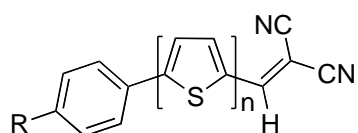# Graphical Abstract

Synthesis and characterization of novel efficient and thermally stable 2-aryl-5-dicyanovinylthiophenes and 5-aryl-5´-dicyanovinyl-2,2´-bithiophenes as potentially promising nonlinear optical (NLO) materials

Cyril Herbivo, Alain Comel, G. Kirsch, A. Maurício C. Fonseca, M. Belsley and M. Manuela M. Raposo[*]

R = H, alkoxy, *N,N*-dialkylamino
n = 1- 2

Synthesis and characterization of novel efficient and thermally stable 2-aryl-5-dicyanovinylthiophenes and 5-aryl-5´-dicyanovinyl-2,2´-bithiophenes as potentially promising nonlinear optical (NLO) materials

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Abstract – Two series of dicyanovinyl-substituted compounds namely 2-aryl-5-dicyanovinyl-thiophenes **4** and 5-aryl-5´-dicyanovinyl-2,2´-bithiophenes **6** were synthesized through Knoevenagel condensation of the corresponding 2-aryl-5-formyl-thiophenes **3** and 5-aryl-5´-formyl-2,2´-bithiophene **5** precursors. On the other hand, precursors **3** were prepared through the Vilsmeier-Haack-Arnold reaction (VHA) starting from inexpensive and easily available precursors such as acetophenones. This method produced the title compounds in higher yields than the recently reported synthesis *via* Suzuki coupling of functionalized aryl boronic acids with 5-bromo-2-formyl-thiophene. Electrochemical studies and characterization of the optical (linear and nonlinear), and thermal properties for compounds **5-6** indicate that, good nonlinearity is complemented by exceptional thermal stability for chromophores **6**, making them potential candidates for several optoelectronic applications such as solvatochromic probes and nonlinear optical materials.

Keywords: Aldehydes, Vilsmeier-Haack-Arnold reaction (VHA), Knoevenagel condensation, Dicyanovinyl-substituted aryl-(bi)thiophenes, Solvatochromic probes, Electrochemisty, Nonlinear optics (NLO), Hyper-Rayleigh scattering (HRS), Thermal stability.

1. Introduction

For the last three decades push-pull substituted heteroaromatic compounds have attracted widespread interest due to their high thermal and chemical stability, exceptional optical properties and good transparency, as well as easy synthesis. Functional oligothiophenes are actually one of the most frequently used π-conjugated materials, in particular as active components in organic electronic devices and molecular electronics [1].

In recent years our research group has reported the synthesis of a large variety of donor-acceptor substituted (oligo)thiophenes through several methods. Experimental and theoretical studies demonstrated that they are strong candidates for potential use in several optoelectronic applications such as: organic semi-conductor materials, solvatochromic and fluorescent probes, nonlinear optical materials and OLEDs [2].

Previously several authors have also reported the synthesis and the characterization of (oligo)thienyl- donor-acceptor chromophores functionalized with the dicyanovinyl moiety as electron acceptor group for nonlinear optical applications [3].

Thiophene derivatives functionalized with the formyl group are versatile building blocks for the synthesis of donor-acceptor substituted π-conjugated systems for several optical applications. Recently, we have reported the synthesis of novel formyl π-conjugated systems (bithiophenes [2a,h], oligothiophenes [2b,h], arylthiophenes [2e,i], thienylpyrroles [4] and arylbithiophenes [5]) through several methods of synthesis such as cross-coupling reactions (Stille [2b], Suzuki [2e,i,5]), metalation followed by quenching with DMF [2a,h], Vilsmeier-Haack formylation [2a] and Vilsmeier-Haack-Arnold reactions [5].

Having in mind our recent work in which we have used formyl heterocyclic systems (bithiophenes, oligothiophenes, and thienylpyrroles) as precursors for the synthesis of dicyanovinyl-derivatives [2a-b,6], for several optoelectronic applications (organic semi-conductors, solvatochromic probes, nonlinear optical materials) we decided to synthesize the new 2-dicyanovinyl-5-arylthiophenes **5** and 5-aryl-5´-dicyanovinyl-2,2´-bithiophenes **6**.

Therefore, compounds **4** and **6** were synthesized and characterized in order to study the influence of the structure modification (*i.e.* the length and the electronic nature of the π-conjugated bridge) on the optical and electrochemical properties of compounds **4** and **6**.

2. Results and discussion

2.1. Synthesis

2.1.1. Synthesis of formyl precursors

Recently we have reported the synthesis of formyl-arylthiophenes through Suzuki coupling reaction [2e] and formyl arylbithiophenes through Vilsmeier-Haack-Arnold reactions [5]. On the basis of our recent results [2e,5] we decided to synthesize formyl-arylthiophenes **3** through Vilsmeier-Haack-Arnold reactions [5,7-10], (Scheme 1, Table 1) in order to choose the most efficient method for the synthesis of theses compounds which will be used as precursors for the synthesis of the corresponding dicyanovinyl-derivatives. Compounds **3b-d** have been previously synthesized by us through Suzuki coupling reaction. All the derivatives were obtained in higher yields though the VHA synthetic methodology compared to the above mentioned method used by us recently (Table 1) [2e].

<div align="center">

<Scheme 1>

<Table 1>

</div>

2.1.2. Synthesis of dicyanovinyl- functionalized compounds 4 and 6 through Knoevenagel condensation

Knoevenagel condensation of aldehydes **3** and **5** with malononitrile in dichloromethane, with a catalytical amount of piperidine, at room temperature, gave dicyanovinyl-derivatives **4** in moderate to good yields (Table 1, 42-83%) and compounds **6** in good to excellent yields (Table 2, 89-95%), (Scheme 2).

The structures of dicyanovinyl-substituted derivatives **4** and **6** were unambiguously confirmed by their analytical and spectral data.

<div align="center">

<Scheme 2>

<Table 2>

</div>

The synthesis of 2-dicyanovinyl-5-(4-methoxyphenyl)thiophene **4b**, 2-dicyanovinyl-5-(4-*N,N*-dimethylaminophenyl)thiophene **4d** and 5-(4´´-*N,N*-dimethylaminophenyl)-5´-dicyanovinyl-2,2´-bithiophene **6d** have been reported by Mignani [12], et al through Knoevenagel condensation of the same aldehyde precursors but using different reaction conditions (ethanol at reflux). Compounds (**4b**, 89%) and (**4d**, 85%) were obtained by Mignani et al in slightly high yields compared to our results (Table 1). On the other hand the synthesis of (**6d**, 45%) was achieved by us in a higher yield (95%) (Table 2). The experimental details and the analytical data concerning compounds **4b**, **4d** and **6d** were very incomplete. The authors reported only the yields, melting points, the λ_{max} and ε in chloroform.

2.2. UV-visible study of dicyanovinyl- derivatives 4 and 6

The electronic spectra of compounds **4** and **6**, recorded in dioxane solutions (10^{-4} M) showed an intense lowest energy charge-transfer absorption band in the UV-visible region (Tables 1-2).

All the dicyanovinyl-substituted compounds **4** and **6** synthesized are deeply colored compounds which exhibit intense absorption in the UV-vis range. The position of this band depended on the electronic nature of the substitutent (H, alkoxy, or *N,N*-dialkylamino) at position 4 of the aryl moiety (Tables 1-2). The reason for the substantial red shift in the investigated compounds **4b-d** and **4f**, (Table 1, entries 2-5) or **6b** and **6d-f**, (Table 2, entries 2-5) functionalized with donor groups, relative to that of unsubstituted derivatives **4a** and **6a** was the strong inductive and conjugative effect of the alkoxy and *N,N*-dialkylamino substituents at the *para* position of the phenyl ring.

The influence of the strength of the donor group was demonstrated for example by comparison of the absorption maxima of compounds **6b** and **6f** as the longest wavelength transition was shifted from 467.0 nm to 521.5 nm (Table 2, entries 2 and 5 respectively). The influence of the strength of the acceptor group was demonstrated for example by comparison of the absorption maxima of compounds **5f** and **6f** as the longest wavelength transition was shifted from 433.0 nm to 521.5 nm (Table 2, entry 5).

