

# Time-resolved Spectroscopy and Structural Properties of Oligothiophene Monomers Combined with Ag Nanoparticles Obtained in Liquid by Ultrashort Laser Ablation



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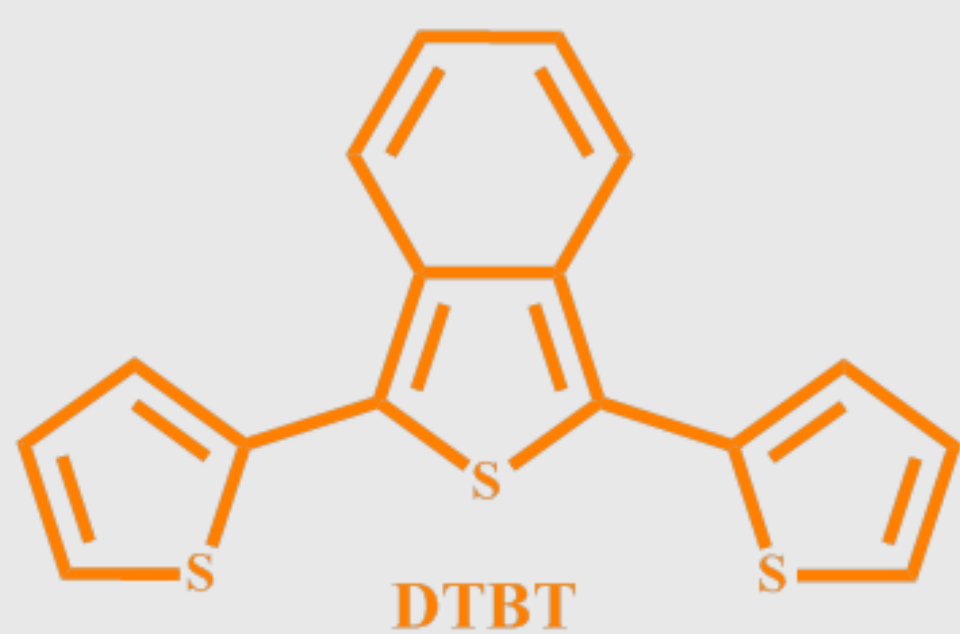
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## OBJECTIVE

Nanocomposites obtained by combining Ag nanoparticles (AgNPs) with oligothiophenes have been investigated via optical, electronic and structural characterizations both in solution and in solid state.

