Intercalation of First Row Transition Metals inside Covalent-Organic Frameworks (COF): a Strategy to Fine Tune the Electronic Properties of Porous Crystalline Materials

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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. However, despite their extraordinary properties, it is difficult to control their electronic properties, thus hindering the potential implementation in electronic devices. A new form of nanoporous material, COFs intercalated with first row transition metal is proposed to address this fundamental drawback - the lack of electronic tunability. Using first-principles calculations, 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: COF-TM-x (where TM=Sc-Zn and x=3-5). This is a significant addition considering that only 187 experimentally COFs structures has been reported and characterized so far. We have investigated their structure and electronic properties. Specifically, we predict that COF's band gap and density of states (DOSs) can be controlled by intercalating first row transition metal atoms (TM: Sc - Zn) and fine tuned by the concentration of TMs. We also found that the *d*-subshell electron density of the TMs plays the main role in determining the electronic properties of the COFs. Thus intercalated-COFs provide a new strategy to control the electronic properties of materials within a porous network. This work opens up new avenues for the design of TM-intercalated materials with promising future applications in nanoporous electronic devices, where a high surface area coupled with fine-tuned electronic properties are desired.

INTRODUCTION

In the 21st century, 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 crystalline organic porous materials 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 that 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/separation,¹⁰⁻¹⁴ photocatalysis,^{15,16} solid state batteries,¹⁷ optoelectronics¹⁸ and even photovoltaics for fuel cells.^{10,16,19-22}

In general, COFs exhibit unique architectures. For example; in 2D-COF, the monomers make 2D layers stacks almost perfectly into infinite 1D columns that are ideal for charge and exciton transport, and such electronic properties have been particularly difficult to engineer in microporous metal-organic frameworks (MOFs) or porous coordination polymers (PCPs).^{23,24} Furthermore the building blocks in COFs have other distinctive advantages. In COFs, building units stack via π - π interactions to form layered structures with well-defined alignment of π -building units to their atomic layers and segregated arrays of π -columns. In such arrays, the intralayer covalent bonds lock the framework, whereas, the interlayer interactions control the stability by non-covalent forces. Thus, various COFs can be created by designing the pore, the skeleton or using complementary control 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 charge-carrier mobility in COFs still impose a great challenge for their applications as porous electronics. Current research has been focused only on the synthesis of various COFs and their application mainly green energy and gas storage/separation.^{10,14} Few

investigations have been reported on the structure-property relationships of COF, specially about the 2D stacking architecture and their electronic properties. This is also limited by only 187 experimentally characterized COFs structures reported and characterized so far.²⁵

Thus, despite COFs extraordinary properties, it is difficult to control their electronic properties, thus hindering the potential implementation in electronic devices. A new form of nanoporous material, intercalated COFs with first row transition metal is proposed to address this fundamental drawback - the lack of electronic tunability. The fundamental research into the intrinsic electronic properties of COFs remains today an open opportunity. Thus, we propose to expand the features of COFs by intercalating transition metals (TM) to dictate the chemical and physical properties as well as to overcome the intrinsic limitations of the material. To date, modification of the COF structures by intercalation with TMs has not been reported in a systemic way. Only a few studies are published on the intercalation of metal ions but not TM. These reports do not focus on the electronic properties but rather on the chemical fuels storage capacities. 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.²⁶ A recent study showed that Ca-intercalated COF is an optimal material for H₂ storage at near-ambient conditions (300 K, 20 bar) compared to pristine COFs.²⁷ Very recently, we computationally showed that the electronic properties of pristine COFs were controlled by intercalating iron atoms between the organic layers in COFs.⁹ Therefore, the fundamental question still arises, what happens if the pristine COFs are intercalated by all first row TM atoms and how the structure-property relationships might be affected? Specially, are the electronic properties tunable significantly? this work focus on the effect of intercalating all first row transition metals, specially the electronic properties as well as the nature of the organic building blocks. Thus, we present a systematic study using all of the first row TM atoms intercalated between boroxine, triazine and benzene rings as building blocks of newly designed COFs.

