

Supporting information

Achieving High Power Efficiency and Low Roll-Off OLEDs Based on Energy Transfer from Thermally Activated Delayed Excitons to Fluorescent Dopants

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1. Experimental Section

General Information. ^1H NMR spectra were measured on a Bruker 500 MHz spectrometer with tetramethylsilane as the internal standard. Mass spectra were recorded on a Shimadzu AXIMA-CFR MALDI-TOF mass spectrometer. Elemental analyses were performed on a flash EA 1112 spectrometer. UV-vis absorption spectra were recorded by a Shimadzu UV-2550 spectrophotometer. Differential scanning calorimetric (DSC) measurements were performed on a NETZSCH DSC204 instrument at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ from 20 to $350\text{ }^\circ\text{C}$ under a nitrogen atmosphere. Thermogravimetric analyses (TGA) were performed on a TA Q500 thermogravimeter by measuring their weight loss while heating at a rate of $10\text{ }^\circ\text{C min}^{-1}$ from 25 to $800\text{ }^\circ\text{C}$ under nitrogen. Cyclic voltammeteries were performed on a BAS 100W instrument with a platinum electrode as the working electrode, a platinum wire as the counter electrode, and an Ag/Ag^+ electrode as the reference electrode with standardized against ferrocene/ferrocenium. The oxidation and reduction potentials were measured in CH_2Cl_2 and DMF solution containing 0.1 M of tetrabutylammonium hexafluorophosphate (TBAPF_6) as a supporting electrolyte at a scan rate of 100 mV s^{-1} , respectively.

Single-Crystal Structure. Diffraction data were collected on a Rigaku R-AXIS-RAPID diffractometer using the ω -scan mode with graphite-monochromator $\text{Mo K}\alpha$ radiation. The structure determination was solved with direct methods using the SHELXTL programs and refined with full-matrix least squares on F^2 .^[1] The corresponding CCDC reference number (CCDC: 1052646) and the data can be obtained

free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Materials. All commercially available reagents were used as received unless otherwise stated. (4s,6s)-2,4,5,6-tetra(9H-carbazol-9-yl)isophthalonitrile (4CzIPN)^[2] and N,N'-di(n-butyl)-2,9-difluoroquinacridone (C₄-DFQA) were synthesized based on the previously reported procedure^[3] and purified by vacuum sublimation prior to use. N,N'-di(n-butyl)-1,3,8,10-tetrakis(trifluoromethyl)-quinacridone (C₄-TCF₃QA) was synthesized by using a key intermediate, diethyl-2,5-bis(3,5-bis(trifluoromethyl)phenylamino)terephthalate according to our previous work^[4].

Synthesis of TCF₃QA: 1,3,8,10-tetrakis(trifluoromethyl)-quinacridone (TCF₃QA) was synthesized according to the reported procedure^[3]. The ¹H NMR spectrum of TCF₃QA was not obtained due to its strong aggregation and poor solubility. MALDI-TOF-MS(M): m/z: 584.7 [M+H]⁺ (calcd: 585.3). Anal. Calcd for C₂₄H₈F₁₂N₂O₂: C, 49.33; H, 1.38; N, 4.79; found: C 49.16, H 1.32, N 4.68.

Synthesis of C₄-TCF₃QA: N,N'-di(n-butyl)-1,3,8,10-tetrakis(trifluoromethyl)-quinacridone (C₄-TCF₃QA): Under nitrogen, sodium hydride (0.84 g, 35 mmol) was added to a suspension of TCF₃QA (2.9 g, 5 mmol) in 50 mL of dry tetrahydrofuran (THF). The mixture was heated to reflux for 1 h, and then 1-bromobutane (1.1 g, 30 mmol) was added. The reaction mixture was continued to heat to reflux for 12 h. After cooling to room temperature, the solvent was removed in vacuum and the residue was added in methanol (30 mL). The resulting suspension was stirred for 1h. The generated orange-red precipitate was filtered off and washed three times with petroleum ether. The

precipitate was then purified by column chromatography using silica gel with chloroform as eluent to give the product. Yield: 80%. ^1H NMR (500 MHz, CDCl_3 , δ): 8.71 (s, 2H), 8.03 (s, 2H), 7.88 (s, 2H), 4.53-4.56 (t, 4H), 1.98-2.04 (m, 4H), 1.63-1.71 (m, 4H), 1.12-1.15 (t, 6H). MALDI-TOF-MS(M): m/z : 695.9 $[\text{M}+\text{H}]^+$ (calcd: 696.2). Anal. Calcd for $\text{C}_{24}\text{H}_8\text{F}_{12}\text{N}_2\text{O}_2$: C, 55.18; H, 3.47; N, 4.02; found: C 55.52, H 3.53, N 4.18.

