



HAL
open science

Gap switching in metal-organic coordination chains

Hassan Denawi, Mathieu Abel, Abdelkader Boukortt, Olivier Siri, Roland Hayn

► **To cite this version:**

Hassan Denawi, Mathieu Abel, Abdelkader Boukortt, Olivier Siri, Roland Hayn. Gap switching in metal-organic coordination chains. *Journal of Magnetism and Magnetic Materials*, 2022, 560 (23), pp.169561. 10.1016/j.jmmm.2022.169561 . hal-03868404

HAL Id: hal-03868404

<https://amu.hal.science/hal-03868404>

Submitted on 22 Jul 2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial 4.0 International License

Gap switching in metal-organic coordination chains

Hassan Denawi^{1,2,3}, Mathieu Abel¹, Abdelkader Boukortt⁴, Olivier Siri⁵ and Roland Hayn¹*

¹Aix Marseille Université, CNRS, IM2NP UMR 7334, 13397, Marseille, France.

²CEA Paris-Saclay, Service de Recherches de Métallurgie Physique, 91191 Gif-sur-Yvette, France

³Centre d'Elaboration de Matériaux et d'Études Structurales (CEMES), Centre National de la Recherche Scientifique (CNRS), Université de Toulouse, Cedex 31055 Toulouse, France.

⁴Laboratoire d'Elaboration et Caractérisation Physico Mécanique et Métallurgique des Matériaux (ECP3M), Abdelhamid Ibn Badis University-Mostaganem, Route nationale N°11, Kharrouba, 27000 Mostaganem.

⁵Aix Marseille Université, CNRS, CINAM, UMR 7325, Campus de Luminy, 13288, Marseille, France.

ABSTRACT

We predict two switchable one-dimensional (1D) spin-polarized semiconductors based on metal-organic coordination chains constructed out of Fe, V, and zwitterionic quinone (ZQ) molecules using first-principal density functional theoretical analysis. The Fe-ZQ coordination chain can be converted from a semiconductor to a half-metal when oxidized by chlorine (Cl). Upon chlorination, the magnetic moment of the Fe-ZQ is increased from $4 \mu_B$ to $5 \mu_B$, per iron atom. In addition, the bimetallic (Fe-ZQ-V-ZQ) ferromagnetic semiconducting coordination chain with a very small energy gap of only 90 meV can be converted to an antiferromagnetic semiconductor

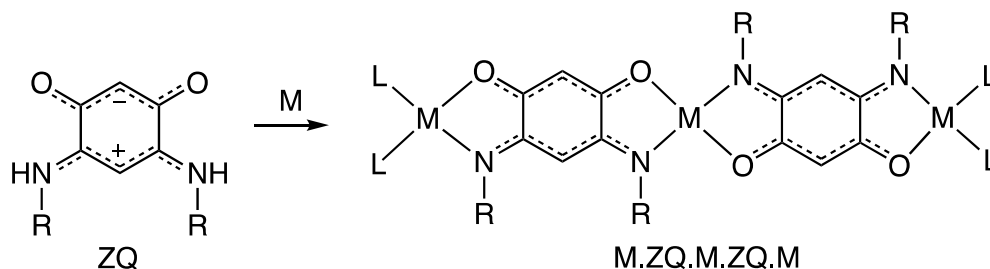
with a large gap of more than 1 eV when oxidized by chlorine. Its magnetic moment is found to be $8 \mu_B$ per heterobimetallic unit (Fe and V) after chlorination, and $7 \mu_B$ without chlorine. These unique properties, namely a switchable or reversible electronic and magnetic characteristics with a transition between different semiconducting states, make these coordination chains to be highly promising candidates for specific applications as multi-functional switch in nanoelectronics and spintronics.

INTRODUCTION

Conducting one-dimensional (1D) systems are of highest importance for future nano-electronics applications. An enormous amount of research work was concentrated on carbon nanotubes which could be useful for that purpose [1–3]. Also, some studies on one-dimensional (1D) metal-organic wires were devoted to sandwich structures with benzene or cyclopentadienyl [4–6]. However, a planar alternative of a molecular conducting wire, as for instance nano-ribbons of carbon,⁴ would be interesting as well. In that respect, the successful synthesis of 1D metal-organic coordination chains on Ag(111) and Au(110) is remarkable [7,8]. These coordination chains are synthesized by co-deposition of Fe together with zwitterionic quinone (ZQ) molecules on the noble metal surface followed by an on-surface coordination reaction under well-chosen conditions. The electronic structure of these Fe-ZQ coordination chains is characterized by a conjugated pi-electron system with local magnetic centers at the Fe-sites. Interestingly, the Fe^{2+} ions (with $3d^6$ electron configuration) can adopt either the $S=1$ or the $S=2$ magnetic state on the Ag(111) and Au(110) substrates, respectively, due to the very different lattice constants of the Fe-ZQ chains being fixed by the different substrates. However, electronic structure calculations of the Fe-ZQ chains taking

properly into account the strong electron correlation of $3d$ electrons predict a semiconducting behavior with gaps of 0.65 and 1.30 eV for the $S=1$ and $S=2$ spin states of Fe, respectively. For future applications of these Fe-ZQ molecular chains as conducting wires it would be very advantageous to reduce the semiconducting gap. We report below ab-initio results, which suggest that this gap reduction can be achieved in two different ways: either by chlorination of the Fe-ZQ chains which leads to half-metallic behavior or by substituting each second Fe by V which reduces the gap drastically. We complete the study by investigating the effect of chlorination on the bimetallic Fe-V chains. We show that attaching a Cl ion to the Fe sites recovers the original gap of Fe-ZQ chains. So, we not only found highly conducting strictly 1D molecular wires with local magnetic centers, but also systems which can be reversibly switched between different electronic and magnetic systems by simple chlorination.

Generally, switchable low-dimensional metallic and magnetic systems are very interesting as potential candidates for future applications in quantum computing, high-density information storage and spintronics. So, spintronics holds a huge potential for the next generation of electronic devices with improved performance and enhanced functionality [9–13]. Nano-structuration is an important tool to find the corresponding nano-structures to be used as spintronic devices [4,5,8,9,14–17]. Here, we will focus on planar magnetic metal-organic chains based on the zwitterionic quinoidal (ZQ) molecule [18]. Taquet et al successfully synthesized metal complexes of ZQ with up to three metal ions [19] (Scheme 1).

