

## One-Dimensional Transition Metal–Benzene Sandwich Polymers: Possible Ideal Conductors for Spin Transport

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**Abstract:** We investigate the electronic and magnetic properties of the proposed one-dimensional transition metal (TM = Sc, Ti, V, Cr, and Mn) –benzene (Bz) sandwich polymers by means of density functional calculations.  $[V(\text{Bz})]_{\infty}$  is found to be a quasi-half-metallic ferromagnet, and half-metallic ferromagnetism is predicted for  $[\text{Mn}(\text{Bz})]_{\infty}$ . Moreover, we show that stretching the  $[\text{TM}(\text{Bz})]_{\infty}$  polymers could have dramatic effects on their electronic and magnetic properties. The elongated  $[V(\text{Bz})]_{\infty}$  displays half-metallic behavior, and  $[\text{Mn}(\text{Bz})]_{\infty}$  stretched to a certain degree becomes an antiferromagnetic insulator. The possibilities to stabilize the ferromagnetic order in  $[V(\text{Bz})]_{\infty}$  and  $[\text{Mn}(\text{Bz})]_{\infty}$  polymers at finite temperatures are discussed. We suggest that the hexagonal bundles composed by these polymers might display intrachain ferromagnetic order at finite temperatures by introducing interchain exchange coupling.

### Introduction

It is expected that the new generation of devices will exploit spin dependent effects, what has been called spintronics.<sup>1,2</sup> A challenge now facing spintronics is transmitting spin signals over long enough distances to allow for spin manipulation. An ideal device for spin-polarized transport should have several key ingredients. First, it should work well at room temperature and should offer as high a magnetoresistance (MR) ratio as possible. In this sense, a half-metallic (HM) ferromagnet with the Curie temperature higher than room temperature is highly desirable since there would be only one electronic spin channel at the Fermi energy.<sup>3</sup> Second, the size or diameter of the materials should be uniform for large scale applications. Carbon nanotubes (CNTs) were considered as promising one-dimensional (1D) spin mediators because of their ballistic nature of conduction and relatively long spin scattering length (at least 130 nm).<sup>4,5</sup> Coherent spin transport has been observed in multiwalled CNT systems with Co electrodes. The maximum MR ratio of 9% was observed in multiwalled CNTs at 4.2 K. However, as the temperature increases to 20 K, the MR ratio goes to zero, preventing any room-temperature applications.<sup>4</sup> A theoretical work suggested that the ferromagnetic (FM) transition metal (TM) /CNT hybrid structures may be used as

devices for spin-polarized transport to further increase the MR ratio.<sup>6</sup> Unfortunately, although a large spin polarization is found in these systems, there is no HM behavior. Another difficulty with CNT is that the devices are unlikely to be very reproducible due to the wide assortment of tube sizes and helicities that are produced during synthesis. Wide variation in device behavior was reported in the CNT experiment.<sup>4</sup>

Recently, an experimental study suggested that the unpaired electrons on the metal atoms couple ferromagnetically in the multidecker organometallic sandwich V-benzene (Bz) complexes, i.e.,  $V_n(\text{Bz})_{n+1}$  clusters.<sup>7</sup> The FM sandwich clusters are supposed to serve as nanomagnetic building blocks in applications such as recording media or spintronic devices. A subsequent density functional study confirmed the FM coupling in multidecker sandwich  $V_n(\text{Bz})_{n+1}$  clusters.<sup>8</sup> Motivated by the above experimental and theoretical studies, we propose that the 1D organometallic sandwich polymers  $[V(\text{Bz})]_{\infty}$  are the possible candidates for spintronic devices for spin-polarized transport since the polymers with an inherently uniform size are supposed to be also FM.

