2003年上海大学博士学位论文 ④

蓝色有机薄膜电致发光器及界面特性的研究

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Study of Blue Organic Thin Film Electroluminescent Devices and Interface Properties

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Major: Materials Science
Supervisor: Prof. Jiang Xueyin

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答辩委员会对论文的评语

有机薄膜电致发光器件（OLED）作为一种理想的平板显示方案已成为目前国际上学术界和产业界普遍关注的一个热点.选择这一前沿性课题作为研究方向,具有十分重要的学术价值和广阔的应用前景.

本文对蓝色有机薄膜电致发光器件及界面特性进行了系统的研究，涉及材料的合成和器件的制备，通过采用不同的器件结构得到了各种不同材料的性能优良的蓝色发光器件,用界面修饰的方法提高了电致发光器件的效率，并对 OLED 中激基复合物的形成进行了系统研究. 创新之处有：①采用阻挡层结构得到了空穴传输型材料的蓝色发光，并采用激子限域结构得到新型 FNPD 的蓝紫色发光；②以蓝光材料 DPVBi 为基质掺杂具有高荧光量子效率的 Perylene，获得了 Perylene 的蓝色发光，最高亮度达到 6123 cd/m^2，未见报道；③通过调节 NPVBi 和电子传输材料 Alq_3 的厚度得到了色度和效率俱佳的蓝色发光器件；④系统地研究了 OLED 中激基复合物形成的条件、特点和规律，特别是采用材料混蒸的方法，人为增加界面，突出激基复合物发光，很有新意；⑤用 C_{60} 对 ITO 与空穴传输层之间的界面进行修饰，提高了有机电致发光器件的效率.

本论文表明作者具有扎实的发光专业基础知识,掌握文献资料丰富，对 OLED 发展动态了解全面，具备了独立从事 OLED 研究的能力. 论文组成合理、分析透彻，达到博士论文水平，是一篇优秀的博士论文. 作者在答辩中叙述清楚，回答问题正确.

答辩委员会表决结果

经答辩委员会表决，全票同意通过朱文清同学的博士学位论文答辩，建议授予工学博士学位.

答辩委员会主席：**夏义本**

2003 年 6 月 19 日

摘　要

有机薄膜发光器件作为新一代的平板显示器件，因其主动发光和宽视角、低压驱动和高效发光、颜色丰富和响应速度快、轻便和成本低廉、可制成柔性屏等优点，引起人们日益浓厚的兴趣，显现出十分诱人的应用前景。至今已取得了较大进展，部分器件实现了商品化. 配上高度集成的专用电路和系统，在不久的将来，必将成为适应信息时代要求的最具竞争力的平板显示器件.

本文主要从材料特性、器件结构、发光机理和过程及界面特性等角度出发，研究蓝色发光器件的结构与性能，激基复合物的发射性质和器件的界面修饰特性. 研究的主要内容包括：

(1) 选用不同的蓝光材料，实现多种不同结构和发光原理的蓝色发光器件.

通过引入电子传输层和复合阴极，改善蓝光材料 8 –羟基喹啉锂为发光层的器件的发光性能. 用电子传输特性的具有高离化势的空穴阻挡层，实现了空穴传输材料的蓝色发光. 研究表明阻挡层器件的稳定性较差. 掺杂型器件中，采用高荧光效率的染料，获得了最高亮度为 6123 cd/m^2 的蓝色发光，然而器件的稳定性无明显改善. 主要原因是基质的玻璃转变温度 T_g 较低，掺杂剂呈平面结构，易聚集. 以联苯乙烯衍生物 NPVBi 为发光层，由于其具有合适的能级位置，通过调节 NPVBi 和电子传输层的厚度，获得了效率和蓝光色度俱佳的蓝色器件. 结果表明，发光层和电子传输层的厚度对载流子的复合和发光区域、发光颜色及效率有重要影响.

对于宽带隙的蓝紫光材料，考虑能级匹配，采用激子限域的多层器件结构，获得了色纯度良好的蓝紫光发射. 同时，选用载流子传输材料时应避免在界面形成激基复合物，以确保蓝紫光色纯度不受激基复合物发射的影响. 用 EL 光谱分解、两种有机物混合膜的PL和EL的比较方法证实了激基复合物的存在. 当产生激基复合物发射影响蓝光色纯度时，隔离形成激基复合物的界面可以避免激基复合物的产生，获得蓝色发光. 选择用较宽带隙的材料形成激基复合物，获得了色纯度较好的蓝光发射.

