

CHAPTER 2
MATERIALS AND INSTRUMENTAL TECHNIQUES

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2.1 Chemicals and solvents:

All chemicals employed in the present study were of analytical grade. Solvents were purified and dried using standard procedures. The materials were procured from Tokyo Kasei, Japan and Lancaster Chemicals, USA. Silica (60-120 mesh) from Spectrochem was used for chromatographic separation. Silica gel G (E-Merck, India) was used for thin layer chromatography (TLC).

2.2 Instruments:

Molar conductance: Molar conductances of the compounds were determined in dichloromethane (10^{-3}M) at room temperature using a MAC-554 conductometer (Macroscientific Works, India).

UV-visible spectroscopy: UV visible absorption spectra of the compounds in chloroform/dichloromethane at different concentrations were recorded on a Shimadzu UV-1601PC spectrophotometer (Shimadzu, Asia Pacific, Pte. Ltd., Singapore). Spectra of the complexes were recorded at room temperature in the wavelength range 200-800nm.

Infrared Spectroscopy: Infrared spectra were recorded on a Perkin Elmer BX series spectrometer on KBr disc in the $400\text{-}4000\text{ cm}^{-1}$ range.

NMR: The ^1H and ^{13}C NMR spectra were recorded on Bruker Advance 400 MHz (Bruker, Kolkata, India) spectrometer in CDCl_3 (chemical shift in δ) solution with Tetramethylsilane (TMS) as internal standard.

CHN analysis: The C, H and N analyses were carried out using Carlo Erba 1108 elemental analyser (Waltham, MA, USA).

FAB mass analysis: Mass spectra were recorded on a JEOL SX-102 (JEOL, Tokyo, Japan) spectrometer with fast atom bombardment.

Magnetic susceptibility measurements: The magnetic susceptibility measurements were carried out at room temperature on Cahn-Faraday electrobalance using

Hg[Co(NCS)₄] as the calibrant or the magnetic measurements were made using SQUID equipment.

Cyclovoltammetry measurement: Cyclic voltammetric (CV) measurements were performed using a computer controlled CHI 660C electrochemical workstation with Pt-disc electrodes with reference to Ag/AgCl using (n-Bu₄N)ClO₄ as supporting electrolyte. All measurements were carried out under nitrogen at 298K in 0.1M acetate buffer of pH 4.7 with a scan rate 0.1V/s.

Thermal Microscopy: The thermal behaviour of the compounds is studied using a thin film of liquid crystalline material sandwiched between glass plate and a cover slip kept in the path of white light beam crossed with polarizers with a polarizing microscope (Nikon optiphot-2-pol, Nikon Corporation, Tokyo, Japan) attached with Instec hot and cold stage HCS302, with STC200 temperature controller configured for HCS302. The accuracies in temperatures are 0.1°C. Since the sample is birefringent, interference colors appeared which resulted in beautiful textures characteristic of molecular arrangement. The phase transition temperatures were detected and associated textures of different liquid crystalline phases were observed. The textures were recorded using photo micrographic equipment attached with the polarizing microscope. The liquid crystalline properties were established by thermal microscopy and the phase transitions were confirmed by differential scanning calorimetry.

Differential Scanning Calorimetry: The thermal behaviour of the compounds was studied using a Perkin-Elmer DSC (Perkin Elmer International, Schwerzenbach, Switzerland) Pyris-1 spectrometer with a heating or cooling rate of 10°C/min.

PXRD study: Variable temperature powder X-ray diffraction (PXRD) studies were carried out using an image plate detector (Mac Science, Japan) equipped with double mirror focusing optics with the sample contained in a Lindmann capillary tube or variable temperature powder X-ray diffraction (PXRD) of the samples were recorded on a Bruker D8 Discover instrument using Cu-K α radiation.

Photoluminescence measurement: Photoluminescence spectra were recorded on a Shimadzu RF-5301PC spectrophotometer. The fluorescence quantum yield in dichloromethane was determined by dilution method using 9, 10-diphenyl anthracene as standard.

DFT study: Quantum chemical calculations were carried out using density functional theory (DFT) as implemented in DMol3package or Gaussian 09 program at B3LYP level.