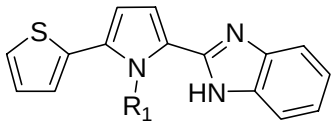
Graphical abstract

New efficient and thermally stable NLO-chromophores **4**-**5** based on a thienylpyrrolyl donor π- conjugated bridge and a benzimidazolyl acceptor moieties were developed by a one step $Na_2S_2O_4$ reduction of substituted *o*-nitroanilines in the presence of formyl-thienylpyrroles.



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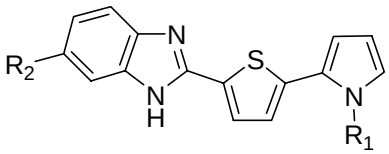

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R_1 = alkyl, aryl
R_2 = H, methoxy, cyano, nitro

Synthesis and second-order nonlinear optical properties of new chromophores containing benzimidazole, thiophene and pyrrole heterocycles

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Abstract – A new series of thermally stable benzimidazole-based nonlinear optical (NLO) chromophores **4-5** has been developed. These chromophores possess a thienylpyrrolyl π-conjugated system attached to functionalized benzimidazole heterocycles. This feature leads to robust chromophores with excellent solvatochromic properties, high thermal stabilities and good molecular optical nonlinearities.

Keywords: thiophene, pyrrole, benzimidazole, auxiliary donors and auxiliary acceptors, 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 attracted much attention in recent years. They have great potential especially for use in optical communication, information processing, frequency doubling and integrated optics.[1] One commonly used strategy to design π-electron chromophores for second-order NLO applications is to end-cap a suitable conjugated bridge with donor (D) and acceptor (A) substituents. In the 90s several authors pointed out that the strength of the electron-donor and -acceptor must be optimized for the specific π-conjugated system, and the loss of aromaticity between the neutral form and the charge separated zwitterionic form of the chromophore is believed to be responsible for the reduced or saturated β values.[2] Therefore, attempts have been made to design chromophores with less aromatic characteristics in the ground state, by

replacing the benzene ring in stilbene derivatives by easily delocalizable five-membered heteroaromatic rings.[3] It has also been demonstrated that the electron density of the π-conjugated system plays a major role in determining second-order NLO response properties. The electron excessive/deficient heterocycles act as auxiliary donors/acceptors while connected to donating/withdrawing groups, and the increase of donor/acceptor ability leads to substantial increase in β values.[4]

Having in mind this idea, several investigators reported on the synthesis and characterization of conjugated heterocyclic systems in which the donor moiety was represented by a π-excessive five-membered heterocycle (pyrrole or thiophene) and the acceptor group was a deficient heterocyclic azine ring. These new heterocyclic derivatives exhibited improved solvatochromic, electrochromic, photochromic, fluorescent and nonlinear optical properties.[5] 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.

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 benzimidazole derivatives,[6] as well as conjugated thiophene and pyrrole heterocycles acting as auxiliary donors, substituted with appropriate acceptor groups,[7-8] whereas ~~Due to the deficiency of electron density on the ring C atoms,~~ the benzimidazole heterocycle acts as an electron-withdrawing group and also as an auxiliary acceptor. Moreover, it extends the conjugation length of the π-electron bridge. Benzimidazole derivatives can also 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).[6a,6d,9] Despite all these promising properties for NLO applications, only a few publications concerning the synthesis and characterization of NLO-chromophores based on benzimidazole derivatives were found in the available literature.[6a-g] Particularly, the synthesis and characterization of new NLO-chromophores, containing a π-excessive thienylpyrrolyl moiety and a ~~electron deficient functionalized~~ benzimidazole heterocycle, has not, to our knowledge, been previously communicated.

