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Electronic and magnetic properties of metal-organic polymers with 4d and 5d-transition metal ions

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ABSTRACT

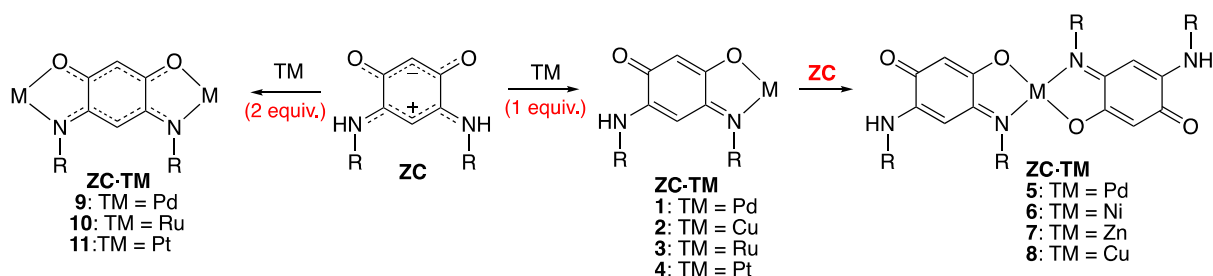
The electronic and magnetic properties of one-dimensional polymers of zwitterionic quinone (ZQ) molecules with 4d and 5d transition metals (TM) are studied using density functional calculations. We present the results of first-principle calculations for the electronic and magnetic properties, including the magnetic anisotropy energy (MAE) of selected 4d- and 5d-ZQ polymers, using the Vienna Ab-initio Simulation Package (VASP). In particular, a pronounced magnetic character is found for TM-ZQ polymers with the TM ions Mo, Ru, Rh, Ag, Re, and Ir, having local magnetic moments between 1 and 4 μ_B and ferromagnetic or antiferromagnetic nearest neighbor exchanges. The large values of spin-orbit coupling lead to high magnetic anisotropy energies (MAE) especially for Rh-ZQ and Re-ZQ, exceeding the MAE of its 3d counterparts considerably. All investigated TM-ZQ polymer chains were found to be spin-polarized semiconductors, which make them, together with the high MAE, excellent candidate materials for spintronics.

INTRODUCTION

The study of metal-ligand molecules or polymers has a long history and is the subject of organometallic chemistry [1–4]. They are of highest importance for biological and technological processes and their investigation is on the upturn at present. The choice of the ligand is here a crucial issue and the monocyclic 2,5-oxoamino-1,4-benzoquinonemonoimines (ZQ, Figure 1), featuring a stable zwitterionic ground state, appeared in this context extremely appealing [5]. The charge separation in ZQ is due to an intramolecular proton transfer that generates two distinct 6π -electron subunits, i.e., a positively charged trimethine cyanine and a negatively charged trimethine oxonol, linked through two single bonds (see ZQ, Scheme 1). According to the coupling principle of polymethine dyes [6], such a ground-state electronic structure is highly stable, generating a large intrinsic dipole (ca. 10 D), that could be exploited for the elaboration of molecular films following adsorption [7–11] or polymerization on metallic surfaces [12–14] along with interfaces [15,16] and, more recently, as interlayers in graphene transistors [17].

Importantly, the use of ZC as a ligand in coordination chemistry has been extensively investigated and clearly demonstrated its efficiency and versatility in solution (Scheme 1). In presence of 1 equiv. of metal precursors (TM), the reaction proceeds by two successive deprotonation/ metalation steps from ZC, affording mononuclear complexes **1-4** with TM = Pd [18], Cu [19], Ru [20] and Pt [21]. Interestingly, mononuclear complexes **5-8** with TM/L ratio of 1/2 could be also obtained when 2 equiv. of ZC was used (M = Pd [18], Ni [18], Zn [22] and Cu [22]). In all cases, each quinoid unit (ZC) is linked to the metal center through two covalent and two coordinative bonds through N and O atoms. As a result, the oxidation state of the metal centers is always +II. Furthermore, the zwitterionic character of the ligand is lost, but its π electrons are now localized. In contrast, the condensation of 2 equiv. of TM precursors on ZC (instead of one) afforded the dinuclear species **9-11** (M = Pd [23], Ru [20],

and Pt [21]) in which the π electrons are still delocalized, a key feature to form conductive materials.



