

# Investigation of new Stilbazolium dye thin films deposited by Pulsed Laser Deposition

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## ABSTRACT

In present work we report the analysis of thin films and targets from new stilbazolium dye E-4-(2-(4-hydroxynaphthalen-1-yl)vinyl)-1-octylquinolinium iodide (**D1**) deposited by Pulsed Laser Deposition (PLD) technique using high power UV TEA N<sub>2</sub> laser. The thin films are deposited onto substrates – KBr, 316L SS alloy, optical glass and aluminum foil. The films were characterized by FTIR spectroscopy, bright field microscopy, fluorescence microscopy and atomic force microscopy (AFM) analysis. FTIR spectroscopic analysis of thin films and target material shows small differences between deposited films and native substance. The films are found to be homogeneous by AFM results and without any cracks and droplets on the surfaces. The present study demonstrates the ability of PLD technique to provide thin films from new stilbazolium dyes with good quality when they are applied as non-linear optical (NLO) organic materials on different type of substrates.

**Keywords:** Non-linear optical organic material; Stilbazolium dye; Pulsed Laser Deposition

## 1. INTRODUCTION

Organic non-linear optical (NLO) thin films with preliminary designed properties and structure are very attractive for applications as fast optical switches, modulators, devices for frequency mixing processes, sensors, integrated optical circuits for telecommunication and medium for optical computing<sup>1-3</sup>.

Thin films of complex organic materials have been deposited by conventional non-vacuum techniques, such as dip coating, spin coating, spray coating, electrochemical deposition, Langmuir–Blodgett method and vacuum methods such as electron beam evaporation, thermally assisted vacuum evaporation, organic molecular beam epitaxy<sup>4,5</sup>. The PLD technique is well known for deposition of complex inorganic thin films<sup>6</sup>.

Recently developed laser based methods, as matrix assisted laser evaporation (MAPLE) using high power UV excimer lasers and resonant infrared PLD (RIR PLD) using free electron laser (FEL), have been found to be very appropriate for deposition of complex organic materials, including polymers, biopolymers, proteins and living cells<sup>7</sup>. The intrinsic disadvantages of these techniques are the necessity to use frozen solutions of the organic compounds as MAPLE target and complex/expensive FEL as ablating source for RIR PLD.

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Relatively low-cost preparation of organic NLO dyes, as well as their active optical properties have stimulated researchers for synthesis of new ones. Stilbazolium salts (hemicyanines) are well known as i) good second order NLO materials with a higher tendency to crystallize in noncentrosymmetric structures than dipolar covalent compounds; ii) fast optical response time; iii) high melting point compounds; iv) architectural flexibility for molecular design<sup>8</sup>. Some authors try to find a way of decreasing the spontaneous self alignment of hemicyanine molecules in the sol-gel fabricated film on silica and hence they expect an enhancement of second harmonic generation (SHG) intensity<sup>9</sup>. Recently, it was reported for the enhancement of THz emission by optical rectification on a hemicyanine-self-assembled monolayer deposited on the Au film<sup>10</sup>.

Compared with inorganic NLO materials, there are also some drawbacks to stilbazolium dyes, such as low mechanical strength and thermal stability, difficulty in large single-crystal growth. It should be noted that the highest known value of the SHG is measured for a stilbazolium dye, called DAST, which shows SHG intensity 2 000 times that of urea standard<sup>8</sup>. DAST has been used already in several prototype photonic devices<sup>11-14</sup> and for THz generation and detection<sup>15,16</sup>. In our previous work we have reported a new stilbazolium dye (E)-1-ethyl-4-(2-(4-hydroxynaphthalen-1-yl)vinyl)quinolinium bromide, possessing SHG more than 10 000 times higher than the standard, which makes it an excellent NLO candidate for photonic applications<sup>17</sup>. To the best of our knowledge, it is the first deposition of hemicyanine dye by PLD method. These results inspired us to continue the investigations.

The aim of the present work is to study the chemical composition and the morphology of the surface of thin films obtained by PLD technique. The thin films are composed by new stilbazolium dye with larger  $\pi$ -conjugated electron system.

