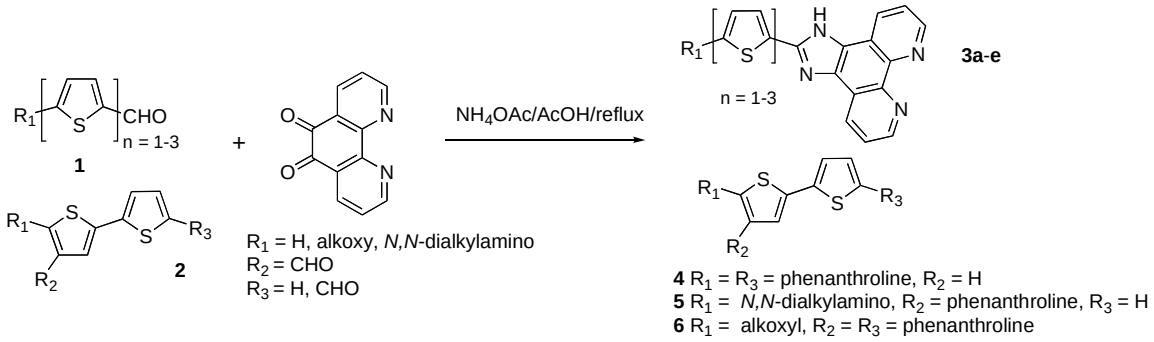
## Graphical Abstract

New thermally stable heterocyclic chromophores **3-6** based on a (oligo)thiophene π-conjugated bridge and a imidazo-phenanthroline moiety were synthesized in moderate to excellent yields by condensation of 5,6-phenanthroline-dione with formyl (oligo)thiophenes **1-2** in the presence of ammonium acetate in glacial acetic acid.



# Synthesis and characterization of novel (oligo)thienyl-imidazo-phenanthrolines as versatile π-conjugated systems for several optical applications

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**Abstract** – A series of new heterocyclic chromophores **3-6** were synthesised in moderate to excellent yields by condensation of 5,6-phenantroline-dione with formyl-thiophene derivatives **1-2** in the presence of ammonium acetate in glacial acetic acid. These chromophores possess a (oligo)thienyl- π-conjugated system attached to an imidazo-phenanthroline moiety. These derivatives were evaluated concerning their solvatochromic properties, thermal stabilities and molecular optical nonlinearities.

**Keywords:** π-conjugated systems, thiophene, imidazole, phenanthroline, solvatochromic probes, hyper-Rayleigh scattering (HRS), thermal stability, nonlinear optics (NLO).

## 1. Introduction

The design and synthesis of organic chromophores as nonlinear optical (NLO) materials has been the focal point of a large amount of recent research in great part due to the potential advances in the fields of optical communication, information processing, frequency doubling and integrated optics that could be realized by materials which display strong second optical nonlinearities together with robust material properties.[1] Donor-acceptor substituted heteroaromatic compounds have attracted widespread interest because it has been experimentally and theoretically demonstrated that they increase the second-order molecular NLO properties of push-pull chromophores with respect to the corresponding aryl analogues. It has also been demonstrated that the electron density of the π-conjugated system plays a

major role in determining second-order NLO response.[2] Electron excessive/deficient heterocycles act as auxiliary donors/acceptors when they are connected to donating/withdrawing groups, and the increase of donor/acceptor strength leads to substantial increase in $\beta$ values.[3]

Oligothiophenes behave as very efficient electron relays almost comparable to polyenes; thiophene has a lower resonance energy than that of benzene, and oligothiophenes have been shown to produce larger values of the molecular hyperpolarizability, $\beta$. The larger nonlinearities were attributed to the bathocromic effect of sulfur, the partial decrease of aromatic character and an increased $\pi$-overlap between the thiophene units. Oligophenylenes attain a rapid saturation beyond the terphenyl unit, whereas oligothiophenes have a strong tendency to increase $\beta$ as the number of thiophene units increases. Aside from the electron transmission efficiency, another merit of oligothiophenes is their inherent stability from which thiophene-based Donor (D)-Acceptor (A) chromophores should benefit.[4] Moreover, these push-pull systems are also excellent solvent polarity indicators due to their positive solvatochromism.[4b-e,g-i,j] This type of compounds can therefore be applied in electro-optical devices.[1]

Triaryl(heteroaryl)- imidazole[2e,5] and benzimidazole[6] based chromophores have received increasing attention due to their distinctive linear and nonlinear optical properties and also due to their excellent thermal stability in guest-host systems. Imidazole derivatives can be further substituted on the nitrogen atom so that the electron density of the chromophore can be changed. This functionalization will remove the possibility of tautomerism and introduces a new potentially useful chemical variable for the optimization of NLO activity of the chromophore (*e.g.* introduction of groups with suitable electronic properties). The imidazole ring can be easily tailored to accommodate functional groups, which allows the covalent incorporation of the NLO chromophores into polyamides leading to NLO side chain polymers.[5a,5d,7] For the practical application of second-order NLO materials, not only a high hyperpolarizability but also good thermal stability is required. In this respect, promising candidates are (benz)imidazole derivatives,[5-6] as well as conjugated (oligo)thiophenes.[4] Despite all these promising properties for NLO applications, only a few publications concerning the synthesis and characterization of NLO-chromophores based on triaryl(heteroaryl)- imidazoles can be found in the available literature.[2e,5a-e,h,m]

Due to their optoelectronic properties, aryl-imidazo-phenanthrolines play important roles in materials science and medicinal chemistry.[8-10] Therefore, they have found application as ligands for the synthesis of metal complexes of ruthenium(II), copper(II), cobalt(II), nickel (II), manganese(II) and several lanthanides especially for nonlinear optical (NLO) applications,[8a-c,g] while in medicinal chemistry they are important building blocks for the synthesis of proton, anion and cation sensors[9] or as ligands for ruthenium(II) and platinum(II) complexes with important and diverse biological applications such as probes of DNA structure or new therapeutic agents due to their capacity to bind or interact with DNA.[10]

New material properties can be achieved when new conjugated systems are composed by different heterocyclic nuclei which allow the fine tuning of important physical and/or photophysical properties. As a result of the optical and conductive properties, conjugated materials containing thiophene, imidazole and phenanthroline heterocycles have found many applications including those described above.[4-5,8-10]

