CHAPTER II

EXPERIMENTATION AND CHARACTERIZATION

2.1 Introduction

The field of coordination polymer research has become an extremely prolific area of chemistry.[6] The interest in this subject has been partly caused by the numerous topologies of metal ions, organic linkers and the bridging co-ligands. Metal-organic frameworks which constructed from 4,4'-bipyridine and monocarboxylato bridging co-ligands, namely formato, acetato and propionato ligands have been prepared to explore the framework motifs and properties of coordination polymers. A number of crystal engineering investigations are aimed at trying to understand how a variety of factors, like the metal ions, reaction conditions and secondary co-ligands,[72] may affect the framework motifs and properties of coordination polymers.[73] This chapter reports the synthesis and characterization of two series of new zinc(II)-**4,4'-bpy**-carboxylato and copper(II)-**4,4'-bpy**-carboxylato compounds.

2.2 Materials and Methods

All reagents were commercial grade materials and were used without further purification. The X-ray single-crystal data were collected at 293(2) K on a 1 K Bruker SMART CCD area detector diffractometer, a Nonius Kappa CCD diffractometer and a Bruker APEX II CCD diffractometer. FTIR spectra were recorded on a Perkin–Elmer Paragon 1000 FTIR spectrophotometer, equipped with a Golden Gate ATR device, using the reflectance technique (4000–300 cm^{-1}). Elemental analyses for C, H and N were performed with a Perkin–Elmer 2400 analyzer. The X-band powder EPR spectra were obtained on polycrystalline samples at room temperature and at 70 K with a Bruker EMXplus spectrometer with DPPH ($g = 2.0036$) as a reference. X-ray powder diffraction (XRPD) data were recorded at room temperature using a Phillips Xpert Pro equipped with an X'celerator, with Cu $K\alpha$ radiation ($\lambda \approx 1.5408$ Å), in the 2θ range 10-45°.

2.3 Preparation of metal organic frameworks

Two series of metal organic frameworks, zinc(II)-**4,4'-bpy**-carboxylato and copper(II)-**4,4'-bpy**-carboxylato compounds were prepared by the mole-ratio method and diffusion layer technique.

2.3.1 A series of zinc(II)-4,4'-bpy-carboxylato compounds

(1) Preparation of $\{[Zn_3(\mathbf{4,4'\text{-}bpy})_{3.5}(\mu\text{-}OOCH)_4(H_2O)_2](ClO_4)_2(H_2O)_2\}_n$ *(1)*

The compound **1** was synthesized as follows. A warm ethanolic solution (10 mL) of **4,4'-bpy** (0. 156 g, 1.0 mmol) was added to a warm aqueous solution (10 mL) of $Zn(NO_3)_2{\bullet}6H_2O$ (0.297 g, 1.0 mmol). An aqueous solution (10 mL) of NaOOCH (sodium formate; 0.136 g, 2.0 mmol) was subsequently added, followed by 0.138 g of $KClO_4$ (1.0 mmol) under continuous heating and stirring. The resulting colorless solution was allowed to stand unperturbed for the slow evaporation of the solvent at room temperature. After several days, colorless crystals were obtained. The crystals were filtered, washed with the mother liquid and dried in air. Yield: 66%. The microcrystalline sample of compound **1** was prepared using the same solvents. The purity and homogeneity were confirmed by X-ray powder diffraction (Appendix A1). Elemental analysis (%) for $C_{39}H_{40}Cl_2N_7O_{20}Zn_3$ (FW 1193.86) calculated (found): C 39.23 (39.22); H 3.37 (3.31); N 8.21 (8.22).

(2) Preparation of $\{[Zn_3(\mathbf{4,4'\text{-}bpy})_{3.5}(\mu\text{-}OOCH)_4(H_2O)_2](PF_6)_2\}_n$ *(2)*

A warm ethanolic solution (10 mL) of **4,4'-bpy** (0.156 g, 1.0 mmol) was added to a warm aqueous solution (10 mL) of $Zn(NO_3)_2{\bullet}6H_2O$ (0.297 g, 1.0 mmol). Next, an aqueous solution (10 mL) of NaOOCH (0.136 g, 2.0 mmol) was subsequently added, followed by KPF_6 (0.184 g, 1.0 mmol) under continuous stirring. The resulting colorless solution was allowed to stand unperturbed for the slow evaporation of the solvent at room temperature. After several days, light pink crystals were obtained. The crystals were filtered, washed with the mother liquid and dried in air. Yield: 60%. The microcrystalline sample of compound **2** was prepared in the same solvents. The purity and homogeneity were confirmed by X-ray powder diffraction (Appendix A2). Elemental analysis (%) for $C_{39}H_{36}F_{12}N_7O_{10}P_2Zn_3$ (FW 1248.84) calculated (found): C 37.51 (37.44); H 2.91 (3.14); N 7.85 (8.01).

(3) Preparation of $\{[Zn_3(\textbf{4,4'-bpy})_{3.5}(\mu\text{-}OOCH)_4(H_2O)_2](BF_4)_2(H_2O)_2\}_n$ *(3)*

A warm solution of **4,4'-bpy** (0.156 g, 1.0 mmol) in ethanol (10 mL) was added to a warm aqueous solution (10 mL) of $Zn(NO_3)_2 \cdot 6H_2O$ (0.297 g, 1.0 mmol). Next, a warm aqueous solution (10 mL) containing NaOOCH (0.136 g, 2.0 mmol) and $NaBF_4$ (0.109 g, 1.0 mmol) were added under continuous stirring. A few drops of HCOOH 98% were subsequently added to the reaction mixture, yielding a clear colorless solution. This solution was allowed to stand unperturbed for the slow evaporation of the solvent at room temperature, producing colorless needle crystals of **3** after a few days. Yield: 70%. The microcrystalline sample of compound **3** was prepared using the same solvents. The purity and homogeneity were confirmed by X-ray powder diffraction (Appendix A3). Elemental analysis (%) for $C_{39}H_{40}B_2F_8N_7O_{12}Zn_3$ (FW 1168.55) calculated (found): C 40.09 (39.53); H 3.45 (3.69); N 8.39 (9.56).