## 2. EXPERIMENTAL

### 2.1. Film deposition

The experimental set-up used for the thin film deposition is typical of the PLD technique and is similar with that described in ref. 18. For the needs of the deposition, an EMG 120 Lambda Physik UV TEA N<sub>2</sub> laser at 337.1 nm with 5 ns pulse duration and repetition rate of 20 Hz was used (pulse energy- 5 mJ). The laser beam was focused by means of a quartz short focus (f=5 cm) lens, while the laser fluence was varied from 200 mJ/cm<sup>2</sup> to 3.5 J/cm<sup>2</sup>. The target holder was rotated with a speed up to 500 rev/min by high speed mini-motor stage fixed on a single axis scanner inside a vacuum chamber. Using of high speed rotation and scanning of target enabled uniform erosion of the target and deposition of the films on relatively large area, up to 10 cm<sup>2</sup> without significant film's thickness gradient. The distance between the target and the substrate (S) was fixed at 4.5 cm. The single bulk dye target was prepared with the aid of a hydraulic press (Perkin Elmer) with 1.2 cm diameter and 0.3 cm thickness. All the experiments were carried out at room temperature and vacuum of 10<sup>-3</sup> mbar, which was achieved by using standard two stage rotary pumps. The microscope glass substrates ("Iimglass" 20x20x0.22 mm), 316L SS alloy, and Al foil were cleaned in an ultrasound bath with pure acetone and ethanol, before the deposition process and were dried with technical nitrogen. Mono crystals KBr, NaCl were used as substrates for the infrared spectroscopy. The choice of substrates was done in order to provide compatibility with NLO devices. The thickness of the deposited films ranged between 80 - 300 nm, measured by interferometric method.

### 2.2. Spectral measurements

The UV-Vis spectrum (1 cm quartz cell and concentration 1×10<sup>-5</sup> M was recorded on Perkin-Elmer Lambda 9 UV-VIS/NIR spectrometer operating between 190 and 900 nm using solvent methanol spectroscopic quality (Uvasol, Merck). Fourier-transform infrared IR spectra were recorded with an IR spectrophotometer VERTEX 70 FT-IR spectrometer (Bruker Optics). The used attenuated total reflectance (ATR) accessory was MIRacle<sup>TM</sup> with a one-reflection ZnSe element (Pike). Thin films onto KBr plate were analyzed with absorbance spectra and the depositions onto 316L SS alloy and aluminum foil by ATR spectra.

### 2.3. Bright field and fluorescence microscopy measurements

An optical study was performed by bright-field fluorescence microscopy (Nikon Eclipse 80i) with maximum magnification 400X and four standard filters in the case of fluorescent mode. Each Nikon triple band fluorescence set

was optimized for use with DAPI and FITC in combination with either TRITC or Texas Red probes. The microscopic imaging was performed by DS Camera Control Unit DS-U2 and DS camera Head DS-Fi 1 with use of imaging software NIS-Elements F 2.30.

#### 2.4. AFM measurements

AFM study in the present work was performed by Veeco DI Nanoscope MultiMode V system (contact mode) with scan size: 10 $\mu$ m x 10 $\mu$ m along *XY* axis and vertical range *Z* axis - of 2.5 $\mu$ m.

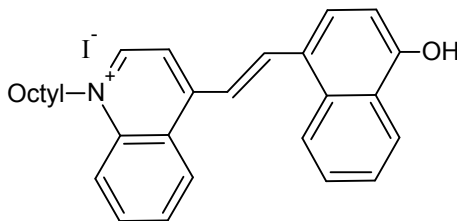
### 3. RESULTS AND DISCUSSION

#### 3.1. NLO organic dye synthesis

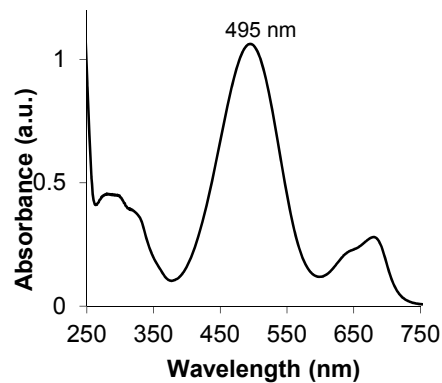
The stilbazolium dye E-4-(2-(4-hydroxynaphthalen-1-yl)vinyl)-1-octylquinolinium iodide (**D1**) is synthesized by Knoevenagel condensation of 4-hydroxynaphthaldehyde and octylpyridinium iodide in the presence of basic catalyst piperidine. Figure 1 shows the chemical structure of the investigated compound.

The dye synthesis methodology is analogous to that one described in ref. 17. Polycrystalline sample of dye **D1** suitable for deposition by the PLD technique is obtained by crystallization from methanol. The melting point (233-4°C) for the target dye is sharp which indicates a high level of purity and a crystalline phase of the resulting salt.