Owing to synthetic difficulties, most of the NLO imidazoles developed so far, namely, 2,4,5-triaryl(heteroaryl)-imidazoles only possess short conjugation pathways (spacers) such as phenyl, thienyl or thiazolyl. [2e,5a-e,h,m] Our approach to the design of new π-conjugated systems for several potential optical applications is based on the use of electron-rich five-membered heteroaromatics such as thiophenes and imidazoles in the conjugation pathway, combined with electron deficient heterocycles such as phenanthroline which also acts as an acceptor group due to the deficiency of electron density on the C ring atoms. Furthermore, the planarity and the extension of conjugation of the phenanthroline moiety with imidazole and oligothienyl units leads to an increase of the overall conjugation. Additionally to the structural characteristics described above they exhibit also high thermal stabilities making them interesting for several applications in materials chemistry.[2e,11]

To the best of our knowledge, this is the first report on the synthesis and evaluation of the solvatochromic and optical (linear and nonlinear) properties of (oligo)thienyl-imidazo-phenanthroline derivatives. We are aware of only one article that reports the synthesis of a thienyl-imidazo-phenanthroline derivative in which the thiophene ring was linked to the imidazo-phenanthroline moiety through its 3-position. This compound was used as ligand on

the synthesis of a polypyridyl ruthenium complex as effective coating agent for the synthesis of gold or silver nanocomposites. [8f]

Following our interest in heterocyclic derivatives for several optical applications (e.g. NLO, OLED´s, etc.)[4b-e,g-k,12] we now report the synthesis and characterization of the thermal and optical properties of the new π-conjugated systems **3-6**, containing a functionalized oligothienyl π-conjugated bridge linked to the imidazo-phenanthroline system, which is original and different from other related reports.[8-10]

## 2. Results and discussion

### 2.1. Synthesis

#### 2.1.1. Synthesis of formyl-(oligo)thiophenes 1-2

The formylation of thiophene and oligothiophene derivatives is usually achieved through two methods: the Vilsmeier reaction,[4a-b,13] (or by a modified procedure of the Vilsmeier formylation using DMF/$POCl_3$ in dichloroethane[14]) or by metalation followed by formyldelithiation using DMF.[4a-b,15] More recently, palladium catalyzed cross-coupling reactions, have also been used in the synthesis of formyl- functionalized (oligo)thiophenes.[4c-d,h-i]

In order to compare the effect of the electronic nature of one or two imidazo-phenanthroline moieties on the optical properties of linear or angular oligothienyl-imidazo-phenanthrolines **3-6**, formyl-oligothiophenes **1-2** containing one or two formyl groups were used as precursors of phenanthrolines **3-6**. Compounds **1b**, **e-f** and **2b** were prepared using two different methods of synthesis: metalation followed by reaction with DMF (**1b** and **2b**) or through Suzuki cross-coupling reactions (**1e-f**).

Therefore, 5-formyl-2-methoxythiophene **1b** was synthesized using our recently reported procedure.[4b] The metalation of 2-methoxythiophene was carried out using 1.2 equivalents of *n*-BuLi in dry ether at 0 $^{o}$C for 1 h. Subsequently, the organolithium derivative was converted to the corresponding formyl thiophene by addition of 1.2 equivalents of DMF followed by refluxing the mixture for 1h, with a 73% yield.

Recently, we have demonstrated that 5-alkoxy- and 5-*N*,*N*-dialkylamino-2,2'-bithiophenes are selectively lithiated at the α-position of the thiophene ring giving only the mono-formylated derivatives, 5'-formyl-5-alkoxy- or 5'-formyl-5-*N*,*N*-dialkylamino-2,2'-bithiophenes, when equimolar amounts of bithiophene and DMF were used.[4b] In order to obtain the diformyl bithiophene **2b** an excess of the metalation reagent (2 equivalents) and also of DMF (2 equivalents) were used. Instead of the diformyl derivative **2b**, as the only product, we obtained a mixture of two compounds (confirmed by TLC and $^1$H NMR). The metalation of 5-methoxy-2,2'-bithiophene using two equivalents of *n*-BuLi in dry ether at 0 $^o$C for 1 h followed by reaction with two equivalents of DMF by refluxing the mixture for 1h produced a mixture of the two formylated derivatives: 5'-formyl-5-methoxy-2,2'-bithiophene[4b] in 42% yield and 5-methoxy-4,5'-diformyl-2,2'-bithiophene **2b** in 31% yield. The methoxy group in phenyl or benzyl derivatives is known as a moderately strong *ortho* directing substituent with electron withdrawing properties in metalation reactions.[15d,16] In 5-methoxy-2,2'-bithiophene **2b**, the methoxy group also demonstrated an *ortho* directing effect on the thiophene ring. Consequently, the formylation in the 4-position of the bithiophene moiety, *ortho* to the methoxy group was also observed for 5-methoxy-2,2'-bithiophene giving the diformylated derivative **2b**.

Compounds **1a** and **1c** were commercially available. The synthesis of 5'-formyl-2-methoxy-2,2'-bithiophene **1d** and 4-formyl-5-piperidino-2,2'-bithiophene **2a** has been reported by us, recently, through metalation followed by reaction with DMF or through Vilsmeier formylation.[4b]

### 2.1.2. Synthesis of (oligo)thienyl-imidazo-phenanthrolines 3-6

Mono- or diformyl (oligo)thiophenes **1-2** with the formyl group at α, β or α and β positions of the thiophene ring were used as precursors of linear and angular phenanthrolines **3-6** in order to evaluate the effect of the position of the phenanthroline group on the optical properties of these chromophores. Therefore, compounds **3-6** with either thienyl, bithienyl or terthienyl moieties (substituted with H, alkoxy or *N*,*N*-dialkylamino donor groups) linked to the imidazo-phenanthroline system, were synthesized in moderate to excellent yields (41-92%, Table 1), through the Radziszewski reaction,[17] of 5,6-phenanthroline-dione with formyl-thiophene derivatives **1-2** and ammonium acetate in refluxing glacial acetic acid for 15 h,

(Scheme 1), in order to evaluate also the effect of the nature of the π-conjugated bridge on the optical (linear and nonlinear) properties of chromophores **3-6**.

In the $^{1}$H NMR spectra of imidazo-phenanthroline derivatives signals at about 13.25-13.91 ppm for compounds **3** were detected. All signals appeared as broad singlets and were attributed to the N-H in the imidazole moiety. A broad correlation could be observed between the donor properties of the oligothienyl group attached to 2-position of the imidazole nucleus and the chemical shift of the nitrogen proton of the imidazole ring in compounds **3** (Table 1). In fact, from the data in Table 1, one may infer that an increase in the chemical shift of the NH proton in the $^{1}$H NMR spectra results from a decrease in donating electronic nature of the (oligo)thiophene moiety. The NH was also identified by IR spectroscopy as a sharp band within the spectral region of 3400-3437 $cm^{-1}$.