We have previously reported several series of donor-acceptor substituted heterocyclic compounds and demonstrated the importance of the thiophene and benz-X-zole rings in enhancing nonlinear response.[8,10-11] Especially, in the case of benzothiazole derivatives, we have studied the effect of the π-conjugated bridge on the fluorescence, solvatochromic, and nonlinear optical properties of bithienyl-,[11a] arylthienyl-[11b] and thienylpyrrolyl-benzothiazoles.[11d] Moreover, in the case of thienylpyrrolyl-benzothiazoles, we have also studied the effect of the position of attachment of the benzothiazole heterocycle on the optical properties of the new chromophores.

Having in mind our recent results and in order to understand better the structure-property relationships for thienylpyrrole substituted benz-X-azole compounds, we decided to investigate the effect of a different benz-X-azole electron deficient heterocycle (benzimidazole) on the linear and nonlinear optical properties of the new NLO-chromophores.

2. Results and discussion

2.1. Synthesis

The most popular synthetic approaches for the synthesis of benzimidazoles generally involve the condensation of an arylenediamine with a carbonyl equivalent.[12] These methods usually use strong acid or alternatively harsh dehydratation conditions often at elevated temperatures, in order to afford benzimidazoles. These conditions are not fully compatible with a broad range of functional groups and desirable substrates. Recently, Yang[13] *et al* reported the synthesis of 2-substituted benzimidazoles by a one step reaction through the $Na_2S_2O_4$ reduction of *o*-nitroanilines in the presence of aryl or heteroaryl (pyridyl and quinolyl) aldehydes. Applying this mild and versatile method of synthesis, we were able to prepare the new benzimidazoles **4**-**5** using as precursors formyl-thienylpyrroles **1**-**2**. The synthesis of compounds **1**-**2** was recently reported by us through formylation of 1-(alkyl)aryl-2-(2'-thienyl)pyrroles[14] using two distinct synthetic methods.[15] Formyl 1-(alkyl)aryl-2-(2'-thienyl)pyrroles **1**-**2** with the formyl group at 5´-position or 5-position of the thiophene or pyrrole ring, respectively, were used as precursors of benzimidazoles **4**-**5** in order to evaluate the effect of the position of benzimidazole group on the optical properties of these chromophores. Therefore, compounds **4**-**5** with either alkyl or aryl donors on the thienylpyrrolyl system and H, OMe, CN or NO_2 groups on the benzimidazole moiety, were prepared by a one step reaction through the $Na_2S_2O_4$ reduction of several *o*-nitroanilines **3** in

the presence of formyl-thienylpyroles **1-2** in DMSO at 120 °C for 15 h (Scheme 1). Under these conditions, compounds **4-5** were obtained in moderate to excellent yields (40-95%) and the structures of these new chromophores were unambiguously confirmed by their analytical and spectral data (Table 1). Although compound **5d** was obtained from a dinitro precursor **3d**, no reduction was observed for the second nitro group.

<Scheme 1>

<Table 1>

In the ^{1}H NMR spectra of benzimidazole derivatives signals at about 11.63 and 12.45-12.47 ppm for compounds **4a** and **5c-d** respectively, were detected. All signals appeared as broad singlets and were attributed to the N-H in the benzimidazole moiety. A broad correlation could be observed between the donor or acceptor properties of the group attached to 6-position of the benzimidazole nucleus and the chemical shift of the nitrogen proton of the benzimidazole ring in compounds **4-5** (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 in a decrease in the basic character of the benzimidazole. The NH was also identified by IR spectroscopy as a sharp band at about 3362-3435 cm^{-1}.

2.2. UV-visible study of benzimidazoles 4-5

The electronic spectra of benzimidazoles **4-5** were recorded in ethanol (Table 1). Communication between the electron donating and acceptor termini can be evaluated by comparing the λ_{max} values. The influence of the position of the benzimidazole group on the pyrrole or on the thiophene ring on λ_{max} of absorption for chromophores **4-5** is noteworthy. The difference in λ_{max} values ($\Delta\lambda_{max}$) between compounds **4b** and **5b** is 39 nm (Table 1, entries 2 and 4). As expected, the introduction of the benzimidazole heterocycle at the 5´-position of the thiophene ring (**5b**), relative to the same acceptor group in the 5-position of the pyrrole ring (**4b**), results in a bathochromic shift in the λ_{max} of absorption for **5b** due to more extensive electron delocalization (Figure 1). This fact probably could be due to less steric hindrance between the imidazole NH group and the thiophene ring, when compared to the steric hindrance between the NH with the alkyl or aryl group substituted on the nitrogen atom of the pyrrole ring.

