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Conjugated polymer nanofibers: effects of nanostructuration on photoemission properties

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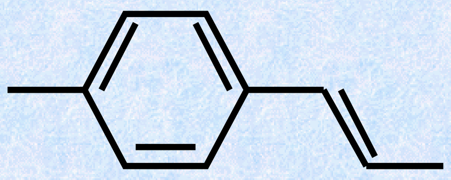
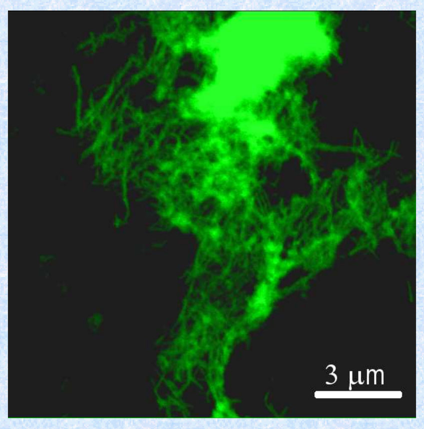
Introduction

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 at the nanometre scale. In this communication, we report on a direct and simple route to elaborate poly-(*p*-phenylene-vinylene) (PPV) filled nanowires or PPV empty nanotubes by varying the concentration of the polymer solution used as precursor for the PPV conversion *poly*(p-*xylene* tetra-hydrothiophenium chloride) (PXA) . PPV nanofibers are prepared by the wetting template method [1] in polycarbonate (PC) nanoporous membranes. PPV nanotubes exhibit a progressively blue-shifted photoluminescence toward 2.81 eV with quantum yield greater than 0.4.

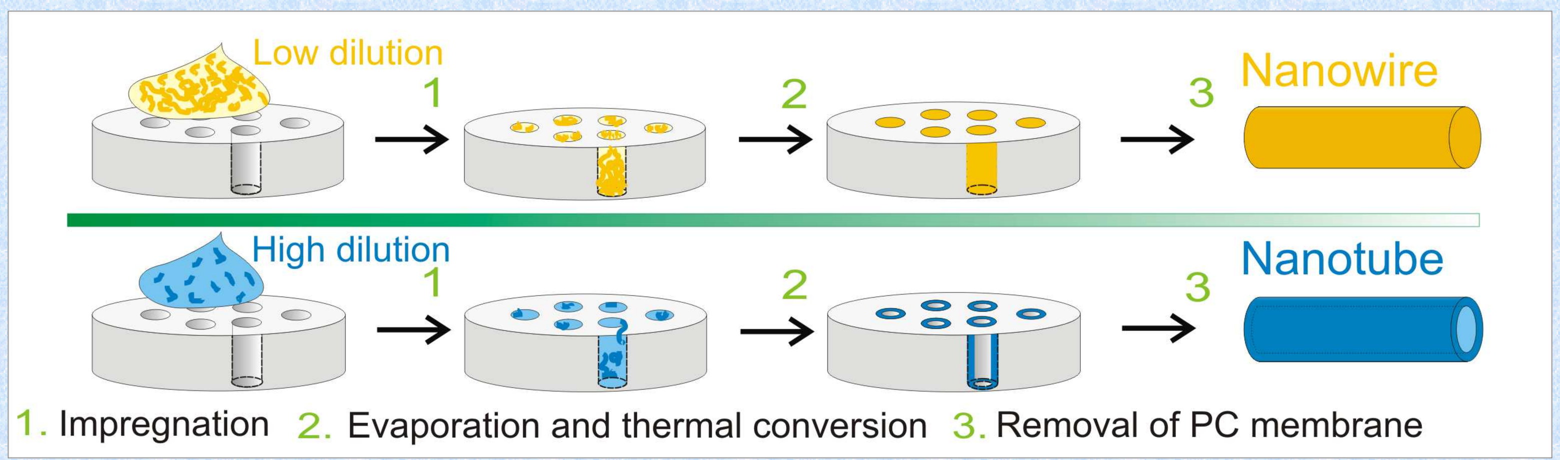


PPV unit cell



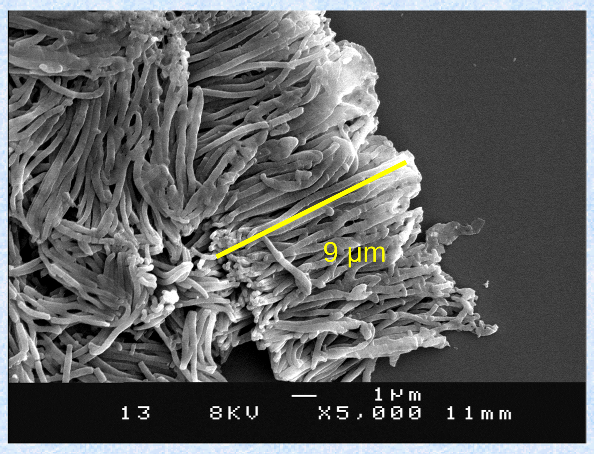
PPV nanofibers epifluorescence image obtained with a laser excitation at 488 nm

