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The spin-filter capability and giant magnetoresistance effect in vanadium–naphthalene sandwich cluster

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ABSTRACT

Using density functional theory and non-equilibrium Green's function technique, we performed theoretical investigations on the magnetic and transport properties of $V_{2n}(C_{10}H_8)_{n+1}$ (n = 1–4) sandwich clusters. For the ground states, our results show that all the clusters are stable and possess ferromagnetic orders. The smaller clusters have higher stabilities, and our predictions are in agreement with the experimental observation. The double exchange mechanism plays an important role in determining the magnetic properties of the systems. Furthermore, with Ni as electrodes, the clusters exhibit interesting transport properties such as significant spin-filter capability, negative differential resistance feature and giant magnetoresistance effect. These findings suggest that $V_{2n}(C_{10}H_8)_{n+1}$ sandwiches are excellent candidates for application in spintronics and organic electronics.

1. Introduction

Since the discovery of ferrocene Fe $(C_5H_5)_2$ in 1951 [1], organic sandwich molecules and clusters have constituted one of the most important subjects in organic chemistry because of their current and potential applications in different areas, such as catalysis, materials science and electronics [2]. With the development of experimental techniques, in recent years many multidecker sandwiches comprised of suitable transition metal (TM) atoms and different monocyclic ligands, including $TM_m(C_5H_5)_n$ and $TM_m(C_6H_6)_n$ (m and n are integers), have been synthesized [3–14]. In parallel with the experiments, the magnetic and transport properties of the finite sandwich clusters and one-dimensional (1D) infinite sandwich nanowires have been investigated theoretically [15–20]. The experimental and theoretical studies revealed that the organic sandwiches have intriguing properties such as spin-filter capability and half-metal behavior, which is a key advantage for their application in spintronics and organic electronics.

It would be interesting to note that the polycyclic organic ligands with more than one carbon ring can also make similar multidecker sandwiches, and they can hold more TM atoms in the sandwich region. Several efforts have been dedicated to this field experimentally and theoretically [21–30]. For example, different-sized vanadium–naphthalene clusters $V_m(C_{10}H_8)_n$ and vanadium–anthracene clusters $V_m(C_{14}H_{10})_n$ have been synthesized by reacting vanadium vapor with naphthalene and anthracene in gas phase [21]. In addition, cobalt–pentalene

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clusters $Co_2(C_8H_6)_2$ and iron-pentalene clusters $Fe_2(C_8H_6)_2$ were prepared and the magnetic properties were discussed [22,23]. Zhang and his coworkers recently explored 1D infinite sandwich nanowire $[V_2(C_{10}H_8)]_\infty$ by using density functional theory (DFT) [24]. They found that the ground state of the nanowire is antiferromagnetic and, more importantly, the magnetic order of the system can be adjusted by changing its charge state. The ground state of $[V_2(C_{14}H_{10})]_\infty$ was predicted to be a typical ferromagnetic half-metal in another study [28]. Furthermore, Peierls phase transition was found in $[Mn_2(C_8H_6)]_\infty$ nanowire [29]. In a word, the sandwich systems with polycyclic organic ligands could exhibit more novel physical and chemical properties since they contain more TM atoms.

In present paper, we perform a theoretical investigation on small $V_{2n}(C_{10}H_8)_{n+1}$ (n = 1–4) sandwich clusters. The reasons for exploring such systems were based on the following two considerations: On one hand, in the mass spectrum, the peaks of $V_{2n}(C_{10}H_8)_{n+1}$ are quite pronounced [21]. However, there is little information about the organic sandwiches so far. Although the structures and magnetic properties of 1D infinite $[V_2(C_{10}H_8)]_\infty$ nanowire were reported [24], according to previous study [30], the finite clusters may be very different from the infinite nanowire owing to the quantum confinement effect and quantum size effect.

On the other hand, as mentioned before, interesting properties such as spin-filter capability and half-metal behavior were found in monocyclic ligand sandwiches. Therefore, the transport properties of $V_{2n}(C_{10}H_8)_{n+1}$ deserve our attention because the sandwiches contain more V atoms and have more complicated interactions. To the best of our knowledge, however, the transport properties of such systems are still open questions, a detailed investigation should be necessary and exciting.

