Excitonic States in Crystalline Organic Semiconductors: A Condensed Matter Approach

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EXCITONIC STATES IN CRYSTALLINE ORGANIC SEMICONDUCTORS: A CONDENSED MATTER APPROACH

A Dissertation Presented

by

Lane Wright Manning

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In this work, a new condensed matter approach to the study of excitons based on crystalline thin films of the organic molecule phthalocyanine is introduced. The premise is inspired by a wealth of studies in inorganic semiconductor ternary alloys (such as AlGaN, InGaN, SiGe) where tuning compositional disorder can result in exciton localization by alloy potential fluctuations. Comprehensive absorption, luminescence, linear dichroism and electron radiative lifetime studies were performed on both pure and alloy samples of metal-free octabutoxy-phthalocyanine (H$_2$OBPc) and transition metal octabutoxy-phthalocyanines (MOBPC), where M = Mn, Co, Ni, and Cu. Varying the ratios of the metal to metal-free OBPcs in all of these studies, as well as looking across a temperature range from 4 Kelvin up to room temperature is essential for quantifying the exciton wavefunction delocalization in crystalline thin films. A comparative study is performed across organic aromatic ringed molecules of different sizes in the same family: phthalocyanine, naphthalocyanine and tetraphenyl porphyrin. In an analogy to nanocrystals and their size effects, variations in π-conjugated ring sizes imply an altering in the number of delocalized electrons, impacting the wavefunction overlap between π-π orbitals along the perpendicular axis of neighboring molecules. Finally, complementary measurements that assess crystallinity of the in-house deposited thin films, including individual grain absorption, small angle x-ray scattering images, polarized microscope images and a new unique LD microscopy dual imaging/luminescence technique are also discussed.
This is for my mother and my father.
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Chapter 1

Introduction and Background

This chapter gives an introduction to organic molecules and a brief background to their unique electronic and excitonic dynamics. Properties of molecular crystals in the solid state depend heavily on the packing and orientation of molecules themselves, and therefore bridging the understanding between proposed theoretical models and experimental results will lend insight into and eventual control over these properties.

1.1 Motivation

With increased interest in organic semiconducting systems for many varied research and commercial applications, crystalline thin films of small molecules present an intriguing system for both fundamental and applied studies of electronic properties and exchange interactions in the larger field of organic electronics. Their optical, transport and magnetic properties belong to an intermediate regime where well-established models fail to fully describe the electronic behavior and do not accurately predict the experimental observations.
The processing method, purity, and crystalline quality of the films themselves can also greatly impact exciton behavior. With this in mind, understanding the nature of the dynamics of diffusion and delocalization of excitons (or electron-hole pairs) becomes a necessity for understanding and eventually controlling the behavior of these materials in organic electronic applications. Coupling between polarized light and electronic states in crystalline ordered materials can give insight into directionally polarized excitons, orbital symmetries, exchange interactions, spin dynamics and even collective magnetic behavior through polarization-resolved spectroscopy. Novel solution-processing deposition techniques in tandem with chemical synthesis design of small molecule soluble derivatives represent a viable avenue for exploring these excitons using organic analogues of semiconductor alloyed systems, where excitonic properties could be tunable through alloy concentration.

The main purpose of the work presented in this thesis is to study a system, and more specifically a family of molecular crystals, which can be spectroscopically explored in order to extract insight into intermolecular interactions and exciton behavior, by using a systematic approach of thin film fabrication and a mixture of molecules to purposefully inhibit exciton delocalization and then subsequently tune this behavior through mixtures of slightly different organic small molecules.

1.2 Organic Molecules vs. Silicon

Inorganic silicon and gallium arsenide have for decades dominated the conversation regarding semiconductors in electronic applications, and for good reason. The stability and performance of these materials for commercial uses was unparalleled for
decades. However, Tang’s seminal 1986 paper using copper phthalocyanine as the main photon absorbing layer in an organic solar cell is widely seen as the tipping point to accepting organic molecules as an actual viable option for commercial applications (rather than purely a 'research interest') [1]. This was then quickly followed by Tang and VanSlyke’s paper on an organic electroluminescent device, showing that organic molecules were not only efficient absorbers of photons, but also efficient emitters as well, with the additional benefits of fast response and low voltage drive still able to achieve efficient emission [2]. The primary reason for the importance of these two papers is that up until around that time, organic materials had been mostly used only as passive layers (or insulators) and photoresists in actual device applications [3]. Tang and VanSlyke showed that organic molecules could instead be implemented as the active part in devices (usually as a part of a donor/acceptor heterojunction), both as absorbing or emitting layers, and brought to the forefront of the scientific community a whole new class of materials that perhaps had not been previously considered as viable for commercial applications.

This sparked a renaissance of sorts, where organic molecules that had been fairly well-known and well-studied for decades now suddenly reemerged in applications that were never imagined for them. Commercially, the reason that interest spiked so suddenly in these materials stemmed from two major points. The primary benefit of most organic materials is that they are generally less expensive to manufacture than their silicon counterparts for the purposes of commercial applications, and have the additional benefit of being biocompatible. This of course is one of the most pertinent qualities for commercial applications, and is an area that organic electronics typically excel in. While electronic and transport properties are still being improved,
the cost-effectiveness and ease of processing is really the benchmark quality for why these materials continue to be of great interest [3]. The second, and somewhat more recent development is on a broader level, the search for renewable energy sources that have little to no environmental impact, as many commercial and governmental organizations look to move away from more traditional energy sources that have limited stockpiles and increasing costs to acquire and refine [4], [5].

This research has continued since the 1970s and 1980s, specifically on the chemistry side where the properties of organic molecules are tuned through chemical engineering, arguably culminating in the Nobel Prize in Chemistry in 2000 for the recognition of the work of Heeger, MacDiarmid and Shirakawa (which actually began in the late 1970s) where they show the ability to tune properties of polymers (or plastics) through doping in order to actually change from an insulator to becoming electrically conductive [6], [7], [8], and the reporting of electroluminescence from conjugated polymers [9], [10] through chemical engineering as well. It was in fact the ordering of the doped polyacetylene in the solid state that allowed for conductivity, and this idea of new and exciting properties as a result of adjusting molecular packing, side-chains [11], and even doping in thin films and in bulk that has evolved throughout the entire field of organic electronics.

This has led to the development of many novel device applications based on organic semiconductors in the past two decades, as the enhancement of desirable properties in organic molecules has become a reality. In addition to their cost-effectiveness and unique functionalities, organic molecules are also viable due to stability and robustness, most showing little degradation after exposure to air even above room temperature. More specifically, with regard to commercial applications, there are
advantages organic molecules possess over the more typical crystalline silicon or other inorganics used in many devices, and the gap in efficiency between them is closing quickly [12], [13], [14]. Recent commercial applications include, but are not limited to organic photovoltaics, organic LEDs, flexible organic displays and organic field effect transistors [15], [16], [14], [17], [18], [4], [19], [20], [5]. Generally these are categorized based on the function that organics will play in the device, and therefore specific properties that chemical engineering may be able to tailor in these molecules.

Those that involve the absorption of light as the primary function of the organic material, such as solar cells, will benefit from the broad, intense absorption bands in both small molecules and polymers that align with a large part of the solar spectrum. This is typically a result of significant wave function overlap between the ground and lowest excited states, as well as the broadening of absorption bands from geometric relaxations occurring in the excited state [4]. However, as photoexcitation leads to the creation of electron-holes pairs in these materials, a majority of those excitons will be inhibited in their recombination, even as they diffuse through the material [21]. The binding energy of these electron-hole pairs are typically greater than the room temperature thermal energy, therefore the exciton will often only separate in the presence of a heterojunction (the interface between layers of two different species, or a combination of an organic polymer and a molecule) [21], [22], which will either dissociate the exciton, creating free carriers, or by creating polaron pairs that eventually will overcome the Coulomb energy in the presence of an electric potential [23], [14], [17], [5]. Therefore the ability of excitons to reach these heterojunctions (long exciton diffusion lengths) is the critical parameter for device applications, and understanding the dynamics of exciton diffusion in these organic materials, which is often greatly impacted
by the orientation and packing of the molecules in crystalline ordering, is paramount to increased efficiency and performance for organic photovoltaic cells [24], [25], [26].

The importance of alignment and packing of molecules is also essential for field-effect transistor (FET) applications, where the crystalline order and the performance of the device shows a direct correlation [27], [28] [25]. This is thanks to the anisotropy of mobilities in ordered organic molecules, which often self-assemble in either a herringbone structure or a face-to-face one-dimensional chain structure [29] [30], where the intermolecular interaction originating from the $\pi-\pi$ orbital overlap between neighboring molecules dictates electronic properties [31], and the quality of crystallinity and long-range order directly impacts free carriers [32]. In this case purity is essential, as defects or traps act as barriers to charge carriers in the solid state [28], [33], and even more specifically, the density of defects or traps in these solids can even influence or establish different regimes of transport at varying temperatures [34], [35]. In FET devices (as well as applications such as Radio Frequency Identification (RFID) devices [36]) carrier mobilities are not the only important characteristic required, as often times the voltage stability and threshold voltage, as well as on/off current are often the most relevant features for organic materials in FETs [27], [37].

Finally, organic molecules can be applied as the emitting layers in device applications, such as organic light-emitting diodes (OLEDs), in which case short diffusion lengths of excitons will often be preferred to prevent loss of radiative recombination to non-radiative sites within the solid layer [38], [35]. Here the process is an inverse of what is desired for solar-cell devices, where in OLEDs electrons and holes would be injected into the LUMO and HOMO respectively, and at some boundary they recombine to produce luminescence. In this case, device efficiency is reliant on minimizing
barriers for carrier injection and recombination through tuning of the energy levels in the molecular solid state [28].

A diagram of an organic solar-cell, field-effect transistor, and light-emitting diode created from organic discotic molecules are shown in Figure 1.1 below, adapted from [28].

![Diagram of organic solar-cell, field-effect transistor, and light-emitting diode](image)

*Figure 1.1: a) Diagram of organic photovoltaic device with vertical transport geometry b) Diagram of organic field-effect transistor device with lateral transport geometry c) Diagram of organic light-emitting diode, with exciton recombination at the heterojunction. [28]*

Recent incorporation of these organic molecules into devices have produced some exciting flexible displays (using OLEDs) and flexible photovoltaics (as a result of not needing rigid Indium Tin Oxide (ITO) glass or some other non-flexible backing materials in solar cells). Some examples of these exciting new device applications are pictured in Figure 1.2.
1.2.1 **Organic Small Molecules**

It is generally considered that there are two primary families of organic molecules used in device applications, polymers (or "plastics") [43], [44], [45] and small molecules [46], [28], [47]. Often times it is the $\pi$-orbital overlap of these molecules in the solid state that is responsible for enhancement of beneficial properties, including conductivity.
and transport of both free (electrons and holes) carriers and bound states (excitons) [3], [48]. The benefits of polymers themselves are well-studied by many other groups, even to the point of making hybrid silicon/organic polymer blends recently [49], which can open a whole new approach to organic photovoltaics and is fascinating in and of itself, but is beyond the scope of what will be discussed here. Instead, the focus of my research lies within the family of organic small molecules.

Throughout the past decade, organic small molecules have returned to the forefront when discussing new trends in fabrication of organic electronic devices, and the fundamental experimental and theoretical studies aimed at understanding the physics of electrons in these devices and the quantum mechanical interactions taking place at the molecular level in these systems are of great interest [50], [34], [51], [52]. Application development of organic molecules in the solid state is often limited by the quality of the films themselves, where low carrier mobilities may be a result of large numbers of defects in the polymer-based materials [53].

More specifically, certain families of conjugated ringed molecules (such as the acenes, the coronenes, and phthalocyanines) have shown great promise for flexible organic electronics and photovoltaic devices due to their unique broad visible/IR absorption bands and large carrier mobilities [54], [28], [55], [56], [57], [58]. Shown below in Figure 1.3 are some of the most well-known organic small molecules.
A common theme can be seen amongst these organic molecules shown above, which is the conjugation within the carbon rings, where thanks to the Hückel Rule these molecules can be considered aromatic. This is as a result of Hückel Molecular Orbital Theory, which states that "planar monocyclic completely conjugated hydro-
carbons will be aromatic when the ring contains $4n + 2 \pi$ electrons" [59]. Taking, for example, the simplest case of a benzene ring in one of the previously shown molecules, it can be shown that the enthalpy of the cyclic ring is significantly lower than the prediction from the carbon-carbon and carbon-hydrogen bonds in a Kekulé representation (that is with lines representing alternating single and double bonds) [60]. This reduced energy and increased stability of aromatic rings is largely in part due to the delocalization of the electrons.

More specifically, in carbon, its six electrons will fill 2 s orbitals and have the two remaining electrons in the 2p orbital (as $1s^22s^22p_x^12p_y^1$). However in a structure such as benzene, each carbon forms a bond with the two neighboring carbons, as well as a hydrogen, which would require 3 unpaired electrons. In order to satisfy this condition, one of the $2s^2$ electrons is promoted to the empty $2p_z$ orbital, giving four unpaired electrons. In this case, the single $2s$ orbital and two of the $2p$ orbitals will hybridize, and these $sp^2$ orbitals are responsible for creating the sigma bonds between the two other carbons and the single hydrogen in the plane of the ring (which will be oriented as far from each other as possible, $120^\circ$), shown in Figure 1.4a. The remaining p orbital will then be oriented out of the plane of the ring for each carbon (as can be seen in Figure 1.4b), and these remaining six electrons are delocalized through the sideways overlap of the p orbitals, creating a system of covalent $\pi$-bonds in which the electrons are spread over the entire ring in bonding molecular orbitals (shown in Figure 1.4c) [60].
The completely filled set of bonding orbitals then gives the benzene (or similar aromatic molecules) their well-known stability, both thermodynamically and with regards to chemical reactivity. Even in situations where a nitrogen replaces a carbon-hydrogen site (such as for phthalocyanines and porphyrins), molecular orbital calculations show resonance stability is conserved, thus making those molecules extremely stable as well [60]. As these molecules crystallize, the relatively close packing in stacks or herringbone structures allows significant intermolecular overlap of the $\pi$-orbitals, and it is this interaction across adjacent molecules that gives some of the unique properties seen in these organic systems in the solid state.

Building up from the benzene molecule, are antracene, tetracene and pentacene, with three, four and five linearly-fused benzene rings respectively. Pentacene is the most well-studied of these organic small molecules, specifically the more soluble derivative triisopropylsilylethynyl (TIPS) pentacene, and is frequently utilized in devices due to large transistor hole mobilities in the solid state [61] (upwards of 5
Interestingly the most promising avenue of improvement lies in substrate surface treatments, purification and a better understanding of how the packing of molecules influences coherence and band transport \([46], [63]\). This is because the proximity of organic molecules in the solid state leads to variations in \(\pi\)-orbital wave function overlap in adjacent molecules in the crystalline lattice \([64], [61]\), a trend that is seen across the antracene and tetracene and rubrene as well \([33], [65], [66], [67]\). Here the key to scaling up properties for devices and understanding macroscopic properties often relies heavily on understanding both free carriers, and bound electron-hole pairs in these materials \([68], [57], [23], [69]\), specifically where purity and long-range ordering of the material in the crystalline solid plays an integral role in diffusion lengths and mobilities, and how dissociation of the exciton will occur to produce free charge carriers.

In the solid state, many organic \(\pi\)-conjugated small molecules including phthalocyanines, porphyrins, and the acenes mentioned above can be viewed as building blocks self-assembled into arrays that allow probing of how the \(\pi\)-\(\pi\) orbital interactions between adjacent molecules will influence larger macroscopic behavior in the crystal itself \([70], [71], [43], [30], [72], [73], [74]\). Therefore a determining factor for how these organic molecules will perform in device-related applications are their excitonic properties in the solid state, specifically in thin films \([75], [26], [55], [76]\), and understanding the dynamics of exciton diffusion and localization (or delocalization) becomes a necessity.

A variety of deposition techniques can be used to fabricate both bulk and thin film species of organic small molecules. Early methods of film creation, such as chemical vapor deposition, plasma deposition and others, gave thin films that were often
amorphous or polycrystalline, with very little ordering, rendering them very limited in useful studies of interactions between molecules. However, somewhat recently a new family of deposition techniques has allowed for rapid deposition that encourages long-range order in many of these organic small molecules. These include, but are not limited to, spin-coating, blade-casting [77], and a hollow pen-writing capillary technique [78], [79], [80] (which is the deposition method of choice for this work, and will be discussed in-depth later on).

Changes in the molecular packing and therefore structure in organic materials can greatly impact the properties in bulk or thin films, which is often possible through modifications of chemical structure [81], [28]. Crystallization into the solid state can have drastic impact on the electronic wave function overlap between molecules, as opposed to the weak interactions in solution [43]. These increased interactions lead to absorption spectra that often significantly broadened and exhibit more peaks as compared to those in solution as a result of this enhancement [82], [83], [84]. This appears to be a general behavior for many \(\pi\)-conjugated molecular systems in the crystal solid state, where degeneracy is lifted as a result of lowered symmetry, causing a Davydov splitting to be observed [85], [86], [72], [57].

The processing method, the purity, and the crystalline quality of the films themselves can also greatly impact exciton diffusion and other electronic properties, as the enhanced interactions present in the solid state allow impurities to have elevated effects on the system [87]. Chemical methods can help to improve purity and therefore crystal morphology, and even techniques such as thermal and solvent annealing, and solvent additives can influence properties in the solid state [88]. Ultimately one could imagine a spectrum in crystalline samples between the extremes of domain purity
versus domain size that allows for a precise selection of properties determined by the 
pure, blended or alloyed materials [88], where electronic properties could be explored 
experimentally by gradually introducing disorder into well-ordered crystalline films 
to investigate the effects of defects and disorder. Understanding the effect of order 
and crystallinity on the electronic and excitonic properties of organic solids could 
eventually lead to the tuning of these properties and optimization for commercial 
applications based on the individual device need [32], [58], [89].

1.3 EXCITON THEORY

The fundamental inherent property of organic semiconductors which all of the studies 
reported here investigate is the formation of an exciton, or an electron-hole pair, 
generated most often as a result of photoexcitation [90]. When discussing exciton 
theory, one must always begin with Yakov Frenkel, and his prediction in 1931 of what 
is now referred to as the Frenkel exciton. A Frenkel exciton (where the spatial extent 
of the electron-hole pair is quite small as compared to the lattice unit cell in the crystal 
structure) describes a system where the collection of molecules in the crystal are very 
weakly interacting. That is, in the first approximation, any contribution from phonons 
and intermolecular interactions is treated as a small perturbation, and therefore the 
collective excitation in the bulk is often compared directly the electronic excitation of 
a free single molecule. So the excitation of an electron, promoting it most commonly 
from the Highest Occupied Molecular Orbital (HOMO) to the Lowest Unoccupied 
Molecular Orbital (LUMO), is often viewed as isolated from the interactions with the 
rest of the crystal structure, due to the small radius and very localized nature of this
exciton. Shown in Figure 1.5 is a basic diagram of this promotion.

Figure 1.5: Diagram of a Frenkel exciton: promotion of an electron to the Lowest Unoccupied Molecular Orbital (LUMO) from the Highest Occupied Molecular Orbital (HOMO) by an incoming excitation, and excitonic emission from the recombination of the electron-hole pair.

In this picture Frenkel excitons can be viewed essentially as excitations in a series of almost non-interacting molecules in a crystal, where the wave function overlap between nearest neighbors is almost negligible. However, studying the excitations in a bulk crystal in this approximation could give insight into the nature of intermolecular interactions (or lack thereof) in a solid, and determine structural and electronic properties.

For spectroscopy purposes, the exciton is a very interesting phenomenon, due to the fact that when radiative recombination occurs at the bandgap, a photon will be released, often giving important insight into the energy of the bandgap, or possibly the energy of higher states. In the Frenkel picture, this excitation is described more
explicitly in the equation below

\[ \psi_n^f = \phi_n^f \prod_m \phi_m^0 \quad m \neq n. \]  \hspace{1cm} (1.1)

Here \( \psi_n^f \) represents the wave function of a bulk exciton in the crystal, and is simply the product of one excited state electronic wave function of the single excited molecule with the electronic wave functions of the remaining molecules in the ground state, and the superscripts \( \theta \) and \( f \) correspond to the ground state and \( f \)-th excited state respectively [86].

\[ \psi_n^f = \phi_n^f \prod_m \phi_m^0 \quad m \neq n. \]

Figure 1.6: In the Frenkel picture the single excited state molecule is isolated from the adjacent ground state molecules. Adapted from Bardeen et al. [87].

A periodic Bloch function is then defined based on this crystal exciton wave func-
tion in order to satisfy periodic boundary conditions (here we are summing over the lattice vectors of the crystal) [86]

\[ |k f \rangle = N^{-\frac{1}{2}} \sum_n \psi_n^f e^{i kn}. \]  

(1.2)

According to Davydov, and his oriented gas model, exciton states are often treated in an adiabatic approximation, where the influence of phonons (lattice vibrations) or intermolecular interactions in the molecular crystals are treated as perturbations. Therefore the zeroth approximation will assume no influence from phonons (that is, the molecules or lattice are rigidly fixed in space), and as a result the eigenvalues of the Hamiltonian operator will give the energies of the excitons themselves. The Hamiltonian contains only two terms, the electron kinetic energy operators and the operators from the Coulomb interactions of the electrons in the crystal and the fixed atomic nuclei [86].

Not long after Frenkel’s description of this particle-like excitation in a lattice with no net charge transfer, Gregory Wannier and Nevill Francis Mott in 1937 proposed a model where the radius (separation) of the electron-hole pair is in fact quite large [91], such that the wave function of the exciton could extend over many lattice unit cells in the crystal structure itself. This would be used to describe behavior in solids with high dielectric constant, such as inorganic semiconductors. In this case, instead of referring to orbitals in a single molecule as we did with the Frenkel exciton, the Wannier exciton is described in terms of band theory, where an incoming excitation would promote an electron from the filled valence band of the crystal to the empty conduction band, as shown in Figure 1.7 below.
The band structure now appears as a result of ionic or covalent interactions between atoms in a crystalline lattice that can no longer be treated as a perturbation, as was the Frenkel case discussed above. In this Wannier case, the promotion described above leaves behind a hole of positive charge (as before) where the interaction between the electron and hole can be described in terms of a hydrogen-like model, with charge proportional to the dielectric constant, and a reduced mass that combines the new effective mass of the electron in the conduction band and the effective mass of the hole in the valence band [86],

\[ Z = \frac{1}{\epsilon} \]  \hspace{1cm} (1.3)

\[ \frac{1}{m_r} = \frac{1}{m_e^*} + \frac{1}{m_h^*} \]  \hspace{1cm} (1.4)
where $m_e^*$ is the effective mass of an electron in the conduction band of the crystal, while $m_h^*$ is the effective mass of a hole in the valence band of the crystal.

The three-dimensional normalized exciton wave functions for the Wannier model can be written in terms of the Laguerre polynomials as shown in Equation 1.5 [92],

$$\psi_{n,l,m}(r) = -\sqrt{\frac{1}{2\pi n a_0^3}}\frac{(n-l-1)!}{n![(n+l)!]^3}\rho^l e^{-\frac{\rho}{2}}L_{n+l}^{2n+1}(\rho)Y_{l,m}(\theta, \phi).$$  \hspace{1cm} (1.5)$$

Here $\rho$ is written in terms of the Bohr radius and the separation of the electron-hole pair as

$$\rho = \frac{2r}{na_0}. \hspace{1cm} (1.6)$$

Recent experiments performed on ordered crystalline organic small molecule thin films [93], [94], [95], [96], where the presence of impurities and defects has been significantly eliminated prove that these systems belong to an intermediate regime between the Frenkel and Wannier cases, where the spatial extent of the exciton wave function extends over a small number of lattice sites. However, this theory of a single bandgap that separates the valence and conduction bands in bulk systems is also inadequate to describe the interactions and mixing in organic semiconducting molecular systems, as it does for most common inorganic semiconductors [87]. More recently, some improvements have been made to these models in similar organic systems that account for significant $\pi-\pi$ orbital interactions, in which the coupling between the excitons and the lattice vibrations (or phonons) are weighted as heavily as the Coulombic interactions between the electron-hole pairs [97], [98], [99].

For instance, here the original Frenkel wave function is rewritten in Equation 1.7,
with the Born-Oppenheimer approximation, so that the electronic and vibrational parts of the wave function are included

\[ \psi_{n\nu}^f = \phi_n^f \chi_{n\nu}^f \prod_m \phi_m^0 \chi_m^0 \quad m \neq n. \tag{1.7} \]

The vibrational wave function of the \(n\)th molecule is described by \(\chi_{n\nu}^f\) in its \(f\)th electronic state and \(\nu\)th vibrational state [98]. This allows for the phonon contribution to be weighted depending on intermolecular interactions, allowing for them to be weighted as heavily as the Coulombic interaction piece, which is often true in the case of these strongly-interacting organic crystalline solids.

1.4 Reconciling Unique Behavior in Strongly-Coupled Aggregate and Crystal Systems

As of late, an effort has been made to reconcile recent experimental results that cannot seem to be explained with models of weakly interacting molecules, such as 5 \(\mu\)m exciton diffusion lengths in rubrene crystalline samples [65] or superradiance in tetracene thin films [68], where experimental observations indicate a long-range coherence or interaction that cannot be described by a weakly-interacting Davydov model, or through some sort of short-range exciton hopping between adjacent molecules.

Spano and Mukamel were some of the first to describe a strongly coupled system of aggregates in which the electronic excitation is delocalized, with a more general
comment referring to "...entities exhibiting properties which are between those of an isolated molecule and the bulk crystal" [100]. They treat the system using an effective Hamiltonian method in which each molecule can be treated as a linear harmonic oscillator dipole that interacts with adjacent molecules through a classical dipole electric field, but with the addition of the linearized Lehmer equation to describe the spectroscopy results (such as fluorescence and more specifically, superfluorescence). In this way, they propose a specific type of fluorescence involving M aggregates of N coupled monomers, a superradiant process, but one that does not include all molecules (MN) coherently cooperating in the sample (as superradiance had been previously defined), instead coupling over a finite number of N monomers, equal to tens or hundreds of molecules. In this manner, they began attempts to describe behaviors of coherence between finite numbers of molecules within a coupled system.

