

## Investigations of morphology and optical properties of thin films of TiOPc/PTCDA donor acceptor couple

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### Properties

#### ABSTRACT

**Purpose:** The aim of this work is studying surface topography and optical properties of organic thin films of TiOPc and PTCDA blends deposited by thermal vacuum evaporation.

**Design/methodology/approach:** Thin films of blends of organic materials are provided as donor/acceptor couples in bulk heterojunction based organic solar cells. Thin films of TiOPc - PTCDA mixture have been deposited by thermal vacuum evaporation from one source with various ratios of blends components and deposition rates used. Both the chemical composition and technological parameters of the deposition process have appeared to influence on optical properties, UV-Vis absorption spectra in particular, and surface morphology of the as-prepared thin films. The paper reveals the methodology of deposition thin films of TiPc-PTCDA donor/acceptor blends and the influence of deposition parameters on their properties.

**Findings:** Thin films of such blends can be used for the research on the planar heterojunction solar cells based on donor-acceptor couple active layers. Results of these investigations suggest that blends of TiOPc and PTCDA can be suitable materials for preparing organic photovoltaic devices.

**Research limitations/implications:** Deposition parameters and proportions of the blend components used determine the properties of TiOPc/PTCDA thin films.

**Originality/value:** The goal of this paper is also to define relations connecting the surface morphology and optical properties of thin films of TiOPc-PTCDA blend prepared with their composition and parameters of the evaporation process.

**Keywords:** Organic thin films; Thermal evaporation; Donor acceptor couple; Phthalocyanine; PTCDA, UV-Vis spectroscopy, AFM microscopy

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## 1. Introduction

Organic materials for electronics, optoelectronics and photovoltaics can strongly reduce the costs associated with the production of photovoltaic components. On the other hand, this makes possibility to use their properties such as low density, flexibility in conjunction with electrical conductivity and semiconductor properties [1,2].

The main issue in case of the technology of organic photovoltaic devices is developing the cheap and efficient technology of preparing the thin film structures containing the p-n junction [3,4].

However, it is necessary to find the relevant materials characterized by the appropriate electrical properties as well as high processability and low price [5].

Preparing high efficiency organic solar cells requires also the use of adequate production technology and development of technological parameters [5-7].

There are the structures of organic cells with the use of bulk heterojunction thin film consisting the mixture of the p-type and n-type semiconductors based on insoluble organic semiconductor materials with low molecular weight (Fig. 1) [8].

Bulk heterojunction can be interpreted as network of electron donor and acceptor materials. Inside such a film, the blends particles of electron donor and electron acceptor are spaced apart by less than 10 nm (the diffusion range of excitons) within the entire volume, which makes greater the contact surface between the two semiconductors. Such an active layer may have the thickness much greater than 20 nm, even up to 100nm, and high efficiency [8-13].

In photovoltaic devices phthalocyanine serves as an electron donor to the materials with high electron affinity, being electron acceptors, such as C60 fullerene or perylene derivative [11-13].

Metal phthalocyanines are often used as absorbing material due to their high absorption coefficient  $10^5 \text{ cm}^{-1}$  in a wide spectrum range of solar radiation and their high photochemical stability and charge transport properties [13].

## 2. Experimental

### 2.1. Material

As organic materials in this study 3, 4, 9, 10-perylene tetracarboxylic dianhydride (PTCDA) and titanyl phthalocyanine (TiOPc) were chosen. In all the layers evaporated from one source where the two materials were blended, PTCDA acts as an electron acceptor, while TiOPc being the electron donor.

Revealing a similar range of evaporation temperature, these materials can be prepared by the thermal vacuum evaporation technique.

Organic thin films of PTCDA: TiOPc blends were evaporated onto boron-silicate glass substrates (BK7). Before the evaporation process, all the substrates were cleaned following the standard procedure, which includes: rinsing with deionized water, washing in organic solvent in an ultrasonic washer, washing in acetone and methanol.

