Chapter 2

MATERIALS AND METHODS

2.1 Materials

2.1.1 Chemical substances

Materials from Fluka

1. 2,2′-Bipyridine, $C_{10}H_8N_2$, A.R. grade
2. 2-aminopyrimidine, $C_4H_5N_3$, A.R. grade
3. nitrosobenzene, C_6H_5NO, A.R. grade
4. Ammonium chloride, NH_4Cl, A.R. grade

Materials from Merck

1. Silica gel 60 (0.040-0.063 nm) GF_{254}
2. Sodium hydroxide, NaOH, A.R. grade

Materials from Aldrich

1. 2-aminopyridine, $C_5H_6N_2$, A.R. grade
2. Nitrosobenzene, C_6H_5NO, A.R. grade
3. *N,N*-dimethyl-4-nitrosoaniline, $C_8H_{10}N_2O$, A.R. grade
4. *N,N*-diethyl-4-nitrosoaniline, $C_{10}H_{14}N_2O$, A.R. grade
5. Ruthenium(III) chloride hydrate, $RuCl_3 \cdot 3H_2O$, A.R. grade

Material from Riedel-de Haen

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

Material from Hopkin & Williams

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

2.1.2 Solvents

Solvents from Lab-scan analytical sciences

1. Dimethyl sulfoxide, $(CH_3)_2SO$, A.R. grade
2. Acetonitrile,CH_3CN, A.R. grade
3. Toluene, C_7H_8, A.R. grade
4. Hexane, C_6H_{12}, A.R. grade
5. Methanol, CH_3OH, ,A.R. grade

Solvents from Analytical Carlo Erba

1. Chloroform, $CHCl_3$, A.R. grade
2. Ethyl acetate, $C_4H_8O_2$, A.R. grade
3. *N,N*-dimethylformamide, C_3H_7NO, A.R. grade

Solvents from Merck

1. Acetone, C_3H_6O, A.R. grade
2. Dichloromethane, CH_2Cl_2, A.R. grade
3. Absolute ethanol, C_2H_5OH, A.R. grade

Solvent from T.J. Baker

1. Ether, $(C_2H_5)_2O$, A.R. grade

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

2.2 Instruments

2.2.1 Melting point of all compounds were measured on an Electrothermal melting point apparatus (Electrothermal 9100).

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

2.2.3 Electrospray (ES-MS) mass spectra were measured on VG Qauttro triple qaudrupole system mass spectrometer (Wollogong University, Australia) and Fast-atom bombardment (FAB) mass spectra were recorded on a VG Autospec instrument (University of Bristol).

2.2.4 Infrared spectra were recorded on a Perkin Elmer Spectrum GX FT-IR spectrophotometer from 370 to 4000 cm^{-1}. All samples were prepared in the KBr pellets.

2.2.5 Nuclear magnetic resonance spectra (^{1}H, ^{13}C NMR, ^{1}H ^{1}H COSY and HMQC) were recorded in acetone-d_6 on a Varian UNITY SNOVA 500-MHz FTNMR spectrometer at ambient temperature. Tetramethylsilane (TMS) was used as an internal reference.

2.2.6 UV-Visible absorption spectra were recorded in the range 200-820 nm by Hewlett Packard 8452A array spectrophotometer and SPECORD S100 spectrophotometer.

2.2.7 Electrochemical measurements were carried out using cyclic voltammetric technique. The mesurements were obtained from EChem 1.5.1. Cyclic voltammograms were obtained using a glassy carbon working electrode, a platinum disc auxiliary electrode and a platinum wire reference electrode. At the end of each experiment, ferrocene was added as an internal standard. All potentials were pouted vs the ferrocene/ferrocenium couple (Fc/Fc^{+}). The supporting electrolyte was tetrabutylammonium hexafluorophosphate (TBAH) in acetonitrile (0.1 M). The argon gas was bubbled through the solution prior to each measurement.

