Electronic Supplementary Information (ESI)

Materials and Instruments

All the chemicals and reagents were purchased from commercial sources and used as received without further purification. ^{1}H and ^{13}C NMR spectra were measured on a Bruker AV 500 spectrometer in $CDCl_3$ at room temperature. High resolution mass spectra (HRMS) were recorded on a GCT premier CAB048 mass spectrometer operating in MALDI-TOF mode. Single crystals of CC6-DBP-PXZ were grown in CH_2Cl_2-methanol mixtures and single crystal X-ray diffraction intensity data were collected at 173 K on a Bruker–Nonices Smart Apex CCD diffractometer with graphite monochromated MoKα radiation. Processing of the intensity data was carried out using the SAINT and SADABS routines, and the structure and refinement were conducted using the SHELTL suite of X-ray programs (version 6.10). UV-vis absorption spectra were measured on a Shimadzu UV-2600 spectrophotometer. PL spectra were recorded on a Horiba Fluoromax-4 spectrofluorometer. PL quantum yields were measured using a Hamamatsu absolute PL quantum yield spectrometer C11347 Quantaurus_QY. The ground-state geometries were optimized using the density function theory (DFT) method with BMK hybrid functional at the basis set level of 6-31G*, and then the ΔE_{ST} values were calculated by time-dependent DFT (TDDFT) method at the same level. All the calculations were performed using Gaussian09 package.

Additional Spectra

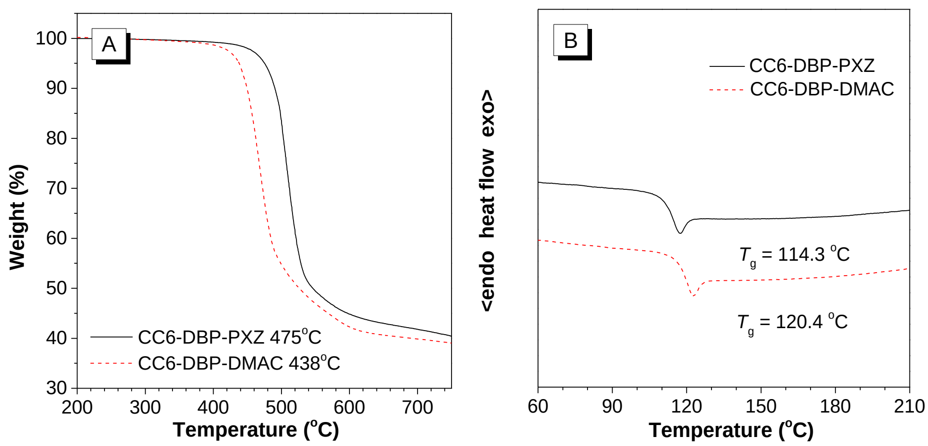

Fig. S1 (A) TGA and (B) DSC thermograms of CC6-DBP-PXZ and CC6-DBP-DMAC, measured under nitrogen at a heating rate of 20 and 10 °C min^{-1}, respectively.

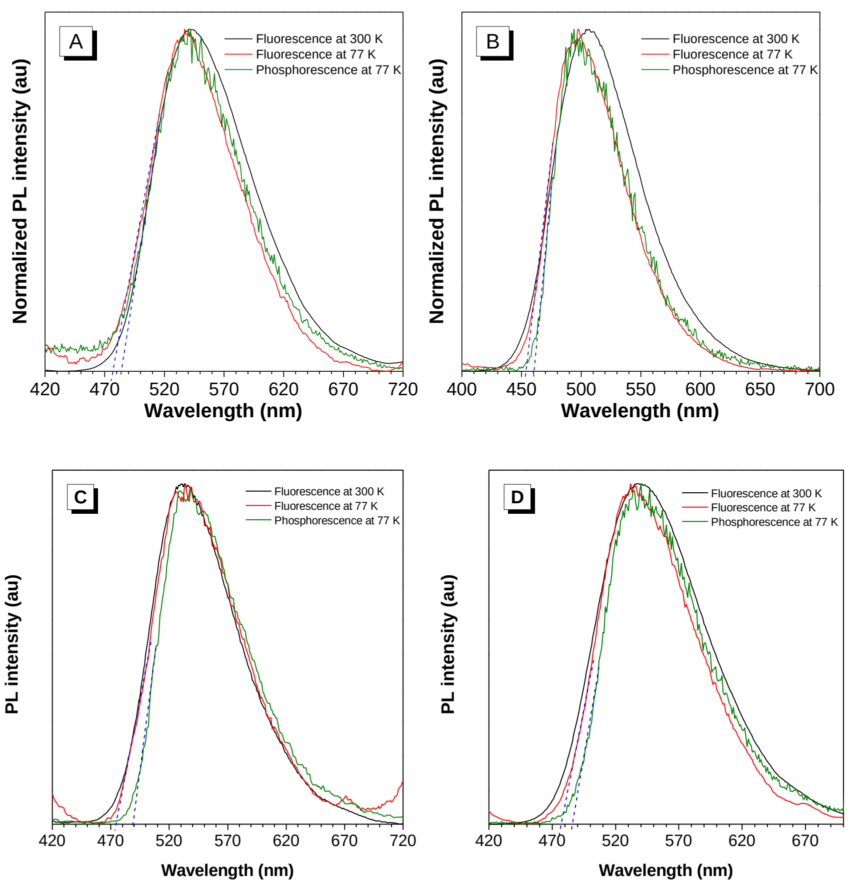

Fig. S2 Fluorescence and phosphorescence spectra of (A) CC6-DBP-PXZ neat film, (B) CC6-DBP-DMAC neat film, (C) 30 wt% CC6-DBP-PXZ:CBP doped film and (D) 30 wt% CC6-DBP-DMAC:CBP doped film.