We have designed a total of 31 new types of COFs made of boroxine, triazine and ben-

zene rings, including intercalation of all first-row transition metal atoms (Sc-Zn) using first-principles calculations. First, we have investigated the equilibrium structures and geometries of these COFs using first-principles calculations at the level of periodic dispersion-corrected density functional theory or DFT-D for short.^{9,28-32} We have computationally studied how their structure (intercalation distances, bond lengths, ring geometries; see Figure 1-2) and electronic properties (band structures, density of states (DOSs), band gaps; see Figure 3-6) were changed due to the intercalation with first-row TM atoms.

Starting with a pristine COF made of benzene, boroxine and triazine rings (Figure 1), we intercalate all first row TM atoms (i.e. TM = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn), to obtained additionally 30 different types of TM intercalated-COF (Figure 1-4 and Figure S1-S3). These are (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, in which three TM atoms were placed at the centroid of each benzene ring, 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 in which the first three were placed between the benzene ring, the fourth TM between a boroxine ring, and the fifth TM between a triazine ring (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 intercalated with first row TM atoms. This is accomplished by using quantum mechanical (QM) calculations to study the effects on the structural and electronic properties, more specifically how the *d*-electrons from the TM atoms might control the electronic properties of the designed COF-TM. We have focused on the most stable conformers configurations of the TM-intercalated COFs, and other less stable conformers configurations of the TM-intercalated COFs are excluded from this manuscript.

Figure 1: Optimized crystal structures of (a) Pristine COF and intercalated COFs with Sc: (b) COF-Sc-3, (c) COF-Sc-4, and (d) COF-Sc-5. The unit cells are highlighted by a parallelogram.

This article is organized as follows: we first describe computational methods in detail, as well as the design principles for the new COFs. Then, we discuss about the structural changes and electronic properties tuned by the use of TMs. Finally, we provide a short conclusion with a focus on the structure-property relationships.

METHODS AND COMPUTATIONAL DETAILS

Periodic Density Functional Theory (DFT): Calculations of energetics, geometry and electronic properties of the pristine COF and COF-TM-x (where TM = Sc - Zn and x = 3 - 5) have been performed using first-principles calculations at the level of unrestricted DFT with the hybrid B3LYP functional²⁸⁻³⁰ as implemented in the *ab initio* CRYSTAL14 suite code.³³ The van der Waals weak interactions were taken account using the semi-empirical Grimme's (-D2) dispersion corrections.^{9,23,31,34-37} In summary, we have used dispersion corrected unrestricted hybrid DFT with the B3LYP functional; UDFT-B3LYP-D2,^{9,28-32,37-40} which is termed DFT-D throughout the text for simplicity. 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).⁴¹ The convergence of energy, electron density and forces were set to 10^{-7} a.u. for all geometry optimizations. The spins states were allowed to relax in the unrestricted wave functions calculations. The harmonic vibrational frequencies at the optimized geometries were analyzed to verify a stable structure. This method was used for geometry optimization because densities and energies obtained with the method are less affected by spin contamination than other approaches, and it has been proved effective for related materials calculations.^{38,39,42-45}

Integrations inside of the first Brillouin zone were sampled on $4 \times 4 \times 16$ Monkhorst-Pack⁴⁶ k-mesh grids for all the COFs during geometry optimization, and a $20 \times 20 \times 20$ Monkhorst-Pack k-mesh grids for the calculations of band structure and density of states. In other words, 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: $\Gamma - K - M - H - A - L - M - \Gamma$ (Figures 5 - 6). The total density of states was plotted using the atomic orbitals of carbon (C), hydrogen (H), nitrogen (N), boron (B), oxygen (O), and intercalated first row transition metal (TM) atoms; where TM = Sc to Zn. The *d*-subshells of the TM were computed in total DOSs and plotted in the right-hand side of Figures 5 - 6.