2.3 Syntheses of ligands

2.3.1 2-(phenylazo)pyridine (azpy)

The synthesis of 2-(phenylazo)pyridine ligand 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 mmol) 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 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 25M NaOH in hot toluene. Then, *N*,*N*-dimethyl-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 5x50 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 2-(4′-*N*,*N*-diethylaminophenylazo)pyridine (deazpy)

This ligand was prepared by similar procedure to that of dmazpy ligand, except that *N*,*N*-dimethyl-4-nitrosoaniline was replaced by an equivalent amount of *N*,*N*-diethyl-4-nitrosoaniline (1.60 g, 0.01 mol). The yield was 0.32 g (13 %, mp 109-110 °C).

2.3.4 2-(phenylazo)pyrimidine (azpym)

The 2-(phenylazo)pyrimidine was synthesis 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 2-(4′-*N,N*-diethylaminophenylazo)pyrimidine (deazpym)

The 2-(4′-*N,N*-diethylaminophenylazo)pyrimidine was synthesis by using the similar procedure as 2-(phenylazo)pyridine. But 2-aminopyrimidine and *N,N*-diethyl-4-nitrosoaniline were used instead of 2-aminopyridine and nitrosobenzene, respectively. The yield was 0.01 g (5 %, mp 96-97 ^{o}C).

2.4 Syntheses of complexes

2.4.1 *cis*-$Ru(bpy)_2Cl_2$

This compound was prepared by a published method (Sullivan, *et al.*, 1978) with a modified purification procedure (Ji, *et al.*, 2000). Commercial $RuCl_3.3H_2O$ (1.311 g, 5 mmol), 2,2′-bipyridine (1.510 g, 10 mmol), and LiCl (2.105 g, 50 mmol) were heated by refluxing in dimethylformamide (25 mL) for 8 h. The reaction was stirred magnetically throughout this period. The reaction mixture was cooled to room temperature and a mixture of 200 mL 1:1 acetone-water was added. Dark green crystals were obtained by filtration. The solid was added into 200 mL water and stirred for 10 h followed by filtration. The product was washed three times with 25-mL portions of water followed by three 25-mL portions of ether, and then it was dried by suction. The yield was 80 %.

2.4.2 $[Ru(bpy)_2azpy](BF_4)_2$

The following modification of the preparation of this complex developed by Goswami (Goswami, *et al.*, 1981) was utilized to give good yields of the complex. The $Ru(bpy)_2Cl_2.2H_2O$ complex (0.121 g, 0.25 mmol) was suspended in a 1:1 (volume) water-methanol (40 mL) and heated for 10 min. An aqueous solution (10 mL) of $AgNO_3$ (0.087 g, 0.51 mmol), and 2-phenylazopyridine(Azpy) ligand (0.048 g, 0.26 mmol) in methanol (10 mL) were added, and then Ar gas was purged through the hot solution for 15 min. The reaction mixture was refluxed for 2 h. The solution turned violet and red. Then AgCl was filtered off. An excess ligand of azpy was extracted with hexane. The solution was evaporated and the residue was extracted with dichloromethane. The solvent was removed from the red solution by a rotary evaporator. The dried product was dissolved in a 10 mL of hot water and the aqueous solution (2 mL) of NH_4BF_4 (0.087 g, 0.83 mmol) was added. The solution was standed overnight at room temperature. The red solid was collected by suction filtration and washed with hexane followed by ether. The yield was 81 %. The red solid was recrystallized in acetonitrile and toluene.

2.4.3 $[Ru(bpy)_2dmazpy](BF_4)_2$

The dmazpy analogue was prepared using the same reactant stoichiometry and procedure except that the reaction mixture was refluxed for 6 h prior to the filtration of AgCl. The yield was 80 %.

