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Magnetic and electronic properties of porphyrin-based molecular nanowires

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Using spin-polarized density functional theory calculations, we performed theoretical investigations on the electronic and magnetic properties of transition metal embedded porphyrin-based nanowires (TM-PNWs, TM = Cr, Mn, Co, Ni, Cu, and Zn). Our results indicate that Ni-PNW and Zn-PNW are nonmagnetic while the rest species are magnetic, and the magnetic moments in TM-PNWs and their corresponding isolated monomer structures are found to be the same. In addition, the spin coupling in the magnetic nanowires can be ignored leading to their degenerate AFM and FM states. These results can be ascribed to the weak intermetallic interactions because of the relatively large distances between neighbor TM atoms. Among all TM-PNW structures considered here, only Mn-PNW shows a half-metallic property while the others are predicted to be semiconducting. The present work paves a new way of obtaining ferromagnetic porphyrin-based nanowires with TM atoms distributed separately and orderly, which are expected to be good candidates for catalysts, energy storage and molecular spintronics. © *2016 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License.* [http://dx.doi.org/10.1063/1.4941073]

I. INTRODUCTION

Molecular spintronics has emerged as an attractive field with wide applications from high-capacity information-storage devices to quantum computers.[1–4] One important issue in this area is to obtain 100% spin-polarized currents at the Fermi level. It has been shown that half-metals, which are semi-conducting or insulating for one spin channel and conducting for the opposite one, can meet this demand.[5] Up to now, substantial efforts have been devoted to obtain half-metallic materials both theoretically and experimentally. Among their various forms, metal-free half metals[6–18] have attracted special research attention with the development of nano-carbon materials.[19,20] For example, zigzag graphene nanoribbon is predicted to show half-metallic properties by applying an external electronic field,[6] edge medication[8,11] or B/N doping.[7,12] Although numbers of graphene- or nanotube-based half metals[7,8,10–13,15,21,22] have been suggested as excellent candidates for applications in spintronics, it is still a big challenge to achieve these structures experimentally because of the difficulties in the control of dopant or functionalization.

Other potential half-metal materials are predicted to be those containing transition metals (TMs).[23,24] These TMs usually have partly occupied subshells, which make it possible to generate spin-polarized electronic states at different channels. Numerous of such half-metals have been proposed and predicted to exhibit excellent spin-filtering abilities.[25–32] One important issue for

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these metal-contained structures is to prevent metal atoms from aggregating, especially for metal-decorated systems,[32] to maintain their structural characters and the corresponding half-metallic performance. To achieve this, interactions between metal atoms and other substructures such as organic ligands in those materials should be strong enough.

Porphyrin has been shown to be a good candidate for hosting metal atoms, affording the possibility of constructing porphyrin-based half-metals. The structural and physicochemical properties of metalloporphyrins and their derivatives[33–36] have been extensively investigated. In addition, multiporphyrin arrays[37,38] have also attracted much attention in the past decades for the feasibility of tuning their geometries and properties by introducing different metal atoms and ligands during the synthetic process. The success in the synthesis of porphyrin oligomers[39–42] should promote future attempts of obtaining porphyrin-based molecular nanowires (PNWs) for their extraordinary electro-optical and nonlinear optical properties resulting from the π-conjugation systems.[43] Introducing different metal atoms into the porphyrin cores would generate various porphyrin-based organometallic nanowires, the properties of which may vary depending on the electronic configurations of metal atoms. Due to the difficulties in preparing such molecular wires in experiments, a detailed theoretical understanding on the magnetic and electronic behaviors of those structures are of great importance for further development and practical applications.

In this paper, we present our theoretical studies on the electronic and magnetic properties of porphyrin-based molecular nanowires with $3d$ transition metals (TM = Cr, Mn, Co, Ni, Cu, and Zn) embedded in the porphyrin cores, via spin-polarized density functional theory calculations. Our results show that the ground states of these TM embedded PNWs are nonmagnetic when TM is Ni or Zn, and magnetic for the rest of the TM species investigated here. The total magnetic moments of TM-PNWs are calculated to be approximately 4.0, 4.8, 1.0, 0, 1.0, and 0 μB per unit cell for TM = Cr, Mn, Co, Ni, Cu, and Zn, respectively. For the magnetic frameworks, the antiferromagnetic (AFM) and ferromagnetic (FM) coupling states are almost degenerate because of the tiny energy difference between these two different spin-coupling states. These results indicate the weak intermetallic interactions in TM-PNWs, making it possible to achieving frameworks with TM atoms distributed separately and orderly. In addition, we found that Mn-PNW is half-metallic while the other TM-PNWs are semiconducting. The present work suggests a new type of porphyrin-based materials, which can be expected to be good candidates for catalysts, energy storage and molecular spintronics.

