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Synthesis, ellipsometry and non-linear optical features of substituted 1,3,5triphenylpyrazolines

Ewa Gondek^{1,*}, Jacek Nizioł², Andrzej Danel³, Mateusz Kucharek³, Jarosław Jedryka⁴, Paweł Karasiński⁵, Natalia Nosidlak¹, Andrij A.Fedorchuk⁶

- 1 Institute of Physics, Cracow University of Technology, ul. Podchorążych 1, 30-084 Kraków, Poland
- 2 AGH University of Science and Technology, Faculty of Physics and Applied Computer Science, al. Mickiewicza 30, 30-059 Krakow, Poland
- 3 Institute of Chemistry, Department of Food Technology, University of Agriculture, ul. Balicka 122, Krakow, Poland
- 4 Institute of Optoelectronics and Measuring Systems, Faculty of Electrical Engineering, Czestochowa University Technology, ul. Armii Krajowej 17, Czestochowa, Poland
- 5 Department of Optoelectronics, Silesian University of Technology, ul. B. Krzywoustego 2, 44-100 Gliwice, Poland
- 6 Department of Inorganic Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya Str., 6, 79005, Lviv, Ukraine

(*) corresponding author: egondek@pk.edu.pl

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Abstract: Ellipsometric and nonlinear optical properties of new, differently substituted, 1,3,5triphenylpyrazolines dyes, were studied. Results of theoretical calculation within a framework of density functional theory (DFT) technique were verified by spectroscopic ellipsometry and optical second harmonic generation (SHG) experiment at fundamental laser wavelength 1064 nm. Absorption bands and complex refractive indices were determined. Principal role of 2thienyl substituent for first order nonlinear optical properties was demonstrated.

1. Introduction

Compounds containing azole groups represent an important part of organic materials applied in modern organic electronics. For example thiazole derivatives have been successfully applied in organic field-effect transistors [1], phosphorescent OLEDs [2] and in organic solar cells [3]. Similarly, pyrazole derivatives have been incorporated in electroluminescent devices [4, 5] and studied because of their nonlinear optical (NLO) properties [6]. A particular case present 1,3,5-triarylpyrazolines. At the early stage of investigations they were exploited as photo- and radio-luminophores [7, 8] or as optical brighteners [9]. Recently they have been used also for fabrication of plastic scintillators [10]. Because of excellent photoemissive properties, an array of 1,3,5 triarylpyrazolines have been also applied as sensitive material for detection of various ions, for example Cd^{2+} , Zn^{2+} [11] or Hg^{2+} [12] and in OLEDs of strong bright blue-green emission [13].

Unfortunately triarylpyrazolines have a tendency to crystallization, but this inconvenience disappears if they are chemically bounded to a polymer. The DFT (*density functional theory*) calculations for pyrazoline derivatives revealed large ground state dipole moment magnitude. Such a feature is an important asset to fabricate bulk materials with NLO

properties using electrical poling process [14]. For several pyrazoline derivatives substituted with –CN and nitro groups the phenomenon of amplified spontaneous emission and two-photon absorption [14] also was observed. An efficient light second harmonic generation (SHG) was found to be typical for push-pull systems of 1-phenyl-2-pyrazolines substituted with nitro-styryl groups [15]. Nevertheless, despite their promising potential, triarylpyrazolines have not yet been sufficiently well studied in domain of nonlinear optics. The last factor has motivated us to pursue studies of 1,3,5-triphenylpyrazolines and the impact of different substituents on optical properties.

Here we report on chemical synthesis, theoretical calculations related to electronic structure, experimental measurements involving ellipsometry and SHG. The obtained results suggest that 1,3,5-triphenylpyrazolines may be an interesting alternative to already known molecules in domain of nonlinear optics.

2. Materials

2.1 Synthesis

The synthesis reaction is depicted in Fig. 1. The starting aldehydes **1** or **4** were prepared by reaction of appropriate pyrazolines with DMF/POCl₃. Aroylacetonitriles

2a or **2b** were synthesized from acetonitrile and methyl thiophene-2-carboxylate or methyl 4methoxybenzoate and sodium hydride. In the final step the aldehydes have been condensed with carbonyl compounds in the presence of catalytic amount of piperidine.



