

**T.R.**  
**GEBZE TECHNICAL UNIVERSITY**  
**GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES**

**THEORETICAL STUDY OF THERMOELECTRIC PROPERTIES OF  
COVALENT ORGANIC FRAMEWORKS**

**GÖKHAN BAYRAM**  
**A THESIS SUBMITTED FOR THE DEGREE OF**  
**DOCTOR OF PHILOSOPHY**  
**DEPARTMENT OF PHYSICS**

**GEBZE**

**2021**

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**THESIS SUPERVISOR**  
**PROF. DR. YURII CHUMAKOV**

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**2021**

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**GEBZE TEKNİK ÜNİVERSİTESİ**  
**FEN BİLİMLERİ ENSTİTÜSÜ**

**KOVALENT ORGANİK ÇERÇEVELERİN**  
**TERMoeLEKTRİK ÖZELLİKLERİNİN**  
**TEORİK İNCELENMESİ**

**GÖKHAN BAYRAM**  
**DOKTORA TEZİ**  
**FİZİK ANABİLİM DALI**

**DANIŞMANI**  
**PROF. DR. YURII CHUMAKOV**

**GEBZE**  
**2021**

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| <b>GEBZE TEKNİK ÜNİVERSİTESİ</b> | <b>DOKTORA JÜRİ ONAY FORMU</b> |
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GTÜ Fen Bilimleri Enstitüsü Yönetim Kurulu'nun 08/01/2021 tarih ve 2021/02 sayılı kararıyla oluşturulan jüri tarafından 28/01/2021 tarihinde tez savunma sınavı yapılan Gökhan Bayram'ın tez çalışması Fizik Anabilim Dalında DOKTORA tezi olarak kabul edilmiştir.

### **JÜRİ**

ÜYE

(TEZ DANIŞMANI) : Prof. Dr. Yurii Chumakov

ÜYE

: Prof. Dr. Osman Öztürk

ÜYE

: Dr. Öğr. Üyesi Eşe Akpınar

ÜYE

: Prof. Dr. Savaş Berber

ÜYE

: Doc. Dr. Betül Canımurbey

### **ONAY**

Gebze Teknik Üniversitesi Fen Bilimleri Enstitüsü Yönetim Kurulu'nun  
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## SUMMARY

In this thesis, thermoelectric properties of different covalent organic frameworks constructed from metallophthalocyanine (MPc) and metalloporphyrin (MP) units with various transition metal atoms (Co, Cu, Zn, and Ni) have been theoretically studied. We performed ab initio calculations within the ABINIT simulation package that works with the density functional theory (DFT) framework using plane-wave basis and pseudopotentials. We used the BoltzTraP code that uses Boltzmann transport theory with constant relaxation time to calculate the thermoelectric properties of the compounds. To obtain thermoelectric electronic fitness function (EFF) we used TransM code.

The thermal conductivity displays remarkably low for all studied compounds which is necessary to enhance the ZT value. For COF 366 and 66, we found that the presence of the Ni atom increases the bandgap. It is observed that in COF 366 a considerable improvement in thermoelectrical figure of merit ZT with presence of central atom Ni, as well as, an increase in the Seebeck coefficient. We show that COF 366 with a central atom Ni could reach a value of  $ZT = 0.998$  around 300 K with proper stacking. As for MPc COFs, CoPc COF have maximum ZT value among these compounds with a value of 0.978 at 780 K along the in-plane direction. The maximum Seebeck coefficient values for MPc COF as follows: 770  $\mu\text{V/K}$  for CoPc COF, -423  $\mu\text{V/K}$  for Cu-Pc COF, and -315  $\mu\text{V/K}$  for ZnPc COF. The calculations showed that all maximum values are in the in-plane directions.

**Key Words:** density functional theory, semiclassical Boltzmann transport theory, thermoelectric materials, covalent organic frameworks.

## ÖZET

Bu tez çalışmasında merkezlerinde çeşitli geçiş metalleri bulunan metalloftalosiyenin ve metalloporfirin birimlerinden türetilmiş kovalent organik çerçevelerin termoelektrik özellikleri teorik olarak incelendi. Ab initio hesaplamaları, yoğunluk fonksiyonelleri kuramı kapsamında, düzlem dalga ve psödopotansiyel yöntemleri kullanılarak ABINIT simülasyon paketi ile yapıldı. Bileşiklerin termoelektrik özellikleri, sabit rahatlama zamanı ile Boltzmann transport kuramını kullanan Boltztrap yazılımı ile hesaplandı. Son olarak bileşiklerin termoelektrik elektronik uygunluk fonksiyonu da TransM kodunu kullanılarak elde edildi.

Tüm incelenen bileşiklerin termal iletkenlikleri çoğu gözenekli malzemelerden beklendiği gibi önemli ölçüde düşük çıktı. COF 366 ve COF 66'nın bant boşluklarının eklenen merkez atomla beraber düştüğü belirlendi. Kullanılan merkez atom Ni'nin ayrıca COF 366'nın termoelektrik değer katsayısının (ZT) önemli ölçüde geliştirdiği gözlemlendi. Uygun dizilime sahip bir COF 366 yapısının, kullanılan Ni merkez atomuyla birlikte 0.998 ZT değerine ulaşabildiği belirlendi. 780 K'da 0.978 ZT değerine ulaşabilen CoPc COF, MPc COF'lar içerisinde en iyi termoelektrik performansı gösteren malzeme oldu. Ayrıca MPc COF'ların hesaplanan Seebeck katsayısı değerleri şu şekilde oldu: CoPc COF için 770  $\mu\text{V/K}$ , Cu-Pc COF -423  $\mu\text{V/K}$  ve ZnPc COF için -315  $\mu\text{V/K}$ .

**Anahtar Kelimeler:** yoğunluk fonksiyonel kuramı, yarı-klasik Boltzmann taşıma kuramı, termoelektrik malzemeler, kovalent organik çerçeveler.

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## LIST of ABBREVIATIONS and ACRONYMS

| <u>Abbreviations<br/>and Acronyms</u> | <u>Explanations</u>                                      |
|---------------------------------------|----------------------------------------------------------|
| $\Pi$                                 | : Peltier coefficient                                    |
| $\tau$                                | : Thomson coefficient                                    |
| $\kappa_e$                            | : Electrical thermal conductivity                        |
| $\kappa_l$                            | : Lattice thermal conductivity                           |
| $\sigma$                              | : Electrical conductivity                                |
| $\mu$                                 | : Charge carrier mobility                                |
| $\eta$                                | : Efficiency                                             |
| $f_0$                                 | : Fermi-Dirac distribution function                      |
| $\rho(r)$                             | : Electron density                                       |
| $\rho\uparrow(r)$                     | : Spin-up electron density                               |
| $\rho\downarrow(r)$                   | : Spin-down electron density                             |
| B3LYP                                 | : Becke, 3-parameter, Lee-Yang-Parr                      |
| BDBA                                  | : Benzenediboronic acid                                  |
| CBM                                   | : Conduction band minimum                                |
| COF                                   | : Covalent organic framework                             |
| DFT                                   | : Density functional theory                              |
| DOS                                   | : Density of states                                      |
| EFF                                   | : Electronic Fitness Function                            |
| GGA                                   | : Generalized gradient approximation                     |
| LDA                                   | : Local density approximation                            |
| LSDA                                  | : Local spin-density approximation                       |
| MPc COF                               | : Metallophthalocyanine covalent organic framework       |
| MP COF                                | : Metalloporphyrin covalent organic framework            |
| PAW                                   | : Projector augmented wave method                        |
| PBE                                   | : Perdew–Burke–Ernzerhof exchange-correlation functional |
| PDOS                                  | : Projected density of states                            |

|     |   |                               |
|-----|---|-------------------------------|
| TM  | : | Thermoelectric module         |
| TEG | : | Thermoelectric generator      |
| UEG | : | Uniform electron gas          |
| VBM | : | Valence band maximum          |
| ZT  | : | Dimensionless figure of merit |

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# 1. INTRODUCTION

Due to the increase in the global population and economic growth, World's energy resources are getting continuously scarcer. It will therefore be necessary to diversify our energy resources while minimizing their negative effects on the environment. More than 75% of the world primary energy consumption is non-renewable which is produced mainly from fossil fuels such as oil, natural gas, and coal. Over 60% of these energy consumption is released into the atmosphere in the form of waste heat [1], [2]. Thermoelectricity that makes it possible to convert waste heat into electric energy, has become the most promising approach to the achievement of energy-saving and environmental protection. Thermoelectric materials provide an alternative route to convert solar energy into electrical power, besides the technology of photovoltaic and thermionic energy conversion. Because thermoelectric modules (TM) do not have any moving parts to wear out, vibrate and/or make any noise like other generators, they are quiet, reliable, maintenance-free, and vibration-free [3].

Despite the recent developments in research on the topic, thermoelectric devices used in everyday life are still based on a limited number of materials. In this thesis, we performed a computational analysis of covalent organic frameworks to evaluate their electronic and thermal capacities to serve as a potential thermoelectric material.

## 2. BACKGROUND

### 2.1. Thermoelectricity

The thermoelectric (TE) effect is the direct and reversible conversion of temperature differences to electric voltage and is governed by the following three thermoelectric material parameters: thermopower or Seebeck coefficient, electrical conductivity, and thermal conductivity [4]. The conversion of temperature difference into electrical energy using thermoelectric materials is typically called thermoelectric energy harvesting. These materials work on Seebeck or Peltier effect [5].

Three scientists made major contributions to the study of thermoelectricity. Hence these three thermoelectric effects are named after these scientists who first described them.

#### 2.1.1. Seebeck effect

The Seebeck effect, which is first observed by Thomas Johann Seebeck in 1821, is the direct conversion of heat into electricity. Seebeck found that, if a junction made of two different metals is heated a voltage can be generated (Figure 2.1). The amplitude of the generated voltage is proportional to the temperature difference:

$$\Delta V = S\Delta T \quad (2.1)$$

where  $S$  is the Seebeck coefficient,  $V$  is generated voltage and  $\Delta T$  is the temperature difference.

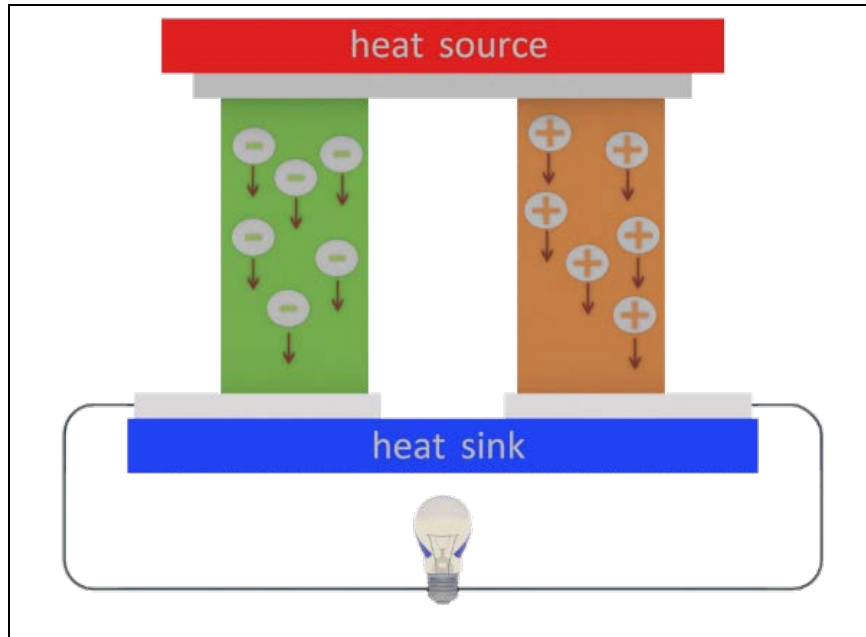


Figure 2.1: Schematic illustration of the Seebeck effect.

### 2.1.2. Peltier effect

In 1834 another thermoelectric phenomenon was discovered by Jean Charles Athanase Peltier. If an electric current passed through a thermocouple, heat is either evolved or absorbed at the junction of the thermocouple depending on the flow of the current (Figure 2.2). This is called as Peltier effect and it is the reverse phenomenon of the Seebeck effect. This effect provides a niche cooling technology which is known as the Peltier cooler.

$$Q = \Pi I \quad (2.2)$$

where  $\Pi$  is the Peltier coefficient,  $Q$  is the thermal current and  $I$  is the electrical current. The Peltier coefficient and the Seebeck coefficient are related to each other by the Onsager relation [6]:

$$\Pi = ST \quad (2.3)$$

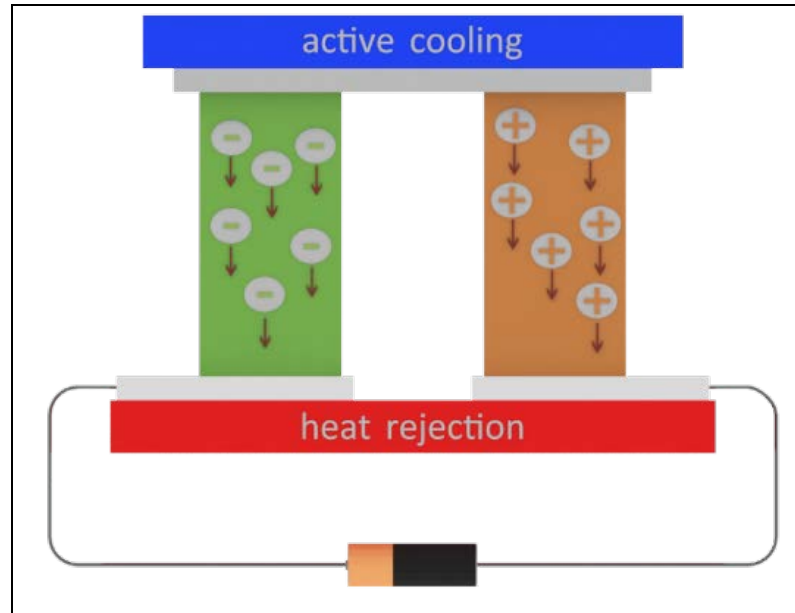


Figure 2.2: Schematic illustration of the Peltier effect.

### 2.1.3. Thomson effect

In 1854, William Thomson analyzed Seebeck and Peltier effects, using the principle of the conservation of energy and empirical results, and proposed a third thermoelectric phenomenon as an extension to the previous studies [7]. This is a reversible thermoelectric effect in which a quantity of heat  $Q_{\text{Thomson}}$ , is liberated or absorbed by a current-carrying conductor if a temperature gradient exists along the conductor.  $Q_{\text{Thomson}}$  is called Thomson heat and it can be shown as

$$Q_{\text{Thomson}} = -\tau I \nabla T \quad (2.4)$$

where  $\tau$  is the Thomson coefficient.

### 2.1.4. Thermoelectric performance

The thermoelectric performance of a material is measured by the dimensionless figure of merit or  $ZT$  which depends on electrical conductivity, thermal conductivity, and Seebeck coefficient. This parameter is written as

$$ZT = \frac{\sigma S^2}{\kappa_e + \kappa_l} T \quad (2.5)$$

where  $\kappa_e$  electronic thermal conductivity,  $\kappa_l$  lattice thermal conductivity,  $T$  temperature,  $S$  the Seebeck coefficient, and  $\sigma$  is the electrical conductivity which is the product of the carrier concentration, the carrier charge and the carrier mobility.

$$\sigma = ne\mu \quad (2.6)$$

The thermoelectrical figure of merit  $ZT$  was first introduced by Abram Fedorovich Ioffe in 1949 and it is considered as the introduction of a modern thermoelectric theory [8]. As is apparent from equation 2.5, a high  $ZT$  value material possesses a high Seebeck coefficient, a high electrical conductivity, and a low thermal conductivity. The Seebeck coefficient or thermopower is an intrinsic property and it is the ratio of the induced voltage that arises due to a temperature difference and thermopower of a semiconductor can be expressed by the Mott formula:

$$S = \frac{8\pi k_B^2}{3eh^2} m^* T \left( \frac{\pi}{3n} \right)^{2/3} \quad (2.7)$$

where  $q$ ,  $k_B$ ,  $m^*$  and  $n$ , the carrier charge, the Boltzmann constant, the effective mass, and the carrier concentration respectively.

For heavily doped semiconductors the Seebeck coefficient generally increases with temperature. Such behavior is not observed in lightly doped semiconductors in which thermopower generally independent of temperature [9]. The Seebeck coefficient may have different signs depending on the type of thermoelectric material. It is negative for n-type and positive for p-type materials. For a thermoelectric material to have a high  $ZT$ , it should have a large Seebeck coefficient, low electrical resistivity, and low lattice thermal conductivity. It is necessary to optimize many of the parameters in the electrical and thermal properties for achieving a high  $ZT$  value.

The first two quantities of equation 2.5 can be combined into the thermoelectric power factor:

$$P_F = \sigma S^2 \quad (2.8)$$

The power factor (PF) of a thermoelectric material measures its ability to extract electrical power from temperature differences [10]. There is a trade-off relationship between  $S$  and carrier concentration ( $n$ ) leads to extremely difficult to enhance PF [11].

The maximum efficiency of a thermoelectric device is independent of the number, shape, or size of the thermoelements. It is also independent of particular values of electrical conductivity, thermal conductivity, Seebeck coefficient but rather dependent on their combination  $ZT$  [12]. As is conventional, for a given thermoelectric device, the efficiency is defined using the following equation:

$$\eta = \frac{T_H - T_C}{T_H} \frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + \frac{T_C}{T_H}} \quad (2.9)$$

where  $T_H$ ,  $T_C$ , and  $ZT$  are the hot side and cold side temperatures, and thermoelectric figure of merit respectively. To obtain a high device efficiency,  $ZT$  must exhibit a large value. In addition, to secure the supply high efficiency as much as possible,  $ZT$  values of the n-type and the p-type parts of the thermoelectric module must be close.

Thermal conductivity has two parts: electronic thermal conductivity and lattice thermal conductivity. The electronic thermal conductivity of a material is defined as [13]

$$k_e = \sigma T \left[ \frac{1}{e^2 T^2} \frac{\sum_v \int \tau v_x^2 f_0 (1 - f_0) (E(k) - E_F)^2 dk^3}{\sum_v \int \tau v_x^2 f_0 (1 - f_0) dk^3} - S^2 \right] \quad (2.10)$$

Equivalently,

$$k_e \equiv \sigma T \left[ \frac{(E - E_F)^2}{e^2 T^2} - S^2 \right] \quad (2.11)$$

where  $\sigma$  is the electrical conductivity,  $\tau$  is the relaxation time of electrons,  $v_x$  is the velocity of electrons,  $f_0$  is the Fermi-Dirac distribution function,  $\bar{E}$  is the average energy responsible for conductivity. Additionally, the lattice thermal conductivity  $k_l$  is expressed by [14]:

$$k_l = \frac{1}{3} C_L v_s \lambda_{ph} \quad (2.12)$$

where  $C_L$  's the specific heat,  $v_s$  is the velocity of sound, and  $\lambda_{ph}$  is the is the mean free path of phonon. Since  $\lambda_{ph}$  in Equation 2.12 is directional, it may have both positive and negative values [15].

The Electronic Fitness Function (EFF) is another critical parameter, especially monitoring the excellent material for thermoelectric applications. The EFF measures the decoupling between electrical conductivity and the Seebeck coefficient. The EFF value of a given material may be calculated using the formula given as follows:

$$t = \left( \frac{\sigma}{\tau} \right) S^2 / N^{2/3} \quad (2.13)$$

Here  $\tau$  is an inverse scattering rate,  $N$  is the volumetric density of states,  $S$  is the Seebeck coefficient,  $\sigma$  is the electrical conductivity. The EFF is doping and temperature dependent. The EFF can be directly calculated via electronic structure calculations and Boltzmann transport theory under the constant relaxation time approximation [16].

## **2.2. Thermoelectric materials**

From a material design perspective, thermoelectric materials consist of two major categories: inorganic and organic semiconductors. Inorganic semiconductors are rigid crystalline, must be exceptionally pure, and require so accurate processing under very demanding conditions such as high reaction temperatures. Organic semiconductors, on the other hand, are non-toxic, flexible, lightweight, and low cost, together with intrinsically low thermal conductivity and high Seebeck coefficient, these materials are considered a promising class of thermoelectric materials.

Based on the fast development of thermoelectricity technology, this thesis aims to comprehensively investigate the selected covalent organic frameworks as promising thermoelectric materials, including their electronic structures and thermoelectric properties.

