SYNTHESIS OF ASYMMETRIC PHTHALOCYANINE DERIVATIVES

By

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ABSTRACT

The overall efficiency in organic photovoltaics (OPVs) is greatly influenced by the nature of the charge injection barrier at the bottom contact. The rate of charge injection can be influenced by the presence of an electroactive monolayer covalently attached to the transparent conducting oxide (TCO). Modification of the TCO/organic interface with an electroactive molecular monolayer (e.g. phthalocyanines or naphthalocyanines) requires the preparation of appropriately substituted asymmetric phthalocyanine (Pc) and naphthalocyanine (Nc) chromophores. The work in this thesis describes improved methods of asymmetrically substituted Pc derivatives synthesis addressing some currently encountered problems including: (1) the need for facile synthesis of asymmetric Pc/Nc hybrids; (2) a lack of general methods for producing asymmetric Pc materials with structural diversity.

Chapter 1 provides a concise review on Pc and Pc/perylenediimide (PDI) derivatives that have been reported as a part of architecture in monochromophoric or multichromophoric molecules for energy and charge transfer studies. In addition, the intrinsic electronic and photophysical properties suitable for OPV applications, such as charge transfer rate, lifetime of charge separated state, and transfer pathway are also discussed.

Chapter 2 details the use of ROMP-Capture-Release to synthesize a small library of asymmetric Pc/Nc hybrids and study of chemical and physical properties of these structurally related asymmetric chromophores and the corresponding symmetric Pc and
Nc in both metalated (Zn) and unmetallated form. The extension of the Pc aromatic core as well as the asymmetry afforded by the unique quadrant can result in modulated physical properties, particularly bathochromic shifted electronic absorption spectra. Further modification of the pendent hydroxyl group on the molecule demonstrated the possibility for covalently grafting Pcs onto inorganic contacts such as ITO and TiO₂.

Chapter 3 reports the investigation of using an asymmetric Pc as the platform for the preparation of a small library of zinc hexatriazolyl-monohydroxyphthalocyanines via CuAAC reaction. The modification of peripheral substituents was demonstrated using azides bearing hydrophobic, photo-crosslinkable, and electroactive moieties. Monitoring the click chemistry by both UV-Vis and FT-IR spectroscopies was performed to provide insight into the role of azide equivalent, reaction time, and catalyst on reaction progress.

Chapter 4 describes the synthesis and characterization of a novel series of Pc-PDI dyads with different perylene bay-functional groups (H, thioether, and sulfonyl), as well as phosphonic acid as an anchoring group connected to the perylene moieties, for the studies of molecular-level heterojunction on transparent conductive oxides. The developed model system for further electrochemical analysis was proved to firmly attach to the ITO surface by ATR-UV/Vis spectroscopy.
CHAPTER 1
INTRODUCTION

1.1 Photovoltaic Technology

Solar energy is a promising terrestrial energy source that can be used in many applications such as solar photovoltaics, solar thermal, and artificial photosynthesis. Among the applications of solar energy, photovoltaic technology has emerged as an attractive part of the solution to the global energy crisis. In photovoltaics, the radiation of sunlight is directly converted into electric current using the photoelectric effect. The first solid state solar cell was constructed by Charles Fritts in 1883 using semiconductor selenium and a thin layer of gold, and the overall efficiency (\(\eta\)) of the prototype selenium cells was determined to be less than 1%. However, the first practical solar cell made of a silicon based semiconductor was developed by Gerald Pearson, Calvin Fuller, and Daryl Chapin in the mid-20th century.\(^1\) In this architecture, the excitons are generated upon irradiation, and diffuse to the \(p-n\) junction where the electron-hole pairs dissociate and travel toward electrodes under an applied electric field.

Photovoltaics are divided into three main generations (Figure 1.1). The first generation photovoltaics, which consist of single crystal or polycrystalline silicon doped with phosphorus and boron in a \(p-n\) junction, have a relatively high energy conversion efficiency and represent the most commercially mature solar cell devices. However, silicon based photovoltaics suffer from high cost of materials and production.
In order to reduce costs, considerable effort has been made to develop second generation photovoltaics, also known as thin film technologies, which are made from other inorganic materials such as amorphous or microcrystalline silicon, copper indium gallium selenide (CIGS), cadmium telluride (CdTe), and gallium arsenide (GaAs).\(^2\)

Taking advantage of thin film technologies, the second generation photovoltaics can be processed by techniques such as sputtering and physical vapor deposition (PVD) to alleviate the cost of materials and production. However, the cells experience a drop in efficiency compared to the first generation photovoltaics.

Third generation photovoltaics are primarily based on organic materials.\(^3\) Organic materials have several advantages relative to inorganic materials: (1) they are relatively inexpensive; (2) they are structurally flexible; (3) they can be processed in
solution and at relatively low temperature for mass production; and (4) due to the high molar absorptivity, they can be used to fabricate solar cells from thin films with thicknesses of only a few hundred nanometers.

1.2 Physical Processes in Organic Photovoltaics (OPVs)

The first bilayer (planar heterojunction) OPV was fabricated in 1986 by Tang, using a copper phthalocyanine (CuPc) as the donor layer and a perylene tetracarboxylic derivative as the acceptor layer (Figure 1.3). Compared to BHJ photovoltaics, the bilayer heterojunction improved the energy conversion efficiency due to the effective charge transfer in separate layers.

![First Bilayer Heterojunction OPV Fabricated in 1986 by Tang](image)

FIGURE 1.2. First Bilayer Heterojunction OPV Fabricated in 1986 by Tang

In a typical planar heterojunction OPV cell, an active layer of two organic materials with specific electron-donating and electron-demanding properties are sandwiched between electrodes with different work functions. The photoconversion
process of bilayer organic solar cells can be divided into four steps (Figure 1.4): (1) photoexcitation and exciton formation, (2) exciton diffusion, (3) exciton dissociation, (4) charge transport and collection.⁸

![Diagram of physical processes in OPVs](image)

**FIGURE 1.3. Physical Processes in OPVs**⁸

In bulk heterojunction (BHJ) photovoltaics, the electron donor and acceptor materials are mixed together, forming a blended domain (Figure 1.2).⁹ While the length scale of the blend is ideally close to the exciton diffusion length, most of the excitons generated in either material can reach the p-n junction interface, where excitons can dissociate efficiently.
FIGURE 1.4. Design of Bulk-Heterojunction OPVs

The bulk heterojunction is usually prepared from spin-coating using a solution of both electron donor and acceptor materials, ideally leading to a well-mixed condensed phase of both components, so that each donor-acceptor interface is within a distance less than the exciton diffusion length.

1.2.1 Photoexcitation and Exciton Formation

The initial step in the photoconversion process involves the absorption of photons and the formation of excitons (bound electron-hole pairs). When light irradiates the donor material though a transparent electrode, an electron is photo-excited from the HOMO to the LUMO (an electronic transition from the ground state ($S_0$) to the excited state ($S_1$)) leaving a hole behind on the HOMO level. The time scale for this electronic transition process is usually on the order of $10^{-15}$ second.

To efficiently trap the sunlight and maximize the formation of photoinduced excitons, the electron donor and acceptor materials chosen for OPVs have to absorb as
much solar radiation as possible, which means broad absorbance profiles and high extinction coefficients.

1.2.2 Exciton Diffusion

Due to the low intermolecular orbital coupling and low dielectric constant for organic materials, the bound electron-hole pairs cannot easily dissociate into free charges before reaching a $p$-$n$ junction.\textsuperscript{10} The migration of excitons towards the Donor/Acceptor interface can be viewed as energy transfer between excitons and neighboring ground state molecules due to the presence of effective overlap of electronic clouds. Only those excitons diffusing to the Donor/Acceptor interface can contribute to exciton dissociation and further photocurrent formation. Therefore, the optimal thickness of a donor or acceptor layer has to be equal to or less than the distance that an exciton can travel during its lifetime, typically ranging from 3 to 40 nm.\textsuperscript{11,12}

1.2.3 Exciton Dissociation

The exciton must overcome the columbic interaction at the Donor/Acceptor interface to undergo the dissociation process, forming a free electron and a hole in the acceptor and donor materials, respectively. The probability of exciton dissociation depends on the relative mobilities of charge carriers, and the energetic offset between the donor and the acceptor LUMOs. However, due to the low charge carrier mobility in organic based solar cells, mainly resulting from the low dielectric constant, the bound electron-hole pairs tend to recombine contributing to a poor efficiency.
1.2.4 Charge Transport and Collection

Since all individual components in the photovoltaic have different electro-chemical potentials, the electrons travel within the acceptor layer towards the anode (e.g. Al), and the holes travel within the donor layer towards the cathode (e.g. ITO) after exciton dissociation at the interface. This process can effectively separate holes and electrons. Once charges reach the electrodes they can be extracted and transferred to the outer circuit, leading to the formation of photocurrent. However, the presence of a rough electrode surface can lead to poor contacts at the interface, resulting in high series resistance and low charge collection efficiency.

1.3 Organic Photovoltaic Components

This section is devoted to the organic active layers, which are composed of electron donor and acceptor materials, sandwiched between two electrodes. Since the original work of Tang in 1986,\textsuperscript{7} great progress has been made in the development of new OPV materials. The materials used for OPVs cover a wide range of materials such as polymers, oligomers, and small molecules. Phthalocyanine (Pc) derivatives and thiophene-based polymers,\textsuperscript{13-17} such as poly(3-hexylthiophene-2,5-diyl) (P3HT), are commonly used as electron donor (\textit{i.e.} hole transporting) materials due to their electronic and photophysical properties (Figure 1.5). The purpose of the donor layer is to harvest incident photons, diffuse the formed exciton to the donor/acceptor interface, and transport charge to the charge collection interface.
Fullerene derivatives\textsuperscript{13-17} such as C\textsubscript{60}, C\textsubscript{70}, and phenyl-C\textsubscript{61}-butyric acid methyl ester (PCBM) are excellent electron acceptor materials due to their relatively low reorganization energy (ca. 0.7 eV), long exciton diffusion length (ca. 77 ± 10 Å), and extraordinarily high electron affinity (Figure 1.6).\textsuperscript{13,18,19}
Perylene derivatives such as perylenediimide (PDI) have also been exploited as the electron acceptor materials. PDI possesses attractive electronic and photophysical properties such as long electron diffusion lengths (30 ± 3 Å), high electron affinities (3.85 eV), large molar absorption coefficients at 490 to 530 nm (5.8 x 10^4 M^{-1}cm^{-1}), and well-defined supramolecular features.\textsuperscript{20-25} The properties of PDIs, depending on their substitution pattern, can include highly exothermic electron affinities, high electron mobilities, and strong fluorescence. These properties have been applied in fundamental studies, including the preparation of OPV devices.\textsuperscript{26-28} In addition, several PDI derivatives have been studied as OPV components for electron transfer and charge
separation,\textsuperscript{29-31} taking advantage of their stability, the intense light absorption, and the remarkable electron accepting properties.\textsuperscript{32-34}

1.4 Phthalocyanines as Electron Donor Materials

An ideal organic electron donor material should (1) absorb strongly and broadly in the solar spectrum; (2) have a long exciton diffusion length (i.e. long exciton lifetime); (3) be easily dissolved and processed from solution at room temperature; and (4) be easily synthesized in large quantities.

Since the first synthesis of metal-free and metallated phthalocyanine (Pc) by Linstead\textsuperscript{35-37} in 1934, an enormous amount of work has been devoted to explore the synthesis and properties of Pcs as an electron donor material. Most organic electron donor materials have an optical band gap around 2 eV, resulting in limited overlap with the solar spectrum which limits light harvesting. However, a typical Pc absorption spectrum is characterized by an intense Q-band lying at 650 to 700 nm with a high molar absorptivity of \(\sim 10^5\) M\(^{-1}\)cm\(^{-1}\), and a less intense B band (Soret band) lying in the UV region (ca. 350 nm). The flexibility of structural modification of Pcs opens a possibility to optimize the related electronic and photophysical properties. Several metallated Pcs and substituted Pcs have been found to intensely absorb in the near-IR region, leading to suitable small band gap materials for OPV.\textsuperscript{38} Another key asset of Pcs for OPV application is their small reorganization energies. In charge transfer reactions, which subsequently evokes an acceleration of the charge separation step.\textsuperscript{39}
Pcs are the most commercially important group of porphyrins because of the intense $\pi$ to $\pi^*$ transitions in the visible region. Due to their outstanding physical and chemical properties, such as thermal stability and structural diversity, Pcs have been widely used in various applications including solar cells,\textsuperscript{7} field effect transistors,\textsuperscript{40} nonlinear optics,\textsuperscript{41} high dielectric materials,\textsuperscript{42} electrochromic devices,\textsuperscript{43} photodynamic therapy (PDT),\textsuperscript{44} and chemical sensors.\textsuperscript{45} The major approaches for Pcs’ structure modification include: (1) coordination with metals ranging from main group to transition metals via the central nitrogen atoms; (2) extension of the $\pi$-system conjugation using fused aromatic rings; and (3) introduction of substituents onto the peripheral or nonperipheral positions with electron donating or withdrawing effects. Due to the versatility of chemical synthesis, various Pc-based materials with desired electronic and structural features have been developed.

In the following sections, we will mainly focus on Pc and Pc/PDI derivatives that have been reported as a part of the architecture in monochromophoric or multichromophoric molecules for energy and charge transfer studies. The intrinsic electronic and photophysical properties relevant for OPV applications, such as charge transfer rate, lifetime of charge separated state, and transfer pathway will be discussed.

### 1.4.1 Functionalized Monochromophoric Pcs for Charge Transfer Studies

One of the key factors in the performance of OPV devices is the charge-injection barrier between the hole-harvesting electrode (e.g. ITO) and the organic semiconductor. Generally, high series resistance arising from the electrical heterogeneity and surface
roughness of the ITO surface often leads to low hole harvesting probabilities at the electrode/donor interface, resulting in poor OPV efficiencies. The presence of a robust ohmic contact at the electrode/donor interface will reduce series resistance and improve OPV efficiencies. Depositing a Pc monolayer to ITO via phosphonic acid (Pc-PA) as the tethering group for creating ohmic contacts was explored by Polaske et al. in 2011(Figure 1.7).  

![Phosphonic Acid Functionalized Asymmetric PCs](image)

**FIGURE 1.7. Phosphonic Acid Functionalized Asymmetric Pc**

It has been found that the phosphonic acid tethering group provides for an efficient linkage between ITO and Pc. The electrochemical result showed near monolayer surface coverage was achieved, although both monomeric and aggregated forms were present in the thin film. Kinetic studies from cyclic voltammetry (CV) experiments showed no significant dependence of the apparent heterogeneous electron transfer rate constants on tether length, which suggests that tunneling through the tethered carbon chain is not the rate-determining step.
Since the orientation distribution of the tethered chromophore thin film was generally not measured during the electron transfer processes, it is difficult to conclude whether there is a definitive correlation between molecular orientation and charge transfer kinetics. The first measurements of electron transfer rates using a combination of waveguide spectroscopy and potential modulated-attenuated total reflectance (PM-ATR) for the previous model system (Pc-PA) as a function of molecular orientation and aggregation was presented by Lin et al. in 2012 (Figure 1.8).

**FIGURE 1.8. Correlation between Orientation and Electron Transfer Rates**

PM-ATR measurements show that the monomeric Pc-PA subpopulation undergoes oxidation/reduction with a rate constant = 2 x 10^2 s^{-1}, independent of Pc orientation. For the aggregated Pc-PA, faster orientation-dependent charge transfer rates are observed. For in-plane-oriented Pc aggregates, the rate constant = 2 x 10^3 s^{-1}, whereas for upright Pc aggregates, the rate constant = 7 x 10^2 s^{-1}. The rates for the
aggregates are comparable to those required for redox-active interlayer films at the hole-collection contact in OPVs.

1.4.2 Pc-Based Multichromophoric Molecules Linked via Covalent Bonds

In a heterojunction solar cell device, efficient photocurrent generation requires uniform blending of electron donor and acceptor on the exciton diffusion length scale. Multichromophoric molecular architectures and arrays, such as dyads, have attracted a considerable amount of scientific interest and been exploited as artificial systems for light harvesting in photovoltaic assemblies.\textsuperscript{48-50} Due to their optoelectronic properties and structural tailor ability, Pc-containing dyads, triads, and higher order arrays have been studied as photoactive donor-acceptor conjugates. In the conjugate systems reported, Pcs were employed as electron donors and PDIs were used as electron acceptors.

