Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

SUPPORTING INFORMATION

Urethane-Acrylate Polymers in High-Resolution Contact Printing

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KEYWORDS: contact printing, polyurethane acrylate, thin-film patterning, additive manufacturing

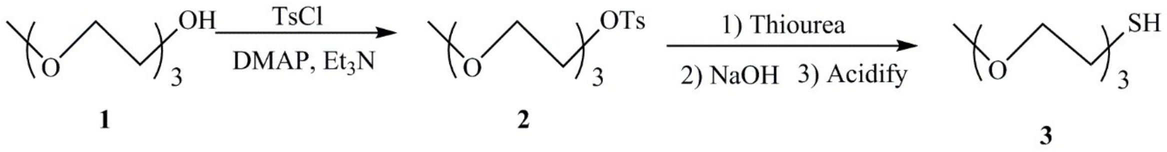
Materials and instrumentation

(1H,1H,2H,2H-tridecafluorooct-1-yl)phosphonic acid (**F-PA**) was purchased from SynQuest Laboratories; 2-propanol was purchased from Fisher scientific Inc; ethanol was purchased from Decon Laboratories. All other reagents and solvents were purchased from Sigma-Aldrich and used as received without further purification. Water was purified with Milli-Q integral systems. All rinsing solvents were filtered through a 0.2 μm PTFE membrane filter before using.

Characterization

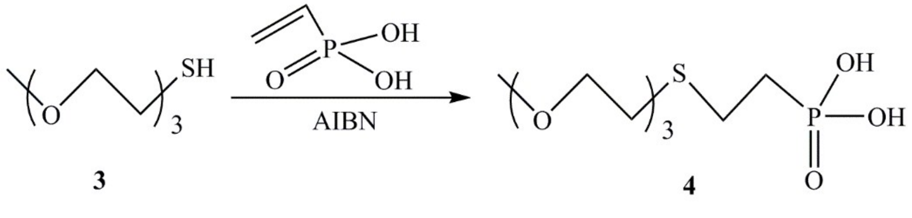
^{1}H-NMR, ^{13}C-NMR and ^{31}P-NMR spectra were recorded on a Bruker Avance 400 MHz NMR spectrometer. Liquid chromatography / mass spectrometry was performed on Shimadzu LC/MS 2010A. DMA analysis was conducted on Solids Analyzer RSA Ⅱ from Rheometrics. The optical images were collected on Zeiss Axio Imager upright microscope under white light, C-DIC or fluorescent illumination. Scanning electron microscopy performed on Zeiss AURIGA-CrossBeam SEM using secondary electron imaging mode. The contact angles were measured on VCA Optima XE goniometer. Polymer surface energy was calculated with SE-2500 surface energy software. Material testing system (MTS) QT/5 with TestWorks 4 software was employed to measure the pull-off force versus temperature and applied pressure of the patterned **PUA** stamp (Load cell value: 5N; Pull-off rate: 10000nm/s; Contact Substrate: 100 Si Wafer with oxygen plasma treatment; Applied pressure range: 1~5N; Repeated 10 times per data point). The surface elemental analysis was conducted on Kratos Axis Ultra XPS spectrometer. The performance 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.

2-(2-(2-Methoxyethoxy)ethoxy)ethanethiol (PEG-SH)



2-(2-(2-methoxyethoxy)ethoxy)ethanethiol (**3**) was synthesized in two steps from 2-(2-(2-methoxyethoxy)ethoxy)ethanol (**1**), following the previously reported procedure.[1] In short, the alcohol **1** was sulfonated by the tosyl chloride to form tosylate **2**, which was reacted with thiourea. Subsequently, sodium hydroxide was added to the reaction mixture, which was acydified with hydrochloric acid. The desired pure product (**3**) was isolated via distillation. The NMR spectra of (**2**) and (**3**) are the same as previously reported.[1]

2,5,8-Trioxa-11-thiatridecan-13-ylphosphonic acid (PEG-PA)



2,5,8-Trioxa-11-thiatridecan-13-ylphosphonic acid (**4**) was synthesized via Michael addition by reacting $(PEG)_3$-SH **3** with vinyl phosphonic acid. As such, 0.0277 mol of **3** (4.99 g) and 0.0277 mol of vinyl phosphonic acid (3.00 g) were dissolved in acetonitrile (30 ml). Subsequently, 9.41×10^{-4} mol of azobisisobutyronitrile (AIBN, 0.154 g) were added to the reaction mixture, which refluxed for 15 hours at 90 ºC under the nitrogen atmosphere. The reaction mixture was cooled to -20 ºC to separate the viscous liquid product, which was dried under high vacuum for 24 hours at 50 ºC to yield final product **4** as a clear viscous liquid (6.78 g, yield 85%).