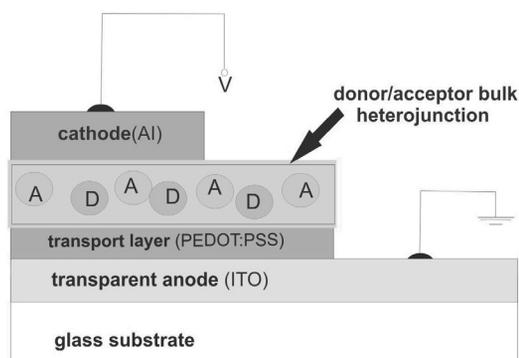


Fig. 1. Scheme of organic solar cell structure with a bulk heterojunction [13]

Blends of perylene derivative and titanyl phthalocyanine (PTCDA/TiOPc) were prepared by mechanical mixing the two components, so that thin films were thermally vacuum evaporated from one sources.

Table 1. Parameters of evaporation process

Sample number	PTCDA/TiOPc mass ratio [%]	Temperature of source [°C]	Deposition rate [nm/sec]
1	75/25	300	0.1
2	75/25	350	0.2
3	75/25	400	0.3
4	50/50	300	0.1
5	50/50	350	0.2
6	50/50	400	0.3
7	25/75	300	0.1
8	25/75	350	0.2
9	25/75	400	0.3

The parameter which was changed during the research works was the temperature of crucible, as it was expected to affect the evaporation rate of the materials in the crucible. To study this temperature dependence, nine various sets of the experimental conditions were chosen, the blends of three various compositions were evaporated at three different temperatures.

Summary of the process parameters chosen are presented in Table 1. The growth rates of the layer depositions were determined by means of a quartz crystal monitor

## 3. Results

UV-Vis absorption spectra taken on PTCDA/TiOPc thin films deposited by the thermal evaporation method are shown in Figs. 2-10. These spectra cover energy interval ranging from 1.5 to 4 eV (420-820 nm).

UV-Vis spectra taken on thin films while evaporated from the blends containing 75% wt. PTCDA and 25% wt. TiOPc at the source temperatures 300 and 350°C (films 1, 2) reveal strong feature characteristic of PTCDA with maximum at about 2.6 eV and smaller one at about 2.3 eV. There are also noticeable in these

spectra small features related to TiOPc. In contrast to these spectra, one can see that spectrum recorded on the film evaporated the source temperature equal to 400°C (film 3) is quite different. This film was deposited with the highest growth rate and its absorption spectrum reveal features related to PTCDA and TiOPc of comparable strengths. Bands peaking at about 1.7 and 2.1 eV as well as those above 3 eV are attributed to TiOPc molecules. It is worth mentioning that the source temperature has appeared to have important impact on the spectrum shape.

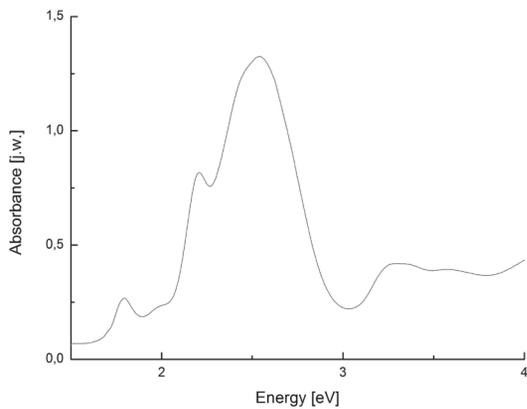


Fig. 2. Spectra of UV-Vis absorption of thin films of sample 1 (evaporated at temperature 300°C from mixture of 75% wt. PTCDA and 25% wt. TiOPc)

