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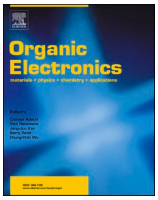

Design of hole transport type host for stable operation in blue organic light-emitting diodes

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ABSTRACT

Molecular design of the hole transport type host for mixed host was investigated to improve the lifetime of the phosphorescent organic light-emitting diodes. A negative polaron stabilizing hole transport type host design was employed and the effect of the negative polaron stabilizing unit was investigated. Dibenzofuran or benzonitrile was introduced as the negative polaron stabilizing unit in the bicarbazole backbone structure of the hole transport type host. Two host materials were synthesized and the comparison of them proposed that the negative polaron stabilizing unit is a key to the lifetime of the phosphorescent organic light-emitting diodes. The dibenzofuran and benzonitrile embedded bicarbazole hosts performed better than the mCBP host. The dibenzofuran and benzonitrile modified bicarbazole hosts demonstrated high external quantum efficiency of 18.6 and 19.1%, respectively and lifetime extension by 30% compared with the conventional host without the negative polaron stabilizing unit.

1. Introduction

Phosphorescent organic light-emitting diodes (PhOLEDs) employing phosphorescent emitters are very popular because of high efficiency close to the theoretical maximum quantum efficiency of OLEDs [1–4]. The PhOLEDs already reached the upper limit of the maximum quantum efficiency. However, the lifetime of the blue PhOLEDs is still far below that of the red and green PhOLEDs, which is a big hurdle for the commercial use of the blue PhOLEDs [5–8].

The short lifetime issues of the blue PhOLEDs can be regarded as the combined effect of the organic materials, carrier transport, carrier recombination and device structure. One of the key factors from the material aspect is the host material. In general, a mixed host consisted of hole transport type (p-type) host and electron transport type (n-type) host has been widely used due to high efficiency and long lifetime in the blue PhOLEDs [9–14]. In particular, the n-type host was a main focus because electrons are mostly trapped by the blue phosphor and high triplet energy n-type hosts are not common. Several n-type type hosts already demonstrated good performances in the blue PhOLEDs [15–18]. For example, triphenylsilyl modified triazine type hosts showed high external quantum efficiency (EQE) about 20% and moderate lifetime [16]. A carbazole and triphenylsilyl co-embedded triazine type host was also effective to extend the device lifetime while achieving high EQE over 20% [18]. Whereas, the development of the p-type host for blue phosphors has not been popular in spite of the importance of the p-type host although several p-type hosts have been documented [19–21]. The n-type hosts can be damaged by positive polarons during light emission process because holes are injected into the host. The electrical burden of the n-type host can be relieved by mixing the p-type host with the n-type host, which can stabilize the devices. As the common direction in the p-type host development was to design strong p-type host, not many strategies were tried. Therefore, further concept and strategy of the hole transport type host for the blue PhOLEDs is strongly required.

Herein, we describe the study of the hole transport type host derived from bicarbazole backbone structure and negative polaron stabilizing unit. The bicarbazole was 9-phenyl-9H,9′H-3,4′-bicarbazole which has linkage between 3 position and 4 position of carbazole. The negative polaron stabilizing units were dibenzofuran and benzonitrile. Two hosts, 9’-(dibenzo[b,d]furan-2-yl)-9-phenyl-9H,9′H-3,4′-bicarbazole (DBFBCz) and 2-(9-phenyl-9H,9′H-[3,4′-bicarbazol]-9′-yl)benzonitrile (BNBCz), were synthesized to trace the role and influence of the negative polaron stabilizing units. It was demonstrated that the negative polaron stabilizing unit is crucial to the device lifetime of the blue PhOLEDs. The dibenzofuran and benzonitrile embedded bicarbazole host performed better than the mCBP host. The DBFBCz and BNBCz hosts demonstrated high EQE of 18.6 and 19.1%, respectively and lifetime extension by 30%

