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



M. González-Lainez^a, M.T. Jiménez-Ruiz^a, N. Martínez de Baroja^a, J. Garín^a, J. Orduna^{a,*}, B. Villacampa^{b,*}, M.J. Blesa^{a,*}

^a Departamento de Química Orgánica-ICMA, Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain

^b Departamento de Física de la Materia Condensada-ICMA, Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain

ARTICLE INFO

Article history:

Received 28 October 2014

Received in revised form

23 February 2015

Accepted 24 February 2015

Available online 25 March 2015

Keywords:

Chromophore

Multichromophore

Linear optical properties

Nonlinear optical materials

Temporal stability

Poled films

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%).

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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 ∞ 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 tricyanovinylidihydrofuran type electron acceptors with different substituents to reach a three dimensional shape chromophore [7].

* Corresponding authors. Tel.: +34 876 553507; fax: +34 976 761194.

E-mail address: mjblesa@unizar.es (M.J. Blesa).

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 thiophene 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 Knoevenagel condensation of the 4-((2-hydroxyethyl) (methyl)amino)benzaldehyde (**Ald 1**) with 1,3-diethyl-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-1-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 formulated 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)phenylamino)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-diethyl-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.

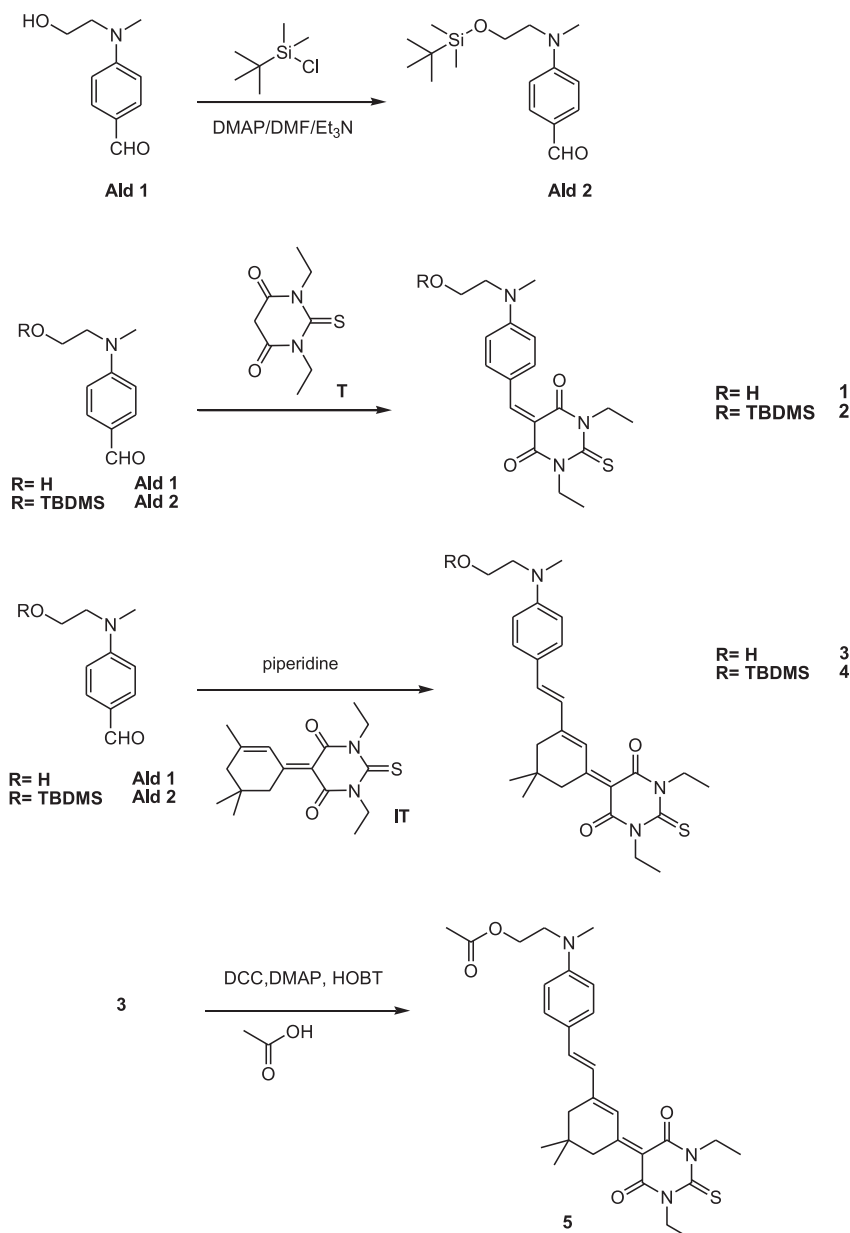
However, compounds **10** and **11** present no shift when the solvent is changed from dichloromethane to dimethylformamide. Thus, the UV spectrum of chromophore **10** was carried out in hydrogen bond acceptor (HBA) solvents such as 1,4-dioxane, ethyl acetate and dimethylsulfoxide (DMSO) and in both 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 bathochromic 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_{T}^{N} , 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_{T}^{N} ($R^2 = 0.98$), 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 ($\mu_{\text{g}} < \mu_{\text{e}}$), 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,



Scheme 1. Synthesis of chromophores 1, 2, 3, 4 and 5.

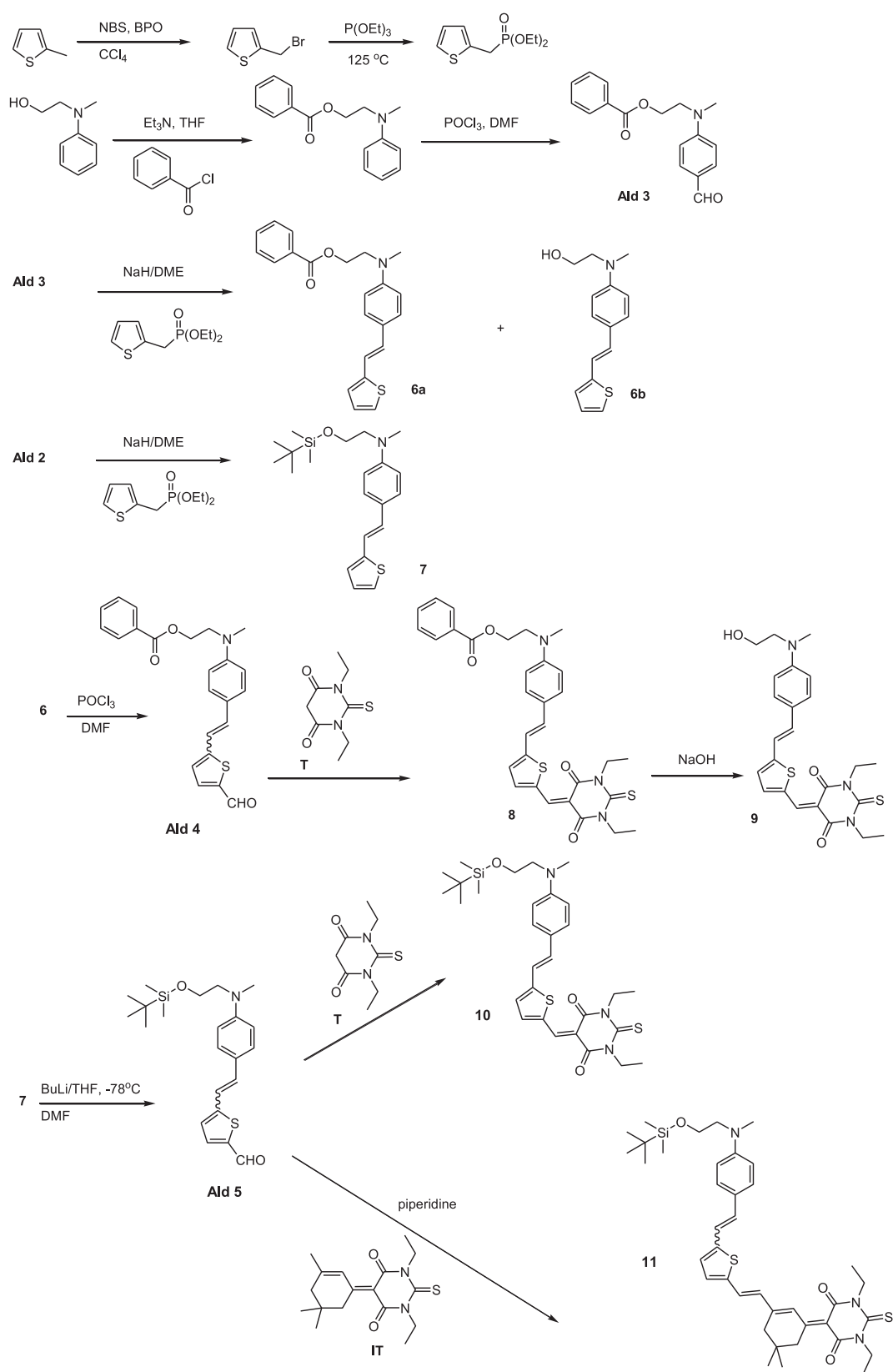
pH = 4.68) gives a relevant change of solution color turning yellowish in acidic medium. The corresponding absorption spectra are gathered in Fig. 1. In this figure, a clear isosbestic point is observed at 515 nm, the specific wavelength at which the two chemical species (acid and basic) have the same molar absorptivity (ϵ).

