

Self-assembly of DNA/cationic polythiophene: chiroptical properties and microscopic morphology

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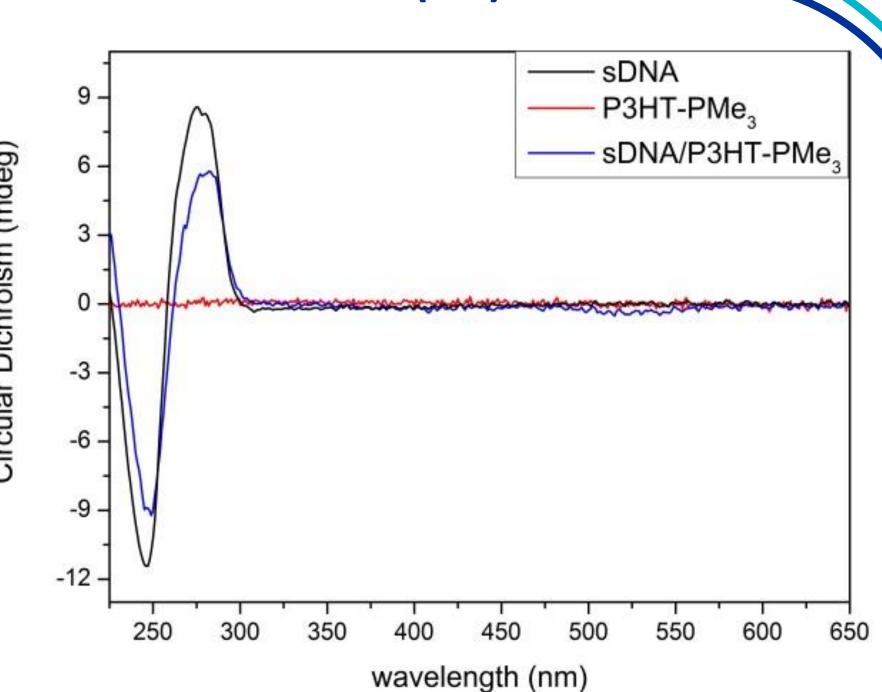
Introduction and objective:

In the family of π -conjugated polyelectrolytes, polythiophenes constitute an interesting class of polymers for biosensing application, as they combine solubility in aqueous media and have sensitive optical properties for the detection of biomolecules like DNA. $^{[1,2]}$

Here, we study the self-assembly of DNA (salmon DNA, sDNA) with a cationic poly[3-(6'-(trimethylphosphonium)hexyl)thiophene-2,5-diyl] (P3HT-PMe₃). We study the chiroptical properties of the complex by Circular Dichroism (CD) and the morphology by Atomic Force Microscopy (AFM) and Confocal Optical Microscopy (COM).

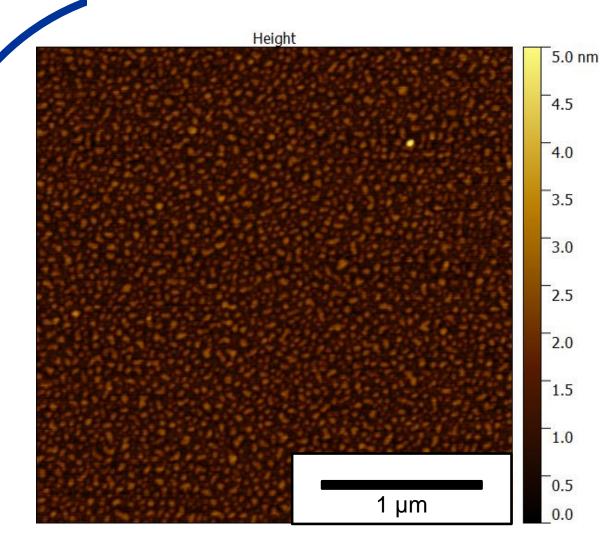
Results: Circular Dichroism (CD) $-dT_{20}$ P3HT-PMe - dT₂₀/P3HT-PMe₃ wavelength (nm) - dsR₄₃ P3HT-PMe₃ - dsR₄₃/P3HT-PMe₃

