

SYNTHESIS AND PHOTOPHYSICAL STUDIES OF PORPHYRIN ARRAYS

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Specially dedicated to:
My Grandma (1927-2001) and Ah Ma (1935-2016) who are always being missed
by us
&
My beloved Parents and Family

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ABSTRACT

Discovering porphyrin compounds capable of harvesting the light had enhanced the research to mimic the energy and electron transfer process in the artificial photosynthetic systems that can be applied in the development of optoelectronic devices. The well-organized porphyrin arrays as electron transfer centers with attached chromophores are important to ensure the ability of controlled energy and electron flow in the porphyrin building blocks which in turn become great challenges. In this study, newly reported porphyrins with appended fluorenone as the light harvesting antennas were synthesized through Adler Longo and Lindsey's condensation reactions, and further being assembled into porphyrin dimer, trimer and pentamer arrays *via* copper-free Sonogashira coupling reaction. Subsequently, the bathochromic shifts in absorption and emission spectra of fluorenone based porphyrins were compared to the reference porphyrin. Afterwards, metallo-porphyrin system with a zinc(II) ion was introduced to influence the electron donating-withdrawing properties by observing the emission population of free base porphyrin. The effect of naphthalene diimide (NDI) in the porphyrin trimer system was also investigated in order to increase the electron push-pull effect and π electron conjugation which caused the quenching of fluorescence quantum yields in more polar solvents. Diphenylacetylene linkage had been used to ensure the overlapping of π electrons between the host porphyrins and promoting the energy transfer in the porphyrin arrays. The roles of the linkages were investigated through comparison of the luminescence spectra of covalent and non-covalently linked compounds. Towards this end, a novel synthetic strategy for alkenyl type porphyrins was developed by using the Tebbe and Petasis reagents, which paved a way to prepare conjugated porphyrins such as vinyl linked porphyrin dimer and *bis*-fluorenylidene porphyrins. These porphyrin compounds were characterized using ^1H and ^{13}C NMR, FTIR, UV-VIS and MALDI-TOF for the structural confirmation. Luminescence properties and fluorescence quantum yields of the targeted compounds were compared with their non-fluorenone and fluorenone porphyrin references. The energy transfer of appended fluorenone into porphyrin system was confirmed by the fluorescence measurement. It was also found that the quantum yields of the porphyrin and NDI building blocks were quenched proposing that electron charge transfer processes occurred in the systems. Overall, a series of porphyrins with appended fluorenone, and the porphyrin dimers, trimers, pentamer and porphyrin-NDI systems newly reported herein were successfully synthesized. The obtained photophysical properties indicated their potential application as materials for photonic devices.