Fig. 1. Principal scheme of the studied pyrazoline derivatives synthesis. "Process" means ethanol/piperidine (cat)/8 hours/boiling.

Synthesis-general procedure.

A round-bottomed flask (25 mL) equipped with a magnetic stirring bar and reflux condenser was filled with 96% ethanol (10 mL), aldehyde **1** or **4** (1 mmol), **aroylacetonitrile 2** (1.2 mmol) and three drops of piperidine as catalyst. Such prepared contents were boiled under reflux condenser for 8 hours. After this the reaction mixture was cooled and the precipitate was filtered off and crystallized from appropriate solvent. The final purification was accomplished with column chromatography filled with silica gel 60 (70-230 mesh) using toluene/ethyl acetate (4:1) as eluent (compound **PR1** and **PR2**) or with preparative TLC (compound **PR3**). The product's contents were confirmed with ¹H NMR spectra and elemental analysis

Compound **PR1**:

Red crystals, 200 mg, 90%, mp. 246-8 °C (toluene). ¹H NMR(600 Hz, DMSO, δ ppm): 8.17(s, 1H, H_{vinyl}), 8.11-8.08(m, 2H), 8.01(d, *J* = 9Hz, 2H), 7.87-7.84(m, 2H), 7.51-7.45(m, 3H), 7.39-7.35(m, 2H), 7.31-7.23(m, 5H), 7.18-7.14(m, 3H), 5.81-5.77(m, 1H_{pyrazoline ring}), 4.09-4.01(m, 1H_{pyrazoline ring}). The peaks from the third proton of pyrazoline ring (ca. 3.20 ppm) were covered with d₆-DMSO signals. Anal. cald for. C₂₉H₂₁N₃OS: C 75.81; H 4.61; N 9.14. Found C 75.96; H 4.73; N 8.97.

Compound PR2:

Yellow crystals, 200 mg, 88%, mp. 178-180 °C (toluene). ¹H NMR(600 Hz, CDCl₃, δ ppm): 7.96(s, 1H_{vinyl}); 7.93(d, J = 9.2Hz, 2H), 7.82-7.81(m, 2H), 7.77-7.76(m, 2H), 7.56(t, J = 7.45Hz, 1H), 7.47(t, J = 7.69 Hz, 2H), 7.43-7.40(m, 3H), 7.35(t, J = 7.41Hz, 2H), 7.29(t, J = 7.37Hz, 1H), 7.26-7.24(m, 2H), 7.12(d, J = 8.2Hz, 2H), 5.44(dd, J = 12.07Hz, 5.35Hz, 1H_{pyrazoline ring}), 3.93(dd, J = 12.1Hz, 17.34Hz, 1H_{pyrazoline ring}), 3.25(dd, J = 5.4Hz, 17.3Hz, 1H_{pyrazoline ring}). Anal. cald for. C₃₁H₂₃N₃O: C 82.10; H 5.11; N 9.26. Found: C 81.76; H 4.97; N 9.05.

Compound **PR3**:

Red crystals, 220 mg, 94%, mp. ¹H NMR(600 Hz, CDCl₃, δ ppm): 8.26(dd, J = 3.9Hz, 1.02Hz, 1H_{thiophene}), 8.19(s, 1H, H_{vinyl}), 7.96(d, J = 9.15Hz, 2H), 7.96(d, J = 9.1Hz, 2H), 7.70(dd, J = 4.97Hz, 1.01Hz, 1H_{thiophene}), 7.49(d, J = 7.2Hz, 2H), 7.39(t, J = 7.21Hz, 4H), 7.32(t, J = 7.27Hz, 2H), 7.26-7.22(m, 3H), 7.17-7.19(m, 1H_{thiophene}), 7.09(d, J = 8.81Hz, 2H), 6.7(d, J = 16.4 Hz, 1H_{stilbene}), 5.42(dd, J = 12.00Hz, 5.21Hz, 1H_{pyrazoline ring}), 3.81(dd, J = 17.1Hz, 12.1Hz, 1H_{pyrazoline ring}), 3.14(dd, J = 17.2Hz, 5.13Hz, 1H_{pyrazoline ring}). Anal. cald for. C₃₁H₂₃N₃OS: C 76.74; H 4.77; N 8.63. Found: C 76.83; H 4.75; N 8.56.

