

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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### 一、中文摘要

**Part A:** 我們合成新穎的芴共聚物，將 DAS 這個具有胺基的發光片段以 sp<sup>3</sup> 垂直交錯的方式接上芴九號碳來得到單體 bis[4-(diphenylamino)styryl]fluorene

，並對材料的熱穩定性、電化學性質以及元件上的表現進行研究。光物理實驗的結果指出，光色改變的原因是因為能量由高能的聚芴主鏈有效轉移 (Förster) 傳給了低能的 DPAS 片段而產生放光。在元件的製作上，以 ITO/PEDOT/EML/TPBI/Mg:Ag 為元件結構，製作以 PF-DPAS 與 PF-TPA-OXD 在不同比例摻混所做的元件，結果發現相較於 PF-TPA-OXD 的單一元件表現有明顯的提升，我們歸咎於此提升的原因是因為光色紅位移與量子效率提升所導致。另外，在比例 1:20 的情況下 EL 光譜上表現出了 DPAS 穩定的光學性質且不受電壓的操作而有所改變，其放射的最高峰在 461 nm 且 CIE 座落為 (0.15, 0.18)。當電壓在 9 V (86.1 mA/cm<sup>2</sup>) 得到最大的外部量子效率 2.08% (2.97 cd/A)，當操作電壓在 13 V 下得到最大亮度 2467 cd/m<sup>2</sup> 且此時電流密度為 361 mA/cm<sup>2</sup>。

**Part B:** 我們合成了兩個具有奎啉與銦金屬配位錯合形成的高效率的磷光金屬錯合物 Ir(DPQ)<sub>2</sub>(acac) 和 Ir(FPQ)<sub>2</sub>(acac)，並且討論其光物理以及電化學性質。利用 X-ray 單晶繞射鑑定 Ir(DPQ)<sub>2</sub>(acac) 的晶體結構，配位基上的氮-氮原子與碳-碳原子相對的位置分別是 trans 及 cis 的排列。相反的，因為具有直鏈烷芴基存在的原因 Ir(FPQ)<sub>2</sub>(acac) 是一個非結晶態 (T<sub>g</sub> = 92 °C) 的固體。因為苯環的導入增長了配位基的共軛平面，改變銦金屬錯合物的 <sup>3</sup>MLCT，導致紅色磷光產生紅位移。最後高分子元件

的設計是將 Ir(FPQ)<sub>2</sub>(acac) 以磷光客發光體的方式摻混加入 PVK/PBD 中，當電流密度 100 mA/cm<sup>2</sup> 得到外部量子效率為 8.16% 和純紅 CIE 為 (0.68, 0.32) 的高效率元件表現。

**Part C:** 我們合成一個 DPVBi[4,4'-bis(2,2-diphenylvinyl)-1,1'-biphenyl] 延伸物，DPVSBF[2,7-bis(2,2-diphenylvinyl)-9,9'-spirobifluorene]，該化合物是在螺旋雙芴的 2,7 碳位置接上 bis(2,2-diphenylvinyl) 基團。並且鑑定其熱性質、電性質 (即是吸收及光激發)，及電化學的表現。接上剛硬的螺旋雙芴基團可成功的提升玻璃轉移溫度及形態的穩定性，且與無螺旋雙芴基的衍生物 DPVBi 的光物理及電性質並無太大的差異。有機電激發光元件的結構為 ITO/NPB/DPVSBF/AlQ/LiF/Al，放光位置 (λ<sub>max</sub>) 為 474nm (CIE 座標: 0.16, 0.24)，且其亮度超過 40,000 cd/m<sup>2</sup>。在 100 mA/cm<sup>2</sup> 時的驅動電壓為 6.4V，亮度為 4110 cd/m<sup>2</sup> 時得到外部量子效率 2.54%，發光效率 4.1 cd/A，發光功率效率 2.01 m/W。此外，以 DPVSBF 為架構的元件其操作壽命為 DPVBi 的 16 倍。