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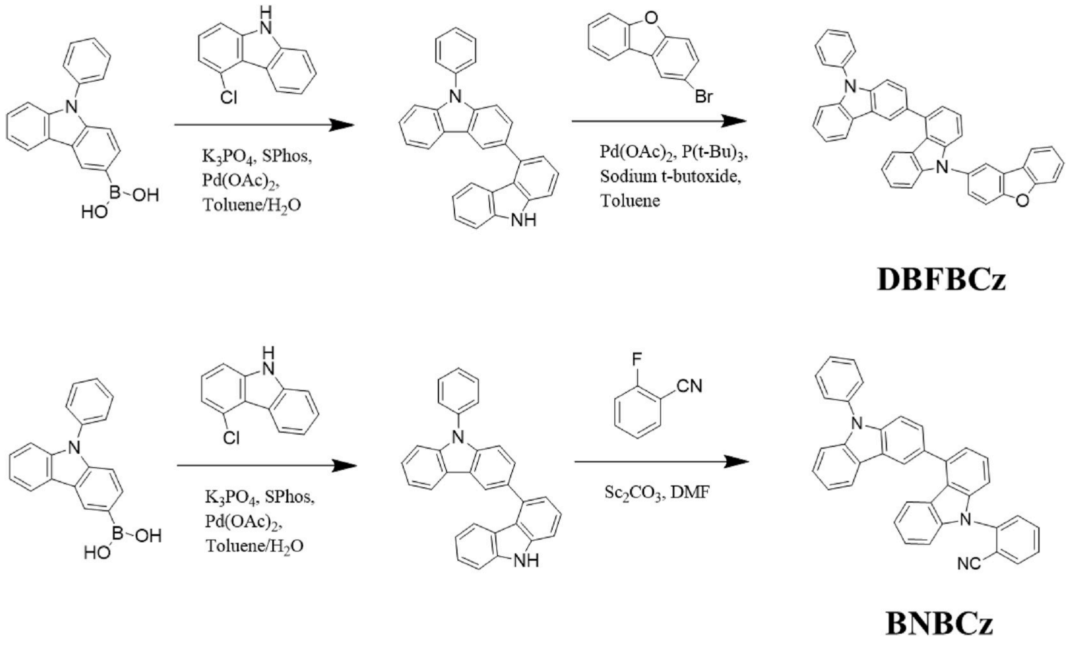

Scheme 1. Synthetic scheme of DBFBCz and BNBCz.

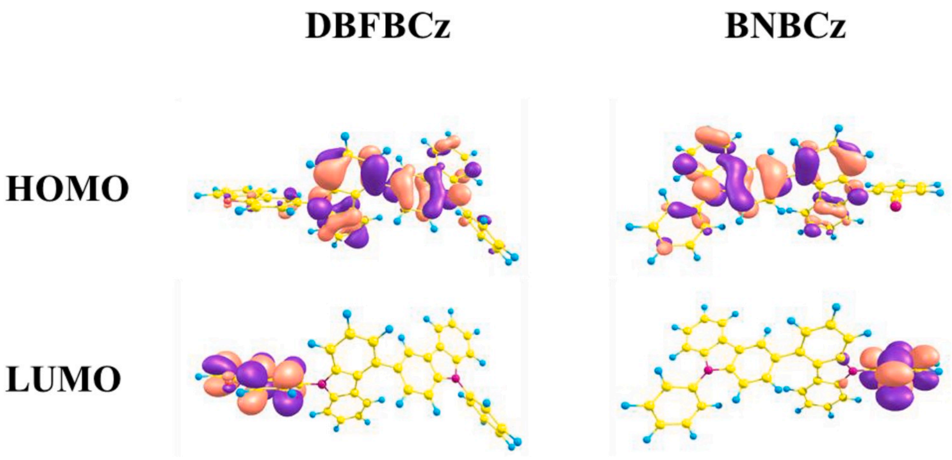

Fig. 1. Calculated HOMO and LUMO distributions of DBFBCz and BNBCz.

relative to the negative polaron stabilizing unit free host.

2. Results and discussion

2.1. Synthesis and orbital calculation

The backbone structure of the host was 9-phenyl-9H,9′H-3,4′-bicarbazole which has linkage between two carbazoles through the 3 and 4 position of the two carbazoles to increase the triplet energy of the host. As the well-known 9-phenyl-9H,9′H-3,3′-bicarbazole is not suitable for blue phosphors due to low triplet energy, the 9-phenyl-9H,9′H-3,4′-bicarbazole backbone structure was employed. As the negative polaron stabilizing unit, weakly electron accepting dibenzofuran and strongly electron accepting benzonitrile units were introduced to correlate the electron accepting units of the hosts with the device performances. Two hosts, DBFBCz and BNBCz, shared the same backbone structure and had different negative polaron stabilizing units. The synthetic process is explained in Scheme 1 and details of the synthesis are described in Experimental section.