(4) Preparation of $\{[Zn(\textbf{4,4'-bpy})(\mu\text{-}OOCH)(H_2O)_2](CF_3SO_3)(H_2O)\}_n$ *(4)*

A warm ethanolic solution (15 mL) containing CF_3SO_3Na (0.172 g, 1.0 mmol) and NaOOCH (0.136 g, 2.0 mmol) was added to a warm aqueous solution (10 mL) of $Zn(NO_3)_2 \cdot 6H_2O$ (0.297 g, 1.0 mmol). Next, a warm ethanolic solution (10 ml) of **4,4'-bpy** (0.156 g, 1.0 mmol) was added under continuous stirring. The resulting colorless solution was allowed to stand unperturbed for the slow evaporation of the solvent at room temperature. After several days, colorless crystals were obtained. The crystals were filtered, washed with the mother liquid and dried in air. Yield: 58%. The microcrystalline sample of compound **4** was prepared in the same solvents. The purity and homogeneity were confirmed by X-ray powder diffraction (Appendix A4). Elemental analysis (%) for $C_{12}H_{15}F_3N_2O_8SZn$ (FW 469.71) calculated (found): C 30.68 (31.09); H 3.22 (3.59); N 5.96 (6.04).

(5) Preparation of $\{[Zn_4(\textbf{4,4'-bpy})_4(\mu\text{-}OOCH)_5(H_2O)_5](NO_3)_3(\textbf{4,4'-bpy})_2(H_2O)_3\}_n$ *(5)*

A warm solution containing **4,4'-bpy** (0.156 g, 1.0 mmol) in ethanol (10 mL) and NaOOCH (0.136 g, 2.0 mmol) in water (10 mL) was added to an aqueous solution (10 mL) of $Zn(NO_3)_2 \cdot 6H_2O$ (0.297 g, 1.0 mmol) under continuous stirring. The resulting colorless solution was allowed to stand unperturbed for the slow evaporation of the solvent at room temperature. After several days, colorless crystals were obtained. The crystals were filtered, washed with the mother liquid and dried in air. Yield: 80%. The microcrystalline sample of compound **5** was prepared using the same solvents. The purity and homogeneity were confirmed by X-ray powder diffraction (Appendix A5). Elemental analysis (%) for $C_{65}H_{69}N_{15}O_{27}Zn_4$ (FW 1753.89) calculated (found): C 44.51 (45.61); H 3.97 (4.80); N 11.98 (12.83).

(6) Preparation of $\{[Zn_3(\mathbf{4,4'\text{-}bpy})_3(\mu\text{-}OOCCH_3)_4(H_2O)_2](PF_6)_2(H_2O)_2\}_n$ *(6)*

A warm aqueous solution (15 mL) of $Zn(NO_3)_2\bullet 6H_2O$ (0.297 g, 1.0 mmol) was added to a hot solution of **4,4’-bpy** (0.156 g, 1.0 mmol) in ethanol (10 mL). Next, a warm aqueous solution (30 mL) containing NaO_2CCH_3 (sodium acetate; 0.164 g, 2.0 mmol) and KPF_6 (0.184 g, 1.0 mmol) was added under continuous heating and stirring. A few drops of CH_3COOH 98% were subsequently added to the reaction mixture, yielding a clear colorless solution. This solution was allowed to stand unperturbed for the slow evaporation of the solvent at room temperature, producing colorless needle crystals of **6** after a few days. Yield: 70%. The microcrystalline sample of compound **6** was prepared in the same solvents. The purity and homogeneity were confirmed by X-ray powder diffraction (Appendix A6). Elemental analysis (%) for $C_{38}H_{44}F_{12}N_6O_{12}P_2Zn_3$ (FW 1258.87) calculated (found): C 36.14 (36.41); H 3.51 (3.23); N 6.66 (6.30).

(7) Preparation of $\{[Zn_3(\mathbf{4,4'\text{-}bpy})_4(\mu\text{-}OOCCH_2CH_3)_4](ClO_4)_2(\mathbf{4,4'\text{-}bpy})_2(H_2O)_4\}_n$ *(7)*

A warm solution of **4,4’-bpy** (0.156 g, 1.0 mmol) in ethanol (10 mL) was added to a hot aqueous solution (10 mL) of $Zn(NO_3)_2\bullet 6H_2O$ (0.297 g, 1.0 mmol). Subsequently, a warm aqueous solution (10 mL) of $NaO_2CCH_2CH_3$ (sodium propionate; 0.192 g, 2.0 mmol) was added, followed by $KClO_4$ (0.138 g, 1.0 mmol) under continuous stirring. Next, a few drops of CH_3CH_2COOH 98% were added, yielding a clear colorless solution, which was allowed to stand unperturbed for the slow evaporation of the solvent at room temperature. Colorless crystals were collected from the solution by filtration after several days. Yield: 68%. The microcrystalline sample of compound **7** was prepared using the same solvents. The purity and homogeneity were confirmed by X-ray powder diffraction (Appendix A7). Elemental analysis (%) for $C_{72}H_{76}Cl_2N_{12}O_{20}Zn_3$ (FW 1696.46) calculated (found): C 50.97 (51.19); H 4.51 (4.84); N 9.91 (9.91).

(8) Preparation of $\{[Zn_3(\textbf{4,4'-bpy})_4(\mu\text{-}OOCC_2H_5)_4(H_2O)_2](PF_6)_2(H_2O)_2\}_n$ *(8)*

Method A. A warm ethanolic solution (15 ml) containing **4,4'-bpy** (0.156 g, 1.0 mmol) was added to an aqueous solution (20 ml) of $Zn(NO_3)_2.6H_2O$ (0.297 g, 1.0 mmol). A warm aqueous solution (10 mL) of $NaO_2CCH_2CH_3$ (0.192 g, 2.0 mmol) was subsequently added, followed by KPF_6 (0.184 g, 1.0 mmol) under continuous stirring. The resulting colorless solution was allowed to stand unperturbed for the slow evaporation of the solvent at room temperature. After several days, light pink crystals were obtained. The crystals were filtered, washed with the mother liquid and dried in air. Yield: 75%. The microcrystalline sample of compound **8** was prepared in the same solvents. The purity and homogeneity were confirmed by X-ray powder diffraction (Appendix A8). Elemental analysis (%) for $C_{52}H_{60}F_{12}N_8O_{12}P_2Zn_3$ (FW 1475.18) calculated (found): C 42.34 (41.43); H 4.10 (4.34); N 7.60 (7.51).

