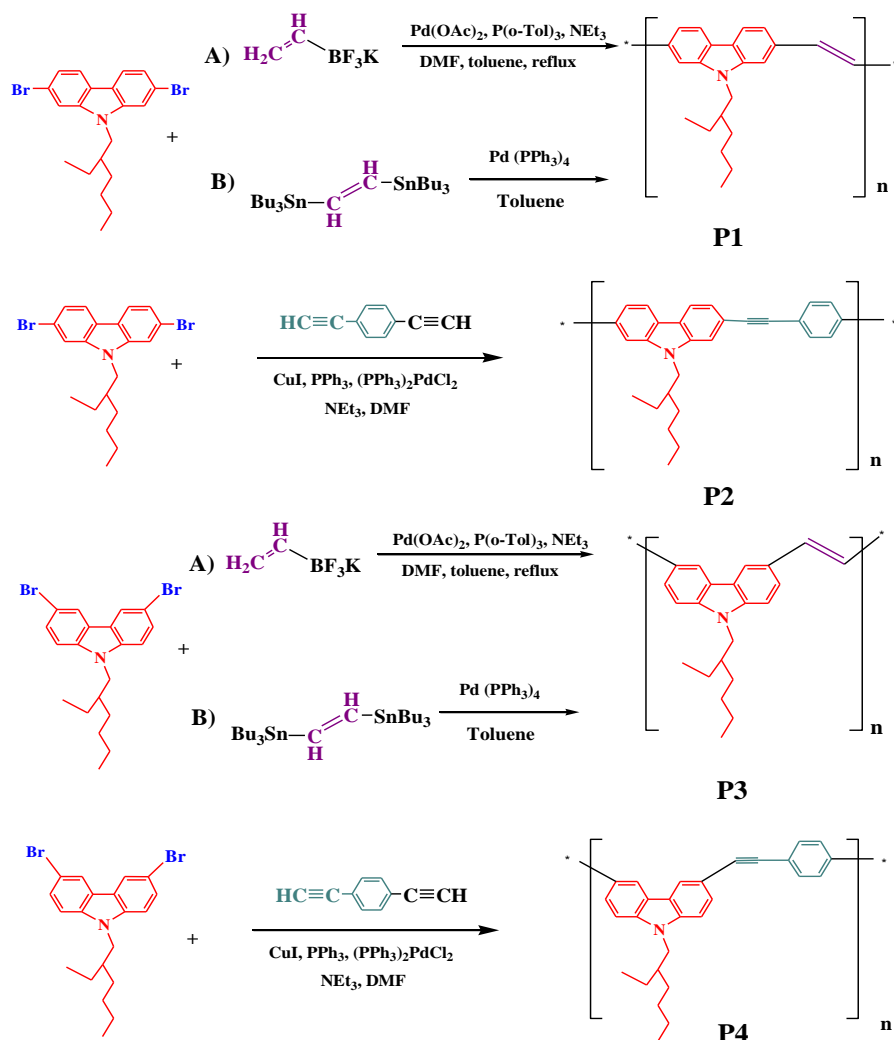


## RESULTS 2013

1. Synthesis and characterization of new conjugated oligomers and polymers with donor groups.
2. Synthesis of photoactive layers from donor oligomers and polymers and acceptors

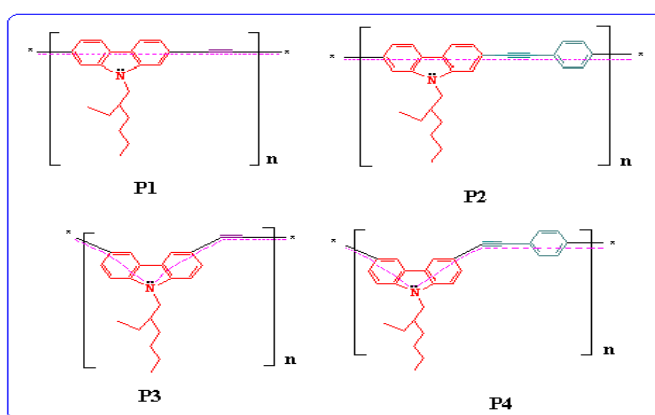
1.a. Polyarylene vinylene and polyarylene ethynylene containing 2,6- and 3,6-carbazolediyl units. A comparative optoelectronic study. Characterization of polymers by FTIR, NMR, optical properties (UV-vis and fluorescence) electronic structure (HOMO and LUMO levels) (by electrochemistry)



Scheme 1. Synthesis of polyarylene vinylene and polyarylene ethynylene containing 2,7- and 3,6-carbazolediyl units

**Table 1.** Optical properties of P1 and P2

Polymer	$\lambda_{\text{absmax}}$ (solution) (nm)	$\lambda_{\text{absmax}}$ (film) (nm)	$\lambda_{\text{emmax}}$ (nm)	E <sub>gop</sub> (eV)
P1	269, 419	272, 418	473	2.46
P2	260, 366	266, 378	419	2.48
P3	344, 373	271, 337, 374	446	2.55
P4	244, 311, 357	243, 362	405	2.64



**Scheme 2.** Conjugation length in polyarylene vinylene and polyarylene ethynylene containing 3,6-carbazolediyl and 2,7-carbazolediyl units

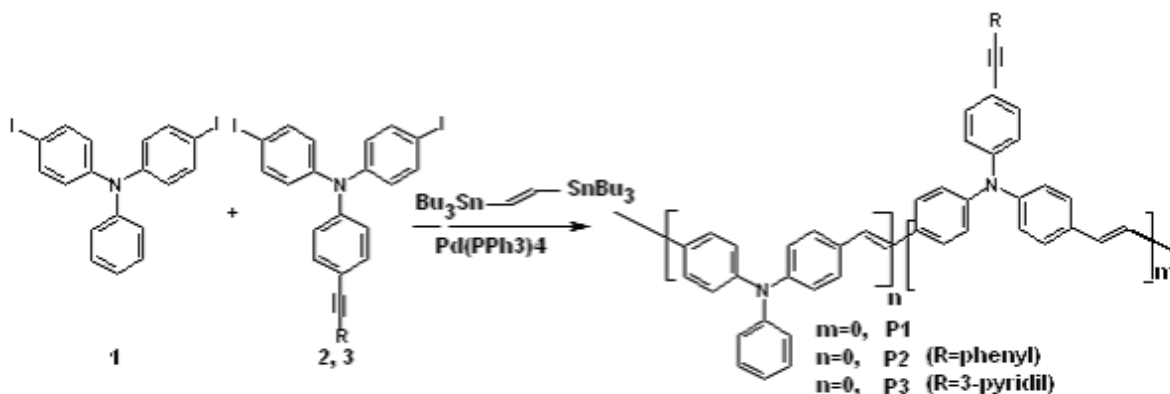
**Table 2.** Electrochemical data of polymers P1-P4

