Electrostatic Spin Crossover and Concomitant Electrically Operated Spin Switch Action in a Ti-Based Endohedral Metallofullerene Polymer

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(Received 10 July 2012; revised manuscript received 26 October 2012; published 18 December 2012)

Herein, we predict that a 1D chain of Ti@C_{32} − C_2 − Ti@C_{32} (TEMF) will act as a spin switch in the presence of an electric field. The spin resolved density of states analyses reveal that, surprisingly, both the low- and high-spin states of TEMF are half-metal; however, the metallic density of states comes from the opposite spin channels of the two spin states. More remarkably, it is found that the electric field driven spin crossover between the low and high state in TEMF is achievable at field strength 1.04 V/nm, which eventually leads to the realization of the first ever electrically operated spin switch device.

DOI: 10.1103/PhysRevLett.109.257204 PACS numbers: 85.75.−d, 71.20.Tx, 75.50.Dd, 75.50.Ee

The quest for materials having spin selective properties and their manipulations in the presence of electric field is the most decisive task of modern spintronics research [1–5]. In spintronics, the spin of an electron acts as an information carrier in addition to its charge degrees of freedom and, after the serendipitous discovery of giant magnetoresistance in certain chromium alloys, the field has blossomed to such an extent that spintronics has started replacing its electronic counterpart [6–8]. Of the many possible device applications, spin valve [9], spin rectifier [10], spin transistors [11,12], spin filter [13], and magnetic tunneling junctions [14] are the ones that have promising potential in high speed data storage, spin-based quantum computing, magnetic sensors, and nonvolatile magnetic random access memory, to mention a few [15–18]. Despite its promising future, the most difficult part of spintronics research is the desired control of the spin state of a molecule or material when the electric field acts as an external stimulus [19]. In this context, Diefenbach and Kim [20] showed that spin multiplicity of certain nonpolar molecules, for example, Ba$(C_6H_6)_2$, could be changed in the presence of a static electric field. More recently, Baadji *et al.* [21] established that electric field induced spin crossover can take place at a modest field strength in polar magnetic molecules through superexchange interaction between two magnetic centers, and this groundbreaking phenomenon is now euphemistically known as electrostatic spin crossover (ESC). The ESC has the tantalizing prospect of developing new spin based devices [22], and one of them is a pure spin-based "off-on" switch, and, needless to say, the realization of a pure molecular spin switch is still elusive.

In this Letter, we will demonstrate that ESC through quintet state superexchange interaction can be accomplished in the unit cell of a Ti-based endohedral metallofullerene (TEMF) polymer, that is, a dimer of Ti@C_{32} bridged by acetylenic moiety ($-C\equiv C-$), at field strength of 1.04 V/nm. The TEMF polymer in its low-spin (LS) state shows half-metallicity [23] with its metallic feature in the up-spin channel and after crossing the threshold field strength, the more stable high-spin (HS) state also furnishes half-metallic character, but in this case, the metallic feature comes from the down-spin channel. This remarkable spin selective half-metal behavior of the LS and HS state of the TEMF polymer in the presence of external electric field is unprecedented and will pave the way to realize the first ever spin coherent "off" and "on" state, that is, a pure molecular spin switch. It is to be noted here that a similar EMF, namely, Ti@C_{28}, has already been synthesized [24].

In principle, if the magnetic centers are well separated and the prevailing interaction is dominated by superexchange through virtual transfer of electrons, the ground-state energies of the LS and HS spin states get modified due to the incorporation of the different magnetic excitations in the respective magnetic ground states. This additional energy correction has significant impact on the electric field induced first and second order Stark energy gain of the LS and HS states. Using the second order perturbation theory—based superexchange model of Baadji *et al.* [21], one can precisely estimate the critical field at which ESC will commence, and the relevant energy expression is

$$\Delta E_{\mathrm{GS}}^{\mathrm{LS,HS}}(V) \sim \Delta E_{\mathrm{GS}}^{\mathrm{LS,HS}} + \frac{1}{2a_0} p_{\mathrm{GS}}^{\mathrm{LS,HS}} V + \frac{1}{4a_0} \alpha_{\mathrm{GS}}^{\mathrm{LS,HS}} V^2, \tag{1}$$

where a_0 denotes the distance between two magnetic centers and the bridge and $\Delta E_{\mathrm{GS}}^{\mathrm{LS,HS}}$ signifies the lowering of the energy of the LS and HS states upon inclusion of magnetic excitations. $p_{\mathrm{GS}}^{\mathrm{LS,HS}}$ and $\alpha_{\mathrm{GS}}^{\mathrm{LS,HS}}$ are the electric dipole moment and polarizability of the LS and HS states, respectively. It is worth noting that the above expression is valid for any combination of LS and HS states, and with an aspiration to achieve electrically controlled spin states higher than triplet, we have applied it to the study of

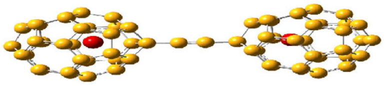

FIG. 1 (color online). Optimized geometry of TEMF.

