UNIVERSITY OF PUERTO RICO FACULTY OF NATURAL SCIENCES DEPARTMENT OF CHEMISTRY RIO PIEDRAS, PUERTO RICO

SYNTHESIS, CHARACTERIZATION, AND STRUCTURAL PROPERTIES OF FLUORINATED METAL PHTHALOCYANINE CHEMIRESISTORS FOR ENVIRONMENTAL PARTS-PER-BILLION DETECTION OF TOXIC GASES

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Synthesis, Characterization and Structural Properties of Fluorinated Metal Phthalocyanine Chemiresistors for Environmental Parts-per-Billion Detection of Toxic Gases

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Dedication

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LIST OF ABBREVIATIONS

DPPF	1,1'-bis(diphenylphosphino)ferrocene	
Acac	Acetylacetone	
AFM	Atomic force microscopy	
Pd(dba) ₂	bis(dibenzylideneacetone)palladium	
LuPc ₂	bis(phthalocyaninato)lutetium	
BBr ₃	Boron tribromide	
CI	Crystallinity index	
CSD	Crystallographic structural database	
Ср	Cyclopentadiene	
DA	Decylamine	
DFT	Density functional theory	
CDCl ₃	Deuterated chloroform	
DBA	Dibenzylamine	
DBVT	Dibromoveratrole	
DCM	Dichloromethane	
DMP	Dimethoxyphthalonitrile	
DMF	Dimethylformamide	
DMSO	Dimethylsulfoxide	
DOA	Dioctylamine	
EDS	Electron diffraction spectroscopy	
ED	Electron donating	
EW	Electron withdrawing	
EPA	Environmental protection agency	
ETE	Equilibrium template effect	
EtOAc	Ethyl acetate	
FFT	Fast Fourier transform	
Fc	Ferrocene	
FIB	Focus ion beam	
FWHM	Full width at half maxima	
F ₁₆ MPc	Hexadecafluorinated MPc complexes	
HRTEM	High resolution TEM	
НОМО	Highest occupied molecular orbital	
IR	Infrarred	

IDE	Interdigitated electrodes
IMF	Intermolecular forces
IEPS	Inverse Emission Photoelectron Spectroscopy
KTE	Kinetic template effect
LDA	Lithium diisopropylamide
Li ₂ Pc	Lithium phthalocyanine
LiTMP	Lithium tetramethylpiperidide
LUMO	Lowest unoccupied molecular orbital
M(OAc) ₂	Metal acetate salt
MPc	Metal phthalocyanine
H ₂ Pc	Metal-free phthalocyanine
NW	Nanowires
NMR	Nuclear magnetic resonance
(OH)8MPc	Octahydroxy metal phthalocyanine
(OCH ₃) ₈ MPc	Octamethoxy metal phthalocyanine
SF ₅	Pentafluorosulfanyl
PVD	Physical vapor deposition
PMHS	polymethylhydrosiloxane
PXRD	Powder X-ray diffraction
PDB	Protein database
SEM	Scanning electron microscopy
sTf	Serum transferrin
S/N	Signal to noise ratio
THF	Tetrahydrofuran
TMEDA	tetramethylethylenediamine
TLC	Thin layer chromatography
TEM	Transmission electron microscopy
TBA	Tributylamine
TEA	Triethylamine
CF ₃	Trifluoromethyl
THB	Turbo-Hauser bases
UV	Ultraviolet
UPS	Ultraviolet photoelectron spectroscopy
VOC	Volatile organic compound
WH	Williamson Hall

Abstract (1)

Air pollution is one of the greatest environmental risks to human health with a death toll of millions every year. The number of total deaths worldwide due to chronic respiratory diseases has increased during the past 3 decades, with an estimated 3.9 million deaths in 2017, accounting for 7% of all deaths worldwide.¹ Gas sensors are crucial components for monitoring and detecting hazardous toxic gases, and ensuring safety, air quality, analyzing environments throughout many different industries. This doctoral thesis aims to produce ultrasensitive gas sensing platforms based on nanomaterials built using synthetic metal phthalocyanine (MPc) nanomaterials. The gas sensing properties are tailored by modifying the MPc nanomaterials chemically through the synthetic attachment of functionalized groups or moieties, thus altering their sensitivity and selectivity towards pollutant gases. This doctoral thesis focuses on the design, synthesis, and extensive characterization of unsubstituted and hexadecafluorinated MPc complexes (F16MPc) with transition metals of the fourth period. We demonstrate a facile and reproducible procedure to synthesize high-purity polycrystalline powder materials possessing exceptional semiconducting properties towards the sensing of pollutant gases. The optimal method to prepare MPc complexes is through a solid-state tetramerization reaction, where the metal centers act as a template for macrocycle formation. This further enables the use of substituted phthalonitrile systems that lead to substituted MPc complexes with enhanced and tailored properties. Sensors from substituted and unsubstituted MPc nanowires were fabricated and tested for ppb gas sensing. Among the materials tested, sensors prepared with F₁₆FePc nanowires showed high sensitivity, reproducibility, recovery, and stability.

Abstract (2)

For applications where a "fast" response is required, the investigated F_{16} FePc nanowire devices offer a ~2% normalized signal change for a response time of ~12 min in the case of 100 ppb, ~20 min in the case of 40 ppb, and a few seconds in the case of 25 ppm. Overall, these results demonstrated the enormous gas sensing potential of synthetic multifluorinated phthalocyanine semiconducting materials towards environmental applications. To our knowledge, this is the first report in the literature that has been able to reach ppb sensing capacities with chemiresistors built from multifluorinated iron and cobalt phthalocyanine systems.²

Motivated by the results obtained in the F_{16} systems, we describe the synthesis and characterization of MPc systems with extended coordination geometries. Four new unreported octahedral MPc complexes were successfully synthesized through a Lewis adduct formation reaction to yield semiconducting platforms suitable for gas sensing and electronic applications. The magnetic anisotropic effect caused by the shielding cones of the macrocyclic portion in the MPc complexes was studied in detail using NMR spectroscopy. The approach was extended to include other unreported primary amine derivatives that could coordinate the axial positions of the iron(II) core in the macrocycles. Both 4-chlorobenzylamine and tyramine were able to be successfully coordinated, the latter showing the most drastic shift due to shielding, with a proton at -7.5 ppm. This study was also able to prove that: (1) primary amines can be coordinated to substituted FePc systems like F_{16} FePc, and (2) primary amines can coordinate to other metal centers in the core of unsubstituted MPc complexes. Lower amounts of product were obtained when using the F_{16} FePc system to coordinate the amine.

Abstract (3)

When Co was used as a core metal ion the macrocycle, the shielding effect of the anisotropic cone is considerably lower that the Fe complex, indicating the metal does in fact influence the magnetic effect of the shielding cone through its nature and electronic configuration. The NMR characterization of MPc metal complexes area where there is still much to be desired. The systems prepared herein open the possibility for a new class of chemiresistive gas sensor based on these octahedral FePc complexes, amongst other derivatives. The successful preparation of these devices can be accomplished by solution deposition methods like drop casting or spin coating, yielding films suitable for sub-ppm detection of coordinating gases like NH₃ and NO₂, which have been proven prior to work successfully as optical sensors.

Due to the enormous need to generate MPc systems with novel substituents, this work describes the design, synthesis, and characterization of two phthalonitrile precursors capable of generating SF₅ and OCH₃ substituted MPc complexes, respectively. The first compound, C₇H₃F₅INS, a pentafluorosulfanyl (SF₅) containing arene, which was synthesized from 4-(pentafluorosulfanyl) benzonitrile and lithium tetramethylpiperidide following a variation to the standard approach, which features simple and mild conditions that allow direct access to tri-substituted SF₅ intermediates that have not been demonstrated using previous methods. Finally, the collection of reactions proposed will serve as the starting point in the pursuit of newly- functionalized materials based on the SF₅ moiety and enhance the properties of existing and relevant materials.³

Abstract (4)

On the other hand, the second MPc precursor, $C_{10}H_8N_2O_2$, is a tetrasubstituted arene molecule that contains two methoxy and two cyano moieties in a 1,2,4,5 arrangement. It was synthesized by a variation of the Pd-catalyzed cyanation reaction of 1,2-dibromoveratrole, which features a one-pot reaction using simple and mild conditions, allowing a direct access to alkoxy-substituted phthalonitrile entities. MPc systems based on the as-obtained high-purity phthalonitrile precursor were obtained by reacting the latter with a metal acetate salt in the solid state at high temperatures. All samples were characterized using UV-Vis, IR, EDX and SEM techniques to confirm the successful formation of the Pc macrocycle and the presence of the metal center. Transformation of the methoxy groups in (OCH₃)₈MPc compounds to their OH counterparts was successfully performed through reduction with sub-stoichiometric amounts of BBr₃, opening a window of possibilities for next-generation materials like 2D and 3D frameworks based on the unreported complexes synthesized here, namely, (OH)₈FePc and (OH)₈CoPc.

Due to the importance of the crystalline structure on gas sensing nanoplatforms, we focused on further improving $F_{16}MPc$ nanowire thin films towards gas sensing through annealing. Crystallographic analyses of $F_{16}MPc$ (M = Fe, Co) show that nanowire films prepared though PVD are composed of highly crystalline and organized nanowires having a distribution of lengths that fluctuates around 250 nm.

Abstract (5)

The interplanar distance changes negligibly for annealed films which supports that the strong π - π interactions between the complexes is robust and resistant to higher temperatures. The as-obtained results offer an in-depth crystallographic and morphological discussion of unreported F₁₆MPc nanowire film crystals, and their sub ppm sensing capabilities towards pollutant gases. The increase was more than two-fold, suggesting that annealing at 100 °C enhances the sensing capacity of these nanowire films the most. The promising results obtained herein are being extended to the less filmogenic F₁₆FePc complex to improve the sensing limit of 40 ppb established prior by our research group, for ultralow detection of NH₃ and other toxic gases. Other gases like NO₂ are also being investigated.

This thesis also presents three important collaboration projects that were key for the development of future crystallographic and spectroscopic accomplishments. All three collaborations resulted in published work and is described further in Appendix A.⁴⁻⁶ The first involves the in-depth characterization of a dithiolene derivative capable of coexisting in various tautomeric forms in solution. The second set of collaborations elucidates the crystallographic properties of a family of ferrocene chalcone derivatives. It performs an in-depth analysis of the literature published so far in this area, in addition to contribute over 10 new crystallographic structures based on these organometallic systems. And lastly, a discussion on the binding in the transferrin protein by classical and non-classicals pathways is offered. The work presented herein resulted in 5 published articles, and 3 that are currently being submitted and awaiting publication; 1 of which is currently being considered for a patent as well.

Chapter 1:

Introduction

I. Metal Phthalocyanine Coordination Complexes (MPc) as Sensing Platforms

Working towards the discovery and development of new multifunctional materials for sensing in which two or more properties co-exist, will enable unprecedented approaches to address challenges in electronics, chemical sensing, and energy conversion/storage.⁷⁻⁸ With the recent advances in technology and the developments in device miniaturization, nanoscale and even molecular scale devices hold the promise of becoming suitable materials for developing sensors due to their small size, high sensitivity and selectivity, low energy consumption, and rapid response.⁹ Classification of sensor types can be accomplished in a variety of ways, following the principles of signal transduction (IUPAC). The following five main types of sensor groups result:

1. Optical: based on absorbance, reflectance, luminescence, fluorescence, refractive index, optothermal effect and light scattering.

2. Electrochemical: metal oxide and organic semiconductors, as well as electrolytic conductivity sensors.

3. Mass-sensitive: piezoelectric devices and cantilevers.

4. Thermometric: mainly for oxygen, based on paramagnetic gas properties.

5. Others: based on emission or absorption of radiation.

Similarly, sensing materials can also be categorized in three general groups: biological, organic, and inorganic materials. Contrasting the latter two, inorganic materials are defined by having inorganic signal generation components that may or may not be further incorporated into a matrix (e.g., metals, metal oxides, semiconductor nanocrystals); whereas organic sensing materials are comprised of dye pigments such as phthalocyanines, polymer/reagent compositions and conjugated/molecularly imprinted polymers.

One of the most popular and well-known organic materials proposed for gas sensing is based on metal phthalocyanines (MPcs, **Figure 1**).¹⁰ MPc are synthetic porphyrin systems from the family of functional dye compounds. Regular dyes are merely used as colorants, whereas functional dyes act as colorants, in addition to possessing semiconducting and multifunctional electronic properties. Both porphyrins and phthalocyanines function as planar tetradentate dianionic ligands that bind metals through four inwardly projecting nitrogen centers. MPcs have been proposed as convenient molecular models for the study of the physicochemical properties of naturally occurring tetrapyrrolic macrocycles including porphyrins due to their structural similarities.¹¹



Figure 1: Metal phthalocyanine coordination complex with relevant positions outlined.

Due to their increased stability, improved spectroscopic characteristics, diverse coordination properties, and architectural flexibility, phthalocyanines have surpassed porphyrins in a number of applications and their immense potential in diverse fields makes them one of the most highly studied macrocyclic and coordination compounds.¹² Copper phthalocyanine is the single largest synthetic colorant produced today.⁹ In addition, phthalocyanines are known catalysts for numerous chemical reactions. In fact, Pc is the only tetrapyrrolic compound used as an industrial catalyst with cobalt phthalocyanine derivatives used in the Merox process for the oxidation of sulfur compounds in gasoline fractions; in addition to nitrido-bridged MPc dimers that are the only catalyst known to date that can mediate the oxidative defluorination of heavily fluorinated organic compounds.¹³⁻¹⁴

The Pc molecule has a two-dimensional π -electron conjugated system (18 electrons) that can incorporate about 70 different metals.¹⁵ Both phthalocyanines and porphyrins can use their empty axial positions to coordinate additional ligands or solvent molecules containing C, O or N donor atoms to generate octahedral complexes and are thus attractive systems for the chemical detection of gases because of their open coordination sites for axial ligation. These chemiresistors exhibit high sensitivity and chemical selectivity toward a variety of analytes.¹⁶ They are particularly attractive for gas sensing, because their sensitivity and response toward various analytes can be tailored by (1) the nature of the central metal atom, (2) the substituents in the aromatic rings, which can impart an *n*-type or *p*-type character to the organic semiconductor material according to their electron- withdrawing/donating capability, and (3) the spatial organization of molecules in the lattice.

II. Electronic Properties of MPc Systems

Electronic structure and bonding in metal phthalocyanines (M= Fe, Co, Ni, Cu, Zn, Mg) was investigated by Scheiner and Liao in detail using a density functional method (DFT).¹⁷ The valence electronic structures of Fe and Co phthalocyanines differ significantly from those of the others. The HOMOs in Fe, Co, and Cu phthalocyanine are metal 3d-like, whereas in Ni and Zn phthalocyanines, the HOMO is localized on the phthalocyanine ring (**Figure 2**). The first ionization removes an electron from the phthalocyanine a_{1u} orbital in all cases, with very little sensitivity of the ionization energy to the identity of the metal.

Similar theoretical studies suggested that the energy required to extract an electron is nearly constant for all MPcs at approximately 6.5 eV; this electron is removed from the Pc HOMO in each case. Fe, Ni, and Cu phthalocyanines have smaller HOMO–LUMO separations than do Zn and Co phthalocyanine. Whereas the first reduction in Fe and Co phthalocyanine occurs at the metal, it is the phthalocyanine that is reduced upon addition of an electron to the other systems (**Figure 2**). It was observed that the nature of M has some influence on the transition energies of the Q and Soret bands when performing UV-Vis, which decrease steadily as M progresses from Fe to Zn.¹⁸ Electronic structures are subject to the influence of strong-field axial ligands, which bind particularly strongly in the case of FePc(CO)₂. The energy of the iron's dz² orbital is destabilized a great deal by the presence of the CO ligands, while some of the other d orbitals are lowered in energy.¹⁹ The resulting reordering shifts electrons and changes the ground electronic state of FePc(CO)₂ as well as CoPc(CO)₂.



Figure 2: Orbital energy levels for the outer orbitals in unsubstituted MPc complexes.

All these electronic and binding properties will contribute to one of the main aspects we seek to exploit in these types of materials: conductivity. Being excellent candidates for conducting applications, these macrocycles will exhibit a change in electronic transitions upon coordinating in the axial positions, which can be detected as a change in resistivity using very sensitive electrodes. This coordination is the driving force for a new type of sensor that will be explained in detail in the proposal section of this work. Conductivity in metal phthalocyanine systems usually depends on the intrinsic properties of a particular kind of phthalocyanine, like the bis(phthalocyaninato)lutetium (LuPc₂) and lithium phthalocyanine (Li₂Pc), which are respectively typical narrow- and broad-band intrinsic molecular semiconductors and have been used for the preparation of devices such as field-effect transistors. Phthalocyanines can be also readily doped by electron acceptors to give *p*-type columnar semiconductors.²⁰

Most of the divalent metals except the zinc ion can form an inner orbital complex of square-planar structure as a result of d²sp³ orbital hybridization. The electronic configuration in the outer orbitals of a metal in phthalocyanine may be expressed as shown in Figure 3. A set of d orbitals of the metal, which are associated with a square-planar arrangement of covalent bonding, must be filled with four electron pairs donated by the ligand nitrogen. For a divalent copper ion, the electronic configuration of the outer orbitals is either $4p^{1}3d^{8}$ or $4p^{0}3d^{9}$ according to whether the unpaired electron is elevated to the 4th orbital or stays in the 3d orbitals. Both configurations are known to be energetically equivalent and capable of forming stable square-planar bonding. Therefore, most of the four-coordinated complexes of zinc ion have a tendency to assume a tetrahedral configuration using 4s4p hybrid. In the case of zinc-phthalocyanine, however, the metal ion is forced to fit into a rigid macrocyclic ring which a priori requires a square-planar configuration. In order to satisfy this requirement, the outer 4d orbital must be used for 4s4p²4d hybridization, resulting in the formation of an outer-orbital complex. Since the stability of this type of complex is generally less than that of an inner complex, it is not unreasonable that the frequency of the metal dependent band for ZnPc is always the minimum as far as the phthalocyanines of divalent first transition metals are concerned.

	3d	4 s	4р	4d
Fe ²⁺	11111	••	•• ••	
Co ²⁺	111111	••	••••	
Ni ²⁺	11111111.	••	••••	
Cu ²⁺ (a)	11111111.	•	•• •• 1	
(ь)	111111111	••	•• ••	••
Zn ²⁺	11111111111	•	•• ••	••

Figure 3: Representation of the electronic configurations of the outer orbitals of divalent metals. *The black points show the electrons donated by ligand nitrogen.

III. Tailoring the Gas Sensing Response of MPc Complexes

MPcs are particularly attractive as gas sensors because both sensitivity and response of MPcs to various analytes is found to depend on the nature of the metal atom and the substituents in the aromatic rings, as well as on the structure and molecular organization of the materials.²¹ Therefore, peripheral substitution of the conjugated macrocycle of MPcs by electron withdrawing or electron-donating groups is a facile way to vary sensitivity and selectivity of these materials toward different analytes.²² Similarly, introduction of different central metals into the MPc ring can significantly alter the material's morphology and offer the possibility to change the metal complex's electrical characteristics and sensor performance. For example, fluorine substituents decrease the electron density of the aromatic ring, which in turn increases the oxidation potential of the MPc molecules.²³ As a result, fluorosubstituted phthalocyanines exhibit a higher sensor response to reducing gases.

There have been numerous reports in the literature about phthalocyanine gas sensors: most of them involve the sensing of oxidizing and reducing gases, although sensing of VOCs with these systems has also been accomplished.²⁴ The interaction mechanism between phthalocyanine films and analyte molecules has also been discussed with respect to analyte basicity.²⁵ Chemical sensors based on MPcs have been developed with respect to two interactions: conductance sensors (based on reversible charge transfer reactions; usually for oxidizing and reducing gases); and capacitance sensors (sorption-based such mass sensitive sensors and quartz crystal microbalance sensors; usually for VOCs). In general, oxidizing gases increase the conductivity of MPcs because they are *p*-type semiconductors and when the oxidizing gases are adsorbed the charge carrier density increases.

The increase of conductivity during exposure to oxidizing gases can be explained as follows: the gas diffuses into the film, displaces other adsorbed species such as oxygen, and then a charge transfer complex is generated between the molecule and the acceptor gas and charge carriers (holes) are created in the film matrix. These charge carriers are responsible for the increase of the conductivity. The intensity and kinetics of the response to a particular gas are therefore related to the nature of the phthalocyanine compound used as the sensitive material.²⁶ The strong bonding of the gas molecules on the surface of the materials causes incomplete desorption of the oxidizing gas, which in turn modifies the subsequent adsorption properties. When the gas is adsorbed, the Pc can be doped by the oxidizing agent, increasing the hole concentration and the conductivity of the material. In contrast, the presence of highly electronegative atoms or groups in fluorinated MPc molecules causes the system to show an increase of conductivity in the presence of donating and/or reducing gases.²⁷ The energy levels which are responsible for the electrical properties of MPcs was determined recently by Ultraviolet Photoelectron Spectroscopy (UPS) and Inverse Emission Photoelectron Spectroscopy (IEPS). The energy gap of non-radical Pcs is approximately 2 eV, which contrasts with LuPc₂, a lutetium derivative that was observed to have a radical nature, capable of easily loosing and gaining an electron and yielding very low activation energies (0.5 eV) for the creation of charge carriers (Figure 4). Moreover, MPc energy levels (HOMO and LUMO) are stabilized from non-substituted to perfluorinated molecules. Pc films are easily oxidized by NOx, forming charge-transfer complexes, which inject holes and increase film currents. The interaction of Pcs with reducing gases, such as NH₃, has the opposite effect. Decreased current upon analyte binding to these films has been attributed to electron donation from the reducing gas to trap charge carriers.²⁸



Figure 4: Effect of fluorination on the energy levels of frontier orbitals (HOMO and LUMO).

The gas sensing behaviors of cobalt phthalocyanine (CoPc) and metal-free phthalocyanine (H₂Pc) thin films were investigated with respect to analyte basicity. There was a transition from physisorption to chemisorption once the analyte exceeded a critical basicity. It was found that the device response for CoPc increased significantly with analyte Lewis basicity, and for H₂Pc, sensor response increased significantly with analyte hydrogen bond basicity. These results support the model that the analyte- phthalocyanine interaction is dominated by the central cavity of the phthalocyanine; coordination chemistry governs CoPc responses, and hydrogen-bonding interactions govern H₂Pc responses. In addition, the interactions of the two phthalocyanines with analytes were found to follow first-order kinetics. The influence of O₂ on the film response was examined, and it was found that competitive binding between analytes and O₂ significantly affects film response and recovery (**Scheme 1**).²⁵



Scheme 1: Chemisorption model of CoPc interaction with oxygen and coordinating analytes L.

Theoretical studies by Density Functional Theory (DFT) were carried out on a series of 3d transition metal(II) phthalocyanines in contact with S–Au wires.²⁹ As expected, the electronic conductance behaves differently in different central metal atom systems. The calculations show how manganese(II) phthalocyanine (MnPc), not only can act as a nearly perfect spin filter, but also has a large transmission around the Fermi level. This confirms that CO, NO, O₂, CO₂, NO₂, and NH₃ molecules, which are of interest for environmental safety and medical purpose, adsorb readily on the central Mn atom of the phthalocyanine ring. The coordination of the particular gas to the MPc metal center will depend on polarity and the interatomic forces between them (Lewis acid-base interactions). Thus, the exchange of the metal center enables a selective detection of different gases while keeping the same platform. Synthetizing MPcs with different substituents around the aromatic macrocycle, and exchanging the metal centers, provides an extremely powerful tool for the synthetic chemist to sense innumerable amounts of gases.

IV. Synthesis and Characterization of MPc Derivatives

There are three general ways of preparing MPc compounds. The first and most simple MPcs are prepared directly from phthalonitrile (1,2-dicyanobenzene) using the metal ion as a template for the cyclotetramerization reaction. Alternatively, a second approach is using phthalic anhydride or phthalamide in the presence of a metal salt, although and a source of nitrogen (urea) and molybdenum catalysts have to be employed for the reaction to go to completion.³⁰ A third, and less employed method, starts from the fairly unreactive free base (H₂Pc) phthalocyanine and through an acid base reaction with triethylamine or tributhylamine (TEA and TBA, respectively), the dianionic Pc²⁻ is generated and later reacted with a metal cation in n-pentanol solution (**Scheme** 2).³¹



Scheme 2: Precursors and transformations leading towards synthetic target (MPc complex) through (a) template reaction starting from 1,2-dicyanobenzene (phthalonitrile), (b) assisted (by nitrogen source and catalyst) template reaction starting from phthalic anhydride and (c) deprotonation and coordination to metal using free base (H₂Pc) MPc.

The first approach can also be extended to include substituted phthalonitriles, which in turn generate substituted phthalocyanine systems. The chemical and physical properties of phthalocyanines are largely dependent on the substituents on the peripheral benzo groups. Electrophilic aromatic substitution reactions can be employed to introduce substituents directly onto the benzo groups of the phthalocyanine.³² In most cases, substituted phthalocyanines are prepared from phthalonitriles containing the desired substituent. With this method, it is the synthesis of the substituted phthalonitrile precursor molecule which presents a synthetic challenge. Even more so when the desired substituents have to be introduced in specific positions in the aromatic ring (α or β). Most approaches focus on obtaining a precursor molecule which contains the desired substituent and a cyano moiety, and later introducing the second cyano group at the ortho position. Other approaches start from the substituted phthalonitrile and work with transforms that affect the substituents and not the nitrile moieties.³³ When assessing the different metals that we can coordinate ion the macrocycle cavity, numerous cations varying oxidation states can be incorporated into the central cavity. The bonding between the central metal atom with a +1oxidation state (Li⁺, K⁺, Na⁺, etc.) and the four nitrogen atoms of the macrocycle is considered to be electrovalent in nature, characterized by its ionic character and relative weakness. The central nitrogen atoms can coordinate two M⁺ atoms. However, in this case, the central nitrogen atoms coordinate two ions. Since both of these cations cannot be accommodated in the central cavity, the metal ions protrude from the plane of the Pc ring. Pc and other alkali metal derivatives possess high solubility in polar organic solvents. In fact, the use of Li₂Pc as a precursor in more convenient owing to the solubility of this complex in acetone and ethanol and the insoluble MPc product is readily collected on completion of the metal-ion-exchange reaction.³⁴

As functional dyes, MPcs possess a wide range of activity in the electromagnetic spectrum, both in the solid state and in solution due to their extensively conjugated 18π system. In the solid state, MPcs have been observed to crystallize in a variety of polymorphs where the square planar molecules are generally arranged in one dimensional molecular column, with interplanar distances ranging from 3-5 Å.³⁵ Thus, crystalline MPc complexes can be studied by powder and single crystal x-ray diffraction (**Figure 5a and 5b**).



Figure 5: Spectroscopic characterization of MPc complexes where (a) and (b) are powder and single crystal examples, respectively. Spectra (c) and (d) correspond to UV-Vis and infrared examples, respectively.

Elucidation of the molecular structure and monitoring reactions by means of optical spectroscopy can challenging in some instances because in solution they are prone to aggregation at moderate-to-high concentrations, so measurements have to be performed at very low concentrations. In the solid state, dye molecules are so close to each other that exciton coupling occurs between the chromophores, which significantly shortens lifetime of the excited state of the dye molecules. Furthermore, their molar extension coefficients are very large (on the order of 10⁵ M⁻¹ cm⁻¹) and most measurements are taken at very low concentrations (10⁻⁶ M): this implies that the reproducibility of spectral measurements might be poor unless their concentrations are accurately controlled.³⁶

The advantages of using optical spectroscopy, however, are numerous and effects like metal ion coordination in the cavity, peripheral substituents and axial coordination can be studied in detail. MPc complexes will display characteristic Soret (B Band) and Q bands in the UV and visible region, respectively. More specifically, the Q band (~670 nm) is an intense absorption band, associated with some less intense satellites at its blue flank (~600-650 nm), that is typical of d- π backbonding transitions present in the coordination bond. Substituting the macrocycle with different peripheral groups is particularly advantageous because it increases the solubility of the complexes in common organic solvents (particularly nonaromatic solvents, which are transparent in a wide spectral range). Solvent effects have been studied previously via absorption measurements of the Q band and the chemical stability of the complexes was also discussed (**Figure 5c**).³⁷ Infrared spectroscopy can be used to characterize ring deformations, bridge vibrations and metal nitrogen stretching, all displayed in the fingerprint region (650-2000 cm⁻¹) of the spectrum (**Figure 5d**).³⁸

V. Nanomaterials Based on MPc Complexes

Solid-state sensors for detecting NO and NO₂, are enormously needed for combustion exhaust control and environmental monitoring. Of such sensors, only an NO sensor using In-doped TiO, is commercially available at present.³⁹ It is emphasized that NO and NO₂, have quite different properties from each other and therefore there should be no gas sensors that respond to both NO and NO₂ at the same sensitivity. Most investigations have so far been devoted to the development of NO₂ sensors at the microscale.⁴⁰ Among the various NO₂ sensors proposed, those using semiconductors appear to be the most promising. More recently, the development of sensors using phthalocyanines has been investigated by many researchers since the first report by the Sadaoka group.⁴¹ These sensors, though often very sensitive to NO₂, appear to have problems in stability and/or response kinetics for practical use. Working towards this end, it is expected that incorporation of MPcs into nanomaterials will enhance their chemiresistive properties. Several nanomaterials based on MPc complexes have been employed for the detection of pollutant gases. Most are based on the optoelectrical sensing of gases that range from pollutant gases to common solvents, and even water.⁴² Working towards chemiresistive sensors, Basova et al. developed thin films of PdPc by organic molecular beam deposition and studied their chemiresistive behavior towards NH₃, with detection limits reaching 10 ppm.⁴³ Alternatively, Altindal and Oruç observed that the exposure to ammonia gas leads to an increase in sensor current, which is unexpected because of the strong electron donating character of ammonia and *p*-type semiconductivity of Pc. They were able to conclude that relative humidity enhances the ammonia adsorption, and the unexpected behavior was found to be related to the change in electronic band structure of the Pc molecule.²⁰
Separately, Gupta and Miura reported nanomaterials for gas sensing based on MPcs, concluding that nanodevices, specifically thin films, exhibit enhanced chemiresistive properties owing to creation of more numbers of interaction sites. Miura further extended this discussion to include other nanomaterials and a variety of gases like CO₂, NO₂, NO, SO_x, fluorocarbons and ozone.⁴⁴⁻⁴⁵ Phthalocyanine thin film conductivity has shown to be sensitive to low concentrations (in the order of 100 ppb) of gases such as NO₂, O₂ and NH₃, among others.⁵⁸ Both the sensitivity and the reversibility of the Pc-based detectors is satisfactory.



Scheme 3: Methods for the development of nanostructures based on MPc complexes.

Metal phthalocyanines are obtained as polycrystalline powders or single crystals, depending on the synthetic method employed. Since chemical sensing is mainly driven by analyte-sensor interactions at the interphase of the material, it is desired that the material employed has high surface area and homogeneous morphology. In addition, preparing MPc-based nanomaterials materials with the methods in **Scheme 3** will improves surface homogeneity and adsorption properties for gas sensing applications. A novel method for the preparation of nanostructures is Physical Vapor Deposition (PVD). Nanowires and nanoribbons can be deposited on a variety of substrates by carefully controlling temperature and pressure at different stages of the furnace oven reactor (**Figure 6**).⁴⁶ The thermodynamic parameters are going to range from 1-10 mmHg pressure and 190-300 °C temperature. The substrate's surface roughness, as well as composition, are going to be of particular interest on the deposition phase of the experiment.⁴⁷ The proposed substrate materials include quartz, glass and aluminum. Manipulation of the as-prepared nanostructures can be achieved with micrometric tweezers or with a Focus Ion Beam (FIB) which allows us to manipulate and create metal contacts with electrodes of interest. The techniques than can be employed for the preparation of nanoscale MPc morphologies also include variations to the physical vapor deposition and organic molecular beam deposition methods, as well recrystallization with enhanced nucleation and supramolecular self-assembly.



Figure 6: (a) Physical Vapor Deposition (PVD) system for the development of nanowires of MPcs (b) Scanning Electron Microscopy images of the process thereof.

