High-resolution electrohydrodynamic jet printing of small-molecule organic light-emitting diodes

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Methods

Materials: ITO glass substrates were purchased from AMG Co. Ltd. and the photoresist for the substrate preparation was purchased from Shipley Co. Ltd. Ortho-dichlorobenzene (Sigma-Aldrich) was used to dilute the TBADN:DPAVBi (Lumtec) ink. PEDOT:PSS (Clevios P VP AI 4083) was used for the hole-injection layer of OLEDs.

Preparation of structured substrates: An ITO coated glass (thickness of ITO, 200 nm; average resistance, ~20 Ω) was cleaned with a detergent and rinsed with deionized water, acetone, and isopropyl alcohol, sequentially. After drying at 100 °C, an SiO$_2$ layer was deposited using a sputter. Then, rectangular photoresist arrays with various dimensions were patterned using photolithography and this patterned photoresist was used as an etching mask for reactive ion etching of the SiO$_2$ layer, followed by photoresist stripping.

Fabrication of OLEDs: PEDOT:PSS was filtered, using a hydrophilic filter with 450 nm pores and then spin-coated on the prepared substrate which was preliminarily UV-ozone-treated before spin coating. Then the substrate was baked at 140 °C for 10 min on a hot plate. After the drying of the PEDOT:PSS layer, the emission layer (TBADN:DPAVBi) was printed using e-jet printing technique. These printed OLED pixel patterns were dried at 130 °C for 30 min. Lastly, a 1 nm-thick LiF and a 150 nm-thick Al layers were deposited using a thermal evaporator as an electron-injection layer and a cathode, respectively.

E-jet printing: The temperature (20 °C) and relative humidity (10%) were constantly maintained during the printing process. An electrically grounded ITO substrate was positioned on a high-resolution translation stage below the nozzle which was preliminarily coated by a thin metal film to generate an electric field within the stage. Nozzles with internal diameters of 1 or 2 μm were used. The stage translated at a speed of 200 μm/s during the printing process. The TBADN:DPAVBi ink was supplied by pneumatic pressure (0.2 psi) from the syringe to the nozzle tip. The distance between the nozzle and the substrate was
fixed at 15 μm and the DC voltage was controlled in the range of 220-360 V. The printing frequency was controlled in the range of 1.5-2.5 kHz depending on the applied voltage. Table S2 summarizes the printing conditions for this work.

**Optical microscopic images of devices at each process step.** Figure S1 shows optical microscopic images of devices with pixels of various dimensions at each process step. Pixel sizes are 20 μm x 30 μm, 10 μm x 10 μm, and 10 μm x 30 μm, respectively. Pixels are defined by patterning SiO$_2$ layers via conventional photolithography. Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) hole-transport layers are spin-coated and 4,4'-bis[4-(di-p-tolylamino)styryl]biphenyl-doped 2-tert-butyl-9,10-di(naphth-2-yl)anthracene (TBADN:DPAVBi (5%)) emitting layers are e-jet printed with precise alignment in ambient environment. Finally, LiF electron-injection layers and Al cathodes are thermally evaporated.

**Optical and electrical characterization of the fabricated OLEDs.** Table S1 summarizes device performances of the e-jet printed TBADN:DPAVBi OLED. Maximum luminance, current efficiency, and external quantum efficiency (EQE) are shown at each corresponding voltage, indicating reasonable operation of the e-jet printed OLED.
**Supporting Figures and Tables**

**Figure S1.** Optical microscopic images of devices at each fabrication step (pixel defining, PEDOT:PSS spin-coating, TBADN:DPAVBi e-jet printing, and LiF/Al thermal evaporation). Pixel sizes are (a) 20 μm x 30 μm, (b) 10 μm x 10 μm, and (c) 10 μm x 30 μm, respectively. All scale bars, 30 μm.
Table S1. Summarized device performances of the e-jet printed OLED.

<table>
<thead>
<tr>
<th></th>
<th>turn-on voltage (V)</th>
<th>maximum luminance (cd/m²)</th>
<th>maximum current efficiency (cd/A)</th>
<th>maximum EQE (%)</th>
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<tbody>
<tr>
<td>E-jet printed OLED</td>
<td>4.5</td>
<td>16872.8</td>
<td>8.7</td>
<td>4.6</td>
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<tr>
<td></td>
<td>(20.0 V)</td>
<td>(17.4 V)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


Table S2. Summarized printing conditions.

<table>
<thead>
<tr>
<th>Dilution</th>
<th>Nozzle inner diameter</th>
<th>Nozzle-substrate distance</th>
<th>Voltage</th>
<th>Pneumatic pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>undiluted-1:20 wt%</td>
<td>1 or 2 μm</td>
<td>15 μm</td>
<td>220-360 V</td>
<td>0.2 psi</td>
</tr>
</tbody>
</table>