Electronic Supplementary Information for:

**Full-solution processed, flexible, top-emitting polymer light-emitting diodes based on the printed Ag electrodes**

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Experimental Section

Materials

Poly(ethylene naphthalate) (PEN) sheets with the thickness of 125 µm were used as the flexible substrates. PEDOT4083 and PH1000, two kinds of conductive Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS), were purchased from Heraeus Clevios. Aqueous PH1000 solution was mixed with 5 wt% dimethyl sulfoxide (DMSO) and 0.5 wt% surfactant (Zonyl FS 300). PH1 solution was achieved from the mixed solution of PH1000 and 0.5% Zonyl FS-300. Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) and Poly[2-(4-(3′,7′-dimethyloctyloxy)-phenyl)-1,4-phenylenevinylene] (P-PPV) were offered by Lijian Corporation (Guangzhou, China). ZnO nanoparticles solution and WO₃ nanoparticals solution was prepared according to the literatures.[7,9] Poly (ethylene glycol) (PEG) (Mw=4000) and potassium peroxodisulfate (KPS) were purchased from Uni-Chem. Ammonium tetrachloropalladate(II) ((NH₄)₂PdCl₄), [3-(methacryloyloxy)propyl] trimethoxysilane (MPS), 2-(methacryloyloxy)ethyl-trimethylammonium chloride (METAC) (80 wt.% aqueous solution), polyethyleneimine (PEI), dimethylsulfoxide (DMSO) and all other chemicals were purchased from Sigma-Aldrich. A thermal crosslinkable urethane liquid rubber compound (Clear Flex 50, from Smooth-On USA, mixed at a weight ratio of 1:2 parts A:B) was used as the elastic encapsulation material, TCPU.

Fabrication of printed Ag cathodes via PAMD

PEN sheets were used directly by tearing off their protective films. They were plasma-treated for 5 min, and immersed into a 0.5 wt% MPS solution (95 wt% EtOH, wt% HAc) for 1 h, followed by rinsing. Then these substrates were immersed into an aqueous solution of 2-(methacryloyloxy)ethyl-trimethylammonium chloride (METAC) (80
wt% aqueous solution) (20 wt%) and potassium peroxodisulfate (KPS) (2.5 g/L), and heated at 60 °C for 60 min for polymerization. Screen printing of catalytic ink (\((\text{NH}_4)_2\text{PdCl}_4\), (100 mg), polyethylene glycol (PEG, 4 g, Mw=4000 g/mol) and deionised (DI) water (1.0 g)) was performed on the PMETAC-modified substrates to form the ink patterns. At the end, the ink-patterned substrates were placed in the dark for 30 min to load \(\text{PdCl}_4^{2-}\) by ion exchange, followed by treating with plasma for 2 min and rinsing with DI water to remove the ink completely. The ELD of Ag was performed in a plating bath consisting of a 1:1 mixture of freshly prepared solution A and B. Solution A contains \(\text{NaOH}\) (12 g/L), and potassium sodium tartrate (29 g/L) in DI water. Solution B is a formaldehyde (40mL/L) aqueous solution. Then the activated \(\text{PdCl}_4^{2-}\)-loaded substrates were immersed in the Ag plating bath ([5 g/L \(\text{Ag(NH}_3)_2\text{NO}_3\) and 50 g/L potassium sodium tartrate aqueous solution) for serves minutes to achieve the printed Ag films at a thickness around 70 nm.

**Fabrication of PLEDs**

70 nm thick PAMD-Ag electrodes on PEN were prepared as described above. ZnO ETL was formed by spin-coating from methanol and methoxyethanol mixed solution of ZnO nanoparticles on the printed Ag electrode and then annealed for 30 min at 80°C. PEI films were made by spin-coating from its 0.5 wt% 2-methoxyethanol solution on ZnO ETL at 3500-5000 rpm for 60 s in a nitrogen-filled glove box and annealed at 80 °C for 30 min. EMLs of PLEDs were spin-coated on ZnO or PEI at different speeds in the glove box from the chlorobenzene solution of MEH-PPV or P-PPV and annealed at 60 °C for 30 min. For the devices using MEH-PPV EML, a buffer layer inserted between MEH-PPV and anode is obtained from PH1 solution. In the devices based on P-PPV, WO\(_3\) film spin-coated on P-PPV was served as HTL. Due to the hydrophobic P-PPV, 0.5 wt% Zonyl FS-300 was doped into isopropanol solution of WO\(_3\) to increase
wettability of the solution. Doped PH1000 was served as top anode, which was spin-coated on EML, PH1 or WO₃ at 1000 rpm for 60 s, and then annealed at 90 °C for 20 min in the glove box to finish the device fabrication. Finally, the TPLEDs were encapsulated using UV curable epoxy resin or Clear Flex 50.

**Characterization**

Ultraviolet photoelectron spectroscopy (UPS) was measured by ESCALAB 250Xi X-ray Photoelectron Spectrometer. Atomic force microscopy (AFM) was performed with Bruker Dimension Edge SPM System by non-contact mode. Scanning electron microscopy (SEM, JEOL JSM-6700F) was also used for surface checking. ZnO nanoparticles were characterized by using transmission electron microscopy (TEM, JEOL JEM-2000). Crystal phase of the samples was examined by X-ray diffraction (XRD) (Bruker, D8-Advance X-ray diffractometer with Cu Kα radiation, λ = 1.54056 Å, 40 kV, 40 mA) from 20 = 5° to 60° at a rate of 0.02° s⁻¹ at room temperature under ambient condition. The current-voltage and light intensity measurements were done on Keithly 2400 source meter and a PR-655 Spectra Scan Spectrophotometers. The fluorescent lifetime of the samples were measured using an Edinburgh Instruments FLS920 Fluorescence Spectrometer. The devices encapsulated by Clear Flex 50 were bended in N₂ glove box with a bending radius of 5.0 mm and then the devices were test in air using a rapid test model.
Fig. S1 Photograph of the printed Ag with different pattern fabricated on PEN sheet.

Fig. S2 SEM images of (a) Printed Ag, (b) Printed Ag/ZnO and (c) Printed Ag/ZnO/PEI.

Fig. S3 TEM images of the ZnO nanoparticles
Fig. S4 (a) UPS spectra of the printed Ag W/O interface modification layers and (b) XRD spectra of the different samples.

Fig. S5 EL spectra of the TPLEDs based on MEH-PPV (a) and P-PPV (b).
Fig. S6 Current efficiency, luminance versus current density characteristics of the PLEDs with a conventional architecture of ITO/PEDOT/P-PPV/LiF/Al.