At this stage, a comparison could also be made between the UV-visible study of 2-dicyanovinyl-5-arylthiophenes **4** with 5´-dicyanovinyl-5-alkoxy- and 5´-dicyanovinyl-5-*N,N*-dialkylamino-2,2'-bithiophenes **7** [2a], recently reported by us (Figure 1). The nature of the thiophenic bridge had a clear influence on the absorption bands of

5

compounds **4**, and **7**. As expected, the obtained results showed that, the substitution of a benzene ring by a thiophene on the π-conjugated bridge, while maintaining the same donor group produced a bathochromic shift of the absorption wavelength maxima (see, for example, the comparison between **4d**, (R = NMe$_2$, λ_{max}= 497.0 nm), with **7d**, (R = NMe$_2$, λ_{max}= 560.0) [2a] both in ethanolic solutions). These observations confirm the previously obtained results, namely that the incorporation of thiophene units in push-pull compounds enhances their charge-transfer properties [13a]. The optical data obtained are not surprising in that they can be explained by considering the bathochromic effect of sulphur, the partial decrease of aromatic character of the thiophene heterocycle compared to benzene and also the increase of the π-overlap between the thiophene units.

<Figure 1>

The wavelength of maximum absorption for compounds **6** compared to compounds **4** was shifted to longer wavelengths (18.5-59.5 nm) as the number of thiophene units increased, as expected from the increase in conjugation. Similar results were obtained for the UV-vis. studies of the corresponding formyl- derivatives precursors **5** reported by us recently [5].

2.3. Solvatochromic study of compounds 6

It has been well recognized that nonlinear optical (NLO) activity of chromophores is determined not only by donor-acceptor strength but more subtly by conjugated electron relays. This can be understood from the difference in relay activities between typical moieties such as polyene and oligophenylene or oligothiophene which bear the same donor-acceptor pair and the same conjugation length; a more pronounced red-shift (in a given solvent), indicative of increased electron transmission, is commonly observed with polyenes in the low energy absorption maximum, λ_{max}, as compared to the oligophenylenes and oligothiophenes. Such a tendency is even more intensified with an increase of solvent polarity. Positive solvatochomism has been regarded as an important indicator of the potential molecular nonlinearity ($\mu\beta$) of NLO chromophores [13]. Previous studies have demonstrated that donor-acceptor substituted oligothiophenes exhibit a positive solvatochromism [2b-d, 2g-h, 13a]. In order to investigate whether compounds **6** exhibit a positive solvatochromism, we carried out a study of the

absorption spectra of compounds **6** in five selected solvents (diethyl ether, ethanol, dioxane, DMF and DMSO) of different solvation character (Table 3). The wavelength maxima λ_{max} and wavenumber maxima ν_{max} of compounds **6** are listed in Table 3 and were compared with π^* values for each solvent, determined by Kamlet et al. [14]. Dicyanovinyl- arylbithiophenes **6** exhibited positive solvatochromism with respect to their CT absorption band, *i.e.* the position of the absorption maximum shifted to longer wavelengths as the polarity of the solvent increased due to a greater stabilization of the excited state relative to the ground state with an increase in the polarity of the solvent. Moreover, compounds **6d** ($\Delta\nu_{max} = 759$ cm^{-1}), **6e** ($\Delta\nu_{max} = 1026$ cm^{-1}) and **6f** ($\Delta\nu_{max} = 810$ cm^{-1}) showed the longest shifts in wavenumber maxima.

<Table 3>

 Therefore, **6e** was submitted to a full solvatochromic study involving 12 solvents (Table 4). Because of the pronounced solvatochromism, good correlation with π^* values by Kamlet and Taft [14], for the solvents investigated and the long wavelength absorption in the visible range, **6d-f** seemed to be very appropriate solvent polarity indicating dyes and also promising nonlinear optical materials.

<Table 4>

2.4. Electrochemical properties of compounds 5-6

To get a deeper insight into the ground state properties and more specifically the mutual donor-acceptor and the π-conjugated system electronic influence, we studied the redox properties of compounds **3-6** by cyclic voltammetry and the results are presented in Tables 5 and 6.

<Tables 5-6>

For formyl-arylthiophenes **3** and formyl-arylbithiophenes **5**, all the voltammograms show the presence of two one-electron reduction waves. For all compounds the first process is reversible and the second process is irreversible except for derivative **5a**. The observed reduction potentials are dependent on the electronic nature of the substituent on the aryl moiety (Tables 5-6).

Comparison of the reduction potentials obtained for formyl-arylthiophenes **3** and formyl-arylbithiophenes **5**, having the same donor groups on the aryl moiety showed the effect of the length and the different nature of the π-conjugated bridge on the electrochemical properties of compounds **3** and **5**. The observed shifts is a direct consequence of the extent of donor-acceptor coupling [6,15-16].

The electrochemical behavior in the region of positive potential for compounds **3** and **5** depends also on the electronic nature of substituent groups on the aryl ring. Therefore, for derivatives **3a-c** and **5a-b** bearing H or alkoxy groups on position 4 of the aryl moiety one irreversible process was observed. The introduction of a more electron-donating substituent results in a decrease of the oxidation potential. For all *N,N*-dialkylamino- derivatives **3d**, **3f** and **5d-f**, two waves are observed. The first oxidation has all the properties of a reversible one-electron transfer process and the second oxidation is irreversible.

The dicyanovinyl-arylthiophenes **4a-d, 4f** and the dicyanovinyl-arylbithiophenes **6a-b** and **6d-f** shows two reduction steps involving one-electron transfer each (Figure 2). The first process is irreversible and the second is reversible. Assuming a large involvement of the dicyanovinyl moiety in both cathodic processes [2d], provided its strong electro-withdrawing nature, one can relate to the reduction at about -1.00 V to the geminal dicyano groups, whereas the second reduction seemingly involves mainly the cross-conjugated vinyl group. The first reduction has all the characteristics of an EC mechanism (electronic transference followed by a chemical step) [16]. A new process of oxidation is observed about -0.5 V vs. fc$^+$/fc. The reduction potential values are only slightly influenced by the nature of the substituent on the aryl moiety. Comparison of the cyclic voltammograms of the unsubstituted derivatives **4a** and **6a**, with compounds having donating groups on the aryl moiety showed that a small cathodic potential shift was induced by these electron-donating groups.

<Figure 2>

Comparison of donor-acceptor systems **4** and **6** having identical donor and acceptor groups but a different π-conjugated bridge shows that, the ground-state donor-acceptor conjugation is, as expected, substantially stronger in aryl-bithiophene derivatives **6** compared to aryl-thiophenes **4** (Tables 5-6).

Electrochemical oxidation data of dicyanovinyl-arylthiophenes **4** and dicyanovinyl-aryl-bithiophenes **6** are similar to that obtained for the corresponding formyl- derivatives **3** and **5** (Figure 3). Therefore, compounds **4a-c** and **6a-b** (bearing H or alcoxy groups on the aryl ring) displayed one irreversible oxidative process corresponding to the oxidation of the thiophene rings [2d]. Compounds **4d**, **4f** and **6d-f** shows two oxidation steps, the first reversible process correspond to the oxidation of the *N,N*-dialkylamino- group and the second irreversible process is attributed to the oxidation of thiophene group. The data obtained for the second process of the oxidation illustrate that there is quite an obvious electrochemical distinction between the compounds depending on the type of donor and acceptor groups, and the length of the π-conjugated bridge (Tables 5-6). However, increase of capacity of the acceptor group result in an increase of the positive shift of the second oxidation potential $^2E_{pa}$. As it was observed before for the formyl derivatives **5**, when compared to **3**, the introduction of the second thiophene ring results in a decrease in the oxidation potential also for the dicyanovinyl compounds **6** compared to **4** due to a higher electronic delocalization in these π-conjugated systems.

<Figure 3>

Electrochemical band gaps were calculated as described previously from the potentials of the anodic (oxidation of thiophene or bithiophene groups) and cathodic processes and agree well with the calculated optical band gaps [6,17-18]. The analysis of the electrochemical data for compounds **3**-**6** showed that several factors have influence on the electronic nature of the π-conjugated systems leading to the decrease of the band gaps values:

    i)   strength of the donor group linked to the aryl moiety (*e.g.* **6b**, 2.26 eV; **6d**, 2.16 eV) (Table 6, entries 2-3);

    ii)   strength of the acceptor group linked to the bithienyl system (*e.g.* **5f**, 2.62 eV; **6f**, 2.16 eV) (Table 6, entry 5);

    iii)   length of the π-conjugated bridge (*e.g.* **4b**, 2.52 eV; **6b**, 2.26 eV).

These results clearly shows that there is much more efficient coupling between the *N,N*-dialkylamino donor groups and the dicyanovinyl acceptor when compared to the formyl acceptor group. The efficient donor-acceptor conjugation leads to a rising and lowering of the HOMO and LUMO levels, respectively, and weaker donor-acceptor coupling, in

contrast, brings about a lowering and an elevation of the HOMO and LUMO levels, respectively.

