



Cyclopenta[def]fluorene based high triplet energy hole transport material for blue phosphorescent organic light-emitting diodes

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ABSTRACT

A cyclopenta[def]fluorene based high triplet energy hole transport material was synthesized as a thermally stable hole transport material for blue phosphorescent organic light-emitting diodes. The cyclopentafluorene type hole transport material showed a high glass transition temperature of 143 °C, high triplet energy of 2.81 eV and the lowest unoccupied molecular orbital of 2.10 eV for electron blocking in blue phosphorescent organic light-emitting diodes. The cyclopentafluorene type hole transport material improved the external quantum efficiency of blue phosphorescent organic light-emitting diodes.

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1. Introduction

The device performances of phosphorescent organic light-emitting diodes (PHOLEDs) typically depend on charge transport materials and emitting materials [1,2]. In particular, triplet energy of the charge transport materials is critical to the quantum efficiency of PHOLEDs because triplet excitons of the emitting material can be quenched by charge transport materials [3–9].

There have been many studies to develop high triplet energy hole transport materials for PHOLEDs [6,10–16]. Carbazole derivatives have been typically used as the hole transport type exciton blocking materials for blue PHOLEDs due to the high triplet energy of the carbazole core [6,10]. 1,3-Di(9H-carbazol-9-yl)benzene (mCP) was originally developed as a host material for blue PHOLEDs [17], but it could also be used as the high triplet energy hole transport type exciton blocking material for PHOLEDs [6,11]. It showed good performances as the high triplet energy hole transport type exciton blocking material for PHOLEDs, but it had a critical problem of poor thermal stability. Other than mCP, 4,4',4''-tris(N-carbazolyl)triphenyl-

amine (TCTA) [8] and 4,4'-(cyclohexane-1,1-diyl)bis(N-phenyl-N-p-tolylaniline) have been used as the high triplet energy hole transport materials [18]. Although they were effective as the high triplet energy hole transport materials for PHOLEDs, further development of high triplet energy hole transport materials is required to improve the device performances of PHOLEDs.

In this work, a novel hole transport material (TPCPF) with a thermally stable tetraphenyl substituted cyclopenta[def]fluorene core was synthesized as the high triplet energy hole transport material for PHOLEDs. The cyclopenta[def]fluorene core was developed as a new core structure for the hole transport material and the device performances of the hole transport material with the cyclopenta[def]fluorene core were investigated. It was demonstrated that cyclopenta[def]fluorene based hole transport material can be effectively used as the hole transport material to obtain high external quantum efficiency blue PHOLEDs.

2. Experimental

General analysis of synthesized material is described in our previous work [16]. All energy levels of materials were measured by our group.

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2.1. Synthesis

Synthetic scheme of TPCPF is described in Scheme 1.

2.2. Synthesis of 4,8-bis(4-bromophenyl)-4,8-diphenyl-4,8-dihydrocyclopenta[def]fluorene

2,2'-Dibromobiphenyl (5.00 g, 16.00 mmol) was dissolved in anhydrous tetrahydrofuran (THF, 30 mL) under a nitrogen atmosphere. The reaction flask was cooled to $-78\text{ }^{\circ}\text{C}$ and *n*-butyllithium (2.5 M in hexane, 14.74 mL) was added dropwise slowly. Stirring was continued for 2 h at $-78\text{ }^{\circ}\text{C}$, followed by addition of a solution of 4-bromobenzophenone (9.62 g, 36.80 mmol) in anhydrous THF (30 mL) under nitrogen atmosphere. The resulting mixture was gradually warmed to ambient temperature and quenched by adding saturated aqueous NaHCO_3 (60 mL). The mixture was extracted with dichloromethane. The combined organic layers were dried over magnesium sulfate, filtered, and evaporated under reduced pressure. A yellow powdery product was obtained. The crude residue was placed in another two-neck flask (250 mL) and dissolved in acetic acid (100 mL). A catalytic amount of H_2SO_4 (12 mL) was then added and the whole solution was refluxed for 12 h. After cooling to ambient temperature, purification by silica gel chromatography using dichloromethane/*n*-hexane gave a white powder which was obtained in 32.2% yield.

