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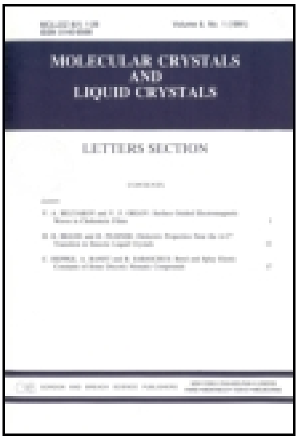

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High Efficiency Green and Blue Phosphorescent Organic Light-Emitting Diodes Using Pyrroloacridine Type Hole Transport Material

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High Efficiency Green and Blue Phosphorescent Organic Light-Emitting Diodes Using Pyrroloacridine Type Hole Transport Material

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A high triplet energy hole transport material with pyrroloacridine core was synthesized and the device performances of green and blue phosphorescent organic light-emitting diodes were studied. The pyrroloacridine type hole transport material showed high triplet energy of 2.90 eV for triplet exciton blocking in phosphorescent organic light-emitting diodes. Green and blue PHOLEDs fabricated using the pyrroloacridine core based hole transport layer showed high quantum efficiency of 17.2% and 20.3%, respectively.

Keywords High efficiency; high triplet energy; hole transport material; pyrroloacridine

Introduction

Organic light-emitting diodes have several organic materials in the device structure [1–6]. Among these, a hole transport material plays a role of transporting holes from a hole injection layer to emitting layer, blocking electron leakage from emitting layer, and suppressing exciton quenching in emitting layer. Therefore, it should possess the highest occupied molecular orbital (HOMO) for hole injection, lowest unoccupied molecular orbital (LUMO) for electron blocking, high singlet and triplet energy for exciton blocking and good hole transport properties. In particular, high triplet energy is required for the hole transport material used in blue phosphorescent organic light-emitting diodes (PHOLEDs) [2, 4, 6].

There have been several reports about high triplet energy hole transport materials for blue PHOLEDs and the most widely used hole transport material for blue PHOLEDs was N,N'-dicarbazolyl-3,5-benzene (mCP) [7–9]. It was originally developed as host materials for blue PHOLEDs7, but it has been commonly used as high triplet energy hole transport material for blue PHOLEDs due to good hole transport properties and high triplet energy. 4,4'-(Cyclohexane-1,1-diyl)bis(N-phenyl-N-p-tolylaniline) (TAPC) is another well-known high triplet energy hole transport material for blue PHOLEDs [2, 10, 11]. TAPC was better than mCP in terms of hole mobility. Other than these, fused carbazole and fused indole based hole transport materials have been synthesized as high triplet

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*Address correspondence to Prof. Jun Yeob Lee, Department of Polymer Science and Engineering, Dankook University, 126, Jukjeon-dong, Suji-gu, Yongin-Si, Gyeonggi-do 448-701 Korea (ROK). Tel.: (+82)31-8005-3585, Fax: (+82)31-8005-3585. E-mail: leej17@dankook.ac.kr energy hole transport materials [12, 13]. Among these materials, fused indole type hole transport materials showed good device performances because of high triplet energy above 2.90 eV, shallow LUMO level for electron blocking and high glass transition temperature [13].

In this work, a high triplet energy hole transport material made up of pyrroloacridine core modified with aromatic amine functional group, 4,4′-(6H-pyrrolo[3,2,1-de]acridine-6,6-diyl)bis(N,N-diphenylaniline) (PADPA), was synthesized as a continuation of our previous work and the device performances of green and blue PHOLEDs with PADPA were studied. High quantum efficiencies of 17.2% and 20.3% were demonstrated in green and blue PHOLEDs using PADPA hole transport material.

Experimental

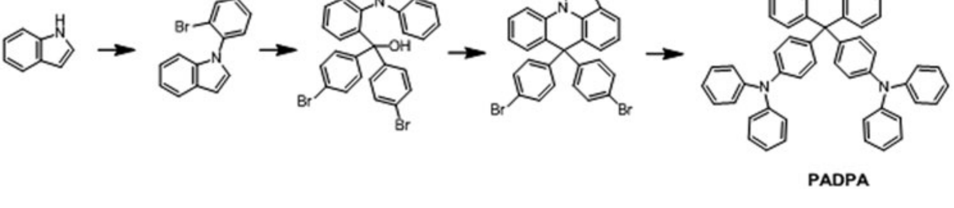
Synthetic scheme of PADPA is shown in Scheme 1. Intermediate compound of PADPA was synthesized according to the procedure reported in previous work [13]. General experimental methods are described in detail in our previous work [13].

