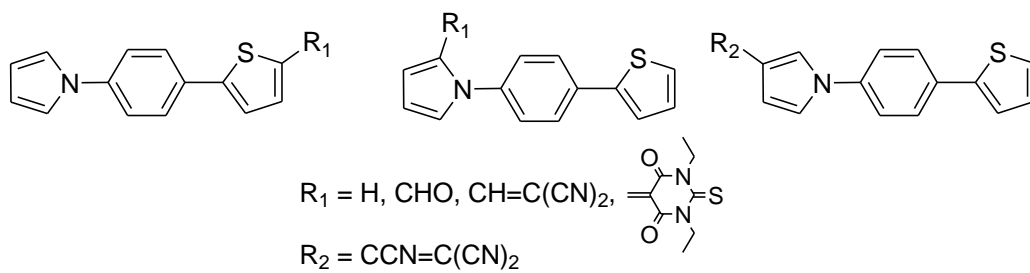


GRAPHICAL ABSTRACT

Synthesis and characterization of novel second-order NLO-chromophores bearing pyrrole as an electron donor group

M. Cidália R. Castro,¹ M. Belsley,² A. Maurício C. Fonseca,¹ and M. Manuela M. Raposo^{1*}



Synthesis and characterization of novel second-order NLO-chromophores bearing pyrrole as an electron donor group

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Abstract- Two series of novel push-pull 1-(4-(thiophen-2-yl)phenyl)-1*H*-pyrroles **3-5** were designed to explore the consequence of using different electron accepting moieties linked to the thiophene at the arylthiophene bridge or to the pyrrole heterocycle which plays the role of donor group. Compound **2** showed a different reactivity behavior in the presence of the Vilsmeier reagent or with tetracyanoethylene (TCNE) giving compounds **4a** and **4b** functionalized respectively at the 2 or on the 3-position of the pyrrole heterocycle. Their optical (linear and first hyperpolarizability), electrochemical and thermal properties have been examined. Hyper-Rayleigh scattering (HRS) in dioxane solutions using a fundamental wavelength of 1064 nm was employed to evaluate their second-order nonlinear optical properties. Of these systems, thiobarbituric acid derivative **5b** functionalized in the thiophene ring exhibits the largest first hyperpolarizability ($\beta = 2480 \times 10^{-30}$ esu, T convention) compared to the corresponding compound **4c** substituted on the pyrrole heterocycle ($\beta = 290 \times 10^{-30}$ esu, T convention). Good to excellent thermal stabilities were also obtained for push-pull compounds **4-5** (270 - 288 °C). This multidisciplinary study shows that modulation of the optical and electronic properties can be achieved by introduction of the acceptor groups in the thiophene of the arylthiophene bridge. The measured molecular first hyperpolarizabilities and the observed electrochemical behavior are quite sensitive to the position of acceptor group on the heterocyclic system (on the thiophene or on the pyrrole ring) as well as the strength of the acceptor moieties. Moreover, the combination of their good nonlinearity and high thermal stability make them good candidates for second order nonlinear optical applications.

Keywords: Push-pull heterocyclic systems, Pyrrole, Thiophene, Reactivity studies, Auxiliary donor heterocycle, First hyperpolarizability (β), Hyper-Rayleigh scattering (HRS), Redox properties, Thermal stability.

1. Introduction

Over the last three decades there has been an intense research effort aimed at improving the nonlinear optical response of push-pull type organic chromophores, motivated by their strong potential to make fundamental improvements in organic modern communication technology, *e.g.* ultrafast image-processing, optical data processing, transmission, and storage.

Several studies have demonstrated that organic materials have ultrafast response times, low dielectric constants, are easier to tailor or process, and possess stronger NLO responses when compared to inorganic compounds. These advantages are in large part due to their optical properties derived from the high electronic polarisation of the π -electrons of the molecules instead of the distortions of the atoms in the crystal lattice, which is a slower process. The ease of synthesis and functionalization of organic compounds allows easy optimization of their structural characteristics which is necessary in order to maximize the NLO properties.

One of the major challenges in the design and optimization of the second-order polarizability of organic NLO materials consists in finding substituents with an optimal combination of their donor/ or acceptor strength for a given parent chromophore.¹

A combination of synthetic innovations² reinforced by theoretical chemical calculations³ and confirmed by structural and optical characterizations has shown that the usage of easily delocalized five-membered heteroaromatic rings (usually thiophene, furan, thiazole and imidazole) instead of benzene ring results in an enhanced molecular nonlinear response as quantified through the first molecular hyperpolarizability β .

Although a large variety of donor, acceptor and spacer groups have been used for the design of NLO chromophores, the use of the pyrrole heterocycle as conjugated bridge and/or as a strong donor moiety has rarely appeared in the NLO literature before 2005^{3a-c,4} probably due to the difficulty of their synthesis. Even rarer are examples of donor-acceptor pyrrole derivatives specifically designed for second-order NLO applications^{3a-b,4a,4c}

Initial work developed in our research group, concerning push-pull functionalized thienylpyrroles,⁵ paved the way for several authors to synthesize and evaluate the first hyperpolarizability β for several chromophores bearing pyrrole as π -bridge or as auxiliary donating group.⁶

Recently, in continuation of our work, we have designed, synthesized and characterized, several series of donor-acceptor substituted 1-alkyl(aryl)-2-thienylpyrroles as donor moieties and/ π -bridge functionalized with different acceptor groups (benzothiazolyl, benzimidazolyl, aryl diazene and thiazolyldiazene). Evaluation of the electrochemical and optical (linear and nonlinear) properties of these novel donor-acceptor systems revealed that they could be used as potential candidates for second-order NLO and photochromic applications.⁷ Furthermore, our experimental and theoretical results concerning the auxiliary donor/acceptor effect of electron rich and electron deficient heterocycles on push-pull thienylpyrrole π -conjugated systems have shown that the position of the acceptor groups such as dicyanovinyl or electron-deficient heterocycles, *e.g.* (benzo)thiazole or benzimidazole on the thienylpyrrolyl system can have a clear influence on the electronic and optical properties of these heterocyclic chromophores.

We were therefore motivated to extend these studies and explore the potential of two new series of push-pull 1-(4-(thiophen-2-yl)phenyl)-1*H*-pyrroles **3-5** bearing pyrrole as donor group and dicyanovinyl, tricyanovinyl and thiobarbituric acid as acceptor moieties linked to the arylthiophene spacer or to the pyrrole ring.

The aim of this work is to demonstrate that combined tuning of optical and electrochemical properties of donor-acceptor thiophen-2-yl-phenyl-pyrroles **3-5** can be achieved by functionalization of these systems with acceptor groups linked to the pyrrole ring (**4**) or to arylthiophene bridge (**3** and **5**). Consequently, two series of structurally related chromophores have been designed and the influence of the different position of the acceptor groups on 1-(4-(thiophen-2-yl)phenyl)-1*H*-pyrroles **4-5** was studied by combined experimental studies of the electronic, linear and nonlinear optical properties of these heterocyclic systems.

Despite the large number of donor-acceptor heterocyclic systems showing NLO properties reported in the literature, the present concept of combining the donor properties of pyrrole heterocycle linked to an arylthiophene bridge functionalized with strong acceptor groups has not, to the best of our knowledge, been previously communicated in the literature.