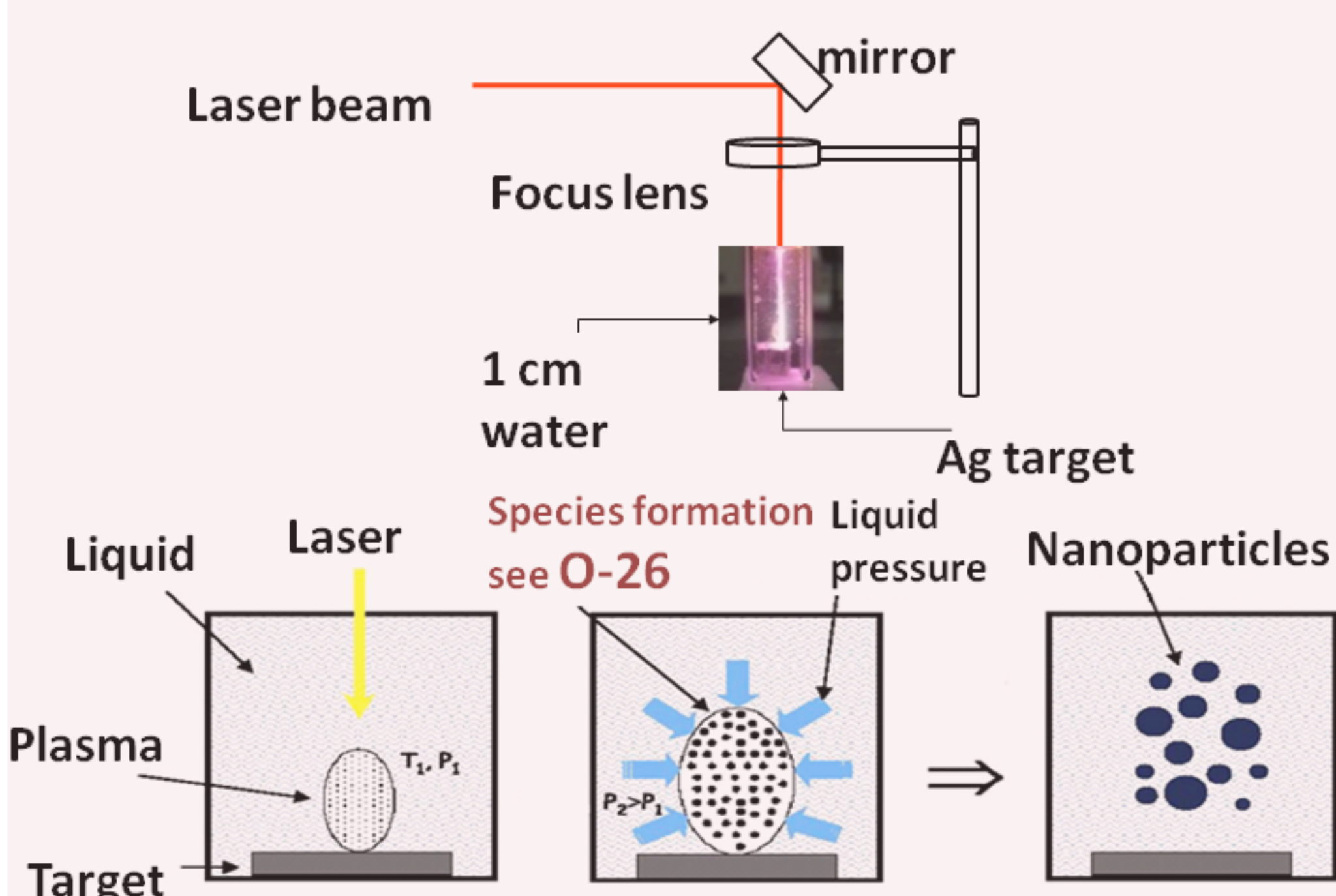


## EXPERIMENTAL PART

### AgNPs synthesis

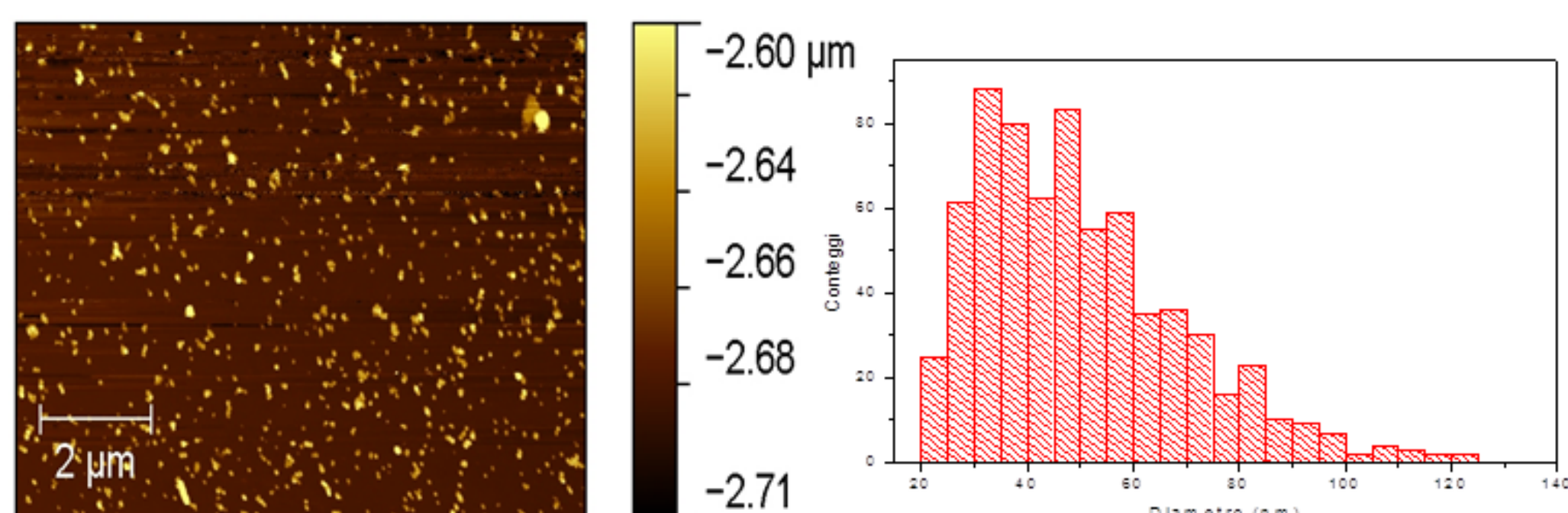
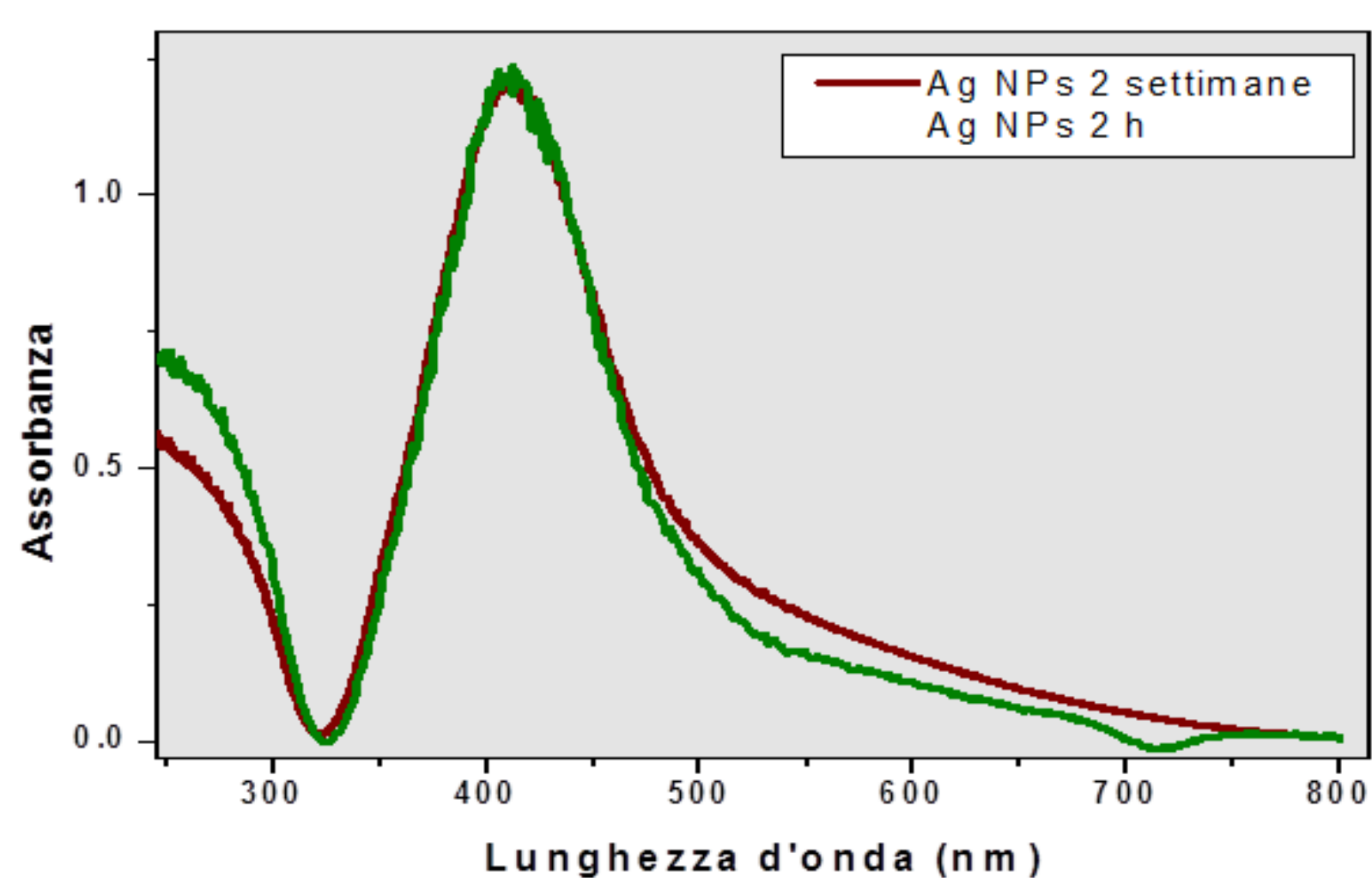
The versatile Pulsed Laser Ablation in Liquid (PLAL) method has been adopted to produce colloidal stable and defined AgNPs solutions.