Method B. An ethanolic solution (5 mL) of **4,4'-bpy** (0.078 g, 0.5 mmol) was carefully layered on mixed aqueous solution (5 mL) containing $Zn(NO_3)_2.6H_2O$ (0.149 g, 0.5 mmol), $NaO_2CCH_2CH_3$ (0.096 g, 1.0 mmol) and KPF_6 (0.092 g, 0.5 mmol) in 12 mL of glass vial. This vial was sealed and allowed to stand undisturbed at room temperature. After four days, light pink crystals of **8** were obtained. Yield: 68%.

(9) Preparation of $\{[Zn_2(\textbf{4,4'-bpy})_2(\mu\text{-}OOCC_2H_5)_2(OH)(H_2O)](BF_4)(H_2O)_2\}_n$ *(9)*

A warm methanolic solution (15 ml) containing **4,4'-bpy** (0.156 g, 1.0 mmol) was added to a warm aqueous solution (20 ml) of $Zn(NO_3)_2.6H_2O$ (0.297 g, 1.0 mmol). A warm aqueous solution (10 mL) of $NaO_2CCH_2CH_3$ (0.192 g, 2.0 mmol) was subsequently added, followed by $NaBF_4$ (0.109 g, 1.0 mmol) under continuous stirring. A few drops of CH_3CH_2COOH 98% were subsequently added to the reaction mixture, yielding a clear colorless solution. This solution was allowed to stand unperturbed for the slow evaporation of the solvent at room temperature, producing colorless needle crystals of **9** after a few days. Yield: 72%. The microcrystalline sample of compound **9** was prepared using the same solvents. The purity and homogeneity were confirmed by X-ray powder diffraction (Appendix A9). Elemental analysis (%) for $C_{26}H_{33}BF_4N_4O_8Zn_2$ (FW 747.15) calculated (found): C 41.81 (41.16); H 4.45 (5.09); N 7.50 (8.12).

(10) Preparation of $\{[Zn_2(\textbf{4,4'-bpy})_2(\mu\text{-}OOCC_2H_5)_2(H_2O)_2](CF_3SO_3)_2\}_n$ *(10)*

Method A. A warm aqueous solution (10 mL) of $Zn(NO_3)_2.6H_2O$ (0.297 g, 1.0 mmol) was added to a warm ethanolic solution (10 mL) of **4,4'-bpy** (0.156 g, 1.0 mmol). A warm aqueous solution (10 mL) of $NaO_2CCH_2CH_3$ (0.192 g, 2.0 mmol) was subsequently added, followed by 0.172 g of CF_3SO_3Na (1.0 mmol) under continuous stirring. The resulting colorless solution was allowed to stand unperturbed for the slow evaporation of the solvent at room temperature. After several days, colorless crystals were obtained. The crystals were filtered, washed with the mother liquid and dried in air. Yield: 68%. The microcrystalline sample of compound **10** was prepared in the same solvents. The purity and homogeneity were confirmed by X-ray powder diffraction (Appendix A10). Elemental analysis (%) for $C_{28}H_{30}F_6N_4O_{12}S_2Zn_2$ (FW 923.46) calculated (found): C 36.42 (36.39); H 3.27 (3.47); N 6.07 (6.92).

Method B. An ethanolic solution (5 mL) of **4,4'-bpy** (0.078 g, 0.5 mmol) was carefully layered on mixed aqueous solution (5 mL) containing $Zn(NO_3)_2.6H_2O$ (0.149 g, 0.5 mmol), $NaO_2CCH_2CH_3$ (0.096 g, 1.0 mmol) and CF_3SO_3Na (0.086 g, 0.5 mmol) in 12 mL of glass vial. This vial was sealed and allowed to stand undisturbed at room temperature. After two days, colorless crystals of **10** were obtained. Yield: 65%.

(11) Preparation of $\{[Zn_3(\textbf{4,4'-bpy})_4(\mu\text{-}OOCC_2H_5)_4(H_2O)_2](NO_3)_2(H_2O)_6\}_n$ *(11)*

A hot solution containing **4,4'-bpy** (0.156 g, 1.0 mmol) and $NaO_2CCH_2CH_3$ (0.192 g, 2.0 mmol) in water-ethanol (10:10 mL) was added to a warm aqueous solution (10 mL) of $Zn(NO_3)_2{\bullet}6H_2O$ (0.297 g, 1.0 mmol) under continuous stirring. A few drops of HNO_3 98% were subsequently added to the reaction mixture, yielding a clear colorless solution. This solution was allowed to stand unperturbed for the slow evaporation of the solvent at room temperature, producing colorless needle crystals of **11** after a few days. Yield: 76%. The microcrystalline sample of compound **11** was prepared using the same solvents. The purity and homogeneity were confirmed by X-ray powder diffraction (Appendix

A11). Elemental analysis (%) for $C_{52}H_{62}N_{10}O_{19}Zn_3$ (FW 1327.27) calculated (found): C 47.06 (47.09); H 4.71 (4.45); N 10.55 (10.59).

2.3.2 Cu^{2+} and Mn^{2+} doped zinc(II)-4,4'-bpy-carboxylato compounds

*(1) Preparation of Cu^{2+} doped $\{Zn_3(\mathbf{4,4'\text{-}bpy})_{3.5}(\mu\text{-}O_2CH)_4(H_2O)_2(ClO_4)_2(H_2O)_2\}_n$ (**1a**) and Mn^{2+} doped $\{Zn_3(\mathbf{4,4'\text{-}bpy})_{3.5}(\mu\text{-}O_2CH)_4(H_2O)_2(ClO_4)_2(H_2O)_2\}_n$(**1b**)*

A warm ethanolic solution (10 mL) of **4,4'-bpy** (0.156 g, 1.0 mmol) was added to a warm aqueous solution (10 mL) of $Zn(NO_3)_2·6H_2O$ (0.297 g, 1.0 mmol). A warm aqueous solution (10 mL) of NaOOCH (0.136 g, 2.0 mmol) was subsequently added, followed by 0.138 g of $KClO_4$ (1.0 mmol) and 0.003 g (0.002 mmol) of $Cu(NO_3)_2·3H_2O$ (or 0.003 g $Mn(NO_3)_2·4H_2O$ (0.002 mmol)) under continuous stirring. The resulting solution was allowed to stand unperturbed for the slow evaporation of the solvent at room temperature. After several days, light-green crystals of **1a** (light-pink crystals for **1b**) were obtained. The crystals were filtered, washed with the mother liquor and dried in air. Yield: 66% (60% for **1b**). The XRPD patterns and IR spectra of **1a** and **1b** are similar to that of **1** (see appendix B).