ABSTRAK

Menemukan sebatian porfirin yang mampu menuai cahaya telah meningkatkan penyelidikan untuk memimik proses pemindahan tenaga dan elektron dalam sistem fotosintetik buatan yang boleh diaplikasikan dalam pembangunan peranti optoelektronik. Tatasusunan porfirin yang bertertib rapi sebagai pusat pemindahan elektron dengan kehadiran kromofor adalah penting untuk memastikan keupayaan aliran tenaga dan elektron terkawal dalam blok binaan porfirin yang seterusnya menjadi suatu cabaran yang besar. Dalam kajian ini, porfirin baharu dengan tambahan fluorenon sebagai antena penuaian cahaya yang disintesis menggunakan tindak balas kondensasi Adler Longo dan Lindsey, dan selanjutnya disusun untuk membentuk tatasusunan porfirin dimer, trimer dan pentamer melalui tindak balas gandingan Sonogashira bebas kuprum. Kemudiannya, anjakan batokrom dalam spektrum serapan dan pancaran untuk porfirin berasaskan fluorenon telah dibandingkan dengan porfirin rujukan. Selepas itu, sistem metalo-porfirin dengan ion zink(II) telah diperkenalkan untuk mempengaruhi sifat pendermaan-penarikan elektron dengan mencerpakan populasi pancaran porfirin bebas logam. Kesan naftalena diimida (NDI) dalam sistem porfirin trimer turut dikaji untuk meningkatkan kesan tolak-tarik elektron dan konjugasi elektron π yang menyebabkan pelindapan hasil kuantum pendarfluor dalam pelarut lebih berkutub. Penghubung difenilasetilina telah digunakan untuk memastikan pertindihan elektron π berlaku di antara porfirin perumah dan meningkatkan pemindahan tenaga dalam tatasusunan porfirin. Peranan penghubung telah dikaji dengan membandingkan spektrum pendarcahaya sebatian terikat kovalen dengan bukan kovalen. Sehubungan itu, strategi sintesis baharu telah dibangunkan untuk porfirin jenis alkenil dengan menggunakan reagen Tebbe dan Petasis, yang merintis laluan kepada penyediaan porfirin berkonjugat seperti porfirin dimer terhubung vinil dan porfirin *bis*-fluorenilidena. Sebatian porfirin ini telah dicirikan menggunakan ^1H dan ^{13}C NMR, FTIR, UV-VIS dan MALDI-TOF untuk pengesahan struktur. Sifat pendarcahaya dan hasil kuantum pendarfluor sebatian sasaran telah dibandingkan dengan porfirin rujukan fluorenon dan bukan fluorenon. Pemindahan tenaga dari tambahan fluorenon ke sistem porfirin telah disahkan melalui pengukuran pendarfluor. Didapati juga bahawa hasil kuantum sistem blok porfirin dan NDI telah dilindapkan yang mencadangkan pemindahan cas elektron telah berlaku dalam sistem. Keseluruhannya, satu siri sebatian porfirin dengan tambahan fluorenon, dan porfirin dimer, trimer, pentamer serta sistem porfirin-NDI baharu yang dilaporkan di sini telah berjaya disintesis. Sifat fotofisikal yang diperoleh menunjukkan potensi penggunaannya sebagai bahan untuk peranti fotonik.

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LIST OF ABBREVIATIONS

ACN	-	Acetonitrile
AMD	-	Age-related Macular Degeneration
Ar	-	Aromatic
BOC	-	Butyloxycarbonyl
BODIPY	-	Boron Dipyrromethene
br	-	Broad
BSN	-	1,1'-dicyano-substituted <i>bis</i> -styrylnaphthalene
COSY	-	Correlation Spectroscopy
d	-	Doublet
D-B-A	-	Donor to Bridge to Acceptor
DCM	-	Dichloromethane
dd	-	Doublet of Doublet
DDQ	-	2,3-dichloro-5,6-dicyano-1,4-benzoquinone
DMF	-	Dimethylformamide
EA	-	Ethylacetate
EET	-	Electronic Energy Transfer
Et	-	Ethyl
<i>et al.</i>	-	et alia (and others)
FRET	-	Förster Resonance Energy Transfer
FTIR	-	Fourier Transform Infrared
g	-	gram
HOMO-LUMO	-	Highest Occupied Molecular Orbital-Lowest Unoccupied Molecular orbital
hr	-	Hour
MALDI-TOF	-	Matrix Assisted Laser Desorption Ionisation-Time of Flight

MeOH	-	Methanol
MHz	-	Megahertz
NBS	-	<i>N</i> -bromosuccinimide
IR	-	Infrared
Hz	-	Hertz
m	-	Multiplet
M	-	Molarity
Me	-	Methyl
mL	-	Milliliter
mmol	-	Milimole
mp	-	Melting Point
nm	-	Nanometer
NMR	-	Nuclear Magnetic Resonance
NDI	-	Naphthalene diimide
NiTPP	-	[5,10,15,20-tetraphenylporphyrinato]nickel (II)
NPAFN	-	<i>bis</i> (4-(<i>N</i> -(1-naphthyl)phenylamino)phenyl) fumaronitrile
OLED	-	Organic Light Emitting Diode
PDT	-	Photodynamic Therapy
PET	-	Photoinduced electron Transfer
Ph	-	Phenyl
ppm	-	Part per Million
PRC	-	Photosynthetic Reaction Centre
PS	-	Photosensitizer
q	-	Quartet
R _f	-	Retention Factor
ROS	-	Reactive Oxygen Species
s	-	Singlet
S _N Ar	-	Aromatic Nucleophilic Substitution
S _n	-	Singlet, n= number of vibrionic state
t	-	triplet
T3TB	-	triphenylamine - functionalized dithienylbenzothiadiazoles

