Dyes and Pigments 99 (2013) 1044-1050

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

# Modular approach to obtaining organic glasses from low-molecular weight dyes using 1,1,1-triphenylpentane auxiliary groups: Nonlinear optical properties

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### ARTICLE INFO

Article history: Received 15 May 2013 Received in revised form 16 August 2013 Accepted 19 August 2013 Available online 30 August 2013

Keywords: Azobenzene Indane-1,3-dione Molecular glass Non-linear optics Glass transition temperature Second harmonic generation

### 1. Introduction

The last decade has witnessed a notable increase in organic nonlinear optical (NLO) materials performance characteristics, making these compounds viable for practical applications in various photonic devices [1,2]. The general structural requirement for NLO activity in materials is the presence of push–pull type chromophores with high molecular hyperpolarizability ( $\beta$ ) values [3]. For the practical applications NLO materials need to meet several criteria such as high optical transparency, good solubility and high chemical and thermal stability. To achieve this, the chromophores are often incorporated into guest–host [4,5] and polymeric [6,7] systems.

The relatively less studied material type is molecular glasses, a compound class where small-molecular compounds are capable of forming a stable amorphous phase [8,9]. This material design approach, however, has several important advantages. Compared to polymeric compounds, where batch to batch synthetic repetition, purification and product characterization are often a difficult

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# ABSTRACT

A new modular synthetic approach to obtain organic glasses from low-molecular weight azobenzenes and stilbenes has been accomplished using 1,1,1-triphenylpentane crystallization preventing auxiliary groups. Six new structures show excellent solubility in non-polar solvents and thin films with good optical qualities have been obtained using a spin-coating technique. The glass transition temperatures of the new amorphous materials were in the range of 73–108 °C. The nonlinear optical activity in thin amorphous films was measured after a corona poling procedure.

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task, the molecular compounds are much easier to obtain, isolate and identify. The general structural requirements regarding the synthesis of the molecular glasses are still not strictly defined, although, some molecular properties as the presence of bulky, nonplanar, heavy and rigid fragments are often taken into the consideration to acquire such materials [10,11].

In the case of NLO materials where the active part of the material is a push—pull type chromophore, the formation of a stable amorphous phase is an even harder task. The chromophores used in such materials are almost always linear, planar and polar molecules which contradict with the general structural requirements of a good glass forming compound. To overcome this, the molecular designs exploiting dendrimeric approach are widely used where the crystallization of compounds is prevented by an increased weight and a complicated geometry of the molecule [12-14]. The success of this method is not always predictable and, in addition, with the increase of molecular weight many dendrimeric compounds, like in the case of polymers, become hard to purify and characterize.

One of the promising directions regarding obtaining molecular glasses from small chromophores is the introduction of phase behavior modifying groups. In particular, groups like mexylamino-triazine [15] and triphenylamine derivatives [16] had been applied for such a use. Recently we have presented an approach where the







<sup>0143-7208/\$ -</sup> see front matter © 2013 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.dyepig.2013.08.020



Scheme 1. Synthetic routes for organic glasses OGL-(1-5). Example compound OGL-0 showing previously presented structural approach is also given.

crystallization of small molecular chromophores is prevented by using triphenylmethyl or triphenylsilyl auxiliary groups [17]. From a structural point of view these triphenyl substituents present several favorable standalone properties like being chemically inert, nonpolar, non-absorbent in the visible light range and solubility enhancing. Unfortunately, in the mentioned paper the triphenyl moieties were bound to the chromophore core by a labile C–O bond making materials susceptible to an acidic hydrolysis (see the structure **OGL-0** given as an example in Scheme 1). While this disadvantage can be overcome by simply avoiding the presence of acids during the processing of materials, this notably limits the possible synthetic routes during the production of compounds. In the present work we describe an improved chemical design for the modular approach introducing 1,1,1-triphenylpentane amorphous phase formation enhancing auxiliary group, where the aforementioned disadvantages are overcome. Using the new modifying moiety, the series of molecular glasses from different low-molecular chromophores frequently used in different NLO studies have been synthesized to show the versatility of the molecular design. The thermoplastic, linear and non-linear optical properties of the materials have been closely studied.

