

Synthesis and Emission Properties of meso-Substituted Porphyrins

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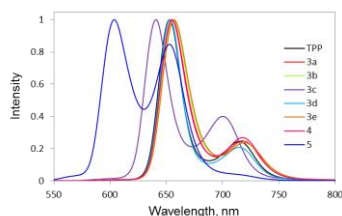
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Graphical abstract



Abstract

Discovering of various organic dyes including porphyrins have attracted considerable attention to mimic the energy and electron transfer process for the artificial photosynthetic model systems which can be applied in developing optoelectronic devices. The accessibility on tailoring porphyrin properties makes them a good candidate to be developed as the red light emitting materials for these applications. Thus, symmetrical and unsymmetrical molecular models of porphyrins with appended fluorenyl components and extended π electrons conjugated system were synthesized towards increasing the efficiency of energy and electron transfer. In the photophysical studies, the emission spectra proposed the evidence of energy transfer of appended fluorenyl arms into the porphyrin macrocyclic, whereas the extension of conjugating system in porphyrins exhibits lower absorption energy and intensified the red fluorescent properties.

Keywords: Porphyrins; fluorenyl; energy and electron transfer; conjugating system

Abstrak

Penemuan pelbagai bahan pewarna termasuk porfirina telah menarik minat untuk menggunakannya dalam meniru sifat semulajadi pemindahan tenaga dan elektron bagi membangunkan sistem fotosintetik buatan, di mana ianya boleh diaplikasi untuk penghasilan peranti optoelektronik. Porfirina sesuai digunakan, sebagai contohnya sebagai bahan pemancar cahaya merah dalam aplikasi tersebut berikutan kemudahan untuk mengubahsui strukturnya bagi mendapatkan sifat fotofizik tertentu. Bagi tujuan meningkatkan keberkesanan pemindahan tenaga dan elektron, porfirina simetri dan tak simetri berasaskan kumpulan fluorenil serta porfirina yang mempunyai sistem berkonjugasi elektron π dipanjangkan telah disintesis. Dalam kajian fotofizik terhadap bahan yang disintesis, spektra pemancaran membuktikan berlakunya pemindahan tenaga daripada kumpulan fluorenil kepada sistem makrosiklik porfirina, manakala pemanjangan sistem konjugasi porfirina memberikan tenaga serapan yang rendah dan meningkatkan sifat pendarfluor merah bahan tersebut.

Kata kunci: Porfirina; fluorenil; pemindahan tenaga dan electron; sistem konjugasi

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1.0 INTRODUCTION

Synthetic porphyrins¹⁻⁴ are a unique class of compounds that are ubiquitous and function in a wide variety of roles ranging from oxygen transport,⁵ electron transfer⁶ and oxidation catalysts to photosynthesis.^{7,8} The luminescence properties of porphyrin have been investigated to be used as light emitting materials for photonic devices such as organic light emitting diodes (OLEDs) based on electron or energy transfer in its rich π -electron conjugating system.^{9,10} For example some fabricated red OLED devices were reported able to generate saturated red emission from triplet excited state (phosphorescence) but no emission from excited singlet state (fluorescence).^{11,12} Although phosphorescence efficiency is encouraging the increase in quantum efficiency of optoelectronic device, the duration of the emitting device will be much shorter without the fluorescence based emission. The most recent study brought up a new non-

dopant red light emitting material which is porphyrin based fluorescence compound appended with fluorenyl and fluorenone.¹³⁻¹⁶ The idea of designing molecular device with satisfying phosphorescence (based on porphyrin) and fluorescence (peripheral fluorene and fluorenone) properties is expected to compromise between colour purity and efficiency of device. In order to obtain high efficient red emissions, the overall porphyrin structure architecture is concerned with chromophores substituents, linker types and pigment connection as well as configuration orientations to optimize the electron and energy transfer. The conjugated symmetrical porphyrins (A_4 , A_2 , and A_2B_2 types) such as tetraphenylporphyrin (TPP),^{17,18} bis-(tertbutylphenyl)porphyrin (TBDPP),¹⁸ [tetra(pentafluoro-phenyl)porphyrinato]platinum(II) (PtF₂₀TPP),¹¹ (diphenylporphyrinato) platinum(II) (PtDPP)¹⁹ have been widely studied for light emitting properties while the unsymmetrical *meso*-substituted porphyrin (A_3B type) study is less frequent. Due to the convenient synthesis

methods, electron donating and withdrawing substituents can be attached as peripheral arms of porphyrin. The electron donor and acceptor appended to porphyrin was being excited selectively to change its flow direction especially for unsymmetrical porphyrin leading to an electron push-pull effect on the macrocyclic ring. In this study, we investigate red emission properties of different

substituted symmetrical and unsymmetrical porphyrins to indicate the energy transfer efficiency. It was found that the emission efficiency of porphyrins was enhanced by extension of π -conjugation system with the evidence of energy transfer from the fluorenyl components to the porphyrin macrocyclic ring.