### Laser ablation in water



**Experimental conditions:**  
Spectra Physics Spitfire Pro XP (Ti:S; 800 nm; 100 fs; 1 kHz);  
Target: 99.95% Ag (Goodfellow).

### AgNPs colloidal solution characterization



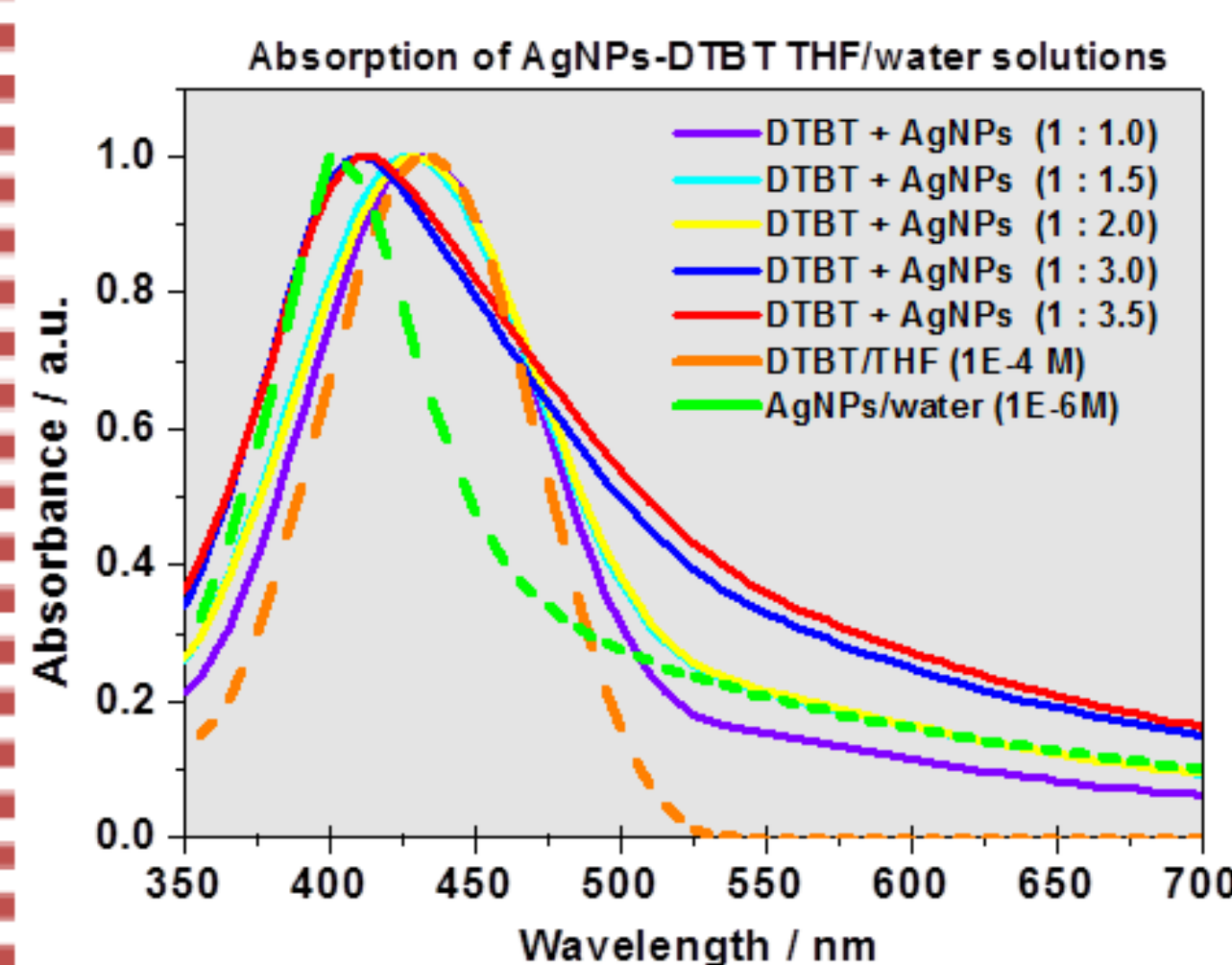
UV-Vis absorption spectra of the colloidal solutions of AgNPs obtained by ablating an Ag target in water using 100 fs laser pulses and AFM image have provided the AgNPs evaluation mean size in the range of 50±20 nm.

