## **Electronic Supplementary Information**

## Solution-Processed Organic Light-Emitting Diodes with Enhanced Efficiency by Using Non-Conjugated Polymer Doped Small-Molecule Hole-Blocking Layer

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**Materials.** Poly(N-vinylcarbazole) (PVK) and PEDOT:PSS (CLEVIOS PVP Al 4083) were purchased from Sigma Aldrich and H. C. Starck Clevios GmbH, respectively, and were used as received. 1,3-Bis[(4-tert-butylphenyl)-1,3,4-oxadiazolyl]phenylene (OXD-7) was purchased from Wuhan Zossin technology Co., Ltd. 2,7-Bis(diphenylphosphoryl)-9,9'-spirobifluorene (SPPO13)<sup>S1</sup> and polyethylene glycol with different molecular weights (PEG 2000, PEG 6000, PEG 10000, and PEG 20000) were purchased from Luminescence Technology Corp. and Alfa Aesar, respectively. Iridium (III) bis(4, 6-difluorophenylpyridinato-N, C2') picolinate (FIrpic) was synthesized in our lab according to the reported procedure.<sup>S2</sup> All the solvents were purchased from Beijing Chemical Works and were distilled before use.

**Fabrication of OLEDs.** The OLEDs were fabricated on patterned ITO-coated glass substrates with a sheet resistance of 10  $\Omega$ /square purchased from CSG Holding Co., Ltd. The ITO-coated glass substrates were cleaned by detergent, then sequentially ultra-sonicated in distilled water, acetone and alcohol. Subsequently, a layer of 40 nm thick PEDOT:PSS was spin-coated onto the precleaned and ultraviolet-ozone (UVO) treated ITO substrates, then annealed at 120 °C for 30 min in a nitrogen filled glove box (H<sub>2</sub>O < 0.1 ppm, O<sub>2</sub>< 0.1 ppm). After that, a chlorobenzene solution containing the mixture of PVK: OXD-7: FIrpic in a total concentration of 15 mg/mL was spin-coated onto the PEDOT:PSS layer and baked at 120 °C for 10 min to form a 80 nm thick emitting material layer (EML). The HBL material composed of SPPO13 and PEG 6000 was dissolved in isopropanol and was spin-coated on the emissive layer to form a 70 nm-thick thin film. Finally, Al (100 nm)

was deposited onto the ETL as a cathode by thermal evaporation under a vacuum of 3  $\times 10^{-6}$  Torr. The chemical structures of the relevant materials and device structure are shown in Figure S1.



**Figure S1.** The chemical structures of the relevant materials and the OLED device structure.

**Measurements.** Film thickness was measured by an Ambios Technology XP-2 profilometer. The current density–luminance–voltage (J-L-V) and luminous efficiency–current density  $(\eta-J)$  were measured using a Keithley 2612B source-measurement unit and a silicon photodiode that is calibrated by a PR-655 SpectraScan spectrophotometer. Electroluminescent spectra were recorded on a Maya 2000Pro

spectrophotometer (Ocean Optics). The atomic force microscopy (AFM) images were obtained from a Veeco DI Dimension V atomic force microscope operating in the tapping mode. For the photovoltaic ( $V_{oc}$ ) measurement, the OLEDs were exposed to light with intensity of 95 mW/cm<sup>2</sup> from a simulated light source (Oriel Sol2A) and measured using a Keithley 2612B source meter. Devices' surface temperatures were measured using a K-type thermocouple and a Keithley 2000 digital multimeter with a Model 2001-TCSCAN thermocouple card.



**Figure S2.** TGA thermogram of PEG 2000, PEG 6000, PEG 10000 and PEG 20000 at a heating rate of 10 °C min<sup>-1</sup>. The inset shows DSC curve of PEG 2000, PEG 6000, PEG 10000 and PEG 20000 at a heating rate of 20 °C min<sup>-1</sup>.



**Figure S3.** AFM images (10  $\mu$ m × 10  $\mu$ m scale) of the surface morphology of the 30% PEG doped SPPO13 thin films without annealing (a) and with annealing temperature of 45 °C (b), 60 °C (c), 80°C (d) and 100 °C (e).



**Figure S4.**  $\eta$ -J characteristics of devices based on the 30% PEG-doped HBL with different molecular weight of PEG (PEG 2000, PEG 6000, PEG 10000, and PEG 20000). (Since these devices were fabricated in a different batch from the devices described in the main text, there is a little difference on the measured value of

luminous efficiency.)



**Figure S5.** Photovoltaic characteristics of devices based on the 30% PEG-doped HBL with different molecular weight of PEG (PEG 2000, PEG 6000, PEG 10000, and PEG 20000).

References:

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- S2. S. Lamansky, P. Djurovich, D. Murphy, F. Abdel-Razzaq, R. Kwong, I. Tsyba, M.
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