The detailed experimental procedure for synthesis of precursors and their important characterization technique used for analyze in the course of investigation are described in this chapter. Further, this chapter discusses the materials and methods employed for synthesis and characterization.

2.1 Chemicals for syntheses

All anhydrous solvents used for the reactions and analyses were purified and dried by standard purification procedure [77,78]. Pyrrole, thiophene and furan were purchased from Sigma-Aldrich and were distilled before use. Selenophene, Tolualdehyde, Mesitaldehyde, p-Chloroanil, DDQ, 2,2’-bithiophene, n-butyllithium, Trifluoroacetic acid, p-Toluenesulphonic acid, methane sulphonic acid and deuterated solvents for NMR measurement were used as received from Sigma-Aldrich. Aluminium oxide and silica gel for column chromatography were purchased from Merck. N,N,N,N-Tetramethylethylenediamine was procured from Sigma-Aldrich and distilled over KOH before use [77]. Tetrabutylammonium hexafluorophosphate was procured from Sigma-Aldrich and vacuum dried in desiccator for more than 2h before use.

2.2 Physico-chemical techniques:

ESI-Mass analysis: Masses of the compounds were recorded by electron spray ionization-mass spectra-Time of flight (ESI-MS-TOF) instrument of Bruker, micrOTOF-QII mass spectrometer.
NMR measurements: NMR spectra were recorded on a Bruker (400 MHz) spectrometer. The NMR protonation titration experiments were carried out with TFA solution quantitatively dissolved in deuterated solvent. Chemical shifts are expressed in parts per million (ppm) relative to TMS, unless otherwise specified.

Spectrophotometer analysis: Steady-state absorption measurement, electronic absorption spectra were recorded with Perkin Elmer – Lambda 750 UV-Visible spectrophotometer and data analyses were done using the UV-winlab software package. Fluorescence spectra were recorded on a Perkin Elmer LS55 Fluorescence spectrometer. Fluorescence quantum yields in solution state were determined using fluorescein in 0.1M NaOH ($\Phi_f = 0.95$) as a reference.

Femto-second Transient Absorption Measurement: The femtosecond time-resolved transient absorption (TA) spectrometer consist of a homemade noncollinear optical parametric amplifier (NOPA) pumped by a Ti:sapphire regenerative amplifier system (Quantronix, Integra-C) operating at 1 kHz repetition rate and an optical detection system. The generated visible NOPA pulses had a pulse width of ~100 fs and an average power of 1mW in the range 500-700 nm which was used as pump pulses. White light continuum (WLC) probe pulses were generated using a sapphire window (3mm of thickness) by focusing of small portion of the fundamental 800 nm pulses which was picked off by a quartz plate before entering to the NOPA. The time delay between pump and probe beams was controlled by making the pump beam travel along a variable optical delay (Newport, ILS250). Intensities of the spectrally dispersed WLC probe pulses are monitored by miniature spectrograph (OceanOptics, USB2000+). The polarization angle between pump and probe beam was set at the magic angle (54.7°) in order to prevent polarization-dependent signals. Cross-correlation fwhm in pump-probe experiments was less than 200 fs and chirp of WLC
probe pulses was measured to be 800 fs in the 400-800 nm region. To minimize chirp, all reflection optics in probe beam path and 2 mm path length of quartz cell were used.

**Two-photon Absorption Measurement:** The TPA measurements were performed using the open-aperture Z-scan method with 130 fs pulses from an optical parametric amplifier (Light Conversion, TOPAS) operating at a 2 kHz repetition rate using a Ti:sapphire regenerative amplifier system (Spectra-Physics, Hurricane X). After passing through a $f=10\text{cm}$ lens, the laser beam was focused to 1 mm-quartz cell. As the position of the sample cell was varied along the laser-beam direction ($z$-axis), the transmitted laser beam from the sample cell was then probed using a Ge/PN photodiode (New Focus, 2033) as used for reference monitoring.

