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## **Multifunctional derivatives of dimethoxy-substituted triphenylamine containing different acceptor moieties**

Dalius Gudeika, Arturs Bundulis, Safia Benhattab, Marwa Ben Manaa, Nicolas Berton, Johann Bouclé, François Tran-Van, Bruno Schmaltz, Dmytro Volyniuk, Martins Rutkis, et al.

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Dalius Gudeika, Arturs Bundulis, Safia Benhattab, Marwa Ben Manaa, Nicolas Berton, et al.. Multifunctional derivatives of dimethoxy-substituted triphenylamine containing different acceptor moieties. *SN Applied Sciences*, 2020, 2 (3), pp.327. <10.1007/s42452-020-2120-x>. <hal-02474140>

**HAL Id: hal-02474140**

**<https://unilim.hal.science/hal-02474140v1>**

Submitted on 7 Oct 2024

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4 **Multifunctional derivatives of dimethoxy-substituted triphenylamine**  
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8 **containing different acceptor moieties**  
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42 *Gražulevičius).*  
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47 **Abstract**  
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52 Two compounds, having dimethoxy-substituted triphenylamino groups and fragments of cyanoacrylic  
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54 acid or rhodanine-3-acetic acid were prepared and characterized. Their optical, photophysical, thermal,  
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56 electrochemical, photoelectrical and nonlinear optical properties were investigated. Both derivatives  
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4 showed ability of glass-formation with glass transition temperatures of 83 and 61 °C. They showed  
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6 comparable ionization potential values of *ca.* 5.20 eV. The compounds showed Kerr and two photon  
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8 absorption effects. The dye containing a rhodanine-3-acetic acid fragment, namely 2-((E)-5-(4-  
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10 (diphenylamino)benzylidene)-tetrahydro-4-oxo-2-thioxothiophen-3-yl)acetic acid, exhibited a  
11  
12 promising power conversion efficiency of 2.09% in dye-sensitized solar cells using the spiro-  
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14 OMeTAD as hole transporting compound.  
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21 **Keywords:** dimethoxy-substituted triphenylamine, cyanoacrylic acid, rhodanine-3-acetic acid, dye-  
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23 sensitized solar cell, two photon absorption effect, Kerr effect.  
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## 28 **Introduction**

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33 In recent years, the investigation on solar cells using organic semiconducting derivatives has  
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35 made considerable advance [1]. Among the promising photovoltaic technologies, dye-  
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37 sensitized solar cells (DSSCs) have received much attention recently due to their low cost and  
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39 relatively high efficiency [2]. Generally, DSSCs are based on a photoelectrode sensitized by a  
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41 dye [3], where photo-induced electron transfers occur [3]. A counter electrode and a liquid  
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43 electrolyte complete the cell [4]. High efficiencies of *ca.* 13% were reached by employing a  
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45 metal complex redox couple (namely Co(II/III)tris(bipyridyl)) and organic dyes [4]. Hole  
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47 transporting materials (HTM) were successfully applied in solid state dye-sensitized solar cells  
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49 (ssDSSCs) which allow to avoid potential leakage problems associated with the volatile nature  
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51 of the liquid electrolyte [5,6]. During the last few years, spiro-OMeTAD has shown ascending  
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53 performance when related with organic dyes such as Y123 (7.2%) [7] and D102 (4.2%) [8].  
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4 However, the synthesis of these dyes requires a multistep procedures which are costly and time  
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6 consuming [9].  
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9 Most conventional organic dyes possess the push-pull structure of “donor-conjugated  
10 bridge-acceptor”. Typically, organic dyes used for efficient solar cells are required to afford  
11 intense and broad absorption in the visible spectral region. Aside from donor units, the electron  
12 acceptor plays a significant role in the performance control of DSSCs [10].  
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19 Recently, derivatives containing triphenylamino moieties as donor units have shown  
20 potential applications in photovoltaic devices [10]. Triphenylamino moiety is able to extend  
21 the light absorption capability of the dyes [11]. Moreover, triphenylamine is sustained as a  
22 perfect donor moiety in organic dyes, since it is able to demonstrate high hole-transporting and  
23 a perfect electron-donating capability [12]. Introducing an additional electron-donating moiety  
24 into derivative of triphenylamine can enhance charge separation, which result in high overall  
25 conversion efficiency [13]. Due to the certain peculiarities of the structure of triphenylamine,  
26 electron acceptor groups can be introduced. They can affect the molar extinction coefficients,  
27 absorption spectra, and the HOMO, LUMO energy levels of the derivatives. Rhodanine 3-  
28 acetic acid and cyanoacetic acid were introduced into triphenylamine-based dyes as acceptor  
29 moieties [14].  
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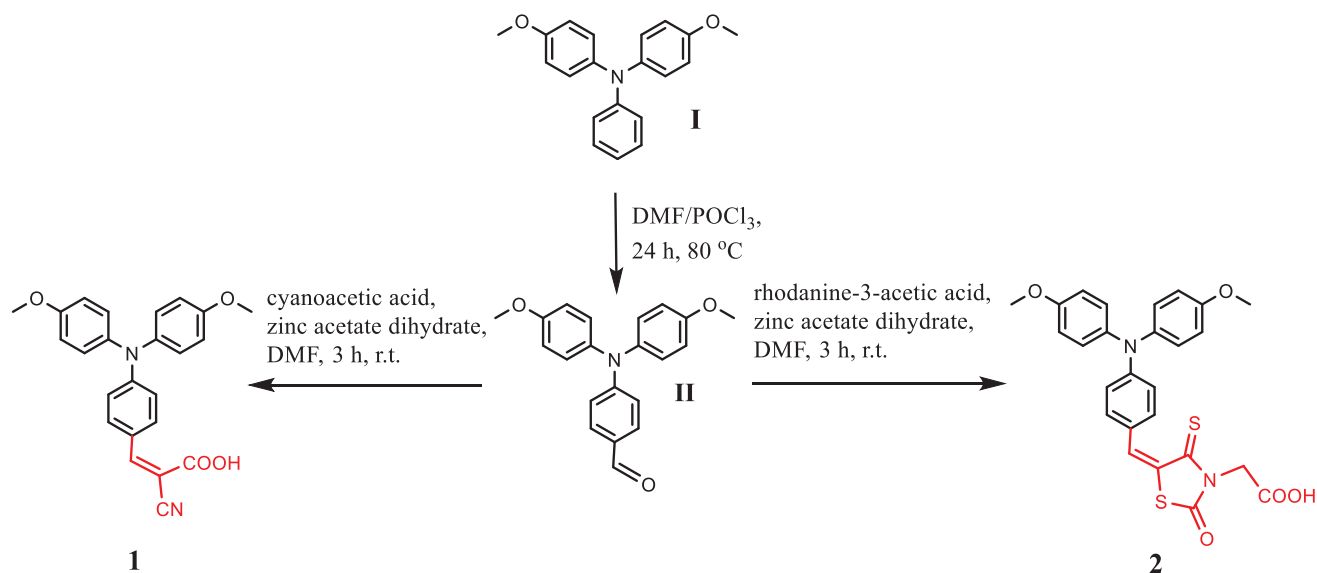
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46 As demand for new nonlinear optical (NLO) materials for optical data storage [15], optical data  
47 processing [16] and other NLO applications grows, more and more researches are dedicated to study  
48 NLO properties of different materials. Organic NLO materials have attracted great interest due to  
49 possibility to tune NLO properties by varying molecular structure. Although vast number of papers has  
50 already been published regarding structure-properties relations of organic NLO materials [17,18,19],  
51 still there is lack of qualitative criteria to theoretically design organic molecules for NLO applications.  
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4 On the other hand, in order to further improve the characteristics of triphenylamine sensitized solar  
5 cells, deeper insight should be committed to the structure-property relationships of triphenylamine-  
6 based of dyes. In this paper, easily synthesized dyes based on dimethoxy-substituted triphenylamines  
7 were obtained by a Knoevenagel condensation. Two different dyes containing cyanoacrylic acid  
8 (compound **1**) and rhodanine-3-acetic acid (compound **2**) moieties as an electron acceptors were  
9 prepared. These dyes show interesting electronic and optoelectronic properties and, as we show,  
10 constitute potential candidates to be used in solid state dye sensitized solar cells based using the  
11 structure of FTO/TiO<sub>2</sub>/Dye/Spiro-OMeTAD/Ag. In addition, we studied Kerr and two-photon  
12 absorption effects of the synthesized derivatives to understand how different acceptor groups influence  
13 NLO properties.  
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## 33 **Results and discussion**

### 34 **Synthesis**

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38 The intermediate derivative (**II**) was prepared by formylation reaction of the derivative of  
39 triphenylamine (**I**). Compounds **1** and **2** were synthesized by Knoevenagel condensation of the formyl  
40 derivative of triphenylamine (**II**) with cyanoacrylic acid or rhodanine-3-acetic acid, respectively in  
41 DMF using zinc acetate dihydrate (Scheme 1). The chemical structures of **1** and **2** were proved by IR,  
42 <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopies, mass spectrometry, elemental analysis. Derivatives are soluble  
43 in acetone, dichloromethane, THF, ethylacetate etc.  
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**Scheme 1.** Synthesis way to derivatives **1** and **2**.

### Thermal properties

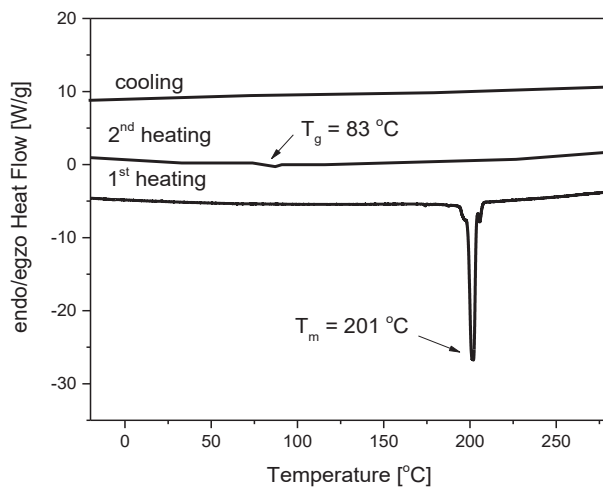
The thermal characteristics of **1** and **2** were obtained by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Derivatives **1**, **2** were obtained after the synthesis and purification as crystalline substances as confirmed by DSC. The DSC thermograms of **1** and **2** are shown in Fig. 1, Fig. S1. When the crystalline samples were heated in the first heating scan, the endothermic peaks due to melting were observed at 201 and 121 °C, respectively. When the melted samples were cooled down and heated again, glass transition temperatures were observed at 83 °C (for **1**) or 61 °C (for **2**). TGA revealed single-stage decomposition of compounds **1**, **2** (Fig. S1). Compound **1** showed considerably higher 5% weight loss temperature of 283 °C as compared with that of compound **2** (195 °C, Table 1). This observation can apparently be explained by the lower thermal stability of the rhodanine-3-acetic acid moiety relative to that of the fragment of cyanoacrylic acid. Higher thermal stability

of compound **1** can also be explained by the stronger intermolecular interaction in the solid state, which is evidenced by considerably higher melting point.