Synthesis

Synthesis of 4,4’-(6H-pyrrolo[3,2,1-de]acridine-6,6-diyl)bis(N,N-diphenylaniline) (PADPA)

Diphenylamine (0.87 g, 4.463 mmol), 6,6-bis(4-bromophenyl)-6H-pyrrolo[3,2,1-de]acri dine (1 g, 1.94 mmol), potassium carbonate (1.09 g, 7.95 mmol), cupper iodide(I) (0.18 g, 0.97 mmol) and dibenzo 18-crown-6 (0.10 g, 0.388 mmol) were dissolved in dimethylformamide under nitrogen atmosphere. The reaction mixture was stirred for 16 h at 150°C. The mixture was diluted with dichloromethane and washed with distilled water three times. The organic layer was dried over anhydrous magnesium sulfate and evaporated in vacuo to give the crude product. The extract was evaporated to dryness affording a white solid, which was further purified by column chromatography using dichloromethane/n-hexane gave a white powder (0.87g, 65%).

Tg 125°C.^{1}H NMR (200 MHz, CDCl$_3$): δ 7.79 (d, 1H, J = 8.00 Hz), 7.63 (d, 2H, J = 8.00 Hz), 7.42 (d, 2H, J = 8.00 Hz), 7.25–6.95 (m, 31H), 6.45 (s, 1H). ^{13}C NMR (200 MHz, CDCl$_3$): δ147.1, 145.9, 140.8, 139.3, 138.4, 132.8, 130.1, 129.1, 128.7, 128.1, 127.7, 124.3, 123.4, 123.0, 122.8, 122.1, 121.7, 57.6. MS (FAB) m/z 691 [(M + H)$^+$]. Anal. Calcd. for $C_{51}H_{37}N_3$: C, 89.06; H, 4.84; N, 6.11. Found: C, 88.55; H, 5.25; N, 6.06.



Scheme 1. Synthetic scheme of PADPA.

Device Fabrication and Measurements

The device structure used in this work was indium tin oxide (ITO, 150 nm)/poly(3,4-ethylenedioxythiophene):polystyrenesulfonate (PEDOT:PSS, 60 nm)/N,N'-di(1-naphthyl)-N,N'-diphenylbenzidine (NPB, 5 nm)/PADPA (10 nm)/emitting layer (30 nm)/diphenylphosphine oxide-4-(triphenylsilyl)phenyl (TSPO1, 25 nm)/LiF(1 nm)/Al(200 nm). Green emitting layer was 9,9'-spirobi[fluorene]-2-yl(9,9'-spirobi[fluorene]-7-yl)methanone (BSFM): iridium (III) tris(2-phenylpyridine) (Ir(ppy)$_3$) and blue emitting layer was (9-(3-(9H-carbazol-9-yl)phenyl)-9H-carbazol-3-yl)diphenylphosphine oxide (mCPPO1):bis((3,5-difluoro-4-cyanophenyl)pyridine) iridium picolinate (FCNIrpic). Doping concentrations of Ir(ppy)$_3$ and FCNIrpic were 10% and 3%, respectively. All devices were encapsulated after metal deposition. Current density-voltage-luminance characteristics of green and blue PHOLEDs were measured with Keithley 2400 source meter and CS1000 spectroradiometer.

Results and Discussion

Pyrroloacridine core was useful as a core structure of high triplet energy hole transport material because of good hole transport properties originated from aromatic amine linkage and short conjugation length caused by sp [3] carbon linkage [13]. Additionally, it could restrict molecular motion due to the rigidity and increase glass transition temperature of hole transport material. Therefore, pyrroloacridine core was used as the core of high triplet energy hole transport material and was combined with hole transporting aromatic amine unit.

