Chapter 2

MATERIALS AND METHODS

2.1 Materials

2.1.1 Chemical substances

Materials from Aldrich Chemical Company, Inc.

1. Ammonium hexafluorophosphate, NH_4PF_6, A.R. grade
2. *N,N*-dimethyl-1,4-nitrisoaniline, A.R. grade
3. *N,N*-diethyl-1,4-nitrisoaniline, A.R. grade
4. Nitrosobenzene, A.R. grade

Materials from BDH Laboratory Supplies, Poole

1. Silver nitrate, $AgNO_3$, A. R. grade

Materials from Carlo Erba

1. *N,N*-dimethylformamide, A.R. grade
2. Cobalt chloride, $CoCl_2.6H_2O$, A.R. grade

Materials from Fluka AG, Switzerland

1. 2-aminopyridine, C_5H_5N, A.R. grade
2. Ruthenium(III)chloride, $RuCl_3.3H_2O$, A.R. grade

Materials from Hopkin and Williams

1. Ammonium tetrafluoroborate, NH_4BF_4, A.R. grade

Materials from Merck

1. 2-aminopyrimidine, $C_4H_5N_3$, A.R. grade

Materials from Riedel-de Haen

1. Lithium chloride, LiCl, A.R. grade

2.1.2 Solvents

Solvents from Lab-Scan

1. Acetone, CH_3COCH_3, A.R. grade
2. Acetonitrile, CH_3CN, A.R. grade
3. Chloroform, $CHCl_3$, A.R. grade
4. Dichloromethane, CH_2Cl_2, A.R. grade
5. Dimethyl sulphoxide, DMSO, A.R. grade
6. Hexane, C_6H_{14}, A.R. grade

Solvents from Merck

1. Ethanol, C_2H_5OH, A.R. grade
2. Hydrochloric acid, HCL, A.R. grade
3. Methanol, CH_3OH, A.R. grade
4. Sodium chloride, NaCl, A.R. grade
5. Sodium hydroxide, NaOH, A.R. grade
6. Tetrabutylammonium hexafluorophosphate, $[NBu_4]PF_6$, A.R. grade

The solvents, dichloromethane, hexane and ethyl acetate, which were reagent grade, used for column chromatography were purified by distillation.

2.2 Instruments

2.2.1 Melting Point Apparatus

Melting Point of the ligands and the complexes were measured on an Electrothermal melting point apparatus (Electrothermal 9100).

2.2.2 Elemental Analysis

Elemental analysis data were obtained by using Carlo Erbra EA 1108 Elemental Analyser (University of Bristol, UK.).

2.2.3 The Electrospray (ES) and the fast-atom bombardment (FAB) Mass Spectrometry

Electrospray (ES) mass spectra were measured on a VG Quattro triple quadrupole system mass spectrometer (University of Wollogong, Australia).

Fast-atom bombardment (FAB) mass spectra were recorded on a VG Autospec instrument (University of Bristol, UK.).

2.2.4 Infrared Spectroscopy

Infrared spectra were obtained by using a Perkin Elmer Spectrum GX FT-IR spectrophotometer from 370 to 4,000 cm^{-1}. All samples were prepared in the KBr pellets.

2.2.5 UV-Visible Absorption Spectroscopy

Ultraviolet and visible absorption spectra were recorded on a Hewlett Packard 8425A diode array spectrophotometer.

2.2.6 Nuclear Magnetic Resonance Spectroscopy

1D and 2D NMR spectra were recorded in acetone-d_6 with a FT-NMR Varian UNITY SNOVA 500-MHz with Me_4Si as an internal standard.

2.2.7 Cyclic Voltammetry

Electrochemical experiments were performed using a EChem 5.1. A glassy carbon working electrode, platinum wire auxilliary electrode, and a platinum reference electrode were used in three-electrode configuration. Electrochemical measurements were carried out in 0.1 M tetra-n-butylammonium hexafluorophosphate ($[NBu_4]PF_6$) in CH_3CN. Ferrocene was added at the end of each experimental as an internal standard. All potentials were quoted vs the ferrocene/ferrocenium couple (Fc/Fc^+). The solvent was used as received. The nitrogen gas was bubbled through the solution prior to each measurement.

2.2.8 X-ray Diffractometer

The X-ray structure of the [Protonated 2-(phenylazo)pyridine and protonated 2-(4-hydroxyphenylazo)pyridine (3:10)]tetrafluoroborate was determined by CCD X-ray diffractometer with Siemens Smart program.

2.3 Syntheses of ligands

2.3.1 Synthesis of 2-(phenylazo)pyridine (azpy)

The synthesis of 2-(phenylazo)pyridine ligands was prepared by modified literature method (Krause and Krause, 1980).

2-Aminopyridine (0.95 g, 0.01 mol) reacted with nitrosobenzene (1.08 g, 0.01 mol) in the mixture of 25M NaOH and 10 mL of benzene. The reaction mixture was warmed on the water bath for 45 min. The mixture was extracted with 3x5 mL of benzene. The solvent was removed and the residue was purified by column chromatography. A mixture of hexane and ethyl acetate was used as eluent. The orange band was collected and solvents were removed. The yield was 0.64 g (35%).

2.3.2 Synthesis of 2-(4'-*N*,*N*-dimethylaminophenylazo)pyridine (dmazpy)

2-Aminopyridine (0.94 g, 0.01 mol) was added to a solution of 11.6 mL of NaOH (25 M) in hot toluene. Then, *N*,*N*-dimethyl-1,4-nitrosoaniline (1.50 g, 0.01 mol) was added to the mixture. After this period the mixture was refluxed for 9 h. The reaction mixture was extracted with 250 mL of toluene. The solvent was removed and the residue was purified by column chromatography. A mixture of hexane and ethyl acetate was used as eluent. The red band was collected and solvents were removed. The yield was 0.63 g (28%).