TBAF	-	Tetra- <i>n</i> -butylammonium fluoride
TEA	-	Triethylamine
TFA	-	Trifluoro Acetic Acid
THF	-	Tetrahydrofuran
TLC	-	Thin Layer Chromatography
TMEDA	-	Tetramethylethylenediamine
TMS	-	Trimethylsilyl
TPP	-	5,10,15,20-tetraphenylporphyrin
TFP	-	5,10,15,20-tetra(flouren-2-yl)porphyrin
TFOP	-	5,10,15,20-tetra(flouren-2-one)porphyrin
TPA	-	Two Photon Absorption
UV-Vis	-	Ultra violet- visible
v/v	-	Volume/Volume
ZnTFOP	-	[5,10,15,20-tetrafluorenoneporphyrinato]zinc (II)
ZnTPP	-	[5,10,15,20-tetraphenylporphyrinato]zinc (II)

LIST OF SYMBOLS

ϵ	-	Molar Absorptivity
α	-	<i>alpha</i>
β	-	<i>beta</i>
$^{\circ}\text{C}$	-	Degree Celsius
δ	-	Delta
μL	-	Microliter
p	-	<i>para</i>
Φ	-	Quantum Yield
ν	-	Wavenumber
η_{std}	-	refractive index of solvent of standard compound
η_S	-	refractive index of solvent of sample
A_{std}	-	Absorbance of standard compound
A_S	-	Absorbance of sample
F_{std}	-	integrated fluorescence intensity of standard compound
F_S	-	integrated fluorescence intensity of sample
λ_{abs}	-	Absorption wavelength
λ_{em}	-	Emission wavelength
λ_{Ex}	-	Excitation wavelength
λ_{max}	-	Maximum wavelength

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Natural occurring photosynthetic system proposed by chlorophylls has inspired the design of various synthetic light harvesting materials for photonic devices based on electron or energy transfer in the light absorbing components. When chlorophylls absorb sun light energy, the exciton is generated and transfer into adjacent molecules lead to oxidation reaction (loss of electron) and reduction reaction (gain electron). The process where the electrons in chlorophylls gained light energy and excited to higher excitation states is called photoexcitation process. To one extend, the electrons gained enough energy and freed to the adjacent molecules which plays the role as electron acceptor. The molecule which lost electrons turned into positively charged ions will further accept electrons from other molecules such as water or oxygen and the process happened continually during the photosynthesis process (Huennekens and Calvin, 1949). The photosynthetic system not only involves light energy transferring process but also includes the electron charge transfer due to redox reaction. Thus, a good mimicked photosynthetic system should be able to harvest energy from sunlight associate with electron donor and acceptor units to assist energy, electron as well as charge transfer. Among the explored artificial photosynthetic systems, porphin (**1**) (Rothemund, 1936; Krol, 1959), was proposed to have the highest similarity to chlorophyll's basic structure other than its parental chlorin (**2**) (**Figure 1.1**)

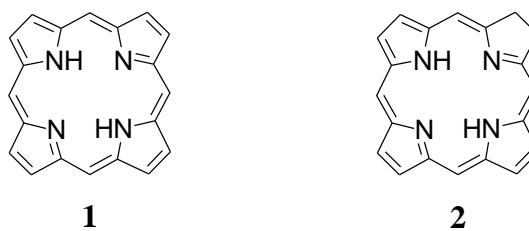


Figure 1.1: Structures of porphin (**1**) and chlorin (**2**)

There are several natural conjugated pigment complexes such as porphyrin, carotenoids, bilins and heme. Conjugated porphyrins have been frequently employed as the light-absorbing and energy transfer components due to its strong and unique absorptions in ultraviolet to visible (UV-VIS) region as well as the fluorescence emission at near infra-red (NIR) region. Porphyrin contains π -electron conjugated macrocyclic ring with available *meso*- and β - free sides to be attached with other fluorescent pigments, makes it an extraordinary material in the luminescent device research (Wang *et al.*, 2011; Shino and Jean, 2009) as the red light emitting materials. Substitution of functional groups or electron donor and acceptor molecules to the porphyrin may alter the photophysical properties of the porphyrin (Victoria Martí'nez-Dí'az *et al.*, 2010; Turro, 1991). In this research, we are concerning with the electronic transitions in ultraviolet, visible and near infrared regions in extended π -conjugating photoluminescence organic compounds to improve the light energy harvesting and energy transmission efficiency. An efficient artificial photosynthetic system must contain the following criteria: (i) posted good light harvesting properties (ii) consists electron hole system and (iii) able to transfer electrons (Grimm *et al.*, 1999).