This continues in 1990, where Spano, Kuklinski, and Mukamel [101] discuss a temperature-dependent coherence domain which has a size directly related to the exciton phonon interaction. They introduce a linear array of N electronically coupled aggregates with periodic boundary conditions that introduce some off-diagonal exciton-phonon coupling in the Hamiltonian. This attempts to explain the temperature-dependent radiative decay in J-aggregates, where fluorescence lifetimes increase with temperature, implying the destruction of coherence as a function of temperature. In this case the radiative decay rate corresponds to a domain size \( N_{eff} \) that is smaller than \( N \) and will similarly decrease with temperature. For a fixed temperature, superradiance is expected as \( N \) increases (here \( N = N_{eff} \)), but at a certain size, \( N_{eff} \) is capped, and remains constant even as \( N \) continues to increase, showing a finite extent of this coherence even in a bulk or 'infinite' system.
Tokihiro et al furthers this idea with a treatment of Frenkel excitons in linear system in 1993 [102], where they ultimately conclude that superradiance from the crystal is a result of an excitation propagating through the chain of atoms by dipolar interactions between adjacent sites. This is as opposed to the previously observed superradiance in gas systems of atoms and molecules, where a periodic array will not be present due to the dilute nature of the gas. While only treating the Frenkel excitons here, they do conclude that as the system size N increases, an increase is seen in the number of multiexcited radiative states, as can be expected. They also propose that superradiance from charge-transfer excitons is an intriguing next step, as the static dipole moment is present in the electronic excited state, and even further, that when excitation transfer is treated in the case of bound excitons at impurities (or traps), that these excitons will interact though dipolar interactions between nearest neighbors (even going so far as to say that eventually one can imagine controlling the excitation transfer by changing the separation of these impurities).

Moving forward to 2002, Meinardi et al [103] describe excitonic luminescence in crystalline oligothiophenes (a planar organic molecule crystallizing in a herringbone structure), where emission is heavily dependent on the orientation of the molecules, a strong correlation is observed in-between adjacent molecules based on the transition dipole moment in the herringbone plane (and as a result, the 0-0 purely electronic transition is observed). This 0-0 transition is only allowed in the orientation where transition dipoles are coherently oriented perpendicular to the molecular site ($\mu_\perp \neq 0$), and displays an intensity of superradiance that increases with the number of molecules emitting in phase (where the number of perpendicular transition dipoles N_c are constructively interfering). They further remark that the delocalization of
the exciton extend over a region which is smaller than the crystalline domain of the sample (again implying a delocalization over a finite number of molecules, but not a complete Frenkel or Wannier-like picture).

Meinardi et al follow up their previous work by focusing on organic molecules (quaterthiophene) that form H-aggregates [104], where planar molecules orient parallel to each other (as opposed to J-aggregates, often characterized by a head-to-tail orientation). Here they report on observations of superradiance in H-aggregates (previously thought to to be not optically allowed), if the molecular symmetry produces an out-of-plane component of the transition dipole moment. They describe the ground state and excited states ($\Psi_G$ and $\Psi_E$) in a molecular crystal as the product of the unit cell wave functions, where molecular wave functions for nonequivalent molecules in the unit cell are described by $\varphi_j'$

$$\varphi = \prod_j \varphi_j'.$$ (1.8)

They then write the ground and excited states in the first order of perturbation theory as

$$\Psi_G = \prod_n \varphi_n$$ (1.9)

and

$$\Psi_E = \frac{1}{\sqrt{N}} \sum_n e^{ik\cdot a_n} \varphi_n^* \prod_{m \neq n} \varphi_m.$$ (1.10)

Here the vectors $a$ and $k$ are the displacement and crystalline momentum vectors.
respectively, and the crystal cells are completely described by \( n \) and \( m \). For simplicity, they leave out exciton-phonon coupling, and so only \( \Delta k = 0 \) are allowed excited states, and they calculate the transition dipole moment for the excitonic recombination (\( \Phi_E \rightarrow \Phi_G \)) in terms of the unit cell transition dipole moment \( \mu_{\text{cell}} \) with the equation

\[
\mu_{\text{agg}}^{\text{GE}} = \left\langle \prod_j \varphi_j \left| \mu_{\text{cell}} \right| \frac{1}{\sqrt{N}} \sum_j \varphi_j^* \prod_{i \neq j} \varphi_i \right\rangle = \sqrt{N} \mu_{\text{cell}}. \tag{1.11}
\]

Meinardi et al mention that in J-aggregates, an in-phase combination of the transition dipole moments relates to the bottom of the exciton band, located at \( k = 0 \) and is allowed. In H-aggregates though, the bottom of the exciton band relates to an out-of-phase combination of the transition dipole moment, and the radiative exciton recombination is forbidden. However, in these particular organic molecules, the transition dipole moment \( \mu \) is not aligned only in the plane of the molecule, and so in the bottom of the exciton band the parallel components (\( \mu_{||} \)) cancel each other, leaving only the coherent perpendicular components (\( \mu_{\perp} \)), and therefore \( \mu_{\text{agg}}^{\text{GE}} = \sqrt{N} c_{\perp} \mu_{\perp} \) which allows the radiative recombination and therefore the observed superradiance from the 0-0 is allowed and proportional to \( N_c \) (the number of coherently emitting dipoles).

Spano further confirms this observation with a full characterization of the excitonic states, including phonon interactions (excitonic polarons) through diagonalization of a Hamiltonian that considers coupling to both nearest neighbors and second nearest neighbors [105], and contends that is can be applied to systems such as anthracene and tetracene where the singlet exciton is entirely polarized along the short molecular axis (or perpendicular direction). This was soon experimentally verified in pentacene by Lim et al [68], where they are able to actually estimate a coherence size of the
delocalized superradiant exciton, which they claim to be approximately 10 molecules in their particular thin film samples. This is done through analysis of the fluorescence signal, where the vibronic line shape and temperature-dependence measure delocalization in a coupled exciton-phonon signal, and matches theoretical calculations quite well, as seen in Figure 1.8.

**Figure 1.8:** Temperature-dependent experimental emission spectra of pentacene b) Temperature-dependent theoretical emission spectra of pentacene from a 3 x 3 pinwheel calculation and Boltzmann distributions, where the arrows indicate the transition dipole moments of the polarized lowest energy exciton. Adapted from [68].

While Lim et al state that improvements are still to be made (including additional vibrational modes and nonequivalence of the tetracene molecules in the unit cell), solid agreement is shown and may point to the possibility of the entire transition dipole moment $\mu$ to be directed in the small short axis (or $\mu_\perp$ as described above), rather than simply a component in some organic small molecule systems [68]. Ultimately it is the confirmation of this perpendicular molecular transition dipole moment that
is allowed in these face-to-face and herringbone aggregates of organic molecules that lends great insight into the work discussed in this thesis.

A few years later, in 2009, Spano has begun to generalize the excitations found in various forms of solid state conjugated organic molecules, stating: "Such excitations, or excitons, are generally spread out over several molecules: a balance between the delocalizing influence of resonant intermolecular coupling and the localizing influence of static and dynamic disorder determines the coherence range of the exciton...To properly understand energy or charge transport, one must treat intermolecular (excitonic) coupling, electron-vibrational coupling, and disorder on equal footing" [106]. This is a significant departure from previous treatments, where lattice vibrations and coupling were simply treated as a perturbation to the system. He uses the Franck-Condon progression (the principle that vibronic wave function overlap dictates vibrational transition probability during an electronic transition, in our case directly relating to the absorption or emission of a photon) to gain insight into the molecular packing and exciton coherence length when going from isolated molecules in solution to an ordered crystalline solid. Spano summarizes by stating that H- and J-aggregates are the two extremes of Franck-Condon distortion that arise from vinyl stretching modes in conjugated molecules in the solid state. However, when a unit cell contains multiple molecules, the top and bottom of the exciton band are generally the origin of oscillator strength, and certain systems may have optical properties resembling both H- and J-aggregate behavior, depending on polarization [107] (an observation believed to be present in the phthalocyanine sample discussed herein).

Yamagata et al extends this proposal to look directly at crystalline pentacene, tetracene, and anthracene, where the presence of two non-equivalent molecules in
the unit cell gives rise to two unique optical transitions that are polarized parallel and perpendicular to the herringbone stacking, as a result of Davydov splitting (and verified experimentally through polarized absorption on the crystal phase) [57]. In an effort to specifically describe the influence of solid state packing on the tetracene molecule, Yamagata et al constructed a exciton model Hamiltonian that contains linear exciton vibrational coupling, more specifically a Frenkel-Holstein Model.

The Holstein Hamiltonian was introduced by Theodore Holstein in 1959 [108] in order to describe polaron motion in a crystalline medium, that is, an electron or hole interacting with vibrations of the crystal lattice. He described a Hamiltonian containing the sum of three terms: \( H = H_e + H_L + H_{int} \). Here the first term \( H_e \) is the electronic component, containing both the kinetic energy of the electron as well as the potential energy form the periodic crystal lattice. \( H_L \) then describes the kinetic and potential energy of the lattice itself, where the kinetic term are the lattice particles and the potential are the particle displacement from equilibrium. The \( H_{int} \) term lastly describes the interaction between the electron and lattice, dependent on the electron coordinate and the displacement of the lattice. He describes the motion of the electron or hole in a one-dimensional molecular-crystal medium in the context of the tight-binding approximation.

This is especially important to organic molecular systems that form into pseudo one-dimensional chains (such as phthalocyanine) in order to introduce a formalism that considers the electron-phonon coupling as weighted more heavily than just a perturbation. This is considered explicitly by Spano and Yamagata for the specific case of a linear chain of face-to-face molecules [109] (as opposed to the herringbone aggregate structure discussed above, and one directly applicable to crystalline ph-
thalocyanine), where their goal is to create a way to directly determine exciton coherence in molecular aggregates. Their site-based Holstein Hamiltonian representing the coupled exciton-phonon system considers an aggregate of N molecules and a single electronic excitation, and is written as

\[ H = \omega_0 \sum_n b_n^\dagger b_n + \omega_0 \lambda \sum_n \langle n | \{ b_n + b_n^\dagger \} + \sum_{n,m} J_{nm} | n \rangle \langle m | + \omega_0 \lambda^2 + \omega_{0-0} + D. \]  

Here the first term has \( b_n^\dagger \) and \( b_n \) as the creation and annihilation operators for the vibrational excitation on the \( n \)th molecule, and \( \omega_0 \) is the symmetric vinyl stretching mode, thus describing the vibrational energy. Secondly is the on-site vibronic coupling, where \( \lambda^2 \) is the Huang-Rhys factor (or electron-phonon coupling constant) and the state \( | n \rangle \) is the electronically excited molecule, with all others in the ground state. The third term is the excitonic coupling, with \( J_{nm} \) as the excitonic coupling between molecules \( n \) and \( m \). Lastly the molecular 0-0 transition frequency is given by \( \omega_{0-0} \) and \( D \) is a gas-to-crystal shift from nonresonant interactions [109].

This model produces some interesting results, in regards to photoluminescence emission in these aggregates, and some that closely match experimental data that will be shown later in phthalocyanine systems. As additional terms are introduced to describe coherence with respect to temperature-dependence for ordered J-aggregates, two calculated photoluminescence spectra are shown in Figure 1.9 that exhibit familiar behavior.
Here a dependence on both coherence over N molecules, as well as a temperature-dependence is seen for the photoluminescence intensity in this aggregate system, where similar behavior will be shown for the phthalocyanine thin films shown later in this thesis. This finally brings us to the most recent work from Spano, Silva, Yamagata, and Hestand. Spano and Silva describe π-conjugated stacks of polymers as displaying unique hybrid photophysical properties of aggregates exhibiting both H- and J-like behavior (with interchain coupling showing H-like behavior and intrachain electronic coupling favoring J-like behavior) [110], and hybrid properties such as these that manifest in the organic systems discussed here.

Yamagata et al [93] have also since refined the complete Hamiltonian discussed above to include four terms

$$H = H_{FE} + H^{(1)}_{CT} + H^{(2)}_{CT} + H_{FE-CT}$$  \hspace{1cm} (1.13)
where the first term is the Holstein Hamiltonian representing the Frenkel exciton including vibronic coupling. The second term describes diabatic energies of charge-transfer excitons and their vibronic coupling, and the third term describes the actual electron and hole transfer that defines charge-transfer excitons. Lastly a term is introduced to describe the coupling between the Frenkel exciton and the charge-transfer states. This model is shown to agree with photophysical behavior in tetraazater-rylene (TAT) π-stack aggregates in the solid state, that show both H- and J-like behavior [93]. Furthermore, Hestand et al consider exciton mobility control in these TAT organic polymer chains through angstrom scale changes in the packing of the crystalline lattice, where they show that unlike the long-range Coulomb coupling, the charge-transfer short-range coupling in these π-stacks are extremely sensitive to the adjustment of slips between adjacent molecules [95] (which is a discussion touched on in Chapter 5 of this work).

Most recently in the work by Hestand and Spano, they tweak the Hamiltonian shown in 1.13 by adjusting the strength of coupling between Frenkel and charge-transfer excitons, and how some systems can transformation from H- to J-like aggregates, considering long axis slip and spatial dependence from packing in the crystalline solid state [94], as well as attempts to fit this model to more recent experimental spectroscopy experiments in crystalline pentacene [96].

Ultimately, a large amount of work in this area still continues, with many attempting to reconcile experimental work with further in-depth theoretical models (Yamagata, Hestand, and Spano), by including terms for charge-transfer excitons, as well a Hamiltonian that can address charge and energy transport in the presence of local vibronic coupling, and the experimental work presented in this thesis will
support the hypothesis of a strong coupling to the lattice in organic small molecule crystalline systems with significant π-orbital interaction between adjacent molecules.

1.5 Interaction with Light and Principles of Optical Spectroscopy in Organic Semiconductors

Polarized light is often used as a powerful spectroscopy tool in order to probe ordered crystalline systems. By restricting the electric field vector of unpolarized light to oscillate either linearly or circularly, information about the crystalline or structural orientation, magnetism, or symmetry of the electronic states of a given sample can be obtained. Polarized light spectroscopy has applications spanning a variety of disciplines, from structural characterization of proteins and DNA to studying magnetism of molecules in the solid state, and often provides insight into ordering and directional properties of these systems.

The Poynting Vector is classically used to describe electromagnetic radiation as the cross-product between its electric and magnetic field components [111]

\[
S = E \times H
\]  

(1.14)

where:

\[
H = \frac{B}{\mu_0}.
\]  

(1.15)
However, when describing the polarization of electromagnetic radiation, only the electric field vector \( \mathbf{E} \) is considered, as the magnetic field vector \( \mathbf{B} \) is always defined with respect to the \( \mathbf{E} \) vector and the direction of propagation. The only case that will be considered here is when the electric field vector is confined to oscillate exclusively in a plane, known as linear polarization

\[
\mathbf{E} = (e_x E_x + e_y E_y) \sin[i(\omega t - \frac{2\pi nz}{\lambda})].
\]  

(1.16)

The direction of the electromagnetic radiation propagation is the \( z \) direction, and therefore \( e_x \) and \( e_y \) are the two remaining orthogonal unit vectors where \( E_x \) and \( E_y \) are the intensity of the electric field vector \( \mathbf{E} \) in the \( x \) and \( y \) directions respectively [112]. In addition, \( \omega \) describes the angular frequency and \( \lambda \) describes the wavelength of \( \mathbf{E} \) traveling through some medium with index of refraction \( n \).

This electromagnetic radiation will interact with a given material or crystalline structure through excitations. That is, it will be absorbed by this material and energy will be transferred to electrons contained within, causing an excitation from the ground state \( (\psi_g) \) to an excited state \( (\psi_e) \), creating an electric dipole transition moment resulting from the Fermi Golden Rule that can be written as

\[
I \propto |\mathbf{E} \cdot \mu_{if}|^2 = |E|^2 |\mu_{if}|^2 \cos^2(\theta).
\]  

(1.17)

Here the intensity will be proportional to the transition dipole moment of the excited electron-hole pair, \( \mu_{if} \), the electric field vector \( \mathbf{E} \), and most importantly the angle \( \theta \) between the direction of the dipole and \( \mathbf{E} \). Thus the orientation between the incident electric field component \( \mathbf{E} \) of the electromagnetic radiation, and the
electric dipole of the material itself gives rise to the intensity of the newly created electric dipole transition. With this in mind, Linear Dichroism (LD) can then be used to probe dipole orientations or the symmetry of states in the material or crystalline structure by measuring the differences or preference of the absorption of polarized light. Selection rules must be followed however, and so not all transitions are possible according to:

\[ \mu_{if} = \langle \psi_i | \mu | \psi_f \rangle \quad (1.18) \]

The transition dipole moment \( \mu_{if} \) is not equal to zero, and \( \mu \) is the electric dipole moment operator. Absorption then occurs when the transition energy is resonant to the energy of the incoming electromagnetic radiation.

As mentioned above, linear dichroism can be used to probe crystalline orientations, and this can be done by looking at the differences in absorption of polarized light in the solid state sample (dichroism). More specifically, linear dichroism measures the difference of absorption of light from a sample where the incoming light is oscillating between two orthogonal planes (often referred to in the lab frame as vertical and horizontal polarization). In our laboratory frame, they are referred to \( x \) and \( y \) linearly polarized light, and the LD signal can be calculated using the equation below [113]

\[ LD(\lambda) = A_x - A_y. \quad (1.19) \]

Here \( A_x \) and \( A_y \) are the absorbance of the \( x \) and \( y \) linearly polarized light respectively. In addition, the linear dichroism is also a function of the wavelength \( (\lambda) \) of the incoming light.
1.5.1 Previous Polarized Photoluminescence Experimental Results

As discussed above, the photoluminescence from these crystalline systems is also expected to be polarized, where components of the optical transition dipole moment $\mu$ can be oriented both within the plane of the discotic molecules, or aligned perpendicular (out-of-plane) along an axis that runs through the face of the molecule itself. This directly correlates to the orientation of the electric dipoles of the excitons created by the incident polarized light, and therefore changes in crystalline orientation and probing of excitons polarized in different directions is possible.

Previous work performed by Dr. Zhenwen Pan, Dr. Naveen Rawat, and myself has experientially verified the existence of two excitons in the phthalocyanine systems, one more localized and polarized in the plane of the discotic molecule, and the second exciton delocalized along the molecular stacking axis as a result of coherence between dipoles in adjacent molecules due to $\pi$-orbital overlap, and polarized in the out-of-plane direction.

This was done through polarized temperature-dependent photoluminescence spectroscopy (described in detail in Chapter 2), where the luminescence from a metal-free octyloxy-phthalocyanine crystalline thin film is shown in Figure 1.10, and fitted with three Gaussian features, labeled (1)-(3) [114], [115].
Figure 1.10: Temperature-dependent photoluminescence of H$_2$OCPc from 5 K to room temperature. Adapted from [114], [115].

Feature (1) was assigned to the singlet exciton emission, as it has very little dependence on temperature, showing only minor changes in peak energy (located at 1.56 eV), intensity and polarization (approximately 40%) going to room temperature. This would correspond to a relatively high exciton binding energy (hundreds of meV), that would not show temperature-dependence, as it would exceed $k_B T$ values even at room temperature, while also confirming that vibronic states are not involved in this specific exciton transition [116].

Feature (2) however shows a significant temperature-dependence in luminescence
intensity, as well as a large change in polarization with temperature (increasing from 20% to 40% at room temperature). The $x$ and $y$ polarized components of the photoluminescence give rise to a net polarization term defined as

$$ P = \frac{I_x - I_y}{I_x + I_y}. $$

(1.20)

The energy and polarization of Feature (2) is plotted as a function of temperature for the two $x$ and $y$ polarized components of the photoluminescence, and shown in Figure 1.11.
Most strikingly, both the energy and net polarization see a significant shift at a 100 K, where above this threshold a increase in peak energy and polarization are observed, and overall luminescence intensity of feature (2) decreases (and is overtaken by the singlet exciton emission of feature (1)). In addition, time-resolved luminescence studies show two distinct lifetimes at 5 K, reinforcing the model of two distinct excitonic states, polarized in the plane of the molecule, and delocalized and polarized along the direction of the stacking axis of the molecules [114], [115].
Previously reported studies in systems such as colloidal nanoparticles have shown observations of optically forbidden luminescence states due to mixing with energetically close allowed excitonic states [117], [118]. In this case however, mixing of these excitonic states here is less likely, as the sharp onset of the temperature-dependent mechanism is inconsistent with this picture. Instead, this behavior is reminiscent of a phase transition in the crystalline solid state, with a significant change in the stacking of the molecules with temperature (further verified in Chapter 2.5), which acts a temperature-dependent switch between the localized and delocalized excitonic states.

In a picture of the electronic band structure in a crystalline solid (as discussed above), the observation of an optically-forbidden excitonic state at low temperatures can be interpreted as a symmetry-lowering change in the crystal lattice with temperature (verified in Chapter 2.5 and [114], [115]). This can be related to a phase transition in the solid that will relax the selection rules of radiative recombination for an exciton polarized along the stacking axis, and at these low temperatures where contributions from vibrational modes are suppressed, this excitonic emission originating from the coherence between intermolecular π-orbital overlap is not only optically allowed, but dominates the photoluminescence spectrum until the 100 K threshold is reached.
1.6 INORGANIC ALLOY SYSTEMS -
A PRECURSOR

The inspiration behind the fabrication of alloys containing these organic phthalocyanine systems in order to lend insight into the excitonic behavior actually originates in the fairly well-known and studied inorganic ternary alloys, including GaAs\textsubscript{1-x}P\textsubscript{x}, Al\textsubscript{x}Ga\textsubscript{1-x}N, Al\textsubscript{x}Ga\textsubscript{1-x}S, In\textsubscript{x}Ga\textsubscript{1-x}N, as well as many others. Lai and Klein in 1980 suggested that not only can the influence of alloy fluctuations in GaAs\textsubscript{1-x}P\textsubscript{x} cause exciton localization, but also reported a new excitonic emission peak (characterized as a more localized Wannier-Mott exciton) and as such, a model that assumes the minimum of the conduction band varying as a function of x (at least locally with respect to the exciton) \[119\].

Yamamoto et al observed a significant increase in photoluminescence intensity with increased disorder in AlAs/GaAs superlattices, as compared to the more ordered lattices, furthering the idea of carrier localization caused by disorder present on the atomic scale \[120\]. This idea was further confirmed by Permogorov and Reznitsky, who conclude that localization of excitons suppresses migration to nonradiative recombination sites, and as a direct result, the quantum yield of radiative recombination which occurs through the localization of exciton states will increase. In addition, they discuss how substitutions of anion or cation nature can influence the valence and conduction bands, and therefore the exciton localization in a large variety of II-VI semiconductor solids \[121\]. The localization of excitons and influence on the photoluminescence spectra through temperature-dependent measurements was further
verified in In$_x$Ga$_{1-x}$N by Chichibu et al [122].

Stringfellow and Chen were among some of the first to suggest that atomic ordering will have significant impact on the fundamental properties of these materials [123], in which they discuss improving electronic and photonic properties in alloys by understanding and controlling the ordering in these materials over large regions. Further, they discuss increasing electron mobilities through eliminating alloy fluctuations, as well as reducing the bandgap as a result of the influence of ordering in these alloys. Yamaguchi et al continued this investigation by noting a significant broadening of photoluminescence linewidth in Al$_{1-x}$In$_x$N that cannot be explained simply by random disorder, instead claiming large inclusions of indium result in the extreme bowing of the bandgap itself, with shifting absorption edges and photoluminescence peaks as a function of indium in the alloys [124].

Recent work has shown an increased complexity in the understanding of the exciton dynamics in ternary alloys as concentrations of the additive are varied. Hwang et al proposing a significant change in the dielectric constant of the material in Al$_x$Ga$_{1-x}$N when a critical concentration x of Al (0.8) is reached [125]. Kim et al observe linearly increasing photoluminescence lifetimes with increased Al concentration in Al$_x$Ga$_{1-x}$N, but decreasing intensity of the PL intensity, which they attribute to loss of carriers to nonradiative paths prior to the localization of the carriers through thermal relaxation [126]. Even further, Lin et al report on an 'inverted S-shape' for the photoluminescence peak energy as a function of temperature in InGaN alloy films, decreasing and then increasing between 40-100 K, and then finally decreasing with increased temperature. They mention other groups making similar observations in III-V ternary semiconductor alloys, and conclude this is a signature of alloy poten-
tial fluctuations, where at low temperatures excitons recombine at states with low potential minima, but as temperature is increased the thermally excited excitons can recombine nonradiatively (decreasing PL intensity) until finally at high enough thermal energy the excitons can be excited to higher localized states and increase PL intensity (and this 'S-shape' PL behavior has become a signature of many ternary alloy systems) [127]. Furthermore, one can now envision tuning specific excitonic properties in organic semiconducting systems in a manner similar to these inorganic systems, most notably through the blending of different species, and creating organic analogues of the inorganic semiconductor alloys.

Ultimately, the dynamics and behavior discussed above have become very well understood for these inorganic alloys, although over the course of over three decades, and with that knowledge came the powerful ability to specifically tune properties for device applications. However, in many of the previously mentioned organic systems, a gap in knowledge exists. Organic semiconductors, and more specifically organic $\pi$-conjugated small molecules provide a unique system in which to better understand the electronic interactions as they are in the inorganic ternary alloys described above. This is due to the fact that many of these organic systems do not fall into the one of the two very-well known exciton descriptions, either a very weakly interacting Frenkel picture, or a strongly interacting Wannier picture. As such, if one can use both chemical engineering as well as unique processing methods to purposefully create systems that vary the intermolecular spacing and therefore the interactions between molecules in a systematic way, allowing in principle probing dynamics that cannot be fully understood within a Davydov-like approach [86], [95], great insight could be given into organic systems that fall into this intermediate regime, and eventually the
understanding that would allow specific tuning of electronic properties in the solid state.
Chapter 2

Experimental Techniques and Equipment

This chapter gives an overview of the experimental techniques and technical specifications of the equipment used for all of the studies contained herein.