ESC between singlet and quintet states. For this purpose, we have selected the dimer of TEMF as the unit cell where each Ti has two unpaired electrons with $3d^2$ configuration, and this makes an ideal background for achieving the quintet state of the system. The geometry of the unit cell is presented in Fig. 1 where two Ti@C_{32} units are coupled by an acetylenic moiety ($-\mathrm{C}\equiv\mathrm{C}-$) that offers a pathway for the quintet state superexchange interaction. The geometry optimizations in the presence and absence of electric field of the pure singlet, broken symmetry (BS), and quintet states are performed with the Becke three-parameter Lee-Yang-Parr (B3LYP) hybrid functional, and the basis sets used are the double-ζ polarization for C and the effective core potential corrected Los Alamos National Laboratory 2-double-ζ (density functional theory) (LANL2DZ) potential for Ti. It has been found that the BS state is more stable than the pure singlet and quintet states. The greater stability of the BS state is an indication of antiferromagentic (AFM) ordering of the TEMF dimer. On the optimized geometries, fresh calculations have been carried out to extract the quantities such as the magnetic coupling constant (J^0_{SQ}), $p^{\mathrm{LS,HS}}_{\mathrm{GS}}$, and $\alpha^{\mathrm{LS,HS}}_{\mathrm{GS}}$ along the direction of the electric field (along the x axis in the present study). In this case, we have relied upon the B3LYP functional since it contains adequate nonlocal HF exchange and the chosen basis sets are triple zeta valence plus polarization function for C and LANL2DZ for Ti. The whole calculation has been implemented in the GAUSSIAN09 suite of programs [25]. To evaluate the different quantities of Eq. (1), we have followed the methodology developed by Baadji *et al.* [21], or in other words, we have performed explicit second order perturbation correction by using the Kohn-Sham orbitals obtained from the ground- and excited-state configurations.

All the relevant quantities for the BS and the HS states are presented in Table I. The sign of the magnetic coupling constant of the TEMF dimer is in favor of antiferromagnetic interaction between the two Ti@C_{32} units, indicating the higher stability of the LS state over the quintet analog. At the same time, it is also evident that both the dipole moment and the polarizability of the HS state (quintet) are greater than that of the LS state, which opens up the possibility of ESC to occur at some critical field strength.

TABLE I. Magnetic coupling constant and dielectric properties of TEMF.

J^0_{SQ} (meV)	p^S_{GS} (a.u.)	p^Q_{GS} (a.u.)	α^S_{GS} (a.u.)	α^Q_{GS} (a.u.)
−0.291	0.0	0.13	869.03	878.74

To evaluate the critical field strength that initiates ESC in TEMF, we have computed the electric field dependent $\Delta E^{\mathrm{LS,HS}}_{\mathrm{GS}}$ following Eq. (1), and the corresponding energy parabolas of the LS and HS states are depicted in Fig. 2, which demonstrates the occurrence of ESC in TEMF at an experimentally achievable field strength of 1.04 V/nm.

Table I clearly dictates that the dipole moment of the BS state is almost zero and is quite compatible with the geometry having a center of inversion. However, the HS state of the TEMF dimer has a dipole moment of 0.13 a.u., and this has happened due to partial symmetry breaking as the number of bonds between Ti and C of the two Ti@C_{32} units are different in the HS state. Earlier, Baadji *et al.* [21] found that an unsubstituted cobaltocene dimer bridged by acetylenic unit ($-\mathrm{C}\equiv\mathrm{C}-$) has insignificant dipole moment in the HS and LS states, and, as a consequence, no ESC has been realized in their unsubstituted system. However, they got a modest difference in the dipole moment of the HS and LS states in a -OMe substituted cobaltocene dimer, which is fair enough to set off ESC at 1.5 V/nm. Moreover, they have also noticed that the critical field strength can further be reduced by a suitable choice of the substituent groups, namely, −CN. Nonetheless, the accomplishment of ESC in unsubstituted TEMF through quintet state superexchange interaction is indeed remarkable and a completely new phenomenon in this field.

