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RESEARCH ARTICLE

# A first-principles study on the electronic structure of one-dimensional $[TM(Bz)]_\infty$ polymer (TM= Y, Zr, Nb, Mo, and Tc)

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A systematic density functional theory (DFT) study has been performed to investigate the electronic and magnetic properties of one-dimensional sandwich polymers constructed with benzene (Bz) and the second-row transition metal (TM = Y, Zr, Nb, Mo, and Tc). Within the framework of generalized gradient approximation (GGA), $[Tc(Bz)]_\infty$ is a ferromagnetic half-metal, and $[Nb(Bz)]_\infty$ is a ferromagnetic metal. With the on-site Coulomb interaction for 4d TM atoms being taken into account, $[Tc(Bz)]_\infty$ keeps a robust half-metallic behavior, while $[Nb(Bz)]_\infty$ becomes a spin-selective semiconductor. The stability of the half-metallic $[Tc(Bz)]_\infty$ polymer is discussed based on magnetic anisotropy energy (MAE). Compared with 0.1 meV per metal atom in $[Mn(Bz)]_\infty$, the calculated MAE for $[Tc(Bz)]_\infty$ is 2.3 meV per metal atom. Such a significantly larger MAE suggests that $Tc(Bz)]_\infty$ is practically more promising than its first-row TM equivalent.

**Keywords** first-principles, half metal, magnetic anisotropy energy, TM(Bz)

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## 1 Introduction

Spintronics, which utilizes both the charge and spin degrees of freedom, holds great promise on enhancing the performance and functionality of electronic devices [1−3]. Among the various spintronics materials studied [4−10], carbon-based materials have attracted a great interest because of their weak spin-orbit coupling (SOC) and long scattering length [4, 8]. Following along this direction, extensive theoretical studies have been devoted to the low-dimensional carbon-based spintronics materials, ranging from the defective carbon films [11] to transition metal (TM) adsorbed graphene [4] or nanotubes [6, 7]. However, experimental realization of such hybrid devices is still a big challenge.

Recently, a new kind of carbon-based spintronics materials, organometallic sandwich V-benzene (Bz) complexes, i.e., $V_n(Bz)_{n+1}$ clusters, have been synthesized in experiment [12]. Their experimentally observed ferromagnetic ordering is very attractive. Many first-principles calculations have been performed to understand the electronic and magnetic properties of such 3D transition metal (TM)–Bz complexes [8−10, 13]. Some of them, such as $[Mn(Bz)]_\infty$, show interesting half metallic behavior, which may lead to perfect spin filter [8]. However, magnetic anisotropy energy (MAE), a measure of the thermal stability of magnetic properties, is very small in such 3d TM–Bz polymer, due to the relatively weak SOC in 3d TMs. As we know, 4d TMs have much stronger SOC, and it is thus expected that 4d TM–Bz organic complexes may be more stable spintronics materials.

Unfortunately, 4d TM–Bz complexes are rarely studied. Mokrousov *et al.* [14] have studied the electronic structures of $[Nb(Bz)]_\infty$, and found that it is a spin-polarized metal. By including SOC, they indeed found that MAE is much larger for 4d Nb than 3d V. However, their study focused on Nb; a systematic study on other 4d TMs is still not available. Additionally, the on-site coulomb interaction has not been considered in their study.

In this paper, we provide a detailed first-principles in-

vestigation on the electronic and magnetic properties of the $[TM(Bz)]_\infty$ polymers with TM = Y, Zr, Nb, Mo and Tc. We find that ferromagnetic (FM) coupling between TM atoms is favorable in $[Nb(Bz)]_\infty$ and $[Tc(Bz)]_\infty$. Besides, $[Tc(Bz)]_\infty$ shows a half-metallic behavior even with the on-site coulomb interaction considered, and it also has a large MAE. Our results thus demonstrate that $[Tc(Bz)]_\infty$ can be a very promising candidate for spintronics.

