CHAPTER 4

EXPERIMENTAL METHODS AND PROCEDURE

In the present chapter experimental methods and procedure for the preparation and characterization of 9,10-anthraquinone based organic compounds and their films have been described. The present chapter has been divided into five sections, namely

4.1 General procedure
4.2 Synthesis of 9,10-anthraquinone based organic compounds
4.3 Preparation of 9,10-anthraquinone based organic films
4.4 Physical measurements
4.5 Molecular device fabrication and characterization.

4.1 General Procedure

Melting points were measured in open glass capillary method using Veego precision Digital Melting Point apparatus (MP-D).\(^{1}\)H NMR spectra were recorded on Bruker AC-200 MHz spectrometer, using tetramethylsilane (TMS) as internal standard and CDCl\(_3\) as solvent. Chemical shifts are expressed as \(\delta\) (ppm) downfield from TMS and \(J\) values in Hz, respectively. Splitting patterns are indicated as \(s\): singlet, \(t\) : triplet, \(q\) : quartet and \(br\) : broad peak. The IR spectra were recorded on Shimadzu FTIR 8300 spectrometer in KBr and mass spectra were recorded on Shimadzu GCMS-QP-2000A spectrometer. The elemental analyses were performed on Perkin-Elmer 240C elemental Analyser. Column chromatography was conducted using silica gel 60-120 or 100-200 mesh. All solvents were purified prior to use.
4.2 Synthesis of organic compounds derived from 9,10-anthraquinone

The 9,10-anthraquinone based compounds: 1,8-bis-(3-hydroxy propylamino)-9,10-anthraquinone; 1-(3-hydroxy-propyl-amino)-910-anthraquinone; 1-(2-amino-ethylamino)-9,10-anthraquinone; 1,4-bis-(2-hydroxyethylamino)-9,10-antraquinone; 1,4-bis-(2-dimethylaminoethylamino)-9,10-anthraquinone are synthesized as described below.

4.2.1 Synthesis of 1,8-bis-(3-hydroxy propylamino)-9,10-anthraquinone

The solution of 1,8-dichloroanthraquinone (1g, 0.003 mol) and 3-amino-1-propanol (2.16g, .028 mol) in acetonitrile (25ml) containing potassium carbonate (996 mg) was refluxed at 90 °C for 28 hours. The completion of the reaction was monitored by thin layer chromatography. After completion of the reaction, the suspended solid was filtered off and the residue was washed with methanol. The combined filtrate and washings were distilled off under vacuum and the residue was crystallized from chloroform. The crude precipitates were column chromatographed over silica gel using hexane, chloroform, methanol and their mixtures as eluents to isolate pure 1,8-bis-(3-hydroxypropylamino)-9,10-anthraquinone. The yield of this process was 50%.

4.2.2 Synthesis of 1-(3-hydroxypropylamino)-9,10-anthraquinone

The solution of 1-chloroanthraquinone (1g, 0.004 mol) and 3-amino-1-propanol (2.5 g, 0.03 mol) in acetonitrile (25 ml) containing suspension of anhydrous potassium carbonate (570 mg) was refluxed with stirring at 363 K for 24-30 hours. After the completion of the reaction, the suspended solid was filtered off and the residue was washed with methanol. The combined filtrate and washings were distilled off under vacuum and residue was crystallized. The crystallized residue was again chromatographed on silica gel column by using hexane, chloroform, ethyl acetate and their mixtures as elements to isolate pure 1-(3-hydroxypropyl amino)-9,10-anthraquinone. The yield was 60%.

4.2.3 Synthesis of 1-(2-aminoethylamino)-9,10-anthraquinone

The solution of 1-chloroanthraquinone (1g,.004 mol) and ethylenediamine (3.48ml,.05mol) in acetonitrile (25 ml) containing suspension of anhydrous potassium carbonate (1.08g) was refluxed with stirring at 363 K for 24-30 hours.
After the completion of the reaction, the suspended solid was filtered off and the residue was washed with methanol and chloroform. The combined filtrate and washing were distilled off under vacuum and residue was crystallized. The crystallized residue was again chromatographed on silica gel column by using hexane, chloroform, ethyl acetate and their mixtures as eluents to isolate pure 1-(2-amino-ethylamino)-9,10-anthraquinone. The yield was 70%.

**4.2.4 Synthesis of 1,4-bis-(2-hydroxyethylamino)-9,10-antraquinone**

Reduction of 1,4-dihydroxyanthracene-9,10-dione with alkaline sodium dithionite in 1,4-dioxane resulted in formation of leucoquinizarin. The oxidative amination of leucoquinizarin with 2-dimethylaminoethyl amine gave desired compound. The yield was 75%.

**4.2.5 1,4-bis-(2-dimethylaminoethylamino)-9,10-anthraquinione**

Oxidative amination of leucoquinizarin with 2-aminoethanol gave this compound. The yield was 70%.

**4.3 Preparation of organic films derived from 9,10-anthraquinone**

The following steps have been taken to prepare the films of the 9,10-anthraquinone based compounds on glass substrates kept at different experimental conditions.