Polimer	E <sub>ox</sub> <sup>onset</sup> (V) vs Ag/AgCl	E <sub>HOMO</sub> (eV)	E <sub>LUMO</sub> (eV)
P1	1.37	-5.74	-3.28
P2	1.32	-5.69	-3.21
P3	1.30	-5.67	-3.12
P4	1.25	-5.62	-2.98

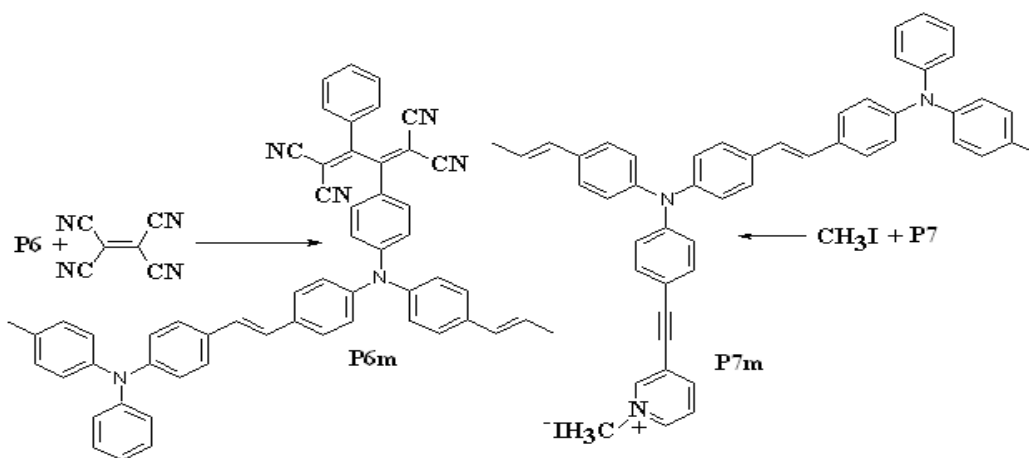
### 1.b. Modification of polymers and oligomers containing arylene ethynylene groups with strong acceptors

New triphenylamine-based polyarylenevinylenes with pendant phenylethynyl- and 3-pyridylethynyl substituents were synthesized by Stille polycondensation of *trans*-1,2-bis(tributylstannyl)ethene with two new ethynyl substituted triphenylamine monomers, i.e., *N,N*-bis(4-iodophenyl)-4'-(phenylethynyl) phenylamine and *N,N*-bis(4-iodophenyl)-4'-(3-pyridylethynyl) phenylamine. The polymers were characterized by spectral methods and cyclic voltammetry and their properties were compared with those of the

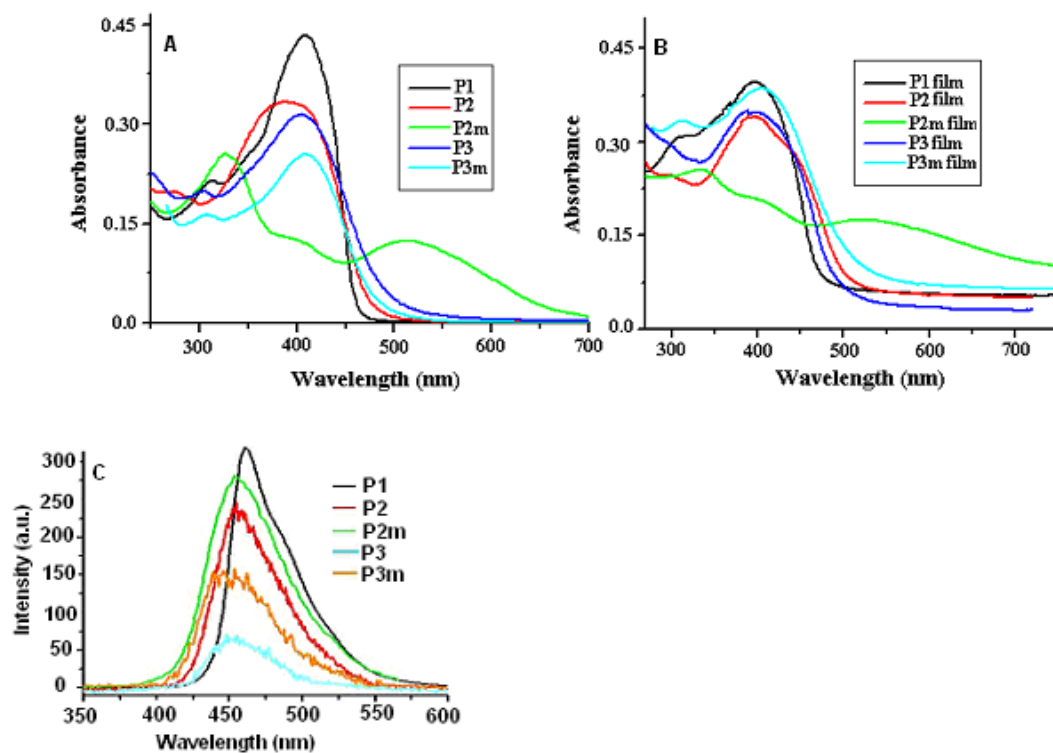
unsubstituted poly(4,4'-triphenylamine vinylene). Chemical post-modifications of the polymers by tetracyanoethylene addition to the triple bond, and quaternization of pyridyl group with accent on the fine-tuning of the optical and electrochemical properties were also studied. Density functional theory calculations provide a reliable interpretation of the observed spectra and electrochemical data.



**Scheme 3.** Synthesis of triphenylamine-based polyarylene vinylenes by Stille coupling polymerization



**Scheme 4.** Chemical modification of functional polyarylene vinylenes by post-reactions



**Figure 1.** Absorption spectra in solution ( $\text{CHCl}_3$ ) (A) and solid state (B) and emission spectra (C) in solution ( $\text{CHCl}_3$ ) of polymers **P1**, **P2**, **P2m**, **P3** and **P3m**.

