Chapter 2

Experimental Methodology

Overview: This chapter highlights the methods used for synthesis and characterization of polynuclear metal clusters and cages (with transition as well as lanthanide metals), metal organic frameworks and their various applications.

2.1. Syntheses of ligands and complexes

All reagents and chemicals were purchased from commercial sources and were used without further purifications.

2.1.1 Synthesis of ligands: The procedure for synthesis of all ligands was mentioned in the respective chapter.

2.1.2 Syntheses of metal complexes: The metal complexes were synthesized either layering or by refluxing techniques and mentioned in the respective chapter.

2.1.3 Syntheses of metal organic frameworks: Most of the metal organic frameworks were synthesized by hydrothermal/solvothermal procedures, *i.e.*, reactions were carried out in closed vessels under autogenous pressure above the boiling point of the solvent. For the present context 25 mL sealed Teflon lined autoclaves were used as closed vessels. Different solvents (*e.g.* methanol, Ethanol, water, dimethyl formamide, dimethylsulphoxide etc.) or mixture of solvents in different ratios were used for different reactions. Temperature as well as the duration of reaction was varied for synthesis of different complexes.

2.2 Characterization of complexes

The ligands and complexes were characterized by following methods:

IR spectroscopy- FT-IR spectra were obtained for all the complexes on a Nicolet MAGNA-IR 750 spectrometer with samples prepared as KBr pellets.

Elemental analysis- C, H and N microanalyses for all the complexes were carried out with a 2400 Series-II CHN Analyzer, Perkin–Elmer, USA.

NMR spectroscopy-Room temperature NMR spectra were recorded on a Bruker Avance 400/500 MHz spectrometer in DMSO solvent.

Thermogrametric Analysis-Thermal analyses were carried out with a TA Instruments SDT Q600 under nitrogenous atmosphere with a flow rate of 100 mL/min in a platinum crucible at a rate of 10 °C/min.

Powder X-ray diffraction-Powder X-ray diffraction (PXRD) measurement was carried out using a Bruker AXS diffractometer (D8 advance) using Cu-Kα radiation (λ= 1.5406 Å), a generator voltage of 40 kV and current 30 mA . Sample was scanned in the range of 2θ= 0-100° with the scan rate 1s/step.

UV−Vis Spectrascopy-UV−visible studies were performed in PerkinElmer Lambda 950 UV−vis instrument.

Fluorescence Spectrascopy- Fluorescence spectra were recorded using a Perkin Elmer luminescence spectrophotometer at 298 K in different solvents.

Diffuse Reflectance Spectra- UV-Vis diffuse reflectance spectra (DRS) were recorded at ambient temperature on a Cary-500 UV-Vis Spectrophotometer along with the usage of different compartment for DRS.

Photoluminescence Spectrascopy-The photoluminescence measurements of solid samples were performed with the Horiba Jobin Yvon Fluoromax-3 spectrometer using steady-state 450 W Xe lamps as the excitation source.

Magnetic Studies-Magnetic data of polycrystalline samples were collected by MPMS (Evercool, 7T) by Quantum Design.

Mass spectrascopy-Mass spectra were recorded on a Q-ToF Micro YA263 high resolution (Waters Corporation) mass spectrometer by positive ion mode electrospray ionization and the spectra were collected in methanol, ethanol, acetonitrile or mixture of solvents.

GC Experiment- GC analysis were performed on Perkin-Elmer gas chromatograph clarus-580 instrument with a thermal conductivity detector and a 5 Å molecular sieve column (2 mm × 2 mm) using Argon as carrier gas.

HRTEM-High resolution transmission microscopy were carried by JEOL 2010EX operated at an accelerating voltage of 200 kV fitted with a CCD camera and the sample is prepared by droping of 10^{-3} M solution on a 300 mesh carbon-coated copper grid, dried under vacuum.

FESEM-FESEM images were JEOL-6700F microscope instrument and the sample is prepared by dropping solution on a glass cover slip, dried under vacuum. Rheology experiment was performed in SDT Q series Advanced Rheometer AR 2000.

Gas Adsorption Studies-Brunauer–Emmett–Teller (BET) surface area were measured using Quantachrome automated gas sorption data acquisition and reduction instruments version 3.0 under bath temperature 77.35 K.

2.3 X-ray crystallography: X-ray diffraction intensities for the complexes were collected either at 120K or at room temperature on Bruker Smart 6K/Bruker APEX-2 CCD diffractometer using Mo-K_α radiation and processed using SAINT. The structures were solved by direct methods in SHELXS and refined by full matrix least squares on F^2 in SHELXL.[1]

2.4 Reference

(1) Sheldrick, G. M. SHELX97, University of Göttingen, Göttingen, Germany, **1997**.