Pyrazole derivatives are difficult to be deposited in form of a thin layer, because they may be crystallized or form other aggregates. A common remedy to this constraint is to disperse molecules inside an optically inert, polymeric matrix, typically in polymethyl metacrylate (PMMA). The synthesized dyes were co-dissolved together with PMMA for each dye in identical molar ratio. Next, thin blend films were deposited on soda-lime microscope slides by spin-coating.

2.2 Quantum chemical theoretical studies

Quantum chemical calculations of dipole moments, first order (β) (at a wavelength of 1064 nm) and second order (γ) molecular nonlinear hyperpolarizabilities as well as determination of HOMO and LUMO, were done using Gaussian W09 computer program package [17] within a

framework of DFT and B3LYP functional supplement with the standard 6-31G(d) basis set. An example of calculated HOMO and LUMO orbitals are depicted for PR1 in Fig.2. Following the DFT calculations it was established that the studied molecules have partial charge transfer, namely - a part of the electron density from a HOMO could be transferred on the 2-thienyl (PR1 and PR3) or on corresponding benzene ring (PR2) at the LUMO, although it is distributed throughout the π -conjugated chain.



Fig. 2 Visualization of modelled theoretically HOMO (a) and LUMO (b) orbitals for PR1.

Numerical results of quantum chemical calculations are compared to experimental data in Table 2, further in the text, in the disscussion of experimental data.

3. Equipment and Methods

Measurements of absorbance, refractive indices n, extinction coefficients κ and film thicknesses d were carried out with application of spectroscopic ellipsometer Woollam M2000 (J.A. Woollam Co. Inc.). Measurements of absorbance were carried out in transmission mode and the other ones were done in reflection mode. The base of ellipsometry is effect of the change in polarization of light reflected on thin film. This effect is determined by the ratio of Fresnel reflection coefficients for both s- and p- polarized light [18]:

$$\rho = \frac{r_p}{r_s} = \tan \Psi e^{i\Delta},\tag{1}$$

where Ψ (amplitude ratio) and Δ (phase shift) are determined for ellipsometry experiment. Determination of optical function from measured ellipsometric angles (Ψ , Δ) requires a model that describes an interaction of the incident light with the film or application of B-spline one, which don't need any assumptions about physical properties of film.

In our studies the dependences of the ellipsometric angles Ψ , Δ on photon energy *E* (dispersion characteristics) were measured with light beam conveyed to the sample at angles 60°, 65° and 70°. The probing light on the sample surface was formed by a beam a spot about 2.5 mm.

The data obtained experimentally (Ψ and Δ) were explored as follows. First, samples thicknesses were deduced using Cauchy approximation to the data from transparent part of the optical spectrum. To exclude noise from the recorded characteristics of the ellipsometric angles, their dispersions were approximated with B-spline functions [19,20]. The number of included free terms was the least possible, necessary to obtain a reasonable mean square error

of the fit. The fitting procedure retained only physical solutions, fulfilling Kramers–Kronig relations. To evaluate dielectric and optical function dispersion (complex permittivity and complex refractive index) in a more rigorous manner, the experimental data are usually parameterized using different theoretical models. In the case of the reported samples, the best matching parameterization of B-spline approximations have been occurred using of Tauc-Lorentz model [21]. This model describes very well optical functions for different amorphous materials like semiconductors [22], insulators [23], many organic [24] or even biological materials [25]. This model simulates the dispersion of imaginary part of the dielectric function ϵ_2 by multiplying the Tauc [26] joint density of states and the ϵ_2 obtained from the Tauc-Lorentz oscillator model. The ϵ_1 (real part) of the dielectric function is derived from ϵ_2 using Kramers–Kronig integration, as shown in Eqs 2 and 3.

$$\varepsilon_{2}(E) = \begin{cases} \left[\frac{AE_{0}B(E-E_{g})^{2}}{(E^{2}-E_{0}^{2})^{2}+B^{2}E^{2}} \cdot \frac{1}{E} \right], & E > E_{g}, \\ 0 & E \le E_{g}. \end{cases}$$
(2)

$$\varepsilon_1(E) = \varepsilon_1(\infty) + \frac{2}{\pi} P \int_{E_g}^{\infty} \frac{x \cdot \varepsilon_2(x)}{x^2 - E^2} \mathrm{d}x.$$
(3)

In the above equations E_g means optical energy band gap, E_0 - principal peak inter-band transition, A - amplitude and B - broadening term, P stands for the Cauchy principal part of the integral. The integral in Eq.(3) can be solved in closed form [21].