Theoretical Calculations. The ground state geometries were fully optimized by the density functional theory (DFT)^[5] method with the Becke three-parameter hybrid exchange and the Lee-Yang-Parr correlation functional^[6] (B3LYP) and 6-31G* basis set using the Gaussian 03 software package.^[7]

Optical characterization of organic thin films. Organic films for optical measurements were fabricated by thermal evaporation under high vacuum onto clean quartz substrates. The spectra of the films, transient PL decay characteristics and absolute fluorescence quantum yields were measured with an Edinburgh Instruments FLS920 spectrometer.

Device Fabrication and Characterization. Before device fabrication, the ITO glass substrates were pre-cleaned carefully and treated by plasma for 5 min. Then the sample was transferred to the deposition system. The devices were prepared in vacuum at a pressure of 5×10^{-7} Torr. The hole-transporting material NPB, exciton blocking material mCP, hole-blocking material BCP and electron-transporting material Bepp₂ were commercially available and thermally evaporated at a rate of 1.0 \AA s^{-1} . After the organic film deposition, 0.5 nm of LiF and 150 nm of aluminum were thermally evaporated onto the organic surface. All of organic materials used were purified by a vacuum sublimation

approach. The electrical characteristics of the devices were measured with a Keithley 2400 source meter. The EL spectra and luminance of the devices were obtained on a PR650 spectrometer. EQE were calculated from the $J-V-L$ characteristics and EL spectra, assuming a Lambertian distribution. The single-carrier devices measurements were performed under dark and ambient conditions. All the devices fabrication and device characterization steps were carried out at room temperature under ambient laboratory conditions.

2. Figures

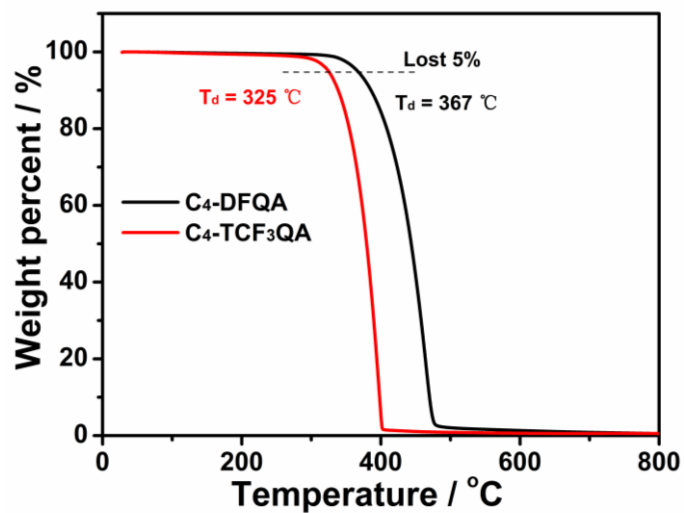


Fig. S1 The TGA graphs of C₄-DFQA and C₄-TCF₃QA.

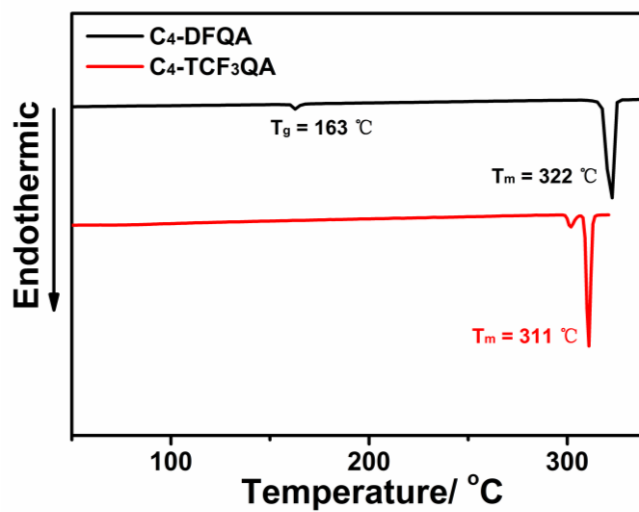


Fig. S2 The DSC graphs of C₄-DFQA and C₄-TCF₃QA.

