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Dibenzo[*b*,*d*]furan and Dibenzo[*b*,*d*]thiophene Molecular Dimers as Hole Blocking Materials for High-Efficiency and Long-Lived Blue Phosphorescent Organic Light-Emitting Diodes[†]

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Novel hole blocking materials (HBMs) based on dibenzo[*b*,*d*]furan and dibenzo[*b*,*d*]thiophene molecular dimers have been rationally designed and synthesized for high-efficiency and long-lived blue phosphorescent organic light-emitting diodes (PhOLEDs). Thermal, optical, and electrochemical analyses show that [2,2 ' -bidibenzo[*b*,*d*]furan]-6,6 ' - diylbis(diphenylphosphine oxide) (DBF-d-PO), [2,2'-bidibenzo[*b*,*d*]thiophene]-6,6'-diylbis(diphenylphosphine oxide) (DBT-d-PO), 6,6'-di(pyridine-3-yl)-2,2'-bidibenzo[*b*,*d*]furan (DBF-d-Py), and 6,6'-di(pyridine-3-yl)-2,2'-bidibenzo[*b*,*d*]thiophene (DBT-d-Py) possess high thermal stability, deep highest occupied molecular orbital energy levels (-6.61 – -6.95 eV), and high triplet energy (E_T) (2.68 – 2.95 eV). Blue PhOLEDs with DBF-d-PO, DBT-d-PO, DBF-d-Py, and DBT-d-Py exhibit low turn-on and operating voltages, excellent external quantum efficiency, and high current and power efficiencies. A blue PhOLED with DBF-d-Py shows the best efficiency of 46.4 lm W⁻¹. In addition, it exhibits an outstanding external quantum efficiency of 22.4% at a practical luminance of 1000 cd m⁻² and a very high maximum luminance of 88,953 cd m⁻² at 12 V. Furthermore, blue PhOLEDs with DBF-d-Py exhibit highly improved lifetimes compared with the conventional HBM, BmPyPB, because of the efficient hole blocking by the deep HOMO energy level and the high thermal stability stabilizing hole blocking layer morphology.

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Phosphorescent organic light-emitting diodes (PhOLEDs), which can use both singlet and triplet excitons for luminescence, have been widely applied in commercial and research areas.¹⁻⁷ Red and green PhOLEDs have satisfactory efficiency and lifetime, but blue phosphorescent ones still do not have an acceptable performance for commercialization.⁸⁻ ¹³ One of the best ways to enhance the efficiency of blue PhOLEDs is to introduce a hole blocking layer (HBL) between the emitting layer (EML) and the electron transporting layer (ETL).¹⁴⁻¹⁸ If the highest occupied molecular orbital (HOMO) energy level of the ETL is not sufficiently deeper than that of the EML, the holes in the EML can be leaked into the ETL. In addition, if the triplet energy (E_T) of the ETL is lower than that of the EML, the triplet excitons of the EML can be quenched by the ETL. Therefore, the leakage of holes and triplet excitons from the EML reduces device efficiency and lifetime. The HBL with a deep HOMO energy level and high E_{T} needs to be

introduced between the EML and ETL to prevent the holes and triplet excitons from migrating into the ETL.¹⁹⁻²⁴

HBMs such as 3-(biphenyl-4-yl)-5-(4-tert-butylphenyl)-4phenyl-4*H*-1,2,4-triazole (TAZ), 1,3-bis(3,5-dipyrid-3-ylphenyl)benzene (BmPyPB), and 1,3,5-tri(m-pyrid-2-yl-phenyl)benzene (TmPyPB), have been developed.²⁵⁻²⁷ However, they possess low thermal stability; hence, they tend to undergo phase transition during PhOLED driving, which is a great obstacle to the development of the PhOLED with a long lifetime.²⁸⁻³⁰ Dibenzo[b,d]furan and dibenzo[b,d]thiophene have recently been used as core molecular structures for PhOLED materials because of their high E_{T} and excellent electron transporting ability.³¹⁻³³ Lee et al. reported HBMs based on 2,6-disubstituted dibenzo[*b,d*]furan and dibenzo[b,d]thiophene for blue PhOLEDs, showing an external quantum efficiency (η_{ext}) of approximately 24%.¹⁹ However, the long-term stability is not sufficient for practical blue PhOLED devices. Therefore, HBMs with excellent device stability and high efficiency must be developed.

Increasing the material stability while maintaining high efficiency is a challenging task and requires a different approach to the design of conventional PhOLED materials. Therefore, designing molecules that satisfy thermal properties as well as HOMO energy levels and E_T is essential. Molecular dimers consisting of two dibenzo[*b*,*d*]furan or dibenzo[*b*,*d*]thiophene molecules jointed by a covalent bond can maximize thermal properties without a large E_T reduction.

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The incorporation of electron-withdrawing groups (EWGs) is essential in designing dibenzo[b,d]furan or dibenzo[b,d]thiophene molecular dimers as effective HBMs. For example, heteroaromatic segments containing a nitrogen atom, such as pyridine, pyrimidine, triazole, and oxadiazole have been used as EWGs.³⁴⁻³⁸ By introducing these kinds of EWGs, the HOMO energy level of HBMs can be deepened, thereby effectively preventing hole diffusion from the EML to the ETL. Moreover, electrons from the ETL can be easily injected into the EML without the charge accumulation in the HBL because of intermolecular interactions such as intermolecular hydrogen bonds. In addition diphenylphosphine oxide or diphenylsilyl groups can be introduced to increase the E_{T} and the bandgap (E_{g}) of the HBMs.^{21,39-41} This can prevent the reduction of E_{T} and E_{g} by disrupting the conjugation of aromatic molecules. However, if the molecular conjugation breaks, the requirements for energy levels can be achieved, but the charge mobility is generally reduced.

