WHITE ORGANIC LIGHT-EMITTING DIODES USING 1,1,2,3,4,5-HEXAPHENYLSILOLE (HPS) AS GREENISH-BLUE EMITTER

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Abstract
White organic light-emitting diodes (WOLEDs) with the structure of ITO/NPB/NPB: DCJTB/HPS/Alq_3/LiF/Al have been fabricated. In this device, the NPB: DCJTB layer was used as the red emitter and the 1,1,2,3,4,5-hexaphenylsilole (HPS) layer was used as the greenish-blue emitter. White light with the Commission Internationale d'Eclairage (CIE) coordinates of (0.33,0.43) was obtained under the driving voltage of 5V. Simultaneously, the luminous efficiency and power efficiency are reaching the maximum value of 12.1cd/A and 7.59lm/W, respectively, with the current density of 1.33mA/cm^2 and luminance of 160cd/m^2. This high efficiency was attributed to the highly efficient greenish-blue emitter-1,1,2,3,4,5-hexaphenylsilole (HPS).

Keywords
White light; organic light-emitting diodes; Hexaphenylsilole

Introduction
White organic light-emitting diodes (WOLEDs) are of interest due to their potential applications as backlights for liquid crystal displays and light sources in fabricating full color displays through color filtering technology. White light emission can be achieved from multi-layer OLED structures [1,2] in which different layers emit different parts of the visible spectrum. In general, white color may result from the combination of three colors (red, blue and green) or two colors (red and blue). It is anticipated that the combination of greenish-blue and red color is also one way to produce white color. Recently, siloles or silacyclopentadiene derivatives have been proposed as a new class of highly efficient greenish-blue fluorescent materials [3-5]. Murata et al. reported an external quantum efficiency (EQE) of 4.8% at a brightness of 100cd/m^2 with undoped active layers-based on silole derivatives (PyPySPyPy, i.e. 2,5-bis(2'2"-bipyridin-6-yl)-1,1-dimethyl-3,4-diphenyl silacyclopentadiene, and 2PSP, i.e. 1,2-bis(1-methyl-2,3,4,5-tetraphenyl silacyclopentadienyl)ethane) with dominating emission peak at about 500nm [4]. 1,1,2,3,4,5-hexaphenylsilole (HPS) has also been reported as a good greenish-blue fluorescent emitter [6]. However, the white emission based on these efficient emitters is rarely reported so far.

In this work, we fabricated a white organic light-emitting diode based on one kind of efficient silole derivatives-1,1,2,3,4,5-hexaphenylsilole (HPS) and demonstrated that very efficient white color emission with CIE coordinates of (0.33,0.43) can be obtained from additive mixture of HPS's greenish-blue emission and red emission from 4-(dicyanomethylene)-2-tert-butyl-6-(1,1,7,7,-tetramethyljulolidin-3-methoxy-4-yl-vinyl)-4H-pyran (DCJTB) doped emitter. The device showed the maximum luminous efficiency of 12.1cd/A under the current density of 1.33mA/cm^2, which was extremely high for the electrofluorescnet white OLEDs.

Experimental details
HPS was synthesized by first reacting diphenylacetylene with an appropriate amount of lithium metal and then reacting the resultant 1,4-dilithiotetraphenylbutadiene with dichlorodiphenylsilane and then purified by recrystallization for use [7,8]. The molecular structures of HPS along with the device structure used in this work are shown in Fig. 1. NPB, Alq_3 and DCJTB are all commercial grades and used as received. The molecular structures of them can be easily found elsewhere [9].

Indium tin oxide (ITO) coated glass was cleaned and plasma-treated as the starting substrates. Details are the same with those reported before [10].

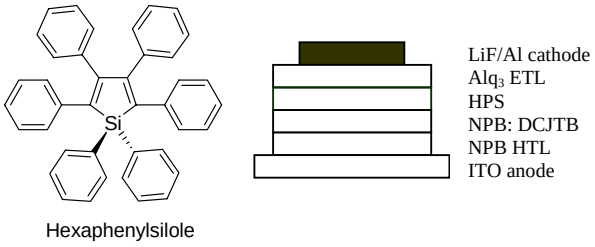

Fig.1. Chemical structure of HPS and schematic device structure used in this work

