Dyes and Pigments 95 (2012) 33-40

Contents lists available at SciVerse ScienceDirect

Dyes and Pigments



Arylmethylene-1,3-indandione based molecular glasses: Third order optical non-linearity

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ARTICLE INFO

Article history: Received 4 January 2012 Received in revised form 8 March 2012 Accepted 9 March 2012 Available online 28 March 2012

Keywords: Indan-1,3-dione derivatives Linked structures Molecular glass Third harmonic generation Third order non-linear susceptibility Polycarbonate

ABSTRACT

The synthesis and new optical features of three indan-1,3-dione class structures is reported. The simple arylmethylene-1,3-indandione structure 2-(4-diethylaminobenzylidene)indan-1,3-dione was used to design two linked structures: 1,3-bis-{3-hydroxy-4-[4-diethylamino-1-(1,3-dioxoindan-2-ylmethylene) benzen-3-yloxy]-1-thiabuthyl}benzene and 4,4'-bis-{{3-hydroxy-4-[4-diethylamino-1-(1,3-dioxoindan-2-ylmethylene) benzen-3-yloxy]-1-thiabutyl}phenyl}sulfide. In contrast to the simple compound, which readily crystallized, the linked derivatives remained in an amorphous phase and are considered as molecular glasses with respective glass transition temperatures 88 and 100 °C. For non-linear optical investigations samples were prepared as a guest-host system in polycarbonate matrix (10%). The Maker-fringe technique was used to investigate the third harmonic generation at a wavelength of 355 nm (YAG laser). Third-order non-linear susceptibility $\chi^{(3)}$ values were extracted $5.75 \cdot 10^{-21}$ m² V⁻², $8.60 \cdot 10^{-21}$ m² V⁻², $16.85 \cdot 10^{-21}$ m² V⁻² for these respective indandiones while modeling the experimental results. To evaluate the susceptibility of the indan-1,3-dione derivatives third harmonic generation a comparative experiment for a reference azodye in polycarbonate was performed. The results show an important feature – higher molecular second order hyperpolarizability for the linked structures. NMR, MS, IR, UV–VIS, XRD and elemental analysis were used to structurally characterize the new compounds and ellipsometry was applied to interpret the non-linear optical results.

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1. Introduction

The development of advanced materials for photonic applications is still a challenging issue. Among new trends, such as inorganic nanostructures or quasi-crystals, organic non-linear optical materials deserve special attention due to their variety and flexibility for structural modifications, relative high susceptibilities and easy integration with optical devices. Frequency conversion is a very important feature for non-linear optical microscopy, nanooptic applications. Indandiones are already well-established materials in photophysics [1]. First manifestation of high optical non-linearity appeared as second harmonic generation in indandione-1,3 pyridinium betaines, where photoinduced intramolecular electron transfer, large change in dipole moment in the excited state and considerable hyperpolarizability were obtained

* Corresponding author. E-mail address: rolandas.tomasiunas@ff.vu.lt (R. Tomašiūnas). [2-4]. Association at high concentration and photo oxidation of betaines motivated the search for new indandione derivatives. Manifesting reduced association within a matrix dimethylaminobenzylidene-1,3-indandione (DMABI) showed increased optical nonlinearity - second harmonic generation - measured by both alloptical and corona poling [5,6]. Langmuir–Blodgett layers of 2-(p-N-hexadecyl-N-methylamino)benzylidene-1,3-indandione produced as alternate chromophore-spacer films having definite orientation to the surface and generating harmonics revealed a model system for designing strong non-linear optical complexes [7]. Our task was to proceed further in the direction of the well-investigated group of DMABI. The methyl group, used to alkylate the amino group, was exchanged with an ethyl group since linking two compounds together with a spacer is more complicated in the first case. Furthermore, the simple arylmethylene-1,3-indandione structure 2-(4-diethylaminobenzylidene)indan-1,3-dione was used to design two linked amorphous structures. This new condition focused our efforts to investigate their non-linear optical properties. Basically flat in an unexcited state indan-1,3-dione class molecules have





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a large dipole moment [6]. The magnitude of the dipole moment and it's change under excitation significantly depends on the substitution pattern. Having more rotational degree of freedom these molecules manifest torsion motion. Twisting around a single bound is responsible for relaxation dynamics and fluorescence properties. It was concluded that linked arylmethylene-1,3indandione derivatives prevents or significantly slows down some non-radiative relaxation pathways [8]. This we valuated as an advantage for enhancement of non-linear optical properties, i.e. harmonic generation.

In this work we extend our non-linear optical knowledge about new material – indan-1,3-dione based molecular glasses – by investigating third order optical non-linearity. Routes of synthesis, chemical structure investigation using spectroscopy and X-ray diffraction, experimental third harmonic generation (THG) – a powerful and almost background free non-linear optical method – and theoretical modeling are presented. Problems and ideas concerned with architecture, chemical properties and physical properties toward higher second order hyperpolarizability are raised.