VI. Unsubstituted and Hexadecafluorinated Square Planar MPc Complexes

The first part of this chapter covers the successful synthesis and characterization of square planar complexes based on unsubsubstituted (H₁₆MPc) and hexadecafluorinated (F₁₆MPc) metal phthalocyanines. It also covers the identification of promising MPc-based NWs that can be used to monitor concentration variations of contaminants in the atmosphere in areas like El Yaguazo Mars, who have been identified as "recovery zones" because of its previous history of contamination. Typical contaminants such as NH₃, NO₂, and VOCs are expected to be above normal levels, but still in the ppb range. For environmental monitoring of toxic gases, fast sensor responses and recovery times are not a main request, as the expected environmental changes in concentration of gases will take place in the range of weeks. However, reduced operation power is desired, as the device will be working for long periods of time, including relatively isolated areas with no access to commercial electrical power. This work presents the facile procedure to fabricate and characterize unambiguously high-purity polycrystalline materials suitable for sensing applications. Highly sensitive conductometric sensors based on unsubstituted and hexadecafluorinated MPc (M = Fe^{2+} and Co^{2+}) NWs was achieved through direct growth on interdigitated electrodes (IDEs) by PVD. In particular, sensors based on FePc and F₁₆FePc NWs were studied and compared with similar ones made from CoPc and F₁₆CoPc, since their response toward NO₂ and NH₃ has not been fully explored, while the unsubstituted CoPc has shown good sensing capabilities toward both gases. This method allows the preparation of sensor prototypes in a single step, producing stable and reproducible devices able to detect NO_2 and NH_3 gases in the low-ppb range.²

VII. Unsubstituted and Hexadecafluorinated Octahedral MPc Complexes

Iron-containing tetrapyrrole macrocycles and their analogues have been found to be capable of mimicking the active sites of a wide variety of biological enzymes.⁸ The possibility of axial coordination and the stability of iron-axial ligand bonds are key features of these systems that play an important role in catalytic and model biological processes. The ability of FePc to coordinate additional ligands or solvent molecules containing N or O donor atoms is well known; in general, the ligands attach above and below the plane of the macrocycle; and solid-state structures for some few examples have been reported.⁴⁸⁻⁵⁰ A large number of bis-axially coordinated low-spin FePc with aliphatic and heterocyclic nitrogen bases, isonitriles, phosphanes, and phosphites has been studied.⁵¹ The available literature suggests that addition of dibenzylamine, decanamine, or dioctylamine, amongst other reagents, accomplishes this task of preparing six-coordinated complexes.⁵² To integrate FePc species in polymer matrices, one approach that has been widely reported in the literature involves the formation of six-fold-coordinated complexes by the addition of N-donor axial ligands such as pyridine, dibenzylamine (DBA), decylamine (DA), or dioctylamine (DOA).⁵³ FePc complexes have been proven to be attractive molecules for the development of optical sensors for detecting NO2 and CO in gas samples. The absorbance spectrum of six-coordinated low-spin FePc shows an absorption maximum, λ_{max} , in the Q-band between 655 and 670 nm, which can be attributed to the substitution of the metal center with two axial ligands (2:1 complex); a shoulder at around 690 nm that can be ascribed to substitution with only one axial ligand (1:1 complex), and a band at around 560 nm, which indicates the formation of the Pc radical cation.⁵⁴ The position of λ_{max} depends upon the donor and acceptor strength of the ligands.

Thus, as a consequence of the exchange of a ligand by a specific gas molecule, the absorption at λ_{max} decreases with the partial pressure of NO₂ or CO, and the absorbance of the shoulder (at around 690 nm) increases with increasing concentration of NO₂ or CO.⁵¹ The six-fold-coordinated complexes formed between FePc and pyridine, 4-methylpyridine, 4-methylpiperidine, and benzylamine (BA) are the only available examples of X-Ray structures containing nitrogen donors.⁵⁵ The (BA)₂FePc complex has also been structurally characterized by NMR methods.⁵³ We have developed efficient and reproducible methods for synthesizing octahedral FePc concepts that highlight the importance of understanding the diamagnetic anisotropy concept under the NMR technique. Systems with pronounced diamagnetic anisotropy are typically aromatic where the induced ring currents are usually underestimated as a source of information. Ring-current effects produce a shielding or deshielding of protons resulting from their orientation with respect to an applied external magnetic field. The circulating π electrons create an induced magnetic field that opposes or reinforces the applied magnetic field in different magnetic zones. The zone where opposition to the applied magnetic field occurs is the shielding zone. Protons located in this region have upfield chemical shifts (lower δ values). On the other hand, protons located in the zone of reinforcement are in the deshielded zone and have downfield chemical shifts (higher δ values).⁵⁶ Inspired by the work of Fernandez et al in the 2000's, where a number of bis adducts and mixedligand ferrous phthalocyanine were isolated and tested as optical gas sensors, we decided to extend the variety of these two families of compounds and synthesize novel MPc and F16MPc sixcoordinate systems as promising candidates for future sensing applications. To date, there is no reported octahedral MPc complexes incorporated into chemiresistive gas sensing platforms to our knowledge, thus increasing the applicability of this approach.

VIII. Multifluorinated Precursors for the Development of Next-Generation MPc Systems

Organic compounds containing the trifluoromethyl (CF_3) or pentafluorothio (SF_5) groups play an important role in organofluorine chemistry because of their special properties including low surface energy, hydrophobicity, high chemical resistance, high thermal stability, and high electronegativity. ⁵⁷⁻⁵⁹ SF₅, coined as the 'super-trifluoromethyl' group, is often preferred to CF₃ as it is more electronegative, lipophilic and chemically stable, and possesses a higher steric effect.⁶⁰ The current interest in the field of drug discovery of fluorinated substituents is based on the possibility of improving both the metabolic stability and bioavailability of receptor binders upon the incorporation of substituents with one or more fluorine atoms.⁶¹⁻⁶³ In fact, several blockbuster drugs include such a group, demonstrating the prominent role of the trifluoromethyl group in the area of drug discovery.⁶⁴⁻⁶⁶ New molecules incorporating the SF₅ group are thus potential alternatives to already existing biologically active molecules containing the CF₃ substitution. Additionally, the chemical robustness of SF₅ has been explored in other areas such as polymer chemistry.⁶⁷ Despite the popularity of the title compound, an important precursor in organofluorine chemistry, its crystallographic characterization, which is an important milestone in the synthesis of next-generation materials containing this motif, has not been reported. Herein, we describe a variation to the synthetic approach and give details of its simple crystallization through slow evaporation methods, yielding X-ray diffraction-quality single crystals. The title compound was obtained as part of our studies toward the synthesis of functionalized arenes containing the SF5 moiety.

The synthesis involves a one-pot reaction in which the interaction of the cyano group in 4the lithium (pentafluorosulfanyl)benzonitrile Lewis acidic to cation in lithium tetramethylpiperidide (LiTMP) allows deprotonation from the nearest ortho-H atom on the arene. The SF5-containing organolithium species is then quenched with iodine to yield the title compound. This reaction pathway was proposed by Iida et al. for the synthesis of SF5-substituted zinc phthalocyanines.⁵⁸ We modified the synthesis by adding tetramethylethylenediamine (TMEDA), an amine additive that serves to break up the lithiated base aggregates, allowing for accelerated reactivity because of the increased basicity. This variation improves the total yield of the title compound by 8%.³ We attempted to further improve the reaction yield by employing Turbo-Hauser bases: amide-magnesium halides (typically Cl) coupled stoichiometrically to LiCl (R₂NMgCl·LiCl).⁶⁸⁻⁶⁹ These mixed Li/Mg metal amides are used as non-nucleophilic bases for metalation reactions of arene substrates. Turbo-Hauser bases (THB) show an enhanced kinetic basicity, excellent regioselectivity, high functional group tolerance and a better solubility in polar aprotic solvents than other metalated amides like LDA.⁷⁰ More specifically, metal amides derived from 2,2,6,6-tetramethylpiperamide (TMP), like (TMP)₂Mg·2LiCl, have proven to be the most powerful and selective of bases in the THB family. Their major advantage is that they can be stored in THF at room temperature (25 °C) for months with no significant reduction of activity.⁷¹ This remarkable feature has made bases best for routine experiments in facilities where low temperature storage is a limitation or is not consistent. Moreover, this procedure can be extended to other tailored synthetic secondary amine derivatives, opening pathways for the exciting and relatively unexplored organometallic chemistry of Turbo-Hauser bases.

IX. Disubstituted Precursors for the Development of Next-Generation MPc Systems

Phthalonitrile (1,2-dicyanobenzene) compounds and the derivatives thereof are the most important precursors for metal phthalocyanine complexes.⁷² The chemical and physical properties of MPcs are largely dependent on the substituents on the peripheral benzo groups.¹⁸ In most cases, substituted phthalocyanines are prepared from phthalonitriles containing the desired substituent. With this method, it is the synthesis of the substituted phthalonitrile precursor molecule which presents a synthetic challenge. A common pathway for the generation of substituted phthalonitriles is the cyano-dehalogenation process known as the Rosenmund-von Braun synthesis.⁷³ This reaction, however, employs harsh conditions, limiting its tolerance towards many functional groups; in addition to forming copper phthalocyanine as biproduct.⁷⁴ Hanack et al. proposed an easier method to prepare substituted catechols via their corresponding aryl bistriflates, which was later expanded to work with halobenzenes thought the employment of transition-metal complexes of the platinum group, especially palladium or nickel complexes.⁷⁵ The displacement of the halide or triflate groups by cyanide anions proceeded in high yields using zinc cyanine and a Pd-based mixed catalyst system. A remarkable feature of this approach is that the reaction can be performed without an inert atmosphere, which is otherwise a necessary condition for other palladiumcatalyzed reactions. This was achieved using a small amount of polymethylhydrosiloxane (PMHS) which is capable of reducing any oxidized Pd back into its 0-oxidation state, thus preserving its catalytic function.

X. Annealing of MPc Nanofilms

Phthalocyanine platforms possess multiple polymorphs, which are often the result of how these substances were crystallized.⁷⁶ The polymorphs of unsubstituted MPc complexes have been studied in detail for most transition metals in the fourth period of the period table.⁷⁷ The temperature dependency of these polymorphs has also been reported, most systems changing from the α metastable to the β stable phase at higher temperatures.⁷⁸ Other phases have been discovered for MPc systems; but regardless of the metal or the ring's substituents, these polymorphs often crystallize in low symmetry crystalline systems like monoclinic and triclinic. The crystalline parameters of nanocrystals deeply influence their surface chemistry. To date, there has been no report on the crystalline behavior of F₁₆MPc nanofilms deposited on substrates like quartz, aluminum, or gold. Powder experiments from cif data of F16MPc complexes suggest a triclinic unit cell for all systems. In addition to develop gas sensing devices, this work also describes the effect of annealing, or heating the nanowire thin films, with respect to their crystallographic and gas sensing properties. The morphological aspects of the films are also explored with respect to annealing temperatures. For application as gas sensing platforms, the nucleation, grain growth and orientation of grain play an important role in determining the final electronic as well as optical properties of nanowire thin films. The understanding and control of the orientation of the grains or crystallites in the film and roughness of film surface allows the regulation of many important properties that depend on grain boundaries, grain size and film roughness. Considering the importance of the F₁₆MPc thin films in future nanotechnology, it was thought worthwhile to study systematically the morphology and molecular orientation in F₁₆MPc nanowire thin films after annealing at a wide range of temperatures from room temperature to temperatures much higher than 300 °C.

XI. Motivation

Numerous scientific studies have closely linked air pollution to a variety of health problems.¹ Towards this end, there have been considerable efforts to lower air pollutant emissions in the last 30 years, evidenced by the most recent studies conducted by the Environmental Protection Agency (EPA) in 2014.⁸⁰ This has been the case for El Yaguazo marsh, located in the San Juan Bay area, who has suffered from elevated levels of air pollution in the last years as a consequence of increased industrial and petrochemical activities (**Figure 7a**). A National Emissions study demonstrated that most of the air pollution comes from fuel combustions and industrial processes (**Figures 7b & 7c**).⁸¹



Figure 7: (a) San Juan Bay area, the red zone includes el Yaguazo marsh and the surrounding zone (b) National Emissions by source pollutant and (c) National NO_x pollutions relative amounts in %.

Preliminary subsoil and air quality analyses show increased levels of volatile organic compounds (VOCs), carbon oxides and nitrogen oxides. A 30-year projection revealed that although there is a decline in national air pollutant emissions, there are millions of tons produced annually, nitrogen oxides (NO_x) having the highest contribution, proving to be the most detrimental factor in air quality in our area of interest.⁸² Adverse health effects have been documented after short-term exposure, as well as long-term exposure to relatively low concentrations of NO_x. Studies have documented that subjects living close to busy roads experience more short- term and long-term effects of air pollution than subjects living further away.⁸³ In urban areas, up to 10% of the population may be living at such "hot spots", which is the case of El Yaguazo marsh, a local 'hot spot' in Puerto Rico's capital city.

For humans, short-term exposures to NO_x are associated with respiratory diseases, while long-term exposures to NO_x further contribute to asthma development and potentially increase susceptibility to respiratory infections, leading to respiratory symptoms, hospital admissions and emergency department visits. The public health burden of such exposures is therefore significant. NO_2 and other NO_x interact with water, oxygen, and other chemicals in the atmosphere to form acid rain, which harms sensitive ecosystems such as lakes, forests, and costal zones. In addition, the nitrate particles that result from NO_x make the air hazy and difficult to see though.⁸³ Nutrient pollution is one of America's most widespread, costly and challenging environmental problems and in coastal areas like the San Juan Bay, NO_2 and NH_3 gases could have the most contribution to nutrient pollution in these coastal waters.

XII. Thesis Summary

The doctoral thesis presented herein starts with an outline of the rich chemistry of MPc semiconducting platforms, presented in Chapter 1. The synthesis of numerous phthalocyanine semiconducting platforms is described in great detail on Chapter 2. Section 1 describes the synthesis of complexes with square planar geometry, more specifically, unsubstituted and hexadecafluorinated. Approaches in solution and solid state are compared and ultimately enhanced to generate polycrystalline powder materials with high degree of purity. On Section 2, we expand the coordination geometry of these systems to include axial-coordinated octahedral complexes. The synthesis of several unreported complexes will be described. The synthesis of phthalonitrile building blocks for the preparation of next generation substituted MPc systems is described on Sections 3 and 4 of Chapter 2, and further discussed in the upcoming Chapters. After successfully achieving the synthesis of high-purity semiconducting platforms, we characterized them readily through spectroscopic, microscopy, and crystallographic methods. An in-depth crystallographic analysis of the polycrystalline powders and nanowires is performed in Chapter 3, in addition to the gas sensing capabilities of the as-described complexes. Chapter 4 addresses the most critical points that were achieved during this thesis project, while Chapter 5 offers a future perspective of the endeavors that can be pursued with the knowledge generated in this thesis. All collaborative efforts are described in Appendix A, while Appendix B contains supplementary characterization data and Appendix C contains the crystallographic tables with respective bond lengths and angles of the published compounds.

Chapter 2:

Experimental Methods

General Treatment of Materials and Reagents

All materials and reagents were purchased from Fisher Scientific. THF and DMF were used as reaction solvents and bought under argon atmosphere. DPPF and Pd(dba)₂ catalysts were also bought under argon atmosphere and stored in the dry box. Dimethoxyphthalonitrile (95% purity), tatrafluorophthalonitrile (98% purity) and pentafluorosulfanyl benzonitrile (95% purity) were all stored in the dry box. The n-buli was bought as a 2.0 M solution in hexanes and stored in a fridge at -10 °C under nitrogen atmosphere. TMP was bought under argon and stored in the dry box as well. Reactions were always charged inside the dry box and transported to a Schlenk system for heating or cooling. TLC using silica stationary ohase was used to monitor all reactions. Column chromatography was carried out using silica 60 Å (70-230 mesh) as stationary phase. The mobile phase solvents (hexane, ethyl acetate or dichloromethane) were always distilled prior to use and stored under molecular sieves. Acetone used for Soxhlet extraction was also distilled prior to use. The organic deuterated solvents used for NMR studies (CDCl₃, MeOD, acetone-d) were all stored in a desiccator at the facilities. All glassware was placed in a heated oven at 180 °C overnight and flamed prior to being charged into the drybox. After being used, the glassware was rinsed with an organic solvent, washed with acid, and then treated with distilled water. All reactions involving strong reducing reagents (hydrides, organolithiums, alkali metals) were quenched with isopropanol, ethanol, methanol, and water, in this order, prior to being disposed. NMR was performed in a multiprobe Bruker 500 MHz spectrometer by diluting samples in deuterated solvents, IR was performed in a Nicolet-500 IR transmission microscope using a KBr plate as sample holder, UV-Vis was performed in a nanodrop 9000 system using a 10 mm cuvette, all Xray studies were performed in a Rigaku XTA Supernova equipped with a Cu source and a shutterless detector, and SEM /EDS was performed in a Nova Nanolab 600 SEM-FIB system.

I. Synthesis and Characterization of H₁₆MPc and F₁₆MPc Square Planar MPc Complexes

a. General Synthesis of MPcs Polycrystalline Powder Samples

Section 1 describes the synthesis and characterization of high-purity microcrystalline MPc complexes for the fabrication of nanowire films thereof. The preparation of these types of phthalocyanine systems is achieved by reacting commercially available phthalonitrile (1,2dicyanobenzene) derivatives with metal acetate salts through a cyclotetramerization (template) reaction at high temperatures under solvent-free conditions.⁸⁴ The complexes can also be prepared in solution through the use of a high-boiling point solvent like ethylene glycol. This approach, however, was demonstrated to be sub-optimal because of solvent removal and the need to employ more rigorous purification controls; in addition to generating a higher amount of waste material. Purification of the complexes is performed through milling and suspending the polycrystalline powders in solvents to remove excess reagents and by products, followed by filtration. Soxhlet extraction with a polar aprotic solvent like acetone is performed on the hexadecafluorinated complexes for 24 hours, after which the remaining solutions are filtered, and solvent removed under pressure to yield high-purity crystalline F₁₆MPc powders. It is worth mentioning that 1,2dicyanobenzene is considered hazardous by the 2012 OSHA Hazard Communication Standard (29-CFR-1910.1200) and thus must be handled with care. The unsubstituted MPcs were prepared with a 4:1 (ligand/metal) ratio, where none of the reagents were in excess with respect to one another. The F₁₆MPc derivatives were prepared by having an excess of metal acetate salt, as to consume completely the less reactive fluorinated phthalonitrile (Scheme 4). After purification, all products were characterized by SEM, EDS, UV-Vis spectroscopy, FTIR, and X-ray powder diffraction.



Scheme 4: Synthetic preparation of (a) unsubstituted and (b) hexadecafluorinated (F₁₆) metal phthalocyanine systems.

b. Synthesis of H₁₆MPc Polycrystalline Powder Samples

A 10 mL round-bottom flask (or similar vessel) was charged with 1,2-dicyanobenzene (512 mg; 4.0 mmol), and Fe(OAc)₂ was added (174 mg; 1 mmol). The vessel was capped with a rubber septum under an argon atmosphere, and the septum was secured with a metal clamp. The reaction was heated until 200 °C and left at this temperature for 4 h, after which a dark-violet solid was obtained. After cooling at room temperature, the as-obtained solid was pulverized using a mortar and pestle and suspended in 100 mL of distilled DCM to remove unreacted 1,2-dicyanobenzene. The suspension was stirred for 15 min at room temperature and vacuum filtered. The solid was washed with ethyl alcohol (5 × 10 mL), and afterward, a second suspension in 100 mL of nanopure water was performed to remove unreacted Fe(OAc)₂, which was stirred for 15 minutes and filtered under vacuum.

The purified product was dried in vacuo overnight, affording 293 mg of H_{16} FePc (52% yield based on 1,2-dicianobenzene). A family of unsubstituted MPc complexes with 3d transition metals was synthesized using this approach and starting from their respective $M(OAc)_2$ salts, where M = Mn, Fe, Co, Ni, Cu and Zn.

c. Synthesis of F₁₆MPc Polycrystalline Powder Samples

A 10 mL round-bottom flask was charged with 3,4,5,6-tetrafluoro-1,2-dicyanobenzene (500 mg; 2.5 mmol), and Fe(OAc)₂ was added (435 mg; 2.5 mmol). The vessel was capped with a rubber septum under an argon atmosphere, and the septum was secured with a metal clamp. The reaction was heated until 250 °C and left at this temperature for 4 h, after which a dark-violet solid was obtained. After cooling at room temperature, the as-obtained solid was pulverized using a mortar and pestle and suspended in 100 mL of distilled hexane to remove unreacted 3,4,5,6-tetrafluoro-1,2-dicyano- benzene. The suspension was stirred for 15 min at room temperature and vacuum filtered. A second suspension in 100 mL of nanopure water was performed to remove unreacted Fe(OAc)₂, which was stirred for 15 min and filtered under vacuum. The crude product obtained upon workup was submitted to extraction with distilled acetone. The dark-violet solid was placed inside a Soxhlet extractor and left extracting with acetone for 24 hours, leaving behind a black coal-like powder containing metal oxides and other impurities present in the crude product obtained before workup. The purified product was further dried in vacuo overnight, yielding 221 mg of F_{16} FePc (41% yield based on 3,4,5,6- tetrafluoro-1,2-dicyanobenzene). A family of hexadecafluorinated MPc complexes with 3d transition metals was synthesized using this approach and starting from their respective $M(OAc)_2$ salts, where M = Mn, Fe, Co, Ni, Cu and Zn.

d. Synthesis of Nanowire Films from Polycrystalline Powder Samples

For the synthesis of nanowire thin films, a PVD procedure was developed based on the ones reported by Ji et al., Liu et al., and Tong et al., respectively.85-87 This was performed in collaboration with Dr. Luis Fonseca's laboratory (NasLab) who designed, tested, and executed the deposition experiments in their PVD facilities (Scheme 5). More specifically, ~20 mg of previously synthesized, purified, and powdered polycrystalline $F_{16}MPc$ precursor is introduced into a long quartz tube reactor in the middle of the right side of a dual oven. The IDE platforms and other substrates are placed at the end of the right zone and the reactor is closed and evacuated to 10⁻² Torr of residual pressure with a mechanical pump. During the PVD procedure, the temperature is raised at a rate of 4.7 °C/min and maintained for 80 min. Throughout the experiment, a constant flow of nitrogen is maintained at a 100 sccm rate, and the pressure is also monitored at 5 Torr inside the reactor. Through these procedures the materials go from solid to gas, losing their crystalline conformation in the process and acquire a new crystalline conformation when they get deposited, which is characteristic and unique of the thermodynamic parameters governing the process, Therefore, accurately controlling temperature and pressure can yield materials with modified and unique morphologies capable of being used for electrochemical applications. Our collaborators at NasLab achieved the successful growth of nanowires from previously synthesized high-purity $F_{16}MPc$ polycrystalline powders by optimization of several parameters during the PVD experiments like carrying gas flow, temperature of evaporation/sublimation, interdigitated electrode (IDE) platform temperature, physical position within the gas reactor, and adequate time of growth. From the synthetic perspective, the purity of the polycrystalline powder sample is the main parameter that must be optimized in order to obtain successful PVD procedures.



Scheme 5: Physical Vapor Deposition System used by NasLab to Synthesize the MPc Nanowires.

e. Fabrication of Gold Interdigitated Electrodes (IDE)

The IDE substrate was designed and fabricated by our collaborators at Dr. Ruben Diaz's Laboratory employing typical photolithographic processes, in which the parameters are critically adjusted to ensure that the pattern transfer process occur with minimal defects (**Figure 8**). The fabricated sensor is further validated through its electrical responses and morphological characteristics. In general, as the distance between the electrodes increases, the working voltage must increase to collect the same current density. Thus, by reducing the distance between the electrodes the devices are able to work at low voltages while passing appreciable measuring current. Different distances, arrangements and patterns in the electrodes lead to distinct sensing capabilities of the devices.

Briefly, a silicon wafer with 380 µm in thickness and 300 nm of thermal oxide was used as the starting substrate. LOR 3A and S1805 were used for the bilayer resist method. The desired pattern was transferred onto the PR by UV exposure using a dark field quartz photomask. The PR and LOR development was performed by submerging the wafer completely in a glass dish containing MF-24A without agitation. To remove any residual photoresist in the critical features, a descuming step was performed in an oxygen plasma for 30 - 60 seconds. The metal deposition was performed with an electron beam evaporator. The deposited thicknesses were 10 nm of Ti and 100 nm of Au. For the lift-off process the wafer was submerged in Remover 1165 at 70 °C for 30 minutes followed by DI water submersion in two consecutive baths and dried with a nitrogen gun.



Figure 8: Fabrication process flow of the IDEs with the bilayer lift-off method.

f. Gas Sensing Experiments

We worked in collaboration with NasLab in order to test the gas sensing properties of our synthetic metal phthalocyanine complexes. The gas sensing facilities are located in our collaborators' laboratory and experiments were conducted by PhD candidate Soraya Flores. Here, IDEs containing nanowire films of our metalated complexes were placed inside the gas sensing chamber and electrically attached to adjustable tungsten tips at room temperature (24 ± 1 °C) (**Scheme 6**). A Keithley 6487 Picoammeter/ Voltage Source was used as the power source and for electrical current measurements. Current measurements were done at 15-second intervals during exposure to a flow of air with and without polluting gas.



Scheme 6: Gas measurement equipment and experiment setup.

The desired pollutant gas concentration was established by combining a flow of air (compressed synthetic air tank -20.4% O₂) and a flow of test gas (100 ppm of ammonia/nitrogen or 100 ppm of NO₂/nitrogen gas tanks) in the proper ratio to define the final concentration in parts per billion by volume for a total gas flow of 500 sccm. The total moisture was determined by the carrier gas (0.036 ppm) with no additional humidity added. In summary, the material is maintained in a constant flux of dried synthetic air, and the ammonia is added to the flux in the desired proportion. To evaluate the sensor's response, the electrical current intensity is measured as a function of time during exposure to an air flow with and without pollutant gas. The normalized sensor response is defined as $S = |I - I_0|/I_0$, where I is the electrical current intensity and I₀ is the initial current intensity before the exposure of the sensor to the pollutant gas. We will employ the Langmuir approximation in order to describe the adsorption kinetics, which is suitable for gas concentrations in the ppb range. Following this assumption, the adsorption process at the surface of the nanowires resulting from gas interaction with the surface-active sites will be a fast process (Equation 1), where adsorption kinetics instead of diffusion controls the time response. The diffusion-controlled slow response was considered using an overall exponential time decay assumption (Equation 2). Both processes are described with the following pair of equations:

$$[\text{Equation 1}] S(t) = A_{1F} \left(1 - e^{-t/\tau_{1F}} \right) + A_{1S} \left(1 - e^{-t/\tau_{1S}} \right)$$
$$[\text{Equation 2}] S(t) = A_{2F} \left(e^{-t/\tau_{1F}} \right) + A_{2S} \left(e^{-t/\tau_{1S}} \right)$$

where A_{1F} , A_{1S} , τ_{1F} , τ_{1S} and A_{2F} , A_{2S} , τ_{2F} , τ_{2S} are the fitting parameters for the response (with ammonia) and the recovery (no ammonia) periods with τ_F and τ_S as the fast and slow time constants, respectively.

II. Synthesis and Characterization of H₁₆MPc and F₁₆MPc Octahedral MPc Complexes

The extension of the coordination geometry of MPc derivatives is reported in Section 2 of this thesis. Scheme 7 shows the reaction of two equivalents of amine with MPc complex in a polar aprotic solvent affords complete conversion to the bis-amine metal complexes.



Scheme 7: Synthesis of octahedral metal phthalocyanine complexes by an adduct-formation rxn.

The corresponding amine (0.3 mmol) was added dropwise to a solution of 1 (85 mg, 0.150 mmol) in THF (5 mL). The reaction mixture was stirred at ambient temperature for 15 min after which time the dark green solution was filtered and concentrated in vacuo. The resulting greenish oil was washed with cold hexane, filtered, and dried in vacuo. This sequence was repeated one more time. Alternatively, the complexes can be prepared in situ in an oven-dried 5 mm NMR tube, by just mixing 0.03 mmol (17 mg) of MPc with 0.06 mmol of the corresponding amine in deuterated THF or chloroform (0.5 mL). After a few minutes the solution turns deep green indicative of the desired transformation.

III. Synthesis of Multifluorinated Precursors for Next-Generation MPc Systems

A novel precursor to unexplored SF5-MPc complexes is reported on Section 3. All solvents and reagents were purified prior to being used. 4-(pentafluorosulfanyl)benzonitrile was obtained commercially and used without further purification (95% purity). A solution of 2.0 M n-Butyl Lithium (n-BuLi) in hexanes was used. Column chromatography was carried out on a column packed with silica gel 70–230 mesh. The synthesis of the title compound was performed through the regioselective ortho-lithiation of 4-(pentafluorosulfanyl) benzonitrile with LiTMP in THF as solvent, favoring the formation of the ortho product (1,2,4-substituted arene) over the meta product (1,3,4-substituted arene) as shown in **Scheme 8**.



Scheme 8: Multistep synthesis of pentafluorosulfanyl arene precursors.

The ortho-metalated product was subsequently quenched with I₂ to afford the iodinated trisubstituted arene. A dry 50 mL Schlenk tube was charged with 4 mL of dry THF and 300 mL of 2,2,6,6-tetramethyl piperidine (1.75 mmol, 2 eq.) and 262 mL of N,N,N,N-tetramethylethylendiamine (1.75 mmol) were added under an inert atmosphere. The solution was cooled to 273 K and 700 μ L of 2.0 M n-n-BuLi in hexane (1.75 mmol, 2 eq.) were added slowly. The reaction mixture was stirred at 273 K for 30 minutes and then cooled to 195 K. A solution containing 200 mg of 4-(penta- fluorosulfanyl)benzonitrile (0.872 mmol, 1 eq.) in 4 mL THF was added dropwise: the solution changed from pale yellow to dark brown upon formation of the metalated intermediary.

After stirring for 1h at 195 K, a solution of 244 mg I₂ (0.960 mmol, 1.2 eq.) in 4 mL THF was added dropwise and stirred for 2 h. The mixture was then warmed to room temperature and stirred for 1 h. The reaction was quenched with water and THF was removed under reduced pressure, followed by extraction with diethyl ether. The combined organic phase was washed with aqueous 0.1 M HCl, 0.1 M Na₂S₂O₃ and brine, then dried over MgSO₄. The crude product was purified by column chromatography (9:1, hexane:EtOAc) to yield 71 mg (46%) of the pure arene product as a yellow solid (m.p. 367–369 K). Block-like yellow crystals suitable for X-ray diffraction were obtained by slow evaporation of a saturated CH₂Cl₂ solution of the 6-sulfanyl)benzonitrile at room temperature over a period of four days. NMR analyses were performed on a Bruker AV-500 spectrometer using deuterated chloroform (CDCl₃) as solvent. The solvent signals at 7.26 and 77.0 ppm were used as internal standards for proton and carbon, respectively. ¹H NMR δ = 8.3 (d, J = 2.1 Hz, 1H), 7.9 (dd, J = 8.6, 2.1 Hz, 1H), 7.8 (d, J = 8.6 Hz, 1H). ¹³C NMR (125 MHz, CDCl₃) δ = 98.2, 117.8, 124.1, 126.1, 134.3, 136.8, 156.1. Similarly, 4-(pentafluorosulfanyl) benzonitrile was combined with (TMP)₂Mg·2LiCl in THF at 0 °C using and ice-water bath. The Turbo-Hauser base was synthesized from LiTMP and (TMP)Mg·LiCl according to Scheme 9 and purified using the same procedure as outlined for the LiTMP synthesis.



Scheme 9: Multistep synthesis of Turbo-Hauser base used for regioselective lithiation.

IV. Synthesis of Difunctionalized Precursors for Next-Generation MPc Systems

The alkoxy-subsituted phthalonitrile precursor on Section 4 is obtained as part of our studies towards functionalized MPc systems containing eight OH groups on the aromatic periphery. The multistep synthesis involves the preparation of phthalonitrile precursor, followed by metal complex formation, and subsequent reduction of the methoxy groups into their hydroxide counterparts. The first step of the synthesis involves the one-pot palladium-catalyzed cyanation bis(dibenzylideneacetone)palladium [Pd(dba)₂] and 1,1'-bis(diphenylphosphino)ferrocene (DPPF) as the catalyst system in dimethylformamide (DMF) as solvent with $Zn(CN)_2$ as cyanating agent at a temperature of 115 °C (**Scheme 10**).

The synthesis was performed by charging a 25 mL 2-necked round bottom flask in the dry box with 1,2-dibromo-4,5-dimethoxybenzene (dibromoveratrole or DBVT) 592 mg, 2 mmol, 1 eq.), Pd(dba)₂ (46 mg, 2 mol% Pd) and DPPF (30 mg, 2.6 mol%). On a separate vial, 4 mL of DMF were combined with 50 µL PMHS and added to the 25 mL round bottom flask. The reaction was taken out of the dry box, heated until 115 °C, and Zn(CN)₂ (294 mg, 5 mmol, 2.5 eq.) was added in 4 portions during the course of 4 hours (1 portion/hour). The remaining solution was left stirring for 1 more hour at 115 °C until TLC revealed no starting material. The reaction was then quenched with EtOAc, organic phase was filtered, washed with water (25 mL x 3) and dried over Na₂SO₄. The crude product was concentrated in vacuo and submitted to column chromatography. The title compound was eluted with CH₂Cl₂ as the mobile phase, affording 346 mg of a pale white solid (92% yield). ¹H NMR (500 MHz, CDCl₃) δ = 7.2 (s, 2H), 3.9 (s, 8H) ppm. ¹³C NMR (125 MHz, CDCl₃) δ = 152.6, 115.7, 114.8, 108.9, 56.6 ppm. IR: ν = 2227 cm⁻¹ (C=N stretching). UV-Vis (in CH₂Cl₂): λ_{max} = 287 nm.



Scheme 10: Dimethoxy-phthalonitrile (4,4-dimethoxy-1,2-dicyanobenzene) precursor synthesis.

A similar approach to the one developed for unsubstituted and hexadecafluorinated was performed, were the phthalonitrile precursor was reacted at high temperatures and pressures, followed by isolation and purification. A methodology following the same pathway was developed in solution using a high boiling point solvent like ethylene glycol (**Scheme 11**). More specifically, 5-dimethoxyphthalodinitrile (5.0 g, 26.6 mmol), M(OAc)₂ salt (7 mmol) were reacted in a pressure-rated vial at 200 °C for 3 hours, followed by repetitive washing with water and DCM. Alternatively, the starting materials can be refluxed in 15 mL of ethylene glycol under argon atmosphere for 24 hours. The mixture is then cooled to room temperature, and 70 mL of water was added to precipitate the (OCH₃)₈MPc. The resulting solid was washed successively with methanol (40 mL \times 5) and acetone (40 mL \times 5) by using a centrifuge to collect precipitate. The product was then dried under vacuum to give (OCH₃)₈MPc as a dark green solid.



