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Electronic Supplementary Information

Boosting electroluminescent efficiency of solution-processed thermally activated delayed fluorescence OLEDs by a versatile hole-transporting layer of organic-inorganic hybrid perovskite

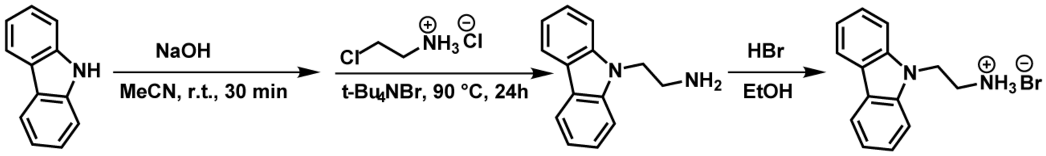
Tao Zhou[a, b], *Chen Liu*[a], *Shaolong Gong**[a], *Yepeng Xiang*[a], *Guohua Xie*[a], *Chuluo Yang**[a, b]

[a] Hubei Key Lab on Organic and Polymeric Optoelectronic Materials, Department of Chemistry, Wuhan University, Wuhan 430072, P. R. China.
*E-mail: slgong@whu.edu.cn, clyang@whu.edu.cn.

[b] Shenzhen Key Laboratory of Polymer Science and Technology, College of Materials Science and Engineering, Shenzhen University, Shenzhen 518060, P. R. China.

1. Experimental section

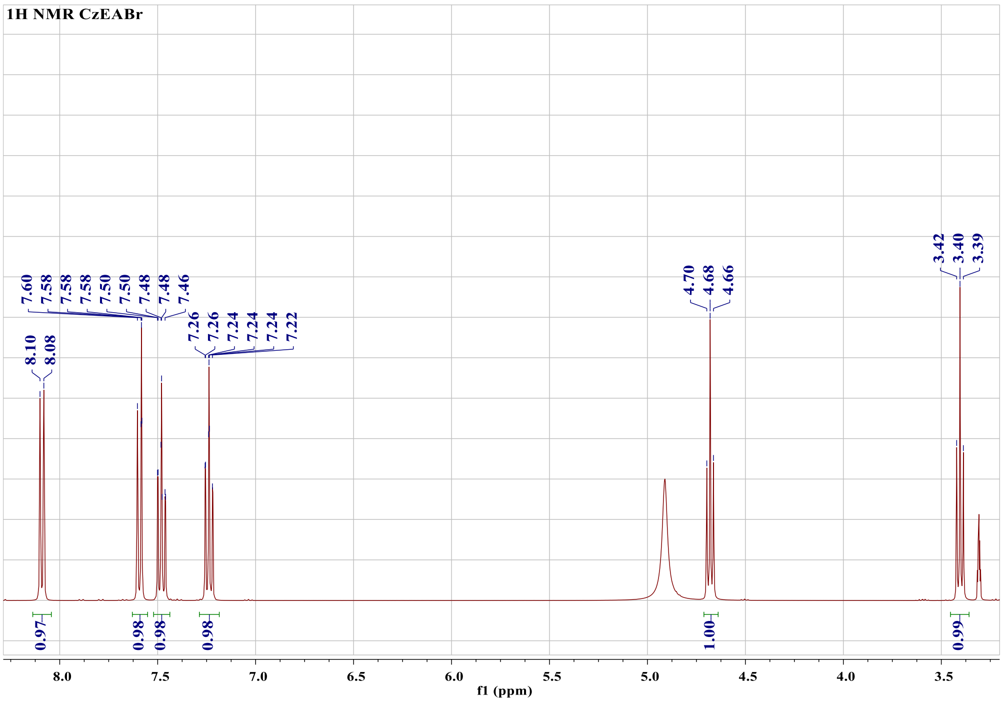
1.1 Synthesis.

