

A Spirobenzofluorene Type Phosphine Oxide Molecule as A Triplet Host and An Electron Transport Material for High Efficiency in Phosphorescent Organic Light-Emitting Diodes

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Abstract

We synthesized a spirobenzofluorene type phosphine oxide (SPPO2) as a new triplet host and an universal electron transport material for phosphorescent organic light-emitting diodes (PHOLEDs). Red PHOLEDs with the SPPO2 host material showed a high quantum efficiency of 14.3 % with a current efficiency of 20.4 cd/A. In addition, the SPPO2 could be applied as an electron transport material which can be matched with any host material due to the lowest unoccupied molecular orbital of 2.4 eV. Electron injection from a cathode to the SPPO2 electron transport layer was better than common electron transport materials. In particular, the SPPO2 was effective as the electron transport material in blue PHOLEDs and the quantum efficiency was more than doubled and driving voltage was lowered by more than 3 V using the SPPO2 instead of common electron transport material.

1. Introduction

Phosphorescent organic light-emitting diodes (PHOLEDs) have been actively developed due to their merits of high efficiency compared with fluorescent organic light-emitting diodes¹. There have been many studies about improving the efficiency red PHOLEDs by developing host and dopant materials. Various iridium or platinum based phenylquinoline or phenylisoquinoline derivatives have been synthesized as dopant materials and high efficiency was reported in the red PHOLEDs^{2,3}.

The energy level of the organic materials has a influence in the PHOLEDs. Depending of energy level of electron transport materials lead to electron injection properties. In addition, it is much more difficult to produce blue emission due to the wide band-gap irrespective of type of materials for blue PHOLEDs.

Although many authors have studied high electron injection materials as it improved current density and efficiency. There have been efforts to develop transport materials to increase electrons. Phosphine oxide functional group is used as a point of saturation between other aromatic compound so that the energy level effected to transfer electrons from cathode to emitting layer. There have been many studies about organic light-emitting devices with phosphine oxide^{4,5}.

In this work, a spirobenzofluorene based phosphine oxide compound (SPPO2) was developed and it was evaluated as a red phosphorescent host material and an electron transport material in blue PHOLEDs.

2. Experimental

The SPPO2 material was synthesized by coupling of diphenylphosphine with spirofluorene unit and detailed synthesis will be reported in other work. We fabricated red PHOLED devices in the following configuration: indium tin oxide (ITO, 150 nm)/poly-3,4-ethylenedioxythiophene:polystyrenesulfonate (PEDOT:PSS, 60 nm)/ N, N'-di(1-naphthyl)-N,N'-

diphenylbenzidine(NPB, 20 nm)/ 4,4',4''-tris(*N*-carbazolyl) triphenylamine (TCTA, 10 nm)/ SPPO2: iridium(III) bis(2-phenylquinoline) acetylacetonate ($\text{Ir}(\text{pq})_2\text{acac}$)(30 nm, x %)/2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline(5 nm)/tris(8-hydroxyquinoline) aluminium(Alq_3 , 20 nm)/LiF(1nm)/Al(200 nm). The doping concentrations of $\text{Ir}(\text{pq})_2\text{acac}$ were 10 %, 15 % and 20 %. A mixed host device with TCTA:PH1 host instead of the SPPO2 was also fabricated as a standard device^[6]. Blue PHOLED devices configuration using the SPPO2 electron transport material was indium thin oxide (ITO)/*N,N'*-diphenyl-*N,N'*-bis-[4-(phenyl-*m*-tolyl-amino)-phenyl]-biphenyl-4,4'-diamine (DNTPD) (60nm) /*N,N'*-di(1-naphthyl)-*N,N'*-diphenylbenzidine (NPB) (20nm)/*N,N'*-dicarbazolyl-3,5-benzene (mCP) (10nm) /mCP: iridium(III)bis[4,6-(di-fluorophenyl)-pyridinato-*N,C2'*]picolate (FIrpic) (30nm,10%)/2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP, 5 nm)/tris(8-hydroxyquinoline) aluminium (Alq_3) (20nm)/LiF (1nm)/Al (100nm). A device with Alq_3 instead of SPPO2 was fabricated as a standard device. The performance of SPPO2 and Alq_3 was compared using the device structure. Chemical structure of SPPO2 and device structure are figure 1. Current density-voltage-luminance and electroluminescence characteristics of the PHOLEDs were measured with Keithley 2400 source measurement unit and CS 1000 spectroradiometer.