II. COMPUTATIONAL METHODS

Our spin-polarized density functional theory (DFT) calculations were performed with the generalized gradient approximation (GGA) method as implemented in the Vienna Ab-initio Simulation Package (VASP).[44] The exchange-correlation potential for GGA was described in the form of Perdew-Burke-Ernzerhof functional (PBE).[45] The projector-augmented wave method[46] with a cut-off energy of 500 eV was employed to describe the ion-electron interaction, and the convergence criterion for energy in the self-consistency process was set to be 10^{-5} eV. Because the standard GGA method cannot well describe strong correlation interactions between the partly occupied d orbitals of transition-metal (TM) atoms in systems considered here, we employed the GGA+U method[47] in the present work. Similar to those used in previous studies,[48–50] the correction energy U and the exchange energy J for TM d orbitals were set to be 4 and 1 eV, respectively. The values of U and J used in this work have been well tested for similar systems. In addition, we have also calculated the magnetic moments of isolated TM-PNW monomers with different values of U from 0.0 to 6.0 eV, to evaluate the effects of U on properties of such systems (See Table S1 of the supplementary material[57]), which indicate that the calculated magnetic moments are the same for each species when the value of U is larger than 3.5 eV. A (2×1) supercell was constructed to investigate the magnetic coupling between TM atoms. The vacuum space along y and z directions were approximately 15 Å, which are sufficiently large to avoid interactions between the nearest images. The Brillouin zone was sampled by a set of $15 \times 1 \times 1$ and $5 \times 1 \times 1$ Monkhorst-Pack meshes[51] of k-points for the unit cell and supercell, respectively. A $30 \times 30 \times 15$ Å^3 box was used in the calculations of isolated TM-PNW monomers. The structures were fully relaxed with no symmetry

constraint until all atomic forces became smaller than 0.01 eV/Å. The ground states for TM-PNW monomers were also investigated at the B3LYP/Def2-TZVPP level of theory as implemented in Gaussian 09 package,[52] which suggest the same spin states for all species as those obtained with GGA+U method described above (See Table S2 of the supplementary material[57]).

III. RESULTS AND DISCUSSION

The TM-PNWs investigated here are composed of porphyrin molecules linked by butadiyne units with 3*d* transition metals (TM = Cr, Mn, Co, Ni, Cu, and Zn) embedded in the porphyrin cores. A number of previous studies have been devoted to electron transport properties of Zn-porphyrin molecular wires,[42,53] which have been successfully obtained in experiment.[41] Because of the fully occupied *d* subshell of Zn atoms, it is usually unnecessary to consider the magnetic properties in such molecular wires. However, substituting Zn with other 3*d* TM atoms such as Cr and Mn, should result in various magnetic behaviors of TM-PNWs, because these TMs have partly occupied *d* subshells, affording their different spin states. The spin states have been shown to have a great influence on the electronic properties of other TM-porphyrin and TM-phthalocyanine nanowires.[49,54] Therefore, we mainly focus our attentions on the magnetic behaviors of TM-PNWs in the present work.

We first investigated the geometric and electronic properties of the metal-free porphyrin nanowire (H_2-PNW), as shown in Fig. 1. A planar structure of H_2-PNW is obtained after a fully geometric optimization, and the lattice constant is calculated to be approximately 13.77 Å. Porphyrin is a well-known aromatic molecule with 26 delocalized π electrons. When porphyrin molecules are linked by butadiyne linkers to form the planar H_2-PNW, π electrons of porphyrin and butadiyne moieties can contribute to the extended π-electron conjugation system over the entire H_2-PNW due to the planar structural character. The extended π-electron conjugation system in H_2-PNW can promote its electrical conduction performance, which has been found in the fused Zn-porphyrin arrays.[53] It has been previously shown that the electronic properties near the Fermi level for species with extended π-electron conjugation systems are mainly contributed by the delocalized π electrons. To demonstrate this, we calculated the projected density of states (PDOS) of H_2-PNW, which clearly indicate the dominant contribution of p_z electrons in determining the electronic features near the Fermi level. Both the valence band maximum (VBM) and the conduction band minimum (CBM) appear at the X (1/2, 0, 0) point of the reciprocal space, leading to a direct energy band gap of approximately 0.6 eV, which indicates the semiconducting properties of H_2-PNW. The rotation of the secondary porphyrin along x-axis can afford another structure of H_2-PNW, in which the nearest