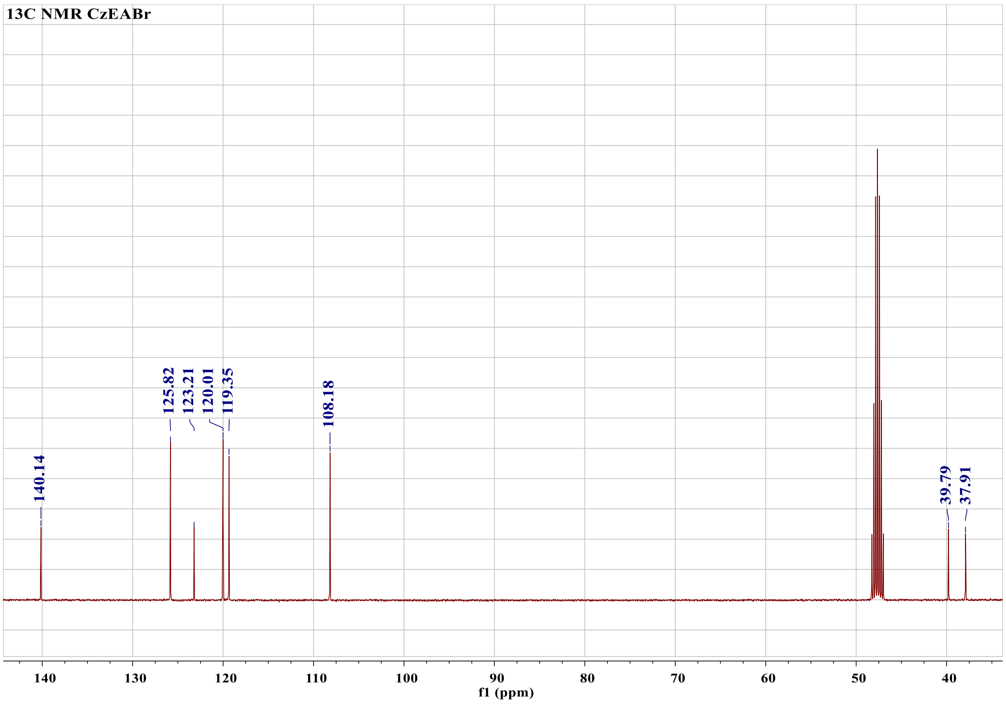


Scheme S1. Synthesis route of CzEABr.

2-(9*H*-carbazol-9-yl)ethanamine (CzEA). CzEA was synthesized through a reported reaction.[1] The received product was a colorless glutinous oil and was directly proceeded into the next stage without further purification.

2-(9*H*-carbazol-9-yl)ethanaminium bromide (CzEABr). CzEABr was synthesized through a simple acid-base neutralization reaction with hydrobromic acid and CzEA. The as-prepared CzEA was diluted in EtOH (40 mL for 5 g carbazole as reactant) and HBr (8 mL, 40 wt.%) was then injected. Massive grey solid was separated out immediately. The received raw product was recrystallized with EtOH for 3 times to afford a pale grey tabular crystal with a yield of 16%. ^{1}H NMR (CD_3OD, 400 MHz) δ (ppm): 8.09 (d, J = 7.8 Hz, 2H; ArH), 7.59 (d, J = 8.2 Hz 2H; ArH), 7.48 (t, J = 7.7 Hz, 2H; ArH), 7.24 (t, J = 7.5 Hz, 2H; ArH), 4.68 (t, J = 6.8 Hz, 2H; CH_2), 3.40 (t, J = 6.8 Hz, 2H; CH_2). ^{13}C NMR (CD_3OD, 400 MHz) δ (ppm): 140.14, 125.82, 123.21, 120.01, 119.35, 108.18, 39.79, 37.91. HR-MS (ESI, m/z): clacd for $C_{14}H_{15}N_2^+$ $[M+H]^+$ 211.12297, found 211.12292.