**<Scheme 1>**

**<Table 1>**

**2.2. UV-visible study of phenanthrolines 3-4**

All the compounds with the exception of *bis*-phenanthrolines **5-6** were soluble enough to allow the UV-visible study. The electronic spectra of phenanthrolines **3-4**, recorded in dioxane solutions ($10^{-4}$ M) showed an intense lowest energy charge-transfer absorption band in the UV-visible region (Table 2-3). The position of this band was strongly influenced by the structure of the compounds, for example by the length of the π conjugated bridge, by the electronic nature of the groups, (H or methoxy), substituted on the oligothienyl moiety and also by the number of the imidazo-phenanthroline moieties substituted on the (oligo)thienyl conjugated system.

Remarkable differences in energy occur upon conversion of formyl-oligothiophenes **1-2** to phenanthrolines **3-6**. For example, formyl-thiophene **1a** ($\lambda_{max}$ = 281.5 nm) is shifted 55 nm (phenanthroline **3a**, $\lambda_{max}$ = 336.5 nm). In the case of introduction of two imidazo-phenanthroline moieties *e.g.* diformyl-thiophene **1f** ($\lambda_{max}$ = 365.5 nm) is shifted 52.5 nm (phenanthroline **4**, $\lambda_{max}$ = 336.5 nm). (Table 3, entries 1 and 6 respectively).

The reason for the red shift in the investigated compound **3b** ($\lambda_{max}$= 346 nm) relative to the unsubstituted thienyl-imidazo-phenanthroline **3a** ($\lambda_{max}$= 336.5 nm) was the strong inductive

and conjugative effect of the alkoxy substituent (Table 3, entries 1 and 2 respectively). In general, the stronger the donor and/or acceptor group, the smaller the energy difference between ground and excited states, and the longer the wavelength of absorption. Comparison of the electronic absorption spectra of thienyl-imidazo-phenanthroline **3a** ($\lambda_{max}$ = 336.5 nm) with bithienyl-imidazo-phenanthroline **3c** ($\lambda_{max}$= 383.5 nm) and terthienyl-imidazo-phenanthroline **3e** ($\lambda_{max}$ = 411.5 nm) revealed that an increase in the number of thiophene units that constitutes the $\pi$ conjugated bridge causes a dramatic red shift of the charge-transfer band. This observation clearly indicates that the incorporation of thiophene units in push-pull compounds enhances their charge-transfer properties. The influence of the number of imidazo-phenanthroline moieties is demonstrated by comparison of the absorption maxima of compounds **3c** and **4** as the longest wavelength transition is shifted from 383.5 nm in 2,2´-bithiophenimidazo[4,5-*f*][1,10]phenanthroline **3c** to 418.0 nm in 2,2'-bithiophene-5,5'-*bis*-imidazo[4,5-*f*][1,10]phenanthroline **4**.

### 2.3. Solvatochromic behavior of phenanthrolines 3-4

Several studies have demonstrated that the replacement of a benzene ring by a less aromatic heterocycle in typical donor-acceptor chromogens of the same chain length and bearing the same D-A pair, results in a significant bathochromic shift (in a given solvent) of the visible absorption spectra. This red shift, obtained for example with thiophene, thiazole and pyrrole rings, suggests an increase of molecular hyperpolarizability, accordingly to theoretical NLO studies. Experimental data confirmed this positive effect, in particular, for the five-membered heterocycles mentioned above.[4c-e,g-i,6h,11] In order to investigate whether compounds **3-4** could act as suitable probes for the determination of solvent polarity, we carried out a study of the absorption spectra of compounds **3-4** in five selected solvents (ethanol, dioxane, chloroform, DMF and DMSO) of different solvation character (Table 2). The wavelength maxima $\lambda_{max}$ and wavenumber maxima $\upsilon_{max}$ of compounds **3-4** are listed in Table 2 and were compared with $\pi^*$ values for each solvent, determined by Kamlet et al..[18] Phenanthrolines **3-4** 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. In view of the strong solvatochromism, the good correlation with $\pi^*$ values for the 5 solvents investigated and the long wavelength absorption in the visible

range, compounds **3b** ($\Delta\nu_{max}$ = 1526 $cm^{-1}$), **3c** ($\Delta\nu_{max}$ = 752 $cm^{-1}$), **3e** ($\Delta\nu_{max}$ = 821 $cm^{-1}$) and **4** ($\Delta\nu_{max}$ = 838 $cm^{-1}$) appear to be quite reliable solvent polarity indicating dyes.

**<Table 2>**

### 2.4. Nonlinear optical properties and thermal stability of phenanthrolines 3-6

We have used the hyper-Rayleigh scattering (HRS) method[19] to measure the first hyperpolarizability $\beta$ of phenanthrolines **3-4** using the 1064 nm fundamental wavelength of a q-switched Nd:YAG laser. Dioxane was used as solvent, and the $\beta$ 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). Compounds **3a** and **3b** displayed exceptionally large amounts of fluorescence near the second harmonic wavelength of 532nm, leading to rather large uncertainties in the corresponding hyperpolarizabilites. The static hyperpolarizability ($\beta_0$) values were calculated using a simple two-level model neglecting damping. They are therefore only indicative and should be treated with caution (Table 3).

From Table 3 it is obvious that the increase of the donor strength of the group substituted on the thiophenic or bithiophenic moieties resulted both in red-shifted absorption maxima and enhanced $\beta$ values for phenanthrolines **3b** and **3d** (R= OMe), compared to derivatives **3a** and **3c** (R=H) (Table 3, entries 1-4). Although the uncertainties in the values for the  are rather high, a comparison of the respective values for **3a** (26 x $10^{-30}$ esu), **3c** (46 x $10^{-30}$ esu) and **3e** (320 x $10^{-30}$ esu) suggests that an increase in the number of thiophenic nuclei[4g] linked to the imidazo-phenanthroline moiety leads to progressively larger nonlinearities (Table 1, entries 1, 3 and 5 respectively).With the exception of *bis*-phenanthrolines **5-6** all the compounds were soluble in most common organic solvents. Therefore, only the latter two compounds were not soluble enough to permit HRS evaluation.