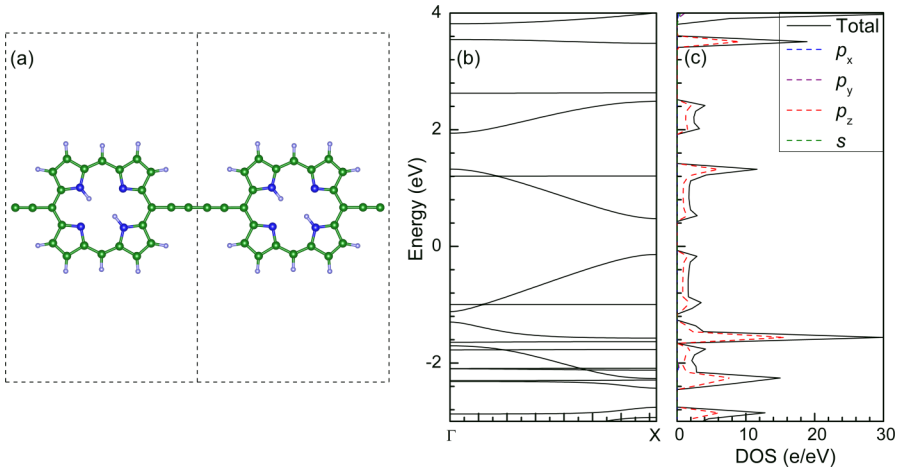


FIG. 1. (a) Geometric structure, (b) band structure, and (c) total and projected density of state of metal-free porphyrin nanowire (H_2-PNW). The Fermi level in panel b and c is shifted to zero. In panel c, only contribution of the delocalized p_z orbital in this species can be found neat the Fermi level while contributions of p_x, p_y and s orbitals are mainly located at energy levels far away from the Fermi level. C, green; H, light blue; and N, blue.

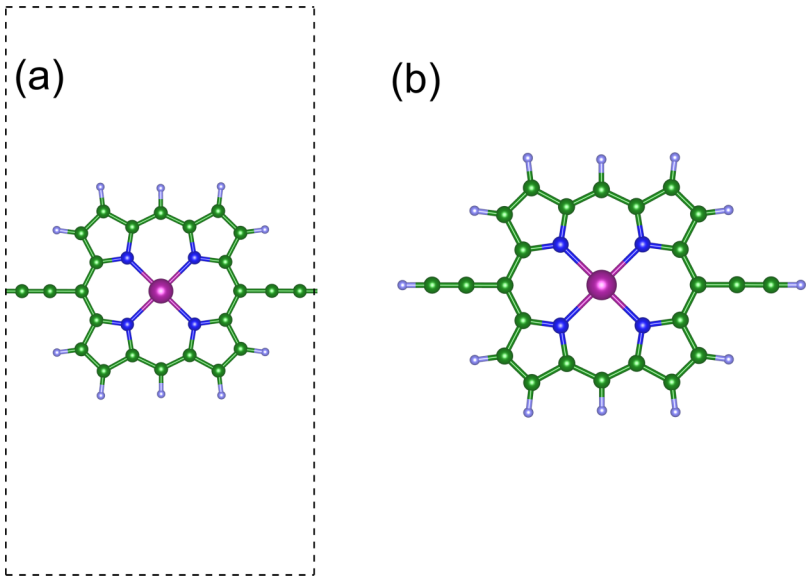


FIG. 2. Geometric structures of (a) TM-PNWs and (b) their corresponding isolated monomers, in which acetenyls are terminated with H atoms. C, green; H, light blue; N, blue; and Transition Metals (TMs), purple.

neighbor porphyrin rings are orthogonal. This atomic arrangement can severely disrupt the extended π-electron conjugation systems, and consequently, damage the electronic performance. Actually, a recent report on the conductance of oligo-porphyrin wires[42] have revealed that the calculated values based on planar porphyrin arrays are more consistent with experimental data than those calculated upon the orthogonal ones. As a consequence, only the planar structures of H_2-PNW and TM-PNWs were considered in this work.