Scheme 11: Template reaction performed for the synthesis of (OCH₃)₈MPc.

One of the most well-known, highly utilized reagents for ether cleavage is boron tribromide (BBr₃), and this reagent is frequently employed in a 1:1 stoichiometric ratio with ethers.⁸⁸ Recent density functional theory calculations predict a new mechanistic pathway involving charged intermediates for ether cleavage in aryl methyl ethers. Moreover, the calculations predict that one equivalent of BBr₃ can cleave up to three equivalents of anisole, producing triphenoxyborane [B(OPh)₃] prior to hydrolysis.⁸⁹ More specifically, (OCH₃)₈MPc (~120 mg, 1.5 mmol) was suspended in 10 mL of dichloromethane, and BBr₃ (1 M, 6 mL, 6 mmol, 6 e.q.) was added under N_2 (Scheme 12). The mixture was stirred for 1 week, and then poured into 50 mL of H₂O. The precipitate was collected by centrifugation. The obtained solid was then dispersed in MeOH (20 mL), shaken vigorously and then centrifuged. The solid was collected and then subjected by MeOH washing using centrifuge for another 4 times. The product was then dried under vacuum to give (OH)₈MPc as a dark green solid. During this work, four new unreported (OCH₃)₈MPc and two (OH)8MPc complexes were designed, synthesized, and characterized; namely, (OCH3)8MPc were M = Mn, Fe, Co, Zn, and (OH)₈MPc were M = Fe, Co. In the literature, only the complexes of Cu and Ni had been reported to date for both (OCH₃)₈MPc and two (OH)₈MPc systems.



Scheme 12: Reduction of (OCH₃)₈MPc to generate (OH)₈MPc metal complexes.

Chapter 3:

Results and Discussion

Section I: Unsubstituted and Hexadecafluorinated Square Planar MPc Complexes

In Section 1 we will cover the synthesis and in-depth crystallographic/spectroscopic characterization of unsubstituted and fluorinated square planar MPc complexes. The results presented herein were published by our research team in 2022 on ACS Nanomaterials.

a. Synthesis of Square Planar MPc Complexes

To this respect, there were numerous other approaches attempted during this thesis for the synthesis of unsubstituted and hexadecafluorinated phthalocyanine systems. An issue that had to be addressed was the enormous variety of synthetic procedures available in the literature to synthesize MPcs, and the plethora of reagents to achieve it. The common factor amongst all these syntheses was the need for strenuous conditions such as high temperatures, long reaction times and complex workup procedures. In solution, most syntheses were performed under inert atmosphere, with the use of high boiling point solvents to achieve temperatures above 150 °C. The solvents would often be extremely toxic like nitrobenzene (bp: 211 °C) and DMF (bp: 153 °C) or would have such a high boiling point that removing it in vacuo under practical conditions was not achievable like ethylene glycol (197 °C). In the solid state, the syntheses needed to be performed under extremely high pressures because the phthalonitrile organic precursors would fuse below 150 °C and sublime in the reaction vessels. Such approach was achieved using solvothermal conditions in a high-pressure Teflon reactor. Although it was a viable approach, there were multiple setbacks that eventually led us to abandon this particular method. Thus, an in-depth discussion to the endeavors of synthesizing MPc complexes is offered with the focus of arriving at an optimal method that enables high purity polycrystalline materials to be produced reproducibly, while maximizing the efficiency of our materials.

We initially started with the preparation of the unsubstituted metal phthalocyanine complexes. Our initial syntheses started from the free-base or metal free phthalocyanine system (H₂Pc). Through this approach, the metal complex product proceeded through an adduct-formation reaction. Here, the deprotonation of H₂Pc generates the dianionic tetradentate ligand Pc²⁻, which reacted subsequently with the metal in M²⁺ form (**Scheme 13**). Three key experimental conditions were modified: (1) solvent (DMF, *n*-pentanol, ethylene glycol), (2) base (TEA, TBA, DBU), (3) metal salt (MCl₂, MNO₃, M(OAc)₂). After the metal salt was added in a high boiling-point solvent and the reaction let to progress for at least 2 hours, the remaining solutions were worked up by filtering the mixture and washing the remaining solid with solvents to remove excess reagents and by-products.



Scheme 13: Metal phthalocyanine synthesis following the deprotonation-metalation pathway.

There were no experimental conditions found that yielded a pure phthalocyanine complex, all attempts led to the metalated complex, with some unreacted H₂Pc present, as confirmed through UV-Vis spectroscopy. Since both metalated and metal-free complexes had a very limited solubility is most organic solvents, separation of one from the other through solvent washing could not be achieved. At this point, we focused more on the purity of the materials, rather than the yield that was being obtained in these reactions. This route was ultimately replaced.

In order to improve the target product purity, a distinct organic precursor and a new reaction pathway was attempted (Scheme 4). Using 1,2-dicyanobenze (phthalonitrile) as precursor proved to be a more favorable pathway because any unreacted phthalonitrile could be washed away with common organic solvents like DCM, THF and EtOAc, improving the overall purity of the product phthalocyanine. Another advantage of this method was that one could start with substituted phthalonitrile precursors and generate a substituted phthalocyanine systems. The reaction proceeded through a metal-mediated mechanism in which the metal acted as a template for macrocycle formation. Scheme 14 serves as a model showing how coordination with the Cu²⁺ plays a role in retaining structure in a conformation favorable to the ring closure by intramolecular nucleophilic attack to form intermediate [Cu(L631)]. Direct elimination of the original nucleophile Y- from [Cu(L631)] is not favored, as this would lead to the dehydrophthalocyanine, which is generally considered as a 16 π -electron system and as such is unstable.⁹⁰ Where copper metal is the reactant, two electrons may be transferred to the metal allowing elimination of Y- to form the stable 18 π -electron copper(II) phthalocyanine CuPc. Consequently, the copper(0) is oxidized to copper(II) as required to participate further in the reaction sequence. When copper(II) is the reactant, so that there is no comparable reducing agent present, it is supposed that Y^+ (in this case the chloronium ion) is eliminated to form CuPc, the driving force for this elimination being the exceptional high stability of CuPc. The eventual formation of [Cu(L629)] in this case is explained by a subsequent electrophilic substitution reaction involving CuPc and the released chloronium ion. When copper(I) chloride reacts, is probable that route (i) is followed initially, the source of the two electrons required being two Cu⁺ ions.

The result of this first phase of the reaction sequence would be the formation of equimolar amounts of CuPc and copper(II) chloride, the latter reacting subsequently in the second phase by route (ii) to give [Cu(L629)].



Scheme 14: Illustration of the kinetic coordination template effect in the synthesis of MPc.

This demonstration is enough to establish the criteria that a metal ion template reaction is one in which coordination of at least one reactant molecule to a metal ion is necessary either for the reaction to proceed, or to change the product distribution in favor of a specific macrocyclic compound. This ultimately means that the presence of the metal is controlling the synthesis. The template effect is demonstrated in two ways, the thermodynamic and the kinetic template effects. The equilibrium (or thermodynamic) template effect (ETE) is when complexation to a metal ion stabilizes one component of a mixture, shifting the equilibrium in favor of production of a metal complex. The kinetic template effect (KTE) is when there is coordination of reactive groups to a metal ion, which then holds these groups in the proper geometry, favors an intramolecular cyclization. In the ETE, the equilibrium lies in favor of the 1,2-dicyanobenzene in the absence of metal ion (M^{2+}), whereas the macrocycle complex (MPc) is formed in >50% yield in the presence of M^{2+} . In the KTE, the favored square- planar coordination about the metal center drives the reaction to give the cyclic product.

In solution, the reaction could be monitored by UV-Vis spectroscopy because metal ligation resulted in a characteristic metal- transition located in the 600-800 nm region of the spectrum. One setback of the solution approach was the need for solvent removal after reaction. Often times the resulting solids, even after hours of strenuous rotary evaporation, required days of vacuum suction at room temperature to be solvent-free. Another challenge was the presence of unreacted metal chloride salt present in the bulk of the crude product. In many instances, washing would not remove the salt completely and would result in non-homogeneous solids. To this end, an ammonium molybdate/urea catalyst system was employed. The catalytic system could be then washed away with solvent during the workup. This theoretically led to the complete consumption of the metal chloride salt, but after careful inspection of the surface/bulk properties of the solids, we always found trace impurities of Mo metal, which were easily detected through Electron Diffraction Spectroscopy (EDS).

An important turning point during the synthesis of the unsubstituted MPc was the employment of metal acetate salts. Since these salts were completely water soluble, they were readily removed during the washing step and the end, with no need to employ a catalytic system for the complete consumption of the metal acetate salt/precursor. Various techniques were performed to optimize the removal of the salt from the crude product. At first, we would wash with warm solvents using gravity or Büchner filtration, followed by drying of the microcrystalline powders. Although we were able to reproducibly obtain favorable results, the filters would often clog and take hours to run the solvent through the solid. To this end, we tried centrifugation which enabled us to create a suspension and subsequent separation of the supernatant. This strategy worked extremely well and enabled a decrease in purification time by more than half but was partially unfavored by the amount of solvent and materials needed. It did, however, yield the best results in terms of purity and led to reproducible synthetic procedures. After exploring the solution synthesis with favorable results, the approach was extended to include a high pressure solvothermal strategy. The latter would reduce the cost of materials, reduce the amount of waste produced, and require little to no solvent elimination after workup. A 50 mL Teflon reactor was used in which the phthalonitrile precursor and metal acetate salt was added; after which the solvothermal apparatus was placed inside an oven at 200 °C. The reaction could be performed with the addition of a minimal amount of solvent, namely 5-10 mL. Under the high-pressure conditions, the number of molecular collisions theoretically increased and improved the reaction rate. This ultimately resulted in higher yields for the same reactions that were performed in solution with normal glassware. Interestingly, we were able to obtain good reproducibility and results even without the use of a solvent. Working towards a more ecosustainable synthetic approach, the solution synthesis was abandoned and replaced in its entirety with the solid state solvothermal syntheses.

For the hexadecafluorinated phthalocyanine systems, a similar reaction pathway was adopted. These systems possessed a wide range of solubility in organic solvents, which made purification easier and more efficient. The phthalonitrile precursor, 3,4,5,6-tetrafluoro-1,2-dicyanobenzene, is heavily deactivated by the inductive nature of the fluorine atoms, and thus required higher reaction temperatures, longer reaction times or an excess of reagents. In order to keep working at a reasonable oven temperature ~ 200 °C and keep the reaction time in the 2–3-hour margin, an excess of metal acetate salt was added. Whereas the original stoichiometry dictated for a 1:4 metal to phthalonitrile ratio, we opted for equimolar ratio of 1:1 which was 3 eq. more than needed for the metal acetate salt. This ultimately meant that an even more rigorous purification procedure had to be established for the removal of the metal acetate salts. Each crude powder would then be pulverized and suspended in solvent, namely water, and left stirring for 15 minutes under nearboiling conditions. The solution was cooled, centrifuged, and the resulting solid suspended and washed again. The process was performed three times until the aqueous solution wash was colorless, indicating no more metal acetate salt was dissolved. The crude powders were later extracted with acetone using Soxhlet extraction, and solvent was removed in vacuo to yield purple microcrystalline MPc complexes. After performing solubility tests, it was determined the complexes were most soluble in polar protic and aprotic solvents; the best ones being acetone, DCM and ethyl acetate. Acetone was mostly used because of its availability and high degree of volatility. A black powder was left behind in the Soxhlet extractor which corresponded to unreacted metal acetate salt and oxides formed from the high temperature reaction thereof. The procedures developed in the beforementioned endeavors resulted in the reproducible synthesis of microcrystalline powders with a high degree of purity.
b. Spectroscopic Characterization of MPc Complexes

Section 1b offers an in-depth analysis of the absorption spectroscopy of square planar MPc complexes. Absorption spectroscopy is one of the most powerful tools for the identification of the different metal coordination systems.⁹¹ The advantages of using absorption spectroscopy to characterize these compounds are numerous, and effects like metal ion coordination in the cavity, peripheral substituents, and axial coordination can be studied in detail. Elucidation of the molecular structure and monitoring reactions by means of absorption spectroscopy can be challenging in some instances, however, because in solution, MPc complexes are prone to aggregation at moderate-to-high concentrations. The molar extinction coefficients of these compounds are very large (on the order of 10⁵ M⁻¹ cm⁻¹),³⁷ and most measurements had to be taken at very low concentrations (10⁻⁶ M). All complexes were studied using UV-Vis and IR spectroscopies. A major experimental challenge for unsubstituted MPc systems in UV-Vis spectroscopy was the need to have the compounds in solution. Their extremely low solubility meant that the solutions had to be filtered thoroughly, and the low amounts of dissolved compounds resulted in signals with low intensities. All complexes displayed absorptions at around 600-800 nm which corresponded to the as-reported values in the literature.¹¹⁹⁻¹²⁰ The more novel hexadecafluorinated complexes possess a wider range of solubilities and were able to be studied readily through UV-Vis spectroscopy. The values for λ_{max} often resulted in lower wavelengths, in comparison to the unsubstituted complexes. All IRs were performed in the solid state using a transmission IR microscope. The need for light to go through the sample meant that the dark microcrystalline solids had to be pressed into a thin film for transmission to occur. Reproducible and well-resolved spectra was obtained for all complexes.

1. UV-Vis Spectroscopy

The Q band absorption of substituted metal phthalocyanines is reported to shift by 100–150 nm to a longer wavelength (lower energy) in comparison to unsubstituted MPcs.³⁵ Gouterman *et al.* showed that to a first approximation the strong Q-band (600 to 750 nm) originates from $\pi \rightarrow \pi^*$ transitions from a_{1u} to e_g^* orbitals (Figure 9). In the case of our synthesized compounds, absorption maxima are moved to longer wavelengths in the order of Co, Ni, Cu, Zn, and Fe, which is in accordance with what is reported.⁹¹ In comparison to the same central metal, non-peripheral substituted phthalocyanines show longer wavelengths than peripheral compounds. In general, H₂Pc's show shorter wavelengths than corresponding MPcs. Metal-free phthalocyanines with bulky substituents, increase the distortion of the molecule because the four central cavity sizes cannot be fixed. Then, the Q band of metal-free will not split. The Q band is known to split into two peaks for high symmetry: the splitting Q band decreases with de-creasing symmetry. Metalfree substituted Pcs display decreased symmetry as a result of the molecular distortion. The Q band shifts depend upon the change in the electron distribution in the phthalocyanine ring caused by substituents and their position, as well as the metal. However, a difference of the Q band in these compounds is low upon studying the different metals in the 4th period. In this case, the nature of the metal only slightly affects the movement to a longer, or shorter wavelengths.



Figure 9: $\pi \rightarrow \pi^*$ transition in MPc complexes showing S (B) and Q bands.

Absorption spectroscopy in the UV–Vis region showed characteristic π – π transitions at 323 and 322 nm for F_{16} FePc and F_{16} CoPc and metal- π transitions in the visible region at 624 and 621 nm for F_{16} FePc and F_{16} CoPc, respectively (Figures 11 and 12). The UV band of both complexes is of lower energy than the UV band of the initial phthalonitrile starting material (Figure 10), indicative of increased conjugation and macrocycle formation. We can observe that the characteristic π - π transitions in the higher energy side of the spectrum possess near-identical values of 323 and 322 nm for F₁₆FePc and F₁₆CoPc, respectively (Figure 13). This indicates the formation of the same macrocyclic ligand. The major difference is on the lower energy metal- π transition, which shows the cobalt complex band is blue shifted with respect to the iron complex band. Both possess a considerable absorbance and clearly demonstrate the successful binding of the metal. Also, there is no ligand transitions observed in the spectra of the complexes, indicating that there are no trace amounts of unreacted precursor left in the bulk of the solid. Dissolved phthalocyanines often show solvatochromic effects, such as changes in the position, intensity, or half- width of the absorption bands.³⁵ New absorption bands appear due to a charge transfer, and the absorption bands can be red or blue-shifted. However, although the absolute position of the absorption bands and their shape was observed to be solvent-dependent, their relative positions remained roughly constant, and usually, the oscillation strength does not vary drastically. The strength of the oscillation is related to the molar absorption coefficient of the absorption bands. In general, to a rough approximation the molar absorption coefficient of the Q-band is in the range of $10^5 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$. Depending on the central metal atom the molar absorption coefficient may change by up to 1 order of magnitude, whereas solvent effects cause only smaller variations.



Figure 10: UV-Vis spectrum of the hexadecafluorophthalocyanine starting material, tetrafluorophthalonitrile (3,4,5,6-tetrafluoro-1,2-dicyanobenzene) in acetone.



Figure 11: UV-Vis spectrum of hexadecafluorinated iron phthalocyanine complex (F₁₆FePc) in acetone.



Figure 12: UV-Vis spectrum of hexadecafluorinated cobalt phthalocyanine complex F₁₆CoPc in acetone.



Figure 13: UV-Vis spectra of the starting material and the two hexadecafluorinated metal phthalocyanine complexes in acetone.

Although the effect of the central metal on the energy of Q band is usually small, absorption maxima are moved to longer wavelengths, and apparently increase with the ionic radius of the central metal. For many other applications, the absorption maxima of MPcs are best if moved near the infrared region. The strongest absorption of MPcs in the visible region can be attributed to the allowed highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) $(\pi \rightarrow \pi^*)$ transition. The Q band of MPcs can be moved by bathochromic effects through extension of the π conjugation system such as seen in naphthalocyanines and anthracyanines but yields of naphthalocyanines and anthracyanines are however usually low.⁹² To overcome this challenge, novel MPcs having non-peripheral substituents have been synthesized in the past and exhibit a high strain structure and no liquid crystal properties, although we will limit our discussion to unsubstituted MPcs for now. The Soret band arises primarily due to an electron di-pole movement that allows π - π * transitions, most common in porphyrin compounds. The broad S-band is caused by transitions between a_{2u} and b_{1u} to eg* orbitals. Most analytical studies of porphyrin-containing moiety can be done using ultraviolet-visible spectroscopy and exciting wavelength at the respective Soret band wavelength. For example, the Soret peak (also known as the B band) is used to describe the absorption of vividly pigmented heme-containing moieties, such as various cytochromes.⁹³ In summary, the Soret band (B Band) absorption is a So-S2 absorption (i.e., ground state to excited state), while the Q band is of S₀-S₁ absorptions, which are lower in energy and can be observed at longer wavelengths (Figure 9).

2. Infrared Spectroscopy

The infrared absorption spectra and their frequencies for phthalocyanine and its divalent metal derivatives was studied as well. These absorption bands can be divided into two groups according to whether or not the wavenumber (as well as the intensity) changed as the species of metal ion are substituted from one to the other. The effect of substitution is best noticed when a close examination is made of these spectra in comparison with those for metal-free phthalocyanine which has two hydrogens in place of a divalent metal ion as shown. Metal-free phthalocyanine shows two strong absorption bands at 716 and 999 cm⁻¹. These two peaks are associated with the N-H out-of-plane de-formation and in-plane deformation respectively. The N-H stretching vibration is expected to show an absorption near 3000 cm⁻¹, and the weak broad band observed at 3200 cm⁻¹ for the metal free phthalocyanine only was assigned to this vibrational mode. It was found that reaction of the ligand with the metal salt did not proceed to completion when using metal chloride salts, in contrast to metal nitrate salts which produced a crude product which had no C-N absorptions in the infrared region (around 2,250 cm⁻¹), characteristic of the C-N bond in the ligand. FT-IR continuum microscope surface mapping revealed that the unreacted ligand cocrystallized upon precipitating the phthalocyanine from the reaction crude.

The MPc complexes are planar molecules of D_{4h} point group symmetry. Assuming a D_{4h} point group for the F₁₆MPc species comprised of 57 atoms, the corresponding vibrational representation reads as:

$$\Gamma_{\text{Vib}} = 14 \text{ } A_{1g} + 13 \text{ } A_{2g} + 14 \text{ } B_{1g} + 14 \text{ } B_{2g} + 13 \text{ } E_g + 6 \text{ } A_{1u} + 8 \text{ } A_{2u} + 7 \text{ } B_{1u} + 7 \text{ } B_{2u} + 28 \text{ } E_{u} + 28 \text{ } E_{u}$$

The A_{1g} , B_{1g} , B_{2g} , E_g modes are Raman active, and the A_{2u} and E_u modes are IR-active. Note that $A_{1g},\,B_{1g},\,B_{2g}$ are in-plane and E_g is an out-of-plane vibration. The positions of some bands are dependent on the type of metal atom. All of the divalent metal phthalocyanine molecules are usually taken to belong to D_{4h} point group, whereas H_2Pc has apparently D_{2h} symmetry. The E_u mode of vibration, which is infrared active for molecules with D_{4h} symmetry, is known to split into two other infrared active modes, B_{2u} and B_{3u} , without too much change in the peak position when the molecules happen to assume D_{2h} symmetry as a result of, for instance, minor substitutions.⁹⁴ Such an effect of splitting is clearly in the lower frequency region. In the higher frequency region, the characterization of doublets was difficult because of the overlapping of a greater number of peaks made the spectra in that region much more intricate. In the case of MPcs, the absorption bands apparently corresponding to those which appeared as the doublets for H_2Pc were detected as singlets which exhibited considerable shifts to higher frequencies. The corresponding absorption peaks are always shifted in the same order: Ni>Co>Fe>Cu>Zn>H₂, strongly indicating that the absorption bands which are affected by the species of substituted metal ion are metal dependent ones. The medium intensity band which appeared as a singlet peak in the range 888 and 919 cm⁻¹ for each specimen is characteristic only of metal derivatives and is strongly dependent on the species of the metal ion.

Since no corresponding absorption peak was observed for H_2Pc , the band of this type can be taken as being associated with the metal-ligand vibrations. These findings, that the metal-ligand absorption bands are observed in such a high frequency region, indicate the extraordinary stability of the metal phthalocyanines due to the strong bonding between the metal ion and the four surrounding nitrogen atoms in the pyrrole rings. More specifically, in the case of unsubstituted MPcs, the fundamentals lying in the spectral region between 1350 and 1500 cm⁻¹ have been identified to be highly sensitive to the nature of the metal ion. Another group of fundamentals of medium intensity at ~1275 cm⁻¹ for F₁₆FePc, F₁₆CoPc, F₁₆NiPc, and F₁₆CuPc, respectively, involves isoindole deformations. Apart from this, the fundamentals in the range 1130-1160 cm⁻¹ are also sensitive to the central metal because they correspond to isoindole ring de-formation coupled with C-N-C and C-N in-plane vibrations. Another group of fundamentals at 937-955 cm⁻ ¹ was attributed to the isoindole breathing along with stretching of M-N. Finally, there are two groups of fundamentals in the wavenumber regions 230-280 cm⁻¹ and 350-400 cm⁻¹ dominated by M-N in-plane and out-of-plane stretching vibrations. In addition, some bands sensitive to the nature of the metal ion are also present in the IR spectra. These fundamentals lie in the wavenumber region 1440-1530 cm⁻¹. The resolution of the IR spectrometer was affected by the dark color of the products, since only a small fraction of the microscope light could go through the sample. This supposes low transmittance values, which translate to low signal to noise ratio (S/N). Additional scans where performed, but after 32 scans the sample's S/N improves negligibly, if anything.

An alternative approach, often more suitable for dark colored samples, is to combine the sample with Nujol in a mortar and pestle or some other device to make a mull (a very thick suspension) and is usually sandwiched between potassium- or sodium chloride plates before being placed in the spectrometer.⁹⁵ Performing IR in solution would be a viable approach, only for those complexes that possess good solubility in common organic solvent. Unfortunately, that would only be the case of the hexadecafluorinated complexes, as the unsubstituted complexes (as well as many other MPc derivatives) are only sparingly soluble in certain solvent, limiting the applicability of this instrumental approach in solution. These fundamentals lie in the wavenumber region 1440-1530 cm⁻¹. More specifically, complexes used herein as gas sensors showed characteristic vibrational bands were observed in the IR-like bridge N vibrations at 1491 and 1500 cm⁻¹ for F₁₆FePc and F₁₆CoPc, and metal–N stretching was observed at 963 and 964 cm⁻¹ for F₁₆FePc and F₁₆CoPc, respectively (**Figures 14-16**).



Figure 14: Infrared spectrum of hexadecafluorinated iron phthalocyanine complex (F₁₆FePc).



Figure 15: Infrared spectrum of hexadecafluorinated cobalt phthalocyanine complex (F₁₆CoPc).



Figure 16: Infrared spectra of the two hexadecafluorinated metal phthalocyanine complexes in acetone, were M = Fe and Co.

c. X-Ray Crystallography of Polycrystalline Powder Samples

An in-depth crystallographic database survey was performed for all systems and single crystal data obtained from cif files was processed to plot the experimentally obtained powder patterns. The Crystallographic Structural Database⁹⁶ was used for such analysis; and processing of the as obtained cifs was performed with Mercury software.⁹⁷ All complexes except F₁₆FePc had cif files that corresponded to the crystallographic analysis of the structures.

Year	Code (CSD)	Polymorph	Space
			Group
1976	FEPHCY	beta monoclinic	P21/a
1936	FEPHCY01	beta monoclinic	P21/n
1986	FEPHCY02	beta monoclinic	P21/n
2013	FEPHCY03	beta monoclinic	P21/c
2013	FEPHCY04	beta monoclinic	P21/c
2014	FEPHCY05	beta monoclinic	P21/n
2018	FEPHCY06	beta monoclinic	P21/n
2018	FEPHCY07	beta monoclinic	P21/n

Table 1: Results of the database survey for reported crystal structures of FePc complexes.

In FePc, two polymorphs (α metastable and β stable) can occur because of the slight differences in the π - π electronic interaction between the neighbor molecules in the lattice (**Table 1**). The main difference between these two polymorphs is the tilt angle of the molecular plane with respect to the stacking *b* axis. In the α -polymorph, the tilt angle is 25-30° with respect to the normal to the molecular ring, whereas in the beta-polymorphs the angle is 45-49°. All β polymorphs crystallize in monoclinic unit cells with one of three distinct space groups: P21/a, P21/c and P21/n; the latter P21/n group being the most common one amongst recent structures (**Figure 17**).



Figure 17: Powder X-ray diffractogram of iron phthalocyanine powder before PVD.

Five polymorphous modifications of CoPc are known; they are designated α , β , ε , π and χ . The α and β polymorphs of MPc are the two common structures reported.⁹⁷ The structures of the χ -CoPc and the π -CoPc have been studied; strong Bragg angles at $2\theta = 7.8^{\circ}$ and 9.5° are observed for the χ -phase, $2\theta = 5.0^{\circ}$, 8.7° and 10.0° for the π -phase were also observed.⁹⁸ The alfa-polymorph is triclinic, with space group *P*-1; whereas the β -form is monoclinic, space group *P*21/*a* (**Table 2**). Other modifications have been described in the literature related to the nanostructures thereof.⁹⁹ All modifications exhibit one-dimensional stacking of the molecules; however, the arrangement of the stacks with respect to one another differs, as illustrated by the model structures of α and β CuPc. α -CoPc consists of columnarly arranged molecules, those of adjacent columns being aligned parallel to each other, whereas a nearly perpendicular arrangement is present in β -CoPc (**Figure 18**).

Year	Code (CSD)	Polymorph	Space
			Group
1980	COPTCY01	beta monoclinic	P21/c
1936	COPTCY02	beta monoclinic	P21/n
1967	COPTCY03	alpha triclinic	P-1
1986	COPTCY04	beta monoclinic	P21/n
1989	COPTCY05	beta monoclinic	P21/c
1991	COPTCY06	beta monoclinic	P21/c
1998	COPTCY07	alpha triclinic	P-1
1998	COPTCY08	beta monoclinic	P21/c
1979	COPTCY10	beta monoclinic	P21/c
2018	COPTCY11	beta monoclinic	P21/n
2018	COPTCY12	beta monoclinic	P21/n

Table 2: Results of the database survey for reported crystal structures of CoPc complexes.

The processing of the powder patterns included a baseline correction, followed by smoothing and a peak fitting analysis. On the diffractograms, the **raw data is displayed in black**, while the **red data represents the processed graph**.



Figure 18: Powder X-ray diffractogram of cobalt phthalocyanine powder before PVD.

In the powder X-ray diffraction (PXRD) patterns, the α and β polymorphs of MPc are the two common structures reported.¹⁰⁰ All modifications exhibit one-dimensional stacking of the molecules; however, the arrangement of the stacks with respect to one another differs. The α polymorph consists of columnar arranged molecules, those of adjacent columns being aligned parallel to each other, whereas a nearly perpendicular arrangement is present in the β polymorph.¹⁰¹ In FePc, two polymorphs (α metastable and β stable) can occur, while five polymorphic modifications of CoPc are known; they are designated α , β , ε , π , and χ .⁹⁸ The α polymorph is triclinic, with space group P1; whereas the β form is monoclinic, with space groups P21/a, P21/c, and P21/n reported. Other modifications have been described in the literature related to the nanostructures thereof. The β phase is often converted to the α phase by dry grinding in the presence of additives and heat. All modifications can be transformed into the most stable form by heating in a high-boiling, inert solvent or through annealing.¹⁰² During the synthesis of the powders, the β modification was primarily formed, as observed from the diffraction patterns of FePc and CoPc (Figures 17 and 18). Some unidentified phases could also be present but are lost and non-existent in the nanostructures formed from these materials thereof. Thus, the most stable modification at high temperatures was formed, as expected. For the F₁₆MPc complexes, the data suggest that there is a distribution of crystallite sizes, as suggested by the peak broadening. These diffractograms possessed lower amounts of signals that can be attributed to lower Bragg angles. Although both presented a total of 4 signals, the main peak in F₁₆FePc possesses a considerably higher intensity at the principal peak around $2\Theta = 5.42^{\circ}$ than the broader one at 26.79° (Figure **19**). This is in contrast to F_{16} CoPc which possess nearly the same intensity for the peaks at around $2\Theta = 6.23^{\circ}$ and 26.87° (Figure 20).



Figure 19: Powder X-ray diffractogram of hexadecafluorinated iron phthalocyanine powder before PVD.



Figure 20: Powder X-ray diffractogram of hexadecafluorinated cobalt phthalocyanine powder before PVD.

d. X-Ray Crystallography of MPc Nanowire Films

The formation of thin films composed of nanowires through PVD is a complex process that is influenced by many factors such as the material's properties, deposition parameters, and external constraints resulting in multiple film microstructures ranging from single crystals, to polycrystalline and amorphous films.¹⁰³ The nanowire growth on our substrates is performed at high temperatures above 400 °C; at these temperatures, molecules have an increased kinetic and can easily migrate to lower energy sites, creating a high amount of nucleation points and resulting in polycrystalline structures with various crystallite sizes, most in the nm range with wire morphology. During synthesis, the most stable modification is formed; in the case of CoPc and FePc this is the beta-modification. The beta modification is often converted to the alfa modification by dry grinding in the presence of additives and heat.

All modifications can be transformed into the most stable form by heating in a high-boiling, inert solvent. The beta phase was the predominant one with regards to the microcrystalline powder samples of both iron and cobalt complexes, however, some minor diffractions were observed that could correspond to alternate phases. When performing the deposition process, both samples lose their crystallographic arrangement upon transitioning into the gas phase. The deposition process on the substrate thus determines the new crystallographic arrangement and orientation. The asobtained nanowires were compared to the already-reported phases and determination of the crystallographic structure was performed through comparison with empirical data.

FePc nanowires in **Figure 21** show the characteristic XRD peaks at $2\theta = 7.05$ and 9.25° corresponding to the interatomic-plane separations of β -FePc, $d_{100} = 12.49$ Å and $d_{-102} = 9.55$ Å, respectively (**Table 3**).



Figure 21: Powder X-ray diffractogram of iron phthalocyanine nanowires after PVD.

FEPHCY	FEPHCY 04	FEPHCY 06	Our Study	Our study
(beta P21/a)	(beta P21/c)	(beta P21/n)	(powder)	(nanowires)
7.06	7.05	7.09	7.05	7.05
9.27	9.25	9.27	9.24	9.25
10.63	10.62	10.63	9.92*	10.61
12.59	12.58	12.61	12.58; 13.60*	12.59
18.21	18.21	18.24	15.58*;16.86*	18.22
18.70	18.67	18.68	19.49*	-
23.89	23.88	23.89	23.86	23.87
26.35	26.34	26.37	26.34	26.33
28.16	28.15	28.17	_	28.18
30.62	30.61	30.61	-	30.59

Table 3: Comparison of the as-reported FePc structures with our synthesized microcrystallineFePc powders and nanowires.

CoPc nanowires shown in **Figure 22** also possess the characteristic XRD peaks at $2\theta = 7.06$ and 9.24° corresponding to the interatomic-plane separations of β -CoPc, $d_{100} = 12.49$ Å and $d_{-102} = 9.55$ Å, respectively (**Figure 22, Table 4**).



Figure 22: Powder X-ray diffractogram of cobalt phthalocyanine nanowires after PVD.

COPTCY12	COPTCY08	COPTCY07	Our Study	Our study
(beta P21/n)	(beta P21/c)	(alfa P-1)	(powder)	(nanowires)
7.09 (100)	7.059 (100)	6.939 (001)	8.85*	7.06
9.39 (-102)	9.254 (-102)	7.33	10.07*	9.24
10.75	10.60	-	-	10.58
12.70	12.60	-	-	12.55
18.35	18.27	15.81	17.53*	18.25
18.93	18.67	16.16	18.23	-
23.98	23.87	24.28	23.81; 25.28*	23.85
26.51	26.31	26.94	26.34	26.30
28.30	28.14	27.98	29.12	28.11
30.82	30.57	-	30.59	30.57

Table 4: Comparison of the as-reported CoPc structures with our synthesized microcrystallineCoPc powders and nanowires.