*(2) Preparation of Cu^{2+} doped zinc(II) compounds **2-11** (**2a-11a**) and Mn^{2+} doped zinc(II) compounds **2-11** (**2b-11b**)*

Compounds **2a-11a** and **2b-11b** were prepared in similar manner as **1a** and **1b** using the corresponding sodium carboxylate salt. The IR spectra and XRPD patterns of the doped compounds are comparable to those of the corresponding parent compounds **2-11** (see appendix B).

2.3.3 A series of copper(II)-4,4'-bpy-carboxylato compounds

*(1) Preparation of $\{[Cu_3(\mathbf{4,4'\text{-}bpy})_3(\mu\text{-}OOCH)_4(H_2O)_2](ClO_4)_2(H_2O)_6\}_n$ (**12**)*

Method A. A warm solution of **4,4'-bpy** (0.156 g, 1.0 mmol) in ethanol (10 mL) was added to a warm aqueous solution (10 mL) of $Cu(NO_3)_2•3H_2O$ (0.241 g, 1.0 mmol). Next, a warm aqueous solution (10 mL) containing NaOOCH (0.136 g, 2.0 mmol) and $KClO_4$ (0.138 g, 1.0 mmol) was added under continuous stirring. A few drops of HOOCH 98% were subsequently added to the reaction mixture, yielding a clear colorless solution. The resulting blue solution was allowed to stand unperturbed for the slow evaporation of the solvent at room temperature, producing blue crystals of **12** after a few days. Yield: 70%. The microcrystalline sample of compound **12** was prepared in the same solvents. The purity and homogeneity were confirmed by X-ray powder diffraction (Appendix A12). Elemental analysis (%) for $C_{34}H_{44}Cl_2Cu_3N_6O_{24}$ (FW 1182.28) calculated (found): C 34.54 (34.56); H 3.75 (4.18); N 7.11 (7.33).

Method B. An ethanolic solution (5 mL) of **4,4'-bpy** (0.078 g, 0.5 mmol) was carefully layered on mixed aqueous solution (5 mL) containing $Cu(NO_3)_2{\bullet}3H_2O$ (0.121 g, 0.5 mmol), NaOOCH (0.068 g, 1.0 mmol) and $KClO_4$ (0.069 g, 0.5 mmol) in 12 mL of glass vial. This vial was sealed and allowed to stand undisturbed at room temperature. After one day, blue crystals of **12** were obtained. Yield: 72%.

(2) Preparation of $\{[Cu_3(\mathbf{4,4'\text{-}bpy})_3(\mu\text{-}OOCH)_4(H_2O)_2](PF_6)_2(H_2O)_6\}_n$ *(13)*

A warm ethanolic solution (10 mL) of **4,4'-bpy** (0.156 g, 1.0 mmol) was added to an aqueous solution (10 mL) of $Cu(NO_3)_2{\bullet}3H_2O$ (0.241 g, 1.0 mmol). A warm aqueous solution (10 mL) of NaOOCH (0.136 g, 2.0 mmol) was subsequently added, followed by KPF_6 (0.184 g, 1.0 mmol) under continuous stirring. A few drops of HOOCH 98% were subsequently added to the reaction mixture, yielding a clear blue solution. The resulting blue solution was allowed to stand unperturbed for the slow evaporation of the solvent at room temperature, producing blue crystals of **13** after a few days. Yield: 74%. Elemental analysis (%) for $C_{34}H_{44}Cu_3F_{12}N_6O_{16}P_2$ (FW 1273.31) calculated (found): C 32.07 (31.38); H 3.48 (3.87); N 6.60 (6.61).

(3) Preparation of $\{[Cu_3(\mathbf{4,4'\text{-}bpy})_3(\mu\text{-}OOCH)_4(H_2O)_2](BF_4)_2(H_2O)_6\}_n$ *(14)*

Method A. A warm solution (20 mL) containing **4,4'-bpy** (0.156 g, 1.0 mmol) and NaOOCH (0.136 g, 2.0 mmol) in water-ethanol (10:10 mL) was added to a hot aqueous solution (10 mL) of $Cu(BF_4)_2{\bullet}H_2O$ (0.346 g, 1.0 mmol) under continuous stirring. A few drops of HOOCH 98% were subsequently added to the reaction mixture, yielding a clear blue solution. The resulting blue solution was allowed to stand unperturbed for the slow evaporation of the solvent at room temperature, producing blue crystals of **14** after a few days. Yield: 62%. The microcrystalline sample of compound **14** was prepared using the same solvents. The purity and homogeneity were confirmed by X-ray powder diffraction (Appendix A13). Elemental analysis (%) for $C_{34}H_{44}B_2Cu_3F_8N_6O_{16}$ (FW 1156.99) calculated (found): C 35.30 (34.88); H 3.82 (4.25); N 7.26 (7.28).

Method B. An ethanolic solution (5 mL) of **4,4'-bpy** (0.078 g, 0.5 mmol) was carefully layered on mixed aqueous solution (5 mL) of $Cu(BF_4)_2 \bullet H_2O$ (0.173 g, 0.5 mmol) and NaOOCH (0.068 g, 1.0 mmol) in 12 mL of glass vial. This vial was sealed and allowed to stand undisturbed at room temperature. After one day, blue crystals of **14** were obtained. Yield: 70%.

(4) Preparation of $\{[Cu_3(\mathbf{4,4'\text{-}bpy})_3(\mu\text{-}OOCH)_4(H_2O)_2](CF_3SO_3)_2(H_2O)_6\}_n$ *(15)*

A warm ethanolic solution (10 mL) containing CF_3SO_3Na (0.172 g, 1.0 mmol) and NaOOCH (0.136 g, 2.0 mmol) was added to a warm aqueous solution (10 mL) of $Cu(NO_3)_2 \bullet 3H_2O$ (0.241 g, 1.0 mmol). Next, a hot ethanolic solution (10 ml) of **4,4'-bpy** (0.156 g, 1.0 mmol) was added under continuous stirring. A few drops of HOOCH 98% were subsequently added to the reaction mixture, yielding a clear blue solution. The resulting blue solution was allowed to stand unperturbed for the slow evaporation of the solvent at room temperature, producing blue crystals of **15** after a few days. Yield: 60%. Elemental analysis (%) for $C_{34}H_{44}Cu_3F_6N_6O_{22}S_2$ (FW 1281.52) calculated (found): C 33.74 (34.60); H 3.46 (3.70); N 6.56 (7.04).