2.1 Chemistry and Purification Techniques

(The purification and synthesis techniques discussed in Chapter 2.1 are courtesy of Dr. Naveen Rawat at the University of Vermont)

Impure 1,4,8,11,15,18,22,25-octabutoxy-29H,31H-phthalocyanine (H\textsubscript{2}OBPc) powder was purchased from Sigma-Aldrich and was chromatographed over silica gel using toluene and ethyl acetate as eluents. After 2 individual columns, the product was collected and recrystallized by dissolving it in acetone. Bright green crystals were
collected and dried under vacuum. The purity was confirmed by NMR and solution absorption, showing good agreement with reported literature [128], [129].

1,4,8,11,15,18,22,25-copper-octabutoxy-phthalocyanine (CuOBPc) was purchased from Sigma-Aldrich and further purified by column chromatography using dichloromethane and diethyl ether (1:10 ratio) and a toluene and ethyl acetate combination as eluents. This was followed by a recrystallization in THF and ethanol. Crystals were then collected and dried for thin film fabrication.

1,4,8,11,1,5,18,22,25-nickel-octabutoxy-phthalocyanine (NiOBPc) was purchased from Sigma-Aldrich and purified using column chromatography in toluene. This was followed by a recrystallization in THF and ethanol. Crystals were then collected and dried for thin film fabrication.

1,4,8,11,15,18,25-cobalt-octabutoxy-phthalocyanine (CoOBPc) was synthesized by starting with cobalt (II) acetate (1.1750 mg, 3.7 mmol, purchased from Sigma Aldrich) and added to a refluxing solution of purified H2OBPc (200mg, .102 mmol) in butanol (15 ml). The solution was maintained at reflux for 2 hours under nitrogen after adding the metal and cooled and column chromatographed twice (in silica gel, using toluene and ethyl acetate as eluents). The green blue fraction was dried under reduced pressure, and further purified by column chromatography, and subsequently was set to recrystallize in THF and ethanol (85% yield). The crystals obtained were then dried under vacuum.

1,4,8,11,15,18,22,25-manganese-octabutoxy-phthalocyanine (MnOBPc) was synthesized by starting with manganese (II) acetate (630mg, 3.7 mmol, purchased from Sigma-Aldrich) and adding it to a refluxing solution of purified H2OBPc (110mg, .102 mmol) in butanol (15 mL). The solution was maintained at reflux for 2 hours
under nitrogen after adding the metal salt, and subsequently cooled and column chromatographed twice (in silica gel, with chloroform and methanol as eluents). The red wine fraction was then dried under atmospheric pressure (60% yield).

2.2 Thin Film Fabrication - The Hollow Pen-Writing Technique

The thin film samples are fabricated using a solution-processed room temperature hollow capillary pen-writing deposition technique developed by Dr. Headrick’s group as the University of Vermont [78], [79], [80], that produce macroscopic grain sizes, enabling ultra-fast spectroscopy studies of excitons and long range order in these materials [115], [130].

The soluble derivatives of phthalocyanine or porphyrin were dissolved in an organic solvent (for these films toluene or chloroform was used), and the solution concentration was determined by product weight (for example a 0.5% solution contained 0.0005 g/100 µl). After sonicating each individual solution for 15 minutes, the solution is loaded into a hollow borosilicate glass capillary pen, while the solution is held inside the pen by capillary forces. Film deposition is then achieved by letting droplets of solution at the end of the pen to make contact with the substrate and then laterally translating the substrate at finely controlled speeds. The substrate is mounted on a one-dimensional Zabar T-LSM050A-S-KT04 linear translation stage, which slowly drags the substrate beneath the meniscus of the solution in the glass capillary at finely controlled and reproducible speeds, leaving a crystalline deposited film behind.

All of the phthalocyanine and porphyrin thin films studied here were deposited
in the convective regime, where well-oriented crystalline films are produced as a result of seeding by the previously deposited crystalline grains as they materialize from the capillary; as opposed to the LLD (Landau-Levich-Derjaguin) regime, where crystallization is dominated by viscous forces that actually pull the solution from the capillary itself, resulting in the rapid formation of sharp grain boundaries, and therefore more severely disordered films [80], [131]. Two pictures of the hollow pen-writing experimental deposition system are shown in Figure 2.1, along with two examples of crystalline thin films deposited from this system.
All c-plane crystalline sapphire slides were pretreated with a triethoxyphenylsilane solution. The deposition grade triethoxyphenylsilane was purchased from Sigma-Aldrich. In order to treat the substrates, they were submerged in a solution of 3% triethoxyphenylsilane/97% toluene and kept under nitrogen for 15 hours at a temperature of 90°C. After the substrate is pulled from the PTS solution, a quick
methanol rinse is performed before thin film deposition. The sapphire substrates were purchased from Meller Optics.

The optimal capillary deposition speeds ranged between 8 and 12 $\mu$m/sec for all of the crystalline thin film samples shown in this work (including the alloyed thin films). The benefit of these specific organic molecules, as well as the solution-processing technique, is the promotion of self-assembly of the molecules in the solid state. In for instance the phthalocyanine derivatives, the discotic molecules will orient themselves 'edge-on' to the substrate, where the stacking axis that runs through the face of the molecules is parallel to the substrate [79]. This is as opposed to the 'face-on' orientation, where the stacking axis is perpendicular to the substrate [28], [25].

A necessity for improving grain size and crystallinity of the thin film samples involves the optimization of the deposition speeds of the solution deposition, as well as the tuning of solution concentration, choice of organic solvent, and the wettability of the substrate itself (which is greatly improved by the PTS treatment discussed above). The average thickness of the thin films was estimated from the calibrated dependence of writing speed on film thickness to be at least 300 nm [79]. Preliminary AFM measurements performed at The University of Vermont Microscopy Imaging Center confirmed the films were on average 400 nm thickness.

Atomic force microscopy was performed at The University of Vermont, with an Asylum Research MFP-3D-BIO (Asylum Research, an Oxford Instruments company; Santa Barbara, CA). Images were obtained in the contact mode in air, using a 225 $\mu$m pyramidal silicon probe containing a silicon tip with tip radius < 10 nm and a spring constant of 0.02 N/m (AppNano, Model Shocon) Imaging parameters in contact mode were, set point 1.00 V, Integral gain 3.00, drive amplitude 100 mV, drive frequency
75 KHz at a 90° scan angle. Images were obtained at scan rates between 0.3 and 1 Hz, with 512 lines per image, and constant image gains. Topographical dimensions of the crystal structure were analyzed using the Igor Pro 6.34 software (WaveMetrics, Portland OR). Shown in Figure 2.2 is a 90 x 90 µm image of a typical crystallized thin film.

Figure 2.2: Atomic Force Microscope image of a crystalline thin film sample of \( H_2OBPc_{0.75}CoOBPc_{0.25} \)

The large valley on the right-hand side of the image is a purposeful cut made with a diamond tipped pen, in order to measure the thickness of a typical hollow-pen deposited thin film. The left-hand side shows the quality of smoothness in most thin film crystalline samples. A cross-sectional height scan was also performed to confirm the thickness of our films, and is shown in Figure 2.3.
The dot-to-dot measurement shown in here estimates the thickness to be roughly 450-500 nm, however it must be noted that by scratching the film in order to estimate the thickness down to the substrate, a pile-up of thickening of the film on either side of the groove is observed. Since that time, profilometer measurements were performed by Kim Hua with the assistance of Dr. Matthew White at the University of Vermont, and confirmed the average film thicknesses to be between 300-400 nm.
2.3 Absorption, Photoluminescence and Time-Resolved Photoluminescence

Spectroscopy as a discipline has become one of a handful of essential measurement techniques used to probe systems both in solution as well as the solid state. Photoluminescence excitation and absorption spectroscopy are the primary tools that are used to probe these crystalline systems, as well as make comparisons as we move from solution into the solid state. Even further, ultrafast photoluminescence spectroscopy is our only way to probe exciton dynamics in these systems. Steady state photoluminescence experiments can give insight into the energy of optically allowed transitions in the crystalline system, as well as information about oscillator strength based on relative intensities of peaks in the photoluminescence spectra.

For solution absorption spectra, the Beer-Lambert Law can be used to calculate absorbance (A), based on molar concentration c, depth of the sample b, and the constant for molar absorptivity ϵ at a particular wavelength

\[ A = \epsilon bc. \]  

(2.1)

For all of the crystalline thin film samples used for the studies discussed within, the absorbance is calculated with following equation,

\[ I = I_o e^{-\alpha d} \]  

(2.2)

where we are not necessarily looking at total light absorbed or transmitted, but
rather relative absorption, and thus when analyzing, we always consider $I/I_o$ on a natural log scale, and this will give the absorbance $\alpha$ (where $d$ is the thickness of the sample studied).

2.3.1 LAMPS AND SINGLE GRAIN ABSORPTION

For the white-light absorption experiments, two different light sources were employed, based on the wavelength range of interest. In the visible range of wavelengths, the preferred light source was a Spectral Products ASBN-D1-W150 Dual Tungsten-Halogen/Deuterium Hybrid Light Source (where for our visible light purposes, the Tungsten-Halogen bulb was the source of illumination). This lamp is shown below in Figure 2.4, and the spectral distribution of this lamp is shown in Figure 2.5.

![Spectral Products Dual Tungsten-Halogen/Deuterium Light Source](spectralproducts.com)
The absorption spectra were measured at room temperature in the range of 400-1100 nm using the quasi-monochromatic (1 nm bandwidth) tunable, incoherent, tungsten halogen light source, and an achromatic 5 cm focal length lens that created an incoherent beam diameter size of approximately 50 µm. A long working distance telescope was used to monitor the beam position on the sample surface, while detection was accomplished using the photodiode detectors discussed below.

For wavelengths deeper into the ultraviolet regime, the preferred light source was a Spectral Products ASB-XE-175 Xenon Light Source. This lamp is shown below in Figure 2.6, and the spectral distribution of this lamp is shown in Figure 2.7.
The typical diffraction-limited diameter of tightly focused laser beams is roughly 5 microns in our experiments, while the incoherent quasi-monochromatic focused white light...
light diameter used in absorption measurements was as small as 50 microns, both of which fit well within the size of the large grains, even for the most disordered films. These beam sizes enable probing of electronic states within a single crystalline grain, free from the interference of defects and disorder (other than alloy fluctuations), using single wavelength techniques for luminescence studies or broad wavelength-tuned incoherent light sources for absorption studies. A diagram of this single-grain absorption experiment is shown in Figure 2.8.

Figure 2.8: Diagram of the single-grain absorption experimental set-up

2.3.2 Spectrometers and Detectors

The photoluminescence spectra for the experiments discussed here were recorded using two different Princeton Instruments spectrometers, the Acton SpectroPro 2500i
and the Acton SpectroPro 2300i, which are 0.5 m and 0.3 m focal length imaging triple grating monochromator/spectrometers respectively. These were coupled to a Princeton Instruments PIXIS 256 CCD (charge-coupled device) camera for imaging and spectroscopy detection. All three are shown below in Figure 2.9.

![Figure 2.9: a) Acton SpectroPro 2500i b) Acton SpectroPro 2300i c) PIXIS 256 CCD camera. Adapted from princetoninstruments.com](image)

Multiple photodiode detectors were also used throughout the experiments that will be discussed in this work. A Thorlabs PDA10CS InGaAs Switchable Gain Detector is used for absorption and LD/MCD experiments using wavelengths toward the IR and near-IR, with a working range of 700-1800 nm. For the UV and visible range, a Thorlabs PDA36A silicon amplified detector is used, with a wavelength range of 350-1100 nm. In addition, for experiments where the beam spot on the detector might need to be adjusted or move throughout a scan or alignment, a Newport 2032 large area silicon photodetector, with a diameter of 5.8 mm is employed, with a wavelength range of 190-1110 nm. Finally, for applications where two balanced outputs might need to be employed, a ThorLabs PDB210A large-area balanced silicon photodetector with a wavelength range of 320-1060 nm is used.
2.3.3 Ultrafast Lasers

For a majority of the photoluminescence experiments addressed here, both room temperature and temperature-dependent, a PicoQuant Diode Laser system is used. The PDL 800-D is a pulsed diode laser driver unit that has various attachable laser heads. It can generate peak powers up to 1 Watt and pulses as short as 50 picoseconds, with repetition rates varying from a single shot up to 80 MHz, as well as continuous wave mode, depending on the laser head attachment. The driver unit features a pulse generator that produces a low jitter clock signal. The clock generator consists of two selectable master oscillators and a frequency divider, which allows a range of producible frequencies from 80 MHz down to 31.25 kHz. This unit is shown below in Figure 2.10.

![Figure 2.10: PDL 800-D - Picosecond pulsed diode laser driver from PicoQuant. Adapted from picoquant.com](image)

Two laser heads were purchased for our system, the LDH-D-C-375 (with an output
wavelength of 375 nm, maximum optical power of 10 mW in continuous wave mode and 3.1 mW at 40 MHz repetition rate, and a minimum pulse width of 59 picoseconds), and the LDH-D-C-730 (with an output wavelength of 734 nm, maximum optical power of 8 mW in continuous wave mode and 2.0 mW at 40 MHz repetition rate, and a minimum pulse width of 98 picoseconds). An example of one of these PicoQuant laser heads is shown below.

![Figure 2.11: Picosecond pulsed diode laser head from PicoQuant. Adapted from pico-quant.com](image)

In addition to the Picoquant system, other lasers were employed in order to select specific excitation wavelengths for various experiment (dependent on the absorption spectra of the specific sample used). For many of the Linear Dichroism Mapping experiments explained in Chapter 4, a Melles Griot HeNe (helium-neon) continuous
wave laser was used, with a wavelength of 632.8 nm and an average output power of 14 mW.

For wavelengths further to the blue, a Coherent CUBE GaN solid state diode laser system was employed, with a wavelength of 402 nm. In continuous wave mode, this system has a maximum output power of 160 mW. However, as our ultrafast spectroscopy experiments require pulsed modes, the Coherent CUBE system was coupled with a Berkeley Nucleonics Model 575 Digital Delay/Pulse generator, that provides multi-channel 250 picosecond resolution pulsing, with an internal low jitter of only 50 picoseconds.

Finally, when a tunable approach was necessary, the largest member of our ultrafast laser family was employed, the Coherent MIRA 900 Ti-Sapphire laser. It was connected to the Coherent VERDI V6 Nd:Vanadate Diode Pump Solid State laser, which produces a continuous wave output at 532 nm and maximum power of 6 Watts, with very low power fluctuation. The output of the MIRA 900 itself can actually vary from 700 nm to 900 nm, with the maximum output at 800 nm. However, in order to probe systems in the visible wavelength range (that is, to generate a pulse with higher energy) a second and third harmonic generator cavity is attached to the output of the MIRA 900. The Photop Technologies TP-2000B Tripler cavity is equipped with a Potassium Titanyl Phosphate (KTP) crystal for single harmonic generation of pulses (around 400 nm), and a Barium Borate Oxide (BBO) crystal in order to generate third harmonic pulses (around 266 nm), with an input from the MIRA of the 800 nm light. This allowed for a tunable wavelength while still retaining high throughput (30 mWatt for 400 nm and 1 mWatt for 266 nm), and more importantly conserving the time profile of the pulses from the MIRA 900 (at 76 MHz for both picosecond and
femtosecond pulses), allowing for time-resolved measurements even while using the tripler cavity. As a digital output for the MIRA is not a viable option, in order to perform time-resolved measurement with this laser, the outgoing beam was split into two components, the first of which was incident on the sample, while the second was directed into a PicoQuant TDA 200 Trigger Diode, which is an optical trigger. With a small portion of the incident beam directed towards the diode, a digital signal is output to the PicoHarp 300 system to synchronize the timing electronics, discussed in detail below.

2.3.4 PicoHarp 300 System

An extremely powerful method of probing exciton dynamics in organic systems involves looking at the time-resolved photoluminescence of a given sample, and therefore in order to perform these measurements a time-correlated single photon counting system was employed. Our system of choice was a PicoHarp 300, a picosecond histogram accumulating real-time processor from PicoQuant, shown below in Figure 2.12:
A time-correlated single photon counting system (TCSPC) operates by collecting data of single photon events collected over many cycles (as opposed to a single shot), where the device then reconstructs a single cycle decay profile. This is possible as a result of a periodic excitation from the laser source, which can then be used to reconstruct a histogram of the single decay from data taken over many cycles. An example of how this histogram is created is shown in Figure 2.13 below:
Because this method relies upon the repetitive measurement of precisely timed single photons from the photoluminescence signal, the exact time difference between the excitation pulse and corresponding photon generated must be known. In order for this to be accomplished, both the trigger signal and photon signal must be converted to an electrical signal.

The trigger signal itself is trivial in most cases, as the PDL 800-D laser head and the Berkeley Nucleonics pulse generator both output an electrical signal to begin with. In the case of the MIRA 900 however, the trigger must be optically activated from
the laser itself, which involved splitting the laser output, sending one path incident on the sample and the other to a PicoQuant TDA 200 trigger diode, which uses a silicon pin photodiode to covert the optical excitation into a voltage signal that can be directly coupled to the PicoHarp 300 TCSPC device in order to synchronize the timing electronics.

The photon signal however, is often less trivial. In order to convert from a single photon to an electrical signal, either a Photomultiplier Tube (PMT) or a Single Photon Avalanche Diode (SPAD) is necessary. In our case, a Micro Photon Devices PDM series detector is used, combining the use of epitaxial silicon SPADs and integrated active quenching circuits, designed and optimized specifically for photon counting experiments. The PDM detector is shown in Figure 2.14.

![Figure 2.14: A Micro Photon Devices PDM series Single Photon Avalanche Diode (SPAD) detector. Adapted from micro-photon-devices.com](image)

This detector is then coupled to the input of the PicoHarp 300 system. A necessary
stipulation is that the probability of registering more than one photon per cycle is low (and in fact many of the cycles will have no photons at all), otherwise a 'pile-up' occurs, in which the earliest photons would be over-represented in the histogram. Instead, the histogram that is created (similar to the one shown above in Figure 2.4) is representative of photon arrivals per time bin, which correlates to the time decay that would have been attained from a single shot time-resolved analog measurement. In the histogram, one memory cell contains the photon counts for one corresponding time bin (or time channel), and as such there is a direct correlation between the counts in a time channel and the resolution of the decay profile. Therefore, for samples with strong luminescence, good signal to noise ratio is often not a time-intensive process, but for sample where photoluminescence is relatively weak, a much longer accumulation time will be necessary [132].

2.4 Temperature Dependent Measurements

It is often useful to perform optical spectroscopy measurements as a function of temperature, as the way that electronic and structural dynamics change with temperature can give additional insight into materials beyond simply performing room-temperature measurements. Properties such as conductivity [133], stress and long-range ordering [134], magneto-optical response [135], electron-phonon interactions [136], and absorption/photoluminescence [137], [138], [139] often have strong temperature-dependence, and as such, experiments where crystalline samples can be cooled to liquid helium temperatures provide the largest range to study these dynamics.
Arguably the most important result of cryogenic temperature experiments is the discovery of superconductivity, where the use of liquid helium was essential in causing a phase transition in mercury below a critical temperature \( T_c \), by Heike Kamerlingh Onnes in 1911 [140]. Interestingly, that same experiment yielded interesting observations of the behavior of the liquid helium itself around 2.2 K by Onnes, which was later shown in 1938 by Jack Allen and Don Misener [141], and Peter Kapitsa [142], to be the first observations of the superfluid transition of liquid helium.

2.4.1 **Oxford Cryostat Coldfinger**

For the temperature-dependent measurements discussed in this work, an Oxford MicrostatHe2 helium optical cryostat was used. This unique, helium-cooled cryostat allows for spectroscopic measurements through optical windows installed in two orthogonal directions, and is shown in Figure 2.15 below:
This versatile cryostat allows for a large variety of optical measurements at liquid helium temperatures, as a result of the optical windows placed on four sides of the samples. A thin film sample is then mounted on the inside of the Oxford cryostat, which itself is mounted on a large xy stage that allows movement of the cryostat (and therefore sample itself) in order to control precisely where the excitation will fall spatially on the sample. A long working-distance objective lens was used to focus the incoming excitation beam, and the emission from the sample is collected through a focusing lens in front of the spectrometer and passed through a long-pass
filter to be sure the excitation beam is not also included in the collected spectra. The SPAD detector is mounted on the backside of the spectrometer for time-resolved measurements. A diagram of this experimental set-up is shown in Figure 2.16.

![Experimental Set-up for Static and Time-Resolved Temperature-Dependant Photoluminescence Measurements](image)

All photoluminescence spectra were corrected for the CCD response and grating reflectivity across the spectral range of interest. A correction factor was also introduced to account for the s and p reflectivity and transmittance of the beam splitter used in the experiments.
2.5 **Linear Dichroism Spatial Mapping**

In order to correlate photoluminescence experiments to actual crystalline ordering in our physical samples, a linear dichroism (LD) spatial mapping experiment was devised. This involved mounting a short focal-length lens directly in front of our sample (which is contained within our cryostat) on a three-dimensional pizeoelastic stage. This stage has micrometer precision in all three dimensions, and the spectrally-resolved spot diameter is approximately 5 \( \mu \text{m} \), thus allowing a focused beam to map a 90 x 90 micrometer area of a crystalline sample. A diagram of this experimental technique is shown in Figure 2.17.

![Diagram of the experimental set-up of the linear dichroism mapping technique.](image)

*Figure 2.17: Diagram of the experimental set-up of the linear dichroism mapping technique.*

In addition, a high-resolution telescope is mounted in front and to the side of
the thin film sample, which allows in-situ monitoring of where the incident beam is striking the sample, which is essential to correlate the LD and absorption spectra spatially with the crystalline grains in the sample, and also to allow probing of the photoluminescence of a particular grain with extreme precision. Linking these experiments together is only possible through such an imaging technique, and hopefully will provide significantly more complete picture than any of the individual experiments on their own. A tighter view of the beam path and short-focal length lens is can be seen in Figure 2.18, where the telescope and polarized lamp are mounted facing the sample as well.
Figure 2.18: Dual pictures of the LD microscopy experimental set-up.
The piezostage on which the 5 cm focal length lens is mounted is connected to a ThorLabs BPC303 Benchtop Controller, which is a three channel piezo controller, able to output 150V/1A per channel (although in our case the maximum travel distance for a 90 $\mu$m movement in a particular axis direction corresponds to 75V output). The stage also had a feedback capability to the controller, making a closed loop system to assure precision when returning to the point of origin on the x-axis while raster-scanning. The BPC303 controller is shown below in 2.19.

![Thorlabs BPC303 piezostage controller.](image)

**Figure 2.19: Thorlabs BPC303 piezostage controller.**

The incoming polarized beam from a Helium-Neon laser (excitation $\lambda = 632.8$ nm) would then pass through both a frequency driven chopper (with a typical frequency of 266 Hz) as well as a PEM100 peizoelastic modulator from Hinds Instruments, shown below, which would modulate the polarization of the incoming light incident on the sample by a typical frequency of 50 kHz.
When the optical piece is compressed, the horizontally polarized component of the light will travel slightly faster through, and lead the vertical component. Alternatively, when the optical piece is stretched, the opposite behavior will occur, with the horizontal component lagging behind the vertical. Through this method, the polarization of the light incident on the sample is modulated between vertical to horizontal at a fixed frequency (as seen in 2.21).
A detector on the transmission side (behind) the mounted sample would then output a signal at two frequencies to dual Signal Recovery 7265 DSP lock-in amplifiers, the 266 Hz modulation as the DC signal and the 50 kHz modulation as the AC signal. These are in turn connected through Stanford Research Systems SR560 low-noise preamplifiers into the desktop computer itself. The Labview routine is then programmed to begin a raster scan in the lower left corner of a selected 90 x 90 µm area, pausing every 1 µm to record both the AC and DC signal at that specific point. Because the resolution of our beam size is slightly larger than 1 µm, we average a
specific raster value with the two adjacent values in the x-direction.

Phthalocyanine and other discotic molecules that crystallize into the solid state have optical transition dipole moments ($\mu$) oriented parallel and perpendicular to the face of the molecule itself (as discussed in detail in Chapter 1). A diagram of this is shown in Figure 2.22.

Figure 2.22: Diagram of the polarization axes of disc-like molecule. Adapted from Rawat et al [115].

Here $\mu_1$ and $\mu_2$ are the polarization axes in the plane of the molecule, $\theta$ is the stacking angle (or the tilt of the normal axis of the molecule with respect to the normal of the substrate) and $\phi$ is the azimuthal angle that represents the difference
in the stacking angle of a particular crystalline grain and the polarizer axis. The 90 \times 90 \mu m raster scans described above can then be plotted as a function of LD using the following equation, where the linear dichroism is expressed using the angles of the molecular stacking shown above.

\[ LD = (\cos^2 \theta)(\sin^2 \phi - \cos^2 \phi). \]  \hspace{1cm} (2.3)

The LD values obtained in these scans can therefore be positive or negative values, depending on the direction of the crystalline stacking in the crystalline grains. Additional LD spatial mapping scans of the pure CoOBPc sample can be found in the Appendix.

2.5.1 **Linear Dichroism Spatial Mapping**

**Experimental Data**

To begin with, shown in Figure 2.23 is a picture taken with the long-focal length telescope of a pure CoOBPc thin film sample mounted within the Oxford cryostat at the center, and in each of the four corners, a HeNe laser spot shown incident on the sample.
Figure 2.23: In-situ image of a thin film CoOBPc sample mounted inside a cryostat. The tightly focused HeNe laser spot is present toward the upper left of the sample.

Each of the four images show the laser positioned at the four corners of the 90 x 90 μm scanning area, with the intention of purposefully mapping across one of the grain boundaries that separate two adjacent crystalline grains. (Unfortunately, as the luminescence is significantly quenched in transition metal phthalocyanines, photoluminescence could not be recorded across different area for this particular sample). This scan of CoOBPc is shown in Figure 2.24, where the map is a function LD (with
the scale shown on the right hand side), along with the actual scanning area on from the telescope image.

