B. TECH. PROJECT REPORT On A Computational Study of Porous

Structure Metal-Organic Frameworks and Covalent-Organic Frameworks

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A Computational Study of Porous Structure Metal-Organic Frameworks and Covalent-Organic Frameworks

A PROJECT REPORT

Submitted in partial fulfillment of the requirements for the award of the degrees

of BACHELOR OF TECHNOLOGY in METALLURGY ENGINEERING AND MATERIALS SCIENCE

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CANDIDATE'S DECLARATION

We hereby declare that the project entitled "A Computational Study of Porous Structure Metal-Organic Frameworks and Covalent-Organic Frameworks" submitted in partial fulfillment for the award of the degree of Bachelor of Technology in Metallurgy Engineering and Materials Science (MEMS) completed under the supervision of Dr. Mrigendra Dubey and Dr. Srimanta Pakhira, IIT Indore is an authentic work.

Further, I declare that I have not submitted this work for the award of any other degree elsewhere.

Signature and name of the student(s) with date

CERTIFICATE by BTP Guide(s)

It is certified that the above statement made by the students is correct to the best of my/our knowledge.

Signature of BTP Guide(s) with dates and their designation

Preface

This report on "A Computational Study of Porous Structure Metal-Organic Frameworks and Covalent-Organic Frameworks" is prepared under the guidance of Dr. Mrigendra Dubey and Dr. Srimanta Pakhira .

Through this report we have studied Porous materials such as Metal Organic Frameworks and Covalent Organic Frameworks computationally, and tried to suggest a method to have better control over certain properties by tweaking the design of the frameworks. In MOFs, we have suggested a method to improve the adsorption capacity of the MOF. Whereas in COFs, we have tried to investigate the electronic properties of COFs by intercalating earth-abundant elements.

I have tried to the best of our abilities and knowledge to explain the content in a lucid manner. I have also added figures and results to make it more illustrative.

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B.Tech. IV Year Discipline of Metallurgical Engineering and Materials Science IIT Indore

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<u>Abstract</u>

Metal-organic frameworks (MOFs) are a new kind of solid porous materials built from metal cations and organic bridging linkers or ligands. We considered a model MOF system using various organic linkers with Zn2+ cations, and studied their equilibrium geometry, structure, potential energy curves (PECs),rotational dynamics, and rotational barriers of the linkers by employing first-principles based DFT methods. We investigated the rotational and dynamical behaviors of the organic linkers in the MOFs. We found that the structural parameters and rotational barrier of the model MOF containing 1,4-benzendicarboxylate (BDC) linker are in excellent agreement with previous experiments. The present computation found that the rotational energy barriers differ considerably depending on the linkers and the substituent effects on them. We envisage that this new class of MOFs with small rotational energy barrier will be beneficial in a variety of applications including H_2 -storage, gas-storage and separation, adsorption, sensors, and many others.

Covalent Organic Frameworks (COFs) have emerged as the new class of nano-porous crystalline materials with applications across various areas of science and technology. The ability of COFs to enable the elaborate integration of organic building blocks into an ordered structure with atomic precision makes them an intriguing platform for the design of porous skeletons with special functionality at the molecular level. Despite the structural tunability of COFs, it is difficult to control their electronic properties. COFs intercalated with Fe atoms is proposed to address this lack of tunability of electronic properties. Using first-principle calculations, we designed new COFs by intercalating Fe atoms between two layers of the COF. For the COF, 1,4benzenediboronic acid (BDBA) is used as the organic linker along BO2C2 rings with benzene and trazine rings. The structural and electrical properties of both the pristine and Fe-intercalated COFs were investigated. The band gap and density of states (DOS) of the COFs were computed and we predict that these properties can be fine-tuned by the concentration of Fe. It was found that the role of d-subshell electron density of Fe plays a main role in altering the electronic properties of COFs. A new strategy to control the electronic properties of crystalline porous materials by intercalated-COFs is studied and this opens up the door for applications of crystalline porous materials in nanoporous electronic devices. We have computationally investigated porous MOFs and COFs and suggested strategies which may lead to applications of porous materials in various directions.

