First Row Transition Metals Intercalation of Covalent-Organic Frameworks: A Promising Route to Tune the Material Structure and Electronic Properties

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Abstract

Covalent organic frameworks (COFs) have emerged as an important class of nanoporous crystalline materials with many potential applications. They are intriguing platforms for the design of porous skeletons with special functionality at the molecular level. A new form of nanoporous material, transition metal intercalated COFs is proposed and its electronic properties are revealed. Using first-principles dispersion-corrected hybrid density functional theory (DFT-D), we have designed 31 new COF materials *in-silico* by intercalating all of the first row transition metals (TMs) with boroxine-linked and triazine-linked COFs. This is a significant addition considering that only 187 experimentally COFs structures has been reported and characterized so far. We have investigated their frameworks properties as well as material properties. Specifically, we predict that COF's band gap and density of states (DOSs) can be fine tuned by intercalating first row transition metal atoms (TM: Sc - Zn). The present DFT-D calculations showed that the *d*-subshell electron density of the TMs plays an important role in determining the material properties of the COFs. The implications of controllable electronic structure and properties of intercalated COF materials for future device applications are discussed. Thus intercalated-COFs provide a new strategy to create semi-conducting and conducting materials within a rigid porous network in a highly controlled and predictable manner. This work opens up new avenues for the efficient production of TM-intercalated materials with promising future applications in nanoporous material science, electronics and chemical sensors.

INTRODUCTION

In the 21st century, porous materials science especially crystalline or amorphous porous materials has already shown a strong impact on our daily life in the forms of porous amorphous carbon for different applications. The linking of organic building units or bridging ligands through strong covalent bonds typically yields poorly crystalline or amorphous solids, thus precluding the characterization of their structures at the atomic level. In recent years,

a new family of porous materials with a well-defined network of building blocks linked by strong covalent bonds, which are called covalent-organic frameworks (COFs), have been characterized and synthesized experimentally.¹⁻⁷ COFs are lightweight, constructed by linking light elements such as carbon, boron, oxygen and silicon through exclusively strong covalent bonds to form periodic frameworks with the faces and edges of molecular subunits exposed to pores.^{1,8,9} An attractive feature of some COFs is the high density of Lewis acidic boron atoms, present in boroxine (B_3O_3) or boronate ester (C_2O_2B) rings, which are an integral component of their frameworks. Due to their high structural regularity and diversity, high surface areas, easy modification of frameworks, unique properties of porosity, and structural flexibility, these COF materials have attracted considerable scientific interest for potential applications in gas storage and separation,¹⁰⁻¹⁴ photocatalysis,^{15,16} solid state batteries,¹⁷ optoelectronics¹⁸ and even photovoltaics for fuel cell.^{10,16,19-22}

In general, COFs exhibit unique architectures such as 2D-COF where the monomers that make up their 2D layers stack almost perfectly into infinite 1D columns that are ideal for charge and exciton transport, and such electronic properties are particularly difficult to engineer in microporous metal-organic frameworks (MOFs) or porous coordination polymers (PCPs).^{23,24} COFs, in which building blocks are precisely integrated into extended structures with periodic skeletons and ordered pores, have other distinctive advantages. In COFs, building units stack via π - π interactions to form the layered structures with well-defined alignment of π -building units to their atomic layers and segregated arrays of π -columns. In such arrays, the intra-layer covalent bonds lock the framework, whereas, interlayer non-covalent interactions control the stability. Thus, from the materials-design perspective, various COFs can be achieved by controlling pore design, skeleton design or using complementary designs of both pores and skeletons. The great promise of COFs is rooted in the idea that the entire structure is organic and thus may be modified through the extensive tools of organic synthesis. However, low intrinsic conductivity and high charge-carrier mobility in COFs still impose a great challenge for their applications in flexible electronics. Current research has

been focused only on the synthesis of various COFs and their application mainly on: green energy applications, gas storage and separation.^{10,14} Few investigations have been reported on the structure-property relationships COF materials, specifically of 2D stacking structure to their electronic properties. This is also limited by 187 experimentally characterized COFs structures so far.²⁵

The fundamental research into COFs' intrinsic properties remains today an open opportunity for material scientists, physicists and chemists. Thus, we propose to expand the applications of COFs by intercalation of transition metals (TM) to dictate the fundamental chemical and physical properties as well as to overcome the limitations of the material. To date, direct modification of the structure of COFs by TM or metal intercalation has not well understood in a systemic way. Only few studies showed how the electronic properties of pristine COFs were changed along with their possible applications. Miyamoto and co-workers computationally designed fullerenes intercalated phthalocyanine Li-doped COFs, and they found that Li-doped COFs are promising candidates for hydrogen storage at room temperature and the intercalation method is an unique way to modify the hydrogen storage performance of the pristine COFs.²⁶ A recent study showed the Ca-intercalated COF is an optimal material for H₂ storage at near-ambient conditions (300 K, 20 bar) compared to pristine COFs.²⁷ Meunier and co-workers computationally showed that the electronic properties of pristine COFs can be controlled by increasing organic chain-links in the framework and they found that the electronic properties do not differ significantly when altering the chain molecules within each family.^{28,29} Very recently, we computationally showed that the electronic properties of pristine COFs were controlled by intercalating the iron atoms between the organic layers in COFs keeping the original hexagonal symmetry ($P-6m2$) of the pristine COF.⁹ Therefore, the question still arises what happens if the pristine COFs are intercalated by other TM atoms and how the structure-property relationships might be affected. As we stipulated in our recent article that the further computational investigations will focus on the effect of all first row transition metals on the electronic properties of the

TM-intercalated COF materials as well as the nature of the organic building blocks, we present here the studies of all the first row TM atoms intercalated with boroxine, triazine and benzene rings in the pristine COF.

