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# First-principle study of metal-organic frameworks of the *4d* and *5d* transition metal series with Phthalocyanine and Tetracyanobenzene

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## Abstract

In the present work, the structural, electronic and magnetic properties of planar frameworks built of Tetracyanobenzene (TCNB) and Phthalocyanine (Pc) with transition metals (TM) of the *4d* and *5d* series (TM = Mo, Ru, Rh, Pd, Ag, Cd, Re, Ir, Pt, and Hg) have been investigated by density functional theory (DFT) including Hubbard-like Coulomb correction terms. In that series, ferromagnetism has been found for Ru-Pc, Re-Pc, Mo-TCNB and Re-TCNB which all are also at least half-metallic with the exception of Mo-TCNB being insulating. The ferromagnetic state is very stable for Mo-TCNB, Re-TCNB, and especially Ru-Pc with an energy difference between ferromagnetic and antiferromagnetic spin arrangements surpassing 100 meV per magnetic ion for Ru-Pc. The prediction of ferromagnetic and half-metallic metal-organic frameworks provides new insight into Pc/TCNB-based nanostructures with potential applications in spintronics.

**Keywords:** Density functional theory; Solid state physics; Spintronics; Electronic structure; Magnetism.

## 1. Introduction

In recent years, great research efforts were devoted to realize long-range magnetic order in low-dimensional materials [1-8, 17]. That research subject is not only fascinating from a fundamental point of view, but could lead to interesting applications in spintronics. Therefore, a half-metallic ferromagnetic material would allow spin-polarized electronic transport and could be used as a spin-filter element. Other applications are magnetic memory elements. Materials with such a perspective are for instance self-organized metal-organic monolayers. Hence, Fe-TCNB and Mn-TCNB networks on Au- and Ag-substrates had been synthesized and a ferromagnetic coupling between the magnetic centers was measured [5, 6] and theoretically confirmed [6, 8]. Mn-TCNB is a precursor material for Mn-Pc which can be obtained by on-surface polymerization [4]. Here, we extend a previous systematic study for

the  $3d$  series [7] of TM-TCNB and TM-Pc to the  $4d$  and  $5d$  series. Our theoretical approach used in the present research has an experimental confirmation, because it is the exact same method used in a previous work [6-8]. We underline that this manuscript is a research incremental from the one described in the cited articles. To be specific, we investigate the following TM elements: Mo, Ru, Rh, Pd, Ag, Cd, Re, Ir, Pt, and Hg. The aim is to find viable candidates which we would then propose to be synthesized. We are not aware of such a systematic study in the scientific literature.

We present an ab-initio and analytical study on the structural, electronic and magnetic properties of free standing TM-TCNB and TM-Pc networks with TM from the  $4d$  and  $5d$  series. We choose density functional theory (DFT) within the spin polarized generalized gradient approximation with Hubbard-like Coulomb correlation terms, i.e. the SGGA+ $U$  method. As will be outlined below, we find several half-metallic and ferromagnetic materials which could be highly relevant in the field of spintronics.

## 2. Theoretical Method

Our present calculations were performed using DFT within the generalized gradient approximation in the form proposed by Perdew and Wang (PW91) [9, 10] and the interpolation formula of Vosko, Wilk, and Nusair (VWN) [11] as implemented in the Vienna Ab-initio Simulation Package (VASP) [12]. We utilized the projected augmented wave (PAW) [13, 14] method and the wave function was expanded in plane waves using a 400 eV energy cut-off. To take into account electron correlation effects, we have included Hubbard-like Coulomb correction terms in the d shell of the TM-TCNB and TM-Pc materials in the form of the SGGA+ $U$  method proposed by Liechtenstein et al. [15]. We did choose the same values of  $U = 5$  eV and  $J = 0.90$  eV for all materials [6-8]. The variation of  $U$  term in the region of  $\pm 2$  eV does not change the results of this paper. We used a Monkhorst-Pack  $6 \times 6 \times 1$  grid of k-points [16].

