硅桥调控的聚茂钒体系电子结构和输运性质

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摘要: 利用密度泛函理论和非平衡格林函数的方法对硅桥调控后的聚茂钒体系 $[V(Cp)_2(SiH_2)_n]_m$ ($n = 1$ (**a**), $n = 2$ (**b**), $n = 3$ (**c**); $m = \infty$; Cp = 环戊二烯基))的电子结构和输运性质进行了研究。研究表明: 随着硅桥的增长, V-V 的铁磁性耦合变弱而反铁磁性耦合增强。**a**和**b**证实为铁磁性基态, 而**c**更倾向为反铁磁性基态。**a**和**b**的铁磁性基态中的每个钒原子的磁距为 $3.0\mu_B$, 超过钒-苯络合物或者纯聚茂钒体系的3倍。**a-c**的输运性质同它们的电子结构相一致, 导电性变化规律为**c** > **b** > **a**。对于**a**和**b**, 自旋向下状态的导电性略强于自旋向上状态。**a**和**c**都发生了明显的负微分电阻效应而**b**却没有, 这主要是由于两个二茂钒的排列取向不同: **a**和**c**(SiH_2 为奇数)中二茂钒呈V-型取向排列, 进而导致了类似于离子键的量子点耦合, 而**b**(SiH_2 是偶数)中二茂钒是平行-型取向排列, 从而导致了类似于共价键的量子点耦合。此外, 由于散射区和两个电极之间的不对称耦合, **a-c**的导电性对电压施加方向较敏感。

关键词: 硅桥键; 聚茂钒; 电子结构; 输运性质; 理论研究

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Silicon Bridge-Tuned Electronic Structures and Transport Properties of Polymetalloenes

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Abstract: Silicon bridge-tuned electronic structures and transport properties of polymetalloenes, $[V(Cp)_2(SiH_2)_n]_m$ ($n = 1$ (**a**), $n = 2$ (**b**), $n = 3$ (**c**); $m = \infty$; Cp = cyclopentadienyl), are studied using the density functional theory (DFT) and non-equilibrium Green's function (NEGF) methods. As the silicon bridge is lengthened, the V-V ferromagnetic (FM) coupling is weakened, while the antiferromagnetic (AFM) coupling is strengthened. Polymetalloenes **a** and **b** favor the FM ground state, while **c** prefers the AFM ground state. Each V atom in the FM state of **a** and **b** has a magnetic moment of $\sim 3.0\mu_B$, three times larger than that in the V-benzene or V-cyclopentadiene multidecker complex. The transport properties of **a-c** are in good agreement with their electronic structures. Their conductivities follow the sequence **c** > **b** > **a**. For **a** and **b**, the spin-down state has slightly higher conductivity than the spin-up state. Polymetalloenes **a** and **c** can both display evident negative differential resistance (NDR) behavior, while **b** cannot. This difference may originate from the orientation of the two $V(Cp)_2$ units, which is V-shaped for **a** and **c** (odd number of SiH_2 units), leading to ionic-like inter-quantum dot coupling, and parallel for **b** (even number of SiH_2 units), leading to covalent-like inter-quantum dot coupling. In addition, the conductivity of **a-c** is sensitive to the current direction because of the asymmetric coupling between the scattering region and two electrodes.

Key Words: Silicon bridge; Polymetalloene; Electronic structure; Transport property; Theoretical study

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1 Introduction

Bridge linked polymetalloenes have attracted continuous interest over the past decade due to their unusual electrical, magnetic, and optical properties^{1–8}. A broad variety of such polymers has been synthesized in laboratory. The bridge moiety can vary from group 13 (B, Al, Ga, In)^{9–12} to group 14 (Si, Ge, Sn)^{13–17}, group 15 (P, As)^{18–20}, and group 16 elements (S, Se)^{21,22}. The metallocene can cover almost the whole first-row transition metal series (Sc–Ni) and some second- and third-row transition metal species (Zr, Hf, Pt)^{23–27}. Much of the interest in these polymers has been focused on the saturated silicon-bridged polymetalloenes; representative examples are the silicon-bridged polyferrocenes^{28–33}. It is confirmed that these copolymers can be utilized as charge dissipation coatings, variable refractive index sensing materials, and magnetic ceramic precursors over a range of length scales^{34–39}.

