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Introduction

Over the past three decades, organic light-emitting devices (OLEDs) have made great progress.¹⁻¹⁰ In particular, OLEDs based on materials displaying phosphorescence and thermally activated delayed fluorescence (TADF) can theoretically achieve 100% internal quantum efficiency.¹¹⁻¹⁶ However, both phosphorescent OLEDs (PHOLEDs) and TADF OLEDs suffer from serious efficiency roll-off issues.¹⁷⁻²⁰ The efficiency roll-off levels of PHOLEDs employing TADF materials as hosts can be greatly alleviated, because the occurrence of the reverse intersystem crossing (RISC) process can prevent triplet-related annihilations from occurring to some extent.²¹⁻²⁴

TADF-based OLEDs do, however, consistently show the disadvantage of poor stability due to unstable moiety in the TADF molecule. For example, the LT50 (time to 50% of an initial luminance of 1000 cd m⁻²) values of TADF-emitter devices have been observed to be 0.1 h for 9,9-dimethyl-9,10-dihydroacridine-2,4,6-triphenyl-1,3,5-triazine, 0.7 h for

Stable and efficient phosphorescent organic lightemitting device utilizing a δ -carboline-containing host displaying thermally activated delayed fluorescence[†]

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Materials displaying thermally activated delayed fluorescence (TADF) can when used as hosts alleviate the serious efficiency roll-off of phosphorescent organic light-emitting devices (PHOLEDs). However, the stability of the device remains challenging due to the unstable moiety in the TADF molecule. Here, a stable and efficient yellow PHOLED based on a δ -carboline-containing TADF host and bis(4-phenylthieno[3,2-c]pyridinato- $C^{2'}$) (acetylacetonato) iridium(III) (PO-01) guest was demonstrated. Compared to the lifetime of the PHOLED with a 4,4'-bis(N-carbazolyl)-2,2'-biphenyl host, a greater than twenty times enhancement of the lifetime of the PO-01-based device was achieved. The LT50 lifetime (time to 50% of initial luminance of 1000 cd m⁻²) of an unpackaged DCb-BPP-based PHOLED reached 424 h, and was accompanied by a maximum external quantum efficiency of 21.5% and an impressive low efficiency roll-off of 17.7% at a high luminance of 10 000 cd m⁻². These values are among the best of those reported for PO-01-based yellow PHOLEDs.

> 10-(4-(4,6-diphenyl-1,3,5-triazin-2-yl) phenyl)-3-phenyl-3,10-dihydropyrrolo[3,2-*a*]carbazole,²⁵ and <4 h for bis(4-(9,9-dimethyl-acridin-10(9H)-yl)phenyl)methanone.26 Poor operational lifetimes of TADFhosted PHOLEDs have also been noted, with LT50 values of 7 h and <2000 h for encapsulated PHOLEDs with 2-phenoxy-4,6-bis(12phenylindolo[2,3-a]carbazole-11-yl)-1,3,5-triazine and 2-benzenecyano-4,6-bis(12-phenylindolo[2,3-a]carbazole-11-yl)-1,3,5-triazine hosts, respectively.²⁷ Most TADF materials are made with donor (D) and acceptor (A) species designed to separate the highest occupied molecular orbital (HOMO) from the lowest unoccupied molecular orbital (LUMO). For example, 10,10'-[5-(6-[1,1'-biphenyl]-4-yl-2-phenyl-4-pyrimidinyl)-1,3-phenylene]bis[9,10-dihydro-9,9dimethyl-acridine] (DMAC-BPP) forms a D-A-D structure, using two acridine-type donor moieties connected by a phenyl group and a pyrimidine.²⁸ The acridine moiety is a strong electron donor, and is oxidized easily when the molecule is transporting holes; and consequently, the material does not display TADF, including the RISC process. Therefore, TADF-hosted PHOLEDs do not display their advantage in efficiency roll-off, and their practical application is limited by their poor stability. To solve this problem, developing stable moieties in TADF molecules with high tolerance to high current density is necessary.

> The well-known carbazole moiety is a strong electron donor.^{29,30} Carboline derivatives have attributes similar to those of the carbazole moiety. However, carboline derivatives are weak donors (when they have a nitrogen heteroatom at the

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Paper

 α - or δ -position) or even acceptors (with a nitrogen heteroatom at the β - or γ -position). The δ -carboline displays the strongest electron donating ability among carbolines, and is suitable as a designed TADF molecule.³⁰ Moreover, due to an intramolecular hydrogen bond, the δ -carboline moiety is a planar structure, which improves the conjugation of the molecule. Therefore, the stability of the δ -carboline-containing TADF host and the corresponding PHOLED is expected to be improved.