## **2.3. Thermoelectric module**

Generally, a thermoelectric module composed of a number of pairs of n- and p-type legs that are alternately arranged and connected in series (Figure 2.3). To establish a high thermoelectric energy conversion efficiency, both legs need to have high thermoelectric performance [17].

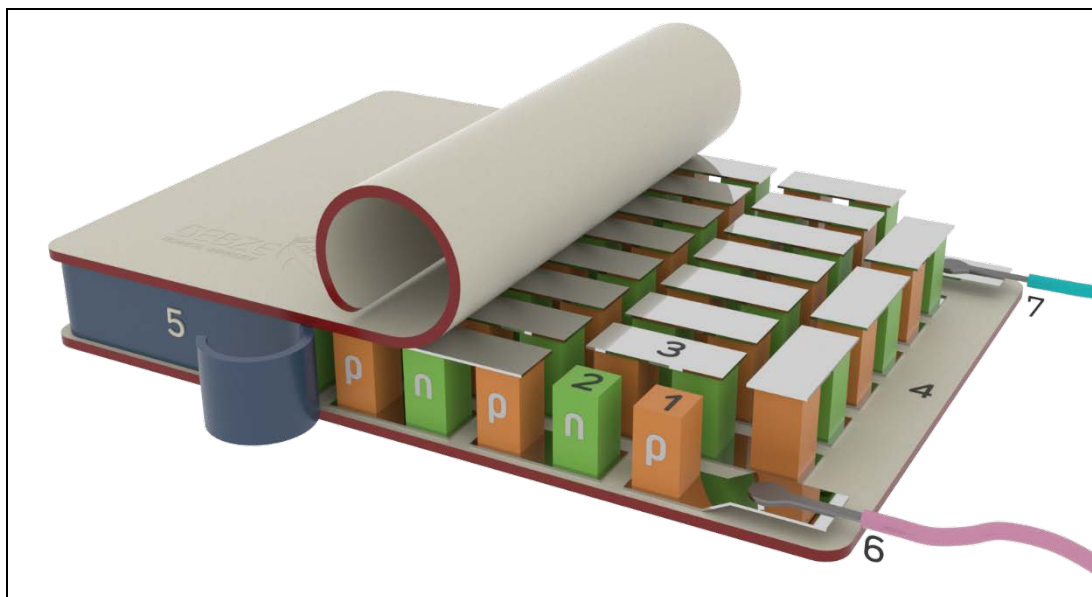


Figure 2.3: A 3D model of a thermoelectric module (TM) with its parts. A TM consists of n-type (1) and p-type (2) thermoelectric materials that are electrically connected in series and connected by a metallic strip (3) and sandwiched between ceramic substrates (4). The edges of the TM can be sealed with epoxy (5) in order to protect it from the moisture. In the case of electrical generation, heat is applied to one side of the thermoelectric generator (TEG), causing the charge carriers to flow through from the hot to the cold side of the TEG (6, 7) and generating an electrical current.

## 2.4. Covalent organic frameworks

Covalent organic frameworks (COFs) are a sub-class of multi-dimensional crystalline organic porous materials assembled by a bottom-up approach from rigid organic molecular building units, namely, linkers and linkages (Figure 2.4), that are linked by strong covalent bonds [18]. Generally, the stability and crystallinity of COFs are related to linkages, whereas, the geometry and pore sizes depend on the linkers' types (Figure 2.4 and 2.5) [19].

Since first synthesized by Yaghi and co-workers in 2005, COFs have attracted considerable attention over the years because of their excellent structural and functional properties including but not limited to facile chemical tunability, structural diversity, high-power density, as well as good architectural and chemical stability and scalability [20], [21]. These excellent properties make COFs potential precise materials for use at gas storage, optoelectronic devices, chemical sensing, separation, and catalysis. In addition to this, developing broadly functional composites by

combining COFs with different materials including different COFs can expand the applications of COFs in various areas. In accordance with this purpose, various types of COFs including, aminal-linked [22], boronate ester-linked [23], dioxin-linked [24], hydrazone-linked, imine-linked, imidazole-linked [25], ketoamine-linked [26], and olefin-linked COFs have been synthesized and developed in recent years.

COFs are reported to have good potentials in thermoelectric applications with satisfactory electrical conductivity, high thermal stability, and permanent porosity characteristics [27]. Crystallinity and porosity are two vital properties that make a material particularly suitable for thermoelectric applications [28]. In favor of their highly crystalline structure, COFs' internal segments have close interactions with each other.

To evaluate the thermoelectrical suitability of COFs in general we studied metallophthalocyanine (MPc COFs) (Figure 2.4) and metalloporphyrin (Figure 2.5) based COFs (COF-66 and -366) containing different transition metals (Co, Cu, Zn, and Ni). Pc-COFs have the same macro appearance compared with the COF-366 and COF-66, only with the difference of the nodes and spacers. Phthalocyanine and porphyrin units which are used as nodes in the studied COFs here are structurally related to each other in the sense that they possess tetrapyrrolic macrocycles [29]. Among the other organic semiconductors, the phthalocyanine (Pc) is a versatile class of organic semiconducting materials with interesting charge transport and optical properties. Literature reported that the Seebeck coefficients of phthalocyanines fall into the range of 0.6–1.8 mV K<sup>-1</sup> and the charge carrier mobilities in single-crystal Pcs by Hall measurement is on the order of cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>. The highest field-effect mobility of holes in thin films of TiOPc was reported to be 10 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>. The high charge carrier mobilities and the large Seebeck coefficients suggest that metal phthalocyanines could be potential thermoelectric materials. Therefore, the phthalocyanine-based covalent organic frameworks may become a very promising class of thermoelectric materials because they combine thermal stability, hole, electron, and ambipolar conductivity, and high charge mobility [30], [31]. On the other hand, it is known that a layered crystal structure is well suited to thermoelectric materials [32]. The aligned bicontinuous  $\pi$ -conjugated intra- and inter-layer arrangement of Pc COFs lead to long-distance charge delocalization and exceptional long-term charge retention that

may cause the electrical current due to temperature gradient. MPc COFs are distinguished by the occupancy of a transition metal ion (e.g. Co, Cu, or Zn) in the formal oxidation state 2+ in their phthalocyanine unit's central cavity.

The conducting functions of COFs are strongly depending on the nature of the nodes and linkers and spatial arrangement of layers. Therefore, our research aimed to calculate the TE properties of COFs as candidates for thermoelectric materials and investigate the influence of metal and linkers on these properties.

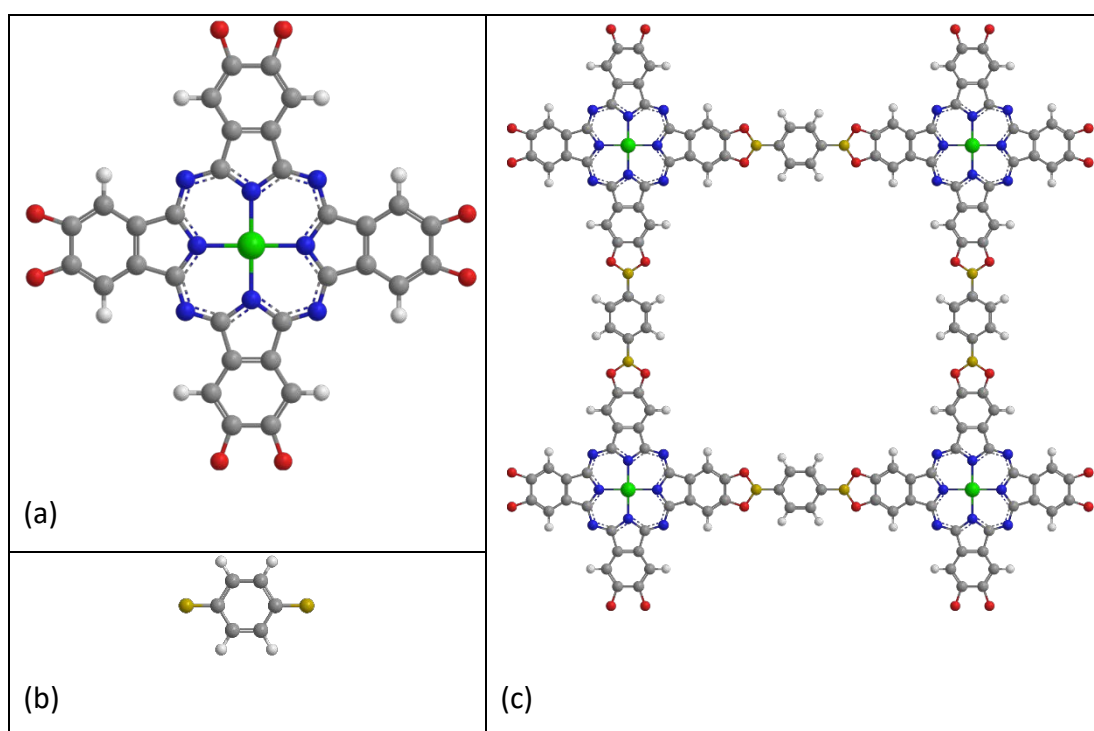


Figure 2.4: Building blocks of MPc COFs investigated a) phthalocyanine unit b) benzendiboronic acid BDDBA c) MPc COF.

COF-366 (Figure 2.5 c), which has a chemical formula  $C_{60}H_{38}N_8$ , formed with imine bond between Ni-TAPP, 5,10,15,20-tetrakis-(p-aminophenyl)-porphine-Ni (Figure 2.5 a) and terephthalaldehyde (Figure 2.5 b). COF-366 has the highest carrier mobility among semiconducting COFs; this is attributed to imine bond which improves the conjugation of the framework [33]. Imine based COFs known for their exceptional thermal stability [34]. COF-66 with a chemical formula of  $C_{72}H_{42}B_4N_4O_8$  (Fig 2.5 f) is a boronate ester-linked COF. Its building blocks are Ni-TBPP (5,10,15,20-

tetrakis-(p-boronic acid-phenyl)-porphine-Ni and THAn, 2, 3, 4, 5-tetrahydroxy anthracene (Figure 2.5) [35]. COF-66 has a smaller interlayer spacing than that of COF-366, yet falls behind when it comes to the ion carrying capability [36].

Nickel porphyrin unit of Ni COF -366 and -66 is a molecular complex consisting of a central nickel atom. It is also a porphyrin macrocycle which is formed by four pyrrole rings located in the same plane. As a result, the nickel porphyrin complex and thus Ni COF has a planar structure [37].

### **2.4.1. Pore size**

It is worthy to further discuss the importance of the pore structure on thermoelectric performance. One of the most distinct material properties of COFs is the large pore volume. The ratio of the pore volume should have an interesting and strong impact on the lattice thermal conductivity. The phthalocyanine COFs stack in an eclipsed fashion within the COF to form 2.3 nm pores. The crystalline structure of NiPc COF shows that there are open micropores of 1.9 nm in width. The pore sizes of COF -366 and -66 obtained from the crystal structures are 2 and 2.3 nm respectively [35]. The pore sizes of NiPc COF lie between those of COF -366 and -66 compounds. NiPc-BTDA COF has tetragonal pores with a width of 2.2 nm.

Simulations of heat transport across aligned square pores of Si reveal that the thermal conductivity can be decreased by increasing the pore size [38]. Moreover, the molecular dynamics simulations show that pores as small as several nanometers in diameter can make lower the phononic thermal conductivity up to two orders of magnitude. The presence of pores leads to a shortening of the median free path of thermal phonons, which results in a substantial reduction of the thermal conductivity of porous materials [39]. Therefore, the pore sizes of the porous material are expected to play an important role in the thermoelectric performance. To clarify the role of the large pore volume on the thermoelectric properties, we will estimate the figure of merit ZT along in-plane and out-of-plane directions using the calculated lattice thermal conductivity. This estimation will allow us to find the high-performance n-and p-type thermoelectric material for thermoelectric applications.

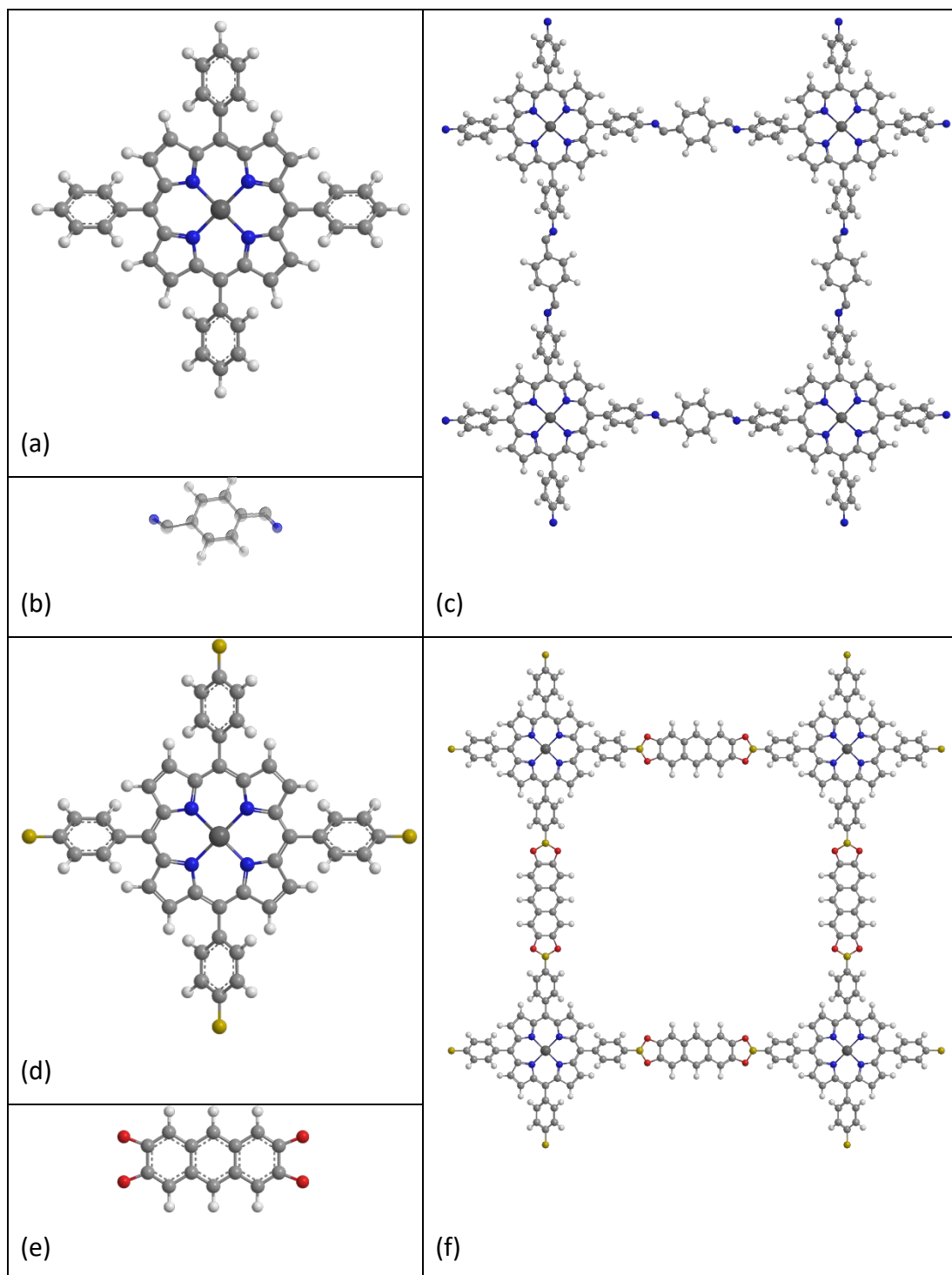


Figure 2.5: Building blocks of COF-66 and -366 with a central atom of Ni. Colors used for identification: Ni dark gray; N blue; C gray; H white; B yellow; O red. a) The porphyrin unit of COF-366 b) The linker unit of COF-366. c) The entire diagram of COF-366. d) The porphyrin unit of COF-66. e) The linker unit of COF-66. f) COF-66.

### 3. THEORETICAL METHODS

In this chapter, the methods which the computational studies rely upon shall be addressed.

#### 3.1. Density functional theory

Density functional theory (DFT) is the most efficient and widely used method for the ab initio calculations of the many-body Schrödinger equation. In DFT, the Hamiltonian of the atomic system is reformulated by using electron density  $\rho(r)$  instead of the many body wavefunction. It may be noted that the density depends on only three spatial coordinates rather than  $3N$  as for the wavefunction and has a big computational advantage. Also, unlike the wave function, the electron density of a quantum mechanical system is an observable and physically measurable quantity, by experimental methods such as positron annihilation spectroscopy, X-ray diffraction [40], [41]. Thus, density functional theory is ideally suited for calculations involving large systems.

The idea behind using such a model is nearly old as quantum mechanics itself. Indeed, already during the beginning years of quantum mechanics Thomas and Fermi independently postulated a density involving theory that seems relevant in approximating the electron distribution using a statistical model. It has further been shown that the TF model provides good estimates at moderate temperatures [42], [43].

The Hamiltonian for the system with  $M$  nuclei and  $N$  electrons is given by

$$H = \sum_{i=1}^N -\frac{1}{2} \Delta_{r_i} + \sum_{i=1}^N V_{ext}(r_i; \{R_I\}) \quad (3.1)$$

Here,  $V_{ext}$  is the external potential, that is the interaction of the electrons with the atomic nuclei.

### 3.1.1. The Hohenberg–Kohn theorem

The theoretical basis of DFT which has become a fundamental tool for electronic structure calculations is constituted with the theorems initially put forward and proven by Hohenberg and Kohn. The electron density determines the ground state properties of a many-electron system. According to this theorem, the electronic density which depends only on three coordinates ( $r$ ) alone is enough to determine all observable quantities of the systems.

Consider an enclosed large system in which  $N$  electrons moving under an external potential  $v(r)$ . For this system, the electronic Hamiltonian written as

$$H = T + V + U \quad (3.2)$$

Here,  $T$  is the kinetic energy of the  $N$  electrons

$$T = \frac{1}{2} \int \nabla \psi^*(r) \nabla \psi(r) dr \quad (3.3)$$

$V$  is the potential energy of the  $N$ -electron system

$$V = \int v(r) \psi^*(r) \psi(r) dr \quad (3.4)$$

$W$  is the electron-electron interaction energy associated with the  $N$ -electron system

$$W = \sum_{i < j}^N \frac{1}{r_{ij}} \quad (3.5)$$

$T$  and  $W$  are universal parts of all electronic Hamiltonians and external potential  $v(r)$  is a system-specific part.

Also, the energy of the ground state is a functional of charge density,  $\rho(r)$ .

$$E[\rho] = F_{HK}[\rho] + \int \rho(r)V_{EXT}(r)dr \quad (3.6)$$

Here  $V_{EXT}$  is the external potential and it can be written in terms of the electronic density as:

$$V_{EXT} = \int \rho(r)v(r)dr \quad (3.7)$$

So, the energy of the ground state can also be written as

$$E[\rho] = F_{HK}[\rho] + \int v[\rho](r)\rho(r)d^3r \quad (3.8)$$

Here,  $F_{HK}[\rho]$  is the HK functional and it is written as

$$F_{HK}[\rho] = \langle \Psi[\rho] | T + W | \Psi[\rho] \rangle \quad (3.9)$$

and,

$$F_{HK}[\rho] = T[\rho] + \frac{e^2}{2} \iint \frac{\rho(r)\rho(r')}{|r - r'|} d^3r d^3r' + E_{XC}[\rho(r)] \quad (3.10)$$

Here, T is the kinetic energy, W is the many-particle interactions, and the final term  $E_{XC}[\rho(r)]$  is the exchange-correlation energy. The exchange-correlation energy is a functional of the density  $\rho(r)$  or -in a spin-polarized system- of the separate up and down spin densities  $\rho \uparrow (r)$  and  $\rho \downarrow (r)$  [44]. If the exchange-correlation energy is known, it is possible simultaneously to calculate the total energy of the system in its ground state, using electron density [45].  $F_{HK}[\rho]$  is independent of  $v(r)$ . So, it can be said that  $F_{HK}$  is a universal functional of the particle density.

$E_{xc}[\rho(r)]$  functional hard to compute, so we need approximations. Local density approximation (LDA), local spin-density approximation (LSDA), generalized gradient approximation (GGA), and their variants are the most popular approximations used for exchange-correlation functional.