2. Samples

2.1. 2-(4-Diethylaminobenzylidene)-1,3-indandione (ID1, C₂₀H₁₉NO₂)

4-Diethylaminobenzaldehyde (5.0 g, 28 mmol) and 1,3indandione (4.1 g, 28 mmol) were dissolved in 90 mL of ethanol. The solution was left stirring at room temperature. After the termination of the reaction (TLC, acetone: *n*-hexane, 5:18) obtained red crystals were filtered off and washed with 2-propanol and recrystallized from the mixture (1:1) of THF and 2-propanol. The yield was 88% (7.6 g); m.p.: 154.5–156 °C (154–155 °C in Ref. [9]).

¹H NMR (300 MHz, CDCl₃, δ , ppm): 8.52 (d, *J* = 9.0 Hz, 2H, *p*-Ph); 7.95–7.86 (m, 2H, 4,7-H of indandione); 7.76 (s, 1H, CH=); 7.74–7.65 (m, 2H, 5,6-H of indandione); 8.52 (d, *J* = 9.0 Hz, 2H, *p*-Ph); 3.49 (q, *J* = 7.13 Hz, 4H, NCH₂); 1.26 (t, *J* = 7.13 Hz, 6H, CH₃).

APCI-MS: m/z (%): 306 [M + H]⁺ (100).

Elemental analysis. Calcd. for C₂₀H₁₉NO₂ (%): C 78.66; H 6.27; N 4.59. Found (%): C 78.55; H 6.17; N 4.57.

2.2. 4-Diethylamino-2-oxiranylmethoxybenzaldehyde (1, $C_{14}H_{19}NO_3$)

2.5 g (12.9 mmol) of 4-diethylamino-2-hydroxybenzaldehyde, 0.36 g (1.29 mmol) of benzyl triethylammonium chloride and 50 mL (647 mmol) of epichlorohydrin were placed into a round bottom flask. The reaction mixture was intensively stirred at the reflux temperature for 15 min. After the termination of the reaction (TLC, acetone: *n*-hexane, 1:4), the reaction mixture was treated with chloroform and washed with distilled water. The organic layer was dried over anhydrous MgSO₄, filtered and solvent and excess of epichlorohydrin were removed. The residue was treated with diethyl ether. The obtained crystals were filtered off and washed with diethyl ether. The yield was 86% (2.5 g); m.p.: 62–63 °C (diethyl ether).

IR (KBr), *v*, cm⁻¹: 3104, 3058 (CH_{arom}), 2980, 2957, 2921, 2901, 2870 (CH_{aliph}), 1655 (C=O), 1553, 1523 (C=C), 1273, 1243, 1214, 1025 (C−O−C).

¹H NMR (300 MHz, CDCl₃, δ , ppm): 10.18 (s, 1H, HC=O); 7.72 (d, J = 9.0 Hz, 1H, 6-H Ph_{1,2,4-subst.}); 6.31 (dd, J = 9.0 Hz, 2.3 Hz, 1H, 5-H of Ph_{1,2,4-subst.}); 6.11 (d, J = 2.3 Hz, 1H, 3-H of Ph_{1,2,4-subst.}); 4.34 (dd, $J_{AM} = 11.2$ Hz, $J_{AX} = 3$ Hz, (H_A), 1H, one of CH₂O protons); 4.05

(dd, J_{MA} = 11.2 Hz, J_{MX} = 5.6 Hz, (H_M), 1H, another of CH₂O protons); 3.47–3.36 (m, 5H, CHO, NCH₂); 2.95 (dd, $J_{A'M'}$ = 4.5 Hz, $J_{A'X}$ = 4.5 Hz (H_{A'}), 1H, one proton of CH₂O of oxirane); 2.81 (dd, $J_{M'A'}$ = 4.5 Hz, $J_{M'X}$ = 2.7 Hz, (H_{M'}), 1H, another proton of CH₂O of oxirane); 1.22 (t, J = 7.1 Hz, 6H, CH₃).

APCI-MS: m/z (%): 250 [M + H]⁺ (100).

Elemental analysis. Calcd. for C₁₄H₁₉NO₃ (%): C 67.45; H 7.68; N 5.62. Found (%): C 67.38; H 7.59; N 5.42.

2.3. 4-Diethylamino-2-oxiranylmethoxy-1-(1,3-dioxoindan-2ylmethylene)benzene (2, C₂₃H₂₃NO₄)

1,3-indandione (5.0 g, 34 mmol) and compound **1** (8.56 g, 34 mmol) were dissolved in 90 mL of ethanol. The solution was left stirring at room temperature over night. Obtained red crystals were filtered off and washed with 2-propanol and diethyl ether. The yield was 92% (12 g); m.p.: 148.5–150 °C (THF: 2-propanol, 1:1).

IR (KBr), $\bar{\nu}$, cm⁻¹: 3033 (CH_{arom}), 2969, 2962, 2869 (CH_{aliph}), 1708, 1660 (C=O), 1547, 1512 (C=C), 1278, 1252, 1209, 1072 (C=O-C); 810, 742 (CH=CH of 1,2-di- and 1,2,4-trisubstituted benzenes).