2.5. Nonlinear optical properties and thermal stability of compounds 4 and 6

We have used the hyper-Rayleigh scattering (HRS) method [19] to measure the first hyperpolarizability β of dicyanovinyl chromophores **4** and **6** using the 1064 nm fundamental wavelength of a q-switched Nd:YAG laser. Dioxane was used as solvent, and the β values were measured against a reference solution of *p*-nitroaniline (*p*NA) [20] 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).

As is common practice, we have extrapolated the measured hyperpolarizabilities to the static (zero frequency) limit using the simple two-level model neglecting damping as proposed by Oudar and Chemla [21]. The resultant values quoted in Table 7 are therefore only indicative and should be treated with caution. This is especially true in the cases of compounds **6d**, **6e** and **6f** which have absorption bands that overlap the generated second harmonic signal. As no correction was made for any possible absorption of the HRS signal as it propagated through the solution, the actual values may in fact be larger than those quoted. Unfortunately we were unable to reliably measure the hyperpolaribilties of compounds **4d**, **4f** and **6b** due to the presence of a significant multiphoton absorption of the incident laser light leading to subsequent fluorescence that spectrally overlapped and overwhelmed the hyper-Rayleigh scattered light.

In general the variations in the measured hyperpolarizabilities reflect the enhancement due to the red-shift of the absorption maxima as the donor strength or conjugation length is increased. The extrapolated β_0 values are surprisingly similar for the different compounds measured.

Although there have been reports in the literature of molecules with a similar acceptor moiety having significantly higher static hyperpolarizabilities, they are all due to compounds that have a significant zwitterionic character in the ground state [22]. The values obtained for compounds **4** and **6** represent reasonably efficient second-order nonlinear molecular responses for compounds which display a positive solvachromatic shift indicative of an increase in the molecular dipole moment of the excited electronic state relative to the ground state.

Nonetheless it is possible to conclude from Table 7 that functionalization of derivatives **6d-f** (R= *N,N*-dialkylamino), with donor groups at the position 4 on the aryl moiety resulted both in red-shifted absorption maxima ($\Delta\lambda_{max}$ = 17-71 nm) and a corresponding enhancement of the β values (772-1650 x 10^{-30} esu) compared to the unsubstituted compound **6a** (285 x 10^{-30} esu) (Table 7, entries 1-2, 4-6). Most if not all of the enhancement of the measured β values appears to be the result of the resonance enhancement from the red-shift of the absorption band as indicated by the extrapolated β_0 values. Noteworthy also is the effect of the length of the π-conjugated bridge on the β values for the dicyanovinyl-arylthiophene **4a** (171x 10^{-30} esu) compared to dicyanovinyl-arylbithiophene **6a** (285x 10^{-30} esu). We had expected to observe a similar effect between the pairs of compounds (**4b**, **6b**), (**4d**, **6d**) and (**4f**, **6f**) but we are unable to drawn definitive conclusions due to the difficulty of obtaining a reliable hyperpolarizabiltiy for compounds **4d**, **4f** and **6b** using incident light with a wavelength of 1064nm.

<Table 7>

The thermal stabilities of chromophores were evaluated by thermal gravimetric analysis (TGA) under nitrogen, with a heating rate of 20 ºCmin^{-1} under a nitrogen atmosphere. The results obtained revealed the exceptional thermal stability for all compounds, which could be heated up to T$_d$ = 300–413 ºC (Table 7). Compounds **6d**-**f** functionalized with a *N,N*-dialkylamino donating groups are more thermally stable than the unsubstituted or the alkoxy derivatives **6a** and **6b**, respectively, exhibiting higher temperatures (T$_d$ = 309–413 ºC). Similar phenomena were observed in our previous cases [2e,g]. This property would benefit the practical applications of these chromophores on optical devices.

3. Conclusions

Formyl-arylthiophenes **3** were synthesized through the Vilsmeier-Haack-Arnold reaction (VHA) starting from inexpensive and easily available precursors such as acetophenones. This method gave the title compounds in higher yields compared to the synthesis *via*

Suzuki coupling of functionalized aryl boronic acids with 5-bromo-2-formyl-thiophene reported recently by us.

Push-pull arylthiophenes **4** and arylbithiophenes **6** have been synthesized, in good to excellent yields from the easily available formyl-substituted derivatives **3** and **5**, and low cost commercially available reagents, using simple and convenient procedures.

Chromophores **6** exhibit excellent solvatochromic properties, exceptional thermal stabilities and good NLO responses. The nonlinearieties of compounds **5** and **6** depend on the length of the π-conjugated bridge and also on the type of substituents on the arylthienyl moiety.

Electrochemical studies and characterization of the optical (linear and nonlinear), and thermal properties for compounds **5**-**6** indicate that, good nonlinearity-thermal stability is well balanced for chromophores **6**, making them potentially promising candidates for several optoelectronic applications such as solvatochromic probes and nonlinear optical materials.

4. Experimental

4.1. General

All melting points were measured on a Gallenkamp melting point apparatus and are uncorrected. TLC analyses were carried out on 0.25 mm thick precoated silica plates (Merck Fertigplatten Kieselgel 60F$_{254}$) and spots were visualised under UV light. Chromatography on silica gel was carried out on Merck Kieselgel (230-240 mesh). IR spectra were determined on a BOMEM MB 104 spectrophotometer using KBr discs or nujol. UV-visible absorption spectra (200 – 800 nm) were obtained using a Shimadzu UV/2501PC spectrophotometer. NMR spectra were obtained on a Varian Unity Plus Spectrometer at an operating frequency of 300 MHz for ^{1}H NMR and 75.4 MHz for ^{13}C NMR or a Bruker Avance III 400 at an operating frequency of 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR using the solvent peak as internal reference. The solvents are indicated in parenthesis before the chemical shift values (δ relative to TMS and given in ppm). (Braga, Portugal). ^{1}H NMR spectra were also recorded on a AC Bruker 250 MHz spectrometer. ^{13}C NMR spectra were run in the same instrument at 62.9 MHz using the solvent peak as internal reference (Metz, France). 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. Mass spectrometry analyses were performed at the "C.A.C.T.I. - Unidad de Espectrometria de Masas" at the University of Vigo, Spain. Elemental analyses were carried out on a Leco CHNS 932 instrument. Voltammetric measurements were 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 typically 1-2 mmol dm^{-3} and 0.1 mol dm^{-3} [NBu$_4$][BF$_4$] was used as the supporting electrolyte in *N,N*-dimethylformamide solvent. The potential is measured with respect to ferrocinium/ferrocene as an internal standard. Acetophenones **1a**-**b** were purchased from Aldrich and Acros and used as received. The synthesis of acetophenones **1c-d** and **1f** [5,7-9] and the synthesis of arylacrylaldehydes **2a-d** and **2f** [5,10] was described elsewhere.

4.2. General procedure for the synthesis of 2-formyl-5-arylthiophenes 3a-d and f

To a solution of Na$_2$S.9H$_2$O (10.5 g, 43.8 mmol) and DMF (140 ml) was added β-aryl-chloroacroleine (43.8 mmol). The mixture was stirred at 60 °C during 2 hours. Chloroformaldehyde (5.6 ml, 43.8 mmol) was added rapidly and the reaction was stirred during 3 hours at 60 °C. K$_2$CO$_3$ (6.05g, 43.8 mmol) was dissolved in water (5 ml) and added to the reaction. The mixture was stirred during 10 minutes at 60°C, cooled at room temperature and quenched in water. The solid obtained was filtered and the crude product was washed with water and recristalysed from ethanol.

4.2.1. 2-Formyl-5-phenylthiophene (3a). Pale yellow solid (30%). Mp 101-102 °C (lit. [11] 89 °C). Other analytical data were identical to those reported for the same compound.

4.2.2. 2-Formyl-5-(4-methoxyphenyl)thiophene (3b). Pale yellow solid (73%). Mp 118-119 °C (lit. [23] 119-120 °C). Other analytical data were identical to those reported for the same compound [2e,22].

4.2.3. 2-Formyl-5-(4-ethoxyphenyl)thiophene (3c). Pale yellow solid (80%). Mp 106-107 °C (lit. [2e] 104-105°C). Other analytical data were identical to those reported for the same compound.

4.2.4. 2-Formyl-5-(4-*N*,*N*-dimethylaminophenyl)thiophene (3d). Yellow solid (80%). Mp 190-191°C (lit. [2e] 188-190 °C). Other analytical data were identical to those reported for the same compound.