**Table 1.** Thermal characteristics of derivatives **1** and **2**.

Derivative	$T_m$ , [°C]	$T_g$ , [°C] (2 <sup>nd</sup> heating)	$T_{ID-5\%}$ , [°C]
<b>1</b>	201	83	283
<b>2</b>	121	61	195

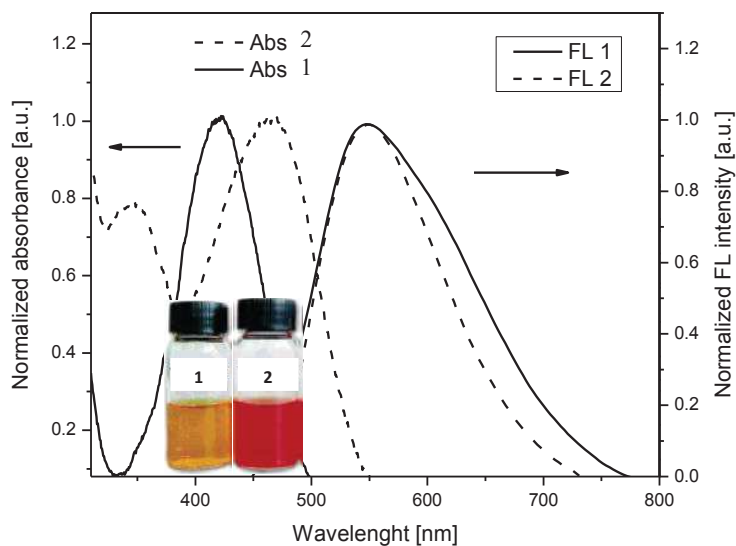
$T_g$  - glass transition point,  $T_m$  - melting point (10 °C/min, nitrogen atmosphere).  $T_{ID-5\%}$  is 5% (20 °C/min under nitrogen).



**Figure 1.** DSC thermograms of **1**.

## Optical properties

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4 UV absorption spectra of the dilute solutions of **1** and **2** in toluene ( $10^{-5}$  M) are shown in Fig.  
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31 **Figure 2.** Normalized UV and FL spectra of dilute solutions of **1** and **2** in toluene at 298 K.  
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36 Absorption intensity maxima at 424 and 466 nm observed in UV spectra of the solutions of  
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38 **1** and **2** can be assigned to an intramolecular charge transfer (ICT) between cyanoacrylic acid  
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40 or rhodanine-3-acetic acid moieties and triphenylamino unit [20,21]. UV spectrum of the  
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42 solution of compound **2** exhibited red-shift with respect of that of the solution of compound **1**.  
43  
44 The solution of compound **1** having cyanoacrylic acid moiety exhibited higher molar extinction  
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46 coefficients at the maximum absorption wavelength compared to those of compound **2**  
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48 containing rhodanine-3-acetic acid fragment. The relatively high molar extinction coefficient  
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50 of the solution of **1** ( $2.4 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ) indicates its good ability for light harvesting. The  
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52 optical band gap ( $E_{\text{opt}}^g$ ) of the solution of **1** (2.28 eV) was found to be lower than that of the  
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54 solution of **2** (2.52 eV, Table 2).  
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**Table 2.** UV and emission data of dilute solutions ( $10^{-5}$  M) of **1** and **2** in toluene.

Compound	$\lambda_{\max}^a$ , nm	$\varepsilon^b$ ( $10^4 \text{ M}^{-1} \text{ cm}^{-1}$ )	$\lambda_{\max}^c$ , nm	$\Phi_F^d$ , %	Stokes shift, nm	$E_g^{op}$ /eV <sup>e</sup>
<b>1</b>	424	2.4	552	19.56	128	2.28
<b>2</b>	466	1.8	553	14.25	87	2.52

<sup>a</sup> Wavelength of absorption maximum. <sup>b</sup>  $\varepsilon$  is the extinction coefficient at  $\lambda_{\max}$  of absorption. <sup>c</sup> Wavelength of photoluminescence emission maximum. <sup>d</sup> Fluorescence quantum yield. <sup>e</sup>  $E_g^{op} = 1240/\lambda_{\text{edge}}$ , where  $\lambda_{\text{edge}}$  is the wavelength of absorption edge in long wave direction.

The wavelengths of emission intensity maxima of the solutions of **1** and **2** were found to be close (552 and 553 nm, respectively). The Stokes shift of the solution of compound **1** (128 nm) was found to be considerably larger than that of the solution of **2** (87 nm). This observation can be attributed to the geometrically more relaxed structure of derivative **1** upon excitation [22]. The solutions of materials **1** and **2** showed relatively low fluorescence quantum yields (19.56 and 14.25%, respectively).

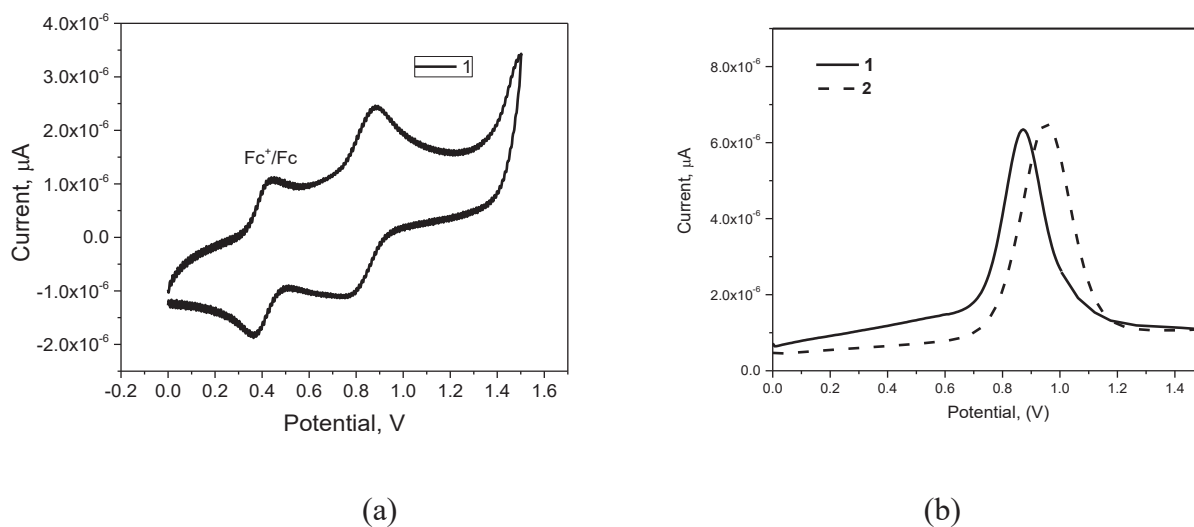
### Frontier orbitals, photoelectrical and electrochemical properties

Electrochemical properties of derivatives **1** and **2** were investigated by cyclic voltammetry (CV) using their  $1 \times 10^{-6}$  M solutions in dichloromethane. CVs of the derivatives are present in Fig. 3a, Fig. S2. The onset oxidation potential vs. Fc together with the values of the electron affinity ( $EA_{CV}$ ) and ionization potential ( $IP_{CV}$ ) values are listed in Table 3.

**Table 3.** Electrochemical characteristics of derivatives **1** and **2**.

Derivative	$E_{onset}^{ox}$ vs Fc/V <sup>a</sup>	IP <sub>CV</sub> /eV <sup>b</sup>	EA <sub>CV</sub> /eV <sup>b</sup>	IP <sub>PE</sub> /eV <sup>c</sup>
<b>1</b>	0.43	5.23	-2.91	5.26
<b>2</b>	0.38	5.18	-2.70	5.29

<sup>a</sup>  $E_{onset}^{ox}$  is oxidation potential vs. Fc/Fc<sup>+</sup>; <sup>b</sup> Ionization potential, electron affinity values estimated according to the equation  $IP_{CV} = -(E_{onset}^{ox} + 4.8)$ ; (where  $E_{onset}^{ox}$  is onset oxidation potential vs. the Fc<sup>+</sup>/Fc);  $EA_{CV} = -(|IP_{CV}| - E_g^{opt})$ ; <sup>c</sup> The values of ionization potentials (IP<sub>PE</sub>).



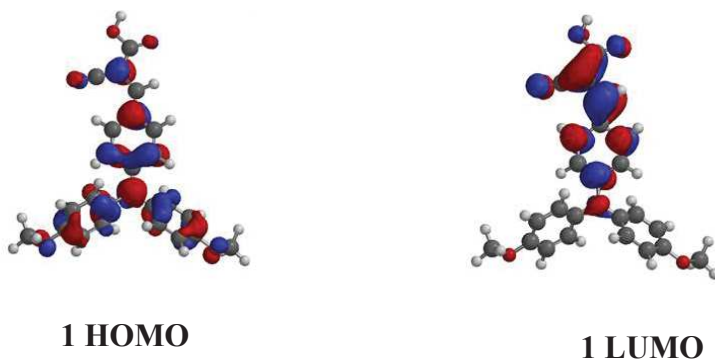
**Figure 3.** (a) CV of **1** recorded in an inert atmosphere (100 mV/s vs Ag/Ag<sup>+</sup>); (b) DPV curves of  $1 \times 10^{-6}$  M of compounds **1** and **2** in 0.1M Bu<sub>4</sub>NBF<sub>6</sub>/DCM electrolyte.