The silicon linkages possess a remarkable ability to tune the physicochemistry property of the resulting bridged polymetalloenes. The frontier orbitals of a metallocene largely preserve the *d* character of the transition metal atom; the cyclic π -coordinated carbon ligands confine the *d* states, making the metal atom an intrinsic molecular quantum dot. The saturated silicon bridges block the adjacent metallocene units spatially and energetically, ensuring the quantum dot behavior of the metal atom⁴⁰. Quantum dots are of great interest in many research applications such as transistors, solar cells, light emitting diodes (LEDs), and diode lasers because electron transport through quantum dots can be precisely controlled by tailoring the molecular size^{41,42}. The length of the silicon bridge plays a significant role in the interdot coupling. For example, Dement'ev *et al.*⁴³ have shown that the Fe–Fe interaction decreases with increasing of the bridge length in a series of silicon-bridged biferrocenes. Experiments have demonstrated that the conducting behavior of ferrocenylsilane polymers is highly dependent on the length of silicon bridge⁴⁴. Studying the silicon moiety effect on the electronic and transport properties of the silicon-bridged polymetalloenes is desirable for the generation of functioned molecular devices.

Recently, polymers derived from sandwiched vanadium complexes are of particular hot topics owing to the high density of unpaired spins of V atoms which are expected to exhibit remarkable physical properties with regard to magnetism or conductivity¹⁹. So far, much effort has been invested in the synthesis of silicon bridged polymers of vanadium complexes. Pioneering work in this area includes that of Elschenbroich *et al.*^{44–49} and Braunschweig *et al.*^{50–52}, who were the first to obtain such silicon bridged polymers by using ring-opening polymerization method of $[\text{V}(\eta^6\text{-C}_6\text{H}_5)_2\text{SiMePr}]$ and $[\text{V}(\eta^5\text{-C}_5\text{H}_5)(\eta^7\text{-C}_7\text{H}_7)\text{SiMePr}]$. They demonstrated that these polymers show a pronounced intramolecular electronic and magnetic communication. The silicon bridged vanadium containing polymers $[\text{V}(\text{Cp})_2(\text{SiH}_2)_n]_m$ are expected to be excellent candidates for exploring novel functional materials with fantastic magnetism and conductivity. Similar to the case in ferrocenylsilane polymers⁴¹, the silicon bridge length *n* in $[\text{V}(\text{Cp})_2(\text{SiH}_2)_n]_m$ may play important role in governing the electronic and transport properties.

In this context, three polyvanadocenes, $[\text{V}(\text{Cp})_2(\text{SiH}_2)_n]_m$ (*n* = 1, 2, 3; Cp = cyclopentadienyl), are the major focus of our studies by using density functional method (DFT) and non-equilibrium Green's function (NEGF) methods (Fig.1). We first investigate the electronic properties of their infinite long systems (*n* = ∞), followed by computing the transport properties of their two-probe devices by curving out one supercell (*n* = 2) sandwiched between two Au electrodes. For the sake of facilitating discussions, we denote infinite long systems of $[\text{V}(\text{Cp})_2(\text{SiH}_2)]_\infty$, $[\text{V}(\text{Cp})_2(\text{SiH}_2)_2]_\infty$, and $[\text{V}(\text{Cp})_2(\text{SiH}_2)_3]_\infty$ as **a**, **b**, and **c**, respectively (Fig.1(a)); we also denote two-probe devices of $\text{Au}/[\text{V}(\text{Cp})_2(\text{SiH}_2)]_2/\text{Au}$, $\text{Au}/[\text{V}(\text{Cp})_2(\text{SiH}_2)_2]_2/\text{Au}$, and $\text{Au}/[\text{V}(\text{Cp})_2(\text{SiH}_2)_3]_2/\text{Au}$ as **D-a**, **D-b**, and **D-c** (Fig.1(b)). We find that the length of the silicon moiety has notable effects on the electronic and transport properties of the silicon bridged polyvanadocenes.

2 Models and computational methods

For computing electronic structures, the infinite long systems

Fig.1 (a) Optimized structures of polymetalloenes a, b, c and (b) the two-probe devices D-a, D-b, D-c for electron transport computation

Table 1 Calculation results of reaction energy ($\Delta E_{\text{reaction}}$), supercell length (L), total energy in the FM and AFM states ($E_{\text{Tot,FM}}$ and $E_{\text{Tot,AFM}}$), energy difference between FM and AFM states ($\Delta E_{\text{FM-AFM}}$), magnetic moment (S) for **a**, **b**, **c**, **D-a**, **D-b**, and **D-c**