2. Results and discussion

2.1. Synthesis

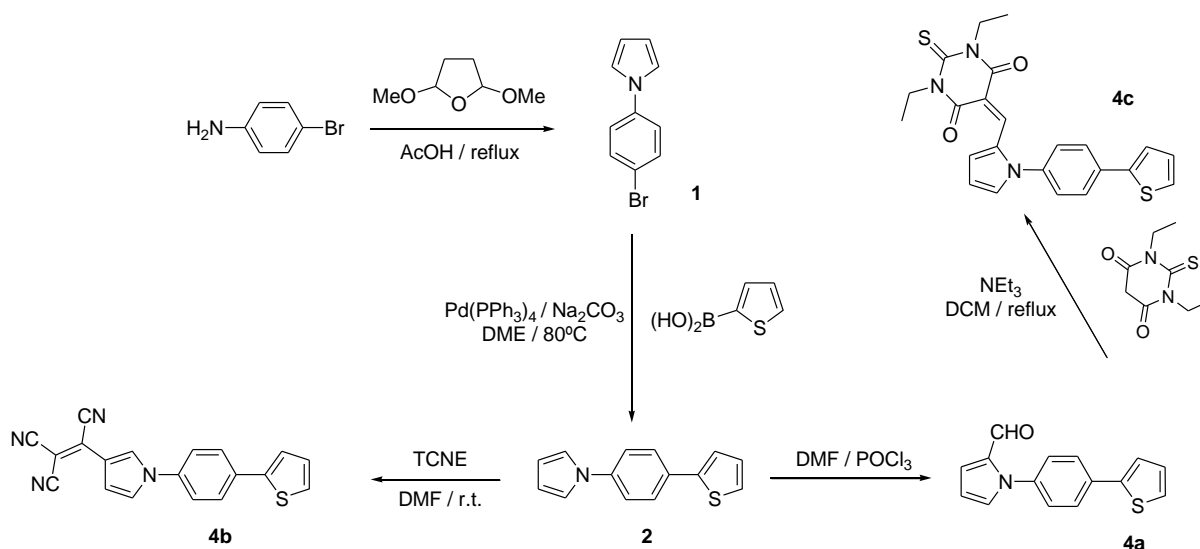
During the past years we have investigated the reactivity of thienylpyrrole systems. Electrophilic substitution reactions of thienylpyrroles were found to be very selective. The reactivity of these systems has been demonstrated with the use of electrophilic reactions (Vilsmeier formylation, tricyanovinilation, azo coupling) producing derivatives with the electrophile substituted primarily on the pyrrole ring.^{5,7d-e,8}

In order to prepare two series of 1-(4-(thiophen-2-yl)phenyl)-1*H*-pyrroles **2-5** functionalized selectively on the thiophene or on the pyrrole heterocycles different synthetic methodologies were applied (Schemes 1-2). Having in mind our earlier results^{5a-b,8} we decided to study the reactivity of the 1-(4-(thiophen-2-yl)phenyl)-1*H*-pyrrole **2** through electrophilic substitution aiming for the preparation of pyrrole derivatives functionalized selectively on the pyrrole heterocycle. In first place, the 4-bromophenylpyrrole precursor **1** (Ref. 9) was prepared through Paal-Knorr reaction from 2,5-dimethoxy-tetrahydrofuran and 4-bromoaniline in high yield (93%). Suzuki cross-coupling reactions of **1** with thiophen-2-yl boronic acid or 5-formylthiophen-2-yl boronic acid gave respectively compounds **2** and **3** in 32 and 61% yields. Compound **2** was used as precursor for the reactivity studies with several electrophiles. Therefore, Vilsmeier formylation of compound **2**, with DMF/POCl₃, proceeded selectively in position 2 of the pyrrole ring to form the corresponding formyl-pyrrole **4a** in 59% yield. On the other hand, tricyanovinilation reaction of **2** with TCNE in DMF using a similar previously reported procedure^{5b} gave compound **4b** bearing the tetracyanovinyl group on position 3 of the pyrrole ring in 43% yield. A possible explanation for the different regioselectivity observed for compound **2** with TCNE could be probably due to the possible steric influence of the bulky tricyanovinylethylene as well as their pre-coordination to the substrate.

Additionally the thiobarbituric derivative **4c** functionalized on the pyrrole ring was prepared through Knoevenagel reaction of aldehyde **4a** with 1,3-diethyl-2-thiobarbituric in 39% yield (Scheme 1).

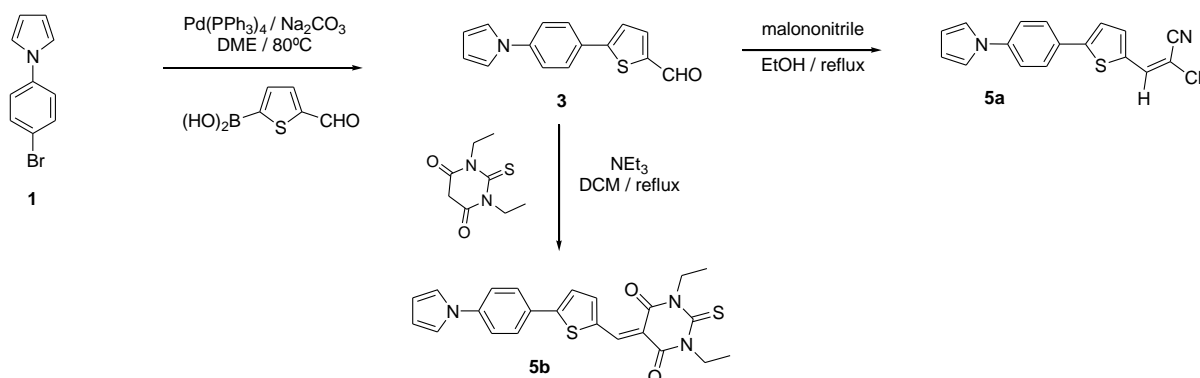
The structures of pyrroles **4a-c** were unambiguously confirmed by their analytical and spectral data. The ¹H NMR spectra of compounds **4a** and **4c** exhibit two sets of doublets and an apparent triplet due to protons 4, 3 and 5 respectively. In the case of compounds **4a** and **4c** functionalized with the acceptor groups on the 2-position of the pyrrole ring the signal with a higher chemical shift is a doublet of doublets attributed to 3-H with coupling constants in the

range of 3.3-3.6 Hz and 1.2-1.5 Hz. Protons 4 in compounds **4a** and **4c** appear also as doublet of doublets with coupling constants in the range of 3.3-3.6 Hz and 2.7-2.8 Hz. On the other hand, for compound **4b** the signal with a higher chemical shift appears as an apparent triplet with a coupling constant of 1.5 Hz which was attributed to 2-H.



Scheme 1. Synthesis of pyrroles **2** and **4a-c**.

Knovenagel condensation of precursor **3** with malononitrile and 1,3-diethyl-2-thiobarbituric gave compounds **5a-b** selectively functionalized with the acceptor groups on the thiophene ring in 43 and 65% yields respectively (Scheme 2).



Scheme 2. Synthesis of 1-(4-(thiophen-2-yl)phenyl)-1H-pyrroles **3** and **5a-b**.

Derivatives **2** and **5** in which the pyrrole ring is functionalized only in position 1 showed two ^1H NMR signals at about 6.38-6.41 and 7.12-7.17 ppm. Both signals appear as multiplets. These signals were attributed respectively, to protons 3 and 4 and 2 and 5 in the pyrrole moiety. In all of the ^1H NMR spectra of derivatives **3** and **5a-b** two doublets at about 7.42-7.56 and 7.76-7.87 ppm with coupling constants of about 3.9-4.2 Hz were detected. These signals were attributed respectively, to the 4 and 3-H protons of the thiophene moiety.