*Figure 2.24: LD microscopy image of CoOBPc.*
The maximum LD was taken at a spatial location on the sample of approximately (60,45) and found to be 0.548, which corresponds to a $\theta = 42.3^\circ$. The ordering of the molecules is clearly visible, with two large regions of crystalline grains.

To further emphasize the quality of samples such as this, take as a counter-example some of the earliest deposition attempts of octabutoxy-naphthalocyanine in the solid state, where solubility was extremely poor, and no long-range order was established. Instead of large crystalline grains, crystalline islands of OBNPc only microns in size are somewhat isolated throughout a completely amorphous thin layer of OBNPc, as seen in the microscope image in Figure 2.25.
Figure 2.25: Polarized microscope image of H$_2$OBNPc and four LD microscopy focusing scans of a H$_2$OBNPc sample.

Beneath the microscope image of the thin film are four focusing scans. These are
shown as an example of the calibration that had to be performed to precisely image grain boundaries and ordering. The four scans were taken with the short-focal length microscope lens at four different focusing distances from the sample. Small changes in the focusing distance (in the direction perpendicular to the face of the sample) can influence the resolution significantly, as can be seen in the first three images. The final image in the bottom right shows a quality focusing, where one can resolve multiple small aggregates, where the more poorly focused scans show only single large aggregates.

In addition, thanks to the luminescence of OBNPc, photoluminescence (PL) was also able to be correlated spatially in scans on this sample. Three spots were chosen for the PL spectra, one of each of two aggregates that show contrasting linear dichroism, and one on the amorphous background. These three PL spectra, as well as the LD scanning map is shown in Figure 2.26.
Figure 2.26: Polarized photoluminescence spectra correlated to an LD microscopy scan of OBNPc.

While this particular sample is not ordered in any long-range crystalline manner, this technique allows the probing of luminescence in very well spatially defined areas, and therefore the luminescence within a single aggregate is able to be probed. While this particular sample does not show a large difference in polarization between the two aggregates (as a result of the lack of ordering in the sample), a strong contrast can be shown between the aggregates and the background, where a strong broad emission
is observed in the isolated aggregates, and several sharp emission peaks are observed in the amorphous H$_2$OBNPc background.

I was also able to perform a handful of scans on the first alloy phthalocyanine film fabricated, the H$_2$OBPc$_{0.5}$CuOBPc$_{0.5}$ thin film sample shown later in Chapter 4. In this case it was possible to correlate the photoluminescence to various spots on the sample, which allows additional insight to be made into the dynamics within the crystalline sample. Shown in Figure 2.27 is one of the LD spatial maps, with a plot of both the LD and the angle matrix (corresponding to $\phi$, the angle between the stacking axis of the molecules and the polarization of the incoming light) included for the same 90 x 90 $\mu$m scanning area.
As can be seen, the scanning area can be plotted as a function of either LD or $\phi$, however the image and contrast based on the orientation of adjacent grins will remain the same. In addition, the photoluminescence in three different spots was recorded, one inside each of the two adjacent crystalline grains, and one directly on the grain.
boundary between the two. A compilation of these spectra are shown in Figure 2.28.

Figure 2.28: Luminescence correlated to three different spots on a linear dichroism mapping of $\text{H}_2\text{OBP}_{0.83}\text{CuOBP}_{0.17}$.
In the luminescence spectra, the two curves are labeled as VV and VH, which correspond to an incoming polarization of vertical light with an analyzing polarization of vertical and horizontal, respectively. Comparing the two luminescence spectra at spatial locations of (50,20) and (50,75) of the 90 x 90 µm scanning area, corresponding to adjacent grains with different stacking axis orientations, we see a flipping in the polarization of the emitted spectra. This is in contrast to the grain boundary emission, where the polarization of the analyzer has little effect on the luminescence intensity.

This not only implies the excitonic recombination emission is polarized (which has been previously verified by Dr. Zhenwen Pan, Dr. Naveen Rawat, and myself as discussed in Chapter 1 [114], [115], for the pure species of phthalocyanines), but also that adjacent crystalline grains in these thin films oriented in different directions will have excitons polarized in different directions as well. This is an expected result, as the orientation of the molecules in the crystalline solid state should directly impact polarization direction of the excitons themselves.

Lastly, the grain boundary photoluminescence emission verifies this, as the grain boundaries should contain randomly oriented molecules [143] of phthalocyanines, and as such any long-range order or directional effects on the excitons, specifically polarization direction of the exciton emission should be lost, and as one can see the spectra from the (50,43) spatial location shows no preferential polarization of the emission in any direction, confirming the random orientation at the grain boundaries.
2.5.2  Temperature-Dependent Linear Dichroism Spatial Mapping

Thanks to the samples being mounted in the Oxford cryostat, this linear dichroism experiment also has the ability to be performed simultaneously at liquid helium temperatures, and allows the ability for temperature-dependent measurements. The prediction that there will be a reorientation of the molecules in the crystalline solid as a function of temperature is able be probed with this experimental technique.

With this in mind, shown in Figure 2.29 is the very first sample that was attempted with the temperature-dependent version of this technique, performed on a crystalline thin film samples of H$_2$OBPc.
Figure 2.29: Temperature-dependent LD microscopy study of a pure $H_2OBPc$ thin film. Adapted from Rawat et al [115].

There is a clear temperature-dependence on the ordering of the molecules, where the change in linear dichroism is a function of the change in $\cos^2 \theta$ from Equation 2.3, where $\theta$ corresponds to the molecular tilt (or the angle between the normal of the substrate and the normal of the face of the molecule). For this particular sample, a calculation from Equation 2.3 shows that the stacking angle $\theta$ changes a maximum of 25° at low temperatures to 65° as the temperature is raised [115]. The change in
this stacking angle also implies a change in the $\pi$-$\pi$ orbital overlap between adjacent molecules, as this is directly impacted by the change in $\theta$.

Now as a comparison to this H$_2$OBPc crystalline film, we will next consider a pure CoOBPc crystalline thin film, similar to the sample shown above. To begin, shown in Figure 2.30 is an in-situ telescope image of a CoOBPc thin film with the LD scanning area marked in red, and the corresponding room temperature linear dichroism spatial map of that area shown above.
Here the crystalline grain boundaries running vertically in the sample are well-
resolved, and long-range order is observed. With this image in mind, shown in Figure 2.31 is the same 90 x 90 micron area, spatially mapped at 5 different temperatures, from 5 K up to 250 K.

Figure 2.31: Temperature-dependent LD microscopy study of a pure CoOBPc thin film.
A remarkable lack of change in linear dichroism is observed here. Clearly the reorientation present in the H$_2$OBPc sample is completely absent here, implying that in the CoOBPc thin films, the stacking angle of the molecules does not change with temperature at all. As mentioned before, the CoOBPc thin films do not luminescence, and as such photoluminescence spectra unfortunately cannot be correlated to the crystalline grains shown, however even for non-luminescent samples, the insight that can be given into reorientation of crystalline ordering as function of temperature is extremely valuable.

If the specific angles of the orientation of molecules in crystalline solids can be followed as a function of temperature, coupled with photoluminescence studies, this tool can be extremely powerful. Giving insight into the correlations between excitonic states and the ordering of organic molecules in the solid state is of extreme interest for devices, as the purity and reduction of grain boundaries seems to be an essential property for many commercial applications [87]. If more information is known about the crystalline ordering and molecular interactions, then more information may be gained about the behavior of excitons in similar systems, and mechanisms of limiting exciton delocalization will be better understood, whether through grain boundaries, traps in the films, or other mechanisms related to disorder in crystalline solid state organic semiconducting systems.
2.6 Grazing Incidence X-Ray Diffraction Experiments

In order to investigate the crystallinity of the thin film samples, I submitted a proposal to the Cornell High Energy Synchrotron Source (CHESS) facility in order to perform grazing incidence x-ray diffraction (GIXRD) experiments on the thin film samples discussed herein, and was awarded time in December of 2013.

GIXRD measurements were performed at the CHESS facility, on the G2 line, with x-rays at 10.05 ± 0.01 keV ($\lambda = 1.2337$ Å), and the scattering data collected using a 640-element one-dimensional diode-array. A set of Soller slits were used on the detector arm to provide an in-plane resolution of 0.2 °. GIXRD patterns were collected on the same thin films previously characterized with the spectroscopy experiments mentioned above.

In the spirit of exploring these films as a possible analogs of inorganic semiconducting alloys, we performed grazing incidence x-ray diffraction studies on these thin film samples at the Cornell High Energy Synchrotron Source (CHESS). Shown below is a diagram of the experimental diffraction mapping set-up.
Figure 2.32: Experimental set-up for grazing incidence x-ray measurements performed at the Cornell High Energy Synchrotron Source. Adapted from Smilgies et al. [144]

Here $k$ is related to the wavelength of the beamline through

$$k = \frac{2\pi}{\lambda}. \quad (2.4)$$

Ultimately, we aim to transform these scattering angles into reciprocal space maps with can then be further analyzed. This is possible through the two equations listed below, where $Q$ is the component of the scattering vector parallel to the substrate, and $q_z$ is the perpendicular (or out-of-plane) component of the scattering vector

$$Q = k[\cos(\alpha)^2 + \cos(\beta)^2 - 2\cos(\alpha)\cos(\beta)\cos(\psi)]^{-1/2} \quad (2.5)$$
\[ q_z = k[\sin(\alpha) + \sin(\beta)]. \] (2.6)

The two-dimensional reciprocal space maps shown in Figure 2.33 were recorded for a series of concentrations in while rotating the sample 100° around an axis perpendicular to the plane of the thin film and substrate, in order to emulate a powder diffraction spectrum and capture as many reflections as possible [144]. Resolution limited strong reflections are observed for all thin films (including the alloys discussed later), confirming the samples are crystalline.

Shown below in Figure 2.33 is a GIXRD scattering map of pure metal-free octabutoxy-phthalocyanine as an example of the data taken at the CHESS facility.
Only a handful of diffraction peaks shown here are labeled, which is purposeful in order to discuss the process that was used to identify them. Here \((hkl)\) are the Miller Indices which represent planes that are orthogonal to the reciprocal lattice vectors \(b_i\)

\[ h \mathbf{b}_1 + k \mathbf{b}_2 + l \mathbf{b}_3. \]  \hspace{1cm} (2.7)

In order to correlate these scattering maps to actual physical properties of the
crystalline packing and structure, we employ Bragg’s Law

\[ n\lambda = 2d \sin \theta. \]  \hspace{1cm} (2.8)

Bragg’s Law describes the conditions for strongest constructive interference, where \( \lambda \) is the wavelength of the incoming x-ray (for our experiments the value of \( \lambda = 1.2337 \) Å, which corresponds to an energy of 10.05 keV). In order to correlate the \( \theta \) values to the reciprocal space \( Q \) vectors, the following equation is used

\[ Q = \frac{4\pi \sin \theta}{\lambda}. \]  \hspace{1cm} (2.9)

In addition, we are also able to relate the reciprocal space vector \( Q \) to the spacing \( d \) of the planes described by Bragg’s Law through the following relation

\[ Q = \frac{2\pi}{d}. \]  \hspace{1cm} (2.10)

The \( \text{H}_2\text{OBPc} \) molecule is a triclinic structure, and as such the following equation is the complete description of the \( d \)-spacing with respect to the volume, and the unit cell lengths, \( a \), \( b \), and \( c \) (in Å) and \( \alpha \), \( \beta \), and \( \gamma \) are the angles between the vectors \( b-c \), \( a-c \), and \( a-b \) respectively

\[ \frac{1}{d_{hkl}^2} = \frac{1}{V^2} \left[ h^2b^2c^2 \sin^2 \alpha + k^2a^2c^2 \sin^2 \beta + l^2a^2b^2 \sin^2 \gamma + 2hkabc^2(\cos \alpha \cos \beta - \cos \gamma) + 2kla^2bc(\cos \beta \cos \gamma - \cos \alpha) + 2hlab^2c(\cos \alpha \cos \gamma - \cos \beta) \right]. \]  \hspace{1cm} (2.11)
Chapter 3

Characterization and Spectroscopic Studies of Pure Octabutoxy-Phthalocyanine Thin Films

3.1 The Phthalocyanine Molecule

The central focus of most studies discussed here are based on the molecule phthalocyanine (or tetrabenzotetraazaporphyrin). Phthalocyanine are planar (pseudo-two dimensional) 18 \( \pi \)-electron aromatic ring systems that contain four isoindole subunits (a benzo-fused pyrrole) at each corner, connected together by a series of nitrogen atoms [145], [146], [59], [147], [13]. This conjugated ring system is aromatic, by nature of Hückel’s rule (as discussed in Chapter 1). This causes the ring system to be
extremely stable, due to the presence of the large number of delocalized electrons [59].

The phthalocyanine family, a well-known and very well-studied small molecule of the \( \pi \)-conjugated organic semiconductor family, offer the advantage of tuning the bandgap without changing the molecular structure of the carbon-nitrogen ring, through chemical engineering such as attaching side-chains at various positions around the ring in order to alter crystalline packing in the solid state or substitution of atoms at the center of the carbon-nitrogen ring. Phthalocyanine serves as a parent molecule for an entire family of derivatives, where one can attach varying alkylated side-chains to increase solubility, shift Q-band absorption peak, or adjust intermolecular distances along the \( \pi-\pi \) stacking direction in the crystalline phase [128], [148], [12]. They have very intense absorption maxima and high extinction coefficients in the visible and near IR spectral domain [147], [12], [149], with the Q-band extending into the 600-800 nm wavelength range, making them ideal candidates for photovoltaic devices, as this overlaps exactly with the maximum solar photon flux spectral window [14], [150], [151], as seen in Figure 3.1.
Figure 3.1: a) Maximum solar flux output from the Sun [152] b) Absorption spectra of thin film $\text{H}_2\text{OBPe}$.

This is in contrast to many other organic semiconductors whose maximum absorption and extinction coefficients are blue-shifted to lower wavelengths in the visible range. The central hydrogen atoms of the metal-free phthalocyanine molecule can
also be replaced with over 70 different metals (the focus here will be on d-shell transition metals), allowing for significant variation in electronic, magnetic and structural properties \[12\], \[153\], \[154\], \[74\], \[155\]. In addition, dielectric constant of metal-free phthalocyanine range from 4.22 - 4.55 in the solid state, depending on the polymorph of the crystalline structure \[156\].

3.2 Metal-Free

Octabutoxy-Phthalocyanine

Phthalocyanines can be chemically engineered to tune particular electronic and optical properties, through the addition of numerous side chains that also increase solubility, and result in an adjustment of the packing distance and tune the bandgap \[128\], \[157\]. Shown below in Figure 3.2 is one of the most common derivatives of phthalocyanine, with octabutoxy side chains attached at the non-peripheral positions (para-substitution) around the molecule.
These specific octabutoxy chains are of benefit due to a drastic increase in solubility, but also have the additional effect of being an electron donating group, and thus contributing some of their electron density into the $\pi$-conjugated phthalocyanine ring itself. This metal-free octabutoxy phthalocyanine ($\text{H}_2\text{OBPc}$) is the molecule purchased commercially from Sigma-Aldrich and used experimentally in a majority of these studies after the purification method discussed in Chapter 2.

Significant changes occur in the excitonic properties of phthalocyanines (and other similar organic small molecules) in the solid state, including broadening of spectroscopic features [82], [72], and the presence of a delocalized exciton as a result of $\pi-\pi$
interactions between molecules [115], [68], [158]. In these thin films the H$_2$OBPc molecules will order in pseudo one-dimensional chains, with the stacking axis parallel to the substrate [115], [79], [30], [84], in a co-facial arrangement along a crystalline axis as a result of van-der-Waals interactions between molecules that are maximized in this orientation [147], [13], [74].

The orientation of the π-π stacking axis in reference to the unit cell axis changes drastically from one phthalocyanine derivative to another [115], [159] making it impossible to directly infer information of the structural and electronic properties from the better-known insoluble parent molecules. The different orientations of these stacking axes in adjacent grains will give rise to the contrast seen in the images in Figure 3.4 [78]. The stacking axis also coincides with the axis of greatest mobility [160], [161], [162], [163], and recent low-temperature spectroscopy studies indicated the presence of exciton delocalization along this same axis [115], [130].
The crystal structure of H$_2$OBPc is triclinic and the space group is P ̅1. It has two molecules per unit cell, according to the powder spectrum, and lattice parameters are $a = 14.0135$ Å, $b = 14.3092$ Å and $c = 16.9072$ Å and the lattice angles are $\alpha = 71.9900^\circ$, $\beta = 85.8280^\circ$, and $\gamma = 73.4420^\circ$. The nearest neighbor separation along the stacking axis is equal to $d_1 = 4.84$ Å and $d_2 = 4.96$ Å [159].

After solution-deposition of all of the thin film samples discussed here, the first step of characterization is polarized microscope imaging to verify macroscopic grain size and long-range ordering. For the H$_2$OBPc thin film, these images are shown in...
Figure 3.4 for one of the crystalline thin films.

Figure 3.4: Polarized microscope image of a crystalline thin film of metal-free octabutoxyphthalocyanine.

Long-range order is evident in these films, approaching millimeter-size length in certain directions, which is well above the size needed for spectroscopic studies. The polarized images also show quality films with very few aggregates and holes. To further investigate the ordering, GIXRD was performed on this thin film, and the scattering map is shown in Figure 3.5 below.
For this pure H$_2$OBPc film, the assignments of the brightest reflections were made in a similar manner as discussed in Chapter 2, and are in agreement with powder x-ray data listed in the Cambridge Crystallographic Data Center (CCDC) [159]. A comparative table of these values can be found below, where the powder values for Q are listed from the CCDC as well our experimental Q values from the thin films taken at the CHESS facility and the d-spacings solved using those experimental values.
<table>
<thead>
<tr>
<th>Plane (hkl)</th>
<th>Qpowder (CDCC) (Å$^{-1}$)</th>
<th>Qexp (CHESS) (Å$^{-1}$)</th>
<th>d-spacing$_{exp}$ (Å)</th>
</tr>
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<tbody>
<tr>
<td>(100)</td>
<td>0.468</td>
<td>0.468</td>
<td>13.43</td>
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<tr>
<td>(001)</td>
<td>0.41</td>
<td>0.411</td>
<td>15.29</td>
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<tr>
<td>(110)</td>
<td>0.57</td>
<td>0.575</td>
<td>10.93</td>
</tr>
<tr>
<td>(011)</td>
<td>0.52</td>
<td>0.519</td>
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<td>0.613</td>
<td>0.612</td>
<td>10.27</td>
</tr>
<tr>
<td>(111)</td>
<td>0.611</td>
<td>0.611</td>
<td>10.28</td>
</tr>
<tr>
<td>(110)</td>
<td>0.759</td>
<td>0.758</td>
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<td>0.778</td>
<td>0.781</td>
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<td>(111)</td>
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<td>(102)</td>
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<td>0.91</td>
<td>6.9</td>
</tr>
<tr>
<td>(200)</td>
<td>0.934</td>
<td>0.939</td>
<td>6.7</td>
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<td>1.25</td>
<td>1.245</td>
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</tr>
<tr>
<td>(211)</td>
<td>0.953</td>
<td>0.956</td>
<td>6.57</td>
</tr>
<tr>
<td>(201)</td>
<td>1.02</td>
<td>1.021</td>
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<td>5.13</td>
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<td>(202)</td>
<td>1.23</td>
<td>1.218</td>
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</tr>
<tr>
<td>(302)</td>
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<tr>
<td>(323)</td>
<td></td>
<td>1.71</td>
<td>3.67</td>
</tr>
<tr>
<td>(133)</td>
<td>1.51</td>
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<tr>
<td>(124)</td>
<td>1.57</td>
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</tr>
<tr>
<td>(332)</td>
<td>1.7</td>
<td>1.704</td>
<td>3.69</td>
</tr>
<tr>
<td>(324)</td>
<td>1.94</td>
<td>1.954</td>
<td>3.21</td>
</tr>
</tbody>
</table>
After the deposition of a thin film of purified H$_2$OBPc, absorption measurements are performed, both in the newly deposited thin films, but also in solution (using the purified product that the thin films were fabricated from). Both the solution and solid state absorption spectra of the H$_2$OBPc are shown in Figure 3.6.

![Figure 3.6: Absorption spectra of purified H$_2$OBPc in solution and the solid state.](image)

As can be seen from the spectrum, a splitting in the maximum peak of the absorption is observed, as a result of the two isoindole nitrogens that carry hydrogens in
the center of the aromatic ring that cause a lowering of the symmetry, thus splitting
the polarized band in the x and y direction to make a point group symmetry of \( D_{2h} \)
in the \( \text{H}_2\text{OBPc} \) molecule [12], [145], and as a result one can observe three peaks in
the broad Q-band absorption at 705 nm, 745 nm, and 805 nm, while the solution
absorption shows only one main peak at 757 nm.

This thin film sample was also analyzed through Magnetic Circular Dichroism
(MCD) by my colleague Dr. Naveen Rawat in the Furis lab at the University of Ver-
mont. MCD measures the difference in absorption of polarized light, similar to LD
discussed in Chapter 2, but now using left and right circularly polarized light and in
the presence of a strong magnetic field aligned parallel with the propagation vector of
the incident light. As opposed to linear or circular dichroism, introducing the mag-
netic field probes the interaction between the polarized light and net magnetization
(electron orbital angular momentum) in the solid state sample. His MCD data and
subsequent fitting are shown in Figure 3.7.
Figure 3.7: 10 K MCD spectra and fitting of crystalline thin film of H$_2$OBPc. Courtesy of the PhD Thesis of Dr. Naveen Rawat from the University of Vermont [164]

The 10 K MCD fitting performed by Dr. Rawat shows at least seven different transitions, indicating the significant mixing of electronic states in the band structure induced by the magnetic field. For instance, when two states mix, the presence of MCD bands with opposite sign is observed, and for mixing to occur the states must be connected through a magnetic dipole operator and be associated with allowed electronic transitions. Therefore for this specific crystalline H$_2$OBPc sample, there must be contributions from lower lying states below the valence band that are mixing with the valence band itself, contributing to the addition of multiple other states.
This discussed in more detail in his PhD Thesis [164].

In addition, a temperature-dependent luminescence study is performed on the same pure crystalline thin film of H$_2$OBPc, shown in Figure 3.8, with an excitation wavelength of $\lambda = 393$ nm.
Figure 3.8: Temperature-dependent photoluminescence spectra of a crystalline thin film sample of $H_2OBPc$.

It is important to note the change in excitonic luminescence features as the temper-
ature is raised. The very strong emission seen at temperatures below approximately 150 K located at 930 nm begins to decrease in intensity, and finally disappears as we pass a threshold of roughly 200 K. This gives way to the more well-known weaker intensity room-temperature phthalocyanine exciton emission located at around 900 nm. The low-temperature exciton emission is polarized along the stacking axis and exhibits the typical behavior of a delocalized bulk exciton, strongly coupled to lattice phonons, that dominates the low temperature spectra. The second, higher-energy, more localized and temperature independent exciton, polarized perpendicular to the stacking axis, dominates the room temperature spectrum [115], [130].

This transition in luminescence from low to high temperatures in phthalocyanines has been previously explored by Dr. Zhenwen Pan in his PhD thesis as discussed in Chapters 1 and 2 of this work. He did a comprehensive study on both luminescence and photoluminescence lifetimes at 4.4 K of the octyloxy-phthalocyanine, and observed significantly longer lifetimes of this intense low temperature feature, as well as a reduction in linear polarization, a large redshift with increased temperature, and disappearance of this feature at higher temperatures (above 100 K). He then concluded that this must be an optically forbidden transition that becomes partially allowed at low temperatures, and most likely corresponds to an exciton with an electronic dipole polarized along the stacking axes of the molecules in the solid state [114].
Figure 3.9: A model of rotation in organic molecules. Created by Roy Anderson (UVM) and adapted from the PhD thesis of Dr. Zhenwen Pan at the University of Vermont [114].

Shown in Figure 3.9 is a theoretical model constructed by a former student in the Furis lab at the University of Vermont, Roy Anderson. It attempts to reconcile the Davydov Oriented Gas Model with the forbidden transitions observed in H$_2$OBPc and H$_2$OCPc at low temperatures, and the result indicates that in fact for an electronic band structure picture, the presence of the dark (forbidden) state can be interpreted as relaxation of the selection rules for radiative recombination, a product of the lowering of the symmetry by a distortion of the crystal lattice or structural phase transition that would lift the degeneracy of the exciton ground state [165], [115].

A fitting of the temperature-dependent photoluminescence was also conducted, using the Arrhenius equation below to fit the normalized peak luminescence at every temperature.
Here, I(T) is the intensity of the luminescence at a given temperature T, and C_i is a weighing constant for each individual activation EA_i. The fitting with the Arrhenius equation is used to extract the activation energy of the luminescence quenching mechanism, and this fitting is shown in 3.10, where two distinct activation energies are clearly seen.

\[
I(T) = \frac{I_o}{1 + \sum_i C_i e^{\left(\frac{-EA_i}{k_B T} \right)}}
\]  

(3.1)

\[ EA_1 = 3.9 \text{ meV} \]
\[ EA_2 = 35 \text{ meV} \]

Figure 3.10: Temperature-dependent Arrhenius fitting of H_2OBPc.

A smaller activation energy of EA_1 = 3.9 meV and a significantly larger activa-
tion energy $EA_2 = 35$ meV are observed in this temperature-dependent spectra, and further discussion of this can be found in Chapter 5.

In addition, time-resolved photoluminescence experiments were also performed on this thin film sample throughout the temperature-dependent study, and the 4 K and room temperature spectra are shown below in Figure 3.11 for the main excitonic emission in the sample.

![Figure 3.11: Lifetime of the major luminescence feature at 4 K and room temperature from thin film $H_2OBPc$.](image)

Where the radiative lifetimes $\tau$ can be extracted from the normalized intensity plotted on a natural log scale versus temperature using the following equation

116
\[ I(t) = I_0 e^{\left( \frac{t}{\tau} \right)}. \]  

(3.2)

Here, lifetimes of the excitonic recombination have a temperature dependence, with the lower temperature showing a longer lived state for the 930 nm feature, and with increase in temperature, giving a shortest lived state for the 905 nm feature that was recorded at room temperature.

