

有機發光二極體之芴與螺結雙芴螢光材料

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中文摘要

第二章：設計並合成出結合 diphenylamino 推電子性及 dicyanovinyl 拉電子性的稀有螢光芴衍生物。由 **pTSPDCV**, 2-di(4-tolyl)amino-7-dicyanovinyl-9,9'-(2,2'-biphenyl)fluorene 和 **PhSPDCV** (2-diphenylamino-7-dicyanovinyl-9,9'-(2,2'-biphenyl)fluorene) 單晶 x 光繞射結構顯示於固態時，除了長距離分子偶極-偶極吸引力外只有微弱的凡得瓦力接觸力。引進龐大的 9,9'-螺結雙芴取代和非共平面雙苯胺基一樣具有阻止偶極效應芴分子的聚集。比起色彩不鮮明的 Nile Red and DCM (4-(dicyanomethylene)-2-methyl-6-[4-(dimethylaminostyryl)-4H-pyran]) 固體，此芴衍生物明顯具有更亮的螢光。這些與其他摻入物不同且獨特的光物理性質使得此類紅色芴衍生物更適合製成非摻入式紅光有機發光二極體。以 **pTSPDCV** 或 **PhSPDCV** 成功製作成非摻入式紅色有機發光二極體。此紅色電激發光(CIE, $x = 0.65$, $y = 0.35$) 展現出最大亮度超過 12000 cd/m^2 ，於 20 mA/cm^2 時具有超過 600 cd/m^2 的高放光亮度，3.6% 的最大外部量子效率更是值得注意。

第三章：我們發表一個新的有關合成純的 2,2'-dibromo-9,9'-spirobifluorene 方法，避免了容易出現副反應的 9,9'-螺結雙芴直接雙溴化或是經由以 2,2'-diamino-9,9'-spirobifluorene 進行 Sandmeyer 反應。進一步合成一系列多個不同螢光化合物，化合物結構中具有一組推拉電子對兩兩互相垂直而不相交。我們選擇三組共六個螺結雙芴化合物作為研究對象，分別是紅色的 **PhSPDCV** 和其二聚分子

BisPhSPDCV、綠色的 **PhSPCHO** 和其二聚分子 **BisPhSPCHO**、藍色的 **PhSPDPV** 和其二聚分子 **BisPhSPDPV**。此二聚螺結雙苄分子結構中含有一組兩個兩兩互相垂直而不相交的片段。我們預期分子中的兩片段相互的影響微弱，在製成有機發光二極體元件時兩個發光團應該會使元件效率加倍。然而對於紅色和綠色的發光團而言，二聚分子的分子偶極卻比單聚分子來的大。因此我們仔細的研究包含由理論計算的分子偶極、螢光的溶劑色移現象、螢光量子效率、單晶晶體結構和元件結果等物理性質。發現具有強偶極的 **PhSPDCV** 和 **PhSPCHO** 其相對的二聚分子 **BisPhSPDCV** 和 **BisPhSPCHO** 不論是元件效率或是螢光量子效率都比單聚分子差很多，但 **PhSPDPV** 和 **BisPhSPDPV** 的差別卻不大。因分子內或鄰近分子偶極所引起的區域電場會影響電激發光性質。特別是高極性 **BisPhSPDCV** 和 **BisPhSPCHO** 的螢光驟熄現象應該是由於其分子內的兩組推拉電子對各自所產生的能量轉移互相影響所產生的內部電場所引起的。因此為了避免電場所引起的螢光驟熄現象，分子的偶極需要有限度的控制。我們以 0.5 wt% **PhSPDCV** 製成摻入式發光元件，得到高效率（3.4%的外部量子效率、9.4 cd/A 的發光效率、8.2 lm/W 的電能效率）、高亮度（在 20 mA/cm² 的電流密度下約 1800 cd/m²）的飽和黃色電激發光元件（1931 CIE 座標參數 $x = 0.50$ ， $y = 0.48$ ）。此外，以 **PhSPDPV** 製成非摻入式發光元件，得到高效率（3.4%的外部量子效率、5.4 cd/A 的發光效率、5.7 lm/W 的電能效率）、高亮度（在 20 mA/cm² 的電流密度下約 910 cd/m²）的藍色電激發光元件（1931 CIE 座標參數 $x = 0.14$ ， $y = 0.22$ ）。