### 2. Experimental

### 2.1. Starting materials and general procedures

If not further specified, the starting reagents and solvents were obtained commercially from Alfa Aesar and used as received. The

following compounds were prepared according to known methods: 5,5,5-Triphenylpentan-1-ol (1) [18], 4-trityldiazobenzene-4'-diazonium tetrafluoroborate [19], 4-nitrobenzenediazonium tetrafluoroborate, 4-tritylbenzenediazonium tetrafluoroborate [17], 1,3indandione [20], 2-Dicyanomethylene-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran (**TCF**) [21], diazomethane [22], 4-(*tert*-butyl) phthalic acid [23]. The solvents used were reagent grade, DMF was distilled from P<sub>2</sub>O<sub>5</sub> and THF from CaH<sub>2</sub> before use. <sup>1</sup>H NMR spectra were obtained using Bruker Avance 300 MHz spectrometer using TMS as an inner standard. Low-resolution mass spectra were acquired on Waters EMD 1000 MS detector (ESI+ mode, cone voltage 30 V). The elemental analysis was carried out with Costech Instruments ECS 4010 CHNS-O Elemental Combustion System. The glass transition temperatures of the compounds were determined using Mettler Toledo DSC-1/200 W, by DSC thermograms acquired at heating rate 10 °C/min, initially the heating samples to decomposition onset temperatures and then cooling at the rate 50 °C/min. Decomposition temperatures were obtained using a Perkin Elmer STA 6000 thermal analyzer.

### 2.2. Synthesis

### 2.2.1. 1,1,1-Triphenylpentan-5-iodide (2)

1,1,1-Triphenylpentan-5-ol (14 g, 44.4 mmol), triphenylphosphine (17.41 g, 66.4 mmol) and imidazole (6.02 g, 88.6 mmol) were dissolved in anhydrous THF (100 mL). The solution was cooled to 0 °C and iodine (16.87 g; 66.4 mmol) was added in small portions. The resulting mixture was stirred at room temperature for 24 h. The formed precipitate was filtered off and washed with THF (3 × 10 mL). The solution was evaporated under reduced pressure to 30 mL volume and ethanol (70 mL) was added. After the repeated evaporation to 30 mL volume light-yellow precipitate formed and was filtered off. The crude product was crystallized from ethanol and **2** was obtained as white flakes (13.8 g, 73%). IR (KBr, *v* cm<sup>-1</sup>): 3053, 2951, 1489, 1443, 1262, 1183. <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>, 300 MHz): 1.12 (2H, m), 1.76 (2H, quin, <sup>3</sup>J = 7.3 Hz), 2.49 (2H, m), 2.99 (2H, t, <sup>3</sup>J = 7.3 Hz), 7.06–7.21 (15H, m). Elemental analysis. Calcd. for C<sub>23</sub>H<sub>23</sub>I: C, 64.80, H, 5.44. Found: C, 65.12, H, 5.50.

### 2.2.2. N,N-bis(5,5,5-Triphenylpentyl)aniline (3)

Aniline (1.1 g, 12.7 mmol) and compound **2** (12.0 g, 28.2 mmol) were dissolved in acetone (20 mL). Powdered K<sub>2</sub>CO<sub>3</sub> (4.0 g, 29 mmol) was added and the mixture was heated under reflux for 48 h. The precipitate was filtered, washed with acetone and the resulting solution was evaporated under reduced pressure. The obtained yellow oil was purified by column chromatography over silica gel using toluene/petroleum ether (2/1) as eluant to give **3** as clear viscous oil (8.50 g, 97%). The excess of reagent **2** was quantitatively recovered. IR (KBr,  $v \text{ cm}^{-1}$ ): 3056, 2942, 2870, 1504, 1492, 1446, 1367, 1264. <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>, 300 MHz): 0.97 (4H, m), 1.42 (4H, quin, <sup>3</sup>*J* = 7.3 Hz), 2.47 (4H, m), 2.94 (4H, t, <sup>3</sup>*J* = 7.7 Hz), 6.44 (2H, d, <sup>3</sup>*J* = 8.4 Hz), 6.53 (1H, t, <sup>3</sup>*J* = 7.2 Hz), 7.03–7.24 (32H, m). Calcd. for C<sub>52</sub>H<sub>51</sub>N: C, 90.52, H, 7.45, N, 2.03. Found: C, 90.81, H, 7.20, N, 2.14%.