**Quantum Mechanical Calculations:** All calculations were carried out using the Gaussian 09 program. Initial geometries were obtained from X-ray structures. All structures were fully optimized without any symmetry restriction. The calculations were performed by the density functional theory (DFT) method with restricted B3LYP (Becke’s three-parameter hybrid exchange functionals and the Lee-Yang-Parr correlation functional) level, employing a basis set 6-311G (d,p). The nucleus independent chemical shift (NICS) values were obtained with the GIAO method at the B3LYP/6-311G (d,p) level. The global ring centers for the NICS values were designated at the non-weighted means of the carbon and sulfur coordinates on the peripheral positions of macrocycles. In addition, NICS values were also calculated on centre of other local cyclic structures [79-82].

**X-ray Diffraction Analysis:** The single crystals for the X-ray analysis were grown by appropriate solvents. X-ray data were recorded on a BRUKER-APEX X-ray diffractometer equipped with a large area CCD detector in 100 K. The structures were solved by Patterson synthesis and refined with the SHELX-97 programs [83]. These data can be obtained free of charge from the Cambridge crystallographic data centre via www.ccdc.cam.ac.uk/data_request.cif.
Dynamic light scattering: DLS analyses were carried out with a Zeta sizer Nano from Malvern Instruments at 25°C.

Scanning electron microscope: SEM analysis was carried out using Zeiss Carl instrument.

Voltammetry: Cyclic voltammetry and differential pulse voltammetry (CV & DPV) experiments were done on CHI model 620B, CH-instruments Inc., interfaced to computer. Three electrode system was used which consist of glassy carbon working electrode, platinum counter electrode and Ag/AgNO₃ reference electrode.

2.3 Experimental Procedure:

The essential precursors required for the synthesis of core-modified macrocycles described in this thesis such as bridged & fused expanded porphyrin [84-87] and expanded calixphyrin [88,89] are described in Scheme 1-7.

Tetrabromothiophene (1):

22 ml (0.431mol) Br₂ was slowly added into the mixture of 8 mL (8.4 g, 0.1 mol) thiophene and 3 mL CHCl₃ in 2h on ice bath. The reaction mixture was refluxed for 5h, then, cooled to ambient temperature. To the reaction mixture 5 mL of 2N NaOH was added and
vigorously stirred for 30 min. The solid product was separated, washed with water and crystallized over hot CHCl₃. The white crystals of 1 were obtained in 75% yield (16.0 g)

\[
\text{13}^\text{C NMR (100 MHz, CDCl}_3, 298 K): \delta (\text{ppm}): 117.10, 110.44
\]

3,4-dibromo-2,5-diformylthiophene (2):

An oven-dried, three-necked round-bottomed flask (1L) was equipped with a magnetic stir bar, a low temperature thermometer, a rubber septum and a three-way stopcock. Under a gentle flow of argon, the flask is added with tetrabromothiophene (16.0 g, 40.0 mmol) and freshly-distilled tetrahydrofuran (200 mL). The solution was cooled in a methanol/2-propanol bath with an internal temperature of less than −65 °C and a solution of n-butyllithium (50 mL, 1.6 M in hexane, 80 mmol) was added via syringe. The addition proceeds at a rate that keeps the internal temperature below −60° C, usually taking 15 min. When the addition was complete, the brown solution was stirred at about −65 °C for 30 min., anhyd. N-formylpiperidine (10 mL, 90 mmol) was added quickly by syringe to the reaction mixture, which was then allowed to warm slowly to ambient temperature overnight. The reaction mixture was cooled to 0° C in an ice-water bath, and hydrochloric acid (100 mL, 6 M) was added slowly to the reaction mixture, causing a yellow precipitate to form. The mixture was stirred at 0 °C for 45 min then filtered immediately under vacuum through a sintered-glass funnel. The solid was washed with water (150 mL) and dried in the funnel under vacuum for 30 min before being dried further in a vacuum desiccator (25 mmHg, overnight, silica gel desiccant with moisture indicator) to give 2 in 70% yield (8.8 g).

\[
\text{1H NMR (400 MHz, CDCl}_3, 298 K): \delta (\text{ppm}): 10.12 (s, 2H)
\]
Dithieno[3,2-b:2′,3′-d]thiophene-2,6-dicarboxylic acid diethyl ester (3):