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Chapter 1

Introduction :

In this project, we have computationally studied Metal Organic Frameworks and Covalent Organic Frameworks and how changing their structure can affect certain material and electrical properties.

Metal-organic frameworks (MOFs) are a new kind of solid porous materials built from metal cations and organic bridging linkers or ligands. Recently, metal-organic frameworks (in short MOFs) have appeared as a widespread class of porous crystalline materials consisting of metal cations or clusters coordinated to organic bridging ligands/linkers or rotational groups, which form extended crystalline network structures; i. e. the organic ligands/units link to the inorganic building units to form well-defined porous network structures. These MOF materials have garnered attention and research interest in modern porous materials science over the last decade as exciting nanoporous materials because of their high structural regularity, high porosity and pore volume, their ultrahigh specific surface area, tailorable pore size and structural flexibility, which can find a large number of potential applications in many areas of materials science and nanoscience.[1–4] Due to the high pore volume along with sizable pore areas of these MOF materials, the guest molecules can absorb into their internal surfaces, and lead to reflection on enormous potential applications such as catalysis, gas storage (especially hydrogen storage), gas adsorption, energy storage, CO2 capture, selective gas separation, water purifications, sensing, molecular recognition, control of chemical reaction in MOF channels, radical polymerization in MOF nano-channels, drug adsorption, drug delivery, etc.[5-8] It has been observed that these MOF materials can be used to test the effect of pore size and functionality on the capacity of H₂-storage in hydrogen fuel cell (HFC) due to their adjustable porous structure and unparalleled strength. Therefore, the versatile nature of MOFs chemistry by altering the organic bridging ligands or linkers and metal cations can be considered for allowing various functionalities and pore dimensions, which needs to be obtained.

In the 20th century, the field of organic chemistry faced a challenge, the synthesis of crystalline extended 2D and 3D organic solids. This was an under-developed area of research until 2005, when Omar M. Yaghi and coworkers reported the first crystalline extended organic frameworks using reticular chemistry. These frameworks were the first ones to be synthesised of what are known as COFs today. COFs contain Earth abundant elements (such as H, B, C, N and O) and combine the functionality of organic units with the strength of covalent bonds. COFs are constructed from light elements and hence offer low density. In COFs, large rigid polyatomic molecules are used as linkers, and strong covalent bonds between the linkers leads to porous structures with high internal surface area and low density. COFs show enhanced stability compared to MOFs because of the presence of robust covalent bonds in their structure. An attractive feature of COF is that it gives more control to synthesize crystalline, extended, nano-porous materials by making use of basic organic building units. Due to its low density, high porosity, stability and its modularity, COFs have found importance in the applications such as Gas Storage/Separations, Catalysis, Environmental Remediation, Sensors, solid state batteries, Optoelectronics. In addition, COFs also drive electronic interactions between the nearest neighbouring sheets due to their π -stacked layer structures. However, due to low intrinsic conductivity and charge-carrier mobility of COFs, it is difficult to control their electronic properties. Due to this, controlling their band gap and optical properties at the atomic scale has been a difficult task.

Problem Definition :

In the last few years, many kinds of MOF materials were prepared and their properties investigated both experimentally and theoretically, where the linkers were used to bridge with the inorganic building units.[9,10] Recently Chun et al.[9] synthesized a new kind of MOF with different aromatic di-carboxylates

organic ligands or linkers. They experimentally determined the structure and showed the storage capacity of H2 molecules inside the MOFs. In short, 1,4-benzenedicarboxylate (BDC), a simple organic linker, was used to construct MOFs. It was observed that the BDC linker of both MOFs has a planar conformation. The breathing behavior of the [$Zn_2(BDC)_2DABCO$] MOF in presence of guest molecules such as C_6H_6

