

Top-down and bottom-up organic semiconductors nanostructures: Near-field lithography and molecular self-organisation as enabling tools for organics nanotechnology

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I will start the paper by presenting an approach to high-resolution lateral patterning of an electroluminescent conjugated polymer, based on near-field lithography with apertured probes. The technique is based on the spatially selective inhibition of the solubility of the polymer precursor by exposure to the ultraviolet optical field present at the apex of scanning fibre double-tapered, gold-coated probes [aperture diameters between 40 and 80 nm (± 5 nm)]. After development in methanol and thermal conversion under vacuum we obtain features with a minimum dimension of 160 nm. We have recently demonstrated the use of the technique for the direct writing of two-dimensional periodic structures with intentional defects and a periodicity relevant to applications in the visible range [1].

Insulated molecular wires [2] made with conjugated-polymers-based polyrotaxanes offer an example of a "bottom-up" approach to electroluminescent nanostructures, which I will describe in more detail in the second part of the talk. An attractive feature here is that this class of materials is engineered at a supramolecular level by threading a conjugated macromolecule, such as poly(*para*-phenylene), poly(4,4'-diphenylene vinylene) or poly(9,9'-fluorene) through α - or β -cyclodextrin rings, so as to reduce intermolecular interactions and solid-state packing effects, that red-shift and partially quench the luminescence. Such a supramolecular approach preserves the fundamental semiconducting properties of the conjugated wires, and is effective at both increasing the photoluminescence efficiency and blue-shifting the emission of the conjugated cores, in the solid state, while still allowing charge-transport. We used the polymers to prepare single-layer light-emitting diodes with Ca and Al cathodes, and observed blue and green emission. The reduced tendency for polymer chains to aggregate shows in both solid-state films, as well as in solution (as clearly demonstrated by the study of fluorescence decay via time-correlated single-photon counting experiments) and allows solution-processing of individual polyrotaxane wires onto substrates, as revealed by scanning-force microscopy [2].

[1] R. Riehn, A. Charas, J. Morgado and F. Cacialli. "Near-field optical lithography of a conjugated polymer". *Appl. Phys. Lett.* **82**, 526-528 (2003).

[2] F. Cacialli, J.S. Wilson, J. J. Michels, C. Daniel, C. Silva, R. H. Friend, N. Severin, P. Samorì, J. P. Rabe, M. J. O'Connell, P. N. Taylor, H. L. Anderson. "Cyclodextrin-threaded conjugated polyrotaxanes as electroluminescent insulated molecular wires with reduced interstrand interactions". *Nature Materials* **1**, 160-164 (2002).

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