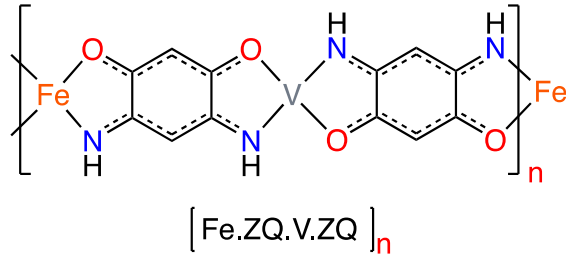


Scheme 1: The zwitterionic quinoidal (ZQ) molecule before (left) and after (right) the complex building reaction.

Further on, the synthesis of micrometer long coordination chains of Fe-ZQ on the Ag(111) and the Au(110) surfaces was reported [7,8,20]. Koudia et al [21] synthesized a single-layer 1D periodic Fe-ZQ framework through a metal-directed surface reaction, and the samples were characterized using scanning tunneling microscopy (STM). They also pointed out that the synthesis procedure is flexible for other central metal atoms. The recent success in embedding transition metal (TM) atoms in 1D TM-ZQ coordination chains provides a novel pathway for achieving the long-standing dream of 1D atomic sheets with regularly and separately distributed TM atoms for catalysis and spintronics. In that spirit, we predict here by theoretical ab-initio calculations switchable metal-organic wires based on ZQ due to a chlorination reaction. The advantage of the present system with respect to alternative proposals found in the scientific literature is that very similar systems have already been synthesized [6,22].

In this work, based on systematic density functional theory (DFT) calculations, we report on half-metallic behavior due to chlorination of Fe-ZQ coordination chains and we show that the (Fe-ZQ-V-ZQ) coordination chain can be converted from a ferromagnetic semiconductor with a very small gap to an antiferromagnetic semiconductor with a considerable gap of more than 1 eV after oxidation of the Fe site and the change of its coordination sphere (geometry) by chlorination (Cl).

Importantly, the magnetic moment is then increased from $7 \mu_B$ for $(\text{Fe-ZQ-V-ZQ})_n$ (see scheme 2) to $8 \mu_B$ for $(\text{FeCl-ZQ-V-ZQ})_n$ per unit cell. So, we find reversible alterations of the electrical and magnetic properties of highly promising 1D metallic or semi-conducting magnetic chains.



Scheme 2: Structure of the bimetallic $(\text{Fe-ZQ-V-ZQ})_n$ coordination chain

METHOD

In this paper, we perform a comprehensive first principles study of the structural, electronic and magnetic properties for the proposed 1D coordination chains. Our theoretical calculations are performed within spin-polarized Density Functional Theory (DFT) with the Generalized Gradient Approximation (SGGA) of Perdew and Wang (PW91) [23,24] for the exchange and correlation potential and the Projector Augmented Wave (PAW) pseudo potentials [25,26]. The first-principle calculations have been performed using the pseudo potential code VASP (Vienna Ab initio Simulation Package) to study the metal-organic 1D chains. Due to the well-known problems of standard spin polarized DFT in describing strongly correlated systems, we choose the VASP code being based on a plane-wave basis and consider the strong correlation of the electrons in the $3d$ shell by a Hubbard U term added to the spin polarized generalized gradient approximation (SGGA+ U) method. The SGGA+ U corrections were introduced by Liechtenstein et al, [26] where U and J enter as independent corrections in the calculations. The value of $J = 0.9$ eV is fixed by

the properties of the TM atom and only slightly reduced with respect to the value for a free atom. On the other hand, the correlation energy U for a $3d$ orbital is considerably screened in a solid and not easy to determine. We choose here $U = 5$ eV as it was justified for TM-ZQ coordination chains [8,20,27]. The electronic wave functions are expanded in plane waves with a kinetic energy cutoff of 480 eV, the coordination chains are relaxed until the residual forces are below 10^{-6} eV/Å and the convergence criteria for the energy deviations is 10^{-7} eV. The Brillouin zone is determined by a set of $8 \times 1 \times 1$ k -points in the unit cell using the Monkhorst-Pack points [28]. The Gaussian smearing method is used in these calculations and a width of 0.01 eV is adopted. We now present first the study of chlorination of Fe-ZQ coordination chains before going over to bimetallic (Fe-ZQ-V-ZQ) coordination chains. The geometry optimization was performed by relaxing all atomic coordinates for a fixed lattice constant.

CHLORINATION OF Fe-ZQ COORDINATION CHAINS

The geometry optimization for coordination chains was performed with the variable lattice parameter and the full relaxation of the coordinates. It consists of Fe-ZQ coordination chains with Cl being attached to the Fe sites (see Figure 1). After relaxation, the Fe ions depart slightly from the strictly planar situation of free standing Fe-ZQ coordination chains which had been calculated before [8,20].

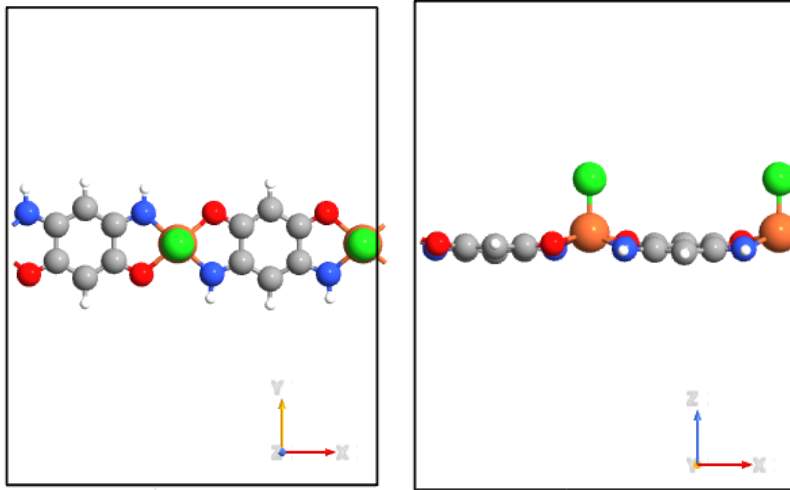


Figure 1: *Ab-initio structure of free-standing 1D coordination chains of (FeCl-ZQ). The color code for the different atoms is as follows: Fe – orange, Cl – green, N – blue, O – red, C – dark grey, H – white.*

Here, we calculated the total energy of isolated FeCl-ZQ chains as a function of the lattice constant.

We found three different spin states corresponding to $S=1/2$, $S=3/2$ and $S=5/2$ which is possible for a $3d^5$ electron configuration of the Fe center. From that we can already conclude, that Cl is in the Cl^- charge state and gets one electron from the Fe site. Therefore, by chlorination, the Fe valence changes from Fe^{2+} to Fe^{3+} .