On the figure 2 is presented the UV-Vis spectrum of dye **D1** measured in methanol solution at concentration 1 $\times$ 10<sup>-5</sup> mol/L. The absorbance spectrum shows a band with  $\lambda_{\text{max}} = 495$  nm, while that measured in fluorescence spectrum shows a maximum at 631 nm. A very large Stokes's shift of 136 nm (4354 cm<sup>-1</sup>) in methanol solution is observed. Generally, a large Stokes shift is attributed to the different charge distribution in the excited state compared to the ground state<sup>19,20</sup>. This large charge displacement is an indication of a large polarizability<sup>21,22</sup>. Therefore, the new stilbazolium dye can be interesting as a very promising material for NLO application.



**Figure 1.** Chemical structure of the investigated dye **D1**.

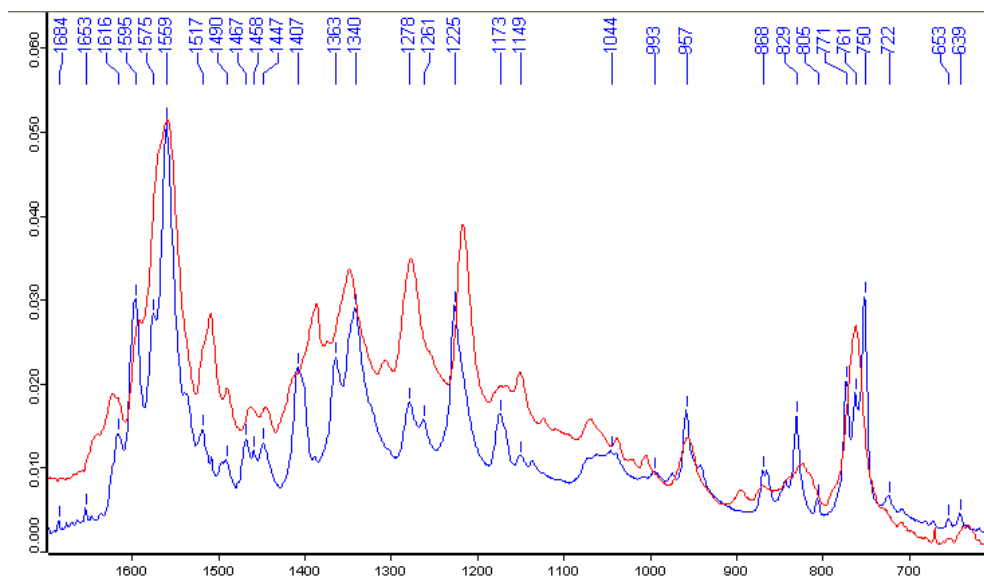


**Figure 2.** a) Absorption spectrum of dye **D1** in methanol solution.

#### 3.2. FTIR spectral analysis

The spectral analysis of the new stilbazolium dye deposited by PLD on various substrates is based on comparison of the spectral bands of the obtained thin films with those of the native materials in a region where most of the characteristic fundamental vibrations appear. For this study the 1700 – 600 cm<sup>-1</sup> spectral interval is selected as it includes the fingerprint region and the region of aromatic ring vibrations. The spectral analysis will be illustrated with the detail comparison of two spectra of hemicyanine dye **D1**.

The 1700-600  $\text{cm}^{-1}$  region of the IR spectrum of dye **D1** deposited onto KBr plate is shown in figure 3 (spectral line in red) together with the spectrum of a drop of dye methanol solution dried onto AgBr plate (spectral line in blue).



**Figure 3.** IR Absorbance spectra of dye **D1**: the spectral line in red is the spectrum of thin film (the substrate is a KBr plate), and the spectral line in blue –that of a drop of dye **D1**'s methanol solution dried onto AgBr plate.

