Bicarbazole-Derived High Triplet Energy P-type Host for Blue Thermally Activated Delayed Fluorescence Organic Light-Emitting Diodes

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Abstract

Three p-type hosts with a high triplet energy (~3.06 eV) were synthesized and evaluated for thermally activated delayed fluorescence organic light-emitting diodes. The three hosts were designed to have a high triplet energy and controlled intermolecular interactions through molecular distortion by introducing bulky blocking groups into the 3,3'-bicarbazole core structure. The blue devices achieved a high external quantum efficiency of 25.6%.

Author Keywords

Blue host; P-type host; Organic light emitting diodes

1. Objective and Background

For successful commercialization of blue organic light-emitting diodes (OLEDs) display, achieving high efficiency and low driving voltage is necessary. Recently, thermally activated delayed fluorescence (TADF) materials have gained great attention in OLEDs due to their high efficiency. These materials have small singlet-triplet energy gap and they can convert triplet excitons into singlet excitons. As a result, they can achieve an internal quantum efficiency of up to 100%.(1)

In TADF OLEDs, it is important to select an appropriate combination of emitter and host. Since the host material usually occupies most of the emissive layer (EML), the development of excellent host materials is necessary. In blue OLEDs, it is important to have a host material with a high triplet energy of about 3.0 eV for efficient energy transfer from the host to the emitter, and a shallow highest occupied molecular orbital (HOMO) level is advantageous for easy hole injection from the anode to the EML.(2) In general, carbazole moiety is used in host materials because of its high triplet energy and shallow HOMO level for hole injection. Among the carbazole derivatives, 9'-diphenyl-9*H*,9'*H*-3,3'-bicarbazole (BPCz) structure is commonly used for p-type host material in green and sky-blue OLEDs.(3) However, the BPCz core is difficult to be used in blue OLEDs because π-π stacking easily occurs and triplet energy decreases due to the high planarity of the structure itself.

In this work, we introduced bulky blocking groups into the 2 position of the BPCz core structure for high triplet energy. Newly synthesized host materials, 9,9'-diphenyl-2-(3-(triphenylsilyl)phenyl)-9*H*,9'*H*-3,3'-bicarbazole (mSi-BPCz), 2-(2-(9*H*-carbazol-9-yl)phenyl)-9,9'-diphenyl-9*H*,9'*H*-3,3'-bicarbazole (oPCz-BPCz), and 2-(3-(9*H*-carbazol-9-yl)phenyl)-9,9'-diphenyl-9*H*,9'*H*-3,3'-bicarbazole (mPCz-BPCz), were prepared to have three different blocking groups of tetraphenylsilane, ortho-phenylcarbazole, and meta-phenylcarbazole, respectively. The bulky blocking groups induce intramolecular steric hindrance and suppress conjugation extension. Likewise, it can prevent intermolecular aggregation in film state, thereby inhibiting π-π stacking and intermolecular interactions. As a result, high triplet energy host materials which can be applicable to blue devices were accomplished. We fabricated TADF devices using three host materials and confirmed that the *ortho*-connected 9-phenylcarbazole moiety worked best as a blocking group. Blue TADF OLEDs with oPCz-BPCz showed the lowest driving voltage of 5.0 V, highest EQE of 25.6%, and lowest efficiency roll-off.

2. Results

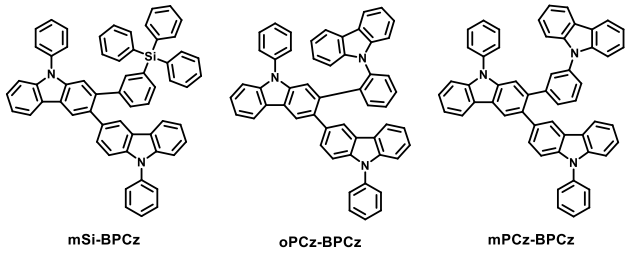

Figure 1. Molecular structure of mSi-BPCz, oPCz-BPCz, and mPCz-BPCz.

Three P-type host materials, mSi-BPCz, oPCz-BPCz, and mPCz-BPCz were successfully synthesized through cascade Suzuki-Miyaura cross-coupling, demethylation and triflation of alcohol. The chemical structures of BPCz-based host materials are illustrated in **Figure 1**. As blocking groups of mSi-BPCz, oPCz-BPCz, and mPCz-BPCz, which were introduced at 2-position of backbone structure, tetraphenylsilane, *ortho*- and *meta*-functionalized 9-phenylcarbazole moieties were selected, respectively. We focused on the differences between aromatic silane and aromatic carbazole moieties, as these may affect the molecular packing mode and charge carrier mobility in the solid state. The tetraphenylsilane group is well known as an effective blocking group because silicon atom generates tetrahedral structure to inhibit intramolecular π-conjugation.(4) The 9-phenylcarbazole group was also used as a bulky side group, but it differs from the tetraphenylsilane group in that it has good hole transport ability.

