

Luminescence and structural properties of thermally evaporated benzanthrone dyes thin films

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We report optical and luminescence properties of 3-N, N-diacetylaminobenzanthrone thin films deposited on glass substrate by thermal evaporation. The structural and optical properties of organic thin films were studied by means of the confocal microscope with an input of femtosecond laser radiation, X-ray diffractometer, and scanning electron microscope (SEM). Intense luminescence with the maximum at 530 nm was observed when excited by laser radiation with the wavelengths 458, 476, 488, 496, 514 nm. In addition, the luminescence caused by two-photon absorption of femtosecond (fs) laser radiation has been investigated. Semi empirical calculations by AM1 and ZINDO/S methods and ab initio calculations using Gaussian software were carried out to estimate the electron system of structure. The calculations show planar configurations for the aromatic core and diacetylamino fragment of this compound. The study of the structure of benzanthrone derivative thin films with X-ray diffraction (XRD) methods, indicates the distance between molecular layers and ordered molecular fragments.

Keywords: Benzanthrone dyes, organic thin films, solid-state luminescence.

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1. Introduction

Organic thin films are used in a number of scientific and technical applications one of which is producing cheap and large scale electronic and optical devices [1–3]. Due to their interesting structural, electronic, and optical properties thin crystalline films of organic molecules on inorganic substrates have attracted considerable attention. These hybrid structures also appear promising for new applications [4]. Scientific investigations have shown that donor-acceptor *p*-conjugated organic substances exhibit interesting photoelectric properties associated with high charge carrier mobility and structural layout of molecular layers. Improvements of these properties make an important factor for a wide use of organic films as prospective materials in biochemical fluorescent technology, nonlinear optics, solar cells, etc. Development of organic materials with high solid-state luminescence efficiency plays a crucial role in advancing techniques for optics and optoelectronics. It appears that solid layers of these compounds could exhibit interesting optical properties that may be different from those of the dissolved dye. This was the reason to study the luminescent properties of benzanthrone dyes in the solid thin film state. Using the method of thermal deposition in vacuum allows for some control of the dye distribution inside the matrix, leading to solid thin films containing non-aggregated dye molecules. The suppression of aggregates is a key issue to

avoid fluorescence quenching. The goal of the research presented herein is to investigate the optical and structural properties of thermally evaporated 3-N,N-diacetylaminobenzanthrone thin films, because the solid-state optical properties and physical characteristics of organic films are important in order to consider them in the development of new luminescent materials.

2. Experimental details

The synthesis of 3-N,N-diacetylaminobenzanthrone (Fig. 1) is described in Ref. 5. Organic thin films were obtained by thermal evaporation of the substance in polycrystal state onto BK-7 3×3 inch glass substrates in the vacuum of $\sim 10^{-5}$ Torr. For thermal deposition of organic films a transparent quartz cell heated to the desired temperature with the help of tungsten filaments was used. Deposition was carried out at the bulk substance melting point (250–260°C) with the rate about 5 nm/sec. The results presented here correspond to the optimised conditions of deposition with a gradual increase in temperature to the melting point and maintain the temperature at about constant level to avoid decomposition of the molecules. Thickness of the prepared film was about 1 μ m. Monitoring of organic film thickness was conducted after the process of evaporation with the help of a Z-scan technique on the confocal microscope (Leica LSM TCSP-5). The thickness was determined from the shift of the maximum of the scanning laser beam signal reflected from the surfaces of the film and substrate.

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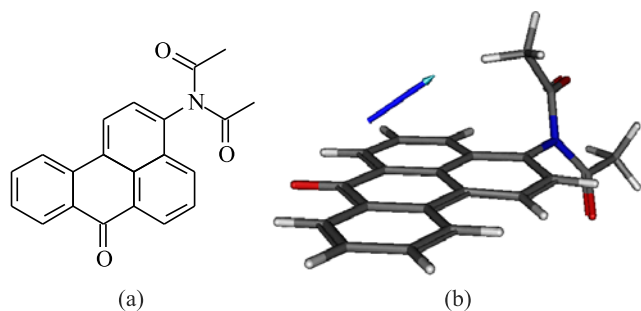


Fig. 1. (a) Chemical structure of 3-N,N-diacetylaminobenzanthrone; (b) Optimized molecular geometry and dipole moment vector.

