

Supporting Information

High-Resolution Organic Light Emitting Diodes Patterned via Contact Printing

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All reagents and solvents were purchased from Sigma-Aldrich and used as supplied unless otherwise stated. Ethanol, isopropanol and deionized water were filtered through a 0.2 μm filter before use. Optical images were collected on Zeiss Axio Imager upright microscope under white light or fluorescent illumination and on a custom-built upright microscope equipped with a long working distance objective. Scanning electron microscopy was performed on Zeiss AURIGA-CrossBeam SEM using secondary electron imaging mode. AFM images were recorded on NTMDT AFM Microscope, using tapping mode with silicon probes (Bruker AFM Probes).

OLED FABRICATION

Modified ITO substrates were loaded into a custom-built vacuum chamber for thin film deposition. All the organic materials for thin film deposition were purified by entrainer gas sublimation before use. Cell fabrication was carried out in the vacuum chamber where the entire layer sequence: **hole injection layer** (HIL): 1nm molybdenum oxide (MoOx); **hole transport layer** (HTL): 30 nm 1,4,7-triazacyclononane- N,N',N'' -triacetate (TCTA); **electroluminescent layer** (EML): 20 nm tris[2-phenylpyridinato- C2,N]iridium(III) (Ir(ppy)_3 , green triplet emitter) hosted in TCTA; **electron transport layer** (ETL): 30 nm bathophenanthroline (BPhen); **electron injection layer** (EIL): 1 nm lithium fluoride (LiF); **cathode**: 100nm aluminum. The electroluminescence of fabricated OLEDs was characterized via SpectraScan PR650 and Keithley 2400 SourceMeter to get the current density-luminance-voltage curve, the electroluminescence spectra, and the curve of external quantum efficiency (EQE)-current density. The substrates of the contact printing experiments were fabricated by depositing 1nm of MoOx and 30 nm of TCTA on the ITO electrode. After the printing of the **EML** layer, the devices were completed by depositing 30 nm of BPhen, 1nm of LiF , and 100nm of Al.

To test how the dopant concentration in the **EML** affects the EQE, a series of vacuum deposited devices was fabricated with 1–11% Ir(ppy)_3 concentrations. **Figure S1** shows the EQE as a functional of the current density and dopant concentration.

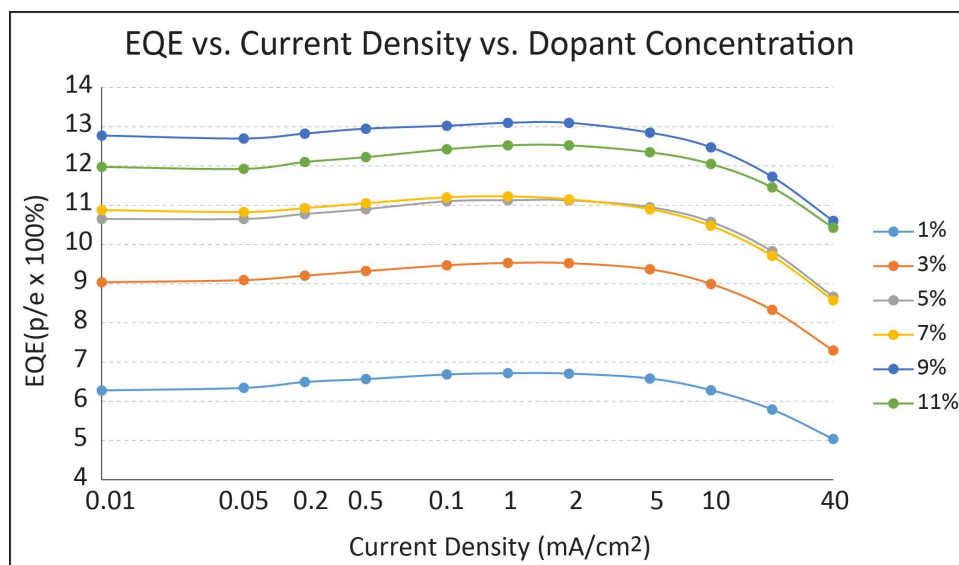


Figure S1. EQE of the vacuum deposited OLEDs as a functiona of the current density and dopant (Ir(ppy)_3) concentration.