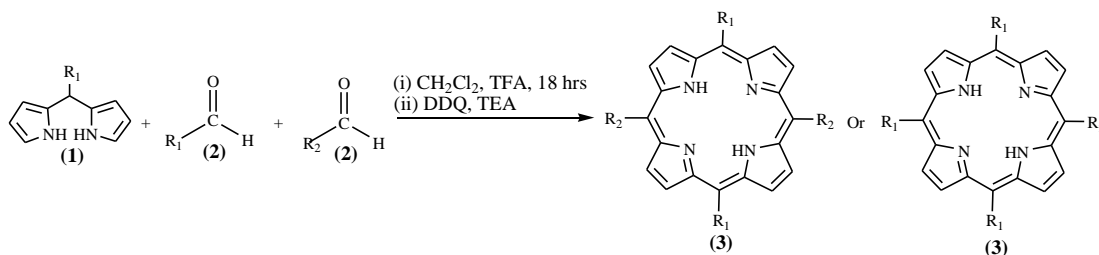
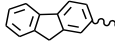
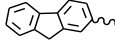
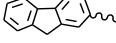
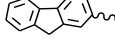


Figure 1 Condensation reaction with types of “2+2” and “2+1+1”

Table 1 Condensation reaction using dipyrromethanes

R ₁		R ₂	Product
1	2		
Ph 1a	 2a	-	3a
HCCPh 1b	 2a	-	3b
H 1c	HOPh 2b	-	3c
 1d	 2a	HCCPh 2c	3d
Ph 1a	Ph 2d	BrPh 2e	3e

2.0 RESULTS AND DISCUSSION

2.1 Syntheses of Dipyrromethanes and Porphyrins

Synthetic porphyrins were prepared through Adler Longo's²⁰ and Lindsey's^{21,22} procedures. Adler Longo's procedure provides a straight forward and convenient route to produce identical substituents tetra-substituted porphyrin (A₄ type porphyrins), for example tetraphenylporphyrin (TPP). In order to construct A₂B₂, A₂ and also A₃B type porphyrins without producing mixture, “2+2” and “2+1+1” condensation reaction (Figure 1) have been performed under Lindsey's condition using dipyrromethane precursor **1a-d**. The dipyrromethanes were initially prepared from pyrrole and their respective aldehydes (Figure 5). The light sensitive and less stable dipyrromethane **1c** were reacted under nitrogen purged and crystal was obtained upon heating in vacuum using Kugelrohr glass oven at 180 °C. The crystal form of **1c** was unable to be obtained through trituration in *n*-hexane and recrystallization in ethanol/water mixture, unlike dipyrromethanes **1a, b** and **d**. A high yield of novel 5-(4-fluorenyl-2-yl)dipyrromethane (**1d**) was obtained which could be used as the precursors in synthesizing other fluorenone derivatives for π conjugating system.

The symmetrical A₂ and A₂B₂ type porphyrins could be obtained through “2+2” condensation reaction. Porphyrins **3a-c** were synthesized through condensation of respective dipyrromethanes and aldehydes (Table 1). The synthetic route had paved a pathway to produce symmetrical A₂ and A₂B₂ type porphyrins without the presence of other mixtures.

On the other hand, “2+1+1” condensation reaction could be a specific route to produce A₃B type porphyrins. The mixture of **1d** together with fluorenyl-2-ylcarbaldehyde (**2a**) and 4-ethynylbenzaldehyde (**2c**) has undergone “2+1+1” condensation reactions to form 5-(4-ethynylphenyl)-10,15,20-(trifluorenyl-2-yl)porphyrin (**3d**) which could act as useful binding site to form dimer. The ethynyl and fluorenyl peripheral groups of **3d** were expected to have extended π electron conjugating system to lower the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) band gap. Another porphyrin **3e** with peripheral bromophenyl group has been synthesized through “2+1+1” condensation reactions using 5-phenyldipyrromethane (**1a**) as the precursor. The bromide functional group is useful as a precursor to synthesize dimer porphyrin *via* Suzuki^{23,24} and Sonogashira^{25,26} coupling reactions. In addition, metallation was performed on **3e** to obtain [5-(4-bromophenyl)-10,15,20-triphenylporphyrin-ato] zinc (II) (**5**) to

increase the planarity of the compound. Since the peripheral polycyclic aromatic fluorenyl extended the π conjugation system of the host molecule, it was expected to lower HOMO and LUMO band gap, which lead to the bathochromic shift in absorption wavelength of the porphyrins. The 5,15-difluorenone-10,20-diphenylporphyrin(**4**) was synthesized by oxidizing the fluorenyl 9-H position of 5,15-di(fluorene-2-yl)-10,20-diphenylporphyrin(**3d**) to compared the fluorescence properties with the other porphyrins.¹⁶

2.2 Photophysical Properties

2.2.1 Absorption Spectra

The measurement of UV-VIS absorption spectra of the porphyrins **TPP**, **3a-e**, **4** and **5** were performed at a room temperature in tetrahydrofuran (THF), as shown in Figure 2. The UV-VIS absorption spectra of free base *meso*-substituted porphyrins exhibited an intense *Soret* band around 420 nm and four weaker Q bands in the range of 480–680 nm (inset figure in Figure 2). The absorption patterns of Q bands are generally formed with Q_x (0,0 and 0,1) and Q_y (0,0 and 0,1).²⁷ The absorption spectra of Zn(II) porphyrins displays a single Q band absorption which is the combination of Q_x and Q_y bands due to the D_{4h} symmetry of metal porphyrins instead of the D_{2h} symmetry of free base porphyrins.²⁸ Hence, **5** exhibited an intense *Soret* band with 2 Q bands.

