SYNTHESIS AND PHOTOPHYSICAL CHARACTERIZATION OF COVALENT AND SELF-ASSEMBLED OLIGO (PHENYLENEVINYLENES) AND RELATED MULTICHROMOPHORE-CONTAINING ASSEMBLIES

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SYNTHESIS AND PHOTOPHYSICAL CHARACTERIZATION OF COVALENT
AND SELF-ASSEMBLED OLIGO (PHENYLENEVINYLENES) AND RELATED
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ABSTRACT

The growing need for cheap, reliable, economical, and environmentally safe sources of energy has prompted extensive research into the field of organic photovoltaics. Oligo(p-phenylenevinylene) (OPVs) are model compounds for the polymer poly (p-phenylenevinylene). These compounds are a highly conjugated, hole conductive materials used in both organic photovoltaics and organic light emitting diodes. Unfortunately, little research exists concerning the effects of nano- and microstructure on organic photovoltaic performance. In other words, how does the spatial relationship between adjacent OPV chains influence photoconductivity? The first project of this dissertation was comprised of two parts. The first part dealt with the need to improve the asymmetric synthesis of OPV chains. By modifying the current literature approach towards asymmetric OPVs, the total overall yield of these chromophores has been optimized to values that are 15 – 30% higher than current literature values. The methodology and synthetic steps are explored. This project became the basis for the second part, which was the synthesis of two OPV units attached cofacially to bridging groups, in order to study energy and electronic transfer between the two units as a function of interchain distance, angle, and/or orbital overlap.

The second project of this dissertation dealt with the creation of liquid crystalline perylene diimide (PDI) aggregates through non-covalent interactions. Perylene diimides
have been utilized as optimal n-type materials for photoconductive organic devices, and have strong intermolecular π-π interactions that induce specific packing orientations. The nature of the packing can be influenced by the substituent at the cyclic imide portion of the chromophore. This unit has no real effect on the ground state electronic properties of the individual chromophore because it is located at a node in the PDI interacting molecular orbitals. The PDI therefore behaves as an isolated chromophore with minimal to no ground state mixing with the imide substituent. Nevertheless, the structure of that substituent can greatly influence the bulk properties of the chromophore by directly affecting the transverse and longitudinal packing in the solid state. The utilization of a hydrazide linkage could direct the self-assembly of appropriately substituted PDIs through both hydrogen bonding and π-π stacking, into ordered arrays. The synthesis and photophysical properties of these hydrazide-linked PDIs are presented.

The third and final project in this dissertation involves the self-assembly of a multichromophoric perylene diimide. Various self-assembly techniques were used to construct this assembly, including hydrogen bonding, π-π stacking, and ligation of metal-complexes, all of which provide site-specific platforms for the organized assembly of a multi-chromophoric system. The synthesis of this compound is presented.
DEDICATION

I dedicate this work to my loving wife Denise. She has stood by my side throughout this experience and without her love and support this work could never have been possible.
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CHAPTER I

INTRODUCTION

The growing need for cheap, efficient, reliable, and renewable fuel sources is becoming a major concern in modern society. In order to generate such a fuel supply, research is increasingly turning to alternative energy sources. One such source of energy is the sun, which, as a potential energy source, does not have the detrimental impact fossil fuels have on the environment. Currently, the primary method of converting solar energy into usable energy is through the use of photovoltaic cells. Inorganic photovoltaic devices are the current state of the art in this field. Unfortunately, these devices suffer from high production costs that do not allow them to economically compete with oil, gas, or coal in providing energy for our society. Polymer-based photovoltaic devices have the potential to greatly reduce the manufacturing costs of producing photovoltaic devices, potentially replacing fossil fuels to a large extent in our society.\textsuperscript{1-2} However, the efficiencies of the current polymer-based photovoltaic devices are still considerably lower than their inorganic counterparts, and are therefore not cost-effective. Nevertheless, advances in improving device performance and fine tuning the existing organic materials used in photovoltaic devices are occurring at a rapid rate.\textsuperscript{1, 6}
Studies of organic photovoltaic devices typically focus on either the interface between the electron donor (D) and electron acceptor (A) groups that are integral to these devices,\textsuperscript{1} or on the process of the self-assembly of these two components in solution or in the solid state.\textsuperscript{1-4} Studies aimed at understanding the interactions between a donor and acceptor in D-A compounds in solution are highly relevant since they mimic the interaction that constitutes the charge-separation between the D-A materials in organic photovoltaic devices. In particular, the D-A interface is where charge-separation occurs subsequent to exciton formation by light absorption of the donor (Figure 1).\textsuperscript{2} The fate of the exciton after it is formed ultimately determines the efficiency of the cell. In this regard, charge-separation followed by charge migration toward the electrodes yields an effective device.

One area of research in organic photovoltaic materials focuses on making greater surface area contact between the D-A components by spin-coating them in a blend.\textsuperscript{1,7} These blended materials not only have greater surface contact between the D-A components, but can also have shorter distances for the migration of the exciton towards the electrode, as illustrated in Figure 2.\textsuperscript{8} Another factor that strongly influences device performance is the orientation of the D-A components relative to one another within the material, as well as that of the D-D and A-A interactions. These interactions can effect the photophysical properties of the material, the movement of charge within the material, and the overall efficiency of the device.\textsuperscript{5} Therefore, a study designed to explore a well-defined system composed of pairs of either donors or acceptors would enable the determination of how morphology effects the photophysical response of a photovoltaic device.
Figure 1. The general mechanism for the generation (top) of an exciton in an organic solar cell upon absorption of light, and the subsequent electron transfer of an electron from an excited electron donor to an electron acceptor within the cell. HOMO refers to the highest occupied molecular orbital, while LUMO refers to the lowest unoccupied molecular orbital.
The research described in this dissertation is divided into four parts. The first part involves the improved synthesis and the steady state absorption and fluorescence properties of tetrameric and pentameric oligo(p-phenylenevinylene) (OPVs) (Figure 3). The second part involves the synthesis and photophysical characterization of OPVs in two different dimeric cofacial structures (Figure 4). In these dimers, the “bite-angles” of the two cofacial compounds are different from one another, and experiments designed to give information about how the distance and angle between OPV segments within polymer chains affect the photophysical response of the system have been performed.
Examining the differences between these dimeric chromophores and their monomeric counterparts using absorption and fluorescence experiments provides information about how distance and angle influences electronic properties.

Figure 3. The general structures for the monomeric oligo(\textit{p}-phenylenevinylene)s synthesized in this work (R = OC\textsubscript{8}H\textsubscript{17} while R’ and R’’ are methoxy, nitro, amine, and hydrogen.
Figure 4. Cofacial OPVs 95 and 96 were synthesized to examine the interactions between closely associated OPV chains (R = C\textsubscript{10}H\textsubscript{21}).

The third part of this dissertation involves the synthesis and photophysical characterization of a perylene diimide (PDI) bearing three liquid crystal segments and a hydrazide group capable of hydrogen bonding (Figure 5). The work described in this section demonstrates the effect that H-bonding has on the self-assembly of these PDIs in solution and in the solid state. The solid state results, in particular, show a high degree of order, potentially providing a platform to generate highly ordered solid state materials.

Figure 5. The hydrazide perylene diimide (HPDI).
The fourth part of this dissertation involves the self-assembly of multichromophoric perylene diimide and pyromellitimide complexes. Various site specific self-assembly techniques were used to construct these complexes, including hydrogen bonding, π-π stacking, and metal ligation (Figures 6 and 7). The syntheses of these complexes are presented. The photophysical properties of these assemblies will eventually be studied using a combination of steady state absorption and fluorescence spectroscopy, and by time correlated single photon counting (TCSPC) and transient absorption spectroscopies to determine the rate constants and efficiencies of electron transfer.
Figure 6. Perylene diimide (PDI) multichromophoric assembly 113. The complex is composed of OPV and zinc porphyrin electron donors, and a PDI electron acceptor.
Figure 7. Pyromellitimide (PI) multichromophoric assembly 114; the complex is composed of OPV and zinc porphyrin electron donors, and a PDI electron acceptor.
2.1 Natural Photosynthesis

Photosynthesis is a photoinduced process that occurs naturally in green plants and cyanobacteria. These organisms utilize solar energy to supply the chemical energy required to perform cellular processes. Both green plants and cyanobacteria share similarities in their photosynthetic apparatus. Of the two, cyanobacterial photosynthesis is better understood, since only one photosynthetic reaction center (PRC) is present instead of the two PRCs present in green plants. Photosynthesis in purple bacteria is a cyclic process that ultimately results in production of adenosine triphosphate (ATP), that is subsequently used as cellular energy. Photosynthesis in green plants, on the other hand, leads to (a) oxidation of water to molecular oxygen, (b) reduction of NAD to NADH, and (c) reduction of carbon dioxide into sugars for cellular growth, as well as a myriad of other cellular processes. Bacterial photosynthesis is therefore an ideal model for designing devices intended for solar energy conversion. In particular, understanding how bacteria harvest solar energy using the light harvesting complexes (LHC I & LHC II), and then funnel that energy into the PRC to produce usable energy, can greatly aid in the construction of synthetic devices that could be used to generate electricity.
2.1.1 The Bacterial Photosynthetic Process

Photosynthesis begins with the absorption of visible light by the membrane bound chromophores referred to as bacteriochlorophylls (BChl) that form the so-called antenna complexes or light harvesting complexes.\(^9\)\(^-\)\(^10\) Purple bacteria contain two LHC complexes, an outer complex (LH2) and an inner complex (LH1).\(^9\)\(^-\)\(^10\) Both LH1 and LH2 are composed of various bacteriochlorophyll \(a\) (Bchl \(a\)) molecules. In LH2, the Bchl \(a\) groups are arranged in a cyclic manner using the non-covalent interactions of a protein matrix.\(^11\) Similarly, LH1 is also composed of a cyclic array of Bchl \(a\) molecules encircling the PRC.\(^11\),\(^13\)

The components present in the PRC are shown in Figure 8.\(^10\) The so-called special pair (SP) is composed of a pair of cofacially positioned bacteriochlorophyll \(a\) molecules (Bchl \(a\)) having a \(C_2\) symmetry axis.\(^10\),\(^13\)\(^-\)\(^15\) Adjacent to the SP on either side are a second Bchl \(a\) and a bacteriopheophytin (BPheo). Also present in the PRC are a pair of quinones, one of which is the membrane bound ubiquinone A (QA) and the other a non-membrane bound menaquinone (QB). A non-heme iron is positioned between the two quinones.\(^16\) The \(C_2\) symmetry axis present in the PRC leads to two potential pathways for ET, termed the L and the M paths, with electron transfer occurring along the L side.\(^9\)\(^-\)\(^22\) The L/M designation originates from the different molecular weights of the protein scaffolding on each side of the PRC.\(^10\)
Electronic excitation of the SP initiates an electron transfer to Bchl $a$, which is followed by secondary ET to the BPheo via a superexchange mechanism with a time constant of $\sim 2.8$ ps. Subsequent electron transfer from BPheo to $Q_A$ occurs in $\sim 200$ ps, followed by the fourth electron transfer step, from $Q_A$ to the $Q_B$, that occurs in $\sim 0.1$ ms. The cycle repeats itself a second time reducing $Q_B$ to the dianion, which becomes protonated and diffuses out of the PRC to the cytochrome $bc_1$ complex, where $Q_B$ is then oxidized. The quantum yield of the electron transfer cascade is near unity, partly because $Q_B$ undergoes the final transmembrane step, partly because the process is energetically downhill, and partly because the oxidized PRC is reduced to its neutral electronic state by the water oxidation process (in green plants). The transferred electrons create a redox potential in the cytochrome $bc_1$ complex that subsequently drives
a proton motive force across the bilayer that is used for generation of adenosine triphosphate (ATP).\textsuperscript{9a, 21}

2.2 Basic photophysical processes

Electronic excitation of an electron donor promotes an electron from the highest occupied molecular orbital (HOMO) to the un-filled lowest unoccupied molecular orbital (LUMO), setting the stage for the light-driven reactions (electron and energy transfer) occurring in nature. Both electron and energy transfer depend on orbital overlap and electronic exchange between a donor and acceptor molecules. Energy transfer can also occur by a through space interaction from oscillating dipoles in an electric field.\textsuperscript{31} The next sections describe the processes of electron and energy transfer in more detail.

2.2.1 Electron Transfer

Photoinduced electron transfer (ET, Figure 9) involves the transfer of an electron from an electronically excited electron donor (D\textsuperscript{*}) to an electron acceptor (A), generating a charge separated (CS) state in the case of intramolecular ET, or a radical ion pair for an intermolecular ET. The lower ionization potential (IP) and higher electron affinity (EA) of an excited state molecule enables this process to occur. If the free energy for electron transfer is negative (exothermic), then the process will be favored, as opposed to a positive free energy change (endothermic) that results in an unfavored process.\textsuperscript{31}
Figure 9. Excitation of an electron donor \((D)\) into the donor excited singlet \((S_1)\) state, followed by electron transfer to an electron acceptor \((A)\). The resulting radical ion pair (or in the case of an intramolecular ET, the charge separated (CS) state) can then undergo charge recombination (CR), regenerating the ground state via back electron transfer. The excited donor \((D^*)\) can also fluorescence (FL) or undergo internal conversion (IC) to the ground state.\(^{31}\)

Electron transfer can be described using the Gibbs free energy as implemented in the Weller equation (Equation 1):

\[
\Delta G = (E_D - E_A) + \frac{e^2}{4\pi\varepsilon_0\varepsilon_s}[\frac{1}{2R_D} + \frac{1}{2R_A} - \frac{1}{R_{DA}}] - \frac{e^2}{4\pi\varepsilon_0\varepsilon_s}[\frac{1}{2R_D} + \frac{1}{2R_A} - \frac{1}{R_{DA}}] - E_{1D}
\]

Equation 1

Where, \(E_D\) and \(E_A\) represent the one electron oxidation and reduction potentials of the electron donor and electron acceptor, respectively; \(\varepsilon_0\) is the permittivity of free space, \(e\) is the electronic charge, \(\varepsilon_s\) and \(\varepsilon_i\) represent the dielectric constant of the reference and sample solvents; \(R_A\) represents the radius of the electron acceptor, \(R_D\) represents the radius of the electron donor, and \(R_{DA}\) is the center to center distance of the D-A complex.
The term $E_{1D}$ refers to the excited state energy of the electron donor, and is an important term in determining whether the electron transfer will be exergonic or endergonic. The Weller equation can be simplified in polar solvents (high dielectric constant), or in molecules having large D-A distances (Equation 2).\(^\text{22}\)

$$
\Delta G_{ET} = (E_D - E_A) - E_{1D}
$$

Equation 2

The rate of electron transfer is dependent on several factors, including: (1) the free energy of activation, (2) the degree of electronic coupling of the D-A pair, (3) the distance between that pair, and (4) the outer and inner sphere reorganization energy. The rate constant for electron transfer as postulated by Marcus and Hush is shown in Equation 3.\(^\text{10,23}\)

$$
k_{ET} = \left(\frac{2\pi}{h}\right) V_{DA} \left[ \frac{1}{(4\pi\lambda k_B T)^{1/2}} \right] \exp\left[ -\frac{(\Delta G^0 + \lambda)^2}{4\lambda k_B T} \right]
$$

Equation 3

where the free energy of activation is given as $\Delta G^0$, $\lambda$ is the total reorganization energy (the combined nuclear $\lambda_r$ and solvent reorganization $\lambda_s$ energies), $V_{DA}$ is the electronic coupling matrix for the donor and acceptor, $h$ is Planck’s constant, $k_B$ is the Boltzmann constant, and $T$ is the temperature in Kelvin.\(^\text{24}\)

The nuclear reorganization energy, sometimes called the inner sphere reorganization energy, represents the changes in bond lengths occurring during ET. The solvent reorganization energy, also called the outer-sphere reorganization energy, represents the dipolar rearrangement of the solvent molecules around the electron donor and acceptor molecules occurring as a result of charge formation on the donor and the acceptor. The degree of orbital overlap plays a critical role in the probability for ET, and is reflected in the electronic coupling matrix, $V_{DA}$.\(^\text{33}\) which in turn is a function of the
distance and the nature of the spacer group that is used to connect the D-A pair together, i.e., a conjugated or a non-conjugated spacer. Conjugated spacers increase the orbital overlap in a D-A complex by delocalizing electron density over the intervening atoms of the bridge, thereby facilitating electron transfer, while a non-conjugated spacer may potentially place the interacting orbitals into an orientation that minimizes the rate of electron transfer by placing the orbitals orthogonal to one another. Nevertheless, in simple systems the electronic coupling matrix will decrease exponentially as the distance between the D and A complex is increased. The rate of ET as a function of that distance is represented by Equation 4:

\[ k_{\text{ET}} = k_0 \exp[-\beta(r - r_0)] \exp[-(\Delta G^0 + \lambda)^2/4\lambda R T] \]  

In this equation \( r \) represents the actual center to center D-A distance, while \( k_0 \) represents the maximum rate of ET at the close contact distance \( (r_0) \), and \( \beta \) is the ability of the solvent to facilitate ET. The maximum rate of ET occurs when the D-A groups are within van der Waals contact of one another, and when the free energy of ET and reorganization energy are equal.

Marcus described the rate of ET as a parabolic function of the free energy \( (\Delta G_{\text{ET}}) \) and reorganization energy \( (\lambda) \). The parabola resulting from the application of Marcus theory yields three regions (Figure 10) when the rate of ET is plotted as a function of the free energy of reaction. The first region is called the normal region, where \(-\Delta G_{\text{ET}} < \lambda \) (Figure 10a), the second region is called the activationless region, where \(-\Delta G_{\text{ET}} = \lambda \) (Figure 10b), and the third is the inverted region, where \(-\Delta G_{\text{ET}} > \lambda \) (Figure 10c). The value of \( k_{\text{ET}} \) increases in the normal region until reaching a
maximum value in the activationless region (Figure 10b). The rate of electron transfer occurring in the inverted region (Figure 10c) decreases as $-\Delta G_{\text{ET}}$ becomes much larger than $\lambda$.

![Figure 10](Image)

*Figure 10. The parabolic curve used by Marcus to relate $-\Delta G_{\text{ET}}$ to $k_{\text{ET}}$. The first curve (a) represents the normal region, (b) the activationless region, and (c) represents the inverted region. The fastest rates of ET occur in the activationless region, where the free energy is equal to the reorganization energy.*

2.2.2 Energy Transfer

The process of energy transfer occurs when an excited energy donor (D) transfers its energy to a ground state energy acceptor (A) through either (1) a radiative mechanism, (2) Dexter energy transfer, or (3) Förster energy transfer. The radiative mechanism occurs when an energy donor molecule (D) absorbs and then emits a photon of light,
while a nearby energy acceptor molecule (A) absorbs that photon of light and is subsequently excited (Equations 5 and 6):\[^{31}\]

\[
D^* \rightarrow D + h\nu \tag{5}
\]

\[
h\nu + A \rightarrow A^* \tag{6}
\]

This mechanism is not common, but is most effective when there is an overlap of the emission of the energy donor and the absorption of the energy acceptor.

The second mechanism for energy transfer is Dexter energy transfer\[^{31,32}\]. This mechanism occurs when the singly occupied orbital of the excited state donor (\(\Psi_{2D}\), Figure 11) transfers an electron to the LUMO orbital of the acceptor (\(\Psi_{2A}\)), while an electron in the doubly occupied orbital of the acceptor (\(\Psi_{1A}\)) is simultaneously transferred back to \(\Psi_{1D}\) (Figure 11)\[^{31}\].

![Figure 11. The Dexter mechanism of energy transfer. An electron in the \(\Psi_{2D}\) orbital of the excited donor is transferred to the \(\Psi_{2A}\) of an acceptor, while an electron is simultaneously transferred from the \(\Psi_{1A}\) orbital of the acceptor to \(\Psi_{1D}\) of the donor.\[^{31,39}\]](image)

The rate constant and efficiency of Dexter energy transfer is mainly dependent on overlap of the wavefunction of the energy donor and acceptor, although diffusional motion (in the case of intermolecular EET), and distance between the donor and acceptor are important. The rate constant for energy transfer in this mechanism normally drops off
exponentially as the distance \( R_{DA} \) between the donor and the acceptor increases. If the solvent is capable of stabilizing energy migration, then larger separations between the D-A pair can still support this mechanism.\(^3\) The rate constant of energy transfer via the Dexter mechanism can be described according to Equation 7:

\[
K_{EnT} = K J \exp \left( -\frac{2R_{DA}}{L} \right) \tag{7}
\]

where \( K \) represents the specific orbital interactions between the donor and acceptor and \( J \) is the spectral overlap integral. The distance between the donor (D) and acceptor (A) is represented by \( R_{DA} \), and \( L \) is the combined van der Waals radii of D and A.

The third mechanism for energy transfer is the Förster mechanism, which is a dipolar transfer occurring through a coulombic interaction between an energy donor (D) and an energy acceptor (A).\(^3\) The Förster mechanism is a through space mechanism that is capable of operating over distances up to ~100 Å.\(^3\) This mechanism occurs when an excited state energy donor (\( D^* \)) induces a resonant dipole interaction with the energy acceptor (A), causing the energy acceptor to become promoted to its corresponding excited state (\( A^* \)) (Figure 12).

\[
\begin{align*}
\Psi_{1D} & \quad \Psi_{2D} \\
\Psi_{1A} & \quad \Psi_{2A} \\
D^* & \quad A \\
D & \quad A^*
\end{align*}
\]

Figure 12. The oscillating electrons in excited state donor (D*) induce a dipole-dipole interaction in the acceptor (A), producing the excited state of the acceptor (A*), while the donor relaxes back to the ground state.\(\text{\textsuperscript{31, 39}}\)
The equation used to describe the rate constant for this mechanism is shown in Equation 8:\textsuperscript{10}

\[ k_{\text{ET}} = E^2 \sim (\mu_D \mu_A)^2 / R_{DA}^6 \]  

(8)

In this equation, the transition dipole moments for the donor and the acceptor are represented by \( \mu_D \) and \( \mu_A \), respectively, while \( E^2 \) represents the interaction energy, or the transition dipoles of the donor (D) and acceptor (A). The rate is inversely proportional to the distance \( (R_{DA}) \) between D and A to the sixth power, and the efficiency is therefore a function of the oscillator strength of the D and A components.\textsuperscript{10}

2.3 Photovoltaic Devices

The initial discovery of the photovoltaic effect was in 1839 by Bacquerel.\textsuperscript{40} He discovered that when a platinum electrode was coated with silver chloride, dipped into an electrolytic solution with another electrode, possibly platinum, and illuminated with light the silver chloride electrode generated electrical current.\textsuperscript{40} In 1954, Fuller, Pearson, and Chapin at AT&T laboratories made the first \( p-n \) silicon single crystal photovoltaic device.\textsuperscript{41} These workers mixed \( p \)-type silicon, which is silicon doped with a minute amount of a group 13 element, usually gallium, that generates electron deficient sites that increase the conductivity of the silicon, in the presence of an \( n \)-type base (i.e., an electron rich material). Illumination of this material generates charge carriers that migrate to their respective electrodes. This device suffered from low photo-conversion and a high cost of manufacturing, but opened the floodgates for semiconductors in photovoltaic research. The use of semiconductive inorganic substances such as silica in photovoltaic devices
have become increasingly popular because of the inherent physical properties of the material obtained upon doping.

Inorganic materials generally have one of the three band structures shown in Figure 13. Band structure is a term used to describe electronic structure of a material when individual molecular orbitals (MOs) become close enough in energy to one another that they attain a great enough density of states so as to be continuous, or band-like. The upper band (the black rectangle) in Figure 13 is called the conduction band, while the lower band is called the valence band. Electronic excitation from the valence band into the conduction band leads to delocalization of the excited electron. Delocalization of both the electron and the complementary hole in the valence band over various sites within the semiconductive material leads to the production of an electrical current. The energy separation between the two bands is called the band gap, and is the amount of energy needed for the generation of charge carriers.
Figure 13. This figure represents different band structures such as (a) the basic band structure of an insulator, (b) a metal where the conductive and valence bands overlap, and (c) a semiconductor. The black band represents the conduction band (unfilled), while the white band represents the valence band (filled).