#### 2.2.3. 4-(bis(5,5,5-Triphenylpentyl)amino)benzaldehyde (4)

DMF (1.41 g, 18.8 mmol) was cooled in an ice bath and phosphoryl chloride (2.89 g, 18.8 mmol) was added dropwise. After 1 h the solution of compound **3** (10 g, 14.5 mmol) in DMF (5 mL) was added and the resulting mixture was stirred at 70 °C temperature for 4 h. The water (2 mL) solution of NaOH (3.01 g, 75.3 mmol) was then added and stirred for 30 min. The mixture was poured into water (150 mL), and the product was extracted with toluene  $(3 \times 50 \text{ mL})$ . The combined extract was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated under reduced pressure. The crude product was purified by column chromatography over silica gel using toluene, then toluene/ethyl acetate (2/1) eluents to yield **4** as white amorphous solid (8.10 g; 78%). IR (KBr, v cm<sup>-1</sup>): 3083, 2941, 2870, 1670, 1542, 1492, 1443, 1164. <sup>1</sup>H NMR (δ, CDCl<sub>3</sub>, 300 MHz): 0.99 (4H, m), 1.43 (4H, quin,  ${}^{3}J = 7.3$  Hz), 2.47 (4H, m), 2.99 (4H, t,  ${}^{3}J = 7.7$  Hz), 6.40 (2H, d,  ${}^{3}J = 9.0$  Hz), 7.03–7.21 (30H, m), 7.56 (2H, d,  ${}^{3}J = 8.8$  Hz), 9.59 (1H, s). Calcd. for C<sub>53</sub>H<sub>51</sub>NO: C, 88.66, H, 7.16, N, 1.95. Found: C, 88.30, H, 7.05, N, 2.06%.

# 2.2.4. N,N-bis(5,5,5-Triphenylpentyl)-4-(-(4-(-(4-tritylphenyl) diazenyl)phenyl)diazenyl) aniline (**OGL-1**)

General procedure A. Aniline 3 (0.65 g, 0.94 mmol) was dissolved in acetic acid (5 mL) and 4-trityldiazobenzene-4'-diazonium tetrafluoroborate (0.76 g, 1.15 mmol) was added to the solution at room temperature, followed by addition of sodium acetate (0.23 g, 2.3 mmol). After stirring for 12 h ethanol (50 mL) was added to the solution and a red precipitate formed that was collected by filtration and air dried. The crude product was purified by column chromatography over silica gel using DCM/petroleum ether (2/1) as eluant. After the evaporation of solvent from the clean fractions, the obtained red glass was dissolved in DCM and ethanol was added. DCM was fractionally removed under reduced pressure and the red precipitate was filtered to yield **OGL-1** as red powder (0.80 g, 74%). IR (KBr,  $\nu$  cm<sup>-1</sup>): 3053, 2914, 2871, 1494, 1445, 1389, 1361, 1142. <sup>1</sup>H NMR (δ, CDCl<sub>3</sub>, 300 MHz): 1.02 (4H, m), 1.48 (4H, m), 2.49 (4H, m), 3.05 (4H, t, <sup>3</sup>*J* = 7.5 Hz), 6.48 (2H, m), 7.06–7.23 (45H, m), 7.33 (2H, d,  ${}^{3}J = 8.7$  Hz), 7.72–7.84 (4H, m), 7.87–7.94 (4H, m). Elemental analysis. Calcd. for C<sub>83</sub>H<sub>73</sub>N<sub>5</sub>: C, 87.41, H, 6.45, N, 6.14. Found: C, 87.15, H, 6.41, N, 6.52%.