In difference to the situation without Cl, there are not two stable spin states as a function of the lattice constant. After chlorination the high spin state $S=5/2$ is the lowest one for all values of the lattice constant being about 1 eV lower than the $S=3/2$ solution and about 2 eV lower (per formula unit) than the $S=1/2$ solution. Therefore, we concentrate the remaining analysis on the $S=5/2$ case exclusively.

The $3d^5$ situation with local spins of $S=5/2$ is also realized in Mn-ZQ coordination chains. Therefore, both systems, i.e., Mn-ZQ and chlorinated FeCl-ZQ are predicted to have very similar electronic structures. Especially, they are both predicted to be metallic. The formal proof is presented in Figure 2 where the total and partial densities of states are shown. One indeed remarks

a very large similarity to the electronic structure of Mn-ZQ coordination chains [20] with a half-metallic behavior for the ferromagnetic arrangement of the local spins.

In addition, we used the SGGA+ U (SGGA) methods, to evaluate the Fe-ZQ spin stabilities after chlorination; this is achieved by comparing the energies of the FM and AFM states in both original and a double unit. Without Cl, for the Fe-ZQ structure, the AFM state is much more stable than the FM state with an energy lowering of 8.8 meV per iron and after Cl oxidation, the AFM state is even more stable than the FM state by 22.6 meV (see Table 1). These results show that both Fe-ZQ and its chlorinated counterpart are AFM materials.

Table 1. Lattice constants (a , in Å), distances between the central Fe atoms and the ligands N (d_{Fe-N} , in Å), O (d_{Fe-O} , in Å) and Cl (d_{Fe-Cl} , in Å), exchange energies ($E_{ex} = E_{FM} - E_{AFM}$, in meV), total magnetic moments (M per Fe atom, in μ_B), local magnetic moments of the d orbital at the Fe atoms (M_d per Fe atom, in μ_B), local magnetic moments at the Cl atoms (M_{Cl} per Cl atom, in μ_B), local magnetic moments at the Fe atoms (M_m per Fe atom, in μ_B), energy band gaps for spin up (E_a) and spin down (E_b , in eV) for 1D (Fe-ZQ), and (FeCl-ZQ), coordination chains in the SGGA+ U method.

	Fe-ZQ	FeCl-ZQ
a	15.90	15.49
d_{Fe-O}	2.080	2.037
d_{Fe-N}	2.020	2.027
d_{Fe-Cl}	---	2.200
E_{ex}	8.8	22.6
M	4	5
M_d	3.670	4.086
M_{Cl}	---	0.188
M_m	3.720	4.155
E_a	1.20	No gap
E_b	1.30	0.78

The analysis of the total and partial densities of states (DOS) is very instructive for a detailed understanding of the remarkable electronic and magnetic properties of FeCl-ZQ coordination chains. First, as shown in Figure 2a, there is no gap at the Fermi level which indicates that the coordination chain is a half-metal. It can be seen from the calculated density of states of oxidized

FeCl-ZQ (Figure 2b) that Cl orbitals are almost degenerate and located just near the Fermi level which means that Cl has captured an electron from the Fe atom and its orbitals are now completely filled with spin-up but almost empty of spin-down electrons. As a result, the magnetic moment of (Fe-ZQ) is shoot up from $4 \mu_B$ to $5 \mu_B$ after Cl oxidation (see Figure 2c). It should be noted that the buckling of chlorinated Fe-ZQ is not essential for its magnetic and electronic properties since we obtain nearly identical results without buckling.