Here, based on first-principles calculations, we have designed a total thirty one (31) new types of COFs made of boroxine, triazine and benzene rings, and intercalating all first row transition metal atoms (Sc-Zn) between two organic layers in the pristine COF. First, we have investigated the equilibrium structures and geometries of these COFs using first-principles calculations based on the periodic dispersion-corrected density functional theory (DFT-D)^{9,30-34} method. In the present article, we have computationally studied how their electronic/material properties (i.e. band structures, band gaps, density of states (DOSs), intercalation distances) were changed due to the addition of first row TM atoms intercalation between two organic layers of the pristine COF. The material properties were altered by the addition of all the first row TM atoms between two organic layers in the pristine COF.

Through addition of all first row TM atoms (i.e., Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn) between layers of a pristine COF, thirty different types of TM intercalated-COF materials were created computationally (Figure 1, and Figure S1-S4): **(i) COF-TM-3**; three TM atoms were intercalated per one unit cell and they were placed at the centroid of three benzene rings (i.e. COF-Sc-3, COF-Ti-3, COF-V-3, COF-Cr-3, COF-Mn-3, COF-Fe-3, COF-Co-3, COF-Ni-3, COF-Cu-3 and COF-Zn-3), **(ii) COF-TM-4**; four TM atoms were intercalated per one unit cell, whereas three Fe atoms were placed at the centroid of three benzene rings, and one TM atom was placed at the centroid of the boroxine ring; (i.e. COF-Sc-4, COF-Ti-4, COF-V-4, COF-Cr-4, COF-Mn-4, COF-Fe-4, COF-Co-4, COF-Ni-4, COF-Cu-4 and COF-Zn-4), and **(iii) COF-TM-5**; five TM atoms were intercalated per unit cell (i.e. COF-Sc-5, COF-Ti-5, COF-V-5, COF-Cr-5, COF-Mn-5, COF-Fe-5, COF-Co-5, COF-Ni-5, COF-Cu-5 and COF-Zn-5). Thus, this work presents the first comprehensive investigation of bulk crystalline porous COF materials with intercalated first row TM atoms. Therefore, to provide a fundamental atomic level quantum mechanical (QM) insight, we have

computationally analyzed the electronic and material properties of the total aforementioned 31 materials (COF-TM) by introducing all of first row transition metal (Sc-Zn) atoms intercalation in the pristine COF material. Here we addressed how the first row transitional metals affects the material as well as electronic properties, more specifically how the d -subshells electron density of the TM atoms direct the changing of the electronic properties of the new COF-TM materials. We have also studied how the TM atoms affect on the surface area (S_A), pore volume (V_p), and density (ρ) i.e. the structure property of the COF frameworks. These materials are promising for electronic and nanoporous material applications. We have focused mainly on the most stable conformer of the TM-intercalated COFs here, and other less stable conformers of the TM-intercalated COFs were excluded from this manuscript.

This article is organized as follows: we first describe and provide methods, technical and computational details. Then, we discuss about the results and discussions including the band structures, band gap, density of states and the effects of first row transition metals intercalation and electron density of the d -subshells of the transition metals. Finally we provide a short conclusion with the analysis of structure-property relationships.

METHODS AND COMPUTATIONAL DETAILS

Periodic Density Functional Theory (DFT): Calculations of energetics, electronic structures, geometry and material properties of aforementioned studied materials (pristine COF and COF-TM-x) have been performed using first-principles calculations based on unrestricted hybrid DFT (UB3LYP)^{30–32} implemented in the *ab initio* CRYSTAL14 suite code, which makes use of localized Gaussian basis sets.³⁵ As there are many van der Waals (vdW) weak interactions between various atoms in the layers of the COFs, semi-empirical Grimme’s (-D2) dispersion corrections were added in the present computation.^{9,23,33,36–39} Thus, to summarize we have used dispersion corrected unrestricted B3LYP hybrid DFT method; UB3LYP-D2,^{9,30–34,39–42}. For simplicity, this is termed DFT-D throughout the text.

Figure 1: Optimized crystal structures of (a) Pristine COF and Sc-intercalated (b) COF-Sc-3, (c) COF-Sc-4, and (d) COF-Sc-5 COF materials. The COFs have hexagonal $P-6m2$ symmetry and the unit cells of the COFs are highlighted by a parallelogram.

Unrestricted wave functions were considered due to the $3d$ orbital electrons of all the TM atoms (where TM = Sc-Zn). In the present computation, triple-zeta valence with polarization quality (TZVP) Gaussian basis sets were used for H, B, C, N, O, and TM atoms (where TM = Sc-Zn).⁴³ The convergence of energy, electron density and forces were set to 10^{-7} a.u. for all geometry optimizations and other convergence calculations. The spins were set at the beginning of SCF cycles calculations but later they were allowed to relax. The harmonic vibrational frequencies at the optimized geometries were analyzed at the respective levels of theory to reveal the nature of the stable minima. The DFT-D method was used for geometry optimization because densities and energies obtained with the method are less affected by spin contamination than other approaches.^{40,41,44-47}

Integrations inside of the first Brillouin zone were sampled on $4 \times 4 \times 16$ Monkhorst-Pack⁴⁸ k-mesh grids for all the COFs during geometry optimization, and $20 \times 20 \times 20$ Monkhorst-Pack k-mesh grids for the calculations of band structure and density of states. The reciprocal space for all the structures was sampled by a Γ -centered Monkhorst-Pack scheme with a resolution of around $2\pi \times 1/60 \text{ \AA}^{-1}$. The band pathway followed the symmetry points: $\Gamma - K - M - H - A - L - M - \Gamma$ (Figure 4 - 13). The total DOSs were plotted using the atomic orbitals of carbon (C), hydrogen (H), nitrogen (N), boron (B), oxygen (O), and intercalated transition metals (TM) atoms; where TM = Sc - Zn. To investigate the contribution of the d -subshell electron density of the intercalated TM atoms in the total DOSs, the DOSs of the d -subshells were computed and plotted in the right handside of Figure 4 - 13. Visualization and analysis were performed using VESTA.⁴⁹