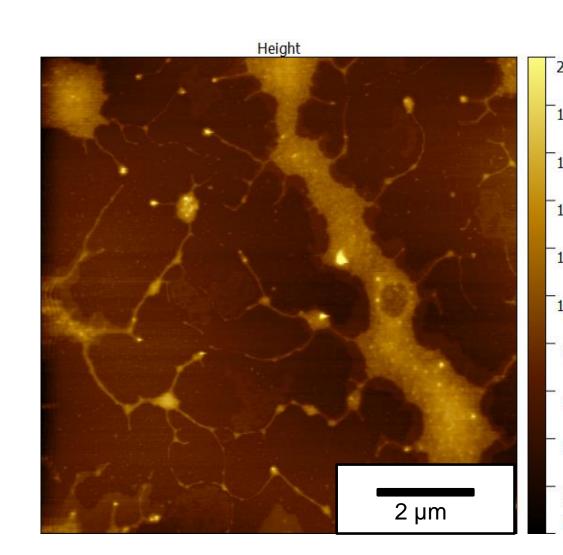
wavelength (nm)

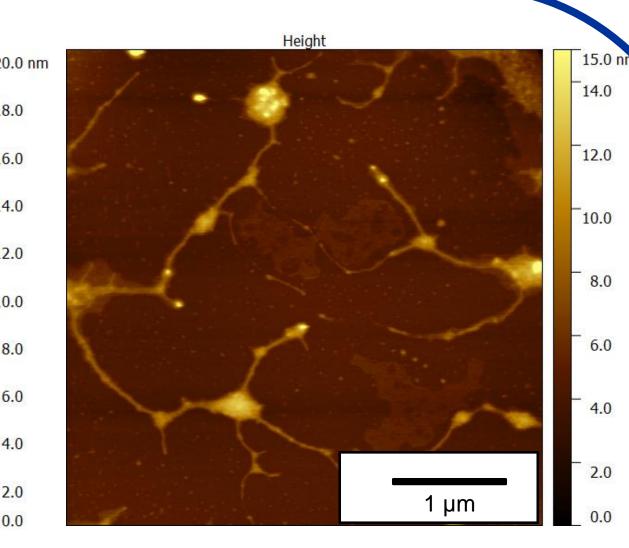


CD spectra of dT_{20} , sDNA, dsR_{43} , P3HT-PMe₃ and $dT_{20}/P3HT-PMe_3$, sDNA/P3HT-PMe₃ and $dsR_{43}/P3HT-PMe_3$ complex at a 1:1 DNA/polymer charge ratio. A righthanded conformation is obseved with a ssDNA (dT_{20}) in the polymer region (400-600) nm) and a left-handed conformation for double strand DNA (dsR₄₃ and sDNA) is observed.