### 3.1.2. The local density approximation

To solve the Kohn–Sham equation, it is necessary to construct definitive exchange and correlation functionals. Local density approximation (LDA) proposed by Kohn and Sham in 1965 is a widely used approximation for the exchange-correlation energy. The LDA is the simplest approximation for the exchange-correlation energy used in DFT [46]. Dividing the overall non-uniform electron region in the system into multiple local sub-regions and approximating these local regions as a uniform electron gas (UEG) is the basic idea behind the LDA. The UEG is an important system from which the LDA for the exchange energy functional can be developed. With the UEG, it is possible to calculate the exchange energy exactly, and it is possible to determine the correlation energy using numerical techniques. The total exchange-correlation functional  $E_{xc}^{LDA}[\rho]$  can be written as

$$E_{xc}^{LDA}[\rho] = \int \varepsilon_{xc}^{UNIFORM}[\rho(r)]\rho(r)d^3r \quad (3.11)$$

here  $\varepsilon_{xc}^{UNIFORM}$  is the exchange-correlation energy for a particle in a uniform electron gas with density  $\rho$ , and it can be divided into two parts: exchange and correlation components,

$$\varepsilon_{xc}^{UNIFORM}[\rho(r)] = \varepsilon_x^{UNIFORM}[\rho(r)] + \varepsilon_c^{UNIFORM}[\rho(r)] \quad (3.12)$$

So, equation 1.1 can be written as:

$$E_{xc}^{LDA}[\rho] = \int \varepsilon_x^{UNIFORM}[\rho(r)]\rho(r)d^3r + \int \varepsilon_c^{UNIFORM}[\rho(r)]\rho(r)d^3r \quad (3.13)$$

By inserting spin dependence into LDA one can move to a further level of this approximation: Local spin density approximation (LSDA). The exchange-correlation energy within LSDA is expressed as

$$E_{xc}^{LSDA}[\rho] = \int \varepsilon_{xc}^{UNIFORM}[\rho \uparrow(r), \rho \downarrow(r)][\rho \uparrow(r) + \rho \downarrow(r)] d^3r \quad (3.14)$$

where  $\rho \uparrow(r), \rho \downarrow(r)$  and  $\varepsilon_{xc}^{UNI}$  are spin up and spin down electron density and exchange-correlation energy in the presence of spin polarization.

Application of LDA should be limited essentially to situations with a slowly varying density. While the local density scheme suffices for most areas, it fails to give accurate results in situations where the electron density is changing very rapidly such as in molecules. In such a case one must look for an approximation that considers the gradient of the electron density.

### 3.1.3. The generalized-gradient approximation

The generalized gradient approximation (GGA) exchange-correlation energy introduced by Becke, Perdew, and others is defined as [47], [48];

$$E_{xc}^{GGA}[\rho] = \int f[\rho(r), \nabla \rho(r)] d^3r \quad (3.15)$$

The GGA also can be separated into two exchange and correlation parts:

$$\varepsilon_{xc}^{GGA}[\rho(r)] = \varepsilon_x^{GGA}[\rho(r)] + \varepsilon_c^{GGA}[\rho(r)] \quad (3.16)$$

With this separation approach many novel hybrid exchange-correlation functionals such as B3LYP (the Becke, 3-parameter, Lee-Yang-Parr) or HSE06 (the Heyd-Scuseria-Ernzerhof), have been introduced.

### 3.1.4. BoltzTrap code

This section is dedicated to the theoretical background and working principle of our calculation approach to obtain thermoelectric properties of COFs which is followed by the description of the simulation package built by BoltzTraP [49].

Thermoelectrical properties have been calculated by BoltzTraP code which performed the Fourier expansion on the band energies calculated by ABINIT through the semi-classical Bloch-Boltzmann transport theory. The Boltzmann transport equation under the relaxation time approximation can be written as follows:

$$\mathbf{v}_k \frac{\partial f_k}{\partial T} \nabla \mathbf{T} + \mathbf{v}_k (-e) \frac{\partial f_k}{\partial \epsilon_k} \mathbf{E} = \frac{f_k^0 - f_k}{\tau_k} \quad (3.17)$$

where  $f_k^0$  is the electronic distribution and it is given by:

$$f_k^0 = \frac{1}{e^{(\epsilon_k - \mu)/k_B T} + 1} \quad (3.18)$$

BoltzTrap code calculated transport properties according to the following expressions:

Electrical conductivity:

$$\sigma(\mu, T) = e^2 \int \left( -\frac{\partial f_0}{\partial E} \right) \tau(E, T) \Xi(E) dE \quad (3.19)$$

The Seebeck coefficient:

$$S(\mu, T) = e \sigma^{-1} \int \left( -\frac{\partial f_0}{\partial E} \right) \left( \frac{E - \mu}{T} \right) \tau(E, T) \Xi(E) dE \quad (3.20)$$

And thermal conductivity:

$$\kappa_e(\mu, T) = \frac{1}{e^2 T} \int \left( -\frac{\partial f_0}{\partial E} \right) (e - \mu)^2 \tau(E, T) \Xi(E) dE \quad (3.21)$$

The BoltzTrap code gives electrical ( $\sigma/\tau$ ) and thermal ( $\kappa/\tau$ ) conductivities per relaxation time. With BoltzTrap it is also possible to obtain the Seebeck coefficient ( $S$ ) without the relaxation time. Constant scattering time approximation (CSTA) makes it possible to get the Seebeck coefficient which is independent of relaxation time [50].

### 3.1.5. Computational details

The calculation stages are as follows: (i) geometry optimization of the compounds to be studied. (ii) calculation of the compounds' electronic band structures. (iii) calculating thermoelectric properties using BoltzTrap code with the constant relaxation time approximation (iv) calculating the electronic fitness function using transM code.

Geometry optimization and electronic structure calculations were carried out with the density functional theory (DFT) as implemented in the ABINIT 8 suite. ABINIT is a first-principles code based on pseudopotentials and a plane-wave basis and freely available under the GNU General Public License (GPL). Structure optimizations and molecular dynamics simulations were performed using the projector augmented wave (PAW) method with the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional [51]. It is known that this widely used functional provides decent results for molecules, solids, interfaces, and surfaces. Molecules were treated with a supercell technique using a plane-wave expansion of the orbitals with a cut-off energy of 30 Hartrees and Troullier-Martins (TM) norm-conserving (NC) pseudopotentials. All pseudopotentials used in this study were provided by the ABINIT package. The lattice parameters of the samples were optimized with a non-shifted Monkhorst and Pack k-sampling grid for both electronic structure and geometry optimization calculations. The k-point mesh used to sample the Brillouin zone has been set to 14×4×4 for MPc COFs and 3×6×3 for M/P COFs. The atomic structures were relaxed using an augmented plane-wave method scheme as implemented in the ABINIT code until the forces on all unconstrained atoms were

lower than 0.01 mRy/Å. The unit cell parameters obtained from geometry optimizations are given shown in Table 3.1. These cell parameters have been used in the calculations of the electronic structures.

Table 3.1: The calculated lattice parameters of studied COFs.

| <i>Compound</i>           | <i>a (Å)</i> | <i>b (Å)</i> | <i>c (Å)</i> |
|---------------------------|--------------|--------------|--------------|
| <i>CoPc COF bulk</i>      | 6.7434       | 23.084       | 23.084       |
| <i>CoPc COF monolayer</i> | 23.084       | 23.084       | 15.000       |
| <i>CuPc COF bulk</i>      | 6.7434       | 23.0839      | 23.084       |
| <i>CuPc COF monolayer</i> | 23.084       | 23.0840      | 15.000       |
| <i>ZnPc COF bulk</i>      | 6.7434       | 23.0839      | 23.084       |
| <i>ZnPc COF monolayer</i> | 23.084       | 23.0840      | 15.000       |
| <i>COF-366 bulk</i>       | 25.417       | 12.3770      | 25.417       |
| <i>COF-366 monolayer</i>  | 25.417       | 25.4170      | 14.159       |
| <i>COF-66 bulk</i>        | 28.984       | 28.9840      | 3.813        |
| <i>COF-66 monolayer</i>   | 28.984       | 28.9840      | 13.032       |
| <i>Ni COF-366</i>         | 25.298       | 12.3199      | 25.290       |
| <i>Ni COF-66</i>          | 40.989       | 40.989       | 3.813        |

The temperature dependence of the four transport coefficients, i.e., the electrical conductivity ( $\sigma$ ), the thermal conductivity ( $k$ ), Seebeck coefficient ( $S$ ), and the dimensionless figure of merit ( $ZT$ ), of COFs have been calculated by BoltzTraP code which performed the Fourier expansion on the band energies calculated by ABINIT through the semi-classical Bloch-Boltzmann transport theory [49]. These coefficients are anisotropic, meaning that they depend on the directions. The BoltzTrap code provides the ratios of thermal conductivity ( $\kappa_{\varepsilon}$ ) and electrical conductivity ( $\sigma$ ) over relaxation time ( $\tau$ ). To obtain exact values of the  $\kappa_{\varepsilon}$  and  $\sigma$  we used the estimated relaxation time ( $\tau = 54.11$  fs) from the data in Chumakov (2016) [27]. The doping-dependent electronic fitness functions (EFF) were obtained using the TransM code.

## 4. RESULTS and DISCUSSIONS

In this chapter, the results of the computational studies done to obtain the electronic density of states (DOS), the band structures (BS), and the thermoelectrical properties of various types of COFs are presented and interpreted.

### 4.1. Phthalocyanine-Based COFs

As reported previously metallophthalocyanine based covalent organic frameworks, in which the conduction path originates from  $\pi$ -macrocycle columns, prefer a slipped stacking arrangement (Figure 4.1 b), and thus calculations for these compounds performed accordingly [30], [52].

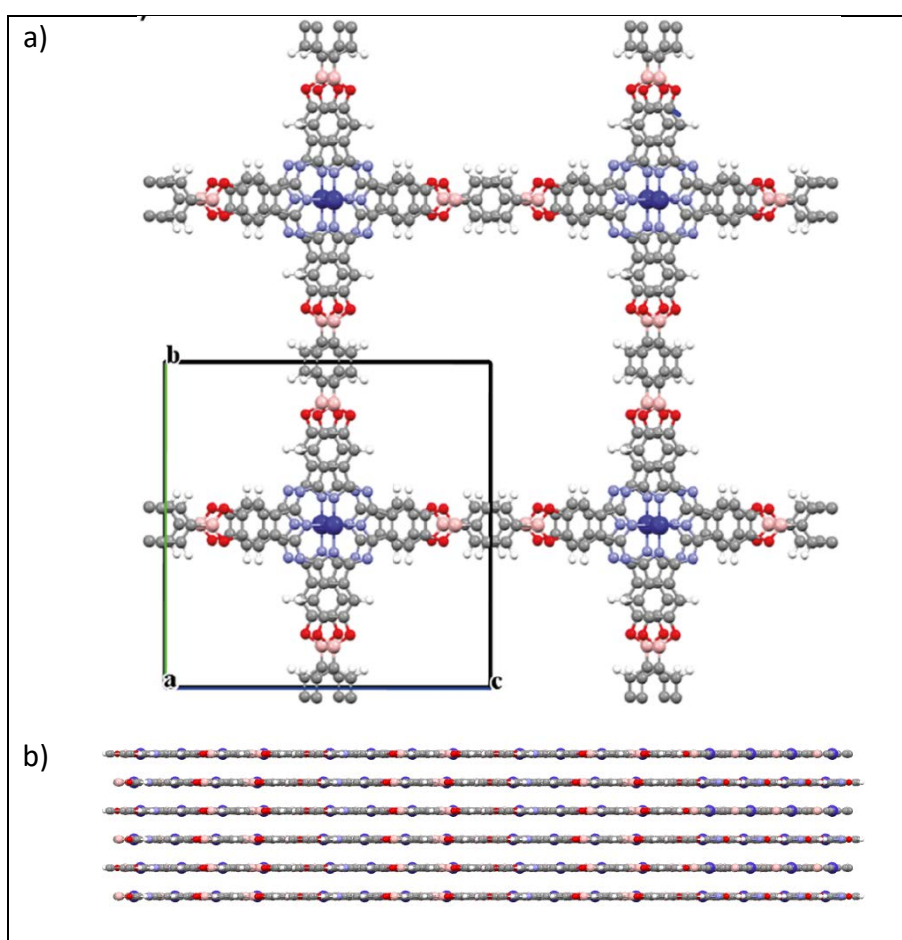


Figure 4.1: a) 2D view of MPc COFs. b) Layered structure along the crystallographic 010 plane. The sheets are shifted by 0.8 Å along c-axis.

#### 4.1.1. Band structure and DOS

First, we concentrated on calculating the density of states and the band structures. The density of electronic states or more precisely, the density of electronic states with respect to energy, simply gives the number of occupied states for electron per unit energy range. The thermoelectric properties strongly depend on the electronic structure of the materials. From the electronic structure, it is possible to estimate the thermoelectric performance of a crystal as energy bands give some important clues regarding its carrier transport properties. In this thesis, all the DOS and band figures are plotted with the Fermi level being zero.

Evidence for the influence of transition metals on the electronic structure of studied compounds has been revealed through the analysis of band structures and density of states (DOS). It has been found that both CuPc-COF and ZnPc-COF compounds are narrow-band direct semiconductors whereas CoPc-COF exhibits a semi-metallic feature. For semimetals and narrow gap semiconductors, the important physical and chemical reactions often occur vicinity of the Fermi level since charge carriers near this level are more active.

Energy curves varying along different symmetry points in Brillouin Zone visualized by the band structure. Band structure and density of states calculations for samples Co-, Cu-, and ZnPc-COF along the high symmetry points with the path  $\Gamma$ -Y-T-Z- $\Gamma$ -X-S-R-U are depicted on Figs. 4.2(a) through 2(c). The sub-bands of the VB and CB as well as their DOS are given in blue. Here the reciprocal coordinates of high-symmetry points are  $\Gamma = (0, 0, 0)$ ,  $X = (0.5, 0, 0)$ ,  $Y = (0, 0.5, 0)$ ,  $Z = (0, 0, 0.5)$ ,  $S = (0.5, 0.5, 0)$ ,  $U = (0.5, 0, 0.5)$ ,  $T = (0, 0.5, 0.5)$ ,  $R = (0.5, 0.5, 0.5)$ .

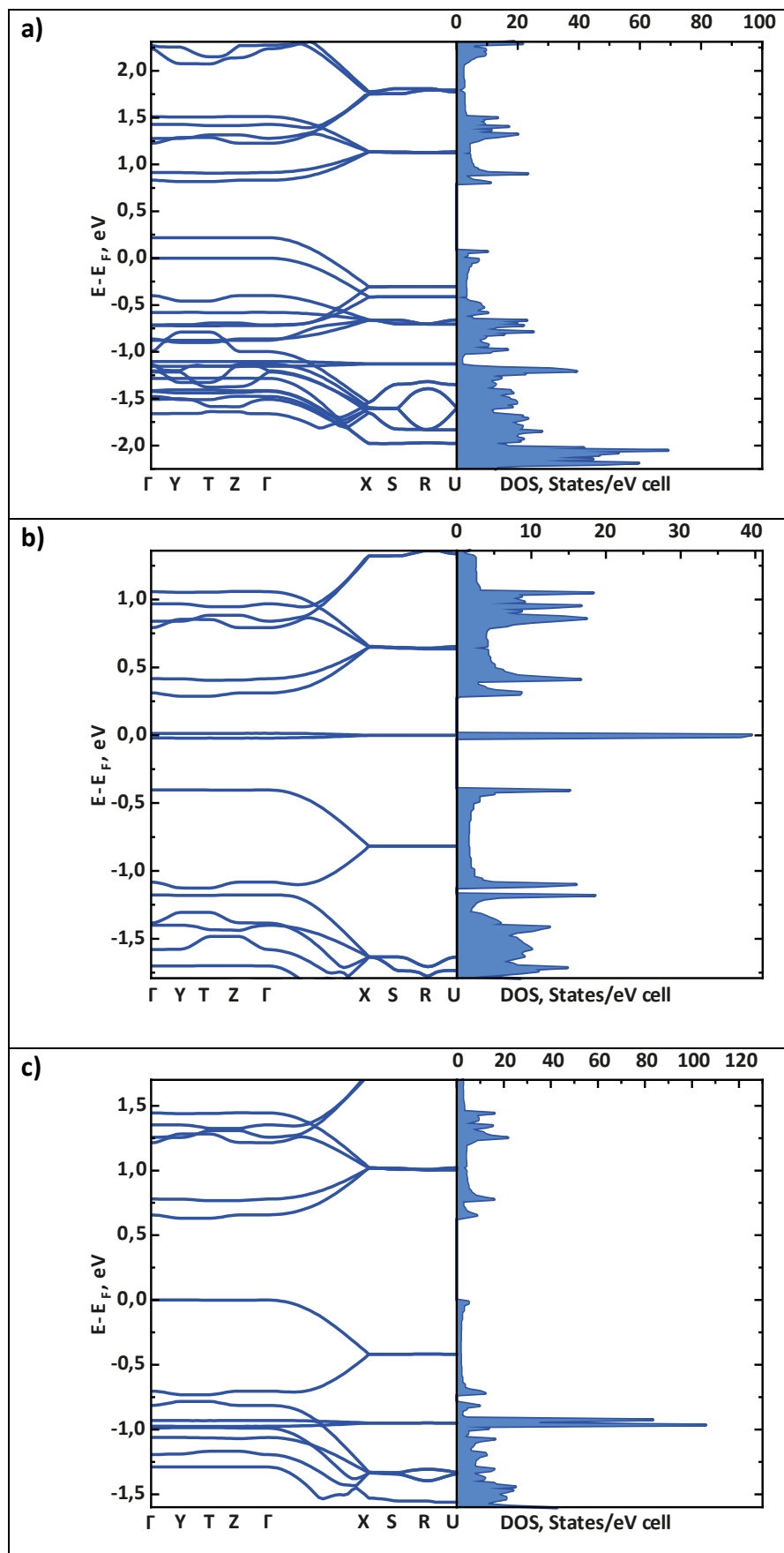


Figure 4.2: Band structures and DOS of (a) CoPc-COF, (b) CuPc-COF, (c) ZnPc-COF.

The energy band structure of CoPc COF, determined in the calculation yields a semimetal. For this compound, around high symmetry point  $X$ , there is a small overlapping between the conducting band and valence band (Fig 4.2a). Overlapping between energy sub-bands indicates that the outer valence band has an antibonding character. Flat energy bands exist along a continuum ranging from  $\Gamma$ - $Y$ ,  $Y$ - $T$ ,  $T$ - $Z$ , and  $Z$ - $\Gamma$  high symmetry lines in valence and conducting bands of CoPc-COF. This feature is not restricted to CoPc-COF but is observed in the other studied compounds. The existence of flat bands is quite typical for molecular crystals [53]. The near-zero slope nature of these sub-bands makes DOS peaks sharper and suggests that very high effective masses (thus very low mobility) appear along  $-y$  and  $-z$  directions. This also increases the Seebeck coefficient as well since it is related to effective mass. However, the  $\Gamma$ - $X$  branch of the band structure showing the nonlinear slopes in both valence and conducting bands of CoPc-COF. The slopes mean a smaller effective mass of electrons (holes) and then a smaller exciton binding energy along the  $x$ -direction. Along the  $X$ - $S$ ,  $S$ - $R$ , and  $R$ - $U$  high symmetry lines, the dispersion bands are parallel. This is the case for both valence and conduction bands (except some energy sub-bands around  $-1.5$  eV in valence band) of CoPc-COF. As the dispersion varies from slope to flat, the effective mass becomes larger and hence decreases the electrical conductivity.

The calculated band structure and density of states for CuPc-COF are shown in Figure 4.2(b). The valence band maximum (VBM) and conducting band minimum (CBM) are located at the same high symmetry point  $Y$  and seem to be extended towards  $T$  which indicates CuPc-COF is a direct bandgap semiconductor. The energy band between VBM and CBM is 0.285 eV. Both Cu-, and ZnPc-COF's band structure, as in CoPc-COF's, have a corrugated character. ZnPc-COF is a direct bandgap semiconductor with a bandgap of 0.634 eV. Both the VBM and CBM locate at high symmetry point  $Z$  for ZnPc-COF. ZnPc COF shows that the CBs are farther to the  $E_F$  than the other two compounds, which resulted in a small peak of DOSs around the Fermi level. In all three compounds, light bands are mainly observed along the stacking direction while heavy bands are dominating over light bands in the  $yz$ -plane. It is known that light bands favorable for electrical conduction. Moreover, it is also

known that the presence of heavy bands enhances the Seebeck coefficient. These two facts will be demonstrated in the next section.

