DOCTORAL THESIS

Synthesis, characterization and photophysics of alkynyl-derived inorganic and organometallic materials comprising group 13,14 and 16 elements

Poon, Suk Yue

Date of Award:
2005

Synthesis, Characterization and Photophysics of Alkynyl-Derived Inorganic and Organometallic Materials Comprising Group 13, 14 and 16 Elements

POON Suk Yue

A thesis submitted in partial fulfillment of the requirements
for the degree of
Doctor of Philosophy

Principal Supervisor: Dr. WONG Wai Yeung, Raymond

Hong Kong Baptist University

September 2005

Abstract

The molecular design, synthesis, spectroscopic and photophysical characterization of some metal-containing oligomeric and polymeric acetylide compounds comprising group 14 and 16 elements are discussed. Besides, the chemistry of new π-conjugated organoboranes with intriguing optoelectronic properties is also presented.

Chapter 1 contains a brief review on metal acetylide complexes and polymers with reference to their preparations, characterization, properties as well as their applications in the materials industry. The chemistry of some main group element-containing compounds is also outlined.

Chapter 2 presents the synthetic methodology and characterization of a series of new oligoacetylenic silanes and germanes containing the 9,9-dihexylfluorene and 9-butylcarbazole moieties. Full characterization of these molecules was accomplished by FTIR, NMR (^{1}H, ^{13}C, ^{29}Si), UV/Vis and fluorescence spectroscopies and FAB mass spectrometry. The single-crystal X-ray structures of selected oligoacetylenic silane and germanes have been determined.

A full account of the synthesis, characterization, photophysical and thermal properties of some platinum(II)-containing oligomeric and polymeric alkynylsilanes and alkynylgermanes are presented in Chapter 3. Soluble and thermally stable platinum(II) alkynylsilane and alkynylgermane polymers were successfully synthesized in good yields by CuI-catalyzed condensation polymerization of *trans*-$[PtCl_2(PBu_3)_2]$ with our new ligands discussed in Chapter 2. The regiochemical structure of these polymers was studied by NMR (^{1}H, ^{13}C, ^{29}Si and ^{31}P) spectroscopy. We report the optical absorption and photoluminescence spectra of these metal-based organosilicon and

organogermanium polymers and compare the data with their mono-, di- and triplatinum(II) acetylide model complexes. Our studies have led to a novel approach of using silyl and germyl functionalities as effective conjugation-interrupters to limit the conjugation length in metal polyynes, resulting in much larger radiative decay rate constant. This indicates that our newly synthesized polyplatinaynes can greatly boost the phosphorescence decay rate, which is essential in light energy harvesting from the triplet excited state.

Chapter 4 presents a series of novel and thermally stable group 10–12 metal alkynyl complexes and polymers containing different group 16 conjugation-interrupting units. The regiochemical structures of these angular-shaped polymers were studied by NMR spectroscopy and by single-crystal X-ray analyses for the related metal diyne compounds. Our investigations indicate that harvesting of the organic triplet emissions can be achieved by the strong heavy-atom effect of group 10–12 transition metals which allows very efficient intersystem crossing from the singlet excited state S_1 to the triplet excited state T_1. The influence of metal (viz. Pt, Au, Hg) and chalcogen-based conjugation-interrupters on the intersystem crossing rate and the spatial extent of the lowest singlet and triplet excitons were also fully elucidated.

In Chapter 5, a novel class of π-conjugated organboranes was prepared and an investigation of their optical, physical and redox properties is also presented. These compounds possess donor-π-acceptor (D-π-A) or acceptor-π-donor-π-acceptor (A-π-D-π-A), structural motifs where the trivalent boron protected by two mesityl groups acts as the acceptor. All of them are highly luminescent and exhibit interesting photophysical and electrochemical properties.

Chapters 6 and 7 present the concluding remarks and the experimental details of the work presented in Chapters 2–5.

of the Department of Chemistry.

I would like to acknowledge the Hong Kong Research Grants Council (Grants HKBU 2054/02P) and the Hong Kong Baptist University for financial support of this work. The award of a Li Po Chun Charitable Trust Fund Postgraduate Scholarship (2004–2005) administered by the University is also gratefully acknowledged.

Last but not least, my wordless and wholehearted gratitude must be dedicated to my family in particular to my mother for their care, comfort and continuous support during my course of study.

Table of Contents