TERPYRIDINE-BASED METALLO-SUPRAMOLECULAR ARCHITECTURES:
FROM STRUCTURE TO FUNCTION

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TERPYRIDINE-BASED METALLO-SUPRAMOLECULAR ARCHITECTURES:
FROM STRUCTURE TO FUNCTION

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Dissertation

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ABSTRACT

The research and applications of functional materials continue to grow rapidly in order to match the materials and energy needs of an increasing population. In this regard, perylene is a stable, organic material that possesses a rich chemistry and unique chemical, physical, and electronic properties. The molecular organization into predesigned geometries such as: cages, dendrimers, macrocycles and polymers, can add a profound enhancement to the material functional characteristics. At the heart of metallosupramolecular chemistry, \(<\text{tpy-M-tpy}>\) binding is a pivotal tool to construct complex and functional architectures. This dissertation reviews the chemical, structural, physical, and electrochemical properties of perylene with an emphasize on its metallosupramolecular chemistry.

The synthesis of perylene-containing \(\text{bis}\)-, \(\text{tetrakis}\)-, and \(\text{hexakis}\)-terpyridine ligands along with their corresponding heteroleptic \(\text{tpyRu}^{II}\text{tpy}>\) complexes was achieved. These high molecular weight nano-dendritic architectures were characterized using \(^1\text{H NMR}\), \(^{13}\text{C NMR}\), COSY, and ESI-MS. These complexes exhibit broad absorption spectra (250-625 nm) and high molar absorption coefficients that are proportional to the number of photoactive units.

The synthesis of supramolecular dyes based on \(\text{tpy-Ru}^{II}-\text{tpy}>\) motifs connected to perylene-core either in \(\text{bay}\)- or \(\text{peri}\)-positions was demonstrated.
The structures of these materials were confirmed using a combination of $^1$H NMR, $^{13}$C NMR, COSY, ESI-MS, and their electrochemical properties were studied via Cyclic Voltametry. These dyes were utilized as active ingredients for DSSCs, of which the photovoltaic properties were described.

Fluorescent cyclic metallosupramolecular architectures were obtained via \(<\text{tpyZn}^{II}\text{tpy}>\) mediated self-assembly of two aminobisterpyridine containing perylene ligands that were synthesized in a multistep procedure, the chemical structure and purity of both ligands and complexes were assured using a combination of $^1$H NMR, $^{13}$C NMR, COSY, and ESI-MS. DOSY was utilized to investigate the dimensions of the metallocycles that were compared to the values obtained from the energy minimized molecular modeling. The photophysical properties of these macrocycles showed strong fluorescence suggesting their potential use in LED.

The formation of novel cyclic complexes including trimer and heteroleptic tetramers was achieved. The UV-Vis absorption and emission spectra of these materials were studied, and their chemical structures were illucidated via a combination of spectroscopic techniques including $^1$H NMR, ESI-MS, and MALDI-TOF-MS. Molecular modeling simulation of these nanosized complexes revealed cavities that can be used for host-guest chemistry.
DEDICATION

I would like to dedicate this dissertation to my mother Eisha for here endless prayers, my wife Mona who sacrificed so much for me, my daughter Khadija, and my son Ahmed for their care support and understanding all these years.
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CHAPTER I
PERYLENE-BASED MATERIALS: SYNTHESIS, STRUCTURE, AND METALLOSUPRAMOLECULAR CHEMISTRY

1.1 Introduction

Perylene and perylenediimide (PDI) constitute a class of functional dyes and pigments that continue to receive a growing interest in both industry and academia. They exhibit outstanding structural and functional properties including high electron mobility, high photo- and thermal stability, high fluorescence quantum yield, and high electron affinity. These materials also possess a rich chemistry, for example, perylene fluorination decreases the LUMO energy level and enhances the material resistance to oxidation. These properties make perylene-based materials\textsuperscript{1-5} interesting candidates for a wide range of applications,\textsuperscript{6-20} such as porous materials,\textsuperscript{21} dye lasers,\textsuperscript{22} single molecule spectroscopy,\textsuperscript{23} organic field effect transistors (OFET),\textsuperscript{24,25} light emitting devices,\textsuperscript{7,26-28} photochromic,\textsuperscript{29,30} sensors,\textsuperscript{31} dyes and pigments,\textsuperscript{32,33} fluorescent markers,\textsuperscript{2,30,34} solar energy collectors,\textsuperscript{30,35-37} and liquid crystals.\textsuperscript{38} While, numerous reviews have appeared in the literature detailing their diverse chemistry applications,\textsuperscript{2,30,31,39-42} we will review the synthetic aspects (Fig. 1.1) of bay-, peri-, and ortho-substituted perylenes, and their core-enlarged (i.e., framework-
expanded) products. The structural and functional properties of these materials will be described, along with their metallosupramolecular chemistry.

![Diagram][1]

Figure 1.1. Diagram shows the perylene chemistry and properties that will be reviewed.

1.2 Historical Synthetic Aspects of Perylene

In 1913, Kardos\textsuperscript{43} reported in a German patent the first synthesis of perylene (Scheme 1.1). This industrial scale production procedure began with the catalytic oxidation of acenaphthalene 1 to generate the naphthalenedicarboxylic acid anhydride 2, which was subsequently reacted with ammonia to generate (80\%) the corresponding 1,8-naphthalimide 3. Reaction of two equivalents of imide 3 with KOH followed by air oxidation gave (60\%) the perylene 4 that was next hydrolyzed (H\textsubscript{2}SO\textsubscript{4}) to afford the commercially available perylenetetracarboxylic acid dianhydride 5.
Scheme 1.1. Early commercial procedure for the production of perylene.\textsuperscript{43}

1.3 Substituted Perylenes.

Perylene can be considered as the fusion of two naphthalene rings at the 1,8-positions; it is a planar, $\pi$-conjugated system comprised of 12 functionalizable carbon atoms (Fig. 1.2), which are comprised of three different types: Bay- ($C_{1,6,7,12}$), Peri- ($C_{3,4,9,10}$), and Ortho- ($C_{2,5,8,11}$) positions.

![Diagram of perylene framework with substituent positions labeled](image)

**Figure 1.2.** Numbering and descriptive terminology for substituents on perylene framework.
1.3.1. *Peri*-Substituted Perylenes.

The early versions of perylene derivatives 6 were obtained through the condensation of perylenetetracarboxylic acid dianhydride 5 with diverse aliphatic or aromatic amines\textsuperscript{44,45} in a high boiling point solvents, such as quinoline. These materials are slightly soluble in organic solvents and are commercially used as high performance pigments and paints in textile and automotive industries.\textsuperscript{46} Reduced solubility of these materials results from the packing of the flat perylene structures, that can be minimized by incorporating branched or bulky groups.\textsuperscript{47}

Scheme 1.2. *Peri*- (imide) position substitution of perylene.\textsuperscript{47-49}

1.3.2. *Bay*-Substituted Perylenes.

The *Bay*-substitution of perylene was first reported by Seybold\textsuperscript{50} where 1,6,7,12-tetrachloro PDI (7) was synthesized by treating PDI 6 with a mixture of sulfuryl chloride, iodine, and iodobenzene, in nitrobenzene at 80 °C. The pure product can be isolated from the trichloro- and pentachloro-intermediates by chromatography. A mixture of isomers including 1,6- and 1,7-dibromo PDI isomers are produced; however when 2.4 equiv. Br\textsubscript{2} are used, the pure 1,7-dibromo PDI 8 isomer can be separated by chromatography,\textsuperscript{51} followed by
recrystallization. Noteably, the increased steric hindrance within the halo-bay substituents distort the perylene’s flat structure and thereby increase solubility. Nucleophilic halogen exchange of 7 produces tetrafluorinated PDI\textsuperscript{52-54} 10 that was used as active material in OFET.\textsuperscript{24}

Scheme 1.3. Synthesis of 1,6,7,12-PDI derivatives 7,9,10 and 1,7-dibromo PDI 8.\textsuperscript{51,52,55-59}

Nucleophilic halogen substitution of 7 or 8 with substituted phenols\textsuperscript{59} and K\textsubscript{2}CO\textsubscript{3}, in N-methylpyrrolidone (NMP) at 80 °C affords either 9 or 11, respectively, these products possess higher solubility compared to their starting materials. A series of products 12a-c was obtained via reacting the dibromoperylene 8 with either Zn(CN)\textsubscript{2}, piperidine\textsuperscript{55} or pyrrolidine,\textsuperscript{60} respectively, at elevated temperatures. Dibromoperylene 8 also undergoes a
Sonogashira$^{61}$ or Suzuki$^{62}$ coupling reaction with substituted acetylenes and boronic acid to afford the corresponding substituted PDIs 13 and 14, respectively.

Scheme 1.4. Bay-position substitution of perylene via reactions of 1,7-dibromo-PDI.$^{55,59,61-63}$

1.3.3. Ortho-Substitution.

In 2009, the first ortho-substituted perylene derivative 15 was synthesized$^{64}$ through the reaction of PDI 6 with trimethylvinylsilane at 165 °C for 60 h in mesity using [RuH$_2$(CO)(PPh$_3$)$_3$] catalyst. 15 showed an intense red solid state fluorescence. This previous Ru catalyst was also used for the synthesis of a library of 2,5,8,11-tetrasubstituted arylperylenes 16 from PDI and arylboronates$^{65}$ in mesitylene at 140 °C. The Müllen group also reported$^{66}$ the efficient synthesis of tetraboronated PDI 17, which was shown to be a key derivative for the synthesis of chloro-, bromo-, iodo-, and cyano-substituted
perylenes 18a-d, respectively. Diiodo-PDI 18c was subsequently reacted with octylamine to afford 20. The oxidation of 17 with hydroxylamine hydrochloride in EtOH at 25 °C afforded (82%) of the tetrahydroxy PDI 19. The OH groups form intramolecular hydrogen bonds with the juxtaposed carbonyl groups, that induces a significant blue shifted absorption spectrum.

Scheme 1.5. Synthesis of 2,5,8,11-derivatives of PDI.

1.3.4. Ortho and Bay Substitution

The highly electron-deficient octachloro PDI 21 was synthesized (79%) by the I₂ catalyzed chlorination of PDI 5 using chlorosulfonic acid and chlorine at 80
°C for 24 h. This semiconductor was utilized to fabricate $n$-channel OFET; the high performance of this device was attributed to the high charge mobility created by the high molecular order.\textsuperscript{72}

![Scheme 1.6. Synthesis of 1,2,5,6,7,8,11,12-octachloro PDI.\textsuperscript{72}](image)

1.3.5. Core-enlarged Perylenes

The electrochemical and photophysical properties of perylene can be altered by delocalization of the $\pi$ electrons. This larger core can be constructed along the perylene long axis (peri-core extension) to give higher rylene (terylene, quat-, penta-, and hexa-rylene) with red shifted absorption or the short axis (Bay-core extension)\textsuperscript{39} (Fig.1.2) to give coronene, dibenzocoronene, aneled PDI, graphene nanoribbons.

![Figure 1.3. Depiction of the expandable regions on the perylene framework.](image)
1.3.5.1. *Peri*-extended Perylene

Perylene monoimide PMI\textsuperscript{39,73} 22 was synthesized by decarboxylation of PDI 5 using 12 wt% KOH, at 230 °C for 18 h. PMI was then reacted with bromine in afforded the monobromo 23\textsuperscript{10} or tribromo 24\textsuperscript{73} products depending on the solvent, molar ratios, and specific reaction conditions.\textsuperscript{74} Indenoperylene 25 was constructed from the Suzuki coupling reaction of PMI 23 and 2-bromophenylboronic acid in toluene/EtOH at 75 °C, followed by Pd-catalyzed dehydrohalogenation.\textsuperscript{75} The reaction of tribromoperylene 24 with substituted phenol and K\textsubscript{2}CO\textsubscript{3} in DMF results in the formation of 26 (the key building block for the core-enlarged perylene). Quaterylene diimide 36 (QDI) was synthesized by a Yamamoto coupling of two equivalents of 23 with Ni(cod)\textsubscript{2} in DMF at 60 °C for 48 h, followed by oxidative cyclization. The resulting product showed a broad absorption spectrum in Near Infra-red (NIR).\textsuperscript{76,77} Hexarylenes 28 was also synthesized\textsuperscript{77} by the Suzuki coupling reaction of 26 with dibromoperylene.\textsuperscript{77} This core extension shifted the absorption 615 nm for perylene to 1050 nm for hexarylene.
Scheme 1.7. Perylene peri enlargement to produce 25, 27, 28. Additional heterocyclic structures can be appended to perylene via reaction of 5 with diverse diamines 29 in quinoline at 220 °C for 3h to produce a mixture (87%) of syn and anti isomers 30.

Scheme 1.8. Synthesis of perylene diamidine via reaction of 5 with diamines 29.
1.3.5.2. Bay-extended Perylene.

The core can also be extended along the short axis (Bay-core-expansion) to afford an array of novel perylene-based materials, such as coronenes,\textsuperscript{61,61} e.g., 32 or dibenzocoronene 34. Coronene 32 was synthesized starting from 1,7-dibromo-PDI by a Suzuki coupling reaction with diverse 1-alkynes in THF/Et\textsubscript{3}N, and in the presence of Pd(0) and CuI to afford dialkyne PDI 31. Cyclization of 31 was achieved \textit{via} reaction with DBU in toluene. This core expansion causes an alternation in HOMO-LUMO energies and lead to a blue shift in the absorption spectrum. In contrast, dibenzocoronene was synthesized by Suzuki coupling reaction of 8 with 2-bromophenylboronic acid, Pd(0), and K\textsubscript{2}CO\textsubscript{3} in toluene at 75 °C for 12 h to afford 33 which was cyclized using DBU (cyclodehydrohalogenation) at 160 °C in DME for 12 h. to give dibenzocoronenes 34 in 10% yield. Diels-Alder reaction of 8 with arynes improved the yield\textsuperscript{82} of 34, which has yellow color and strong fluorescence Φ = 80\%.\textsuperscript{75}
Scheme 1.9. *Bay*-extension of perylene to produce coronenes 32 and benzocoronenes 34.\(^{61,80}\)

Annelated perylenes 36 were synthesized (75%) via a Pd(0) catalyzed Stille coupling reaction of 8 with \(t\)-butylstannylthiophene in toluene at 110 °C for 24h.\(^{83,84}\) Molecular modeling of 36 revealed a steric interaction between the thiophene sulfur and ring hydrogen, yet it showed a fully planar, conjugated structure that leads to the observed low solubility. Similarly, Pd(0) catalyzed Suzuki coupling of 8 with pyridineboronic acid in THF generated 35. In contrast, a multistep synthetic approach was utilized for the synthesis of 37, 38, and 39. This procedure includes the reaction of 8 with either imidazole, triazole or pyrazole, in toluene at 100 °C, followed by photo-cyclization in CH\(_2\)Cl\(_2\) to afford the corresponding \(N\)-heterocoronenes.\(^{83,85}\)
Scheme 1.10. Perylene bay-extension to produce N-heterocoronenes.84,86,87

The double S-annelated heterocyclic structure 40 was synthesized (72%) via Pd-catalyzed reaction of tetrachloro-PDI 7 with (SnBu3) in refluxing toluene for 10 h. Heterocycle 48 is a planer structure that is soluble in CH2Cl2, toluene, and CHCl3. This material has a strong absorption spectrum at λmax = 480 nm (ε = 82,000 M⁻¹cm⁻¹) due to the allowed π-π* transition. A red co-crystal of 40 with pyrene (1:1) was grown using CH2Cl2, which was included in the crystal.
Scheme 1.11. Bay-extension of perylene to produce S-annelated PDI 40.\textsuperscript{88}

The planer and twisted ladder conjugated \textit{n}-type semiconducting materials PDI 42 and 43 were synthesized. The I\textsubscript{2}-catalyzed regioselective photocyclization of biperylene 41 either with DDQ in toluene or oxygen in CH\textsubscript{2}Cl\textsubscript{2} affords oligoperylenes 42 or 43, respectively.\textsuperscript{89} The solubility of these products was enhanced by incorporating tricosanes into the imide position.
A combination of Ullman reaction\textsuperscript{90-92} and C-H bond transformation was implemented in order to construct $N$-type graphene nanoribbons. The synthesis started from tetrachloro- or tetrabromo-PDI (7 or 8) self-coupling using CuI, $L$-proline, and $K_2CO_3$ in DMSO at 75 - 110 °C for 12-15 h to afford a series of fully conjugated $bay$ region fused di-, tri- and tetra-PDI 44-48. These materials possess an extremely strong electron-accepting and enhanced broad absorption in UV-NIR regions suggesting their use in organic electronics.
Scheme 1.13. Perylene bay-extension to produce graphene nanoribbon.93-95

1.3.6. Water-soluble Derivatives.

Single molecule tracking for biological systems requires highly fluorescent, photo-stable water-soluble fluorescent markers that do not show aggregation induced fluorescence quenching in an aqueous medium. Water solubility30 was achieved via functionalization of perylene in the bay, peri, and ortho position with hydrophilic moieties, such as: phosphate,96 carboxylate,97 sulphate,98,99 sugars,100 quaternary ammonium salts,66 hyperbranched polymers,101 and dendrons.102
1.4 Structural Properties

This crystal structures confirmed that, in the solid state, the twisting angle and hence the solubility is a function of the bulkiness of the bay substituents. The dihedral angle depends on the substitution, for instance, 1,7-dibromo, dihydroxyphenyl, and diphenoxy perylene have a dihedral angle of 21°-23.3°, 18.9-1.2°, and 17°, respectively. Disubstituted perylene 14 showed a flat structure in solid state even though it carries bulky 2,6-diphenylphenoxy-moieties at the 1,7-positions, the bulky groups shielded the perylene π system from the stacking, di fluorinated PDI show small twisting 4° compared to the large asymmetric twisting in the tetrafluoro PDI (18°, 28°).

In comparison, tetrachloro and tetraphenoxy groups cause the central ring to twist by 25° and 36.7°, respectively; this is very similar to the octachloroPDI 21 twisting (37°). In contrast, X-ray analysis of the imide substituted- 6 and S-heterocyclic annelated-PDI 40 show that the molecule regenerates its planer structure. Even though ortho-substituted PDI 16 shows highly planer core structure with mean plane deviation of 0.015 Å, the crystal structure revealed the absence of π-π stacking because of the steric hindrance of the substituents.
1.5 Redox and Optical Properties

In general, PDIs are stable, electron-deficient molecules that are difficult to oxidize and easy to reduce. Figure 1.5 shows the one-electron reversible oxidation and reduction process for PDI. The substituents in the imide position impose a negligible effect on the absorption and emission properties of substituted perylene; whereas, the arylated bay-position substitution shows a pronounced influence on the photophysical properties. For instance, the substitution produced a core twisting to cause a substantial bathochromic shift. In contrast to the bay substitution effect, the ortho-substitution causes slight bathochromic shifts.
compared to the parent unsubstituted perylene suggesting weak ground state electronic interactions between the substituents and perylene π system.

![Diagram of oxidation and reduction processes](image)

**Figure 1.5.** Oxidation $E_{1,o}$ and reduction $E_{1,r}$, and $E_{2,r}$ of PDI.$^{111}$

1.6 Perylene, as a Building Block, in Supramolecular Chemistry.

In 1987, the Nobel Prize was awarded to Professor Jean-Marie Lehn for his contributions to supramolecular chemistry,$^{112}$ which is founded on non-covalent interactions that have been employed in many cases to build the complicated functional architectures of Nature.$^2$ Metal-ligand coordination is an attractive supramolecular approach. The bond strength of such coordination complexes can be tuned by altering the metal. For instance, Ru$^{II}$ forms very strong bonds with tpy; whereas, Zn$^{II}$ and Cd$^{II}$ exhibit weak coordination. Porphyrins, C$_{60}$, and carbon nanotubes have been implemented to form functional architectures via a metallosupramolecular approach. Perylene bisimide (PBI) is useful in this
regard as a functional material due to its exceptional structural, photophysical, thermal, and electrochemical properties. The decoration of PBI with terpyridine, pyridine, and other suitable ligands instills further metal-mediated, self-assembly\textsuperscript{113,114} of these building blocks into cages, polymeric materials, amino acid conjugates, nanomaterials, and circular multichromophoric arrays that mimic natural photosynthetic light harvesting systems.

1.6.1 Metallo-supramolecular Chemistry of Perylene and Diazaperylene.

Perylene-bipyridine ligand \textbf{49} containing polyethylene side chains was self-assembled in aqueous media to form nanofibers that subsequently further associated and formed a three-dimensional network resulting in the generation of a chemical and thermal stimuli responsive gel.\textsuperscript{115} The network was utilized as a recyclable membrane for size selective separation of metal and semi-conductor nanoparticles.\textsuperscript{116} Charge transfer in the dyad system containing PDI and Ru\textsuperscript{II}bipyridine \textbf{50} was studied using femtosecond transient absorption spectroscopy, that showed ultrafast (<150 fs) intramolecular charge transfer from Ru\textsuperscript{II} to PDI,\textsuperscript{117} followed by charge recombination (64 ps). In order to apply this system for artificial photosynthesis devices, Ru\textsuperscript{II} photo-oxidation life time of Ru\textsuperscript{II}complex needs to be longer.
Figure 1.6. Structure of bipyridyl PDI ligand 49 and complex 50.\textsuperscript{3,115}

The construction of supramolecular architectures containing two Ru\textsuperscript{II}-porphyrin\textsuperscript{118} (or Zn\textsuperscript{II}-phthalocyanine\textsuperscript{119}) and one pyridyl-functionalized PDI 52, 53 (or dibenzodiazaperylene)\textsuperscript{120} in high yield was reported. The photophysical properties of these assemblies were also studied. These complexes exhibit a wavelength dependent electron-transfer behavior; thus, altering the wave length (from 585 to 530 nm) caused the change from intramolecular electron-transfer into triplet energy-transfer, which is inaccessible in free PDI chromophores due to the high fluorescence quantum yield and negligible intersystem crossing. The intramolecular sensitization imposed by the axial molecular arrangement facilitates the high efficiency access to this triplet state.\textsuperscript{121}
Scheme 1.14. Synthesis of \textbf{52} and \textbf{53} via axial coordination of \textbf{51} to Ru$^{II}$-porphyrin or Zn$^{II}$-phthalocyanine, respectively.$^{122-124}$

El-khouly et al.$^{125}$ reported that the axial coordination of pyridyl- or imidazolyl-functionalized PDI with Zn$^{II}$phthalocyanine afforded either \textbf{54} or \textbf{55}, respectively, that were reported by Bay substituted and unsubstituted PDIs were implemented, to investigate the effect of substitution on the electron-transfer rates. The moderately stable complexes absorbed light in visible and NIR wavelength, resulting in a charge separated state involving PDI radical anion (PDI$^{-}$) and Zn$^{II}$ naphthacyanine radical cation (ZnNc$^{+}$). The charge-separation and recombination rates of these molecules were determined in non-polar solvents where the bay-substituted PDIs showed longer excited state life times and slower charge recombination. The application of these molecules as photosynthetic models was also proposed. Zn$^{II}$porphyrin PDI dyad was also synthesized and utilized as active material for DSSC,$^{4}$ this multichromophore based solar device
exhibited moderate efficiency compared to separate chromophores and this was attributed to the co-sensitization and directional electron-transfer.

![Diagram of ZnII-phthalocyanine-PDI 54 and 55, and their energy transfer diagrams.](image)

Figure 1.7. Structures of ZnII-phthalocyanine-PDI 54, and 55, and their energy transfer diagrams.

Jiménez et al. reported the synthesis of the supramolecule 58 containing four bay-substituted pyridyl-PDI (PDIpy₄) electron-acceptor unit 57 connected to and enveloped by four RuII-phthalocyanine (RuCOPc) electron-donor units 56. The absorption, emission, time-resolved, and electrochemical spectroscopy of this system were also studied, it showed strong electronic interaction between the donor and acceptor units in the ground and excited states. Excitation of either the electron donor or acceptor moieties to S₁ produces a radical ion pair S₁ with short life time that underwent intersystem crossing to T₁ (Fig. 1.7).
Figure 1.8. Synthesis of RuⅡ-phthalocyanine-PDI 58, and energy transfer diagram depicting the relaxation routes upon excitation using 530 nm (left) or 630 nm (right).