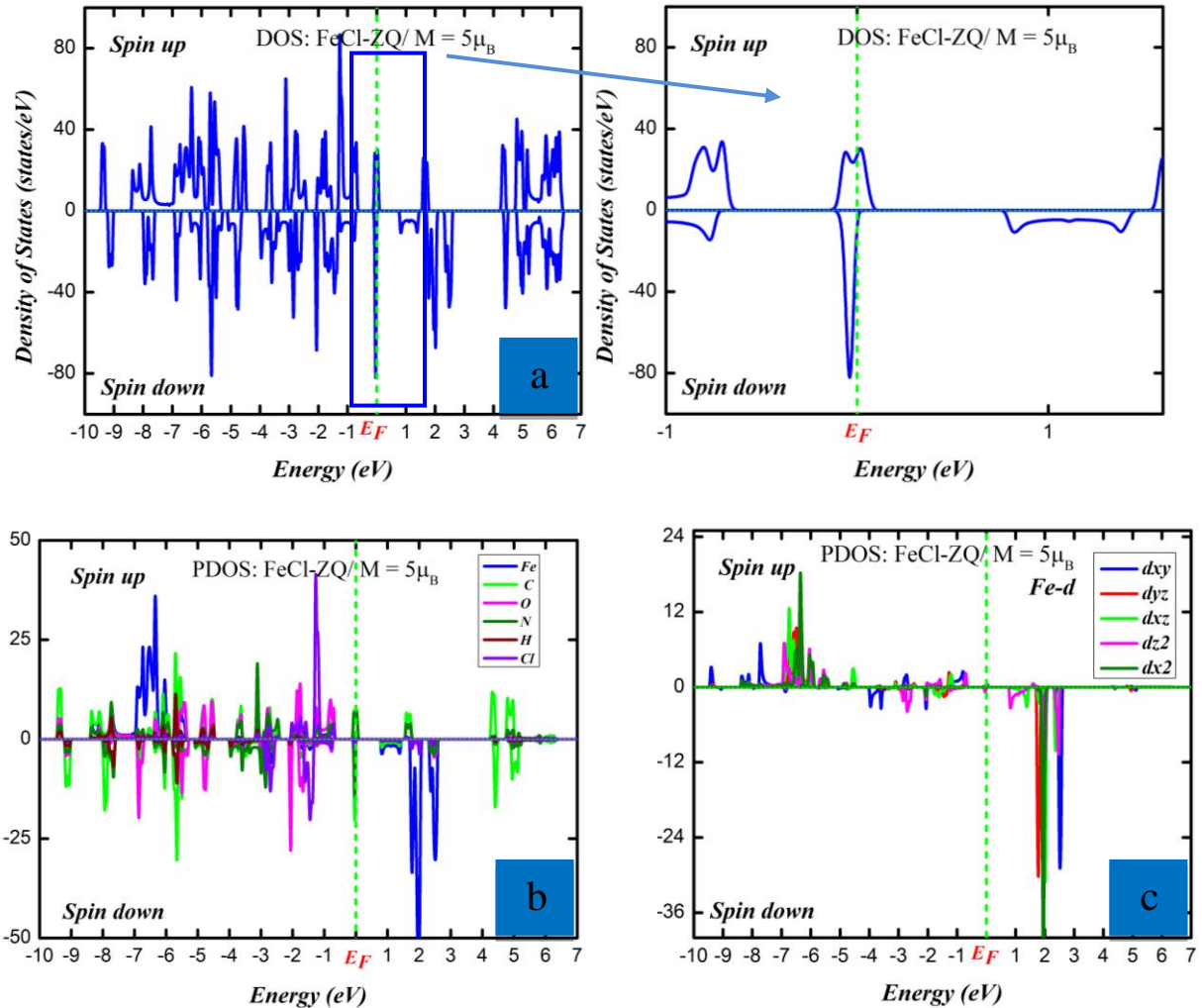


Figure 2: (a) Total DOS (b) projected DOS of the atoms (Fe, C, O, N, H), (c) the d orbitals at the Fe atoms in the 1D (FeCl-ZQ) coordination chains.

BIMETALLIC CHAINS

In this part, we study the 1D-coordination chains of (Fe-ZQ-V-ZQ) with and without chlorine, and Figure 3 shows a 1D top representation and a side view of the coordination chains. We checked several absorption sites for the Cl atom and found the Fe site to be the most preferable one which will be discussed further on (absorption energies in eV on Fe: -3.11, on V: -2.52, and on C: -1.49).

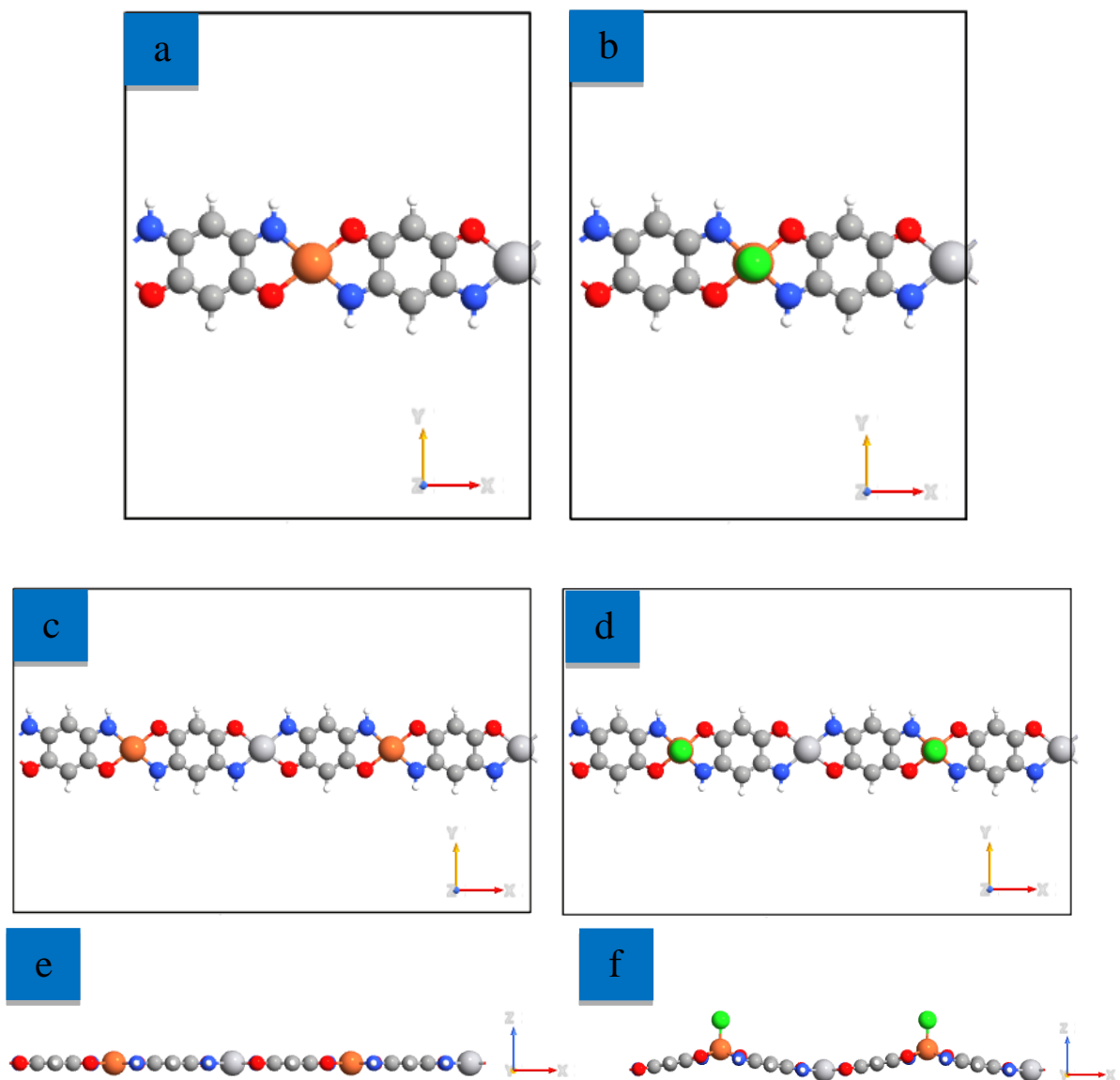


Figure 3: Ab-initio structure of free-standing 1D coordination chains of (Fe-ZQ-V-ZQ) in single (a,b) or doubled (c,d,e,f) unit cells. Panels b,d, and f show the structure with one Cl atom attached to a Fe atom after relaxation. The color code for the different atoms is as follows: Fe – orange, V – light grey, Cl – green, N – blue, O – red, C – dark grey, H – white.