Scheme 1

This metal (TM) -ligand (L) assembly was recently investigated by some of us on surface to obtain polymers with full delocalization of the electrons. The on-surface polymerization of Fe and zwitterionic quinone (ZQ) to long polymer chains was indeed successfully reported and attracted considerable attention [13]. Remarkably, this polymerization reaction could not be realized in the gas phase or under wet conditions but only on the surface of noble metals like Ag or Au [14,24]. The polymer chains mentioned above are interesting for spintronics applications in the prospect of spin-polarized one-dimensional (1D) electron transport. With the rapid miniaturization of the semiconductor industry, molecular-sized components will be used in the foreseeable future in hybrid electronics or spin electronics (spintronics) devices. The Fe-ZQ polymers are also remarkable, since they can be adapted to very different substrates in connection with a predicted spin-state transition and they build different 1D or 2D arrangements [14,24]. There is certainly no experimental difficulty to replace Fe by other transition metal (TM) atoms and the whole class of 3d TM-ZQ polymer chains was studied theoretically [25] predicting most of them to be antiferromagnetic semiconductors with the exception of metallic behavior for Mn-PC.

But to fully use the capacity of magnetic organometallic polymer chains for spintronics applications, a high value of the magnetic anisotropy energy (MAE) would be crucial. It may

stabilize a potential magnetic ordering and opens the possibility of molecular magnetic information storage. Magnetic monolayers of organometallic polymers could be interesting for two different classes of applications. A high MAE of single magnetic units of molecular size qualifies them as candidates for magnetic molecular memory where the best examples are found at present in rare earth ions packed into sandwich complexes [26] or C_{80} molecules [27]. Alternatively, if it would be possible to obtain monolayers or thin films which are ferromagnetically ordered, they also could serve in magnetic tunnel junctions where a large magnetic anisotropy barrier is useful for spintronic devices [28].

For that reason, 4d and 5d TM materials become interesting, in the form of atomic chains [29,30] or as Rh-Phthalocyanine nanojunctions [31]. Since the amount of spin-orbit coupling increases with the atomic number, these 4d and 5d TM materials have usually higher MAE (up to the order of several tens of meV) than the corresponding 3d series. For that reason, we investigate here selected 4d and 5d TM-ZQ polymers and can indeed confirm high MAE's for some of them. Especially remarkable are the significant MAE's for Rh-ZQ and Re-ZQ. Furthermore, we study in detail the structural, electronic, and magnetic properties of 4d and 5d TM-ZQ polymers.

METHOD

We used the Vienna Ab-initio Simulation Package (VASP) [32] at the level of the spin-polarized generalized-gradient approximation in the form of the Perdew and Wang PW91 functional [33,34]. It is well known that the standard Density Functional Theory (DFT) has difficulties to describe correctly the electronic structure of transition metal compounds, especially for 3d but to a lesser amount also for 4d and 5d transition metal ions. For that reason, we apply here the Spin polarized Generalized-Gradient Approximation with Hubbard term U (SGGA+U). The SGGA+U corrections were introduced by Liechtenstein et al. [35] Unfortunately, the value of U is not very well known. We take in the following $U = 5$ eV and

an exchange energy of $J = 0.90$ eV as it was justified for Fe-ZQ. That has to be understood as an upper bound for the U value since that parameter is certainly reduced in 4d and 5d systems with respect to 3d compounds. The necessity of the SGGA + U method for metal–organic compounds with transition metal ions is proven by many examples such as TM-TCNB [36,37] or TM-TCNQ [38], TM-ZQ [25] where TM is a transition metal. We also perform calculations without the Hubbard U correction, i.e. we apply the SGGA method, to compensate the uncertain knowledge of the U parameter. In such a way we can justify the calculated MAE values and estimate their uncertainty.

The interaction between the valence electrons and ionic cores was described within the framework of the projector augmented wave (PAW) method [39–42]. The electronic wave functions were expanded in plane waves with a kinetic energy cutoff of 480 eV, the polymers were relaxed until the residual forces were below 10^{-6} eV/Å and the convergence criteria for the energy deviations was 10^{-7} eV. The relaxation of all atomic positions guaranties the structural stability of the polymers. The Gaussian smearing method was used in these calculations and a width of 0.01 eV was adopted. The Brillouin zone was determined by a set of $8 \times 1 \times 1$ k-points in the unit cell using the Monkhorst-Pack points [43]. The geometry optimization was performed by relaxing all atomic coordinates for a fixed lattice constant (see Figure 1). The geometry optimization was performed without spin-orbit coupling. But a relativistic calculation with spin-orbit coupling was necessary to calculate the orbital moments and the MAE's.

