Scanning near-field optical lithography (SNOL) of organic semiconductors

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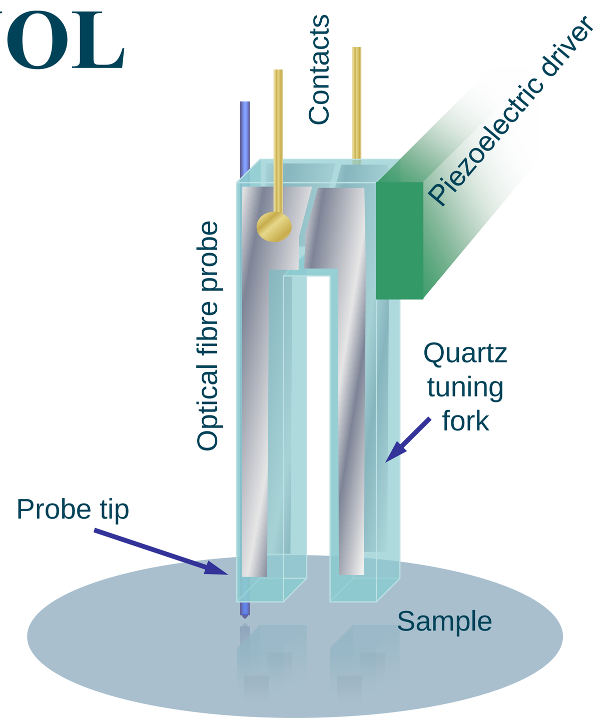
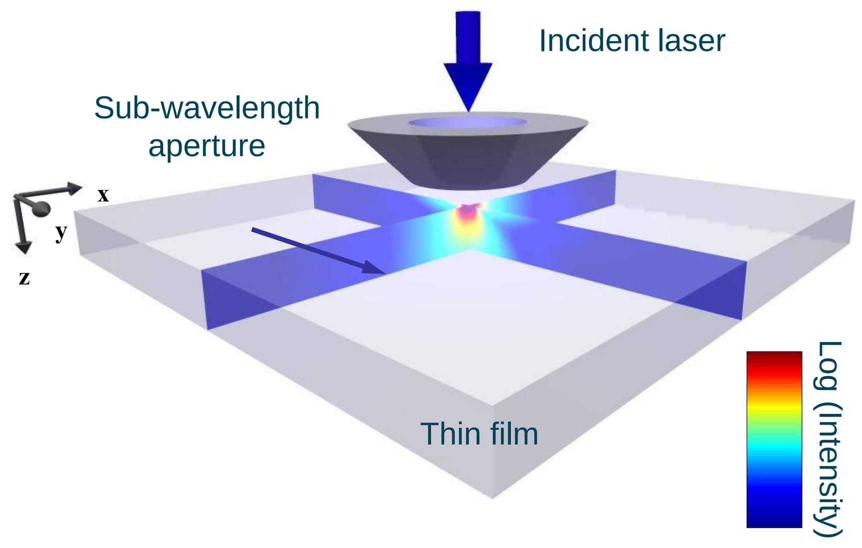
Scanning near-field optical lithography (SNOL) has been shown to provide a versatile method for patterning materials over lengths well below the classical diffraction limit. We apply this technique to thin films of organic semiconductors. These optically and electronically active materials are chemically tuneable, flexible, and can often be processed directly from solution.

For applications in photonic devices and nano-electronics, achieving lithographic resolution on the nano-scale is vital. Using a home-built SNOL system, we demonstrate how thin films of the widely studied polymer poly(para-phenylene-vinylene) (PPV), and the cross-linkable oxetane derivatives F8Ox and BTOx can be patterned to any predetermined design.