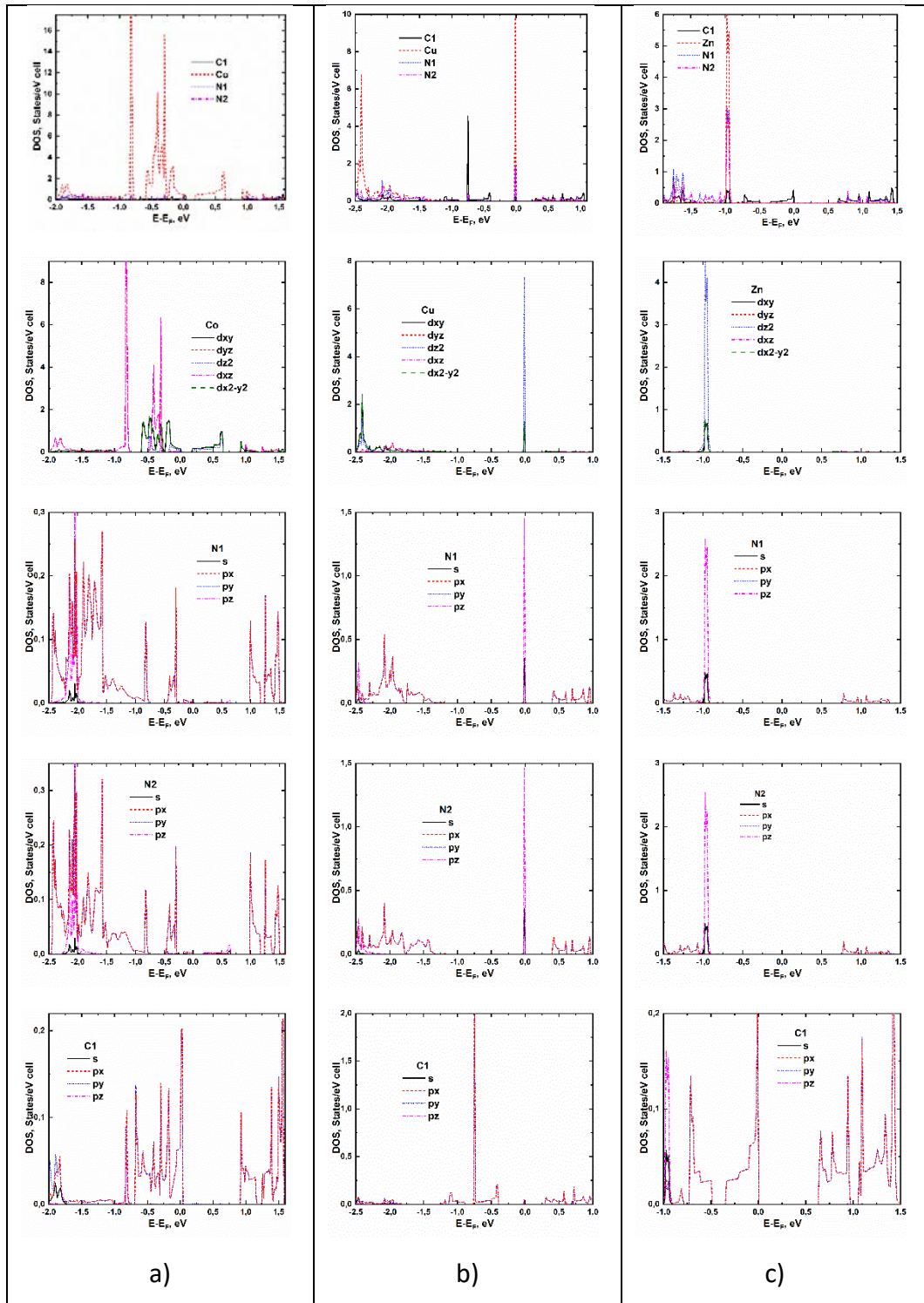


Figure 4.3: The projected density of states (PDOS) of a) CoPc COF, b) CuPc COF, c) ZnPc COF, with m-decomposition.

To reach a further understanding of the electronic structure, partial densities of states (PDOS) of Co-, Cu-, and ZnPc COF are plotted in Figure 4.3. Analysis of the PDOS showed that Co atom's d states in CoPc COF dominate in the ranges of  $-2$  –  $-0.75$  and  $-0.6$  –  $0$  eV, due to contributions from individual  $d_{xz}$ ,  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals. The highest peak is at around  $-0.8$  eV and  $d_{xz}$  orbital is the main contributor to this peak. d states of Co atom are significantly hybridized with s and  $p_x$  states of the organic ligand in the valence band. Both  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals contribute to the edge of the valence band. d states lie in the range  $0.2$  –  $0.65$  eV in the conduction band while the main contribution comes from  $d_{xz}$  and  $d_{z^2}$  orbitals within the energy range of  $0.9$  –  $1.6$  eV. It is found that there is a hybridization between the d states of the central atom Co's s and organic ligand's  $p_x$  orbitals.

In CuPc COF, contribution to the DOS on the Fermi level mainly comes from  $d_{z^2}$  orbital of the Cu atom with a small admixture of the Ni atom's  $p_z$  states. Cu atom's d states in CuPc COF dominate in the range of  $-2.5$  –  $-1.1$  eV while the s and p states of the organic ligand mostly contribute to the range of  $-2.5$  –  $-0.4$  eV, which leads to hybridization between the d states of Cu atom with s and  $p_x$  orbitals of the organic ligand. The conduction band is essentially dominated by the organic ligand's s and  $p_x$  states with a small contribution of the central atom Cu's  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals.

In ZnPc COF, the highest peak of PDOS is located in the range of  $-0.9$  –  $-1.5$  eV in the valence band region. Also, the majority  $d_{z^2}$  state of the Zn atom which overlaps with  $p_z$  states of the organic ligand seems to be a bit too close to the Fermi level. In ZnPc COF, the energy interval between the conduction band edge and  $1.5$  eV is dominated by  $p_x$  orbitals of the organic ligand. From PDOS it is learnt that in CoPc COF and CuPc COF the contribution to the valence band maximum (VBM) and the conduction band minimum (CBM) is mainly from d states whereas in ZnPc COF, the VBM and the CBM are composed by p states of the organic ligand. Furthermore, because of orbital hybridization, all MPc COFs show strong covalent bond (Figure 4.4).

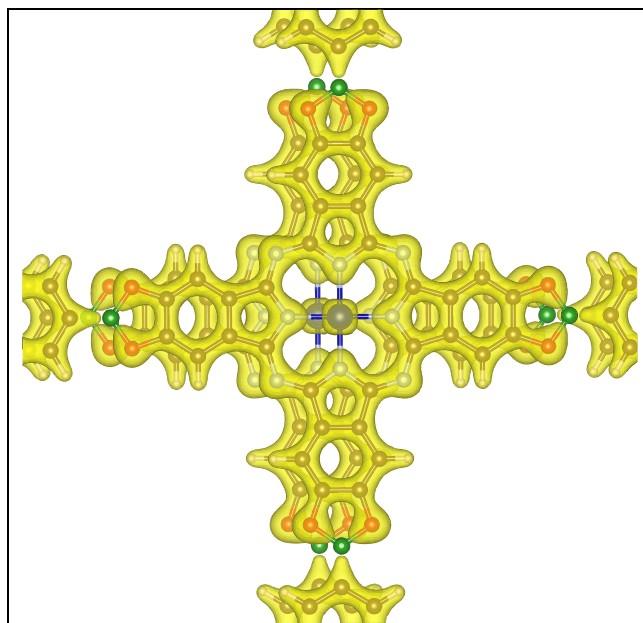


Figure 4.4: Isosurfaces of electron charge densities for MPc COFs showing the highly covalent bonds between the atoms.

#### 4.1.2. Thermoelectric coefficients

The thermoelectric (TE) effect is the direct and reversible conversion of temperature differences to an electric voltage. This effect can occur in all conductive substances and has motivated the study of significant thermoelectrical factors, such as the calculation of electrical and thermal conductivity, the Seebeck coefficient, and the figure of merit  $ZT$  in Pc COFs. The anisotropic band structure of MPc-COFs, ( $M = \text{Co}, \text{Cu}, \text{and Zn}$ ) is expected to exhibit anisotropic electronic transport coefficients. The calculated thermal coefficients of the studied compounds confirm the anisotropic behavior.

Temperature dependences of electronic thermal ( $\kappa_e$ ) and electrical conductivity ( $\sigma$ ) coefficients across a wide range of temperature of MPc COFs along the three crystalline directions are shown in Fig. 4.5 and Fig 4.6. The results of calculations show that for all three studied compounds, the temperature dependence of  $\kappa_e$  and  $\sigma$  have similar character towards -b and -c directions. However, the values in these directions are significantly lower than the corresponding values in the a-direction. As depicted in Figures 4.6a-c, the electrical conductivity values of the samples show the following order in the studied temperature range for a-axis:  $\sigma_{\text{CoPc-}}$

COF >  $\sigma_{\text{ZnPc-COF}}$  >  $\sigma_{\text{CuPc-COF}}$ . The  $\sigma$  values of all compounds increase gradually with increasing temperature except for CuPc COF. As can be seen from Figure 4.5 b for this compound the electrical conductivity along the a-axis decreased with increasing temperature until around 550 K and then increased. The change at 550 K is not very sharp, but it is the temperature interval at 400 K to 700 K. We have taken its average as 550 K. Below 550 K, electrical conductivity decreases with temperature indicating that CuPc COF may become metallic below 550 K, as shown in Fig. 4.5 b. These results also agree with electronic band structures and the density of states of studied compounds discussed above.

The temperature dependence of thermal conductivity of MPc COFs has been investigated from room temperature to well beyond 900 K. Plots of thermal conductivity versus temperature shown in Figure 4.6. The thermal conductivity characteristics of MPc COFs depending on temperature also shows a very similar tendency as that of the electronic conductivity. It increases with increasing temperature in the order of CoPc COF, ZnPc COF, and CuPc COF as shown in Figure 4.6. As has been briefly outlined in the Introduction it is expected that COFs will have a very low thermal conductivity as they have many voids that largely disturb phonon transport in a long-range. It is found that thermal conductivity for all three samples is lower than 7 W/mK in the entire temperature range, which is relatively low for a thermoelectric material. Thermal conductivities for all compounds increase as temperature increases as depicted in Figure 4.6. Evidently, the thermal conductivity comes mainly from electronic thermal conductivity.

The thermal conductivity of CuPc COF is nearly zero from 200 to 400 K and sharply increases to 0.6 W/mK at 800 K. However, this compound has the lowest thermal conductivity among the three studied compounds at any temperature. At room temperature, the calculated thermal conductivities along the stacking direction are 2.1 W/mK for CoPc COF, 0.0014 W/mK for CuPc COF, and 0.7 W/mK for ZnPc COF, respectively. With the temperature increasing to 900 K, the thermal conductivities reach 7.2 W/mK for CoPc COF, 1.1 W/mK for CuPc COF, and 3.4 W/mK for ZnPc COF, respectively. CoPc exhibits higher thermal conductivity at any temperature as compared to the other two that can be attributed to high carrier concentration in this compound.

The calculated results for ZnPc COF are of particular interest since, due to the small influence of the Zn atom on the electronic structure, ZnPc COF exhibits very similar characteristics as those of central-metal-free Pc COF [12]. The evolution of the thermal and electronic conductivity of ZnPc COF as a function of temperature (see Figures 4.5 c and 4.6 c agree with what has been found in a previous study in which the conductivity specifications of the metal-free Pc COFs were reported [4].

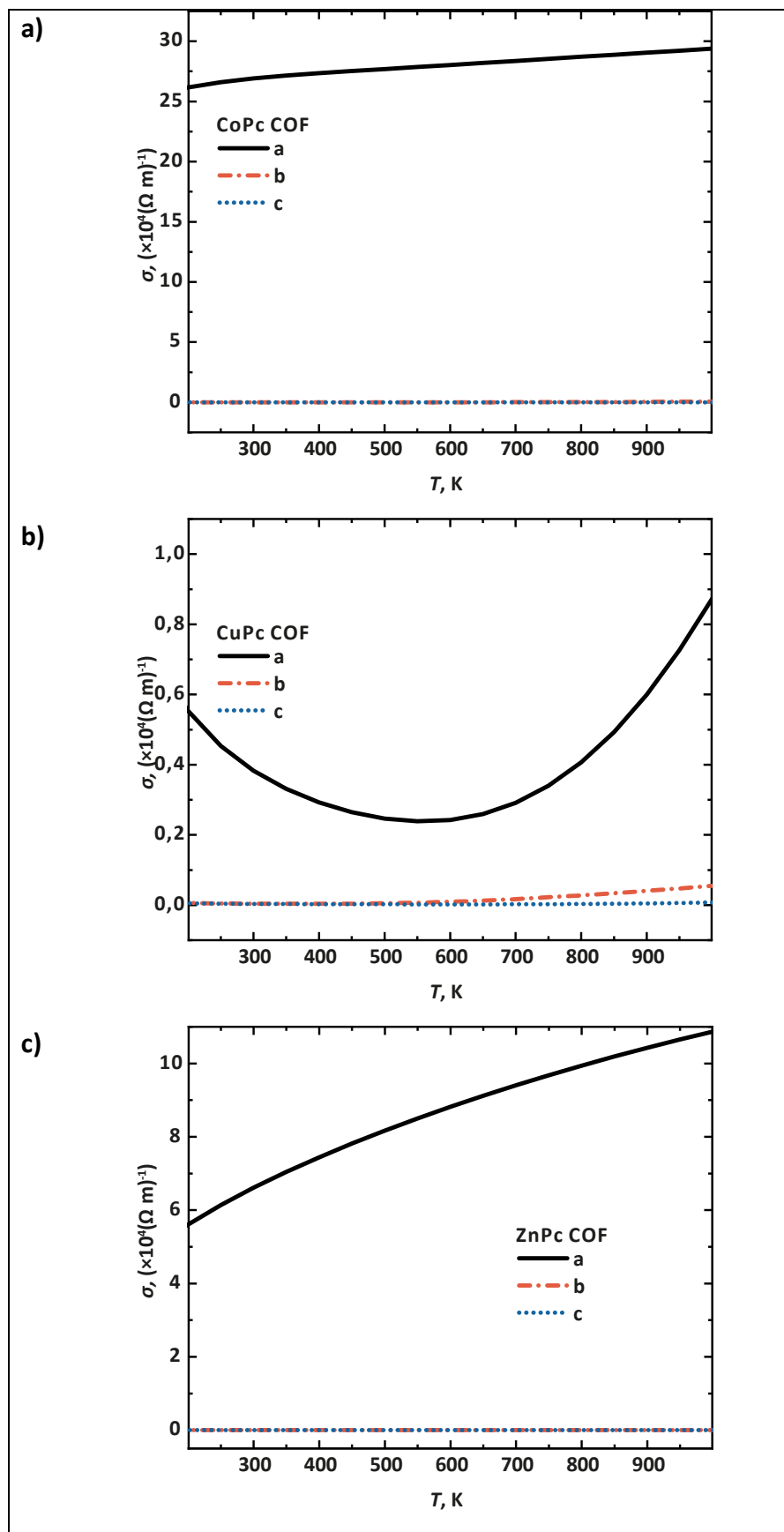


Figure 4.5: Calculated electrical conductivity of a) CoPc COF, b) CuPc COF, c) ZnPc COF.

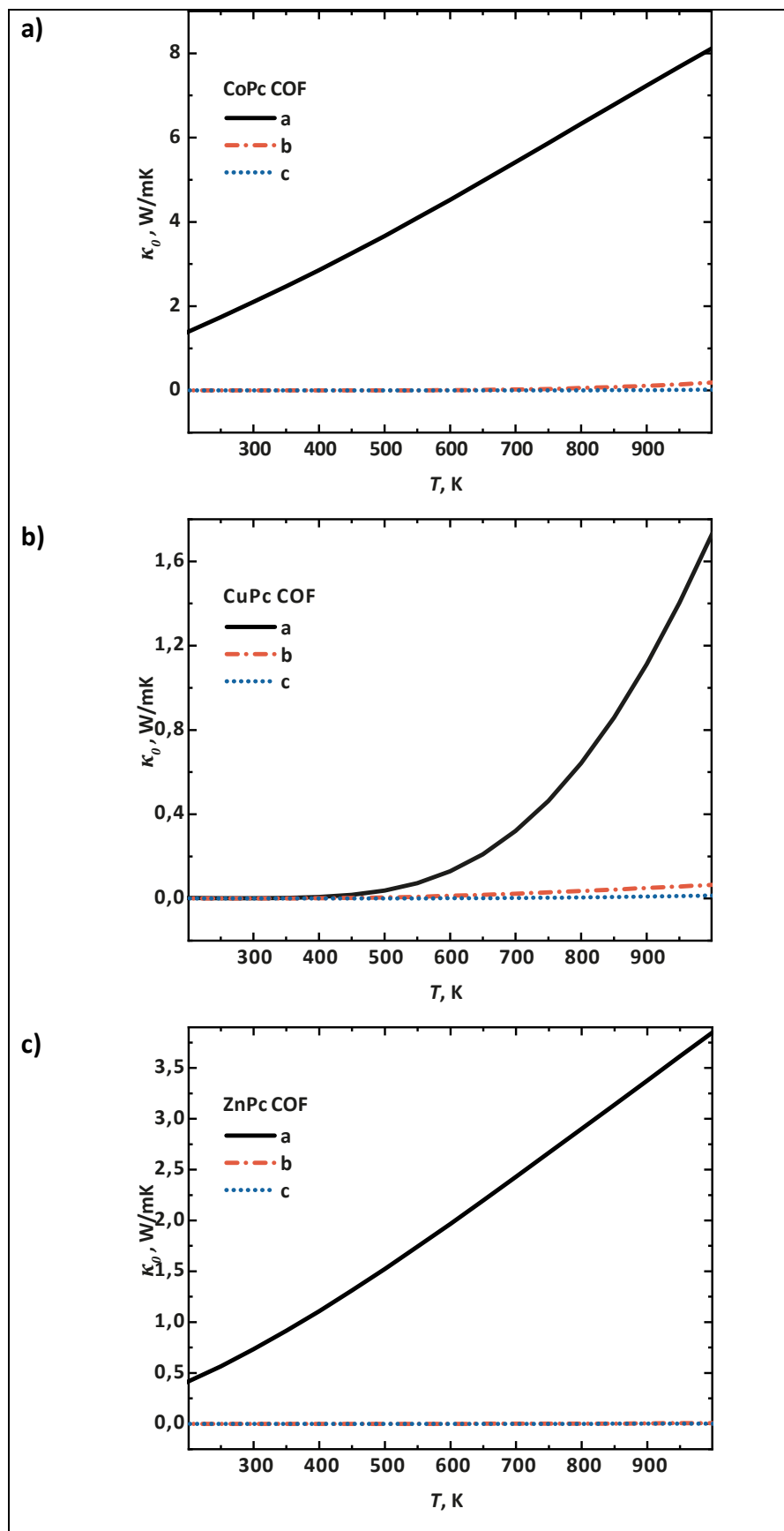


Figure 4.6: Calculated thermal conductivity of a) CoPc COF, b) CuPc COF, c) ZnPc COF.

Bulk effects such as grain morphology and synthesis techniques can influence electrical conductivity. The Seebeck coefficient is not as vulnerable to bulk effects, so it is more reliable to indicate conduction modes [54]. The Seebeck coefficient of all the compounds does not vary much as a function of temperature until 400 K (Figure 4.7). Beyond 400 K, in in-plane directions, a rapid increase in the Seebeck coefficient is observed with temperature, especially between 600 K and higher temperatures. Thermopower values along the stacking directions are less significant compared to those of in-plane directions for all studied compounds.

It is a known fact that the asymmetry of the electron distribution around the Fermi level dictates whether the sign of the Seebeck coefficient is positive or negative. That is the sign of the Seebeck coefficient determined by the majority of charge carriers. The magnitude of the Seebeck coefficient is also influenced by this asymmetry. CoPc COF exhibits a steep slope at the Fermi level, thus indicating an improved Seebeck coefficient (Fig 4.7 a). The calculated values of the Seebeck coefficient for CoPc COF are positive along with all directions, pointing to holes as the main charge carriers. The maximum thermopower value was found to be 770  $\mu\text{V/K}$  at 590 K for this compound along the in-plane b direction. Such a situation is not unique to CoPc COF but also the other two compounds' maximum thermopower values placed on the b-direction. CuPc COF has a negative Seebeck coefficient indicating a predominant electronic conduction mechanism (Fig. 4.7 b). The significant localized density of electronic states in the vicinity of the Fermi level and the presence of pseudo gaps in the valence band seem to be possible explanations for this feature of CuPc COF. The maximum thermopower value was found to be 423  $\mu\text{V/K}$  at 650 K for this compound. ZnPc COF exhibits nearly temperature-independent thermopower along the stacking direction (Fig 4.7 c). For all the compounds in this study, the thermopower rate changing with temperature is minimal along the -a direction. The mean value of thermopower for ZnPc COF along this direction is 156  $\mu\text{V/K}$ , which is much lower than those of along b and -c directions. Furthermore, the maximum thermopower value is -315  $\mu\text{V/K}$  at 920 K along the in-plane direction b.