This *in silico* anticipation of ESC in TEMF through quintet state superexchange has far-reaching consequences in spintronic device applications, and one such possibility is the design of a molecular spin switch that operates in the presence of electric field. To establish the spin coherent off-on switch action, we have chosen the one-dimensional polymer chain of TEMF. Considering the unit cell geometry as depicted in Fig. 1, we have performed periodic boundary calculations on the AFM and ferromagnetic (FM) states using Amsterdam Density Functional 2012.01a package [26]. In this case, we have used the

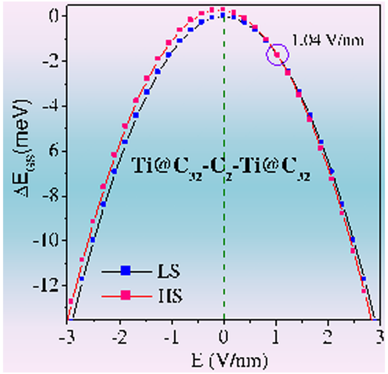

FIG. 2 (color online). Variation of ΔE_{GS} (scaled with respect to singlet) for the BS and quintet states of TEMF as a function of external electric field. Violet circle represents spin crossover point.

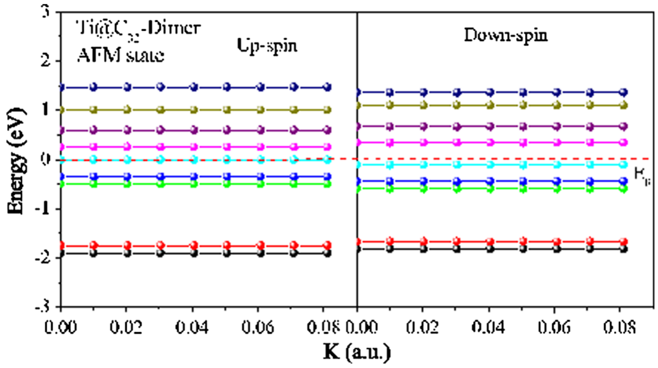

FIG. 3 (color online). Band structure of TEMF polymer in AFM state at zero field.

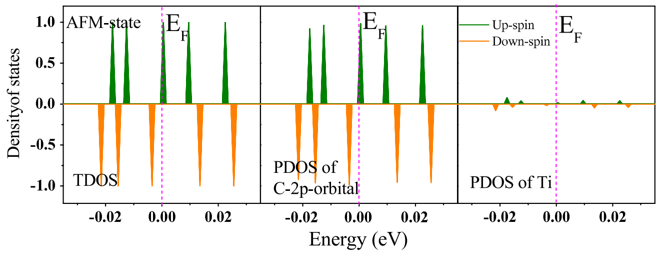

FIG. 5 (color online). DOS of AFM state of TEMF polymer at zero field.

Hubbard U–corrected generalized gradiant approximation (GGA) functional (GGA + U), more precisely, revPBE + U (where PBE is the Perdew-Burke-Ernzerhof functional), and the basis set used is triple zeta with double polarization function for both C and Ti. The U values are taken as 0.280 and 0.355 a.u. for C and Ti, respectively. While the spin-flip density functional theory (DFT) method ensures the capture of the AFM state properly, the FM state is achieved by taking into account the high- spin state of the unit cell. The spin-polarized band structures of both the AFM and FM states of a TEMF polymer are presented in Figs. 3 and 4. Across the Fermi level, all the bands of the AFM and FM states of the TEMF polymer are quite flat, indicating Ti-encaged fullerene moieties are weakly interacting and thus creating a proper environment for superexchange interaction. Albeit, flatband ferromagnetism is already observed in a number of materials [27–29], its AFM counterpart is still missing, and in the absence of electric field, the stable AFM state of the TEMF polymer with noticeable flatband is of profound importance in condensed matter physics. Normally, interacting electrons with flatband prefer to stay at the FM state; however, the dominant interaction in the TEMF polymer is superexchange type and the superexchange pathway is a linear one that helps stabilize the AFM state even with the flatbands. The electric field free band structures of the more stable AFM state of the TEMF polymer also reveal an appealing feature, that is, the presence of a particular energy band just at the Fermi level in one spin channel and the absence of the same in the other. This feature also persists in the FM state of the TEMF polymer at a field strength 1.04 V/nm, when the FM state becomes more stable than the AFM state.