In this work, we design and synthesize novel HBMs based on dibenzo[b,d]furan and dibenzo[b,d]thiophene molecular dimers, [2,2 -bidibenzo[b,d]furan]-6,6 diylbis(diphenylphosphine oxide) (DBF-d-PO), [2,2 bidibenzo[*b*,*d*]thiophene]-6,6 ' -diylbis(diphenylphosphine 6,6 ′ (DBT-d-PO), -di(pyridine-3-yl)-2,2 oxide) bidibenzo[b,d]furan (DBF-d-Py), and 6,6'-di(pyridine-3-yl)-2,2'bidibenzo[b,d]thiophene (DBT-d-Py), for blue PhOLEDs with high-efficiencies and long lifetimes. We successfully synthesized dimeric intermediates using dibenzo[b,d]furan and dibenzo[b,d]thiophene segments and incorporated pyridine and phosphine oxide functional groups as EWGs for the HBMs. A computational simulation was used to investigate optimal structure, orbital distribution, the and physicochemical properties of the HBMs. Thermal, optical, and electrochemical analyses show that DBF-d-PO, DBT-d-PO, DBFd-Py, and DBT-d-Py possess high thermal stability, deep HOMO energy levels (-6.61 – -6.95 eV), and high E_{T} (2.68 – 2.95 eV) values. Moreover, their electron-only device (EOD)

characteristics indicate that DBF-d-Py and DBT-d-Py with pyridine EWGs have better electron mobility than DBF-d-PO and DBT-d-PO with phosphine oxide EWGs. Blue PhOLEDs with DBF-d-PO, DBT-d-PO, DBF-d-Py, and DBT-d-Py as HBLs exhibit low turn-on and operating voltages, excellent external quantum efficiency, and high current and power efficiencies. A blue PhOLED with DBF-d-Py shows the best efficiency with a maximum external quantum efficiency ($\eta_{\text{ext,max}}$) of 24.3%, a maximum current efficiency ($\eta_{ce,max}$) of 44.3 cd A⁻¹, and a maximum power efficiency ($\eta_{pe,max}$) of 46.4 lm W⁻¹. It also exhibits an outstanding η_{ext} of 22.4% at a practical luminance of 1000 cd m⁻² and a very high maximum luminance of 88,953 cd m⁻² at 12 V. Furthermore, blue PhOLEDs with DBF-d-Py and DBT-d-Py exhibit a highly improved lifetime compared with the conventional HBM, BmPyPB, with a pyridine electron transport unit and a phenyl core structure.

Results and discussion

We designed novel HBMs based on dibenzo[b,d]furan and dibenzo[b,d]thiophene molecular dimers to achieve excellent thermal stability and high E_T values. Two dibenzo[b,d]furan or dibenzo[b,d]thiophene segments were connected through the *meta*-positions of each segment to form molecular dimers. Therefore, the thermal stability can be increased without decreasing E_T . Pyridine and phosphine oxide EWGs were introduced into the dibenzo[b,d]furan and dibenzo[b,d]thiophene dimers for deep HOMO energy levels and excellent electron transporting properties.

Scheme 1 depicts the synthetic routes of DBF-d-PO. DBT-d-PO. DBF-d-Py, and DBT-d-Py. First, 6-bromo-2iododibenzo[*b*,*d*]furan (compound 1) and 6-bromo-2iododibenzo[b,d]thiophene (compound 1') were synthesized from 4-bromodibenzo[b,d]furan and 4bromodibenzo[*b*,*d*]thiophene. Subsequently, 2-(6bromodibenzo[b,d]furan-2-yl)-4,4,5,5-tetramethyl-1,3,2dioxaborolane (compound and 2-(6-2)

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Fig. 1 Optimized molecular structures, HOMO and LUMO distributions, and calculated bandgaps of DBF-d-PO, DBT-d-PO, DBF-d-Py, and DBT-d-Py.

bromodibenzo[b,d]thiophene-2-yl)-4,4,5,5-tetramethyl-1,3,2dioxaborolane) (compound 2 ') were prepared through the Miyaura borylation. Next, though the Suzuki reaction, 6,6 'dibromo-2,2 '-bidibenzo[b,d]furan (compound 3) and 6,6 'dibromo-2,2 '-bidibenzo[b,d]thiophene (compound 3 ') were synthesized by reacting compound 1 (or 1') with compound 2 (or 2'). Two bromo functional groups of compound 3 and 3' were substituted to diphenylphosphines. Finally, DBF-d-PO and DBT-d-PO were successfully synthesized by oxidizing the diphenylphosphines. DBF-d-Py and DBT-d-Py were synthesized by reacting compound 3 and 3' with pyridine-3-boronic acid through the Suzuki reaction. All the synthesized compounds were confirmed by gas chromatography - mass spectrometry (GC-MS) and nuclear magnetic resonance (NMR) spectrometry. DBF-d-PO, DBT-d-PO, DBF-d-Py, and DBT-d-Py were highly purified using a train sublimator.

The molecular calculations of DBF-d-PO, DBT-d-PO, DBF-d-Py, and DBT-d-Py were conducted using the density functional theory simulation based on Becke, three-parameter, Lee-Yang-Parr (B3LYP) 6-31G* as a basis set. Fig. 1 depicts the optimized molecular structure, HOMO and lowest unoccupied molecular orbital (LUMO) distribution, and energy levels of DBF-d-PO, DBT-d-PO, DBF-d-Py, and DBT-d-Py. For DBF-d-PO and DBF-d-Py, the dihedral angles between the two dibenzo[b,d]furan segments were 40.5° and 40.1°, respectively. For DBT-d-PO and DBT-d-Py, the dihedral angles between the two dibenzo[b,d]thiophene segments were equally calculated at 39.3°. Significant distortions between the dibenzo[b,d]furan and dibenzo[b,d]thiophene molecular dimers may result in a reduced degree of the effective conjugation in the molecular orbital. Thus, the decrease of E_{g} and $E_{\rm T}$ can be minimized while maximizing the thermal stability. In addition, the dihedral angles of DBF-d-PO and DBF-d-Py were larger than those of DBT-d-PO and DBT-d-Py, suggesting E_g and E_T of DBF-d-PO and DBF-d-Py were higher than those of DBT-d-PO and DBT-d-Py. For DBF-d-Py and DBT-d-Py with two pyridine EWGs, their HOMO distributions extended to electron-deficient pyridine segments such that both compounds had deeper HOMO energy levels than DBF-d-PO

and DBT-d-PO with phosphine oxide EWGs. The LUMO distributions of the phosphine oxide-based compounds were completely blocked in the central dibenzo[b,d]furan and dibenzo[b,d]thiophene dimers, but those of DBF-d-Py and DBT-d-Py were greatly extended toward the pyridine EWGs. The electron density of DBF-d-Py and DBT-d-Py was higher than that of DBF-d-PO and DBT-d-PO; hence, the electron transporting ability of DBF-d-Py and DBT-d-Py is expected to be better than that of DBF-d-PO and DBT-d-PO.