(2) 从材料结构，界面能级，发射特性等方面研究了激基复合物形成和发射基本规律.

以空穴传输材料 TPD 和电子传输材料 PBD 组成双层器件和混合层器件时，EL 光谱包含不同成份的多重发射，并且电荷复合物的形成和衰减均随外电场呈现不同的变化规律，表明由于TPD/PBD异质结界面和TPD:PBD混合发射层的差异造成电场对各激发过程的影响不同.

研究表明双层器件中激基复合物仅发生在 TPD/PBD 界面. 双层器件的 EL 光谱各成份随电流增加呈现不同的变化规律，致使 EL 光谱发生红移. 在电流密度小于 32 mA/cm^2 时为白光区域. 混合层器件中由于 TPD:PBD 混合层增加了形成激基复合物的界面和发射比例. 两种结构器件的 EL 光谱均呈现出随偏置变化的特点.

在 ITO/J0503/PBD/Al 器件中表现出 electroplex 的近白光发射，说明在光激发和电激发下该器件内部载流子产生和复合的物理过程是不同的.

通过激基复合物(TPD/PBD)或 electroplex(J0503/PBD)的发射在双层器件中获得白光，可大大简化器件的制备工艺和结构.

形成激基复合物需要组成分子的有利的构型和取向. 采用非平面性的具有大取代基和立体结构特征的分子，有可能阻碍激基复合物的形成.

用具有不同离化势的空穴传输材料(HTM)与固定的电子传输材料 BBOT 组成结构为 ITO/HTM/BBOT/Al 的双层器件，用 PL 和 EL 光谱的比较证明在 HTM/BBOT 界面形成了激基复合物. 解释了 EL 光谱随偏置增强而蓝移的原因.

在 HTM/BBOT 器件中激基复合物的峰值能量 $h\nu_{exm}$ 与对应的 HTM 的离化势 I_p 成线性关系，说明激基复合物的发射波长 ν_{exm} 取决于电子给体的离化势和电子受体的亲和势之差. 通过激基复合物的发射可以有规律地调节器件的发光颜色. 这种类型的器件提供了调节器件发光颜色的有效方法.

(3) 在 ITO 与空穴传输层界面间采用界面修饰层，提高了器件的发光效率.

采用具有蒸发性的富勒烯 C_{60} 在结构为 ITO/C_{60}/TPD/Alq_3/LiF/Al 的器件中作为空穴注入修饰层. 研究表明适当厚度的 C_{60} 可以改善器件效率. 在 C_{60} 厚度为 1.6 nm 时，器件发光效率最高，在电流密度为 100 mA/cm^2 时，该器件的发光效率比没有修饰层器件的效率提高了近一倍.

关键词 有机薄膜，电致发光，蓝色发光，稳定性，激子限域，激基复合物，electroplex，颜色调节，界面修饰，效率

Abstract

Organic thin film electroluminescent devices have attracted more and more interests as a new generation of flat panel displays with particular advantages such as self-luminous, low driving voltage, high luminescence efficiency, more colorful and rapid response, portable, flexible and low cost, and thus, exhibiting a great application potential. Great progresses have been made in this field and some of the devices are put into practical application so far. Equipped with large scale integrated circuits and systems, organic electroluminescent devices will become one of the most competitive flat panel displays of information epoch in the near future.

In this dissertation, blue device structures and properties, the nature of exciplex emission and interface modification properties are investigated on the basis of properties of organic materials, device structures, luminescence mechanisms and interface properties. The main contents include:

(1) Several blue organic electroluminescent devices with different structures and diverse luminescence principles are realized according to the properties of different organic materials.

The performance of a device using blue lithium 8-hydroxyquinoline(Liq) as an emissive layer has been improved by introduction of an electron transport layer and a composite cathode. The blue emission is achieved from a hole transport layer by use of electron

transport hole-blocking layer with high ionization potential. However, the stability of this type of device is poor. The highest blue luminance of 6123cd/m^2 has been obtained in a doped device using fluorescent dopant of high quantum efficiency. But, there is no significant improvement on the device stability. The main reasons for the low stability of the doped device are the low glass transition temperature T_g of the host and the planer structure of the dopant having a high tendency to aggregate. Devices with a novel distyrylarylenes derivative, 4,4′-bis[2,2-(1-naphthyl,phenyl)vinyl]-1,1′-biphenyl(NPVBi), as an emitting layer have been prepared. By adjusting the thickness of the NPVBi and electron transport layer, blue emission with both high efficiency and a good color purity is achieved. It is proved that luminescence properties of the devices can be controlled by the thickness of the emitting layer NPVBi and electron transport layer.