## 3. Results and Discussion

### 3.1. Series of TM-Pc polymers

Let us first present the results for the TM-Pc polymer series which has a considerable higher binding energy than the corresponding TM-TCNB one (see Table 1, where all compounds are listed for which a solution had been found). The two-dimensional ( $2D$ ) structure of TM-Pc is shown in Fig. 1 on the right-hand side and can be obtained from the TM-TCNB framework by rotating the benzene rings by 30 degrees and establishing new C-N bonds by on-surface

polymerization reaction. For each network, the atomic positions and the lattice constants are optimized.

In Table 1, the magnetic moments for the ground state solutions are shown. Sometimes, several magnetic states with different lattice constants are possible as for instance for Ru-Pc, Re-Pc, and Mo-Pc. In these cases, only the solution with lowest energies are indicated in Table 1. The Ru-Pc polymer has two solutions: a fundamental state (IS) with a total magnetic moment  $M = 2 \mu_B$  and a lattice constant about 10.77 Å. The other solution is a non-magnetic solution (LS) with a lattice constant of 10.73 Å and about 1.99 Å Ru-N distance. In this situation, the calculated energy difference  $\Delta E$  between the two possible configurations is 1.36 eV.

The Re-Pc monolayer has two possible states of spin with a difference in energy of 0.95 eV: a stable state  $S = 3/2$  ( $a = 10.79$  Å and Re-N = 2.03 Å) and an excited state  $S = 1/2$  ( $M = 1\mu_B$ ,  $a = 10.75$  Å and Re-N = 2.00 Å). To finish this part, the Mo-Pc polymer has three possible solutions: the most stable state (HS) with  $S = 2$ , and two meta-stable states  $S = 1$  (IS,  $M = 2.00 \mu_B$ ) and  $S = 0$  (LS,  $M = 0 \mu_B$ ). The energy difference  $\Delta E_1$  ( $E_{S=1} - E_{S=2}$ ) and  $\Delta E_2$  ( $E_{S=0} - E_{S=2}$ ) are respectively 461.41 meV and 560.64 meV. These three states have the same lattice constant and the Mo-N distance, which are respectively 10.85 Å and 2.07 Å. We found that Hg-Pc polymer has the largest lattice constant and the Hg-N distance in the whole series of transition metals  $4d$  and  $5d$  described in Table 1. Several materials are non-magnetic (NM), namely Pd-Pc, Cd-Pc, Pt-Pc, and Hg-Pc. The three structures Rh-Pc, Ag-Pc and Ir-Pc have a total magnetic moment about  $M = 1 \mu_B$  and their lattice constants are respectively 10.76 Å, 10.82 Å and 10.75 Å. The local magnetic moments at the central TM atom of all frameworks are illustrated in Table 1.

For all TM-Pc structures, the lattice constant decreases in going from  $d^4$  to  $d^8$  and increases again at the end of the series. That is true for the  $4d$  and the  $5d$  series, as well for TM-Pc as for TM-TCNB. So, for the TM-Pc structures, the lattice constants are in an interval of 10.72 Å to 10.92 Å while the TM-N distances varies from 1.99 Å to 2.13 Å. For TM-Pc, the local and total magnetic moments are very close. From Rh to Pd (from Ir to Pt), the local magnetic moments are always low spin (LS). The polymers of Rh-Pc, Pd-Pc, Ag-Pc, Cd-Pc, Ir-Pc, Pt-Pc and Hg-Pc have an insulating character with a large energy band gap. On the other hand, Mo-Pc, Ru-Pc and Re-Pc networks have a half-metallic behavior (metallic in the minority

spin direction and insulating in the majority spin direction). The magnetic exchange couplings will be discussed later on in Section 3.3.

### 3.2. Series of the TM-TCNB metal-organic networks

We treated the 2D arrays TM-TCNB based on a metal-ligand bond (with TM = Mo, Ru, Pd, Cd, Re, Pt and Hg) of the 4d and 5d series. Indeed, we have not found solutions for Rh-TCNB, Ag-TCNB and Ir-TCNB, related to several stability structure factors.