Organic photovoltaic devices (OPDs) are also known as excitonic photovoltaic devices. An excitonic photovoltaic device operates by the generation of an exciton upon photo illumination. An exciton is a tightly bound electron-hole pair, and has a high binding strength because of the inherently large bandgap in organic materials. As depicted in Figure 1, photoexcitation leads to promotion of an electron from the ground state of the donor (D) molecule into the donor excited state (D*). The electron in the
excited state is coupled to the ground state by a positive hole, and an energy barrier must be overcome for the electron to escape from the excitonic state to generate a charge separated state. Most organic materials have too low of a dielectric constant to stabilize a charge separated state. In order to efficiently generate and then stabilize a charge separated state, the donor (D) must be mixed with an acceptor material (A) with a high electron affinity.\(^7\) The energetic difference between the donor and the acceptor generates one of the driving forces in CS state formation at the interface between the two materials.\(^7\) Careful selection of the D-A pair can therefore enable efficient charge separation at the interface, and subsequent migration, leading to an efficient photovoltaic device.\(^30\) The criteria that must be met for an organic photovoltaic device to operate efficiently are:

1. Efficient photon absorption and exciton generation
2. Diffusion of the exciton to the D-A interface
3. Efficient charge separation at the D-A interface
4. The diffusion of the electron and hole to the cathode and anode electrodes
5. Collection of charges at the electrodes

2.3.1 Charge Transport in Conjugated Polymers

The type of conjugated system, as well as the intermolecular interactions between adjacent polymer chains, governs the electronic and photophysical properties of conjugated polymers. The absence of sp\(^3\) bonds throughout the backbone of a conjugated polymer results in an overlapping set of \(p\)-orbitals that leads to delocalization of electrons through the chain. The most famous example of this type of system is polyacetylene.
2.4 Polyacetylene

In 1977, Shirikawa, Heeger, and coworkers at The University of Pennsylvania found that doped polyacetylene (PA) films were conductive.\textsuperscript{34,43} In this work, crystalline films of PA when doped with either AsF$_5$ or iodine produced conductivities between 220 to 160 $\Omega^{-1}$cm$^{-1}$.\textsuperscript{34} The degree of conductivity depended on the concentration of the dopant used, as illustrated in Figure 14 (with AsF$_5$ as the dopant).\textsuperscript{34} The conductivity of the films was found to increase as the concentration of AsF$_5$ increased, with a maximum reached at 0.10 M.\textsuperscript{34} The doping of the polyacetylene chain allowed for greater conductivity due to delocalization of electrons throughout the chain. The theoretical basis for this phenomenon comes from Hückel Molecular Orbital theory (HMO).
Conjugated molecules can be described at a first approximation using Hückel Molecular Orbital theory (HMO). In Figure 15, the \( \pi \) molecular orbitals (MOs) for four types of butadiene molecules are shown, where \( n = 1, 2, 3, \ldots \) infinite and \( n \) is equal to the number of repeating butadiene units.\(^{33} \) In order to understand the electronic behavior of conjugated chains, it is instructive to first begin with the smallest common denominator, \( i.e. \), more theoretically manageable fragments, before extending the theory towards an infinitely long polymer. In the case of poly(acetylene) (PA), the four MOs of butadiene,
the monomer of PA, are a representative starting point \((n = 1)\) and are shown in Figure 15a. In this diagram, the lowest two orbitals, \(\Psi_1\) and \(\Psi_2\), are filled (\(\Psi_2\) is the HOMO), while the highest two MOs (\(\Psi_3\) and \(\Psi_4\)) are unoccupied, with \(\Psi_3\) being the LUMO. In Figure 15b and Figure 15c, the chain length is extended by the addition of successive butadiene units, with the MOs becoming both higher and lower in energy as a result of the in-phase and out-of-phase combinations of the constituent AOs. These changes to the MOs cause the energy difference between different MOs to decrease, resulting in more closely spaced energy levels. In Figure 15d \((n = \text{infinite})\), the filled (and unfilled) MOs become close enough in energy to form a metallic-like band appearance in infinite PA.\(^{33}\) Because of the infinitely small HOMO-LUMO gap, the bandgap \((E_g)\) for PA would appear, according to Figure 15f, to be zero. Contrary to this drawing, PA is not an organic metal, but rather it has been found to be a semiconductive material.
Figure 15. Evolution of band structures from $\pi$ MOs in (a) butadiene, to (f) a band system in infinite $\pi$ systems (poly-acyetylene). At each increment the chain is extended by one butadiene unit, thereby increasing the $\pi$ system from (a) $n=1$ (butadiene), (b) $n=2$, (c) $n=3$, (d) and (e) $n>1000$, to (f) where $n=\infty$ (infinite poly(acyetylene)). The discrete nature of the MOs break down at large $n$, generating closely spaced energy levels that eventually merge into a continuous band system as represented by (f) with all of the blocks merging into one band. In this figure, $\Psi_1$ and $\Psi_2$ correspond to bonding orbitals, while $\Psi_3$ and $\Psi_4$ represent anti-bonding orbitals.

One assumption made in HMO theory is that all bond lengths in PA are equivalent, when in reality PA is not completely delocalized and is composed of alternating long (1.45 Å) and short (1.35 Å) bonds. This phenomenon results from the Peierls distortion, analogous to the Jahn-Teller distortion, caused by electron-electron repulsion, thereby creating a band gap. As the C-C distance is shortened, the interaction between neighboring electrons becomes stronger, destabilizing the conjugated system.
By allowing one bond in the conjugated system to lengthen, the unfavorable repulsive interaction is minimized, thereby stabilizing the shorter bond. This effect breaks the symmetry of the molecules regenerating the band gap, $E_g$. The result of the structural changes are the semi-conductive properties observed in PA, as well as those of other analogous conjugated organic materials.

PA films have been shown to become highly conductivity ($10^8$ S/cm) when doped by introducing a charge into the conjugated material. The extra holes or electrons ($p$ or $n$ doping, respectively) that are introduced delocalize through a segment of the chain, reducing the Peierls distortion in the vicinity of the charge and making the polymer more conductive. In addition to delocalizing the charge in an intra-chain fashion, the inter-chain movement of charges can also occur. The intra-chain movement of charge results from the structural properties of the polymer such as defects in the chain and breaks in conjugation. The inter-chain mobility, also known as inter-chain “hopping”, is dependent on the distance, angle, and orientation of the chains relative to one another in the solid state.

Despite the early promise of PA films, they have mainly functioned as an important model for other highly conjugated systems. The primary reasons PA films have not been of practical use includes solubility issues, difficulty in processing the polymer, and the brittle nature of PA films, all of which limit their effectiveness in photovoltaic devices. Nevertheless, PA has opened the doors to research in highly conjugated polymers.
2.5 Poly-(phenylenevinylene) and Oligo-(phenylenevinylene)

In 1990, the electroluminescence of poly (p-phenylenevinylene) (PPV) was demonstrated by Burroughs and co-workers.\textsuperscript{35} PPV polymers (Scheme 1) have been shown to have great promise as electroluminescent materials because of (a) the high quality of the films cast from doped PPV, and (b) the strong photoluminescence band observed near 2.2 eV, which is just below the threshold for $\pi \rightarrow \pi^*$ transitions.\textsuperscript{35} These polymers can also be synthesized in high purity and with high molecular weights (MW).\textsuperscript{45} However, PPV suffers from limited solubility because of inter-chain $\pi-\pi$ stacking interactions. Substitution on the PPV phenyl rings with alkyl substitutes has been shown to increase the solubility, while at the same time enhancing the fluorescence and electroluminescence of the polymer.\textsuperscript{45}

Scheme 1. The Wessling synthesis of PPVs.\textsuperscript{45}
The first synthesis of PPV was achieved through a step-growth polymerization (Scheme 1). This polymerization suffered from significant amounts of unreacted end groups, low degrees of polymerization, and a mix of cis and trans isomers throughout the chain.\textsuperscript{45} In 1960, Campbell and McDonald utilized a Wittig-type coupling (Scheme 2) between the bisphosphonium salt of 1,4-bis(bromomethyl)benzene and 4-formylbenzaldehyde to generate oligomers of PPV with an average degree of polymerization of 3-9.\textsuperscript{46} While an improvement over the previous method, the approach still produced low degrees of polymerization of PPV.

\begin{center}
\begin{tikzpicture}
  \node at (0,0) {OHC-\(\begin{array}{c}
  \text{CHO}
  \end{array}\) + \(\begin{array}{c}
  \Phi
  \end{array}\) \(\begin{array}{c}
  \text{Ph}_3\text{PH}_2\text{C-}\end{array}\) \(\begin{array}{c}
  \text{CH}_2\text{Ph}_3
  \end{array}\) \(\rightarrow\) \(\begin{array}{c}
  \text{[}
  \begin{array}{c}
  \text{[}
  \begin{array}{c}
  \text{R}
  \end{array}
  \end{array}
  \end{array}\)
  \(\begin{array}{c}
  \text{n}
  \end{array}\)
  \end{array}\)
  \end{tikzpicture}
\end{center}

Scheme 2. Synthesis of PPV using Wittig Coupling.\textsuperscript{45}

\begin{center}
\begin{tikzpicture}
  \node at (0,0) {OHC-\(\begin{array}{c}
  \text{CHO}
  \end{array}\) \(\rightarrow\) \(\begin{array}{c}
  \text{OHC-}
  \end{array}\) \(\begin{array}{c}
  \text{CHO}
  \end{array}\) \(\begin{array}{c}
  \text{[}
  \begin{array}{c}
  \text{R}
  \end{array}
  \end{array}\)
  \(\begin{array}{c}
  \text{R}
  \end{array}\) \(\begin{array}{c}
  \text{[}
  \begin{array}{c}
  \text{Ti}
  \end{array}
  \end{array}\)
  \(\text{R}
  \end{array}\) \(\end{array}\)
  \end{tikzpicture}
\end{center}

Scheme 3. The McMurray coupling used for the synthesis of soluble PPV derivatives. This synthesis utilizes a low-valent titanium complex to facilitate the deoxygenative coupling of two aldehydes.\textsuperscript{47}
Rehahn and Scluter were the first to synthesize a high MW PPV via a McMurray deoxygenative coupling (Scheme 3). This protocol produced good results, but suffered from a mixture of cis and trans linkages throughout the chain. The reaction scheme did, however, allow for various PPV analogs to be prepared.

The Heck reaction, involving the redox coupling between an aryl halide and an unsubstituted or monosubstituted alkene introduces the double bond as a part of the growing chain. Griener and coworkers used this technique to polymerize ethylene with aromatic dibromides to produce PPV and soluble derivatives. While this reaction is appealing due to the ease of synthesis of the starting materials, it also suffers from the fact that one of the reagents is a gas that must be added in a controlled manner. In addition, ethylene undergoes side reactions that makes the purification of PPV compounds prepared by this method more tedious (Scheme 4). Using a styrene derivative such as 1,4-divinylbenzene reduces the side reactions encountered in the Heck reaction with ethylene, however, these modified conditions require the preparation of the necessary monomer, making this method less appealing.

\[
\begin{align*}
\text{Br} & \quad \longrightarrow \quad \text{Pd catalyst} \\
\text{Br} & \quad \longrightarrow \\
\hline
\text{Pd catalyst} & \quad \longrightarrow \\
\end{align*}
\]

Scheme 4. A reaction showing the Heck reaction of ethylene with dibromobenzene.

Meier, et al. utilized a Siergrist reaction to form PPV and its derivatives. This reaction takes advantage of a Schiff base that is reacted with an aldehyde to generate double bonds in relatively good yields (Scheme 5). The conversion of an aldehyde to
an imine increases the reactivity of that methylene carbon allowing for the deprotonated carbon on the xylene to attack, generating a double bond.

\[
\text{OHC} - \text{CH}_2\text{-CHO} + \text{ArNH}_2 \xrightarrow{120 \degree \text{C}} \text{Dean-Stark App} \quad \xrightarrow{-\text{H}_2\text{O}} \quad \text{N} \equiv \text{N} \quad \xrightarrow{\text{t-BuOK}} \quad \text{PPV} \quad n
\]

Scheme 5. General scheme for the utilization of the Siergrist reaction to form PPV. The initial step involves formation of the imine followed by reaction with \( p \)-xylene to generate PPV.\(^{45}\)

The best route to high purity PPVs is still the Wessling synthesis shown in Scheme 1. Wessling and Zimmerman\(^{50}\) found that sulfonium salts could be treated with base to produce an electrolyte solution that, when subjected to dialysis and the addition of excess base, generated PPV polymers in high purity. The first step involves the nucleophilic substitution of the tetrahydrothiophene to the \( \alpha,\alpha' \)-dichloro-1,4-xylene. This reaction is followed by the deprotonation of one of the methylene protons, and is followed by the 1,6-elimination of one sulfide group to form a reactive \( p \)-xylylene intermediate. Lahti and coworkers\(^{51, 55}(a)\) proved that the polymerization proceeded by a radical mechanism using experiments that indicated the addition of TEMPO dramatically lowered the polymer MW and yields. Controversy, nonetheless, remains as to whether the reactive species is a biradical formed from two quinoidal \( p \)-xylylene intermediates, or a mono-radical species.\(^{45, 144}\)
Currently, the synthesis of PPVs is performed using either thermal elimination of a sulfide group under vacuum or nitrogen, or by a base catalyzed elimination.\textsuperscript{45, 145–147} The thermal elimination has been shown to occur at a variety of temperatures, depending on the nature of the counterion. Using bromide as a counterion, elimination has been shown to occur at 120°C, while temperatures of 200°C have been used for chloride and fluoride counterions, and above 300°C for the acetate counterion.\textsuperscript{45, 145–147} Eliminations of the sulfide and chloride leaving groups are not always concerted, and side reactions can therefore occur that limit the extent to which the sulfide and its counterions are removed.\textsuperscript{45, 145–147} These processes have been confirmed by elemental analysis,\textsuperscript{52} but more work is needed to elucidate the exact mechanism.

PPVs generated by the Wessling method can have ill-defined molecular structures as a result of the random nature of the sulfide elimination. In addition, incomplete conversions (5-50% of the total polymer is typically converted into PPV using these techniques) creating traps in the polymer chain, and ultimately leading to poor device properties.\textsuperscript{35} Clearly, a method devised to synthesize a PPV chain prior to casting of the thin film would aid in creating PPV chains that are extremely pure and contain better photophysical/device properties.

Because of the problems encountered with the products produced by existing synthetic methods, researchers have sought to explore the synthesis of substituted PPV analogs prepared by different synthetic methods. When side chains are introduced at the 2,5-positions of the phenyl groups in PPV (Figure 16), the stability of the doped polymers are found to be improved, and are more easily oxidized by dopants of lower oxidizing power (i.e., iodine).\textsuperscript{45} Electron donating alkoxy side chains are typically used to diminish
the band gap and the oxidation potential of the compound.\textsuperscript{53} Finally, these derivatives have been found to have higher conductivity values compared to PPV in the presence of most oxidants.\textsuperscript{45} Such alkoxy-substituted derivatives have been synthesized in a manner similar to PPV, as shown in Scheme 6 for the mono-methoxy PPV.\textsuperscript{53}

\begin{scheme}
\centering
\includegraphics[width=\textwidth]{scheme6.png}
\caption{The synthesis of a mono-methoxy substituted PPV chain (PMPV) under Wessling conditions.\textsuperscript{53}}
\end{scheme}

The most common PPV analog, poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) can be synthesized by anionic polymerization as shown in Schemes 7 and 8.\textsuperscript{54} This method is a modified Gilch route utilizing a non-polymerizable acidic additive (4-tert-butylbenzylchloride (2)).\textsuperscript{54} The presence of 2 affects the MW of the MEH-PPV polymer by terminating the reaction by dimerization giving 4,4'-di-tert-butylstilbene. The amount and concentration of 2 used in the reaction, consistent with an anionic polymerization mechanism, is inversely proportional to the MW of the polymer.\textsuperscript{54} The reaction begins upon deprotonation of the benzylic carbon of 1, followed by a 1,6-elimination to produce reactive intermediate 4. Subsequent attack
by 3 on 4 initiates the anionic polymerization process. Nucleophilic attack of the anion-terminated chain on 2 terminates the growing polymer.\textsuperscript{54–55}

Scheme 7. The anionic polymerization method used to generate MEH-PPV.\textsuperscript{54}

Scheme 8. The steps involved in the anionic polymerization involved in the synthesis of MEH-PPV. The generation of the reactive p-xylylene intermediate 4 is necessary for generation of high MW PPV compounds.\textsuperscript{54}

In order to conduct a study of structure as a function of the electronic and optical properties of PPV and its analogs, it is relevant to study homologs of PPV (i.e., oligo (\(p-\))
phenylenevinylene) (OPV)). These lower homologs have well defined structures, and at certain chain lengths, \( n = 5 \) and greater, the physical properties mimic the parent PPV polymer.\(^{57}\)

![Figure 16. Representative examples of oligo-(phenylenevinylens) (OPVs): 5 (a) represents the non-substituted oligomer, while 5 (b) and 5 (c) represent the alkyl and alkoxy substituted oligomers.](image)

OPVs suffer from the same insolubility problems traditionally associated with PPV because of chain rigidity and a planar structure that leads to stacking of the chains. Similar to PPV, adding alkyl or alkoxy substituents on the phenyl groups enhances both
solubility and processability.\textsuperscript{56} Oligo($\rho$-phenylenevinylene)s also enable the researcher to tune the electronic properties of the oligomers using step-by-step synthetic approaches in the OPV synthesis. The incorporation of electron donating or electron withdrawing groups, or a combination of the two, onto the OPV chain can significantly alter the absorption, fluorescence, and redox properties of the resulting oligomers.\textsuperscript{56}

The synthesis of OPVs is commonly performed using one of two basic methodologies: 1) a step-wise approach, where the phenylene vinylene groups are added together one at a time, which is the most common method employed,\textsuperscript{58} and 2) a polymer approach where known polymerization methods are used, with early termination of the growing chain.\textsuperscript{56} The most common stepwise method involves making alkene bonds using the Wittig-Horner reaction. This reaction takes advantage of phosphorous ylides and their reactivity to carbonyl containing compounds. Phosphorous ylides have been known since the work of Michaelis and Gimborn in the 1890s,\textsuperscript{57} but were not useful synthetically until 1954 when Wittig discovered phosphorous-stabilized ylides could be used to form alkenes from aldehydes or ketones.\textsuperscript{57} The mechanism of the Wittig reaction is outlined in Scheme 9.
Scheme 9. The generally accepted reaction (a) and reaction mechanism (b) for the Wittig reaction. In this reaction, the phosphorous ylide (9) reacts with a carbonyl compound to produce an betaine intermediate (10) followed by formation of an oxaphosphetane intermediate (11), before cyclization to undergo elimination of triphenylphosphine oxide (13) to form the alkene (12).\textsuperscript{57}

In general, ylide 9 is generated by addition of a strong base that subsequently deprotonates the labile proton on the methylene carbon of the phosphonium salt 8 (previously prepared by addition of triphenyl phosphine 6 to an alkyl halide 7). Attack of the resonance stabilized ylide at the carbonyl carbon of the electrophile produces the charge-separated betaine intermediate 10 that quickly collapses to the oxaphosphetane intermediate 11. This intermediate in turn decomposes to form the alkene 12 and the triphenylphosphine oxide 13 by-product.\textsuperscript{57}
If rotation of betaine 10 can occur prior to collapse to the anti-oxaphosphetane 11, then syn-elimination yields the E alkene (Scheme 10). If the betaine 10 rotates into the syn-oxaphosphetane 14 on the other hand, elimination results in the Z alkene. Numerous effects can induce either conformation to become predominant; however, the thermodynamically favored state is most commonly the anti-oxaphosphetane that produces the E alkene. The effect of substitution around the phosphonium salt can determine the relative orientation of the forming alkene, i.e., resonance stabilized or non-stabilized ylids. If the substituent bound to the carbon of the ylid 9 is an electron donor, i.e., alkyl or alkoxy groups, then cleavage of triphenylphosphine oxide is slowed allowing an equilibrium to favor the anti-betaine orientation, and thereby increasing the amount of E alkene. However, if a protic solvent or Lewis acid is present in the reaction mixture, then the Z alkene begins to predominate. Coordination to the oxygen atom of the betaine 14 can also hinder rotation giving rise to the Z alkene.
Another common approach used in the synthesis of alkenes is the Heck reaction. This reaction involves the palladium catalyzed coupling of an aryl halide or an aryl triflate with an activated alkene in the presence of a triphenylphosphine base, producing a predominately trans-oriented alkene. This reaction mechanism is outlined in Scheme 11.
Scheme 11. The accepted mechanistic cycle for the Heck reaction. The initial oxidative addition of an aryl halide with a palladium (0) catalyst generates a palladium (II) species that generates a π complex with a vinylene compound. Following π complexation is insertion of the double bond into the palladium (II) complex. Elimination of the β-H of the palladium-σ intermediate generates a trans alkene. The remaining palladium (II) species undergoes reductive elimination to palladium (0), thereby reentering the reaction cycle.57, 63

The Heck reaction begins with the generation of a palladium (0) complex (Pd⁰) by the addition of triphenylphosphine ligands across the metal center (Pd(OAc)₂). This complex undergoes an oxidative addition from an aryl or alkyl bromide to generate a Pd
(II) species. The Pd (II) species forms a π complex with an activated alkene, followed by insertion of the alkene into the palladium complex forming a Pd-σ intermediate. The Pd-σ intermediate then undergoes a β-hydrogen elimination to generate a π-complex, that is quickly followed by elimination of the newly formed alkene and reductive elimination of the Pd(II) complex to regenerate the Pd(0) catalyst. The observed $E$ selectivity in this reaction results from the β-hydrogen elimination, which requires a β-hydrogen to be in a syn-periplanar conformation with respect to the halopalladium complex. The reversibility of this elimination allows for the more thermodynamically stable $E$ isomer to form.

Current syntheses of OPV compounds generally involve either of these two methods, or a mixture of the two as outlined in Schemes 12 – 14. Both approaches rely on the synthesis of an asymmetric central unit that allows for the fine-tuning of the physical and optical properties of the final OPV. Substitution on the OPV backbone or at the termini with solubilizing groups has enabled the study of the absorption, fluorescence, and photoelectron spectroscopy of OPV chains having varying degrees of conjugation and chain length (Figure 17).
Scheme 12. (i) 4-Methylbenzaldehyde, LiOEt/EtOH, DMF, rt; (ii) NBS, CCl₄, 80°C; (iii) PPh₃, Toluene, 110°C; (iv) LiOEt/EtOH, DMF, rt.\(^{58}\)
Scheme 13. (i) NaH, DME, reflux; (ii) Pd(OAc)$_2$, P(o-tolyl)$_3$, NBu$_3$, DMF, reflux.$^{56}$
Scheme 14. (i) Aniline, reflux; (ii) KOr-Bu, DMF, reflux; (iii) n-BuLi, DMF, 0°C → rt; (iv) DOWEX 50WX, MeOH, rt; (v) A, KOr-Bu, DMR, reflux.56
Müllen and coworkers performed the first study on substituted OPVs, investigating the degree of conjugation (n) and the effect it has on the photophysical properties. These workers found that increasing the n value leads to red shifts in the absorption spectra that plateaus around n > 5. The fluorescence spectra also exhibited a blue-shift in fluorescence relative to PPV. The blue-shifted fluorescence bands were found to result from conformational twisting of the PPV chain forcing segments of the polymer chain to be non-planar (Figure 18).
Figure 18. Some of the conformations calculated for PPV-type conjugated polymers (A, random coil; B, molten globule; C, toroid; D, rod; E, defect-coil; and F, defect-cylinder). Reproduced with permission from *Acc. Chem. Res.* 2005, 38 (7), 602. Copyright (2005) American Chemical Society.

Experiments designed to understand conformational effects on the spectroscopy of PPV have been conducted with single molecule spectroscopy. Single molecule spectroscopy has enabled researchers to study complex conjugated polymers one molecule at a time. Barbara and Yu resolved the problem of the blue shift in fluorescence by studying the individual emissions from a single chain of MEH-PPV, and found that by lowering the temperature to 20K, the emission from MEH-PPV gave both “red” and “blue” emissions. Barbara proposed that the “red” sites result
from π stacking of neighboring chromophores, leading to low lying states capable of emitting at a longer wavelengths. The “blue” sites stemmed from individual chains of MEH-PPV that had an average conjugation length of 10-17 phenylene units, and resembled the emission spectrum oligomeric MEH-PPV.\textsuperscript{61–62} The realization that emission from MEH-PPV was identical to OPV derivatives indicated the potential that oligomers have for electronic materials.

2.6 Donor/Acceptor Systems

Organic photovoltaic cells require fast electron transfer, as well as an energy gradient that supports extended charge separation, in order to be efficient. Upon charge-separation, the resulting electrons and holes must migrate towards the respective electrodes to complete the electrical circuit. Consequently, the majority of research in this field concerns studying donor and acceptor dyads systems that lead to long-lived charge separated states. Careful consideration of the donor and acceptor used in the dyad is therefore necessary to construct materials that are capable of efficient ET events with subsequent charge separation. Several commonly used donor and acceptor systems for photovoltaic applications are shown in Figure 19.