Dependence of transmission, reflection and absorption on wavelength for the studied films was obtained with the help of a micro spectrophotometer (MSP500, Anstronm Sun Tech., spectral resolution 1 nm). For calculating refraction index (Fig. 2) on the basis of the obtained data, the formula $R = (n - 1)^2 / (n + 1)^2$ for reflection coefficient R from the surface with refractive index n for light with normal incidence was used.

The fluorescence excitation and emission spectroscopic measurement were performed using spectrofluorometer (FS920 Edinburgh) equipped with an Xe-lamp source (spectral resolution 1 nm). Investigation of luminescence spectra of organic thin films induced by laser radiation (with the spectral resolution of 3 nm) were carried out by the confocal microscope (Leica LSMTC SP-5) with an external input of a tuneable near-infrared femtosecond laser beam (Chameleon Ultra, 280 fs pulses, 80 MHz repetition frequency, $\lambda = 690\text{--}1040$ nm). For luminescence excitation $\lambda = 458, 476, 488, 496,$ and 514 nm wavelengths of Ar laser and for two-photon luminescence $\lambda = 800, 900, 1000$ nm wavelengths of fs-laser were used. The quantum chemical calculations were performed by using the AM1 [6], ZINDO/S [7] and *ab initio* (using DFT approach [8]) methods. The imaging of the surface were performed by atomic force microscope (AFM) in a non-contact mode (NX10 Park System Corp.). Surface morphology of benzanthrone films after coating a ~ 10 nm layer of Al was observed by the TESCAN-VEGA LMU II scanning electron microscope (SEM). The structural properties of the thin films were

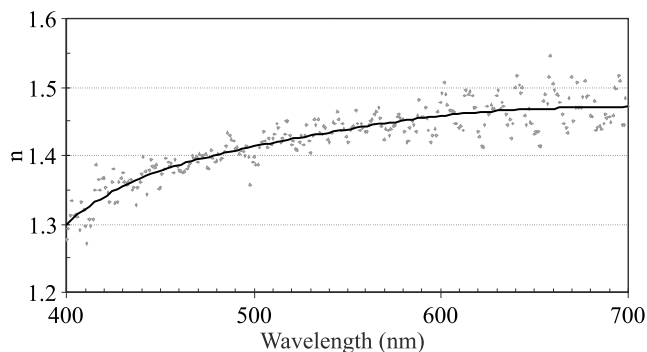


Fig. 2. Spectral dependence of refractive index for 3-N,N-diacetylaminobenzanthrone film.

determined by X-ray diffraction (XRD) by using the Smart-Lab RIGAKU diffractometer. The data were collected at $\lambda = 1.543 \text{ \AA}$ (Cu-K α line) within the range of $4^\circ < 2\theta < 30^\circ$ with a high resolution ($0.002^\circ/\text{step}$) from the 5×5 mm area.

3. Results and discussion

Figure 3 shows a typical transmission spectrum of the 3-N,N-diacetylaminobenzanthrone films which visually have a bright yellow or yellow-orange colour, depending on the film thickness.

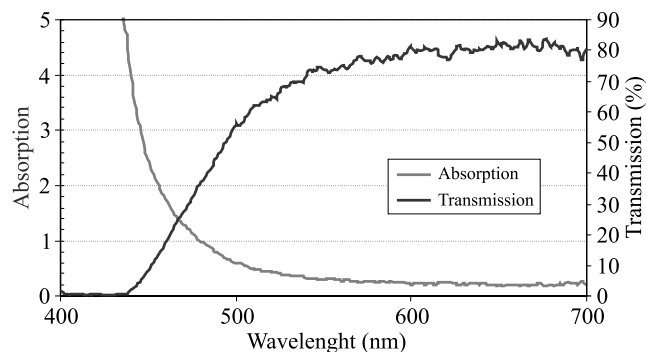


Fig. 3. Spectral dependence of transmission and absorption for $1 \mu\text{m}$ 3-N,N-diacetylaminobenzanthrone film.