In this research, a stable yellow PHOLED with a 5,5'-[5-(6-[1,1'-biphenyl]-4-yl-2-phenyl-4-pyrimidinyl)-1,3-phenylene]bis-5H-pyrido[3,2-b]indole (DCb-BPP) host was demonstrated. For comparison, the yellow PHOLEDs with a DMAC-BPP TADF host and traditional 4,4'-bis(N-carbazolyl)-2,2'-biphenyl (CBP) host were also prepared. Compared to DMAC-BPP, with its two acridines as strong electron donors, the DCb-BPP used includes two δ -carbolines as weak electron donors. All of the PHOLEDs show high external quantum efficiency levels, of around 20%. And the PHOLEDs with a TADF-displaying host present a lower efficiency roll-off. More importantly, the stability of the DCb-BPP-based PHOLED is significantly better than those of the other tested PHOLEDs. From an initial brightness of 1000 cd m⁻², the unpackaged DCb-BPP-based PHOLED has a lifetime of 424 h, twenty times those of DMAC-BPP-based and CBP-based PHOLEDs.

Results and discussion

Electrochemical and thermal properties

In order to investigate the influence that δ -carboline has on the energy levels, the electrochemical properties of the TADF materials DCb-BPP and DMAC-BPP were evaluated using cyclic voltammetry (CV), where the potentials were calibrated against a ferrocenium/ferrocene (Fc⁺/Fc) redox couple, as shown in the inset in Fig. 1. The HOMO and LUMO energy levels were then estimated using the onset potentials of the oxidation and reduction, respectively. The HOMO/LUMO energy levels of DCb-BPP were in this way determined to be -5.90/-2.73 eV, while those of DMAC-BPP were found to be -5.38/-2.46 eV.

The thermal stability of DCb-BPP was assessed by performing thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) under a nitrogen atmosphere. As shown in Fig. 1, DCb-BPP exhibits superior thermal stability with a high decomposition temperature (T_d) of 514 °C and a high glass



Fig. 1 TGA, DSC (left inset), and CV (right inset) curves of DCb-BPP and DMAC-BPP.



Scheme 1 Synthetic route to DCb-BPP and DMAC-BPP. Inset: Possible intramolecular hydrogen bond existing in DCb-BPP.

transition temperature (T_g) of 173 °C. In contrast, the T_g and T_d values of DMAC-BPP were measured to be 220 and 419 °C, respectively. Therefore, DCb-BPP was clearly found to be more stable than DMAC-BPP, which can be attributed to the hydrogen bonding of δ -carboline,²⁹ as shown in Scheme 1 (inset).

Optical properties

Fig. 2a shows the acquired absorption and photoluminescence (PL) spectra of DCb-BPP. The DCb-BPP sample exhibits strong absorption in the range of 250 to 350 nm. As shown in Fig. 2a, the fluorescence spectrum of DCb-BPP at room temperature shows a peak at 452 nm displaying a typical Gaussian distribution curve and a large full width at half maximum (FWHM) of 70 nm, while the low-temperature fluorescence spectrum of DCb-BPP shows three peaks: a fluorescence emission at 407 nm and phosphorescence signals at 488 and 520 nm. Quite an overlap was observed between the signals of the 77 K phosphorescence spectrum and 300 K fluorescence spectrum. From the peaks of the 77 K-phosphorescence spectrum and 300 K fluorescence spectrum, the energy levels of the singlet and triplet states of DCb-BPP were determined to be 2.74 and 2.54 eV, respectively. This result indicates a $\Delta E_{\rm ST}$ value of only 0.20 eV and relatively high similarity between the triplet energy level of DCb-BPP and that of its singlet energy level. DCb-BPP was concluded from these results to have the potential to be a TADF material. Compared with the bluish-green-light-emitting TADF material DMAC-BPP, DCb-BPP shows blue-shifted fluorescence emission, attributed to its electron-deficient δ-carboline moiety.

The transient fluorescence characteristics of the PMMA: 0.1 wt% DCb-BPP film were also investigated at room temperature to prove the occurrence of the TADF process. As shown in Fig. 2b (inset), the data for the very initial decay was fitted with a single-exponential function with a lifetime of 3 ns. This rapid initial decay may be due to the planar δ -carboline with high rigidity having improved the molecular conjugation, increasing



Fig. 2 (a) UV-vis absorption and fluorescence spectra at 300 K, and fluorescence and phosphorescence PL spectra at 77 K of DCb-BPP. (b) Transient decay spectra of a PMMA:0.1 wt% DCb-BPP film showing (inset) initial lifetime and delayed lifetime.

the intensity of the fluorescence emission. As shown in Fig. 2b, the delayed emission shows a lifetime of 2.1 μ s. As shown in Fig. S1 (ESI†), the delayed emission at 1 μ s is red-shifted compared with the initial emission at 10 ns. All of these results provided strong evidence of the TADF characteristics of DCb-BPP.