**4.3.1 Substrate preparation**

The properties of the films are greatly influenced by the nature of the substrate upon which films is to be grown. The blue star micro slides PIC-I obtained from polar industrial corporation Bombay (India) having dimensions 75x25x1.3 mm were used as glass substrates. The slides were thoroughly washed with detergent solution of sodium hydroxide and later with dilute nitric acid. The slides were washed with distilled water and then ultrasonically cleaned by ultrasonic cleaner VS-120 obtained from Vibronics (INDIA). The slides were then kept in desiccators for further use.

**4.3.2 Film Preparation**

The vacuum coating unit 12A4H supplied by Hind High Vacuum Co (India) was used for deposition of films. The coating system consists of vacuum chamber
having stainless steal base plate and bell jar. Figure 3.1 shows the outline diagram of vacuum coating unit. The base plate is fitted on to the three stage oil diffusion pump through liquid nitrogen trap. The oil diffusion pump is backed by two stage mechanical rotary pump. An electromagnetic isolation cum air admittance is provided just above the rotary pump to minimize the accidental back sucking of rotary pump oil in vacuum line and diffusion pump. Butterfly valves are provided to select the vacuum path to the chamber either direct or through diffusion pump. In addition to this the 12A4H unit is equipped with dual pirani gauge, penning gauge, 10 Amp-220 V AC supply for radiant heater, 100 Amp 20 volt and 200Amp 10 volt L.T supply to heat boat, filament or evaporation source directly or indirectly, 2.5 kV-500mA HT supply for DC sputtering and cleaning. Few Monitors and auto switches are employed in the monitor and to avoid accidents.

Two techniques have been used for the preparation of the films from 9,10-anthraquinone, namely thermal evaporation and Hot Wall technique.

4.3.2.1 Thermal evaporation technique

This method of evaporating the thin films has been very popular for long time. Various evaporation sources like helix, basket, boat, crucible etc usually made of refractory metal wires or sheets are used. The choice of evaporation source is made on the basis of nature and physical form of material to be evaporated. For thermal evaporation of organic compounds, a tungsten boat was fitted on LT electrodes. The substrate, glass slides, on which the films was to be deposited was place on the holder, while organic powder to be evaporated was taken into boat in pellet from. To form the pellets of organic compound a high pressure was applied using hydraulic press. To measure the thickness of the films the digital thickness monitor (DTM 101) obtained from Hind High Vacuum Co India was used. On attaining the vacuum of the order of $10^{-5}$ Torr, a constant current was passed through Tungsten boat mounted on LT electrodes. The thickness monitor continuously monitored the film thickness. When desired thickness was reached then evaporation was stopped. The thickness of the films was also measured after deposition, by using depth profiler (Dek Tek) and found to lie in range 1-1.6 μm. To anneal the films for some time radiant heater was switched on for some time.
4.3.2.2 Hot Wall Technique

Otero (1978) developed the Hot wall epitaxy technique (HWE) for IV-VI compounds. This technique allows the films to attain thermal equilibrium to a considerable extent under high vapour pressure with minimum loss of material. This technique helped to grow more ordered and of relatively higher conducting films than that obtained with thermal evaporation. Figure 4.2 represents the general outline for the HWE set up which was fabricated in the laboratory. The compound was placed at the bottom of the sealed quartz tube of HWE system. The substrate was kept over the open end at the top. The substrate acts as a lid to the closed tube. Radiant heater was switched on prior to film deposition so that better vacuum could be obtained. Different heaters were used to heat the compound, wall and substrate and their temperature were controlled independently using K-type thermocouples obtained from Omega Engg. USA. The whole apparatus was fitted onto the base plate of vacuum chamber of vacuum coating unit 12AH in such a way that substrate could be moved either way so that desired distance can be maintained. The tube was held in a straight position and organic material was taken into the tube and evacuated to a pressure of about $10^{-5}$ Torr. Prior to depositing of films entire vacuum chamber gadgets were heated upto 470K, to degas the chamber for one hour.

On attaining the required experimental conditions, the source heater was switched on and the substrate holder was moved on to the top of the tube such that it is effectively close to the tube and forms a closed system. After precalculated time, the substrate holder was raised above and moved aside. The thickness of the films was measured by depth profiler (Dek Tek) and found to lie in the range 1-1.6 μm.

4.4 Physical Measurements

This section provides different techniques used for measurement of structural, electrical and optical characterization of organic films deposited onto the glass substrate. The different methods for measurements of physical properties like electrical resistivity, carrier concentration and optical properties have been discussed in this section.

