

行政院國家科學委員會補助專題研究計畫 成果報告

二極發光體有機材料的研究(3/3)

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一、中文摘要

Part A: **TFTPA** 是一個新穎的主發光體材料，其主要結構以 triphenylamine 做為核心主體並且在周圍修飾上三個 9-phenyl-9-fluorenyl 的官能基。合成的步驟主要是經由 Friedel-Crafts 的取代反應所製備而成。由於 9-phenyl-9-fluorenyl 這個巨大立體障礙官能基的存在導致 **TFTPA** 具有高度的玻璃轉移溫度(186 °C)以及良好形態與電化學上的穩定性。此外，透過原子力顯微鏡的測量可以發現，銜金屬客發光體的堆疊現象在 **TFTPA** 當中可以有效的被抑制，使得磷光元件可以達到高效率的表現。特別是在藍光以及紅光的電激磷光元件方面，以 **TFTPA** 做為主發光體的元件，其效率遠高於那些以 mCP 或者 CBP 為主發光體的元件。在藍光元件的部份，我們採用 Firpic 為客發光體，其外部量子效率和功率效率達到 12% (26 cd/A) 以及 18 lm/W，同時亮度為 100 cd/m²。而在紅光元件的部份，則以 Ir(piq)₂acac 做為客發光體，該元件展現出相當低的驅動電壓(2.6 V)。相較於以 CBP 為主發光體的元件，該元件的功率效率(9.0 lm/W)已大幅提昇至原本的三倍。(Adv. Funct. Mater. 2007, 17, 3514.)

Part B: 高效率藍色螢光材料 2-tert-butyl-9,10-bis[4-(1,2,2-triphenylvinyl)phenyl]anthracene (**TPVAn**) 已經被成功的合成與鑑定。**TPVAn** 的分子結構主要以蔥做為中心結構，並且在分子兩端修飾上 tetraphenylethylene 之官能基。由於 tetraphenylethylene 具有高度立體障礙，因此致使 **TPVAn** 表現出高度的玻璃轉移溫度(155 °C)以及良好的形態穩定性。利用 **TPVAn** 這個材料所製備而成的電激發光

元件，其放射波長座落在飽和藍光區域[其 CIE 座標為 (0.14, 0.12)]。最大量子效率高達 5.3% (5.3 cd/A)，為至今最好的藍色有機電激發光元件。此外藉由在 **TPVAn** 當中摻雜少量橘紅光的螢光材料來製備白色電激發光元件，其元件可達最大外部量子效為 4.9% (13.1 cd/A) 與 CIE 座標為 (0.33, 0.39)。(Adv. Funct. Mater. 2007, 17, 3141.)

關鍵詞：有機電激發光二極體，電激磷光元件，主發光體材料，蔥，三苯胺，非摻雜，藍光，蔥。

Abstract

Part A: **TFTPA** (tris[4-(9-phenylfluorene-9-yl)phenyl]amine), a novel host material that contains a triphenylamine core and three 9-phenyl-9-fluorenyl peripheries, was effectively synthesized through a Friedel-Crafts-type substitution reaction. Owing to the presence of its sterically bulky 9-phenyl-9-fluorenyl groups, **TFTPA** exhibits a high glass transition temperature (186 °C) and is morphologically and electrochemically stable. In addition, as demonstrated from atomic force microscopy measurements, the aggregation of the triplet iridium dopant is significantly diminished in the **TFTPA** host, resulting in a highly efficient full-color phosphorescence. The performance of **TFTPA**-based devices is far superior to those of the corresponding mCP- or CBP-based devices, particularly in blue- and red-emitting electrophosphorescent device systems. The efficiency of the Firpic-based blue-emitting device reached

12% (26 cd A⁻¹) and 18 lm W⁻¹ at a practical brightness of 100 cd m⁻²; the Ir(piq)₂acac-based red-emitting device exhibited an extremely low turn-on voltage (2.6 V) and a threefold enhancement in device efficiency (9.0 lm W⁻¹) relative to those of reference devices based on the CBP host material.