## AgNPs-oligothiophene nanocomposites characterizations

### SOLUTIONS

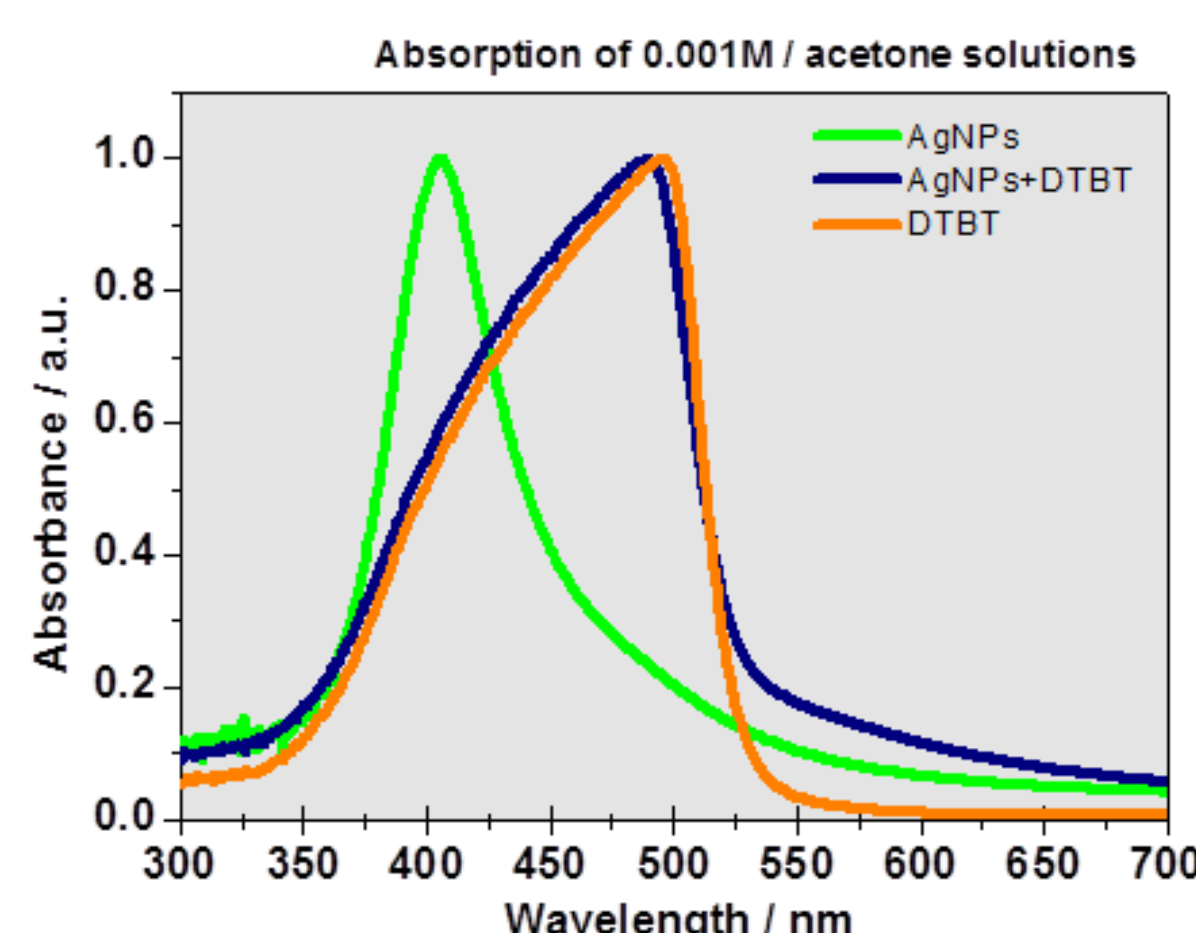
#### Steady-state UV-Vis: absorption and emission