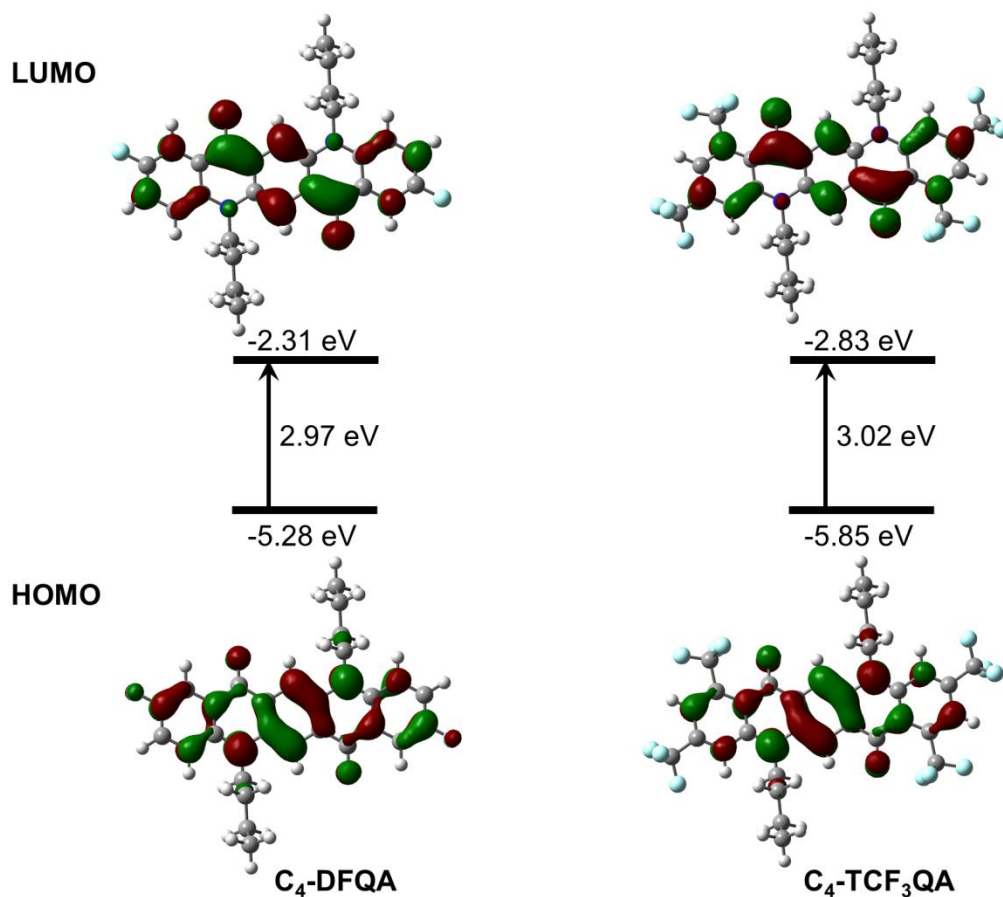


Fig. S3 Calculated spatial distributions of the HOMO and LUMO levels for $\text{C}_4\text{-DFQA}$ and $\text{C}_4\text{-TCF}_3\text{QA}$.