4.2.5. 2-Formyl-5-(4-pyrrolidinophenyl)thiophene (3f). Yellow solid (81%). Mp 184-185°C. IR (KBr) ν 3088, 2923, 2895, 2803, 1646 (C=O), 1606, 1539, 1442, 1369, 1237, 1059, 802 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$) δ 2.05 (m, 4H, N(CH$_2$CH_2)$_2$, 3.35 (m, 4H, N(CH_2CH$_2$)$_2$, 6.58 (d, 2H, J=8.7Hz, 3'-H and 5'-H), 7.23 (d, 1H, J=3.9Hz, 4-H), 7.55 (d, 2H, J=8.7Hz, 2'-H and 6'-H), 7.68 (d, 1H, J=3.9Hz, 3-H), 9.81 (s, 1H, CHO). ^{13}C NMR δ 25.4, 46.5, 111.8, 120.1, 121.2, 127.6, 138.1, 139.7, 148.7, 156.5, 182.4. MS (EI) *m/z* (%): 257 (M$^+$, 100), 256 (77), 201 (29), 187 (7), 115 (7). HRMS: m/z (EI) for C$_{15}$H$_{15}$NOS; calcd 257.0874; found: 257.0866.

4.3. General procedure for the synthesis of 2-dicyanovinyl-5-arylthiophenes 4 from the corresponding 2-formyl-5-arylthiophenes 3 by Knoevenagel condensation with malononitrile

To a solution of malononitrile (0.08 g, 1.2 mmol) and 2-formyl-5-arylthiophenes **3** (1.0 mmol) in dichloromethane (25 ml) was added piperidine (1 drop). The solution was stirred at room temperature during different reaction times (15 min.- 3 h), then petroleum ether was added and the 2-dicyanovinyl-5-arylthiophenes **4** precipitate and were filtrate. The crude residue was submitted to 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.

4.3.1. 2-Dicyanovinyl-5-phenylthiophene 4a. Yellow solid (50%). Mp 171-173 °C. UV (Dioxane): λ_{max} nm (ε, /M^{-1} cm^{-1}) 391.0 (16,274). IR (nujol) ν 2221 (CN), 1578, 1434, 1360, 1324, 1265, 1244, 1138, 1069, 934, 806, 749, 679 cm^{-1}. ^{1}H NMR (DMSO-d$_6$) δ 7.48-7.51 (m, 3H, 3´-H, 4´-H, 5´-H), 7.80-7.84 (m, 3H, 2´-H, 6´-H and 4-H), 7.95

(d, 1H, J=4.5 Hz, 3-H), 8.68 (s, 1 H, CH=C(CN)$_2$). ^{13}C NMR (Acetone-d$_6$) δ 76.9, 114.4, 115.1, 126.0, 127.3, 130.3, 130.9, 133.2, 135.4, 142.3. MS (EI) m/z (%): 237 (M$^+$+1, 64), 236 (M$^+$, 70), 209 (47), 197 (81), 155 (41), 154 (100). HRMS: m/z (EI) for C$_{14}$H$_8$N$_2$S; calcd 237.0486; found: 237.0493. Anal. Calcd. for C$_{14}$H$_8$N$_2$S : C, 71.16; H, 3.41; N, 11.86; S, 13.57. Found: C, 70.89; H, 3.76; N, 11.55; S, 13.12.

4.3.2. 2-Dicyanovinyl-5-(4-methoxyphenyl)thiophene 4b. Orange solid (77%). Mp 189-190 ^{o}C (lit. [12] 195 °C). UV (Dioxane): λ_{max} nm (ε, /M^{-1} cm^{-1}) 423.0 (33,887). IR (KBr) ν 3024, 2984, 2959, 2913, 2220 (CN), 1686, 1598, 1567, 1495, 1419, 1065, 1222, 1255, 1025, 816 cm^{-1}. ^{1}H NMR (DMSO-d$_6$) δ 3.81 (s, 3H, OCH_3), 7.05 (d, 2H, J=9.0Hz, 3'-H and 5'-H), 7.70 (d, 1H, J=3.9Hz, 4-H), 7.75 (d, 2H, J=9.0Hz, 2'-H and 6'-H), 7.90 (d, 1H, J=3.9Hz, 3-H), 8.59 (s, 1H, CH=C(CN)$_2$). ^{13}C NMR (DMSO-d$_6$) δ 55.4, 73.6, 114.0, 114.7, 114.9, 124.4, 128.1, 133.2, 142.7, 152.6, 155.5, 160.9. MS (EI) m/z (%): 266 (M$^+$, 100), 251 (82), 223 (55), 196 (12). HRMS: m/z (EI) for C$_{15}$H$_{10}$N$_2$OS; calcd 266.0514; found: 266.0525.

4.3.3. 2-Dicyanovinyl-5-(4-ethoxyphenyl)thiophene 4c. Red solid (62%). Mp > 185°C. UV (Dioxane): λ_{max} nm (ε, /M^{-1} cm^{-1}) 416.0 (35,847). IR (KBr) ν 3038, 2948, 2224 (CN), 1614, 1581, 1501, 1382, 1052, 1180, 1253, 1052, 792 cm^{-1}. ^{1}H NMR (DMSO-d$_6$) δ 1.33 (t, 3H, J=6.9Hz, OCH$_2$CH_3), 4.09 (q, 2H, J=6.9Hz, OCH_2CH$_3$), 7.03 (d, 2H, J=8.7Hz, 3'-H and 5'-H), 7.70 (d, 1H, J=4.5Hz, 4-H), 7.72 (d, 2H, J=8.7Hz, 2'-H and 6'-H), 7.90 (d, 1H, J=4.5Hz, 3-H), 8.59 (s, 1 H, CH=C(CN)$_2$). ^{13}C NMR (DMSO-d$_6$) δ 63.4, 73.6, 114.0, 114.8, 115.3, 124.3, 124.4, 128.1, 133.1, 142.7, 152.6, 155.5, 160.3. MS (EI) m/z (%): 280 (M$^+$, 40), 252 (100), 223 (12), 83 (18). HRMS: m/z (EI) for C$_{16}$H$_{12}$N$_2$OS; calcd 280.0670; found: 280.0677.

4.3.4. 2-Dicyanovinyl-5-(4-N,N-dimethylaminophenyl)thiophene 4d. Green solid (83%). Mp > 209 ^{o}C (lit. [12] 217°C). UV (Dioxane): λ_{max} nm (ε, /M^{-1} cm^{-1}) 485.0 (33,586). IR (KBr) ν 3025, 2943, 2211 (CN), 1701, 1607, 1579, 1503, 1439, 1365, 1062, 1231, 803 cm^{-1}. ^{1}H NMR (DMSO-d$_6$) δ 2.99 (s, 6H, N(CH_3)$_2$), 6.76 (d, 2H, J=8.7Hz, 3'-H and 5'-H), 7.61 (d, 1H, J=3.9Hz, 4-H), 7.64 (d, 2H, J=8.7Hz, 2'-H and 6'-H), 7.85 (d, 1H, J=3.9Hz, 3-H), 8.49 (s, 1H, CH=C(CN)$_2$). ^{13}C NMR (DMSO-d$_6$) δ 46.4, 73.6, 114.0, 114.7, 115.4, 124.4, 124.5, 128.0, 133.4, 142.5, 152.4, 155.6, 160.7.

MS (EI) m/z (%): 279 (M$^+$, 100), 278 (66), 263 (21). HRMS: m/z (EI) for C$_{16}$H$_{13}$N$_3$S; calcd 279.0830; found: 279.0832.

4.3.5. 2-Dicyanovinyl-5-(4-pyrrolidinophenyl)thiophene 4f. Green solid (42%). Mp > 226 ^{o}C. UV (DMSO): λ_{max} nm (ε, /M^{-1} cm^{-1}) 503.0 (42,143). IR (KBr) ν 3027, 2968, 2215 (CN), 1656, 1604, 1565, 1493, 1411, 1391, 1067, 1191, 797 cm^{-1}. ^{1}H NMR (DMSO-d$_6$) δ 1.97 (m, 4H, N(CH$_2$CH$_2$)$_2$), 3.31 (m, 4H, N(CH$_2$CH$_2$)$_2$), 6.62 (d, 2H, J=8.7Hz, 3'-H and 5'-H), 7.59 (d, 1H, J=3.9Hz, 4-H), 7.64 (d, 2H, J=8.7Hz, 2'-H and 6'-H), 7.85 (d, 1H, J=3.9Hz, 3-H), 8.48 (s, 1H, CH=C(CN)$_2$). ^{13}C NMR (DMSO-d$_6$) δ 24.9, 47.3, 112.1, 114.6, 115.3, 118.5, 122.3, 127.9, 131.2, 143.5, 149.0, 151.8, 158.2. MS (EI) m/z (%): 305 (M$^+$, 100), 304 (74), 301 (17), 262 (11), 249 (35), 235 (11), 164 (11), 149 (15). HRMS: m/z (EI) for C$_{18}$H$_{10}$N$_2$S$_2$; calcd 305.0987; found: 305.0992.

