2.1. Materials

The required starting materials and reagents for the synthesis of 5-substituted dipyrrromethane and porphyrin are commercially available with purity. Pyrrole, 2,4,6-trimethylbenzaldehyde, 9-anthracenecarboxyaldehyde, 4-nitrobenzaldehyde, trifluoroacetic acid (TFA), 2-methoxy-1-naphthaldehyde, 2,3-dichloro-5,6-dicyano-p-benzoquinone (DQQ) were purchased from Sigma Aldrich and used as received except the pyrrole. For the synthesis of dipyrrromethane, pyrrole was distilled from calcium hydride (CaH$_2$) and used for further reactions. Triethylamine (TEA), borontrifluoride–etharate complex (BF$_3$.OEt$_2$), sodium hydroxide (NaOH) were obtained from CDH chemicals, India and used as received. For the synthesis of porphyrins, ACS grade chloroform (CHCl$_3$) and dichloromethane (DCM) were purchased from Merck, India and used without prior distillation. For column chromatography, silica gel 60-120 mesh and neutral alumina were purchased from CDH chemicals, India. For spectral measurements, HPLC grade DCM was purchased from Merck, India. For all other purpose laboratory grade CHCl$_3$, DCM, petroleum ether were purchased and distilled prior to use.

2.2. Instrumentation

UV-Vis absorption spectra were recorded in Perkin Elmer Lambda 35 spectrophotometer. Steady-state fluorescence spectra measurements were made by using Agilent Cary Eclipse Fluorescence spectrofluorimeter. Fluorescence-lifetime measurements were carried out on a time correlated single photon counting (TCSPC) setup (FluoroLog-3 Triple Illuminator, IBH Horiba Jobin Yvon) employing a light emitting diode laser (NanoLED, λ$_{ex}$= 250 and 445 nm) as excitation sources. The data were fitted with help of DAS6 v 6.6 software.


$^1$H and $^{13}$C NMR spectra were recorded in Burker 400 MHz NMR spectrometer by using trimethylsilane as an internal standard. MALDI-TOF spectrum was recorded in Voyager DE Pro (Applied Biosystems) and ESI-MS spectrum was recorded in Fischer Scientific.

Electrochemical measurements were carried out with CHI model electrochemical workstation. Two compartments, three electrode cell (Glassy carbon (GC) - working electrode, pseudo silver wire-reference electrode, Platinum- counter electrode) were used for the electrochemical measurements. All measurements were carried out under nitrogen atmosphere. The GC electrode was polished with 0.50 and 0.05μm alumina slurry and the cleanliness of the electrode was checked with $K_4[Fe(CN)_6]$ in 0.1 M KCl. For cyclic voltammetry (CV), scan rate of 100 mV/s is used for scanning and in case of differential pulse voltammetry (DPV) a pulse width of 0.05 s and amplitude of 0.05 V was applied.

2.3. Computational Details

Synthesized molecules were initially optimized with density functional theory (DFT) method using the Becke, three parameter, Lee-Yang-Parr (B3LYP) level of theory, Becke Three–Parameter Perdew/Wang 91 (B3PW91) theory and 6-31G (d) basis set in gas phase.\(^1\)\(^-\)\(^2\) Thereafter, single point energy calculation was done using same method, theory and basis set with dichloromethane as solvent.\(^3\) Time-dependent density functional theory (TD-DFT) method was opted to study the excited state properties. TD-DFT calculations were computed using B3LYP theory and 6-31G (d) basis set.\(^4\)\(^-\)\(^5\) Transition density cube (TDC) methods are performed to study the excited state electronic population. All quantum chemical calculations were carried out in Gaussian 09.\(^6\)
2.4. Quantum Yield Calculation

The quantum yield of the donors and acceptors of the dyads in the present study were calculated by the comparative method proposed by the William et. al.,\(^7\) and the equation 2.1 is used to calculate the quantum yield of the standards and samples in dichloromethane.

\[
\phi_x = \phi_{\text{std}} \left( \frac{\text{Grad}_x}{\text{Grad}_{\text{std}}} \right) \left( \frac{\eta_x}{\eta_{\text{std}}} \right)^2
\]  \hspace{1cm} (2.1.)

