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Synthesis and optical properties of novel, thermally stable phenanthrolines bearing an arylthienyl-imidazo conjugation pathway

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ABSTRACT

Six new hyperpolarizable chromophores based on functionalized arylthiophene donors and an imidazo-phenanthroline acceptor moiety have been designed and synthesized for the first time in good to excellent yields by condensation of 5,6-phenantroline-dione with formyl-arylthiophene derivatives in the presence of ammonium acetate in glacial acetic acid. The thermal stability, solvatochromic and nonlinear optical properties of these compounds were evaluated.

1. Introduction

For the last three decades the design and synthesis of organic nonlinear optical (NLO) chromophores has been one of the fastest growing areas of research, being connected with important advances in the fields of medicine, signal processing and optical computation. In particular much interest has been focused on the potential of organic chromophores as versatile, easy to synthesize electro-optic (EO) materials. To be technologically attractive NLO-chromophores should be endowed with important material properties including high thermal and chemical stability, large nonlinearity and good transparency, as well as easy synthesis [1].

The standard approach to obtaining organic molecules with strong hyperpolarizabilities is to connect donor and acceptor moieties with a π-conjugated bridge. While initial efforts concentrated on using benzene moieties to construct the bridge, it has been recently realized that by modulating the aromatic stabilization energy along the conjugated bridge, dramatically increased hyperpolarizabilities can be obtained. Several experimental and theoretical studies have indicated that the use of easily delocalizable five-membered heterocycles (*e.g.* thiophene [2] and pyrrole [3] as electron-rich and (benzo)thiazole [4] and (benz)-imidazole [5] as electron deficient moieties) instead of benzene rings results in enhanced molecular hyperpolarizabilities of the donor/acceptor substituted compounds. The modulation of the electron density along the π-conjugated system seems to play a major role in localizing the eigenfunctions on different parts of the molecules. In effect, electron excessive/deficient heterocycles act as auxiliary donors/acceptors when they are connected to donating/withdrawing groups, and the enhancement of donor/acceptor strength can lead to substantial increases in the hyperpolarizability [6].

Chromophores based on triaryl(heteroaryl)-imidazoles display interesting optical properties, as well as excellent thermal stability and their application in guest–host systems has been the subject of various reports in recent years [5]. For the practical application of second-order NLO materials, good thermal stability and high hyperpolarizability is required. In this respect, promising candidates are imidazole derivatives [5], as well as conjugated push-pull arylthiophenes [4c] and (oligo)thiophenes [2]. 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 were found in the available literature [5a–h].

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Due to their strong optoelectronic responses, aryl-imidazo-phenanthrolines have been actively investigated from a materials science perspective [7]. In particular they have been employed as ligands in the synthesis of a variety of metal complexes, which have been developed for use in NLO applications [7a–c,e]. The nonlinear optical studies showed that the more efficient systems were ruthenium complexes containing as ligands aryl-imidazo-phenanthrolines in which the aryl rings were functionalized with nitro groups at *para* position [7a,c].

2,4,5-Triaryl(heteroaryl)-imidazoles bearing more than one aryl or an heteroaryl moiety (thiophene or thiazole) as spacers [5] are a synthetic challenge and therefore most of the NLO imidazoles developed so far possess short conjugation pathways (spacers). To circumvent this limitation and augment the effective conjugation we have used a functionalized arylthiophene together with a imidazo moiety in the conjugation pathway, combined with the phenanthroline heterocycle instead of the diaryl system. The latter moiety acts as an acceptor group due to the electron density deficiency on the ring C atoms. Furthermore, the planarity [5a] and the extension of conjugation of the phenanthroline moiety with imidazole and arylthiophene units lead to an enhancement of the overall conjugation with a subsequent increase in the molecular hyperpolarizabilities. Especially noteworthy is the fact that all the synthesized compounds have absorption maxima in the near ultraviolet region of the spectrum, in sharp contrast to the vast majority of strong nonlinear optical chromophores that absorb strongly in the red portion of the visible spectrum. Thus our design strategy may provide a means of circumventing the usual trade-off between strong hyperpolarizability and transparency that plague most other approaches. We feel that the synthesis and characterization of new arylthienyl-imidazo-phenanthrolines represents an original contribution in the field of heterocyclic based solvatochromic probes and NLO-chromophores.

A number of factors prompted us to synthesize and study the properties of arylthienyl-substituted imidazo-phenanthrolines **3**–**4**:

(i) despite the growing interest in NLO heteroaromatic chromophores, relevant information concerning the relation between molecular structure and effective material properties for these NLO systems is still scarce;
(ii) our experience in the chemistry of functionalized heterocycles, namely (oligo)thiophenes [2a–c], thienylpyrroles [3b–d], benzothiazoles [4a,4c–d] and benzimidazoles [5i];
(iii) the limited presence in the available literature of related systems [5a–h,7];
(iv) the high thermal stabilities of compounds derived from imidazole and thiophene, which is an important characteristic for the prospective technological applications of these molecules.

Accordingly and as part of our continuing interest in developing chromophores for several optical applications, we describe here the synthesis, thermal stability, solvatochromic and nonlinear optical properties of a series of heterocyclic chromophores of the imidazo-phenanthroline type containing a arylthienyl moiety substituted with various groups such as alkoxy, *N*,*N*-dialkylamino, cyano and nitro which is original and different from other related reports [5a–h,7].