It can be seen that the two spectral curves look pretty similar and the bands of dye **D1** at 1559  $\text{cm}^{-1}$ , 1340  $\text{cm}^{-1}$ , 1278  $\text{cm}^{-1}$  and 957  $\text{cm}^{-1}$  are preserved in the spectrum of the thin film. The most prominent IR-bands at 1559  $\text{cm}^{-1}$  and 1595  $\text{cm}^{-1}$  correspond to the strongly coupled  $\nu_{\text{C}=\text{C}}$  and 8a, 8b in-plane vibrations of the quinolinium fragment in the molecule<sup>17</sup>. These are the characteristic bands that are strongly influenced by the charge redistribution effects. On the other side, some of the bands are shifted up to 10  $\text{cm}^{-1}$ , which is to be expected as the compound is embedded into the crystal structure of KBr. The strong bands of this type are 1225  $\text{cm}^{-1}$  (in plane deformation vibration of quinolinium moiety) shifted to 1216  $\text{cm}^{-1}$  and 750  $\text{cm}^{-1}$  (skeleton deformation vibrations of both, quinolinium and naphthalene fragments) shifted to 760  $\text{cm}^{-1}$ , respectively. The interaction of the deposited dye with the substrate is also a reason for widening of most of the bands. In this case two or three bands close in the compounds spectrum can appear as one (usually unsymmetrical) band in the thin film spectrum. In figure 3 these are 1595  $\text{cm}^{-1}$  and 1559  $\text{cm}^{-1}$  couple, 1363  $\text{cm}^{-1}$  and 1340  $\text{cm}^{-1}$  couple and 771  $\text{cm}^{-1}$ , 761  $\text{cm}^{-1}$  and 750  $\text{cm}^{-1}$  triad.

There are two bands in the spectrum of the deposited compound that cannot be explained as a result of deposition – these are the strong 1508  $\text{cm}^{-1}$  band and the 1149  $\text{cm}^{-1}$  band. The only explanation is that a partial degradation of the deposited compound happened.

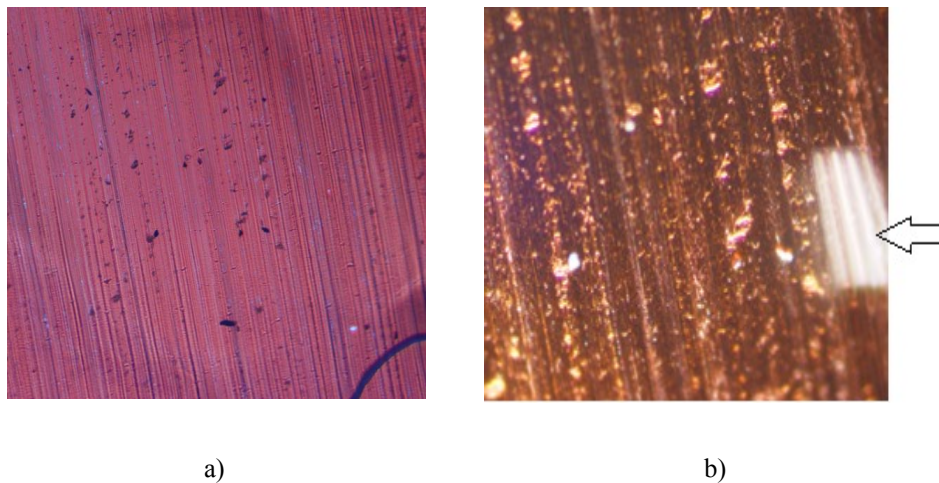
As a whole, the high laser fluence (3.5  $\text{J}/\text{cm}^2$ ) used for dye deposition has not decomposed heavily the target material. The high fluence shortens the deposition process thus decreasing its cost.

### 3.3. Surface analysis

An optical and optical fluorescent analyses were performed of thin films of the investigated new stilbazolium dye **D1** deposited onto substrates from KBr, 316L SS alloy, optical glass and aluminum foil.

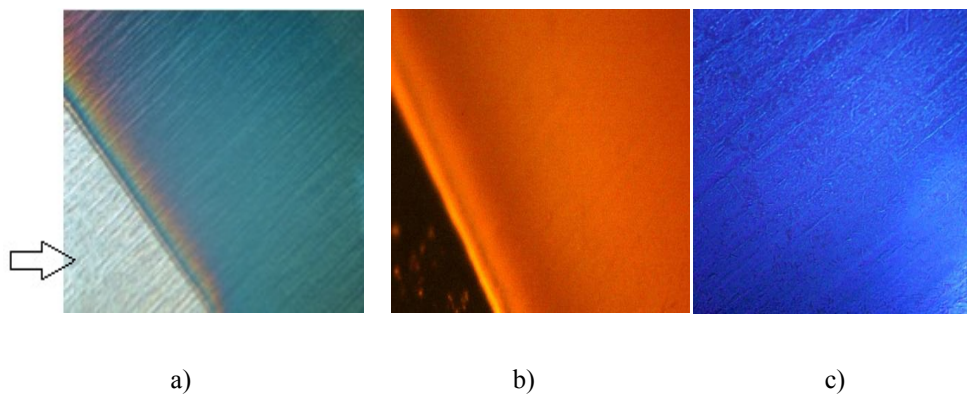
As can be seen from figure 4, polycrystalline layers grown on aluminum foil substrate from the vapor phase under vacuum usually exhibit a uniform “single-crystal-like” orientation. Optical micrographs show that the layers are essentially polycrystalline. However, the numerous crystals composing the layers show the same morphology and the same orientation with respect to the Al foil sliding direction (figure 4b). The arrow shows the clean surface of the substrate indicating the Al foil sliding direction. These micrographs clearly indicate that a specific nucleation occurs at