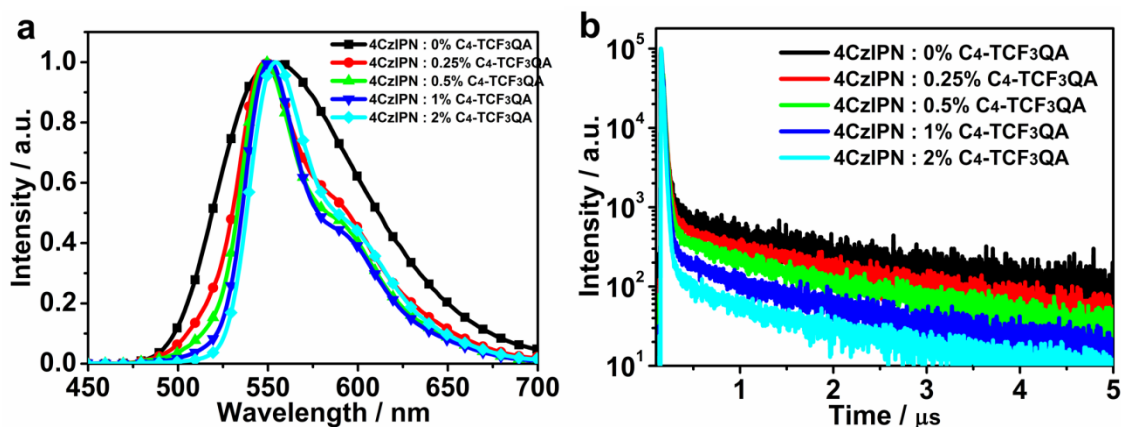


Fig. S4 a) The PL spectra of the 4CzIPN: $\text{C}_4\text{-TCF}_3\text{QA}$ films. b) The PL transient decay curves of the 4CzIPN: $\text{C}_4\text{-TCF}_3\text{QA}$ films observed at 552 nm.

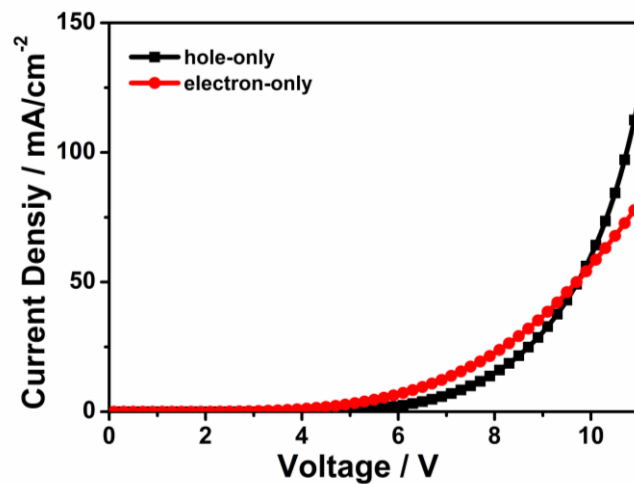


Fig. S5 Current density versus voltage characteristics of the hole-only [ITO/NPB (35 nm)/mCP (5 nm)/4CzIPN (30 nm)/NPB(10 nm)/Al (150 nm)] and electron-only devices [ITO/BCP (10 nm)/4CzIPN (30 nm)/BCP (5 nm)/BePP₂ (40 nm)/LiF (0.5 nm)/Al (150 nm)].