2.3. 4,4'-(4,8-diphenyl-4,8-dihydrocyclopenta[def]fluorene-4,8-diyl)bis(*N,N*-diphenylaniline)(TPCPF)

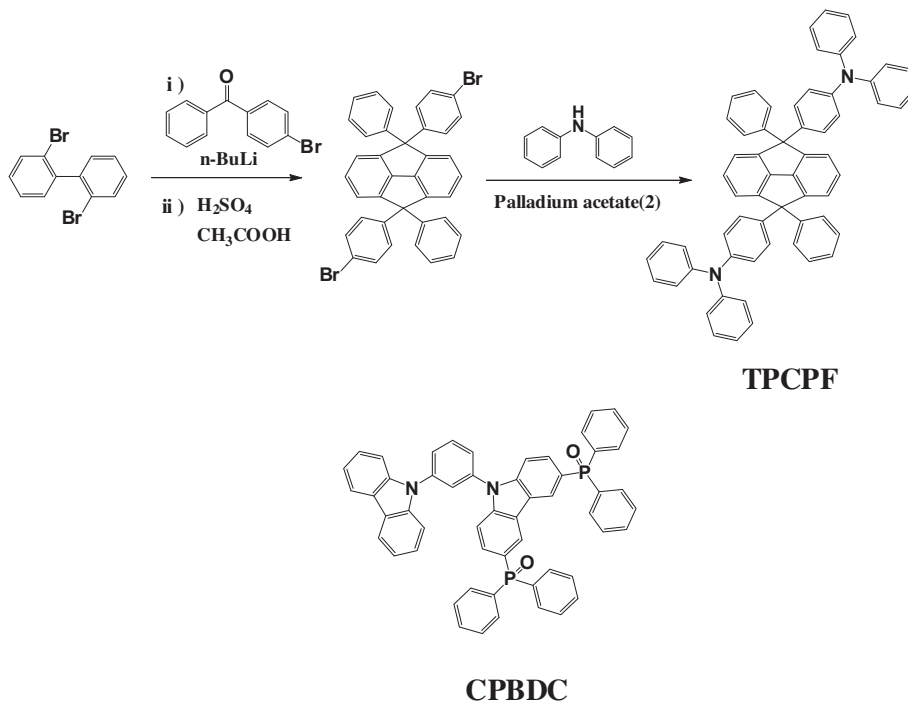
4,8-Bis(4-bromophenyl)-4,8-diphenyl-4,8-dihydrocyclopenta[def]fluorene (0.70 g, 1.09 mmol), diphenylamine

(0.46 g, 2.73 mmol) and palladium acetate (0.01 g, 0.07 mmol) were dissolved in anhydrous toluene (20 mL) under a nitrogen atmosphere. To the reaction mixture was added a solution of tri-*t*-butylphosphine (1 M, 0.21 g, 1.09 mmol) and sodium-*t*-butoxide (0.26 g, 2.73 mmol) dropwise slowly. The reaction mixture was stirred for 12 h at $100\text{ }^{\circ}\text{C}$. The mixture were 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, which was purified by column chromatography using *n*-hexane. The final yellowish powdery product was obtained in 0.5 g (56%) yield.

^1H (200 MHz, CDCl_3): 7.39–6.85 (m, 44H). ^{13}C (200 MHz, CDCl_3): 152.7, 148.1, 146.5, 144.0, 140.1, 139.4, 138.5, 138.0, 131.4, 130.0, 129.0, 128.1, 125.2, 124.3, 123.5, 122.6, 64.7. MS (FAB) m/z 818 $[(\text{M}+\text{H})^+]$. Anal. Calcd for $\text{C}_{62}\text{H}_{44}\text{N}_2$: C, 91.14; H, 5.52; N, 3.43. Found: C, 90.95; H, 5.52; N, 3.35.