The photophysical behavior of the polymers has been studied in dilute chloroform solution ( $1 \times 10^{-5} \text{M}$ ) or in solid state as thin films obtained by drop-casting method from  $\text{CHCl}_3$  or DMSO (**P3m**). The optical characteristics are summarized in Table 3

**Table 3 .** Optical and electrochemical properties of pristine and modified polymers

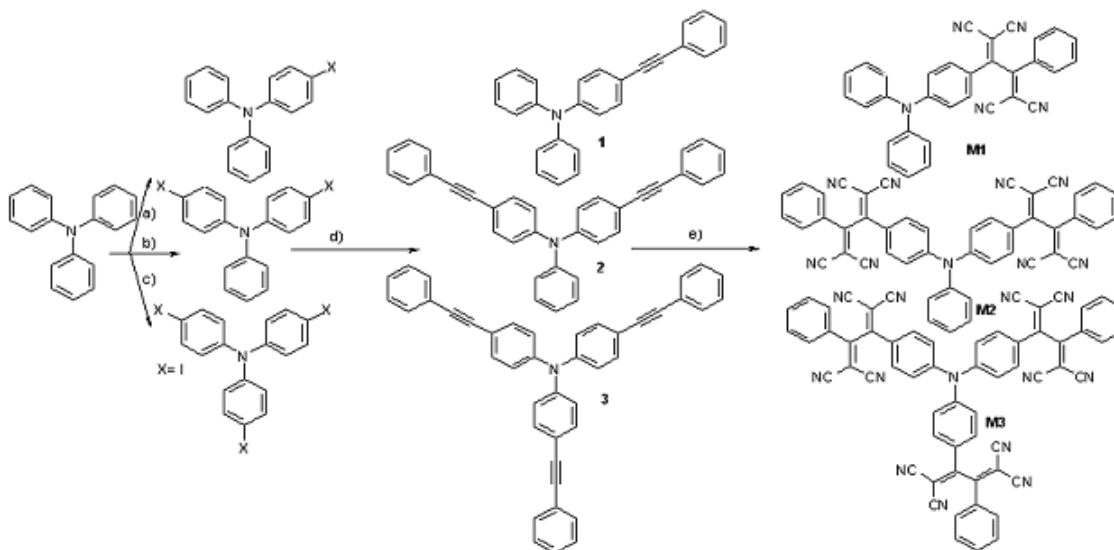
Sample	$\lambda_{\text{abs}}^{\text{max}}$ (nm)		$E_{\text{g}}^{\text{opt}}$ (eV)	$\lambda_{\text{em}}^{\text{max}}$ (nm)	$E_{\text{ox}}^{\text{onset}}$ (V) vs Ag/AgCl	$E_{\text{HOMO}}$ (eV)	$E_{\text{LUMO}}$ (eV)
	Solution	Film					
P5	313; 357(sh.), 408	308 (sh) 410	2.51	460	0.73	-5.10	-2.59
P6	312; 405	407	2.48	459	0.70	-5.07	-2.59
P6m	330; 394 (sh.), 564	322; 391 (sh), 600	2.41	461	0.71	-5.08	-2.67
P7	308,394	400	2.38	451	0.66	-5.03	-2.65
P7m	310; 403	403	2.37	453	0.56	-4.93	-2.56

The absorption and emission spectra, HOMO and LUMO energy levels and gaps energies can be fine-tuned by chemical modification of polymers using addition of

tetracyanoethylene at electron rich triple bond or by protonation and alkylation of pyridine ring. In both cases an intramolecular charge transfer complex is formed between acceptor pendant groups and triphenylamine from conjugated chain. The variation in the absorption and emission wavelengths and redox properties of polymers after chemical modification shows the possibility of fine-tuning optoelectronic properties of arylenevinylene copolymers.

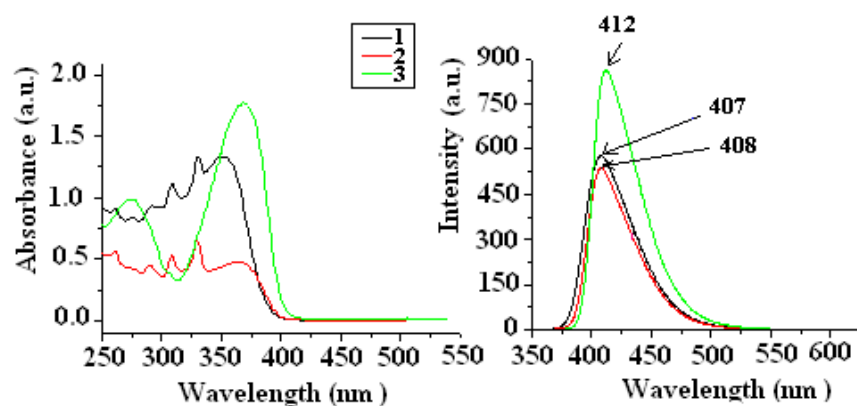
### 1.c. Oligomers with acceptor properties

Three novel triphenylamine-based compounds containing strong electron acceptor groups have been synthesized and their comparative photophysical properties are presented. These compounds were obtained by a two-step method: (i) triphenylamine compounds with one, two and three phenylacetylene arms were synthesized by Sonogashira reaction between iodine-substituted triphenylamines and phenylacetylene, followed by (ii) post-modification of these electron-rich alkynes by addition of the strong electron acceptor, tetracyanoethylene. Characterization of all oligomers was made by FTIR,  $^1\text{H-NMR}$ , UV-Vis and fluorescence spectroscopy. A bathochromic shifting of the UV and photoluminescence maxima was observed with increasing of the acceptor group number. The electrochemical behavior was studied by cyclic voltammetry. The cyclic voltammograms have evidenced that triphenylamine-phenylacetylene compounds undergo only oxidation processes while compounds modified with tetracyanoethylene show both oxidation and reduction peaks associated with donor and acceptor groups, respectively. The donor-acceptor compounds coordinate metal ions (i.e.,  $\text{Hg}^{2+}$ ,  $\text{Sn}^{2+}$ ) by cyano groups resulting in the decreasing of charge transfer band intensity, and they can be used as chemosensors.

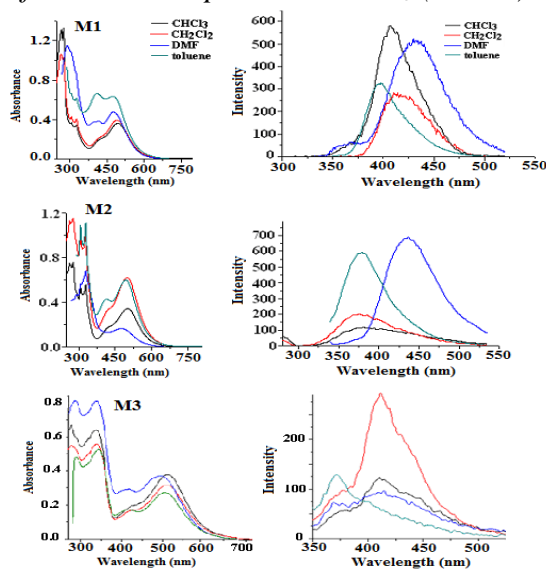


**Scheme 5.** Synthesis of oligomers M1-M3.

*a,b,c*) –  $\text{KI}/\text{KIO}_3$ ,  $\text{AcOH}$ ,  $85^\circ\text{C}$ , 5h; *d*) –  $[(\text{PPh}_3)_2\text{PdCl}_2, \text{CuI}, \text{PPh}_3]$ , TEA, phenylacetylene,  $50\text{-}60^\circ\text{C}$ , 24h; *e*) – TCNE,  $\text{CCl}_4$ .