Materials Design of COFs: All of the COFs presented here were designed as ideal honeycomb-like structures with the **bnn** topology. The final material consisted of connecting one triazine, one boroxine, and three benzene rings in one unit cell with the $P-6m2$ space group symmetry. We found that the **gra** topology is less stable once the TM are added between the layers. The reason for this combination of building units is to maximize the environment of different TMs and organic rings, while maintaining experimental synthesis feasibility. The first row TM atoms (Sc-Zn) were intercalated between organic layers of the pristine COFs to make a sandwich-like structure. Throughout the intercalation process, we have maintained the original hexagonal symmetry of the pristine COF (Figure 1-3). Through the addition of all first row TM atoms between layers, 30 new intercalated-COF materials were designed and studied computationally (Figure 4, and Figures S1-S3). These materials are thermodynamically stable at room temperature according to their vibrational analysis, i.e. there are no negative or imaginary frequencies.

RESULTS AND DISCUSSIONS

We calculated the optimized bulk crystal structures of the pristine COF (Figure 3) and TM-intercalated COFs; COF-TM-x, where TM = Sc-Zn and x=3-5 (Figure 4), at the UDFT-B3LYP-D2 level of theory. 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 results prompted the hypothesis that it is possible to intercalate TM atoms between the adjacent organic layers in the pristine COF. Accordingly, 3 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 in COF-TM-3 (Figure 1b and Figures S1-S3). This is to maximize symmetry configurations and complexity. We have previously shown that the intercalated structure is generally more stable, when the more number of TM atoms

are intercalated in the system. The COF structures reported are the most stable, *i.e.* the 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-4A, which we showed in our recent published article where TM is iron (Fe).⁹ This was also done for the COF-TM-5 structures. Thus, all the other less stable conformation structures were excluded from the present manuscript.

Now, we discuss the structural information of both the pristine COF and COF-TM-x materials. Due to the similar crystal structure but slightly different chemistry as well as geometry, it is interesting to compare the 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 intercalation distance (d , the average distance between two organic layers) are reported in Table 1. On the other hand, the electronic properties including band structures, band gap (E_g), density of states (DOSs) 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 angles of the rings in the linkers were also altered by intercalation of TM atoms. The angles in boroxine; $\angle OBO$, $\angle BOB$, and triazine; $\angle CNC$, $\angle NCN$ were about 113.5° , 126.5° , 116.3° and 123.7° , respectively in the pristine COF. These angles changed slightly to 118.5° , 121.5° , 124.5° , and 124.5° , respectively, due to Sc intercalation to form COF-Sc-3. A similar trend is observed when intercalating any of the other TMs. In general, the boroxine and triazine rings are slightly different from the benzene rings. To give an 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.⁴⁷⁻⁴⁹

The distances d between two identical organic layers in COFs; COF-TM-3, COF-TM-4,

Table 1: Structural properties of COFs: 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-pure	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

and COF-TM-5 is increased the more TM atoms are added between the layers (see Table 1). The lattice constants (a , b and c) were also increased in the intercalated COFs compared to the pristine material. Similarly, other average covalent bonds distances C-C, B-O and C-N were slightly increased and the C-B bond distances were decreased (Table 1). Thus, the addition of the first row TM atoms (Sc-Zn) between boroxine rings has 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. Therefore, the COF structure can be affected by intercalation of TMs by using different rings in the structure (linkers), concentration and configurations of TMs (order of addition of TM).

Next in designing new materials is to estimate their thermodynamic stability. Consequently, we have estimated the binding energy as $\Delta E = E_{\text{COF-TM-}x} - E_{\text{COF}} - x \cdot E_{\text{TM}}$; where x is the number of TM atoms intercalated in the COF. The $E_{\text{COF-TM-}x}$, E_{COF} , E_{TM} are the electronic energies of the TM-intercalated COFs, pristine COF and the TM atom, respectively. Similarly, the binding energy, ΔE , of the pristine bilayer COF is calculated by $\Delta E = E_{\text{COF}} - nE_{\text{Single-Layer-COF}}$; where n is the number of organic layers 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 and reported in the Supporting Information. The binding energy (ΔE) of each TM-intercalated COF was calculated with respect to the pristine COF in Table 2 and plotted in Figure 2a. This plot shows that the ΔE varies non-linearly. Specifically, we found that the ΔE is negative for all these COFs, suggesting that they may be synthesized experimentally, with COF-Ti-5 showing the lowest binding energy (about -67.57 eV). The case of Zn-intercalated COFs (COF-Zn- x) is a special case because ΔE is slightly positive, which suggests that COF-Zn-3, COF-Zn-4 and COF-Zn-5 are not stable thermodynamically at these conditions. Conversely, the negative value of ΔE for all other COFs (i.e. COF-TM- x ; where TM=Sc-Cu and $x=1-3$) predicts exothermic reactions. As a word of caution, the relative energies are calculated with respect to the neutral form of the TM; thus, the binding energies might vary if a different source of TM is used in the experiments.

