

Introduction

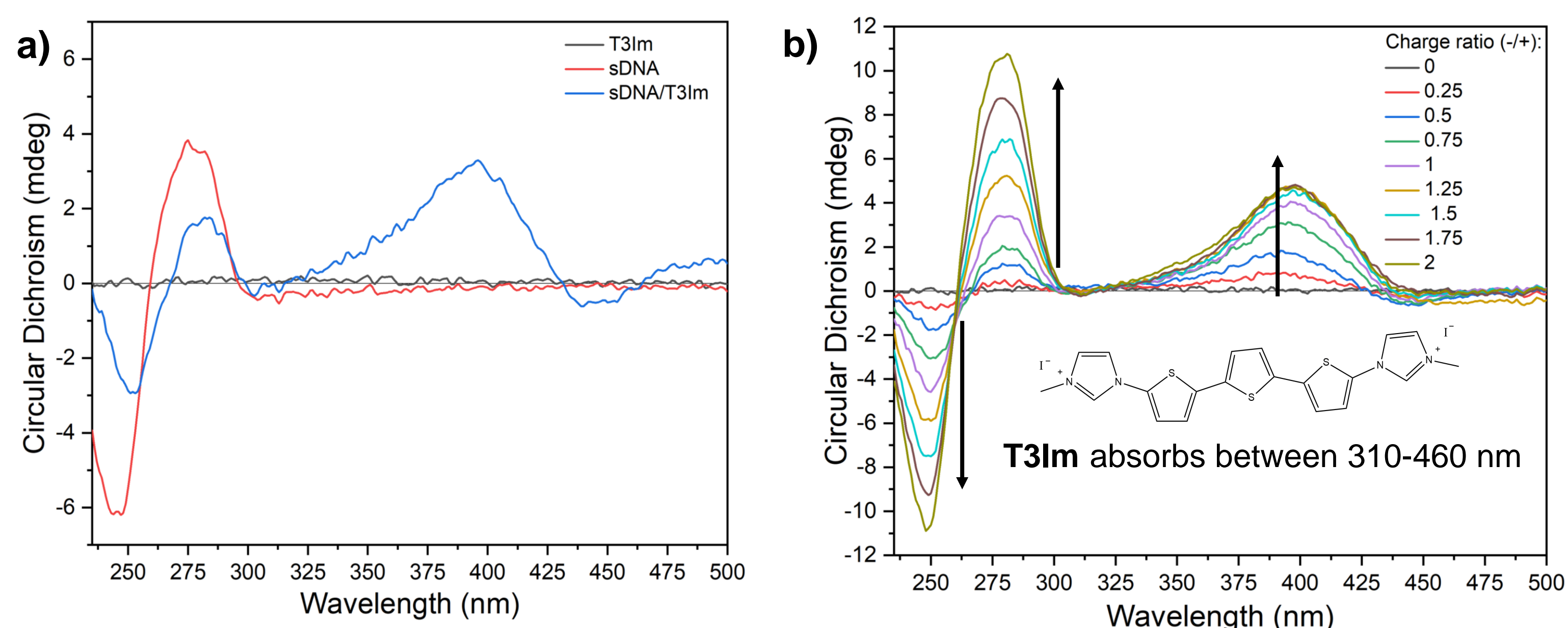
Cationic π -conjugated oligothiophenes are appealing candidates as molecular materials for optical detection and imaging of DNA, as they combine:

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

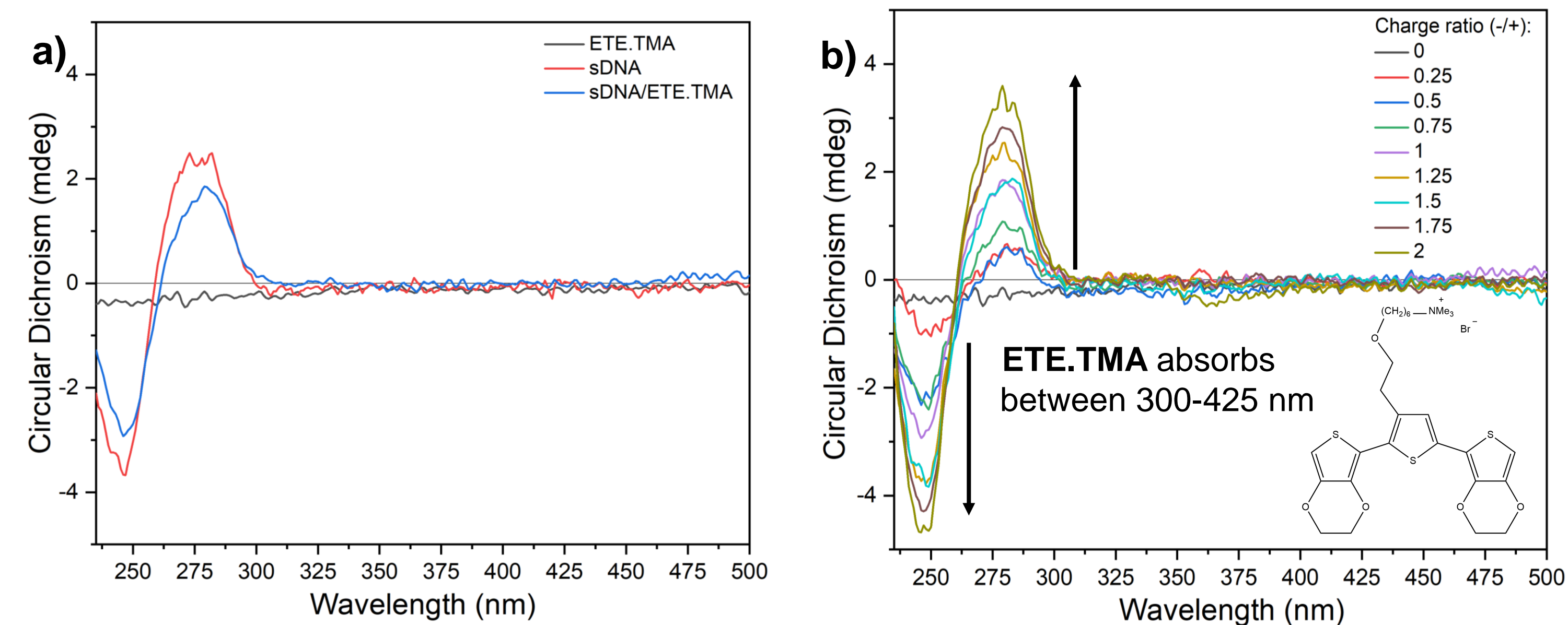
Here, we have studied complexes formed by supramolecular self-assembly between a series of newly designed cationic π -conjugated oligothiophenes, **T3Im** and **ETE.TMA**, (Scheme 1) and DNA (salmon DNA, **sDNA**).