Buckminsterfullerenes (fullerenes, C\textsubscript{60}) have been used extensively in photovoltaic applications because of their low reorganization energy that leads to long-lived charge separated states.\textsuperscript{63–67} Because of this low reorganization energy, fullerene based photovoltaic cells benefit from the ultra-fast electron transfer to the fullerene that occurs upon electronic excitation of an appropriate donor, as well as the slow charge recombination that results after electron transfer. The fullerene radical anion has a
characteristic absorption at 1070 nm,\cite{63-67} that allows electron transfer to be monitored in transient absorption experiments. The low reorganization energies of fullerenes\cite{64-67} results from the rigid structure and the triply degenerate lowest unoccupied molecule orbital (LUMO).\cite{64-67}

![Diagram of molecular structures]

Figure 19. Representative examples of commonly used materials in organic photovoltaic devices; P3HT = poly-(3-hexylthiophene); MDMO-PPV = poly(2-methoxy-5-(3,7-dimethyloxy)-1,4-phenylenevinylene); APFO = poly\{2,7-(9,9-dioctylfluorene)-alt-5,5-(4,7-di-2’-(3-decyloxy)-thienyl-2,1,3-benzothiadiazole)\}; PTCDA = perylene tetracarboxylic dianhydride; Zn-TPP = Zinc tetraphenylporphyrin; \( \text{C}_60 \) = Buckminsterfullerene.\cite{63}
Studies using dyads composed of porphyrin-OPV,\textsuperscript{69-70} porphyrin C\textsubscript{60}-OPV,\textsuperscript{71} C\textsubscript{60}-OPV,\textsuperscript{72-74} PDI-OPV,\textsuperscript{75-76} and PPV-C\textsubscript{60}\textsuperscript{63,77-78} have been described. The main goal in this work has been to optimize forward electron transfer, generating a charge separated state, and charge migration at the expense of charge recombination. Several examples of dyads used for studying charge transfer for PPV type systems stem in part from work with the porphyrin/fullerene,\textsuperscript{78} tetrathiafulvalene/fullerene,\textsuperscript{79} and heteroaromatic/fullerene dyads\textsuperscript{79} shown in Figure 20.
The work on these model dyads has provided information regarding the effects of D-A distance, as well as how the bridging group between the D-A groups affects the generation of the charge separated state. Gust and Moore et al.\textsuperscript{80} were the first to introduce a porphyrin-fullerene dyad with a rigid hydrocarbon spacer group (29). Dyad (29) was capable of both ET and rapid singlet-singlet energy transfer.\textsuperscript{81} In toluene, these
workers found that excitation of the porphyrin lead to singlet-singlet energy transfer (EET) to the fullerene with a rate constant of $k_{EET} = 4.5 \times 10^{10} \text{ s}^{-1}$. The fullerene was then shown to undergo intersystem crossing to give the fullerene triplet state. All attempts to study the charge separated state failed in non-polar solvents, in which ET was not a thermodynamically favored process. However, in benzonitrile, ET was observed to occur with a rate constant of $k_{ET} = 1.3 \times 10^{10} \text{ s}^{-1}$. This process was slower than singlet energy transfer ($k_{EET} = 1.8 \times 10^{11} \text{ s}^{-1}$). The end result of electron transfer was the generation of a charge separated state with nearly 99% efficiency. The decay of this charge separated state occurred with a rate constant of $k_{CR} = 3.4 \times 10^{9} \text{ s}^{-1}$, that was significantly smaller than ET because of the small reorganization energy associated with fullerenes.80
Gust and Moore \(^{82-83}\) also examined acetylene and amide spacer groups in porphyrin-C\(_{60}\) dyads (Figure 21). Photoexcitation of the porphyrin resulted in quenching of the porphyrin emission by electron transfer. Quantum yields of \(\Phi_{FL} = 0.012\) for 30 and \(\Phi_{FL} = 0.037\) for 31 were observed in tetrahydrofuran (THF), while in the more polar DMF the quantum yields were \(\Phi_{FL} = 0.039\) for 30 and \(\Phi_{FL} = 0.069\) for 31. For comparison, the quantum yield of zinc tetraphenyl porphyrin (ZnTPP) is \(\Phi_{FL} \sim 0.03\). \(^{82-83}\)
Energy transfer from the excited porphyrin ($^1$P-$\text{C}_60$) was ruled out as a competitive pathway, since no emission from C$_60$ was observed. Time resolved fluorescence lifetime data indicated monoexponential decays for the porphyrin in both systems ($\tau_{\text{FL}} = 27$ ps and \( \tau_{\text{FL}} = 75 \) ps in THF for 30 and 31, and \( \tau_{\text{FL}} = 33 \) ps and \( \tau_{\text{FL}} = 75 \) ps in DMF for 30 and 31). The rate constants for electron transfer were obtained from the fluorescence lifetime measurements and showed that electron transfer was three times faster in the acetylene bridge as compared to the amide spacer group (\( k_{\text{ET}} = 3.72 \times 10^{10} \text{ s}^{-1} \) in THF compared to \( k_{\text{ET}} = 1.28 \times 10^{10} \text{ s}^{-1} \) in THF for 30 and 31 respectively). The acetylene bridge allows for greater orbital overlap between the porphyrin and C$_60$, while the amide bond resulted in
the D-A dyad being orthogonal to each other, thereby minimizing the orbital overlap and slowing the ET rate. Imahori 83 showed that using more polar solvents could generate the charge separated state more quickly, because the charge separated state was lower in energy as a result of the greater ionizing ability of the polar solvent.82 – 83

The work of Imahori and Gust has reinforced the idea that conjugated systems serve as better scaffolds to generate a charge separated state. Conjugated systems have a more rigid architecture that minimizes the back-folding process that potentially enhances charge recombination.79 The advantages to using fullerene-containing dyads is the low reorganization energy of C60. Although C60 combinations are clearly useful in photovoltaic applications, their high cost leads to high manufacturing costs. The high cost outweighs the advantages of these combinations, thereby deterring from the cost advantages proposed for organic based solar cells. Research into other acceptor models, such as perylene diimides (PDIs) is therefore a current area of research.75

Photovoltaic systems using perylene diimides (PDIs) take advantage of the PDIs high molar absorptivity, high quantum yield of fluorescence, and stability to chemical and photophysical processes.84 Charge separated states in the realm of several microseconds have been obtained using PDIs as electron acceptors.75 However, the use of covalently bonds to connect an electron donor and acceptor is a time-consuming process requiring extensive synthetic work.

Nature has utilized non-covalent interactions to align chromophores throughout various light harvesting complexes using protein scaffolding, hydrogen bonding, and π-π stacking. Materials scientists have begun to exploit these self-assembly techniques in
order to organize large chromophoric systems capable of harvesting solar energy and using it to create a usable devices.

2.7 Self-Assembled Chromophoric Systems

Taking advantage of non-covalent interactions like hydrogen bonding, π-π stacking, and ligation of metal complexes gives supramolecular control of chromophore alignment. These interactions could in principle improve the performance of optoelectronic devices, as well as enable the rapid assembly of large systems with site-specific alignment. The cyanuric acid/melamine hydrogen bonding motif has previously been employed to combine OPVs with a perylene diimide (Figure 22) to study energy transfer.
Figure 22. Hydrogen-bonding via a melamine/cyanuric acid motif is used to align two OPV units (melamine part) with a PDI (cyanuric acid part) generating OPV-PDI-OPV.

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Excitation of the OPV group in **OPV-PDI-OPV** leads to quenching of the OPV fluorescence.\(^6\) Concentration dependent studies on **OPV-PDI-OPV** were also conducted and revealed aggregate formation. The results showed that increasing the concentration of the OPV segment (above \(10^{-5}\) M) increased the formation of PDI aggregates, resulting in a blue shift in the absorption maxima of the PDI chromophores together with a new red shifted band at \(~590\) nm in the absorption spectra. These results were attributed to \(H\)-type aggregate formation.\(^4\) OPVs have also been used to self-assemble with metallo-porphyrins (Figure 23) generating complexes that undergo efficient energy and electron transfer.\(^6-\)\(^8\)
Meijer and co-workers studied the self-assembled system 32 in Figure 23. This D$_2$-A triad used hydrogen bonding via the cyanuric acid/melamine motif. In order to confirm that the 1:2 complex formed in methylene chloride (instead of self-complexation of oligo-(p-phenylenevinylene)-n-triazines (OPV4T) (33) that can self-assemble in methylene chloride at concentrations as low as 2 × 10$^{-5}$ M) these workers measured the fluorescence spectra of 33 as a function of concentration of the OPV segment. The aggregated fluorescence spectra of 33 shifts relative to the non-aggregated spectra (Figure 24). Keeping the concentration of 33 lower than 2 × 10$^{-5}$ M was found to inhibit
self-aggregation. Addition of the porphyrin was then found to quench the fluorescence of 33, with an optimal concentration of porphyrin of $4.5 \times 10^{-5}$ M. The complete quenching of the OPV at this concentration indicated energy transfer from 33 to the porphyrin occurs in 99% yield.

Figure 24. A plot of OPV4T concentration vs. degree of aggregation showing self-assembly of 33 in MCH with porphyrin (squares) (32); with cyanuric acid derivative (circles); with itself (triangles) using concentration-dependent fluorescence data. The insert shows the quenching of the fluorescence of the 33 compound as a function of increasing porphyrin concentration. Reproduced by permission of Org. Biomol. Chem., 2006, 4, 4460. Reproduced by permission of The Royal Society of Chemistry http://dx.doi.org/10.1039/D0OB00908K.

Hydrogen bonding is an ideal method for preparing supramolecular assemblies because of specific binding interactions that lead to orientational and directional control of chromophores in the solution and solid state. Hydrogen bonding motifs used in
nature and self-assembly include double hydrogen bonds, triple hydrogen bonds, quadruple hydrogen bonds, or combinations of each bonding system (Figures 25 – 27).89

![Figure 25. The self-association of 2-acrylamidopyridine in solution via a double hydrogen bond system.](image)

![Figure 26. The proposed geometry of the triple hydrogen-bonding motif in the assembly of bis(acetylamino)triazene with N-propylthymine.](image)
Studies\textsuperscript{89–90} to probe double hydrogen bonds were performed on 2-acrylamidopyridine (34) (Figure 25), triple hydrogen bonds with melamine/cyanuric acid derivatives (35) (Figure 26), and bis(acylamino)triazene compounds (36) for quadruple hydrogen bonds (Figure 27).\textsuperscript{89–90} These systems offer numerous advantages by making once insoluble components into soluble complexes by allowing for the self-assembly into cyclic arrays such as 37 instead of extended insoluble materials.\textsuperscript{89–90}
Metallo-complexes have also been used to self-assemble chromophoric materials. One commonly used method is axial ligation of a metalloporphyrin with Lewis bases. Specifically, axial ligation of a zinc-porphyrin with pyrindine associates in a 1:1 ratio due to a five coordinate zinc porphyrin complex (Figure 28). A well known system utilizing this self-assembly technique is represented by 38.
Figure 28. A 1:1 pyridine:zinc porphyrin complex.

The binding constants for bis-porphyrin-pyromellitimide complex (38) were determined using UV-Vis absorption titration studies. The 1:1 complex was confirmed, with an association constant of $K_a = 2.6 \times 10^6 \text{ dm}^3 \text{ mol}^{-1}$. Excitation of the porphyrins at 428 nm resulted in quenching of the porphyrin emission ($\Phi_{FL} = 0.08$). The rate constants for electron and back electron transfer in this complex were determined using transient absorption measurements, yielding values of $k_{ET} = 2.1 \times 10^{10} \text{ s}^{-1}$ and $k_{CR} = 1.3 \times 10^{10} \text{ s}^{-1}$. The rate constants were found to be slower than similar covalently linked systems. However, this study did not explore the effect that changing the environment surrounding the self-assembled triad had on electron transfer. The environment surrounding a self-assembled system has been shown to drastically affect electron and or energy transfer.
Work on PDI/OPV systems have shown there can be fast electron transfer via non-covalent interactions along with charge recombination rates that are on the same timescale or orders of magnitude slower than their covalent counterparts.\textsuperscript{92} One such self-assembled system (39) is shown in Figure 29. The first fluorescence spectrum shown in the inset (upper left) of Figure 29 shows the fluorescence of the OPVs without the PDI acceptor present. The absorption spectrum of the isolated OPVs shows the main absorption band in methylene chloride at 436 nm (Figure 30). The fluorescence spectrum was characterized by an emission of $\lambda_{\text{max}} \sim 502$ nm with vibrational features extending to 531 nm (Figure 30). Dissolving this OPV in methylcyclohexane (MCH) resulted in a blue shift of the main absorption band to $\lambda = 419$ nm, along with the appearance of a red shoulder at $\lambda = 500$ nm, indicative of formation of an $H$-type aggregate (Figure 31) of OPV chromophores.\textsuperscript{93}
Figure 30. The absorption and fluorescence spectra of the self-assembled OPV compound in Figure 29 with increasing concentration. As the concentration is increased, a blue shift of the main absorption peak is seen along with a red shift in the emission and quenching of the OPV fluorescence. Reproduced by permission of Hoeben, F.J.M.; Zhang, J.; Lee, C.C.; Pouderoijen, M.J.; Würthner, F.; Schenning, A.P.H.J.; Meijer, E.W.; De Feyter S. Visualization of Various Supramolecular Assemblies of Oligo(para-phenylenevinylene)-Melamine and Perylene Bisimide. *Chem. Eur. J.* 2008, 14, 8579. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

Figure 31. *H*- and *J*-type aggregate forms are shown for a hypothetical rigid rod.
When the assembly of OPV/PDI (39) was performed in methylcyclohexane, the spectral features associated with J-type aggregates were observed. Thus, the fluorescence from the OPV segment of 39 was observed to be nearly quenched upon irradiation, indicating electron transfer from the OPV to the PDI. The decrease in fluorescence of the OPV segment was similar to experiments on a closely related covalent system, although ET in the covalent system was found to be more efficient in methylcyclohexane. However, determination of the rates for charge-separation was not possible from the femtosecond transient absorption spectra. Meijer and co-workers were able, however, to determine the rate constants for charge separation and charge recombination for a similar system (Figure 23) in methylcyclohexane and toluene, for which they found that charge separation occurred with $k_{ET} > 10^{12}$ s$^{-1}$. Charge recombination was two orders of magnitude higher in the covalent system in toluene as compared to the non-covalently linked system. Therefore, linking chromophores via self-assembly can generate a system that has photophysical properties that are comparable, or better than a covalently linked system.
CHAPTER III
RESULTS AND DISCUSSION

3.1 Asymmetrical Oligo (p-phenylenevinylenes)

Emissive conjugated oligomers based on p-phenylenevinylene have gained widespread attention in recent years due to their potential use in organic photovoltaic devices,\textsuperscript{96 – 97} field effect transistors,\textsuperscript{98} organic light emitting diodes,\textsuperscript{99} and non-linear optical devices.\textsuperscript{100} The photophysical properties of oligo (p-phenylenevinylene) can be tuned by varying the substitution pattern on either the phenylene or vinylene portion of the compound (Figure 32).

![Figure 32](image_url)

\( R_{1-3, 7-9} = \text{H, OCH}_3, \text{t-butyl, etc.} \)
\( R_{5-6} = \text{H, OCH}_3, \text{OAlkyl, t-butyl, etc.} \)
\( R_4 = \text{H, CN} \)

Figure 32. Various substitution patterns that have been prepared along the phenyl or vinylene positions of an oligo (p-phenylenevinylene) chromophore. The substituents can be mixed and matched depending on the synthetic approach employed.
Increasing the asymmetry of an OPV can induce a high degree of polarizability in the molecule, shifting both the absorption and fluorescence spectra. The shifted spectra often result in larger optical Stokes shifts, and these compounds have found applications in non-linear optical materials. The optimized, scalable, and reproducible synthesis of highly pure asymmetric OPV materials is clearly highly desirable. The most popular way to prepare asymmetric OPVs is shown in Scheme 16. Nierengarten optimized the synthesis of 41, obtaining 10 g of 41 in 50% overall yield from the dialkoxybenzene starting material. Other synthetic methodologies based on 40 have only moderately improved the overall yield of 41 (to 53% overall yield) from the dialkoxybenzene starting material. The initial step in this synthesis involves the di-iodination of a dialkoxybenzene with iodine and periodic acid in acetic acid, a reaction that occurs with an average yield of 67% for 40. The mono-lithiation of 40 with n-BuLi, followed by its conversion to the formyl group with DMF, yields 41 in approximately 70% yield. The overall yield of 41 in this process from the dialkoxy starting material is 47% yield. Currently, the synthesis of an asymmetric unit like 41 does not exceed production of more than 15 grams. Potential causes of the available yields are scalability problems and the potential hazards of running formylation reactions with n-BuLi on large enough scales to produce larger quantities of 41. In any case, any synthetic approach that increases the yield of asymmetric OPVs and increases the scale at which OPVs could be produced, is highly desirable. The preparation of asymmetric OPVs in higher yields with greater versatility comprises the first part of this dissertation.
Scheme 16. A representative example towards the synthesis of an asymmetric central subunit in traditional OPV synthesis.\textsuperscript{102}

By modifying the current literature approach towards asymmetric OPVs, the Smith-Modarelli method\textsuperscript{114} towards asymmetric OPV synthesis increases the overall yield to values 15-30\% higher than currently reported.\textsuperscript{102} In this synthetic approach, an asymmetric focal point, 43, was first prepared (Scheme 17). The selective oxidation of methyl benzyl ether with DDQ\textsuperscript{103} is an integral step in the preparation of 43, and therefore OPV synthesis. Several asymmetric tetrameric and pentameric OPVs were then synthesized to illustrate the utility of 42 as a highly useful substrate for the generation of asymmetric OPVs. The Smith-Modarelli\textsuperscript{114} methodology has been employed to generate quantities of 43 from 100 mg to 50 g with minimal work-up, producing pure product by \textsuperscript{1}H NMR, \textsuperscript{13}C NMR, and mass spectroscopies upon recrystallization from 95\% ethanol.

Scheme 17. The synthesis of an asymmetric central subunit for OPV synthesis is shown above.
The proposed mechanism for the oxidation of methyl benzyl ether with DDQ is depicted in Scheme 18.\textsuperscript{103} The rate limiting step for this reaction is the formation of the charge-transfer complex with DDQ. The subsequent reduction of DDQ generates the aldehyde 55. The asymmetry in the molecule is conserved due in part to the less favored formation of a second charge-transfer complex of 55 with a second equivalent of DDQ, thereby allowing isolation of pure 55 in good yields.

\[ \text{H}_3\text{CO-CH}_2\text{OCH}_3 \xrightarrow{\text{slow}} \text{H}_3\text{CO-CH}_2\text{C(NC)Cl}_2\text{OCl}_2 \]

Scheme 18. The proposed mechanism for the DDQ oxidation of methyl benzyl ethers.\textsuperscript{103}

Wang performed this synthetic step on various substituted benzyl ethers.\textsuperscript{103} He showed that the oxidation of benzyl ethers with DDQ is enhanced by the presence of ortho-substituents (compared to the rate with meta- and para-substituents).\textsuperscript{103} The time required for the complete conversion of starting material 42 to 43 was determined by varying the reaction time and comparing the relative intensities of the methylene proton peaks in the \textsuperscript{1}H NMR spectra with the relative intensity of the mono- and di-aldehyde peaks.
peaks. This study showed that the starting dimethyl benzyl ether was completely consumed within 12 – 15 min, and that the mono-aldehyde product 43 was produced in quantitative yields. Longer reaction times resulted in the generation of a terephthaldehyde by-product. This synthetic method not only provided the desired central sub-unit used in this work (43) in quantitative yields, it also allowed for extremely fast reaction times that resulted in the synthesis of multiple OPV derivatives.

3.1.1 Tetrameric and Pentameric Oligo-(phenylenevinylene) (OPVs)

A series of tetrameric and pentameric OPVs were synthesized using 42 as the central building block towards the generation of tetrameric and pentameric OPVs shown in Chart 1. The synthesis of the 44 – 50 are shown in Scheme 19 and 20, while the synthesis of 51 - 54 are shown in Scheme 21.
Chart 1. Asymmetrical OPVs 44 – 54.

Scheme 19. Synthetic scheme for the synthesis of 44 – 47.
Scheme 20. The synthetic scheme of tetramers 48 – 50.

1,4-Di-(octyloxy)-2,5-bis-(methylmethoxy) benzene 42 was prepared in 96 % yield from 1,4-di-(octyloxy)-2,5-bis-(bromomethyl) benzene by reaction with sodium
methoxide in dry methanol. The DDQ oxidation of 42 to 43 was performed by reacting 42 with 1.5 equivalents of DDQ in a 10:1 mixture of methylene chloride and water at room temperature for 15 min. The conversion was found to be greater than 99% complete by $^1$H NMR, and upon extraction with NaHCO$_3$ to remove the hydroquione by-product, produced 43 in quantitative yields. Horner-Wadsworth-Emmons (HWE) coupling of 43 with aryl phosphonate ester 56 produced 57 (a) in 92% yield. The ether group in 57 (a) was oxidized with DDQ to produce aldehyde 57 (b) in 96% yield. Aldehyde 57 (b) was reacted using two different reaction pathways to prepare tetramers 44 - 50 and pentamers 51 - 54. These two sets of OPV products were prepared to illustrate the synthetic versatility of precursor 53.

The synthesis of tetramers 54 - 57 are shown in Scheme 14. In these reactions, stilbene bromide 67 (b) was reacted with para-substituted aryl phosphonate esters 57 - 59 under HWE coupling conditions to produce trimers 60 - 62. The aryl phosphonate esters 57 - 59 were synthesized by reacting the precursor benzyl bromide with triethyl phosphite under Arbuzov conditions to generate the phosphonate esters 57 - 59 in excellent yields. The Heck coupling reaction of 60 - 62 with styrene produced tetramers 44 - 46 in 50-75% yields. The nitro-substituted tetramer 46 was converted to its amine-substituted analog 47 by reduction with SnCl$_2$ in ethanol in 60% yield.

Scheme 20 shows the synthesis of tetramers 48 - 50. Aldehyde 57 (b) was reacted under Heck coupling conditions with para-nitrostyrene to give the trimeric aldehyde 64 in ~50% yield. The para-nitrostyrene used in Scheme 20 was prepared by taking para-nitro-benzyl phosphonium salt and reacting with 37% formaldehyde in water with sodium carbonate as the base. Upon column purification by chromatography, para-
nitrostyrene was produced in 50% yield. The HWE coupling of either benzyl phosphonate ester 56 or 59 provided the corresponding methoxy-nitro substituted tetramer 48, and bromo-nitro-substituted tetramer 49, which were both purified by column chromatography in 67-69% yield. The bromo-nitro-substituted tetramer 49 was converted to the amine-substituted analog 50 using SnCl₂ in ethanol in ~60% yield, similar to the conversion of 46 to 47.

The syntheses of pentamers 51 - 54 are shown in Scheme 16. The formylation of 65 and 66 was conducted at -78°C by the slow addition of n-BuLi to a solution of 65 and 66 in anhydrous THF, followed by the addition of DMF to produce the crude aldehyde that was purified by column chromatography to produce 67 and 68 in moderate yields. These aldehydes were then coupled with the stilbene phosphonate esters 69, 70, and 71 under HWE conditions producing pentamers 51 - 54 in 58%, 67%, 76%, and 74% yields respectively.
Figure 33. Normalized steady state absorption spectra of $44 - 47$ in methylene chloride. All spectra are normalized to the absorption band with the highest intensity value to illustrate the shifts in the $\lambda_{\text{max}}$ upon substitution of the OPV chromophore.
Figure 34. Normalized steady state fluorescence spectra of 44 – 47 in methylene chloride. All spectra are normalized to illustrate the relative shifts of the $\lambda_{\text{max}}$ upon changing the end group on the OPV.

The UV-Vis spectra of tetramers 44 - 50 are shown in Figures 33 and 34. These spectra clearly illustrate that varying the substitution around an OPV chain can fine tune the spectral properties the compound. OPV 44 illustrates the typical absorption spectra of an OPV with $\lambda_{\text{max}} = 411$ nm, accompanied by a higher energy absorption band at 351 nm. The fluorescence spectrum of 44 is characterized by an emission maximum at $\lambda_{\text{em}} \sim 460$ nm with a low energy shoulder at $\sim 495$ nm. The absorption spectra of 45 is similar to 44, except for the more pronounced absorption at 351 nm resulting from the placement of the methoxy group on the 4–position of the benzene ring. The fluorescence spectrum of 45 is red-shifted by 10 nm from 44, with $\lambda_{\text{em}} \sim 470$ nm. These results coincide with the results
obtained from Zhu and co-workers on trimeric unsubstituted OPVs and methoxy substituted OPVs.\textsuperscript{104} In this work, the placement of an electron-withdrawing group at the ends of the OPV chain red-shifted the absorption and fluorescence spectra. In the case of nitro substituted trimer, 74\textsuperscript{(a)}, a decrease in the amount of fluorescence was also observed.\textsuperscript{104} Similar quenching of the fluorescence has been observed in numerous nitro-substituted stilbene and higher conjugated OPV compounds, and has been attributed to either charge transfer in the excited state or to a trans to cis isomerization resulting from intersystem crossing to the triplet state.\textsuperscript{104\textsuperscript{(b-c)}} This effect is clearly illustrated in Figures 33 and 35, where both the absorption and fluorescence spectra of nitro substituted 46 are red-shifted relative to 44, 45, and 47. The fluorescence spectra for 44 - 47 are comparable to similarly symmetrically substituted trimeric OPV molecules, albeit slightly red shifted because of the extension of the conjugation by one phenylene vinylene unit.\textsuperscript{104} The relevant absorption ($\lambda_{\text{max}}$), fluorescence maxima ($\lambda_{\text{em}}$), Stokes shifts, and fluorescence quantum yields ($\Phi_{\text{Fl}}$) for 44 – 47 are tabulated in Table 1.

In organic light emitting diode (OLED) research the ability to shift the absorbance and fluorescence of a chromophore is critical to proper device fabrication. The absorbance of nitro-substituted OPV 46 is red-shifted by 29 nm relative to 44. In comparison, the dinitro substituted trimer 74\textsuperscript{(a)} (Figure 35) has an absorption maximum that is red-shifted ~51 nm relative to the unsubstituted trimer 74\textsuperscript{(b)}. Similarly, the fluorescence of 46 ($\lambda_{\text{max}} = 507$ nm) is red-shifted by 40 nm relative to 44. These results indicate that changing the symmetry of OPVs can affect the absorption and fluorescence response of these molecules.\textsuperscript{104}
Figure 35. Zhu’s trimeric nitro-substituted OPV 74 (a) along with an H-end substituted OPV 74 (b). The fluorescence maxima for 74 (a) was observed at 610 nm, while the maxima for 74 (b) was observed at 444 nm.

Table 1. The steady state absorption and fluorescence data for samples 44 – 47.