**關鍵詞：**聚芴高分子；銦金屬錯合物；螺旋雙芴分子；電激發二極體。

### Abstract

**Part A:** We have synthesized a novel polyfluorene copolymer (PF-DPAS) by attaching an amino-substituted DAS dye, bis[4-(diphenylamino)styryl]fluorene, orthogonally onto the C-9 position of a fluorene unit, and have investigated this

polymer's thermal properties, electronic properties (*viz.* absorption and photoluminescence), and electrochemical behavior. Photoluminescence studies indicate that color tuning can be achieved through efficient Förster energy transfer from the higher-energy polyfluorene backbone to the lower-energy pendent DPAS units. We have fabricated LED devices having the structure ITO/PEDOT/emitting layer/TPBI/Mg:Ag. The devices based on blends of PF-DPAS in PF-TPA-OXD exhibit significant improvements in device performance relative to that of the pure PF-TPA-OXD device; we attributed this improvement to both a red shift of the EL spectra and an enhancement in quantum efficiency. At a blend ratio of 1:20, the EL spectrum is voltage-independent and stable and exhibits the characteristic emission of a DPAS moiety: a peak at 461 nm and CIE coordinates of (0.15, 0.18). The maximum external quantum efficiency is 2.08% (2.87 cd/A) at a bias of 9 V (86.1 mA/cm<sup>2</sup>) with a brightness of 2467 cd/m<sup>2</sup>; the maximum brightness (6916 cd/m<sup>2</sup>) occurs at an applied voltage of 13 V and a current density of 361 mA/cm<sup>2</sup>. (Su, H. -J.; Wu, F. -I.; Tseng, Y. -H.; Shu, C. -F. "Color Tuning of Light-Emitting Polymer: Polyfluorene Containing Pendant Amino-Substituted Distyrylarylene Units" *Adv. Funct. Mater.* 2005, 15, 1209.)

**Part B:** We have synthesized two highly efficient phosphorescent iridium metal complexes, Ir(DPQ)<sub>2</sub>(acac) and Ir(FPQ)<sub>2</sub>(acac), which are based on cyclometalated quinoline ligands, and discuss details of their electrochemical behavior and photophysical properties (*viz.* absorption and photoluminescence). Single-crystal X-ray diffraction studies of Ir(DPQ)<sub>2</sub>(acac) reveal a distorted octahedral geometry, in which the quinoline N atoms and the C atoms of the orthometalated phenyl groups are located at the mutual trans and cis positions, respectively. In contrast, Ir(FPQ)<sub>2</sub>(acac) is an amorphous solid and undergoes a glass transition at 92 °C, which

we attribute to the presence of the long di-*n*-octyl chains in the fluorenyl groups. The phosphorescence of these Ir complexes originates from the dominant <sup>3</sup>MLCT excited state shifts to red that occur upon introducing a phenyl substituent and/or a large conjugating aromatic ring into the ligand. A polymer light-emitting diode (PLED) device that uses Ir(FPQ)<sub>2</sub>(acac) as a phosphorescent dopant and a PVK/PBD blend as the host material produces very high efficiency (an external quantum efficiency of 8.16% at 100 mA/cm<sup>2</sup>) and a pure-red emission with 1931 CIE (Commission Internationale de L'Eclairage) chromaticity coordinates of (*x* = 0.68, *y* = 0.32). (Wu, F. -I.; Su, H. -J.; Shu, C. -F.; Luo, L.; Diao, W. -G.; Cheng, C. -H.; Duan, J. -P.; Lee, G. -H. "Tuning the Emission and Morphology of Cyclometalated Iridium Quinoline Complexes and Application to Organic Light-Emitting Diode" *J. Mater. Chem.* 2005, 15, 1035.)

**Part C:** We have synthesized a spirobifluorene-based **DPVBi** [4,4'-bis(2,2-diphenylvinyl)-1,1'-biphenyl] analogue, **DPVSBF** [2,7-bis(2,2-diphenylvinyl)-9,9'-spirobifluorene], in which the bis(2,2-diphenylvinyl) groups are connected through the 2 and 7 positions of the spirobifluorene framework, and have characterized its thermal properties, electronic properties (*viz.* absorption and photoluminescence), and electrochemical behavior. The presence of the rigid spirobifluorene linkage imparts significant improvement in the material's glass transition temperature and morphological stability, while preserving most of the photophysical and electronic properties of its non-spiro, biphenyl analogue, **DPVBi**. Organic electroluminescent devices having the structure ITO/NPB/**DPVSBF**/AIQ/LiF/Al display bright emissions with a  $\lambda_{\text{max}}$  at 474 nm (CIE coordinates: 0.16, 0.24) and exhibit maximum luminescence exceeding 40,000 cd/m<sup>2</sup>. At a driving current density of 100

mA/cm<sup>2</sup> (6.4 V), a luminance of 4110 cd/m<sup>2</sup> was obtained with external quantum efficiency of 2.54%, luminance efficiency of 4.1 cd/A, and power efficiency of 2.0 lm/W. Moreover, the **DPVSBF**-based device exhibits a 16-fold enhancement in the operation lifetime relative to that of a similar device based on **DPVBi**. (Wu, F.-I.; Shu, C.-F.; Wang, T.-T.; Diao, E. W.-G.; Chien, C.-H.; Chuen, C.-H.; Tao, Y.-T. "Bis(2,2-diphenylvinyl)spirobifluorene: An Efficient and Stable Blue Emitter for Electroluminescence Applications" *Synth. Met.* 2005, 151, 285)