(benzene) and C_3H_8O (propan-2-ol) was investigated both experimentally and theoretically or computationally as well,[17–19] and moreover density functional theory(DFT) based molecular mechanical (MM) force field parameters of this MOF were used in molecular dynamics (MD) simulations to explain the breathing behavior.[18] So, the dynamical behavior of various organic linkers or bridging ligands in MOF materials should play an important role in controlling the pore size, pore volume, and gas storage capacity. In the last decade, a novel type of MOF materials denoted by $[M_2(X)_2DABCO]$, (where M is Cu or Zn, and X is organic linker) were experimentally prepared by introducing various substituent groups onto the organic bridging linkers or bulkier rotational groups. It has been observed that the crystal structure and frameworks

the MOFs. Recently, Pakhira et al. computationally studied the rotational barrier of the $[Zn_2(1,4-NDC)_2(DABCO)]$ MOF considering a model system with an artificial rigid constraint planar structure, and they found that the barrier is about 30 kJ/mol lower than experimental value. Therefore, it seems that the constraint planar rigid structure of the $[Zn_2(1,4-NDC)_2(DABCO)]$ MOF is not suitable to find out its rotational barrier, and there is no other computational work to support the previous experimental

properties of these kinds of MOFs completely depend on the organic linkers and metal-ions in

observations of the rotational energy barrier of the NDC linker in MOFs.

As mentioned in the introduction, controlling the band gap and optical properties at the atomic scale has been a difficult task. To address this challenge, Zhu and Meunier studied the electronic properties of 2D COFs and they showed that their band gap can be fine-tuned by appropriate modifications of their structures, specifically by increasing organic chain-links in the framework. Meng and his coworkers proposed Calcium-intercalated COF (Ca-COF) and they used DFT methods to compute equilibrium structures and density of states (DOSs) of the Ca-COF. They found that this Ca-COF is useful for H2 storage. However, we suggest that, instead of modifying the COF structures or increasing the organic linkers in the frameworks, we intercalate Fe atoms between the organic layers in COFs to tune the electronic properties by controlling the Fermi energy level (E_f). In this work, 1,4-benzenediboronic acid (BDBA) is used as the organic linker along BO₂C₂ rings. Both the modelling and quantum chemical calculations lead to a deeper understanding of many phenomena found in porous framework materials and are becoming increasingly important for both the discovery of new materials and the understanding of their properties. Using DFT-D, we computationally studied how their structure (intercalation distances, bond lengths, and ring geometries; see Fig. 1 and Scheme 1) and electronic properties (band structures, density of states (DOS), and band gaps; see Fig. 2) were changed due to the intercalation of Fe atoms. The electronic properties of COFs are tuned by intercalating Fe atoms between the two organic layers in the pure COF, while keeping the same space group symmetry.

Objectives:

To the best of our knowledge, there is no detailed study of the electronic structure calculations, rotational and dynamical behaviour of various kinds of MOFs considering a model system containing Zn^{2+} metal cations and different kinds of organic linkers. The main motivation to advance MOF material applications is the development of new pathways and strategies to construct novel types of MOFs as platforms suitable for the desired application in modern materials science. Towards this effort, we have developed a new approach for construction of MOFs based on the rigid organic ligands or linkers and metal cations. We computationally investigated the equilibrium geometry, electronic structure, stability, flexibility, potential energy curves (PECs), and rotational barrier energy of seven types of various organic linkers (the linkers are BDC, DFBDC^I, DFBDC^{II}, TFBDC, DMBDC, DBrBDC and NDC) in the [Zn₂(X₂)DABCO] MOFs. In these cases, the computational studies are carried out by considering a model MOF system noted as [Zn₂(X)₂(Y)₆(NH₃)₄], where X = rotational group, and Y= (HCO₂) due to their big size.

As mentioned in the previous section, due to the limited research in exploring the structure-property relationships of COFs, especially electronic properties, using DFT, we computationally study, how intercalation of Fe atoms between the two organic layers of a COF can be used to tune the electronic and material properties of the material. We analyse the effect of intercalating Fe atoms on the crystal structures by calculating their electrical and material properties such as band gap, density, pore volume, etc. of different COFs. The role of d-subshells electron density of the Fe atoms in improving the semi-conducting properties of the new materials is also analyzed. These materials would have interesting applications in nanoporous materials, electronic devices and thermoelectric materials if they can be fabricated.