Metal–ligand molecules have been the subject of many studies in the past decade.<sup>9–16</sup> Especially, TM–Bz complexes

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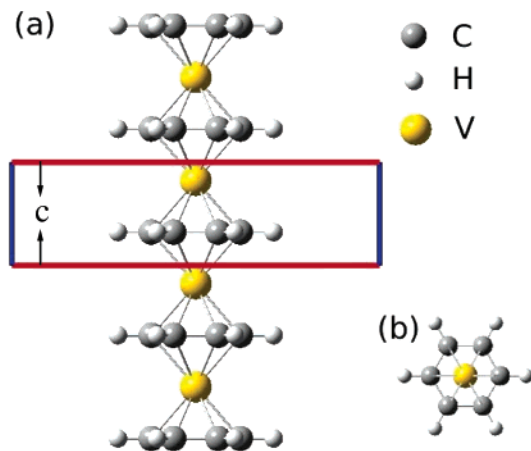
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( $M_n(\text{Bz})_m$ ) are the prototypical organometallic complexes for studying the  $d-\pi$  bonding interactions. Depending on the metal, there are two types of structures for  $M_n(\text{Bz})_m$ : multiple-decker sandwich structures and metal clusters fully covered with Bz molecules (rice-ball structures). The former sandwich structure is characteristic of the complexes for early transition metals (Sc–V), whereas the latter is formed for late transition metals (Fe–Ni).  $\text{Cr}(\text{Bz})_2$  and  $\text{Mn}(\text{Bz})_2$  with a sandwich structure are also observed experimentally.<sup>12</sup> Although the multidecker sandwich  $M_n(\text{Bz})_m$  clusters have been extensively studied theoretically,<sup>13–16</sup> studies of the 1D  $[\text{TM}(\text{Bz})]_\infty$  polymers are still very lacking. To our knowledge, only one semiempirical Hückle calculation was performed to examine the thermodynamical stability of the 1D  $[\text{TM}(\text{Bz})]_\infty$  polymers.<sup>9</sup> The electronic and magnetic properties of the 1D  $[\text{TM}(\text{Bz})]_\infty$  polymers remain to be explored using ab initio quantum mechanics methods. Moreover, the differences in bonding, energetics, and magnetic properties between  $[\text{TM}(\text{Bz})]_\infty$  polymers with different TM atoms are to be clarified since the properties of TM–Bz sandwich clusters depend on the number of the 3d electrons of the TM atoms.

## Discussion

In this paper, we perform a comprehensive first principles study on the electronic and magnetic properties for the proposed 1D sandwich polymers. Only the  $[\text{TM}(\text{Bz})]_\infty$  polymers with TM = Sc, Ti, V, Cr, and Mn are considered since Fe, Co, and Ni usually react with Bz to form the rice-ball structures.<sup>10,12</sup> Our theoretical calculations are performed within spin-polarized density-functional theory (DFT) with the generalized gradient approximation (GGA) PW91 functional.<sup>17</sup> The Vienna ab initio simulation package (VASP),<sup>18,19</sup> a plane-wave based program, is used. We describe the interaction between ions and electrons using the frozen-core projector augmented wave approach.<sup>20</sup> The plane-wave basis set cutoff is 400 eV. In a typical calculation, a 1D periodic boundary condition is applied along the polymer axis (the  $z$  direction) with Monkhorst–Pack<sup>21</sup>  $k$ -point sampling.

There are two typical structural configurations for the sandwich polymers. One is a normal sandwich structure with  $D_{6h}$  symmetry, in which the TM atom and Bz rings are arranged alternatively, as shown in Figure 1 for the  $D_{6h}$   $[\text{V}(\text{Bz})]_\infty$  polymer. The other is a staggered sandwich structure ( $D_{6d}$  symmetry) in which one of the Bz rings is rotated by 30% with respect to the other ring. Our preliminary calculations for both  $D_{6h}$  and  $D_{6d}$   $[\text{V}(\text{Bz})]_\infty$  polymers indicate that the electronic and magnetic properties of the  $D_{6d}$  conformer differ little from those of the corresponding  $D_{6h}$  one. The qualitative similarity between the  $D_{6d}$  and  $D_{6h}$  configurations is also found in a previous study on the sandwich clusters.<sup>14</sup> So hereafter we mainly focus on the polymers with  $D_{6h}$  symmetry.



**Figure 1.** Structure of the  $D_{6h}$   $[\text{V}(\text{Bz})]_\infty$  sandwich polymer (a) side view and (b) top view. The enclosed region in part a indicates the unit cell of the polymer, and  $c$  denotes the lattice constant.