**Keywords:** polyfluorene; iridium metal complexes; spirobifluorene; OLED.

## 二、Introduction

**Part A:** Organic light-emitting polymers continue to be the subject of intense academic and industrial research because of their potential applications in flat-panel displays.<sup>1</sup> The main advantages of organic polymers, when compared with inorganic or molecular organic materials, are the ability to fine-tune the luminescence properties of polymers by manipulating their chemical structure and the feasibility of utilizing spin-coating and printing processes for preparing large-area display devices. Polymers having large-energy band gaps that emit blue light efficiently are of special interest because these materials are desirable either as a blue light sources in full-color displays or as host materials for generating other colors through energy transfer to lower-energy fluorophores.<sup>2</sup>

Because of their high photoluminescence and electroluminescence efficiencies and good thermal stabilities, solubilities, and film-forming capabilities, polyfluorenes (PFs) are very promising candidates for preparing blue light-emitting materials.<sup>3</sup> Facile methods for functionalizing the C-9 position of the fluorene unit also offer an ability to tune the optoelectronic properties of PFs through

macromolecular engineering.<sup>4-6</sup> In conjugated polymers, Förster energy transfer is fast and efficient between two chromophore segments that have different energies and it shifts the emission to longer wavelengths.<sup>7,8</sup> In addition, such low-energy sites act as effective energy traps for excitons formed at the higher-energy segments.<sup>9</sup> Significant effort have been made to tune the colors of fluorene-based polymers to longer wavelengths. Most color-tunable polyfluorene derivatives that have been developed so far have been synthesized by incorporating low-band-gap comonomers in the polyfluorene main chain.<sup>10-12</sup> Only a few studies have concerned the attachment of narrow-band-gap dyes as pendent side groups,<sup>12,13</sup> even if this route has the advantage of permitting the incorporation of a high concentration of dyes without affecting the electronic properties of the polyfluorene backbone.<sup>12</sup> In this paper, we report the synthesis of a color-tunable fluorene copolymer by attaching an amino-substituted DAS dye, bis[4-(diphenylamino)styryl]fluorene (DPAS), orthogonally onto the C-9 position of a fluorene unit. We chose DAS as the side chain dye because of its intense blue fluorescence and its impressive performance in organic light-emitting diodes (OLEDs).<sup>14</sup> Because of the good spectral overlap between the emission spectrum of polyfluorene and the absorption spectrum of the pendent DPAS units, an efficient Förster energy transfer from the higher-energy polymer backbone to the lower-energy side chain occurs, which leads to emission solely, or predominantly, from the latter. Consequently, the photoluminescence (PL) of the copolymer is fine-tuned to a blue region and the  $\lambda_{\text{max}}$  of the emission is red-shifted from 418 nm for poly(dialkylfluorene),<sup>15</sup> which is located at wavelengths where the human eye is not very sensitive, to 467 nm, which is closer to

the maximum of a relative photopic luminous efficiency function.<sup>16</sup> This moderate red shift in turn results in a higher luminance efficiency. The fluorene copolymer, when used as a dopant in PLED devices, gives a bright blue emission from the dopant.

**Part B:** Recently, tremendous efforts have been focused on improving the efficiency of organic light-emitting diodes (OLEDs) through either the development of better materials or improvements in device structure. During the electrical operation of OLEDs, both holes and electrons are injected from opposing electrodes and then they combine together to form singlet and triplet excitons. In a typical fluorescent OLED system, only singlet excitons provide a radiative pathway for electron-hole recombination; the radiative decay of triplet excitons is very inefficient because it is inhibited by the rule of spin conservation.<sup>1</sup> Electrophosphorescent materials incorporating complexes of third-row transition-metal elements have attracted a great deal of attention because of their potential applications as highly efficient electroluminescent (EL) emitters.<sup>2-6</sup> The strong spin-orbit coupling induced by the heavy metal promotes an efficient intersystem crossing from the singlet to the triplet excited state manifold, which then facilitates strong electroluminescence by harnessing both singlet and triplet excitons after the initial charge recombination. EL devices based on these phosphors allow both singlet and triplet excitons to be harvested and the internal efficiency, theoretically, can reach as high as 100%.<sup>7</sup>