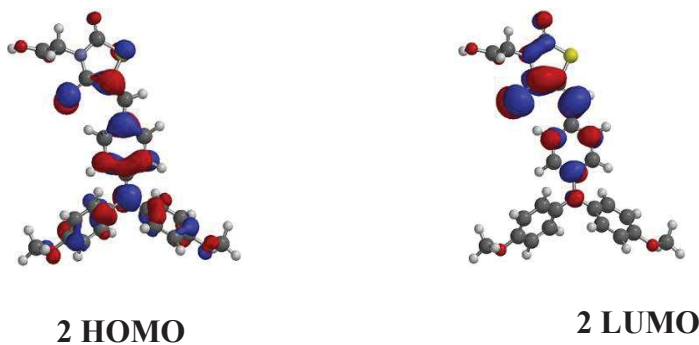
Oxidation of **1** and **2** is apparently related to the loss of electrons of TPA moiety, resulting in radical cations (one redox system) [23]. No reduction potentials were detected. Compound **1**

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4 displayed a reversible oxidation potential in positive potential range at 0.43 V, whereas **2**  
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6 showed a quasi-reversible oxidation potential at 0.38 V vs Fc. The presence of cyanoacrylic  
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8 acid moiety in compound **1** resulted in slightly higher oxidation potential and thus slightly  
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10 higher  $IP_{CV}$  value. The calculated  $EA_{CV}$  values for derivatives **1** and **2** were found to be -2.91  
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12 and -2.70 eV, respectively. In compound **1** the acceptor moiety apparently has stronger  
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14 influence on the electrochemical properties as compared to **2**. For this reason, **1** showed higher  
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16  $IP_{CV}$  values than compound **2**. These results are in agreement with the results of density  
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18 functional theory (DFT) calculations. The low energy absorption band of **1** appeared at lower  
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20 energy than that of **2**.

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27 Differential pulse voltamperometric (DPV [24]) spectra (Fig. 3b) of compounds **1** and **2**  
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29 showed peaks of oxidation processes. The oxidation potential peak (0.87 V) of **1** having  
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31 cyanoacrylic acid moiety was observed at a slightly higher potential compared to that of  
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33 compound **2** containing rhodanine-3-acetic acid moiety (0.96 V).  
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37 To investigate electron distribution of the compounds, their structures were optimized using DFT  
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39 calculations with Spartan 14 program [25]. The calculations were performed with the B3LYP under 6-  
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41 31G (d) basis set. Fig. 4 presents the frontier molecular orbitals of the compounds.

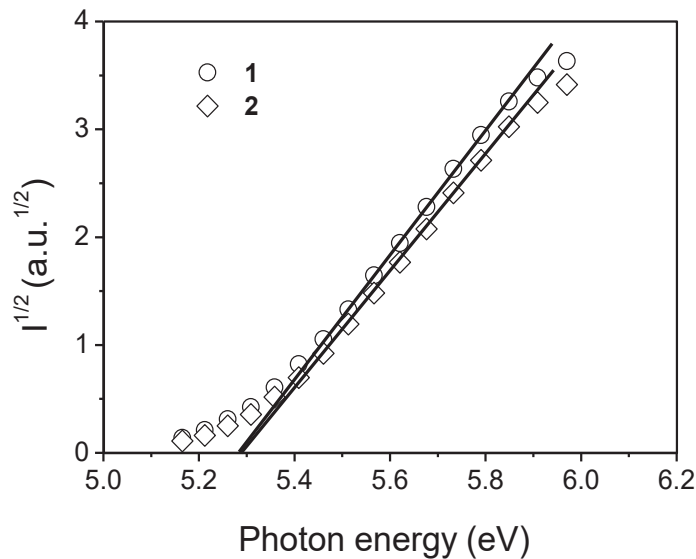




**Figure 4.** Molecular orbital distributions of **1** and **2**.

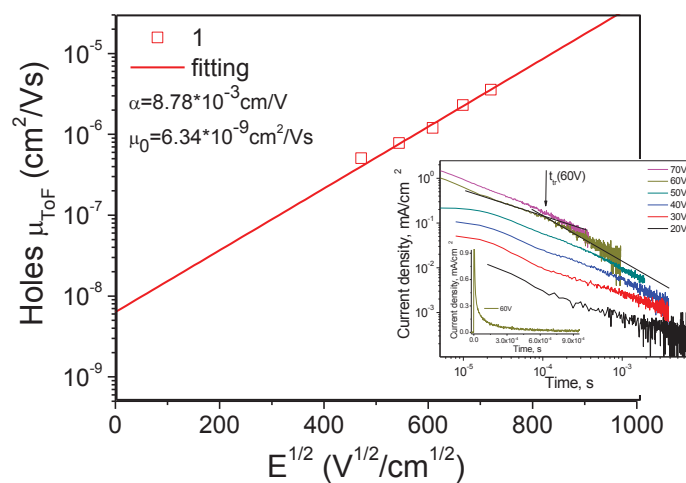
For both **1** and **2**, HOMOs are distributed over the whole molecular structures. LUMO of **1** and **2** are mainly concentrated on cyanoacrylic acid and rhodanine moieties, especially on carbonyl and thiocarbonyl groups, as well as on the neighbouring benzene rings. The energies of HOMO and LUMO for **1** were found to be -5.15 and -2.12 eV, respectively, and those estimated for **2** were -5.02 and -2.48 eV, respectively. It was found that the calculated values are in good agreement with the experimental CV data.

Ionization potential values of thin solid layers ( $IP_{PE}$ ) of derivatives **1**, **2** were estimated by photoelectron emission spectrometry. Photoelectron emission spectra of the solid layers of **1**, **2** are depicted in Fig. 5. The  $IP_{PE}$  values of the solid samples of **1** and **2** were found to be comparable (5.26 and 5.29 eV, respectively).



**Figure 5.** Photoelectron emission spectra of the solid films of **1** and **2**.

Charge-transporting properties of the layers of compound **1** were studied by time-of-flight (TOF) technique. To prepare the sample with the structure of ITO/organic layer/Al, the layer of compound **1** the sample was deposited by thermovacuum method. It was not possible to prepare the sample of compound **2** for the TOF measurements by the same method, apparently due to its relatively low thermal stability (Table 1). Hole drift mobility of  $3.4 \times 10^{-6} \text{ cm}^2/\text{Vs}$  at electric field of  $5.2 \times 10^5 \text{ V/cm}$  was obtained for compound **1**. Hole mobilities of the layer of **1** were found to be strongly dependent upon electric field. This dependence could be well described by a Poole-Frenkel type mobility using formula  $\mu = \mu_0 e^{\alpha \sqrt{E}}$  [26]. Zero-field mobilities ( $\mu_0$ ) and field dependence parameter ( $\alpha$ ) are given in Fig. 6. Relatively high dependence of hole mobilities versus electric field for derivative **1** can apparently be explained by the dispersive hole transport which is betrayed by TOF transients shown in the insert of Fig. 6.



**Figure 6.** Electric field dependence of hole drift mobility for the layer of derivative **1**. Insert shows TOF transients for hole transport and one of the transient curves in the linear plot.

## NLO properties

Kerr and two-photon absorption effects describe materials refractive index and absorption changes, respectively, due to optical irradiance:

$$n = n_0 + n_2 I, \quad (1)$$

$$\alpha = \alpha_0 + \alpha_2 I, \quad (2)$$

where  $n_0$  is linear refractive index,  $\alpha_0$  - linear absorption coefficient,  $n_2$  - Kerr coefficient,  $\alpha_2$  is TPA coefficient and  $I$  is optical intensity.

We studied Kerr and two-photon absorption effects of selected molecules to better understand how different acceptor groups influence third-order NLO properties. Organic molecules were dissolved in chloroform and contained in 2 mm thick optical quartz cells.

To study Kerr and two-photon absorption effects we implemented the Z-scan method. Details regarding experimental setup can be found in reference [27]. Laser beam was focused using lens with 11 cm focal length. Light transmitted through sample was measured simultaneously with open-aperture detector and closed-aperture detector with 1 mm aperture separating less than 1 % of incident light. Laser beam waist radius at focus was calculated to be  $w_0=26 \mu\text{m}$ . This allowed to employ thin-sample approximation for data fitting [27]. To acquire Kerr and two-photon absorption coefficients from experimental data we employed analytical expressions derived using Gaussian decomposition method [28]. During Z-scan experiment we measured how materials transmittance changes due to optical irradiance. For Kerr effect transmittance can be expressed as:

$$T(z)=1+\frac{4\Delta\Phi\frac{z}{z_0}}{\left(\frac{z^2}{z_0^2}+1\right)\left(\frac{z^2}{z_0^2}+9\right)}, \quad (3)$$

where  $z$  - sample position,  $z_0$  - Rayleigh length and  $\Delta\Phi$  is phase change defined as:

$$\Delta\Phi=kn_2L_{\text{eff}}I, \quad (4)$$

where  $k$  - wave number and  $L_{\text{eff}}$  - effective sample length defined as:

$$L_{\text{eff}}=\frac{1-e^{-\alpha L}}{\alpha}, \quad (5)$$

In case of TPA, transmittance of measured medium can be expressed as:

$$T(z)=\sum_{m=0}^{\infty}\frac{\left(\frac{q}{\left(1+\frac{z^2}{z_0^2}\right)}\right)^m}{(m+1)^{3/2}}, \quad (6)$$

where  $q$  is TPA amplitude defined as:

$$q=\alpha_2L_{\text{eff}}I, \quad (7)$$

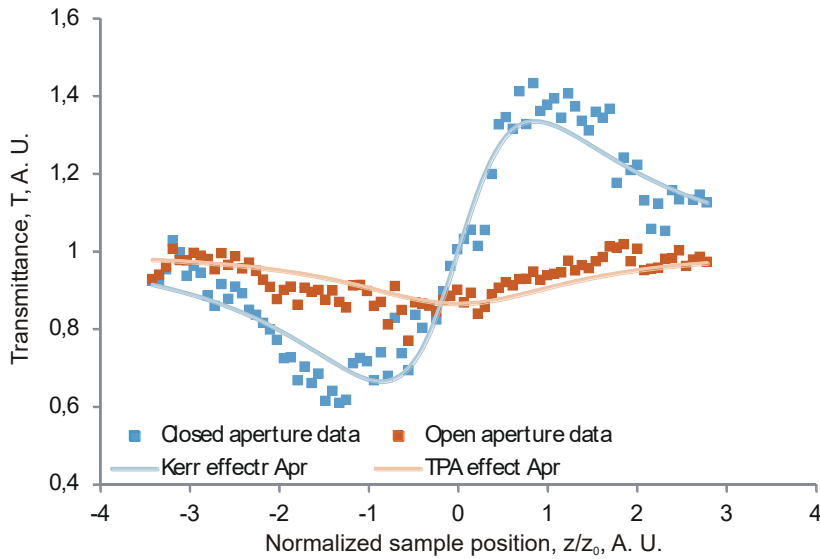
While TPA coefficient allows us to compare different NLO sample, it does not allow us to compare molecules. For this we calculated two-photon absorption cross-section values that characterize single