Luminescence of organic compounds is basically based on the π electron delocalization in the molecular structure. These organic molecules can be classified into: (i) aromatic hydrocarbons—anthracene, pyrene, naphthalene, stilbene (ii) five and six membered heterocyclic compounds—carbazole, pyrazoline (iii) compounds with carbonyl groups—coumarins, naphthalimides and (iv) organic ligands formed with metals (Tsutsui and Adachi, 2006). Organic materials which consist any of the photoluminescence properties mentioned above are capable to be developed into photonic devices. Moreover the luminescence of organic compounds is determined

by the π -electron systems and hence the luminescence properties remained or similar in solid state, amorphous aggregation or even in vapour phase. The luminescence resulted by energy emission from excited singlet states to ground state is called fluorescence while the energy transmitted to triplet excited states and emitted as phosphorescence energy. These luminescence energies were produced by employing different kinds of excitation methods and named as photoluminescence, electroluminescence and chemiluminescence (Tsutsui and Adachi, 2006).

Electronic energy transfer (EET) or Förster resonance energy transfer (FRET) mechanism was implied in the explanation of energy donor-acceptor system associated in photosynthetic system. The excited donor usually generates exciton and interacts coulombically to an acceptor either through bond or space. The general requirements for excitation energy transfer between a donor and an acceptor are: (i) the energy of donor excited state should be higher than that of acceptor excited state and (ii) the rate of energy transfer should be more rapid than the decay rate of the donor excited state (Ayyappanpillai *et al.*, 2008). In this study, the donor-acceptor systems were introduced based on extended conjugation of porphyrins *via* diphenylacetylene linkers to generate promising energy transfer efficiency within the porphyrinic oligomers. Covalently *sp meso-meso* linked porphyrin conjugated systems were reported as the essential π -overlapping connections for more effective electron and energy transmission (Ambrose *et al.*, 2000; Yu and Lindsey, 2001). The light harvesting fluorenone pendants also acted as the energy donating groups transferred the energy towards porphyrins and methoxy or methylbenzoate porphyrin acceptors through the diphenylacetylene bonds.

Other than EET and FRET, photoinduced electron transfer (PET) is also being studied for photoluminescence organic compounds especially supramolecular structures. PET usually involves oxidative and reductive electron transfer from electron donor and acceptor to generate electron-hole and form charge separation and recombination in the electronic excited states. In simple words, energy transferred from singlet to triplet excited states which involved charge separation and recombination (Harvey, 2003a) is categorized as PET. Other than detecting the redox reactions in the molecules, observation of large fluorescence quenching usually

indicates the occurrence of PET as well. High electron affinity naphthalene diimide (NDI) compound which is also redox active has been widely studied in supramolecular chemistry (Sessler *et al.*, 1998; Wallin *et al.*, 2010; Robotham *et al.*, 2013; Villamaina *et al.*, 2013). The bulk delocalization electrons presence in NDI making it a good electron acceptor when binds to another electron donor. The extraordinary optoelectronic properties of NDI have very much contribution to the molecular energy and electron charge transferring systems.

1.2 Problem Statement

Shorter wavelength blue and green light emitting materials for the usage of OLED have been well developed. Most of the blue light emitting materials were giving bright and pure colour although the fluorescent lifetime and stabilities were less efficient. In contrast, the usage of red fluorescent emitting materials in OLED were still limited due to the difficulties to compromise between colour purity and efficiency of device. The light emitting materials were generally categorized in two forms, host emitter which emits light itself without doping process and dopant that incorporated onto host such as *tris*(8-hydroxyquinolinato)aluminium (Alq₃) (**3**) (Chen, 2004). One of the most vital host emitting non-doped red fluorescent materials was the donor-acceptor incorporated conjugated compounds such as D-CN (**4**) (Kim *et al.*, 2001) BSN (**5**) (Hung and Chen, 2002), NPAFN (**6**) (Yeh *et al.*, 2003) and T3TB (**7**) (Thangthong *et al.*, 2015) as shown in **Figure 1.2**. These red fluorophores were reported to offer better red light emitting characteristics due to the intensified charge-transfer efficiency as the results of the existence of electron donor-acceptor groups. However, the drawback of this kind of red fluorophores is that usually they have high polarity and accessible to aggregation in solid state due to dipole-dipole interactions. As the results, the performance of non-doped red emitters still falls below the host incorporated red emitters and the non-doped red fluorescent materials were still remained shortage.

