-spin electrons with respect to α electrons, considering that the unpaired electrons associated with the Fe^{II} center have α spin.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Transmission spectra for the fixed electrodes (Figure S1), effect of changing the Au−S distance (Figure S2), and dependence of the fixed-electrode transmission spectra on the applied bias (Figure S3); transmission spectra for the less stable on-top and bridge Au−S coordination contacts (Figure S4); and atomic coordinates and energies for the calculated systems. This material is available free of charge via the Internet at http://pubs.acs.org.

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