For full-color display applications, red-, green-, and blue-emitting materials that have sufficient luminous efficiency and proper chromaticity must be developed. While great success has been achieved in the development of green phosphorescent materials, the design and synthesis of efficient red emitters is intrinsically more difficult because their luminescence quantum

yields tend to decrease as the emission wavelength increases in accordance with the energy gap law.<sup>8</sup> The cyclometalated iridium complexes used in EL devices are octahedral, with a 3+ oxidation state, and exhibit strong phosphorescence primarily from a triplet metal-to-ligand charge-transfer (<sup>3</sup>MLCT) or a ligand-centered <sup>3</sup> $\pi$ - $\pi^*$  transition.<sup>4</sup> The emission colors from these complexes, which range from blue to red, are strongly dependent on the choice of the cyclometalating ligand.<sup>4,9,10</sup> The purpose of the present study was the molecular design of highly efficient red phosphorescent emitters based on iridium(III) phenylquinoline complexes. By extending the  $\pi$ -electron delocalization of the aromatic ligand chromophore, the energy gap between the ground and lowest excited states can be reduced effectively to provide emitters that have a saturated red color. In addition, these quinoline-based Ir complexes possess relatively short phosphorescence lifetimes that suppress triplet-triplet (TT) annihilation and polaron-triplet (PT) annihilation, which results in improved device quantum efficiency at a high current density.<sup>11</sup> Furthermore, the incorporation of a 9,9-di-*n*-octylfluorene group into the ligand gives rise to an amorphous Ir complex that improves the compatibility between the phosphorescent dopant and the polymer host and leads to highly efficient electrophosphorescent polymer light-emitting devices.<sup>12</sup>

**Part C:** Since their discovery by Tang et al.,<sup>1</sup> research into multi-layered organic light-emitting diodes (OLEDs) has been actively pursued because of their potential applications in flat-panel displays.<sup>2</sup> Considerable attention has been directed toward the development of new conjugated organic materials that function as efficient light emitters and/or charge transporters.<sup>3</sup> Organic light-emitting materials having large band-gap energies, which emit blue light efficiently, are of particular interest, because they are desired for use as blue light sources

in full-color display applications. In addition, they are able to serve as energy-transfer donors in the presence of lower-energy fluorophores.<sup>4</sup> Recently, efficient organic blue- and white-light-emitting diodes have been prepared by utilizing a blue-emitting distyrylarylene derivative, 4,4'-bis(2,2-diphenylvinyl)-1,1'-biphenyl (**DPVBi**), to function as the electroluminescent layer.<sup>5,6</sup> The active emitting material in these devices is characterized by its high solid-state photoluminescence efficiency. Amorphous films of **DPVBi** fabricated by vacuum evaporation have a tendency, however, to crystallize.<sup>7</sup> This inherent problem presents a limitation for its LED applications because crystal formation destroys film homogeneity and crystal boundaries raise the resistance of the sample, which eventually leads to device failure.<sup>8</sup>

Amorphous materials that possess high  $T_g$  values are often less vulnerable to heat-induced morphological changes and this characteristic makes them more desirable for fabricating molecular LEDs.<sup>8,9</sup> Our goal was to attain a material that resembles **DPVBi** in its electroluminescence and charge transport properties, but possesses a significantly higher glass transition temperature and a reduced tendency toward crystallization. Herein, we report the synthesis of a spirobifluorene-based **DPVBi** analogue, **DPVSBF**, in which the two 2,2-diphenylvinyl groups are connected at the 2 and 7 positions of the spirobifluorene framework. Because the spirobifluorene linkage enhances molecular rigidity and hinders close packing and intermolecular interactions, we expected the glass transition temperature to increase and the tendency for crystallization to reduce.<sup>10,11</sup> In addition, most of the desired electronic and optical properties of the corresponding biphenyl molecule will remain substantially unchanged because of the tetrahedral nature of the carbon atom at the spiro center, which connects the conjugated moieties through a  $\sigma$ -bonded network.<sup>12</sup> Molecular weight is

another limiting factor that must be considered when designing materials for OLED applications: molecules that have very high molecular weights tend to be difficult to evaporate — they may even decompose — during the thermal evaporation used to deposit materials in the OLED fabrication process. The low molecular weight of **DPVSBF**, relative to that of 2,2',7,7'-tetrakis(2,2-diphenylvinyl)-9,9'-spirobifluorene (**Spiro-DPVBi**),<sup>13</sup> leads to its lower sublimation temperature. In fact, **DPVSBF** can be sublimed smoothly in a vacuum chamber without thermal decomposition, whereas the sublimation conditions required for **Spiro-DPVBi** are quite harsh.<sup>13a</sup> We have prepared electroluminescent devices based on **DPVSBF** and have compared them with those based on **DPVBi**. Besides a bright blue emission with similar or better performance characteristics, we observed a significant improvement in device lifetime when using **DPVSBF**. The morphological stability is believed to contribute to the extended lifetime.