The photophysical properties and energy levels of the hosts were forecast before synthesis to judge the appropriateness of the host design for blue device application. The frontier molecular orbital (FMO) simulation results of the DBFBCz and BNBCz are displayed in Fig. 1. The FMO calculation results were similar in the two hosts in that the HOMO was in the bicarbazole backbone structure and the LUMO was found in the negative polaron stabilizing unit. The LUMO localization in the dibenzofuran or benzonitrile unit suggests that the negative polaron related properties would be governed by the negative polaron stabilizing units. The calculated highest occupied molecular orbital (HOMO)/ lowest unoccupied molecular orbital (LUMO) values of the DBFBCz and BNBCz hosts were −5.11/-1.17 eV and −5.21/-1.60 eV, respectively. The LUMO levels of the two hosts indicate that the BNBCz is a strongly electron accepting hole transport type host and the DBFBCz is a weakly electron accepting hole transport type host.

The two hosts were prepared by the similar synthetic pathways coupling the negative polaron stabilizing unit to the 9-phenyl-9H,9′H-3,4′-bicarbazole backbone structure produced by Suzuki coupling reaction between (9-phenyl-9H-carbazol-3-yl)boronic acid and 4-chloro-9H-carbazole. The synthetic yield of the bicarbazole backbone structure was 60%, while that of the DBFBCz and BNBCz from the bicarbazole

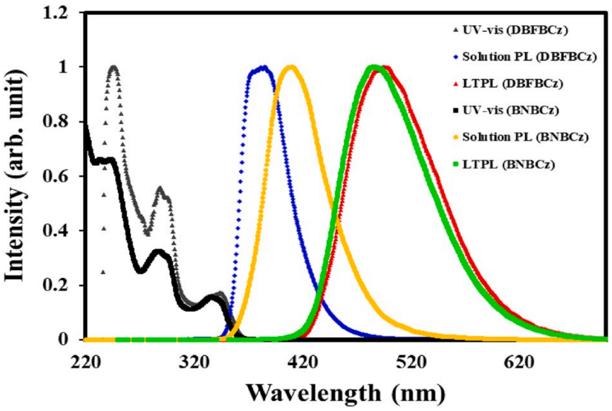

Fig. 2. UV–vis and PL spectra of DBFBCz and BNBCz.

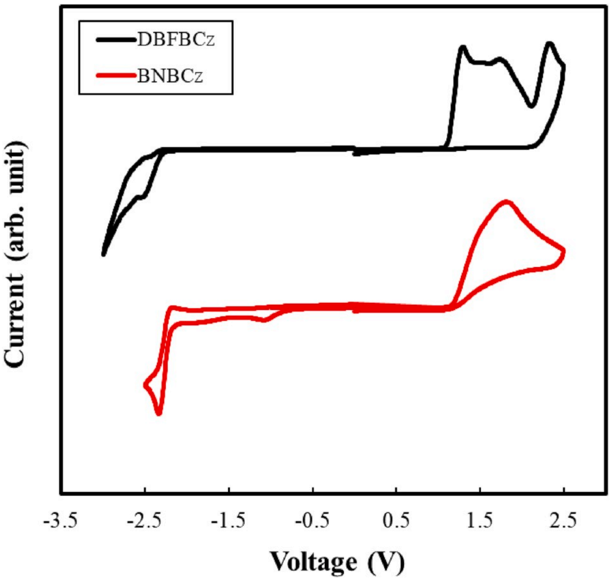

Fig. 3. Cyclic voltammetry (CV) data of DBFBCz and BNBCz.

intermediate was 40 and 55%, respectively. Multi-step purification processes of column chromatography, recrystallization, and sublimation were engaged to afford the final hosts for device lifetime study. The identification of the final compounds was conducted using ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectrometer, mass spectrometer and elemental analysis.