**Figure 2.** UV and fluorescence spectra in  $\text{CHCl}_3$  ( $10^{-5}$  M) of compounds **1-3**.

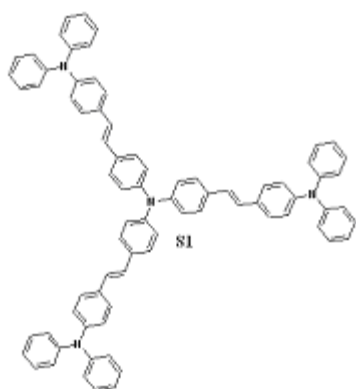


**Figure 3.** UV-Vis and fluorescence spectra of compounds **M1**, **M2**, and **M3** in different solvents.

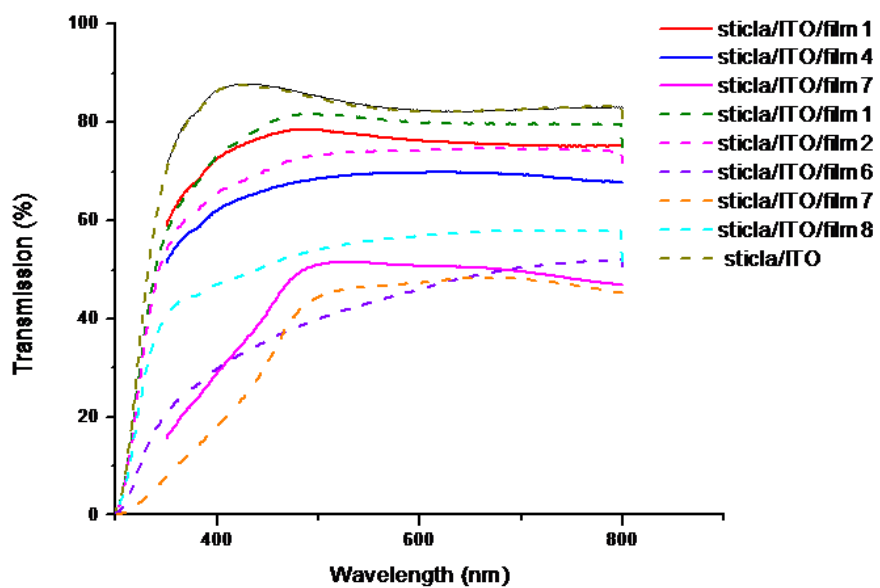
## 2. Synthesis of photoactive films of conjugated oligomers and polymers with donor groups and small molecular acceptors. Morphological study of composite films deposited by different techniques. Photoelectrical properties of composite films

### 2.a. Star oligomer S1

Compound S1 (its synthesis and characterization was presented in 2012 Report) was used for obtaining of heterostructures by MAPLE and drop-casting techniques. A film of copoly(aniline-co-anilineN-propylsulfonic acid) or PEDOT/PSSNa was used as intermediary layer between ITO and organic material. The copoly(aniline-co-anilineN-propylsulfonic acid) film was obtained by electrochemical polymerization of a mixture of monomers (aniline/aniline N-propylsulfonic acid =3/1) at different times (eight films were deposited) and their transmission spectra are presented in Figure 4.

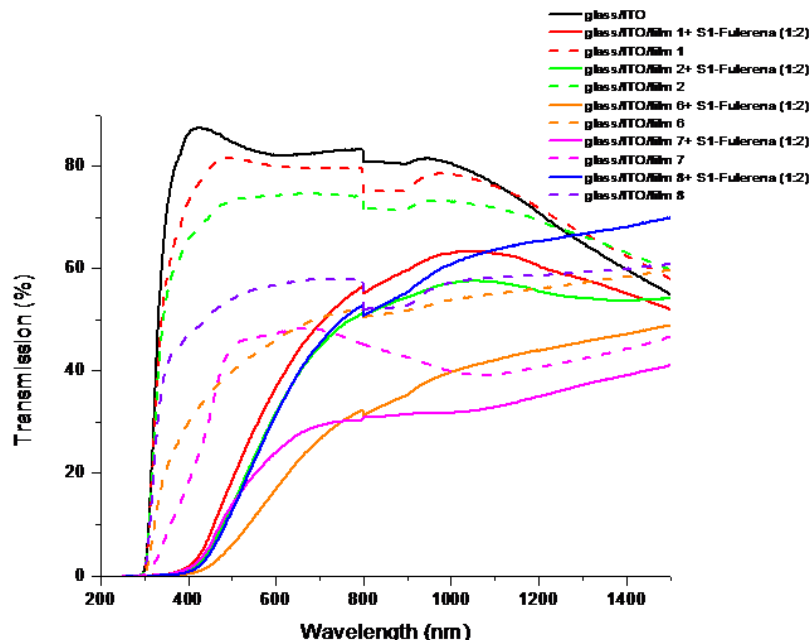


Structure of star oligomer S1

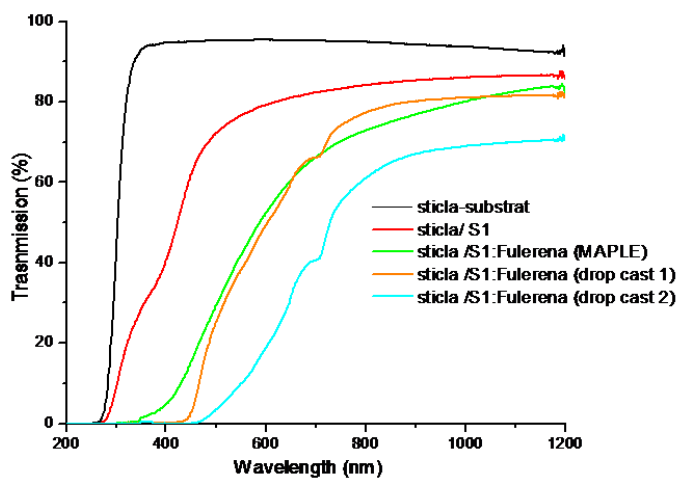


**Figure 4.** Transmission spectra of copoli(aniline/aniline-N-popil sulfonic acid) deposited by electropolymerization on ITO electrode

On these layers, S1 and S1/fullerene (1/2 molar ratio) were deposited by MAPLE technique and their transmission spectra are in Figure 5.



