

Supplementary Material

Perylene-Based Solution Processed Single Layer WOLED with Adjustable CCT and CRI

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Contents

Synthesis and Characterization of Perylene Derivatives

Space Charge Limited Current (SCLC) Measurements of Carrier-Only Devices

Synthesis and Characterization of Perylene Derivatives

1. Materials

Iodobutane and 1,8-diazabicyclo(5.4.0)undec-7-ene (DBU) were from ABCR Chemicals and TCI Chemicals, respectively. Hydrochloric acid, sodium hydroxide, 1-butanol, 2-ethylhexylamine, methanol, hexane, chloroform, dichloromethane (DCM), N,N-dimethyl-formamide (DMF), silica gel 0.040–0.063 mm were obtained from Sigma-Aldrich, and perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA), ferrocene (Fc) and tetrabutyl ammonium hexafluorophosphate (TBAPF₆) were purchased from Fluka. All the other chemicals used were of analytical grade.

2. Method

¹H-NMR spectra were recorded on a Bruker 400 MHz spectrometer and cyclic behavior was determined by using CH Instrument CHI 660B.

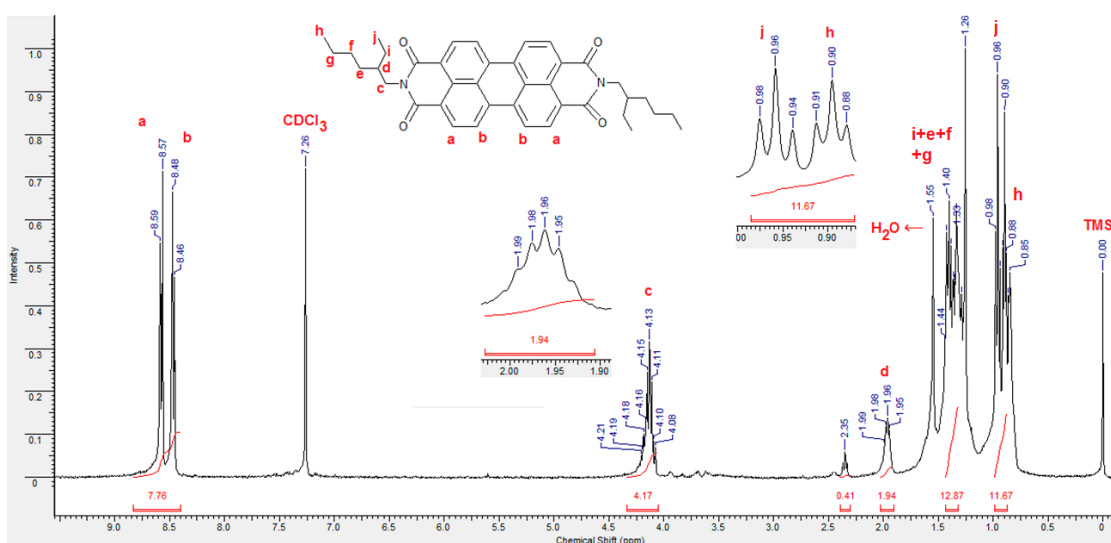
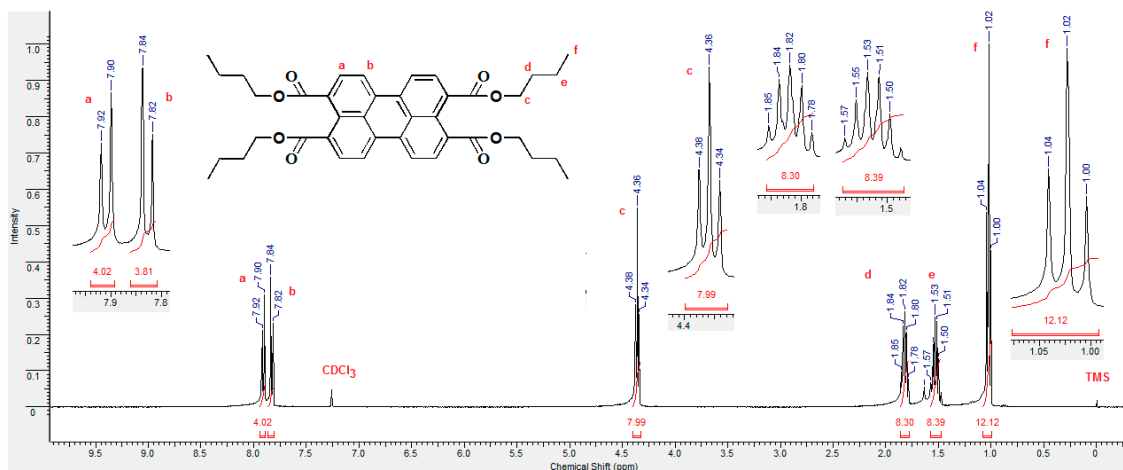
The synthetic path reported in our previous studies was followed [1, 2]. The reactions were terminated by monitoring the TLC of samples taken from the reaction medium.