**<Table 3>**

All the oligothienyl-imidazo-phenanthrolines **3-6** are thermally stable, high melting materials, with melting points above 320 ºC. Thermal stability of compounds **3-6** was estimated by thermogravimetric analysis (TGA), measured at a heating rate of 20 ºC $min^{-1}$ under a nitrogen

atmosphere. The results obtained revealed the exceptional thermal stability for all compounds, which could be heated up to $T_d$ = 341–467 ºC (phenanthroline derivatives **3a**-**e**) or 389–725 ºC (*bis*-phenanthroline derivatives **4**-**6**). The increase of the number of thiophenic units, *e.g.,* as in **3c** ($T_d$ = 451 ºC) and **3e** ($T_d$ = 467 ºC) and especially the incorporation of a second phenanthroline moiety, e.g. comparison of **3c** ($T_d$ = 451 ºC ) with **4** ($T_d$ = 690 ºC), leads to highly thermal stable materials.

## 3. Conclusions

For the first time, a variety of donor-acceptor substituted phenanthrolines **3** and **5** and *bis*-phenanthrolines **4** and **6** have been synthesized, in moderate to excellent yields from easily available formyl-oligothiophenes **1**-**2** and low cost commercially available reagents, using simple and convenient procedures.

These materials exhibit good solvatochromic properties, exceptional thermal stabilities but modest NLO responses. The chromophore nonlinearieties depend primarily on the length of the π-conjugated bridge and secondarily on the type of substituents on the (oligo)thienyl moiety.

Our results concerning the nonlinear optical properties of phenantrolines **3**-**6** showed that, the resultant values for the hyperpolarizability $\beta$ are modest. Moreover, the hyperpolarizability $\beta$ of some compounds (specially compounds **3a** and **3c)** have rather high relative uncertainties due to the fact that the detected signals were relatively small and the amount of fluorescence was high. Althrough imidazo-phenanthroline derivatives have been of interest in the field of coordination chemistry for a number of years[8-10] only platinum and ruthenium complexes of aryl-imidazo-phenanthroline have been reported so far from different perspectives, mainly directed at studies of interactions with DNA. Therefore, some of the new phenantrolines **3**-**6**, due to their fluorescence, could be used for other interesting optical applications such as proton, anion and cation sensors with environmental, biological and medicinal applications and also as ligands for the synthesis of several metal complexes for diverse applications which are already underway.[23]

## 4. Experimental

### 4.1. General

Reaction progress was monitored by thin layer chromatography (0.25 mm thick precoated silica plates: Merck Fertigplatten Kieselgel 60 F254), while purification was effected by silica gel column chromatography (Merck Kieselgel 60; 230-400 mesh). 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). Mps were determined on a Gallenkamp apparatus and are uncorrected. Infrared spectra were recorded on a BOMEM MB 104 spectrophotometer. UV-vis absorption spectra (200 – 800 nm) were obtained using a Shimadzu UV/2501PC spectrophotometer. Elemental analyses were carried out on a Leco CHNS 932 instrument. Mass spectrometry analyses were performed at the "C.A.C.T.I. -Unidad de Espectrometria de Masas" at the University of Vigo, Spain.

All the solvents were of spectrophotometrical grade. Light petroleum refers to solvent boiling in the range 40-60 ºC. Compounds **1a** and **1c** were commercially available. The synthesis of formyl-oligothiophenes **1d** and **2a** was described elsewhere.[4b]

### 4.2. Procedures for the synthesis of formyl- derivatives 1b and 2b *via* metalation with *n*-BuLi followed by reaction with DMF

**4.2.1. Synthesis of 5-formyl-2-methoxythiophene (1b).** A 2.5 M solution of *n*-BuLi in hexanes (0.44 mL, 1.1 mmol) was dropped under Ar at 0 ºC to a stirred solution of 2-methoxythiophene (1.0 mmol) in anhydrous ether. The reaction mixture was then stirred 1 h at 0 ºC and was allowed to stand 15 min at room temperature. DMF (0.05 mL, 1.0 mmol) dissolved in anhydrous ether (2 mL) was added dropwise at room temperature. The mixture was heated at reflux for 1 h. The mixture was poured into water (20 mL) and extracted with (3 × 50 mL) of ethyl acetate. The combined organic extracts were washed with $H_2O$ (100 mL), dried with $MgSO_4$ and the solvent was evaporated under reduced pressure to give the crude 5-formyl-2-methoxythiophene **1b** which was purified by "flash" chromatography on silica with increasing amounts of diethyl ether in light petroleum as eluent. Compound **1b** was obtained as a brown oil (95%). UV (dioxane): $\lambda_{max}$ nm (log ε) 309.0 (3.95), 253.0 (3.57). IR (liquid film) $\nu$ 2931, 1657 (C=O), 1540, 1478, 1418, 1338, 1231, 1211, 1052, 988, 782 cm$^{-1}$. $^{1}$H

NMR ($CDCl_3$) δ 3.97 (s, 3H, OC*H*$_3$), 6.32 (d, 1H, *J*= 4.5 Hz, 3-H), 7.49 (d, 1H, *J*= 4.2 Hz, 4-H), 9.63 (s, 1H, C*H*O). $^{13}$C NMR ($CDCl_3$) δ 60.49, 106.29, 130.03, 137.65, 175.90, 182.28. MS (EI) *m/z* (%): 142 ($M^+$, 13), 141 (10), 99 (11), 86 (65), 84 (100), 71 (13). HRMS: (EI) *m/z* (%) for $C_6H_6O_2S$; calcd 142.0089; found 142.0093.

