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Patterned Luminescence of Organic Light-Emitting Diodes by Hot Microcontact Printing (HμCP) of Self-Assembled Monolayers

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Modification of the anode (usually Sn-doped In_2O_3, ITO)−organic interface in organic light-emitting diode (OLED) structures by chemisorption/self-assembly of nanoscopic adsorbate layers can effect dramatic enhancements in device performance for reasons that are variously associated with balancing hole-electron injection fluences,[1] altering the anode work function,[2] electric field effects,[3] anode chemical passivation,[1a] improving anode wetting by the hole transport layer,[4] and smoothing interlayer HOMO energetic discontinuities.[5] In principle, the nanoscale charge-blocking modulation possible via such interfacial effects combined with soft lithographic techniques such as microcontact printing (μCP)[6] should offer an easily implemented alternative/complement to/improvement over current approaches[7−13] for patterning OLEDs. The attraction versus several current approaches includes smaller feature sizes, parallel rather than serial fabrication, nanoscale interface tailorability, and potential molecular recognition characteristics. However, achieving rapid, contiguous anode coverage requires addressing poorly understood features of ITO surface chemistry which appear to limit efficient chemisorption.[2,14] We report here an approach to OLED anode patterning using *high-temperature microcontact printing* (or hot microcontact printing, HμCP) which readily affords pixel features down to 1.0 μm dimensions[15] and which, by virtue of the length scale-dependent carrier tunneling through SAM structures,[16] affords tunability in luminescent patterns.

The mold for the PDMS μCP "stamp" was fabricated using standard photolithographic techniques and a vapor-deposited, $CF_3(CF_2)_5CH_2CH_2SiCl_3$-derived release SAM.[6b,17] The test pattern consisted of arrays of cylinders with diameters ranging from 1 to 40 μm and with 100 μm center-to-center distances. A series of freshly distilled $RSiCl_3$ reagents (R = n-$CH_3(CH_2)_n$− (n = 21, 17, 7), n-$CF_3(CF_2)_5CH_2CH_2$−) as solutions in dry hexane were used as "inks", and were applied under rigorously anaerobic conditions to the PDMS stamp, followed by spinning at 2000 rpm for 60 s. After application of the test patterned SAMs to cleaned, 3−4 nm rms roughness, 2.5 cm^2 ITO-glass substrates (vide infra), standard OLED structures were fabricated in a double evaporator-interfaced glovebox as described elsewhere[1a,18] using vapor deposited layers of gradient sublimed TPD (50 nm) and Alq_3 (60 nm) as hole transport and electron transport/emission layers, respectively. Vapor deposition of a 70−100 nm Al cathode completed the device. Device characterization was carried out in the continuous dc mode using a Tektronix PS281 power supply and a calibrated Si photodiode. I−V responses were recorded using a Keithley 2400 current source.

Initially, all attempts to transfer an $RSiCl_3$-derived pattern to ITO substrates using standard μCP methodologies (stamping performed in ambient or in a glovebox; ink in various solvents at various concentrations; stamping for short or long times using an actuator capable of varying the pressure; use of a variety of R groups) and on a variety of ITO surfaces (sonicated in acetone, then ethanol; sonicated in detergent; cleaned in an oxygen plasma) resulted in irreproducible, poorly resolved or marginally visible luminescent patterns as imaged by optical microscopy. This was despite the fact that well-resolved test pattern features are readily imaged by SEM on single-crystal silicon substrates having a native oxide layer. These results and circumstantial evidence in the literature suggest that ITO surfaces are poorly nucleophilic and that the formation of the chemisorptive bonds[19] to the surface is sluggish.[2,14] Subsequent, successful experiments employed ITO sonicated in acetone, then ethanol, and held at temperatures of 80−100 °C during the contact printing process (2−4 s contact time with light pressure).

Figure 1a shows typical current−voltage and light output−voltage data for an OLED device patterned with an R = n-$CH_3(CH_2)_{21}SiCl_3$-based SAM applied by the present HμCP technique. The turn-on voltage is found to be ~8.0 V (typical of ITO/TPD/Alq_3/Al devices),[1a] and the pixel arrays become visible to the eye at ~12 V. Maximum light output of 3250 cd/m^2 is recorded at 25 V, which is ~10× brighter than typical cathode ray tube displays. Figure 1b shows an image of 40 μm pixel arrays at 24 V, observed under an optical microscope and recorded using a CCD camera. Note that the SAM masked area exhibits negligible emission even with the device illuminated at a level of >3000 cd/m^2. Given that the soft lithography creates no visible