Materials Design of COFs: All of the COFs presented here were designed as ideal honeycomb-like structures with the **bnn** topology, and the final material consisted of one triazine, one boroxine, and three benzene rings in one unit cell with the $P - 6m2$ space group symmetry. The reason for this combination is to maximize the explanation of different TMs and organic rings, which can explore the effects of TMs in the different rings. The

first row TM atoms (Sc-Zn) were intercalated in between two organic layers of the pristine COFs. During the intercalation process we have maintained the original hexagonal symmetry ($P-6m2$) of the pristine COF. Through the addition of all first row TM atoms between layers, thirty different types of TM intercalated-COF materials were designed and studied computationally: (i) COF-TM-3; three TM atoms were intercalated per one unit cell and they were placed at the centroid of three benzene rings, (ii) COF-TM-4; four TM atoms were intercalated per one unit cell, whereas three TM atoms were placed at the centroid of three benzene rings, and one TM atom was placed at the centroid of the boroxine ring, and (iii) COF-TM-5; five TM atoms were intercalated per unit cell at the centroid of three benzene rings, one boroxine ring and one triazine ring as shown in Figure 1, and Figure S1-S4 in the Supporting Information, respectively. These materials are thermodynamically stable at room temperature according to their vibrational analysis, i.e. there are not negative frequencies and this indicates that they are likely for synthesis.

RESULTS AND DISCUSSIONS

The optimized bulk crystal structures of the pristine COF and TM-intercalated COFs, COF-TM-x (where TM = Sc-Zn and x=3-5), are shown in Figures 1 and S1-S3 in the Supporting Information, respectively. First, we have considered the interaction between the adjacent organic layers in the pristine and TM-intercalated COF materials during the optimization, and we found that the equilibrium distance between the adjacent organic COF layers is 3.241 Å. This computation indicates that it is possible to intercalate TM atoms between the adjacent organic layers in the pristine COF. Three atoms of same TMs (Sc-Zn) have been placed at the centroid of three benzene rings between two organic layers in one unit cell of the pristine COF resulting COF-TM-3; see Figure 1b and Figure S1-S3 in the Supporting Information. This was due to symmetry and to avoid configuration and complexity. We have previously shown that the intercalated structure is generally more stable when it has

more number of TM atoms which were intercalated in the system. The fourth TM atom was placed at the centroid of the boroxine ring in COF-TM-3 to form COF-TM-4 as shown in Figure 1c and Figure S1-S3. Similarly, the fifth TM atom was placed at the centroid of the triazine ring in COF-TM-4 to form COF-TM-5 (Figure 1d) and Figure S1-S3. The coordinates of the optimized pristine COF and COF-TM-x crystal structures are reported in the Supporting Information. The COF materials studied here were energetically stable. Other conformations of TM intercalation in COF-TM-3 at the centroid of the triazine ring to form COF-TM-4B are also possible but they are energetically less stable than COF-TM-4, which we showed in our recent published article where TM is Fe.⁹ Thus all the other conformation structures of the COF-TM-4B were excluded from the present manuscript.

Now we discuss the structural information of both the pristine COF and COF-TM-x materials. The optimized unit cells with the equilibrium geometries of these materials are shown in Figure 1 and Figure S1-S3 in the Supporting Information, where the unit cells of these materials were highlighted by a parallelogram. Due to the similar crystal structure but slightly different chemistry as well as geometry, it is interesting to compare the basic electronic structures and properties of all the TM intercalated COFs studied here. The equilibrium lattice constants (a , b , and c), various average equilibrium bond distances (C-C, B-O, C-B, C-N) and the average distance between two organic layers i.e. intercalation distance (d) are reported in Table 1. On the other hand, the electronic properties (i.e. band structures, electronic band gap (E_g), and density of states (DOSs)), state and binding energies (ΔE) are shown in Table 2. The lattice constants and various bond distances gradually changed when the TM (TM = Sc - Zn) atoms were added inside the COFs. The present DFT-D calculations found that the angles $\angle OBO$ and $\angle BOB$ in the boroxine ring of the pristine COF were about 113.5° and 126.5° , respectively. Similarly the angles $\angle CNC$ and $\angle NCN$ in the triazine ring were about 116.3° and 123.7° , respectively. These angles were changed due to TM atoms intercalation the pristine COF. For example, the angles $\angle OBO$, $\angle BOB$, $\angle CNC$ and $\angle NCN$ were about 118.5° , 121.5° , 124.5° , and 124.5° , respectively due to

Table 1: The lattice constants (a , b , c), average bond distances, and intercalation distance (d) between layers of COFs. The lattice constants and all the bond distances are expressed in Å.