2.1. Synthesis of Perylene-3,4,9,10-tetracarboxy tetrabutylester (PTE):

Firstly, 1g (2.54 mmol) PTCDA, DMF (13 mL), DBU (1.52 mL) and n-butanol (1.86 mL) were added to a 2-neck reaction flask. The reaction was stirred in argon atmosphere at 60 °C for half an hour. Then, dissolved iodobutane (1.84 g, 10 mmol) in DMF (10 mL) was slowly added. Subsequently, the reaction was stirred at 60°C for more than 4 hours and then cooled to room temperature. The mixture was slowly added into distilled water (120 mL) and the solid was filtered. The solid material was dried (75°C) and purified by column chromatography (silica gel, DCM). Yield: 1.52g (92%). FTIR (KBr) (Figure 1): ν_{\max} = (C_A-H): 2960 cm⁻¹, (C-H): 2872 cm⁻¹, (C=O): 1724 cm⁻¹, (C-O): 1276- 1172 cm⁻¹. ¹H NMR (400 MHz, Chloroform-d, TMS/ppm) δ : 7.92 (d, J: 8.0 Hz, 4H), 7.84 (d, J:8.0 Hz, 4H), 4.36 (t, J: 8.0 Hz, 8H), 1.85-1.78 (m, J: 8.0 Hz, 8H), 1.57-1.48 (m, J: 8.0 Hz, 8H), 1.02 ppm (t, J: 8.0 Hz, 12H) (Figure S1a).

2.2. Synthesis of N,N'-bis[2-ethylhexyl]perylene-3,4,9,10-dicarboxylic dimide (PDI):

Here, 0.4 g (1 mmol) of PTCDA was transferred to a 50 mL 2 neck reaction flask. After adding 20 mL of DMF to the reaction flask, it was stirred at 60 °C for 15 minutes. 1.3 mL (7.9 mmol) of 2-ethyl-1-hexylamine was added and the temperature was then increased to 140°C. After the reaction was stirred in reflux for 24 hours, the reaction temperature was turned off and after reaching room temperature, the solution was slowly poured into a 1 M 100 mL HCl(aq) solution and then stirred at room temperature for 1 night. The suspension mixture was filtered through filter flasks-funnels and then washed extensively with 1 M hot NaOH(aq) solution (the unreacted green dianhydride and mono anhydrides dissolved away). It was then washed with plenty of water to neutralize the pH of the medium. The solid was dried for 2 days at 80°C. The solid was purified by column chromatography (CHCl₃/SiO₂). Yield: 0.56 grams (92%). FTIR (KBr) (Figure 1): ν_{\max} = (C_{Ar}-H): 2959-2930 cm⁻¹, (C-H): 2872-2856 cm⁻¹, (C=O): 1697-1651 cm⁻¹. ¹H NMR (400 MHz, Chloroform-d, TMS/ppm) δ : 8.59-8.57, 8.48-8.46 (d, d J: 8Hz, 8H-perylene core C_{Ar}-H), 4.13 (m, 4H), 1.96 (m, 2H), 1.4 (m, 13H aliphatic-H), 0.96-0.90 (m, m, 12H) (Figure S1b).



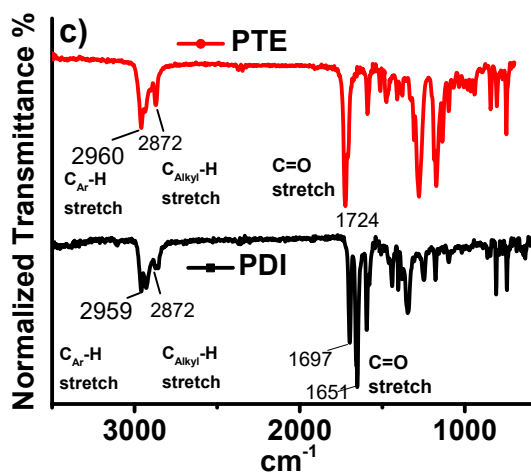


Figure S1. ¹H-NMR spectra of a) PTE, b) PDI and c) FTIR spectra of PTE and PDI.