Embedding $3d$ TM atoms into the porphyrin cores in H_2-PNW can afford the generation of one-dimensional TM-PNWs (TM = Cr, Mn, Co, Ni, Cu and Zn), the geometric structures of which are shown in Fig. 2. Porphyrin ring is a good host for these TM atoms. These TM ions in TM-PNWs are in +2 valence states and coordinated to the nitrogen atoms. The strong coordination interactions and relatively large distances resulting from the butadiyne linkers between neighboring metal atoms in TM-PNWs can efficiently prevent the aggregation of these atoms, which is much challenging in Mn-doped silicon systems.[55,56] As a result, these TM atoms can distribute separately in TM-PNWs, which can induce the intrinsic magnetic properties of TM-PNWs, making them potential candidate for constructing nanodevices of spintronics.

To reveal the magnetic behaviors of TM-PNWs, spin-polarized DFT calculations were performed, and the results are listed in Table I. For Ni-PNW and Zn-PNW, their ground states are unpolarized with a total magnetic moment of 0.0 μ_B per unit cell. While for the rest of TM-PNWs, their ground states are found to be spin-polarized. The total magnetic moments of these TM-PNWs are calculated to be 4.0, 4.8, 1.0, and 1.0 μ_B per unit cell, for Cr-PNW, Mn-PNW, Co-PNW, and Cu-PNW, respectively. We have also investigated the magnetic properties of the monomeric structures of these TM-PNWs to evaluate the influence of junction on their magnetic moments. As Table I shows, when these TM-porphyrin monomers are connected to TM-PNWs, the spin states are not changed. For example, the spin states for nickel species are unpolarized in both

TABLE I. Total magnetic moments (M, in μ_B) for TM-PNWs and their monomers, and exchange energies (E_{ex}, in meV) per supercell for the magnetic TM-PNWs.

TM	Cr	Mn	Co	Ni	Cu	Zn
M (monomer)	4.0	5.0	1.0	0.0	1.0	0.0
M (TM-PNW)	4.0	4.8	1.0	0.0	1.0	0.0
E_{ex}	1.0	30.0	0.0	-	0.0	-

Ni-porphyrin monomer and nanowire. In addition, the total magnetic moments of spin-polarized species are nearly the same for both TM-porphyrin monomer and TM-PNW (TM = Cr, Mn, Co, Cu), indicating that the formation of nanowires has little influence on the magnetic moments of TM-porphyrins. This can be ascribed to the fact that the long distances (~ 13.5 Å in the optimized structures) between neighbor TM atoms in TM-PNWs leading to their weak interactions. For the magnetic TM-PNWs, the central TM atoms carry most of the magnetic moment and their neighbor N atoms have slightly antiferromagnetic polarizations, except for Cu-PNW, in which Cu and N atoms are polarized ferromagnetically. These spin-polarized characteristics have also been found in TM embedded phthalocyanine frameworks,[48,49] in which the chemical environment for TM atoms are resemble to those considered here.

For the magnetic TM-PNWs, it is usually necessary to investigate the magnetic coupling between the central TM atoms. A supercell containing two repeats of the monomer of TM-PNW (TM = Cr, Mn, Co and Cu) was constructed and the energies upon these structures were calculated at both antiferromagnetic (AFM) and ferromagnetic (FM) coupling states (Fig. 3). The exchange energy E_{ex} (= $E_{AFM} - E_{FM}$), which defines the energy difference between AFM and FM state, are summarized in Table I. A positive (negative) E_{ex} value means a FM (AFM) ground state for the investigated system. It was found that the energy difference between AFM and FM states for Cr-PNW, Co-PNW and Cu-PNW is almost 0. Even in the case of Mn-PNW, which prefers FM coupling state, the exchange energy is not too large (30.0 meV). As a consequence, the AFM and FM coupling states are almost degenerate for all magnetic TM-PNWs investigated here, which is caused by the relatively large intermetallic distances making the spins difficult to be coupled. Because of the degenerate character of different spin states, the ferromagnetic state can be accomplished under suitable conditions such as an external magnetic field and low temperatures, which has been expected for TM-porphyrin arrays.[54] And consequently, we will then calculate their electronic structures in the ferromagnetic ground state.