COFs	a	b	c	C-C	C-B	B-O	C-N	d
COF	14.85	14.85	3.31	1.39	1.53	1.38	1.34	3.241
COF-Sc-3	14.88	14.88	3.72	1.46	1.51	1.39	1.35	3.715
COF-Sc-4	15.06	15.06	3.76	1.47	1.51	1.46	1.35	3.760
COF-Sc-5	15.21	15.21	3.77	1.47	1.50	1.47	1.42	3.769
COF-Ti-3	14.86	14.86	3.39	1.47	1.51	1.39	1.35	3.387
COF-Ti-4	15.07	15.07	3.41	1.47	1.50	1.46	1.35	3.408
COF-Ti-5	15.22	15.22	3.43	1.47	1.49	1.46	1.41	3.427
COF-V-3	14.86	14.86	3.34	1.46	1.51	1.47	1.35	3.357
COF-V-4	15.05	15.05	3.39	1.46	1.51	1.46	1.35	3.388
COF-V-5	15.19	15.19	3.39	1.46	1.51	1.46	1.41	3.393
COF-Cr-3	14.93	14.93	3.37	1.45	1.51	1.39	1.35	3.366
COF-Cr-4	15.08	15.08	3.41	1.45	1.50	1.45	1.35	3.406
COF-Cr-5	15.17	15.17	3.44	1.45	1.50	1.45	1.41	3.445
COF-Mn-3	14.86	14.86	3.55	1.46	1.51	1.39	1.35	3.554
COF-Mn-4	14.99	14.99	3.60	1.46	1.49	1.45	1.34	3.602
COF-Mn-5	15.08	15.08	3.67	1.47	1.48	1.45	1.45	3.667
COF-Fe-3	14.83	14.83	3.44	1.44	1.51	1.39	1.34	3.443
COF-Fe-4	14.95	14.95	3.45	1.44	1.50	1.43	1.34	3.448
COF-Fe-5	15.03	15.03	3.45	1.43	1.51	1.43	1.39	3.450
COF-Co-3	14.86	14.86	3.41	1.46	1.51	1.39	1.35	3.411
COF-Co-4	14.95	14.95	3.47	1.46	1.48	1.45	1.35	3.471
COF-Co-5	15.02	15.02	3.51	1.46	1.49	1.44	1.42	3.510
COF-Ni-3	14.91	14.91	3.50	1.45	1.50	1.39	1.35	3.505
COF-Ni-4	14.92	14.92	3.69	1.45	1.47	1.43	1.35	3.569
COF-Ni-5	14.99	14.99	3.59	1.45	1.50	1.44	1.39	3.587
COF-Cu-3	14.91	14.91	3.50	1.46	1.50	1.39	1.35	3.461
COF-Cu-4	14.92	14.92	3.69	1.47	1.46	1.45	1.35	3.492
COF-Cu-5	14.99	14.99	3.59	1.45	1.46	1.44	1.39	3.539
COF-Zn-3	14.91	14.91	3.50	1.51	1.49	1.40	1.35	3.537
COF-Zn-4	14.92	14.92	5.88	1.45	1.54	1.39	1.34	5.879
COF-Zn-5	14.99	14.99	5.91	1.42	1.53	1.38	1.36	5.905

three Sc atoms intercalated in the pristine COF i.e. COF-Sc-3. Of all the intercalated-COFs studied here, the boroxine and triazine rings are slightly different from the benzene rings. For example, both the boroxine and triazine rings are not perfect hexagonal rings in COF-Sc-3, since the angles $\angle BOB$ and $\angle NCN$ are about 121.6° and 124° , respectively, which is a small deviation from the expected 120° . This is because the electronegativity of the O and N atoms is stronger (i.e. there is a lone pair of electrons) than that of the B and C atoms, and both the boroxine and triazine rings have less aromatic character compared to pure benzene rings.⁵⁰⁻⁵² The distances d between two identical organic layers in COF, COF-TM-3, COF-TM-4, and COF-TM-5 is increased as more TM atoms were added between the layers (see Table 1). The lattice constants (a, b and c) were also increased in the intercalated COF materials compared to the pristine one due to intercalation. Similarly other covalent bonds distances C-C, B-O and C-N were increased and the C-B bond distances were decreased except COF-Zn-4, COF-Zn-5 materials as depicted in Table 1. Thus, we can say that the addition of the first row TM atoms (Sc-Zn) between two boroxine rings had a different effect than the addition of same TM atoms between benzene and triazine rings in the intercalated COFs, which is likely due to the different aromaticity of the each rings in the COF materials.

In designing new materials especially the TM-intercalated COFs, the energetic stability of these systems is one of the most important aspects to be examined. In order to examine the stability of the COFs against the formation or binding energy ΔE , we have estimated the binding energy as $\Delta E = E_{\text{COF-TM-}x} - E_{\text{COF}} - xE_{\text{TM}}$; where x is the number of TM atoms intercalated in the COFs. The $E_{\text{COF-TM-}x}$, E_{COF} , E_{TM} are the energies of the TM-intercalated COFs, pristine COF and the TM atom. Similarly, ΔE of the pristine bilayer COF is calculated by the mathematical expression $\Delta E = E_{\text{COF}} - nE_{\text{Single-Layer-COF}}$; where n is the number of organic layers in the pristine COF (here $n = 2$) and $E_{\text{Single-Layer-COF}}$ is the energy of the single organic layer of the pristine COF. The total energy of the systems was computed using the aforementioned DFT-D method; and these values are reported in the Supporting Information. The binding energy (ΔE) of each TM-intercalated COF was calcu-

lated with respect to the pristine COF as reported in Table 2. The binding energy for all the TM-intercalated COF materials has been plotted w.r.t. all the first row TM (Sc - Zn) atoms and shown in Figure 2a. This plot shows that how the ΔE of the intercalated COF materials varies with the all the first row TM atoms, and COF-Ti-5 is the most favorable material as it shows the lowest binding energy (about -67.57 eV) among all the materials studied here. In the present study, we found that the ΔE of the TM-intercalated COFs (where TM = Sc-Cu) are negative and it suggests that they may be synthesized experimentally except for COF-Zn-x. In the case of Zn-intercalated COFs (COF-Zn-x), the ΔE is slightly positive and this result indicates that these three COF-Zn-3, COF-Zn-4 and COF-Zn-5 materials are not stable and may not be synthesized experimentally, because the synthesis processes are endothermic reactions. Conversely, the negative value of ΔE for all other COFs (i.e. COF-TM-x; where TM = Sc-Cu) indicates that these Sc-Cu atoms intercalated COFs are more stable than COF-Zn-x crystals, and the synthesis processes are exothermic reactions. A word of caution, the relative energies are calculated with respect to the neutral atomic form of TM; thus the binding energies might vary if a different source of TM is used in experiment.