In an oven-dried 500-mL, two-necked round-bottomed flask equipped with a magnetic stir bar, nitrogen inlet and rubber septum, 2 (8.0 g, 26.9 mmol) was suspended in anhydrous N,N-dimethylformamide (250 mL), anhydrous potassium carbonate (9.65 g, 69.8 mmol) and ethyl 2-mercaptoacetate (6 mL, 55 mmol) were added to the slurry, causing a slight exotherm, and the reaction mixture was stirred under nitrogen at ambient temperature for three days. The dark solution was poured into a beaker containing 500 mL of water stirred with a magnetic stir bar, and a yellow precipitate forms. The aqueous suspension was extracted with CH$_2$Cl$_2$ (3 × 250 mL). The red organic extracts were combined, washed with brine (4 × 500 mL) and dried over anhydrous magnesium Sulphate. After filtration through fluted filter paper, the solvent was evaporated on a rotary evaporator and a yellow solid begins to form. When the volume of solvent remain about 100 mL, yellow color solid formed and it was filtered under vacuum on a Büchner funnel, washed with water (100 mL) and dried in a vacuum desiccator overnight (7–8 mm Hg, silica gel desiccant with moisture indicator) to give the crude diester. Yield: 6.5 g, 74%

$^1$H NMR (400 MHz, CDCl$_3$, 298 K): δ (ppm): 8.03 (s, 2H); 4.44 (q, 4H); 1.42 (t, 6H)

Synthesis of 2,6-dibromo dithieno[3,2-b;2′,3′-d]thiophene (4):

To a suspension of DTT-diester 3 (2.5g, 7.3mmol) 40 mL of 1M aqueous solution of LiOH was added. The reaction mixture was refluxed for 3h and water was added to give a clear brownish yellow solution. Excess N-bromosuccinimide (6.28g, 35.3mmol) was then added and the reaction mixture was stirred overnight at ambient temperature. The reaction mixture was then extracted with CH$_2$Cl$_2$. The organic layers were washed with saturated NaHCO$_3$ water and brine, and dried with anhydrous sodium sulphate. After the solvent was
removed under reduced pressure, the residue was precipitated with ethanol and then filtered to give a white solid (1.7 g, 85%). The melting point was recorded to be 164° C. (lit m.p. 162-163° C).

1H NMR (400 MHz, CDCl3, 298 K): δ (ppm): 7.279 (s, 2H)

\[\text{Scheme 2}\]

5,5'-Bis-(mesitylhydroxymethyl)-dithienothiophene–(DTT diol) (5):

To a solution of 4 (0.7 g, 3.5 mmol) in 50 ml THF, n-Butyllithium (5 ml 1.6 M, 7.8 mmol) was added slowly at -78 °C under inert atmosphere. It was allowed to stir for 1h. Mesitaldehyde (1.154 g, 7.8 mmol) in 30 ml of THF was added drop wise at 273 K. The mixture was allowed to warm to room temperature and stirred further for 1h. To the reaction mixture 75 ml of saturated ammonium chloride solution was added and extracted with diethyl ether. The organic layers were combined, washed with brine and dried over sodium sulphate. After evaporation, the crude was subjected to silica gel column (100-200 mesh) chromatography with ethyl acetate: Hexane (1:5) afforded 5 in 63% yield.

1H NMR (400 MHz, CDCl3, 298 K) δ (ppm): 6.88 (s, 4H), 6.78 (s, 2H), 6.51 (s, 2H), 2.35 (s, 12H), 2.29 (s, 6H); ESI-MS: m/z: 492.36 [M]+, Calcd for C_{28}H_{28}O_{3}S_{3}: 492.13
5,5’-Bis-(tolylhydroxymethyl)-dithienothiophene-DTT diol (6):

Following the procedure of 5, diol 6 was prepared by using tolualdehyde instead of mesitaldehyde.

