



# Triphenyl group containing molecular glasses of azobenzene for photonic applications



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## ABSTRACT

D- $\pi$ -A type organic molecules have attracted considerable attention of scientists due to their potential applications in nonlinear optics and holographic data storage as light, flexible and low-cost photonic materials. To provide a better understanding on the relation between the compound chemical structure and their physical properties necessary for the mentioned purposes, eight glassy triphenyl group containing derivatives of azobenzene with incorporated 5,5-dimethylcyclohex-2-enylidene or 4*H*-pyran-4-ylidene structural fragments and dicyanomethylene, indene-1,3-dione and pyrimidine-2,4,6 (1*H*,3*H*,5*H*)-trione acceptor groups have been synthesized and investigated.

Thermal stability of synthesized glasses is no lower than 250 °C and glass transition in higher than 70 °C which both further increases (up to 120 °C) by additional number of attached triphenyl-moieties and incorporated structural fragments. Almost all of the synthesized azodyes form good optical quality transparent amorphous films from volatile organic solvents with their light absorption in thin solid films in the range of 400–660 nm. Azocompounds with sterically small cyclohex-2-ene-1-ylidene fragment in their molecules proved to be most efficient materials for holographic data storage and nonlinear optics with diffraction efficiency up to 20.40%, self diffraction efficiency up to 12.94% and NLO coefficient  $d_{33}$  up to 125.7 pm/V. Azodyes with no additionally incorporated structural fragments and indene-1,3-dione electron acceptor group were least efficient materials for these purposes, however may show potential as photoactive components in organic solar cells due to their remarkable light absorption properties in the solid state.

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## 1. Introduction

In the last two decades the small organic molecules where the electron acceptor fragment is bonded through  $\pi$ -conjugated system with electron donating fragment have been studied due to their potential applications as a new generation optical materials for nonlinear optics (NLO) and holographic information data storage due to their flexibility, light weight and low-cost fabrication possibility [1–8].

Standard design for such materials with nonlinear optical activity requires the incorporation of chromophore fragments with high hyperpolarizability, thermal and chemical stabilities [1,2,8–15]. Organic materials with azobenzene fragment in their structures makes them possible to form holographic volume and diffraction

gratings due to a reversible *trans-cis-trans* photoisomerization processes after exposure to laser radiation, which could be useful for information storage [10,12,16–21]. Various synthetic modification possibilities for organic compounds has provided numerous approaches regarding the placement of azobenzene fragment containing or NLO active chromophores, most commonly in polymer [1,2,8–21], dendrimeric [22,23] and host-guest systems [12,24].

For NLO applications inorganic crystals were widely used, however their production is expensive and complicated [1,2,8]. Organic polymers obtained through synthesis are light, flexible and simple to produce, but possess several other drawbacks. The repeated synthesis of the exactly the same polymer is a challenging task [1,2,12] as the obtained products always will have different physical properties. In case chromophore molecules are doped in a polymer matrix, phase separation problem may occur. This resulting in decrease of optical transparency in the polymer composite films.

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Recently it was demonstrated [25–27] that by the incorporation of bulky triphenyl groups in the low molecular mass organic compounds enables their excellent solubility in non-polar organic solvents and enhances the ability to form good optical quality transparent glassy films by solution processing. Such organic compounds with nonlinear optical [25,26] and holographic information storage properties were obtained [27]. The mentioned approach and have a certain and well defined structure and good synthetic repeatability. The investigated triphenyl group containing molecular materials could be used either for NLO or optical information storage but never for both purposes at the same time. Therefore to provide with a better understanding on the relation between the compound chemical structure and their physical properties, eight glassy triphenyl group containing derivatives of azobenzene with incorporated different structural fragments and functional acceptor groups have been synthesized and investigated in this work for potential applications in NLO and holographic information storage.

## 2. Experimental

All necessary reagents were purchased as commercial products from Acros Organics, Sigma-Aldrich and Alfa-Aesar. Organic solvents (pyridine, dichloromethane, chloroform, triethylamine and piperidine) were dried by refluxing with calcium hydride and distilled.

### 2.1. Syntheses of compounds

Full synthesis and characterization and/or relevant references of all organic compounds is presented and available in [Supplementary Information](#).