The detailed structural information of both the pristine and TM-intercalated COFs are listed in Table 1 along with the intercalation distances d of the organic layers. The properties of the frameworks i.e. surface area (S_A), pore volume (V_p) and density (ρ) of all the COF materials studied here, have been calculated by rolling a H_2 molecule with an initial diameter of 2.80 Å, over the framework’s internal surface. As expected, the surface area and pore volume of the COF-TM-x (TM = Sc-Cu) COFs were decreased by the intercalated TM atoms compared to the pristine one except COF-Zn-4 and COF-Zn-5. This is due to the interaction between the organic COF layers and TM atoms, thus the intercalation distance d increases in the COF materials depending on the type of the TM atoms. Among these intercalated COFs, COF-Zn-4 possesses the lowest density and highest pore volume and accessible surface area. All these properties of the COF-Zn-4 indicate that the gas storage

capacity may be enhanced by the intercalated four Zn atoms, but this compound is not stable thermodynamically.

The pore surface area (S_A), pore volume (V_p) and density (ρ) of the COF-TM-x (TM = Sc - Zn and x = 3 - 5) along with the pristine COF were estimated and reported in Table 3. Interestingly, our present DFT-D study found that COF-TM-x have large surface area, and plotted in Figure 2b along with the pore volume (V_p) and density (ρ) as depicted in Figure 2c and Figure 2d, respectively. This calculation indicated that the in general pore surface area of the COF-TM-x was decreased when the larger TM atom was intercalated in the pristine COF except COF-Zn-x. It means that COF-Zn-4 has the largest pore surface area and COF-Cu-5 has the lowest pore surface area; see Table 3 and Figure 2. We also observed that the pore volume of the COF-TM-x materials decreases as the size of the TM atoms increases; except COF-Zn-x.

Once the equilibrium structures of both the pristine and TM-intercalated COFs are determined, we are ready to investigate how the ground state electronic properties of the materials are changed by intercalating the first row transition metals (Sc-Zn). The band structure of these materials was plotted along a high symmetric k -direction in the first Brillouin zone, $\Gamma - K - M - H - A - L - M - \Gamma$. Although it has a similar topological structure to graphene, the electronic properties are completely different.^{40,41,53} It was found that the pristine bulk COF material behaves like an insulator (Figure 1a), and we showed that it has a high band gap of around 2.60 eV in our recent work,⁹ thus its detailed band structures and density of states (DOSs) calculations are excluded from the present manuscript. Inspection of the density of states and band structure (See Figure 3 and Figure 3a in reference⁹) reveals that the bulk structure boroxine and triazine linked pristine COF with a benzene ring attains an indirect band gap of ~ 2.60 eV (see Table 2), which is well below boroxine-linked pristine COF (3.55 eV).²⁹ In both the band and DOSs calculations, the energy values are normalized i.e. the band energy and DOSs are plotted with respect to the Fermi energy of zero. This calculation indicates that the pristine COF is an insulator as shown in the band structure

Table 2: The band gap energy E_g and binding energy (ΔE) of the pristine COF and first row transition metal (TM) atoms intercalated-COFs, COF-TM-x (where TM = Sc-Zn and x=3-5) materials. The band gap energy and binding energy are expressed in eV. Note that the ΔE of the TM intercalated COFs are calculated w.r.t. the pristine COF i.e. the reference is pristine COF.

COFs	E_g	ΔE	Material
COF	2.60	-2.84	Insulator
COF-Sc-3	0.00	-25.39	Conductor
COF-Sc-4	0.00	-29.67	Conductor
COF-Sc-5	0.00	-37.44	Conductor
COF-Ti-3	0.00	-43.93	Conductor
COF-Ti-4	0.00	-53.84	Conductor
COF-Ti-5	0.00	-67.57	Conductor
COF-V-3	0.00	-21.89	Conductor
COF-V-4	0.00	-24.46	Conductor
COF-V-5	0.00	-30.55	Conductor
COF-Cr-3	0.00	-19.48	Conductor
COF-Cr-4	0.93	-22.98	Semi-conductor
COF-Cr-5	0.59	-28.39	Semi-conductor
COF-Mn-3	1.71	-2.17	Semi-conductor
COF-Mn-4	0.00	-0.16	Conductor
COF-Mn-5	0.00	-0.12	Conductor
COF-Fe-3	1.16	-14.47	Semi-conductor
COF-Fe-4	1.12	-17.93	Semiconductor
COF-Fe-5	1.18	-19.70	Semiconductor
COF-Co-3	1.21	-8.12	Semi-conductor
COF-Co-4	1.33	-7.82	Semi-conductor
COF-Co-5	1.43	-9.53	Semi-conductor
COF-Ni-3	1.26	-9.38	Semi-conductor
COF-Ni-4	1.94	-12.66	Semi-conductor
COF-Ni-5	1.70	-13.64	Semi-conductor
COF-Cu-3	1.26	-12.93	Semi-conductor
COF-Cu-4	0.00	-16.01	Conductor
COF-Cu-5	0.00	-20.72	Conductor
COF-Zn-3	0.30	7.32	Semi-conductor
COF-Zn-4	2.22	1.02	Semi-conductor
COF-Zn-5	1.93	0.56	Semi-conductor

Table 3: Properties of the frameworks used in this work: Surface Area (S_A), Pore Volume (V_p), and Density (ρ). S_A and V_p were estimated from rolling an H_2 molecule with an initial diameter of 2.80 Å to simulate a solvent molecule, over the framework’s surface.

