

稳定的蓝色及白色有机薄膜电致发光器件

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摘要: 报道了一种稳定的蓝色和白色有机薄膜电致发光器件, 蓝色器件最大亮度为 $7\ 526\text{cd}/\text{m}^2$, 最大效率 $1.45\text{lm}/\text{W}$, 半亮度寿命 $1\ 035\text{h}$ (初始亮度 $100\text{cd}/\text{m}^2$)。白色器件的最大亮度为 $14\ 850\text{cd}/\text{m}^2$, 最大效率 $2.88\text{lm}/\text{W}$, 色度 $x = 0.31, y = 0.38$, 且色度不随电流增大而变化, 半亮度寿命为 $2\ 860\text{h}$ (初始亮度 $100\text{cd}/\text{m}^2$)。

关键词: 有机薄膜电致发光; 蓝色、白色 EL 器件; 稳定性

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1 引 言

有机薄膜电致发光作为新型的平板显示器件受到人们广泛的关注。目前绿色已进入了实用化阶段。进一步奋斗的目标是实现彩色显示。在实现彩色显示中, 红、蓝、绿及白四种器件都是重要的。虽然对这些器件报道得不少, 然而能否得到稳定的红、蓝、绿、白的器件则是关系能否真正实用的问题。对于绿色器件, J. M. Shi 等^[1]报道的初始亮度 $7\ 000\text{cd}/\text{m}^2$ 下寿命 $1\ 400\text{h}$ 仍是最好的结果, V+En Choohe 等^[2]最近使用混合的方法得到 $100\text{cd}/\text{m}^2$ 初始亮度下 $70\ 000\text{h}$ 的寿命。我们也报道了 $100\text{cd}/\text{m}^2$ 下 $14\ 000\text{h}$ 寿命的绿色器件^[3]。各大公司在量产化中都是以绿色为突破口, 表明绿色器件已达实用水平。关于红色器件有不少报道, 但不涉及寿命^[4-5]。我们首先报道了寿命 $7\ 500\text{h}$ (初始亮度 $50\text{cd}/\text{m}^2$) 的红色器件^[6], 最近 P. E. Burrows 等^[7]根据推算得到寿命大于 10^7h (初始亮度 $48\text{cd}/\text{m}^2$) 的红色器件, 都表明红色器件的稳定性已有了很大进展, 可能已经不是制约彩色发展的瓶颈。然而蓝色和白色稳定性仍有相当大的差距。1995 年日本出光兴产^[8]报道了寿命 $5\ 000\text{h}$ 的蓝光器件后, 以后的蓝光器件的报道^[9-10]未涉及稳定性。白色器件的报道^[11-15]基本没有涉及到稳定性。

在本文中, 我们报道一个稳定性较好的蓝色器件, 在初始亮度 $100\text{cd}/\text{m}^2$ 下, 它的半亮度寿命

可达 $1\ 035\text{h}$ 。在这个蓝色器件的基础上, 我们制成了白色器件, 它可达到初始亮度 $100\text{cd}/\text{m}^2$ 下, 半亮度寿命 $2\ 860\text{h}$ 。这是我们所知道的最好的白光器件稳定性。

2 实 验

将 ITO 玻璃衬底经清洗及 plasma 处理后放入 $1.33 \times 10^{-4}\text{Pa}$ 的真空室内, 相继蒸发缓冲层、空穴传输层、发光层及电子传输层, 然后制作金属电极 Mg: Ag (1: 9), 其中掺杂的发光层及金属电极均采用双源蒸发的方法, 最后器件密封测量。器件的亮度, 色度及光谱通过 PR650 光谱扫描色度计测量, 亮度-电压, 电流-电压特性用 2400 Source Meter 及相关线路测量。所用有机材料的分子结构示于图 1。

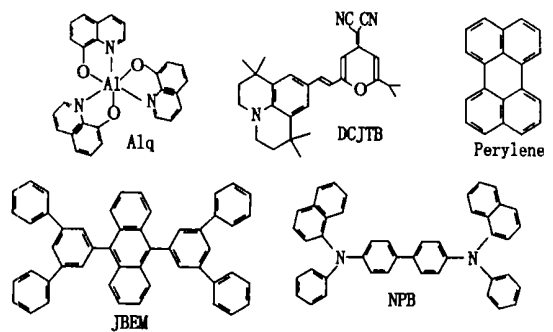


图 1 所用有机材料的分子式

Fig. 1 Molecular structures of organic materials used.