Several strategies have been carried out to construct the Pc-based molecular arrays, such as polymer blending,\textsuperscript{51,52} chemical linking via covalent bonds,\textsuperscript{53-58} and self-assembly.\textsuperscript{59-61} However, materials tend to segregate when blended, leading to discontinuous paths and traps for charge transport. The most effective route is to link donor material and acceptor material via either a covalent or non-covalent bond to combine them together and prevent phase separation as well.

Synthesis of Pc-Based Multichromophoric Molecules Using Click Chemistry

Though there are many reports on the peripheral modification of Pcs,\textsuperscript{62-74} a general method remains scarce in the preparation of Pc based arrays linking via covalent
bonds. A practical route for Pc modification would (1) circumvent the low yielding Linstead cyclization step, which is often accompanied by tedious purification; (2) allow modification with substituents that would otherwise not survive the Linstead cyclization conditions; and (3) be amenable to scale up. The Cu-catalyzed azide–alkyne cycloaddition (CuAAC) “click” reaction has recently been demonstrated by us and others as a mild and straightforward method for functional modification of Pcs.\textsuperscript{44,76-80}

A paper published in 2010 by Rowan described the synthesis and photophysical characterization of a series of phthalocyanine-perylenediimide (Pc-PDI) octad molecules in which eight perylene moieties were attached to a Pc core through different linkers (Figure 1.9).\textsuperscript{54}

![Figure 1.9. Multichromophoric Phthalocyanine-(Perylenediimide)$_8$ Molecules\textsuperscript{54}](image)

The experimental results in this disclosure demonstrated how the photophysical properties might be altered by the changes of structure and the arrangement (e.g. monomer or aggregate) of the molecules. Transient absorption (TA) spectroscopy revealed that photoexcitation of the PDIs led to rapid energy transfer to the Pc center,
which was strongly favored over charge separation between moieties. The presence of aggregates in solution was proven by dynamic light scattering (DLS) experiments. In octad monomers, the Pc singlet excited-state decays within tens of ps, whereas the excitons are stabilized in the aggregated form of the molecules, typically with lifetimes in the order of 1-10 ns. In addition, the intramolecular interactions between adjacent PDI units were found to highly depend upon the tails of the PDI moieties. In the case of the PDI units with steric hindrance of incompatible glycol tails, the $\pi$-$\pi$ interactions and intermolecular aggregation were suppressed, resulting in a more straightforward photophysical interaction of Forster resonance energy transfer (FRET) between the PDI moieties and relatively non-radiative Pc core.

**Covalently Bonded Pc-PDI-Pc Ensembles**

In 2007, a covalently linked donor-acceptor array composed of two Zn(II)-phthalocyanines connected to the 1,7-positions of a perylenediimide moiety was assembled by palladium chemistry for artificial photosynthetic reaction studies (Figure 1.10).\textsuperscript{57}
FIGURE 1.10. Covalently Bonded ZnPc-PDI-ZnPc (through Bay) Triad

The molecular structure of this triad was designed to be favorable for electron or hole transportation in a solar cell system due to the strong intermolecular $\pi-\pi$ stacking interaction and for the elimination of the effect of phase separation on the device performance. In this triad, the two Pcs were bound to the PDI-bay region, so that the system was found to be electronically coupled, with the PDI component profoundly influenced by the presence of the two Pcs. The PDI transitions, which typically occur at 464, 495, and 529 nm, were red shifted to 540 and 570 nm due to the substitution by conjugated ethynyl groups at the PDI bay and the presence of two bulky Pcs, leading to a strong influence on the planarity of the PDI chromophore. Strong fluorescence quenching for both ZnPc and PDI moieties in ZnPc-PDI-ZnPc was observed. The transient spectra were indicative of the ZnPc singlet excited state, which was formed with a rate constant of $>1 \times 10^{12}$ s$^{-1}$. The resulting singlet excited state features decayed slowly (3.0 ns; $3.3 \times 10^{8}$ s$^{-1}$) to the energetically lower lying triplet excited state, predominantly via intersystem crossing (ZnPc triplet quantum yield = 0.7). Transient
absorption at 840 and 1000 nm in the near-IR region was observed, which corresponded to the ZnPc radical cation, resulting from a thermodynamically allowed (0.52 eV) electron transfer. By following the temporal changes of the radical ion pair (ZnPc$^{+}$-PDI$^{-}$-ZnPc) features, a lifetime of 224 ps ($4.4 \times 10^9$ s$^{-1}$) was derived. In toluene/pyridine, the lifetime increases to 517 ps ($1.9 \times 10^9$ s$^{-1}$).

A similar ZnPc-PDI-ZnPc triad system linked through the PDI imide nitrogens was also synthesized in 2007 by coupling 3,4,9,10-perylene-tetracarboxylic dianhydride with zinc tri-tert-butyl-aminophthalocyanine and the lifetime of the charge separated state was estimated as 25 ns in toluene and 20 ns in benzonitrile (Figure 1.11).$^{58}$

![Covalently Bonded ZnPc-PDI-ZnPc (through Imide) Triad](image)

**FIGURE 1.11.** Covalently Bonded ZnPc-PDI-ZnPc (through Imide) Triad$^{58}$

Similar to the triad linked through the bay position, when the ZnPc moiety was excited with 670 nm light, the fluorescence intensity of ZnPc at 670 nm decreased compared with that of ZnPc reference in toluene, indicating quenching of the singlet excited-state of the ZnPc moiety ($^{1}\text{ZnPc}^{*}$) by the appended PDI entity. When exciting the PDI moiety at 490 nm, no ZnPc fluorescence was detected. This finding is helpful to rule
out the transfer of the singlet excited-state energies from $^1\text{PDI}^*$ to ZnPc in ZnPc-PDI-ZnPc, although this process is energetically feasible with a higher energy level of $^1\text{PDI}^*$ than that of $^1\text{ZnPc}^*$ by 0.31 eV. In addition, the shortening of the fluorescence lifetimes for the PDI moiety was observed from 5.0 to 0.2 ns. These observations suggest that efficient charge separation is taking place in ZnPc-PDI-ZnPc via both $^1\text{ZnPc}^*$ and $^1\text{PDI}^*$.

FIGURE 1.12. HOMO, HOMO-1, and LUMO of ZnPc-PDI-ZnPc (through Imide) Triad Calculated by B3LYP/3-21G Methods$^{58}$

The molecular orbital calculations show that the majority of the HOMO is localized in the ZnPc ring, and the majority of the LUMO is localized on the PDI unit.
These observations suggest the existence of a charge separated state (ZnPc$^{+}$-PDI$^{-}$-ZnPc), which is generated by transferring an electron from the ZnPc unit to the PDI moiety. Since the decay of the $^{1}$PDI$^{+}$ moiety at 980 nm can be attributed to rapid electron transfer followed by charge recombination of ZnPc$^{+}$-PDI$^{-}$-ZnPc to the ground state but not to the triplet states (no triplet states were observed), the rates of the charge recombination were evaluated as 4.0 x 10$^{7}$ s$^{-1}$ in toluene and 5.1 x 10$^{7}$ s$^{-1}$ in benzonitrile.

**Pc-Based Multichromophoric Molecules with a Long-Lived Charge-Separated State**

Generally, the systems of Pc-PDI dyads have energetically low-lying triplet excited states which prevent the generation of persistent charge-separated states, resulting in short lifetimes in the picosecond or nanosecond range.$^{57,58,81,82}$ However, in some cases, the presence of Mg$^{2+}$ as a stabilizer to the PDI moiety in the dyad systems has resulted in charge-separated states energetically more stable than corresponding triplet excited states, resulting in relatively long lifetimes for charge-separated states in the range of hundreds of microseconds.$^{39,81-83}$ In 2012, Sastre-Santos et al. reported the first example of a Pc-PDI dyad in which the corresponding charge separated state was lower in energy than the triplet excited state of the Pc and PDI in the absence of Mg$^{2+}$ (Figure 1.13).$^{55}$ The molecular design included a peripherally substituted Pc unit with phenoxy groups (electron rich) and a PDI bay substituted with sulfonyl groups (electron poor) were needed. The lifetime of the resulting charge-separated state of the dyad was 72 μs, confirmed by nanosecond laser flash photolysis.
Sastre-Santos’ model system formed by combining an electron donating Pc subunit with an electron demanding PDI via a short linker also benefits from a few other advantages such as the high absorption coefficients over most of the visible region as well as a possible driving direction for photoinduced electron transfer from Pc to PDI.

1.4.3 Pc-Based Multichromophoric Molecules Linked via Self-Assembly

Supramolecular chemistry can be applied to build highly complex chemical systems where molecular components interact by non-covalent, intermolecular forces. It has been found an attractive strategy for constructing large and complex entities that are multifunctional starting with simple molecular building blocks. Hydrogen bonding is among several non-covalent interactions used to construct supramolecular architectures. Highly selective as well as directional, it is often used as a tool to construct nanostructures of well-defined shape, size, and composition.

**Hydrogen-Bonded Multichromophoric Assemblies**
To better understand the non-covalent donor-acceptor properties of PCs in multicomponent systems focusing on the fundamental charge-transfer studies, a Pc with a ditopic melamine moiety bound to a complementary PDI by means of triple hydrogen bonding was reported by Torres and co-workers (Figure 1.14).\textsuperscript{61}

![Figure 1.14. Melamine-Mediated Pc–PDI Supramolecular Assembly\textsuperscript{61}](image)

The absorption spectrum of the melamine ZnPc itself in chloroform displayed a broad Q-band with shoulders at 740 and 840 nm, suggesting the presence of aggregated species in solution. Upon addition of PDI, the Q-band sharpened with concomitant reduction of the aggregation bands, indicating the formation of ZnPc-PDI-ZnPc assembly. The PDI fluorescence decreased exponentially in the presence of variable concentrations of melamine ZnPc. Throughout the titration, the PDI fluorescence was subjected to a 60% quenching in THF, while in benzonitrile the overall quenching amounts to 40%. The exponential concentration/fluorescence relationship revealed the affinity constants corresponding to the formation of ZnPc-PDI-ZnPc assembled from PDI and ZnPc to be 2
x $10^5$ M$^{-1}$ and 7 x $10^4$ M$^{-1}$ in THF and benzonitrile, respectively. When ZnPc-PDI-ZnPc was excited at either 530 or 680 nm, the singlet excited state features were observed, suggesting the successful formation of either $^{1}\text{PDI}^*$ or $^{1}\text{ZnPc}^*$. However, instead of intersystem crossing, the $^{1}\text{PDI}^*$ decayed with a lifetime of about 3.0 ns, which is ascribed to an intraensemble energy transfer. On the other hand, the $^{1}\text{ZnPc}^*$ in ZnPc-PDI-ZnPc converts into the corresponding triplet excited state. However, there is not enough evidence for the formation of a charge transfer state.

**Coordinated Multichromophoric Supramolecule**

In 2006, a supramolecular electron donor-acceptor hybrid was reported with axial coordination of a PDI moiety, bearing two 4-pyridyl substituents at the imide positions, to the ruthenium(II) metal centers of two Pcs (Figure 1.15). This modular protocol enabled access to electron donor-acceptor ensembles with potentially great design flexibility.

![FIGURE 1.15. Supramolecular Bis(rutheniumphthalocyanine)-PDI Ensembles](84)
Insertion of the PDI unit between the two RuPc rings completely eliminated any appreciable aggregation from the RuPc precursor. The UV/Vis spectrum of the supramolecular triad is best described as the sum of its molecular components in a 2:1 ratio, suggesting no electronic coupling between the RuPc and PDI subunits in the ground state. In addition, no absorption that might be attributable to a ground state charge transfer state is observed in the recorded range of up to 900 nm. Laser photoexcitation of either chromophore leads to a product that is essentially identical for both pathways, evolving from the RuPc or PDI singlet excited state. Features of the photoproduct are new transient maxima at 530 and 725 nm, plus transient minima at 580 nm and 650 nm, indicating the formation of a radical ion pair state (RuPc$^{+}$-PDI$^{-}$-RuPc) with a lifetime on the order of 115 ns.

1.5 Summary

The overall efficiency in OPVs is greatly influenced by the nature of the charge injection barrier at the bottom contact. The rate of charge injection can be influenced by the presence of an electroactive monolayer covalently attached to the transparent conducting oxide (TCO). Modification of the TCO/organic interface with an electroactive molecular monolayer (e.g. Pc) requires the preparation of appropriately substituted asymmetric Pc and naphthalocyanine (Nc) chromophores. The work in this dissertation includes the use of ROMP-Capture-Release to synthesize a small library of asymmetric Pc/Nc hybrids and study of chemical and physical properties of these
structurally related asymmetric chromophores and the corresponding symmetric Pc and Nc in both metalated (Zn) and unmetallated form. The extension of the Pc aromatic core as well as the asymmetry afforded by the unique quadrant can result in modulated physical properties, particularly bathochromic shifted electronic absorption spectra. Further modification of the pendent hydroxyl group on the molecule demonstrated the possibility for covalently grafting Pcs onto inorganic contacts such as ITO and TiO₂. In addition, the investigation of using an asymmetric Pc as the platform for the preparation of a small library of zinc hexatriazolyl-monohydroxyphthalocyanines via Cu-catalyzed azide–alkyne cycloaddition (CuAAC) will be reported herein. The modification of peripheral substituents was demonstrated using azides bearing hydrophobic, photo-crosslinkable, and electroactive moieties. Finally, the synthesis and characterization of a novel series of Pc-PDI dyads with different perylene bay-functional groups (H, thioether, and sulfonyl), as well as phosphonic acid as an anchoring group connected to the perylene moieties, for the studies of molecular-level heterojunction on transparent conductive oxides will also be described in this dissertation.

1.6 References


CHAPTER 2
SYNTHESIS OF ASYMMETRIC NAPHTHALOCYANINES AND PHTHALOCYANINE/NAPHTHALOCYANINE HYBRIDS

2.1 Introduction

Phthalocyanines (Pcs) are synthetic, 18 $\pi$ electron macrocyclic molecules, which have attracted a lot of attention since their initial characterization in the 1930s by Linstead and Robertson.\textsuperscript{1,2} They are the most commercially important group of porphyrins due to the intense $\pi$ to $\pi^*$ transitions in the visible region. Pcs are widely used in various applications including solar cells,\textsuperscript{3} field effect transistors,\textsuperscript{4} nonlinear optics,\textsuperscript{5} high dielectric materials,\textsuperscript{6} electrochromic devices,\textsuperscript{7} photodynamic therapy (PDT),\textsuperscript{8} and chemical sensors\textsuperscript{9} due to their outstanding physical and chemical properties, such as thermal stability and structural diversity.

For a number of applications, Pcs with two or more different substituents on the exterior of the macrocyclic system would be advantageous. However, most Pcs and naphthalocyanines (Ncs) prepared are symmetric due to the relative ease to synthesize them from a single precursor compared to asymmetric ones which need more than one precursor. Molecular structure plays an important role in the molecular arrangement in the condensed phase, as well as the properties making asymmetric Pcs increasingly relevant to applications.\textsuperscript{10} In addition, recent work with asymmetrically substituted Pcs has been found to improve photodynamic properties and nonlinear optical effects.\textsuperscript{11} Asymmetric Pcs are also amenable to appending with functionalities, such as phosphonic
acid which is useful as an anchoring group for attachment to the surface of ITO or ZnO. \(^{12,13}\) However, asymmetrically substituted Pcs and Ncs involve difficult purification after the crossover Linstead macrocyclization \(^{14}\) of the corresponding phthalonitriles (Pns) and naphthalonitriles (Nns) due to small differences in polarity among the products. To explore the relationship between chemical structure and physical properties, and also achieve the requirement of different functionalities on a single molecule for their applications in materials science, a simple and general synthetic route to afford asymmetric Pc or Nc chromophores is required.

The following sections will briefly summarize several examples of asymmetric Pcs and several reported methods for the synthesis of asymmetric Pc chromophores.