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4 molecule contribution to two-photon absorption effect. Two-photon absorption cross-section can be  
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6 calculated using the following equation [29]:  
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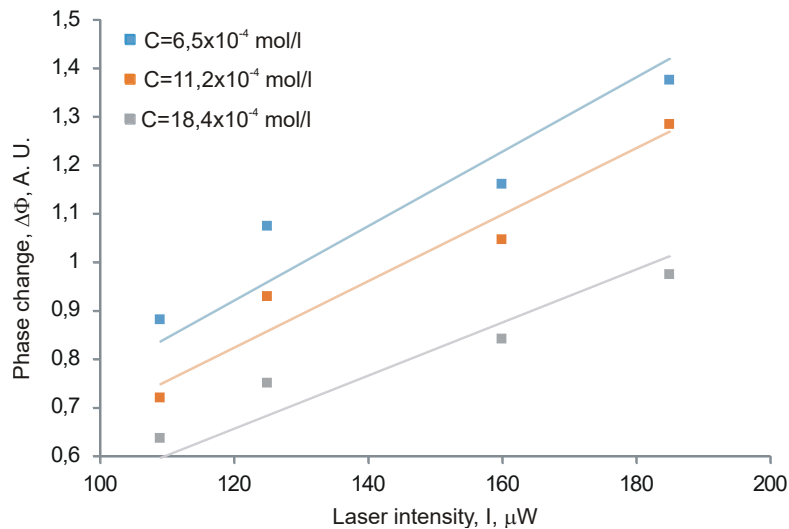
$$\sigma_{\text{TPA}} = \frac{h\nu}{N} \alpha_2, \quad (8)$$

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11 where  $h\nu$  is photon energy and  $N$  molecule concentration per  $\text{cm}^3$ . To use analytical equations (3) and  
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13 (6) NLO medium needs to fit weak nonlinear model for which two conditions need to be satisfied -  
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15 phase change  $|\Delta\Phi| < \pi$  and two-photon absorption amplitude  $|q| < 1$  [28].  
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20 Example for compound **1** experimental data is shown in Fig. 7. Phase changes for different  
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22 concentration samples in case of **1** are shown in Fig. 8. It is evident that by increasing compound **1**  
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24 concentration the phase changes decrease. This leads to conclusion that compound **1** possess negative  
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26 Kerr coefficient. Acquired values for NLO coefficients for all molecules are listed in Table 4.  
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52 **Figure 7.** Z-scan experimental data for **1** fitted with corresponding analytical  
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54 approximations (Apr).  
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**Figure 8.** Phase change  $\Delta\Phi$  as function of laser intensity.

**Table 4.** Kerr, TPA and two-photon absorption cross-section values of studied molecules.

Compound	M, g/mol	$n_2$ , $\text{cm}^2/\text{W} \cdot 10^{-12}$	$\alpha_2$ , $\text{cm}/\text{W} \cdot 10^{-8}$	$\sigma_{\text{TPA}}$ , GM
<b>I</b>	305.37	$0.106 \pm 0.023$	-	-
<b>II</b>	333.38	$0.249 \pm 0.035$	-	-
<b>1</b>	400.427	$-1.875 \pm 0.22$	$7.10 \pm 0.86$	$592 \pm 72$
<b>2</b>	506.593	$-1.93 \pm 0.20$	-	-

Real and imaginary parts of third-order susceptibility can be defined as [30]:

$$\chi_{\text{Re}}^{(3)} = \left(4 \cdot \frac{\varepsilon_0 \cdot c \cdot n_0^2}{3}\right) \cdot n_2 \left(\frac{\text{m}}{\text{W}}\right), \quad (9)$$

$$\chi_{\text{Im}}^{(3)} = \left(\frac{\varepsilon_0 \cdot c \cdot n_0^2 \cdot \lambda}{3 \cdot \pi}\right) \cdot \alpha_2 \left(\frac{\text{m}}{\text{W}}\right), \quad (10)$$

where  $\lambda$  - laser wavelength,  $\varepsilon_0$  - vacuum dielectric constant,  $n_0$  - refractive index and  $c$  - speed of light.

Additionally, we carried out quantum chemical calculations of second-order hyperpolarizability real

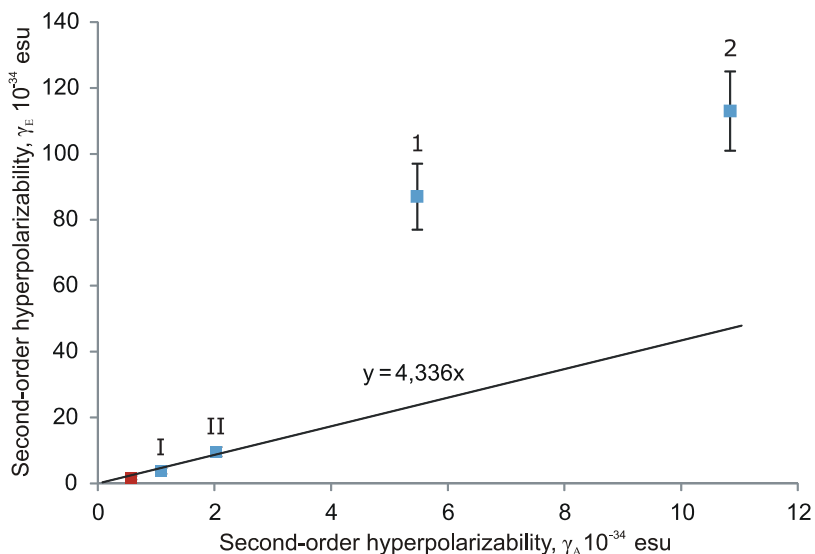
part  $\gamma_A$  using CPKS method in Gaussian 9. Further information about calculation parameters can be found in [27]. Experimental values for second-order hyperpolarizability were calculated using equation (11) and presented alongside third-order susceptibility values in Table 5 [31].

$$\gamma_E = \frac{\chi_{Re}^{(3)}}{\left[\frac{1}{3}(n_0^2+2)\right]^4 \cdot N}, \quad (11)$$

**Table 5.** Real and imaginary part of third order susceptibility and absolute experimental and quantum calculation values of second-order hyperpolarizability. For the comparison, the second-order hyperpolarizability values of triphenylamine are given.

Compound	$\chi_{Re}, m^2/V^2 \cdot 10^{-19}$	$\chi_{Im}, m^2/V^2 \cdot 10^{-19}$	$\gamma_A, esu \cdot 10^{-34}$	$ \gamma_E , esu \cdot 10^{-34}$
Triphenylamine				
[27]			0.58	1.69±0.57
<b>I</b>	1.085±0.24	-	1.09445	3.74±0.81
<b>II</b>	2.55±0.35	-	2.0351	9.6±1.4
<b>1</b>	-19.2±2.2	6.23±0.76	5.47653	87±10
<b>2</b>	-19.8±2.1	-	10.84	113±12

From all of the molecules only compound **1** possesses two-photon absorption coefficient due to considerable absorption at 532 nm. By comparing the values of Kerr coefficient it is evident that by adding a stronger acceptor group we increase the magnitude of Kerr effect. Experimental and quantum calculation values for second-order hyperpolarizability are shown in Fig. 9.



**Figure 9.** Experimental and quantum calculation values of second-order hyperpolarizability. Blue point indicate molecules studied in this paper while red dot indicates triphenylamine studied in our previous paper [32].

It is evident that derivatives **I** and **II** gives a similar slope values as other derivatives of triphenylamine reported in other papers [27,32]. At the same time, derivatives **1** and **2** displays much larger difference between experimental and quantum calculation values. We speculate that this is due to aggregation processes that can lead to larger third-order NLO values. Similar enhancement of NLO properties due to aggregation has been previously reported in literature [33].

### Photovoltaic properties

The photovoltaic properties of compounds **1** and **2**, used as dyes, were investigated by fabricating solid-state dye sensitized solar cells with spiro-OMeTAD as p-type organic hole transporting material (HTM). The device structure was FTO/TiO<sub>2</sub>/Dye/Spiro-OMeTAD/Ag.

Knowing the IP values of 5.23 and 5.18 eV and the EA values of 2.91 and 2.70 eV, respectively for **1** and **2**, we can expect that these dyes would be suitable i) for electron transfer to the TiO<sub>2</sub> nanostructured electrode as well as ii) to be regenerated by HTM. In comparison, IP and EA values of **D102** are 5.32 and 3.38 eV respectively [34]. EA values of the new dyes are expected to prevent any electron transfer from the dye to the LUMO of the spiro-OMeTAD (EA value of the HTM is 2.05 eV) [35]. In summary, the energy levels of the synthesized dyes are clearly well suited for FTO/TiO<sub>2</sub>/Dye/Spiro-OMeTAD/Ag device.

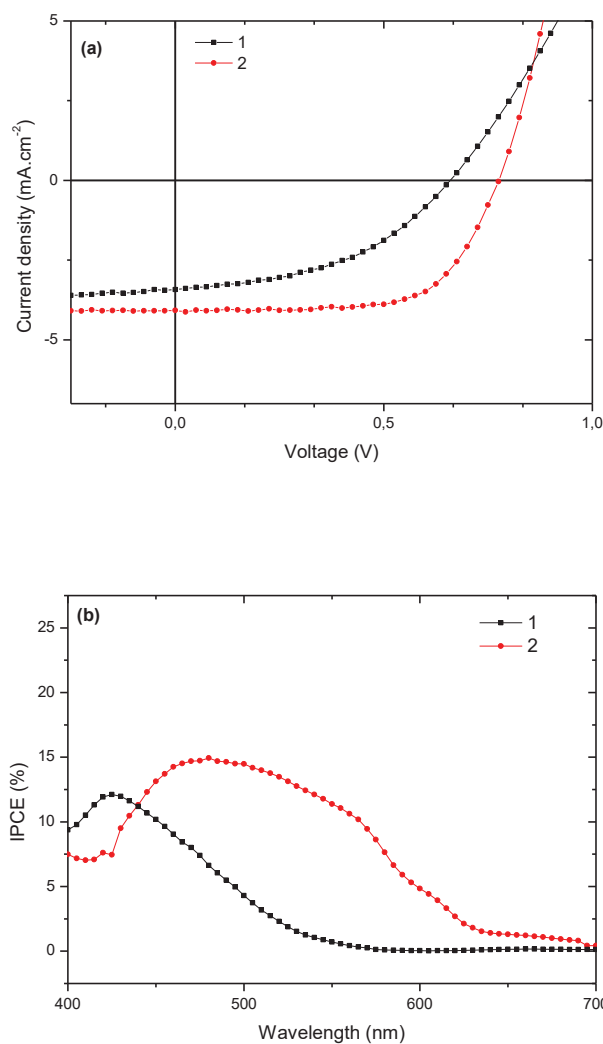
Usually, the solvent used to prepare the solution of **D102** is a mixture of acetonitrile and *tert*-butanol (ACN/*tert*-BuOH). The solution of dye **1** has been prepared and deposited under these conditions. Nevertheless, dye **2** was found to be hardly soluble in this solvent mixture. That is why THF as solvent was preferred for dye **2**. The same dye concentration (0.06 mM) was chosen for both compounds **1** and **2**.