Golubkov et al. reported the synthesis of three terpyridinyl PDI metal complexes 60-62, based on a single amphiphilic motife 59 containing perylene photoactive material, terpyridine and PEG group to enhance the water solubility. This ligand was then complexed with, PdⅡ, PtⅡ or AgⅡ to afford the corresponding PDI-Metal complexes 60, 61 or 62, respectively. These materials were shown to form diverse self-assembled structures in water/THF (9:1 v/v). For instance, ligand 69 self-assembled into long fibers, whereas, complex 60, 61 or 62 assembled into fiber-like structure, vesicular aggregates, or nanoplatelets respectively. The nanoassemblies were characterized using Cryo-TEM and visualized by molecular modeling. The functional properties of these complexes were studied using femtosecond transient absorption; they also showed high exciton mobilities.
Scheme 1.15. Complexation of 59 with various metal centers reported by Golubkov,\textsuperscript{127} A) Cryo-TEM of 59 (scale bar is 40 nm) segmented ribbon-like fibers; B) suggested structure of fibers of 59; C) Cryo-TEM (scale bar is 20 nm) of 60 nanotubes; D) Suggested structure of nanotube cross section; E) Cryo-TEM image of 61 (Scale bar is 10 nm) nanoplatelet; F) Molecular model of the bilayer formed by 61 (Reprinted with permission from ref\textsuperscript{127}, Copyright 2009 Wiley-VCH).

Tidhar et al.,\textsuperscript{128} also reported the synthesis of stable amphiphilic terpyridinyl-Pt\textsuperscript{II}PDI-containing peptide conjugates 63 that were formed via Pt\textsuperscript{II}-S binding. This complex exhibited kinetically controlled self-assembly behavior in aqueous medium, where the ratio of water/THF mixture altered the conjugates aggregation pathways from fibrous to helical to cylindrical nanostructures. CD, UV-Vis, and TEM were utilized to characterize the self assembly of this conjugate along with molecular modeling.
Figure 1.9. PDI-Pt\textsuperscript{II}-peptide conjugate 63; Molecular models of A) a single stack fiber; B) tube-like fiber; C) Schematic presentation of pathway dependent self-assembly of 63 (Reprinted with permission from ref\textsuperscript{128}, Copyright 2011 Wiley-VCH).

In order to efficiently generate the triplet excited-state of PDI (which improves the performance of PDI-based photo-voltic devices), Rachford \textit{et al.}\textsuperscript{129} synthesized three Pt\textsuperscript{II}-containing square planar complexes 64-66 in which the PDI moiety is attached to Pt\textsuperscript{II} \textit{via} bay-substituted acetylene group which is known to induce strong spin-orbital coupling and hence facilitating intersystem crossing. Following light absorption, the PDI fluorescence was quenched and the transient absorption spectrum showed long excited-state life time (from 246 ns to 1 µs), indicative of the triplet state. The authors anticipated that this finding will pave the road for higher performance solar cells that harness perylene triplet state. The
same group\textsuperscript{130} reported another example to investigate the triplet state of four heteroleptic acetylene-functionalized PDI connected to \textit{Pt}\textsuperscript{II}(terpyridine, bipyridine, and diphenylacetylyphosphine) that have emission in the Near IR region at approximately 1270 nm.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Chemical structures of PDI-Pt\textsuperscript{II} complexes 64, 65, and 66 reported by Rachford.\textsuperscript{129}}
\end{figure}

Dobrawa, Stepanenko \textit{et al.}\textsuperscript{131,132} synthesized asymmetric PDI containing monoterpyridine ligands with diverse substituents in the bay- and peri-positions. These ligands were self-assembled using Zn\textsuperscript{II} in a mixed solvent of CHCl\textsubscript{3}/MeOH to afford 68. The structural characterization was carried out using $^1$H NMR, $^{13}$C NMR, DOSY, and MALDI-TOF MS. UV-Vis absorption at $\lambda > 350$ nm was unaltered by complexation of ligand 67, whereas, a small increase at $\lambda = 250$-350 nm was observed due to tpy-Zn\textsuperscript{II}complexation. Ligand 67 and complex 68 are strongly fluorescent materials with $\Phi = 0.92$ and 0.90, respectively, in CHCl\textsubscript{3}. In contrast, stable, and non-luminescent supramolecular dimer was formed upon using excess Fe\textsuperscript{II} instead of Zn\textsuperscript{II}.  

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Scheme 1.16. Formation of perylene-terpyridine Zn$^{II}$ complexes 68,\textsuperscript{131,133}

PDI containing phenanthroline Ru$^{II}$ dye 69 was synthesized by Liu et al.,\textsuperscript{2} which showed a broad absorption spectrum and high molar absorption coefficient. The dye was adsorbed on TiO$_2$ via COOH anchoring groups and was utilized to build DSSC of which the photovoltaic properties was studied and showed lower output performance than expected. This was attributed to the electron withdrawing effect of the Imid group that resulted in the unbeneificial photogenerated electron transfer directionality. A series of perylene-containing polypyridyl ligands were synthesized\textsuperscript{134} and reacted with tpy-Ru$^{II}$ adduct to afford the corresponding PDI-containing phenanthroline-Ru$^{II}$ complexes 70 and 71 in order to investigate the coupling of one electron organic material (perylene) to two electrons catalyst (Ru) as an artificial photosynthetic system. These materials electrocatalyzed the transformation of isopropyl alcohol into acetone in the dark, whereas, the reaction rate showed a small enhancement upon illumination. The photocatalytic activity of these materials was demonstrated\textsuperscript{135} by photooxidation reaction of DMF.
Costa et al.\textsuperscript{2,27} reported the synthesis of pheanthroline-Ir\textsuperscript{III} PDI complex 72 along with its application as an active layer in light emitting electrochemical cells. This material showed high external electro-luminescent efficiency in the deep red region, which was attributed to the collaboration between the ionic nature of Ir\textsuperscript{III} (that function as hole conducting phosphorescence emitter) and PDI red fluorescence (that acted as an electron conductor). The PDI-containing phenylpyridinyl-Ir\textsuperscript{III} complex 73 was also synthesized, and it’s photophysical properties were reported\textsuperscript{138}. In case of CF\textsubscript{3} substituted PDI, an ultrafast electron transfer from the Ir\textsuperscript{III} site to PDI was observed and electrochemical studies showed irreversible oxidation currents that indicate the stability of the catalytic site upon attachment to perylene. These materials were used as catalysts for water oxidation.
Kammer et al. reportd the multistep synthesis and self-assembly to diazperylene (Dper) 77. The synthesis started with the halogenation of 74 with POCl₃ to give 75 which uderwent a Ni-catalyzed coupling reaction to afforded the bisquinoline 76. The reductive cyclization of 76 afforded the corresponding dialkylated diazaperylene 77 that was then reacted with Cu¹ to affod the corresponding bisdiazaperylene-Cu¹ complex 78. A single crystal of this compound showed that the complex formed a supraolecular columnar structures via π-π stacking forces that caused strong intermolecular electronic interactions.
Scheme 1.17. Synthesis of diazaperylene 77 and its Cu(I)-mediated self-assembly, and crystal structure of 78 (R=iPr). (Reprinted with permission from ref\textsuperscript{139}, Copyright 2009 Wiley-VCH).

Chouai \textit{et al.}\textsuperscript{140} reported the synthesis of Ru\textsuperscript{II} and Os\textsuperscript{II} homo and heteroleptic complexes. Ru\textsuperscript{II} and Os\textsuperscript{II} trisperylen complexes 79 were synthesized by the reaction of Dper 77 with Ru\textsuperscript{II} and Os\textsuperscript{II}, respectively. The heteroleptic complexes 80 and 81 were also synthesized where the single crystal of 80 showed that the ligands are arranged in propeller shape. The absorption spectrum of these complexes showed that the $\lambda_{\text{max}}$ of MLCT band increase in intensity and decrease in energy as the number DPer ligands increase, Ru\textsuperscript{II}(Dper)$_2$bpy 80 caused the photogenerated DNA plasmid cleavage. The same group also reported\textsuperscript{141} the synthesis of Fe\textsuperscript{II} and Ni\textsuperscript{II}Dper octahedral complexes with either BF\textsubscript{4} or PF\textsubscript{6} counter ions. The single crystal of these compounds have strong intermolecular $\pi-\pi$ interactions that direct the metallosupramolecules into honeycomb nanochannel structures that run along the crystal C-axis. The light absorption and redox properties of these materials were also studied.
Scheme 1.18. Self-assembly of 77 and bpy using Ru$^{II}$, Ni$^{II}$, Fe$^{II}$, Os$^{II}$: A) Uv-vis spectra of 77 (black), 81 (blue), 80 (green), and 79 (red) (Reprinted with permission from ref$^{140}$, Copyright 2005 American Chemical Society); B) Honeycomb structure of 79 (M=Ni) (Reprinted with permission from ref$^{142}$, Copyright 2005 Wiley-VCH).

A supramolecular heterostructure 82 was synthesized by Schmelz et al$^{143}$ to study the electronic interactions at the nanoscale interface. This system includes ZnS-CdSe core-shell nanocrystal coated with TOPO 81 ligands, that were exchanged with Dper ligands 77 (3-20 ligands attached to the nanoparticles). Dper dye 77 was synthesized starting from LDA dimerization of isoquinoline to form biisoquinoline that was subsequently reduced and cyclized with K in DME to give the targeted dye (74%). The fluorescence of the nanocrystal was quenched upon the formation of this NC/dye supramolecular structure at any dye coverage, whether the dye or the nanocrystal is photoexcited. This observation was explained by the possible formation of an interfacial energy state that leads to the nonradiative energy dissipation.
Scheme 1.19. Phosphate ligand displacement with diazaperylene 77 in CdSe-NP 82.\textsuperscript{143}

Kammer \textit{et al.}\textsuperscript{144} also reported the synthesis and X-ray structure characterization of a series of heteroleptic Dper-Ir\textsuperscript{III} complexes 83. In solid state the \(\pi-\pi\) stacking forces either form supramolecular channels or 2-D layer structures, CH-\(\pi\) interactions also contributed significantly to the solid state structure stability. In addition, ESI-MS was implemented to study the complexation of Dper to transition metals series including Os\textsuperscript{II}, Ru\textsuperscript{II}, Fe\textsuperscript{II}, Ni\textsuperscript{II}, and Cu\textsuperscript{I} in the gas phase. The binding affinity of this ligand was the highest compared to bipyridine and phenanthroline, due to its planar structure. The collision-induced dissociation study showed that the binding strength of these metals-Dper bond increase in the following order (Os\textsuperscript{II} > Ru\textsuperscript{II} > Fe\textsuperscript{II} = Ni\textsuperscript{II} = Cu\textsuperscript{I}).
Elbatal *et al.* reported the synthesis of peri-substituted linear and angular PDI-containing bisterpyridine ligands 87 and 88 *via* reaction of perylene 84 with amino-terpyridine 85 and 86, respectively, in quinolone at 220 °C. These ligands were then introduced to the reaction with RuII-terpyridine adducts 89 in DMF to afford the corresponding metallosupramolecules 90 or 91. Diocetyldibromo PDI 92 was also synthesized and underwent a Suzuki coupling reaction with terpyridine boronic acid 84, in a refluxing mixture of t-Bu-OH:toluene:H2O (3:3:1) to give a mixture of 1,6- and 1,7-bisterpyridine PDI 41. The pure 1,7-isomer 94 was isolated by iterative recrystallization cycles (CHCl3/MeOH). This bisterpyridine was then reacted with adduct 89, under reducing conditions followed by chromatographic purification steps to afford the bay-substituted RuII complex 95. The photophysical and electrochemical properties of these materials were studied along with their application as sensitizers for DSSCs. The solar devices showed low overall performance that was attributed to the presence of two strong electron withdrawing groups that make the non-directional electron injection.
Elbatal \textit{et al.}\textsuperscript{145} also reported the synthesis of a series of complexes including \textit{bis-}, \textit{tetrakis-} and \textit{hexakis-}terpyridine ligands 98, 99, and 100 via the reaction of perylene bisanhydride 84 with either amino mono-, \textit{bis-}, or \textit{tris-}terpyridines 95, 96 or 97 respectively in quinoline at 220 °C. The corresponding Ru\textsuperscript{II}\textit{bisterpyridine} metallodendrimers 101, 102 or 103 were then achieved through the reaction of adduct 89 with ligands 95, 96 or 97, respectively, in DMF at 80 °C. These materials were characterized using \textsuperscript{1}H NMR, COSY, \textsuperscript{13}C NMR, and ESI-MS. The photophysical properties of these ligands and complexes were studied, the ligands showed a broad absorption spectrum with $\lambda_{\text{max}} = 579, 543, 447, 267,$ and 289 nm, and strong emission at $\lambda_{\text{max}} = 582, 617,$ and 671 nm, whereas,
complexes exhibited a band at 497 corresponding to MLCT, the molar absorption coefficient of which is proportional to the number of Ru\textsuperscript{II}bistpyridine complexes. The authors suggested the use of these materials as potential candidates for solar energy collecting devices.

Scheme 1.21. Synthesis of perylene-based, *bis*-*, tetrakis*-*, and *hexakis*-terpyridine ligands 98, 99, and 100, and their Ru\textsuperscript{II} complexes 101, 102, and 103.\textsuperscript{145} The ditopic perylene containing terpyridine ligand 104 was self-assembled with Zn\textsuperscript{II} in MeCN/CHCl\textsubscript{3} to afford the fluorescent trimeric metallomacrocyle\textsuperscript{146} 105. The structure of this compound was confirmed using DOSY and \textsuperscript{1}HNMR titration experiments in addition to MALDI-TOF MS. These metallocycles underwent a second level of self-assembly to form two-dimensional honeycomb networks. AFM was implemented to study their morphology on HOPG surface.
Scheme 1.22. Zn$^{II}$bisterpyridinyl PDI metallocyles formation and AFM images of 105 on HOPG: A) and B) height images; C) Fast Fourier transform analysis of image B; D) Zoomed hexagonal unit; E) Proposed model for the trimer 105 arrangement in honeycomb structure. (Reprinted with permission from ref$^{146}$, Copyright 2008 Wiley-VCH).

Würthner et al.$^{147}$ reported the dynamic equilibrium between molecular triangles 109b and squares 109a upon the self-assembly of bay-functionalized diazadibenzoperylene ligand 107 with pd$^{II}$ and Pt$^{II}$ phosphane triflate 108 in CH$_2$Cl$_2$ at 25 °C. The equilibrium was depicted using variable-temperature $^1$H NMR, $^{31}$P NMR, and ESI-MS. This equilibrium was influenced using solvent, metal, and was shifted towards the square structure 109a when the bulky t-butyl bay-substituents were introduced. The stability of these complexes was also investigated using the UV-Vis study that showed the dependence of absorption and emission properties on the metal used, where higher stability was achieved with Pt(II) complexes compared to Pd(II) complexes.
Scheme 1.23. Self-assembly of 107 and 108 to produce equilibrium mixture of trimer 109b and tetramer 109a structures.\textsuperscript{147}

Tetrannuclear macrocyclic including Pt(II) and Pd(II) diazadibenzoperylene 112 were reported by Stang \textit{et al}.\textsuperscript{148} These squares were formed by the reaction of dibenzodiazaperylene 110 with (Et\textsubscript{3}P)\textsubscript{2}Pt(OTf)\textsubscript{2} 111 in MeNO\textsubscript{2} at 25 °C. Their characterization using \textsuperscript{1}H NMR and \textsuperscript{19}F NMR showed the presence of symmetric structure that was assigned to square 112. This result contradicts the previous examples that showed equilibrium shift from trimeric to tetrameric species as a function of the \textit{bay}-substituents bulkiness of, which suggest that the trinuclear species should dominate in absence of any \textit{bay}-substituents. This may be attributed to the lack of any MS analysis that can support the proposed structure.
Scheme 1.24. Synthesis of tetranuclear PtII and PdII diazadibenzoperylene macrocycles 112.\textsuperscript{148}

Professor Stang group\textsuperscript{149} also reported the synthesis of bispipyridylperylened ligand 113 via a Sonogashira coupling as well as its self-assembly with either Pt-clip 114 or cis-(PMe\textsubscript{3})\textsubscript{2}Pt(OTf)\textsubscript{2} 115 in acetone to yield the corresponding rectangle 116 or rhomboid 117 structure, respectively. These complexes were characterized using \textsuperscript{1}H NMR, \textsuperscript{31}P NMR, ESI-MS, and UV-Vis spectroscopy which showed an enhanced absorption of the macrocycles compared to the free ligand. Molecular modeling showed a Pt-Pt distance of 3.5 nm and PDI-PDI-distance 0.76 nm for rhomboid structure 117, compared to the larger rectangle 116 pore size of 4.5 nm.
Scheme 1.25. Self-assembly of 113 with 114 or 115 to produce Pt$^{II}$-pyridyl-PDI rectangle 116 or rhombus 117 metallomacrocycles.\textsuperscript{149}

Quantitative formation of supramolecular squares 118 was reported.\textsuperscript{150} These complexes were formed upon the self assembly of diverse bay-functionalized pyridine-PDI ligand 59 with Pt(II) or Pd(II) salts in CH$_2$Cl$_2$ at 25 °C followed by precipitation with Et$_2$O. These squares were characterized using $^1$H, $^{31}$P NMR, UV-Vis spectroscopy, ESI-MS, and cyclic voltametry. These complexes posses high molecular weights ~12 kDa (pyrene substituents) and the molecular modeling showed dimensions of (2.4 x 2.4 nm), this large pore size has potential for guest enclosure. The energy transfer in molecular square with pyrene bay-substituents was investigated using emission and excitation spectroscopy\textsuperscript{151} that exhibited ultrafast and efficient energy-electron transfer\textsuperscript{152} process that is only matched by solid materials. This fast transfer rates were attributed the formation of solid like molecular ensembles formed by close packing of aggregates containing 20 chromophoric units. In case Ferrocene functionalize PDI
Pt$^{\text{II}}$ molecular square$^{153}$ 118, the electrochemical studies showed that the redox behavior of ferrocene units was influenced by the square superstructure.

Scheme 1.26. Pt$^{\text{II}}$-mediated self-assembly of 59 to produce substituted PDI-tetranuclear metallomacrocycles 118.$^{154-157}$

Elbatal et al. synthesized two perylene-containing terpyridine ligands 121 or 123 via reaction of perylene 119 with either bisterpyridine ligands 120 or 122 in quinoline at 220 °C followed by workup and chromatographic purification. The resulting low yield of ligand 121 compared to 123 was attributed to the direct electronic interaction with the two terpyridine in 120 that decrease the reactivity compared to 123 that contains $n$-propyl spacer. The ligands were then self-assembled using Zn$^{\text{II}}$, in MeOH/CHCl$_3$ (1:3) to give an equilibrium mixture of macrocycles 124. The structure was studied using $^1$HNMR and TWIM-MS that showed the major product is 5- and 6-membered rings. Dosy NMR also revealed the presence of two molecular species with diffusion coefficients of 2.5 and 3X10$^{-10}$ m$^2$S$^{-1}$ that corresponds to calculated hydrodynamic radius of 3.1 and 3.5 nm respectively. The molecular modeling diminsions of the pentameric and hexameric structures were in agreement with the calculated dimensions. The photophysical properties of these ligands and complexes were also studied. The
Emission spectroscopy of 124 showed that these materials are strongly photoluminescent; the fabrication of OLED of these materials was also proposed by the authors.

![Scheme 1.27. Synthesis of PDI-bis-terpyidine ligands 121 and 123 and Zn^{II}-mediated self-assembly of 123 to give macrocycles 124.](image)

Dibromo- 127a and tetrachloro-pyridine-PDI 127b were self-assembled with dicarboxylic acids 125 and Zn (II) to form paddlewheel\(^{158}\) crystalline material 127a and 127b. The crystal structures showed large accessible porous volume (55%) and the adsorption measurements revealed BET surface area of 195 (127a) and 91 (127b) m\(^2\)/g. These porous MOF investigated for their ability to store gases such as H\(_2\) at ambient pressures, in addition to the proposed application as sensing and solid state fluorescent materials.
Diporphyrine zinc perylene triads 128 were synthesized by condensation of amino porphyrine with Perylenedianhydride and zinc acetate in quinoline at 180 °C for 16 h. The UV-Vis spectra of these materials showed strong absorption at $\lambda_{\text{max}} = 425$ and 500-650 nm due to the absorption of porphyrine and perylene, respectively. Substituted diazadibenzoperylene (DABP) 107 was synthesized and its crystal structure was investigated, this triad was then self-assembled with diaza ligand 107 in CHCl$_3$ to afford photo-functional rigid oligomeric zigzag assemblies 129 (n ~ 6) of alternating porphyrine and perylene dyes. The authors reported that the molecular modeling calculations suggested that the
twisting of perylene ligand 107 disfavor the formation of rectangular supramolecular structure. The emission properties of 129 revealed strong luminescence at $\lambda_{\text{max}} = 496, 522$ nm with $\Phi = 0.75$, it worth noting that the $^1$HNMR of the 129 is shape and represents a single molecular species; this paper did not offer enough evidence (such as MS) to justify the absence of the molecular square species.

Scheme 1.29. Self-assembly of PDI-Zn$^{II}$-porphyrin triad 128 with dibenzodiazaperylene 107 to form coordination polymer 129.$^{159}$

Trials to investigate the polymerization of 130 with Ag(I) were not possible because the chain growth of this polymer was hindered by interchain $\pi-\pi$ stacking (that led to precipitation and thus individual chains cannot be observed). In order to investigate single chains bay-position was functionalized with G$_1$, G$_2$, and G$_3$ Fréchet type dendrons$^{102}$ DABP 130 were synthesized and polymerized using Ag$^+$ to afford G$_1$ and G$_2$ dendronized rod-like polymers 131. In comparison, G$_3$ dendronized ligand resisted polymerization due to the spatial shielding of aza-
groups by dendritic wedges. The polymer structures were characterized using DOSY-NMR which showed large decrease of diffusion coefficients upon addition of 1 equivalent of Ag(I). AFM images showed long rod like structures corresponding to polymer chains for $G_1$ and $G_2$ Ag-DABP polymer chains.

Scheme 1.30. The synthesis of $G_1$-$G_3$ dendronized diazadibenzoperylene ligand 130 and Ag-mediated rigid polymer formation 131, and AFM height image on HOPG (scale bar is 200 nm) of polymer 131. (Reprinted with permission from ref 102, Copyright 2006 Wiley-VCH).

A linear Perylene-containing terpyridine ligand 133 was used as a building block for the fabrication of a multilayer Fe$^{II}$-Ligand functional self-assembled monolayers (SAML) on a gold surface. The process started by the fictionalization of gold surface with terpyridine to give 132a. Dipping this gold wafer in FeSO$_4$ solution gave the corresponding Fe(II)-adduct 132b, which was then dipped in perylene-containing solution to afford 132c (SAML). This process was then repeated for x-times to give x-layers perpendicular self-assembled chains on the gold surface.$^{160,161}$ The formation of the multilayers was then investigated using AFM measurement of the patterned samples, which confirmed the upright growth.
The photophysical studies showed that perylene moieties absorbed energy and then injected it (in sub-picosecond time scale) to the gold surface.

Scheme 1.31. The growth of self-assembled monolayers 132e and AFM image and line cross section of 4-layers pattern. (Reprinted with permission from ref160, Copyright 2009 Royal Society of Chemistry).

Hassan et al.2 reported the formation of novel fluorescent cellulose nano-whiskers 134c. In this approach, the hydroxyl groups on 134a were introduced to the reaction with chloroterpyridine. The tpy-functionalized nanomaterial was then reacted with RuCl₃·nH₂O to give the corresponding paramagnetic Ru³⁺-adduct which was purified to give 134b. Compound 87 was then reacted with 134b to produce cellulose functionalized perylene, which was further reacted with RuCl₃·nH₂O followed by azide-functionalized tpy to afford the perylene containing cellulose nanocomposite 134c. This material has potential for further functionalization using click chemistry with cancer targeting moieties to harness the excellent fluorescence properties of 134c for cancer imaging.
Würthner group\textsuperscript{131,133} reported the synthesis of Zn\textsuperscript{II}bis-terpyridine perylene photoluminescent polymers \textbf{136} or \textbf{137} via reaction of Zn triflate with either ditopic ligands (1:1) \textbf{135} or \textbf{87}, respectively. The dynamic nature of these polymers was proved by the addition of a second equivalent of Zn\textsuperscript{II} to give bis-Zn\textsuperscript{II} adduct \textbf{138} or \textbf{139}. These rigid polymers were soluble in DMF and were deposited on mica and HOPG surfaces. AFM studies on these surfaces showed that the polymers aligned along the graphite axis and the average chain length of the polymer is 30-35 repeating units. Current imaging tunneling spectroscopy showed periodicity of 2.2 nm between Zn\textsuperscript{II} centers which was in excellent matching with molecular modeling calculations (2.3 nm). Finally a multilayer alternating film of the two metallopolymers was deposited and the surface densities of perylene in these films were studied.
Scheme 1.33. The formation and dissociation of coordination polymers by Zn$^{II}$-mediated self-assembly of PDI ligands 87, 135 and AFM image (scale bar is 100 nm) of thin film prepared by spin-coating 137 on HOPG. (Reprinted with permission from ref$^{133}$, Copyright 2009 Royal Society of Chemistry).