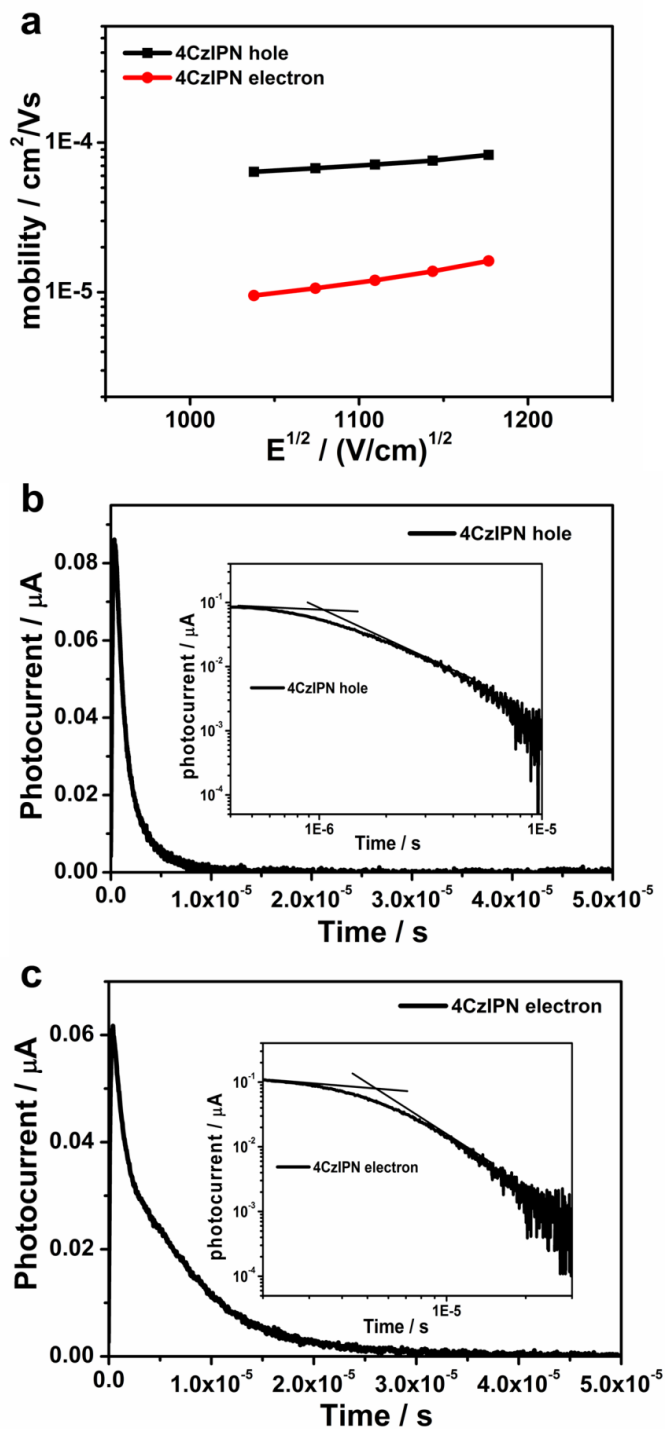


Fig. S6 a) Hole and electron mobility of 4CzIPN as a function of the square root of the electric field. b) Typical transient photocurrent signal for hole. c) Typical transient photocurrent signal for electron. The device used for TOF measurement was prepared through vacuum deposition with a tri-layer structure of ITO/4CzIPN (2 μm)/Al (150 nm).

