Supplementary Information (SI) for Journal of Materials Chemistry C.

Supporting Information for

Copolyfluorene containing 4,4’-bis[4-(di-*p*-tolylamino)styryl]biphenyl as chromophore for efficient blue polymer light-emitting diodes

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Materials

Toluene used for Suzuki polycondensation was purified according to standard procedures and distilled in nitrogen before use. Other commercially available reagents were used without further purification. 2,7-dibromo-9,9-dioctylfluorene (F-Br_2), 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (F-$Bpin_2$), N,N'-Bis(4-*t*-butylphenyl)-N,N'-bis(4-bromophenyl)biphenyl-4,4'-diamine (TD-Br_2), and 4-((4-Bromophenyl)(4-(t-butyl)phenyl)amino) benzaldehyde were synthesized with reference to our previous article [*J. Mater. Chem. C*, 2018, **6**, 12355]. 4,4-Bis(diethylphosphonomethyl)biphenyl was purchased from J&K Scientific Co. The DPAVBi (99.5%) were purchased from Changchun Tuocai Technology Co., Ltd.

General procedures of Suzuki polymerization, using PF-DPAVBi0.5 as an example

Monomer F-$Bpin_2$ (321.3 mg, 0.5 mmol), monomer F-Br_2 (260.5 mg, 0.475 mmol), monomer TD-Br_2 (18.5 mg, 0.02 mmol), monomer DPAVBi-Br_2 (4.8 mg, 0.005 mmol), palladium acetate (4 mg), and tricyclohexylphosphine (8 mg) were dissolved in toluene (20 mL) and tetraethyl ammonium hydroxide aqueous solution (20 wt/v%, 2 mL) at a nitrogen atmosphere. The mixture reacted at 85 ºC for 24 h and then end-capped by phenylboronic acid (25 mg) and bromobenzene (0.2 ml) successively. After cooling, the solution was dropwise added into 500 ml stirring methanol and then filtered out. The crude polymers were washed with methanol, acetone and n-hexane in a Soxhlet apparatus and dried under a vacuum to yield the resulting polymers as a light-yellow floccule. ^1H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.85 (br, ArH), 7.68 (br, ArH), 7.60-7.30 (m, ArH), 7.26-7.05 (m, ArH), 2.15 (br, CH2), 1.35 (m, CH_2), 1.28-1.00 (m, CH_2, CH_3), 0.82 (m, CH_3).

PF-DPAVBi01

Monomer F-Bpin$_2$ (321.3 mg, 0.5 mmol), monomer F-Br$_2$ (257.8 mg, 0.47 mmol), monomer TD-Br$_2$ (18.5 mg, 0.02 mmol), monomer DPAVBi-Br$_2$ (9.6 mg, 0.01 mmol). ^{1}H NMR (500 MHz, CDCl$_3$) δ (ppm): 7.84 (br, ArH), 7.68 (br, ArH), 7.60-7.30 (m, ArH), 7.26-7.05 (m, ArH), 2.13 (br, CH2), 1.35 (m, CH$_2$), 1.28-1.00 (m, CH$_2$, CH$_3$), 0.82 (m, CH$_3$).

PF-DPAVBi2

Monomer F-Bpin$_2$ (321.3 mg, 0.5 mmol), monomer F-Br$_2$ (252.3 mg, 0.46 mmol), monomer TD-Br$_2$ (18.5 mg, 0.02 mmol), monomer DPAVBi-Br$_2$ (19.2 mg, 0.02 mmol). ^{1}H NMR (500 MHz, CDCl$_3$) δ (ppm): 7.83 (br, ArH), 7.68 (br, ArH), 7.60-7.30 (m, ArH), 7.26-7.05 (m, ArH), 2.15 (br, CH$_2$), 1.35 (m, CH$_2$), 1.28-1.00 (m, CH$_2$, CH$_3$), 0.82 (m, CH$_3$).