1H NMR CzEABr
8.10
8.08
7.60
7.58
7.58
7.58
7.50
7.50
7.48
7.48
7.46
7.26
7.26
7.24
7.24
7.24
7.22
4.70
4.68
4.66
3.42
3.40
3.39
0.97
0.98
0.98
0.98
1.00
0.99
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
f1 (ppm)


13C NMR CzEABr
140.14
125.82
123.21
120.01
119.35
108.18
39.79
37.91
140
130
120
110
100
90
80
70
60
50
40
f1 (ppm)

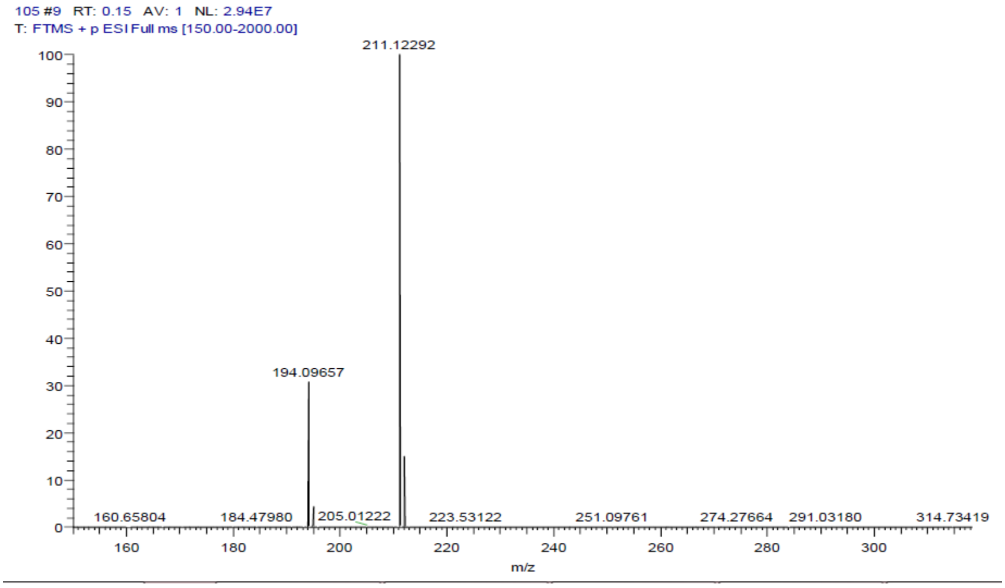


Fig. S1 ^{1}H NMR, ^{13}C NMR and HR-MS spectra of CzEABr.

1.2 Materials.

All materials commercially available were used as received without further purification. Hydrobromic acid was purchased from Acros Organics. The hole injecting material, poly(styrene sulfonic acid)-doped poly(3,4-ethylenedioxythiphene) (PEDOT: PSS) (Heraeus Clevios™ P VP AI 4083), the host material, 1,3-bis(carbazol-9-yl) benzene (mCP), the green TADF emitter, 2,4,5,6-tetrakis(carbazol-9-yl)-1,3-dicyanobenzene (4CzIPN), electron injecting material, lithium 8-hydroxyquinolinolate (Liq) were purchased from Xi'an Polymer Light Technology Corp.. The electron-transporting material, 1,3,5-tri[(3-pyridyl)-phen-3-yl] benzene (TmPyPB) was purchased from Jilin OLED Material Tech Co., Ltd.

1.3 Device fabrication.

The ITO coated glasses were cleaned with acetone and ethanol in an ultrasonic bath. 10 minutes of ultraviolet light-ozone treatment (UVO) was then loaded with PL16 series (SenLights Corporation) UV-ozone surface processor. PEDOT:PSS were spin coated onto ITO surface under 3000 rpm and then baked at 120 °C for 10 minutes. The substrates were then transferred into a N_2 filled glove box. CzEAP was spin coated using a precursor solution with 100 mg/mL $CzEA_2PbBr_4$ DMSO solution under 3000 rpm. During the spin coating, a drop of chloroform was added onto the glass as anti-solvent. 3 minutes of 80 °C baking was then conducted. Afterward, the emitting layer was spin coated using 10 mg/mL chlorobenzene solution under 1000 rpm, followed with a baking at 40 °C. The electron-transporting layer (TmPyPB), the electron injecting layer (Liq) and aluminum cathode were consecutively evaporated in a vacuum chamber under 10^{-5} mbar. The as-fabricated device was unsealed and measured in ambient air.