(5) Preparation of $\{[Cu(\mathbf{4,4'\text{-}bpy})(\mu\text{-}OOCH)(NO_3)]\}_n$ *(16)*

A warm solution containing **4,4'-bpy** (0.156 g, 1.0 mmol) in ethanol (10 mL) and NaOOCH (0.136 g, 2.0 mmol) in water (10 mL) was added to an aqueous solution (10 mL) of $Cu(NO_3)_2 \bullet 3H_2O$ (0.241 g, 1.0 mmol) under continuous stirring. A few drops of HCOOH 98% were subsequently added to the reaction mixture, yielding a clear blue solution. The resulting blue solution was allowed to stand unperturbed for the slow evaporation of the solvent at room temperature, producing blue crystals of **16** after a few days. Yield: 82%. The microcrystalline sample of compound **16** was prepared in the same solvents. The purity and homogeneity were confirmed by X-ray powder diffraction (Appendix A14). Elemental analysis (%) for

$C_{12}H_9CuN_3O_5$ (FW 326.75) calculated (found): C 40.43 (40.02); H 2.78 (3.01); N 12.86 (12.86).

(6) Preparation of $\{[Cu_2(\mathbf{4,4'\text{-}bpy})_2(\mu\text{-}OOCCH_3)_3](ClO_4)(H_2O)\}_n$ ***(17)***

A hot ethanolic solution (10 mL) of **4,4'-bpy** (0.156 g, 1.0 mmol) was added to an aqueous solution (10 mL) of $Cu(NO_3)_2{\bullet}3H_2O$ (0.241 g, 1.0 mmol). A warm aqueous solution (10 mL) of NaO_2CCH_3 (0.164 g, 2.0 mmol) was subsequently added, followed by $KClO_4$ (0.138 g, 1.0 mmol) under continuous stirring. A few drops of CH_3COOH 98% were subsequently added to the reaction mixture, yielding a clear blue solution. The resulting blue solution was allowed to stand unperturbed for the slow evaporation of the solvent at room temperature, producing colorless needle crystals of **17** after a few days. Yield: 66%. Elemental analysis (%) for $C_{26}H_{27}ClCu_2N_4O_{11}$ (FW 734.06) calculated (found): C 42.54 (42.40); H 3.71 (3.69); N 7.63 (7.80).

(7) Preparation of $\{[Cu_2(\mathbf{4,4'\text{-}bpy})_2(\mu\text{-}OOCCH_3)_3](PF_6)(H_2O)\}_n$ ***(18)***

Method A. A hot aqueous solution (10 mL) of $Cu(NO_3)_2{\bullet}3H_2O$ (0.241 g, 1.0 mmol) was added to a solution of **4,4'-bpy** (0.156 g, 1.0 mmol) in ethanol (10 mL). Next, a warm aqueous solution (10 mL) containing NaO_2CCH_3 (0.164 g, 2.0 mmol) and KPF_6 (0.184 g, 1.0 mmol) was added under continuous stirring. A few drops of CH_3COOH 98% were subsequently added to the reaction mixture, yielding a clear blue solution. The resulting blue solution was allowed to stand unperturbed to allow slow evaporation of the solvent at room temperature, producing colorless needle crystals of **18** after a few days. Yield: 72%. The microcrystalline sample of compound **18** was prepared using the same solvents. The purity and homogeneity were confirmed by X-ray powder diffraction (Appendix A15). Elemental analysis (%) for $C_{26}H_{27}Cu_2F_6N_4O_7P$ (FW 779.57) calculated (found): C 40.06 (39.76); H 3.49 (3.50); N 7.19 (6.94).

Method B. An ethanolic solution (5 mL) of **4,4'-bpy** (0.078 g, 0.5 mmol) was carefully layered on mixed aqueous solution (5 mL) containing $Cu(NO_3)_2{\bullet}3H_2O$ (0.121 g, 0.5 mmol), NaO_2CCH_3 (0.082 g, 1.0 mmol) and KPF_6 (0.092 g, 0.5 mmol) in 12 mL of glass vial. This vial was sealed and allowed to stand undisturbed at room temperature. After one day, blue crystals of **18** were obtained. Yield: 78%.

(8) Preparation of $\{[Cu_2(\mathbf{4,4'\text{-}bpy})_2(\mu\text{-}OOCCH_3)_3](BF_4)(H_2O)\}_n$ ***(19)***

A warm mixture of **4,4'-bpy** (0.156 g, 1.0 mmol) in ethanol (10 mL) and NaO_2CCH_3 (0.164 g, 2.0 mmol) in water (10 mL) was added to a warm aqueous solution (10 mL) of $Cu(BF_4)_2{\bullet}H_2O$ (0.346 g, 1.0 mmol) under continuous stirring. A few drops of CH_3COOH 98% were subsequently added to the reaction mixture, yielding a clear blue solution. The resulting blue solution was allowed to stand unperturbed to allow slow evaporation of the solvent at room temperature, producing colorless needle crystals of **19** after a few days. Yield: 70%. Elemental analysis (%) for $C_{26}H_{27}BCu_2F_4N_4O_7$ (FW 721.41) calculated (found): C 43.29 (42.82); H 3.77 (3.77); N 7.77 (7.44).

(9) Preparation of $\{[Cu_2(\mathbf{4,4'\text{-}bpy})_2(\mu\text{-}OOCCH_3)_3](CF_3SO_3)(H_2O)\}_n$ ***(20)***

A hot solution of **4,4'-bpy** (0.156 g, 1.0 mmol) in ethanol (10 mL) was added to a warm aqueous solution (10 mL) of $Cu(NO_3)_2{\bullet}3H_2O$ (0.241 g, 1.0 mmol). Next, a warm aqueous solution (10 mL) containing NaO_2CCH_3 (0.164 g, 2.0 mmol) and CF_3SO_3Na (0.172 g, 1.0 mmol) was added under continuous stirring. A few drops of CH_3COOH 98% were subsequently added to the reaction mixture, yielding a clear blue solution. The resulting blue solution was allowed to stand unperturbed for the slow evaporation of the solvent at room temperature, producing colorless needle crystals of **20** after a few days. Yield: 58%. Elemental analysis (%) for $C_{27}H_{27}Cu_2F_3N_4O_{10}S$ (FW 783.68) calculated (found): C 41.38 (41.22); H 3.47 (3.59); N 7.15 (7.39).