PATTERNED SI/SIO₂ MASTER FABRICATION

NR9-1500PY (Futurrex) was spun on a clean silicon chip at 3000 rpm for 40 sec. The resulting substrate was baked on a digital hot plate at 155°C for 2 min to produce 180 nm of the resist on Si. Photolithography (Karl Suss MA6/BA6) was performed using a photomask (Photo Sciences, Inc.) bearing 16 μm hexagons with an exposure time of 11.5 sec. After UV exposure, the substrate was baked on a digital hot plate at 105°C for 70 sec, developed in RD6 (Futurrex) for 11 sec and immediately rinsed with water. The dried substrate was baked in an oven at 110 °C for 5 min and descumed in oxygen plasma for 1 min at 100 watts and 6×10^{-1} mbar O_2 pressure (Emitech K-1050X plasma asher). The oxide layer was etched away through the opening in photoresist using reactive ion etching (Trion Technology Phantom II) for 22 min using CF_4 and O_2 . Any remaining oxide was removed using buffered oxide etch (BOE). The negative resist was removed with nanostrip (55 °C, 2 min) producing a patterned silicon/ SiO_2 master.

PUA PRINTING STAMPS

PUA stamps were prepared using patterned Si/SiO₂ masters and polycarbonate CD masters according to the previously published protocol.^[1] **Figure S2** shows PUA composition and optical and SEM images of the masters and corresponding PUA stamps.

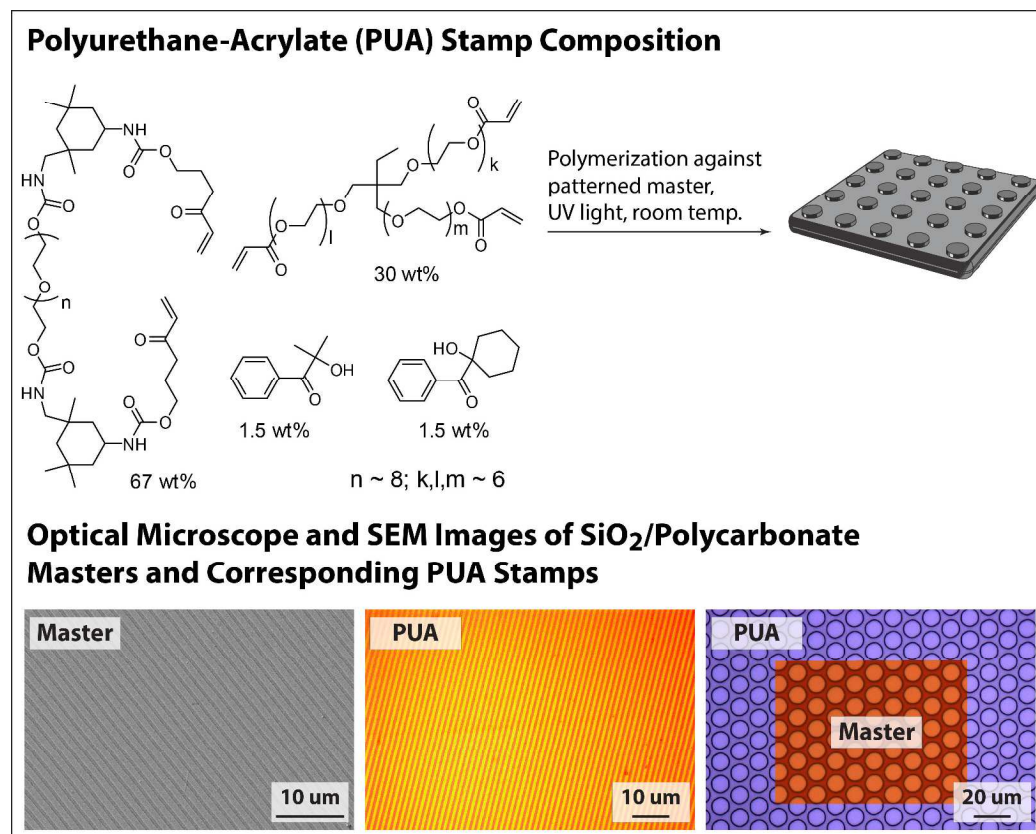


Figure S2. PUA composition and optical and SEM images of the patterned masters and corresponding PUA stamps.

STAMPING PROTOCOL

The corresponding patterned PUA stamps were sonicated in micro-filtered isopropanol to thoroughly remove any dust and contaminations, rinsed with water, ethanol and isopropanol and dried with filtered nitrogen. Subsequently, a thin layer of the emitting layer was deposited in vacuum on the stamp surface. The stamp was pressed against TCTA on ITO (at 110 kPa for 10 min), in a nitrogen filled oven preheated to a desired temperature. Following the printing, the stamp was manually separated from the substrate.