1.4 Measurements.

The ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded with Bruker Advanced II (400 MHz) NMR spectrometer. The high-resolution mass spectra (HR-MS) were collected with Thermo Scientific LTQ Orbitrap XL and ESI ion source.

The powder X-ray diffraction spectra were collected with Rigaku Miniflex600 X-ray diffractometer. The ultraviolet-visible absorption spectra were recorded using Shimadzu UV-2700 spectrometer. The ultraviolet photoelectron spectra (UPS, He I as source) were collected with Thermo Fisher ESCALAB 250Xi X-ray photoelectron spectrometer. The photoluminescence quantum yield was measured with a Quantaurus-QY measurement system (C9920-02, Hamamatsu Photonics). The PLQY values of different samples were collected under a 300 nm light excitation. The transient photoluminescence spectra were recorded with Edinburgh Instruments FLS920 at a detection wavelength of 520 nm under a picosecond pulsed ultraviolet laser (377 nm) as source. The electroluminescence properties were measured with Photoresearch SpectraScan PR735 spectrometer and Keithley 2400 source meter. The operational lifetimes of OLEDs were measured with a customized lifetime measruement system under a constant current density (20 mA cm^{-2}) mode.

2. Characterization of CzEAP and its heavy-atom effect.

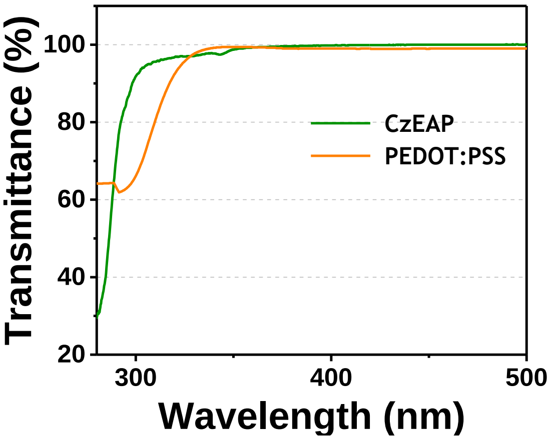


Fig. S2 Transmittance of CzEAP and PEDOT:PSS films.

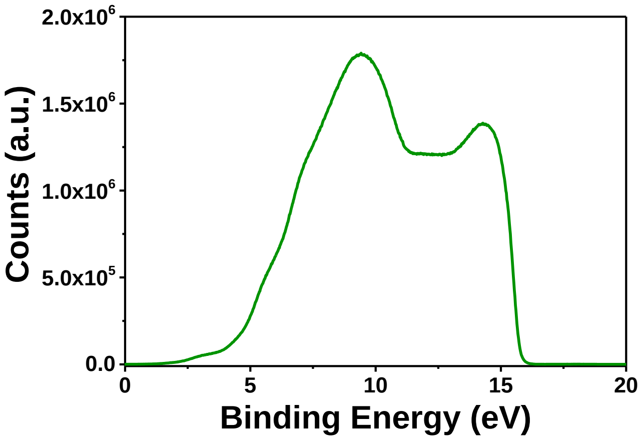


Fig. S3 UPS spectra of CzEAP.

2.2 Hole mobility measurement.

The hole mobility was calculated from SCLC model and the following equation:

$$J=\frac{9\varepsilon_0\varepsilon_r\mu V^2}{8d^3} \tag{S1}$$

where J refers to the current density, ε_0 refers to vacuum dialect constant, ε_r refers to the relative dialect constant of the transporting material, μ refers to the charge mobility, V refers to the applying voltage, d refers to the thickness of transporting material.