# 2.2.5. 4-((4-Nitrophenyl)diazenyl)-N,N-bis(5,5,5-triphenylpentyl) aniline (**OGL-2**)

Compound was prepared according to *General procedure A* described above to yield **OGL-2** as red powder (0.64 g, 82%). IR (KBr,  $v \text{ cm}^{-1}$ ): 3054, 2939, 2870, 1515, 1419, 1331, 1131. <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>, 300 MHz): 1.03 (4H, m), 1.49 (4H, m), 2.50 (4H, m), 3.06 (4H, t, <sup>3</sup>*J* = 7.3 Hz), 6.48 (2H, d, <sup>3</sup>*J* = 8.5 Hz), 7.05–7.23 (30H, m), 7.79 (2H, d, <sup>3</sup>*J* = 8.7 Hz), 7.85 (2H, d, <sup>3</sup>*J* = 9.0 Hz), 8.23 (2H, d, <sup>3</sup>*J* = 9.0 Hz). MS (ESI+) *m/z*: 840.7 (M+, requires 840.1). Elemental analysis. Calcd. for C<sub>58</sub>H<sub>54</sub>N<sub>4</sub>O<sub>2</sub>: C, 83.02, H, 6.49, N, 6.68. Found: C, 82.39, H, 6.37, N, 6.33%.

# 2.2.6. N,N-bis(5,5,5-Triphenylpentyl)-4-((4-tritylphenyl)diazenyl) aniline (**OGL-3**)

Compound was prepared according to *General procedure A* described above to yield **OGL-3** as yellow powder (0.79 g, 89%). IR (KBr,  $v \text{ cm}^{-1}$ ): 3054, 2940, 2870, 1494, 1444, 1394, 1363, 1140. <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>, 300 MHz): 1.00 (4H, m), 1.47 (4H, m), 2.49 (4H, m), 3.03 (4H, t,  ${}^{3}J = 7.2 \text{ Hz}$ ), 6.46 (2H, d,  ${}^{3}J = 8.2 \text{ Hz}$ ), 7.04–7.23 (45H, m), 7.27 (2H, d,  ${}^{3}J = 8.7 \text{ Hz}$ ), 7.64 (2H, d,  ${}^{3}J = 8.7 \text{ Hz}$ ), 7.72 (2H, d,  ${}^{3}J = 7.7 \text{ Hz}$ ). MS (ESI+) *m/z*: 1037.6 (M+, requires 1037.4). Elemental analysis. Calcd. for C<sub>77</sub>H<sub>69</sub>N<sub>3</sub>: C, 89.23, H, 6.71, N, 4.05. Found: C, 89.19, H, 6.69, N, 4.00%.

### 2.2.7. 2-(4-(bis(5,5,5-Triphenylpentyl)amino)benzylidene)-1Hindene-1,3(2H)-dione (**OGL-4**)

Aldehyde **4** (0.80 g, 1.11 mmol) and indane-1,3-dione (0.20 g, 1.36 mmol) were dissolved in n-butanol (10 mL) and a drop of piperidine was added. After heating under reflux for 4 h, the product was precipitated by addition of ethanol (50 mL), filtered, washed with methanol and dried. After the purification by column chromatography over silica gel using DCM as eluant and following precipitation from DCM with ethanol, compound **OGL-4** was obtained as orange powder (0.60 g, 64%). IR (KBr,  $v \text{ cm}^{-1}$ ): 3057, 2941, 2869, 1713, 1667, 1552, 1512, 1445, 1351, 1182. <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>, 300 MHz): 1.02 (4H, m), 1.49 (4H, m), 2.49 (4H, m), 3.07 (4H, t, <sup>3</sup>*J* = 7.7 Hz), 6.48 (2H, d, <sup>3</sup>*J* = 9.0 Hz), 7.07–7.22 (30H, m), 7.84 (2H, m), 7.88 (1H, s), 8.05 (2H, m), 8.60 (2H, d, <sup>3</sup>*J* = 8.3 Hz). MS (ESI+) *m/z*: 847.6 (M+, requires 847.1). Elemental analysis. Calcd. for C<sub>62</sub>H<sub>55</sub>NO<sub>2</sub>: C, 88.01, H, 6.55, N, 1.66. Found: C, 87.75, H, 6.47, N, 1.68%.