The calculated results for all the $(\text{Fe-ZQ-V-ZQ})_n$ coordination chains, including their structural, energetic, electronic, and magnetic properties, are summarized in Table 2. The structural parameters are found after relaxation of all atomic positions as described in the section before. Remarkable is the reduction of the distances between Fe and its nearest neighbor ligands (O and N) after chlorination. That is not the case for the distances between V and its ligands which remain the same and are considerably larger than for Fe. The high-spin state is the lowest in energy at a lattice constant of 16.02 Å (15.60 Å) for the Fe-ZQ-V-ZQ (FeCl-ZQ-V-ZQ) coordination chains. The total magnetic moment increases from $7 \mu_B$ to $8 \mu_B$ per unit cell with one Fe and one V ion. As can be seen from the local magnetic moments at the metallic sites that increase by chlorination is due to an increase of the magnetic moment at the Fe site which increases from about $3.7 \mu_B$ to about $4.1 \mu_B$. Taking into account magnetic moments in the neighborhood of the Fe site that can be interpreted as an increase from a local spin $S = 2$ (or $4 \mu_B$ corresponding to a $3 d^6$ configuration of the Fe(II) center) to $S = 5/2$ (or $5 \mu_B$ corresponding to a $3 d^5$ configuration of the Fe(III)). Highly interesting is the electronic structure that we calculate for a parallel arrangement of all magnetic moments, i.e. a ferromagnetic state. Please note, however, that due to principal reasons there can be no magnetic long-range order in 1D systems at finite temperature, not ferro- nor antiferromagnetic order [29]. We find a small gap of 90 meV for spin up electrons for $(\text{Fe-ZQ-V-ZQ})_n$ which increases considerably after chlorination to 1.05 eV, turning $(\text{FeCl-ZQ-V-ZQ})_n$ into an antiferromagnetic semiconductor. This property could be highly interesting for future spintronics applications. We also calculated the energy difference $E_{ex} = E_{FM} - E_{AFM}$ between a ferromagnetic (FM) and an antiferromagnetic (AFM) state (the moments in the doubled unit cell are Fe-up V-up, Fe-down and V-down) and found the FM arrangement more stable for the (Fe-

ZQ-V-ZQ) $_n$ coordination chain ($E_{ex} = -4.1$ meV per unit cell with one V and one Fe) whereas $E_{ex} = 27.5$ meV becomes positive after chlorination, corresponding to an AFM state. To calculate the AFM state, we used a doubled unit cell which is shown in Figure 3.

Table 2. Lattice constant (a , in Å), distances between the central TM (Fe and V) atoms and the ligands N (d_{TM-N} , in Å), O (d_{TM-O} , in Å) and Cl (d_{Fe-Cl} , in Å), exchange energies ($E_{ex} = E_{FM} - E_{AFM}$, in meV), energy difference between NM and FM solution ($\Delta_E = E_{NM} - E_{FM}$, in eV), total magnetic moments (M per cell, in μ_B), local magnetic moments of the d orbital at the TM atoms (M_d per TM atom, in μ_B), local magnetic moments at the Cl atoms (M_{Cl} per Cl atom, in μ_B), local magnetic moments at the TM atoms (M_m per TM atom, in μ_B), energy band gaps for spin up (E_a) and spin down (E_b , in eV) for 1D (Fe-ZQ-V-ZQ), and (FeCl-ZQ-V-ZQ), coordination chains in the SGGA+U method. The values for a , E_{ex} , Δ_E , and M are given for one unit cell with one Fe and one V ion.

	Fe-ZQ-V-ZQ	FeCl-ZQ-V-ZQ
a	16.02	15.60
d_{Fe-O}	2.07	2.03
d_{Fe-N}	2.03	2.02
d_{Fe-Cl}	---	2.20
d_{V-O}	2.10	2.10
d_{V-N}	2.10	2.10
E_{ex}	-4.1	27.5
Δ_E	9.004	7.478
M	7	8
M_d	Fe : 3.659 V : 2.678	Fe : 4.087 V : 2.690
M_{Cl}	---	0.178
M_m	3.727 2.771	4.156 2.783
E_a	0.09	1.36
E_b	1.39	1.05

We show in Figures 4 and 5 the total valence charge density ($\uparrow + \downarrow$) and spin density ($\uparrow - \downarrow$) contour plots for the ferromagnetic coordination chains. The density plots are given along the coordination chains. The isovalue for the charge density in the (Fe-ZQ-V-ZQ) $_n$ coordination chain is $1.55 e^- \text{Å}^{-3}$ and $0.08 e^- \text{Å}^{-3}$ for the spin density. As it is clearly seen from the plots of the spin density distribution, the magnetic moments are mainly distributed around the Fe and V atoms, while the Cl atoms contribute little to the magnetism. The magnetic density (see Figure 4b)

indicates a quite localized positive magnetic moment at the Fe atom ($4 \mu_B$) and $3 \mu_B$ for the V atom. Our computations specify the total magnetic moment of $7 \mu_B$ per unit cell for the most stable state of $(\text{Fe-ZQ-V-ZQ})_n$. For $(\text{FeCl-ZQ-V-ZQ})_n$, there is a magnetic moment of about $8 \mu_B$ per unit cell.

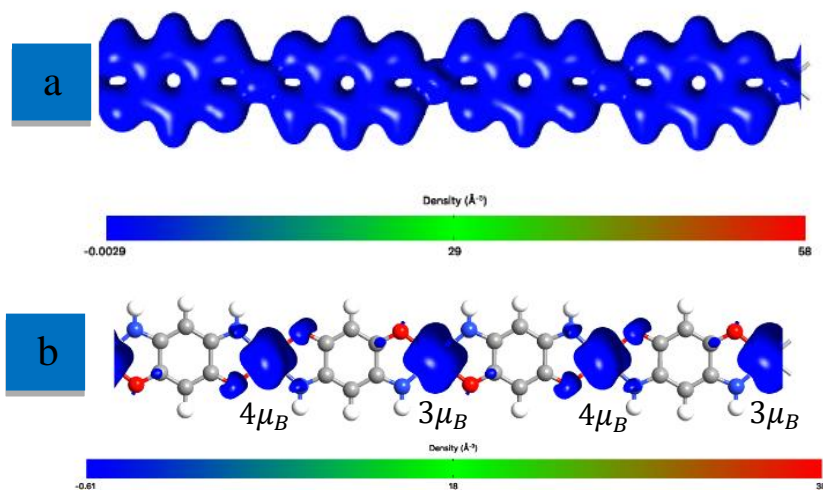


Figure 4: (a) Charge density (isovalue = $1.55e^- \text{ \AA}^{-3}$) and (b) spin density (isovalue = $0.08e^- \text{ \AA}^{-3}$) of the $(\text{Fe-ZQ-V-ZQ})_n$ coordination chain.