<table>
<thead>
<tr>
<th>H₂OBPc Lifetimes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecule</td>
</tr>
<tr>
<td>-----------</td>
</tr>
<tr>
<td>H₂OBPc</td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>

### 3.3 Transition Metal Octabutoxy-Phthalocyanine Molecules

There is a large variety of derivatives that arise from substituting a transition metal in the center of the ring (replacing the two hydrogens), and it has been shown that this substitution can encompass up to 70 different metal atoms [12]. When a metal atom is substituted for the 2 hydrogen atoms at the center of the ring, it is important to note the change in symmetry.
The metal-free phthalocyanine has a point group symmetry of pseudo $D_{2h}$ due to the offset nature of the two hydrogens, while a metal substitution will enhance the symmetry to four-fold, giving a pseudo $D_{4h}$ point group symmetry in the metal-phthalocyanines.

In the pure open d-shell metal species of phthalocyanines, the luminescence in the solid state is significantly quenched at room-temperature due to the opening of nonradiative-recombination pathways via d-d transitions [148], [166], [167], [168], which precludes us from investigating the nature of excitonic states via luminescence in these species. As a result, the limits of probing the pure species with spectroscopy is limited to absorption and GIXRD, while the magnetic circular dichroism spectra
is of great interest, and is covered in full by my colleague Dr. Naveen Rawat in his PhD Thesis [164].

3.3.1 Cobalt Octabutoxy-Phthalocyanine

Cobalt is the first transition-metal phthalocyanine discussed here. The synthesis and purification of the cobalt octabutoxy-phthalocyanine was performed by Dr. Naveen Rawat, with the assistance of Dr. Anthony Wetherby, in the laboratory of Dr. Rory Waterman in the Chemistry department at the University of Vermont. The two hydrogens at the center of the phthalocyanine ring have been replaced with a Co$^{2+}$ metal ion with a ground state spin $S = 1/2$. The molecular structure is shown in Figure 3.13.
Solution-deposition of CoOBPc was performed using toluene as a solvent, and similar to the other thin films discussed herein, deposition speeds fell between 8-12 µm/s. Thanks to the fine work of Dr. Rawat, the purification of the powder was excellent, and as a result, long-range crystalline order was easily achieved in the solid state, as seen in Figure 3.14.
Large grains approaching the millimeter scale are shown, with very few aggregates and holes. As before, to further investigate the ordering, GIXRD was performed on this thin film, and the scattering map is shown in Figure 3.15 below (the large peak in the upper right is the c-plane cut sapphire substrate).
In the absence of a powder or single crystal structure for the CoOBPc molecule, the assignments in 3.15 were limited to the (001) and (100) reflections. There are three additional unidentified strong reflections that are also marked with diamonds which can be followed as a function of concentration. In the pure CoOBPc film, we observe two distinct (001) reflections, indicating the presence of crystalline grains with two distinctly different orientations. Q-values and associated d-spacing for the
assigned peaks were calculated from the scattering map, and are shown in the table below.

<table>
<thead>
<tr>
<th>Plane (hkl)</th>
<th>Q_{exp} (CHESS) (Å^{-1})</th>
<th>d-spacing_{exp} (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(001)</td>
<td>0.409</td>
<td>15.36</td>
</tr>
<tr>
<td>(100)</td>
<td>0.495</td>
<td>12.7</td>
</tr>
</tbody>
</table>

As a result of the luminescence being significantly quenched in the solid state for CoOBPc (as previously discussed), exploration was limited to absorption studies for the thin film and solutions samples, and those results are included in Figure 3.16.
The absorption spectra of CoOBPc contains a Q-band of 725 nm in solution, and a broad peak centered at 755 nm in the solid state, with fewer resolved peaks than the metal-free derivative shown above, a result of the increased symmetry in all the metal-phthalocyanine derivatives. That is, the change in symmetry from pseudo $D_{2h}$ to pseudo $D_{4h}$ will leave the states degenerate, thus any splitting present in the $H_2OBPc$ will now be absent in any of the transition metal species of phthalocyanines.
The absorption is significantly broadened and peaks slightly shifted as we deposit metal OBPC from solution into thin films, a common trend for all transition metal phthalocyanine species studied here.

3.3.2 Copper Octabutoxy-Phthalocyanine

The next phthalocyanine derivative is the very-well known copper substitution of the phthalocyanine molecule. It was the CuPc molecules that was main absorbing layer in Tang’s 1986 paper discussed previously [1]. The dielectric constant of copper phthalocyanine range from 4.05 - 4.44 in the solid state, depending on the polymorph of the crystalline structure [156]. The octabutoxy substituted derivative of the CuPc was commercially purchased from Sigma-Aldrich and purified using the method mentioned in Chapter 2. Here the two hydrogens at the center of the phthalocyanine ring have been replaced with a Cu$^{2+}$ metal ion with a ground state spin $S = 1/2$. The molecular structure is shown in Figure 3.17.
Figure 3.17: Molecular structure of copper octabutoxy-phthalocyanine.

The crystal structure of CuOBPc is monoclinic and the space group is $P 2_1/c$, with four molecules per unit cell [169].
CuOBPc has lattice parameters of $a = 13.7406 \, \text{Å}$, $b = 26.7373 \, \text{Å}$ and $c = 16.6902 \, \text{Å}$ and the lattice angles are $\alpha = 90^\circ$, $\beta = 101.278^\circ$, and $\gamma = 90^\circ$. The nearest neighbor separation along the stacking axis is approximately $d_1 = 3.46 \, \text{Å}$ and $d_2 = 4.9 \, \text{Å}$ [169].

Thin film deposition of CuOBPc proved more difficult than some of the other transition metal derivatives of phthalocyanine. First attempts of the pure CuOBPc film are included in Figure 3.19.
A noticeable difference can be seen in this image compared to the previously shown thin film samples. Any crystalline order is on a scale of only tens of microns at best, as opposed to the significantly longer-range order shown previously. This is most likely a result of the purity of commercially purchased product, even after a column purification, or a poor choice of organic solvent used for the solution deposition. Further evidence of this lack of order was the results of GIXRD performed on the same CuOBPc thin film.
As can be seen from figure above, the diffraction spectra appear have more powder character than crystalline character, implying the significant lack of long-range order in this particular sample.

Since that time, further purification and film deposition was performed, and significant improvement was made in the quality and lone-range order in the thin films, as evidenced by Figure 3.21.
Absorption experiments were also performed both in solution (toluene) and on the crystalline thin films samples. Again, the typical broadening going from solution to thin film is observed, with the characteristic large Q-band absorption at 710 nm in the solid state and 735 nm in solution. This can be seen in Figure 3.22.
3.3.3 Nickel Octabutoxy-Phthalocyanine

The nickel substituted phthalocyanine was the final commercially available derivative of phthalocyanine with octabutoxy side-chains, which was purchased from Sigma-Aldrich. Here the two hydrogens at the center of the phthalocyanine ring have been replaced with a Ni$^{2+}$ metal ion with a ground state spin believed to be $S = 0$. The molecular structure is shown in Figure 3.23.
The purification of NiOBPc is discussed in Chapter 2, and the deposition was performed from a toluene solution at speeds between 8-10 µm/s. Polarized microscope images of a pure NiOBPc are shown in Figure 3.23.
The crystal structure of NiOBPc has been previously solved, and the unit cell and stacking of the molecules is included below.
The crystal structure of NiOBPc is triclinic and the space group is P 1̅. NiOBPc has lattice parameters of $a = 14.107 \, \text{Å}$, $b = 14.121 \, \text{Å}$ and $c = 16.871 \, \text{Å}$ and the lattice angles are $\alpha = 86.52^\circ$, $\beta = 72.52^\circ$, and $\gamma = 73.30^\circ$. The nearest neighbor separation along the stacking axis is approximately $d_1 = 3.8 \, \text{Å}$ and $d_2 = 4.9 \, \text{Å}$ [170].

Absorption experiments were performed both in solution (toluene) and on the crystalline thin films samples. The typical broadening going from solution to thin film is observed, and both spectra can be seen in Figure 3.26.
The peak absorption wavelength for NiOBPc is located at 730 nm in solution and the two peaks in the solid state appear at 670 nm and 717 nm. An interesting observation can be seen in the splitting of the main Q-band absorption peak in the solid. The NiOBPc has a D\(_{4h}\) symmetry, therefore the behavior seen in the H\(_2\)OBPc is not expected in a molecule of higher symmetry, which is true for the solution absorption, but in the crystalline thin film a splitting of the main bandgap absorption peak is clearly seen, implying some lifting of degeneracy. Therefore it is unlikely that the symmetry of the molecule is the origin of this splitting, implying that intermolecular interactions occurring in the crystalline solid state will cause this splitting of the main
absorption feature in the NiOBPc thin film.

3.3.4 Manganese Octabutoxy-Phthalocyanine

Finally the manganese substituted OBPc, which was synthesized and purified in the laboratory of Dr. Rory Waterman in the Chemistry department at the University of Vermont, was performed by Dr. Naveen Rawat, with the assistance of Dr. Anthony Wetherby. The two hydrogens at the center of the phthalocyanine ring have been replaced with a Mn$^{2+}$ metal ion with a ground state spin S = 3/2. The molecular structure is shown in Figure 3.27.

![Molecular structure of manganese octabutoxy-phthalocyanine](image)

*Figure 3.27: Molecular structure of manganese octabutoxy-phthalocyanine.*
The MnOBPc derivative actually turned out to be the most difficult species to work with for deposition purposes, not easily giving long-range order seen in previous films. Solubility in toluene seemed to be very good, a possible reason being the purity of the synthesized product itself, or perhaps the solution-deposition speed and concentration. Shown in Figure 3.28 is one of the highest quality MnOBPc films fabricated.
While long-range crystalline order is clearly present in this samples, the grain boundaries character look much more chaotic, overlapping and limiting crystalline grain size to tens of microns laterally, and hundreds of microns in length at the very best. GIXRD was also performed on this pure MnOBPc sample (as shown in Figure
3.29) to verify crystallinity, and while the presence of some nicely resolved peaks indicate crystalline order, there is also some significant streaking that would indicate disorder present in the thin film as well.

![GIXRD spectra of a thin film of manganese octabutoxy-phthalocyanine.](image)

*Figure 3.29: GIXRD spectra of a thin film of manganese octabutoxy-phthalocyanine.*

Just like the other samples discussed above, solution and thin film absorption experiments were performed on the purified product in toluene and the solution-
The peak absorption wavelength for MnOBPc is located at 805 nm in solution and the two peaks in the solid state appear at 795 nm and 873 nm. Again, similar to the NiOBPc thin films spectra, a splitting is seen in the main Q-band absorption peak in the solid. As mentioned above, similar to the NiOBPc, the MnOBPc will have a $D_{4h}$ symmetry, and as such any lifting of the degeneracy should be suppressed. Which is true for the solution absorption, but in the crystalline thin film a clear splitting
of the main bandgap absorption peak is clearly seen, implying some lifting of the degeneracy. Similar to the NiOBPc case, the symmetry of the molecule is most likely not the origin of this splitting, and therefore the most likely scenario is intermolecular interactions occurring in the solid state film that will cause the peaks to be resolved.

3.3.5 Comprehensive Absorption Comparison Across MOBPc Molecules

It is important to show consider all of the absorption spectra together, in order to see the shift brought on by different substitution of these transition metals into the phthalocyanine ring. To begin with shown in Figure 3.31 is the solution spectra (in toluene) of all four transition-metal species discussed above.
Figure 3.31: Solution absorption spectra of transition metal OBPc species in toluene.

In the solution spectra, the CoOBPc is blue-shifted the most, followed very closely by NiOBPc and CuOBPc, which seem to follow their pattern on the periodic table. The MnOBPc however is red-shifted significantly compared to the other three species. The characterization Q-band absorption is present in all four species, slightly broadened in the MnOBPc species.

In the solid state, where interactions are drastically enhanced as discussed above, the absorption spectra also vary significantly from the solution, but also with respect...
to each in energy (wavelength). This is seen in Figure 3.32.

Figure 3.32: Thin film absorption spectra of pure transition-metal OBPC species.
The order of blue and red shifts do not follow the same pattern as seen in the solution spectra. Here the NiOBPc thin film is the furthest blue-shifted in the solid state, followed by CuOBPc and CoOBPc. In addition, a broadening of the absorption Q-band is observed, as a result of intermolecular interactions, although shifts to the blue or the red will vary depending on the MOBPc molecule. What is consistent across both the absorption and thin film spectra however is the significant red-shift the MnOBPc. In both cases a red-shift of approximately 70 nm in solution (0.15 eV) and up to 160 nm in the thin film (0.31 eV) is observed for the MnOBPc species.

This furthers the idea that a tunable band-gap absorption could be possible through the introduction of varying transition-metal species of phthalocyanines. While only four species are discussed here, one can imagine the myriad of substitutions that could be made with phthalocyanine and other ringed molecules, that could tune absorption spectra very precisely for device applications [12] [153] [154] [74] [155].
Chapter 4

Octabutoxy-Phthaloxygenine Alloys

This chapter gives a complete overview of a comprehensive and systematic fabri-
cation of an entire family of crystalline thin films of $H_2OBP_c_xMOBP_{c_{1-x}}$, using the
established room temperature solution-processed technique previously discussed, that
produces large crystalline grain sizes even at very low mixing ratios (high MOBPc
content). The range of different metal-free to metal OBPc ratios was varied from
$x = 0.5$ ($1:1 \text{ H}_2\text{CoOBPc}$) to $x = 0.001$ ($1000:1 \text{ H}_2\text{CoOBPc}$). For every different
concentration, a new customized deposition optimization was completed.
4.1 Fabrication of Metal/Metal-free Octabutoxy-Phthalocyanine Alloys

The purpose of these studies focus on quantifying the spatial range of intermolecular interactions and exciton delocalization that can directly impact carrier mobilities and exciton diffusion in organic small molecule semiconductors. The approach is inspired by a wealth of studies in inorganic semiconductor alloys (such as AlGaN, InGaN, SiGe etc.) [171], [122], [172], [126], [119], [127], [173], [121], [174], [124], [120], where compositional disorder can result in exciton localization by alloy potential fluctuations, as well as recent reports of successful donor/acceptor organic alloys containing two molecular species with similar geometries [77]. This pursuit benefits from a solution-processed deposition technique developed at the University of Vermont (discussed in Chapter 2) [78], [79], [80], that can accommodate a wide range of molecules for rapid fabrication of alloyed organic thin films with macroscopic crystalline grain sizes.

Alloyed thin film samples of $\text{H}_2\text{OBPc}_{1-x}\text{MOBPC}_x$ (with $0.5 \geq x \geq 0.001$) were fabricated from solution mixtures of $\text{H}_2\text{OBPc}$ combined with various transition-metal octabutoxy-phthalocyanines. The choice of transition metal species include cobalt(II) (CoOBPC), copper(II) (CuOBPC), nickel(II) (NiOBPC) and manganese(II) (MnOBPC) octabutoxy phthalocyanine.

As previously discussed in Chapter 3, the phthalocyanine molecules self-assemble into one-dimensional chains in the solid state. With this in mind, a picture can be created where in a ideal scenario the insertion of the MOBPc molecules will occur at regular intervals throughout the $\text{H}_2\text{OBPc}$ chain. This idealized picture is shown by
the diagram in Figure 4.1.

![Diagram of ideal mixing picture for various concentrations of H_2OBPc_x MOBPc_{1-x} in a 1D chain.]

Figure 4.1: Diagram of an ideal mixing picture for various concentrations of H_2OBPc_x MOBPc_{1-x} in a 1D chain.

This diagram is not likely a realistic picture of the actual stacking of molecules across the entire crystal structure, but simply an aid to illustrate how the insertion of metal-phthalocyanines into the one-dimensional chain might occur, where in actuality one would imagine regions of the crystalline film that are more H_2OBPc rich and regions that are more MOBPc rich. The goal of this project is ideally to use the mixing concentration of these alloys as control for electronic and excitonic properties.
in the solid state, and more specifically the spatial extent of the wavefunction (and indirectly the diffusion of the delocalized exciton) and crystallinity.

For a typical mixed phthalocyanine film, the individual H₂OBPc and MOBPc purified products were each dissolved in a 0.5% by weight solution (for ex. 0.0005 g/100 µl) in identical solvents (typically toluene). After sonicating each individual solution for 15 minutes, they were combined by volume into another solution (using the appropriate ratio desired), and then this combined solution was sonicated for an additional 20 minutes to assure complete mixing. The mixed solution was then immediately deposited at room temperature onto a PTS treated c-plane cut sapphire substrate using the hollow capillary pen-writing technique. Following the recipe listed above, a complete series of thin films were fabricated, with the transition-metal phthalocyanine concentration "x" varying from x = 0.5 all the way to x = 0.001 (the most dilute of the samples), for M = Co, Cu Ni, and Mn. The solvent of choice for all samples was toluene, with deposition speeds all in the range between 8-12 µm/s.

4.2 Characterization and Spectroscopic Studies on Crystalline Thin Film Octabutoxy-Phthalocyanine Alloys

4.2.1 H₂OBPcₓCoOBPC₁₋ₓ Alloys

This discussion will begin with the cobalt phthalocyanine alloyed films. They were the most straightforward crystalline thin films to fabricate, while the synthesis of
the molecule was perhaps the most difficult (a special thanks here to Dr. Naveen Rawat for all of his hard work on the cobalt phthalocyanine molecule). To begin, it is extremely important to show how the dynamics of deposition can effect the crystallinity of the thin film, specifically the deposition speed.

The grain size and crystallinity are largely controlled by solubility, the volatility of organic solvent, concentration of the solution before deposition, deposition speed, and wettability of the sapphire substrates which was improved using a triethoxyphenyloxysilane (PTS) surface treatment mentioned in Chapter 2. As an example of this in Figure 4.2 is a small insight into the optimization process that went into making each alloyed thin film for this project. Polarized microscope images of H$_2$OBPc$_{0.75}$CoOBPc$_{0.25}$ at various solution deposition speeds are included, and it is important to note both the smoothness of grain boundaries (or lack thereof) and aggregation in the thin film samples.
Figure 4.2: Polarized optical microscope images of H$_2$OBPc$_{0.75}$CoOBPc$_{0.25}$ at various deposition speeds. a) 6.25 µm/s b) 7.59 µm/s c) 8.48 µm/s d) 9.82 µm/s. Slower speeds a) and b) are prone to producing aggregates, while faster speeds, d) give rise to uneven and overlapping grain boundaries. In this case the optimum speed of deposition was determined to be c) 8.48 µm/s.

These polarized microscope images indicate the larger grain size originally observed in the pure phthalocyanine species is retained even in samples with high concentration of the transition-metal phthalocyanines. Increasing disorder is observed with increasing MOBPc concentration, but the films still retain crystalline grain sizes large enough for spectroscopic measurements. While thin films of phthalocyanines combined with porphyrins or other phthalocyanine species have been reported previ-
ously [175], [176], [177], [178], these studies mostly dealt with amorphous or highly disordered films created by thermal or vapor deposition, that lacked long-range order. Our studies indicate that the solution-processing technique discussed here preserves the crystalline quality to a much more significant extent.

Relatively small changes (on the order of 10%) in deposition speed cause significant differences in crystalline grain size and frequency of grain boundaries as seen in the H$_2$OBp$_{0.75}$CoOBp$_{0.25}$ thin films shown in Figure 4.2, while promoting the formation of aggregates (visible as bright green areas in a) and b) in Figure 4.2).

An optimization similar to this was continued for all other concentrations 'x' of CoOBp in the alloys H$_2$OBp$_{1-x}$CoOBp$_x$. Interestingly, the alloy concentration hardly influences the optimal deposition speed, as evidenced by polarized microscope images of alloyed thin films with various MOBPc concentrations shown in Figure 4.3.
Figure 4.3: Polarized optical microscope images of alloyed thin films with various concentrations. a) $H_2OBPC_{0.67}CoOBPC_{0.33}$  b) $H_2OBPC_{0.98}CoOBPC_{0.02}$  c) $H_2OBPC_{0.99}CoOBPC_{0.01}$.

Long-range ordering with large grain size is achieved even at high concentrations of MOBPc.

In order to investigate whether a new alloyed film is in fact created, comprehensive optical spectroscopy and x-ray diffraction characterization studies were performed. Specifically a series of spatially resolved single grain UV-VIS absorption
spectra were measured from various grains within a thin film sample. The typical diffraction-limited diameter of tightly focused laser beams is roughly 5 microns in our experiments, while the incoherent quasi-monochromatic focused white light diameter used in absorption measurements was as small as 50 microns, both of which fit well within the size of the large grains, even for the most disordered ($x = 0.5$) films. These beam sizes enable probing of electronic states within a single crystalline grain, free from the interference of defects and disorder using single wavelength techniques for luminescence studies or broad wavelength-tuned incoherent light sources for absorption studies.

**Single-Grain Absorption Studies**

In order to compare the newly formed alloy to the pure thin films of H$_2$OBPc and pure CoOBPc, single-grain absorption experiments were performed on all three. Shown in Figure 4.4 is a comparison of the pure H$_2$OBPc, pure CoOBPc, and H$_2$OBPc$_{0.83}$CoOBPc$_{0.17}$ single-grain thin film absorption spectra.
Figure 4.4: Room-temperature absorption spectra of $\text{H}_2\text{OBPC}$, $\text{CoOBPC}$ and $\text{H}_2\text{OBPC}_{0.83}\text{CoOBPC}_{0.17}$ thin films. The alloyed system spectrum bears the signature of an enhanced bandgap exciton feature (marked with an arrow), previously encountered in the metal-free species.

It is important to note that while the alloyed system retain certain absorption features from both pure $\text{H}_2\text{OBPC}$ and pure $\text{CoOBPC}$ thin films, it is clearly a unique absorption spectrum. Most notable, the bandgap excitonic absorption feature at 860 nm, a hallmark of the metal-free phthalocyanine, is also present in the alloyed system, with an enhanced intensity relative to the other features seen in the spectrum.

Further investigation was performed to verify whether the alloyed samples are in fact uniform on the macroscopic scale, free from large pure metal or metal-free
phthalocyanine aggregates. This was accomplished by recording spatially-resolved single grain absorption spectra from various randomly chosen grains within the same thin film. To ensure the 50 µm incoherent focused white light beam was in fact located within a single grain, a long distance telescope, equipped with a CCD camera was used to monitor the focused beam position on the thin film surface. The absorption spectra for eight different randomly selected grains within the H$_2$OBPc$_{0.83}$CoOBPc$_{0.17}$ are shown in Figure 4.5.

Figure 4.5: Room temperature absorption spectra of H$_2$OBPc$_{0.83}$CoOBPc$_{0.17}$, recorded for eight different crystalline grains within the single sample.
The absorption spectrum shape is preserved across all grains, with minor differences in the overall absorbance due to variations in the film thickness. Most importantly, the distinct bandgap exciton absorption feature at 860 nm is consistently present in all surveyed grains within the sample, indicating there are no grains of pure H$_2$OBPc or CoOBPc species. It is important to note the consistency across the relative peak ratios, with some exception occurring at the thicker edges of the film, where re-absorption is expected to occur. This accounts for the two curves where relative peak intensity ratios are not consistent with the rest of the spectra. The bandgap exciton feature (located at 860 nm) is not only present in every alloyed sample studied here, but also evolves as function of MOBp concentration.

Shown in Figure 4.6 are the complete set of single-grain absorption spectra for all concentrations of the cobalt alloyed phthalocyanine thin films, along with the pure H$_2$OBPc and CoOBPc thin films.
Figure 4.6: Absorption spectra of seven different concentrations of $H_2OBPc_{1-x}CoOBPc_x$ thin films at room temperature. In addition, absorption spectra from each pure thin film is shown for comparison.

An evolution is clearly observed as the concentration is varied from $x = 0.5$ (1:1 $H_2OBPc$:MOBPc ratio), to $x = 0.001$ (1000:1 $H_2OBPc$:MOBPc ratio). The $H_2OBPc$ bandgap exciton absorption feature at 860 nm broadens and becomes less prominent...
with increasing MOBPc concentration. Similar behavior is observed for the absorption spectra of the copper, nickel, and manganese alloyed films that are shown later in this chapter.

More importantly, the absorption spectra shown in Figure 4.6 point toward the existence of a threshold in the concentration that fundamentally alters the nature of the bandgap exciton states. For the cobalt alloyed samples this threshold is \( x = 0.09 \) (or 10:1 \( \text{H}_2\text{OBPc:CoOBPc} \)) (while for the copper alloyed films the threshold appears at a concentration of approximately \( x = 0.17 \)). Below this threshold (for \( x < 0.09 \) in cobalt samples), the 860 nm bandgap feature dominates the spectra.

**Grazing Incidence X-Ray Diffraction Studies**

All of these \( \text{H}_2\text{OBPc}_{1-x}\text{CoOBPc}_x \) thin film samples were brought to the CHESS facility at Cornell for characterization through GIXRD experiments. To begin with, shown in Figure 4.7 is the pure \( \text{H}_2\text{OBPc} \), \( \text{H}_2\text{OBPc}_{0.5}\text{CoOBPc}_{0.5} \) and pure \( \text{CoOBPc} \) GIXRD scattering maps.
Figure 4.7: Powder mode grazing incidence x-ray scattering map of 3 thin film samples. a) H$_2$OBPc  b) H$_2$OBPc$_{0.5}$CoOBPc$_{0.5}$  c) CobaltOBPc. Peaks assigned to the H$_2$OBPc are marked with circles, and those assigned to CoOBPc with diamonds.
Assignments made previously in Chapter 3 for the pure H$_2$OBPc can be seen in the H$_2$OBPc$_{0.5}$CoOBPc$_{0.5}$ thin film, as well as the (100) and (001) reflections from the pure CoOBPc sample (additional CoOBPc peaks are also observed, but as they are unable to be definitively assigned, are simply marked with diamonds). Despite the high concentration of CoOBPc, the film is still very well ordered, showing many familiar, well-resolved peaks of both pure species labeled.