SNOL



- The SNOL probe: a sharpened, metal-coated optical fibre with a sub-wavelength aperture defined at the apex
- 325nm HeCd laser launched into the fibre.
- Optical near-field generated around the aperture
- Contact is maintained using shear-force feedback



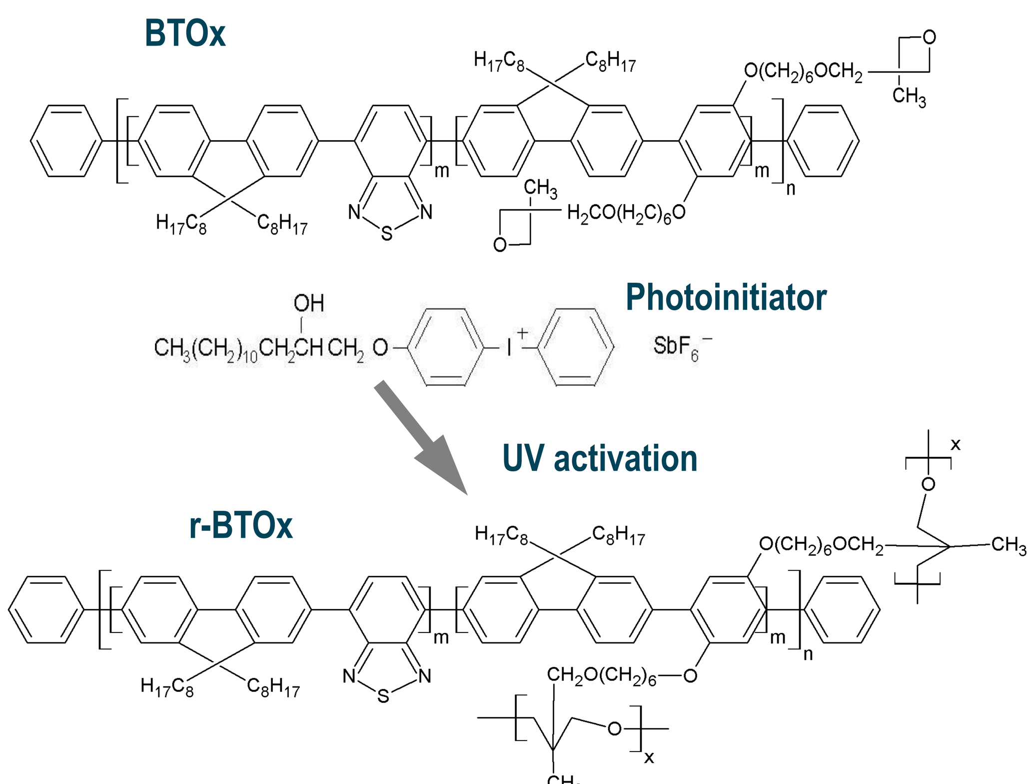
(Right) 3-dimensional representation of the optical field strength in a thin film placed below the tip of an apertured SNOL probe.
Optical intensity distribution is calculated with the Bethe-Bouwkamp model (λ = 325nm, aperture diameter 50nm, film thickness 20nm and film refractive index 1.73 + 0.067*i*.)

BTOx

Poly{2,7-(9,9-dioctylfluorene-alt-benzothiadiazole)-co-1,4-(2,5-bis-(methyl-4'-(6-(3-methyloxetan-3-yl)methoxy)hexyloxy)benzene)}

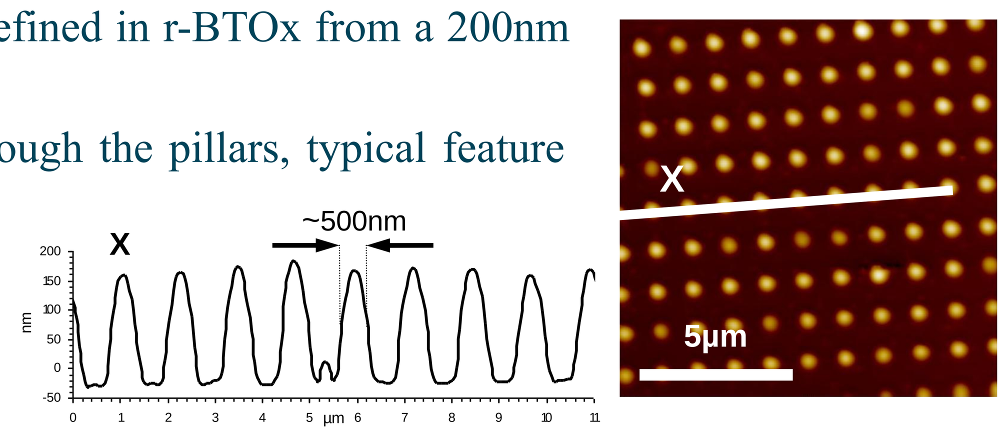
A copolymer based around the common green-emitting polymer **F8BT**.

