Combined wet lithography and fractional precipitation as a tool for fabrication of spatially

controlled nanostructures of poly(3-hexylthiophene) ordered aggregates

Lorena Di Silvio, Eugenio Lunedei, Denis Gentili, Marianna Barbalinardo, Ilse Manet, Silvia Milita, Fabiola Liscio, Alessandro Fraleoni-Morgera & Massimiliano Cavallini

SUPPORTING INFORMATIONS

Experimental

All experimental procedures were carried out at room temperature and in air.

Materials

The solution used contains P3HT ((Mw = 50,000 - 100,000 Da, regioregular 90%), and PDCB (99+%) in CHCl3(99.9+%), with concentrations of 1 mg/ml and 300 mg/ml respectively. The substrates were made Si/SiO₂ wafers with 200 nm of thermal SiO₂.^{1,2}

Stamp

Stamps were prepared by replica moulding of a blank compact disk in PDMS (Sigma Aldrich). The stamps motif consists of parallel protruding lines 220 nm thick, 750 nm wide with a $1.5 \,\mu$ m pitch.^{3,4}



Figure SO AFM image of the stamp

Lithographically Controlled Wetting (LCW)

In LCW, the stamp is placed in contact with 10 μ l of liquid film of a solution on a substrate (Figure 1a). The menisci form under the stamp protrusions due to capillary forces. As the solvent evaporates, the solution remains pinned to the protrusions and the contact line between solution and substrate recedes due to faster solvent evaporation in the region between protrusions (Figure 1b). This makes the region between the protrusions free of solution. As the critical concentration is reached, the solute precipitates onto the substrate only below the protrusions (Figure 1c), giving rise to a structured thin film that replicates the positive pattern on the stamp (Figure 2).

Characterization techniques

Atomic force microscopy. AFM imaging were performed on a Multimode 8 microscope equipped with a Nanoscope V controller and a type JV piezoelectric scanner. Samples were scanned in PeakForce mode with NTMDT-NSG10 probes (Spectrum Instruments, Ireland). Raw images were processed with Gwyddion 2.48 (http://gwyddion.net/).

Grazing incidence X-ray diffraction. GIXRD measurements were performed at the XRD1 beamline of ELETTRA synchrotron facility in Trieste (Italy). The X-ray beam was characterized by a wavelength of 0.7 Å and a beam size of 200x200 μ m². The XRD profiles have been obtained by radially integrating the diffracted intensity of the (001) reflection recorded on the 2D-GIWAXS images. The detector was a 2MPilatus silicon pixel X-ray detector (DECTRIS Ltd.) was positioned perpendicular to the incident beam, at a distance of 260 mm from the sample.

Confocal Fluorescence Imaging. Confocal fluorescence imaging was performed on an inverted Nikon Ti-E microscope (Nikon Co., Shinjuku, Japan) using an argon-ion CW laser as well as 405 nm pulsed/CW diode lasers (PicoQuant GmbH, Berlin, Germany). Images were collected using a Nikon Plan Apo VC 60X oil immersion objective with NA 1.40. Filters were set to register the fluorescence intensity in the 500-550 nm, 560-610 nm and 665-735 nm ranges. A Nikon A1 spectral module with

a precisely corrected 32-PMT array detector was used for spectral imaging. Wavelength resolution was set to 6 nm per PMT. Spectral images were obtained by exciting the sample at 405 nm in CW mode.



Figure S1. Sketch of the last steps in the formation of P3HT structures on a silicon surface, via progressive PDCB sublimation, the bluish crystals progressively disappearing. The imaged crystals were prepared by drop casting a CHCl₃/P3HT/PDCB solution (P3HT:PDCB ratio w/w 1:300) in air at room temperature.



Figure S2. SEM image of large area printed P3HT stripes of sample type 2.



Figure S3. (a) 3D-plot of the current $I_{SD}[\mu A]$ flowing inside OFET channel, during successive sweps in V_G (with V_G from 0V to -50V, in 51 steps) at fixed V_{SD} value (V_{SD} from 0V to -50V in 26 steps). (b) I_{SD} isocurrent lines as calculated from a. The current value (in μA) is indicated for some representative values of I_{SD} . (c) OFET transfer curves (V_G=0V,...,-50V), as measured at fixed values of V_{SD} (V_{SD} from 0V to -50V). (d) OFET leakage current (I_G), upon V_G scan. 26 curves are traced, one for each fixed value of V_{SD}. The leakage current I_G across the dielectric layer neverexceeded 1/100th of channel current value at any V_{SD}

- C. C. Cedeno, J. Seekamp, A. P. Kam, T. Hoffmann, S. Zankovych, C. M. S. Torres, C. Menozzi, M. Cavallini, M. Murgia, G. Ruani, F. Biscarini, M. Behl, R. Zentel and J. Ahopelto, *Microelectron. Eng.*, 2002, 61-62, 25-31.
- S2. M. Cavallini and F. Biscarini, *Review of Scientific Instruments*, 2000, **71**, 4457-4460.
- S3. M. Cavallini, I. Bergenti, S. Milita, J. C. Kengne, D. Gentili, G. Ruani, I. Salitros, V. Meded and M. Ruben, *Langmuir*, 2011, **27**, 4076-4081.
- S4. C. Albonetti, J. Martinez, N. S. Losilla, P. Greco, M. Cavallini, F. Borgatti, M. Montecchi, L. Pasquali, R. Garcia and F. Biscarini, *Nanotechnology*, 2008, **19**, 435303.