$^1$H NMR (400 MHz, CDCl$_3$, 298 K) δ (ppm) : 7.3 (d, 4H), 7.22 (d, 2H), 7.02 (s, 2H), 6.04 (s, 2H), 7.36 (d, $^3$J= 8Hz, 2H), 7.19 (d, $^3$J=8Hz, 2H) 6.51 (s, 2H), 2.32 (s, 6H); ESI-MS: m/z: 436.24 (54%)[M]$^+$, Calcd for C$_{24}$H$_{20}$O$_2$S$_3$: 436.16
Chapter – 2 : General experimental methods and technique

DTT-Mes-dipyrrane (7)

5, 5'-bis-(mesitylhydroxymethyl)dithienothiophene (DTT-mes-diol) 5 (0.5g, 1.01mmol), pyrrole (3.66 ml, 56.5mmol) was added and the mixture was degassed by bubbling nitrogen gas. To this solution TFA (0.03, 0.38mmol) was added and the reaction mixture was stirred for about 30 min at room temperature. After completion of the reaction, CH$_2$Cl$_2$ (100 ml) was added and the reaction mixture was neutralized with 0.1M NaOH solution. The organic layer was separated and washed two times with water (50 ml) then dried over sodium sulphate. The solvent and excess pyrrole was removed by vacuum. The crude product obtained was purified by silica gel (100-200 mesh) column chromatography with ethyl acetate/hexane (8:92, vol/vol) 7 was obtained as yellow semi-solid. Yield:85%.

ESI-MS: m/z (%): calcd for C$_{36}$H$_{34}$N$_2$S$_3$+H$: 590.1884; found: 590.1127; $^1$H NMR (400 MHz, CDCl$_3$, 298 K), δ [ppm]: 8.24 (brs, 2H), 7.05 (s, 2H), 6.79 (s, 4H), 6.73 (s, 2H), 6.26-6.23 (m, 6H), 2.29 (s, 12H), 2.16 (s, 6H).
DTT-Tol-dipyrrane (8)

The above procedure was used with 5, 5’-bis-(tolylhydroxymethyl)dithienothiophene (DTT-tolyl-diol) (0.5g, 1.15mmol). The crude product obtained was purified by silica gel (100-200 mesh) column chromatography with ethyl acetate/hexane (8:92, vol/vol) 8 was obtained as yellow semi-solid. Yield: 82%.

8: ESI-MS: m/z (%): m/z calcd for C_{32}H_{26}N_{2}S_{3}+H^+: 534.1258; found: 534.1378; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}, 298 K), δ [ppm]: 7.89 (brs, 2H), 7.01 (s, 2H), 7.00 (s, 2H), 6.87 (s, 2H), 6.85 (d, J=8Hz, 4H), 6.68 (d, J=8Hz, 4H), 6.18-6.09 (m, 6H), 2.28 (s, 6H).
2, 5 bis-(mesitylhydroxymethyl)thiophene (9):

To a solution of N,N,N',N'-tetramethylethylene diamine (4.03 mL, 26.75 mmol) in dry n-hexane (80 mL), n-butyllithium (1.6 M hexane, 17.8 mL, 26.75 mmol) was added followed by thiophene (0.72 mL, 8.9 mmol) under argon atmosphere. The reaction mixture was stirred at room temperature for an hour and later heated under reflux for 1h. The reaction mixture was then allowed to attain the room temperature. Then, it was ice cooled and a solution of Mesitaldehyde (3.28 mL, 22.28 mmol) in dry THF (12.5 mL) was added drop wise to it under continuous stirring. After the addition was over, the reaction mixture was allowed to attain room temperature and saturated ammonium chloride solution was added and it was then extracted with ether solvent. The organic layers were combined and washed with brine (60 mL) and dried over anhydrous sodium sulphate. The crude product obtained on evaporation of the solvent was purified by silica gel chromatography (100-200 mesh) with ethyl acetate: hexane (20:80), 9 was obtained as white solid. Yield: 55%.

\[
\text{1}^1\text{H NMR (400 MHz, CDCl}_3, \text{298 K): } \delta (\text{ppm}) = 1.65 \text{ (brs, 2H), 2.27 (s, 6H), 2.32 (s, 12H), 6.37-6.41 (m, 4H), 6.84 (s, 4H)}
\]