Synthetic scheme of PADPA is shown in Scheme 1. Brominated pyrroloacridine core was prepared according to the synthetic method reported in previous work, which was reacted with diphenylamine to produce PADPA [13].

Photophysical properties of PADPA were measured using ultraviolet-visible (UV-Vis) and photoluminescence (PL) spectrometer. Figure 1 shows UV-Vis, solution PL and low temperature PL spectra of PADPA. The UV-Vis and PL measurements of PADPA were carried out using 1×10^{-4} M tetrahydrofuran solution at room temperature and low temperature PL measurement was performed at 77 k using liquid nitrogen. Excitation wavelength of PL spectrum was 295 nm. PADPA exhibited strong UV-Vis absorption peak at 295 nm which is assigned to $\pi-\pi^*$ absorption of pyrroloacridine core and diphenylamine. Additionally, n-π^* transition was observed between 320 nm and 360 nm. Optical bandgap was calculated from absorption edge of UV-Vis spectrum, which was 3.62 eV. Solution PL emission of PADPA was observed at 366 nm. Low temperature PL measurement of PADPA was carried out at low temperature to measure triplet energy of PADPA. The triplet energy was calculated from the first phosphorescent emission peak of low temperature PL spectrum, which was 2.90 eV. The triplet energy of PADPA was higher than that of blue emitting FCNIrpic dopant and PADPA is expected to suppress triplet exciton quenching by hole transport layer.

Molecular orbital simulation of PADPA was performed to study HOMO and LUMO distribution. A suite of Gaussian 03 program and the nonlocal density functional of Becke's 3-parameters employing Lee-Yang-Parr functional (B3LYP) with 6–31G* basis sets were used for the calculation. Fig. 2 shows HOMO and LUMO distribution of PADPA. HOMO of PADPA was localized on diphenylamine unit, while LUMO was dispersed over pyrroloacridine core. As diphenylamine unit is strong hole transport moiety due to strong electron donating character of aromatic amine, HOMO was distributed over diphenylamine moiety.

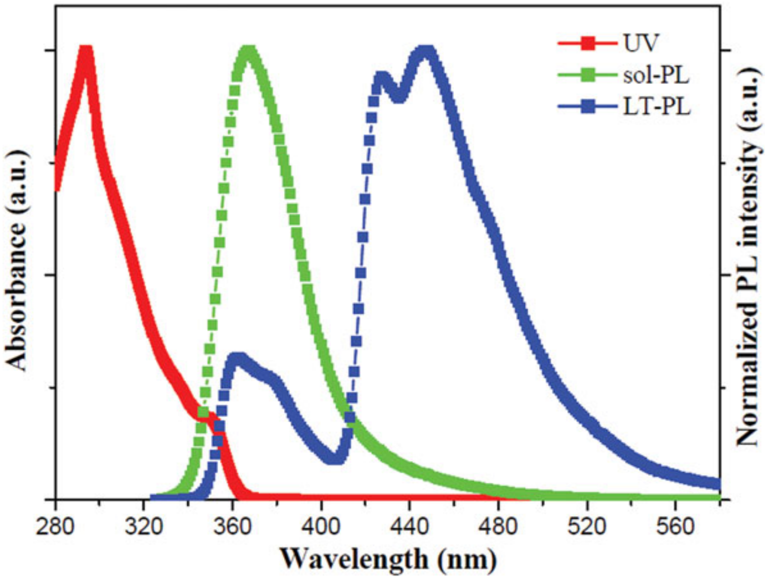


Figure 1. UV-Vis, PL and low temperature PL spectra of PADPA.

On the contrary, LUMO was distributed over pyrroloacridine core, indicating poor electron transport properties PADPA hole transport material.

HOMO level of PADPA was determined by cyclic voltametry (CV) method which uses electrochemical oxidation for HOMO measurement. Figure 3 shows CV curves of PADPA. HOMO level of PADPA was −5.77 eV from CV oxidation curve and LUMO level of −2.15 eV was obtained from HOMO level and optical bandgap determined by UV-Vis absorption edge. The HOMO level of PADPA was suitable for hole injection from hole injection layer to emitting layer and the LUMO level of PADPA was good enough for electron blocking from common emitting layer.

