

Synthesis and nonlinear optical properties of linear and Λ -shaped pyranone-based chromophores

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Abstract

New, pyranone-based chromophores were synthesized and their (nonlinear) optical properties were measured. The chromophores were prepared by first condensing an electron withdrawing group with pyranone, followed by reaction with an aldehyde-functionalized π -conjugated bridged donor molecule. This approach enables one to easily incorporate the pyranone moiety and to prepare both linear and Λ -shaped chromophores. The (nonlinear) optical properties were measured using femtosecond hyper-Rayleigh scattering. These measurements demonstrated the advantages of this approach.

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1. Introduction

The continuous interest in poled polymers for nonlinear optical (NLO) applications has resulted in the development of numerous chromophores and a profound understanding of their structure–property relationship.^{1,2} Most chromophores are linear, rigid, π -conjugated molecules, end-capped with an electron donating and electron withdrawing group. The $D\pi A$ -structure, present in these molecules, triggers their large second-order hyperpolarizabilities. Apart from linear $D\pi A$ chromophores, also Λ -shaped chromophores have been developed.^{3–11} Their assets are double. First, depending on the angle between the constituting linear $D\pi A$ parts, the hyperpolarizability of Λ -shaped chromophores can be higher than the hyperpolarizability of the individual, linear chromophores they consist of. Second, unlike linear chromophores, which are usually incorporated as side-chains in polymer systems,

Λ -shaped chromophores can be built-in into accordion-type polymers.^{6,9,11,12} After poling—to obtain the necessary macromolecular noncentrosymmetry—accordion polymers tend to relax slower, resulting in a more stable NLO response.

Some 2,6-dimethyl-4*H*-pyran-4-on (pyranone)-based chromophores, both linear and Λ -shaped, have already been prepared and studied. The advantage of the incorporation of the pyranone unit is that it not only extends the π -conjugation in comparison with analogous chromophores, which lack this group, but also that it gives the possibility to prepare both linear and Λ -shaped chromophores.^{3,10,11} The Λ -shaped pyranone-based chromophores, which have been prepared and studied before, were typically equipped with rather moderate electron withdrawing groups (usually a dicyanomethylene group) and/or a poor variety of rather simple π -conjugated systems.

In this manuscript, the synthesis and (nonlinear) optical properties of some new linear and Λ -shaped chromophores are described. They all consist of a pyranone unit, which is functionalized with different electron withdrawing groups and one (linear) or two (Λ -shaped) amino-substituted

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π -conjugated system(s). A variety of moderate to excellent electron withdrawing groups are used, together with an extended π -conjugated bridge. The (nonlinear) optical properties of both types of chromophores are compared and evaluated in detail.

2. Results and discussion

2.1. Chromophore design

Several parameters in the design of the chromophores were taken into account. A general structure of the chromophores is presented in Figure 1. All chromophores contain an amino functionality as donor, while four different acceptor groups were incorporated. Special attention has been given to the π -conjugated bridge, in which a central thiophene moiety was incorporated. The choice of the thiophene moiety can be motivated as follows: on one hand, Marder et al. have shown that very easily polarizable spacers, such as polyenic spacers, when substituted with strong electron donating and electron withdrawing groups, show minor NLO properties.¹³ Moreover, polyenic chromophores tend to have low thermal and photochemical stabilities. Aromatic spacers based on benzene, on the other hand, show superior stability, but are much less polarizable. Thiophene-based chromophores, however, have shown to combine the necessary stability with large second-order nonlinear hyperpolarizabilities.^{14–21} As mentioned earlier, a pyranone unit was incorporated to further extend the conjugation length.

Next, also the shape of the (linear) chromophores was taken into account. When incorporated to further extend the polymer system, the highly dipolar chromophores interact with each other above a critical chromophore concentration, resulting in a centrosymmetric, NLO inactive, ensemble. These unwanted interactions can be diminished by carefully substituting the linear chromophore with alkyl groups, resulting in an ellipsoidal shape.²² Moreover, these alkyl groups increase the solubility of the chromophore.

Finally, the chromophores are substituted with one (linear chromophores) or two (Λ -shaped chromophores) alcohol functionalities, allowing them to be covalently attached to a polymer backbone (linear chromophores) or to be built-in in accordion polymers (Λ -shaped chromophores). The synthesis and nonlinear optical properties of those polymers, including the influence of the molecular structure of the polymer (linear vs accordion) on their properties, are now under investigation.

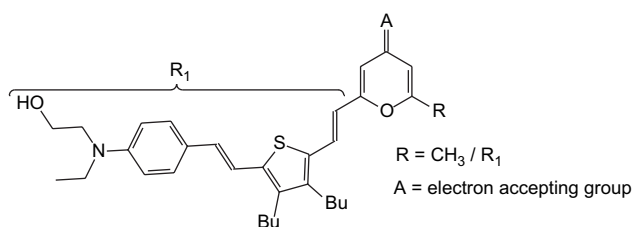


Figure 1. General structure of the chromophores.

2.2. Chromophore synthesis

The synthesis of the chromophores is displayed in Scheme 1. First, aldehyde **1** is reduced with NaBH_4 to the corresponding alcohol **2**, which is converted into the phosphonium salt **3** in a one-step reaction with triphenyl phosphonium bromide. Next, **3** was reacted with **4** using a Wittig reaction, rendering **5** as a cis/trans mixture. Although a Horner reaction would result in pure trans-alkene, a Wittig reaction was preferred to introduce a double bond. The reason for this approach is the fact that we encountered great difficulties in converting the alcohol **2** into its corresponding chloride. Presumably, polymerization of the benzylic halide occurs. Compound **5** was protected as an acetate ester, after which the aldehyde functionality was introduced by a Vilsmeier reaction. After deprotection of **7**, the building block **8** was obtained, still as a mixture of cis and trans isomers.

The key step in the chromophore synthesis is the Knoevenagel condensation of **9a–d** with aldehyde **8**. This renders all-trans chromophores. Compounds **9a–d** were prepared by a Knoevenagel condensation of **10** with the appropriate acceptor molecules (Scheme 2).

Although it would be advantageous for the synthesis of these particular chromophores to first condense **10** with **8** and then react the acceptor molecules **11–14** with **15** (since that approach would reduce the total number of reaction steps, Scheme 3), the former pathway was preferred, since it allows to condense a large number of different aldehydes with **9a–d**. Consequently, this is an easy, fast and general way to prolong the conjugation length of already existing chromophores—which are typically synthesized by condensing their corresponding aldehydes with the appropriate acceptor molecules—by two double bonds. It is worthwhile to mention that it was also tried to condense **10** first with **8** and then react the acceptor molecules with **15**. Unfortunately, this synthesis failed at the first stage.

In the condensation reaction of the pyranone derivatives **9a–d** with aldehyde **8**, both mono and di-reaction takes places, resulting in the linear (**a1–d1**) and Λ -shaped (**a2–d2**) chromophores, respectively. In all cases, they could easily be separated by column chromatography.

During the synthesis of **d1**, **9d**, which is asymmetric, can react with the aldehyde at each of both methyl groups, resulting in two different mono-reacted chromophores. Unfortunately, both isomers could not be separated and purified; therefore, that chromophore was not further investigated.

2.3. Linear optical properties

The optical properties of the chromophores are listed in Table 1. In order to avoid the influence of the intramolecular H-bridge between the terminal OH and the amino functionality, which weakens the electron donating capacity of the dialkyl-amino functionality, the alcohol groups of the chromophores **a–d** were converted into acetate groups for this study. The acylation was performed with acetic anhydride (Scheme 4). No base was added to prevent nucleophilic attack on the

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