The Ag NPs-oligothiophene nanocomposites solutions have been characterized by fluorescence and absorption techniques

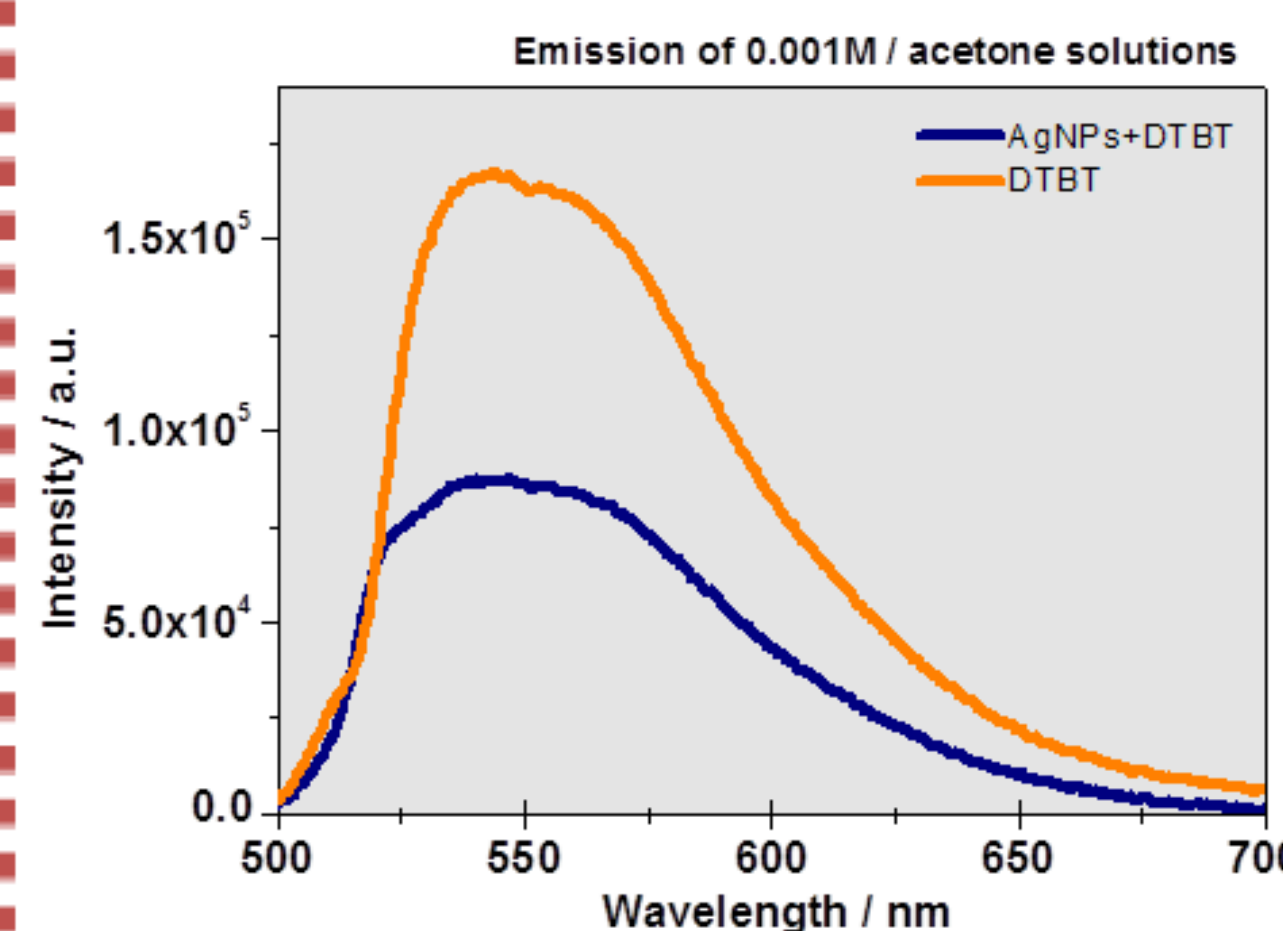


#### OBSERVED EFFECTS AFTER ADDITION OF AgNPs TO DTBT SOLUTION:

- The hybrid nanocomposites used have shown a blue shift with the increase of the concentration of metal nanoparticles;
- AgNPs - oligothiophene composite aggregation occurs.