All organic thin films were prepared in a vacuum chamber at low pressure of ~3×10^{-7} Torr. Firstly, a 65 nm thick film of N,N'-diphenyl-N,N'-(2-napthyl)-(1,1'-phenyl)-4,4'-diamine (NPB) was deposited onto ITO and used as the hole transport layer (HTL). A 6nm thick film of NPB doped with DCJTB (0.1%, 1% and 2% by weight) was used as the red emitting layer followed by a 40nm thick film of HPS that was functioned as the greenish-blue emitting layer. 8-hydroxyquinoline aluminum (Alq_3) film with thickness of 5nm was served as electron transport layer (ETL) interposing between the emitter and cathode. Finally, the cathode consisting of 1nm LiF followed by 150nm of Al was deposited through shadow

mask in another vacuum chamber with base pressure of ~1×10^{-6} Torr. The active area of the devices was ~6.4mm^2. The doping layer was achieved by co-evaporation from two separated sources. The typical deposition rates of organic thin films and metal films were 0.1-0.2nm/s and 0.2-0.3 nm/s, respectively. Quartz oscillators monitored film thickness *in situ*.

100nm thick film of HPS was also deposited on glass substrates for spectroscopic characterization. UV absorption spectra were measured on a Milton Roy Spectronic 3000 Array spectrophotometer. Photoluminescence spectra were recorded on a Perkin-Elmer *LS 55* spectrofluorometer using 370nm as the excitation wavelength. The electroluminescent (EL) spectra of the devices were obtained by a Photoresearch PR650 spectrometer. The luminance-current density-voltage (L-J-V) characteristics were measured using an Advanced R6145 DC Voltage-Current source and Fluke 45 Dual Display multi-meter combined with the PR650 controlled by software. All the measurements were performed in ambient atmosphere at room temperature without device encapsulation.

Results and discussion

Fig.2 show the UV absorption spectra of HPS thin film together with the PL spectra and also the EL spectra of the device based on the HPS emission with the structure of ITO/NPB/HPS/Alq_3/LiF/Al. The maximum absorption and photoluminescence of HPS is located at ~366nm and ~485nm, respectively. The EL spectra of the device are similar to that of PL spectra, which shows a greenish-blue color. We here also show the EL characteristics of this device in Fig. 3 aiming at verifying the highly EL efficiency and intensity of the HPS. As can be seen that the maximum brightness is more than 75,000 cd/m^2 under the driving voltage of 17V. The highest luminous efficiency of the device is reaching 20cd/A with the current density of 0.4mA/cm^2 that is similar as reported before [6]. It is anticipated that using an efficient fluorescent red emitter together with this HPS can be a good way to produce white light emission.

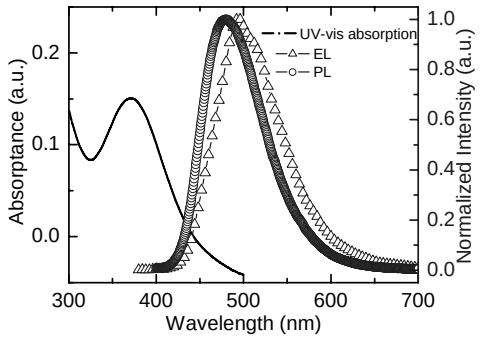

Fig.2. Optical absorption and PL spectra of thin film of HPS and EL spectra of devices only based on HPS emission with structure of ITO/NPB/HPS/Alq_3/LiF/Al

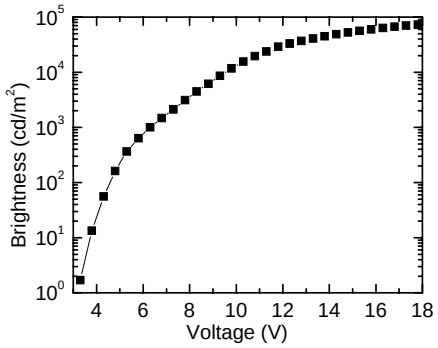

Fig.3. L-V characteristics of EL device only based on HPS emission

DCJTB is a well-known red fluorescent dopant material [11] and always used inside WOLEDs [12]. NPB has a large energy gap of ~ 3.1ev (the difference of energy between LUMO and HOMO) and can be served as a candidate of host [9]. Particularly, the absorption spectra of DCJTB have a relatively large overlapped with the fluorescent spectra of NPB, which means the Förster energy transfer from NPB to DCJTB will be much enhanced [9]. Additionally, the fact that NPB could act as both the HTL and host of DCJTB will reduce the species of organic materials used and also simplifies the device fabrication. Therefore, we selected NPB: DCJTB as the red emitter and fabricated the device with the structure of ITO/NPB(65nm)/NPB: DCJTB (6nm, x%wt)/HPS(40nm)/Alq_3(5nm)/LiF(0.8nm)/Al(150nm). X is equal to 0.1, 1 and 2 for device A, B and C, respectively.