Single-carrier devices

To evaluate the hole and electron transport properties of the host materials, a hole-only single carrier device with an ITO/ MoO₃ (2 nm)/TcTa (5 nm)/host material (100 nm)/TcTa (5 nm)/ MoO₃ (2 nm)/Ag (120 nm) structure and electron-only device with a similar structure, specifically ITO/LiF (2 nm)/TmPyPB (5 nm)/host material (100 nm)/TmPyPB (5 nm)/LiF (2 nm)/Mg: Ag (12:1, 120 nm), were fabricated. TcTa with MoO₃ and TmPyPB with LiF were used to block the electrons and holes injected from the cathode and anode, respectively. Besides DCb-BPP, three other host materials, namely CBP, DMAC-BPP and TcTa:45wt% DCb-BPP, were also investigated for comparison. The acquired current density-voltage curves of these single-carrier devices are shown in Fig. 3. Compared to CBP and DMAC-BPP, DCb-BPP was found to much more easily transport electrons. However, the hole transport ability of DCb-BPP was still far worse



Fig. 3 The current density-voltage curves of electron-only and holeonly devices for (a) CBP, (b) DMAC-BPP, (c) DCb-BPP, and (d) TcTa:45 wt% DCb-BPP. (Insets) The molecular structures of the host materials.

than its electron transport ability. Therefore, we doped TcTa into DCb-BPP in order to balance the transport of carriers. As clearly seen in Fig. 3d, TcTa:45% DCb-BPP showed a more balanced transport ability than did the other host materials, as its electron-only current density was nearly identical to its hole-only current density.

Performances of the PHOLEDs

To prove the advantage of the stable TADF materials, OLEDs employing DCb-BPP as a host were fabricated and their performances were studied. Here, the device structure was ITO/MoO₃ (3 nm)/TAPC (30 nm)/TcTa (5 nm)/host: 5 wt% PO-01 (20 nm)/ TmPyPB (50 nm)/LiF (0.5 nm)/Mg:Ag (12:1, 120 nm). For comparison, the four hosts CBP, DMAC-BPP, DCb-BPP and TcTa:45 wt% DCb-BPP were used, and the corresponding OLEDs were marked as Devices 1–4, respectively. MoO₃, TAPC, TcTa, TmPyPB, and LiF acted as, respectively, the hole-injecting layer, hole-transporting layer, electron-blocking layer, electron-transporting layer, and electron-injecting layer in these devices.

A shown in Fig. 4a, the HOMO of PO-01 was determined to be deeper than those of the above-described four host materials, so PO-01 would trap the holes at the TcTa/EML interface. In Device 1, the classical host material CBP was better at transporting holes than at transporting electrons, which causes Device 1 needs a high driving voltage. In Device 2, there was a barrier of 0.24 eV between DMAC-BPP and TmPyPB, but no barrier between PO-01 and TmPyPB. Thus, PO-01 could promote injection of electrons, and then transfer them to the host. As a result, the turn-on voltage of Device 2 was lower than that of Device 1. In Device 3, the LUMO of DCb-BPP was determined to be almost the same as that of TmPyPB and slightly lower than that of PO-01. Most of the electrons were transferred onto DCb-BPP, and then recombined with holes trapped by PO-01 at the interface. All of these results were reflected in the voltage-current density curves, shown in Fig. 4b. Besides the suitable energy level, the high electron-mobility of DCb-BPP was helpful for decreasing the



Fig. 4 (a) Energy levels of the tested materials. (b) Current density–voltage and brightness–voltage curves of the tested devices. (c) Electroluminescence (EL) spectra of the tested PHOLEDs. (d) Brightness–efficiency curves of Devices 1–4.

turn-on voltage in Device 3. As a result, the efficiency of Device 3 was still very high. However, such an unbalanced transport ability usually leads a narrow recombination region. This characteristic was confirmed according to the transient EL response of Device 3 as shown in Fig. S2 (ESI[†]). Even so, the efficiency roll-off of Device 3 ($B_{1/2} = 52\,000$ cd m⁻², with $B_{1/2}$ defined as the brightness observed when the efficiency dropped to half of the maximum value of the external quantum efficiency) was still better than that of Device 1 ($B_{1/2}$ = 37 000 cd m⁻²), which may have been due to the TADF of DCb-BPP. As for the TADF host, the efficiency roll-off of Device 2 ($B_{1/2}$ = 77 000 cd m⁻²) was the best, but its external quantum efficiency (EQE) was not the highest (EQE = 19.8%). The efficiency of Device 3 was still higher than that of Device 2 under 6000 cd m^{-2} . In Device 4, the doped TcTa was beneficial in that it improved the carrier balance in the emitting layer so that the recombination region became much wider. In addition, the TADF of DCb-BPP of the host mixture was still able to alleviate the efficiency roll-off caused by triplet-related annihilations. As a consequence, compared with the turn-on voltage of Device 3, that of Device 4 was slightly greater, but its efficiency roll-off was still much better ($B_{1/2} = 72\,000$ cd m⁻²), due to the improvement of carrier balance. Because of the low turn-on voltage, Device 3 and Device 4 achieved high maximum power efficiency (PE) values of 70 lm W⁻¹ and 74 lm W⁻¹, as shown in Fig. 4b. However, the maximum PE of Device 2 was only 52 lm W^{-1} due to the high turn-on voltage ($V_{\rm ON}$ = 2.85 V). The detailed performance measures of the devices are summarized in Table 1.