Results and discussion

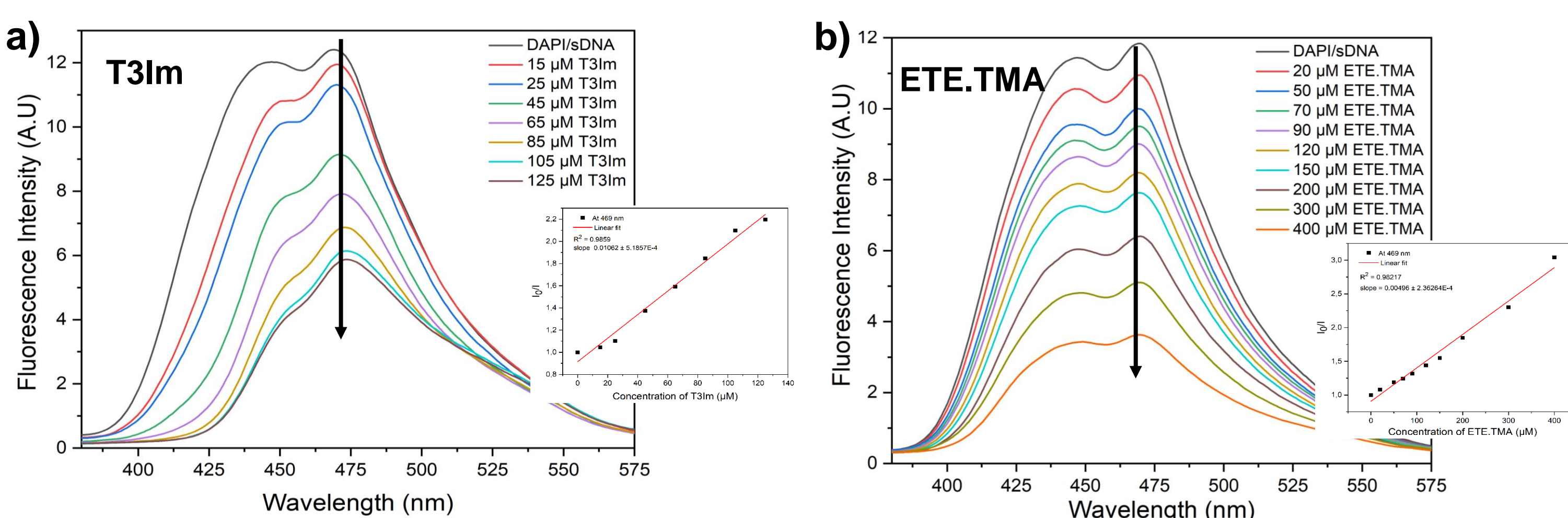
1. Chiroptical properties of oligothiophene/DNA complexes



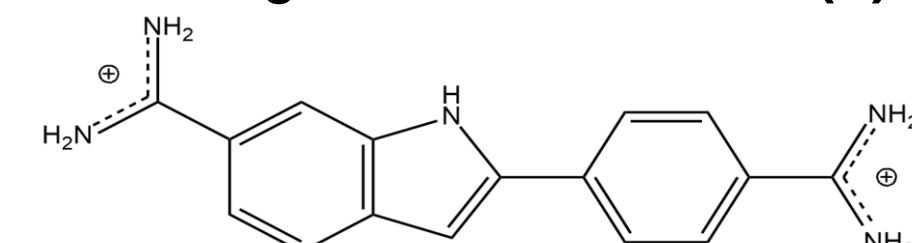
These results point to the interaction between DNA and the cationic π -conjugated oligothiophene.