3 实验结果

(1) 蓝色器件: 我们使用新的蓝色发光材料作

为基质制作了蓝色器件,其结构为ITO/CuPc/NPB/JBEM: perylene/Alq/MgAg。其中JBEM是蓝光材料9,10-bis(3',5'-diaryl)phenyl anthracene^[15],并在其中掺入了perylene,器件的电致发光光谱示于图2。发光是perylene的特征蓝色,色度为 $x = 0.14, y = 0.21$ 。

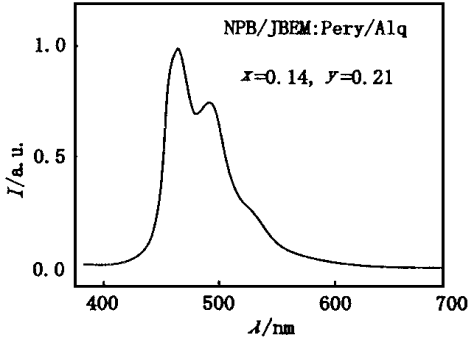


图 2 蓝色器件电致发光光谱

Fig. 2 Electroluminescent spectra of the blue OLED.

亮度-电压、电压-电流关系示于图3。由图可知,器件在18V达到最大亮度,其值为 $7548\text{cd}/\text{m}^2$,器件在电流密度 $20\text{mA}/\text{cm}^2$ 的驱动下亮度为 $408\text{cd}/\text{m}^2$,最大效率 $1.45\text{lm}/\text{W}$ 。

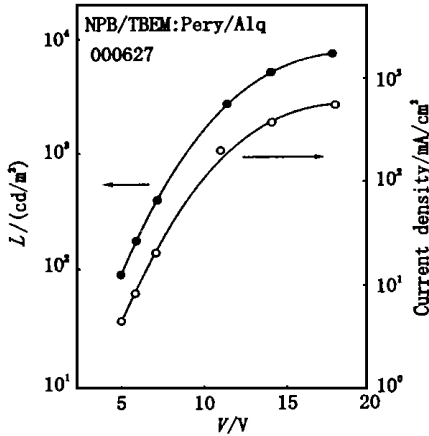


图 3 蓝色器件的亮度-电压、电流-电压曲线

Fig. 3 Dependence of luminance and current density on applied voltage of blue cell.

蓝色器件的老化曲线及恒流条件下驱动电压的经时变化示于图4。由图可见,在 $12\text{mA}/\text{cm}^2$ 恒定电流驱动下,初始亮度 $230\text{cd}/\text{m}^2$ 下,亮度降至一半是450h,若初始亮度按 $100\text{cd}/\text{m}^2$ 计,半亮度寿命1035h。驱动电压在500h内升高2V,电压变化率为 $4\text{mV}/\text{h}$,说明老化过程中,界面势垒有升高。这个器件显示了较好的稳定性。

(2) 白色器件:在蓝色器件的基础上,我们研制了白色器件。在蓝色器件的发光层JBEM中除

掺入蓝色染料Perylene外,还掺入红色染料DCJT B,当改变DCJT B浓度时可得到不同色度的电致发光光谱。利用JBEM向DCJT B的不完全能量传递实现白光。器件结构为ITO/CuPc/NPB/JBEM: perylene: DCJT B/Alq/MgAg。