Species	$\Delta E_{\text{reaction}}/\text{eV}$	L	$E_{\text{Tot,FM}}/\text{eV}$	$E_{\text{Tot,AFM}}/\text{eV}$	$\Delta E_{\text{FM-AFM}}/\text{meV}$	S/μ_B
a	-5.24	14.548	-7715.78088	-7715.77500	-5.88	6.003
b	-17.94	18.500	-8138.27056	-8138.27045	-0.11	6.02
c	-36.90	22.250	-8560.88640	-8560.88693	0.53	-0.009
D-a	—	—	-131051.08489	-127779.70929	-3.27	—
D-b	—	—	-131510.23977	-128196.96583	-3.31	—
D-c	—	—	-128612.62842	-131908.65216	3.30	—

of **a**, **b**, and **c** are modeled *via* using the periodic condition in the axial direction (Fig.1(a)). Each repeated cell included two vanadocene units. Such supercell could facilitate to consider the magnetic coupling between V atoms. The polymers are separated by ~ 2.4 nm from each other to neglect inter-chain interaction. All the periodic systems are fully optimized until the maximum absolute force is less than $0.2 \text{ eV} \cdot \text{nm}^{-1}$.

For computing transport properties, the two-probe devices of **D-a**, **D-b**, and **D-c** are adopted (Fig.1(b)). We carved out one supercell, i.e., $[\text{V}(\text{Cp})_2(\text{SiH}_2)]_2$, $[\text{V}(\text{Cp})_2(\text{SiH}_2)_2]_2$, and $[\text{V}(\text{Cp})_2(\text{SiH}_2)_3]_2$, as the central scatter region based on the optimized periodic structures to be sandwiched between two Au electrodes. The semi-infinite Au electrodes were modeled by two Au(111)- (3×3) surfaces, and five layers were used for the left and right sides. As the sulfur atom has good affinity with the gold surface, dithiolate derivatives have been used for the construction of metal/molecule/metal junctions in general^{53–56}. Therefore, in the present work, we also used the sulfur atom as the junction to link the Au electrode and the bivanadocene system. The sulfur atom was set to the hollow site of the electrode as most of the studies had elucidated that the hollow site was more favorable in energy than the top and bridge adsorption sites^{53–56}. In this model, the S–Au distance was set as 0.2341 nm according to the reported literature^{57,58}. Calculations were carried out by changing the applied bias in the step of 0.2 V in the range of $-1.0 - 1.0$ V.

All the computations for the infinitely long and two-probe systems are performed using an *ab initio* code package, Atomistix ToolKit (ATK), which is based on combination of DFT and NEGF methods^{59–62}. A generalized gradient approximation (GGA) within the Perdew-Burke-Ernzerhof (PBE) formalism is employed to describe the exchange correlations between electrons. Spin polarization of V atom is considered in all calculations. The on-site correlation effects among $3d$ electrons of the V atom are accounted for by using the GGA + U scheme⁶², where the parameter $U-J$ (Ueff)⁶² is set to be 3.4. A double- ζ basis functional with polarization (DZP) is used for all atoms. A $(1 \times 1 \times 100)$ k -point in string Brillouin zone (x, y, z directions, respectively) is employed. 150 Ry cutoff energy is applied to describe the periodic wave function.

3 Results and discussion

The stability of introducing silicon bridge between vanadocenes is evaluated by the reaction energy ΔE as given following:

Fig.2 Computed projected density of states (PDOS) of polymetalloenes **a**, **b**, and **c**

The calculated $\Delta E_{\text{reaction}}$ are listed in Table 1. These values of $\Delta E_{\text{reaction}}$ are all negative indicating exothermic reaction. Hence, inserting silicon bridge between vanadocenes is energetically reasonable.

In this section, we first show results of magnetism and band structures of **a**–**c**, followed by transport properties computed based on the two-probe devices of **D-a**–**D-c**.

3.1 Magnetism

Both the AFM state and FM state of **a**–**c** are considered. The calculated energy differences $\Delta E_{\text{FM-AFM}}$ between the FM and AFM states are listed in Table 1. The values of $\Delta E_{\text{FM-AFM}}$ are -5.88 , -0.11 , and 0.53 meV for **a**, **b**, and **c**, respectively. This case clearly demonstrates that the length of the silicon bridge plays important role in governing the magnetism. With the lengthening of the silicon bridge, the V-V FM coupling is weakened while the AFM coupling is enhanced. The polymers **a** and **b** favor the FM ground state while **c** prefers the AFM state. The same case is also