The detailed structural information of both the pristine and intercalated COFs is listed in Table 1. The framework properties of these materials; surface area (S_A) and pore volume (V_p), have been calculated by rolling a H_2 molecule with an initial diameter of 2.80 Å over the framework’s internal surface. The surface area and pore volume of the COF-TM-x decreased by intercalating TM atoms compared to the pristine analogue except for COF-Zn-4 and COF-Zn-5. Due to the interaction between the organic COF layers and TM atoms, the intercalation distance (d) changes depending on the type of the TM atoms. As with the binding energy, the COF-Zn-x cases present special cases, for example COF-Zn-4 possesses the lowest density, and highest pore volume and accessible surface area (Table 2). These properties of COF-Zn-4 are desirable for gas storage capacity, but this compound is not stable thermodynamically at normal pressure and temperature.

The surface area (S_A), pore volume (V_p) and density (ρ) of the pristine and intercalated COFs are reported in Table 2. Somehow surprising, we found that COF-TM-x (TM = Sc - Zn and x = 3 - 5) have large surface area from around 700-2,000 m²/g (Figure 2b). Likewise, pore volume (V_p) varies between 0.58-1.0 cm³/g and it is mostly monotonically decreasing except for the Zn cases (Figure 2c). The density (ρ) of these COFs is between 1.0-1.6 g/cm³, and the trend is expected, where the more TM the higher the density (Figure 2d), the special case is again Zn, where the volume increases as well which makes them have a smaller density. In general, the surface area and pore volume of COF-TM-x decreased when a larger TM atom was intercalated in the pristine COF. This can be explained by realizing that when one insert TMs in between layers, not all the surface area of the intercalated atom gets exposed because some is already used as interaction sites with the linkers of the COFs. Once again an exception to this trend is the COF-Zn-x, where the trends get reversed, i.e. the more Zn is added the S_A and V_p is increased.

Now we discuss how the ground state electronic properties of the materials are changed by intercalating the first row transition metals. The band structure of these materials were plotted along a high symmetric k -direction in the first Brillouin zone, $\Gamma - K - M - H - A - L -$

Table 2: Properties of COFs: Band gap E_g , binding energy (ΔE), 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 $m^2\ g^{-1}$	V_p $cm^3\ g^{-1}$	ρ $g\ cm^{-3}$	E_g eV	ΔE eV	Material State
COF-pure	1081	0.948	1.055	2.6	-2.84	Insulator
COF-Sc-3	986	0.822	1.216	0	-25.39	Conductor
COF-Sc-4	990	0.786	1.273	0	-29.67	Conductor
COF-Sc-5	945	0.744	1.345	0	-37.44	Conductor
COF-Ti-3	867	0.726	1.377	0	-43.93	Conductor
COF-Ti-4	835	0.698	1.432	0	-53.84	Conductor
COF-Ti-5	798	0.661	1.513	0	-67.57	Conductor
COF-V-3	844	0.790	1.265	0	-21.89	Conductor
COF-V-4	810	0.678	1.475	0	-24.46	Conductor
COF-V-5	765	0.637	1.571	0	-30.55	Conductor
COF-Cr-3	856	0.721	1.387	0	-19.48	Conductor
COF-Cr-4	822	0.637	1.569	0.93	-22.98	Semiconductor
COF-Cr-5	779	0.639	1.565	0.59	-28.39	Semiconductor
COF-Mn-3	876	0.716	1.396	1.71	-2.17	Semiconductor
COF-Mn-4	832	0.696	1.436	0	-0.16	Conductor
COF-Mn-5	793	0.658	1.520	0	-0.12	Conductor
COF-Fe-3	850	0.713	1.403	1.16	-14.47	Semiconductor
COF-Fe-4	791	0.659	1.518	1.12	-17.93	Semiconductor
COF-Fe-5	731	0.609	1.643	1.18	-19.7	Semiconductor
COF-Co-3	829	0.697	1.434	1.21	-8.12	Semiconductor
COF-Co-4	782	0.650	1.538	1.33	-7.82	Semiconductor
COF-Co-5	716	0.606	1.651	1.43	-9.53	Semiconductor
COF-Ni-3	854	0.723	1.384	1.26	-9.38	Semiconductor
COF-Ni-4	837	0.690	1.450	1.94	-12.66	Semiconductor
COF-Ni-5	740	0.618	1.617	1.7	-13.64	Semiconductor
COF-Cu-3	823	0.687	1.455	1.26	-12.93	Semiconductor
COF-Cu-4	765	0.633	1.579	0	-16.01	Conductor
COF-Cu-5	694	0.586	1.707	0	-20.72	Conductor
COF-Zn-3	811	0.696	1.437	0.3	7.32	Semiconductor
COF-Zn-4	2089	1.028	0.973	2.22	1.02	Semiconductor
COF-Zn-5	1144	0.940	1.063	1.93	0.56	Semiconductor