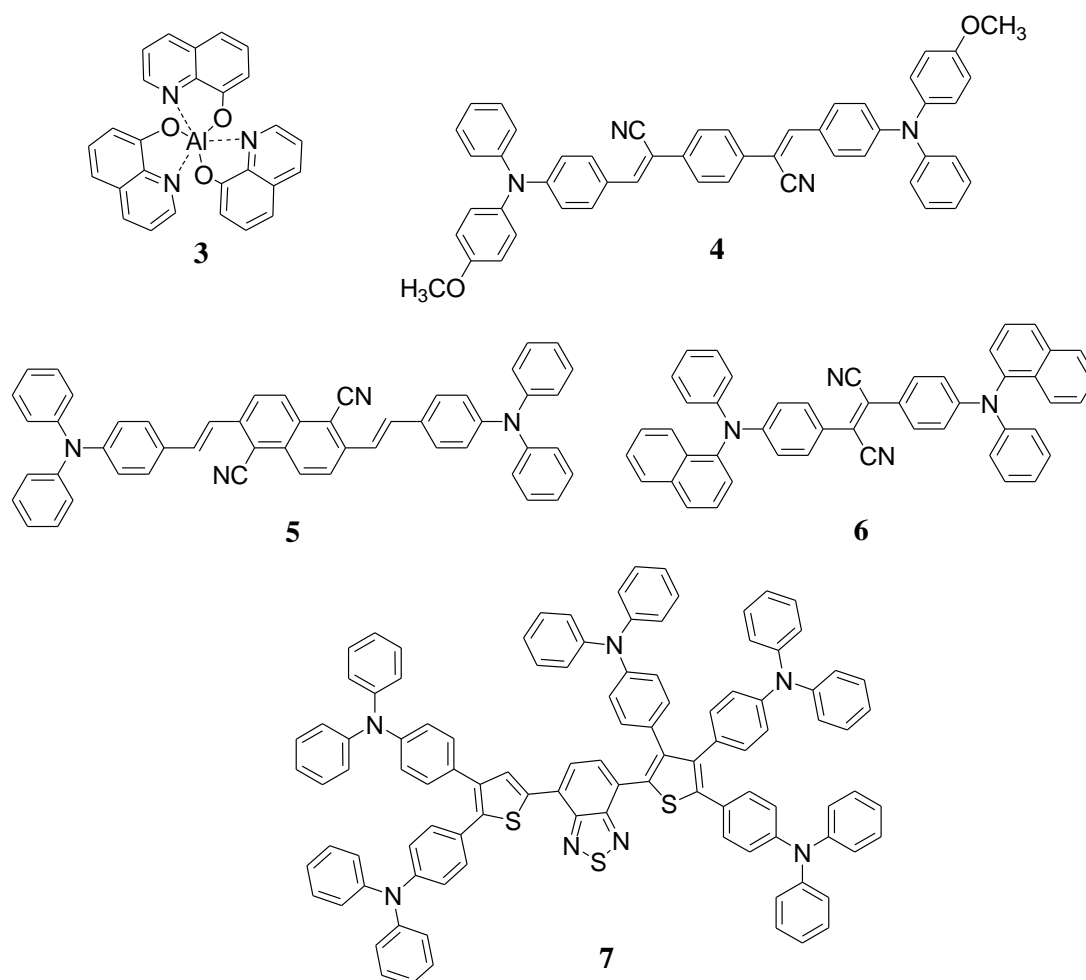


Figure 1.2: *tris*(8-Hydroxyquinolinato)aluminium (Alq₃) (**3**) and non-doped red fluorescent materials (**4-7**)