Synthesis of PPV nanofibers

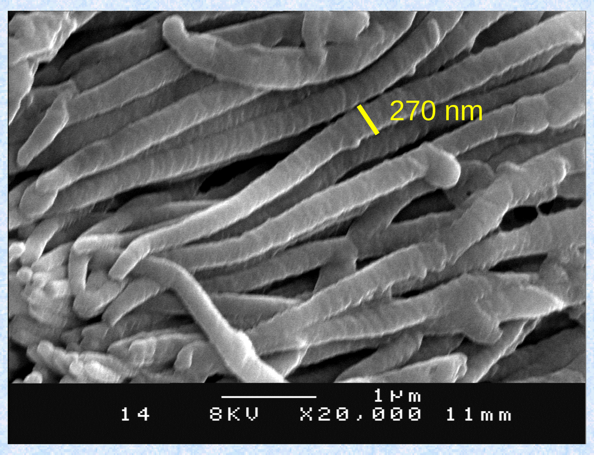


Morphological studies

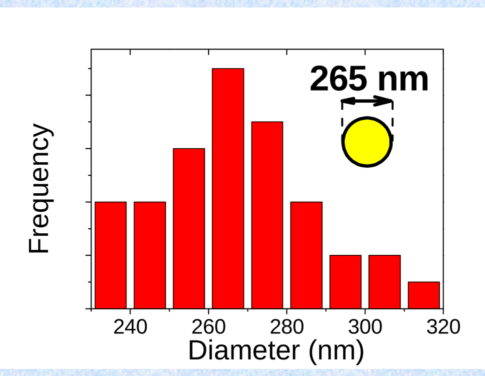
Nanowires prepared from low dilution



- Rough surface replicating that of the PC pore walls
- Nanofibers length corresponding to the membrane thickness (10 µm)

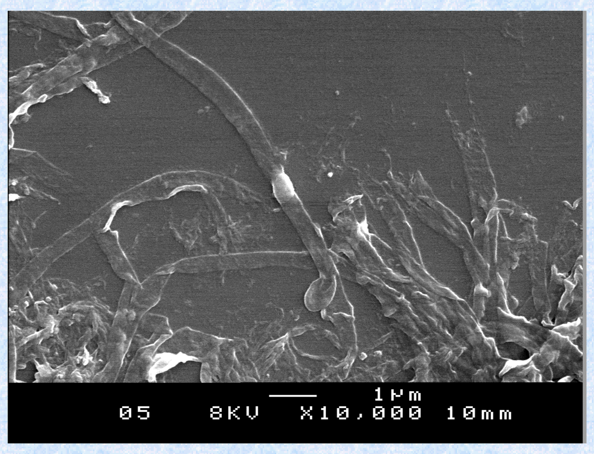


- Cigare shape like the pore shape of the PC membrane

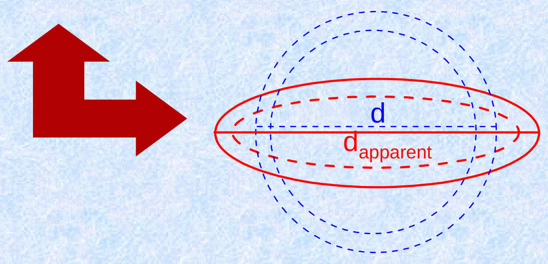


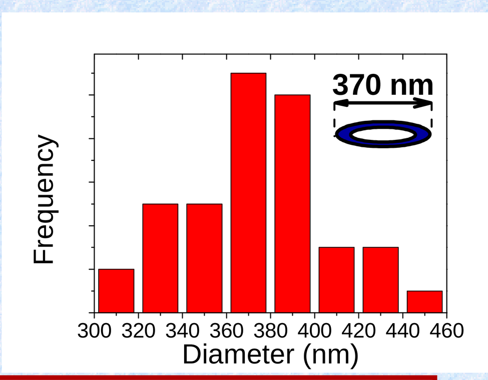
- Nanowires obtained with a mean diameter d ≈ 265 nm

Nanotubes prepared from high dilution



- Flattened nanotubes with an apparent diameter broader than the actual diameter d of PPV nanowires