COFs	S_A , m ² gm ⁻¹	V_p , cm ³ gm ⁻¹	ρ , gm cm ⁻³
COF	1081	0.948	1.055
COF-Sc-3	986	0.822	1.216
COF-Sc-4	990	0.786	1.273
COF-Sc-5	945	0.744	1.345
COF-Ti-3	867	0.726	1.377
COF-Ti-4	835	0.698	1.432
COF-Ti-5	798	0.661	1.513
COF-V-3	844	0.790	1.265
COF-V-4	810	0.678	1.475
COF-V-5	765	0.637	1.571
COF-Cr-3	856	0.721	1.387
COF-Cr-4	822	0.637	1.569
COF-Cr-5	779	0.639	1.565
COF-Mn-3	876	0.716	1.396
COF-Mn-4	832	0.696	1.436
COF-Mn-5	793	0.658	1.520
COF-Fe-3	850	0.713	1.403
COF-Fe-4	791	0.659	1.518
COF-Fe-5	731	0.609	1.643
COF-Co-3	829	0.697	1.434
COF-Co-4	782	0.650	1.538
COF-Co-5	716	0.606	1.651
COF-Ni-3	854	0.723	1.384
COF-Ni-4	837	0.690	1.450
COF-Ni-5	740	0.618	1.617
COF-Cu-3	823	0.687	1.455
COF-Cu-4	765	0.633	1.579
COF-Cu-5	694	0.586	1.707
COF-Zn-3	811	0.696	1.437
COF-Zn-4	2089	1.028	0.973
COF-Zn-5	1144	0.940	1.063

Figure 2: (a) Binding energy (ΔE in eV); (b) Pore surface area (S_A , $\text{m}^2 \text{gm}^{-1}$); (c) Pore volume (V_p , cm^3); and (d) Density (ρ , gm cm^{-3}) of the COF-TM-x (where TM = Sc - Zn and x = 3 -5) were plotted with respect to the pristine COF and first row TM atoms. Note that “Pristine” indicates the pristine COF in all the (a)-(d) figures.

and DOSs calculations displayed in Figure 3.

Figure 3: Optimized crystal structures of pristine COF. The band structure and total density of states (DOSs) are shown at the right hand side.

The electronic properties of the COF-TM-x ($x = 3 - 5$ and TM = Sc - Mn) materials are shown in Figure 4 - 8 along with the pore structure of the TM-intercalation. The band structure calculations showed that the valance and conduction bands are overlapped and crossed the Fermi Energy level (E_F) when the pristine COF was intercalated by Sc, Ti and V atoms as depicted in Figure 4 - 6. The shape of the band structures of the TM-intercalated COFs were completely changed due to TM atoms intercalation in the pristine COF. The present computation found that a large electron density appeared around the Fermi Energy level making them conductor as shown in their DOSs. An interesting phenomenon was observed in the electronic properties of the COF-Cr-4 and COF-Cr-5 materials. The band structures and DOSs found that COF-Cr-3 showed conducting behavior where as the COF-Cr-4 and COF-Cr-5 materials showed semi-conducting behavior as they have direct band gap (E_g) at M -point about 0.93 and 0.59 eV, respectively as shown in Figure 7b-c and Table 2. These results indicate that boroxine and triazine rings are not conducting like benzene rings and they have less aromatic character than the pure benzene rings given that the 4th and 5th Cr atoms are intercalated at the centroid of the boroxine and triazine rings of the COF-Cr-3, respectively. An opposite phenomenon was observed in the COF-Mn-3, COF-Mn-4 and COF-Mn-5 materials. The present calculations found that COF-Mn-3 is a semiconductor with a band gap about 1.71 eV, while the COF-Mn-4 and COF-Mn-5 are conductors as the bands are overlapped with a large electron density appeared around the Fermi energy level as shown in Figure 8. In this case, the concentration of the Mn atoms plays an important role to control the electronic properties of the COF and it transforms the pristine COF from insulator to a conductor. We have found that the concentration of the TM atoms increases the stability and binding energy (ΔE) as reported in Table 2. This calculation also reveals that COF-Ti-5 is the most stable COF (Figure 5) as it shows the lowest binding energy among all the TM-intercalated COFs and in general the stability increases when the concentration of the TM atoms increase. However, in the case of COF-Mn-4 and COF-Mn-5, the stability decreased although Mn concentration increased.

Figure 4: Optimized crystal structures of Sc-intercalated COFs: (a) COF-Sc-3, (b) COF-Sc-4, and (c) COF-Sc-5. The band structure and DOSs are shown. The contribution of d -subshell electrons of Sc in total DOSs is shown in the far right hand, as ‘Sc d’.

Figure 5: Optimized crystal structures of Ti-intercalated COFs: (a) COF-Ti-3, (b) COF-Ti-4, and (c) COF-Ti-5. The band structure and DOSs are shown. The contribution of d -subshell electrons of Ti in total DOSs is shown in the far right hand, as ‘Ti d’.

Figure 6: Optimized crystal structures of V-intercalated COFs: (a) COF-V-3, (b) COF-V-4, and (c) COF-V-5. The band structure and DOSs are shown. The contribution of d -subshell electrons of V in total DOSs is shown in the far right hand, as ‘V d’.

Figure 7: Optimized crystal structures of Cr-intercalated COFs: (a) COF-Cr-3, (b) COF-Cr-4, and (c) COF-Cr-5. The band structure and DOSs are shown. The contribution of d -subshell electrons of Cr in total DOSs is shown in the far right hand, as ‘Cr d’.

Figure 8: Optimized crystal structures of Mn-intercalated COFs: (a) COF-Mn-3, (b) COF-Mn-4, and (c) COF-Mn-5. The band structure and DOSs are shown. The contribution of d -subshell electrons of Mn in total DOSs is shown in the far right hand, as ‘Mn d’.