2. Binding affinities of oligothiophene ligands for DNA



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



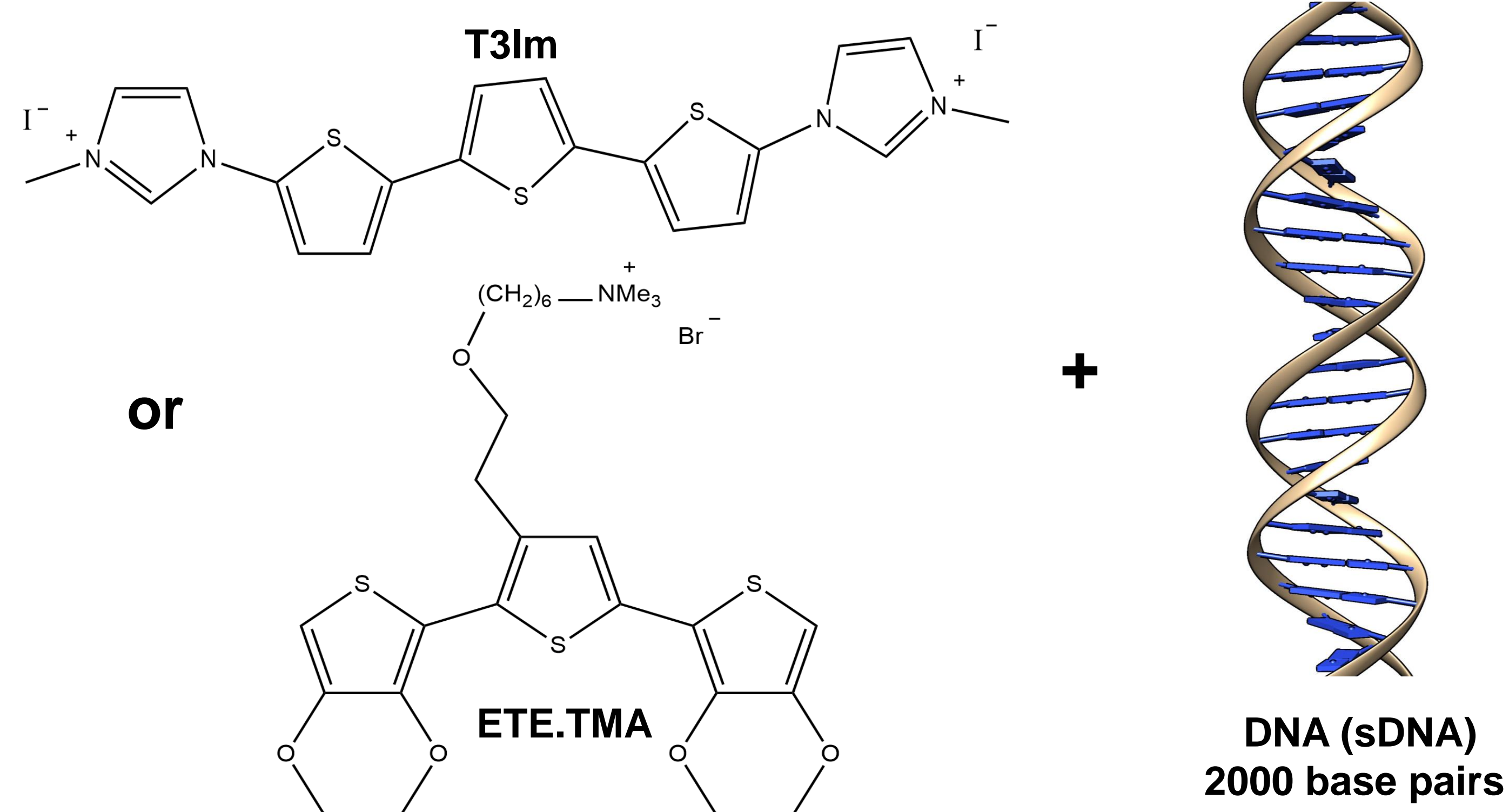
Scheme 2: Chemical structure of DAPI.

	T3Im	ETE.TMA
K_a (L.mol ⁻¹)	1.26×10^4	3.86×10^3

- Fluorescence titration experiments point to an interaction between ligands and the DNA minor groove.
- T3Im ligands showed a higher binding affinity for salmon DNA.

Conclusion

- 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.



Scheme 1: Chemical structures of the two cationic π -conjugated oligothiophenes.