Following the printing step, the substrate was transferred into a nitrogen atmosphere and annealed on a hot plate for 10 min (or without annealing). Subsequently, the substrate was return

to the PVD chamber to complete the final OLED device. Figure 3S Shows the energy diagram of the fabricated OLEDs. **Figure 3S** shows fluorescent image of the printed **EML** pixels (after annealing, but before device completion), optical micrograph and histogram of the corresponding Si/SiO₂ master (histogram shows the background-to-feature ratio averaged over >1200 features), electroluminescent micrographs of the completed devices (after 100 °C annealing and without annealing), and the energy diagram of the completed OLED.

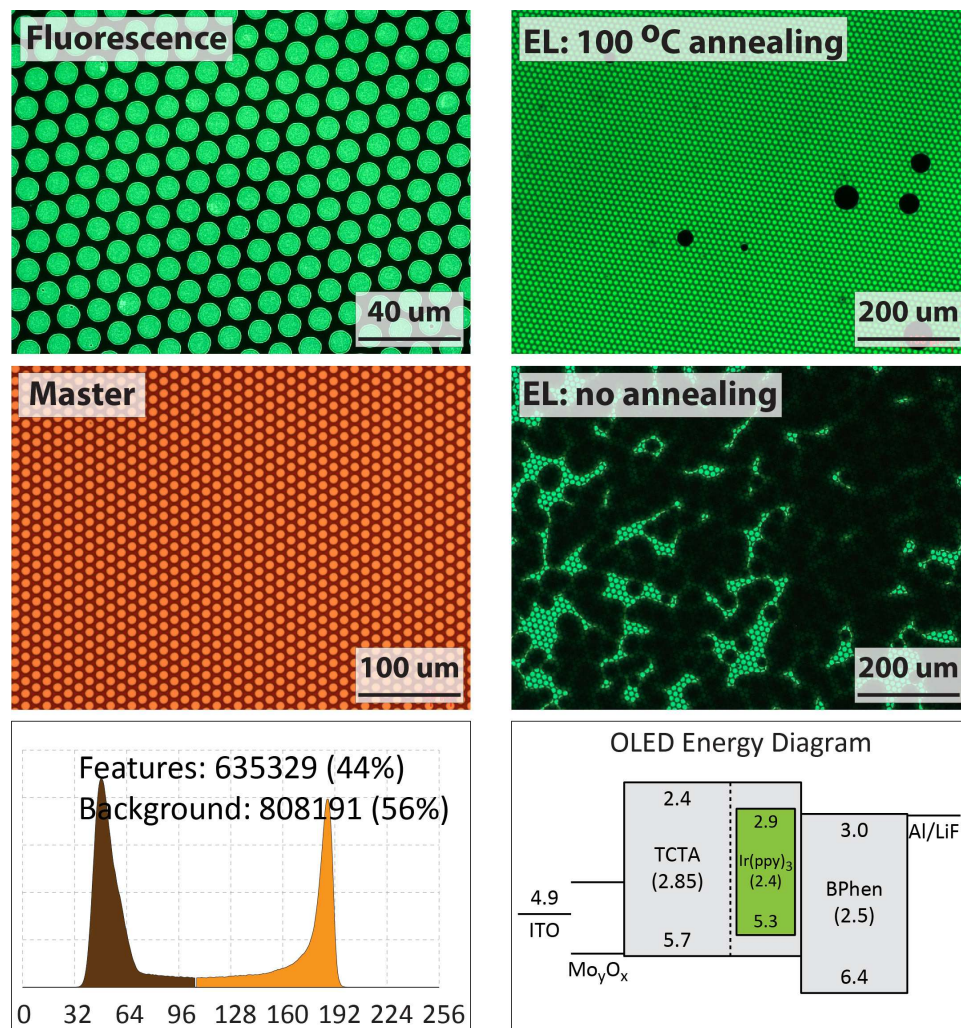


Figure S3. Fluorescent and electroluminescent images of the patterned pixels and OLED devices, optical micrograph and pixel intensity histogram of the corresponding master, OLED energy diagram

COMPARISON OF THE VACUUM-DEPOSITED AND PRINTED OLEDs.

For this comparison we used a printed **PP** OLED with 57/43 distribution of the background to pixel areas. We also used vacuum deposited **EV** devices with the emitting layer (equivalent structure to the pixel area in the **PP** OLED, two devices were used for the comparison), and vacuum-deposited **BV** devices without the emitting layer (equivalent structure to the background area in the **PP** OLED, two devices were used for the comparison). Our goal was to use **EV** and **BV** devices to calculate the efficiency of a hypothetical, vacuum-deposited **PV** OLED that has the same feature-background area ratio as the printed **PP** device.