Porphyrin compounds such as 5,10,15,20-tetraphenylporphyrin (TPP, **8**) and 5,15-[2,5-*bis*(*tert*butyl)diphenyl]porphyrin (**9**) were often used as the red light emitting dopant in the OLEDs (Chen, 2004; Xu *et al.*, 2014). The nature of porphyrinic fluorescent materials showed highly emissive tendency in solution but tend to weakly or non-emissive in solid states due to aggregation or intermolecular π -stacking. As the urge to change the current situation, some porphyrin based non-doped red light emitting materials had been developed. The introduction of fluorene (TFP) and fluorenone (TFOP) red chromophoric porphyrin monomers were approaching stronger fluorescence than TPP became potential candidates as red light emitting materials (**Figure 1.4**) (Christine and Simonneaux, 2006). The dendritic fluorene porphyrin was previously prepared to achieve higher luminescence outcome

by substituting more fluorene based chromophores but failed to present higher fluorescence quantum yield than its monomer (Samuel and Christine, 2009). Although the star branched polymeric compounds may propose larger harvesting potential, the steric hindrance of large molecules may cause star burst effect which failed to attach more antennas on the host. Therefore, different porphyrin arrays are need to be investigated.

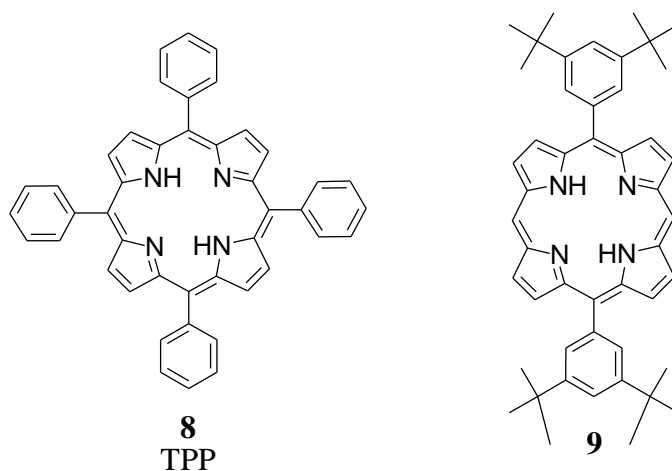


Figure 1.3: Porphyrinic red light dopant in OLED

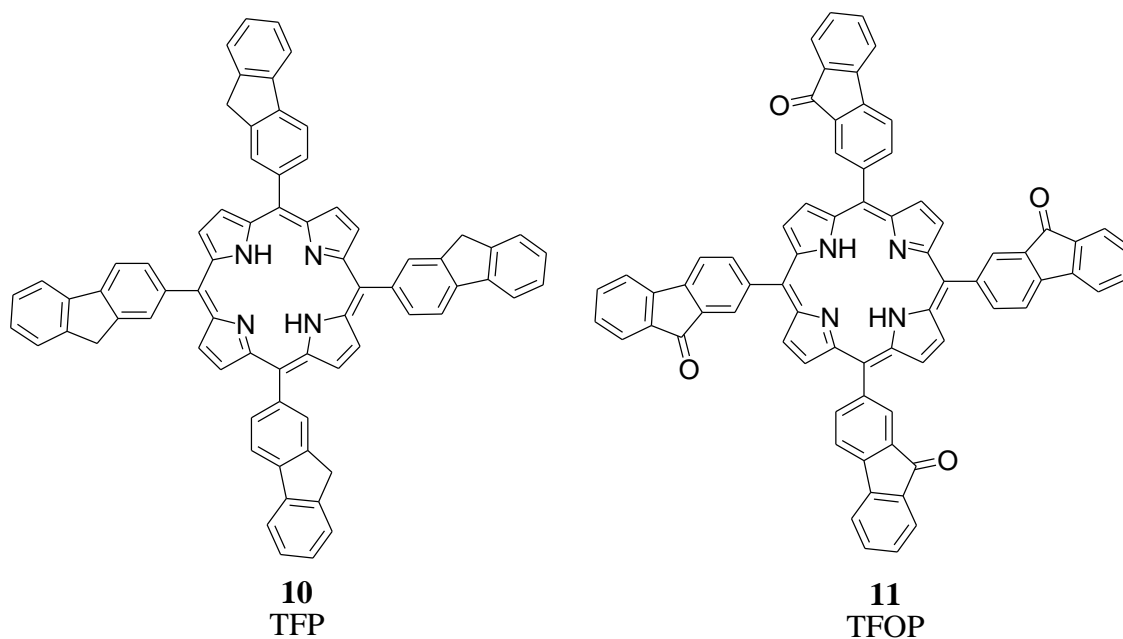


Figure 1.4: Structure of TFP (10) and TFOP (11)

