DOCTORAL THESIS

Synthesis, characterization and photophysical properties of platinum(II) metallopolyyne polymers for photovoltaic applications

Li, Li

Date of Award:
2011

Synthesis, Characterization and Photophysical Properties of Platinum(II) Metallopolyyne Polymers for Photovoltaic Applications

LI Li

A thesis submitted in partial fulfillment of the requirements

for the degree of

Doctor of Philosophy

Principal Supervisor: Professor WONG Wai Yeung, Raymond

Hong Kong Baptist University

March 2011

Abstract

The molecular design, synthesis, spectroscopic and photophysical characterization of a new series of transition metal-containing complexes and polymers incorporating different π-conjugated chromophores are discussed. The applications of some of these compounds in solar cells and materials science are also outlined.

In chapter 1, a brief overview of the development of solar cells is given. The techniques to optimize the performance of organic solar cells are highlighted.

Chapter 2 describes the synthesis and characterization of a series of donor-based metallopolyyne polymers of platinum(II), which contain electron-rich chromophores. All the polymers exhibit good thermal stability and have a moderate to high degree of polymerization. Both optical absorption and photoluminescence properties of newly synthesized ligands and polymers and model complexes have been studied. In addition, the photovoltaic behavior of some of the polymers was examined, and the results indicate that the polymers are suitable materials for photovoltaic cell applications.

In chapter 3, a versatile system was developed for preparing fluorene-based conjugated metallic copolymers with tunable optical absorption, electrochemical and electronic properties for polymer solar cells (PSCs). The photophysical, charge-transporting, and electrical properties of our organometallic polymers can be

easily manipulated by variation of the oligothienyl chain length. This in turn can improve the performance of the resulting PSCs through extending the oligothienyl chain length in strongly absorbing polyplatinynes.

In chapter 4, ten solution-processable Pt(II) acetylide polymers functionalized with electron-deficient spacers were prepared and characterized. Optical spectroscopy and electrochemical data reveal narrow bandgap systems for most of the polymers. Inclusion of thiophene fragments into the electron-deficient units further expands the spectral width of absorption appropriate for sunlight harvesting in **P22**, **P25** and **P30**, which in turn can raise the performance of the resulting PSCs. For **P21** and **P22**, biological studies show that the metallopolymers are non-cytotoxic *in vitro* of up to 50 μg mL^{-1} against HaCaT human skin keratinocytes and liver derived Hep3B cells. All these results reveal that such Pt(II) acetylide polymers can be a promising and safe material for the development of stable PLEDs. Based on their attractive physical, chemical and biological features, we could further make use of them for various purposes in photovoltaic and textile technologies.

In chapter 5, several heterobimetallic metallopolyyne polymers have been designed, successfully synthesized and fully characterized by spectroscopic and photophysical measurements. We examined the photovoltaic behavior of some of the polymers and found that they have the ability to convert solar energy to electricity, although the PCEs are not very high. The PCE of **P36** with V_{oc} = 0.59 V, J_{sc} = 0.98 mA cm^{-2} and FF = 0.25 and **P37** with V_{oc} = 0.54 V, J_{sc} = 1.21 mA cm^{-2} and FF = 0.27 are 0.14% and 0.18%, respectively, indicating that they have the potential to be used for solar cell applications.

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

Table of Contents

Chapter 5

Synthesis and Properties of Heterobimetallic Metallopolyyne Polymers