Supplementary Information

Effect of bipolar charge transport of derivatives of 1phenyl-1H-benzo[d]imidazole with horizontal molecular orientation on the performance of OLEDs based on thermally activated delayed fluorescence or phosphorescence

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Instrumentation

Chemical composition of synthesized compounds was investigated via 1H (400 MHz) and 13C (101 MHz) NMR spectroscopy, the NMR spectra were recorded with Bruker Avance III apparatus. NMR samples were prepared according to general procedure: 25 mg of compound was dissolved in 0.6 ml of deuterated solvent (dimethyl sulfoxide or chloroform). Mass spectra were recorded with Waters ZQ 2000 apparatus.

Thermal characteristics of synthesized compounds were studied using TA Instruments DSC Q2000 series thermal analyzer for differential scanning colorimetry (DSC) and TA Instruments TGA Q50 apparatus for thermogravimetric analysis (TGA). The sample heating rate for DSC experiments was 10 °C/min under N2 flow, the sample heating rate for TGA experiments was 20 °C/min under N2 flow.

Cyclic voltammetry (CV) measurements were performed utilizing Bio-Logic SAS and a micro-AUTOLAB Type III apparatus. Electrode structures were used as follows: Pt for the counter electrode (CE), Ag for the reference electrode (RE), and C for the working electrode (WE). Tetrabutylammonium hexafluorophosphate (0.1M) in dry CH2Cl2 was used as the electrolyte solution.

Absorption spectra were recorded using Avantes AvaSpec-2048X spectrometer. Photoluminescence spectra were recorded using Edinburgh Instruments FLS980 Fluorescence Spectrometer. Photoluminescence quantum yields were measured in air by the absolute method using an integrated sphere and FLS980. Photoluminescence decay curves were recorded using FLS980 and the microsecond lamp or PicoQuant LDH-D-C-375 laser with the excitation wavelength of 374 nm as a source of photoexcitation. Photophysical measurements at different temperatures were done using the Oxford Instruments OptistatDN-2 cryostat.

Charge-transporting properties of vacuum-deposited films of 1tCzBzCN and 2tCzBzCN were studied by the time-of-flight (TOF) method at room temperature 57. The sample configuration was indium tin oxide (ITO) /organic layer/Al. The thicknesses (d) of the layers of 1tCzBzCN and 2tCzBzCN were measured by ProFilm3D profilometer (Figure S7). A laser (EKSPLA) with a wavelength of 355 nm, the precision 6517B electrometer (Keithley), and the TDS 3032C oscilloscope (Tektronix) were used in the TOF setup. The samples were excited by the laser from the ITO side. Positive or negative voltages (V) were applied to ITO to record hole carrier transients with visible transit times (ttr) at the different electric fields (E). Hole and electron mobilities (μ h) of 1tCzBzCN and 2tCzBzCN were calculated using the formula μ h = d2 / (V × ttr).

Computational strategies

Quantum chemical calculations were performed to gain comprehensive insights into the groundstate and excited-state properties of the developed compounds, employing a combination of density functional theory (DFT) and time-dependent DFT (TD-DFT) methodologies. These calculations provided valuable information on electronic structures, energy levels, and transitions, which are critical for understanding the photophysical behavior of the compounds. The electronic structure optimization of the compounds in their ground state was conducted using the widely recognized B3LYP functional which combines the exchange functional of Becke¹ and the correlation functional of Lee, Yang, and Parr², paired with the 6-31G** basis set³. These calculations were carried out using the Gaussian program⁴. To investigate excited-state properties and photophysical transitions, the TD-DFT approach was employed with the range-separated functional LC- ω PBE⁵, with 6-31G^{**} basis set. This functional is particularly suitable for capturing long-range electronic effects, which are often pivotal in charge-transfer systems. The range separation parameter " ω " is tuned for the gaseous medium. The tuned ω value is 0.178 Bohr⁻¹ for 1tCzBzCN and 0.155 Bohr⁻¹ for 2tCzBzCN. Spin-orbit coupling (SOC) matrix element between first singlet and triplets below first singlet $(S_1|Hso|T_n)$ are computed using $\omega B97XD^6$ functional and same 6-31G** basis set implemented in ORCA program ^{7,8}. The ωB97XD functional was chosen for its excellent performance in describing dispersion interactions and excited-state properties, ensuring accurate SOC predictions critical for understanding the delayed fluorescence mechanisms of compounds.



Figure S1. PL decay curves of the deoxygenated toluene solutions of compounds 1tCzBzCN (a) and 2tCzBzCN (b)



Figure S2. PL decay curves of the films of 1tCzBzCN and 2tCzBzCN measured in vacuum.



Figure S3. PL spectra of the films of the compounds 1tCzBzCN (a) and 2tCzBzCN (b) measured in air and vacuum.