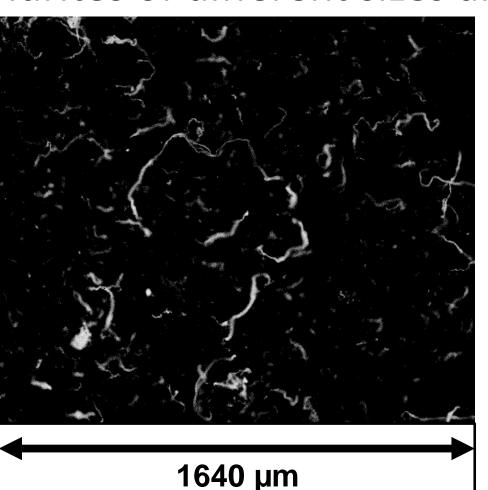
AFM and **COM**

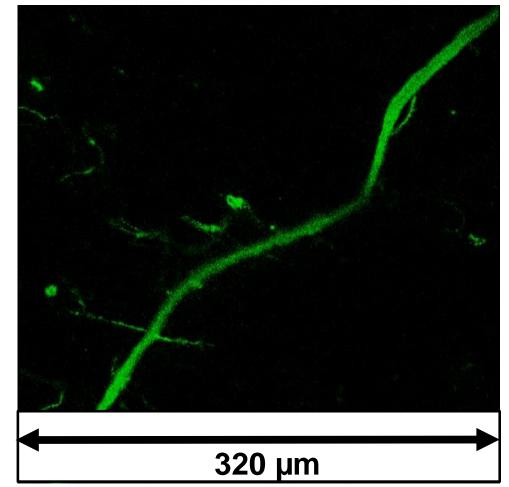


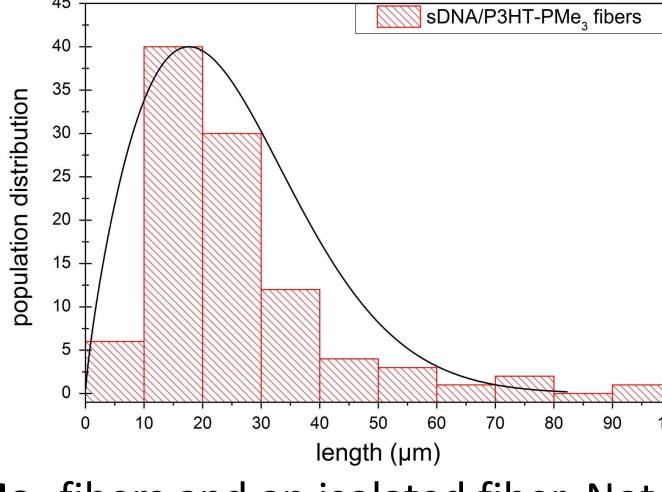




AFM images of pure P3HT-PMe₃ and sDNA/P3HT-PMe₃ complex. A tree-like structure with dendrites of different sizes are present.







Fluorescence images of a large group of sDNA/P3HT-PMe₃ fibers and an isolated fiber. Note that pure DNA is not fluorescent. The average size of the fibers (in the image of the left) is 28 μM and more of the half-population have a size between "0" μM and 40 μM .

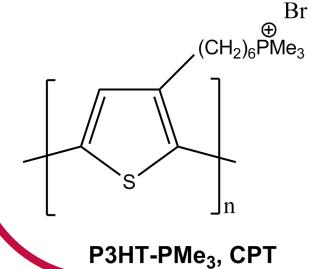
References:

- [1] J. Rubio-Magnieto et al , Chem. Commun. 2013, 49, 5483-5485.
- [2] J. Rubio-Magnieto et al, Soft Matter **2015**, 11, 6460-6471
- [3] Lv. Fengting *et al, small,* **2016**, 12, 696-705

Preparation:

DNA and P3HT-PMe₃ samples were dissolved in TE buffer. The concentration of the DNA was determined by UV-vis (ε_{260}) and the charge ratio between polymers and DNA were adjusted using this concentration.

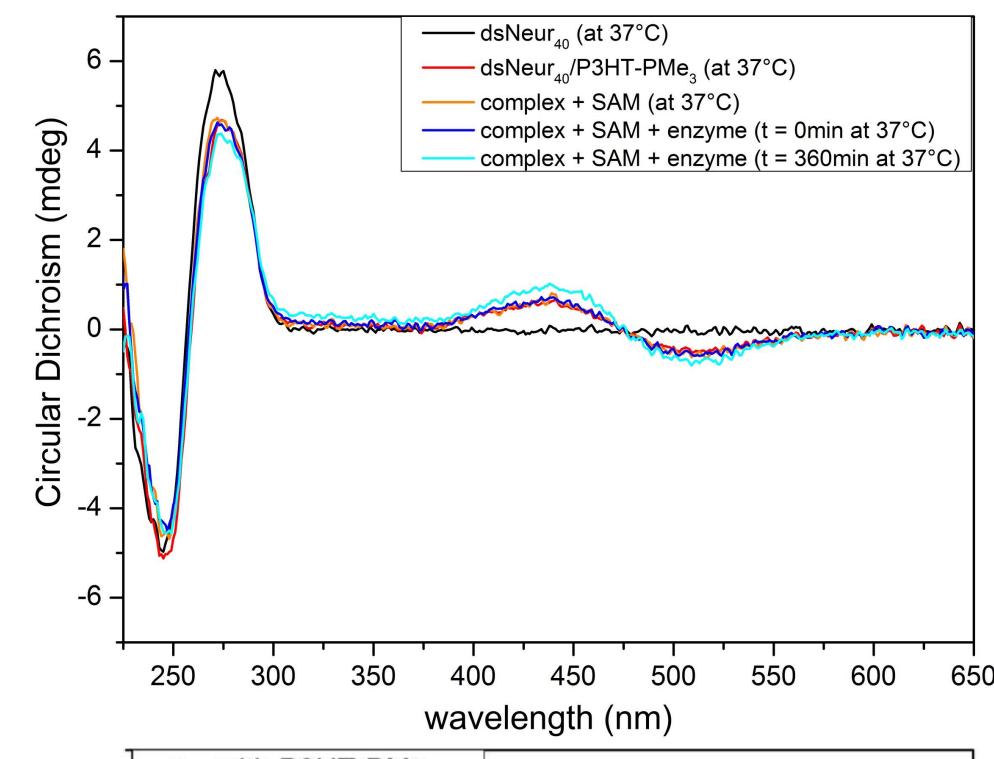
Thin deposits were prepared by sinking mica plates into a solution of DNA/polymer during 5-10 min, rinsed with MQ water and dried with N₂ gaz.