The equivalence point, or stoichiometric point, corresponds to the mixing of stoichiometrically equivalent amounts of acid and base. As an indication of the sharpness of color change, it should be mentioned that the solution at pH = 2.85 is green and clearly different from both solutions at pH = 3.04 (light blue) and at pH = 2.72 (yellow). Thus, this chromophore solution has a potential use as pH-indicator in the range 2.72–3.04. On the other hand, the titration of KOH with the same solution of compound **9** in EtOH (2×10^{-5} M) was also carried out and the blue color disappeared when the pH was changed from 10 to 11 value (See S-43. Supporting Information). This behavior is reversible.

2.3. Electrochemistry

The redox properties of the target compounds were measured by cyclic voltammetry (CV) in CH_2Cl_2 (Table 3). Chromophores **1–5**, **8–11** show one oxidation and one reduction waves corresponding to the electron processes of oxidation of the electron donor unit and reduction of the electron acceptor fragment, respectively. Oxidation process is reversible or quasi-reversible.

The lengthening of the π -spacer gives rise to a decrease of the $E_{1/2}$ and $E_{p,c}$ values. On chain lengthening, the smaller the interaction between the electron donor and electron acceptor end groups, the easier both oxidation and reduction processes. In particular, as an oxidation process is concerned, this process is favored when either an isophorone (**3, 4**) or a thiophene (**9, 10**) ring are introduced on the π -spacer to get a better delocalization of the charge. Thus, the easiest oxidation was obtained with the compound with both isophorone and thiophene ring (**11**).



Scheme 2. Synthesis of chromophores 8, 9, 10 and 11.

Table 1
UV/Vis data of the chromophores **1–11**.

	Experimental						Theoretical calc. ^c		
	CH ₂ Cl ₂			DMF			CH ₂ Cl ₂		
	λ_{\max}^a	ΔE_{01}^b	$\log \epsilon$	λ_{\max}^a	ΔE_{01}^b	$\log \epsilon$	λ_{\max}^a	ΔE_{01}^b	f
1	493	2.51	4.88	504	2.46	4.72	425	2.92	1.37
2	496	2.50	4.89	503	2.46	4.84	432	2.87	1.63
3	564	2.20	4.42	597	2.08	4.64	536	2.31	1.96
4	579	2.14	4.66	593	2.09	4.62	536	2.31	1.95
5	563	2.20	4.56	579	2.14	4.54	523	2.38	1.94
8	584	2.12	4.71	589	2.10	4.63	518	2.39	1.69
9	587	2.11	4.61	602	2.06	4.56	548	2.26	1.69
10	599	2.07	4.70	599	2.07	4.68	548	2.26	1.72
11	599	2.07	4.55	599	2.07	4.48	566	2.19	1.81

^a nm.^b eV.^c TD-PCM-M06-2X/6-311+G(2d,p) on M06-2X/6-31G* PCM CH₂Cl₂ geometries.

These observed trends in $E_{1/2}(E_{p,c})$ are confirmed by theoretical calculations (PCM, CH₂Cl₂), which show that the E_{HOMO} (E_{LUMO}) values increase (decrease) with the length of the spacer. The variation of the $E_{1/2}$ values is more noticeable than that of $E_{p,c}$ in agreement with the trends shown by the energy levels of the frontier orbitals.

The comparison between the D- π -A compounds with a hydroxyl group and the ones functionalized with a silicon group show no important variation on the redox behavior.

2.4. Nonlinear optical properties

The second-order NLO properties of the prepared compounds have been measured by electric-field-induced second harmonic generation (EFISH) technique in CH₂Cl₂ at 1907 nm. The measured $\mu\beta$ values, together with the corresponding static $\mu\beta_0$ values calculated using the two-level model (TLM) [37,38], are gathered in Table 4 (for the sake of comparison and as a reference, $\mu\beta_0 = 480 \cdot 10^{-48}$ esu has been obtained for *Disperse Red 1* under the same experimental conditions). TLM is widely used to estimate zero-frequency $\mu\beta_0$ values from single-frequency measurements, in particular when one-dimensional systems, in which one excited state dominates the nonlinearity, are involved. The $\mu\beta_0$ values calculated using coupled perturbed Hartree-Fock (CPHF) theory (gas phase) [39] are also collected in Table 4.

The experimental values show that the lengthening of the spacer using isophorone or thiophene heterocycles gives rise to the increase of the NLO response in the series **1** < **3** < **9**. An analogous behavior is observed for the corresponding compounds bearing the alkylsilyl group **2** < **4** < **10**. The electron-donor character of alkylsilyl groups causes a higher NLO response of silylated compounds compared to their hydroxyl analogous with the exception of compound **2**.

When the chromophores **10** and **11** are compared, the extra isophorone ring does not enhance the NLO response of the

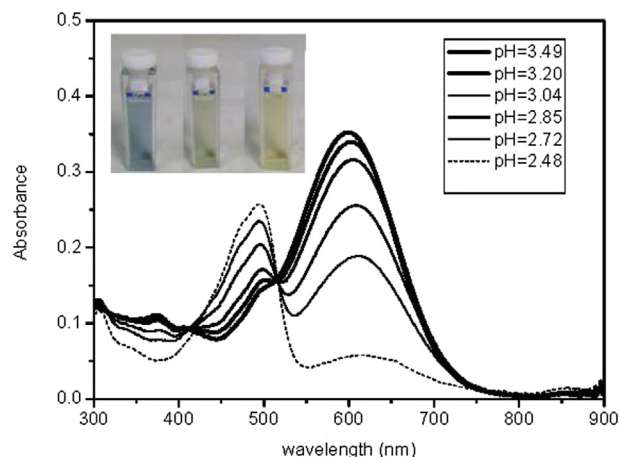


Fig. 1. a) Isosbestic plot: Titration of 0.01 M HCl to a blue solution of chromophore **9** in EtOH ($2 \cdot 10^{-5}$ M). b) Solution color: blue (pH = 3.04), green (pH = 2.85), yellow (pH = 2.72). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

chromophore and, regarding their UV/Vis spectra, both compounds show the band maxima at the same wavelength in CH₂Cl₂ and DMF. Although the π -spacer length is increased by the introduction of the isophorone ring, these results could be explained by both the distortion of the planarity of the chromophore and the difficulties to align the μ and β vectors. Similar effects of an analogous structural modification have been previously reported and explained for the compounds reported in Ref. [40]. The better stability of compound **10** compared with compound **11** makes compound **10** more adequate chromophore for further applications.