2.2. Material characterization

The basic properties of the hosts were analyzed by photophysical, electrochemical, and thermal characterizations. The photophysical analysis results of the hosts are presented in Fig. 2. Absorption, fluorescence and phosphorescence of the hosts were characterized using tetrahydrofuran solution (1.0×10^{-5} M) of the hosts. The absorption behavior in the ultraviolet–visible (UV–vis) region was similar in the two hosts because the main UV–vis absorption is from the bicarbazole backbone structure which is shared in the two hosts. The fluorescence of the hosts collected at room temperature was slightly different in that the fluorescence spectrum of the BNBCz was relatively broad and red-shifted because of charge transfer (CT) character by the strongly electron accepting benzonitrile unit. Bathochromic shift of the fluorescence spectrum by 13 nm resulted from the CT character. Whereas, the phosphorescence spectra of the two hosts gathered at 77 K after delay time of 1 ms agreed each other and provided high triplet energy of 2.90 eV. The linkage via the 3 and 4 positions of the bicarbazole core allowed the high triplet energy in the two hosts.

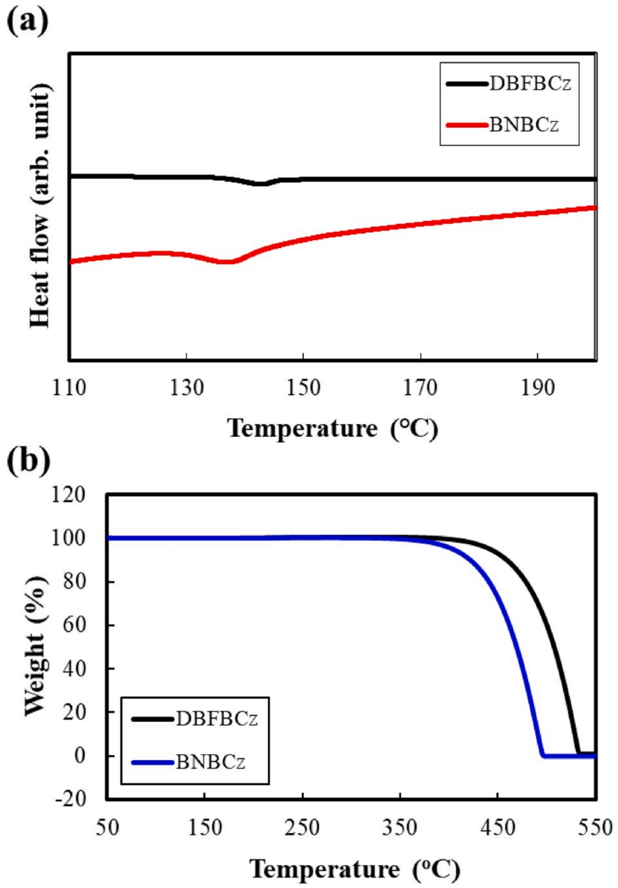

Fig. 4. (a) DSC (Differential Scanning Calorimetry) and (b) TGA (Thermogravimetric analysis) data of DBFBCz and BNBCz at a heating rate of 10 °C/min in a nitrogen atmosphere.

The electrochemical characterization data of the two hosts are shown in Fig. 3. Both oxidation and reduction of the hosts were detected during cyclic voltage scan. The conversion of the oxidation and reduction potentials of the hosts into the energy levels using the ferrocene standard material provided the HOMO/LUMO levels of −5.98/-2.59 eV and −6.06/-2.64 eV for the DBFBCz and BNBCz hosts, respectively. The strongly electron accepting nature of the benzonitrile slightly deepened the HOMO and LUMO levels of the BNBCz host.

The thermal characterization of the hosts was performed to evaluate the potential of the hosts in terms of electrical operation stability and thermal evaporation process stability. Glass transition temperature (T_g) and thermal decomposition temperature (T_d) at 5% weight loss indirectly guide the thermal stability of the hosts. The thermal characterization data in Fig. 4(a) and (b) enabled the determination of the T_g/T_d as 143/442 and 138/385 °C in the DBFBCz and BNBCz hosts, respectively. The high T_g and T_d of the two hosts confirmed the thermal stability of them in the operation and fabrication processes. All material characterization data explained above proved that the DBFBCz and BNBCz hosts would perform as the hosts for the blue phosphors.