# 2.2.8. (E)-2-(4-(4-(bis(5,5,5-Triphenylpentyl)amino)styryl)-3cyano-5,5-dimethylfuran-2(5H)-ylidene)malononitrile (**OGL-5**)

Compound 4 (1.38 g, 2.0 mmol) and TCF (0.40 g, 2.0 mmol) were dissolved in DMF (10 mL) and two drops of piperidine were added to the mixture. After stirring for 12 h at 80 °C temperature the solvent was evaporated under reduced pressure till 2 mL volume and ethanol (50 mL) was added. The blue precipitate was filtered, dried and purified by column chromatography over silica gel using DCM/hexane (6/1) as eluant. After the evaporation of the solvent from the clean fractions, the obtained blue glass was dissolved in DCM and ethanol was added. DCM was fractionally removed under reduced pressure and the blue precipitate was filtered to yield OGL-**5** as blue powder (0.40 g, 22%). IR (KBr,  $\nu$  cm<sup>-1</sup>): 3053, 2938, 2871, 2220, 1559, 1517, 1448, 1367, 1273, 1161. <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>, 300 MHz): 1.02 (4H, m), 1.44 (4H, m), 1.67 (6H, s), 2.49 (4H, m), 3.05  $(4H, t, {}^{3}J = 7.6 \text{ Hz}), 6.41 (2H, d, {}^{3}J = 9.0 \text{ Hz}), 6.64 (1H, d, {}^{3}J = 15.8 \text{ Hz}),$ 7.07–7.21 (30H, m), 7.38 (2H, d,  ${}^{3}J = 8.7$  Hz), 7.51 (1H, d, <sup>3</sup>*J* = 15.8 Hz). MS (ESI+) *m/z*: 900.8 (M+, requires 900.2). Elemental analysis. Calcd. for C<sub>64</sub>H<sub>58</sub>N<sub>4</sub>O: C, 85.49, H, 6.50, N, 6.23. Found: C, 85.48, H, 6.49, N, 6.07%.

### 2.2.9. Dimethyl 4-(tert-butyl)phthalate (6)

In a well-ventilated fume hood to the solution of 4-(*tert*-butyl) phthalic acid (10 g; 45.0 mmol) in methanol/water (10/1, 100 mL)

freshly prepared diazomethane MTBE solution was added dropwise. When the mixture had turned light yellow and the release of gas bubbles was no more observed, the addition was stopped and the solvent was removed under reduced pressure. The resulting oil was dissolved in MTBE and washed with 5% NaHCO<sub>3</sub> solution. The organic layer was then dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated under reduced pressure. The crude product was purified by column chromatography over silica gel using DCM as eluant to give **6** as clear viscous oil (7.0 g, 62%). IR (KBr, v cm<sup>-1</sup>): 2955, 2907, 2871, 1725, 1434, 1292, 1281, 1247. <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>, 300 MHz): 1.26 (9H, s), 3.81 (3H, s), 3.84 (3H, s), 7.46 (1H, dd, <sup>3</sup>*J* = 8.1 Hz, <sup>4</sup>*J* = 2.1 Hz), 7.60 (1H, d, <sup>4</sup>*J* = 2.1 Hz), 7.63 (1H, d, <sup>3</sup>*J* = 8.3 Hz). Elemental analysis. Calcd. for C<sub>14</sub>H<sub>18</sub>O<sub>4</sub>: C, 67.18, H, 7.25. Found: C, 67.25, H, 7.29.

# 2.2.10. 2-(4-(bis(5,5,5-Triphenylpentyl)amino)benzylidene)-5-(tertbutyl)-1H-indene-1,3(2H)-dione (**OGL-6**)

To the compound 6 (7.0 g, 28.0 mmol) small lumps of sodium (1.21 g, 52 mmol), anhydrous ethanol (0.14 mL) and ethyl acetate (6.77 mL) were added and the mixture was heated under reflux for 8 h. Ethanol (20 mL) was then added and the mixture was left to stir for 1 h. The solvent was removed under reduced pressure and the resulting brown glass was added in small portions to the boiling water (125 mL). The water solution was then cooled to 70 °C and after 1 h sulfuric acid/water mixture (1/3, 25 mL) was added dropwise. The mixture was cooled and extracted with MTBE. The organic layer was then dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated under reduced pressure. The crude product was then dissolved in n-butanol (10 mL) along with aldehyde 4 (1 g, 1.40 mmol) and a drop of piperidine was added. After heating under reflux for 4 h, the product was precipitated by addition of ethanol (50 mL), filtered, washed with methanol and dried. After the purification by column chromatography over silica gel using DCM as eluant and following precipitation from DCM with ethanol, compound OGL-6 was obtained as orange powder (0.48 g). IR (KBr,  $v \text{ cm}^{-1}$ ): 3055, 2948, 1713, 1670, 1554, 1511, 1445, 1365, 1323, 1173.  $^1\mathrm{H}$  NMR (  $\delta$ CDCl<sub>3</sub>, 300 MHz): 1.02 (4H, m), 1.34 (9H, 2 signals representing *E*/*Z* isomers with integral intensity 1:1), 1.46 (4H, m), 2.50 (4H, m), 3.07  $(4H, t, {}^{3}J = 7.5 \text{ Hz}), 6.46 (2H, d, {}^{3}J = 9.2 \text{ Hz}), 7.08 - 7.23 (30H, m), 7.66$ (1H, d), 7.67-7.71 (1H, m), 7.78 (1H, m), 7.87 (1H, m), 8.39 (2H, d,  ${}^{3}J = 8.5$  Hz). MS (ESI+) m/z: 903.6 (M+, requires 903.2). Elemental analysis. Calcd. for C<sub>66</sub>H<sub>63</sub>NO<sub>2</sub>: C, 87.86, H, 7.04, N, 1.55. Found: C, 87.25, H, 7.14, N, 1.42%.