2. Results and discussion

2.1. Synthesis

2.1.1. Synthesis of formyl-arylthiophenes 1d and 1e

Formyl and diformyl-arylthiophenes **1a**–**f** functionalized with several groups (methoxy, *N*,*N*-dimethylamino, cyano and nitro), were used as precursors in the synthesis of phenanthrolines **3** and **4**, in order to evaluate the influence of the different electron donor and acceptor strengths of these groups on the solvatochromic and nonlinear optical properties of donor/acceptor systems **3** and **4**.

The formyl-arylthienyl derivatives **1d** and **1e** were synthesized by $Pd(PPh_3)_4$ catalyzed cross-coupling reaction of 5-formylthiophene boronic acid with 1-bromo-4-cyanobenzene or 1-bromo-4-nitrobenzene to give formyl-arylthiophenes **1d** (82% yield) and **1e** (60% yield), respectively (Scheme 1).

2.1.2. Synthesis of arylthienyl-imidazo-phenanthrolines 3 and 4

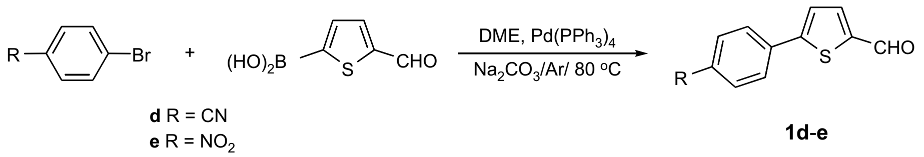
A series of phenanthrolines **3**–**4** was synthesized with either hydrogen, methoxy- and *N*,*N*-dimethylamino-donors or cyano and nitro acceptor groups on the arylthienyl system. Compounds **3**–**4** were synthesized in good to excellent yields (50–95%), by a standard cyclo-condensation reaction of 5,6-phenanthroline-dione **2** with formyl-arylthiophenes **1a**–**e** or diformyl-arylthiophene **1f** and ammonium acetate in refluxing glacial acetic acid [8] for 4 h (Scheme 2, Table 1).

In the ^{1}H NMR spectra of phenanthroline derivatives **3**–**4** signals in the range of 13.79–14.00 ppm 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 electronic nature of the functionalized arylthienyl moiety attached to position 2 of the imidazole nucleus and the chemical shift of the nitrogen proton of the imidazole ring in compounds **3**–**4** (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 functionalized arylthiophene moiety. The NH was also identified by IR spectroscopy as a sharp band at about 3410–3480 cm^{-1}.

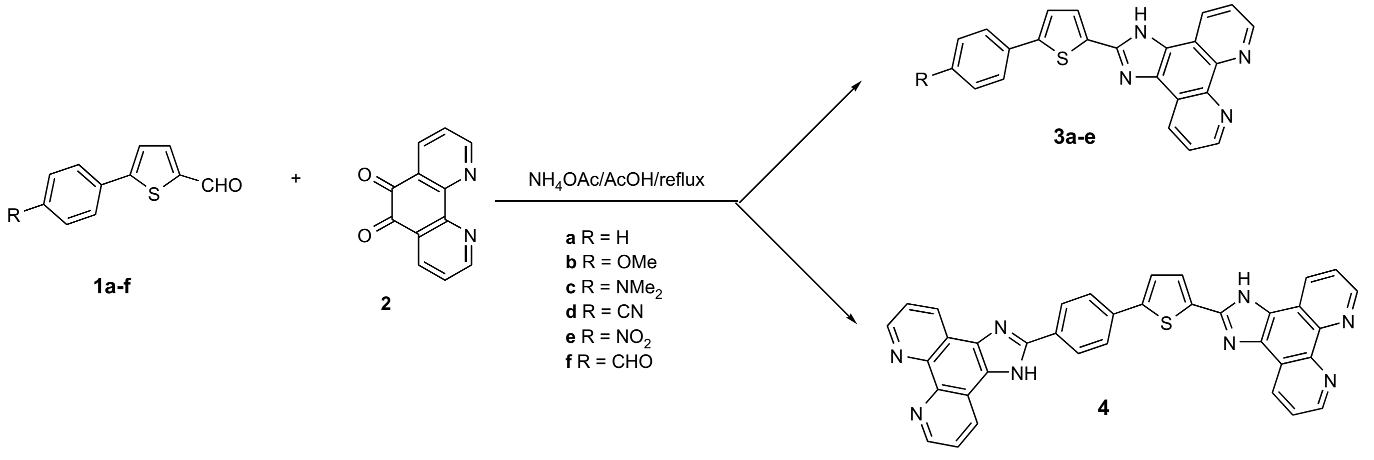
2.2. UV–visible study of arylthienyl-imidazo-phenanthrolines 3–4

The interesting photophysical properties of compounds such as arylthienyl-imidazo-phenanthrolines can be attributed to the presence in their molecules of different chromophores: imidazole, phenanthroline and the functionalized arylthienyl systems.