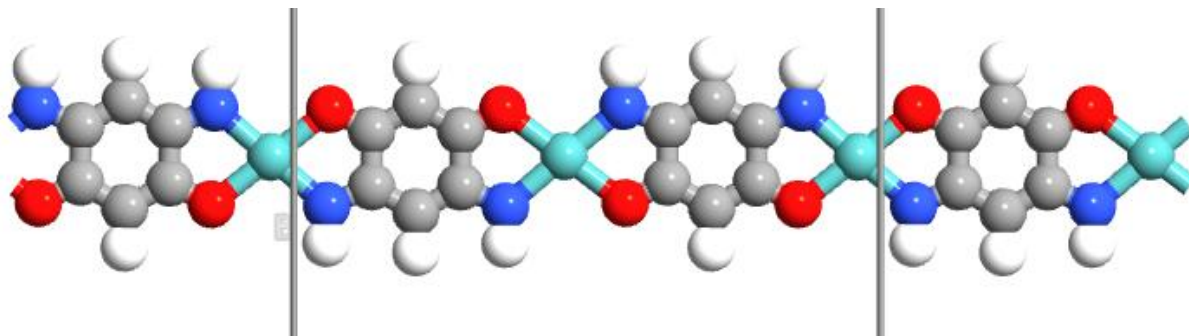


Figure 1: Geometrical structure of a free-standing polymer chain of TM atoms and zwitterionic Quinone (C: grey, O: red, N: blue, H: white, and TM: light blue).

RESULTS AND DISCUSSION

A. Electronic and magnetic properties of TM-ZQ polymers

We first report the results of the SGGA+U calculation without spin-orbit (SO) coupling and summarize the results in Table 1. The valence of the TM can be deduced from the local occupation numbers and was found to be +2 for all investigated polymers. Also, all TM-ZQ compounds were magnetic with the exception of the two TM's with d^8 configuration, Pd-ZQ and Pt-ZQ, which have a nonmagnetic ground-state. Two possible spin states, namely a high-spin ($S = 2$) solution and an intermediate spin ($S = 1$) solution, were found for Mo-ZQ by the variation of the lattice constant. That is visible in two different curves of total energy vs. lattice constant for Mo-ZQ which are given in the supplemental material (Fig. S1) for all investigated materials. The energetically lowest state for Mo-ZQ is the high-spin state ($S = 2$) but that is an exception since all other investigated 4d and 5d TM-ZQ polymers realize the intermediate or no spin state in difference to the 3d series of TM-ZQ [25]. The optimized lattice constants for TM-ZQ range from 15.74 to 16.30 Å, corresponding to the trend of the atomic radii of the metal which generally decrease with the atomic number in the 4d or 5d series. The same trend is also visible in the interatomic distances $d_{\text{TM-N}}$ and d_{TM} as shown in Table 1.

Table 1: Distance between the central TM Atoms and the N Atoms (d_{TM-N} , in Å), Distance between the central TM Atoms and the O Atoms (d_{TM-O} , in Å), Lattice constant (a , in Å), Exchange Energies ($E_{ex}=E_{FM}-E_{AFM}$ per TM atom, in meV), Total Magnetic Moments (M per TM atom, 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 TM atoms (M_m per TM atom, in μ_B), Energy Band Gaps (spin up (E_a) and spin down (E_b), in eV), Total Energy gaps (E_g , in eV), for 1D TM-quinone polymer in the SGGA+U method for the TM-ZQ polymer.