<table>
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<tr>
<th>Sample</th>
<th>Solvent</th>
<th>$\lambda_{\text{max Abs}}$ (nm)</th>
<th>$\lambda_{\text{max Fl}}$ (nm)</th>
<th>$\Delta \lambda$ (nm)</th>
<th>$\Phi_{\text{Fl}}$</th>
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<td>481</td>
<td>68</td>
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</table>

*Excited at 400 nm. Quinine sulfate used as quantum yield reference.*

The steady state absorption and fluorescence spectra of pentamers 51 – 54 and reference compound 72 are shown in Figures 36 – 38. Unsubstituted pentamer 51 was observed to have $\lambda_{\text{abs}} = 420$ nm and $\lambda_{\text{em}} = 484$ nm in methylene chloride, corresponding to a Stokes shift of 65 nm; in DMAc 51 was observed to have $\lambda_{\text{abs}} = 421$ nm and $\lambda_{\text{em}} = 498$ nm, corresponding to a Stokes shift of 77 nm. The unsubstituted symmetrical
reference compound 72 in methylene chloride has $\lambda_{\text{abs}} = 426$ nm and $\lambda_{\text{em}} = 483$ nm, corresponding to a Stokes shift of 58 nm. In DMAc, compound 72 was observed to have $\lambda_{\text{abs}} = 427$ nm and $\lambda_{\text{em}} = 485$, corresponding to a Stokes shift of 58 nm. Upon changing the position of the dialkoxy phenyl group from the third repeat unit in 72 to the second repeat unit in 51, the main absorption band is seen to red-shift slightly, while the emission band red-shifts ~10 nm in DMAc and ~17 nm in methylene chloride. The absorption, florescence, Stokes shifts, and fluorescence quantum yields ($\Phi_F$) in compounds 51 – 54, along with the absorption maxima and fluorescence maxima of symmetric reference compounds 72 and 73, are tabulated in Table 2.
Figure 36. Normalized steady state absorption spectra of pentamers 51 - 54 in (a) methylene chloride and (b) dimethylacetamide (DMAc).
Figure 37. The normalized steady state fluorescence spectra of 51 – 54 in (a) methylene chloride and (b) DMAc.
Table 2. The steady state absorption, fluorescence, and Stokes shifts for 51 – 54, and 72 – 73 in methylene chloride (CH$_2$Cl$_2$) and DMAc.

<table>
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<tr>
<th>Sample</th>
<th>Solvent</th>
<th>$\lambda$ Abs (nm)</th>
<th>$\lambda$ Fl (nm)</th>
<th>$\Delta\lambda$ (nm)</th>
<th>$\Phi$ Fl</th>
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<tr>
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<tr>
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<td>498</td>
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<td>DMAc</td>
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</table>

* Excited at 400 nm. " Quinine sulfate used as quantum yield reference.\textsuperscript{149}
Figure 38. A comparison of the normalized steady state (a) absorbance, and (b) fluorescence of 51 to 72 in methylene chloride.
3.2 Synthesis and Photophysical Characterization of Cofacial and Branched OPVs

Since the fundamental work of Shirakawa, MacDiarmid, and Heeger\textsuperscript{108} over 20 years ago, exploration into the use of conjugated materials has increased significantly. Commercialization of $\pi$-conjugated materials for organic light emitting diodes\textsuperscript{109} (OLED) has driven research to understand the photophysical properties of these $\pi$-conjugated materials in both solution and the solid state.\textsuperscript{96, 110} Further experiments in this area are important for studying excited state energy delocalization and migration among closely spaced chromophores. Interactions such as these are important in closely spaced OPV groups, an area that is of interest because of the potential for these excited state processes to influence the photophysical response in photovoltaic materials.

Recent theoretical work\textsuperscript{96, 106, 111, 112} has focused on understanding how distance and orientation of neighboring OPV and PPV chains can affect the photophysical responses of closely associated molecules relative to isolated molecules. Bazan and co-workers\textsuperscript{96, 106, 111, 112} synthesized dimeric OPV paracyclophane models 75 – 75 (Figure 39), where the OPV groups were spaced close together, in order to study these interactions experimentally.\textsuperscript{96, 106, 111, 112} Photophysical experiments on these compounds confirmed several theoretical predictions such as spectral splitting upon close association of neighboring stilbene molecules; however, completely cofacial OPV model compounds have not yet been synthesized. A cofacial OPV such as 78 would allow for examination of the effect distance and orbital overlap has on the photophysical properties of OPVs under similar conditions to those found in thin films.\textsuperscript{96, 106, 111, 112} The work presented in this section includes the synthesis of cofacial oligomers with a high degree of interchain
orbital overlap to compare how geometry and alignment of stilbene, tetrameric OPV, and pentameric OPV chains can effect the photophysical response of an OPV system.

Figure 39. Paracyclophane stilbene molecules designed by Bazan and coworkers.\textsuperscript{96, 106, 111, 112} Stilbenes 75 – 76 have an inter-stilbene distance of \(~3.5\) Å.\textsuperscript{96, 106, 111, 112}
Theoretical work at the INDO level\textsuperscript{96, 106, 111, 112} has shown that when the interchain distance between a pair of conjugated molecules is decreased from 16 Å to 3 Å, the molecular orbitals between neighboring chains begin to overlap, causing the electronic wavefunction to be delocalized between the two chains. Such an interaction leads to a splitting of the ground state energy levels, resulting in red shifted absorption bands. However, at distances shorter than 4 Å, the lowest predicted absorption occurs from the $S_0 - S_5$ transition instead of the analogous $S_0 - S_1$ and $S_0 - S_2$ transitions.\textsuperscript{96, 106, 111, 112} The optimal interchain distance\textsuperscript{96, 106, 111, 112} between cofacial stilbenes or related conjugated chains is 4 Å in terms of optimizing orbital overlap and minimizing extraneous close contact interactions.

In order to study interchain excited state interactions within cofacial OPV oligomers, we decided to prepare cofacial OPVs tethered to a xanthene bridge 79 (Figure 40). The distance between two OPV chains attached to this bridge is $\sim$4.4 Å (AM1 level), similar to the optimal separation for interchain interactions calculated by Brédas, et al.\textsuperscript{96, 106, 111, 112} A benzofuran bridge 80 (Figure 42) was also used in order to provide a larger interchain bite angle (36°) and greater interchain distances, that range from 4.5 –
10 Å (at the chain terminus). The synthesis of OPV compounds having these bridges are described in the following section.

Figure 40. The two types of bridges utilized in this study. Xanthene 79 was used to place the OPV molecules into a cofacial arrangement, while benzofuran 80 orients is the OPV molecules into a Y-shaped orientation.

The precursor anchors\textsuperscript{113} 83 and 84 were synthesized according to Scheme 22. Suzuki coupling of 4-formyl boronic acid with either 81\textsuperscript{113} or 82\textsuperscript{113} in a 1:1 mixture of toluene and ethanol and a catalytic amount of tetrakis-triphenylphosphine palladium (0) ((Ph\textsubscript{3}P)\textsubscript{4}Pd) produces 83 and 84 in 80\% and 86\% yields, respectively.
The syntheses of stilbenes 87 and 88 are shown in Scheme 23. The HWE olefination of 3,5-di-tert-butylbenzyl phosphonate ester with 4-bromobenzaldehyde produces compound 85 in 77% yield. Bromostilbene 85 was subsequently reacted with tert-butyl lithium, followed by trimethylborate to produce boronic acid 86 in 75% yield. Suzuki coupling of boronic acid 86 with either 81 or 82 then produced xanthene distilbene 87 and benzofuran distilbene 88 in 82% and 81% yields, respectively.
Scheme 23. (i) THF, potassium tert-butoxide; (ii) tert-BuLi, THF; (iii) B(OMe)_3, 3M HCl; (iv) Toluene/EtOH, 81, Pd(PPh_3)_4, K_2CO_3; (v) Toluene/EtOH, 82, Pd(PPh_3)_4, K_2CO_3.

The synthetic route to prepare precursor phosphonate ester 94 is outlined in Scheme 24. The HWE olefination of 89 with 90 produces an intermediate methyl benzyl ether stilbene, that was oxidized with DDQ purified by column chromatography to produce 91 in 73% overall yield. This aldehyde was then reacted with diethyl 4-(diethoxymethyl)benzylphosphonate in THF with potassium tert-butoxide until TLC.
analysis indicated the disappearance of the starting aldehyde. The reaction was quenched with aqueous HCl, neutralizing the reaction as well as cleaving the acetal protecting group. The deprotected aldehyde was then reacted with diethyl 4-(diethoxymethyl)-benzylphosphonate again to extend the conjugation in the chain one more unit.

![Chemical structures and reactions](image)

Scheme 24. (i) THF, potassium tert-butoxide; (ii) DDQ, methylene chloride/water; (iii) diethyl 4-(diethoxymethyl)benzylphosphonate, THF, potassium tert-butoxide; (iv) 3M HCl; (v) diethyl 4-(diethoxymethyl)benzylphosphonate, THF, potassium tert-butoxide; (vi) 3M HCl; (vii) NaBH₄, THF:H₂O; (viii) thionyl chloride, pyridine, methylene chloride, producing 93; (ix) triethyl phosphite, 180 °C.

When TLC indicated completion, the reaction was quenched with aqueous HCl with subsequent cleavage of the acetal protecting group. This crude aldehyde was collected and dried. Reduction of this intermediate aldehyde in wet THF produced benzyl alcohol.
after column chromatography in 17% overall yield from \( \text{91} \). Alcohol \( \text{92} \) was then reacted with equimolar amounts of thionyl chloride and pyridine in dry methylene chloride to produce benzyl chloride \( \text{93} \) in 98% yield. Benzyl chloride \( \text{93} \) was reacted with triethyl phosphite at 180 °C for 12 h, and then vacuum distilled to isolate tetrameric phosphonate ester \( \text{94} \) in 95% yield.

\[
\begin{align*}
\text{93} & \quad + \quad \text{83} \\
& \quad \xrightarrow{\text{i}} \quad \text{95}
\end{align*}
\]

Scheme 25. The synthesis of \( \text{95} \): (i) THF, potassium \( \text{tert} \)-butoxide.

Schemes 25 and 26 show the synthetic routes used to prepare compounds \( \text{95} \) and \( \text{96} \) respectively. The pentameric oligo (\( p \)-phenylenevinylene) (POPVs) \( \text{95} - \text{96} \) were synthesized by a Horner-Wadsworth-Emmons (HWE) olefination reaction of phosphonate ester \( \text{93} \) with either \( \text{83} \) or \( \text{84} \) in THF with potassium \( \text{tert} \)-butoxide, producing \( \text{95} \) and \( \text{96} \) in 75% and 70% yields, respectively.
Scheme 26. The synthesis of 96: (i) Potassium tert-butoxide, THF, reflux.

The last cofacial OPV synthesized was a tetrameric version 98 (Figure 41).

Compound 98 was synthesized by the Horner-Wadsworth Emmons coupling of phosphonate ester 99 with 83, producing 98 in 76% yield (Scheme 27).
Figure 41. The structure of cofacial tetramer 98 along with reference compound 44.

Scheme 27. The synthesis of 98: (i) Potassium tert-butoxide, THF, reflux.

3.2.1 Steady State Absorption and Fluorescence Spectroscopy of 87 and 88

The steady state absorption spectra and fluorescence spectra of cofacial stilbene 87, 88, and reference stilbene 100 (a) in methylene chloride are shown in Figures 42 and 43. The absorption spectra in both compounds are dominated by the $S_0 \rightarrow S_1$ transition of
the stilbene. Cofacial dimer 87 showed an absorption maximum at $\lambda_{\text{max}} = 330$ nm together with a shoulder at $\sim 300$ nm, while 88 had $\lambda_{\text{max}} = 338$ nm with a shoulder at $\sim 312$ nm. The $S_0 \rightarrow S_1$ absorption band in both compounds was red-shifted from stilbene 100 (a), for which $\lambda_{\text{max}} \sim 298$ nm. The steady state fluorescence spectra of 87 has a band at $\lambda_{\text{em}} = 398$ nm with a shoulder at $\sim 421$ nm, while 88 has a fluorescence band at $\lambda_{\text{em}} = 396$ nm along with a shoulder at $\sim 377$ nm and a second low energy shoulder at $\sim 419$ nm (Figure 43). The fluorescence spectrum of stilbene 100 (a) has $\lambda_{\text{em}} \sim 348$ nm along with a shoulder $\sim 368$ nm and a higher energy shoulder at $\sim 334$ nm. The fluorescence quantum yields of both 87 ($\Phi_{\text{fl}} = 0.63$) and 88 ($\Phi_{\text{fl}} = 0.81$) are significantly reduced from that of the conformationally constrained trans-stilbene analog 100 (b), $\Phi_{\text{fl}} = 1.0$, but larger than that of trans-stilbene 100 (a) ($\Phi_{\text{fl}} = 0.05$) probably resulting from a conformationally constrained structure. The absorption, fluorescence, and quantum yield data for 87, 88, and 100 (a) are tabulated in Table 3.
<table>
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<tr>
<th>Sample</th>
<th>Solvent</th>
<th>$\lambda_{\text{max Abs}}$ (nm)</th>
<th>$\lambda_{\text{em Fl}}$ (nm)</th>
<th>$\Phi_{\text{fl}}$</th>
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<td>CH$_2$Cl$_2$</td>
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<td>88</td>
<td>CH$_2$Cl$_2$</td>
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<td>100 (a)</td>
<td>CH$_2$Cl$_2$</td>
<td>298</td>
<td>348</td>
<td>0.05</td>
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</table>

Excited at 320 nm. Quinine sulfate used as quantum yield reference.

The differences in the absorption and fluorescence spectra of 87, 88, and stilbene 100 (a) can be explained in terms of the theoretical work of Brédas, et al., as well as in the context of the spectra of the analogous compounds (75 – 77) prepared by Bazan and coworkers. Brédas has calculated the geometries of OPVs and cofacially positioned OPVs at the INDO/S level to examine interchain electronic interactions. These calculations focused on varying the distance between cofacial stilbenes, and predicting the electronic interactions and photophysical response of these cofacial chains. The calculations were also expanded to include longer chain OPVs, as well as the effect that the “bite” angle between the two cofacial chains, and the resultant photophysical properties of these compounds. These calculations predicted a small red shifted band in the absorption spectra of the cofacial dimer arising from the individual chains. This shift occurs because the chains become more planar upon approaching one another due to the more constrained environment. These calculations also predicted the appearance of a blue-shifted band resulting from the cofacial interaction between the two chains. This shift is due to excitonic coupling between the two chains causing higher energy absorptions to become more probable. Brédas also argued that blue shifted band may
not be intense enough to be seen experimentally, therefore the experimental results of cofacially aligned stilbenes or OPVs could show only a red shift in their absorption spectra and an absence of a blue shift.

Both red and blue shifted absorption bands have been observed in the closely associated cofacial stilbene 75 (a). The absorption band for this compound was split into two different bands having $\lambda_{\text{max}} \sim 264$ nm and $\sim 325$ nm. The cofacial dimer 76 (a) exhibited only one band that was red shifted 13 nm relative to model compound 77, indicating excitonic coupling as a result of interactions between the two stilbene chromophores. Cofacial trimers 75 (b) and 76 (b) also showed a 15 nm red shift relative to 77, which was also attributed to excitonic coupling. The difference in the spectroscopic properties of 75 (a) and 76 (a) has been attributed to energy transfer between the excited state of the stilbene chromophore with the lower energy inter-ring excited state of the [2,2] paracyclophane core.

The red-shifted absorption bands in 87 and 88 can also be interpreted in the context of Brédas’ computations. Brédas has predicted an exponential increase in excitonic splitting and charge transfer (CT) contributions as the interchain distance between two stilbenes is decreased from 4 Å to 3.5 Å, with the lowest excited state transition (i.e. $S_0 \rightarrow S_1$) becoming optically forbidden by symmetry. In this interpretation, higher energy transitions ($S_0 \rightarrow S_n$, $n = 2, 3$, etc) become more probable, leading to the blue-shifted absorbance spectra. Cofacial dimer 75 (a) is highly constrained with a computed intermolecular distance of 3.82 Å (measured at the alkene bonds). Dimer 76(a), on the other hand only has orbital overlap between the cyclophane phenyl groups, and therefore considerably less orbital overlap between the
stilbene groups than 75 (a). Cofacial dimer 75 (a) was also observed to have a fluorescence maxima at 412 nm compared to 77 ($\lambda_{em} = 355$ nm), and a large Stokes shift that was indicative of an excimer.

The absorption and fluorescence spectra of 87 and 88 resemble those of 76 (a), 75 (b), and 76 (b). Compounds 87 and 88 both exhibit red-shifted absorbance (Figure 42) and fluorescence bands relative to monomer 100 (a) (Figure 43).

![Absorption spectra of 87, 88, and 100 (a) in methylene chloride.](image)

However, while the fluorescence in 75 (a), 75 (b), 76 (a), and 76 (b) are quite similar to one another, the spectra of 87 and 88 are significantly different from one another (Figure 43). The shape of the fluorescence curve of 88 resembles that of the isolated chromophore 100 (a), containing shoulders at both higher and lower energies, while the
spectrum for 87 no longer has the pronounced shoulder to the blue of the most intense band at ~370 nm. These spectral changes suggest that the $S_3 \rightarrow S_0$ transition in 88 decreases in probability compared to that of 87.\textsuperscript{31,32} Calculations done by Brédas also support this concept because of the relaxation of selection rules governing optical transitions for the excited state and ground state of cofacial stilbenes.\textsuperscript{96,106,111,112} These results lead to the speculation that the two chains in 88 are forming an excimer in the excited state, while 87 is not.\textsuperscript{151} The work of Löwe and Weder\textsuperscript{151} on excimer formation in short chain OPV chromophores further indicates that this assumption could be right. These workers found that excimer formation led to a red-shift, and inversion of intensity, in the fluorescence bands of a cofacial short chain OPV.\textsuperscript{151} Compound 88 exhibited similar effects, with the 0,0 and 1,0 fluorescence bands changing intensity and becoming red-shifted. Compound 87, on the other hand, exhibited a fluorescence signal more typical of a non-aggregated stilbene.\textsuperscript{151} The red-shift in the absorption spectra of 87 and 88, compared to 100 (a), can be explained as resulting from either excitonic coupling between the cofacial OPVs, or the enforcement of a more rigid environment that results in more planar OPVs. If the red-shift results from excitonic coupling, then the two chains would have to be aligned in an edge-to-edge orientation relative to one another in order to attain a $J$-aggregate conformation.\textsuperscript{96,106,111,112,151} Calculations on the geometry of both 87 and 88 would help to confirm this hypothesis.
Figure 43. The normalized steady state fluorescence spectra of 87, 88, and 100 (a) in methylene chloride.

Computational work at the AM1 level for 88\textsuperscript{113} indicates that the distance between the phenyl rings on the stilbene chromophores adjacent to the benzofuran bridge (Figure 44) is \( \sim 4.5 \, \text{Å} \). This distance is within the limit for orbital interaction between neighboring stilbene molecules.\textsuperscript{96, 106, 111, 112} At the terminus of each chain, the distance separating the chains increases to \( \sim 8.8 \, \text{Å} \), suggesting the interchain orbital interactions should be reduced at greater distances from the dibenzofuran core. Evaluation of the molecular orbital interactions between the stilbene groups in 88 is currently in progress. The calculated geometry of 87\textsuperscript{113} has an inter-stilbene distance of \( \sim 4.3 \, \text{Å} \) (Figure 45) that does not change appreciably along the chain length. Brédas calculated and the INDO/S level that the ideal distance to study the effect of neighboring stilbene chromophores was
~4.0 Å. The calculations did indicate that between 4.0 and 5.0 Å the change in the electronic interaction between the cofacial stilbenes was minimal. Therefore, a model system with a separation distance between 4.0 and 5.0 Å will give experimental results on the interaction between closely associated stilbenes that fall within the ideal conditions that Brédas calculated. Calculations to determine the amount of electronic delocalization between the two stilbene groups is also in progress for this molecule.

Figure 44. The optimized geometry of 88 at the AM1 level without the tert-butyl groups attached. The arrows indicate the center to center distances in Å between the phenyl rings.
3.2.2 Steady State Absorption and Fluorescence Spectra of 95 – 97

The steady state absorption and fluorescence spectra of 95 – 97 are shown in Figures 46 and 47, respectively. The absorption spectrum of reference compound 97 shows $\lambda_{\text{max}} = 421$ nm along with a higher energy shoulder at ~374 nm. The cofacial
dimer 95 is characterized by an absorption band that is red-shifted relative to 97, with λ\text{max} = 428 nm and with the absence of any higher energy shoulder. The cofacial dimer 96 is characterized by an absorption band that is blue shifted relative to 97, with λ\text{max} = 416 nm and a higher energy shoulder at ~362 nm. The steady state fluorescence spectrum of 97 has a single emission band at λ\text{em} = 503 nm. The fluorescence spectrum of 95 is characterized by an emission band that is blue-shifted 5 nm relative to 97, to λ\text{em} = 498. The fluorescence spectrum of 96 has an emission maxima at still higher energy (λ\text{em} = 492 nm). The emission of both 95 and 96 are both slightly broader tha that of 97. The steady state fluorescent quantum yields of 95 – 96 were similar to one another and slightly smaller than 97: Φ_\text{fl} = 0.74 (95), 0.75 (96), and 0.82 (97). The absorption, fluorescence, and quantum yield data for 95 – 97 are tabulated in Table 4.
Figure 46. The normalized steady state absorption spectra of 95 – 97 in methylene chloride. The inset is an expanded view of 95 – 97 in the 400 – 500 nm range.
Figure 47. The normalized steady state fluorescence spectra of 95 – 97 in methylene chloride. The inset is an expanded view of the fluorescence spectra in the 460 nm to 530 nm region.

Table 4. The absorption, fluorescence, and quantum yield data for 95 – 97 in methylene chloride.

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*Excited at 400 nm. Quinine sulfate used as quantum yield reference.149*

The optimized geometries at the AM1 level of 95 – 97 without the alkoxy side groups indicate the OPV chains in 95 are less twisted out of plane than those of 96. The more planar geometry results in a more highly conjugated molecule which may account...
for the red shifted absorption spectrum observed in 95. 96, 106, 111, 112 The band broadening observed in the shorter wavelength region could potentially mask any possible blue-shifted shoulder that may be present in this dimer. The absorption spectrum of 96 is also broadened, and is blue-shifted relative to 97. The shift in the absorbance spectrum to higher energy in 96 is attributed to torsional rotation in 96 along the OPV vinyl bonds. Such a rotation along the OPV chain would disrupt the \( \pi \)-conjugation, causing a blue shift in both the absorption and fluorescence spectra, a phenomenon that has been observed in polymeric diaminoazobenzene chromophores. 107 The same twisting is not observed in the optimized geometry of 95 because of the close proximity of the two OPV groups, that effectively hinders chain distortion and rotation. Another factor that may account for the observed blue-shift in absorption of 96, and the broadened absorption band in 95, is torsional displacement of the OPV chains by the trialkoxy end groups. Alternatively, the trialkoxy end groups may force the OPV groups into a slipped orientation relative to one another, potentially leading to an \( H \)- or \( J \)-type aggregate arrangement between the cofacial pair of OPVs that results in the shifted absorption and fluorescence spectra. 95, 115 Such a result is supported by theory. 116 Deviations from a perfectly cofacial arrangement between two conjugated chains causes a splitting of energy levels. 95, 115 Depending on the type of aggregate formed, spectral shifts can be attributed to either aggregate state, or a mixture of the two. Spano 116 has argued that a small red-shifted emission can be attributed to \( J \)-type aggregates, but did not predict the spectral response for an \( H \)-type aggregate. Future work on 95 and 96 would be to use Spano’s theoretical model to predict the spectral response of an \( H \)-type aggregate with the already predicted \( J \)-type aggregate.
Nevertheless, the data suggests that 95 adopt a geometry that places the two chains in a side to side alignment as seen below. The result of this alignment would generate spectra that resemble a \(J\)-aggregate in solution, i.e., red-shifted absorption, broadened fluorescence spectrum, and slightly quenched fluorescence. Similar spectral results were obtained for self-assembled OPV chromophores.\(^{152}\) These OPV compound self-assembled into large helical aggregates that placed the individual chains in an edge-to-edge orientation relative to one another.\(^{152}\) Meijer\(^{152}\) studied two different aggregating systems. One system formed a highly ordered helical aggregate, while another formed a more disordered helical aggregate. The disordered helical aggregate exhibited absorption and fluorescence spectra that were very similar to 95.\(^{152}\) Compound 96 exhibited spectral features that do not match any observed for aggregates of OPV compounds. Therefore, analysis of the molecular orbitals at the AM1 level on 95 and 96 will allow for a better understanding and confirmation of alignment of the two chains in 96 and 95, respectively. It is also anticipated that these results will indicate the amount of orbital overlap present between the OPV groups 95 and 96 and this should help to explain the fluorescence quenching observed in both systems.
The quantum yield data indicates the $\Phi_{Fl}$ values for 95 and 96 are smaller than that of model OPV 97, although the reason for the decreased amount of fluorescence is presently unclear. Potential sources for the decreased $\Phi_{Fl}$ values are interchain interactions, the torsional constraints that distort the OPVs in the cofacial geometry, or energy transfer to the core. The latter is not so likely since the absorption maxima of the dibenzofuran and xanthene linker groups are both at higher energy than that of the OPV, indicating the singlet excited state energy of the linker is also higher than that of the OPVs. Fluorescence lifetime measurements will also be determined for 95 – 97 to further understand the decay pathways in each compound.

3.2.3 Steady State Absorption and Fluorescence Spectra of 98

The last cofacial system to be studied was 98 with the complementary reference compound 44. The steady state absorption and fluorescence spectra of 98 and 44 are shown in Figure 48. The absorption spectrum of reference tetramer 44 showed $\lambda_{\text{max}} = 411$ nm, with a second higher energy band at $\sim 354$ nm. The absorption spectrum of 98 is characterized by an absorption band at 410 nm, with a second higher energy and lower intensity peak to the blue at $\sim 360$ nm. The low energy band in 98 is also significantly broadened with a red-shifted tail that extends the absorption to $\sim 490$ nm. The steady state fluorescence spectrum of 98 has two peaks of almost identical intensity, with emission peaks at 482 and 501 nm. Reference compound 44 has a similar emission spectrum with peaks at 467 and 490 nm although in this compound the higher energy
band emission band at 467 nm is more intense (Figure 48). The steady state fluorescence quantum yield of 98 was $\Phi_{fl} = 0.47$, while 44 was observed to have a $\Phi_{fl} = 0.84$.

