

行政院國家科學委員會專題研究計畫 成果報告

二極發光體有機材料的研究

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計畫主持人：許慶豐

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詢

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行政院國家科學委員會專題研究計畫成果報告

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一、中文摘要

Part 1(A): 我們以 Suzuki coupling 反應法合成了以聚萸物為主幹的共聚高分子，在此共聚高分子中每兩個交替的單元中就包含了一個碳 9 位置取代的螺結環烷官能基；此剛硬螺結環烷官能基的存在不僅能阻礙分子堆疊發生，還能保持高分子的剛硬性，進而使此高分子具有較高的玻璃轉移溫度並改善其熱穩定度與放光位置穩定性。當我們將此高分子經過一恆溫熱處理(150°C for 20 小時)之後再去量測其光學性質時可發現，一般高分子加熱後因堆疊所產生的激發複合體已被有效抑制；將此具有螺結結構的聚萸衍生物當發光層作成兩層的元件後可證明其是一個發藍光的 OLED 材料。

Part 1(B): 我們合成了一具有高效率的藍光共聚高分子，此共聚高分子在萸分子的碳 9 位置上分別具有一個龐大的電洞傳輸基團 triphenylamine (TPA) 與另一個電子傳輸基團 oxadiazole (OXD)；從光致發光與電化學的量測結果上皆可發現，在此共聚高分子中不論是側鏈或是聚萸物的主鏈都各自保有其原來基團的電子結構特性；此共聚高分子在經過恆溫熱處理(150°C for 20 小時)之後再去量測其光學性質時並不會產生堆疊或激發複合體的現象，因此仍呈現出純藍色的放光。另外，在電激發光的結果上也證明了導入這些官能團有效的改善電荷注入與平衡電荷的傳輸；以此共聚高分子為發光層製成單層元件時，其最大外部量子效應為 1.21 % (亮度 354 cd/m² 驅動電壓 7.6 V)；最大亮度可達到 4080 cd/m² (電壓 12 V 電流密度 640 mA/cm²)。

Part 2(A): 在螺結雙萸分子中心兩側連接兩個垂直萸發光團可合成 spiro-FPA 新的藍

光發光材料。在 spiro-FPA 中導入螺結結構，使得結晶趨勢減緩且增加其玻璃轉移溫度。此外，在螺結中心的碳原子其四面體結構之特性，維持了原本萸的光與電化學特性。藉由原子力顯微鏡之量測可證明，具良好與穩定的形態之 spiro-FPA 可利用真空蒸鍍製備高度非晶相的薄膜。利用 1.0wt%TBP 摻混在 spiro-FPA 發光層中製成的有機電激發光元件產生高螢光效率 4.9cd/A(2.07lm/W)之藍光。

Part 2(B): 我們合成以螺結雙萸分子為基礎的 pyrazoloquinilines，分別為 spiro-PAQ-Me 跟 spiro-PAQ-Ph 的。在這些化合物中，兩個相同的發光團被一 sp³ 混成碳原子所連結並相互垂直。導入剛硬的螺結雙萸導致玻璃轉移溫度提升，其範圍在 240-280 °C。這些新型材料展現 mono-pyrazoloquinilines 衍生物的特徵吸收，每個材料在 420nm 皆擁有一個寬並且低能量的吸收，而放射螢光效率坐落在藍光區域。電化學研究顯示這些化合物還原為可逆的，並且擁有低的 LUMO 能階，是由於 pyrazoloquiniline 環缺電子的特性所致。多層的有機電激發光元件使用 spiro-PAQ-Ph 當作客發光體於發光層中產生很亮的藍光放射，其最大亮度為 20 000 cd m⁻²。在摻雜 2.0%的元件中，電流密度為 20mA cm⁻²，電壓為 7.0V 時可得最大的外部量子效率為 3.6%(4.5 cd A⁻¹, 2.02 lm W⁻¹)，CIE 為(0.14, 0.17)。

關鍵詞：聚萸高分子；螺結雙萸分子；電激發二極體。

Abstract

Part 1(A): We have synthesized polyfluorene-based copolymers containing spiro-cycloalkyl groups functionalized on the C-9 position of alternate fluorene units using the Suzuki coupling reaction. The presence of the rigid spiro-cycloalkyl pendent groups not only hinders the close packing and intermolecular interactions between polymer chains, but also preserves the molecular rigidity of the polymer, leading to polyfluorenes with high glass transition temperatures and improved thermal and spectral stabilities. The results of photoluminescence measurements of the isothermally heated spiro-polyfluorene thin films (150 °C for 20 h) show that the commonly observed aggregate/excimer formation is suppressed effectively in these polymers. Blue electroluminescence was demonstrated in a double-layer LED device using the spiro-derivatized polyfluorene as the emitting layer. (Wu, F. -I.; Dodda, R.; Jakka, K.; Huang, J. -H.; Hsu C. -S.; Shu, C. -F. *Polymer* **2004**, *45*, 4257.)