To explore further on π -conjugating extended light harvesting arrays, new synthetic pathway to generate connections between π -electrons rich porphyrins including sp and sp^2 orbitals overlapping linkages are of interests. Other than $C\equiv C$ bond, unsaturated alkenyl bond also plays similar role to the π -electron rich porphyrins. Hence exploration of new methods to prepare ethenyl anchoring porphyrins as well as alkenyl linked extended conjugated porphyrins is important. Thus far, titanium based reagents have been used on small organic molecule reactions with good yields, but not much application on porphyrinic compounds has been reported. As a result, titanium based methylenation and alkenylation reagents were selected to be applied directly on formyl porphyrins to investigate its reactivity towards π -electron rich porphyrins as the potential new pathway of porphyrin functionalization.

1.3 Significance of Study

Due to the limitations and non-flexibility of red light emitting materials, exploration of non-doped red fluorescent materials had become demanding. To enhance the performance of porphyrin as the red light emitters, fluorenone was chosen as the fluorophore enhancer which encouraged by the studies of extended fluorenyl-porphyrin conjugating systems and also initial study of fluorenone porphyrins. The extended π -conjugating porphyrin monomers were expected to gain higher fluorescence outcomes which also promoted the red light saturation and purity. Furthermore the limitation due to the rigidity of molecular structure for dendritic fluorenyl-porphyrins had also inspired the idea of generating linearly linked conjugating porphyrin systems. The covalently linked conjugating porphyrin oligomers were expected to alter the spectral coverage across visible to near infrared region. With longer emission wavelength, the colour purity could be achieved by the novel fluorenone based porphyrin oligomers as the red fluorescent materials. Considering the nature of photosynthesis system proposed by Mg-chlorophylls, metalation such as Zn, Ni, Cu became vital in terms of luminescence studies. Nevertheless, introduction of metalated porphyrins to the extended conjugation light harvesting arrays also promotes the rigidity and planarity of porphyrins. Besides, the

energy gradient generated between the metalated porphyrin and free base unit assisted in directing the energy flow from donor groups to the acceptors.

The development of our design porphyrin oligomers was extended to the syntheses of porphyrin-NDI systems and study of their photophysical properties. Electron deficient NDI substituted in between two porphyrin hosts to act as an electron acceptor was anticipated to promote efficient electron-charge transfer. Among the porphyrin-NDI compounds being developed, most of the binding linkages were formed at the diimide nitrogen group of NDI and their triplet states transition was very much concerned. A few core-substituted porphyrin-NDI compounds were being studied recently as a result of successfully obtaining brominated NDI acted as the convenient binding sites. At this current stage, no acetylene linked core-substituted porphyrin-NDI dimer and trimer has been synthesized and being applied as the red light emitting materials. The carbon-carbon *sp* hybridization bonds between porphyrin and NDI allowed overlapping π -electron directly into the aromatic system provided more efficient electronic energy transfer (EET) than carbon-nitrogen bond.

In this research, the porphyrin based compounds were investigated as the organic red light emitting materials. The conjugated fluorenone based porphyrin oligomers and porphyrin-NDI compounds together with the porphyrin monomers and other related intermediates were synthesized and used to improve the red light intensity, fluorescence quantum yield efficiency and energy transfer. Moreover, alkenyl and methenyl functionalization methods using titanium based reagents which were rarely reported to porphyrins were carried out to explore different conjugated porphyrin arrays. The overall significant of this research would be:

- i. Molecular designation to promote energy flow efficiency by implementing light harvesting energy donors, π -electron rich linkages, adjacent and central porphyrin or NDI energy acceptors.
- ii. Extending the π -conjugating system of porphyrin by connecting porphyrin units with *sp* covalent bonds to form porphyrin oligomers which will absorb at longer absorption wavelength to increase the light intensity and reduce the excitation energy.