![Figure 48. The normalized steady state absorption (top) and fluorescence (bottom) spectra of 98.](image)
The absorption and fluorescence results for 98 correlate well with the theoretical work of Brédas.\textsuperscript{96, 106, 111, 112} The increase in intensity of the absorption band at 360 nm suggests a ground state interaction between the cofacial OPVs. The red-shifted emission band in the fluorescence spectrum of 98 is also consistent with Brédas predictions; specifically, excitonic coupling in this interpretation produces the shifts observed in 98.\textsuperscript{96, 106, 111, 112} The significant decrease in the fluorescence quantum yield of 98 relative to 44 (~37% decrease) suggests a pathway for ES deactivation different than enhanced IC resulting from vibrational relaxational. It is known that cofacially overlapped chromophores in the solution state experience fluorescence quenching similar to what is observed for monomers in the solid state,\textsuperscript{95, 115} indicating the close proximity of the two OPV groups may lead to the decrease in the quantum yield.

The red-shifted fluorescence and the increase in the intensity of the higher energy absorption band for 98 indicates an excimer, similar to what has been observed by Bazan with cyclophane 75 (a).\textsuperscript{96, 106, 111, 112} Extension of the OPV chain in 76 (a) eliminated the excimer-like spectral response, leading Bazan to attribute the excimer behavior of 75 (a) to energetic interactions between the paracyclophane core and the stilbene chromophores.\textsuperscript{96, 106, 111, 112} The results from 98 indicate that this assumption may have been incorrect. The spectral changes observed for 98 are not as dramatic as those found for 75 (a), but the relative shifts nonetheless indicate that an excited state excimer interaction, and to a lesser extent a ground state interaction exists for 98, despite the longer conjugation length of \( n = 4 \). The change in the fluorescence spectrum for 98, relative to 44, matches the change observed when a solution of an OPV is evaporated into a highly ordered thin film where the OPVs are oriented cofacial to one another.\textsuperscript{150 – 151}
The OPVs in these films were found to have ordered into $H$-aggregates, with an $\sim 3 – 4$ Å distance between chains, and had blue-shifted absorption spectra. The OPVs in cofacial dimer 98 have a calculated interchain distance of $\sim 4.5$ Å. The increase in the 360 nm absorption band is similar to the blue shifted absorption observed in thin films, consistent with energy delocalization between the OPV chains in 98. The broadening of the absorption band in 98 is also consistent with results in aggregated systems that have been suggested to undergo $\pi-\pi$ stacking interactions. The red-shift and change in peak intensities observed in the fluorescence spectrum of 98 are also consistent with excimer formation. However, the absorption differences in 44 and 98 can not be explained by excimer formation, and an explanation having the two chains in 98 oriented cofacial to one another in an $H$-type dimer is more plausible. Further studies exploring the excited state properties of 98 through calculations aimed at understanding spectral shifts are in progress. Additional information gained from time correlated single photon counting (TCSPC) experiments could validate the existence of a cofacial alignment of the OPV chains in 98 by giving lifetime measurements that resemble that of excimers.

3.3 Hydrazide Perylenediimide (HPDI)

Semi-conducting organic materials with high thermal stability and charge carrier mobility have found uses in nano-electronics, organic photovoltaic cells, field-effect transistors, and light emitting diodes. Using non-covalent interactions to self-assemble chromophoric systems into functional materials is an exciting area of research worldwide. Perylene diimides (PDIs) have been used extensively in these areas of research. These compounds are good electron acceptors that
can act as \( n \)-type materials for photoconductive organic devices\(^{117,118} \) and can also self-assemble into large aggregates as a result of strong intermolecular \( \pi-\pi \) interactions.\(^{125,129-130} \) The type of aggregate formed, \( H \)- or \( J \)-type, is influenced by the substituent at the cyclic imide portion of the molecule.\(^{125} \) This substituent helps to determine the bulk physical properties of the chromophore by affecting the transverse and longitudinal packing in the solid state, as well as the solution phase electronic properties such as absorption and fluorescence.\(^{125} \)

It is known that a simple hydrazide linkage can enhance molecular assemblies through hydrogen bonding.\(^{131} \) It has also been shown that substituting a perylene diimide with trialkoxy benzene groups can induce liquid crystallinity in the solid state, primarily because trialkoxy benzenes have long greasy alkyl chains that interact with one another causing the substituted PDIs to aggregate, and in the process facilitating \( \pi-\pi \) interactions between the perylene diimide cores. These cooperative effects can make ordered layers that move slightly relative to one another due to the presence of the alkyl chains.\(^{125} \) Our group has postulated that using a hydrazide linking group between a trialkoxybenzene and the PDI core could influence the one, and possibly two, dimensional packing of the PDIs in the solid and solution state. The work presented in this section describes the results of using hydrazide linking groups in conjunction with trialkoxy benzene substituted PDI.

Hydrazide perylene diimide containing compounds 101 - 103 were synthesized as shown in Scheme 28. Compounds 106 – 107 were synthesized by the substitution reaction of methyl 3,4,5-trihydroxybenzoate (104) with a \( C_8-\text{C}_{12} \) alkylbromide in the presence of potassium carbonate as base, forming 105 (a-c) in 80 – 82% yields.
Compounds 105 (a-c) were then reacted with hydrazine in ethanol at reflux to produce 106 – 107 in 90 – 92% yields. The condensation of hydrazides 106 - 108 with perylene tetracarboxylic dianhydride (PCTDA) in quinoline with zinc acetate as a Lewis acid catalyst produced 101 – 103 in ~20% yields (Scheme 28). Compound 112 was prepared in order to illustrate the photophysical properties of a non-aggregated PDI chromophore in various solvents, and was synthesized in 32% yield (Scheme 29). In this scheme, reaction of the trisubstituted benzyl bromide 109 with cyanomethanaminium chloride produced 110, which was subsequently reduced with hydrogen gas in the presence of 10% palladium on carbon to produce amine 111 in a quantitative yield. The condensation of 111 with perylene tetracarboxylic dianhydride (PCTDA) in quinoline with zinc acetate as a Lewis acid catalyst produced 112 (Scheme 29). PDI 112 contains the same number of atoms between the cyclic imide position and the trialkoxybenzene unit, however, the added bulkiness of having two trialkoxybenzene units, together with not having the hydrazide hydrogen bonding motif, should inhibit aggregation in solution. All of these compounds were purified by silica gel column chromatography using 5% methanol/dichloromethane as the eluant.

The $^1$H NMR spectra of compounds 101 and 112 are shown in Figures 49 and 50. PDI 101 exhibits a broadening at the 9,10-bay position peaks ($\delta$ 8.09 – 8.90 ppm) of the perylenediimide core (Figure 49) indicative of aggregation. This result contrasts with compound 112, where the 9,10-bay protons appear as a sharp peak at $\delta$ 8.616 ppm (Figure 50).
Scheme 28. Synthetic scheme for the preparation of PDIs 101 – 103.
Scheme 29. The synthetic scheme for the preparation of PDI 112.
Figure 49. The $^1$H NMR spectrum of 101 in CDCl$_3$. The 9,10 bay positions (a) in this spectrum are broadened and split into two peaks.\textsuperscript{148}
Figure 50. The $^1$H NMR spectrum of compound 112 in CDCl$_3$. The protons for the 9,10 bay positions (a) of the PDI are at 8.63 ppm and are a singlet.$^{148}$

The solid state properties of 101 were studied using scanning electron microscopy (SEM) imaging and wide-angle x-ray diffraction (XRD). The solid state samples used in these experiments were prepared in two ways. Compound 101 was divided into two samples, with one sample undergoing a slow precipitation from a mixed solvent system (methanol/methylene chloride). The other sample was dissolved into dichloromethane and placed under a steady stream of nitrogen to quickly evaporate the solvent. The first approach was used in order to form a more ordered solid-state structure, because of the slower evaporation of the solution under these conditions, as well as the propensity of the PDI to precipitate from methanol. The second sample, in methylene chloride, would in
all likelihood be disordered because of the relatively quick evaporation of
dichloromethane. These two methods produced two different colored samples, \textbf{101 purple} and \textbf{101 red}, which had identical \textsuperscript{1}H NMR spectra and mass spectral results. The solid state experimental results, along with the steady state absorption and fluorescence measurements, yielded different results for \textbf{101 purple} and \textbf{101 red}. We therefore decided to study \textbf{101 purple} and \textbf{101 red} to determine if they are two polymorphs of the same compound.

The SEM images of \textbf{101 purple} and \textbf{101 red} are shown in Figures 51 and 52, respectively. PDI \textbf{101 purple} formed long ribbons with an average length of 50 μm. PDI \textbf{101 red}, on the other hand, was significantly more disordered, and lacked the ribbon-like structures observed for \textbf{101 purple} and resembled a sheet. These results indicate a greater degree of order in the slowly precipitated \textbf{101 purple}. This gives order on the micron scale with the hope that larger scale ordering can also be obtained from this compound. To further understand the degree of ordering in the solid state of \textbf{101 purple} and \textbf{101 red}, X-ray diffraction studies were conducted.
Figure 51. SEM image of 101 purple indicating long ribbons. The average length of the ribbons was found to be ~50 μm.
Figure 52. SEM image of 101 red indicating a sheet morphology and the absence of ribbons.\textsuperscript{148}

Wide angle X-ray diffraction (Figure 53) was performed to observe the degree of order and liquid crystallinity present in the solid state of 101 purple and 101 red. Compound 101 purple (Figure 53) exhibited a diffuse halo in the wide angle region with a $d$ spacing of 3.99 Å that corresponds to a disordered alkyl region.\textsuperscript{95, 115} An additional sharp peak with a $d$ spacing of 3.31 Å indicates a higher degree of order in this compound.\textsuperscript{95, 115} These results correspond with closely spaced PDIs that exhibit an
ordered hexagonal columnar mesophase.\textsuperscript{95, 115} The 3.31 Å $d$ spacing in 101 purple has been observed for other PDI chromophores in the literature that are known to aggregate.\textsuperscript{95,132} An explanation for the closer contact distance could be the result of H-bonding between the neighboring amide bonds, as indicated in Figure 49 by a shift in the NMR spectrum for the amide bond from a predicted value of 9.2 ppm to 8.9 ppm. The wide angle X-ray diffraction pattern of 101 red (Figure 53) had a longer $d$ spacing of ~3.5 Å that is representative of $\pi$-$\pi$ stacking in PDI chromophores.\textsuperscript{133} The presence of a diffuse halo in the 4.32 Å region is consistent with disordered alkyl chains.\textsuperscript{133} The small angle region of both compounds indicates the edge-to-edge distance between two PDI molecules in the longitudinal and transverse directions.\textsuperscript{133} The spacing observed for 101 purple was found to be 21.65 Å, while that of 101 red was found to be 31.52 Å. These results indicate that 101 purple has a higher degree of packing in the solid state between interacting PDI molecules as observed in other PDI systems.\textsuperscript{133} The XRD pattern for both 101 purple and 101 red are consistent with aggregated liquid crystalline perylene diimides.\textsuperscript{133, 157} The crystal structure of 101 purple and 101 red may resemble a rhombus arrangement (shown below) due to the similarity in XRD data compared to literature values on perylene diimide compounds.\textsuperscript{158–160} Characteristic patterns in the XRD with
peaks at $2\theta = \sim 10, 20, \text{and} 25$ are indicative of this type of crystal arrangement. The XRD data for \textbf{101 purple} shows only two out of the three matching peak intensities for a rhombus crystal packing, but broadening of the spectrum between the $2\theta = 9 - 18$ region could mask the peak intensity at $2\theta = 10$.\textsuperscript{158} The XRD data for \textbf{101 red} shows all three indicative intensities along with matching other lower intensity bands as well.\textsuperscript{158} The fluorescence data of rhombus perylene diimide crystals matched exactly with the fluorescence data of both \textbf{101 purple} and \textbf{101 red}. The fluorescence spectra of the rhombus perylene crystals exhibited the same spectral shifts and band intensities of both \textbf{101 purple} and \textbf{101 red}.\textsuperscript{158} To further understand the nature of the aggregation of \textbf{101 purple} and \textbf{101 red}, steady state absorption and fluorescence measurements were conducted to explore the nature of the aggregation ($J$- or $H$-type) in solution.
Figure 53. The XRD data for 101 purple (top) and 101 red (bottom).\textsuperscript{148}
The absorption spectrum of 101 purple in toluene\textsuperscript{148} (Figure 54) showed the characteristic PDI absorption bands,\textsuperscript{95} with the 0 → 0 band at $\lambda_0 \rightarrow 0 = 528$ nm, the 0 → 1 band at $\lambda_0 \rightarrow 1 = 496$ nm, and a high energy 0 → 2 band at $\lambda_0 \rightarrow 2 = 459$ nm. The absorption spectrum of 101 red in toluene (Figure 54) was identical to that of 101 purple. The steady state absorption spectra of 101 purple and 101 red in heptane\textsuperscript{148} are shown in Figure 55. Compound 101 purple in heptane has a 0 → 1 band at $\lambda_0 \rightarrow 1 = 496$ nm, a shoulder at ~543 nm that is attributed to the 0 → 0 band, and the 0 → 2 band at ~459 nm. In addition, the absorption spectrum of 101 red in heptane is no longer exactly the same as that of 101 purple, with a 0 → 1 band at $\lambda_0 \rightarrow 1 = 493$ nm, along with a 0 → 0 band at ~535 nm and the 0 → 2 band at ~477 nm. The shape of the absorption spectrum of 101 purple was also slightly broader than 101 red in heptane. To determine that these results were not solely the result of heptane, the steady state absorption spectrum of 112 was acquired in heptane (Figure 56). This PDI exhibited a non-aggregated absorption spectrum with the 0 → 0 band at $\lambda_0 \rightarrow 0 = 528$ nm, along with higher energy 0 → 1 and 0 → 2 bands at ~490 nm and ~459 nm, respectively.

The fluorescence spectrum of 101 purple (Figure 57) in toluene\textsuperscript{148} is well defined, with the most intense emission band at 538 nm, as well as lower energy bands at ~579 nm and ~630 nm. The steady state fluorescence spectrum of 101 red (Figure 57) in toluene was identical to that of 101 purple. The fluorescence spectra of 101 red and 101 purple (Figure 58) in heptane were different from one another and from the spectra in toluene. The fluorescence spectrum of 101 purple in heptane exhibited a red-shifted maximum at $\lambda_{em} = 671$ nm along with a less intense and higher energy shoulder at ~644 nm, while 101 red had a red-shifted maximum at $\lambda_{em} = 680$ nm and a shoulder at ~644
nm. Both fluorescence spectra were significantly broadened from the results in toluene, with the spectrum of 101 red broader than 101 purple with a low energy tail that trails out to ~800 nm. The fluorescence spectrum of 112 in heptane is shown in Figure 59, and is identical to those of 101 red and 101 purple in toluene. The quantum yields of 101 purple and 101 red were recorded in toluene. PDI 101 purple has a $\Phi_{fl} = 0.73$, while 101 red has a $\Phi_{fl} = 0.67$. The fluorescence for 101 purple and 101 red in heptane are nearly quenched (Figure 58), thereby making the quantum yields too low for an accurate measurement. The quantum yield of 112 was $\Phi_{fl} = 0.89$ in heptane. The spectra in heptane are consistent with aggregation of PDIs.95

Changes in absorption and fluorescence spectra of PDI compounds in certain solvents have been correlated with aggregation, i.e., $H$- or $J$-type.95 These shifts due to aggregation have been explained by the point dipole model of Kasha.153–156 This model predicts that a red or blue shift observed in an absorption spectrum results from the orientation of the transition dipoles of the molecules involved along with the angle of the center-to-center vector of the aggregated molecules.153–156 If the transition dipoles are not completely parallel then a red and blue shifted absorption should be observed for the system under study.153–156 The spectral features of 101 purple and 101 red resemble a previously studied perylene diimide aggregate system that had the perylene diimide cores stacked on top of each other with a 30° angle between the transition dipoles.153 They determined that their system was an $H$-type aggregate. Conversely, $J$-type aggregates are characterized by absorption and fluorescence spectra that are both red-shifted compared to the non-aggregated spectra of the PDI under study. $J$-aggregates are also known to exhibit measurable fluorescence quantum yields.95 $H$-type aggregates, on the other hand,
are characterized by blue-shifted absorption spectra, red-shifted fluorescence spectra, and significantly quenched fluorescence. The absorption and fluorescence changes observed in 101 purple and 101 red indicate H-type aggregation in heptane. The spectral results are summarized in Table 5.

![Normalized steady state absorption spectra of 101 purple and 101 red in toluene.](image)

Figure 54. The normalized steady state absorption spectra of 101 purple and 101 red in toluene.148
Figure 55. The normalized steady state absorption spectra of **101 purple** and **101 red** in heptane.\textsuperscript{148}
Figure 56. The normalized steady state absorption spectrum of 112 in heptane. 148
Figure 57. The normalized steady state fluorescence spectra of 101 purple and 101 red in toluene.148
Figure 58. The normalized steady state fluorescence spectra of 101 purple and 101 red in heptane. 

\[ \text{Normalized fluorescence spectrum of 101 purple and 101 red in heptane.} \]
Figure 59. The normalized steady state fluorescence of 112 in heptane.\textsuperscript{148}
Table 5. Absorption and emission data for 101 purple and red in toluene and heptane.148

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<td>Aggregate</td>
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<td>Aggregate</td>
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*a* Excited at 450 nm.  
*b* Quantum yields (Φ_Fl) were determined using Quinine Sulfate as a standard.149

Binding constants associated with aggregation yield information regarding the strength of association between neighboring chromophores. Our group148 explored two different methods for determining the binding constant of both 101 purple and 101 red. The first method involved temperature dependent steady state absorption spectroscopy. Increasing the temperature of an aggregated solution often results in dissociation of the aggregate, with the spectra changing from aggregated to non-aggregated. The isobestic points in the spectra can then be used to plot the changes in concentration as a function of temperature, and can be fit using non-linear regression to obtain a binding constant.112, 134

However, absorption experiments on 101 purple and 101 red in heptane (b.p. 98 °C), at temperatures as high as 70 °C did not result in aggregate dissociation. Accordingly, a
second technique, using NMR spectroscopy, was used to determine the binding constant. In this set of experiments, the chemical shift of the amide N-H absorption was examined as a function of added CD$_3$OD used to hydrogen bond in place of the hydrazines. These experiments were also inconclusive, as the reproducibility of the results were not reliable because of the exchange of the amide hydrogen with the CD$_3$OD (as opposed to the desired monitoring of the shifting of the N-H absorption). Further studies aimed at obtaining a binding constant for self-assembly of 101 purple and 101 red are currently underway with using solvent mixtures as a function of aggregate dissociation. Würthner recently published work on an amide linked perylenediimide chromophore having switchable $J$- or $H$-type aggregation, the nature of which depended on the length of the alkyl substituent on the trialkoxybenzene groups.\textsuperscript{112(a)} In this work, the alkoxy side chain was shown to influence the nature of the aggregate. Chiral alkoxy groups, or achiral alkoxy groups having one methoxy group, were shown to prefer a $J$-type aggregate. This aggregate had the characteristic bathochromic shift in the absorption spectrum, along with a red-shifted absorption band at 621 nm. If the alkoxy chains were achiral or non-methyl groups, then $H$-type aggregates were found to form. These aggregated structures were characterized by a hypsochromic shift of the absorption band, accompanied by a the appearance of a weak band at 555 nm.\textsuperscript{112(a)} The spectral properties of Würthners $H$-type aggregates resemble the spectral properties observed for 101 red and 101 purple, indicating an $H$-type aggregation state. Another group\textsuperscript{153} studied the spectral changes incurred in certain $H$-type aggregates of perylene diimides. In this work, the absorption spectrum was found to lose all fine vibrational features, and undergo a change in the intensity pattern, with the blue peak becoming more intense. The band to
the red of this was found to shift to lower energy.\textsuperscript{153} They also performed molecular mechanics calculations on their aggregated perylene diimide system to confirm the nearly cofacial arrangement of the PDI chromophores. Those results confirmed their initial deduction about the cofacial alignment obtained from the spectral shifts observed in the absorption spectrum.\textsuperscript{153} Their results nearly match the results obtained for \textbf{101 purple} and \textbf{101 red}. This further piece of evidence leads to the conclusion that \textbf{101 purple} and \textbf{101 red} are forming $H$-aggregates in solution.

Hydrazide linked perylenediimdes \textbf{101 - 103} form stable $H$-type aggregates capable of forming highly ordered structures in the solid state. Further studies on the stability and macromolecular structures of these aggregates through calculations, the photophysical properties of thin films from spin-cast solutions of \textbf{101 purple}, as well as lifetime measurements of the monomer and aggregate species are on-going areas of research in our group.

3.4 Self-Assembled Multi-Chromophoric Perylene Diimide and Pyromellitimide

The utilization of non-covalent interactions to direct the self-assembly of multi-chromophoric materials is an active area of research.\textsuperscript{84–87} The self-assembly of such multi-chromophoric systems requires careful planning, in order to allow for site-specific alignment of various chromophores without allowing competing interactions to inhibit the degree of assembly. In Chapter II, recent efforts in this field to self-assemble PDIs, OPVs, and porphyrins were explored. The goal of this project was to use self-assembly to align three different chromophores at specific regions in space to make triad \textbf{113} (Figure 60), in order to facilitate donor-acceptor systems for artificial photosynthetic
applications. The specificity of the self assembly in these molecules is controlled by the non-competitive site-specific nature of the self-assembly techniques employed.
Figure 60. Self-assembled perylene diimide multichromophoric 113. In principle, the trimeric OPV self assembles with the uracil component of the PDI via triple hydrogen bonding, while the zinc porphyrin axially ligates to the pendant pyridine of the PDI, thereby generating a site-specific multichromophoric system.
The chromophores chosen for this study were a perylene diimide, trimeric oligo
\((p\text{-phenylenevinylene})\) and zinc tetraaryl porphyrin (Figure 61). Appending pyridine and
uracil groups to a PDI is expected to lead to the trimeric OPV hydrogen bonding with the
uracil (Figure 60). At the same time, the pyridine should axially ligate with the zinc
porphyrin 115 as shown in Figure 60. The target PDI 117, together with standard
samples 117 – 119 are shown in Figure 62. However, the synthesis of 118 and 119
revealed severe solubility problems that limited the utility and potential for self-assembly
of these systems. The main source of insolubility in these materials was thought to come
from the high degree of \(\pi-\pi\) stacking that occurs in a planar perylene diimide. To
overcome this problem the central unit in the system was changed to the pyromellitimide
(PI) group shown in Figure 63. In this system, the goal was to use the same trimeric OPV
and zinc porphyrin, assembled via hydrogen bonding with a pendant uracil group and
axial ligation with a pendant pyridine. The central core group, as stated earlier, is the
appropriately functionalized PI. The PI would function as the final electron acceptor in
this self-assembled system, the same role the perylene diimide was to perform in the
structure in Figure 60. The end result of photoexcitation of the trimeric OPV chromphore
would be photo-induced electron transfer to the zinc porphyrin followed by electron
transfer to the PI (Scheme 30). The final target complexes as well as the reference
compounds for this project are shown in Figure 64. The syntheses of core-containing
complexes (118 – 122) are explored below.
Figure 61. Chromophores used in the self-assembled perylene diimide complex 113. In complex 113, the zinc porphyrin 115 would self-assemble by axial ligation to a pendant pyridine, while OPV 116 would hydrogen bond with the uracil group.
Figure 62. The structures of model compounds 120 – 122.
Figure 63. The final pyromellitimide containing self-assembled multi-chromophoric complex 114. This complex consists of a PI core, and OPV self-assembled by hydrogen bonding to the pendent uracil group on the core, and a zinc porphyrin self-assembled by axial ligation of the metallo-porphyrin with the pendant pyridine.
Scheme 30. This illustrates the cascade of electron transfer events that should occur in 114.

Figure 64. Core PI group 120 bearing a pendant uracil and pyridine groups, and model compound 121 capable of hydrogen bonding to the hydrogen bond acceptor 116.

3.4.1 Synthesis of Self-Assembled Multichromophoric Systems
Compound 118 was synthesized as shown in Scheme 31. In the first step of the synthesis, 3-nitrobenzoyl chloride was reacted with 4-aminopyridine in dry THF and in the presence of triethylamine to produce 122 in 86% yield. Compound 122 was converted to amine 123 by catalytic hydrogenation with 3 atm of H₂ in the presence of 10% Pd/C in a methanol/1,4-dioxane solvent mixture. After 16 h at 3 atm, the reaction mixture was poured through a layer of celite to remove the palladium catalyst and upon removal of the solvent produced 123 in 97% yield. The imidization of 123 with PTCDA was carried out in quinoline in the presence of zinc acetate at 160 °C for 16 h. This reaction was poured into aqueous methanol producing a violet precipitate that was isolated by filtration and washed with copious amounts of methanol. This crude material was stirred with 2M Na₂CO₃ to remove any residual PTCDA and recrystallized with DMF to produce compound 118. This compound proved to be quite insoluble in most organic solvents even upon heating. The ¹H NMR was taken in d-DMSO with a microliter amount of trifluoroacetic acid (TFA). The TFA disrupts the aggregation of 118 allowing for its dissolution in the d-DMSO for analysis. However, the concentration of TFA had to be kept low in order to avoid distortion of the NMR signal. Nevertheless, the mass spectral results indicate the parent ion peak at 783.29 m/z, indicating the presence of 118.
Scheme 31. The synthetic scheme for 118.

The synthesis of 119 is outlined in Scheme 32. The reaction of 3-nitrobenzoyl chloride with 5-aminouracil in THF at reflux for 1 h produces upon cooling a precipitate. This crude precipitate is collected by vacuum filtration and washed with ethanol and ether to produce 124 in 76% yield. Reduction of 124 was done by reacting with granular tin in the presence of concentrated hydrochloric acid to produce 125 in 60% yield. The imidization of 125 occurred in the same way as 123, but instead of quenching the reaction with aqueous methanol the reaction was instead poured into 1M HCl. The crude precipitate was vacuum filtered and washed with additional 1M HCl and methanol before stirring with 2M Na₂CO₃ to remove residual PTCDA. The recrystallization of crude 119 was attempted with DMF. This material again proved to be insoluble like 118. The ¹H NMR of 119 was conducted in a similar manner as 118. The mass spectral data on 119 is being conducted.
Scheme 32. The synthetic scheme to 119.

