

Improving Efficiency by Doping PtOEP into Spiro Light-Emitting Devices*

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Abstract: To investigate effective means of improving the efficiency of organic light-emitting devices (OLEDs) by making full use of triplet emission, a phosphorescent material Pt (II) Octaethylporphine (PtOEP) is doped into polymer host polyspirobifluorene (Spiro) to allow radiative recombination of triplet excitons. The current and brightness characteristics of the devices are tested and the electroluminescent spectra are described. Both fluorescence and phosphorescence are observed, and an obvious increase in external quantum efficiency is realized compared to undoped devices when different phosphorescent dopant concentrations are tried. Thus, the phosphorescent emission from triplet excited states might be an effective way to increase the efficiency of OLEDs when the concentration of the phosphorescent dopant is properly controlled.

Key words: external quantum efficiency; triplet; organic light-emitting device

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1 Introduction

Organic light-emitting devices (OLEDs) have been intensively investigated for their applications in high efficiency, low voltage, and full-color large-area flat-panel displays. In OLEDs, the emission processes are mediated by molecular excitons. In small molecule systems, the fractions of formed singlet and triplet excitons under electrical excitation are 25% and 75%, respectively^[1]. In polymer systems, the exciton formation rate has been found to be spin-dependent and therefore the 25% to 75% ratio is not accurate. The reason for this is still under investigation. However, singlet formation rates of greater than 50% have been measured^[2]. Due to the low molecular weight of the atoms in most organic semiconductors, radiative decay from the triplet state to the ground singlet state is spin forbidden. This leaves theoretical maximum internal quantum efficiency for the small molecule OLEDs at only 25%. The external quantum efficiency (η_E) of OLEDs is limited to $\sim 5\%$ when also considering the $\sim 20\%$ optical out-coupling efficiency of devices.

In addition to using a polymer emission system, one method of overcoming 25% efficiency limitation is to introduce a phosphorescent dopant into the system. Phosphorescent material allows for a radiative transition to occur between the lowest energy triplet state and the singlet ground state. By using phospho-

rescent materials that harvest both singlet and triplet excitons, the η_E can approach 100% and we anticipate a four-fold increase of η_E up to 20%^[3].

Emission from the phosphorescent dye can be achieved in three ways^[4]: charges trapped directly on the phosphorescent dye, and Förster and Dexter energy transfer of singlet excitons from host molecules to the dopants. The most commonly used dyes are those incorporating either platinum (Pt) or iridium (Ir)^[3-5]. To achieve a phosphorescent device with good performance, in addition to efficient emitting dopants, there are several requirements for the host material, such as a large energy-gap, high carrier mobility, and morphological stability^[6-8]. The efficiency of OLEDs is influenced by many complicated factors^[9-14]. In this work, based on the efficiency of OLEDs using Pt (II) Octaethylporphine (PtOEP) as a phosphorescent dopant and polyspirobifluorene (Spiro) as the carrier-transporting host for the emissive layer, we demonstrate the influence of PtOEP concentration on η_E of OLEDs rather than upgrading the efficiency by optimizing the device structure and experimental conditions.

2 Experiment

The structure of the OLED is ITO/PEDT : PSS (30nm)/PtOEP : Spiro (150nm)/Ba (5nm)/Al (50nm), where polyethylene dioxythiophene-polystyrene sulfonate (PEDT : PSS) is provided in an aqueous solu-

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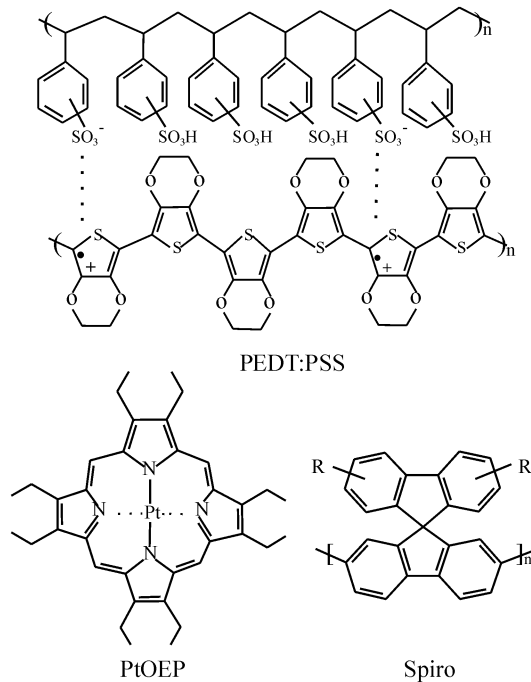