Moreover, when compounds **3** and **9** are compared with the analogous with alkoxysilyl group, an improvement of the molecular NLO response is observed (compounds **4** and **10**). As the λ_{\max} is scarcely modified, the presence of the silicon group improves the transparency-efficiency trade-off.

The calculations correctly reproduce the $\mu\beta$ increasing tendency associated with the lengthening of the π -spacer and the effect of the incorporation of the silyl group in chromophores **3** and **9**. However, the predicted increase of $\mu\beta_0$ for **2** compared to **1** has not been observed experimentally.

2.5. Thermal stability

The thermal stabilities of the chromophores were studied by thermogravimetric analysis (TGA) under nitrogen at a heating rate of 10 °C/min. The decomposition temperature (T_d) was estimated as the temperature at the intercept of the leading edge of the weight loss with the baseline of the TGA scans.

The results [T_d (°C): **1**, 220; **3**, 266; **9**, 224; **2**, 258; **4**, 296; **10**, 246; **11**, 284] show that the compounds have acceptable thermal

Table 2
UV/Vis data of the chromophores **10** and **11** on hydrogen bond acceptor (HBA) solvents and on hydrogen bond acceptor (HBA)-hydrogen bond donor (HBD) solvents.

	1,4-Dioxane			Ethyl acetate			DMSO			Acetonitrile			Ethanol		
	λ_{\max}^a	ΔE_{01}^b	$\log \epsilon$	λ_{\max}^a	ΔE_{01}^b	$\log \epsilon$	λ_{\max}^a	ΔE_{01}^b	$\log \epsilon$	λ_{\max}^a	ΔE_{01}^b	$\log \epsilon$	λ_{\max}^a	ΔE_{01}^b	$\log \epsilon$
10	576	2.15	4.73	579	2.14	4.74	609	2.04	4.15	585	2.12	4.56	596	2.08	4.30
11	567	2.19	4.14	570	2.17	4.23	^c	^c	^c	573	2.16	4.49	598	2.07	4.45

^a nm.^b eV.^c Decomposed.

Table 3
Electrochemical data^a, E_{HOMO} and E_{LUMO} values.^b

	$E_{1/2}^c$ (V)	ΔE_p (mV)	$E_{p,c}$ (V)	$E_{\text{HOMO}}/E_{\text{LUMO}}$ (eV)
1	1.13	80	−1.08	−6.95/−1.94
2	1.16	130	−0.93	−6.77/−1.84
3	0.74	80	−0.85	−6.26/−2.14
4	0.77	130	−0.89	−6.26/−2.14
5	0.84	80	−0.88	−6.35/−1.98
8	0.80	65	−0.88	−6.30/−2.24
9	0.74	90	−0.81	−6.19/−2.22
10	0.77	135	−0.83	−6.20/−2.22
11	0.65	115	−0.77	−6.01/−2.26

^a 10^{-3} M in CH_2Cl_2 versus Ag/AgCl (KCl 3 M), glassy carbon working electrode, Pt counter electrode, 20 °C, 0.1 M NBu_4PF_6 , 100 mV s^{-1} scan rate. Ferrocene internal reference $E_{\text{ox}} = +0.51$ V. $\Delta E_p = 0.160$ V.

^b Calculated at the PCM M06-2X/6-31G level in CH_2Cl_2 .

^c $E_{\text{ox}} = E_{1/2}$, net oxidation.

stabilities for the high temperature poling processes carried out to induce macroscopic NLO response [41,42].

In every case it can be observed that thermal stability improves with both the presence of the silicon group and the isophorone ring [43–46] in the NLO chromophore.

2.6. Electric field poling and macroscopic nonlinear properties

In order to undertake a further study, the two chromophores with the best NLO molecular response studied in this work were incorporated into a polymeric matrix. Both chromophores, **4** and **10**, contain bulky silicon groups and the presence of bulky groups is expected to minimize the electrostatic interactions. Moreover, their thermal stabilities, discussed above, make them suitable for high temperature poling in order to examine their macroscopic NLO response.

The optical properties of thin films of the chromophores **4** and **10** have been studied. These chromophores have been embedded in polybisphenol A carbonate (PC) ($M_w = 6400$, $T_g = 150$ °C) and thin films, with different chromophore content, from 4% up to 20 %wt, were prepared by *spin coating* [47–49]. The UV/Vis spectra exhibited a strong absorption in the visible region as it is shown in Fig. 2 for PC_10 films. The measurements of the different films have been scaled by the thickness. Very similar band shape was observed when the results for different chromophore concentration were compared. A slight increase of the bandwidth is observed with the chromophore content which could indicate some molecular aggregation; however, it does not seem to be very important. Moreover, the maximum absorption values scale essentially as

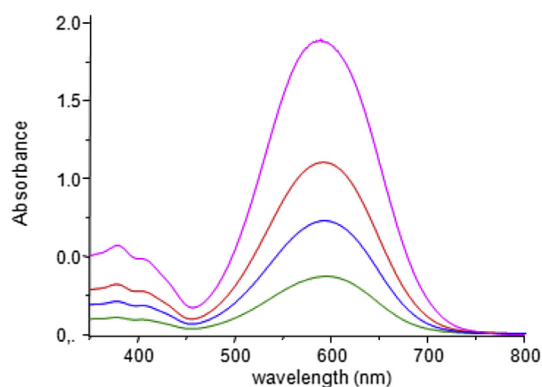


Fig. 2. Absorption spectra of thin films with different content of compound **10** embedded in polycarbonate PC_10_X% (X = **4** (green), **8** (blue), **12** (red) and **20** (pink)). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

4:8:12:20, which indicates that the amount of the chromophore in the matrix corresponds with the nominal content.

Following with the optical characterization of thin films, refractive index measurements (mode coupling method) were performed at 1306 nm. In addition to providing information on the initial state of the films (chromophore content, optical anisotropy ...), refractive index evolution reflects the changes of molecular orientation, as the ones associated with the electric field poling processes [50].

The refractive indices of the doped polymer films are gathered in Table 5. The thickness of the films was in the range 1.5–2.0 μm . On the one hand, it is observed the expected increase of the index values with the chromophore content, due to the optical absorption contribution. On the other hand, the measurements revealed that the index value measured with light polarization parallel to the film plane (n_o) is somewhat higher than that corresponding to light polarization perpendicular to the plane (n_e). This initial anisotropy, which indicates a preferential in-plane order, can be attributed to the film preparation conditions.

The PC_4 and PC_10 films were poled by using electric field “corona” poling process (see Supporting Information). The UV/Vis spectra taken at normal incidence showed a decrease of the absorption of the poled films as compared with the “as prepared” ones. In order to estimate the degree of the induced orientation, an order parameter, defined as $\phi = 1 - (\text{ABS}_{\text{poled}}/\text{ABS}_{\text{unpoled}})$, is usually given [51,52]. In the present work, ϕ values about 0.16 and 0.14 have been obtained for compounds **4** and **10**, respectively. In accordance

Table 4
Experimental and CPHF-calculated NLO properties and TDDFT-calculated^a parameters.

	Experimental		Theoretical calc.			
	$\mu\beta^b$ [10^{-48} esu]	$\mu\beta_0^c$ [10^{-48} esu]	$\mu\beta_0^d$ [10^{-48} esu]	μ_g [D]	E [eV]	$\Delta\mu_{\text{ge}}(z)$ [D]
1	340	230	184	8.90	2.92	8.60
2	330	220	358	12.99	2.87	7.39
3	1320	780	1254	15.96	2.31	13.35
4	1900	1090	1321	16.23	2.31	13.11
5	1100	650	1085	11.29	2.37	13.60
8	1880	1060	1221	13.80	2.39	11.41
9	1400	790	1549	14.04	2.26	14.38
10	2500	1375	1647	13.68	2.26	14.70
11	2540	1390	1744	13.23	2.19	16.24

^a Calculated at the M06-2X/6-311+G(2d,p) level in CH_2Cl_2 /PCM-M06-2X/6-31G*.