Figure S4. PL spectra of the films of the compounds **1tCzBzCN** (a) and **2tCzBzCN** (b) measured in Argon at various temperatures.



Figure S5. Natural transition orbitals of selected excited states of 1tCzBzCN and 2tCzBzCN at TD/LC- ω *PBE/6-31G(d,p) theoretical level (tuned ω in gaseous medium).



Figure S6. Energy levels of S₁ and triplets below S₁ excited states with their computed spin-orbit coupling values for compounds at TD/LC- ω *PBE/6-31G(d,p). **Abbreviations:** benzonitrile (BN), benzoimidazole (BzIm) *tert*-butyl carbazole (tBCz),



Figure S7. Interaction of 2tCzBzCN with picric acid and their molecular orbitals at LC- $\omega PBE/6-31G(d,p)$ level.







Figure S8 PLQY measurement of the films of the molecular mixtures of Ir(ppy)₂acac (10 wt.%) and compounds **1tCzBzCN** (a), **2tCzBzCN** (b).



Figure S9. TOF transients of vacuum-deposited film of the compound **2tCzBzCN** under applied negative voltages for electrons at optically transparent electrode ITO.





(b)

Figure S10. Thicknesses measurement data of TOF samples of the compounds 1tCzBzCN (a) and 2tCzBzCN (b).

Table S1. Comparison of the efficiencies of PhOLEDs	with Ir(ppy) ₂ (acac) or FIrpic as emitters
and host materials based on benzimidazole	

Host	Hole drift mobility, cm ² /V·s	Emitter	EQE,	Reference
1tCzBzCN	2.34·10 ⁻⁶ at 8.7·10 ⁵ V/cm	Ir(ppy) ₂ (acac)	13.0	This study
1tCzBzCN	2.34·10 ⁻⁶ at 8.7·10 ⁵ V/cm	FIrpic	10.2	This study
2tCzBzCN	8.75·10 ⁻⁷ at 8.7·10 ⁵ V/cm	Ir(ppy) ₂ (acac)	4.4	This study
DCzMzSi	-	FIrpic	3.3	9
CbzNBI	$<<3.10^{-5}$ at 6.4.10 ⁵ V/cm	FIrpic	13.5	10
mCPNBI	$<<3.10^{-5}$ at 6.4.10 ⁵ V/cm	FIrpic	16.3	10
o-mCPBI	-	FIrpic	20.2	11
o-mCPBI	-	Ir(ppy) ₂ (acac)	22.7	11
m-mCPBI	-	FIrpic	15.0	11
m-mCPBI	-	Ir(ppy) ₂ (acac)	18.0	11
<i>p</i> -mCPBI	-	FIrpic	7.6	11
<i>p</i> -mCPBI	-	Ir(ppy) ₂ (acac)	6.2	11
DTAFNBI	1.10 ⁻⁵ at 8.7.10 ⁵ V/cm	FIrpic	9.4	12
<i>m</i> -DTAFNBI	3.10 ⁻⁵ at 8.7.10 ⁵ V/cm	FIrpic	9.6	12
DTAFCBI	1.10 ⁻⁵ at 6.4.10 ⁵ V/cm	FIrpic	2.9	12
<i>m</i> -DTAFCBI	1.10 ⁻⁵ at 4.3.10 ⁵ V/cm	FIrpic	5.9	12
BII–BCz	-	FIrpic	29.4	13
BII–BCz	-	Ir(ppy) ₂ (acac)	$Ir(ppy)_2(acac)$ 27.8 ¹³	
BII–TPA	-	FIrpic	FIrpic 21.2 ¹³	
BII–TPA	-	Ir(ppy) ₂ (acac)	$Ir(ppy)_2(acac)$ 26.4 ¹³	

Table S2. Excited state parameters computed at TD/LC- ω *PBE/6-31G(d,p) theoretical level (tuned ω) for **1tCzBzCN** and **2tCzBzCN**. Theoretical vertical excited state energies are red-shifted by 0.4 eV for **1tCzBzCN** and 0.2 eV for **2tCzBzCN**.

Molecules	Excited State	Energy (eV)	Oscillator strength	Nature of Excitation
1tCzBzCN	\mathbf{S}_1	3.01	0.0525	$LE_{BN} + CT$
	T ₁	2.61	0	$LE_{BN+BzIm} + CT$
	T ₂	2.81	0	LE _{tBCz}
	T ₃	2.88	0	$LE_{BN+BzIm} + CT$
	T ₄	2.98	0	LE _{BN+tBCz}
2tCzBzCN	S ₁	2.66	0.0846	$LE_{BN} + CT$
	T ₁	2.51	0	$LE_{BN+BzIm} + CT$
	T ₂	2.55	0	$LE_{BN+BzIm} + CT$

Abbreviations: benzonitrile (BN), benzoimidazole (BzIm) tert-butyl carbazole (tBCz).

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