^{1}H-NMR (DMSO-d$_6$) δ ppm: 1.78(2H, m, C$\mathbf{H}_2$-P), 2.65(4H, m, C$\mathbf{H}_2$-S-C$\mathbf{H}_2$), 3.25(3H, s, C$\mathbf{H}_3$-O), 3.42-3.60(10H, m, O-C$\mathbf{H}_2$C$\mathbf{H}_2$-O-C$\mathbf{H}_2$C$\mathbf{H}_2$-O-C$\mathbf{H}_2$), 8.08(2H, s, PO(O$\mathbf{H}$)$_2$). ^{13}C-NMR (DMSO-d$_6$) δ ppm: 24.6(1C, s, S-$\mathbf{C}$H$_2$-CH$_2$-P), 29.9(1C, d, $\mathbf{C}$H$_2$-P, $J_{c\text{-}p}$=130.7Hz), 31.7(1C, s, OCH$_2$$\mathbf{C}H_2$-S), 59.18(1C, s, $\mathbf{C}$H$_3$-O), 70.4-72.4(5C, m, O-$\mathbf{C}$H$_2$CH$_2$-O-$\mathbf{C}$H$_2$$\mathbf{C}H_2$-O-$\mathbf{C}H_2$). ^{31}P-NMR (DMSO-d$_6$) δ ppm: 25.0(1P, s). LC/MS (MeOH): m/z [M+H$^+$] calculated = 289.08, found = 288.65.

Polyurethane acrylate (PUA) prepolymer

Isophorone diisocyanate (83.8 ml), tin(II) 2-ethylhexanoate (0.128 ml) and 4,4′-methylenebis(2,6-di-tert-butylphenol) (0.18 g) were mixed together in a beaker, which was wrapped in aluminum foil. Polyethylene glycol (70.92 ml) was added dropwise to the reaction mixture at 50°C, which was then stirred for 3 hours at 55°C. Subsequently, the temperature was gradually increased to 70°C and the hydroxypropyl acrylate (49.3 ml) was added dropwise. The reaction mixture was slowly heated to 75°C and sirred at this temperature for another 3 hours.

After the reaction, the mixture was cooled down to 65°C and diluted with 102 g of trimethylolpropane ethoxylate triacrylate. Stirring was continued at 65°C for additional 20 min. The reaction mixture was cooled down to 50°C and mixed with photoinitiators: 5g of 1-hydroxycyclohexyl phenyl ketone and 4.64 ml of 2-hydroxy-2-methylpropiophenone. Stirring was continued for 5 min at 50°C to yield the final PUA prepolymer mixture.

PUA stamps

PUA prepolymer (1.5 ml) in a 20 ml glass vial was degassed under vacuum. The prepolymer was applied to a substrate (flat Si wafer or patterned Si/SiO$_2$ master or separated polycarbonate CD disc) using a plastic syringe and covered with a glass slide wrapped in parafilm. The stamp thickness was controlled using glass slide spacers. The stamp was polymerized under UV light at 365 nm in a UV reactor for 3 hours (Chromato-VUE Cabinet, Model CC-10). Subsequently, the top glass slide and the parafilm were removed and the stamp was exposed to UV light for additional 3 hours. The PUA stamp was peeled off from the substrate and rinsed with water, ethanol and isopropanol. Patterned Si/SiO_2 masters were reused multiple times. After each application, they were cleaned in Nanostrip at 75 °C for 45 minutes, rinsed with copious amount of water and isopropanol and dried with filtered nitrogen. To fabricate fluorinated hydrophobic **F-PUA** stamps, before the degassing step, 1.5 ml of the prepolymer were mixed with 150 µL of 1H,1H-pentadecafluorooctylamine while slightly heating. The hydrophilic **PEG-PUA** stamp was fabricated by mixing 75 µL of **PEG-SH** with 1.5ml of the PUA prepolymer before the degassing step. The degassing, molding and polymerization steps were the same as for the unmodified **PUA** stamp.

Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis was conducted to study the temperature-dependence of storage modulus of PUAs. **PUA**, **F-PUA** and **PEG-PUA stamps** were polymerized between a flat Si wafer and a glass slide. All the stamps were cut into identical pieces with the following dimensions: 8 mm x 35 mm x 1.27 mm. During the measurement, a dynamic strain sweep was run at least 3 times to pick the force and strain for the dynamic temperature ramp test. The tests were conducted under the nitrogen atmosphere.

Substrate pretreatment

ITO substrates (~ 1 cm x 1 cm) on silicon were manufactured by coating silicon wafers with 2000Å ITO using an RF dielectric sputter system (Kurt Lesker PVD 75). The ITO on glass or silicon was either cut into 1cm x 1cm square (for SAM printing) or used as received (from Tinwell Technology LTD, surface resistance 15 Ω/sq with ~90% optical transparency, for all thin film work), rinsed with water, ethanol and isopropanol, and dried with filtered nitrogen. After cleaning, ITO was oxidized with oxygen plasma (PC-2000 Plasma Cleaner, South Bay Technology Inc.) for 5 minutes at 200 mTorr of pressure, 40W of the forward power and 1-3W of the reflected power.