The synthesis of the PI self-assembled system (Figure 52) was conducted as shown in Scheme 33. Benzene tetracarboxylic acid 126 was reacted with leucine in acetic acid at reflux for 16 h producing 127 upon cooling and washing the solid product with water. Compound 127 was reacted with thionyl chloride overnight at reflux to produce 128, which was reacted with 1 equivalent of 5-aminouracil producing 129. Compound 129 was DCC coupled with 1-citronellol to produce 120.

The synthesis of 121 is outlined in Scheme 33. Compound 129 was reacted with 1 equivalent of 4-aminopyridine in DMF in the presence of DCC and 4-DMAP. When the reaction was complete, water was added, and the precipitate was filtered and washed with 95% ethanol. The resulting white solid was dried. The material proved to be insoluble like 118. The $^1$H NMR of 120 was conducted in DMSO and the mass spectral results are currently being collected.
Scheme 33. (i) AcOH, reflux; (ii) Thionyl chloride, reflux; (iii) 5-aminouracil, THF, NEt₃; (iv) DCC, methylene chloride, citronellol; (v) DCC, DMF, 4-aminopyridine.

The synthesis of these self-assembled systems has been described. Further studies aimed at exploring the binding constants, absorption and fluorescence properties as well as the rates of electron transfer are ongoing projects. Compounds 118 and 119 pose particular problems due to their lack of solubility in conventional self-assembling solvents, i.e. solvents of low polarity; therefore synthetic modification of the perylene diimide core may be necessary to increase solubility of 118 and 119. The 3,4:9,10 positions of the perylene could be brominated and reacted with phenol undergoing an S_NAr reaction generating a system with substantially increased solubility.
CHAPTER IV
EXPERIMENTAL

General Methods: All reactions were run under a nitrogen atmosphere unless otherwise indicated. THF was dried over the Na-benzophenone ketyl. Methylene chloride was distilled from calcium hydride and stored over 4 Å molecular sieves. DMF was passed through an alumina column and collected over 4 Å molecular sieves. Triethyl amine (TEA) was distilled from CaH₂ prior to use. All other reagents were used as received. Flash chromatography was performed on silica gel (230 – 400 mesh), neutral alumina (60 – 325 mesh) or basic alumina (60 – 325 mesh). All melting points were taken using a Thomas-Hoover capillary melting point apparatus and are uncorrected. Proton and carbon nuclear magnetic resonance spectra were recorded with a 300 MHz and 75 MHz Varian Spectrometer, respectively. All spectra were recorded in CDCl₃ and referenced to the residual CHCl₃ peak at 7.27 ppm. The abbreviations utilized to denote the multiplicity are s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sex (sextet), and m (multiplet). IR spectra were recorded on a Win-Bomem MB100 spectrometer. High resolution mass spectrometry experiments were performed on an ESI-TOF mass 134 spectrometer equipped with an orthogonal electrospray source (Z-spray) operated in positive ion mode. Sodium iodide was used for mass calibration for a calibration range of m/z 100-2000. Optimal ESI conditions were found using a capillary voltage 3000 V, a
source temperature of 110 °C, and a cone voltage of 40 V. The ESI gas was nitrogen and all ions transmitted into the pusher region of the TOF analyzer were scanned over m/z 700-1200 with a 1s integration time. Data was acquired in continuum mode until acceptable averaged data was obtained. High resolution electrospray ionization measurements were done at the Mass Spectrometry and Proteomics Facility at The Ohio State University or at the Mass Spectrometry Facility at The University of Akron.

Absorption spectra were recorded on a Shimadzu Model UV-1601 spectrophotometer. Steady-state fluorescence spectra were acquired on an ISA Jobin Yvon-SPEX Fluorolog 3-22 fluorometer having dual input and output monochrometers and are uncorrected. Fluorescence spectra were collected using argon-saturated solutions in S/R mode to correct for changes in the lamp output intensity.

From the steady state absorption and fluorescence data obtained, energies of the excited states were calculated from experimental data by averaging the energy of the longest wavelength absorption and the energy of the shortest wavelength emission.

Samples for the transient absorption experiments were prepared with optical densities less than 0.1 at the excitation wavelength to increase the intensity signal and used a 2 mm path length cell. Time-resolved fluorescence experiments were performed using the time-correlated single-photon counting (TCSPC) technique. The experimental apparatus utilizes the pulses from a Coherent 700 dye laser pumped by the 527 nm output of ~5 ps (FWHM) Nd:YLF Quantronix 4217ML mode-locked 76 MHz laser. The fluorescence signals were detected at 54.7° with an emission polarizer and depolarizer, using a Hamamatsu R3809U-51 red-sensitive microchannel plate detector. Data collection and analysis were accomplished using an Edinburgh Instruments data collection system. All
experiments were run under argon-saturated conditions. High resolution electrospray ionization measurements were done at the Mass Spectrometry and Proteomics Facility at The Ohio State University and The University of Akron. Steady state absorption, fluorescence, and quantum yield measurements on 101 purple and 101 red were performed by Mrs. Sarah Phillips. Compounds 81 – 86 were prepared by Mr. Wongwit Wongwitwichote.

The $^1$H and $^{13}$C NMR data of (nitrobenzyl)triphenylphosphonium salt, 1-nitro-4-vinylbenzene$^{135}$, diethyl[4-(diethoxymethyl)phenyl]phosphonate$^{136}$ diethyl 4-methoxybenzylphosphonate (59)$^{137}$, 2,5-bis(bromomethyl)-1,4-di(octyloxy)benzene, and 1,4bis(octyloxy)-2-(E)-styryl-5-((E)-4-(E)-styrylstyryl)benzene$^{139}$ and 1,4-bis(octyloxy)diethyl 3,4,5-tris(decyloxy)benzylphosphonate, 3-nitro-N-(4-pyridinyl)benzamide (122)$^{142}$ and 3-amino-N-(4-pyridinyl)benzamide$^{142}$ all matched the reported literature values.

1,4-Bis(methoxymethyl)-2,5-bis(octyloxy)benzene (42): 2,5-Bis(bromomethyl)-1,4-dioctyloxybenzene (13.7 g, 26.3 mmol) was added to a solution of sodium methoxide (7.12 g, 0.13 mol) in dry methanol (120 mL) in a round-bottomed flask. This solution was brought to reflux for 6 h. The solution was then cooled to room temperature and diluted with water (300 mL). The organic phase was extracted with ether (3 × 100 mL) and dried over sodium sulfate. The solvent was removed under vacuum and the resulting solid was recrystallized with 95% EtOH to produce 42 (10.3 g, 93%) as a white solid (M.p. 62-63 °C). $^1$H NMR: (CDCl$_3$, 300 MHz) δ (ppm): 0.87-1.78 (m, 15H), 3.43 (s, 6 H), 3.93-3.97 (t, 4H, $J$ = 6 Hz), 4.50 (s, 4H), 6.92 (s, 2H). $^{13}$C NMR: (CDCl$_3$, 75 MHz),
4-(Methoxymethyl)-2,5-bis(octyloxy)benzaldehyde (43): To a flame dried 3-neck flask was added 1,4-Bis(methoxymethyl)-2,5-bis(octyloxy)benzene (42) (3.00 g, 7.10 mmol) in a 0.02 M solution of methylene chloride and water (10:1). To this vigorously stirred solution was added DDQ (2.26 g, 9.97 mmol), and allowed to stir for 13 min. A saturated solution of sodium bicarbonate (100 mL), was then added and the organic layer was extracted with sat. NaHCO₃ (3 × 100 mL), brine (3 × 100 mL), and then dried with sodium sulfate. The solvent was removed under reduced pressure and the resulting solid was recrystallized with 95% EtOH and filtered to yield 43 (2.77 g, 96%) as a yellow solid (M.p. 38-39 °C). ¹H NMR: (CDCl₃, 300 MHz) δ (ppm): 0.87-1.85 (m, 15H), 3.50 (s, 3H), 3.95-3.99 (t, 2H, J = 6 Hz), 4.05-4.10 (t, 2H, J = 6 Hz), 7.11 (s, 1H), 7.26 (s, 1H), 10.46 (s, 1H). ¹³C NMR: (CDCl₃, 75 MHz), δ (ppm): 14.38, 22.92, 26.33, 29.49, 29.57, 32.07, 59.16, 68.77, 69.44, 108.68, 112.48, 123.86, 156.81, 189.87. m/z 429.2976; calcd: C₂₅H₄₂O₄: 429.2981.

(E) 1-(Bromostyryl)-2,5-bis(octyloxy)benzaldehyde (57(b)): To a flame dried 3-neck flask equipped with a dropping funnel and condenser was added diethyl 4-bromobenzylphosphonate (2.48 g, 7.70 mmol) under a nitrogen atmosphere. Dry THF (48.0 mL), and potassium tert-butoxide (1.78 g, 1.58 mmol) were added. The solution was allowed to stir at room temperature for 10 min. A solution of 4-(methoxymethyl)-2,5-bis(octyloxy)benzaldehyde (3.00 g, 7.39 mmol) in dry THF (8.60 mL) was added dropwise via a canula over a 5 min interval. The solution was allowed to stir for 12 h. The solution was then diluted with ether (50.0 mL), washed with water (200 mL), brine
(200 mL), and the organic phase was dried with sodium sulfate. The solvent was removed and the resulting crude material was run through a short plug of silica with methylene chloride as the solvent. The solvent was then removed and the crude material was dissolved in a 0.07 M solution of methylene chloride and water (10:1). To this solution was added DDQ (2.00 g, 8.83 mmol) and the mixture was stirred at room temperature for 24 h, before being quenched with a sat. NaHCO₃ soln. (200 mL), and washed with brine (200 mL). The solvent was removed under reduced pressure and the resulting material was purified by silica gel chromatography using (95:5) hexane/ethyl acetate as the eluent. (E) 1-(1-Bromostyryl)-2,5-bis(octyloxy)benzaldehyde (57(b)) was isolated in 69% overall yield (2.40g) as a light yellow solid (M.p. 46-48 °C) ¹H NMR: (CDCl₃, 300 MHz) δ (ppm): 0.89-1.85 (m, 15H), 4.02-4.06 (t, 2H, J = 6 Hz), 4.09-4.13 (t, 2H, J = 7 Hz), 7.15-7.52 (m, 8H), 10.46 (s, 1H). ¹³C NMR: (CDCl₃, 75 MHz), δ (ppm): 14.35, 22.90, 26.34, 29.48, 29.57, 32.03, 69.34, 69.46, 107.72, 110.36, 110.89, 128.53, 131.18, 132.12, 134.01, 150.98, 156.38, 189.42. m/z 565.2305; calcd: C₃₁H₄₃BrO₃: 565.2293.

**General Horner-Wadsworth Emmons Couplings (51 – 54, 61 – 63, and 73):** To a flame dried 3-neck flask equipped with a dropping funnel and condenser was added substituted phosphonate (1.20 equiv) under a nitrogen atmosphere. Dry THF (2.00 mL), and potassium tert-butoxide (1.50 equiv) were added and the solution was allowed to stir at room temperature for 10 min. A solution of 57(b) (0.11g, 0.20 mmol) in dry THF (2.00 mL) was added dropwise over a 5 min interval at which time the solution was stirred at room temperature for 12 h. The solution was diluted with ether (20.0 mL), washed with water (20.0 mL), brine (20.0 mL), and the organic phase was dried with
sodium sulfate. The solvent was removed under reduced pressure to give a crude solid that was recrystallized with 95% EtOH. The solid product was filtered and the mother liquor was concentrated down under reduced pressure and dissolved in toluene (4.00 mL). To this solution was added a catalytic amount of iodine and was brought to reflux for 12 h. Upon cooling to room temperature the solution was washed with brine (50.0 mL), water (50.0 mL), and sat. NaHCO₃ (50.0 mL). The organic phase was dried with sodium sulfate and concentrated down to give a crude material that was recrystallized with 95% EtOH to give a second crop of product. The overall yield of 1-((E)-4-bromostyryl)-2,5-bis(octyloxy)-4-(E)-styrylbenzene (61) was 0.102 g (82%).

1-((E)-4-Bromostyryl)-2,5-bis(octyloxy)-4-(E)-styrylbenzene (61): Isolated in 82% yield (0.102 g) as yellow solid (M.p. 88-90 °C). ¹H NMR: (CDCl₃, 300 MHz) δ (ppm): 0.87-1.92 (m, 30H), 4.03-4.09 (t, 4H, J = 7 Hz), 7.05-7.56 (m, 15H). ¹³C NMR: (CDCl₃, 75 MHz), δ (ppm): 14.36, 22.95, 26.59, 29.59, 29.70, 29.81, 32.10, 69.93, 111.07, 123.83, 126.78, 127.24, 127.64, 128.89, 129.06, 138.27, 151.42.

1-((E)-4-Bromostyryl)-4-((E)-4-methoxystyryl)-2,5-bis(octyloxy)benzene (62): Isolated in 84% yield as a yellowish-orange solid (0.112 g) (M.p. 104-106 °C). ¹H NMR: (CDCl₃, 300 MHz) δ (ppm): 0.87-1.92 (m, 30H), 3.85 (s, 3H), 4.03-4.08 (t, 4H, J = 6 Hz), 6.90-7.49 (m, 14H). ¹³C NMR: (CDCl₃, 75 MHz), δ (ppm): 14.36, 22.95, 26.59, 29.59, 29.70, 29.81, 32.10, 69.93, 111.07, 123.03, 126.78, 127.24, 127.65, 128.89, 129.06, 138.27, 151.42.

1-((E)-4-Bromostyryl)-4-((E)-4-nitrostyryl)-2,5-bis(octyloxy)benzene (63): Isolated in 74% yield as a reddish solid (0.135 g) Yield: 0.135 (M.p. 113-114 °C). ¹H NMR: (CDCl₃, 300 MHz) δ (ppm): 0.87-1.91 (m, 30H), 4.04-4.11 (t, 4H, J = 7 Hz), 7.08-7.67
(m, 12H), 8.22-8.25 (d, 2H, J = 9 Hz). $^{13}$C NMR: (CDCl$_3$, 75 MHz), δ (ppm): 14.36, 22.94, 26.55, 29.58, 29.71, 32.08, 69.71, 69.82, 110.78, 111.20, 121.58, 124.28, 124.41, 125.97, 126.68, 127.00, 128.16, 128.29, 128.47, 128.58, 132.05, 136.98, 144.98, 146.80, 151.32, 151.83.

1,4-bis(octyloxy)-2-(E)-styryl-5-((E)-4-((E)-4-(E)-styrylstyryl)styryl)benzene (51): Isolated in 76% yield (0.125 g) as a yellow solid. $^1$H NMR: (CDCl$_3$, 300 MHz) δ (ppm): 0.90 – 1.89 (m, 30H), 4.06 – 4.09 (t, 4H, J = 6 Hz), 7.15 – 7.54 (m, 28H). $^{13}$C NMR: (CDCl$_3$, 75 MHz) δ (ppm): 14.38, 22.96, 26.58, 29.60, 29.70, 29.79, 32.10, 69.88, 100.26, 110.90, 126.78, 127.13, 128.55, 128.90, 128.97, 151.41. m/z 742.794; calc: C$_{54}$H$_{62}$O$_2$: 742.475.

1-((E)-4-methoxystyryl)-2,5-bis(octyloxy)-4-((E)-4-((E)-4-(E)-styrylstyryl)styryl)benzene (52): Isolated in 74% yield as a yellow solid (0.142 g). $^1$H NMR: (CDCl$_3$, 300 MHz) δ (ppm): 0.90 – 1.91 (m, 30H), 3.85 (s, 3H), 4.04 – 4.09 (t, 4H, J = 7 Hz), 6.90 – 6.93 (d, 2H, J = 9 Hz), 7.14 – 7.55 (m, 27H). $^{13}$C NMR: (CDCl$_3$, 75 MHz) δ (ppm): 14.40, 22.96, 26.59, 29.60, 29.71, 29.81, 32.11, 55.57, 69.87, 110.71, 110.91, 114.37, 121.67, 123.78, 126.70, 126.78, 127.10, 127.65, 127.90, 127.99, 128.19, 128.36, 128.54, 128.64, 128.82, 128.96, 131.08, 136.66, 136.91, 137.77, 151.20, 151.46. m/z 772.802; calc: C$_{55}$H$_{64}$O$_3$: 772.486.

1-((E)-4-((E)-4-((E)-4-methoxystyryl)styryl)styryl)-2,5-bis(octyloxy)-4-(E)-styrylbenzene (53): Isolated in 75% yield as a yellow solid (0.104 g). $^1$H NMR: (CDCl$_3$, 300 MHz) δ (ppm): 0.90 – 1.91 (m, 30H), 3.85 (s, 3H), 4.06 – 4.09 (t, 4H, J = 6 Hz), 6.91 – 6.93 (d, 2H, J = 6 Hz), 6.96 – 7.56 (m, 27H). $^{13}$C NMR: (CDCl$_3$, 75 MHz) δ (ppm): 14.40, 22.96, 26.59, 29.60, 29.71, 29.81, 32.11, 55.57, 69.87, 110.71, 110.91, 114.37, 121.67, 123.78, 126.70, 126.78, 127.10, 127.65, 127.90, 127.99, 128.19, 128.36, 128.54, 128.64, 128.82, 128.96, 131.08, 136.66, 136.91, 137.77, 151.20, 151.46. m/z 772.802; calc: C$_{55}$H$_{64}$O$_3$: 772.486.
114.37, 121.67, 123.78, 126.70, 126.78, 127.10, 127.65, 127.90, 127.99, 128.19, 128.36, 128.54, 128.64, 128.82, 128.96, 131.08, 136.66, 136.91, 137.77, 151.20, 151.46. m/z 772.803; calcd: C₅₅H₆₄O₃: 772.486.

1-((E)-4-bromostyryl)-2,5-bis(octyloxy)-4-((E)-4-((E)-4-styrylstyryl)styryl)benzene (54): Isolated in 73% yield as a yellow solid (0.121 g). ¹H NMR: (CDCl₃, 300 MHz) δ (ppm): 0.89 – 1.92 (m, 30H), 4.06 – 4.10 (t, 4H, J = 7 Hz), 7.08 – 7.54 (m, 27H). ¹³C NMR: (CDCl₃, 75 MHz) δ (ppm): 14.40, 22.97, 26.60, 29.71, 32.11, 69.87, 110.80, 121.80, 123.67, 126.76, 127.15, 127.31, 128.22, 128.63, 128.95, 132.06, 136.32, 136.62, 136.76, 137.65, 151.45. m/z 820.466; calc: C₅₄H₆₁BrO₂: 820.386.

1-((E)-4-((E)-4-methoxystyryl)styryl)-2,5-bis(octyloxy)-4-((E)-4-(E)-styrylstyryl)styryl)benzene (73): Isolated in 71% yield as a yellow solid (0.132 g). ¹H NMR: (CDCl₃, 300 MHz) δ (ppm): 0.91 – 1.90 (m, 30H), 3.85 (s, 3H), 4.08 (m, 4H), 6.91 – 7.53 (m, 29H). ¹³C NMR: (CDCl₃, 75 MHz) δ (ppm): 14.42, 22.98, 26.59, 29.62, 29.71, 29.78, 32.11, 55.60, 69.85, 110.80, 114.41, 123.38, 126.81, 127.10, 127.99, 128.64, 128.97, 137.66, 151.44. m/z 772.707; calc: C₅₅H₆₄O₃: 772.486.

General Heck Coupling procedure for tetramers 44 – 46: To a flame-dried 3-neck round bottomed flask equipped with a dropping funnel and a condenser was added palladium acetate (catalytic), potassium carbonate (1.50 equiv), and dry dimethylacetamide (52.0 mL) under a nitrogen atmosphere. The solvent was purged with excess nitrogen for 5 min, at which time a solution of 61 – 63 (1.00 equiv) and styrene (2.80 equiv) in dry DMA (10.0 mL) was added dropwise over a 10 min interval. When the addition was completed, the reaction was heated to 140 °C for approximately 16 h and
monitored by TLC. Upon disappearance of the starting material, the reaction was poured into an Erlenmeyer flask containing water (200 mL), and then extracted with EtOAc (3 × 50 mL). The organic phase was washed with brine and dried with sodium sulfate. The solvent was removed under vacuum and the crude material was purified by silica gel chromatography using hexanes and progressing to (95:5) hexanes/ethyl acetate.

1,4-Bis(octyloxy)-2-(E)-styryl-5-((E)-4-(E)-styrylstyryl)benzene (44): Isolated in 60% yield as a yellow solid (1.25 g) (M.p. 110-112 °C). Spectral results matched that already reported in the literature.\(^\text{114}\)

1-((E)-4-Methoxystyryl)-2,5-bis(octyloxy)-4-((E)-4-(E)-styrylstyryl)benzene (45):
Isolated in 75% yield as a yellow solid (1.02 g) (M.p. 104-106 °C). \(^1\)H NMR: (CDCl\(_3\), 300 MHz) δ (ppm): 0.90-1.89 (m, 30H), 3.85 (s, 3H), 4.07 (t, 4H, \(J = 6\) Hz), 6.88-6.90 (d, 2H, \(J = 6\) Hz), 7.13-7.53 (m, 19H). \(^{13}\)C NMR: (CDCl\(_3\), 75 Hz), δ (ppm): 14.40, 22.97, 26.57, 29.60, 29.70, 29.79, 32.10, 55.58, 66.43, 69.85, 110.65, 114.34, 121.62, 126.66, 126.74, 127.07, 127.59, 127.98, 128.32, 128.62, 128.96, 131.05, 137.64, 137.71, 151.16, 151.41, 159.42. \(m/z\) 671.00; calcd. C\(_{47}\)H\(_{58}\)O\(_3\): 670.98.

1-((E)-4-Nitrostyryl)-2,5-bis(octyloxy)-4-((E)-4-(E)-styrylstyryl)benzene (46):
Isolated in 50% yield as a oily reddish solid (0.087 g). \(^1\)H NMR: (CDCl\(_3\), 300 MHz) δ (ppm): 0.90-1.93 (m, 30H), 4.05-4.12 (t, 4H, \(J = 7\) Hz), 7.14-7.68(m, 19H), 8.22-8.25 (d, 2H, \(J = 6\) Hz). \(^{13}\)C NMR: (CDCl\(_3\), 75 MHz), δ (ppm): 14.37, 22.56, 29.59, 29.69, 29.73, 32.08, 69.66, 69.85, 110.56, 111.20, 123.34, 124.41, 125.65, 126.47, 126.76, 126.97, 127.11, 127.19, 127.93, 128.51, 128.61, 128.84, 128.97, 129.43, 136.97, 137.38, 137.55, 144.90, 146.71, 151.86, 151.86. \(m/z\) 708.4042; calcd. C\(_{46}\)H\(_{55}\)NO\(_4\): 708.4029.
**General Procedure for synthesis of tetrarners 48 and 49:** To an oven dried 3-neck round-bottomed flask was charged with sodium acetate (1.66 equiv) and carefully flame dried and placed under nitrogen. A solution of 57 (b) (1.00 equiv), 4-vinyl nitrobenzene (2.83 equiv), dimethylguanidine (0.04 equiv), and DMAc (30.0 equiv) were added via canula. To this suspension is added a catalytic amount of palladium acetate, and the reaction was then heated to 140 °C for 20 h. The reaction was cooled to room temperature, poured into water, and then extracted with methylene chloride (3 × 50 mL). The organic layer was then dried with sodium sulfate, concentrated down under vacuum, and the crude material was then reacted in the next step without further purification. The crude material was then placed into a round bottomed flask and dissolved in dry THF (100 equiv). To a flame-dried 3-neck round-bottomed flask equipped with a dropping funnel and condenser was added the substituted phosphonate ester (56 or 59) (1.20 equiv) under a nitrogen atmosphere. Dry THF (20.0 mL), potassium tert-butoxide (1.50 equiv) were added and the solution was allowed to stir at room temperature for 10 min. The solution of crude nitro trimer (1.00 equiv) in dry THF (20.0 mL) was added dropwise over a 5 min interval at which time the solution was stirred at room temperature for 12 h. The solution was diluted with ether (80 mL), washed with water (80 mL), brine (80 mL), and the organic phase was dried with sodium sulfate. The solvent was removed under reduced pressure to give a crude solid that was recrystallized with 95% EtOH. The solid product was filtered and the mother liquor was concentrated down under reduced pressure and dissolved in toluene (20 mL). To this solution was added a catalytic amount of iodine, and the solution was brought to reflux for 12 h. Upon cooling to room temperature, the solution was washed with brine (100 mL), water (100 mL), and saturated
NaHCO₃ (100 mL). The organic phase was dried with sodium sulfate and concentrated down to give a crude material that was recrystallized with 95% EtOH to give a second crop of product. The overall yield of compounds 48 and 49 over these two steps was 34% and 35%, respectively.

1-((E)-4-Methoxystyryl)-4’-((E)-4″-((E)-4‴-nitrostyryl)styryl)-2,5-bis(octyloxy)benzene (48): Isolated in 34% yield as a reddish solid (0.042 g) (M.p. 125-126 °C). ¹H NMR: (CDCl₃, 300 MHz) δ (ppm): 0.90-1.90 (m, 30H), 3.85 (s, 3H), 4.06-4.10 (t, 4H, J = 6 Hz), 6.91-6.93 (d, 2H, J = 6 Hz), 7.13-7.66 (m, 16H), 8.22-8.25 (d, 2H, J = 9 Hz); ¹³C NMR: (CDCl₃, 75 MHz), δ (ppm): 14.45, 22.98, 26.57, 29.77, 32.09, 48.28, 69.87, 107.79, 110.54, 110.86, 112.50, 114.32, 121.50, 124.45, 127.05, 127.19, 127.67, 127.99, 128.80, 130.97, 145.88, 151.13, 162.97. m/z 738.4150; calcd.: C₄₇H₅₇NO₅: 738.4134.