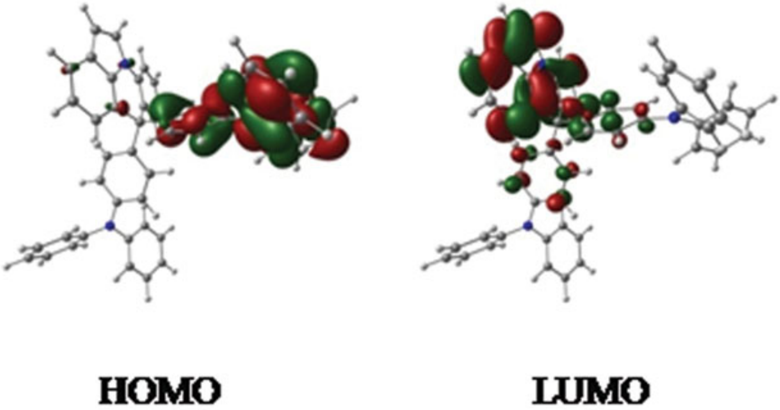


Figure 2. HOMO and LUMO distribution of PADPA.

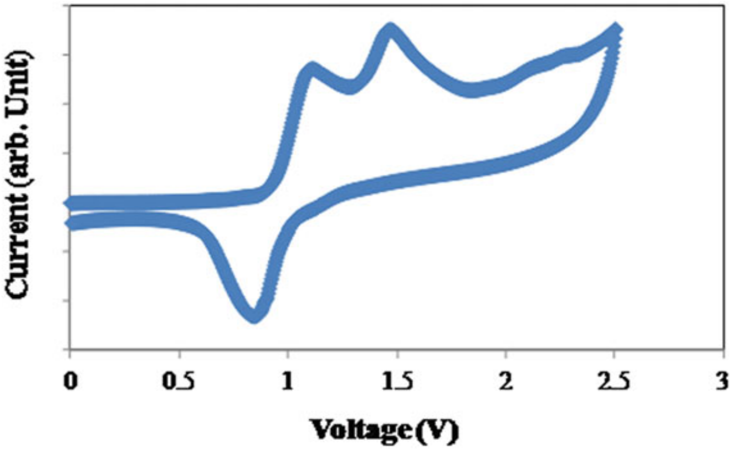


Figure 3. CV oxidation curve of PADPA.

Differential scanning calorimeter (DSC) measurement of PADPA was carried out to obtain glass transition temperature of PADPA. Glass transition temperature of PADPA was 125°C. As rigid pyrroloacridine unit was used as the core structure of PADPA, high glass transition temperature was obtained.

Green and blue PHOLEDs were fabricated using PADPA as hole transport materials. Green emitting layer was $Ir(ppy)_3$ doped BSFM, while blue emitting layer was FCNIrpic doped mCPPO1. Figure 4 shows current density-voltage-luminance curves of green and blue PHOLEDs with PADPA hole transport layer. The current density and luminance of green PHOLED were higher than those of blue PHOLED, which is due to low energy barrier for hole injection in green PHOLEDs as shown in energy level diagram in Fig. 5. HOMO level of BSFM was −5.90 eV and there exists 0.13 eV energy barrier for hole injection from PADPA to BSFM in green PHOLED. However, the energy barrier is increased to

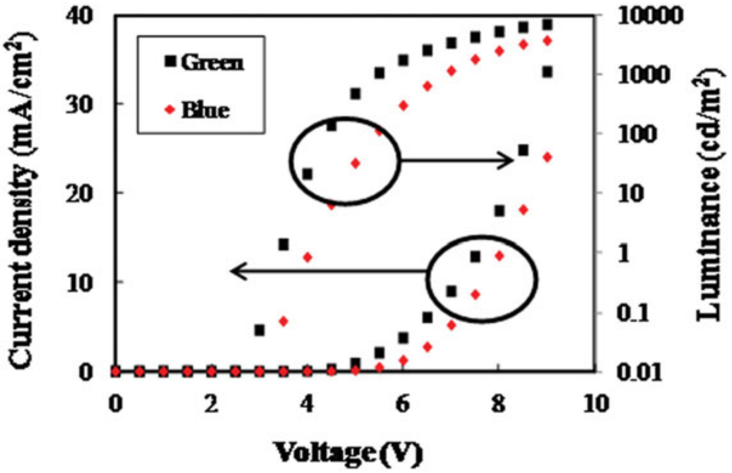


Figure 4. Current density-voltage-luminance curves of green and blue PHOLEDs with the PADPA hole transport layer.