2.3. Device analysis

Device evaluation of the two hosts was carried out by doping fac-tris (3-(1-(2,6-diisopropylphenyl)-1H-imidazole-2-yl)benzonitrile)iridium (CNIm) phosphor in the mixed hosts. The CNIm was reported as a blue phosphor realizing high EQE and long device lifetime in our previous work and was also used in this work for EQE and lifetime study of the

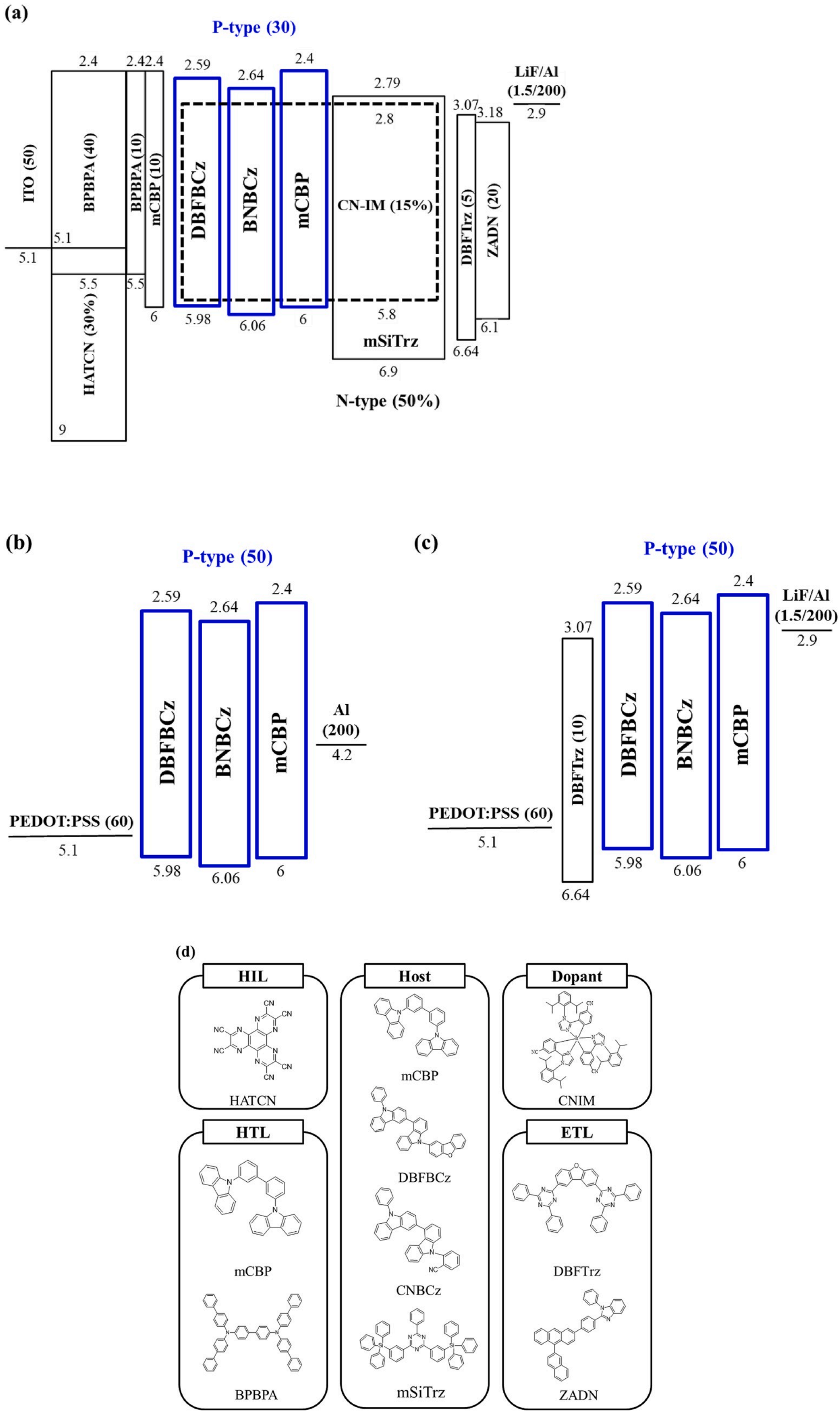

Fig. 5. Energy level diagram of the blue PhOLEDs (a), device structure of hole only device (b) and electron only device (c), and chemical structure of the materials (d).