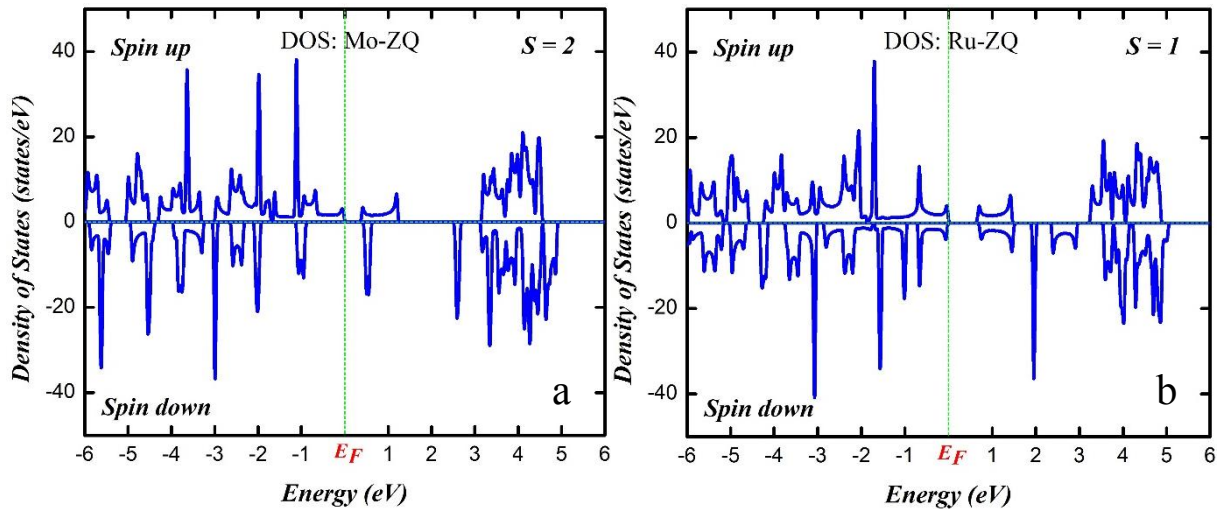
	Mo	Ru	Rh	Pd	Ag	Re	Ir	Pt
	$4d^4$	$4d^6$	$4d^7$	$4d^8$	$4d^9$	$5d^5$	$5d^7$	$5d^8$
d_{TM-N}	2.18	2.06	2.01	2.00	2.10	2.06	1.97	1.99
d_{TM-O}	2.15	2.06	2.03	2.03	2.20	2.03	1.99	2.02
a (Å)	16.48	16.03	15.797	15.74	16.3	16.11	15.75	15.74
E_{ex}	48.950	4.663	19.229	-	14.546	-3.463	-3.468	-
M	4	2	1	0	1	3	1	0
M_d	3.357	1.725	0.863	0	0.473	3.084	1.125	0
M_m	3.493	1.816	0.873	0	0.471	3.250	1.143	0
E_a	0.35	0.63	0.85	0.76	1.2	0.35	0.41	0.41
E_b	1.2	0.69	0.94	0.76	0.35	1.07	0.31	0.41
E_g (FM)	0.43	0.63	0.85	0.76	0.35	0.08	0.05	0.41
E_g (AFM)	0.88	0.69	1	-	0.56	0.37	0.00	-

Based on the most stable structures of TM-ZQ, we systematically study their magnetic and electronic properties. The corresponding magnetic moments are listed in Table 1, as well as the exchange energy ($E_{ex} = E_{FM} - E_{AFM}$) which is the difference between the antiferromagnetic and ferromagnetic states. The two polymers (Re, Ir)-ZQ have ferromagnetic ground states (E_{ex} is negative), with an energy difference between the FM and AFM states of -3.463 and -3.468 meV/TM respectively. Further, the polymers (Mo, Ru, Rh, Ag)-ZQ have an antiferromagnetic ground states (E_{ex} is positive) which is more stable than the FM state by an energy difference of 48.950, 4.663, 19.229 and 14.546 meV per TM atom, respectively, as summarized in Table 1. We also give in Table 1 the band gap values of all compounds which are all direct band gap semiconductors within the SGGA+U density functional. The band gaps of Re-ZQ and Ir-ZQ polymers are very small (0.08 and 0.05 eV respectively). The physical parameters which were calculated by SGGA+U are confirmed by the SGGA method (without U, see Table S1 in the Supplementary material). That is especially true for all structural parameters (not all are shown). Also, the exchange energies E_{ex} have the same sign and the

same order of magnitude without or with U for all investigated compounds. As it can be expected, the modulus of E_{ex} is larger in SGGA than in SGGA+U with the only exception Rh-ZQ. Different are the band gaps which are reduced in SGGA for the Ru-, Pd-, Re- and Pt-ZQ polymers and even absent (metallic behaviour) for the Mo-, Rh- and Ir-ZQ polymers while half-metallic for the Ag-ZQ polymer (see Table S1).

B. Density of states

In order to understand in more detail the magnetic properties of TM-ZQ polymers, we plot the density of states (DOS) and the atomic site projected density of state (PDOS) in Figures 2 and 3. The density of states is an important physical quantity that is very often calculated in solid state physics. We now analyze the electronic structure, i.e., the total densities of states (DOS), of the ground state solution for the TM-ZQ polymer network more in detail to understand the behaviors of TM-ZQ polymers. The total DOS for these polymers are shown in Figure 2 and reveal that the spin-up and spin down states are not symmetrical near the Fermi level for magnetic systems. While for Pt- and Pd-ZQ, they are symmetrical, these two polymers are therefore non-magnetic materials. It is remarkable that all the studied polymers are semiconductors.