Conventional OLEDs are fabricated by thermal vacuum evaporation; thus, the thermal stability of the synthesized HBMs must be investigated. In addition, when OLEDs are driven, the change in thin film morphology caused by the endothermic process is critical to the efficiency and lifetime of the OLEDs. Therefore, OLED materials with high thermal stability must be developed. Fig. 2, S12, and Table 1 show the thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and differential thermal analysis (DTA) results. The decomposition temperature (T_d) values of DBF-d-PO, DBT-d-PO, DBF-d-Py, and DBT-d-Py were 484, 514, 380, and 400 °C, respectively. The DSC results showed that DBF-d-PO and DBT-d-PO had high glass transition temperature (T_g) values of 142 and 162 °C, respectively. The DTA measurement results exhibited that DBF-d-Py and DBT-d-Py had T_g values of 134 and 135 °C, respectively. Moreover, to investigate the thermal stability and morphological durability against thermal stress, an atomic force microscopy (AFM) study of HBM films was performed. AFM images of DBF-d-PO, DBT-d-PO, DBF-d-Py and DBT-d-Py films were measured before and after thermal annealing treatment (85 °C, 24 h). As shown in Fig. S13 and S14, before thermal annealing treatment, the root-meansquare roughness (R_{rms}) values of DBF-d-PO, DBT-d-PO, DBF-d-Py, and DBT-d-Py films were 0.274, 0.283, 0.302 and 0.287 nm, respectively. After thermal annealing treatment for 24 h, the R_{rms} values of DBF-d-PO, DBT-d-PO, DBF-d-Py, and DBT-d-Py films were 0.278, 0.288, 0.306, and 0.320 nm, respectively. They showed a negligible change in their $R_{\rm rms}$ values before and after thermal annealing treatment, indicating that they

possess high thermal and morphological stability against heat. Therefore, it is expected that DBF-d-PO, DBT-d-PO, DBF-d-Py,

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 Table 1 Physical properties of DBF-d-PO, DBT-d-PO, DBF-d-Py, and DBT-d-Py.

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HBMs	T _d ª/T _g [°C]	λ _{max,abs} d [nm]	λ _{onset,abs} e [nm]	λ _{max,FL} f [nm]	E _g g [eV]	E _T ^h [eV]	HOMO ⁱ /LUMO ^j [eV]
DBF-d-PO	484/142 ^b	258	351	367	3.53	2.95	-6.75/-3.22
DBT-d-PO	514/162 ^b	254	370	387	3.35	2.70	-6.61/-3.26
DBF-d-Py	380/134 ^c	246	350	366	3.54	2.74	-6.95/-3.41
DBT-d-Py	400/135 ^c	256	374	379	3.32	2.68	-6.71/-3.39

^a obtained from TGA. ^b obtained from DSC. ^c measured from DTA. ^d measured from UV-vis absorption spectrum. ^e measured from the absorption onset in film. ^f measured from fluorescent emission spectrum. ^g deduced from absorption onset in film. ^h estimated from phosphorescent spectrum. ¹ estimated from the LUMO energy level and E_{g} . ¹ estimated from the reduction potential in CV.



Fig. 2 TGA traces of DBF-d-PO, DBT-d-PO, DBF-d-Py, and DBT-d-Py with a heating rate of 10 °C min⁻¹.

and DBT-d-Py can maintain a uniform and stable film morphology during device operation.

The optical properties of DBF-d-PO, DBT-d-PO, DBF-d-Py, and DBT-d-Py were investigated by UV-vis absorption spectrometry and photoluminescence (PL) spectrometry. Fig. 3 displays their absorption and PL spectra. DBF-d-PO, DBT-d-PO, DBF-d-Py, and DBT-d-Py showed major absorption bands around 250 and 300 nm because of the π - π * transition. DBT-d-PO and DBT-d-Py exhibited a long-wavelength absorption tail because of the n- π * transition of the sulfur atom.^{19,42} The E_g values of DBF-d-PO, DBT-d-PO, DBT-d-PO, DBT-d-PO, Were estimated as 3.53, 3.35, 3.54, and 3.32 eV, respectively from their absorption spectra in film (Fig. S15). The maximum fluorescent emission wavelengths of DBF-d-PO, DBT-d-PO, DBF-d-PO, DBF-d-PO, DBT-d-PO, DBF-d-PO, DBT-d-PO, DBF-d-PO, DBT-d-PO, DBF-d-PO, DBF-d-PO, DBT-d-PO, DBF-d-PO, DBT-d-PO, DBF-d-PO, DBT-d-PO, DBF-d-PO, DBT-d-PO, DBF-d-PO, DBT-d-PO, DBF-d-PO, DBT-d-PO, DBF-d-PO, DBF-d-PO, DBT-d-PO, DBF-d-PO, DBF-d-PO, DBT-d-PO, DBF-d-PO, DBF-d-P

The $E_{\rm T}$ values of DBF-d-PO, DBT-d-PO, DBF-d-Py, and DBT-d-Py were determined by low temperature PL emission spectra in tetrahydrofuran (THF) at 77 K. As shown in Fig. 3b, they exhibited the highest energy sub-bands at 420 (DBF-d-PO), 459 (DBT-d-PO), 452 (DBF-d-Py), and 462 nm (DBT-d-Py). The corresponding $E_{\rm T}$ values were calculated as 2.95, 2.70, 2.74, and 2.68 eV, respectively. This result clearly indicates that all compounds possessed high $E_{\rm T}$ values suitable for blue PhOLEDs. Moreover, DBF-d-PO and DBT-d-PO showed higher



Fig. 3 (a) UV-vis absorption and fluorescence spectra in THF at room temperature and (b) phosphorescence spectra in THF at 77 K.