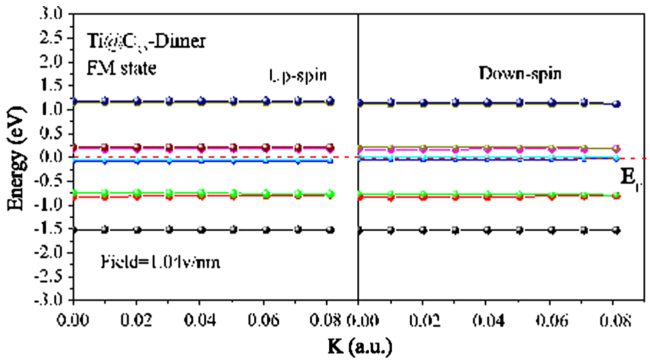

FIG. 4 (color online). Band structure of TEMF polymer in FM state at 1.04 V/nm.

To inspect such an unusual finding more rigorously, we need to analyze the spin-resolved total density of states (TDOS) and partial density of states (PDOS) of all the elements involved in the formation of the TEMF polymer in its AFM and FM states. The zero field DOS and PDOS of the TEMF polymer in the AFM state is presented in Fig. 5, and the same for the FM state at electric field strength 1.04 V/nm is shown in Fig. 6. Figure 5 illustrates the presence of finite DOS at the Fermi level of the up-spin channel while the existence of DOS at the Fermi level is completely absent in the down-spin channel.

This clearly indicates that the TEMF polymer in the AFM configuration at zero field strength should behave as a metal in the up-spin channel, keeping the down-spin electrons in the insulating state, or in other words, the TEMF polymer will act as an antiferromagnetic half-metal in the absence of electric field. Most remarkably, the stable FM state of the TEMF polymer after crossing the critical electric field also shows half-metallic behavior. However, in this case, the metallic feature comes from the down-spin electrons and it is clearly reflected from Fig. 6, which indicates the presence of appreciable DOS at the Fermi level of the down-spin channel in contrast to its up-spin analog.

This electric field controlled spin selective half-metallicity in the AFM and FM state of the TEMF polymer

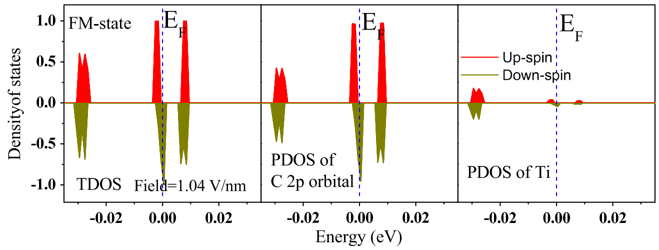

FIG. 6 (color online). DOS of FM state of TEMF polymer at 1.04 V/nm.

is the only one of its kind and opens up new avenues for developing a high speed molecular spin switch. The possibility of achieving such device action is quite rational since the spin-polarized current in the AFM state will come from the up-spin electron while the same for the FM state will be originated from the down-spin electron. A meticulous examination of the PDOS of C and Ti spells out another surprising phenomenon associated with the spin selective half-metallicity of the TEMF polymer in the AFM and FM states. Figures 5 and 6 elucidate that the half-metal behavior in both of the magnetic configurations arises out of the $2p$ electrons of C even when a $3d$ transition metal, Ti, is present in the system. This metal free magnetism in a transition metal containing carbon compound is unparalleled. To justify this unique C-based magnetism in the TEMF polymer, we have evaluated the magnetic moment of the TEMF unit cell in its FM state and found that the total magnetic moment is $4\mu_B$, which is fully consistent with the HS state of the dimer. However, out of this $4\mu_B$, the two C_{32} rings contribute approximately $3\mu_B$, indicating a strong bonding interaction between Ti and C_{32} facilitates the transfer of charge from Ti to the C_{32} cage. This unusual magnetic property of TEMF is fully consistent with the spin density mapping as depicted in Fig. 7.