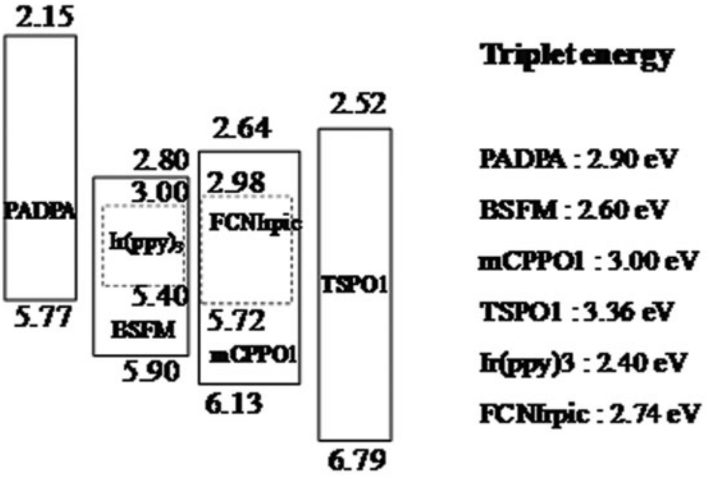


Figure 5. Energy level diagram of green and blue PHOLEDs.

0.36 eV in blue PHOLED, resulting in low current density at the same driving voltage. Turn on voltages of green and blue PHOLEDs were 3.0 V and 3.5 V, respectively.

Quantum efficiency-luminance curves of green and blue PHOLEDs are shown in Fig. 6. Maximum quantum efficiencies of green and blue PHOLEDs were 17.2% and 20.3%, while the quantum efficiencies at 1,000 cd/m^2 were 15.7% and 18.4%. There was less than 10% decrease of quantum efficiency at 1,000 cd/m^2 compared with that of maximum quantum efficiency. The high quantum efficiency of green and blue PHOLEDs can be explained by high triplet energy, efficient hole injection and electron blocking by

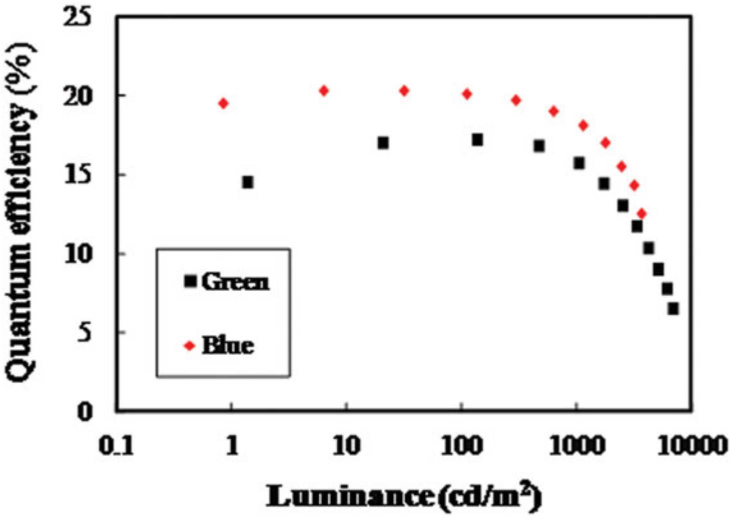


Figure 6. Quantum efficiency-luminance curve of green and blue PHOLEDs with the PADPA hole transport layer.