^b $\mu\beta$ values determined in dichloromethane at 1907 nm (experimental accuracy $\pm 10\%$).

^c Experimental $\mu\beta_0$ values calculated using the two level model and the λ_{max} values gathered in Table 1.

^d Calculated at the CPHF/6-31G* level in gas phase/M06-2X/6-31G*.

Table 5
Refractive indices n_o and n_e measured at 1306 nm before film poling.

PC film	Chromophore amount (% wt)	n_o	n_e	$\Delta n = (n_e - n_o)$
PC_10	4	1.564	1.550	−0.014
PC_10	12	1.579	1.567	−0.012
PC_10	4	1.571	1.558	−0.013
PC_10	12	1.585	1.572	−0.013
PC_10	20	1.604	1.594	−0.020

with that, index measurements revealed that the sign of the anisotropy is reversed upon the poling, and a positive birefringence (between 0.01 and 0.02) has been obtained.

The nonlinear optical properties of the poled films were evaluated by SHG measurements at 1907 nm. Two different polarizations (s and p) of the excitation light were used in order to obtain the d_{31} and d_{33} coefficients. Table 6 depicts the mentioned coefficients, calculated from the fitting of the harmonic signal measurements (Maker fringes) performed 24 h after the poling process. It can be seen that d_{33}/d_{31} ratios near to 3 have been obtained, which is in accordance with an essentially isotropic host matrix arrangement and the assumption of low poling electric field. [53].

On the other hand, the comparison of d_{ij} values of the three PC_10 films, allows assuming a similar polar order degree, regardless of the chromophore content. Thus, macroscopic nonlinear coefficients increase almost linearly with the chromophore content and, in accordance with UV/Vis results, saturation of the response has not been observed up to 20% for PC_10 films (expected, for example, if aggregation were relevant).

As the molecular relaxation tends to gradually reduce the polar ordering in poled guest-host polymeric systems, the NLO response of films was characterized after different intervals of time once the poling process was finished. After a week, a reduction of about 5–8% respect to the coefficients shown in Table 6 has been observed for the films. The NLO signal (as well as the optical anisotropy) of the films with the highest chromophore content was monitored over longer times. Measurements performed up to eight months after the poling showed that the polar order was maintained in a fairly high degree, obtaining d_{ij} values over 80% of that measured just after the poling.

3. Conclusions

A new series of aniline electron donor-based chromophores with a thiophene or an isophorone ring in the π -spacer group have been synthesized and show a combined high/moderate nonlinear optical activities (NLO) with good transparency. Both experimental and theoretical results show the improvement of $\mu\beta_o$ values when the silicon substituent is placed on the electron donor moiety. The alkylsilyl group has improved the NLO response as well as the thermal stability. This functionalization contributes to increase the solubility of these compounds, key factor in order to further macroscopic studies.

Table 6
Nonlinear coefficients of poled films with compounds 4 and 10.

Compound	Number density N^a	$\mu\beta^b$	d_{31}^c	d_{33}^c
4_4%	0.48×10^{20}	1900	0.9	2.8
4_12%	1.45×10^{20}		2.4	7.2
10_4%	0.49×10^{20}	2500	1.1	3.3
10_12%	1.48×10^{20}		3.0	9.0
10_20%	2.22×10^{20}		5.7	17

^a Chromophore molecules cm^{-3} .

^b From EFISH at 1.9 μm , in CH_2Cl_2 , in $\times 10^{-48}$ esu.

^c In pm V^{-1} , d_{ij} coefficients have been calculated from the Maker fringes measured at about 24 h after the poling (experimental accuracy $\pm 15\%$).

The incorporation of chromophores 4 and 10 in a polycarbonate matrix allowed the preparation of good optical-quality films by spin coating. UV/Vis studies showed no evidence of aggregation for the different concentrations explored, from 4% up to 20%. Corona poling processes were undertaken and quite efficient polar order was achieved. Nonlinear coefficients as high as 17 and 5.6 pm V^{-1} (d_{33} and d_{31} , respectively) were obtained for films with 20%wt content of chromophore 10. Concerning the stability of the polar order, it should be noted that 8 months after the poling d_{ij} values over 80% of those measured just after the poling were obtained.

4. Experimental

4.1. Detailed synthetic procedures

4.1.1. 1,3-Diethyl-5-(4-((2-hydroxyethyl) (methyl)amino)benzylidene)-2-thiobarbituric acid (1)

A solution of 1,3-diethyl-2-thiobarbituric acid, **T** (400 mg, 2.00 mmol) and 4-((2-hydroxyethyl) (methyl)amino)benzaldehyde, **Ald 1**, (358 mg, 2.00 mmol) was prepared in 30 mL ethanol. The mixture was refluxed under argon atmosphere with exclusion of light for 1 h. After cooling, the residue was filtered and washed with cold ethanol. A red solid was obtained (642 mg, 89%). Molecular weight (g/mol): 361.46.

m.p. ($^\circ\text{C}$) at 760 mmHg: 209. **IR** (KBr) (cm^{-1}): 1685 (C=O), 3453 (O–H). **^1H NMR** (400 MHz, CDCl_3) δ : 1.29–1.34 (m, 6H), 3.21 (s, 3H), 3.69 (t, $J = 5.5$ Hz, 2H), 3.91 (t, $J = 5.5$ Hz, 2H), 4.55–4.62 (m, 4H), 6.77 (d, $J = 9.26$ Hz, 2H), 8.39–8.41 (m, 3H). **^{13}C NMR** (100 MHz, CDCl_3) δ : 12.4, 12.5, 39.5, 43.4, 44.0, 54.2, 60.2, 110.7, 111.3, 121.9, 139.9, 154.3, 159.7, 162.2. **HRMS** (ESI^+) m/z 362.1521 [$\text{M}+\text{H}$] $^+$; [$\text{C}_{18}\text{H}_{24}\text{N}_3\text{O}_3\text{S}$] $^+$ requires 362.1533. **UV–Vis data** λ_{max} (CH_2Cl_2) (nm): 493, molar extinction coefficient ϵ_{max} ($\text{mL}^{-1}\text{dm}^3\text{cm}^{-1}$): 76. **Elemental analysis** found C 59.52; H 6.61; N 11.49; S 8.90%; molecular formula $\text{C}_{18}\text{H}_{23}\text{N}_3\text{O}_3\text{S}$ requires C 59.81; H 6.41; N 11.63; S 8.87%.