Fig. 1 Molecular structure of materials used in the OLED

tion, and PtOEP and Spiro are supplied in soluble solid form. The molecular structure of the organic material is shown in Fig. 1. The PtOEP doped Spiro (PtOEP: Spiro) solution is made prior to sample fabrication by first dissolving 10mg PtOEP and Spiro in 1mL chlorobenzene separately, and then adding the PtOEP solution to the Spiro solution in different weight ratios to determine a compromise between turn on voltage and quantum efficiency. All the solutions were stirred with magnetic bars for at least two hours to ensure a complete blend.

For fabrication of the samples, ITO coated glasses were cut into 15mm × 10mm sheets and etched to form a central band of ITO (~7mm wide) along the sample for the foundation of devices to prevent short-circuiting between the ITO and cathode when in the test rig. After etching, the ITO substrate was cleaned with detergent, acetone, and isopropanol by stirring each for 5min in an ultrasonic bath. Then it was dried with a jet of compressed N₂ and exposed to UV ozone for 3min in a Jelight 42 - 220 UVO-Cleaner. The PEDT : PSS film was spin coated onto the etched substrate in ambient conditions at 1500rpm for 60s. This yields a 30nm thick layer, measured by a Tencor Alpha-Step 2000 thickness profiler. After baking the sample over 10h at 50°C in a vacuum oven, the PtOEP : Spiro solution in different concentrations was spin coated onto the PEDT : PSS film under the same conditions, yielding a PtOEP : Spiro film about 150nm thick. The barium and aluminum film were deposited under 8×10^{-6} torr by thermal evaporation. The thickness and evaporation rate were monitored by a cali-

brated quartz thickness monitor. The barium was capped with aluminum to reduce the rate of oxidation onset. The substrates were placed behind a shadow mask to pattern the top cathode. Typically, the area of overlap between the cathode and anode (hence device area) is 1.5mm². After fabrication, all samples were stored in a glove box before testing to reduce the risk of contamination.

OLEDs are studied by testing various characteristics of the samples including current and brightness versus voltage, electroluminescent (EL) spectrum, and external quantum efficiency. The test samples were mounted in a test-rig and held under a dynamic vacuum (10^{-4} mbar) at ambient temperature.

3 Results and discussion

The characteristics of OLEDs are sensitive to fabrication conditions. For comparison, the samples with different PtOEP concentrations in the PtOEP : Spiro active layer were fabricated under the same conditions, such as the bake of PEDT : PSS, spin-casting of polymer solution, and evaporation of barium and aluminum. For different samples of the same group fabricated under the same conditions, different PtOEP concentrations are tried to find a compromise between turn on voltage and quantum efficiency, and four devices were obtained from every sample for optimized confirmation of the OLED characteristics.

Typically, Figure 2 shows the characteristics of group 1 OLEDs, where the PtOEP concentrations in the active layer are expressed as weight ratios of PtOEP to Spiro solution:

G1S1: PtOEP : Spiro = 0 : 100

G1S2: PtOEP : Spiro = 5 : 95

G1S3: PtOEP : Spiro = 10 : 90

G1S4: PtOEP : Spiro = 15 : 85

Figure 2 shows that for group 1, the PtOEP content is on the high side, the PtOEP peak is dominant in the EL spectrum, and η_e of the PtOEP: Spiro samples (G1S2 ~ G1S4) are lower than that of the pure Spiro sample (G1S1). For sample G1S2 with the lowest PtOEP content, the Spiro EL peak is relatively high, while its quantum efficiency is the highest in the PtOEP : Spiro samples. For high dopant concentrations, the interaction of doped molecules may induce obvious concentration quenching^[15], and thus reduce the light-emitting efficiency.