¹H NMR (300 MHz, CDCl₃, δ, ppm): 9.34 (d, J = 9.3 Hz, 1H, 6-H Ph_{1,2,4-subst.}); 8.42 (s, 1H, Ph-CH=C); 7.90–7.83 (m, 2H, 5,6-H of indandione), 7.71–7.63 (m, 2H, 4,7-H of indandione); 6.40 (dd, J = 9.3 Hz, J = 2.4 Hz, 1H, 5-H of Ph_{1,2,4-subst.}); 6.13 (d, J = 2.4 Hz, 1H, 3-H of Ph_{1,2,4-subst.}); 6.13 (d, J = 2.4 Hz, 1H, 3-H of Ph_{1,2,4-subst.}); 4.39 (dd, $J_{AM} = 11.1$ Hz, $J_{AX} = 3.1$ Hz, (H_A), 1H, one of CH₂O protons); 4.10 (dd, $J_{MA} = 11.1$ Hz, $J_{MX} = 5.4$ Hz, (H_M), 1H, another of CH₂O protons); 3.46 (m, 5H, CHO, NCH₂); 2.98 (dd, $J_{A'M'} = 4.5$ Hz, $J_{A'X'} = 4.5$ Hz, (H_{A'}), 1H, one of CH₂O protons); 2.86 (dd, $J_{M'A'} = 4.5$ Hz, $J_{M'X} = 2.7$ Hz, (H_{M'}), 1H, another of CH₂O protons); 1.24 (t, J = 7.1 Hz, 6H, CH₃).

APCI-MS: m/z (%): 378 [M + H]⁺ (100).

Elemental analysis. Calcd. for C₂₃H₂₃NO₄ (%): C 73.19; H 6.14; N 3.71. Found (%): C 72.95; H 6.27; N 3.57.

2.4. 1,3-Bis-{3-hydroxy-4-[4-diethylamino-1-(1,3-dioxoindan-2ylmethylene)benzen-3-yloxy]-1-thiabuthyl}benzene (ID2, C₅₂H₅₂N₂S₂O₈)

Epoxy compound **2** (2.0 g, 5.3 mmol) and benzene-1,3-dithiol (0.35 g, 2.65 mmol) were dissolved in 5 mL of THF. Then 0.14 mL (1.06 mmol) of triethylamine was added. The mixture was stirred intensively at the reflux temperature for 20 min. After the termination of the reaction (TLC, acetone: *n*-hexane, 7:18) solvent was evaporated. The residue was purified by column chromatography using 1:4 acetone: *n*-hexane as the eluent. The resultant red oil was dissolved in 15 mL of THF and then poured with intensive stirring into 200 mL of *n*-hexane to obtain amorphous product **ID2**. The yield was 84% (1.9 g).

IR (KBr), $\bar{\nu}$, cm⁻¹: 3358 (OH), 3072 (CH_{arom}), 2970, 2927, 2870 (CH_{aliph}), 1707, 1660 (C=O), 1613, 1594, 1543, 1507 (C=C) 1275, 1253, 1154, 1077 (C=O-C), 810, 786, 735 (CH=CH of 1,2-di-, 1,3-di- and 1,2,4-trisubstituted benzenes).

¹H NMR (300 MHz, CDCl₃, δ , ppm): 9.26–9.17 (m, 2H, 6-H Ph_{1,2,4-subst.}); 8.29–8.24 (m, 2H, Ph-CH=C); 7.82–7.52 (m, 8H, Ar), 7.29–7.12 (m, 4H, Ar); 6.29–6.17 (m, 2H, 5-H of Ph_{1,2,4-subst.}); 5.90–5.83 (m, 2H, 3-H of Ph_{1,2,4-subst.}); 4.85–4.40 (m, 2H, OH); 4.28–4.06 (m, 2H, CHO); 4.06–3.88 (m, 4H, OCH₂); 3.45–3.21 (m, 8H, SCH₂, NCH₂); 1.22–1.12 (m, 12H, CH₃).

APCI-MS: m/z (%): 897 [M + H]⁺ (45).

Elemental analysis. Calcd. for C₅₂H₅₂N₂O₈S₂ (%): C 69.62; H 5.84; N 3.12. Found (%): C 69.56; H 5.88; N 3.76.

2.5. 4,4'-Bis-{{3-hydroxy-4-[4-diethylamino-1-(1,3-dioxoindan-2ylmethylene)benzen-3-yloxy]-1-thiabutyl}phenyl}sulfide (ID3, C₅₈H₅₆N₂O₈S₃)

Synthesis of compound **ID3** was carried out according to the procedure described for **ID2** except that 3.86 g epoxy compound **1** (10 mmol), 4,4'-thiobisbenzenedithiol (1.25 g, 5 mmol) and 0.29 mL (2 mmol) of triethylamine were used. The yield was 83% (4.2 g).