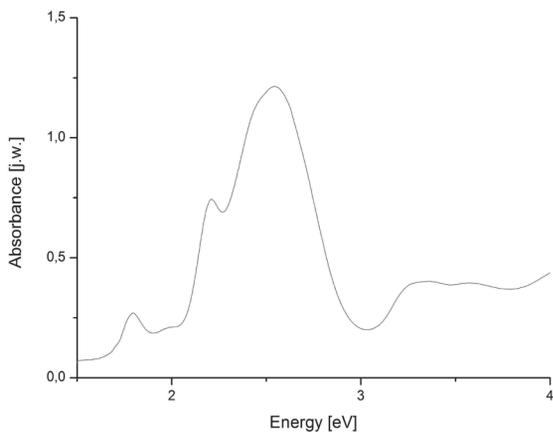


Fig. 3. Spectra of UV-Vis absorption of thin films of sample 2 (evaporated at temperature 350°C from mixture of 75% wt. PTCDA and 25% wt. TiOPc)

UV-Vis spectra of thin films samples deposited from the mixtures containing 50% PTCDA and 50% TiOPc (samples 4, 5, 6) also reveal similar tendencies as those discussed above on the spectra taken of thin films prepared from 25% wt. PTCDA and 75% wt. TiOPc blends. However, the spectra of films no 4 and 5 reveal stronger features related to TiOPc than those observed in the spectra of films 1 and 2, respectively. However, in contrast to the spectrum of film 3, the features related to TiOPc are dominant over those coming from PTCDA.

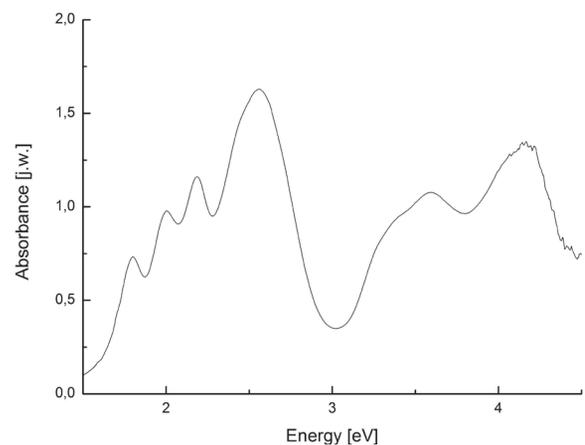


Fig. 4. Spectra of UV-Vis absorption of thin films of sample 3 (evaporated at temperature 400°C from mixture of 75% wt. PTCDA and 25% wt. TiOPc)

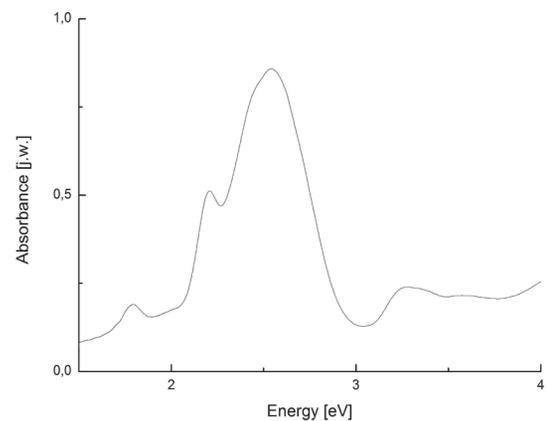


Fig. 5. Spectra of UV-Vis absorption of thin films of sample 4 (evaporated at temperature 300°C from mixture of 50% wt. PTCDA and 50% wt. TiOPc)

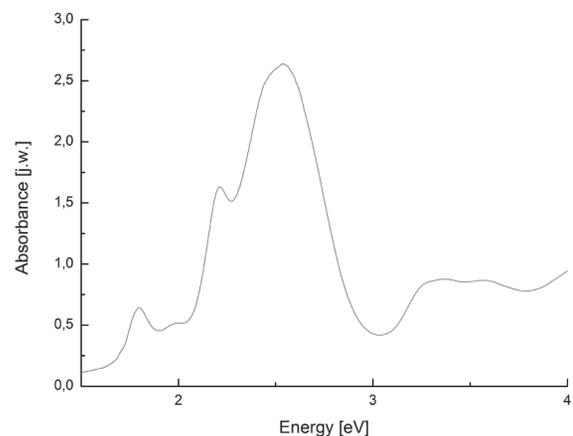


Fig. 6. Spectra of UV-Vis absorption of thin films of sample 5 (evaporated at temperature 350°C from mixture of 50% wt. PTCDA and 50% wt. TiOPc)