As can be seen in Fig. 4c, compared with the peak in the electroluminescence spectrum of Device 1, a 4 nm red-shift of the peak was discerned for Device 2. This shift was caused by the polarity of the TADF material with a D–A structure. At the same time, the red-shifts for Device 3 and Device 4 were each only 1 nm. This smaller red-shift was related to the molecular mass of DCb-BPP ($M_{\text{DCb-BPP}} = 680$) being smaller than that of DMAC-BPP ($M_{\text{DMAC-BPP}} = 762$). In general, a host with a smaller molecular mass could more effectively impede the rotation of a guest molecule, decreasing the red-shift.³¹

Simulation of annihilation in PHOLEDs

To investigate the effect of the annihilation process, which mainly involved triplet–triplet annihilation (TTA) and triplet-polaron annihilation (TPA), on the efficiency roll-off levels of the PHOLEDs, we simulated the contribution of the TTA and TPA to the efficiency loss of each PHOLED by solving the rate equations for the triplet and polaron density.³² As is shown in



Fig. 5 Simulated IQE, TTA, TPA, triplet density (N_t), and polaron density (N_p) plotted against current density for (a) Device 3 and (b) Device 4.

Fig. 5a, the efficiency loss of the DCb-BPP-based Device 3 was calculated to have been mainly caused by TPA. This result might be attributed to the asymmetric carrier transport ability of DCb-BPP. A decreased TPA was calculated for Device 4, compared to that of Device 3. This decease can be attributed to its balanced carrier transport properties. However, a more serious TTA was indicated for Device 4, and this result might be attributed to its higher triplet density. As shown in Fig. S3(c) (ESI⁺), Device 4 displays a higher N_t/N_p than Device 3, so that more triplets are formed in Device 4.

Stability levels of the devices

To assess the stability of the PHOLED based on the DCb-BPP host, we determined the operational lifetimes of the four devices under a constant current in atmospheric conditions (Fig. 6a). The experimental conditions were a temperature of 300 K and a 40% relative humidity of the air. Compared to the other three PHOLEDs, Device 3 shows a more than twenty times greater LT50 lifetime, of 424 h. The extended LT50 lifetime of Device 3 can be mainly attributed to the planar structure and weak electron-donating properties of the δ -carboline group, which improve molecular conjugation and reduce the likelihood of oxidation occurring. At the same time, the short initial lifetime (τ_0) led to efficient Förster resonance energy transfer, further decreasing the amount of time an exciton stays on the host. Thus, DCb-BPP remains excited for a shorter time. Besides this, compared with the HOMO/LUMO levels of CBP and DMAC-BPP, those of DCb-BPP are more suitable for TcTa and TmPyPB, leading to a shorter barrier in Device 3. In Device 1, hole-trapping on PO-01 and electron-transporting on CBP consume energy during carrier transport. In Device 2, there is a barrier between DMAC-BPP and TmPyPB, which improves the driving voltage and wastes energy. The wasted energy is eventually converted into heat, which is harmful to the stability of the devices. The luminances of

Table 1 Performances of	the	PHOLEDs
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	$V_{\rm on}/{ m V}$	$L_{\rm max}/{ m cd}~{ m m}^{-2}$	EQE ^{max/a/b/c} /%	$J_{1/2}$ /mA cm $^{-2}$	$B_{1/2}/cd m^{-2}$	
Device 1	2.97	110 000	22.9/21.9/17.6/4.8	108	37 000	
Device 2	2.85	116 000	19.8/19.7/17.9/8.2	256	77 000	
Device 3	2.37	120 000	21.5/20.6/17.7/6.3	162	52 000	
Device 4	2.56	174000	24.5/24.2/20.8/10.2	188	72 000	

Abbreviation: V_{on} : turn-on voltage. L_{max} : maximum luminance. EQE: external quantum efficiency. max/a/b/c: recorded at max luminance, 1000 cd m⁻², 10000 cd m⁻², and 100000 cd m⁻². $J_{1/2}$ ($B_{1/2}$): the current density (brightness) at which the quantum efficiency drops to half of the maximum value.