Electronic absorption spectra of all phenanthroline derivatives **3**–**4** in dioxane showed an intense lowest energy charge-transfer absorption band in the UV–visible region. The position of this band depended on the electronic nature of the substitutent at position 4 of the arylthiophene moiety (Table 1). The reason for the substantial red shift in the investigated compounds **3b**–**c**, functionalized with donor groups, $\lambda_{max} = 370.0–391.0$ nm, and **3d**–**e**, functionalized with acceptor groups, $\lambda_{max} = 386.0–408.0$ nm, relative to that of unsubstituted phenanthroline **3a** ($\lambda_{max} = 361.0$ nm) was the strong inductive and conjugative effect of the methoxy, *N*,*N*-dimethylamino, cyano or nitro substituent at the *para* position of the phenyl ring.



Scheme 1. Synthesis of formyl-arylthiophenes **1d** and **1e** through Suzuki coupling.



Scheme 2. Synthesis of arylthienyl-imidazo-phenanthrolines **3** and **4**.

The influence of the strength of the donor group was demonstrated by comparison of the absorption maxima of compounds **3b** and **3c** as the longest wavelength transition was shifted from 370.0 nm in 4-methoxyphenythienyl-imidazo-phenanthroline **3b** to 391.0 nm in 4-*N*,*N*-dimethylaminophenylthienyl-imidazo-phenanthroline **3c**. The influence of the phenanthroline moiety was demonstrated by comparison of the absorption maxima of compounds **3a** and **4** as the longest wavelength transition was shifted from 361.0 nm in phenylthienyl-imidazo-phenanthroline **3a** to 399.0 nm in phenylthienyl-bis-phenanthroline **4**.

The shifts of the absorption maxima were proportional to the intramolecular charge-transfer between the electron-releasing and withdrawing groups. 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. The increase of the β values, characteristic of the strength of the NLO response, is accompanied by an increase in the wavelength of the absorption maximum λ_{max} in the UV–visible spectra, *i.e.* a decrease in the intramolecular charge-transfer (ICT) values [2c,e,9].

2.3. Solvatochromic behavior of arylthienyl-imidazo-phenanthrolines 3–4

Several studies have showed that donor/acceptor substituted oligothiophenes, arylthiophenes and (benz)imidazoles exhibit strong positive solvatochromic behavior [2b–c,e,4a,4c–d,5i]. In order to investigate if 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 λ_{max} and wavenumber maxima ν_{max} of compounds **3**–**4** are listed in Table 2 and were compared with π^* values for each solvent, determined by Kamlet et al. [10]. 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 the increase of polarity of the solvent. In view of the good solvatochromism and the long wavelength absorption in the visible range, compounds **3a** ($\Delta\nu_{max} = 815\ cm^{-1}$), **3e** ($\Delta\nu_{max} = 1024\ cm^{-1}$) and **4** ($\Delta\nu_{max} = 693\ cm^{-1}$) appear to be quite reliable solvent polarity indicating dyes.

2.4. Nonlinear optical properties and thermal stability of arylthienyl-imidazo-phenanthrolines 3–4

We have used the hyper-Rayleigh scattering (HRS) method [11] to measure the first hyperpolarizability β of phenanthrolines **3**–**4** using the 1064 nm fundamental wavelength of a laser beam. Dioxane was used as solvent, and the β values were measured against a reference solution of *p*-nitroaniline (*p*NA) [12] in order to obtain quantitative values, while care was taken to properly

Table 1
Yields, IR and ^{1}H NMR spectra, UV–visible absorption, β and β_0 values and T_d data for arylthienyl-imidazo-phenanthrolines **3**–**4**

Formyl-arylthiophene	Arylthienyl-phenanthroline	R	Yield (%)	IR, ν (cm^{-1})	δ_H (ppm)[d]	UV–visible, λ_{max} (nm)[e] (log ε)	β (10^{-30} esu)[f]	β_0 (10^{-30} esu)[g]	T_d (°C)[h]
1a	**3a**	H	95	3441[c]	13.86	361.0 (4.16)	41	20	470
1b	**3b**	OMe	50	3410[c]	13.84	370.0 (4.48)	145	66	431
1c	**3c**	NMe_2	60	3450[b]	13.80	391.0 (4.34)	189	75	448
1d	**3d**	CN	75	3480[b]	Not visible	386.0 (4.45)	91	38	465
1e	**3e**	NO_2	86	3453[a]	14.00	408.0 (4.12)	45	16	450
1f	**4**	–	80	3435[a]	13.79, 13.89	399.0 (4.30)	–	–	739
–	*p*NA	–	–	–	–	352.0	16.9	8.5	–

[a] For the NH stretching band (recorded in KBr).
[b] For the NH stretching band (recorded in Nujol).
[c] For the NH stretching band (recorded in liquid film).
[d] For the N*H* proton of the imidazole ring for compounds **3**–**4** (DMSO-d_6).
[e] Experimental hyperpolarizabilities and spectroscopic data measured in dioxane solutions.
[f] All the compounds are transparent at the 1064 nm fundamental wavelength.
[g] 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 [13].
[h] Decomposition temperature (T_d) measured at a heating rate of 20 °C min^{-1} under nitrogen atmosphere, obtained by TGA.

