Chapter 2

Experimental Section
2.1. Chemicals and materials

All the starting materials and reagents used in this study were commercially available with high purity. Pyrrole, mesitaldehyde, 4-nitrobenzaldehyde, ferrocencarboxaldehyde, pentafluorobenzaldehyde and 2,3-dichloro-5,6-dicayano-
p-benzoquinone were purchased from Aldrich and used as received. Thiophenol (TP), benzene-1,4-dithiol (BDT), p-aminothiophenol (ATP), p-hydroxythiophenol (HTP), and p-toluenethiol (TTP) purchased from TCI, Tokyo Kasei, Japan were used without further purification. Boron trifluoride-etherate complex (BF₃-OEt₂), triethylamine and ethyl acetate were purchased from SRL, India and used as received. Chloroform, dichloromethane and ethyl acetate were purchased from Merck, India and distilled by usual procedure before using. Hyrdochloric acid and shulphuric acid were purchased from Fischer chemicals, India and are of analytical grade. For spectral measurements, spectroscopic grade of dichloromethane, chloroform and N,N'-dimethylformamide were purchased from Merk India. meso-tetraphenylporphyrin and meso-tetrakis-(4-sulfonatophenyl)porphyrin were purchased from Fluka and used as received. Stannous chloride was purchased from Merk, India and used as received.

3 mm glassy carbon electrode (GC) disk electrode, 1 mm Ag wire and 0.5 mm Pt wire were purchased from CH Instruments (CHI, USA, Texas). Ag/AgCl (KCl sat.) electrode was purchased from Bioanalytical Systems (BAS), USA. The disposable screen-printed carbon electrodes (SPCEs) with geometrical area of 0.2 cm² were purchased from Zensor R & D, Taichung, Taiwan.
2.2. Instrumentation

Perkin Elmer Lambda 35 spectrophotometer was used to record the UV-vis absorption spectra. Perkin Elmer LS 55 model fluorimeter was used for fluorescence spectral measurements. FT-IR and ATR-FT-IR measurements were carried out on an FT-IR spectrophotometer, JASCO FT-IR 460 Plus model equipped with an ATR attachment with a horizontal ZnSe crystal (Pike Technologies). NMR spectra were recorded using Bruker 300 MHz and mass spectra using GC-MS (Applied BioSystems 3200 Q TRAP LC/MS/MS System) and MALDI-TOF (Voyager-DE PRO Biospectrometry Workstation).

All the electrochemical measurements were carried out with CHI Model 643B (Austin, TX, USA) electrochemical workstation. Two-compartment three-electrode cell was used for the electrochemical measurements. All the electrochemical measurements were carried out under nitrogen atmosphere unless otherwise it is specified. The GC electrode was polished with 0.50 and 0.05 μm alumina slurries and sonicated in double distilled water for 10 min and the cleanliness of the electrode was checked with K3[Fe(CN)6] in 0.1 M KCl. A pulse width of 0.05 s and amplitude of 0.06 V were applied for differential pulse voltammetry (DPV) studies. Laser flash photolysis experiments were carried out using the Nd-YAG laser source employing nanosecond pulses (8 ns) of 355 nm light and the energy of the laser pulse was around 150 mJ. All optical components were made of quartz to enable the full spectral range from the UV to the near IR to
be covered. The basic output from the system is a profile of change in absorbance vs. time at a given wavelength. Fluorescence lifetime spectrometer (Model 5000U, IBH, UK) was used to measure lifetime of the porphyrin and anthracene emissions. The second harmonic (425 nm) output from the Tsunami mode locked picosecond laser and LEDs were used as the exciting sources. Fluorescence decay analysis was carried out by the software provided by IBH (DAS-6) which is based on reconvolution technique and iterative non-linear least square methods. Atomic force microscope (AFM) images were recorded by Digital Instruments Nanoscope IV, Veeco. High resolution transmission electron microscopy (HR-TEM) images were obtained using JEOL JEM 3010 operating at 200 kV.