For a purplish blue fluorescent material, a multiplayer exciton confinement device has been constructed based on the match of energy levels and purplish blue light with good color purity is obtained. In addition, to insure the color purity of blue light, appropriate carrier layers should be selected to avoid the exciplex formation at the interface between the carrier layers and the emissive layer. The existence of exciplexes was evidenced by the decomposition of electroluminescent spectrum, and by comparison of photoluminescence(PL) and electroluminescence(EL) of the blends of constituent organic materials. When exciplexes occurred at interface of constituent organic materials, the color purity of blue emission could be affected. To prevent exciplex formation, inserting

an thin layer between this interface is effective.

On the other hand, science exciplex emission has a bathochromic shift relative to the fluorescence of the constituent organic materials, a blue emission of exciplex with good color purity has been obtained by using of large band gap constituent organic materials.

(2) The elementary principle of exciplex formation and emission have been investigated on the basis of the material structures, energy levels at interface and emission properties.

By use of hole transport material TPD(N,N′-diphenyl-N,N′- bis (3-methylphenyl)-1,1′-biphenyl -4,4′-diamine) and electron transport material PBD(2-(4′-biphenyl)-5-(4″-tert-butylphenyl)-1,3,4- oxadiazole), a bilayer and a mix-layer device were fabricated, respectively. The EL spectra the devices show different multiple components; and the formation and decay of charge complexes are dependent on the applied electric field. These facts indicate that the differences between the TPD/PBD heterostructure and the mixed TPD:PBD emissive layer result in the different influences of the electric field on the exciting process.

It is demonstrated that exciplex takes places only at the interface of TPD/PBD. Each component of the emission in bilayer device changes with increasing current density in different ways, resulting in a redshift in EL emission. The emission color is white when the current density is less than 32mA/cm^2. In the mix-layer device, TPD:PBD mixed layer increases the interface for exciplex formation and thus increases the proportion of exciplex emission. The EL spectra of these two devices

are characterized by the different behaviors of color tuning with the bias.

The electroplex emission in ITO/0503/PBD/Al bilayer device suggests that different physical processes of carriers generation and recombination under optical excitation and electrical excitation. The EL emission color is white, close to greenish blue, in the CIE diagram 1932.

Manufacturing process and device structures of white light device can be greatly simplified by employing exciplex or electroplex emission from bilayer device.

Formation of exciplex requires a favorable configuration and orientation of constituent molecules. The non-planar molecules with bulky substituents and steric hindrance seem to impede the formation of exciplex.

A fixed electron transport material BBOT(2,5-bis(5-tert-butyl-2-benzoxazolyl)thiophen) and six hole transport materials(HTMs) with varying ionization potentials were utilized to construct ITO/HTM/BBOT/Al bilayer devices. In all of devices, exciplex formation at the interfaces of HTMs/BBOT are confirmed by comparison between PL and EL spectra. The reasons for blueshift of EL emission with the increasing bias are also described.

The energy of the peak emission $h\nu_{exm}$ versus ionization potentials I_p of those HTMs gives a linear relationship for a fixed electron transport layer, indicating that the wavelength of exciplex emission $h\nu_{exm}$ is determined by the energy difference between the ionization potential of the electron donor and the electron affinity of the electron

acceptor. Emission color can be tuned feasibly from exciplex by varying ionization potential of hole transport layer for a fixed electron transport layer in organic electroluminescent devices. This types of devices provide an effective method for tuning of emission color.

(3) Luminescent efficiency is effectively improved by insertion of a modification layer at the interface between indium tin oxide(ITO) and hole transport layer in organic electroluminescent devices.

Vacuum evaporable fullerene C_{60} is utilized to act as a hole injection modification layer in the device structure of ITO/C_{60}/TPD/ Alq_3(tris(8-hydroxyquinoline) aluminum)/LiF/Al. It is demonstrated that an appropriate thickness of C_{60} can improve the efficiency of this device and the optimized thickness is 1.6nm. EL efficiency of the device, which contains 1.6nm C_{60} buffer, has been doubled in comparison with the device without buffer at a current density of 100mA/cm^2.

Key words organic thin film, electroluminescent devices, blue light emission, exciton confinement, stability, exciplex, electroplex, color tuning, interface modification, efficiency

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