 $E_{\rm T}$ values than DBF-d-Py and DBT-d-Py because the phosphine oxide EWG completely broke the aromatic conjugation. Interestingly, DBF-d-PO with the dibenzo[*b*,*d*]furan dimer and phosphine oxide EWG showed the highest $E_{\rm T}$ compared with those of DBT-d-PO, DBF-d-Py, and DBT-d-Py and was expected to effectively suppress the triplet exciton leakage in the EML.

Cyclic voltammetry (CV) was performed using the ferrocene couple (Fe/Fe⁺) as an internal standard to investigate the HOMO and LUMO energy levels of DBF-d-PO, DBT-d-PO, DBF-d-Py, and DBT-d-Py. Fig. S13 illustrates their reductive traces on the CV measurements. The LUMO energy levels of HBMs



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Fig. 4 Current density traces of EODs with DBF-d-PO, DBT-d-PO, DBF-d-Py, and DBT-d-Py.

were deduced though the reduction potential onset in the cyclic voltammograms.

The HOMO energy levels of HBMs were calculated by their LUMO energy levels and $E_{\rm g}$ s. Table 1 lists the energy levels. DBF-d-PO and DBT-d-PO exhibited the first reductive onset of -1.01 and -0.97 V, respectively, implying the LUMO energy levels of DBF-d-PO and DBT-d-PO were -3.22 and -3.26 eV, respectively. The first reductive onset of DBF-d-Py and DBT-d-Py was shown at -0.82 and -0.84 V. The LUMO energy levels of DBF-d-Py and DBT-d-Py were -3.41 and -3.39 eV, respectively. The oxygen atom was more electronegative than the sulfur atom; hence, DBF-d-PO and DBF-d-Py had deep HOMO energy levels compared with DBT-d-PO and DBT-d-Py. Moreover, DBF-d-Py and DBT-d-Py exhibited lower energy levels compared with DBF-d-PO because the pyridine EWG did not block the π -conjugation, and the HOMO/LUMO distributions were extended to the pyridine EWG. Considering

that the HOMO energy level of the host and <u>higheridopant</u> materials of the conventional blue PhOLEDs Was below C6:0 eV, the HOMO energy levels of DBF-d-PO, DBT-d-PO, DBF-d-Py, and DBT-d-Py were deep. Thus, they were expected to effectively confine the holes in the EML for highly efficient blue PhOLEDs.

EODs were fabricated with the following device structure to evaluate the electron transporting properties of DBF-d-PO, DBT-d-PO, DBF-d-Py, and DBT-d-Py: ITO/Ca (5 nm)/HBMs (30 nm)/LiF (1 nm)/Al (150 nm). Fig. 4 displays traces of the current density vs. voltage of the EODs. The electron transporting properties of DBF-d-Py and DBT-d-Py were superior to those of DBF-d-PO and DBT-d-PO because of the excellent intermolecular interaction derived from the intermolecular hydrogen bonds between the pyridine segments.⁴³⁻⁴⁴ All compounds exhibited high current densities up to a practical voltage range; therefore, they are expected to easily transport the electrons in OLED devices without electron accumulation.

Blue PhOLEDs were fabricated with the following device structure to evaluate the performances of DBF-d-PO, DBT-d-PO, DBF-d-Py, and DBT-d-Py as HBMs : ITO/ BPBPA:HATCN (40 nm, 30% co-evaporation of HATCN)/BPBPA (10 nm)/PCZAC (10 nm)/mCBPCN:oCBP:CNIr (30 nm, 50% and 10% doping of oCBP and CNIr, respectively)/ DBF-d-PO (device 1, 5 nm), DBT-d-PO (device 2, 5 nm), DBF-d-Py (device 3, 5 nm), DBT-d-Py (device 4, 5 nm), or BmPyPB (device 5, 5 nm)/ZADN (20 nm)/LiF (1 nm)/AI (200 nm).¹⁹ A mixed layer consisting of N,N,N',N'tetra[(1,1'-biphenyl)-4-yl]-(1,1'-biphenyl)-4,4'-diamine (BPBPA) and 1, 4, 5, 8, 9, 11-hexaazatriphenylene hexacarbonitrile (HATCN) was used as a hole injecting layer. BPBPA was used as HTL.9,9-Dimethyl-10-(9-phenyl-9H-carbazol-3-yl)-9,10an dihydroacridine (PCZAC) was introduced as an exciton blocking layer.45 9-(3'-(9H-Carbazole-9-yl)-5-cyano[1,1'-biphenyl]-3-yl)-9H-carbazole-3-carbonitrile (mCBPCN) and 9,9'-biphenyl-2,2'-



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Fig. 6 (a) Current density and luminance traces vs. voltage, (b) external quantum efficiency traces vs. luminance, (c) current and power efficiency traces vs. luminance, and (d) electroluminescence spectra of the blue PhOLEDs with DBF-d-PO, DBT-d-PO, DBT-d-PO, and BmPyPB.

Table 2 EL performance of devices 1-5.