To investigate the material properties, density functional theory (DFT) calculations were performed at B3LYP/6-31G(d) level. **Table 1** summarizes the calculated material properties of three hosts including HOMO, lowest unoccupied molecular orbital

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(LUMO), singlet energy, triplet energy, and reorganization energy (λ_{Reorg}). The λ_{Reorg} of host materials was calculated at optimized ground state and cationic geometries.[5] In the DFT calculation data, mSi-BPCz showed the shallowest HOMO and the highest triplet energy. To investigate the effect of each blocking group on the hole transport, the total reorganization energy values of the synthesized materials were calculated. The calculations suggested that the mSi-BPCz, oPCz-BPCz, and mPCz-BPCz hosts possess the reorganization energies of 0.3013, 0.2090, and 0.1929 eV, respectively. The calculated data shows that the host introduced with a tetraphenylsilane group has a large λ_{Reorg}, while the host introduced with 9-phenylcarbazole group has a relatively small λ_{Reorg}. These data demonstrate that the 9-phenylcarbazole group is a better choice than tetraphenylsilane group as a blocking group in terms of hole mobility.

Table 1. Summarization of DFT calculations of mSi-BPCz, oPCz-BPCz, and mPCz-BPCz.

	HOMO (eV)	LUMO (eV)	S_1 (eV)	T_1 (eV)	λ_{Reorg}[(a)] (eV)
mSi-BPCz	-5.01	-0.83	3.67	3.00	0.3013
oPCz-BPCz	-5.04	-0.96	3.57	2.94	0.2090
mPCz-BPCz	-5.09	-0.98	3.59	2.97	0.1929

(a) Reorganization energy calculated between optimized S_0 and cationic geometries.

Photophysical and electrochemical properties of the host materials are summarized in **Table 2**. Cyclic voltammetry (CV), ultraviolet-visible (UV-Vis) absorption, and photoluminescence (PL) analysis were performed to measure the HOMO, LUMO, singlet energy (E_S), and triplet energy (E_T) of mSi-BPCz, oPCz-BPCz, and mPCz-BPCz. The HOMO level was measured by CV, and the LUMO level was estimated by optical bandgap (E_{opt}) and HOMO. The absorption and fluorescence spectra were measured in a 10^{-5} M tetrahydrofuran solution at room temperature and the phosphorescence spectrum was measured at 77 K under a nitrogen atmosphere. E_S and E_T were calculated with the onset position of each PL emission spectrum. The peak wavelengths of the emission were observed at 406, 408, and 409 nm for mSi-BPCz, oPCz-BPCz, and mPCz-BPCz, respectively. The HOMO level of mSi-BPCz and oPCz-BPCz was relatively shallower than that of mPCz-BPCz. Shallow HOMO is generally favorable in p-type host as it promotes easier hole injections from the anode, resulting in efficient hole transport. Triplet energy of mSi-BPCz was the lowest, and both oPCz-BPCz, and mPCz-BPCz showed triplet energy higher than 3.0 eV. Triplet energy of three host materials is appropriate for blue OLEDs.

Table 2. Summary of electrochemical and photophysical properties of mSi-BPCz, oPCz-BPCz, and mPCz-BPCz.

	HOMO (eV)	LUMO (eV)	E_{opt} (eV)	E_S (eV)	E_T (eV)
mSi- BPCz	-5.89	-2.53	3.36	3.39	2.97
oPCz-BPCz	-5.89	-2.52	3.33	3.38	3.03
mPCz-BPCz	-5.97	-2.6	3.41	3.4	3.06

(a) optical bandgap obtained from onset UV-Vis absorption

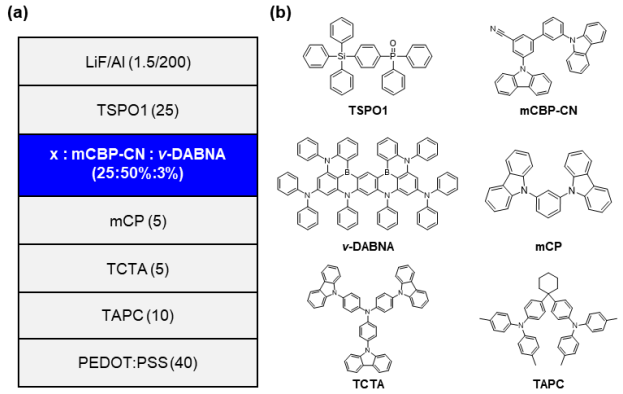

Figure 2. (a) Device structure of the mSi-BPCz, oPCz-BPCz, and mPCz-BPCz host based blue TADF OLEDs. (b) Chemical structures of the materials used in the device.

Table 3. Device Performance of mSi-BPCz, oPCz-BPCz, and mPCz-BPCz based blue TADF OLEDs at 1000 cd m^{-2}.