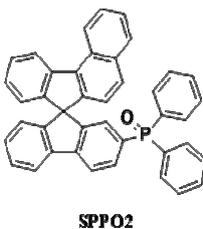
Al(200 nm)	Al(100 nm)	 <p style="text-align: center;">SPPO2</p>
LiF (1 nm)	LiF (1 nm)	
Alq_3 (20 nm)	SPPO2 (20 nm)	
BCP (5 nm)	BCP (5 nm)	
SPPO2: $\text{Ir}(\text{pq})_2\text{acac}$ X% (30 nm)	mCP:Firpic 10% (40 nm)	
TCTA (10 nm)	mCP (10 nm)	
NPB (20 nm)	NPB (20 nm)	
PEDOT : PSS (60 nm)	DNTPD (60 nm)	
ITO	ITO	
(a)	(b)	

Fig. 1. Chemical structure of SPPO2 and device structures used in this work. a) Red PHOLEDs, b) Blue PHOLEDs.

3. Results and discussion

The SPPO2 host material has good film forming ability with a surface roughness less than 1 nm due to a glass transition temperature of 119 °C and a twisted structure of the rigid spirobenzofluorene unit. The

highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the SPPO2 were 6.0 eV and 2.4 eV, respectively. The HOMO level of SPPO2 is eligible for hole injection and the electron transporting property of the phosphine oxide and the spirobenzofluorene unit is appropriate for balancing holes and electrons in the emitting layer. Figure 2 shows the quantum efficiency of the red PHOLEDs with SPPO2 as a host. The efficiency was compared with that of the TCTA:PH1 host reported in previous work. The triplet energy bandgap of the SPPO2 measured from low temperature photoluminescence is 2.4 eV which is suitable for triplet energy transfer from the SPPO2 to red emitting $\text{Ir}(\text{pq})_2\text{acac}$ with a triplet bandgap of 2.2 eV. The quantum efficiency of SPPO2 used red PHOLED was 14.3 % at 100 cd/m^2 with a current efficiency of 20.4 cd/A and the SPPO2 device showed better quantum efficiency than the mixed host device over all luminance range investigated. This indicates that the SPPO2 host is better than the TCTA:PH1 mixed host in terms of charge balance in the emitting layer.

The SPPO2 was also evaluated as an electron transport layer in green & blue PHOLEDs. Figure 3 a) shows current density-voltage curves of green PHOLEDs with SPPO2 based electron transport layer. The SPPO2 devices showed lower driving voltage than common Alq_3 devices because electron injection from a cathode to the SPPO2 electron transport layer was better than Alq_3 electron transport materials.

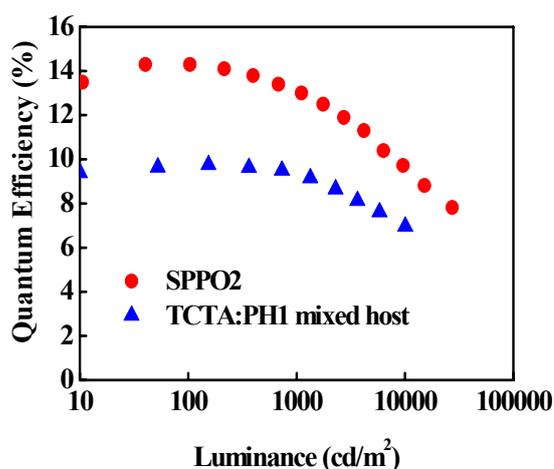


Fig. 2. Quantum efficiency of red PHOLEDs with SPPO2 and TCTA:PH1 as a host.