Figures 23 and 24 display a comparison of both iron and cobalt metal phthalocyanine complexes with their respective nanowire materials. In the patterns of CoPc and FePc nanowires grown using our method, the locations of the peaks are somewhat different from the powder precursor, which contains mostly the β -MPc phases and some others which could not be identified. All nanowire diffractograms contain an excellent signal to noise ratio and display well defined peaks that could be assigned to each respective phase. As the Bragg angles increases, the intensity of the signals decreases, as expected. For all samples, the most intense peak is between 6° - 8° 2 θ and corresponds to the main interplanar spacing between the metal centers in our MPc complexes. Most signals remained unchanged for the iron complex. Most notably, the signal at $2\theta = 9.25^{\circ}$ increased considerably, which shows that the nanowires have increased crystalline planes or domains corresponding to this interplanar distance. There was a more drastic effect observed at lower Bragg angles for the cobalt complex. The nanowires of CoPc are purely composed of the beta-phase, whereas in the microcrystalline powered the main diffraction peak at lower angles is shifted towards higher angles. There was no polymorph in the literature that corresponded to these Bragg angles, suggesting that a new crystalline phase could be present within the microcrystalline powder of the CoPc complex. Most importantly, these results demonstrate that the microcrystalline powder that is produced during the synthesis contains mainly the stable beta-polymorph for both complexes, with some unidentified phases; whereas the nanowire structures of both complexes are, to the most part, arranged in the beta phase or polymorph. These results are consistent with what is expected to be obtained at high deposition temperatures like the ones produced during PVD.



Figure 23: Comparison of powder X-ray diffractograms of iron phthalocyanine powder and nanowires (before and after PVD).



Figure 24: Comparison of powder X-ray diffractograms of cobalt phthalocyanine powder and nanowires (before and after PVD).

A search for F₁₆MPc diffraction data performed in the Cambridge Structural Database (CSD) reveals a total of four structures of F₁₆MPc (M = Co, Cu, Zn and Pd). All these compounds crystallize in the triclinic $P_{\underline{1}}$ space group and contain an antiparallel arrangement of molecules isostructural to the α and β polymorph in unsubstituted systems (**Table 5**). F₁₆CoPc, specifically, displays characteristic XRD peaks at $2\theta = 6.32^{\circ}$ and 28.19° . Basova et al. has also reported the powder pattern for F₁₆CoPc which reveals Bragg peaks at $2\theta = 6.20^{\circ}$ and 12.14° , corresponding to the (001) and (002) planes.¹⁰⁴ Peaks with a very low intensity were observed at 11.96°, 16.93° and 22.58° for the F₁₆ZnPc system, corresponding to the (002), (003), and (004) planes respectively.¹⁴⁴ There is no F₁₆FePc diffraction data (nor of F₁₆MnPc or F₁₆NiPc) reported to date in the CSD, to our knowledge. A recent publication by Denekamp et al. shows diffraction peaks of $2\theta = 27.70^{\circ}$ and 27.65° for F₁₆CoPc and F₁₆FePc, respectively.⁸⁴

Year	Code (CSD)	F ₁₆ MPc metal	Unit Cell	Space Group
2010	FUJPUW	Cu	triclinic	P-1
2014	OHADIM	Со	triclinic	P-1
2014	OHADUY	Zn	triclinic	P-1
2018	BEGNOT	Pd	triclinic	P-1

Table 5: Results of the database survey for reported crystal structures of F₁₆CoPc complexes.

The F₁₆FePc nanowires observed in **Figures 25 and 26** show characteristic XRD peaks at $2\theta = 6.31^{\circ}$ and 28.52° corresponding to the interatomic-plane separations of d₀₀₁ = 14.08 Å and d₀₀₄ = 3.09 Å, whereas F₁₆CoPc nanowires in **Figures 27 and 28** show characteristic XRD peaks at $2\theta = 6.25$ and 28.49° corresponding to the interatomic-plane separations of d₁₀₀ = 14.12 Å and d₀₀₄ = 3.13 Å, respectively. Both obtained powder XRD patterns display characteristic Bragg angles of the triclinic crystal system consistent with previous reports in the literature.¹⁰⁴⁻¹⁰⁵



Figure 25: Powder X-ray diffractogram of hexadecafluorinated iron phthalocyanine nanowires.



Figure 26: Comparison of powder X-ray diffractograms of hexadecafluorinated iron phthalocyanine powder and nanowires (before and after PVD).



Figure 27: Powder X-ray diffractogram of hexadecafluorinated cobalt phthalocyanine nanowires after PVD.



Figure 28: Comparison of powder X-ray diffractograms of hexadecafluorinated cobalt phthalocyanine powder and nanowires (before and after PVD).

The locations of the peaks in the powder XRD of our nanowires are also different from the powder precursor, which shows similar diffraction peaks at $2\theta \approx 6^{\circ}$ and 27° but displaced at lower Bragg angles, indicative of longer interplanar distances (**Tables 6 and 7**).

Our Study	Our study
(powder)	(nanowires)
5.42	6.31; 7.20*
-	9.16
11.97	12.57; 15.39*
-	16.43*
17.03	18.09
-	20.04*
26.79	27.80
-	28.52
-	-
-	-

Table 6: Comparison of the synthesized microcrystalline F₁₆FePc powders and nanowires.

OHADIM	Our Study	Our study
(triclinic P-1)	(powder)	(nanowires)
6.32	6.23	6.25
9.18	-	9.20
9.51	-	-
12.64	-	12.61
17.65	-	17.71
18.06	18.09	18.11
22.73	21.48	22.73
27.85	27.87	-
28.19	-	-
28.45	-	28.49
29.07	-	-
29.37	-	-

Table 7: Comparison of the as-reported F_{16} CoPc structures with our synthesized microcrystalline F_{16} CoPc powders and nanowires.

e. Electron and Atomic Force Microscopy MPc Nanowire Films

Figure 29a shows a scanning electron microscope (SEM) image of as- grown nanowires on IDEs; as observed in the image, a uniform coverage of the IDE is achieved. The wires' size distribution includes <100 nm wires and >150 nm belts and bundles (**Figures 29 b-d**).



Figure 29: Electron microscopy analysis of as-prepared F_{16} FePc nanowires. (a) Lowmagnification SEM image showing uniform coverage of the electrodes. (b) TEM image of nanowire bundles on holey carbon grids. (c) HRTEM image of a single nanowire. (d) Electron diffraction pattern.

1. Scanning Electron Microscopy (SEM) of MPc Nanowire Films

SEM images of the as grown F_{16} FePc nanowires on the interdigitated gold electrodes show preferential growth of the nanowires at the gold electrode surface (see red circles in **Figure 30a**). Nanowires with diameters <100 nm and belts of larger width but <100 nm thickness are observed in **Figures 30 b-d**.



Figure 30: (a) and (b): SEM image of the electrodes area shows a high percentage of connecting NWs between adjacent electrodes. (c) and (d): Nanowires with diameters <100 nm, belts and bundles are forming the chemiresistor network.

Optical microscopy inspection shows a larger density of wires close to gold electrode areas, and in SEM closeup images (**Figure 31**), preferential growth from the gold electrodes is shown with a large concentration of smaller size nanowires making direct contact between adjacent electrodes. The preferred formation of MPc nanowires directly on the surface of the gold electrodes is consistent with previous reports where the effect on nucleation upon the use of gold substrates for growing MPc nanostructures with a diversity of shapes was examined.¹⁰⁶⁻¹⁰⁷



Figure 31: (a) and (b): SEM image of the electrodes area shows F₁₆CoPc (c) and (d): SEM image of the electrodes area shows FePc.

2. Transmission Electron Microscopy (TEM) of MPc Nanowire Films

Figure 32 shows the high-resolution transmission electron microscope (HRTEM) image of a ~54 nm F₁₆FePc wire. The crystal planes spanning the observed region confirm the highly crystalline quality also obtained in the electron diffraction pattern shown in **Figure 33**. Multiple measurements were performed on Figure 33 that revealed a distance of ~1.4 nm between crystalline planes (**Figures 34-36**). Spectra and mappings of the different elements in a selected nanowire support the F₁₆FePc chemical composition. TEM images are consistent with SEM and AFM findings by showing single nanowires and larger belts with >100 nm thickness, and bundles.



Figure 32: TEM images of F_{16} FePc nanowires. Left: a distribution of nanowires. Those with larger width are belts, thinner ones are nanowires. Right: A ~120 nm single nanowire. Image shows a uniform and compact structure.



Figure 33: TEM images of F₁₆FePc nanowires showing well-defined crystalline planes.

Both SEM and TEM analyses reveal the successful deposition of nanowires on our IDG. TEM images reveal the highly crystalline nature of one discreet wire, where the interatomic planes can be clearly seen and calculated using processing software. Ideally, the interplanar distance will be proportional to the distance obtained through powder diffraction analysis of both microcrystalline powders and nanowire samples.

3. Fast Fourier Transform (FFT) Measurements of MPc Nanowire Films

Using the image processing program ImageJ,¹⁰⁸ we performed FFT measurements to distinct regions in the as-obtained TEM images. The spatial calibration was carried out using the scale bar at the bottom of the images.

After the distance: pixels ratio was calculated, a profile plot was generated using a fixed set of planes. The cycles were manually counted, and the distance was divided by the number of cycles on the plot (shown in red at the top-left corner of each plot).



Figure 34: TEM image and profile plot of 10 atomic planes selected for the calculation.



Figure 35: TEM image and profile plot of 5 atomic planes selected for the calculation.

Using the same program but the "Roi Manager" tool, the distance between the planes was estimated knowing the scale of the image. To get an average, 8 measurements of different parts of the image and 5 parallel planes were considered, the average was 1.39 nm.



Figure 36: TEM image of where selected 8 measurements that have 5 atomic planes and table of this dataset.

The profile plots were performed in different regions to confirm the reproducibility of the measurements. Interestingly, the interplanar distance correlates with a Bragg angle of 6.31° , which is the one precisely observed in the powder diffractograms of these materials. The results show the microscopy and diffraction techniques are in agreement with the crystalline arrangement and distances of respective F₁₆FePc motifs in microcrystalline powders/nanowires.

4. Atomic Force Microscopy (AFM) of MPc Nanowire Films

Atomic force microscopy (AFM) is a powerful technique that enables the imaging of almost any type of surface and is useful to measure and localize many different forces, including adhesion strength, magnetic forces and mechanical properties. Nanowires can even be manipulated using AFM to generate intricate and extremely conductive nanostructures that operate as nanoelectrodes, although the latter approach was beyond the scope of this thesis work. Atomic force microscopy (AFM) mappings of larger wires show that larger structures are belts or bundles with thickness in the nanoscale. **Figure 37** shows the AFM mapping of a single nanowire with a diameter of \sim 80 nm (left side) and a bundle of two nanowires (right side). One wire of the bundle is a belt with a \sim 200 nm width and a \sim 70 nm thickness. Nanobelts show some surface roughness.



Figure 37: AFM mapping of F_{16} FePc nanowires. Left: a nanowire with ~80 nm diameter. The image shows another wire bundled at the top. Right: A bundle of two wires. One is a belt with ~70 nm thickness.

f. Energy Dispersive X-ray Spectroscopy (EDX) of Metal Phthalocyanine Nanowire Films

Energy-dispersive X-ray spectroscopy (EDS) was used for the elemental analysis and chemical characterization of all our samples (**Figure 38**). Spectra and mappings of the different elements in a nanowire supports F_{16} FePc chemical composition as shown in **Table 8** as an example. EDS for all other MPc systems is located in the appendix, showing the presence of the metal in our materials.



Figure 38: EDS analysis. EDS spectrum, TEM image and elemental mappings for the F₁₆FePc.

Element	series	Net	[wt.%]	[norm. wt.%]	[norm. at.%]	Error in wt.% (3 Sigma)
Carbon	K-series	6762	69	69	78	6.8
Oxygen	K-series	225	1	1	1	0.4
Iron	K-series	471	4	4	1	0.8
Fluorine	K-series	2958	18	18	12	2.0
Nitrogen	K-series	1045	18	18	8	1.0
		Sum:	100	100	100	

Table 8: Normalized quantitative weight percentages for the elements in the yellow region of the F_{16} FePc nanowire.

Vibrational spectroscopies (IR and Raman) have been shown to be very useful for study of the surface structure and properties of thin films and powders. These techniques are particularly suitable in the case of F₁₆MPc compounds with unknown crystal structure because the commonly employed X-ray diffraction methods are not always able to fully characterize these substances. Raman spectra of as prepared FePc, F₁₆FePc and F₁₆CoPc materials are shown in **Figure 39**. Many of unsubstituted metallic phthalocyanines and fluorosubstituted phthalocyanines such as MPc (M= Co, Cu, Fe, Ni, Mn) among others, are planar molecules of group D_{4h} symmetry and their vibrational modes corresponds to:

$$\Gamma_{vib} = 14 \ A_{1g} + 13 \ A_{2g} + 14 \ B_{1g} + 14 \ B_{2g} + 13 \ E_g + 6 \ A_{1u} + 8 \ A_{2u} + 7 \ B_{1u} + 7 \ B_{2u} + 28 \ E_u,$$

where the active modes in Raman are A_{1g} , B_{1g} , B_{2g} (in the plane) and E_g (out the plane). Difference in the spectral behavior of the different MPc is due to the influence of the central cation. In the group of bands between 1350 cm⁻¹ and 1500 cm⁻¹, a slight displacement product of the metal ion is observed.¹⁵¹ In our case, in F₁₆FePc it is 1531 cm⁻¹, in F₁₆CoPc it is 1528 cm⁻¹ and in FePc it is 1534 cm⁻¹. Insertion of sixteen F substituents in MPc entails to a change in intensities and wavenumbers of the vibrations due to the contribution of C-F vibrations, this change is noticeable in the bands ranging from 1450 cm⁻¹ to 1640 cm⁻¹ that are associated with the stretching vibrations of C = N and C = C in the benzene rings. Another group of bands from 600 cm⁻¹ to 1250 cm⁻¹ is also associated with macroring or isoindole deformations due to the contribution of C-F vibrations.¹⁵²



Figure 39: Experimental Raman spectra for F₁₆FePc, F₁₆CoPc and FePc.

The vibrations observed in our data are assigned according to data found in the literature.¹⁰⁹ The experimentally measured vibrational wavenumbers of F_{16} MPc molecules coincide well with DFT theoretical predictions performed by Basova *et al.* The RMS difference between the calculated and experimental wavenumbers was around 20 cm⁻¹. The fundamentals in the spectral region around 900-1100 cm⁻¹ are characterized by high contribution of C-F stretching vibrations. The stretching vibrations of C=C (1590-1640 cm⁻¹) in benzene rings of the MPc molecule are also quite sensitive to the change of the molecular packing. The modes below 200 cm⁻¹ belong to the lattice vibrations and are also dependent on. The phase composition and molecular packing.
h. Gas Sensing Measurements of MPc Nanowire Films

Gas sensing in MPc complexes relies on a charge transfer reaction in which the oxidizing or reducing gas binds to the transition metal center through a coordinate-covalent bond. The focus of this thesis is to produce semiconducting platforms based on the MPc complexes that are capable of detecting pollutant gases in relevant concentrations, in the order of ppm and ppb. Gas testing revealed that the F₁₆MPc complexes had a noticeable increase in the electrical current under constant voltage when exposed to ppb concentrations of ammonia gas (**Figure 40**). Measurements were performed until stabilization was observed, followed by a similar recovery period. For all nanowire films deposited on IDEs, this time was around 55 hours, which may be too large for some applications were instant responses are required. To this end, environmental monitoring of gases happens over a range of days and the sensor has to be able to measure the concentration of a gas in the field for prolonged times.



Figure 40: Comparison between the F₁₆FePc and F₁₆CoPc sensors' response (Normalized S) to (a) 100 ppb of NH₃ for 75 h and (b) 500 ppb of NH₃ for 3 h.

As suggested in the experimental section, there are two processes that contribute to the gas sensing response of the semiconducting nanofilms, a fast and a slow one. The semiconductivity of our metal complexes is tailored by chemically modifying the substituents on the periphery of the aromatic rings. While unsubstituted MPcs show *p*-type semiconductivity, replacing all H atoms for F atoms transforms it into an *n*-type semiconductor. In our novel $F_{16}MPc$ nanowires, surface ionized oxygen reacts with the ammonia gas, and the oxygen-localized electrons are released, increasing the density of free electrons in the conduction band, thus reducing the electrical resistance. The time constants for the slow and fast processes were calculated and curve fittings were performed, revealing that the time constant for the slow process resulted to be larger than the recovery time constant. An overall linear dependence was observed, consistent with the adsorption-controlled linear approximation outlined in the experimental section. The distance between active sites in MPc coordination complexes is significantly larger than in typical inorganic metal oxide chemiresistors, thus justifying the use of the linear approximation in this condition. Figure 41 shows the response of F₁₆FePc nanowire sensors when exposed to 100 ppb of NH₃ gas in air.



Figure 41: (a) Comparison between the F₁₆FePc and FePc normalized sensors' response to 100 ppb of NH₃. (b) Normalized response (Normalized S) of the FePc sensor at 100 ppb of NO₂.

Similar saturation behavior is observed, but the sensitivity toward ammonia of the cobalt-based material is significantly reduced when compared with the iron complex. A similar result is observed at higher concentrations of 500 ppb of NH₃ concentration in a shorter period of time. When comparing the recovery time of the unsubstituted FePc sensors to their hexadecafluorinated counterparts, it was observed that the recovery time is very slow, and a total recovery was not obtained in within the testing times for this system. The response of FePc nanowire sensors to 100 ppb of NO₂ in nitrogen carrier gas shows a reduction of the electrical resistance when exposed to the oxidizing gas. The response is significant (18% in \sim 2 h), and the recovery is relatively slow, indicating a stronger interaction between the gas molecules and the metal center of the complex. Tests were conducted down to 40 ppb in concentration, showing remarkable results in the material's ability to detect ammonia gas. During the course of 3 hours, the sensor was able to detect 40 ppb of ammonia and recover to its original base current. Cycling tests at 100 ppb over the course of 90 minutes revealed that the material could detect and recover in less than 30 minutes. Over multiple cycles, the normalized current gave reproducible values, which correlated linearly to the ammonia concentration. This demonstrates the reproducibility of the sensor under sub ppm concentrations, and that we are able to obtain fast and slow responses from our systems, depending on the metal center and the substituents on the MPc rings. This Chapter resulted in an ACS Nanomaterials publication with enormous potential to serve as the foundation for future publications:

Flores, S. Y.; Gonzalez-Espiet, J. C.; Cintrón, J.; Villanueva, N. D. J.; Camino, F. E.; Kisslinger, K.; Piñero Cruz, D. M.; Díaz Rivera, R.; Fonseca, L. F. Fluorinated Iron and Cobalt Phthalocyanine Nanowire Chemiresistors for Environmental Gas Monitoring at Parts-per-Billion Levels. *ACS Applied Nano Materials*. **2022**, *5* (4), 4688-4699. DOI: 10.1021/acsanm.1c04039.

Section II: Unsubstituted and Hexadecafluorinated Octahedral MPc Complexes

Section 2 presents the extension MPc geometry into their octahedral counterparts. An in-depth study using NMR was performed to elucidate the chemical environment of axial ligands. Four new unreported complexes were prepared using the methodology described herein.

a. Synthesis and NMR Characterization of (amino)₂H₁₆FePc

MPc octahedral complexes were achieved by coordinating a primary amine to the two empty axial positions, thus extending their coordination geometry, and potentially making them more labile and prone to substitution via dissociative mechanisms. The characterization of the octahedral metal complexes based on MPcs can be successfully achieved by nuclear magnetic resonance (NMR). NMR of coordination complexes is unique, interesting, and relatively unexplored. Electrons in π systems (e.g., aromatics, alkenes, alkynes, carbonyls etc.) interact with the applied field which induces a magnetic field that causes the anisotropy.⁵⁶ As a result, the nearby protons in an NMR experiment will experience 3 fields: (1) the applied magnetic field (by the NMR magnet), (2) the shielding field of the valence electrons, and (3) the field due to the π system. Depending on the position of the proton in this third field, it can be either shielded (smaller δ) or (larger δ), which implies that the energy required for, and the frequency of the absorption will change. When an O or N donor coordinates to the empty axial positions, the protons are in the deshielding cone of the aromatic system, which possess a high electron density due to the delocalization of the π aromatic system and shifts the signals towards lower ppm. In fact, there are signals that can be located at negative ppm values, a highly unusual feature when performing routine NMR experiments. This requires the spectroscopist to broaden the spectral window and calibrate the frequency axis with

great precision. The experiments performed herein were carried out in a 500 MHz Multiprobe Bruker NMR, a high-resolution spectrometer that possess the capacity to probe these protons at negative ppms and assess the coordination of the octahedral complexes, in addition to being able to monitor the reaction progress and calculate stoichiometrically the amount of complex being formed. Initial studies based on unsubstituted FePc octahedral complexes were performed in deuterated THF, an expensive solvent when compared to other deuterated ones used in NMR like CDCl₃, acetone-d⁶ and acetonitrile-d³. The reason for this was that most MPc complexes were insoluble in most solvents, and very sparingly soluble in THF. One of the goals of the present approach is to increase the applicability of these octahedral systems by making them more accessible through their synthesis in other solvent systems. Unsubstituted MPc complexes readily aggregate due to the strong π - π interactions in the aromatic systems. This makes the dissolution process unfavorable since we need to break the solute-solute interactions with the solvent. Thus, the solubility of MPc systems is very limited in numerous solvents.



Figure 42: Example of the magnetic anisotropic cone model for FePc complex and benzylamine.

When placing FePc in deuterated chloroform, no signals were observed in the NMR spectrum because the compound was not in solution, but rather precipitated in the NMR tube. If it were dissolved, we would expect two signals that correspond to the alfa and beta hydrogens of the aromatic π system of the macrocycle. When adding a primary amine, the transparent CDCl₃ solution turns dark green, indicating the complex has been dissolved as shown in **Figure 42**. This can be attributed to the deaggregation of solute molecules due to disruption in their π system interactions, which ultimately leads to a higher degree of solubility in organic solvents. We can confirm this by monitoring the progress in the NMR tube as it happens. The spectrum now reveals both signals of the FePc hydrogens and the signals of the primary amine derivative shifted towards lower ppms (signals f and g, Figure 43). Since our spectral window had to be large enough (negatively) for us to study the hydrogens in the anisotropic cone of the MPc macrocycle, the spectral width was increased to 24 ppms and the range set for -12 to 12 ppms; twice as broad as a routine NMR spectrum. An exciting and interesting feature that could not have been explored prior to current technological advances and opens a window of possibilities to study systems in these anisotropic environments. We used the (BA)₂FePc systems that was already published as a reference and to calibrate the spectral/synthetic parameters for our new (amine)₂FePc systems. Using these approaches we designed, synthesized, and characterized these novel octahedral derivatives, thus extending the coordination geometry of MPc systems.



Figure 43: (benzylamine)₂FePc NMR spectrum displaying shielded benzylamine protons.

b. Synthesis and NMR Characterization of Unreported (amino)₂H₁₆FePc Complexes

The octahedral metal complexes synthesized during this study were based on two distinct primary amine systems, 4-chlorobenzylamine and 4-(2-aminoethyl)phenol (tyramine). These were readily available in our laboratory and had an acceptable reagent purity, making them suitable for chemical synthesis (**Figure 44**). All complexes were able to be synthesized in less than 1 hour, and when left stirring in solution for 24 hours, no change in spectra were observed, demonstrating these compounds are stable and can be further isolated (**Figure 45**).







Figure 45: (4-chlorobenzylamine)₂FePc NMR spectrum displaying shielded protons c and d.

Since the alkyl chain on the amino group on tyramine has an extra -CH₂ (signal c, **Figure 46**), we can observe it suffers from the shielding effect of the anisotropic cone of the FePc macrocycle, but not to the same extent as protons *d* and *e* who are in closer proximity to the cone. Protons on the benzene ring of tyramine get shielded to the least extent, due to them being furthest from the aromatic π system of FePc. The tyramine-FePc systems was also shown to be stable after 24 hours stirring in solution. Deuterated solvents offered the advantage of serving as a medium for the reaction, but also to characterize the molecules in the solvent they were synthesized in. To this end, CDCl₃ proved to be the best solvent because it is cheap, readily available, and of high purity, making it suitable for chemical synthesis. Regular chloroform was also proven to be successful, although it lacked the NMR advantage.

Regular and deuterated THF were found to be suitable, but THF-d⁸ is very expensive, while regular THF is a Lewis basic solvent that could later compete with the coordinated amine through ligand exchange reactions.



Figure 46: (tyramine)₂FePc NMR spectrum displaying shielded protons d and e.

A summary of the octahedral complexes synthesized during this study is presented on **Figure 47**. All complexes were successfully synthesized, characterized, and further isolated in their solid state. The complexes possessed a high purity and a stoichiometric ratio of 2:1 amine to complex, demonstrating the coordination of the primary amine derivative to the Fe(II) metal center. The low spin complexes reveal how the strong magnetic anisotropic effects alter the chemical shifts of protons in the vicinity of the conjugated pi aromatic system of the FePc macrocycle. Out of the three complexes synthesized, (tyramine)₂FePc octahedral complexes showed the greatest shift due to magnetic anisotropy of the shielding cones, with ppms shifting upfield to values up to -7.5 ppm. This is an even more drastic effect than the one observed for the already reported benzylamine complex with shifts up to -7.5 ppm. The new octahedral derivatives synthesized herein possess exceptional solubility in organic solvents because of decreased aggregation of molecules in the solid state, increasing their applicability in many fields.



Figure 47: Stacked spectra of amine coordinated octahedral FePc complexes.

c. Synthesis and NMR Characterization of Octahedral Fluorianted and Cobalt Complexes

To further explore the chemistry of octahedral metal phthalocyanine complexes, two experiments were performed with the hexadecafluorinated iron complex and unsubstituted cobalt complex synthesized in the prior study. We wanted to conceptually prove two major aspects with the latter experiments: (1) primary amines can be coordinated to substituted FePc systems like $F_{16}FePc$, and (2) primary amines can coordinate to other metal centers in the core of unsubstituted MPc complexes. Both experiments proved to be successful, however, not to the same extent. On **Figure 48** we can clearly observe the benzylamine protons in a shielded environment due to the anisotropic cone of the $F_{16}FePc$ system. The signal-to-noise ratio was lower relative to the unsubstituted MPc complexes, which could be due to a lower amount of product formed during the reactions. On the other hand, unsubstituted CoPc was able to coordinate readily with benzylamine, showing an excellent signal-to-noise ratio and successful synthesis of the complex. The greatest remark about the spectrum is the chemical shift of the benzylamine protons at -1.8 ppm and -3.6, when compared to the benzylamine proton shift of the Fe complex which was -1.9 and -7.0.



Figure 48: (a) NMR of (benzylamine)₂F₁₆FePc (b) NMR of (benzylamine)₂CoPc.

Section III: Multifluorinated Precursors for Next-Generation MPc Systems

Section 3 of this thesis describes the organometallic synthesis of SF₅-substituted precursors for next-generation MPc complexes. The structural characterization of the precursor compound was studied through X-ray crystallography/spectroscopic methods and published in 2019 on the crystallographic journal Acta Crystallographica.

a. Structural Commentary of 2-iodo-(pentafluorosulfanyl)benzonitrile Precursor

Figure 49 shows the molecular structure of the title compound, which crystallizes in the space group P_{nma} Its asymmetric unit consists of a single molecule lying on a mirror plane perpendicular to [010] containing the iodo, cyano, and the sulfur and axial fluorine of the pentafluorosulfanyl substituent in the plane of the molecule. Fluorine atoms from the pentafluorosulfanyl group at equatorial positions lie above and below the plane in a staggered fashion relative to the two hydrogens ortho to the substituent; of those, two of the four florine atoms are symmetrically generated by the mirror plane. The S1-F_(eq) bond distances differ from each other depending on the side of the molecule the bond is located at (**Table 9**). Bond S1-F2_(eq) and its symmetry analogue F2ⁱ_(eq) (symmetry code: (i) x, -y+3/2, z) are on the same side of the iodine and exhibit a longer bond distance of 1.573(2) Å in comparison to S1-F1_(eq) and its symmetry analogue F1ⁱ_(eq) (symmetry code: (i) x,-y+3/2, z) which are further away from the iodine and have a shorter bond length distance of 1.561(4) Å. The S1-F3_(ax) bond length of 1.582(5) Å is consistent with that of similar structures (1.588(2) Å and 1.573(3) Å from Du *et al.*, 2016).

$S1-F1_{(eq)}$ and $S1F1_{(eq)}^{i}$	1.561 (4)
$S1-F2_{(eq)}$ and $S1-F2_{(eq)}^{i}$ $S1-F3_{(ax)}$	1.572 (3) 1.582 (5)
$\begin{array}{c} C4 - S1 - F2_{(eq)} \\ C4 - S1 - F1_{(eq)} \end{array}$	92.0 (2) 92.2 (2)

Symmetry code: (i) x, $-y + \frac{3}{2}$, z.

Table 9: Selected bond lengths and angles for 2-iodo-4-(pentafluorosulfanyl)benzonitrile.



Figure 49: Molecular structure of 2-iodo-4-(pentafluorosulfanyl)benzonitrile, including atom labelling. Displacement ellipsoids are drawn at the 50% probability level. Atoms generated by the mirror plane [symmetry code: (i) x, -y + 32, z] are depicted in dark green.

b. Supramolecular Features of DMP Precursor

The packing of the compound is consolidated through a series of intermolecular interactions which can be classified as in-plane and out-of-plane (**Table 10**). Each molecule acts as a C-H donor through the hydrogen atoms in the ortho and meta positions of each phenyl ring counter to the iodine atom. Propagating along the plane perpendicular to [010], there are two C-H···F hydrogen bonds between adjacent molecules creating an in-plane network, one from C5-H5···F3 and the other between C6-H6···F3 with a contact distance of 2.573 Å and 2.558 Å, respectively (**Figure 50**). Both H5 and H6 atoms are highly acidic due to the electron withdrawing effects of the -SF5 and -CN substituents. Additionally, significant in-plane intermolecular interactions attributed to halogen bonding between N1···I1 from neighboring molecules is observed, with a contact length of 3.408 Å.¹¹⁰ Out-of-plane intermolecular interactions arise primarily from F····π ring interactions at one of the corners of the ring **Figure 51**). The F···π intermolecular contact occur between F2···C3 with a distance of 3.123 Å along [010].



Figure 50: A view along the *b* axis of crystal packing of 2-iodo-4 (pentafluorosulfanyl) benzonitrile showing in-plane contacts.



Figure 51: Partial packing diagram for 2-iodo-4 (pentafluorosulfanyl) benzonitrile viewed along the *a* axis showing out-of-plane interactions.

$D - H \cdot \cdot \cdot A$	D-H	$H \cdot \cdot \cdot A$	$D \cdots A$	$D - H \cdot \cdot \cdot A$
$C5-H5\cdots F3^i$	0.93	2.57	3.501 (1)	174
$C6-H6\cdots F3^{ii}$	0.93	2.56	3.476 (1)	169

Symmetry codes: (i) $x - \frac{1}{2}, -y + \frac{3}{2}, -z + \frac{3}{2}$; (ii) $x - 1, -y + \frac{3}{2}, z$.

Table 10: Hydrogen-bond geometry (Å, °) of 2-iodo-4 (pentafluorosulfanyl)benzonitrile.

c. Hirshfeld Surface Analysis of DMP Precursor

The Hirshfeld surface¹¹¹ for the title compound mapped over d_{norm} is shown in **Figure 52** while **Figure 53** shows the associated two-dimensional fingerprint plots,²³ both generated with Crystal-Explorer17.¹¹² Red spots on the Hirshfeld surface mapped over d_{norm} in the color range -0.4869 to 1.4157 arbitrary units confirm the previously mentioned main intermolecular contacts. The fingerprint plots are given for all contacts and those delineated into F…H/H …F (29.4%; Fig. **53b**), F…I/I…F (15.8%; **Fig. 53c**), F…N/N…F (11.4%; **Fig. 53d**), H…N/N…H (6.3%; **Fig. 53e**), I…N/N…I (5.6%; **Fig. 53f**), C…F/F…C (4.5%; **Fig. 53g**), C…H/H…C (4.5%; **Fig. 53h**), I…H/H…I (3.3%; **Fig. 53i**), C…N/N…C (1.6%; **Fig. 53j**), C…C (9.5%; **Fig. 53k**), F…F (6.0%; **Fig. 53l**) and I…I (2.2%; **Fig. 53m**) interactions. Thus, the Hirshfeld surface analysis indicates that the most significant contributions arise from F…H and F…I contacts.



Figure 52: A view of the Hirshfeld surface of 2-iodo-4 (pentafluorosulfanyl) benzonitrile mapped over d_{norm} with the four main intermolecular contacts in the crystal lattice.