For measuring fluorescence spectra the signal reflected from films was used. The average penetration depth d_λ of excitation light with the wavelength λ into a film depends on the value of absorption D_λ for this wavelength and defined as $d_\lambda = d_0 / D_\lambda$. For the films under study the assumed penetration depth is $d_\lambda \sim 400$ nm ($d_0 = 1 \mu\text{m}$, $D_\lambda = 2.5$) for the excitation wavelength $\lambda = 450$ nm. Thus the reflected fluorescence signal for excitation wavelength is determined by a thin borderline layer and does not very much depend on film thickness and reabsorption or scattering effects. This was proved by the experiment data. Taking into account the above said, the article considers optical properties of films of the same thickness ($1 \mu\text{m}$), except measurement of fluorescence spectra in two-photon absorption was carried out using a $3 \mu\text{m}$ film. Due to a high intensity of the focused scanning fs laser beam (average measured power of the scanning beam is ~ 40 mW and the calculated peak power is $\sim 10^4$ W) parameters of the $1 \mu\text{m}$ thick film were changing in course of experiment. We were able to find equal experiment conditions for three fs laser wavelengths (800, 900, 1000 nm) only in case of the $3 \mu\text{m}$ thick film. These results of the experiment are given in the graph of Fig. 8.

Normalized excitation and fluorescent emission spectra of thermally deposited films are shown in Figs. 4 and 5. The excitation spectrum is quite broad and shows two peaks at 350 and 450 nm. The excitation spectra were obtained while registering the fluorescence signal at the wavelength of $\lambda = 540$ nm, which corresponds to the maximum of fluorescence spectra (Fig. 4).

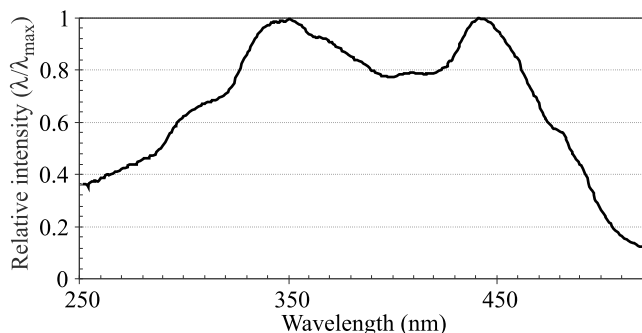


Fig. 4. Normalized excitation spectra of 3-N,N-diacetylaminobenzanthrone film by registration of the fluorescence at 540 nm.

To better understand the nature of electronic spectra of benzantrone, the quantum chemical calculations were carried out. For studied compound the geometry optimization was performed by the AM1 method (Fig. 6).

The molecular orbital positions are important information for understanding the spectral properties of the investigated dye. The electronic spectrum of compound was calculated by using the ZINDO/S method. Calculations show an intensive (oscillator strength is about 0.53), long-wavelength absorption band at 360 nm. This absorption is generally an electron shift from HOMO to LUMO (transition from 61 orbital to 62 orbital, e.g., $S_0 \rightarrow S_1$). Both orbitals are mainly localized in the benzantrone fragment Fig. 6(b), whereas the amide group investment in this shift is insignificant. It is calculated that energy difference in ground and excited state for investigated dye is about 7.3 eV.

Long-wavelength absorption causes a notable increase of the system dipole moment by about 3D. As the molecule is a polar compound, it is not surprising that in real spectra, the long-wavelength absorption band is shifted by about 90 nm due to strong intermolecular interactions mainly by π - π -stacking. The lowest-energy absorption band is result from a twisted intramolecular charge-transfer between the amino group and benzantrone moiety [9].

The next notable band for investigated dye is at about 260 nm. These bands are characterized by a not so strong absorption (oscillator strength is about 0.28), and these mostly consist of the electron shift between different orbitals (transitions from 61 orbital to 63, 64 or 66 orbitals).