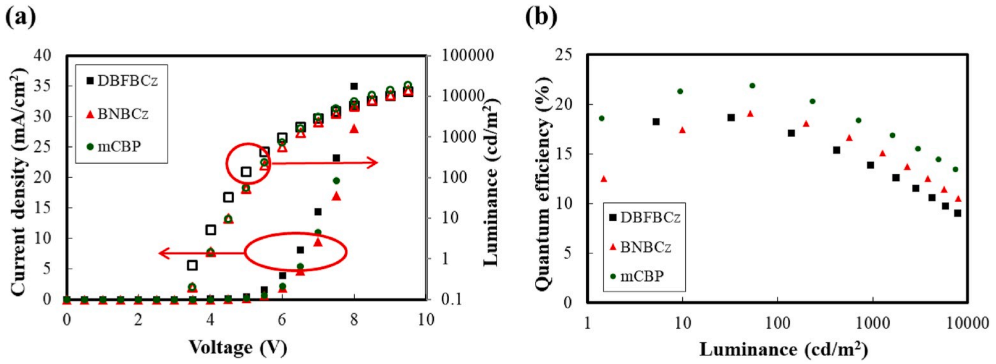

Fig. 6. (a) The current density and luminance according to driving voltage and (b) the external quantum efficiency (EQE) according to luminance of the PhOLEDs.

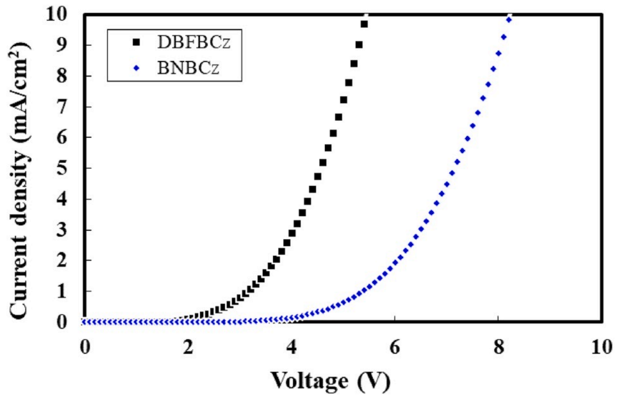

Fig. 7. Hole current density of non-doped DBFBCz and BNBCz hole only devices.

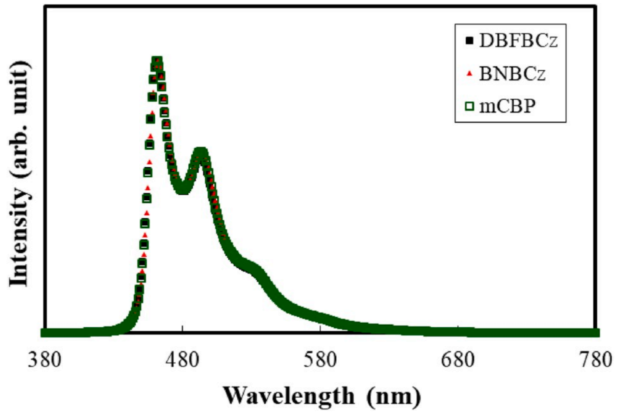

Fig. 8. EL spectra of DBFBCz, BNBCz, and mCBP device at 1000 cd/m^2.

hosts [22]. As the DBFBCz and BNBCz were developed as the p-type hosts in the mixed host, they were mixed with a 2-phenyl-4,6-bis(3-(triphenylsilyl)phenyl)-1,3,5-triazine (mSiTrz) n-type host reported in our previous work [16]. The device structure is schematized in Fig. 5 including the energy levels and chemical structure of the organic materials. The device evaluation data of the DBFBCz and BNBCz hosts are presented in Fig. 6. In the current density and luminance characterization data according to driving voltage, the current density and luminance of the DBFBCz device were higher than those of the BNBCz device. Hole only devices were fabricated to confirm the current density discrepancy in the two hosts, which showed that the better hole transport properties of the DBFBCz host are responsible for the high current density of the DBFBCz device (Fig. 7). The low hole current density of the BNBCz device might be due to the strongly electron accepting character of the benzonitrile unit. The driving voltages of the DBFBCz and BNBCz devices at 1000 cd/m^2 were 6.0 and 6.3 V, respectively.