Measurements of non-linear optical properties for the studied materials were carried out using measurement system presented in Fig. 3. The studied powder-like chromophore were electrically poled and oriented in the dc-electric field about 8 kV/cm. The sample orientation controlled by polarimetry was equal to about 83 % in terms of observed optical polarization variation.



Fig. 3 A measuring set-up for determination of the second harmonic generation efficiency versus the varying fundamental energy power density at wavelength of 1064 nm.

The second harmonic generation (SHG) were observed for *s-p* polarization of the incident light. The samples were illuminated with fundamental 1064 nm pulsed beam from a Nd:YAG 10 ns nanosecond laser (Spectra-Physics Lasers Inc., USA, Quanta Ray INDI), pulse duration 12 ns, repetition rate 12 Hz and energy 60 mJ. The laser energy density was continuously tuned by Glan polarizers up to 150 J/m². All the measurements were carried out in classical architecture with rotation stage as outlined in Fig. 3 and already explained in Ref. 16.

4. Experimental results and discussion

In Fig. 4 are shown absorption spectra for the studied chromophore embedded in PMMA matrix, measured using transmission. The first absorption maxima occur at ca. 2.5eV (λ =495.6 nm). However PR2, in contrast to the two remaining chromophore, features two distinct absorption maxima in the available wavelength range and the first one is apparently weaker than for the case of PR1 and PR3. The PR2 dye contains a phenyl pendant group instead of 2-thienyl as PR1 and PR3. This observation may indicate a crucial role of 2-thienyl group on significant variation of electronic levels.



Fig. 4. Typical absorbance spectra for the studied molecules in PMMA matrix. The spectra are re-scaled vertically, but relative magnitudes are retained.

In Fig. 5 are plotted as an example, experimentally obtained Ψ and Δ dependence versus light energy. This picture illustrates level of noises occurred during the experiment studies and accuracy of B-spline approximation (dashed lines). The part of data (energies lower than 2 eV, compare to Fig.4) used to determine thicknesses of the sample were characterized by particularly low noise.



Fig. 5 Ellipsometric angles Ψ (a) and Δ (b) functions dispersions measured for PR2 embedded in PMMA matrix. Solid lines represent experimental data while dashed ones are B-spline fits. Labels on graphs correspond to the probing light incidence angle.

Although Cauchy parameterization allows to calculate thickness and real part of refractive index, it does not provides any parameters describing observed electronic molecular transitions. That is why (as it was explained earlier in this report), the experimental data were fitted using of Tauc-Lorentz model. An example of experimental data fitted with Tauc-Lorentz are depicted in Fig. 6. In the case of PR2 dye two spectral peaks had to be included in the model contrary to the two other dyes. However, it was not possible to parameterize unambiguously the tail originating from spectral resonances appearing in vacuum UV spectral ranges. So it was excluded from calculations. However, Tauc-Lorentz fits very well agreed to the B-spline plot.



Fig. 6 Dispersion relations of refractive index (left), extinction coefficient (right) for PR2 chromophore dispersed in PMMA matrix,. Solid lines represent data derived from B-spline fits, while dashed lines depict data obtained from Tauc-Lorentz parameterization.

In this way, values parameters necessary to interpret results of SHG experiment were obtained. Calculated energies of optical band gap E_g , transition energies E_0 , absorptions and real part of refractive indices for the wavelengths of interest are summarized in Table 1.

Parameter/Sample	PR1	PR 2	PR 3
Thickness [nm]	81.2	54.5	80.3
E_g [eV]	1.946 ± 0.002	1.882 ± 0.001	1.819 ± 0.010
$E_0(1)$ [eV]	2.477 ± 0.001	2.537 ± 0.006	2.459 ± 0.001
$E_0(2)$ [eV]		3.185 ± 0.008	
abs (λ =532nm)	0.151	0.040	0.153
<i>n</i> (λ=532nm)	1.784	1.690	1.716
<i>n</i> (λ=1064nm)	1.551	1.546	1.548

Table 1 Samples thickness and parameters in Tauc-Lorentz parameterization deduced from ellipsometry data.