4.1.2. 5-(4-((2-*tert*-butyldimethylsilyl)oxi)etil) (methyl)amino benziliden)-1,3-diethyl-2-tioxodihydropyrimidine-4,6(1H,5H)-dione (2)

A solution of 1,3-diethyl-2-thiobarbituric acid, **T** (100.13 mg, 0.5 mmol) and **Ald 2** (146 mg, 0.5 mmol) were solved in ethanol (9 mL). The reaction mixture was stirred at 80 $^\circ\text{C}$ during 75 min with exclusion of light. The precipitated was filtered and 232.8 mg (0.4893 mmol) of a red solid was obtained with a yield of 98%. Molecular weight (g/mol): 475.72.

m.p. ($^\circ\text{C}$) at 760 mmHg: 151. **IR** (Nujol) (cm^{-1}): 820 (Si-(CH_3) $_2$), 1653 (C=O). **^1H NMR** (400 MHz, CDCl_3) δ 0.00 (s, 6H), 0.86 (s, 9H), 1.29–1.34 (m, 6H), 3.19 (s, 3H), 3.64 (t, $J = 5.6$ Hz, 2H), 3.84 (t, $J = 5.6$ Hz, 2H), 4.55–4.62 (m, 4H), 6.74 (d, $J = 8.8$ Hz, 2H), 8.41–8.42 (t, $J = 8.8$ Hz, 3H). **^{13}C NMR** (100 MHz, CDCl_3) δ −5.5, 12.4, 12.5, 18.1, 25.8, 39.8, 43.4, 43.9, 54.7, 60.5, 110.4, 111.4, 121.8, 139.9, 154.2, 159.6, 162.2, 178.8. **HRMS** (HR-ESI^+) m/z 476.2401 [$\text{M}+\text{H}$] $^+$; [$\text{C}_{24}\text{H}_{38}\text{N}_3\text{O}_3\text{SSi}$] $^+$ requires 476.2398. **UV–Vis data** λ_{max} (CH_2Cl_2) (nm): 496, molar extinction coefficient ϵ_{max} ($\text{mL}^{-1}\text{dm}^3\text{cm}^{-1}$): 78. **Elemental analysis** found C 60.32, H 7.85, N 8.99, S 6.53%; molecular formula $\text{C}_{24}\text{H}_{37}\text{N}_3\text{O}_3\text{SSi}$ requires C 60.59, H 7.84, N 8.83, S 6.74%.

4.1.3. (E)-1,3-Diethyl-5-(3-(4-((2-hydroxyethyl) (methyl)amino)esteryl)-5,5-dimethyl-2-cyclohex-2-en-1-yliden)-2-thiobarbituric acid (3)

To a solution of 4-((2-hydroxyethyl) (methyl)amino)benzaldehyde, **Ald 1**, (90 mg, 0.50 mmol) and the acceptor **IT** (160 mg, 0.50 mmol) in dry acetonitrile (7.5 mL) piperidine (0.05 mL, 0.5 mmol) was added. The mixture was refluxed under argon atmosphere with exclusion of light for 7 h (TLC monitoring). After

cooling, acetonitrile was distilled, and CH_2Cl_2 was added (200 mL). The organic layer was washed with HCl 0.1 M (2×70 mL) and water (2×70 mL), dried (MgSO_4) and the solvent evaporated. The crude product was purified by flash chromatography on silica gel (40–60 μm) with hexane: ethyl acetate (1:1) as eluent and a dark blue solid was obtained (170 mg, 70%). Molecular weight (g/mol): 481.65.

m.p. ($^\circ\text{C}$) at 760 mmHg: 90. **IR** (Nujol) (cm^{-1}): 1657 ($\text{C}=\text{O}$), 3434 (OH). **^1H NMR** (400 MHz, CDCl_3) δ : 1.06 (s, 6H), 1.27–1.34 (m, 6H), 1.58 (s, 1H), 2.46 (s, 2H), 3.08 (s, 3H), 3.10 (s, 2H), 3.58 (t, $J = 5.6$ Hz, 2H), 3.86 (t, $J = 5.6$ Hz, 2H), 4.50–4.58 (m, 4H), 6.78 (d, $J = 7.3$ Hz, 2H), 7.03 (c, $J = 16.1$ Hz, 2H), 7.43 (d, $J = 8.8$ Hz, 2H), 8.39 (s, 1H). **^{13}C NMR** (100 MHz, CDCl_3) δ : 12.6, 28.6, 31.9, 39.0, 43.6, 43.7, 44.9, 54.9, 60.1, 111.5, 112.3, 127.2, 127.5, 129.6, 137.5, 160.8, 161.2, 171.1, 178.0. **HRMS** (ESI^+) m/z 482.2481 $[\text{M}+\text{H}]^+$; $[\text{C}_{27}\text{H}_{36}\text{N}_3\text{O}_3\text{S}]^+$ requires 482.2472. **UV–Vis data** $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)$ (nm): 564, molar extinction coefficient $\epsilon_{\text{max}}(\text{mL}^{-1}\text{dm}^3\text{cm}^{-1})$: 26. **Elemental analysis** found C 67.45, H 7.50, N 8.55, S 6.75%; molecular formula $\text{C}_{27}\text{H}_{35}\text{N}_3\text{O}_3\text{S}$ requires C 67.33, H 7.32, N 8.72, S 6.66%.

4.1.4. (E)-5-(3-(4-((tert-butyl(dimethylsilyl)oxy)ethyl) (methyl) amino)styryl)-5,5-dimethylcyclohex-2-en-1-yliden)-1,3-diethyl-2-tioxodihydropyrimidine-4,6(1H,5H)-dione (4)

To a stirred solution of **Ald 2** (586.95 mg, 2 mmol) in dry acetonitrile (8 mL) piperidine (0.1975 mL, 2 mmol) was added. After 15 min, **IT** (640.9 mg, 2 mmol) was also added. The mixture was refluxed during 1 h. The solvent was removed and the residue was solved in dichloromethane (200 mL) and washed with H_2O –HCl (9:1) (2×70 mL) and twice with water and dried. After concentration under reduced pressure, the residue was purified by column chromatography hexane-ethyl acetate (1:0.1) on silica gel (40–60 μm) and the desired product was isolated as a dark blue solid 0.280 g with a yield of 24%. Molecular weight (g/mol): 595.33.

m.p. ($^\circ\text{C}$) at 760 mmHg: 76. **IR** (KBr) (cm^{-1}): 861 ($\text{Si}-\text{CH}_3$), 1180 ($\text{C}=\text{S}$), 1657 ($\text{C}=\text{O}$). **^1H NMR** (400 MHz, CDCl_3) δ : 0.02 (s, 6H), 0.87 (s, 9H), 1.07 (s, 6H), 1.28–1.35 (t, 6H), 2.46 (s, 2H), 3.11 (s, 2H), 3.13 (s, 3H), 3.55 (t, 2H), 3.87 (t, 2H), 4.47–4.60 (m, 4H), 6.95–7.10 (m, 4H), 7.48 (d, $J = 8.8$ Hz, 2H), 8.39 (s, 1H). **^{13}C NMR** (100 MHz, CDCl_3) δ : –5.5, 12.6, 18.2, 25.8, 28.6, 31.9, 39.1, 43.6, 43.7, 44.8, 60.1, 129.5, 172.2, 173.9, 174.2, 177.5, 178.9, 179.9. **HRMS** (ESI^+) m/z 596.3342 $[\text{M}+\text{H}]^+$; $[\text{C}_{33}\text{H}_{50}\text{N}_3\text{O}_3\text{SSi}]^+$ requires 596.3337. **UV–Vis data** $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)$ (nm): 579, molar extinction coefficient $\epsilon_{\text{max}}(\text{mL}^{-1}\text{dm}^3\text{cm}^{-1})$: 46. **Elemental analysis** found C 66.70, H 8.52, N 6.84, S 5.24%; molecular formula $\text{C}_{33}\text{H}_{49}\text{N}_3\text{O}_3\text{SSi}$ requires C 66.51, H 8.29, N 7.05, S 5.38%.