The calculated spin-polarized total density of states (DOS) of TM-PNWs are shown in Fig. 4. The features of total DOS clearly demonstrate the spin states of TM-PNWs. For example, the total DOS of the spin-up and spin-down channels are symmetrical for Ni-PNW and Zn-PNW, indicating their non-polarized spin states. On the other hand, for Cr-PNW, Mn-PNW, Co-PNW and Cu-PNW, their spin-up and spin-down states are asymmetrical, implying the magnetic characteristics of these systems. It should be noted that the total DOS of both spin channels for Cr-PNW, Co-PNW, Ni-PNW, Cu-PNW and Zn-PNW are not occupied in the energy region slightly above the Fermi level, which indicates that these TM-PNWs are semiconducting for both spins. Because of the asymmetrical DOS occupation of spin-up and spin-down states in Cr-PNW, Co-PNW and Cu-PNW, the energy gaps of two spin channels in these systems are slightly different. In terms of Mn-PNW, there is a band gap for the spin-up channel while the spin-down channel is gapless, which allows

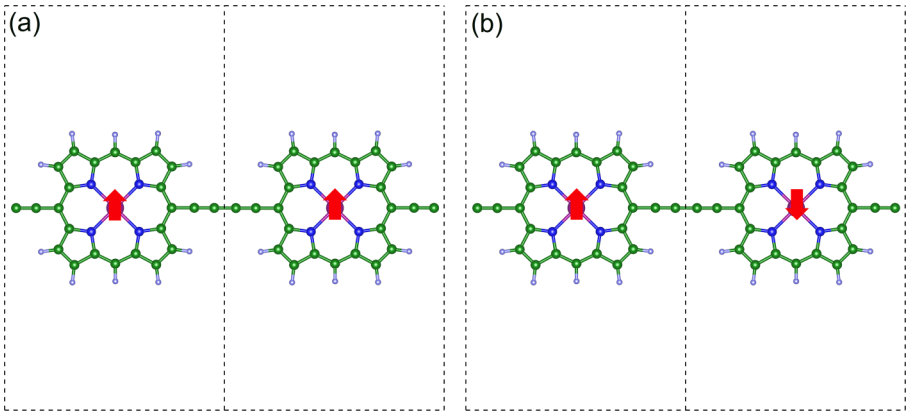


FIG. 3. Schematic representations of (a) ferromagnetic and (b) antiferromagnetic coupling states between central TM atoms, in which arrows denote spin directions of the neighbor TM atoms. C, green; H, light blue; N, blue; and Transition Metals (TMs), purple.

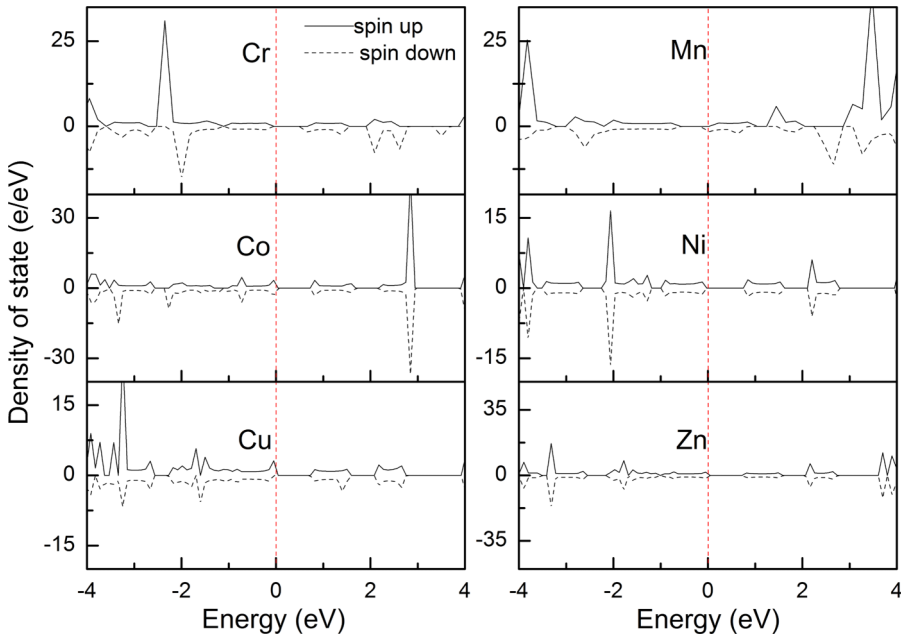


FIG. 4. Spin-polarized total DOS of TM-PNWs. The red dashed lines denote the Fermi level, which has been shifted to zero.

electron transport freely. Furthermore, the spin polarization approaches 100% based on the equation $P = (N_{\downarrow}(E_F) - N_{\uparrow}(E_F))/(N_{\downarrow}(E_F) + N_{\uparrow}(E_F))$, where $N(E_F)$ is the DOS occupation of the spin states at the Fermi level. These results demonstrate the half-metallic properties of Mn-PNW, which can be used to construct spin filter devices to obtain electrons in a pure spin state.