## ≡ 、 Results and Discussion

**Part A:** We have synthesized a polyfluorene copolymer (PF-DPAS) containing pendent amino-substituted DAS dye units that are attached orthogonally to the C-9 positions of fluorene units. The presence of the rigid spiro pendent units imparts a substantial increase in the material's glass transition temperature. PL studies demonstrate that most of the excitons formed in the polyfluorene main chain by direct photoexcitation migrate to the lower-energy pendent groups, from which emission occurs. In addition, in the PF-DPAS/PF-TPA-OXD blend, an efficient cascade energy transfer takes place from the excited TPA and OXD substituents of the host polymer to the pendent DPAS units of the doping polymer mediated by the PF backbone. Because of color tuning as well as enhancements in

quantum efficiency, the EL devices based on blends of PF-DPAS in PF-TPA-OXD exhibit significant improvements in device performance when compared with the pure PF-TPA-OXD device. The device prepared at a blend ratio of 1:20 displays the characteristic emission spectrum of the amino-substituted DAS dye and exhibits a voltage-independent and stable EL spectrum with a peak at 461 nm, which corresponds to CIE color coordinates of (0.15, 0.18) that are located in the pure blue region. The maximum external quantum efficiency of 2.08% (2.87 cd/A), with a brightness of 2467 cd/m<sup>2</sup>, was obtained at a current density of 86.1 mA/cm<sup>2</sup>, and the maximum brightness of 6916 cd/m<sup>2</sup> was achieved at an applied voltage of 13 V.

**Part B:** We have designed cyclometalated iridium complexes, Ir(DPQ)<sub>2</sub>(acac) and Ir(FPQ)<sub>2</sub>(acac), which contain two cyclometalated quinoline ligands and an ancillary acetylacetonate ligand, that are suitable for use as red-emissive materials in PLEDs. In contrast to the fact that Ir(DPQ)<sub>2</sub>(acac) is a crystalline solid, Ir(FPQ)<sub>2</sub>(acac) is an amorphous solid and undergoes a glass transition at 92 °C, which we attribute to the presence of the long di-*n*-octyl chains in the fluorenyl groups. Our electrochemical studies reveal that the HOMO and LUMO of these Ir complexes are located mainly at the Ir-phenyl center and the electron-accepting heterocyclic portion of the ligands, respectively. By introducing a phenyl substituent and/or a large conjugating aromatic ring into the ligand, the phosphorescence of the Ir complexes, which originates from the dominant <sup>3</sup>MLCT excited state, shifts to red. We have demonstrated the preparation of efficient, bright-red electrophosphorescent light-emitting diodes (LEDs) employing Ir(FPQ)<sub>2</sub>(acac) doped into a blend of PVK and 30 wt% of PBD. The electroluminescence emission is characteristic of Ir(FPQ)<sub>2</sub>(acac), with a maximum at 627 nm and CIE color coordinates of (0.68, 0.32); these coordinates

are very close to those of the standard red (0.67, 0.33) demanded by the NTSC. At a current density of 10.7 mA/cm<sup>2</sup> (brightness of 1180 cd/m<sup>2</sup>), the external quantum and luminous efficiencies were 10.27% and 11.0 cd/A, respectively. Even at a higher current density of 100 mA/cm<sup>2</sup>, the device maintains a high efficiency (8.16%) and brightness (8746 cd/m<sup>2</sup>).

**Part C:** We have prepared a new blue emitter, **DPVSBF**, that possesses most of the photophysical and electronic properties of **DPVBi**, but has a higher glass transition temperature as a result of the presence of its spirobifluorene linking group. This material also has a much longer operation lifetime, relative to that of **DPVBi**, when incorporated into an electroluminescent device; this property makes **DPVSBF** a more practical material. In a standard three-layer configuration and at a driving current of 100 mA (6.4 V), the device exhibited a luminance of 4110 cd/m<sup>2</sup> with an external quantum efficiency of 2.54%, a luminance efficiency of 4.1 cd/A, and a power efficiency of 2.0 lm/W.

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