Our theoretical results obtained via SGGGA+ $U$  approach are mentioned in Table 1. The frameworks of Pd-TCNB, Cd-TCNB, Pt-TCNB and Hg-TCNB are non-magnetic, have a local spin  $S_d$  equal to 0 ( $S_d = S$ ) and their lattice constants are respectively 12.00 Å, 12.34 Å, 11.88 Å and 12.36 Å. The fundamental state of the 2D structure of Mo-TCNB has a lattice constant of 12.24 Å, and the local magnetic moment of the Mo site is  $3.27 \mu_B$ . The Mo-TCNB has another excited state ( $M = 0.05 \mu_B$ ,  $M_d = 1.64 \mu_B$ ) and the lattice constant and the Mo-N distance are respectively 12.22 Å and 2.13 Å. This value of 426.94 meV is the energy difference between the two possible states in the case of Mo-TCNB network. The metal-organic network Ru-TCNB has a single state (IS) with a local magnetic moment of  $1.45 \mu_B$  and a lattice constant of 12.00 Å. The Ru-N distance associated with this state is 2.01 Å.

As already mentioned, going from Re to Pt, the TM-N distances and the lattice constants decrease whereas for TM = Hg, these two parameters increase. For TM = Mo, Ru (and Re), the local moment are HS, and IS respectively.

The magnetic monolayers of Mo-TCNB, Ru-TCNB and Re-TCNB have an incomplete screening effect of the local magnetic moment (the total and local magnetic moments are not equal). The local magnetic moment of the central atom TM is screened by the electrons of the organic ligands (with a spin anti-parallel to the local spin) as it was explained before for Mn-TCNB and Fe-TCNB [8, 6]. Such an incomplete screening effect does not occur for the TM-Pc structures. The metal-organic networks of Pd-TCNB, Cd-TCNB, Re-TCNB, Pt-TCNB and Hg-TCNB have a metallic character in both directions of spin. In contrast, Mo-TCNB and Ru-TCNB materials have an insulating behavior with a high energy band gap  $E_\alpha$ . In the following paragraph, we treat the exchange energies for all magnetic systems.

### 3.3. Exchange energies for both 2D systems

We recall briefly some basic concepts for the determination of the exchange energy for our structures using the SGGA+ $U$  approximation. We employed a supercell ( $2 \times 2$ ) which contains 4 TM ions and calculated the total energies for ferromagnetic (FM) and antiferromagnetic (AFM) arrangement of such a supercell,  $E_{\text{FM}}$  and  $E_{\text{AFM}}$ , respectively. The exchange energy  $E_{\text{ex}}$  is the difference between the total energies for FM and AFM order per magnetic ion, i.e.  $E_{\text{ex}} = (E_{\text{AFM}} - E_{\text{FM}})/4$ . For  $E_{\text{ex}} > 0$ , the ground state (GS) is FM, otherwise ( $E_{\text{ex}} < 0$ ), the GS is AFM.

The polymers of Mo-Pc, Rh-Pc, Ag-Pc and Ir-Pc have an antiferromagnetic coupling with a low exchange energy. In contrast, the half-metallic magnetic structures of Ru-Pc and Re-Pc have a ferromagnetic (FM) ground state. The Ru-Pc material has a high exchange energy in the order of 153.5 meV. It represents a half-metallic electronic properties and ferromagnetic long-range order. The experimental synthesis of this polymer will prove useful in various applications in the fields of nanoelectronics and spintronics.

From Table 1, the 2D magnetic TM-TCNB materials are FM. The 2D metallic magnetic material Re-TCNB has a high exchange energy with 75 meV, which will play a major role for future development in spintronics applications to store and process information. Furthermore, the Mo-TCNB system has an insulating character and an exchange energy around of 71.8 meV.

In order to resume our most interesting theoretical results, the Fig. 2 describes the total magnetic moments as a function of the lattice parameters of the two monolayers (TM-Pc and TM-TCNB). The nature of the magnetic coupling is specified in the same figure. The structures of Rh-Pc, Ag-Pc and Ir-Pc have the same total magnetic moment ( $1\mu_{\text{B}}$ ) and represent the same ground state (AFM).

## 4. Conclusions

In summary, we have performed a systematic, theoretical study of the 4d and 5d TM series of 2D metal-organic networks TM-Pc and TM-TCNB using the SGGA+ $U$  method. We found several favorable candidate materials for ferromagnetic order and high exchange energy being the total energy difference between FM and AFM order per magnetic ion. Especially interesting are the predictions of the FM half-metallic state in Ru-Pc with  $E_{\text{ex}} = 153.5$  meV, the FM metallic state in Re-TCNB with  $E_{\text{ex}} = 75$  meV and of the FM insulator Mo-TCNB

with  $E_{\text{ex}} = 71.8$  meV. Our results unveil that these 2D metal-organic monolayers have an important impact because they have conductive and magnetic properties. This study can provide an efficient reference for the design and the synthesis of these magnetic materials. These remarkable systems could be a key enabler for promising applications in spintronics and molecular electronics.