IR (KBr), $\bar{\nu}$, cm⁻¹: 3407 (OH), 3072 (CH_{arom}), 2970, 2928, 2870 (CH_{aliph}), 1709, 1661 (C=O), 1613, 1594, 1542, 1507 (C=C) 1275, 1253, 1155, 1077 (C=O-C), 810, 788, 736 (CH=CH of 1,2-di-, 1,4-di- and 1,2,4-trisubstituted benzenes).

¹H NMR (300 MHz, CDCl₃, δ , ppm): 9.26 (d, *J* = 9.3 Hz, 1H, 6-H Ph_{1,2,4-subst.} of one diastereomer); 9.23 (d, *J* = 9.3 Hz, 1H, 6-H Ph_{1,2,4-subst.} of other diastereomer); 8.27 (s, 1H, Ph-CH=C of one diastereoisomer); 8.26 (s, 1H, Ph-CH=C of other diastereoisomer); 7.84–7.72 (m, 4H, Ar), 7.64–7.57 (m, 4H, Ar); 7.35–7.29 (m, 4H, Ar); 7.19–7.13 (m, 4H, Ar); 6.31 (dd, *J* = 9.3 Hz, *J* = 2.2 Hz, 2H, 5-H of Ph_{1,2,4-subst.}); 5.86 (m, 2H, 3-H of Ph_{1,2,4-subst.}); 4.34–4.10 (m, 6H, OCH₂CH); 3.44–3.21 (m, 8H, SCH₂, NCH₂); 2.80–2.25 (m, 2H, OH); 1.21 (t, *J* = 7.1 Hz, 12H, CH₃).

APCI-MS: *m*/*z* (%):1005 [M + H]⁺ (38).

Elemental analysis. Calcd. for C₅₈H₅₆N₂O₈S₃ (%): C 69.30; H 5.61; N 2.79. Found (%): C 69.24; H 5.55; N 2.67.

2.6. Preparation of films composed with polymer matrix

Three different samples of the indan-1,3-dione class molecules (**ID1**, **ID2**, **ID3**) and DR1 dye (Dispersed Red 1, $C_{16}H_{18}N_4O_3$, SIGMA-ALDRICH, product number 344206) dispersed in polycarbonate matrix for THG experiments were prepared by spin-coating technique. It concerned 500 cycles per min for the first 6 s followed up by 2000 for the next 20 s. Silica glass plates used as substrates were degreased in ethanol, washed in distilled water and dried. Polycarbonate Iupilon Z-200 with $T_g = 189$ °C was chosen as a matrix material for these molecules to create guest-host system. In order to avoid aggregation, 10% (wt%) loading density of chromophores in all samples was chosen. Finally, drying via two steps (25 min at room temperature followed up by 45 min at 80 °C) was performed. Film thickness measurement provided by AFM (BioScope II) revealed values: ~4.5 µm for **ID1**, ~3.5 µm – **ID2**, ~2.6 µm – **ID3** and ~0.8 µm – DR1 dye sample.

3. Experimental

¹H NMR spectra were measured on Varian Unity Inova spectrometer (300 MHz) in CDCl₃. IR spectra of the samples in KBr pellets were recorded on a Perkin Elmer Spectrum GX FT-IR System spectrometer. Mass spectra were recorded on Waters (Micromass) 2Q 200. Absorption spectra of the material *THF* solutions (10^{-4} M) placed in 1 mm path length microcell were recorded on Perkin Elmer Lambda 35 UV/VIS spectrometer. Thermal properties were examined by using Netzsch STA 409 PC Luxx apparatus at heating rate of 10 K/min under nitrogen atmosphere. Glass transition temperatures (T_g) were determined from second heating. XRD analysis was performed using diffractometer DRON-UM2. Diffraction patterns were recorded at 30 kV and 20 mA in 1 deg/s detector movement speed, intensity was measured every $2\Theta = 0.02^{\circ}$. Flat diffracted beam pyrolitic graphite monochromator was used to remove fluorescent X-rays.

The course of reactions was monitored by TLC on Merck TLC aluminum Silica gel 60 F₂₅₄ sheets and developed with I₂ or UV light. Silica gel (grade 62, 60–200 mesh, 150 Å, Aldrich) was used for column chromatography. Elemental analyses were performed with Exeter Analytical CE-440 Elemental Analyzer. Melting points were determined in capillary tubes on capillary melting point apparatus Electrothermal MEL-TEMP[®].