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Device (HBM)	V _{on} ^a /V ₁₀₀ ^b /V ₁₀₀₀ ^c [V]	$\eta_{\mathrm{ext,100}^{\mathrm{b}}}/\eta_{\mathrm{ext,1000}^{\mathrm{c}}}/\eta_{\mathrm{ext,max}^{\mathrm{d}}}$ [%]	$\eta_{c,100}{}^{b}/\eta_{c,1000}{}^{c}/\eta_{c,max}{}^{d}$ [cd A ⁻¹]	$\eta_{p,100}{}^{b}/\eta_{p,1000}{}^{c}/\eta_{p,max}{}^{d}$ [lm W ⁻¹]	L _{max} [cd m ⁻² / V]
Device 1 (DBF-d-PO)	3.0/3.6/4.5	20.3/18.7/20.7	37.3/34.3/38.6	32.9/24.1/40.4	48,445 / 11.0
Device 2 (DBT-d-PO)	3.0/3.7/4.8	12.3/12.3/12.3	21.5/21.7/21.7	18.3/14.4/22.7	39,977 / 11.0
Device 3 (DBF-d-Py)	3.0/3.5/4.3	24.1/22.4/24.3	43.8/40.5/44.3	39.4/30.0/46.4	88,953 / 12.0
Device 4 (DBT-d-Py)	3.0/3.5/4.5	20.6/18.5/20.7	37.1/33.1/37.2	33.1/23.4/33.3	80,941 / 12.5
Device 5 (BmPyPB)	3.0/3.7/4.8	21.9/19.5/22.3	38.3/33.9/39.1	32.9/22.4/40.9	55,610 / 14.0

^a voltage at 1 cd m⁻². ^b voltage, external quantum efficiency (η_{ext}), current efficiency (η_c), power efficiency (η_p) at 100 cd m⁻². ^c voltage, η_{ext} , η_c , and η_p at 1000 cd m⁻². ^d maximum η_{ext} , η_{cr} and η_p .

diylbis-9*H*-carbazole (oCBP) were used as the EML host materials. fac-Tris(1-(2,6-diisopropylphenyl)-2-(3-cyanophenyl)-1*H*-imidazolyl)iridium (III) (CNIr) was adopted as a blue phosphorescent dopant. 2-[4-(9,10-Di-naphthalen-2-yl-anthracene-2-yl)-phenyl]-1-phenyl-1*H*-benzimidazole (ZADN) was used as an ETL. A blue PhOLED with a conventional pyridine-based HBM (BmPyPB) was also fabricated as the standard device (device 5). Fig. 5 depicts the chemical

structure and energy level diagrams of the materials used in the OLED fabrication.

Fig. 6 shows the current density and luminance vs. voltage, η_{ext} , current efficiency (η_{ce}), and power efficiency (η_{pe}) vs. luminance, and electroluminescence (EL) spectra of the blue PhOLEDs. Table 2 lists their device performances. Device 1 and 2 with DBF-d-PO and DBT-d-PO showed a similar current density from 0 to 10 V. The turn-on voltage of devices 1 and 2

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Fig. 7 Lifetime test of devices 1-5 at an initial luminance of 200 cd m⁻².

with DBF-d-PO and DBT-d-PO was 3.0 V. The driving voltages at 1000 cd m⁻² of devices 1 and 2 with DBF-d-PO and DBT-d-PO were 4.5 and 4.8 V, respectively. These results clearly indicated that DBF-d-PO and DBT-d-PO did not create any problems such as electron trapping. However, the luminance of device 1 with DBF-d-PO was higher than that of device 2 with DBT-d-PO. Device 1 with DBF-d-PO showed a maximum external quantum efficiency ($\eta_{ext,max}$) of 20.7%, a maximum current efficiency ($\eta_{pe,max}$) of 38.6 cd A⁻¹, and a maximum power efficiency ($\eta_{pe,max}$) of 40.4 lm W⁻¹, whereas device 2 with DBT-d-PO showed an $\eta_{ext,max}$ of 12.3%, an $\eta_{ce,max}$ of 21.7 cd A⁻¹, and an $\eta_{pe,max}$ of 22.7 lm W⁻¹. The efficiency of device 1 with DBF-d-PO was higher than that of device 2 with DBT-d-PO. This result can be attributed to the high E_{T} and the deep HOMO energy level of DBF-d-PO compared with DBT-d-PO.

Device 3 with DBF-d-Py showed the best efficiency with an $\eta_{\text{ext,max}}$ of 24.3%, an $\eta_{\text{ce,max}}$ of 44.3 cd A⁻¹, and an $\eta_{\text{pe,max}}$ of 46.4 Im W⁻¹, whereas device 4 with DBT-d-Py displayed an $\eta_{\text{ext.max}}$ of 20.7%, an $\eta_{\rm ce,max}$ of 37.2 cd A^-1, and an $\eta_{\rm pe,max}$ of 33.3 Im W^-1. Note that the HBMs with pyridine EWGs exhibited higher efficiency than the HBMs with phosphine oxide EWGs. This result can be due to a significant increase in the electron transporting property of the HBMs with pyridine EWGs compared with the HBMs with phosphine oxide EWGs. Furthermore, device 3 with DBF-d-Py exhibits an excellent η_{ext} of 22.4% at a practical luminance of 1000 cd m⁻² and a very high maximum luminance of 88,953 cd m⁻² at 12 V. In contrast, the standard device 5 with BmPyPB showed an η_{ext} of 19.5% at a practical luminance of 1000 cd m⁻² and a maximum luminance of 55,610 cd m⁻² at 14 V. This result confirmed that device 3 with DBF-d-Py was far superior to device 5 with BmPyPB in terms of driving voltage, luminance efficiency, power efficiency, and maximum luminance. This result confirmed that DBF-d-Py can successfully confine the holes in the EML and suppress triplet quenching because of its deep HOMO energy level and high E_{T} . Furthermore, as shown in Fig. 6d, the EL spectra of devices 1-4 exhibited the same emission peaks at 460 and 490 nm, which were consistent with the blue PhOLED with a CNIr dopant.⁴⁶ This result indicates that DBF-dPO, DBT-d-PO, DBF-d-Py, and DBT-d-Py completely Acceptined the triplet excitons in the EML.

