DOCTORAL THESIS

The chemistry of luminescent mercury (II) alkynyl complexes and their platinum (II) and gold (I) counterparts

Liu, Li

Date of Award:
2005

The Chemistry of Luminescent Mercury(II) Alkynyl Complexes and Their Platinum(II) and Gold(I) Counterparts

LIU Li

A thesis submitted in partial fulfillment of the requirements

for the degree of

Doctor of Philosophy

Principal Supervisor: Dr. Raymond W. Y. WONG

Hong Kong Baptist University

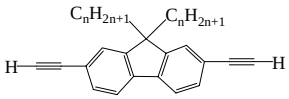
June 2005

Abstract

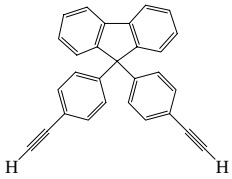
Several new series of thermally stable group 10 platinum(II) and group 12 mercury(II) polyyne polymers containing substituted fluorene and carbazole spacers were prepared in good yields by the Hagihara's dehydrohalogenation reaction of the corresponding metal chloride precursors with the relevant alkynyl ligands (**L_1**–**L_{12}**) at room temperature. Among these, the first examples of soluble well-defined high-molecular weight mercury(II) polyyne polymers with 9,9-dialkylfluorene groups were identified, from which we have been able to directly trigger phosphorescence localized on the organic system through efficient intersystem crossing by ligation to the Hg(II) moiety. The optical and electronic properties of these polymetallaynes were investigated and the results were compared with their dinuclear model complexes as well as the group 11 gold(I) counterpart. The structural properties of selected model complexes have been studied by X-ray crystallography. The influence of the heavy metal atom in these metal alkynyl systems on the intersystem crossing rate and the spatial extent of lowest singlet and triplet excitons were systematically characterized. Our investigations indicate that the organic triplet emissions can be harvested by the heavy-atom effect of group 10–12 transition metals (viz. Pt, Au, Hg) which enables efficient intersystem crossing from the S_1 singlet excited state to the T_1 triplet excited state.

Moreover, mononuclear mercury(II) alkynyl complexes containing substituted fluorene and bithiazole as the linking groups were successfully synthesized from **L_{13}** and **L_{14}** and fully characterized by common spectroscopic methods. Their photophysical properties were studied using UV/Vis and photoluminescence spectroscopies. The high extinction coefficient makes these mercury complexes suitable for HPLC analysis using

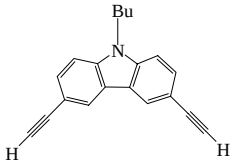
UV detection. The exploitation of these mercury(II) alkynyl complexes in the development of simple and inexpensive procedures for the determination of inorganic mercury and methylmercury was described. All of the ligands **L_1–L_{14}** employed in the present research are shown below:



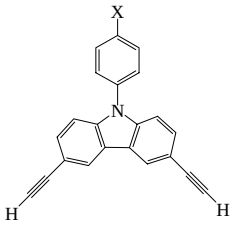
n = 6 **L_1**
n = 8 **L_2**
n = 16 **L_3**



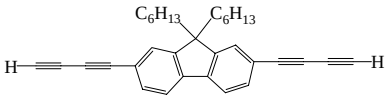
L_4



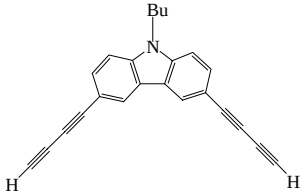
L_5



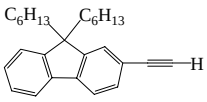
X = Me **L_6**
X = OMe **L_7**
X = Cl **L_8**
X = H **L_9**
X = F **L_{10}**