4.4. General procedure for the synthesis of 5-aryl-5´-dicyanovinyl-2,2´bithiophenes 6 from the corresponding 5-aryl-5´-formyl-2,2´bithiophenes 5 by Knoevenagel condensation with malononitrile

To a solution of malononitrile (0.08 g, 1.2 mmol) and 5-aryl-5'-formyl-bithiophenes **5** (1.0 mmol) in dichloromethane (25 ml) was added piperidine (1 drop). The solution was stirred at room temperature during different reaction times (15 min.-2 h), then petroleum ether was added and the 5-aryl-5'-dicyanovinyl-2,2´-bithiophenes **6** precipitate and were filtrate. The crude residue was submitted to silica gel column chromatography using mixtures of chloroform and light petroleum of increasing polarity. The fractions containing the purified product were collected and evaporated under vacuum.

4.4.1. 5-Phenyl-5´-dicyanovinyl-2,2´-bithiophene 6a. Dark red solid (93%). Mp > 84 ^{o}C. UV (DMSO): λ_{max} nm (ε, /M^{-1} cm^{-1}) 463.5 (21,575), 321.5 (9,966) inf. 376.5 (2,242). IR (nujol) ν 2223 (CN), 1572, 1539, 1482, 1461, 1449, 1367, 1346, 1261, 1227, 1187, 1147, 1078, 1056, 934, 882, 788, 755, 722, 697, 684, 608 cm^{-1}. ^{1}H NMR (DMSO-d$_6$) δ 7.34 (m, 1H, 4"-H), 7.44 (m, 2H, 3"-H and 5"-H), 7.61 (d, 1H, J=3.9Hz, 4-H), 7.65 (d, 1H, J=3.9Hz, 3'-H), 7.71 (d, 1H, J=3.9Hz, 3-H), 7.73 (m, 2H, 2"-H and 6"-H), 7.90 (d, 1H, J=3.9Hz, 4'-H), 8.64 (s, 1H, CH=C(CN)$_2$). ^{13}C NMR (DMSO-d$_6$) δ 74.2, 113.9, 114.6, 125.3, 125.6, 128.6, 129.2, 132.5, 133.3, 133.6, 142.4, 146.1, 147.5,

152.2. MS (EI) *m/z* (%): 318 (M$^+$, 15), 283 (17), 257 (28), 236 (35), 213 (29), 185 (32), 155 (63), 152 (32), 129 (38), 127 (71), 111 (55), 98 (66), 97 (100), 83 (82), 71 (68). HRMS: *m/z* (EI) for C$_{18}$H$_{10}$N$_2$S$_2$; calcd 318.0285; found: 318.0291.

4.4.2. 5-(4´´-Methoxyphenyl)-5´-dicyanovinyl-2,2´-bithiophene 6b. Red Solid (95%).

Mp > 180 ^{o}C. UV (DMSO): λ_{max} nm (ε/M^{-1} cm^{-1}) 482.0 (21,738), 312.0 (6,861) inf. 474.0 (2,918). IR (nujol) v 2221 (CN), 1882, 1608, 1580, 1542, 1512, 1484, 1349, 1309, 1289, 1275, 1253, 1232, 1193, 1179, 1163, 1146, 1124, 1112, 1078, 1063, 1031, 960, 943, 884, 862, 817, 799, 785, 722, 693, 646, 630, 604, 587, 555 cm^{-1}. ^{1}H NMR (DMSO-d$_6$) δ 3.79 (s, 3 H, OC*H$_3$*), 7.00 (d, 2H, *J*=8.7Hz, 3''-H and 5''-H), 7.51 (d, 1H, *J*=3.9Hz, 4-H), 7.62 (d, 1 H, *J*=3.9Hz, 3'-H), 7.67 (m, 3H, 3-H, 2''-H and 6''-H), 7.90 (d, 1H, *J*=3.9Hz, 4'-H), 8.62 (s, 1H, C*H*=C(CN)$_2$). ^{13}C NMR (DMSO-d$_6$) δ 55.33, 77.80, 114.05, 114.70, 124.46, 125.06, 125.27, 127.09, 129.38, 132.46, 133.08, 142.69, 146.54, 148.00, 152.26, 159.73. MS (EI) *m/z* (%): 348 (M$^+$, 100), 333 (85), 305 (42), 271 (6), 203 (5), 174 (4). HRMS: *m/z* (EI) for C$_{19}$H$_{12}$ N$_2$OS$_2$; calcd 348.0391; found: 348.0395.

4.4.3. 5-(4´´-*N,N*-Dimethylaminophenyl)-5´-dicyanovinyl-2,2´-bithiophene 6d.

Brown solid (95%). Mp > 180 ^{o}C (lit. [12] 215°C). UV (DMSO): λ_{max} nm (ε/M^{-1} cm^{-1}) 530.0 (18,868), 364.5 (13,732) inf. 421.0 (7,308). IR (nujol) v 2223 (CN), 1872, 1606, 1578, 1551, 1542, 1486, 1352, 1310, 1266, 1231, 1201, 1146, 1075, 959, 939, 876, 810, 790, 745, 721, 687, 629, 608, 573, 550 cm^{-1}. ^{1}H NMR (DMSO-d$_6$) δ 3.05 (s, 6H, N(C*H$_3$*)$_2$) 6.84 (d, 2H, *J*=9.0Hz, 3''-H and 5''-H), 7.38 (d, 1H, *J*=3.9Hz, 4-H), 7.56 (d, 1H, *J*=3.9Hz, 3'-H), 7.62 (d, 2H, *J*=9.0Hz, 2''-H and 6''-H), 7.64 (d, 1H, *J*=3.9Hz, 3-H), 7.94 (d, 1H, *J*=3.9Hz, 4'-H), 8.40 (s, 1H, C*H*=C(CN)$_2$). ^{13}C NMR (DMSO-d$_6$) δ 73.0, 112.0, 113.8, 114.4, 120.1, 122.4, 124.3, 126.4, 129.1, 130.7, 132.4, 142.0, 148.0, 150.3, 151.6. MS (EI) *m/z* (%): 361 (M$^+$, 100), 345 (100), 318 (15), 180 (5), 172 (4), 97 (4). HRMS: *m/z* (EI) for C$_{20}$H$_{15}$N$_3$S$_2$; calcd 361.0707; found: 361.0708. Anal. Calcd. for C$_{20}$H$_{15}$N$_3$S$_2$: C, 66.45; H, 4.18; N, 11.62; S, 17.74. Found: C, 66.01; H, 4.05; N, 11.47; S, 17.39.

4.4.4. 5-(4´´-*N,N*-Diethylaminophenyl)-5´-dicyanovinyl-2,2´-bithiophene 6e. Green

solid (87%). Mp > 184 ^{o}C. UV (DMSO): λ_{max} nm (ε/M^{-1} cm^{-1}) 546.5 (18,298), 369.0

(14,277) inf. 430.0 (8,079). IR (nujol) ν 2219 (CN), 1603, 1572, 1541, 1272, 1193, 1159, 1093, 1072, 1054, 955, 932, 880, 806, 776, 740, 732, 684, 628, 605, 568, 549, 517 cm^{-1}. ^{1}H NMR (DMSO-d$_6$) $\delta\Box$ 1.22 (t, 6H, J=5.4Hz, N(CH$_2$CH_3)$_2$), 3.38 (q, 4H, J=5.4Hz, N(CH_2CH$_3$)$_2$), 6.71 (d, 2H, J=6.6Hz, 3"-H and 5"-H), 7.32 (d, 1H, J=3.0Hz, 4-H), 7.49 (d, 2H, J=6.6Hz, 2"-H and 6"-H), 7.52 (d, 1H, J=3.0Hz, 3-H), 7.58 (d, 1H, J=3.0Hz, 3'-H); 7.88 (d, 1H, J=3.0Hz, 4'-H), 8.50 (s, 1H, CH=C(CN)$_2$). ^{13}C NMR (DMSO-d$_6$) δ 43.4, 72.8, 111.5, 113.8, 114.4, 119.2, 122.0, 124.1, 126.6, 129.1, 130.4, 132.3, 142.0, 147.7, 148.2, 148.4, 151.5. MS (EI) m/z (%): 389 (M^{+}, 56), 374 (100), 345 (59), 326 (36), 236 (24), 152 (18), 137 (20), 129 (29), 123 (32), 111 (50), 97 (90), 83 (92), 81 (78), 71 (72). HRMS: m/z (EI) for C$_{22}$H$_{19}$N$_3$S$_2$; calcd 389.1020; found: 389.1009. Anal. Calcd. for C$_{22}$H$_{19}$N$_3$S$_2$: C, 67.83; H, 4.92; N, 10.79; S, 16.46. Found: C, 67.40; H, 4.84; N, 10.65; S, 16.37.