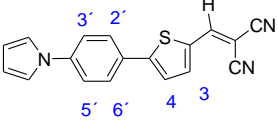
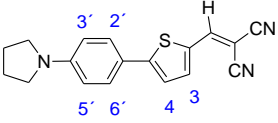
2.2. Electronic structure analysis

The structures and charge transfer transitions of the pyrrole derivatives were first analyzed by ^1H NMR spectroscopy and cyclic voltammetry.

The ^1H NMR chemical shifts reflect a charge separation in the ground state, consequently the analysis of these data in donor-acceptor compounds such as pyrroles **4-5** bearing dicyanovinyl, tricyanovinyl and thiobarbituric acid moieties also confirms their push-pull character with a significant intramolecular charge transfer (ICT) from the donor pyrrole heterocycle to the acceptor groups and a high polarizability of the whole donor-acceptor derivatives. This interpretation is supported by the observation that the chemical shifts of the protons in compounds **5a-b** bearing stronger acceptor groups on the arylthiophene spacer, exhibit signals that are downfield relative to the unsubstituted derivative **2** indicating CT from the donor to the acceptor group. On the other hand, stronger acceptor groups substituted on position 2 or 3 of the pyrrole ring on series of compounds **4** also lead to upfield signals for all protons thus again demonstrating the ease of electron communication within the whole heterocyclic system.

At this stage, a comparison can also be made between the ^1H NMR data of the new pyrrole **5a** with 2-dicyanovinyl-5-(4-pyrrolidinophenyl)thiophene **6**,¹⁰ recently reported by us (Table 1). The electronic nature of the donor group, *N,N*-dialkylamino for **6** or heteroaromatic for **5a** had a clear influence on the ^1H NMR data of these compounds. Compound **6** bearing a pyrrolidino moiety as donor group exhibits signals that are shifted upfield relative to the corresponding pyrrole derivative **5a** indicating the weaker donor ability of the pyrrole heterocycle when compared to a *N,N*-dialkylamino group. The electronic data obtained can be explained by realizing that the pyrrole electron pair is involved in the aromatic system and, thus, not available for delocalization to the acceptor dicyanovinyl group.

Table 1. Chemical shifts of protons of the arylthiophene derivatives **5a** and **6**¹⁰ in deuterated chloroform at 400 MHz, with chemical shift values in ppm.

Comp.	4-H	3-H	3'-H + 5'-H	2'-H + 6'-H
<p>5a</p> 	7.45	7.80	7.48	7.75
<p>6</p> 	7.28	7.63	6.64	7.60

We used cyclic voltammetry to investigate the redox behavior of compounds **2-5** and obtain their HOMO and lowest occupied molecular orbital (LUMO) energy levels. The redox properties of compounds were measured using 0.1 mol dm⁻³ DMF/TBABF₄ solutions (Table 2). Compounds **2-5** show an irreversible oxidation process associated with the oxidation of the pyrrole group. The oxidation potentials are influenced by the acceptor group substituted on the pyrrole or on the thiophene ring. Therefore, derivatives **3-5** functionalized with strong acceptor groups exhibit an anodic shift compared to the unsubstituted precursor **2**. For example, in their reduction traces the cyclic voltammetry of compound **2** exhibit two quasi reversible one-electron reduction processes at -2,23 e -2,55 V. On the other hand compound **5a** showed reduction potentials at -1.40 and -2.00 V. Derivatives bearing tricyanovinyl (**4b**), dicyanovinyl (**5a**) or thiobarbituric acid group (**5b**) have a different electrochemical behavior. As an example, Figure 1 shows the cyclic voltammetry waves recorded for compounds **4b** and **5a**.

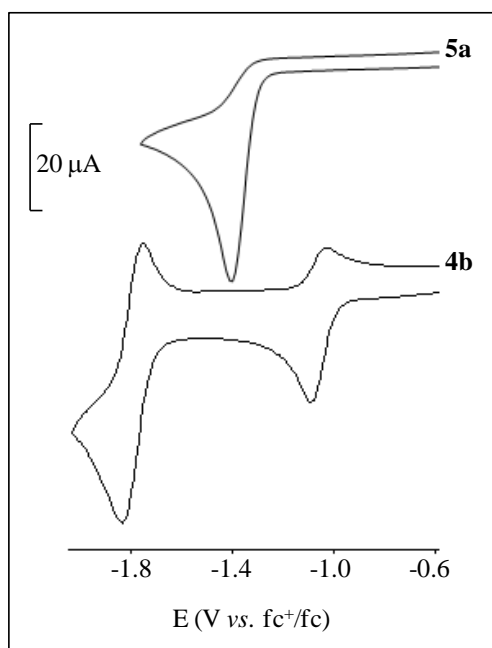


Figure 1. Cyclic voltammograms of compounds **4b** and **5a** (1.0×10^{-3} mol dm $^{-3}$) in DMF, 0.1 mol dm $^{-3}$ [NBu $_4$][BF $_4$] at a vitreous carbon electrode, scan rate 0.1 V s $^{-1}$.

The electrochemical response of the tricyanovinyl compound **4b** consists of stable cathodic processes. The first reduction process near -1.10 V is attributed to the tricyanovinyl group due to its strongest electron withdrawing nature. The first sight of the reduction at -1.10 V can be related to the geminal terminal (CN) $_2$ groups, whereas the second reduction apparently involves mainly the cross-conjugated CN group.¹¹

For compounds **5a-b**, we observe that the first reduction process is irreversible (Figure 1). In these compounds, after the reduction, negative charges in the anionic species are mainly concentrated in the vicinity of the electron withdrawing moieties. For example, in the vinyl C(H)-atom linked the dicyano group, for **5a**, or to other acceptor groups such as in compound **5b**. Therefore those anion radicals might react between them forming dimer molecules by generation of new C-C bonds. Thus the difference in the reduction behavior for these vinylic derivatives could be attributed to the presence of a quite labile hydrogen atom.^{5c,11-12}

Comparison of compound **4c** and **5b** bearing a thiobarbituric acid moiety on the pyrrole or on the thiophene moiety, respectively showed that the functionalization of the thiophene ring by the acceptor group results in a larger shift to less reduction potentials (*e.g.* $^1E_{pc} = -1.29$ V for **4c** and $^1E_{pc} = -1.24$ V for **5b**).

At this moment another comparison can also be made between dicyanovinyl derivatives **5a** and **6**.¹⁰ The substitution of a pyrrolidino donor group (**6**) by the pyrrole ring (**5a**) results in a decrease of the reduction potentials (*e.g.* $E_{pc} = -1.40$ V for **5a** and $E_{pc} = -1.50$ V for **6**) that could be due to the stronger electron-donating ability of pyrrolidino group compared to the pyrrole heterocycle. These results are in agreement with the previous ¹H NMR analysis that showed increased electron densities for compound **6** compared to **5a**.

