

# Spectroscopic properties of laser induced Ag nanoparticle-oligothiophene nanocomposites

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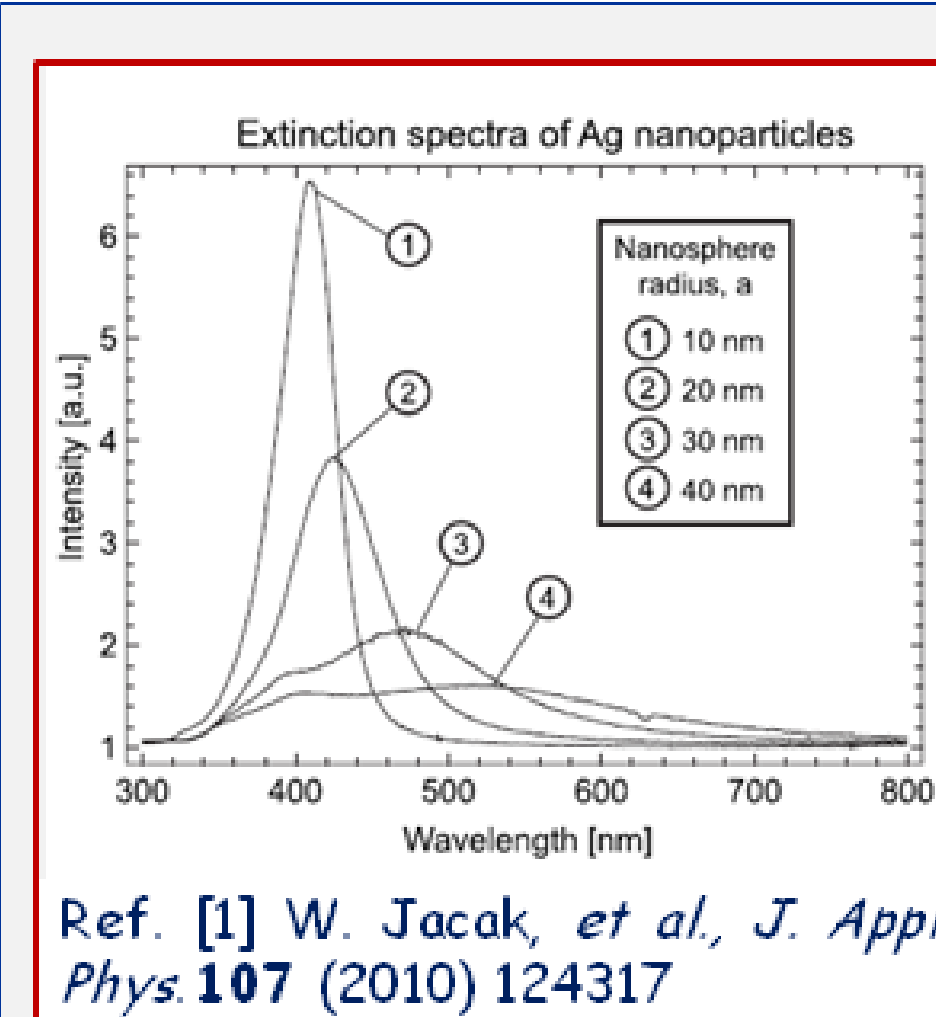