The device lifetime of the blue PhOLEDs was investigated by operating the devices at an initial luminance of 200 cd m⁻². Fig. 7 shows the results. The lifetime characteristics such as T_{90} (corresponding to the degradation time of 10% luminance loss) and T_{50} (corresponding to the degradation time of 50% luminance loss) of devices 1-4 were compared with those of device 5 with BmPyPB. The T_{50} lifetime of devices 1 and 2 with DBF-d-PO and DBT-d-PO was 72.2 h and 49.8 h, respectively. This short lifetime may be due to the chemically unstable C-P bond of the phosphine oxide segments in DBF-d-PO and DBTd-PO.⁴⁷ However, The T₉₀ lifetime of devices 3 and 4 with DBFd-Py and DBT-d-Py was 88.5 and 63.9 h, respectively. The halflifetime (T_{50}) of devices 3 and 4 with DBF-d-Py and DBT-d-Py was approximately 1070 h. On the contrary, device 5 with BmPyPB initially exhibited steep luminance degradation. The T_{90} and T_{50} lifetimes of device 5 with BmPyPB were 27.8 and 429.5 h, respectively. This result clearly verified that the blue PhOLEDs with DBF-d-Py and DBT-d-Py as HBMs showed a highly enhanced lifetime compared with BmPyPB with an HBM.

The efficient hole blocking by the deep HOMO energy level and the high thermal stability stabilizing HBL morphology can be considered as major factors for the lifetime improvement of devices 3 and 4 with DBF-d-Py and DBT-d-Py.

Conclusions

In summary, we designed and synthesized herein four HBMs based on dibenzo[b,d]furan and dibenzo[b,d]thiophene dimers, 2,2'-bidibenzo[b,d]furan and 2.2'molecular bidibenzo[b,d]thiophene, (i.e. DBF-d-PO, DBT-d-PO, DBF-d-Py, and DBT-d-Py) for high-efficiency and long-lived blue PhOLEDs. We successfully synthesized dimeric intermediates using dibenzo[b,d]furan and dibenzo[b,d]thiophene segments and incorporated pyridine and phosphine oxide functional groups as EWGs for HBMs. A computational simulation was used to investigate the optimal structure, orbital distribution, and physicochemical properties of the HBMs. Thermal, optical, and electrochemical analyses showed that DBF-d-PO, DBT-d-PO, DBF-d-Py, and DBT-d-Py possessed high thermal stability, deep HOMO energy levels (-6.61 – -6.95 eV), and high $E_{\rm T}$ (2.68 – 2.95 eV) values. Moreover, their EOD measurements indicated that DBF-d-Py, and DBT-d-Py with pyridine EWGs had better electron mobility than DBF-d-PO and DBT-d-PO with phosphine oxide EWGs. The blue PhOLEDs with DBF-d-PO, DBT-d-PO, DBF-d-Py, and DBT-d-Py as HBLs exhibited low turnon (3.0 V) and operating voltages (4.3 - 4.8 V), excellent external quantum efficiency, and high current and power efficiencies. A blue PhOLED with DBF-d-Py showed the best efficiency with an $\eta_{\text{ext,max}}$ of 24.3%, an $\eta_{\text{ce,max}}$ of 44.3 cd A⁻¹, and an $\eta_{\rm pe,max}$ of 46.4 Im W^-1. It also exhibited an outstanding $\eta_{\rm ext}$ of 22.4% at a practical luminance of 1000 cd m⁻² and a very high maximum luminance of 88,953 cd $\,m^{-2}$ at 12 V. Furthermore, blue PhOLEDs with DBF-d-Py and DBT-d-Py exhibited a highly improved lifetimes compared with the conventional HBM, BmPyPB, with a pyridine electron

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transport unit and a phenyl core structure. We anticipate that novel HBMs based on dimeric dibenzo[*b*,*d*]furan and dibenzo[*b*,*d*]thiophene molecules will be key materials for the commercialization of high-performance blue PhOLEDs.

Experimental

General information

Chemicals such as starting materials and solvent used in this study were purchased commercially and used without further purification. The NMR (¹H, ¹³C) spectra were collected by using an AVANCE III 400 NMR spectrometer. The molecular masses of synthesized molecules were measured by using a 5977B gas chromatography/mass selective detector. TGA and DSC were performed by using a TA Instruments - Waters LLC and -DISCOVERY units with the scanning rate of 10 °C min⁻¹. DTA was carried out by using Rigaku - TG-DTA 8120 instrument with the scanning rate of 5 °C min⁻¹. AFM images were obtained from Park systems - XE7 unit. The absorption and photoluminescence spectra were recorded on an Agilent - Cary 500 and - Eclipse spectrophotometers. Low temperature phosphorescent spectra were measured from a PerkinElmer -LS-55 spectrophotometer at 77 K. The electrochemical analysis of the compounds was carried out in the dichloromethane (DCM) solution by using a BioLogic - VMP3 unit. A platinum (Pt) and silver/silver chloride (Ag/AgCl) were used as a counter and reference electrodes, respectively. When investigating the electrochemical properties, the ferrocene was used as an internal standard.

Synthesis

Synthetic routes of DBF-d-PO, DBT-d-PO, DBF-d-Py, and DBTd-Py are described in Scheme 1. The synthesis of 6-bromo-2iododibenzo[b,d]furan (compound 1) was carried out through previously reported literature.¹⁹

Synthesis of compound (1')

Under N₂ condition, 4-bromodibenzo[*b*,*d*]thiophene (5.00 g, 19.00 mmol), iodobenzene diacetate (3.06 g, 9.50 mmol), and iodine (2.41 g, 9.50 mmol) were stirred in acetic acid (25 ml) and acetic anhydride (25 ml). Several drops of the sulfuric acid were added to reaction mixture and the reaction mixture was stirred for 24 hours at room temperature. Then, the methanol (200 ml) was poured and the reaction mixture was filtered. The purified compound (3.12 g, 8.02 mmol, 42%) was obtained as the white solid. ¹H NMR (400 MHz, chloroform-d₃, δ): 7.44 (dd, 1H), 8.07-8.05 (dd, 1H), 7.78-7.75 (dd, 1H), 7.65-7.62 (m, 2H), 7.39-7.35 (t, 1H). ¹³C NMR (100 MHz, chloroform-d₃, δ): 141.48, 138.45, 138.06, 135.69, 135.38, 131.20, 129.97, 126.02, 124.42, 120.38, 116.27, 89.20. GC/MS *m/z*: [M]⁺ calcd for C₁₂H₆BrIS, 389.84; found, 389.8.