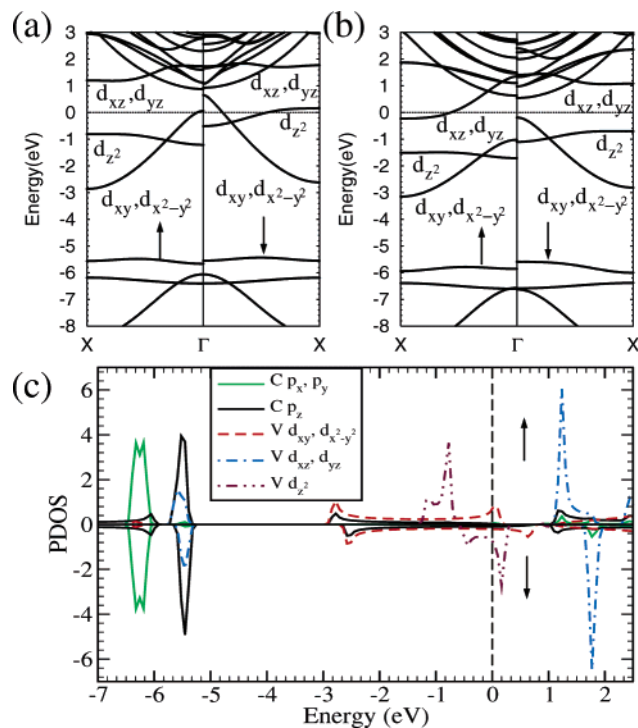
**Table 1.** Calculated Lattice Constant ( $c$ ), Binding Energy ( $E_b$ ), Total Magnetic Moment per Unit Cell ( $M$ ), Electronic Ground State (GS), and the Energy Difference between the FM and AFM States for the  $[\text{TM}(\text{Bz})]_\infty$  Sandwich Polymers (TM = Sc, Ti, V, Cr, and Mn) ( $\Delta E = E(\text{FM}) - E(\text{AFM})$ )

TM	$c$ (Å)	$E_b$ (eV/TM)	$M$ ( $\mu_B$ )	GS	$\Delta E$ (eV/TM)
Sc	3.78	4.844	0.00	PM metal	
Ti	3.58	5.317	0.00	AFM metal	0.006
V	3.37	5.334	0.80	FM metal	−0.084
Cr	3.30	2.181	0.00	NM insulator	
Mn	3.37	1.714	1.00	FM metal	−0.250

## Results

Our results for different  $[\text{TM}(\text{Bz})]_\infty$  polymers are summarized in Table 1. We can see that the sandwich  $[\text{TM}(\text{Bz})]_\infty$  polymers display rich electronic and magnetic properties. All  $[\text{TM}(\text{Bz})]_\infty$  polymers studied here are metallic except that  $[\text{Cr}(\text{Bz})]_\infty$  is a nonmagnetic (NM) insulator with a 0.71 eV direct energy gap at  $\Gamma$ .  $[\text{Sc}(\text{Bz})]_\infty$  is paramagnetic (PM). For  $[\text{Ti}(\text{Bz})]_\infty$ , the AFM state is slightly favorable by 6 meV/Ti over the FM state. The ground state for  $[\text{V}(\text{Bz})]_\infty$  and  $[\text{Mn}(\text{Bz})]_\infty$  is the robust FM state. The diversity of the magnetic properties for the sandwich clusters with different TM atoms has been found by previous theoretical studies. The NM insulating property for  $[\text{Cr}(\text{Bz})]_\infty$  accords with the singlet state for  $\text{Cr}(\text{Bz})_2$  due to the 18-electron rule.<sup>13</sup> For  $[\text{V}(\text{Bz})]_\infty$  and  $[\text{Mn}(\text{Bz})]_\infty$ , the FM ground state also agrees qualitatively with the doublet ground state for  $\text{V}(\text{Bz})_2$  and  $\text{Mn}(\text{Bz})_2$ .<sup>15,13</sup> However, two distinct cases are Sc and Ti. A previous study showed that  $\text{Sc}(\text{Bz})_2$  is a doublet state in contrast with the PM state for  $[\text{Sc}(\text{Bz})]_\infty$  found here. On the other hand,  $\text{Ti}(\text{Bz})_2$  is a singlet state contrasting sharply to the AFM ground state for  $[\text{Ti}(\text{Bz})]_\infty$ . The binding energy of the  $[\text{TM}(\text{Bz})]_\infty$  polymers as given in Table 1 is defined as follows:  $E_b = E(\text{Bz}) + E(\text{TM}) - E([\text{TM}(\text{Bz})]_\infty)$ , where  $E(\text{TM})$  is the energy of the isolated TM atom. We can see that  $[\text{V}(\text{Bz})]_\infty$  has large thermodynamic stability with the largest binding energy (5.334 eV/V atom). The trend of the lattice constant for the  $[\text{TM}(\text{Bz})]_\infty$  polymers is similar with that of the distance of the TM atoms from the center of the Bz ring in  $\text{TM}(\text{Bz})_2$ .<sup>13</sup>  $[\text{Cr}(\text{Bz})]_\infty$  has the smallest lattice constant (3.30 Å) but not a very large binding energy, which might result from the stable  $3d^5 4s^1$  valence configuration for the Cr atom.