For refractive index evaluation spectral ellipsometer SOPRA GES-5 with rotating polarizer was used. Chromophores dispersed in polycarbonate were deposited on BK7 glass substrate covered with gold (100 nm) using spin-coating technique. Film thickness 4 μ m, 4.3 μ m and 11.5 μ m for **ID3**, **ID2** and **ID1**, respectively, was measured by profilometer DEKTAK 150. Ellipsometry measurements were carried out in spectral range from 400 to 1700 nm. Optical constants were determined from ellipsometry data and analyzed by SOPRA program Winelli using multi-layer model. Cauchy function for refraction index:

$$n = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4},\tag{1}$$

was used in regression analysis to obtain optical constants $A = 1.831 \pm 4.937 \cdot 10^{-3}$, $B = 9.7 \cdot 10^{-3} \ \mu\text{m}^2$ (**ID1**), $A = 1.752 \pm 8.751 \cdot 10^{-3}$, $B = 5.7 \cdot 10^{-3} \ \mu\text{m}^2$ (**ID2**) and $A = 1.642 \pm 3.736 \cdot 10^{-3}$, $B = 1.4 \cdot 10^{-2} \ \mu\text{m}^2$ (**ID3**) [10].

Third harmonic generation was measured using Maker-Fringes technique, which consist of the analysis of THG intensity oscillations on incidence angle variation from a 'substrate-film' structure. The setup and method used may be found described in Ref. [11].

4. Results and analysis

The synthesis route to the arylmethylene-1,3-indandione derivatives ID1-ID3 is shown in Fig. 1. Thus, parent simple structure 2-(4-diethylaminobenzylidene)indan-1,3-dione (**ID1**) was prepared in good yield via condensation of 1,3-indandione with 4-diethylaminobenzaldehyde, whereas the twin structures **ID2** and **ID3** required three steps. In the first step, an intermediate 4-diethylamino-2-oxyranylmetoxybenzaldehyde (1) was produced by reaction of commercially available 2-hydroxy-4-diethylaminobenzaldehyde with epichlorohydrin in presence of benzyl trimethylammonium chloride. During the second step, condensation of 1 with 1,3-indandione at room temperature even in the absence of a catalyst led to the derivative 2 containing an epoxy group. Finally, the desired products 1,3-bis{3-hydroxy-4-[4diethylamino-1-(1,3-dioxoindan-2-ylmethylene)benzen-3-yloxy]-1-thiabuthyl}benzene (**ID2**) and 4,4'-bis{{3-hydroxy-4-[4diethylamino-1-(1,3-dioxoindan-2-ylmethylene)benzen-3-yloxy]-1-thiabutyl}phenyl}sulfide (ID3) were synthesized by reaction of the oxirane function of 2 with difunctional nucleophilic linking agents 1,3-benzenedithiol and 4,4'-thiobisbenzenedithiol in presence of a catalytic amount of triethylamine (TEA).

All our attempts to crystallize **ID2** and **ID3** were unsuccessful, while the structure **ID1** was crystallized from ethanol. The two former materials were purified by column chromatography followed by precipitation. Chemical structure of the arylmethylene-1,3-indandione derivatives **ID1–ID3** were confirmed by IR, ¹H NMR, UV and APCI-MS spectroscopy. Splitting of some individual downfield peaks in the ¹H NMR spectra indicates that isolated linked compounds **ID2** and **ID3** containing several stereogenic centers, were isolated as mixtures of diastereomers, which could not be separated by purification procedures. The IR spectra of **ID1–ID3** are characterized by occurrence of two carbonyl absorptions in the range of 1710–1707 cm⁻¹ and 1662–1660 cm⁻¹. This is in accordance with the reports in the literature assigning the two



Fig. 1. Synthesis route to the arylmethylene-1,3-indandione derivatives ID1-ID3.

different signals to symmetrical (higher frequency) and asymmetrical (lower frequency) stretching mode of carbonyl groups [12]. In addition, the hydroxyl groups of twin **ID2** and **ID3** participating in hydrogen bonding give rise to a broad oscillation at $3600-3100 \text{ cm}^{-1}$.

Existence of several diastereoisomers, possibility of intermolecular hydrogen bonding and flexibility of aliphatic linking chains make crystallization in solid state difficult ascribing twin arylmethylene-1,3-indandione molecules **ID2** and **ID3** to low molar mass compounds with a stable amorphous phase above room temperature. Such compounds are called molecular glasses or amorphous molecular materials [13]. They form uniform, transparent amorphous thin films by spin-coating method. In contrast to crystalline compounds, which show anisotropic properties, these amorphous materials exhibit isotropic as well as homogeneous properties due to the absence of grain boundaries. In contrast to polymers, they are pure materials with well-defined molecular structure and definite molecular weight without any distribution. X-ray diffraction pattern of **ID2** and **ID3** show only broad halos (see Fig. 2) in contrast to structure **ID1**.

The formation of a glassy state for **ID2** and **ID3** was confirmed by differential scanning calorimetry (DSC). These investigations revealed that both investigated 2-(4-diethylamino-2-hydroxyphenylmethylene)-1,3-indandione based molecular glasses were found only in the amorphous phase (see Fig. 3). No crystallization took place at first heating of **ID2**, only glassing temperature (T_g) was revealed at 88 °C during the second heating. This is a common feature for both **ID2** and **ID3**. T_g of **ID3** is higher (100 °C) than of **ID2** due to thiobisbenzene unit at the linking fragment.