Note: Replacing sodium formate and sodium acetate with a larger monocarboxylate group, i.e. sodium propionate, in the preparation of Cu(II)-**4,4'-bpy-propinato** compounds was unsuccessful.

2.4 Characterization of the Products

All metal organic frameworks in two series have been characterized by X-ray structure analysis, elemental microanalysis, infrared, electronic diffuse reflectance and EPR spectra as well as X-ray powder diffraction. The preliminary results are reported in Tables 2.1 and 2.2, respectively. This section will describe the characterization and summarize the obtained products.

2.4.1 The products of zinc(II)-4,4'-bpy-carboxylato system

Eleven zinc(II)-**4,4'-bpy**-carboxylato compounds, $\{[Zn_3(\textbf{4,4'-bpy})_{3.5}(\mu\text{-}OOCH)_4(H_2O)_2](X)_2\}_n$ when X = $ClO_4^-\cdot H_2O$ (**1**), PF_6^- (**2**), $BF_4^-\cdot H_2O$ (**3**), $\{[Zn(\textbf{4,4'-bpy})(\mu\text{-}OOCH)(H_2O)_2](CF_3SO_3)(H_2O)\}_n$ (**4**), $\{[Zn_4(\textbf{4,4'-bpy})_4(\mu\text{-}OOCH)_5(H_2O)_5](NO_3)_3(\textbf{4,4'-bpy})_2(H_2O)_3\}_n$ (**5**), $\{[Zn_3(\textbf{4,4'-bpy})_3(\mu\text{-}OOCCH_3)_4(H_2O)_2](PF_6)_2(H_2O)_2\}_n$ (**6**), $\{[Zn_3(\textbf{4,4'-bpy})_4(\mu\text{-}OOCCH_2CH_3)_4](ClO_4)_2(\textbf{4,4'-bpy})_2(H_2O)_4\}_n$ (**7**), $\{[Zn_3(\textbf{4,4'-bpy})_4(\mu\text{-}OOCC_2H_5)_4(H_2O)_2](PF_6)_2(H_2O)_2\}_n$ (**8**), $\{[Zn_2(\textbf{4,4'-bpy})_2(\mu\text{-}OOCC_2H_5)_2(OH)(H_2O)](BF_4)(H_2O)_2\}_n$ (**9**), $\{[Zn_2(\textbf{4,4'-bpy})_2(\mu\text{-}OOCC_2H_5)_2(H_2O)_2](CF_3SO_3)_2\}_n$ (**10**), and $\{[Zn_3(\textbf{4,4'-bpy})_4(\mu\text{-}OOCC_2H_5)_4(H_2O)_2](NO_3)_2(H_2O)_3\}_n$ (**11**) were prepared by the mole ratio method and diffusion layer technique using zinc(II) salts, **4,4'-bpy** and corresponding sodium or potassium salt as starting reagents. All products suitable for X-ray analysis were crystallized using EtOH/H_2O or MeOH/H_2O mixed solvents. The analytical data and spectroscopic properties, given in Table 2.1, are consistent with those of the authentic compounds. In order to investigate the functions these coordination polymers, the crystal structures (for compounds **1**, **6** and **7**), infrared spectra, EPR spectra, thermal and optical properties, as well as the catalytic reactivity are studied in detail and will be reported in Chapter 3, together with the dynamic structural transformation and anion-exchange behavior.

Table 2.1 Physical properties of zinc(II)-**4,4'-bpy**-carboxylato compounds and structural types

Compound	Type	Geometry	Color/ Shape	IR (cm^{-1})^a
$\{[Zn_3(\mathbf{4,4'\text{-}bpy})_{3.5}(\mu\text{-}OOCH)_4(H_2O)_2](ClO_4)_2(H_2O)_2\}_n$ (**1**)	3D	Oct.	Colorless, Prismatic	ν_{as}(COO) 1588, ν_s(COO) 1413, δ(O-C-O) 630, (ClO_4) 1089-1040
$\{[Zn_3(\mathbf{4,4'\text{-}bpy})_{3.5}(\mu\text{-}OOCH)_4(H_2O)_2](PF_6)_2\}_n$ (**2**)	3D	Oct.	Light pink, Prismatic	ν_{as}(COO) 1564, ν_s(COO) 1417, δ(O-C-O) 645, (PF_6) 834-823
$\{[Zn_3(\mathbf{4,4'\text{-}bpy})_{3.5}(\mu\text{-}OOCH)_4(H_2O)_2](BF_4)_2(H_2O)_2\}_n$ (**3**)	3D	Oct.	Colorless, Prismatic	ν_{as}(COO) 1580, ν_s(COO) 1417, δ(O-C-O) 647, (BF_4) 1041-1009
$\{[Zn(\mathbf{4,4'\text{-}bpy})(\mu\text{-}OOCH)(H_2O)_2](CF_3SO_3)(H_2O)\}_n$ (**4**)	2D	Oct.	Colorless, Prismatic	ν_{as}(COO) 1564, ν_s(COO) 1413, δ(O-C-O) 638, (CF_3SO_3) 1252-1218
$\{[Zn_4(\mathbf{4,4'\text{-}bpy})_4(\mu\text{-}OOCH)_5(H_2O)_5](NO_3)_3(\mathbf{4,4'\text{-}bpy})_2(H_2O)_3\}_n$ (**5**)	2D	Oct.	Colorless, Prismatic	ν_{as}(COO) 1575, ν_s(COO) 1417, δ(O-C-O) 649, (NO_3) 1384
$\{[Zn_3(\mathbf{4,4'\text{-}bpy})_3(\mu\text{-}OOCCH_3)_4(H_2O)_2](PF_6)_2(H_2O)_2\}_n$ (**6**)	2D	Oct.	Colorless, Prismatic	ν_{as}(COO) 1520, ν_s(COO) 1419, δ(O-C-O) 643, (PF_6) 846-838
$\{[Zn_3(\mathbf{4,4'\text{-}bpy})_4(\mu\text{-}OOCCH_2CH_5)_4](ClO_4)_2(\mathbf{4,4'\text{-}bpy})_2(H_2O)_4\}_n$ (**7**)	2D	Oct.	Colorless, Prismatic	ν_{as}(COO) 1578, ν_s(COO) 1466, δ(O-C-O) 631, (ClO_4) 1067-1046
$\{[Zn_3(\mathbf{4,4'\text{-}bpy})_4(\mu\text{-}OOCC_2H_5)_4(H_2O)_2](PF_6)_2(H_2O)_2\}_n$ (**8**)	1D	Oct.	Colorless, Prismatic	ν_{as}(COO) 1567, ν_s(COO) 1417, δ(O-C-O) 643, (PF_6) 834-820
$\{[Zn_2(\mathbf{4,4'\text{-}bpy})_2(\mu\text{-}OOCC_2H_5)_2(OH)(H_2O)](BF_4)(H_2O)_2\}_n$ (**9**)	2D	Oct.	Colorless, Prismatic	ν_{as}(COO) 1580, ν_s(COO) 1417, δ(O-C-O) 647, (BF_4) 1041-1012
$\{[Zn_2(\mathbf{4,4'\text{-}bpy})_2(\mu\text{-}OOCC_2H_5)_2(H_2O)_2](CF_3SO_3)_2\}_n$ (**10**)	1D	TBP	Colorless, Prismatic	ν_{as}(COO) 1568, ν_s(COO) 1417, δ(O-C-O) 650, (CF_3SO_3) 1257-1200
$\{[Zn_3(\mathbf{4,4'\text{-}bpy})_4(\mu\text{-}OOCC_2H_5)_4(H_2O)_2](NO_3)_2(H_2O)_3\}_n$ (**11**)	1D	Oct.	Colorless, Prismatic	ν_{as}(COO) 1575, ν_s(COO) 1417, δ(O-C-O) 649, (NO_3) 1384