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**Figure 2.** Electronic band structures for (a)  $[\text{V}(\text{Bz})]_{\infty}$  and (b)  $[\text{Mn}(\text{Bz})]_{\infty}$ . Part c shows the C and V PDOS for  $[\text{V}(\text{Bz})]_{\infty}$ .

Since  $[\text{V}(\text{Bz})]_{\infty}$  and  $[\text{Mn}(\text{Bz})]_{\infty}$  have robust ferromagnetism, which is crucial for practical spintronic applications, the detailed electronic and magnetic properties are examined carefully. The band structures for  $[\text{V}(\text{Bz})]_{\infty}$  and  $[\text{Mn}(\text{Bz})]_{\infty}$  are shown in Figure 2. For  $[\text{V}(\text{Bz})]_{\infty}$ , there is a gap just above the Fermi level for the spin-up component indicating a quasi-HM behavior. The V, Mn 4s orbitals lie in the conduction band with very high energy, and the bands around the Fermi level are mainly contributed by the TM 3d orbitals. The bands which are mainly composed by the TM 3d orbitals are labeled by their 3d components in Figure 2. In the crystal field of the Bz ligands, the TM 3d bands split into three parts: A 2-fold degenerated band D1 contributed mainly by TM  $3d_{xy}$  and  $3d_{x^2-y^2}$  orbitals, a nonbonding band D2 with TM  $3d_{z^2}$  character, and a 2-fold degenerated antibonding band D3 due to TM  $3d_{xz}$  and  $3d_{yz}$ . The dispersive D1 band crosses the localized D2 band. And the D3 band with high energy is separated from the other two bands. For  $[\text{V}(\text{Bz})]_{\infty}$ , in the majority part, the D2 band is fully occupied and there is a small hole in the D1 band, and both D1 and D2 bands are partly filled in the minority part. Such 3d orbitals occupation results in a  $0.80 \mu_{\text{B}}$  total magnetic moment for  $[\text{V}(\text{Bz})]_{\infty}$ . Since a Mn atom has two valence electrons more than a V atom, both D1 and D2 bands are fully occupied in both spin components in  $[\text{Mn}(\text{Bz})]_{\infty}$ . The remaining one valence electron half fills the D3 band in the spin majority part. Such a picture of the orbital occupation leads to the peculiar HM FM behavior in  $[\text{Mn}(\text{Bz})]_{\infty}$  with a total magnetic moment  $1.00 \mu_{\text{B}}$ .