**4.2.2. Synthesis of 4,5'-diformyl-5-methoxy-2,2'-bithiophene (2b).** A 2.5 M solution of *n*-BuLi in hexanes (2.16 mL, 5.4 mmol) was dropped under Ar at 0 ºC to a stirred solution of 2-methoxythiophene (2.70 mmol) in anhydrous ether. The reaction mixture was then stirred 1 h at 0 ºC and was allowed to stand 15 min at room temperature. DMF (0.42 mL, 5.4 mmol) dissolved in anhydrous ether was added dropwise at room temperature. The mixture was heated at reflux for 1 h. The mixture was poured into water (20 mL) and extracted with (3 × 50 mL) of ethyl acetate. The combined organic extracts were washed with $H_2O$ (100 mL), dried with $MgSO_4$ and the solvent was evaporated under reduced pressure to give a mixture of 5-methoxy-5'-formyl-2,2'-bithiophene and 4,5'-diformyl-5-methoxy-2,2'-bithiophene **2b** which was purified by "flash" chromatography on silica with increasing amounts of diethyl ether in light petroleum as eluent. The first compound eluted was 5-methoxy-5'-formyl-2,2'-bithiophene[4b] (42%). The second compound eluted was 4,5'-diformyl-5-methoxy-2,2'-bithiophene **2b** as a green solid (27%). Mp: 170-172 ºC. UV (dioxane): $\lambda_{max}$ nm (log ε) 367.0 (4.80), 242.0 (4.75). IR (liquid film) $\nu$ 1665 (C=O), 1553, 1523, 1501, 1386, 1270, 1237, 1224, 1179, 1066, 1000, 973, 858, 827, 797, 666 $cm^{-1}$. $^1$H NMR ($CDCl_3$) δ 4.17 (s, 3H, OC*H*$_3$), 7.16 (d, 2H, *J*= 3.9 Hz, 4'-H), 7.46 (s, 1H, 3-H), 7.67 (d, 1H, *J*= 4.2 Hz, 3'-H), 9.86 (s, 1H, CHO), 9.93 (s, 1H, CHO). $^{13}$C NMR ($CDCl_3$) δ 62.48, 121.79, 122.18, 123.34, 123.80, 137.18, 141.76, 146.13, 176.51, 182.08, 182.32. MS (EI) *m/z* (%): 252 ($M^+$, 100), 237 (73), 209 (9), 153 (13), 137 (15), 127 (5), 109 (6). HRMS: (EI) *m/z* (%) for $C_{11}H_8O_3S_2$; calcd 251.991488; found 251.990697.

### 4.3. General procedure for the synthesis of formyl-(oligo)thiophenes 1e-f through Suzuki cross-coupling

2-Bromo-5-formylthiophene and 5-bromo-2,2'-bithiophene (1.2 mmol) were coupled to 5-formylthiophene boronic acid (1.6 mmol), in a mixture of DME (15 mL) and aqueous 2 M $Na_2CO_3$ (1 mL) and $Pd(PPh_3)_4$ (6 mol %) at 80 ºC under a argon atmosphere during 5-12 h. After cooling the mixture was filtered. Ethyl acetate and a saturated solution of NaCl were

added and the phases were separated. The organic phase was washed with water (3 × 50 mL) and a aqueous solution of NaOH (10%). The organic phase obtained was dried ($MgSO_4$), filtered and solvent removal gave a crude mixture which was submitted to column chromatography on silica with increasing amounts of diethyl ether in light petroleum as eluent, affording the coupled products **1e**-**f**.

**4.3.1. 5-Formyl-2,2':5'2''-terthiophene (1e)**. Orange solid (63%). Mp: 141.8-143.1 ºC. UV (dioxane): $\lambda_{max}$ nm (log ε) 396.0 (4.06), 267.0 (3.48). IR (KBr) $\nu$ 3095, 2959, 1728, 1650 (C=O), 1459, 1285, 1223, 1048, 833, 795, 708 $cm^{-1}$. $^1H$ NMR ($CDCl_3$) δ 7.06 (m, 1H, 4''-H), 7.13 (d, 1H, *J*= 3.9 Hz, 3''-H), 7.23-7.25 (m, 2H, 4'-H and 5''-H), 7.28-7.29 (m, 2H, 3'-H and 3-H), 7.68 (d, 1H, *J*= 3.9 Hz, 4-H), 9.87 (s, 1H, C*H*O). MS (FAB) *m/z* (%): 276 ($[M+H]^+$, 27), 275 ($M^+$, 26), 167 (22), 154 (38). HRMS: (FAB) *m/z* (%) for $C_{13}H_9OS_3$; calcd 275.9737; found 275.9745.

**4.3.2. 5,5'-Diformyl-2,2'-bithiophene (1f)**. Orange solid (40%). Mp: 215.9-217.2 ºC. UV (dioxane): $\lambda_{max}$ nm (log ε) 365.5 (4.45), 290.0 (3.71), 260.0 (3.69). IR (KBr) $\nu$ 3097, 2922, 1655 (C=O), 1511, 1437, 1385, 1277, 1225, 1053, 889, 799, 751, 676 $cm^{-1}$. $^1H$ NMR ($CDCl_3$) δ 7.77 (d, 2H, *J*= 4.2 Hz, 3'-H and 3-H), 8.05 (d, 2H, *J*= 3.9 Hz, 4'-H and 4-H), 9.93 (s, 2H, 2 × C*H*O). $^{13}C$ NMR ($CDCl_3$) δ 126.46, 136.91, 143.84, 144.82, 182.55. MS (EI) *m/z* (%): 223 ($M^+$+1, 20), 222 ($M^+$, 100), 220 (78), 192 (20), 149 (13), 133 (22), 83 (16). HRMS: (EI) *m/z* (%) for $C_{10}H_6O_2S_2$; calcd 221.9809; found 221.9815.

**4.4. General procedure for the synthesis of (oligo)thienyl-imidazo-phenanthrolines 3-6**

A mixture of formyl-(oligo)thiophene (1.2 mmol), $NH_4OAc$ (20 mmol) and 1,10-phenanthroline-5,6-dione (1 mmol) in glacial acetic acid (20 mL) was stirred and heated at reflux for 4h. The mixture was then cooled to room temperature and the product precipitated during neutralization with $NH_4OH$ 5 M. The precipitate was filtrated, washed with water and diethyl ether, recrystalized from methanol and dried at 50 ºC in *vacuo* to give the pure product.

**4.4.1. 2-Thiophenimidazo[4,5-*f*][1,10]phenanthroline (3a)**. Yellow solid (90%). Mp > 320 ºC. UV (dioxane): $\lambda_{max}$ nm (log ε) 336.5 (4.36), 282.5 (4.46), 247.0 (4.40). IR (KBr) $\nu$ 3430 (NH), 1668, 1561, 1295, 1237, 1130, 1075, 923, 853-795, 736 $cm^{-1}$. $^1H$ NMR (DMSO-$d_6$) δ

7.27-7.29 (m, 1H, 4'-H), 7.76 (dd, 1H, *J*= 4.8 and 1.2 Hz, 3'-H), 7.82 (br s, 2H, 5-H and 10-H), 7.90 (dd, 1H, *J*= 4.0 and 1.2 Hz, 5'-H), 8.84 (br s, 2H, 4-H and 11-H), 9.02 (dd, 2H, *J*= 4.4 and 1.2 Hz, 6-H and 9-H), 13.84 (s, 1H, N*H*). $^{13}$C NMR (DMSO-$d_6$) δ 119.06, 123.29, 126.07, 126.25, 128.31, 129.53, 133.39, 135.51, 143.54, 146.24, 147.81. MS (EI) *m/z* (%): 303 ($M^+$+1, 15), 302 ($M^+$, 100), 301 (9), 193 (5). HRMS: (EI) *m/z* for $C_{17}H_{10}N_4S$; calcd 302.0626; found 302.0623.

