CHAPTER 1 INTRODUCTION

Metallomesogens (metal-based liquid crystals [1-4]) involving first-row transition metals have the combined advantage of anisotropy and fluidity of liquid crystals with useful properties associated with the presence of polarizable *d* electrons, such as tunable geometry and colour, thermal stability, electronic conductivity, and magnetic and redox properties. Such metallomesogens are potential low-dimensional photonic, electronic, spintronic, and/or catalytic materials.

Current research interest is on thermally-stable and low-temperature functional metallomesogens. Two strategies may be adopted in designing the desired materials. The first is to induce self-assembly through the formation of H-bonds by replacing at least one of the alkanoates with an aroate carrying an -OH or -NH_2 functional group. The second is to lower the melting temperature by lowering the molecular symmetry [5] and by using ligands with long or non-linear alkyl chains [1,6]. The research concept is based on copper(II) homocarboxylates, $[Cu_2(\mu\text{-}RCOO)_4]$, where R is a long linear or branched hydrocarbon chain. Examples are $[Cu_2(\mu\text{-}CH_3(CH_2)_{14}COO)_4]$ and $[Cu_2(\mu\text{-}(CH_3(CH_2)_6)_2CHCOO)_4]$, with melting temperature of 112^oC and lower than -20^oC, respectively; the linear chain complex was found to exhibit a columnar discotic mesophase (D_{ho}) [6].

This research was focused on the one-pot synthesis and characterization of copper(II) mixed-carboxylates, $[Cu_2(RCOO)_n(R'COO)_{4-n}]$, where R = *p*-$NH_2C_6H_4COO$, R' = $CH_3(CH_2)_{14}$, and n = 1, 2 and 3, as thermally stable, magnetic and redox-active metallomesogens. The chemical formulas of these

complexes were deduced from CHN elemental analyses, FTIR and UV-vis spectroscopies, and molar conductance. The thermal and metallomesogenic properties were studied using thermogravimetry (TGA), differential scanning calorimetry (DSC), and optical polarized microscopy (OPM), the magnetic susceptibility by the Gouy method, and the redox properties by cyclic voltammetry (CV).

Some of the findings of this research were published in one ISI journal, one was submitted for publication in an ISI journal, and were presented either orally or as posters at three international and three local conferences (**Appendix 1**):

1. Ahmad Nazeer Che Mat, Norbani Abdullah, Hamid Khaledi and Jia Ti Tee, *Bis(μ-hexadecanoato-κ^2O:O)bis[(2,2'-bipyridine-κ^2N,N')(hexadecanoato-κO)copper(II)] methanol, disolvate*, Acta Cryst., (2011) E**67**, m599–m600;
2. N. Abdullah, A.N.C Mat, M.I. Mohamadin, R. Ngatten, *Bis(p-aminobenzoato)bis(hexadecanoato)dicopper(II): a low-temperature and thermally-stable functional metallomesogen*, Journal of Coordination Chemistry (Manuscript ID: GC00-2010-0596);
3. A poster entitled, *Copper(II) Mixed-Carboxylates as Solvents-cum-Catalysts Ionic Liquids: $Cu_2[(p\text{-}H_3NC_6H_4COO)_2(CH_3(CH_2)_{14}COO)_2]X_2$, where $X=NO_3^-$, CH_3COO^-, SO_4^{2-} and Cl^-*, 2nd International Conference and Workshop on Basic and Applied Sciences and Regional Annual Fundamental Science Seminar (ICORAFSS) (2009);

4. An oral paper, "*[Cu_2(p-$H_3NC_6H_4COO$)($RCOO)_3$](CH_3COO) as Functional Metal Containing Ionic Liquids"*, Regional Conference on Ionic Liquids (RCiL09) (2009);
5. An oral paper, "*Metallomesogenic trans-bis(2,2'-bipyridine)tetrakis(hexadecanoato)dicopper(II): Synthesis, Crystal Structure and Characterization*", 5th International Conference on Surfaces, Coatings & Nanostructures Materials, France (2010);
6. An oral paper, "*Copper(II) Mixed-Carboxylates as Solvent-cum-Catalyst Ionic Liquids: [$Cu_2(CH_3(CH_2)_{14}COO)_n$(p-$H_3NC_6H_4COO)_{4-n}$]($CH_3COO)_n$, where n=1,2 or 3",* 10th Asian Conference on Analytical Sciences and 22nd Malaysian Symposium on Analytical Chemistry (ASIANALYSIS X/SKAM 22) (2009);
7. An oral paper, "*Synthesis, structural elucidation, thermal, magnetic and electrochemical properties of trans-bis(μ-p-aminobenzoato)bis(μ-hexadecanoato)dicopper(II)",* 23rd Regional Symposium of Malaysian Analytical Sciences (SKAM 23) (2010); and
8. A poster, "*Bis(p-aminobenzoato)bis(hexadecanoato)dicopper(II): A Thermally-Stable Magnetic Metallomesogen",* Bilateral Symposium between University of Malaya and University of Hyderabad (2010).

This report is divided into five chapters. Chapter 1 introduces the objectives of the research and publications of research findings. Chapter 2 presents the relevant theory and literature reviews on copper(II) carboxylates, metallomesogens, and the instrumental techniques used to characterize the

complexes, namely elemental analysis, FTIR and UV-vis spectroscopies, molar conductivity, TGA, DSC, OPM, magnetic susceptibility and CV. Chapter 3 presents the experimental part of the research covering the methods used to synthesize the complexes and the instrumental techniques used to characterise them. Chapter 4 contains the results and discussions, and Chapter 5 presents the conclusions and suggestions for future works. A list of references is included at the end of each chapter. The appendices are included at the end of the report.

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