The HOMO and LUMO energies of all compounds were calculated according to the energy level of the ferrocene reference (4.8 eV below vacuum level)¹³⁻¹⁴ Accordingly, the HOMO energy levels of **2-5** were between -5.68 eV and -5.78 eV, showing the variations resulting from the presence of different electron-withdrawing substituents on the pyrrole or on the thiophene heterocycles. The LUMO energy levels of **2-5** were all located between -2.57 and 3.70 eV thus, the energy of this orbital is strongly influenced by the presence of electron withdrawing groups in the system. In addition, the electrochemical bandgaps, estimated from the difference between the onset potentials for oxidation and reduction, were in the range 2.03–3.13 eV. The efficient donor-acceptor conjugation leads to a lowering of the HOMO and the LUMO levels in **3** and **5a-b**, revealing a more efficient coupling between the 1-(4-(thiophen-2-yl)phenyl)-1*H*-pyrrole system and the formyl, dicyanovinyl and thiobarbituric acceptor groups.

The analysis of the electrochemical data for compounds **2-5** showed that the functionalization of compound **2** with acceptor groups leads to two series of push-pull chromophores **4** and **5** and in both cases the electronic acceptor strength has a strong influence on the electronic delocalization of the π -conjugated systems. Moreover, as expected the stronger acceptor substituents leads to smaller band gaps values.

Table 2. Electrochemical data for compounds **2-5**.

Comp.	Reduction ^a				Oxidation ^a		HOMO ^c (eV)	LUMO ^c (eV)	Band gap ^d (eV)	
	⁻¹ E _{pc} (V)	ΔE ^b (mV)	⁻² E _{pc} (V)	ΔE ^b (mV)	⁻³ E _{pc} (V)	ΔE ^b (mV)				E _{pa} (V)
2	2.23	180	2.55	220	—	—	0.88	-5.68	-2.57	3.13
3	2.10	130	2.60	—	—	—	0.91	-5.71	-2.70	3.01
4a	2.15	63	2.56	—	—	—	0.91	-5.71	-2.65	3.06
4b	1.10	60	1.84	70	2.90	190	0.93	-5.73	-3.70	2.03
4c	1.29	72	2.21	—	—	—	0.95	-5.75	-3.51	2.24
5a	1.40	—	2.00	—	—	—	0.92	-5.72	-3.40	2.32
5b	1.24	—	1.94	70	—	—	0.98	-5.78	-3.56	2.22

^a Measurements made in dry DMF containing 1.0 mM in each compounds and 0.10 M [NBu₄][BF₄] as base electrolyte at a carbon working electrode with a scan rate of 0.1 V s⁻¹. All E values are quoted in volts vs the ferrocenium/ferrocene -couple. E_{pc} and E_{pa} correspond to the cathodic and anodic peak potentials, respectively.

$$^b \Delta E = |E_{\text{red}} - E_{\text{ox}}|.$$

^c E_{HOMO} and E_{LUMO} were calculated according to the energy level of the ferrocene reference 4.80 eV below vacuum level. E_{HOMO} = -(4.80 + E_{pa}) (eV) and E_{LUMO} = -(¹E_{pc} + 4.80) (eV).

^d Band gap calculated from the difference between E_{LUMO} and E_{HOMO}.¹⁰

2.3. Optical properties

Pyrrole derivatives **2-5** showed good solubility in common polar and non-polar organic solvents such as dioxane, diethyl ether, ethanol, DMF and DMSO. The extinction coefficients (ϵ) and the wavelength maxima λ_{max} of compounds **2-5** in several solvents, are summarized in Table 3 and were compared with the π^* values for each solvent, as determined by Kamlet and Taft.¹⁵ All chromophores exhibit broad and intense CT absorptions in the visible region from 306 nm to 465 nm in dioxane solutions. The position of this band was strongly influenced by the electronic nature of the acceptor moiety and also by the position of substitution of this group in the π -bridge (on the pyrrole or on the thiophene heterocycle). Therefore, the absorption maxima (λ_{max}) of pyrrole-based chromophores **4a-c**, in dioxane are located at the range of 308 to 433 nm, on the other hand compounds **3** and **5a-b** bearing the acceptor group on the thiophene moiety exhibit absorption maxima (λ_{max}) located at the range of 349 to 465 nm probably due to more extensive electron delocalization. As observed earlier for other pyrrole push-pull systems, a bathochromic shift in the UV-Vis. spectra is observed when stronger acceptor groups are linked to the heterocyclic system.^{5,7a-b, 7d-e} For example, the substitution of a hydrogen for a thiobarbituric acid moiety leads to a red shift of 127 nm from 306 nm (**2**) to 433 nm (**4c**), furthermore a larger red-shifted λ_{max} (159 nm) was obtained for derivative **5b** bearing the acceptor group on the thiophene ring when compared with the same compound **2**.

Within the two series of compounds **4a**, **4c** and **3** and **5a-b** the CT bands moves to lower energies as the electron accepting ability of the acceptor moiety increases, in the order CHO < dicyanovinyl < thiobarbituric acid (Figure 2). These results agree with the band gap calculations based on the redox properties (Table 2), which show decreased band gaps for derivatives **4b**, **4c** and **5a-b** functionalized with strong electron acceptor groups.

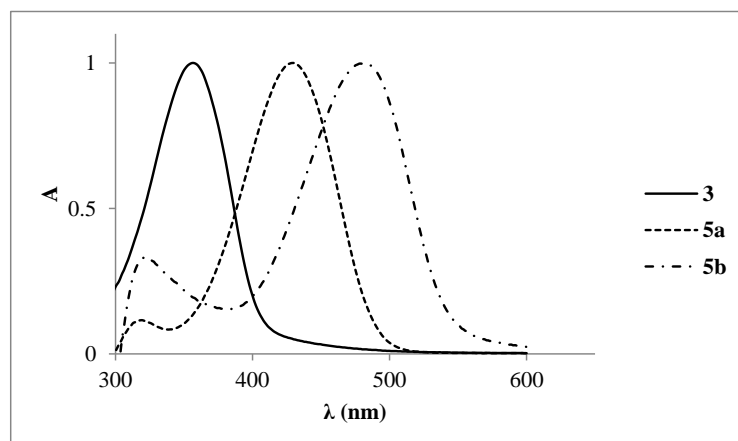


Figure 2. Comparative absorption spectra of **3** and **5a-b** in dioxane at room temperature.

Compounds **2-5** exhibit positive solvatochromism ($\Delta\nu_{\max} = 529\text{-}1019\text{ cm}^{-1}$) with respect to their CT absorption band, that is, the position of the absorption maximum shifts to longer wavelengths as the polarity of the solvent increases due to a greater stabilization of the excited state relative to the ground state with increasing polarity of the solvent (Table 3).

Table 3. Solvatochromic data [λ_{\max} (nm) and $\Delta\nu_{\max}$ (cm^{-1}) of the charge-transfer band] for pyrroles **2-5** in 5 solvents with π^* values by Kamlet and Taft.¹⁵

Comp.	Diethyl ether (0.54) λ_{\max} (nm)	1,4-Dioxane (0.55) λ_{\max} (nm)	Chloroform (0.76) λ_{\max} (nm)	DMSO (1.00) λ_{\max} (nm)	$\Delta\nu_{\max}^a$ (cm^{-1})	ε (Dioxane) ($\text{M}^{-1}\text{cm}^{-1}$)
2	305	306	307	310	529	39,720
3	345	349	350	357	974	32,740
4a	306	308	309	313	731	28,420
4b	400	403	413	417	1019	31,990
4c	430	433	441	445	784	45,790
5a	415	416	425	430	841	39,180
5b	461	465	478	479	815	45,790

$$^a \Delta\nu_{\max} = \nu_{\max}(\text{diethyl ether}) - \nu_{\max}(\text{DMSO}) / \text{cm}^{-1}$$

The molecular first hyperpolarizabilities β of compounds **2-5** were measured by hyper-Rayleigh scattering (HRS) method¹⁶ at a fundamental wavelength of 1064 nm of a laser beam. Dioxane was used as the solvent, and the β values were measured against a reference solution of *p*-nitroaniline (*pNA*)¹⁷ in order to obtain quantitative values, while care was taken to properly account for possible fluorescence of the dyes (see experimental section for more details). The static hyperpolarisability β_0 values¹⁸ were calculated using a very simple two-level model neglecting damping. They are therefore only indicative and should be treated with caution (Table 4).