Table 2
Solvatochromic data [λ_{max} (nm) and ν_{max} (cm^{-1}) of the charge-transfer band] for phenanthrolines **3–4** in selected solvents with π^* values by Kamlet et al. [10]

Solvent[a]	π^*	**3a**		**3b**		**3c**		**3d**		**3e**		**4**	
		λ_{max}	ν_{max}	λ_{max}	ν_{max}	λ_{max}	ν_{max}	λ_{max}	ν_{max}	λ_{max}	ν_{max}	λ_{max}	ν_{max}
EtOH	0.54	362.0	27,624	367.0	27,247	388.0	25,773	380.0	26,316	399.0	25,062	393.0	25,445
Dioxane	0.55	361.0	27,700	370.0	27,027	391.0	25,575	386.0	25,906	408.0	24,510	399.0	25,063
$CHCl_3$	0.76	359.0	27,855	360.5	27,739	388.0	25,773	387.0	25,839	407.0	24,570	390.0	25,641
DMF	0.88	371.0	26,954	371.0	26,954	391.0	25,575	388.0	25,773	413.0	24,213	400.0	25,000
DMSO	1.00	373.0	26,809	375.0	26,666	393.0	25,445	390.0	25,641	416.0	24,038	404.0	24,752

[a] Solvents used as received.

account for possible fluorescence of the dyes (see Section 4 for more details). The static hyperpolarisability β_0 values were calculated using a very simple two-level model neglecting damping. They are therefore only indicative and should be treated with caution (Table 1).

From Table 1 it is clear that the progression of donor substituents from phenylthienyl-, 4-methoxyphenylthienyl- and 4-*N*,*N*-dimethylaminophenylthienyl- resulted both in red shifted absorption maxima and enhanced nonlinearities as anticipated from the donor strengths of the substituents. Therefore, compounds **3b** and **3c** (having the methoxy- or *N*,*N*-dimethylamino group at *para* position on the aromatic ring) showed higher β values compared to the unsubstituted derivative **3a** which has a β value that is 2 times that of *p*NA. The β values for **3b** and **3c** are 9–11 times that of *p*NA, whereas the β_0 values are 8–9 times that of *p*NA (Table 1). Comparison of the β values for the alkoxy-arylthienyl-imidazo-phenanthroline **3b** with *N*,*N*-dimethylamino-substituted arylthienyl-imidazo-phenanthroline **3c** shows that the amino donor substitution results in greatly enhanced nonlineariaties which are in agreement with the findings of Moylan et al. [14].

On the contrary, comparison of the β values for compounds **3d** ($\beta = 91 \times 10^{-30}$ esu) and **3e** ($\beta = 45 \times 10^{-30}$ esu), with inverse polarization, showed that the acceptor substituents on the arylthienyl moiety lead to smaller nonlinearities compared to derivatives functionalized with donor groups namely compound **3b** ($\beta = 145 \times 10^{-30}$ esu) and **3c** ($\beta = 189 \times 10^{-30}$ esu) (Table 1). Thus the electronic nature of the group substituted on the arylthienyl moiety can either dramatically enhance or decrease the overall molecular nonlinearity of the system. One must therefore view the arylthienyl moiety not simply as the conjugated segment but also as a structural unit, which affects the overall electron transfer properties of the system. While the aromaticity of heteroaromatics affects the electron transfer between donor and acceptor groups, the electron excessive or electron deficient nature of the heterocyclic ring systems may also play a major role in determining the overall electron-donating and accepting ability of the substituents: electron-rich heterocycles act as auxiliary donors and electron deficient heterocycles act as auxiliary acceptors [6]. The arylthienyl moiety will act as auxiliary donor while the imidazo-phenanthroline moiety, due to the deficiency of electron density on the phenanthroline C atoms, will act as electron-withdrawing group and also as an auxiliary acceptor. Arylthiophene, being an electron-rich system, counteracts the electron-withdrawing effect of the cyano or nitro groups, resulting in a decrease in β. These findings are in accordance with theoretical and experimental studies reported before [6,15], and also with our recent work [3c–d,4d,5i] which concluded that the increase or decrease of the molecular nonlinear activity of heteroaromatic systems depends not only on the electronic nature of the (hetero)aromatic rings but also on the position of substitution of the donor or acceptor groups on these systems.

In 1993 Moylan et al. [5a] reported the synthesis and study of the nonlinear optical properties of 3,6-disubstituted 2-phenyl-phenanthro[9,10-*d*]imidazoles (planar analogues of 2,4,5-triphenyl-substituted imidazole heterocyclic systems) in which the phenanthrene moiety had always electron-donating substituents in positions 3 and 6 and the imidazo-phenyl system had an electron-acceptor substituent at position 2. The related series of compounds with the opposite donor/acceptor relationship, *i.e.* donor at the 2-aryl ring and acceptors at the 4-aryl and 5-aryl rings was not synthesized but theoretical studies involving molecular orbital calculations revealed that those compounds should possess smaller hyperpolarizabilities. Our nonlinear optical study of our functionalized arylthienyl-imidazo-phenanthrolines **3** has yielded results that go against this prediction. These results could be due to the deficient electronic character of the phenanthroline heterocycle similar to heterocyclic azines [6b].