4.1.5. (E)-2-((4-(2-(3-(1,3-diethylthiobarbituric)-5,5-dimethyl-1-cyclohexen-1-yl)vinyl)phenyl) (methyl)amino)ethyl acetate (5)

To a solution of **acetic acid** (0.012 mL, 0.21 mmol) in dry dichloromethane (30 mL), 1-hydroxybenzotriazole (**HOBT**), (28 mg, 0.21 mmol), 4-dimethylaminopyridine (**DMAP**) (51 mg, 0.42 mmol) and 1,3-dicyclohexylcarbodiimide (**DCC**) (86 mg, 0.42 mmol) were added successively under nitrogen atmosphere and after 15 min compound **3** (100 mg, 0.21 mmol) was also added. The reaction mixture was stirred at room temperature during 4 days with exclusion of light. The mixture was filtered and dichloromethane (200 mL) was added. The organic phase was washed several times with both NH_4Cl and water and it was dried with MgSO_4 . After concentration under reduced pressure, the residue was purified by column chromatography (CH_2Cl_2) on silica gel (40–60 μm) and the ester was isolated as a dark blue solid (40 mg, 36%). Molecular weight (g/mol): 523.68.

m.p. ($^\circ\text{C}$) at 760 mmHg: 135. **IR** (Nujol) (cm^{-1}): 1271 ($\text{C}-\text{O}$), 1651 ($\text{C}=\text{O}$), 1739 ($\text{C}=\text{O}$). **^1H NMR** (400 MHz, CDCl_3) δ : 1.06 (s, 6H), 1.28–1.34 (m, 6H), 2.01 (s, 3H), 2.46 (s, 2H), 3.06 (s, 3H), 3.10 (s, 2H),

3.66 (t, $J = 5.9$ Hz, 2H), 4.27 (t, $J = 5.9$ Hz, 2H), 4.50–4.58 (m, 4H), 6.71 (d, $J = 9.0$ Hz, 2H), 6.98 (d, $J = 15.9$ Hz, 1H), 7.07 (d, $J = 15.9$ Hz, 1H), 7.43 (d, $J = 9.0$ Hz, 2H), 8.39 (s, 1H). **^{13}C NMR** (100 MHz, CDCl_3) δ : 12.6, 20.9, 28.7, 31.9, 38.7, 39.1, 43.7, 45.0, 50.8, 61.3, 112.1, 124.6, 127.1, 127.5, 129.7, 137.8, 150.2, 159.2, 160.9, 161.2, 170.9, 171.2, 178.1. **HRMS** (MALDI^+) m/z 524.2564 $[\text{M}+\text{H}]^+$; $[\text{C}_{29}\text{H}_{38}\text{N}_3\text{O}_4\text{S}]^+$ requires 524.2578. **UV–Vis data** $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)$ (nm): 563, molar extinction coefficient $\epsilon_{\text{max}}(\text{mL}^{-1}\text{dm}^3\text{cm}^{-1})$: 36. **Elemental analysis** found C 66.70, H 7.34, N 7.88, S 6.32%; molecular formula $\text{C}_{29}\text{H}_{37}\text{N}_3\text{O}_4\text{S}$ requires C 66.51, H 7.12, N 8.02, S 6.12%.

4.1.6. 2-((4-formylphenyl) (methyl)amino)ethyl benzoate (Ald 3)

POCl_3 (1.0 mL, 10.92 mmol) was added dropwise to (2.0 mL, 25.83 mmol) of freshly distilled DMF at 0°C in argon atmosphere. A solution of (2.500 g, 9.80 mmol) of N-2-benzoxoethyl-N-methyl-aniline (20 mL) was added dropwise to the POCl_3/DMF complex at room temperature. The reaction mixture was stirred at 90°C for 6 h. After the completion of the reaction (monitored by TLC), the reaction mixture was cooled to rt and poured into ice water. The crude product was extracted with dichloromethane (3×100 mL) and the organic layer was washed with sodium acetate and water and dried over anhydrous sodium sulfate. After removing the solvent under reduced pressure, the residue was purified by column chromatography (eluent: dichloromethane/ethyl acetate, 95: 5) on silica gel to afford the desired compound as an yellow oil (1.58 g, 57% yield). Molecular weight (g/mol): 283.32.

IR (cm^{-1}): 1272 ($\text{C}-\text{O}$), 1678 ($\text{C}=\text{O}$), 1720 ($\text{C}=\text{O}$). **^1H NMR** (400 MHz, CDCl_3) δ : 3.15 (s, 3H), 3.84 (t, $J = 5.9$ Hz, 2H), 4.52 (t, $J = 5.9$ Hz, 2H), 6.80 (d, $J = 9.0$ Hz, 2H), 7.41 (t, $J = 7.9$ Hz, 2H), 7.55 (tt, $J_1 = 7.5$ Hz, $J_2 = 1.3$ Hz, 1H), 7.73 (dt, $J_1 = 9.0$ Hz, $J_2 = 1.9$ Hz, 2H), 7.94–7.96 (m, 2H), 9.74 (s, 1H). **^{13}C NMR** (100 MHz, CDCl_3) δ : 39.0; 50.8; 61.0; 111.3; 125.8; 128.5; 129.6; 132.1; 133.2; 153.4; 166.5; 190.3. **HRMS** (HR-ESI^+) m/z 306.1104 $[\text{M}+\text{Na}]^+$; molecular formula $\text{C}_{17}\text{H}_{17}\text{NNaO}_3$ requires $[\text{M}+\text{Na}]^+$ 306.1100.

Elemental analysis found C 72.15, H 6.04, N 4.92%, molecular formula $\text{C}_{17}\text{H}_{17}\text{NO}_3$ requires C 72.07, H 6.05, N 4.94%.

4.1.7. 2-(methyl(4-(2-(thiophen-2-yl)vinyl)phenyl)amino)ethyl benzoate (6a) and 2-(methyl(4-(2-(thiophen-2-yl)vinyl)phenyl)amino)ethanol (6b)

To a dried, three-necked, 100 mL round-bottom flask were added 1,2-dimethoxyethane (15 mL) and sodium hydride, 60% (156 mg, 4.06 mmol) under nitrogen. The mixture was stirred for 5 min, and compound **Ald 3** (575 mg, 2.03 mmol) in 1,2-dimethoxyethane (10 mL) was then added. The diethyl 2-thenylphosphonate (471 mg, 2.03 mmol) in 1,2-dimethoxyethane (10 mL) was added slowly to the reaction mixture. The resulting solution was overnight at room temperature and then poured into crushed ice (40 g) under nitrogen. The mixture was extracted with dichloromethane (3×30 mL). The organic layer was washed with water (3×50 mL). After removing the solvent, the crude product was chromatographed using hexane/diethyl ether (7: 3) to yield compound **6a** as yellow solid (143 mg, 0.39 mmol) yield: 19%. Molecular weight (g/mol): 363.47.

m.p. ($^\circ\text{C}$) at 760 mmHg: 104. **IR** (Nujol) (cm^{-1}): 1277 ($\text{C}-\text{O}$), 1713 ($\text{C}=\text{O}$). **^1H NMR** (400 MHz, CDCl_3) δ : 3.08 (s, 3H), 3.78 (t, $J = 5.9$ Hz, 2H), 4.51 (t, $J = 5.9$ Hz, 2H), 6.77 (d, $J = 8.8$ Hz, 2H), 6.86 (d, $J = 16.0$ Hz, 1H), 7.00–6.96 (m, 2H), 7.04 (d, $J = 16.0$ Hz, 1H), 7.12 (d, $J = 4.8$ Hz, 1H), 7.36 (d, $J = 8.8$ Hz, 2H), 7.42 (t, $J = 7.7$ Hz, 2H), 7.55 (t, $J = 7.4$ Hz, 1H), 7.97 (d, $J = 7.4$ Hz, 2H). **^{13}C NMR** (100 MHz, CDCl_3) δ : 38.8; 51.2; 62.1; 112.4; 117.9; 123.1; 124.6; 127.5; 127.6; 128.4; 128.5; 129.6; 133.0. **HRMS** (HR-ESI^+) m/z 364.1367 $[\text{M}+\text{H}]^+$; molecular formula $\text{C}_{22}\text{H}_{22}\text{NO}_2\text{S}$ requires $[\text{M}+\text{H}]^+$ 364.1366. **Elemental analysis** found C 72.97, H 5.80, N 3.84, S 8.84%, molecular formula $\text{C}_{22}\text{H}_{21}\text{NO}_2\text{S}$ requires C 72.70, H 5.82, N 3.85, S 8.82%.