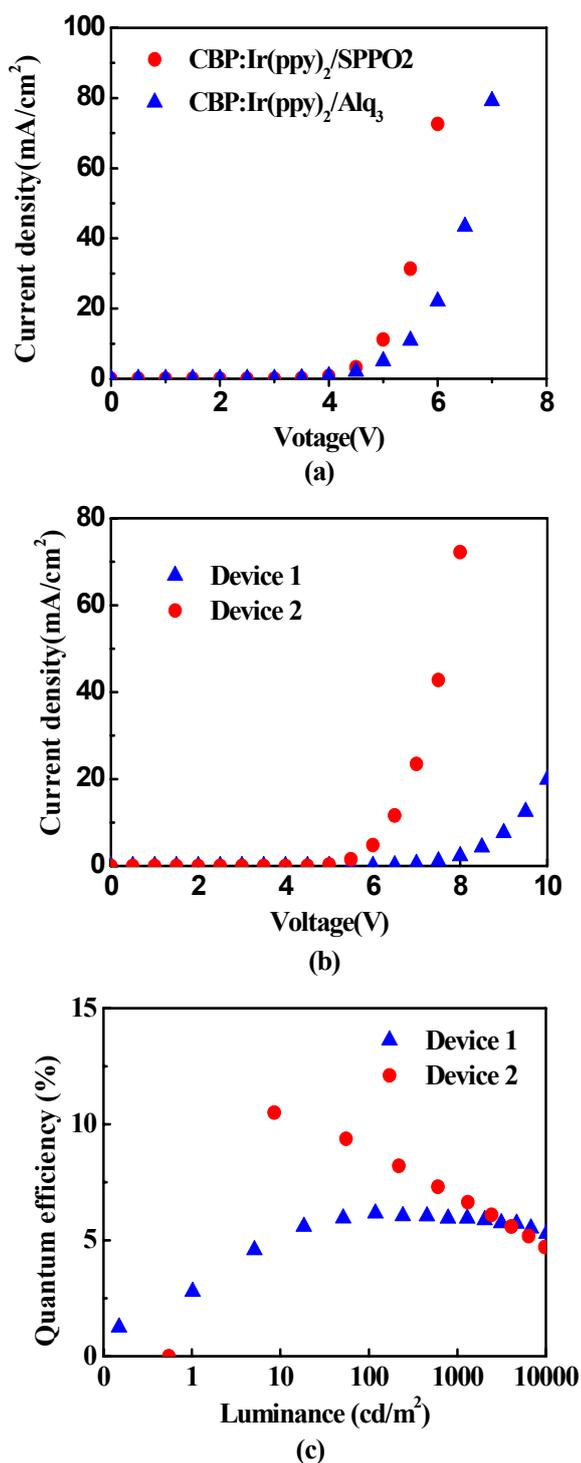


Fig. 3. a) Current density-voltage characteristics for Green PHOLEDs with SPPO2 as a electron transport material. b) Current density-voltage and c) Quantum efficiency of Blue PHOLEDs with SPPO2 as a electron transport material. Device1(triangle) : ITO/DNTPD/NPB/mCP:FIrpic/BCP/Alq₃/LiF/Al, Device 2 (circle): ITO/DNTPD/NPB/mCP:FIrpic/SPPO2/LiF/Al.

Figure 3 b) shows current density-voltage curves of blue PHOLEDs with SPPO2 based electron transport layer. Driving voltage of the SPPO2 devices was lowered by more than 3 V using the SPPO2 instead of common electron transport material because the electron injection from the SPPO2 with the LUMO level of 2.4 eV to the mCP emitting layer with the LUMO level of 2.4 eV. There was no energy barrier between SPPO2 and mCP, while there was 0.4 eV energy barrier between BCP & mCP, resulting on much higher current density on the blue PHOLED with the SPPO2 ETL. Figure 3 c) shows quantum efficiency of blue PHOLEDs with SPPO2 as a electron transport material. The quantum efficiency of the SPPO2 devices was more than doubled because of efficient electron injection.

4. Summary

A phosphine oxide derivative with a spirobenzofluorene backbone structure, SPPO2, was effective as a red phosphorescent host and it was better than common mixed host structure in terms of quantum efficiency. A high quantum efficiency of 14.3% and a current efficiency of 20.4 cd/A were obtained due to a triplet bandgap of 2.4 eV for efficient energy transfer and a charge balance in the light-emitting layer. The SPPO2 showed a smooth surface roughness less than 1 nm and a high glass transition temperature of 119 °C. It was also evaluated as an electron transport material and lowered the driving voltage of the blue PHOLED by 3 V. The quantum efficiency was 10.9 % and the power efficiency was 19 lm/W. Therefore, the SPPO2 could be used as a versatile material which shows good performances both as a host and an electron transport materials. In particular, the SPPO2 could give good device performances irrespective of the energy level of host materials and can be used as universal electron transport material.

5. Acknowledgements

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