Measurements

Thermal gravimetric analysis and differential scanning calorimetry (DSC) measurements were carried out under a nitrogen flow using a NETZSCH DSC204 and a NETZSCH TGA-209 thermal analyzer, respectively. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX 500 spectrometer at 500 MHz and 100 MHz, respectively. Cyclic voltammetry (CV) was performed on a CHI800C electrochemical workstation equipped with a glass carbon working electrode, a Pt wire counter electrode and a saturated calomel served as reference electrode and used 0.1 mol L^{-1} tetrabutylammonium hexafluorophosphate (Bu$_4$NPF$_6$) acetonitrile solution as the electrolyte. The PL lifetime of PFO and PF-DPAVBi were measured by the FLS-920 (Edinburgh Instrument Ltd). Atomic force microscopy (AFM) measurements were carried out Bruker Multimode 8 in scanasys mode. The thickness and cross-section profile of the polymer layers were measured by a Dektak 150 surface profiler. A Keithley 2400 digital source meter was used to record *J-V* characteristics and given the driving voltage when measured by the EL spectra. The EL spectra, luminous intensity and CIE coordinates were taken by a Photo Research PR745 spectroradiometer. The operating lifetime of devices were driven by Keithley 2400 digital source with constant current and recorded by a CS-200 spectrophotometer (Konica Minolta). The trPL of ITO/PEDOT:PSS/DPAVBi1 and quartz/PF-DPAVBi1/CsF/Al were measured by Fluorolog-QM (HORIBA).

Fabrication and characterization of PLEDs

The fabrication of the single-layer PLEDs followed a well-established process. First, the ITO glass substrates were sequentially cleaned with acetone, isopropanol, detergent, deionized water and isopropanol, and then baked at 120 °C for 2 h. Then a 35-nm PEDOT:PSS (Al 4083) layer was spin-coated onto the clean ITO substrate, which had been treated by oxygen plasma for 90 s. The PEDOT:PSS film was dried by baking at 150 °C for 15 min. Afterwards, an 80-nm EML from *p*-xylene solution was spin-coated directly on the PEDOT:PSS, the film was then annealed at 100 °C for 20 min to remove the residue solvent. Finally, the cathode with a 1-nm CsF and a 100-nm Al was evaporated onto the emissive layer through a shadow mask defined active area of 5.16 mm^2 under a vacuum of 1×10^{-6} Pa. The thickness was monitored using an STM-100/MF Sycon quartz crystal. Except for the cleaning of the substrate and the preparation of PEDOT:PSS layer, other procedures were carried out in an inert atmosphere with oxygen and moisture below 10 ppm. Before testing, all the devices were encapsulated with UV-cured epoxy resin and cover glass.