Chapter 2 :

Methodology:

Metal Organic Frameworks :

The equilibrium structures, geometries, calculations of energetics and rotational barriers of various linkers in the MOF model system $[Zn_2(X)_2(Y)_6(NH_3)_4]$, (where X is organic linkers such as BDC, DFBDC^I, DFBDC^{II}, TFBDC, DBrBDC, DMBDC and NDC and Y = (HCO₂), were computed by using hybrid density functional theory (DFT) B3LYP and M06-2X methods with cc-pVDZ type Gaussian basis set for C, H, N, O and F atoms, and cc-pVDZ-pp basis set for both Zn and Br atoms. Frequency (i. e. harmonic vibrational analysis) and thermodynamic calculations were done to get the Gibbs free energy and Zero-Point vibrational Energy (ZPE) using the same methods and basis sets. To reduce the spin contamination effects in the present calculations, the DFT methods were used for all the computations studied here. The lattice constant along the direction of MOF nanochannel, Zn1-Zn2, Zn3-Zn4 and N-N distances; and other distances such as Zn1-Zn3 and Zn2-Zn4, and O-Zn-O-C dihedral angles were fixed during the optimization to keep the MOF structure without any distortion. The negative frequencies i. e. imaginary frequencies were cautiously eliminated i.e. structures are optimized and confirmed to be a minimum on the potential energy curves with zero negative eigen value of the Hessian matrix.



Figure 2.1. The equilibrium optimized structures of the model MOFs containing (A) 1,4-benzenedicarboxylate (BDC)

Optimizing the MOFs, the rotational energy barriers were estimated for those model systems as depicted in Figure 1, by using the same B3LYP and M06-2X DFT methods and basis sets as accomplished in the suite code Gaussian 09. The rotation of the organic bridging linkers in the MOFs is defined as a continuous transition where the three-dimensional arrangement of an organic linker is transformed by tuning around a rotational axis i.e. along the axis of MOF nanochannels. The initial geometry optimization gave eclipsed Zn clusters at

the two ends of those MOF models. Then the organic linkers are rotated around the Zn cluster-cluster axis (dihedral angle χ (C1-C2-C3-O1) as shown in Figure 1) to scan the potential energy curves (PECs) and the dihedral angle χ in the range of 0° to 90° with 5.0° increments relative to the clusters constrained to remain eclipsed. During the scan, all the degrees of freedom were relaxed with the dihedral angle constraint. This relaxed scan was performed to compute the PECs and to find out the most stable and unstable structure of the aforementioned model MOFs with BDC, DFBDCI, DFBDCII, TFBDC, DMBDC, DBrBDC, and NDC organic linkers. The rotational barrier was computed as the energy difference between the most stable and unstable states as followed by the works of Pakhira et al.

Covalent Organic Frameworks

Calculations of energetics, geometry and electronic properties of the pure COF and COF-Fe-x, (where x = 4,6,7) were performed using first-principles calculations at the level of unrestricted DFT with the Grimme's dispersion correction i.e. hybrid B3LYP-D2 method as implemented in the ab initio CRYSTAL17 suite code. In summary, we have used dispersion corrected unrestricted hybrid DFT with the B3LYP functional. The convergence of energy, electron density and forces were set to 10-7 a.u. for all geometry optimizations. The mathematical expression used to calculate the binding energy, ΔE , is given below:

 $\Delta E = E_{\text{COF}-\text{Fe}=0} - nE_{\text{Fe}};$



Figure 2.2: Optimized crystal structures of the a) Pure COF and b) COF-Fe-4A

where n is the number of Fe atoms intercalated in the COFs. The harmonic vibrational frequencies at the optimized geometries were analyzed to verify the stable structure. This method was used for geometry optimization because the densities and energies obtained by the method are less affected by spin contamination than those by other approaches, and it has been proved effective for related materials calculations. The Fe atoms were intercalated between the organic layers of the pure COFs to make a sandwichlike structure. During

the intercalation process, we have maintained the original hexagonal symmetry of the pure COF. The electronic properties of these materials were calculated at the optimized equilibrium structures of the pure COF and intercalated-COF materials using the same level of theory (i.e. UB3LYP-D2). The total DOSs was plotted using the atomic orbitals of carbon (C), hydrogen (H), nitrogen (N), boron (B), oxygen (O), and intercalated iron (Fe) atoms. The DOSs of the d-subshells of Fe atoms were computed and plotted to investigate the contribution of the d-subshell electron density of the intercalated Fe atoms in the total DOSs. Visualization and analysis were performed using VESTA. These materials are thermodynamically stable at room temperature according to their vibrational analysis, i.e. there are no negative or imaginary frequencies. The binding energy is negative, which shows that their formation is favorable.

