

Supporting Information

Solution-processable orange-red thermally activated delayed fluorescence emitters with 3,6-disubstituted carbazole for highly efficient OLEDs with ultra-low efficiency roll-off

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General methods

¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were measured on a Bruker Ascend 400 spectrometer using CDCl₃ as a solvent and the spectral data were reported in ppm relative to tetramethylsilane (TMS) as an internal standard. Molecular weights were measured with a Bruker Autoflex III MALDI-TOF mass spectrometer. Elemental analyses of carbon, hydrogen, and nitrogen were performed on a Vario EL III microanalyzer. Thermogravimetric analysis (TGA) was undertaken with a TA instrument Q600 at a scanning rate of 10 °C/min under nitrogen atmosphere. Differential scanning calorimetry (DSC) was performed on a Mettler Toledo DSC1 STArE system with nitrogen flow at 20 mL/min. Samples were preheated to above their melting points, and then cooled down to –30 °C at –100 °C/min before the second heating and cooling scans were recorded at 20 °C/min. The atomic force microscopy (AFM) was conducted on a Bruker Dimension ICON. UV-vis absorption spectra were recorded on a Perkin-Elmer Lambda-900 spectrophotometer. PL spectra were measured on a Hitachi F-7000 fluorescence spectrophotometer and phosphorescence spectra at 77 K were recorded on a Perkin-Elmer LS 50B spectrofluorometer. The absolute PL quantum yields were measured using a Hamamatsu C9920-02G integrating sphere system coupled with a 150 W xenon lamp and a PMA-12 photonic multichannel analyzer. The transient PL decay measurements were performed using an Edinburgh Instruments FLS980 spectrometer. CV was carried out using nitrogen-purged anhydrous THF for the reduction and dichloromethane (DCM) for the oxidation scan at room temperature with a CHI voltammetric analyzer. Tetrabutylammonium

hexafluorophosphate (TBAPF₆) (0.1 M) was used as the supporting electrolyte. The conventional three-electrode configuration consists of a glassy carbon working electrode, a platinum wire counter electrode, and a saturated calomel reference electrode (SCE) with ferrocene/ferrocenium (Fc/Fc⁺) as the internal standard. The working electrode surface was previously polished with alumina slurry on a micro cloth. The dilute sample solutions exhibit reduction and oxidation scans against the Ag/AgCl reference electrode. Cyclic voltammograms were obtained at a scan rate of 100 mV/s. The reduction and oxidation potentials, E_{1/2}(red) and E_{1/2}(oxd), relative to Fc/Fc⁺ were used to calculate the LUMO and HOMO levels as $-4.80 - qE_{1/2}(\text{red})$ eV and $-4.80 - qE_{1/2}(\text{oxd})$ eV, respectively, where q is electron charge. All calculations were performed utilizing the Gaussian 09 program package. Geometry optimizations were conducted in the framework of the density functional theory (DFT) at the B3LYP level. The 6-31G(d,p) basis set was used for all the elements. The molecular orbitals were visualized using Gaussview.

Equations for calculation of rate constants

$$k_r = \Phi_p k_p + \Phi_d k_d \quad (1)$$

$$k_{nr} = \frac{1 - \Phi_{PL}}{\Phi_{PL}} k_r \quad (2)$$

$$k_{ISC} \approx \frac{\Phi_d}{\Phi_p \Phi_{PL}} k_r \quad (3)$$

$$k_{RISC} \approx \frac{k_p k_d}{k_r} \Phi_{PL} \quad (4)$$

Device fabrication and characterization

The fabricated devices were grown on clean glass substrates pre-coated with a 180-

nm thick layer of ITO with a sheet resistance of 15–20 Ω/sq . The ITO surface underwent a wet-cleaning course in an ultrasonic solvent bath, and then was dried at 120 °C before the UV-Ozone treatment for 20 min. A 40 nm thick PEDOT:PSS layer used as a hole- injecting layer was spin-coated on the ITO substrate under 3000 rpm and then baked inside the glove-box at 120 °C for 10 min. The EML was prepared from 10 mg mL⁻¹ toluene solution by spin-coating at 1500 rpm on top of the PEDOT:PSS layer. The electron-transporting, electron-injecting, and cathode layers were sequentially deposited in a vacuum chamber. Current–brightness–voltage characteristics were measured using Keithley source measurement units (Keithley 2400 and Keithley 2000) with a calibrated silicon photodiode. The EL spectra were measured using a SpectraScan PR650 spectrophotometer. External quantum efficiencies were calculated from the luminance, current density, and EL spectrum, assuming a Lambertian distribution. All the measurements were carried out in an ambient atmosphere.

Table S1 Summary of solution-processable orange-red TADF emitters

Emitter	λ_{EL} (nm)	CIE (x, y)	EQE (%, Max./@1000)	Ref.
D(DPXZ-Cz)-DCPP	600	(0.57, 0.43)	21.6/18.7	This work
D(DCz-Cz)-DCPP	560	(0.45, 0.54)	19.5/17.1	This work
NAI_R3	622	(0.60, 0.40)	22.5/3.4	[1]
DDPhCz-DCPP	578	(0.48, 0.50)	20.6/–	[2]
PXZPDO	570	(0.47, 0.50)	20.1/18.5	[3]
oDTBPZ-DPXZ	612	(0.60, 0.40)	18.5/–	[4]
TAT-DBPZ	604	(0.56, 0.44)	15.4/8.2	[5]
pDTBPZ-DPXZ	608	(0.59, 0.41)	14.4/–	[4]
DDTPACz-DCPP	646	(0.61, 0.38)	13.6/–	[2]
TPXZBM	582	(0.48, 0.49)	12.7/9.9	[3]
TS-1	608	(0.58, 0.41)	12.58/–	[6]
NAI_R2	610	(0.57, 0.42)	11.5/3.9	[1]
tDBBPZ-DPXZ	620	(0.62, 0.37)	10.1/–	[7]
pDBBPZ-DPXZ	612	(0.60, 0.40)	9.3/–	[4]
TAT-FDBPZ	611	(0.58, 0.41)	9.2/7.4	[5]
FDQPXZ	600	(0.53, 0.46)	9.0/6.1	[8]
NAI_R1	616	(0.58, 0.41)	9.0/4.3	[1]
DTPAB	605	–	8.2/3.5	[9]
TPA-AQ	612	(0.60, 0.40)	7.5/–	[10]
BPXZBM	598	(0.50, 0.46)	7.05/4.0	[3]
TS-2	614	(0.58, 0.41)	6.92/–	[6]
DPhCzB	587	–	6.7/6.1	[9]
4t-BuCzTTR	592	(0.54, 0.45)	6.2/–	[11]
Cz-AQ	572	(0.50, 0.49)	5.8/–	[10]
BTZPP	600	(0.56, 0.43)	3.4/–	[12]

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