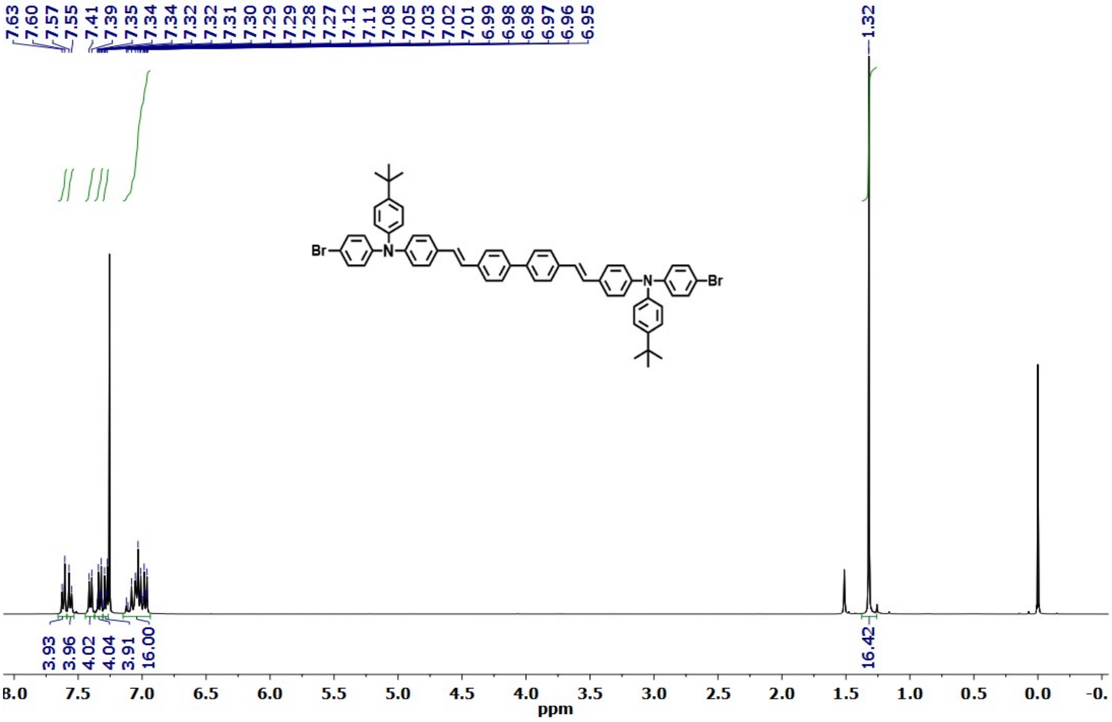

Fig. S1 ^{1}H NMR spectrum of DPAVBi-Br$_2$.

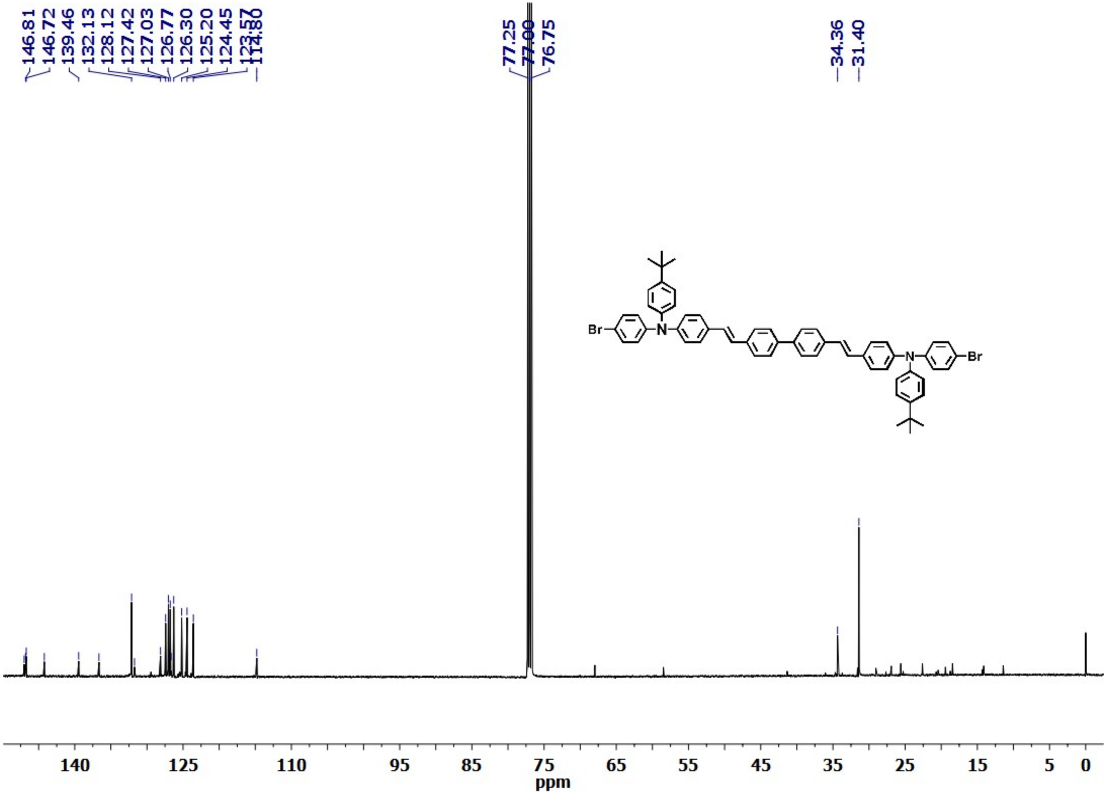

Fig. S2 ^{13}C NMR spectrum of DPAVBi-Br$_2$.

