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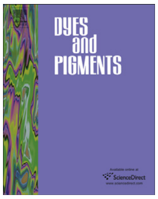

Using functionalized nonlinear optical chromophores to prepare NLO-active polycarbonate films

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ABSTRACT

Novel functionalized second order nonlinear optical (NLO) chromophores have been prepared with functionalized aniline as electron donor, thiophene or isophorone as a π-spacer and 1,3-diethyl-2-thiobarbituric acid as electron acceptor. The films prepared from dyes with alkylsilyl bulky groups gave better performance than the corresponding non functionalized chromophores due to the reduction of the intermolecular electrostatic interactions. The incorporation of chromophores **4** and **10** in a polycarbonate matrix allowed the preparation of good optical-quality films. Nonlinear coefficients d_{33} and d_{31} as high as 17 and 5.6 pm V^{-1}, respectively, were obtained. Moreover, the temporal stability of these host-guest films was confirmed up to eight months (>80%).

1. Introduction

During the last decades, organic materials have been proposed as promising candidates for a variety of nonlinear optical (NLO) applications, such as frequency doublers, optical storage devices, and electro-optic (EO) switches and modulators [1]. High NLO susceptibility, fast response time, low dielectric constant, small dispersion in refractive index, structural flexibility, and ease of material processing have brought organic materials to the forefront of NLO research. To achieve good device functionality, the NLO chromophore must simultaneously possess high microscopic molecular hyperpolarizability (β), good thermal and photostability, low optical absorption, high solubility in polymer hosts and weak intermolecular electrostatic interactions in a given host matrix [2]. However, a relevant obstacle to the development of organic materials is the difficulty of translating the high hyperpolarizability of chromophores into an adequate macroscopic property. At high chromophore density, dipole–dipole interactions between the chromophores favor centrosymmetric arrangements and therefore the polar order of the material is difficult. Modification of chromophore shape with bulky substituents would make them more spherical and hence limits intermolecular electrostatic interaction. Thus, the resulting material will be easier to be polarized. Polymers provide systems with high synthetic versatility and easy processability. Strategies for the design second order nonlinear polymers not only imply the incorporation of dipolar, highly polarizable electron donor-π-acceptor molecules (normally used as NLO-phores) into a macromolecular structure but also a non-centrosymmetric organization. The experimental technique used for this purpose is based on the electric field poling; after the poling NLO chromophores show a preferential orientation along the field direction, defining an optical axis perpendicular to the film surface (C∞υ symmetry) [3], [4].

Polar chromophores with a common structural characteristic of flat highly conjugated system have high $\mu\beta$ values. However, the resulting dipole moment makes the chromophores aggregate. Several studies have been carried out to solve this problem, for example, by attaching side chains to polymers, by incorporating the chromophore inside a dendrimer structure separating the chromophores with bulky peripheral chains [5,6] and by modifying tricyanovinyldihydrofuran type electron acceptors with different substituents to reach a three dimensional shape chromophore [7].

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Having this in mind, we suggest to simply functionalize hydroxyl chromophores with *tert*-butyldimethylsilyl group (TBDMS) with the aim to inhibit electrostatic interactions among "high $\mu\beta$" chromophores.

In this paper, we report the synthesis and the optical properties of hydroxyl functionalized push–pull systems bearing an aniline ring as an electron donor [8–12], a conjugated tiophene bridge system [13,14] or a isophorone ring [15] in the spacer group and one strong electron acceptor, the 1,3-diethyl-2-thiobarbituric acid. The choice of an aniline ring results in the possibility of having more planar rigid structures due to the intramolecular interactions between the thiophene and the aniline rings which can affect the electronic properties and hence the nonlinear response of the chromophores. In a similar way we have studied the effect of silylation of the hydroxyl group in the nonlinear optical behavior of these derivatives and finally silylated chromophores have been incorporated to a polycarbonate host matrix to evaluate their macroscopic NLO response.

2. Results and discussion

2.1. Synthesis

The detailed synthetic procedure of chromophores **1**–**11** is presented in Schemes 1 and 2.

The protection of the hydroxyl group of **Ald 1** gave **Ald 2** following the method describe in the literature [16,17].

The compound **1** was prepared by Knovenagel condensation of the 4-((2-hydroxyethyl) (methyl)amino)benzaldehyde (**Ald 1**) with 1,3-diethy1-2-thiobarbituric acid (**T**). The compound **3** was synthesized in successive steps. Firstly, the electron acceptor 1,3-diethyl-5-(3,5,5-trimethyl-2-cyclohexen-l-ylidene)-2-thiobarbituric acid (**IT**) was prepared by the method described by Brooker [18,19]. Secondly, the electron acceptor **IT** was reacted with **Ald 1** in the presence of piperidine to give chromophore **3**. The conditions used to prepare this compound were analogous to that described in the literature [15,20,21]. Analogous reactions were carried out with 4-((2-(((1,1-dimethylethyl)dimethylsilyl)oxy) ethyl)methylamino)-benzaldehyde (**Ald 2**) to produce chromophores **2** and **4** (Scheme 1).