2.3. Computational studies

*ab-initio* calculations were performed to probe the electronic and geometrical structure of the compounds. Structural optimization and energy calculation were carried out using MOPAC, GAMESS and Gaussian 03W softwares. The output of the calculations were visualized using ChemDraw 8.0, ChemGraft 3.0 and GaussianView 3.7 softwares. Semiempirical calculations were done by using MOPAC 2000 version 1.0 at the PM3 level theory for aromatic thiols and 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ). *ab-initio* calculations were done by using the Gamess US program by HF model at the 6-311G level of theory for aromatic thiols. The structures were optimized using same level of theory. The output of the *ab-initio* calculations were visualized using
ChemCraft 1.5 software. DFT B3LYP/3-21G(*) method was used to probe the electronic and geometry of the bis-ferrocenyl porphyrins.

2.4. Synthesis of 5-substituted dipyrromethanes

5-Substituted dipyrromethanes were synthesized using the modified procedure of Naik and coworkers [1]. Pyrrole (25.0 mL, 360 mmol) and aldehyde (14.4 mmol) were taken in a dry round-bottomed flask with 50 ml of the mixture of n-hexane and chloroform in the ratio of 8:2. The mixture was degassed with a stream of argon (Ar) gas for 5 min. Amberlyst 15 (4g) was then added and the solution was stirred under argon atmosphere at room temperature for 5 hr and then filtered. The filtrate was evaporated under reduced pressure. The residue was washed with n-hexane to remove the excess pyrrole. The resultant solid was recrystallized from ethanol giving desired dipyrromethane.

2.5. Synthesis of meso-substituted bis-ferrocenylporphyrins

meso-Substituted bis-ferrocenyl porphyrins were synthesized using MacDonald type condensation [2]. Samples of dipyrromethane (0.40 mmol) and ferrocenecarboxaldehyde (0.40 mmol) were dissolved in 40 mL of chloroform. To the resulting solution, BF$_3$-Et$_2$O (93 μL, 1.2 mmol) was added and the reaction was stirred at room temperature. After 30 min, the supernatant was decanted and THF (20 mL) was added to the residue followed by Et$_3$N (167 μL, 1.2 mmol). Both organic fractions were combined and DDQ (136 mg, 0.60 mmol) was added as a solution in THF and the reaction mixture was stirred for 1 hr. The crude
mixture was filtered through a silica pad (dry column vacuum chromatography, 60 × 150 mm, chloroform/ethylacetate, 95:5, then 90:10). After evaporation, the crude product was dissolved in chloroform and chromatographed (silica, CH₂Cl₂ then CH₂Cl₂/ethylacetate, 99:1, then 97:3, 95:5). The resulting solid was crystallized from CHCl₃/cyclohexane to obtain pure porphyrin.

2.6. Synthesis of meso-tetramesitylporphyrin (MTMP)

MTMP was synthesized according to the reported procedure [3]. Freshly distilled pyrrole (0.694 mL, 10 mmol) and mesitaldehyde (1.475 mL, 10 mmol) were dissolved in 1 L of chloroform and purged with a stream of Ar gas for 10 minutes. 2.5 M of BF₃·Et₂O (3.3 mmol) was added to the reaction mixture with constant stirring. After 2 hr the mixture was quenched by the addition of one equivalent (0.460 mL, 3.3 mmol) of triethylamine and then DDQ (1.7g, 7.5 mmol) was added. The content was refluxed at boiling condition for an hour. The solvent was evaporated using a rotary evaporator and washed with methanol to remove polypyrrromethanes and quinol derivatives. The crude product was washed with dichloromethane and the filtrate was evaporated to dryness. The purple solid (meso-tetramesitylporphyrin) obtained was subjected to column chromatography on silica gel using dichloromethane and ethyl acetate mixture (9:1) as eluent. The yield was 540 mg (23%). ¹H NMR (CDCl₃) δ -2.51 (s, 2H, NH), 1.85 (s, 24H, o-CH₃) 2.62 (s, 12H, p-CH₃), 7.27 (s, 8H, m-ArH), 8.61 (s, 8H, β-pyrrole).
2.7. Synthesis of *meso*-tetrakis(4-nitrophenyl)porphyrin (MTNP)