Recently, using the same method described above, we studied the nonlinear optical properties of arylthienyl-benzothiazoles NLO-chromophores **5** (Fig. 1) [4c], having the benzothiazole acceptor group attached to functionalized arylthiophene systems. For those derivatives the same trend was observed *i.e.* the compounds substituted with an alkoxy- or *N*,*N*-dialkylamino group at *para* position on the aromatic ring exhibited the highest β values. On the other hand, comparison of the β values of arylthienyl-benzothiazoles **5a** (R = OMe, $\beta = 136 \times 10^{-30}$ esu) and **5e** (R = *N*,*N*-dimethylamino, $\beta = 299 \times 10^{-30}$ esu) with phenanthrolines **3b** (R = OMe, $\beta = 145 \times 10^{-30}$ esu) and **3c** (R = *N*,*N*-dimethylamino, $\beta = 189 \times 10^{-30}$ esu) which have the same arylthienyl moieties showed that although compounds **3b** and **3c** contain a longer π-conjugating system constituted by the imidazo-phenanthroline moiety, their values are similar to (in the case of **3b**) or lower than (in the case of **3c**) the β values of the corresponding benzothiazoles. These results could possibly be due to the different electronic nature of imidazo-phenanthroline heterocyclic system compared to benzothiazole [16].

At this stage, a comparison could also be made between the nonlinear optical data of the new arylthienyl-imidazo-phenanthrolines **3–4** and (oligo)thienyl-imidazo-phenanthrolines **6**, recently reported by us [17] (Fig. 2). The results obtained showed that, the substitution of a benzene ring by a thiophene on the π-conjugated bridge, maintaining the same donor group produced a bathochromic shift on the absorption wavelength maxima and larger values of the molecular hyperpolarizability β (see, for example, the comparaison between **3b**, R = OMe, $\lambda_{max} = 370.0$ nm, $\beta = 145 \times 10^{-30}$ esu and **6d**, R = OMe, $\lambda_{max} = 393.0$ nm $\beta = 170 \times 10^{-30}$ esu). The optical data obtained are not surprising

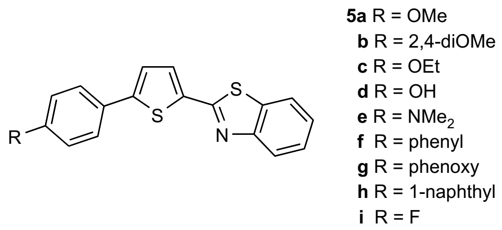


Fig. 1. Structure of arylthienyl-benzothiazoles **5** [4c].

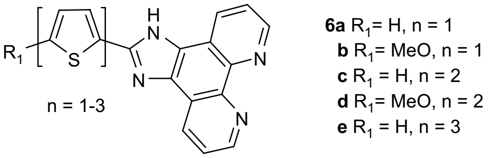


Fig. 2. Structure of (oligo)thienyl-imidazo-phenanthrolines **6** [17].

and could be explained having in mind the bathochromic effect of sulfur, 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 [2].

Thermal stability of compounds **3**–**4** was estimated by thermogravimetric analysis (TGA), measured at a heating rate of 20 °C min^{-1} under a nitrogen atmosphere. The results obtained revealed the exceptional thermal stability for all compounds, which could be heated up to $T_d = 431$–470 °C (phenanthroline derivatives **3a**–**e**) or 739 °C (bis-phenanthroline derivative **4**). The incorporation of a second phenanthroline moiety, *e.g.* comparison of **3a** ($T_d = 470$ °C) with **4** ($T_d = 739$ °C), leads to the material with the highest thermal stability.

3. Conclusions

The donor/acceptor π-conjugated phenanthrolines **3** and bis-phenanthroline **4** described in this report meet several of the criteria required for organic materials used for several optical applications.

(i) Compounds **3** and **4** were synthesized in good to excellent yields from easily available formyl-arylthiophenes **1** and low cost commercially available reagents, using simple and convenient procedures;

(ii) The absorption bands of these compounds are in the near ultraviolet region. This later property is particularly interesting, since a strong second-order nonlinear response it typically associated with molecules that absorb in the visible region. The reported compounds **3** and **4** thus represent an appealing promise to circumvent the nonlinearity-transparency trade-off which plagues the majority of molecules with a strong second-order nonlinear response. In addition, these compounds display good solvatochromic properties which together with their good solubility make them interesting potential indicators of local polarity. This characteristic could be of use in characterizing the local microenvironment of heterogeneous materials such as sol–gel derived media.

(iii) Due to the interesting optical properties exhibited by the new arylthienyl-imidazo-phenanthrolines **3**–**4** they could have other optical applications. These compounds have interesting prospects to be employed as proton, anionic and cationic sensors in analytical, environmental and/or biological applications. In addition they could also serve as ligands for the synthesis of a variety of metal complexes, such as ruthenium(II) and osmium(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 [18] which we are currently exploring [19].

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 100.6 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–visible absorption spectra (200–800 nm) were obtained using a Shimadzu UV/2501PC spectrophotometer. Mass spectrometry analyses were performed at the "C.A.C.T.I. – Unidad de Espectrometria de Masas" at the University of Vigo, Spain.

