



Second order nonlinear optical networks with excellent poling stability from a new trifunctional thiophene based chromophore

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ABSTRACT

Two new trifunctional thiophene based dyes suited for crosslinking were synthesised from the same structural core, i.e. 4-[[5-[(4-nitrophenyl)azo]-2-thienyl]azo]benzenamine. Crystal structure and second order nonlinear optical properties were determined on a related difunctional dye that can be considered as a representative and simplified model of the trifunctional compounds, determining on it the $\mu\beta$ value of 4950×10^{-48} esu ($6111 \times 10^{-80} \text{ C}^2 \text{ m}^4 \text{ V}^{-2}$).

The presence of three acrylic or hydroxyl functional groups in the dyes allowed to incorporate the chromophoric fragment into two different kinds of crosslinked materials possessing "frozen" long-lasting dipole order. The traditional guest-host approach used for one of them was exceeded by covalently anchoring the chromophore to a functionalised polymer in a three-dimensional unique network. In this way a promising NLO active material was obtained. The value of the d_{33} coefficient (determined by SHG measurement using the Maker fringe technique) was 11 pm/V for the poled/crosslinked film. Very good thermal and temporal stability of the chromophore poling-induced dipole alignment was attained.

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1. Introduction

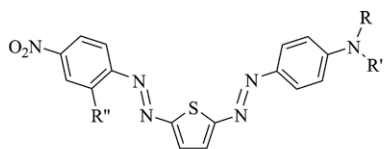
Compounds exhibiting disazo-thiophene groups have been extensively investigated, especially for their properties of colouring textiles and plastics or in general as dispersed pigments [1,2]. More recently, thiophene has been largely used as electron-rich molecule for a variety of optical and electrooptical applications [3–5]. Thiophene based dyes typically contain aromatic rings linked by unsaturated moieties. The influence on electron donor effects of the thiophene ring has been extensively examined [6] and the use of this heterocycle in compounds for nonlinear optics has

gained increasing consideration [7–9]. In particular, theoretical investigations indicated that the replacement of a phenyl ring with a thiophenic one significantly improves the values of molecular hyperpolarizability [10–12]. Thiophene not only behaves as one of the most effective heterocyclic rings in enhancing NLO properties of typical push-pull chromophores even in relatively short conjugated systems, but also prompts the desirable targets of high solubility of the dyes and easy processability of materials.

In this work, we report the synthesis of three functionalised derivatives having the same core, 4-[[5-[(4-nitrophenyl)azo]-2-thienyl]azo]benzenamine (C type compounds in Fig. 1) and their precursors (C' type compounds in Fig. 1).

In the new dyes the thiophene ring is interposed between two highly conjugated moieties bringing donor and acceptor substituents. The unsaturated moieties are

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$R = \text{CH}_3$; $R' = \text{CH}_2\text{CH}_2\text{OCOCH}=\text{CH}_2$; $R'' = \text{OH}$	$\mathbf{C}'_{\text{Diacr}}$
$R = R' = \text{CH}_2\text{CH}_2\text{OCOCH}=\text{CH}_2$; $R'' = \text{OH}$	$\mathbf{C}'_{\text{Triacr}}$
$R = R' = \text{CH}_2\text{CH}_2\text{OH}$; $R'' = \text{OH}$	$\mathbf{C}'_{\text{Triox}}$
$R = \text{CH}_3$; $R' = \text{CH}_2\text{CH}_2\text{OCOCH}=\text{CH}_2$; $R'' = \text{OCOCH}=\text{CH}_2$	$\mathbf{C}_{\text{Diacr}}$
$R = R' = \text{CH}_2\text{CH}_2\text{OCOCH}=\text{CH}_2$; $R'' = \text{OCOCH}=\text{CH}_2$	$\mathbf{C}_{\text{Triacr}}$
$R = R' = \text{CH}_2\text{CH}_2\text{OH}$; $R'' = \text{OCH}_2\text{CH}_2\text{OH}$	$\mathbf{C}_{\text{Triox}}$

Fig. 1. Chemical diagrams of the chromophores (**C** type compounds) and their precursors (**C'** type compounds).

azo bridges, that are claimed to be the most efficient ones in push–pull systems [13].

In contrast with the extended use of thiophene in NLO active polymers and materials [14–16], only a few examples of disazo-thiophene dyes for the synthesis of NLO active materials are known [17,18]. To our knowledge no example of disazo-thiophene dye in crosslinked materials was reported.