### 2.1.1 Solution-Phase Statistical Condensation

The synthesis of asymmetric Pc chromophores via a solution-phase approach is most commonly performed by statistical condensation of two different phthalonitriles, diiminoisoindoles, or related derivatives. This theoretically yields a mixture of six corresponding Pc derivatives (Scheme 2.1). \(^{15}\) The ratios of products are related to the stoichiometry of the reaction and the relative reactivity of the starting materials. \(^{16,17,18}\)
Usually, the solution phase statistical condensation of two different phthalonitriles or diiminoisoindoles involves difficult and tedious purification work due to the similar chemical and physical properties among the resulting products, asymmetrically substituted Pcs or Ncs. One method to facilitate purification is to alter polarity among the resulting adducts to aid in isolating the desired product by column chromatography. To prepare hydroxyl-functionalized asymmetric Pcs using statistical condensation, we took advantage of the $p$-methoxybenzyl (PMB) protecting group, and its subsequent removal, to distinguish the targeted product from the reaction mixture (Scheme 2.2).\textsuperscript{12}
SCHEME 2.2. Synthesis of Asymmetric Pcs via PMB Method\textsuperscript{12}

PMB-protected Pn was condensed during a statistical macrocyclization. The PMB group served not only as a protecting group during the statistical condensation in the solution phase, but also was cleaved under mild acidic conditions (50% TFA/DCM). The resulting free hydroxyl group facilitated the purification because of the increased polarity afforded to the asymmetric Pc. Further peripheral modification with phosphonic acid for ITO surface deposition was explored.\textsuperscript{12,13}

2.1.2 Solid-Phase Approach

In solid-phase synthesis of asymmetric Pcs, one of the Pn precursors is tethered to an insoluble solid support, such as polystyrene or polyethylene glycol, via a cleavable linker (Scheme 2.3). The resulting solid-supported Pn is then treated with an excess amount of another Pn to give AB\textsubscript{3}-type asymmetric Pc bound to the solid support, while
B₄-type symmetric Pc forms in solution. The B₄-type symmetric Pc can be removed by Soxhlet extraction. Subsequent cleavage of the linker from the solid support affords the desired AB₃-type asymmetric Pc.

**SCHEME 2.3. Concept of Solid-Phase Synthesis of Asymmetric Pcs**

The first synthesis of asymmetric Pcs via the solid-phase approach was reported in 1982 by Leznoff et al.¹⁹ In their contribution, a cross-linked divinylbenzene-styrene copolymer was used as the solid support in the preparation of the AB₃-type, asymmetric 2-(6’-hydroxyhexoxy)-9,16,23-triisopropoxyphthalocyanine (Scheme 2.4).
One of the challenges of the solid-phase approach is the requirement for long-term washing via Soxhlet extraction to remove the symmetric B₄-type Pc from the hydrophobic solid support. For example, Leznoff et al. reported that four to five days of Soxhlet extraction are required to remove symmetric B₄-type Pc during the preparation of the AB₃-type, asymmetric 2-(6'-hydroxyhexoxy)-9,16,23-triisopropoxyphthalocyanine. A subsequent paper reported the failure of an even more extensive Soxhlet extraction to completely remove the hydrophobic B₄ Pc from the solid support. This resulted in a contaminated asymmetric AB₃-type Pc after cleavage from the solid support, and additional column chromatography was required to obtain the targeted AB₃-type Pc in purified form.
Another challenge of the solid-phase approach is the potential formation of $A_2B_2$-type Pc due to intra-resin reactions. Reaction between Pn active sites tethered to the solid support can be similar in rate to the reactions between activated Pn species in solution and resin-bound Pns (Scheme 2.5). A significant amount of undesired $A_2B_2$-type Pc can result.

![Scheme 2.5. Formation of $A_2B_2$-Type Pcs in Solid Support](image)

### 2.1.3 Ring Expansion Approach

In addition to solution-phase and solid-phase approaches, the ring expansion reaction of geometrically constrained boron subphthalocyanines (SubPcs), first disclosed by Kobayashi et al. in 1990 (Scheme 2.6), provides another possibility for preparing asymmetric $AB_3$-type Pcs. SubPcs are homologues of Pcs, consisting of a tripyrrolic macrocycle. The loss of an aromatic unit results in a hypsochromic shift in the Q-band of...
the electronic spectra from 680 to 560-580 nm, which gives a reddish purple color to the solutions of these SubPcs.

SCHEME 2.6. Synthesis of Asymmetric Pcs via Ring Expansion Approach$^{22}$

The ring expansion reaction of SubPcs is a multistep reaction which greatly depends on the nature of the substituents on the SubPcs, the reactivity of the 1,3-diiminoisoindoline, the solvent, and the reaction conditions used. Typically, the reaction proceeds through partial or total fragmentation of the SubPcs followed by statistical ring closure of the fragments. This leads to the formation of a mixture of differently substituted Pcs, hence making purification difficult (Scheme 2.7).$^{23}$
2.1.4 Synthesis of $A_2B_2$-Type Phthalocyanines

In addition to the synthesis of $AB_3$-type asymmetric Pcs, several approaches have been developed for the formation of $A_2B_2$-type (ABAB or AABB) Pcs. In 1990, Young and Onyebuagu reported cross-condensation between 1,3-diiminoisoindoles and 6/7-nitro-1,3,3-trichloroisooindolenine to provide ABAB-type, opposite substituted Pcs in which six of the eight nitrogens on the inner perimeter of the macrocycle were provided by the diiminoisoindole (Scheme 2.8).^24

SCHEME 2.8. Synthesis of ABAB-Type Pcs by Cross-Condensation^24
Two methods have been developed to selectively obtain AABB-type, adjacent substituted, Pcs. The first approach is often referred to as the “lithium method” (Scheme 2.9).\textsuperscript{25,26}

\begin{center}
\includegraphics[width=0.7\textwidth]{scheme29.png}
\end{center}

**SCHEME 2.9. Synthesis of AABB-Type Pcs by Lithium Method**\textsuperscript{26}

Reaction of a Pn containing phenyl groups at the non-peripheral positions with a strong base, such as lithium alkoxide, results in the formation of a half-Pc. Since homocyclization is disfavored by the steric hindrance between neighboring phenyl substituents, the subsequent condensation of a half Pc intermediate with a second type of Pn results in the selective formation of AABB-type Pc.

AABB-type Pcs can be also achieved by side-strapped bisphthalonitriles.\textsuperscript{27,28} In 1994, Leznoff et al. developed a "constrained" approach where bisphthalonitriles linked by 2,2-disubstituted propan-1,3-diol precursors produced pure 1,11,15,25-tetrasubstituted Pc derivatives upon homocyclization (Scheme 2.10).\textsuperscript{29} The difficulty in this approach was that polymerization competed with dimerization. It was found that condensation of
bispenthalonitriles under high dilution and high temperatures for short reaction times led
to the desired AABB-type Pcs.

\[ \text{SCHEME 2.10. Synthesis of AABB-Type Pcs by Side-Strapped Bispenthalonitriles}^{29} \]

2.1.5 ROMP-Capture-Release

Ring-opening metathesis polymerization (ROMP) is olefin metathesis-based
chain-growth polymerization of cyclic olefins such as norbornene or cyclopentene.\(^{30-32}\)
ROMP has been used to provide a wide range of polymers by converting cyclic olefins
into linear polymers containing olefins in the backbone. The concept of ROMP-Capture-
Release was initially introduced by Hanson et al. in 2002 as an approach to facilitate
product purification in the Mitsunobu reaction (Scheme 2.11).\(^{31}\)

\[ \text{SCHEME 2.11. Synthesis of O-Alkylhydroxylamines via ROMP-Capture-Release}^{31} \]
In their contribution, Mitsunobu reaction was first carried out to bond a variety of alcohols onto an oxonorbornenyl \( N \)-hydroxysuccinimide monomer, followed by subjection of the resulting crude reaction mixture to ROMP, giving a polymer, which was precipitated from methanol and isolated from the Mitsunobu byproducts. Treating the corresponding polymer with hydrazine released the targeted \( O \)-alkylhydroxylamines from the water-soluble polymer.

ROMP-Capture-Release strategy was applied to synthesize asymmetric porphyrazines (Pz) by Barrett and Hoffman in 2005 (Scheme 2.12).\(^{33,34}\)

**SCHEME 2.12. Synthesis of Asymmetric Pz via ROMP-Capture-Release\(^ {34}\)**
Norbornyl-tagged diaminomaleonitrile and dipropylmaleonitrile generated crude mixtures of porphyrazines containing diamino-hexapropylporphyrazine magnesium complexes. The resulting mixtures were subjected to ROMP to yield the insoluble diaminoporphyrin-functionalized polymers which were isolated by filtration and extensively washed with CH$_2$Cl$_2$ to remove soluble symmetric B$_4$-type porphyrazine. Subsequent treatment of the corresponding polymers with acid released the asymmetric AB$_3$-type diaminoporphyrin with minimized purification.

Chen et al. previously reported the ROMP-Capture-Release synthesis of asymmetric Pcs with six solubilizing groups and one hydroxyl group on the peripheral position (Scheme 2.13).$^{35}$

\[
\begin{align*}
\text{R} = \text{C}_3\text{H}_7 & + \\
\text{NC} & \text{CN} \\
\text{NC} & \text{CN} \\
\text{OR} & \text{OR} \\
\text{1. Statistical Condensation} & \\
\text{2. ROMP} & \\
\text{3. Acidic Cleavage} & \\
\text{Scheme 2.13. Synthesis of Asymmetric Pc via ROMP-Capture-Release$^{35}$} & \\
\end{align*}
\]

Using crossover-Linstead macrocyclization between Pn and corresponding norbornyl tagged Pn, followed by ROMP with isolation by cleavage under acidic conditions, the asymmetric Pc was obtained with minimal purification. Furthermore, the
remaining hydroxyl group on the molecule was found reactive enough to alkylate, thus opening the possibility for covalently grafting Pcs onto inorganic contacts such as ITO and TiO$_2$.\textsuperscript{12,13}

\subsection*{2.1.6 Research Goals}

We report herein the use of ROMP-Capture-Release to synthesize a small library of asymmetric Pc/Nc hybrids and study of chemical and physical properties of these structurally related asymmetric chromophores (2.2-2.5) and the corresponding symmetric Pc (2.1) and Nc (2.6) in both metalated (Zn) and unmetallated form. The extension of the Pc aromatic core as well as the asymmetry afforded by the unique quadrant can result in modulated physical properties, particularly bathochromic shifted electronic absorption spectra (Scheme 2.14).
The ROMP-Capture-Release method for Pc synthesis entails statistical condensation of a norbornenyl-tagged Pn or Nn (A) and corresponding Pn or Nn (B) in an optimized ratio to provide a mixture of norbornenyl-tagged AB₃ and B₄. ROMP on the resulting mixture in the presence of a cross-linker affords an insoluble matrix of polymer-bound AB₃ chromophore. The polymer tag can be subsequently cleaved under acidic conditions to produce asymmetric AB₃-type Pc. The ROMP-Capture-Release method facilitates the synthesis of asymmetric Pc chromophores by taking advantage of both solution and solid-phase synthetic methods, giving a simplified purification and a reproducible synthetic method.
2.2 Synthesis of Asymmetric Pc Derivatives via ROMP-Capture-Release

The targeted asymmetric Pc/Nc derivatives 2.2-2.5 are composed of several key precursors (Scheme 2.15): phthalonitrile (Pn 2.7), naphthalonitrile (Nn 2.8), norbornenyl-tagged phthalonitrile (T-Pn 2.9), and norbornenyl-tagged naphthalonitrile (T-Nn 2.10).

![Scheme 2.15](image)

**SCHEME 2.15. Key Precursors for the Synthesis of Asymmetric Pc Derivatives**

The embedded benzyl group in the norbornenyl-tagged moieties is cleavable, which enables the release of the resulting asymmetric molecules from the insoluble matrix under acidic conditions. To ensure the targeted asymmetric Pc/Nc hybrids’ solubility in common organic solvents for further analysis, pentylyphenyl groups were also introduced to the Pc periphery. The high solubility of the resulting asymmetric Pc/Nc hybrids was designed to facilitate the characterization of products by NMR and the manipulation by solution phase processing.

Pn derivatives 2.7 and 2.9 were prepared according to literature procedures.\(^\text{35}\) Nn derivatives 2.8 and 2.10 were prepared as shown (Scheme 2.16). Coupling of Nn 2.11\(^\text{36}\) and commercially available \(p\)-pentylyphenol by a nucleophilic aromatic substitution
mechanism under basic conditions, provided Nn \textbf{2.8} in 37% yield. Alkylation of potassium salt Nn \textbf{2.12}\textsuperscript{37} with benzyl chloride \textbf{2.13}\textsuperscript{33} under basic conditions provided norbornenyl-tagged Nn \textbf{2.10} (T-Nn) in 96% yield.

\begin{center}
\begin{化学方程式}
{\text{Nn}}_{2.12} \xrightarrow{\text{HO-}C_8H_{11}, \text{DMF, } Cs_2CO_3, 37\%} {\text{Nn}}_{2.8} \\
{\text{Nn}}_{2.12} \xrightarrow{\text{Nal, DMF, } K_2CO_3, 96\%} {\text{T-Nn}}_{2.10}
\end{化学方程式}
\end{center}

\textbf{SCHEME 2.16. Synthesis of Nn 2.8 and T-Nn 2.10}

\subsection{2.2.1 Macrocyclization Analyzed by MALDI Mass Spectroscopy}

Crossover macrocyclization of Pn \textbf{2.7} and T-Nn \textbf{2.10} under basic conditions in the presence of a metal template was performed initially as a model system and yielded a mixture of symmetric Pn \textbf{2.1a}, asymmetric norbornenyl-tagged Pn \textbf{2.14}, as well as minor products with multiple tags (i.e. A\textsubscript{2}B\textsubscript{2} Pcs, not shown) (Scheme 2.17).
To ensure a high purity product after being cleaved from the insoluble matrix, an optimized ratio of Pn 2.7 (A) to T-Nn 2.10 (B) had to be determined so that the crossover condensation resulted in minimal amounts of A$_2$B$_2$ which contains multiple polymerizable groups. A trend of decreasing amount of A$_2$B$_2$ was observed by matrix-
assisted laser desorption/ionization (MALDI) mass spectroscopy analysis while increasing the ratio of Pn 2.7 (A) to T-Nn 2.10 (B) (Figure 2.1).
Macrocyclization of Pn 2.7 and T-Nn 2.10 in a 1:1 stoichiometric ratio were performed and the crude product mixture was composed of symmetric Pc 2.1a (B₄) as the most abundant product, but with significant amounts of asymmetric 2.14 (AB₃) containing one norbornenyl-tagged group and bis-tagged A₂B₂ (Figure 2.1a). In the case of A:B = 5:1 (Figure 2.1c), the major products were 2.1a and 2.14 with a trace of bis-tagged A₂B₂, presumably as a mixture of adjacent and opposite substituted isomers. Based on the results, a ratio of A:B = 5:1 was employed for all targeted asymmetric chromophores to minimize incorporation of A₂B₂ in the resulting polymer.

Treatment of the crude mixture of symmetric Pc 2.1a (B₄) and norbornenyl-tagged 2.14 (AB₃) with second generation Grubbs’ catalyst in the presence of crosslinker 2.15 provided crosslinked polymeric 2.16 which was insoluble in all organic solvents. Polymer 2.16 was subsequently washed by extensive Soxhlet extraction in DCM for seventy-two hours to remove symmetric Pc 2.1a (B₄). Cleavage under acidic conditions was then accomplished using 10% trifluoroacetic acid in dichloromethane to afford the asymmetric Pc/Nc hybrid 2.3a in 8% yield over three steps. Macrocycles 2.4a and 2.5a were obtained in an analogous manner from Nn 2.8 and norbornyl-tagged T-Pn 2.9 and T-Nn 2.10 (Scheme 2.18).
SCHEME 2.18. Synthesis of Asymmetric Pc Derivatives 2.4a and 2.5a via ROMP-Capture-Release Method
The optimized 5:1 ratio of Nn 2.8 to the corresponding T-Pn 2.9 or T-Nn 2.10 was followed, leading to a trace amount of A₂B₂ derivative incorporated into polymers 2.19 and 2.20 during the crossover condensation. After removal of symmetric Nc 2.6a by Soxhlet extraction, acidic cleavage with 10% trifluoroacetic acid afforded asymmetric Pc/Nc hybrid 2.4a in 10% yield and asymmetric Nc 2.5a in 8% yield after 3 steps.

### 2.2.2 Synthesis of Asymmetric Free-Base Pc Derivatives

Removing the central metal on these molecules was performed to examine the change of physical properties between metallated and metal-free asymmetric chromophores. To prepare the metal-free Pc derivatives, compounds 2.3a-2.6a were allowed to react with pyridine-HCl and pyridine to give the corresponding products 2.3b-2.6b, respectively (Scheme 2.19).
2.2.3 Synthesis of Phosphonic Acid Tethered Pc/Nc Hybrid

The hydroxyl group in the unique quadrant of 2.3-2.5 can be alkylated to introduce functionality to the asymmetric chromophores. For example, phosphonic acid works well as an anchoring group attached to the surface of ITO or TiO$_2$. The remaining hydroxyl group on asymmetric Pc/Nc hybrid 2.4a was efficiently converted to an alkyl phosphonic acid in two steps, thus opening the possibility for grafting Pcs onto oxide substrates (Scheme 2.20).
SCHEME 2.20. Preparation of Phosphonic Acid Tethered Asymmetric Hybrid

Nucleophilic substitution between compound \(2.4a\) and phosphonate \(2.21\) under basic conditions and in the presence of potassium iodide as a catalyst produced phosphonate-tethered asymmetric \(\text{Pc/Nc}\) hybrid \(2.4c\). Trimethylsilyl bromide (TMSBr) was used to convert phosphonate \(2.4c\) into phosphonic acid \(2.4d\), obtained in 66% yield over two steps from \(2.4a\).