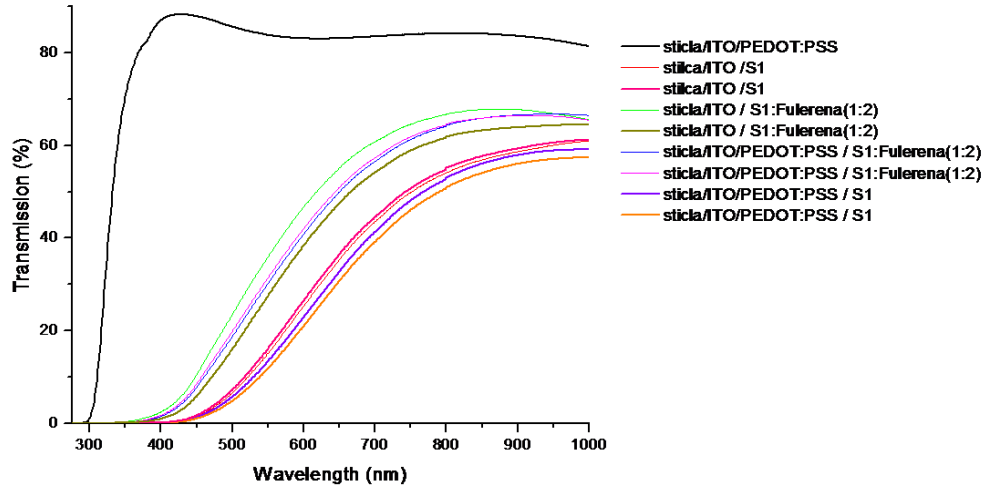
**Figure 5.** Transmission spectra of S1/fullerene (1:2) deposited by MAPLE on glass/ITO/copoly(aniline/aniline-N-popol sulfonic acid)



**Figure 6.** Transmission spectra of S1 and S1/fullerene (1:2) deposited by MAPLE and drop-casting methods on glass substrate

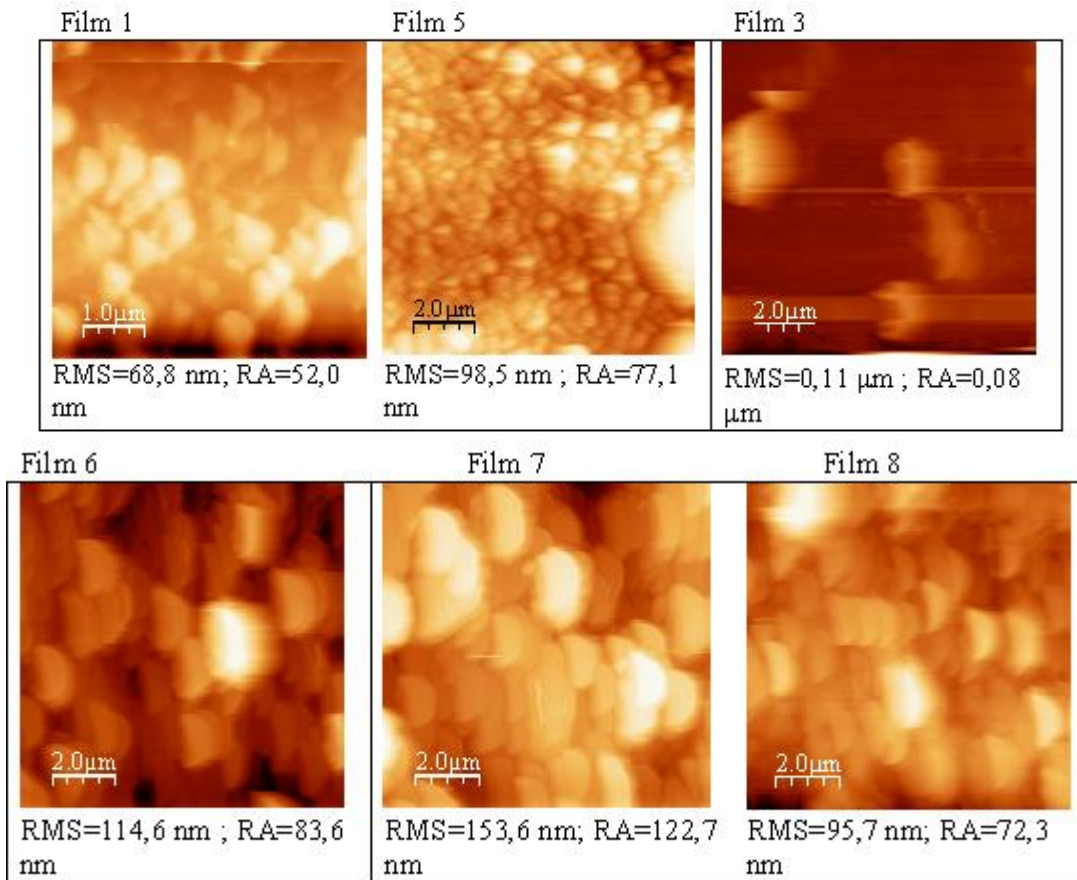
For comparison, S1 and S1/fullerene were deposited by MAPLE on glass/ITO/PEDOT:PSS (Figure 7).



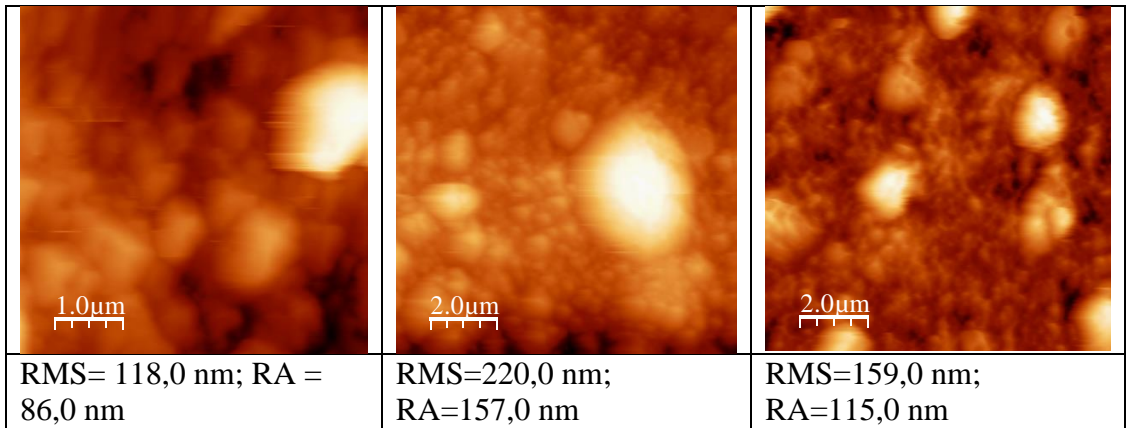


**Figure 7.** Transmission spectra of S1 and S1/fullerene (1:2) on glass/ITO/PEDOT:PSS substrate.

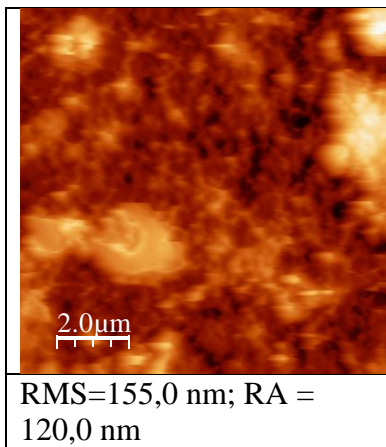
An important factor that influences photovoltaic properties is morphology of the films.