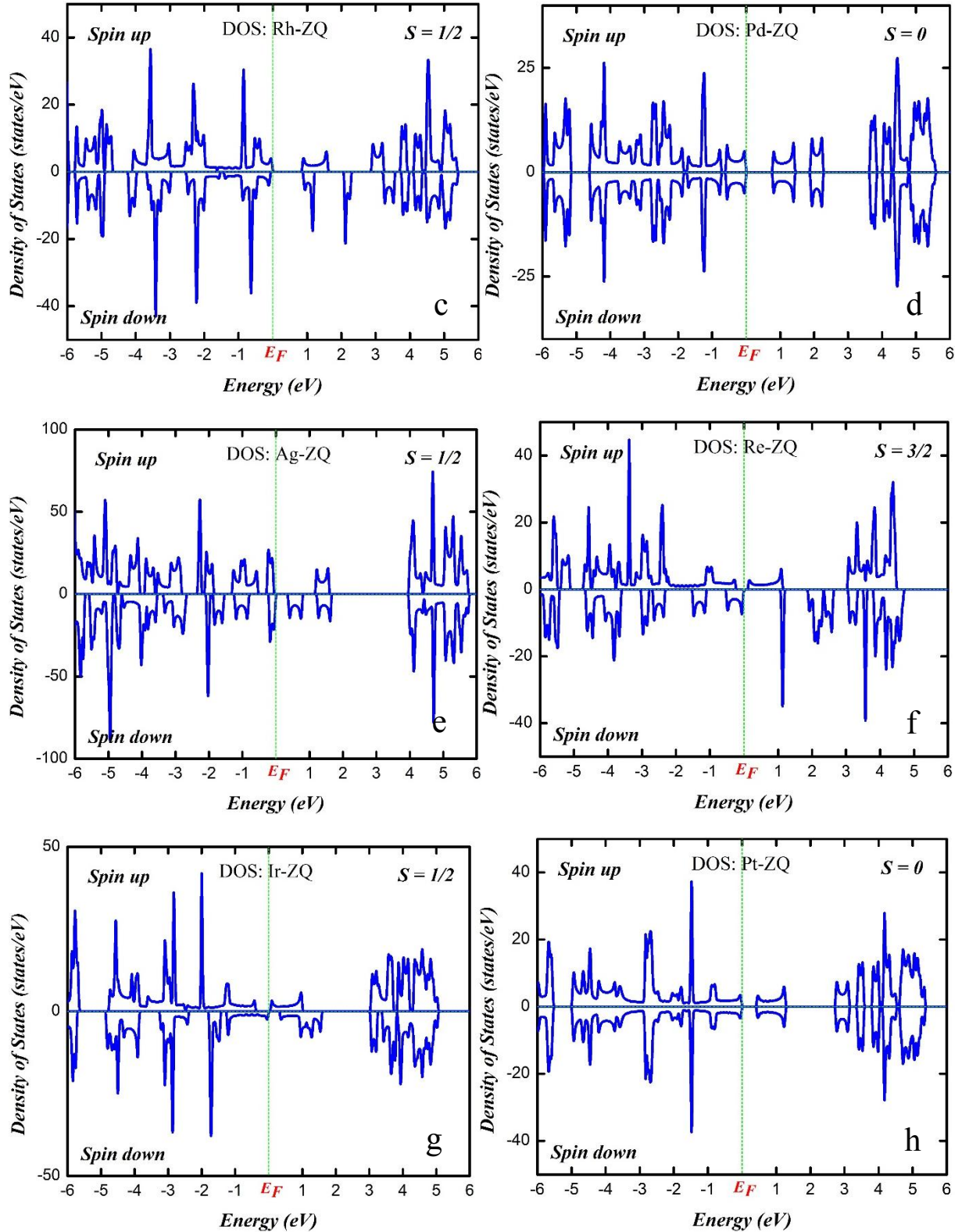
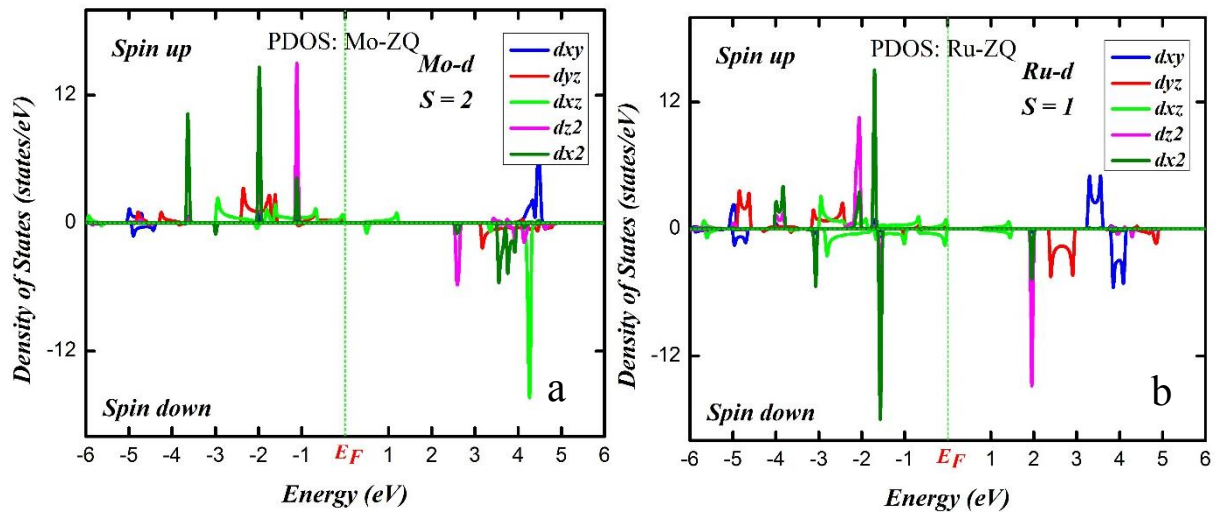