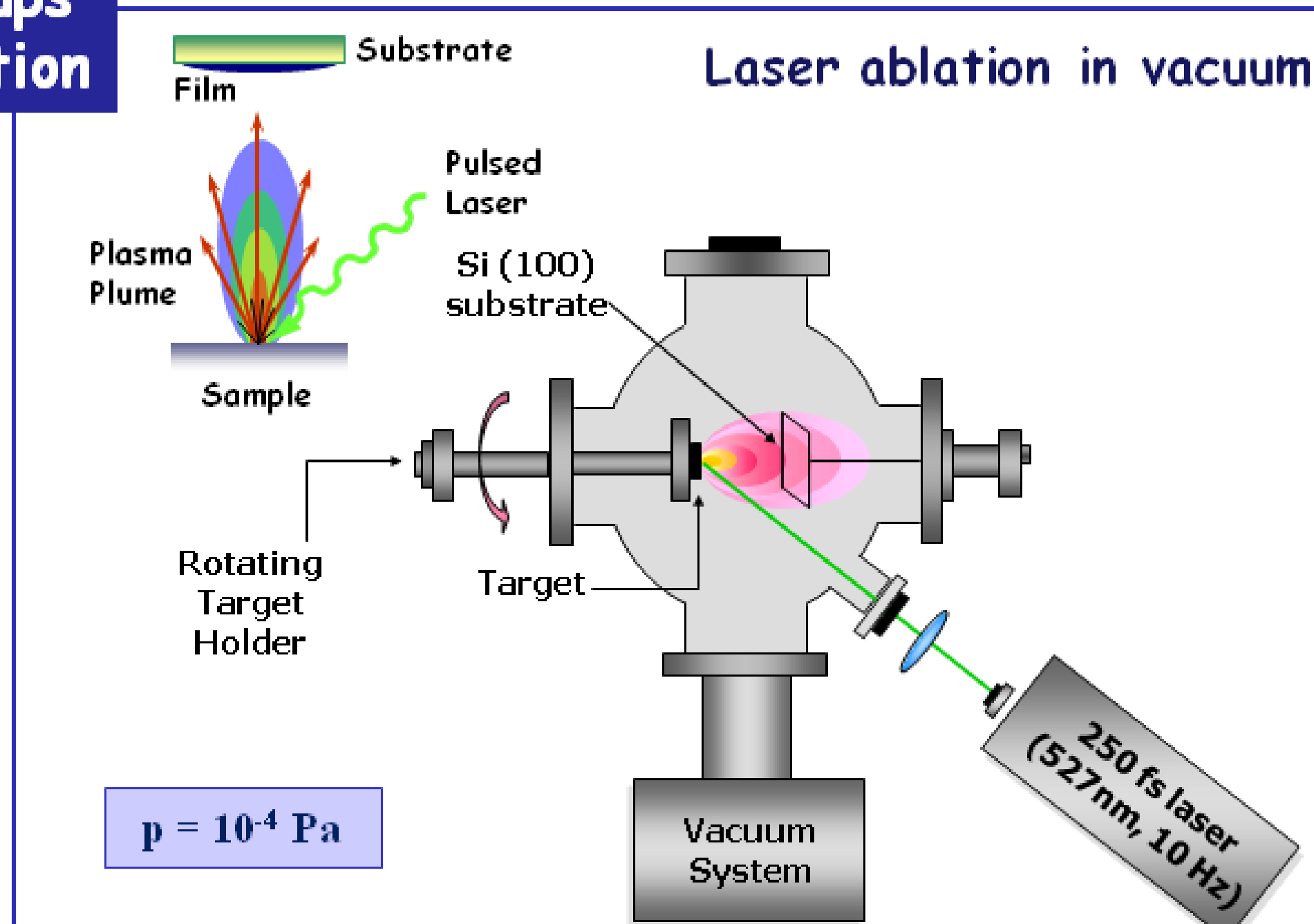
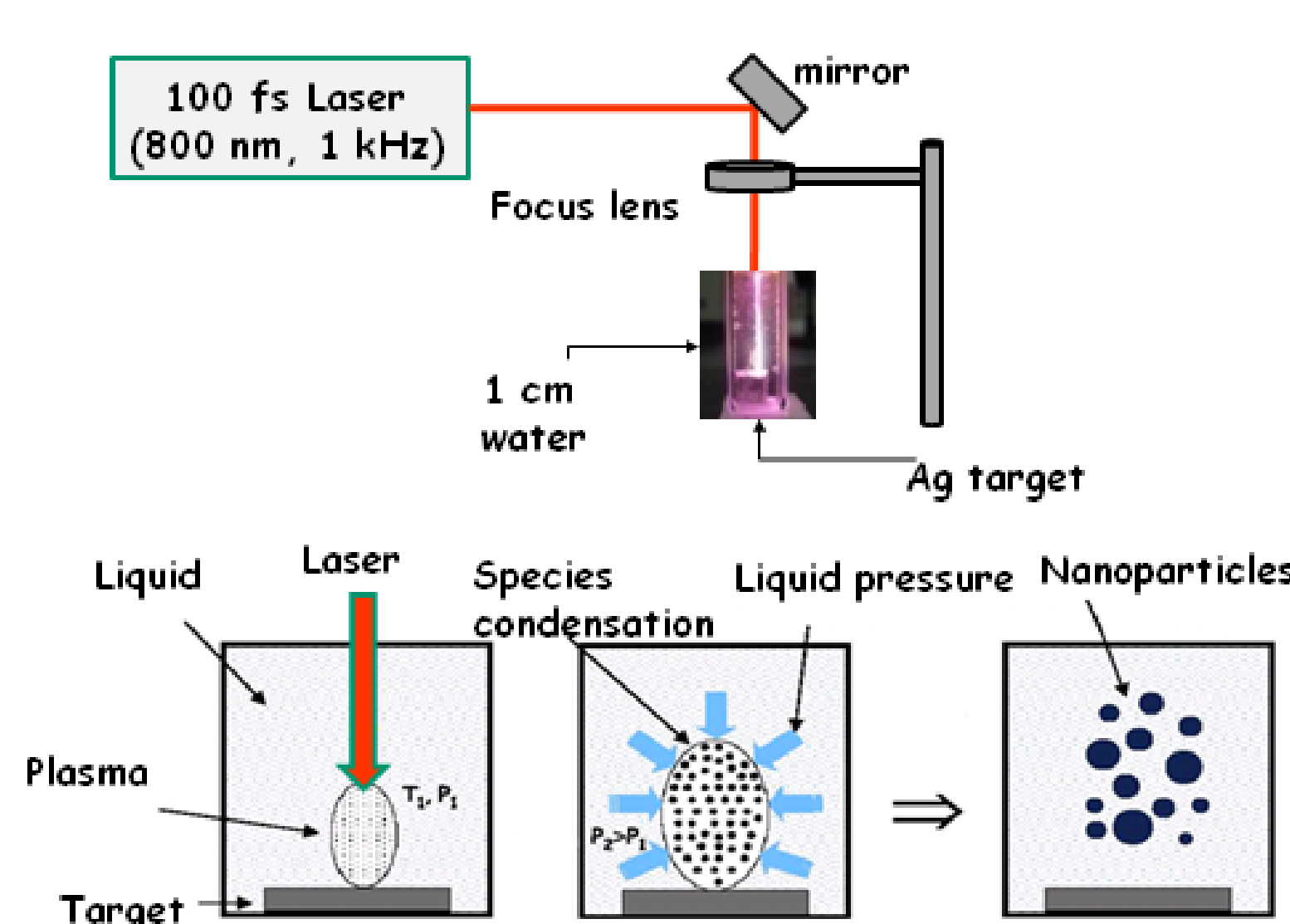
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## Abstract