4.4.5. 5-(4´´-Pyrrolidinophenyl)-5´-dicyanovinyl-2,2´-bithiophene 6f. Brown solid (89%). Mp > 214 ^{o}C. UV (DMSO): λ_{max} nm (ε/M^{-1} cm^{-1}) 544.5 (18,365), 369.5 (14,309) inf. 429.0 (7,329). IR (nujol) ν 2214 (CN), 1603, 1569, 1548, 1538, 1512, 1487, 1438, 1231, 1212, 1188, 1164, 1144, 1061, 966, 927, 880, 862, 814, 789, 775, 722, 688, 645, 634, 602 cm^{-1}. ^{1}H NMR (DMSO-d$_6$) δ 1.96 (m, 4H, N(CH$_2$CH_2)$_2$), 3.72 (m, 4H, N(CH_2CH$_2$)$_2$), 6.57 (d, 2H, J=8.7Hz, 3"-H and 5"-H), 7.37 (d, 1H, J=3.9Hz, 4-H), 7.52 (d, 2H, J=8.7Hz, 2"H and 4"-H), 7.57 (d, 1H, J=4.2Hz, 3'-H), 7.63 (d, 1H, J=3.9Hz, 3-H), 7.87 (d, 1H, J=4.2Hz, 4'-H), 8.57 (s, 1H, CH=C(CN)$_2$). ^{13}C NMR (DMSO-d$_6$) δ 24.9, 47.2, 72.8, 111.9, 114.1, 114.8, 119.4, 122.3, 124.4, 126.7, 129.6, 130.4, 132.4, 142.8, 147.8, 148.5, 148.6, 151.9. MS (EI) m/z (%) 387.09 (M^{+}, 6), 368 (18), 355 (27), 327 (15), 311 (15), 283 (22), 257 (35), 255 (23), 243 (24), 239 (27), 237 (22), 236 (35), 229 (23), 211 (17), 165 (23), 156 (16), 155 (100), 127 (96). HRMS: m/z (EI) for C$_{22}$H$_{17}$N$_3$S$_2$; calcd 387.0864; found: 387.0851.

4.5. Nonlinear optical measurements for compounds 4 and 6 using the hyper-Rayleigh scattering (HRS) method [19a]

Hyper-Rayleigh scattering (HRS) was used to measure the first hyperpolarizability β of the molecules studied. The experimental set-up for hyper-Rayleigh measurements is similar to that presented by Clays et al [19a]. The incident laser beam came from a Q-switched Nd:YAG laser operating at a 10 Hz repetition rate with approximately 10 mJ

of energy per pulse and a pulse duration (FWHM) close to 12 ns at the fundamental wavelength of 1064 nm. The incident power could be varied using a combination of a half wave-plate and Glan polarizer. The incident beam was weakly focused (beam diameter ~0.5 mm) into the solution contained in a 5 cm long cuvette. The hyper-Rayleigh signal was collimated using a high numerical aperture lens passed through an interference filter centred at the second harmonic wavelength (532 nm) before being detected by a photomultiplier (Hamamatsu model H9305-04). The current pulse from the photomultiplier was integrated using a Stanford Research Systems gated box-car integrator (model SR250) with a 20 ns gate centred on the temporal position of the incident laser pulse. The hyper-Rayleigh signal was normalized 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. Dioxane was used as a solvent, and the β values were calibrated using a reference solution of p-nitroaniline (pNA) [20] also dissolved in dioxane at a concentration of 10^{-2} M (external reference method). The hyperpolarizability of pNA dissolved in dioxane is known from EFISH measurements carried out at the same fundamental wavelength [20]. The concentrations of the solutions under study were chosen so that the corresponding hyper-Rayleigh signals fell well within the dynamic range of both the photomultiplier and the box-car integrator. All solutions were filtered (0.2 μm porosity) to avoid spurious signals from suspended impurities. The small hyper Rayleigh signal that arises from dioxane was taken into account according to the expression

$$I_{2\omega} = G\left(N_{solvent}\left\langle\beta^2_{solvent}\right\rangle + N_{solute}\left\langle\beta^2_{solute}\right\rangle\right)I^2_{\omega}$$

where the "instrumental factor", G, 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) as well as local field corrections due to the solvent. The brackets indicate an average over the spatial orientations of the molecules.
We took particular care to avoid reporting artificially high hyperpolarizibilities due to a possible contamination of the hyper Rayleigh signal by molecular fluorescence near 532 nm. Measurements were carried out using two different interference filters with different transmission pass bands centred near the second harmonic at 532 nm. The transmission band of the narrower filter (CVI model F1.5-532-4) was 1.66 nm (full

width at half maximum) with a transmission of 47.6% at the second harmonic, while the corresponding values for the wider filter (CVI model F03-532-4) were 3.31 nm, with a transmission of 63.5% at the second harmonic. The transmission of each filter at the second harmonic wavelength was carefully determined using a crystalline quartz sample. We assume that any possible fluorescence emitted from the solutions is essentially constant over the transmission of both interference filters. Then by comparing the signals obtained with the two different filters we can determine the relative contributions of the hyper-Rayleigh and possible fluorescence signals. More concretely the overall detected signal can have contributions from both the second harmonic signal and any possible fluorescence that is emitted within the passband of the filter. Denoting S_{NB} as the actual signal measured (after correction for the solvent contribution) using the "narrow" band interference filter (CVI model F1.5-532-4), we have

$$S_{NB} = T_{NB}S^{2\omega} + A_{NB}S^{F}$$

while the corresponding signal obtained using the "wide" (CVI model F03-532-4) band interference filter is

$$S_{WB} = T_{WB}S^{2\omega} + A_{WB}S^{F}.$$

Here $S^{2\omega}$ is the second harmonic signal incident on the filters while S^{F} is the average fluorescence signal over the passband of the filters. We assume the fluorescence component is broad enough that the average fluorescence signal is essentially identical for both filters. The transmissions T_{NB} and T_{WB} are respectively the transmission of the "narrow" and "wide" band interference filters at the second harmonic wavelength (47.6% and 63.5%), while A_{NB} and A_{WB} represent the integrated area under the respective filter's transmission curve. The transmission curves were obtained using a dual-beam spectrophotometer with slits adjusted to give 0.1 nm resolution. We obtained values of 1.29 nm and 2.18 nm for A_{NB} and A_{WB} respectively. Solving the above equations for $S^{2\omega}$ and S^{F} we arrive at the following expression for the actual hyper-Rayleigh and fluorescence contribution to the signal obtained using the narrow band interference filter:

$$S_{NB}^{2\omega} = \left(\frac{S_{NB}A_{WB} - S_{WB}A_{NB}}{T_{NB}A_{WB} - T_{WB}A_{NB}} \right) T_{NB}$$

$$S_{NB}^{F} = \left(\frac{S_{WB}T_{NB} - S_{NB}T_{WB}}{T_{NB}A_{WB} - T_{WB}A_{NB}} \right) A_{NB}$$

This allows us to determine if fluorescence is present and to reliably correct for its presence provided that the integrated contribution is less than 80% of the total detected signal within the temporal gate of the box-car integrator (20 ns). The resultant values for the hyperpolarizability and the associated uncertainties are reported in Table 7. The uncertainties have been calculated using the measured variances in the signals obtained using the narrow and wide band filters for the compound under study, the background obtained from the measurements on pure dioxane and the pNA reference solution.

When using the "narrow" band filter the estimated fraction of the total detected signal due to fluorescence together with the estimated experimental uncertainty is listed in Table 8.

<Table 8>

For compounds **4d**, **4f** and **6b**, the absorption and emission spectral curves overlap at the second harmonica wavelength of 532 nm, making our experimental method unreliable. For compounds **6e** and **6f** we also expect significant two-photon absorption of the incident laser light at 532 nm although the subsequent emission is red-shifted beyond the transmission of our interference filters. The simple two-level model that we use to extrapolate the β_0 values predicts a significant resonance enhancement for these compounds. However as damping was neglected, the β_0 values quoted for these compounds are less trustworthy.