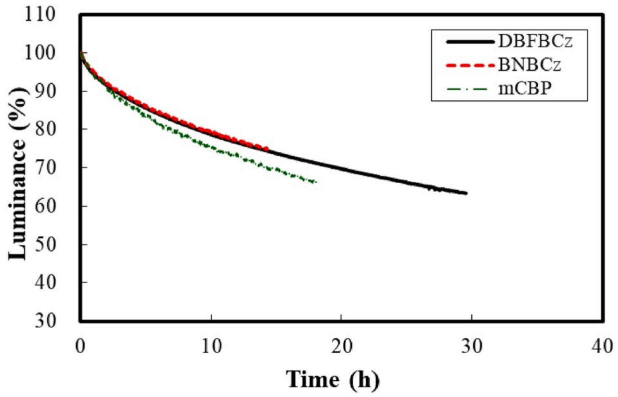

Fig. 9. Lifetime data of CNIm doped DBFBCz, BNBCz, and mCBP devices.

The EQE of the blue PhOLEDs is presented according to the luminance of the devices. The EQE of the BNBCz device was slightly higher than that of the DBFBCz device possibly due to balanced carrier density triggered by the low hole carrier density of the BNBCz hole only device considering the same triplet energy of the two hosts. As shown Fig. 8, the same EL spectra presenting pure CNIm emission in the two devices support the exclusion of the energy transfer as the factor for the disagreement of the EQE. The maximum EQEs of the DBFBCz and BNBCz devices were 18.6 and 19.1%, respectively. The CIE color coordinates of the DBFBCz and BNBCz devices were (0.15,0.25) and (0.15,0.26), respectively.

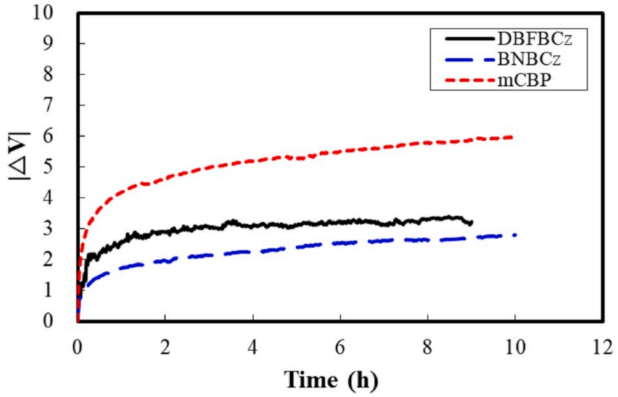

Fig. 10. The change of driving voltage according to time in electron only devices of DBFBCz, BNBCz and mCBP.

The device lifetime of the DBFBCz and BNBCz devices was evaluated at a constant current driving condition. A conventional p-type host without the negative polaron stabilizing unit, mCBP, was a standard material to validate the host design strategy. The device lifetime data are presented in Fig. 9. The device lifetime of the DBFBCz and BNBCz devices was longer than that of the mCBP control device. The lifetime values of the DBFBCz, BNBCz, and mCBP devices up to 80% of initial luminance were 8.8, 9.3, and 6.8 h, respectively. In order to understand the origin of the lifetime extension by the DBFBCz and BNBCz hosts, device analysis was carried out by tracing the negative polaron stability of the hosts. The stability test of the hosts against the polarons was performed by stressing the electron only devices of the hosts. The negative polaron stability of the DBFBCz and BNBCz hosts was compared with that of the mCBP host. The data of polaron stability test are presented in Fig. 10. In the negative polaron stability test using electron only devices, the change of driving voltage according to time in DBFBCz and BNBCz devices was smaller than that of the mCBP device. This indicates that DBFBCz and BNBCz have better negative polaron stability than mCBP. The benzonitrile and dibenzofuran units made the hosts stable under negative polarons because they tend to accept electrons and their electron deficiency can stabilize injected electrons. Therefore, the DBFBCz and BNBCz hosts showed enhanced negative polaron stability and extended the device lifetime.

3. Conclusions

The negative polaron stabilizing hole transport type hosts of DBFBCz and BNBCz were designed and synthesized as high triplet energy host with a triplet energy above 2.90 eV. In blue PhOLEDs, the DBFBCz and BNBCz showed high EQE of 18.6 and 19.1%, respectively, and extended device lifetime compared with the mCBP. The improved negative polaron stability of the hosts by the dibenzofuran and benzonitrile units was responsible for the improved device lifetime. This result revealed that negative polaron stability of hole transport type hosts play an important role in improving the driving lifetime.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.orgel.2020.105724.

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