found for the two-probe devices **D-a**, **D-b**, and **D-c** (Table 1). In fact, the short SiH_2 unit in **a** serves as a FM coupling unit for two spin V atoms to be FM coupled. However, in **c**, the V spin dots are separated far away by the long $(\text{SiH}_2)_3$ segment, direct V-V FM coupling is destroyed. The FM state of **a** and **b** shows a magnetic moment $S \sim 6.0\mu_{\text{B}}$ per supercell, i.e., $\sim 3.0\mu_{\text{B}}$ per V atom (Table 1), three times larger than that of the V-benzene or V-cyclopentadiene multidecker complex⁶³. This value is in agreement with that in vanadocene⁶⁴. The magnetic behavior of the FM and AFM states is reflected in the projected density of states (PDOS) shown in Fig.2. For the FM state of **a** and **b**, the majority spin below the Fermi level (E_{f}) is greater than the minority spin. The spin polarization is mainly due to the V atoms. For the AFM state of **c**, the majority spin and the minority spin are nearly the same near the E_{f} so that their net magnetic moments are nearly zero. These novel magnetic properties of **a**–**c** may have potential applications for magnetic nanodevices.

Fig.3 Computed band structures (left panels) of (a, b) polymetalloccene a, (c, d) polymetalloccene b, and (e, f) polymetalloccene c and the Kohn-Sham orbitals (right panels) corresponding to the energy levels (highlighted in color lines) near E_{f} at the Γ point

The iso-surface value is $5 \text{ e} \cdot \text{nm}^{-3}$.

3.2 Band structure

Fig.3 plots the band structures of **a–c**. It is known that in vanadocene the five *d* orbitals of V atom split into a d_{z^2} (a_1) orbital and two sets of doubly degenerate d_{xy,x^2-y^2} (e_2) and $d_{xz,yz}$ (e_1) orbitals under the Cp ligand field. Here, the **a–c** supercell contains two V atoms which contribute ten *d* orbitals to couple with the Cp π orbitals, thereby resulting in ten bands: two a_1 -like bands, four e_2 -like bands, and four e_1 -like bands. In the spin-up state of **a** and **b**, the a_1 -like bands and the e_2 -like bands are occupied while the e_1 -like bands are unoccupied. However, in the spin-down state, all the a_1 -, e_2 -, and e_1 -like bands are unoccupied. Therefore, each vanadocene unit in **a** and **b** possesses a magnetic moment of $S \sim 3.0\mu_B$, in line with the computed magnetism. Clearly, the spin-down state has a slightly lower band gap than the spin-up state, suggesting a slightly stronger conductivity in the spin-down state of **a** and **b**. In the AFM **c**, the spin-up state and the spin-down state exhibit a symmetrical band gap. The band gaps are in the order of **a** > **b** > **c**, indicating that the conductivity should follow the sequence of **c** > **b** > **a**. Another feature can be found that the valence and conduction bands in the spin-down state of **b** display larger dispersion owing to the good coupling between the vanadocene unit and the silicon bridge while those of **c** show evident flat character due to the block effect of the long silicon bridge. From the PDOS, one can see that the valence band mainly comes from the V *d* state, while the conduction band stems from both V *d* and Si *p* states. Therefore, the silicon σ orbitals can also participate in conducting by accepting electrons from the V atom.

3.3 Transport properties

To confirm the predication of the transport property based on the electronic structures, we have also computed transport properties of two-probe devices **D-a**, **D-b**, and **D-c** by sandwiched finite-sized **a**, **b**, and **c** between two Au electrodes (c.f. Fig.1(b)). The computed current–voltage (*I–V*) curves based on the two-probe devices are shown in Fig.4, from which several characteristics attributable to silicon bridge can be found at the bias voltage of $-1.0 - 1.0$ V.

First, the silicon bridge could remarkably tune the magnitude of total current (Fig.4(a)). Overall, the two-probe system **D-c** shows the highest conductivity, followed by **D-b**, while **D-a** is the lowest. This is in good agreement with the band structure analysis. Fig.5(a) gives the transmission spectra (TS) at 0.0 V bias voltage. Clearly, near the E_F , **D-c** shows the largest TS peak, while **D-a** has the smallest.

Second, **D-a** and **D-b** systems show spin polarized transport property, i.e., the spin-down state gives a higher conductivity than the spin-up state (Fig.4(b, c)). In contrast, for **D-c**, the spin-up state and the spin-down state exhibit close magnitude of current under a certain bias voltage, suggesting an unpolarized transport property. These results are consistent with electronic structures of their infinitely long systems. Fig.5(a) also indicates that the spin-down states of **D-a** and **D-b** offer larger TS peaks than the spin-up state near E_F , while the spin-up state and spin-down state in **D-c** devote similar TS contributions.