The cyclic behaviors of PTE and PDI were determined by the use of a cell containing glassy carbon working electrode, and a platinum auxiliary (counter) electrode and 0.1M[(TBA)⁺(PF6)⁻] supporting electrolyte (scan rate: 100mV/s) (**Figure S2a**). The solutions were purged with nitrogen before starting the measurement. The electrochemical characterization of the perylene derivatives gave two reduction peaks. Lowest unoccupied molecular orbital (LUMO) was calculated by the use of Eq. (1):

$$ELUMO = -e(E_{1/2}(\text{red, dye}) - E_{1/2}(\text{Fc}) + 4.8) \quad (1)$$

The value of 4.8 eV for ferrocene with respect to the vacuum level and onset potentials of the first reduction peaks were used. Highest occupied molecular orbital (HOMO) energy levels were simply found by adding the optical band gap calculated from the off-set of absorption bands of the perylene derivatives (2.50 eV and 2.28 eV for PTE and PDI, respectively) (**Figure 2b**). The electrochemical stability of PTE and PDI was demonstrated by the comparison with the first and 52nd CV measurements (degassed) (**Figure S2c and S2d**).

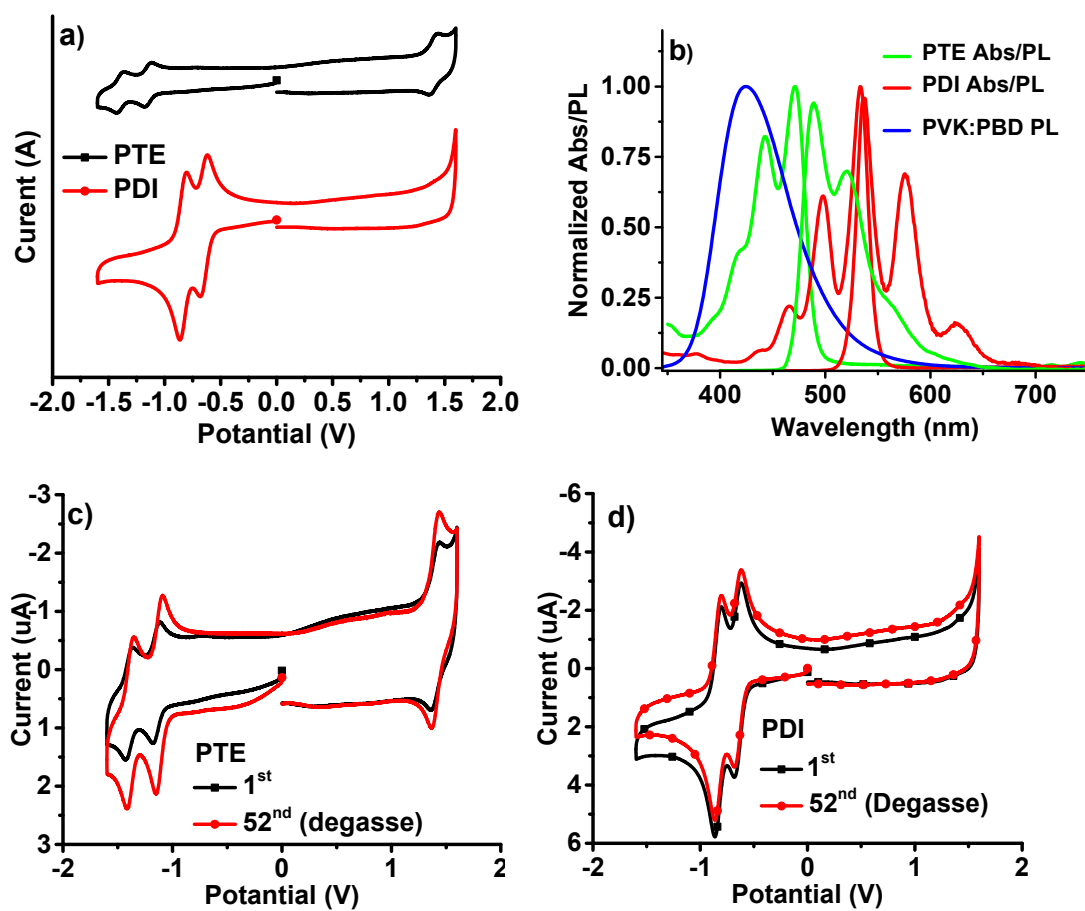


Figure S2. a) Cyclic behavior and b) absorption spectra of PDI and PTE, electrochemical stability of c) PTE and d) PDI.

Space Charge Limited Current (SCLC) Measurements of Carrier-Only Devices

ITO/PEDOT:PSS/HOST/Au and Al/HOST/LiF/Al devices were prepared to detect hole and for electron mobility values, respectively. Electron and hole mobility were calculated using a drift regime (Mott–Gurney law). Frequency-varying capacitance values were determined up to 10^6 Hz. Permittivity and mobility were found according to following equation:

$$C = \frac{\epsilon A}{d}, \quad \mu = \frac{J_{SCLC}}{V^2} d^3 \frac{8}{9\epsilon}$$

where film thickness (d) (Table S1) and area (A) are known, capacitance (C) is measured, current density (J) and V voltage measured, the electrical permittivity (ϵ) is calculated. Frequency versus mobility curves are provided in Figure S3.

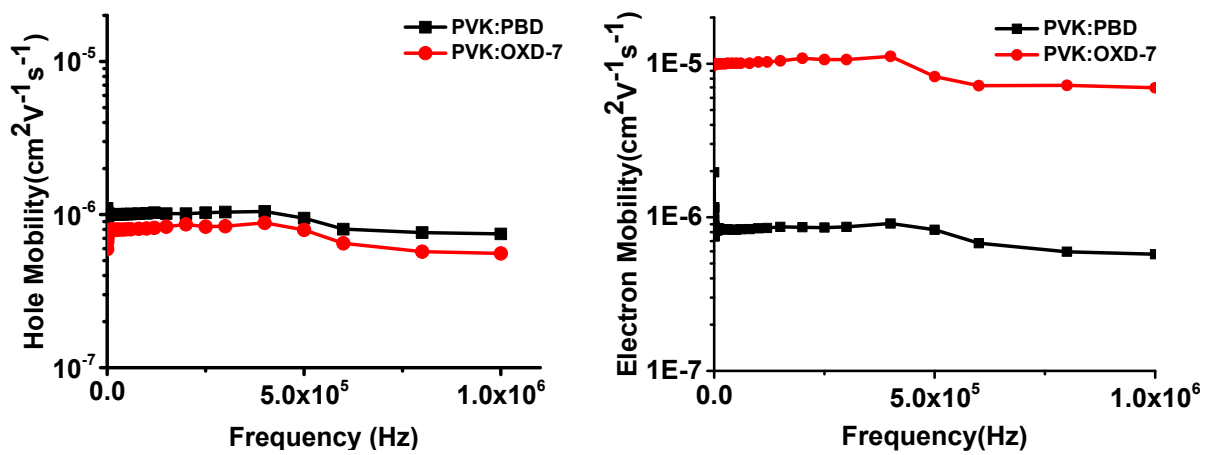


Figure S3. Hole and electron mobility of PVK:PBD and PVK:OXD-7 hosts.