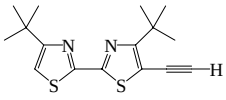
L_{11}



L_{12}



L_{13}



L_{14}

Table of Contents

Declaration i

Abstract ii

Acknowledgements iv

Table of Contents v

List of Tables x

List of Figures xiii

List of Schemes xxi

List of Abbreviations and Symbols xxiii

Chapter 1 Introduction 1

1.1 Background of Research 1

1.2 General Overview of Complex and Polymer Synthesis 2

1.3 Optical Properties, Electronic Structures and Bonding of Transition Metal Alkynyl Complexes 8

1.4 Metallated Molecular Materials of Fluorene Derivatives and Their analogues 16

1.4.1 Fluorene Groups 16

1.4.1.1 C-Donors 16

1.4.1.2 N-Donors 19

1.4.1.3 O-Donors 22

1.4.1.4 Mixed C, N-Donors 24

1.4.2 Carbazole 26

1.4.2.1 C-Donors 27

1.4.2.2 N-Donors 29

1.5 Scope of Thesis 30

1.6 References 31

Chapter 2 Synthesis, Characterization and Properties of Fluorene-, Carbazole- and Bithiazole-Functionalized Alkyne Ligands 40

2.1 Introduction 40

2.2 Synthesis 42

2.3 Spectroscopic Characterization 47

2.4 Absorption and Emission Properties of Alkyne Ligands 54

2.5 Concluding Remarks 61

2.6 References 61

Chapter 3 Synthesis, Characterization and Properties of Dinuclear and Polymeric Metal Complexes Containing Substituted Fluorenes as the Linking Groups 64

3.1 Introduction 64

3.2 Reactions of Fluorene-Functionalized Alkynes with 66

Group 10-12 Transition Metals

3.2.1 Synthesis of Dinuclear Mercury(II) Complexes 66

3.2.2 Synthesis of Polymeric Mercury(II) Complexes 66

3.2.3 Synthesis of Polymeric Platinum(II) Complexes 67

3.2.4 Synthesis of Dinuclear Platinum(II) Complexes 68

3.2.5 Synthesis of Dinuclear Gold(I) Complexes 69

3.3 Spectroscopic and Structural Characterization 69

3.4 Absorption and Emission Properties 83

3.5 Thermal Analysis 109

3.6 Concluding Remarks 123

3.7 References 124

Chapter 4 Synthesis, Characterization and Properties of Dinuclear and Polymeric Metal Complexes Containing Substituted Carbazoles as the Linking Groups 129

4.1 Introduction 129

4.2 Reactions of Carbazole-Functionalized Alkynes with Group 10-12 Transition Metals 131

4.2.1 Synthesis of Dinuclear Mercury(II) Complexes 131

4.2.2 Synthesis of Polymeric Mercury(II) Complexes 131

4.2.3 Synthesis of Polymeric Platinum(II) Complexes 132

4.2.4 Synthesis of Dinuclear Platinum(II) Complexes 133

4.2.5 Synthesis of Dinuclear Gold(I) Complexes 134

4.3 Spectroscopic and Structural Characterization 135

4.4 Absorption and Emission Properties 150

4.5 Thermal Analysis 166

4.6 Concluding Remarks 181

4.7 References 181

Chapter 5 Synthesis, Characterization, Luminescent Properties and Analytical Applications of Mononuclear Mercury Alkynyl Complexes Containing Substituted Fluorene and Bithiazole as the Linking Groups 186

5.1 Introduction 186

5.2 Synthesis 190

5.2.1 Synthesis of Mercury(II) Monoyne Complexes 190

5.2.2 Synthesis of Mercury(II) Bis(alkynyl) Complexes 190

5.3 Spectroscopic and Structural Characterization 191

5.4 Absorption and Emission Properties 199

5.5 Analytical Applications 203

5.5.1 General Background 203

5.5.2 General Derivatization Procedure 207

5.5.3 Chromatographic Analysis 207

5.6 Concluding Remarks 212

5.7 *References* *213*

Chapter 6 Experimental Details 219

6.1 *General* *219*

6.2 *Materials* *221*

6.3 *Experimental Details for Chapter 2* *221*

6.4 *Experimental Details for Chapter 3* *243*

6.5 *Experimental Details for Chapter 4* *250*

6.6 *Experimental Details for Chapter 5* *260*

6.7 *References* *261*

Chapter 7 Conclusions 264

Curriculum Vitae 267