The above analysis based on the crystal field theory qualitatively describes the electronic and magnetic properties of the two polymers. However, the large dispersion of the D1 band and the FM mechanism in these systems remain to be clarified. To penetrate into this problem, we plot the projected density of states (PDOS) for  $[\text{V}(\text{Bz})]_{\infty}$  in Figure 2c. We can see there is a considerable contribution to the V D1 band near X from C  $2p_z$

orbitals; however at  $\Gamma$  the V  $3d_{xy}$  and  $3d_{x^2-y^2}$  orbitals could only hybrid with C  $2p_x$  and  $2p_y$  orbitals due to the symmetry matching rule. The C  $2p_z$  orbitals of a Bz hybrid with V  $3d_{xy}$  and  $3d_{x^2-y^2}$  orbitals resulting in bonding states near X, and antibonding-like states near  $\Gamma$  arise due to the weak hybridization between Bz  $2p_x$  and  $2p_y$  states and these V 3d orbitals. Such hybridization leads to the large dispersion of the D1 band with the highest energy at  $\Gamma$  in the whole Brillouin zone. Clearly, the contribution from Bz orbitals to the states near the Fermi level is very small, and the holes are mainly of TM 3d character, so ferromagnetism in such systems is identified to be due to the double exchange (DE) mechanism.<sup>22,23</sup>

The spin densities for both  $[\text{V}(\text{Bz})]_{\infty}$  and  $[\text{Mn}(\text{Bz})]_{\infty}$  are shown in Figure 3a and b, respectively. The spin density for  $[\text{V}(\text{Bz})]_{\infty}$  clearly indicates the  $3d_{z^2}$  character, which is in accord with the band structure. Yet, the spin density for  $[\text{Mn}(\text{Bz})]_{\infty}$  is mainly due to Mn  $3d_{xz}$  and  $3d_{yz}$  orbitals, as discussed above. An interesting phenomenon should be noted: The spin polarization not only is located around the TM atoms but also has a small negative contribution from the Bz  $2p_z$  orbitals. The spin injection to Bz is due to the hybridization effect. More occupied hybridized bands will lead to a larger spin polarization of Bz. Since the D3 band of the spin up component is also half filled, the spin polarization of Bz in  $[\text{Mn}(\text{Bz})]_{\infty}$  is  $(0.090 \mu_{\text{B}})$  larger than that  $(0.067 \mu_{\text{B}})$  in  $[\text{V}(\text{Bz})]_{\infty}$ . The spin injection to Bz has also been found by Muhida et al. in the study of  $\text{TM}(\text{Bz})_2$  (TM = Mn, Fe, and Co).<sup>15</sup> However, the six C atoms in a Bz ring contribute equally to the spin polarization in both  $[\text{V}(\text{Bz})]_{\infty}$  and  $[\text{Mn}(\text{Bz})]_{\infty}$ , contrasting sharply to their results that two of the C atoms contribute much larger than the others.<sup>15</sup>

In the above paragraphs, we have shown that the ground state of both  $[\text{V}(\text{Bz})]_{\infty}$  and  $[\text{Mn}(\text{Bz})]_{\infty}$  polymers is FM. We now turn to study the magnetic properties of  $[\text{V}(\text{Bz})]_{\infty}$  and  $[\text{Mn}(\text{Bz})]_{\infty}$  polymers at finite temperatures. Unfortunately, there is no long-range FM or AFM order in any infinite strictly 1D isotropic system with a finite range exchange interaction at any nonzero temperature.<sup>24</sup> However, there are several mechanisms for the occurrence of FM or AFM order in 1D or quasi-1D systems at finite temperatures: barriers due to the magnetic anisotropy, finite size, and interchain couplings. Large magnetic anisotropy energy can block the thermal fluctuation and stabilize long-range FM order; e.g., 1D monatomic chains of Co constructed on a Pt substrate exhibit long-range FM order below the blocking temperature 15 K.<sup>25</sup> However, our calculated results show that the magnetic anisotropy energy in both  $[\text{V}(\text{Bz})]_{\infty}$  and  $[\text{Mn}(\text{Bz})]_{\infty}$  polymers is smaller than  $0.1 \text{ meV/TM}$ , indicating that the ferromagnetism in these polymers might be stabilized only at extremely low temperatures by the magnetic anisotropy induced barrier. There are also some reports indicating the existence of FM in 1D chains with finite lengths, where the length of the chains is related to the range of the exchange interaction.<sup>25</sup> The most relevant work related to the current study is the discovery of FM in 1D  $\text{V}_n(\text{Bz})_{n+1}$  sandwich clusters by Miyajima et al.<sup>7</sup> as mentioned above. Since here we mainly focus on infinite 1D polymers, thus we will not discuss more on this point. The interchain coupling is found to be an important