3. Microscopic morphology of oligothiophene/DNA complexes

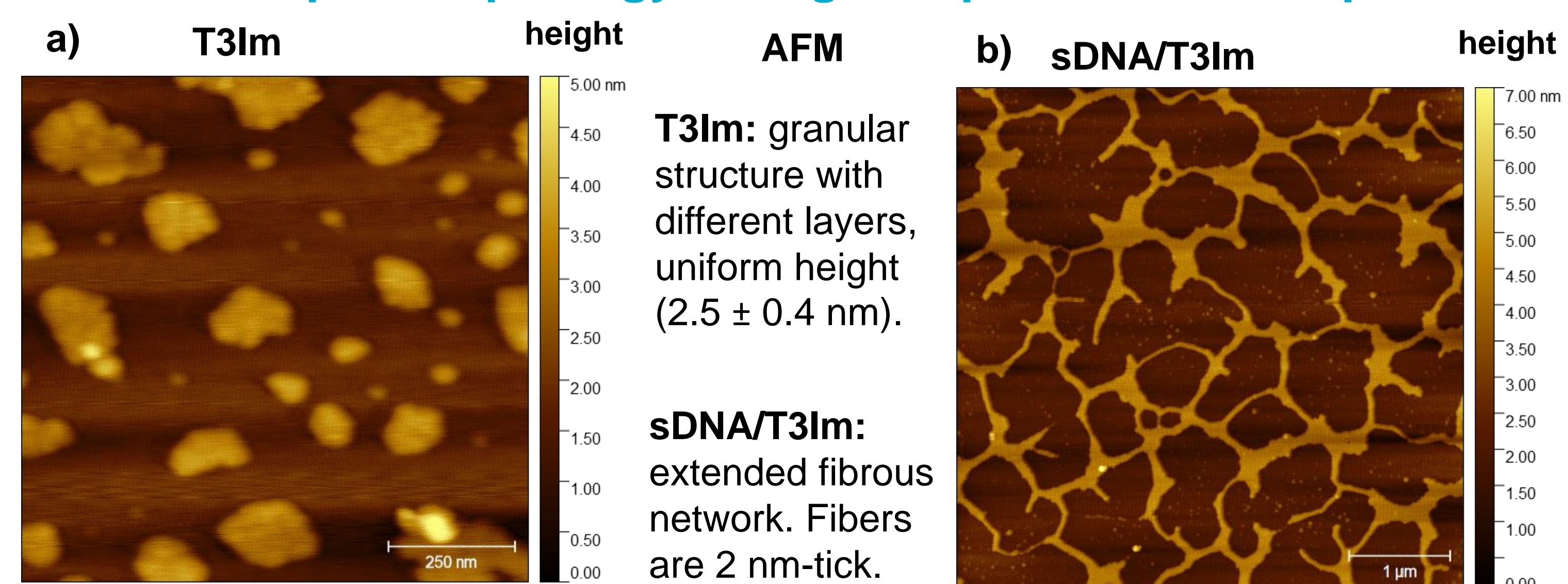


Figure 4: AFM images of thin deposits **a)** pure T3Im and **b)** sDNA/T3Im mixing on mica substrate. [T3Im]=120 μ M and [sDNA]=0.06 μ M.