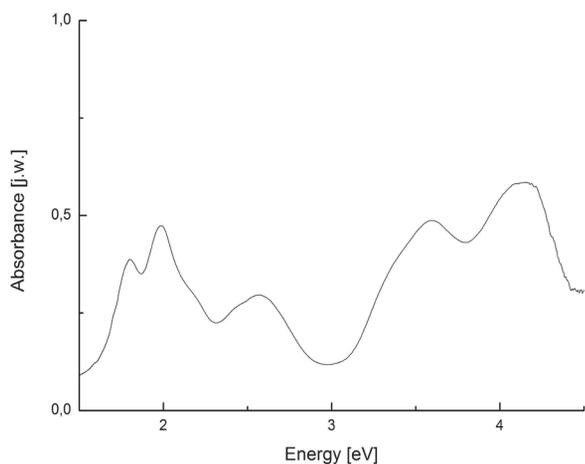


Fig. 7. Spectra of UV-Vis absorption of thin films of sample 6 (evaporated at temperature 400°C from mixture of 50% wt. PTCDA and 50% wt. TiOPc)

UV-Vis spectra of thin films samples deposited from the mixtures containing 50% PTCDA and 50% TiOPc (samples 4, 5, 6) also reveal similar tendencies as those discussed above on the spectra taken of thin films prepared from 25% wt. PTCDA and 75% wt. TiOPc blends. However, the spectra of films no 4 and 5 reveal stronger features related to TiOPc than those observed in the spectra of films 1 and 2, respectively. However, in contrast to the spectrum of film 3, the features related to TiOPc are dominant over those coming from PTCDA.

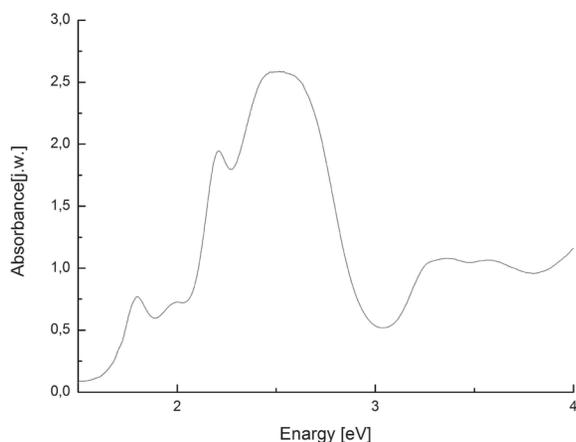


Fig. 8. Spectra of UV-Vis absorption of thin films of sample 7 (evaporated at temperature 300°C from mixture of 25% wt. PTCDA and 75% wt. TiOPc)

UV-Vis spectrum of a thin film evaporated from the source being a blend containing 25wt% PTCDA and 75wt% TiOPc and kept at 300°C (film 7) reveals strong feature characteristic of PTCDA, whose shape is modified probably due to rather important contribution from TiOPc. The spectrum shown in Fig. 9, reveals spectrum of rather medium strength but dominated

by PTCDA feature with distinct involvement of TiOPc molecules (film 8). In contrast to them the spectrum shown in Fig. 10, which was recorded on film 9 evaporated from the source kept at temperature 400°C, reveals features characteristic of TiOPc with very weak feature related to PTCDA.