2.3 Characterization of Asymmetric Naphthalocyanines and \(\text{Pc/Nc}\) Hybrids

The targeted products were characterized by NMR, UV/Vis spectroscopy (DCM), MALDI mass spectrometry, elemental analysis, and gel permeation chromatography (THF). \(^1\)H and \(^{13}\)C NMR spectra of asymmetric chromophores were recorded in \(\text{CD}_2\text{Cl}_2\) with 5% \(d_6\)-DMSO as co-solvent to prevent aggregation. However, in the \(^1\)H NMR spectra, the aromatic protons were not well resolved as sharp peaks, indicating aggregation of chromophores. In an effort to sharpen the proton signals, additional \(^1\)H spectroscopic NMR experiments under various conditions were performed, such as
adding other co-solvents (e.g. \(d_5\)-pyridine and trifluoroacetic acid), extending the delay time in the pulse sequence, and diluting samples, but no improvement was observed in any case. In the \(^{13}\)C NMR spectra of free-base asymmetric chromophores, the signals of aromatic carbon atoms were unobserved, likely due to aggregation of chromophores. \(^{13}\)C NMR spectra under diluted conditions only showed a few peaks corresponding to the peripheral substituents even after extended scanning.

2.3.1 UV/Vis Absorption Spectroscopy

Metallated compounds 2.1a-2.6a showed characteristic Q and B bands in the UV/Vis absorption spectra (Figure 2.2). The Q band results from the electronic transition from the HOMO (\(a_{1u}\)) to the LUMO (\(e_g\)) of the molecule. The B band arises due to the electronic transition from a deeper level \(\pi\)-orbital, HOMO-1, to the corresponding LUMO.\(^{38,39}\) The absorption spectra of symmetric Pc 2.1a and Nc 2.6a exhibited a singlet Q band due to structural symmetry at 681 and 763 nm, respectively, with the bathochromic shift from 2.1a to 2.6a related to the greater conjugation in the Nc chromophore. Based upon the UV/Vis absorption spectra of 2.3a-2.5a, a 25 nm bathochromic shift was observed per additional benzene ring attached to central core due to the extended conjugation. The UV/Vis spectra of lower symmetry analogs 2.3a and 2.5a, showed a split Q-band, which was attributed to the electronic transition from HOMO to a doubly non-degenerate LUMO and LUMO+1.\(^{40}\) However, low symmetry analog Pc/Nc hybrid 2.4a, showed a sharp singlet Q band in the UV/Vis spectrum, indicating that the LUMO and LUMO+1 are likely coincidentally degenerate.
The metal-free Pc derivatives are relatively lower in symmetry, and the corresponding LUMO levels ($b_{3g}$, $b_{2g}$) are no longer degenerate, causing two possible electronic transitions and hence a more complex Q band. Metal-free compounds 2.1b-2.6b also showed characteristic Q and B bands in the UV/Vis absorption spectra (Figure 2.2). Similar to the metallated derivatives, a 25 nm bathochromic shift was also observed per additional benzene ring attached to central core. Due to the loss of the central metal, the asymmetric Pcs 2.1b and 2.2b exhibited a split Q band at around 700 and 670 nm. The UV/Vis spectra of asymmetric Pc/Nc hybrids 2.3b and 2.4b exhibited multiple Q band absorptions which are attributed to both the loss of the central metal and its structurally low symmetry as well as the presence of two proton tautomeric forms of each chromophore. Asymmetric Nc 2.5b showed a split and broad Q band at 783 and 727 nm suggesting the presence of aggregation due to both the $\pi-\pi$ interaction and intermolecular
hydrogen bonding. However, the relatively low symmetry analog compared to symmetrically metallated Nc 2.6a, symmetrically metal-free Nc 2.6b, only showed a sharp singlet Q band in the UV/Vis spectrum, indicating that the LUMO and LUMO+1 might be coincidentally degenerate.

In contrast to alcohol 2.4a and phosphonate 2.4c, a significantly broad Q band near 733 nm for the phosphonic acid tethered asymmetric Pc/Nc hybrid 2.4d was observed (Figure 2.3). It is likely that the presence of the phosphonic acid group results in aggregation.

FIGURE 2.3. UV/Vis Absorption Spectra of Chromophores 2.4a, 2.4c, and 2.4d

2.4 Conclusion
We have demonstrated the synthesis of asymmetric Pc/Nc hybrids and asymmetric Ncs using the ROMP-Capture-Release strategy as a simple and general route. To achieve this goal, statistical condensation of norbornenyl-tagged T-Pn or T-Nn (A) and the corresponding Pn or Nn (B) in an optimized ratio led to a mixture of norbornenyl-tagged AB₃ and symmetric B₄. Subsequent ROMP on the resulting mixture was carried out in the presence of a cross-linker, which led to an insoluble matrix of polymer-tagged AB₃. The polymer tag was subsequently cleaved under acidic conditions to produce asymmetric AB₃-type Pc/Nc hybrid. The ROMP-Capture-Release method facilitated the synthesis of asymmetric Pc/Nc chromophores by taking advantage of both solution and solid-phase synthesis methods, giving the simplified purification and a reproducible synthetic route. This methodology effectively eliminates the significant formation of symmetric Pc and Nc as side products. In addition, the extension of the Pc aromatic core does result in perturbed molecular properties, particularly bathochromically shifted electronic absorption.

2.5 Experimental Section

All reactions were run under a nitrogen or argon atmosphere unless otherwise noted. All chemicals were purchased from commercial sources and used without further purification unless otherwise noted. Compounds 2.1a, 2.1b, 2.2a, 2.2b, 2.7, 2.9, 2.11, 2.12, 2.13, 2.15, and 2.21 were prepared according to the literature.¹²,³⁵-³⁷ DMSO was dried over freshly activated 4 Å molecular sieves. Anhydrous CH₂Cl₂ was distilled from CaH₂ under argon. Anhydrous THF was distilled from sodium and benzophenone under
argon. $^1$H NMR / $^{13}$C NMR spectra were recorded on commercially available instrumentation. $^1$H NMR spectra were obtained in either CDCl$_3$ or CD$_2$Cl$_2$:DMSO-$d_6$ (95:5) as noted and calibrated using residual CHCl$_3$ ($\delta = 7.26$ ppm) or CHDCl$_2$ ($\delta = 5.32$ ppm) as an internal reference respectively, with chemical shifts reported in ppm from TMS. $^{13}$C NMR spectra were obtained either in CDCl$_3$ or CD$_2$Cl$_2$:DMSO-$d_6$ (95:5) as noted and calibrated using CDCl$_3$ ($\delta = 77.0$ ppm) or CD$_2$Cl$_2$ ($\delta = 53.8$ ppm) as an internal reference, respectively. Gel permeation chromatography (GPC) was performed in a CH$_2$Cl$_2$ mobile phase on two Jordi FlashGel DVB columns 500Å (10 mm × 500 mm) operating at 3 mL/min. UV/Vis spectroscopy was performed using a Shimadzu UV-2401PC spectrometer. Mass spectra were obtained from the Mass Spectrometry Facility, Department of Chemistry and Biochemistry, the University of Arizona. Combustion analyses were performed by NuMega Resonance Labs Inc., San Diego, CA. Flash column chromatography and TLC were performed using silica gel 60 and Silica Gel 60 F$_{254}$ plates respectively from EMD.

**Asymmetric Pc/Nc Hybrid Zn-3Pn/1T-Nn (2.3a)**

A mixture of Pn 2.7 (1.91 g, 4.22 mmol), T-Nn 2.10 (343 mg, 0.844 mmol), DBU (0.771 g, 5.06 mmol), Zn(OAc)$_2$ (232 mg, 1.27 mmol), and 70 mL 1-pentanol was heated at reflux under Ar for 10 h. The reaction mixture was allowed to cool to RT, poured into methanol, and the resulting precipitate was filtered, washed with methanol, air dried and then chromatographed (SiO$_2$, 100% CH$_2$Cl$_2$). The green elution was collected and concentrated in vacuum. The resulting green residue (containing 2.1a and 2.14) (1.47 g),
and crosslinker 2.15 (0.147 g, 0.560 mmol) were dissolved in dry CH₂Cl₂ (20 mL) under Ar. To this solution was added 2nd generation Grubbs’ catalyst (4 mg, 5 μmol), and the mixture was maintained at reflux for 6 h. A combination of CH₂Cl₂ (3.0 mL), CH₃CN (1.5 mL), and ethyl vinyl ether (1.5 mL) was added, and the resulting mixture was heated to 40 °C for another 1 h. The mixture was filtered and the insoluble cross-linked polymer was washed with CH₂Cl₂ (100 mL) and further extracted with CH₂Cl₂ ( Soxhlet) for 72 h. To the resulting polymer (2.16) CH₂Cl₂ (20 mL) and trifluoroacetic acid (2 mL) was added, and the mixture was allowed to stir at RT under Ar for 1 h. The reaction mixture was then washed with water (20 mL), saturated aqueous NaHCO₃ (20 mL), and the organic layer was dried over MgSO₄, filtered, and concentrated in vacuum. The crude product was purified by flash column chromatography (SiO₂, 5% methanol in CH₂Cl₂) to give compound 2.3a (103 mg, 8% yield based on T-Nn 2.10) as a green solid: ¹H NMR (500 MHz, 5% DMSO-d₆ in CD₂Cl₂) δ 9.48 (br s, 1H), 9.19 (s, 1H), 9.11 (s, 1H), 8.59 (dd, J = 16.1, 3.2 Hz, 6H), 8.18 (d, J = 8.8 Hz, 1H), 7.69 (s, 1H), 7.45 (dd, J = 8.7, 2.3 Hz, 1H), 7.34 – 7.13 (m, 24H), 2.66 (m, 12H), 1.77 – 1.59 (m, 12H), 1.48 – 1.31 (m, 24H), 1.02 – 0.87 (m, 18H); ¹³C NMR (125 MHz, 5% DMSO-d₆ in CD₂Cl₂) δ 156.9, 156.4, 156.39, 156.36, 156.0, 155.2, 154.8, 152.5, 152.2, 151.8, 150.7, 150.4, 150.2, 150.1, 149.9, 149.8, 149.7, 138.6, 138.2, 138.1, 138.17, 138.08, 138.0, 136.5, 136.3, 136.0, 134.6, 134.4, 134.38, 134.2, 133.4, 131.9, 130.1, 130.07, 130.0, 129.9, 129.1, 128.6, 125.7, 122.4, 120.5, 120.3, 119.0, 118.5, 118.4, 118.3, 118.26, 114.3, 113.5, 111.7, 35.7, 35.65, 35.6, 34.5, 32.1, 32.0, 31.8, 30.5, 30.1, 29.6, 23.0, 22.99, 21.2, 14.30, 14.31; MS
Asymmetric Pc/Nc Hybrid H-3Pn/1T-Nn (2.3b)

A mixture of compound 2.3a (0.100 g, 61.8 μmol), pyridine-HCl (3.00 g, 26.0 mmol), and 6 mL pyridine was stirred and heated at 120 °C under Ar for 18 h. The reaction was removed from the heat, and water (10 mL) was added immediately. The resulting precipitate was collected by centrifugation and washed with water, methanol, and dried under high vacuum. The crude product was purified by flash column chromatography (SiO2, 100% CH2Cl2) to give compound 2.3b (50.1 mg, 52% yield) as a green solid: 1H NMR (500 MHz, 5% DMSO-d6 in CD2Cl2) δ 9.10 (br s, 1H), 8.69 (br s, 3H), 8.24 (br s, 6H), 8.01 (br s, 2H), 7.46 (br s, 3H), 7.28 (m, 23H), 2.70 (m, 12H), 1.74 (m, 12H), 1.47 (m, 24H), 1.02 (m, 18H); MS (MALDI) m/z: [M]+ Calcd for C102H104N8O7: 1552.803. Found 1552.742; Anal. Calcd for C102H104N8O7: C, 78.84; H, 6.75; N, 7.21. Found: C, 78.44; H, 7.15; N, 7.11.

Asymmetric Pc/Nc Hybrid Zn-3Nn/1T-Pn (2.4a)

Following the procedure for compound 2.3a, Nn 2.8 (1.20 g, 2.39 mmol), T-Pn 2.9 (0.170 g, 0.477 mmol), DBU (0.436 g, 2.87 mmol), Zn(OAc)2 (0.175 g, 0.955 mmol), and 30 mL 1-pentanol gave compound 2.4a (81.0 mg, 10% yield based on T-Pn 2.9) as a green solid: 1H NMR (500 MHz, 5% DMSO-d6 in CD2Cl2) δ 9.26 – 9.16 (br s, 1H), 9.09 – 8.98 (br s, 1H), 8.98 – 8.87 (br s, 1H), 8.82 (br s, 2H), 8.76 – 8.58 (m, 2H), 8.52 – 8.40
Asymmetric Pc/Nc Hybrid H-3Nn/1T-Pn (2.4b)

Following the procedure for compound 2.3b, compound 2.4a (40.5 mg, 23.6 μmol), pyridine-HCl (1.50 g, 13.0 mmol), and 3 mL pyridine gave compound 2.4b (22.2 mg, 57% yield) as a green solid: \(^1\)H NMR (500 MHz, 5% DMSO-\(d_6\) in CD\(_2\)Cl\(_2\)) \(\delta\) 8.04 – 6.66 (br m, 32H), 2.61 (br m, 12H), 1.70 – 1.34 (br m, 36H), 0.87 (br m, 18H); MS (MALDI) \(m/z\): [M]\(^+\) Calcd for C\(_{110}\)H\(_{106}\)N\(_8\)O\(_7\)Zn: C, 76.93; H, 6.22; N, 6.52. Found: C, 76.98; H, 6.51; N, 6.49.

Asymmetric Phosphonate Tethered Pc/Nc Hybrid Zn-3Nn/1T-Pn (2.4c)

A mixture of compound 2.4a (0.240 g, 0.139 mmol), KI (11.6 mg, 69.6 μmol), anhydrous K\(_2\)CO\(_3\) (28.9 mg, 0.209 mmol), diethyl(10-bromodecyl)phosphonate 2.21 (74.6 g, 0.209 mmol), and anhydrous DMF (5 mL) was stirred at 120 °C for 2 h under Ar. To the resulting mixture methanol (5 mL) and water (5 mL) was added to give a precipitate. The crude product was collected by centrifugation and purified by flash column chromatography (SiO\(_2\), 5% methanol in CH\(_2\)Cl\(_2\)) to give phosphonate 2.4c (0.200 g, 72% yield) as a green solid: \(^1\)H NMR (500 MHz, 5% DMSO-\(d_6\) in CD\(_2\)Cl\(_2\)) \(\delta\) 8.87 – 7.01 (br m, 38H), 4.45 – 3.48 (br m, 6H), 2.11 – 1.00 (br m, 90H); \(^{31}\)P NMR (202 MHz, (br s, 1H), 7.79 (m, 3H), 7.67 (m, 3H), 7.49 (m, 1H), 7.41 – 7.05 (m, 25H), 2.81 – 2.63 (m, 12H), 1.75 (m, 12H), 1.44 (m, 24H), 1.06 – 0.90 (m, 18H); MS (MALDI) \(m/z\): [M]\(^+\) Calcd for C\(_{110}\)H\(_{106}\)N\(_8\)O\(_7\)Zn: C, 76.93; H, 6.22; N, 6.52. Found: C, 76.98; H, 6.51; N, 6.49.