4.6. Thermogravimetric analysis of compounds 6

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 ºC min^{-1} heating rate and were characterized between 25 and 800 ºC.

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Captions

Scheme 1. Synthesis of formyl-arylthiophenes **3** through Vilsmeier-Haack-Arnold reaction.

Scheme 2. Synthesis of dicyanovinyl-arylthiophenes **4a-d**, **4f** and dicyanovinyl-arylbithiophenes **6a-b**, **6d-f** through Knoevenagel condensation of the corresponding formyl precursors **3** and **5**, respectively, with malononitrile.

Table 1. Yields, ^{1}H NMR, IR and UV-vis data of formyl-arylthiophenes **3** and dicyanovinyl-arylthiophenes **4**.

[a] For the C*H*O proton for formyl-arylthiophenes **3** (300 MHz, CDCl$_3$).

[b] All the spectra were recorded in nujol.

[c] For the C*H*=(CN)$_2$ proton for dicyanovinyl-arylthiophenes **4** (400 MHz, DMSO-d$_6$).

[d] All the UV-vis spectra were recorded in dioxane.

Table 2. Yields, ^{1}H NMR, IR and UV-vis data of dicyanovinyl-arylbithiophenes **6** and UV-vis data of compounds **5**.

[a] All the UV-vis spectra were recorded in dioxane.

[b] For the C*H*=(CN)$_2$ proton for dicyanovinyl-arylbithiophenes **6** (400 MHz, DMSO-d$_6$).

[c] For the CN stretching band (recorded in nujol).

Table 3. Solvatochromic data [λ_{max} (nm) and υ_{max} (cm^{-1}) of the charge-transfer band] for dicyanovinyl-arylbithiophenes **6** in 5 solvents with π^* values by Kamlet and Taft [14].

[a] Solvent used as received.

Table 4. Solvatochromic data [λ_{max} (nm) and υ_{max} (cm^{-1}) of the charge-transfer band] for dicyanovinyl-arylbithiophenes **6e** in 12 solvents with π^* values by Kamlet and Taft [14].

[a] Solvent used as received.

[b] The correlation coefficient *r* obtained for the linear solvatation energy relationship with π^* values by Kamlet and Taft for solvents was *r* = 0.9607 for **6e**. This value was obtained without ethylacetate, dioxane, acetonitrile and chloroform which deviate slightly from the regression line [2b].

Table 5. Electrochemical data for formyl-arylthiophenes **3** and dicyanovinyl-arylthiophenes **4**.

[a] Measurements made in dry dimethylformamide containing 1.0 mM in each compounds and 0.10 M [NBu$_4$][BF$_4$] as base electrolyte at a carbon working electrode with a scan rate of 0.1 V s^{-1}. Ferrocene was added as an internal standart at the end of each measurement, and all E values are quoted in volts *versus* the ferrocinium/ferrocene-couple. E_{pc} and E_{pa} correspond to the cathodic and anodic peak potentials, respectively.

[b] $\Delta E_p = E_{ox} - E_{red}$, where the subscripts ox and red refer to the conjugated oxidation and reduction steps, respectively.

[c] $E_{HOMO} = 4.39 + E_{pa}$ (eV) and $E_{LUMO} = E_{pc} + 4.39$ (eV).

[d] Values obtained from the difference between the $^2E_{pa}$ (oxidation of thiophenic ring) and the $-^1E_{pc}$.

Table 6. Electrochemical data for formyl-arylbithiophenes **5** and dicyanovinyl-arylbithiophenes **6**.

[a] Measurements made in dry dimethylformamide containing 1.0 mM in each compounds and 0.10 M [NBu$_4$][BF$_4$] as base electrolyte at a carbon working electrode with a scan rate of 0.1 V s^{-1}. Ferrocene was added as an internal standard at the end of each measurement, and all E values are quoted in volts *versus* the ferrocinium/ferrocene-couple. E_{pc} and E_{pa} correspond to the cathodic and anodic peak potentials, respectively.

[b] $\Delta E_p = E_{ox} - E_{red}$, where the subscripts ox and red refer to the conjugated oxidation and reduction steps, respectively.

[c] $E_{HOMO} = 4.39 + E_{pa}$ (eV) and $E_{LUMO} = E_{pc} + 4.39$ (eV).

[d] Values obtained from the difference between the $^2E_{pa}$ (oxidation of bithiophenic moiety) and the $-^1E_{pc}$.

Table 7. UV-vis absorptions, β and β_0 values and T$_d$ data for dicyanovinyl-arylthiophenes **4** and dicyanovinyl-arylbithiophenes **6**[a].

[a] Experimental hyperpolarizabilities and spectroscopic data measured in dioxane solutions.

[b] All the 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 [21].

d Decomposition temperature (T$_d$) measured at a heating rate of 20 ºC min^{-1} under a nitrogen atmosphere, obtained by TGA.

* The values obtained for these compounds were unreliable. We believe this is due to the overlap of the two-photon absorption and subsequent fluorescence emission for an incident wavelength of 1064 nm.

Table 8. Estimates of the amount of fraction of the detected signal that is due to fluorescence when using the narrow band interference filter, S_{NB}^{F} / S_{NB} for compounds **4** and **6**.
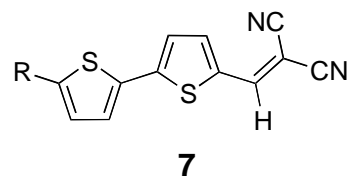
Figure 1. Structure of compounds **7** [2a].

Figure 2. Cyclic voltammograms of compound **6e** (1.0x10^{-3} mol dm^{-3}) in DMF, 0.1 mol dm^{-3} [NBu$_4$][BF]$_4$ at a vitreous carbon electrode, scan rate 100 mV s^{-1}. A - between -1.1 V and -1.7 V *vs*. fc$^+$/fc; B - between -1.1 V and -3.3 V *vs*. fc$^+$/fc.

Figure 3. Cyclic voltammograms of compounds **6d** (cyclic voltammograms A and B) and **6b** (cyclic voltammogram C) obtained in DMF, 0.1 mol dm^{-3} [NBu$_4$][BF]$_4$ with a vitreous carbon electrode, scan rate 100 mV s^{-1}and concentration of compound 1.0x10^{-3} mol dm^{-3}.
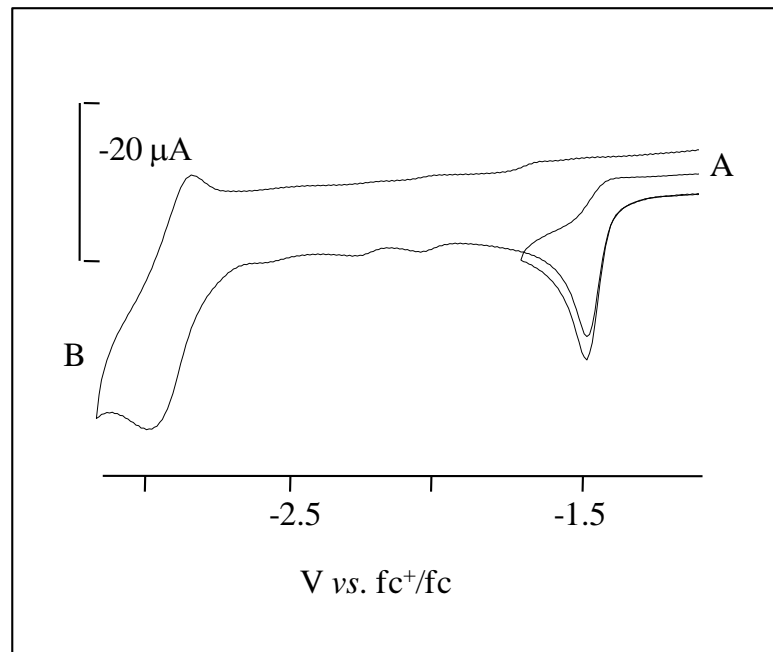
Figures

Figure 1

7

b R = MeO
c R = EtO
d R = NMe$_2$
e R = NEt$_2$

Figure 2

Figure 3

20 µA

B

C

A

-0.5

0.5

V *vs.* fc⁺/fc

Table 1

R	Formyl-arylthiophene 3	Yield (%)	δ_H (ppm)[a]	IR ν (cm^{-1})[b]	Dicyanovinyl-arylthiophene 4	Yield (%)	δ_H (ppm)[c]	IR ν (cm^{-1})[b]	λ_{max} (nm)[d]
H	a	30, 30 [11]	---	---	a	50	8.68	2221 (CN)	391.0
MeO	b	73, 15 [2e]	---	---	b	77	8.59	2219 (CN)	423.0
EtO	c	80, 66 [2e]	---	---	c	62	8.59	2216 (CN)	416.0
NMe$_2$	d	80, 26 [2e]	---	---	d	83	8.49	2217 (CN)	485.0
Pyrrolidino	f	81	9.81	1657 (C=O)	f	42	8.48	2215 (CN)	503.0