2. Computational methods

Geometry optimization and electronic structure calculation of sandwich were performed by using DFT method as implemented in DMOL^3 code [31]. The spin-polarized generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) functional [32] and double numerical basis set with polarization functions (DNP) were employed. The combination of PBE/DNP has been successfully applied to investigate sandwich systems in our recent study [33]. For a given sandwich, all the possible magnetic orders were examined during the optimization. Take $V_4(C_{10}H_8)_3$ as example, the initial structure and possible magnetic orders, including non-magnetic (NM), ferromagnetic (FM) and antiferromagnetic (AFM) orders, are given in Fig. 1a and b. The Jahn–Teller distortion was considered for the cluster with high symmetry and the vibrational frequencies were analyzed to ensure that the optimized structures are stable.

The transport properties of sandwiches were calculated by using ATK code [34]. The functional was set to be the same as that used in the electronic structure calculations. Optimized basis set of the double-ζ quality including polarization functions (DZP) was adopted with the real-space mesh cutoff 300 Ry. To carry out the transport calculations, the non-equilibrium Green's function (NEGF) technique was employed and the two-probe molecular junction used here is shown in Fig. 1c. Although similar two-probe model was described in our previous study [33], a brief introduction should be necessary. In present study, current–voltage relationship, spin filter efficiency (SFE) and giant magnetoresistance (GMR) effect at different bias voltages were investigated. The SFE value at zero bias voltage is calculated from the transmission by its definition

$$\mathrm{SFE} = \frac{T_\uparrow(E_F) - T_\downarrow(E_F)}{T_\uparrow(E_F) + T_\downarrow(E_F)} \times 100\% \quad (1)$$

where $T_\uparrow(E_F)$ and $T_\downarrow(E_F)$ are the transmission spectrum at Fermi energy E_F of spin-up (↑) and spin-down (↓) channels under zero bias voltage, respectively. Because nanodevices always work at various electrical biases, the spin-polarized current I_σ (σ = ↑ or ↓) at finite bias voltage can be calculated by using the Landauer-Büttker formula [35]

$$I_\sigma = \frac{e}{h}\int T_\sigma(E, V_b)[f_L(E, V_b) - f_R(E, V_b)]dE \quad (2)$$

where $T_\sigma(E, V_b)$ represents the spin-polarized transmission spectrum calculated at bias voltage V_b, while $f_{L(R)}(E, V_b)$ is the Fermi–Dirac distribution function for the left (right) electrode. The total current can be then obtained from $I = I_\uparrow + I_\downarrow$. Different from Eq. (1), the SFE at the finite bias voltage is defined as

$$\mathrm{SFE} = \frac{I_\uparrow - I_\downarrow}{I_\uparrow + I_\downarrow} = \frac{I_\uparrow - I_\downarrow}{I} \times 100\% \quad (3)$$

It is well known that the choice of metal electrodes is an important issue for designing nanodevices [36]. Such issue is very complicated because different metal electrodes will give rise to specific characteristics of the nanodevices, e.g., the bonding nature between the metal electrode and the cluster could determine the so-called contact conductance, while the contact conductance will further severely influence the transport properties of the system. In order to choose suitable electrodes, we considered different magnetic metals, i.e. Fe, Co and Ni, as electrodes to construct three kinds of molecular junctions. The calculated SFE values of the three systems under zero bias are listed in Table 1. One can see that the Ni electrodes could well match with the outermost $C_{10}H_8$ ligands of $V_4(C_{10}H_8)_3$ and lead to largest SFE value. Therefore, Ni electrodes were adopted here.

For different mutual alignments of the magnetization of Ni electrodes, the electrical conductance was investigated and the GMR was then calculated by the definition

$$\mathrm{GMR} = \frac{G_P - G_{AP}}{G_{AP}} \times 100\% \quad (4)$$

where G_P and G_{AP} are the conductance of the molecular junction with the mutual magnetization orientation of the Ni electrodes parallel (P) alignment or antiparallel (AP) alignment to each other, respectively (see Fig. 1d). A similar treatment was used to investigate the magnetoresistance in graphene naondevices recently [37]. From Table 1, it is obvious that the molecular junction based