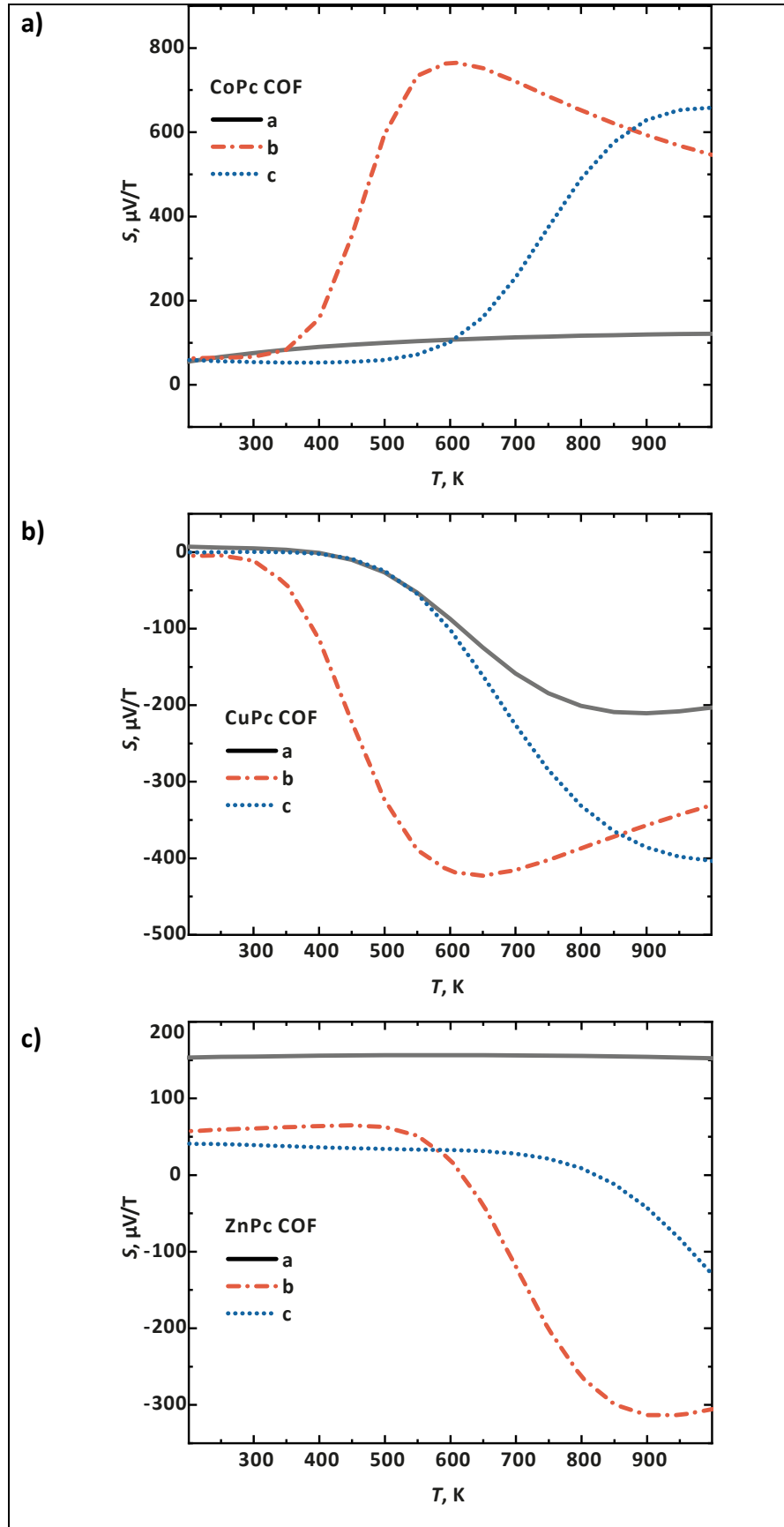


Figure 4.7: Calculated Seebeck coefficients of a) CoPc COF, b) CuPc COF, c) ZnPc COF.

The figure of merit ZT as a function temperature for CoPc COF, CuPc COF, ZnPc COF are shown in Figure 4.9. Electrical conductivity, thermal conductivity, and Seebeck coefficient calculations reveal that the maximum figure of merit ZT value can be expected for the composition CoPc COF, which reaches 0.972 at a temperature of 780 K. The maximum ZT value for this compound is observed along -b direction. The room temperature ZT values for the three samples are CoPc COF $\approx$ 0.24, CuPc COF $\approx$ 0.35, and ZnPc COF $\approx$ 0.02. The maximum ZT values for all three compounds are at high temperatures, suggesting the MPc COFs will be useful at high temperatures.

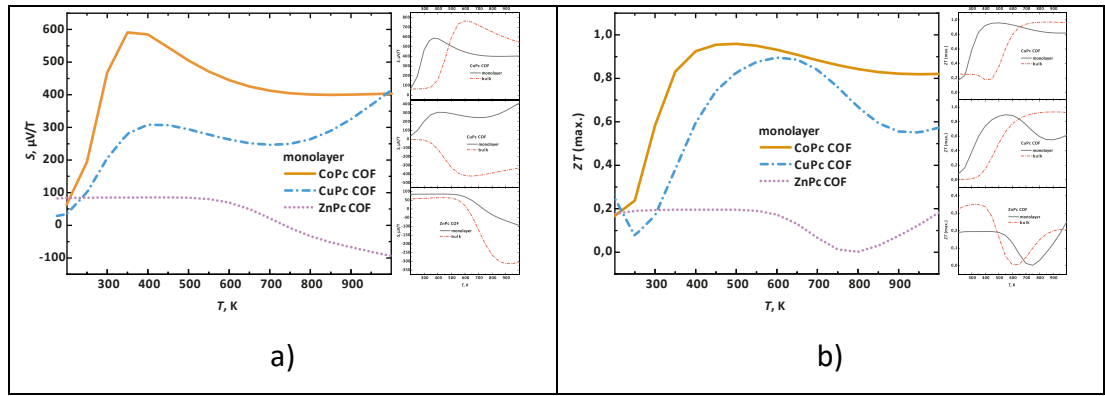


Figure 4.8: a) Seebeck coefficient and b) ZT values for monolayer MPc COFs and their comparisons with bulk counterparts.

Temperature-dependent Seebeck coefficient and ZT values of monolayer MPc COF (M=Co, Cu, Zn) compounds are shown in Fig. 4.8. At room temperature, monolayer Co-, Cu- and ZnPc COF exhibit a ZT value of 0.583, 0.168, and 0.194 respectively while the highest ZT values they possess are 0.959 (500 K), 0.895 (600 K), and 0.195 (450K) respectively. This order is also found for the Seebeck coefficients of the same monolayer compounds. The maximum Seebeck coefficient is observed to be about 591  $\mu\text{V/K}$  (350 K) for CoPc COF, 414 (1000 K)  $\mu\text{V/K}$  for CuPc COF, and -94  $\mu\text{V/K}$  (1000 K) for ZnPc COF. We find that the monolayer structure of CuPc COF is a p-type semiconductor, whereas it becomes an n-type semiconductor in its bulk state. Evidence from the electronic band structure suggests that it may be related to the Fermi level corresponding to the CBM and VBM of the monolayer structure. Shifting downwards of the FL from the CBM to VBM may be resulting in a transformation from the n-type to p-type behavior.

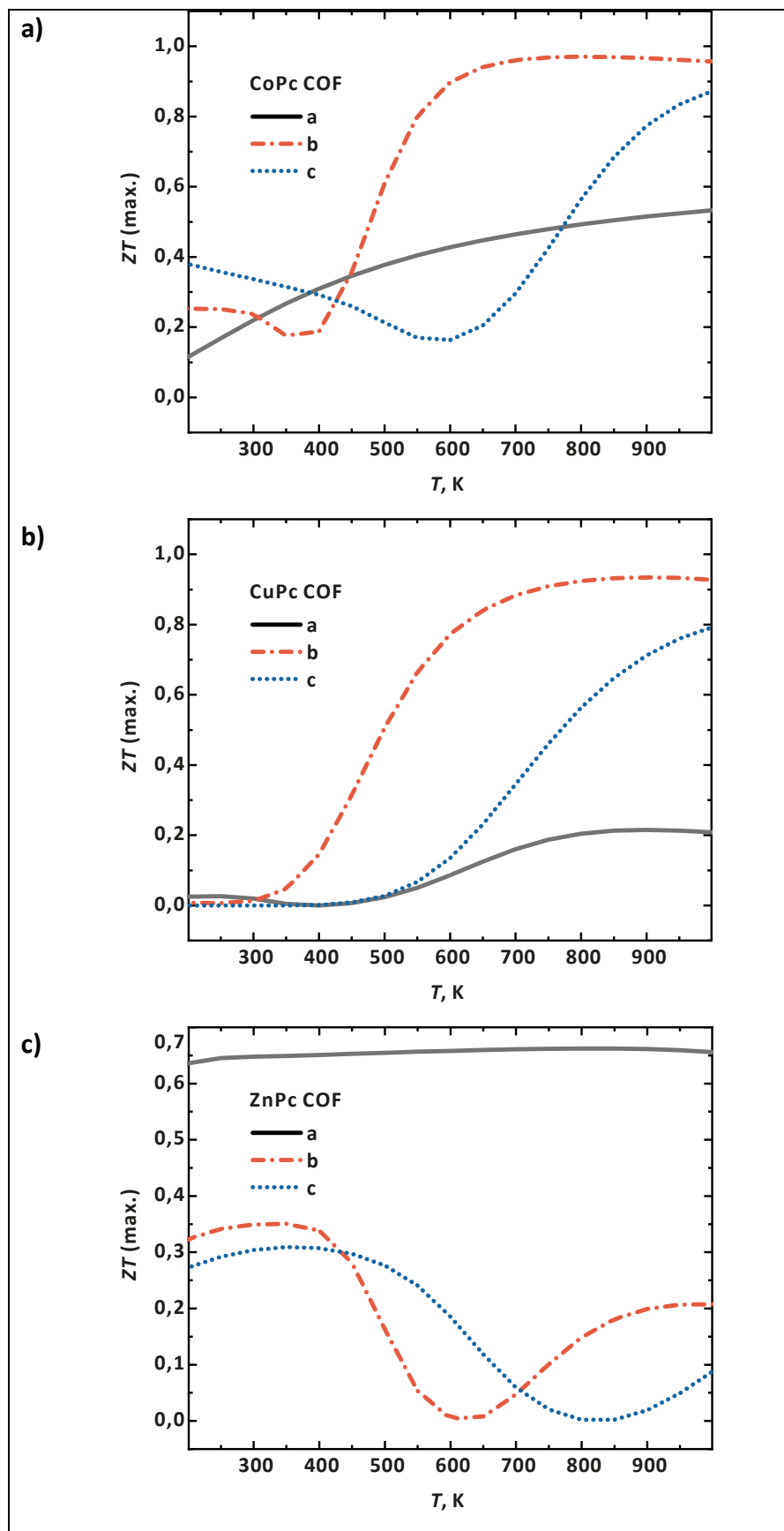


Figure 4.9: Calculated ZT of a) CoPc COF, b) CuPc COF, c) ZnPc COF.

Further, to demonstrate the electronic aspect of ZT in order to find the high-performance thermoelectric material, we calculated the electronic fitness function (EFF) of three MPc COF compounds as a function of n-type (Figure 4.10-a and -b) and p-type (Figure 4.10-c and -d) doping level. In Figure 4.10 a and d we present the electronic fitness function (EFF) with respect to the carriers' concentration at 300 and 800 K for MPc COFs. For all n-type doped MPc COFs, it is observed that EFF increases with temperature. All compounds show larger n-type EFF values along the stacking direction. Among n-type materials, ZnPc COF possesses the highest thermoelectric performance along the stacking direction while CoPc COF possesses the best performance in the in-plane -b direction at 300 K. However, ZnPc COFs in-plane direction EFF values are insignificant compared with those of out-of-plane direction.

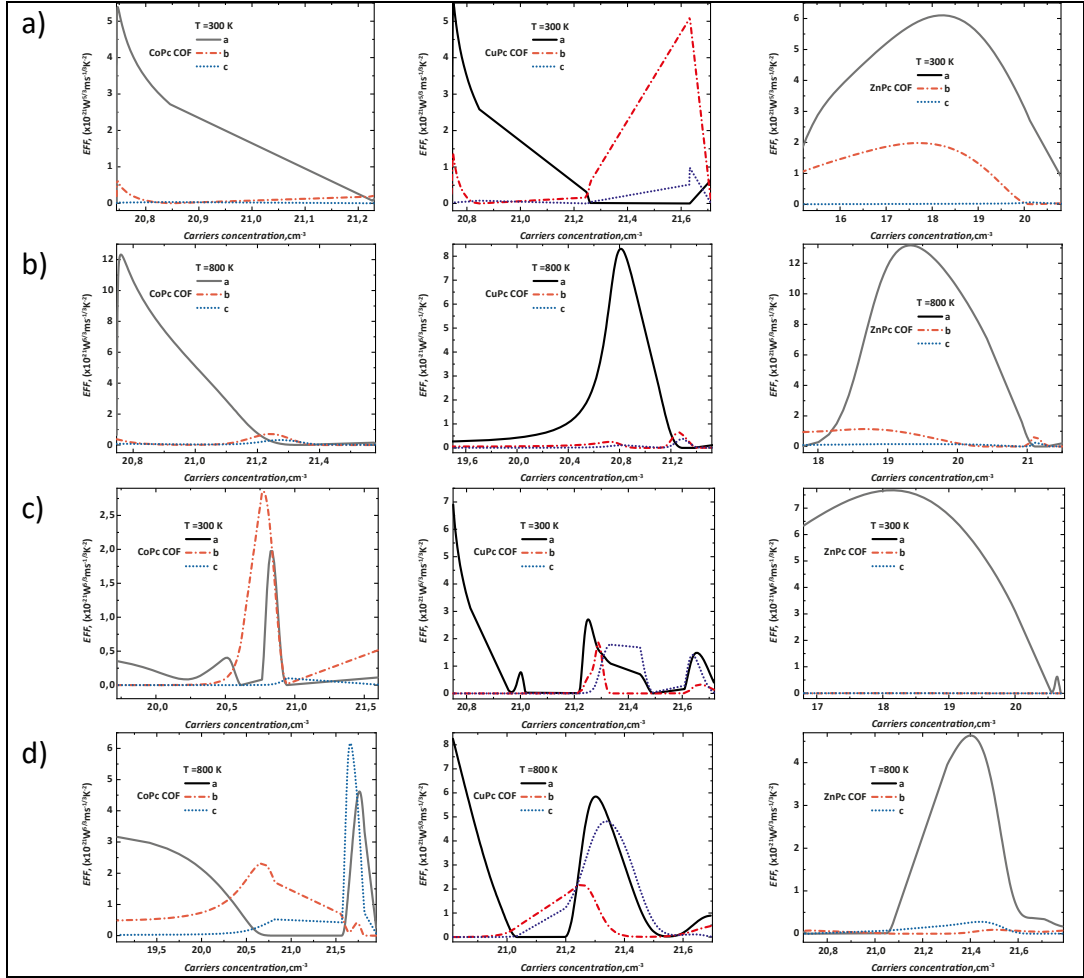


Figure 4.10: Calculated electronic fitness functions (EFF) with respect to the carrier concentration of n-type of compounds at a) 300 K and b) 800K and p-type compounds at c) 300 K and d) 800K.

Figure 4.10-a to -d showing the EFF variation with electron concentration at different temperatures and along the a-, b- and c-axes. P-type doping compounds possess more anisotropic electronic fitness function in comparison with n-type doping compounds at 300 and 800K. ZnPc COF is the only compound that exhibits a larger EFF value along stacking direction than in-plane directions at both temperatures. Moreover, this compound shows the best TE performance at 300 K among all studied compounds. For CoPc COF, the maximum values of EFF are found to be along -b direction and at high concentration along, -c direction at 300 and 800 K respectively. Among all the p-doped compounds CuPc COF have the best TE performance at 800 K. the maximum value that CuPc COF possesses is along the stacking direction.

Based on the Mott formula mentioned in the introduction section, we can conclude that when calculating the thermopower of a material, it is necessary to take into account the influence of the carrier concentration. n- and p-type doping of MPc COFs are effective to increase the Seebeck coefficient at both 300 and 800 K. The Seebeck coefficient as a function of carrier concentration at 300 and 800 K for CoPc COF, CuPc COF, ZnPc COF are shown in Figure 4.11. At 300 K, CoPc COF and CuPc COF show maximum values of thermopower along with all crystallographic directions and the values range from -700 till -800  $\mu\text{V/K}$ . The ZnPc COF shows the maximum value of thermopower (1300  $\mu\text{V/K}$ ) along c-direction, among all n-type compounds. However, increasing temperature causes a decrease in the Seebeck coefficient for all n-type doping MPc COFs. At 300 K the maximum values of Seebeck coefficients for p-doping compounds (Figure 4.11 c and d) are found along b-, c- (in-plane) and a- (out-of-plane) directions for CoPc COF, CuPc COF, and ZnPc COF respectively. The maximum thermopower values are between 700 and 800  $\mu\text{V/K}$  for all studied compounds. The Seebeck coefficient value decreasing with temperature is observed in p-type doping MPc COFs as well, which is coherent. The maximum values of S at 800 K are observed along with in-plane directions for all MPc COFs. In the framework of rigid band structure, the chemical potential shifts with the doping. Consequently, humps observed in the Seebeck coefficient dependences in the plots may be caused by an increase in the effective mass in a local range of carrier concentration. As was foreseeable, the Seebeck coefficients are lower with higher amounts of carrier density.

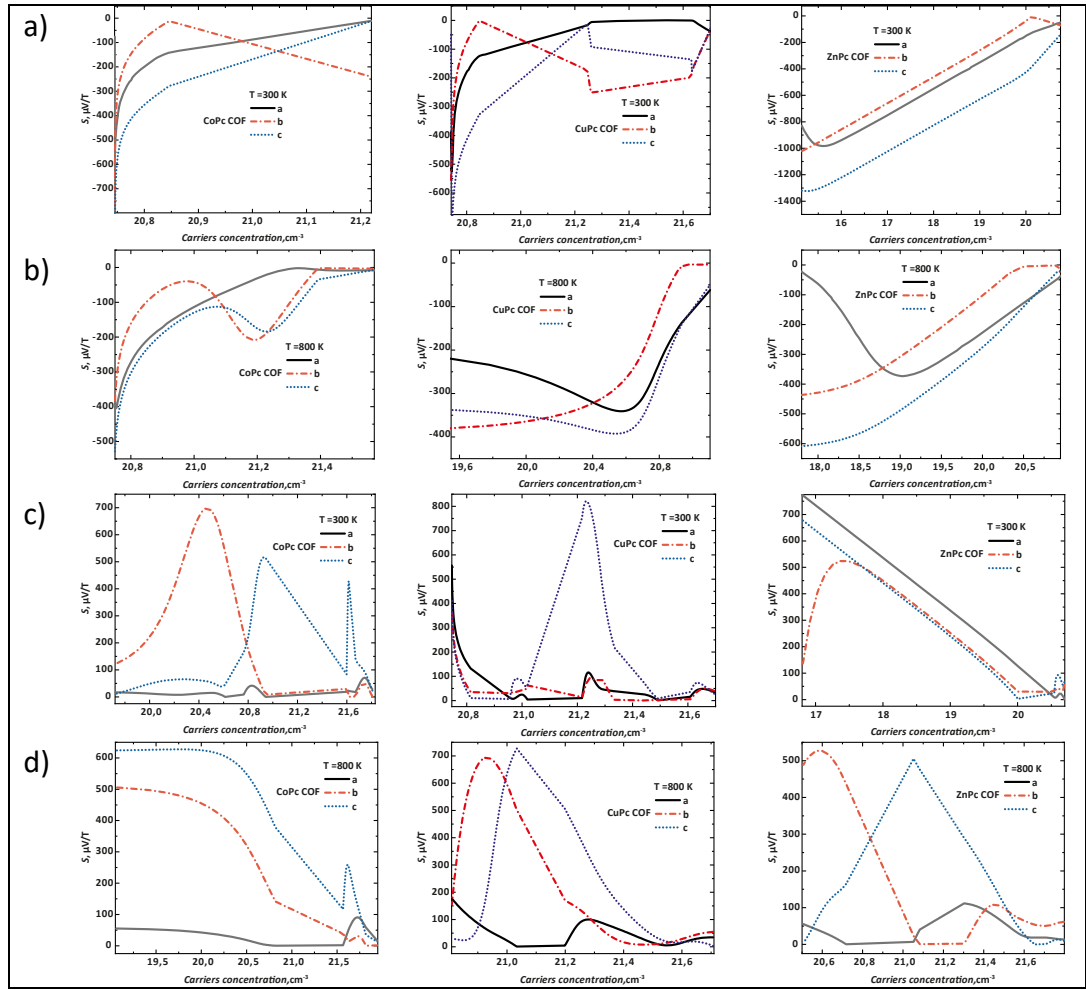


Figure 4.11: Carrier concentration dependent Seebeck coefficient for n-type compounds at a) 300 K, b) 800 K and p-type compounds at c) 300 K, d) 800 K.