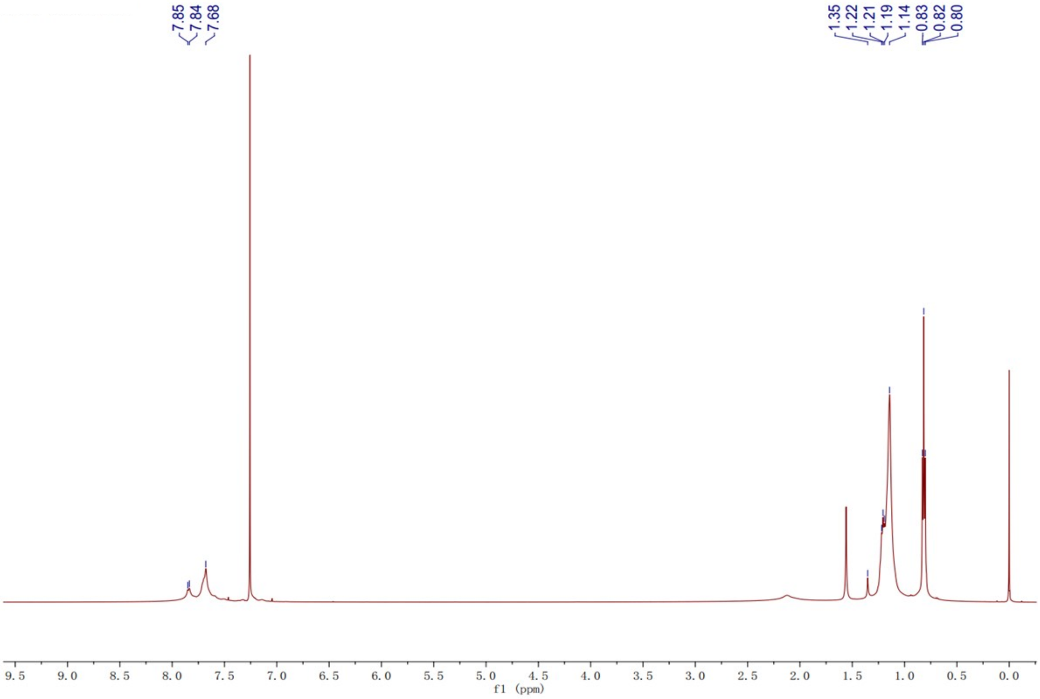

Fig. S3 ^{1}H NMR spectrum of PF-DPAVBi0.5.

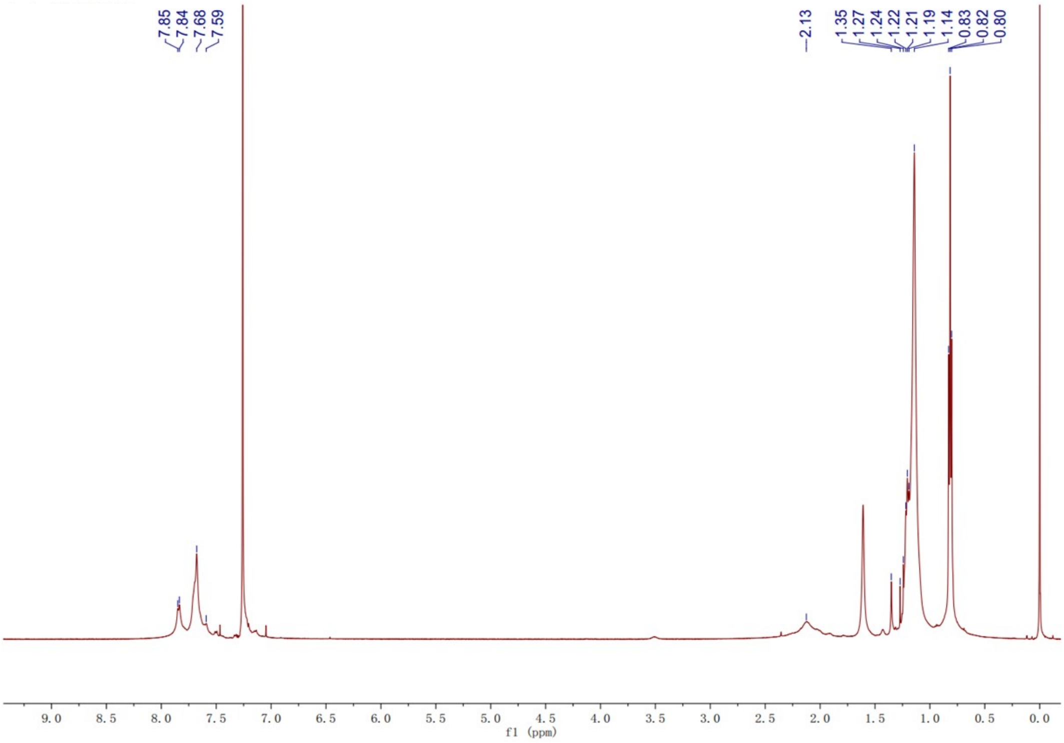

Fig. S4 ^{1}H NMR spectrum of PF-DPAVBi1.