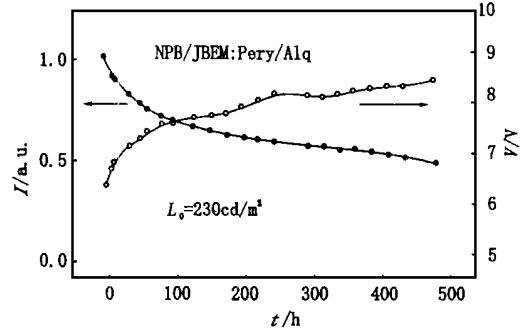


图 4 在 $12\text{mA}/\text{cm}^2$ 恒定电流驱动下,蓝色器件的亮度及施加电压随时间的变化

Fig. 4 Luminance degradation and the change of driving voltage with the time under $12\text{mA}/\text{cm}^2$ continuous operation.

图5是不同DCJT B浓度时器件的电致发光光谱。由图可见,当DCJT B浓度较小时,JBEM只有一部分能量传递,这时蓝色的发射仍有保留,蓝光和DCJT B发的红光合成白光。当DCJT B浓度大时,蓝光被传递而减弱,红光增强。在掺杂浓度为0.2%时光谱色度为 $x = 0.32, y = 0.38$,浓度为0.5%和2%时色度分别为 $x = 0.34, y = 0.40$ 和 $x = 0.46, y = 0.47$ 。器件的光谱向红偏移,不再是白光。

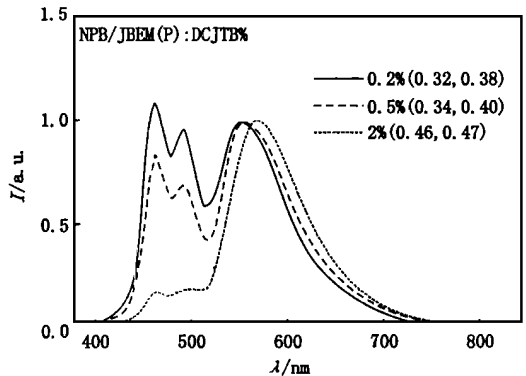


图 5 不同DCJT B浓度下的电致发光光谱

Fig. 5 Electroluminescent spectra of the devices with different concentrations of DCJT B.

器件的光谱随电流变化示于图6。如图所示,这种器件的色度随电流变化很小,电流由 $4\text{mA}/\text{cm}^2$ 变化至 $20\text{mA}/\text{cm}^2$ (这是最常用的电流范围)色度没有变化。这对于实际应用是重要的。

器件的亮度-电压, 电流-电压曲线示于图 7。由图可知, 器件的最大亮度为 $14\ 800\text{cd}/\text{m}^2$, 它是在 20V 达到的。在电流密度 $20\text{mA}/\text{cm}^2$ 下的亮

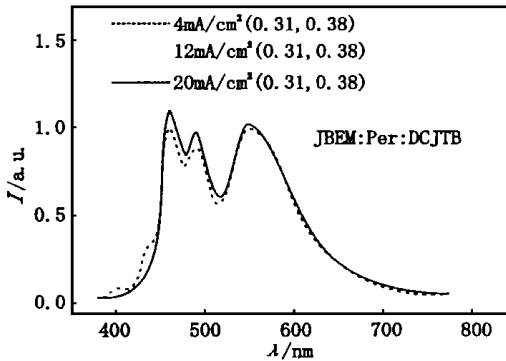


图 6 不同电流下的光谱

Fig. 6 Electroluminescence spectra under different current density.

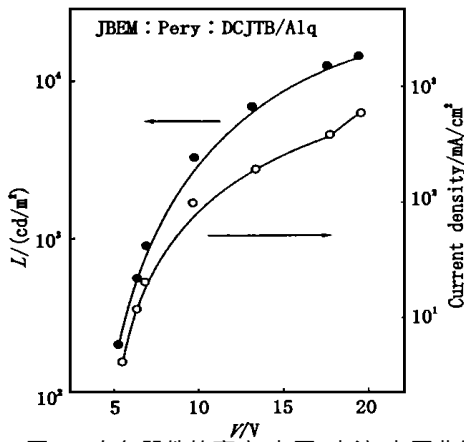


图 7 白色器件的亮度-电压, 电流-电压曲线

Fig. 7 Dependence of luminance and current density on applied voltage of white cell.