- Nanotubes obtained with a mean diameter $d_{apparent}$ ≈ 370 nm

References:

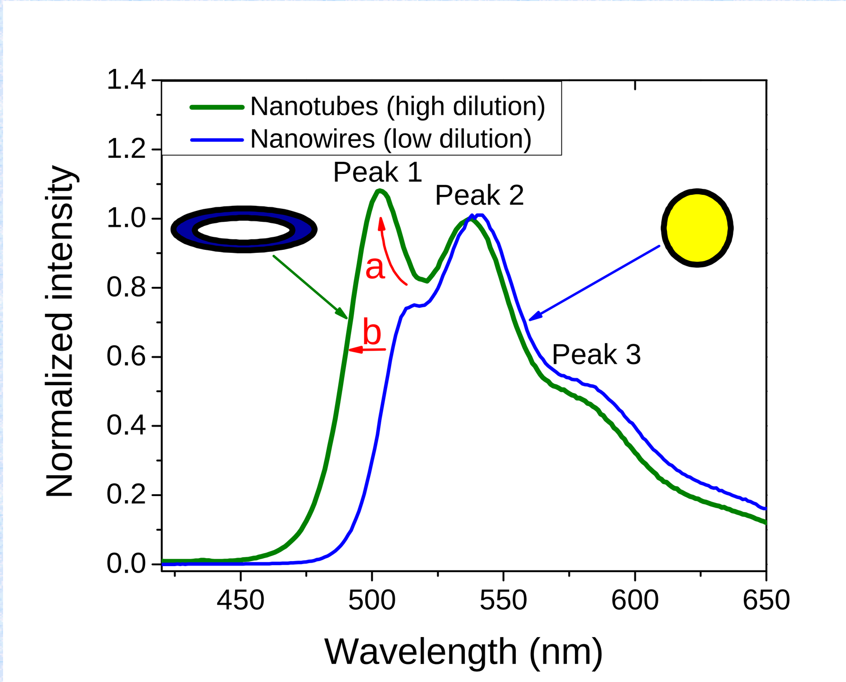
[1] M. Steinhart, J.H. Wendorff, A. greiner, R.B. Wehrspohn, K. Nielsch, J. Schilling, J. Choi, U. Gösele, Science, **296**, 1997 (2002).

[2] F. Massuyeau, E. Faulques, H. Athalin, S. Lefrant, J.-L. Duvail, J. Wéry, E. Mulazzi, and R. Perego, submitted to J. Chem. Phys. (2008).

Photoluminescence (PL) studies

Steady-state PL

PL spectrum by varying dilution



Steady-state PL tunability of PPV nanofibers ensembles in PC membranes obtained by varying the PXA concentration.
λ_{exc} = 400 nm.
Three main peaks are observed at low PXA dilution:
- *Peak 1 : 515 nm*
- *Peak 2 : 540 nm*
- *Peak 3 : 580 nm*

By increasing dilution → a) Ratio $\frac{I_{Peak1}}{I_{Peak2}}$ increases

→ b) Blue shift of the PL (≈10 nm)

The effective conjugation length of PPV nanofibers decreases i) by incrasing the PXA dilution ii) on going from nanowires to nanotubes