Figure 2: Total DOS of the 1D transition-metal (TM) atoms zwitterionic quinoidal polymer with the PAW-SGGA+U method, when TM is (a) Mo (b) Ru, (c) Rh, (d) Pd, (e) Ag, (f) Re, (g) Ir, (h) Pt.

To analyse further the magnetic properties, we plot the projected density of states (PDOS) of the d orbitals of the TM atom. For the TM^{+2} configurations of TM-ZQ, the d_{xy} orbital is totally

empty because it is the highest in energy and located very far from the other orbitals (see Figure 3). That is the reason for the nonmagnetic state of the d^8 configuration and the intermediate spin state in most 4d and 5d TM-ZQ polymer. For the Mo-ZQ polymer, we can observe that the spin up d_{yz} , d_{xz} , d_{z^2} and d_{x^2} orbitals are all occupied, and that the five spin down d orbitals are empty, while for the Ru atom the two spin down d_{xz} and d_{x^2} orbitals are occupied. Therefore, the total magnetic moments of the Mo and Ru atom become 4 and $2 \mu_B$ respectively. As for the Rh-ZQ polymer, the spin up d_{xz} , d_{yz} , d_{z^2} , and d_{x^2} orbitals are almost occupied, as well as the d_{xz} , d_{z^2} , and d_{x^2} spin down orbitals, resulting in an effective spin $\frac{1}{2}$ (total magnetic moment of $1\mu_B$). All the d orbitals of the Ag atom are occupied, while only the spin down d_{xy} orbital is empty. The Ir ion is isoelectronic to the Rh ion and has a similar electronic configuration. Therefore, also the total magnetic moments of the Ag-ZQ and Ir-ZQ polymers become $1\mu_B$. Moreover, for the Re-ZQ polymer, the spin up d_{xy} orbital is completely empty. Therefore, the total magnetic moment of Re-ZQ is $3 \mu_B$. For Pt- and Pd-ZQ, the spin-up and spin down states are symmetrical near the Fermi level since the system constitute non-magnetic materials.