The chromophore was synthesized by esterification of **3** with **acetic acid**. This reaction was carried out following the experimental procedure described by Hudhomme [22] in the presence of dicyclohexylcarbodiimide (DCC), 4-(dimethylamino)-pyridine (DMAP), and 1-hydroxybenzotriazole (HOBT). This esterification afforded the corresponding compound **5**.

The synthesis of chromophores **8**, **9**, **10** and **11** was depicted in Scheme 2. To begin with the synthesis of **9**, aldehyde **Ald 4** is used. The previously unreported aldehyde **Ald 4** was prepared by a convergent method described in the literature [23–25]. On one hand, 2-bromomethylthiophene was prepared by the bromination of 2-methylthiophene with *N*-bromosuccinimide. Next, diethyl 2-thiophenylmethylphosphonate was prepared by the Arbuzov reaction of 2-bromomethylthiophene with triethylphosphite [26–28]; on the other hand, 2-(methylphenylamino) ethanol was protected using benzoyl chloride to give 2-(methyl(phenyl)amino)ethylbenzoate and then was formilated by the Vilsmeier reaction to produce the previously unreported **Ald 3**. Then, the 4-(*N*-ethyl-*N*-((benzoyl-oxy)ethyl)amino)benzaldehyde (**Ald 3**) reacted with the described phosphonate derivative through the Horner–Emmons reaction [29] to give the compound (*E*)-2-methyl(4-(2-thiophen-2-yl)vinyl)phenyl)amino)ethyl benzoate (**6**) and the corresponding alcohol due to a partial hydrolysis caused by the formed NaOH. The Vilsmeier–Haack formylation [30] of the benzoate gave the aldehyde **Ald 4**. In a similar way, a lithiation was carried out starting from the corresponding aniline protected by the *tert*-butyl dimethyl silyl group (**7**) and using BuLi followed by the addition of DMF. This aniline derivative was selectively formylated and **Ald 5** was obtained [31]. It should be notice that both aldehydes, **Ald 4** and **Ald 5**, were obtained as a mixture *E* and *Z*. Finally, chromophores **8** and **10** were isolated as an all *E* isomer after a Knoevenagel reaction between the electron acceptor 1,3-diethy1-2-thiobarbituric acid **(T)** and the aldehydes **Ald 4** and **Ald 5**, respectively [32]. At the end, compound **8** was hydrolyzed to produce chromophore **9**. Finally, the electron acceptor **IT** was reacted with **Ald 5** in the presence of piperidine to give chromophore **11** in low yield. The characterization of compound **11** was not complete due to its instability in solution.

2.2. Linear optical properties

The linear optical properties of chromophores dissolved in organic solvents were studied by Ultraviolet–visible (UV/Vis) spectroscopy. The UV/Vis absorption data of the studied compounds are collected in Table 1.

Inspection of the spectra reveals some common trend; all compounds show strong intramolecular charge–transfer transitions in the visible region and in every series the λ_{max} values increase on lengthening the spacer.

Solvatochromic effect is related with the molecular nonlinearity of NLO chromophores [33]. The comparison between the D–π–A compounds with a hydroxyl group (**1**, **3**, **9**) and functionalized compounds with a *tert*butyldimethylsilyl group (**2**, **4**, **10**) depicts a red shift in dichloromethane and a slight blue shift in dimethylformamide (DMF). The compounds **1**–**5** and **8, 9** present a positive solvatochromic effect on passing from dichloromethane to dimethylformamide. This positive solvatochromic shift serves as an indicator of the increased dipole moment upon excitation [34]; thus confirming the CT character of these transitions [35] and indicating positive hyperpolarizability.

However, compounds **10** and **11** present no shift when the solvent is changed from dichloromethane to dimethylformamide. Thus, the UV spectrum of chromophore **10** was carried out in hydrogen bond acceptor (HBA) solvents such as 1,4-dioxane, ethyl acetate and dimethylsulfoxide (DMSO) and in both hydrogen bond acceptor (HBA) and donor (HBD) solvents such as acetonitrile and ethanol (Table 2).

A positive solvatochromic shift is observed on passing from 1,4-dioxane to ethyl acetate or DMSO and also on passing from acetonitrile to ethanol. Thus, the chromophore **10** confirms the batochromic behavior.

In order to obtain further information about the ground state structure of chromophore **10**, the transition energy plot as a function of solvent polarity was studied. The scales Z-scale, E^N_T, p* and ET(30) have been evaluated [35,36]. It has been established linear correlations of transition energy with the typical solvent parameter (Z-scale ($R^2 = 0.97$), E^N_T ($R^2 = 0.98$), p* ($R^2 = 0.97$) or ET(30) ($R^2 = 0.98$)). Therefore, the transition energy plot as a function of solvent polarity decreases linearly with increasing the solvent polarity. (See S-37, S-38, S-39, S-40. Supporting Information). The declining transition energy with increasing solvent polarity is indicative of an increase of the dipole moment upon excitation ($\mu_g < \mu_e$), suggesting the predominance of the neutral form in the ground state structure.

2.2.1. pH dependence on the absorption of chromophore 9

Among the compounds studied, chromophore **9** showed an absorption spectrum strongly dependent on pH. The titration of HCl with a blue solution of chromophore **9** in EtOH ($2\ 10^{-5}$ M,