Figure 2: Properties of COF-TM-x *vs.* all first row TMs (COF-TM-x where TM=Sc-Zn and x=3-5): (a) Binding energy (ΔE), (b) Surface area (S_A), (c) Pore volume (V_p), and (d) Density (ρ). Note that “Pristine” indicates the pristine COF or the pure COF without TM.

M – Γ . In the band structure, the energy values are normalized, i.e. they are plotted with respect to the vacuum. Although these COFS has a similar topological structure to graphene, the electronic properties are completely different.^{38,39,50} We found that the pristine bulk COF material behaves like an insulator (Figure 3) with a large band gap of around 2.60 eV (Table 2), which is well below boroxine-linked pristine COF (3.55 eV).^{9,51}

The equilibrium structure of the COF-TM-x (TM=Sc-Mn and x=3-5) materials are shown in Figure 4 and their electronic properties are shown in Figures 5. When the pristine COF was intercalated by Sc, Ti and V atoms are conductors. Specifically, their band structure showed that the valence and conduction bands are overlapped and crossed the E_F

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

(Figure 5a-c). The large electron density around the Fermi Energy level in their DOSs is consistent with a conductor.

An interesting phenomenon was observed in the electronic properties of the COF-Cr-x. The band structures and DOSs found that COF-Cr-3 showed close to a conducting behavior whereas COF-Cr-4 and COF-Cr-5 are semiconductors with a direct band gap (E_g) at the M -point of 0.93 and 0.59 eV, respectively (Figure 5d and Table 2). These results suggest that boroxine and triazine rings are not as effective as benzene rings at sharing electrons with Cr. This is also consistent with the boroxine and triazine rings 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 to form COF-Cr-4 and COF-Cr-5, respectively. The opposite phenomenon was observed in COF-Mn-3, COF-Mn-4 and COF-Mn-5; the more TM in the structure the more conductor the material becomes. COF-Mn-3 is a semiconductor with a band gap of about 1.71 eV, while COF-Mn-4 and COF-Mn-5 are conductors (Figure 5e). However, at this level of theory, the highly correlated electrons effects usually observed in Cr and Mn compounds might not be captured. In general the higher concentration of the TM atoms increases the stability and binding energy (ΔE), however, in the case of COF-Mn-4 and COF-Mn-5, the stability decreased the more Mn are added (Table 2). Among all of COF-TM-x; COF-Ti-5 is the most stable with the highest relative energy as it shows the lowest binding energy among all the TM-intercalated COFs (Figure 4b).

Next, we use the transition metals Fe, Co and Ni atoms for intercalation in the pristine COF (Figure 4f-h and Figure 6a-c). The detailed discussions about the COFs intercalated

Figure 4: Optimized crystal structures of intercalated COFs: (a) COF-Sc-x, (b) COF-Ti-x, (c) COF-V-x, (d) COF-Cr-x, (e) COF-Mn-x, (f) COF-Fe-x, (g) COF-Co-x, (h) COF-Ni-x, (i) COF-Cu-x, and (j) COF-Zn-x; where x=3-5.