All absorption bands except **3c** tend to be red shifted compared to **TPP** due to the expanding conjugating system of porphyrins. Appended fluorenyl and fluorenone arms on porphyrins **3a,b,d** and **4** showed strong $\pi-\pi^*$ absorptions in the range of 240–300 nm; where **TPP** and **3c** displayed much weaker absorptions in that range. The absorption of fluorenone arms was more intense than the fluorenyl arms due to the presence of C=O functional group at 9-H position of fluorene. The higher photon absorption tendency of fluorenyl appended arms was anticipated to transfer energy into porphyrin conjugated system. The sign of energy transfer is discussed in the emission spectra. Addition of an extra fluorenyl arms on porphyrin **3d** exhibited most red shifted absorption spectra (17 nm) from **TPP**. Porphyrins **3a**, **b**, **d**, **e** and **4** proposed photon absorption at lower energy due to closer HOMO-LUMO band gaps.

Absorption spectra of **3e** were red shifted from **TPP** and proposed second highly red shifted compound due to the presence of bromophenyl group. However, **5** which is the result of metallated **3e** proposing slightly blue shifted absorption bands due to the restoration of electron conjugation in the macrocyclic ring. On the other hand, porphyrin **3c** with appended hydroxylphenyl group showed blue shifted absorption band compared to **TPP** where higher energy is needed to excite the electrons during the electronic transition process.

2.2.2 Emission Spectra

To confirm the fluorescence properties of porphyrins **TPP**, **3a-e**, **4** and **5**, emission spectra result from excitation of absorption *Soret* bands of respective compounds have been normalized as shown in Figure 3. The emission spectra were measured using a spectrofluorometer where the excitation wavelengths were set up to a peak top of absorption value in the range of 255–285 and 400–425 nm of the respected compound. The emission bands of **TPP**, **3a-e**, **4** and **5** were detected in the region 550–800 nm with the respective excitation wavelength.

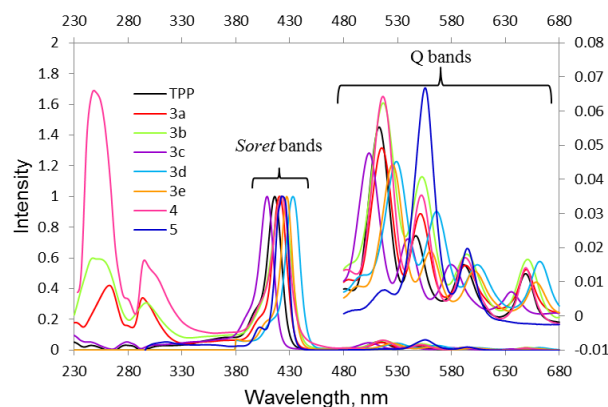


Figure 2 Absorption spectra of **TPP**, **3a-e**, **4** and **5** in THF at room temperature (normalized at *Soret* bands)

All compounds showed emission bands centered at a red visible region. The emission spectra of the porphyrin compounds were compared to the emission spectrum of **TPP** ($\lambda_{Em} = 653$ nm, 716 nm). Compound **TPP** was excited at $\lambda_{Ex} = 416$ nm and produced an emission at 653 and 716 nm due to S_1 to S_0 electronic transitions. Light absorption process can lead to excitons (coulombically bound electron-hole pairs)²⁹ which produce separated charges from charge transfer from electron-donor to electron-acceptor components^{30,31} such as materials used in the semiconductors, solar cells and other biological systems. As the π -electron conjugation of porphyrins extended, the absorption energies reduced due to the HOMO and LUMO electronic levels came closer.

Porphyrin **3a** ($\lambda_{Ex} = 420$ nm) and **d** ($\lambda_{Ex} = 422$ nm) showed strong emission bands at 655 and 653 nm; a weaker band at 718 and 715 nm. Both emission spectra are corresponded to the electron rich porphyrin macrocyclic ring. Both compounds **3a** and **d** were then excited at 270 nm to investigate the role of appended fluorenyl arms in energy transferring process. As anticipated, the emission spectra in both excitation wavelength ($\lambda_{Ex} = 270$ and 420 nm) were identical indicated the energy transfer from appended fluorenyl and phenyl group into the porphyrin system. An efficient energy transfer between the substituents and porphyrin took place in compounds **3a** and **d** where there was almost no residual emission of fluorene unit occurred at the region around 300 nm.¹⁶ Porphyrin **3b** with appended conjugating fluorenyl and also ethynyl group ($\lambda_{Em} = 656$ and 719 nm) contributed red shifted absorption and emission bands, indicating the well extension of π electron conjugation in the porphyrin system. The red shifting of the bands were contributed by the relaxation of electrons in $\pi-\pi^*$ transition states of fluorene and fluorenone. Compounds **3b** and **4** ($\lambda_{Em} = 654$ nm, 717 nm) were both excited at $\lambda_{Ex} = 269$ and 256 nm also presenting similar emission properties with **3a**.

Observing from Figure 4, **3e** was surprisingly exhibiting the most red shifted emission bands at 657 and 719 nm which is contrast to **5** ($\lambda_{em} = 604$ and 653 nm). The emission of **3e** was displayed in the red region while emission of **5** was remarkably blue shifted (more than 60 nm) towards a green region. The Zn(II) insertion of **5** restored the rigidity and conjugation of the electron rich system, resulting higher energy emissions of the porphyrin. Porphyrin **3c** ($\lambda_{Ex} = 408$ nm) displayed also a blue shifted emission wavelength from **TPP** at 641 and 700 nm due to the $n-\sigma^*$ transition of hydroxyl group. Apparently, the hydroxyl substituents have the electron withdrawing effect on the porphyrin π electron system, which caused the HOMO-LUMO band gap wider.