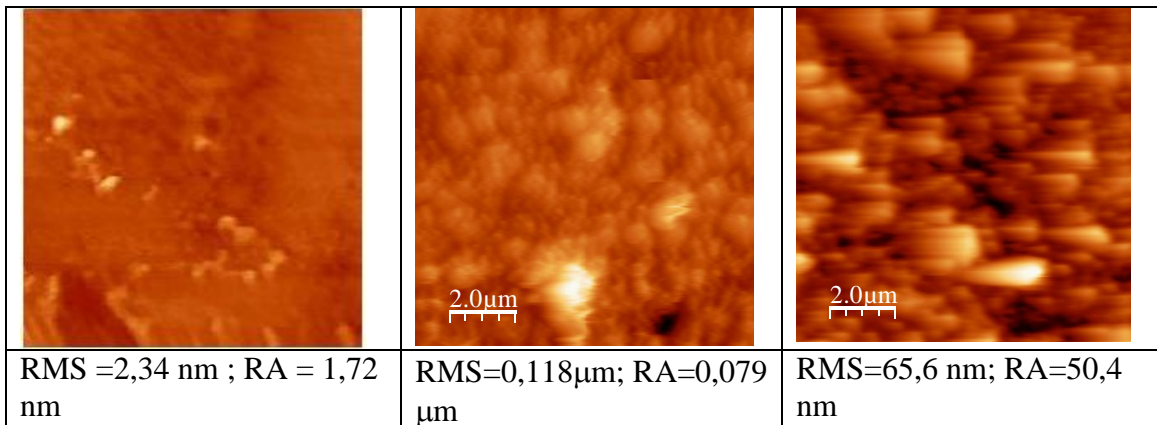
**Figure 7.** AFM images of copoly(aniline/aniline-N-popol sulfonic acid) layers on glass/ITO



sticla/ITO/ film 8/ S1:Fulerena(1:2)

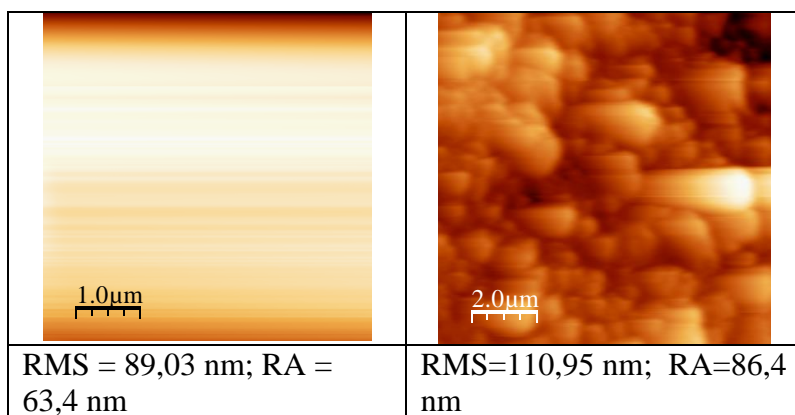


**Figure 8.** AFM images of s1 and S1/fullerene layers deposited by MAPLE on copoli(aniline/aniline-N-popil sulfonic acid) layers /glass/ITO

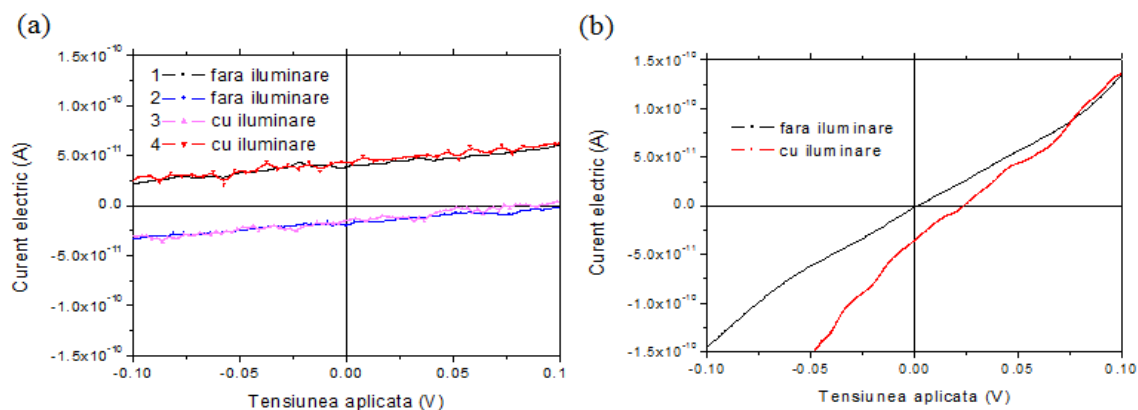


Sticla /ITO/PEDOT:PSS

Sticla/ITO/PEDOT:PSS/S1:Fulerena



**Figure 9.** AFM images of SI and SI/fullerene layers deposited by MAPLE method on glass/ITO/PEDOT:PSS.



**Figure 10.** I-V characteristics for heterostructure glass/ITO/PEDOT:PSS/SI:fullerene (1:2) (a) after formation of heterostructure (curbele 2 si 3 sau corectie de offset); (b) after a period of time

## 2.b. Arylene vinylene polymers containing 3,6- and 2,7-carbazolyldiyl groups

Polymers P1-P4 (Scheme 1) were deposited on glass/ITO or glass/ITO/PEDOT-PSS substrate by spin coating method from dichloroethane solution.