In the above equation \(X\) and \(\text{std.}\) refers the sample and standard respectively. \(\phi\) is the fluorescence quantum yield, Grad is the gradient from the plot of integrated fluorescence intensity Vs absorbance and \(\eta\) is the refractive index of the solvent. 5,10,15,20-tetraphenylporphyrin and 5,10,15,20-tetramesitylporphyrin are taken as acceptor standards, 2-methoxynaphthalene and anthracene are taken as donor reference compounds. The refractive indexes of solvents used in the calculation are 1.496 for toluene, 1.445 for chloroform and 1.424 for dichloromethane.\(^7\)\(^8\)

2.5. Synthesis of 5-Substituted Dipyrrromethane

The important precursors involved in the porphyrins synthesis are 5-substituted dipyrrromethanes. The required dipyrrromethanes for the synthesis of 5, 15-bis(2-methoxynaphthal-1-yl)10,20-dimesitylporphyrin (MNMP), 5-(9-anthryl)-15-(4-nitrophenyl)-10,20-diphenylporphyrin (AnNPP) and 5-(9-anthryl)-15-(4-nitrophenyl)-10,20-bisferrocenylporphyrin (AnFcP) are 5-mesityldipyrrromethane, 5-(4-nitrophenyl)dipyrrromethane and 5-(9-anthracenyl)dipyrrromethane. They were synthesized according to the reported procedure.\(^9\)\(^-\)\(^10\)
2.5.1. Synthesis of 5-mesityldipyrromethane

![Chemical structure](image1)

**Scheme 2.1.** Synthesis of 5-mesityldipyrromethane.

In a 100 mL two-necked round-bottomed flask, pyrrole (475 mmol; 33 mL) and mesitaldehyde (19 mmol; 2.8 mL) were taken and purged with nitrogen for 10 minutes. It was followed by the addition of TFA (1.9 mmol; 0.15 mL) and stirred for 1 hour. The reaction mixture was neutralized with 0.1 M sodium hydroxide. Ethyl acetate was added and the organic layer was washed with water. Organic layer was dried over MgSO$_4$. Excess pyrrole and solvent were removed under vacuum by rotary evaporator. The crude was subjected to column chromatography and the product was eluted by using petroleum ether/CHCl$_3$ mixture (70:30). Finally, the product was recrystallized from CHCl$_3$/hexane mixture. White crystalline solid was obtained, yield: 16.9% (0.8529 g).

2.5.2. Synthesis of 5-(4-nitrophenyl)dipyrromethane

![Chemical structure](image2)

**Scheme 2.2.** Synthesis of 5-(4-nitrophenyl)dipyrromethane.
In a 100 mL two-necked round-bottomed flask, pyrrole (500 mmol; 34.6 mL) and 4- nitrobenzaldehyde (20 mmol; 3.0224 g) were taken and purged with nitrogen for 10 minutes. This was followed by the addition of TFA (2 mmol; 0.15 mL) and stirred for 15 minutes. The reaction mixture was neutralized with triethylamine. Excess pyrrole was removed under vacuum by rotary evaporator. The crude was recrystallized from ethyl acetate/hexane mixture. Yellow crystalline solid, yield: 27% (1.4508 g).

2.5.3. Synthesis of 5-(9-anthracenyl)dipyrromethane

\[
\text{Scheme 2.3. Synthesis of 5-(9-anthracenyl)dipyrromethane}
\]

In a 100 mL two-necked round-bottomed flask, (20 mmol; 4.1248 g) of 9-anthracenecarboxaldehyde and (500 mmol; 34 mL) of pyrrole were taken together and purged with nitrogen for 10 minutes. Then, (2 mmol; 0.15 mL) of TFA was added and stirred for 1 hour at room temperature. The reaction was quenched by the addition of 0.1 M sodium hydroxide and ethyl acetate was added. The organic layer was washed with water and dried over MgSO₄. The crude was purified by column chromatography over silica gel using petroleum ether/DCM (70/30) as eluent and yellow solid was obtained, yield: 373 mg (12%).
2.6. Synthesis of Porphyrins