## 2 Computational method

The spin-polarized generalized gradient approximation (GGA) [15] and GGA+$U$ [16] ($U$ = on-site Coulomb repulsion strength) electronic structure calculations were performed by means of the density functional theory as implemented in the Vienna ab initio simulation package (VASP) [17−19]. Perdew–Wang functional known as PW91 [20] was used in GGA, and Dudarev *et al.*'s approach [21] was adopted for GGA+$U$ calculations. The GGA+$U$ functional depends only on the difference ($U_{\text{eff}}$) of Hubbard parameter $U$ and screened exchange parameter $J$, and $J$ was fixed at 0 eV during GGA+$U$ calculations. The projector augmented wave method [22] in its Kresse–Joubert implementation [23] was used to describe the electron-ion interaction. The plane-wave basis set energy cutoff was 500.0 eV. The convergence thresholds for energy and force were $10^{-5}$ eV and 0.01 eV/Å, respectively. A 1×1×20 Monkhorst–Pack $k$-point grid [24] was used to sample the one-dimensional Brillouin zone. Initial structures for geometry optimization were constructed referring to the stable structures of the first-row TM–Bz polymers predicted by previous calculations [8−10].

## 3 Results and discussion

The geometric structure of the 4d TM–Bz complexes is shown in Fig. 1. The lattice constant ($c$) for different TM elements is listed in Table 1. $c$ generally decreases with the increase of the atomic number and atomic radius of the TM elements, except Mo and Tc. Binding energy $E_b$ of $[TM(Bz)]_\infty$ is defined as: $E_b = E(\text{TM}) + E(\text{Bz}) - E(\text{TM–Bz})$, where the $E$(TM) and $E$(Bz) are energies for isolated TM atoms and Bz molecules. Large binding energies are obtained for 4d TM–Bz polymers. We notice that very small binding energies have been reported by Shen *et al.* [9]. However, we fail to reproduce their result with the same set of computational parameters.

Both $[Y(Bz)]_\infty$ and $[Mo(Bz)]_\infty$ are paramagnetic (PM). However, the former is a metal, while a 0.685 eV direct energy gap at $\Gamma$ is predicted for the latter. Similar with the $[Cr(Bz)]_\infty$ case [8], the insulating behavior is resulted from the 18-electron rule. $[Zr(Bz)]_\infty$ is an AFM metal. Most interestingly, FM ground state is predicted for $[Nb(Bz)]_\infty$ and $[Tc(Bz)]_\infty$, and the magnetic moment per TM atom is 0.48 and 0.97 $\mu_B$, respectively. The calculated magnetic moment is smaller than that of their corresponding 3d TM–Bz polymer, which means that Tc and Nb atoms have a stronger interaction with the benzene molecule than V and Mn. This is confirmed by the binding energy data. As shown in Table 1, $E_b$ of $[Tc(Bz)]_\infty$ is nearly 2 eV larger than that of $[Mn(Bz)]_\infty$ [8], indicating a more stable structure.

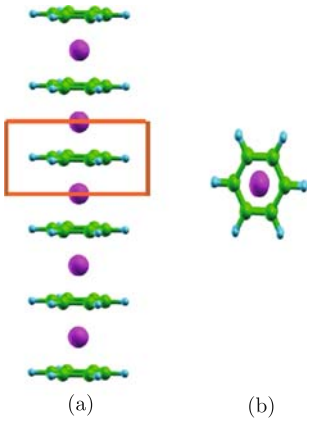


**Fig. 1** **(a)** Side view and **(b)** top view of the schematic structure of the $D_{6H}$ $[TM(Bz)]_\infty$ sandwich polymer. The enclosed region in **(a)** indicates a unit cell. Carbon atoms are in green, hydrogen atoms in sapphire, and TM atoms in purple.

