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Synthesis of new thiophene compounds with large second order optical non-linearities

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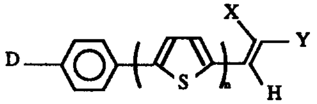
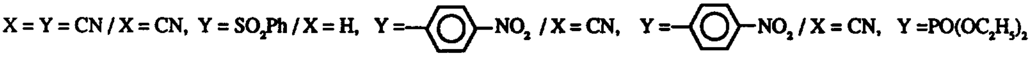
Abstract

A synthesis of new thiophenes with large second order optical non-linearities is described. These products display a very good stability under irradiation.

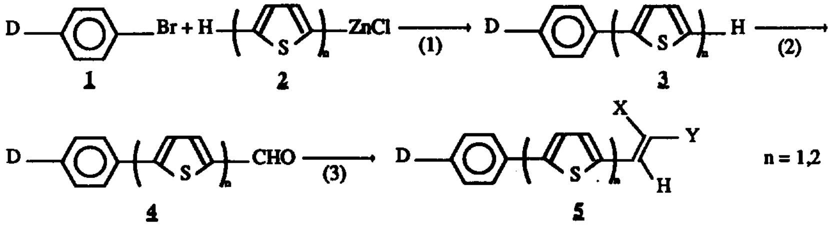
Organic and organometallic compounds have attracted great interest for their important large non-linear susceptibilities rising from delocalized π-electrons. These products allow the creation of new materials for very specific applications (communication, optical information and integrated optics). The second order non-linear optical (NLO) effects require molecular fragments which have a large hyperpolarizability β and are non centrosymmetically ordered [1].
In this paper, we would like to report the synthesis, characterization and properties in non-linear optic applications of new thiophene products with the following formula [2].



n = 1,2 D = $-N(CH_3)_2$, $-OCH_3$



It is known that polyaromatics and polyheteroaromatics like polythiophenes have an extended conjugated π-system which represents good optical properties [3].
Donor and acceptor groups have been attached to the α and α' positions of thiophene or bithienyl heterocycles in order to obtain large β values. The synthesis of these new materials is schematically represented below.



REAGENTS AND CONDITIONS

(1) Catalyst Pd (DBA)$_2$ / TPP, (1% mol• 1/4), THF, reflux - 16h.
(2) a) n-BuLi, THF, 0°C-1h.
    b) DMF, room temperature-16h.
(3) X – CH$_2$ – Y, Ethanol, reflux-3h, catalyst piperidine (1 - 5% w)

The first step is the cross coupling reaction between bromo-derivatives and the organometallic compounds catalysed by palladium [4]. All compounds **3** were transformed into their aldehydes **4** by successive reaction of n-BuLi and DMF. (Table 1).

Table 1

Entry	Halide compounds **1**	Thienyl compounds **2**	Products **3** (%)	Yield [5] **4** (%)
a	D = –N (CH$_3$)$_2$	n = 1	**3a** (64)	**4a** (91)
b	D = –OCH$_3$	"	**3b** (59)	**4b** (80)
c	D = –N (CH$_3$)$_2$	n = 2	**3c** (51)	**4c** (40)

The conversion of **4** to **5** was performed under standard conditions by the reaction of activated methylene compounds with the aldehydes **4** (catalyst piperidine) (Table 2).

The data of the non-linear optical properties are listed in Table 3. The product βs•μ (μ = dipole moment in the ground state, βs = hyperpolarizability extrapoled at zero frequency) is usually obtained from an EFISH experiment [6] and a two level model [7]. In our case, however the molecules are incorporated into a PMMA thin film (13 μm) sandwiched between two semitransparent electrodes (SiO$_2$ and gold). The guest molecules are oriented by an electrical field above the glass temperature Tg [8]. The product βs•μ is deduced from the interferometric measurement of the electrooptical effect at λ = 633 nm [9] and compared with the value of Disperse Red one **6**. These results show that the the substituted thiophenes are an interesting familly for NLO applications. The thiophene fragment is a good π electron patheway and therefore interesting for the synthesis of new compounds with large second order optical properties. All materials displayed a very good stability under irradiation.

Table 2

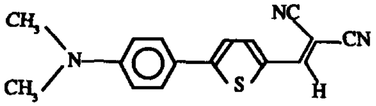
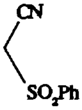
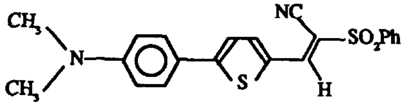
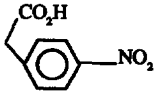
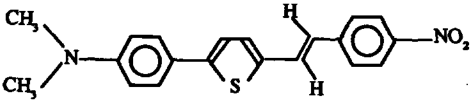
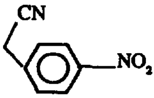
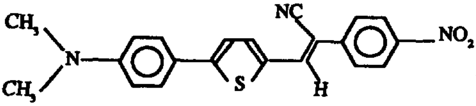
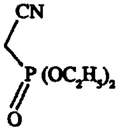
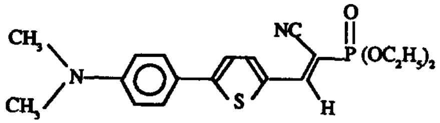
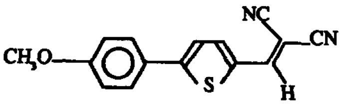
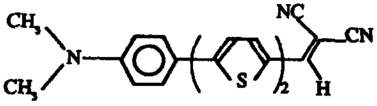
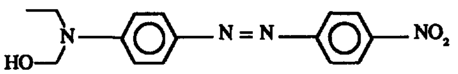
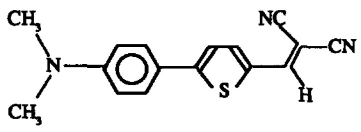
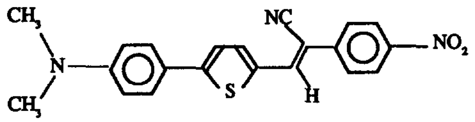
Entry	Compounds **4**		Compounds **5**	Yield % [5] **5**	mp (°C)	λ max nm (ε), $CHCl_3$
a	**4a**			85	217	510 (40700)
b	"			91	211	498 (36400)
c	"			50	240	457 (28200)
d	"			49	298	499 (37500)
e	"			85	155-156	464 (25900)
f	**4b**			89	195	430 (36900)
g	**4c**	"		45	215	540 (-)

Table 3

Entry	Compounds	$\beta_s \cdot \mu$ (10^{-48} esu)
a	 6	409 [10]
b		604
c		260

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