

Chapter 2

MATERIALS AND METHODS

2.1 Materials

2.1.1 Chemical substances

Materials from Fluka

2,6-diaminopyridine, $C_5H_7N_3$, A.R. grade

2,2'-bipyridine, $C_{10}H_8N_2$, A.R. grade

Nitrosobenzene, C_6H_5NO , A.R. grade

Materials from Merck

Silica gel 60 (0.040-0.063 nm) GF₂₅₄

Sodium hydroxide, NaOH, A.R. grade

1,10-phenanthroline-monohydrate, $C_{12}H_8N_2 \cdot H_2O$, A.R. grade

Materials from Aldrich

Nitrosobenzene, C_6H_5NO , A.R. grade

Ruthenium(III) chloride hydrate, $RuCl_3 \cdot 3H_2O$, A.R. grade

Materials from Hopkin & Williams

Ammonium tetrafluoroborate, NH_4BF_4 , A.R. grade

Materials from Fisher Chemicals

1,10-phenanthroline hydrate, A.R. grade

Materials from AnalaR

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

2.2 Instruments

2.2.1 Melting Point Apparatus

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

2.2.2 Elemental Analysis

Elemental analysis data were obtained by using Carlo Erba EA 1108 Elemental Analyser (University of Bristol, U.K.).

2.2.3 Fast-atom bombardment (FAB) Mass spectrometry

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

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 in the range 200-800 nm by Hewlett Peckard 8425A diode array spectrophotometer.

2.2.6 Nuclear Magnetic Resonance Spectroscopy

1D and 2D NMR spectra were recorded in acetone- d_6 and CDCl_3 with a Varian UNITY SNOVA 500-MHz FT-NMR spectrometer and Bruker AVANCE 300-

MHz. Tetramethylsilane (Me_4Si) was used as an internal standard.

2.2.7 Cyclic Voltammetry

Electrochemical experiments were carried out using cyclic voltammetry technique. The program was 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 quoted 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.

2.2.8 X-ray Diffractometer

The structures of the 2,6-(diphenylazo)pyridine ligand and the $[\text{Ru}(\text{diazpy})(\text{bpy})_2](\text{BF}_4)_2$ complex were determined by Smart APEX CCD diffractometer with Shelxt program.

2.3 Syntheses of ligands

2.3.1 2-(phenylazo)pyridine (azpy)

The 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 mol) in the mixture of 20 M NaOH and 10 mL of benzene. The reaction mixture was warmed on the water bath for 45 min. The mixture was extracted with 3×5 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 an eluent. The orange band was collected and solvents were removed. The yield was 0.64 g (35 %).

2.3.2 2,6-(diphenylazo)pyridine (diazpy)

The 2,6-(diphenylazo)pyridine ligand was obtained from the reaction of 2,6-diaminopyridine and nitrosobenzene. The 2,6-diaminopyridine (0.109 g, 1 mmol) was added to 3 mL 20 M NaOH containing 10 mL benzene with stirring on water bath. Then the nitrosobenzene (0.214 g, 2 mmol) was added to the solution. The mixture was refluxed for 5 h and was extracted with 7×20 mL of benzene. Purification was carried out by column chromatography on silica column. The red-orange ligand was eluted with the mixture of hexane and ethyl acetate. The yield was 0.131 g (45 %).

2.4 Syntheses of complexes

2.4.1 [Ru(diazpy)Cl₂]

The 2 mg (0.1 mmol) of RuCl₃·3H₂O and 58 mg (0.2 mmol) of 2,6-(diphenylazo)pyridine was added to 50 mL of absolute ethanol in a 100 mL round-bottom flask. The mixture was heated at reflux for 3 h with stirring. The solvent was removed. The product was purified by column chromatography. A mixture of a 2:1 (by volume) toluene and acetonitrile was used as an eluent. The first green band was collected. The resulting precipitate was separated from solution by vacuum filtration

and washed with hexane and ether. The procedure produced of dry black solid 0.033 g was obtained. A typical yield for this method was 71 %.

2.4.2 [Ru(diazpy)(azpy)₂](BF₄)₂

The [Ru(diazpy)Cl₂] complex 30 mg (0.065 mmol) was suspended in methanol 30 mL and heated. Then 23 mg (0.13 mmol) of AgNO₃ and 24 mg (0.13 mmol) of 2-(phenylazo)pyridine (azpy) in methanol 10 mL were added. The reaction mixture was refluxed for 8 h, then the color was changed from green to red. The AgCl was filtered off. An excess ligand of azpy was extracted with hexane. The solution was removed less solvent, then 90 mg of NH₄BF₄ (0.86 mmol) was added to the red solution. The small black solid precipitated after 3 days, the resulting precipitate from methanol was separated from solution by vacuum filtration, washed with ether. The yield was 80 %.

2.4.3 [Ru(diazpy)(bpy)₂](BF₄)₂

The [Ru(diazpy)Cl₂] complex 24 mg (0.05 mmol) was suspended in methanol 40 mL and heated. Then 24 mg (0.13 mmol) of the 2,2'-bipyridine (bpy) ligand in methanol 10 mL was added. The triethylamine was used as reducing agent. The reaction mixture was refluxed for 5 h, then the color was changed from green to dark-red. The solution was evaporated and dissolved in H₂O 10 mL, then an excess ligand of phen was extracted with CH₂Cl₂. The solvent was removed from the solution by a rotary evaporator. The dried product was dissolved in acetone/H₂O (3:1 by volume) and 90 mg of NH₄BF₄ (0.86 mmol) was added to the dark-red solution. The small black solid precipitated after 3 days. The resulting precipitate was separated

from solution by vacuum filtration and washed with hexane and ether. The yield was 85 %.

2.4.4 $[\text{Ru}(\text{diazpy})(\text{phen})_2](\text{BF}_4)_2$

The synthesis was similar to that of $[\text{Ru}(\text{diazpy})(\text{bpy})_2](\text{BF}_4)_2$ complex. Only bpy was replaced by an equivalent amount of 1,10-phenanthroline (phen). The yield was 82 %.