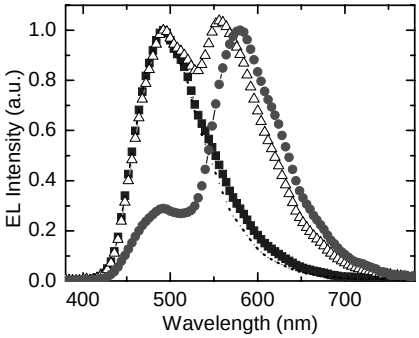

Fig. 4. EL spectra of device A (solid square), B (hollow triangle) and C (solid circle) along with that of device only based on HPS emission (dash line)

Fig. 4 shows the EL spectra of three devices under the current density of 1.33mA/cm^2. It is clear that there is much difference for the spectra of three devices caused by different doping concentration for each device. As for device A, its spectrum is almost the same with that of greenish-blue device only based on HPS emission. This fact is caused by too little DCJTB molecules doping in

the host introduces very little red fluorescence. As for device B and C, we can observe two emission peaks, one is 492nm and the other is 565nm for B and 580nm for C, respectively. Undoubtedly, the former peak is originating from HPS and the latter one is from DCJTB. The peak shift from 565nm for device B to 580nm for device C can be attributed to medium effect in a solid state solution which is typical for the polar and donor-acceptor type red dyes [13].

We also find that only device B shows the comparative two peaks leading to good color purity similar to pure white in comparison with the other two devices. It is necessary to mention that the color shift does exist in these devices even for device B that has the optimum doping concentration in terms of color purity and EL performance. Fig. 5 shows the CIE coordinates of device B under different driving voltage (4V to 16V). Color shows a reddish shift with increasing the voltage, however, the emission still looks like white light. This phenomenon is ascribing to the change of ratio of emission from HPS and DCJTB caused by the change of internal electric field distribution as well as the intrinsic fluorescent efficiency of these two materials.

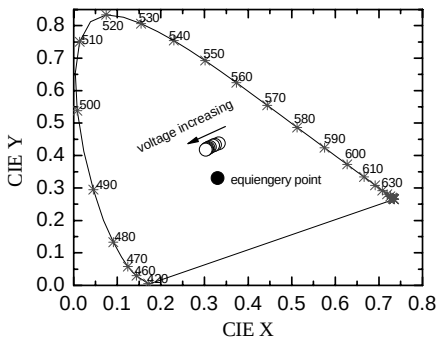

Fig.5. Variation of CIE coordinates with applied voltage for device B

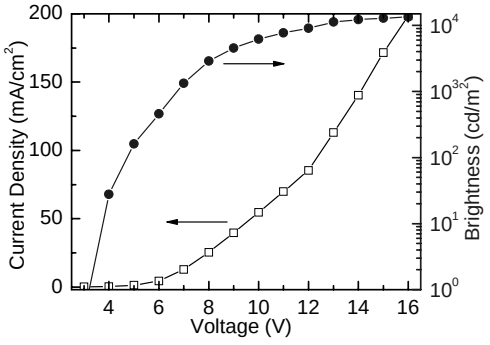

Fig.6. J-V-L characteristics of device B

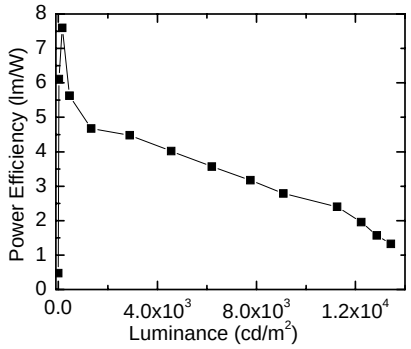

Fig.7. Power efficiency versus luminance for device B

Fig. 6 shows the J-V-L characteristics of device B. As can be seen that the white light emission is very efficient. The device turns on at ~3.5V (1cd/m^2) and reaches the maximum luminance of 13,500cd/m^2 at 16V. The maximum luminous efficiency is about 12.1cd/A under the driving current density of 1.33mA/cm^2. Shown in Fig. 7 is the power efficiency versus luminance curve. The power efficiency is reaching the maximum value of 7.59lm/W with the luminance of 160cd/m^2. These characteristics are very attractive for application use and are almost the best results to my knowledge for WOLEDs based on fluorescence reported so far. Actually, these results are preliminary ones and the better performance, such as little color shift or even higher luminous efficiency, is expected in the future work.