First, the current density-voltage (J-V) plots of the **EV** and **BV** devices were fitted to the polynomial equations to calculate their current densities at the voltages of the **PP** OLED and to calculate the J-V dependence of the **PV** device using the following equation:

$$J_{PV} = J_{BV} * 0.57 + J_{EV} * 0.43 \text{ (at constant V of the PP device)}$$

The calculated J values of the **EV** and **BV** devices were also used as the pixel and background current densities in the **PV** device at the voltages of the printed **PP** OLED (**Figures S4 and S5** top plots and **Figure 5**).

We then fitted spectral radiances (L) of the **EV** and **BV** OLEDs measured at different wavelengths and current densities to the linear L -J equations ($L = a * J$) to recalculate L values of the **EV** and **BV** devices at the calculated current densities of the pixel and background areas in the **PV** OLED. **Figures S4 and S5** show calculated and measured spectral radiances of **EV** and **BV** (compared at different current densities!) and the accuracy of the L -J fits through the coefficient of determination (R^2) dependence on the wavelength

The calculated spectral radiances of the **EV** and **BV** devices were then used to calculate the radiances of the **PV** OLED at the voltages of the **PP** device (**Figure S6**, **PV**: orange lines, **PP**: blue lines, compared at the same voltages but different current densities) and the overall EQE values of the **PV** OLED using the following equations:

$$L_{PV} = L_{BV} * 0.57 + L_{EV} * 0.43 \text{ (at constant } \lambda \text{ and V of the PP device)}$$

$$\text{EQE} = \text{SUM}(\text{EQE}_S) * 4 * 100\% \quad \text{EQE}_S = L_{PV} * \pi / (E * e) \quad e = J_{PV} * 6.241509 * 10^{19} \quad E = hc / \lambda$$

EQE_S: spectral efficiency E: photon energy e: number of electrons

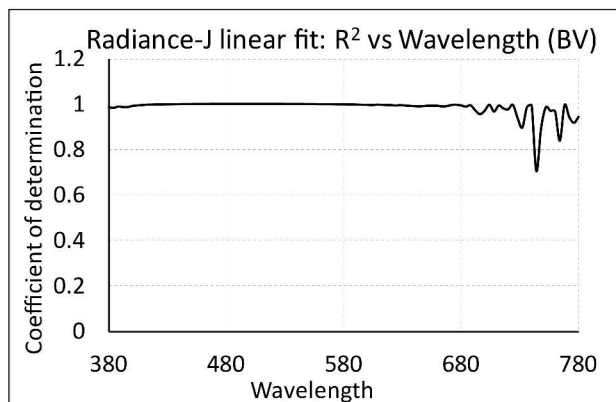
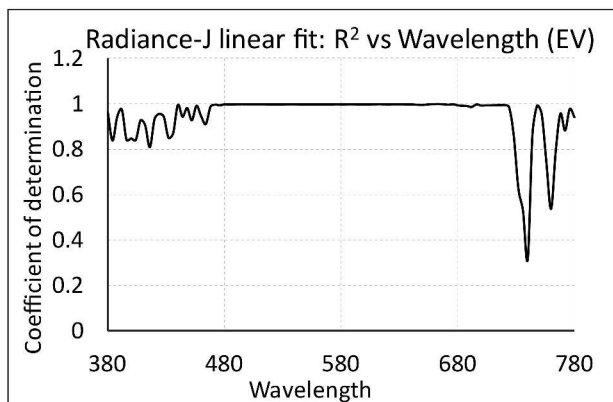
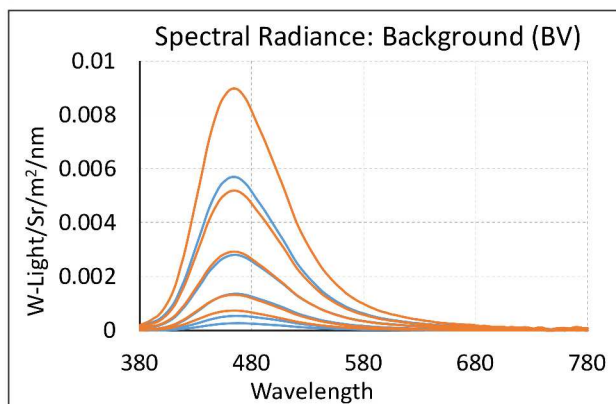
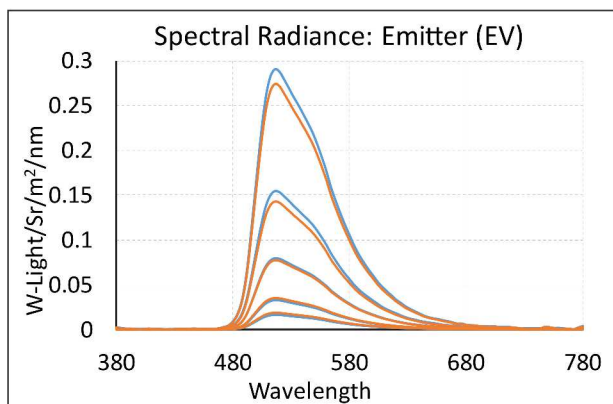
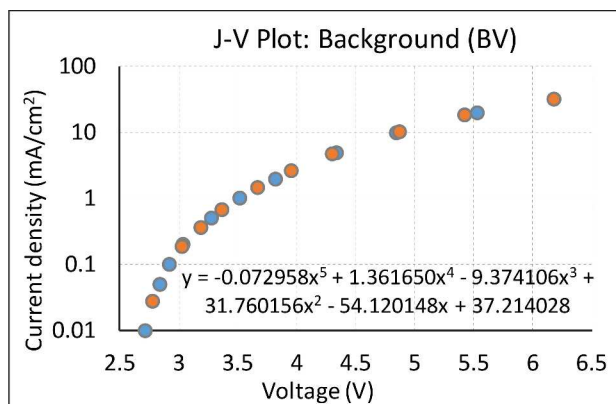
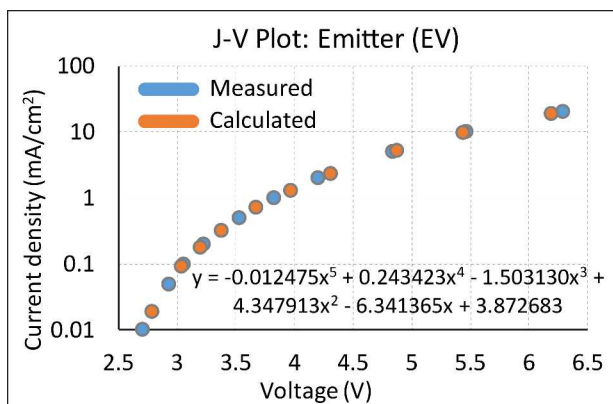