- Cross-linking through oxetane side-chains activated via a photoacid initiator.
- Cross-linked reticulated network (r-BTOx) forms.
- Development in THF removes the unexposed polymer.

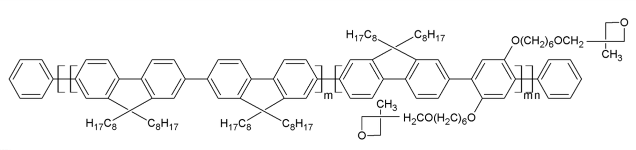


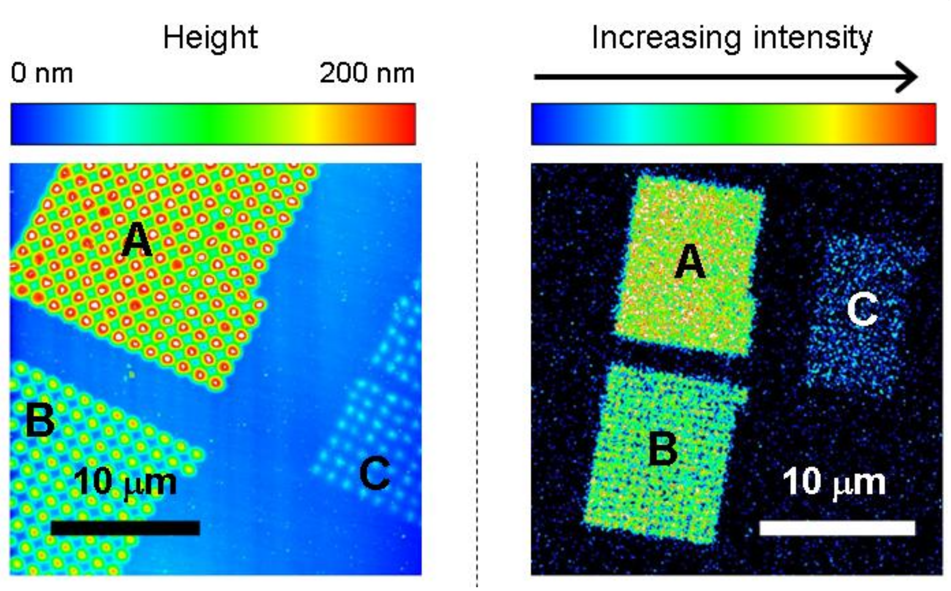
(Right, top) An array of pillars defined in r-BTOx from a 200nm film using a 60nm probe aperture

(Right, bottom) cross section through the pillars, typical feature size of around 500nm.