Table 2

Entry	Formyl-arylbithiophene 5	R	λ_{max} (nm)[a]	Dicyanovinyl-arylbithiophene 6	Yield (%)	δ_H (ppm)[b]	IR ν (cm^{-1})[c]	λ_{max} (nm)[a]
1	**a**	H	382.5	**a**	93	8.64	2223	450.5
2	**b**	MeO	394.5	**b**	95	8.62	2221	467.0
3	**d**	NMe$_2$	424.0	**d**	95	8.40	2223	509.5
4	**e**	NEt$_2$	435.5	**e**	93	8.39	2219	520.0
5	**f**	Pyrrolidino	433.0	**f**	89	8.57	2214	521.5

Table 3

Solvents[a]	π^*	6a		6b		6d		6e		6f	
		λ_{max} (nm)	υ_{max} (cm^{-1})	λ_{max} (nm)	υ_{max} (cm^{-1})	λ_{max} (nm)	υ_{max} (cm^{-1})	λ_{max} (nm)	υ_{max} (cm^{-1})	λ_{max} (nm)	υ_{max} (cm^{-1})
Diethyl ether	0.27	449.5	22,247	465.0	21,505	509.5	19,627	517.5	19,324	521.5	19,175
Ethanol	0.54	453.5	22,051	471.0	21,231	517.5	19,324	533.0	18,762	529.0	18,904
Dioxane	0.55	450.5	22,198	467.0	21,413	509.5	19,627	520.0	19,231	521.5	19,175
Dimethylformamide	0.88	455.5	21,954	476.0	21,008	522.5	19,139	540.5	18,501	536.5	18,639
Dimethylsulfoxide	1.00	463.5	21,575	482.0	20,747	530.0	18,868	546.5	18,298	544.5	18,365

Table 4

Solvents[a]	π^{*b}	Compound **6e**	
		λ_{max} (nm)	υ_{max} (cm^{-1})
Diethyl ether	0.27	517.5	19,324
Toluene	0.54	532.0	18,797
Ethanol	0.54	533.0	18,762
Dioxane	0.55	520.0	19,231
Ethyl acetate	0.55	523.0	19,120
Tetrahydrofuran	0.58	530.5	18,850
Acetone	0.71	532.0	18,797
Acetonitrile	0.75	524.0	19,084
Chloroform	0.76	552.0	18,116
Dichloromethane	0.82	540.5	18,501
Dimethylformamide	0.88	540.5	18,501
Dimethylsulfoxide	1.00	546.5	18,298

Table 5

Entry	Formyl-arylthiophene 3	R	Electrochemical data[a] oxidation $^{1}E_{pa}$ (V)	$^{2}E_{pa}$ (V)	reduction $-^{1}E_{pc}$(V)	$-^{2}E_{pc}$ (V)	band gap (eV)[c]	Dicyanovinyl-Arylthiophene 4	Electrochemical data[a] oxidation $^{1}E_{pa}$ (V)	$^{2}E_{pa}$ (V)	reduction $-^{1}E_{pc}$ (V)	$-^{2}E_{pc}$ (V)	band gap (eV)[c]
1	a	H	—	—	2.05 (67)[b]	2.75	—	a	—	—	1.40	3.04 (90)[b]	—
2	b	MeO	1.00	—	2.11 (64)[b]	2.82	3.11	b	1.06	—	1.46	3.29 (90)[b]	2.52
3	c	EtO	0.96	—	2.14 (71)[b]	2.84	3.10	c	1.00	—	1.47	3.30 (80)[b]	2.47
4	d	NMe$_2$	0.36 (60)[b]	0.81	2.22 (65)[b]	—	3.03[d]	d	0.42 (63)[b]	0.88	1.50	—	2.38[d]
5	f	Pyrrolidino	0.35 (67)[b]	0.83	2.21 (64)[b]	—	3.04[d]	f	0.38 (61)[b]	0.86	1.50	—	2.36[d]

Table 6

Entry	Formyl-arylbithiophene 5	R	Electrochemical data[a]				band gap (eV)[c]	Dicyanovinyl-Arylbithiophene 6	Electrochemical data[a]				band gap (eV)[c]
			oxidation		reduction				oxidation		reduction		
			$^1E_{pa}$ (V)	$^2E_{pa}$ (V)	$-^1E_{pc}$(V)	$-^2E_{pc}$ (V)			$^1E_{pa}$ (V)	$^2E_{pa}$ (V)	$-^1E_{pc}$ (V)	$-^2E_{pc}$ (V)	
1	**a**	H	—	—	1.93 (62)[b]	2.40 (55)[b]	—	**a**	1.01	—	1.36	2.67 (90)[b]	2.36
2	**b**	MeO	0.79	—	1.95 (58)[b]	2.48	2.74	**b**	0.87	—	1.39	2.77 (110)[b]	2.26
3	**d**	NMe$_2$	0.27 (55)[b]	0.63	1.99 (64)[b]	2.54	2.67[d]	**d**	0.28 (56)[b]	0.76	1.40	2.84 (130)[b]	2.16[d]
4	**e**	NEt$_2$	0.23 (63)[b]	0.60	2.04 (72)[b]	2.59	2.68[d]	**e**	0.26 (70)[b]	0.74	1.44	2.93 (120)[b]	2.18[d]
5	**f**	Pyrrolidino	0.26 (56)[b]	0.68	1.94 (54)[b]	2.75	2.62[d]	**f**	0.27 (75)[b]	0.75	1.41	2.88 (105)[b]	2.16[d]

Table 7

Entry	R	Dicyanovinyl-arylthiophene 4	λ_{max} (nm)[a]	β (10^{-30}esu)[b]	β_0 (10^{-30}esu)[c]	Dicyanovinyl-arylbithiophene 6	λ_{max} (nm)[a]	β (10^{-30}esu)[b]	β_0 (10^{-30}esu)[c]	T_d (ºC)[d]
1	H	a	391.0	171 ± 12	68 ± 5	a	450.5	285 ± 30	67 ± 7	306
2	MeO	b	420.0	138 ± 12	44 ± 4	b	467.0	*	*	300
3	EtO	c	416.0	162 ± 12	53 ± 4	c	---	---	---	---
4	NMe$_2$	d	484.0	*	*	d	509.5	1050 ± 65	69 ± 5	328
5	NEt$_2$	---	---	---	---	e	520.0	772 ± 50	26 ± 2	309
6	Pyrrolidino	f	503.0	*	*	f	521.5	1650 ± 135	51 ± 4	413
7	pNA	---	352.0	16.9 [20]	8.5	---	---	---	---	---

Table 8

Entry	R	Dicyanovinyl-arylthiophene **4**	λ_{max} (nm)[a]	S_{NB}^{F} / S_{NB}	Dicyanovinyl-arylbithiophene **6**	λ_{max} (nm)[a]	S_{NB}^{F} / S_{NB}
1	H	**a**	391.0	0.18 ($\pm$ 0.08)	**a**	450.5	0.37 ($\pm$ 0.11)
2	MeO	**b**	420.0	0.10 (+0.12-0.10)	**b**	467.0	*
3	EtO	**c**	416.0	0.11 ($\pm$ 0.08)	**c**	---	---
4	NMe$_2$	**d**	484.0	*	**d**	509.5	0.32 ($\pm$ 0.05)
5	NEt$_2$	---	---	---	**e**	520.0	0.45 ($\pm$ 0.05)
6	Pyrrolidino	**f**	503.0	*	**f**	521.5	0.53 ($\pm$ 0.11)
7	*p*NA	---	352.0	16.9 [20]	---	---	---

Schemes

POCl$_3$ / DMF / 60 °C

Na$_2$S.9 H$_2$O / DMF / 60 °C

ClCH$_2$CHO / K$_2$CO$_3$

1a-d, **f**

2a-d, **f**

3a-d, **f**

a R = H
b R = MeO
c R = EtO
d R = NMe$_2$
f R = pyrrolidino

Scheme 1

32

3a-d, f

CH₂CN₂ / EtOH / CH₂Cl₂

piperidine / r.t.

5a-b, d-f

a R = H
b R = MeO
c R = EtO
d R = NMe₂
e R = NEt₂
f R = pyrrolidino

4a-d, f

6a-b, d-f

Scheme 2