1-((E)-4-Bromostyryl)-4’-((E)-4″-((E)-4‴-nitrostyryl)styryl)-2,5-bis(octyloxy)benzene (49): Isolated in 35% yield as a reddish brown solid (0.053 g) (M.p. 76-77 °C). ¹H NMR: (CDCl₃, 300 MHz) δ (ppm): 0.88-1.91 (m, 30H), 4.05-4.09 (t, 4H, J = 6 Hz), 7.06-7.66 (m, 18H), 8.22-8.25 (d, 2H, J = 9 Hz); ¹³C NMR: (CDCl₃, 75 MHz), δ (ppm): 14.39, 22.95, 26.56, 29.59, 29.67, 29.73, 32.09, 69.77, 110.86, 121.36, 124.44, 126.12, 126.98, 127.04, 127.11, 127.24, 127.67, 127.91, 128.22, 128.41, 132.00, 133.19, 135.48, 137.12, 138.86, 144.17, 146.90, 151.38, 151.42.

General procedure for synthesis of amine containing compounds (47 and 50): In a flame-dried round-bottomed flask was placed nitro compound (49) (1.00 equiv), absolute EtOH (247 equiv), and tin chloride dihydrate (5.00 equiv). This solution was heated to 70 °C for 18 h. Upon cooling to room temperature, the solution was poured onto 25.0 g
of ice and diluted with 5% NaHCO₃ to bring the pH to 8. This solution was extracted with EtOAc (3 × 50 mL) and the organic layer was dried with sodium sulfate. The solvent was removed under reduced pressure and the crude material was purified by column chromatography using 5% EtOAc/Hexanes to 50% EtOAc/Hexanes as eluant.

**4-((E)-2,5-Bis(octyloxy)-4’-((E)-4''-(E)-styrylstyryl)styryl)benzenamine (47):**

Isolated in 61% yield as an oily yellowish solid (0.045 g). ¹H NMR: (CDCl₃, 300 MHz) δ (ppm): 0.88-1.90 (m, 30H), 3.76 (s, 2H), 4.05-4.09 (t, 4H, J = 6 Hz), 6.68-6.71 (d, 2H, J = 9 Hz), 7.04-7.55 (m, 19H). ¹³C NMR: (CDCl₃, 75 MHz), δ (ppm): 14.41, 22.96, 26.56, 29.59, 29.70, 29.79, 32.10, 66.43, 69.83, 110.51, 110.87, 115.47, 120.08, 123.77, 126.74, 127.07, 127.99, 128.05, 128.55, 128.64, 128.95, 129.15, 136.56, 137.65, 137.78, 146.25, 151.05, 151.44.  m/z 656.4425; calcd: C₄₆H₅₇NO₂: 656.4467.

**4-((E)-4’-((E)-4''-((E)-4'''-Bromostyryl)-2,5-bis(octyloxy)styryl)styryl)benzenamine (50):**

Isolated in 60% as a yellowish-brown solid (0.0402 g) (M.p. 72-73 °C). ¹H NMR: (CDCl₃, 300 MHz) δ (ppm): 0.88-1.91 (m, 30H), 3.77 (s, 2H), 4.06-4.07 (t, 4H, J = 7 Hz), 6.68-6.71 (d, 2H, J = 9 Hz), 7.11-7.53 (m, 18H). ¹³C NMR: (CDCl₃, 75 MHz), δ (ppm): 14.44, 22.95, 26.57, 29.74, 32.11, 69.76, 110.88, 115.52, 121.24, 126.63, 127.07, 127.61, 128.07, 128.21, 128.96, 132.00, 136.81, 137.22, 137.47, 146.42, 151.41.  m/z 734.3569; calcd: C₄₆H₅₆BrNO₂: 734.3567.

**General procedure for synthesis of formyl groups via n-butyllithium (67 and 68):**

To an oven dried 3-neck round-bottomed flask was added 65 or 66 (1.00 equiv), and the solid was cooled under a constant stream of nitrogen. When the flask had reached room temperature, dry THF (10 mL) was added, and the solution was cooled to -78 °C with a dry ice/acetone bath. To this solution n-BuLi (1.50 equiv) was added drop-wise over 10
min at -78 °C. One hour after the addition of n-BuLi, dry DMF (2.00 equiv) was introduced all at once and the flask was allowed to warm to room temperature over 2 h. At this point the reaction was quenched by addition of water (400 equiv) and the solid product was filtered and washed with MeOH. The crude product was chromatographed on silica gel with 20% EtOAc/hexanes as the eluant to produce 67 and 68 in 58% and 42% yields, respectively. The compounds were sufficiently pure by 1H NMR and were taken on to the next step without further purification.

4-((E)-2,5-Bis(octyloxy)-4′-(E)-styrylstyril)benzaldehyde (67): Isolated in 58% yield as a yellow solid (0.102 g). 1H NMR: (CDCl3, 300 MHz) δ (ppm): 0.90 – 1.91 (m, 30H), 4.06 – 4.12 (dt, 4H, J = 4 Hz), 7.15 – 7.70 (m, 13H), 7.88 – 7.91 (d, 2H, J = 9 Hz), 10.02 (s, 1H). 13C NMR: (CDCl3, 75 MHz) δ (ppm): 14.39, 22.94, 26.37, 26.45, 29.51, 29.55, 29.62, 32.07, 69.36, 69.43, 110.33, 110.66, 122.98, 124.41, 126.79, 127.14, 127.50, 128.02, 128.37, 128.98, 129.19, 132.07, 134.53, 136.81, 137.44, 137.53, 150.96, 156.46, 189.44.

4-((E)-4′-methoxy styryl)-2,5-bis(octyloxy)styryl)benzaldehyde (68): Isolated in 42% yield as a yellow solid (0.097 g). 1H NMR: (CDCl3, 300 MHz) δ (ppm): 0.89 – 1.89 (m, 30H), 3.85 (s, 3H), 4.04 – 4.11 (dt, 4H, J = 4 Hz), 6.90 – 6.93 (d, 2H, J = 9 Hz), 7.13 – 7.86 (m, 10H), 7.86 – 7.89 (d, 2H, J = 9 Hz), 10.00 (s, 1H).

General Suzuki Coupling Procedure (87 and 88): To an oven-dried 3-neck round-bottomed flask was added bromo derivative (81 or 82) (1.00 equiv), dry toluene (200 equiv), palladium tetrakis(triphenylphosphine) (3.00% mol equiv). The solution was degassed with dry nitrogen for 15 min. A solution of boronic acid 86 (2.00 equiv/bromine) in absolute EtOH was added via a syringe, followed by 2 M potassium
carbonate (2.00 equiv/bromine). The solution was then brought to reflux for 16 h. After the reaction was finished as judged by TLC, the reaction was cooled to room temp and filtered. Diethyl ether (100 equiv) was added to this solution and the organic layer was washed with brine and dried with sodium sulfate. The organic layer was then concentrated under reduced pressure and recrystallized from 95% EtOH.

**2,7-Di-tert-butyl-4,5-bis(4-((E)-3,5-di-tert-butylstyryl)phenyl)-9,9-dimethyl-9H-xanthene (87):** Isolated in 82% yield as a whiteish-red solid (0.101 g). $^1$H NMR: (CDCl$_3$, 300 MHz) δ (ppm): 1.38 (s, 54H), 1.75 (s, 3H), 7.10 – 7.46 (m, 22H). $^{13}$C NMR: (CDCl$_3$, 75 MHz) δ (ppm): 31.65, 31.74, 31.85, 33.07, 33.07, 34.89, 35.14, 120.98, 121.14, 121.49, 122.45, 124.43, 126.23, 126.36, 127.16, 127.30, 127.75, 129.74, 130.11, 130.27, 150.76, 151.33, 155.78.

**4,4’-(benzofuran) (E)-1,3-di-tert-butyl-5-styrylbenzene (88):** Isolated in 81% yield as an off-white solid (0.100 g). $^1$H NMR: (CDCl$_3$, 300 MHz) δ (ppm): 1.38 (s, 36H), 7.24 – 8.06 (m, 24H). $^{13}$C NMR: (CDCl$_3$, 75 MHz) δ (ppm): 31.74, 35.14, 119.93, 121.19, 122.46, 123.65, 125.22, 125.48, 126.70, 126.97, 127.80, 129.04, 130.33, 135.44, 136.70, 137.34, 151.30, 153.51. m/z 748.4; calcd for C$_{26}$H$_{16}$O$_3$: 748.4.

**Synthesis of (E)-2,5-bis(octyloxy)-4-(3,4,5-tris(decyloxy)styryl)benzaldehyde (91):**

To an oven-dried 3-neck round-bottomed flask was added 89 (1.20 equiv) and dry THF (200 equiv). This solution was cooled to 0 °C and potassium tert-butoxide (1.50 equiv) was added, and the solution was allowed to warm to room temperature with stirring. A solution of 90 (1.00 equiv) in dry THF (50.0 equiv) were added drop-wise, and the solution was brought to reflux for 3 h. When the reaction was complete by TLC, the solution was diluted with 3 M HCl (300 equiv), and the solid was filtered and washed.
with cold MeOH. This crude solid was placed into a round-bottomed flask. To this flask a 10:1 methylene chloride:water solution (0.10 M) was added along with DDQ (1.20 equiv). The reaction was stirred until TLC indicated disappearance of starting material and the reaction was quenched by addition of saturated NaHCO₃. The organic layer was washed with saturated NaHCO₃ (3 × 50 mL), brine (3 × 50 mL), and dried. The organic layer was concentrated under reduced pressure and chromatographed with silica gel using 5% EtOAc/hexanes as the eluant to produce 91 in 73% overall yield. Isolated in 73% yield as a yellow solid (4.132 g). \(^{1}H\) NMR: (CDCl₃, 300 MHz) \(\delta\) (ppm): 0.83-1.91 (m, 95H), 3.97-4.13 (m, 10H), 6.75 (s, 2H), 7.12-7.36 (m, 4H), 10.45 (s, 1H); \(^{13}C\) NMR: (CDCl₃, 75 MHz) \(\delta\) (ppm): 14.29, 22.88, 26.33, 29.56, 29.63, 29.80, 29.86, 29.94, 30.56, 32.11, 69.35, 73.70, 105.75, 126.38, 126.86, 130.36, 131.89, 132.62, 135.32, 139.23, 143.70, 153.55, 191.57.

**Synthesis of (4-((E)-4’-((E)-2,5-bis(decyloxy)-4”-(3,4,5-tris(decyloxy)styryl)styryl)phenyl)methanol (92):** To an oven-dried 3-neck round-bottomed flask was added diethyl 4-(diethoxymethyl)benzylphosphonate (1.00 g, 3.69 mmol, 1.20 equiv), dry THF (44.3 g, 614 mmol, 200 equiv). The solution was cooled to 0 °C and potassium tert-butoxide (0.52 g, 4.63 mmol, 1.50 equiv) was then added. To this dark solution was added a 1 M solution of 91 (3.04 g, 3.07 mmol, 1.00 equiv), at which point the reaction was refluxed for 4 h and monitored by TLC. When the starting material had disappeared by TLC, the reaction was cooled to room temperature, quenched with 3 M HCl, and stirred for and additional 1 h. The resulting yellow solid (1.66 g) was collected and washed with cold MeOH. This crude product was dried under vacuum and used in the next step without further purification. To a dried
3-neck round-bottomed flask was added 4-(diethoxymethyl)benzylphosphonate (0.50 g, 1.84 mmol, 1.20 equiv), dry THF (22.0 g, 304 mmol, 200 equiv), and potassium tert-butoxide (0.26 g, 2.32 mmol, 1.50 equiv) at 0 °C. To this solution was added a 1 M solution of the crude aldehyde from the previous step (1.66 g, 1.52 mmol, 1.00 equiv), and the reaction was brought to reflux and monitored by TLC. When consumption of the crude starting aldehyde was complete as indicated by TLC, the reaction was quenched with 3 M HCl, and stirred for an additional 1 h. The yellow solid was filtered and washed with cold MeOH. This crude aldehyde (1.14 g, 0.96 mmol, 1.00 equiv) was placed in a round-bottom flask and diluted with a 33:1 THF:water (0.02 M) solution, and then sodium borohydride (0.02 g, 0.48 mmol, 0.50 equiv) was added at room temperature. The reaction was stirred at room temp for 2 h and then quenched with water and extracted with methylene chloride (3 × 50 mL). The organic extracts were combined and concentrated under reduced pressure to give a crude yellow solid that was chromatographed on silica gel with 10% EtOAc/hexanes as the eluant to produce 92 (0.3874 g) in 17% overall yield as a yellow solid. ^1H NMR: (CDCl₃, 300 MHz) δ (ppm): 0.87-1.88 (m, 96H), 3.96-4.09 (m, 10H), 4.72-4.73 (d, 2H, J = 3 Hz), 6.74 (s, 2H), 7.10-7.55 (m, 16H); ^13C NMR: (CDCl₃, 75 MHz) δ (ppm): 14.38, 22.96, 26.43, 29.64, 32.19, 68.69, 69.80, 84.58, 107.62, 111.82, 115.86, 120.33, 122.86, 123.85, 126.95, 127.68, 128.74, 138.04, 147.11, 150.56, 151.67, 153.54, 163.35, 165.16, 170.32. m/z 1195.352 [M + H]; calcd: C₈₁H₁₂₆O₆: 1194.955

**Synthesis of 5-((E)-4-((E)-4'-(chloromethyl)styryl)styryl)-2,5-bis(decyloxy)styryl)1,2,3-tris(decyloxy)benzene:** To an oven-dried 3-neck round-bottomed flask was added 92 (0.387 g, 0.32 mmol, 1.00 equiv), dry methylene chloride
(0.15 M), and pyridine (33.0 μL, 0.41 mmol, 1.28 equiv). To this solution was added thionyl chloride (30.0 μL, 0.41 mmol, 1.28 equiv), and the reaction was stirred for 16 h at room temperature. When the starting material has disappeared by TLC, the reaction was concentrated under reduced pressure, and redissolved in diethyl ether. This solution was washed with water, brine, and dried with magnesium sulfate. The magnesium sulfate was removed by vacuum filtration, and the organic solution was concentrated under reduced pressure to produce the title compound in 98% yield as a yellow solid (0.39 g) (M.p. 121 – 122 °C). \(^1\)H NMR: (CDCl\(_3\), 300 MHz) δ (ppm): 0.87-1.89 (m, 95H), 3.98-4.09 (m, 10H), 4.62 (s, 2H), 6.74 (s, 2H), 7.11-7.54 (m, 16H); \(^1\)C NMR: (CDCl\(_3\), 75 MHz) δ (ppm): 14.37, 22.95, 26.42, 28.38, 29.64, 30.00, 30.35, 32.19, 35.77, 38.82, 59.43, 59.91, 67.52, 100.81, 127.05, 129.38, 130.54, 137.07, 144.59, 146.51, 155.51, 167.34 177.37. \(m/z\) 1213.374 [M + H]; calcd: C\(_{81}\)H\(_{125}\)O\(_5\)Cl: 1212.9216

**Synthesis of Diethyl-4-\(\text{(E)}\)-4'-(\(\text{E}\))-2,5-bis(allyloxy)-4''-(\(\text{E}\))-3,4,5-tris(allyloxy)styryl)styryl)benzylphosphonate (93):** To a round-bottom flask was added 5-\(\text{(E)}\)-4-\(\text{(E)}\)-4'-(chloromethyl)styryl)styryl)-2,5-bis(allyloxy)styryl)1,2,3-tris(allyloxy)benzene (0.39 g, 0.32 mmol, 1.00 equiv) and triethyl phosphite (4.80 mL, 82.0 equiv). This solution was brought to reflux for 16 h and then vacuum distilled to remove any unreacted triethyl phosphite. Upon cooling a yellow precipitate formed in the round-bottom flask giving 93 in 95% yield as a yellow solid (0.40 g). \(^1\)H NMR: (CDCl\(_3\), 300 MHz) δ (ppm): 0.88-1.85 (m, 95H), 3.13-3.20 (d, 2H, \(J = 21\) Hz), 3.97-4.07 (m, 10H), 6.73 (s, 2H), 7.10-7.51 (m, 16H); \(^1\)C NMR: (CDCl\(_3\), 300 MHz) δ (ppm): 14.38, 16.62, 16.70, 22.95, 26.42, 26.59, 29.64, 29.73, 29.78, 29.88, 29.94, 30.62, 32.18, 62.39, 62.48, 69.38, 69.83, 73.80, 105.43, 126.91, 127.09, 128.20, 128.53, 130.33,
General Procedure for the synthesis of 95 – 97: To an oven-dried 3-neck round-bottomed flask was added 93 (2.20 equiv), dry THF (200 equiv), and potassium tert-butoxide (3.00 equiv). To this solution was added a 1M solution of 116, 118, or benzaldehyde (1.00 equiv) in dry THF. The reaction was brought to reflux for 4 h and monitored by TLC. Upon disappearance of the starting aldehyde, the reaction was quenched with 3 M HCl, and the solid was collected by vacuum filtration. The crude solid was chromatographed on silica gel with 5% EtOAc/hexanes as the eluant giving the title compounds 95, 96, and 97 in 75%, 70%, and 71% yields, respectively.

4,5-Bis((E)-4-((E)-2,4-bis(decyloxy)-4’-((E)-3,4,5-tris(decyloxy)styryl)styryl)styryl)styryl)-2,7-di-tert-butyl-9,9-dimethyl-9H-xanthene (95): Isolated in 75% yield as a yellow solid (44.0 mg). Yield: 44 mg  

\[\text{Isolated in 75\% yield as a yellow solid (44.0 mg).} \]

Yield: 44 mg  

\[\text{1H NMR: (CDCl}_3, 300 \text{ MHz) } \delta \text{ (ppm): 0.87-1.92 (m, 214H), 3.98-4.07 (m, 20H), 6.74 (s, 4H), 7.02-7.54 (m, 52H);} \]

\[\text{13C NMR: (CDCl}_3, 75 \text{ MHz) } \delta \text{ (ppm): 14.81, 23.38, 26.85, 27.02, 30.06, 30.16, 30.31, 30.38, 31.04, 32.25, 32.61, 37.03, 62.39, 65.39, 69.80, 70.26, 74.23, 103.39, 127.53, 128.93, 133.87, 153.94.} \]

\[m/z 2853.539 \text{ [M + H]} \text{; calcd: C}_{200}\text{H}_{288}\text{O}_{10}: 2852.182.} \]

4,5-Bis((E)-4-((E)-2,4-bis(decyloxy)-4’-((E)-3,4,5-tris(decyloxy)styryl)styryl)styryl)styryl)-benzofuran (96): Isolated in 70% yield as a yellow solid (40 mg).  

\[\text{1H NMR: (CDCl}_3, 300 \text{ MHz) } \delta \text{ (ppm): 0.89-1.93 (m, 190H), 3.98-4.06 (m, 20H), 6.28 (s, 1 H), 6.74 (s, 4H), 7.02-7.53 (m, 54H);} \]

\[\text{13C NMR: (CDCl}_3, 75 \text{ MHz) } \delta \text{ (ppm): 14.31, 15.71, 22.89, 26.37, 26.54, 29.57, 29.67, 29.82, 29.89, 32.12,} \]

\[166 \]
5-((E)-2,5-Bis(decyloxy)-4-((E)-4’-((E)-4’’-(E)-styrylstyrly)styryl)styryl)-1,2,3-
tris(decyloxy)benzene (97): Isolated in 71% yield as a yellow solid (82 mg). ^1H NMR: (CDCl$_3$, 300 MHz) δ (ppm): 0.87-1.88 (m, 95H), 3.96-4.09 (m, 10H), 6.75 (s, 2H), 7.14-7.53 (m, 23H); ^13C NMR: (CDCl$_3$, 75 MHz) δ (ppm): 14.36, 22.95, 26.40, 29.94, 29.62, 29.94, 32.18, 33.55, 34.76, 38.68, 42.55, 44.65, 46.03, 46.25, 50.03, 52.39, 54.43, 54.80, 56.33, 66.15, 91.82, 130.37, 106.00, 123.39, 127.12, 128.53, 137.04, 139.30, 151.79, 184.10. m/z 1267.520 [M + H]; calcd: C$_{88}$H$_{130}$O$_5$: 1266.992

Synthesis of diethyl 4-((E)-2,5-bis(octyloxy)-4’-(E)-styrylstyrly)benzylphosphonate (99): To an oven-dried 3-neck round-bottomed flask was added 67 (2.00 g, 3.53 mmol, 1.00 equiv) and dry THF (50.0 mL). To this solution was added sodium borohydride (0.20 g, 5.30 mmol, 1.50 equiv), and the reaction was stirred until TLC indicated disappearance of the starting material. The reaction was then quenched with water (50.0 mL), and the aqueous solution was extracted with methylene chloride (3 × 20 mL). The organic layer was washed with brine, dried with sodium sulfate, and concentrated under reduced pressure to produce a crude benzyl alcohol that was dried under vacuum. This alcohol (2.00 g, 3.53 mmol, 1.00 equiv) was dissolved in dry methylene chloride (50.0 mL), and cooled to 0 °C. To this solution was added thionyl chloride (0.63 g, 5.30 mmol, 1.50 equiv), and pyridine (0.42 g, 5.30 mmol, 1.50 equiv). The reaction was allowed to warm to room temperature overnight. The reaction was quenched by the addition of water. The organic layer was extracted with saturated NaHCO$_3$, dried with sodium sulfate, and concentrated under reduced pressure to produce 1-((E)-4-
(chloromethyl)styryl)-2,5-bis(octyloxy)-4-(E)-styrylbenzene (1.02 g, 49% overall yield). This crude benzyl chloride (1.02 g, 1.74 mmol, 1.00 equiv) and triethylphosphite (8.00 mL, 27.0 equiv) were heated to reflux for 16 h, cooled, and vacuum distilled under reduced pressure to produce 99 in 98% yield as a yellow solid (1.17 g). \( ^1 \)H NMR: (CDCl\(_3\), 300 MHz) \( \delta \) (ppm): 0.87-1.88 (m, 95H), 3.98-4.09 (m, 10H), 4.62 (s, 2H), 6.74 (s, 2H), 7.11-7.54 (m, 16H); \( ^{13} \)C NMR: (CDCl\(_3\), 75 MHz) \( \delta \) (ppm): 14.36, 16.68, 22.92, 26.50, 26.53, 29.53, 29.56, 29.66, 29.74, 32.03, 32.06, 34.78, 62.32, 62.46, 69.74, 69.82, 90.53, 110.77, 110.91, 123.58, 126.73, 126.87, 127.62, 128.51, 128.86, 128.98, 129.09, 130.23, 130.32, 138.16, 151.29.

**Synthesis of 4,5-bis(4-((E)-4′-((E)-2,5-bis(octyloxy)-4″-(E)-styrylstyryl)styryl)phenyl)-2,7-di-tert-butyl-9,9-dimethyl-9H-xanthene (98):**

To an oven-dried 3-neck round-bottomed flask equipped with a condenser and nitrogen outlet was added diethyl 4-((E)-2,5-bis(octyloxy)-4′-(E)-styrylstyryl)benzylphosphonate (99) (0.50 g, 0.73 mmol, 2.20 equiv), potassium tert-butoxide (0.10 g, 0.89 mmol, 2.60 equiv), and dry THF (5.00 mL). The solution was cooled to 0 °C and a solution of 83 (0.18 g, 0.34 mmol, 1.00 equiv) was added, and the solution was then warmed to room temperature, and then refluxed for 8 h. The reaction was quenched with 3 M HCl (20 mL) and the product was extracted with methylene chloride (3 × 50 mL). The organic layer was dried with sodium sulfate and concentrated under reduced pressure. The crude greenish solid was recrystallized with 95% EtOH to produce 98 in 76% yield as a greenish solid (0.54 g). \( ^1 \)H NMR: (CDCl\(_3\), 300 MHz) \( \delta \) (ppm): 0.87-1.88 (m, 95H), 3.98-4.09 (m, 10H), 4.62 (s, 2H), 6.74 (s, 2H), 7.11-7.54 (m, 16H); \( ^{13} \)C NMR: (CDCl\(_3\), 75 MHz) \( \delta \) (ppm): 14.36, 16.68, 22.92, 26.50, 26.53, 29.53, 29.56, 29.66, 29.74, 32.03, 32.06, 34.78, 62.32, 62.46, 69.74, 69.82, 90.53, 110.77, 110.91, 123.58, 126.73, 126.87, 127.62, 128.51, 128.86, 128.98, 129.09, 130.23, 130.32, 138.16, 151.29.
MHz) δ (ppm): 14.80, 23.36, 24.66, 27.00, 30.06, 30.28, 32.03, 32.24, 32.55, 126.38, 127.18, 128.85, 129.46, 131.27, 141.23. m/z 1600.3 [M + H]; calcd: C_{115}H_{138}O_{5}: 1599.0.

**General Synthesis of 106 – 108**: These compounds were made by a slightly different method than one previously reported. To an oven-dried single neck round-bottomed flask equipped with a reflux condenser was added 105 (a – c) (10.0 mmol, 1.00 equiv) and EtOH (100 mL). A solution of hydrazine in water (0.37 M, 30 mL, 1.11 equiv) was added through the top of the condenser and the reaction was heated to reflux for 18 h. The reaction was then cooled to room temperature and placed into an ice bath to precipitate the product. The solid was collected by vacuum filtration and washed with water and EtOH to produce hydrazide products 106 – 108.