第四章：設計合成 **PhSPDPV** 和 **PhSP_{N2}DPV** 並研究其熱性質、光物理性質、電化學性質及電機發光元件性質。**PhSPDPV** 和 **PhSP_{N2}DPV** 兩者具有非常類似的玻璃轉移溫度(T_g 約 120 °C)和光物理性質。由單傳輸電洞和電子元件得知，**PhSP_{N2}DPV** 具有比 **PhSPDPV** 更佳的電子傳輸和注入能力。相對於 **PhSPDPV** 的電機放光元件，**PhSP_{N2}DPV** 具有較佳的電激放光元件效率(最大亮度為 60500 cd/m²、最大外部量子效率為 4.9%)。**PhSP_{N2}DPV** 的高元件效率是因為分子中的 diaza 官能基可以促進分子電子傳輸和電子注入能力，進而平衡元件中的電洞和電子，而增加電子電洞的再結合率。

第五章：設計並合成出一系列含有 benzothiazole 的雙苯胺基芴或螺結雙芴螢光體。利用在雙苯胺基的鄰位上引進甲基、氯、或是氟取代基可以輕易的改變螢光體的光色，將之藍位移由 470 nm 到 439 nm。這些螢光體具有高達 54 - 74 % 的螢光放光效率，適合做為藍色電激發光的材料。以 **PhFBT** 摻入 MADN 中製成摻入式藍色電機放光元件，當摻入濃度為 10 ~ 20% 時，在 20 mA/cm² 的電流密度驅動下可達到 4.7% 的外部量子效率 (摻入濃度為 10% 時) 及高達 28300 cd/m² 的亮度，相對應的最大放光波長位置在 454-458 nm，CIE 座標參數 $x = 0.14-0.14$ ， $y = 0.13-0.15$ 。有趣的是，此電激放光元件因為能量未能完全由主體 MADN 完全轉移到的摻入物 **PhFBT**，而使得摻入物 **PhFBT** 和主體 MADN 共同放光。



Fluorene and Spirobifluorene Fluorophores for Organic Light-Emitting Diodes

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Abstract

Chapter 2: Rare red fluorescent fluorene derivatives were designed and synthesized. The long wavelength red fluorescence was achieved by incorporating di(4-tolyl)amino or diphenylamino electron donor and dicyanovinyl electron acceptor. Single crystal x-ray structure of **pTSPDCV**, 2-di(4-tolyl)amino-7-dicyanovinyl-9,9'-(2,2'-biphenyl)fluorene and **PhSPDCV**, 2-diphenylamino-7-dicyanovinyl-9,9'-(2,2'-biphenyl)fluorene indicates only weak non- π van der Waals contact in addition to long distance dipole-dipole interaction of red fluorene molecules in solid state. The aggregation of the dipolar fluorene was largely suppressed by introducing bulky 9,9'-substituents (spiro-fused bifluorene) as well as the non-planar di(4-tolyl)amino or diphenylamino group. In solid state, these fluorenes derivatives all showed red fluorescence brightly compared with the dull red dopants of Nile Red and DCM (4-(dicyanomethylene)-2-methyl-6-[4-(dimethylaminostyryl)-4*H*-pyran]). The unique photophysical properties of red fluorene derivatives differ from other known red dopants and facilitate the fabrication of non-doped red organic light-emitting diodes (OLEDs). Authentic red (CIE, $x = 0.65$, $y = 0.35$) electro-luminescence with brightness over 12000 cd/m^2 (or $> 600 \text{ cd}/\text{m}^2$ at $20 \text{ mA}/\text{cm}^2$) and remarkable external quantum efficiency as high as 3.6% was observed for the red OLEDs with **pTSPDCV** or **PhSPDCV** as the sole host emitter.

Chapter 3: Pure 2,2'-dibromo-9,9'-spirobifluorene was synthesized by a method that did