Fig. 6 (a) Luminance as a function of time for each device in the air without any protection, $L_0 = 1000$ cd m⁻². Inset: The changes in voltage relative to the initial value with time. (b) Cole–Cole plot of the impedance from the integrated OLED before (solid line) and after (dotted line with symbols) aging. Inset: The equivalent OLED circuit. (c) Transient decay spectra of undoped devices with DCb-BPP and DMAC-BPP EMLs both before and after stress was applied.

Device 2 (LT50 = 17 h) and Device 4 (LT50 = 12 h) were also seen to decrease very rapidly after 7 h, indicating that the degradation of the devices was not only caused by water and oxygen. Thus, we made a simple package for Device 2 and for Device 3, as shown in Fig. S4(a) (ESI⁺). After being packed, the LT50 of Device 2 increased by 35% and that of Device 3 increased by nearly 100%. The package did not make much difference for Device 2. Here, the intrinsic degradation of the host itself is apparently much faster than the erosion caused by water and oxygen from the environment. The lifetime of the device is more primarily determined by the stability levels of the materials. Although Device 4 shows the highest efficiency and lowest efficiency roll-off, the stability of TcTa did not lead to a long operational lifetime, which has been proved that the TcTa-related interface exciplex is much more stable than the TcTa-related bulk exciplex.33-35 When we selected CBP as the co-host with DCb-BPP, an LT50 of 271 h was achieved, which proves the stability of DCb-BPP, as shown in Fig. S4(b) (ESI⁺).

Impedance spectroscopy (IS) data of the devices at various modulation frequencies were collected using a small modulation of the signal ($V_{\rm rms}$ = 100 mV). The IS results revealed the degradation mechanism of devices to some degree. The aging process involved stressing the devices under 5 V for 12 h. Except for the emission layer (EML), the structures of these devices were the same. We acquired IS data from these devices both before and after applying stress. The Cole-Cole plot of the impedance of each device is shown in Fig. 6b and the detailed results are summarized in Table 2. At high frequency, the impedance (Z) of the device was approximately equal to the contact resistance (R_s) . As shown in Table 2, the R_s values were almost equal. At low frequency, $Z \approx R_{\rm s} + R_{\rm j}$, where $R_{\rm j}$ could reflect the carrier transport properties in the OLEDs.³⁶ The large changes in R_i (ΔR_i) of Device 2 and Device 4 indicate the significant change in the electrical properties of the aged

Table 2 IS test data of D1–D4

	LT50/h	$R_{ m s}/\Omega$	$R_{\rm j}/\Omega$	Aged- R_j/Ω	$\Delta R_{\rm j}/\Omega$
Device 1	21	50	356	642	286
Device 2	17	50	335	1505	1170
Device 3	424	51	248	328	80
Device 4	12	50	204	1091	887

DMAC-BPP and aged TcTa molecules. Device 3 shows the lowest ΔR_j value, providing further evidence for the electrical stability of DCb-BPP.

To further assess the stability, or lack thereof, of the acridine-based molecules, we acquired transient decay spectra of the undoped devices before and after applying stress. Here, the device structure was ITO/MoO₃ (3 nm)/TAPC (30 nm)/TcTa (5 nm)/host (20 nm)/TmPyPB (50 nm)/LiF (0.5 nm)/Mg:Ag (120 nm), and the host materials were DCb-BPP, DMAC-BPP, DMAC-BP, and DMAC-DPS, respectively. The aging process involved stressing the devices under 1.5 mA for 2 h. The microsecond level decay represented the delayed emission of TADF. As shown in Fig. 6c, there was almost no difference between the results obtained before and after application of stress for DCb-BPP, but the TADF of DMAC-BPP decreased obviously. DMAC-BP and DMAC-DPS displayed the same phenomena, as shown in Fig. S5 (ESI†).

Conclusion

A stable and efficient phosphorescent organic light-emitting device utilizing a δ -carboline-containing TADF-displaying host was demonstrated. The PHOLED based on a DCb-BPP host not only achieved high efficiency and low efficiency roll-off, but also a long operational lifetime. We attributed the enhancement of the lifetime to the planar structure and weak electron-donating property of δ -carboline, which improved molecular conjugation and reduced the likelihood of oxidation occurring. At the same time, the short initial lifetime and suitable energy levels also benefited the stability of the DCb-BPP-based PHOLEDs. The design concept of this stable material displaying TADF provides a promising method to achieve TADF-based OLEDs featuring high efficiency, low efficiency roll-off, and long operational lifetime values.