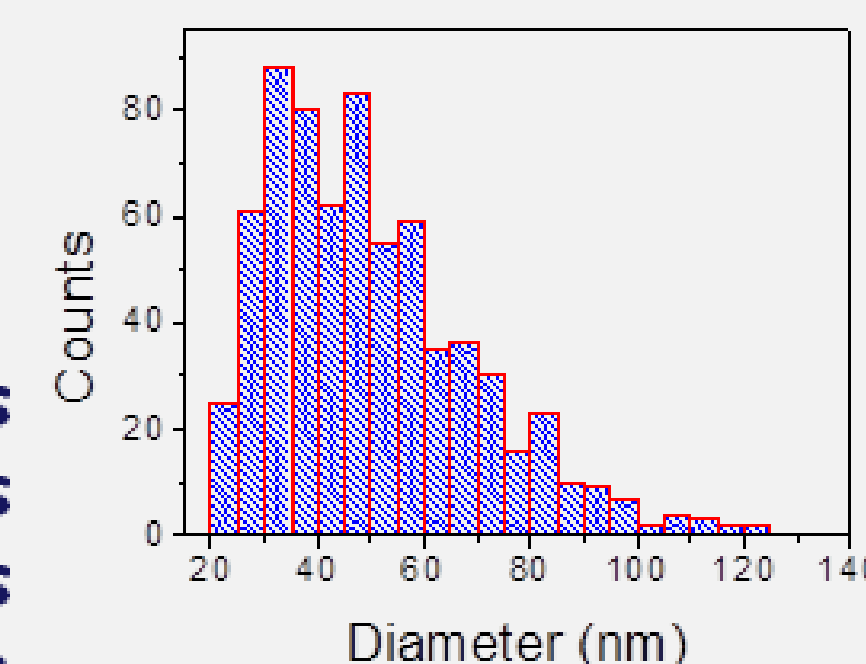
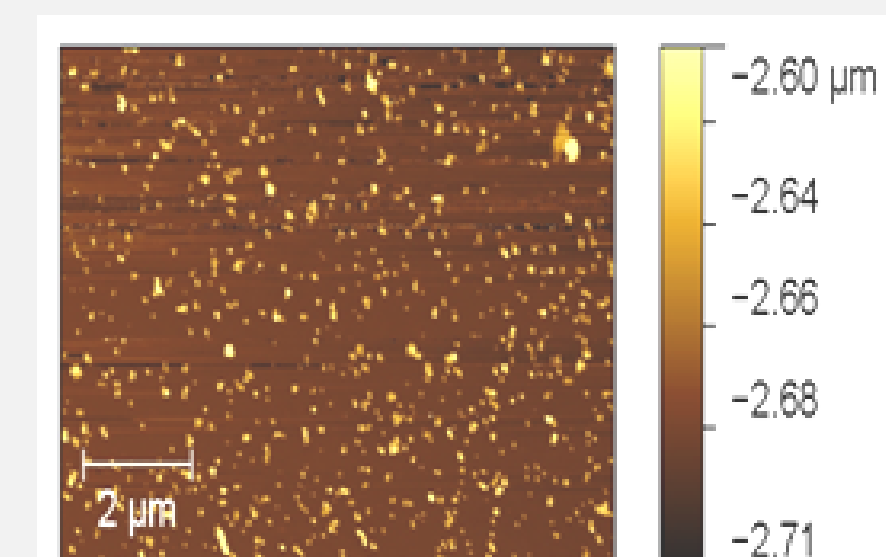
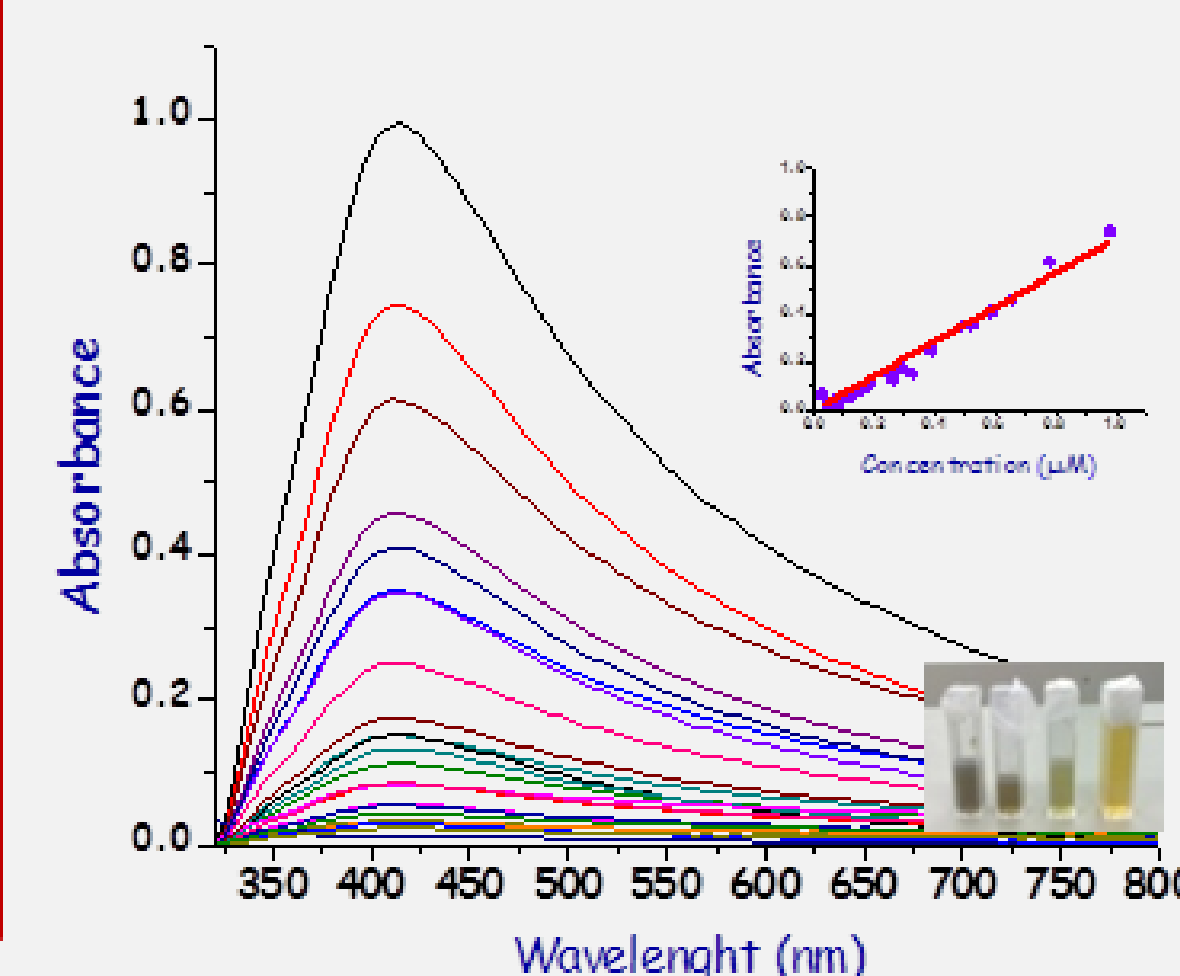
In this work, the quite new and versatile Laser Ablation in Liquid method, for producing colloidal stable and well defined Ag nanoparticle (NP) solutions has been adopted. UV-vis absorption spectra of these Ag NP solutions obtained by ablating an Ag target in water using 100 fs laser pulses have provided the NPs evaluation mean size ( $50 \pm 20$  nm) and concentration (up to  $3.6 \mu\text{M}$ ). The formation of nanocomposites was obtained by combining the laser induced Ag NPs with oligothiophenes. Ag NP-oligothiophene nanocomposite solutions have been characterized by steady-state photoluminescence and absorption spectroscopy (250–800 nm). Metal-polythiophene hybrid nanocomposites have shown an enhancement of the photoluminescence intensity as well as spectral modulation by either varying the concentration of  $\pi$ -conjugated organic system or changing the metal NPs features. For defining the kind of interaction occurring between Ag NPs and oligothiophenes the Surface Enhanced Raman Spectroscopy (SERS) technique has been employed. With this purpose Ag NPs were firstly deposited on Si (100) substrates by pulsed laser ablation ( $\tau = 250$  fs) performed in vacuum ( $10^{-4}$  Pa) and, afterwards, on these, different Ag-oligothiophene nanocomposite thin films were produced by drop casting of oligothiophene solutions. The results show a change in SERS spectra when oligothiophenes benzo-substituent is present which suggests that different conformational orientation of the oligothiophenes may occur during their interaction with the Ag NPs.