Light petroleum refers to solvent boiling in the range 40–60 °C. The synthesis of formyl-arylthiophenes **1b**, **1c** and **1f** was described elsewhere [4c].

4.2. General procedure for the synthesis of formyl-arylthiophenes ***1d***–***e*** through Suzuki cross-coupling

1-Bromo-4-cyanobenzene and 1-bromo-4-nitrobenzene (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 °C under an argon atmosphere for 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 an aqueous solution of NaOH (10%) (3 × 50 mL). The organic phase obtained was dried ($MgSO_4$), filtered and solvent removal gave a crude mixture which was submitted to column chromatography, using mixtures of diethyl ether–light petroleum of increasing polarity, affording the coupled products **1d**–**e**, which were recrystallized from ethyl acetate and *n*-hexane.

4.2.1. 2-Formyl-5-(4′-cyanophenyl)thiophene (***1d***)

Yellow solid (82%). Mp: 190.8–193.1 °C. UV (dioxane): λ_{max} nm (log ε) 332.0 (3.26). IR (liquid film) ν 2923, 2220 (CN), 1668 (C=O), 1450, 1229, 1064, 838, 799 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 7.51 (d, 1H, *J* = 4.2 Hz, 3-H), 7.71–7.79 (m, 5H, 2′-H, 6′-H, 3′-H, 5′-H, 4-H), 9.93 (s, 1H, C*H*O). ^{13}C NMR ($CDCl_3$) δ 112.56, 118.26, 125.82, 126.77, 132.93, 137.08, 137.16, 144.07, 150.93, 182.73. MS (EI) *m*/*z* (%): 213 (M^+, 66), 212 (100), 185 (5), 140 (30). HRMS: (EI) *m*/*z* (%) for $C_{12}H_7NOS$: calcd 213.0248; found 213.0244.

4.2.2. 2-Formyl-5-(4′-nitrophenyl)thiophene (***1e***)

Yellow solid (60%). Mp: 176.3–178.0 °C. UV (dioxane): λ_{max} nm (log ε) 346.0 (3.45). IR (liquid film) ν 1672 (C=O), 1600, 1510, 1447, 1341, 1217, 1121, 1067, 847, 805, 748 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 7.55 (d, 1H, *J* = 3.9 Hz, 3-H), 7.80–7.84 (m, 3H, 2′-H, 6′-H and 4-H), 8.30 (d, 2H, *J* = 6.9 Hz, 3′-H and 5′-H), 9.95 (s, 1H, C*H*O). ^{13}C NMR ($CDCl_3$) δ 124.54, 126.31, 126.96, 137.06, 139.01, 144.49, 147.84, 150.34, 182.74. MS (EI) *m*/*z* (%): 233 (M^+, 20), 203 (100), 202 (38), 174 (13), 130 (20). HRMS: (EI) *m*/*z* (%) for $C_{11}H_7NO_3S$: calcd 233.0147; found 233.0153.

4.3. General procedure for the synthesis of arylthienyl-imidazo-phenanthrolines ***3***–***4***

A mixture of formyl-arylthiophenes **1** (1.2 mmol), NH_4OAc (20 mmol) and 1,10-phenanthroline-5,6-dione **2** (1 mmol) in glacial acetic acid (20 mL) was stirred and heated at reflux for 4 h. The mixture was then cooled to room temperature and the crude product precipitated during neutralization with NH_4OH 5 M. The precipitate was filtered, washed with water and diethyl ether, recrystalized from methanol and dried at 50 °C in vacuo to give the pure product.

4.3.1. 2-(1″-Phenyl-2′-thienyl)-imidazo[4,5-f][1,10]phenanthroline (**3a**)

Yellow solid (95%). Mp: >320 °C. UV (dioxane): λ_{max} nm (log ε) 361.0 (4.16), 286.0 (4.08). IR (liquid film) ν 3441 (NH), 1657, 1600, 1438, 1300, 1224, 1133, 1092–1072, 1029, 919, 801, 752–738, 684 cm^{-1}. ^{1}H NMR (DMSO-d_6) δ 7.33–7.39 (m, 1H, 4″-H), 7.43–7.49 (m, 2H, 3″-H and 5″-H), 7.66 (d, 1H, J = 3.9 Hz, 3′-H), 7.76–7.88 (m, 5H, 4′-H, 2″-H, 6″-H, 5-H and 10-H), 8.78–8.85 (m, 2H, 4-H and 11-H), 9.02 (dd, 2H, J = 4.5 and 1.8 Hz, 6-H and 9-H), 13.86 (s, 1H, N*H*). ^{13}C NMR (DMSO-d_6) δ 119.05, 123.46, 124.79, 125.48, 126.21, 126.27, 127.28, 128.26, 129.30, 129.38, 132.43, 133.17, 135.65, 143.52, 143.61, 144.93, 145.95, 147.91. MS (FAB) m/z (%): 379 ([M + H]$^+$, 100), 378 (M$^+$, 31), 154 (18). HRMS: (FAB) m/z for $C_{23}H_{15}N_4S$: calcd 379.1017; found 379.1018.