2.3.3 Synthesis of 2-(4'-*N,N*-diethylaminophenylazo)pyridine (deazpy)

The 2-(4'-*N,N*-diethylaminophenylazo)pyridine was synthesized by using the same procedure as 2-(4'-*N,N*-dimethylaminophenylazo)pyridine ligand. But *N,N*-diethyl-1,4-nitrosoaniline (1.60 g, 0.01 mol) was replaced *N,N*-dimethyl-1,4-nitroso aniline. The yield was 0.32g (12.7%).

2.3.4 Synthesis of 2–(phenylazo)pyrimidine (azpym)

The 2-(phenylazo)pyrimidine was was synthesized by using the similar procedure as 2-(phenylazo)pyridine. But 2-aminopyrimidine was used instead of 2-aminopyridine. The yield was 0.10 g (27%).

2.3.5 Synthesis of 2-(4'-*N,N*-diethylaminophenylazo)pyrimidine (deazpym)

The 2-(4'-*N,N*-diethylaminophenylazo)pyrimidine was synthesized by using the similar procedure as 2-(phenylazo)pyridine. But 2-aminopyrimidine and *N,N*-dimethyl-1,4-nitrosoaniline were used instead of 2-aminopyridine and nitrobenzene, respectively. The yield was 0.01 g (5.33%).

2.3.6 Synthesis of [Protonated 2-(phenylazo)pyridine and protonated 2-(4-hydroxy phenylazo)pyridine (3:1)]tetrafluoroborated

Concentrated HCl 2.5 mL was added to the aqueous solution containing $CoCl_2.H_2O$ 0.5 mmol. 2-(Phenylazo)pyridine (azpy) 1.5 mmol in ethanolic solution was added to the cobalt solution. The mixture was stirred at room temperature for 10 min. Then 30% H_2O_2 3.5 mL and NH_4BF_4 2.5 mmol were added to the solution

mixture. Single crystals of the protonated azpy were grown at 25°C by slow diffusion of hexane into the reaction mixture. The yield was 0.21 g (54.84%)

2.4 Syntheses of complexes

2.4.1 Synthesis of *cis*-$Ru(phen)_2Cl_2$

The *cis*-$Ru(phen)_2Cl_2$ complex was prepared by using literature method. (Sullivan, *et al.*, 1978)

$RuCl_3.3H_2O$ (0.50 g, 2.4 mmol), 1,10-phenanthroline (0.95 g, 5 mmol) and LiCl (0.03 g, 0.6 mmol) were heated at reflux in reagent grade dimethylformamide 30 mL for 8 h. After the reaction mixture was cooled to room temperature, 70 mL of acetone was added and the resultant solution cooled at 0°C overnight. The solid was filtered and washed with 75 mL of water followed by 75 mL of diethyl ether. The yield was 0.45 g (33.8%).

2.4.2 Synthesis of $[Ru(phen)_3](BF_4)_2$

cis-$[Ru(phen)_2Cl_2]$ (0.11 g, 0.2 mmol) and 1,10-phenanthroline (0.03 g, 0.15 mmol) were added to dimethylformamide 25 mL. The solution was heated at reflux with stirring for 4 h, evaporated to dryness and dissolved in a 20 mL of ethanol. A saturated aqueous NH_4BF_4 (0.05 g, 0.2 mmol) was added to the solution. The yield was 0.01 g (77.38%).

2.4.3 Synthesis of $[Ru(phen)_2azpy](BF_4)_2$

cis-$[Ru(phen)_2Cl_2]$ (0.06 g, 0.1 mmol), azpy (0.03 g, 0.15 mmol) and $AgNO_3$ (0.04 g, 0.15 mmol) were suspended in 20 mL of ethanol and water (3:1, v/v). Then, this mixture was degassed by bubbling the argon gas for 10 min and refluxed for 2 h. AgCl was filtered from the reaction mixture. An aqueous solution of NH_4BF_4 (0.04 g, 0.2 mmol) and ethanol 15 mL were added to the solution. It was cooled to 4°C in a refrigerator. After 3 days, the brown-red solid was collected and washed with a small amount of hexane, water and ether respectively, then dried at 110°C. The yield was 0.07 g (81.10 %).

2.4.4 Synthesis of $[Ru(phen)_2dmazpy](PF_6)_2$

This complex was prepared by using the same method as $[Ru(phen)_2azpy](BF_4)_2$ complex. The azpy ligand and NH_4BF_4 were replaced by dmazpy ligand and NH_4PF_6, respectively. The yield was 0.09 g (92.04 %).

2.4.5 Synthesis of $[Ru(phen)_2deazpy](PF_6)_2$

This complex was prepared by using the same method as $[Ru(phen)_2$ - dmazpy$](PF_6)_2$ complex. The dmazpy ligand was replaced by deazpy ligand. The yield was 0.09 g (89.55%).

2.4.6 Synthesis of $[Ru(phen)_2azpym](PF_6)_2$

This complex was prepared by using the same method as $[Ru(phen)_2dmazpy](PF_6)_2$ complex. The dmazpy ligand was replaced by azpym ligand. The yield was 0.08 g (90.3 %).

2.4.7 Synthesis of $[Ru(phen)_2deazpym](PF_6)_2$

This complex was prepared by using the same method as $[Ru(phen)_2$ - dmazpy$](PF_6)_2$ complex. The dmazpy ligand was replaced by deazpym ligand. The yield was 0.08 g (81 %).