Figure 5: The electronic properties calculated for: (a) COF-Sc-x, (b) COF-Ti-x, (c) COF-V-x, (d) COF-Cr-x, and (e) COF-Mn-x. In each inset: (left) band structure, (middle) total density of states (DOSs) and (right) the contribution from the transition metal in the DOSs; “TM d”.

Figure 6: The electronic properties calculated for: (a) COF-Fe-x, (b) COF-Co-x, (c) COF-Ni-x, (d) COF-Cu-x, and (e) COF-Zn-x. In each inset: (left) band structure, (middle) total density of states (DOSs) and (right) the contribution from the transition metal in the DOSs; “TM d”.

with Fe were recently published.⁹ We found that COF-Fe-3 and COF-Fe-4 have an indirect band gap of about 1.16 eV and 1.12 eV, respectively. Their band structure show that their edge bands slightly touch each other about 0.15 - 0.11 eV above E_F in the high symmetric $M-H-A-L-M$ direction accompanied by a large electron density reflected in the total DOSs(Figure 6a). The shape of the conduction band was slightly changed and pushed down towards the E_F in COF-Fe-5 (Figure 6a right-hand side), leading to a small direct band gap of about 1.18 eV. This is well below the value for the pristine 3D-COFs calculated by Lukose et al. (2.3 - 4.2 eV).⁵² The electronic properties of the Co-intercalated COFs (i.e. COF-Co-x; x= 3 - 5) were changed due to intercalation of Co atoms in the pristine COF (Figure 6b), for which the band gap was gradually increasing by increasing the Co concentration in the pristine COF. Similar phenomenon was observed in the electronic properties of the Ni-intercalated COFs (COF-Ni-x; x = 3 - 5) as the E_g was increased gradually from 1.26 to 1.70 eV (Figure 6c), with a more significant 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 6d and 6e, respectively. The band gap of the COF-Cu-3 was found to be about 1.26 eV, which is essentially the same as COF-Ni-3 at the same level of theory. 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 valence bands with higher electron density around the Fermi level (Figure 6d). In a similar fashion to previous compounds, 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. A band gap again appeared in the COFs when the pristine COF was intercalated with Zn atoms (Figure 6e). COF-Zn-3 has a direct band gap at the Γ -point of about 0.30 eV whereas COF-Zn-4 and COF-Zn-5 have E_g of about 2.22 eV and 1.93 eV, respectively, which resemble a large band gap semiconductor or an insulator. This makes COF-Zn-4 the compound with the largest band gap in the COF-TM-x (Table

2). However, the binding energy showed that the Zn-intercalated COFs are not stable as they have positive values of ΔE (Table 2). A possible alternative to make Zn-derivatives thermodynamically stable might be to change the source of Zn atoms or to create the COF-Zn-x materials at higher pressure, specially if applied along the crystallographic z-axis.

We have further investigated the contribution of the *d*-orbitals of the first row TM atoms in the total DOS of all the designed COF-TM-x (TM=Sc-Zn and x=3-5). The large electron density around the E_F is due largely to the *d*-subshell electrons of all the TM atoms (right-hand side of Figure 5 - 6). In other words, all the TM atoms modify the band structure of the COFs. The TM atoms caused the COFs to become semiconductors or even conductors by pushing down the conduction bands toward the Fermi level. Additionally, not all the intercalations are the same, i.e. intercalation between benzene rings makes the TM to interact more with the COFs structures. This effect is less prominent when the TM is placed between triazine rings followed by boroxine rings. Thus, this work shows that the first-row TM atoms intercalated in pristine COFs are playing the main role to tune the electronic as well as structure properties.