**Table 6.** Photovoltaic characteristics of the devices FTO/TiO<sub>2</sub>/Dye/Spiro-OMeTAD/Ag with dye **1** (in ACN/*tert*-butanol) and **2** (in THF).

Parameters	<b>1</b>	<b>2</b>
<b>V<sub>oc</sub> (V)</b>	0.65	0.68
<b>J<sub>sc</sub> (mAcm<sup>-2</sup>)</b>	3.39	4.08
<b>FF</b>	0.46	0.66
<b>PCE (%)</b>	1.02	2.09

Fig. 10a shows photocurrent-voltage curves and IPCE spectra of **1**- and **2**-sensitized DSSCs. Photovoltaic parameters are summarized in Table 6. Photocurrent of the **2**-sensitized DSSC is

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4 higher than that of the **1**-sensitized one, which is due to more delocalized electron distribution  
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6 in the HOMO state (see Fig. 4). The open-circuit voltage ( $V_{OC}$ ) are of ca. 0.65 V for both dyes.  
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8 The higher  $V_{OC}$  (0.80 V) observed for the organic **D102** dye (Table S1) is probably related to  
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10 the recombination kinetics at the  $TiO_2$ /Dye/HTM interface. Indeed, the energy offset for  
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12 electron injection from the LUMO level of the dye to the  $TiO_2$  conduction band is found to be  
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14 much larger for compounds **1** and **2** compared to **D102**, which can explain a substantial energy  
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16 loss of the photo-excited electrons. Moreover, the energy difference between the LUMO of  
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18 compound **2** (and in less extend of compound **1**) and LUMO level of spiro-OMeTAD is largely  
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20 reduced compared to **D102** (Fig. S3). The energy barrier for direct electron injection to spiro-  
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22 OMeTAD is therefore reduced, which can favor charge recombination and prevent efficient  
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24 charge injection. Such phenomenon is in agreement with the larger dark current observed  
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26 under reverse applied voltage (see Fig. S4). Finally, although the power conversion efficiency  
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28 of the devices with dye **1** is quite low (1.02%), the devices built with dye **2** show interesting  
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30 PCE (2.09%), close to that **D102** reference (2.47%). The limited PCE for the devices built with  
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32 dye **1** is most likely due to the blue-shift in optical absorption, which is less favorable for  
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34 efficient charge generation. Since the maximum of absorption of **1** is shifted to lower  
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36 wavelengths compared to those of **D102** and **2**, we can observe the beginning of a screen effect  
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38 (overlapping of both dye and HTM absorption). Although several devices have been prepared  
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40 (Fig. S5) and even if the PCE are lower than that of the **D102** reference dye without further  
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42 optimizations (i.e. in concentration), the results show a promising tendency for both dyes.  
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**Figure 10.** (a) Photocurrent density-voltage curves under illumination and (b) incident photon-to-current conversion efficiency (IPCE) spectra of **1**- and **2**-sensitized DSSCs.

Fig. 10b shows the external quantum efficiency (EQE) spectra of the solid-state DSSC [FTO/TiO<sub>2</sub>/Dye/Spiro-OMeTAD/Ag] containing **1** and **2**, recorded under the monochromatic illumination. The devices based on **2** show a broad response which extends up to 650 nm, while compound **1** only exploits incoming photons up to 520 nm. The IPCE spectra are in

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4 agreement with the optical absorption data, where the maximum absorption of dye **1** is blue-  
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6 shifted leading to an increased screening effect of the solar light. IPCE shows clearly that dye **2**  
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8 is better suited in terms of absorption for solid-state DSSC.  
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## 10 11 12 13 14 **Conclusions**

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19 Dimethoxy-substituted triphenylamine derivatives containing cyanoacrylic acid and rhodanine-  
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21 3-acetic acid moieties were synthesized by Knoevenagel condensation. The target derivatives  
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23 form molecular glasses with glass transition temperatures of 83 and 61 °C. They show  
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25 moderate thermal stability with the temperatures of degradation onsets of 283 and 195 °C. The  
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27 cyclic voltammetry measurements revealed close ionization potential (5.23 and 5.18 eV) and  
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29 electron affinity values (-2.91 and -2.70 eV) in the solid state. The layer of derivative  
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31 containing cyanoacrylic acid moiety showed time-of-flight hole drift mobility of  $3.4 \times 10^{-6}$   
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33  $\text{cm}^2/\text{Vs}$  at electric field of  $5.2 \times 10^5$  V/cm. This compound also showed two-photon absorption  
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35 effect as it was the only compound exhibiting considerable absorption at 532 nm. Compounds  
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37 containing acceptor groups possessed larger nonlinear refractive index values than dimethoxy  
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39 substituted triphenylamines. Dye sensitized solar cells with the structure FTO/TiO<sub>2</sub>/Dye/Spiro-  
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41 OMeTAD/Ag were fabricated using the synthesized compounds as dyes. The photovoltaic  
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43 properties of the devices were found to be in agreement with the electronic and optical  
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45 properties. The dye containing a rhodanine-3-acetic acid moiety exhibited a promising power  
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47 conversion efficiency of 2.09% in solid state dye sensitized solar cell using the spiro-OMeTAD  
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49 as hole transporting compound.  
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4 **Compliance with ethical standards**  
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9 *Conflict of interest.* The authors declare that they have no conflict of interest.  
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14 **Acknowledgements**  
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19 This research was funded by the Région Centre, the Tunisian ministry of research, University of  
20 Monastir and the French ministry of Higher Education and Research. J. Bouclé would like to thank the  
21 Sigma-Lim LabEx environment for financial supports, and the PLATINOM facility at XLIM  
22 laboratory regarding device fabrication and characterizations. This research was funded by a grant  
23 (No. S-LZ-19-2) from the Research Council of Lithuania.  
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## 53 LIST

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56 **Table 1.** Thermal characteristics of derivatives **1** and **2**.

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59 **Table 2.** UV and emission data of dilute solutions ( $10^{-5}$  M) of **1** and **2** in toluene.  
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6 **Table 3.** Electrochemical characteristics of compounds **1** and **2**.

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8 **Table 4.** Kerr, TPA and TPA cross-section values of studied molecules.

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10 **Table 5.** Real and imaginary part of third order susceptibility and absolute experimental and quantum  
11 calculation values of second-order hyperpolarizability. For the comparison, the second-order  
12 hyperpolarizability values of triphenylamine are given.  
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16 **Table 6.** Photovoltaic characteristics of the devices FTO/TiO<sub>2</sub>/Dye/Spiro-OMeTAD/Ag with dye **1** (in  
17 ACN/*tert*-butanol) and **2** (in THF).  
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21 **Figure 1.** DSC thermograms of **1**.

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23 **Figure 2.** Normalized UV and FL spectra of dilute solutions of **1** and **2** in toluene at 298 K.

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25 **Figure 3.** (a) CV of **1** recorded in an inert atmosphere (100 mV/s vs Ag/Ag<sup>+</sup>); (b) DPV curves of  
26 1×10<sup>-6</sup> M of compounds **1** and **2** in 0.1M Bu<sub>4</sub>NBF<sub>6</sub>/DCM electrolyte.  
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30 **Figure 4.** Molecular orbital distributions of **1** and **2**.

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32 **Figure 5.** Photoelectron emission spectra of the solid films of **1** and **2**.

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34 **Figure 6.** Electric field dependence of hole drift mobility for the layer of derivative **1**. Insert shows  
35 TOF transients for hole transport and one of the transient curves in the linear plot.  
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39 **Figure 7.** Z-scan experimental data for **1** fitted with corresponding analytical approximations (Apr).  
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43 **Figure 8.** Phase change  $\Delta\Phi$  as function of laser intensity.

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45 **Figure 9.** Experimental and quantum calculation values of second-order hyperpolarizability. Blue  
46 point indicate molecules studied in this paper while red dot indicates triphenylamine studied in our  
47 previous paper [35].  
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51 **Figure 10.** (a) Photocurrent density-voltage curves under illumination and (b) incident photon-to-  
52 current conversion efficiency (IPCE) spectra of **1**- and **2**-sensitized DSSCs.  
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## LIST OF TABLES

**Table 1.** Thermal characteristics of derivatives **1** and **2**.

Derivative	T <sub>m</sub> , [°C]	T <sub>g</sub> , [°C] (2 <sup>nd</sup> heating)	T <sub>ID-5%</sub> , [°C]
<b>1</b>	201	83	283
<b>2</b>	121	61	195

T<sub>g</sub> - glass transition point, T<sub>m</sub> - melting point (10 °C/min, nitrogen atmosphere). T<sub>ID-5%</sub> is 5% (20 °C/min under nitrogen).

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**Table 2.** UV and emission data of dilute solutions (10<sup>-5</sup> M) of **1** and **2** in toluene.

Compound	λ <sub>max</sub> <sup>a</sup> , nm	ε <sup>b</sup> (10 <sup>4</sup> M <sup>-1</sup> cm <sup>-1</sup> )	λ <sub>max</sub> <sup>c</sup> , nm	Φ <sub>F</sub> <sup>d</sup> , %	Stokes shift, nm	E <sub>g</sub> <sup>op</sup> /eV <sup>e</sup>
<b>1</b>	424	2.4	552	19.56	128	2.28
<b>2</b>	466	1.8	553	14.25	87	2.52

<sup>a</sup> Wavelength of absorption maximum. <sup>b</sup> ε is the extinction coefficient at λ<sub>max</sub> of absorption. <sup>c</sup> Wavelength of photoluminescence emission maximum. <sup>d</sup> Fluorescence quantum yield. <sup>e</sup> E<sub>g</sub><sup>op</sup> = 1240/λ<sub>ed</sub><sub>ge</sub>, where λ<sub>edge</sub> is the wavelength of absorption edge in long wave direction.