Fig. 7 Dependences of the SHG output versus the fundamental laser energy density for the studied materials.

Fig. 7 presents the results of the SHG signal dependences versus the fundamental energy density. The observed SHG intensities from the studied samples are significantly lower than the reference Nd:BiB₃O₆ crystals [27]. because poling process was not the subject of optimization. To eliminate the scattering background the additional interferometer filters at 520 nm and 542 nm have been applied. Additionally to evaluate the parasitic fluorescence background the rare earth doped glasses have been applied [28]. Nevertheless, the dependence is close to parabolic, as expected theoretically. The least intense signal was observed for PR2, despite the lowest absorption at wavelength 532 nm. This observation again points out the role of 2-thienyl substituent.

Table 2 Comparison of experimental and theoretical parameters. The dipole moments *D* and first order molecular hyperpolarizabilities β were theoretically calculated, while values of second order susceptibility $\chi^{(2)}$ were deduced from results of SHG studies obtained for PMMA blends with the studied dyes.

Parameter/sample	PR1	PR2	PR3
Dipole moment (D) [Debye]	11.82	11.47	11.81
First order hyperpolarizability (β) [esu] $\times 10^{-28}$	5.35	4.11	7.58
Second order susceptibility $\chi^{(2)}$, [pm/V]	2.12	1.69	2.67

In Table 2 are summarized results of theoretical calculations concerning molecular electronic properties and values of second order susceptibilities $\chi^{(2)}$, deduced from SHG measurements. As can be seen, all three molecules have a similar dipole moments *D*, but hyperpolarizibility β increases in the following order – PR2, PR1 and PR3. It follows then, that 2-thienyl is more efficient donor. In addition the case of PR3 confirms, that the extension of π -conjugated length in the opposite end of molecule, converts this side to a more efficient acceptor. The similar order was found for susceptibilities $\chi^{(2)}$. Taking into account similar dipole moments and molecular volume of all three dyes, poling efficiency can be supposed identical for PMMA films blended with these dyes. For this reason susceptibilities $\chi^{(2)}$ can be directly related to hyperpolarizibility β . In other words, results of DFT calculations were confirmed by SHG experiment. The obtained values are commensurable with other organic dyes [30,31], however they have more smooth dispersions of the optical functions which do they more applicable.

5. Conclusions

Joint theoretical and experimental studies concerning linear and nonlinear optical properties of new 1,3,5-triphenylpyrazolines have been reported. Since steric architecture may be crucial for poling efficiency, three similar molecules were synthesized. The sole difference was in extremities of push-pull system. It was established how this differences may enhance (or decrease nonlinear optical properties). It was established that the extension of π -conjugated length in the opposite end of molecule, converts this side to a more efficient acceptor. The similar order was found for susceptibilities $\chi^{(2)}$. The crucial role of 2-thienyl substituent was demonstrated.

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References

- [1] Ortiz RP, Yan H, Facchetti A, Marks JT, Azine- and Azole-Functionalized Oligo´ and Polythiophene semiconductors for organic thin-film transistors, Materials 2010;3:1533-1558. doi: 10.3390/ma3031533.
- [2] Xu F, Kim JH, Kim HU, Mi D, Cho YJ, Lee JY, Yoon UC, Hwang DH, Phosphorescent organic light-emitting diodes fabricated using iridium complexes with carbazole-based benzothiazole ligands, Synthetic Met, 2013; 178: 10-17. https://doi.org/10.1016/j.synthmet.2013.06.023.
- [3] Mohammad L, Chen Q, Mitul A, Sun J, Khatiwada D, Vaagensmith B, Zhang C, Li J, Qiao Q, Improved Performance for Inverted Organic Photovoltaics via Spacer between Benzodithiophene and Benzothiazole in Polymers, J Phys Chem C, 2015;119:18992-19000. doi:10.1021/acs.jpcc.5b05608.
- [4] Niziol J, Danel A, Gondek E, Armatys P, Sanetra J, Boiteux G, Pyrazoloquinolines -Alternative chromophores for organic LED fabrication, Macromol Sy 2004:212:473-478. https://doi.org/10.1002/masy.200450860.
- [5] Gondek E, Niziol J, Danel A, Szlachcic P, Plucinski K, Sanetra J, Kityk IV, Influence of chromophore dipole moments in parameterts of organic light emitting devices based on

phenyl and methyl modified pyrazoloquinoline, Spectrochim Acta A-M 75(5) (2010) 1501-1505. doi:10.1016/j.saa.2010.02.006.