Figure 53: Full (a) and individual (b)–(m) two-dimensional fingerprint plots showing the 12 intermolecular contacts present in the crystal structure.

d. Crystallographic Database Survey of DMP Precursor

A search of the Cambridge Structural Database⁹⁶ revealed no matching compounds with the title compound substructure and the three substituents. However, a search for SF₅ aryl compounds fragment revealed about 85 hits: 77 of these structures were reported in the last 10 years, which shows the increasing interest in the SF₅ group. Most of these compounds are used as reagents in the synthesis and modification of pharmaceuticals, such as the antimalarial agent mefloquine and the anti-obesity drug fenfluramine.¹¹³⁻¹¹⁴

e. Crystal Structure Refinement of DMP Precursor

Data collection, crystal data and structure refinement parameters are summarized in **Appendix B**. H atoms were included in geometrically calculated positions and refined as riding atoms with C-H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$.

f. Synthesis and Crystallization of DMP Precursor

The direct selective functionalization of C-H bonds has been one of the major efforts in the synthetic community for the preparation of complex molecules.¹¹⁵ Ortho-metalation followed by quenching with an electrophile was discovered independently by Gilman and Wittig and has since proven to be one of the most important and versatile transformations in organic synthesis.¹¹⁶ Traditionally, electrophilic substitution of aromatic rings could lead to a mixture of products depending on the nature of the substituents in the ring. Since organometallic reagents function as powerful nucleophiles, interaction of the metal cation with a Lewis basic substituent in the ring allows for selective metal hydrogen exchange, yielding the ortho metalated arene. The high regioselectivity in these reactions arises from a complex-induced proximity effect generated by the coordination of the metal cation with a Lewis basic substituent on the ring, directing deprotonation at the ortho position.¹¹⁷ The cyano group functions as an ideal direct metalating group (DMG) because the electron pair on the nitrogen can coordinate the metal cation and the group is polar enough to stabilize the anionic character. Furthermore, its electron- withdrawing character increases the acidity of the protons in the ortho positions, enhancing their reactivity in the deprotonation process.

The reactivity of the newly formed carbon-metal bond will be highly dependent on the reduction potential of the metal, lithium and magnesium being the most reactive. The relatively high ionic character of the C-Li bond renders them strong nucleophiles that can react with polar multiple bonds, especially carbonyl groups, and provide synthetic routes to a variety of alcohols and ketones.¹¹⁸ Other electrophiles such as alkyl halides, CO₂, epoxides, organotin and organophosphate chlorides could readily react to give the corresponding products (**Scheme 15**).



Scheme 15: Organolithium reactions for the functionalization of new materials using 2-iodo-4-(pentafluorosulfanyl)benzonitrile.

Indeed, organolithium compounds have been proven to outperform other organometallic nucleophiles in many cases due to the large difference in electronegativity in C-Li bonds.¹¹⁹ The electronegativity of atoms, however, changes depending on the hybridization of the orbital being employed. A higher s character on an atom that employs an sp^x hybrid orbital for bonding, will make that bond more heavily polarized, as in our case. Both the target molecule and the lithiated intermediate possess large potential as reagents in the chemical synthesis of novel SF5-containing arenes. Recent milestones in the development of methods for the direct functionalization of C-H bonds further motivated the synthesis of 2-iodo-4-(pentafluorosulfanyl)benzonitrile.¹²⁰ Aryllithiums, specifically, are often employed as precursors for other organometallic compounds (B, Sn, Zn) that are also used extensively in cross- coupling processes (Scheme 16). They have also been found to have a prominent role as reagents in pharmaceutical asymmetric processes.¹²¹ Feringa et al. recently demonstrated that the high reactivity of newly synthesized aryllithiums is beneficial in cross-coupling reactions to obtain a fast coupling of highly hindered poly substituted arenes.¹²² More recently, they also demonstrated that the nucleophilic properties of aryllithiums can be used to perform 1,2-additions to amides yielding masked ketones, giving access to substituted benzophenones which are extensively used in cosmetics due to their UV protecting properties.¹²³ Finally, another synthetic endeavor of great interest tackled by Chen et al. included the functionalization of C-H bonds in the presence of free N-H bonds from secondary amines. Previous approaches were limited to protected or tertiary amines, however, earlier this year they were able to achieve the functionalization of cyclic N-H amines using aryllithium reagents.¹²⁴ The latter enabled a protecting-group free approach that required no transition metals and offered high regioselectivity, a major achievement in the synthesis of nitrogen containing compounds.



Scheme 16: Potential transmetallation pathways for the attachment of the SF₅-aryl moiety onto relevant organic scaffolds.

In addition to react with a wide variety of organic substrates, the lithiated intermedite serves as a precursor for the preparation of other organometallic reagents. Organoboron, organosilicon, organocopper, organozinc, organotin, organophosphorus, organocerium, and organosulfur compounds are frequently prepared by reacting organolithium reagents with appropriate electrophiles.¹²⁵ Potentially, transmetalation of the title compound will favor new metal–carbon bonds under mild conditions and serves to alter the reactivity of the organometallic intermediate. A wide variety of organometallic derivatives can be prepared using metal exchange in which a given metal is either moved to a new location of replaced by a new metal.

The exchange process of the lithium cation to form the new C-MgBr bond, for example, undergoes an equilibrium that favors the metal halide in which the metal has the greater negative reduction potential (LiBr in our case).¹²⁶ Treatment of the organomagnesium derivative with zinc salts in dioxane generates a dioxane complex of the magnesium halide that precipitates and leaves the arylzinc derivative of the title compound in solution (**Scheme 17**).



Scheme 17: Transmetallation with Mg and Zn of ortho-lithiated 4-pentafluorothiobenzonitrile.

Although they are much less reactive than their organomagnesium counterparts, these compounds have been particularly adaptable to enantioselective additions.¹²⁷ An attractive feature of organozinc reagents is that many functional groups that would interfere with organolithium and organomagnesium reagents can be present in organozinc chemistry. Furthermore, the reactions are frequently catalyzed with Lewis acids and chiral ligands to increase the selectivity and application of these reagents.¹²⁸ The coupling of Grignard reagent in **Scheme 5** with alkyl, vinyl, or aryl halides under nickel or palladium catalysis provides a direct route for introducing our aromatic SF₅-containing moiety into countless systems under milder conditions.

A major advantage in the Kumada Coupling is that it avoids additional reaction steps such as the conversion of the Grignard reagent to organozinc compounds for use as starting materials in the Negishi Coupling. Future advancements in the field of catalysis even enabled these reactions to be carried out at milder conditions. Chen et al. performed the Kumada cross-coupling reaction on a variety of inactivated aryl chlorides, vinyl chlorides, and heteroaryl chlorides, catalyzed by nickel (II) complexes containing pyridine-functionalized NHC ligands and found that the catalysts were so active that the reactions proceed at room temperature in excellent yields.¹²⁹ This reaction has been proven to be an excellent method of choice for the low-cost synthesis of unsymmetrical biaryls under mild reaction conditions. Halogenation of organolithium reagents is a powerful tool for the formation of C-X bonds in a highly regioselective manner. It is particularly important in the halogenation of an electron-deficient aromatic molecules like the lithiated intermediate, which will not readily undergo electrophilic aromatic substitution. Moreover, functionally substituted aryllithiums are only stable at low temperatures, and thus require trapping with a reactive electrophile. In contrast to the aromatic C-H bond in the SM, the aromatic C-I bond of the 4-(pentafluorothio)-2-iodobenzonitrile renders it a powerful reagent that can be used in a variety of reactions that mainly involve the activation of the iodo group with transition metals for coupling reactions.¹³⁰ When comparing it to the C-H bond in the starting compound, the longer and more polarized C-I bond readily undergoes oxidative addition with palladium (0) to form the first organopalladium intermediate. This species subsequently reacts with a base, giving another intermediate, which via transmetallation with the coupling partner forms an organopalladium species that undergoes reductive elimination, yielding the product and regenerating the catalyst. The oxidative addition step breaks the carbon-halogen bond and is the rate determining step of the catalytic cycle in most cases.¹³¹

Since the bond dissociation energy increases as the difference in the electronegativity of the bonded atoms increases, C-I bonds in aryl iodides are more easily broken than any other aryl halogen bond. Moreover, first step is key in the synthesis of chiral targets because oxidative addition initially forms the cis-palladium complex, which rapidly isomerizes to the trans complex. This process in aryl halides proceeds with inversion of stereochemistry, in comparison to vinyl halides which proceeds with retention of stereochemistry.¹³² The advantages of palladium couplings (**Table 12**) over alternative reactions include mild reaction conditions, a wide range of organometallic coupling partners, and most reactions are scalable and cost-effective for use in the synthesis of intermediates for pharmaceuticals.

F ₅ S	L + X	Pall Ca	adium talyst	Product
Coupling Reaction	X	Catalyst	Conditions	Product
Suzuki (Organoboron)	(HO) ₂ B — Ph	Pd(dba) ₃	KOH/ THF	P55 CN
Stille (Organotin)	Bu ₃ Sn	PdCl ₂ (MeCN) ₂	DMF/ -78°C	F55 CN
Sonogashira (Terminal alkynes)	HR	(PPh ₃) ₂ PdCl ₂	DMSO/ Cul/ ET ₃ N	F ₂ 5
Castro- Stephens (Organocopper)	Cu ————————————————————————————————————	-	Pyridine/ Reflux	Fys CN
Negishi (Organozinc)	RZnX	(PPh ₃) ₂ PdCl ₂ or Ni(PPh ₃) ₄	Pyridine/ Reflux	E ₅ S CN
Hiyama (Organosilicon)	(MeO) ₃ Si	Pd(OAc) ₂	THF/ Reflux	F ₅ S
Heck (Terminal olefins)	CO ₂ Et	Pd(PPh ₃) ₄	DMF/ ET ₃ N	F ₁ S
Carbonylation	CO, Nuc.	Pd(OAc) ₂	DMF/ K ₂ CO ₃	P ₄ 5 ON

Table 11: Potential Pd-catalyzed reactions of 2-iodo-(pentafluorosulfanyl) benzonitrile.

Section 3 of this thesis was published in 2020 on the crystallographic journal Acta Crystallographica:

Gonzalez Espiet, J. C.; Cintron Cruz, J. A.; Piñero, D. M. Structural characterization and Hirshfeld surface analysis of 2-iodo-4-(penta-fluoro-λ6-sulfan-yl)benzo-nitrile. *Acta Cryst.* **2020**, *E76*, 231-234. DOI: 10.1107/S2056989020000365

Section IV: Difunctionalized Precursors for Next-Generation MPc Systems

Section 4 of this thesis describes the fundamental study performed with regards to the synthesis and characterization of alkoxy substituted precursors and MPc complexes, which were later transformed into their hydroxide counterparts. The structural characterization of the precursor compound was studied through X-ray crystallography/spectroscopic methods and published is currently being submitted for publication on the crystallographic journal Acta Crystallographica. Other unreported complexes in this chapter have yet to be published.

a. Structural Commentary of DMP Precursor

Figure 54 shows the molecular structure of the title compound, which crystallizes in the monoclinic space group P21/c with one molecule per asymmetric unit. Its chemical structure consists of a tetrasubstituted benzene ring with two cyano and two methoxy units in a 1,2,4,5 arrangement. The cyano moieties are ortho with respect to each other and nearly lineal, possessing bond angles of 178.82° and 179.21° for C2-C8-N2 and C1-C7-N1, respectively. The methoxy groups are also ortho with respect to each other and display characteristic bent geometries of sp³-hybridized oxygens; with lower bond angles of 116.97° and 117.88° for C4-O1-C9 and C5-O2-C10, respectively. The methyl groups on the oxygen atoms are oriented in opposite directions with respect to one another, minimizing the interplanar repulsions between the latter two groups. All the substituents completely lie on the plane of the aromatic ring.



Figure 54: ORTEP molecular structure of 4,5-dimethoxy-1,2-dicyanobenzene, including atom labelling. *Displacement ellipsoids are drawn at the 50% probability level.

b. Supramolecular Features of DMP Precursor

The title compound exhibits multiple intermolecular interactions, namely four N-H and two O-H contacts (**Figure 55**, **Table 13**) that propagate thought the *ac* plane to generate an extended network of rings. The two O-H interactions that lie on the plane of the ring are exclusively performed through one methoxy substituent, namely O1-H9b, while the other methoxy group exhibits no short contact interactions. This interaction has a length of 2.482 Å and propagates in the *c* direction specifically.

This contrasts with the four N-H interactions that take place on both cyano moieties, namely between N1-H3 and N2-H6. The latter interactions propagate on the *b* direction and are longer, with distances of 2.619 Å and 2.643 Å for N1-H3 and N2-H6, respectively. Short contacts from neighboring molecules. The aromatic entities extend in zig-zag fashion through the *ac* plane forming a network with all rings coplanar to each other. The interaction between the molecules generates hexagonal clusters that are linked to the next through two molecules.



Figure 55: Crystal packing of the title compound 4,5-dimethoxy-1,2-dicyanobenzene along the *c* axis with short-contact interactions shown as dashed lines.

Table 12: N-H and O-H short contacts in 4,5-dimethoxy-1,2-dicyanobenzene.

Short contact	Distance (Å)
O1 H9	2.482
N1 H3	2.619
N2 H6	2.643

CrystalExplorer17¹¹² was used to generate the Hirshfeld surface¹¹¹ for the title compound mapped over d_{norm} and the associated two- dimensional fingerprint plots (**Figure 57**). **Figure 56** shows the molecules involved in the four closest contacts. Red spots on the Hirshfeld surface mapped over d_{norm} in the color range d_{norm} 0.1517 to 1.2369 arbitrary units confirm the previously mentioned main intermolecular contacts. The fingerprint plots are given for all contacts (**Figure 57a**) and those decomposed into nine individual interactions: H…N/N…H (39.2%; **Figure 57b**), H…H (18.4%; **Figure 57c**), H…C/C…H (13.9%; **Figure 57d**), H…O/O…H (12.8%; **Figure 57e**), C…C (6.5%; **Figure 57f**), C…N/N…C (5.9%; **Figure 57g**), C…O/O…C (2.8%; **Figure 57h**), O…O (0.4%; **Figure 57i**) and N…N (0.1%; **Figure 57j**). The Hirshfeld surface analysis for the title compound indicates that the most significant contributions arise from H-N/N-H and H-H contacts.¹³³⁻¹³⁴



Figure 56: Hirshfeld surface of 4,5-dimethoxy-1,2-dicyanobenzene mapped over d_{norm} with the four main intermolecular contacts in the crystal lattice shown.



Figure 57: Full (a) and individual (b)–(j) two-dimensional fingerprint plots showing the nine intermolecular contacts present in the crystal structure.

d. Database Survey of DMP Precursor

A search of the Cambridge Structural Database⁹⁶ revealed no matching compounds with the title compound substructure. However, a search for disubstituted (OR)₂-phthalonitrile compounds (R = any atom or substituent) revealed a total of 51 hits, 46 in which the R group was an sp²-hybridized aromatic carbon; the other 5 compounds contained crown ether substituents. There are no aliphatic carbons chains nor hydrogens directly bonded to the oxygens, to our knowledge; our compound would be the first to contain such aliphatic motif through the methyl (-CH₃) moiety.

e. Refinement of DMP Precursor

Data collection, crystal data and structure refinement parameters are summarized in **Appendix B**. H atoms were included in geometrically calculated positions and refined as riding atoms with C-H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$.

f. Synthesis and Spectroscopic Characterization of DMP Precursor

The synthesis was monitored through NMR methods using a Bruker 500 MHz spectrometer. The starting material (DBVT) had two singlets that were shifted downfield when Br atom underwent replaced by CN moieties (**Figure 58**). This is expected because of the strong electron-withdrawing nature of the CN groups on the arene carbons. The purification of the compound involved filtration to remove the catalyst, washing of the organic layer to remove DMF, and column chromatography. Fractions eluting from the column had to be meticulously analyzed through TLC because both compounds were transparent, ultimately yielding high-purity reagent grade product which was later crystallized and analyzed through spectroscopic and crystallographic methods (**Figures 59-63**).



Figure 58: Progress of 3,4-dimethoxyphthalonitrile synthesis monitored through ¹HNMR spectroscopy.



Figure 59: ¹H-NMR spectrum of 1,2-dicyano-4,5-dimethoxybenzene CDCl₃ (0-12 ppm).



Figure 60: ¹³C-NMR spectrum of 1,2-dicyano-4,5-dimethoxybenzene in CDCl₃ (0-200 ppm).



Figure 61: FTIR spectrum of 1,2-dicyano-4,5-dimethoxybenzene (650-3500 cm⁻¹).



Figure 62: FTIR spectrum of 1,2-dicyano-4,5-dimethoxybenzene (650-1700 cm⁻¹).

Bond	Mode	Frequency (cm ⁻¹)
С-Н	stretch (aromatic)	3126, 3096, 3069
С-Н	stretch (aliphatic)	2974, 2941
CEN	stretch (nitrile)	2227
C=C	stretch (aromatic)	1591, 1562, 1520
C-H	bend (methyl)	1446
C-O	stretch (aromatic)	1395, 1358
C-O	stretch (aliphatic)	1293, 1235, 1090
C=C	bend (aromatic)	1017, 972, 880, 829

Table 13: Summary of selected vibration frequencies observed in Figures 61 and 62.



Figure 63: UV-Vis spectrum of 1,2-dicyano-4,5-dimethoxybenzene in CH₂Cl₂ (250-850 nm).
g. Synthesis and Characterization of (OCH₃)₈MPc Complexes

The assembly of OH functional groups to the MPc platforms begins by the preparation of the phthalonitrile precursor. The high-purity product synthesized prior was reacted with metal acetate salt through a similar approach as that described in the F_{16} MPc. Inspired by the successful results of this approach for other substituted MPc systems, we developed a series of 6 (OCH₃)₈MPc complexes, namely M = Mn, Fe, Co, Ni, Cu, Zn. The compounds were purified by washing with solvents to remove excess reagents and by products, namely, any unreacted phthalonitrile precursor or metal acetate salt. The as obtained powders were dried in vacuo and characterized by spectroscopic methods. All the samples had very limited solubility, if any, in multiple polar protic and aprotic organic solvents. Their solubility is similar to that of unsubstituted MPc complexes (H₁₆MPc), were DMSO, DMF and THF partially dissolved all complexes from 4th period metals. **Figure 64** displays the Q-band in the absorption spectra of the iron complexes F₁₆FePc and (OCH₃)₈FePc in THF.



Figure 64: UV-Vis spectra of iron Pc complexes containing F₁₆ and (OCH₃)₈ substituents.

The absorption spectrum of the newly synthesized complex containing eight methoxy (OCH₃) groups displays a band at 710 nm that is redshifted in comparison to the 610 nm band of $F_{16}FePc$ by 85 nm. Since the metal was the same, we can see the net effect of the electron-donating nature of the methoxy groups, in comparison to the electron-withdrawing nature of the fluorine groups. The Q band for the other (OCH₃)₈MPc complexes was 671, 672, 687, 710 nm for Mn, Zn, Cu, and Ni, respectively (**Appendix B**). For all complexes, the Q band was barely visible, even though the measurements were performed at high concentrations. As seen on Figure 64 the Q band is about a tenth of the intensity of the $F_{16}FePc$ complex at the same concentration (~10⁻⁵ M). The S-band of the complexes at the higher energy side of the spectrum however had an intense absorption that was blueshifted 35 nm with respect to the starting material phthalonitrile precursors (**Figure 65**). The complexes also displayed shoulders at around 290 and 340 nm for Co and Fe, respectively. All other complexes of the (OCH₃)₈MPc family were successfully characterized using UV-Vis.



Figure 65: UV-Vis spectra of (OCH₃)₈MPc complexes comparing arene π - π transitions in the S band of Fe and Co with phthalonitrile precursor starting material.

Vibrational spectroscopy was also performed on the as obtained powders using a Nicolet transmission IR microscope. The dark, intense color of the powder samples made it challenging to perform the measurements, since little to no transmittance could be obtained. Reflectance measurements were also performed with no success. Milling the powders and dispersing a small amount of the dust-like material onto the KBr plate proved to be successful and gave spectra with highly resolved peaks for all complexes. More specifically, in the lower frequency 500-1800 cm⁻¹ region the complexes displayed characteristic C=C and C=N, ring deformation, and metal-N stretching frequencies. In **Figures 66 and 67** we can observe metal-N diagnostic bands for the Fe-N and Co-N frequencies, respectively. Most of the bands in the displayed region are higher in frequency for the Co complex than for the Fe complex. The morphology of the bands as well as the number of bands is identical for the Fe and Co complexes. This same trend was also observed for the IR spectra of the other (OCH₃)₈MPc (M = Mn, Ni, Cu and Zn).

The identity of all complexes was unambiguously characterized by IR since the starting phthalonitrile (4,5-dimethoxyphthalonitrile) has no absorption frequencies below 800 cm⁻¹. All complexes displayed 2-3 well defined frequencies below 800 cm⁻¹ that enabled the characterization of the metal-nitrogen linkage, complementing the results obtained in UV-Vis spectroscopy. The frequencies between 1000-2000 cm⁻¹ also showed drastic changes in the number of signals, as well as the location and morphology of the signals when compared to the phthalonitrile starting materials. Other complementary methods to confirm the metal-nitrogen linkage in our systems support the validity of the obtained results through absorption and vibrational spectroscopies.



Figure 66: IR spectrum of (OCH₃)₈FePc highlighting 500-1800 cm⁻¹ region.



Figure 67: IR spectrum of (OCH₃)₈CoPc highlighting 500-1800 cm⁻¹ region.

The elemental composition of each sample was assessed through Electron Diffraction X-ray (EDX) spectroscopy, which reveals the presence of the metal, in addition to characteristic C, N and O atoms. The technique was coupled to SEM in order to observe the surface morphology of the as-obtained powder samples. **Figures 68 and 69** show the EDS and SEM of (OCH₃)₈FePc and (OCH₃)₈CoPc, respectively. All powders had a homogeneous appearence with plates and blocks of 1-10 µm sizes. Appendix B contains the ata for all other complexes in the (OCH₃)₈MPc family.



Figure 68: EDX spectrum and SEM image of (OCH₃)₈FePc complex.



Figure 69: EDX spectrum and SEM image of (OCH₃)₈CoPc complex.

The results of this study demonstrate that (OCH₃)₈MPc complexes can be reduced with BBr₃ to generate (OH)₈MPc complexes suitable for applications like building reticular networks. The highly reactive nature of BBr₃ in solution limited the applicability of this approach because the reagent would react readily with the most minimal amount of any atmospheric water to form boric acid and hydrobromic acid. Nonetheless, sub-stoichiometric amounts of BBr₃ were able to be used in place of one full equivalent, enabling the use of BBr₃ in total synthesis (OH)₈MPc complexes. The transient (BBr₂)₈MPc species was hydrolyzed with water and purified by washing with solvents to remove excess reagent and by products, followed by drying in vacuo (**Scheme 18**). Inspired by the successful results obtained for the F₁₆MPc complexes, we decided to focus on Fe and Co metals. These were also unreported complexes that have yet to be published in the literature, in contrast to the (OH)₈MPc complexes of Ni and Cu which have been previously prepared using a different synthetic approach.



Scheme 18: Reduction pathway of novel (OH)8MPc complexes with BBr3.

The OH substituents gave the (OH)₈MPc complexes a high degree of solubility in multiple organic solvents, increasing their applicability where solubility is of interest. Thus, the reaction products were readily characterized through NMR spectroscopy in CDCl₃. They displayed two singlets: δ = 8.8, 10.3 ppm for the Co complex, and δ = 7.9, 9.9 ppm for the Fe complex (**Figure 70-71**). The signals for the Co complexes were better resolved and the spectrum overall displayed a higher purity and were further downfield suggesting the metal has an influence on the chemical shift of both protons.



Figure 70: ¹HNMR spectrum of (OH)₈FePc highlighting the 7.5-10.5 ppm region.



Figure 71: ¹HNMR spectrum of (OH)₈CoPc highlighting the 7.5-10.5 ppm region.

Section V: Crystallography and Gas Sensing of Annealed MPc Nanofilms

The fifth Section of this doctoral thesis provides a detailed analysis of the crystalline structure and morphology of F_{16} MPc nanowires deposited on substrates and annealed at different temperatures. The results presented herein are the foundation for a patent regarding the improvement of the gas sensing platforms developed in Chapter 1.

a. X-ray Crystallography of Hexadecafluorinated Metal Phthalocyanine Annealed Nanofilms

The F_{16} MPc nanowire films were prepared using the PVD technique described before on quartz glass and aluminum substrates. The F_{16} MPc nanowire films were heated in a high vacuum chamber by using a dual chamber oven at the annealing temperatures for 30 minutes. The as obtained nanowire films deposited on quartz were then analyzed through PXRD, giving the diffractograms shown in **Figures 72-75**. All diffractograms are clearly resolved in suitable for crystallographic calculations, a limitation that had to be addressed in comparison to our prior crystallographic studies based on this same material, particularly for F_{16} FePc which proved to be significantly less filmogenic substance than F_{16} CoPc, which forms nanowire films more readily.



Figure 72: PXRD patterns of F_{16} FePc nanowire thin films deposited on quartz substrates, annealed at 100, 200 and 300 °C, respectively.



Figure 73: Selected region (from 10-50 2θ) PXRD patterns of F₁₆FePc nanowire thin films deposited on quartz substrates, annealed at 100, 200 and 300 °C, respectively.



Figure 74: PXRD patterns of F₁₆CoPc nanowire thin films deposited on quartz substrates, annealed at 100, 200 and 300 °C, respectively.



Figure 75: Selected region (from 10-50 2 θ) PXRD patterns of F₁₆CoPc nanowire thin films deposited on quartz substrates, annealed at 100, 200 and 300 °C, respectively.

As seen from **Figures 72-75**, the powder pattern of both the iron and cobalt complex presents 5 diffractions which change negligibly between the annealing temperatures. For both complex the lowest angle signal at around $2\Theta \sim 6^{\circ}$ corresponds to the annealing temperature of 100 °C. Temperatures above 300 °C sublimed the nanowire films completely from the substrate. A broad signal was observed that corresponded to a combination of signals that were broadened most likely do to microstrain and nanocrystalline grains in the nanowire films. These results showcase the robustness and stability of the nanowire films at different temperatures since the crystallinity of the materials is consistent and suffers little-to-no transformations. In many MPc systems, this increase in temperature leads to an alteration in the crystalline structure, and ultimately, could compromise the performance of the materials at higher temperatures.

Peak broadening is due to the instrument and the sample, after subtracting the instrument's contribution, the broadening is mostly due to the sample:

 β (total)= β (instrument)+ β (sample)

(**Equation 3**): $\beta(\text{total}) \sim \beta(\text{sample})$

The broadening in the sample is due to crystallite size and microstrain:

 β (sample)= β (crystallite size)+ β (lattice strain)

While broadening due to crystallite size is given by the Scherrer equation (**Equation 4**), broadening due to lattice strain is given by **Equation 5**:

(Equation 4): $D=k\beta\cos\theta$; which rearranges to $\beta(\text{cryst. size})=kD\cos\theta$

(Equation 5): $\mathcal{E}=\beta 4\tan\theta$; which rearranges to $\beta(\text{lattice strain})=4\mathcal{E}\tan\theta$

Combining equations 4 and 5 into the sample broadening gives:

(**Equation 6**): $\beta(\text{sample}) = kD\cos\theta + 4\xi\tan\theta$

Since $\tan\theta = (\sin\theta)/(\cos\theta)$, the equation then becomes:

(Equation 7): $\beta(\text{sample})^*\cos\theta = kD + 4\varepsilon\sin\theta$

Rearranging the above the equation to solve as a function of theta:

(Equation 8): $\beta(\text{sample})^*\cos\theta = \mathcal{E}(4\sin\theta) + kD$

where \mathcal{E} is the lattice strain, β (total) is the particle size broadening, D is the crystallite size, K is a dimensionless shape factor (0.94), λ is the X-ray wavelength for Cu K α radiation (1.5406 Å) and θ is Bragg angle in degree.

The resulting equation has the behavior of a straight line: y = mx + b. Hence, by plotting the graph of $\beta(\text{total})^*\cos\theta$ against $4\sin\theta$, we get a linear regression were the lattice strain ε is equal to the slope of the graph (m) and the crystallite size (D) is obtained from the y-intercept (b) using this expression: c = kD. Individual peaks were fitted non-linearly using the Gaussian method. The full width half maxima (FWHM) and 2θ were obtained from the fit, and the associated errors were registered. The Williamson-Hall (WH) plot was used to estimate the crystallite size and lattice strain of the samples using Equation 6. The macroscopic properties of material are largely affected by the microstructure. The microstructure contains various aspects that influence specific properties in a synergistic manner. These aspects include grain morphology and size, crystallographic texture, internal residual stresses, and defects, which are largely dislocations in nature. Dislocation densities in metals and their alloys can be measured through the direct method of Transmission Electron Microscopy (TEM) or indirect methods such as X-ray diffraction (XRD) and neutron diffraction techniques. While the method of TEM can be used for dislocation analysis, it only reveals information about microscopic areas of samples, which raises questions on how representative these areas are of the entire sample volume. Under such situations, XRD is a very appropriate technique to investigate the microstructure as it gives information from a macroscopic area in a statistically averaged manner. An ideal diffraction pattern consists of narrow, symmetrical, delta function peaks positioned according to a particular hkl plane of a unit cell. The aberrations from the ideal pattern are perceived as peak broadening.



Figure 76: Diffraction peak fittings of F_{16} FePc used to calculate the crystallite size and lattice strain of annealed nanowire thin films at different temperatures.



Figure 77: Williamson-Hall plots of F_{16} FePc used to calculate the crystallite size and lattice strain of annealed nanowire thin films at different temperatures.



Figure 78: Diffraction peak fittings of F_{16} CoPc used to calculate the crystallite size and lattice strain of annealed nanowire thin films at different temperatures.



Figure 79: Williamson-Hall plots of F_{16} CoPc used to calculate the crystallite size and lattice strain of annealed nanowire thin films at different temperatures.

The crystallite size is an important parameter as the sizes of the crystals determine whether the material is soft (small crystallites) or brittle (large crystallites) and affects their macroscopic behavior. As the crystallite size gets smaller, the peak gets broader. Factors that affect K (Scherrer constant) and crystallite size:

- (1) how the peak width is defined (FWHM vs. integral breadth)
- (2) how crystallite size is defined
- (3) the shape of the crystal,
- (4) the size distribution.

The crystallite size is usually taken as the cube root of the volume of a crystallite, which assumes that all crystallites have the same size and shape. For a distribution of sizes, the mean size can be defined as (i) the mean value of the cube roots of the individual crystallite volumes, and (ii) the cube root of the mean value of the volumes of the individual crystallites.

Annealing T (°C)	Crystallite size from XRD for F ₁₆ FePc (nm)	Crystallite size from XRD for F ₁₆ CoPc (nm)
25	241.9	241.7
100	238.0	241.1
200	242.5	242.5
300	241.4	240.5

Table 14: Average crystallite size for the as deposited $F_{16}MPc$ (M = Fe, Co) nanowire thin films (deposited on quartz substrates at room temperature) and films annealed at different temperatures obtained from the WH plots.

Crystallite size is different from particle size, oftentimes a particle is made up of several different crystallites. Crystallite size often matches grain size. Though the shape of crystallites is usually irregular, we can approximate them as spheres, cubes, tetrahedra, or octahedra; parallelepipeds such as needles or plates; and prisms or cylinders. The broadening of a single diffraction peak is the product of the crystallite dimensions in the direction perpendicular to the planes that produced the diffraction peak. Very small nanocrystallites like the ones found in our nanowire films produce weak signals because the specimen broadening will be significantly larger than the instrumental broadening. In this case, the signal: noise ratio is more important than the instrumental profile.



Figure 80: Representation of crystallites and domains in a single nanowire structure.

Though the shape of crystallites is usually irregular, we can approximate them as spheres, cubes, tetrahedra, or octahedra; parallelepipeds such as needles or plates; and prisms or cylinders. The broadening of a single diffraction peak is the product of the crystallite dimensions in the direction perpendicular to the planes that produced the diffraction peak. Very small nanocrystallites produce weak signals because the specimen broadening will be significantly larger than the instrumental broadening. In this case, the signal: noise ratio is more important than the instrumental profile. Microstrains are very common in nanocrystalline materials. Microstrain broadening is the product of lattice strains from displacements of the unit cells about their normal positions often produced by dislocations, domain boundaries, surfaces etc. There are several contributions to microstrain broadening: (1) Non-uniform lattice distortions, (2) Dislocations, (3) Antiphase Domain Boundaries, and (4) Grain surface relaxation. This gives rise to non-uniform lattice distortions. Rather than a single d-spacing, the crystallographic plane has a distribution of dspaces. This produces a broader observed diffraction peak. Such distortions can be introduced by surface tension of nanocrystals, morphology of crystal shape (such as nanotubes or nanowires), and interstitial impurities.

Annealing T (°C)	Microstrain & for F ₁₆ FePc (lin ⁻² m ⁻²)*10 ⁻⁴	Microstrain & for F ₁₆ CoPc (lin ⁻² m ⁻²)*10 ⁻⁴
25	15.96	15.96
100	15.95	15.96
200	15.97	15.97
300	15.96	15.96

Table 15: Values of microstrain (E) calculated from XRD data for annealed nanowire films.

Crystallinity index (CI), defined as the volume fraction of the crystallinity of one phase in a given sample is quantitative. indicator of crystallinity. It represents the average crystallite size, perfection and ordering of a crystal.

Annealing T (°C)	Crystallinity index for F ₁₆ FePc (%)	Crystallinity index for F16CoPc (%)
25	81.02	84.56
100	85.49	85.60
200	84.25	87.00
300	84.96	86.56

Table 16: Values of crystallinity index calculated from XRD data for annealed nanowire films.

The quantification of dislocation density via the XRD method relies on this broadening of diffraction peaks that occurs when atoms in crystal unit cells are displaced from their ideal position due to small crystallite (size broadening) below one micrometer and an abundance of lattice defects (strain broadening) such as dislocations. The dislocation density (δ), defined as the length of dislocation lines per unit volume of the crystal, was evaluated from the formula $\delta = 1/D^2$.