Tetra-Zn$^{II}$-porphyrin functionalized perylene ligand 142 was synthesized by the DCC condensation reaction of perylene 140 with porphyrine (TPP), in CH$_2$Cl$_2$ for 7 days. Porphrin 141 metallation was achieved via reaction with Zn(OAc)$_2$ in CH$_2$Cl$_2$/MeOH at 25 ºC for 24h. 142 was then self assembled with DABCO 143 in CHCl$_3$ to form sandwich structure using 1:1 ratio to form 144 or 2:1 ratio to form 144$^{160}$ This multichromophore double decker structure and properties were examined using $^1$H NMR, DOSY, UV-Vis spectroscopy, and AFM imaging. The DOSY obtained dimensions is (1.56 nm), which is in perfect match with the molecular modeling calculated dimensions (1.54 nm). AFM data showed the formation of monodisperse nanoparticles on HOPG surface (4.7 nm.
length and 3.4 nm width), this 2-D nanopattern can have potential electro-optical applications.

Scheme 1.34. Diagram of DABCO 143 mediated two-step self-assembly of 142 and AFM images (scale bar is 60 nm): A) Height AFM image of 144b spin-coated on HOPG; B) Magnified region of image A yellow frame; C) Cross-section analysis along the yellow line in B. (Reprinted with permission from ref\textsuperscript{160}, Copyright 2010 Wiley-VCH).

Indelli \textit{et al.}\textsuperscript{162} reported the synthesis of multichromophore heterometallic molecular box 146. The synthesis started from dipyridyl Zn\textsuperscript{II}-porphyrine complexation with Ru\textsuperscript{II} to give 145, which was axially coordinated with PDI 51 in CH\textsubscript{2}Cl\textsubscript{2}. The \textit{bay}-substituents in PDI 51 have a great influence on the structural, photophysical, and electrochemical properties of the so formed complexes. X-ray structures showed that pyrrolidine \textit{bay}-substituted PDI, formed a perfect rectangle shape, whereas, the bulkier \textit{t}-butylphenol substituted PDI showed a highly distorted box structures in which Zn\textsuperscript{II}-porphyrin was twisted and the PBI units
were in a close proximity to each other (3.9 Å), leaving a cavity that can establish π stacking and electronic interactions with guest molecules.

Scheme 1.35. The synthesis molecular box 146 and cartoon representation of its solid state structures. (Reprinted with permission from ref \textsuperscript{162}, Copyright 2010 American Chemical Society).

Oliva \textit{et al.}\textsuperscript{163} harnessed the axial coordination approach to form double-decker cages 148\textsuperscript{a} and 148\textsuperscript{b}. In this approach bispyridinyl-PDI 51 was reacted with \textit{tris}-Zn\textsuperscript{II}-porphyrine 147 to afford a mixture of fully- 148\textsuperscript{a} and partially-assembled 148\textsuperscript{b} triagonal prism type product. 148\textsuperscript{a} was the predominant species in CH\textsubscript{2}Cl\textsubscript{2}, whereas, the partially assembled compound 148\textsuperscript{b} was the major product in toluene. The photophysical and electrochemical properties of this mixture showed that the porphyrine fluorescence was quenched upon the excitation of either PDI (acceptor) or porphyrine (donner). In case of partially-assembled structure, the photophysical behavior of uncoordinated Zn\textsuperscript{II}-porphyrine was same as free unit. The rate of charge transfer was independent of the solvent whereas the charge recombination life time was solvent dependent.
Scheme 1.36. Axial coordination of 59 and 151 to form cage structures 148a and 148b.\textsuperscript{163}

1.7 Concluding Remarks.

PDI is a material that posses rich chemistry and potential for versatile applications, which make it the focus of academic research and industrial activity. The application spectrum of this material spans the electronic, physical, chemical, medical and biological fields. Enhancing the efficiency of PDI in several applications can be achieved via construction of highly ordered structures, in this regard, metallosupramolecular chemistry can be considered one of the most important tools to create a plethora of controlled shapes such as cage, cyclic, and polymeric architectures. Exploring the chemistry, properties, and applications of PDI will continue to expand and play an increasing role in the chemistry, physics and material science.
CHAPTER II
PERYLENE-BASED, BIS-, TETRAKIS-, AND HEXAKIS-TERPYRIDINE LIGANDS AND THEIR RUTHENIUM(II)BIS-TERPYRIDINE COMPLEXES:
SYNTHESIS AND PHOTOPHYSICAL PROPERTIES†

2.1 Introduction

Perylene bisimide is an organic chromophore with exceptional characteristics,\textsuperscript{164-166} including high quantum yield, photoluminescence, thermal and photochemical stability, as well as good optical and electronic properties,\textsuperscript{167} leading to applications\textsuperscript{168} in fields such as: fluorescent markers,\textsuperscript{169} photonics,\textsuperscript{170} organic electronics,\textsuperscript{31,171,172} and solar devices.\textsuperscript{31,168-174} Their use in the construction of multichromophoric dye arrays (cyclic or incorporating branches) embraces the promise of enhancing the light harvesting efficiency; this goal can be achieved by instilling a supramolecular\textsuperscript{113,175} approach using hydrogen bonding,\textsuperscript{176} hydrophobic,\textsuperscript{177} and \( \pi-\pi \) interactions, and metal-ligand binding approaches to control the shape and size of the assembled architectures. Numerous examples of <ligand-M-ligand> connectivity have been reported by Newkome,\textsuperscript{178-180} Stang,\textsuperscript{181} Schmittel,\textsuperscript{182,183} Fujita,\textsuperscript{184,185} and others.\textsuperscript{186-188}

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More specifically, 2,2’:6’,2”-terpyridine (tpy) ligands have gained increasing utility in metal-ligand coordination, particularly <tpyRuIItpy> complexes\textsuperscript{146,189,190} due to their potential utilitarian applications\textsuperscript{191,192} and interesting possible topologies, which include macrocycles\textsuperscript{193} and dendrimers.\textsuperscript{191,192,194} Metalloendritic architectures are monodisperse, well-defined branched structures, and since light absorbing chromophores can be incorporated into their core and/or branches, the resultant materials can possess enhanced optical characteristics. Our objective is to synthesize materials with maximized photofunctional properties through the non-covalent combination of multichromophores. Herein, we present the synthesis, isolation, and characterization of three novel perylene-containing tpy ligands,\textsuperscript{127} as well as their heteroleptic <tpyRuIItpy> complexes. The perylene unit is employed as the core and the <tpyRuIItpy> as the termini. The structures of these materials were studied by NMR spectroscopy, MS, UV-Vis absorption, and photoluminescence.

2.2 Results and Discussion

Construction of the desired complexes necessitated access to the requisite amino-(mono-, bis-, and tris)terpyridine ligands. The mono- and bis-terpyridines were prepared via reported procedures.{Chan, 2010 119 /id;Wang, 2004 64 /id;Chan, 2010 119 /id} Synthesis of tristerpyridine 6 (Scheme 2.1) was accomplished by the alkylation of phenol 1\textsuperscript{195} with N-(3-propyl)phthalimide 2 and K$_2$CO$_3$ in MeCN at 80 °C for 8 h to give (85%) imide 3, which was reacted with 4-terpyridinylphenylboronic acid 4 in toluene:H$_2$O:t-BuOH (3:3:1) at 100 °C for
3d. The crude product was purified by column chromatography (Al$_2$O$_3$), eluting with CHCl$_3$, followed by deprotection with hydrazine in EtOH to afford 6 (80%).

Scheme 2.1. Synthesis of tristerpyridine 6: a) K$_2$CO$_3$, MeCN, 80 °C, 8h; b) Pd$^{II}$, K$_2$CO$_3$, toluene:H$_2$O:t-BuOH (3:3:1), Ar, 100 °C, 72h; c) N$_2$H$_4$, EtOH, 80 °C, 8h.

The two-step synthesis of complexes 14 - 16 is illustrated in Scheme 2.2. Initially, the bisanhydride 1 was reacted with aminoterpyridine 8, 9 or 6 in quinoline at 220 °C for 4 days. The crude products were precipitated using AcOH, filtered, washed with water and EtOH, and then subsequently purified by column chromatography (Al$_2$O$_3$), eluting with CHCl$_3$, followed by recrystallization (CHCl$_3$/MeOH) to afford 10 (67%), 11 (55%), and 12 (40%), respectively. The structures were confirmed using $^1$H, $^{13}$C, and COSY NMR spectroscopy, as well as electrospray ionization mass spectrometry (ESI-MS). $^1$H NMR spectrum of bisterpyridine 10 revealed a singlet at 8.87 ppm (3',5'), two doublets at 8.74 ppm (6,6'') and 8.64 ppm (3,3''), two multiplets at 7.78 (4,4'') and 7.33 ppm (5,5''), and a single perylene proton at 8.19 ppm. In comparison, the $^1$H NMR spectrum of the tetrakisterpyridine 11 showed the following tpy resonance frequencies: 8.70-8.69 (3',5' and 6,6''), 7.84 (4,4'') and 7.30 ppm (5,5''), and a single perylene proton at 8.12 ppm; whereas, hexakisterpyridine 12 revealed the presence of two electronically non-equivalent sets of tpy protons with (2:1) integration ratio, four
electronically equivalent perylene protons, and a singlet at 3.23 ppm corresponding to CH$_3$. The observed integration ratios for all the ligands were as anticipated. The identity and purity of the tpy ligands were further assured by ESI-MS spectra, which led to peaks at $m/z$ 1712.8 [M]$^+$ (Calcd. $m/z$ = 1717.7) for 10, 2174.8 [M]$^+$ (Calcd. $m/z$ = 2174) for 11, and 3149.2 [M]$^+$ (Calcd. $m/z$ = 3149.2) for 12.

The Ru$^{II}$tpy(MeCN)$_3$ 13 (Scheme 2.3) was constructed by refluxing terpyridine 17 in an ethanolic solution of RuCl$_3$·3H$_2$O for 12h to afford the paramagnetic Ru$^{III}$tpy adduct, which was washed with EtOH, dehalogenated and reduced to Ru$^{II}$tpy(MeCN)$_3$ by refluxing in a AgNO$_3$ solution of MeOH:MeCN (1:1) for 12 h. Reagent 13 was column chromatographed (SiO$_2$) eluting with a mixture of MeCN:H$_2$O:KNO$_3$ (20:1:1). The $^1$H NMR spectrum of 13 revealed a singlet at 8.66 ppm (3',5'), two doublets at 8.94 ppm (6,6''), and 8.58 ppm (3,3''), as well as three singlets at 2.76, 2.49, and 2.13 ppm corresponding to tpy-CH$_3$ moieties, equatorial and axial MeCN ligands, respectively.
Scheme 2.2. Synthetic route to ligands 10 - 12 along with their corresponding \textit{<tpyRu}^{II}tpy\textit{>} complexes 14 - 16: a) quinoline, Ar, 220 °C, 4 days; b) DMF, Ar, 110 °C, 2 days (complexes 14 - 16 were isolated with \textit{NO}_3^− counterions).

The heteroleptic complexes 14 - 16 were prepared by the reaction of tpy ligands 10 - 12 with adduct 13 (1.2 eq. per tpy) in DMF at 110 °C for 48 h., the solvent was removed \textit{in vacuo} and complexes 14 - 16 were column chromatographed (SiO\textsubscript{2}) eluting with a mixture of MeCN:H\textsubscript{2}O:KNO\textsubscript{3} (30:1:1) for 14 (80%), (20:1:1) for 15 (70%), and (15:1:1) for 16 (55%).
Scheme 2.3. Synthesis of Ru\textsuperscript{II}tpy adduct 13: a) RuCl\textsubscript{3}3H\textsubscript{2}O, EtOH, 12h; b) AgNO\textsubscript{3}, MeCN/MeOH (1:1).

Finally, the counter ion was exchanged (NO\textsubscript{3}\textsuperscript{−} to PF\textsubscript{6}\textsuperscript{−}) modifying the solubilities from MeOH/CHCl\textsubscript{3} (NO\textsubscript{3}\textsuperscript{−}) to MeCN/CHCl\textsubscript{3} and DMF, respectively. Complexes 14 - 16 were characterized \textsuperscript{1}H NMR, \textsuperscript{13}C NMR, COSY, and MALDI-TOF MS spectroscopy. The \textsuperscript{1}H NMR spectra of both complexes 14 and 15 showed two sets of distinct resonance frequencies attributed to the internal and terminal tpy. The tpy\textsuperscript{H\textsubscript{3,5}} resonances showed slight down-field shifts when compared to the corresponding free ligands at 9.22, 9.16 ppm (14); 9.87, 9.54 ppm (15). In contrast, the tpy\textsuperscript{H\textsubscript{6,6\textsuperscript{\prime}}} resonances showed dramatic upfield shifts compared to the corresponding free ligands at 6.99 ppm (14); 7.98-7.94, 7.87-7.86 ppm (15). Hexakisadduct 16 exhibited a complicated \textsuperscript{1}H NMR spectroscopy pattern with the following resonance frequencies: four tpy\textsuperscript{H\textsubscript{3,5}} at 9.04, 8.98, 8.95, 8.94 ppm; perylene proton at 8.08 ppm; three CH\textsubscript{3} and one C(CH\textsubscript{3})\textsubscript{3} at 2.98, 2.85, 2.27 and 1.29 ppm, respectively, with the correct integration ratios. The structures were further confirmed by ESI-MS (Fig. 2.1) with peaks for multiply charged ions of 14 at \textit{m/z} 902.60 [M - 3PF\textsubscript{6}\textsuperscript{−}]\textsuperscript{3+} (Calcd. \textit{m/z} = 902.60) and 640.70 [M - 4PF\textsubscript{6}\textsuperscript{−}]\textsuperscript{4+} (Calcd. \textit{m/z} = 640.71), which resulted from the loss of PF\textsubscript{6}\textsuperscript{−} counter ions. Tetrakisadduct 15 formation was confirmed with signals at (\textit{m/z}): 1113.7, 861.9,
694.1, 674.1, and 484.3 for charge states +4 to +8, respectively. Finally, the hexakiscomplex 16 (Fig. 2.1) was confirmed by the presence of signals at (m/z): 1342.9, 1094.9, 917.7, 784.9, 681.6, 598.8, 530.9, and 474.9 for charge states +5 to +12, respectively.

Figure 2.1. ESI-MS of 14 (a), 15 (b), and 16 (c).

The absorption (DMF) and emission spectra (CHCl₃) of the metallodendrimers and the corresponding ligands along with their photophysical data are shown in Fig. 2.2, and Table 2.1. It is known that the electronic properties
of perylene are unaltered by substituents in the imide position. Thus, one can expect the UV-vis spectra of the ligands and complexes to be a superimposition of perylene and \(<\text{tpyRu}^{\text{II}}\text{tpy}>\) absorptions with peak heights proportional to the number of termini. Ligands 10 - 12 are bright red materials that show absorption spectra with \(\lambda_{\text{max}}\) at 579, 543, and 447 nm corresponding to \(S_{0}-S_{1}\) and \(S_{0}-S_{2}\) transitions, respectively, in addition to the expected tpy ligand centered (LC, \(\pi\rightarrow\pi^{*}\)) absorption at 267 and 289 nm.

In comparison, emission spectra of ligands 10 - 12 are mainly attributed to perylene emission bands with maxima at 582, 617, and 671 nm. Moreover, the ruthenium-containing heterocomplexes 14 - 16 are dark red solids exhibiting bands at 497 nm corresponding to the allowed metal-to-ligand charge transfer (\(1^{\text{MLCT}}\)) transitions \([\log \varepsilon = 4.88\ (14); 4.90\ (15); 4.92\ (16)]\); 288, 313 nm corresponding to (LC, \(\pi\rightarrow\pi^{*}\)) absorption \([\log \varepsilon = 3.28, 5.25\ (14); 5.29, 5.30\ (15); 5.30, 5.32\ (16)]\); 570 nm corresponding to perylene \(S_{0}-S_{1}\) absorption band \([\log \varepsilon = 4.72\ (14); 4.62\ (15); 4.44\ (16)]\). The observed progressive increase of the molar extinction coefficient \((14 < 15 < 16)\) at the following absorption bands: 288, 313, and 497 nm is consistent with the increase in the number of ligands and Ru\(^{\text{II}}\) metal centers.
2.2. Normalized absorption (DMF) and emission spectra (CHCl$_3$) of ligands 10-12 and the corresponding complexes 14-16 at 25 °C. The emission spectra were recorded with excitation wave length at 580 nm and slit width of 5nm.

Table 2.1. Photophysical properties of ligands 10-12 and metallodendrimers 14-16.

<table>
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<th>Compds.</th>
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<th>$\lambda_{\text{max}}$ em./nm</th>
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<td>16</td>
<td>288 (5.30), 313 (5.32), 497 (4.92), 570 (4.44)</td>
<td>582, 617, 671</td>
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<tr>
<td>15</td>
<td>288 (5.29), 313 (5.30), 497 (4.90), 570 (4.62)</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>288 (3.28), 313 (5.25), 497 (4.88), 570 (4.72)</td>
<td></td>
</tr>
<tr>
<td>12</td>
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<td>582, 617, 671</td>
</tr>
<tr>
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<td>582, 617, 671</td>
</tr>
<tr>
<td>10</td>
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<td>582, 617, 671</td>
</tr>
</tbody>
</table>

2.3. Conclusions

A series of new photofunctional branched ligands as well as their $<\text{tpyRu}^\text{II} \text{tpy}>$ metallomacromolecules, based on a perylene central core, has been designed and synthesized. These nanoscale dendritic architectures possess large
molecular weights and broad absorption spectra (250-625 nm) as well as molar absorption coefficients directly related to the number of photoactive scaffolds. The broad absorption and high molar absorption coefficients of 14-16 make them interesting potential dyes for solar devices.

2.4. Experimental Section

**General Procedures.** Chemicals were purchased and used without further purification. Thin layer chromatography (TLC) was conducted on flexible sheets (Bakerflex) precoated with Al$_2$O$_3$ (IB-F) or SiO$_2$ (IB2-F) and visualized by UV light. Column chromatography was conducted using basic Al$_2$O$_3$, Brockman Activity I (60-325 mesh) or SiO$_2$ (60-200 mesh) from Fisher Scientific. Melting points were determined on Electrothermal 9100 heater. $^1$H and $^{13}$C NMR spectra were recorded on either a Varian Mercury 300 or a Varian NMRS 500 spectrometer. Mass spectra were obtained on a Synapt HDMS quadrupole/time-of-flight (Q/TOF) mass spectrometer (Waters Corp., Milford, MA); the sprayed solution was prepared by dissolving the sample (1 mg) in a MeCN/MeOH (1:1, v/v) solvent mixture (1 mL). ESI-MS of 13-16 were recorded with PF$_6^-$ counterions. The absorption and emission spectra were normalized by dividing the absorption values of each spectrum by the maximum absorption of compound 16 and 10, respectively.

**Synthetic procedures:**

**3,4,5-Tribromo-2,6-dimethylphenol**$^{195}$ (1): To Br$_2$ (144 gm, 0.9 mol) at 0 °C, was added molten 2-xylenol (18.3 gm, 150 mmol) dropwise with stirring. The reaction temperature was raised to 25 °C and the stirring continued for 2 h. Excess Br$_2$ was removed using a preheated water bath and air stream. The product was recrystallized
(CHCl₃) to afford a yellow powder (47 mg, 90%): m.p. 206-207 °C; ¹H NMR (500 MHz, CDCl₃): δ 4.90 (s broad), 1H, OH), 2.42 (s, 6H, CH₃); ¹³C NMR: δ 151.45, 125.85, 125.30, 119.77, 18.54; ESI-MS: m/z 356.48 (calcd [M+H]+ = 355.80).

O-(3-Phthalimidopropyl)-3,4,5-tribromo-2,6-dimethylphenol (3): To a stirred mixture of N-(3-bromopropyl)phthalimide 2 (1.35 gm, 5 mmol), and K₂CO₃ (3.7 gm, 26.8 mmol) in MeCN (50 mL) was added 3,4,5-tribromo-2,6-dimethylphenol 1 (1.5 gm, 4.4 mmol). The mixture was stirred at 80 °C for 4 h. The solvent was removed in vacuo and residue was dissolved in CHCl₃, washed with water, and dried (MgSO₄). The solvent was evaporated in vacuo and the crude product was recrystallized CHCl₃/hexanes to afford 3, as a white powder (1.9 gm, 85%): m.p. 151-152 °C; ¹H NMR (500 MHz, CDCl₃): δ 7.88-7.86 (m, 2H, Phth H), 7.74-7.73 (m, 2H, Phth H), 3.96 (t, 2H, J = 7 Hz, CH₂), 3.80 (t, 2H, J = 6.5 Hz, CH₂), 2.41 (s, 6 H, CH₃), 2.22 (m, 2 H, CH₂); ¹³C NMR: δ 168.51, 155.32, 134.28, 133.25, 132.30, 126.10, 124.09, 123.54, 71.21, 35.55, 29.43, 19.20; ESI-MS: m/z 542.81 (calcd [M]+ = 542.87).

O-(3-Phthalimidopropyl)-3,4,5-tris((4-phenyl)-4'-[2,2':6',2"]terpyridinyl)-2,6-dimethylphenol (5): To a mixture of O-(3-phthalimidopropyl)-3,4,5-tribromo-2,6-dimethylphenol (3; 250 mg, 461 μmol), and 4′-(4-boronatophenyl)[2,2’:6’,2”]terpyridine (4; 586 mg, 1.6 mmol) in toluene: tBuOH: H₂O (2:1:1), was added K₂CO₃ (1g, 7.2 mmol). The mixture was freeze-pump-thawed (3x) and backfilled with argon; then Pd(PPh₃)₂Cl₂ (12 mol%) was added. After refluxing for 72 h under argon, the mixture was cooled to 25 °C. The solvent was removed in vacuo to give a solid, which was dissolved in CHCl₃, washed (H₂O), and dried (MgSO₄). The crude product was column chromatographed (Al₂O₃) eluting with CHCl₃ to give 5, as a white solid powder: (130 mg, 23%); m.p. 174-175 °C; ¹H NMR (300 MHz, CDCl₃): δ 8.68 (s, 4H, PyH₃₃), 8.66 (d, 4H, J = 4 Hz, PyH₇), 8.60 (d, 4H, J = 8 Hz, PyH₆₆), 8.57 (d, 2H, J = 5 Hz, PyH₆₆), 8.54 (s,
2H, PyH¿, 8.51 (d, 2H, J = 8 Hz, PyH3,5¿), 7.90-7.87 (m, 2H, PhthH), 7.82 (m, 4H, PyH4,4¿), 7.78-7.72 (m, 8H, PhthH, PyH4,4¿, ArH), 7.50 (d, 2H, J = 8 Hz, ArH), 7.29 (m, 4H, PyH3,3¿), 7.24-7.18 (m, 6H, ArH, PyH4,4¿, ArH), 7.29 (m, 4H, PyH5,5¿), 7.22 (s, 6H, CH3); ¹³C NMR: δ 168.51, 156.56, 156.51, 155.91, 155.71, 155.35, 150.09, 149.78, 149.18, 149.07, 141.70, 141.5, 140.22, 136.82, 136.68, 136.25, 135.22, 135.09, 134.11, 132.35, 131.86, 131.01, 128.97, 126.82, 125.94, 123.74, 123.43, 121.39, 121.30, 119.00, 118.81, 70.22, 35.80, 29.66, 14.86; ESI-MS: m/z 1231.26 (calcd [M+H]+= 1231.46).