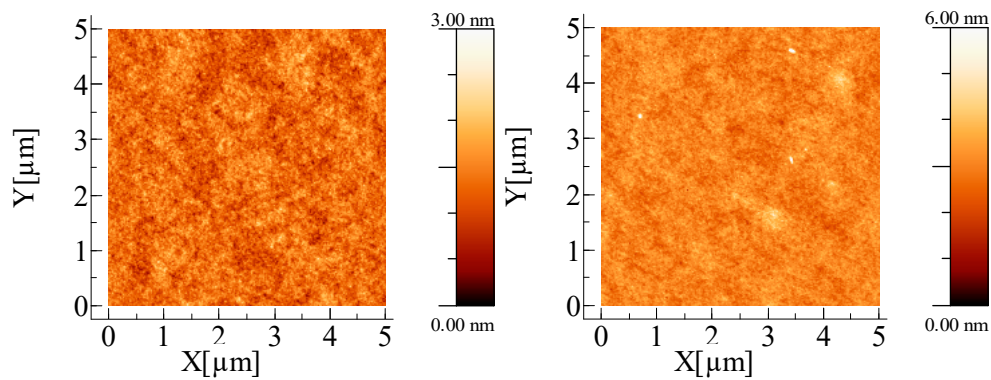
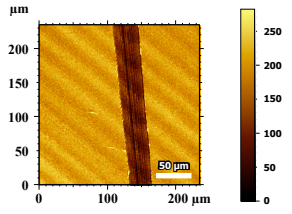
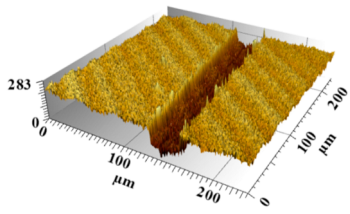
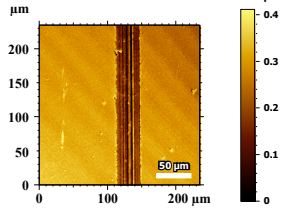
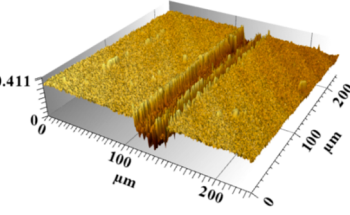
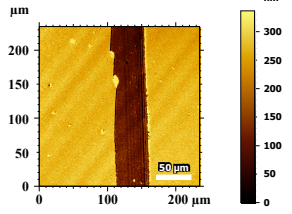
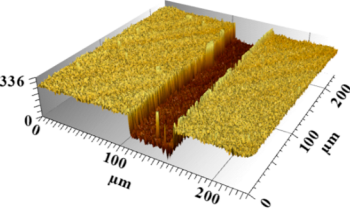
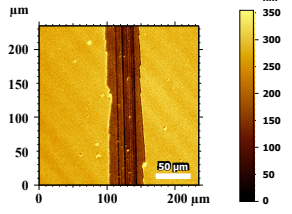
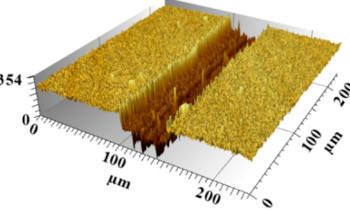
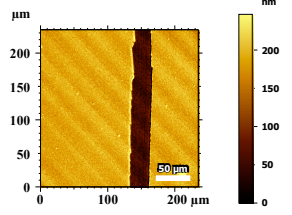
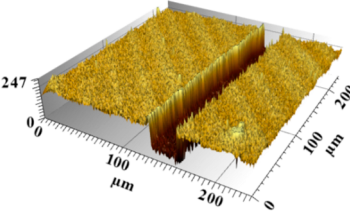
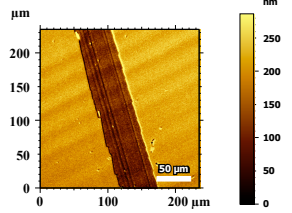
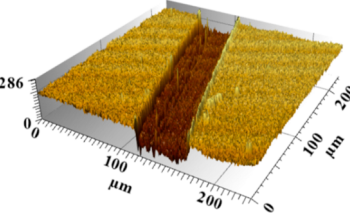
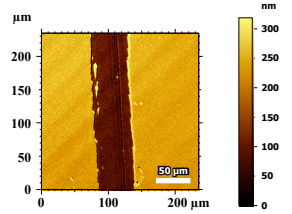
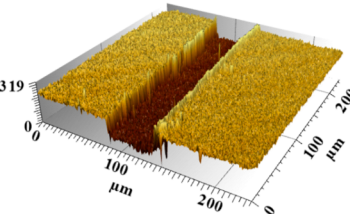


Figure S4. a) AFM images of PVK:PBD and b) PVK:OXD-7 films.