Synthesis of 2,5 bis-(mesitylhydroxymethyl)selenophene (10):

Following the procedure of 9, 10 was synthesized by using selenophene in 48% yield.

\[
\text{1}^1\text{H NMR (400 MHz, CDCl}_3, \text{298 K): } \delta (\text{ppm}) = 1.62 \text{ (brs, 2H), 2.25 (s, 6H), 2.31 (s, 12H), 6.34 (s, 1H), 6.35 (s, 1H), 6.50 (s, 1H), 6.52 (s, 1H), 6.82 (s, 4H)}
\]

Synthesis of 5,10 dimesityl-16-thiatripyrrane (11):

A mixture of 9 (1g, 2.63 mmol) and pyrrole (7.3 mL, 105.28 mmol) was degassed by bubbling nitrogen gas. Trifluoroacetic acid (TFA) (0.06 mL, 0.79 mmol) was added to this solution and the mixture was stirred for about 30 min at room temperature. After completion
of the reaction, CH$_2$Cl$_2$ (100 mL) was added and the reaction mixture was neutralized with 0.1M NaOH solution. The organic layer was separated and washed two times with water before drying over sodium sulphate. The solvent and excess pyrrole was removed by vacuum. The crude product was purified by silica gel column chromatography (100-200 mesh) with ethyl acetate and petroleum ether (3:97) gave the desired tripyrrane 11 as a yellow band in 90% yield.

$^1$H NMR (400 MHz, CDCl$_3$, 298 K): $\delta$ (ppm): 2.11 (s, 12H), 2.26 (s, 6H), 5.98-6.02 (m, 4H), 6.13-6.156 (m, 2H), 6.60-6.64 (m, 4H), 6.84 (s, 2H), 7.84 (brs, 2H)

**Synthesis of 5,10-dimesityl-16-selenatripyrrane [12]:**

2,5-bis(mesityl hydroxymethyl) selenophene 10 (1 g, 2.34 mmol), pyrrole (5 ml, 93.6 mol) and TFA (0.018 ml, 0.235 mmol) under similar reaction conditions as mentioned above gave dark yellow semi solid identified as 12 in 90% yield.

$^1$H NMR (400 MHz, CDCl$_3$, 298 K): $\delta$ (ppm): 2.12 (s, 12H), 2.24 (s, 6H), 6.0 (s, 2H), 6.05 (s, 2H), 6.12-6.16 (m, 2H), 6.61 (m, 2H), 6.79 (s, 2H), 6.83 (s, 4H), 7.84 (brs, 2H)

**Synthesis of 2,5-thiophene dicarboxaldehyde (13):**

A suspension of 2,5–dilithiothiophene was prepared by the addition of n-butyllithium (18.6 mL, 30 mmol) at room temperature to a mixture of N,N,N',N'-tetramethyl ethylenediamine (TMEDA (4.5 ml, 30 mmol), thiophene ( 1 g, 11.9 mmol) and n-
hexane (30ml). The temperature of thus obtained yellow suspension was raised to 40ºC and
the conversion was completed by refluxing for 30 min. Then 15 mL of THF was added, the
solution was cooled to -40ºC and excess DMF (2.3 mL, 32 mmol) was added over a period
of 10 min. The temperature of the mixture was gradually raised to room temperature and
stirring was continued for 30 min. The suspension was then poured into a mixture of 30%
HCl and H₂O at -20 to -50 ºC under vigorous stirring. Saturated NaHCO₃ solution was added
until the aqueous layer pH becomes 6. The organic layer was separated and the aqueous layer
was extracted with diethyl ether. The organic solution was evaporated by a rotavapour. The
crude product thus obtained was purified by silica gel (100-200 mesh) chromatography; an
orange band eluted with ethylacetate/hexane (20:80) identified as 13 51% yield.