O-(3-Aminopropyl)-3,4,5-tris((4-phenyl)-4′-2,2′:6′,2″]terpyridinyl)-2,6-dimethylphenol (6): To a stirred suspension of 5 (341 mg, 270 μmol) in EtOH (40 mL), was added hydrazine (64%, 1.5 mL, excess). The mixture was refluxed for 12 h. The solvent was evaporated in vacuo to give the residue that was partitioned in (CH2Cl2/H2O). The aqueous layer was extracted (4x) with CH2Cl2, and the combined organic layer was washed (H2O), brine, and dried (MgSO4). The solvent was removed in vacuo to afford 6, as a white powder: (243 mg, 80%); m.p. 210-212 °C; ¹H NMR (500 MHz, CDCl3): δ 8.71 (s, 4H, PyH3,5¿), 8.69 (d, 4H, J = 4 Hz, PyH6,6¿), 8.64 (d, 4H, J = 8 Hz, PyH3,3¿), 8.62 (d, 2H, J = 5 Hz, PyH6,6¿), 8.57 (d, 2H, J = 8 Hz, PyH3,3¿), 8.56 (s, 2H, PyH5,5¿), 7.87 (m, 4H, PyH4,4¿), 7.81 (m, 2H, PyH4,4¿), 7.78 (d, 4H, J = 8 Hz, ArH), 7.52 (d, 2H, J = 8 Hz, ArH), 7.33 (m, 4H, PyH5,5¿), 7.28 (m, 2H, PyH5,5¿), 7.21 (d, 4H, J = 8 Hz, ArH), 7.01 (d, 2H, J = 8 Hz, ArH), 4.06 (t, 2H, J = 6 Hz, CH2), 3.73 (t, 2H, J = 6.5 Hz, CH2), 2.19 (m, 2H, CH2), 2.17 (s, 6H, CH3); ¹³C NMR: δ 156.56, 156.50, 156.47, 155.92, 155.90, 155.72, 155.35, 150.09, 150.06, 149.19, 149.18, 149.08, 141.67, 141.53, 140.26, 136.85, 136.81, 16.71, 136.32, 136.27, 136.10, 131.86, 131.01, 128.90, 126.79, 125.94, 123.76, 123.57, 121.41, 121.32, 19.01, 118.83, 70.67, 39.56, 14.85, 14.81; ESI-MS: m/z 1101.26 (calcd [M+H]+= 1101.46).
Synthesis of terpyridine-perylene ligands 10 - 12. General Procedure. A stirred mixture of 1,6,7,12-tetra(p-t-butylphenoxy)perylene-3,4,9,10-tetracarboxylic acid bisanhydride\(^{196}\) (7; 1 eq.), aminoterpyridine (8,\(^{197}\) 9,\(^{198}\) or 6; 3 eq.), and quinoline (20 mL) under Argon was heated at 220 °C for 4 days. The mixture was then cooled to 25 °C, precipitated with glacial AcOH (50 mL), filtered, washed with water (500 mL), and lastly EtOH several times. The product was column chromatographed (Al\(_2\)O\(_3\)) eluting with CHCl\(_3\).

\(N,N'\)-Bis[O-(3-propyl)phenyl-4-[(2,2':6',2'')terpyridinyl]-1,6,7,12-tetra(p-t-butylphenoxy)-3,4:9,10-perylenetetracarboxydiimide (10): red powder (67%); m.p. 188-190 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)): δ 8.74 (d, 4H, \(J = 4.5\) Hz, Py\(\text{H}^{6,6''}\)), 8.67 (s, 4H, Py\(\text{H}^{3,3''}\)), 8.64 (d, 4H, \(J = 7.5\) Hz, Py\(\text{H}^{3,3'}\)), 8.19 (s, 4H, Pery\(\text{H}\)), 7.86 (m, 4H, Py\(\text{H}^{4,4''}\)), 7.78 (d, 4H, \(J = 9\) Hz, Ar\(\text{H}\)), 7.33 (m, 4H, Py\(\text{H}^{5,5''}\)), 7.16 (d, 8H, \(J = 8.5\) Hz, Ph\(\text{H}\)), 6.86 (d, 4H, \(J = 9\) Hz, Ar\(\text{H}\)), 6.80 (d, 8H, \(J = 8.5\) Hz, Ph\(\text{H}\)), 4.43 (t, 4H, \(J = 6.5\) Hz, CH\(_2\)), 4.15 (t, 4H, \(J = 6\) Hz, CH\(_2\)), 2.36 (m, 4H, CH\(_2\)), 1.25 [s, 36H, C(CH\(_3\))\(_3\)]; \(^{13}\)C NMR: δ 163.77, 159.89, 156.60, 156.17, 153.09, 149.88, 149.32, 147.42, 136.98, 133.09, 130.85, 128.53, 126.79, 123.91, 122.56, 121.50, 120.83, 120.15, 119.63, 119.53, 118.43, 115.02, 66.44, 38.35, 34.54, 31.65, 28.13; ESI-MS: \(m/z\) 1712.86 (Calcd. [M]+ = 1712.72).

\(N,N'\)-Bis[O-(3-propyl)phenyl-3,5-bis[(2,2':6',2'')terpyridinyl]-1,6,7,12-tetra(p-t-butylphenoxy)-3,4:9,10-perylenetetracarboxydiimide (11). Red powder (55%); m.p. 221-222 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)): δ 8.70-8.69 (2s, 16H, Py\(\text{H}^{3,5'}\), Py\(\text{H}^{6,6'}\)), 8.62 (d, 8H, \(J = 8\) Hz, Py\(\text{H}^{3,3'}\)), 8.12 (s, 4H, Pery\(\text{H}\)), 7.88 (s, 4H, Ar\(\text{H}\)), 7.84 (m, 8H, Py\(\text{H}^{4,4'}\)), 7.30 (m, 8H, Py\(\text{H}^{5,5'}\)), 7.27 (s, 4H, Ar\(\text{H}\)), 7.07 (d, 8H, \(J = 8.5\) Hz, Ph\(\text{H}\)), 6.66 (d, 8H, \(J = 9\) Hz, Ph\(\text{H}\)), 4.48 (t, 4H, \(J = 6.5\) Hz, CH\(_2\)), 4.34 (t, 4H, \(J = 5.5\) Hz, CH\(_2\)).
2.33 (m, 4H, CH$_2$), 1.21 [s, 36H, C(CH$_3$)$_3$]; $^{13}$C NMR: δ 163.61, 159.74, 156.18, 155.90, 155.77, 153.02, 149.98, 149.09, 146.84, 140.76, 136.71, 132.71, 126.38, 123.70, 122.19, 121.32, 120.70, 20.20, 119.42, 119.20, 119.14, 118.82, 113.91, 105.03, 66.65, 38.35, 34.24, 31.41, 27.88; ESI-MS: m/z 2174.935 (Calcd. [M$^+$] = 2174.884).

$N,N'$-Bis[O-(3-propyl)-2,6-dimethylphenyl-3,4,5-tris[(2,2':6',2")-terpyridinylphenyl]-1,6,7,12-tetra(p-t-butylphenoxy)-3,4,9,10-pylenetetracarboxydiimide] (12). Red powder (40%); m.p. > 250 °C; $^1$H NMR (500 MHz, CDCl$_3$): δ 8.68 (s, 4H, Py$_3'$,5'), 8.65 (d, 4H, $J = 4$ Hz, Py$_3'$,5'), 8.61-8.58 (m, 6H, Py$_6'$,6'', Py$_3'$,3'', Py$_3'$,5'), 8.53 (s, 2H, ArH, Py$_3'$,5'), 8.27 (s, 4H, PeryH), 7.83 (m, 4H, 6H, 7H, 8H), 7.78-7.73 (m, 6H, 6H, 7H, 8H), 7.57 (s, 2H, ArH, Py$_3'$,5'), 7.49 (d, 2H, $J = 8$ Hz, ArH), 7.29 (m, 4H, Py$_3'$,5'), 7.24-7.21 (m, 6H, ArH, Py$_3'$,5'), 7.18 (d, 4H, $J = 8$ Hz, ArH), 6.98 (d, 2H, $J = 8$ Hz, ArH), 6.86 (d, 4H, $J = 8.5$ Hz, ArH), 4.46 (t, 2H, $J = 6.5$ Hz, CH$_2$), 4.07 (t, 2H, $J = 6$ Hz, CH$_2$), 2.34 (m, 2H, CH$_2$), 2.13 (s, 6H, CH$_3$), 1.27 [s, 36H, C(CH$_3$)$_3$]; $^{13}$C NMR: δ 163.66, 156.20, 155.66, 155.4, 155.36, 153.02, 150.1, 149.86, 148.96, 148.78, 147.51, 141.81, 140.11, 137.14, 137.09, 136.09, 136.06, 134.89, 133.11, 131.91, 131.16, 131.05, 129.03, 126.83, 126.79, 125.94, 125.91, 123.84, 123.82, 123.67, 122.57, 121.54, 121.51, 121.48, 120.76, 120.10, 119.54, 119.13, 119.1, 118.96, 70.85, 38.51, 34.50, 31.59, 29.31, 14.86, 14.16; ESI-MS: m/z 3149.37 (Calcd. [M$^+$] = 3149.29).

TerpyridineRu(II) adduct 13. A stirred mixture of 4'-(4-methylphenyl)-2,2':6',2''-terpyridine (17; 500 mg, 2.24 mmol) and RuCl$_3$·3H$_2$O (697.5 mg, 3.3 mmol) in EtOH (50 mL) was refluxed for 12 h, then allowed to cool to 25 °C. The precipitate was filtered, washed with EtOH, then CHCl$_3$ and dried in vacuo to afford a black powder. The Ru-terpyridine adduct (930 mg, 1.7 mmol) was refluxed with Ag(NO$_3$) (2.1 g, 10.5 mmol) in 1:1 mixture of MeCN/MeOH (200 mL) in the dark for 12 h. The mixture was filtered through Celite, dried in vacuo, and column chromatographed (SiO$_2$), eluting with
KNO₃:MeCN:H₂O mixture (1:20:1) to afford (840 mg, 80%) 13, as a brown powder: m.p. > 300 °C; ¹H NMR (500 MHz, CD₃CN): δ 8.94 (d, 2H, J = 5 Hz, PyH₃,5), 8.66 (s, 2H, PyH₆,6”), 8.58 (d, 2H, J = 8 Hz, PyH₃,3”), 8.20 (m, 2H, PyH₄,4”), 7.76 (d, 2H, J = 8 Hz, ArH), 7.50 (d, 2H, J = 8 Hz, ArH), 7.50 (m, 2H, PyH₅,5”), 7.49 (d, 2H, J = 8 Hz, ArH), 7.49 (m, 2H, PyH₆,6”) 7.26 (s, 3H, CH₃), 2.49 (s, 3H, CH₃(eq.)); ¹³C NMR: δ 159.84, 149.67, 155.45, 142.27, 139.97, 134.36, 131.19, 128.97, 128.59, 125.13, 121.49, 21.36, 4.77, 4.03; ESI-MS (PF₆¯): m/z: 1712.86 (Calcd. [M]+ = 1712.72).

**Synthesis of terpyridineperylene Ruᴵᴵ complexes 14 - 16. General Procedure.**

A stirred mixture of ligand 10, 11 or 12 (1 eq.) and adduct 13 (1.2 eq. per terpyridine) in DMF (20 mL) was heated at 110 °C for 2 days and the solvent was removed in vacuo. The residue was column chromatographed (SiO₂) eluting with H₂O:KNO₃:MeCN mixture (30:1:1) for 14; (20:1:1) for 15; (15:1:1) for 16, the counter ions were exchanged by adding NH₄PF₆, and then the product was filtered, washed with water, and dried in vacuo. [(5)Ru₂(12)₂][NO₃⁻]₄ (14): red powder (80%), m.p. > 300 °C; ¹H NMR (500 MHz, CD₃OD): δ 9.22 (s, 4H, PyH₃,3”), 9.16 (s, 4H, PyH₃,5), 8.85 (d, 4H, J = 8 Hz, PyH₃,3”), 8.80 (d, 4H, J = 8 Hz, PyH₃,5), 8.38 (s, 4H, PeryH), 7.67 (d, 4H, J = 8 Hz, ArH), 7.64 (d, 4H, J = 8 Hz, ArH), 7.51-7.47 (m, 8H, PyH₄,4”), 7.04 (d, 4H, J = 8 Hz, ArH), 6.99 (m, 8H, PyH₆,6”), 6.80-6.75 (m, 16H, ArH, PyH₅,5”), 6.67 (d, 4H, J = 8 Hz, ArH), 6.40 (d, 4H, J = 8 Hz, ArH), 4.34 (t, 4H, J = 6 Hz, CH₂), 4.24 (t, 4H, J = 6 Hz, CH₂), 2.53 (s, 6H, CH₃), 2.24 (m, 4H, CH₂), 1.28 [s, 36 H, C(CH₃)₃]; ¹³C NMR: δ 164.30, 162.08, 159.44, 156.87, 156.55, 156.41, 154.10, 152.96, 150.11, 149.69, 148.34, 141.99, 139.22, 134.75, 131.21, 129.98, 128.74, 128.50, 127.50, 125.77, 123.18, 122.20, 121.67, 120.77, 120.27, 116.42, 67.32, 35.13, 31.96, 28.76, 21.47; ESI-MS (as PF₆⁻) (m/z): 902.04 [M - 3PF₆⁻]³⁺ (Calcd. m/z = 902.60), 640.70 [M - 4PF₆⁻]²⁺ (Calcd. m/z = 640.71).
[(6)Ru₄(12)]₂[NO₃]₈ (15): red powder (70%), m.p. > 300 °C; ¹H NMR (500 MHz, CD₂OD): δ 9.87 (s, 8H, PyH³,5), 9.54 (s, 4H, PyH³,5), 9.44 (d, 8H, J = 10 Hz, PyH³,3'), 9.21 (d, 8H, J = 10 Hz, PyH³,3'), 8.71 (s, 4H, PeryH), 8.53 (d, 10H, J = 8 Hz, PhH, ArH), 8.46-8.40 (m, 20H, PhH, PyH³,5), 7.98-7.94 (m, 16H, ArH, PyH⁺,5), 7.87-7.86 (m, 8H, PyH⁶,6'), 7.75-7.68 (m, 24H, PhH, PyH³,5), 7.31 (d, 8H, J = 10 Hz, PhH), 3.84 (t, 4H, J = 6 Hz, CH₂), 3.77 (t, 4H, J = 6 Hz, CH₂), 2.97 (s, 12H, CH₃), 1.74 (m, 4H, CH₂), 1.69 [s, 36 H, C(CH₃)₃]; ¹³C NMR: δ 164.14, 161.36, 158.78, 158.55, 156.57, 155.79, 153.49, 152.65, 152.13, 149.95, 148.95, 147.94, 141.81, 140.03, 138.97, 138.89, 133.89, 133.51, 130.93, 128.52, 128.36, 128.00, 127.16, 125.95, 125.32, 122.91, 122.86, 121.72, 121.35, 120.02, 120.08, 119.76, 116.06, 105.56, 67.27, 34.75, 31.70, 30.06, 28.67, 21.53; ESI-MS (as PF₆⁻) (m/z): 1113.74 [M - 4PF₆⁻]⁺ (Calcd. m/z = 1113.73), 861.99 [M - 5PF₆⁻]⁵⁺ (Calcd. m/z = 861.99), 694.16 [M - 6PF₆⁻]⁶⁺ (Calcd. m/z = 694.17), 574.14 [M - 7PF₆⁻]⁷⁺ (Calcd. m/z = 574.29), 484.37 [M - 8PF₆⁻]⁸⁺ (Calcd. m/z = 484.38).

[(7)Ru₄(12)]₂[NO₃]₁₂ (16): red powder (55%), m.p. > 300 °C; ¹H NMR (500 MHz, CD₂CN): δ 9.04 (s, 8H, PyH³,5), 8.98 (s, 8H, PyH³,5), 8.95 (s, 4H, PyH⁺,5), 8.94 (s, 4H, PyH⁺,5), 8.69 (d, 12H, J = 8 Hz, PyH³,3'), 8.61 (d, 8H, J = 8 Hz, PyH³,3'), 8.5 (d, 4H, J = 8 Hz, PyH³,3'), 8.19 (d, 8H, J = 8 Hz, ArH), 8.09 (d, 8H, J = 4 Hz, ArH), 8.08 (s, 4H, PeryH), 8.06 (d, 4H, J = 8 Hz, ArH), 7.95 (d, 4H, J = 8 Hz, ArH), 7.87 (m, 8H, PyH⁺,5), 7.81 (m, 8H, PyH⁺,5), 7.78 (m, 4H, PyH⁺,5), 7.67 (m, 4H, PyH⁺,5), 7.61-7.54 (m, 20H, J = 8 Hz, ArH), 7.39-7.35 (m, 32H, ArH, PyH⁺,5), 7.31 (d, 4H, J = 6 Hz, PyH⁺,5), 7.27 (d, 4H, J = 6 Hz, PyH⁺,5), 7.12 (m, 8H, PyH⁺,5), 7.03 (m, 12H, PyH⁺,5), 6.96 (d, 10H, J = 8 Hz, ArH), 6.88 (m, 2H, PyH⁺,5), 4.46 (m, 4H, CH₂), 4.18 (m, 4H, CH₂), 2.98 (s, 12H, CH₃), 2.85 (s, 6H, CH₃), 2.27 (s, 12H, CH₃), 2.21 (s, 4H, CH₂), 1.29 [s, 36 H, C(CH₃)₃]; ¹³C NMR: δ 164.54, 159.26, 157.09, 156.49, 156.37, 154.18, 153.18, 149.87, 149.40.
148.55, 144.20, 142.16, 139.24, 137.75, 134.73, 134.07, 133.77, 132.77, 131.38, 130.15, 128.63, 128.38, 127.77, 125.94, 125.74, 123.73, 122.56, 122.2, 121.70, 120.83, 120.44, 35.67, 35.26, 32.12, 30.53, 30.21, 21.82, 15.44; ESI-MS (as PF₆⁻) (m/z):

1342.9 [M - 5PF₆⁻]⁺ (Calcd. m/z = 1342.8), 1094.9 [M - 6PF₆⁻]⁶⁺ (Calcd. m/z = 1094.8), 917.7 [M - 7PF₆⁻]⁷⁺ (Calcd. m/z = 917.7), 784.9 [M - 8PF₆⁻]⁸⁺ (Calcd. m/z = 784.9), 681.6 [M - 9PF₆⁻]⁹⁺ (Calcd. m/z = 681.6), 598.8 [M - 10PF₆⁻]¹⁰⁺ (Calcd. m/z = 598.9), 530.9 [M - 11PF₆⁻]¹¹⁺ (Calcd. m/z = 531.3), 474.9 [M - 12PF₆⁻]¹²⁺ (Calcd. m/z = 474.9).
CHAPTER III

TERPYRIDINE-MODIFIED, PERYLENE-RU(II) COMPLEXES: SYNTHESIS, ELECTROCHEMICAL AND PHOTOVOLTAIC PROPERTIES†

3.1 Introduction

Perylene-diimides (PDIs) have been widely studied due to their stability and attractive electronic properties.\textsuperscript{31,113,164-167,170,171} Elegant work by Würthner \textit{et al.}\textsuperscript{113} has resulted in the synthesis of a plethora of functional supramolecular architectures using ionic self-assembly, hydrogen-bonding, π-π interactions, and metal-ligand directed self-assembly.\textsuperscript{128,146} Metal-terpyridine connectivity\textsuperscript{194,201} is also an attractive approach to build functional materials due to the rich coordination chemistry and the incorporation of redox, photophysical, and electrochemical properties into the resulting supramolecules. As a result, terpyridine (tpy) coordination has permitted the exploration of diverse materials used in construction of solar devices.\textsuperscript{189} This, along with the unique properties of perylene, provided the inspiration to synthesize perylene-containing tpy ligands\textsuperscript{173} and their Ru\textsuperscript{II} complexes. Herein, we report the synthesis of \textit{bis}(terpyridinyl)perylene, heteroleptic Ru\textsuperscript{II} complexes, and their use in the fabrication of dye-sensitized solar cell (DSSC) devices.

\footnote{Parts of this chapter are the product of collaboration with Dr. Juan Manriquez and his research group including Perla F. Méndez and Luis A. Godínez}
3.2 Results and Discussion

Synthesis began with the construction of aminoterpyridines 2 and 4, which were obtained from the reduction of the corresponding known nitroterpyridines using Pd/C and hydrazine hydrate. The reaction of perylenetetracarboxylic acid dianhydride (1) with 2 gave (51%) the linear bisterpyridine-perylene ligand (Scheme 3.1), which was confirmed by absorptions at 8.79 (3',5'-tpy), 8.74 (6,6''-tpyH), 8.30 [perylene(peryH)], and 1.27 ppm [C(CH₃)₃], in addition to the electrospray ionization mass spectrometry (ESI-MS) peak at m/z 1597.38 (calcd. [M+H]⁺ = 1597.64). The isomeric 5 was similarly synthesized (60%) and exhibited ¹H NMR peaks at 8.76 (3',5'-tpyH), 8.70 (6,6''-tpyH), 8.30 (peryH), and 1.27 ppm [C(CH₃)₃], as well as ESI-MS peaks at m/z 1596.71 (calcd. [M]⁺ = 1596.64).

The Ru³⁺tpy adduct 7 was obtained (88%) from terpyridine 6 with RuCl₃·nH₂O (Scheme 3.1). Complexes 8 and 9 were generated from Ru³⁺tpy adduct 7 (2.2 eq.) with bisterpyridine ligands 3 and 5, respectively, in MeOH and N-ethylmorpholine, as a reducing agent. After counter ion exchange, the desired PF₆⁻ complexes were isolated (78%), as dark red solids.
Scheme 3.1 Reagents and conditions: a) quinoline, 220 °C, 72 h, N₂; b) EtOH/CHCl₃, N-ethylmorpholine, 12 h, NH₄PF₆; c) EtOH, RuCl₃·3H₂O, 12 h.

The ¹H NMR spectrum for bis-complex 8 revealed a pair of singlets at 9.53 (3',5'-tpyH) and 9.46 (3',5'-peryH) ppm that were shifted downfield (Δδ = +0.65 Hz) when compared to that of the free ligands 3 and 6. It also revealed a multiplet at 9.14 (3,3"-tpyH and 3,3"-peryH) ppm, a peak at 7.81 (6,6"-tpyH and 6,6"-peryH) ppm, with a significant upfield shift resulting from the ring current shielding effect upon complexation, as well as two singlets with an integration ratio of 1:6 at 2.90 (tpy-CH₃) and 1.66 [C(CH₃)₃] ppm. In the case of the isomeric 9, the ¹H NMR spectrum showed three singlets with an integration ratio of 1:1 at
9.01 (3',5'-tpyH), 9.01 (3',5'-peryH) and 8.99 (peryH) ppm along with two doublets at 8.63 (3,3''-tpyH) and 8.60 (3,3''-peryH) ppm. The spectrum also revealed a multiplet at 7.43-7.44 (6,6''-tpyH and 6,6''-peryH) ppm in addition to two singlets at 2.54 (tpy-CH₃) and 1.29 [C(CH₃)₃] ppm with an integration ratio of 1:6, respectively. The structure was further confirmed by ESI-MS peaks at m/z 611.4 [M-4PF₆⁻]⁺⁺ (Calcd. m/z = 611.51), 863.51 [M-3PF₆⁻]³⁺ (Calcd. m/z = 863.61), and 2881.11 [M-PF₆⁻]¹⁺ (Calcd. m/z = 2881.5) for 8, and m/z 2881.01 [M-PF₆⁻]¹⁺ (Calcd. m/z = 2881.10) for 9.