3,4,5-tris(octyloxy)benzohydrazide (106): Isolated in 92% yield as an off-white solid (4.79 g). \(^1\)H and \(^{13}\)C NMR data is in accordance with previously made compound.\(^{141}\)

3,4,5-tris(decyloxy)benzohydrazide (107): Isolated in 90% yield as an off-white solid (5.44 g). \(^1\)H and \(^{13}\)C NMR data is in accordance with previously made compound.\(^{141}\)

3,4,5-tris(dodecyloxy)benzohydrazide (108): Isolated in 90% yield as an off-white solid (6.20 g). \(^1\)H and \(^{13}\)C NMR data is in accordance with previously made compound.\(^{141}\)

**General synthesis of 101 – 103**: To a 3-neck round-bottomed flask attached to a nitrogen outlet is added 106 – 108 (5.00 mmol, 2.50 equiv). To this solid was added perylene tetracarboxylic dianhydride (2.00 mmol, 1.00 equiv), zinc acetate (2.01 mmol, \(~1.00\) equiv), and quioline (67.0 mL, 0.03M). The solution was heated to 160 °C for 18 h, at which point the solution was cooled to room temperature and 3 M HCl was added. The solution was then stirred at 50 °C for 1 h, cooled to room temperature, and the dark
A purplish-red solid was collected by vacuum filtration. The solid was washed with water, EtOH, and dried under reduced pressure. The solid was chromatographed on neutral alumina with a gradient of methylene chloride to 5% MeOH/methylene chloride as the eluant producing 101 – 103 as reddish solids. The solids were then split into two portions. One portion was dissolved into a minimum amount of methylene chloride. To this solution was slowly added methanol to the top of the solution. This mixed solvent system was left undisturbed for 3 days producing purplish solids of 101 – 103. The $^1$H, $^{13}$C, and mass spectral data for both the red and purple compounds were identical.

**Perylene-3,4:9,10-bis((3,4,5-trus(octyloxy)benzohydrazide)-dicarboximide) (101):**

Isolated in 20% yield as a red solid (0.56 g). $^1$H NMR: (CDCl$_3$, 300 MHz) δ (ppm): 0.88 – 1.75 (m, 90H), 3.93 – 4.03 (m, 12H), 7.31 (s, 4H), 8.07 – 8.92 (m, 10H). $^{13}$C NMR: (CDCl$_3$, 75 MHz) δ (ppm): 14.39, 22.97, 26.09, 26.41, 29.69, 29.85, 29.99, 30.11, 30.21, 30.75, 31.02, 32.22, 69.36, 70.88, 73.73, 73.85, 101.80, 106.22, 122.81, 123.34, 131.75, 152.66, 153.60, 164.97. m/z 1419.9077 [M + Na]; calcd: C$_{86}$H$_{116}$N$_4$O$_{12}$: 1396.8590.

**Perylene-3,4:9,10-bis((3,4,5-trus(decyloxy)benzohydrazide)-dicarboximide) (102):**

Isolated in 20% yield as a red solid (0.625 g). $^1$H NMR: (CDCl$_3$, 300 MHz) δ (ppm): 0.88 – 1.75 (m, 114H), 3.92 – 4.03 (m, 12H), 7.28 (s, 4H), 8.10 – 8.93 (m, 10H). $^{13}$C NMR: (CDCl$_3$, 75 MHz) δ (ppm): 14.39, 20.44, 22.97, 26.42, 29.70, 29.99, 30.76, 32.21, 69.38, 73.76, 101.33, 106.16, 122.16, 123.43, 125.57, 131.99, 140.60, 153.58. m/z 1588.0219 [M + Na]; calcd: C$_{98}$H$_{140}$N$_4$O$_{12}$: 1565.04672.

**Perylene-3,4:9,10-bis((3,4,5-trus(dodecyloxy)benzohydrazide)-dicarboximide) (103):**

Isolated in 20% yield as a red solid (0.69 g). $^1$H NMR: (CDCl$_3$, 300 MHz) δ (ppm): 0.86 – 1.82 (m, 138H), 3.99 – 4.04 (m, 12H), 6.94 – 7.04 (m, 4H), 8.29 – 8.66 (m, 8H), 9.08
(s, 2H). $^{13}$C NMR: (CDCl$_3$, 75 MHz) δ (ppm): 14.39, 20.44, 22.97, 26.42, 29.70, 29.99, 30.76, 32.21, 69.38, 73.76, 101.33, 106.16, 122.16, 123.43, 125.57, 131.99, 140.60, 153.58. $m/z$ 1756.2229 [M + Na]; calcd: C$_{110}$H$_{164}$N$_4$O$_{12}$: 1733.2345

**Synthesis of [bis-(3,4,5-tris-dodecyloxy-benzyl)-amino]-acetonitrile (110):** To a 3-neck round-bottomed flask equipped with a reflux condenser was added 109 (2.05 g, 2.83 mmol, 2.04 equiv), cyanomethanaminium chloride (0.13 g, 1.40 mmol, 1.00 equiv), potassium carbonate (0.43 g, 3.09 mmol, 2.20 equiv), and acetonitrile (30.0 mL). The solution was heated to reflux overnight and quenched by pouring into water (200 mL). The solid precipitate was filtered by vacuum filtration and washed with water and EtOH. The crude solid was chromatographed on neutral alumina with 50/50 hexanes/methylene chloride as eluant producing 110 in 86% yield as a white waxy solid (1.88 g). $^1$H NMR: (CDCl$_3$, 300 MHz) δ (ppm): 0.87 – 1.83 (m, 138H), 3.41 (s, 2H), 3.62 (s, 4H), 3.92 – 3.99 (m, 12H), 6.57 (s, 4H). $^{13}$C NMR: (CDCl$_3$, 75 MHz) δ (ppm): 14.39, 22.96, 26.44, 29.65, 29.75, 29.94, 30.00, 30.62, 32.20, 58.61, 69.36, 73.68, 107.29, 132.43, 153.51. $m/z$ 1364.958 [M + Na]; calcd: C$_{88}$H$_{160}$N$_4$O$_6$: 1342.222.

**Synthesis of N1,N1-bis-(3,4,5-tris-dodecyloxy-benzyl)-ethane-1,2-diamine (111):** Compound 110 (1.80 g, 1.34 mmol, 1.00 equiv) was placed into a hydrogenation flask with a 1,4-dioxane:methanol solution (1:1) (30.0 mL) and 10% palladium on carbon (0.20 g). The flask was purged with hydrogen gas three times and evacuated to remove any residual air from the solution. The flask was then filled with hydrogen gas to a pressure of 60 PSI and shaken overnight. Upon completion of the reaction, the flask was evacuated and filtered over celite to remove the palladium catalyst. The organic solution
was concentrated down to produce 111, which subsequently was used in the next step without need for further purification.

**Synthesis of Perylene-3,4:9,10-bis((N1,N1-Bis-(3,4,5-tris-dodecyloxy-benzyl)-ethane-1,2-diamine) -dicarboximide) (112):** To a 3-neck round-bottomed flask equipped with a nitrogen outlet was added 111 (1.00 g, 0.74 mmol, 2.20 equiv), perylene tetracarboxylic dianhydride (0.13 g, 0.33 mmol, 1.00 equiv), zinc acetate (0.120 g, 0.66 mmol, 2.00 equiv), and quionline (11.0 mL, 0.03M). The solution was heated to 160 °C overnight, cooled to room temperature, and quenched with 3 M HCl (50.0 mL). The solution was stirred at 50 °C for 1 h, and the orange solid was filtered, and then washed with water and EtOH. The crude solid was chromatographed on neutral alumina with methylene chloride as the eluant to produce 112 in 32 % yield as an organge solid (0.32 g). $^1$H NMR: (CDCl$_3$, 300 MHz) $\delta$ (ppm): 0.88 – 1.86 (m, 276H), 2.91 (s, 4H), 3.54 – 3.94 (m, 32H), 4.39 (s, 4H), 6.45 (s, 8H), 8.62 (s, 8H). $m/z$ 3070.5711 [M + Na]; calcd: C$_{200}$H$_{332}$N$_4$O$_{16}$: 3047.696.

**Synthesis of perylene-3,4:9,10-bis((3-Amino-N-pyridin-4-yl-benzamide) -dicarboximide) 118:** To a 3-neck round-bottomed flask was added 123 (1.00 g, 5.07 mmol, 1.20 equiv), tetracarboxylic perylene dianhydride (0.80 g, 2.11 mmol, 1.00 equiv), zinc acetate (0.91 g, 4.22 mmol, 2.00 equiv), and quinoline (141 mL). The solution was heated to 180 °C overnight, and then cooled to room temperature. To the purplish solution was added 3 M HCl (200 mL), and stirred for an additional 1 h at room temperature. The solid formed was filtered, washed with methanol, and dried under vacuum to give 118 in 25% yield as a purple solid (0.41 g). The purple solid was then dissolved in $d$-DMSO by addition of TFA. $^1$H NMR: (DMSO/TFA, 300 MHz) $\delta$ (ppm):
7.756 (s, 2H), 8.09 - 8.15 (m, 4H), 8.28-8.29 (d, 6H, \( J = 3 \) Hz), 8.51 - 8.53 (d, 4H, \( J = 6 \) Hz), 8.75 – 8.77 (d, 8H, \( J = 6 \) Hz), 11.56 (s, 2H). \( m/z \) 782.288 \([\text{M}]\); calcd: \( C_{48}H_{26}N_6O_6 \): 782.191

**Synthesis of N-(2,4-dioxo-1,2,3,4-tetrahydro-pyrimidin-5-yl)-3-nitro-benzamide (124):** To a 3-neck round-bottomed flask equipped with a reflux condenser was added 3-nitrobenzoyl chloride (1.05 g, 5.67 mmol, 1.20 equiv), THF (50.0 mL), triethylamine (0.57 g, 5.67 mmol, 1.20 equiv), and 5-aminouracil (0.60 g, 4.72 mmol, 1.00 equiv). The reaction was then heated to reflux for 2 h. The progress of the reaction was monitored by TLC. When the starting material was consumed as indicated by TLC, the mixture was cooled to room temperature and quenched with the addition of water. The solid obtained was filtered and washed with water, 95% EtOH, and ether. The solid was dried under vacuum to produce 124 in 60% yield as a whiteish solid (0.78 g). This compound was used in the next step without further purification. \(^1\)H NMR: (DMSO, 300 MHz) δ (ppm): 7.78 – 7.93 (m, 2H), 8.32 – 8.44 (m, 2H), 8.71 (s, 1H), 9.79 (s, 1H), 10.90 (s, 1H), 11.49 (s, 1H).

**Synthesis of 3-amino-N-(2,4-dioxo-1,2,3,4-tetrahydro-pyrimidin-5-yl)-benzamide (125):** To a round-bottomed flask equipped with a reflux condenser was added 124 (0.78 g, 2.83 mmol, 1.00 equiv), tin (II) chloride (2.00 g, 8.86 mmol, 3.13 equiv), and concentrated HCl (10.0 mL). The reaction was heated to reflux for 2 h, cooled to room temperature, and then poured onto 40.0 g of crushed ice. To this ice mixture was added 10 M NaOH until the solution was basic. The solid formed was filtered and washed with water, and 95% EtOH producing 125 in 80% yield as a grayish solid (0.70 g). The solid was dried and used in the next step without further purification. \(^1\)H NMR: (DMSO, 300 MHz) δ (ppm):
MHz) \( \delta \) (ppm): 4.40 (s, 2H), 7.41 – 7.52 (m, 2H), 7.50 – 7.90 (m, 2H), 7.92 (s, 1H), 9.30 (s, 1H), 10.97 (s, 1H), 11.479 (s, 1H).

**Synthesis of perylene-3,4:9,10-bis((3-Amino-N-(2,4-dioxo-1,2,3,4-tetrahydro-pyrimidin-5-yl)-benzamide) -dicarboximide) (119):** To a 3-neck round-bottomed flask was added 125 (0.70 g, 2.84 mmol, 2.40 equiv), tetracarboxylic perylene dianhydride (0.45 g, 1.19 mmol, 1.00 equiv), zinc acetate (0.51 g, 2.37 mmol, 2.00 equiv), and quinoline (40.0 mL). The mixture was heated to reflux overnight and then cooled to room temperature. To this purple solution was added 3 M HCl, and this solution was allowed to stir for an additional 1 h at room temperature. The solid formed was filtered, washed with water, and dried to produce a crude 119 in ~20% yield as a purple solid (0.20 g). The crude solid was dried and dissolved in \( d\)-DMSO by addition of TFA. \(^1H\) NMR: (DMSO/TFA, 300 MHz) \( \delta \) (ppm): 7.97 – 8.40 (m, 18H), 9.10 – 9.35 (m, 6H).

**Synthesis of 2-[6-(1-carboxy-3-methyl-butyl)-1,3,5,7-tetraoxo-3,5,6,7-tetrahydro-1H-pyrrolo[3,4-f]isoindol-2-yl]-4-methyl-pentanoic acid (127):** This molecule was synthesized by a slightly modified procedure than what has been reported.\(^{143}\) A round-bottomed flask equipped with a reflux condenser was added 126 (5.00 g, 19.6 mmol, 1.00 equiv), AcOH (50.0 mL), and L-leucine (7.80 g, 59.4 mmol, 3.00 equiv). This solution was heated to reflux for 16 h. After that time, the solution was cooled to room temperature, diluted with water (200 mL), and filtered. The solid was washed with water and dried to give 127 in 96% yield as a white solid (8.20 g). The spectral characteristics matched literature values.\(^{143}\)

**Synthesis of 2-[6-(1-chlorocarbonyl-3-methyl-butyl)-1,3,5,7-tetraoxo-3,5,6,7-tetrahydro-1H-pyrrolo[3,4-f]isoindol-2-yl]-4-methyl-pentanoyl chloride (128):** This
molecule was synthesized by a slightly modified procedure than what has been reported. Compound 127 (5.00 g, 11.2 mmol, 1.00 equiv) was placed into a round-bottomed flask. To this flask was added thionyl chloride (10.0 mL, 12.0 equiv). The solution was heated to reflux for 16 h, whereupon the excess thionyl chloride was removed by vacuum distillation to provide an off-white solid 128 in 98 % yield (5.28 g). The spectral characteristics matched the literature values.

Synthesis of 2-{6-[1-(2,4-dioxo-1,2,3,4-tetrahydro-pyrimidin-5-ylcarbamoyl)-3-methyl-butyl]-1,3,5,7-tetraoxo-3,5,6,7-tetrahydro-1H-pyrrolo[3,4-f]isoindol-2-yl]-4-methyl-pentanoic acid (129): Compound 128 (1.00 g, 2.07 mmol, 1.00 equiv) was placed into a 3-neck round-bottomed flask. To this flask was added dry THF (20.0 mL), 5-aminouracil (0.26 g, 2.06 mmol, 1.00 equiv), and triethylamine (0.231 g, 2.10 mmol, 1.05 equiv). The reaction was stirred at room temperature until consumption of starting material was indicated by TLC, then the reaction was quenched by addition of water (50 mL). The precipitate that formed was filtered, washed with water, and chromatographed on silica with methanol as the eluant. The product 129 was obtained as an off-white solid in 50% yield (0.57 g). 1H NMR: (DMSO, 300 MHz) δ (ppm): 0.88 – 0.89 (m, 12H); 1.35 – 1.50 (m, 2H); 1.89 (m, 2H); 4.84 – 4.88 (dd, 1H, J = 6 Hz); 5.07 – 5.10 (dd, 1H, J = 6 Hz); 7.80 – 7.82 (d, 1H, J = 6 Hz); 8.29 – 8.33 (dd, 2H, J = 6 Hz); 9.44 (s, 1H); 10.72 (s, 1H); 11.42 (s, 1H). 13C NMR: (DMSO, 75 MHz) δ (ppm): 20.87, 21.03, 23.22, 23.38, 24.80, 25.12, 37.02, 38.67, 38.96, 39.24, 39.51, 39.79, 40.07, 40.35, 51.02, 53.14, 55.03, 112.65, 118.40, 118.60, 132.17, 136.78, 136.92, 137.21, 150.15, 165.98, 166.39, 167.94, 170.69.
Synthesis of 2-{6-[1-(2,4-dioxo-1,2,3,4-tetrahydro-pyrimidin-5-ylcarbamoyl)-3-methyl-butyl]-1,3,5,7-tetraoxo-3,5,6,7-tetrahydro-1H-pyrrolo[3,4-f]isoindol-2-yl]-4-methyl-pentanoic acid 3,7-dimethyl-oct-6-enyl ester (120): To a 3-neck round-bottomed flask was added 129 (0.50 g, 0.90 mmol, 1.00 equiv), dry DMF (10.0 mL), and (R)-3,7-dimethyl-oct-6-en-1-ol (0.141 g, 0.90 mmol, 1.00 equiv). The solution was cooled to 0 °C, and DCC (0.204 g, 0.99 mmol, 1.10 equiv) was added. The reaction was allowed to warm to room temperature overnight monitored by TLC (1:4 EtOAc: hexanes as the eluant). When the reaction was complete by TLC, the reaction was quenched by the slow addition of water. The precipitate that formed was filtered and washed with water, and 95% EtOH. The product was dried under vacuum to provide 120 as an off-white sticky solid in 52% yield (0.32 g). \(^1\)H NMR: (DMSO, 300 MHz) δ (ppm): 0.74 – 2.14 (m, 33H), 2.31 – 2.38 (t, 1H, \(J = 6 \) Hz), 4.18 – 4.19 (m, 2H), 5.01 – 5.07 (m, 2H), 8.25 – 8.29 (d, 2H, \(J = 12 \) Hz), 8.47 (s, 1H), 9.83 (s, 1H), 10.36 (s, 1H).

Synthesis of 4-methyl-2-{6-[3-methyl-1-(pyridin-4-ylcarbamoyl)-butyl]-1,3,5,7-tetraoxo-3,5,6,7-tetrahydro-1H-pyrrolo[3,4-f]isoindol-2-yl]-pentanoic acid (2,4-dioxo-1,2,3,4-tetrahydro-pyrimidin-5-yl)-amide (121): To a 3-neck round-bottomed flask was added 129 (0.50 g, 0.90 mmol, 1.00 equiv), dry DMF (10.0 mL), and 4-aminopyridine (0.09 g, 0.90 mmol, 1.00 equiv). The solution was cooled to 0 °C and DCC (0.20 g, 0.99 mmol, 1.10 equiv) was added. The reaction was allowed to warm to room temperature overnight monitored by TLC (1:4 EtOAc: hexanes as the eluant). When the reaction was complete by TLC, the reaction was quenched by the slow addition of water. The precipitate that formed was filtered and washed with water, and 95% EtOH. The product was dried under vacuum to provide 121 as an off-white solid in 31%
yield (0.18 g). $^1$H NMR: (DMSO, 300 MHz) δ (ppm): 0.85 – 1.92 (m, 18H), 4.17 – 4.20 (m, 1H), 4.96 – 5.17 (m, 1H), 8.30 – 8.47 (m, 2H), 8.47 (s, 1H), 9.83 (s, 1H), 10.36 (s, 1H). $^{13}$C NMR: (DMSO, 75 MHz) δ (ppm): 17.83, 19.51, 19.57, 21.17, 23.29, 24.53, 24.97, 25.12, 25.40, 25.54, 25.78, 25.90, 26.15, 29.65, 29.69, 31.27, 33.24, 33.51, 34.05, 35.41, 37.06, 49.33, 51.70, 64.94, 118.97, 119.20, 124.56, 131.61, 137.24, 165.80, 166.37, 169.37.
CHAPTER V
SUMMARY

The synthesis and photophysical characterization of a series of oligo(\(p\)-phenylenevinylene) were performed. The goal was to improve the overall yield of asymmetrical OPVs. It was determined from this work that the Smith-Modarelli method for synthesis of asymmetric OPVs increases the overall yield as compared to current literature methods. This synthetic approach has the potential to be used for large scale synthesis of asymmetric OPVs for commercial applications.

The next part of this dissertation dealt with the synthesis and photophysical characterization of cofacial and branched OPV chains. Understanding the relationship between closely associated cofacial, or branched, chains can aid in improving photovoltaic device performance. This study focused on synthesizing different length OPV chains and attaching these chains to a xanthene or benzofuran bridge. These bridges served as scaffolds to align the OPV chains in either a cofacial, or branched, alignment, respectively. The steady state absorption and fluorescence spectra were obtained. Upon decreasing the chain length from \(n = 5\) to \(n = 4\), the steady state fluorescence spectrum of 98 showed a significant red-shift in fluorescence maxima. This shift, along with the absence of any shift in the steady state absorption spectrum of 98, indicates a possible excited state interaction between the neighboring OPV chains.
Further studies with TCSPC will indicate the exact type of interaction that is occurring in 98, and the other cofacial and branched OPV systems.

The synthesis and photophysical characterization of hydrazide-based perylene diimides (HPDIs) were also performed. These compounds showed a high degree of aggregation in heptane. The spectral shifts observed for these compounds indicated an $H$-type aggregate. The steady state absorption spectra indicated the 0-1 band was blue-shifted along with increasing in intensity, while the 0-0 band became red-shifted and decreased in intensity. These spectral features are all indicative of an $H$-type aggregate. Studies aimed at understanding the binding constant for aggregate formation along with photophysical experiments to study the aggregated state is an on-going project.

The synthesis of a self-assembled pyromellitimide (PI) compound has been done. The self-assembling units were chose to be a pyridine, for axial ligation of a metallo-porphyrin, and a uracil derivative that was chosen to undergo hydrogen bonding with a triazene functionalized OPV. This molecule should undergo ET from the OPV to the zinc porphyrin with the final electron acceptor being the PI. Studies aimed at understanding the mechanism of ET within this model, along with observation of the self-assembly, are on-going research projects within our group.
REFERENCES


113. Wongwitwichote, W.; Modarelli, D.A. Unpublished data.


APPENDICES
Figure A.1  Steady state absorption spectra of 44 – 47 in methylene chloride. All spectra are normalized to the absorption with the highest absorption value to illustrate the shifts in the $\lambda_{\text{max}}$ upon substitution of the OPV chromophore.
Figure A.2  Steady state absorption spectra of pentamers 51 - 54 in (top) methylene chloride (DCM) and (bottom) dimethylacetamide (DMAc).
Figure A.3  The steady-state absorbance spectra of 51 and 73 in DCM.
Figure A.4  The absorption spectra of 87, 88, and 100 (a) in DCM. Both 87 and 88 are red shifted relative to 100 (a) indicating a ground state interaction between the neighboring chromophores.
Figure A.5  The steady state absorption spectra of 98.
Figure A.6  The steady state absorption spectra of 101 purple and 101 red in toluene.
Figure A.7  The steady state absorption spectra of **101 purple** and **101 red** in heptane.
Figure A.8  The steady state absorption spectrum of 112 in heptane.
Figure B.1  Steady state fluorescence spectra of 44 – 47 in methylene chloride. All spectra are normalized to illustrate the relative shifts of the $\lambda_{\text{max}}$ upon changing the end group on the OPV.
Figure B.2  The steady state fluorescence spectra of 51 – 54 in both (top) DCM and (bottom) DMAc.
Figure B.3  The absorbance fluorescence spectra of 51 to 73 in DCM.
Figure B.4  The steady state fluorescence spectra of 87, 88, and 100 (a) in DCM.
Figure B.5  The steady state fluorescence spectra of 95 – 97 in methylene chloride (DCM). The inlet is an expanded view of the fluorescence spectra in the 460 nm to 530 nm region.
Figure B.6  The steady state fluorescence spectra of 44 and 98.
Figure B.7  The steady state fluorescence spectra of 101 purple and red in toluene.
Figure B.8  The steady state fluorescence spectra of 101 purple and red in heptane.
Figure B.9  The steady state fluorescence of 112 in heptane.
APPENDIX C

ABBREVIATIONS

A    Acceptor
ATP  Adenosine tri-phosphate
CS   Charge Seperated
CR   Charge Recombination
CT   Charge separated state
D    Donor
D*   Excited state donor
DCM  Dichloromethane
DMAc N,N-Dimethylacetamide
DMF  N,N-dimethylforamide
DMSO Dimethylsulfoxide
EA   Electron affinity
EET  Electronic energy transfer
ET   Electron transfer
Fl   Fluorescence
HMO  Hückel Molecular Orbital
HOMO Highest Occupied Molecular Orbital
<table>
<thead>
<tr>
<th>Abbreviation</th>
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<tbody>
<tr>
<td>HPDI</td>
<td>Hydrazide perylene diimide</td>
</tr>
<tr>
<td>HWE</td>
<td>Horner-Wadsworth-Emmons</td>
</tr>
<tr>
<td>INDO</td>
<td>Hartree-Fock Intermediate Neglect of Differential Overlap</td>
</tr>
<tr>
<td>IP</td>
<td>Ionization potential</td>
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<tr>
<td>LHC</td>
<td>Light harvesting complex</td>
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<tr>
<td>LUMO</td>
<td>Lowest Unoccupied Molecular Orbital</td>
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<tr>
<td>MEH-PPV</td>
<td>Poly[2-methoxy-5-(2’-ethylhexyloxy)-1,4-phenylenevinylene]</td>
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<tr>
<td>MO</td>
<td>Molecular orbitals</td>
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<tr>
<td>MW</td>
<td>Molecular weight</td>
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<tr>
<td>OLED</td>
<td>Organic light emitting diode</td>
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<tr>
<td>OPD</td>
<td>Organic photovoltaic device</td>
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<tr>
<td>OPV</td>
<td>Oligo(p-phenylenevinylene)</td>
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<tr>
<td>PA</td>
<td>Polyacetylene</td>
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<tr>
<td>PDI</td>
<td>Perylene diimide</td>
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<tr>
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<td>PRC</td>
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<td>PTCDA</td>
<td>Perylene tetracarboxylic dianhydride</td>
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<td>Ph</td>
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