

## Structure-dependent tuning of electro-optic and thermoplastic properties in triphenyl groups containing molecular glasses



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### HIGHLIGHTS

- Triphenylmethyl groups can be used to reduce solid phase dipole interactions in organic molecular materials.
- NLO efficiency of a poled material is higher, if a number of present triphenyl groups increases.
- NLO efficiency of materials decreases, if polarity of used chromophores increases.
- Thermal stability of polar order up to 108 °C can be achieved in poled organic glasses.

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### ABSTRACT

The series of seven molecular compounds composed of D- $\pi$ -A chromophores and triphenylmethyl auxiliary groups were characterized by UV-Vis spectroscopy, differential scanning calorimetry and quantum chemical calculations. Nonlinear optical (NLO) properties of compounds were determined by second harmonic generation measurements in corona poled thin glassy films. The results show that triphenylmethyl auxiliary groups are effective at shielding undesirable dipole interactions in solid phase thus increasing NLO efficiency of materials. Thermal stability up to 108 °C was achieved for a polar order in poled samples.

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## 1. Introduction

During the last two decades the research of organic nonlinear optical (NLO) materials has resulted in a notable performance increase for organic NLO devices, making them viable for various practical applications [1,2]. For example, effective organic electro-optic modulators for fiber optical communication systems have been demonstrated [3].

A macroscopic NLO activity in an organic material can be observed if several structural requirements are met. At the microscopic level the material must contain molecules with large molecular hyperpolarizability ( $\beta$ ) values. Such a property is common to donor-acceptor (D-A) dyes, and is to a great extent determined by a

donor or acceptor group strength [4], or by a length of  $\pi$ -electron chain in the D-A conjugation system [5]. Another important requirement for NLO materials is the noncentrosymmetric arrangement of NLO active structural elements. The molecules with large  $\beta$  values usually also have large dipole moment ( $\mu$ ), so in the solid state they tend to pack centrosymmetrically due to dipole-dipole interactions. The required polar order in the material is typically achieved by an electric field poling procedure. Unfortunately, dipole interactions limit the poling efficiency, and the achievable degree of polar order is low. To overcome this, the principle of site isolation is applied, modifying the molecule, so that polar interactions between molecules are shielded by bulky structural groups [6–9]. The known approaches are effective to just a certain degree and the intermolecular interactions still limit the attainable efficiency of organic NLO compounds. Therefore the search for materials with large structural noncentrosymmetry through means of molecular engineering is still one of the main

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challenges in the development of in NLO devices applicable organic materials.

Recently we have demonstrated a new structural approach to obtaining amorphous phase forming molecular materials, also known as molecular glasses, from different organic dyes [10,11]. The method is based on attaching triphenylmethyl-substituents to polar D-A organic dyes that otherwise would crystallize in the solid state. Such materials have potential in NLO [10,11], light emission [12] and holographic recording [13] applications. The structure of bulky and non-polar triphenylmethyl-substituents by concept could provide an effective sterical isolation of polar chromophores, falling within the idea of site isolation principle and making such materials particularly promising for use in NLO devices. In this study a series of triphenyl groups containing molecular glasses are investigated and structure-NLO performance relations are analysed. The acquired results could provide us with a better understanding of general structural requirements for a design of high-performance NLO materials.

## 2. Experimental

### 2.1. Materials and sample preparation

Chemical structures of the studied compounds are given in Fig. 1. The synthesis, spectral data and thermoplastic properties of materials **Azo-1** [14], **Pyr-1**, **Pyr-2** [12], **Pyr-3** [15] and **Iph-1**, **Iph-2** [16] are published in separate papers.

#### 2.1.1. Synthesis of compound **Azo-2**

The synthesis of compound **Azo-2** is outlined in Scheme 1.

Starting materials were purchased from Acros and Alfa Aesar. Solvents, DMF and  $\text{CH}_2\text{Cl}_2$ , were dried over  $\text{P}_2\text{O}_5$ , MeCN and Py - over  $\text{CaH}_2$ . Compound **4** was prepared according a known procedure [17]. The UV-Vis spectra were recorded with Perkin Elmer Lambda 35 spectrometer. IR spectra were recorded with Perkin Elmer Spectrum 100 FT-IR spectrometer using UATR accessory, NMR spectra were obtained on a Bruker Avance 300 MHz or Varian 6 Unity Inova 600 MHz spectrometers using solvent residue as an internal reference. Reaction mixture analysis was carried out on HPLC-MS system consisting of Waters Alliance 2695 chromatograph equipped with XTerra<sup>®</sup> MS C18 5  $\mu\text{m}$  2.1  $\times$  100 mm column, Waters 2996 PDA detector, Waters EMD 1000 (ESI) mass spectrometer. The elemental analysis was carried out with Costech Instruments ECS 4010 CHNS-O Elemental Combustion System.