Synthesis of compound (2)

Under N_2 condition, compound 1 (5.00 g, 13.41 mmol), bis(pinacolato)diboron (4.43 g, 17.43 mmol), potassium

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(3.95 40.22 acetate g, mmol), and Article Inthe bis(diphenylphisphino)ferrocene]dichloPopalladiams9TC0268(AP) complex with dichloromethane (Pd(dppf)Cl₂·CH₂Cl₂, 0.55 g, 0.67 mmol) were stirred in dioxane (200 ml) and refluxed for 12 hours. Then, the distilled water and dichloromethane were added to the reaction mixture and the organic phase was extracted. The extracted organic phase was evaporated and the crude mixture was purified by column chromatography using hexane and dichloromethane as the eluents. The purified compound (4.01 g, 10.75 mmol, 80%) was gained as the beige solid. ¹H NMR (400 MHz, chloroform-d₃, δ): 8.43 (s, 1H), 7.98-7.95 (dd, 1H), 7.91-7.89 (dd, 1H), 7.66-7.64 (dd, 1H), 7.62-7.60 (dd, 1H), 7.25-7.21 (t, 1H), 1.40 (s, 12H). GC/MS m/z: [M]⁺ calcd for C₁₈H₁₈BBrO₃, 372.05; found, 372.2.

Synthesis of compound (2')

Under N₂ condition, compound 1' (3.12 g, 13.41 mmol), bis(pinacolato)diboron (2.65 g, 10.43 mmol), potassium acetate (2.36 g, 24.06 mmol), and Pd(dppf)Cl₂·CH₂Cl₂ (0.33 g, 0.40 mmol) were stirred in dioxane (200 ml) and refluxed for 12 hours. Then, the distilled water and dichloromethane were added to the reaction mixture and the organic phase was extracted. The extracted organic phase was evaporated and the crude mixture was used for the next reaction without further purification.

Synthesis of compound (3)

Under N₂ condition, compound 1 (4.00 g, 10.72 mmol), (4.00 g, 2 10.72 mmol), compound palladium tetrakis(triphenylphosphine) (Pd(PPh₃)₄, 0.62 g, 0.54 mmol), and sodium carbonate (Na $_2CO_3$, 2.27 g, 21.45 mmol) were stirred in dioxane (150 ml) and distilled water (75 ml) and refluxed for 12 hours. Then, the distilled water and dichloromethane were added to the reaction mixture and the organic phase was extracted. The extracted organic phase was evaporated and the crude mixture was washed by methanol and dichloromethane. The purified compound (2.67 g, 5.43 mmol, 51%) was gained as the white solid. ¹H NMR (400 MHz, chloroform-d₃, δ): 8.20-8.19 (dd, 2H), 7.98-7.96 (dd, 2H), 7.81-7.79 (dd, 2H), 7.77-7.75 (dd, 2H), 7.67-7.65 (dd, 2H), 7.30-7.28 (t, 2H, a peak of triplet is masked in the CHCl₃). ¹³C NMR (100 MHz, chloroform-d₃, δ): 155.53, 153.81, 136.84, 130.31, 127.62, 125.69, 124.82, 124.13, 119.84, 119.73, 112.33, 104.61. GC/MS *m/z*: [M]⁺ calcd for C₂₄H₁₂Br₂O₂, 492.2; found, 492.0.

Synthesis of compound (3')

Under N₂ condition, compound 1' (3.12 g, 8.02 mmol), crude compound 2' (3.12 g, 8.02 mmol, assumed that the theoretical yield of the previous reaction is 100%), Pd(PPh₃)₄ (0.46 g, 0.40 mmol), and Na₂CO₃ (1.70 g, 16.04 mmol) were stirred in dioxane (150 ml) and distilled water (75 ml) and refluxed for 12 hours. Then, the distilled water and dichloromethane were added to the reaction mixture and the organic phase was extracted. The extracted organic phase was evaporated. The crude mixture washed by methanol and dichloromethane and was used for the next reaction without further purification. GC/MS m/z: [M]⁺ calcd for C₂₄H₁₂Br₂S₂, 523.87; found, 524.0.

Synthesis of DBF-d-PO

Under N₂ condition, compound 3 (3.00 g, 6.10 mmol) were dissolved in tetrahydrofuran (THF, 100 ml) and the solution was cooled to -78 °C. The 2.5 M n-butyllithium in hexane (5.85 ml, 14.63 mmol) was added to the cooled solution and the reaction mixture was stirred for 1.5 hours at -78 °C. After 1.5 hours, the diphenylphosphine chloride (3.23 g, 14.63 mmol) was added to the reaction mixture at -78 °C and stirred for 12 hours at room temperature. Then, the reaction mixture was quenched with the distilled water and dichloromethane. The organic phase was extracted and stirred with the hydrogen peroxide (10 ml) for 3 hours. Next, the distilled water (100 ml) was added and the organic phase was extracted. The extracted organic phase was evaporated and the crude mixture was purified by column chromatography using ethyl acetate and hexane as the eluents. The purified compounds (2.50 g, 8.13 mmol, 61%) was gained as the white solid. ¹H NMR (400 MHz, chloroform-d₃, δ): 8.23-8.21 (dt, 2H), 8.18-8.17 (d, 2H), 7.86-7.80 (m, 10H), 7.69-7.67 (dd, 2H), 7.59-7.55 (m, 4H), 7.53-7.45 (m, 12H). GC/MS m/z: [M]⁺ calcd for C₄₈H₃₂O₄P₂, 734.18; found, 734.4.