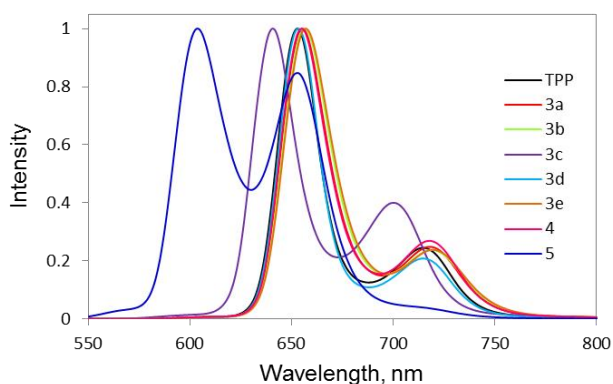


Figure 3 Normalized emission spectra of **TPP** ($\lambda_{\text{Ex}} = 416$ nm), **3a** ($\lambda_{\text{Ex}} = 420$ nm), **3c** ($\lambda_{\text{Ex}} = 408$ nm), **3e** ($\lambda_{\text{Ex}} = 405$ nm), **5** ($\lambda_{\text{Ex}} = 410$ nm), **3b**, **3d** and **4** ($\lambda_{\text{Ex}} = 422$ nm) in THF at room temperature

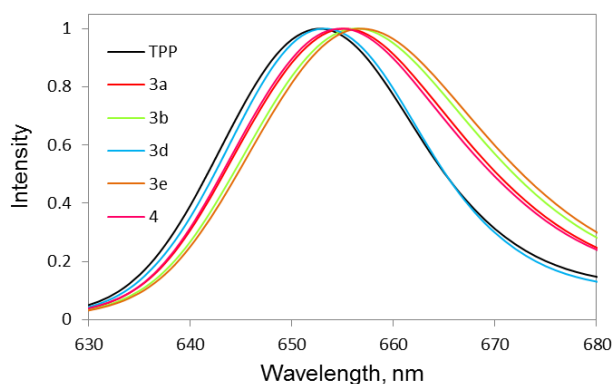


Figure 4 Expanded normalized emission spectra of **TPP** ($\lambda_{\text{Ex}} = 416$ nm), **3a** ($\lambda_{\text{Ex}} = 420$ nm), **3c** ($\lambda_{\text{Ex}} = 408$ nm), **3e** ($\lambda_{\text{Ex}} = 405$ nm), **5** ($\lambda_{\text{Ex}} = 410$ nm), **3b**, **3d** and **4** ($\lambda_{\text{Ex}} = 422$ nm) in THF at room temperature

3.0 EXPERIMENTAL

3.1 Material, Method and Measurement

Characterization of the synthesized porphyrin compounds was performed using Fourier transform infrared (FT-IR) spectrometer model a Perkin Elmer to determine the infrared vibrations of the compounds. The ratio of samples with potassium bromide (KBr) powder in 1:100 was mixed and pressurized for 5 minutes. The absorption and emission spectra were measured through Perkin Elmer Lambda 25 Ultraviolet/ Visible (UV/VIS) spectrometer and Jasco spectrofluorometer model a FP 8500. The samples were dissolved and diluted in analytical grade THF, and THF was used as the blank throughout the instrument. The emission wavelengths were obtained and normalized to the maximum intensity of the respected compounds. Merck pre-coated silica gel (60 F₂₅₄) thin layer chromatography (TLC) plates were used with the assist of Vilber Lourmat UV lamp (365 nm) to observe the spots of the compounds in a reaction and purification. Proton and carbon nuclear magnetic resonance (400 MHz for ¹H NMR and ¹³C NMR for 100 MHz) Bruker Avance were used to obtain the splitting patterns of the atoms in porphyrin compounds. The compounds were dissolved in deuterated chloroform (CDCl₃) during the measurement. Besides, Barnsfoad Electrothermal 9100 was used for the measurement of melting points of the solid products. Glass oven Buchi 585 was used to perform fractional distillation to obtain pure dipyrromethane. All chemicals were used in the form

of directly purchased without any purification unless otherwise stated.

3.2 Meso Substituted Dipyrromethanes

The experiment was performed according to the method reported by Joydev K. L. *et al.* as shown in the Figure 5.³² Distilled pyrrole (100 equivalent) and aldehyde (1 equivalent) were stirred under nitrogen purge in dark condition. Indium (III) chloride (InCl₃, 0.1 equivalent) was then being added into the mixture and stirred for another 2 hours. The solution was then stirred for 45 minutes with sodium hydroxide (NaOH) to neutralize the solution. The solution was filtered to remove the remained InCl₃ and NaOH. A small amount of pyrrole was used to wash the filtrate and the excess pyrrole then removed from the solution to obtain a yellowish viscous solution. The crude viscous solution was triturated with 50 mL *n*-hexane for 3 times and the solvent was evaporated to obtain pale yellow solids. Crystallization was performed by adding warm ethanol and water (4:1) to dissolve the solids and filtered immediately. The filtrate was allowed to stay overnight at room temperature to obtain pale yellow crystal.