not involve troublesome dibromination of 9,9'-spirobifluorene or Sandmeyer reaction of 2,2'-diamino-9,9'-spirobifluorene. A series of donor-acceptor orthogonally substituted 9,9'-spirobifluorene was subsequently prepared showing rich variation of fluorescence in solution and solid state. Here we study a series of strong fluorescence donor-acceptor-substituted spirobifluorene compounds, red **PhSPDCV** (2-diphenylamino-7-dicyanovinyl-9,9'-spirobifluorene), green **PhSPCHO** (2-diphenylamino-7-formyl-9,9'-spirobifluorene), and blue **PhSPDPV** (2-diphenylamino-7-diphenylvinyl-9,9'-spirobifluorene), together with their spiro "dimer" analogs, **BisPhSPDCV** (2,2'-diphenylamino-7,7'-dicyanovinyl-9,9'-spirobifluorene), green **BisPhSPCHO** (2,2'-diphenylamino-7,7'-diformyl-9,9'-spirobifluorene), and blue **BisPhSPDPV** (2,2'-diphenylamino-7,7'-diphenylvinyl-9,9'-spirobifluorene), respectively. The "dimeric" molecules are two identical units orthogonally linked in the spirobifluorene structure. The electronic interaction between the two molecular halves is expected to be weak, and thus the light-emitting density could be assembly doubled. However the dipole moments are also increased in the corresponding "dimeric" molecules in the red and green fluorophores. The physical properties including dipole moment from quantum chemistry calculation, emission solvatochromism, fluorescence quantum yield (Φ_f), crystal packing X-ray structure, and OLED performance of these materials are examined and analyzed in details. We found that the fluorescence quantum yield as well as the OLED performance of the strongly dipolar red **PhSPDCV** and green **PhSPCHO** series decrease significantly in the "dimeric" structures (**BisPhSPDCV** and **BisPhSOCHO**), but not in the weakly dipolar **BisPhSPDPV**. The electroluminescence is closely correlated with the local electric field, which is induced by the dipole moments of nearby molecules or internal molecular halves. Particularly, the fluorescence quenching of highly polar "dimeric" **BisPhSPDCV** or **BisPhSOCHO** is likely due to the strong local electric field arising from the donor-acceptor functionalized molecular halves, with which a charge-transfer associated quenching channel may become feasible. To avoid electric field-induced fluorescence

quenching, the molecular dipole moments should be limited. Within the context, dopant-based OLED containing 0.5% **PhSPDCV** light-emitter exhibited one of the most efficient (maximum external quantum efficiency of 3.4%, luminance efficiency of 9.4 cd/A, or power efficiency of 8.2 lm/W), bright (~ 1800 cd/m² at 20 mA/cm²) saturated yellow (CIE, $x = 0.50$, $y = 0.48$) electroluminescence. On the other hand, non-dopant-based OLED containing **PhSPDPV** light-emitter exhibited very efficient (maximum external quantum efficiency of 3.4%, luminance efficiency of 5.4 cd/A, or power efficiency of 5.7 lm/W), bright (~ 910 cd/m² at 20 mA/cm²) blue (1931 CIE, $x = 0.14$, $y = 0.22$) electroluminescence.

Chapter 4: The synthesis, thermal, optical physical, electrochemical and electro-luminescent properties of **PhSPDPV** and **PhSP_{N2}DPV** were investigated. Both **PhSPDPV** and **PhSP_{N2}DPV** exhibit similar high glass-transition temperatures ($T_g \sim 112$ °C) and similar optical physical properties either in solution or solid state. Hole- and electron-only devices of these two compounds were reported that **PhSP_{N2}DPV** exhibit electron transporting and injecting ability better than **PhSPDPV**. Compared with **PhSPDPV** OLED, a significantly improved OLED performance was achieved for **PhSP_{N2}DPV** (maximum brightness of 60500 cd/m² and maximum η_{EXT} of 4.9%). The diaza moiety improved the electron transporting and injecting ability of **PhSP_{N2}DPV** and further enhanced the hole-electron charge recombination leading to more charge balance in **PhSP_{N2}DPV** OLED.

Chapter 5: A series of benzothiazole-carrying diarylamino fluorene or spirobifluorene fluorophores were successfully prepared and investigated. By introducing methyl, chloro, or fluoro substituent to the ortho-position of diphenylamino donor, the fluorescence wavelength of chromophores can easily to blue-shifted from 472 nm to 439 nm. These fluorene or spirobifluorene fluorophores show high fluorescent quantum yields in a range of 54-74% which are reasonably good for high efficiency blue OLEDs. High performance blue OLEDs containing **PhFBT**-doped **MADN** has been obtained with high dopant concentration of 10~20% with remarkable external quantum efficiency value of 4.7% (dopant concentration of

10 %) at the current density of 20 mA/cm². The devices of the dopant concentration of 10~20% showed the emission λ_{\max} at 454-458 nm corresponding to CIE coordinate, $x = 0.14-0.14$, $y = 0.13-0.15$ with highly brightness over than 28300 cd/m². It is interesting that the blue EL emission is attributed to both **PhFBT** dopant and MADN host due to the incomplete Förster energy transfer or similar charge-trapping ability of the two materials.