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**Table 3.** Electrochemical characteristics of derivatives **1** and **2**.

Derivative	$E_{onset}^{ox}$ vs Fc /V <sup>a</sup>	IP <sub>CV</sub> /eV <sup>b</sup>	EA <sub>CV</sub> /eV <sup>b</sup>	IP <sub>PE</sub> /eV <sup>c</sup>
<b>1</b>	0.43	5.23	-2.91	5.26
<b>2</b>	0.38	5.18	-2.70	5.29

<sup>a</sup>  $E_{onset}^{ox}$  is oxidation potential vs. Fc/Fc<sup>+</sup>; <sup>b</sup> Ionization potential, electron affinity values estimated according to the equation  $IP_{CV} = -(E_{onset}^{ox} + 4.8)$ ; (where  $E_{onset}^{ox}$  is onset oxidation potential vs. the Fc<sup>+</sup>/Fc);  $EA_{CV} = -(|IP_{CV}| - E_g^{opt})$ ; <sup>c</sup> The values of ionization potentials (IP<sub>PE</sub>).

**Table 4.** Kerr, TPA and TPA cross-section values of studied molecules.

Compound	M, g/mol	$n_2$ , cm <sup>2</sup> /W*10 <sup>-12</sup>	$\alpha_2$ , cm/W*10 <sup>-8</sup>	$\sigma_{TPA}$ , GM
<b>I</b>	305.37	0.106±0.023	-	-
<b>II</b>	333.38	0.249±0.035	-	-
<b>1</b>	400.427	-1.875±0.22	7.10±0.86	592±72
<b>2</b>	506.593	-1.93±0.20	-	-

**Table 5.** Real and imaginary part of third order susceptibility and absolute experimental and quantum calculation values of second-order hyperpolarizability. For the comparison, the second-order hyperpolarizability values of triphenylamine are given.

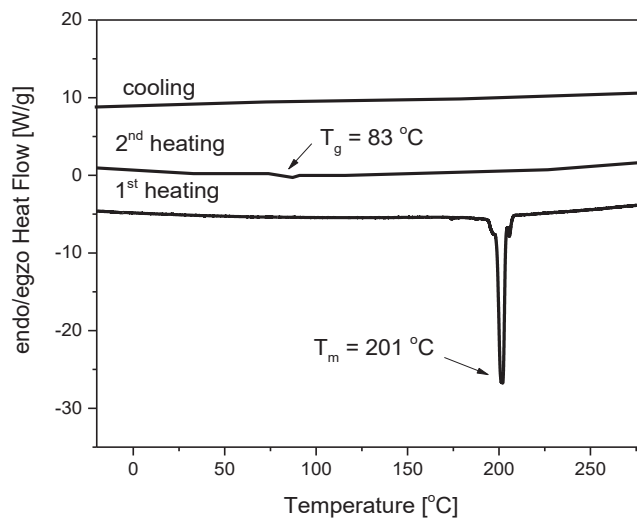
Compound	$\chi_{Re}, m^2/V^2 \cdot 10^{-19}$	$\chi_{Im}, m^2/V^2 \cdot 10^{-19}$	$\gamma_A, esu \cdot 10^{-34}$	$ \gamma_E , esu \cdot 10^{-34}$
Triphenylamine				
[22]			0.58	1.69±0.57
<b>I</b>	1.085±0.24	-	1.09445	3.74±0.81
<b>II</b>	2.55±0.35	-	2.0351	9.6±1.4
<b>1</b>	-19.2±2.2	6.23±0.76	5.47653	87±10
<b>2</b>	-19.8±2.1	-	10.84	113±12

**Table 6.** Photovoltaic characteristics of the devices FTO/TiO<sub>2</sub>/Dye/Spiro-OMeTAD/Ag with dye **1** (in ACN/*tert*-butanol) and **2** (in THF).

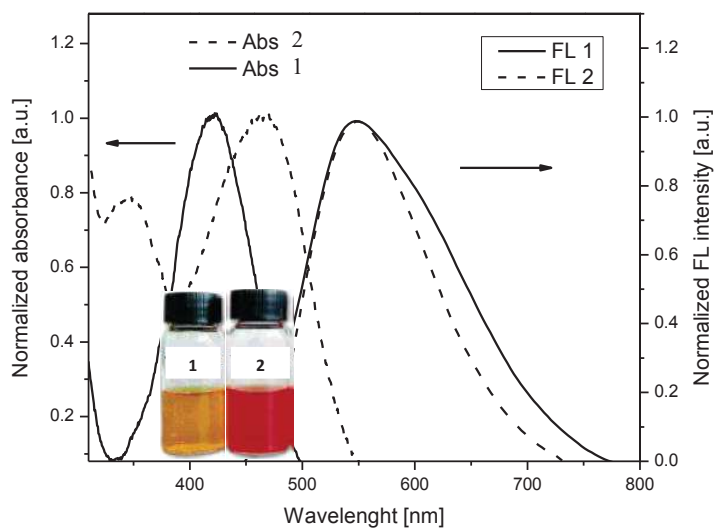
Parameters	<b>1</b>	<b>2</b>
<b>V<sub>oc</sub> (V)</b>	0.65	0.68
<b>J<sub>sc</sub> (mAcm<sup>-2</sup>)</b>	3.39	4.08
<b>FF</b>	0.46	0.66
<b>PCE (%)</b>	1.02	2.09

## LIST OF FIGURES

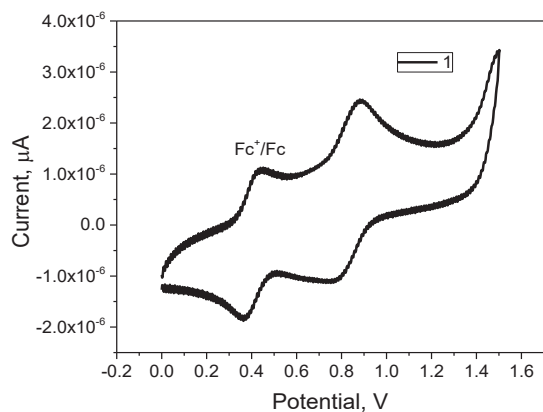
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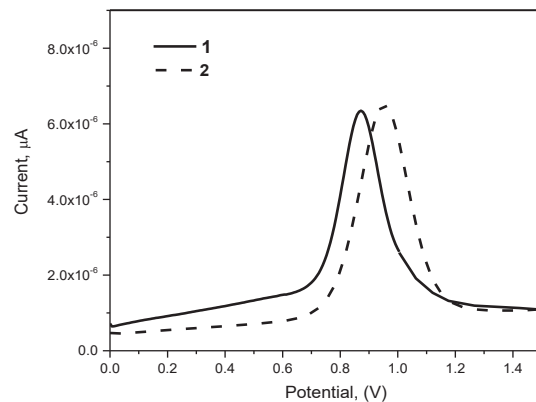
**Figure 1.** DSC thermograms of **1**.



**Figure 2.** Normalized UV and FL spectra of dilute solutions of **1** and **2** in toluene at 298 K.

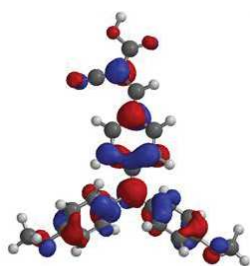
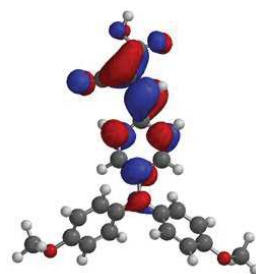
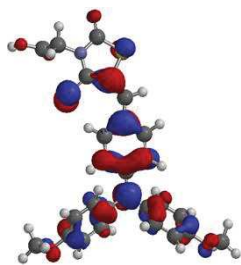
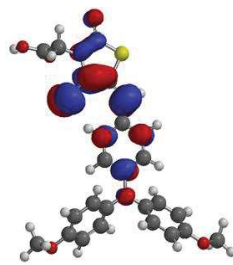


(a)

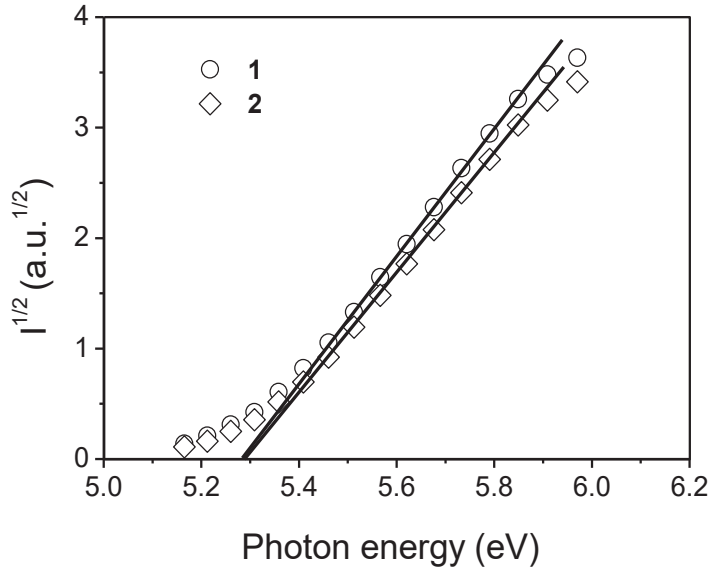


(b)

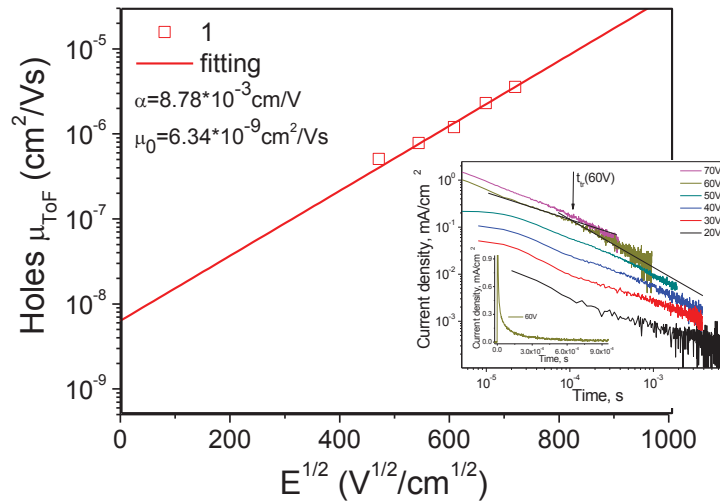
**Figure 3.** (a) CV of **1** recorded in an inert atmosphere (100 mV/s vs Ag/Ag<sup>+</sup>); (b) DPV curves of  $1 \times 10^{-6}$  M of compounds **1** and **2** in 0.1M Bu<sub>4</sub>NBF<sub>6</sub>/DCM electrolyte.