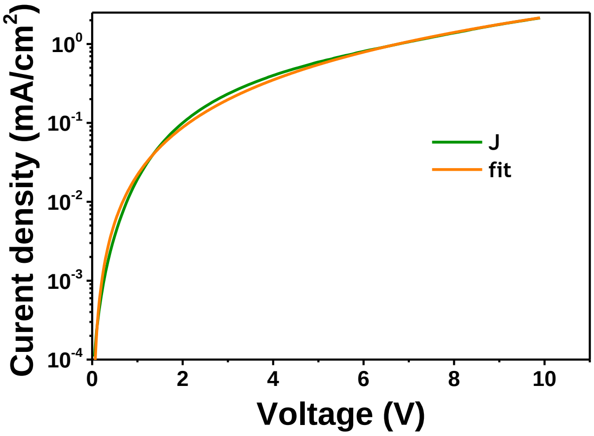


Fig. S4 Current density-voltage curve of monocharge device and SCLC fitting.

Table S1. PLQYs of mCP:4CzIPN (10 wt.%) on different substrates.

Substrate	quartz	PEDOT:PSS	PEDOT:PSS/ PMMA	CzEAP	PEDOT:PSS/ CzEAP
PLQY[a] [%]	85	40	50	73	39
Abs [%]	68	69	60	68	65

[a] PLQY measurements were conducted in an integrating sphere filled with argon.

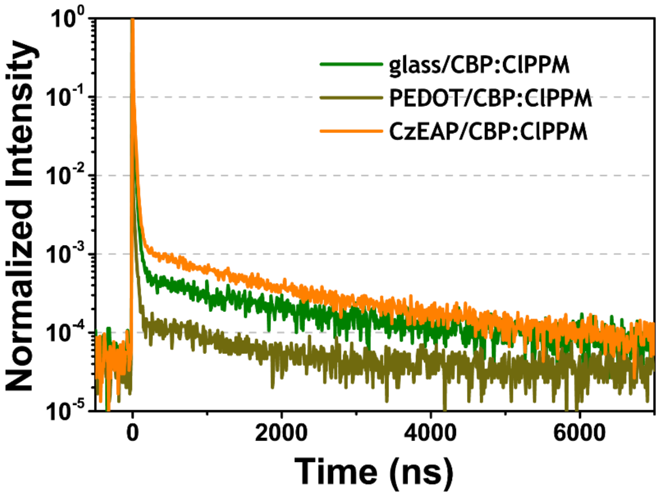


Fig. S5 Transient PL spectra of CBP:ClPPM on different substrates.

3. Device operational stability

The operational lifetimes of OLEDs were conducted using pristine emitting layer (EML) of mCP:4CzIPN (10 wt.%) or CzEABr doped EML (1 wt.%) under a constant current density of 20 mA cm^{-2}. The LT$_{50}$ (the time as the device luminance drops to the 50% of the initial luminance) of OLEDs with pristine EML was 0.7 h (initial luminance of 1105 cd m^{-2}); while OLEDs with CzEABr doped EML exhibited the better operational stability with a LT$_{50}$ of 2.1 h (initial luminance of 1012 cd m^{-2}).

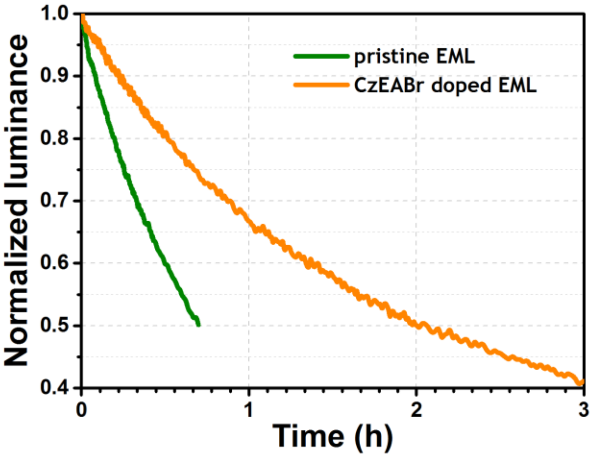


Fig. S6 The decay of normalized luminance as a function of operational lifetime under a constant current driving for OLEDs with pristine emitting layer or CzEABr doped emitting layer.

References

1 A. M. Cuadro, M. P. Matia, J. L. Garcia, J. J. Vaquero and J. Alvarez-Builla, *Synth. Commun.*, 1991, **21**, 535.