Experimental

Synthesis of 3,5-dibromobenzaldehyde (A)

A suspension of 1,3,5-tribromobenzene (4.0 g, 12.7 mmol) in anhydrous diethyl ether (100 mL) at -78 °C was treated dropwise with butyllithium (5.3 mL, 13.5 mmol). After 45 min, dimethylformamide (2.8 g, 38.3 mmol) was added to the mixture, which was then stirred for a further 1 h. Diluted HCl (40 mL, 2 mol L⁻¹) was added to the stirred mixture, and then organic phase was removed, and a brown solid was obtained. The crude product was recrystallized from diethyl ether/hexane to give needles for compound 1 (2.4 g, 70%). 3,5-Dibromobenzaldehyde (1), yield (2.4 g, 70%). ¹H NMR: δ (CDCl₃, ppm): 9.91, s, 1H, CHO, 7.94, (d, 2H, Ar-H), 7.92, (t, 1H, Ar-H).

Synthesis of 2-propen-1-one,1-[1,1'-biphenyl]-4-yl-3-(3,5-dibromophenyl) (C)

Into 1300 mL of ethanol, 50.8 g (192 mmol) of 3,5-dibromobenzaldehyde and 37.8 g (192 mmol) of 4-acetylbiphenyl were added. The mixture was stirred at room temperature and then an aqueous solution of 14.2 g (356 mmol) of sodium hydroxide in 70 mL of water was gradually dropped into the reaction solution. After stirring for 2 h at room temperature, the reaction solution was allowed to stand overnight. The precipitate was collected by performing filtration, dispersed in water and then in ethanol for washing, and afterwards vacuum dried to obtain 82.9 g (99% yield) of the desired chalcone compound as a pale yellow solid. ¹H NMR: δ (CDCl₃, ppm): 8.10–8.12, d, 1H, 8.02–8.04, (d, *J* = 1.6 Hz, 2H, Ar-H), 7.62–7.75, (m, 8H), 7.25–7.58 (m, 4H).

Synthesis of pyrimidine, 4-[1,1'-biphenyl]-4-yl-6-(3,5-dibromophenyl)-2-phenyl (E)

Into 1000 mL ethanol, 82.8 g (187 mmol) of compound C and 30.2 g (192 mmol) of benzamidine hydrochloride (D) were added. The mixture was stirred at room temperature and then an aqueous solution of 15.2 g (374 mmol) of sodium hydroxide in 70 mL of water was gradually dropped into the reaction solution. After stirring for 8 h at room temperature, the reaction solution was allowed to stand overnight. The precipitate was collected by filtration, dispersed in water and then ethanol for washing, and vacuum dried, to obtain 46.9 g (55% yield) of the aimed chalcone compound as a pale white solid. ¹H NMR: δ (CDCl₃, ppm): 8.72–8.73, d, 2H, 8.36–8.44, (d, 4H), 8.01–8.04, (d, 1H), 7.98 (s, 1H), 7.79–7.84 (m, 3H), 7.69–7.71 (m, 3H), 7.26–7.57 (m, 12H).

Synthesis of DCb-BPP. 5,5'-[5-(6-[1,1'-biphenyl]-4-yl-2-phenyl-4pyrimidinyl)-1,3-phenylene]bis-5*H*-pyrido[3,2-*b*]indole

Into a 1000 mL flask, 46.2 g (85.2 mmol) of compound E, 34.2 g (204 mmol) of 5H-pyrido[3,2-b]indole, 1.6 g (8.5 mmol) of CuI and 54.3 g (256 mmol) of K_3PO_4 were added. After replacing the inner atmosphere with Ar gas, a volume of 300 mL of dry 1,4-dioxane was added into the flask. The temperature was raised to 70 °C and the contents were stirred. To the reaction liquid was added 1.9 g (17.4 mmol) of trans-1,2-cyclohexanediamine, and the resulting mixture was heated at the reflux temperature for 24 h. The resulting reaction liquid was concentrated, the precipitated solid was dissolved in toluene, and the insolubles were removed using filtration. The collected filtrate was concentrated under pressure. The precipitated solid was recrystallized twice from toluene, and a mass of 40 g (70% yield) of yellow solid was obtained. ¹H NMR: δ (CDCl₃, ppm): 8.70, (d, 2H,), 8.58, (s, 2H), 8.41 (d, 2H), 8.13 (s, 1H), 7.75 (d, 2H), 7.71 (d, 2H), 7.51 (m, 10H), 6.78-7.21 (m, 10H), 1.71 (s, 12H).