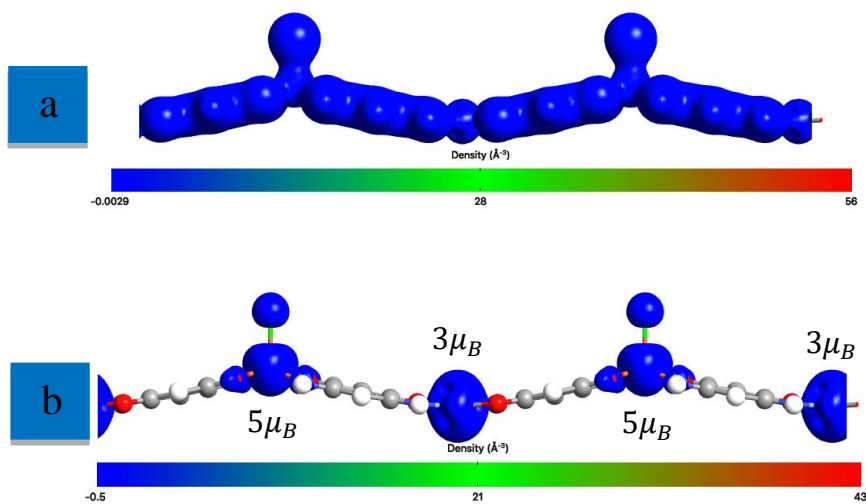


Figure 5: (a) Charge density (isovalue = $1.55e^- \text{ \AA}^{-3}$) and (b) spin density (isovalue = $0.08e^- \text{ \AA}^{-3}$) of $(\text{FeCl-ZQ-V-ZQ})_n$ coordination chain.

The corresponding local densities of states (DOS), projected DOS of the atoms (Fe, V, C, O, N, H) and the d orbitals at the Fe and V atoms in the 1D $(\text{Fe-ZQ-V-ZQ})_n$ and $(\text{FeCl-ZQ-V-ZQ})_n$ coordination chains, respectively, with the PAW-SGGA+ U method are shown in Figures 6 and 7. It is evident that the $(\text{Fe-ZQ-V-ZQ})_n$ coordination chain is a ferromagnetic semiconductor, the band gap is around 0.09 eV for spin up and 1.39 eV for spin down. The general band gap increases very much from 0.09 eV to 1.05 eV for the chlorinated coordination chain. More in detail, it is 1.36 eV for spin up and 1.05 eV for spin down for $(\text{FeCl-ZQ-V-ZQ})_n$. Figure 7 shows the electronic structure for $(\text{FeCl-ZQ-V-ZQ})_n$ in the ferromagnetic state to distinguish better between the majority and minority spin channels. The antiferromagnetic state is energetically slightly lower (see Table 2) but has a very similar energy gap of about 1 eV.

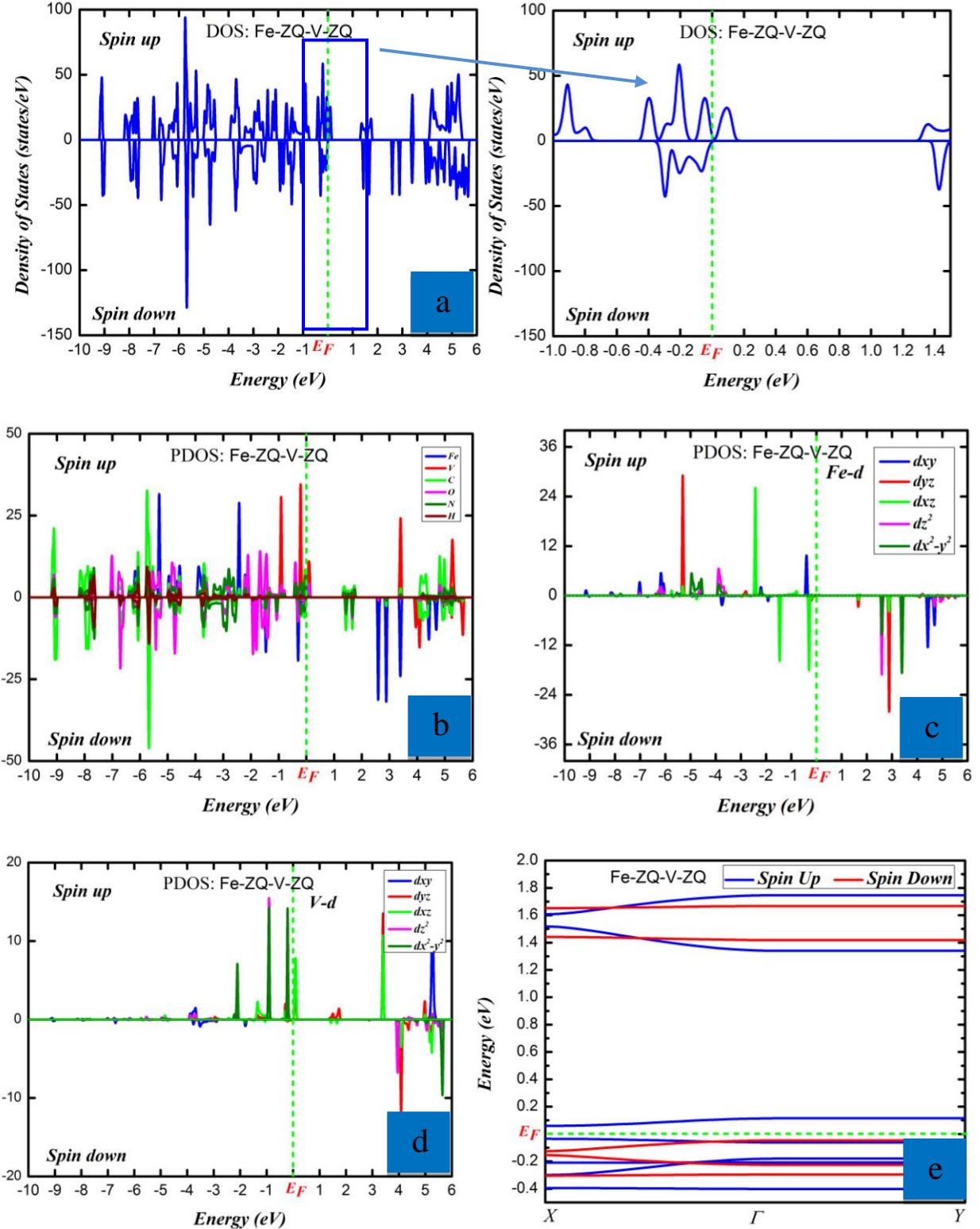


Figure 6: (a) Total DOS (b) projected DOS of the atoms (Fe, V, C, O, N, H), (c, d) the d orbitals at the Fe and V atoms and (e) band structure of the 1D (Fe-ZQ-V-ZQ) coordination chain with the PAW-SGGA+U method with high-spin.