1H NMR (400 MHz, CDCl₃, 298 K): δ (ppm): 7.85 (s, 2H); 10.05 (s, 2H)

Synthesis of 2,5-bis(dipyrrolylmethyl)thiophene (14):

A mixture of 13 (0.05 g, 3.6 mmol) and pyrrole (9.14 g, 143 mmol) was stirred under
argon atmosphere for 5 min. To this solution trifluoroacetic acid (TFA) (0.1 mL, 0.86 mmol)
was added and stirring was continued for 30 min. The reaction was quenched by adding 30
mL of CH₂Cl₂ and 20 mL of 0.1N NaOH. The organic layer was separated and washed with
water. The excess pyrrole and solvent was removed by vacuum distillation. The residue was
purified by chromatography on silica gel column (100-200) with ethyl acetate/petroleum
erther (1:4) gave an orange band eluted of 14 in 47% yield.

1H NMR (400 MHz, CDCl₃, 298 K), δ (ppm): 7.98 (br, 4H), 6.72
(s, 2H), 6.68 (m, 4H), 6.14 (m, 4H) 6.02 (m, 4H), 5.64 (s, 2H).
Synthesis of Bithiophene (15):

To a solution of thiophene (1 g, 12 mmol) in 1:1 mixture of dry ether (20 mL) and dry THF (20 mL), n-BuLi (8.4 mL, 13 mmol) was added at -70 °C and allowed to stir for 2h at same temperature. After 2h CuCl₂ (2.88 g, 21 mmol) was added to the above mixture and it was quenched with saturated NH₄Cl (25 mL) solution at 0 °C. The reaction mixture was then extracted with ethyl acetate. The organic layers were combined and washed with brine. The crude product obtained on evaporation was purified by silica gel column chromatography (100-200 mesh). A colorless fraction eluted with petroleum afforded 15 as a white solid in 30% yield.

\[ ^1H \text{NMR (400 MHz, CDCl}_3, \text{RT): } \delta (\text{ppm}): 7.21 (d, J = 1.2 \text{ Hz, 1H}); 7.20 (d, J = 1.2 \text{ Hz, 1H}); 7.18 (dd, 2H), 7.03 (dd, 2H) \]

Synthesis of 5,5’-bis-(mesitylhydroxymethyl)-2,2’-bithiophene(16):

To a solution of N, N, N’,N’-tetramethylethylenediamine (TMEDA) (2.7 mL, 18 mmol) in dry THF (40 mL), n-butyllithium (11 mL, 18 mmol) was added followed by 2,2’-bithiophene (1 g, 6 mmol) under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 1h and later heated under reflux for 1h. The reaction mixture was then allowed to attain 25 °C. Mesitaldehyde (2.2 mL, 15 mmol) in dry THF was added drop wise to the reaction mixture at 0 °C. After addition was over, the reaction mixture was allowed to attain room temperature and saturated ammonium chloride (100 ml) was added to quench the reaction. The reaction mixture was extracted with diethylether. The organic layers were
combined and washed with brine and dried over anhydrous sodium sulphate. The crude product obtained on evaporation of solvent was purified by silica gel column chromatography (100-200 mesh). A yellow band eluted with ethyl acetate/petroleum ether (1:5) afforded the diol 3 as pale solid. Yield: 1.5 g, 54%

\[ ^1H \text{NMR} \ (400 \text{ MHz, CDCl}_3, \ 298 \text{ K}): \delta \ (\text{ppm}): \ 6.91 \ (d, J = 3.6 \text{ Hz}, 2H), 6.86 \ (s, 4H), 6.51 \ (m, 2H), 6.39 \ (d, J = 3.6 \text{ Hz}, 2H), 2.33 \ (s, 12H), 2.28 \ (s, 6H), 1.57 \ (s, 2H). \]

