**Supplementary Information**

**Thermally activated delayed fluorescence emitters with a \(m,m\)-di-\(\text{tert}\)-butyl-carbazolyl benzoylpyridine core achieving extremely high blue electroluminescence efficiencies**

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**General Information**

The \(^1\)H and \(^{13}\)C NMR spectra were recorded by using Varian mercury 400 spectrometer. The HRMS were measured using MAT-95XL HRMS or MStation. The UV-visible absorption spectra were taken on a Hitachi U-3300 spectrophotometer. Fluorescence and phosphorescence spectra were recorded on a Hitachi F-7000 spectrophotometer. The decomposition temperature was determined by TGA using TG/DTA Seiko SSC-5200 instrument. Transient PL measurement of the materials in solution were obtained using 355 nm pulsed laser (Nd:YAG laser, INDI-40-10, Spectra-Physics) as the excitation source and the sample was excited by the optical fiber (77532, Newport Corp). A highpass filter (GG-400-25.4, Lamda) at 410 nm in front of the photodiode (DET10A/M, Thorlabs) was used to prevent the scattering of 355-nm laser. The electronic signal was recorded by an oscilloscope (WaveSurfer 24MXs-B, LeCroy). The absolute PL quantum efficiency of the doped films were determined using an integrating sphere under \(\text{N}_2\) atmosphere. The electrochemical properties were measured by using CH Instruments 600A electrochemical analyzer. The oxidation measurements were measured using a glassy carbon electrode as the
working electrode, an Ag/Ag⁺ (0.01 M AgNO₃) as the reference electrode and a Pt wire as the counter electrode in dichloromethane. The HOMO energy level were determined from the onset of the oxidation potential using the equation -(4.8 eV + E_{ox} (vs Fc_{ox})).

**DFT Calculation**

Molecular geometry optimizations and electronic properties were carried out by using the Gaussian 03 program with density functional theory (DFT) and time-dependent DFT (TDDFT) calculations in which the Becke’s three parameter functional combined with Lee, Yang, and Parr’s correlation functional (B3LYP) hybrid exchange-correlation functional with the 6-31G* basic set were used.¹ The molecular orbitals were visualized using Gaussview 4.1 software.

**OLEDs Fabrication and Measurement**

The organic materials used in device fabrication were purified by sublimation. Devices were fabricated by vacuum deposition onto pre-coated ITO glass with sheet resistance of 15 Ω/square at a pressure lower than 10⁻⁶ Torr. The organic materials were deposited at the rate of 0.5~1.2 Å s⁻¹. LiF and Al were deposited at the rate of 0.1 Å s⁻¹, 3-10 Å s⁻¹, respectively. The rest of the procedures are similar to the reported method.²

The transient EL measurements were carried out on a function generator (Agilent 8114A) and an indigenously developed time-resolved emission spectrometer. The devices were driven by a voltage pulse 6 V with a repetition rate of 20 kHz and pulse width of 10 μs. The emission decay curves at specific wavelengths were gained using a cooled photomultiplier tube (PMT) detector (Becker & Hickl GmbH PMC-100) integrated with a 300 nm focal length monochromator (Princeton Instruments Acton SP2300). The time-resolved photon counting was done via a multi-channel scaling (MCS) card (Becker & Hickl GmbH MSA-300) with a time resolution of 5 ns.
The whole system was synchronized with a digital delay generator (Stanford Research Systems DG645).

**Table S1.** Main transitions and electron contour plots of molecular orbitals of 4BPy-\textit{m}DTC

<table>
<thead>
<tr>
<th>Transition</th>
<th>Orbitals</th>
<th>Probabilities</th>
<th>(f^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(S_0\rightarrow S_1)</td>
<td>HOMO→LUMO, HOMO-1→LUMO</td>
<td>0.67741, 0.18881</td>
<td>0.0185</td>
</tr>
<tr>
<td>(S_0\rightarrow S_2)</td>
<td>HOMO→LUMO</td>
<td>0.19037, 0.67830</td>
<td>0.0079</td>
</tr>
<tr>
<td>(S_0\rightarrow S_6)</td>
<td>HOMO→LUMO+1, HOMO→LUMO+2, HOMO-1→LUMO+1, HOMO-1→LUMO+2</td>
<td>0.49121, 0.30790, 0.29808, 0.24116</td>
<td>0.2187</td>
</tr>
</tbody>
</table>

\[\text{Diagram:}
\begin{align*}
\text{HOMO} & \quad \text{HOMO-1} & \quad \text{LUMO} & \quad \text{LUMO+1} & \quad \text{LUMO+2} \\
\end{align*}\]