#### 2.3. Sample film preparation

The typical procedure involved the preparation of a compound solution with concentration 100 mg/mL. The solution was then dropped onto indium tin oxide (ITO) covered glass substrates and spin-coated with a Laurell WS-400B-6NPP/LITE (starting speed – 0 rpm, terminal speed – 300 rpm, acceleration – 200 rpm/s<sup>2</sup>, spinning time – 1 min). The resulting films were 1–2  $\mu$ m thick. The samples for absorption spectra were 0.05–0.1  $\mu$ m thick and were made from 5 times more diluted solutions.

### 2.4. Linear and non-linear optical measurements

The NLO properties of films were characterized by means of the Maker fringe technique with an excitation at 1064 nm. The thickness, refractive indexes and absorption coefficients of amorphous films were determined in advance. The NLO coefficients  $d_{33}$ ,  $d_{31}$  and  $d_{15}$  were calculated by Herman and Hayden [24] approach using an *x*-cut quartz crystal as a reference ( $d_{11} = 0.3 \text{ pm/V}$ ) and taking into the account the absorption of film at 532 nm. The more detailed descriptions of these procedures could be found in our previous studies [17,25].

### 3. Results and discussion

The main task in this study was to improve the chemical stability of our previously presented compounds that contain triphenylmethyl (trityl) auxiliaries as amorphous phase formation ensuring groups (see example structure **OGL-0**) [17]. The logical synthetic step in this direction was to replace the labile C–O bond with a more stable C–C bond. Following our structural approach presented previously this new molecular fragment should be connected to an aniline nitrogen atom to form the basis of an electron donating part of a chromophore. To achieve this the alkylating agent 1,1,1-triphenylpentane-5-iodide (2) was synthesized from the known intermediate 1,1,1-triphenylpentane-5-ol (1) [18] and was reacted with aniline to obtain the key building block for molecular glasses N,N-bis(5,5,5-triphenylpentyl)aniline (3) (Scheme 1). The choice of a four carbon atom long connecting bridge between a trityl group and nitrogen was not coincidental. While not described here in the detail, we performed initial synthetic routes involving propane and butane analogs of compound 2. In the first case the alkylation did not proceed due to steric hindrance of electrophilic center by trityl group. The second synthetic approach resulted in the products with relatively poor solubility and glass formation ability.

The aniline **3** was azo-coupled with the series of diazonium salts to yield final products **OGL-1,2,3**. Compounds **OGL-1,3** contain an additional triphenyl group in the acceptor part of chromophore what could result in a better phase behavior and thermoplastic properties. In addition, sterically large groups in close proximity to the chromophores have been shown to increase the macroscopic NLO performance of materials [26]. This so called site isolation principle is based on the prevention of dipole–dipole interactions of polar chromophore moieties. The NLO activity of chromophore systems is ensured by ordering these molecules noncentrosymmetrically by an external electric field poling. If molecules are not sufficiently isolated dipoles tend to spontaneously align centrosymmetrically leading to a decreased poling efficiency and stability of a poled system.