**Asymmetric Phosphonic Acid Tethered Pc/Nc Hybrid Zn-3Nn/1T-Pn (2.4d)**

A solution of compound 2.4c (0.200 g, 0.100 mmol), trimethylsilyl bromide (0.154 g, 1.00 mmol), and 5mL CH₂Cl₂ was stirred at RT for 18 h under Ar. To the resulting mixture methanol (5 mL) and water (5 mL) was added to give a precipitate. The crude product was collected by centrifugation and washed with acetone twice to give phosphonic acid 2.4d (0.179 g, 92% yield) as a green solid: ¹H NMR (500 MHz, 5% DMSO-d₆ in CD₂Cl₂) δ 7.17 (br m, 38H), 4.14 (br s, 12H), 2.71 (br s, 12H), 1.72 – 0.96 (br m, 64H); ³¹P NMR (202 MHz, CDCl₃) δ 32.50; MS (MALDI) m/z: [M]⁺ Calcd for C₁₂₀H₁₂₇N₈O₁₀PZn 1934.870. Found 1934.881.

**Asymmetric Metallated Naphthalocyanine (2.5a)**

Following the procedure for compound 2.3a, Nn 2.8 (3.81 g, 7.59 mmol), T-Nn 2.10 (0.617 g, 1.52 mmol), DBU (1.39 g, 9.11 mmol), Zn(OAc)₂ (0.556 g, 3.04 mmol), and 30 mL 1-pentanol gave compound 2.5a (210 mg, 8% yield based on T-Nn 2.10) as a green solid: ¹H NMR (500 MHz, 5% DMSO-d₆ in CD₂Cl₂) δ 7.36 – 6.86 (br m, 37H), 2.70 (br m, 12H), 1.72 – 1.26 (br m, 36H), 0.95 (br m, 18H); MS (MALDI) m/z: [M]⁺ Calcd for C₁₁₄H₁₀₈N₈O₇Zn 1764.763. Found 1764.545; Anal. Calcd for C₁₁₄H₁₀₈N₈O₇Zn: C, 77.47; H, 6.16; N, 6.34. Found: C, 77.70; H, 6.31; N, 6.31.
Asymmetric Metal-Free Naphthalocyanine (2.5b)

Following the procedure for compound 2.3b, compound 2.5a (0.100 g, 56.6 μmol), pyridine-HCl (3.00 g, 0.477 mmol), and 6 mL pyridine gave compound 2.5b (53.0 mg, 55% yield) as a green solid: \(^1\)H NMR (500 MHz, 5% DMSO-\(d_6\) in CD\(_2\)Cl\(_2\)) \(\delta\) 8.04 – 6.48 (br m, 34H), 2.10 – 0.84 (br m, 66H); MS (MALDI) \(m/z\): [M]\(^+\) Calcd for C\(_{114}\)H\(_{110}\)N\(_8\)O\(_7\) 1702.850. Found 1702.949; Anal. Calcd for C\(_{114}\)H\(_{110}\)N\(_8\)O\(_7\): C, 80.35; H, 6.51; N, 6.58. Found: C, 79.96; H, 6.91; N, 6.31.

Symmetric Metallated Naphthalocyanine (2.6a)

A solution of CH\(_2\)Cl\(_2\) used to clean the insoluble cross-linked polymers from making compound 2.4a and 2.5a was collected and concentrated under reduced pressure. The crude product was purified by flash column chromatography (SiO\(_2\), 100% CH\(_2\)Cl\(_2\)) to give compound 2.6a as a green solid: \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.81 (br s, 8H), 7.68 (br s, 8H), 7.29 (d, \(J = 8.5\) Hz, 16H), 7.18 (d, \(J = 8.4\) Hz, 16H), 2.71 (t, \(J = 8.5\) Hz, 16H), 1.79 – 1.63 (m, 16H), 1.50 – 1.33 (m, 32H), 1.05 – 0.85 (m, 24H); MS (MALDI) \(m/z\): [M]\(^+\) Calcd for C\(_{136}\)H\(_{136}\)N\(_8\)O\(_8\)Zn 2072.977. Found 2072.742; Anal. Calcd for C\(_{136}\)H\(_{136}\)N\(_8\)O\(_8\)Zn: C, 78.68; H, 6.60; N, 5.40. Found: C, 78.28; H, 6.70; N, 5.37.

Symmetric Metal-Free Naphthalocyanine (2.6b)

Following the procedure for compound 2.3b, compound 2.6a (0.100 g, 48.2 μmol), pyridine-HCl (3.00 g, 26.0 mmol), and 6 mL pyridine gave compound 2.6b (59.1
mg, 61% yield) as a green solid: $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.47 (br s, 8H), 7.42 (br s, 8H), 7.37 – 7.10 (m, 34H), 2.77 (t, $J = 7.4$ Hz, 16H), 1.81 (m, 16H), 1.59 – 1.46 (m, 32H), 1.05 (t, $J = 6.6$ Hz, 24H); MS (MALDI) m/z: [M]$^+$ Calcd for C$_{136}$H$_{138}$N$_8$O$_8$ 2011.064. Found 2011.205; Anal. Calcd for C$_{136}$H$_{138}$N$_8$O$_8$: C, 81.16; H, 6.91; N, 5.57. Found: C, 81.36; H, 7.31; N, 5.74.

6,7-Bis(4-pentylphenoxy)naphthalene-2,3-dicarbonitrile (2.8)

A mixture of anhydrous K$_2$CO$_3$ (11.1 g, 80.0 mmol), 4-pentylphenol (3.61 g, 22.0 mmol), 6,7-dibromonaphthalene-2,3-dicarbonitrile 2.11 (3.36 g, 10.0 mmol), and anhydrous DMF (60 mL) was stirred at 100 °C for 18 h under Ar. The reaction mixture was cooled to room temperature and poured into water (200 mL). The solution was extracted with CH$_2$Cl$_2$ (3×100 mL), and the combined organic layers were dried over MgSO$_4$ and filtered. The filtrate was concentrated in vacuum and purified by flash column chromatography (SiO$_2$, 20% ethyl acetate in hexanes) to give Nn 2.8 (1.85 g, 37% yield) as a white solid: $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.03 (s, 2H), 7.26 (m, 4H), 7.18 (s, 2H), 7.07 (m, 4H), 2.67 – 2.62 (m, 4H), 1.70 – 1.62 (m, 4H), 1.36 (dd, $J = 7.2$, 3.7 Hz, 8H), 0.92 (dd, $J = 8.4$, 5.7 Hz, 6H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 152.7, 152.6, 140.3, 133.9, 130.1, 130.1, 120.1, 116.0, 113.2, 108.8, 35.3, 31.5, 31.2, 22.5, 14.1; MS (MALDI) m/z: [M + H]$^+$ Calcd for C$_{34}$H$_{35}$N$_2$O$_2$ 503.270. Found 503.269.

6-((4-((1R,4R)-bicyclo[2.2.1]hept-5-en-2-ylmethoxy)benzyl)oxy)naphthalene-2,3-dicarbonitrile (2.10)
A mixture of anhydrous \( \text{K}_2\text{CO}_3 \) (0.980 g, 7.10 mmol), NaI (1.03 g, 7.10 mmol), potassium 6,7-dicyanonaphthalen-2-olate 2.12 (1.65 g, 7.10 mmol), norbornenyl tagged benzyl chloride 2.13 (1.77 g, 7.10 mmol), and anhydrous DMF (70 mL) was stirred at 75 °C for 18 h under Ar. The reaction mixture was cooled to room temperature and poured into water (200 mL). The solution was extracted with \( \text{CH}_2\text{Cl}_2 \) (3\( \times \)100 mL), and the combined organic layers were dried over MgSO\(_4\) and filtered. The filtrate was concentrated in vacuum and purified by flash column chromatography (SiO\(_2\), 100% \( \text{CH}_2\text{Cl}_2 \)) to give T-Nn 2.10 (2.76 g, 96% yield) as a white solid: \(^1\text{H} \text{NMR (500 MHz, CDCl}_3\)) \(\delta\) 8.21 (d, \(J = 27.7\) Hz, 2H), 7.87 (d, \(J = 9.1\) Hz, 1H), 7.46 (dd, \(J = 9.0, 2.1\) Hz, 1H), 7.38 (t, \(J = 8.6\) Hz, 2H), 7.29 (s, 1H), 6.96 (d, \(J = 8.5\) Hz, 1H), 6.92 (d, \(J = 8.6\) Hz, 1H), 6.20 – 6.13 (m, 1H), 6.12 (s, 1H), 5.95 (dd, \(J = 5.6, 2.8\) Hz, 1H), 5.15 (d, \(J = 5.0\) Hz, 2H), 4.05 (dd, \(J = 9.1, 6.1\) Hz, 1H), 3.86 (t, \(J = 9.1\) Hz, 1H), 3.73 (dd, \(J = 9.0, 6.5\) Hz, 1H), 3.56 (t, \(J = 9.1\) Hz, 1H), 3.04 (s, 1H), 2.86 (d, \(J = 9.4\) Hz, 1H), 2.57 (dd, \(J = 9.8, 4.3\) Hz, 1H), 1.96 – 1.87 (m, 1H), 1.55 (s, 1H), 1.49 (d, \(J = 8.3\) Hz, 1H), 1.37 (d, \(J = 7.7\) Hz, 1H), 1.31 (d, \(J = 8.3\) Hz, 1H), 1.25 (d, \(J = 11.5\) Hz, 1H), 0.66 – 0.59 (m, 1H); \(^{13}\text{C} \text{NMR (125 MHz, CDCl}_3\)) \(\delta\) 160.4, 159.5, 137.6, 136.9, 136.4, 135.4, 135.1, 134.3, 132.3, 130.3, 129.4, 128.7, 127.1, 124.1, 116.2, 114.8, 110.7, 107.6, 72.4, 71.6, 70.5, 49.4, 45.0, 43.8, 42.2, 41.6, 38.4, 29.7, 29.0 ppm; MS (MALDI) \(m/z\): [M + Na]\(^+\) Calcd for \( \text{C}_{27}\text{H}_{22}\text{N}_2\text{O}_2\text{Na}\) 429.16. Found 429.16; Anal. Calcd for \( \text{C}_{27}\text{H}_{22}\text{N}_2\text{O}_2\): C, 79.78; H, 5.46; N, 6.89. Found: C, 79.35; H, 5.80; N, 7.05.

2.6 References


CHAPTER 3
CLICK CHEMISTRY MODIFICATION OF ASYMMETRICALLY ALKYNE-
FUNCTIONALIZED PHTHALOCYANINES

3.1 Introduction

Phthalocyanines (Pcs) are 18 π-electron tetrapyrrolic macrocycles and highly
conjugated synthetic porphyrin analogues that exhibit high extinction coefficients, hole
mobility, and strong π-π interactions. Due to their unique physical and chemical
properties, Pcs have been applied in a number of advanced technologies including optical
limiting devices, photodynamic therapy (PDT), organic field-effect transistors
(OFETs), and organic photovoltaic (OPV) devices. Near-IR-absorbing and emitting
Pcs, in particular, have potential application in both detecting and treating cancer since
mammalian tissues are transparent in the near-IR spectrum (700–900 nm). These
molecules are also used as xerographic materials, in photovoltaic windows, and in
organic solar cells. These applications require optimization of chemical, physical, and
photophysical properties such as absorption, solubility, partition ratio, and
electrochemical potentials. Though there are many reports on the modification of Pcs, a general method remains scarce. A practical route for Pc modification would (1) allow modification with substituents that otherwise would not survive the Linstead cyclization conditions; and (2) be amenable to scale up. The Cu-catalyzed azide–alkyne
cycloaddition (CuAAC) “click” reaction has recently been demonstrated as a mild and
straightforward method for functional modification of Pcs.
McGrath and coworkers have disclosed the modification of Pc chromophores with click chemistry and the subsequent use of installed functional groups to create robust cross-linked photo-patterned and imprinted nanostructures.\textsuperscript{40} In 2010, Rowan et al. described the synthesis and photophysical characterization of a series of phthalocyanine-perylene diimide (Pc-PDI) octad molecules in which eight perylene moieties were attached to a Pc core with different linkers.\textsuperscript{41} Notably, a correlation between intermolecular aggregation and the presence of long-lived excitations on the Pc cores was observed in this disclosure.

In 2011, we reported the use of an symmetrically octaalkynyl-substituted Pc precursor for the creation of a small library of peripherally substituted Pc derivatives by click chemistry methodology (Scheme 3.1).\textsuperscript{42}
In this disclosure, a near-IR absorbing soluble Pc bearing eight alkyne moieties as side chains of the chromophore with suitable length of alkyne-linker was designed to be soluble in most organic solvents (e.g., CH₂Cl₂, CHCl₃, and THF). Substitution at the β (peripheral) positions of Pcs with arylthio moieties generally shift the absorption towards the near-IR region around 30 nm relative to analogous aryloxy-substituted Pcs. The resulting Pc was used as a scaffold for functional modification using alkyne-azole click chemistry with various azides, leading to a small library of Pcs bearing photo-crosslinkable, dendritic, and hydrophilic moieties starting from a single Pc molecule.

In addition to symmetrically substituted Pcs, of particular interest is the development of asymmetrically substituted AB₃ Pcs, which can possess improved photodynamic properties and unique second-order nonlinear optical effects. Asymmetric AB₃-type Pcs containing active functional groups in the odd quadrant such as hydroxy, amino, carboxylic acid, isothiocyanate, azide, and alkyne serve as building blocks in the design of phthalocyanine-based molecular systems. Recently, we have used asymmetric AB₃ Pcs as components of a model system to investigate charge capture at oxide interfaces from typical OPV donor materials. However, efficient production and purification of Pc materials with structural diversity, including AB₃ asymmetry, still remains an open challenge, especially for Pcs with sensitive substituents that are not compatible with the conditions of cyclization of Pc precursors.
In light of the previous success in the production of symmetrically substituted Pc derivatives via click chemistry, Chen from the McGrath group had made some attempts on the synthesis of asymmetrically modified Pc chromophores using an CuAAC reaction (Scheme 3.2).

**SCHEME 3.2. Attempts at the Synthesis of Asymmetrically Modified Pc Chromophores through Click Chemistry**

However, an inefficient metal-insertion was observed by both MS-MALDI and UV-Vis during the synthesis, leading to a mixture of metallated and metal-free Pc. Neither increasing the stoichiometric equivalents of metal template nor prolonged reaction times were successful in driving the metal-insertion to completion.
3.2 Research Goals

The behavior of Pcs as materials is highly dependent on short- and long-range organization of the molecules induced by either self-assembly (bottom-up)\textsuperscript{21,59} or nano-patterning (top-down) approaches,\textsuperscript{40,60} both of which can be facilitated by the modification of Pcs with suitable functional groups. Therefore, the application of Pcs for advanced technologies demands synthetic methods that can generate numerous precisely tailored Pc derivatives with high fidelity. This chapter details the investigation of using an asymmetric Pc as the platform for the preparation of a small library of zinc hexatriazolyl-monohydroxyphthalocyanines via click chemistry (Scheme 3.3). Monitoring the CuAAC reaction by both UV-Vis and FT-IR spectroscopies was performed to provide insight into the role of azide equivalent, reaction time, and catalyst on reaction progress.
3.3 Click Chemistry Modification of Asymmetrically Alkyne-Functionalized Pc

Herein, we report the modification of asymmetrically clickable hexaalkynyl AB$_3$-type Pc through the CuAAC reaction. We have previously reported the macrocyclization of alkyne-containing phthalonitriles (Pn) under basic Linstead conditions afforded symmetric alkylnyl Pc which possesses good solubility in common organic solvents such as THF, DCM, acetone, and Et$_2$O$^{40,42}$ Protection of the terminal alkyne moieties was not necessary during the macrocyclization reaction, providing a relatively simple way to incorporate acetylenic moieties into a Pc scaffold.

Recent work in the McGrath group has utilized statistical cyclization but with a modification aimed at simplifying asymmetric Pc purification. We have described the
synthesis of asymmetric AB$_3$-type Pcs by statistical macrocyclization using 4-methoxybenzyl (PMB)-protected Pn$^{58}$ to yield asymmetric AB$_3$ Pcs with a unique phenolic quadrant that can be more readily isolated. Clickable AB$_3$-type Pc 3.6 was prepared accordingly via statistical macrocyclization bis(alkynyl) Pn 3.2 of and PMB-protected Pn 3.3, followed by deprotection using acidic conditions (Scheme 3.4).$^{58}$

![Scheme 3.4](image)

**SCHEME 3.4. Synthesis of Asymmetrically Clickable Pc 3.6**

Statistical macrocyclization of bis(alkynyl) Pn 3.2$^{40}$ and PMB-protected Pn 3.3$^{58}$ ($3.2:3.3 = 3:1$) in the presence of 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU) as a base and zinc acetate (Zn(OAc)$_2$) as a metal template provided a chromatographically inseparable mixture of asymmetrically PMB-protected AB$_3$-type Pc 3.4 and symmetric B$_4$-type Pc 3.5. The crude mixture was chromatographed to remove DBU and excess metal salt from the crude Pc mixture. MALDI mass spectral analysis of the obtained
crude mixtures revealed the presence of PMB-protected Pc 3.4 and symmetric Pc 3.5. Subjecting the mixtures to PMB deprotection conditions, 10% trifluoroacetic acid (TFA) in DCM, yielded a mixture of symmetric Pc 3.5 and asymmetrically clickable Pc 3.6. Due to the increased polarity afforded by the unique phenolic quadrant in the asymmetric AB3-type Pc, the resultant mixture was easily separable by flash chromatography to provide the desired macrocycle 3.6, in an overall yield of 20% from Pn 3.3.