2.4. Device fabrication and measurements

A basic device structure of indium tin oxide (ITO, 50 nm)/poly(3,4-ethylenedioxythiophene): polystyrenesulfonate (PEDOT-PSS, 60 nm)/TCTA or TPCPF (10 nm)/9-(3-(9H-carbazole-9-yl)phenyl)-3,6-bis(diphenylphosphoryl)-9H-carbazole (CPBDC); iridium (III) bis((3,5-difluorophenyl)pyridine) picolinate (Flrpic) (30 nm, 3%)/diphenylphosphine oxide-4-(triphenylsilyl)phenyl (TSPO1, 25 nm)/LiF(1 nm)/Al(200 nm) was used for device fabrication. The synthesis and device performances of CPBDC were reported in other work [19]. Chemical structure of CPBDC is shown in Scheme 1. All devices were fabricated by vacuum evaporation and were encapsulated with a glass lid. The device



Scheme 1. Synthetic scheme of TPCPF and chemical structure of CPBDC.

performances of the PHOLEDs were measured with Keithley 2400 source measurement unit and CS1000 spectroradiometer.

3. Results and discussion

TPCPF was designed as the hole transport material to obtain high glass transition temperature and high triplet energy. The core of TPCPF was cyclopenta[def]fluorene unit substituted by four phenyl groups. Cyclopenta[def]fluorene plays a role of the high triplet energy unit and the tetraphenyl groups improve the thermal stability of the core structure while keeping the high triplet energy of cyclopenta[def]fluorene. The four phenyl groups were attached to sp^3 carbon of cyclopenta[def]fluorene and did not extend the conjugation of the cyclopenta[def]fluorene. Diphenylamine units were introduced to enhance the hole transport properties and manage the energy levels of the hole transport materials.

TPCPF was prepared by amination of brominated cyclopenta[def]fluorene core synthesized by one step ring closing reaction of 2,2'-dibromobiphenyl and 4-bromobenzophenone using H_2SO_4 . 2,2'-Dibromobiphenyl was lithiated by 1-butyllithium and reacted with 4-bromobenzophenone to prepare tetraphenyl substituted cyclopenta[def]fluorene. Synthetic scheme of TPCPF is shown in Scheme 1.

As TPCPF was designed as a thermally stable hole transport material, thermal transition temperature of TPCPF was measured using differential scanning calorimeter (DSC). DSC thermogram of TPCPF is shown in Fig. 1. A melting transition of TPCPF was not observed in the DSC thermogram up to 400 °C and glass transition temperature was 143 °C. Considering that common hole transport materials showed glass transition temperature around 100 °C [20], TPCPF was better than other hole transport materials in terms of glass transition temperature. As explained above, TPCPF had rigid cyclopenta[def]fluorene core structure, enhancing the glass transition temperature of the hole transport material.

Molecular simulation of TPCPF was carried out to correlate molecular orbital distribution with photophysical properties of TPCPF. Density functional theory calculation was performed using a suite of Gaussian 03 program. The nonlocal

density functional of Becke's 3-parameters employing Lee–Yang–Parr functional (B3LYP) with 6–31G* basis sets was used for the calculation. Fig. 2 shows the HOMO and lowest unoccupied molecular orbital (LUMO) distribution of TPCPF. The HOMO of TPCPF was mainly localized on the triphenylamine unit which is connected to cyclopenta[def]fluorene. This indicates that the hole transport and the HOMO level of TPCPF are mainly dominated by the triphenylamine units attached to cyclopenta[def]fluorene. In contrast to the HOMO distribution, the LUMO was dispersed over the cyclopenta[def]fluorene core with little distribution in the triphenylamine unit. As diphenylamine is a strong electron donating unit, the LUMO was localized on the weakly electron deficient cyclopenta[def]fluorene core. Calculated HOMO and LUMO levels of TPCPF were -4.90 eV and -0.71 eV, respectively.