the ordered Al foil surface giving very likely a peculiar crystallographic plane in contact with the substrate. The average orientation of these crystals will be deduced from powder X-ray diffraction in our future work.



**Figure 4.** Optical micrographs of the **D1** thin film on aluminum foil substrate: a) 100X; b) 200X. The arrow shows the clean surface of the substrate indicating the Al foil sliding direction.

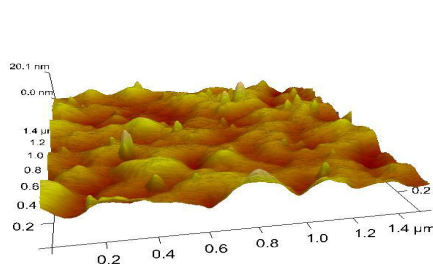
The surface quality of thin film of dye **D1** onto samples from stainless steel 316L are shown on figure 5. A similar orientation, such as the above mentioned one, is observed in layers with thickness 180 nm on a stainless steel substrate (figures 5a and 5c). The arrow shows the clean surface of the substrate indicating the stainless steel sliding direction. When the thickness of layers increases, a completely disordered structure can be observed (figure 5b). It is known that the NLO properties of the crystalline layers depend of their molecular orientation<sup>23, 24</sup>.



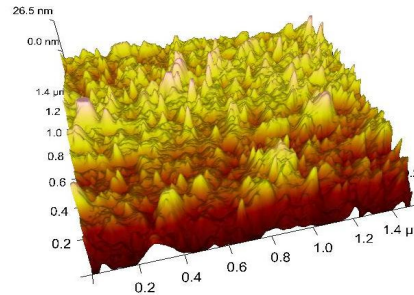
**Figure 5.** Bright field and fluorescence micrographs of dye **D1** as thin film onto samples from stainless steel 316L: a) 100X; b) 200X by filter Texas Red; c) 200X by filter DAPI. The arrow shows the clean surface of the substrate indicating the stainless steel sliding direction.

AFM is useful tool for studying surfaces because it may provide real volumetric film morphology and nanostructures. Figures 6 and 7 show the ability of AFM to visualize and characterize surfaces of the stilbazolium dye **D1** deposited by PLD on glass substrates and aluminum foils with thickness 220 nm, respectively. *X* and *Y* axes are graduated in  $\mu\text{m}$  and show the area of the scanned sample. *Z* axis is graduated in nm and shows the roughness of the sample.

The surface topology showed a different mode of the growing of crystals in the deposited films in relation to substrates nature. The film on glass substrate is extremely uniform with deviation of no more than 20 nm (figure 6), while that one deposited onto aluminum foil showed a deviation of more than 30 nm (figure 7) and preference for growing in vertical axis. The crystal structure of aluminum foil defines the direction of deposited film<sup>23</sup>. The films have highly-ordered uniform morphology and a layered structure; the organic molecules stand nearly vertical in the case of metal (aluminium foil) substrates and planar in the case of dielectric substrates, such as optical glass and mono crystals from KBr.



**Figure 6.** AFM 3D image of a surface of the thin film of dye **D1** deposited by PLD on glass substrate.



**Figure 7.** AFM 3D image of a surface of the thin film of dye **D1** deposited by PLD on aluminum foil.

## CONCLUSION

A successful deposition of thin films from stilbazolium dye with larger conjugated system than the well-known DAST is described. The thin-film deposition technique is PLD using high power UV N<sub>2</sub> laser. The films have highly-ordered uniform morphology and a layered structure. They are homogeneous and their surface has a roughness of no more than 40 nm which is still enough and compatible for NLO applications. This preliminary study and the previous one<sup>17</sup> afford an interesting possibility to compose new stilbazolium dye - inorganic nanocomposites for direct photonics applications.

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