- [6] Miller RD, Moylan CR, Reiser O, Walsh CA, Heterocyclic azole nonlinear optical chromophores. 1. Donor-acceptor substituted pyrazole derivatives, Chem Mater 1993;5:625-632. doi:10.1021/cm00029a009.
- [7] Sandler SR, Loshaek S, Broderick E, Tsou KC, 1,3,5-triaryl-2-pyrazolines as wave length shifters in scintillation plastics, J Phys Chem 1962;66:404-408. doi: 10.1021/j100809a006.
- [8] Buryakovskaya EG, Tsukerman SV, Lavrushin VF, Poduzhailo VF, Heterocyclic analogs of 1, 3, 5-triphenyl-Δ2-pyrazoline as spectrum shifters for liquid scintillators, J Appl Spectrosc 1967;7:500-502. https://doi.org/10.1007/BF00604542.
- [9] Krasovitskii BM, Bolotin BM, Heterocyclic compounds as organic luminophores (review), Chem Heterocycl Compd 1974;10:1269-1284. https://doi.org/10.1007/BF01175078.
- [10] Bliznyuk VN, Seliman AF, Ishchenko AA, Derevyanko NA, Devol TA, New Efficient Organic Scintillators Derived from Pyrazoline, ACS Appl Mater Interfaces 2016;8:12843-12851. doi: 10.1021/acsami.6b02719.
- [11] Ciupa A, Mahon MF, De Bank PA, Caggiano L, Simple pyrazoline and pyrazole "turn on" fluorescent sensors selective for Cd²⁺ and Zn²⁺ in MeCN, Org Biomol Chem 2012; 10(44): 8753-8757. doi:10.1039/C2OB26608C.
- [12] Wang SQ, Liu SY, Wang HY, Zheng XX, Yuan X, Liu YZ, Miao JY, Zhao BX, Novel pyrazoline-based selective fluorescent sensor for Hg²⁺, J Fluoresc 2014;24:657-663. doi: 10.1007/s10895-013-1339-y.
- [13] Sano T, Nishio Y, Hamada Y, Takahashi H, Usuki T, Shibata K, Design of conjugated molecular materials for optoelectronics, J Mater Chem 2000;10:157-161. doi:10.1039/A903239H.
- [14] J. Myśliwiec, A. Szukalski, L. Sznitko, A. Miniewicz, K. Haupa, K. Zygadlo, K. Matczyszyn, J. Olesiak-Banska, M. Samoc, Synthesis, optical and nonlinear optical properties of new pyrazoline derivatives, Dyes and Pigments 2014;102:63-70. https://doi.org/10.1016/j.dyepig.2013.10.027.
- [15] Szukalski A, Parafiniuk K, Haupa K, Goldeman W, Sahraoui B, Kajzar F, Myśliwiec J, Synthesis and nonlinear optical properties of push-pull type stilbene and pyrazoline based chromophores, Dyes and Pigments 2017;142:507-515. http://dx.doi.org/10.1016/j.dyepig.2017.04.009.
- [16] Kityk IV, Alzayed N, Berdowski J, Tylczynski Z, Fuks-Janczarek I, Miedzinski R, Lakshminarayana G, Photoinduced effects in γ-glycine nanocrystallites embedded in polymer matrices, Opt Commun 2011;284:1575-1577. doi:10.1016/j.optcom.2010.11.002.
- [17] Frisch MJ, Trucks GW, Schlegel HB, e. al., Gaussian G09, Gaussian, Inc., Wallingford CT2009.
- [18] Azzam RMA, Bashara NM, Ellipsometry and polarized light, North-Holland, Amsterdam 1987.
- [19] Johs B, Hale JS, Dielectric function representation by B-splines, Phys Status Solidi A, 2008;4:715-719. https://doi.org/10.1002/pssa.200777754.
- [20] Likhachev DV, Selecting the right number of knots for B-spline parametrization of the dielectric functions in spectroscopic ellipsometry data analysis, Thin Solid Films 2017;636:519-526. https://doi.org/10.1016/j.tsf.2017.06.056