Part 1(B): A highly efficient blue light-emitting copolymer with bulky hole-transporting triphenylamine (TPA) and electron-transporting oxadiazole (OXD) pendant groups at the C-9 position of fluorene was synthesized. The results from photoluminescence and electrochemical measurements reveal that both the side chains and the polyfluorene main chain retain their own electronic characteristics in the copolymer. It shows a pure blue emission with no aggregates or excimers formed even after being annealed at 150 °C under nitrogen for 20 h. In addition, it also demonstrates improved charge injection and balanced charge transport in electroluminescence. The maximum external quantum efficiency of a single-layer device using this copolymer as the emitting layer is 1.21 % (at a brightness of 354 cd/m² with driving voltage of 7.6 V). The maximum luminance of the device reaches

4080 cd/m² at a bias of 12.0 V and a current density of 640 mA/cm². (Shu, C.-F.; Dodda, R.; Wu, F.-I.; Liu, M. S.; Jen, A. K.-Y. *Macromolecules* **2003**, *36*, 6698.)

Part 2(A): Spiro-FPA, a novel blue emitter, in which two identical anthracene luminophores are linked orthogonally around a spirobifluorene core, has been synthesized and characterized. The introduction of a spiro linkage into the structure of spiro-FPA leads to a reduction in crystallization tendency and an increase in glass transition temperature relative to the monomeric units. In addition, the tetrahedral nature of the carbon atom at the spiro center preserves the optical and electrochemical characteristics of the pristine anthracene units. As demonstrated by AFM measurements, high-quality amorphous films of spiro-FPA with good morphological stability can be prepared by vapor deposition. Organic EL devices constructed using a 1.0-wt% TBP-doped spiro-FPA emitting layer produce bright blue emissions with a high luminescence efficiency of 4.9 cd/A (2.07 lm/W). (Shen, W. -J.; Dodda, R.; Wu, C. -C.; Wu, F. -I.; Liu, T. -H.; Chen, H. -H.; Chen, C. H. Shu, C. -F. *Chem. Mater.* **2004**, *16*, 930.)

Part 2(B): We report the synthesis of spirobifluorene-based pyrazoloquinolines, spiro-PAQ-Me and spiro-PAQ-Ph, in which two identical luminophores are connected through an *sp*³-hybridized carbon atom (a spiro center) and are orthogonally arranged. The incorporation of the rigid spirobifluorene linkage results in significant increases in the glass transition temperatures, which are in the range 246–280 °C. These new materials display the characteristic absorptions of the mono-pyrazoloquinoline (i.e., non-spiro) derivatives, each with a broad, low-energy absorption at ca. 420 nm, and emit photoluminescence efficiently in the blue region. Electrochemical studies reveal that these compounds exhibit reversible reductions and low-lying LUMO

energy levels that originate from the electron-deficient nature of the pyrazoloquinoline ring. Multilayer organic electroluminescent devices constructed using spiro-PAQ-Ph as a dopant in the emitting layer produced bright blue emissions with maximum luminescence exceeding 20,000 cd m⁻². For the 2.0%-doped device, a high external quantum efficiency of 3.6% (4.5 cd A⁻¹, 2.02 lm W⁻¹) was achieved at 20 mA cm⁻² and 7.0 V with color coordinates of (0.14, 0.17). (Chen, C. -H.; Wu, F. -I.; Shu, C. -F.; Chien C. -H.; Tao, Y. -T. *J. Mater. Chem.* **2004**, *14*, 1585.)

Keywords: polyfluorene; spirobifluorene; LED device.