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### **Competing financial interests**

The authors declare no competing financial interests.

### **Appendix A. Supplementary data**

Additional material comprising full details of the total density of states (DOS) and Projected DOS of TM-Pc and TM-TCNB networks.

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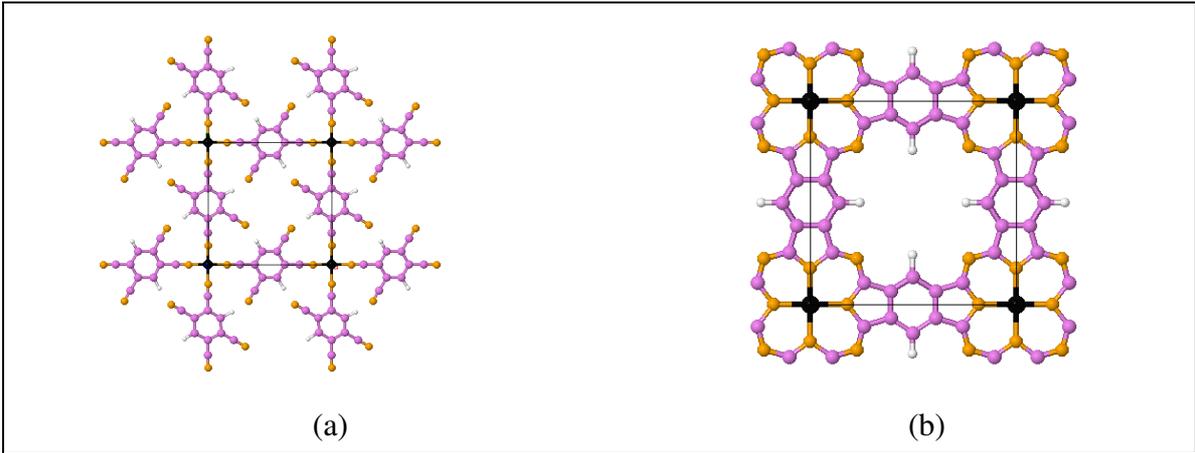


Figure 1. Structures of TM-TCNB metal-organic networks (a) and 2D TM-Pc polymers (b). The TM, N, C, and H atoms are highlighted in black, orange, violet, and white respectively.