Synthesis of DBT-d-PO

Under N₂ condition, compound 3' (2.00 g, 3.81 mmol) were dissolved in THF (100 ml) and the solution was cooled to -78 °C. The 2.5 M n-butyllithium in hexane (3.66 ml, 9.16 mmol) was added to the cooled solution and the reaction mixture was stirred for 1.5 hours at -78 °C. After 1.5 hours, the diphenylphosphine chloride (2.02 g, 9.16 mmol) was added to the reaction mixture at -78 °C and stirred for 12 hours at room temperature. Then, the reaction mixture was guenched with the distilled water and dichloromethane. The organic phase was extracted and stirred with the hydrogen peroxide (10 ml) for 3 hours. Next, the distilled water (100 ml) was added and the organic phase was extracted. The extracted organic phase was evaporated and the crude mixture was purified by column chromatography using ethyl acetate and hexane as the eluents. The purified compounds (2.20 g, 2.87 mmol, 75%) was gained as the white solid. ¹H NMR (400 MHz, chloroform-d₃, δ): 8.45-8.42 (m, 4H), 7.92-7.89 (d, 2H), 7.80-7.74 (m, 10H), 7.62-7.57 (m, 4H), 7.55-7.44 (m, 12H). GC/MS m/z: [M]+ calcd for C₄₈H₃₂O₂P₂S₂, 766.13; found, 766.3.

Synthesis of DBF-d-Py

Under N_2 condition, compound 3 (2.00 g, 4.06 mmol), pyridine-3-boronic acid (1.20 g, 9.75 mmol), Pd(dppf)Cl₂·CH₂Cl₂ (0.35 g, 0.41 mmol), and potassium carbonate (K₂CO₃, 2.81 g, 20.32 mmol) were stirred in dioxane (100 ml) and distilled water (50 ml) and refluxed for 12 hours. Then, the distilled water and dichloromethane were added to the reaction mixture and the organic phase was extracted. The extracted organic phase was evaporated and the crude mixture was purified by column chromatography using Paper

dichloromethane and methanol as the eluents. The purified compound (1.20 g, 2.46 mmol, 60%) was better as a solid. ¹H NMR (400 MHz, chloroform-d₃, δ): 9.20-9.19 (dd, 2H), 8.70-8.69 (dd, 2H), 8.30-8.27 (m, 4H), 8.09-8.06 (dd, 2H), 7.82-7.80 (dd, 2H), 7.72-7.70 (d, 2H), 7.67-7.65 (dd, 2H), 7.53-7.48 (m, 4H). ¹³C NMR (100 MHz, chloroform-d₃, δ): 155.65, 153.88, 149.66, 148.89, 136.71, 135.95, 132.14, 127.30, 126.74, 125.18, 124.59, 123.56, 123.50, 122.51, 120.65, 119.55, 112.07. GC/MS *m/z*: [M]⁺ calcd for C₃₄H₂₀N₂O₂, 488.15; found, 488.2.

Synthesis of DBT-d-Py

Under N₂ condition, compound 3 ' (2.00 g, 4.06 mmol), pyridine-3-boronic acid (1.13 g, 9.16 mmol), Pd(dppf)Cl₂·CH₂Cl₂ (0.31 g, 0.38 mmol), and K_2CO_3 (2.64 g, 19.07 mmol) were stirred in dioxane (100 ml) and distilled water (50 ml) and refluxed for 12 hours. Then, the distilled water and dichloromethane were added to the reaction mixture and the organic phase was extracted. The extracted organic phase was evaporated and the crude mixture was purified by column chromatography using dichloromethane and methanol as the eluents. The purified compound (1.50 g, 2.88 mmol, 76%) was obtained as a white solid. ¹H NMR (400 MHz, chloroform-d₃, δ): 9.10-9.00 (dd, 1H), 8.73-8.72 (dd, 1H), 8.51 (d, 1H), 8.35-8.33 (dd, 1H), 8.14-8.11 (m, 1H), 7.99-7.97 (dd, 1H), 7.87-7.84 (dd, 1H), 7.67-7.63 (t, 1H), 7.54-7.52 (dd, 1H), 7.51-7.47 (dd, 1H). ¹³C NMR (100 MHz, chloroform-d₃, δ): 149.36, 149.30, 139.32, 138.50, 138.03, 136.47, 136.35, 136.21, 135.52, 133.59, 127.30, 126.76, 125.42, 123.55, 123.13, 121.39, 120.51. GC/MS *m*/*z*: [M]⁺ calcd for C₃₄H₂₀N₂S₂, 520.11; found, 520.2.

Calculation of molecular energy level

The LUMO energy levels of HBMs were deduced though the reduction potential onset ($E_{onset, red}$) with the redox potential of ferrocene/ferrocenium ($E_{1/2, Fe}$) couple in the cyclic voltammograms. The HOMO energy levels of HBMs were calculated by their LUMO energy levels and bandgaps in films (E_g^{film}). The calculated equations are shown below.

$$E_{LUMO} (eV) = -4.80 - (E_{onset, red} - E_{1/2, Fe})$$
(1)

$$E_{HOMO} (eV) = E_{LUMO} (eV) - E_g^{film} (eV)$$
(2)

Device fabrication and analysis

The electron-only devices and blue phosphorescent OLEDs with four compounds were fabricated with the following configuration: ITO/Ca (5 nm)/four compounds (30 nm)/LiF (1 nm)/Al (150 nm), ITO/ BPBPA:HATCN (40 nm, 30% co-evaporation of HATCN)/BPBPA (10 nm)/PCZAC (10 nm)/mCBPCN:oCBP:CNIr (30 nm, 50% and 10% doping of oCBP and CNIr, respectively)/HBMs (5 nm)/ZADN (20 nm)/LiF (1 nm)/Al (200 nm). When fabricating the device, the organic layers were fabricated by the thermal vacuum deposition at 1.0×10^{-7} torr and devices were protected from the oxygen and moisture by encapsulating the devices using the CaO getter. The current density and luminance vs. voltage of the devices were recorded by Keithley 2400 source meter unit and Konica Minolta CS-2000 spectroradiometer unit.

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Conflicts of interest

There are no conflicts to declare

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