Table 4. UV-vis absorptions, β and β_0 values and T_d data for pyrrole derivatives **2-5**^a and thienylpyrrole **7**.^{5c}

Compounds	Yield (%)	λ_{\max} (nm)	β^b (conv T) (10^{-30} esu)	β_0^c (conv T) (10^{-30} esu)	T_d^d ($^{\circ}$ C)
2	32	309	* ¹	* ¹	194
3	41	349	66	34	199
4a	59	308	* ¹	* ¹	---
4b	43	403	225	82	288
4c	39	433	290	82	---
5a	65	416	2200	725	277
5b	65	465	2480	474	270
6 ¹⁰	---	503	* ²	* ²	---
7 ^{5c}	---	450	860	200	---
<i>pNA</i>	---	352	40	20	---

^a Experimental first hyperpolarizabilities β and spectroscopic data measured in dioxane solutions.

^b All compounds are transparent at the 1064 nm fundamental wavelength.

^c Data corrected for resonance enhancement at 532 nm using the two-level model with $\beta_0 = \beta [1 - (\lambda_{\max}/1064)^2][1 - (\lambda_{\max}/532)^2]$; damping factors not included 1064 nm.¹⁸

^d Decomposition temperature (T_d) measured at a heating rate of 20 $^{\circ}$ C min⁻¹ under a nitrogen atmosphere, obtained by thermogravimetric analysis (TGA).

*¹ Due to a combination of low signals and fluorescence it was not possible to measure the β value.

*² Due to fluorescence it was not possible to measure the β value.

It was not possible to measure the β value for compounds **2** and **4a** due to a combination of low absolute signals and fluorescence contamination at 532 nm. From Table 4 it is clear that the progression of acceptor substituents from formyl, dicyanovinyl and thiobarbituric acid results in enhanced nonlinearities as anticipated from the acceptor strengths of the substituents. As expected compounds **5b** and **4c** exhibit the highest β values.

Moreover β values for compounds having the acceptor groups on the thiophene ring are 55-62 times greater than *p*NA, whereas the respective β_0 are 24-36 times greater. On the other hand compounds **4** functionalized with acceptor moieties on the pyrrole ring exhibit smaller β values when compared to the corresponding compounds **5**. For example, **5b** exhibits a β value of 2480×10^{-30} esu while for **4c** the β value is 8 times smaller (290×10^{-30} esu). The results obtained show that the location of the acceptor group on the pyrrole or on the thiophene ring alone can dramatically alter the overall molecular nonlinearity of the system. Pyrrole, being the most electron-rich five-member heteroaromatic ring, counteracts the electron withdrawing effect of the acceptor groups, resulting in a decrease in β . These findings are in accordance with our recent work related to push-pull thienylpyrroles^{5c, 7a-b} where it was concluded that the increase or decrease of the molecular nonlinear activity in these systems depends on the electronic nature of the heterocycles as well as the location of the acceptor groups in these heterocyclic systems.

The thermal stability of chromophores **2-5** was characterized by thermogravimetric analysis (Figure 3). The samples had moderate to high decomposition temperatures ($T_d = 199 - 288$ °C), measured at a heating rate of 20 °C min^{-1} under a nitrogen atmosphere. Experimental results indicate that good nonlinearity–thermal stability is well balanced for these chromophores, specially for compounds **5a-b** which possess a β values at the range of $2200-2480 \times 10^{-30}$ esu and high decomposition temperatures ($T_d = 270 - 277$ °C).

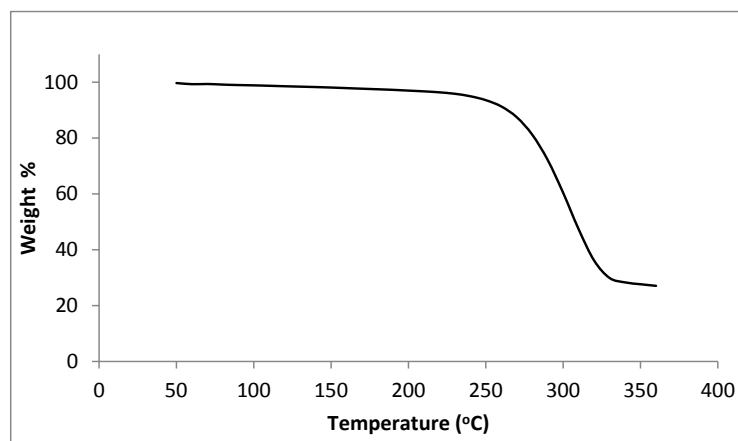


Figure 3. Thermal analysis data for compound **5a** through TGA recorded under a nitrogen atmosphere, measured at a heating rate of 20 °C min⁻¹.

3. Conclusions

In conclusion we have developed two new series of push-pull pyrrole NLO-heterocyclic systems functionalized with acceptor groups on the pyrrole (**4a-c**) or on the thiophene heterocycles (**3** and **5a-b**).

Reactivity studies of compound **2** in the presence of different electrophiles (Vilsmeier reagent or with tetracyanoethylene) showed that the strongest and bulky electrophile react in position 3 of the pyrrole heterocycle to produce compound **4b** while the Vilsmeier reagent give rise to the derivative **4a** functionalized on position 2 of the pyrrole ring.

By varying the position of linkage of the acceptor moiety the electrochemical properties of compounds **4-5** as well as the linear and nonlinear optical properties of these push-pull π -conjugated systems can be readily tuned.

Electrochemical studies and characterization of the optical (linear and nonlinear), and thermal properties for compounds **2-5** indicate that, good nonlinearity-thermal stability is well balanced for chromophores **5a-b**, making them good candidates for several optoelectronic applications such as solvatochromic probes and second order nonlinear optical materials.

4. Experimental

4.1. Materials

Thiophen-2-yl-boronic acid, 5-formyl-thiophen-2-yl-boronic acid, 4-bromoaniline and 2,5-dimethoxytetrahydrofuran used as precursors for the synthesis of pyrroles **1-5** were purchased from Aldrich and Fluka and used as received. TLC analyses were carried out on 0.25 mm thick precoated silica plates (Merck Fertigplatten Kieselgel 60F₂₅₄) and spots were visualised under UV light. Chromatography on silica gel was carried out on Merck Kieselgel (230-240 mesh).

4.2. Synthesis

Compound **1** was synthesized using the experimental procedure described earlier.⁹

1-(4-Bromophenyl)-1H-pyrrole 1. Pale brown solid (242 mg, 93%). ¹H NMR (CDCl₃) δ 6.36-6.38 (m, 2H, 3-H and 4-H), 7.05-7.07 (m, 2H, 2-H and 5-H), 7.28 (d, 2H, *J*=8.6 Hz 2'-H and 6'-H), 7.55 (d, 2H, *J*=8.6 Hz, 3'-H and 5'-H).

