

CHAPTER 5 CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORKS

5.1 Conclusions

(a) One-pot reaction

The one-pot reaction may be used to prepare the ionic complexes of general formula, $K_n[Cu_2(p-OC_6H_4COO)_n(CH_3CH=CHCOO)_{4-n}]$, where $n = 1$ and 2 , but not $n = 3$, and to prepare $K_n[Cu_2(p-OC_6H_4COO)_n(CH_2(CH_3)=CHCOO)_{4-n}]$, where $n = 2$ and 3 , but not $n = 1$.

All of the anionic complexes have the paddle-wheel structure and square pyramidal geometry at both Cu(II) centres. Their optical band gap energy ranges from 2.89 eV to 3.11 eV, and independent on the ratio of arylcarboxylate:alkylcarboxylate ligands. Also, there is no correlation between thermal stability and the ratio of aromatic to unsaturated aliphatic carboxylates.

All complexes exhibit antiferromagnetic behavior. The antiferromagnetic interaction is stronger for complexes with *syn-syn* bridging carboxylate ligand than for *syn,anti*- and/or chelating carboxylate ligand; and with a higher ratio of unsaturated aliphatic carboxylate ligand. All complexes showed quasireversible redox properties.

(b) Ligand-exchange reaction

The ligand-exchange reaction was successfully used to prepare the ionic precursor complexes $[Cu_2(p-HOC_6H_4COO)_n(CH_3CH=CHCOO)_{4-n}]$, where $n = 1$ and 3 , but not $n = 2$. The complexes were dinuclear with square pyramidal geometry at the two Cu(II) centres. Their optical band gap energy ranges from 2.31 eV to 2.63 eV. The complex with a higher ratio of arylcarboxylate ligand ($n = 3$) has a wider band gap energy, higher thermal stability and is antiferromagnetic, while that with a lower ratio ($n = 1$) has a

narrower band gap energy, lower thermal stability and is ferromagnetic. All complexes undergo quasireversible redox reaction.

The ligand-exchange reaction may also be used to prepare ionic precursor complexes of general formula $[\text{Cu}_2(p\text{-HOC}_6\text{H}_4\text{COO})(\text{RCOO})_3]$, where R is = $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7$, $(\text{CH}_3)_3\text{C}$, $\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{CH}_2\text{CH}_3)$ and $\text{CH}_3(\text{CH}_2)_7\text{CH}(\text{CH}_2)_5$. The complexes were dinuclear with bridging carboxylates ligands. The geometry at Cu(II) depends on the steric factor (larger number of alkyl groups of the alkylcarboxylates leads to a lower coordination number). Their optical band gap energy ranges from 2.18 eV to 2.29 eV and independent on the size of the alkylcarboxylate ligands. The thermal stability of these complexes depends on geometry at Cu(II) centre and degree of saturation of the alkylcarboxylate ligands. The square pyramidal complexes are antiferromagnetic while the tetrahedral complex is ferromagnetic. All complexes showed quasireversible redox properties.

The precursor complex $[\text{Cu}_2(p\text{-HOC}_6\text{H}_4\text{COO})(\text{RCOO})_3]$, where R is $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7$, could not be converted to the corresponding ionic complex $(\text{K}[\text{Cu}_2(p\text{-OC}_6\text{H}_4\text{COO})(\text{RCOO})_3])$, using KOH.

5.2 Suggestions for Future Works

The one-pot reaction seems to be more suitable to synthesize ionic binuclear copper(II) mixed-carboxylates complexes than the ligand-exchange reaction. Hence, this method may be adopted to prepare low-temperature copper(II) mixed carboxylates by replacing K^+ ion with an organic cation, such as shown in **Figure 5.1**.

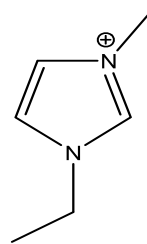


Figure 5.1 Structural formulas of organic cations

It would be interesting to do similar study for copper(II) mixed carboxylates made up of arylcarboxylate ligand substituted with other ionisable group, such as -NH_2 , and $\text{-SO}_3\text{H}$, or with strongly electron-attracting group (NO_2) to replace the -OH group used in this project, and to lower the band gap by using conjugated polymeric organic ligands, such as shown in **Figure 5.2**.

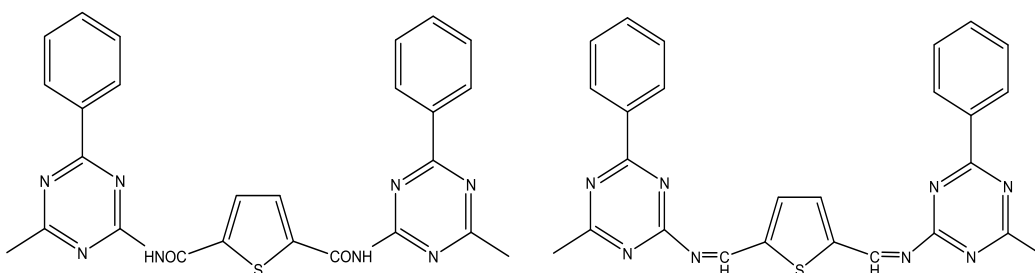


Figure 5.2 Conjugated ligands

The study of low band gap materials may be extended to mixed-valence complexes, such as $[\text{Cu(II)Cu(I)(4-XC}_6\text{H}_4\text{COO)}_3]$ and $[\text{Fe(III)Fe(II)(4-XC}_6\text{H}_4\text{COO)}_5]$, mixed-metal complexes, such as $[\text{CuFe(4-XC}_6\text{H}_4\text{COO)}_2\text{L}]$, where $\text{X} = \text{OH, NH}_2, \text{NO}_2$, and spin-crossover complexes, such as $[\text{M(cyclam)(RCOO)}_2]$, where $\text{M} = \text{Co(II), Fe(II), Mn(II)}$; and $\text{R} =$ linear and branched alkyl with $n > 6$.

The photoluminescence study should be repeated using samples in the form of thin films, and excited at higher energy than the LMCT transition, and using life-time fluorescence spectrometer.