共軛有機分子材料奈米結構及有機-無機混成自組裝奈米複合材料之合成及光電特性探討

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摘要

本研究主要係探討合成及定性分析含有螢光的共軛有機小分子，並透過自組裝的手法製備出發螢光的奈米粒子及有機無機奈米複合材料。本論文擬分成以下兩部分討論：

第一部分主要合成出一系列的含螢光特性的有機小分子及軟段硬段塊式分子(rod-coil molecules)，並探討其有機合成路徑、奈米粒子的形成機制以及形成奈米粒子前後的光物理特性變化。在分子的結構設計上，共軛有機部份主要採用寡聚 1,4-伸苯基乙烯的衍生物(oliogophenylene vinylene derivatives)做為主體，並透過吸收與放射光譜(UV, PL), 掃描式及穿透式電子顯微鏡(SEM、TEM)以及飛秒雷射(Time-Resolved studies)等分析的技術來鑑定其形成奈米粒子後所表現出的特殊光物理特性。奈米粒子的製備方法為在水及四氫呋喃的不同體積分率的混合溶液中，透過相分離效應而形成懸浮物，以達到自組裝的目的。經由電子顯微鏡的觀測(SEM)，可發現不論是對於 PPB 系列的奈米粒子、CNDSB 的奈米帶或者是 HPS 的奈米花而言，當形成奈米粒子之後，其放射強度相較於原本的巨觀分子，將有大幅度的提升。對於胺基-二苯乙烯(amino-stilbene)的衍生物來說，更可觀察到所謂的螢光淬滅效應(Fluorescence quenching)。化合物 DSB-C8 顯現出類

似蟲狀的微胞奈米結構，此奈米結構對於其光致發光的強度將有增強的貢獻。這些奈米粒子的粒徑、化學結構及其相關的光物理特性將於第一部分中有詳細的探討與分析。再者，本研究同時合成了所謂的軟段硬段塊式分子(rod-coil molecules)，其硬段的區塊主要係採用 OPV 衍生物，軟段係採用親水性的聚環氧乙烷(polyethylene oxide，PEO)，以此為主體於水/四氫呋喃共溶液中所製備出來的奈米粒子，即使其本身於溶液態中的發光強度相當的弱，其粒徑的不同亦強烈的影響了其本身的光物理特性。

本研究第二部分主要係討論以溶膠-凝膠(sol-gel)製程製備出自組裝的有機-無機混成奈米複合材料。在分子的結構設計上，有機端主要採用以二苯乙烯及芴的衍生物(PPP-C11，FL-Stilbene-$(C11)_2$)，此有機單體本身具有親水及疏水兩性性質，其末端的羥基可在酸性環境下與無機矽的前驅物作用，透過 Bergman 環化聚合法將螢光有機分子包圍於矽的六角柱之中，以構成所謂的有機-無機奈米複合材料。以 PPP-C11 and FL-Stilbene-$(C11)_2$ 這兩種材料，透過旋轉塗佈及溶液蒸發而導致的自組裝現象所製備出的有機/無機奈米薄膜，由於螢光分子相當規則的被限制在矽的奈米六角柱之中，其所表現出的光致發光強度以及絕對量子效率，相較於原本的有機材料薄膜均有大幅的提升，同時此奈米結構亦強烈的影響發光分子的光物理特性。此結果對於一般有機分子於薄膜態時常因分子間互相堆疊而導致的發光效率降低現象或許將有某種程度的改進。此兩種奈米複合材料於掃描式電子顯微鏡的觀察下分別呈現出奈米板及奈米棒的型態。而本論文所呈現的此藉由矽基材將有機螢光分子規則且有效的控制於奈米洞中的手法，經由溶液蒸發

而導致的自組裝現象所製成的薄膜，亦可視為另一種提高發光物質的薄膜態量子效率的嶄新方法。藉由此法可藉由矽與有機分子的連結來提高有機小分子於固態時的成膜性，此高規則度的奈米薄膜將可望應用於電激發光元件製程中，以製備出高亮度及高效率的有機發光元件。

Synthesis and Characterization of Nanostructures of Conjugated Organic Light Emitting Compounds and Organic-Inorganic Hybrid Self-assembled Nanocomposites

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Abstract

The goal of this research is to study the synthesis and characterization of fluorescent organic nanoparticles and self-assembled nanocomposites.

This thesis consists of two parts:

The first part of this study gives a brief introduction about fluorescent organic nanoparticles and their photophysical properties and contains the results and discussion along with the experimental section of the synthesis and nanoparticles formation of conjugated organic compounds and rod-coil molecules. We synthesized a series of conjugated organic compounds, especially the oliogophenylene vinylene derivatives, and have observed the fascinating photophysical properties of their fluorescent organic nanoparticles and these were studied by several characterization techniques. These nanoparticles were prepared by reprecipitation in solutions of water

and THF at various volume fractions. We observed formation and strong emission of PPB nanoparticles, CNDSB nanobelts, HPS nanoflowers. Fluorescence quenching was observed for amino-stilbene derivatives. DSB-C8 showed worm-like micellar nanostructures which contributed to the enhancement of photoluminescence intensity. Overall size and nanostructure dependent photophysical properties were observed for these organic compounds. Moreover, we synthesized rod-coil molecules with OPV derivatives as rods showed different sizes of the nanoparticles in water dispersions and they too showed the size-dependent photophysical properties in nanoparticles even though their molecular solutions were very weak or no fluorescent.

The second part, gives a brief introduction about the self-assembled organic-inorganic functional hybrid nanocomposites and “Design, Synthesis and Characterization of Organic Surfactant Amphiphilic Monomers with Chromophoric Functional Groups and their Self-assembly with Inorganic Precursors” and includes the experimental section of the present work. We have demonstrated the preparation of chromophoric amphiphile/silica self-assembled nanocomposite films of PPP-C11 and FL-Stilbene-$(C11)_2$ with enhanced emission; thus tried to solve the problem of soild-state quenching of the organic chromophores to some extent. These nanocomposites showed nanosheet or nanorod morphology. The ability to tailor the orientation of the chromophore surfactant amphiphiles within the mesoscopic structures by solvent evaporation induced self-assembly in thin films and subsequent formation of well ordered chromophore nanopackets in this fashion dramatically impacts the photophysical properties of these materials. This method is free of chromophore leaching problem which is common in

inclusion chemistry. The demonstration of ‘controlled’ chromophoric aggregation induced emission enhancement in self-assembled functional hybrid nanocomposites may stimulate new molecular engineering endeavours in the design of luminescent organics with highly emissive aggregation states. Moreover, we have demonstrated Bergman cyclopolymerization of polymerizable amphiphilic surfactant monomer within the hexagonal channels of functional hybrid nanocomposite formed by evaporation-induced self-assembly. Such a technique allows the patterned polymerization of the polymer precursor material directly onto a surface, thus avoiding solubility related problems that may be encountered when attempting to directly coat the pristine polymeric material, which is often insoluble, thereby facilitating its use in device fabrication.

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