二、Introduction

Part 1(A): Since the discovery of poly(phenylene vinylene)-based polymer light-emitting diodes (PLEDs) in 1990,¹ organic light-emitting polymers have been the subject of intensive investigations because their luminescent properties may be fine-tuned by manipulating their chemical structures and because spin-coating and printing processes may be used to prepare large-area-display devices.² Blue-emitting polymers are of special interest, since they can be used either as a blue light source in full-color displays or as the host material for generating other colors through energy transfer to lower-energy fluorophores.³ Because of their high photoluminescence and electroluminescence efficiencies, polyfluorenes (PF's) are very promising candidates for blue-light-emitting materials.⁴ A major problem with polyfluorenes, however, is their poor spectral stability; an additional emission band appears between 500 and 600 nm upon exposure to heat.⁵ This phenomenon leads to a major issue of color instability of the light emitted from LEDs fabricated with polyfluorenes. The formation of interchain excimers has been suggested as the cause of the undesirable long-wavelength emission. Recently, List

et al. reported that keto-defects, which result from the thermal oxidation of the polymers, might also be the source of the low-energy emission bands.⁶

Several chemical approaches have been utilized to reduce the excimer formation and enhance the color stability of polyfluorenes, including introducing low-band-gap chromophores to the end and/or middle of the polymer chain,^{7,8} end-capping with cross-linkable moieties or hole-trapping groups,^{9,10} and encapsulating the polymer backbone with bulky/dendrimer side chains.^{11,12} It has been demonstrated that incorporating alicyclic substituents into the polymer backbone of polyimides improves their solubility effectively without sacrificing their excellent thermal properties, such as their glass transition temperatures (T_g).¹³ Previous studies also have shown that incorporating spirobifluorene pendent groups in an alternating polyfluorene copolymer enhances both its T_g and luminescent stability.¹¹ In light of these observations, we chose to synthesize novel alternating polyfluorene copolymers containing spiro-cycloalkanes at the C-9 position of every other fluorene repeating unit. The presence of the rigid spiro-cycloalkyl substituent not only hinders close packing and intermolecular interactions between polymers, but also preserves their molecular rigidity. As a result, the stability of the amorphous state in polymer films can be enhanced by suppressing the formation of aggregates and interchain excimers, leading to polyfluorene-based blue-light-emitting materials with improved thermal and spectral stabilities.

Part 1(B): The development of blue light-emitting polymers has been the subject of intense academic and industrial research due to their potential for full-color flat panel displays. They can be used either as the active layer in polymer light-emitting diodes (PLEDs) or as the host material for generating other colors through energy transfer to lower energy fluorophores.¹⁻⁴

Polyfluorenes (PF), with their high thermal stability and exceptionally high solution and solid state fluorescence quantum yields are very promising candidates for blue LEDs.⁴⁻⁸ Recently, a fluorene homopolymer, poly(9,9-di-n-octylfluorene) (POF) has been demonstrated as an effective blue emitter.⁹ However, this type of polyfluorenes tends to form aggregates and/or excimers during device fabrication and operation, leading to both a red-shifted emission and lower efficiency.¹⁰ This can be overcome by introducing bulky substituents at the C-9 position of the fluorene.¹¹⁻¹⁵ Such structural features could minimize the close chain packing of molecules in solid state. In addition, the saturated sp³ carbon (C-9) on the fluorene ring can also effectively block the conjugation between the side chains and the polymer backbone. As a result, the pure blue emission from the PF main chain can be preserved.

More recently, we reported the synthesis of a fluorene-based alternating copolymer, PF-OXD, which contains oxadiazole (OXD) moieties with their phenyl end group directly attached to the C-9 carbon in every alternating fluorene unit.¹⁵ The electron deficient OXD derivatives were introduced to improve both electron injection and transport. The results from the photoluminescence (PL) measurements of the isothermally heated PF-OXD thin film (150 °C for 20 h) show that the commonly observed aggregate/excimer formation in polyfluorene was effectively suppressed in this polymer due to its 3-D structure. The LED device using this polymer also shows a low turn-on voltage, high brightness and efficiency due to a more balanced charge recombination in the polymer emissive layer. However, the ionization potential for PF-OXD is 5.76 eV, which is very similar to

that of POF (5.8 eV). This means that there is a significant energy barrier for hole-injection from the conducting polymer, polyethylene dioxythiophene:polystyrene sulphonate (PEDOT:PSS) modified ITO (~ 5.2 eV) to PF-OXD, and it needs to be improved in order to further enhance the device performance. Here we report the synthesis, characterization, and device performance of a new statistical copolymer PF-TPA-OXD containing both electron-transporting OXD moieties and hole-transporting triphenylamine (TPA) units that are functionalized at the C-9 position of fluorene. These bipolar substituents provide both functions of suppressing aggregation and improving charge injection simultaneously.