Compound 6b was obtained as a yellow solid (164 mg, 0.63 mmol). Yield: 31%. Molecular weight (g/mol): 259.36.

m.p. (°C) at 760 mmHg: 124. **I.R.** (Nujol) cm^{-1} : 1604 (C=), 3250 (O–H). **^1H NMR** (400 MHz, CDCl_3) δ : 3.01 (s, 3H), 3.51 (t, $J = 5.6$ Hz, 2H), 3.83 (t, $J = 5.6$ Hz, 2H), 6.80 (d, $J = 8.6$ Hz, 2H), 6.86 (d, $J = 16.1$ Hz, 1H), 6.97–7.00 (m, 2H), 7.06 (d, $J = 16.1$ Hz, 1H), 7.13 (d, $J = 5.0$ Hz, 1H), 7.36 (d, $J = 8.6$ Hz, 2H). **^{13}C NMR** (100 MHz, CDCl_3) δ : 39.0; 55.3; 60.1; 113.0; 118.1; 123.2; 124.7; 126.2; 127.4; 128.3; 143.7; 149.2. **HRMS** ($[\text{M}+\text{H}]^+$) m/z 260,1105 $[\text{M}+\text{H}]^+$; molecular formula $\text{C}_{15}\text{H}_{18}\text{NOS}$ requires $[\text{M}+\text{H}]^+$: 260,1104. **Elemental analysis** found C 69.63, H 6.62, N 5.39, S 12.39%, molecular formula $\text{C}_{15}\text{H}_{17}\text{NOS}$ requires C 69.46, H 6.61, N 5.40, S 12.36%.

4.1.8. 2-((4-(2-(5-formylthiophene-2-yl)vinyl)phenyl) (methyl)amino)ethyl benzoate (Ald 4)

POCl_3 (0.05 mL, 0.58 mmol) was added dropwise to (0.29 mL, 3.77 mmol) of freshly distilled DMF at 0 °C in argon atmosphere. A solution of (212 mg, 0.58 mmol) of compound **6a** was added dropwise to the POCl_3/DMF complex at rt. The reaction mixture was stirred at 80 °C for 20 h. After the completion of the reaction (monitored by TLC), the reaction mixture was cooled to rt and poured into ice water. The crude product was extracted with dichloromethane (3×100 mL) and the organic layer was washed with sodium bicarbonate and water and dried over anhydrous sodium sulfate. After removing the solvent under reduced pressure, the residue was purified by column chromatography (eluent: hexane/dichloromethane, 1:1) on silica gel to afford an orange solid (188 mg, 0.48 mmol), 83% yield as a mixture Z/E (46/54). Molecular weight (g/mol): 391.48.

IR (KBr) cm^{-1} : 1262 (C–O), 1649 (C=O), 1714 (C=O). **^1H NMR** (400 MHz, CDCl_3) δ : 3.09–3.11 (m, 6H), 3.77–3.81 (m, 4H), 4.51–4.55 (m, 4H), 6.51 (d, $J = 12.0$ Hz, 1H), 6.68 (d, $J = 12.0$ Hz, 1H), 6.80 (m, 4H), 7.01 (d, $J = 16.0$ Hz, 1H), 7.07–7.11 (m, 3H), 7.27 (d, $J = 8.9$ Hz, 2H), 7.39–7.44 (m, 6H), 7.54–7.56 (m, 3H), 7.64 (d, $J = 3.9$ Hz, 1H), 7.95–8.00 (m, 4H), 9.79 (s, 1H), 9.82 (s, 1H). **HRMS** ($[\text{M}+\text{H}]^+$) m/z 392,1321 $[\text{M}+\text{H}]^+$; molecular formula $\text{C}_{23}\text{H}_{22}\text{NO}_3\text{S}$ requires $[\text{M}+\text{H}]^+$ 392,1315. **Elemental analysis** found C 70.80, H 5.40, N 3.59, S 8.17%, molecular formula $\text{C}_{22}\text{H}_{21}\text{NO}_3\text{S}$ requires C 70.56, H 5.41, N 3.58, S 8.19%.

4.1.9. (E)-2-((4-(2-(5-((1,3-diethylthiobarbituric)-5(2H)-ylidene) methyl)thiophene-2-yl)vinyl)phenyl) (methyl)amino)ethyl benzoate (8)

A solution of the aldehyde, **Ald 4** (103 mg, 0.26 mmol) and 1,3-diethyl-2-thiobarbituric acid, **T** (53 mg, 0.26 mmol) was prepared in 25 mL ethanol. The mixture was refluxed under argon atmosphere with exclusion of light for 1 h. After cooling, the residue was filtered and washed with cold ethanol. A dark blue solid was obtained (83 mg, 55%). Molecular weight (g/mol): 573.73.

m.p. (°C) at 760 mmHg: 175. **IR** (KBr) (cm^{-1}): 1264 (C–O), 1685 (C=O), 1717 (C=O). **^1H NMR** (400 MHz, CDCl_3) δ : 1.32 (t, $J = 7.0$ Hz, 3H), 1.37 (t, $J = 7.0$, 3H), 3.13 (s, 3H), 3.82 (t, $J = 5.9$ Hz, 2H), 4.53 (t, $J = 5.9$ Hz, 2H), 4.56–4.66 (m, 4H), 6.83 (d, $J = 8.8$ Hz, 2H), 7.08 (d, $J = 16.0$ Hz, 1H), 7.22 (d, $J = 4.2$ Hz, 1H), 7.38 (d, $J = 16.0$ Hz, 1H), 7.40–7.43 (m, 2H), 7.44–7.47 (m, 2H), 7.54–7.58 (m, 1H), 7.79 (d, $J = 4.2$ Hz, 1H), 7.95–7.97 (m, 2H), 8.60 (s, 1H). **^{13}C NMR** (100 MHz, CDCl_3) δ : 12.4, 12.6, 39.1, 43.1, 43.9, 51.1, 61.9, 108.7, 112.5, 116.7, 126.3, 128.4, 129.1, 129.6, 129.7, 133.2, 135.4, 135.8, 147.8, 150.0, 160.0, 161.3, 162.3, 166.5, 178.7. **HRMS** ($[\text{M}+\text{H}]^+$) m/z 574.1809 $[\text{M}+\text{H}]^+$; $[\text{C}_{31}\text{H}_{32}\text{N}_3\text{O}_4\text{S}_2]^+$ requires 574.1829. **UV–Vis data** $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)$ (nm): 584, molar extinction coefficient $\epsilon_{\text{max}}(\text{mL}^{-1}\text{dm}^3\text{cm}^{-1})$: 51. **Elemental analysis** found C 65.01, H 5.56, N 7.11, S 11.25%; molecular formula $\text{C}_{31}\text{H}_{31}\text{N}_3\text{O}_4\text{S}_2$ requires C 64.90, H 5.45, N 7.32, S 11.18%.