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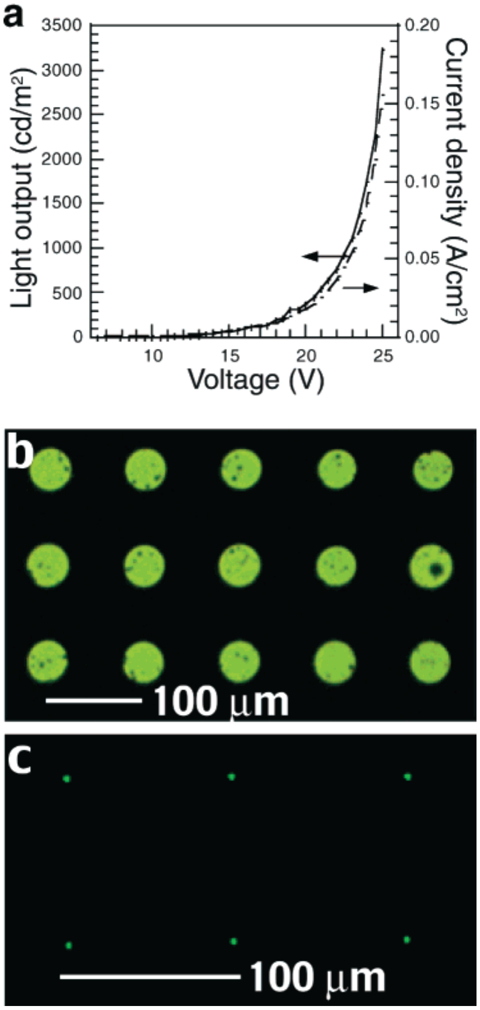

Figure 1. (a) Current density−voltage (−) and light output−voltage (- - -) data for a typical ITO/TPD/Alq_3/Al device, (b) digital image of emitting 40 μm OLED pixel arrays, and (c) digital image of emitting 1.0 μm OLED pixel arrays.

ITO transparency changes, the ∼2.1 nm thick SAM[19,20] clearly impedes hole injection into the TPD layer, rendering the stamped area essentially nonemissive. In regard to accessible pattern dimensions, the present pixel fabrication technique readily produces 1.0 μm diameter features (Figure 1c). Pixel-to-pixel variation in emission intensity and luminescence inhomogeneity within a single pixel is not appreciable for a majority of the stamped area. The occasional dark spots observed in the pixels are likely due to nonemissive defects, commonly observed in OLED devices.[21]

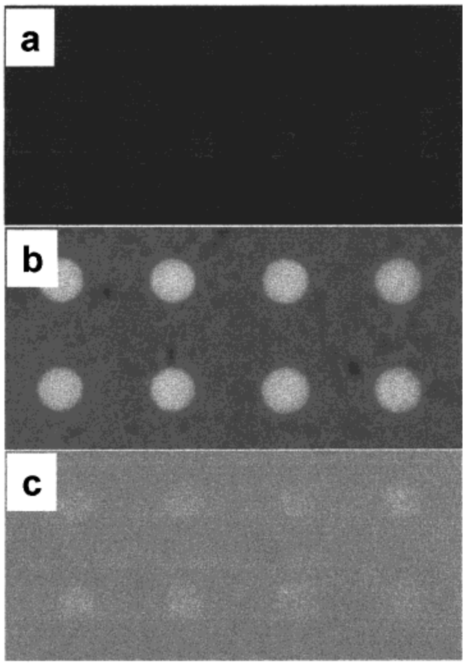

Figure 2. ITO/TPD/Alq_3/Al OLED device with n-$C_{18}H_{37}SiCl_3$-derived 40 μm SAM pixelation biased at (a) 12.0, (b) 16.5, and (c) 20.0 V.

Additionally, the hole injection efficiency as gauged by pattern luminance is a function of SAM alkyl chain length and likely related packing density.[19,20] Thus, in contrast to the above result, a thinner n-$C_{12}H_{25}SiCl_3$ SAM-derived device exhibits patterned emission with substantially lower pixel-to-background contrast at the point of device turn-on due to significant emission through the SAM-coated regions. As the bias is increased, emission from the masked region becomes increasingly intense, rendering the pixels almost indistinguishable from the background. This is presumably because hole tunneling through the SAM[16] becomes progressively more efficient at higher voltages. When n-$C_{18}H_{37}SiCl_3$ is employed as the SAM precursor (Figure 2a), the pattern contrast is enhanced and the nonemissive, SAM-masked background observed up to 16.5 V (Figure 2b) progressively becomes as emissive as the stamp-free areas (Figure 2c). These results also show that the present effects are not simply attributable to ITO etching processes.

In summary, we have demonstrated that HμCP soft lithography can effectively and rapidly transfer nanoscale hole-blocking chemisorptive patterns to OLED anodes, thereby generating luminous feature sizes as small as 1.0 μm. Moreover, this method should be compatible with other OLED fabrication techniques and more elaborate pixelation schemes.

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