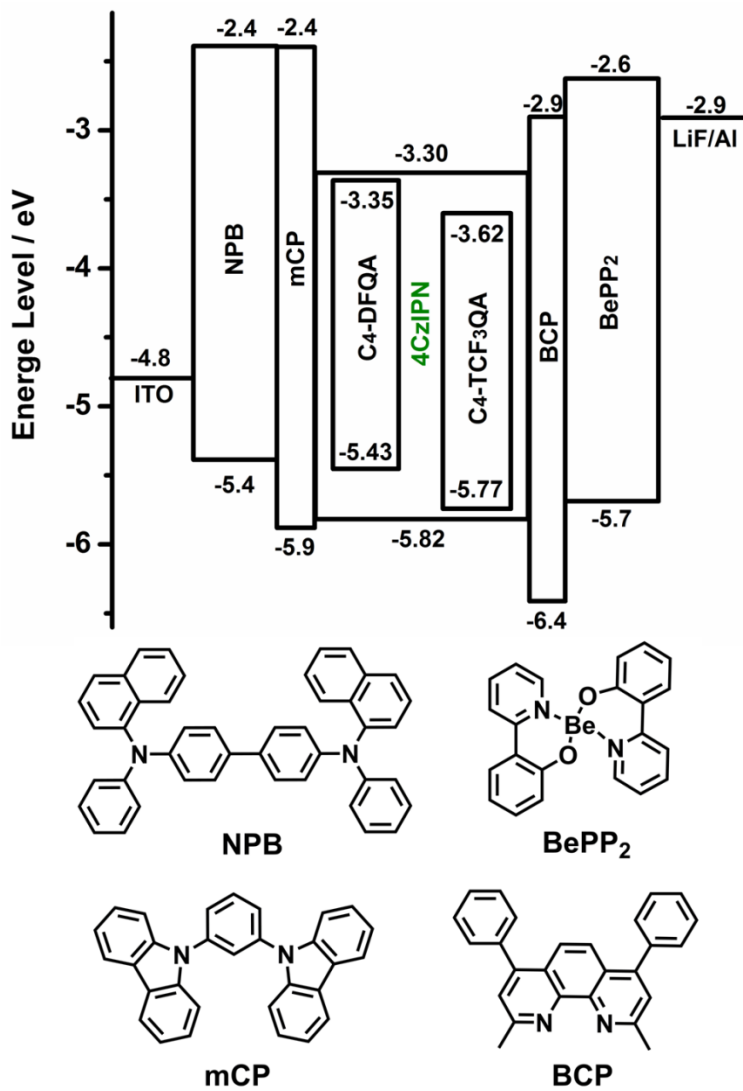


Fig. S7 The energy-level diagram of the multilayer devices and chemical structures of the used materials.

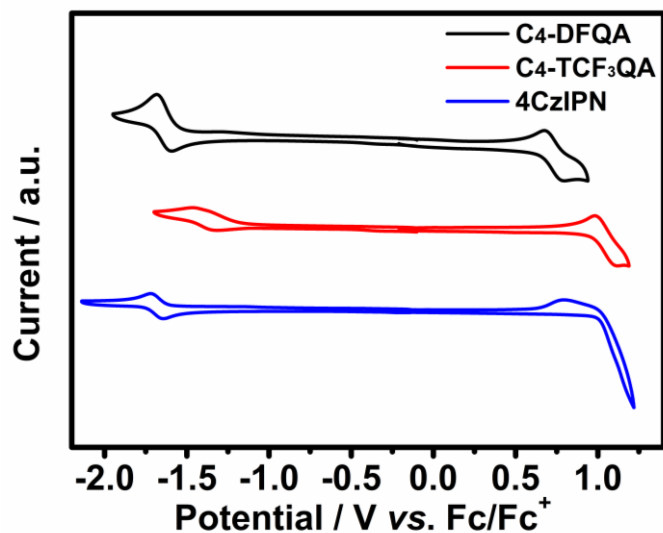


Fig. S8 Cyclic voltammograms of C₄-DFQA, C₄-TCF₃QA and 4CzIPN.