General procedure for the synthesis of pyrroles **2** and **3** through Suzuki cross coupling reaction¹⁹

1-(4-Bromophenyl)-1H-pyrrole **1** (0.90 mmol, 200 mg) was coupled to thiophen-2-yl-boronic acid or 5-formyl-thiophen-2-yl-boronic acid (1.12 mmol) in a mixture of DME (10 ml), aqueous 2 M Na₂CO₃ (1 ml) and Pd(PPh₃)₄ (3 mol %) at 80 °C under nitrogen. The reaction was monitored by TLC, which determined the reaction time (24-32 h). After cooling, the mixture was extracted with chloroform (3×20 ml) and a saturated solution of NaCl were added (20 ml) and the phases were separated. The organic phase was washed with water (3×10 ml) and with a solution of NaOH (10%) (1×10 ml). The organic phase obtained was dried (MgSO₄), filtered, and the solvent removed to give a crude mixture. The crude product was purified through a silica gel chromatography column using mixtures of chloroform and light petroleum of increasing polarity to afford the coupled products **2** or **3**. Recrystallization from light petroleum/ether gave the pure compounds.

1-(4-(Thiophen-2-yl)phenyl)-1H-pyrrole 2. Pale beige solid (65 mg, 32%). Mp 215-216 °C. ¹H NMR (CDCl₃) δ 6.38-6.39 (m, 2H, 3-H and 4-H), 7.11 (dd, 1H, *J*=5.2 and 3.6 Hz, 4''-H), 7.12-7.14 (m, 2H, 2- and 5-H), 7.29-7.33 (m, 2H, 3''-H and 5''-H), 7.42 (d, 2H, *J*=9.0 Hz, 2'-H and 6'-H), 7.68 (d, 2H, *J*=9.0 Hz, 3'-H and 5'-H). ¹³C NMR (CDCl₃) δ 110.6, 119.2, 120.7, 123.1, 124.9, 127.0, 128.1, 131.9, 139.9, 143.4. λ_{max} (Dioxane)/nm 306 (ε/dm³ mol⁻¹ cm⁻¹)

39,720). IR (CHCl₃): ν 3139, 1886, 1605, 1538, 1509, 1333, 1252, 1133, 1079, 854, 819, 703 cm⁻¹. MS (ESI) m/z (%) = 226 ([M+H]⁺, 100), 225 (64), 209 (38), 203 (37). HMRS: m/z (ESI) for C₁₄H₁₁NS; calcd 226.0685; found: 226.0684. Anal. Calcd for C₁₄H₁₁NS: C, 74.63; H, 4.92; N, 6.22; S, 14.23. Found: C, 74.85; H, 5.30; N, 6.55; S, 14.60.

5-(4-(1H-Pyrrol-1-yl)phenyl)thiophene-2-carbaldehyde 3. Orange solid (210 mg, 61%). Mp. 205-206°C. ¹H NMR (CDCl₃) δ 6.39-6.41 (m, 2H, 3''-H and 4''-H), 7.14-7.16 (m, 2H, 2''- and 5''-H), 7.42 (d, 1H, $J=4.2$ Hz, 4-H), 7.47 (d, 2H, $J=8.9$ Hz, 3'-H and 5'-H), 7.74 (d, 2H, $J=8.9$ Hz, 2'-H and 6'-H), 7.76 (d, 1H, $J=4.2$ Hz, 3-H), 9.91 (s, 1H, CHO). ¹³C NMR (CDCl₃) δ 111.1, 119.1, 120.6, 123.9, 127.7, 130.2, 137.5, 141.3, 142.4, 153.2, 182.7. λ_{\max} (Dioxane)/nm 349 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 32,740). IR (CHCl₃): ν 3442, 3148, 2945, 1648, 1605, 1536, 1480, 1449, 1330, 1233, 1001, 919, 826, 805, 730 cm⁻¹. MS (ESI) m/z (%) = 254 ([M+H]⁺, 100). HMRS: m/z (ESI) for C₁₅H₁₁NOS; calcd 254.0634; found: 254.0630. Anal. Calcd for C₁₅H₁₁NOS: C, 71.12; H, 4.38; N, 5.53; S, 12.66. Found: C, 71.29; H, 4.57; N, 5.85; S, 13.00.

Synthesis of compound **4a**

POCl₃ (0.44 mmol) was added to DMF (0.44 mmol) at 0 °C and the mixture was stirred for 15 min. at 0 °C. After this time pyrrole 2 (0.44 mmol) dissolved in DMF (2 ml) were added dropwise with stirring. The reaction mixture was then heated 4 h at 60 °C. The solution was then poured slowly into 10 ml saturated sodium acetate aqueous solution and stirred 30 min.. The organic layer was diluted with ether (25 ml), washed with saturated NaHCO₃ aqueous solution (2×25 ml), and dried with anhydrous MgSO₄. Evaporation of the organic extract under reduced pressure gave the crude aldehyde **4a** which was purified through a silica gel chromatography column using mixtures of chloroform and light petroleum of increasing polarity to afford aldehyde **4a**. Recrystallization from light petroleum/ether gave the pure compound.

1-(4-(Thiophen-2-yl)phenyl-1H-pyrrole-2-carbaldehyde 4a. Pale beige solid (66 mg, 59%). Mp 215-216 °C. ¹H NMR (CDCl₃) δ 6.44 (dd, 1H, $J=3.6$ and 2.8 Hz, 4-H), 7.11-7.13 (m, 2H, 5-H and 4''-H), 7.19 (dd, 1H, $J=3.6$ and 1.2 Hz, 3-H), 7.34 (dd, 1H, $J=5.2$ and 1.2 Hz, 5''-H), 7.37-7.39 (m, 3H, 3'-H, 5'-H and 3''-H), 7.70 (d, 2H, $J=8.6$ Hz, 2'-H and 6'-H), 9.62 (s, 1H, CHO). ¹³C NMR (CDCl₃) δ 111.0, 122.7, 123.8, 125.5, 126.4, 128.2, 131.1, 132.4, 134.4, 137.8, 143.0, 179.0, 192.5. λ_{\max} (Dioxane)/nm 308 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 28,420). IR (CHCl₃): ν

3123, 1766, 1673, 1660, 1533, 1523, 1318, 1303, 1280, 1261, 1238, 1210, 1195, 1091, 1036 cm^{-1} . MS (ESI) m/z (%) = 254 ($[\text{M}+\text{H}]^+$, 100). HMRS: m/z (ESI) for $\text{C}_{15}\text{H}_{12}\text{NOS}$; calcd 254.0634; found: 254.0632. Anal. Calcd for $\text{C}_{15}\text{H}_{11}\text{NOS}$: C, 71.12; H, 4.38; N, 5.53; S, 12.66. Found: C, 71.29; H, 4.57; N, 5.85; S, 12.88.

Synthesis of compound **4b**

A solution of compound **2** (0.22 mmol, 50 mg) in DMF (1.5 ml) was cooled at 0°C and then tetracyanoethylene (0.44 mmol, 57 mg) was added slowly. The reaction mixture was stirred at room temperature for about 2 hours. After this time the mixture was poured into ice/water (5 ml) and the organic layer was diluted in chloroform (10 ml), washed with water (2×20 ml), and dried with anhydrous MgSO_4 . Evaporation of the solvent under reduced pressure gave the crude product, which was recrystallized from chloroform giving the pure product **4b**.