Electron transition from ground to excited state in **ID1–ID3** gives the main absorption maxima at *ca*. 483 nm for the **ID1** and at *ca*. 490 nm for the linked structures (Fig. 4). The red shift for linked structures relates to known length effects. Relative absorption maxima at wavelengths 205, 241 and 249 nm describe the absorption to higher excited states with different vibrational levels.



Fig. 2. X-ray diffraction patterns of ID1 and ID2 molecules.



Fig. 3. DSC second heating curves of ID1-ID3 molecules (heating rate 10 K/min).

Since **ID2** and **ID3** contain several isolated π -electron systems, the total light absorption spectra is a sum of spectra of separate molecule fragments. The comparison of spectra for compound ID2 with ID3 shows that ID3 gives an extra maxima at ca. 275 nm due to the lone pairs of sulfur atom between two phenyl groups in the central linking fragment, i.e. the 4,4'-thiobisbenzenethiol. In the spectra of molecules dispersed in polycarbonate and prepared as film same characteristic peaks and shifts appeared, however, due to relative high concentration of chromophores in ID1 sample larger absorption coefficient and broader spectra was registered. This higher concentration is an issue of preparing the films, since for identical loading density of chromophores more than one third of weight correspond to the spacer in the linked compounds. From the analysis of ellipsometry data dispersion curves were built, what gave us the refractive index values for 1,3-indandione based molecules 1.948 (355 nm) ID1, 2.067 (355 nm) ID2 and 2.067 (355 nm) ID3 (Fig. 5). They were used later as a basis for modeling the $\chi^{(3)}$.

To determine the third order non-linear optical susceptibility $\chi^{(3)}$ a model describing the THG from a structure immersed between two linear media was used [14]. The THG intensity in our case from air-substrate-film follows a complex expression:

$$\begin{split} I_{3\omega} &= \frac{64\pi^4}{c^2} \Big| e^{i(\psi_{\omega}^{\rm S} + \psi_{3\omega}^{\rm S})} \Big| \frac{\chi^{(3)}}{\Delta\varepsilon} \Big|_{\rm S} \Big[T_1 \Big(1 - e^{-i\Delta\psi_{\rm S}} \Big) \\ &+ \rho T_2 e^{i\varphi} \Big(e^{i\Delta\psi_{\rm F}} - 1 \Big) \Big] \Big|^2 (I_{\omega})^3, \end{split}$$
(2)



Fig. 4. UV_VIS absorption spectra of 1,3-indandione based molecules ID1 (black), ID2 (gray), ID3 (light gray) (THF, $c = 10^{-4}$ M) (a) and them dispersed in polycarbonate (b). Thin lines represent 4,4'-thiobisbenzenethiol (a) and polycarbonate itself (b).



Fig. 5. Refractive index dispersion $n(\lambda)$ for 1,3-indandione based molecules dispersed in polycarbonate ID1 (black), ID2 (gray), ID3 (light gray).

where

$$\begin{split} \Delta\psi_{S} &= \psi_{\omega}^{S} - \psi_{3\omega}^{S} = \frac{3\omega l_{S}}{c} \left(n_{\omega}^{S} \cos \Theta_{\omega}^{S} - n_{3\omega}^{S} \cos \Theta_{3\omega}^{S} \right), \\ \Delta\psi_{F} &= \psi_{\omega}^{F} - \psi_{3\omega}^{F} = \frac{3\omega l_{F}}{c} \left(n_{\omega}^{F} \cos \Theta_{\omega}^{F} - n_{3\omega}^{F} \cos \Theta_{3\omega}^{F} \right), \\ \rho &= \left| \frac{(\chi^{(3)} / \Delta \epsilon)_{F}}{(\chi^{(3)} / \Delta \epsilon)_{S}} \right|, \\ T_{1} &= \left(\frac{2n^{(1)} \cdot \cos \Theta^{(1)}}{n^{(1)} \cdot \cos \Theta^{(1)} + n_{\omega}^{S} \cdot \cos \Theta_{\omega}^{S}} \cdot \frac{2n_{\omega}^{S} \cdot \cos \Theta_{\omega}^{S}}{n_{\omega}^{S} \cdot \cos \Theta_{\omega}^{S} + n_{\omega}^{F} \cdot \cos \Theta_{\omega}^{F}} \right)^{3} \\ &\cdot \frac{N_{3\omega}^{S} + N_{3\omega}^{S}}{N_{3\omega}^{S} + N_{3\omega}^{F}}, \\ T_{2} &= \left(\frac{2n^{(1)} \cdot \cos \Theta^{(1)}}{n^{(1)} \cdot \cos \Theta^{(1)} + n_{\omega}^{S} \cdot \cos \Theta_{\omega}^{S}} \right)^{3} \cdot \frac{2n_{3\omega}^{F} \cdot \cos \Theta_{3\omega}^{F}}{n_{3\omega}^{F} \cdot \cos \Theta_{3\omega}^{F} + n^{(1)} \cdot \cos \Theta^{(1)}} \\ &\cdot \frac{N_{3\omega}^{F} + N_{\omega}^{F}}{N_{3\omega}^{F} + N_{3\omega}^{(1)}}, \end{split}$$