#### 2.1.1. General method of synthesis of azoaldehydes **4a-b** [21]

To a suspension of 2.0 g (16.50 mmol) 4-amino-benzaldehyde (**2**) [28] in 34.0 mL distilled water a 4.0 mL of concentrated hydrochloric acid was slowly added in a period of 30 min while the solution was cooled down to 0.5 °C temperature. Afterwards a 1.20 g (16.70 mmol) NaNO<sub>2</sub> dissolved in 4.0 mL distilled water were added over a period of another 30 min. The obtained solution was stirred at a 0.5 °C temperature over 40–60 min until the suspension fully dissolves. To the afforded clear solution a 16.30 mmol of respective N,N-disubstituted aniline was added and the reaction mixture was stirred further over a period of 24 h, then poured into ~300 mL distilled water and neutralized with KHCO<sub>3</sub> until pH ~ 7. The formed solid were filtered, washed and dried.

#### 2.1.2. General method of synthesis of azocompounds **6a-b** [29]

To a solution of indene-1,3-dione (**5**) (0.49 g, 3.37 mmol) and (E)-4-((4-(ethyl(2-hydroxyethyl)amino)phenyl)diazanyl)benzaldehyde (**4a**) (1.00 g, 3.37 mmol) in dry ethanol (30.0 mL) was added piperidine (0.43 mL, 4.37 mmol). The reaction mixture was refluxed for 8 h, then cooled overnight to the room temperature. The afforded solid was filtered, washed and dried.

#### 2.1.3. General method of synthesis of azocompounds **WE-1**, **WE-2**, **WE-3** and aldehydes **7a-b** [29]

To a solution of trityl-chloride or triphenylsilyl-chloride (1.50 mmol or 3.00 mmol) in dry pyridine (5.0 mL) was added triethylamine (1.50 mmol, 0.21 mL) and the respective hydroxyl group containing azocompound (1.00 mmol). Depending on the reactants the reaction mixture was either refluxed for 2 h or stirred for 24 h at a room temperature. The formed slurry was poured either in ~200 mL ethanol or distilled water. The afforded solid were filtered, dried and then purified.

2.1.3.1. (E)-2-(4-((4-(ethyl(2-(trityloxy)ethyl)amino)phenyl)diazanyl)benzylidene)-1H-indene-1,3(2H)-dione (**WE-1**). Yield: 73%; m.p. 175 °C; IR (KBr)  $\nu$ , cm<sup>-1</sup>: 3468, 2924, 1719, 1698, 1683, 1605, 1583, 1557, 1516, 1350, 1316, 1259, 1222, 1204, 1192, 1162, 1137. <sup>1</sup>H-NMR (200 MHz; CDCl<sub>3</sub>)  $\delta$ , ppm.: 1.15 (3H, t, <sup>3</sup>J = 7.69 Hz), 3.33 (2H, t, <sup>3</sup>J = 5.13 Hz), 3.43–3.58 (4H, m), 6.63 (2H, d, <sup>3</sup>J = 9.0 Hz), 7.10–7.40 (15H, m), 7.70–8.00 (9H, m), 8.57 (2H, d, <sup>3</sup>J = 8.5 Hz). Elemental analysis: calcd. for **WE-1** (C<sub>45</sub>H<sub>37</sub>N<sub>3</sub>O<sub>3</sub>): C, 80.94; H, 5.58; N, 6.29, found C, 80.12; H, 5.58; N, 5.97.

2.1.3.2. (E)-2-(4-((4-(bis(2-(trityloxy)ethyl)amino)phenyl)diazanyl)benzylidene)-1H-indene-1,3(2H)-dione (**WE-2**). Yield: 90%; m.p. 239 °C; IR (KBr)  $\nu$ , cm<sup>-1</sup>: 3083, 3055, 2922, 2871, 2859, 1724, 1682, 1598, 1582, 1557, 1513. <sup>1</sup>H-NMR (400 MHz; CDCl<sub>3</sub>)  $\delta$ , ppm.: 3.30 (4H, t, <sup>3</sup>J = 5.46 Hz), 3.62 (4H, t, <sup>3</sup>J = 5.5 Hz), 6.55 (2H, d, <sup>3</sup>J = 9.4 Hz), 7.10–7.40 (30H, m), 7.75 (3H, m, <sup>3</sup>J = 8.6 Hz), 7.97 (2H, m), 8.56 (2H, d, <sup>3</sup>J = 8.6 Hz). Elemental analysis: calcd. for **WE-2** (C<sub>64</sub>H<sub>51</sub>N<sub>3</sub>O<sub>4</sub>): C, 83.00; H, 5.55; N, 4.54, found C, 83.27; H, 5.57; N, 4.62.