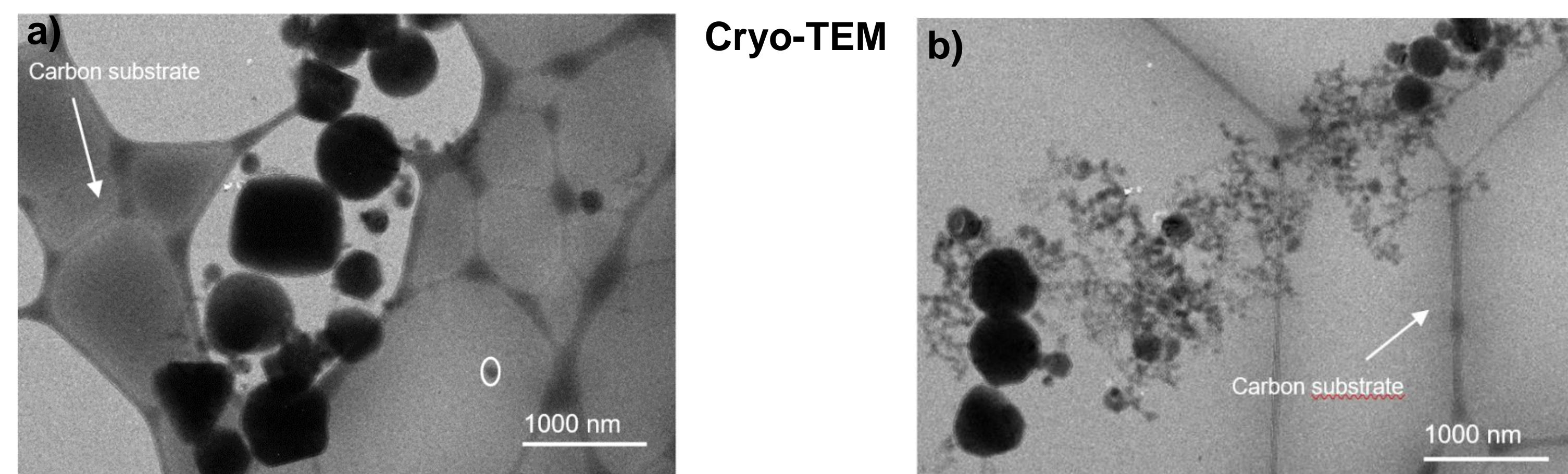


Figure 5: Cryo-TEM images of **a)** pure T3Im and **b)** sDNA/T3Im mixing at the hydrated state. [T3Im]=120 μ M and [sDNA]=0.06 μ M.

- T3Im: grains and crystals.

- sDNA/T3Im: extended fibers network.

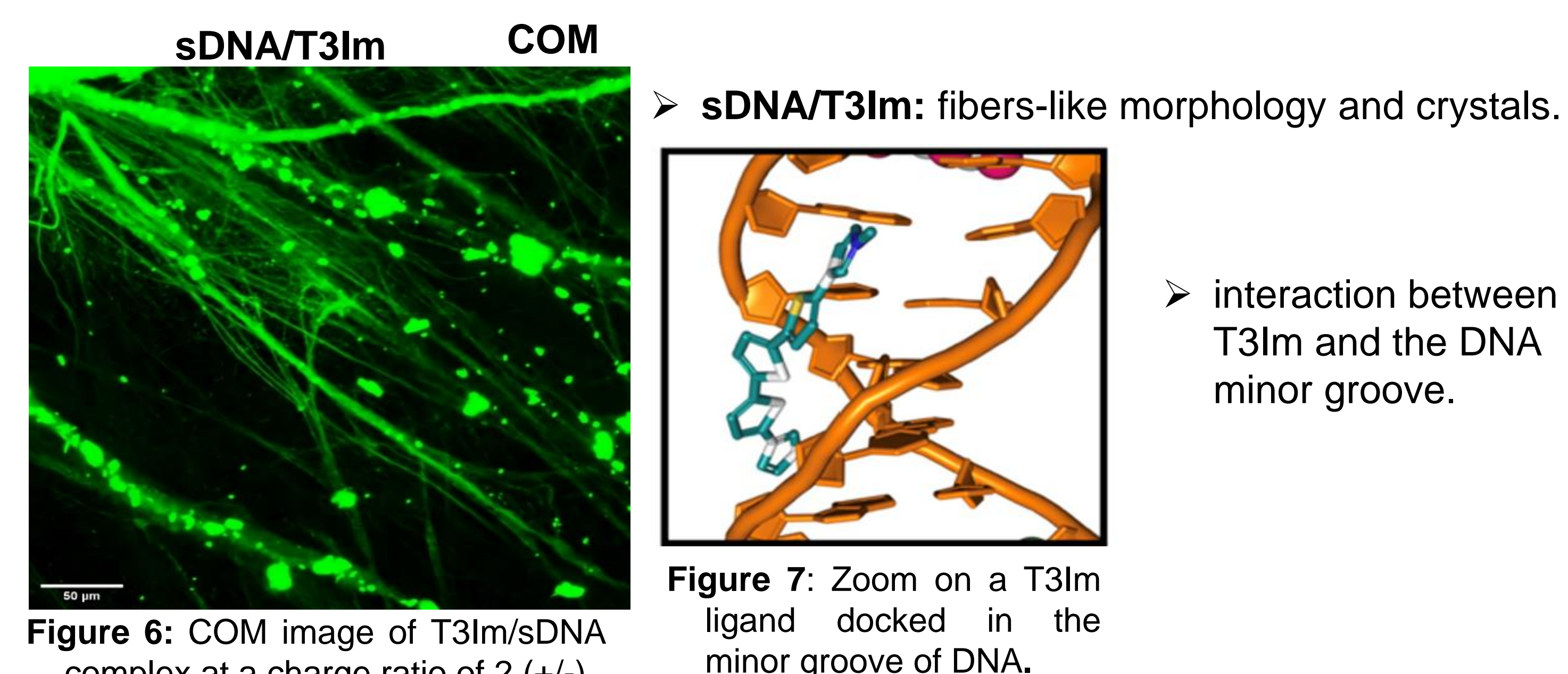


Figure 6: COM image of T3Im/sDNA complex at a charge ratio of 2 (+/-).

