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# **Supramolecular assemblies of DNA/oligothiophene** binding, chiroptical properties and microscopic morphology



DNA (sDNA)

2000 base pairs

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## Introduction

Cationic  $\pi$ -conjugated oligothiophenes are appealing candidates as molecular materials for optical detection and imaging of DNA, as they combine:

- solubility in aqueous media.
- tunable design to achieve targeted supramolecular recognition.[1,2]  $\bullet$
- sensitivity of their chiroptical properties to minor perturbations that can their conformation, interactions influence such as the with a biomacromolecule.[2]

Here, we have studied complexes formed by supramolecular self-assembly between a series of newly designed cationic  $\pi$ -conjugated oligothiophenes,



T3Im and ETE.TMA, (Sheme 1) and DNA (salmon DNA, sDNA).

## **Results and discussion**

#### **1. Chiroptical properties of oligothiophene/DNA complexes**



Figure 1: a) CD spectra of T3Im, sDNA and a T3Im/sDNA mixture at a charge ratio of 1. b) CD spectra of T3Im titration by sDNA. The spectra were recorded in a TE buffer solution (pH=7.4) at 20°C. [T3Im]=120 µM.

— ETE.TMA

These results point to the interaction between DNA and the cationic  $\pi$ -conjugated oligothiophene.

Charge ratio (-/+

**Scheme 1:** Chemical structures of the two cationic  $\pi$ -conjugated oligothiophenes.

### 3. Microscopic morphology of oligothiophene/DNA complexes



Figure 4: AFM images of thin deposits a) pure T3Im and b) sDNA/T3Im mixing on mica substrate.  $[T3Im] = 120 \ \mu M$  and  $[sDNA] = 0.06 \ \mu M$ .



Cryo-TEM b)

a)



Figure 2: a) CD spectra of ETE.TMA, sDNA and ETE.TMA/sDNA mixture at a charge ratio of 1. b) CD spectra of ETE.TMA titration by sDNA. The spectra were recorded in a TE buffer solution (pH=7.4) at 20°C. [ETE.TMA]= 120 µM.

#### 2. Binding affinities of oligothiophene ligands for DNA





Figure 5: Cryo-TEM images of a) pure T3Im and b) sDNA/T3Im mixing at the hydrated state.  $[T3Im] = 120 \ \mu M$  and  $[sDNA] = 0.06 \ \mu M$ .

> **T3Im:** grains and crystals.



Figure 6: COM image of T3Im/sDNA complex at a charge ratio of 2 (+/-). ETE.TMA height a

SDNA/T3Im: extended fibers network.



the

b)



ligand docked in

minor groove of DNA.

AFM

**ETE.TMA:** granular

interaction between T3Im and the DNA minor groove.

height

1.60

1.00

0.60

0.40

0.20

sDNA/ETE.TMA



Wavelength (nm)

Figure 3: Fluorescence spectra of DAPI bounded by sDNA in the absence of T3Im (a) /ETE.TMA (b) and the presence of increasing amounts of T3Im (a) /ETE.TMA (b).

$$\frac{I_0}{I} = 1 + K_{sv} \cdot [L]$$

Conclusion



**K<sub>a</sub> (L.mol<sup>-1</sup>)**  $1.26 \times 10^4$   $3.86 \times 10^3$ 

- Scheme 2: Chemical structure of DAPI.
- $\succ$  Fluorescence titration experiments point to an interaction between ligands and the DNA minor groove.
- $\succ$  T3Im ligands showed a higher binding affinity for salmon DNA.



Figure 8: AFM images of thin deposits a) pure ETE.TMA and b) sDNA/ETE.TMA on mica substrate.  $[ETE.TMA] = 120 \ \mu M and [sDNA] = 0.06 \ \mu M.$ 

### References

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[1] G. Barbarella, M. Melucci, G. Sotgiu, Adv.

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[2] Conjugated Polyelectrolytes: Fundamentals and

> Nature, position and number of cationic substituents influence the interactions and the binding affinities towards DNA.

> Binding of T3Im to DNA shows promising fluorescence properties as a result of a preferential adsorption along DNA minor grooves.

This communication is supported financially by the FNRS grant.