**Table S2.** Main transitions and electron contour plots of molecular orbitals of 3BPy-\textit{m}DTC

<table>
<thead>
<tr>
<th>Transition</th>
<th>Orbitals</th>
<th>Probabilities</th>
<th>(f^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(S_0\rightarrow S_1)</td>
<td>HOMO→LUMO, HOMO-1→LUMO</td>
<td>0.66142, 0.23662</td>
<td>0.0231</td>
</tr>
<tr>
<td>(S_0\rightarrow S_2)</td>
<td>HOMO→LUMO</td>
<td>0.23857, 0.66268</td>
<td>0.0056</td>
</tr>
<tr>
<td>(S_0\rightarrow S_6)</td>
<td>HOMO→LUMO+1, HOMO→LUMO+2, HOMO→LUMO+4, HOMO-1→LUMO+1, HOMO-1→LUMO+2</td>
<td>0.36942, 0.27188, 0.20215, 0.37119, 0.24757, 0.19548</td>
<td>0.2152</td>
</tr>
</tbody>
</table>
Table S3. Main transitions and electron contour plots of molecular orbitals of 2BPy-mDTC

<table>
<thead>
<tr>
<th>Transition</th>
<th>Orbitals</th>
<th>Probabilities</th>
<th>$f^a$</th>
</tr>
</thead>
</table>
| $S_0 \rightarrow S_1$ | HOMO→LUMO  
HOMO-1→LUMO | 0.67045  
0.21482 | 0.0105 |
| $S_0 \rightarrow S_2$ | HOMO→LUMO  
HOMO-1→LUMO | 0.21511  
0.67151 | 0.0043 |
| $S_0 \rightarrow S_6$ | HOMO→LUMO+1  
HOMO→LUMO+2  
HOMO-1→LUMO+1 | 0.50359  
0.10802  
0.46807 | 0.0284 |
Table S4. Main transitions and electron contour plots of molecular orbitals of BP-mDTC

<table>
<thead>
<tr>
<th>Transition</th>
<th>Orbitals</th>
<th>Probabilities</th>
<th>$f^a$</th>
</tr>
</thead>
</table>
| $S_0 \rightarrow S_1$ | HOMO→LUMO  
HOMO-1→LUMO | 0.68062  
0.17147 | 0.0250 |
| $S_0 \rightarrow S_2$ | HOMO→LUMO  
HOMO-1→LUMO | 0.17480  
0.68138 | 0.0093 |
| $S_0 \rightarrow S_6$ | HOMO→LUMO+1  
HOMO-1→LUMO+1 | 0.55396  
0.40185 | 0.2362 |

Fig. S1 Absorption (Abs.) and fluorescence (Fl.) spectra of 3BPymDTC (a) and 2BPymDTC (b) in toluene ($10^{-5}$ M) solution measured at room temperature and phosphorescence (Phos.) spectra in toluene ($10^{-5}$ M) measured at 77 K.
Fig. S2 Absorbance spectra and fluorescence spectra of 4BPy-\textit{m}DTC (a and b), 3BPy-\textit{m}DTC (c and d) 2BPy-\textit{m}DTC (e and f) and BP-\textit{m}DTC (g and h) in various solvents at RT (10^{-5} \text{ M}).
**Fig. S3** Oxidization potentials of a) 4BPy-\textit{m}DTC, b) 3BPy-\textit{m}DTC, c) 2BPy-\textit{m}DTC and d) BP-\textit{m}DTC and were measured in 10^{-3} \text{ M} DCM. The electrode potentials were measured versus Ag/Ag\textsuperscript{+} electrode.
**Fig. S4** Fluorescence (Fl.) and phosphorescence (Phos.) spectra of 7 wt% a) 4BPy-mDTC, b) 3BPy-mDTC, c) 2BPy-mDTC and d) BP-mDTC doped in mCBP films. Fluorescence spectra were measured at room temperature and phosphorescence spectra were measured at 77 K.

**Fig. S5** The thermogravimetric thermograms of 4BPy-mDTC, 3BPy-mDTC, 2BPy-mDTC and BP-mDTC.

**Fig. S6** Transient PL characteristics of co-doped films (7 wt% 4BPy-mDTC, 3BPy-mDTC, or 2BPy-mDTC doped in mCBP host) at 300 K.
Fig. S7 Structures of the materials used in devices and schematic representation of devices A-E.

Fig. S8 a) The current efficiency vs luminance, b) power efficiency vs luminance of devices A-D.

Fig. S9 El spectra at various voltages of a) device A, b) device B, c) device C, and d) device D.
**Fig. S10** a) EQE vs luminance and b) electroluminescence spectra of device E.

**Fig. S11** Transient electroluminescence characteristics of devices B and C.
Fig. S12 Chromatograms of HPLC analysis of a) 4BPy-\textit{m}DTC, b) 3BPy-\textit{m}DTC, c) 2BPy-\textit{m}DTC and d) BP-\textit{m}DTC.

References