Annealing T (°C)	Dislocation density for F_{16} FePc (x10 ⁻⁵ nm ⁻²)	Dislocation density for F ₁₆ CoPc (x10 ⁻⁵ nm ⁻²)
25	1.709	1.712
100	1.765	1.720
200	1.700	1.700
300	1.716	1.729

Table 17: Values of dislocation density (δ) calculated from XRD data for annealed nanowire films.

All nanowire films from both iron and cobalt complexes displayed nearly identical crystallographic properties, namely, crystallite size, microstrain, crystallinity index and dislocation density. The crystallite size is between 238 and 242 nm, which is in good agreement with the SEM and TEM images presented on the prior section. The microstrain values were around 15.95 lin⁻² $m^{-2} * 10^{-4}$, in comparison to the unsubstituted MPc complexes that contain lower strains around 8-12 lin⁻² $m^{-2} * 10^{-4}$. A notable feature was that for both complexes, the crystallinity index as well as the dislocation density increased for the films annealed at 100 °C specifically. When performing gas sensing measurements on the most filmogenic material, F₁₆CoPc, there was a considerable increase in the initial current, as well as sensing current. The increase was more than two-fold, suggesting that annealing at 100 °C enhances the sensing capacity of these nanowire films the most. The promising results obtained herein are being extended to the less filmogenic F₁₆FePc complex in order to improve the sensing limit of 40 ppb established prior by our research group, for ultralow detection of NH₃ and other toxic gases.



Figure 81: Gas sensing comparison between nanowire films of F₁₆CoPc 1 ppm NH₃ for 2.5 hours.

Chapter 4:

Conclusions

In Section 1 of Chapter 3 we designed, synthesized, and extensively characterized unsubstituted and hexadecafluorinated MPc complexes with transition metals of the fourth period. We demonstrated a facile and reproducible procedure to produce high-purity polycrystalline powder materials possessing exceptional semiconducting properties towards the sensing of pollutant gases. The optimal method to prepare MPc complexes is through a solid-state tetramerization (or template) reaction, where the metal centers act as a template for macrocycle formation. This further enables the use of substituted phthalonitrile systems that lead to substituted MPc complexes with enhanced and tailored properties. The purification of the complexes is best achieved through repetitive washing following an enhanced protocol that involves milling the powders to increase their surface area and suspending them in solvents, followed by centrifugation and filtration. The F₁₆MPc complexes were found to be exceptionally soluble in a variety of organic solvents, and these could further be purified through Soxhlet extraction procedures, yielding exceptionally pure microcrystalline powders. The fabrication of highly sensitive conductance sensors by the direct growth of MPc nanowires on interdigitated electrodes was performed by physical vapor deposition. This single-step procedure avoids the use of solvents for the deposition of the nanowires on the device, resulting in a better electrical contact between the nanowires and the electrodes. Moreover, preferential growth of the thinner nanowires at the gold electrodes is observed, thus increasing the percentage of nanowires in direct electrical contact between adjacent electrodes. The procedure was successful for substituted and unsubstituted metal phthalocyanine nanowires including different metals (Fe²⁺ and Co²⁺).

Sensors from substituted and unsubstituted MPc nanowires were fabricated and tested for ppb gas sensing. Among the materials tested, sensors prepared with F₁₆FePc nanowires showed high sensitivity, reproducibility, recovery, and stability. For applications where a "fast" response is required, the investigated F_{16} FePc nanowire devices offer a ~2% normalized signal change for a response time of ~ 12 min in the case of 100 ppb, ~ 20 min in the case of 40 ppb, and a few seconds in the case of 25 ppm. F₁₆FePc nanowire devices are thus ideal for applications related to the monitoring of "recovery zones" where the testing periods are longer and in the range of days and months. For such long-term applications, the response of these sensors can take advantage of the slow response that expands the detection limit below 20 ppb (the presented data show detection values above 20% for 100 ppb and 10% for 40 ppb for \sim 3 h detection periods). The fact that these sensors based on MPc nanowires operate at room temperature and consume minimal power makes them appropriate for very low energy consumption, free-standing, long-term operations. Scalability and production methods are not within the scope of this article and should be considered in future works. Overall, these results demonstrate the enormous gas sensing potential of synthetic multifluorinated phthalocyanine semiconducting materials towards environmental applications. It should be clearly emphasized that the sensing response of a material is not solely determined by the bond strength between the central metals of the molecules of thin film and the analyte. On the contrary, many other factors can contribute noticeably like the number of active sites in a layer, details of sorption-desorption processes and, particularly, thickness and morphology of the film. To our knowledge, this is the first report in the literature that has been able to reach ppb sensing capacities with chemiresistors built from multifluorinated iron and cobalt phthalocyanine systems.

Four new unreported octahedral MPc complexes were successfully synthesized through a Lewis adduct formation reaction to yield semiconducting platforms suitable for gas sensing and electronic applications (Section 2, Chapter 3). The magnetic anisotropic effect caused by the shielding cones of the macrocyclic portion in the MPc complexes was studied in detail using NMR spectroscopy. The novel complexes were able to be synthesized in less than one hour using a onepot approach and simple workup procedures. All could be isolated in the solid state and obtained as dry powders for further applications. The initially studied unsubstituted complex based on FePc was found to be completely insoluble in most organic solvents, however, upon coordination of the primary amine derivate, the as-produced octahedral complex weas exceptionally soluble in a multitude of organic solvents. Thus, coordination of an N-donor like an amine increases the solubility of square planar unsubstituted FePc complexes because of lower aggregation of solute molecules. The approach was extended to include other unreported primary amine derivatives that could coordinate the axial positions of the iron(II) core in the macrocycles. Both 4chlorobenzylamine and tyramine were able to be successfully coordinated, the latter showing the most drastic shift due to shielding, with a proton at -7.5 ppm. This study was also able to prove that: (1) primary amines can be coordinated to substituted FePc systems like F_{16} FePc, and (2) primary amines can coordinate to other metal centers in the core of unsubstituted MPc complexes. Lower amounts of product were obtained when using the $F_{16}FePc$ system to coordinate the amine. When Co was used as a core metal ion the macrocycle, the shielding effect of the anisotropic cone is considerably lower that the Fe complex, indicating the metal does in fact influence the magnetic effect of the shielding cone through its nature and electronic configuration. The NMR characterization of MPc metal complexes area where there is still much to be desired.

The title compound, C7H3F5INS, a pentafluorosulfanyl (SF5) containing arene, was synthesized from 4-(pentafluorosulfanyl)benzonitrile and lithium tetramethylpiperidide following a variation to the standard approach, which features simple and mild conditions that allow direct access to trisubstituted SF₅ intermediates that have not been demonstrated using previous methods (Section 3, Chapter 3). The molecule displays a planar geometry with the benzene ring in the same plane as its three substituents. It lies on a mirror plane perpendicular to [010] with the iodo, cyano, and the sulfur and axial fluorine atoms of the pentafluorosulfanyl substituent in the plane of the molecule. The equatorial F atoms have symmetry- related counterparts generated by the mirror plane. The pentafluorosulfanyl group exhibits a staggered fashion relative to the ring and the two hydrogen atoms ortho to the substituent. S—F bond lengths of the pentafluorosulfanyl group are unequal: the equatorial bond facing the iodo moiety has a longer distance [1.572 (3) Å] and wider angle compared to that facing the side of the molecules with two hydrogen atoms [1.561 (4) Å]. As expected, the axial S—F bond is the longest [1.582 (5) Å]. In the crystal, in-plane C—H…F and N…I interactions as well as out-of-plane F…C interactions are observed. According to the Hirshfeld analysis, the principal intermolecular contacts for the title compound are $F \cdots H$ (29.4%), F…I (15.8%), F…N (11.4%), F…F (6.0%), N…I (5.6%) and F…C (4.5%). The structural and electronic effects observed by incorporating the iodo group in the 4-(pentafluorothio)-2iodobenzonitrile evidence how this group, along with the cyano and pentafluoro substituents, possess the capability to alter the geometry and non-covalent interactions of materials of this type. Finally, the collection of reactions proposed will serve as the starting point in the pursuit of newlyfunctionalized materials based on the SF5 moiety and enhance the properties of existing and relevant materials.

The title compound, $C_{10}H_8N_2O_2$, is a tetrasubstituted arene molecule that contains two methoxy and two cyano moieties in a 1,2,4,5 arrangement. It was synthesized by a variation of the Pdcatalyzed cyanation reaction of 1,2-dibromoveratrole, which features a one-pot reaction using simple and mild conditions, allowing a direct access to alkoxy-substituted phthalonitrile entities (Section 4, Chapter 3). Single crystals of the title compound were obtained by slow evaporation of a concentrated solution in THF. It crystallizes in the monoclinic space group P_{21n} and contains a network of rings that propagates along the b axis through N-H and O-H short contact interactions. Hirshfeld surface analyses reveal N-H interactions contribute the most to the packing of the title compound, with a total contribution of 39.2%; while O-H interactions contribute 18.4%. Both interactions combined account for over half of the interactions that consolidate the overall crystalline structure of the title compound. MPc systems based on the as-obtained high-purity phthalonitrile precursor were obtained by reacting the latter with a metal acetate salt in the solid state at high temperatures. This approach was later extended to include a synthesis in solution using ethylene glycol; the advantage of this approach over the prior ones reported in the literature is that (1) a metal acetate salt is used, which offers better removal opportunities upon workup, and (2) no catalyst is used that could later compromise the purity of our product. All samples were characterized using UV-Vis, IR, EDX and SEM techniques to confirm the successful formation of the Pc macrocycle and the presence of the metal center. Transformation of the methoxy groups in (OCH₃)₈MPc compounds to their OH counterparts was successfully performed through reduction with sub-stoichiometric amounts of BBr3, opening a window of possibilities for next-generation materials like 2D and 3D frameworks based on the unreported complexes synthesized here, namely, (OH)8FePc and (OH)8CoPc.

Section 5 of Chapter 3 describes the crystallographic analysis and morphology of $F_{16}MPc$ (M = Fe, Co) thin films prepared though PVD, which are composed of highly crystalline and organized nanowires having a distribution of lengths that fluctuates around 100-300 nm. The interplanar distance changes negligibly, if anything, for annealed films which supports that the strong π - π interactions between the complexes is robust and resistant to higher temperatures. The relative peak intensity and position remained unchanged, while structural values changed slightly. After recording the PXRD diffractograms directly on the substrate material, smoothing, baseline correction, and peak fitting was employed to calculate each peaks area and FWHM value. By using the equations described, a WH plot was created for each annealed film, which allowed the calculation of crystallographic parameters. All nanowire films from both iron and cobalt complexes displayed nearly identical crystallographic properties, namely, crystallite size, microstrain, crystallinity index and dislocation density. A notable feature was that for both complexes, the crystallinity index as well as the dislocation density increased for the films annealed at 100 °C specifically. When performing gas sensing measurements on the most filmogenic material, F_{16} CoPc, there was a considerable increase in the initial current, as well as sensing current. The increase was more than two-fold, suggesting that annealing at 100°C enhances the sensing capacity of these nanowire films the most. The promising results obtained herein are being extended to the less filmogenic F_{16} FePc complex to improve the sensing limit of 40 ppb established prior by our research group, for ultralow detection of NH₃ and other toxic gases. Other gases like NO₂ are also being investigated. The reproducibility of the results will be confirmed to elucidate the most optimal conditions for annealing and film enhancement. The as-obtained results offer an in-depth crystallographic and morphological discussion of unreported F₁₆MPc nanowire film crystals, and their sub ppm sensing capabilities towards pollutant gases.

Chapter 5:

Future Work

The doctoral thesis opens multiple pathways to advance the synthesis, characterization, and gas sensing capabilities of MPc platforms. To this end, the materials produced in this work are the foundation for the next-generation semiconducting nanoplatforms based on MPc complexes. Electron-donating substituents on the macrocycles of MPc complexes like octamethoxy and octahydroxy, which were prepared in this work, have not been used to prepare nanoplatforms like nanowires, and their gas sensing capabilities remain unknown in the scientific community. The crystal structure of these compounds also remains undetermined. Future experiments through PVD methods could produce crystalline nanostructures of these MPc materials based on ED substituents on the periphery of the macrocycle. If future experiments prove to be unsuccessful, other deposition methods to produce nanostructures from these materials can be attempted. For the preparation of thin nanofilms, the solid samples can be suspended in water using sonication, and later drop-casted onto interdigitated gold electrodes like the ones used in this work. Samples like unexplored and newly synthesized (tyramine)₂FePc, (4-chlorobenzylamine)₂FePc, the (benzylamine)₂CoPc and (benzylamine)₂F₁₆FePc, which are soluble in volatile organic solvents, can also be drop casted or spin coated onto interdigitated gold electrodes. Studies developing chemiresistive gas sensors based on octahedral systems has yet to be reported and could further expand the approach presented in this work. The thickness and morphology of the films can be readily characterized by microscopic methods like AFM and SEM/TEM, respectively.

Electron-withdrawing substituents prepared in this work, namely hexadecafluorianted, proved to be the most sensitive of materials capable of detecting ppb concentrations of NH₃. Preliminary studies have suggested that the F_{16} platforms have not responded to CO gas, suggesting a certain selectivity for the gases published in this work, namely NH3 and NO2. Further tests are thus needed in the F_{16} platforms to specify which gases is this platform suitable for. MPc complexes substituted with other EW groups can also be achieved through the synthetic endeavors presented herein. Pentafulorosulfanyl precursors studied crystallographically in this work present a starting point for phthalonitriles that can be converted into the SF5MPc systems. Unfortunately, because of their availability, the fate of certain SF₅ compounds has been compromised, thus limiting their synthesis. Nonetheless, their gas sensing capabilities or the preparation of their nanostructure remains unknown. Future endeavors should be focused on finding other MPc platforms suitable for detecting CO and H₂S, which we did not get to explore during this work. When such nanomaterials have been discovered it is encouraging to think about a sensing device that could have multiple IDE connected simultaneously to the main board, to allow for sensitive detection of multiple gases. There is still much to be desired in the development and testing of MPc platforms, particularly the ones developed in this project. These encouraging results must be sustained by field tests with the as-prepared sensing devices. To date, there has been no reports of any concentration of NH₃ or NO₂ in the coastal communities in Puerto Rico, making our gas sensing platforms based on F₁₆FePc the most promising material for the detection of such gases in areas of interest such as the coastal zones in Puerto Rico and other parts of the world with compromised air quality.

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Appendix A:

Collaborations

I. Introduction

Dithiolene systems are a versatile family of compounds in coordination chemistry because of their redox non-innocent behavior.¹³⁵ These compounds are electronically flexible and contribute to the stability of several redox processes observed in metal complexes, which are not necessarily 'metalbased'.¹³⁶ Their electronic spin states can easily be clarified with the combined insights afforded by spectroscopic data, X-ray crystallography and computational analysis.¹³⁷⁻¹³⁸ Dithiolene derivatives such as tetrathiafulvenylacetylacetonate (TTFSacacH) have been reported as electroactive ligands with interesting redox properties.¹³⁹ Most of these compounds employ the zinc-thiolate complex bis(tetrabutylammonium)bis(1,3- dithiole-2-thione-4,5-dithiolato)zinc (II), [TBA]₂[Zn(dmit)₂]²⁻, as a key starting material to achieve the synthesis of interesting metal complexes.¹⁴⁰ Herein, the reduction of the $[Zn(dmit)_2]^{2-}$ dithiolene complex is utilized to aid the formation of a novel thiocarbonyl compound by its reaction with 3-chloro-2,4-pentadiyl)bis(sulfanediyl)]bis(4-hydroxypent-3-en-2-one), the di-enol tautomer of 3,3-[(2sulfanylidene-1,3-dithiole-4,5-diyl)bis(sulfanediyl)]bis(pentane-2,4-dione). The electrophilic nature of the acetylacetone (acac) motif and the high electron density on the sulfur atoms drive the nucleophilic substitution to completion. The title compound is a double β -dicarbonyl compound that contains two acetylacetone moieties, which are found in their enolic form in the solid state. Concerning the reactivity of the title compound, it is able to undergo acid or base-catalyzed α hydrogen substitution reactions, in which the rate-determining step is the formation of the enol or enolate anion.⁴

Compared to the acid-catalyzed process, the self- enolization of most ketones is negligible. The double β -dicarbonyl compound described herein also undergoes tautomerization; however, in the solid phase, the enol tautomer predominates in this equilibrium as it is stabilized relative to the keto form via resonance through the conjugated π -system and by intramolecular hydrogen bonding in the solid-state. This aspect is confirmed by its FT–IR and NMR spectra.¹⁴¹⁻¹⁴²

II. Experimental Methods

The synthesis of the title compound was carried out by refluxing 1 eq. of $[TBA]_2[Zn(dmit)_2]$ and 4 eq. of 3-chloro-2,4- pentanedione in 100 mL of acetonitrile under argon for 1 h, after which it was cooled and left under stirring overnight (**Figure A1**). Activated carbon was added and stirring continued for 1 h. The resulting mixture was filtered and washed with cold acetonitrile. The solvent was evaporated under reduced pressure, and ethyl acetate was added to precipitate ZnCl₂. The remaining solution was filtered, followed by evaporation of the solvent, giving a yellow crystalline solid (67.3% yield). NMR analyses were performed on a Bruker AV-700 spectrometer using chloroform-d (CDCl₃) as solvent. The solvent signals at 7.26 and 77.0 ppm were used as internal standards for proton and carbon, respectively. ¹HNMR (700 MHz, CDCl₃) δ 15.4 (s, 1H, interchangeable), 2.5 (s, 12H). ¹³CNMR (176 MHz, CDCl₃) δ 24.9, 102.3, 131.4, 197.7, 209.1.



Figure A1: Chemical synthesis of dmit(acac)₂ compound through SN₂ reaction.

III. Results and Discussion

1. Structural Commentary

The title compound crystallizes in the triclinic space group P₁ with one molecule in the asymmetric unit (**Figure A2, Table A1**). Its chemical structure consists of two 4-hydroxy-3-penten-2-one units connected to a 1,3-dithiol-1-thione ring moiety through a C—S single bond. In the unit cell, two molecules are related by an inversion center. The central thione ring is conformed by a C2-C3 carbon–carbon double bond, which is in the same plane as the C1 S1 bond characteristic of the thione substituent. The angles C2—S3—C6 and C3—S4—C11 are 101.45 (7)° and 103.72 (7)°, respectively. The torsion angles S4—C3—C2—S3 and S2—C2—C3—S5 are 176.18 (8)° and 0.54 (18)°, respectively; the difference in the torsion angles is due to the effects of steric hindrance from the 4-hydroxy-3- penten-2-one moiety. The S4—C3 and S3—C2 bond lengths are 1.7608 (16) and 1.7679 (16) Å, respectively.



Figure A2: The title compound dmit(acac)₂ with displacement ellipsoids drawn at 50% probability level and hydrogen bonds (O-H···O) in the asymmetric unit indicated.

2. Supramolecular Features

The title compound exhibits numerous intermolecular interactions, namely four C-H···O, three C—H···S, three C···O, one S···C, and one S···S interaction (Figure A3, Tables A1 and A2). The five-membered thiocarbonyl-containing rings lie almost parallel to the c axis and extend in a sheetlike fashion, forming a network that propagates along the axis with all rings following the same orientation. The sheets are linked by out-of-plane C13-H13B...S1 short contacts, generating stacks along the *a* axis with S···S short contacts between adjacent molecules $[S5 \cdots S5_{iv} = 3.5688]$ (6) Å]. In addition, the nucleophilic atom S3 is oriented towards the electrophilic C5, leading to an S3…C5_{iii} [3.471 (2) Å] contact, further contributing to the extension of the network along the c-axis direction. Molecules of the title compound also associate with neighboring molecules above and below the thiocarbonyl ring planes through the acac backbone by C4-H4...S1 and C9-H9...S1 contacts. The acac backbone lies nearly perpendicular to the rings, and there are several key interactions between the carbonyl oxygen atoms (O1, O2, and O3) and neighboring methyl hydrogen atoms (H8A and H8C) with lengths in the range 2.56-2.66 Å. However, atom O4 is not involved in any interactions with hydrogen atoms, and instead makes short contacts with both C12 and C13.

 $C \cdots O$, $S \cdots C$ and $S \cdots S$ short contacts (Å).

$C10 \cdot \cdot \cdot O1^i$	3.178 (2)	$S3 \cdot \cdot \cdot C5^{iii}$	3.471 (2)
$C12 \cdots O4^{ii}$	3.180 (2)	$S5 \cdot \cdot \cdot S5^{iv}$	3.5688 (6)
$C13 \cdots O4^{ii}$	3.219 (2)		

Symmetry codes: (i) x, y - 1, z; (ii) -x + 1, -y, -z + 1; (iii) -x + 1, -y + 1, -z + 2; (iv) -x, -y + 1, -z + 1.

Table A1: Short contact interactions in dmit(acac)₂.



Figure A3: Crystal packing of dmit(acac)₂, indicating the intermolecular $O \cdots H - C$, $O \cdots C$ and $S \cdots C$, $C - H \cdots S$ and $S \cdots S$ short contacts, viewed along the *b* axis.

$D - H \cdot \cdot \cdot A$	D-H	$H \cdot \cdot \cdot A$	$D{\cdots}A$	$D - H \cdot \cdot \cdot A$
$O2-H2\cdots O1$	0.82	1.67	2.4228 (17)	151
$O4-H4\cdots O3$	0.82	1.69	2.4406 (17)	151
$C13-H13C\cdots O3^{v}$	0.96	2.60	3.374 (3)	138
$C8-H8C\cdots O3^{vi}$	0.96	2.66	3.522 (2)	150
$C8-H8A\cdots O2^{vii}$	0.96	2.66	3.612 (2)	170
$C8-H8C\cdots O1^{v}$	0.96	2.56	3.228 (3)	127
$C9-H9B\cdots S1^{viii}$	0.96	2.90	3.5184 (19)	123
C13-H13 B ···S1 ^{iv}	0.96	2.89	3.7165 (19)	144
$C4-H4A\cdots S1^{viii}$	0.96	2.90	3.7987 (19)	156

Symmetry codes: (iv) -x, -y + 1, -z + 1; (v) x - 1, y, z; (vi) x - 1, y + 1, z; (vii) -x, -y + 2, -z + 2; (viii) -x + 1, -y + 1, -z + 1.

 Table A2: H-bond geometry of dmit(acac)2.

3. Hirshfeld Surface Analysis

The Hirshfeld surface¹¹¹ for the title compound mapped over d_{norm} is shown in **Figure A4** while **Figure A5** shows the associated two-dimensional fingerprint plots¹³³, both generated with Crystal Explorer17¹¹². Red spots on the Hirshfeld surface mapped over d_{norm} in the color range 0.0820 to 1.5568 arbitrary units confirm the above-mentioned primary intermolecular contacts. The fingerprint plots are given for all contacts and those delineated into S…H/H…S, (**Fig. A5b**), H…H (25.8%; **Fig. A5c**), O…H/H…O (**Fig. A5d**), C…H/H…C (9.3%; **Fig. A5e**), S…C/C…S (4.9%; **Fig. A5f**), S…O/O…S (4.8%; **Fig. A5g**), S…S (4.0%; **Fig. A5h**), O…C/C…O (2.0%; **Fig. A5i**), O…O (1.1%; **Fig. A5j**), and C…C (0.7%; **Fig. A5k**) interactions. Thus, the Hirshfeld surface analysis indicates that the most significant contributions arise from S…H and H…H contacts.



Figure A4: Hirshfeld surface of dmit(acac)₂ mapped over d_{norm} with the four main intermolecular contacts in the crystal lattice shown.



Figure A5: Full (a) and individual (b)–(m) two-dimensional fingerprint plots showing the ten intermolecular contacts present in the crystal structure of dmit(acac)₂.

4. Database Survey

A search of the Cambridge Structural Database (CSD Version 5.40, September 2019 update; Groom et al., 2016) for the title compound revealed 46 hits comprising structures including metal complexes and organic compounds. Of the latter, 31 hits are for C–S bicyclic compounds and four hits are for mono- cyclic C–S crystal structures.

Monocyclic structures related to the title compound are bis(5-(mesitylthio)-1,3-dithiole-2- thione)-4,4-disulfide dihydrate (LOBXEF)¹⁴³, 4,4 -disulfanediylbis{5-[(2,4,6-triisopropylphenyl)sulfanyl]-1,3-dithiole-2-thione} (NUMXOJ)¹⁴⁴ and 4,5-bis(2,4-dinitrophenylthio)-1,3-dithiole-2thione (YISBOR; Qi et al., 1994 and YISBOR10; Qu et al., 1995). The dihedral angles in YISBOR/YISBOR10 and LOBXEF are similar to those exhibited by the title compound, unlike in NUMXOJ, which is completely different. For the mentioned compounds, the lack of C—H···O and C—H···S short contacts means they are not comparable to the title compound. The four comparative compounds show similar S···C short contacts, which involve the sulfur atoms of the thione ring and the carbon atoms from the substituents. In contrast to YISBOR/YISBOR10, the structures of LOBXEF and NUMXOJ exhibit an S···S short contact analogous to that in the title compound. The structure of NUMXOJ exhibits π - π stacking of the thione rings of neighboring molecules, similar to the title compound, and unlike LOBXEF (in which π - π stacking occurs between the benzene and thione rings) and YISBOR/YISBOR10 (where there π - π stacking between the thione ring and one benzene ring).

5. Refinement

Crystal data, data collection and structure refinement details are summarized in **Table A4**. H atoms were included in geometrically calculated positions for the alkyl groups while the hydrogen atoms from OH groups were located from the difference-Fourier map and refined as riding: O-H = 0.82 Å, C-H = 0.93-0.98 Å with $U_{iso}(H) = 1.5U_{eq}(O, C-methyl)$ and $1.2U_{eq}(C)$ for other H atoms.

Identification code	dpc037
Empirical formula	$C_{13}H_{14}O_4S_5$
Formula weight	394.54
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	7.18430(10)
b/Å	9.91980(10)
c/Å	12.5230(2)
α/°	84.3190(10)
β/°	83.5740(10)
γ/°	69.1510(10)
Volume/Å ³	827.11(2)
Z	2
$\rho_{calc}g/cm^3$	1.584
μ/mm ⁻¹	6.588
F(000)	408.0
Crystal size/mm ³	0.3 imes 0.28 imes 0.06
Radiation	$CuK\alpha \ (\lambda = 1.54184)$
2Θ range for data collection/°	7.118 to 138.192
Index ranges	$-8 \le h \le 8, -12 \le k \le 12, -15 \le l \le 15$
Reflections collected	45972
Independent reflections	$3086 [R_{int} = 0.0477, R_{sigma} = 0.0169]$
Data/restraints/parameters	3086/0/206
Goodness-of-fit on F ²	1.048
Final R indexes [I>=2 σ (I)]	$R_1 = 0.0265, wR_2 = 0.0722$
Final R indexes [all data]	$R_1 = 0.0268, wR_2 = 0.0725$

Table A4: Crystal structure refinement of dithiolene title compound.

6. Spectroscopic Characterization

Without basic catalysis, the self-enolization of most ketones is negligible and the keto form is favored almost exclusively.¹⁴¹ However, β-dicarbonyl compounds, which can also undergo tautomerization, are stabilized in the enol tautomer via resonance of the conjugated π -system and intramolecular hydrogen bonding. Furthermore, the enol is the less polar of the two tautomers because the intramolecular hydrogen bond reduces the dipole-dipole repulsion of the two carbonyls in the keto form. The equilibrium of β -dicarbonyl compounds has been studied extensively and it has been shown that tautomeric interconversion between the diketo and enol forms is relatively slow and can be observed by NMR. Under normal conditions, the enolic form predominates in equilibrium.¹⁴⁵ This effect was demonstrated to be solvent and concentration dependent. An NMR study of keto–enol tautomerism in β-dicarbonyl compounds revealed that for the unsubstituted and symmetrical β -dicarbonyl compound pentane-2,4-dione, the equilibrium constant at 310 K has a value of 2.95 with 93.3 enol % (acetone exists as 0.00025% enol).¹⁴⁶ In addition, as these compounds are progressively diluted with non- polar solvents, the enol content of the system increases. The progressive dilution with more polar solvents than the solute was observed to increase the stability of the keto form.



Figure A6: Tautomeric effect observed in the acetylacetonate portion of dmit(acac)₂.

In the case of the ¹HNMR study of the title compound in deuterated chloroform at 298 K, the predominant form was observed to be the enol tautomer. NMR was used to confirm the underlying symmetry the title compound possesses in solution, in which the enol tautomer predominates, as can be observed in **Figure A6**. The lowest frequency signal in the ¹HNMR spectrum integrates to twelve and corresponds to the methyl protons of the compound, indicating that the latter are chemically equivalent. Similarly, the enol form of the compound was observed crystallographically and in solution, exhibiting intramolecular hydrogen bonding and renders both methyl groups, as well as both carbonyls, chemically equivalent. When studying the proton spectrum, the conjugation in the six-membered pseudo-aromatic ring deshields the signal of the interchangeable proton, giving rise to a low field signal at 15.4 ppm that is lost in the baseline. Looking further into the baseline at higher fields, around 5.1 ppm, it reveals a wide signal that is almost lost in the noise and that can be assigned to the interchangeable proton in the keto tautomer (**Figure A7**).



Figure A7: ¹H NMR spectrum of dmit(acac)₂ with inserts of the baseline expansions near 15.4 and 5.1 ppm, respectively.

The formation of this hydrogen-bridge bond is promoted by the planar structure of the enolcarbonyl resonance system because this leads to an ideal spatial orientation of the hydroxy group and carbonyl group in order to construct a strong hydrogen-bridge bond. Therefore, the monoenolic form of a β-dicarbonyl compound has a planar, six-membered cyclic structure stabilized by resonance. Decreasing the concentration of the solute in non-polar solvents has been proven to increase the concentration of the enol tautomer. ¹³CNMR spectrum displayed a single signal at 24.8 ppm for the methyl carbons, and a single signal at 197.7 ppm for the carbonyl carbons, supporting the statement that there is chemical equivalency between the methyl groups and, most importantly, between both carbonyl moieties. This effect has been previously demonstrated by comparing the ¹³CNMR spectra of the enol forms of symmetrical and unsymmetrical derivatives of β -diketones, where a different chemical shift was observed for the two carbonyls in the unsymmetrical case. It is possible to conclude that the three signals of the 2,4pentanedione portion of the title compound, as well as the chemical shifts observed, are indicative of a symmetrical system that results from intramolecular hydrogen-bonding in the enol tautomer. IR peaks at 2,962 and 2,876 cm⁻¹ are assigned to the C—H stretches (**Figure A8**). The peaks between 1,575 and 1,402 cm⁻¹ correspond to the C-C bond in the enol form. Moreover, hidden under this peak there is also the C-O stretch in the enol form, which is lowered by conjugation to the C-C bond and the O atom of the –OH group, respectively. OH stretches for β - diketones are tabulated from 3,200 to 2,400cm⁻¹; however, in the case of symmetric acac compounds where the enol form predominates and the interchangeable hydrogen is located between the two carbonyls, the dipole change associated to the symmetric OH stretch is null, and the signal is minimal to nonexistent. Thus, evidence from NMR and IR spectroscopy indicates that the compound exists almost entirely in its enol form.



Figure A8: IR spectrum of the title compound dmit(acac)₂.

IV. Conclusions

The reaction between $[TBA]_2[Zn(dmit)_2]$ and 3-chloro-2,4-pentanedione yielded single crystals of the title compound, (3E,3E)-3,3-[(2-sulfanylidene- 1,3-dithiole-4,5-diyl)bis(sulfanediyl)]bis(4hydroxypent-3-en-2-one), $C_{13}H_{14}O_4S_5$, after solvent evaporation. The title compound crystallizes in the triclinic space group P₁ with two molecules related by an inversion center present in the unit cell. The central thione ring moiety contains a carbon–carbon double bond covalently linked to two sulfoxide substituents located outside of the plane of the ring. The S—C—C—S torsion angles are 176.18 (8)° and 0.54 (18)°. Intramolecular hydrogen bonds occur within the two dione substituents (1.67–1.69 Å). Adjacent asymmetric units are linked by C—H…S (2.89–2.90 Å), S…S [3.569 (1) Å] and O…H [2.56–2.66 Å between non-stacked thione rings] short contacts.

My major contribution to this work was from the spectroscopic perspective. The design, execution and in-depth analysis of the NMR and vibrational spectra were two of the greatest challenges we were able to overcome with my expertise. More specifically, the elucidation of the underlying chemistry of the tautomeric forms of the dicarbonyl compound described herein, and the unambiguous assignment of all signals in both ¹H and ¹³C NMR spectra. In the 1H NMR spectrum the signals were either hidden or broadened, an endeavor that was resolved using an instrument with a significantly potent magnetic field sensitive enough to detect them (700 MHz). I performed the Hirshfeld surface analysis and database survey, which ultimately revealed that the compound is consolidated through S…H and H…H short contact interactions.