## Experimental set-ups for Ag NPs production

### Laser ablation in water



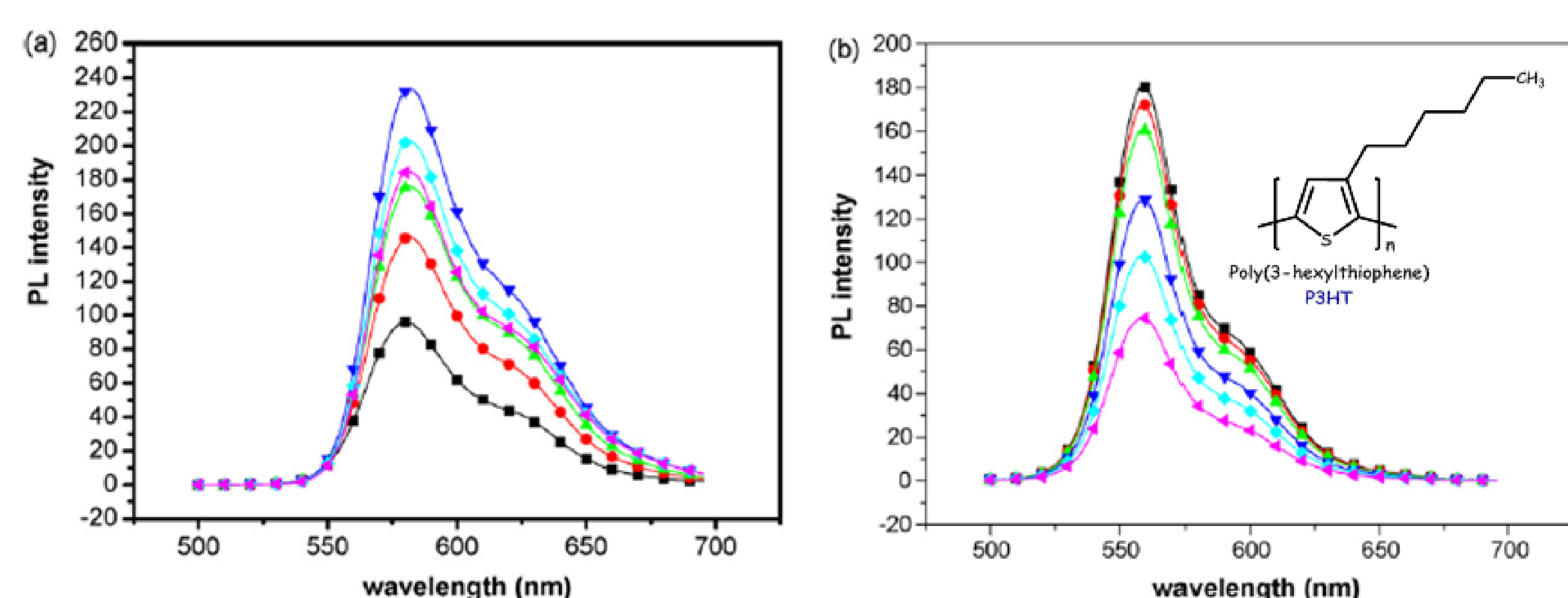
Ref. [1] W. Jacak, *et al.*, *J. Appl. Phys.* **107** (2010) 124317