Chapter 3:

Results and Discussions:

Metal Organic Frameworks:

The optimized structural parameters of the model MOFs: $Zn_4(BDC)(HCO_2)_6(NH_3)_4$ Zn₄(DFBDCI)(HCO₂)₆(NH₃), Zn₄(DFBDC^{II})(HCO₂)₆(NH₃)₄, $Zn_4(TFBDC)(HCO_2)_6(NH_3)_4$, Zn₄(DBrBDC)(HCO₂)₆(NH₃)₄, Zn₄(DMBDC)(HCO₂)₆(NH₃)₄, and Zn₄(NDC)(HCO₂)₆(NH₃)₄ computed with the first-principles based DFT B3LYP and M06-2X methods, are tabulated in Table 1 along with the earlier reported theoretical and experimental values for comparison wherever available. The equilibrium optimized geometries of the model MOFs containing BDC and TFBDC organic linkers obtained by B3LYP method are shown in Figure 2.1. The present study found that the model MOF containing BDC linker is the most stable planar structure with the dihedral angle (c (C1-C2-C3-O1)) of the BDC ligand with respect to the metal ligands is 0.0°.

Organic		Computatio	Others			
linkers in MOFs	Rotational energy barrier at 90.0°		Rotational energy barrier at 0.0°		Expt.	Theo.
	B3LYP	M06-2X	B3LYP	M06-2X		
BDC	56.54	62.24	—	—	47.5±8.4 ^a	51.04-60.67 ^b
DFBDC ^I	43.62	55.43	—	—	—	
DFBDC ^{II}	46.40	52.36	—	—	—	—
TFBDC	15.30	17.40	16.20	10.70	—	—
DBrBDC	30.19	47.13	7.72	3.86		
DMBDC	30.80	38.70	1.10	1.20	_	
NDC	53 70	55 51	54 20	61.07	53°	

Table 1: The rotational barriers of various organic linkers in the model MOFs. (The energy barriers are expressed in kJmol⁻¹.)

^aReference 22 (In IRMOF-1), ^bReference 23 (In IRMOF-1 model system), ^cReference 24 and 25.

The optimized dihedral angles c(C1-C2-C3-O1) of aforementioned model MOFs calculated using both DFTs are reported in Table 2 along with the earlier experimental results of Matsuda et al. to draw a comparison. Here, it should be mentioned that the experiment was achieved by using Cu metal cations instead of Zn ions with the same types of organic linkers in the MOFs. The present computation found that the equilibrium dihedral angle c of the organic linkers BDC, DFBDC^I, and DFBDC^{II} in the model MOF materials computed at both the levels of theory, B3LYP and M06-2X, is 0.0° which reveals that these three organic bridging linkers are situated in the same plane with the Zn-cation clusters. This study shows that these MOF structures are very similar to the MOFs containing Cu metal cations. The dihedral angle of the model MOF containing TFBDC computed at B3LYP overestimates the experimental values by about 4.0° whereas the value calculated at M06-

2X level of theory is well harmonized with the experiment. To the best of our knowledge, there is no experimental study of the MOFs containing DBrBDC and DMBDC organic linkers for comparison, whereas Pakhira et al. computationally studied these two model MOFs considering rigid planar constraints structure. The dihedral angles of the DMBDC in the model MOF containing DMBDC computed at both levels of theory are the same as the model MOF containing DBrBDC computed at M06-2X level. The B3LYP and M06-2X DFTs tend to underestimate the dihedral angle of the model MOF containing NDC about 12.0° with the experimental value.

