Dendrimeric and Molecular Approach Designing Triphenyl Groups Containing Organic Glass NLO Materials

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The last decade has shown the notable breakthrough in the field of organic nonlinear optical (NLO) materials, providing the future prospects for applications in different data transport and processing systems [1]. These materials have many design approaches, most studied being polymer and guest-host systems. Molecular organic glasses, the compound class where amorphous glassy state is formed by relatively small molecules without the presence of plasticizers, are less known despite having advantages as simpler synthesis, characterization and purification. Our group has recently successfully developed NLO materials where amorphous phase stability of molecular compounds is ensured by incorporation of triphenyl substituents [2].

Here we would like to present the series of compounds containing 4-amino-4'-carboxyazobenzene chromophore core. The chemical structures of compounds are given in Figure 1. The synthesized materials can be divided into molecular compounds (**Azo-1,2**) and dendrimeric compounds (**Azo-3,4**). The glass formation ability for the compounds are ensured by the presence of 1,1,1-triphenylpentane fragments. While these groups prevent the crystallization process, the large sterical bulk of triphenyl-substituents could provide shielding of dipole-dipole interactions between chromophore cores. These interactions are unwanted because they order molecules centrosymmetrically while NLO activity is induced by external electric field polling, ordering polar chromophores non-centrosymmetrically [3].

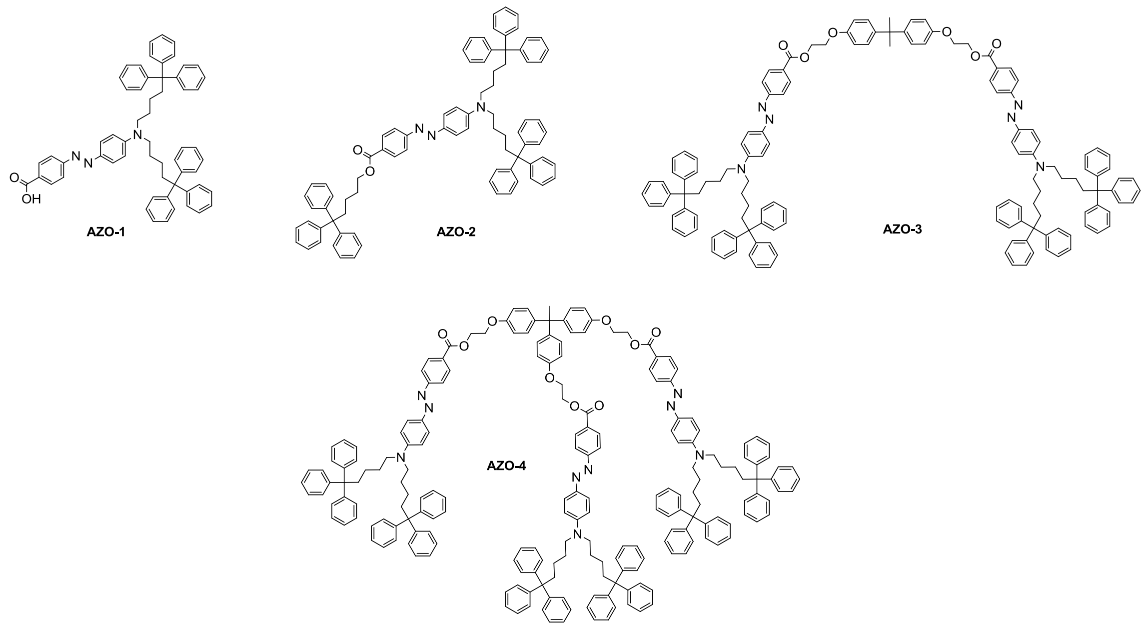

Figure 1. Chemical structures of the synthesized compounds.

The measured linear and nonlinear optical properties of materials are given in Table 1. Measurements were taken in the thin solid films made with spin-coating technique without the use of added plasticizers. As the results show, the best NLO response (d_{33}) is achieved in the case of compound **Azo-4**. This can be attributed to the fact that the star-shaped molecular structure of the compound provides the best prevention of dipole-dipole interactions between the molecules. In all the other cases NLO activity of materials are two times lower. The thermal stability of NLO activity is characterized with a value T_{SHI50}, the temperature at which a half of starting NLO signal strength has diminished. As expected, in this case the higher results are observed for dendrimeric compounds, because branched structure and higher molecular weight increases the energetic demands for the molecular movement.

Table 1. Linear and non-linear optical properties of materials in solid films.

Compound	**λ_{max}, nm**	**T_{SHI50}, °C**	**RI_{532}**	**RI_{1064}**	**$d_{33(532)}$, pm×V^{-1}**
Azo-1	462	65	2.02	1.65	10.0
Azo-2	455	59	1.81	1.60	11.2
Azo-3	462	72	1.65	1.55	10.1
Azo-4	457	85	1.76	1.58	20.2

In the conclusion, with the use of a similar chromophore core, the increase of NLO activity and thermal stability was observed in materials if dendrimeric approach was used instead of simple molecular design.

References:

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