The purpose of this work is to predict the properties of first-row TM-intercalated COFs; COF-TM-x (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 most of these materials are stable, which suggest their possible synthesis. The frequency analysis and binding energy have been shown to be reliable quantities to predict material stability and synthesis.^{20,32,38,39} Hence, we expect that these TM-intercalated COFs to be readily fabricated experimentally by first row TM atoms intercalation between weakly bound COF layers, except for Zn. Although Ca-intercalated COFs were reported in the past, no transition metal was used. In the Ca-intercalated COFs, Meng and co-workers²⁷ used benzene and boroxine linkers and they proposed that Ca-intercalated COFs could be useful for H₂ storage materials. In the current work, we used triazine organic linkers in the design of the new materials, and we studied the electronic properties by using first prin-

ciples quantum mechanical calculations rather than force field methods. Additionally, our new materials are not intended for H₂ storage, but rather for increasing the conductivity and reducing the band gap in COFs by tuning the structure-property relationships. For this purpose, we proposed that many first row TM intercalated in COFs may be useful to obtain small band gap materials, which is an important property that has been lacking in crystalline porous materials. We designed these compounds with the triazine included because it has π electrons to facilitate orbital overlap with the d -orbitals of TMs and electron conductivity, while the boroxine ring does not have a high level of π electrons. We hypothesized that the intercalation of transition metal atoms would also improve the conductivity of COFs by injecting some of the d -electron density into the periodic system. These two components (triazine and all first row TM atoms) form a unique idea which can be used as a way to improve conductivity and stability in nanoporous materials. In other words, benzene (C₆H₆) and triazine (C₃N₃) rings are more useful to tune properties, than boroxine (B₃O₃) rings. However, the major factor is the identify of the TM intercalated in the COFs, which controls the electronic properties and the distance between layers. The ongoing search for crystalline porous materials such COFs that are good semiconductors or conductors is of paramount importance if these materials are to be used as chemical sensors due to their surface area or other applications that require highly porous conductors.

The result for the new proposed materials that intercalates first-row TM atoms is a promising way to tune the band gap from large to small. Our findings suggest a new type of porous materials having entirely different electronic properties compared to pristine porous material. In other words, the present study shows how the insulating pristine COF is converted to a direct band gap semiconductor or even a conductor when intercalating the right TM atom. The main contributing component in the total DOSs was the d -subshell electron density of TM. This approach of intercalation of TM broadens the scope and complexity of nanoporous COF, 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 might be suitable for semiconducting applications.

CONCLUSIONS

In conclusion, we have presented the intercalation of TMs inside COFs as a strategy to dictate the structural changes and intrinsic electronic properties of the porous material. Specifically, we have designed 31 new COF materials belonging to a new class of porous crystalline COFs by intercalating first-row transition metal atoms (COF-TM- x , where TM=Sc-Zn and $x=3-5$) inside the pristine COF using first-principles calculations. These TM-intercalated COFs have well-defined crystal structures and most of them are predicted to be thermodynamically stable. The structural and electronic properties of these new kind of materials are reported. We have carried out a systematic study of their stability and found that the more TMs are added in the COFs and the compound becomes more stable. Transition metal atoms prefer to bind to aromatic organic units i.e. benzene (C_6H_6) followed by triazine (C_3N_3) and boroxine (B_3O_3) connecting rings in the COF-TM- x . Intercalation compounds allow incorporation or exchange of external atoms into the voids of the host lattices in two-dimensional space and represent an important frontier in solid state chemistry. The structural diversity of these solids gives rise to a vast array of applications. Our work suggests that TM atoms intercalation is a promising approach for converting an insulating COF to a semiconductor or conductor porous material. None of the materials studied here have been synthesized experimentally, however, the calculated vibrational frequencies and binding energies predict that most of these materials are stable, which has been proven as enough evidence for likely synthesis in previous work. Understanding the properties and behavior of intercalated-COF materials will allow us to improve design principles for other applications in the near future.

For the structure-property relationship, the method of intercalating TM is another approach to rationally design the structure, the band structure, density of states, and Fermi energy level. We envisage that this new class of porous crystalline materials, with a high

density of active metal sites, could prove useful in a variety of future applications including as a electrical or chemical sensors, and as thermoelectrics. The open metal sites might also serve as additional catalytic sites for unexplored chemical reactions. Intercalation of TM has extensive potential for extending the design space of materials and will promote further research in porous materials. We predict this approach will serve to synthesize a new generations of COFs with the next frontier being COFs made of hetero-structures and co-intercalation of multi-TMs.

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Supporting Information: Equilibrium structures with the unit cell of the pristine and 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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