4.1.10. (E)-1,3-Diethyl-5-((5-(4-((2-hydroxyethyl) (methyl)amino) styryl)-2-thiophen-2-yl)methylen)-2-thiobarbituric acid (9)

To a solution of the **8** compound (67 mg, 0.12 mmol) in 2 mL ethanol, NaOH was added (0.5 mL, 20%). The reaction mixture was stirred at room temperature during 14 h with exclusion of light. The residue was filtered and the solvent was removed. Chloroform (200 mL) was added and the organic phase was washed several times with both NH_4Cl and water and dried. After concentration under reduced pressure, a dark green solid was obtained (34 mg, 63%). Molecular weight (g/mol): 469.62.

m.p. (°C) at 760 mmHg: 210. **IR** (Nujol) (cm^{-1}): 1377 (C=S), 1644 (C=O), 3497 (O–H). **^1H NMR** (400 MHz, CDCl_3) δ : 1.32 (t, $J = 7.0$ Hz, 3H), 1.36 (t, $J = 7.0$ Hz, 3H), 3.09 (s, 3H), 3.58 (t, $J = 5.6$ Hz, 2H), 3.87 (t, $J = 5.6$ Hz, 2H), 4.56–4.67 (m, 4H), 6.79–6.86 (m, 2H), 7.09 (d, $J = 16.0$ Hz, 1H), 7.21 (d, $J = 4.3$ Hz, 1H), 7.38 (d, $J = 16.0$ Hz, 1H), 7.45 (d, $J = 8.9$ Hz, 2H), 7.78 (d, $J = 4.3$ Hz, 1H), 8.60 (s, 1H). **^{13}C NMR** (100 MHz, CDCl_3) δ : 12.4, 12.6, 29.7, 43.1, 44.0, 126.6, 129.0, 147.6, 149.0, 160.0, 161.2, 178.7. **HRMS** ($[\text{M}+\text{H}]^+$) m/z 470.1552 $[\text{M}+\text{H}]^+$; $[\text{C}_{24}\text{H}_{28}\text{N}_3\text{O}_3\text{S}_2]^+$ requires 470.1567. **UV–Vis data** $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)$ (nm): 587, molar extinction coefficient $\epsilon_{\text{max}}(\text{mL}^{-1}\text{dm}^3\text{cm}^{-1})$: 41. **Elemental analysis** found C 61.28, H 5.76, N 9.10, S 13.50%; molecular formula $\text{C}_{24}\text{H}_{27}\text{N}_3\text{O}_3\text{S}_2$ requires C 61.38, H 5.80, N 8.95, S 13.65%.

4.1.11. (E)-5-((5-(4-((2-((tert-butyldimethylsilyl)oxi)ethyl) (methyl)amino)styryl)thiophen-2-yl)methylen)-1,3-dimethyl-2-tioxodihydropyrimidine-4,6(1H,5H)-dione (10)

To a stirred solution of 1,3-diethyl-2-thiobarbituric acid, **T** (50 mg, 0.250 mmol) in ethanol (6 mL), **Ald 5** (100 mg, 0.250 mmol) solved in ethanol (12 mL) was added. The reaction mixture was heated at 70 °C during 2 h with exclusion of light. The precipitated was filtered and washed with cold ethanol. 0.120 g (0.205 mmol) of a dark blue solid were obtained with a yield of 82%. Molecular weight (g/mol): 583.88.

m.p. (°C) at 760 mmHg: 140 (d). **IR** (Nujol) (cm^{-1}): 1266 (C–O), 1382 (C=S), 1652 (C=O). **^1H NMR** (400 MHz, CDCl_3) δ : 0.02 (s, 6H), 0.88 (s, 9H), 1.31 (t, $J = 7.2$ Hz, 3H), 1.36 (t, $J = 7.2$ Hz, 3H), 3.07 (s, 3H), 3.53 (t, $J = 5.6$ Hz, 2H), 3.80 (t, $J = 5.6$ Hz, 2H), 4.58 (c, $J = 6.8$ Hz, 2H), 4.62 (c, $J = 6.8$ Hz, 2H), 6.72 (d, $J = 8.8$ Hz, 2H), 7.04 (d, $J = 16$ Hz, 1H), 7.19 (d, $J = 4.4$ Hz, 1H), 7.37 (d, $J = 16$ Hz, 1H), 7.42 (d, $J = 8.8$ Hz, 2H), 7.76 (d, $J = 4.4$ Hz, 1H), 8.58 (s, 1H). **^{13}C NMR** (100 MHz, CDCl_3) δ : 5.4, 12.4, 12.6, 25.8, 39.4, 43.1, 43.9, 54.7, 60.4, 108.4, 112.2, 116.0, 126.0, 129.1, 136.2, 147.9, 148.8, 150.2, 161.3, 162.8, 178.6. **HRMS** ($[\text{M}+\text{H}]^+$) m/z 584.2392 $[\text{M}+\text{H}]^+$; $[\text{C}_{30}\text{H}_{42}\text{N}_3\text{O}_3\text{S}_2\text{Si}]^+$ requires 584.2431. **UV–Vis data** $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)$ (nm): 599, molar extinction coefficient $\epsilon_{\text{max}}(\text{mL}^{-1}\text{dm}^3\text{cm}^{-1})$: 50. **Elemental analysis** found C 61.58, H 7.25, N 7.05, S 11.05%, molecular formula $\text{C}_{30}\text{H}_{41}\text{N}_3\text{O}_3\text{S}_2\text{Si}$ requires C 61.71, H 7.08, N 7.20, S 10.98%.

4.1.12. 5-(3-((E)-2-(5-((E)-4-((2-((tert-butyldimethylsilyl)oxi)ethyl) (methyl)amino)styryl)thiophen-2-yl)vinyl)-5,5-dimethylcyclohex-2-en-1-yliden)-1,3-diethyl-2-tioxodihydropyrimidine-4,6(1H,5H)-dione (11)

To a stirred solution of **Ald 5** (150 mg, 0.373 mmol) in dry acetonitrile (8 mL) piperidine (0.037 mL, 0.373 mmol) was added. After 15 min, the acceptor **IT** (119.68 mg, 0.373 mmol) was also added. The mixture was heated at 70 °C during 1 h. The solvent was removed and the residue was solved with dichloromethane (200 mL) and washed with H_2O –HCl (9:1) (2×70 mL) and twice with water. The residue was dried and purified with two consecutive column chromatography hexane-ethyl acetate (8:1) on silicagel (40–60 μm). The desired product was obtained as a dark blue solid with a yield of 6%. Molecular weight (g/mol): 704.07.

m.p. (°C) at 760 mmHg: 97. **IR** (KBr) (cm^{-1}): 1361 (C=S), **¹H NMR** (400 MHz, CDCl_3) δ 0.02 (s, 6H), 0.84 (s, 9H), 1.07 (s, 6H), 1.29–1.34 (m, 6H), 2.41 (s, 2H), 3.10 (s, 2H), 3.25 (s, 3H), 3.55 (t, 2H), 4.05 (t, 2H), 4.50–4.60 (m, 4H), 6.92 (d, J = 16 Hz, 2H), 7.06 (d, J = 4 Hz, 1H), 7.10 (d, J = 4 Hz, 1H), 7.14 (d, J = 16 Hz, 1H), 7.22 (d, J = 16 Hz, 1H), 7.57 (d, J = 8.4 Hz, 2H), 7.78 (d, J = 8.4 Hz, 2H), 8.38 (s, 1H). **¹³C NMR** (100 MHz, CDCl_3) δ –5.40, 12.6, 18.2, 25.9, 28.6, 29.7, 31.8, 38.9, 43.6, 43.7, 44.6, 60.0, 112.6, 124.1, 126.4, 128.0, 128.6, 129.4, 130.4, 131.0, 140.1, 156.8, 160.7, 161.1, 170.1, 178.1. **HRMS** (HR-ESI^+) m/z 704.3351 $[\text{M}+\text{H}]^+$; $[\text{C}_{39}\text{H}_{54}\text{N}_3\text{O}_3\text{S}_2\text{Si}]^+$ requires 704.3370. **UV–Vis data** λ_{max} (CH_2Cl_2) (nm): 599, molar extinction coefficient ϵ_{max} ($\text{m}^{-1}\text{dm}^3\text{cm}^{-1}$): 35. **Elemental analysis** found C 66.60, H 7.31, N 6.20, S 4.12%; molecular formula $\text{C}_{39}\text{H}_{53}\text{N}_3\text{O}_3\text{S}_2\text{Si}$ requires C 66.53, H 7.59, N 5.97, S 3.99%.

Acknowledgments

Financial support from MICINN-FEDER (CTQ2011-22727 and MAT2011-27978-C02-02) and Gobierno de Aragón-Fondo Social Europeo (E39 and E04) and also anonymous referees for helpful discussions are gratefully acknowledged.

Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.dyepig.2015.02.026>.

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