In contrast, complex 13 was synthesized via a Suzuki coupling of dibromide 10 (Scheme 3.2) with 4-terpyridinylphenylboronic acid 11 in a solvent mixture of toluene:H₂O:η-BuOH (3:3:1) at 100 °C for 3 days. The solvent was evaporated in vacuo and the residue was column chromatographed Al₂O₃, eluting with CHCl₃ and then recrystallized (5x) CHCl₃/MeOH to eliminate the 1,6-bisterpyridine-substituted perylene isomer and afford (55%) the pure 1,7-bisterpyridine perylene ligand 12, as a red solid. The ¹H NMR spectrum of 12 showed resonances at 8.88 (3',5'-tpyH), 8.79 (6,6''-tpyH), 8.74 (3,3''-tpyH), and 8.69 (peryH); its ESI-MS possessed a peak at m/z 1229.64 [M+H]⁺ (Calcd. m/z = 1229.54) confirming the molecular composition. Finally, bisterpyridine 12 was treated with 7 in refluxing EtOH/CHCl₃ (2:1) with N-ethylmorpholine for 12 h, followed by counter ion exchange (NO₃⁻ to PF₆⁻) to afford (78%) 13, as a dark red solid. The ¹H NMR of bis-complex 13 exhibited three singlets at 9.35 (3',5'-tpyH), 9.18 (3',5'-peryH), and 8.26 (peryH) ppm, two doublets at 8.91 (3,3''-tpyH) and 8.83 (3,3''-peryH) ppm, a multiplet at 7.54 (6,6''-tpyH and 6,6''-peryH) ppm,
and a singlet at 2.54 ppm for the tpy-CH₃ moieties. ESI-MS further confirmed 13 with peaks at m/z 519.70 [M-4PF₆⁻]^{4+} (Calcd. m/z = 519.65), 741.20 [M-3PF₆⁻]^{3+} (Calcd. 741.19).

Scheme 3.2 Reagents and conditions: a) K₂CO₃, toluene:H₂O:t-BuOH (3:3:1), Ar, 100 °C, 48 h; b) EtOH/CHCl₃, N-ethylmorpholine, 12 h, NH₄PF₆.

Finally, complex 14 (Fig. 3.1) was synthesized according to the literature procedure.₁⁴⁵

Figure 3.1 Chemical structure of complex 14.

The CV responses of 8 (Figure 3.2A) and 9 (Figure 3.2B) show two signals at -2.2 and -1.4V that are associated with one-electron consecutive reductions for the two pairs of inner and outer tpy moieties. Two additional reversible signals were also observed between -1.3 and -0.6V that are associated with two-electron consecutive reduction processes for perylene,¹¹¹ (black-marked
in Scheme 3.1) (E_{1r} and E_{2r} in Scheme 3.3-B). Similarly, 14 (Figure 3.2C) and 13 (Figure 3.2D) show irreversible signals for the consecutive reduction previously described for the tpy moieties (red- and blue-marked in Scheme 3.2 and Figure 3.1, between -2.2 and -1.4V), and for perylene (black-marked in Scheme 3.2 and Figure 3.1, between -1.3 and -0.6V).

Comparing the cathodic behavior for the couples 8 and 9 (Figures 3.2A and 3.2B) to that of 13 and 14 (Figures 3.2D and 3.2C) strongly suggests that the reversible electrochemical responses for tpy and perylene moieties are observed only if these two types of groups are connected through the peri-positions. This supports the thermodynamically favorable electronic communication based on tpy-perylene conjugation.\textsuperscript{208} Inspection of the oxidation processes (Figures 3.2A and 3.2B) reveals two small shoulders at +0.5 and +0.7V associated an one-electron oxidation process reported for the characteristic bay-positions perylene\textsuperscript{111} (E_{1,o} in Scheme 3.3)\textsuperscript{111} and for the tpyRu\textsuperscript{II}tpy moieties, respectively.\textsuperscript{207}

Thus, the low intensities observed for these two types of oxidation could be associated with very short life-times for the perylene radical anions due to favorable e-transfer to Ru\textsuperscript{III}tpy units. In contrast, a comparison between Figures 3.2C and 3.2D show irreversible overlapped signals between +0.6 and +1.4V, possibly due to the consecutive oxidation reactions previously described for perylene and Ru\textsuperscript{II}tpy.
Figure 3.2 CV responses for 8 (A), 9 (B), 14 (C), and 13 (D) using a glassy carbon electrode at 25°C (dE/dt = 25 mVs⁻¹).

**Preparation of 8, 9, 13, and 14-Sensitized Solar Cells.** Nanoparticulate TiO₂ electrodes (80-roughness factor, η, and 2 μm thick, d, estimated according to measurements of the electroactive area, Aₑ, and profilometry, respectively) were obtained by electrophoretic deposition of TiO₂ nanoparticles (P25 Degussa, 21 nm diameter), as previously reported. Cathodes were obtained as follows: 8 μL/cm² of a 10 mM H₂PtCl₆·6H₂O (Strem Chemicals, 99.9%-Pt) solution in 2-propanol (J.T. Baker, 99.97%) was homogeneously spread on the surface of optically transparent electrodes (OTE) based on indium-doped tin oxide (TEC15,
Hartford Glass Co., USA). The cathodes were subsequently dried at 25 °C and finally annealed in air at 380 °C for 30 min.\textsuperscript{210} TiO\textsubscript{2} electrodes were dyed by immersion in 0.40 mM solutions of (a) 8 and 9 both in MeOH (J.T. Baker, HPLC grade), (b) 14 in MeOH/CHCl\textsubscript{3} (3:1), or (c) 13 in MeOH/CHCl\textsubscript{3} (5:1), at 25 °C for 6 days. DSSCs were assembled in a sandwich arrangement using a 160 μm-thick o-ring (6 mm i.d.), home-made from a commercial transparency sheet (CG3700 3M, typically used as projecting transparencies) in order to avoid premature short circuit. A solution of 0.3 M LiI (Aldrich, 99.9%) + 0.015 M I\textsubscript{2} (J.T. Baker, ACS reagent) in propylene carbonate (Aldrich, 99.7%) was employed as the electrolytic medium in the photovoltaic cells (Fig. 3.6). An effective geometric area of 0.28 cm\textsuperscript{2} was illuminated for all the photoelectrochemical experiments. These results indicate that the \textit{ocp} for the DSSC containing 8 (Figure 3.4-iA) or 14 (Figure 3.4-iiA) is constant under illumination, as function of time; however, the \textit{ocp} for photocells sensitized by 9 (Figure 3.4-iB) and 13 (Figure 3.4-iiB) is rapidly deactivated under the same condition. These last results indicate that the oxidized states for the dyes 9 and 13 are not efficiently reduced by I\textsuperscript{-} ions contained in the cell electrolyte.\textsuperscript{211}

As predicted by their electrochemical responses, a comparison between the Figures 3.3A and 3.3B, indicates that the output power obtained from DSSC assembled with 14 or 13 are higher than for 8 or 9. This behavior is reflected by the photovoltaic parameters compiled in Table 1; whereas, the global photovoltaic efficiencies (\(\eta\)) follow the same tendencies. Despite the well-known photophysical and electrochemical properties of both <tpyRu\textsuperscript{II}tpy> and perylene,
the observed low efficiencies of the DSSC can be attributed to the presence of two strong electron-withdrawing imide groups leading to a non-directional\textsuperscript{173} transfer of the generated photoelectrons. Notably for all the dyes studied, there is an absence of anchoring groups (such as CO$_2$H) that can promote an efficient injection of photo-generated electrons into nanostructured TiO$_2$ photoanodes.\textsuperscript{212}

The photo-stability for the sensitizers was studied by means of open-circuit-potential transients (\textit{ocp} vs. time plots) obtained for all the DSSC upon repetitive illumination-dark (ON-OFF) cycles. Figures 3.4-\textit{i} and 3.4-\textit{ii} show the \textit{ocp} transients obtained for 8 and 9 (Figures 3.4-\textit{iA} and 3.4-\textit{iB}) and for 14 and 13 (Figures 3.4-\textit{iiA} and 3.4-\textit{iiB}), respectively.

![Discharge curves](image)

Figure 3.3 Discharge curves obtained from DSSC containing the couples of dyes (A) 8 (-o-) and 9 (-\Delta-), and (B) 14 (-o-) and 13 (-\Delta-), as sensitizers.
Table 3.1 Performance data obtained for DSSC having 8, 9, 13 or 14-dyed TiO$_2$ electrodes.

<table>
<thead>
<tr>
<th>Photoanode</th>
<th>$-E_{OC}$(V)</th>
<th>$j_{sc}$/µA cm$^{-2}$</th>
<th>$a_{ff}$</th>
<th>$b$ η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$/8</td>
<td>0.29</td>
<td>51.78</td>
<td>0.38</td>
<td>0.08</td>
</tr>
<tr>
<td>TiO$_2$/9</td>
<td>0.23</td>
<td>46.07</td>
<td>0.39</td>
<td>0.05</td>
</tr>
<tr>
<td>TiO$_2$/13</td>
<td>0.26</td>
<td>149.64</td>
<td>0.28</td>
<td>0.14</td>
</tr>
<tr>
<td>TiO$_2$/14</td>
<td>0.24</td>
<td>140.71</td>
<td>0.36</td>
<td>0.16</td>
</tr>
<tr>
<td>TiO$_2$(bare)</td>
<td>0.03</td>
<td>1.07</td>
<td>0.21</td>
<td>3.5$\times$10$^{-4}$</td>
</tr>
</tbody>
</table>

$^a$Fill-factor was calculated using the Eq. $ff=P_{max}/\left|V_{oc}\times j_{sc}\right|$ where $P_{max}$ is the maximum output power cell and $j_{sc}$ is the short-circuit photocurrent. $^{213}$

$^b$Global photovoltaic conversion was calculated using the Eq. 

$$
\eta \%(\%)=\left[\frac{P_{max}}{0.82\times P_0}\right]\times 100
$$

where $P_0$ is the power of the incident photon flux (9.21mWcm$^{-2}$). $^{213}$ The constant 0.82 represents the effective transmittance when the photon flux passes through the OTE.

Figure 3.4. Open-circuit-potential (ocp) transients obtained for DSSC containing the couples of dyes (i) 8 (A) and 9 (B) or (ii) 14 (A) and 13 (B), as sensitizers.

To support the results shown in Figures 3.4-iA and 3.4-iiA, the steady-state-photocurrent spectra (IPCE vs. wavelength plots, Figure 3.5) were obtained and compared for the DSSCs containing the dyes. The photocurrents subsequently obtained from photocells constructed with 8 and 14 predominantly resulted from injection by perylene at or near 470, 500, and 550 nm, respectively. $^{212,214}$
Finally, the spectra shown in Figure 3.5 demonstrate that \(<\text{tpyRu}^\text{II} \text{tpy}>\) units contained in 8 and 14 have no direct contribution to the photocurrent generation, thereby suggesting that only perylene groups can establish a successful electronic connection with Ti bonding orbitals in the TiO₂ photoanodes.

![Figure 3.5](image)

Figure 3.5. Steady-state-photocurrent spectra obtained from DSSC containing 8 (-o-) and 14 (-Δ-), as sensitizers.

We propose that the mechanism for photo-current generation and transfer in this DSSCs (Fig. 3.6) starts with photon absorption by \(<\text{tpy-Ru}^\text{II}-\text{tpy}>\) moiety generating photoelectron, that transferred to TiO₂ electrode through PDI core.
3.3 Conclusions

In conclusion, dyes 8, 9, 13, and 14 were synthesized, their structures were confirmed using $^1$H and $^{13}$C NMR, COSY, and ESI-MS, and their electrochemical, photoelectrochemical, and photovoltaic properties were studied. These complexes were successfully incorporated in the assembly of DSSCs for which global conversion efficiencies were obtained. Photovoltaic results demonstrated that the perylene moieties of these dyes were responsible for the photoactivated electron injection into TiO$_2$ collectors. As well, the $<$tpyRu$^\text{II}$tpy$>$ complexes were simultaneously deactivated by the presence of the perylene radical cations formed by photoactivation, thus inhibiting charge injection into the TiO$_2$. 

Figure 3.6. A) Picture of DSSc; B) the proposed charge transfer mechanism for DSSC, using TiO$_2$ electrodes sensitized with 14.
3.4 Experimental Section

**General Procedures.** Chemicals were commercially purchased and used without further purification. Thin layer chromatography (TLC) was conducted on flexible sheets (Baker-flex) percolated with Al₂O₃ (IB-F) or SiO₂ (IB2-F) and visualized by UV light. Column chromatography was conducted using basic Al₂O₃, Brockman Activity I (60-325 mesh) or SiO₂ (60-200 mesh) from Fisher Scientific. Melting points were determined on an Electrothermal 9100 heater. ¹H and ¹³C NMR spectra were recorded on either a Varian Mercury 300 or a Varian NMRS 500 spectrometer. Mass spectra were obtained on a Synapt HDMS quadrupole/time-of-flight (Q/TOF) mass spectrometer (Waters Corp., Milford, MA); the sprayed solution was prepared by dissolving 1 mg of sample in 1 mL of a MeCN/MeOH (1:1) solvent mixture.

**Electrochemistry.** Cyclic voltammetry (CV) experiments were performed at 25 °C and 25 mV/s by means of a BAS Epsilon potentiostat-galvanostat. A glassy carbon working-disc-electrode (1.5 mm-diameter) was immersed in a typical three-electrode cell containing DMF (99.8%, J.T. Baker) + 0.1 M Bu₄NPF₆ (Fluka, 98%) for testing complexes 8 and 9. Electrolytic mixtures of MeOH/CHCl₃ (5:1) + 0.1 M Bu₄NPF₆ and MeOH/CHCl₃ (3:1) + 0.1 M Bu₄NPF₆ were used for obtaining the CV responses for samples 13 and 14, respectively. Experimental setup was completed when silver and platinum wires were inserted in the electrochemical cell as pseudo- and counter-electrodes, respectively. All solutions were purged with ultra-pure nitrogen (Praxair, 99.999%) for 15 min. prior to conducting the experiments. Potentials were referenced to the
ferrocinium/ferrocene redox scale (denoted as Fc\(^+\)/Fc). PDIs are stable, electron-deficient molecules, which are difficult to oxidize and easy to reduce. Scheme 3.3-A shows the one-electron reversible oxidation (as revealed by CV) and Scheme 3.3-B shows the reduction process reported for PDI.\(^ {111} \)

Scheme 3.3. (A) One-electron oxidation and (B) two-electron reduction processes reported for a perylene group.\(^ {111} \)

Fig. 3.7 shows the structure of the commercially available perylene dye; it has twelve functionalizable carbon atoms. Substituents at C (3, 4, 9, and 10) are known as Peri-substituents; whereas, C (1, 6, 7, and 12) are known as the Bay-positions. Finally C (2, 5, 8, and 11) are known as the ortho-positions.
Figure 3.7. Bay and peri-positions in perylene.

Photoelectrochemistry. Discharge curves were obtained for the DSSCs utilizing a variable resistance of 52 kΩ upon polychromatic illumination emitted by a MR16 50W 12V lamp (GE) equipped with an EXN dichroic reflector to diffuse the light. Power of the light source was 9.21 mW/cm² (ca. 0.1 Sun). Steady-state photocurrent spectra were obtained upon monochromatic illumination (400-650 nm) using a 6257 100W Xe lamp coupled to a 77250 monochromator, both purchased from Thermo-Oriel and calibrated by means of a 17043 Eppley Thermopile. Incident-photon-to-current efficiencies (IPCE) were estimated according to Eq. 3.1, where $\lambda$, $j_{\text{ph},\lambda}$, and $I_{0,\lambda}$ denote incident photon wavelength (in nm), photocurrent density (in $\mu$A/cm²), and incident photon flux (in W/cm²), respectively.^{210} The constant 0.82 corresponds to the effective transmittance of the incident photon flux through the OTE. All these experiments were conducted on an IM6 BAS-Zahner potentiostat-galvanostat in order to measure open-circuit-potentials or steady-state-photocurrents.

$$IPCE(\lambda) = \frac{(1240eV \cdot nm) j_{\text{ph},\lambda}}{0.82 I_{0,\lambda}}$$

Eq. 3.1 Calculation of incident-photon-to-current efficiencies (IPCE).
Synthesis of terpyridine-perylene ligands (3 and 4). General procedure.

A mixture of 1,6,7,12-tetra(p-t-butylphenoxy)perylene-3,4:9,10-tetracarboxylic acid bisanhydride \(^{196,215,216}\) (500 mg, 0.5 mmol) and aminoterpyridine \(^{202}\) or \(^{4}\) \(^{203}\) (1.31 g, 4.06 mmol) in quinoline (50 mL) was stirred at 220 °C under argon for 3 days. The mixture was cooled to 25 °C, precipitated with AcOH (50 mL), filtrated, and washed with water, and MeOH. The product was column chromatographed (Al\(_2\)O\(_3\)) eluting with a mixture of CHCl\(_3\)/hexane (2:1).

\[N,N'-Bis[4-([2,2':6,2"]terpyridin-4'-yl)phenyl]-1,6,7,12-tetra(p-t-butylphenol)perylene-3,4:9,10-tetracarboxylic acid bisanhydride\] \(^{317}\) (3): red powder, 51%; mp > 350 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.79 (s, 4H, Py\(_{3',5'}\)), 8.74 (d, 4H, \(J = 4.2\) Hz, Py\(_{6,6'}\)), 8.68 (d, 4H, \(J = 7.8\) Hz, Py\(_{3,3'}\)), 8.30 (s, 4H, Pery\(_H\)), 8.06 (d, 4H, \(J = 8.4\) Hz, Ar\(_H\)), 7.89 (m, 4H, Py\(_{4,4'}\)), 7.43 (d, 4H, \(J = 8.4\) Hz, Ar\(_H\)), 7.36 (m, 4H, Py\(_{5,5'}\)), 7.25 (d, 8H, \(J = 9\) Hz, Ar\(_H\)), 6.88 (d, 8H, \(J = 9\) Hz, Ar\(_H\)), 1.27 (s, 36 H, C\(_{6}\)H\(_3\)); \(^{13}\)C NMR \(\delta\) 163.75, 156.40, 156.28, 153.07, 149.68, 149.37, 147.70, 139.19, 137.09, 136.21, 133.41, 129.44, 128.46, 126.93, 124.06, 122.79, 121.61, 121.08, 120.51, 120.05, 119.60, 119.27, 105.23, 34.59, 31.65; ESI-MS: \(m/z\) 1597.38 (calcd. [M+H]\(^+\) = 1597.64).

\[N,N'-Bis[3-([2,2':6,2"]terpyridin-4'-yl)phenyl]-1,6,7,12-tetra(p-t-butylphenol)perylene-3,4:9,10-tetracarboxylic acid bisanhydride\] \(^{146}\) (5): red powder, 60%; mp > 350 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.76 (s, 4H, Py\(_{3',5'}\)), 8.70 (d, 4H, \(J = 4.73\) Hz, Py\(_{6,6'}\)), 8.66 (d, 4H, \(J = 7.77\) Hz, Py\(_{3,3'}\)), 8.3 (s, 4H, Pery\(_H\)), 8.02 (d, 2H, \(J = 7.09\) Hz, Ar\(_H\)), 7.86 (m, 4H, Py\(_{4,4'}\)), 7.83 (t, 2H, \(J = 1.69\) Hz, Ar\(_{2''}\)), 7.67 (t, 2H, \(J = 7.76\) Hz, Ar\(_H\)), 7.37 (d, 2H, \(J = 6.75\) Hz, Ar\(_H\)),
7.33 (m, 4H, PyH$_{5,5}$), 7.25 (d, 8H, $J = 9.12$ Hz, ArH), 6.89 (d, 8H, $J = 8.78$ Hz, ArH), 1.27 (s, 36 H, CH$_3$); $^{13}$C NMR δ 163.54, 156.16, 156.03, 152.90, 149.21, 149.11, 147.39, 139.92, 136.77, 136.05, 133.18, 129.85, 129.18, 126.67, 123.78, 122.56, 121.30, 119.37, 118.91, 105.02, 34.35, 31.42; ESI-MS: $m/z$ 1596.71 (calcd. [M]$^+$ = 1596.64).

$[\text{Ru(6)Cl}_3]^{218}$ (7). 4'-(4-Methylphenyl)[2,2':6',2"]terpyridine 6 (200 mg, 890 µmol) was treated with RuCl$_3$·3H$_2$O (251.7 mg, 1.21 mmol) in EtOH (20 mL), then the suspension was refluxed for 12 h. After the mixture was cooled, the resultant dark brown solid was filtered, washed with cold EtOH, and dried in vacuo to give 7: 290 mg (88%). This material was used without further purification.

**Synthesis of complexes 8, 9, and 13. General Procedure:** Bis(terpyridine) ligand (3, 5 or 12) (40 mg, 31 µmol) was added to a suspension of Ru$^{III}$tpy 7 (25 mg, 69 µmol) in a mixed solvent (20 mL) of EtOH/CHCl$_3$ (2:1), then N-ethylmorpholine (500 µL) was added. The mixture was refluxed for 12 h. After cooling, the resulting deep red solution was filtered (Celite), solvent was removed in vacuo and the residue was column chromatographed (SiO$_2$), eluting with H$_2$O:KNO$_3$:MeCN (1:35:1). The counter ion was exchanged by adding NaPF$_6$, and then the product was filtered, washed with water, and dried in vacuo.

$[(3)\text{Ru}_2(6)_2][\text{PF}_6]_4$ (8): red powder, 50 mg (78%), m.p. > 350 °C; $^1$H NMR (500 MHz, CD$_3$OD) δ: 9.44 (s, 4H, PyH$_{3,5}$), 8.36 (s, 4H, PyH$_{3,5}$), 9.05 (t, 8H, $J = 6$ Hz, PyH$_{3,3}$), 8.62 (d, 4H, $J = 8$ Hz, ArH), 8.06 (s, 4H, PeryH), 8.36 (d, 4H, $J = 8$ Hz, ArH), 8.27 (m, 4H, PyH$_{4,4}$), 7.93 (d, 4H, $J = 8$ Hz, ArH), 7.81 (m,
4H, ArH), 7.71 (m, 4H, PyH^{6,6’}), 7.56 (m, 16H, ArH, PyH^{5,5’}), 7.22 (d, 8H, J = 8.5 Hz, ArH), 2.81 (s, 6H, CH₃), 1.57 (s, 36H, CH₃); ¹³C NMR δ: 163.56, 157.86, 157.80, 155.01, 151.63, 149.36, 147.99, 147.45, 141.14, 138.30, 138.25, 137.17, 136.80, 135.14, 133.03, 130.19, 129.88, 127.82, 127.70, 126.46, 124.72, 124.63, 121.54, 121.04, 121.01, 120.99, 120.08, 120.05, 119.69, 119.15, 34.04, 30.92, 29.31; ESI-MS (m/z): 2881.1 [M - PF₆⁻]⁺ (Calcd. m/z = 2881.5), 863.5 [M - 3PF₆⁻]³⁺ (Calcd. m/z = 863.6), 611.4 [M - 4PF₆⁻]⁴⁺ (Calcd. m/z = 611.5).

[(5)Ru₂(6)₂][PF₆]₄ (9): red powder, 50 mg (78%); m.p. > 350 °C; ¹H NMR (500 MHz, CD₃CN) δ 9.04 (s, 4H, PyH^{3,3’}), 9.02 (s, 4H, PyH^{3,3’}), 8.66 (d, 4H, J = 8 Hz, PyH^{3,3’}), 8.63 (d, 4H, J = 8Hz, PyH^{3,3’}), 8.32 (d, 2H, J = 7.5Hz, ArH), 8.18 (s, 2H, ArH), 8.14 (m, 8H, PeryH, ArH), 7.92 (m, 10H, ArH, PyH^{3,3’}), 7.64 (d, 2H, J = 8 Hz, ArH), 7.58 (d, 4H, J = 8 Hz, ArH), 7.41 (m, 8H, PyH^{6,6’}), 7.36 (d, 8H, J = 7 Hz, ArH), 7.16 (m, 8H, PyH^{5,5’}), 6.96 (d, 8H, J = 7 Hz, ArH), 2.57 (s, 6H, CH₃), 1.32 (s, 36H, CH₃); ¹³C NMR δ: 163.50, 157.80, 157.73, 156.05, 155.26, 154.95, 152.61, 151.57, 149.29, 147.38, 141.08, 138.18, 137.10, 136.73, 133.07, 132.6, 130.13, 129.81, 128.42, 127.75, 127.67, 127.19, 126.42, 124.57, 122.12, 12.47, 120.97, 120.92, 120.01, 119.62, 119.08, 33.97, 30.93, 29.24; ESI-MS (m/z): 2881.0 [M - PF₆⁻]⁺ (Calcd. m/z = 2881.1).