	V_d [(a)] (V)	J [(b)] (mA cm^{-2})	EQE (%) 1000 cd m^{-2}	EQE (%) max	Roll-off [(c)] (%)	CIE (x, y)
mSi-BPCz	5.4	8.2	14.2	24.9	43.0	(0.114,0.119)
oPCz-BPCz	5.0	6.3	17.5	25.6	31.6	(0.113,0.125)
mPCz-BPCz	5.5	7.1	16.1	26.5	39.2	(0.113,0.121)

(a) Driving voltage. (b) Current density. (c) $(EQE_{max} - EQE_{1000\ cd\ m-2})/(EQE_{max})$.

Blue TADF OLEDs were fabricated to evaluate three p-type host materials. As n-type host, 3,3′-di(carbazol-9-yl)-5-cyano-1,1′-biphenyl (mCBP-CN) was used. As a blue TADF emitter, N^7,N^7,N^{13},N^{13},5,9,11,15-octaphenyl-5,9,11,15-tetrahydro-5,9,11,15-tetraaza-19b,20b-diboradinaphtho[3,2,1-*de*:1′,2′,3′-jk]pentacene-7,13-diamine (*v*-DABNA) was used. The doping concentration of *v*-DABNA was set to 3 wt%. **Figure 3** shows the device structure of the mSi-BPCz, oPCz-BPCz, and mPCz-BPCz host based blue TADF OLEDs, and chemical structures of the materials used in the device. All devices achieved high EQE_{max} by harvesting both singlet and triplet excitons of *v*-DABNA. In particular, the mPCz-BPCz device showed the highest EQE_{max} of 26.5%. Whereas EQE of the oPCz-BPCz device was the highest at 1000 cd m^{-2} because of the low EQE roll-off caused by high hole mobility. The oPCz-BPCz device showed a driving voltage of 5.0 V, which was much lower than that of the mPCz-BPCz device (5.5 V). The low operating voltage is due to the improved charge balance resulting from the high hole mobility of oPCz-BPCz.

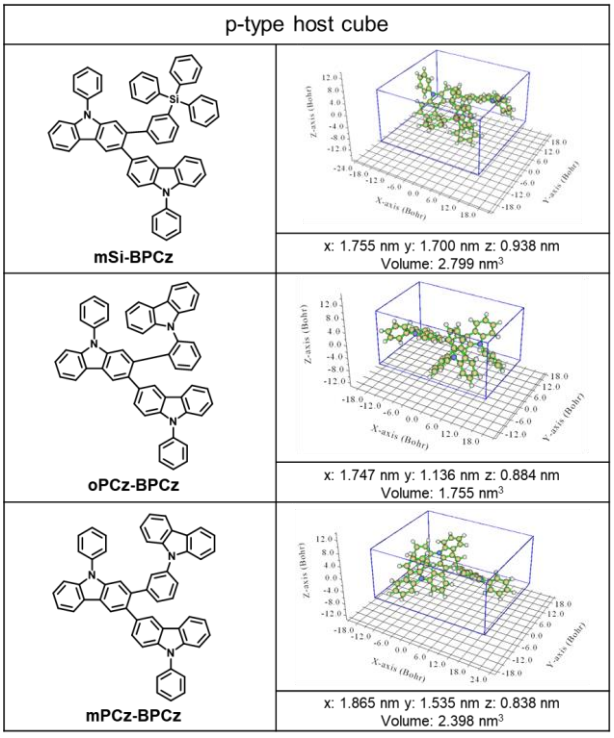

Figure 2. Calculated molecular cubic volume of mSi-BPCz, oPCz-BPCz, and mPCz-BPCz by Multiwfn program in which van der Waals surface is defined by the lengths of the three side of the cube based on the optimized geometries by Gaussian 16 program.

To investigate the reason for low driving voltage and low EQE roll-off in the oPCz-BPCz device, calculations of the molecular cubic volume of three host materials were performed by Multiwfn program.[6] The effective cubic volumes were calculated to be 2.799, 1.755, and 2.398 nm^3 for mSi-BPCz, oPCz-BPCz, and mPCz-BPCz, respectively. oPCz-BPCz showed the smallest effective cubic volume compared to the other host molecules. The small effective volume of the host induced the fast recombination.[7] This suggests that the spherical structure of the host molecules can be densely packed within the EML to form an effective charge transport path, which can enhance the hole mobility and achieve low driving voltage and low EQE roll-off. These results demonstrate that the use of *ortho*-phenylcarbazole as a blocking group can achieve an appropriate HOMO level and E_T, maintain an appropriate distance for efficient charge transport within the EML due to its low effective cubic volume, resulting in excellent device performance.

3. Impact of Research

In this study, three p-type host materials were synthesized and evaluated in TADF OLEDs. The bulky group was introduced at the 2 position of the BPCz core structure to suppress intermolecular interactions and achieve high E_T. All three hosts showed high E_T near 3.0 eV, which is suitable for blue devices. TADF OLEDs with oPCz-BPCz, having low reorganization energy and small effective cubic volume, showed the highest EQE at 1000 cd m^{-2} and the lowest driving voltage and EQE roll-off. This suggests that the p-type host with high hole mobility and small effective cubic volume is important for low driving voltage, low EQE roll-off, and high EQE in blue TADF OLEDs.

4. References

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