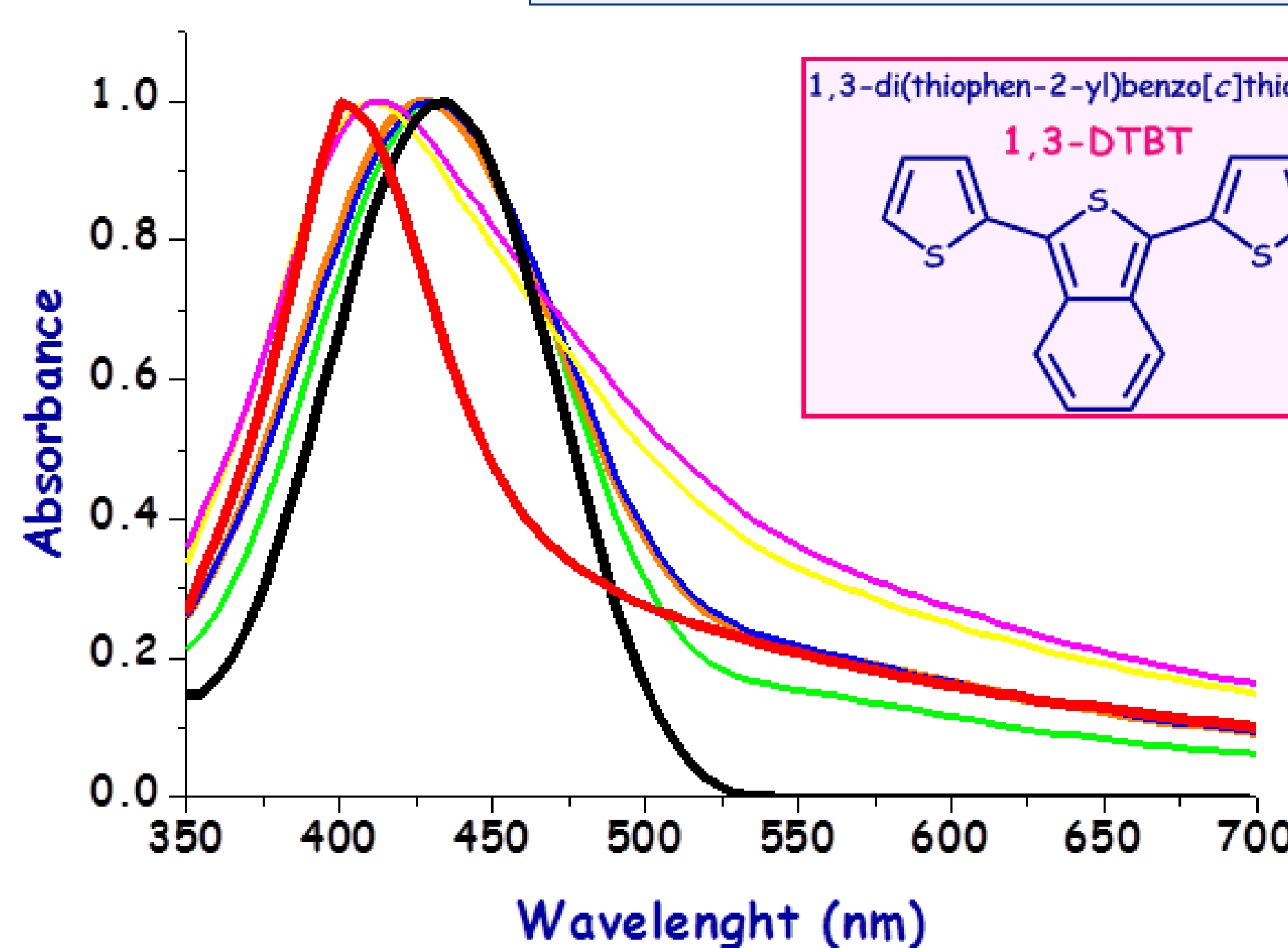
All Ag colloidal water solutions were characterized by NPs diameters within the range of  $50 \pm 20$  nm. These results were confirmed by experimental AFM surveys as well as the good agreement of UV-vis absorbance spectra with theoretical prediction of Ref. [1].