**Synthesis of dithieno[3,2-b;2',3'd]thiophene-2,5-dicarbaldehyde (17):**

To a solution of 4 (0.5 g, 1.41 mmol) in 50 ml THF at -78 °C, n-Butyllithium (1.6 M in Hexane), (4.4 ml, 5.64 mmol) was added drop wise. After keeping the same temperature for 3 h, N,N'-dimethylformamide (DMF) (0.3 ml, 4.23 mmol) was added. The reaction mixture was warmed up slowly to room temperature and stirred for about 1h. After quenching with water, 5% citric acid was used to keep the pH at 5. The reaction mixture was extracted with CHCl$_3$. Organic layers were combined and washed with NaHCO$_3$ and brine and dried over anhydrous sodium sulphate. The crude product thus obtained was purified by silica gel column chromatography (100-200 mesh) with ethyl acetate/petroleum ether (1:4) in 25% yield.

\[ ^1H \text{NMR} \ (400 \text{ MHz, DMSO-d6, 298K}): \delta \ (\text{ppm}): \ 8.53 \ (s, 2H); 10.05 \ (s, 2H) \]
Synthesis of 2,5-bis(dipyrromethyl)dithienothiophene (18):

A mixture of 17 (0.2 g, 0.8 mmol) and pyrrole (2.14g, 32 mmol) were stirred under inert atmosphere for 5 minutes. Trifluoroacetic acid (0.015 ml, 0.2 mmol) was added and the stirring was continued for 3h. The reaction was quenched by adding 30 mL of CH$_2$Cl$_2$ and 20 mL of 0.1N NaOH. The organic layers were separated and washed with brine and water and solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (100-200 mesh). A pink band eluted with ethyl acetate and hexane (15:85) gave a reddish-brown solid which was identified as 18 in 41% yield.

![1H NMR spectrum](image)

$^1$H NMR (400 MHz, CDCl$_3$, 298 K): δ (ppm): 8.03 (brs, 4H) 7.04 (s, 2H), 6.72 (m, 4H), 6.18 (m, 4H), 6.10 (m, 4H), 5.78 (s, 2H).
2,5-bis(diphenylhydroxymethyl)thiophene (20):

N,N,N',N'-tetramethylethlenediamine (1.6ml, 2.5mmol) was dissolved in dry hexane under argon atmosphere. n-Butyllithium (1.875ml, 3mmol) was added drop wise and followed by addition of thiophene (0.79ml, 1mmol) and allowed to stir at ambient temperature for 1h and refluxed for 2h. The mixture was brought back to room temperature. Finally, the mixture was kept in an ice-bath and then benzophenone (0.432g, 2.3mmol) in dry hexane was added drop wise to the above reaction mixture and allowed to stir for 2h. The work up was done using water and saturated brine solution. The organic layer was then extracted with CH$_2$Cl$_2$ and dried over anhydrous sodium sulphate. The solvent was removed by using rotary evaporator. The crude product was purified by silica gel column chromatography (100-200 mesh) and eluted with petroleum ether: ethyl acetate (17:3) afforded 65% yield.

$^1$H NMR (400 MHz, CDCl$_3$, 298 K) δ (ppm): 7.38-7.26 (m, 20H), 6.55 (s, 2H), 2.91 (s, 2H).
2,5-bis(diphenylpyrrolylmethyl)thiophene (21):

2,5-bis(diphenylhydroxymethyl)thiophene 20 (1 g, 2.23 mmol) was added to pyrrole (7.73 ml, 111.5 mmol) under argon atmosphere and after 10 min TFA (0.053 ml, 0.69 mmol) was added and stirred for 30 min in ambient temperature. CH₂Cl₂ (30 ml) and KOH were added to quench and neutralize the acid respectively. The organic layer was then extracted with CH₂Cl₂ and dried over anhydrous sodium sulphate. The solvent was removed by rotary evaporator. The crude product was purified by silica gel column chromatography (100–200 mesh) with petroleum ether/ethyl acetate (95:5) gave yellow color semi-solid in 45% yield.

ESI-MS: m/z calcd for C₃₈H₃₀N₂S: 546.2130; found: 546.2143, ¹H NMR (400 MHz, CDCl₃, 298 K) δ ppm: 7.92 (brs, 2H), 7.28-7.09 (m, 20H), 6.73-6.71 (m, 2H), 6.58 (s, 2H), 6.15-6.13 (m, 2H), 5.96-5.95 (m, 2H).