- iii. Creating energy gradient and promote structural rigidity as well as planarity by introducing zinc (II) into the porphyrin macrocyclic rings.
- iv. Introducing the red light chromophores: fluorenone pendants peripheral to the porphyrins and acted as the energy donors at the same time.
- v. Implementing strong electron withdrawing NDI as the electron accepting groups.
- vi. Promoting the energy transfer from the fluorenone into porphyrin hosts as well as from one fluorenone porphyrin to another.
- vii. Improving the fluorescence quantum yield efficiency by employing extended fluorenone based porphyrins.
- viii. Developing new synthetic pathway to generate extended π -conjugating porphyrin arrays with new electron acceptor system to be explored as organic photonic device materials.

1.4 Objectives of Research

This research embarks on the following objectives:

- i. To develop the synthetic methods in constructing the conjugated porphyrin model based on different donor-acceptor orientation and structural conformation.
- ii. To study the fundamental luminescence effect of the appended substituents such as fluorenone and ethynyl groups to the porphyrin monomers as well as all synthesized porphyrin oligomers and compare to their parental references.
- iii. To prepare linearly linked fluorenone based porphyrin dimers, trimers, pentamer and porphyrin-NDI energy, electron donating and accepting systems.
- iv. To generate intramolecular energy gradient by substituting different functional groups to the energy acceptors and by introducing zinc (II) metals to the porphyrin donors.
- v. To investigate the reactivity of titanium based reagents to the fluorenone and formylporphyrin compounds and further synthesize extended π -conjugating

porphyrin arrays using titanium based methylation and alkenylation reagents

1.5 Scope of Study

This research is aim to study the potential porphyrin based materials to be applied as non-doped red fluorescent host emitters. The synthesized porphyrin arrays were expected to be used as red light emitting materials with satisfaction on light harvesting, energy transferring, lower HOMO-LUMO energy gaps and electron donating-accepting properties. Initially, the fluorenyl and fluorenone based porphyrins with effective binding sites such as ethynyl and brominated groups were synthesized. The fundamental absorption and emission properties were studied and compared to determine appropriate energy donating and accepting groups. Fluorenone pendant arms which absorbed energy at shorter wavelength than porphyrin and other functional groups were chosen as the energy and electron donating groups. The ethynyl anchoring fluorenone based porphyrin monomers also proposed red shifted absorption wavelength which indicated lower HOMO-LUMO band gaps and excitation energy. The positive results of luminescence studies had encouraged the further exploration of extended conjugating porphyrin arrays.

The idea of designing light harvesting porphyrin arrays in linear form was inspired by previous reported literatures. To overcome the structural steric hindrance and “star burst” effect of dendritic porphyrin arrays, linearly linked fluorenone appended porphyrin dimers, trimers, pentamer together with porphyrin-NDI compounds which were covalently linked by diphenylacetylene bridges were prepared through Lindsey optimized copper free Sonogashira coupling reactions. Extended conjugation arrays by substituting more than one porphyrin units were anticipated to offer red shifted absorption and emission bands which also indicated more saturation red fluorescence with lower excitation energy. Additionally, the roles of energy or electron donor and acceptor were determined through the luminescence studies. Zinc (II) metalation was introduced to the porphyrin donors within the extended π -conjugating system that had altered the luminescence

properties of the respective compounds. Zinc (II) metal was chosen to be inserted into the porphyrin macrocyclic ring due to its appropriate cation size as compared to larger Ni(II), Cu(II) cations as well as the convenience and milder Zn(II) metal insertion method. Furthermore, the metalated compounds allowed the observation of changing in fluorescence emission as compared to the free base porphyrin arrays. The energy transfer efficiency was determined by fluorescence spectra upon excitation at different absorption wavelengths in same concentration, excitation on porphyrin oligomers and their non-covalently linked monomer references and fluorescence studies on emission in different solvent polarities. Besides, the fluorescence quantum yield efficiency of the extended conjugated compounds was studied.

Moreover, new synthetic methods to produce vinyl and ethenyl linked porphyrins have been explored using titanium based reagent. Tebbe and Petasis reagents were applied to the formylporphyrins to prepare vinyl porphyrin and ethenyl linked dimeric porphyrin. Another optimized low valent titanium reagent was employed on formylporphyrins as well as fluorenone porphyrin (McMurry reaction) to form extended π -conjugating porphyrin arrays. The research is the first stage involved proof-of-concept to develop and improve the efficiency of non-doped red light emitting materials in terms of light intensity, fluorescence intensity and energy transfer efficiency which towards the end useful for OLED application.

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