



Efficient second-order nonlinear optical chromophores based on dithienothiophene and thienothiophene bridges



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Dedicated to the memory of our colleague Christian Claessens

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ABSTRACT

Two series of push–pull systems bearing dithienothiophene or thienothiophene as (part of) π -conjugated spacer have been synthesized. These compounds combine high second-order molecular nonlinearities with good thermal stabilities, showing one of the thienothiophene (TT) derivative the highest $\mu\beta_0$ value found for a 4*H*-pyranilidene-containing merocyanine.

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1. Introduction

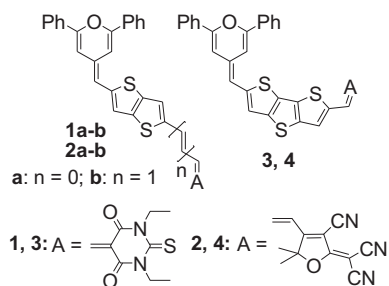
Over the last decades great efforts have been dedicated to obtain materials exhibiting good second-order nonlinear optical (NLO) properties due to their potential application in optical devices.¹ Following this trend, many high performing organic systems (specially donor- π -acceptor (D- π -A) type molecules) have been synthesized, but the combination of high molecular hyperpolarizabilities and good thermal stability in the same system is still a subject of interest in materials science. Polyene-type structures have often been included in the conjugated spacer between the donor and the acceptor moieties because they provide the best conjugation pathway for the charge transfer, but poor thermal stabilities are associated with the presence of these olefinic fragments.² The reverse situation is found for aryl-type spacers. Then, the replacement of aryl rings by heteroaromatic rings with lower resonance energies is the common way to obtain

a good balance between nonlinear optical response and thermal stability.³ In this context, thiophenes are among the most studied heterocyclic spacers for D- π -A systems,^{3b,4} due to their relatively low resonance energies, and have allowed the preparation of chromophores with high stabilities and nonlinearities. On the other hand, conjugated spacers based on fused thiophene rings have been much less studied in this field, even though thieno[3,2-*b*]thiophene (TT)⁵ and dithieno[3,2-*b*:2',3'-*d*]thiophene (DTT)⁶ show a lower resonance energy per electron when compared to thiophene⁷ and allow to increase conjugation, which typically results in increased NLO responses. Just a few chromophores bearing these fused heterocycles as (part of) the electron relay have been reported.^{3a,8,9} Moreover, just one of the papers^{8a} approaches these systems from the standpoint of the establishment of structure–activity relationships, and it is focused on the comparison between thiophene and thieno[3,2-*b*]thiophene moieties.

In this work we focus our attention on the synthesis, characterization, and study of six new fused thiophene derivatives **1–4**, which are expected to be efficient NLO chromophores and to show high thermal stability. New D- π -A molecules bear the proaromatic 4*H*-pyran-4-ylidene unit as donor¹⁰ and two common strong organic acceptors. To the best of our knowledge, no such merocyanines

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with a 4*H*-pyran-4-ylidene moiety and dithienothiophene or thienothiophene relays in their structure have been previously reported. The influence of these fused heterocycles on the optical and thermal properties is discussed and compared with that exerted by a single thiophene unit in the π -spacer.

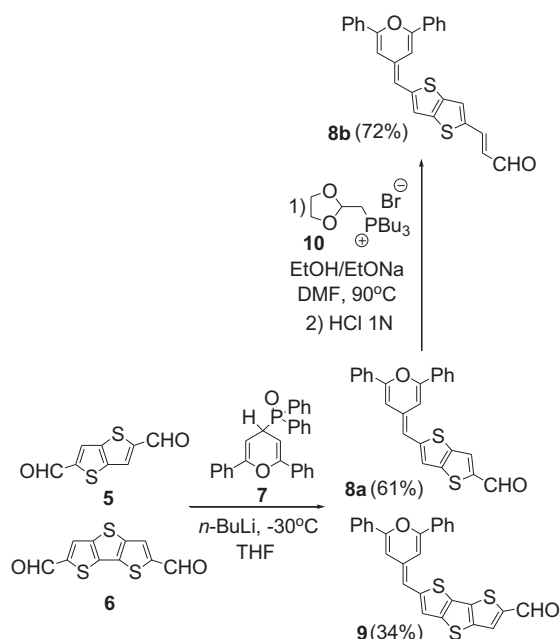


Scheme 1. Synthesis of aldehyde precursors **8** and **9**.