A permanent band gap was found when Fe, Co and Ni atoms were intercalated in the pristine COF, i.e. COF-TM- x (where TM = Fe, Co and Ni; $x = 3 - 5$) and their band structures and DOSs were shown in Figure 9 - 11. The detailed discussions about the Fe-intercalated COFs were recently published in our recent article.⁹ The DFT-D calculations found that the COF-Fe-3 and COF-Fe-4 COFs have an indirect band gap about 1.16 eV and 1.12 eV. The band structure calculations show that two conduction bands slightly touch each other about 0.15 - 0.11 eV above the Fermi energy level (E_F) in the high symmetric $M - H - A - L - M$ direction accompanied by a large electron density reflected in the total DOSs computation as shown in Figure 9a-b. The shape of the CB structure was slightly changed in the COF-Fe-5 due to the addition of the 5th Fe atom to the COF-Fe-4 at the centroid of the triazine ring. The band structure of the COF-Fe-5 showed that one conduction band is overlapped with the Fermi energy level in the $\Gamma - K - M$ direction resulting in a large electron density around the E_F , which was reflected in the total DOSs as shown in Figure

9c. The present study found that the COF-Fe-5 has a small direct band gap of about 1.18 eV (see Table 2), resulting it in a semiconductor. This value was well below the values for the pristine 3D-COFs calculated by Lukose et al. (2.3 - 4.2 eV).⁵⁴ The electronic properties of the Co-intercalated COFs (i.e. COF-Co-x; x= 3 - 5) were changed due to the Co atoms intercalation in the pristine COF, and the band gap was increased by about 0.05 - 0.25 eV compared to Fe-intercalated COFs as shown in Table 2 and in Figure 10. In the case of the COF-Co-x, the band gap was gradually increasing by increasing the Co concentration in the pristine COF. This calculation indicates that both the triazine and boroxine rings in COF-Co-5 do not help to increase the semi-conductivity character of the COF, where as the benzene rings are more favorable for increasing the conductivity character of the COFs than the triazine and boroxine rings. Similar phenomenon was observed in the electronic properties of the Ni-intercalated COFs (i.e. COF-Ni-x; x = 3 - 5) and the E_g was increased gradually from 1.26 - 1.70 eV in the COFs as shown in Figure 11, with more effect when adding the TM atoms to the benzene rings.

The band structures and DOSs of the Cu- and Zn-intercalated COFs are shown in Figure 12 and 13, and the E_g was displayed in Table 2. The band gap of the COF-Cu-3 was found to be about 1.26 eV, which is the same as COF-Ni-3 and it is about 0.05 eV higher than COF-Co-3. The band gap disappeared when the 4th and 5th Cu atoms were intercalated in the COF-Cu-3 to form COF-Cu-4 and COF-Cu-5 due to the overlapping of the conduction and valance bands (see Figure 12) with higher electron density around the Fermi energy level. In this case, the Cu concentration determines the conductivity of the Cu-intercalated COFs. We also report the properties of COF-Zn-x at the same level of theory although they are predicted to be not as stable as the other COF-TM-x. Band gap again appeared in the COFs when the pristine COF was intercalated by Zn atoms; see Figure 13. The highest band gap was found in the COF-Zn-4 material among all others as reported in Table 2. COF-Zn-3 has a direct band gap at Γ -point and it is about 0.30 eV whereas the COF-Zn-4 and COF-Zn-5 COFs have the value of E_g about 2.22 eV and 1.93 eV, respectively. But the binding energy

Figure 9: Optimized crystal structures of Fe-intercalated COFs: (a) COF-Fe-3, (b) COF-Fe-4, and (c) COF-Fe-5. The band structure and DOSs are shown. The contribution of d -subshell electrons of Fe in total DOSs is shown in the far right hand, as ‘Fe d’.

Figure 10: Optimized crystal structures of Co-intercalated COFs: (a) COF-Co-3, (b) COF-Co-4, and (c) COF-Co-5. The band structure and DOSs are shown. The contribution of d -subshell electrons of Co in total DOSs is shown in the far right hand, as ‘Co d’.

Figure 11: Optimized crystal structures of Ni-intercalated COFs: (a) COF-Ni-3, (b) COF-Ni-4, and (c) COF-Ni-5. The band structure and DOSs are shown. The contribution of *d*-subshell electrons of Ni in total DOSs is shown in the far right hand, as ‘Ni d’.

calculations showed that these Zn-intercalated COFs are not stable as they have positive values of ΔE as reported in Table 2. A possible alternative to make Zn-derivatives stable could be to change the source of Zn or to create the COF-Zn-x materials at higher pressure, specially along the z-axis.

The present computations found that the TM atoms, which were intercalated in the pristine COFs, are playing the main important role to tune the electronic as well as structure properties of the COFs. We have further investigated in detail the contribution of the *d*-orbitals of the first row TM atoms (Sc-Zn) in the total DOSs of all the COF-TM-x (where $x = 3 - 5$) studied here. The large electron density around the E_F is due largely to the *d*-subshell electrons of all the TM atoms considered here as depicted in the *d*-subshell DOSs calculations shown in Figure 4 - 13. Thus, the present study reveals that the all the TM atoms changed the band structure of the COFs depending on the intercalation of the first row TM atoms. The TM atoms caused the COFs to become semiconductors, pushed down

the conduction bands, and caused the CB to move toward the Fermi energy level. We have also discovered that not all the intercalations are the same, i.e. for intercalation in benzene rings the TM seems to interact more with the COFs structures i.e. organic layers of the COFs. This effect is less prominent in triazine rings followed by boroxine rings.

Figure 12: Optimized crystal structures of Cu-intercalated COFs: (a) COF-Cu-3, (b) COF-Cu-4, and (c) COF-Cu-5. The band structure and DOSs are shown. The contribution of *d*-subshell electrons of Cu in total DOSs is shown in the far right hand, as ‘Cu d’.