Oct. = distorted octahedral; TBP = distorted trigonal bipyramidal; ^{a}see Figure 3.22

Table 2.2 Physical properties of copper(II)-**4,4'-bpy**-carboxylato compounds and structural types

Compound	Type	Geometry	Color/ Shape	IR (cm^{-1})^b	Electronic spectrum (kK)^c	EPR	
						RT	70 K
{[Cu$_3$(**4,4'-bpy**)$_3$(μ-OOCH)$_4$(H$_2$O)$_2$](ClO$_4$)$_2$(H$_2$O)$_6$}$_n$ (**12**)	2D	Oct.	Blue, Needle	ν_{as}(COO) 1569, ν_s(COO) 1417, δ(O-C-O) 643, (ClO$_4$) 1104-1045	15.8 12.5 (sh)	$g_{//} = 2.224$ $g_{\perp} = 2.090$	$g_{//} = 2.224$ $g_{\perp} = 2.090$
{[Cu$_3$(**4,4'-bpy**)$_3$(μ-OOCH)$_4$(H$_2$O)$_2$](PF$_6$)$_2$(H$_2$O)$_6$}$_n$ (**13**)^a	2D	Oct.	Blue, Needle	ν_{as}(COO) 1567, ν_s(COO) 1417, δ(O-C-O) 643, (PF$_6$) 834-820	15.5 12.5 (sh)	$g_{//} = 2.225$ $g_{\perp} = 2.090$	$g_{//} = 2.224$ $g_{\perp} = 2.090$
{[Cu$_3$(**4,4'-bpy**)$_3$(μ-OOCH)$_4$(H$_2$O)$_2$](BF$_4$)$_2$(H$_2$O)$_6$}$_n$ (**14**)	2D	Oct.	Blue, Needle	ν_{as}(COO) 1580, ν_s(COO) 1417, δ(O-C-O) 647, (BF$_4$) 1041-1012	15.8 12.5 (sh)	$g_{//} = 2.224$ $g_{\perp} = 2.090$	$g_{//} = 2.223$ $g_{\perp} = 2.090$
{[Cu$_3$(**4,4'-bpy**)$_3$(μ-OOCH)$_4$(H$_2$O)$_2$](CF$_3$SO$_3$)$_2$(H$_2$O)$_6$}$_n$ (**15**)^a	2D	Oct.	Blue, Needle	ν_{as}(COO) 1564, ν_s(COO) 1413, δ(O-C-O) 638, (CF$_3$SO$_3$) 1252-1212	15.5 12.5 (sh)	$g_{//} = 2.225$ $g_{\perp} = 2.090$	$g_{//} = 2.224$ $g_{\perp} = 2.090$
{[Cu(**4,4'-bpy**)(μ-OOCH)(NO$_3$)]}$_n$ (**16**)	2D	Oct.	Blue, Needle	ν_{as}(COO) 1575, ν_s(COO) 1416, δ(O-C-O) 644, (NO$_3$) 1374	15.5	$g_{\perp} = 2.183$ $g_{//} = 2.046$	$g_{\perp} = 2.186$ $g_{//} = 2.046$
{[Cu$_2$(**4,4'-bpy**)$_2$(μ-OOCCH$_3$)$_3$](ClO$_4$)(H$_2$O)}$_n$ (**17**)^a	2D	Oct. + TBP	Blue, Needle	ν_{as}(COO) 1564, ν_s(COO) 1417, δ(O-C-O) 646, (ClO$_4$) 1067-1038	16.5, 12.5 (sh)	$g_i = 2.060$	$g_i = 2.058$
{[Cu$_2$(**4,4'-bpy**)$_2$(μ-OOCCH$_3$)$_3$](PF$_6$)(H$_2$O)}$_n$ (**18**)	2D	Oct. + TBP	Blue, Needle	ν_{as}(COO) 1564, ν_s(COO) 1417, δ(O-C-O) 645, (PF$_6$) 834-823	16.5, 12.5 (sh)	$g_{\perp} = 2.229$ $g_{//} = 2.090$	$g_{\perp} = 2.217$ $g_{//} = 2.090$
{[Cu$_2$(**4,4'-bpy**)$_2$(μ-OOCCH$_3$)$_3$](BF$_4$)(H$_2$O)}$_n$ (**19**)	2D	Oct. + TBP	Blue, Needle	ν_{as}(COO) 1564, ν_s(COO) 1417, δ(O-C-O) 644, (BF$_4$) 1024-1001	16.5, 12.5 (sh)	$g_{\perp} = 2.229$ $g_{//} = 2.095$	$g_{\perp} = 2.230$ $g_{//} = 2.079$
{[Cu$_2$(**4,4'-bpy**)$_2$(μ-OOCCH$_3$)$_3$](CF$_3$SO$_3$)(H$_2$O)}$_n$ (**20**)^a	2D	Oct. + TBP	Blue, Needle	ν_{as}(COO) 1568, ν_s(COO) 1417, δ(O-C-O) 650, (CF$_3$SO$_3$) 1257-1200	16.5, 12.5 (sh)	$g_{//} = 2.170$ $g_{\perp} = 2.060$	$g_{//} = 2.175$ $g_{\perp} = 2.060$