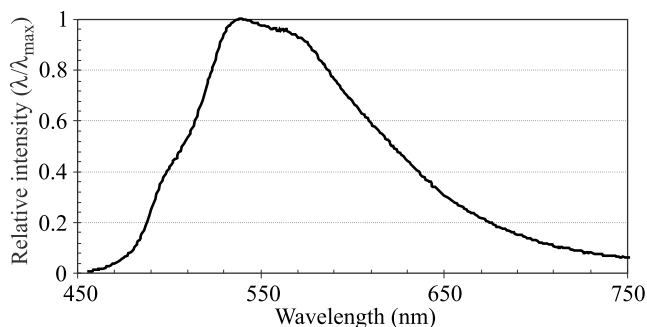


Fig. 5. Normalized emission fluorescence spectra of 3-N,N-diacetylaminobenzanthrone film by 442 nm excitation of krypton lamp.

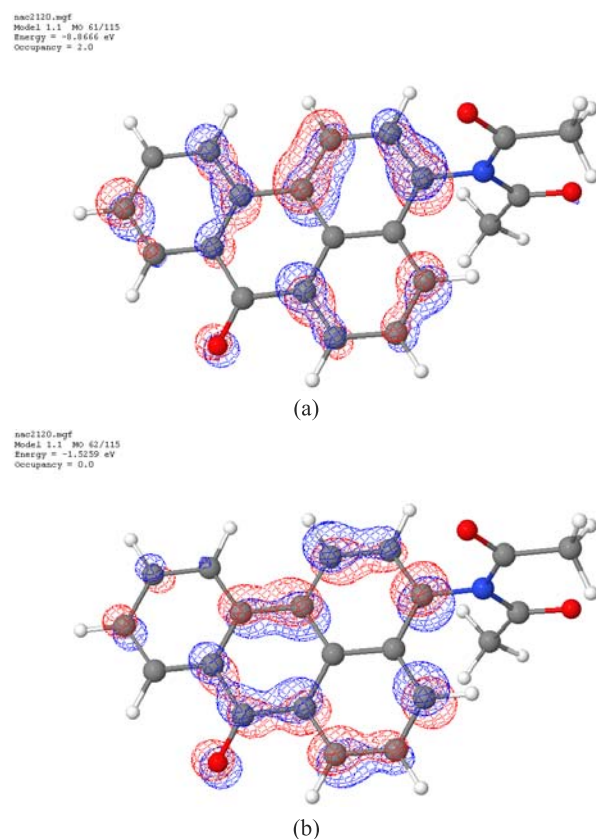


Fig. 6. Representation of calculated HOMO (a) and LUMO (b) states (ZINDO/S) of 3-N,N-diacetylaminobenzanthrone molecule.

This calculated absorption band is also shifted from real band by about 90 nm due to intermolecular interactions.

It is known that the lowest singlet excited state for benzantrone is S_{np}^* in gas state or in a non-polar solvent, but $S_{\pi\pi}^*$ in polar media due to dipole-dipole interactions. The calculated excitation energy to the $S_{\pi\pi}^*$ state is 3.52 eV corresponds well to the maximum of the UV-absorption spectrum at 3.29 eV measured in hexane [10].

Photophysical behaviour of the 3-substituted benzantrones is basically related to the polarization of the benzantrone molecule. The polarization occurring upon irradiation results from the electron donor-acceptor interaction between the electron-donating substituents at the 3-position and the electron-accepting carbonyl group of the chromophorous system [11,12].

The fluorescence excitation bands of 3-N,N-diacetylaminobenzanthrone can be ascribed to the electronic transitions from the lowest vibronic level of the ground state to different vibronic levels of the singlet excited states. In this case, the long-wavelength absorption band in the visible region is a band of charge transfer, due to $\pi \rightarrow \pi^*$ electron transfer on $S_0 \rightarrow S_1$ transition. Upon photoexcitation at the absorption maximum, these organic films emit strong yellow-green fluorescence with a broad peak at 540 nm with a pronounced vibronic structure.

Normalized single photon emission (SPE) spectra for different laser excitation wavelength are presented in Fig. 7.