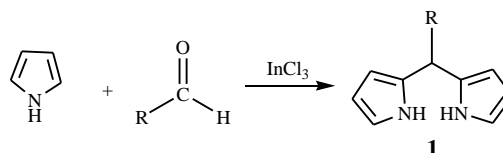


Figure 5 Synthesis of dipyrromethanes

3.2.1 5-phenyldipyrromethane (1a)³³

The reaction was carried out according to general procedure 3.2 with pyrrole (173.32 mL, 2.5 mol) and benzaldehyde (**2d**) (2.55 mL, 25.0 mmol) to obtain yellow crystal (3.92 g, 71%): m.p. = 99-100°C (lit. from Lee and Lindsey at 1994, 100-101 °C); ¹H NMR δ_{H} ppm (400 MHz, CDCl₃): $\delta = 5.50$ (s, 1H, H_D), 5.94 (t, $J = 0.8$ Hz, 2H, H_A), 6.18 (q, $J = 2.8$ Hz, 2H, H_C), 6.71 (dd, $J = 1.2$ Hz and 2.8 Hz, 2H, H_B), 7.30 (m, 5H, H_{A'}, H_{B'}, H_{C'}), 7.95 (br s, 2H, N-H); IR ν (cm⁻¹) (KBr): 3342.77 (N-H), 3138.40 (Ar-C-H), 3507.44 (sp² C-H), 2863.43 (sp³ C-H), 1553.66 (Ar-C=C), 1454.97 (C=C).

3.2.2 5-(4-ethynylphenyl)dipyrromethane (1b)²²

The reaction was carried out according to general procedure 3.2 with pyrrole (138.5 mL, 2.0 mol) and 4-ethynylbenzaldehyde (**2d**) (2.6 g, 20.0 mmol) to obtain yellow crystal (1.48 g, 30%): m.p. = 106-107°C (lit. from Rao *et al.* at 2000, 109-110°C); ¹H NMR δ_{H} ppm (400 MHz, CDCl₃): $\delta = 3.08$ (s, 1H, sp C-H), 5.48 (s, 1H, H_D), 5.91 (s, 2H, H_A), 6.18 (q, $J = 2.8$ Hz, 2H, H_B), 6.72 (s, 2H, H_C), 7.19 (d, $J = 8.4$ Hz, 2H, H_{B'}), 7.46 (d, $J = 8.0$ Hz, 2H, H_{A'}), 7.96 (br s, 2H, N-H); IR ν (cm⁻¹) (KBr): 3332.35 (N-H), 3135.72 (Ar-C-H), 3059.03 (sp² C-H), 2963.20 (sp³ TMS-C-H), 2898.72 (sp³ C-H), 2160.55 (C≡C), 1496.28 (Ar-C=C).

3.2.3 5-(4-fluoren-2-yl)dipyrromethane (1d)

The reaction was carried out according to general procedure 3.2 with pyrrole (173.32 mL, 2.5 mol) and fluoren-2-yl carbaldehyde (**2a**) (4.85 g, 25.0 mmol) to obtain yellow crystal (6.17 g, 80%): m.p. = 146.5-148.5°C; ¹H NMR δ_{H} ppm (400 MHz, CDCl₃): $\delta = 3.89$ (s, 2-H, H_K), 5.57 (s, 1H, H_D), 6.00 (m, 2H, H_A), 6.23 (q, $J =$

2.8 Hz, 2H, H_B), 6.74 (m, 2H, H_C), 7.28 (dd, $J = 7.6$ Hz, 1H, H_H), 7.34 (td, $J = 7.2$ Hz and 7.6 Hz, 1H, H_I), 7.41 (m, 2H, H_G and H_J), 7.57 (d, $J = 7.6$ Hz, 1H, H_F), 7.76 (d, $J = 7.6$ Hz, 1H, H_E), 7.81 (d, $J = 7.2$ Hz, 1H, H_L), 7.97 (br s, 2H, N-H); ¹³C NMR δ_{H} ppm (100 MHz, CDCl₃): $\delta = 36.92, 44.12, 107.22, 108.48, 117.20, 119.83, 119.93, 125.04, 126.67, 126.78, 127.15, 132.71, 140.72, 141.35, 143.34, 143.80$; IR ν (cm⁻¹) (KBr): 3438.93 (N-H), 3097.47 (sp² C-H), 3010.98 (sp³ C-H), 1614.79 (C=C), 1465.96 (Ar-C=C).

3.2.4 Dipyrrromethane (1c)³⁴

Paraformaldehyde (0.03 g, 1.0 mmol) and pyrrole (3 mL, 43.0 mmol) were stirred in nitrogen gas condition. The solution was heated to 50°C and TFA (8 μ L, 0.1 mmol) was added immediately right after the heat source was removed. A sharp increase in the temperature which was 8 to 10°C was observed and the solution became darker rapidly. After the stirring process, the solution was diluted with dichloromethane (DCM) and quenched with sodium hydroxide solution. The organic layer was dried and excess pyrrole was removed. The crude product was collected using Kugelrohr glass oven Buchi 585 at 180°C to give pale yellow dipyrrromethane (3.5 g, 21%): m.p. = 73°C (lit. from Kamaljit *et al.*, 2005, 75°C): ¹H NMR δ_{H} ppm (400 MHz, CDCl₃): $\delta = 3.97$ (s, 2H, CH₂), 6.01 (m, 2-H, pyrrolic H), 8.18 (q, 2-H, pyrrolic H), 8.67 (m, 2-H, pyrrolic H), 7.82 (br, 2H, N-H); IR ν (cm⁻¹) (KBr): 3342.77 (N-H), 3138.40 (Ar-C-H), 3507.44 (sp² C-H), 2863.43 (sp³ C-H), 1553.66 (Ar-C=C), 1454.97 (C=C).