Figure 7: Zoom on a T3Im ligand docked in the minor groove of DNA.

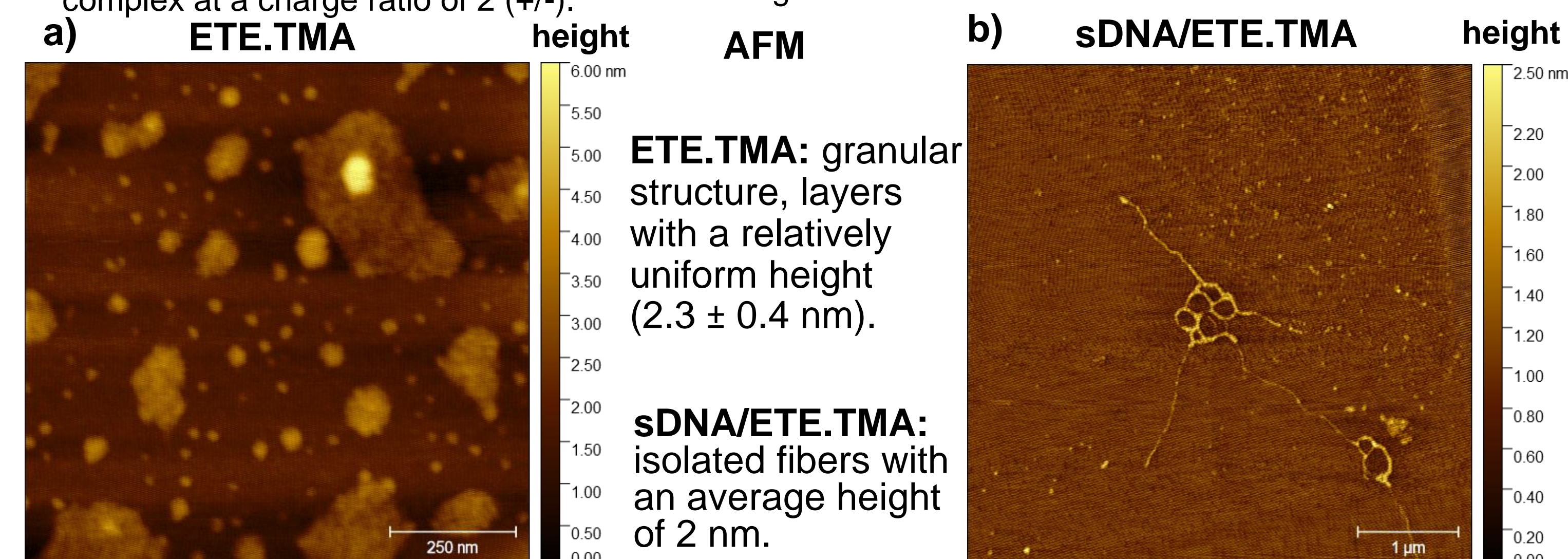


Figure 8: AFM images of thin deposits **a)** pure ETE.TMA and **b)** sDNA/ETE.TMA on mica substrate. [ETE.TMA]=120 μ M and [sDNA]=0.06 μ M.

References

- [1] G. Barbarella, M. Melucci, G. Sotgiu, *Adv. Mater.*, **2005**, 17, 1581-1593.
- [2] Conjugated Polyelectrolytes: Fundamentals and Applications, edited by Liu, B. & Bazzan, G. C., Wiley-VCH, **2013**.