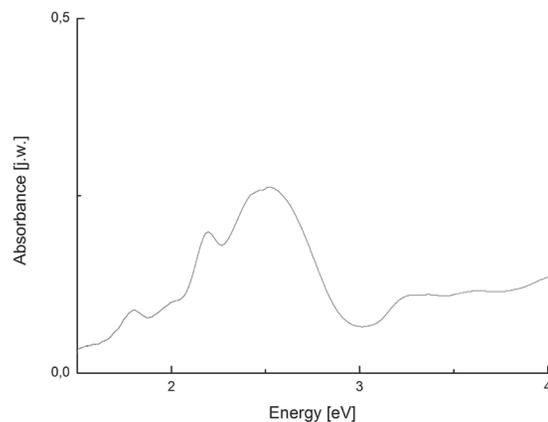


Fig. 9. Spectra of UV-Vis absorption of thin films of sample 8 (evaporated at temperature 350°C from mixture of 25% wt. PTCDA and 75% wt. TiOPc)

While comparing all these spectra one can notice that transport of TiOPc molecules towards the substrate is of rather low intensity when the source temperature is equal to 300 or 350°C. For these reasons, the spectra coming from thin films 1, 2, 5, 6 and 7 reveal dominant features related to PTCDA, even in the case of its being minority component of the blend. The peaks in the absorption spectrum of this film at about 1.7, 2.1, 3.6 and 4.2 eV are attributed to TiOPc, while very faint broad feature with the maximum at about 2.6 eV comes from PTCDA. The strongest peaks characteristic for titanylphthalocyanine appear in film deposited with highest deposition rate (sample 9) and spectra of this film reveals lowest intensity of peaks characteristic for PTCDA.

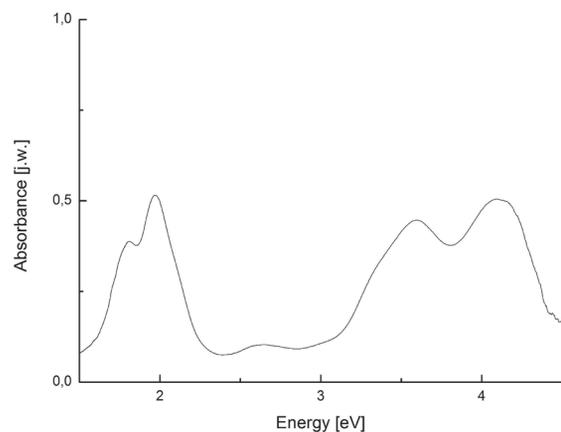


Fig. 10. Spectra of UV-Vis absorption of thin films of sample 9 (evaporated at temperature 400°C from mixture of 25% wt. PTCDA and 75% wt. TiOPc)

While comparing spectra shown in Figs. 4, 7 and 10, one can see that the strength of absorption bands is the highest in Fig. 4, the two others revealing nearly coinciding strengths. It is attributed to high intensity of PTCDA in the stream due to higher contents in the blend and higher temperature, which impinging onto the substrate surface concur with the stream of TiOPc molecules whose intensity become important at temperature 400°C.

The spectra shown in Figs. 9 and 10 compared, one may expect that relatively lower strength of PTCDA peak at about 2.6 eV is due to higher impact of the source temperature rather than lower content of perylene derivative in the source blend (50 wt%). Thus, one might expect that evaporating power of PTCDA can be smaller than that of TiOPc at 400°C.

It is also interesting to notice that at temperatures 300 and 350°C evaporation of PTCDA is dominant independently of its contents in the source material.

The morphology of thin films was examined with the use of Atomic Force Microscope (AFM), a main tool for the research surface morphology of organic thin layers. While taking surface morphology images AFM worked in non-contact mode to overcome rather low hardness of the as-deposited films of the organic blends under discussion. Topographic images, which illustrate surfaces of the as-deposited thin films of PTCDA/TiOPc blends, are shown in Figs. 11-19.