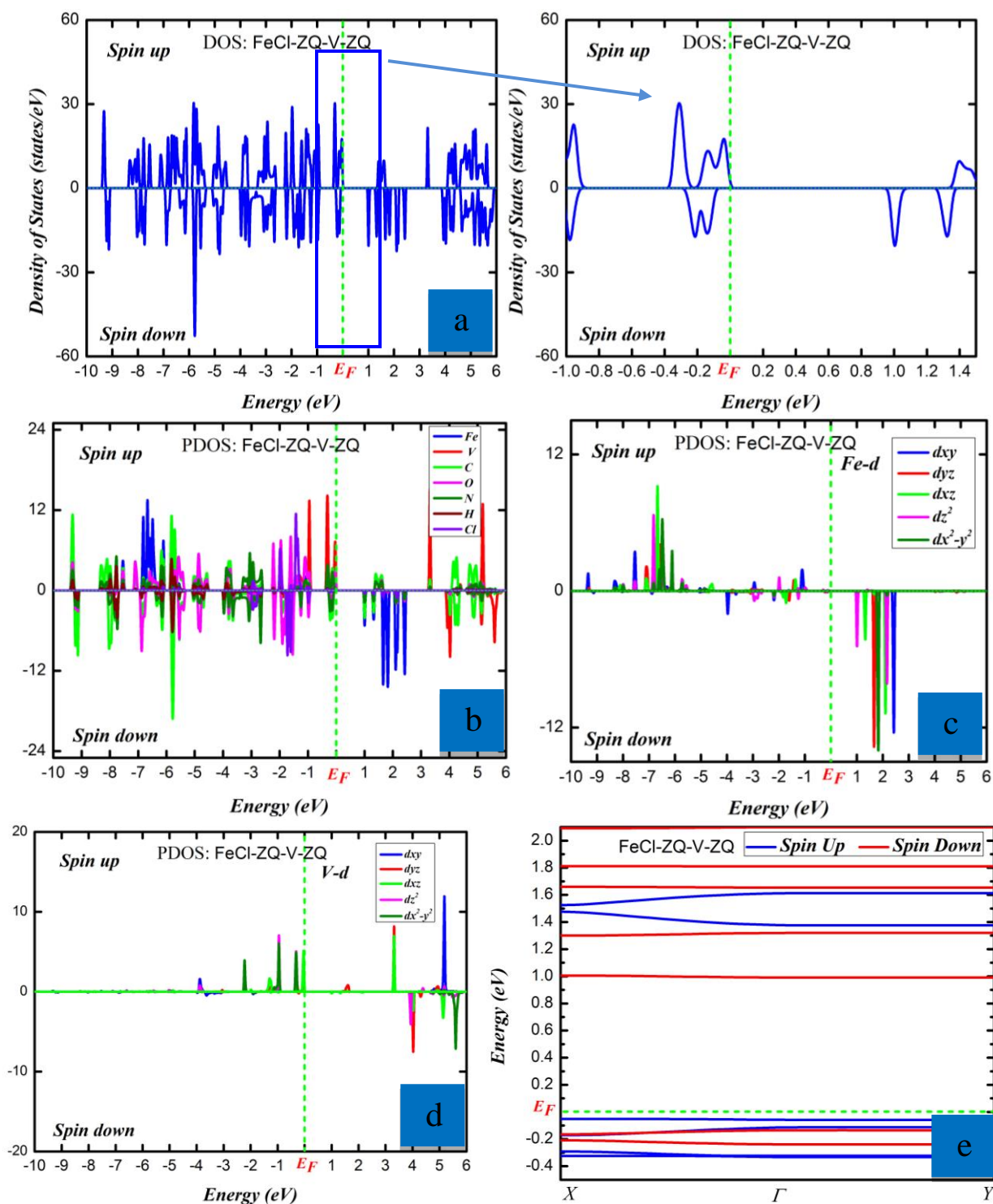


Figure 7: (a) Total DOS (b) projected DOS of the atoms (Fe, V, C, O, N, H), (c, d) the d orbitals at the Fe and V atoms and (e) band structure in the 1D (FeCl-ZQ-V-ZQ) coordination chain with the PAW-SGGA+ U method with high-spin.

CONCLUSIONS

In summary, we analyzed in detail the structural, energetic, electronic, and magnetic properties of the $(\text{Fe-ZQ})_n$ and $(\text{Fe-ZQ-V-ZQ})_n$ coordination chains with and without chlorine, obtained within a DFT framework. The coordination chain $(\text{Fe-ZQ})_n$ chain can be converted reversibly from semiconducting to half-metallic states using chlorine as oxidant. Moreover, the $(\text{Fe-ZQ-V-ZQ})_n$ coordination chain can be converted reversibly from a ferromagnetic semiconductor with a very small energy gap of 90 meV to an antiferromagnetic semiconductor with a gap of about 1 eV upon chlorination of the Fe center. The small energy gap of 90 meV would allow a high conductivity already at room temperature, which could reversibly be converted to the conductance behavior of an ordinary semiconductor. In addition, the change in the electronic properties is connected with a transition between ferromagnetic and antiferromagnetic behavior. The present theoretical prediction concerns only the short-range magnetic correlations since a magnetic long-range order is principally impossible in strictly 1D systems. However, it could be induced by an external magnetic field or an adapted substrate. Due to all these reasons, the $(\text{Fe-ZQ-V-ZQ})_n$ coordination chain with and without chlorine could be an interesting building unit in the design and the assembly of nano-systems and nano-spintronics. The current theoretical study may provide a guide for future experimental and theoretical studies to stimulate researchers to extend the use of these ligands and their corresponding complexes to embrace new discoveries.

AUTHOR INFORMATION

Corresponding Author

*E-mail: hassan.denawi@cea.fr (H.D.)

ACKNOWLEDGEMENTS

This work was supported by the Computer resources of the Centre Informatique National de l'Enseignement Supérieur (CINES), Project No. A0020906873 and the High Performance Computing (HPC) resources of Aix-Marseille University financed by the project Equip@Meso (ANR-10-EQPX-29-01). We thank M. Koudia for helpful discussions.

Conflict of interest

The authors declare that they have no conflict of interest.