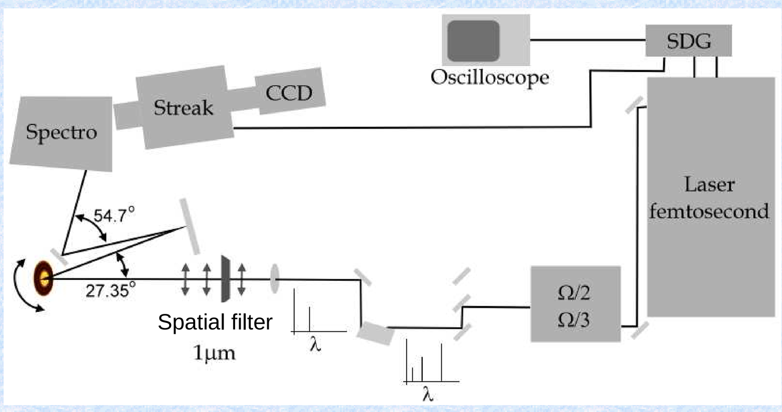
PL quantum yield by varying dilution

Measured with an integrating sphere

PPV film converted at 110°C : 30% PPV nanowires : 29 % PPV nanotubes : 46%

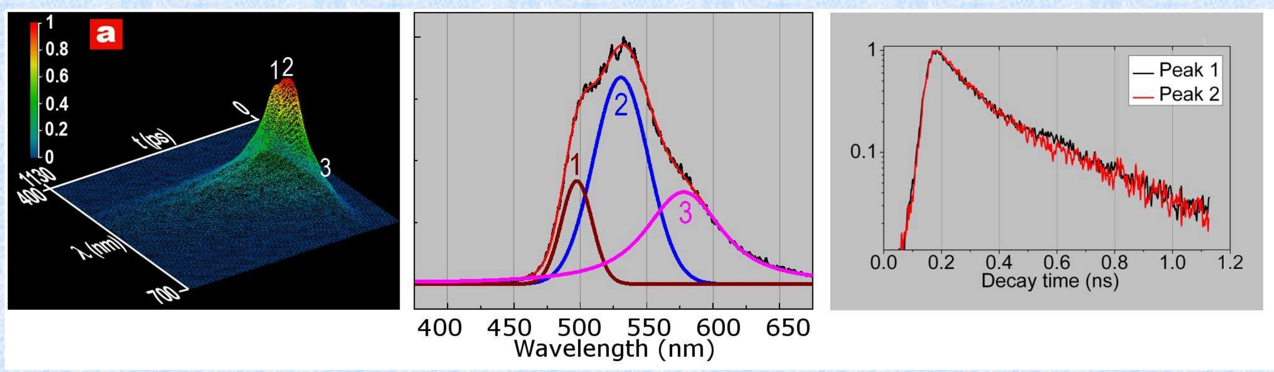
Enhancement of the PL QY from PPV nanowires to PPV nanotubes

Time-resolved PL with a confocal resolution



- *Excitation : 400 nm*
- *Pulse duration : 100 fs at 1kHz*
- *Fluence : 1 µJ/pulse at regen output*
- *Transient signals sent in a monochromator and detected with a streak camera (C7700) of temportal resolution < 5 ps*

PPV film converted at 110°C

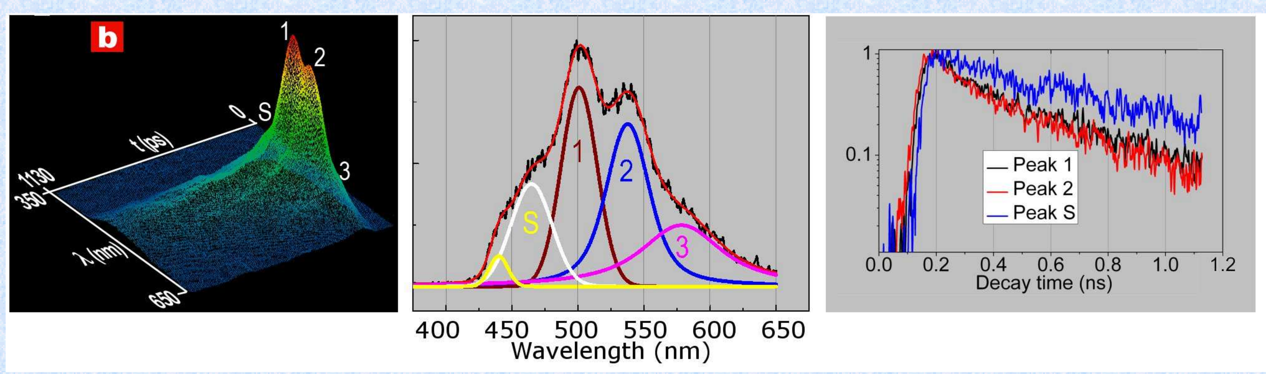


Left column: 3-D streak images. Middle column: corresponding transient spectra on a wavelength scale. Right column: corresponding PL decays.

- Peak 1 (505 nm) and 2 (529 nm) → Non exponential decay

The non-radiative decay channel is favored by excitonic migration from short segments to longer segments

PPV nanotubes converted at 110°C



Left column: 3-D streak images. Middle column: corresponding transient spectra on a wavelength scale. Right column: corresponding PL decays.

- Compared to PPV film, a new band S appears at ≈ 450 nm
- Peak 1 (501 nm) and 2 (534 nm) → Non exponential decay
- Peak S (457 nm) → Mono-exponential decay

Monoexponential decay characteristic of a localization of the electron-hole pairs on very short isolated chain segments (repeat unit ≈ 3)[2]

Conclusion

- **Easy and low costt method: wetting template**
- **Controlled wall thickness by varying the dilution of the PPV precursor**
- **Yellow-green to blue photoluminescence tunability with high efficiency from PPV nanowires to PPV nanotubes**

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