Figure S4. Measured and calculated parameters of the **EV** OLED

Figure S5. Measured and calculated parameters of the **BV** OLED

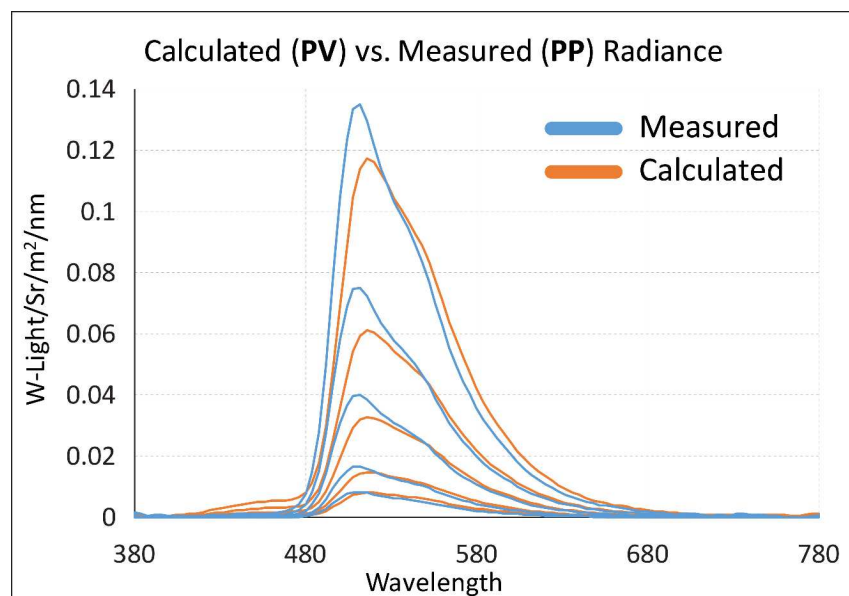


Figure S6. Measured spectral radiance of the **PP** OLED and calculated spectral radiance of the hypothetical **PV** OLED.

REFERENCES

1. Shestopalov, A. A.; Morris, C. J.; Vogen, B. N.; Hoertz, A.; Clark, R. L.; Toone, E. J., Soft-Lithographic Approach to Functionalization and Nanopatterning Oxide-Free Silicon. *Langmuir* **2011**, 27 (10), 6478-6485.