References

- [1] H. Jiang, M. Bai, P. Wei, L. Sun, Z. Shen, S. Hou, Half-metallic properties of single-walled polymeric manganese phthalocyanine nanotubes, *Sensors*. 12 (2012) 8438–8446.
- [2] K. Tsukagoshi, B.W. Alphenaar, H. Ago, Coherent transport of electron spin in a ferromagnetically contacted carbon nanotube, *Nature*. 401 (1999) 1998–2000.
- [3] S. Frank, P. Poncharal, Z.L. Wang, W.A. De Heer, Carbon nanotube quantum resistors, *Science*. 280 (1998) 1744–1746.
- [4] L. Shen, S.-W. Yang, M.-F. Ng, V. Ligatchev, L. Zhou, Y. Feng, Charge-Transfer-Based Mechanism for Half-Metallicity and Ferromagnetism in One-Dimensional Organometallic Sandwich Molecular Wires, *Journal of the American Chemical Society*. 130 (2008) 13956–13960.
- [5] X. Zhang, Z. Tian, S.W. Yang, J. Wang, Magnetic manipulation and half-metal prediction of one-dimensional bimetallic organic sandwich molecular wires $[\text{CpTM1CpTM2}]_{\infty}$ (TM1 = Ti, Cr, Fe; TM2 = Sc-Co), *Journal of Physical Chemistry C*. 115 (2011) 2948–2953.
- [6] H. Da, H. Mei jin, K. Hwa Lim, V. Ligatchev, M. Ng, K. Hong khoo, S. Yang, Half metal reversible switch in bimetallic sandwich molecular wire via redox reactions, *Nano Energy*. 1 (2012) 297–302.
- [7] H. Denawi, E. Nardi, M. Koudia, O. Siri, M. Abel, R. Hayn, Magnetic Polymer Chains of Iron and Zwitterionic Quinoidal Ligands on the Ag(111) Surface, *The Journal of Physical Chemistry C*. 124 (2019) 1346–1351.
- [8] H. Denawi, M. Koudia, R. Hayn, O. Siri, M. Abel, On-Surface Synthesis of Spin Crossover Polymeric Chains, *Journal of Physical Chemistry C*. 122 (2018) 15033–15040.
- [9] S.A. Wolf, D.D. Awschalom, R.A. Buhrman, J.M. Daughton, S. von Molnar, M.L. Roukes, A.Y. Chtchelkanova, D.M. Treger, Spintronics: a spin-based electronics vision for the future, *Science*. 328 (2016) 80–83.
- [10] Q. Tang, Y. Li, Z. Zhou, Y. Chen, Z. Chen, Tuning electronic and magnetic properties of wurtzite ZnO nanosheets by surface hydrogenation, *ACS Applied Materials and Interfaces*. 2 (2010) 2441–2447.
- [11] Y. Ma, Y. Dai, M. Guo, C. Niu, Y. Zhu, B. Huang, Evidence of the existence of magnetism in pristine VX₂ monolayers (X = S, Se) and their strain-induced tunable magnetic properties, *ACS Nano*. 6 (2012) 1695–1701.
- [12] A. Du, S. Sanvito, S.C. Smith, First-principles prediction of metal-free magnetism and intrinsic half-metallicity in graphitic carbon nitride, *Physical Review Letters*. 108 (2012) 197207 (1–5).

- [13] H. Grün, T. Berer, J. Bauer-Marschallinger, R. Nuster, G. Paltauf, P. Burgholzer, Spintronics: Fundamentals and applications, *Reviews of Modern Physics*. 76 (2004) 323–410.
- [14] E. Kan, W. Hu, C. Xiao, R. Lu, K. Deng, J. Yang, H. Su, Half-metallicity in organic single porous sheets, *Journal of the American Chemical Society*. 134 (2012) 5718–5721.
- [15] A.L. Elias, A.R. Botello-Méndez, D. Meneses-Rodríguez, V.J. González, D. Ramírez-González, L. Ci, E. Muñoz-Sandoval, P.M. Ajayan, H. Terrones, M. Terrones, Longitudinal cutting of pure and doped carbon nanotubes to form graphitic nanoribbons using metal clusters as nanoscalpels, *Nano Letters*. 10 (2010) 366–372.
- [16] J. Zhou, Q. Wang, Q. Sun, X.S. Chen, Y. Kawazoe, P. Jena, Ferromagnetism in Semihydrogenated Graphene Sheet, *Nano Letters*. 9 (2009) 3867–3870.
- [17] B. Huang, Y.-W. Son, G. Kim, W. Duan, J. Ihm, Electronic and Magnetic Properties of Partially Open Carbon Nanotubes, *J. Am. Chem. Soc.* 10 (2009) 366–372.
- [18] O. Siri, P. Braunstein, Unprecedented zwitterion in quinonoid chemistry, *Chemical Communications*. 2 (2002) 208–209.
- [19] J. Taquet, O. Siri, P. Braunstein, R. Welter, L. Pasteur, B. Pascal, F.-S. Cedex, Stepwise Synthesis, Structures, and Reactivity of Mono-, Di-, and Trimetallic Metal Complexes with a $6\pi + 6\pi$ Quinonoid Zwitterion, *Inorganic Chemistry*. 43 (2004) 2680–2685.
- [20] H. Denawi, M. Abel, R. Hayn, Magnetic Polymer Chains of Transition Metal Atoms and Zwitterionic Quinone, *Journal of Physical Chemistry C*. 123 (2019) 4582–4589.
- [21] M. Koudia, E. Nardi, O. Siri, M. Abel, On-surface synthesis of covalent coordination polymers on micrometer scale, *Nano Research*. 10 (2017) 933–940.
- [22] S. Nagao, A. Kato, A. Nakajima, K. Kaya, Multiple-decker sandwich poly-ferrocene clusters, *Journal of the American Chemical Society*. 122 (2000) 4221–4222.
- [23] J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh, C. Fiolhais, Atoms, molecules, solids, and surfaces: Applications of the generalized gradient approximation for exchange and correlation, *Phys. Rev. B*. 48 (1993) 4978.
- [24] J.P. Perdew, Y. Wang, Accurate and simple analytic representation of the electron-gas correlation energy, *Physical Review B*. 13 (1992) 244–249.
- [25] G. Kresse, J. Furthmüller, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set, *Physical Review B*. 54 (1996) 11169–11186.
- [26] A.I. Liechtenstein, V.I. Anisimov, Z. J., Density-functional theory and strong interactions: Orbital ordering in Mott-Hubbard insulators, *Physical Review B*. 52 (1995) 5467–5471.
- [27] H. Denawi, M. Abel, O. Siri, R. Hayn, Electronic and magnetic properties of metal–organic polymers with 4d and 5d-transition metal ions, *Journal of Magnetism and Magnetic Materials*. 537 (2021) 168183.
- [28] H.J. Monkhorst, J.D. Pack, special points for Brillouin-zone integrations, *Physical Review B*. 13 (1976) 5188–5192.
- [29] L.D. Landau, E.M. Lifshitz, *Course of Theoretical Physics, Statistical Physics*, Elsevier, Amsterdam, 5 (1951).