4.3.2. 2-(4″-Methoxy-1″-phenyl-2′-thienyl)-imidazo[4,5-f][1,10]phenanthroline (**3b**)

Orange solid (50%). Mp: 303.9–306.1 °C. UV (dioxane): λ_{max} nm (log ε) 370.0 (4.48), 291.0 (4.32), 245.0 (4.42). IR (liquid film) ν 3410 (NH), 2996, 1655, 1605, 1570, 1487, 1448, 1289, 1252, 1177, 1028, 802, 738 cm^{-1}. ^{1}H NMR (DMSO-d_6) δ 3.81 (s, 3H, OC*H*$_3$), 7.04 (d, 2H, J = 8.7 Hz, 3″-H and 5″-H), 7.55 (d, 1H, J = 3.9 Hz, 3′-H), 7.72 (d, 2H, J = 8.7 Hz, 2″-H and 6″-H), 7.78–7.81 (m, 2H, 5-H and 10-H), 7.86 (d, 1H, J = 3.9 Hz, 4′-H), 8.83–8.87 (m, 2H, 4-H and 11-H), 9.03 (dd, 2H, J = 3.6 and 1.2 Hz, 6-H and 9-H), 13.84 (s, 1H, N*H*). ^{13}C NMR (DMSO-d_6) δ 55.30, 114.69, 119.08, 123.29, 123.49, 125.86, 126.20, 126.91, 127.36, 129.57, 129.78, 131.20, 135.62, 143.34, 143.43, 145.17, 146.17, 147.83, 159.39. MS (EI) m/z (%): 409 (M$^+$ + 1, 30), 408 (M$^+$, 100), 393 (50), 365 (18), 217 (27), 191 (23), 172 (15), 165 (22), 111 (39), 97 (50), 83 (56). HRMS: (EI) m/z for $C_{24}H_{16}N_4OS$: calcd 408.1045; found 408.1046.

4.3.3. 2-(4″-N,N-Dimethylamino-1″-phenyl-2′-thienyl)-imidazo[4,5-f][1,10]phenanthroline (**3c**)

Dark green solid (60%). Mp: >320 °C. UV (dioxane): λ_{max} nm (log ε) 391.0 (4.34), 382.5 (4.33), 275.5 (4.19), 345.5 (4.28). IR (liquid film) ν 3450 (NH), 2946, 1651, 1665, 1491, 1441, 1370, 1231, 1194, 1060, 805, 740 cm^{-1}. ^{1}H NMR (DMSO-d_6) δ 3.00 (s, 6H, 2 × NC*H*$_3$), 7.45–7.70 (m, 4H, 3″-H, 5″-H, 3′-H and 4′-H), 7.82–7.91 (m, 4H, 5-H, 10-H, 2″-H and 6″-H), 8.83 (m, 2H, 4-H and 11-H), 9.03 (m, 2H, 6-H and 9-H), 13.80 (broad s, 1H, N*H*). MS (FAB) m/z (%): 423 ([M + 2H]$^+$, 46), 422 ([M + H]$^+$, 38), 408 (23), 231 (100), 217 (24), 154 (46). HRMS: (FAB) m/z for $C_{25}H_{20}N_5S$: calcd 422.1439; found 422.1421.

4.3.4. 2-(4″-Cyano-1″-phenyl-2′-thienyl)-imidazo[4,5-f][1,10]phenanthroline (**3d**)

Orange solid (75%). Mp: 234.5–236.8 °C. UV (dioxane): λ_{max} nm (log ε) 386.0 (4.45), 286.0 (4.29), 244.0 (4.31). IR (nujol) ν 3480 (NH), 2220 (CN), 1700, 1601, 1297, 1175, 1071, 1030, 921, 801, 722 cm^{-1}. ^{1}H NMR (DMSO-d_6) δ 7.76–7.81 (m, 3H, 3′-H, 5-H and 10-H), 8.87–7.91 (m, 5H, 4′-H, 3″-H, 5″-H, 2″-H and 6″-H), 8.80 (dd, 2H, J = 7.8 and 2.1 Hz, 4-H and 11-H), 8.99 (dd, 2H, J = 4.2 and 1.5 Hz, 6-H and 9-H). ^{13}C NMR (DMSO-d_6) δ 109.90, 118.79, 121.47, 123.28, 125.09, 125.87, 127.13, 127.23, 128.50, 129.57, 131.53, 133.14, 135.32, 137.54, 142.06, 143.62, 146.09, 147.77. MS (FAB) m/z (%): 405 ([M + 2H]$^+$, 11), 404 ([M + H]$^+$, 34), 403 (M$^+$, 11), 307 (36), 289 (16), 155 (32), 154 (100). HRMS: (FAB) m/z for $C_{24}H_{14}N_5S$: calcd 404.0970; found 404.0964.