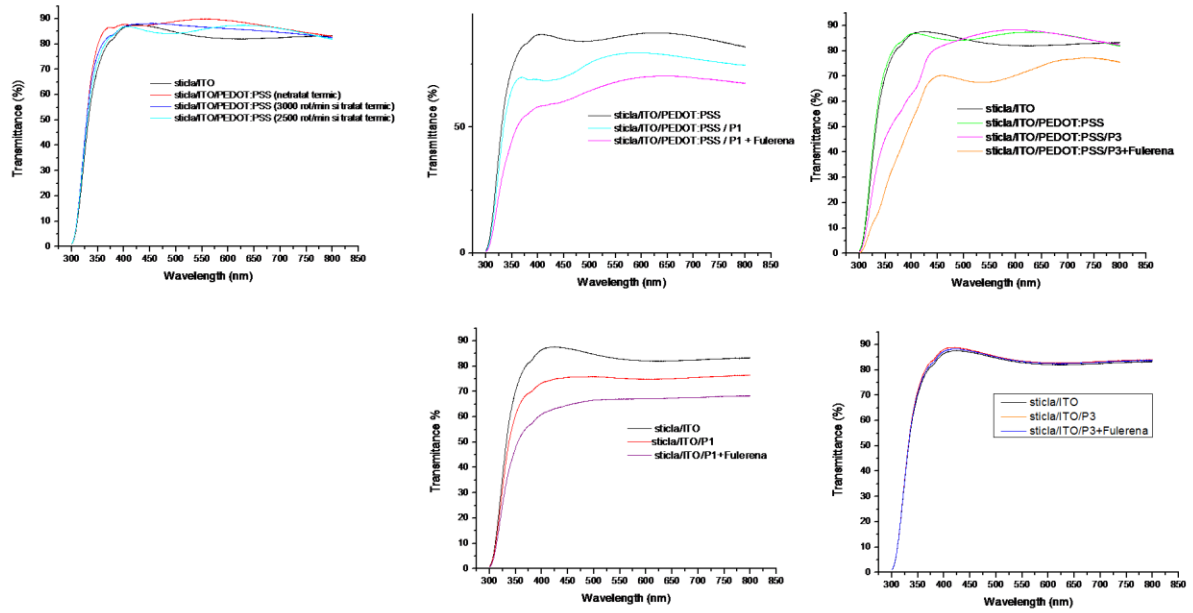


Figure 11. Transmission spectra of layers deposited on glass/ITO substrates by spin-coating.

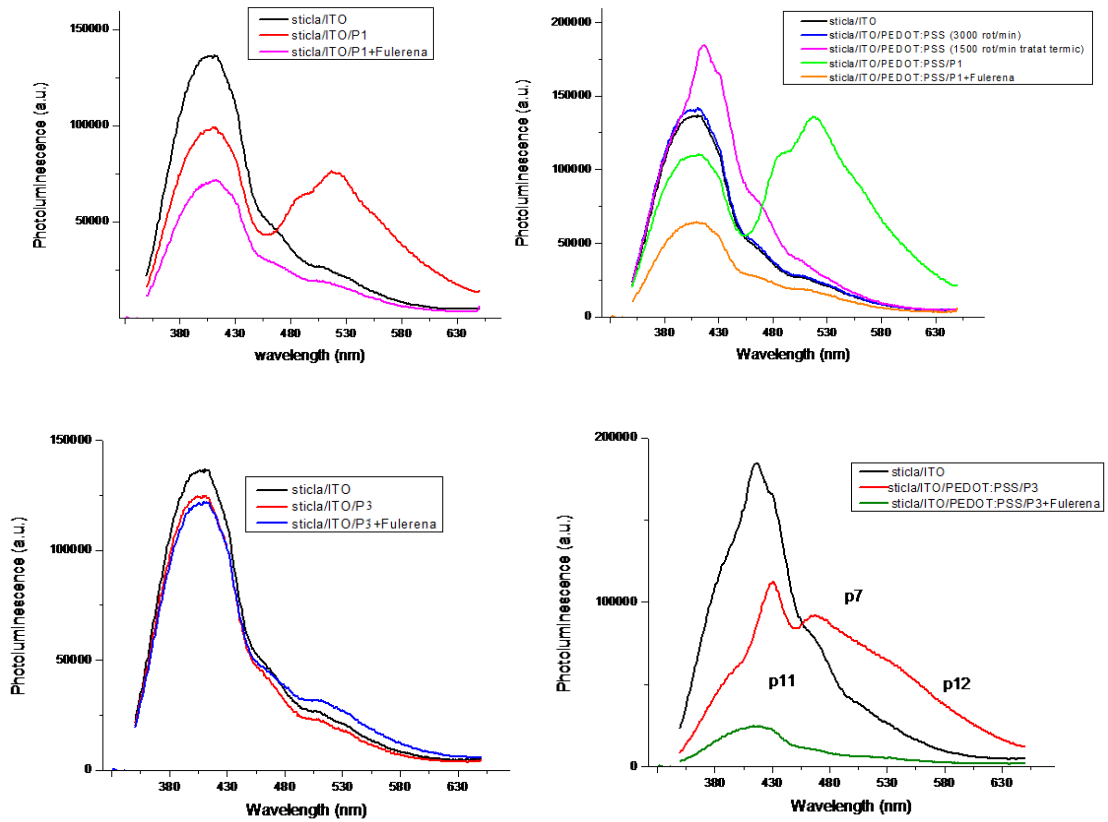


Figure 12: Photoluminescence spectra of spin-coating layers ( $\lambda_{ex}=335\text{ nm}$ )