Ref. [2] I-Shuo Liu, *et al.*, *J. Photochem. Photob. A* **199** (2008) 291

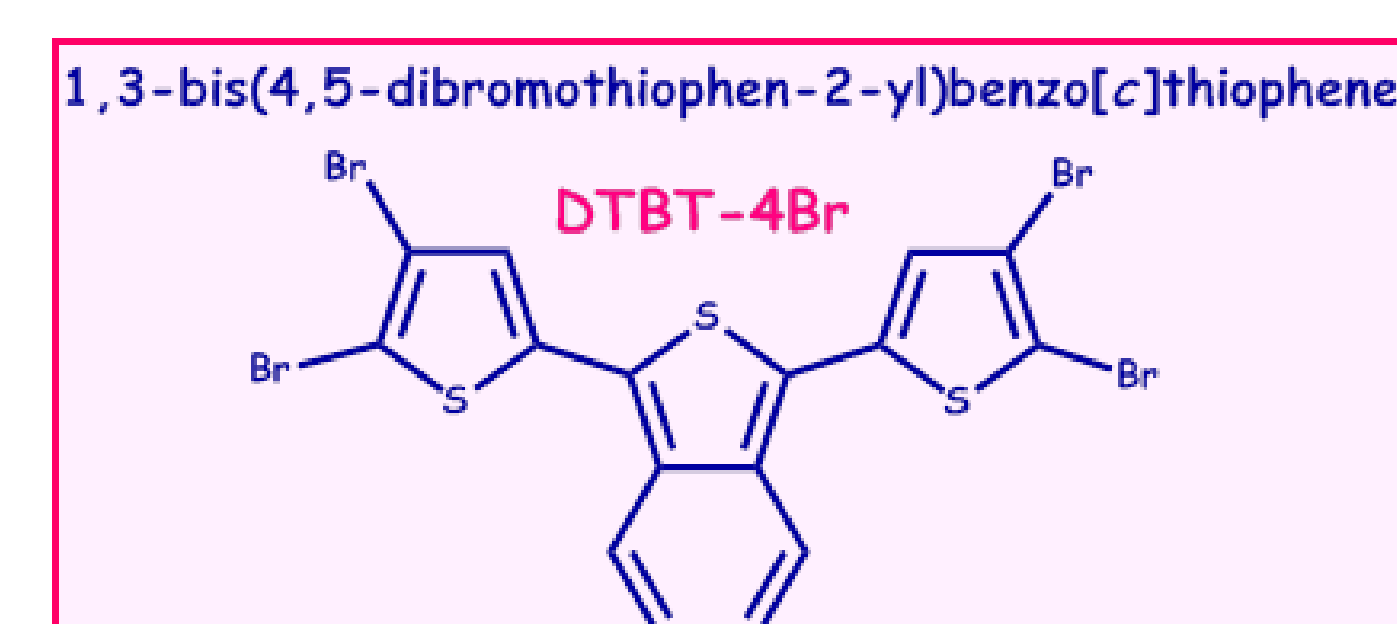
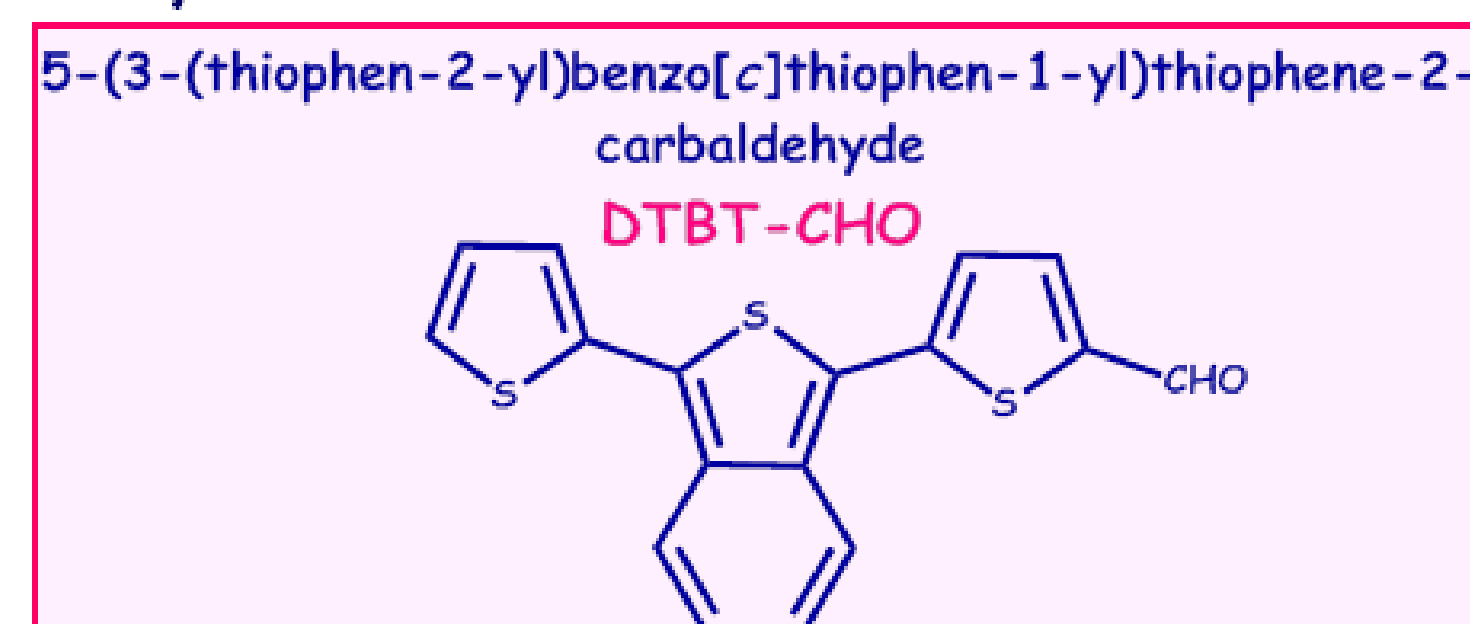
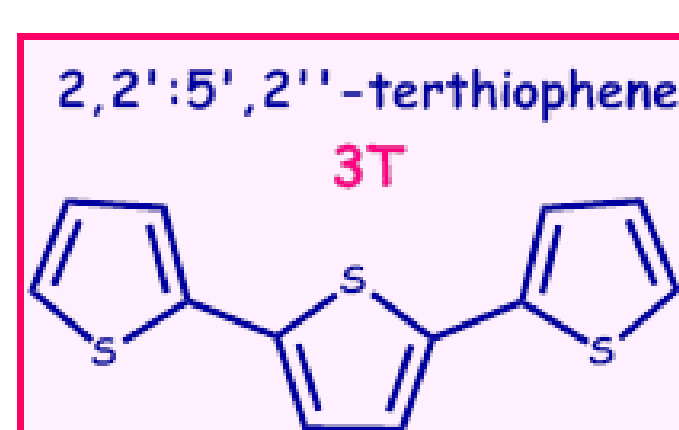
The amount of metal NPs can induce either enhancement or quenching of the  $\pi$ -conjugated system photoluminescence. Enhancement is observed when scattering comes from metal NPs surface plasmon resonance. Conversely quenching is appreciated when metal NPs surface plasmon resonance comes from absorption of the organic component. Different photoluminescence spectral modulation can be as well connected to diverse organic component concentrations.