MTNP was synthesized using the reported procedure for MTMP [3]. Freshly distilled pyrrole (0.694 mL, 10 mmol) and 4-nitrobenzaldehyde (1.51g, 10 mmol) were dissolved in 1 L of chloroform and purged with a stream of Ar gas for 10 min. 2.5 M of boron trifluoride-etherate complex (BF$_3$-Et$_2$O) (3.3 mmol) was added to the reaction mixture with constant stirring. After 2 hr the mixture was quenched by the addition of one equivalent (0.460 mL, 3.3 mmol) of triethylamine and then DDQ (1.7g, 7.5 mmol) added. The content was refluxed at boiling condition for an hour. The solvent was evaporated using a rotary evaporator and washed with methanol to remove polypyrromethanes and quinol derivatives. The crude product was washed with dichloromethane and the filtrate was evaporated to dryness. The purple solid (*meso*-tetramesitylporphyrin) obtained was subjected to column chromatography on silica gel using dichloromethane and ethyl acetate mixture (9:1) as eluent. The yield was 520 mg (21%). $^1$H NMR (CDCl$_3$) $\delta$ -2.84 (s, 2H, NH), 8.39, 8.67 (d, d, $J = 8.0$ Hz, 16H, C$_6$H$_4$), 8.81 (s, 8H, $\beta$-pyrrole). IR: 1500, 1330 (NO$_2$) cm$^{-1}$.

2.8. Preparation of charge transfer complexes of aromatic thiols with DDQ

The solid CT complexes of DDQ with different aromatic thiols were prepared by mixing 5 mmol of the donor in dichloromethane with 4 mmol of acceptor in the same solvent for 1:1 complex and 10 mmol of the donor in dichloromethane with 4 mmol of acceptor in the same solvent for 2:1 complex.
The mixture was stirred at room temperature for 2 hr. After evaporation of solvent, solid product was collected and washed with dichloromethane.

2.9. Preparation of MTMP thin film

A thin film of MTMP on glass plate was prepared using 0.01 M MTMP in dichloromethane by dip coating method. A clean glass plate (0.8 mm x 300 mm) was immersed in the MTMP solution at a withdrawal rate of 12 cm/min using home made stepper and dried at room temperature under nitrogen atmosphere. Standard dry HCl gas (19 ppm) diluted with nitrogen was used for J-aggregate formation. The MTMP thin film was exposed for a minute to hydrogen chloride (HCl) vapor to obtain the aggregated structure. The quantum yield of MTMP thin film and aggregates were determined using fluorescence lifetimes.

2.10. Preparation of TPPS thin film

A thin film of TPPS on glass plate was prepared using 0.01 M TPPS in 9:1 ethanol and water mixture by spin coating method. A clean glass plate (0.8 mm x 300 mm) was placed on a rotating plate with 3000 rpm and 0.1 mL of 0.001 M TPPS added to the surface. The plate was dried at room temperature under nitrogen atmosphere. Standard dry HCl gas (19 ppm) diluted with nitrogen was used to expose the TPPS thin film for J-aggregate formation. The quantum yield of TPPS thin film and aggregates were determined using fluorescence lifetimes.
2.11. Detection of HCl gas

The solid state sensor for HCl gas detection was fabricated by depositing a thin film of a porphyrin on cleaned glass plate (0.8 mm x 300 mm) using dip coating method. Clean glass plate was immersed in the MTMP solution at the rate of 12 cm /min and dried at room temperature under nitrogen atmosphere. A home made pulsed generator with a stepper at a withdrawal speed of 12 cm /min was used to deposit a thin film of porphyrin on glass plate. The same procedure was followed for sensor fabrication using meso-tetraphenylporphyrin (MTPP) and MTNP. The porphyrin deposited glass plate was dried at room temperature under nitrogen atmosphere for 10 min. Standard dry HCl gas (19 ppm) diluted with nitrogen was used and the concentration of HCl gas was controlled by mixing the standard gas with nitrogen. Mass flow controller was used to mix the desired amount of HCl gas with dry nitrogen. All measurements were performed at 30°C.

2.11.1. Flow cell set up for detection of HCl gas

![Flow cell diagram]

Figure 2.1. Experimental setup for detection of HCl gas.
2.12. References