Rotational Behaviour and Energy Barrier of the Organic Linkers in the Model MOFs :

The rotational energy barriers of these model MOFs with the above mentioned organic linkers calculated by the B3LYP and M06-2X DFT methods are reported in Table 3. The potential energy curves (PECs) of the BDC and TFBDC linkers obtained by the B3LYP methods are depicted in Figure, revealing the most stable and unstable positions of these two organic linkers in MOFs. Our present computation found the stable structure of the BDC linker containing model MOF is planar i. e. the dihedral angle (χ (C1-C2-C3-O1)) with respect to the Zn_2^+ cluster metal cations of BDC linker is zero as depicted in Figure. On the other hand, the stable structure of the model MOF containing TFBDC linker is non-planar and the equilibrium dihedral angle χ is about 36.0°, as shown in below Figures. The B3LYP and M06-2X PECs of the model MOF containing BDC show that it has only one unstable point at the dihedral angle 90.0°. The rotational barrier energy of the BDC linker computed by both the B3LYP and M06-2X methods agrees with the earlier experimental value of Gould et al. and the theoretical value of Winston et al. Similarly, the model MOFs containing DFBDCI and DFBDCII have only one stable and one unstable state at the dihedral angles 0.0° and 90.0°, respectively. The present computational study reveals that the distances (Zn1-Zn2, Zn-Zn and Zn-O) and angles (Zn-O-C2 and O-Zn-O) of the MOFs containing various linkers such as BDC, DFBDC, TFBDC, DMBDC, DBrBDC, and NDC linkers do not differ significantly with substitution or replacement of the organic linkers or rotational groups. The stable structures of the model MOFs containing BDC, DFBDC^I, and DFBDCII are planar i. e. the dihedral angle of the aforementioned organic linkers in the model MOFs is zero. This is due to several hydrogen bond (O…H) interactions between the H atoms in benzene and O atoms in carboxylate groups; see Figure 1A, Meanwhile, in the model MOFs containing DFBDC^I, DFBDC^{II}, and TFBDC, there is also a strong electrostatic repulsion force between the fluorine (F) atoms in the linkers or rotational groups (i. e. DFBDC^I, DFBDC^{II}, and TFBDC) and oxygen (O) atoms in the carboxylate groups. Due to this strong repulsion between these O and F atoms in the TFBDC linker, it is inclined at about a 36.0° angle. Similarly, there is a solid electrostatic repulsion force between the O and Br atoms in the DBrBDC linker of the model MOF.

Organic Bridging	Meth	nods	Others	
Linkers in MOFs	B3LYP	M06-2X	Expt. ^{†a}	
BDC	0.0	0.0	0.0	
DFBDC ^I	0.0	0.0	0.0	
DFBDC ^{II}	0.0	0.0	0.0	
TFBDC	40.4	35.8	36.0	
DBrBDC	27.2	20.6	—	
DMBDC	19.5	18.8	_	
NDC	36.9	36.1	49.0	

Table 2. The optimized dihedral angle of all the model MOFs containing different kinds of organic bridging linkers with respect to Zn cluster-cluster axis. (The dihedral angles (γ) were expressed in degrees.)

Strong electrostatic repulsion forces have many important roles in determining the equilibrium structure of the model MOF materials containing NDC organic linker. The strong electrostatic repulsion force acts between the C atoms in the naphthalene ring (i. e. NDC linker) and O atoms in the carboxylate groups, and there are strong vdW repulsion forces between the C and H atoms in the naphthalene and several O atoms in the ligands. There are several kinds of vdW interactions between H, O, and C atoms in the linkers (here NDC) and carboxylate groups in the model MOFs.



Figure 3.1. (A) Potential energy curve (PEC) i. e. the scan of the PEC of the rotation of the BDC organic linker in the model MOF computed at the B3LYP level of theory; (B) PEC of the model MOF containing TFBDC computed at the B3LYP level of theory. The rotational dihedral angle χ vs. relative energy has been plotted for both the BDC and TFBDC linkers at the B3LYP level of theory.