**4.4.2. 2-(5'-Methoxy-2'-thiophene)-imidazo[4,5-*f*][1,10]phenanthroline (3b)**. Dark red solid (92%). Mp > 320 ºC. UV (dioxane): $\lambda_{max}$ nm (log ε) 346.0 (3.84), 285.5 (3.93). IR (KBr) $\nu$ 3435 (NH), 1651, 1504, 1200, 1087, 968, 799, 730 cm$^{-1}$. $^1$H NMR (DMSO-$d_6$) δ 3.97 (s, 3H, OC$H_3$), 6.49 (d, 1H, *J*= 4.2 Hz, 4'-H), 7.58 (d, 1H, *J*= 4.2 Hz, 3'-H), 7.78-7.82 (m, 2H, 5-H and 10-H), 8.80 (dd, 2H, *J*= 8.4 and 1.8 Hz, 4-H and 11-H), 9.01 (dd, 2H, *J*= 6.0 and 1.8 Hz, 6-H and 9-H), 13.25 (s, 1H, N*H*). $^{13}$C NMR (DMSO-$d_6$) δ 60.36, 105.04, 119.02, 119.18, 123.16, 123.39, 124.90, 125.94, 129.44, 129.64, 135.29, 143.23, 143.44, 146.62, 147.70, 167.50. MS (FAB) *m/z* (%): 333 ([M+H]$^+$, 100), 332 ($M^+$, 33), 307 (17), 289 (12), 155 (20), 154 (63). HRMS: (FAB) *m/z* for $C_{18}H_{13}N_4OS$; calcd 333.0810; found 333.0808.

**4.4.3. 2-(2',2''-Bithiophene)-imidazo[4,5-*f*][1,10]phenanthroline (3c)**. Orange solid (88%). Mp > 320 ºC. UV (dioxane): $\lambda_{max}$ nm (log ε) 383.5 (4.45), 288.0 (4.23), 249.0 (4.35). IR (KBr) $\nu$ 3437 (NH), 3071, 1572, 1489, 1426, 1401, 1353, 1231, 1130, 1094, 1028, 926, 805, 739, 721, 686 cm$^{-1}$. $^1$H NMR (DMSO-$d_6$) δ 7.14-7.20 (m, 1H, 4''-H), 7.45 (d, 1H, *J*= 3.9 Hz, 3'-H), 7.48 (dd, 1H, *J*= 3.2 and 1.2 Hz, 3''-H), 7.60 (dd, 1H, *J*= 4.8 and 1.2 Hz, 5''-H), 7.76-7.82 (m, 2H, 5-H and 10-H), 7.84 (d, 1H, *J*= 3.9 Hz, 4'-H), 8.84 (d, 2H, *J*= 7.5 Hz, 4-H and 11-H), 9.00-9.08 (m, 2H, 6-H and 9-H), 13.90 (s, 1H, N*H*). $^{13}$C NMR (DMSO-$d_6$) δ 123.35, 124.89, 126.28, 127.05, 128.60, 129.54, 131.80, 134.40, 135.92, 138.13, 140.55, 143.62, 145.76, 147.93. MS (EI) *m/z* (%): 384 ($M^+$, 26), 192 (5), 147 (7), 138 (7), 99 (7), 63 (11), 62 (100). HRMS: (EI) *m/z* for $C_{21}H_{12}N_4S_2$; calcd 384.0503; found 384.0521.

**4.4.4. 2-(5''-Methoxy-2',2''-bithiophene)-imidazo[4,5-*f*][1,10]phenanthroline (3d)**. Brown solid (76%). Mp > 320 ºC. UV (dioxane): $\lambda_{max}$ nm (log ε) 393.0 (4.44), 276.5 (4.33), 249.0 (4.39). IR (KBr) $\nu$ 3400 (NH), 3078, 2935, 1655, 1573, 1501, 1425, 1351, 1250, 1200, 1131, 1091, 1052, 1029, 991, 925, 805 cm$^{-1}$. $^1$H NMR (DMSO-$d_6$) δ 3.90 (s, 3H, OC$H_3$), 6.37 (d,

1H, *J*= 4.2 Hz, 4''-H), 7.14 (d, 1H, *J*= 4.2 Hz, 3''-H), 7.26 (d, 1H, *J*= 3.9 Hz, 3'-H), 7.79 (d, 1H, *J*= 3.9 Hz, 4'-H), 7.80-7.90 (m, 2H, 5-H and 10-H), 8.75-8.90 (m, 2H, 4-H and 11-H), 9.00-9.10 (m, 2H, 6-H and 9-H), 13.90 (s, 1H, N*H*). $^{13}$C NMR (DMSO-$d_6$) δ 60.38, 105.23, 112.76, 118.65, 121.92, 122.75, 122.97, 126.78, 129.26, 130.39, 135.35, 138.72, 143.49, 145.67, 147.62, 165.45. MS (EI) *m/z* (%): 414 ($M^+$, 4), 384 (6), 186 (15), 165 (20), 151 (28), 137 (31), 123 (37), 110 (48), 98 (98), 97 (55), 84 (92), 83 (100), 68 (63). HRMS: (EI) *m/z* for $C_{22}H_{14}N_4OS_2$; calcd 414.0609; found 414.0620.