Estimation of Basic Photophysical Data

The quantum efficiencies and rate constants were determined using the following equations according to the following equations:

$\Phi_{prompt} = \Phi_F R_{prompt}$ (1)

$\Phi_{delayed} = \Phi_F R_{delayed}$ (2)

$k_F = \Phi_{prompt}/\tau_{prompt}$ (3)

$\Phi_F = k_F/(k_F + k_{IC})$ (4)

$\Phi_{prompt} = k_F/(k_F + k_{IC} + k_{ISC})$ (5)

$\Phi_{IC} = k_{IC}/(k_F + k_{IC} + k_{ISC})$ (6)

$\Phi_{ISC} = k_{ISC}/(k_F + k_{IC} + k_{ISC}) = 1 - \Phi_{prompt} - \Phi_{IC}$ (7)

$\Phi_{RISC} = \Phi_{delayed}/\Phi_{ISC}$ (8)

$k_{RISC} = (k_p k_d \Phi_{delayed})/(k_{ISC}\Phi_{prompt})$ (9)

$k_p = 1/\tau_{prompt}$; $k_d = 1/\tau_{delayed}$ (10)

Table S1. Transient PL decay data of THF solutions and neat films of CC6-DBP-PXZ and CC6-DBP-DMAC at 300 K under nitrogen.[a]

compound	state	$<\tau>$ (ns)	τ_1 (ns)	τ_2 (ns)	A_1	A_2	R_{prompt} (%)	$R_{delayed}$ (%)
CC6-DBP-PXZ	THF solution	2.0	1.9	28.6	61783	15.048	~100	~0
	neat film	244.9	22.9	1212.8	40350.8	175.0	81	19
CC6-DBP-DMAC	THF solution	60.7	19.7	217.2	6505.02	154.58	79	21
	neat film	1294.8	25.7	2882.1	31778	226.3	56	44

[a] The transient PL decay data were fitted by multiple-exponential function and the mean fluorescence lifetimes ($<\tau>$) were calculated by $<\tau> = \Sigma A_i\tau_i^2/\Sigma A_i\tau_i$, where A_i is the pre-exponential for lifetime τ_i. R_{prompt} and $R_{delayed}$ are individual component ratio for prompt and delayed fluorescence. $R_{prompt} = \tau_1 A_1/(\tau_1 A_1 + \tau_2 A_2 + \tau_3 A_3)$, $R_{delayed} = 1 - R_{prompt}$.

Table S2. Photophysical data of neat films and doped films in CBP (30 wt%) of CC6-BP-PXZ and CC6-BP-DMAC.[a]

	CC6-DBP-PXZ		CC6-DBP-DMAC	
	neat film	30 wt% in CBP	neat film	30 wt% in CBP
Φ_F (%)	38.3	59.0	59.5	69.1
τ_{prompt} (ns)	22.9	24.5	25.7	29.4
$\tau_{delayed}$ (μs)	1.2	1.6	2.9	6.4
$R_{delayed}$ (%)	19.0	28.6	44.0	43.4
Φ_{prompt} (%)	31.0	37.8	33.3	39.1
$\Phi_{delayed}$ (%)	7.3	15.2	26.2	30.0
Φ_{ISC} (%)	19.0	28.6	44.0	43.4
Φ_{RISC} (%)	38.4	53.0	59.5	69.1
k_F ($\times 10^6$ s^{-1})	13.5	15.4	13.0	13.3
k_{IC} ($\times 10^6$ s^{-1})	21.8	13.7	8.8	5.9
k_{ISC} ($\times 10^6$ s^{-1})	8.3	11.7	17.1	14.7
k_{RISC} ($\times 10^6$ s^{-1})	3.2	3.3	2.1	1.1

[a] Abbreviations: Φ_{PL} = absolute photoluminescence quantum yield; τ_{prompt} and $\tau_{delayed}$ = lifetimes calculated from the prompt and delayed fluorescence decay, respectively; $R_{delayed}$ = the ratio of delayed components; Φ_{prompt} and $\Phi_{delayed}$ = fluorescent and delayed components, respectively, determined from the total Φ_{PL} and the proportion of the integrated area of each of the components in the transient spectra to the total integrated area; Φ_{ISC} = the intersystem crossing quantum yield; K_F = fluorescence decay rate; K_{IC} = internal conversion decay rate from S_1 to S_0; K_{ISC} = intersystem crossing decay rate from S_1 to T_1; K_{RISC} = the rate constant of reverse intersystem crossing process.

Table S3. The theoretically calculated maximum η_{ext} values for nondoped OLEDs of CC6-DBP-PXZ and CC6-DBP-DMAC.

	Φ_{prompt} (%)	Φ_{ISC} (%)	Φ_{RISC} (%)	η_{ext}[a] (%)	η_{ext}[b] (%)
CC6-DBP-PXZ	31.0	19.0	38.4	7.7-11.5	7.73
CC6-DBP-DMAC	33.3	44.0	59.5	12.8-19.2	9.02

[a] Theoretical maximum η_{ext} values, calculated according to the following equations (1) and (2):

$$\eta_{ext} = \eta_{int} \times \eta_{out} \quad (1)$$

$$\eta_{int} = \gamma \times [\eta_S \times \Phi_{prompt} + (\eta_S \times \Phi_{ISC} + \eta_T) \times \Phi_{RISC}] \quad (2)$$

where η_{int} denotes the internal quantum efficiency, η_{out} is the optical out-coupling factor (typically 0.2~0.3), γ is the charge balance factor (ideally γ = 1.0), and η_S and η_T are the fractions of singlet and triplet excitons (25% and 75%, respectively).

[b] Experimental maximum η_{ext} values.