Diversity of Rotational Energy Barrier :

This study reveals that the rotational energy barriers are independent of the position of the substituted H atoms by F atoms inside the organic linkers of both the model MOF materials. The B3LYP barrier at 90.0° of the MOFs containing DBrBDC and DMBDC are almost the same. The barriers of the model MOF containing

DMBDC at 0.0° are very small and lie below the chemical accuracy. The present theoretical investigation displays that the rotational barrier of both the BDC and NDC linkers is almost equal. The modification of the ligands or linkers with substituent groups can change not only the electrostatic effect and equilibrium structure but also the rotational energy barrier of the organic bridging linker or bulkier rotational group in the MOFs. Therefore, we can say that the rotational barrier notably fluctuates between 15–56 kJ/mol according to the linkers. It is clear from the study that the hydrogen substitution by other atom or group in the BDC rotational linker plays a vibrant role in determining the barrier in the model MOFs, which provides an important information of the flexibility of the MOF materials. In other words, if the linkers in MOFs have higher values of rotational energy barriers, then the MOFs is less flexible. It indicates that rotational barrier governs the flexibility of the linkers in MOFs. The rotation of the organic bridging linkers is one of the most important properties of flexible MOFs, as it solely controls the property of flexibility of MOF materials. It has been shown that the rotation of the organic linkers starts the expansion of the pore windows, i. e. pore size and pore volume in MOFs, and some in cases the size of adsorbed molecules was greater than anticipated from the MOFs. The rotation of organic bridging linkers in the MOFs has a strong influence on the gas storage and selectivity of various guest molecules, and also it controls the breathing behaviour of porous MOF materials. During the rotation of linkers in MOFs, the core framework remains stable, i. e. the crystal structure of MOFs is not affected by the rotation of linkers and it only causes the expansion of pore windows of MOFs.

Thus, this computational study suggests that MOF materials can be synthesized with a variety of pore volumes/sizes by altering the organic linkers for specific applications while keeping the permanent framework. The present study shows that the MOFs with TFBDC linker are the most flexible among all the MOFs studied here as TFBDC linker has the lowest rotational barrier. Here, we used two DFT methods B3LYP and M06-2X to study the model MOF systems and compute the structural parameters and rotational barriers. The computed values obtained by both the DFT methods are well harmonized with the previous experiment and theory wherever available.

Covalent Organic Frameworks :

The crystal structures of Pure COF and Fe-intercalated COFs, COF-Fe-3, COF-Fe-4A, COF-Fe4B were optimized. The final material consisted of connecting one triazine, benzene and BO_2C_2 in the one-unit cell with the P6-m2 space group symmetry. Fe atoms were intercalated between the organic layers of the pristine COFs to make a sandwich-like structure, while maintaining the original hexagonal symmetry of the pristine COF. The Fe atoms are placed at the centroid of the respective rings. These materials are thermodynamically stable at room temperature according to their vibrational analysis, i.e. there are no negative or imaginary frequencies. The P–6m2 space group symmetry of the pure COF was maintained even after intercalation of Fe atoms. The designed COFs were found to be energetically stable. Structural properties such as the equilibrium

lattice constants (a, b, c), various average equilibrium bond distances (C-C, B-O, C-B, C-N) and the average distance between two layers i.e. intercalation distance (d) were measured to compare the basic electronic structures and properties of the COFs and are reported in Table 1. In the Fe-intercalated COFs, the contribution by the d-subshells of Fe atoms to the electron density was also computed and is plotted in Figure 2 (b), (c), (d). The band structure was plotted along a high symmetric k-direction in the first Brillouin zone, given by $\Gamma - K - M - H - A - L - M - \Gamma$. In all the figures, Fermi level was normalized to 0 and bands were adjusted accordingly. As observed from the band gap plot, COF-pure was found to have a band gap of 1.99 eV. For Pristine COF, Fermi level was found to be closer to the Valence band. However, the intercalation of Fe atoms caused the alteration of band gap of other COFs.