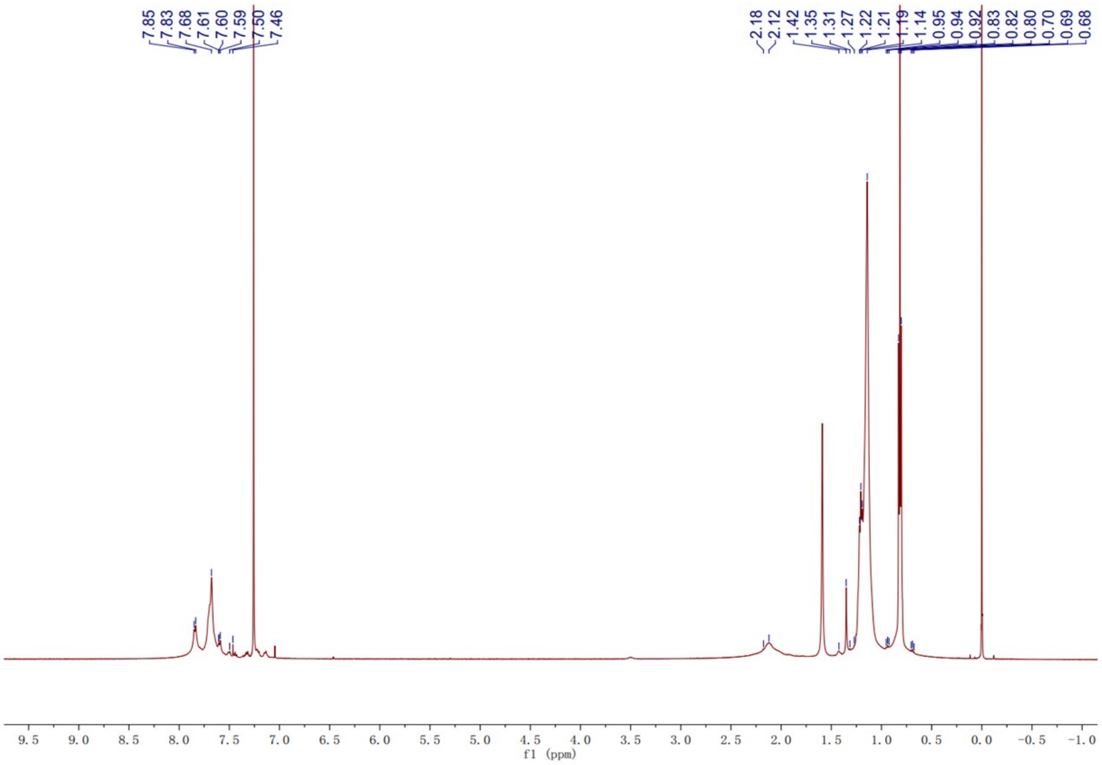

Fig. S5 ^{1}H NMR spectrum of PF-DPAVBi2.