Printing of organic molecules

An ink solution (10 mM solution of **Alk-PA** in 2-propanol, 10 mM solution of **F-PA** in 2-propanol or 10 mM solution of **PEG-PA** in methanol) was filtered with a 0.2-µm PTFE

Fisherbrand syringe filter and spin-coated three times onto a corresponding stamp at 1000 rpm for 1 minute. The printing was conducted manually by placing the inked stamp onto the ITO substrate for 1 minute and applying small initial pressure to ensure a conformal contact. The stamp was removed from the ITO substrate, the substrate and the stamp were rinsed with isopropanol and water and dried with filtered nitrogen. The same stamps were reused multiple times.

Wet etching of ITO

Aqueous solution of oxalic acid (0.05M) was filtered through a 0.2-μm PTFE syringe and used to etch the ITO substrate bearing patterns of **Alk-PA** for 30 seconds at room temperature with slight agitation to achieve a more uniform etching. The etched substrate was rinsed with water and isopropanol and analyzed by SEM and C-DIC microscopy after drying.

Wetting of patterned SAMs on ITO

To test the dewetting ability of the patterned **Alk-PA** SAMs on ITO, the patterned substrate was exposed to a saturated water vapors. The condensed water on the ITO surface was imaged immediately using optical microscopy.

To test wetting ability of **PEG-PA** SAMs, the ITO substrate was rinsed with isopropanol, dried, oxidized with oxygen plasma, and immersed into a 10 mM solution of **F-PA** in isopropanol for 1 min to form a continuous hydrophobic SAM. Subsequently, the modified substrate was used in microcontact printing with the **PEG-PUA** stamp and 10 mM **PEG-PA** solution in methanol. Following the printing, the substrate was exposed to the saturated water vapor and imaged using optical microscopy. The pattern of **PEG-PA** on **F-PA** ITO was imaged by SEM.

Comparison of printing and solution-deposited SAMs

SAMs of **Alk-PA**, **F-PA**, and **PEG-PA** were deposited on ITO substrates either from the corresponding 10 mM isopropanol (methanol for PEG-PA) solutions overnight at room temperature, or by the contact printing using the previously described conditions and flat **PUA**, **F-PUA** and **PEG-PUA** stamps. The functionalized substrates were rinsed with water and isopropanol, dried with filtered nitrogen, and analyzed by XPS.

Printing of organic thin films

ITO glass substrates (110 nm, 15 Ω/sq) were sonicated in water for 10 min, and cleaned in mixture of acetone and ethanol (3:1) for 10 min, and with a stream of filtered nitrogen. Oxygen plasma was then used to remove the remaining organic contaminations.

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 (see next section) was deposited in vacuum on the stamp surface. The stamp was pressed against TAPC 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.

Organic thin film deposition

All films were prepared through thermal deposition ($<10^{-6}$ Torr) using custom-made physical vapor deposition (PVD) equipment. 20 nm of tris(4-carbazoyl-9-ylphenyl)amine (TCTA) with 15% of bis[2-(4,6-difluorophenyl)pyridinato-C2,N](picolinato)iridium(III) (FIrpic) or 20 nm of Tris(4-carbazoyl-9-ylphenyl)amine (TCTA) with 10% of green dopant $Ir(ppy)_3$ was evaporated onto the patterned PUA stamps (**PUA**, **F-PUA** and **PEG-PUA**) as a light emitting layer. To prepare the printing substrates, 1nm of MoO_x was first deposited onto ITO as hole injection layer, followed by thermal deposition of 30nm film of 4,4-cyclohexylidenebis[N,N-bis(4-methylphenyl)benzenamine] (TAPC) as hole transport layer.

OLEDs fabrication

Following the printing step, the substrate was transferred into a nitrogen atmosphere and annealed on a hot plate at 100 ºC for 10 min (or without annealing). Subsequently, the substrate was return to the PVD chamber and 30 nm of TPBi, 20 nm of TmPyPb, 20 nm of Bphen, 1 nm of LiF and 100 nm of Al were deposited onto the substrate to manufacture the device. Figure 1S Shows the energy diagram of the fabricated OLEDs.

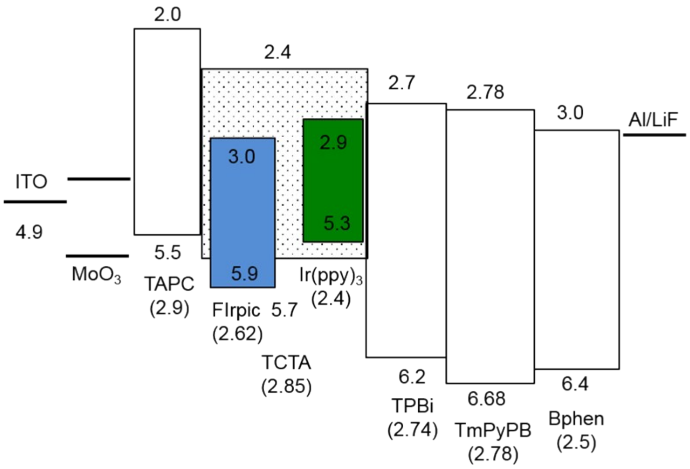


Figure 1S. Energy diagram of the fabricated OLED devices

References:

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