[21] Jellison GE Jr, Modine FA, Parameterization of the optical functions of amorphous materials in the interband region, Appl Phys Lett, 1996; 69(3): 371-373. https://doi.org/10.1063/1.118064.
Jellison GE Jr, Modine FA, Erratum:"Parameterization of the optical functions of amorphous materials in the interband region" [Appl Phys Lett 1996;69: 371-373], Appl

Phys Lett, 1996; 69 (14): 2137. https://doi.org/10.1063/1.118155.

- [22] Jellison GE Jr, Merkulov VI, Puretzky AA, Geohegan DB, Eres G, Lowndes DH, Caughman JB, Characterization of thin-film amorphous semiconductors using spectroscopic ellipsometry, Thin Solid Films 2000;377-378:68-73. https://doi.org/10.1016/S0040-6090(00)01384-5.
- [23] Von Blanckenhagen B, Tonova D, Ullmann J, Application of the Tauc-Lorentz formulation to the interband absorption of optical coating materials, Appl Opt 2002;41:3137-3141. https://doi.org/10.1364/AO.41.003137.
- [24] Schmiedova V, Heinrichova P, Zmeskal O, Weiter M, Characterization of polymeric thin films for photovoltaic applications by spectroscopic ellipsometry, Appl Surf Sci 2015;349: 582-588. https://doi.org/10.1016/j.apsusc.2015.05.027.
- [25] Nizioł J, Thermal treatment effects imposed on solid DNA cationic lipid complex with hexadecyltrimethylammonium chloride, observed by variable angle spectroscopic ellipsometry, J Appl Phys, 2014; 116(23): 234701. https://doi.org/10.1063/1.4904196.
- [26] Tauc J, Grigorovici R, Vancu A, Optical properties and electronic structure of smorphous germanium, Phys Status Solidi B, 1966;15:627-637. https://doi.org/10.1002/pssb.19660150224.
- [27] Brenier, A, Kityk IV, Majchrowski A, Evaluation of Nd³⁺-doped BiB₃O₆ (BIBO) as a new potential self-frequency conversion laser crystal, Opt Commun, 2002; 203: 125-132. https://doi.org/10.1016/S0030-4018(01)01740-0.
- [28] Kityk IV, Wasylak J, Dorosz J, Kucharski J, Eu³⁺-doped glass materials for red luminescence, Opt Laser Technol, 2001; 33: 157-160. https://doi.org/10.1016/S0030-3992(01)00012-3.
- [29] Kityk IV, Wasylak J, Kucharski J, Dorosz D, PbO-Bi₂O₃-Ga₂O₃-BaO-Dy³⁺ glasses for IR luminescence, J Non Cryst Solids, 2002;297:285-289. https://doi.org/10.1016/S0022-3093(01)00930-9.
- [30] Liu J, Gao W, Kityk IV, Liu X, Zhen Z, Optimization of polycyclic electron donors based on julolidinyl structure in push-pull chromophores for second order NLO effects, Dyes and Pigments, 2015;122:74-84. https://doi.org/10.1016/j.dyepig.2015.06.007.
- [31] Kulhanek J, Bures F, Kuznik W, Kityk IV, Mikysek T, Ruzicka A, Ferrocene-Donor and 4,5-Dicyanoimidazole-Acceptor Moieties in Charge- Transfer Chromophores with p Linkers Tailored for Second-Order Nonlinear Optics. Chem Asian J, 2013;8:465-475. https://doi.org/10.1002/asia.201200963.

<u>Highlights</u>

- New, differently substituted, 1,3,5-triphenylpyrazolines dyes, were synthesised.
- DFT calculations for pyrazoline derivatives were made.
- Optical properties of the new materials were determined via ellipsometric way.
- Nonlinear properties of studied materials were determined.