and the indexes (1), S and F refer to air (vacuum), substrate and film, ω and 3ω – to fundamental and harmonic wave, respectively; *c* is the speed of light in vacuum; $\omega/c = 2\pi/\lambda_{\omega}$; $N = n \cdot \cos\Theta$; $\Delta\psi$ is the phase mismatch between the fundamental ($\lambda_{\omega} = 1064$ nm) and third ($\lambda_{3\omega} = 355$ nm) harmonic; *l* is the thickness; Θ is the propagation angle; $\Delta\varepsilon = \varepsilon_{\omega} - \varepsilon_{3\omega}$ is the dielectric constant dispersion; φ is the phase of the film susceptibility ($\chi_{F}^{(3)} = |\chi_{F}^{(3)}| \cdot e^{i\varphi}$); *I* is the fluence.

THG intensity as a function of the incidence angle measured in the silica substrate revealed a symmetric structure of spikes in a train. Calculation using optical parameters for silica (see Table 1) shows good agreement with the measurement (Fig. 6), which proves the model used.

We succeeded to get a best fit of THG experimental results for indan-1,3-dione derivatives (Fig. 7). The offset of THG signal is defined by $\chi^{(3)}$ of the film, the fringes - of the substrate, when the film thickness l_F is much less than the coherence length $L_{c,F} = \lambda_{\omega}/[6 \cdot (n_{3\omega}^F - n_{\omega}^F)]$ [14]. In our case of indan-1,3-dione derivatives the fringes should appear for both, the film and the substrate, providing superposition since the condition is not fulfilled (see Table 1). This may influence the reduced amplitude of scattering of experimental points. The situation differs for DR1,

38 Table 1

Sample	ID1	ID2	ID3	DR1		SiO ₂
l _F [μm]	4.5	3.5	2.6	0.8	l _s [μm]	1000
n_{ω}^{F}	1.730 ^a	1.849 ^a	1.836 ^a	1.6028 ^b	$\boldsymbol{n}_{\omega}^{S}$	1.44967 ^c
$n_{3\omega}^F$	1.993 ^d	2.087 ^d	2.062 ^d	1.658	$n_{3\omega}^{S}$	1.4762 ^e
T_1	28	28	28	28		28
$T_2 \ \chi_F^{(3)} \ [m^2/V^2]$	$1 \\ 5.75 \cdot 10^{-21} \\ 2.25 \cdot 10^{-21} \\ f$	$1 \\ 8.60 \cdot 10^{-21} \\ 3.45 \cdot 10^{-21f}$	$\begin{array}{c} 1 \\ 16.85 \cdot 10^{-21} \\ 7.3 \cdot 10^{-21 \mathrm{f}} \end{array}$	$1 \\ 29.6 \cdot 10^{-21} \\ 24.70 \cdot 10^{-21}$	$\chi^{(3)}_S \; [m^2/V^2]$	2.0·10 ^{-22e}
L _{c,F} [μm]	0.67	0.73	0.76	3.2	L _{c,S} [μm]	6.7

Parameters used for modeling the experimental third harmonic generation for indan-1,3-dione based molecules **ID1–ID3** and DR1 dye dispersed in polycarbonate and the SiO₂ plate (substrate) using Eq. (2).

^a From ellipsometry data.

^b $\lambda = 1053$ nm, 13 wt% [23].

^c [21].
^d From ellipsometry data, adjusted while modeling.

^e [21].

^f Calc. using Eq. (3).

where the condition is valid and the amplitude of the fringes is well expressed. From modeling, 2-to-3 times higher $\chi^{(3)}$ value for the linked samples (ID2,ID3) than for the simple compound ID1 sample was obtained. Whereas the samples were equally loaded by weight (percentage), a larger number of chromophores was expected for ID1. This would predict less susceptibility for ID2 and **ID3** since each is composed of two **ID1** moieties and a linking spacer. Interconnected via aliphatic junction the **ID1** are treated isolated with their π -electron conjugated system. Probably, these evaluations are lacking of one factor - the intramolecular charge transfer, which could significantly contribute to the cubic nonlinearity [15]. The simple 1,3-indandione compounds having donor and acceptor group form an ascentric system characterized by higher second order hyperpolarizability than symmetrically shaped donor-donor or acceptor-acceptor pairs [16]. The fact of relative increase of third order susceptibility observed for ID2 and **ID3** samples in our case could be a proof that simple additivity of second order hyperpolarizabilities within complex systems couldn't be sufficient. Moreover, our results indicate that the longer the spacer the larger increase of susceptibility was obtained, despite less quantity of chromophores in the sample **ID3.** Similar indications noted when measuring charge carrier drift in similar derivatives: despite the lower concentration of chromophores, the hole drift mobilities measured in these molecular glasses exceeded the parameters of the analogous with higher concentration of photoconductive moieties [17]. Two possible arguments: close packaging feature and intramolecular charge transfer contribution to conductivity for multimers were discussed [18]. Another aspect supporting the increase of optical



Fig. 6. Third harmonic generation for silica plate. Lines are modeling results using Eq. (2) explained in the text.

non-linearity for linked compounds is the glass transition temperature. It was confirmed that T_g increase for amorphous molecular glasses enhances surface relief grating formation property [19].