Part B: A highly efficient blue-emitting material,

2-*tert*-butyl-9,10-bis[4-(1,2,2-triphenylvinyl)phenyl]anthracene (**TPVAn**), which contains an anthracene core and two tetraphenylethylene end-capped groups, has been synthesized and characterized. Owing to the presence of its sterically congested terminal groups, **TPVAn** possesses a high glass transition temperature (155 °C) and is morphologically stable. Organic light-emitting diodes (OLEDs) utilizing **TPVAn** as the emitter exhibit bright saturated-blue emissions [Commission Internationale de L'Eclairage (CIE) chromaticity coordinates of $x = 0.14$ and $y = 0.12$] with efficiencies as high as 5.3% (5.3 cd/A)—the best performance of non-doped deep blue-emitting OLEDs reported to date. In addition, **TPVAn** doped with an orange fluorophore served as an authentic host for the construction of a white-light-emitting device that displayed promising electroluminescent characteristics: the maximum external quantum efficiency reached 4.9% (13.1 cd/A) with CIE coordinates located at (0.33, 0.39).

Keywords: OLED, Electrophosphorescent Device, Host Material, Fluorene, Triphenylamine, Non-doped, Blue-emitting, Anthracene.

二、Introduction

Part A: Organic light-emitting diodes (OLEDs) are being investigated widely for their potential applications within full-color flat-panel displays.^[1] Among these devices, the use of phosphorescent emitters has

stimulated the development of efficient heavy metal-containing electroluminescent guest systems.^[2,3] The ability of these phosphorescent dyes to harvest both singlet and triplet excitons can, theoretically, increase the internal efficiency of devices up to 100%.^[4-6] In these phosphorescent OLEDs, the triplet emitters are normally used as emitting guests in a host material to reduce the self-quenching associated with the relatively long excited state lifetimes of triplet emitters and triplet-triplet annihilation; consequently, the choice of host materials is of vital importance for the preparation of efficient phosphorescent OLEDs. The carbazole-based molecule 4,4'-bis(9-carbazolyl)-2,2'-biphenyl (CBP) [glass transition temperature (T_g) = 62 °C]^[7] has been used frequently as a host material in green- and red-emitting phosphorescent devices—even though the triplet energy of CBP (2.56 eV) is lower than that of the general blue triplet emitters (> 2.62 eV), resulting in an inefficient energy transfer from host to guest.^[8] To overcome this obstacle, structurally modified host molecules, such as 1,3-bis(9-carbazolyl)benzene (mCP), which has a higher-value E_T (2.90 eV), have typically been utilized to fabricate blue-emitting OLEDs; bis[(4',6'-difluorophenyl)pyridinato-*N,C*^{2'}]iridium(III) picolate (FIrpic; $E_T = 2.65$ eV) is the most popular choice for the dopant.^[8] Although mCP possesses a suitable triplet energy, its relatively low thermal and morphological stability [glass transition temperature (T_g) = 60 °C]^[7] may hinder its application as a host material in OLEDs. In attempts to overcome these problems and realize efficient blue-emitting devices, several carbazole derivatives have been prepared, but their syntheses often suffer from drawbacks such as complicated reaction conditions and moderate to low yields.^[9,10]

In this report, we describe the facile synthesis of a novel fluorene/triarylamine hybrid (tris[4-(9-phenylfluoren-9-yl)phenyl]amine,

TFTPA)—through a simple one-step reaction from commercially available starting materials—and its superior characteristics that make it suitable for use as a host material in full-color phosphorescent devices. The design of **TFTPA** was based on triphenylamine and fluorene both possessing large triplet energy gaps (3.04 and 2.95 eV, respectively).^[11,12] Because the triphenylamine unit is connected to the sp³-hybridized carbon atom at the C-9 position of the fluorene moiety, which serves as a spacer to block extended π -conjugation,^[13] the conjugation length and triplet energy of each individual building block in the resulting composite should remain essentially unperturbed. In addition, the 3-D cardo structure of substituted fluorene derivative should improve the system's rigidity and hinder any unwanted aromatic π -stacking interactions, resulting in an amorphous material possessing enhanced morphological stability. More importantly, we expected that the sterically hindered phenyl-substituted fluorene peripheries of **TFTPA** would alleviate the triplet-triplet annihilation and concentration quenching arising from strong bimolecular interactions of the phosphor at high doping levels,^[14,15] leading to highly efficient phosphorescent devices.