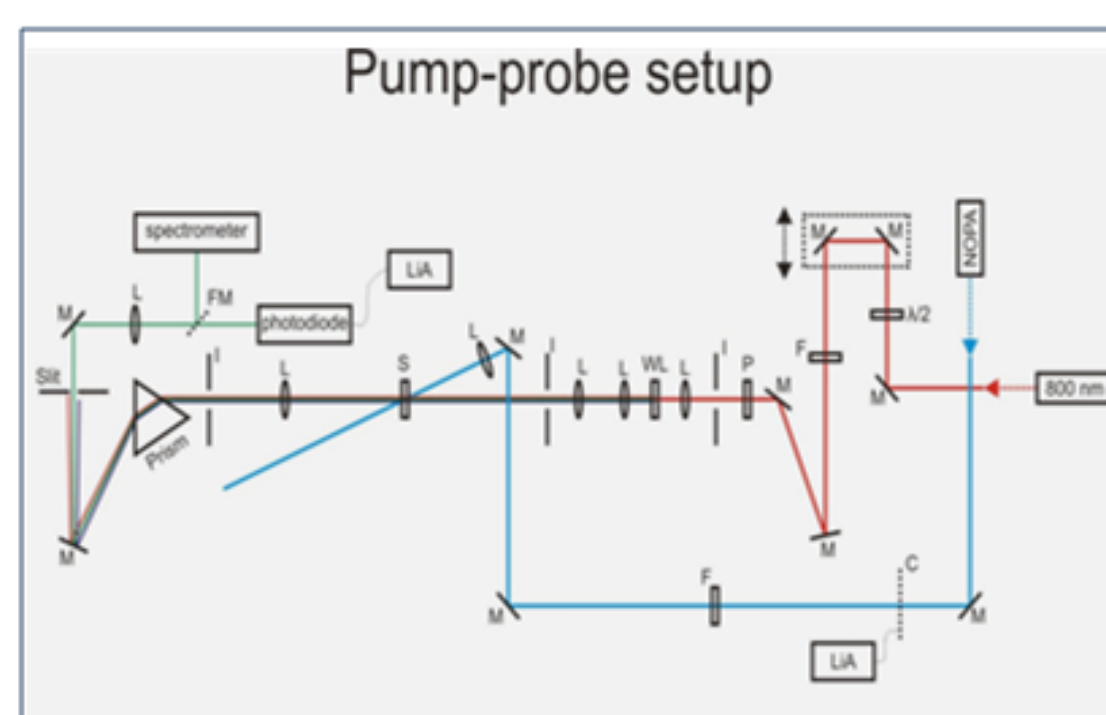
- The nanocomposite absorption spectrum is not just due to the sum of the two single spectra;
- It is observed AgNPs-oligothiophene composite aggregation effects as well a slight blue-shift.



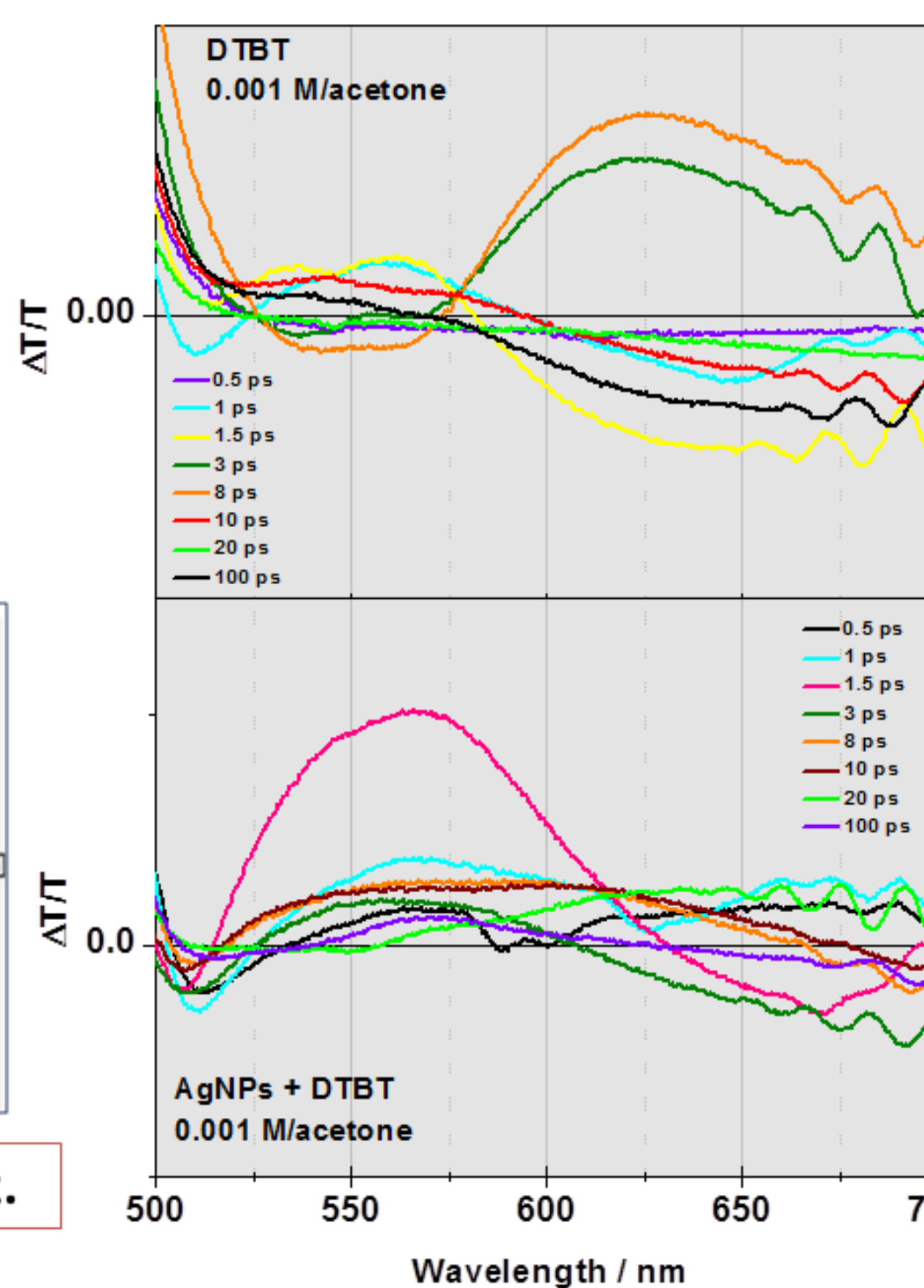
- Fluorescence quenching;
- Broadening around 500-700 nm;
- Red-shifted shoulder.