Based on this result, group 2 is tried with further lower PtOEP to Spiro concentrations:

G2S1: PtOEP : Spiro = 0 : 100

G2S2: PtOEP : Spiro = 1.5 : 98.5

G2S3: PtOEP : Spiro = 3.0 : 97.0

G2S4: PtOEP : Spiro = 4.5 : 95.5

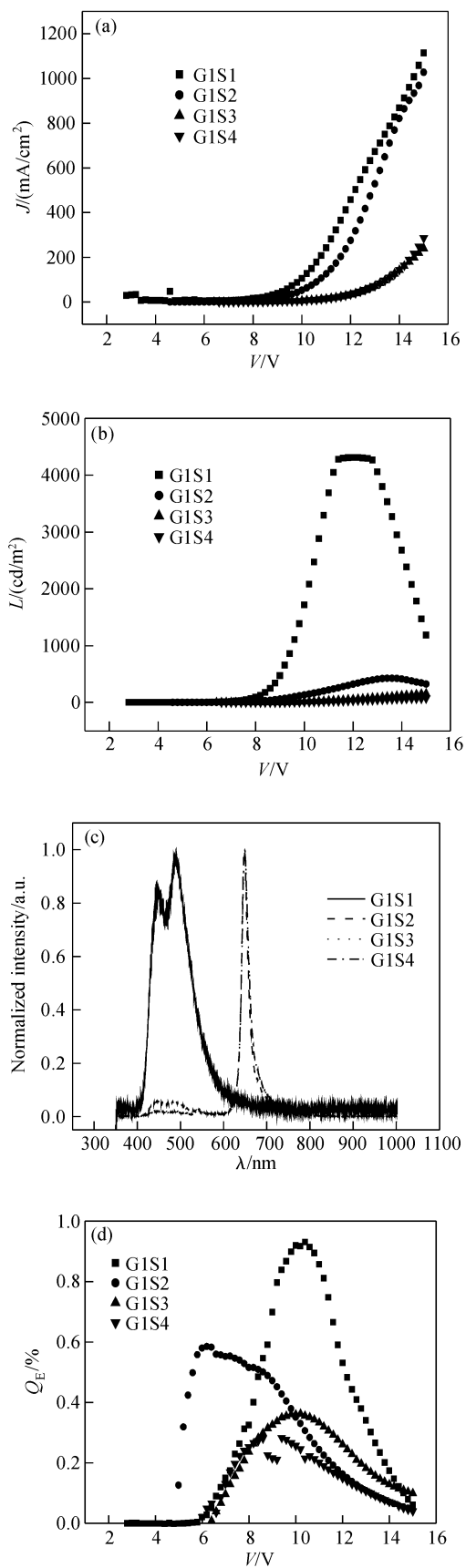


Fig.2 Characteristics of group 1 OLEDs (a) Current density versus voltage; (b) Luminescence versus voltage; (c) Electroluminescent spectra; (d) External quantum efficiency versus voltage