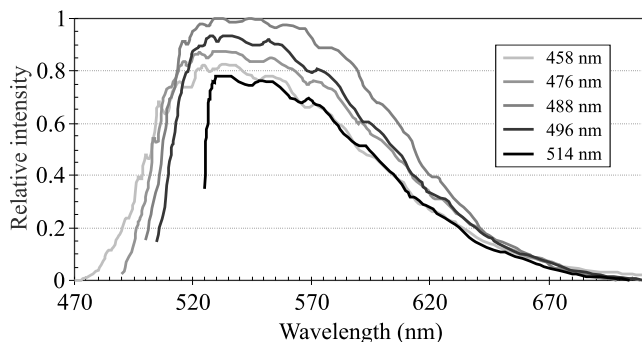


Fig. 7. Normalized fluorescence spectra of 3-N,N-diacetylaminobenzanthrone film at different exciting laser wavelength.

For determining the luminescence spectrum, the signal reflected from the film and directed towards the exciting laser beam was used. A band-stop-filter with a narrow band (~ 10 nm), which overlaps the laser line, is used for cutting off the luminescence signal from the reflected laser beam in the microscope. The filter slightly changes the short-wavelength segment of the spectrum (Fig. 7). Since the luminescence spectrum was obtained for the reflected beam, it is possible to claim that reabsorption does not influence the form of the spectrum. Determination of the luminescence spectrum for thin films is accompanied by interferential changes in the form of wave-shaped spectra which is particularly noticeable in the case of two-photon absorption (Fig. 8). The film is nearly transparent for the infrared emission of an *fs* laser, and interference in it is not neutralized at the expense of absorption. The graph (Figs. 5, 7 and 8) shows that the derivative of benzanthrone dyes with a diacetyl amino group is characterized by a high solid state luminescence efficiency emitting in the green region ($\lambda_{\max} \sim 540$ nm) in contrast with non-luminescent solutions of this dye in organic solvents.

Quantum yield was calculated on the assumption that the luminescence intensity is the same in all directions, and only that part of luminescence is registered that is caught by the objective of a microscope with a known numerical aperture. An integral luminescence signal was compared with a weakened laser radiation of a known intensity. Using the obtained data and taking into account the spectrum content of luminescence and the absorption, a valuation calculation of the quantum yield was performed; it was $\eta = 0.36$ for $\lambda = 476$ nm.

Two-photon absorption characterizes the probability of simultaneous absorption of two photons whose energies add up to match the molecular transition energy. Two-photon absorption is governed by quantum-mechanical rules other than those of one-photon absorption, and, as a result, the two photon emission (TPE) spectra are often different in shape from their one-photon counterparts, especially in the case of organic compounds, what mainly depends on the location of the electronic states.

The fluorescence spectra of the studied dye films induced by TPE are presented in Fig. 8. TPE fluorescence

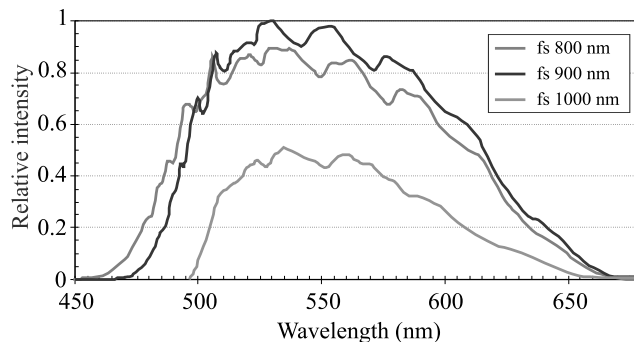


Fig. 8. Normalized fluorescence spectra of 3-N,N-diacetylaminobenzanthrone film with excitation of two-photon absorption of femtosecond laser radiation.

maxima are situated between 530 and 560 nm and the shapes of SPE and TPE fluorescence spectra are close. It is known that the locations of the one- and the two-photon states are related to the symmetry of a studied molecule or crystals. For example, researchers [13] found that locations of the one- and the two-photon states are related to inversion symmetry: in non-centrosymmetric octupolar molecules both one- and two-photon transitions to the same electronic state were allowed, but in centrosymmetric quadrupolar molecules the two-photon state was above the lowest one-photon state.