### Transient time-resolved absorption: Pump-Probe

Pump-Probe have provided insights on the electronic structure, and excitation de-excitation mechanisms involved. The spectroscopic time evolutions of the formed hybrid nanocomposites obtained have been studied and their comparison has been drawn.



Ti:S ; 800 nm; 30-100 fs; 1mJ; 1KHz.



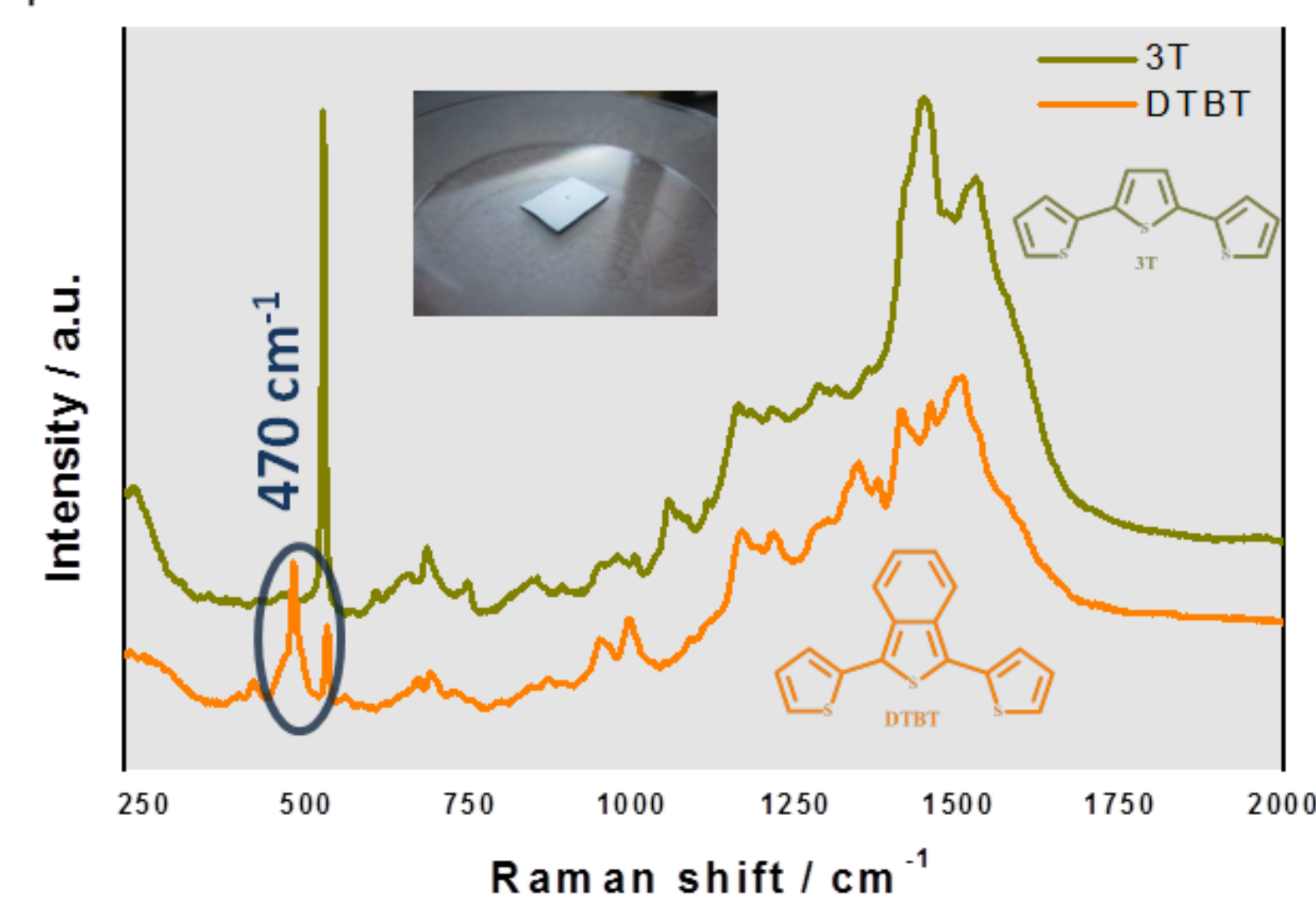
## CONCLUSIONS

The preliminary results here reported have evidenced the existence of AgNPs-DTBT bond by SERS, High Resolution XPS and absorbance of nanocomposites. Spectroscopic experimental results support that a linkage between Ag and DTBT oligothiophene could occur and this hypothesis is even strengthened by Pump-Probe transient absorption results in which a completely different behavior can be observed between the bare oligothiophene and the nanocomposite system.