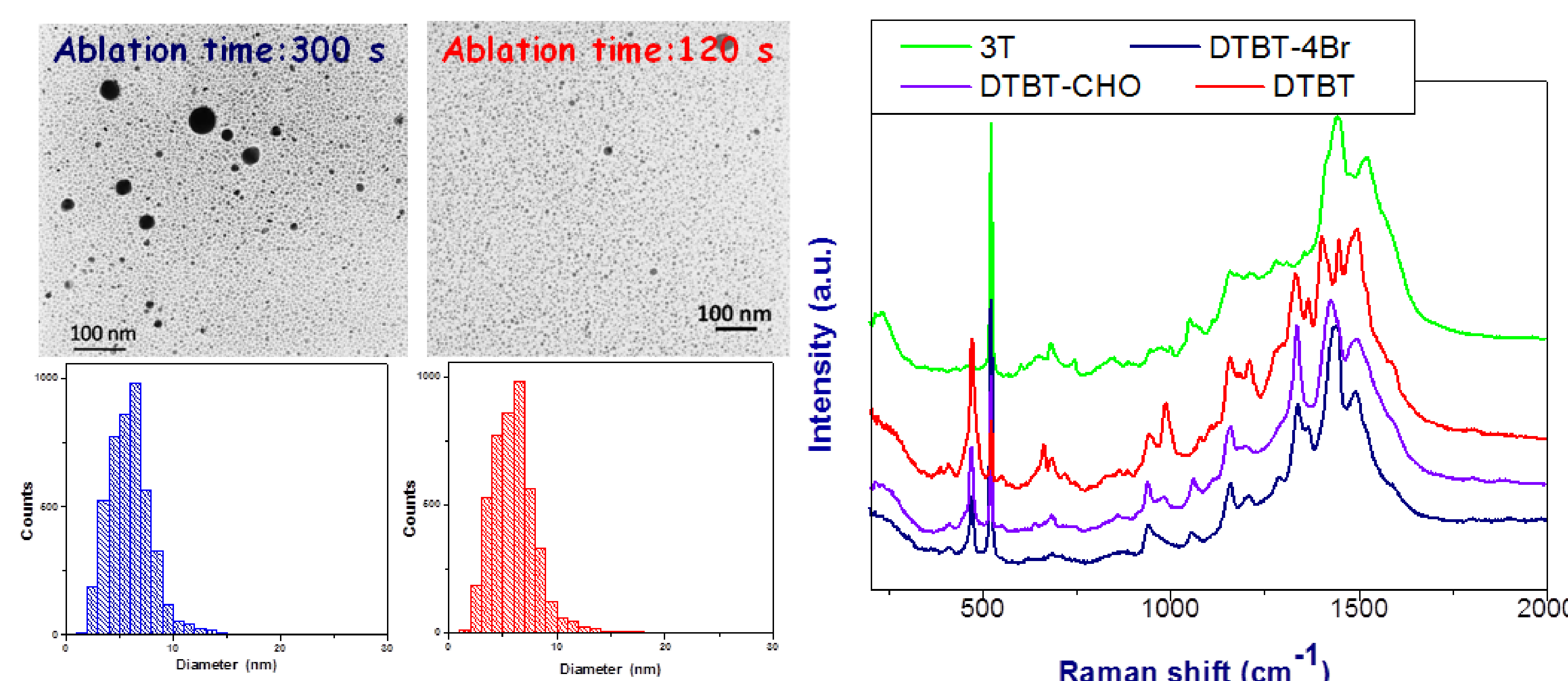
Photoluminescence spectra of (a) high (0.08 wt.%) and (b) low ( $1.48 \times 10^{-5}$  wt.%) poly(3-hexylthiophene) concentration with different amount of metal NPs. ■ Pure P3HT; ● NPs  $3.06 \times 10^{-4}$  wt%, ▲ NPs  $1.22 \times 10^{-3}$  wt%, ▼ NPs  $3.67 \times 10^{-3}$  wt%, ◆ NPs  $6.11 \times 10^{-3}$  wt%, ◆ NPs  $8.56 \times 10^{-3}$  wt%.



Different concentrations of Ag NPs generated in water mixed with 1,3-DTBT/THF solutions have shown a quenching absorption effect together with a spectral modulation of the absorption band. The above spectra have been normalized for a better view of the modulation behaviour. Commercial (3T) and other synthesized oligothiophene systems have shown similar behaviours.