The influence of the strength of the acceptor group is demonstrated by comparison of the absorption maxima of compounds **5a** and **5c-d** (Figure 2) as the longest wavelength transition is shifted from 369.0 nm in benzimidazole **5a** (R_2 = H, Table 1, entry 3) to 391.0 nm for benzimidazole **5d** (R_2 = NO_2, Table 1, entry 6). This effect has been attributed to the stabilization of LUMO by the electron-withdrawing groups.[10c]

<Figure 1>

2.3. Solvatochromic behavior of benzimidazoles 4-5

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, pyrrole and thiazole 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. It is widely recognized that low energy bands in the UV-vis spectra and large solvatochromism are good indicators of potential NLO properties.[8a-b,d,10,11,16] Donor-acceptor substituted thienylpyrroles,[8a-b,d] bithienyl-, arylthienyl- and thienylpyrrolyl-benz-X-azoles[11] have been known to demonstrate strong solvatochromic behavior. In order to determine the best solvatochromic probe, we carried out a preliminary study of the absorption spectra for compounds **4-5** in solvents with different polarities (diethyl ether, ethanol, chloroform and DMSO). The highest energy transitions were found with nonpolar solvents. More polar solvents such as DMSO resulted in lower energy transitions. This behavior has been defined as a positive solvatochromic response. Compounds **5a-b** and **5d** showed the largest energy shifts in the absorption band ($\Delta\nu$ = + 607 cm^{-1} for **5a**, $\Delta\nu$ = + 731 cm^{-1} for **5b** and $\Delta\nu$ = + 1142 cm^{-1} for **5d**), so a full solvatochromic study involving 13 solvents was carried out. The maxima of the wavenumbers ν_{max} for chromophores **5a-b** and **5d** as well as the corresponding wavelength λ_{max} are listed in Table 2 and compared to the solvent π^* values determined by Kamlet and Taft.[17] Noteworthy is the behavior of **5a-b** and **5d** in chlorinated solvents such as chloroform, which slightly deviates from linearity.[8a,10b] In view of the pronounced solvatochromism and the good correlation with π^* values for the 13 solvents investigated, compounds **5a** ($\Delta\nu$ = + 685 cm^{-1}), **5b** ($\Delta\nu$ = + 807 cm^{-1}) and **5d** ($\Delta\nu$ = + 1277 cm^{-1}) seem to be very appropriate solvent polarity indicating dyes (Table 2).

<Table 2>

2.4. Nonlinear optical properties and thermal stability of benzimidazoles 4-5

We have used the hyper-Rayleigh scattering (HRS) method[19-20] to measure the first hyperpolarizability β of benzothiazoles **4-5**. *p*-Nitroaniline (*p*NA) was used as standard[21-22] in order to obtain quantitative values, while care was taken to properly account for possible fluorescence of the dyes (see experimental section for more details). The static hyperpolarisability β values were calculated using a very simple two-level model neglecting damping. They are therefore only indicative and should be treated with caution (Table 3).

As expected, the β values for benzimidazoles **4a-b** increase with the donor strength of the group attached to the nitrogen atom on the pyrrole ring in the order *n*-propyl < 4-MeO-phenyl.