1,6/1,7-Dibromo-3,4,9,10-perylenetetracarboxylic acid bisanhydride.⁸,²⁸,⁵¹,⁵⁵,²¹⁹ A mixture of 3,4,9,10-perylenetetracarboxylic acid bisanhydride (4 g, 10 mmol) and H₂SO₄ (60 mL) was stirred at 55 °C for 18 h. Then I₂ (80 mg, 300 µmol) was added and the mixture was stirred for 5 h at 55 °C. Br₂ (3.5 g, 20 mmol) was added, the reaction mixture was stirred for 48 h at 85
°C, followed by cooling to 0 °C. Excess Br₂ was removed using air stream in the hood. The product was precipitated with cold water (30 mL), filtrated, washed with water, EtOH and then dried in vacuo to afford (89%) an orange powder: 5 g. The product was used in the next step without further purification.

\[N, N'-\text{Bis}(n\text{-octyl})-1,6/1,7\text{-dibromo-3,4,9,10-perylenetetracarboxy-diimide}^{51,55} \ (10)\]. To a mixture of 1,6/1,7-dibromo-3,4,9,10-perylenetetracarboxylic acid bisanhydride\(^{219}\) (2.5 g, 4.5 mmol) and \(n\text{-octylamine} \) (5.8 g, 44.8 mmol), was added a solvent mixture of 2-BuOH:H₂O (80 mL, 1:1). The reaction mixture was stirred under argon at 65 °C for 12 h, cooled to 25 °C, precipitated with MeOH (150 mL), and filtered. The product was dried in vacuo and column chromatographed (SiO₂) eluting with CHCl₃ to give \(10\), as an orange powder: 5 g (89 %); \(^1\)H NMR (500 MHz, CDCl₃) \(\delta \) 9.43 (d, 4H, \(J = 8 \) Hz, PeryH), 8.87 (s, 4H, PeryH), 8.65 (d, 4H, \(J = 8 \) Hz, PeryH), 4.20 (m, 8H, \(CH₂\)), 1.75 (m, 8H, \(CH₂\)), 1.44-1.26 (m, 48H, \(CH₂\)), 0.89 (t, 12H, \(CH₃\)); \(^{13}\)C NMR \(\delta \) 163.39, 163.01, 162.51, 162.14, 138.27, 138.15, 133.32, 133.08, 132.93, 132.52, 130.16, 130.02, 129.36, 128.64, 128.27, 127.88, 127.08, 123.54, 123.35, 122.92, 122.61, 121.79, 120.97, 41.16, 41.04, 40.93, 32.04, 29.54, 29.43, 28.30, 27.38, 27.33, 27.29, 22.86, 14.31; MALDI-MS: \(m/z \) 770.20 (calcd. \(M^+ = 770.13\)).

\(N, N'-\text{Bis}(n\text{-octyl})-1,7\text{-di}[4-\table{2,2':6,2''\text{y}]terpyridin-4'-yl}phenyl]-3,4,9,10-perylenetetracarboxydiimide \ (12)\). To a mixture of \(10\) (250 mg, 500 \(\mu\)mol) and \(4'-(4\text{-boronatophenyl})[2,2':6,2''\text{y}]terpyridine \(11\) (485 mg, 1.3 mmol) in toluene:t-BuOH:H₂O (2:1:1; 80 mL), was added K₂CO₃ (3.5 g, 27.4 mmol). The system was freeze-pump-thawed (3x) and backfilled with argon; then Pd(PPh₃)₂Cl₂ (16
mg) was added. After refluxing for 72 h under argon, the mixture was cooled to 25 °C, solvent was removed in vacuo and the residue was dissolved in CHCl₃ and filtered. After concentration in vacuo, the residue was purified by column chromatography (Al₂O₃), eluting with CHCl₃, followed by recrystallization from CHCl₃/MeOH (5x) to give (31%) 15, as a red solid: m.p. > 300 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.88 (s, 4H, PyH³,⁵), 8.79 (m, 4H, J = 4 Hz, PyH⁶,⁶'), 8.74 (d, 4H, J = 8 Hz, PyH³,³'), 8.69 (s, 2H, PeryH), 8.23 (d, 2H, J = 8 Hz, PeryH), 8.11 (d, 4H, J = 8 Hz, ArH), 7.95 (m, 6H, PeryH, PyH⁴,⁴'), 7.76 (d, 4H, J = 8 Hz, ArH), 7.42 (m, 4H, PyH⁵,⁵'), 4.20 (t, 4H, J = 8 Hz, CH₂), 1.43-1.27 (m, 23H, CH₃), 0.87 (m, 6H, CH₃); ¹³C NMR δ 163.55, 163.42, 140.44, 135.30, 134.90, 133.36, 132.88, 130.60, 130.12, 129.86, 129.46, 129.42, 127.98, 124.71, 122.66, 122.34, 40.81, 31.99, 29.51, 29.36, 28.32, 27.29, 22.79, 14.23; ESI-MS: m/z 1229.64 (calcd. [M+H]+ = 1229.54).

[(10)Ru₂(6)₂][PF₆]₄ (13): red powder, (78%), m.p. > 350 °C; ¹H NMR (500 MHz, CD₃OD): δ 9.35 (s, 4H, PyH³,⁵), 9.18 (s, 4H, PyH³,⁵), 8.91 (d, 4H, J = 8 Hz, PyH³,³'), 8.83 (d, 4H, J = 8 Hz, PyH³,³'), 8.69 (s, 2H, PeryH), 8.49 (d, 4H, J = 8 Hz, ArH), 8.26 (d, 2H, J = 8 Hz, PeryH), 8.13 (d, 4H, J = 8 Hz, ArH), 8.02-7.96 (m, 14H, ArH, PeryH, PyH⁴,⁴'), 7.54 (m, 8H, PyH⁶,⁶'), 7.51 (d, 4H, J = 5 Hz, ArH), 7.30 (m, 8H, PyH⁵,⁵'), 4.23 (t, 4H, CH₂), 2.54 (s, 6H, CH₃), 1.77 (m, 8H, CH₂), 1.46-1.25 (m, 23H, CH₂), 0.86 (m, 6H, CH₃); ¹³C NMR δ 162.72, 157.84, 157.75, 155.14, 155.12, 154.84, 151.62, 151.35, 148.88, 140.62, 137.94, 137.87, 137.78, 137.77, 137.74, 133.09, 127.42, 127.36, 126.75, 126.68, 124.64, 124.31, 121.37, 121.35, 120.76, 31.24, 28.71, 28.60, 28.54, 27.44, 26.53, 21.96, 20.18,
13.03; ESI-MS (m/z): 519.70 [M-4PF_6]^{4+} \ (\text{Calcd. } m/z = 519.65), \ 741.20 \ [M-3PF_6]^{3+} \ (\text{Calcd. } 741.19).
CHAPTER IV
NOVEL NANOSIZED, LUMINESCENT PERYLENE FUNCTIONALIZED
BISTERPYRIDINE ZN(II) METALLOMACROCYCLES

4.1 Introduction

Supramolecular chemistry\textsuperscript{175} is a powerful tool for the construction of both complex and highly functionalized materials. This approach implements diverse types of bindings, such as: $\pi-\pi$-interactions, hydrogen bonding, and metal-to-ligand binding. Coordination binding between polypyridine ligands, especially terpyridine\textsuperscript{194,201} with transition metals is an attractive route to cyclic trimers,\textsuperscript{220} tetramers, pentamers,\textsuperscript{193} hexamers,\textsuperscript{179,221} polygons,\textsuperscript{178} and other cyclic architectures.\textsuperscript{180,190} Ru(II) and Fe(II) salts react with terpyridine to afford a mixture of kinetic products; whereas, the terpyridine reaction with weakly binding metals [Cd(II) and Zn(II)] produces the thermodynamically most stable product in quantitative yield or produces a library of complexes in equilibrium.\textsuperscript{222,223}

The redox or luminescent functional properties of the metals and the ligands are incorporated into the resulting metallosupramolecule.\textsuperscript{191,224} Thus, several functional derivatives, such as: porphyrin,\textsuperscript{225} phthalocyanine,\textsuperscript{226} fluorene,\textsuperscript{227,228} truxene,\textsuperscript{190} HBC,\textsuperscript{229} and perylene-functionalized terpyridine\textsuperscript{131,228} have been reported. Perylene is an electron-deficient polyaromatic conjugated dye.
with desirable photophysical, electrochemical properties that can be multiplied by metal-mediated, self-assembly multichromophores.

4.2 Results and Discussion

Herein, we report the synthesis of fluorescent cyclic metallosupramolecular architectures. These macrocycles were constructed from perylene-substituted bisterpyridine ligands and self-assembled using Zn(II). The synthesis of these ligands necessitated the prior access to the novel aminobisterpyridine. The multi-step synthesis of 7 is illustrated in Scheme 4.1. Nitroisophthalic acid 1 was reduced with BH$_3$·THF in dry THF at 0 °C for 1 h, followed by reflux for 6h. The crude product was then neutralized (Na$_2$CO$_3$), extracted (CHCl$_3$), and the solvent was evaporated in vacuo to give (25%) 2$^{230}$. Diol 2 was oxidized with pyridiniumchlorochromate (PCC) in CH$_2$Cl$_2$ at 25 °C for 5h. The crude product was filtered (Celite), concentrated in vacuo and the residue was column chromatographed (SiO$_2$) eluting with EtOAc/hexanes (1:3) to afford (90%) bisaldehyde 3$^{231}$. Condensation of 3 with 2-acetylpyridine under basic conditions in MeOH at 0 °C for 7h afforded crude product that was filtered, and recrystallized (CHCl$_3$/MeOH) to give (41%) 4. Enone 4 was then refluxed with N-\{1-(2′-pyridyl)-1-oxo-2-ethyl\}pyridinium iodide$^{232}$ in EtOH for 48 h, followed by the addition NH$_4$OH and stirring at 75 °C for 8h. Solvent was removed in vacuo and the residue was column chromatographed (Al$_2$O$_3$), eluting with CHCl$_3$ to give 6 (44%). The reduction of 6 into aminobisterpyridine 7 was conducted using hydrazine hydrate and was catalyzed with Pd/C in refluxing
EtOH for 4h. The mixture was then filtered (Celite) and concentrated in vacuo to give (44%) 7.

The structure of the nitro-(6) was elucidated (^1H NMR) that showed the following resonance frequencies: (8.83 ppm, tpy H^3',5'), (8.76 ppm, tpy H^3'''), (8.72 ppm, tpy H^6'''), (7.92 ppm, tpy H^4''), (7.39 ppm, tpy H^5'''). In contrast, amino-bisterpyridine (7) revealed the following signals: (8.77 ppm, tpy H^3'), (88.79 ppm, tpy H^3''), (8.70 ppm, tpy H^6''), (8.05 ppm, tpy H^4''), (8.53 ppm, tpy H^5''). In addition to the ESI-MS peaks at m/z 586.2 (calcd [M+H]^+ = 586.19) for nitrobieterpyridine 6 and m/z 556.3 (calcd [M+H]^+ = 556.2), 578.3 (calcd [M+Na]^+ = 578.2) for aminobieterpyridine 7.

Scheme 4.1. Synthesis of nitro-(6), and amino-2,2',6',2''-terpyridine (7).

Moreover, the shape-persistent perylene-containing bisterpyridine ligand 10 was prepared by the condensation of perylene 8 with aminobieterpyridine 7 in
quinoline at 220 °C under an inert atmosphere for 4 days. The crude product was precipitated with glacial MeCO₂H, filtered, washed (H₂O), and column chromatographed (Al₂O₃) eluting with CHCl₃ to afford 9. The low observed yield of ligand 10 (18%) can be attributed to the presence of two electron-withdrawing tpy groups electronically communicating to amino group of 9 raising the energy barrier for its condensation reaction with 8. Bisterpyridine 11 was obtained similarly by the condensation of aminopropylbisterpyridine 9 with perylene 8. Ligand 11 was isolated (60 %) as a red powder. The enhanced yield of 11 compared to that of 10 is due to the introduction of propyl spacer that eliminated the electronic communication between the two tpys and amino group. The structure and purity of these ligands were assured using ¹H NMR, ¹³C NMR, and ESI-MS.

The ¹H NMR spectrum of 10 showed the following terpyridine peaks: singlet (8.82 ppm, tpyH³'₅'), doublet (8.67 ppm, tpyH³',3''), doublet (8.70 ppm, tpyH⁶',6''), two singlets at (8.30, and 8.27 ppm PeryH), this splitting is due to the asymmetric substitution of perylene with terpyridine on one side and octyl group on the other position, respectively.
Scheme 4.2. Synthesis of bis[terpyridinyl]-perylene ligands 10 and 11.

The asymmetric substitution of perylene was further confirmed from the [C(CH$_3$)$_3$] two singlets at 1.31 and 1.26 ppm with an 1:1 integration. In comparison, perylene 11 showed the following resonance values: tpy $H^{3,5'}$ and tpy $H^{6,6'}$ (8.69 ppm), tpy $H^{3,3'}$ (8.61 ppm) in addition to Pery$H$, singlets, at 8.18 and 8.14 ppm, in addition to [C(CH$_3$)$_3$] at 1.31 ppm and 1.26 ppm with 1:1 integration that proves the asymmetric nature. ESI-MS of 10 showed peaks at $m/z$ 1633.74 (calcd. [M]$^+$ = 1633.74), 1634.72 (calcd. [M+H]$^+$ = 1634.74), 3267.47 (calcd
[2M]$^+$ = 3267.48). This last peak reveals that the strong intermolecular $\pi-\pi$ for 10 in gas phase leads to the formation of dimeric species. Finally, the ESI-MS of 11 showed a peak $m/z$ 1690.72 (calcd. [M]$^+$ = 1690.78).


Tpy ligand 11 was reacted with adduct 12 at 90 °C in DMF, the solvent was evaporated in vacuo, and the crude product was column chromatographed (SiO$_2$) eluting with a mixed solvent of MeCN:KNO$_3$:H$_2$O (35:1:1) to afford (70%) a dark red powder; the counter ion was exchanged (NO$_3^-$ to PF$_6^-$) by adding NH$_4$PF$_6$. The $^1$H NMR spectrum showed two sets of resonance frequencies at 9.32 and 9.21 corresponding to the terminal and internal tpyH$_{3',5'}$ respectively, with 1:1 integration. The [C(CH$_3$)$_3$] and PeryH were split into two singlets at (8.26, 6.32 ppm) and (1.25, 1.29 ppm), respectively. The structure of 13 was further confirmed using ESI-MS (as PF$_6^-$) that showed multiple charged ions at $m/z$: 895.25 [M - 3PF$_6^-$]$^{3+}$ (Calcd. $m/z$ = 895.28), 635.19 [M - 4PF$_6^-$]$^{4+}$ (Calcd. $m/z$ = 635.22).
The $120^\circ$ tpy ligand 11 was cyclized using Zn(OTf)$_2$ in a solvent mixture of MeOH/CHCl$_3$ (1:3, v/v) followed by precipitation using Et$_2$O to afford (80%) the metallosupramolecule 14, as red powder.

Scheme 4.4. Zn$^{II}$–mediated self-assembly of ligand 11.

Previous literature noted that the self-assembly of 60$^\circ$, 120$^\circ$, and 180$^\circ$ **bisterpyridine** with labile metals, such as Cd$^{II}$ and Zn$^{II}$, results in trimeric,$^{220}$ hexameric,$^{221,233,234}$ or polymeric products,$^{217}$ respectively. In some cases, however, the product were reported to be a mixture of cyclic structures$^{235}$ that were characterized using Travelling Wave Ion Mobility-MS (TWIM-MS) in this technique, different compounds are separated, based on their authentic drift time.$^{236}$

The $^1$H NMR of 14 confirms the absence of free ligand resonance and shows broad bands indicative of rapid dynamic equilibrium on NMR time-scale and aggregation typical for perylene moieties $\pi-\pi$ stacking.$^{237}$ The broad peak at 9.0-8.9 ppm is attributed to $\text{tpyH}^{3',5'}$ with the expected downfield shift ($\Delta\delta = +0.31$) compared to free ligand upon complexation with Zn$^{II}$.
Moreover, the ESI-MS (Fig. 4.1) depicted the presence of two series of peaks in perfect match with the corresponding calculated values for pentameric and hexameric species. The peaks at \( m/z \): 2934.1 \([M - 4\text{OTf}^-]^{4+}\) (Calcd. \( m/z = 2934.1 \)), 2317.4 \([M - 5\text{OTf}^-]^{5+}\) (Calcd. \( m/z = 2317.4 \)), 1905.3 \([M - 6\text{OTf}^-]^{6+}\) (Calcd. \( m/z = 1905.1 \)), 1611.2 \([M - 7\text{OTf}^-]^{7+}\) (Calcd. \( m/z = 1611.66 \)), 1391.6 \([M - 8\text{OTf}^-]^{8+}\) (Calcd. \( m/z = 1391.6 \)), 1391.6 \([M - 8\text{OTf}^-]^{8+}\) (Calcd. \( m/z = 1220.4 \)), resulting from the iterative loss of OTf counter ions from the hexameric structure under the MS-ionization conditions. Peaks at \( m/z \): 2420.2 \([M - 4\text{OTf}^-]^{4+}\) (Calcd. \( m/z = 2420.2 \)), 1905.3 \([M - 5\text{OTf}^-]^{5+}\) (Calcd. \( m/z = 1905.3 \)), 1562.7 \([M - 6\text{OTf}^-]^{6+}\) (Calcd. \( m/z = 1567.7 \)), 1319.2 \([M - 7\text{OTf}^-]^{7+}\) (Calcd. \( m/z = 1318.2 \)) are assigned for the pentamer.
The 2D-DOSY NMR spectrum was recorded in a solvent mixture of CDCl$_3$/CD$_3$OD (3:1) at 298 °K revealing the presence of two species with diffusion coefficient of 2.5×10$^{-10}$ and 3×10$^{-10}$ m$^2$s$^{-1}$. Stokes-Einstein equation was implemented to obtain the experimental molecular hydrodynamic radius of the pentamer (3.1 nm) and hexamer (3.5 nm). The mean radius of pentameric and hexameric metallocyclic macrocycles was calculated using energy minimized molecular modeling (Fig. 4.2), the calculated values from molecular modeling matched with the DOSY experimental radius. The modeling show that the cyclic structure adopt a disc-like structure with the perylene substituents bending above and below the disc plan causing the observed small molecular radius.

![Figure 4.2. Molecular modeling of metallocycles 14.](image)

*Bi*sterpyridine ligand 11 and metallocycles 14 are bright red materials. The absorption and emission spectra (DMF) of these compounds are shown (Fig. 4.3). The absorption properties of perylene ligand 11 are similar to complex 14. Ligand 11 and complex 14 show absorption with $\lambda_{\text{max}}$ at 579, 543, 447, 267, and 289 nm corresponding to $S_0$-$S_1$, $S_0$-$S_2$, and (LC, $\pi\rightarrow\pi^*$) transitions, respectively. The observed enhancement of complex 14 absorption compared to
the free ligand 11 can be attributed to the Zn$^{II}$-terpyridine coordinative interaction.

In comparison, emission spectra of 10 and 14 are identical to perylene emission with intense red fluorescence with maxima at 617 and 671 nm. The observed negligible effect on fluorescent properties upon Zn$^{II}$ complexation is due to the absence of any electronic interactions between tpyZn$^{II}$tpy and the perylene moieties.

Figure 4.3. Uv-vis and fluorescence (Excitation wavelength = 580 nm) spectra of 11 and 14.

4.3. Conclusions
Amino-bis-terpyridine ligands containing 7 and 9 were synthesized in multistep procedures and reacted with perylene 8 to afford the corresponding perylene-containing bis-terpyridine ligands 10 and 11, respectively. In addition, ligand 11 was reacted with tpyRu$^{II}$ adduct 12 to afford the asymmetric complex 13; whereas, 11 reacted with Zn(OTf)$_2$ to produce a mixture of five- and six-membered metallomacrocyclics 14. The chemical structure and purity of the ligands and complexes were shown using $^1$H NMR, $^{13}$C NMR, and MS.
Photophysical properties revealed broad absorption spectrum and strong red luminescence of complex 14 suggesting its application in LED devices.

4.4. Experimental Section

**General Procedures.** Chemicals were purchased and used without further purification. Thin layer chromatography (TLC) was conducted on flexible sheets (Baker-flex) precoated with Al₂O₃ (IB-F) or SiO₂ (IB2-F) and visualized by UV light. Column chromatography was conducted using basic Al₂O₃, Brockman Activity I (60-325 mesh) or SiO₂ (60-200 mesh) from Fisher Scientific. Melting points were determined on Electrothermal 9100 heater. ¹H and ¹³C NMR spectra were recorded on either a Varian Mercury 300 or a Varian NMRS 500 spectrometer. Mass spectra were obtained on a Synapt HDMS quadrupole/time-of-flight (Q/TOF) mass spectrometer (Waters Corp., Milford, MA); the sprayed solution was prepared by dissolving 1 mg of sample in 1 mL of a MeCN/MeOH (1:1) solvent mixture.

**3,5-Bis(hydroxymethyl)nitrobenzene (2).** To a stirred solution of 5-nitroisophthalic acid 1 (45 g, 21 mmol) in dry THF (400 mL) under Ar at 0 °C, BH₃-THF (1M; 471 mL, 49 mmol) was added dropwise over 30 minutes. The mixture was stirred for 1 h at 0 °C, then allowed to warm to 25 °C, followed by reflux for 6 h, then cooled to 0 °C. The mixture was neutralized with aq. Na₂CO₃ and extracted with CHCl₃. The combined organic fraction was dried (MgSO₄) and concentrated *in vacuo* to afford 2, as white powder: 25 g (65%); m.p. 84-86 °C
(Lit.\textsuperscript{230} m.p. 91-92 °C); \textsuperscript{1}H NMR (300 MHz, DMSO-\textit{d}_6): δ 8.04 (s, 2H, \textit{ArH}\textsubscript{2,6}), 7.69 (s, 1H, \textit{ArH}\textsubscript{4}), 5.49 (t, 2H, \textit{J} = 5.7 Hz, \textit{OH}), 4.62 (d, 4H, \textit{J} = 5.7 Hz, \textit{CH}_2).

\textbf{5-Nitroisophthaldehyde (3).} To a stirred solution of 3,5-\textit{bis}(hydroxymethyl)nitrobenzene 2 (20 g, 100 mmol) in CHCl\textsubscript{3} (500 mL) was added a mixture of PCC (60.7 g, 280 mmol) and Celite (60 g). The mixture was stirred at 25 °C for 5 h., filtered (Celite), and the solvent was removed \textit{in vacuo} to give a residue that was column chromatographed (SiO\textsubscript{2}) eluting with an EtOAc/hexane mixture (1:3) affording 3, as yellow powder: 17.5 g (90%); m.p. 108-110 °C (Lit.\textsuperscript{231} m.p. 128-129 °C); \textsuperscript{1}H NMR (300MHz, CDCl\textsubscript{3}): δ 10.21 (s, 2H, \textit{CHO}), 8.95 (d, 2H, \textit{J} = 1.5 Hz, \textit{ArH}\textsubscript{2,6}), 8.72 (t, 1H, \textit{J} = 1.5 Hz, \textit{ArH}\textsubscript{4}).