Third, **D-a** and **D-c** give rise to evident negative differential

Fig.4 (a) Total *I–V* curves of **D-a**, **D-b**, and **D-c** two-probe devices; (b, c, d) Spin polarized *I–V* curves of **D-a**, **D-b**, and **D-c** two-probe devices, respectively

Fig.5 (a) Transmission spectra (TS) of **D-a**, **D-b**, and **D-c** two-probe devices at 0.0 V bias voltage; (b) TS of **D-a** two-probe device at 0.0, 0.2, and 0.4 V bias voltages; (c) TS of **D-b** two-probe device at 1.0 and -1.0 V bias voltages

resistance (NDR) peaks at the considered bias voltage $-1.0 - 1.0$ V, while **D-b** cannot. In fact, in metallocene polymers, the Cp ligands confine the d states of metal atom, making the metal atom an intrinsic molecular dot. Experiments have demonstrated that the metal-to-metal communication plays an important role in the conducting behavior⁶⁵⁻⁶⁷. Fig.6 plots the calculated electrostatic potential for **D-a**, **D-b**, and **D-c** two-probe devices. Evidently, in **D-a** and **D-c**, the saturated silicon bridge blocks the two vanadocene units effectively, leading to an ionic-like interdot coupling.

Fig.6 Computed contour plot of potential distribution for **D-a**, **D-b**, and **D-c**

Electronic transport through ionic-like coupled quantum dots are covered by Coulomb blockade theory^{68,69}, which usually results in NDR behavior. In contrast, electron delocalization through silicon bridge becomes easier for the parallel orientation compared to the V-shape. The covalent-like interdot coupling occurs in **D-b** owing to the high electron delocalization through the silicon bridge. The strong covalent-like interdot coupling in **D-b** induces a coherent tunneling, and thus cannot give a significant NDR behavior. The above differences may be originated from the orientation of the two $V(Cp)_2$, which is V-shape for **a** and **c** (odd-numbered SiH_2 unit) and parallel for **b** (even-numbered SiH_2 unit). The NDR phenomenon of **D-a** and **D-c** is of important application in multiple-valued logic devices. For **D-a**, NDR peaks appear at 0.2 and -0.8 V; and for **D-c**, NDR peaks locate at 0.6 and -0.8 V. This NDR feature can be further interpreted from the TS distribution exemplified by **D-a** in Fig.5(b). Clearly, at 0.2 V and near the E_f , the magnitude of the TS of **D-a** is much larger than that of 0.4 V, resulting in the sharp dropping of the current from 0.2 to 0.4 V.

Last, the conductivity is sensitive to the current direction owing to the asymmetric coupling between the scatter region and the two electrodes. The magnitude of the current under a negative bias voltage is evidently larger than that under a corresponding positive bias voltage. This phenomenon can be reflected from the TS in Fig.5(c). Take **D-b** as an example, clearly, TS peaks near E_f at $V = -1.0$ V are larger than those at $V = 1.0$ V.

4 Conclusions

Silicon bridge tuned electronic and transport properties of polymetalloenes, $[V(Cp)_2(SiH_2)_n]_m$ ($n = 1$ (**a**), $n = 2$ (**b**), $n = 3$ (**c**); $m = \infty$; Cp = cyclopentadienyl), are studied using DFT and NEGF methods. With the lengthening of the silicon bridge, the V-V FM coupling is weakened while the AFM coupling is enhanced. **a** and **b** favor the ferromagnetic (FM) state ground state, while **c** prefers the antiferromagnetic (AFM) ground state. Each V atom in the FM

state of **a** and **b** shows a magnetic moment of $\sim 3.0\mu_B$, three times larger than that in the V-benzene or V-cyclopentadiene multidecker complex. The transport properties of **a–c** are in good agreement with the electronic structures. The conductivity follows the sequence of **c** > **b** > **a**. For **a** and **b**, the spin-down state has a slightly stronger conductivity than the spin-up state. **a** and **c** can both give rise to evident negative differential resistance behavior while **b** cannot. This difference may be originated from the orientation of the two V(Cp)₂: V-shape for **a** and **c** (odd-numbered SiH₂ unit) leading to ionic-like interdot coupling while parallel for **b** (even-numbered SiH₂ unit) leading to covalent-like interdot coupling. In addition, the conductivity of **a–c** is sensitive to the current direction owing to the asymmetric coupling between the scatter region and the two electrodes.

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