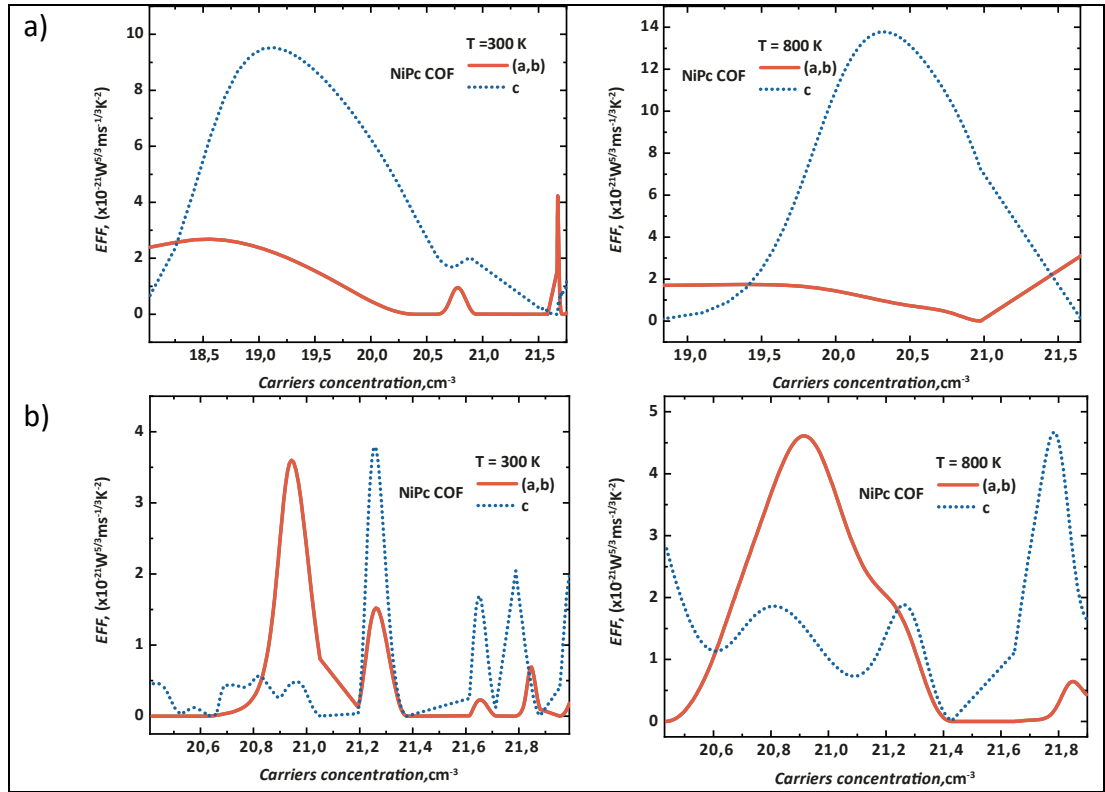


Figure 4.12: Calculated electronic fitness functions (EFF) with respect to the carrier concentration of a) n-type doping and b) p-type doping NiPc COFs at 300 and 800 K.

For the sake of the comparison, we have also performed calculations for the eclipsed AA stacking structure of NiPc COF. Band structure and density of state calculations show that this compound is an indirect bandgap material. Unlike the other MPc COFs, NiPc COF shows less anisotropy, due to its stacking-dependent electronic properties. The results obtained from the EFF calculations indicate that NiPc COF is close to optimum doping at 800 K.

Figure 4.12 shows the electronic fitness function variation with electron concentration at different temperatures and along both the a-, b- and c-axes. For NiPc COF, which has the best thermoelectric performance among MPc COFs, the EFF has the same value along the in-plane a- and b- directions. The EFF exhibits significant values along in-plane (a- and b-) as well as along stacking direction (c-) at 300 and 800 K. Figure 4.13 shows the Seebeck coefficient variation with electron concentration at different temperatures and along both the a-, b- and c-axes. Like the other MPc COF compounds mentioned here, NiPc COF's thermopower value is decreasing with

increasing temperature. At 800 K the maximum  $S$  value is observed along in-plane a- and b- directions.

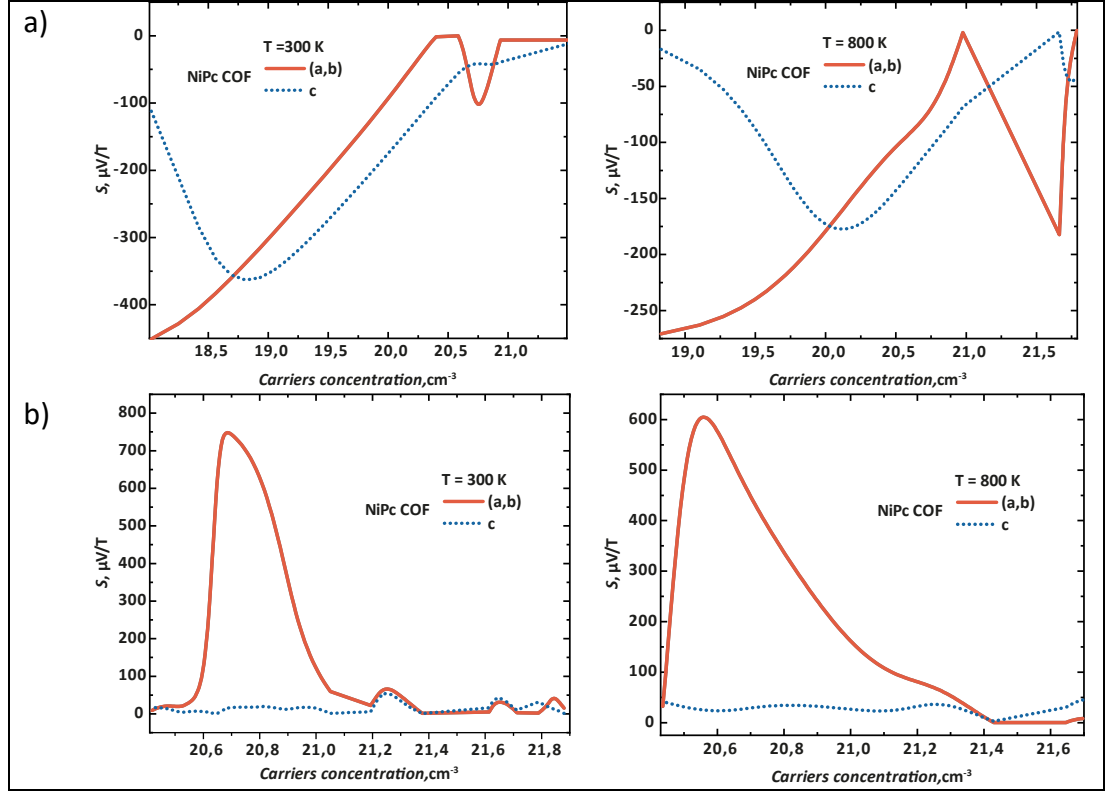


Figure 4.13: Calculated Seebeck coefficients with respect to the carrier concentration of a) n-type doping and b) p-type doping NiPc COFs at 300 and 800K.

## 4.2. Porphyrin-Based COFs

Porphyrin-Based COFs are other candidates, thermoelectric material identified in the present calculations. In contrast to the three compounds discussed above, metalloporphyrin COFs prefer an eclipsed stacking. They possess simultaneously low thermal conductivity and high electrical conductivity, indicating promising thermoelectric materials.

Table 4.1: Summary table for bandgap information of porphyrin-based COFs.

| <i>Material</i>  | Minimum optical gap (eV) | Fundamental gap (eV) |
|------------------|--------------------------|----------------------|
| <i>COF-366</i>   | 0.0097                   | 0.0097               |
| <i>NiCOF-366</i> | 0.2194                   | 0.2194               |
| <i>COF-66</i>    | 1.1775                   | 0.5266               |
| <i>NiCOF-66</i>  | 1.2477                   | 1.2073               |

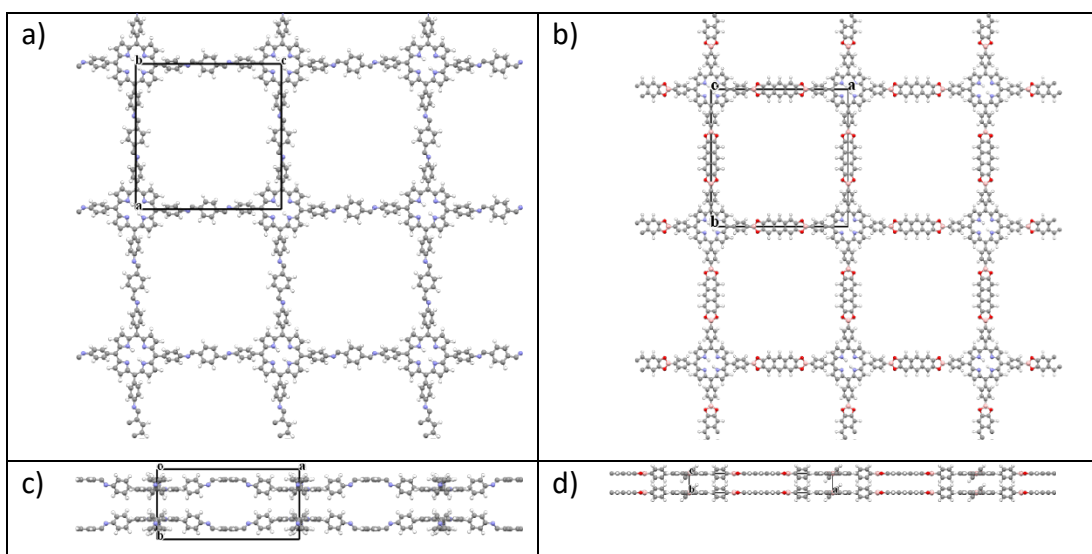


Figure 4.14: Top view of a) COF-366 and b) COF-66, side view of c) COF-366 and d) COF-66 with AA packing.

#### 4.2.1. Band structure and DOS

MP COFs are relatively less studied materials. In order to gain insight into the transport properties of COF -366 and -66, we plotted band structure as well as density of states. The calculated electronic band structure and corresponding density of electronic states for the COF-366 and -66 are shown in Figures 4.15 a and 4.15 b, respectively. The reciprocal coordinates of high-symmetry points for bulk COF-366 are X (0.5, 0, 0),  $\Gamma$  (0, 0, 0), Y (0, 0.5, 0), V (0.5, 0.5, 0),  $\Gamma$  (0, 0, 0), Z (0, 0, 0.5), R (0.5, 0.5, 0.5),  $\Gamma$  (0, 0, 0) and for bulk COF-66 are X (0.5, 0, 0),  $\Gamma$  (0, 0, 0), Y (0, 0.5, 0), V (0.5, 0.5, 0),  $\Gamma$  (0, 0, 0), Z (0, 0, 0.5). COF-366 has an almost dispersionless electronic band structure along the entire path of the irreducible Brillouin zone. It is found that COF

366 is a semimetal with a substantial overlap between conduction and valence bands. According to the obtained results, COF-66 is an indirect bandgap semiconductor with the valence band top at the  $\Gamma$  high symmetry point and with the conduction band bottom at the R high symmetry point. Moreover, its bandgap is 1.178 eV (Table 4.1).

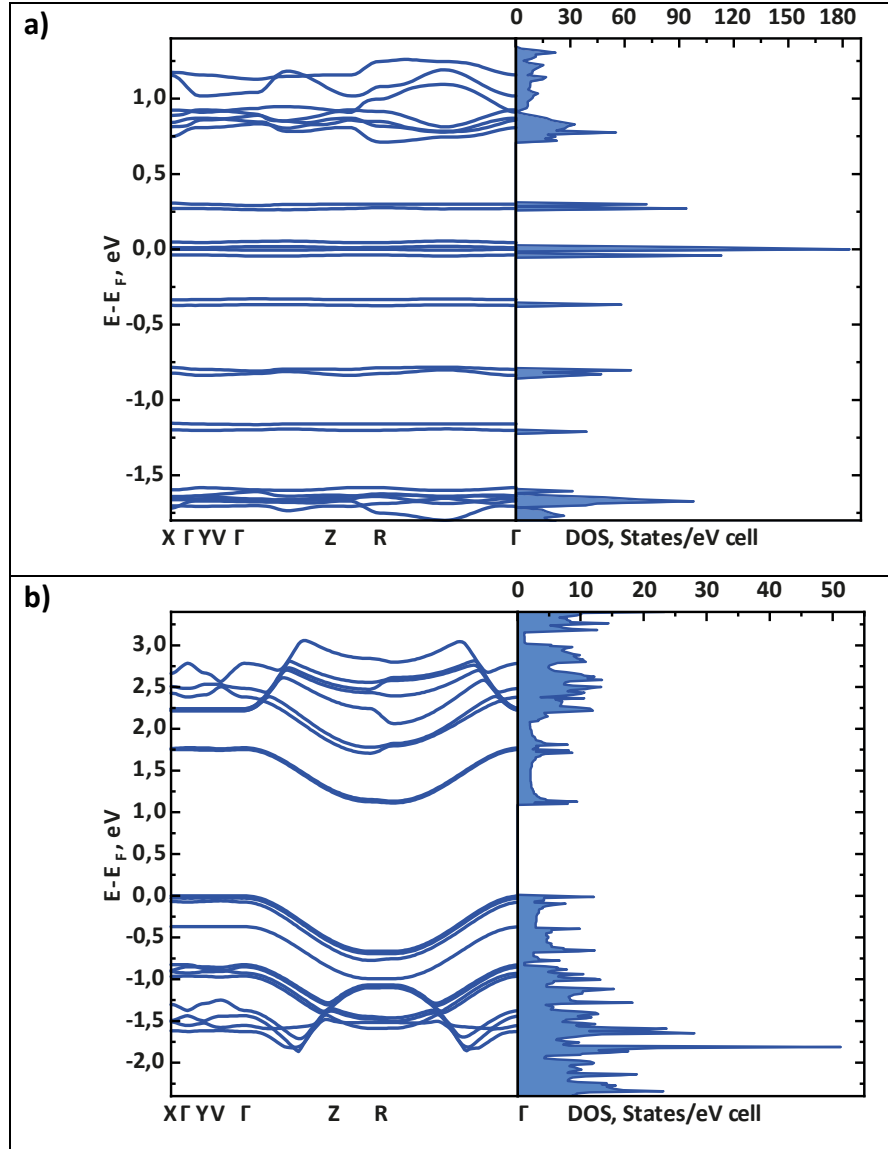


Figure 4.15: Band structures and DOS of bulk (a) COF-366, (b) COF-66.

In Figure 4.16 we display the electronic band structures of both monolayer COF-366 and -66. The reciprocal coordinates of high-symmetry points for this structures in the irreducible part of the first Brillouin zone are X (0.5, 0, 0),  $\Gamma$  (0, 0, 0), Y (0, 0.5,

0), V (0.5, 0.5, 0),  $\Gamma$  (0, 0, 0) and,  $\Gamma$  (0, 0, 0), Y (0, 0.5, 0), V (0.5, 0.5, 0),  $\Gamma$  (0, 0, 0) respectively.

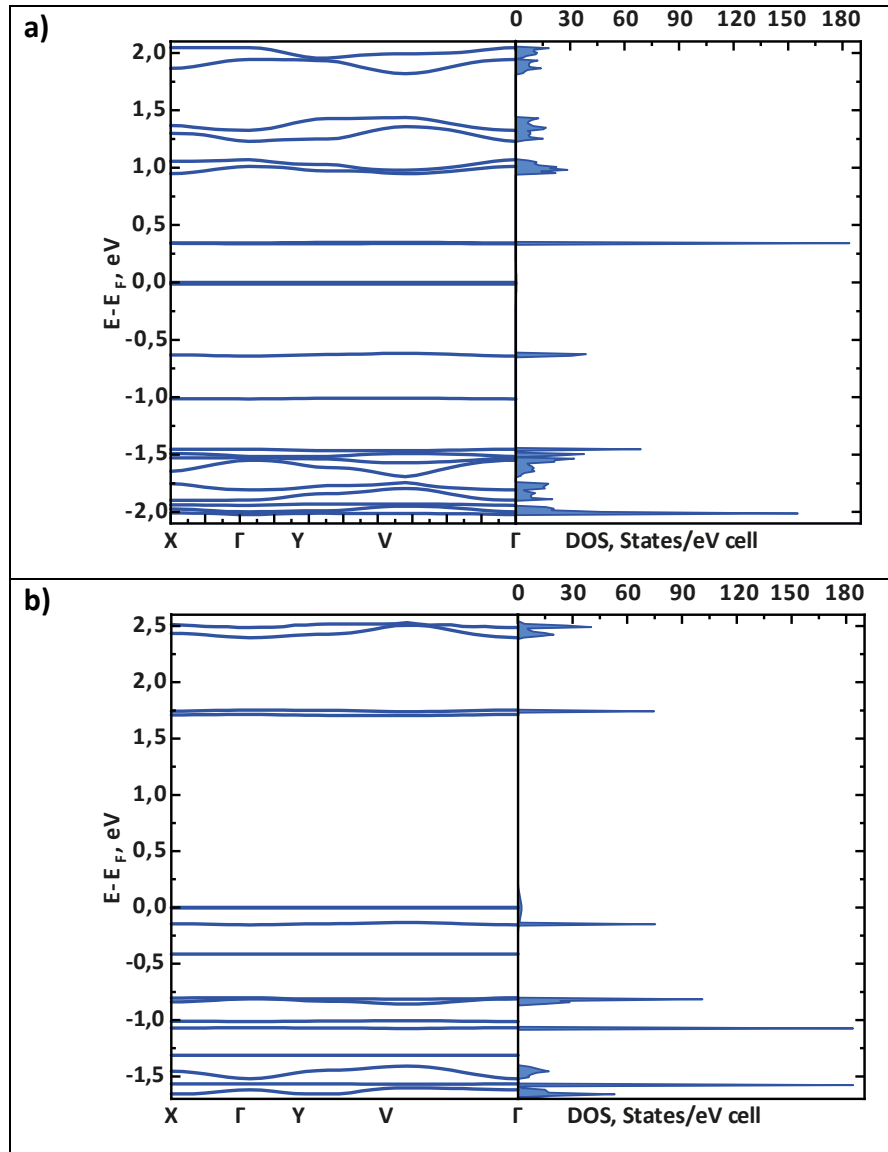


Figure 4.16: Band structures and DOS of the monolayer (a) COF-366, (b) COF-66.

The electronic band structures of COF 366 and COF 66 monolayers along the high-symmetry X  $\Gamma$  Y V  $\Gamma$  directions of the first Brillouin zone are calculated. Selected energy bands of COF 366 and COF 66 monolayers in the energy range  $\pm 2$  eV are plotted in Fig. 4.16-a and -b respectively.