GIXRD was performed on all concentrations of H$_2$OBPc$_{1-x}$CoOBPc$_x$, and a summary of concentrations can be found below in Figure 4.8 (with the remaining spectra included in the Appendix).
Figure 4.8: Powder mode grazing incidence x-ray scattering map of 6 thin film samples. a) H$_2$OBPc b) H$_2$OBPc$_{0.98}$CoOBPc$_{0.02}$ c) H$_2$OBPc$_{0.91}$CoOBPc$_{0.09}$ d) H$_2$OBPc$_{0.75}$CoOBPc$_{0.25}$ e) H$_2$OBPc$_{0.5}$CoOBPc$_{0.5}$ f) CobaltOBPc. Peaks assigned to the H$_2$OBPc are marked with circles, and those assigned to CoOBPc with diamonds.

Even in the absence of a solved CoOBPc single crystal structure, the evolution of these reflections can still be followed as a function of CoOBPc concentration. For thin films with concentrations of $x = 0.02$ and below, the scattering maps show reflections characteristic of the pure H$_2$OBPc crystal structure. In this case, one can consider these thin films as an analogy of a doped semiconductor, with the CoOBPc molecules randomly substituting for the H$_2$OBPc molecules in a single phase crystalline struc-
In contrast, for \( x = 0.09 \) and above, one can observe the presence of reflections that belong to both pure \( \text{H}_2\text{OBPc} \) and \( \text{CoOBPc} \) crystal structures, with slightly shifted \( Q \) vectors, indicating two crystalline phases are simultaneously present. If we correlate x-ray data with the absorption spectra shown in Figure 4.6, we conclude that as the concentration of \( \text{CoOBPc} \) increases above \( x = 0.09 \), two crystalline phases coexist in the film, and the absorption experiments indicate one of these phases is \( \text{H}_2\text{OBPc} \) rich, while the other is \( \text{CoOBPc} \) rich.

For example, the reflection associated with the (110) peak in the pure \( \text{H}_2\text{OBPc} \) (Figure 4.8a) gradually decreases in intensity with increasing \( \text{CoOBPc} \) concentration, and finally disappears in the pure \( \text{CoOBPc} \) as expected. Similarly, following evolution of the (001) peak as a function of concentration from the pure \( \text{CoOBPc} \) (Figure 4.8f), one will observe a gradual decrease in intensity as more \( \text{H}_2\text{OBPc} \) is introduced. Finally, this feature is completely absent for \( \text{CoOBPc} \) concentrations lower than \( x = 0.09 \). (This is immediately apparent in Figure 4.11, showing the peak GIXRD reflection intensity vs. concentration of \( \text{CoOBPc} \) plot). We also attempted to estimate a domain size of alloy fluctuations by analyzing the FWHM of (110) peaks of the \( \text{H}_2\text{OBPc} \) as a function of \( \text{CoOBPc} \) concentration (shown in Figure 4.9 and 4.10).
Figure 4.9: \( (110) \) \( \text{H}_2\text{OBPc} \) GIXRD Peak Intensity vs. \( Q \) perpendicular for varying concentrations of \( \text{H}_2\text{OBPc}_{1-x}\text{CoOBPc}_x \) thin film samples.
Figure 4.9 and 4.10 show both a decreasing intensity and increasing full-width at half-maximum for the (110) $H_2\text{OBPc}$ peak as the concentration of $\text{CoOBPc}$ in the crystalline sample is increased, which is to be expected. Taking this one step further, the peak intensity value for two well-resolved features, the (101) for the pure $H_2\text{OBPc}$ and the (001) for the pure $\text{CoOBPc}$, was followed as a function of $\text{CoOBPc}$ concentration in the thin films, shown below in Figure 4.11.
As one might anticipate, the peak intensity of each of the two peaks representative of a major feature in the pure species decreases consistently with the introduction of the other species (or increases as the sample becomes more "pure"). The evolution of in-plane and out-of-plane domain sizes extracted from the (110) peak (shown in Figure 4.12 and 4.13, respectively) indicate there is a trend of decreasing domain size for CoOBPc concentrations larger than x = 0.09.
Figure 4.12: Estimated in-plane domain size vs. concentration of CoOBPc for the (110) GIXRD reflections of H$_2$OBPC$_{1-x}$CoOBPc$_x$ crystalline thin film samples. Error bars are on the order of the estimated domain sizes, as a result of the resolution limit of the experiment.
For \( x < 0.09 \) the reflections are very narrow in Q-space, and our experimental resolution is not sufficient to exactly determine the domain size (see error bars in Figure 4.12 and 4.13). This decrease in domain size with increasing CoOBPc concentration is expected with the formation of a random alloy [179], [123]. The coexistence of the two crystalline phases, and the reduction in domain size, can have serious implications on the excitonic states in this system, especially in the context of previous low-temperature photoluminescence findings that revealed the presence of two
bandgap exciton states in pure H$_2$OBPc thin films [115] [130], as discussed in Chapters 1 and 3.

**Temperature-Dependent Photoluminescence Studies**

The absorption experiments shown above in Figure 4.6 indicate a possible correlation between concentration of MOBPc and the nature of excitonic states, however only low-temperature luminescence spectroscopy experiments can unambiguously probe the delocalized exciton. This is as a result of the reorientation of molecules in the crystalline lattice relaxing the selection rules, and previously optically forbidden exciton (the delocalized exciton) becomes optically allowed at low temperatures [115]. Comprehensive temperature-dependent luminescence characterization was therefore conducted on all alloyed thin films, using four different transition-metal species of octabutoxy-phthalocyanines (Co, Cu, Ni, Mn). As mentioned in Chapter 3, for metal species of phthalocyanines, the luminescence in the solid state is significantly quenched [148], [166], [167], [168], which precludes investigating the nature of excitonic states via luminescence in these species. This is the primary reason why concentrations of MOBPc above $x = 0.5$ (corresponding to 1:1 H$_2$OBPc:MOBPc) were not explored in these studies.

For these measurements, samples were placed in an Oxford continuous flow cold-finger cryostat, cooled to liquid helium temperatures, and subsequently heated in incremental steps up to room temperature. Photoluminescence spectra and spectrally-resolved PL decay curves were recorded at each selected temperature using a diffraction limited focused excitation laser beam (diameter of 5 µm). To begin, shown in Figure 4.14 is a temperature-dependent study of the H$_2$OBPc$_{0.91}$CoOBPc$_{0.09}$ thin film.
Figure 4.14: Temperature-dependent photoluminescence of $H_2OBPc_{0.91}CoOBPc_{0.09}$ from a) 10 K to 150 K and b) 175 K - 293 K.
A few observations are immediately apparent from this spectra. First, at low temperatures, the signature photoluminescence feature of the delocalized exciton that was present at low temperatures at 930 nm in the pure H$_2$OBPc remains present here, and similar to that pure sample, this feature decreases with temperature, eventually dying at approximately 150 K. As the temperature is raised from 5 K, the well-known, blue-shifted localized exciton at 900 nm that is polarized perpendicular to the stacking axis appears and continues to dominate the spectra until room temperature. It has been previously established that this behavior is due to phonon coupling and a change in the stacking angle for temperatures larger than 150 K [115], and as seen in Figure 3.9 in Chapter 3.

The other remarkable trait of all alloyed films is the presence of a sharp luminescence emission feature located at 850 nm (feature (1)), never before reported in pure H$_2$OBPc thin films. The feature is strongly temperature-dependent, with a full-width at half-maximum (FWHM) rapidly increasing, and an energy rapidly decreasing, with temperature. In some of these samples (such as x = 0.5 and x = 0.09), the lowest temperature spectrum even exhibits multiple vibrational replicas of the main luminescence peak.

The sharpness of this feature and its temperature dependence is reminiscent of emission from localized states (or bound excitons) in bulk semiconductors, where the $\Delta k = 0$ selection rule for optical recombination results in the presence of strong phonon replicas for these transitions. In contrast, for delocalized (or free) excitons, the selection rules are relaxed due to strong phonon coupling already present in the system (as mentioned previously).

As a result of excitonic emission being significantly quenched in the solid state for
MOBPc molecules, this sharp emission cannot simply be associated with luminescence from the CoOBPc dopants. Instead, this feature is likely associated with an optical transition involving one of the delocalized π-orbitals of the H2OBPc chain and an electronic state localized on the CoOBPc molecule. It can possibly be regarded as an intermolecular charge transfer exciton where either the hole or electron is delocalized along the H2OBPc chain, while the other carrier is largely localized on the MOBPc molecule.

A second interpretation of this unique 850 nm emission feature involves orbital interactions between the MOBPc molecules and the H2OBPc chains. As discussed further below, this 850 nm exciton luminescence is present in every H2OBPc1−xMOBPcx alloy film shown in this work, meaning this feature is entirely dependent on the presence of the MOBPc in the alloy films. The cobalt, nickel and copper phthalocyanines all contain an a1u molecular orbital at almost identical energy levels with respect to vacuum [153], while the LUMO of each metal derivative is either a b1g or an eg orbital. If some interaction is occurring at the interface between the H2OBPc and MOBPc molecules, then a lifting of the eg orbital degeneracy is possible, allowing hybridization between the b orbitals of the conduction band in the H2OBPc with the now non-degenerate b orbitals that make up the LUMO in the MOBPc, and some excitonic recombination could be induced at a higher energy. The oscillator strength itself must be coming from the H2OBPc molecules, but this hybridization coming from the lifting of degeneracy in the LUMO of the MOBPc could be the origin of this unique exciton emission.

As a direct comparison, we will now consider the H2OBPc0.5CoOBPc0.5 sample, where there is a 1:1 ratio between molecules of H2OBPc and CoOBPc in the thin
film. The temperature-dependent luminescence of the $\text{H}_2\text{OBPc}_{0.5}\text{CoOBPc}_{0.5}$ thin film is shown in Figure 4.15.

![Temperature-dependent photoluminescence of $\text{H}_2\text{OBPc}_{0.5}\text{CoOBPc}_{0.5}$ from a) 4 K to 75 K and b) 100K - 293K.](image)

*Figure 4.15: Temperature-dependent photoluminescence of $\text{H}_2\text{OBPc}_{0.5}\text{CoOBPc}_{0.5}$ from a) 4 K to 75 K and b) 100K - 293K.*

A significant difference is immediately apparent in this spectra as compared to the
H$_2$OBP$_{c0.91}$CoOBP$_{c0.09}$ sample. In the H$_2$OBP$_{c0.5}$CoOBP$_{c0.5}$ film, where picturing a scenario similar to the diagram shown in Figure 4.1, the probability of having a nearest neighbor of the opposite species is 50%, and in that case, the $\pi$-$\pi$ stacking and vibrational coupling that lead to the observation of the delocalized exciton in the pure H$_2$OBPc is completely inhibited, and one observes only the contribution from the localized exciton polarized in the plane of the molecule. This is a universal behavior observed for all of the d-shell transition-metal ions studied (Co, Cu, Ni, Mn phthalocyanine alloys), as all the four alloyed systems exhibited a similar trend with increasing MOBPc concentrations (included below in this chapter is the spectra for Cu, Ni and Mn). Observations also indicated the concentration that characterizes the switch from localized to delocalized excitons is slightly different for the various transition metals studied in these alloyed thin films, most likely as a result of the somewhat different packing structure of molecules in the various MOBPc crystalline alloys.

In addition, the intensity of the sharp 850 nm luminescence feature is strongly enhanced in the H$_2$OBP$_{c0.5}$CoOBP$_{c0.5}$ sample. It must be emphasized that unlike previous studies of disordered pure H$_2$OBPc thin film systems performed by Dr. Zhenwen Pan at the University of Vermont [130] [114], the 850 nm feature is not a result of disorder at the grain boundary or some other type of defect in the sample. The focused beam luminescence experiments confirm the presence of this feature everywhere inside the grains in the crystalline films. While there is no consistent trend for the evolution of the intensity of this feature with the H$_2$OBPc to MOBPc mixing concentration, its relative intensity with respect to the excitonic recombination, is much larger in the higher concentration thin films ($x = 0.09$ and above), confirming
it is related to the presence of MOBPc molecules. This feature is present in all alloyed films studied, regardless of concentration, and its presence in all the crystalline grains of any given thin film provides further evidence that these samples are not simply H₂OBPc thin films with inclusions of pure MOBPc aggregates.

This sharp feature is very much present even in the lower concentrations (x = 0.02 and below), dispelling the idea that we might simply be looking at emission at a grain boundary between nanometer size MOBPc inclusions and the H₂OBPc matrix. If the metal-free and metal OBPc were completely phase separated, we would either record luminescence of pure H₂OBPc or no luminescence at all, which is clearly not the case here. Instead, as mentioned in detail above, a gradual extinction of the delocalized exciton, in favor of an enhancement in the localized exciton is observed with increasing MOBPc concentration at low temperatures.

With this in mind, shown in Figure 4.16 is a compilation of photoluminescence as a function of CoOBPc concentration at liquid helium temperatures and room temperature.
Figure 4.16: Luminescence spectra of eight different ratios of $H_2OBPc_{1-x}CoOBPc_x$ at 5 K and at room temperature.

For all concentrations, with the notable exception of $x = 0.5$ (1:1 $H_2OBPc$:CoOBPc
ratio), the photoluminescence spectra exhibit a feature associated with the delocalized bulk exciton that was previously identified in pure H$_2$OBPc thin films at low temperature (labeled as feature (3) in Figure 4.16) [115]. As we follow the evolution of the luminescence spectra as a function of CoOBPc concentration, we notice the shape of the delocalized exciton feature (3) does not appear to change in any dramatic fashion, until we reach the x = 0.09 concentration (10:1 H$_2$OBPc:CoOBPc ratio). For all concentrations x > 0.09, feature (3) becomes sharper and loses intensity until it completely disappears in the x = 0.5 thin film. In contrast, the localized exciton, feature (2), that was always absent at low temperatures from the spectra of the pure metal-free species dominates the low temperature spectrum for the x = 0.5 film.

This is reminiscent of inorganic semiconductors, where the excitonic behavior in the lightly doped systems retain the properties of the pure material, while alloyed systems can have distinct properties that in many cases are due to a new crystalline phase. However, in stark contrast to inorganic alloys where the excitonic line-width broadens, and the overall intensity decreases due to alloy fluctuations [172], [126], [121], the narrowing of the exciton line-width and its blue shift at large MOBPc concentrations indicate that the formation of the delocalized exciton is inhibited altogether.

This observation correlates with the previous GIXRD spectra (Figure 4.8), and the absorption spectra (Figure 4.6), that infers a significant change in the structural ordering for the films with CoOBPc concentration larger than x = 0.09. One could then conclude in the cobalt phthalocyanine alloys, the critical concentration of CoOBPc at which the delocalized exciton disappears is approximately 9%. Since the presence of a delocalized exciton is exclusively due to the $\pi$-$\pi$ stacking in the
ordered H$_2$OBPc chain, as well as the coupling to the lattice vibrations, we can infer that the average distance between two CoOBPc molecules becomes roughly equal to the spatial extent of the exciton delocalization around approximately $x = 0.09$ (10:1 H$_2$OBPc:CoOBPc).

The correlation between the delocalized exciton state and the compositional fluctuations cannot simply be understood through an analogy to inorganic alloy semiconductors. This is because in phthalocyanines, the coupling of $\pi$-states to lattice vibrations is most likely responsible for the existence of the delocalized exciton, through the coherence discussed in Chapter 1. The presence of compositional fluctuations in the system does not merely create an alloy potential fluctuation that could trap the bandgap exciton (as is the case for inorganic systems) [171], [122], [172], [119], [127], [125], but more importantly disturbs the long-range vibrational coupling, inhibiting the formation of the delocalized exciton altogether.

For CoOBPc concentrations larger than $x = 0.09$, the $\pi$-$\pi$ stacking along the molecular chain will be significantly different, since the probability of having a nearest neighbor of the opposite species becomes larger. The $\pi$-$\pi$ overlap along the stacking axis is now perturbed on a length scale comparable to the exciton delocalization in the pure species. Therefore in these alloys, the compositional fluctuations will gradually diminish the spatial extent of the delocalized exciton at low temperatures, for concentration $x > 0.09$. If one assumes a perfectly random distribution of these molecules, the result implies the spatial extent of the delocalized exciton is on average approximately 10 lattice spacings (or roughly 40 Å) along the stacking axis in the pure H$_2$OBPc crystalline films. This interpretation is also supported by the spectrum of the H$_2$OBPc$_{0.5}$CoOBPc$_{0.5}$ film shown above, where as mentioned, the delocalized
exciton in the pure H$_2$OBPc is completely inhibited, only the contribution from the localized exciton is present.

**Time-Resolved Photoluminescence Studies**

Additional insight into the luminescence discussed above can be gained by performing time-resolved luminescence experiments on these thin films. The discussion above regarding excitonic properties in the organic alloy formation is supported by the low-temperature evolution of radiative lifetimes in the H$_2$OBPc$_{1-x}$CoOBPc$_x$ alloy films shown in Figure 4.17.
Figure 4.17: a) Time-resolved delocalized excitonic photoluminescence decay for eight different ratios of \( \text{H}_2\text{OBPC}_{1-x}\text{CoOBPC}_x \) at 5 K. The corresponding concentration of CoOBPC are listed next to each spectrum. b) Time-resolved excitonic photoluminescence decay for the three features present in the \( \text{H}_2\text{OBPC}_{0.91}\text{CoOBPC}_{0.09} \) film spectrum at 5 K.
The most notable finding in this data is the evolution of the bandgap exciton recombination lifetime as a function of concentration at 5 K shown in Figure 4.17a. For most of the alloyed films, the delocalized exciton lifetimes are similar to the one measured in pure H$_2$OBPc films, decreasing slightly with increasing CoOBPc concentration, while the 850 nm feature shown in Figure 4.17b decays on the same scale as the bulk excitons. The only remarkable difference is seen for the x = 0.5 alloy film bandgap exciton, whose lifetime is much longer than any decay ever measured at low temperature in the pure H$_2$OBPc film, with the delocalization inhibited by the lack of nearest neighbors of the same species.

4.2.2 H$_2$OBPc$_{1-x}$CuOBPc$_x$ ALLOYS

A complete set of H$_2$OBPc$_{1-x}$CuOBPc$_x$ alloys were also fabricated, in order to compare to the set of cobalt phthalocyanine alloys as a function of changing the central transition metal ion. Purification of the CuOBPc was performed as described in Chapter 2, and the films were deposited from a toluene solution. A significant portion of the behavior observed for the H$_2$OBPc$_x$CoOBPc$_{1-x}$ films is also true for the H$_2$OBPc$_x$CuOBPc$_{1-x}$ samples (as well as the nickel and manganese alloys discussed below), and as such, the focus here will only be on the differences between the two series of films.

As mentioned above, a completely new deposition optimization was necessary, but coincidentally the choice of solvent (toluene) was consistently able to be used for all alloy discussed in this chapter. Show below in Figure 4.18 is a polarized microscope image of H$_2$OBPc$_{0.83}$CuOBPc$_{0.17}$ (the very first alloyed film that was fabricated for this study).
This particular sample was essential in the studies described here, as the characterization techniques developed for these alloys were actually first employed to study just this film. For instance, the single-grain absorption technique was necessary to verify that a complete mixing had occurred, and not just regions of pure $\text{H}_2\text{OBPc}$ and CuOBPc (as mentioned above in more detail). An in-situ image of this film while the single-grain absorption measurement was occurring is shown in 4.19.
While using this in-situ telescope technique to monitor the beam spot on the sample, probing of individual grains became possible as the spot size of the lamp falls well inside an individual grain (covered in much more detail in Chapter 2). So with this in mind, eight different single-grain absorption spectra are shown in Figure 4.20.
Figure 4.20: Room temperature absorption spectra of $H_2OBPc_{0.83}CuOBPc_{0.17}$, recorded for eight different crystalline grains within a single sample.

Again, the absorption spectrum shape is fairly consistent across all grains, with minor differences in the overall absorbance due to variations in the film thickness. As with the cobalt alloys, the bandgap exciton absorption feature at 860 nm is consistently present in all surveyed grains within the sample, indicating there are no grains of pure $H_2OBPc$ or $CuOBPc$ species. Also, the two curves where relative peak intensity ratios are not consistent with the rest of the spectra are located at the very edge of the films, where the film is much thicker and spectra is altered due to re-absorption.

In addition, for the sample of $H_2OBPc_{0.83}CuOBPc_{0.17}$, the single grain absorption
measurement technique was also used to measure the linear dichroism in those eight grains as well (where as discussed in Chapter 1, linear dichroism lends insight into the mixing of electronic states in the band structure and the orientation of optical transition dipole moments in the crystalline sample), shown in Figure 4.21.

![Linear Dichroism Spectra](image)

*Figure 4.21: Room temperature linear dichroism spectra of $H_2OBPc_{0.83}CuOBPc_{0.17}$, recorded for eight different crystalline grains within a single sample.*

A complete analysis of this and many other linear dichroism and circular dichroism spectra can be found in the PhD Thesis of Dr. Naveen Rawat [164], but it is simply important to point out the consistency of the LD spectra throughout the sample, with
the exception of one scan, which was located on the edge of the film, where thickness and uniformity are quite different.

After fabrication of a complete set of $\text{H}_2\text{OBPC}_{1-x}\text{CuOBPC}_x$ alloys is completed (optimizing to reduce aggregation and increase uniformity of grain boundaries) this same single-grain absorption is performed on all crystalline samples, and shown here in Figure 4.22.
Temperature-dependent photoluminescence was performed on a smaller set of H$_2$OBPc$_{1-x}$CuOBPc$_x$ thin films, and those results are included in Figure 4.23, where the same 3 main luminescence features observed in the H$_2$OBPc$_{1-x}$CoOBPc$_x$ luminescence spectra are again indicated with arrows here.
Figure 4.23: Luminescence spectra of four different ratios of $\text{H}_2\text{OBPc}_{1-x}\text{CuOBPc}_x$ at 5 K and at room temperature. The corresponding concentration of CuOBPc are listed next to each spectrum. Excitation wavelength is equal to 734 nm.

The first observation that can be made of the low temperature spectra is that sharp localized emission located at 850 nm is clearly present, as it was in the $\text{H}_2\text{OBPc}_{1-x}\text{CoOBPc}_x$ samples, with what appears to be an even stronger dependence on the concentration of CuOBPc in the alloyed sample. In addition, the inhibition
of the delocalized exciton that was observed in the H$_2$OBPc$_{0.5}$CoOBPc$_{0.5}$ sample is clearly observed in the H$_2$OBPc$_{0.5}$CuOBPc$_{0.5}$ sample here, where the only emission observed at 5 K is from the localized exciton at 890 nm.

However, perhaps the most interesting difference between the cobalt and the copper alloys is the shape of the delocalized excitonic feature (at 930 nm) as a function of MOBPc concentration. One should recall that in the H$_2$OBPc$_{1-x}$CoOBPc$_x$ samples a clear transition occurs past a concentration of $x = 0.09$ (or 10:1 H$_2$:CoOBPc) in the photoluminescence spectra. In the case of the H$_2$OBPc$_{1-x}$CuOBPc$_x$ there appears to be almost no change in the shape of the delocalized exciton emission as we move from a CuOBPc concentration of $x = 0.09$ to $x = 0.17$. This indicates that this critical concentration must be below $x = 0.17$ (or 5:1 H$_2$:CoOBPc). This is assumed to be as a result of the different packing of the molecules in CuOBPc as opposed to CoOBPc. While the number of unit cells is unknown for CoOBPc, as the crystal structure has not been solved, the CuOBPc packs four molecules into the unit cell, as opposed to the H$_2$OBPc, which contains just two molecules per unit cell. The packing of the molecules in these alloys systems significantly influences excitonic properties as discussed in detail previously in Chapter 1, and that influence will have direct impact on what critical MOBPc concentration influences a change in the luminescence spectra.

Again, time-resolved luminescence experiments were also performed simultaneously with the temperature-dependent luminescence on these H$_2$OBPc$_{1-x}$CuOBPc$_x$ thin films. The discussion above regarding excitonic properties in the organic alloy formation is supported by the low-temperature evolution of radiative lifetimes in the H$_2$OBPc$_{1-x}$CuOBPc$_x$ alloy films shown in Figure 4.24.
Figure 4.24: Time-resolved exciton photoluminescence decay for four different ratios of \(H_2OBPC_{1-x}CuOBPC_x\) at 5 K and room temperature. The corresponding mixing ratios of metal-free to metal are listed next to each spectrum, as well as the specific exciton wavelength.
Here for the \( \text{H}_2\text{OBPc}_{1-x}\text{CuOBPc}_x \) films, the evolution of the bandgap exciton recombination lifetime as a function of CuOBPc is almost negligible at 5 K. The delocalized exciton lifetimes are similar to the one measured in pure \( \text{H}_2\text{OBPc} \) films, and 850 nm feature decays on the same scale as the bulk excitons. The only remarkable difference is seen for the \( x = 0.5 \) alloy film bandgap exciton at room temperature, where the exciton lifetime appears to be moderately longer lived compared to the other alloys, possibly due to a confinement from the CuOBPc molecules adjacent to the \( \text{H}_2\text{OBPc} \) molecules.

4.2.3 \( \text{H}_2\text{OBPc}_{1-x}\text{NiOBPc}_x \) Alloys

The fabrication of phthalocyanine alloys now moves to NiOBPc, which was the last commercially available octabutoxy derivative available from Sigma-Aldrich, but was the second set of alloy created (following the cobalt alloys). Purification was performed as described in Chapter 2, and the films were deposited from a toluene solution in a similar manner as the other alloyed films. As before, single-grain absorption experiments were performed on all the crystalline thin film samples, and the results as a function of NiOBPc concentration are contained in Figure 4.25.
Figure 4.25: Absorption spectra of seven different concentrations of $\text{H}_2\text{OBPc}_{1-x}\text{NiOBPc}_x$ thin films at room temperature. In addition, absorption spectra from each pure thin film is shown for comparison.

Similar to the two sets of cobalt and copper alloys alloys above, a consistent trend is observed as the concentration of NiOBPc is increased. However, the hallmark 860 nm absorption feature from the $\text{H}_2\text{OBPc}$ is clearly always present until we reach the
pure NiOBPc absorption.

Temperature-dependent luminescence studies on these \( \text{H}_2\text{OBPc}_{1-x}\text{NiOBPc}_x \) thin films is shown in Figure 4.26.
Figure 4.26: Temperature-dependent photoluminescence of $H_2OBPc_{1-x}NiOBPc_x$ from a) 10 K to 150 K and b) 175 K - 293 K.