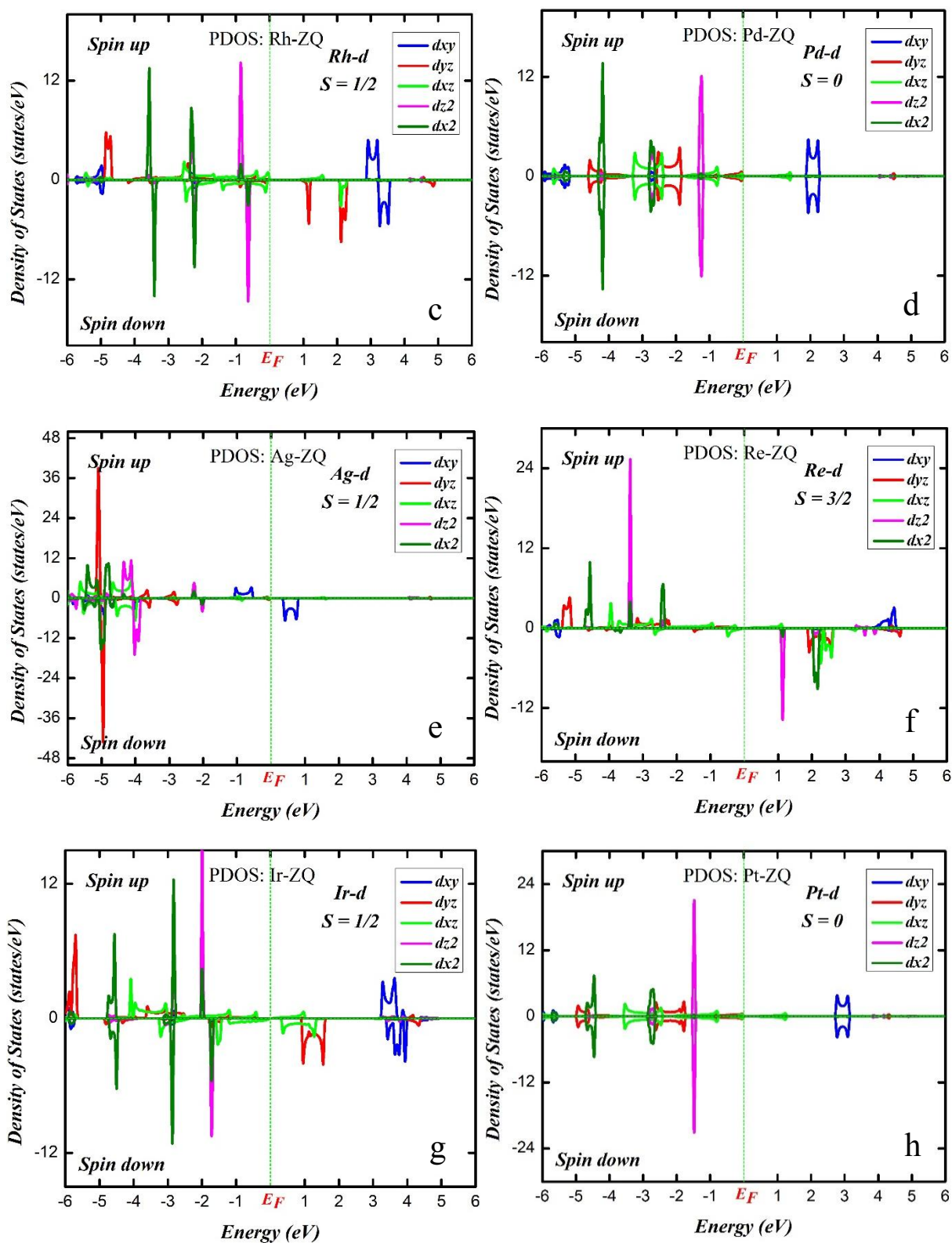


Figure 3: Projected DOS of the d orbitals on the TM atoms in the 1D zwitterionic quinoidal polymer with TM atoms with the PAW-SGGA+ U method.

C. Magnetic anisotropy energy

The electronic structures of TM-ZQ are completed by SOC calculations. The initial directions of magnetization are along the x, y, z orientations, where the chains run along the x-direction and the z-axis is perpendicular to the plan of the polymers. For the TM-ZQ polymer, three different directions of magnetization are considered in the SOC calculations. The energy difference for the magnetizations lying in the x- and z-directions defines the magnetic anisotropy energy (MAE) which for the magnetic chains with Mo, Ru, Rh, Re and Ir takes rather important values of 5.37, 4.80, 143.25, 93.45 and 64.56 meV/atom (see Table 2). We calculated the FM and AFM chains at zero temperature. It is known that the isotropic Heisenberg model allows no long-range order at any finite temperature in one or two dimensions. However, a large MAE can stabilize long-range magnetic order in low dimensions. Furthermore, a large MAE would lead to interesting magnetic properties even above a hypothetical long-range ordering temperature. The local magnetic centers react then independently of each other to a magnetic field. But for such large MAE's as reported here, there might exist a magnetic blocking temperature and magnetic hysteresis due to the large energy barriers between different directions of the local magnetic moments. As summarized in Table 2, the easy axis of TM-ZQ follows the direction of the lowest energy. In addition to the local spin moments M_d , Table 2 shows also the atomic orbital magnetic moments M_L . The SOC generally reduces the local spin moments by a few percent in 4d and 5d but induces a large orbital magnetic moment in the polymers Ru-, Rh-, and Ir-ZQ; see Table 2. We verified the large MAE's calculated with SGGA+U+SO by fully relativistic SGGA calculations, or SGGA+SO (see Table S2 in the supplementary material). In general, the MAE's without the U correction confirm the results summarized in Table 2. First of all, they confirm the easy axis behaviour of most compounds. The only exception is Ag-ZQ for which the MAE changes sign between SGGA+SO and SGGA+U+SO, but the magnitude of MAE is very small in that

case since we have just one hole in the d shell. Interesting are the large MAE's for Re-ZQ (108.1 meV/atom) and Rh-ZQ (41.8 meV/atom) confirming the large values of Table 2 where the U correction is included. The MAE of Ir-ZQ reduces from 64.6 meV/atom (with U) to 11.3 meV/atom (without U) but even 11.3 meV/atom is a rather large MAE for d ions. For Mo-ZQ and Ru-ZQ, the SGGA+SO values are even larger than in SGGA+U+SO.