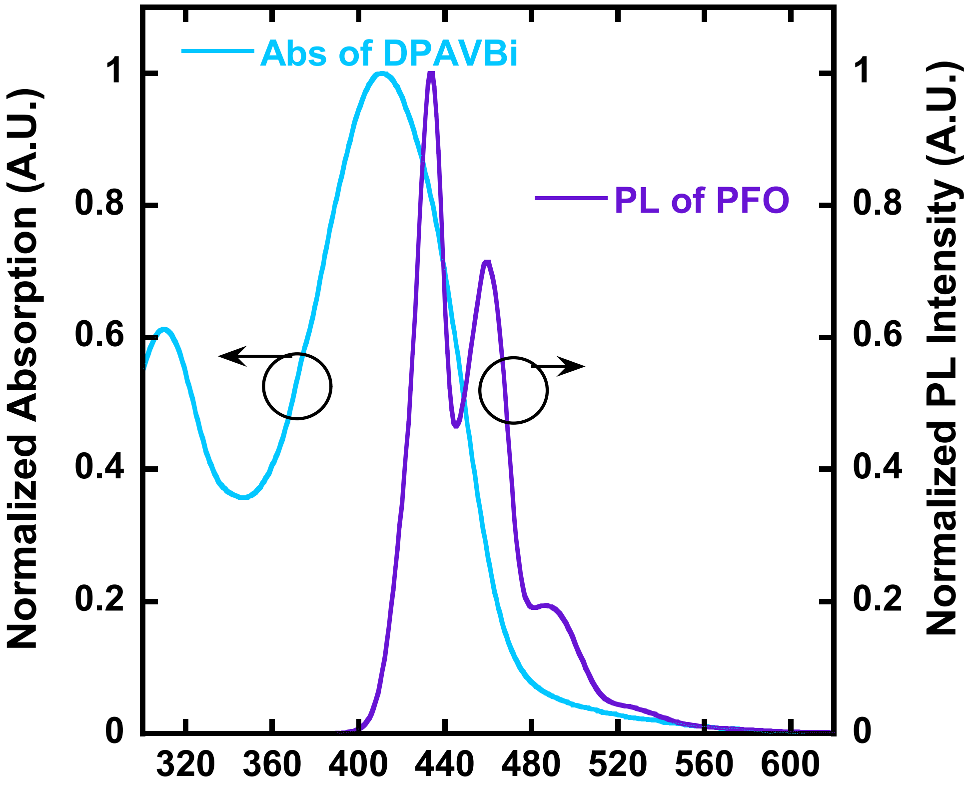

Fig. S6 The absorption of DPAVBi and PL of PFO in films.

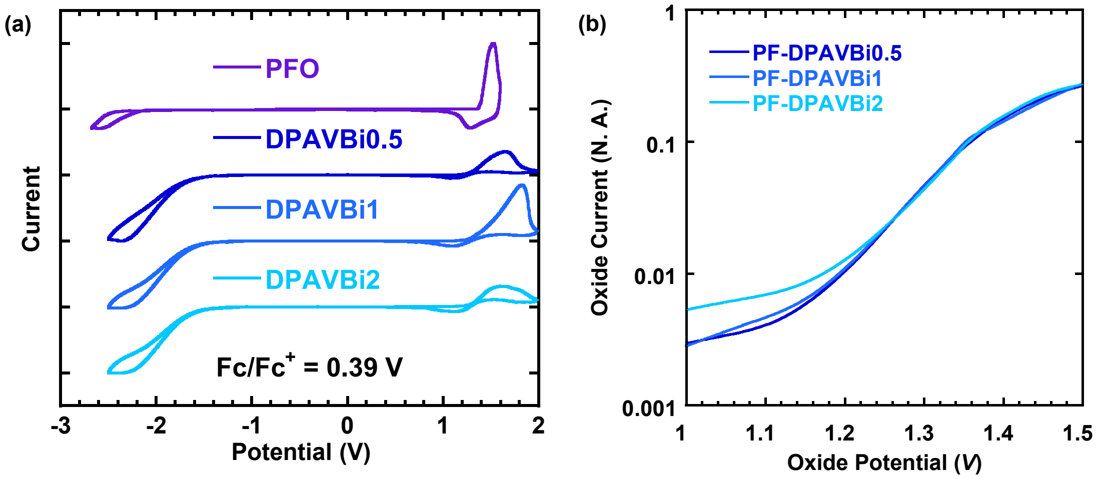

Fig. S7 Electrochemical characterization of PFO and PF-DPAVBi*x* copolymers. (a) Cyclic voltammetry curves and (b) zoomed-in view of the oxidation currents for the three copolymers.