度为 $878\text{cd}/\text{m}^2$, 最大效率 $2.88\text{lm}/\text{W}$ 。白色器件的老化曲线及恒流条件下驱动电压的经时变化示于图 8。由图可见, 初始亮度 $493\text{cd}/\text{m}^2$ 下, 亮度降至一半是 580h , 若初始亮度按 $100\text{cd}/\text{m}^2$ 计, 半亮度寿命 $2\ 860\text{h}$ 。驱动电压在 500h 内升高 2V , 电压变化率为 $4\text{mV}/\text{h}$, 说明老化过程中, 界面势垒有升高。由此可见, 一个稳定的、光谱不随电流变化的白色器件实现了。

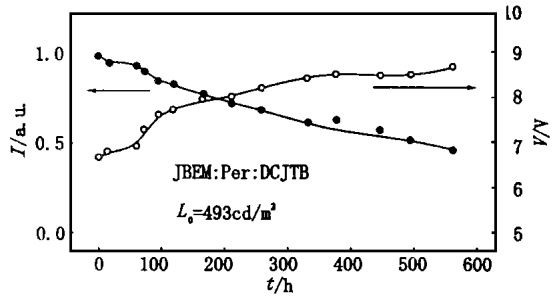


图 8 白色器件亮度及驱动电压随时间的变化

Fig. 8 Luminance degradation and the change of driving voltage with the time under $12\text{mA}/\text{cm}^2$ continuous operation.

4 结 论

利用一种新的蓝色材料制成了稳定的蓝色和白色有机薄膜电致发光器件, 蓝色器件最大亮度为 $7\ 526\text{cd}/\text{m}^2$, 最大效率 $1.45\text{lm}/\text{W}$, 半亮度寿命 $1\ 035\text{h}$ (初始亮度 $100\text{cd}/\text{m}^2$)。白色器件的最大亮度为 $14\ 850\text{cd}/\text{m}^2$, 最大效率 $2.88\text{lm}/\text{W}$, 色度 $x = 0.31, y = 0.38$, 且色度不随电流增大而变化, 半亮度寿命为 $2\ 860\text{h}$ (初始亮度 $100\text{cd}/\text{m}^2$)。

参 考 文 献:

- [1] Shi J M, Tang C W. Doped organic electroluminescent devices with improved stability [J]. *Appl. Phys. Lett.*, 1997, **70**(13): 1665-1667.
- [2] Choche V, En, Shi Song, Curless Jay, et al. Organic light-emitting diode with a bipolar transport layer [J]. *Appl. Phys. Lett.*, **75**(2): 172-174.
- [3] Zhang Zhilin, Jiang Xueyin, Zhang Buxin, et al. Multi-color organic light emitting diodes and its stability [J]. *Chinese J. Lumines.*, 2000, **21**(4): 308-314 (in Chinese).
- [4] Sakakibara Y, Okutsu S, Enokida T, et al. Red organic electroluminescence devices with a reduced porphyrin compound, tetraphenylchlorin [J]. *Appl. Phys. Lett.*, 1999, **74**(18): 2587-2589.
- [5] Hamada Y, Kanno H, Tsujioka T, et al. Red organic light emitting diodes using an emitting assist dopant [J]. *Appl. Phys. Lett.*, 1999, **75**(12): 1682-1684.
- [6] Jiang Xueyin, Zhang Zhilin, Zhang buxin, et al. High stable red organic emitting diode [J]. *Chin. J. Lumines.*, 2000, **21**(2): 174-176.
- [7] Burrows P E, Forrest S R. Operating lifetime of phosphorescent organic light emitting devices [J]. *Appl. Phys. Lett.*, 2000, **76**(18): 2493-2495.
- [8] Hosokawa C, Higashi H, Nakamura H, et al. Highly efficient blue electroluminescence from a distyrylarylene emitting layer with a new dopant [J]. *Appl. Phys. Lett.*, 1995, **67**(26): 3853-3855.
- [9] Gao Z Q, Lee C S, Bello I, Lee S T. Bright-blue electroluminescence from a silyl-substituted ter-(phenylene-vinylene)