Vilsmeier formylation of compound 3 yielded 4-(bis(5,5,5triphenylpentyl)amino)benzaldehyde (4), a building block for styrene dyes. The Knoevenagel condensations of 4 with 1,3indandione and TCF yielded products OGL-4,5. To reduce the intermolecular dipole interactions and improve the NLO performance of the material a sterically bulky tert-butyl group in the 5 position of indane-1,3-dione was introduced according to Scheme 2. The esterification of 4-(tert-butyl)phthalic acid (5) by convenient methods was unsuccessful and was accomplished by the use of diazomethane. After the subsequent cyclization the acquired 5tert-butylindane-1,3-dione, without isolation, was condensed with 4 to yield OGL-6. The <sup>1</sup>H NMR spectra revealed that a 1:1 mixture of E/Z isomers was obtained depending on the *tert*-butyl group placement in the indanedione ring. It was not separable with both the flash chromatography and HPLC and the further measurements were taken for the mixture of isomers.

The acquired compounds **OGL-(1–6)** all show a good glass formation ability and an excellent solubility in non-polar organic solvents, so the films with a high optical quality can be easily acquired by spin-coating from concentrated solutions using volatile solvents like chloroform without the use of added plasticizers. The thermoplastic properties of the compounds were examined by DSC. The glass transition temperatures (Fig. 1) were acquired on the second heating cycle after the samples were initially heated to the temperatures where a decomposition onset was observed (Table 1). In the all cases no other peaks than  $T_g$  were observed during the repeated heating. Moreover, only samples **OGL-2** and **OGL-3** revealed the presence of a crystalline phase during the initial



Scheme 2. Synthetic route for 5-tert-butylindane-1,3-dione fragment containing compound OGL-6.

heating showing melting peaks at 185 and 171 °C representatively. The acquired  $T_g$  values are close to those we measured for the tritiloxy moieties containing compounds in our previous study [17]. A linear positive correlation between molecular weight and glass transition temperature can be observed for azobenzene dye containing compounds **OGL-(1–3)**, the same can be said for indane-1,3-dione fragments containing **OGL-4,6** as with the introduction of *tert*-butyl substituent the glass transition temperature increases by 15 °C.

Despite the relatively low molecular weight, the highest  $T_g$  value of 108 °C was measured for compound **OGL-5**. Taking into the consideration the highest calculated dipole momentum value for this compound (see Table 1), the increased heat resistance of the glass can be explained by a strong intermolecular chromophore  $\pi$ –  $\pi$  stacking in the solid phase, a property that is known for the given dye system [27]. The obtained solid phase UV–Vis absorption spectra reassure this assumption (Fig. 2) as **OGL-5** shows a distinctive pair of absorption bands. The band with a peak at 577 nm is comparable to the absorption of the compound in CH<sub>2</sub>Cl<sub>2</sub> (the maximum value at 575 nm) and likely represents nonaggregated molecules while bathochromically shifted band at 619 nm can be attributed to the aggregates. For the other compounds no notable multimodality is observed in the absorption



**Fig. 1.** Acquired DSC thermograms showing *T*<sub>g</sub> peaks.

bands. These observations of the absorption spectra suggest that with the increase of chromophore polarity the trityl auxiliary groups bound at the donor part of the chromophore cannot ensure sufficient chromophore shielding from dipole—dipole interactions and further molecular modifications at the acceptor part of the molecules are necessary.

The measured nonlinear coefficients for compounds are given in Table 1. To evaluate the relative performance of materials several



**Fig. 2.** Absorption spectra and maxima in thin films for azobenzene (a) and stilbene (b) chromophores containing compounds.

Table 1

Calculated hyperpolarizabilities and dipole moments; measured thermoplastic, linear and nonlinear optical properties in solid films.

Compound	$\beta_{(0)}$ , $10^{30}~\mathrm{esu^a}$	$\mu$ , D <sup>a</sup>	$T_{\text{decomp.}}$ , °C	T <sub>SHI50</sub> , °C	RI <sub>532</sub>	RI1064	$d_{31(532)}$ , pm $ imes$ V $^{-1}$	$d_{ m 33(532)}$ , pm $ imes$ V $^{-1}$	$d_{33(0)}$ , pm $ imes$ V $^{-1}$
OGL-1	32.7 <sup>b</sup>	2.81	331	92	2.55	1.63	11.5	24.2	1.9
OGL-2	40.3 <sup>b</sup>	9.85	320	66	2.15	1.61	28.7	117.7	11.0
OGL-3	20.1 <sup>b</sup>	2.59	355	73	1.71	1.59	2.1	10.8	3.0
OGL-4	31.0	4.00	298	74.5	1.95	1.66	32.6	84.8	7.7
OGL-5	60.1	18.3	279	86	1.04	1.72	7.5	24.9	5.7
OGL-6	27.7 <sup>c</sup>	3.15 <sup>c</sup>	290	75	1.99	1.64	25.8	57.4	6.2