Part B: Organic light-emitting devices (OLEDs) have been attracting considerable attention because of their potential application within flat-panel displays.^[1,2] Efficient blue-light OLEDs are of particular interest because they are desired for use as blue light sources in full-color display applications;^[3-8] furthermore, they can also serve as hosts for exothermic energy transfer to lower-energy fluorophores to realize white-light OLEDs.^[9-13] Although the use of dopant emitters in the guest-host system can improve the electroluminescence (EL) efficiency significantly,^[14-16] the addition of dopants is usually a complicated and expensive process during the mass production of OLEDs. Because phase

separation upon heating is an important cause of performance degradation in some guest (or dopant)-host systems^[17-19] and considering that some of these OLEDs will be operated under harsh conditions (e.g., at high temperatures), the use of a single-component host emitting layer may be more pragmatic for application than the use of guest-host-type emitting layers. Although several blue host emitters have been reported for the fabrication of non-doped blue OLEDs,^[4-8,20,21] high-performance blue-light-emitting materials exhibiting ideal color purity, good stability, and high fluorescence efficiency remain relatively rare.

Because anthracene derivatives possess outstanding photoluminescence and electroluminescence properties, they have been used widely as emitting materials in OLEDs.^[12,15,22-25] Herein, we report the synthesis and characterization of a novel, deep-blue-emitting material, 2-*tert*-butyl-9,10-*bis*[4-(1,2,2-triphenylvinyl)phenyl]anthracene (**TPVAn**, Scheme 1), for use in non-doped blue-light OLEDs. In **TPVAn**, two tetraphenylethylene groups are end-capped at the 9- and 10-positions of the central anthracene core to increase structural bulk and non-planarity through the tendency of the phenyl rings to twist. The non-planarity of this molecular structure effectively diminishes its degree of intermolecular π - π stacking and reduces concentration quenching; meanwhile, the sterically bulky units facilitate the formation of stable amorphous films.^[25,26] In addition, we expected that the introduction of a *tert*-butyl unit at the C2 position of the anthracene moiety might enhance the morphological stability of this material's thin films during annealing processes.^[25,27] In comparison with other blue-light-emitting materials for non-doped OLEDs, **TPVAn** provides higher thermal stability, good color purity, and better emitting efficiency.

≡ 、 Results and Discussion

Part A: We have developed a facile

synthetic route for the preparation of a novel host material, **TFTPA**, which contains a **TPA** core with three 9-phenyl-9-fluorenyl groups attached at its peripheries. This one-step Friedel–Crafts-type reaction is not only simple but, because of the use of inexpensive reactants and mild operating conditions, it is also cost effective. Using this synthetic strategy, **TFTPA** can be produced readily on a large scale. Owing to the presence of the sterically bulky 9-phenyl-9-fluorenyl groups, **TFTPA** exhibits a high glass transition temperature (186 °C) and is morphologically and electrochemically stable. AFM measurements suggested that the aggregation of the triplet iridium dopant was depressed significantly when **TFTPA** was used as the host. As a result, self-quenching is effectively reduced leading to highly efficient phosphorescent devices at high dopant concentrations (optimized at 21 wt%). The performance of the **TFTPA**-based devices is far superior to those of the corresponding mCP- or CBP-based devices, particularly in the blue- and red-emitting electrophosphorescent device systems. The efficiencies of the blue-emitting device reached 12% (26 cd A⁻¹) and 18 lm W⁻¹ at a practical brightness of 100 cd m⁻²; these values are among the highest ever reported for blue electrophosphorescent devices. In addition, the red-emitting device exhibited an extremely low turn-on voltage (2.6 V) and a threefold enhancement in the power efficiency (9.0 lm W⁻¹) relative to those of reference devices based incorporating CBP as the host material. As well as yielding highly efficient full-color phosphorescence, our present approach should be attractive for the development of commercial applications because the simple device structure promises low-cost manufacturing.

Part B: We have realized efficient deep-blue non-doped OLEDs based on a novel highly thermally stable blue-light-emitting material, **TPVAn**, which

comprises a 2-*tert*-butylanthracene core and two sterically bulky tetraphenylethylene peripheral groups. The **TPVAn**-based non-doped devices exhibited satisfying deep-blue emissions with CIE coordinates located at ca. (0.14, 0.11), very close to the standard blue CIE coordinates. Moreover, these devices displayed excellent EL efficiency: the maximum external quantum efficiency reached 5.3% (5.3 cd/A) at 4.09 mA/cm²—the best performance reported to date for non-doped deep-blue-light-emitting OLEDs. In addition to achieving highly efficient blue fluorescence, we demonstrated that **TPVAn** doped with an orange fluorophore could serve as an authentic host for the construction of a white-light-emitting device that displayed promising EL characteristics: CIE coordinates located at (0.33, 0.39) and maximum external quantum efficiency reaching 4.9% (13.1 cd/A).

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