**Table 1** Calculated lattice constant ($c$), total magnetic moment per unit cell ($M$), energy difference [$\Delta E = E(\text{FM}) - E(\text{AFM})$] between the FM and AFM states in eV per unit cell, electronic ground state (GS), and biding energy $E_b$ for the $[TM(Bz)]_\infty$ sandwich polymers (TM = Y, Zr, Nb, Mo, and Tc).

| TM | $c$/Å | $M(\mu_B)$ | $\Delta E$/eV | GS | $E_b$/(eV/TM) |
|---|---|---|---|---|---|
| Y | 4.20 | 0.00 | | PM metal | 4.467 |
| Zr | 3.95 | 0.00 | 0.28 | AFM metal | 5.783 |
| Nb | 3.78 | 0.48 | −0.005 | FM metal | 5.039 |
| Mo | 3.62 | 0.00 | | PM insulator | 4.065 |
| Tc | 3.73 | 0.97 | −0.138 | FM half metal | 3.814 |

The electronic structure of the FM $[Nb(Bz)]_\infty$ and $[Tc(Bz)]_\infty$ are examined in more detail, since they have possible applications in spintronics. Their band structures are shown in Fig. 2. The 5s orbitals of Nb or Tc form a conduction band with very high energy, and the bands in the vicinity of Fermi level are mainly composed by TM 4d orbitals. Because of the crystal-field effect, the fivefold degenerated 4d levels are split into three energy levels, consisting of one singlet $4d_{z^2}$ and two doublets [($4d_{xz}$, $4d_{yz}$) and ($4d_{xy}$, $4d_{x^2-y^2}$)], according to the symmetry [8−10]. We denote these three bands as $D_0$, $D_1$, and $D_2$, respectively. No energy gap is observed for $[Nb(Bz)]_\infty$, indicating a metallic behavior. In the spin-up channel, the localized $D_0$ band is fully occupied and there is a small hole in the $D_2$ band. While in the spin-down channel, both $D_0$ and $D_2$ bands are

partially occupied. The occupied $D_0$ bands are nearly flat, which means that the corresponding orbitals have weak hybridization with the benzene molecules. On the other hand, $[Tc(Bz)]_\infty$ is a half metal. The dispersed $D_2$ band crosses the localized $D_0$ band, and both of them are fully occupied in the two spin channels. Around the Fermi level, the $D_1$ band in the spin-up channel is partial occupied. The large dispersion of the $D_1$ band demonstrates a strong interaction between the Tc atoms and benzene molecules.

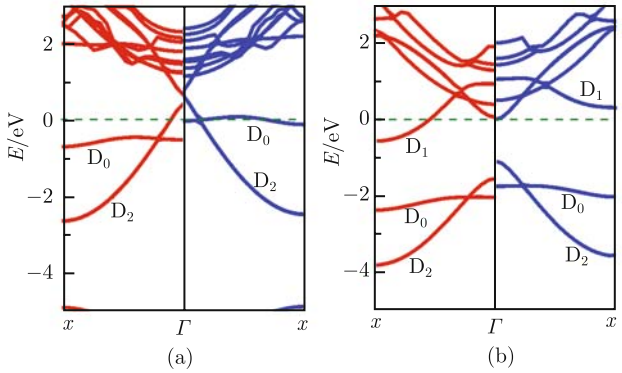


**Fig. 2** Band structure calculated with generalized gradient approximation (GGA) for **(a)** $[Nb(Bz)]_\infty$ and **(b)** $[Tc(Bz)]_\infty$. Red lines are spin-up bands, and blue lines for the down-spin channel.