3.3.1 Modification of Asymmetric Pcs via Click Chemistry

Modification of the periphery of asymmetric Pc 3.6 chromophore with CuAAC click chemistry was examined (Scheme 3.5).

**SCHEME 3.5. Click Reaction between Asymmetric Pc 3.6 and Azide 3.7a-3.7d**
We expected that zinc-metallated clickable Pc 3.6 would prevent the inherent copper-insertion reaction in the preparation of clicked Pcs and therefore allow the use of a sub-stoichiometric amount of copper catalyst. Similar conditions described in previous literature were first applied to reactions with azide 3.7a-3.7c (CuI/DIPEA/THF). Due to the poor solubility of perylene azide 3.7d in THF, the synthesis of clicked Pc 3.1d was carried out in CHCl₃ instead. Using a 10:1 azide-alkyne ratio under these conditions, a reaction time at ambient temperature of sixteen hours was sufficient to provide hexatriazenyl Pc 3.1a-3.1d in yields of 24~44% from clickable Pc 3.6.

### 3.3.2 Characterization of Asymmetric Pcs

Asymmetrically clicked Pcs 3.1a-3.1d were readily soluble in CH₂Cl₂, CHCl₃, and THF; hence the purification was accomplished by a combination of precipitation and flash chromatography. Asymmetrically clicked Pcs 3.1a-3.1d were structurally characterized by MALDI mass spectrometry, combustion analysis, and UV/Vis spectroscopy. ¹H and ¹³C NMR spectra of clicked Pcs were recorded in CD₂Cl₂ with 5% d₆-DMSO as co-solvent to prevent aggregation. However, in ¹H NMR spectra, the aromatic protons were not well resolved as sharp peaks indicating aggregation of chromophores. In an effort to sharpen the proton signals, additional ¹H NMR spectroscopic experiments under various conditions were performed, such as adding other co-solvents (e.g. d₅-pyridine and trifluoroacetic acid), extending the delay time in the pulse sequence and diluting samples, but no improvement was observed in all cases.
In $^{13}$C NMR spectra of all clicked Pcs, the signals of aromatic carbon atoms were unobserved, likely due to aggregation of chromophores. $^{13}$C NMR spectra under diluted conditions only showed a few peaks corresponding to the peripheral substituents even after 24 h.

The appearance of the Q and B bands in the UV/Vis spectra were similar for all clicked Pcs and clickable precursor 3.6, consistent with the identical nature of the central Pc chromophore in all five compounds (Figure 3.1).

![UV/Vis Absorption Spectra of Pc 3.6 and 3.1a-3.1d (ca. 10 μM in CHCl₃), Normalized at Q-Band $\lambda_{max}$](image)

The UV/Vis absorption spectra exhibited a singlet Q-band at around 685 nm, indicating the existence of metallated Pcs. Clicked Pc 3.1d showed absorption at 530,
490, and 460 nm due to the incorporation of chromophoric perylenediimides (PDIs). No charge transfer bands were evident at longer wavelengths, indicating lack of electronic communication between the Pc and PDI chromophores.

3.3.3 Impact of Catalyst and Stoichiometry on Click Reaction

Monitoring of the click reaction above indicated poor solubility of the copper catalyst. Continuous stirring was employed due to the heterogeneous nature of the reaction mixture. Our intent to use this click process to ultimately modify Pcs on solid surfaces, such as ITO and TiO$_2$,\textsuperscript{58,61} led us to explore the use of a more soluble catalyst which would be amenable to use in a flow through apparatus for surface deposition and subsequent spectroelectrochemical studies. Soluble copper source Cu(PPh$_3$)$_3$Br\textsuperscript{40} was compared with CuI in side by side reactions between clickable Pc \textbf{3.6} and perylene azide \textbf{3.7d}. Both reactions were followed by UV/Vis spectroscopy on isolated product mixtures at selected time intervals (Figure 3.2).
FIGURE 3.2. UV/Vis Absorption Spectra Normalized upon Pc Q-Band of Isolated Clicked Products (ca. 10 μM in CHCl$_3$) after Indicated Reaction Times Using (a) CuI and (b) Cu(PPh$_3$)$_3$Br as Catalysts.
The quenched mixture was purified by flash column chromatography to remove excess azide 3.7d and isolate the resulting Pc containing species. UV/Vis spectra were normalized to the absorbance of the Pc Q-band to indicate the increase of perylene chromophore absorption ($\lambda = 530$ nm) from the clicked products. A plot of $A_{530}/A_{685}$ ratio of perylene to Pc Q-band absorbance for both catalysts indicates the perylene absorbance arriving at a constant similar value within ten hours (Figure 3.3). The $A_{530}/A_{685}$ ratio reached 2.68 and 2.66 for CuI and Cu(PPh$_3$)$_3$Br catalyzed click reactions, respectively. Two fitting curves shown in Figure 3.3 were generated by KaleidaGraph using the exponential rise method.

FIGURE 3.3. The Perylene Absorbance at 530 nm Normalized to Pc Q-Band Absorbance at 680 nm with Reaction Time for CuI and Cu(PPh$_3$)$_3$Br as Catalyst
Both curves suggest that the progression of the click reaction was complete after six hours under those reaction conditions. Visual inspection of the click reaction at the various time points showed a clear progression of color as more perylenes were incorporated on the Pc periphery (Figure 3.4).

FIGURE 3.4. Digital Image of Isolated Mixtures at Selected Time Intervals (ca. 100 μM in CHCl₃): 1 h, 2 h, 3 h, 6 h, 50 h (Left to Right), Catalyzed by Cu(PPh₃)₃Br

Monitoring of the click reaction by FT-IR also showed reaction progress and verified consumption of the terminal alkyne moieties by disappearance of the peaks including $sp$-hybridized C-H stretching at 3291 cm$^{-1}$ and C-C triple bond stretching at 2119 cm$^{-1}$ (Figure 3.5).
FIGURE 3.5. FT-IR Spectra of Clickable Pc 3.6 (Top) and Clicked Pc 3.1d at the Reaction Time of Six Hours (Bottom), Using Cu(PPh$_3$)$_3$Br as Catalyst

The impact of the number of azide equivalents on the modification of asymmetrically clickable Pc 3.6 was also studied in a similar fashion to the copper source. Keeping all other reaction conditions constant (Cu(PPh$_3$)$_3$Br/room temperature/chloroform), the influence of varying the ratio of azide 3.7d to alkyne moiety on Pc 3.6, from one to three to ten was performed (Figure 3.6). Three fitting curves shown in Figure 3.6 were generated by KaleidaGraph using exponential rise method.
The reaction progress was clearly expedited by an increased number of azide equivalents, with ten equivalents showing apparent reaction completion within six hours while three equivalents of azide afforded the fully clicked product with reaction times up to three days. The use of equimolar amounts of azide and alkyne yielded a perylene-phthalocyanine ratio of only 2.18, which was significantly lower than with ten equivalents of azide.

### 3.3.4 Condensed Phase Absorption Spectral Comparison

A comparison of the condensed phase UV/Vis absorption spectra of 3.6, 3.1d, 3.7d with the corresponding solution phase spectra indicated a degree of frustration of
aggregation of both Pc and PDI chromophores by combination into the single \textbf{3.1d} structure (Figure 3.7).

![Figure 3.7](image)

**FIGURE 3.7.** Condensed Phase UV/Vis Spectra of Clickable Pc 3.6, Clicked 3.1d, and Perylene Azide 3.7d Spin Coated on Glass from Chloroform

Broadening and blue shifting in the condensed phase spectrum of Pc \textbf{3.6} relative to the solution spectrum was clearly indicative of chromophore aggregation. Similarly, the broadening and increased absorbance of the perylene peak at 490 nm when prepared as a condensed phase thin film of \textbf{3.7d} indicated increased chromophores aggregation as well. In contrast, the condensed film of \textbf{3.1d} exhibits a UV/Vis spectrum in which Pc aggregation was observed to have decreased. The Q-band is comparable to that observed in the solution UV/Vis spectrum of \textbf{3.6} and \textbf{3.1a-3.1d}. The UV/Vis absorbance in the
PDI region, however, still indicates chromophore aggregation in the thin film of 3.1d, but less than that seen for 3.7d. These differences suggest that peripheral substitution with perylenes through click chemistry can provide sufficient steric hindrance to prevent central Pc aggregation, although perylene aggregation still occurs.

### 3.4 Conclusion

The modification of peripheral substituents under CuAAC conditions was successfully demonstrated on an asymmetric Pc scaffold using azides bearing hydrophobic, photo-crosslinkable, and electroactive moieties. The asymmetrically clicked Pc derivatives were constructed from the single clickable Pc and different azides under mild conditions within six hours as mentioned by UV/Vis and FT-IR spectroscopies. Both CuI and Cu(PPh$_3$)$_3$Br were observed to be efficient catalysts, and azide-alkyne stoichiometry had an expected influence on reaction rate. The utility of using the CuAAC click reaction as a means to introduce various functionalities onto the periphery of the Pc chromophore holds much promise in the preparation of multifunctional Pc derivatives. Further modification of the hydroxyl group will also be the subject of future research.

### 3.5 Experimental Section

All reactions were run under a nitrogen or argon atmosphere unless otherwise noted. All chemicals were purchased from commercial sources and used without further purification unless otherwise noted. Compounds 3.2, 3.3, 3.7a, 3.7b, 3.7c, and 3.7d were
prepared according to the literature. DMSO was dried over freshly activated 4 Å molecular sieves. Anhydrous CH₂Cl₂ was distilled from CaH₂ under argon. Anhydrous THF was distilled from sodium and benzophenone under argon. ¹H NMR / ¹³C NMR spectra were recorded on commercially available instrumentation. ¹H NMR spectra were obtained in either CDCl₃ or CD₂Cl₂:DMSO-d₆ (95:5) as noted and calibrated using residual CHCl₃ (δ = 7.26 ppm) or CHDCl₂ (δ = 5.32 ppm) as an internal reference respectively, with chemical shifts reported in ppm from TMS. ¹³C NMR spectra were obtained in either CDCl₃ or CD₂Cl₂:DMSO-d₆ (95:5) as noted and calibrated using CDCl₃ (δ = 77.0 ppm) or CD₂Cl₂ (δ = 53.8 ppm) as an internal reference, respectively. UV/Vis spectroscopy was performed using a Shimadzu UV-2401PC spectrometer. Mass spectra were obtained from the Mass Spectrometry Facility, Department of Chemistry and Biochemistry, the University of Arizona. Combustion analyses were performed by NuMega Resonance Labs Inc., San Diego, CA. Flash column chromatography and TLC were performed using silica gel 60 and Silica Gel 60 F₂₅₄ plates respectively from EMD.

**Zinc 2,3,9,10,16,17-Hexa(4-(4-(1-dodecyl-1 H-1,2,3-triazol-4-yl)-butoxy)phenoxy)-23-hydroxyphthalocyanine (3.1a)**

To a solution of asymmetrically clickable Pc 3.6 (50.0 mg, 0.029 mmol), azide 3.7a (368 mg, 1.74 mmol) and dry THF (20 mL) was added N,N-diisopropylethylamine (45.0 mg, 0.349 mmol) and CuI (13.3 mg, 0.0698 mmol). The mixture was degassed and backfilled with argon three times before stirring overnight at room temperature. The reaction mixture was diluted with CH₂Cl₂ followed by washing with 0.1 M EDTA (3 x
100 mL), 1 M HCl (3 x 100 mL), and brine (3 x 100 mL). The organic layer was concentrated and the crude product was purified by flash column chromatography (SiO$_2$, CH$_2$Cl$_2$:MeOH = 95:5) followed by recrystallization from CH$_2$Cl$_2$/MeOH to give Pc 3.1a as a green solid (21.0 mg, 24%): $^1$H NMR (500 MHz, 5% DMSO-$d_6$ in CD$_2$Cl$_2$) δ 8.86 (br s, 2H), 7.07-6.77 (br m, 34H), 4.13-3.73 (br m, 24H), 1.66 (br s, 24H), 1.12 (br s, 120H), 0.76 (br s, 30H); MS (MALDI) $m/z$: [M]$^+$ Calcd for C$_{176}$H$_{238}$N$_{26}$O$_{13}$Zn 2987.805. Found: 2987.774. Anal. Calcd for C$_{176}$H$_{238}$N$_{26}$O$_{13}$Zn: C, 70.67; H, 8.02; N, 12.17. Found: C, 70.49; H, 8.26; N, 11.83.

Zinc 2,3,9,10,16,17-Hexa(4-(4-(1-(3-phenylpropyl)-1 H-1,2,3-triazol-4-yl)butoxy)phenoxy)-23-hydroxyphthalocyanine (3.1b)

Following the procedure for Pc 3.1a, asymmetrically clickable Pc 3.6 (50.0 mg, 0.029 mmol), azide 3.7b (281 mg, 1.74 mmol), dry THF (20 mL), $N,N$-diisopropylethylamine (45.0 mg, 0.349 mmol), and CuI (13.3 mg, 0.0698 mmol) gave Pc 3.1b as a green solid (27.0 mg, 35%): $^1$H NMR (500 MHz, 5% DMSO-$d_6$ in CD$_2$Cl$_2$) δ 8.83 (br s, 6H), 7.09-6.68 (br m, 57H), 3.99-3.69 (br m, 24H), 2.33 (br s, 12H), 1.90 (br s, 12H), 1.49 (br m, 12H), 0.76 (br m, 24H); MS (MALDI) $m/z$: [M]$^+$ Calcd for C$_{158}$H$_{154}$N$_{26}$O$_{13}$Zn 2687.148. Found: 2687.164. Anal. Calcd for C$_{158}$H$_{154}$N$_{26}$O$_{13}$Zn: C, 70.53; H, 5.77; N, 13.54. Found: C, 70.47; H, 6.14; N, 13.19.

Zinc 2,3,9,10,16,17-Hexa(4-(4-(1-(3-ethoxy-3-oxoprop-1-en-1-yl)-phenoxy)propyl)-1H-1,2,3-triazol-4-yl)butoxy)phenoxy)-23-hydroxyphthalocyanine (3.1c)
Following the procedure for Pc 3.1a, asymmetrically clickable Pc 3.6 (20 mg, 0.012 mmol), azide 3.7c (200 mg, 0.726 mmol), dry THF (20 mL), N,N-diisopropylethylamine (45.0 mg, 0.349 mmol), and CuI (13.3 mg, 0.0698 mmol) gave Pc 3.1c as a green solid (17 mg, 44%): 1H NMR (500 MHz, 5% DMSO-d6 in CD2Cl2) δ 8.97 (br s, 6H), 7.56-6.25 (br m, 70H), 4.22-3.81 (br m, 48H), 2.19-1.29 (br m, 66H); MS (MALDI) m/z: [M + H]+ Calcd for C188H191N26O31Zn 3372.346. Found 3372.121. Anal. Calcd for C188H190N26O31Zn: C, 66.90; H, 5.67; N, 10.79. Found: C, 66.84; H, 5.90; N, 10.51.

**Compound 3.1d using CuI as catalyst**

To a solution of asymmetrically clickable Pc 3.6 (21 mg, 0.012 mmol) and azide 3.7d (493 mg, 0.752 mmol), and dry CHCl3 (10 mL) was added N,N-diisopropylethylamine (50 mg, 0.388 mmol) and CuI (13 mg, 0.068 mmol). The mixture was degassed and backfilled with argon three times before stirring overnight at room temperature. The reaction mixture was diluted with CHCl3 followed by washing with 0.1 M EDTA (3 x 100 mL), 1 M HCl (3 x 100 mL), and brine (3 x 100 mL). The organic layer was concentrated and the crude solid was loaded to column chromatography and first flushed with 5% v/v ethyl acetate in CH2Cl2 until excess azide 3.7d eluted completely. The product was eluted with 5% v/v MeOH in CH2Cl2, and after evaporation of solvent under reduced pressure the resulting residue was recrystallized from CHCl3/MeOH to give Pc 3.1d as a dark purple solid (24 mg, 35%): MS (MALDI) m/z:
[M + H]⁺ Calcd for C_{344}H_{335}N_{38}O_{37}Zn 5653.479. Found 5653.870. Anal. Calcd for C_{344}H_{334}N_{38}O_{37}Zn: C, 73.02; H, 5.95; N, 9.41. Found: C, 73.02; H, 5.91; N, 9.08.