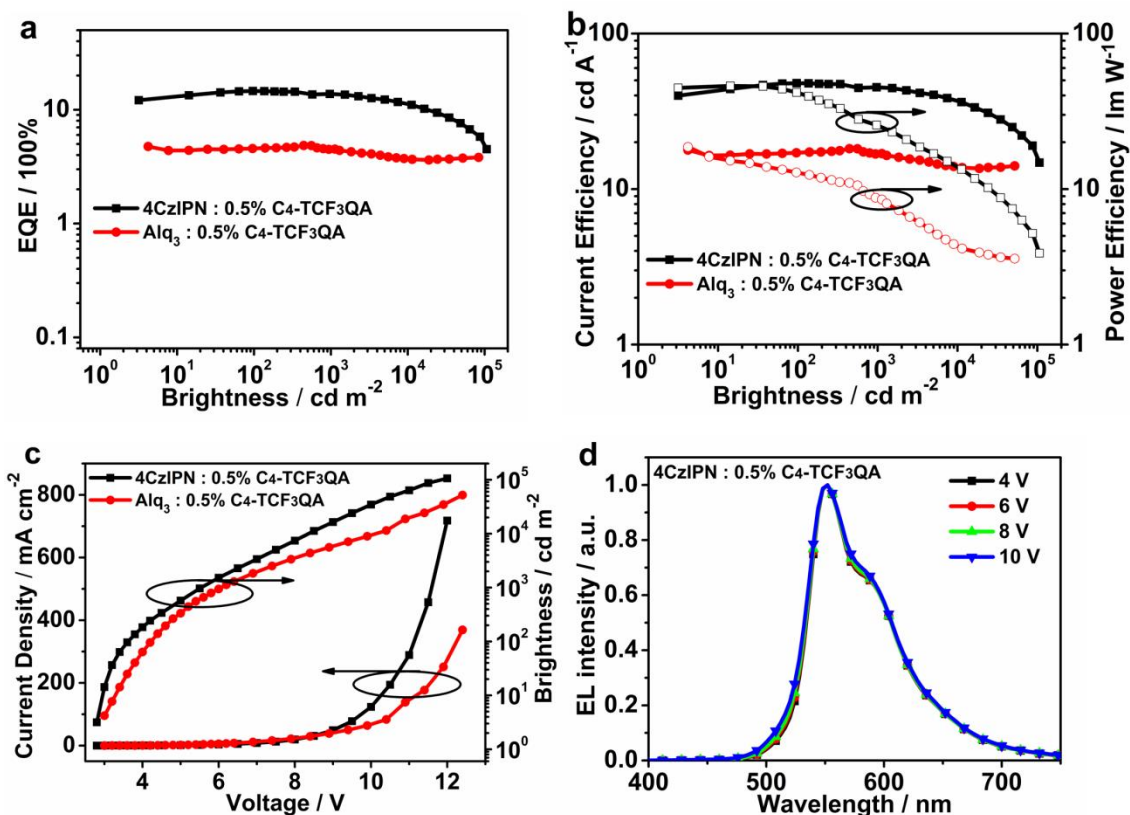


Fig. S9 The EL characteristics of devices based on C₄-TCF₃QA. a) External quantum efficiency versus brightness characteristics. b) Current efficiencies and power efficiencies versus brightness characteristics. c) Current density–voltage–brightness (*J–V–L*) characteristics. d) The EL spectra operated at different voltages of the device.

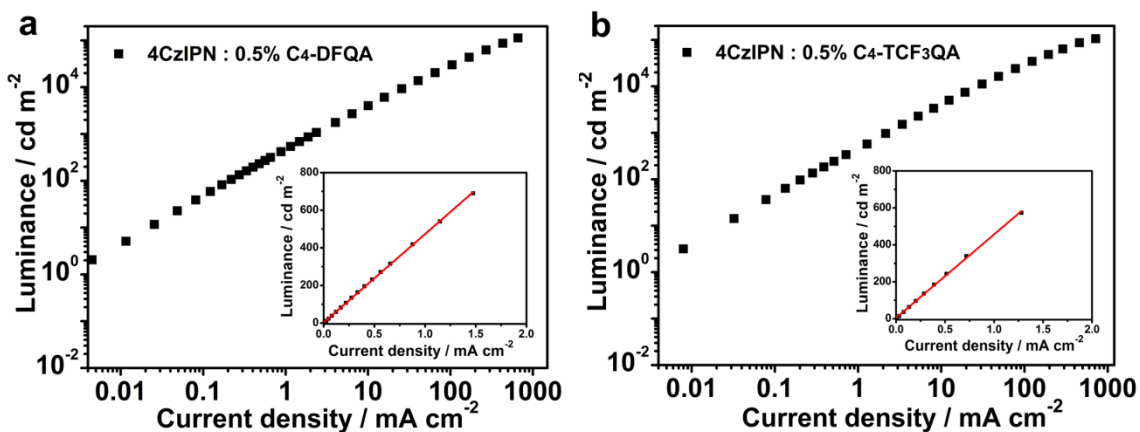


Fig. S10 Luminance-current density characteristics for the devices. Inset shows luminance-current density characteristics at low current density region.

3. Tables

Table S1. The PL efficiency of 4CzIPN:C₄-DFQA (C₄-TCF₃QA) films.^{a)}

Doping concentration	Φ_{PL} of 4CzIPN:C ₄ -DFQA	Φ_{PL} of 4CzIPN: C ₄ -TCF ₃ QA
0%	0.52	0.52
0.25%	0.64	0.69
0.5%	0.78	0.82
1%	0.76	0.78
2%	0.68	0.73

^{a)} Absolute PL quantum yield evaluated using an integrating sphere. The excitation wavelength of the films was 415 nm.

4. References:

[1] SHELXTL, Version 5.1; Siemens Industrial Automation, Inc., 1997; G. M. Sheldrick, SHELXS-97, Program for Crystal Structure Solution, University of Göttingen, Göttingen 1997.

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