Thus, the emission centres are the same in case of both SPE and TPE fluorescence. It is known that a planar geometry does not interfere with electron transfer across the molecule, and the less the electron transfer is impeded, the better the molecule should absorb and emit light. Therefore, the high TPE for the investigated dye can be ascribed to the extended p-delocalization system and its highly molecular planarity.

Figure 9 shows the XRD spectra of the investigated thin films. A few peaks in the XRD diagram indicate some crystalline of the obtained organic film, the main peak ($2\theta = 13.97^\circ$, $d = 6.34$ Å) and the additional peak ($2\theta = 23.22^\circ$, $d = 3.83$ Å). From our previous investigation of crystal structure [5] by X-ray diffraction methods, it is known that molecules in mono crystal of 3-N,N-diacetylaminobenzanthrone are packed into parallel layers showing head-to-tail arrangement.

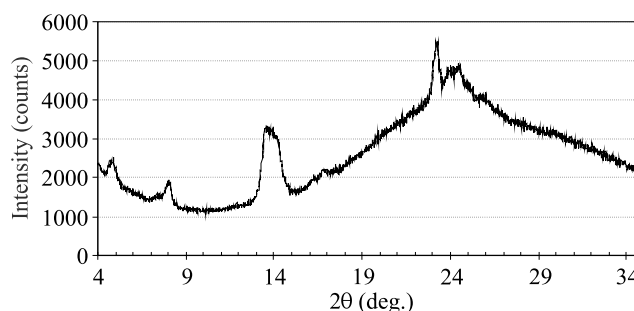


Fig. 9. XRD pattern of benzanthrone film received by thermal deposition method.

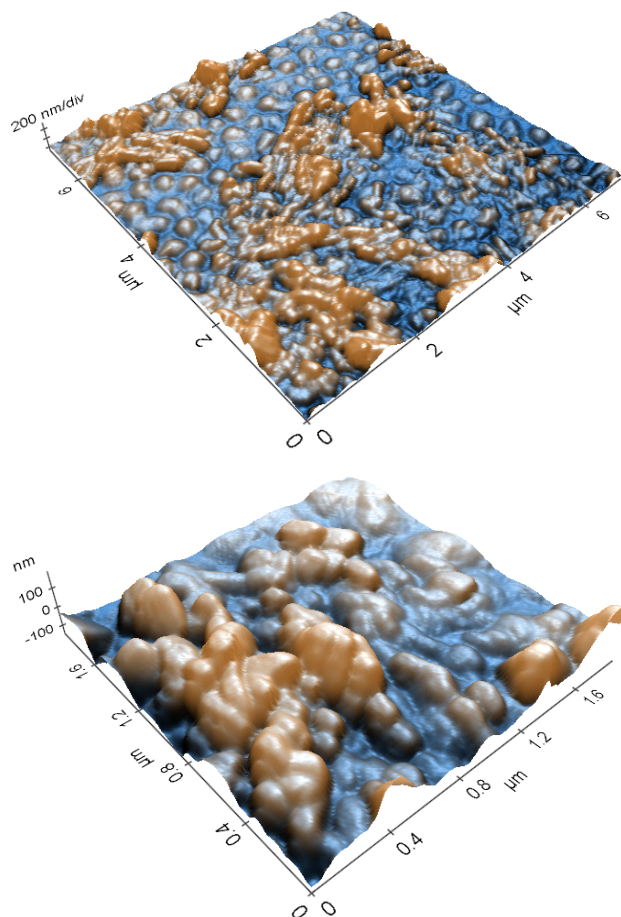


Fig. 10. AFM images of the surface of the benzanthrone film, obtained by a thermal evaporation in vacuum.

These layers are held together due to moderate π - π stacking interactions in the crystal structure between benzanthrone systems connected by the centre of inversion. The distance between parallel benzanthrone planes is 3.36 Å. The molecular structure of the studied dye consists of two planar fragments, the benzanthrone system and N, N-diacetyl amino group. The dihedral angle between these fragments is 81.3°, and deviation of the N atom from the benzanthrone system plane is 0.09 Å.

