

Chapter 2

MATERIALS AND METHODS

2.1 Materials

2.1.1 Chemical substances

Materials from Aldrich Chemical Company, Inc.

Ammonium hexafluorophosphate, NH_4PF_6 , A.R. grade

Nitrosobenzene, A.R. grade

Materials from BDH Laboratory Supplies, Poole

Silver nitrate, AgNO_3 , A.R. grade

Materials from Carlo Erba

N,N-dimethylformamide, A.R. grade

Materials from Fluka AG, Switzerland

2-Aminopyridine, $\text{C}_5\text{H}_5\text{N}_2$, A.R. grade

2-Aminopyrimidine, $\text{C}_4\text{H}_5\text{N}_3$, A.R. grade

Ruthenium(III)chloride trihydrate, $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$, A.R. grade

2,2'-Bipyridine, $\text{C}_{10}\text{H}_8\text{N}_2$, A.R. grade

Materials from Hopkin and Williams

Ammonium tetrafluoroborate, NH_4BF_4 , A.R. grade

Materials from Merck

Silica gel 60 (0.040-0.063 nm) GF_{254}

1,10-Phenanthroline, $\text{C}_{12}\text{H}_8\text{N}_2 \cdot \text{H}_2\text{O}$, A.R. grade

Sodium hydroxide, NaOH , A.R. grade

Sodium chloride, NaCl, A.R. grade

Tetrabutylammonium hexafluorophosphate, [NBu₄]PF₆, A.R. grade

Materials from Riedel-de Haen

Lithium chloride, LiCl, A.R. grade

2.1.2 Solvents

Solvents from Lab-Scan analytical sciences

Acetone, CH₃COCH₃, A.R. grade

Acetonitrile, CH₃CN, A.R. grade

Chloroform, CHCl₃, A.R. grade

Dichloromethane, CH₂Cl₂, A.R. grade

Dimethyl sulfoxide, DMSO, A.R. grade

Hexane, C₆H₁₄, A.R. grade

Solvents from Merck

Ethanol, C₂H₅OH, A.R. grade

Hydrochloric acid, HCl, A.R. grade

Methanol, CH₃OH, A.R. grade

Solvents from J. T. Baker

Ether, (C₂H₅)₂O, A.R. grade

The solvents for using with column chromatography such as dichloromethane, hexane and ethyl acetate were purified by distillation prior to use.

2.2 Instruments

2.2.1 Melting Point Apparatus

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

2.2.1 Elemental Analysis

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

2.2.3 The Fast-atom bombardment (FAB) Mass Spectrometry

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

2.2.4 Infrared Spectroscopy

Infrared spectra were measured on 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 measured on UV-Vis Spectrophotometer SPECORD S100.

2.2.6 Nuclear Magnetic Resonance Spectroscopy

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

2.2.7 Cyclic Voltammetry

Electrochemical experiments were measured using MacLab (4e AD Instruments) with potentiostat (Serial No p068). The program was EChem 1.5.1. A glassy carbon working electrode, platinum wire auxiliary electrode, and platinum reference electrode were used in three-electrode configuration. The supporting electrolyte was tetra-*n*-butylammonium hexafluorophosphate ($[\text{NBu}_4]\text{PF}_6$) in CH_3CN . Ferrocene was added at the end of each experiment as an internal standard. All potentials were quoted vs the ferrocene/ferrocenium couple (Fc/Fc^+). The solvent was used as received. The argon gas was bubbled through the solution prior to each measurement.

2.2.8 X-ray Diffractometer

The X-ray structure of $[\text{Ru}(\text{azpy})_3](\text{PF}_6)_2$, $[\text{Ru}(\text{azpy})_2\text{bpy}](\text{PF}_6)_2$ and $[\text{Ru}(\text{azpy})_2\text{phen}](\text{BF}_4)_2$ complexes were determined by Smart APEX CCD diffractometer.

2.3 Syntheses of ligands

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

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

2-Aminopyridine (0.45 g, 4.78 mmol) reacted with nitrosobenzene (0.60 g, 5.60 mmol) in the mixture of 25 M NaOH 13.5 mL and 10 mL of benzene with stirring. The reaction mixture was heated on the water bath for 45 min. The reaction mixture was extracted five times with 5 mL portions of benzene, then the solvent was removed by rotary evaporation. The residue was purified by column chromatography on a silica gel. A mixture of hexane and ethylacetate as the eluting solvent. The orange band was collected. Evaporation of solvent gave a gummy mass of the ligand. The yield was 35%.

2.3.2 Synthesis of 2-(phenylazo)pyrimidine (azpym)

The 2-(phenylazo)pyrimidine was synthesized by using the similar procedure as 2-(phenylazo)pyridine, but 2-aminopyrimidine was used instead of 2-aminopyridine. The yield was 24%.

2.4 Synthesis of complexes

2.4.1 Synthesis of α -Ru(azpy)₂Cl₂

The mixture of 0.10 g (0.48 mmol) of RuCl₃·3H₂O and 0.20 g (1.09 mmol) of 2-(phenylazo)pyridine and 0.20 g (4.72 mmol) of LiCl in dimethylformamide (30 mL) was refluxed, with magnetic stirring for 10 h. The solution mixture was filtered and solvent was removed. The residue was dissolved in a minimum volume of dichloromethane and purified by column chromatography on silica gel. Three isomeric of Ru(azpy)₂Cl₂ was isolated. The blue (*ctc*-Ru(azpy)₂Cl₂) band was selected and eluted by using a mixture of dichloromethane and ethylacetate (9:1) resulting in 30% of *ctc*-Ru(azpy)₂Cl₂ complex.

2.4.2 Synthesis of [Ru(azpy)₃](PF₆)₂

ctc-Ru(azpy)₂Cl₂ (0.07 g, 0.13 mmol), 2-(phenylazo)pyridine (0.03 g, 0.16 mmol) and AgNO₃ (0.05 g, 0.29 mmol) were suspended in 50 mL mixture of ethanol and water (3:1,v/v). The argon gas was passed for 15 min through the solution and then the solution was refluxed for 7 h. After AgCl was removed by filtration, a aqueous solution of NH₄PF₆ (0.042 g, 0.27 mmol) was added to the filtrate. Then the solvent was removed by rotary evaporation, the resulting precipitate from methanol was separated by filtration, washed with hexane and ether respectively, and dried at 110 °C. The yield was 79%.

2.4.2 Synthesis of $[\text{Ru}(\text{azpy})_2\text{azpym}](\text{PF}_6)_2$

This complex was synthesized by using the same method as $[\text{Ru}(\text{azpy})_3](\text{PF}_6)_2$ complex, but the azpy ligand was replaced by azpym ligand. The yield was 70%.

2.4.3 Synthesis of $[\text{Ru}(\text{azpy})_2\text{bpy}](\text{PF}_6)_2$

This complex was synthesized by using the same method as $[\text{Ru}(\text{azpy})_3](\text{PF}_6)_2$ complex, but the azpy ligand was replaced by 2,2'-bipyridine (bpy) ligand. The yield was 76%.

2.4.4 Synthesis of $[\text{Ru}(\text{azpy})_2\text{phen}](\text{BF}_4)_2$

This complex was synthesized by using the same method as $[\text{Ru}(\text{azpy})_3](\text{PF}_6)_2$ complex, but the azpy ligand and NH_4PF_6 were replaced by 1,10-phenanthroline (phen) ligand and NH_4BF_4 respectively. The yield was 73%.