### THIN FILMS

#### SERS on AgPLD

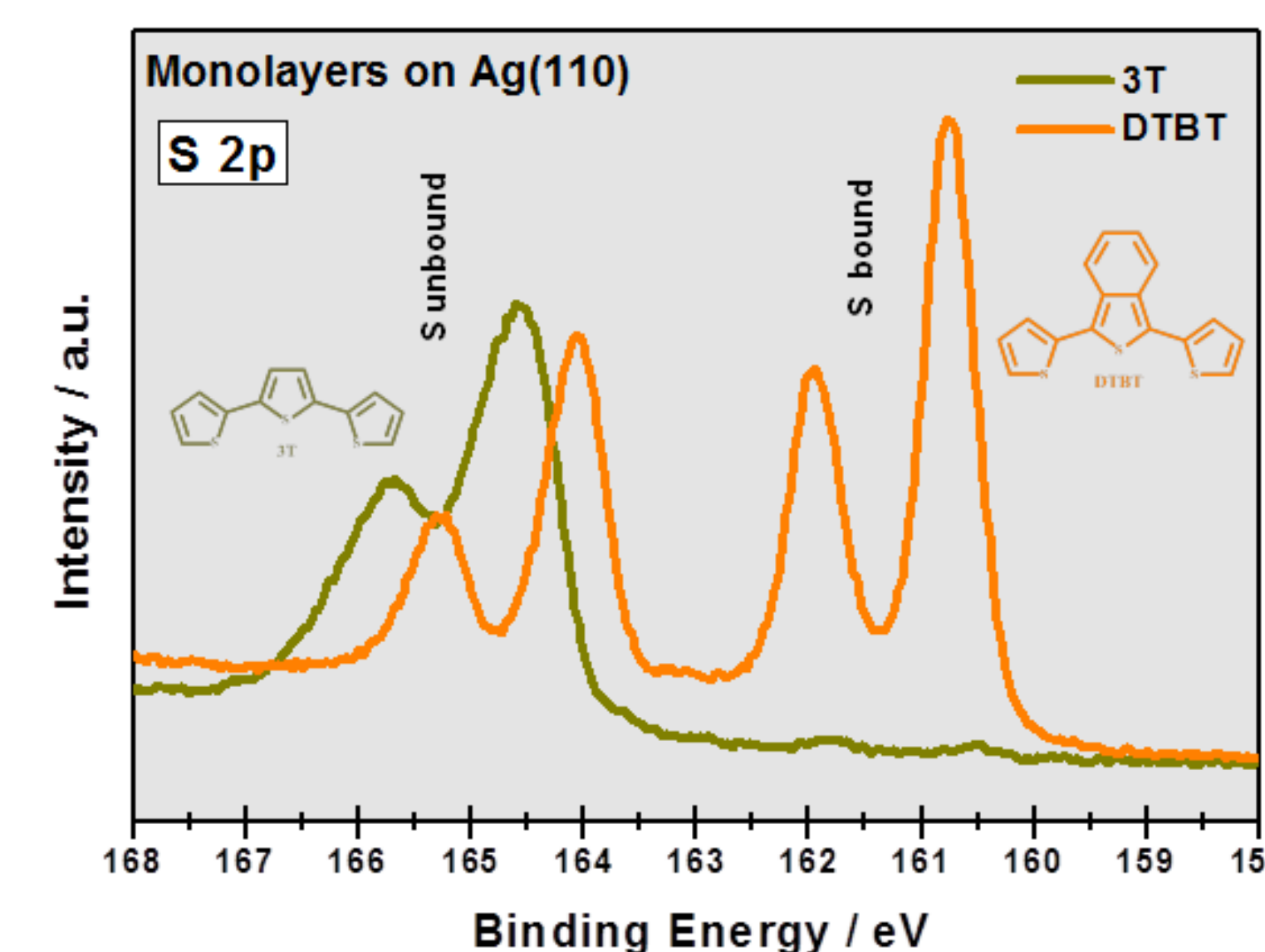
In order to investigate vibrational mode differences due to the interaction between the AgNPs surfaces and monomer's first monolayers, Surface Enhanced Raman Spectroscopy (SERS) measurements have been performed.



SERS signals	3T (cm <sup>-1</sup> )	DTBT (cm <sup>-1</sup> )
C-S		470
		664
	683	685
		939
C-H bending		987
	1050	1073
	1156	1155
		1210
		1331
C-C stretching	1416 (shoulder)	
		1365
C=C simm. stretching	1444	1447
		1399
C=C asimm. stretching		1499
		1522

The SERS spectra have shown that the benzene ring condensed on the oligothiophene can play a key role on Raman active modes which can be likely related to the benzo-fused group. In particular, the DTBT signal at 470 cm<sup>-1</sup> together with other differences of SERS spectra compared to 3T can be related to a different interaction with AgNPs (maybe a S-Ag linkage is involved) and, therefore, affecting reactivity, electronic properties and applications of nanocomposites of this kind.

### XPS on Ag(110)



Looking to XPS spectra made after Ultra High Vacuum (UHV) deposition of one monolayer of DTBT (about 3 Å) on Ag(110) we can conclude that two main species of sulphur are present and the one at lower binding energy could be related to sulphur bound to Ag surface showing in this way a possible linkage in the Ag-DTBT composite material.

### Acknowledgements

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