Part 2(A): Since the discovery of multi-layered organic light-emitting diodes (OLEDs) by Tang et al.,¹ electroluminescent devices have been the subject of intensive investigation because of their applications in full-color displays.² Recently, various studies have been focused on improving the durability of OLEDs. The tendency of small molecules to crystallize spontaneously upon exposure to heat presents a limitation for LED applications, since crystal formation destroys film homogeneity and crystal boundaries raise the resistance of the sample, eventually leading to electrical shorting.³ A considerable amount of evidence indicates that an amorphous thin film (in OLEDs) with a high glass transition temperature (T_g) is less vulnerable to heat and, hence, the device performance is more stable.⁴ Different synthetic approaches have been pursued to confer a higher stability to the glass state of low-molecular-weight compounds. Several distinct classes of glass-forming small molecules with elevated values of T_g have been synthesized, including spiro-shaped,

“star-burst”, dendritic, tetrahedral, and cardo molecules.⁵⁻⁹ Salbeck et al. have synthesized spiro-type molecules based on 9,9'-spirobifluorene,^{4b,5a-c} which consists of two identically substituted-fluorene moieties connected through an sp^3 -hybridized carbon atom: the spiro center. In the spiro segment, the rings of the connected bifluorene entities are arranged orthogonally.¹⁰ This structural feature not only hinders close packing and intermolecular interactions, but also increases the molecular rigidity. As a result, the introduction of a spirobifluorene linkage into the structure of small molecules leads to a reduction in the tendency to crystallize, an enhancement in solubility, and an increase in glass transition temperature. In addition, the tetrahedral nature of the carbon atom at the spiro center connects the conjugated moieties through a σ -bonded network, which in turn serves as a conjugation interrupt, and, thus, most of the desired electronic and optical properties of the corresponding non-spiro molecules are preserved.¹¹

Organic light-emitting materials with large band gap energies that emit blue light efficiently are of special interest, because they are desired for use as blue light sources in full-color display applications and also because they can serve as energy-transfer donors in the presence of lower-energy fluorophores.¹² Among the blue fluorescent materials, 9,10-diphenylanthracene (**DPA**), which has near unity fluorescence quantum efficiency in solution,¹³ is attractive, but it has the inherent problem of crystallizing when deposited as a thin film in a device.¹⁴ To avoid the formation of polycrystalline films and to improve its thermal properties, our aim was to introduce the 9,9'-spirobifluorene linkage into **DPA** without altering its photophysical characteristics. Herein, we report the synthesis and characterization of a high- T_g

and efficient blue-emitting material, 2,2'-bis(10-phenylanthracen-9-yl)-9,9'-spirobifluorene (spiro-**FPA**), in which the two identical luminophores are aligned orthogonally through bonding to an sp^3 -hybridized carbon atom: a spiro center. Additionally, we report the fabrication and performance of blue-emitting OLEDs using spiro-**FPA** as the emitter itself or as a host emitting material doped with 2,5,8,11-tetra-*tert*-butylperylene (**TBP**).¹⁵

Part 2(B): Since the discovery of multi-layered organic light-emitting diodes (OLEDs) by Tang et al.,¹ research into OLEDs has been pursued intensively because of their potential for applications in, among other things, flat-panel displays.²⁻⁶ With such an application in mind, full-color displays would require three primary-color emissions—i.e., red, green, and blue. Organic light-emitting materials having large band-gap energies that emit blue light efficiently are of particular interest, because they are desired for use as blue light sources in full-color display applications and also because they can be used to achieve green and red color emission by several pathways, such as dopant emission or fluorescent down-conversion.⁷⁻¹⁰ A range of pyrazole-containing derivatives have been demonstrated to exhibit efficient blue photoluminescence,¹¹⁻¹³ and some of them have been utilized as emitting materials in the fabrication of electroluminescent (EL) devices, in which they provide bright blue EL emission.¹⁴⁻²¹