1-(1-(4-(Thiophen-2-yl)phenyl)-1H-pyrrol-2-yl)ethene-1,2,2-tricarbonitrile 4b. Dark orange solid (21 mg, 43%). Mp $257\text{--}259^\circ\text{C}$. ^1H NMR (Acetone- d_6) δ 7.21(dd, 1H, $J=5.1$ and 3.9 Hz, 4''-H), 7.29 (dd, 1H, $J=2.7$ and 2.1 Hz, 4-H), 7.58 (dd, 1H, $J=5.1$ Hz and 1.2 Hz, 5''-H), 7.62 (dd, 1H, $J=3.0$ Hz and 1.2 Hz, 3''-H), 7.76 (dd, 1H, $J=2.7$ and 2.1 Hz, 5-H), 7.86 (2H, d, $J=9.0$ Hz 3'-H and 5'-H), 7.92 (2H, d, $J=9.0$ Hz 2'-H and 6'-H), 8.38 (t, 1H, $J=1.8$ Hz, 2-H). ^{13}C NMR (CDCl_3) δ 81.9, 109.7, 113.2, 113.3, 114.0, 118.9, 121.5), 124.7, 125.7, 126.6, 128.7, 129.1, 133.5, 133.6, 136.7, 141.9. λ_{max} (Dioxane)/nm 403 ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ 31,990). IR (Nujol): ν 3570, 2246, 2210, 1653, 1610, 1538, 1506, 1329, 1296, 1266, 1249, 1209, 1075, 978, 930, 841, 828 cm^{-1} . MS (EI) m/z (%) = 326 ($[\text{M}]^+$, 100), 301 (27), 300 (32), 185 (10), 121 (22). HMRS: m/z (EI) for $\text{C}_{19}\text{H}_{10}\text{N}_4\text{S}$; calcd 326.0626; found: 326.0626. Anal. Calcd for $\text{C}_{19}\text{H}_{10}\text{N}_4\text{S}$: C, 69.92; H, 3.09; N, 17.17; S, 9.82. Found: C, 70.02; H, 3.39; N, 17.40; S, 10.05.

Synthesis of compound **4c**

A solution of aldehyde **4a** (0.20 mmol, 50 mg) and 1,3-diethyl-2-thiobarbituric acid (0.26 mmol, 52 mg) and triethylamine (2 drops) in dichloromethane (7 ml) was refluxed for 5 hours. The mixture was poured into water (20 ml) and extracted with chloroform (2×50 ml). The organic layer was dried with anhydrous MgSO_4 and evaporated under reduced pressure to give the crude product which by crystallization with petroleum ether gave the pure product **4c**.

1,3-Diethyl-dihydro-5-((1-(4-thiophen-2-yl)phenyl)-1H-pyrrol-2-yl)methylene)-2-thioxopyrimidine-4,6(1H,5H)-dione 4c. Brown solid (33 mg, 39%). Mp $230\text{--}232^\circ\text{C}$. ^1H NMR

(Acetone- d_6) δ 1.24-1.28 (m, 6H, 2xNCH₂CH₃), 4.50-4.52 (m, 4H, 2xNCH₂CH₃), 6.76 (dd, 1H, $J=3.3$ and 2.7 Hz, 4-H), 7.17 (dd, 1H, $J=4.5$ and 3.6 Hz, 4''-H), 7.58 (d, 2H, $J=8.7$ Hz, 3'-H and 5'-H), 7.60 (dd, 1H, $J=5.1$ Hz and 1.2 Hz, 5''-H), 7.68 (dd, 1H, $J=3.0$ and 1.2 Hz, 3''-H), 7.85 (t_{ap}, 1H, $J=1.8$ Hz, 5-H), 7.98 (d, 2H, $J=8.7$ Hz, 2'-H and 6'-H), 8.32 (s, 1H, C=CH), 8.80 (dd, 1H, $J=3.3$ and 1.5 Hz, 3-H). λ_{\max} (Dioxane)/nm 433 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 45,790). IR (CHCl₃): ν 1691, 1657, 1557, 1282, 1106, 1044, 824, 784 cm⁻¹. MS (ESI) m/z (%) = 436 ([M+H]⁺, 23). HMRS: m/z (ESI) for C₂₃H₂₂N₃O₂S₂; calcd 436.1148; found: 43.1132. Anal. Calcd for C₂₃H₂₂N₃O₂S₂: C, 63.28; H, 5.08; N, 9.62; S, 14.69. Found: C, 63.47; H, 5.22; N, 9.85; S, 14.35.

Synthesis of compound **5a**

To a solution of malononitrile (0.24 mmol, 0.016 g) and aldehyde **3** (0.19 mmol, 0.50 mg) in ethanol (10 ml) was added piperidine (1 drop). The solution was stirred at reflux during 3 hours. After cooled to room temperature the mixture was evaporated to dryness and the organic layer was extracted with chloroform (2 \times 20 ml). and dried over anhydrous MgSO₄. The product was purified through a silica gel column chromatography using mixtures of chloroform and light petroleum of increasing polarity. The fraction containing the purified product were collected and evaporated under vacuum. Recrystallization from light petroleum/ether gave the pure compound.

2-((5-(4-(1H-Pyrrol-1-yl)phenyl)thiophen-2-yl)methylene)malononitrile **5a**. Yellow solid (25 mg, 43%). Mp 221-223°C. ¹H NMR (CDCl₃) δ 6.40-6.41 (m, 2H, 3''-H and 4''-H), 7.15-7.17 (m, 2H, 2''-H and 5''-H), 7.45 (d, 1H, $J=3.9$ Hz, 4-H), 7.48 (d, 2H, $J=9$ Hz, 3'-H and 5'-H), 7.80 (d, 1H, $J=3.9$ Hz, 3-H), 7.78 (d, 2H, $J=9$ Hz, 2'-H and 6'-H), 7.81 (s, 1H, C=CH). ¹³C NMR (CDCl₃) δ 111.4, 113.3, 114.1, 118.9, 120.5, 124.4, 127.9, 129.2, 134.2, 140.0, 141.9, 150.5, 155.4. λ_{\max} (Dioxane)/nm 416 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 39,180). IR (CHCl₃): ν 3179, 3051, 2221, 1606, 1530, 1568, 1494, 1325, 1264, 1245, 1210, 1141, 1069, 945, 919, 832, 817, 807, 606 cm⁻¹. Anal. Calcd. for C₁₈H₁₁N₃S: Found: C, 71.58; H, 3.69; N, 13.72. % CHNS requires: C, 71.74; H, 3.68; N, 13.94.

Synthesis of compound **5b**

A solution of aldehyde **3** (0.20 mmol, 50 mg) and 1,3-diethyl-2-thiobarbituric acid (0.26 mmol, 52 mg) and triethylamine (0.02 mmol) in dichloromethane (5 ml) was refluxed for 4 hours. The mixture was poured into water (20 ml) and extracted with chloroform (2 \times 50 ml).

The organic layer was dried with anhydrous MgSO_4 and evaporated under reduced pressure to give the crude product which by crystallization with hexane we obtain the pure product **5b**.

