

DOCTORAL THESIS

Synthesis, characterization and properties of self-assembled metal complex nanosheets heterostructured organic microrods

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Abstract

Molecular self-assembly or ligand-metal assembly is a process in which several individual molecules and metal ions organize themselves into an ordered arrangement without external stimuli, the defined structures can lead to distinctive electronic and photonic performances. In the meantime, as the scale of materials decreases, various unique properties arise from their minute scaled dimensions, such as surface effect, volume effect, quantum effect and dielectric confinement effect, etc. Therefore, the design and fabrication of the micro- and nanomaterial via the technique of molecular self-assembly or ligand-metal assembly is becoming an emerging research field, for the purpose of meeting the increased demands of multi-functional materials.

Chapter 1 gives an overview of the advanced materials prepared by either molecular self-assembly or ligand-metal assembly. We described the interaction nature in detail, and enumerated the applications as well as developments of this scientific field. Furthermore, the detailed classifications as well as previous work of these advanced materials we researched on, such as two dimensional nanosheets, hetero-structured materials and cyclometalated iridium(III) complexes were also amply summarized.

Two-dimensional nanosheets have always been a research hotspot since graphene was discovered and isolated. In contrast, molecule-based organometallic nanosheets through bottom-up method exhibit more inner structures. In Chapter 2, we constructed two classes of organometallic nanosheets with different

intermolecular forces, one is metal–ligand coordination, while the other one is the aromatic (π - π) interaction. Two-dimensional nanosheets with Hg-acetylide linkages, bis(dipyrrinato)metal linkages as well as bis(terpyridine)metal linkages were synthesized and characterized by UV-Vis absorption spectroscopy, FT-IR spectroscopy, optical and electron microscopy, photoluminescence spectroscopy, thermal gravimetric analysis, X-ray photoelectron spectroscopy and so on. In addition, the potential applications were explored as well, including the tests of charge mobility and current capacitance. Meanwhile we also investigated the two-dimensional nanosheets self-assembled by aromatic (π - π) interaction. The morphology characterizations, crystal form measurements, besides elemental analyses were conducted. By means of surface control, the hybrid nanosheets could achieve many superior performances, like super hydrophobicity, high conductivity and soft magnetism.

In Chapter 3, we firstly mentioned that organic hetero-structured micro- or nanomaterials are widely attractive on account of its extensive applications in lasers, bipolar transistors, field effect transistors and solar cells. In our work, we focus on the diverse microrods assembled from π -conjugated small molecules, especially in the construction of heterogeneous organic heterojunction materials with specific components distribution. Two novel kinds of heterostructure, multilayer core-shell structured heterojunction and heterogeneous rod-tail helix were fabricated and developed both via a stepwise seeded-growth route, in which the different constituents possess different colors of luminescence. Through the

media of fluorescence microscopy and confocal microscopy, the core-shell hetero-structures can be observed, testified and recorded quite distinctly. Furthermore, the prepared method by employing seeded-precursor could give us a revelation about constructing more sophisticated and functional organic luminescent heterogeneous materials.

Chapter 4 focuses on the syntheses and characterization of eight cyclometalated iridium(III) complexes, Ir(TPY)₂(Dipyrrinato), Ir(PIQ)₂(Dipyrrinato), Ir(Ligand 1)₂(Dipyrrinato), Ir(Ligand 2)₂(Dipyrrinato), Ir(Ligand 3)₂(Dipyrrinato), Ir(PPY)₂(Dipyrrinato), Ir(m-PPY)₂(Dipyrrinato) and Ir(PPY-m)₂(Dipyrrinato). As is known, iridium(III) complexes can exploit the energy of both 25% singlet and 75% triplet excited states. Due to their highly efficient applications in phosphorescent OLEDs, these materials are considered as one of the potential candidates for flexible display screen as well as clearing luminary. Among those full-color light-emitting iridium(III) phosphors, near-infrared (NIR) phosphors are broadly utilized in phototherapy as well as biosensors. Herein, our eight synthetic cyclometalated iridium(III) complexes all gave photoluminescence at 680 - 700 nm in solution, which could be attributed to the NIR region. We continuously tune the extensive conjugation on the C^N ligands in order to make longer wavelength emitting phosphors. The HOMO and LUMO of eight synthetic iridium(III) phosphors were also calculated according to their cyclic voltamograms (CV). The design and preparation strategy in this thesis can inspire us to develop near-infrared as well as higher-performance organometallic phosphors.

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