F8Ox



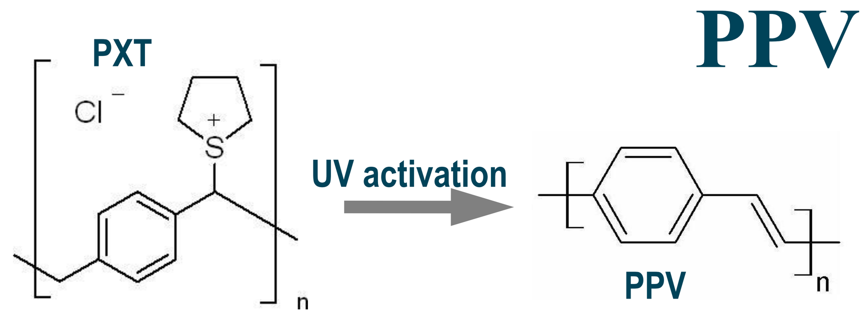


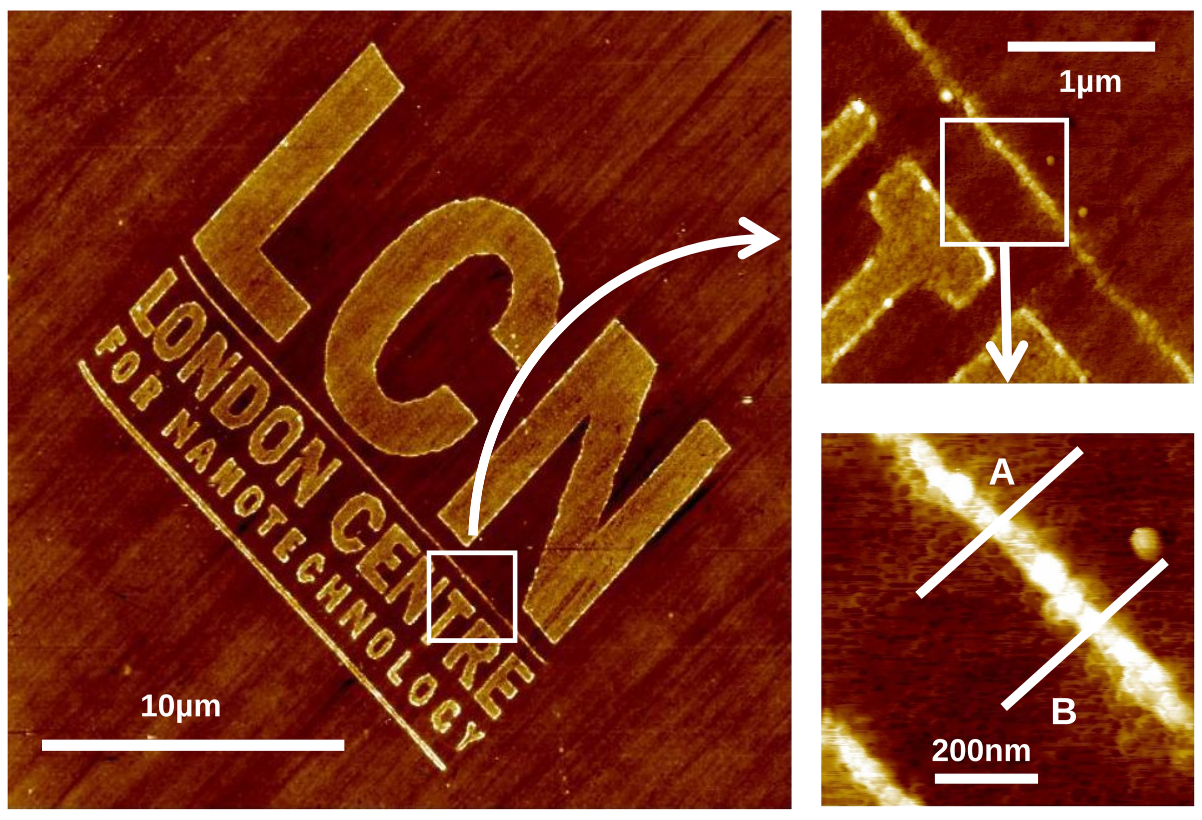
- Oxetane side chains (analogue to BTOx).
- Blue-emitting.
- Photoluminescence preserved during lithography.
- Under-exposure results in poorly positioned features (area C).

(Left) Arrays of pillars defined in r-F8Ox from a ~200 nm film using a 60 nm probe aperture. Exposure decreases from A (200 ms) to B (50 ms) to C (20 ms). (Right) Confocal photoluminescence images of the same areas.