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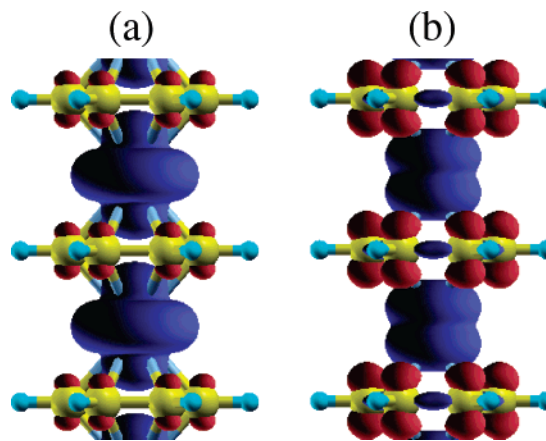
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mechanism to stabilize long-range FM or AFM order in quasi-1D systems. Some quasi-1D systems have been discovered to display FM<sup>26,27</sup> or AFM<sup>28</sup> order at finite temperatures. Here we study the hexagonal bundles composed of  $[\text{V}(\text{Bz})]_{\infty}$  or  $[\text{Mn}(\text{Bz})]_{\infty}$  polymers. The optimized distance between the centers of neighbor polymers is about 6.95 Å for both V–Bz and Mn–Bz bundles. Our results indicate that these bundles are energetically more favorable (by about 31 and 17 meV for Mn–Bz and V–Bz bundles, respectively) than their corresponding 1D isolated chains. It is well-known that there is spin frustration for an AFM spin configuration in a hexagonal lattice. Here we refer to the spin configuration where some neighbor chains couple antiferromagnetically and some neighbor chains couple ferromagnetically as the AFM one. The AFM coupling between V–Bz chains is slightly more favorable by about 3 meV/TM than the FM coupling. In contrast, the interchain coupling in Mn–Bz bundles is found to be FM (with the energy about 5 meV/TM lower than the AFM coupling). The different coupling manners between these two cases might originate from the different characters of their spin densities. From the energy difference between the AFM and FM coupling in these bundles, the interchain coupling  $J$  is estimated to be about 0.75 or 1.25 meV/TM for V–Bz and Mn–Bz bundles, respectively. The interchain coupling should be large enough to stabilize the intrachain FM at finite temperature since it is significantly larger than that in other typical quasi-1D magnetic systems; for example, the interchain coupling  $J$  was estimated to be about 0.1 K (0.009 meV) in *p*-nitrophenyl nitronyl nitroxide (*p*-NPNN) with a Curie temperature of 0.65 K.<sup>27</sup>

The intrachain exchange coupling is an important parameter in describing the magnetic properties in quasi-1D magnetic systems. Here we derive the exchange parameters in  $[\text{V}(\text{Bz})]_{\infty}$  and  $[\text{Mn}(\text{Bz})]_{\infty}$  isolated polymers using total energy calculations for different spin configurations. The intrachain coupling in their bundles is expected to have a similar magnitude as that in isolated polymers. Since the distance between a TM atom and its next nearest neighbor TM is larger than 6.0 Å, the magnetic coupling between them should be negligible. Considering only the nearest magnetic coupling, the effective Heisenberg Hamiltonian for the 1D  $[\text{TM}(\text{Bz})]_{\infty}$  polymer can be written as  $H_{\text{eff}} = -\sum_i J \mathbf{e}_i \cdot \mathbf{e}_{i+1}$ , where  $J$  is the effective exchange parameter between the nearest neighbor TM atoms and  $\mathbf{e}_i$  is the unit vector pointing in the direction of the magnetic moments at site  $i$ . Here we term  $J$  as an effective exchange parameter but not a pure exchange parameter, since  $J$  also includes the magnitude of the magnetic moment of the TM atoms. One might expect that  $J$  could be deduced from the energy difference between the AFM state and FM state. However, we find that the local magnetic moments for V and Mn atoms in the AFM state differ significantly from those in the FM state, so the above method to obtain  $J$  might be questionable. We circumvent this problem by considering another magnetic configuration: The magnetic configuration is  $\uparrow\uparrow\downarrow\downarrow$  with the periodicity 4 times that for the FM case. In this case, the local magnetic moments for V and