The strategy generally used to produce NLO active materials with enduring polar order involves the synthesis of polymers crosslinkable under electric field [19,20]. Alternatively, polyfunctionalised monomers, eventually pre-polymerised, are poled and crosslinked under poling conditions to give the final network [21,22].

In our case, according to the last approach, $\mathbf{C}_{\text{Triacr}}$ was simply reacted with non NLO active polyfunctional monomers under an electric field. For $\mathbf{C}_{\text{Triox}}$ another recently proposed approach [23] was implemented. The dispersed chromophore, polyglycidyl methacrylate (PGMA) and a passive co-crosslinker were thermally seized by covalent bonding in a single network under poling conditions. The most promising crosslinked material presented in this paper was achieved in this case, getting materials with both high NLO activity and excellent temporal stability of the dipolar alignment.

The difunctional compound $\mathbf{C}_{\text{Diacr}}$ was tailored as a model compound for EFISH and spectroscopic measurements. X-ray single crystal diffraction analysis was also effected, in order to relate crystal structure and optical properties and to achieve information on the factors affecting solubility.

2. Results and discussion

2.1. Synthesis and characterization of dyes

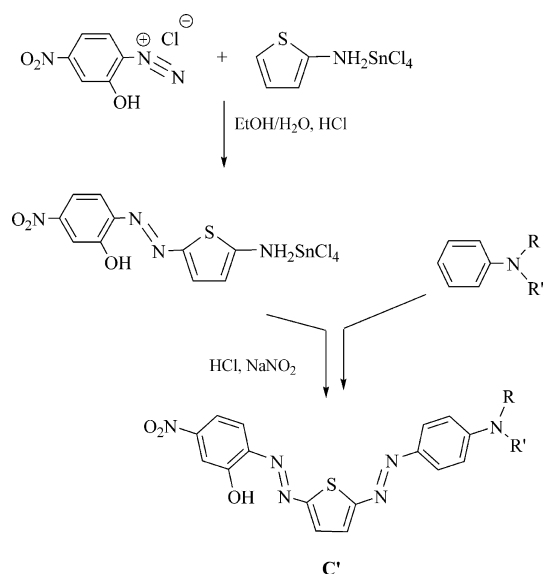
Three thiophene based functionalised push–pull chromophores ($\mathbf{C}_{\text{Diacr}}$, $\mathbf{C}_{\text{Triacr}}$ and $\mathbf{C}_{\text{Triox}}$ in Fig. 1) were synthesised and characterized. The dye skeleton includes a nitro acceptor group and a substituted amino donor group on

phenyl rings linked by a conjugated system made up of two azo bridges and one thiophene unit. The syntheses of similar 2,5-disazo-thiophene compounds reported in literature [18,24] is often cumbersome. We have followed a synthetic pathway somehow different and simplified respect to the previously described ones [8,15,18]. According to a previous report [8], a nitro group in 2 position on a thiophene ring can be converted into an aminic one by reduction with tin. Isolation of a SnCl_4 -aminothiophene hydrochloride complex avoided the use of the poorly stable free 2-aminothiophene. The complex was then converted into the acetamido derivative that was successively nitrated and then deprotected to nitroamine [8]. In our case, we have directly copulated 2-hydroxy-4-nitrobenzenediazonium chloride with SnCl_4 -aminothiophene hydrochloride, the metal group acting as a protector group in the synthesis of the first azo bridge. We built the second azo bridge by amine diazotation on this metalated intermediate after easy de-protection in mildly acid solution. Thus, such use of the not isolated intermediate complex allowed easy and fast *one-pot* synthesis of the **C'** type chromophores (Scheme 1), that were used as precursors of **C** type ones.

Starting from **C'** chromophores, three different dyes (**C** type compounds, Fig. 1) were easily obtained as acrylic or hydroxylic derivatives. The trifunctional compounds, $\mathbf{C}_{\text{Triacr}}$ and $\mathbf{C}_{\text{Triox}}$, were designed to be employed in the synthesis of two kinds of crosslinked materials.

The three chromophores are all crystalline greenish gray solids, affording blue solutions in chloroform. The ^1H NMR spectra gave evidence of high purity for all products. In particular, the singlet pertaining to the thiophene proton, observed at 8.36 ppm, can be considered diagnostic. Thermodynamic data for **C** chromophores and their precursors **C'** are reported in Table 1.

According to thermogravimetric analyses, the 5% weight loss temperatures are higher than 200 °C for all



Scheme 1. Synthetic pathway for **C'** type compounds.

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