PPV

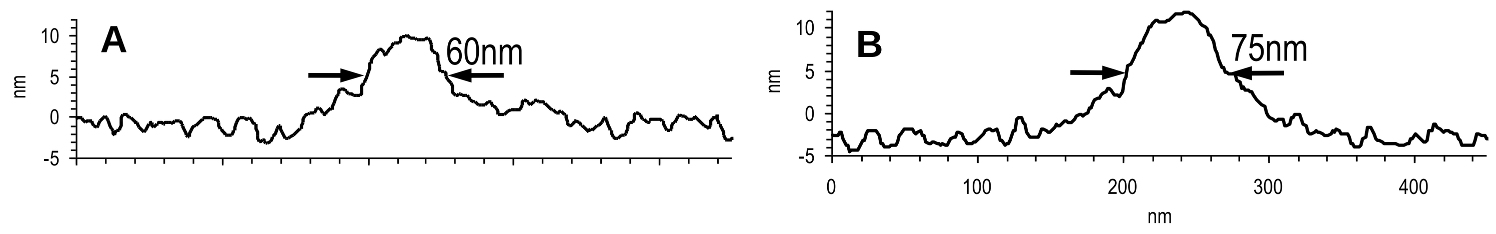
PPV structures fabricated via a Wessling-type precursor process using SNOL to convert poly(p-xylene tetrahydrothiophenium chloride) (PXT) in-situ into conjugated PPV. Unexposed PXT removed using methanol





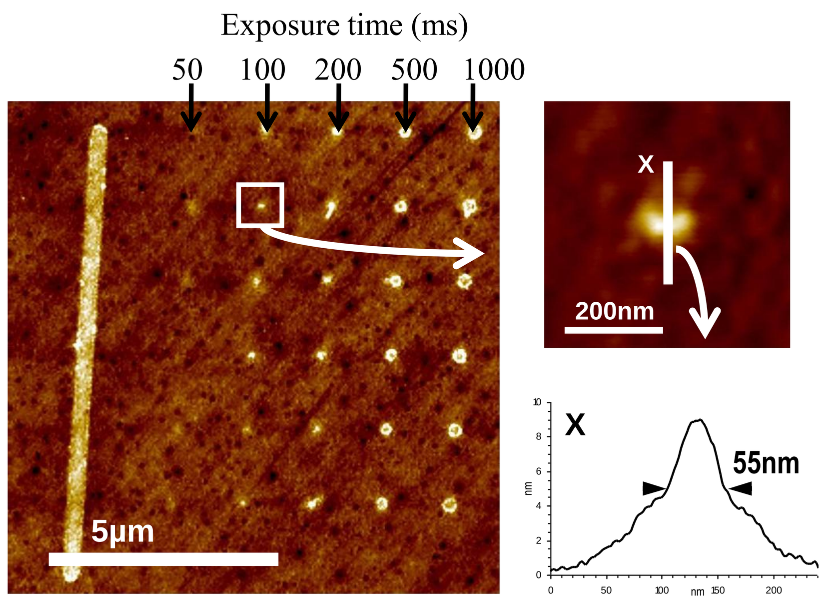
(Left) AFM scan of a features drawn in PPV on a variety of length scales, from a ~15nm thick precursor film using a 50nm near-field probe.

(Below) Cross-sections of the finest features.



- Structure of 65,000 pixels.
- Minimum resolution 60 nm.