**1 HOMO****1 LUMO****2 HOMO****2 LUMO**

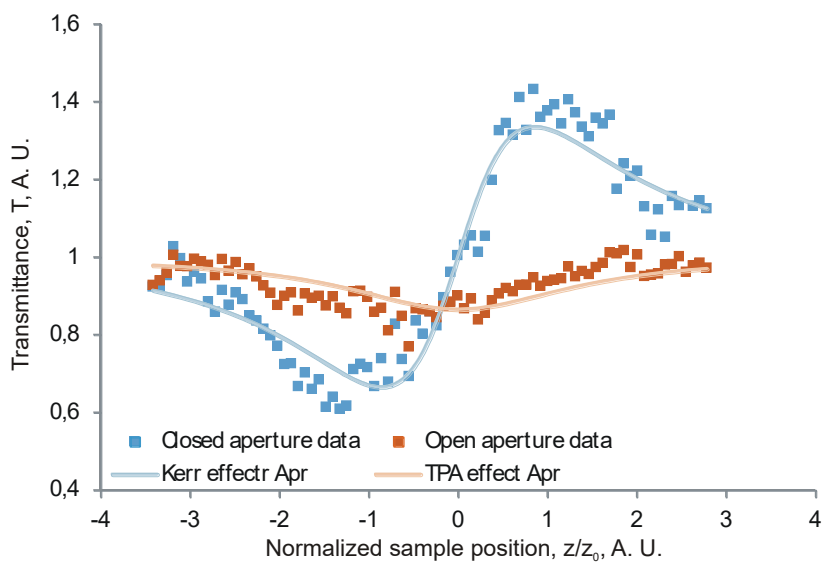
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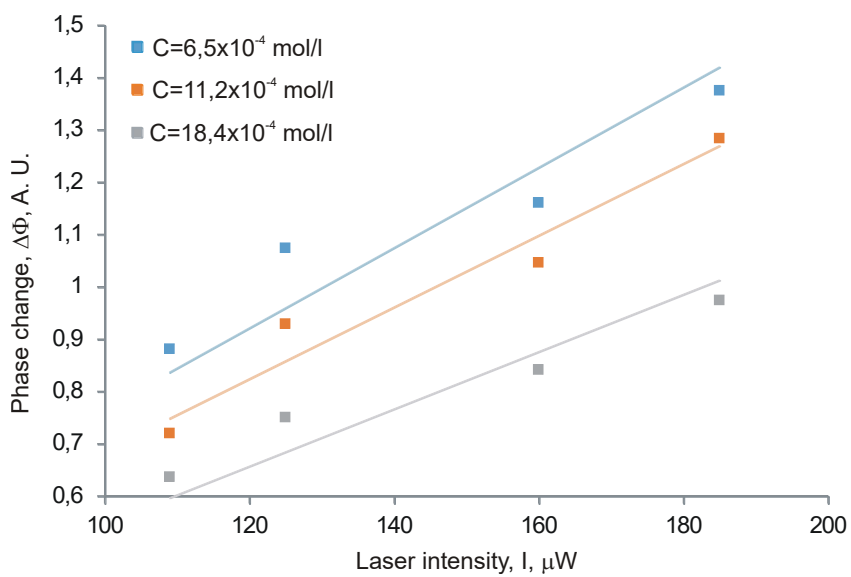
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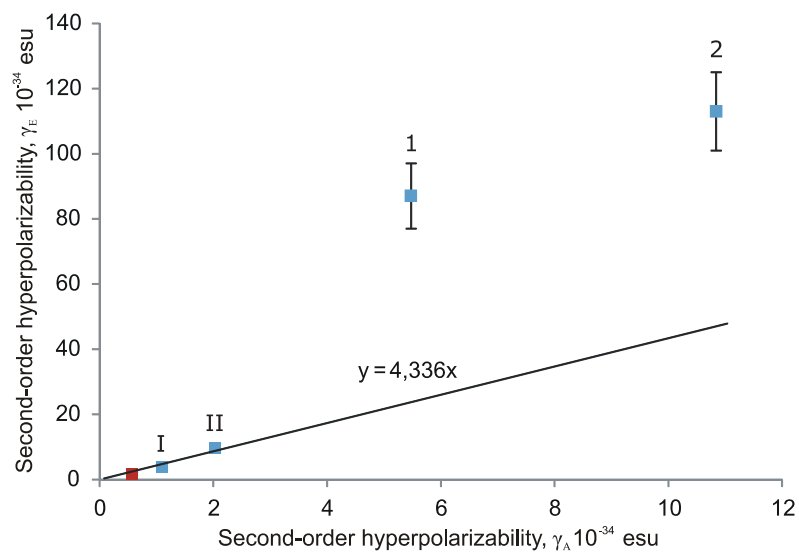


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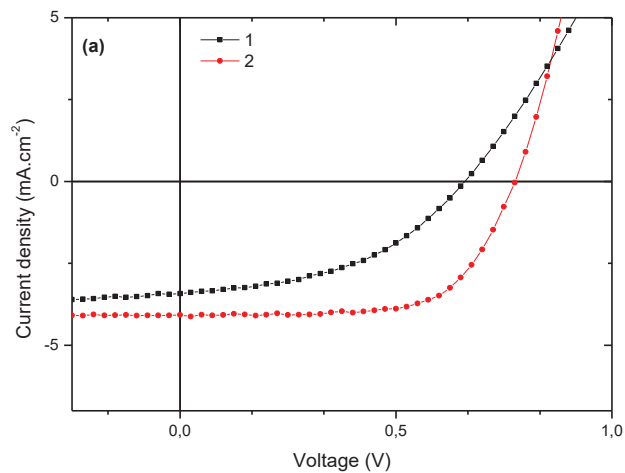


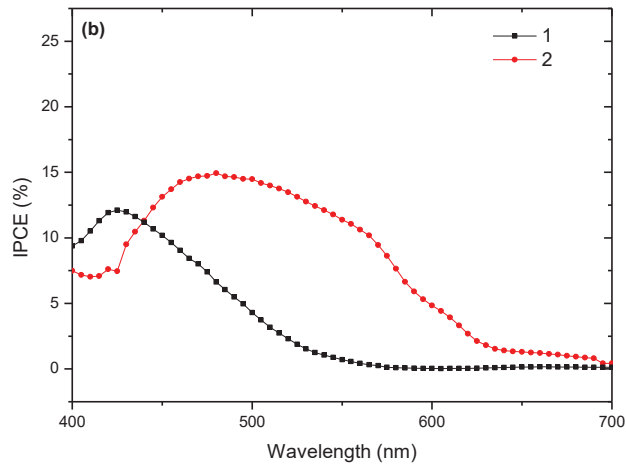
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**Figure 9.** Experimental and quantum calculation values of second-order hyperpolarizability. Blue point indicate molecules studied in this paper while red dot indicates triphenylamine studied in our previous paper [35].





**Figure 10.** (a) Photocurrent density-voltage curves under illumination and (b) incident photon-to-current conversion efficiency (IPCE) spectra of **1**- and **2**-sensitized DSSCs.

**Table 1.** Thermal characteristics of derivatives **1** and **2**.

Derivative	T <sub>m</sub> , [°C]	T <sub>g</sub> , [°C] (2 <sup>nd</sup> heating)	T <sub>ID-5%</sub> , [°C]
<b>1</b>	201	83	283
<b>2</b>	121	61	195

T<sub>g</sub> - glass transition point, T<sub>m</sub> - melting point (10 °C/min, nitrogen atmosphere). T<sub>ID-5%</sub> is 5% (20 °C/min under nitrogen).

**Table 2.** UV and emission data of dilute solutions ( $10^{-5}$  M) of **1** and **2** in toluene.

Compound	$\lambda_{\text{max}}^{\text{a}}$ , nm	$\epsilon^{\text{b}}$ ( $10^4 \text{ M}^{-1} \text{ cm}^{-1}$ )	$\lambda_{\text{max}}^{\text{c}}$ , nm	$\Phi_{\text{f}}^{\text{d}}$ , %	Stokes shift, nm	$E_{\text{g}}^{\text{opt}}$ /eV <sup>e</sup>
<b>1</b>	424	2.4	552	19.56	128	2.28
<b>2</b>	466	1.8	553	14.25	87	2.52

<sup>a</sup> Wavelength of absorption maximum. <sup>b</sup>  $\epsilon$  is the extinction coefficient at  $\lambda_{\text{max}}$  of absorption. <sup>c</sup>

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$1240/\lambda_{\text{edge}}$ , where  $\lambda_{\text{edge}}$  is the wavelength of absorption edge in long wave direction.