3.3 Symmetrical and Asymmetrical Porphyrins

3.3.1 5,10,15,20-tetraphenylporphyrin (TPP)³⁵

Pyrrole (1.39 mL, 0.02 mol) and **2d** (2.04 mL, 0.02 mol) were refluxed in propionic acid (100 mL) for 45 min according to Adler Longo's condensation reaction. The resulting mixture was left overnight. The precipitate material was filtered off and washed with methanol to afford 5,10,15,20-tetraphenylporphyrin as purple solid (0.30 g, 10%): m.p. > 400°C. $R_f = 0.75$ (DCM/*n*-hexane 1:1); ¹H NMR δ_{H} ppm (400 MHz, CDCl₃): $\delta = -2.76$ (s, 2H, N-H), 7.76 (m, 12H, *ortho*, *para*-phenyl H), 8.23 (d, $J = 6.7$ Hz, 8-H, *meta*-phenyl H), 8.85 (s, 8-H, β -H); IR ν (cm⁻¹) (KBr): 3319.00 (N-H), 3051.23 (Ar-C-H), 1598.00 (C=C aromatic), 1220.84 (C-N); UV-Vis (DCM): λ_{max} (log ϵ) = 416 (5.44), 512 (4.19), 546 (3.81), 591 (3.59), 649 (3.55); Fluorescence (THF): λ_{Em} nm = 653, 716.

3.4 General Procedure for "2+2" Condensation Reaction

1 equiv. of dipyrrromethane derivative and 1 equiv. of aldehyde were dissolved in dried DCM and stirred in dark condition and under nitrogen purge. Trifluoroacetic acid (0.1 equivalent) was added to the solution. The solution was allowed to stir for 18 hours at ambient temperature. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 1.2 equivalent) which was suspended in dried DCM was added into the solution to oxidize the solution. Triethylamine (1 mL) was added to terminate the reaction. After stirring for 15 minutes, the DCM was reduced using rotator evaporator. The crude product was separated through silica gel and DCM/*n*-hexane or ethylacetate (EA)/*n*-hexane was used as the eluent. Recrystallization was performed with DCM and methanol (1:3) to obtain purple crystals of porphyrins.

3.4.1 5,15-di(fluoren-2-yl)-10,20-diphenyl-porphyrin (3a)³⁶

1a (2.0 g, 9.0 mmol) and **2a** (1.75 g, 9.0 mmol) were dissolved in dried DCM and continued with general procedure 3.4.2 to obtain

purple crystal 5,15-di(fluoren-2-yl)-10,20-diphenylporphyrin (0.68 g, 10%): m.p. > 400°C; $R_f = 0.35$ (EA/*n*-hexane, 1:10 v/v); ¹H NMR δ_{H} ppm (400 MHz, CDCl₃): $\delta = -2.68$ (t, $J = 16.4$ Hz, 2H, N-H), 4.22 (s, 4H, H_G), 7.46 (t, $J = 7.4$ Hz, 2H, H_E), 7.55 (t, $J = 7.4$ Hz, 2H, H_D), 7.72 (d, $J = 7.6$ Hz, 2H, H_F), 7.87 (m, 6H, H_A, H_B), 8.07 (d, $J = 7.2$ Hz, 2H, H_C), 8.17 (d, $J = 7.6$ Hz, 2H, H_B), 8.25 (d, $J = 6.8$ Hz, 6H, H_A, H_C), 8.40 (s, 2H, H_H), 8.88-8.94 (d, $J = 24$ Hz, 8H, β -H_A, β -H_B); IR ν (cm⁻¹) (KBr): 3428.88 (N-H), 3049.45 (Ar-C-H), 2851.64 (sp³ C-H) 1634.34 and 1453.82 (Ar-C=C), 1347.07 (C-N); UV-Vis (THF): λ_{max} nm (log ϵ) = 263 (3.16), 293 (5.00), 420 (5.47), 515 (4.16), 551.19 (3.94), 593 (3.64), 649 (3.60); Fluorescence (THF): λ_{Em} nm = 655, 718.

3.4.2 5,15-di (4-ethynylphenyl) - 10, 20 - di (fluoren-2-yl)porphyrin (3b)

1b (0.56 g, 2.5 mmol) and **2a** (0.48 g, 2.5 mmol) were dissolved in dry DCM and continued with general procedure 3.4.2 to obtain purple crystal 5,15-di(4-ethynylphenyl)-10,20-di(fluoren-2-yl)porphyrin (0.18 g, 9%): m.p. > 400°C; $R_f = 0.38$ (EA/*n*-hexane, 1:10 v/v); ¹H NMR δ_{H} ppm (400 MHz, CDCl₃): $\delta = -2.71$ (t, $J = 21.4$ Hz, 2H, N-H), 3.33 (s, 2H, sp C-H), 4.22 (s, 4H, H_G), 7.48 (t, $J = 7.0$ Hz, 2H, H_E), 7.56 (t, $J = 7.2$ Hz, 2H, H_D), 7.72 (d, $J = 7.2$ Hz, 2H, H_F), 7.91 (d, $J = 8.0$ Hz, 4H, H_A), 8.08 (d, $J = 6.8$ Hz, 2H, H_C), 8.20 (m, 8H, H_A, H_B, H_B), 8.39 (s, 2H, H_H), 8.85 (d, $J = 4.8$ Hz, 4H, H_B), 8.95 (d, $J = 4.8$ Hz, 4H, H_A); IR ν (cm⁻¹) (KBr): 3289.34 (N-H), 2104.39 (C≡C), 1603.94 and 1453.81 (Ar-C=C), 1348.15 (C-N); UV-Vis (THF): λ_{max} nm (log ϵ) = 247 (5.32), 297 (5.06), 422 (5.57), 517 (4.37), 552 (4.18), 594 (3.83), 650 (3.79); Fluorescence (THF): λ_{Em} nm = 656, 719.