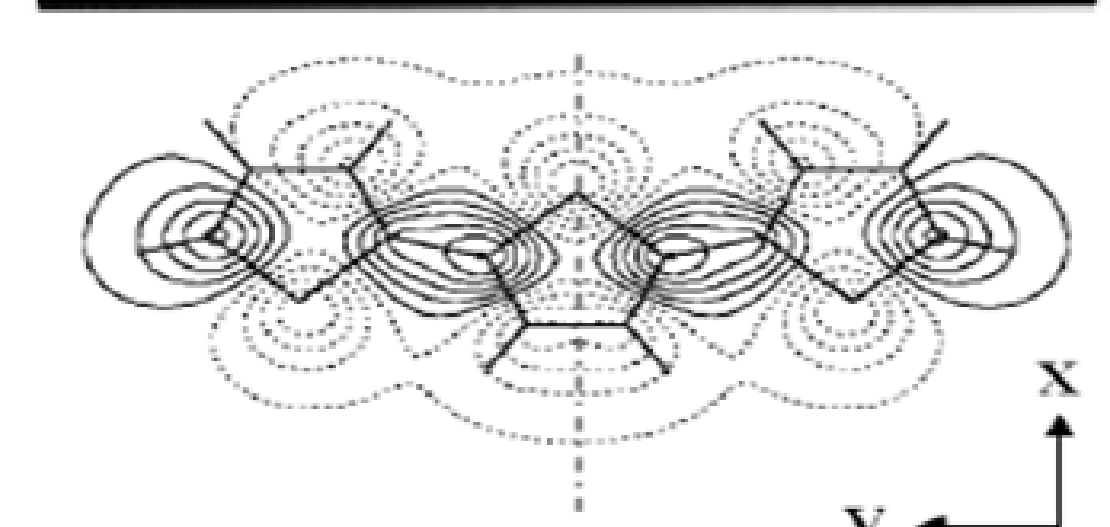
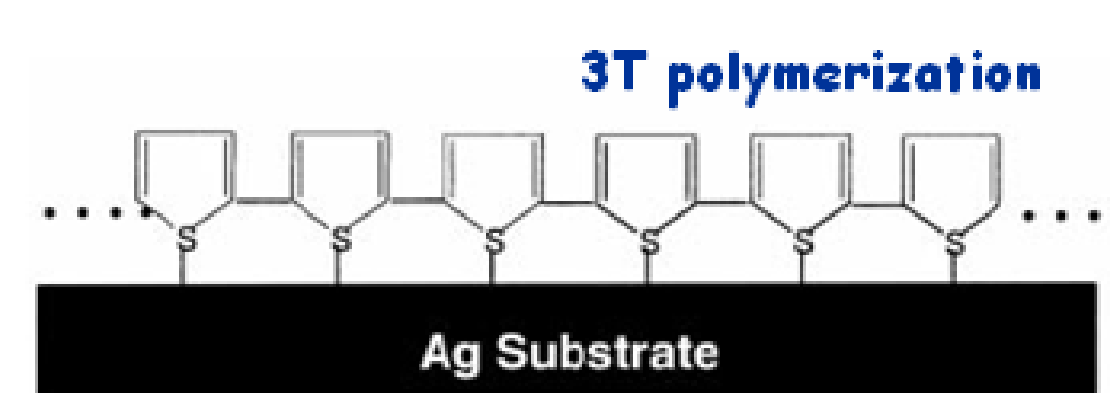
The surface plasmon resonance effect taking place when Ag NPs are combined with the reported four different oligothiophenes has been evaluated by Surface Enhanced Raman Spectroscopy (SERS). With this aim Ag NPs have been deposited on Si (100) by direct ablation of Ag target in vacuum ( $p: 10^{-4}$  Pa; laser: 250 fs, 527 nm, 10 Hz), afterwards the oligothiophenes have been deposited by drop casting.



Independently from the Ag NPs dimension the SERS spectra have shown that the oligothiophene substituent can play a key role on Raman active modes. In the region  $1100\text{--}1300\text{ cm}^{-1}$  a very complex pattern of weak lines appears although for 3T, compared to the benzo-substituted systems they are rather negligible. DTBT, DTBT-CHO and DTBT-4Br show well defined signals at 490 and  $1334\text{ cm}^{-1}$  which can be likely related to the benzo-substituent.

SERS spectra suggest that 3T and DTBT-CHO could involve a similar conformational arrangement where sulphur atoms are bound to Ag-NPs' surface inducing polymerization.

Ref. [3] E.A. Bazzouzi, *et al.*, *J. Raman Spectrosc.* **177** (1998) 29;  
Ref. [4] G. Compagnini *et al.*, *Phys. Chem. Chem. Phys.* **2** (2000) 5298



Oligothiophene	3T	DTBT-CHO	DTBT-4Br	DTBT
SERS active modes				
Benzo-substituent feature		469	467	470
				664
C-S	683	684	688	685
		939	937	939
				987
C-H bending	1050	1060	1057	1073
	1156	1157	1158	1155
			1209	1210
			1291	
		1334	1333	1331
			1366	1365
				1399
C-C stretching	1416(shoulder)	1425		
C=C symm. stretching	1444	1444(shoulder)	1444	1447
		1497	1490	1499
C=C asymm. stretching	1522			

3T LUMO plot shows a bonding interaction in the inter-ring connection which can be strongly affected by distortion. DTBT and DTBT-4Br provide pretty different SERS spectra which can be related to a changed interaction with Ag-NPs and, therefore, LUMO and optical property variations.

## Conclusions

It is expected that the oligothiophene substituents can play a fundamental role with Ag-NPs during formation of relative nanocomposites and consequently their features (e.g. photoluminescence or absorption spectral modulation) could be likely planned by a proper choice of them.

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