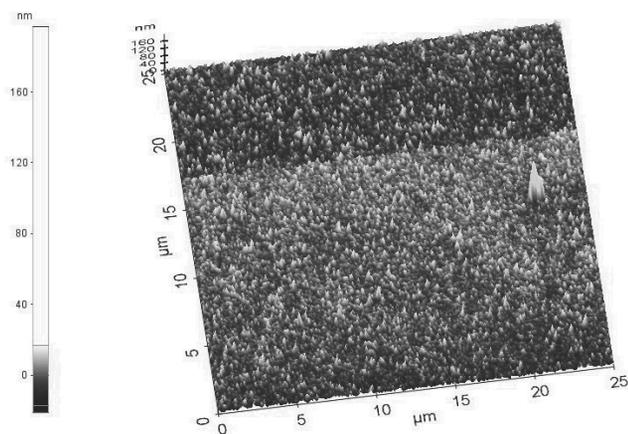


Fig. 11. Topographical image of a surface of sample 1 (evaporated at temperature 300°C from mixture of 75% wt. PTCDA and 25% wt. TiOPc)

Thin films deposited from source blends containing 25 wt.% TiOPc and 75 wt.% PTCDA (samples 1, 2, 3) present rather homogeneous granular morphology with surface roughness within -25 to 25 nm limits with also homogeneous distribution of higher structures up to 160 nm. In case of the film no2, the image is very similar, though the medium roughness is within -25 to 25 nm limits with higher structures up to about 75 nm. The surface morphology of a film 3 deposited with highest source temperature is also granular with visible coalescence of granules revealing rather plane surface. On the surface of this film one can see randomly distributed coarse objects or hills.

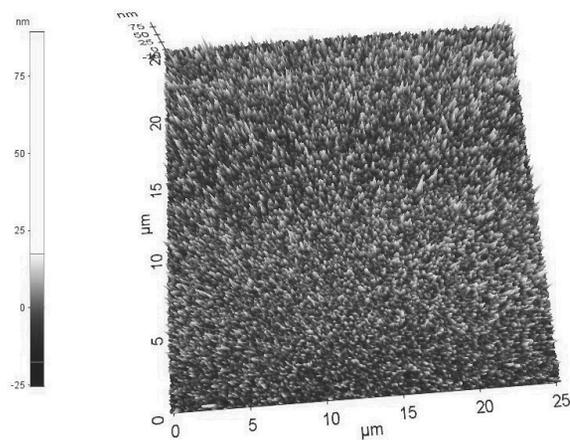


Fig. 12. Topographical image of a surface of sample 2 (evaporated at temperature 350°C from mixture of 75% wt. PTCDA and 25% wt. TiOPc)

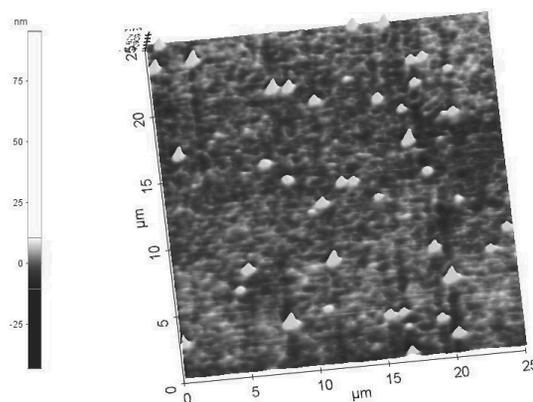


Fig. 13. Topographical image of a surface of sample 3 (evaporated at temperature 400°C from mixture of 75% wt. PTCDA and 25% wt. TiOPc)

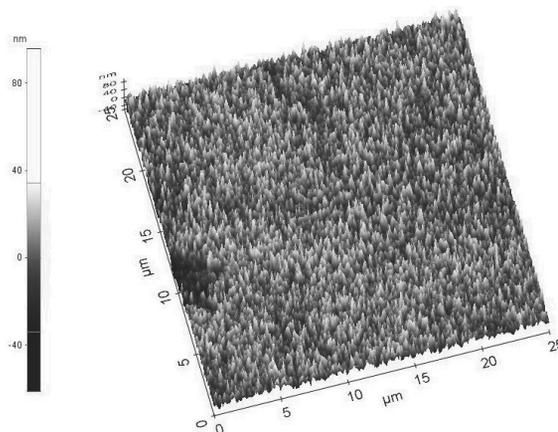


Fig. 14. Topographical image of a surface of sample 4 (evaporated at temperature 300°C from mixture of 50% wt. PTCDA and 50% wt. TiOPc)