**4.4.5. 2-(2',2'':5'',2'''-Terthiophene)-imidazo[4,5-*f*][1,10]phenanthroline (3e)**. Brown solid (83%). Mp > 320 ºC. UV (dioxane): $\lambda_{max}$ nm (log ε) 411.5 (4.43), 393.0 (4.44), 275.0 (4.31), 253.0 (4.41). IR (KBr) *ν* 3426 (NH), 3071, 2926, 2851, 1723, 1655, 1565, 1487, 1391, 1271, 1131, 1029, 926, 792, 738 cm$^{-1}$. $^1$H NMR (DMSO-$d_6$) δ 7.10-712 (m, 1H, 4'''-H), 7.30-7.41 (m, 4H, 3'-H, 3''-H, 4''-H and 3'''-H), 7.55 (dd, 1H, *J*= 4.2 and 1.2 Hz, 5'''-H), 7.77-7.82 (m, 3H, 4'-H, 5-H and 10-H), 8.80-8.84 (m, 2H, 4-H and 11-H), 8.97-8.99 (m, 2H, 6-H and 9-H). $^{13}$C NMR (DMSO-$d_6$) δ 121.71, 123.18, 123.31, 124.48, 125.10, 125.55, 125.90, 126,63, 127,34, 128.50, 129.54, 130.52, 131.88, 133.39, 134.05, 134.86, 135.87, 136.83, 138.05, 141.07, 143.49, 144.04, 146.78, 147.49. MS (FAB) *m/z* (%): 467 ($[M+H]^+$, 16), 466 ($M^+$, 7), 441 (15), 391 (18), 316 (34), 288 (46), 154 (23). HRMS: (FAB) *m/z* for $C_{25}H_{15}N_4S_3$; calcd 467.0459; found 467.0446. $C_{25}H_{14}N_4S_3$: calcd. C 64.35, H 3.02, N 12.01, S 20.62; found C 64.28, H 3.07, N 12.12, S 20.79.

**4.4.6. 2-(2',2''-Bithiophene)-*bis*[imidazo[4,5-*f*][1,10]phenanthroline] (4).** Orange solid (79%). Mp > 320 ºC. UV (dioxane): $\lambda_{max}$ nm (log ε) 418.0 (3.84), 321.0 (3.49), 262.0 (3.79). IR (KBr) *ν* 3435 (NH), 3065, 1651, 1563, 1481, 1427, 1352, 1232, 1131, 1029, 927, 805, 739 cm$^{-1}$. $^1$H NMR (DMSO-$d_6$) δ 7.68 (d, 1H, *J*= 4.0 Hz, 3'-H or 4'-H), 7.73 (d, 1H, *J*= 4.0 Hz, 3'-H or 4'-H), 7.80-7.90 (m, 6H, 3'-H, 4'-H, 2 × 5-H and 2 × 10-H), 8.80-8.88 (m, 4H, 2 × 4-H and 2 × 11-H), 9.00-9.08 (m, 4H, 2 × 6-H and 2 × 9-H), 13.93 (s, 1H, N*H*), 14.00 (s, 1H, N*H*). $^{13}$C NMR (DMSO-$d_6$) δ 123.42, 123.62, 125.95, 127.31, 127.94, 129.70, 130.00, 134.49, 136.42, 137.49, 144.74, 145.28, 148.09. MS (FAB) *m/z* (%): 603 ($[M+H]^+$, 5), 460 (7), 413 (8), 307 (36), 289 (18), 232 (24), 155 (30), 154 (100). HRMS: (FAB) *m/z* for $C_{34}H_{19}N_8S_2$; calcd 603.1174; found 603.1165. $C_{34}H_{18}N_8S_2$: calcd. C 67.76, H 3.01, N 18.59, S 10.64; found C 67.65, H 3.09, N 18.63, S 10.75.

**4.4.7. 2-(5''-Piperidino-2',2''-bithiophene)-imidazo[4,5-*f*][1,10]phenanthroline (5).** Brown solid (41%). Mp > 320 ºC. IR (KBr) $\nu$ 3421 (NH), 3061, 2932, 2851, 2797, 2363, 1665, 1572, 1493, 1445, 1376, 1124-1020, 803, 740, 691 $cm^{-1}$. $^1H$ NMR (DMSO-$d_6$ with TFA-*d*) δ 1.80-2.10 (m, 6H, 3 × C$H_2$), 2.20-2.60 (m, 4H, 2 × NC$H_2$), 7.21 (br s, 1H, 4'-H), 7.40-7.60 (m, 1H, 5''-H), 8.41-8.60 (m, 4H, 4''-H, 3''-H, 5-H and 10-H), 9.42-9.57 (m, 4H, 4-H, 6-H, 9-H and 11-H). MS (FAB) *m/z* (%): 468 ($[M+H]^+$, 23), 467 ($M^+$, 10), 307 (26), 289 (17), 232 (61), 157 (96), 154 (100). HRMS: (FAB) *m/z* for $C_{26}H_{22}N_5S_2$; calcd 468.1317; found 468.1317. $C_{26}H_{21}N_5S_2$: calcd. C 66.78, H 4.53, N 14.98, S 13.71; found C 66.71, H 4.62, N 15.05, S 13.59.

**4.4.8. 2-(5'-Methoxy-2',2''-bithiophene)-*bis*[imidazo[4,5-*f*][1,10]phenanthroline] (6).** Dark brown solid (80%). Mp > 320 ºC. IR (KBr) $\nu$ 3430 (NH), 3071, 2917, 1631, 1481, 1424, 1398, 1316, 1226, 1017, 805, 738, 720 $cm^{-1}$. $^1H$ NMR (DMSO-$d_6$ with TFA-*d*) δ 4.28 (s, 1H, $OCH_3$), 8.12-8.27 (m, 6H, 2 × 5-H, 2 × 10-H, 3'-H and 4'-H), 9.01-9.29 (m, 9H, 2 × 4-H, 2 × 11-H, 2 × 6-H, 2 × 9-H and 3''-H). MS (FAB) *m/z* (%): 633 (**[**$M+H]^+$, 4), 316 (10), 308 (10), 307 (38), 289 (18), 288 (14), 155 (30), 154 (100). HRMS: (FAB) *m/z* for $C_{35}H_{21}N_8OS_2$; calcd 633.1280; found 633.1279. $C_{35}H_{20}N_8OS_2$: calcd. C 66.44, H 3.19, N 17.71, S 10.14; found C 66.36, H 3.27, N 17.75, S 10.30.

## 4.3. Nonlinear optical measurements for compounds 4-5 using the hyper-Rayleigh scattering (HRS) method[19a]

Hyper-Rayleigh scattering (HRS) was used to measure the first hyperpolarizability $\beta$ of response 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 25 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 $\beta$ values were calibrated using a reference solution of *p*-nitroaniline (*p*NA)[19b] also dissolved in dioxane at a concentration of $1 \times 10^{-2}$ M (external reference method). The hyperpolarizability of *p*NA 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 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 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" (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 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 (25 ns). The resultant values for the hyperpolarizability and the associated uncertainties are reported in table 3. The uncertainties take have been calculated using the measured variances in the signals obtained using the

narrow and wide band filters for both the compound and the background obtained from the measurements on pure dioxane and the *p*NA reference solution. Measurements for compound **3c** and especially compound **3a** have rather high relative uncertainties due to the fact that detected signals were relatively small and the amount of fluorescence is high. Once the fluorescence and the background from the dioxane solvent are discounted, the remaining contribution is not much greater than the combined the statistical fluctuations of the signals from the compound and references.