To establish the possibility of achieving a purely electrically controlled spin switch, we have further performed spin-polarized quantum transport calculation, and the calculations are implemented within Atomistix Toolkit 12.2.2 [30]. The nonequilibrium Green function—based transport calculations are carried out in combination with a double-ζ polarized basis function and a spin-polarized PBE functional. The relevant results are depicted in Fig. 8. The current-voltage (I-V) characteristics manifestly demonstrate a strong switch action between the AFM and the FM state. In the low bias region (<1.0 V), the current obtained from the AFM state is significantly smaller than that of the FM state at bias >1.0 V. A closer inspection of the I-V curve reveals that I_{FM}/I_{AFM} could be as high as 380, indicating that the present TEMF-based two-probe setup is a perfect choice for realizing the electrically operated spin switch. The contour plot of the dominant molecular projected self-consistent Hamiltonian (MPSH) states involved with the transport process are also shown in Fig. 8, which shows that the dominant transport path of the AFM state is much more localized than the FM state and offers an explanation of the origin of the strong switch action. Furthermore, to justify whether or not the field strength required for initiating the ESC in TEMF is observable in a molecular junction experiment, we have evaluated the potential drop (ΔV_{Ti}) between the two Ti atoms of TEMF in the applied bias range 0.01–1.5 V. The variation of ΔV_{Ti} with applied bias is shown in the inset of Fig. 8, which illustrates that an applied bias of 1.5 V produces a relative change of the on-site energy of the Ti atoms by an amount of 0.7 V. Moreover, the distance between the two Ti atoms is 0.9 nm, and therefore the accomplishment of ESC in TEMF is quite feasible by means of a two-probe experiment in a STM setup.

Based on the foregoing discussions, we conclude that electrostatic spin crossover through quintet state superexchange interaction will commence in the unit cell of a TEMF polymer at an experimentally achievable electric field strength of 1.04 V/nm. By exploiting this heuristic ESC phenomenon, the spin switch action in TEMF is realized since a finite bias 1.04 V/nm has favored the FM state that displays half-metallicity with a metallic down-spin channel, while in the absence of electric field, the more stable AFM state behaves as metal and the metallic behavior comes from the up-spin electron only. More surprisingly, our study also reveals that the $3d$ electrons of a Ti atom do not make any significant contribution in the density of states and the spin coherent "off" and "on" action is solely guided by the $2p$ electrons of C of the fullerene cage. Furthermore, the quantum transport calculation clearly demonstrates that both ESC and the spin switch action in TEMF could be made possible in a real two-probe experimental setup. In brief, the quintet state superexchange interaction induced ESC and the concomitant electric field driven spin selective half-metallicity in

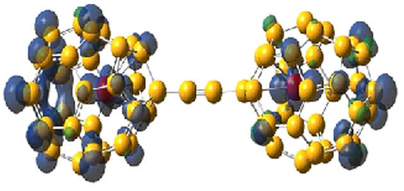

FIG. 7 (color online). Spin density mapping of TEMF polymer in FM state.

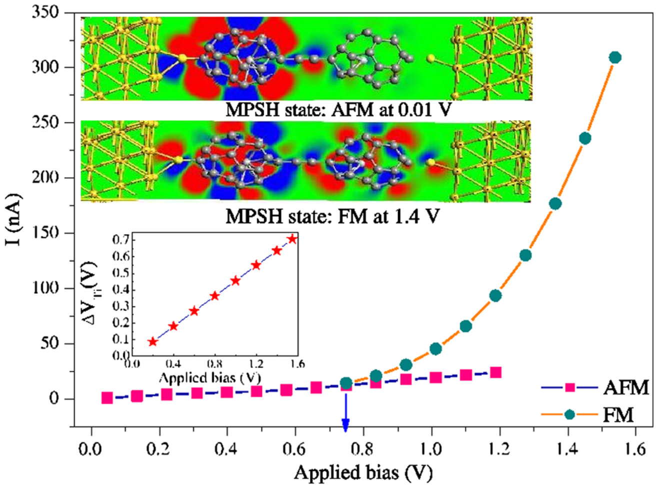

FIG. 8 (color online). I-V characteristics of TEMF connected with the hollow sites of Au(111) electrodes. Inset represents the change in potential drop between two Ti atoms against applied bias; MPSH state of the system in AFM state (0.01 V) and FM state (1.4 V).

the AFM and FM state of the TEMF polymer *vis-à-vis* spin switch action at experimentally measurable electric field strength is completely unprecedented.

The authors convey their special thanks to Professor Stefano Sanvito for helping us understand many critical aspects of electrostatic spin crossover phenomena. M. C. thanks CRNN, University of Calcutta. M. A. thankfully acknowledges CSIR, Government of India, for support through a senior research fellowship. S. S. thankfully acknowledges DST, Government of India for the Fast Track Project.

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