

## CONJUGATED POLYMER NANOFIBERS: EFFECTS OF NANOSTRUCTURATION ON PHOTOEMISSION PROPERTIES

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The controlled elaboration of well-defined nanostructures made of conjugated photo-electroluminescent organic polymers is very challenging for the fields of organic light emitting diodes (OLEDs), optoelectronics, photonics, and sensors. One of the most studied electroluminescent and photoconductive polymer in photonics is poly-(*p*-phenylene-vinylene) (PPV) which is the insoluble archetype of the  $\pi$ -conjugated polymers now used in OLEDs. The fabrication of thin films and the bulk optical properties of PPV and its related derivatives are at present quite well documented. Nanoscale systems make possible to integrate and tune desirable attributes of molecular and bulk regimes, through confinement effects, localization versus delocalization, exciton binding energy, exchange interaction and exciton fine structure, exciton-vibration coupling and dynamics of excitons.

Nanowires and nanotubes of poly-(*p*-phenylene-vinylene), a prototypical photo- and electroluminescent  $\pi$ -conjugated polymer, have been prepared by the wetting template method in nanoporous membranes with an easy all-in-solution polymer precursor route. Both nanowires and nanotubes were obtained by varying the dilution of the polymer precursor in methanol prior to thermal conversion, as shown by a morphological study by scanning and transmission electron microscopies (fig.1). The effect of dilution has been addressed for PPV thin film in previous studies [1] and is compared to the case of PPV nanostructures. A polarized infra-red absorption spectroscopy (PIRAS) study indicated a preferential orientation of the PPV chains along the wire axis (fig.2). Nanofibers are highly luminescent (fig.3). Photoemission properties have been determined by steady-state and time-resolved photoluminescence (PL) spectroscopies. The time-resolved PL set-up is equipped with a confocal nanoprobe equipment, which results in a very small probe size. PPV nanotubes exhibit blue-shifted emission, higher quantum yield, and longer fluorescence lifetime with respect to PPV films. Interestingly, a new band appears at higher energy (447 nm) for the PPV nanotubes (fig.4) [2]. These effects are attributed to the cancellation of interchain interactions, that are consistent with nanoscale tubular structures formed from isolated short polymer chain segments.

### References:

[1] Optical properties of poly(para-phenylene vinylene) and single-walled carbon nanotube composite films: Effects of conversion temperature, precursor dilution, and nanotube concentrations.

F. Massuyeau, H. Aarab, L. Mihut, S. Lefrant, E. Faulques, J. Wery, E. Mulazzi and R. Perego, *J. Phys. Chem. C*, **111** (41), 15111 (2007).

[2] Controlling shape of conjugated polymer nanofibers for tunable photoemission properties. F. Massuyeau, J.L. Duvail, H. Athalin, J.M. Lorcy, , S. Lefrant, J. Wery and E. Faulques, *Advanced materials*, in submission.

Figures:

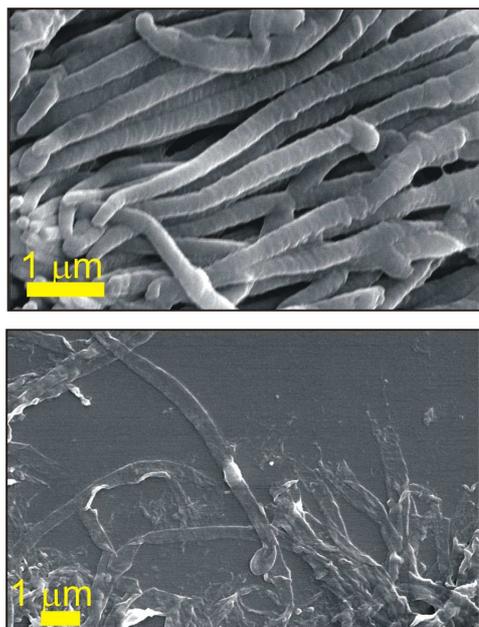


Figure 1: up: nanowires ; down : nanotubes.

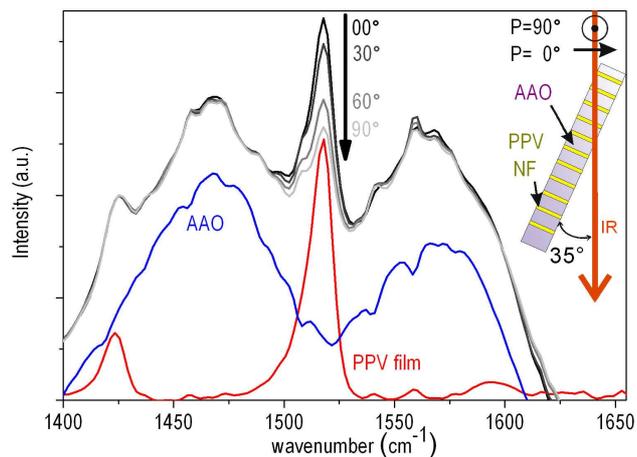


Figure 2: Micro-PIRAS recorded on PPV nanowires for different orientations of polarization.

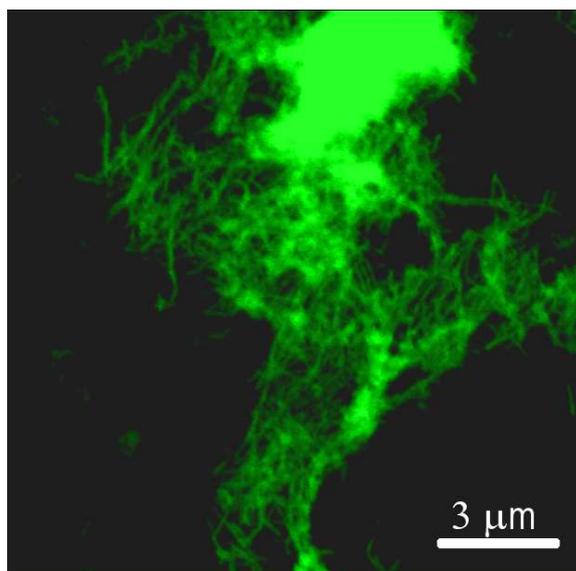


Figure 3: Epifluorescence image of PPV nanowires.

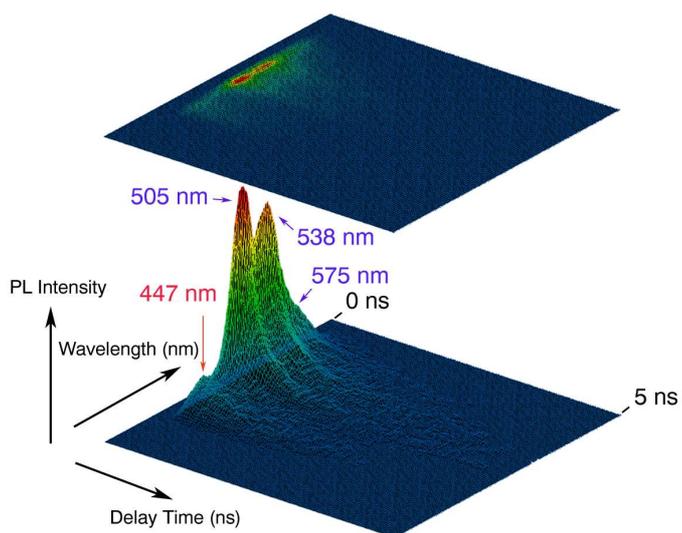


Figure 4: 3D time-resolved PL image of PPV nanotubes.