The HOMO of TPCPF measured by cyclic voltammetry was -5.72 eV. The HOMO level of TPCPF was suitable for hole injection into phosphorescent emitting layer because common host materials for PHOLEDs have the HOMO level in the range from -5.8 eV to -6.3 eV [7,9,10]. Bandgap of TPCPF was calculated from the edge of ultraviolet–visible (UV–Vis) absorption spectra in Fig. 3 and was 3.62 eV. The bandgap of TPCPF was much wider than that of other hole transport materials such as NPB (3.1 eV) and TCTA (3.3 eV). The wide bandgap of TPCPF is due to isolation of the triphenylamine unit by sp^3 carbon in the backbone structure. As the conjugation of the backbone structure was not extended to the aromatic amine unit, the wide bandgap was obtained in TPCPF. The LUMO level of TPCPF could be calculated from the HOMO and bandgap, and it was 2.10 eV. Considering that the LUMO level of NPB and TCTA is 2.4 eV, the LUMO level of TPCPF is suitable for electron blocking. The LUMO level of triplet host materials for PHOLEDs is within the range from 2.4 eV to 3.0 eV, indicating that there exists at least 0.3 eV energy barrier for electron leakage from emitting layer to TPCPF hole transport layer. Therefore, TPCPF can be effective as the hole transport material to block electron leakage from the emitting layer to the hole transport layer.

Photophysical properties of TPCPF were analyzed using UV–Vis absorption and photoluminescence (PL) emission measurement. Fig. 3 shows UV–Vis absorption and PL emission spectra of TPCPF. Strong UV–Vis absorption was observed at 305 nm, which is assigned to the $\pi-\pi^*$ transition of TPCPF core. As the cyclopenta[def]fluorene core was isolated, diphenylamine unit could not contribute to the UV–Vis absorption. Bandgap was calculated from the absorption edge of the UV–Vis spectrum and was 3.62 eV. PL emission peak of TPCPF was observed at 369 nm due to the wide optical bandgap. Low temperature PL measurement was also carried out to measure triplet energy of TPCPF hole transport material. The triplet energy of TPCPF was 2.81 eV from the low temperature PL emission peak at 441 nm. The triplet energy of TPCPF was higher than that of common blue phosphorescent dopants such as Flrpic (2.65 eV). Therefore, TPCPF can be used as the hole transport type triplet exciton blocking material in blue PHOLEDs. TPCPF can suppress triplet exciton quenching by the hole transport layer due to the high triplet energy and block electron leakage due to the LUMO level of 2.1 eV.

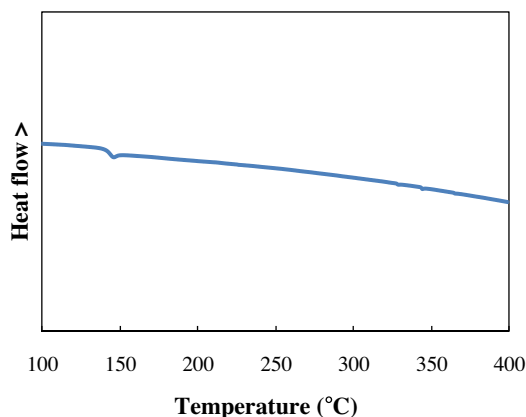


Fig. 1. DSC thermogram of TPCPF.