The purpose of this work is to suggest the synthesis and predict the properties of these TM-intercalated COFs i.e. COF-TM-*x* (where TM = Sc - Zn and *x* = 3 - 5). While none of the materials studied here have been synthesized experimentally, the calculated vibrational frequencies and binding energies predict that these materials are stable. The frequency analysis and binding energy has been shown to be effective quantities to predict material stability and a *posteriori* synthesis in previous work.^{20,34,40,41} Thus, we expect these TM-intercalated COFs to be readily fabricated experimentally by all the first row TM atoms intercalation between weakly bound pristine COF layers except Zn. Although Ca-intercalated COFs were reported in the past, the base materials and linkers are different than those in the current

Figure 13: Optimized crystal structures of Zn-intercalated COFs: (a) COF-Zn-3, (b) COF-Zn-4, and (c) COF-Zn-5. The band structure and DOSs are shown. The contribution of *d*-subshell electrons of Zn in total DOSs is shown in the far right hand, as ‘Zn d’.

work. In the Ca-intercalated COFs, Meng and co-workers²⁷ used benzene and boroxine linkers. More specifically, they used benzene diboronic acid as an organic linker and they proposed that Ca-intercalated COFs could be useful for H₂ storage materials. In the current TM-intercalated COFs, we used triazine organic linkers in the design of the new materials. Additionally, our new materials are not intended for H₂ storage, but rather for increasing the conductivity and reducing the band gap in COFs for tuning the structure-property relationships. Here we proposed that many TM-intercalated COFs may be useful for small band gap materials as a semiconductor, which is an important property of crystalline porous materials. We designed these compounds with the triazine included because it has π electrons to facilitate electron diffusion, while the boroxine ring does not have π electrons. We imagined that the intercalation of transition metal atoms would also improve the conductivity of COFs. These two elements (triazine and all first row TM atoms) form a unique idea which can be used in semi-conducting technology as a way to improve conductivity and stability

in nanoporous materials in future applications. In other words, benzene (C_6H_6) and triazine (C_3N_3) rings are useful to tune the conductive properties, while boroxine (B_3O_3) are more useful for tuning the band gap opening and capacitors properties. The ongoing search for the COFs that are semi-conductors or conductors is of paramount importance if these materials are to be used as chemical sensors due to their surface area.

The results for the new proposed intercalated-COF materials are quite interesting and suggest the TM-intercalation approach is a promising way to tune the band gap from big to small while keeping the original symmetry of the pristine COF. Our findings suggest a new type of porous materials having entirely different electronic properties compared to usual porous materials such as pristine COFs. The present study also shows how the insulating pristine COF is converted to a direct band gap semiconductor or conductor when COF is intercalated by all first row TM atoms. In the present work, we, specifically, have focused and carried out an investigation on the fundamental properties required from a semiconductor to make it usable as an electronic component by tuning their electronic properties, such as band structures, DOSs and bandgap. The main contributing component in the total DOSs was investigated by computing the *d*-subshell electron density of the first row TM (Sc-Zn) atoms. This TM atoms intercalation approach broadens the scope and complexity of nanoporous COF materials, and opens the door to a more informed search for new electronic organic materials that combine the features of a porous framework structure with tunable electronic properties which are suitable for semiconducting applications.

CONCLUSIONS

In conclusion, we have presented intercalation of COFs with TMs as an strategy to dictate the fundamental chemical and physical properties as well as to overcome the limitations of the intrinsic material. We have designed 31 new COF materials belonging to a new class of porous crystalline COFs by intercalating first row transition metal atoms (Sc-Zn) in the

pristine COF using first-principles dispersion-corrected unrestricted hybrid DFT method. These TM-intercalated COFs have well-defined crystal structures and they are chemically stable compounds. The equilibrium structures, framework properties and electronic properties of these new kind of TM-intercalated COF materials were studied and investigated computationally. We have carried out a systematic study of their stability as compared with the corresponding COF-TM-x COFs. Transition metal atoms prefer to bind to aromatic organic units i.e. benzene (C_6H_6) followed by boroxine (B_3O_3) and triazine (C_3N_3) connecting rings in COF-TM-x COFs. Intercalation compounds allow incorporation or exchange of foreign atoms or molecules into the voids of various topologies in the host lattices such as cages (COFs, zeolites and so on), channels and two-dimensional (2D) spaces and represent an important frontier in solid state chemistry. The structural diversity of these solids gives rise to a vast array of applications too extensive to summarize. Our work indicates that all the TM atoms intercalation is a promising approach for converting an insulating pristine COF to semiconducting porous materials for device applications based on its electronic properties. None of the materials studied here have been synthesized experimentally, however, the calculated vibrational frequencies and binding energies predict that these materials are stable, which has been proven in later experimental synthesis in previous work. Understanding the new properties and behavior of these intercalated-COF materials will allow us to design new COFs that are intercalated by other transition elements in the periodic table for other applications in the near future.

For the structure-property relationship, the TM intercalation method is another approach to rational designs of the band structure, density of states, Fermi energy level, carrier density, and for inducing magnetic properties. We envisage that this new class of COF-TM-x porous materials, with a high density of active metal sites, could prove useful in a variety of future applications including semi-conductors, conductors, gas adsorption, sensors, and as thermoelectric. There is no doubt that intercalation chemistry still has extensive space for the 2D layered COF materials researchers. Finally, we have studied the effect of intercalants

on the electronic structure of the COF, where we conclude that intercalating the TM atoms in the COFs can open the door of TM-intercalated COFs which will enhance the science behind the porous materials and their behavior. It will provide a unique contribution and new knowledge to promote further research in porous materials and their applications in nanoporous material science. We predict this approach will serve to synthesize a new generations of COFs and applications, with the next frontier being hetero-structures COFs and multi-TMs intercalation materials.

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Supporting Information: Equilibrium structures with the unit cell of the COF-TM-x (TM = Ti - Zn and x = 3 -5); and the optimized crystallographic information (.cif) files of the pristine and TM-intercalated COF materials and detailed structural information of COF-TM-x (TM = Sc-Zn), and the total energies of these materials.

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