**Table 3.** Electrochemical characteristics of derivatives 1 and 2.

Derivative	$E_{\text{onset}}^{\text{ox}}$ vs Fc/V <sup>a</sup>	IP <sub>CV</sub> /eV <sup>b</sup>	E <sub>ACV</sub> /eV <sup>b</sup>	IP <sub>PE</sub> /eV <sup>c</sup>
<b>1</b>	0.43	5.23	-2.91	5.26
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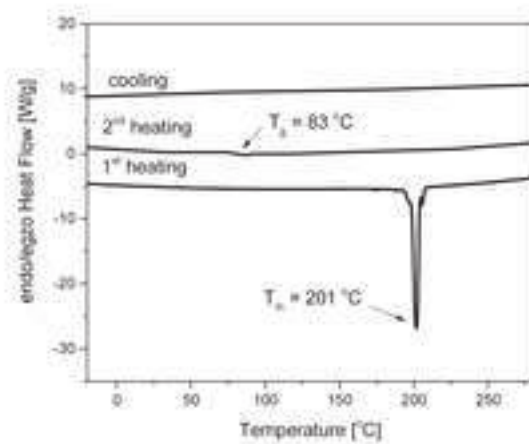
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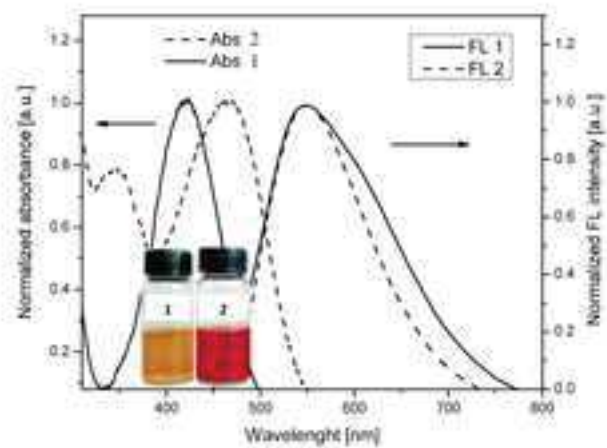
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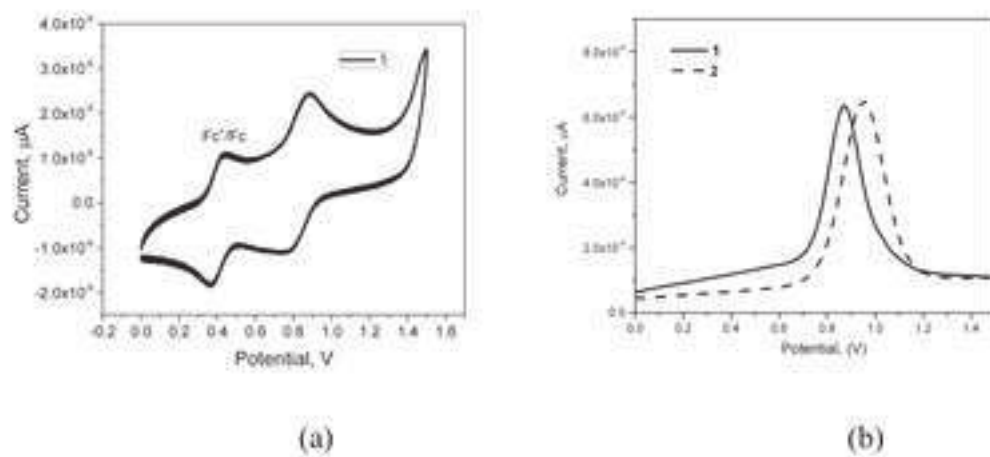
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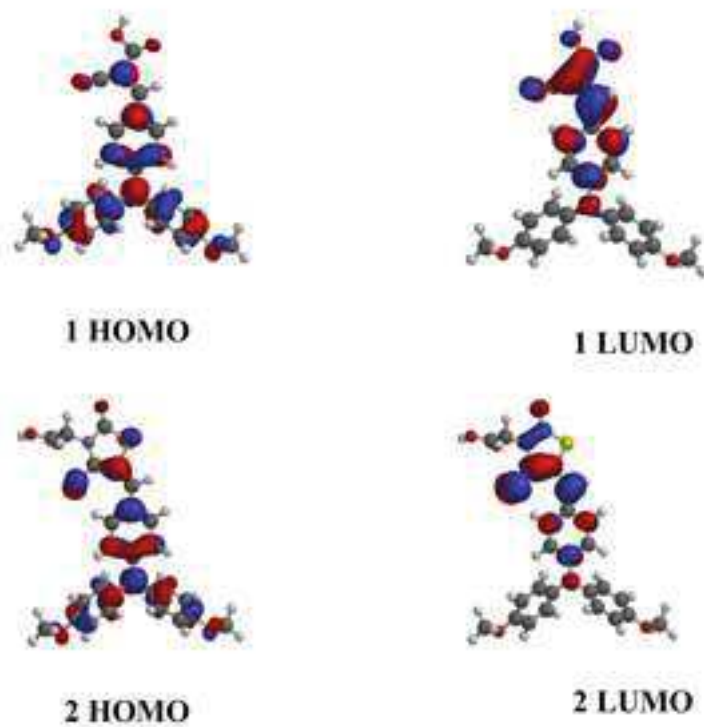
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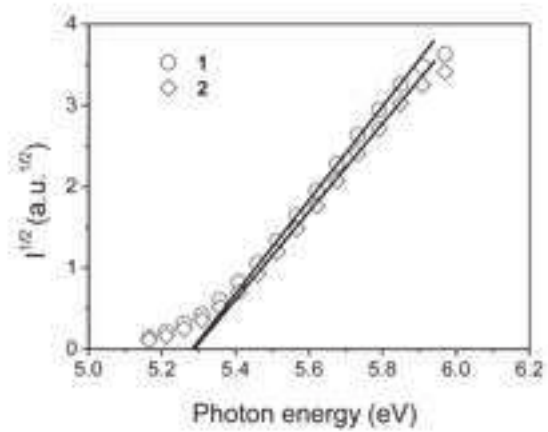
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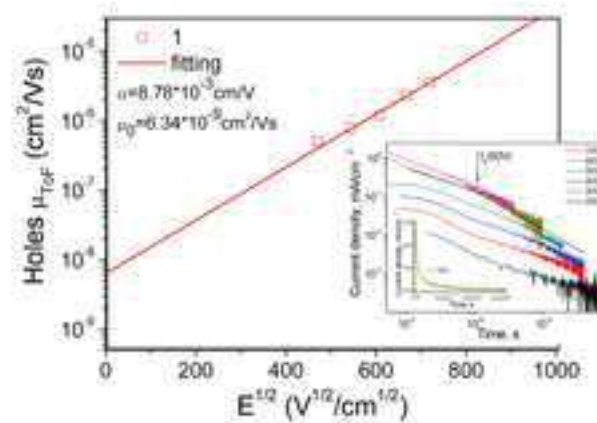
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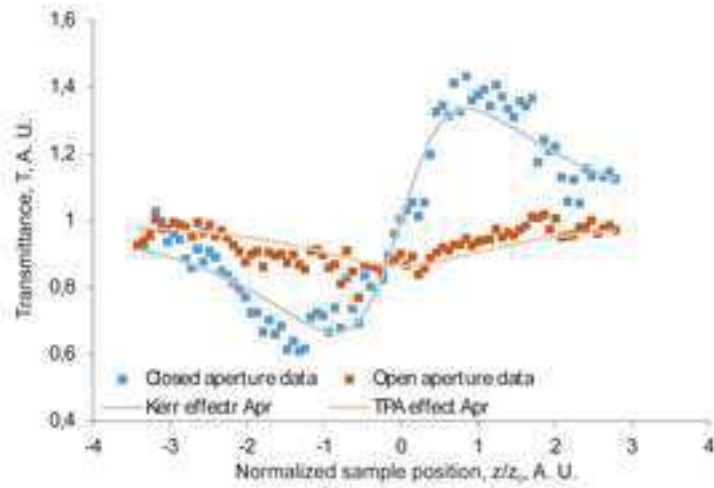
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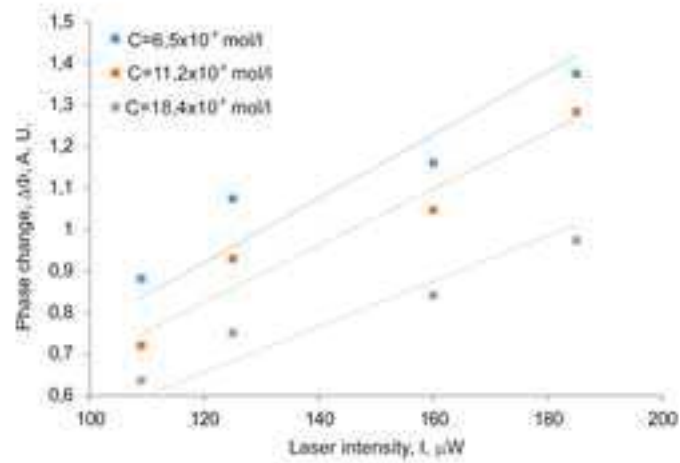
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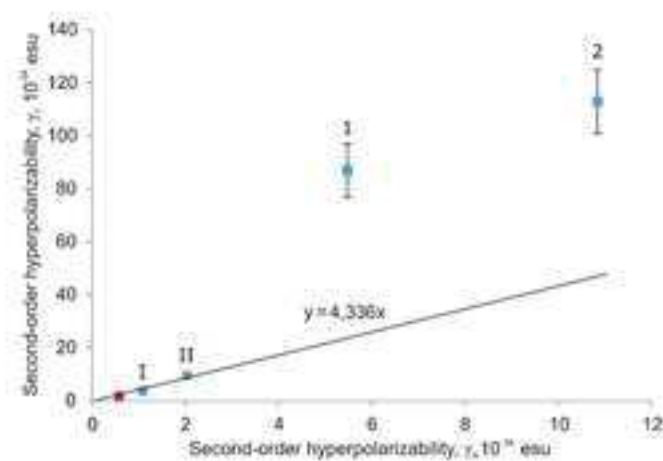
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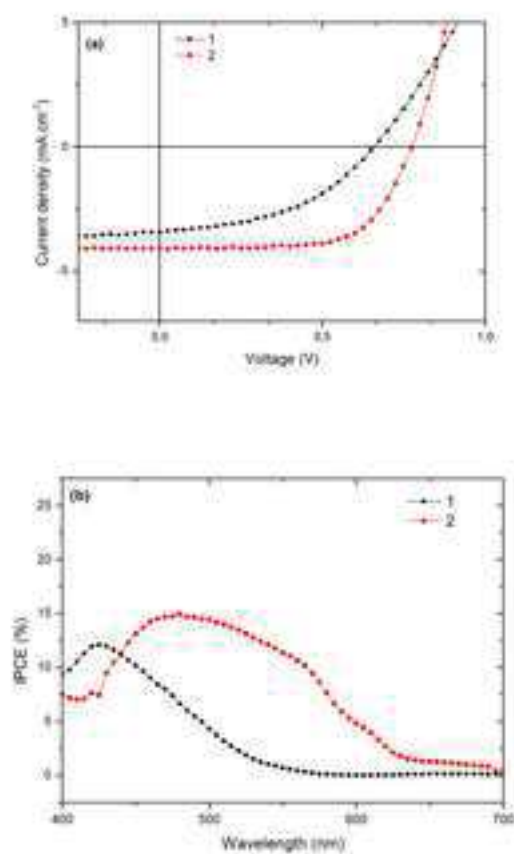
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This paper is elaborated at the Centre of Excellence in Advanced Material Research and Technology Transfer of the Institute of Solid State Physics, University of Latvia executing project CAMART<sup>2</sup> that has received funding from the Horizon 2020 Framework Programme H2020-WIDESPREAD-01-2016-2017-TeamingPhase2 under grant agreement No. 739508