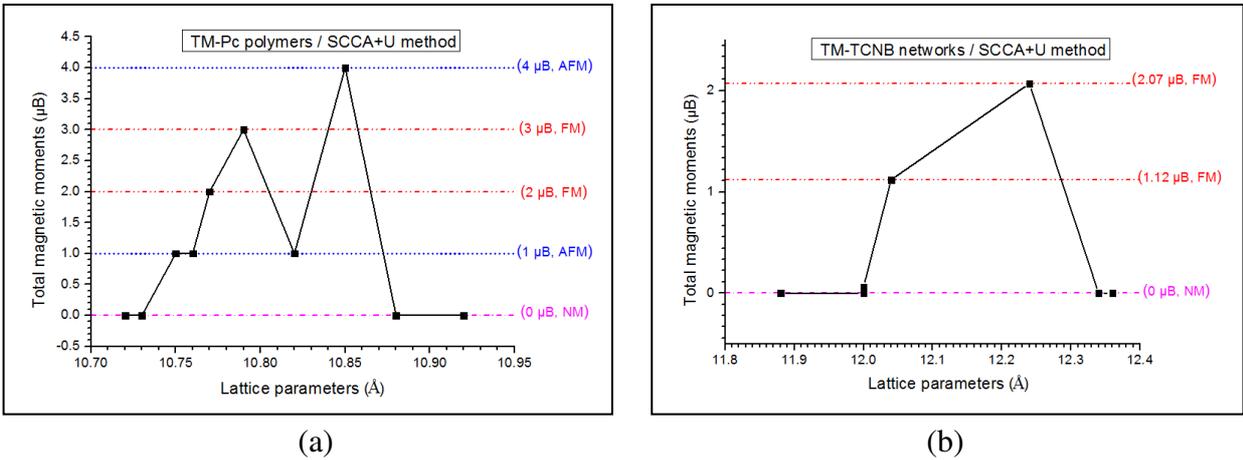


Figure 2. Total magnetic moments ( $\mu_B$ ) as a function of lattice parameters ( $\text{\AA}$ ) for TM-Pc polymers (a) and TM-TCNB materials (b) via SGGA+U approach. The horizontal lines (pink, red, and blue) describe the ground state of structures.

Table 1. Lattice constants  $a$ , TM-N distances, total magnetic moments  $M$  per unit cell, local magnetic moments  $M_d$  at TM site, energy  $E$ , energy gap ( $E_\alpha$ : spin-up,  $E_\beta$ : spin-down), exchange energy  $E_{ex}$  per magnetic ion of magnetic materials using SGGA+ $U$  method.

System	TM <sup>2+</sup> ( $d^n$ )	$a$ (Å)	TM-N (Å)	$M$ ( $\mu_B$ )	$M_d$ ( $\mu_B$ )	$E$ (eV)	( $E_\alpha, E_\beta$ )/HM/M (eV)	$E_{ex}$ (meV)	Type	
TM-Pc	Mo ( $d^4$ )	10.85	2.07	4.00	3.20	0	H-M, $E_\alpha = 0.6842$	-8.5	AFM	
	Ru ( $d^6$ )	10.77	2.02	2.00	1.71	0	H-M, $E_\alpha = 0.4874$	153.5	FM	
	Rh ( $d^7$ )	10.76	2.01	1.00	0.84	–	$E_\alpha = 0.4272,$ $E_\beta = 0.4336$	-0.002	AFM	
	Pd ( $d^8$ )	10.73	2.00	0	0	0	$E_\alpha = E_\beta = 0.4065$	–	NM	
	Ag ( $d^9$ )	10.82	2.06	1.00	0.49	–	$E_\alpha = 0.3560,$ $E_\beta = 0.3880$	-1.4	AFM	
	Cd ( $d^{10}$ )	10.88	2.10	0	0	0	$E_\alpha = E_\beta = 0.3520$	–	NM	
	Re ( $d^5$ )	10.79	2.03	3.00	3.01	0	H-M, $E_\alpha = 0.4357$	7.5	FM	
	Ir ( $d^7$ )	10.75	2.01	1.00	0.84	–	$E_\alpha = 0.4754,$ $E_\beta = 0.4834$	-0.004	AFM	
	Pt ( $d^8$ )	10.72	1.99	0	0	0	$E_\alpha = E_\beta = 0.4522$	–	NM	
	Hg ( $d^{10}$ )	10.92	2.13	0	0	0	$E_\alpha = E_\beta = 0.3856$	–	NM	
TM-TCNB	Mo ( $d^4$ )	12.24	2.14	2.07	3.27	6.58	$E_\alpha = 2.0036,$ $E_\beta = 0.8360$	71.8	FM	
	Ru ( $d^6$ )	12.00	2.01	0.06	1.45	7.28	$E_\alpha = 1.8495,$ $E_\beta = 0.6017$	<sup>b</sup>		
	<sup>a</sup> Rh ( $d^7$ )	–								
	Pd ( $d^8$ )	12.00	2.01	0	0	8.72	M	–	NM	
	<sup>a</sup> Ag ( $d^9$ )	–								
	Cd ( $d^{10}$ )	12.34	2.11	0	0	6.58	M	–	NM	
	Re ( $d^5$ )	12.04	2.02	1.12	2.15	7.02	M	75	FM	
	<sup>a</sup> Ir ( $d^7$ )	–								
	Pt ( $d^8$ )	11.88	1.95	0	0	8.69	M	–	NM	
	Hg ( $d^{10}$ )	12.36	2.23	0	0	6.60	M	–	NM	

M: metallic, H-F: half-metallic, FM: ferromagnetic, AFM: antiferromagnetic and NM: non-magnetic.

<sup>a</sup> solutions not found. <sup>b</sup> solutions not calculated since the total magnetic moment is very small.