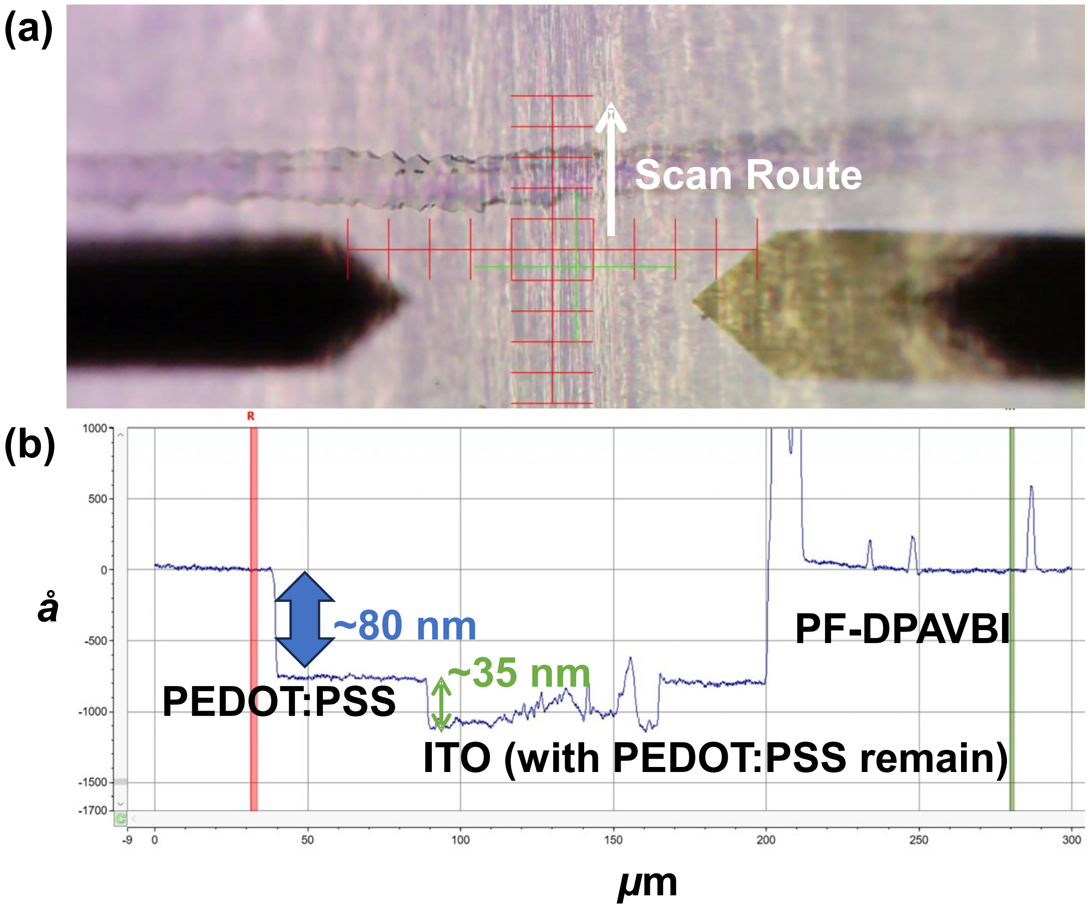

Fig. S8 (a) The optical image of scratched area of the film and the scan route of step profiler. (b) The cross-sectional validation of the ITO/PEDOT:PSS/PF-DPAVBi1. Due to the deliquescence of CsF, the CsF/Al cathode was removed.

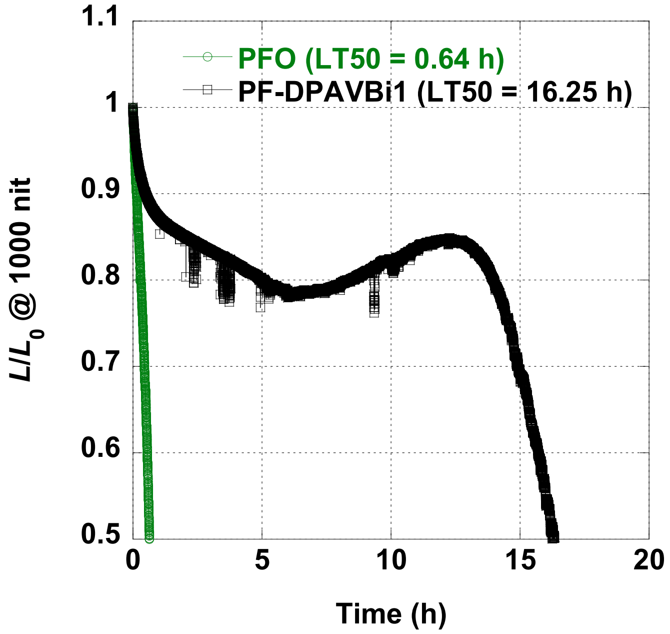

Fig. S9 The operating lifetime of PLEDs initial at 1000 nit. The device structure is ITO/PEDOT:PSS/EML/CsF/Al, encapsulated with epoxy and glass sheet.