<sup>a</sup> Quantum chemical calculations (RHF with basis set 6-31G(p,d) in the vacuum by Gaussian 09W).

<sup>b</sup> Trans configuration for all azo dyes was energetically preferable, so given values correspond to this conformer.

<sup>c</sup> Both isomers (E/Z) have almost the same molecular hyperpolarizability.



Fig. 3. The temperature induced decay of second harmonic intensity in poled films.

factors need to be taken into the consideration. The general macroscopic NLO activity for a compound is proportional to an active chromophore hyperpolarizability and accentric chromophore order. Additionally, the measured second harmonic (SH) generation efficiency is frequency dependent and approaching the lowest chromophore charge-transfer transition (CT) the resonance enhancement takes place and inflates the acquired  $d_{33}$  values. The extrapolation to the zero frequency  $d_{33(0)}$  according to the two level model [28] is often used to benchmark different chromophores, however, if SH and CT frequencies are close the precision of this model falls drastically [29]. Overall, the measured  $d_{33}$  and  $d_{33(0)}$ values show good correlation with calculated  $\beta$  values with the notable exceptions being compounds OGL-4 and OGL-5. In the case of OGL-5 the low measured nonlinearity despite the highest calculated  $\beta$  can be attributed to the formation of aggregates discussed previously, resulting in lowered accentric chromophore order. The opposite situation is observed for compound **OGL-4** where the  $d_{33}$  value exceeds expected. With a comparable structure, compound OGL-6 was predicted to perform better due to tertbutyl group providing improved shielding from dipole-dipole interactions. And if compared with our previously synthesized indane-1,3-dione containing molecular glasses [17] this was the case as the increase by close to 50% was achieved regarding materials NLO performance. However, OGL-4 performs notably better. A specific structure related anisotropic self assembly and resulting increase in non-centrosymmetry is proposed as the cause of this, but additional experiments are planned to examine this feature in detail. The temperature dependent decay of SH intensity was also measured (Fig. 3) and the values  $T_{SHI50}$  were obtained (Table 1) representing the temperatures at which a half of starting SH intensity has vanished. These values should be close to the measured glass transition temperatures as the steep increase in molecular motion leads to the loss of chromophore accentric order. However, the measured  $T_{SHI50}$  values are notably lower than  $T_g$  for most compounds. This can be partly explained by the different glass formation conditions (spin-coating and melting) and the resulting structural differences for the amorphous materials and a lower thermodynamic stability of supercooled system in the poled film. The highest *T*<sub>SHI50</sub> value of 92 °C was measured for compound **OGL**-1 what was expected as it is the compound with the highest molecular weight.

### 4. Conclusions

We have shown that the phase behavior modifying 1,1,1triphenylpentane substituents can be successfully used to obtain stable organic glasses from small-molecular chromophores. The obtained compounds show good solubility in non-polar solvents and good optical quality films can be prepared using a simple spin-coating procedure. Glass transition temperatures in the range of 73–108 °C were measured depending on the chromophore. Generally, the heat resistance of the compound increases with the molecular weight, although the high chromophore dipole momentum and the resulting partial  $\pi - \pi$  stacking also contribute to increased  $T_g$  values. After the poling procedure the materials showed nonlinear optical activity. For the chromophores with relatively low hyperpolarizability the measured NLO performance is in the expected range, but for more polar chromophores it falls due to the reduced polar order of chromophores as it was illustratively observed for compound **OGL-5**. Additional site isolating groups are suggested to improve materials performance in these cases.

# Acknowledgments

This work has been supported by the European Social Fund within the project "Support for the implementation of doctoral studies at Riga Technical University", and National Research Program "Development of Innovative Multifunctional Materials, Signal Processing and Information Technologies for Competitive Science Intensive Products".

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