2. Results and discussion

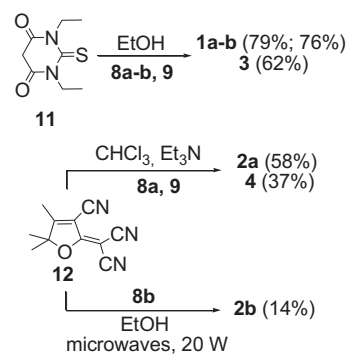
2.1. Synthesis

For the synthesis of the target systems **1–4**, the previously unreported aldehydes **8a,b** and **9** were chosen as precursors. Compounds **8a, 9** were prepared by a Horner reaction between pyranylphosphine oxide **7**¹¹ and dicarbaldehydes **5**¹² and **6**,^{9b} respectively (Scheme 1). Reaction conditions were carefully tuned (temperature, order of slow addition of reagents) in order to minimize the formation of pyranylidene-disubstituted derivatives as by-products. Thus, a yield of 61% could be achieved for **8a**, whereas lower yields were obtained for **9** due to the insolubility of dicarbaldehyde **6**. Aldehyde **8b** was obtained from reaction of **8a** and tributylphosphonium salt **10**¹³ in the presence of sodium ethoxide and a subsequent acid hydrolysis.



Scheme 1. Synthesis of aldehyde precursors **8** and **9**.

The Knoevenagel reaction between acceptors **11** and **12** (2-dicyanomethylene-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran, TCF)¹⁴ and aldehydes **8a,b, 9** afforded the six new D- π -A compounds **1–4** (Scheme 2).



Scheme 2. Synthesis of chromophores **1–4**.

It is worth noting that the reaction of aldehyde **8b** and acceptor **12** under the same conditions used for aldehydes **8a** and **9** afforded compound **2a** instead of the expected **2b**. This vinylenes-shortening reaction has already been reported for other Knoevenagel-type reactions by us¹⁵ and other authors.¹⁶ Different reaction conditions reported¹⁷ for Knoevenagel reactions involving acceptor **12** were tried with the same result. To overcome this drawback, the reaction between aldehyde **8b** and acceptor **12** was tested under microwave conditions.¹⁸ In this approach the addition of a base is not necessary, and therefore the aforementioned side-reaction is less likely to happen. Using this procedure compound **2b** was eventually isolated in low yield.

2.2. ¹H NMR studies

Compounds **1b, 2a,b**, and **4** have an *all-trans* geometry along the spacer according to ³J_{HH} coupling constant analysis. Whereas the *s-trans* conformation for the bond linking the donor moiety to the thieno[3,2-*b*]thiophene spacer is confirmed by selective ge-1D NOESY experiments carried out on model compound **8a** (300 MHz, CDCl₃, rt), the same conformation can be assumed for NLO chromophores **1–4**.

¹H NMR data also provide valuable information about ground-state polarization of the studied D- π -A systems. The chemical shifts of the H atoms along the polyenic spacer show the typical oscillatory behavior¹⁹ of a merocyanine-like compound, and the high ³J_{HH} values for the =CH–CH= protons in the olefinic part of the spacer for compounds **1b** and **2b** (12.8 Hz for compound **1b** (CDCl₃); 11.4 Hz for **2b** (CD₂Cl₂)) show the contribution of their zwitterionic form to their electronic ground states.

A slight downfield shift for the protons of the pyranylidene ring of compound **2a** when compared to **2b** was observed (6.61 and 7.23 ppm for **2a** and 6.56 and 7.20 ppm for **2b** in CD₂Cl₂). This finding indicates a higher contribution of the aromatic pyrylium form for the shortest system, in agreement with other D- π -A systems with a 4*H*-pyran-4-ylidene unit previously described.^{10,15c,20}

¹H NMR spectra of DTT derivatives **3, 4** were recorded in different conditions as a result of their low solubility, leaving them out of the comparison with **1–2**.

2.3. Calculated structures

For a better understanding of the role of fused thiophene conjugated spacers in these chromophores, natural bond orbital (NBO) atomic charge calculations for the target compounds and for analogous systems bearing a single thiophene spacer **13, 14**²⁰ (Fig. 1) were carried out. The resulting charges for comparable systems are shown in Fig. 2. It can be seen that part of the net positive charge of the push–pull system is supported by the thiophene relays, in agreement with previously reported results.^{9d}

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