4.4.1 Structural Measurements
The structural measurements of the films were carried out by using Scanning Electron Microscopy (SEM) and X-ray diffraction (XRD). The JEOL JSM-6100 (Japan) scanning microscope and Phillips diffractometer were used for these purposes, respectively. For SEM analysis the films deposited on to the glass substrates were first coated with gold films (100Å) and then studies were carried out. X-ray diffractogram has been recorded in the range 5°-60° (2θ) at a scanning speed of 1° per minute. All these structural measurements were performed at room temperature.
4.4.2 Electrical resistivity

Two probe method was used to measure the resistivity of the films. To make this measurement a lower electrodes was deposited by evaporating silver using mask and then film was deposited. Silver paste was used for making the upper electrode. The resistivity measurements were carried out in the temperature range 295-415K at different substrate temperature. The ohmic nature of the contacts were established for the field applied during measurements. Fig. 4.3 shows the outline for the two probe set up. The resistivity of the film was calculated by using the expression

$$R = \rho \frac{L}{bt}$$

where ‘L’ is the distance between the electrodes, ‘b’ is the breadth and ‘t’ is the thickness of the film. The measurements of the film for electrical resistivity were carried out in vacuum cup designed in the laboratory. The cup is fitted with cryogen circulation and a heater capable of varying temperature of the films The steady state value of current was recorded at regular intervals of 5 K using an electrometer (Keithley 6517 A). Silver contacts were used to connect electrical leads to the films. The temperature of the sample was measured with K-type thermocouple obtained from Omega Engg. Inc (USA) fitted in the cup.

![Diagram of two probe setup](image)

**Figure 4.3 : Two probe set up for measurement of electrical resistivity**
4.4.3 Carrier concentration

The charge carrier concentration is determined using the relation (Wahed & Mankhly, 1996)

\[ n = 2(2\pi m^+ kT/h^2)^{3/2} \exp(-\Delta E/2kT) \]

Where \( m^+ \) is the effective mass of the charge carrier and is assumed to be equal to the real mass of the electron, \( \Delta E \) is the activation energy, \( k \) is Boltzmann’s constant and \( h \) is the Planck’s constant.

4.4.4 Optical Properties

In order to study the photo conversion behaviour, it is highly desirable to determine optical band gap of films. To study of optical properties, the transmittance and absorbance spectra of the samples were obtained at room temperature in the photoenergy range 1.12-4.13 eV by using UV-1601 PC (Shimadzu) spectrophotometer. The films samples obtained on the glass substrates were used as such for the optical measurements and the incident light was kept normal to their basal plane. The absorption coefficient \( \alpha \), was determined from the transmittance \( T \) by using the relation (Moss, 1959)

\[ T = (1-R)^2 \exp(-\alpha d) \]

The extinction coefficient (k) and refractive index (n) of films has also been determined from absorption coefficient and refractivity of organic materials.

4.5 Molecular Devices

The effort has been extended to fabricate molecular devices based on anthraquinones. For this fluorine doped tin oxide/anthraquinone/aluminium schottky barrier has been fabricated. The transparent fluorine doped tin oxide (FTO) layer having high optical transmittance and electrical conductivity has been used as window material for photovoltaic applications.

4.5.1 Synthesis of Molecular Devices

Spray pyrolysis technique (Athwal and Bedi, 1986) has been used for making FTO films. Figure 4.4 shows the outlines for the experimental set up. This technique involves the spraying of solution onto the hot substrate. Usually aqueous solution containing double salts of constituent atoms of desired compounds, dopant and some carrier liquid is used. In common practice the solution is sprayed by
atomizer using suitable carrier gas or ultrasonic sprayer (Mavrodiev et. al., 1984; Shanthi et. al., 1980). The sprayed droplet at hot substrate undergoes pyrolytic decompositon resulting in the formation of desired comound and some volatile byproducts. The byproducts escape whereas the atoms of the desired compounds stick to the substrate. The high substrate temperature provides the the thermal energy for recrystallization of the resulting compounds.

In present case an aqueous solution containing 0.6 M SnCl₄, 9 M isopropanol with different concentrations of NH₄F has been prepared. The so prepared solution was sprayed by an atomizer onto the glass substrate, kept at 720K using oxygen as carrier gas. The following chemical reaction ( Siefert, 1984; Athwal and Bedi, 1985) takes place

\[ \text{SnCl}_4 + 2\text{H}_2\text{O} \rightarrow \text{SnO}_2 + 4\text{HCl} \]

And SnO2 gets displaced over the substratre. The FTO/ anthraquinones/ Al devices have been prepared by depositing the anthraquinones layers using hot wall technique over the F:SnO₂ coated glass substrate kept at 348K temperature followed by aluminium (Al) layer to make the sandwitch type FTO / anthraquinone / Al device.

4.5.2 Current Voltage characteristics of Molecular devices

In order to measure current –voltage characterisics of molecular devices, the sample was mounted on the aluminium block and K-type thermocouple was fixed along with it. Dots of silver paste was applied over top electrodes to ensure better conduction. The current through the junction was measured by electrometer. The voltage from the power supply was increased linearly and corresponding current value recorded. Both dark and illuminated current voltage characterisitcs were recorded at room temperature. A 1000W halogen lamp was used for the illumination and intensity was recorded by Lux meter. The effect of functional derivatives of 9,10-anthraquinone on the J-V characterized were also measured.
Figure 4.4: Spray Pyrolysis set up