An intermolecular contact between the O atom of aromatic carbonyl group and the carbon atom of C = O in the acetyl group should be noted, and this distance is 3.04 Å. Taking into account the data about mono crystal packing, we think that the main peak in the film XRD diagram is connected with the layers formed by acetyl groups, and the additional peak corresponds to the inter planar distance $d = 3.83$ Å between benzanthrone planes with less densely packing comparing to that in the mono crystal.

Figure 10 shows AFM images of the organic film surface. In order to provide a more detailed description of the film structure, SEM images of the film surface also is presented (Fig. 11). It is clearly seen that in a polycrystalline organic structure, the crystallite size have reached about 200–300 nanometers.

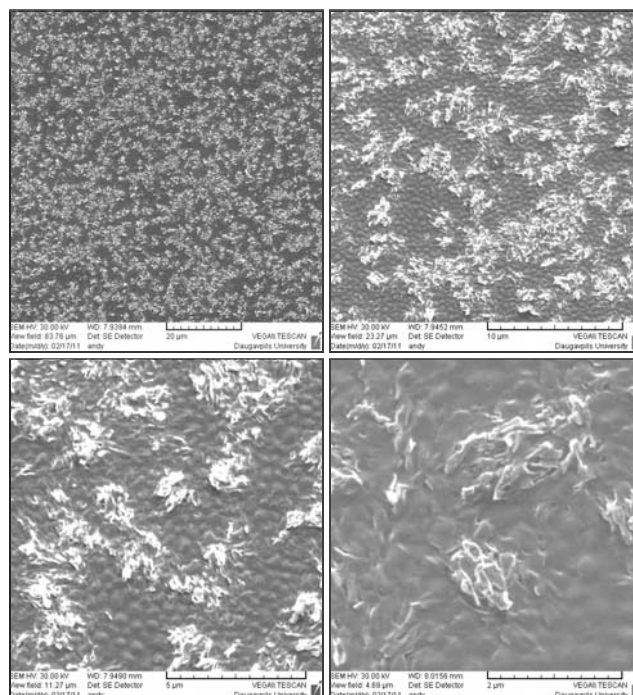


Fig. 11. SEM images of surface of benzanthrone film, obtained by a thermal evaporation in vacuum.

From the presented results, we can conclude that anti-parallel packing of molecules in the crystal plane contributes to the high luminescence intensity. Such package allows for an efficient interaction between the π -electron of aromatic system with the neighbouring molecules of benzanthrone, as well as donor-acceptor interaction between nitrogen atoms and the carbonyl oxygen. In previous studies [5,14], it was shown that in other molecular crystals, packaging of benzanthrone derivatives demonstrated a low intensity of luminescence of these compounds in the solid state. In addition, it was found that the other studied 3-N-derivatives of benzanthrone (with substituted amino and amidino groups) were not able to form ordered thin films.

The films of other benzanthrone derivatives (3-N-[N', N'-Dimethylbenzamidino]benzanthrone; 3-N-[N', N'-Dimethylformamidino]benzanthrone) were obtained by thermal deposition in vacuum and studied. They are characterised by interesting optic and fluorescence properties, but the film structure is completely amorphous, that is why we believe that in comparison with those, the structured films 3-N, N-diacetylaminobenzanthrone have more potential to be used in applied opto-electronics and photonics.

4. Conclusions

The thin films of 3-N, N-diacetylaminobenzanthrone, prepared by a thermal deposition method, show an intense green luminescence with the maximum of $\lambda_{\max} \sim 530$ nm. The films are transparent in the region corresponding to the fluorescence emission and at higher wavelengths, what is very interesting for optical applications. These films have

a polycrystalline structure with the crystallite size of up to ~300 nm. It was found that the obtained films are highly ordered materials forming the molecular layers with inter planar distance $d = 3.83 \text{ \AA}$ and $d = 6.34 \text{ \AA}$. The possibility of combining the deposition of benzanthrone dyes films with the other optical inorganic and nanostructured materials in the same reactor by changing the deposition conditions opens the way to the fabrication of complex photonic devices for different applications. Further experiments of thermal deposition of films on nano-structured substrates, as well as a study of their structure and electrical properties, are planned in future.

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