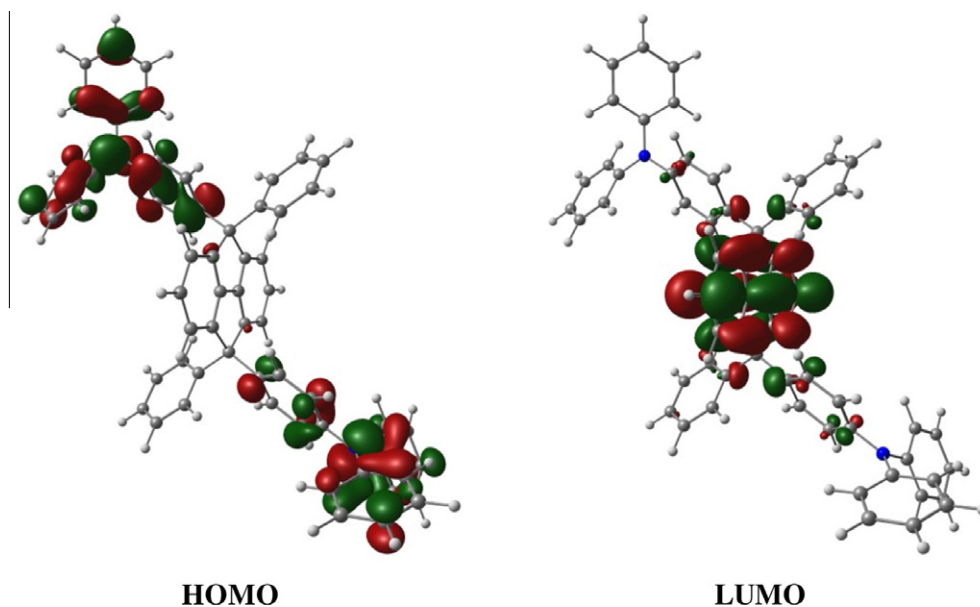


Fig. 2. Simulated HOMO and LUMO distribution of TPCPF.

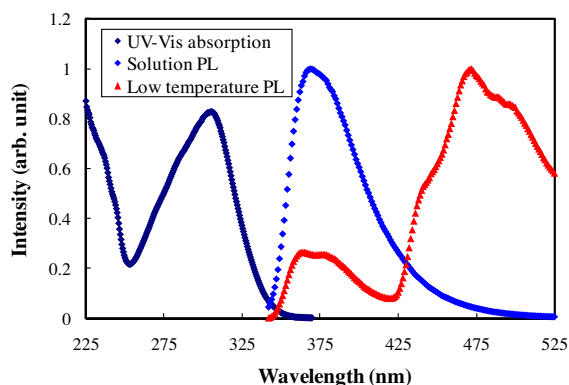


Fig. 3. UV-Vis, solution PL and low temperature PL spectra of TPCPF.

TPCPF was used as the high triplet energy hole transport layer in blue PHOLEDs. It was compared with TCTA as the high triplet energy hole transport material. Fig. 4 shows current density–voltage–luminance curves of blue PHOLEDs with TCTA and TPCPF as the hole transport materials. TPCPF device showed similar current density to TCTA device in blue PHOLEDs. The current density is generally dominated by energy barrier for charge injection and charge transport properties of materials. Considering the energy barrier for hole injection, TPCPF has similar energy barrier to TCTA because of similar HOMO level of TPCPF (5.72 eV) and TCTA (5.70 eV). This indicates that hole transport properties of TPCPF is comparable to that of TCTA. The luminance of TPCPF was a little higher than that of TCTA device, which is due to high recombination efficiency of TPCPF device.

Quantum efficiency–luminance curves of TPCPF and TCTA devices are shown in Fig. 5. The quantum efficiency

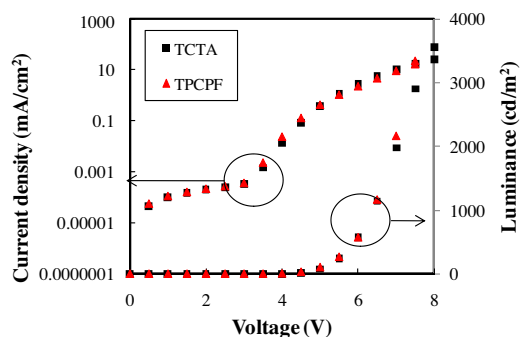


Fig. 4. Current density–voltage–luminance curves of the blue PHOLEDs with TCTA and TPCPF hole transport layers.

of TPCPF device was higher than that of TCTA device over all luminance range. It has been known that the quantum efficiency is mainly affected by the charge balance and charge leakage in the emitting layer [6]. As there was little difference of current density in TPCPF and TCTA devices, there may be little difference of charge balance in TPCPF and TCTA devices. Therefore, the high quantum efficiency of TPCPF device can be explained by the charge leakage in the emitting layer. Blue host material, CPBDC, has the LUMO level of 2.55 eV, while the LUMO of TPCPF is 2.10 eV. There exists 0.45 eV energy barrier for electron injection from CPBDC emitting layer to TPCPF hole transport layer. Therefore, electrons can be confined inside the emitting layer due to the large energy barrier for electron leakage. However, there is only 0.15 eV energy barrier for electron injection from CPBDC host material to TCTA hole transport layer, leading to less effective charge confinement inside the emitting layer. This can be confirmed in electroluminescence (EL) spectra of TPCPF and TCTA de-