5-((5-(4-(1H-Pyrrol-1-yl)phenyl)thiophen-2-yl)methylene)-1,3-diethyl-dihydro-2-thioxopyrimidine-4,6(1H,5H)-dione **5b**. Red solid (86 mg, 65%). Mp 280-282 °C. ^1H NMR (CDCl_3) δ 1.26-1.39 (m, 6H, $2 \times \text{NCH}_2\text{CH}_3$), 4.57-4.64 (m, 4H, $2 \times \text{NCH}_2\text{CH}_3$), 6.39-6.41 (m, 2H, 3''-H and 4''-H), 7.16-7.17 (m, 2H, 2''-H and 5''-H), 7.47 (d, 2H, $J=8,0$ Hz, 3'-H and 5'-H), 7.56 (d, 1H, $J=4.0$ Hz, 4-H), 7.87 (d, 2H, $J=8,0$ Hz, 2'-H and 6'-H), 7.89 (d, 1H, $J=4.0$ Hz, 3-H) 8.67 (s, 1H, C=CH). ^{13}C NMR (CDCl_3) δ 12.4, 12.5, 43.2, 43.9, 110.3, 111.3, 118.9, 120.4, 124.6, 128.1, 130.2, 136.7, 141.7, 157.3, 149.6, 159.9, 160.2, 161.0, 178.7. λ_{max} (Dioxane)/nm 465 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 45,790). IR (Nujol): 2350, 1684, 1662, 1606, 1548, 1491, 1413, 1334, 1267, 1247, 1105, 1077, 787 cm^{-1} . MS (ESI) m/z (%) = 436 ($[\text{M}+\text{H}]^+$, 20), 387 (11), 386 (39), 382 (20), 381 (70), 360 (29), 359 (84), 354 (14), 353 (44), 342 (37), 341 (100), 331 (14), 314 (14), 285 (12), 268 (27), 267 (89), 240 (14) and 239 (35). HMRS: m/z (ESI) for $\text{C}_{23}\text{H}_{22}\text{N}_3\text{O}_2\text{S}_2$; calcd 436.1148; found: 43.1155. Anal. Calcd for $\text{C}_{23}\text{H}_{22}\text{N}_3\text{O}_2\text{S}_2$: C, 63.28; H, 5.08; N, 9.62; S, 14.69. Found: C, 63.10; H, 5.30; N, 9.87; S, 14.91.

4.3. Instruments

NMR spectra were obtained on a Varian Unity Plus Spectrometer at an operating frequency of 300 MHz for ^1H NMR and 75.4 MHz for ^{13}C NMR or a Bruker Avance III 400 at an operating frequency of 400 MHz for ^1H NMR and 100.6 MHz for ^{13}C NMR using the solvent peak as internal reference at 25 °C. All chemical shifts are given in ppm using $\delta_{\text{H}} \text{Me}_4\text{Si} = 0$ ppm as reference and J values are given in Hz. Assignments were made by comparison of chemical shifts, peak multiplicities and J values and were supported by spin decoupling-double resonance and bidimensional heteronuclear HMBC and HMQC correlation techniques. IR spectra were determined on a BOMEM MB 104 spectrophotometer using KBr discs. UV-visible absorption spectra (200 – 800 nm) were obtained using a Shimadzu UV/2501PC spectrophotometer. Mass spectrometry analyses were performed at the “C.A.C.T.I. -Unidad de Espectrometria de Masas” at the University of Vigo, Spain. Thermogravimetric analysis of samples was carried out using a TGA instrument model Q500 from TA Instruments, under high purity nitrogen supplied at a constant 50 mL min^{-1} flow rate. All samples were subjected to a 20 $^\circ\text{C min}^{-1}$ heating rate and were characterized between 25 and 500 $^\circ\text{C}$. All melting points were measured on a Gallenkamp melting point apparatus and are uncorrected. Cyclic

voltammetry (CV) was performed using a potentiostat/galvanostat (AUTOLAB /PSTAT 12) with the low current module ECD from ECO-CHEMIE and the data analysis processed by the General Purpose Electrochemical System software package also from ECO-CHEMIE. Three electrode-two compartment cells equipped with vitreous carbon-disc working electrodes, a platinum-wire secondary electrode and a silver-wire pseudo-reference electrode were employed for cyclic voltammetric measurements. The concentration of the compounds were 1 mmol dm⁻³ and 0.1 mol dm⁻³ [NBu₄][BF₄] was used as the supporting electrolyte in dry *N,N*-dimethylformamide solvent. The cyclic voltammetry was conducted usually at 0.1 Vs⁻¹, or at different scan rates (0.02-0.50 Vs⁻¹), for investigation of scan rate influence. The potential is measured with respect to ferrocenium/ferrocene as an internal standard.

4.4. Solvatochromic study

The solvatochromic study was performed using 10⁻⁴ mol dm⁻³ solutions of compounds **2-5** in several solvents at room temperature using a Shimadzu UV/2501PC spectrophotometer.

4.5. Nonlinear optical measurements using the hyper-Rayleigh scattering (HRS) method

Hyper-Rayleigh scattering (HRS) was used to measure the first hyperpolarizability β of response of the molecules studied. The experimental set-up for hyper-Rayleigh measurements employed a q-switched Nd:YAG laser and is similar to the one presented by Clays *et al.*¹⁶ Details of the experimental procedure used have been previously published.¹⁰ We emphasize that particular care was taken to avoid reporting artificially high first hyperpolarizabilities by using a pair of interference filters to estimate and correct for the presence of a possible contamination of the hyper Rayleigh signal by molecular fluorescence near 532 nm. Further cautions include normalizing the hyper-Rayleigh signal at each pulse using the second harmonic signal from a 1 mm quartz plate to compensate for fluctuations in the temporal profile of the laser pulses due to longitudinal mode beating and the filtering of the solutions, using a 0.2 μ m porosity filter, to avoid spurious signals from suspended impurities.

Dioxane was used as a solvent for all measurements. The small hyper-Rayleigh signal that arises from dioxane was taken into account according to the expression

$$I_{2\omega} = G(N_{solvent}\langle\beta_{solvent}^2\rangle + N_{solute}\langle\beta_{solute}^2\rangle)I_{\omega}^2$$

where the factor G is an instrumental factor that takes into account the detection efficiency (including geometrical factors and linear absorption or scattering of the second harmonic light on its way to the detector) and local field corrections. The concentrations of the solutions

under study were chosen so that the corresponding hyper-Rayleigh signals fell well within the dynamic range of detection system. We have assumed that molecules could be treated as linear donor-acceptor chromophores with a first hyperpolarizability tensor dominated by a single longitudinal element, $\beta_{333} = \beta$, associated with the charge transfer axis. In this case the measured HyperRayleigh signal is related to the value of the dominant tensor element through the relation $\beta = \sqrt{\langle \beta_{HRS}^2 \rangle} = \sqrt{\langle \beta_{ZZZ}^2 \rangle + \langle \beta_{XZZ}^2 \rangle}$ where the angle brackets denote an average for the random molecular orientations in the solution. Here we have adopted a laboratory reference frame in which the incident fundamental light propagates along the X axis and was vertically polarized along the Z direction, while no polarization discrimination was carried out in the detection arm which is orientated along the laboratory frame Y axis. To calibrate our system a reference solution of *p*-nitroaniline (*p*NA) dissolved in dioxane at a concentration of 1×10^{-2} mol dm⁻³ (external reference method). Kaatz and Shelton^{20a} have measured the value of β_{333} of *p*NA in dioxane at 1064 nm to be 40×10^{-30} esu using the so-called Taylor convention for the first hyperpolarizability.^{20b} This value includes a correction factor of 1.88 that accounts for the most recent measurement of the CCl₄ hyper-Rayleigh scattering signal which was used as a reference.²¹

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