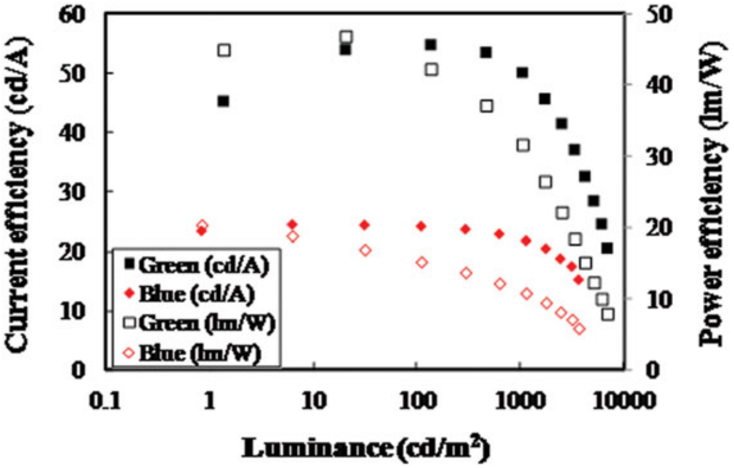


Figure 7. Current efficiency-luminance and power efficiency-luminance curves of green and blue PHOLEDs with the PADPA hole transport layer.

PADPA hole transport layer. The triplet energy of PADPA was 2.90 eV, which was high enough for triplet exciton blocking of green (triplet energy: 2.40 eV) and blue (triplet energy: 2.74 eV) phosphorescent emitting materials. Therefore, triplet excitons can be confined inside the emitting layer, resulting in high quantum efficiency. Electron blocking of PADPA also contributes to the charge confinement in the emitting layer. As the LUMO level of PADPA was −2.15 eV, electron leakage from emitting layer to PADPA layer can

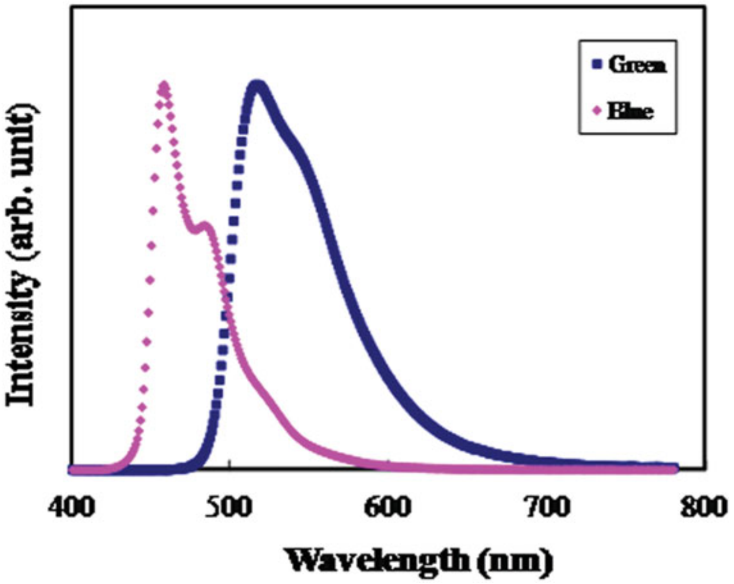


Figure 8. Electroluminescence spectra of green and blue PHOLEDs with the PADPA hole transport layer.

be effectively blocked by PADPA, leading to high recombination efficiency in the emitting layer.

Current efficiency and power efficiency curves of the green and blue PHOLEDs with the PADPA hole transport layer are shown in Fig. 7. The maximum current and power efficiencies of green devices were 54.7 cd/A and 46.8 lm/W, respectively, while those of blue PHOLEDs were 24.4 cd/A and 20.3 lm/W, respectively. High current efficiency was obtained in the green and blue PHOLEDs, but the power efficiency was rather low due to high driving voltage. The quantum efficiency and power efficiency of the PADPA device were in between those of mCP and TAPC.

Electroluminescence (EL) spectra of green and blue PHOLEDs are shown in Fig. 8. Only the emission of $Ir(ppy)_3$ and FCNIrpic was observed without any emission of PADPA or other charge transport materials, indicating exciton confinement inside the emitting layer. Therefore, it can be concluded that the PADPA hole transport mateiral can effectively confine electrons and excitons in the emitting layer.

Conclusions

A high triplet energy hole transport material based on pyrroloacridine core, PADPA, was synthesized and showed high quantum efficiency in green and blue PHOLEDs. High triplet energy, HOMO level for hole injection and LUMO level for electron blocking of PADPA contributed to the high quantum efficiency of green and blue PHOLEDs. It is expected that the pyrroloacridine core derivatives can be effectively used as the core structure of high triplet energy hole transport materials.

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