To understand the different electronic behavior of TM-PNWs, we have also calculated the projected density of states of *d* orbitals of central metal atoms and *p* orbitals of carbon and nitrogen atoms. As shown in Fig. 5, the electronic states for Mn-PNW and Cr-PNW near the Fermi level

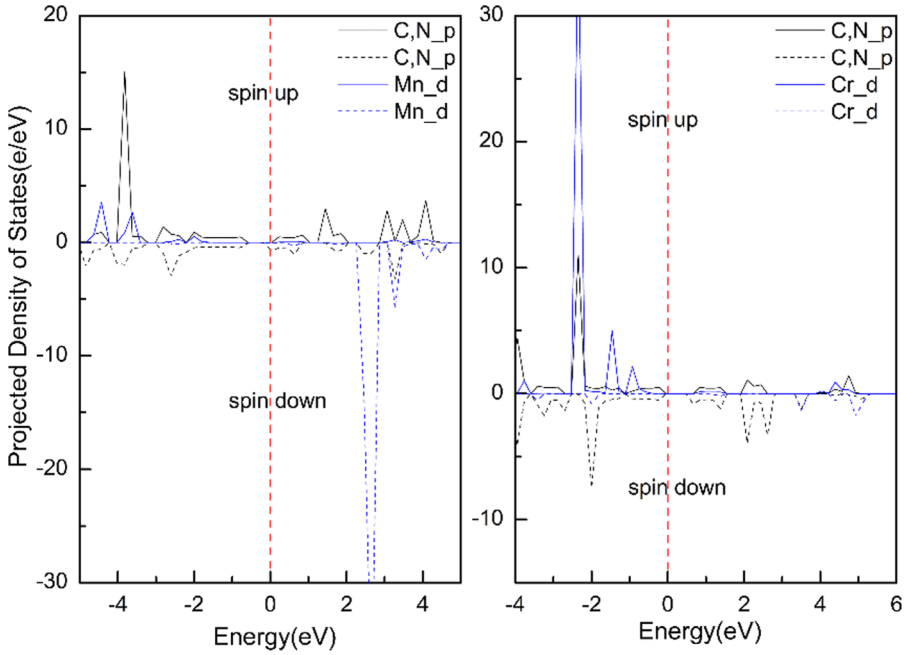


FIG. 5. Projected density of states of Mn-PNW and Cr-PNW. Contributions of d orbitals are presented in five-fold to describe the electronic features near the Fermi level (denoted by red dished lines) more clearly.

are mainly contributed by the p orbitals of C and N. In addition, because of the introducing of metal atoms, the spin states of p orbitals become unsymmetrical. The d orbitals in Mn-PNW and Cr-PNW exhibit different behaviors. In the case of Cr-PNW, four 4d electrons occupy the spin-up states below the Fermi level, resulting in a magnetic moment of 4 μ_B for this species. Besides, no occupied state can be found across the Fermi level, which makes Cr-PNW a semiconductor. Similar contributions of d and p orbitals to the density of states also hold for other semiconducting TM-PNWs (TM=Co, Cu, Ni and Zn, See Fig. S1 of the supplementary material[57]). However, in Mn-PNW, the conductive spin-down channel is found to be slightly contributed by d orbitals, which were further characterized to be the d_{xy} orbital with delocalized characters. The coupling between delocalized p and d orbitals across the Fermi level provide the channels for electron transfer in Mn-PNW, rendering it a half-metal. Because of the slight contribution of d orbital to spin-down states, the total magnetic moment of Mn-PNW is less than 5 μ_B (Table I).

IV. CONCLUSION

In summary, we have systematically investigated the electronic and magnetic properties of TM-PNWs (TM = Cr, Mn, Co, Ni, Cu and Zn) based on spin-polarized DFT calculations. The ground states of these systems are found to be nonmagnetic for Ni-PNW and Zn-PNW, and magnetic for the others, the total magnetic moments of which are equal to their corresponding isolated monomer structures. The AFM and FM spin coupling states are almost degenerate for the magnetic nanowires, making it possible to tune their spin directions with an external magnetic field. These results indicate that the intermetallic interactions in TM-PNWs are relatively weak because of the large distances between neighbor TM atoms, which can sufficiently prevent these TM atoms from aggregation. In addition, the ferromagnetic Mn-PNW is half-metallic with 100% spin polarization at the Fermi level, while the other frameworks are semiconducting. The present work suggests a new way of obtaining ferromagnetic porphyrin-based nanowires with TM atoms distributed separately and orderly, which are expected to be good candidates for catalysts, energy storage and molecular spintronics.

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