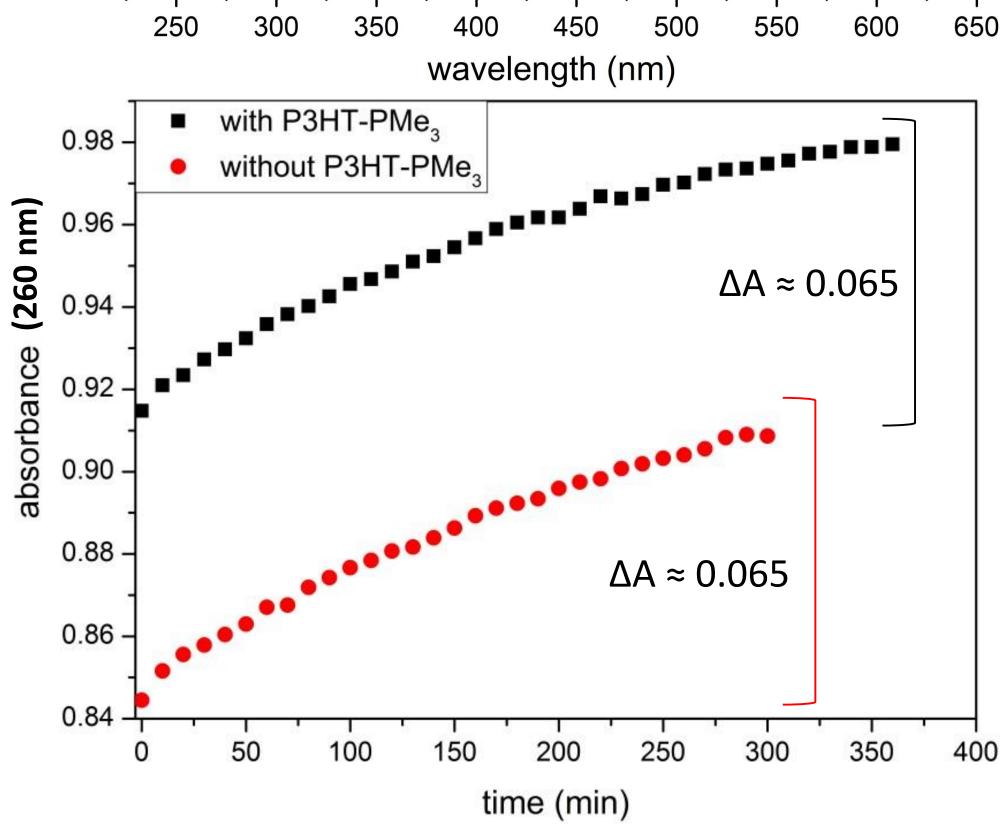


(CH₂)₆PMe₃ dT₂₀: 5'-TTT-TTT-TTT-TTT-TTT-3' dsR₄₃: 5'-CGT-CAC-GTA-AAT-CGG-TTA-ACA-AAT-GGC-TTT-CGA-AGC-TAG-CTT-C-3' Salmon DNA (sDNA): double Strand DNA, 2000 base pairs (bp)

Conclusion and perspectives:

- The DNA CD signal (220-300 nm) decreased when it interacts with polymer.
- > An induced CD signal appeared in the polymer region (400-600 nm) with both DNA.
- AFM images showed that the sDNA/polymer complexation leads to a fiber-like morphology.
- > COM showed us the homogenous fluorescence within the self-assembled fibers.
- > These results could be useful for studying structural modifications of DNA through the (chir)optical and fluorescence properties of the for detection polymer (e.g. DNA of methylation).[3]
- dsNeur40 : 5'-GAG-CTG-ATC-TGA-TCG-CCG-GCG-ACAT-CACT-CAG-GAG-ACC-GG-3'





- > (+) and (-) CD signals of the polymer slightly increased during the methylation.
- \triangleright The **P3HT-PMe₃**, self assembled with the **dsR**₄₃, did not seem to disturb the enzymatic activity.