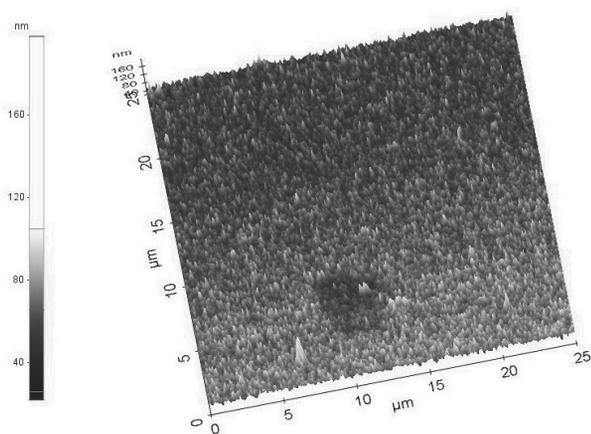


Fig. 15. Topographical image of a surface of sample 5 (evaporated at temperature 350°C from mixture of 50% wt. PTCDA and 50% wt. TiOPc)

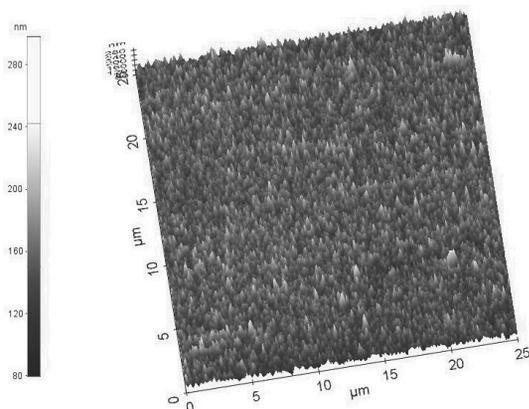


Fig. 16. Topographical image of a surface of sample 6 (evaporated at temperature 400°C from mixture of 50% wt. PTCDA and 50% wt. TiOPc)

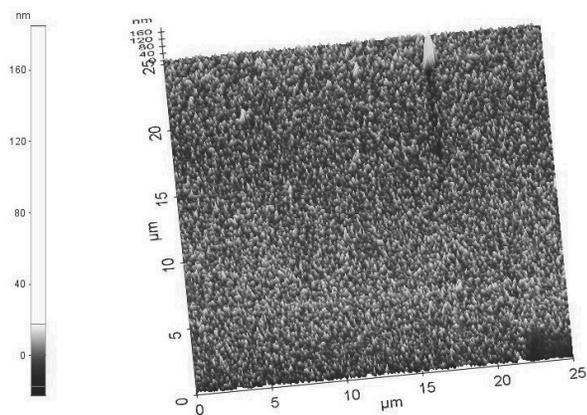


Fig. 17. Topographical image of a surface of sample 7 (evaporated at temperature 300°C from mixture of 25% wt. PTCDA and 75% wt. TiOPc)

Such roughness of the film surface may indicate on the possible clusters formation, but it seems difficult to attribute them to PTCDA or TiOPc, though some contribution from TiOPc might be taken into consideration.

In the case of blends containing 50 wt.% TiOPc and 50 wt.% PTCDA (samples 4, 5, 6) the film growth rate is thought to affect their surface morphologies. Thin films evaporated at lower source temperature (samples 4 and 5) seem to have more inhomogeneous morphology of their surfaces than it was the case for films deposited from source blends containing 25 wt.% TiOPc and 75 wt.% PTCDA.

Thin films prepared at the highest temperature of the source blend (sample 6) have similar surface morphology as films deposited with lower growth rates. However, inhomogeneities of the surface morphology of this film are lower than in the case of film evaporated from the source blend of PTCDA 25 wt.%/TiOPc 75 wt.% (samples 1, 2, 3).