3.4.3 5,15-di(4-hydroxyphenyl)porphyrin (3c)³⁷

1c (0.58 g, 4.0 mmol) and 4-hydroxybenzaldehyde (**2b**) (0.49 g, 4.0 mmol) were dissolved in 200 mL dried DCM and continued with general procedure 3.4.2 to obtain purple crystal 5,15-di(4-hydroxyphenyl)porphyrin (0.06 g, 3.0%): m.p. > 400°C; $R_f = 0.45$ (EA/*n*-hexane, 1:3, v/v); ¹H NMR δ_{H} ppm (400 MHz, Aseton-D): $\delta = -3.01$ (s, 2H, N-H), 7.38 (d, $J = 8.0$ Hz, 4H, H_A), 8.15 (d, $J = 7.6$ Hz, 4H, H_B), 9.03 (br s, 2H, O-H), 9.16 (d, $J = 4.8$ Hz, 4H, β -H_B), 9.59 (d, $J = 3.6$ Hz, 4H, β -H_A), 10.54 (s, 2H, *meso*-H_C); IR ν (cm⁻¹) (KBr): 3373.62 (N-H), 3297.08 (O-H), 3109.89 (Ar-C-H), 1608.31 (Ar-C=C), 1238.33 (C-O), 1171.63 (C-N); UV-Vis (THF): λ_{max} nm (log ϵ) = 409 (5.22), 503 (3.79), 539 (3.35), 579 (3.01), 635 (2.22); Fluorescence (THF): λ_{Em} nm = 641, 700.

3.5 General Procedure for "2+1+1" Condensation Reaction

Dipyrrromethane (2 equivalent) and aldehyde (1 equivalent) were dissolved in dried dichloromethane (DCM) and stirred in dark condition and under nitrogen purge. Trifluoroacetic acid (0.1 equivalent) was added to the solution. The solution was allowed to stir for 18 hours at ambient temperature. DDQ (1.2 equivalent) which was suspended in dried DCM was added into the solution to oxidize the solution. Triethylamine (1 mL) was added to terminate the reaction. After stirring for 15 minutes, the DCM was reduced using rotator evaporator. The crude product was separated through silica gel and DCM/*n*-hexane or ethylacetate (EA)/*n*-hexane was used as the eluent. Recrystallization was performed with DCM and methanol (1:3) to obtain purple crystals of porphyrins.

3.5.1 5-(4-ethynylphenyl)-10,15,20-(trifluorenyl)-porphyrin (3d)

1d (1.24 g, 4.0 mmol), **2a** (0.388 g, 2.0 mmol) and **2c** (0.26 g, 2.0 mmol) were dissolved in dried DCM and continued with general procedure 3.4.3 to obtain purple crystal 5-(4-ethynylphenyl)-10,15,20-(trifluorenyl)-porphyrin (0.22 g, 12%): m.p.> 400°C; $R_f = 0.54$ (DCM/*n*-hexane, 1:1 v/v); $^1\text{H NMR } \delta_{\text{H}}$ ppm (400 MHz, CDCl_3): $\delta = -2.65$ (t, $J = 20.4$ Hz & 22 Hz, 2H, N-H), 3.34 (s, 1H, sp C-H), 4.23 (s, 6H, H_G), 7.46 (m, 3H, H_E), 7.55 (m, 3H, H_D), 7.72 (d, $J = 7.2$ Hz, 3H, H_F), 7.91 (d, $J = 8.4$ Hz, 2H, H_A), 8.08 (d, $J = 7.2$ Hz, 3H, H_C), 8.18 (d, $J = 7.6$ Hz, 3H, H_B), 8.23 (t, $J = 3.6$ Hz, 2H, H_B), 8.28 (d, $J = 6.4$ Hz, 3H, H_A), 8.41 (s, 3H, H_H), 8.86 (d, $J = 4.8$ Hz, 2H, $\beta\text{-H}_A$), 8.96 (d, $J = 6.0$ Hz, 6H, $\beta\text{-H}_B$); $^{13}\text{C NMR } \delta_{\text{H}}$ ppm (100 MHz, CDCl_3): 37.14, 117.95, 120.30, 125.29, 127.08, 130.51, 131.39, 133.54, 134.45, 140.63, 141.31, 141.54, 141.72, 143.78; IR ν (cm^{-1}) (KBr): 3428.57 (N-H), 3298.46 (sp C-H), 3027.47 (Ar-C-H), 2921.60 (sp³ C-H), 2346.15 (C \equiv C), 1602.21 and 1453.60 (Ar-C=C); UV-Vis (THF): λ_{max} nm (log ϵ) = 433 (5.98), 529 (4.63), 566 (4.47), 604 (4.16), 662 (4.18); Fluorescence (THF): λ_{Em} nm = 653, 715.