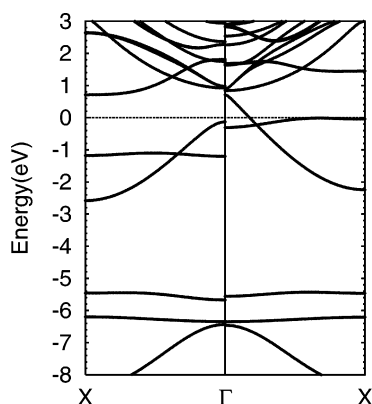
**Figure 3.** Spin density for (a)  $[\text{V}(\text{Bz})]_{\infty}$  and (b)  $[\text{Mn}(\text{Bz})]_{\infty}$ . The isovalues for the red and blue isosurfaces are  $-0.014$  and  $0.014 e/\text{\AA}^3$ , respectively.

Mn atoms are almost the same as those in the FM state. The energy difference between this configuration and the FM state is  $J$  per TM atom. The estimated effective exchange parameter for  $[\text{V}(\text{Bz})]_{\infty}$  and  $[\text{Mn}(\text{Bz})]_{\infty}$  is 24 and 62 meV respectively, which is larger than the intrachain exchange coupling (about 0.4 meV) in *p*-NPNN.<sup>27</sup> The relatively large effective exchange parameter for  $[\text{V}(\text{Bz})]_{\infty}$  and  $[\text{Mn}(\text{Bz})]_{\infty}$  is due to the DE mechanism, which usually leads to FM with a relatively high Curie temperature; e.g., the relative high Curie temperature (about 228–370 K)<sup>29</sup> for Mn doped GaN is due to the DE mechanism.<sup>23,30</sup>

Pressure is well-known to have a drastic effect on the electronic and magnetic properties of the magnetic materials.<sup>31</sup> Here, the effect of pressing and stretching on the electronic and magnetic properties of  $[\text{V}(\text{Bz})]_{\infty}$  and  $[\text{Mn}(\text{Bz})]_{\infty}$  is examined by changing the lattice constant. It is found that the electronic and magnetic properties of  $[\text{V}(\text{Bz})]_{\infty}$  and  $[\text{Mn}(\text{Bz})]_{\infty}$  change little when they are compressed to a reasonable degree. However, stretching can dramatically change their electronic and magnetic properties.  $[\text{V}(\text{Bz})]_{\infty}$  turns into HM FM when the lattice constant is in the range 3.47 to 3.78 Å. To show the HM FM behavior, we plot the band structure of  $[\text{V}(\text{Bz})]_{\infty}$  with a lattice constant 3.55 Å in Figure 4. Clearly, the energy gap opens in the spin majority part in the stretched  $[\text{V}(\text{Bz})]_{\infty}$  polymer, in contrast to a gap opening in the spin minority part in  $[\text{Mn}(\text{Bz})]_{\infty}$ . Along with the increase of the lattice constant, the hybridization between TM and Bz is weakened. The bandwidth of the D1 band, especially in the spin majority part, becomes narrower. In the spin majority part the downshift of the D1 band near  $\Gamma$  makes the D1 band fully occupied and the system HM ferromagnetic. We note that turning the  $[\text{V}(\text{Bz})]_{\infty}$  polymer into HM FM through stretching experimentally the polymer is possible. The stress in a hexagonal bundle composed by  $[\text{V}(\text{Bz})]_{\infty}$  polymers with lattice constants  $a = 6.95$  Å and  $c = 3.55$  Å is about 4.8 GPa, which could be easily realized experimentally. By increasing the lattice constant of  $[\text{Mn}(\text{Bz})]_{\infty}$  to the critical value 3.48 Å, the HM behavior disappears. With