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 the following table:

| Compound | $S_{NB}^{F} / S_{NB}$ |
|---|---|
| **3a** | 0.87 (+0.13, -0.66) |
| **3b** | 0.59 (±0.24) |
| **3c** | 0.73 (±0.51) |
| **3d** | 0.59 (±0.10) |
| **3e** | 0.63 (±0.07) |

The higher level of uncertainty for compounds **3a** and **3c** is also reflected in the estimated uncertainty of the fluorescence contribution for these compounds.

### 4.4. Thermogravimetric analysis of compounds 3-6

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 phenanthrolines **3-6** by condensation of 5,6-phenanthroline-dione with formyl (oligo)thiophenes **1-2** in the presence of ammonium acetate in glacial acetic acid.

**Table 1.** Yields, IR absorption spectra and $^1$H RMN spectra of phenanthrolines **3-6**.

[a] For the NH stretching band (recorded in KBr).

[b] For the NH proton of the imidazole ring for compounds **3-6** (DMSO-$d_6$).

**Table 2**. Solvatochromic data [$\lambda_{max}$ (nm) and $\upsilon_{max}$ ($cm^{-1}$) of the charge-transfer band] for phenanthrolines **3-4** in selected solvents with $\pi^*$ values by Kamlet et al.[18a]

[a] Solvents used as received.

**Table 3**. UV-visible absorption for formyl-(oligo)thiophenes **1-2** and phenanthrolines **3-6**, $\beta$ and $\beta_0$ values and $T_d$ data for phenanthrolines **3-6**.[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.

[e] Due to insolubility it was not possible to obtain the UV-visible spectrum.

[f] Due to insolubility it was not possible to obtain the first hyperpolarizability, $\beta$ value.

**Table 1**

| Entry | Formyl-oligothiophene | Oligothienyl-phenanthroline | $R_1$ | n | Yield (%) | IR ν ($cm^{-1}$)[a] | $\delta_H$ (ppm)[b] |
|---|---|---|---|---|---|---|---|
| 1 | **1a** | **3a** | H | 1 | 90 | 3430 | 13.84 |
| 2 | **1b** | **3b** | MeO | 1 | 92 | 3435 | 13.25 |
| 3 | **1c** | **3c** | H | 2 | 88 | 3437 | 13.91 |
| 4 | **1d** | **3d** | MeO | 2 | 76 | 3400 | 13.90 |
| 5 | **1e** | **3e** | H | 3 | 83 | 3426 | not visible |
| 6 | **1f** | **4** | --- | 2 | 79 | 3435 | 13.93, 14.00 |
| 7 | **2a** | **5** | Piperidino | 2 | 41 | 3421 | not visible |
| 8 | **2b** | **6** | MeO | 2 | 80 | 3430 | not visible |

**Table 2**

| Solvent[a] | π* | Compound | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | **3a** | | **3b** | | **3c** | | **3d** | | **3e** | | **4** | |
| | | $\lambda_{max}$ | $\nu_{max}$ | $\lambda_{max}$ | $\nu_{max}$ | $\lambda_{max}$ | $\nu_{max}$ | $\lambda_{max}$ | $\nu_{max}$ | $\lambda_{max}$ | $\nu_{max}$ | $\lambda_{max}$ | $\nu_{max}$ |
| EtOH | 0.54 | 333.0 | 30030 | 339.0 | 29498 | 377.0 | 26525 | 389.0 | 25706 | 406.0 | 24630 | 413.0 | 24213 |
| dioxane | 0.55 | 336.5 | 29717 | 346.0 | 28902 | 383.5 | 26075 | 393.0 | 25445 | 411.5 | 24301 | 418.0 | 23923 |
| $CHCl_3$ | 0.76[18b] | 337.0 | 29673 | 348.0 | 28736 | 381.0 | 26246 | 391.0 | 25575 | 410.0 | 24390 | 413.8 | 24166 |
| DMF | 0.88 | 336.0 | 29761 | 356.5 | 28050 | 386.0 | 25906 | 393.0 | 25445 | 419.0 | 23866 | 421.0 | 23753 |
| DMSO | 1.00 | 337.0 | 29673 | 357.5 | 27972 | 388.0 | 25773 | 394.0 | 25380 | 420.0 | 23809 | 427.8 | 23375 |

**Table 3**

| Entry | Formyl-oligothiophene | UV-Vis. $\lambda_{max}$ (nm)[a] | Oligothienyl-phenanthroline | $R_1$ | n | UV-Vis. $\lambda_{max}$ (nm)[a] (log ε) | $\beta/10^{-30}$ (esu)[b] | $\beta_0/10^{-30}$ (esu)[c] | $T_d$ ($^oC$)[d] |
|---|---|---|---|---|---|---|---|---|---|
| 1 | **1a** | 281.5 | **3a** | H | 1 | 336.5 (4.36) | 26 (+63, -26) | 14 | 441 |
| 2 | **1b** | 309.0 | **3b** | MeO | 1 | 346.0 (3.84) | 110 (±40) | 57 | 341 |
| 3 | **1c** | 349.5 | **3c** | H | 2 | 383.5 (4.45) | 46 (±43) | 19 | 451 |
| 4 | **1d** | 375.5 | **3d** | MeO | 2 | 393.0 (4.44) | 170 (±40) | 67 | 423 |
| 5 | **1e** | 396.0 | **3e** | H | 3 | 411.5 (4.43) | 320 (±60) | 110 | 467 |
| 6 | **1f** | 365.5 | **4** | --- | 2 | 418.0 (3.84) | --- | --- | 690 |
| 7 | **2a** | 335.6 | **5** | Piperidino | 2 | ---[e] | ---[f] | --- | 389 |
| 8 | **2b** | 367.0 | **6** | MeO | 2 | ---[e] | ---[f] | --- | 725 |
| 9 | --- | --- | *p*NA | --- | --- | 352.0 | 16.9 | 8.5 | --- |

## Schemes

**Scheme 1**