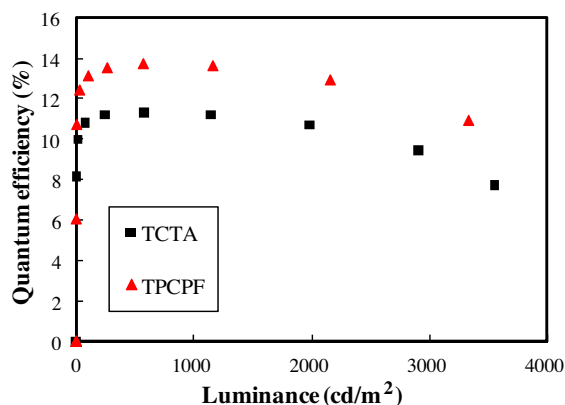


Fig. 5. Quantum efficiency–luminance curves of the blue PHOLEDs with TCTA and TPCPF hole transport layers.

vices (Fig. 6). In the case of TPCPF device, there was no emission of TPCPF around 400 nm, implying no electron leakage out of the emitting layer to TPCPF hole transport layer. However, TCTA device showed weak TCTA emission between 400 and 430 nm due to electron leakage from the emitting layer to TCTA hole transport layer. The weak emission of TCTA was confirmed by comparing the emission spectrum of TPCPF device with that of pure TCTA emission and the sum of pure TCTA emission and TPCPF device emission. TCTA PL emission spectrum is shown in Fig. S1 (supporting information). Therefore, the effective electron blocking of TPCPF confined electrons in the emitting layer and improved the quantum efficiency of the blue PHOLED. The high triplet energy of 2.81 eV of TPCPF was also effective to enhance the quantum efficiency of the blue PHOLED because of triplet exciton blocking effect. The triplet energy of TPCPF was higher than that of Irpic, suppressing the triplet exciton quenching by TPCPF. In

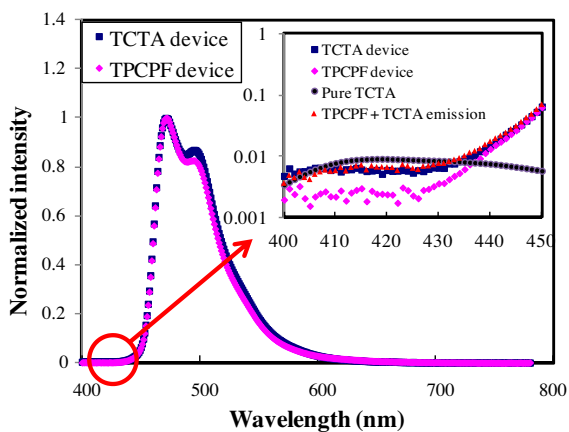


Fig. 6. Normalized electroluminescence spectra of the blue PHOLEDs with TCTA and TPCPF hole transport layers. Normalized electroluminescence spectra between 400 and 450 nm was enlarged in log scale to clarify TCTA emission. Pure TCTA photoluminescence emission spectrum and calculated spectrum from the sum of pure TCTA emission and TPCPF device emission were also added for comparison.

particular, the recombination zone of the device is close to the hole transport layer, indicating that the triple energy of hole transport material is critical to the quantum efficiency of blue PHOLED. Therefore, high quantum efficiency could be obtained in TPCPF device.

EL spectra of TPCPF and TCTA devices are shown in Fig. 6. Both devices showed similar EL spectra with a main emission peak at 469 nm and a shoulder at 490 nm although TCTA device exhibited weak TCTA emission due to the electron leakage.

4. Conclusions

In conclusion, TPCPF with a new cyclopenta[def]fluorene core structure was effectively synthesized as a thermally stable high triplet energy hole transport material. A high glass transition temperature of 143 °C and LUMO level of 2.10 eV for efficient electron blocking were achieved in TPCPF. In addition, TPCPF enhanced the quantum efficiency of blue PHOLED by blocking electron leakage and triplet exciton quenching. New cyclopenta[def]fluorene core can be effectively used as the rigid core structure for high glass transition temperature in organic electronic materials.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.orgel.2012.03.006>.

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