**2.1.1.1. 4-[N-(2-hydroxyethyl)-N-(2-trityloxyethyl)amino]-4'-nitroazobenzene (2).** Compound **1** (3.00 g, 9.0 mmol) was dissolved in abs. Py (100 mL) and tritylchloride (2.53 g, 9.0 mmol) and  $\text{NEt}_3$  (2.6 mL, 18 mmol) were added. Resulting solution was heated at 100 °C for 6 h, and water (400 mL) was added to the cooled reaction mixture. The next day a formed precipitate was filtered and dried, then it was mixed with  $\text{CH}_2\text{Cl}_2$ , unreacted insoluble starting material **1** was filtered off, filtrate was chromatographed on silica gel with  $\text{CH}_2\text{Cl}_2$  then 10% EtOAc/ $\text{CH}_2\text{Cl}_2$  as eluent. Yield 2.59 g (50%) of deep red crystals, *mp* 161–163 °C.

Elem. anal. calcd. for  $\text{C}_{35}\text{H}_{32}\text{N}_4\text{O}_4$ : C 73.41; H 5.63; N 9.78; found: C 73.27; H 5.87; N 9.56%.

MS ESI + *m/z* calcd.  $\text{C}_{35}\text{H}_{33}\text{N}_4\text{O}_4$  573.2  $[\text{M}+\text{H}]^+$ , found 573.3  $[\text{M}+\text{H}]^+$ .

<sup>1</sup>H NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.27 (d, *J* = 8.8, 2H), 7.86 (d, *J* = 8.8,

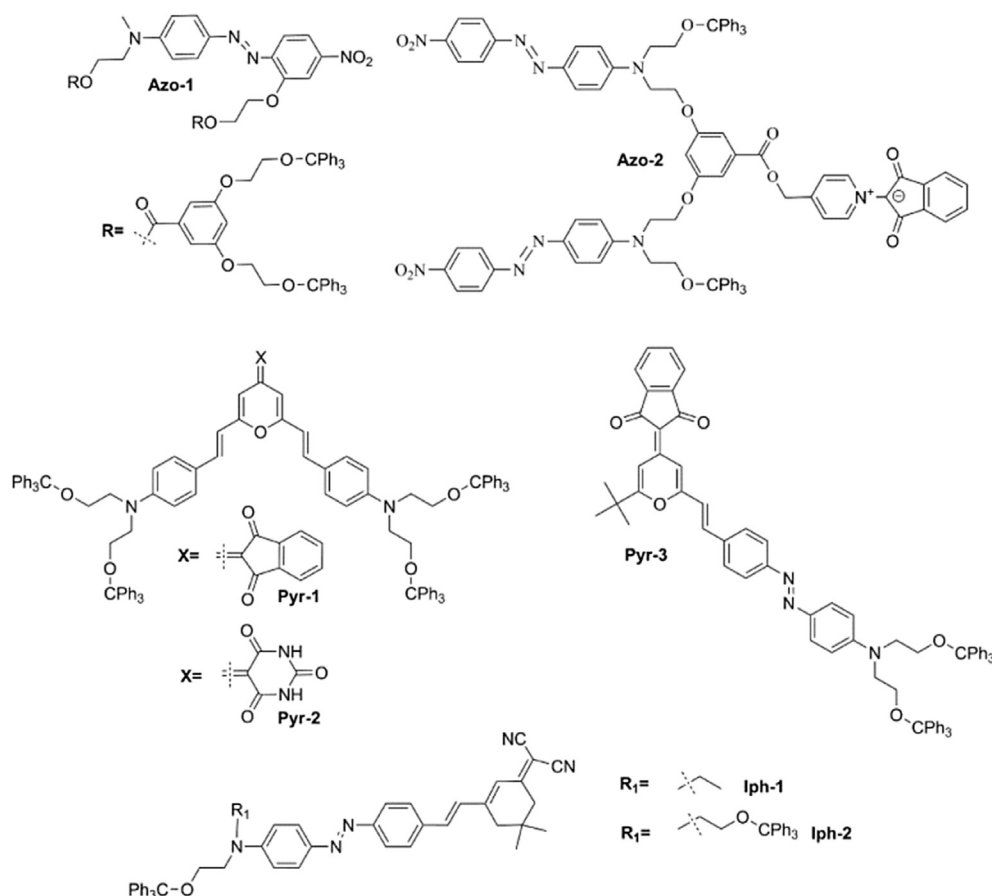


Fig. 1. Structures of the studied compounds.

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