3.5.2 5-(4-bromophenyl)-10,15,20-triphenylporphyrin (3e)³⁸

1a (0.89 g, 4.0 mmol), **2d** (0.20 mL, 2.0 mmol) and 4-bromobenzaldehyde (**2e**) (0.37 g, 2.0 mmol) were dissolved in dried DCM and continued with general procedure 3.4.3 to obtain purple crystal 5-(4-bromophenyl)-10,15,20-triphenylporphyrin (0.19 g, 28%): m.p.> 400°C; $R_f = 0.6$ (DCM/*n*-hexane, 1:1 v/v); $^1\text{H NMR } \delta_{\text{H}}$ ppm (400 MHz, CDCl_3): $\delta = -2.80$ (t, $J = 10$ Hz, 2H, N-H), 7.79 (m, 9H, H_D , H_E), 7.92 (m, 2H, H_A), 8.10 (m, 2H, H_B), 8.23 (m, 6H, H_C), 8.87 (m, 8H, $\beta\text{-H}_A$, $\beta\text{-H}_B$); IR ν (cm^{-1}) (KBr): 3433.01 (N-H), 3120.87 (Ar-C-H), 1632.38 and 1472.65 (Ar-C=C); UV-Vis (THF): λ_{max} nm (log ϵ) = 427 (5.88), 525 (4.53), 560 (4.16), 601 (4.00), 658 (3.88); Fluorescence (THF): λ_{Em} nm = 657, 719.

3.6 [5-(4-bromophenyl)-10,15,20-triphenylporphyrinato] zinc (II) (5)³⁹

3e (0.07 g, 0.1 mmol) was dissolved in 50 mL of dichloromethane. The solution was allowed to stir and 2 drops of TFA added followed by adding excess amount of zinc acetate hydrate. The solution was then being reflux for an hour and the total consumption of reactant was controlled using TLC. The mixture was filtered and the solvent was evaporated. The product obtained was purple crystal of [5-(4-bromophenyl)-10,15,20-triphenylporphyrinato] zinc (II) (0.062 g, 83%): m.p.> 400°C; $R_f = 0.24$ (DCM/hexane, 1:1, v/v); $^1\text{H NMR } \delta_{\text{H}}$ ppm (400 MHz, CDCl_3): $\delta = 7.77$ (m, 9H, H_D , H_E), 7.91 (m, 2H, H_A), 8.11 (m, 2H, H_B), 8.25 (m, 6H, H_C), 8.95 (m, 8H, $\beta\text{-H}_A$, $\beta\text{-H}_B$); IR ν (cm^{-1}) (KBr): 3049.45 (Ar-C-H), 1629.64 and 1482.37 (Ar-C=C); UV-Vis (THF): λ_{max} nm (log ϵ) = 423 (5.51), 556 (4.34), 595 (3.80); Fluorescence (THF): λ_{Em} nm = 604, 653.

3.7 5,15-difluorenone-10,20-diphenylporphyrin (4)

3a (0.24 g, 0.3 mmol) was further dissolved in *n*-heptane. 30% Sodium hydroxide---->sodium hydroxide solution and Aliquat 336 were added to the solution to oxidize the **3a**. The solution was allowed to stir vigorously for four days. TLC check was performed to investigate the **3a** consumption. The organic layer was then be separated and filtered through silica gel to remove the impurities. Column chromatography was performed using eluent EA/*n*-hexane (1:10 v/v). Recrystallization with DCM and methanol (1:3) had obtained purple crystal 5,15-difluorenone-

10,20-diphenylporphyrin (0.024 g, 10%): m.p.> 400°C; $R_f = 0.55$ (EA/*n*-hexane, 1:3 v/v); $^1\text{H NMR } \delta_{\text{H}}$ ppm (400 MHz, CDCl_3): $\delta = -2.74$ (s, 2H, N-H), 7.45 (t, $J = 7.4$ Hz, 2H, H_E), 7.66 (t, $J = 7.6$ Hz, 2H, H_D), 7.81 (m, 10H, H_F , H_A , H_B , H_C), 7.93 (d, $J = 7.6$ Hz, 2H, H_B), 8.24 (d, $J = 6.8$ Hz, 4H, H_C), 8.33 (d, $J = 7.6$ Hz, 2H, H_A), 8.52 (s, 2H, H_H), 8.90 (m, 8H, $\beta\text{-H}_A$, $\beta\text{-H}_B$); DEPT Q NMR δ_{H} ppm (400 MHz, CDCl_3): $\delta = 99.99, 118.80, 120.81, 124.60, 127.86, 129.47, 129.54, 132.78, 134.61, 134.82, 135.05, 140.32, 141.93, 143.27, 143.93, 144.41, 194.53$; IR ν (cm^{-1}) (KBr): 3316.42 (N-H), 3053.03 (Ar-C-H), 1714.50 (C=O), 1600.36 and 1455.18 (Ar-C=C), 1349.40 (C-N), 1105.94 (C-O); UV-Vis (THF): λ_{max} nm (log ϵ) = 248 (5.78), 295 (5.33), 422 (5.56), 516 (5.10), 552 (4.11), 593 (3.79), 649 (3.71); Fluorescence (THF): λ_{Em} nm = 654, 717.6----> 717.

4.0 CONCLUSION

Different types of porphyrin precursors **1a-d** were successfully synthesized through convenient condensation reaction. The dipyrromethanes were useful to construct symmetrical and asymmetrical porphyrins **3a-e**, **4** and **5** with various functional groups. A newly reported 5-(4-fluorenyl)-dipyrromethane (**1d**) could amplify the synthesis route of fluorenyl based porphyrins and also the other fluorenyl based organic compounds. The extension of conjugating system intensified the red fluorescence properties with the lower absorption energy compared to electron withdrawing hydroxyphenyl group. The side appended fluorene and fluorenone arms porphyrins have more saturated red light emitting properties and higher energy transfer efficiency compared to **TPP**. We suggest that the terminal bromophenyl porphyrin (**3e** and **5**) and ethynylphenyl porphyrins (**3b** and **d**) could be used as the precursors to form extended conjugating porphyrin dimer or trimer in future study.

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