Oct. = distorted octahedral; TBP = distorted trigonal bipyramidal; ^{a}proposed structures (see Chapter 4); ^{b}see Figure 4.19; ^{c}kK = 1000 cm^{-1}

2.4.2 The products of copper(II)-4,4'-bpy-carboxylato system

Nine copper(II)-**4,4'-bpy**-carboxylato compounds were obtained and were characterized crystallographically to be a copper(II)-**4,4'-bpy**-formato/acetato compound, $\{[Cu_3(\textbf{4,4'-bpy})_2(\mu\text{-OOCH})_4(H_2O)_2](X)_2(H_2O)_6\}_n$ when $X = ClO_4^-$ (**12**), PF_6^- (**13**), BF_4^- (**14**), $CF_3SO_3^-$ (**15**), $\{[Cu(\textbf{4,4'-bpy})(\mu\text{-OOCH})(NO_3)]\}_n$ (**16**), $\{[Cu_2(\textbf{4,4'-bpy})_2(\mu\text{-OOCCH}_3)_3](X)(H_2O)\}_n$ when $X = ClO_4^-$ (**17**), PF_6^- (**18**), BF_4^- (**19**), $CF_3SO_3^-$ (**20**). All products were successfully synthesized by the mole-ratio method and diffusion layer technique, using copper(II) salts, **4,4'-bpy** and corresponding sodium or potassium salt as starting reagents, in a similar manner to those of the zinc(II)-**4,4'-bpy**-carboxylato compounds. The analytical data and spectroscopic properties, given in Table 2.2, are consistent with those of the authentic compounds. The crystal structures (for compounds **12** and **18**), infrared, reflectance and EPR spectra, thermal and optical properties, as well as their catalytic reactivity are investigated in detail and reported in Chapter 4, together with the dynamic structural transformation and anion-exchange behavior.

2.5 Conclusions

Two series of the metal organic frameworks, zinc(II)-**4,4'-bpy**-carboxylato and copper(II)-**4,4'-bpy**-carboxylato compounds containing the 4,4'-bipyridine as organic linker and monocarboxylate as co-ligands are described in the present work:

(1) A series of zinc(II)-**4,4'-bpy**-carboxylato compounds. Compounds $\{[Zn_3(\textbf{4,4'-bpy})_{3.5}(\mu\text{-OOCH})_4(H_2O)_2](X)_2\}_n$ when $X = ClO_4^- \bullet H_2O$ (**1**), PF_6^- (**2**), $BF_4^- \bullet H_2O$ (**3**), $\{[Zn(\textbf{4,4'-bpy})(\mu\text{-OOCH})(H_2O)_2](CF_3SO_3)(H_2O)\}_n$ (**4**), $\{[Zn_4(\textbf{4,4'-bpy})_4(\mu\text{-OOCH})_5(H_2O)_5](NO_3)_3(\textbf{4,4'-bpy})_2(H_2O)_3\}_n$ (**5**), $\{[Zn_3(\textbf{4,4'-bpy})_3(\mu\text{-OOCCH}_3)_4(H_2O)_2](PF_6)_2(H_2O)_2\}_n$ (**6**), $\{[Zn_3(\textbf{4,4'-bpy})_4(\mu\text{-OOCCH}_2CH_3)_4](ClO_4)_2(\textbf{4,4'-bpy})_2(H_2O)_4\}_n$ (**7**), $\{[Zn_3(\textbf{4,4'-bpy})_4(\mu\text{-OOCC}_2H_5)_4(H_2O)_2](PF_6)_2(H_2O)_2\}_n$ (**8**), $\{[Zn_2(\textbf{4,4'-bpy})_2(\mu\text{-OOCC}_2H_5)_2(OH)(H_2O)](BF_4)(H_2O)_2\}_n$ (**9**), $\{[Zn_2(\textbf{4,4'-bpy})_2(\mu\text{-OOCC}_2H_5)_2(H_2O)_2](CF_3SO_3)_2\}_n$ (**10**), and $\{[Zn_3(\textbf{4,4'-bpy})_4(\mu\text{-OOCC}_2H_5)_4(H_2O)_2](NO_3)_2(H_2O)_3\}_n$ (**11**) suitable for X-ray structure analysis were successfully synthesized and characterized for their composition. The structures, thermal and optical properties, potential cation-exchange properties with structure retention by doping zinc(II)

compounds with copper (II) and manganese(II), dynamic structural transformation by removal and reintroduction of guest molecules, anion-exchange and catalytic reactivity of all frameworks will reported in detail in Chapter 3.

(2) A series of copper(II)-**4,4'-bpy**-carboxylato compounds. Compounds $\{[Cu_3(\mathbf{4,4'\text{-}bpy})_2(\mu\text{-}OOCH)_4(H_2O)_2](X)_2(H_2O)_6\}_n$ when $X = ClO_4^-$ (**12**), PF_6^- (**13**), BF_4^- (**14**), $CF_3SO_3^-$ (**15**), and $\{[Cu(\mathbf{4,4'\text{-}bpy})(\mu\text{-}OOCH)(NO_3)]\}_n$ (**16**), $\{[Cu_2(\mathbf{4,4'\text{-}bpy})_2(\mu\text{-}OOCCH_3)_3](X)(H_2O)\}_n$ in which $X = ClO_4^-$ (**17**), PF_6^- (**18**), BF_4^- (**19**), $CF_3SO_3^-$ (**20**) were successfully synthesized and crystallographically characterized for four compounds, namely **12**, **14**, **16** and **18,** while those of the remaining ones characterized from an elemental analysis and spectroscopic properties and the results are reported in the present Chapter 2. The crystal structures, infrared, reflectance and EPR spectra, thermal and optical properties, as well as their catalytic reactivity have been investigated in detail and are reported in Chapter 4, together with the dynamic structural transformation and anion-exchange behavior.

All metal organic frameworks of both series were prepared directly by the mole-ratio method and diffusion layer technique and have been characterized by X-ray structure analysis, elemental microanalysis, infrared, electronic diffuse reflectance and EPR spectra and X-ray powder diffraction as the preliminary results.