2.1.3.3. (E)-2-(4-((4-(bis(2-(triphenylsilyloxy)ethyl)amino)phenyl)diazanyl)benzylidene)-1H-indene-1,3(2H)-dione (**WE-3**). Yield: 41%; m.p. 236 °C; IR (KBr)  $\nu$ , cm<sup>-1</sup>: 3065, 2929, 2860, 1724, 1683, 1599, 1581, 1557, 1514, 1429. <sup>1</sup>H-NMR (400 MHz; CDCl<sub>3</sub>)  $\delta$ , ppm.: 3.47 (4H, t, <sup>3</sup>J = 5.9 Hz), 3.86 (4H, t, <sup>3</sup>J = 6.3 Hz), 6.32 (2H, d, <sup>3</sup>J = 9.4 Hz), 7.20–7.50 (30H, m), 7.62 (2H, d, <sup>3</sup>J = 9.0 Hz), 7.76 (2H, m), 7.88 (3H, m, <sup>3</sup>J = 8.2 Hz), 7.97 (2H, m), 8.56 (2H, d, <sup>3</sup>J = 8.6 Hz). Elemental analysis: calcd. for **WE-3** (C<sub>62</sub>H<sub>51</sub>N<sub>3</sub>O<sub>4</sub>Si<sub>2</sub>): C, 77.71; H, 5.36; N, 4.39, found C, 76.70; H, 5.31; N, 4.43.

2.1.3.4. (E)-4-((4-(ethyl(2-(trityloxy)ethyl)amino)phenyl)diazanyl)benzaldehyde (**7a**). Yield: 76%; m.p. 171 °C; IR (KBr)  $\nu$ , cm<sup>-1</sup>: 3435, 3061, 3024, 2980, 2966, 2928, 2914, 2871, 2835, 2740, 1687, 1594, 1560, 1518, 1491, 1425, 1407. <sup>1</sup>H-NMR (200 MHz; CDCl<sub>3</sub>)  $\delta$ , ppm.: 1.14 (3H, t, <sup>3</sup>J = 5.5 Hz), 3.32 (2H, q, <sup>3</sup>J = 6.3 Hz), 3.44–3.52 (4H, m), 6.62 (2H, d, <sup>3</sup>J = 9.4 Hz), 7.10–7.40 (15H, m), 7.78 (2H, d, <sup>3</sup>J = 9.4 Hz), 7.85–7.97 (4H, m), 10.00 (1H, s).

2.1.3.5. (E)-4-((4-(bis(2-(trityloxy)ethyl)amino)phenyl)diazanyl)benzaldehyde (**7b**). Yield: 52%; m.p. 225 °C; IR (KBr)  $\nu$ , cm<sup>-1</sup>: 3084, 3054, 3021, 2945, 2921, 2891, 2876, 2849, 2259, 1694, 1592, 1560, 1518, 1490. <sup>1</sup>H-NMR (200 MHz; CDCl<sub>3</sub>)  $\delta$ , ppm.: 3.29 (4H, t, <sup>3</sup>J = 7.0 Hz), 3.6 (3H, t, <sup>3</sup>J = 5.5 Hz), 6.5 (2H, d, <sup>3</sup>J = 9.4 Hz), 7.10–7.40 (30H, m), 7.73 (2H, d, <sup>3</sup>J = 7.4 Hz), 7.85–7.97 (4H, m), 10.00 (1H, s).

#### 2.1.4. General method of synthesis of azocompounds **IWK-2M** and **IWK-2D** [29,30]

To a solution of 3,5,5-trimethylcyclohex-2-enone (**8**) (1.84 g or 2.0 mL, 13.30 mmol) and malononitrile (**9**) (0.87 g, 13.30 mmol) in 3.0 mL DMFA was added piperidine (0.20 mL) and catalytic amount of acetic acid (2 drops) and acetic anhydride (1 drop). The reaction mixture was stirred at room temperature for one hour and at a 70 °C for another hour. To the heated reaction mixture the respective trityl group containing azoaldehyde (**7a** or **7b**) (2.50 mmol) and additional 4.0 mL DMFA were added. The obtained solution was stirred under reflux for one hour, then cooled to the room temperature and poured in ~200 mL ethanol. The afforded solid were filtered, dried and then purified.

2.1.4.1. 2-(3-(4-((E)-4-(ethyl(2-(trityloxy)ethyl)amino)phenyl)diazanyl)styryl)-5,5-dimethylcyclohex-2-enylidene)malononitrile (**IWK-2M**). Yield: 21%; m.p. 188 °C; IR (KBr)  $\nu$ , cm<sup>-1</sup>: 3448, 3082, 3032, 2969, 2957, 2927, 2872, 2217, 1600, 1563, 1518, 1406. <sup>1</sup>H-NMR (300 MHz; CDCl<sub>3</sub>)  $\delta$ , ppm.: 1.01 (6H, s), 1.13 (3H, t,

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