The synthesis of 5, 15-bis(2-methoxynaphth-1-yl)10,20-bis(mesityl)porphyrin (MNMP), 5-(9-anthryl)-15-(4-nitrophenyl)-10,20-diphenylporphyrin (AnNPP) and 5,15-bis(mesityl)-10,20-bisferrocenylporphyrin (BMBFP) are carried out according to reported procedure.\textsuperscript{11}

2.6.1. Synthesis and Characterization of 5, 15-bis(2-methoxynaphth-1-yl)10,20-bis(mesityl)porphyrin (MNMP)

\begin{center}
\includegraphics[width=\textwidth]{Scheme24.png}
\end{center}

\textbf{Scheme 2.4.} Synthesis of MNMP.

In a 250 mL round-bottomed flask, 5-mesityldipyromethane (1.732 mmol; 0.4579 g) and 2-methoxy-1-naphthaldehyde (1.732 mmol; 0.3225 g) were taken and dissolved in 173 mL ACS grade chloroform. The entire solution was purged with nitrogen for 10 minutes and BF\textsubscript{3}.OEt\textsubscript{2} (3.3 mM; 0.5709 mmol; 0.0718 mL) was slowly added. The whole mixture was stirred at dark for 1 hour. After 1 hour, DDQ (2.598 mmol; 0.5897 g) was added and stirred for another 1 hour. Finally the reaction was quenched by adding TEA (0.5709 mmol; 0.080 mL). The solution was passed through alumina and eluted with chloroform. Solvent was removed and crude was dissolved in 25 mL of toluene and DDQ (0.866 mmol; 0.1966 g) was added, refluxed for 1 hour. Toluene was removed under reduced pressure. Crude was passed through
alumina and eluted using chloroform. Finally purification was carried out using silica
gel in column chromatography by eluting with petroleum ether and chloroform
mixture (85: 15). Purple solid, yield: 278 mg, 37% (include both isomers).

\( \alpha,\alpha\)-and \( \alpha,\beta\)-isomer: \(^1\)H NMR (CDCl\(_3\), 400 MHz) \( \delta \) (ppm): 8.56 (d, \( J = 4.8 \) Hz, 8H), 8.49 (d, \( J = 4.4 \) Hz, 8H), 8.31 (d, \( J = 9.2 \) Hz, 4H), 8.06 (d, \( J = 8 \) Hz, 4H), 7.34 (t, \( J = 7.2 \), 7.2 Hz, 4H), 7.72 (d, \( J = 8.8 \) Hz, 4H), 7.02 (t, \( J = 4 \) Hz, 4H), 6.95 (d, \( J = 8.4 \) Hz, 2H), 6.91 (d, \( J = 8.4 \) Hz, 2H), 7.21 (s, 8H), 3.63 (s, 6H), 3.62 (s, 6H), 2.57 (s, 12H), 1.86, 1.84
and 1.83 (s, 24H), -2.32 (br s, 4H)

\(^1\)H NMR (CDCl\(_3\), 400 MHz) \( \delta \) (ppm): 8.56 (d, \( J = 4.8 \) Hz, 4H), 8.49 (d, \( J = 4.4 \) Hz, 4H), 8.30 (d, \( J = 8.8 \) Hz, 2H), 8.05 (d, \( J = 8.0 \) Hz, 2H), 7.71 (d, \( J = 9.2 \) Hz, 2H), 7.34 (t, \( J = 0.8 \), 1.2 Hz, 2H), 7.02 (t, \( J = 0.8 \), 2, 1.2, 0.8 Hz, 2H), 6.95 (d, \( J = 8.8 \) Hz, d), 7.29 (s, 4H), 3.61 (s, 6H), 2.57 (s, 6H), 1.83 & 1.86 (s, 12H), -2.31 (s, 2H)