<Table 3>

Noteworthy is the effect of the electronic nature of the group that substitutes the benzimidazole heterocycle at 6-position. From Table 3 it is obvious that the increase of the acceptor strength of the groups mentioned above, along the series H < CN < NO_2, results both in red-shifted absorption maxima and enhanced β values for benzimidazoles **5a** and **5c-d**. The β values for compounds **4a-b** and **5a** having the unsubtituted benzimidazole group on the pyrrole or on the thiophene ring respectively, are 2-3 times greater than *p*NA, whereas the β values for compounds having the ~~methoxyl,~~ cyano and nitro groups on the benzimidazole heterocycle substituted on the thiophene ring (5~~b~~**c-d**) are 7~~-17~~ times greater than *p*NA. Electron deficient heterocycles act as auxiliary acceptors, withdrawing electron density from acceptor substituents and hence increasing the acceptor ability. This increased acceptor ability leads to a substantial increase in NLO response.

These findings are in accordance with theoretical and experimental studies reported before for related compounds,[3h,5a-b,6e,26] and also with our recent work[8b,8d,11d] where it was concluded that the increase or decrease of the molecular nonlinear activity of heteroaromatic systems depends substantially on the electronic nature of the (hetero)aromatic rings.

The measured β value for compound **5b** is abnormally large (290×10^{-30} esu), when compared to compounds **5a**,**c-d**; this may be due to a two-photon resonance effect, so no value is given in Table 3.

Recently, using the same method described above, we have studied the nonlinear optical properties of thienylpyrrolyl-benzothiazoles NLO chromophores **6-7** (Figure 3),[11d] having the benzothiazole acceptor group attached to the thiophene or on the pyrrole heterocycles. In the case of benzimidazoles **4-5** and contrarily to the results obtained for benzothiazoles **6-7**, no effect was observed on the β values for compounds **4b** ($\beta = 58 \times 10^{-30}$ esu) and **5a** ($\beta = 60 \times 10^{-30}$ esu) having the benzimidazole moiety substituted on the pyrrole or on the thiophene rings respectively.

These results can probably be explained by the different electronic nature of benzimidazole heterocycle compared to benzothiazole. In fact, earlier studies by Pagani[26] *et al* concerning the electron-acceptor properties of π-deficient heteroaromatics in a series of 2-benzylazoles (thiazole, oxazole and imidazole) and their corresponding benzo-fused analogs showed that the charge demand c_x, a quantity representing the fraction of π negative charge withdrawn (delocalizated), is particularly small for imidazole and benzimidazole heterocycles c_{imidaz} (0.382 for *N*-methylbenzimidazol-2-yl) compared to c_{thiaz} (0.457-0.471 for benzothiazol-2-yl). Several theoretical and experimental studies[3h-k,5a-b,27] could also explain the smaller nonlinearities of thienylpyrrolyl-benzimidazoles **4-5** compared to thienylpyrrolyl-benzothiazoles **6**-7 with similar structures.[11d]

<Figure 3>

Thermal stability of chromophores **4-5** 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 good thermal stability for all compounds, which could be heated up to T_d = 326–401 ºC ~~without decomposition or sublimation (*e.g.* thermogram for compound **5b**, Figure 4).~~

Although alternative methods to prepare composite matrices do not require high temperatures, *e.g.* the use of high pressures, great thermal stability is much desirable for device applications.[28]

Our hyper-Rayleigh and thermal stability studies indicate that good nonlinearity-thermal stability trade-off is achieved for chromophores **5~~b~~c-d**, which possess β values from 114 × 10^{-30} to 121 × 10^{-30} esu and higher decomposition temperatures. Specifically, the combination of 4-MeO-phenyl- electron-donating group substituted on the nitrogen atom of the pyrrole ring with acceptor groups on the benzimidazole heterocycle (**5~~b~~c-d**) provides a very efficient

method to optimize both the molecular nonlinearities and thermal stabilities for these type of NLO-chromophores.

~~<Figure 4>~~

3. Conclusions

The donor-acceptor π conjugated benzimidazoles **4-5** reported meet several of the criteria requested for organic materials used for second order NLO applications:

i) compounds **4-5** were synthesized in moderate to excellent yields from easily available formyl-thienylpyrroles **1-2** and low cost commercially available anilines, using simple and convenient procedures;

ii) they showed excellent solvatochromic properties and thermal stabilities as well as good solubility in usual organic solvents;

iii) although the NLO activity is only moderate, their thermal stability is very high.