Table S1. Thickness measurements of layers

Active area	2D	3D	Average thickness
PEDOT:PSS			75±3.2 nm
PVK:OXD7			126±4.3 nm
PVK:PBD			84±2.0 nm
PVK:OXD-7: PDI(0.1 wt%)			135±4.9 nm
PVK:PBD:PDI (0.1 wt%)			89±3.4 nm
PVK:PBD:PTE (0.1 wt%)			87±2.8 nm
PVK:PBD:PDI (0.1 wt%): PTE (0.1 wt%)			87±2.1 nm

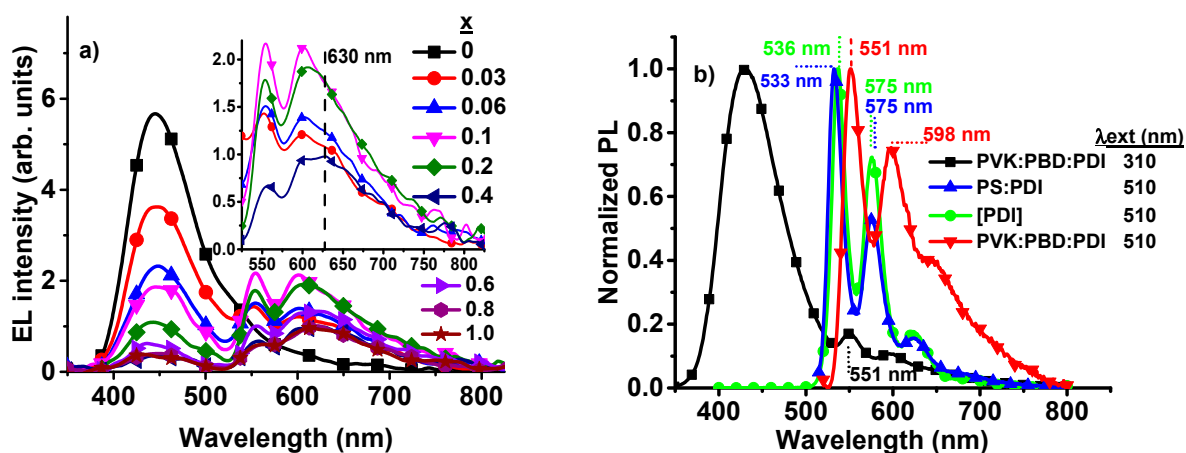


Figure S5. a) EL versus wavelength spectra of PVK:PBD:x wt%PDI devices (inset: EL intensity change at the orange–red region for the x values between 0.03 and 0.4) and b) PL curves of polystyrene (PS):PDI (λ_{exc} =510 nm), PS:PVK:PBD:PDI (λ_{exc1} = 510 and λ_{exc2} = 310 nm), films and PDI solution in $CHCl_3$.

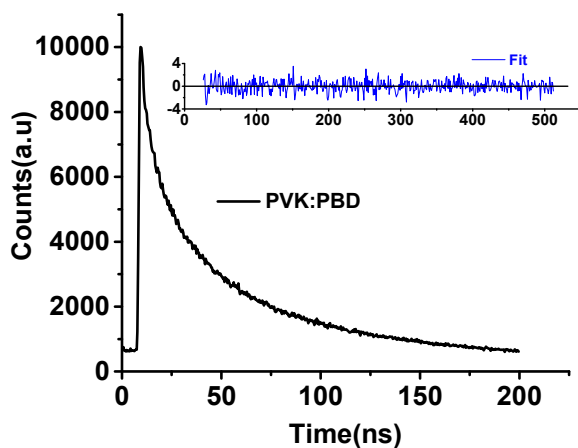


Figure S6. Lifetime measurement of the PVK:PBD matrix.