Device fabrication

 MoO_3 and LiF powder, and small-molecule organic materials 1,1-bis[(di-4-tolylamino)phenyl]cyclohexane (TAPC), 4,4',4"-tris-(carbazol-9-yl)triphenylamine (TCTA), and 1,3,5-tri(*m*-pyrid-3-yl-phenyl)benzene (TmPyPB) were purchased from Luminescence Technology Corporation, while yellow phosphor iridium(III)

bis(4-phenylthieno[3,2-c]pyridinato-N,C²)acetylacetonate (PO-01) was obtained from Xi'an p-OLED. In the work described in this paper, all of the devices were fabricated on ITO-coated glass substrates. Before depositing the function film, the substrates were cleaned. First, the substrates were rinsed with Decon 90, swelled with deionized water, put in deionized water cleaning for ultrasonic cleaning three times, each time for 5 min, dried in an oven at 120 °C for 10 min, and finally processed in a plasma cleaner chamber (PDC-32G, Harrick) for 5 min. At last, organic layers and cathode materials were deposited on the substrates sequentially under vacuum of 5.0×10^{-4} Pa. The deposition rates for MoO₃, the organic layer and LiF were 0.2–0.5 Å s⁻¹, 1–2 Å s⁻¹, and 0.1-0.3 Å s⁻¹, respectively. The metal electrode was evaporated at a rate of 1.5–2.0 Å s^{-1} . The cathode was defined using shadow masks and coated with ITO to make four completely consistent 10 mm² devices on every substrate.

Characterization and device measurements

Voltage-current-brightness curves and electroluminescence spectra of the unprotected devices were acquired using a Goniophotometric Measurement System based on a spectrometer (GP-500, Otsuka Electronics Co. Osaka, Japan) and with a test condition of being in the air at room temperature simultaneously. The PL decay was measured by using an imaging spectrometer (HORIBA, IHR320, Japan). The operational lifetime was measured by using an OLED aging tester (Shanghai University, ZJZCL-1, China).

Conflicts of interest

The authors declare no conflict of interest.

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Notes and references

- 1 M. G. Helander, Z. B. Wang, J. Qiu, M. T. Greiner, D. P. Puzzo, Z. W. Liu and Z. H. Lu, *Science*, 2011, 332, 944–947.
- 2 Z. W. Yu, J. X. Zhang, S. H. Liu, L. T. Zhang, Y. Zhao,
 H. Y. Zhao and W. F. Xie, ACS Appl. Mater. Interfaces, 2019, 11, 6292–6301.
- 3 X. Zhang, S. H. Liu, L. T. Zhang and W. F. Xie, *Adv. Opt. Mater.*, 2019, 7, 1800857.
- 4 Z. W. Yu, H. W. Feng, J. X. Zhang, S. H. Liu, Y. Zhao,
 L. T. Zhang and W. F. Xie, *J. Mater. Chem. C*, 2019, 7, 9301–9307.
- 5 K. H. Kim, J. L. Liao, S. W. Lee, B. Sim, C. K. Moon, G. H. Lee, H. J. Kim, Y. Chi and J. J. Kim, *Adv. Mater.*, 2016, 28, 2526–2532.

- 6 S. H. Liu, H. W. Yu, Q. Y. Zhang, F. S. Qin, X. Zhang,
 L. T. Zhang and W. F. Xie, *J. Mater. Chem. C*, 2019, 7, 5426–5432.
- 7 K. T. Ly, R. W. Chen-Cheng, H. W. Lin, Y. J. Shiau, S. H. Liu,
 P. T. Chou, C. S. Tsao, Y. C. Huang and Y. Chi, *Nat. Photonics*, 2017, **11**, 63–68.
- 8 J. X. Zhang, X. Zhang, H. W. Feng, Z. W. Yu, J. M. Zhang, S. H. Liu, L. T. Zhang and W. F. Xie, *J. Mater. Chem. C*, 2019, 7, 1991–1998.
- 9 K. H. Kim, S. Lee, C. K. Moon, S. Y. Kim, Y. S. Park, J. H. Lee, J. W. Lee, J. Huh, Y. You and J. J. Kim, *Nat. Commun.*, 2013, 5, 4769.
- 10 X. Zhang, T. Pan, J. X. Zhang, L. T. Zhang, S. H. Liu and W. F. Xie, ACS Photonics, 2019, 6, 2350–2357.
- 11 C. Y. Xiang, W. Koo, F. So, H. Sasabe and J. Kido, *Light: Sci. Appl.*, 2013, **2**, e74.
- 12 C. Adachi, Jpn. J. Appl. Phys., 2014, 53, 060101.
- A. Tsuboyama, H. Iwawaki, M. Fruugori, T. Mukaide, J. Kamatani, S. Igawa, T. Moriyama, S. Miura, T. Takiguchi, S. Okada, M. Hoshino and K. Ueno, *J. Am. Chem. Soc.*, 2003, 42, 12971–12979.
- 14 T. Hatakeyama, K. Shiren, K. Nakajima, S. Nomura, S. Nakatsuka, K. Kinoshita, J. Ni, Y. Ono and T. Ikuta, *Adv. Mater.*, 2016, 28, 2777–2781.
- 15 J. Sun, K. Kim, C. Moon, J. Lee and J. Kim, *ACS Appl. Mater. Interfaces*, 2016, **8**, 9806–9810.
- 16 D. F. O'Brien, M. A. Baldo, M. E. Thompson and S. R. Forrest, *Appl. Phys. Lett.*, 1999, 74, 442–444.
- 17 H. Tanaka, K. Shizu, H. Miyazaki and C. Adachi, *Chem. Commun.*, 2012, **48**, 11392–11394.
- 18 Q. Zhang, J. Li, K. Shizu, S. Huang, S. Hirata, H. Miyazaki and C. Adachi, *J. Am. Chem. Soc.*, 2012, **134**, 14706–14709.
- 19 T. L. Wu, M. J. Huang, C. C. Lin, P. Y. Huang, T. Y. Chou, R. W. Chen-Cheng, H. W. Lin, R. S. Liu and C. H. Cheng, *Nat. Photonics*, 2018, **12**, 235–240.
- 20 G. Mehes, H. Nomura, Q. Zhang, T. Nakagawa and C. Adachi, *Angew. Chem., Int. Ed.*, 2012, **51**, 11311–11315.