\textbf{3,5-Bis[(1-(2-pyridyl)-2-propen-1-one]nitrobenzene (4).} To a stirred solution of 5-nitroisophthaldehyde 3 (3.5 g, 190 mmol) in MeOH (250 mL) at 0 °C, aq. NaOH (10%, 1 mL) was added, followed by the addition of cold 2-acetylpyridine (4.72 g, 390 mmol) in EtOH (25 mL) dropwise over 4 h. After 7 h, the white powder was filtered, washed with MeOH, and recrystallized (CHCl\textsubscript{3}/MeOH) to afford the product 4, as white powder: 3.1 g, (41%); m.p. 120 °C; \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}): δ 8.81 (d, 2H, \textit{J} = 4.2 Hz, PyH\textsubscript{6,6'}, 8.60 (d, 2H, \textit{J} = 1.2 Hz, ArH\textsubscript{2,6}), 8.52 (d, 2H, \textit{J} = 15.9 Hz, CH), 8.26 (s, 1H, ArH\textsubscript{4}), 8.24 (d, 2H, \textit{J} = 8.1 Hz, PyH\textsubscript{3,3'}, 8.00 (d, 2H, \textit{J} = 16.2 Hz, CH), 7.92 (dd, 2H, \textit{J} = 15.9 Hz, PyH\textsubscript{1,4}), 7.57 (m, 2H, PyH\textsubscript{5,5'}); \textsuperscript{13}C NMR: δ 188.85, 153.59, 149.01, 140.79, 137.68, 137.16, 134.05, 127.32, 124.46, 123.59, 123.05; ESI-MS: \textit{m/z} 386.1 (calcd [M+H]\textsuperscript{+} = 386.11).
5'-Nitro-3,5-bis[4'-[2,2':6',2''-terpyridinyl]benzene (6). To a stirred mixture of 4 (1.8 g, 4.6 mmol) in EtOH (200 mL) under Ar, 1-(2-pyridylcarbonylmethyl)pyridinium iodide\textsuperscript{232} (3.2 g, 9.8 mmol) was added, the mixture was stirred at 75 °C for 48 h with the addition of NH\textsubscript{4}OH (20 mL) over 8 h intervals. The solvent was removed \textit{in vacuo} to give a residue that was washed with H\textsubscript{2}O, MeOH, and column chromatographed (Al\textsubscript{2}O\textsubscript{3}) eluting with CHCl\textsubscript{3} to afford 6, as yellow powder: 1.2 g (44%); m.p. 165 °C; \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}): δ 8.83 (s, 4H, Py\textsubscript{3',5'}), 8.81(s, 2H, Ar\textsuperscript{2}), 8.76 (d, 4H, \textit{J} = 4.2 HZ, Py\textsuperscript{3,3'}), 8.72 (d, 4H, \textit{J} = 8.1 Hz, Py\textsuperscript{6,6'}), 8.64 (s, 1H, Ar\textsuperscript{4}), 7.92 (t, 4H, \textit{J} = 7.5 Hz, Py\textsuperscript{1,4}), 7.39 (t, 4H, \textit{J} = 7.2 Hz, Py\textsuperscript{5,5'}); \textsuperscript{13}C NMR: δ 156.542, 155.69, 149.22, 147.78, 141.57, 136.96, 131.93, 124.13, 122.51, 121.42, 119.05; ESI-MS: m/z 586.2 (calcd [M+H]\textsuperscript{+} = 586.19).

5'-Amino-3,5-bis[4'-[2,2':6',2''-terpyridinyl]benzene (7). A stirred suspension of nitrobi-terpyridine 6 (1 g, 1.7 mmol) and Pd/C (2 g) in EtOH (100 mL) under Ar was refluxed for 4 h, followed by the injection of hydrazine hydrate (5 mL). The reaction was further refluxed, filtered (Celite), washed (3x) with water and the combined organic fraction was dried (MgSO\textsubscript{4}), then concentrated \textit{in vacuo} to afford 7, as yellow powder: 700 mg (74%); \textsuperscript{1}H NMR (500 MHz, DMSO-d\textsubscript{6}): δ 8.79 (d, 4H, \textit{J} = 5 Hz, Py\textsuperscript{3,3'}), 8.77 (s, 4H, Py\textsuperscript{3,3'}), 8.70 (d, 4H, \textit{J} = 5 Hz, Py\textsuperscript{6,6'}), 8.05 (dd, 4H, \textit{J} = 5 Hz, Py\textsuperscript{1,4}), 8.53 (dd, 4H, \textit{J} = 5 Hz, Py\textsuperscript{5,5'}), 7.48 (s, 1H, Ar\textit{H}), 7.32 (s, 2H, Ar\textit{H}); \textsuperscript{13}C NMR: δ 156.08, 155.45, 151.07, 150.31, 149.81, 139.78, 137.93, 124.98, 121.41, 118.37, 113.51, 112.68; ESI-MS: m/z 556.3 (calcd [M+H]\textsuperscript{+} = 556.2), 578.3 (calcd [M+Na]\textsuperscript{+} = 578.2).
Synthesis of terpyridine-perylene ligands 10 and 11. **General Procedure.** A stirred mixture of *N*-octyl-1,6,7,12-tetra(*p*-t-butylphenoxy)-perylene-3,4-anhydride-9,10-tetracarboxylic imide \(^8\) (1 g, 1.1 mmol) and aminobisterpyridine 7 or \(^9\) (2.2 mmol) in quinoline (20 mL) under Ar was heated at 220 °C for 4 d. The mixture was cooled to 25 °C, precipitated with glacial MeCO\(_2\)H (150 mL), filtered, washed with water (500 mL), and EtOH. The product was column chromatographed (Al\(_2\)O\(_3\)) eluting with CHCl\(_3\) to give 10 and 11.

\(*\text{N-[5-(1,3-phenylene)bis-2,2':6',2''-terpyridinyl]-N'-octyl-1,6,7,12-tetra(*p*-t-butylphenoxy)perylene-3,4:9,10-tetracarboxydiimide (10): red powder; m.p. > 300 °C; (18%);}^1\text{H NMR (500 MHz, CDCl}_3^\text{):} \delta 8.82 \text{ (s, 4H, PyH}_3^\text{,5'),} 8.70 \text{ (d, 4H, J = 4.6 Hz, PyH}_6^\text{,6'''),} 8.67 \text{ (d, 4H, J = 8 Hz, PyH}_3^\text{,3''),} 8.43 \text{ (s, 1H, ArH)}, 8.30 \text{ (s, 2H, PeryH)}, 8.27 \text{ (s, 2H, PeryH)}, 7.87 \text{ (m, 6H, PyH}_8^\text{,8''),} 7.34 \text{ (m, 4H, PyH}_5^\text{,5''),} 7.25 \text{ (m, 4H, ArH)}, 6.88 \text{ (m, 4H, ArH)}, 4.13 \text{ (t, 2H, J = 7.8 Hz, CH}_2^\text{),} 1.68 \text{ (m, 2H, CH}_2^\text{),} 1.55 \text{ [s (broad), 8H, CH}_2^\text{],} 1.31 [s, 18H, C(CH}_3^\text{)\text{3}], 1.26 [s, 18H, C(CH}_3^\text{)\text{3}], 0.86 (m, 5H, CH}_2^\text{, CH}_3^\text{);} ^{13}\text{C NMR:} \delta 163.46, 156.13, 152.97, 152.91, 149.14, 147.30, 140.97, 136.81, 136.77, 128.33, 126.67, 123.80, 122.42, 121.34, 120.47, 119.88, 119.39, 119.32, 119.24, 34.61, 34.58, 31.70, 31.65, 29.51, 29.41, 28.36, 27.37, 22.84; ESI-MS: \text{m/z} 1633.7417 (calcd [M]+ = 1633.7429), 1634.7233 (calcd [M+H]+ = 1634.7429).\)\n
\(*\text{N-Octyl-N'-[O-(3-propyl)-3,5-bis[(4'-(2,2':6',2'')terpyridinyl)]-1,6,7,12-tetra(*p*-t-butylphenoxy)perylene-3,4:9,10-tetracarboxydiimide (11): red powder; m.p. > 300 °C; (60%);}^1\text{H NMR (500 MHz, CDCl}_3^\text{):} \delta: 8.69 \text{ (s, 8H,}
Py$H^{3,5}$, Py$H^{6,6''}$), 8.61 (d, 4H, $J = 8$ Hz, Py$H^{3,3''}$), 8.18 (s, 2H, PeryH), 8.14 (s, 2H, PeryH), 7.87 (s, 1H, ArH), 7.83 (m, 4H, Py$H^{4,4''}$), 7.31 (d, 2H, $J = 8$ Hz, ArH), 7.17-7.12 (m, 8H, PhH), 7.74 (d, 4H, $J = 8.5$ Hz, PhH), 4.47 (t, 2H, $J = 6.5$ Hz, CH$_2$), 4.33 (t, 2H, $J = 5.5$ Hz, CH$_2$), 4.12 (t, 2H, $J = 7.5$ Hz, CH$_2$), 2.32 (m, 4H, CH$_2$), 1.69 (m, 8H, CH$_2$); $^{13}$C NMR: $\delta$ 163.82, 163.63, 159.92, 156.38, 156.16, 156.09, 155.94, 153.21, 1153.12, 150.16, 149.29, 147.31, 147.20, 140.92, 136.88, 133.02, 132.95, 126.73, 126.68, 123.88, 122.61, 122.46, 121.50, 120.89, 120.71, 120.23, 119.69, 119.54, 119.41, 119.33, 118.98, 114.07, 66.86, 40.86, 38.59, 34.52, 34.48, 32.00, 31.66, 31.61, 29.91, 29.50, 29.41, 28.38, 28.01, 27.38, 22.82, 14.27; MALDI-MS: m/z 1690.72 (calcd [M]$^+$ = 1690.78).

**TerpyridineRu(II) adduct 12.** A stirred mixture of 4'-((4-methylphenyl)[2,2':6',2"]terpyridine $^{200}$ (500 mg, 2.24 mmol) and RuCl$_3$·3H$_2$O (697.5 mg, 3.3 mmol) in EtOH (50 mL) was refluxed for 12 h, allowed to cool to 25 °C. The precipitate was filtered, washed with EtOH, then CHCl$_3$ and dried in vacuo to afford a black powder. The Ru$^{III}$-terpyridine adduct (930 mg, 1.7 mmol) was refluxed with AgBF$_4$ (2.1 g, 10.5 mmol) in 1:1 mixture of MeCN/MeOH (200 mL) in the dark for 12 h. The mixture was filtered through Celite, dried in vacuo, and column chromatographed (SiO$_2$) eluting with KNO$_3$:MeCN:H$_2$O mixture (1:20:1) to afford (80%) 12, as a brown powder: m.p. > 300 °C; $^1$H NMR (500 MHz, CD$_3$CN) $\delta$: 8.94 (d, 2H, $J = 5$ Hz, Py$H^{6,6''}$), 8.66 (s, 2H, Py$H^{3,5}$), 8.58 (d, 2H, $J = 8$ Hz, Py$H^{3,3''}$), 8.20 (m, 2H, Py$H^{4,4''}$), 7.76 (d, 2H, $J = 8$ Hz, ArH),
7.75 (m, 2H, PyH\textsuperscript{5,5'}), 7.50 (d, 2H, J = 8 Hz, ArH), 2.76 (s, 3H, CH\textsubscript{3}), 2.49 (s, 3H, CH\textsubscript{3(eq)}), 2.13 (s, 6H, CH\textsubscript{3(ax)}); \textsuperscript{13}C NMR δ: 159.84, 149.67, 155.45, 142.27, 139.97, 134.36, 131.19, 128.97, 128.59, 125.13, 121.49, 21.36, 4.77, 4.03; MALDI-MS (PF\textsubscript{6}¯): \textit{m/z}: 1712.86 (calcd [M]\textsuperscript{+} = 1712.72).

**Terpyridineperylene Ru(II) complexes 13.** A stirred mixture of 11 (1 eq) and adduct 12 (1.2 eq) in DMF (20 mL) was heated at 110 °C for 2 days and the solvent was removed in vacuo. The residue was column chromatographed (SiO\textsubscript{2}) eluting with H\textsubscript{2}O:KNO\textsubscript{3}:MeCN mixture (1:1:30), the counter ions were exchanged by adding NH\textsubscript{4}PF\textsubscript{6} and then the product was filtered, washed with water, and dried in vacuo to afford (70%) 13 as a red powder: m.p. > 300 °C; \textsuperscript{1}H NMR (500 MHz, CD\textsubscript{3}CN) δ: 9.23 (s, 4H, PyH\textsuperscript{3,5'}), 9.12 (s, 4H, PyH\textsuperscript{3,5'}), 8.76 (m, 8H, PyH\textsuperscript{3,3'}), 8.24 (s, 2H, PeryH), 8.22 (s, 2H, PeryH), 7.67 (d, 4H, J = 8 Hz, ArH), 7.64 (d, 4H, J = 8 Hz, ArH), 7.51-7.47 (m, 8H, PyH\textsuperscript{4,4'}), 7.04 (d, 4H, J = 8 Hz, ArH), 6.99 (m, 8H, PyH\textsuperscript{6,6'}), 6.80-6.75 (m, 16H, ArH, PyH\textsuperscript{5,5'}), 6.67 (d, 4H, J = 8 Hz, ArH), 6.40 (d, 4H, J = 8 Hz, ArH), 4.34 (t, 4H, J = 6 Hz, CH\textsubscript{2}), 4.24 (t, 4H, J = 6 Hz, CH\textsubscript{2}), 2.53 (s, 6H, CH\textsubscript{3}), 2.24 (m, 4H, CH\textsubscript{2}), 1.28 [s, 36 H, C(CH\textsubscript{3})\textsubscript{3}]\textsuperscript{3+}; \textsuperscript{13}C NMR δ: 164.30, 162.08, 159.44, 159.44, 156.87, 156.55, 156.41, 154.10, 152.96, 150.11, 149.69, 148.34, 141.99, 139.22, 134.75, 131.21, 129.98, 128.74, 128.50, 127.50, 125.77, 123.18, 122.20, 121.67, 120.77, 120.27, 116.42, 67.32, 35.13, 31.96, 28.76, 21.47; ESI-MS (as PF\textsubscript{6}¯) (\textit{m/z}): 895.25 [M - 3PF\textsubscript{6}¯]\textsuperscript{3+} (Calcd. \textit{m/z} = 895.28), 635.19 [M - 4PF\textsubscript{6}¯]\textsuperscript{4+} (Calcd. \textit{m/z} = 635.22).
[Zn₈(11)₈][OTf]₁₆ (14). To a solution of Zn(OTf)₂ (2.3 mg, 6.5 µmol) in MeOH (1 mL) was added ligand 11 (11 mg, 6.5 µmol) in CHCl₃, (3 mL). The mixture was stirred at 25 °C for 1 h and the solvent was removed in vacuo to afford (95%) 14 as a red powder: ¹H NMR [500 MHz, CDCl₃/CD₃OD (3:1)]: δ 9.00 (br, 4H, PyH₃,5'), 8.69 (br, 4H, PyH₂,3'), 8.18 (s, 2H, PeryH), 8.14 (s, 2H, PeryH), 7.87 (s, 1H, ArH), 7.83 (m, 4H, PyH₄,4''), 7.31 (m, 4H, PyH₅,5''), 7.24 (d, 2H, J = 8 Hz, ArH), 7.17-7.12 (m, 8H, PhH), 7.74 (d, 4H, J = 8.5 Hz, PhH), 4.47 (t, 2H, J = 6.5 Hz, CH₂), 4.33 (t, 2H, J = 5.5 Hz, CH₂), 4.12 (t, 2H, J = 7.5 Hz, CH₂), 2.32 (m, 4H, CH₂), 1.69 (m, 8H, CH₂), 1.27 [s, 18H, C(CH₃)₃], 1.22 [s, 18H, C(CH₃)₃], 0.86 (m, 5H, CH₂, C(CH₃)₃); MALDI-MS: m/z 1690.72 (calcd [M]⁺ = 1690.78). ESI-MS (as OTf⁻) (m/z): 2934.1 [M - 4OTf⁻]⁴⁺ (Calcd. m/z = 2934.1, hexamer), 2420.2 [M - 4OTf⁻]⁵⁺ (Calcd. m/z = 2420.2, pentamer), 2317.4 [M - 5OTf⁻]⁵⁺ (Calcd. m/z = 2317.4, hexamer), 1905.3 [M - 5OTf⁻]⁶⁺ (Calcd. m/z = 1905.3, pentamer), 1905.3 [M - 6OTf⁻]⁶⁺ (Calcd. m/z = 1905.1, hexamer), 1611.2 [M - 7OTf⁻]⁷⁺ (Calcd. m/z = 1611.6, hexamer), 1562.7 [M - 6OTf⁻]⁶⁺ (Calcd. m/z = 1567.7, pentamer), 1391.6 [M - 8OTf⁻]⁸⁺ (Calcd. m/z = 1391.6, hexamer), 1319.2 [M - 7OTf⁻]⁷⁺ (Calcd. m/z = 1318.2, pentamer).
CHAPTER V
PERYLENE-CONTAINING RU(II) BIS-TERPYRIDINE
METALLOMACROCYCLES: SYNTHESIS, MOLECULAR MODELING AND
PHOTOPHYSICAL PROPERTIES

5.1. Introduction

Design and construction of highly organized dye arrays\(^{23}\) that mimic the biological photosynthetic systems\(^{241}\) has gained considerable attention. Supramolecular chemistry is a simple and unique strategy to achieve the goal of building 2D\(^{242}\) and 3D\(^{243}\) complex structures via self-assembly of predesigned building blocks. Several chemists have contributed significantly to this chemistry including Lehn,\(^{175}\) Schubert,\(^{227}\) Newkome,\(^{244}\) Stang,\(^{245}\) Mirkin,\(^{246}\) Fujita,\(^{247}\) Müllen,\(^{248}\) Aida,\(^{249}\) and others.\(^{107,182,183,250}\) 2,2’:6’,2’’-Terpyridine (tpy) has strong binding affinity towards transition metals, such as: Fe\(^{II}\), Ru\(^{II}\), and Os\(^{II}\) and the resulting tpy-M\(^{II}\)-tpy complexes can exhibit significant functional properties: catalytic, photophysical, electrochemical, photovoltaic, and light harvesting. In addition, tpy-M\(^{II}\)-tpy complexes were extensively employed to fabricate diverse structures such as: metallo-dendrimers,\(^{145}\) cages, and metallomacrocycles including tri-,\(^{220}\) tetra-,\(^{251}\) penta-,\(^{193}\) and hexa-gonal\(^{252}\) shapes. Incorporation of versatile chromophores such as: porphyrin,\(^{253}\) phthalocyanine,\(^{226}\) squarine,\(^{254}\) fluorene,\(^{227}\) pyrene,\(^{255}\) HBC,\(^{229}\) naphthalene\(^{256}\) or perylene into the cyclic self-
assembled structures was achieved. Perylenediimide (PDI)\textsuperscript{2,30,39-42} is a chromophore with outstanding properties including thermal, photo-, and electro-stability; strong light absorption and emission properties, as well as important applications in organic electronics and photovoltaics.\textsuperscript{31,171,257}

Herein, the synthesis of perylene containing tpy ligands and their Ru\textsuperscript{II}-mediated self-assembly into trimeric and heteroleptic tetrameric metallomacrocycles along with their photophysical properties and molecular simulation data are reported.

5.2. Results and discussions

The synthesis of ligand\textsuperscript{28} 7 started with reaction of 3-bromoaniline (1) with dibromoperylenetetracarboxylic acid dianhydride 2\textsuperscript{258} in propionic acid at 155 °C for 72 h; the mixture was cooled to 25 °C, precipitated (H\textsubscript{2}O), filtered, and washed (MeOH) to give (80%) 3. Compound 3 was introduced to reaction with t-octylphenol 4, K\textsubscript{2}CO\textsubscript{3} in N-methylpyrrolidone (NMP) at 80 °C for 48 h, the mixture was then cooled to 25 °C, precipitated with a mixture of (H\textsubscript{2}O/HCl), filtered, washed (H\textsubscript{2}O and MeOH), and dried \textit{in vacuo}. The crude product was column chromatographed (SiO\textsubscript{2}) eluting with CHCl\textsubscript{3}/hexane (9:1) to give 5 (57%). Bisterpyridine 7 was obtained \textit{via} Suzuki reaction of 5 with 4-terpyridinylphenylboronic acid 6,\textsuperscript{145} K\textsubscript{2}CO\textsubscript{3}, Pd(0) in DMF at 100 °C for 48 h. The reaction mixture was cooled to 25 °C and precipitated (H\textsubscript{2}O), filtered, washed with (H\textsubscript{2}O and MeOH), and dried \textit{in vacuo}. The crude product was column chromatographed (Al\textsubscript{2}O\textsubscript{3}) eluting with CHCl\textsubscript{3}/hexane (8:2), followed by recrystallization (CHCl\textsubscript{3}/MeOH) to give (53%) 7. This product required several
recrystallization cycles to eliminate the contamination with 1,6-disubstituted PDI isomer from the targeted product 7. In contrast, ligand 8 was synthesized and purified according to the literature procedure.\textsuperscript{252}

The structures of these compounds were confirmed \textsuperscript{1}H NMR, \textsuperscript{13}C NMR, and electrospray ionization mass spectrometry (ESI-MS). \textsuperscript{1}H NMR of 5 showed the following resonance frequencies: two doublets at 9.70 and 8.8 ppm, and a singlet at 8.68 ppm corresponding to perylene protons. In comparison, bisterypyridine ligand 7 revealed the following tpy resonance values: multiplet at 8.74 ppm (PyH\textsuperscript{6,6’}, PyH\textsuperscript{3,3’}), doublet at 8.67 ppm (PyH\textsuperscript{3,3’}), multiplet at 7.90 ppm (PyH\textsuperscript{4,4’}), at 7.73-7.66 ppm (PyH\textsuperscript{5,5’}) in addition to three sets of perylene proton resonance at: 8.74, 9.65, and 8.35 ppm, and the \textit{t}-octyl protons: singlets at 1.76 ppm (CH\textsubscript{2}), 1.40 ppm [C(CH\textsubscript{3})\textsubscript{2}], 0.76 ppm [C(CH\textsubscript{3})\textsubscript{3}]. Finally, ESI-MS shows a peak at \textit{m/z} 1566.10 (cald [M+H]\textsuperscript{+}=1566.65).

\begin{center}
\includegraphics[width=\textwidth]{Scheme_5_1.png}
\end{center}

\textbf{Scheme 5.1.} Synthetic route to bisterypyridine ligand 7: a) propionic acid, Ar, 150 °C, 72h; b) NMP,K\textsubscript{2}CO\textsubscript{3}, 80 °C, 48h; c) DMF, Pd(PPh\textsubscript{3})\textsubscript{4}, K\textsubscript{2}CO\textsubscript{3}, Ar, 120 °C , 48 h.
Figure 5.1. Single crystal X-ray structure of 4-terpyridinylphenylboronic acid 6 (as sodium salt).

The single crystal of 6 was obtained by slowly evaporating 4-terpyridinylphenylboronic acid 6 in MeOH. The crystal data of 6 are summarized in Table 5.1 and the single crystal is shown in Fig. 5.1.

Table 5.1. Crystal data of 4-terpyridinylphenylboronic acid 6.

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<th>Empirical formula</th>
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<td>Formula weight</td>
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<td>b (Å)</td>
<td>5.2511(2)</td>
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<tr>
<td>Temperature (K)</td>
<td>100(2) K</td>
<td>c (Å)</td>
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<td>Wavelength (Å)</td>
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</tr>
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<td>Crystal system</td>
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<tr>
<td>Space group</td>
<td>P2(1)/c</td>
<td>γ (°)</td>
<td>90°</td>
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<tr>
<td>Volume (Å$^3$)</td>
<td>2262.09(17)</td>
<td>Density (Mg/m$^3$)</td>
<td>1.319</td>
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</table>
The trimetallic complex 9 was synthesized via the reaction of 8 with RuCl$_2$(DMSO)$_4$ (1.1 equ.) in DMF (800 mL) at 90 °C for 24 h. The solvent was removed in vacuo and the residue was column chromatographed (SiO$_2$) eluting with a mixture of H$_2$O/MeCN/KNO$_3$(aq) (1:25:1). The counter ions were then exchanged (NO$_3^-$ to PF$_6^-$), to give (9 %) 9 (Scheme 5.1).

The $^1$H NMR of 9 showed a singlet at 9.00 ppm (Py$^3$,5$'$), doublet at 8.61 ppm (Py$^3$,3$''$), multiplets at 7.92 ppm (PyH$^{4,4''}$), 7.4-7.37 ppm (PyH$^{6,6''}$), and 7.16 ppm (PyH$^{5,5''}$), in addition to perylene protons at 8.13 ppm and a singlet at 1.30 ppm [(CH$_3$)]. The Maldi-TOF-MS of 9 showed peaks at m/z 5819.1 (calcd. [M–(H+PF$_6^-$)]$^+$ = 5819.6), 5838.0 (calcd. [H+M–2PF$_6^-$])$^+$ = 5837.8, 1843.7 (calcd. [M–3PF$_6^-$]$^{3+}$ = 1843.7, 1374.8 (calcd. [M–4PF$_6^-$]$^{4+}$ = 1374.4).