4.3.5. 2-(4″-Nitro-1″-phenyl-2′-thienyl)-imidazo[4,5-f][1,10]phenanthroline (**3e**)

Dark red solid (86%). Mp: >320 °C. UV (dioxane): λ_{max} nm (log ε) 408.0 (4.12), 283.0 (4.11), 241.5 (4.16). IR (nujol) ν 3453 (NH), 1651, 1590, 1338, 849, 803, 722 cm^{-1}. ^{1}H NMR (DMSO-d_6) δ 7.82–7.87 (m, 2H, 5-H and 10-H), 7.93–7.95 (m, 2H, 3′-H and 4′-H), 8.03 (d, 2H, J = 8.8 Hz, 2″-H and 6″-H), 8.29 (d, 2H, J = 8.8 Hz, 3″-H and 5″-H), 8.82 (broad d, 2H, J = 7.6 Hz, 4-H and 11-H), 9.03 (dd, 2H, J = 4.4 and 1.6 Hz, 6-H and 9-H), 14.00 (s, 1H, N*H*). ^{13}C NMR (DMSO-d_6) δ 123.37, 124.52, 124.55, 126.13, 127.23, 127.50, 127.95, 127.99, 129.57, 135.28, 138.98, 139.38, 141.85, 143.72, 144.01, 145.40, 146.36, 147.42, 149.11. MS (FAB) m/z (%): 424 ([M + H]$^+$, 12), 307 (36), 289 (16), 155 (32), 154 (100). HRMS: (FAB) m/z for $C_{23}H_{14}N_5O_2S$: calcd 424.0868; found 424.0875.

4.3.6. (1″-Phenyl-2′-thienyl)-bis[imidazo[4,5-f][1,10]phenanthroline] (**4**)

Orange solid (80%). Mp: >320 °C. UV (dioxane): λ_{max} nm (log ε) 399.0 (4.30), 316.5 (3.49), 300.0 (4.01). IR (KBr) ν 3435 (NH), 1646, 1565, 1478, 1447, 1398, 1353, 1246, 1125, 1071, 1030, 805, 739 cm^{-1}. ^{1}H NMR (DMSO-d_6) δ 7.79–7.89 (m, 5H, 2 × 5-H, 2 × 10-H and 3′-H), 7.95 (d, 1H, J = 3.9 Hz, 4′-H), 8.03 (d, 2H, J = 8.7 Hz, 2″-H and 6″-H), 8.36 (d, 2H, J = 8.7 Hz, 3″-H and 5″-H), 8.78–8.93 (m, 4H, 2 × 11-H and 2 × 4-H), 9.01–9.03 (m, 4H, 2 × 6-H and 2 × 9-H), 13.79 (s, 1H, N*H*), 13.89 (s, 1H, N*H*). ^{13}C NMR (DMSO-d_6) δ 119.02, 119.25, 123.19, 123.44, 125.45, 125.91, 126.91, 127.33, 129.47, 129.63, 133.00, 134.00, 135.70, 135.93, 143.57, 143.66, 144.12, 145.85, 147.86, 147.92, 149.94, 151.71. MS (FAB) m/z (%): 597 ([M + H]$^+$, 17), 316 (11), 307 (40), 289 (19), 288 (15), 246 (10), 155 (30), 154 (100). HRMS: (FAB) m/z for $C_{36}H_{21}N_8S$: calcd 597.1610; found 597.1603.

4.4. Nonlinear optical measurements for compounds **3–4** using the hyper-Rayleigh scattering (HRS) method

Hyper-Rayleigh scattering (HRS) [11a] was used to measure the first hyperpolarizability β of response of the molecules studied. The experimental set-up for hyper-Rayleigh measurements is similar to the one presented by Clays and Persoons [11a]. 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 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 β values were calibrated using a reference solution of *p*-nitroaniline (*p*NA) [11b] also dissolved in dioxane at a concentration of 1×10^{-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 [12]. 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

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

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

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

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

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

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:

$$\begin{aligned} S_{\mathrm{NB}}^{2\omega} &= \left(\frac{S_{\mathrm{NB}} A_{\mathrm{WB}} - S_{\mathrm{WB}} A_{\mathrm{NB}}}{T_{\mathrm{NB}} A_{\mathrm{WB}} - T_{\mathrm{WB}} A_{\mathrm{NB}}}\right) T_{\mathrm{NB}} \\ S_{\mathrm{NB}}^{F} &= \left(\frac{S_{\mathrm{WB}} T_{\mathrm{NB}} - S_{\mathrm{NB}} T_{\mathrm{WB}}}{T_{\mathrm{NB}} A_{\mathrm{WB}} - T_{\mathrm{WB}} A_{\mathrm{NB}}}\right) A_{\mathrm{NB}} \end{aligned}$$

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). When using the “narrow” band filter the estimated fraction of the total detected signal due to fluorescence is listed in the following table:

Compound	$S_{\mathrm{NB}}^{\mathrm{F}}/S_{\mathrm{NB}}$
3a	49 ± 58%
3b	66 ± 9%
3c	67 ± 15%
3d	67 ± 19%
3e	94 ± 15%

With the exception of compound **3a**, the error associated with the fluorescence measurement is less than 30% of the value quoted. Compound **3a** has a high uncertainty due to low level of signal measured.

The corresponding uncertainties associated with the determination of the hyperpolarizability are also typically within 30% of the values quoted in the above shown table. The two exceptions are compounds **3a** and **3e** which are in any case the compounds displaying the smaller and therefore less interesting optical nonlinearities.

4.5. Thermogravimetric analysis of compounds **3–4**

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

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