V. References

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Cordero Gimenez, K. T.; Soto Diaz, V. Y.; <u>Gonzalez Espiet, J. C.</u>; Lavin Flores, A.; Bas Concepcion, J.; Rivera Cruz, K. E.; Rodriguez Ayala, D. L.; Pinero Cruz, D. M. Crystal structure, Hirshfeld surface analysis and spectroscopic characterization of the di-enol tautomeric form of the compound 3,3'-[(2-sulfanylidene-1,3-dithiole-4,5-diyl)bis(sulfanediyl)]bis(pentane-2,4-dione). *Acta Cryst.* **2020**, *E76*, 1427-1432. DOI: 10.1107/S2056989020010695

I. Introduction

Recent efforts in the field of medicinal organometallic chemistry have been driven by a high interest in the synthesis of metal ethynyl complexes, particularly because of their biological activity.¹⁴⁷ In addition, phenyl- ethyne-derived compounds display active electrochemical properties such as the generation of stable redox forms, regeneration at low potentials and good electrochemical reversibility.¹⁴⁸⁻¹⁴⁹ 1-Ferrocenyl-2- (4-nitrophenyl)ethyne has previously been prepared in moderate-to-high yields (52–92%) by applying Sonogashira coupling reactions. However, all of them used 4-iodo-1- nitrobenzene or 4-triflate-1-nitrobenzene and a variety of solvents, catalysts, and conditions, under an inert atmosphere. The reaction time varied from 25 min to 4 h.¹⁴⁹⁻¹⁵³ Other approaches involved the use of iodoferrocene and 4-ethynyl-1-nitrobenzene.¹⁵⁰ Our approach focuses on performing copper-free Sonogashira coupling between ethynylferrocene and 4-bromo- 1-nitrobenzene without the need of inert atmosphere protocols and obtaining moderate-to-high yields, by following green chemistry protocols.

II. Experimental Methods

The synthesis of all Fc-chalcone derivatives was performed by PhD candidate Sara Delgado from Dr. Ingrid Montes' Lab through a Sonogashira coupling or Crossed Aldol condensation, followed by chromatography and subsequent recrystallization with acetone/water.

III. Results and Discussion

1. Structural Commentary

Figure A9 shows the molecular structure of the title compound, which crystallizes in space group P21/n. The substituted ferrocene (Fc) system is linked to a *p*-nitrobenzene moiety by an acetylenic bridge between C11 and C12 with a bond distance of 1.202 (2) Å, which is comparable to those in similar complexes, *e.g.*, 1.202 (2) Å,¹⁵⁴ 1.197 (3) Å¹⁵⁵, and 1.193 (2) Å.¹⁵⁶ The unit cell is comprised of four molecules with one molecule present per asymmetric unit. The substituted Cp and phenyl rings are almost parallel to each other, subtending a dihedral angle of 6.19 (10) °, in contrast to (phenyl-ethynyl)ferrocene, which has no substituent in the para position and exhibits a nearly perpendicular dihedral angle of 89.06 (3)°.



Figure A9: Molecular structure of the title compound, including atom labelling. Displacement ellipsoids are drawn at the 50% probability level.

The distances of the Fe1 atom from the centroids of the substituted and unsubstituted Cp rings are 1.6461 (8) and 1.6584 (8) Å, respectively. The Cg1—Fe1—Cg2 angle is 179.27°, where Cg1 and Cg2 are the centroids of substituted and unsubstituted Cp rings, respectively. The Cp rings in the ferrocene system are thus almost parallel, since the angle between the Cp ring planes is $1.03 (13)^{\circ}$. In addition, the Cp rings display a nearly eclipsed conformation with a slight deviation, as demonstrated by the average C—Cg1—Cg2—C torsion angle of 12.26°. The C—C bond distances in the Cp rings range from 1.417 (2) to 1.436 (2) Å, while the Fe—C bond lengths range between 2.038 (2) and 2.055 (2) Å.

2. Supramolecular Features

The title compound exhibits π – π stacking interactions between one of the Cp rings from the Fc moiety and the p-nitrophenyl substituent, allowing the formation of a zigzag structure; atom pairs involved relate C6_(Cp) and C7_(Cp) to C17_(p-nitrophenyl) and C18_(p-nitrophenyl) of a neighboring molecule, with short contacts of 3.340 (2) and 3.397 (2) Å, respectively. This interaction can be described as pairs of molecules being interrupted by two C3_(Cp)…H8—C8_(Cp) interactions from a different interconnected pair of perpendicularly oriented Fc moieties with short contact distances of 2.83 Å each short contacts with neighboring molecules establishing a distinctive interconnected pair between a corner of the Cp ring and one of the oxygen atoms from the p-nitrophenyl substituent yield a closed arrangement of atoms. Short contacts involve H6—C6_(Cp) …O1_(p-nitrophenyl) at a distance of 3.461 (2) Å.



Figure A10: Crystal packing of the title compound along the *a* axis with short-contact interactions shown as dashed lines.

Another interconnection is found between adjacent p-nitrophenyl groups, yielding a ring arrangement involving pairs from H17—C17_(p-nitrophenyl)…O2_(p-nitrophenyl) with a distance of 2.727 (2) Å and pairs from O1_(p-nitrophenyl)…H15—C15_(p-nitrophenyl) with a distance of 2.716 (2) Å. In addition, a chain is formed by short contacts from the C17—H17_(p-nitrophenyl)…O1_(p-nitrophenyl) interaction belonging to the p-nitrophenyl substituent with a distance of 3.203 (19) Å. Numerical details of the hydrogen-bonding interactions are given in Table 1 and the packing is shown in **Figure A10**.

3. Hirshfeld Surface Analysis

CrystalExplorer17¹¹² was used to generate the Hirshfeld surface¹¹¹ for the title compound mapped over d_{norm} and the associated two- dimensional fingerprint plots.¹³⁴ Figure A11 shows the molecules involved in the four closest contacts. Red spots on the Hirshfeld surface mapped over d_{norm} in the color range -0.2315 to 1.1417 arbitrary units confirm the previously mentioned main intermolecular contacts.



Figure A11: A view of the Hirshfeld surface of the title compound mapped over d_{norm} with the four main intermolecular contacts in the crystal lattice.

The fingerprint plots are given for all contacts (**Figure A12a**) and those decomposed into nine individual interactions: H…H (46.9%; **Fig. A12b**), C…H/ H…C (21.9%; Fig. **A12c**), O…H/ H…O (18.7%; **Fig. A12d**), C…C (7.5%; Fig. **A12e**), C…O/O…C (1.6%; **Fig. A12f**), C…N/N…C (1.2%; Fig. **A12g**), N…O/O…N (0.9%; Fig. **A12h**), O…O (0.9%; **Fig. A12i**) and N…H/H…N (0.5%; **Fig. A12j**). The Hirshfeld surface analysis for the title compound indicates that the most significant contributions arise from H…H and C…H contacts (González *et al.*, 2020; McKinnon *et al.*, 2004, 2007; Spackman & McKinnon, 2002).



Figure A12: Full (a) and individual (b)–(j) two-dimensional fingerprint plots showing the nine intermolecular contacts present in the crystal structure.

4. Database Survey

A search of the Cambridge Structural Database (Version 5.41, updated November 2019)⁹⁶ revealed 142 related compounds with the 1-ferrocenyl-2-phenylethyne backbone. Of those structures, 41 contain substituents in the para position of the phenyl ring, as in the title compound. One of the reasons for such a high number of reported structures for methynylferrocene and its derived compounds is attributed to their substantial interest as chromophores, mainly because of their electronic communication capacity through the alkyne linkage to the Fe center. When comparing the effect of the substituent on the molecular structure, one of the main features is the dihedral angle that is formed between the substituted Cp ring of the ferrocene group and the phenyl moiety. The orientation can range from almost parallel (1.01°: YOHSIY) to completely perpendicular (90.00°: YOHSUK01). Table 2 gives the dihedral angles for previously reported compounds; our compound having the second lowest dihedral angle and a nearly parallel conformation. Exchanging the hydrogen atoms in the methyl group for fluorine atoms shifts the dihedral angle from 1.01° to 90.00° in the case of methyl and trifluoromethyl substituents, respectively.

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. H atoms were included in geometrically calculated positions, C—H = 0.93 Å, and refined as riding on their parent C atom with $U_{iso}(H) = 1.2U_{eq}(C)$.

6. Crystallography of Other Ferrocene Chalcone Derivatives

The crystal structure of other members of the Fc-chalcone family was also resolved with publishable R1 and completeness values (Table A5). An in-depth crystallographic analysis is being performed to determine the structural features and trends in these pyridine-substituted systems, namely, their dihedral angles and IMFs in their crystal lattices.

FC SYSTEM	R1 VALUE (%)	COMPL. (%)	STRUCTURE
F1	6.27	98	FC
F1	5.18	99	Fc N
F1	2.93	100	Fc N
F1	2.57	100	Fc CH3 CH3
F1	2.2	100	Fc NO ₂
F3	2.6	100	Fc
F3	2.58	100	FC
F3	2.31	99	FC
F3	4.18	100	Fc
F3	4.07	100	Fc NO ₂

Table A5: Solved structures of pyridine-derived ferrocene chalcones systems.

IV. Conclusions

The title ferrocene derivative, $[Fe(C_5H_5)_2(C_8NO_2)]$, including an alkyne bonded to a paranitrophenyl substituent, which was synthesized from a copper-free Sonogashira cross-coupling reaction between ethynylferrocene and 4-bromo-1- nitrobenzene, crystallizes in the P21/n space group. In the ferrocene unit, the pentadienyl (Cps) rings are in an eclipsed conformation. The angle of rotation between the substituted cyclopentadienyl ring and the p-nitrophenyl group is 6.19 (10)° yielding a quasi-linear extension of the ferrocenyl substitution. Important intermolecular interactions arise from π - π stacking between the Cp rings and the *p*-nitrophenyl, from corners of the Cp rings that are perpendicularly aligned, and between the O atoms from the nitro substituent and carbons at the corners of the Cp rings, propagating along all three crystallographic axes. My contribution to this work was directly related to the X-ray crystallographic analyses, elucidating the solid-state chemistry of these compounds, starting from the structural and supramolecular features to the Hirshfeld analysis of interactions, database surveys, and refinements. The fascinating area of Fc-chalcone compounds still leaves much to be desired because of their rich and diverse structural chemistry. Part of the work presented herein was published for 1 of the compounds in 2020 on Acta Crystallographica; the data of the other 10 compounds is currently being prepared for submission. This work ultimately establishes the foundation for the future crystallographic analysis of Fc-chalcone compounds, which is an exciting and relatively unexplored field in X-ray crystallography.

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Section III: Exploring Serum Transferrin Regulation of Nonferric Metal Therapeutic Function and Toxicity

I. Introduction

The sTF protein houses N and C-lobes that are divided into two subdomains (N1 and N2, and C1 and C2) that form the two metal binding sites for Fe(III). In mixed-metal TF systems, as well as diferric and iron-free TF, there is a pH dependency that will affect the binding of these metals to the protein in both lobes.¹⁵⁷ Moreover, the binding sites at the C and N lobes will have different affinity for the same metal. For example, when observing the dependency of iron binding with pH, the C-terminal site of the protein remains attached at pH values down to 4.8, whereas the N-site cannot bind below pH 5.7.158 In addition, at physiological pH (7.4) the stoichiometric binding constant of N-terminal site is 5 times lower than the C-terminal site.¹⁵⁹ Although there have been several reports on nonferric coordination to apo-Tf, vanadium is perhaps the first metal ion that most scientists agreed bound to sTf unlike any other metal ion. Both V(IV) and V(V) bring with them the oxide anion as a synergistic anion and, in addition, can bind to proteins via other exogeneous ligands present in the body.¹⁶⁰ Most evidence supports that most of the vanadium in the serum is bound to hTF, however, the issue of how V(IV) is transported in the form of V(IV)O carrier complexes is not fully understood, as well as how relevant this is for up-take of vanadium by target cells.¹⁶¹⁻¹⁶² There is still much needed information regarding the conformational changes that sTf undergoes upon metal binding and dissociation. This information is crucial to understanding the endocytosis route and the subsequent fate of the transported metal.

II. Canonical vs. Noncanonical Fe(III) Binding Model for Human Serum Transferrin⁶

The primary sphere of coordination of Fe(III) consists of two tyrosines, one histidine, and one aspartic acid; the remainder of the sites are occupied by bidentate carbonate anions (CO_3^{2-}), also known as the synergistic anion. The anion in the form of its conjugate pair, bicarbonate (HCO_3^{-}) is prevalent in our blood and stabilizes Fe(III) in said connective tissue.¹⁶³ This is referred to as the canonical modality of metal binding (**Figure A13**). The canonical binding that occurs at physiological pH can also be performed by substituting the bicarbonate anions for carboxylate ligands. The main difference between the affinity of Fe(III) for both sites in sTf is due to the intermolecular forces (IMFs) within the secondary sphere of coordination. Upon binding to Fe(III), the lobes in the protein experience a change from open to closed conformation, which ultimately leads to stabilization and a different surface charge. X-ray crystallography has enabled the elucidation of a non-canonical modality of Fe(III) binding to sTf. In which the metal is bound by other protein residues or synergistic anions, resulting in open or semi-open conformations.¹⁶⁴



Figure A13. (A) Canonical (closed) and (B) noncanonical (open) Fe(III) binding to serum transferrin (C) Representation of sTf metal affinity that suggests the capacity for additional nonferric metal.

III. Conclusions

This work described herein was a collaborative endeavor between members of the Metals in Medicine course, led by Dr. Arthur Tinoco and his laboratory. My contribution to this work was on the first section, describing the canonical and non-canonical binding of other transition metals. More specifically, vanadium, chromium, aluminum, and rare earth metals. Our group worked on Figure A13, which was generated with PDB data, and the results obtained from out literature research. Overall, this resulted in a comprehensive publication that encompasses numerous topics during the last years of sTf binding research and challenges the notions of this protein to only have one binding modality with physiological relevance.

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Appendix B:

Supplemental Figures and Tables

Appendix B contains data relevant to the characterization of $F_{16}MPc$ complexes and (OCH₃)8MPcs described in Chapter 3, in addition to the precursor phthalonitriles. Firstly, the IR and UV-Vis spectra of F16MPc compounds (M = Mn, Ni, Cu, Zn) is presented, followed by their corresponding PXRD patterns. The corresponding SEM/EDS data of the $F_{16}MPc$ complexes follows. Supplemental gas sensing graphs generated by PhD candidate Soraya Flores and Dr. Luis Fonseca at Naslab. NMR spectra of 2-iodo-4-pentafluorothiobenzonitrile and 4-pentafluorothiophtalontrile is presented afterwards, with the respective crystallographic refinement tables of 2-iodo-4-pentafluorothiobenzonitrile. The SEM, EDS, IR, and UV-Vis of (OCH₃)8MPc complexes is presented herein as well.



Wavenumber (cm⁻¹)

Figure B1: IR spectra of synthetic F₁₆MPc complexes.



Figure B2: UV-Vis spectra of synthetic F₁₆MPc complexes in ethyl acetate (EtOAc).



Figure B3: UV-Vis spectra of synthetic F₁₆MPc complexes in tetrahydrofuran (THF).

Sample	S- Band (w/ EtOAc) (nm)	S- Band (w/ THF) (nm)	Q- Band (w/ EtOAc) (nm)	Q- Band (w/ THF) (nm)
TFDCB	298	235, 300	-	-
F ₁₆ MnPc	320	305	635	635
F ₁₆ NiPc	258, 382, 318	235, 290, 320, 345	635, 660	600, 665
F ₁₆ CuPc	258	235, 355	-	-
F ₁₆ ZnPc	-	355	-	645, 675

Table B1: Summary of Q and S bands for synthetic F₁₆MPc complexes.



Figure B4: X-ray powder diffraction patterns of synthetic F₁₆MPc complexes.



Figure B5: SEM/EDS of as-synthesized F₁₆FePc microcrystalline powder.



Figure B6: SEM/EDS of as-synthesized F₁₆CoPc microcrystalline powder.



Figure B7: SEM/EDS of as-synthesized F₁₆NiPc microcrystalline powder.



Figure B8: SEM/EDS of as-synthesized F₁₆CuPc microcrystalline powder.



Figure B9: Includes the as measured electrical current intensity as a function of time of a representative F_{16} FePc nanowires sensor prototype during 100 ppb NH₃ testing. **Figure 2** in the paper was obtained from this data.



Figure B10: (a) Normalized $F_{16}FePc$ sensor response (Normalized S) as a function of time at different NH₃ concentrations for exposure times < 3 h. (b) Model fittings (continuous red lines) for the $F_{16}FePc$ sensor fast response as a function of time at different NH₃ concentrations.



Figure B11: (a) Inverse of the time constant for the fast response process $(1/\tau 1F)$ as a function of the NH₃ concentrations. (b) Fast response saturation values (A1F) as a function of the NH₃ concentrations.



Figure B12: (a) Normalized response (Normalized S) of the F_{16} FePc nanowire sensor to ON and OFF 100 ppb NH₃ gas cycles. Exposure time < 30 min including three repetitions. (b) Normalized response (Normalized S) of the F_{16} FePc nanowire sensor to 40 ppb of NH₃ gas exposure at room temperature.



Figure B13: (a) Comparison between the F_{16} FePc and FePc normalized sensors' response (Normalized S) to 100 ppb of NH₃. (b) Normalized response (Normalized S) of the FePc sensor at 100 ppb of NO₂.

In summary, for the detection of NH₃, two processes with significantly different time constants were identified in the response of the sensor. For a 100 ppb NH₃ concentration in air at room temperature, the fast component ($\tau_{fast} \approx 2.25$ h) was assigned to the interaction of the analyte with the adsorbed oxygen at the surface of the nanowires. The slow component ($\tau_{slow} \approx 30.41$ h) was assigned to the diffusion of the ammonia through the bundles' interfaces and the reduced surface porosity of the nanowires. Among all the materials studied, F₁₆FePc nanowires showed improved stability and recovery.



Figure B14: ¹H-NMR spectrum of 2-iodo-4-pentafluorothiobenzonitrile.



Figure B15: ¹H-NMR spectrum of 4-pentafluorothiophthalonitrile.

Empirical formula	C7H3F5INS
Formula weight	355.06
Temperature/K	300.00
Crystal system	orthorhombic
Space group	Pnma
a/Å	8.06340(10)
b/Å	7.70880(10)
c/Å	16.4410(3)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	1021.96(3)
Z	4
$\rho_{calc}g/cm^3$	2.308
µ/mm ⁻¹	26.993
F(000)	664.0
Crystal size/mm ³	$0.258 \times 0.17 \times 0.117$
Radiation	$CuK\alpha \ (\lambda = 1.54184)$
2@ range for data collection/°	10.762 to 137.584
Index ranges	$-9 \le h \le 9, -9 \le k \le 9, -19 \le l \le 19$
Reflections collected	9403
Independent reflections	1020 [$R_{int} = 0.0823$, $R_{sigma} = 0.0311$]
Data/restraints/parameters	1020/0/85
Goodness-of-fit on F ²	1.033
Final R indexes [I>=2 σ (I)]	$R_1 = 0.0417, wR_2 = 0.1098$
Final R indexes [all data]	$R_1 = 0.0435, wR_2 = 0.1114$
Largest diff. peak/hole / e Å ⁻³	0.74/-1.77

 Table B2: Crystal structure data for 2-iodo-4-(pentafluorosulfanyl)benzonitrile.

Identification code	DPC_JCG319_auto
Empirical formula	$C_{10}H_8N_2O_2$
Formula weight	188.187
Temperature/K	300.00(10)
Crystal system	monoclinic
Space group	P21/c
a/Å	4.5860(1)
b/Å	12.8423(3)
c/Å	16.7698(5)
α/°	90
β/°	90.734(3)
γ/°	90
Volume/Å ³	987.57(4)
Z	4
$\rho_{calc}g/cm^3$	1.266
µ/mm ⁻¹	0.753
F(000)	393.4
Crystal size/mm ³	0.23 imes 0.06 imes 0.06
Radiation	$Cu K\alpha (\lambda = 1.54184)$
2@ range for data collection/°	8.68 to 136.84
Index ranges	$-5 \le h \le 4, -15 \le k \le 15, -20 \le l \le 20$
Reflections collected	9363
Independent reflections	1766 [$R_{int} = 0.0310$, $R_{sigma} = 0.0266$]
Data/restraints/parameters	1766/0/129
Goodness-of-fit on F ²	1.054
Final R indexes [I>=2σ (I)]	$R_1 = 0.0420, wR_2 = 0.1237$
Final R indexes [all data]	$R_1 = 0.0530, wR_2 = 0.1345$

Table B3: Crystal data and structure refinement for 4,5-dimethoxy-1,2-dicyanobenzene.



Figure B16: SEM/EDS of as-synthesized (OCH₃)₈MnPc microcrystalline powder.



Figure B17: SEM/EDS of as-synthesized (OCH₃)₈FePc microcrystalline powder.



Figure B18: SEM/EDS of as-synthesized (OCH₃)₈CoPc microcrystalline powder.



Figure B19: SEM/EDS of as-synthesized (OCH₃)₈NiPc microcrystalline powder.



Figure B20: SEM/EDS of as-synthesized (OCH₃)₈CuPc microcrystalline powder.



Figure B21: SEM/EDS of as-synthesized (OCH₃)₈ZnPc microcrystalline powder.



Figure B22: SEM image of as-synthesized (OCH₃)₈ZnPc microcrystalline powder showing a well-defined and homogeneous morphology.



Figure B23: IR spectrum of as-synthesized (OCH₃)₈MnPc microcrystalline powder.



Figure B24: IR spectrum of as-synthesized (OCH₃)₈NiPc microcrystalline powder.



Figure B25: IR spectrum of as-synthesized (OCH₃)₈CuPc microcrystalline powder.



Figure B26: IR spectrum of as-synthesized (OCH₃)₈ZnPc microcrystalline powder.



Figure B27: UV-Vis spectrum of (OCH₃)8MnPc microcrystalline powder in DMSO.



Figure B28: UV-Vis spectrum of (OCH₃)₈NiPc microcrystalline powder in DMSO.



Figure B29: UV-Vis spectrum of (OCH₃)₈MnPc microcrystalline powder in DMSO.



Figure B30: UV-Vis spectrum of (OCH₃)₈MnPc microcrystalline powder in DMSO.

Appendix C:

Crystallographic Tables

Atom	Atom	Length/Å
I1	C2	2.076(6)
S1	F3	1.582(5)
S1	F2	1.572(3)
S1	F21	1.572(3)
S1	F11	1.561(4)
S1	F1	1.561(4)
S1	C4	1.823(7)
C4	C3	1.388(9)
C4	C5	1.374(10)
C3	C2	1.399(8)
C2	C1	1.388(9)
C1	C7	1.442(10)
C1	C6	1.406(11)
C7	N1	1.136(10)
C5	C6	1.353(11)

 Table C1: Bond lengths for 2-iodo-4-pentafluorothiobenzonitrile.

 Table C2: Bond angles for 2-iodo-4-pentafluorothiobenzonitrile.

Atom	Atom	Atom	Angle/°
F3	S1	C4	179.4(3)
F21	S1	F3	87.52(18)
F2	S1	F3	87.52(18)
F21	S1	F2	89.4(3)
F2	S1	C4	92.04(19)
F21	S1	C4	92.04(19)
F11	S1	F3	88.3(2)
F1	S1	F3	88.3(2)
F1	S1	F21	90.4(2)

F1	S1	F2	175.8(2)
F11	S1	F2	90.4(2)
F11	S1	F21	175.8(2)
F11	S 1	F1	89.5(4)
F11	S1	C4	92.2(2)
F1	S1	C4	92.2(2)
C3	C4	S 1	118.3(5)
C5	C4	S 1	119.8(5)
C5	C4	C3	121.8(6)
C4	C3	C2	118.4(6)
C3	C2	I1	118.9(5)
C1	C2	I1	121.2(5)
C1	C2	C3	119.9(6)
C2	C1	C7	121.6(6)
C2	C1	C6	119.5(6)
C6	C1	C7	118.9(7)
N1	C7	C1	178.4(9)
C6	C5	C4	119.8(7)
C5	C6	C1	120.6(7)

 Table C3: Bond lengths for 4,5-dimethoxyphthalonitrile.

Atom	Atom	Length/Å
09	C6	1.3443(17)
09	C10	1.4376(17)
07	C1	1.3501(17)
07	C8	1.432(2)
C6	C1	1.417(2)
C6	C5	1.3733(19)
C1	C2	1.379(2)

C5	C4	1.389(2)
C4	C3	1.395(2)
C4	C11	1.432(2)
C3	C2	1.389(2)
C3	C13	1.436(2)
N14	C13	1.143(2)
C11	N12	1.140(2)

 Table C4: Bond angles for 4,5-dimethoxyphthalonitrile.

Atom	Atom	Atom	Angle/°
C10	09	C6	117.11(11)
C8	07	C1	117.97(14)
C1	C6	09	115.69(12)
C5	C6	09	124.77(12)
C5	C6	C1	119.54(13)
C6	C1	07	115.10(12)
C2	C1	07	125.31(13)
C2	C1	C6	119.59(13)
C4	C5	C6	120.78(13)
C3	C4	C5	119.72(13)
C11	C4	C5	120.02(13)
C11	C4	C3	120.26(13)
C2	C3	C4	119.88(13)
C13	C3	C4	119.24(14)
C13	C3	C2	120.88(13)
C3	C2	C1	120.47(13)
N14	C13	C3	179.13(16)
N12	C11	C4	179.00(16)

Atom	Atom	Length/Å
S4	C11	1.7700(16)
S4	C3	1.7608(16)
S2	C2	1.7385(16)
S2	C1	1.7389(16)
S5	C3	1.7479(16)
S5	C1	1.7225(16)
S1	C1	1.6424(17)
S3	C6	1.7653(16)
S3	C2	1.7679(16)
03	C10	1.267(2)
O2	C7	1.287(2)
01	C5	1.278(2)
O4	C12	1.303(2)
C11	C12	1.399(2)
C11	C10	1.435(2)
C6	C7	1.415(2)
C6	C5	1.424(2)
C12	C13	1.489(2)
C10	C9	1.495(2)
C7	C8	1.483(2)
C2	C3	1.351(2)
C5	C4	1.491(2)

 Table C5: Bond lengths for dithiolene compound dmit(acac)2.

 Table C6: Bond angles for dithiolene compound dmit(acac)2.

Atom	Atom	Atom	Angle/°
C3	S4	C11	103.72(7)
C2	S2	C1	97.02(7)

C1	S5	C3	97.48(7)
C6	S3	C2	101.45(7)
C12	C11	S4	119.52(12)
C12	C11	C10	119.34(14)
C10	C11	S4	120.87(12)
C7	C6	S 3	120.13(12)
C7	C6	C5	119.32(14)
C5	C6	S 3	120.55(12)
O4	C12	C11	120.13(15)
O4	C12	C13	115.14(14)
C11	C12	C13	124.71(15)
03	C10	C11	120.25(15)
03	C10	С9	118.05(15)
C11	C10	C9	121.69(14)
O2	C7	C6	119.97(15)
O2	C7	C8	116.18(15)
C6	C7	C8	123.84(15)
S2	C2	S 3	118.79(9)
C3	C2	S2	116.65(13)
C3	C2	S 3	124.56(13)
S5	C3	S4	120.39(9)
C2	C3	S4	123.78(13)
C2	C3	S5	115.69(12)
S5	C1	S2	113.10(9)
S1	C1	S2	122.31(9)
S1	C1	S5	124.58(10)
01	C5	C6	119.46(15)
01	C5	C4	117.29(15)
C6	C5	C4	123.24(15)

Atom	Atom	Length/Å
Fe1	C1	2.0431(17)
Fe1	C2	2.0454(16)
Fe1	C3	2.0505(16)
Fe1	C4	2.0491(16)
Fe1	C5	2.0375(16)
Fe1	C6	2.0552(16)
Fe1	C7	2.0546(16)
Fe1	C8	2.0515(17)
Fe1	С9	2.0489(17)
Fe1	C10	2.0488(16)
01	N1	1.2301(17)
O2	N1	1.2312(17)
N1	C16	1.464(2)
C1	C2	1.435(2)
C1	C5	1.437(2)
C1	C11	1.427(2)
C2	C3	1.422(2)
C3	C4	1.422(2)
C4	C5	1.418(2)
C6	C7	1.422(2)
C6	C10	1.418(3)
C7	C8	1.421(2)
C8	С9	1.417(2)
C9	C10	1.423(3)
C11	C12	1.202(2)
C12	C13	1.432(2)
C13	C14	1.402(2)
C13	C18	1.403(2)

Table C7: Bond angles for Fc-alkyne title compound.

C14	C15	1.385(2)
C15	C16	1.389(2)
C16	C17	1.385(2)
C17	C18	1.380(2)

Table C8: Bond lengths for Fc-alkyne title compound.

Atom	Atom	Angle/°
Fe1	C2	41.09(6)
Fe1	C3	68.60(6)
Fe1	C4	68.76(6)
Fe1	C6	108.20(7)
Fe1	C7	128.28(7)
Fe1	C8	166.33(7)
Fe1	C9	151.89(7)
Fe1	C10	118.21(7)
Fe1	C3	40.62(7)
Fe1	C4	68.63(7)
Fe1	C6	119.18(7)
Fe1	C7	108.59(7)
Fe1	C8	128.09(7)
Fe1	C9	165.58(7)
Fe1	C10	152.64(7)
Fe1	C6	153.07(7)
Fe1	C7	119.24(7)
Fe1	C8	108.37(7)
Fe1	C3	40.58(7)
Fe1	C6	165.33(7)
Fe1	C7	152.40(7)
Fe1	C8	118.25(7)
	Atom Fe1 Fe1	AtomAtomFe1C2Fe1C3Fe1C4Fe1C6Fe1C7Fe1C8Fe1C10Fe1C3Fe1C4Fe1C3Fe1C4Fe1C4Fe1C6Fe1C7Fe1C6Fe1C7Fe1C8Fe1C9Fe1C10Fe1C6Fe1C7Fe1C6Fe1C7Fe1C8Fe1C3Fe1C3Fe1C3Fe1C6Fe1C7Fe1C8Fe1C3Fe1C6Fe1C6Fe1C6Fe1C3Fe1C6Fe1C6Fe1C6Fe1C6Fe1C6Fe1C6Fe1C6Fe1C6Fe1C6Fe1C6Fe1C6Fe1C7Fe1C8