Almost twice less $\chi^{(3)}$ value was obtained when applying another method proposed by Wang [20] (see Table 1). This simplified method based on comparison of $\chi_{\rm F}^{(3)}$ between material of interest and reference (silica):

$$\frac{\chi_{\rm F}^{(3)}}{\chi_{\rm S}^{(3)}} = \frac{2}{\pi} \cdot \frac{L_{\rm c,S}}{l_{\rm F}} \cdot \sqrt{\frac{I_{3\omega,\rm F}}{I_{3\omega,\rm S}}},\tag{3}$$

where $L_{c,S}$ is the coherence length and $\chi_S^{(3)} = 2.0 \cdot 10^{-22} \text{m}^2/\text{V}^2$ [21] both for the reference; l_F is the thickness of film; $I_{3\omega,F}$ and $I_{3\omega,S}$ are the third harmonic intensities of the film and the reference, respectively. The deviation from the first approach may concern some conditions ignored in Eq. (3) and could be important due to THG spectra position in our case. Same ratio of deviation was observed by Sahraoui (see Table 3 in Ref. [11]). Nevertheless, the result should be valuated as reasonable and supporting the order of magnitude for the third order optical non-linearity of 1,3-indandione based molecular glasses.

Using both approaches we should consider the estimated $\chi^{(3)}$ for 1,3-indandione derivatives as a lower limit. The task to investigate frequency conversion at YAG laser third harmonic (wavelength 355 nm) meant the situation "close or within the resonance" for 1,3-indandiones, i.e. the THG quantum energy corresponded to the transition between the ground and first excited state, and the ground and higher excited state (see Fig. 4). Together with some marginal absorption observed in the spectra this may imply also non-linearity dispersion effects.

In order to rank the optical non-linearity of arylmethylene-1,3indandione molecular glasses a reasonable comparison with DR1 dye in polycarbonate was made. Due to the similarity of the absorption spectra (eg [22].) the same conclusion as made for 1,3indandiones about the limit for the $\chi^{(3)}$ value to DR1 could be applied. The obtained $\chi^{(3)}$ for DR1 is almost 1.5 times higher than for DR1 doped DNA films [22]. However, the twice higher concentration of chromophores used in our case makes the approximate balance. Based on that one could conclude that the third order optical non-linearity of 1,3-indandione derivatives is quite close to recognized dye molecules. Moreover, the molecular structure of the presented 1,3-indandione based molecular glasses prevents crystallization and allows preparation of stable films for non-linear optics without a binder or with a low binder concentration. Such experiments are currently underway.



Fig. 7. Third harmonic generation for 1,3-indandione based molecules ID1 (top, left), ID2 (top, right), ID3 (bottom, left) and DR1 (bottom, right) dye dispersed in polycarbonate. Lines are modeling results using Eq. (2) explained in the text.

5. Conclusions

New linked structures 1,3-bis-{3-hydroxy-4-[4-diethylamino-1-(1,3-dioxoindan-2-ylmethylene)benzen-3-yloxy]-1-thiabuthyl} benzene (ID2) and 4,4'-bis-{{3-hydroxy-4-[4-diethylamino-1-(1,3dioxoindan-2-ylmethylene)benzen-3-yloxy]-1-thiabutyl}phenyl} sulfide (ID3), which appeared as molecular glass featuring glass transition temperatures 88 °C and 100 °C, respectively, revealed higher third order optical non-linearity than the model simple arylmethylene-1,3-indandione structure 2-(4-diethylaminobenzylidene)indan-1,3-dione (ID1). Lengthening of linking spacer in ID2 and ID3 appeared to enhance significantly the molecular second order hyperpolarizability. Samples prepared as host-guest system in polycarbonate were investigated by means of third harmonic generation. Third order non-linear susceptibility $\chi^{(3)}=$ 16.85 $\cdot 10^{-21}~m^2/V^2$ (wavelength 355 nm) obtained for the linked structure ID3 demonstrated potential for 1,3-indandione based molecular glasses be applied in organic optoelectronics for optical frequency conversion. Evaluation of $\chi^{(3)}$ was performed via modeling the experimental results and analyzed using two approaches.

Acknowledgments

This work was partially supported by a grant from the Lithuanian State Science and Studies Foundation (project Mulatas 2), by the Agency of International Science and Technology Development in Lithuania and by the EU COST Action MP0702. GS acknowledges the STSM grant Nr.4695. The authors wish to express their appreciation to G.Medeišiene for sample preparation.

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