**Compound 3.1d using Cu(PPh₃)₃Br as catalyst**

Following the procedure for Pc 3.1d using CuI as catalyst, asymmetrically clickable Pc 3.6 (21 mg, 0.012 mmol), azide 3.7d (493 mg, 0.752 mmol), dry CHCl₃ (10 mL), N,N-diisopropylethylamine (50 mg, 0.388 mmol), and Cu(PPh₃)₃Br (63 mg, 0.068 mmol) gave Pc 3.1d as a dark purple solid (21 mg, 31%).

**Zinc 2,3,9,10,16,17-Hexa-(4-(hex-5-ynyloxy)phenoxy)-23-hydroxyphthalocyanine (3.6)**

A mixture of Pn 3.2 (600 mg, 1.13 mmol), Pn 3.3 (100 mg, 0.4 mmol), DBU (200 mg, 1.43 mmol), Zn(OAc)₂ (140 mg, 0.7 mmol), and 60 mL 1-pentanol was refluxed under Ar for 8 h. The reaction mixture was allowed to cool to RT, then poured into MeOH (150 mL). The precipitate was filtered, washed with MeOH, air dried and then chromatographed (SiO₂, CH₂Cl₂:MeOH = 99:1). The green fraction was collected and concentrated under reduced pressure. A solution of the resulting green residue, TFA (2 mL), and CH₂Cl₂ (20 mL) was stirred at RT under Ar for 4h. The reaction mixture was then washed with water (50 mL), aqueous NaHCO₃ (50 mL), and the organic layer was dried over MgSO₄, filtered, and evaporated under reduced pressure. The crude product was purified by flash column chromatography (SiO₂, CH₂Cl₂:MeOH = 99:1) to give Pc 3.6 (130 mg, 20% yield) as a green solid: ¹H NMR (500 MHz, CD₂Cl₂:DMSO-d₆ = 95:5)
δ 9.77 (s, 1H), 8.80-8.40 (m, 8H), 7.51(d, J = 8 Hz, 1H), 7.36-7.35(m, 4H), 7.29-7.24 (m, 8H), 7.06-7.02(m, 4H), 6.98-6.95 (m, 8H), 4.07-4.00 (m, 12H), 2.35-2.30 (m, 12H), 2.08-2.06 (m, 6H), 2.00-1.91 (m, 12H), 1.81-1.73 (m, 12H); $^{13}$C NMR (125 MHz, CD$_2$Cl$_2$;DMSO-d$_6$ = 95:5) δ 160.2, 156.0, 155.8, 155.58, 155.52, 154.2, 153.3, 152.5, 151.8, 151.8, 151.64, 151.58, 151.2, 151.1, 151.0, 150.9, 150.5, 150.3, 149.9, 149.8141.0, 134.4, 134.3, 133.9, 130.7, 124.1, 120.8, 119.9, 119.8, 119.7, 119.6, 118.21, 116.0, 115.8, 113.74, 113.65, 113.5, 112.2, 112.0, 108.668.93, 68.87, 68.3, 68.23, 68.18, 30.0, 28.8, 25.5, 25.51, 25.47, 18.48, 18.45; MS (MALDI) Calcd for C$_{104}$H$_{91}$N$_8$O$_7$ [M + H]$^+$: m/z 1659.67. Found 1659.72. Anal. Calcd for C$_{104}$H$_{90}$N$_8$O$_7$Zn: C, 72.49; H, 5.15; N, 6.50. Found: C, 72.01; H, 5.60; N, 6.51.

3.6 References

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CHAPTER 4
SYNTHESIS OF PHTHALOCYANINE-PERYLENEDIIMIDE DYADS
WITH LONG-LIVED CHARGE-SEPARATED STATES

4.1 Introduction

The overall efficiency in organic photovoltaics (OPVs) is greatly influenced by the nature of the electron injection barrier at each interface. Photoinduced electron transfer from an electron-donating unit to another electron-accepting unit is one of the most important processes taking place in OPVs.\textsuperscript{1-3} To better understand the factors that control interfacial electron transfer rates, a molecular level heterojunction can be developed. A model molecular level heterojunction using organic donor-acceptor dyads can be built on the surface of electrode materials. To further create a molecular level understanding of the organic / transparent conductive oxide (TCO) interface and the factors that control interfacial electron transfer rates, in terms of the charge separated state lifetime, from structure to function.

4.1.1 Molecular Level Heterojunction Based on Pc and PDI Moieties

Phthalocyanine (Pc) and perylenediimide (PDI) are popular materials for a number of advanced technologies due to their outstanding photo-physical properties.\textsuperscript{4} Due to these properties, such as thermal stability and intense $\pi$ to $\pi^*$ transitions in the visible region, Pcs have been widely used in various applications including solar cells,\textsuperscript{5} field effect transistors,\textsuperscript{6} nonlinear optics,\textsuperscript{7} high dielectric materials,\textsuperscript{8} electrochromic
devices, photodynamic therapy (PDT), and chemical sensors. The properties of PDIs, depending on their substitution pattern, can include highly exothermic electron affinities, high electron mobilities, and strong fluorescence. These properties have been exploited in fundamental studies of optoelectronic devices and systems for biological applications. In addition, several PDI derivatives have been studied as components for electron transfer and charge separation, as subjects for single-molecule fluorescence studies, and as components of organic electronic materials with applications in devices including field effect transistors and solar cells, taking advantage of their stability, intense light absorption, and electron accepting properties.

These two types of compounds have been used as pigments since their discovery early last century. They are chemically and thermally stable and exhibit intense absorptions and fluorescence in the visible region. Though the non-substituted Pcs and PDIs are insoluble in most common organic solvents, simple structural modifications can increase their processability. The architecture formed by combining both units, composed of an electron donating Pc subunit linked to a strongly electron accepting PDI via covalent bond, benefit from several advantages, such as the high absorption coefficients over most of the visible region and a possible driving direction for photoinduced electron transfer from Pc to PDI.

A model of molecular level heterojunction using organic dyads can be built on the surface of electrode materials. To successfully deposit organic dyads onto inorganic oxide surfaces, a proper surface active functional group is needed and embedded in the structure (Scheme 4.1). Hence, a Pc-PDI dyad with an anchoring group at the terminus is
a promising candidate for photophysical studies, such as the dark electron transfer rate from a radical ion charge separated state (\(i.e. \text{Pc}^{\ddagger}\text{-PDI}^{-}\)).

**SCHEME 4.1. Model System for Interfacial Electron Transfer Studies**

### 4.1.2 Pc-PDI Dyads

Donor-acceptor dyads have been studied as artificial systems for energy harvesting in biological and photovoltaic assemblies\(^{30-32}\). Several strategies have been carried out to mimic molecular arrays using Pc and PDI moieties, such as polymer blending\(^{33,34}\), chemical linking via covalent bonds\(^{29,35-38}\), and self-assembly\(^{27,28,39}\). In most systems, photoexcitation is followed by energy transfer from one molecule to another.

Generally, Pc-PDI dyads have energetically low-lying triplet excited states which prevent the generation of a persistent charge-separated state, resulting in short charge-separated lifetimes in the picosecond or nanosecond range\(^{36,40-42}\). However, in some cases, the presence of Lewis acids (e.g. Mg\(^{2+}\)) has produced stable charge-separated states.
below the corresponding triplet excited states, hence giving relatively long lifetimes for charge-separated states in the range of hundreds of microseconds.\textsuperscript{40,42-44}

4.1.3 Sastre-Santos’ Molecular Design

In 2012, Sastre-Santos et al. reported the first example of a Pc-PDI dyad with a charge separated state lower in energy than the triplet excited state of either the Pc or PDI (Scheme 4.2).\textsuperscript{37} The molecular design consisted of a peripherally substituted Pc unit with phenoxy groups (electron rich) and a bay substituted PDI with sulfonyl groups (electron poor). The lifetime of the resulting charge-separated state of the dyad was 72 \( \mu \text{s} \), confirmed by nanosecond laser flash photolysis.

![Scheme 4.2. Pc-PDI Dyad with a Long-Lived Charge-Separated State\textsuperscript{37}]

4.1.4 Research Goals

To create a molecular level understanding of the organic / TCO interface and the factors that control interfacial electron transfer rates, a model of a molecular level heterojunction will be constructed using Pc/PDI dyads based on Sastre-Santos’ design.
Since the rate of electron injection can be greatly influenced by the presence of an electroactive monolayer covalently attached to the TCO, a proper anchoring group (i.e., phosphonic acid) will be included in our molecular design based on Sastre-Santos’ molecule as our targeted model system (Scheme 4.3).

A series of Pc-PDI dyads will be constructed as shown in Scheme 4.3. Pc and PDI moieties will be coupled via a short alkyl linker, and a phosphonic acid anchoring group will be included on the PDI moiety to allow surface deposition to TCOs such as ITO, ZnO, and TiO$_2$. The Pc moiety will have electron rich alkylphenoxy groups on the periphery. The PDI will be substituted with three different bay substituents including the sulfonyl group explored by Sastre-Santos. However, due to the electron withdrawing effect of the sulfonyl group, we anticipate that the LUMO level of the PDI might be too low to line up with the Fermi level of ZnO, prohibiting electron injection. Hence, we
decided to manipulate the substitution to tune the LUMO levels of PDIs by changing the bay area groups with protons and thioether groups in the dyad models. Herein, the syntheses and preliminary photophysical analyses of these dyad molecules are reported.

4.2 Synthesis of Pc-PDI Dyads with an Anchoring Group

The general approach to PC-PDI dyads with a surface active phosphonic acid group entailed condensation of the appropriately bay-substituted perylene dianhydride (4.3a-c) with monoamino Pc 4.2 (Scheme 4.4). This was then followed by condensation with aniline derivative 4.5 to install the phosphonate moiety.
SCHEME 4.4. Synthesis of 4.1a-c Phosphonic Acid Tethered Pc-PDI Dyads

Compound 4.2, 4.3a-c, and 4.5 were prepared according to the literature.\textsuperscript{37,45} To minimize the undesired Pc-PDI-Pc triad during the imidization reaction in the formation of dyad 4.4a, only 0.9 equivalents of Pc 4.2 was used relative to perylene 4.3a. Subsequent workup using acetic acid yielded Pc-perylene anhydride 4.4a in 30\% yield, leaving the opposite end of the perylene moiety as an anhydride. Condensation of dyad anhydride 4.4a with phosphonate functionalized aniline 4.5\textsuperscript{45} under basic conditions produced Pc-PDI-phosphonate 4.6a. The resulting dyad phosphonate 4.6a was then
allowed to react with trimethylsilyl bromide (TMSBr) to give the desired phosphonic acid tethered Pc-PDI dyad 4.1a in an overall yield of 28% over two steps. Target dyad 4.1a was deposited onto an ITO surface for electrochemical analysis without any further purification. Synthesis of dyad 4.1b followed the procedures for 4.1a.

Similarly, coupling of perylene 4.3c with Pc 4.2 was carried out with excess 4.3c to optimize the formation of bay-substituted dyad 4.4c (bay-sulfonyl). However, the reaction conditions used for the synthesis of dyad 4.4c and 4.6c had to be changed from DMF/imidazole to NMP/AcOH. Based on mass spectroscopic data, the sulfonyl group at the perylene bay position was found to be sensitive to basic conditions, even as mild as pyridine and imidazole. The mass spectra indicated that the sulfonyl group did fall off under DMF/imidazole conditions and generated the partially unsubstituted dyads. Using o-xylene under reflux was also investigated, resulting in a 25% product yield of 4.6c which is comparable to NMP/AcOH (28%).

### 4.3 Characterization of Pc-PDI Dyads

Pc-PDI dyads 4.1a-c were characterized by NMR, UV/Vis spectroscopy (dichloromethane), fluorescence spectroscopy (dichloromethane), attenuated total reflectance UV/Vis (ATR-UV/Vis) spectroscopy, and MALDI mass spectrometry. $^1$H and $^{13}$C NMR spectra of dyads were recorded in CD$_2$Cl$_2$ with 5% $d_6$-DMSO as co-solvent to prevent aggregation. However, in the $^1$H NMR spectra, the aromatic protons were not well resolved as sharp peaks indicating aggregation of chromophores. In an effort to sharpen the proton signals, additional $^1$H NMR spectroscopic experiments under various
conditions were performed, such as adding other co-solvents (e.g. $d_5$-pyridine and trifluoroacetic acid), extending the delay time in the pulse sequence and diluting samples, but no improvement was observed in all cases. In $^{13}$C NMR spectra of all dyads, the signals of aromatic carbon atoms were unobserved, likely due to aggregation of chromophores. $^{13}$C NMR spectra under diluted conditions only showed a few peaks corresponding to the peripheral substituents.

4.3.1 UV/Vis Absorption and Fluorescence Spectroscopy

The steady-state UV/Vis absorption spectra of dyad anhydrides (4.4a to 4.4c), dyad phosphonates (4.6a to 4.6c), and dyad phosphonic acids (4.1a to 4.1c) with different substituents, ranging from electron donating group to electron withdrawing group, in perylene moiety are shown in Figure 4.1. All spectra were normalized at the Pc Q-band ca. 685 nm.
FIGURE 4.1. UV/Vis Absorption Spectra of (a) Dyad Anhydrides in DCM, (b) Dyad Phosphonates in DCM, and (c) Dyad Phosphonic Acids in THF

The bay-thioether substituted perylene moiety in dyad 4.4b absorbed at 570 nm, a red-shift of ca. 5 nm compared to the chromophore itself (Figure 4.1a). The bay-unsubstituted and bay-sulfonyl substituted perylene moieties (in monoimide form) in dyad 4.4a and 4.4c absorbed at 530 nm, which are comparable to the chromophores themselves. The main difference among 4.4a-c in Figure 4.1a is the PDI absorbance of the bay-thioether versus the bay-unsubstituted and bay-sulfonyl which are the identical.

Comparing dyad phosphonates 4.6a and 4.6c to dyad anhydrides 4.4a and 4.4c respectively, a red-shift of ca. 5 nm was observed in the absorption of the perylene moiety due to extended conjugation (Figure 4.1b). No other significant difference was found between these two stages, indicating that dyad 4.4a/4.4c, and 4.6a/4.6c remained
unaggregated in solution. In contrast, the bay-thioether substituted perylene moiety in dyad 4.6b aggregated to be as evidenced by its broadened absorption peak, while the Pc moieties at the phosphonate stage remained monomeric in solution.

Phosphonic acid dyads 4.1a-c exhibited absorption profiles with several marked differences relative to dyad anhydrides 4.4a-c and phosphonates 4.6a-c (Figure 4.1c). Absorption at 630 nm in dyad phosphonic acids (4.1a-c) indicated significant aggregation of the Pc units. The perylene moieties in dyads 4.1a-c also behaved like aggregates as indicated by the ratio of peak intensity of vibronic 0-1 and 0-0 transitions. The aggregation exhibited in the UV/Vis spectrum of dyad phosphonic acids was partially attributed to hydrogen bonding between phosphonic acids.

The fluorescence spectra of dyad phosphonates 4.6a-c and the corresponding reference PDIs 4.7a-c with different substituents in the bay position are recorded in Figure 4.2.
FIGURE 4.2. Emission spectra of (a) dyad 4.6a, (b) 4.6b, (c) 4.6c and the corresponding reference PDIs 4.7a-c (λ_{ex} = 522, 567, and 522 nm, respectively) in DCM, (inset) structure of the reference PDI. All fluorescence spectra were recorded in DCM at 2 \times 10^{-6} \text{M}.