Again, it appears that the sharp localized emission at low temperatures located
at 850 nm is clearly present, as it was in the cobalt and copper OBPC alloys, however not with the same strong dependence on concentration as was seen in the previous samples. More importantly, the inhibition of the delocalized exciton that was observed in the other two sets of samples is clearly observed in the H$_2$OBPc$_{0.5}$NiOBPc$_{0.5}$ sample here, however it appears that at 5 K multiple states appear to be contributing to the luminescence spectra, but most prominently the familiar 900 nm localized exciton emission previously observed. The critical concentration for the H$_2$OBPc$_{1-x}$NiOBPc$_x$ appears to occur at roughly $x = 0.09$ (10:1 H$_2$:NiOBPc), similar to the observed behavior in the cobalt alloy films. The NiOBPc contains two molecules in the unit cell, identical to the H$_2$OBPc, which also contains two molecules per unit cell. This could help lend insight into the behavior of the H$_2$OBPc$_{1-x}$CoOBPc$_x$ thin films, perhaps even indicting that the CoOBPc contains two molecules per unit cell, similar to the NiOBPc.

Time-resolved data was also taken on the luminescence features throughout these temperature-dependent studies, and so in Figure 4.27 we see this data at liquid helium temperatures as well as room temperature.
Figure 4.27: Time-resolved photoluminescence of $H_2OBPc_{1-x}NiOBPc_x$ at a) 4 K and b) 293 K.
Here, just as in the H$_2$OBPc$_{1-x}$CoOBPc$_x$ systems, the evolution of the bandgap exciton recombination lifetime has a dependence on concentration at 5 K. The delocalized exciton lifetimes are similar to the one measured in pure H$_2$OBPc films, decreasing slightly with increasing CoOBPc concentration, while the 850 nm feature shown in Figure 4.17b decays on the same scale as the bulk excitons. Again, we see that the x = 0.5 alloy film bandgap exciton at 5 K longer lived than any of the other H$_2$OBPc$_{1-x}$NiOBPc$_x$ films, where the delocalization is considered to be inhibited by the lack of nearest neighbors of the same H$_2$OBPc species. In addition, at room temperature, a clear transition is seen above a concentration of x = 0.17, where the three concentrations above this threshold have significantly longer lived excitons, while concentrations of NiOBPc x = 0.09 and below are significantly shorter lived. As mentioned above, this could have to do with the chances of having a nearest neighbor molecule of the same or different species of phthalocyanine.

4.2.4 H$_2$OBPc$_x$MnOBPc$_{1-x}$ Alloys

The final set of phthalocyanine alloys was fabricated using MnOBPc, which was synthesized by Dr. Naveen Rawat (as discussed in Chapter 2), and the films were deposited from a toluene solution in a similar manner as the other alloyed films. As opposed to the first three sets of alloyed phthalocyanine films, the H$_2$OBPc$_x$MnOBPc$_{1-x}$ alloys were considerably more difficult to solution-deposit in order to create the large grain sizes that were so familiar in the previous samples. This is often a result of the purity of the molecules themselves, or possibly the deposition conditions that were used. For more insight, Figure 4.28 contains polarized microscope images of six different concentrations of H$_2$OBPc$_x$MnOBPc$_{1-x}$.
Figure 4.28: Optical microscope images of H$_2$OBP$_{c_x}$MnOBP$_{c_1-x}$ thin film alloys at concentrations of a) $x = 0.001$ b) $x = 0.02$ c) $x = 0.09$ d) $x = 0.17$ e) $x = 0.25$ f) $x = 0.5$. 

From the images, one can see that large grain sizes in these samples are retained until a concentration of $x = 0.17$ (or 5:1 H$_2$:MnOBPc). Above this concentration of MnOBPc however, any long range order completely lost in these solution deposited samples (not however, for lack of effort, as these high concentration H$_2$OBP$_{c_x}$MnOBP$_{c_1-x}$ thin films were attempted a significantly number of times more...
than other similar samples). The samples at high concentration are in fact crystalline, but the ordering is clearly decreasing with increasing MnOBPc concentration. This is most likely not a result of poor purity of the synthesized MnOBPc product, or the deposition conditions of the thin films. This is because the low concentration samples shown in Figure 4.28 a) - d) still form quality, crystalline samples with long-range order, using the same deposition speeds (between 8-12 µm/s) and yet as the concentration of MnOBPc passes this critical limit, any long-range ordering falls apart. Instead, it is the poor miscibility between the two pure H$_2$OBPc and MnOBPc species themselves that cause this breakdown of long-range order in Figure 4.28 e) and f).

Similar to how the H$_2$OBPc$_x$CuOBPc$_{1-x}$ alloys show a different critical concentration than the H$_2$OBPc$_x$CuOBPc$_{1-x}$ and H$_2$OBPc$_x$NiOBPc$_{1-x}$ alloys in the luminescence spectra, it is completely likely that past a critical concentration of MnOBPc in the H$_2$OBPc$_x$MnOBPc$_{1-x}$ alloys, the formation of the one-dimensional chains in the solid state becomes significantly inhibited, to the point that at $x = 0.25$ (3:1 H$_2$:MnOBPc) and $x = 0.5$ (1:1 H$_2$:MnOBPc) the length of any self-assembly in the solid state will decrease to scales below even microns.

As with the other alloyed samples, single-grain absorption spectra and temperature-dependent photoluminescence studies were used to characterize the H$_2$OBPc$_x$MnOBPc$_{1-x}$ thin films as well, and these studies are shown in Figure 4.29 and 4.30.
Figure 4.29: Absorption spectra of six different concentrations of $H_2OBPc_{1-x}MnOBPc_x$ thin films at room temperature. In addition, absorption spectra from each pure thin film is shown for comparison.

Here we again see a pattern in absorption as a function of MnOBPc concentration, however it is difficult to assign where the bandgap absorption feature is coming from, as the MnOBPc pure film has its largest absorption peak centered at 860 nm as
well. Thus an increase in the absorption spectra at this wavelength is expected with increasing MnOBPc concentration, and is confirmed here.

Temperature-dependent luminescence of these sample is shown in Figure 4.30.
Figure 4.30: Temperature-dependent photoluminescence of $H_2OBPc_xMnOBPc_{1-x}$ at a) 4 K and b) 293 K.

In these $H_2OBPc_xMnOBPc_{1-x}$ samples, the sharp localized emission at low tem-
peratures located at 850 nm is hardly visible in any sample except the x = 0.02 concentration. In the H$_2$OBPc$_x$MnOBPc$_{1-x}$, the luminescence was significantly weaker than in any of the other alloy samples, and as such very large exposure times were needed to clearly resolve the PL with good signal to noise ratio. The large intensity seen incoming from the left side at 800 nm is actually the 734 nm laser line, that despite a long-pass filter, still intrudes on the luminescence spectra when exposure times are large.

Most importantly, we again see the inhibition of the delocalized exciton that was observed in the other three sets of samples is clearly observed here, showing the delocalized exciton is inhibited at low temperatures. The critical concentration for the H$_2$OBPc$_x$MnOBPc$_{1-x}$ appears to occur at roughly x = 0.09 (10:1 H$_2$:MnOBPc), similar to the observed behavior in the cobalt and nickel alloy films. At room temperature, the well-known localized bandgap exciton emission is observed as expected.

4.2.5 CoOBPc$_{0.5}$CuOBPc$_{0.5}$ Thin Film

Most recently, the idea of creating a series of alloy films with two species of transition metal phthalocyanine was proposed. While this project is still in its very preliminary stages, I was able to fabricate a CoOBPc$_{0.5}$CuOBPc$_{0.5}$ alloy thin film, with good crystallinity and long-range order, shown in Figure 4.31.
The ordering previously found in other alloy samples is also seen here, where no H$_2$OBPc is present at all. Some aggregation still remains, as well as some holes in the thin film, but for a preliminary sample it holds great promise. While this project will be taken on by another member of the Furis group at the University of Vermont, I was able to take a thin film absorption spectra on this crystalline sample very recently, seen in Figure 4.32 and then plotted with the thin film absorption spectra of the pure CoOBPc and CuOBPc as well in Figure 4.33.
Figure 4.32: Absorption spectra for a thin film sample of CoOBPc$_{0.5}$CuOBPc$_{0.5}$.

A clear splitting in the main Q-band peak is observed, but in order to put this in proper context, shown in Figure 4.33 is this same thin film absorption of CoOBPc$_{0.5}$CuOBPc$_{0.5}$ plotted with the pure CoOBPc and pure CuOBPc thin film absorption as well.
Interestingly, the CoOBPc\textsubscript{0.5}CuOBPc\textsubscript{0.5} alloy film appears to have both Q-band absorption contributions from the individual CoOBPc and CuOBPc species, but appear to be blue-shifted by almost 100 nm. Further studies will be done on this film and hopefully an entire series of these alloy films of different species of just the transition-metal octabutoxy phthalocyanines, especially to study the magnetic properties, which could provide significantly more insight into the dynamics of these alloy
MOBPcs in the solid state.

4.3 CONCLUSIONS

To summarize this chapter, alloyed crystalline thin films were fabricated from the organic molecule phthalocyanine using varying concentrations of the MOBPc species mixed with H$_2$OBPc while still retaining crystalline ordering (with the exception of the high concentration H$_2$OBPc$_{1-x}$MnOBPc$_x$ alloy thin films). Comprehensive photoluminescence studies were performed as a function of MOBPc concentration that provided an estimation of the spatial extent of the exciton delocalization. Varying the concentration from $x = 0.001$ to $x = 0.5$ introduces changes in the crystalline phase structure that result in a drastic change in excitonic states for $x > 0.09$. At the $x = 0.5$ (1:1 H$_2$OBPc:MOBPc) concentration, the delocalized exciton formation is entirely inhibited due to the lack of long-range vibrational coupling between H$_2$OBPc molecules. This is a universal behavior observed for all alloyed films created from transition-metal species of octabutoxy-phthalocyanines.

This also has implications on the exciton coherence length as introduced in Chapter 1.4 of this thesis [68], [105], [109], where macrolevel properties such as superradiance and superfluorescence are dependent on the intermolecular dipole interactions in these systems, and these alloys could be a direct experimental way to measure coherence lengths in the crystalline solid state. Varying the concentrations of MOBPc will have direct impacts on the crystal structure, resulting in exciton localization for MOBPc concentration $x > 0.09$, and this would imply inhibition or complete destruction of exciton coherence over finite distances. Further investigation into the direct
impact of increasing MOBPc concentration on not only phthalocyanine alloys, but other similar small molecules organic semiconductors could provide a straightforward knob to tune experimentally that could verify predictions of exciton coherence or decoherence discussed in the literature above, and the impact on interesting phenomena desired in commercial applications including superradiance and long diffusion lengths used in devices fabricated from these organic systems.

From a broader perspective, the ease of fabricating crystalline organic alloys for a wide range of molecular concentrations opens up incredible avenues for engineering emergent electronic properties on a length-scale relevant to device applications. Organic alloys are fundamentally different from mixtures that result in bulk heterojunctions, where poor miscibility and phase separation are encouraged. Instead they represent a paradigm shift to systems where large miscibility is highly desirable and results in crystalline films with long-range order. This allows for new electronic properties such as the existence of delocalized excitons, and more importantly, provides a tuning mechanism for this delocalization. Our study also reveals the robustness of this deposition technique that is essentially molecule independent, where the process is governed by solubility, organic solvent and deposition speed, thus accommodating a large variety of small organic molecules. This could then lend itself to designing and engineering properties of organic semiconductors in the solid state, such as carrier mobilities, diffusion lengths and other properties. Our group is already pursuing the characterization of low-temperature magnetism properties in these alloys, and preliminary results hold great promise with regards to the possibility of tuning the spin-exchange interactions between the d-shell metal ions as a function of MOBPc concentration. These results are covered the in the PhD thesis of Dr. Naveen Rawat.
at the University of Vermont [164].
Chapter 5

Correlations between Crystalline Structure and $\pi$-$\pi$ Orbital Interactions in Crystalline Thin Films

As discussed in Chapter 1, candidates for organic electronic applications extend to a plethora of molecules, and as such, additional molecular systems with a variety of conjugated ring sizes are also explored in this work. The aromatic ring size and substituted side-chains can have significant influence over electronic and excitonic properties in these organic semiconducting molecules, as in the solid state both of these properties can greatly influence the packing of molecules and therefore the $\pi$-$\pi$ overlap between adjacent molecules. The electronic delocalization over the $\pi$-electrons in the ring will be altered as a function of the size, and thus it is important to study both extended and reduced conjugated rings. With this in mind the molecules porphine (with a reduced conjugated ring) and naphthalocyanine (with an extended conjugated ring size) will be studied in comparison to the previously discussed phthalocyanine
molecule, as well as the octakis(octyloxy)-phthalocyanine (where the alkylated side chains are attached at the peripheral positions, as opposed to the non-peripheral positions as in the octabutoxy-phthalocyanine).

In the second part of this thesis, tuning of excitonic properties in these organic molecules as a function of \( \pi \)-conjugated ring size and the overlap of \( \pi \)-orbitals due to packing in the solid state is discussed. By performing a comparative study of crystalline thin film samples of these molecules, one can begin to have an understanding of how \( \pi \)-conjugated ring size and peripheral attachment of side-chains can strongly influence the packing and crystalline grain size in solid state samples, and therefore directly influence and possibly even engineer electronic and excitonic properties.

\section*{5.1 Organic \( \pi \)-Conjugated Semiconducting Molecules}

\subsection*{5.1.1 The Octyloxy-Phthalocyanine Molecule}

To begin, consider the example of the aforementioned phthalocyanine molecule, where our commercially purchased product had octabutoxy side chains attached in the non-peripheral positions, which for our purposes greatly increased solubility and allowed for use in the solution-processed pen writing technique. For our first comparison, the same phthalocyanine molecule will be explored, but with the solubility-enhancing side chains attached in the peripheral positions around the ring (ortho-substitution).
While the conjugated ring size itself is not changing for this particular molecule, it is important to show how the change in side chains could effect electronic spectra and photophysical effects in the solid state. Shown in Figure 5.1 is the commercially purchased (Sigma-Aldrich) octyloxy-phthalocyanine molecule.

It must be noted that these side chains are slightly extended as compared to the octabutoxy groups (with an additional four carbons in the chain), but as both groups are electron donating and would have little effect on the delocalization of the electrons in the aromatic ring, a reasonable comparison can be made.

Using the hollow pen-writing technique, crystalline thin films of octyloxy-phthalocyanine were solution deposited using chloroform as a solvent (as opposed to toluene for octabutoxy-phthalocyanine) at a 1% by volume solution. Because of the more volatile
solvent, the writing speeds were significantly faster than the previously deposited films, with an optimal deposition speed of approximately 60 $\mu$m/sec, but it was a necessary choice as the solubility in toluene was less than ideal. Shown in Figure 5.2 is an in-situ image of a thin film of metal-free octyloxy-phthalocyanine (with a diffraction limited laser spot of approximately 5 $\mu$m shown):

![Figure 5.2: In-situ polarized telescope image of crystalline thin film octyloxy-phthalocyanine. The red dot in the center of a crystalline grain represents our focused excitation beam spot.](image)

While crystalline order is clearly evident, it must be noted that the range of that order is of poor quality compared to other thin film samples that were fabricated
and shown previously. This most likely has to do with choice of solvent, because of significantly increased volatility of chloroform compared to toluene, the deposition speed must also be significantly increased, otherwise the solution evaporates in the capillary before it can be deposited on the substrate. This high speed of deposition most likely inhibits the formation of long-range order, as the Landau-Levich-Derjaguin regime is reached, disorder is much more likely as a result of viscous forces pulling the solution out of the pen-writing capillary (and not allowing a natural crystallization to build from the contact line of the meniscus at lower speeds) [80], [180], [181], as discussed in Chapter 2. Still, crystalline grain sizes in the sample were large enough to perform spectroscopic measurements, and we began with the absorption spectra, as shown in Figure 5.3 for both solution and the solid state:
Figure 5.3: Absorption of octyloxy-phthalocyanine in solution and in the crystalline solid state.

A typical broadening of the absorption spectra of the solid state is observed in Figure 5.3, the two peaks at 662 nm and 700 nm observed in solution evolve into a large Q-band absorption spanning almost 250 nm and centered at 735 nm. This molecule was previously well-studied by Dr. Zhenwen Pan in his PhD work here at the University of Vermont [114], and a temperature-dependent luminescence study he performed is shown in Figure 5.4.
As has been discussed previously, both in this work and in Dr. Zhenwen Pan’s thesis [114], in the H$_2$OCPc we see a delocalized bandgap exciton emission at low temperatures centered at 815 nm, and the localized well-known bandgap emission at 215...
770 nm at room temperature.

An Arrhenius fitting on this temperature study was performed, in the same manner as described in Chapter 3, which can be seen in Figure 5.5.

![Arrhenius fitting graph](image)

\[ EA_1 = 1.32 \text{ meV} \]
\[ EA_2 = 42.5 \text{ meV} \]

*Figure 5.5: Temperature-dependent Arrhenius fitting of H$_2$OCPc.*

Similar to the H$_2$OBPc, the photoluminescence quenching is characterized by two activation energies \( EA_1 = 1.32 \text{ meV} \) and \( EA_2 = 42.5 \text{ meV} \).
5.1.2 The Porphine (Porphyrin) Molecule

The porphine (or porphin) molecule is the most well-known and well-studied of the molecules discussed in this work, and is the so-called "parent molecule" to a myriad of other organic small molecules (including porphyrins and the phthalocyanine molecule). Found commonly in nature, porphyrin is a conjugated ringed molecule, and is a key building block of chlorophyll $a$, chlorophyll $b$, and heme (which is found in hemoglobin, myoglobin and other biologically relevant hemeproteins) [59], [165].

Shown below in Figure 4.3 is the most basic porphyrin structure, referred to as porphine.

![Molecular structure of Porphine.](image)

The porphine molecule consists of four Pyrrole rings at each of the four corners, connected together by a series of four methylene bridges (meso carbons) [147]. Similar
to its other derivatives, the porphyrin molecule is planar, with $D_{2h}$ symmetry in the metal-free case (thanks to the two hydrogens at the center of the macrocycle), and $D_{4h}$ symmetry in the case of the substitution of a metal atom at the center of the macrocycle (replacing the two hydrogens), as shown in Figure 5.7.

![Molecular structure of Metalloporphyrin.](image)

A large number of different metal atoms may be substituted into the ring of the porphyrin molecule, the most well-known of which is iron porphyrin, an essential component of the protein complex of hemoglobin, found in red blood cells and responsible for transporting oxygen throughout the body [59].

Similar to phthalocyanines though, porphyrins often require substitution of side-chains in order to enhance solubility, especially in situations where a solution-processed method is used. With this in mind, in order to study the porphyrin molecule properly in the solid state, 5,10,15,20-tetraphenyl-21H,23H-porphine (TPP) crystalline thin
films were fabricated with the previously discussed solution-deposited pen-writing technique for use in this comparative study. The molecular structure of H$_2$TPP is shown in Figure 5.8.

![Molecular structure of Tetraphenyl Porphine.](image)

*Figure 5.8: Molecular structure of Tetraphenyl Porphine.*

The crystal structure of H$_2$TPP is triclinic, and the space group is P ̅1, with two molecules per unit cell, and has a known crystal structure in the CCDC database [182].
Figure 5.9: Unit cell and the molecular stacking of H$_2$TPP. Adapted from the Cambridge Crystallographic Database Center (CCDC) [182].

The H$_2$TPP triclinic structure has lattice parameters of $a = 10.464$ Å, $b = 12.395$ Å and $c = 6.4330$ Å and the lattice angles are $\alpha = 99.332^\circ$, $\beta = 101.209^\circ$, and $\gamma = 95.744^\circ$. The nearest neighbor separation along the stacking axis is equal to approximately 3.8 Å [182].

Purification of commercially purchased tertraphenyl porphine was performed through column chromatography, using 20:1 chloroform to methanol as an eluent. The tetraphenyl porphine was dissolved in chloroform at various concentrations, and deposited onto PTS treated glass slides to find an ideal concentration and deposition speed. After multiple trials, a 0.5% solution was ultimately deposited on PTS treated sapphire at
a deposition speed of 51.3 $\mu$m/sec. Polarized microscope images of the crystalline H$_2$TPP film is shown in Figure 5.10.

![Polarized microscope images of thin film tetraphenyl porphine.](image)

*Figure 5.10: Polarized microscope images of thin film tetraphenyl porphine.*

Again, as with the octyloxy-phthalocyanine, poor solubility prevented fabrication of thin films with uniform grain sizes seen in the octabutoxy-phthalocyanine samples, however the long-range order is still preserved over large enough areas to enable the spectroscopy experiments described in Chapter 2. With this in mind, shown in Figure
5.11 is the thin film and solution absorption spectra of H$_2$TPP.

![Absorption spectra of a crystalline thin film sample of Tetraphenyl Porphine.](image)

*Figure 5.11: Absorption spectra of a crystalline thin film sample of Tetraphenyl Porphine.*

An immediate observation is the blue-shift of the absorption spectra in the solid state, as compared to the octyloxy-phthalocyanine shown previously, reflecting the reduced conjugated ring size of the porphine molecule. In addition to absorption studies, time-resolved and temperature-dependent photoluminescence studies were also performed on the crystalline thin film sample of H$_2$TPP. As with the studies
mentioned previously, the H$_2$TPP sample was mounted in an Oxford continuous flow
cold-finger cryostat, cooled to liquid helium temperatures, and subsequently heated in
incremental steps up to room temperature. A complete photoluminescence spectrum
and spectrally-resolved photoluminescence decay curve was recorded at each selected
temperature using a diffraction limited focused excitation laser beam (\(\lambda = 375\) nm,
20 MHz repetition rate, with a diameter of 5 \(\mu m\)). The complete results of this study
is shown in Figure 5.12 below.
Figure 5.12: Temperature-dependent photoluminescence spectra of a crystalline thin film sample of tetraphenyl porphine.
This temperature-dependent luminescence shows interesting behavior as compared to the larger π-conjugated ring size of octabutoxy-phthalocyanine. The photoluminescence emission is blue-shifted significantly from the larger conjugated ring size molecules, corresponding to the blue shift of the absorption spectra. As compared to the previously shown phthalocyanines however, the H₂TPP thin film sample exhibits some interesting behavior in the luminescence behavior with temperature. First, at low temperatures a sharp emission is observed and localized at 655 nm. This very sharp feature is usually associated with a monomer-like emission (spatially localized within the molecule), and while one observes a decrease in the intensity of luminescence upon raising the temperature from 4 K to 50 K, past this threshold there is no observed temperature-dependence for the wavelength or intensity of the emission, often a signature of localized states.

For further investigation into the H₂TPP low-temperature dynamics, another liquid helium study was performed, but in this case taking much smaller temperature steps (2.5 K) from 5-47.5 K. This was to gain additional information for the Arrhenius fitting, to provide more data at low temperatures. This study is shown in Figure 5.13.
Figure 5.13: Temperature-dependent photoluminescence spectra of a crystalline thin film sample of tetraphenyl porphine from 5 K to 47.5 K.

Very similar behavior is observed to the complete temperature study, but now we have more data points along the way in order to fit the intensities. To begin, shown in Figure 5.14 is the intensity as a function of temperature for both studies mentioned above.
There are only two transitions that reveal any temperature-dependence, located at 655 nm and the shoulder at 660 nm, and even that temperature-dependence is lost after approximately 50 K. This transition temperature of 50 K is also further enforced by the Arrhenius fittings shown in 5.15 for the 655 nm and 720 nm feature.
Figure 5.15: Temperature-dependent Arrhenius fitting of H$_2$TPP for the a) 655 nm and b) 720 nm features.

Only the low temperature photoluminescence (5-50 K) decay changes with respect to temperature, indicating an activated behavior. Above this 50 K temperature, the photoluminescence is essentially temperature-independent, and as such was not fitted.
However, at low temperatures, an activation energy for photoluminescence quenching for two features is found, 3.5 meV for the 655 nm feature, and 4.5 meV for the 720 nm feature.

To further explore this phenomenon, time-correlated photoluminescence was also recorded at every one of the temperature steps shown in Figure 5.12 for the 655 nm feature. The normalized photoluminescence intensity decays are shown in Figure 5.16 as a function of temperature:

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**Figure 5.16:** Time-resolved photoluminescence spectra for the 655 nm feature of a crystalline thin film sample of tetraphenyl porphine at various temperatures.
The most striking result seen in this plot is the significantly longer lifetimes for the 4K and 10K photoluminescence from the 655 nm feature. In addition, there is a transition in lifetimes that accompanies the change in excitonic states that occurs at 50 K.

5.1.3 The Naphthalocyanine Molecule

Moving in the opposite direction of the previous molecule is naphthalocyanine. As opposed to the porphine molecule discussed above, where the removal of a benzene ring at each of the four corners will reduce the π-conjugated ring size, the naphthalocyanine molecule instead adds a benzene ring to each of the four corners (referred to as benzannulation), thus extending the conjugated ring size.

The pure naphthalocyanine molecule itself is relatively insoluble, so in order to do a legitimate comparison the commercially available 5,9,14,18,23,27,32,36-octabutoxy-2,3-naphthalocyanine (H$_2$OBNPc) was purchased (not only for comparisons sake, but also to be able to employ the solution-deposited pen-writing technique). The molecular structure of the product purchased from Sigma-Aldrich is shown below in Figure 5.17.
As with the H$_2$OBPc purchased from Sigma-Aldrich, multiple column chromatography purifications were performed to be sure we were working with pure product in order to fabricate crystalline films. Specifically, purification was performed using 20:1 Chloroform to Methanol as an eluent through column chromatography. The H$_2$OBNPc was dissolved in chloroform at various concentrations, and deposited onto PTS treated glass slides to find an ideal concentration and deposition speed. After multiple trials, a 0.5% solution was ultimately deposited on PTS treated sapphire at a deposition speed of 51.3 $\mu$m/sec. Polarized microscope images of the crystalline H$_2$OBNPc film is shown in Figure 5.18.
The H$_2$OBNPc has a solved crystal structure, and the unit cell and stacking is shown in Figure 5.19.
The crystal structure of H$_2$OBNPc is monoclinic and the space group is P 2$_1$/c, with six molecules per unit cell. The lattice parameters are $a = 8.0487$ Å, $b = 31.630$ Å and $c = 15.884$ Å and the lattice angles are $\alpha = 90^\circ$, $\beta = 102.199^\circ$, and $\gamma = 90^\circ$. The nearest neighbor separation along the stacking axis is equal to approximately 6.64 Å [183].