(b)



Figure 3.2: Optimized crystal structures, band structure and DOSs of a) Pristine-COF, b) COF-Fe-4A and c) COF-Fe-6 and d) COF-Fe-7 materials. The Fe atom was intercalated in order to keep the hexagonal P - 6m2 symmetry of the Fe-intercalated COFs. (Green-Boron, Red-Oxygen, Brown-Carbon, Blue-Nitrogen, Pink-Hydrogen)

In COF-Fe-4A, 2 Fe atoms each were intercalated between layers of Benzene and Triazine rings. This saw a decrease in band gap value by 0.6 eV compared to Pristine COF and Fe d-subshell contributed to the total DOS. Valence band was pushed further away from the Fermi level. In the case of COF-Fe-6, 6 Fe atoms were intercalated between layers of Benzene rings in a unit cell. Band gap value dropped to 1.33 eV and Fe-d

subshell contribution to the total DOS was observed again. Valence band was pushed further away from the fermi level and conduction band almost intersected with Fermi Level. The Fermi Level intersected with the valence band, making it a conductor. The high electron density around E_f is also accompanied by a high DOSs in the d-subshell electrons. Thus, the Fe atoms caused the COFs to become semiconductors. Finally, in the case of COF-Fe-7, the effect of Fe-d subshell contribution was observed yet again, where 7 Fe atoms were intercalated between layers of the COF in a unit cell. As per the calculations for the vibrational frequencies and binding energies, the designed materials are stable. This suggests that the synthesis of Fe-intercalated COFs for semiconductor applications is feasible, although it's never been carried out before. As previously shown by Meng and co-workers, Ca-intercalated COFs using benzene and Borozine linkers can be used for H₂ storage applications. The currently designed Fe-intercalated COFs are intended for semiconductor applications using crystalline porous materials, not H₂ storage.

Chapter 4 :

Conclusions and Future Scope:

We computationally developed a model system of MOF materials $[Zn_2(X)_2(Y)_6(NH_3)_4]$, (where X is organic linkers such as BDC, DFBDC^I DFBDC^{II}, TFBDC, DBrBDC, DMBDC and NDC and Y = (HCO₂)) with various types of organic linkers to investigate the equilibrium geometry, PECs, stability, and rotational barriers of the linkers by using DFT methods with the correlation consistent double ζ -quality gaussian basis sets. Our calculated frameworks and structural properties of the BDC linker in MOF agree with the earlier reported results. Rotational barriers computed at B3LYP level of theory of the model MOF containing BDC linker is in accord with previous experiment and theory. From the results, we can deduce the following conclusion: the rotational energy barrier decreases due to hydrogen substitutions by the heavier halogen atoms (F and Br) and –OCH3 group in the organic linkers has a central role in determining the rotational barriers of the MOFs studied here. This conclusion helps to better understand the rotation of the organic linkers in the MOFs and the effect of the substituents onto the linkers. We can say that the present work also offers a general perspective of rational design of MOFs by substituting organic linkers with expected high porosities and functionalities.

COFs were designed in which Fe atoms were intercalated between layers of pristine COFs. Using dispersioncorrected unrestricted hybrid DFT methods, the structure and electronic properties of the newly designed COFs were studied. It was found that Fe-intercalation is a good approach to tune the band gap of the COF while maintaining the original symmetry of the pristine COFs. Intercalation of pristine COFs by Fe atoms gave rise to entirely different electronic properties from the pristine crystalline porous materials. Increase in intercalation distance, pore volume was observed when Fe atoms were intercalated between BO₂C₂ rings. Fe-intercalation between Benzene and Triazine rings led to decrease in Band Gap value relative to Pristine COFs. The designed COFs had a reduced the band gap compared to the pristine COFs, making them semiconductors at room temperature. It was observed that the Fe-d subshell contribution to the Total DOS was high, showing that intercalation of Fe atoms is affecting the electronic properties of the COFs. This indicates that Fe intercalation is a promising approach for converting an insulating pristine COF to semiconducting porous materials for device applications based on its electronic properties. Further investigation will focus on increasing the number of intercalated Fe atoms per unit cell and examining their effect on structural and electronic properties.

Publications

N. Sinha, I. Deshpande and S. Pakhira., Substituents Effects of Organic Linkers on Rotational Energy Barriers in Metal-Organic Frameworks, *Chemistry Select*, Vol 9, Issue 29, 2019

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