- 21 C. Li, L. Duan, D. Zhang and Y. Qiu, ACS Appl. Mater. Interfaces, 2015, 7, 15154–15159.
- 22 H. Wang, L. Q. Meng, X. X. Shen, X. F. Wei, X. L. Zheng, X. P. Lv, Y. P. Yi, Y. Wang and P. F. Wang, *Adv. Mater.*, 2015, 27, 4041–4047.
- K. P. Guo, H. D. Wang, Z. X. Wang, C. F. Si, C. Y. Peng, G. Chen, J. H. Zhang, G. F. Wang and B. Wei, *Chem. Sci.*, 2017, 8, 1259–1268.
- Y. Tao, K. Yuan, T. Chen, P. Xu, H. H. Li, R. F. Chen, C. Zheng,
 L. Zhang and W. Huang, *Adv. Mater.*, 2014, 26, 7931–7958.
- 25 J. H. Kim, M. Eum, T. H. Kim and J. Y. Lee, *Dyes Pigm.*, 2017, 136, 529–534.
- 26 Q. S. Zhang, D. Tsang, H. Kuwabara, Y. Hatae, B. Li, T. Takahashi, S. Y. Lee, T. Yasuda and C. Adachi, *Adv. Mater.*, 2015, 27, 2096–2100.
- 27 D. D. Zhang, L. Duan, Y. L. Li, H. Y. Li, Z. Y. Bin, D. Q. Zhang, J. Qiao, G. F. Dong, L. D. Wang and Y. Qiu, *Adv. Funct. Mater.*, 2014, 24, 3551–3561.
- 28 H. Wang, C. X. Zang, G. G. Shan, Z. W. Yu, S. H. Liu, L. T. Zhang, W. F. Xie and H. Y. Zhao, *Adv. Opt. Mater.*, 2019, 7, 1801718.
- 29 J. S. Kang, T. R. Hong, H. J. Kim, Y. H. Son, R. Lampande, B. Y. Kang, C. Lee, J. K. Bin, B. S. Lee and J. H. Yang, *J. Mater. Chem. C*, 2016, 4, 4512–4520.
- 30 G. H. Kim, R. Lampande, J. B. Im, J. M. Lee, J. Y. Lee and J. H. Kwon, *Mater. Horiz.*, 2017, 4, 619–624.
- 31 C. Deng, L. Zhang, D. Wang, T. Tsuboi and Q. Zhang, *Adv. Opt. Mater.*, 2019, **7**, 1801644.
- 32 X. M. Peng, H. W. Feng, J. X. Zhang, S. H. Liu, L. T. Zhang and W. F. Xie, *Nanoscale Res. Lett.*, 2018, **13**, 310.
- 33 S. Scholz, D. Kondakov, B. Lüssem and K. Leo, *Chem. Rev.*, 2015, **115**, 8449–8503.
- 34 F. So and D. Kondakov, Adv. Mater., 2010, 22, 3762-3777.
- 35 D. D. Zhang, M. H. Cai, Y. G. Zhang, Z. Y. Bin, D. Q. Zhang and L. Duan, ACS Appl. Mater. Interfaces, 2016, 8, 3825–3832.
- 36 G. W. Lee, H. Kim, J. Park, J. I. Shim and D. S. Shin, *IEEE*, 2018, **30**, 1183–1185.