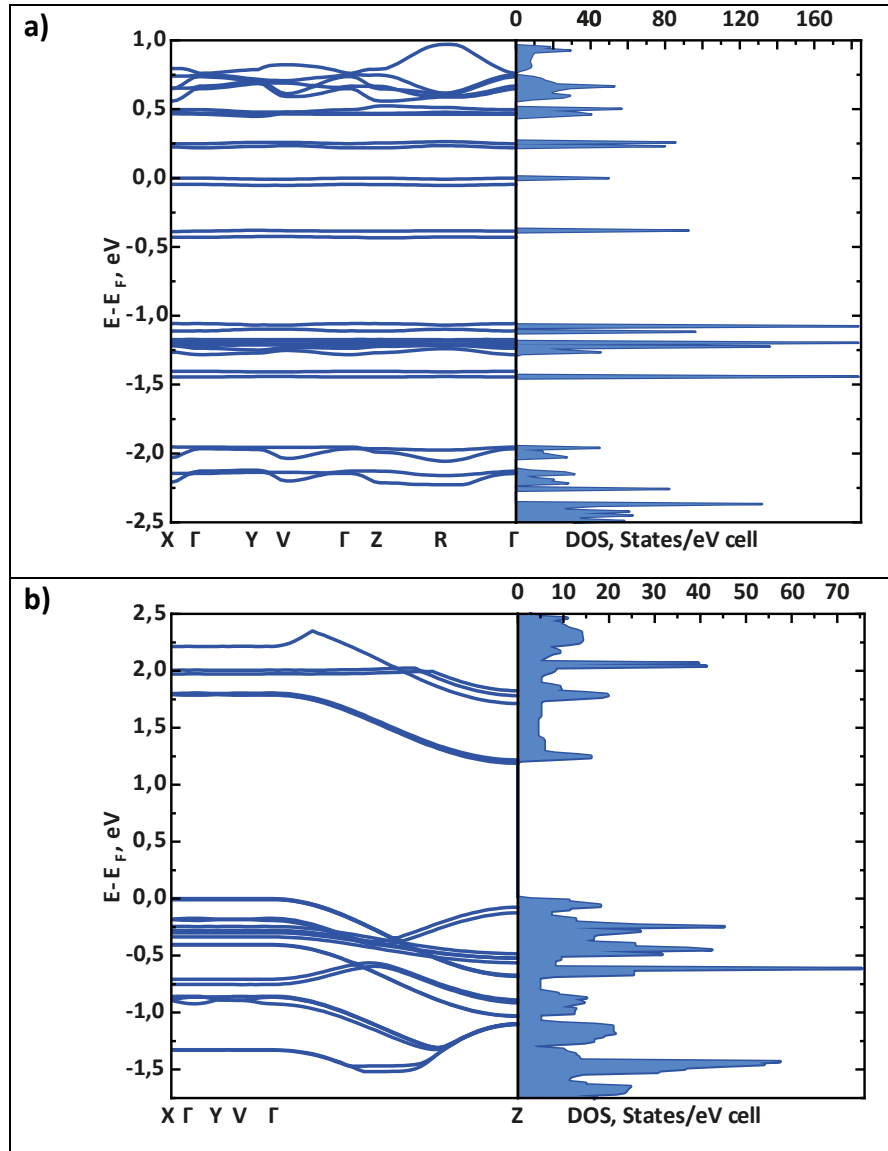


Figure 4.17: Band structures and DOS of (a) Ni COF-366, (b) Ni COF-66.

The band structure of NiCOF-366 shows that the ground state of the compound corresponds to semimetal because of a very small overlap between the bottom of the conduction band and the top of the valence band (Fig. 4.17 a). In both VB and CB, there is complicated parallel dispersion of some bands where the flat subband dispersions exist along all high symmetry lines in the energy interval -1.5 – 0.5 eV. The zero slopes in these subbands cause a sharp DOS structure (Fig. 4.17 a). Therefore, for these nearly flat subbands, the effective masses in the directions of the a-, b-, c-axes as well as along diagonals are very high, which implies that the carriers are localized in the potential wall (quantum size effect regime). However,

there are nonzero and nonlinear slopes along the X- $\Gamma$ , Y-V- $\Gamma$ , and Z-R- $\Gamma$  symmetry lines in the energy interval 0.5 – 1.0, indicating a low effective mass of carriers along with these directions. Thus, the high conductivity in this compound may be associated with light bands, and at the same time, a high Seebeck coefficient may be associated with heavy bands. In VB of given compounds, it is observed four ‘pseudo’ gaps in the interval -2.5 – 0 eV and in CB there are two ‘pseudo’ gaps in the interval 0 – 0.5 eV. The band structure was plotted along a high symmetric k-direction in the first Brillouin zone, given by X- $\Gamma$ -Y-V- $\Gamma$ -Z.

Like the central-metal-free COF 66, it was found that NiCOF 66, is an indirect semiconductor with a bandgap of 1.248 eV (Table 4.1). The flat subband dispersions exist along X- $\Gamma$ , Y-V, and V- $\Gamma$  symmetry lines in the energy interval -1.75 – 2.25 eV. With this respect, one can see that along -a and -b directions, the effective masses are very high. Therefore, the Seebeck coefficients along -a and -b directions are lower than those of along -c directions. At this point it is worth mentioning that,  $\Gamma$  to Z high symmetry lines are of slope nature, suggesting a high Seebeck coefficient and low electrical conductivity along -c direction.

#### 4.2.2. Thermoelectric coefficients

The temperature dependences of thermoelectric coefficients of porphyrin-based COFs showed the same trends as those of MPc COFs.

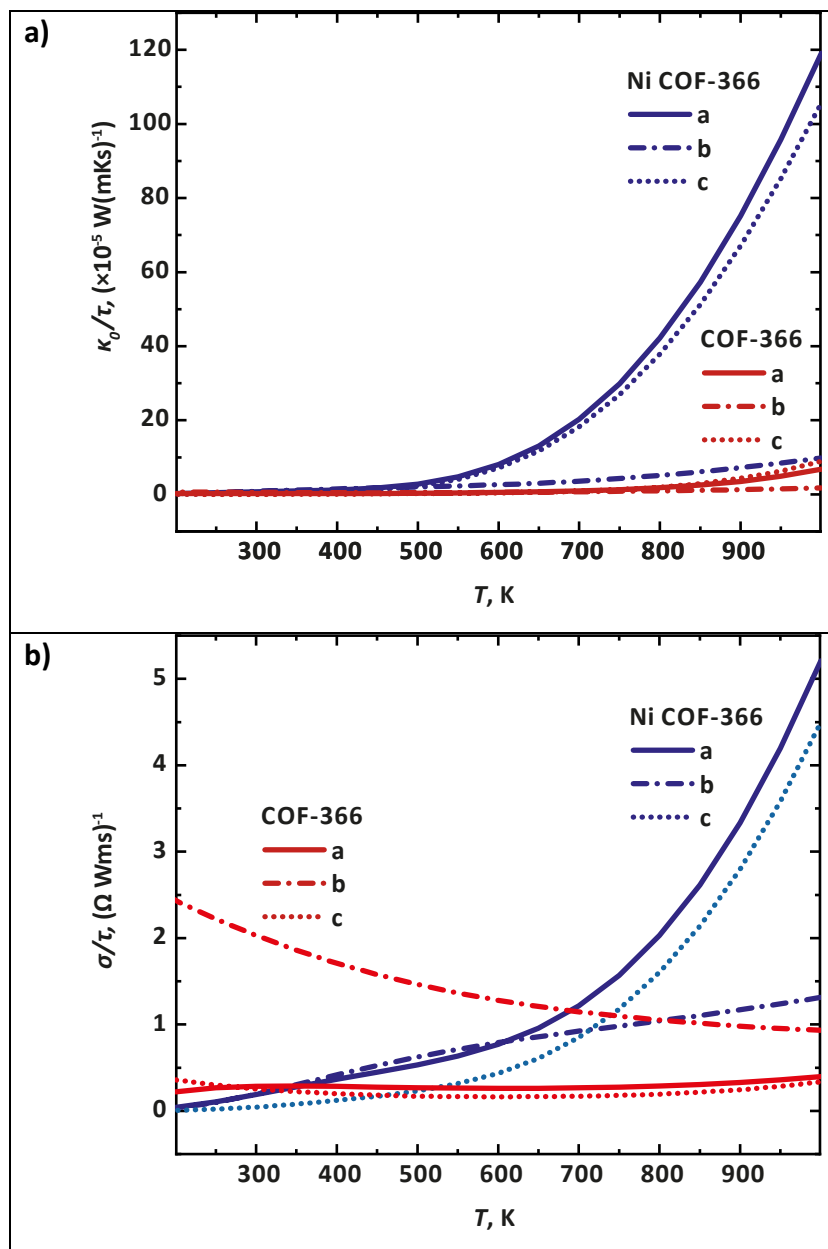


Figure 4.18: Calculated a) electrical conductivity per relaxation time of Ni COF 366 (blue) and COF 366 (red) b) thermal conductivity per relaxation time of Ni COF 366 (blue) and COF 366 (red).

The compound with central atom Ni recorded higher values of thermal conductivity per relaxation time, across the calculated temperature range compared to the compound without a central atom. Thermal conductivity per relaxation time ( $\kappa/\tau$ ) depending on temperature for COF 366 and Ni COF 366 compounds are shown in Fig. 4.18 (b). The calculated thermal conductivity per relaxation time ( $\kappa/\tau$ ) increases

exponentially with temperature for Ni COF 366, while steady thermal conductivity per relaxation time is observed in the whole temperature range for COF-366.

Electrical conductivity per relaxation time ( $\sigma/\tau$ ) depending on temperature for COF 366 and Ni COF 366 compounds are shown in Fig. 4.18 (a). Changing the  $\sigma/\tau$  values of the material is closely related to its corresponding electronic band structure. In this regard, it is worth pointing out that it is noticed from Figure 4.18 b that the values of  $\sigma/\tau$  for the Ni COF 366 are greater than those for COF 366 within the temperature range of 700 K to 900 K, which corresponds to the high value of carrier concentration of Ni COF 366 as compared to COF 366 without central atom. For Ni COF 366 increasing trend of  $\sigma/\tau$  in the whole temperature range can be seen. On the other hand, for COF 366 there is a decreasing trend of  $\sigma/\tau$  with temperature. As depicted in Figures 4.18 a and 4.18 a, the electrical conductivity values of the samples show the following order in the studied temperature range for a-axis:  $\sigma_{\text{COF-66}} > \sigma_{\text{Ni COF-366}} > \sigma_{\text{COF-366}}$ .

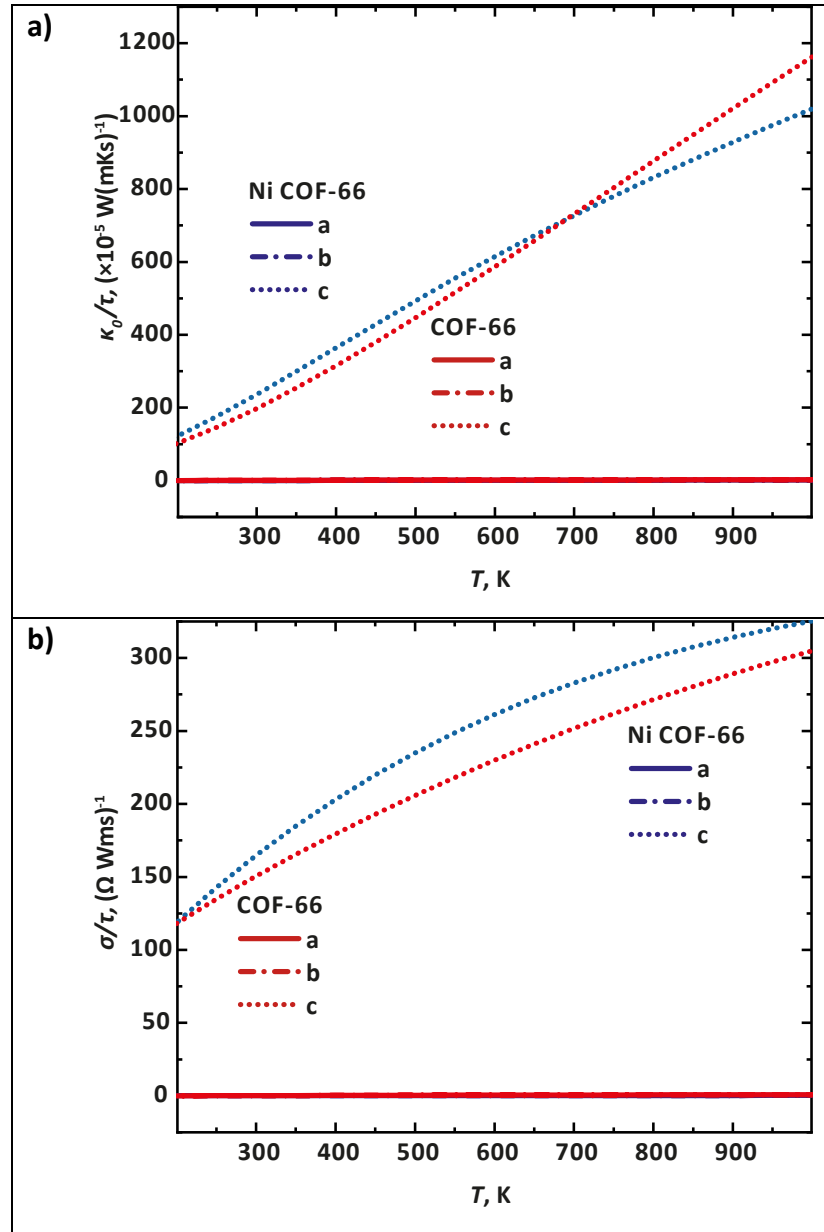


Figure 4.19: Calculated a) electrical conductivity per relaxation time of Ni COF 66 (blue) and COF 66 (red) b) thermal conductivity per relaxation time of Ni COF 66 (blue) and COF 66 (red).

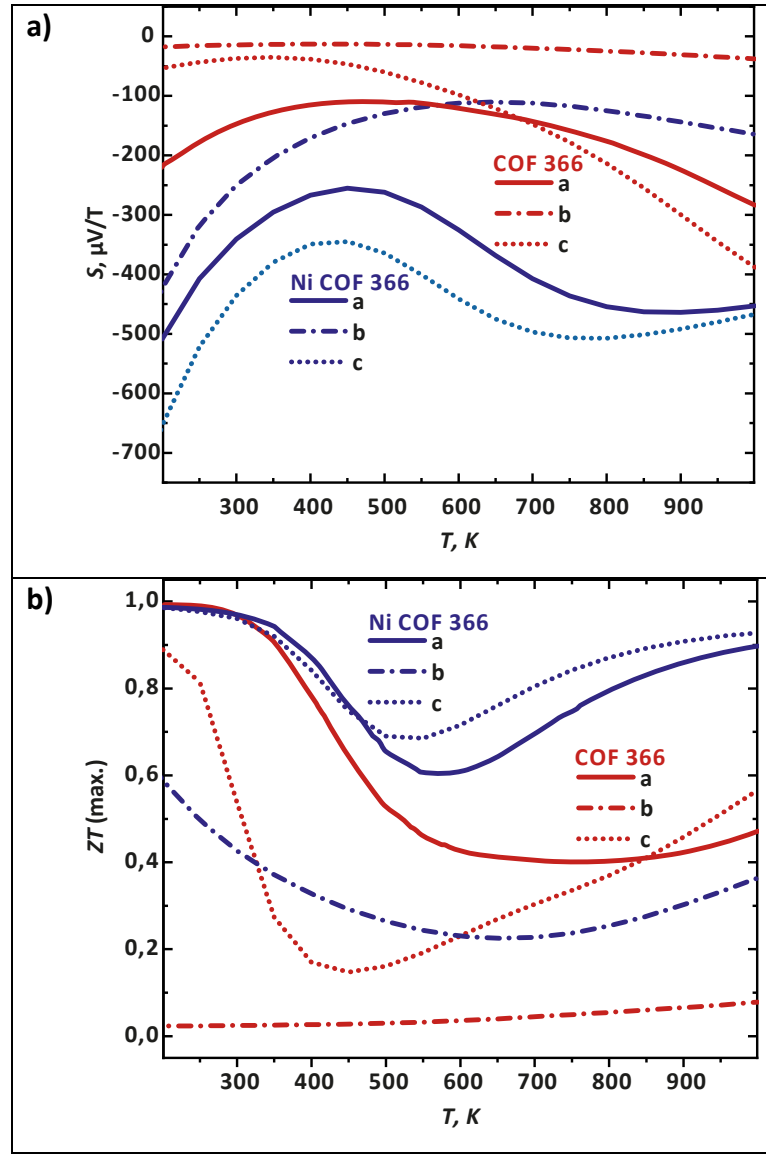


Figure 4.20: Study of the influence of the central atom on COF 366.

We have carried out a set of calculations for comparison of thermoelectric performances for the porphyrin-based COFs with and without a central atom. In Fig. 4.20 we observe the influence of the central atom Ni on the thermoelectric performance of COF 366. It is confirmed that both Ni COF 366 and COF 366 show negative values of thermopower, suggesting that the majority of charge carriers are electrons, hence indicating that they are n-type semiconductors. COF 366 exhibited lower thermopower and negative temperature dependences. The maximum thermopower values they possess are, -508  $\mu\text{V/K}$  at 200 K for NiCOF 366 and -283  $\mu\text{V/K}$  at 1000 K for COF 366. The central atoms effect is also reflected on the

thermoelectric figure of merit ZT values. The room temperature ZT values for NiCOF 366 and COF 366 are 0.970 and 0.971 respectively. The difference becomes more significant as the temperature rises. The ZT value at 900 K obtained for NiCOF 366 sample is 0.859 and this is about twice the 0.423 obtained for COF 366. The maximum ZT value of Ni COF 66 is about 850 K, suggesting this compound will be useful at high temperatures.

We have also compared the performance for monolayer and bulk COFs with the same central atoms.

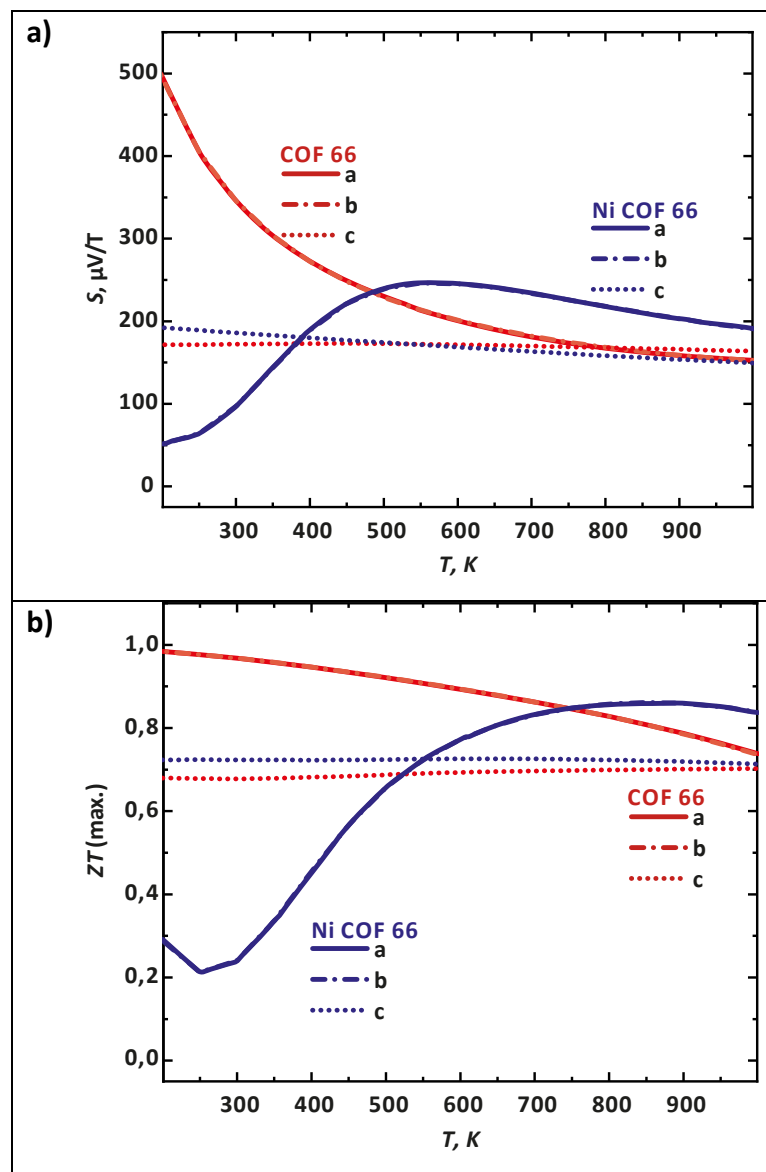


Figure 4.21: Study of the influence of the central atom on COF 66.