Herein, we report the synthesis and characterization of spirobifluorene-based pyrazoloquinolines, in which the two identical luminophores are aligned orthogonally through bonding to an sp^3 -hybridized carbon atom: a spiro center.^{22,23} The introduction of a spirobifluorene linkage not only increases molecular rigidity but also hinders close

packing and intermolecular interactions, so that the tendency for molecules to crystallize may be reduced and the glass transition temperature may be increased.²⁴⁻²⁹ Amorphous materials possessing a high value of T_g , which are less vulnerable to heat-induced morphological changes, are highly desirable for fabricating molecular LEDs, since the tendency of small molecules to crystallize spontaneously during operation has been identified as one reason for LED device failure.³⁰⁻³⁵ Moreover, the tetrahedral nature of the carbon atom at the spiro center connects the conjugated moieties through a σ -bonded network, which in turn serves as a conjugation interrupt, and, thus, most of the desired electronic and optical properties of the corresponding non-spiro molecules are preserved.^{29,36,37} The spirobifluorene-based pyrazoloquinoline was used as a dopant in EL devices, which gave bright blue emission from the dopant. The performance of these devices is discussed.

三、Results and Discussion

Part 1(A): We have developed novel polyfluorene copolymers, **PF-cyclic_a** and **PF-cyclic_b**, with spiro-cycloalkyl groups functionalized on the C-9 position of alternate fluorene units to form a rigid 3-D structure. These polymers possess high values of T_g and very good thermal stability. The results from the photoluminescence measurements of the isothermally heated spiro-polyfluorene thin films (150 °C for 20 h) reveal that the commonly observed aggregate/excimer formation is effectively suppressed in these polymers. We attribute the improved spectral stability to their high values of T_g and their spiro-structures that reduce interchain interactions. Blue electroluminescence was demonstrated in a double-layer LED device using **PF-cyclic_a** as the emitting layer.

Part 1(B): A highly efficient blue-emitter,

PF-TPA-OXD with bipolar pendant groups at the C-9 position of fluorene was synthesized. The incorporation of electron-rich TPA and electron-deficient OXD groups leads to an increase in both hole- and electron- affinities. The polymer shows both a pure blue emission without the formation of aggregates/excimers and a balanced hole- and electron-injection/transport compared to those from the fluorene homopolymer (POF) and copolymer (PF-OXD), which has only the electron-deficient OXD as side chains.

Part 2(A): We have synthesized a novel blue emitter, spiro-**FPA**, in which two identical anthracene luminophores are connected through an sp^3 -hybridized carbon atom, a spiro center, and are orthogonally arranged. These features lead to a reduction in crystallinity and an increase in T_g . As demonstrated by AFM measurements, high-quality amorphous films of spiro-**FPA** with good morphological stability can be prepared by vapor deposition. Multilayer organic EL devices constructed using spiro-**FPA** as an emitting layer produced bright blue emissions. With a 1.0-wt%-**TBP**-doped spiro-**FPA** emissive layer (20 nm), we achieved a high luminescence efficiency of 4.9 cd/A (2.07 lm/W) with CIE coordinates of $x = 0.134$ and $y = 0.207$ at a current density of 20 mA/cm² and a voltage of 7.4 V.

Part 2(B): We have synthesized spirobifluorene-based pyrazoloquinolines, spiro-**PAQ-Me** and spiro-**PAQ-Ph**, by the condensation of 2,2'-diamino-3,3'-dibenzoyl-9,9'-spirobifluorene (**3**) with pyrazolone derivatives, and have discussed details of their thermal properties, electronic properties (*viz.* absorption and photoluminescence), and electrochemical behavior. The presence of the rigid spirobifluorene skeleton imparts significant increases in these materials' glass transition temperatures, while preserving the

optical and electrochemical characteristics of their pristine pyrazoloquinoline units. Multilayer EL devices having ITO/NPB/CBP/TPBI:spiro-PAQ-Ph/TPBI/Mg:Ag configurations display bright blue emissions, with luminescence intensities exceeding 20,000 cd m⁻², caused by the spirobifluorene-based pyrazoloquinoline dopant. At a 2.0-wt% doping level, the device possesses good blue-color purity, with an EL emission maximum at 466 nm, which corresponds to (0.14, 0.17) blue-color chromaticity in CIE coordinates, and exhibits a high luminescence efficiency of 4.5 cd A⁻¹ (2.02 lm W⁻¹) at a current density of 20 mA cm⁻² and a voltage of 7.0 V.

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