The two organo-metallic polymers Re-ZQ and Ir-ZQ have a ferromagnetic nearest neighbour exchange, a very small gap and a large MAE value. Like Fe-ZQ they could probably be deposited on metallic surfaces and build well-ordered monolayers. If they also would show ferromagnetic long range order they could eventually serve in magnetic tunnel junctions. Taking similar distances as in Fe-ZQ on Au(110) [9] one can translate a MAE of 65 meV (for Ir-ZQ) per magnetic ion into a surface (or interface) anisotropy K_i of about 25 mJ/m² which would be an extremely high value.

It is instructive to compare with the MAE's of the 3d series TM-ZQ [25]. There, indeed, all MAE's are smaller than 6 meV/atom with the only exception V-ZQ which reaches an easy plane anisotropy of about -22 meV/atom comparable to the values reported above for the 4d/5d series. But the reason is completely different: in V-ZQ there are two 3d orbitals ($3d_{xz}$ and $3d_{yz}$) which are nearly degenerate and partially filled, leading to a large orbital moment and a large MAE. Therefore, a high MAE is possible despite a small SOC coupling constant for V. A similar degeneration among the d orbitals was not observed in the 4d/5d series of TM-ZQ.

Table 2: Magnetic anisotropy energy (**MAE**, per TM atom in meV), total magnetic moments \mathbf{M}_i , local magnetic moments of the *d* orbitals at the TM site $\mathbf{M}_d(\mathbf{i})$ and orbital moments ($\mathbf{M}_L(\mathbf{i})$ per TM atom in μ_B) for selected 1D TM-ZQ polymers of the 4d and 5d series. The data result from SGGA+U calculations including SO coupling with the magnetic moments directed towards the $\mathbf{i}=\{\mathbf{x},\mathbf{y},\mathbf{z}\}$ direction.

	Mo	Ru	Rh	Pd	Ag	Re	Ir	Pt
MAE ($\mathbf{E}_x-\mathbf{E}_z$)	5.37	4.80	143.25	-	-0.47	93.45	64.56	-
\mathbf{M}_x	3.99	1.63	0.56	-	0.99	2.74	0.78	-
\mathbf{M}_y	3.99	1.92	0.32	-	0.99	2.70	0.47	-
\mathbf{M}_z	3.99	1.73	0.34	-	1	2.63	0.47	-
$\mathbf{M}_d(\mathbf{x})$	3.348	1.411	0.470	-	0.470	2.883	0.976	-
$\mathbf{M}_d(\mathbf{y})$	3.344	1.651	0.264	-	0.470	2.809	0.636	-
$\mathbf{M}_d(\mathbf{z})$	3.343	1.496	0.285	-	0.473	2.779	0.410	-
$\mathbf{M}_L(\mathbf{x})$	-0.056	0.425	0.632	-	0.036	0.047	1.144	-
$\mathbf{M}_L(\mathbf{y})$	-0.056	0.600	0.217	-	0.032	0.024	0.340	-
$\mathbf{M}_L(\mathbf{z})$	-0.082	0.099	0.143	-	0.114	-0.052	0.093	-

CONCLUSIONS

We investigated systematically the structural, electronic, and magnetic properties of organometallic polymers which are built of zwitterion quinone (ZQ) molecules and 4d/5d transition metals. We used fully relativistic SGGA and SGGA+U calculations and found several compounds with surprisingly high MAE. Especially remarkable is the easy axis behaviour of Rh-ZQ and Re-ZQ with MAE's of 143.25 and 93.45 meV/atom in SGGA+U+SOC, respectively (41.28 and 108.1 meV/atom without U correction). Such high values can lead to high blocking temperatures below which one can expect a magnetic hysteresis. It would be very interesting to verify our prediction experimentally. And it could be the basis to use these materials in future devices of magnetic molecular memory.

There is great variation of magnetic properties in the investigated material family: (Re, Ir)-ZQ polymers are FMs, (Mo, Ru, Rh, Ag)-ZQ polymers are AFM, and non-magnetic are Pt-ZQ and Pd-ZQ polymers. We also analyse the electronic structure of all compounds, and find magnetic compounds, which combine local magnetic moments with wide bands characteristic to conjugated polymer compounds. There is a strong variation of MAE within the 4d and 5d

series. Most variations are good understood but not all. They demand further investigations. There is a certain influence of the U parameter on the electronic and magnetic properties, the gaps are reduced, and some insulating compounds become metals. But the MAE's do not strongly depend on U (with the exception of Ir-ZQ). So, the prediction of a significant MAE for Rh-ZQ and Re-ZQ makes them highly interesting candidate materials for practical spintronics applications.

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Conflict of interest

The authors declare that they have no conflict of interest.

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