In order to provide a further understanding of the electronic properties of the two FM polymers, we plot their projected density of state (PDOS) corresponding to TM 4d and C 2p electronic states in Fig. 3. The band splitting due to the crystal-field effect is clearly visible. The energy distributions of the PDOS for Nb $4d_{x^2-y^2}$, $4d_{xy}$ and C $2p_z$ states appears similar, which suggests a strong Nb $4d_{x^2-y^2}$, $4d_{xy}$ hybridization with C $2p_z$. Such

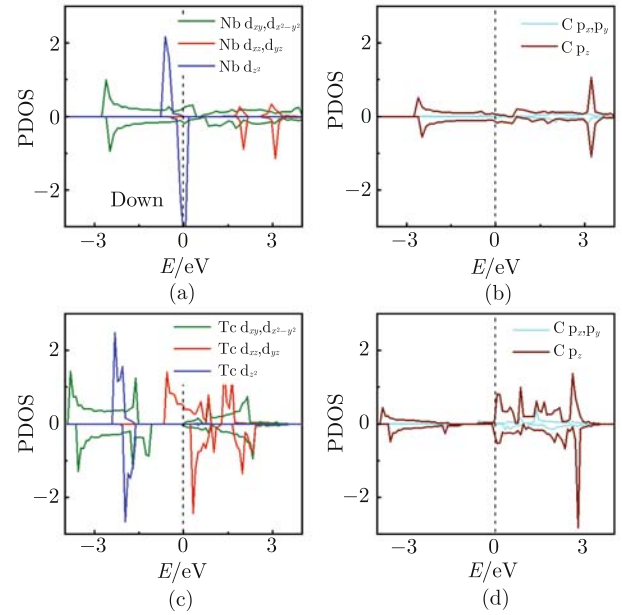


**Fig. 3** The **(a)** Nb and **(b)** C PDOS calculated within the framework of GGA for $[Nb(Bz)]_\infty$, and the **(c)** Tc and **(d)** C PDOS for $[Tc(Bz)]_\infty$.

hybridization leads to a large dispersion of the $D_2$ band. Similar but relatively weaker hybridization can also be observed for $[Tc(Bz)]_\infty$. In energy range from $-1$ to 3 eV, where Tc $4d_{xz}$ and $4d_{yz}$ states dominate, C $2p_z$ states contribute but the PDOS intensity for Tc $4d_{x^2-y^2}$ and $4d_{xy}$ are very low. In Fig. 4, we present the spin densities for both $[Nb(Bz)]_\infty$ and $[Tc(Bz)]_\infty$. It is clear that the spin density of $[Nb(Bz)]_\infty$ mainly exhibits a Nb $4d_{z^2}$ character. On the other hand, the spin density for $[Tc(Bz)]_\infty$ is essentially contributed by Tc $4d_{xz}$ and $4d_{yz}$ orbitals. Furthermore, a little spin polarization has been injected into the Bz ring due to the TM 4d and Bz hybridization effect.

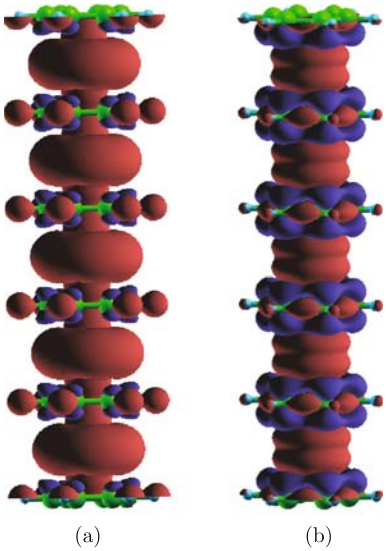


**Fig. 4** Spin density for $[Nb(Bz)]_\infty$ **(a)** and $[Tc(Bz)]_\infty$ **(b)**. The isovalue for the red and blue isosurfaces is 0.002 and $-0.002$ $e/Å^3$, respectively.

On the other hand, we also notice that the bands around the Fermi level are very narrow in energy for $[Nb(Bz)]_\infty$. It is well known that in DFT–GGA calculations the on-site Coulomb interaction has not been properly considered, which however is very important for predicting the electronic and magnetic properties of d and f electron systems [25, 26]. We thus used the GGA+U method to improve the GGA results for $[Tc(Bz)]_\infty$ and $[Nb(Bz)]_\infty$. Hubbard parameter $U$ has been set to 2, 3, or 4 eV, which is reasonable for 4d TM atoms [27, 28].