- derivative [J]. *Appl. Phys. Lett.*, 1999, **74**(6): 865-867.
- [10] Tao X T, Suzuki H, Wada T, *et al.* Lithium tetra-(8-hydroxy-quinolato) boron for blue electroluminescent applications [J]. *Appl. Phys. Lett.*, 1999, **75**(12): 1655-1657.
- [11] Kido J, Kimura M, Nagai K. Multilayer white light emitting organic electroluminescent device [J]. *Science*, 1995, **267**: 1332-1334.
- [12] Forrest S R, Burrows P E, Shen Z, Gu G, Bulovic V. The stacked OLED: a new type of organic device for achieving high resolution full color display [J]. *Synthetic Metals.*, 1997, **91**: 9-13.
- [13] Deshpande R S, Bulovic V, Forrest S R. White light emitting organic electroluminescent devices based on interlayer sequential energy transfer [J]. *Appl. Phys. Lett.*, 1999, **75**(7): 888-890.
- [14] Xie Z Y, Huang J S, Li C N, *et al.* White light emission induced by confinement in organic multiheterostructures [J]. *Appl. Phys. Lett.*, 1999, **74**(6): 641-643.
- [15] Jiang X Y, Zhang Z L, Zhao W M, *et al.* White emitting organic diode with a doped blocking layer between hole- and electron-transporting layers [J]. *J. Phys. D: Appl. Phys.*, 2000, **33**: 473-476.
- [16] Shi Jianmin, *et al.*, US Patent: 5972247, 1999: 10.

Stable Blue and White Organic Light Emitting Diodes

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Abstract: A blue organic light emitting diode (OLED) with rather stability was realized by using a new blue emitting material. In this device, copper phthalocyanine (CuPc) was chosen as a buffer layer, N, N'-bis-(1-naphthyl)-N, N'-diphenyl-1, 1'-biphenyl-4-4'-diamine (NPB) was used as the hole transporting layer, 9, 10-bis(3' 5'-diaryl) phenyl anthracene (JBEM) was used as the emitting layer, in which peryrene was doped, then Alq was used as the electron transporting, MgAg alloy as the cathode. The structure of blue device was ITO/CuPc/NPB/JBEM: Peryrene/Alq/MgAg. Based on the blue device, a white device was constructed in which both perylene and DCJT B were doped in the emitting layer JBEM, the structure was ITO/CuPc/NPB/JBEM: Peryrene: DCJT B/Alq/MgAg.

The luminance, chromaticity and EL spectra of the OLED cells were measured with PR-650 Spectrascan Spectra Colorimeter. The characteristic of current-voltage was measured by using a Keithley 2400 Source Meter. Operation of the encapsulated EL cell was conducted at room temperature using a DC voltage current source in the constant current mode.

For the blue device, maximum luminance of 7 526cd/m², the luminance of 408cd/m² under current density of 20mA/cm², maximum efficiency 1.45 lm/W, the half decay time of 1035h at initial luminance of 100cd/m² were achieved. The white OLED shows the CIE coordinates $x = 0.32$, $y = 0.38$ and the independence of CIE coordinates on the current density. The maximum luminance of 14 852cd/m², the luminance of 878cd/m² under current density of 20mA/cm², maximum efficiency of 2.88 lm/W and half decay time of 2 860h at initial luminance of 100cd/m² were obtained.

Key words: organic emitting diode; blue, white EL devices; high stability