![Scheme 5.2: Synthetic route to biscerpyridine ligand 9](image)

Scheme 5.2. Synthetic route to biscerpyridine ligand 9: a) DMF, Ar, 90 °C, 48 h; b) NH$_4$PF$_6$. 
The Ru\textsuperscript{III}bisterpyridine adduct 11 was constructed by refluxing \textit{t}-butylbisterpyridine 10 with RuCl\textsubscript{3}·4H\textsubscript{2}O in EtOH for 24 h. The mixture was cooled, filtered, washed (EtOH), and dried \textit{in vacuo} to afford (89\%) the paramagnetic Ru\textsuperscript{III}tpy. The heteroleptic tetranuclear macrocycle 12 was prepared by the reaction of ligand 8 with adduct 11 and reduced with drops of \textit{N-}ethylmorpholine in EtOH at 60 °C for 48 h, the solvent was evaporated \textit{in vacuo} and the crude product was column chromatographed (SiO\textsubscript{2}) eluting with a mixture of H\textsubscript{2}O:KNO\textsubscript{3}:MeCN (1:15:1) to give (30\%) 12; the counter ions were exchanged (NO\textsubscript{3}\textsuperscript{−} to PF\textsubscript{6}\textsuperscript{−}).

The \textsuperscript{1}H NMR showed two sets of tpy\textit{H} resonance as following: two singlets at 8.94 and 8.76 ppm (Py\textit{H}\textsuperscript{3,5}), two doublets at 8.55 and 8.36 ppm (Py\textit{H}\textsuperscript{3,3}), multiplet at 7.71 ppm (Py\textit{H}\textsuperscript{4,4}), two multiplets at 7.4-7.37 (Py\textit{H}\textsuperscript{6,6}) and 7.16 ppm (Py\textit{H}\textsuperscript{5,5}), perylene protons appeared as a singlet at 8.16 ppm in addition to the two distinct singlets at 1.61 and 1.30 ppm [C(\textit{CH})\textsubscript{3}]. The structure was further confirmed using MALDI-TOF-MS peak at \textit{m}/\textit{z} = 5806.9 (calcd [2H+M-PF\textsubscript{6}\textsuperscript{−}]\textsuperscript{+}=5806.9).
Scheme 5.3. Synthesis of Ru\textsuperscript{III} bisterpyridine adduct 11 and heteroleptic metallomacrocycle 12: a) RuCl\textsubscript{3}·4H\textsubscript{2}O, EtOH, 24h; b) EtOH:CHCl\textsubscript{3} (1:2), 60 °C, 48h, NH\textsubscript{4}PF\textsubscript{6}.

Figure 5.3 MALDI-TOF-MS spectrum of 12.

The absorption and emission spectra (DMF) of metallomacrocycles (9 and 12) and ligands (7 and 8) are shown (Fig. 5.4) along with their photophysical properties (Table 5.2). Ligand 7 is an orange material; whereas, ligand 8 is a deep red compound, both compounds exhibit strong, broad absorption with maxima at 545, 523, 338, 279 (7); 567, 531, 338, 272 (8). The observed hypsochromic shift...
of perylene bands of 7 at 545, 513 nm with regard to those of 8 at 567, 531 (S₀-S₁ and S₀-S₂ transitions, respectively)¹¹³ is attributed to the lower electron donation of two phenoxy substituents at the bay-positions in 7 compared to that of four phenoxy substituents in 8. Both 7 and 8 show identical tpy ligand centered (LC, π→π*) absorbtions at 338 and 272, this can be explained by the absence of any electronic interaction of perylene rings with substituents on imide-positions. In addition to the previous absorption bands, the dark red complexes 9 and 12 possess metal-to-ligand charge transfer (¹MLCT) transitions at 445 and 447, respectively. The observed enhancement of (¹MLCT:S₀-S₁) absorption intensity [¹² (576:447nm) > 9 (584:445)] is proportional to the increase of tpyRu⁺:perylene units [¹²(2:1) or 9 (1:1)].

Ligand 7 or 8 emits a yellow or pink fluorescence, respectively, under illumination with UV lamp at 365 nm (onset Fig. 5.4). Emission spectra of 7 and 8 were collected upon excitation at 545 (7) and 575 (8), both materials give broad strong fluorescence maxima at (552, 600, and 642 nm) for 7 and (581, 591, 636, and 680 nm) for 8. This luminescence was completely quenched as the tpyRu⁺ complexation took place.
Figure 5.4. Absorption and emission spectra (DMF) of ligands (7 and 8) and complexes (9 and 12) at 25 °C (onset image shows the yellow and pink fluorescence of 7 and 8, respectively.)

Table 5.2. Photophysical data of ligands 7 and 8; complexes 9 and 12.

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<th>Cpd.</th>
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<th>( \lambda_{\text{em}} ) (nm)</th>
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<td>12</td>
<td>576, 533, 492, 447, 334, 292</td>
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</tbody>
</table>

Attempts to grow single crystal of either macrocycles 9 and 12 were unsuccessful; thus, molecular modelling was implemented to gain insight of the structural characteristics and dimensions. Molecular simulation of 12 showed a planar structure with (35.5 x 46.6 Å) outer and (26.8 x 26.9 Å) cavity dimensions; whereas, that of the hexameric trimer 9 depicted an untwisted macrocycle with outer diameter of (42.8 Å) and void diameter of (25.5 Å) (Fig. 5.5).
The perylene core of complex 9 and 12 showed twisted and rigid structures and the cyclization renders them even more rigid.

Figure 5.5. Molecular modelling of metallomacrocycles 9 (A. Side-view and B. Top-view) and 12 (C. Side-view and D. Top-view)

Although the free rotation of perylene around its long axis is allowed; the minimized energy state seems to prefer a conformation in which the perylene aromatic plane is tilted from the horizontal plane, whereas, the t-butyl-phenoxo-groups are directed above and below the macrocycles planes, leaving a void accessible for potential guest molecules encapsulation.
5.3. Conclusions

The successfully prepared novel perylene-containing bisterpyridine ligands underwent Ru$^{II}$-mediated self-assembly to give homo- and heteroleptic metallomacrocycles 9 and 12. $^1$H NMR, ESI-MS, and MALDI-TOF-MS spectroscopy were implemented to elucidate the resulting chemical structures. The molecular modeling of these complexes shows that the rings have an external diameter of 3-4 nm with interior cavity diameter of 2.5 nm. The photophysical properties of these materials show broad intense absorption spectra.

5.4. Experimental Section

**General Procedures.** Chemicals were purchased and used without further purification. Thin layer chromatography (TLC) was conducted on flexible sheets (Baker-flex) precoated with Al$_2$O$_3$ (IB-F) or SiO$_2$ (IB2-F) and visualized by UV light. Column chromatography was conducted using basic Al$_2$O$_3$, Brockman Activity I (60-325 mesh) or SiO$_2$ (60-200 mesh) from Fisher Scientific. Melting points were determined on Electrothermal 9100 heater. $^1$H and $^{13}$C NMR spectra were recorded on either a Varian Mercury 300 or a Varian NMRS 500 spectrometer. Mass spectra were obtained on a Synapt HDMS quadrupole/time-of-flight (Q/TOF) mass spectrometer (Waters Corp., Milford, MA); the sprayed solution was prepared by dissolving the sample (1 mg) in a MeCN/MeOH (1:1, v/v) solvent mixture (1 mL). The absorption and emission spectra were normalized by dividing the absorption values of each specrum by the maximum absorbtion of
compound 12. Molecular modeling was accomplished using the Forcite module in the Materials Studio program v4.2.0.0 available from Accelrys Software, Inc.

**X-ray Structure Determination Details**

A crystal of C$_{21}$H$_{25}$B$_1$N$_3$O$_6$Na 6 was coated in paraffin oil and mounted on a CryoLoop™ and placed on the goniometer head under a stream of nitrogen cooled to 100 °K. The data were collected on a Bruker APEX II Duo CCD system equipped with a Cu ImuS micro-focus source (λ = 1.54178 Å). The unit cell was determined by using reflections from three different orientations. The data were integrated using SAINT. An empirical absorption correction and other corrections were applied to the data using multi-scan SADABS. Structure solution, refinement, and modeling were accomplished by using the Bruker SHELXTL package. The structure was determined by full-matrix least-squares refinement of $F^2$ and the selection of the appropriate atoms from the generated difference map. Hydrogen atom positions were calculated and U$_{iso}$(H) values were fixed according to a riding model.

**Synthetic procedures:**

**1,7-Dibromo-3,4,9,10-perylenetetracarboxylic dianhydride (2)$^{258}$** A mixture of 3,4,9,10-perylenetetracarboxylic dianhydride (4 gm, 10 mmol) and H$_2$SO$_4$ (60 mL) was stirred at 55 °C for 18 h, I$_2$ (80 mg, 300 µmol) was added and the mixture was stirred for 5 h at 55 °C. Br$_2$ (3.5 gm, 20 mmol) was then added, and the reaction mixture was stirred for 48 h at 85 °C, followed by cooling to 0 °C. Excess Br$_2$ was removed using air stream. The product was precipitated with
ice water (30 mL), filtrated, washed (H₂O and EtOH) to give (90%) 2 as an orange powder (5 gm). The product was used in the next step without further purification.

**N,N'-Bis(3-bromophenyl)-1,7-dibromoperylene-3,4:9,10-tetracarboxydiimide** (3) A mixture of 1,7-dibromo-3,4,9,10-perylenetetracarboxylic dianhydride 2 (2 gm, 3 mmol) and 3-bromoaniline (7 gm, 40.6 mmol) in propionic acid (50 mL) was stirred at 155 °C under argon for 48 h. The reaction mixture was cooled to 25 °C, the product was precipitated (H₂O, 200 mL), filtered, and washed (H₂O and MeOH) to give (80%) 3, as orange powder mp > 300 °C (2.5 g). The product was used in the next step without further purification.

**N,N'-Bis(3-bromophenyl)-1,7-di(p-t-octylphenoxy)perylene-3,4:9,10-tetracarboxydiimide** (5). A suspension of **N,N'-bis(3-bromophenyl)-1,7-dibromoperylene-3,4:9,10-tetracarboxydiimide** 3 (1.5 gm, 1.7 mmol), p-t-octylphenol 4 (1.2 gm, 5.8 mmol), K₂CO₃ (570 mg, 4.1 mmol) in NMP (50 mL) under argon was stirred at 80 °C for 48 h. The mixture was cooled, precipitated (H₂O and HCl), filtered, and washed (H₂O and MeOH). The crude product was column chromatographed (SiO₂) eluting with CHCl₃/hexane (9:1), the product was contaminated by 10% 1,6-di(p-t-octylphenoxy) isomer, which was removed by successive recrystallization (CHCl₃/MeOH) to give (57%) 5, as red powder: 1.1 gm; ¹H NMR (300 MHz, CDCl₃) δ: 9.61 (d, 2H, J = 8.49 Hz, PeryH), 8.60 (d, 2H, J = 8.20 Hz, PeryH), 8.30 (s, 2H, PeryH), 7.61 (d, 2H, J = 6.9 Hz, ArH), 7.49-7.38 (m, 6H, ArH, PhH), 7.27 (m, 2H, ArH), 7.10 (d, 4H, J = 8.4 Hz, PhH), 7.15-7.05 (m, 8H, ArH, PhH), 7.00-6.90 (m, 10H, ArH, PhH).
1.77 (s, 4H, CH$_2$), 1.41 (s, 12H, CH$_3$), 0.78 (s, 18H, CH$_3$); ESI-MS: m/z 1107.7 (calcd [M+H]$^+$=1107.2).

$N,N'$-**Bis**(4'-[1,1'-phenyl]-4-yl-(2,2':6',2'')-terpyridinyl)-1,7-di(p-t-octylphenoxy)perylene-3,4:9,10-tetracarboxydiimide (7) A mixture of $N,N'$-bis(3-bromophenyl)-1,7-di(p-t-octylphenoxy)perylene-3,4:9,10-tetracarboxydiimide 5 (200 mg, 180 mmol), boronic acid 4 (191 mg, 542 mmol), K$_2$CO$_3$ (75 mg, 542 mmol) and Pd(PPh$_3$)$_4$ (10 mg, 10 mol%) was stirred under argon in DMF (10 mL) at 100 °C, for 48 h, the solvent was evaporated, the product was redissolved (CHCl$_3$), filtered (Celite), washed (H$_2$O and MeOH), and dried in vacuo. The crude product was column chromatographed (Al$_2$O$_3$) eluting with CHCl$_3$/hexane (8:2) and recrystallized (CHCl$_3$/MeOH) to give (53%) 7, as red powder: 150 mg; $^1$H NMR (300 MHz, CDCl$_3$) δ 8.74 (m, 8H, PeryH, Py$_2$H$_{6,6'}$, PyH$_{3,5'}$), 9.65 (d, 2H, $J = 8.5$ Hz, PeryH), 8.67 (d, 4H, $J = 8.1$ Hz, PyH$_{3,3'}$), 8.35 (s, 2H, PeryH), 7.90 (m, 6H, ArH, PyH$_{4,4'}$), 7.73-7.66 (m, 8H, ArH, PyH$_{5,5'}$), 7.48 (d, 4H, $J = 7.5$ Hz, PhH), 7.45 (m, 6H, $J = 87.5$ Hz, ArH), 7.13 (d, 4H, $J = 87.5$ Hz, PhH), 1.76 (s, 4H, CH$_2$), 1.40 (s, 12H, CH$_3$), 0.76 (s, 18H, CH$_3$); ESI-MS: m/z 1566.10 (calcd [M+H]$^+$=1565.65).

$[\text{Ru}_2(10)\text{Cl}_6]$ (11) Bis(terpyridine) ligand 10 (40 mg, 60 µmol) was added to a solution of RuCl$_3$-3H$_2$O (33 mg, 160 µmol) in EtOH (20 mL), the suspension was refluxed for 24 h. The mixture was cooled to 25 °C and the resultant dark solid was filtered, washed with EtOH and dried in vacuo to give (89%) bis(Ru$^{III}$) adduct, as a dark brown solid: 60 mg; This material was used without further purification.
A mixture of 1,6,7,12-tetra(p-t-butyloxy)perylene-3,4:9,10-tetracarboxylic acid bisanhydride (500 mg, 0.5 mmol), 3-aminoterpyridine (1.31 g, 4.06 mmol) in quinoline (50 mL) was stirred at 220 ºC under argon for 3 days. The mixture was cooled to 25 ºC, precipitated with AcOH (50 mL), filtrated, washed (H₂O and MeOH). The product was column chromatographed (Al₂O₃) eluting with a mixture of CHCl₃/hexane (2:1) to afford (60%) 8 as a red powder; mp > 300 ºC; ¹H NMR (500 MHz, CDCl₃) δ 8.76 (s, 4H, PyH₃',₅'), 8.70 (d, 4H, J = 4 Hz, PyH₆',₆''), 8.66 (d, 4H, J = 7 Hz, PyH₃,₃''), 8.3 (s, 4H, PeryH), 8.02 (d, 2H, J = 7 Hz, ArH), 7.86 (m, 4H, PyH₄',₄''), 7.83 (t, 2H, J = 7 Hz, ArH), 7.37 (d, 2H, J = 6 Hz, ArH), 7.33 (m, 4H, PyH₅,₅''), 7.25 (d, 8H, J = 9 Hz, ArH), 6.89 (d, 8H, J = 8 Hz, ArH), 1.27 (s, 36 H, CH₃); ¹³C NMR δ 163.54, 156.16, 156.03, 152.90, 149.21, 149.11, 147.39, 139.92, 136.77, 136.05, 133.18, 129.85, 129.18, 126.67, 123.78, 122.56, 121.30, 119.37, 118.91, 105.02, 34.35, 31.42; ESI-MS: m/z 1596.71 (calcd. [M]+ = 1596.64).

[Ru₃(10)₃][PF₆]₆ (9). To a solution of 8 (113 mg, 70 µmol) in DMF (800 mL), RuCl₂(DMSO)₄ (500 mg, 1.1 mmol) was added. The mixture was stirred at 90 ºC for 48 h, the solvent was evaporated in vacuo, and the residue was column chromatographed (SiO₂) eluting with H₂O/MeCN/KNO₃(aq) (1:25:1). The counter ions were exchanged (NO₃⁻ to PF₆⁻), then the product was dried in vacuo to afford (9 %) 9 as a red powder: 30 mg; mp > 350 ºC; ¹H NMR (500 MHz, CDCl₃) δ 9.00 (s, 4H, PyH₃',₅'), 8.61 (d, 4H, J = 7 Hz, PyH₃',₃''), 8.23 (s, 4H, ArH),
8.13 (s, 4H, PeryH), 7.92 (m, 8H, ArH, PyH^{4,4'}, 7.67 (d, 2H, J = 7 Hz, ArH), 7.4-
7.37 (m, 4H, PyH^{6,6'}), 7.16 (m, 4H, PyH^{3,5'}), 7.07 (d, 2H, J = 9 Hz, ArH), 6.97 (d, 
8H, J = 8 Hz, ArH), 1.30 (s, 36 H, CH$_3$); Maldi-TOF-MS: m/z 5819.1 (calcd [M–
(H+PF$_6$¯)]$^+$ = 5819.6), 5838.0 (calcd. [H+M–2PF$_6$¯])$^+$ = 5837.8), 1843.7 (calcd. 

[(5)$_2$Ru$_4$(10)$_2$][PF$_6$]$_8$ (12) A mixture of adduct 11 (40 mg, 0.06 mmol), 
bisterpyridine 5 (90 mg, 56 μmole) and drops of N-ethylmorpholine in 
EtOH:CHCl$_3$ (1:2) (600 mL) was stirred at 60 °C for 48h. The mixture was 
filtered (Celite), solvent was evaporated in vacuo and crude product was column 
chromatographed (SiO$_2$) eluting with H$_2$O: KNO$_3$:MeCN, 1:1:20 to afford (30%) 
12 as a dark red powder (50 mg) the counter ion was exchanged (NO$_3$¯ to PF$_6$¯):
mp > 350 °C; $^1$H NMR (500 MHz, CDCl$_3$) δ 8.94 (s, 4H, PyH^{3,5'}), 8.76 (s, 4H, 
PyH^{3,5'}) 8.55 (d, 4H, J = 7 Hz, PyH^{3,5'}), 8.36 (d, 4H, J = 7 Hz, PyH^{3,3'}), 8.16 (s, 
4H, PeryH), 8.08 (d, 4H, J = 7 Hz, ArH), 7.71 (m, 8H, ArH, PyH^{4,4'}), 7.67 (d, 2H, 
J = 7 Hz, ArH), 7.4-7.37 (m, 4H, PyH^{6,6'}), 7.16 (m, 4H, PyH^{5,5'}), 7.67 (d, 2H, J = 
9 Hz, ArH), 6.97 (d, 8H, J = 8 Hz, ArH), 1.30 (s, 36 H, CH$_3$); MALDI-TOF-MS 
:m/z = 5806.9 (calcd [2H+M-PF$_6$¯]$^+$=5806.9).
CHAPTER VI
SUMMARY

A series of metallodendrimers 9-11 as well as their corresponding ligands has been designed and synthesized. These materials integrate perylene, as a functional core, with \(<\text{tpyRu}^{II}\text{tpy}>\) termini; both chromophores are known for their photovoltaic properties. The products were fully characterized using a combination of \(^1\text{H NMR, COSY, }^1\text{C NMR spectroscopy, and MS.}\) Their photophysical properties revealed a broad absorption spectrum with enhanced molar absorption coefficients corresponding to the increase of \(<\text{tpyRu}^{II}\text{tpy}>\) units, suggesting their potential candidates for light harvesting.

Four perylene-based terpyridine-Ru(II) complexes were synthesized using a multistep procedure. These metallo-complexes were then structurally characterized, and their electrochemical and photoelectrochemical properties were studied. These materials were then used for the fabrication of dye-sensitized solar cells. The photovoltaic properties of these DSSCs were investigated.

Novel amino \([2,2':6',2'']-\text{bisterpyridine}\) was synthesized and reacted with perylene to afford a shape-persistent perylene-containing \(\text{bisterpyridine}\) ligand. In addition, aminopropyl\(\text{bisterpyridine}\) was decorated into the imide position of perylene ligand. These ligands were then self-assembled using Zn(II) to afford strong emissive metallomacrocycles. The structures of these compounds were
identified using mass spectroscopy, DOSY NMR spectroscopy and was visualized with molecular modeling.

Finally synthesis of novel extended tpy-containing perylene was established \textit{via} a Suzuki coupling reaction. In addition, the Ru\textsuperscript{II}-containing cyclic trimer and heteroleptic tetramers were also achieved. These materials were structurally and optically characterized, their molecular modeling simulation revealed nano-diminsional metallocycles.
CHAPTER VII

CONCLUSION

The ultimate goal of this dissertation was to design and construct supramolecular dye arrays that mimic natural photosynthetic light harvesting systems along with testing their photophysical properties and their applications in solar devices.

Diverse Ru$^{II}$-based supramolecular architectures including dyes, metallodendrimers and metallomacrocycles have been constructed. In addition, the formation of photoluminescent Zn$^{II}$-containing macrocycles was also reported. All these materials were either applied or showed desirable properties for potential applications in solar energy collectors, light emitting devices or fluorescent markers.

The design and synthesis of terpyridine functionalized bay- and imide-perylenes along with their corresponding tpyRu$^{II}$tpy metallodyes were described. Solar devices, based on these dyes, were fabricated and their photovoltaic properties were studied. Future research on improving the efficiency of these devices requires the control of dye molecules arrangement with respect to TiO$_2$, which can be established via adding carboxylic groups to tether the dyes to TiO$_2$.

In order to maximize the photophysical properties of dye molecules; metallodendritic dye molecules containing two, four and six tpyRu$^{II}$tpy sensitizers
were designed and synthesized, their structures were studied and their light absorption and emission behavior were demonstrated. It was shown that the hexakis-complex possesses the strongest light absorbing properties among these dendrimers.

Multichromophore cyclic dye arrays were formed via tpyRu\textsuperscript{II}tpy assembly of perylene dyes. The chemical structures were elucidated and the photophysical properties showed enhancement of the light harvesting properties. Molecular modeling revealed that these cyclic architectures contain voids that are accessible to guest molecules. Future research can be made to fabricate inclusion complexes with potential for hierarchical self-assembly to fabricate semiconducting nanofibers for potential application in field effect transistors.

Cyclic fluorescent nanomaterials were also synthesized; these materials can be implemented to make red-emitting LEDs. In addition, it is possible to integrate other luminescent dyes via Ir\textsuperscript{III}-mediated assembly for the potential application in the highly desirable white LEDs. The functionalization of these materials with antibodies can extend the application of these materials to the field of targeted cancer imaging.
REFERENCES


APPENDIX

SUPPORTING NMR SPECTRA
$^1$H NMR and $^{13}$C NMR spectra of 1.
$^1$H NMR and $^{13}$C NMR spectra of 3.
$^1$H NMR and $^{13}$C NMR spectra of 5.
$^1$H NMR and $^{13}$C NMR spectra of 6.
$^1$H NMR and $^{13}$C NMR spectra of 10.
$^1$H NMR and $^{13}$C NMR spectra of 1.1.
$^1$H NMR, $^{13}$C NMR, and COSY spectra of 12.
$^1$H NMR and $^{13}$C NMR spectra of 13.
$^1$H NMR, COSY and $^{13}$C NMR spectra of 14.
$^1$H NMR, COSY and $^{13}$C NMR spectra of 15.
$^1$H NMR, COSY and $^{13}$C NMR spectra of 16.
\(^1\)H NMR and \(^{13}\)C NMR spectra of 3
$^{1}$H NMR and $^{13}$C NMR spectra of 5
$^1$H NMR, $^{13}$C NMR, COSY, and ESI-MS spectra of 8
$^1$H NMR, $^{13}$C NMR, COSY, and ESI-MS spectra of 9
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[M-PF₆]⁺
$^{1}$H NMR, $^{13}$C NMR, and COSY spectra of 12
$^1$H NMR, $^{13}$C NMR, COSY, and ESI-MS spectra of 13
$^1\text{H}$ NMR, $^{13}\text{C}$ NMR and COSY spectra of 4
$^1$H NMR, $^{13}$C NMR, COSY and MALDI MS spectra of 6
$^1$H NMR, $^{13}$C NMR and MALDI MS spectra of 7
$^1$H NMR, $^{13}$C NMR and COSY spectra of 10
$^1$H NMR, $^{13}$C NMR and MALDI MS. of 11.
$^1$H NMR and ESI MS spectra of 13.

Theoretical Values

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$^1$H NMR and DOSY spectra of 14.
$^1$H NMR spectrum of 7.
$^1$H NMR spectrum of 9.

$^1$H NMR spectrum of 12.