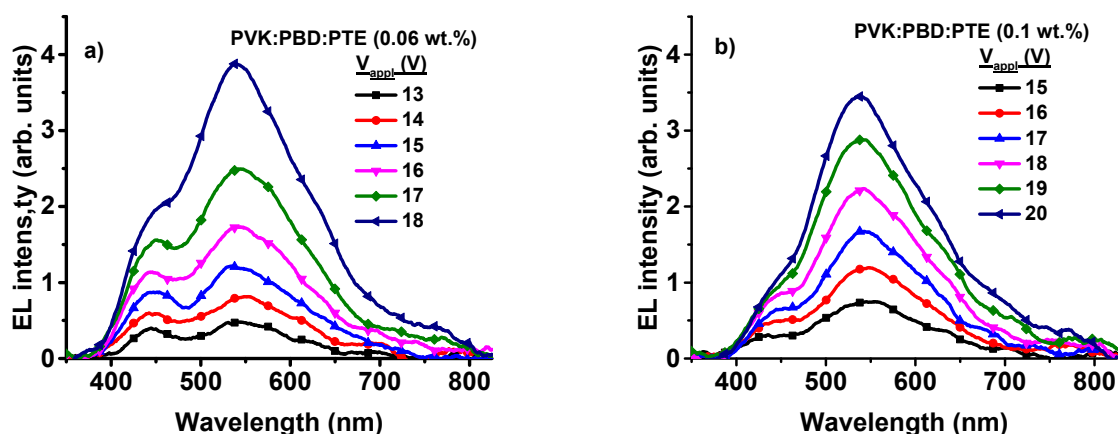


Figure S7. Applied voltage-dependent EL versus wavelength spectra of PVK:PBD:x wt%PTE devices a) x=0.06 and b) x=0.1.

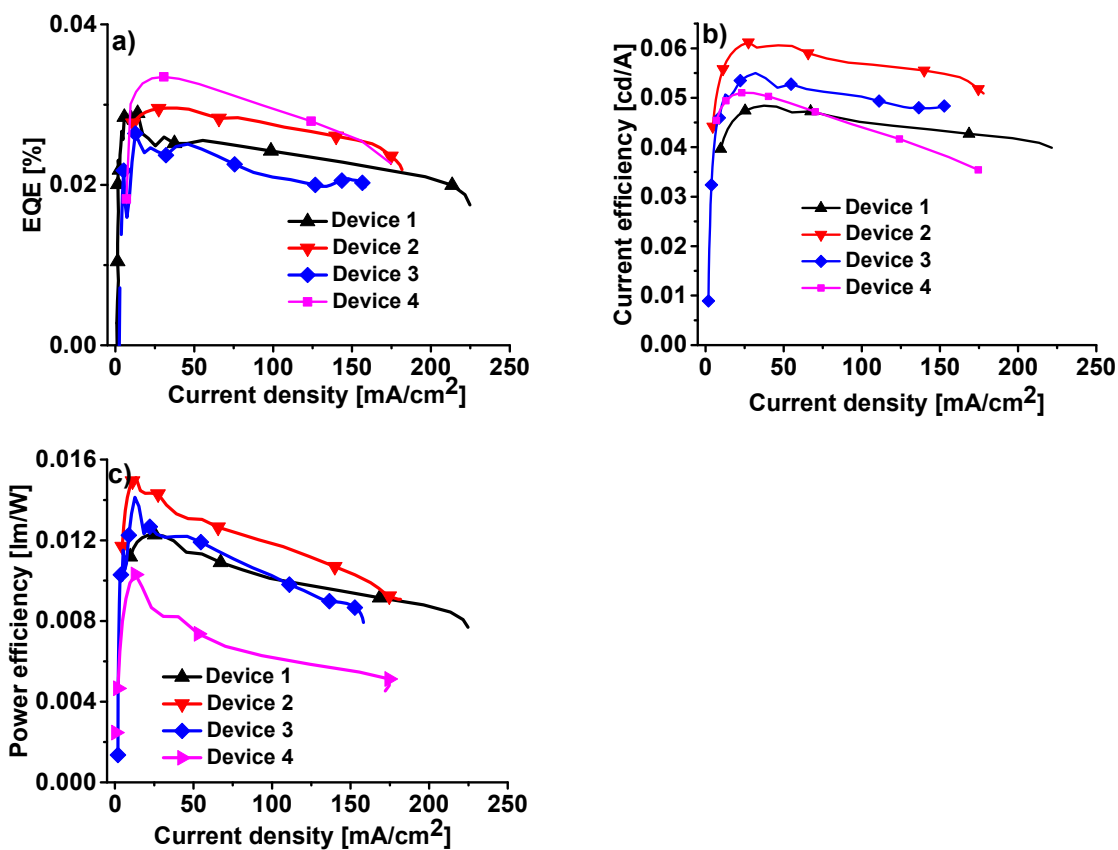


Figure S8. a) External quantum efficiency; b) current efficiency; and c) the power efficiency of Devices 1-4.