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**Figure 4.** Electronic band structure for  $[\text{V}(\text{Bz})]_{\infty}$  with the lattice constant  $c = 3.55 \text{ \AA}$ . It clearly shows the HM behavior in this system.

further increase of the lattice constant of  $[\text{Mn}(\text{Bz})]_{\infty}$  up to a second critical value  $3.70 \text{ \AA}$ , an FM metal to AFM insulator transition takes place. The drastic changes of the electronic and magnetic properties of  $[\text{Mn}(\text{Bz})]_{\infty}$  are also caused by the reduced hybridization. Although the band narrowing of the D1 band also takes place, the downshift of the D3 band near X in the spin majority part plays a crucial role in determining the electronic and magnetic properties of  $[\text{Mn}(\text{Bz})]_{\infty}$ . The disappearance of the HM behavior results from the D1 band partly occupying the spin minority part as a consequence of the downshift of the D3 band in the spin majority part. The FM metal to AFM insulator transition can be reasonably explained as follows: The band narrowing of the D1 band results in a smaller DE effect; thus the superexchange AFM interaction can compete with and even overwhelm the DE interaction, since the former depends on hopping linearly, and the latter, quadratically.

Previous studies indicated that the local density approximation (LDA) and other semilocal GGA functionals fail to describe some conducting polymers. A typical example is the dimerization of *trans*-polyacetylene: LDA predicts almost no carbon–carbon bond length alternation (BLA), whereas Hartree–Fock (HF) produces a too large BLA.<sup>32</sup> It was shown that a hybrid density functional mixed with exact exchange, namely B3LYP,<sup>33</sup> provided dimerization parameters close to experiment.<sup>32</sup> Thus it is interesting to know the electronic and magnetic properties of the polymers within the B3LYP formalism. For this purpose,

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we perform some calculations on these 1D polymers using a CRYSTAL03 code.<sup>34</sup> The results show that both  $[\text{V}(\text{Bz})]_{\infty}$  and  $[\text{Mn}(\text{Bz})]_{\infty}$  are HM FM in their most stable configurations. Although there are some minor differences between the PW91 and B3LYP results, our main conclusions remain valid when using the B3LYP functional. The applicability of the semilocal GGA functional to the 1D  $[\text{TM}(\text{Bz})]_{\infty}$  polymers is not surprising since the current studied systems are not  $\pi$ -conjugated. In fact, LDA has been successfully applied to study the conformation and electronic structure of polyethylene.<sup>35</sup>

## Conclusions

In conclusion, we have performed a comprehensive first principles study on the electronic and magnetic properties for the proposed 1D  $[\text{TM}(\text{Bz})]_{\infty}$  polymers with TM = Sc, Ti, V, Cr, and Mn. We demonstrate that all polymers except  $[\text{Cr}(\text{Bz})]_{\infty}$  are metallic.  $[\text{Sc}(\text{Bz})]_{\infty}$  is PM.  $[\text{Ti}(\text{Bz})]_{\infty}$  is a magnetic system where the FM state is almost isoenergetic to the most stable AFM state.  $[\text{V}(\text{Bz})]_{\infty}$  is quasi-HM FM, and the ground state of  $[\text{Mn}(\text{Bz})]_{\infty}$  is HM FM. In addition,  $[\text{V}(\text{Bz})]_{\infty}$  could be tuned to become HM FM through stretching. The hexagonal bundles composed by  $[\text{V}(\text{Bz})]_{\infty}$  and  $[\text{Mn}(\text{Bz})]_{\infty}$  polymers are studied. The intrachain exchange coupling is very large due to the DE mechanism. We find that the interchain coupling is large enough to stabilize the intrachain ferromagnetic order at finite temperatures. The 1D  $[\text{TM}(\text{Bz})]_{\infty}$  polymers, especially  $[\text{V}(\text{Bz})]_{\infty}$  and  $[\text{Mn}(\text{Bz})]_{\infty}$ , with such peculiar electronic and magnetic properties would be ideal materials for promising spin-polarized transport.

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**Supporting Information Available:** Geometries and energies of  $[\text{TM}(\text{Bz})]_{\infty}$  polymers. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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