For COF 66 existence of central atom Ni, is less significant. It even makes worse the thermoelectric performance at low temperatures. Both ZT and thermopower values for COF 66 have negative temperature dependences along the -a direction. Room temperature Seebeck coefficient values are 345  $\mu\text{V/K}$  for COF 66 and 96  $\mu\text{V/K}$  for NiCOF 66. As temperature rises central atom Ni slightly improves the thermoelectric performance. At 900 K, the values change as follows: 158  $\mu\text{V/K}$  for COF 66 and 203  $\mu\text{V/K}$  for NiCOF 66. For Ni COF 66 the maximum ZT value is 0.860 at 850 K along -a and -b directions, suggesting this compound will be convenient at high temperatures. COF 66's ZT value decreases as temperature increases.

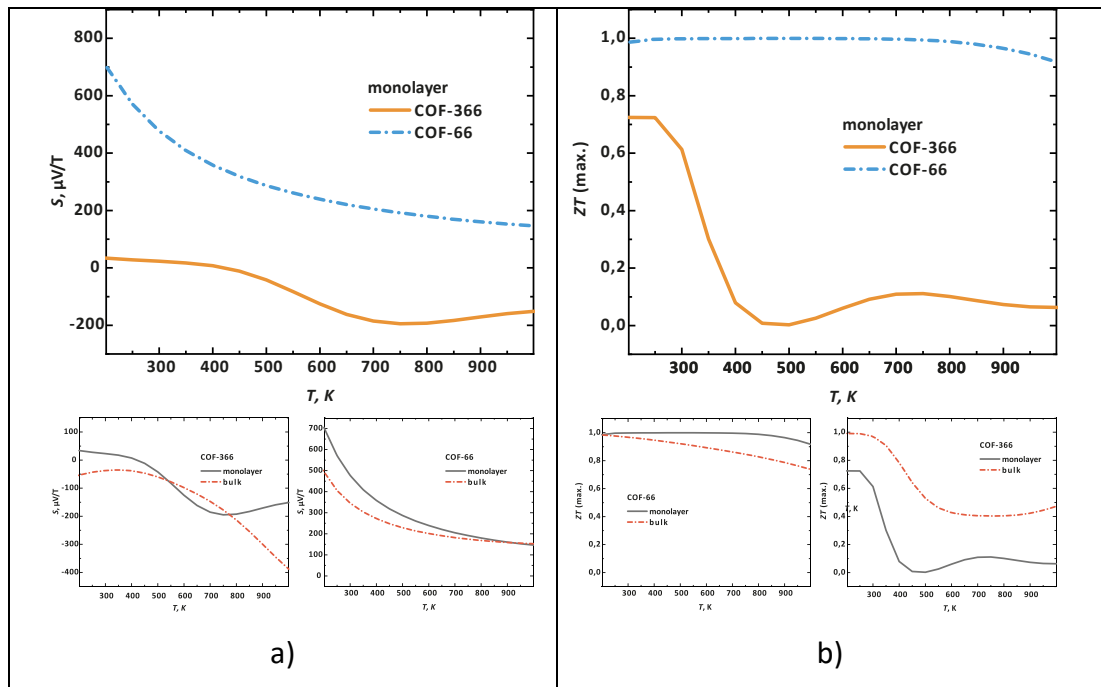


Figure 4.22: Seebeck coefficient and b) ZT values for monolayer P COFs and their comparisons with bulk counterparts.

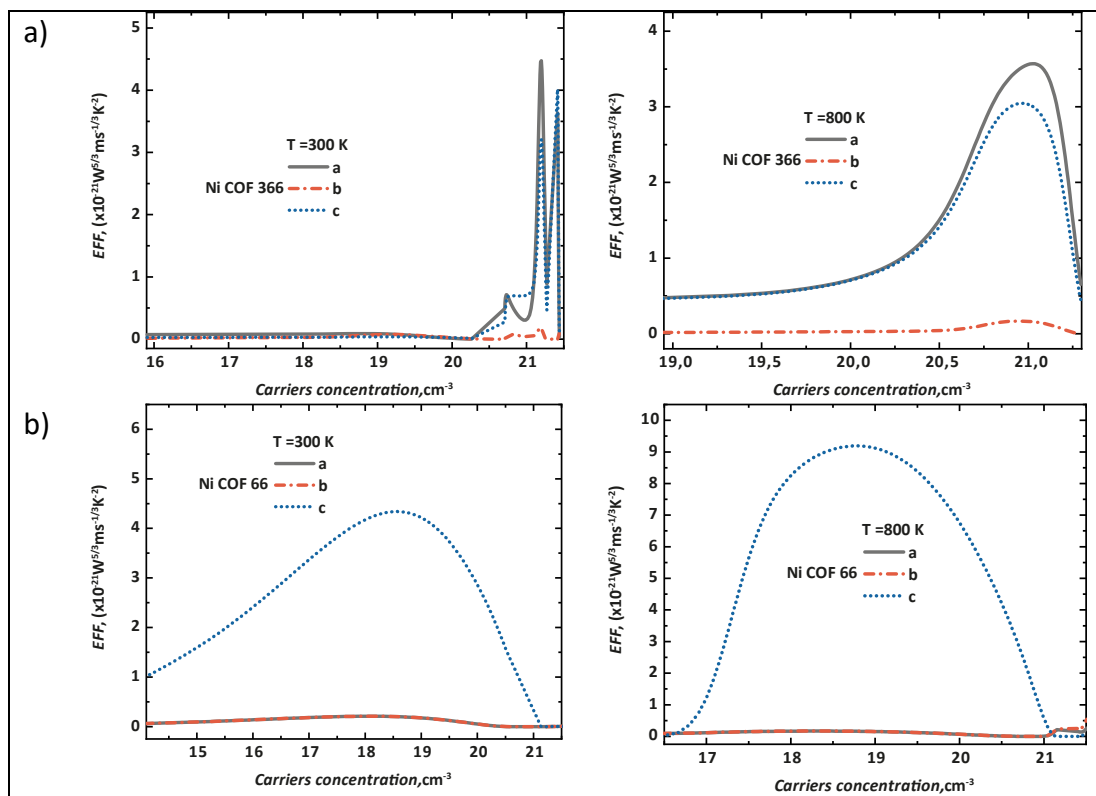


Figure 4.23: Calculated electronic fitness functions (EFF) with respect to the carrier concentration for n-type doping a) Ni COF 366 and b) Ni-COF 66 along with different crystallographic directions.

Figure 4.23 shows the electronic fitness function (EFF) of n-type and Figure 4.24 shows EFF of p-type doping compounds depending on the carrier concentration. The objective is to analyze the behavior of porphyrin-based COFs (COF -366 and -66) at a range of room (300 K) and high temperatures (800K). At 300 K and 800 K, both n-type doping and p-type doping NiCOF 66 shows better EFF. In general Ni COF 66 tends to have high EFF values, increasing with temperature, while Ni COF 366 shows relatively low EFF values, decreasing with temperature. It is obvious that the EFF values of p-type doping higher than n-type doping of COF 366 and -66 at both temperatures; therefore, it can be said that porphyrin-based COFs will be better p-type thermoelectric materials.

The maximum EFF values are observed along the a- crystallographic direction for n- and p-type doping of NiCOF 366 at 300 and 800 K. However, Ni COF 366 has the maximum values along the b- direction. Furthermore, Ni COF 366 shows more anisotropic behavior at both temperatures. For n-type doping NiCOF 366, at 300 and

800 K, the EFF is slightly above  $4.5 \times 10^{21} \text{W}^{5/3} \text{ms}^{-1/3} \text{K}^{-2}$  respectively at higher carrier concentrations. Whereas for p-type doping, the EFF values are nearly the same at both temperatures, and it is around  $4.5 \times 10^{21} \text{W}^{5/3} \text{ms}^{-1/3} \text{K}^{-2}$ .

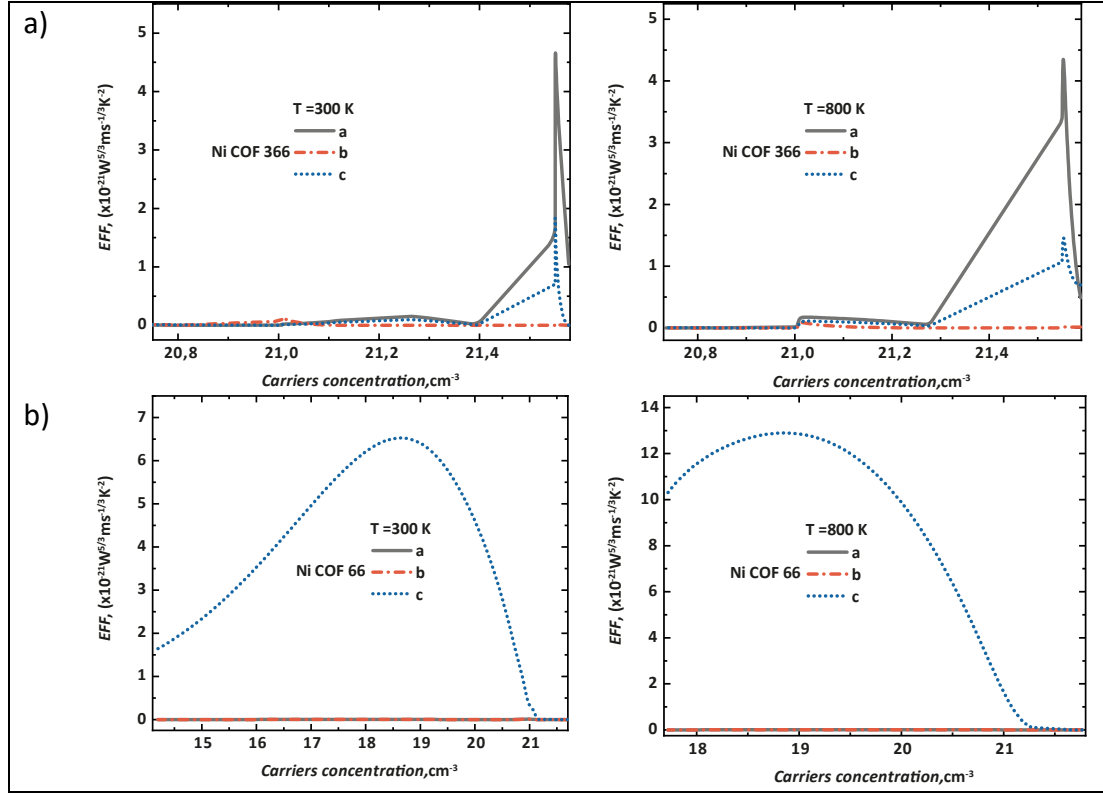


Figure 4.24: Calculated electronic fitness functions (EFF) with respect to the carrier concentration for p-type doping a) Ni COF 366 and b) Ni-COF 66.

Figure 4.25 shows the Seebeck coefficients of n-type and Figure 4.26 shows  $S$  of p-type doping compounds depending on the carrier concentration. As was foreseeable, the Seebeck coefficients are lower with higher amounts of carrier density for all NiP COFs. Both p- and n-type doping have led to the significant development of thermopowers of COF 66 and 366 at 300K and 800 K compared with intrinsic NiP COFs.

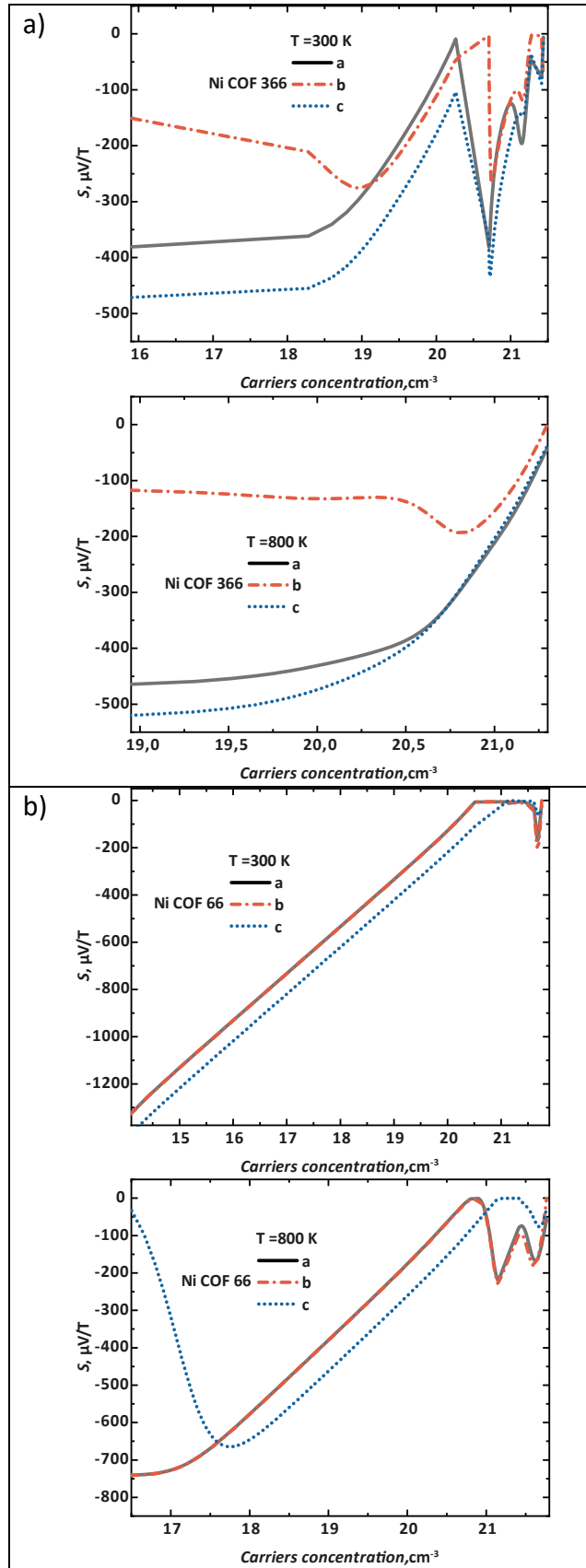


Figure 4.25: Calculated Seebeck coefficients with respect to the carrier concentration for n-type doping a) Ni COF 366 and b) Ni-COF 66.

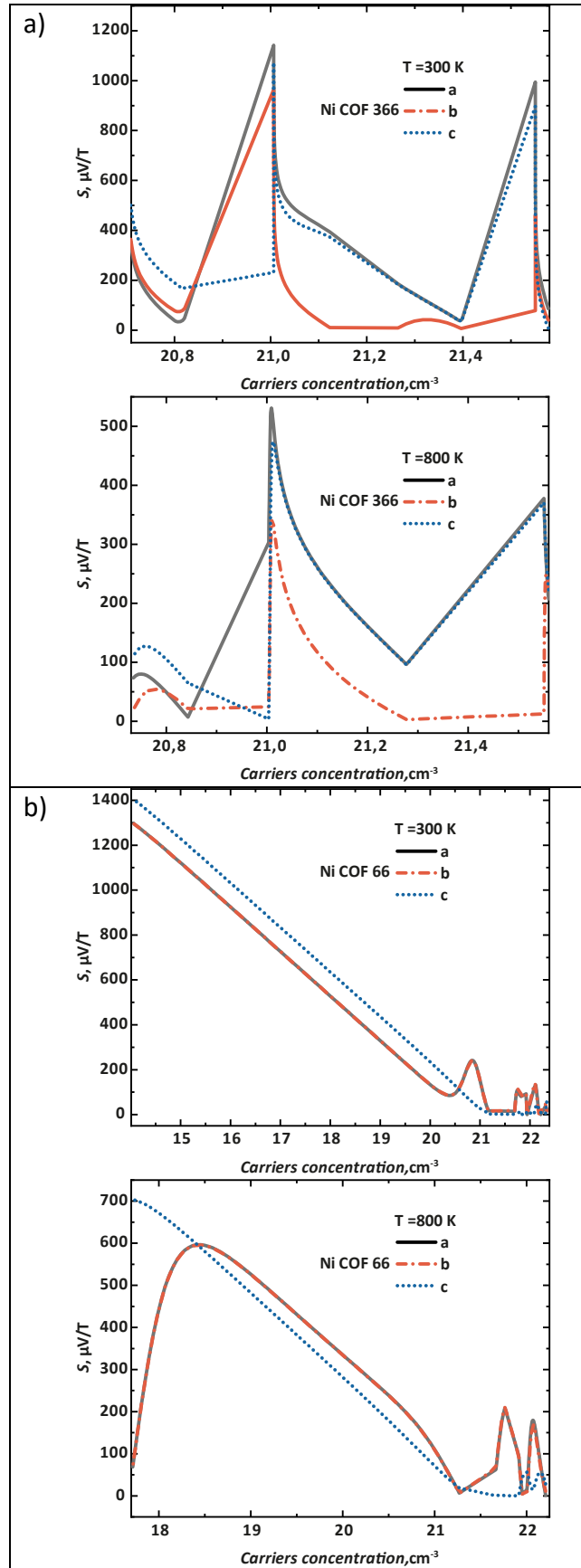


Figure 4.26: Calculated Seebeck coefficients with respect to the carrier concentration for p-type doping a) Ni COF 366 and b) Ni-COF 66.

## 5. CONCLUSIONS

In this study, we theoretically investigated the thermoelectric properties of porphyrin and phthalocyanine-based covalent organic frameworks. Here we used density functional theory together with general gradient approximation and Boltzmann transport equations to compute electronic and transport properties of the investigated materials.

We started by investigating metallophthalocyanine based covalent organic frameworks with four different central atoms (Co, Cu, Zn, and Ni). We investigated the evolution of the thermal conductivity, electrical conductivity, the Seebeck coefficient, and the thermoelectrical figure of merit with temperature. Based on calculated results, for three compounds the Seebeck coefficients are predicted as in the following order:  $|S^{CoPc\ COF}| > |S^{CuPc\ COF}| > |S^{ZnPc\ COF}|$ . These absolute maximum thermopower values are along b- direction. This order is also found for the figure of merit (ZT) values for the same compounds:  $ZT^{CoPc\ COF} > ZT^{CuPc\ COF} > ZT^{ZnPc\ COF}$ . For Co- and CuPc COF the maximum value of ZT is along b- direction while for ZnPc COF is along a- direction.

Then we investigated metalloporphyrin-based COFs (COF 366 and COF 66). We found that for P COFs the absolute maximum values order is,  $|S^{NiCOF\ 366}| > |S^{COF\ 66}| > |S^{COF366}| > |S^{NiCOF66}|$ . Similarly, this order is also reflected in the figure of merit values:  $|ZT^{NiCOF\ 366}| > |ZT^{COF\ 66}| > |ZT^{COF366}| > |ZT^{NiCOF66}|$ .

This study showed that the optimal thermoelectric performance is found in in-plane directions. Future 2D covalent organic frameworks for thermoelectric applications may be designed considering this important finding to obtain better results.

As mentioned in the introduction, porous materials are becoming essential in thermoelectric applications as they are generally possessing low thermal conduction. To further reduce the thermal conductivity a guest atom inserted COF's pore may be used.

Compelling results have been obtained from this study; be that as it may, there are still many aspects that deserve to be investigated to clear up some challenges that yet lie ahead. With this work, we hope to open a door to further investigating

some calculating aspects and understanding some properties for thermoelectric material selection processes. More than that, we also hope that our theoretical study in this work will give rise to an experimental survey of these remarkable thermoelectric materials.

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## **BIOGRAPHY**

Gökhan Bayram is a PhD candidate in the Department of Physics at Gebze Technical University. He received a bachelor's degree in physics from Yıldız Technical University and a master's degree from Gebze Institute of Technology. In 2015 he started his doctoral program and now he is working under the supervision of Prof. Dr. Yurii Chumakov.

## APPENDICES

### Appendix A: Publications

Chumakov Y., Bayram G., (2020), “Theoretical Study of Thermoelectric Properties of Covalent Organic Frameworks with Slipped Arrangement”, *Journal of Electronic Materials*, 49 (9), 5498–5507.

Chumakov Y., Bayram G., (2018), “Theoretical Study of Covalent Organic Frameworks Thermoelectrical Properties: Bulk and Monolayer Structures”, 9<sup>th</sup> International Conference on Materials Science and Condensed Matter Physics (MSCMP 2018), 194, Chisinau, Republic of Moldova, 25-28 September.

Chumakov Y., Bayram G., Demir Kanmazalp S., (2017), “Dft Study of Conducting Phthalocyanine-Based 2d Covalent Organic Frameworks”, Turkish Physical Society 33<sup>rd</sup> International Physics Congress (TPS33), 598, Bodrum, Turkey, 6-10 September.