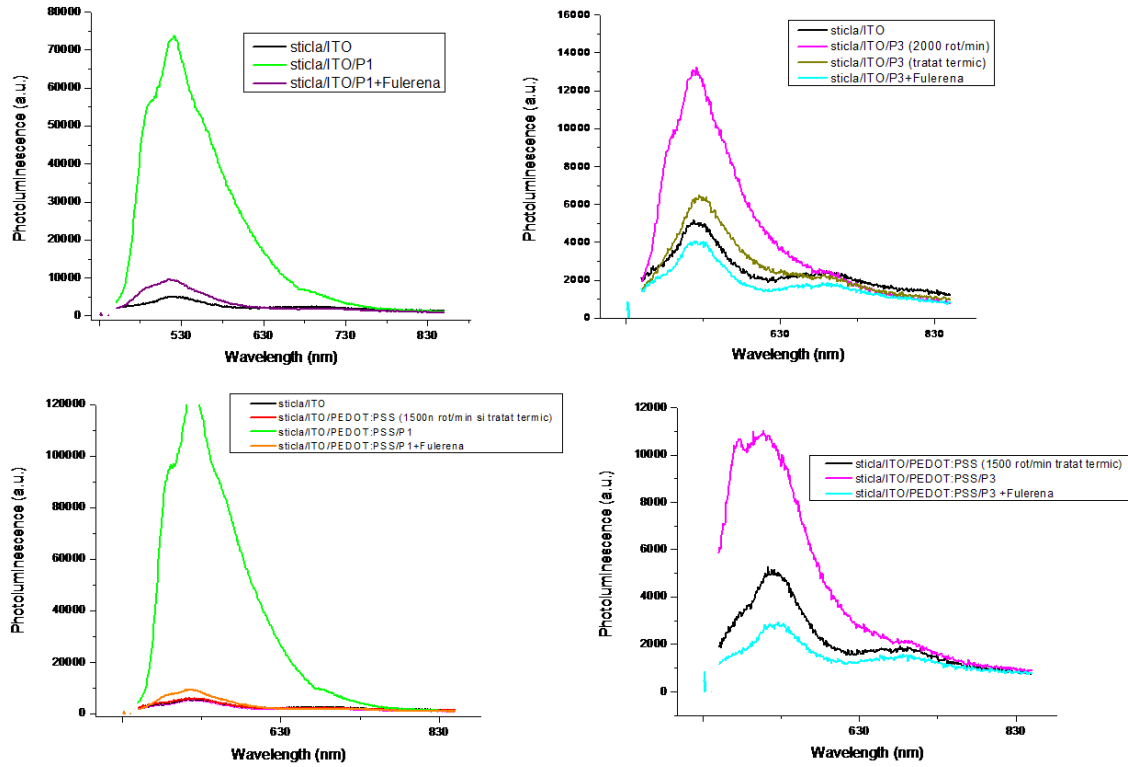
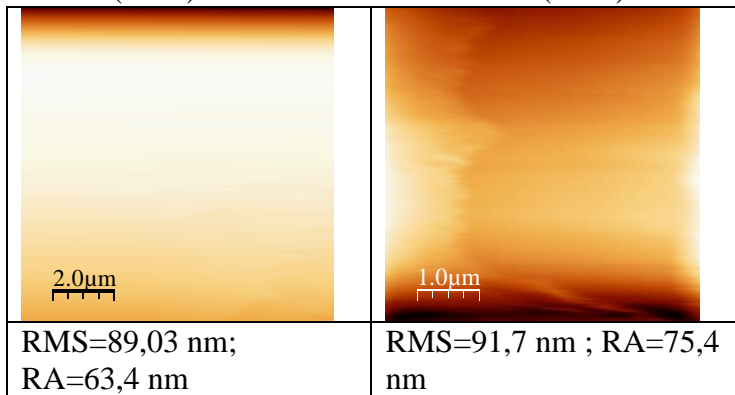


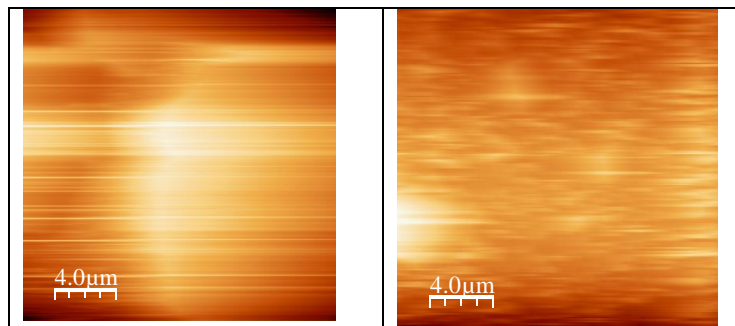
Figure 13: Photoluminescence spectra of spin-coating layers ( $\lambda_{ex}=435\text{ nm}$ )

sticla/ITO/PEDOT:PSS (3000)    sticla/ITO/PEDOT:PSS (1500)



Sticla/ITO/P1

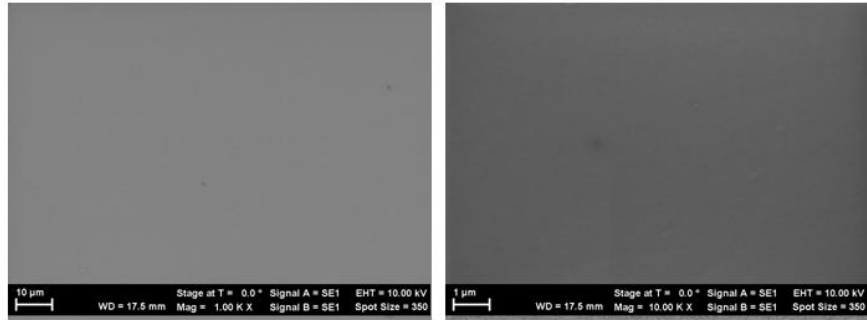
sticla/ITO/PEDOT:PSS/P1



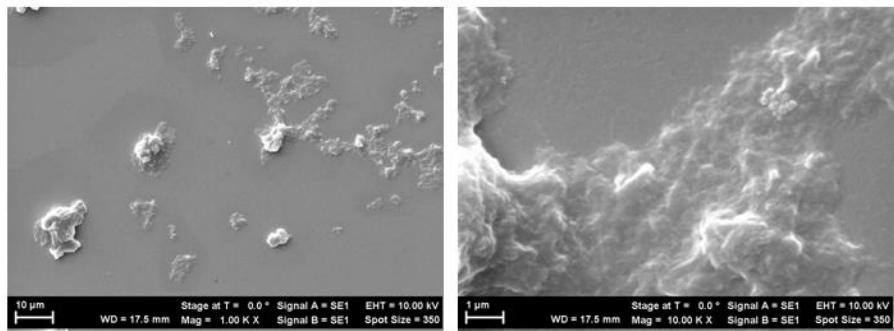
RMS=82,14 nm; RA=64,7 nm	RMS=45,9 nm ; RA=36,2 nm
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**Figure 14.** AFM images of PEDOT:PSS layers deposited on glass/ITO support and P1 , P1/fullerene on glass/ITO or glass /ITO/PEDOT:PSS

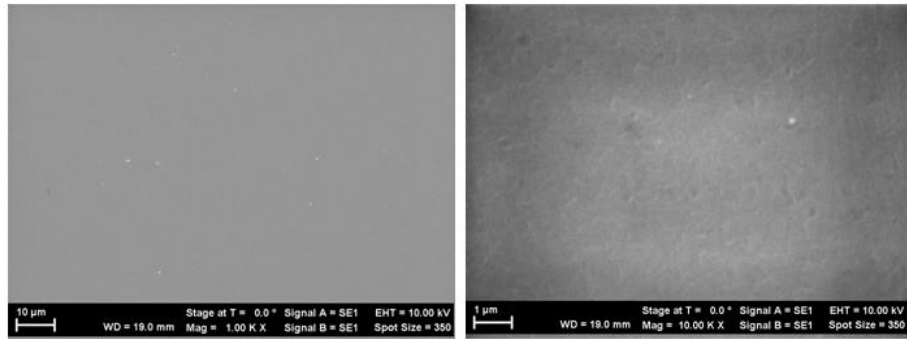
(a) sticla/ITO/PEDOT:PSS (tratata termic)



(b) sticla/ITO/P1



(c) sticla/ITO/P3



**Figure 15.** SEM images for PEDOT:PSS layers (thermally treated at 120 °C, for 5 min) and P1 and P3 deposited by spin-coating on glass/ITO.