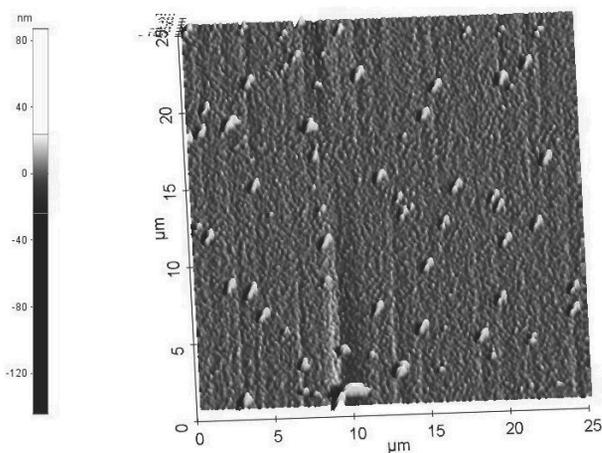


Fig. 18. Topographical image of a surface of sample 8 (evaporated at temperature 350°C from mixture of 25% wt. PTCDA and 75% wt. TiOPc)

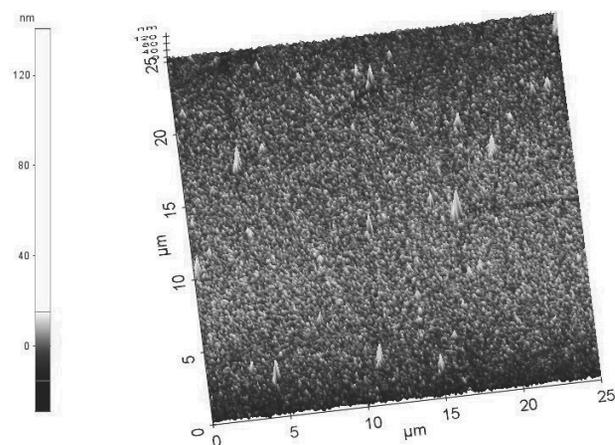


Fig. 19. Topographical image of a surface of sample 9 (evaporated at temperature 400°C from mixture of 25% wt. PTCDA and 75% wt. TiOPc)

Films deposited from mixture containing 75 wt% TiOPc and 25 wt% PTCDA (samples 7, 8, 9) with source temperature 350°C and 400°C reveal more compact surface morphology which suggest rather strong granule coalescence and merging. However, thin film evaporated at the 350°C source temperature, similarly like the film deposited from the blend 25 wt.% TiOPc and 75 wt.% PTCDA may indicate on clusters forming due to some excess of PTCDA evaporative power over that of TiOPc.

## 4. Conclusions

The absorption spectrum of TiOPc reveals energy interval with very low absorption level, which coincides with the same energy range of very PTCDA high absorbance. Then, all the spectra taken on thin films of PTCDA/TiOPc blends reveal larger photon energy area with high absorption level. Essentially one can see it in the spectra of the films no 1 and 9, that energy ranges of high absorption levels of PTCDA and TiOPc films are much narrower.

The UV-vis absorption spectral distribution of thin films of PTCDA:TiOPc deposited by thermal evaporation depends on compositions of the starting material and the source temperature. It can be seen that the absorbance strength of related to any of the two components of PTCDA: TiOPc blends depends on its contents in the source blend material, being essentially proportional to its contents in the source material.

One can see that absorption spectra of thin films evaporated from the of PTCDA/TiOPc blends are distinctly dependent on the source temperature.

Similarly, morphology of the as-deposited films depends on the source temperature affecting the evaporation rate and the film growth rate. In case of all of as-deposited films their surface morphology depends on the film growth rate.

In most cases the lower deposition rate generate the more homogenous film surface morphology. In addition, studying AFM images of the as-deposited films may suggest that high film growth rate produces the surface roughness and inequalities which may be created by lumps of evaporated materials.

Additionally results obtained for as-deposited films may also suggest that surface topography depends of composition of used mixture.

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