With the excitation wavelength at the first perylene absorption (522 nm), the bay-unsubstituted reference PDI 4.7a clearly showed an expected fluorescence profile,\textsuperscript{26,46} exhibiting bands at 533, 575, and 622 nm in dichloromethane (Figure 4.2a). For dyad phosphonate 4.6a, no significant fluorescence emission from either the Pc or PDI moiety was observed. Similar quenching of the fluorescence was also observed in previously reported Pc-PDI dyads and triads with long-lived charge separated states.\textsuperscript{37,43,44} Based on the emission spectrum of dyad 4.6a, the resulting excited dyad \([\text{Pc}^-\text{PDI}^+]\) undergoes non-radiative decay presumably as a result of charge transfer from Pc to PDI with the
formation of the charge separated state $[\text{Pc}^{\bullet+}\text{-PDI}^{\bullet-}]$, followed by the back electron transfer (i.e. recombination) to the ground state.$^{47,48}$

The bay-thioether reference PDI 4.7b revealed a relatively weak fluorescence band located at around 670 nm in the emission spectrum (Figure 4.2b). Compared to the bay-unsubstituted reference PDI, the bay-thioether reference PDI dramatically decreased in fluorescence intensity due to the quadrupolar charge-transfer character from sulfur to perylene.$^{26}$ Similarly, the significant difference in perylene fluorescence between the reference PDI and dyad 4.6b was also observed. Emission of perylene from the bay-thioether substituted dyad 4.6b was not observed presumably due to the charge transfer from Pc to PDI, followed by the recombination to the ground state.

The bay-sulfonyl reference PDI 4.7c showed fluorescence bands located at 545 and 584 nm in dichloromethane (Figure 4.2c). Similar to dyad 4.6a and 4.6b, these emission bands were found to be fully quenched in dyad 4.6c, presumably due to the formation of the charge separated state $[\text{Pc}^{\bullet+}\text{-PDI}^{\bullet-}]$ as a non-radiative decay.

In addition, fluorescence spectra of the three phosphonate dyads (4.6a-c) were also taken at the excitation wavelengths of 680 nm and 355 nm, corresponding to the absorption of Pc Q-band and B-band, respectively. Upon excitation at 680 nm (Figure 4.3a), Pc emission at 690 nm observed in reference Pc 4.2 was absent for all three phosphonate dyads, suggesting the presence of non-radiative relaxation. Quenching of Pc emission was also observed in these dyads when excited at 355 nm (Figure 4.3b).
FIGURE 4.3. Emission spectra of 4.2, 4.6a, 4.6b, and 4.6c in DCM (2x10^-6 M) with excitation wavelength at (a) 680 nm and (b) 355 nm

4.3.2 Attenuated Total Reflectance UV/Vis (ATR-UV/Vis) Spectroscopy
The adsorption of phosphonic acid tethered Pc-PDI (bay-H) dyad 4.1a onto ITO was monitored with ATR-UV/Vis spectroscopy. ATR spectra (Figure 4.8) were acquired as a function of time after injecting a 100 μM solution of dyad 4.1a in acetonitrile/pyridine (1/1, v/v). The absorbance at the Q band maximum (685 nm) of dyad 4.1a increased and reached a plateau ca. 3 h after injection, indicating equilibrium was reached. After flushing the flow cell with acetonitrile/pyridine to remove dissolved and weakly adsorbed dyad 4.1a molecules the absorbance remaining was substantially the same, indicating that phosphonic acid tethered dyad 4.1a was strongly adsorbed to the ITO surface.

FIGURE 4.4. TM polarized ATR-UV/Vis spectra (solid lines) acquired as a function of time after a 100 μM solution of dyad 4.1a (bay-H) was injected into an ATR flow cell with an ITO-coated glass slide. The dashed line is the spectrum acquired after flushing the cell with fresh solvent (acetonitrile/pyridine).
4.4 Conclusion

We have demonstrated the synthesis and characterization of a novel series of Pc-PDI dyads with different perylene bay-functional groups (H, thioether, and sulfonyl), as well as phosphonic acid anchoring groups connected to the perylene moieties for the studies of molecular-level heterojunction on transparent conductive oxides. Boc-protected Pn was chosen for the preparation of asymmetric Pc using statistical macrocyclization since the embedding amines served as the nucleophilic site to couple with perylene moiety. The targeted dyads were prepared by condensation of the electron donating Pc subunit with an electron demanding perylene via a short length of alkyl chain, followed by the introduction of phosphonic acid as the anchoring group. For all three synthesized phosphonate dyads, the preliminary evidence of non-radiative relaxation, presumably suggesting the electron transfer from Pc unit to PDI unit, was found via solution fluorescence spectroscopy. This model system using organic dyads was shown to firmly attach to an ITO surface by ATR-UV/Vis spectroscopy.

4.5 Experimental Section

All reactions were run under a nitrogen or argon atmosphere unless otherwise noted. All chemicals were purchased from commercial sources and used without further purification unless otherwise noted. Compound 4.2, 4.3a-c, 4.5, and 4.7a-c were prepared according to the literature.\textsuperscript{37,45} DMSO was dried over freshly activated 4 Å molecular sieves. Anhydrous CH\textsubscript{2}Cl\textsubscript{2} was distilled from CaH\textsubscript{2} under argon. Anhydrous
THF was distilled from sodium and benzophenone under argon. \(^1\)H NMR / \(^{13}\)C NMR spectra were recorded on commercially available instrumentation. \(^1\)H NMR spectra were obtained in either CDCl\(_3\) or CD\(_2\)Cl\(_2\):DMSO-\(d_6\) (95:5) as noted and calibrated using residual CHCl\(_3\) (\(\delta = 7.26\) ppm) or CHDCl\(_2\) (\(\delta = 5.32\) ppm) as an internal reference respectively, with chemical shifts reported in ppm from TMS. \(^{13}\)C NMR spectra were obtained in either CDCl\(_3\) or CD\(_2\)Cl\(_2\):DMSO-\(d_6\) (95:5) as noted and calibrated using CDCl\(_3\) (\(\delta = 77.0\) ppm) or CD\(_2\)Cl\(_2\) (\(\delta = 53.8\) ppm) as an internal reference, respectively. UV/Vis spectroscopy was performed using a Shimadzu UV-2401PC spectrometer. Mass spectra were obtained from the Mass Spectrometry Facility, Department of Chemistry and Biochemistry, the University of Arizona. Flash column chromatography and TLC were performed using silica gel 60 and Silica Gel 60 F\(_{254}\) plates respectively from EMD.

**ITO Substrate Preparation**

ITO on glass with a layer thickness of \(\sim100\) nm and a sheet resistance of \(\sim15\) \(\Omega/cm^2\) was purchased from Colorado Concept Coatings LLC. The ITO electrodes were cleaned by lightly scrubbing with detergent (diluted Triton X-100) for 1 min, followed by successive sonication in detergent, deionized (DI) water, and ethanol for 15 min each. DI water was obtained from a Barnstead Nanopure system with a measured resistivity of 18.3 M\(\Omega\)\(\cdot\)cm\(^{-1}\). Cleaned ITO electrodes were stored in ethanol. The electrode surface was then activated in an air plasma cleaner (PDC-3XG, Harrick Scientific, Ossining, NY) for 15 min at medium radio frequency (rf) level immediately before use.
Pc-PDI (Bay-H) Dyad Phosphonic Acid (4.1a)

A solution of phosphonate dyad 4.6a (10 mg, 0.005 mmol), trimethylsilyl bromide (154 mg, 1.00 mmol), and CH$_2$Cl$_2$ (5mL) was allowed to stir at RT for 16 h under Ar. The reaction was quenched with water (5 mL) and then methanol (20 mL) was added to give precipitate. The crude product was collected by centrifugation, washed with methanol twice, and dried under reduced pressure to give dyad 4.1a (58 mg, 60%) as a dark purple solid: $^3$P NMR (202 MHz, CDCl$_3$) $\delta$ -11.63; MS (MALDI) m/z: [M]$^+$ Calcd for C$_{130}$H$_{117}$N$_{10}$O$_{14}$PZn 2136.778; Found 2136.798.

Pc-PDI (Bay-Thioether) Dyad Phosphonic Acid (4.1b)

Following the procedure for dyad 4.1a, phosphonate dyad 4.6b (10 mg, 0.005 mmol), trimethylsilyl bromide (154 mg, 1.00 mmol), and 5mL CH$_2$Cl$_2$ gave dyad 4.1b (70 mg, 66%) as a dark blue solid: $^3$P NMR (202 MHz, CDCl$_3$) $\delta$ -13.49; MS (MALDI) m/z: [M + H]$^+$ Calcd for C$_{144}$H$_{130}$N$_{10}$O$_{14}$PS$_2$Zn 2381.816; Found 2381.945.

Pc-PDI (Bay-Sulfonyl) Dyad Phosphonic Acid (4.1c)

Following the procedure for dyad 4.1a, phosphonate dyad 4.6c (10 mg, 0.005 mmol), trimethylsilyl bromide (154 mg, 1.00 mmol), and 5mL CH$_2$Cl$_2$ gave dyad 4.1c (65 mg, 63%) as a dark purple solid: $^1$H NMR (500 MHz, 5% DMSO-$d_6$ in CD$_2$Cl$_2$) $\delta$ 8.95 (br s, 9H), 7.19 (br m, 38H), 4.45 (br m, 4H), 2.53 (br m, 12H), 2.03 (s, 6H), 1.64-0.93 (br s, 54H); $^3$P NMR (202 MHz, CDCl$_3$) $\delta$ -13.14; MS (MALDI) m/z: [M]$^+$ Calcd for C$_{144}$H$_{129}$N$_{10}$O$_{18}$PS$_2$Zn 2444.796; Found 2445.011.
Phthalocyanine-Perylene (Bay-H) Dyad Anhydride (4.4a)

A mixture of Pc 4.2 (310 mg, 0.19 mmol), perylene potassium salt 4.3a (170 mg, 0.38 mmol), imidazole (4.0 g, 59 mmol), and DMF (5 mL) was maintained at 120 °C under Ar for 16 h. The reaction mixture was allowed to cool to RT, and then 10% aqueous citric acid (20 mL) was added. The resulting precipitate was filtered, washed with MeOH, and dried under reduced pressure. The crude product was purified by flash column chromatography (SiO₂, CH₂Cl₂:EtOAc = 95:5) to give dyad 4.4a (120 mg, 31%) as a dark purple solid; ¹H NMR (500 MHz, 5% DMSO-d₆ in CD₂Cl₂) δ 8.79 (br m, 7H), 7.90 (br s, 2H), 7.61 (br s, 2H), 7.27 (br m, 24H), 6.96 (br s, 2H), 6.35 (br m, 4H), 5.07 (br s, 2H), 4.79 (br s, 2H), 2.65 (br m, 12H), 1.72 (br m, 12H), 1.38 (br m, 12H), 1.20 (br m, 12H), 0.85 (br m, 18H); MS (MALDI) m/z: [M]⁺ Calcd for C₁₂₄H₁₁₁N₉O₁₂Zn 1981.764; Found 1981.693.

Phthalocyanine-Perylene (Bay-Thioether) Dyad Anhydride (4.4b)

Following the procedure for dyad 4.4a, Pc 4.2 (310 mg, 0.19 mmol), perylene 4.3b (170 mg, 0.38 mmol), imidazole (4.0 g, 59 mmol), and DMF (5 mL) gave dyad 4.4b (110 mg, 28%) as a dark blue solid; ¹H NMR (500 MHz, 5% DMSO-d₆ in CD₂Cl₂) δ 8.94 (br m, 12H), 7.25 (br m, 32H), 6.55 (br s, 3H), 4.89 (br m, 4H), 2.65 (br m, 12H), 2.19 (s, 6H), 1.68 (br s, 12H), 1.39 (br m, 24H), 0.83 (br m, 18H); MS (MALDI) m/z: [M + H]⁺ Calcd for C₁₃₈H₁₂₃N₉O₁₂S₂Zn 2226.810; Found 2226.706.
Phthalocyanine-Perylene (Bay-Sulfonyl) Dyad Anhydride (4.4c)

A mixture of Pc 4.2 (310 mg, 0.19 mmol), perylene 4.3c (170 mg, 0.38 mmol), and AcOH/NMP (1:1, 5 mL) was maintained at 85 °C under Ar for 18 h. The reaction mixture was allowed to cool to RT, and MeOH (20 mL) was added to give precipitate. The precipitate was filtered, washed with MeOH, and then dried under reduced pressure. The crude product was purified by flash column chromatography (SiO₂, CH₂Cl₂:EtOAc = 95:5) to give dyad 4.4c (106 mg, 27%) as a dark purple solid: \(^1\)H NMR (500 MHz, 5% DMSO-d\(_6\) in CD₂Cl₂) \(\delta\) 8.69 (br m, 10H), 7.55 (br m, 5H), 7.24 (br m, 32H), 5.01 (br s, 2H), 4.81 (br s, 2H), 2.66 (br m, 12H), 2.38 (s, 6H), 1.67 (br s, 12H), 1.32 (br m, 24H), 0.86 (br m, 18H); MS (MALDI) m/z: [M]+ Calcd for C\(_{138}\)H\(_{123}\)N\(_9\)O\(_{16}\)S\(_2\)Zn 2289.782; Found 2289.764.

Pc-PDI (Bay-H) Dyad Phosphonate (4.6a)

A mixture of dyad 4.4a (110 mg, 0.05 mmol), phosphonate 4.5 (36 mg, 0.16 mmol), anhydrous Zn(OAc)\(_2\) (10 mg, 0.053 mmol), and pyridine (1 mL) was maintained at reflux under Ar for 16 h. The reaction mixture was allowed to cool to RT, and then poured into MeOH (20 mL). The resulting precipitate was filtered, washed with MeOH, and dried under reduced pressure. The crude product was purified by flash column chromatography (SiO₂, CH₂Cl₂:THF = 95:5) to give dyad 4.6a (57 mg, 46%) as a dark purple solid: \(^1\)H NMR (500 MHz, 5% DMSO-d\(_6\) in CD₂Cl₂) \(\delta\) 8.87-6.85 (br m, 30H), 4.83-4.11 (br m, 8H), 2.61-2.45 (br m, 18H), 1.64 (br m, 12H), 1.30 (br m, 24H), 0.84 (br
m, 18H); $^{31}$P NMR (202 MHz, CDCl$_3$) $\delta$ 17.72; MS (MALDI) m/z: [M]$^+$ Calcd for C$_{134}$H$_{125}$N$_{10}$O$_{14}$PZn 2192.841; Found 2192.727.

**Pc-PDI (Bay-Thioether) Dyad Phosphonate (4.6b)**

Following the procedure for dyad 4.6a, dyad 4.4b (110 mg, 0.05 mmol), phosphonate 4.5 (36 mg, 0.16 mmol), anhydrous Zn(OAc)$_2$ (10 mg, 0.053 mmol), and pyridine (1 mL) gave dyad 4.6b (50 mg, 43%) as a dark blue solid: $^1$H NMR (500 MHz, 5% DMSO-$d_6$ in CD$_2$Cl$_2$) $\delta$ 8.82 (br m, 6H), 7.77 (br m, 5H), 7.09 (br m, 36H), 5.04 (m, 2H), 4.72 (br s, 2H), 4.06 (br m, 4H), 2.63 (m, 12H), 2.31 (s, 6H), 2.18 (m, 6H), 1.65 (br m, 12H), 1.29 (br m, 24H), 0.90 (br m, 18H); $^{31}$P NMR (202 MHz, CDCl$_3$) $\delta$ 17.79; MS (MALDI) m/z: [M]$^+$ Calcd for C$_{148}$H$_{137}$N$_{10}$O$_{14}$PS$_2$Zn 2436.879; Found 2436.828.

**Pc-PDI (Bay-Sulfonyl) Dyad Phosphonate (4.6c)**

A mixture of dyad 4.4c (110 mg, 0.05 mmol), phosphonate 4.5 (36 mg, 0.16 mmol), and AcOH/NMP (1:1, 1 mL) was maintained at 85 $^\circ$C under Ar for 18 h. The reaction mixture was allowed to cool to RT and then poured into MeOH (20 mL). The precipitate was filtered, washed with MeOH, and dried under reduced pressure. The crude product was purified by flash column chromatography (SiO$_2$, CH$_2$Cl$_2$:THF = 95:5) to give dyad 4.6c (52 mg, 44%) as a dark purple solid: $^1$H NMR (500 MHz, 5% DMSO-$d_6$ in CD$_2$Cl$_2$) $\delta$ 8.95 (br m, 8H), 7.58 (br m, 2H), 7.21 (br m, 32H), 6.70 (br s, 5H), 4.81 (br m, 8H), 2.67 (m, 12H), 2.34 (m, 6H), 1.70 (br s, 12H), 1.34 (br m, 30H), 0.86 (br m,
18H); $^{31}$P NMR (202 MHz, CDCl$_3$) $\delta$ 17.17; MS (MALDI) m/z: [M + H]$^+$ Calcd for C$_{148}$H$_{138}$N$_{10}$O$_{18}$PS$_2$Zn 2501.858; Found 2502.165.

4.6 References


REFERENCES

CHAPTER 1


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CHAPTER 3

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CHAPTER 4