The half-metallic behavior of $[Tc(Bz)]_\infty$ remains under all these different $U$ values. However, the inclusion of on-site coulomb interaction among 4d electrons leads to a significant change in the electronic structure of $[Nb(Bz)]_\infty$, which changes from metal to semiconductor, as shown in Fig. 5. We notice that the obtained energy gap, however, is very small in all our DFT+$U$ calculations with different $U$. The large difference of the dependence of the electronic structure on on-site Coulomb interaction for $[Tc(Bz)]_\infty$ and $[Nb(Bz)]_\infty$ is consistent

with the fact that the GGA band structure of $[Nb(Bz)]_\infty$ show flat bands crossing the Fermi level while this is not the case for $[Tc(Bz)]_\infty$.

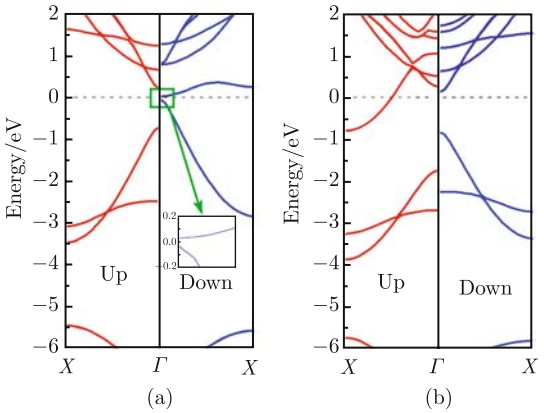


**Fig. 5** Band structures calculated with GGA+$U$ ($U = 3$ eV) for **(a)** $[Nb(Bz)]_\infty$ and **(b)** $[Tc(Bz)]_\infty$. Red lines are spin-up bands, and blue lines for the down-spin channel. Inset of **(a)** shows an enlarged region around the Fermi level.

Thermal stability of magnetism is very important for potential spintronics application. MAE is a quantity closely related to the stability of magnetism against quantum tunneling and thermal fluctuations. By taking SOC into account, we can calculate the energy required to change the magnetization direction. Mokrousov *et al.* have calculated MAE of $[Nb(Bz)]_\infty$, and found that it reaches 1.3 meV per Nb atom [14]. Since $[Tc(Bz)]_\infty$ shows robust half metallic behavior, its MAE is more interesting. In our SOC calculations, two configurations are considered. One is with the spin direction of Tc atoms perpendicular to the one-dimensional polymer, and the other one is with the spin direction parallel with the polymer. Our calculations indicate that spin direction of Tc atoms prefers the perpendicular direction, and the relative energy difference is 2.3 meV per Tc atom. Compared with the value of $[Mn(Bz)]_\infty$, about 0.1 meV per Mn atom, the $[Tc(Bz)]_\infty$ polymer obviously holds a much better thermal stability. This means that it should be a more promising candiate for spintronics compared to 3d TM-benzene polymers.

## 4 Conclusion

In summary, we have studied the electronic and magnetic properties of the one-dimensional $[TM(Bz)]_\infty$ polymers with TM = Y, Zr, Nb, Mo, and Tc using ab initio spin-polarized band structure calculations. Within GGA, all polymers are metallic except $[Mo(Bz)]_\infty$. $[Nb(Bz)]_\infty$ and $[Tc(Bz)]_\infty$ are FM with a total magnetic moment of 0.48 and 0.97 $\mu_B$, respectively. The half-metallic $[Tc(Bz)]_\infty$ predicted by both GGA and GGA+$U$, has a much larger binging energy than the corresponding 3d TM complex ($[Mn(Bz)]_\infty$). MAE calculations show that Tc atoms prefer a magnetization direction perpendicular to the polymer. Compared with $[Mn(Bz)]_\infty$, the much larger MAE (2.3 meV per Tc versus 0.1 meV per Mn) implies that $[Tc(Bz)]_\infty$ has a great potential for future spintronics applications.

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