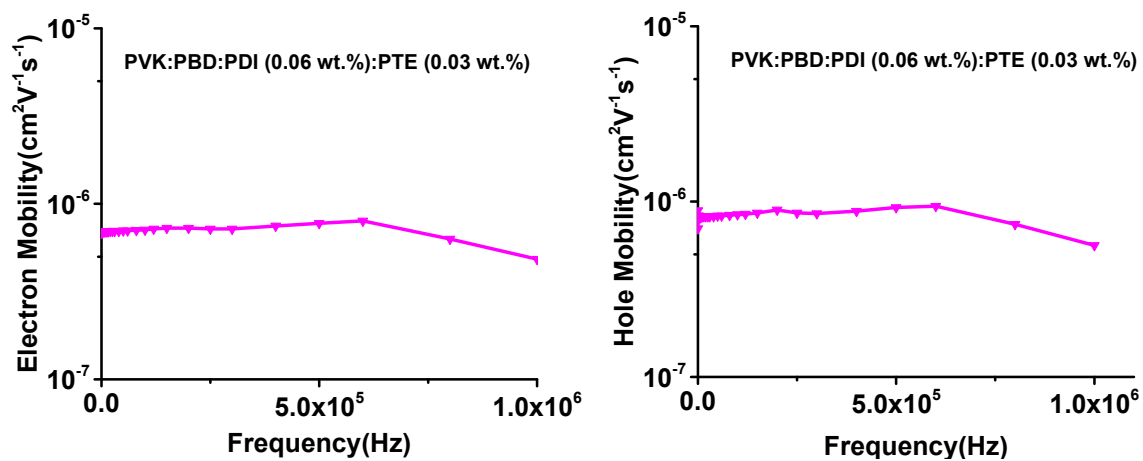


Figure S9. Hole and electron mobility of PVK:PBD: 0.06 wt.% PDI: 0.03 wt.% PTE-based device; Device 4.

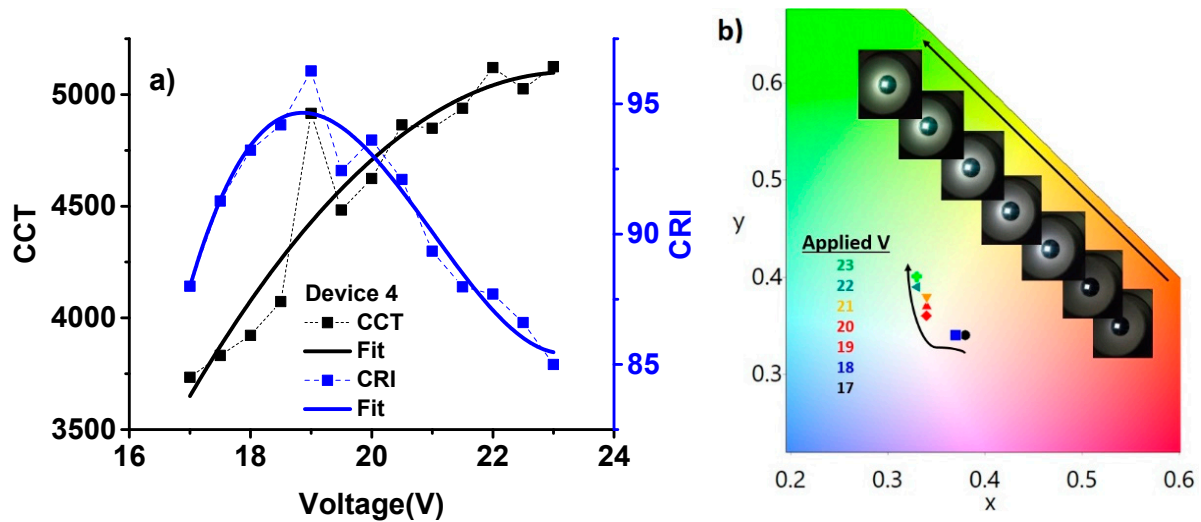


Figure S10. a) Applied voltage-dependent CCT and CRI values; and b) CIE coordinate deviation (inset; applied voltage dependent images) of Device 4.

References

- [1] E. Aksoy, N. Demir, C. Varlikli, White LED light production using dibromoperylene derivatives in down conversion of energy, *Can. J. Phys.* 96 (2018) 734–739. doi:10.1139/cjp-2017-0752.
- [2] T. Guner, E. Aksoy, M.M. Demir, C. Varlikli, Perylene-embedded electrospun PS fibers for white light generation, *Dye. Pigment.* 160 (2019) 501–508. doi:10.1016/j.dyepig.2018.08.040.