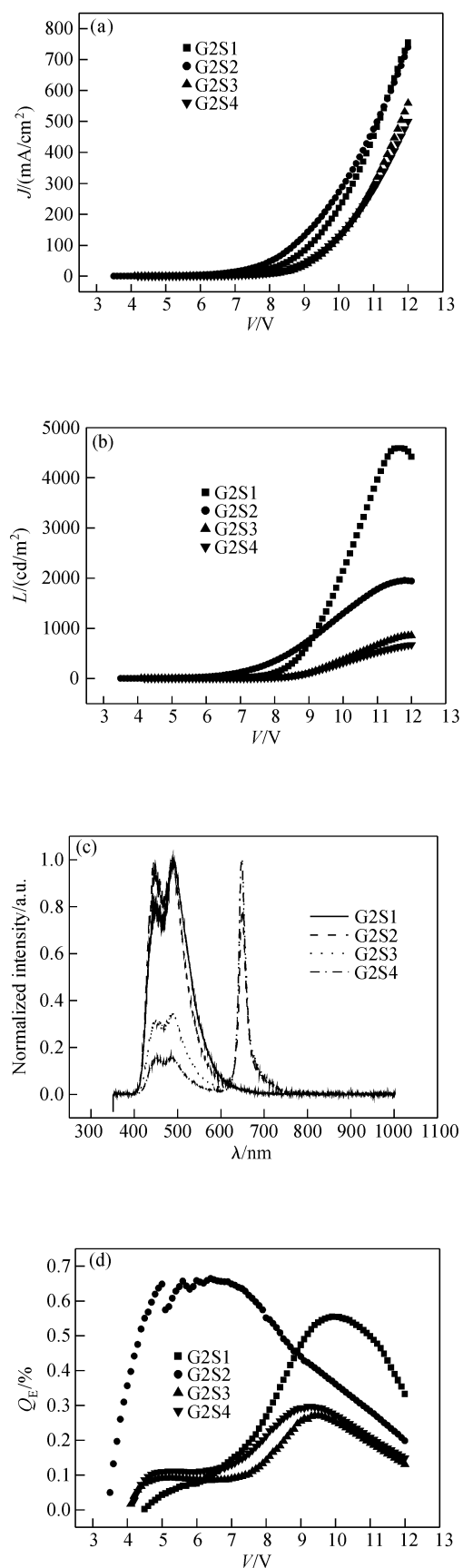


Fig.3 Characteristics of group 2 OLEDs (a) Current density versus voltage; (b) Luminescence versus voltage; (c) Electroluminescent spectra; (d) External quantum efficiency versus voltage

The corresponding results are shown in Fig. 3. The PtOEP and Spiro peaks in the EL spectra are concurrent, and for sample G2S2 with the lowest PtOEP content in the PtOEP: Spiro samples, the Spiro peak is dominant in the EL spectrum, and its η_E is higher than that of the undoped Spiro sample. Thus, when the PtOEP concentration is properly controlled, a PtOEP dopant can elevate the quantum efficiency of the Spiro emitted OLEDs.

These attributes result from the phosphorescent molecule's harnessing of both singlet and triplet states. In addition to the emission from directly trapped triplets, the doped phosphorescent guest emission usually originates from the triplet energy transfer in the donor material^[16]. Moreover, the energy transfer rate depends on the intermolecular distance of the guests and the molecular distance between the host and guest. When the energy acceptor is located at a proper distance, the energy transfer dominates the process^[17]. Theoretical simulation reveals that the rate of the triplet energy transfer exponentially increases with the host-guest molecular distance^[18], which is one of the factors affecting the sensitivity of the quantum efficiency to dopant concentration. The energy transfer and emission mechanism in phosphorescent dye doped OLEDs is complicated, and systematic theoretical and experimental works are expected to improve the efficiency by making full use of triplet emission.

4 Conclusion

In summary, OLEDs with PtOEP doped Spiro as the active layer have been developed. The current and brightness characteristics of the devices were tested and the EL spectra were described. The external quantum efficiencies at ambient temperature were measured and the influences of PtOEP concentration on the external quantum efficiency were demonstrated. Both fluorescence and phosphorescence are observed, and an obvious increase in device efficiency is realized compared to undoped devices when different phosphorescent dopant concentrations are tried. Therefore, the phosphorescent emission from triplet excited states might be an effective way to increase the efficiency of OLEDs when the concentration of the phosphorescent dopant is properly controlled.

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利用 PtOEP 掺杂改善 Spiro 发光器件的发光效率*

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摘要: 为了利用有机三线态发光提高有机发光器件的发光效率,用磷光材料掺杂到聚合物主体中作为发光层,制备有机电致发光器件.在测量器件的电流-电压特性、发光亮度-电压特性和电致发光谱的基础上,计算了器件的外量子效率,研究了磷光材料的掺杂浓度对器件发光效率的影响.结果表明,对特定的材料体系,适当控制掺杂浓度,可以同时观察到荧光和磷光光谱,使掺杂器件的外量子效率在纯聚合物发光器件的基础上得到明显提高.

关键词: 外量子效率; 三线态; 有机发光器件

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