\(^{13}\)C NMR (CDCl\(_3\), 100 MHz), \( \delta \) (ppm): 157.74, 139.56, 139.45, 138.41, 137.90, 137.57, 130.52, 128.57, 127.70, 127.66, 127.55, 126.52, 125.08, 123.52, 117.70, 113.92, 113.06, 56.97, 34.72, 34.57, 26.97, 25.33, 21.81, 21.80, 21.48, 20.76

HR-MS: calculated mass 858.3934, observed mass 859.417

\(^1\)H NMR (CDCl\(_3\), 400 MHz) \( \delta \) (ppm): 8.55 (d, \( J = 4.8 \) Hz, 4H), 8.48 (d, \( J = 4.4 \) Hz, 4H), 8.30 (d, \( J = 9.2 \) Hz, 2H), 8.05 (d, \( J = 8 \) Hz, 2H), 7.71 (d, \( J = 9.2 \) Hz, 2H), 7.33 (t, \( J = 7.2 \) & 7.6 Hz, 2H), 7.21 (s, 4H), 7.02 (t, \( J = 7.6 \) & 7.6 Hz, 2H), 6.91 (d, \( J = 8.8 \) Hz, 2H), 3.62 (s, 6H), 2.57 (s, 6H), 1.84 (s, 12H), -2.31 (s, 2H)
$^{13}$C NMR (CDCl$_3$, 100 MHz), $\delta$ (ppm): 157.72, 139.49, 138.40, 137.90, 137.54, 130.51, 128.55, 127.66, 127.54, 127.46, 126.56, 125.03, 123.50, 117.69, 113.83, 113.01, 56.92, 31.63, 29.76, 22.69, 21.79, 21.46.
Figure 2.1. $^1$H NMR spectrum of MNMP (both $\alpha\alpha$-and $\alpha\beta$-isomers) in CDCl$_3$. 
Figure 2.2. $^1$H NMR spectrum of MNMP (αα-isomer) in CDCl$_3$. 
Figure 2.3. $^{13}$C NMR spectrum of MNMP ($\alpha\alpha$-isomer) in CDCl$_3$. 
Figure 2.4. $^1$H NMR spectrum of MNMP (αβ-isomer) in CDCl$_3$. 
Figure 2.5. $^{13}$C NMR spectrum of MNMP (αβ-isomer) in CDCl$_3$. 
Figure 2.6. HR-MS of MNMP (αα-isomer) (a) Full-view (b) Expanded-view
2.6.2. Protonation and Characterization of 5, 15-bis(2-methoxynaphth-1-yl)10,20-bis(mesityl)porphyrin (MNMP-aa isomer)

Protonation of MNMP- aa isomer was carried out by passing hydrogen chloride gas through the MNMP solution dissolved in dichloromethane. Complete protonation was confirmed from the changes in Soret band shifting to 438 nm and merging of two Q-bands at 593 and 647 nm.

2.6.3. Synthesis and Characterization of 5-(9-anthryl)-15-(4-nitrophenyl)-10,20-diphenylporphyrin (AnNPP)

![Scheme 2.6. Synthesis of AnNPP.](image)

5-(4-nitrophenyl)dipyrrromethane (0.5 mmol; 0.1336 g), 5-anthr-9-yl dipyrrromethane (0.5 mmol; 0.1612 g), benzaldehyde (1 mmol; 0.1 mL) were dissolved in 150 mL of CHCl₃. The entire solution was purged with N₂ for 10 minutes. To this, BF₃.OEt₂ (0.495 mmol; 0.06 mL) was added and stirred at room temperature for 1 hour under dark. This is followed by the addition of DDQ (1.5 mmol; 0.3405 g) and further stirred for another one hour. Finally, triethylamine (0.495 mmol; 0.07 mL) was added in order to neutralize the added acid. The mixture was passed through a pad of alumina and eluted with chloroform. Column purification
over silica gel eluted with petroleum ether/ chloroform (1: 1) gave the desired porphyrin as second band. Red solid, Yield: 45 mg (23%).