2.4.4 $[Ru(bpy)_2deazpy](BF_4)_2$

The complex was obtained by a procedure similar to that described for dmazpy complex. Only 2-(4′-*N*,*N*-dimethylaminophenylazo)pyridine (dmazpy) was

replaced by an equivalent amount of 2-(4′-*N*,*N*-diethylaminophenylazo)pyridine (deazpy). The yield was 82 %.

2.4.5 $[Ru(bpy)_2azpym](BF_4)_2$

The complex was obtained by a procedure similar to that described for the azpy complex. Only 2-(phenylazo)pyridine (azpy) was replaced by an equivalent amount of 2-(phenylazo)pyrimidine (azpym). The yield was 85 %. The red solid was recrystallized in 1:2 (volume) acetonitrile-toluene.

2.4.6 $[Ru(bpy)_2deazpym](BF_4)_2$

The complex was prepared in a manner similar to that reported previously for $[Ru(bpy)_2dmazpy](BF_4)_2$ but using 2-(4′-*N*,*N*-diethylaminophenylazo)pyrimidine (deazpym) in place of dmazpy ligand. The yield was 78 %.

2.5 Methods for structures determination

2.5.1 Electrospray and Fast-atom bombardment mass spectrometry (ES-MS and FAB-MS)

Mass spectrometry is useful technique to confirm molecular structure of compounds by considering their m/z values. The ES technique has been developed to study inorganic and organometallic structures.

2.5.2 Infrared spectroscopy (IR)

IR is commonly used to detect characteristic frequencies of functional groups in compounds. The compounds absorb the infrared frequency range and show vibrational modes of molecule at different frequencies. For this research complexes absorb in the IR region (4000-370 cm^{-1}).

2.5.3 Nuclear Magnetic Resonance spectroscopy (NMR)

NMR is another technique to identify structure of compounds. It is related to molecular arrangement. The chemical shifts (δ) data provide information concerning the electron density of a giving molecules. The resonance frequency of proton is related to its environment. However, other features also affect NMR parameters.

^{1}H NMR spectra exhibit the total number of protons in each complex and their chemical shifts are related to position in complexes which were assigned from ^{1}H-^{1}H COSY spectra. Furthermore, the ^{13}C NMR signals were assigned from HMQC spectra.

2.5.4 UV-Visible absorption spectroscopy (UV-Visible)

UV-Visible absorption is a roughly technique to characterize complexes but useful for describing colored. The chromophoric groups in compounds give rise to absorption to the ultra-violet and visible region (200-800 nm). The colors of transition -metal compounds are usually attributed to electronic transitions involving orbitals. These transitions are of two main types. The first type is "d-d transition" which gives pale colors, an the other type is the "charge transfer transition" which gives dark colors.

2.5.5 Cyclic Voltammetry (CV)

The cyclic voltammetry is an electrochemical method which leads to the knowledge of redox phenomena. It shows current-potential curve, which is called cyclic voltammogram. In general, a typical voltammetric experiment utilizes three types of electrodes (Eklund and Bond, 1998).

The working electrode is the electrode at which the reaction of interest takes place, e.g. the simple one-electrode oxidation-reduction processes are given below.

$$A \rightarrow A^{+} + e^{-} \quad \text{(oxidation)}$$

$$B + e^{-} \rightarrow B^{-} \quad \text{(reduction)}$$

These electrode are typically made of inert and electrically conducting material. The common electrodes are made of platinum and some forms of carbon (i.e. glassy carbon or graphite).

The reference electrode provides a fixed reference couple against the potential of working electrode measured, e.g. the Ag/Ag^{+} electrode which the potential are accurately known relative to the standard hydrogen electrode (SHE).

The counter/auxiliary electrode is consists of a large surface area piece of platinum (wire or gauze) or carbon (disc or rod) placed directly into the test solution. Since the current flows through the counter electrode, it must have sufficiently large surface area relative to working electrode to prevent limitation of current flowing in the circuit. The current measured in a voltammetric experiment flows between the working and counter electrode.