C5Fe1C1 $41.23(7)$ C5Fe1C2 $69.11(7)$ C5Fe1C3 $68.47(7)$ C5Fe1C4 $40.62(7)$ C5Fe1C6 $127.80(7)$ C5Fe1C6 $127.80(7)$ C5Fe1C7 $166.23(7)$ C5Fe1C8 $151.41(7)$ C5Fe1C9 $117.54(7)$ C5Fe1C10 $107.31(7)$ C7Fe1C6 $40.48(7)$ C8Fe1C7 $40.50(6)$ C9Fe1C3 $127.56(7)$ C9Fe1C4 $107.38(7)$ C9Fe1C6 $68.12(7)$ C9Fe1C6 $68.12(7)$ C9Fe1C3 $165.28(7)$ C10Fe1C4 $127.24(7)$ C10Fe1C6 $40.42(7)$ C10Fe1C6 $40.14(7)$ C10Fe1C6 $40.14(7)$ C10Fe1C6 $40.42(7)$ C10Fe1C6 $40.42(7)$ C10Fe1C6 $40.42(7)$ C10Fe1C6 $40.42(7)$ C10Fe1C6 $40.42(7)$ C10Fe1C6 $68.14(7)$ C10Fe1C7 $68.11(7)$ C10Fe1C9 $40.65(7)$ O1N1O2 $123.00(13)$ O1N1O1 $118.36(13)$ O2N1C16 $118.63(13)$ O2C1				
C5Fe1C2 $69.11(7)$ C5Fe1C3 $68.47(7)$ C5Fe1C4 $40.62(7)$ C5Fe1C6 $127.80(7)$ C5Fe1C7 $166.23(7)$ C5Fe1C8 $151.41(7)$ C5Fe1C9 $117.54(7)$ C5Fe1C9 $117.54(7)$ C5Fe1C9 $117.54(7)$ C5Fe1C10 $107.31(7)$ C7Fe1C6 $40.48(7)$ C8Fe1C6 $68.07(7)$ C8Fe1C7 $40.50(6)$ C9Fe1C3 $127.56(7)$ C9Fe1C4 $107.38(7)$ C9Fe1C6 $68.12(7)$ C9Fe1C4 $107.38(7)$ C9Fe1C6 $68.10(7)$ C9Fe1C3 $165.28(7)$ C10Fe1C4 $127.24(7)$ C10Fe1C6 $40.42(7)$ C10Fe1C6 $40.42(7)$ C10Fe1C6 $40.42(7)$ C10Fe1C6 $40.42(7)$ C10Fe1C7 $68.11(7)$ C10Fe1C6 $40.42(7)$ C10Fe1C6 $40.42(7)$ C10Fe1C5 $68.14(7)$ C10Fe1C9 $40.65(7)$ O1N1O2 $123.00(13)$ O1N1C16 $118.36(13)$ O2N1C16 $118.63(13)$ O2C1 <td>C5</td> <td>Fe1</td> <td>C1</td> <td>41.23(7)</td>	C5	Fe1	C1	41.23(7)
C5Fe1C3 $68.47(7)$ C5Fe1C4 $40.62(7)$ C5Fe1C6 $127.80(7)$ C5Fe1C7 $166.23(7)$ C5Fe1C8 $151.41(7)$ C5Fe1C9 $117.54(7)$ C5Fe1C10 $107.31(7)$ C7Fe1C6 $40.48(7)$ C8Fe1C6 $68.07(7)$ C8Fe1C7 $40.50(6)$ C9Fe1C3 $127.56(7)$ C9Fe1C4 $107.38(7)$ C9Fe1C6 $68.12(7)$ C9Fe1C6 $68.12(7)$ C9Fe1C6 $68.10(7)$ C9Fe1C6 $68.10(7)$ C9Fe1C6 $68.10(7)$ C10Fe1C3 $165.28(7)$ C10Fe1C6 $40.42(7)$ C10Fe1C7 $68.11(7)$ C10Fe1C7 $68.11(7)$ C10Fe1C7 $68.11(7)$ C10Fe1C7 $68.11(7)$ C10Fe1C9 $40.65(7)$ O1N1O2 $123.00(13)$ O1N1O2 $123.00(13)$ O2N1C16 $118.63(13)$ C2C1Fe1 $69.54(9)$ C2C1Fe1 $69.18(9)$ C11C1Fe1 $125.49(11)$	C5	Fe1	C2	69.11(7)
C5Fe1C4 $40.62(7)$ C5Fe1C6 $127.80(7)$ C5Fe1C7 $166.23(7)$ C5Fe1C8 $151.41(7)$ C5Fe1C9 $117.54(7)$ C5Fe1C10 $107.31(7)$ C7Fe1C6 $40.48(7)$ C8Fe1C6 $68.07(7)$ C8Fe1C7 $40.50(6)$ C9Fe1C3 $127.56(7)$ C9Fe1C4 $107.38(7)$ C9Fe1C6 $68.12(7)$ C9Fe1C6 $68.12(7)$ C9Fe1C6 $68.12(7)$ C9Fe1C6 $68.12(7)$ C9Fe1C7 $68.10(7)$ C9Fe1C6 $40.42(7)$ C10Fe1C3 $165.28(7)$ C10Fe1C6 $40.42(7)$ C10Fe1C6 $68.14(7)$ C10Fe1C6 $68.14(7)$ C10Fe1C9 $40.65(7)$ O1N1O2 $123.00(13)$ O2N1C16 $118.63(13)$ O2N1C16 $118.63(13)$ O2C1C5107.51(14)C5C1 <td< td=""><td>C5</td><td>Fe1</td><td>C3</td><td>68.47(7)</td></td<>	C5	Fe1	C3	68.47(7)
C5Fe1C6 $127.80(7)$ C5Fe1C7 $166.23(7)$ C5Fe1C8 $151.41(7)$ C5Fe1C9 $117.54(7)$ C5Fe1C10 $107.31(7)$ C7Fe1C6 $40.48(7)$ C8Fe1C6 $68.07(7)$ C8Fe1C7 $40.50(6)$ C9Fe1C3 $127.56(7)$ C9Fe1C4 $107.38(7)$ C9Fe1C6 $68.12(7)$ C9Fe1C6 $68.10(7)$ C9Fe1C6 $68.10(7)$ C9Fe1C7 $68.10(7)$ C9Fe1C8 $40.42(7)$ C10Fe1C3 $165.28(7)$ C10Fe1C4 $127.24(7)$ C10Fe1C6 $40.42(7)$ C10Fe1C6 $68.14(7)$ C10Fe1C9 $40.65(7)$ O1N1O2 $123.00(13)$ O2N1C16 $118.63(13)$ O2N1C16 $118.63(13)$ C2C1Fe1 $69.54(9)$ C2C1C5 $107.51(14)$ C5C1 <td>C5</td> <td>Fe1</td> <td>C4</td> <td>40.62(7)</td>	C5	Fe1	C4	40.62(7)
C5Fe1C7 $166.23(7)$ C5Fe1C8 $151.41(7)$ C5Fe1C9 $117.54(7)$ C5Fe1C10 $107.31(7)$ C7Fe1C6 $40.48(7)$ C8Fe1C6 $68.07(7)$ C8Fe1C7 $40.50(6)$ C9Fe1C3 $127.56(7)$ C9Fe1C4 $107.38(7)$ C9Fe1C6 $68.12(7)$ C9Fe1C7 $68.10(7)$ C9Fe1C3 $165.28(7)$ C10Fe1C4 $127.24(7)$ C10Fe1C6 $40.42(7)$ C10Fe1C7 $68.11(7)$ C10Fe1C9 $40.65(7)$ O1N1O2 $123.00(13)$ O1N1C16 $118.63(13)$ O2N1C16 $118.63(13)$ O2C1C5 $107.51(14)$ C5C1Fe1 $69.18(9)$ C11C1Fe1 $125.49(11)$	C5	Fe1	C6	127.80(7)
C5Fe1C8 $151.41(7)$ C5Fe1C9 $117.54(7)$ C5Fe1C10 $107.31(7)$ C7Fe1C6 $40.48(7)$ C8Fe1C6 $68.07(7)$ C8Fe1C7 $40.50(6)$ C9Fe1C3 $127.56(7)$ C9Fe1C4 $107.38(7)$ C9Fe1C6 $68.12(7)$ C9Fe1C6 $68.12(7)$ C9Fe1C7 $68.10(7)$ C9Fe1C8 $40.42(7)$ C10Fe1C3 $165.28(7)$ C10Fe1C4 $127.24(7)$ C10Fe1C7 $68.11(7)$ C10Fe1C7 $68.11(7)$ C10Fe1C7 $68.14(7)$ C10Fe1C7 $68.11(7)$ C10Fe1C1 $118.36(13)$ O1N1O2 $123.00(13)$ O1N1C16 $118.36(13)$ O2N1C16 $118.63(13)$ C2C1C5 $107.51(14)$ C5C1Fe1 $69.18(9)$ C11C1Fe1 $125.49(11)$	C5	Fe1	C7	166.23(7)
C5Fe1C9 $117.54(7)$ C5Fe1C10 $107.31(7)$ C7Fe1C6 $40.48(7)$ C8Fe1C6 $68.07(7)$ C8Fe1C7 $40.50(6)$ C9Fe1C3 $127.56(7)$ C9Fe1C4 $107.38(7)$ C9Fe1C6 $68.12(7)$ C9Fe1C7 $68.10(7)$ C9Fe1C7 $68.10(7)$ C9Fe1C3 $165.28(7)$ C10Fe1C3 $165.28(7)$ C10Fe1C4 $127.24(7)$ C10Fe1C6 $40.42(7)$ C10Fe1C6 $40.42(7)$ C10Fe1C7 $68.11(7)$ C10Fe1C7 $68.14(7)$ C10Fe1C9 $40.65(7)$ O1N1O2 $123.00(13)$ O1N1C16 $118.36(13)$ O2N1C16 $118.63(13)$ C2C1Fe1 $69.54(9)$ C2C1Fe1 $69.18(9)$ C11C1Fe1 $125.49(11)$	C5	Fe1	C8	151.41(7)
C5Fe1C10 $107.31(7)$ C7Fe1C6 $40.48(7)$ C8Fe1C6 $68.07(7)$ C8Fe1C7 $40.50(6)$ C9Fe1C3 $127.56(7)$ C9Fe1C4 $107.38(7)$ C9Fe1C6 $68.12(7)$ C9Fe1C6 $68.12(7)$ C9Fe1C7 $68.10(7)$ C9Fe1C7 $68.10(7)$ C9Fe1C3 $165.28(7)$ C10Fe1C3 $165.28(7)$ C10Fe1C4 $127.24(7)$ C10Fe1C6 $40.42(7)$ C10Fe1C6 $40.42(7)$ C10Fe1C7 $68.11(7)$ C10Fe1C8 $68.14(7)$ C10Fe1C9 $40.65(7)$ O1N1O2 $123.00(13)$ O1N1C16 $118.36(13)$ O2N1C16 $118.63(13)$ C2C1Fe1 $69.54(9)$ C2C1C5 $107.51(14)$ C5C1Fe1 $69.18(9)$ C11C1Fe1 $125.49(11)$	C5	Fe1	C9	117.54(7)
C7Fe1C6 $40.48(7)$ C8Fe1C6 $68.07(7)$ C8Fe1C7 $40.50(6)$ C9Fe1C3 $127.56(7)$ C9Fe1C4 $107.38(7)$ C9Fe1C6 $68.12(7)$ C9Fe1C6 $68.10(7)$ C9Fe1C7 $68.10(7)$ C9Fe1C8 $40.42(7)$ C10Fe1C3 $165.28(7)$ C10Fe1C4 $127.24(7)$ C10Fe1C6 $40.42(7)$ C10Fe1C7 $68.11(7)$ C10Fe1C7 $68.14(7)$ C10Fe1C7 $68.14(7)$ C10Fe1C9 $40.65(7)$ O1N1O2 $123.00(13)$ O1N1C16 $118.36(13)$ O2N1C16 $118.63(13)$ C2C1Fe1 $69.54(9)$ C2C1Fe1 $69.18(9)$ C11C1Fe1 $125.49(11)$	C5	Fe1	C10	107.31(7)
C8Fe1C6 $68.07(7)$ C8Fe1C7 $40.50(6)$ C9Fe1C3 $127.56(7)$ C9Fe1C4 $107.38(7)$ C9Fe1C6 $68.12(7)$ C9Fe1C7 $68.10(7)$ C9Fe1C7 $68.10(7)$ C9Fe1C8 $40.42(7)$ C10Fe1C3 $165.28(7)$ C10Fe1C4 $127.24(7)$ C10Fe1C6 $40.42(7)$ C10Fe1C7 $68.11(7)$ C10Fe1C7 $68.11(7)$ C10Fe1C8 $68.14(7)$ C10Fe1C9 $40.65(7)$ O1N1O2 $123.00(13)$ O1N1C16 $118.63(13)$ C2C1Fe1 $69.54(9)$ C2C1Fe1 $69.18(9)$ C11C1Fe1 $125.49(11)$	C7	Fe1	C6	40.48(7)
C8Fe1C7 $40.50(6)$ C9Fe1C3 $127.56(7)$ C9Fe1C4 $107.38(7)$ C9Fe1C6 $68.12(7)$ C9Fe1C7 $68.10(7)$ C9Fe1C3 $165.28(7)$ C10Fe1C4 $127.24(7)$ C10Fe1C6 $40.42(7)$ C10Fe1C6 $40.42(7)$ C10Fe1C6 $40.42(7)$ C10Fe1C6 $40.42(7)$ C10Fe1C7 $68.11(7)$ C10Fe1C7 $68.11(7)$ C10Fe1C9 $40.65(7)$ O1N1O2 $123.00(13)$ O1N1C16 $118.36(13)$ O2N1C16 $118.63(13)$ C2C1Fe1 $69.54(9)$ C2C1Fe1 $69.18(9)$ C11C1Fe1 $125.49(11)$	C8	Fe1	C6	68.07(7)
C9Fe1C3 $127.56(7)$ C9Fe1C4 $107.38(7)$ C9Fe1C6 $68.12(7)$ C9Fe1C7 $68.10(7)$ C9Fe1C3 $165.28(7)$ C10Fe1C4 $127.24(7)$ C10Fe1C6 $40.42(7)$ C10Fe1C6 $40.42(7)$ C10Fe1C6 $40.42(7)$ C10Fe1C6 $40.42(7)$ C10Fe1C7 $68.11(7)$ C10Fe1C8 $68.14(7)$ C10Fe1C9 $40.65(7)$ O1N1O2 $123.00(13)$ O1N1C16 $118.36(13)$ O2N1C16 $118.63(13)$ C2C1Fe1 $69.54(9)$ C2C1Fe1 $69.18(9)$ C11C1Fe1 $125.49(11)$	C8	Fe1	C7	40.50(6)
C9Fe1C4 $107.38(7)$ C9Fe1C6 $68.12(7)$ C9Fe1C7 $68.10(7)$ C9Fe1C8 $40.42(7)$ C10Fe1C3 $165.28(7)$ C10Fe1C4 $127.24(7)$ C10Fe1C6 $40.42(7)$ C10Fe1C6 $40.42(7)$ C10Fe1C6 $40.42(7)$ C10Fe1C7 $68.11(7)$ C10Fe1C8 $68.14(7)$ C10Fe1C9 $40.65(7)$ O1N1O2 $123.00(13)$ O1N1C16 $118.36(13)$ O2N1C16 $118.63(13)$ C2C1Fe1 $69.54(9)$ C2C1C5 $107.51(14)$ C5C1Fe1 $69.18(9)$ C11C1Fe1 $125.49(11)$	С9	Fe1	C3	127.56(7)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	С9	Fe1	C4	107.38(7)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	С9	Fe1	C6	68.12(7)
C9Fe1C8 $40.42(7)$ C10Fe1C3 $165.28(7)$ C10Fe1C4 $127.24(7)$ C10Fe1C6 $40.42(7)$ C10Fe1C7 $68.11(7)$ C10Fe1C8 $68.14(7)$ C10Fe1C9 $40.65(7)$ O1N1O2 $123.00(13)$ O1N1C16 $118.36(13)$ O2N1C16 $118.63(13)$ C2C1Fe1 $69.54(9)$ C2C1C5 $107.51(14)$ C5C1Fe1 $69.18(9)$ C11C1Fe1 $125.49(11)$	С9	Fe1	C7	68.10(7)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	С9	Fe1	C8	40.42(7)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	C10	Fe1	C3	165.28(7)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	C10	Fe1	C4	127.24(7)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	C10	Fe1	C6	40.42(7)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	C10	Fe1	C7	68.11(7)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	C10	Fe1	C8	68.14(7)
O1 N1 O2 123.00(13) O1 N1 C16 118.36(13) O2 N1 C16 118.63(13) O2 C1 Fe1 69.54(9) C2 C1 C5 107.51(14) C5 C1 Fe1 69.18(9) C11 C1 Fe1 125.49(11)	C10	Fe1	C9	40.65(7)
O1 N1 C16 118.36(13) O2 N1 C16 118.63(13) C2 C1 Fe1 69.54(9) C2 C1 C5 107.51(14) C5 C1 Fe1 69.18(9) C11 C1 Fe1 125.49(11)	01	N1	O2	123.00(13)
O2 N1 C16 118.63(13) C2 C1 Fe1 69.54(9) C2 C1 C5 107.51(14) C5 C1 Fe1 69.18(9) C11 C1 Fe1 125.49(11)	01	N1	C16	118.36(13)
C2 C1 Fe1 69.54(9) C2 C1 C5 107.51(14) C5 C1 Fe1 69.18(9) C11 C1 Fe1 125.49(11)	O2	N1	C16	118.63(13)
C2 C1 C5 107.51(14) C5 C1 Fe1 69.18(9) C11 C1 Fe1 125.49(11)	C2	C1	Fe1	69.54(9)
C5 C1 Fe1 69.18(9) C11 C1 Fe1 125.49(11)	C2	C1	C5	107.51(14)
C11 C1 Fe1 125.49(11)	C5	C1	Fe1	69.18(9)
	C11	C1	Fe1	125.49(11)

C11C1C2 $127.74(15)$ C11C1C5 $124.74(15)$ C1C2Fe1 $69.37(9)$ C3C2Fe1 $69.37(9)$ C3C2C1 $107.72(14)$ C2C3Fe1 $69.50(9)$ C4C3Fe1 $69.50(9)$ C4C3Fe1 $69.66(9)$ C4C3C2 $108.54(14)$ C3C4Fe1 $69.76(9)$ C5C4C3C2C5C4Fe1 $69.25(9)$ C5C4C3 $108.16(15)$ C1C5Fe1 $69.60(9)$ C4C5Fe1 $69.60(9)$ C4C5Fe1 $69.60(9)$ C4C5Fe1 $69.60(9)$ C4C5Fe1 $69.60(9)$ C4C5Fe1 $69.60(9)$ C4C5Fe1 $69.60(9)$ C4C5C1 $108.06(15)$ C7C6Fe1 $69.74(9)$ C10C6C7 $108.03(15)$ C6C7Fe1 $69.63(9)$ C8C7C6 $107.88(15)$ C7C8Fe1 $69.87(9)$ C8C9Fe1 $69.89(9)$ C9C8C7 $108.12(15)$ C8C9Fe1 $69.67(9)$ C6C10Fe1 $69.68(9)$ C10C9Fe1 $69.68(9)$ C10C6C10Fe1 $69.68(9)$ C10C9Fe1<				
C11C1C5124.74(15)C1C2Fe1 $69.37(9)$ C3C2C1 $107.72(14)$ C2C3C2C1 $107.72(14)$ C2C3Fe1 $69.50(9)$ C4C3Fe1 $69.66(9)$ C4C3C2 $108.54(14)$ C3C4Fe1 $69.76(9)$ C5C4Fe1 $69.25(9)$ C5C4C3 $108.16(15)$ C1C5Fe1 $69.60(9)$ C4C5Fe1 $69.60(9)$ C4C5Fe1 $69.60(9)$ C4C5Fe1 $69.60(9)$ C4C5Fe1 $69.60(9)$ C4C5Fe1 $69.60(9)$ C4C5Fe1 $69.60(9)$ C4C5C1 $108.06(15)$ C7C6Fe1 $69.78(9)$ C10C6C7 $108.03(15)$ C6C7Fe1 $69.78(9)$ C10C6C7 $108.03(15)$ C7C8Fe1 $69.63(9)$ C8C7C6 $107.88(15)$ C7C8Fe1 $69.89(9)$ C9C8C7 $108.12(15)$ C8C9Fe1 $69.89(9)$ C8C9C10 $107.97(15)$ C10C9Fe1 $69.68(9)$ C10C9Fe1 $69.68(9)$ C10C9Fe1 $69.68(9)$ C12C11C1 $177.07(18)$	C11	C1	C2	127.74(15)
C1C2Fe1 $69.37(9)$ C3C2Fe1 $69.88(9)$ C3C2C1 $107.72(14$ C2C3Fe1 $69.50(9)$ C4C3Fe1 $69.50(9)$ C4C3C2 $108.54(14)$ C3C4Fe1 $69.76(9)$ C4C3C2 $108.54(14)$ C3C4Fe1 $69.76(9)$ C5C4Fe1 $69.25(9)$ C5C4C3 $108.16(15)$ C1C5Fe1 $69.60(9)$ C4C5Fe1 $69.60(9)$ C4C5C1 $108.06(15)$ C7C6Fe1 $69.74(9)$ C10C6C7 $108.03(15)$ C6C7Fe1 $69.63(9)$ C10C6C7 $108.03(15)$ C6C7Fe1 $69.63(9)$ C8C7C6 $107.88(15)$ C7C8Fe1 $69.69(9)$ C9C8C7 $108.12(15)$ C8C9Fe1 $69.89(9)$ C9C8C7 $108.12(15)$ C8C9Fe1 $69.67(9)$ C6C10Fe1 $70.03(9)$ C6C10C9 $108.00(15)$ C9C10Fe1 $69.68(9)$ C12C11C1 $177.07(18)$	C11	C1	C5	124.74(15)
C3C2Fe1 $69.88(9)$ C3C2C1 $107.72(14)$ C2C3Fe1 $69.50(9)$ C4C3C2 $108.54(14)$ C3C4C3C2 $108.54(14)$ C3C4Fe1 $69.76(9)$ C5C4Fe1 $69.25(9)$ C5C4C3 $108.16(15)$ C1C5Fe1 $69.60(9)$ C4C5Fe1 $69.60(9)$ C4C5Fe1 $69.60(9)$ C4C5C1 $108.06(15)$ C7C6Fe1 $69.74(9)$ C10C6C7 $108.03(15)$ C6C7Fe1 $69.78(9)$ C8C7Fe1 $69.63(9)$ C9C8C7 $108.12(15)$ C8C9Fe1 $69.69(9)$ C9C8C7 $108.12(15)$ C8C9Fe1 $69.67(9)$ C9C8C7 $108.12(15)$ C8C9C10 $107.97(15)$ C10C9Fe1 $69.67(9)$ C6C10Fe1 $70.03(9)$ C6C10C9 $108.00(15)$ C9C10Fe1 $69.68(9)$ C12C11C1 $177.07(18)$	C1	C2	Fe1	69.37(9)
C3C2C1 $107.72(14)$ C2C3Fe1 $69.50(9)$ C4C3Fe1 $69.66(9)$ C4C3C2 $108.54(14)$ C3C4Fe1 $69.76(9)$ C5C4Fe1 $69.25(9)$ C5C4C3 $108.16(15)$ C1C5Fe1 $69.60(9)$ C4C5Fe1 $69.60(9)$ C4C5Fe1 $70.13(9)$ C4C5C1 $108.06(15)$ C7C6Fe1 $69.74(9)$ C10C6C7 $108.03(15)$ C6C7Fe1 $69.78(9)$ C8C7Fe1 $69.63(9)$ C9C8C7C6C7C8Fe1 $69.69(9)$ C9C8C7 $108.12(15)$ C8C9Fe1 $69.89(9)$ C9C8C7 $108.12(15)$ C8C9Fe1 $69.67(9)$ C6C10Fe1 $70.03(9)$ C6C10Fe1 $69.68(9)$ C12C11C1 $177.07(18)$	C3	C2	Fe1	69.88(9)
C2 $C3$ Fe1 $69.50(9)$ $C4$ $C3$ $Fe1$ $69.66(9)$ $C4$ $C3$ $C2$ $108.54(14)$ $C3$ $C4$ $Fe1$ $69.76(9)$ $C5$ $C4$ $Fe1$ $69.76(9)$ $C5$ $C4$ $Fe1$ $69.25(9)$ $C5$ $C4$ $C3$ $108.16(15)$ $C1$ $C5$ $Fe1$ $69.60(9)$ $C4$ $C5$ $Fe1$ $70.13(9)$ $C4$ $C5$ $Fe1$ $70.13(9)$ $C4$ $C5$ $C1$ $108.06(15)$ $C7$ $C6$ $Fe1$ $69.74(9)$ $C10$ $C6$ $C7$ $108.03(15)$ $C6$ $C7$ $Fe1$ $69.63(9)$ $C8$ $C7$ $Fe1$ $69.63(9)$ $C9$ $C8$ $C7$ $C6$ $C9$ $C8$ $C7$ $108.12(15)$ $C8$ $C9$ $Fe1$ $69.69(9)$ $C9$ $C8$ $C7$ $108.12(15)$ $C8$ $C9$ $C10$ $107.97(15)$ $C10$ $C9$ $Fe1$ $69.67(9)$ $C6$ $C10$ $Fe1$ $70.03(9)$ $C6$ $C10$ $Fe1$ $69.68(9)$ $C12$ $C11$ $C1$ $177.07(18)$	C3	C2	C1	107.72(14)
C4C3Fe1 $69.66(9)$ C4C3C2 $108.54(14)$ C3C4Fe1 $69.76(9)$ C5C4Fe1 $69.25(9)$ C5C4C3 $108.16(15)$ C1C5Fe1 $69.60(9)$ C4C5Fe1 $70.13(9)$ C4C5Fe1 $69.74(9)$ C10C6Fe1 $69.75(9)$ C10C6C7 $108.03(15)$ C6C7Fe1 $69.78(9)$ C8C7Fe1 $69.63(9)$ C9C8C7I08.12(15)C8C9Fe1 $69.69(9)$ C9C8C7 $108.12(15)$ C8C9C10 $107.97(15)$ C10C9Fe1 $69.67(9)$ C8C9C10 $107.97(15)$ C10C9Fe1 $69.68(9)$ C10C9Fe1 $69.68(9)$ C10C9Fe1 $69.68(9)$ C10C9C10Fe1C6C10Fe1 $70.03(9)$ C6C10C9 $108.00(15)$ C9C10Fe1 $69.68(9)$ C12C11C1 $177.07(18)$	C2	C3	Fe1	69.50(9)
C4C3C2 $108.54(14)$ C3C4Fe1 $69.76(9)$ C5C4Fe1 $69.25(9)$ C5C4C3 $108.16(15)$ C1C5Fe1 $69.60(9)$ C4C5Fe1 $70.13(9)$ C4C5C1 $108.06(15)$ C7C6Fe1 $69.74(9)$ C10C6Fe1 $69.78(9)$ C10C6C7 $108.03(15)$ C6C7Fe1 $69.78(9)$ C8C7C6 $107.88(15)$ C7C8Fe1 $69.69(9)$ C9C8C7 $108.12(15)$ C8C9Fe1 $69.89(9)$ C9C8C7 $108.12(15)$ C8C9Fe1 $69.67(9)$ C9C8C7 $108.12(15)$ C8C9Fe1 $69.67(9)$ C6C10Fe1 $70.03(9)$ C6C10C9 $108.00(15)$ C9C10Fe1 $69.68(9)$ C12C11C1 $177.07(18)$	C4	C3	Fe1	69.66(9)
C3C4Fe1 $69.76(9)$ C5C4Fe1 $69.25(9)$ C5C4C3 $108.16(15)$ C1C5Fe1 $69.60(9)$ C4C5Fe1 $70.13(9)$ C4C5C1 $108.06(15)$ C7C6Fe1 $69.74(9)$ C10C6Fe1 $69.78(9)$ C10C6C7 $108.03(15)$ C6C7Fe1 $69.63(9)$ C8C7C6 $107.88(15)$ C7C8Fe1 $69.87(9)$ C9C8C7 $108.12(15)$ C8C9Fe1 $69.89(9)$ C9C8C7 $108.12(15)$ C8C9Fe1 $69.67(9)$ C9C8C7 $108.12(15)$ C10C9Fe1 $69.67(9)$ C6C10Fe1 $70.03(9)$ C6C10C9 $108.00(15)$ C9C10Fe1 $69.68(9)$ C12C11C1 $177.07(18)$	C4	C3	C2	108.54(14)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	C3	C4	Fe1	69.76(9)
C5C4C3 $108.16(15)$ C1C5Fe1 $69.60(9)$ C4C5Fe1 $70.13(9)$ C4C5C1 $108.06(15)$ C7C6Fe1 $69.74(9)$ C10C6Fe1 $69.55(9)$ C10C6C7 $108.03(15)$ C6C7Fe1 $69.78(9)$ C8C7Fe1 $69.63(9)$ C9C8C7C6C9C8C7 $108.12(15)$ C8C9Fe1 $69.89(9)$ C9C8C7 $108.12(15)$ C6C10C9Fe1 $69.67(9)$ C6C10Fe1 $70.03(9)$ C6C10C9I08.00(15)C9C10C9Fe1 $69.68(9)$ C12C11C1 $177.07(18)$	C5	C4	Fe1	69.25(9)
C1C5Fe1 $69.60(9)$ C4C5Fe1 $70.13(9)$ C4C5C1 $108.06(15)$ C7C6Fe1 $69.74(9)$ C10C6Fe1 $69.74(9)$ C10C6C7 $108.03(15)$ C6C7Fe1 $69.78(9)$ C8C7Fe1 $69.78(9)$ C8C7C6 $107.88(15)$ C7C8Fe1 $69.87(9)$ C9C8Fe1 $69.87(9)$ C9C8C7 $108.12(15)$ C8C9Fe1 $69.89(9)$ C9C8C9Fe1C10C9Fe1 $69.67(9)$ C6C10Fe1 $70.03(9)$ C6C10C9I08.00(15)C9C10Fe1 $69.68(9)$ C12C11C1 $177.07(18)$	C5	C4	C3	108.16(15)
C4C5Fe1 $70.13(9)$ C4C5C1 $108.06(15)$ C7C6Fe1 $69.74(9)$ C10C6Fe1 $69.55(9)$ C10C6C7 $108.03(15)$ C6C7Fe1 $69.78(9)$ C8C7Fe1 $69.63(9)$ C8C7C6 $107.88(15)$ C7C8Fe1 $69.69(9)$ C9C8C7 $108.12(15)$ C8C9Fe1 $69.69(9)$ C9C8C7 $108.12(15)$ C8C9Fe1 $69.69(9)$ C9C8C9Fe1C10C9Fe1 $69.67(9)$ C6C10Fe1 $70.03(9)$ C6C10C9 $108.00(15)$ C9C10Fe1 $69.68(9)$ C12C11C1 $177.07(18)$	C1	C5	Fe1	69.60(9)
C4C5C1 $108.06(15)$ C7C6Fe1 $69.74(9)$ C10C6Fe1 $69.74(9)$ C10C6C7 $108.03(15)$ C6C7Fe1 $69.78(9)$ C8C7Fe1 $69.63(9)$ C8C7C6 $107.88(15)$ C7C8Fe1 $69.69(9)$ C9C8C7 $108.12(15)$ C8C9Fe1 $69.89(9)$ C9C8C7 $108.12(15)$ C8C9Fe1 $69.69(9)$ C9C8C7 $108.12(15)$ C8C9Fe1 $69.69(9)$ C9C8C9Fe169.89(9)C10 $107.97(15)$ C10C9Fe1 $69.67(9)$ C6C10Fe1 $70.03(9)$ C6C10C9 $108.00(15)$ C9C10Fe1 $69.68(9)$ C12C11C1 $177.07(18)$	C4	C5	Fe1	70.13(9)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	C4	C5	C1	108.06(15)
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	C7	C6	Fe1	69.74(9)
C10C6C7108.03(15)C6C7Fe169.78(9)C8C7Fe169.63(9)C8C7C6107.88(15)C7C8Fe169.87(9)C9C8Fe169.69(9)C9C8C7108.12(15)C8C9Fe169.89(9)C9C8C7108.12(15)C8C9Fe169.89(9)C8C9Fe169.67(9)C6C10Fe170.03(9)C6C10C9108.00(15)C9C10Fe169.68(9)C12C11C1177.07(18)	C10	C6	Fe1	69.55(9)
C6 C7 Fe1 69.78(9) C8 C7 Fe1 69.63(9) C8 C7 C6 107.88(15 C7 C8 Fe1 69.87(9) C9 C8 Fe1 69.69(9) C9 C8 C7 108.12(15 C8 C9 Fe1 69.89(9) C8 C9 Fe1 69.89(9) C8 C9 Fe1 69.63(9) C8 C9 Fe1 69.69(9) C8 C9 Fe1 69.69(9) C8 C9 C10 107.97(15 C10 C9 Fe1 69.67(9) C6 C10 Fe1 70.03(9) C6 C10 C9 108.00(15 C9 C10 Fe1 69.68(9) C12 C11 C1 177.07(18	C10	C6	C7	108.03(15)
C8 C7 Fe1 69.63(9) C8 C7 C6 107.88(15) C7 C8 Fe1 69.87(9) C9 C8 Fe1 69.69(9) C9 C8 C7 108.12(15) C8 C9 Fe1 69.89(9) C8 C9 Fe1 69.89(9) C8 C9 C10 107.97(15) C10 C9 Fe1 69.67(9) C6 C10 Fe1 70.03(9) C6 C10 C9 108.00(15) C9 C10 Fe1 69.68(9) C12 C11 C1 177.07(18)	C6	C7	Fe1	69.78(9)
C8 C7 C6 107.88(15) C7 C8 Fe1 69.87(9) C9 C8 Fe1 69.69(9) C9 C8 C7 108.12(15) C8 C9 Fe1 69.89(9) C8 C9 Fe1 69.89(9) C8 C9 Fe1 69.89(9) C8 C9 C10 107.97(15) C10 C9 Fe1 69.67(9) C6 C10 Fe1 70.03(9) C6 C10 C9 108.00(15) C9 C10 Fe1 69.68(9) C12 C11 C1 177.07(18)	C8	C7	Fe1	69.63(9)
C7 C8 Fe1 69.87(9) C9 C8 Fe1 69.69(9) C9 C8 C7 108.12(15 C8 C9 Fe1 69.89(9) C8 C9 Fe1 69.89(9) C8 C9 C10 107.97(15 C10 C9 Fe1 69.67(9) C6 C10 Fe1 70.03(9) C6 C10 C9 108.00(15 C9 C10 Fe1 69.68(9) C12 C11 C1 177.07(18	C8	C7	C6	107.88(15)
C9C8Fe169.69(9)C9C8C7108.12(15)C8C9Fe169.89(9)C8C9C10107.97(15)C10C9Fe169.67(9)C6C10Fe170.03(9)C6C10C9108.00(15)C9C10Fe169.68(9)C12C11C1177.07(18)	C7	C8	Fe1	69.87(9)
C9 C8 C7 108.12(15) C8 C9 Fe1 69.89(9) C8 C9 C10 107.97(15) C10 C9 Fe1 69.67(9) C6 C10 Fe1 70.03(9) C6 C10 C9 108.00(15) C9 C10 Fe1 69.68(9) C12 C11 C1 177.07(18)	C9	C8	Fe1	69.69(9)
C8 C9 Fe1 69.89(9) C8 C9 C10 107.97(15 C10 C9 Fe1 69.67(9) C6 C10 Fe1 70.03(9) C6 C10 C9 108.00(15 C9 C10 Fe1 69.68(9) C12 C11 C1 177.07(18	C9	C8	C7	108.12(15)
C8 C9 C10 107.97(15) C10 C9 Fe1 69.67(9) C6 C10 Fe1 70.03(9) C6 C10 C9 108.00(15) C9 C10 Fe1 69.68(9) C12 C11 C1 177.07(18)	C8	C9	Fe1	69.89(9)
C10C9Fe169.67(9)C6C10Fe170.03(9)C6C10C9108.00(15)C9C10Fe169.68(9)C12C11C1177.07(18)	C8	C9	C10	107.97(15)
C6 C10 Fe1 70.03(9) C6 C10 C9 108.00(15) C9 C10 Fe1 69.68(9) C12 C11 C1 177.07(18)	C10	C9	Fe1	69.67(9)
C6C10C9108.00(15)C9C10Fe169.68(9)C12C11C1177.07(18)	C6	C10	Fe1	70.03(9)
C9 C10 Fe1 69.68(9) C12 C11 C1 177.07(18)	C6	C10	C9	108.00(15)
C12 C11 C1 177.07(18	C9	C10	Fe1	69.68(9)
	C12	C11	C1	177.07(18)

C11	C12	C13	178.15(18)
C14	C13	C12	120.19(15)
C14	C13	C18	119.13(15)
C18	C13	C12	120.67(15)
C15	C14	C13	120.74(15)
C14	C15	C16	118.24(14)
C15	C16	N1	118.51(14)
C17	C16	N1	118.86(14)
C17	C16	C15	122.62(15)
C18	C17	C16	118.53(15)
C17	C18	C13	120.73(15)