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ (ppm): -2.58 (s, 2H), 6.92 (t, $J = 6.5$, 8.5 Hz, 2H), 6.98 (d, $J = 8.5$ Hz, 2H), 7.34 (t, $J = 7$, 7.5 Hz, 2H), 7.66-7.61 (m, 6H), 8.11 (d, $J = 7$ Hz, 4H), 8.19 (d, $J = 9$ Hz, 4H), 8.34 (d, $J = 8$ Hz, 2H), 8.57 (d, $J = 8.5$ Hz, 2H), 8.60 (d, $J = 4$ Hz, 2H), 8.68 (d, $J = 4.5$ Hz, 2H), 8.82 (d, $J = 4.5$ Hz, 2H), 8.84 (s, 1H).

$^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ (ppm): 149.30, 147.78, 141.68, 135.52, 135.27, 135.13, 135.10, 134.50, 132.44, 130.87, 130.09, 128.53, 128.49, 128.28, 128.22, 128.19, 127.89, 126.80, 126.77, 125.90, 125.08, 121.89, 121.85, 120.68, 117.19, 116.19.

MALDI-MS (TOF): calculated mass 759.263, observed mass 760.8979.

Fragmentation of $-\text{NO}_2$ group in AnNPP was occurred and the corresponding mass appeared at 745.9787 and 729.9743.\textsuperscript{12}
Figure 2.7. $^1$H NMR spectrum of AnNPP in CDCl$_3$. 
Figure 2.8. $^{13}$C NMR spectrum of AnNPP in CDCl$_3$. 
Figure 2.9. MALDI-TOF spectrum of AnNPP.
2.6.4. Protonation of 5-(9-anthryl)-15-(4-nitrophenyl)-10,20-diphenylporphyrin (AnNPP)

The protonated form, PANP was obtained by passing hydrogen chloride vapor into AnNPP dissolved in dichloromethane. Complete protonation of AnNPP was confirmed by the shift of the Soret band from 420 nm to 447 nm using the UV-vis spectroscopy.

2.6.5. Synthesis and Characterization of 5,15-bis(ferrocenyl)-10,20-bis(mesityl)porphyrin (BFBMP)

Scheme 2.7. Synthesis of BFBMP.

5-mesityl dipyrromethane (0.75 mmol; 0.2418 g), and ferrocenecarboxaldehyde (1.5 mmol; 0.3211 g) were taken together and dissolved in 150 mL ACS grade DCM. The mixture was purged with nitrogen for 10 minutes followed by addition of TFA (0.5 mmol; 0.06 mL). The mixture was stirred at dark for 1 hour. At this stage, where the solution contains porphyrinogen intermediate is converted into porphyrin by addition of TCQ (2.25 mmol; 0.5532 g). Further this solution is stirred for another 1 hour. After the formation of porphyrin, the solution was passed through the alumina in column and eluted with DCM. The fraction is collected until the green band is
eluted fully. Finally the green fraction is purified by column chromatography using PET/CHCl₃ (70/30) as eluent. Green solid. Yield: 70 mg (27%)

^1^H NMR (CDCl₃, 400 MHz) δ (ppm): 9.83 (d, J = 4.8 Hz, 4H), 8.55 (d, J = 4.8 Hz, 4H), 7.29 (s, 4H), 5.48 (s, 4H), 4.798 (s, 4H), 4.16 (s, 10H), 2.63 (s, 12H), 1.86 (s, 6H), -1.54 (s, 2H)

^1^C NMR (CDCl₃, 100 MHz) δ (ppm): 147.99, 139.48, 139.33, 137.72, 131.27, 129.52, 127.86, 118.32, 117.06, 89.34, 77.23, 76.81, 70.74, 69.07, 21.73, 21.61

HR-MS: Calculated mass 914.2734; observed mass 915.2944 (M+H).
Figure 2.10. $^1$H NMR spectrum of BMBFP in CDCl$_3$. 
Figure 2.11. $^{13}$C NMR spectrum of BMBFP in CDCl$_3$. 
Figure 2.12. HR-MS of BMBFP (a) Full-view (b) Expanded-view
2.7. References