Conclusion

In summary, we have reported a very highly efficient white organic light-emitting diode based on the greenish-blue emitter of HPS. The white light emission with the CIE coordinates of (0.33, 0.43) is obtained under driving voltage of 5V. The maxmium luminous efficiency is 12.1cd/A with the current density of 1.33mA/cm^2 and luminance of 160cd/m^2. We attribute the high efficiency of the device to the use of highly efficient greenish-blue emitter-1, 1,2,3,4,5-hexaphenylsilole (HPS). More importantly, it suggests a way to produce white light emission in OLEDs employing other high efficiency fluorescent silole derivatives.

Acknowledgement

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References

[1] S. Liu, J. Huang, Z. Xie, Y. Wang, B. Chen, "Organic white light electroluminescent devices," *Thin Solid Films*, *363*, p.294, (2000).

[2] X. Jiang, Z. Zhang, W. Zhao, W. Zhu, B. Zhang, S. Xu, "White-emitting organic diode with a doped blocking layer between hole- and electron-transporting layers," *J. Phys. D: Appl. Phys, 33,* p.473, (2000).
[3] H. Murata, G. G. Mallizras, M. Uchida, Y. Shen, and Z. H. Kafafi, "Non-dispersive and air-stable electron transport in an amorphous organic semiconductor," *Chem. Phys. Lett., vol. 339,* p.161, (2001).
[4] H. Murata, Z. H. Kafafi, and M. Uchida, "Efficient organic light-emitting diodes with undoped active layers based on silole derivatives," *Appl. Phys. Lett., vol. 80,* p.189, (2002).
[5] L. C. Palilis, A. J. Makinen, M. Uchida, and Z. H. Kafafi, "Highly efficient molecular organic light-emitting diodes based on exciplex emission," *Appl. Phys. Lett., vol. 82,* p.2209, (2003).
[6] Haiying Chen, Junwu Chen, Chengfeng Qiu, Benzhong Tang, Man Wong and Hoi-Sing Kwok, "Efficient and Bright OLED based on Hexaphenylsilole," *SID Symposium Digest,* pp.509-511, (2003).
[7] Yan Ren, Jacky W. Y. Lam, Yongqiang Dong, Ben Zhong Tang, and Kam Sing Wong, "Enhanced Emission Efficiency and Excited State Lifetime Due to Restricted Intramolecular Motion in Silole Aggregates," *J. Phys. Chem. B (2005), 109,* 1135-1140.
[8] Ben Zhong Tang, Xiaowei Zhan, Gui Yu, Priscilla Pui Sze Lee, Yunqi Liu and Daoben Zhu, "Efficient blue emission from siloles," *J. Mater. Chem., (2001), 11,* 2974-2978.
[9] Hiroshi Kanno, Yuji Hamada, and Hisakazu Takahashi, "Development of OLED With High Stability and Luminance Efficiency by Co-Doping Methods for Full Color Displays," *IEEE Journal of Selected Topics in Quantum Electronics, vol.10,* no.1 pp.30-36, January/February (2004).
[10] J. X. Sun, X. L. Zhu, H. J. Peng, M. Wong, and H. S. Kwok, "Highly Efficient Stacked OLED Employing New Anode-Cathode Layer," *SID Symposium Digest,* P-129, (2005).
[11] Tswen-Hsin Liu, Chung-Yeh Iou, and Chin H. Chen, "Doped red organic electroluminescent devices based on a cohost emitter system," *Appl. Phys. Lett, vol.83,* pp.5241-5243, (2003).
[12] C. H. Chuen, Y. T. Tao, F. I. Wu, and C. F. Shu, "White organic light-emitting diodes based on 2,7-bis(2,2-diphenylvinyl)-9,9'-spirobifluorene: Improvement in operation lifetime," *Appl. Phys. Lett., vol. 85,* pp.4609-4611, (2004).
[13] V. Bulovic, R. Deshpande, M. E. Thompson, and S. R. Forrest, "Tuning the color emission of thin film molecular organic light emitting devices by the solid state solvation effect," *Chem. Phys. Lett. 308,* p.317, (1999).