Absorption in solution and the crystalline solid state was performed on the H$_2$OBNPc, and is shown in Figure 5.20.
A red shift in the absorption peaks of 15 nm in both the solution and solid state compared to the octabutoxy-phthalocyanine is seen, with peak of 865 nm in solution and a slightly broadened peak in the thin film centered at 875 nm. This is a well-known result of the extended conjugated ring size of the naphthalocyanine molecule previously seen in solution [148], [184], and now verified in the solid state as well.

In addition to absorption studies, time-resolved and temperature-dependent luminescence studies were also performed on the crystalline thin film sample of H$_2$OBNPc.
As with the previous studies mentioned above, the H$_2$OBNPc sample was mounted in an Oxford continuous flow cold-finger cryostat, cooled to liquid helium temperatures, and subsequently heated in incremental steps up to room temperature. A complete photoluminescence spectrum and spectrally-resolved photoluminescence decay curve was recorded at each selected temperature using a diffraction limited focused excitation laser beam ($\lambda = 735$nm, 40MHz repetition rate, with a diameter of 5$\mu$m). The complete results of this study is shown in Figure 5.21 below.
Figure 5.21: Temperature-dependent photoluminescence spectra of a crystalline thin film sample of octabutoxy-naphthalocyanine.

Again we see the familiar delocalized excitonic emission in the solid state at low
temperatures, centered at 955 nm, giving way to the localized excitonic emission at 885 nm at high temperatures. An interesting observation is the larger energy difference between these two peaks as compared to the other crystalline thin film sample studied previously (70 nm or 0.1 eV), where for example in pure H$_2$OBPc the energy difference between the low and high temperature emission is 32 nm (or 0.047 eV). An intensity plot as a function of temperature is shown in Figure 5.22 for the three main features in the luminescence spectra.

![Intensity plot as a function of temperature for three main features in crystalline thin film octabutoxy-naphthalocyanine.](image)

*Figure 5.22: Photoluminescence intensity versus temperature for three feature in crystalline thin film octabutoxy-naphthalocyanine.*
The 955 nm feature (the delocalized exciton) is the only feature that shows strong dependence on temperature, so with that in mind, an Arrhenius fitting was performed on that luminescence peak, and shown in Figure 5.23 below.

![Arrhenius fitting of the 955 nm feature of octabutoxy-naphthalocyanine.](image)

Figure 5.23: Arrhenius fitting of the 955 nm feature of octabutoxy-naphthalocyanine.

We again see two clear activation energies for luminescence quenching, $EA_1 = 2$ meV and $EA_2 = 19$ meV, which are the smallest of the activation energies seen in the organic molecules studied here. Time-resolved luminescence spectra are contained in the Appendix, where only a minor temperature dependence is shown.
5.2 Influence of \( \pi \)-Orbital Overlap on Photophysical Properties in the Crystalline Solid State

With the investigative spectroscopic studies discussed above, the goal of this work was to compare how the molecular packing due to \( \pi-\pi \) orbital overlap and \( \pi \)-conjugated ring size would compare across these molecules in the crystalline solid state and what influence this would impart on the photophysical properties respectively. To begin this section, a brief reminder of the molecular structure of each molecule in this comparison is shown in Figure 5.24.
Significant work has been previously reported on these molecules, even in comparative studies [185], [128], [148], but it has been limited almost exclusively to either theoretical calculations or studies performed in solution, thus providing a lack of de-
tailed information of these molecules in a comparative study in the crystalline solid state. A direct comparison of optical properties across crystalline thin film samples of these four molecules can help to lend insight into not just the influence of \( \pi \)-conjugated ring size, but also how increased or decreased \( \pi \)-orbital overlap between adjacent molecules in the crystal lattice will influence or even inhibit delocalization of excitonic states in these systems, and even how the strength of exciton-phonon interactions from the crystal lattice can influence electronic and excitonic properties as well.

To illustrate in what way the ring size and side-chains can influence spectroscopic properties, and even the color of these molecules, shown in Figure 5.25 is the complete set of all four molecules in solution.

\[
\text{H}_2\text{TPP} \quad \text{H}_2\text{OCPc} \quad \text{H}_2\text{OBPc} \quad \text{H}_2\text{OBNPc}
\]

\textbf{Figure 5.25: Photograph of organic small molecules in solution used in this study.}

It is important to note that even between the \( \text{H}_2\text{OBPc} \) and \( \text{H}_2\text{OCPc} \) molecules, where the only difference is the side-chains attached to the main phthalocyanine molecule, a significant color change is observed (indicating the changes in absorption of the molecule).
5.2.1 Comparison of Absorption Across \( \pi \)-Conjugated Ring Molecules

The first comparator that will be looked at is the absorption of a quasi-coherent light source across each of the four molecules. These absorption studies are performed in identical fashion as the experimental details in Chapter 2. A compilation of all four species solution absorption and thin film absorption spectra are shown in Figure 5.26 and 5.27 respectively.
Figure 5.26: Solution absorption spectra of a) Tetraphenyl Porphine b) Octabutoxy-
Phthalocyanine c) Octyloxy-Phthalocyanine d) Octabutoxy-Phthalocyanine. A red-shift is observed with increasing π-conjugated ring size.
Figure 5.27: Absorption spectra of crystalline thin film samples of a) Tetraphenyl Porphine b) Octabutoxy-Phthalocyanine c) Octyloxy-Phthalocyanine d) Octabutoxy-Phthalocyanine. The same red-shifting trend that is observed in solution is also seen here as a function of $\pi$-conjugated ring size in the solid state.
A common trend is seen in both the solution and single-grain thin film absorption spectra, namely the increase in \( \pi \)-conjugated ring size causes a red-shift to lower energies for the bandgap exciton absorption peak. This would then imply that the increase in the number of electrons in the conjugated ring and changes in the \( \pi-\pi \) orbital overlap with increasing ring size cause shift toward the IR for the absorption. However, one must also take into account the packing of the molecules when considering \( \pi-\pi \) orbital overlap for adjacent molecules, where as we go from \( \text{H}_2\text{TPP} \) (3.8 Å) to \( \text{H}_2\text{OBPc} \) (4.9 Å on average) to \( \text{H}_2\text{OBNPc} \) (6.64 Å), a clear trend is seen as well. Unfortunately the crystal structure of \( \text{H}_2\text{OCPc} \) is not yet solved, but it is expected that bulkier side-chains will most certainly play a central role in a different molecular packing as evidenced by previous temperature-dependent photoluminescence studies [115]. However, based on the absorption and photoluminescence data, it is likely that the \( \text{H}_2\text{OCPc} \) molecules will have less \( \pi-\pi \) orbital overlap compared to the \( \text{H}_2\text{OBPc} \) molecules, in spite of identical conjugated ring size, due to the bulky octyloxy side-chains that would decrease \( \pi \)-orbital overlap in the solid state.

5.2.2 Comparison of Photoluminescence Across \( \pi \)-Conjugated Ring Molecules

In order to further investigate the influence of aromatic ring size on these molecules in the solid state, temperature-dependent photoluminescence measurements were performed on all four crystalline thin films, with the experimental technique discussed in Chapter 2. Shown in Figure 5.28 is the photoluminescence spectra of all four species, with an excitation wavelength of 734 nm, with the exception of the \( \text{H}_2\text{TPP} \), where
the excitation wavelength was 375 nm.

Figure 5.28: Photoluminescence spectra of crystalline thin film samples of a) Tetraphenyl Porphine b) Octabutoxy-Phthalocyanine c) Octyloxy-Phthalocyanine d) Octabutoxy-Phthalocyanine at 5 K and 293 K.

Figure 5.28: Photoluminescence spectra of crystalline thin film samples of a) Tetraphenyl Porphine b) Octabutoxy-Phthalocyanine c) Octyloxy-Phthalocyanine d) Octabutoxy-Phthalocyanine at 5 K and 293 K.
Again a clear trend is observed as a function of conjugated ring size and π-π orbital overlap in these molecules at low temperatures. As with the absorption, the larger the aromatic ring size and more pronounced the π-π orbital overlap, the further to the red the emission of the exciton is shifted at low temperature. Interestingly, at low temperatures the H$_2$OCPc, H$_2$OBPc and H$_2$OBNPc all have the presence of the delocalized (dark) exciton and as the temperature is raised, it disappears and the localized (or bright) exciton dominates the room temperature spectra. However, the H$_2$TPP does not show this behavior at all, and there is no energy shift in the spectrum with respect to temperature. Time-resolved luminescence was also recorded from the H$_2$TPP, H$_2$OBPc and H$_2$OBNPc samples, presented in the Appendix, where the only unique observation is the significantly longer lived excitonic state of the H$_2$TPP compared to the other two species, which may imply a very localized exciton that when confined has less chance to encounter a defect or grain boundary, and thus would be longer lived than a delocalized exciton in the solid state.

This H$_2$TPP behavior may suggest that there is no reorientation of the molecules with temperature, as previously observed in H$_2$OBPc and H$_2$OCPc, or no significant long-range exciton diffusion at all. Unfortunately the powerful linear dichroism mapping experimental technique discussed previously that images the orientation of the molecules in the solid state was unable to be performed on the crystalline H$_2$TPP film, but further investigation is necessary to confirm what is actually happening to the orientation of the molecules with temperature to give insight into possible exciton delocalization or lack thereof. However is most likely possible that interactions with the lattice are quite large in the other three species, hence their temperature dependence, whereas the H$_2$TPP shows very little influence with temperature, and it
is certainly possible the influence of phonons is relatively weak in this system.

An Arrhenius fitting was performed on the main exciton emission for all four species, and they are contained in Figure 5.29.
Figure 5.29: Arrhenius fittings of the main excitonic emission of a) Tetraphenyl Porphine (at 655 nm) b) Tetraphenyl Porphine (at 720 nm) c) Octabutoxy-Phthalocyanine d) Octyloxy-Phthalocyanine e) Octabutoxy-Phthalocyanine.
The Arrhenius plots show dependence of activation energy on the $\pi$-conjugated ring size. If one imagines a wavefunction for the delocalized exciton that accounts for intermolecular coupling as well as phonon mixing, then a larger coupling to the vibrational exciton-phonon mode from the lattice would cause a decrease in the activation energy, making a dissociation of the exciton easier with increased ring size (and therefore increased $\pi$-$\pi$ interaction). The H$_2$TPP does not show any temperature dependence past 50 K, however the trend in the other three, where the activation energy associated with the photoluminescence quenching of the main exciton feature in the organic system seems to decrease with increasing $\pi$-conjugated ring size (and therefore $\pi$-$\pi$ interaction), points to an increase in the contribution of phonon interactions, and therefore lowering the energy that would be necessary to disrupt the Coulombic interaction between the electron-hole pair of the exciton.

Lastly, the peak wavelength of exciton bandgap absorption and excitonic emission for all four conjugated ring molecules is contained below, reinforcing the overall trend discussed above.
Thin Film Peak Absorption and Photoluminescence

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Bandgap Absorption</th>
<th>Bandgap Exciton Emission</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂TPP (5 K)</td>
<td>655 nm (1.89 eV)</td>
<td>655 nm (1.89 eV)</td>
</tr>
<tr>
<td>H₂TPP (293 K)</td>
<td>655 nm (1.89 eV), 727 nm (1.71 eV)</td>
<td>655 nm (1.89 eV), 727 nm (1.71 eV)</td>
</tr>
<tr>
<td>H₂OCPc (5 K)</td>
<td>710 nm (1.75 eV)</td>
<td>815 nm (1.52 eV)</td>
</tr>
<tr>
<td>H₂OCPc (293 K)</td>
<td>710 nm (1.75 eV)</td>
<td>770 nm (1.61 eV)</td>
</tr>
<tr>
<td>H₂OBPc (5 K)</td>
<td>860 nm (1.44 eV)</td>
<td>934 nm (1.33 eV)</td>
</tr>
<tr>
<td>H₂OBPc (293 K)</td>
<td>860 nm (1.44 eV)</td>
<td>902 nm (1.37 eV)</td>
</tr>
<tr>
<td>H₂OBNPc (5 K)</td>
<td>875 nm (1.42 eV)</td>
<td>955 nm (1.3 eV)</td>
</tr>
<tr>
<td>H₂OBNPc (293 K)</td>
<td>875 nm (1.42 eV)</td>
<td>885 nm (1.4 eV)</td>
</tr>
</tbody>
</table>

5.3 Conclusions

The effects of benzannulation and alkylated side-chains on the electronic properties of organic small molecules in the crystalline solid state is discussed above. Previously observed behavior reported by Kobyashi and Zhang of these molecules in solution [128], [186], [187] is confirmed in the results reported here. The peak bandgap absorption red-shifts to longer wavelengths with increasing π-conjugated ring size in the crystalline thin films, agreeing with the reported work of Kobayashi and Zhang. In addition, this red-shift in absorption decreases in total wavelength (or eV) with increasing π-conjugated ring size, and the splitting of the Q-band itself in solution also decreases with increasing π-conjugated ring size (while in the solid state, typical broadening due to lattice interactions mask traits of similar behavior).
Low-temperature photoluminescence follows a similar red-shifting trend in peak emission wavelength with increasing \( \pi \)-conjugated ring size, but the temperature-dependence reveals a more interesting story. The temperature-evolution of the photoluminescence for the naphthalocyanine shows a larger shift in wavelength going from liquid helium temperatures to room temperature, indicating a more complex behavior of the electronic properties as ring size is increased. The temperature-dependent behavior seems to depend less on the packing of the molecules themselves (and therefore direct intermolecular distance), and more on coupling to lattice vibrations, where the enhanced \( \pi-\pi \) overlap in the naphthalocyanine would have a direct impact.

The effect of benzannulation in the solid state is significantly more complex than in the well-studied single molecule case. Mainly, it is concluded that extended \( \pi \)-conjugated ring size manifests itself through a distinctly different molecular ordering and \( \pi \)-stacking arrangement, which results in unique vibrational modes for each of these different organic small molecules in the crystalline phase. These variations are in turn then responsible for the different temperature-dependent excitonic states seen in these systems. Furthermore, these studies show that benzannulation is critical for the formation of the delocalized phonon-coupled exciton which can be associated with a longer coherence length at low temperatures and can manifest itself in experimentally observed coherent behavior, such as superradiance [102], [101], [104], [68].

In addition, recent work by Anthony et al [188] paint an even more complex picture specifically regarding charge mobilities and transport properties as related to the \( \pi \)-stacking in organic systems, where they contest that the idea of \( \pi \)-stacking leading to higher mobilities is an over-simplification. Instead one must consider multiple factors when discussing the origin of high mobilities. The first is the strong intermolecular
electronic coupling (or coherence as discussed in Chapter 1) in organic systems that results from significant overlap of $\pi$-orbitals of adjacent molecules. Anthony et al however continue, citing work by Jean-Luc Brédas [29], [189], that discusses the consideration of not just spatial overlap of the $\pi$ orbitals, but also the phase relationships between orbitals in adjacent molecules when considering exciton coherence or coupling. Ultimately they conclude that researchers must consider not just the presence of large $\pi$-orbital overlap in organic systems, but more specifically the nature of the $\pi$-stacking and overlap when considering these organic systems in the solid state for device applications.

It can thus be concluded from this work and that reported by other researchers that the nearest neighbor separation by itself is not the only factor that strongly influences intermolecular interactions and coupling to lattice vibrations. In spite of larger intermolecular separation seen in naphthalocyanine (from the solved x-ray crystal structure discussed above) as compared to phthalocyanine, it shows the strongest phonon-coupling to lattice vibrations, as evidenced by shifts in the temperature-dependent photoluminescence and decrease in the activation energy of the luminescence quenching.

These results open an intriguing avenue for future studies, specifically related to the long-range interactions, $\pi$-stacking and delocalized exciton states in small organic molecules in the solid state. From a broader perspective, tuning these interaction in the solid state would allow for engineering new organic thin film systems where the bandgap and exciton mobilities could be fine-tuned in a manner similar to inorganic systems. As previously discussed in Chapter 4, alloys of these organic small molecules are able to be fabricated from the solution-processed deposition technique using the
metal-free phthalocyanine molecule with varying additive concentrations of transition-metal phthalocyanine. One can now envision alloys fabricated not just with various phthalocyanines, but also by mixing different benzannulated $\pi$-conjugated derivatives in various concentrations in order to adjust the bandgap and other electronic properties. This approach will ideally add additional fine-tuning in a very controlled and reproducible way for the $\pi$-$\pi$ orbital overlap and molecular stacking in the context of highly-ordered crystalline thin film samples of organic small molecule systems.
Chapter 6

Conclusions and Future Outlook

The experimental work and results presented in this thesis give an entirely new insight into the physics of organic semiconducting molecules. The somewhat unexpected comeback of these well-known small molecules now being used in cutting-edge technologies makes this an extremely exciting time to be involved with investigating the yet somewhat unexplored fundamental physics of the electronic and excitonic properties of these organic systems in the solid state. The impetus of this newfound excitement in some relatively old systems is made possible by new solution-deposition techniques (one of which is employed heavily in this work) that produce highly-ordered crystalline films where these electronic and exciton properties are able to be isolated from the masking effects of disorder and defects, and systematically studied.

In this work it has been shown that not only can insight be gained into excitonic states and their interactions with lattice vibrations in these organic molecules, but more importantly how to tune these electronic properties by introducing disorder in a controlled way previously not possible in traditional organic thin films. For example, it has been shown here that it is possible to fabricate organic semiconductor alloys
where the interplay between localization and delocalization methods are controlled in a similar manner to well-known semiconductor alloys.

It has also been shown here that these well-ordered films have the ability of adjusting excitonic properties in a much more significant and finely-tuned way than possible in inorganic systems, which has been previously predicted by theory as discussed in Chapter 1. For a given molecule the introduction of alkylated side-chains and benzannulation dramatically changes excitonic properties through changes in the $\pi-\pi$ orbital overlap between adjacent molecules.

The studies discussed here have confirmed some existing theoretical predictions of coherent excitonic states and the appearance of superradiance in these systems. The photoluminescence and linear dichroism studies presented constitute irrefutable experimental evidence in support of theoretical concepts that predict these systems belong to an intermediate regime between a Frenkel and Wannier-like excitonic picture.

In this regime where long-range Coulomb interactions, short-range charge transfer interactions, and coupling to lattice vibrations all have comparable strength, the excitonic state is therefore not only temperature-dependent, but also coherent across up to tens of molecules in the crystalline lattice. This coherence length can be controlled or destroyed through introducing disorder in crystalline samples by alloying in a manner similar to inorganic semiconducting systems. These studies along with previous magneto-optical studies performed by my colleague Dr. Naveen Rawat [164], give a complete picture of the excitonic delocalization and coherence. The measurement of the coherence length reported here completes the picture of a complex molecular system where the long-range interactions and vibrational coupling control both electronic

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and magnetic properties in a way never before observed in inorganic semiconducting systems.

In addition, further investigation into how crystalline packing and $\pi$-orbital overlap of adjacent molecules in the solid states effects the band structure in these systems is essential for developing a theoretical model that encompasses the experimentally observed behavior reported on here and elsewhere. One path could involve the mixing of two species of aromatic ringed molecules with different $\pi$-conjugated ring sizes, to purposefully induce disorder or limitations on coherence and delocalization of excitons, a project whose beginnings have already been undertaken by Kim Hua in the Furis lab at UVM.

Another intriguing path involves the investigation of the electronic bandgap as a function of strain in these crystalline samples. Recent reports have shown how the influence of strain in the solid state could even be used as another parameter in order to tune the bandgap, charge transport, carrier mobilities, or even work functions in organic semiconducting systems [62], [190]. Investigations into inducing this strain through changes in concentrations of the alloy systems discussed here immediately come to mind, where one can envision purposefully inducing lattice mismatch to induce strain, both in system mixing metal and metal-free phthalocyanine derivatives, but also in mixed alloys of different $\pi$-conjugated ring size, where engineering material electronic properties and functions could be accomplished simply by adjusting the alloying concentrations in the solid state.

For a broader perspective from the standpoint of the scientific community at large, these results offer a pathway to customizing electronic properties for many applications. This pathway is not far removed from practical commercial applications
(for instance roll-to-roll processing) as this solution-deposited fabrication method is ideal for fast turn-around times where quickly implementing feedback is essential.

The results reported here however are just the beginning, as there are still many unanswered questions from both an experimental and theoretical standpoint. The success in fabricating crystalline alloys that at the same time exhibit superradiance and tunable low-temperature magnetic exchange, merits further exploration with regards to ways of tuning these properties further in additional alloy systems, but also in terms of understanding how delocalized carriers mediate the magnetic exchange as a function of coherence length in these systems.

Future endeavors might include the exploration of alloy systems where the bandgap tuning is achieved through benzannulation of one of the species, or through side-chain addition (such as electron-withdrawing versus electron-donating, or length of the substituent addition that will influence packing of the molecules in the solid state). As shown in this thesis, a deeper understanding of the influence of these changes on inherent properties of small organic molecules is paramount for practical applications.

More recently the development and improvement of deposition techniques to fabricate films with quality long-range order has prompted scientists in this field to revisit a number of other molecular families such as carbon-nitrogen bonding organics including quinacridone and indigo, which display interesting excitonic properties, such as the possible presence of Wannier excitons. All of the experimental techniques discussed in this work are ideal for pursuing the knowledge about the nature of excitonic states in such systems.

The future seems bright for implementation in commercial technology. Better understanding of the physics in these molecules is necessary, but quick turnarounds
for fabrication give a streamlined route for testing changes and variations. Researchers in the field are currently working on flexible technology that includes encapsulation of these devices, which are primarily made of organic semiconductors, for applications such as biosensors that can be applied directly to human skin [191], [192]. The excitonic properties reported here, along with high mobilities reported previously, enable a vision of future organic electronics beyond that of organic LEDs, solar-cells, or field-effect transistors. This expanded vision includes logical circuits that are not rigorously dependent on silicon bound to rigid substrates, but where instead cost, flexibility, and disposability are superseding the high-speed requirement for everyday electronic applications.
Appendix A

A.1 Temperature Dependent Photoluminescence of $\text{H}_2\text{OBPC}_{1-x}\text{MOBPC}_x$
Figure A.1: Temperature-dependent photoluminescence of a thin film sample of $\text{H}_2\text{OBP}_{0.67}\text{CoOBP}_{0.33}$. 

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Figure A.2: Temperature-dependent photoluminescence of a thin film sample of $H_2OBPc_{0.75}CoOBPc_{0.25}$. 
Figure A.3: Temperature-dependent photoluminescence of a thin film sample of $H_2OBP_{0.83}CoOBP_{0.17}$.
Figure A.4: Temperature-dependent photoluminescence of a thin film sample of $H_2OBP_{c_{0.875}}CoOBP_{c_{0.125}}$. 
Figure A.5: Temperature-dependent photoluminescence of a thin film sample of $H_2O BPc_{0.91}CuOBPc_{0.09}$. 
Figure A.6: Temperature-dependent photoluminescence of a thin film sample of $H_2OBP_{c0.5}NiOBP_{c0.5}$.
Figure A.7: Temperature-dependent photoluminescence of a thin film sample of $H_2OBPc_{0.67}NiOBPc_{0.33}$. 
Figure A.8: Temperature-dependent photoluminescence of a thin film sample of $H_2OBPc_{0.83}NiOBPc_{0.17}$. 
Figure A.9: Temperature-dependent photoluminescence of a thin film sample of $\text{H}_2\text{OBPc}_{0.91}\text{NiOBPc}_{0.09}$. 
Figure A.10: Temperature-dependent photoluminescence of a thin film sample of $H_2OBPc_{0.5}MnOBPc_{0.5}$.
Figure A.11: Temperature-dependent photoluminescence of a thin film sample of $H_2OBP_{0.83}MnOBP_{0.17}$. 
Figure A.12: Temperature-dependent photoluminescence of a thin film sample of $H_2OBPc_{0.91}MnOBPc_{0.09}$. 
A.2 **Time-resolved photoluminescence measurements**

![Time-resolved photoluminescence spectra for the 900 nm feature of a crystalline thin film sample of octabutoxy-naphthalocyanine at various temperatures.](image)

*Figure A.13: Time-resolved photoluminescence spectra for the 900 nm feature of a crystalline thin film sample of octabutoxy-naphthalocyanine at various temperatures.*
Figure A.14: Time-resolved photoluminescence spectra for the 920 nm feature of a crystalline thin film sample of octabutoxy-naphthalocyanine at various temperatures.
Figure A.15: Time-resolved photoluminescence spectra for the 955 nm feature of a crystalline thin film sample of octabutoxy-naphthalocyanine at various temperatures.
Figure A.16: Time-resolved photoluminescence spectra of crystalline thin film samples of a) Tetraphenyl Porphine b) Octabutoxy-Phthalocyanine c) Octyloxy-Phthalocyanine d) Octabutoxy-Phthalocyanine.
A.3 Grazing Incidence X-Ray Spectra

Figure A.17: GIXRD of a thin film sample of H$_2$OBPc$_{0.5}$NiOBPc$_{0.5}$.
Figure A.18: GIXRD of a thin film sample of H$_2$OBPc$_{0.67}$NiOBPc$_{0.33}$.

Figure A.19: GIXRD of a thin film sample of H$_2$OBPc$_{0.83}$NiOBPc$_{0.17}$.
Figure A.20: GIXRD of a thin film sample of H$_2$OBPc$_{0.91}$NiOBPc$_{0.09}$.

Figure A.21: GIXRD of a thin film sample of H$_2$OBPc$_{0.999}$NiOBPc$_{0.001}$. 
A.4 Linear Dichroism Spatial Mapping Scans

Figure A.22: LD microscopy image of CoOBPc
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