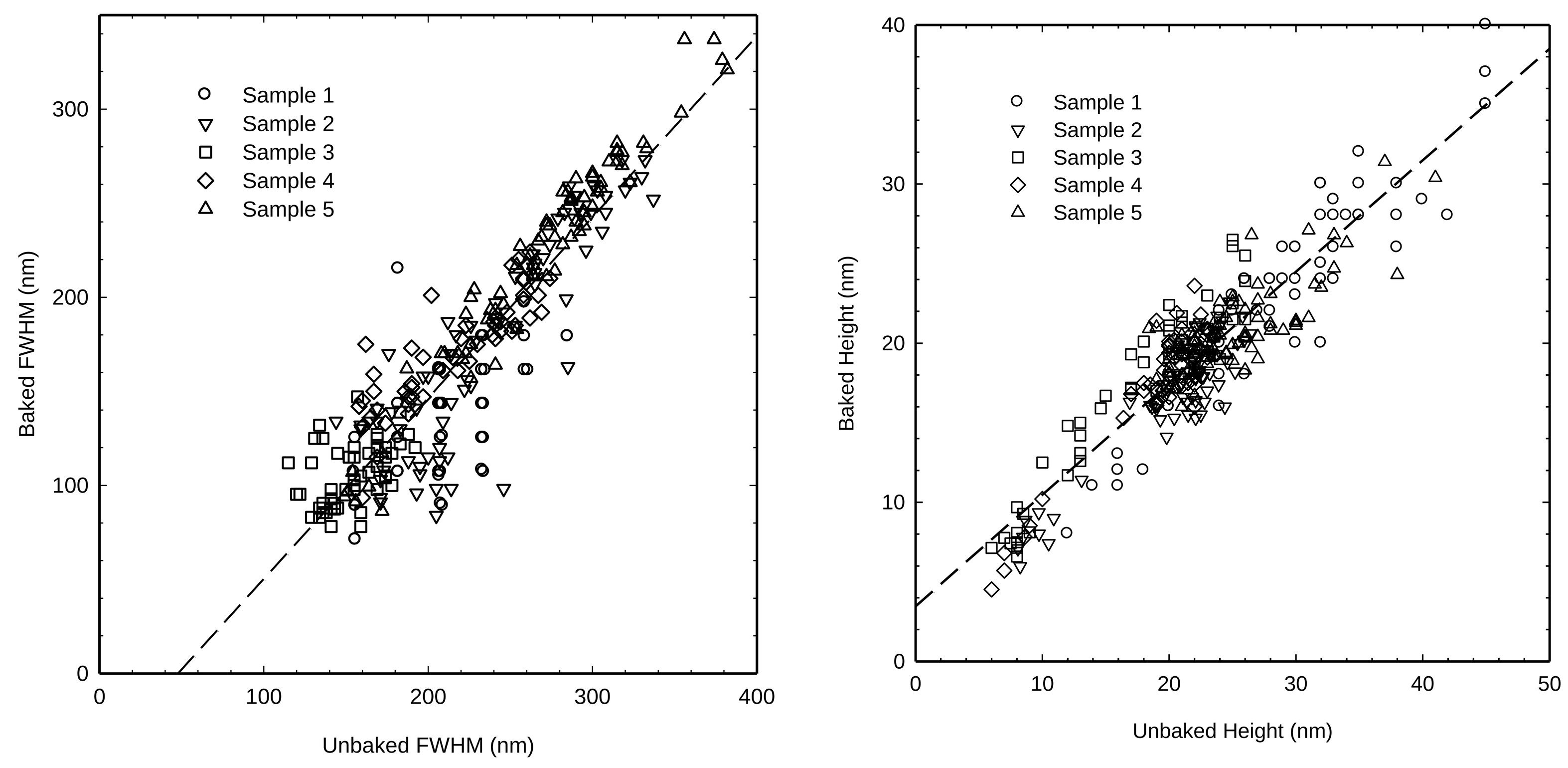
→ Integrity of aperture maintained.



(Left) Dots drawn in PPV from a 15nm film, using a 50nm probe aperture. (Right) Zoom and cross-section through this feature showing FWHM of approximately **55nm.**

Non-uniform shrinkage during baking

- Uniform films shrink ~50% during baking.
- Height and width of nano-sized dots measured *before and after baking*



Linear fits to data give :

$$W_b = W_{ub} - 46nm$$

$$H_b = 0.7 \times H_{ub} + 3nm$$

W = width (FWHM)
H = height
b = baked
ub = unbaked

→ 30% vertical shrinkage

→ Outer layers collapse a ***fixed*** 20-25 nm around the edge (not dependent on lateral dimension)

IN SUMMARY, scanning near-field optical lithography is a powerful tool for patterning materials on the nano-scale. We have investigated the resolution achievable with our system, as applied to the patterning of PPV, and found that a feature size of around 50nm are possible. We have also shown that, in addition to individual small structures, creating large arrays and more complicated designs is equally feasible using SNOL. Finally, we have shown that a variety of other materials are suitable for patterning via this technique, including BTOx and F8Ox, which undergo a very different reaction to PPV.

We thank: the EPSRC; the RS; the EC for funding of the RTN THREADMILL (EU-contract: MRTN-CT-2006-036040); the European Science Foundation EUROCORES Programme SONS with supplementary funds from EPSRC and the EC Sixth Framework Programme (ERAS-CT-2003-980409); as well as the EC Seventh Framework Programme (FP7/2007-2013) under grant agreement N. 212311 (ONE-P).

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