Electronic Supplementary Information (ESI)

1. General

Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under dry nitrogen immediately prior to use. All other chemicals and reagents were purchased from commercial sources and used as received without further purification. NMR spectra were obtained on a Bruker AV 500 or 600 M spectrometer. High resolution mass spectra (HRMS) were recorded a GCT premier CAB048 mass spectrometer operating in MALDI-TOF mode. LC-MS measurements were carried out on a Waters ACQUITY UPLC H-Class_XEVO TQD. Single crystal X-ray diffraction intensity data were collected on a Bruker-Nonices Smart Apex CCD diffractometer with graphite monochromated MoKa radiation. Processing of the intensity data was carried out using the SAINT and SADABS routines, and the structure and refinement were conducted using the SHELTL suite of X-ray programs (version 6.10). The ground-state geometries were optimized using the density functional with B3LYP hybrid functional at the basis set level of 6-31G (d, p). All the calculations were performed using Gaussian 09 package. UV-vis absorption spectra were measured on a SHIMADZU UV-2600 spectrophotometer. Fluorescence spectra were recorded on a Horiba Fluoromax-4 fluorescence spectrophotometer. Fluorescence quantum yields were measured using a Hamamatsu absolute PL quantum yield spectrometer C11347 Quantaurus QY. Fluorescence lifetimes were determined with a Hamamatsu C11367-11 Quantaurus-Tau time-resolved spectrometer.

2. Device fabrication

The multilayer OLEDs were fabricated by the vacuum-deposition method. Organic layers were

deposited by high-vacuum (5 \times 10⁻⁴ Pa) thermal evaporation onto a glass (3 cm \times 4 cm) substrate with indium oxide (ITO) pre-coated tin layer. an Dipyrazinoquinoxaline-2,3,6,7,10,11-hexacarbonitrile (HATCN) was used as the hole-injecting layer, N,N-bis(naphthalene)-N,N-bis(phenyl)benzidine (NPB) was used as the hole-transporting layer (HTL), f-DBP-DBPE and f-DBP-DFLE were the emitting layers, used as 1,3,5-tri(1-phenyl-1*H*-benzo[d]imidazol-2-yl)phenyl (TPBi) was used as the electron-transporting layer (ETL) and LiF/Al was used as the cathode. All organic layers were deposited sequentially. Thermal deposition rates for the organic materials, LiF and Al were 0.5, 0.5 and 1 Å S^{-1} , respectively. The active area of each device was 12 mm². The electroluminescent spectra were measured on a Hitachi MPF-4 spectrofluorometer. The current density-voltage characteristics of the OLEDs were recorded on a Keithley 2400 Source Meter. The current density-voltage-luminance curves characterizations were carried out with a 3645 DC power supply combined with a 1980A spot photometer and they were recorded simultaneously. All measurements were done at room temperature under ambient conditions.

3. Additional Data



Fig. S1 Lifetimes of (A) *f*-DBP-DBP, (B) *f*-DBP-DFLE, (C) DBP-DPy and (D) DBP-DTPA under ambient temperature.