~~The combination of these properties suggests the potential application of benzimidazoles **4-5** for device applications in guest-host systems.~~

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 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). Peak assignments were supported by spin decoupling-double resonance and bidimensional heteronuclear HMBC and HMQC techniques. 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. 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 ºC. The synthesis of formyl-thienylpyrroles **1-2** was described elsewhere.[15]

4.2. General procedure for the synthesis of thienylpyrrolyl-1,3-benzimidazoles 4-5

A solution of *o*-nitroaniline (1 equiv) and formyl-thienylpyrrole (1 equiv) in DMSO (1 mL) was treated with $Na_2S_2O_4$ (3 equiv), dissolved in a small volume of water, and heated at 120 ºC with stirring for 15 h. The mixture was poured into water (20 mL) and extracted with ethyl acetate (3 × 50 mL). The organic layer was dried with magnesium sulphate and evaporated under reduced pressure to give the crude thienylpyrrolyl-benzimidazoles **4-5** which were purified by chromatography on silica with increasing amounts of diethyl ether in light petroleum as eluent.

4.2.1. 2-(1´-Propyl-2´-(2´´-thienyl)pyrrolyl)-1,3-benzimidazole (4a). Pale yellow solid (95%). Mp: 157.6-158.9 ºC. UV (dioxane): λ_{max} nm (log ε) 332.5 (4.53), 242.5 (4.08), 225.5 (4.00). IR (KBr) *v* 3087 (CH), 2951 (CH), 1571, 1433, 1402, 1387, 1339, 1200, 1117, 905, 989, 721, 699 cm^{-1}. ^{1}H NMR (acetone-d_6) δ 0.88 (t, 3H, *J*=7.5 Hz, C*H*$_3$), 1.80-1.84 (m, 2H, $CH_2CH_2CH_3$), 4.86 (t, 2H, *J*=7.5 Hz, $CH_2CH_2CH_3$), 6.41 (d, 1H, *J*=3.9 Hz, 3´-H), 6.97 (d, 1H, *J*=3.9 Hz, 4´-H), 7.19-7.23 (m, 3H, 4´´-H +5-H + 6-H), 7.26-7.28 (m, 1H, 3´´-H), 7.56-7.61 (m, 3H, 5´´-H + 4-H + 7-H), 11.63 (broad s, 1H, N*H*). ^{13}C NMR (acetone-d_6) δ 11.03 (CH_3), 25.33 ($CH_2CH_2CH_3$), 47.89 ($CH_2CH_2CH_3$), 111.66 (C3´), 112.00 (C4´), 116.88 (C7 + C4), 122.71 (C5 + C6), 125.53 (C2´ or C5´), 126.71 (C5´´), 127.27 (C3´´), 128.44 (C4´´), 131.47 (C2´ or C5´), 134.93 (C2´´), 139.18 (C7a), 139.37 (C3a), 147.18 (C2). MS (FAB) *m/z* (%): 308 ($[M+H]^+$, 100), 307 (M^+, 83), 306 (10), 265 (16), 154 (29). HRMS: (FAB) *m/z* (%) for $C_{18}H_{18}N_3S$; calcd 308.1221; found 308.1226.

4.2.2. 2-(1´-(4´´´-Methoxyphenyl)-2´-(2´´-thienyl)pyrrolyl)-1,3-benzimidazole (4b). Dark yellow solid (74%). Mp: 232.7-235.9 ºC. UV (dioxane): λ_{max} nm (log ε) 336.0 (4.45), 283.5 (3.94), 274.5 (3.94), 241.5 (4.16). IR (KBr) *v* 3435 (NH), 1639, 1624, 1511, 1431, 1299, 1249, 1107, 1007, 833, 744, 709 cm^{-1}. ^{1}H NMR (acetone-d_6) δ 3.89 (s, 3H, OC*H*$_3$), 6.66 (d, 1H, *J*=3.9 Hz, 3´-H), 6.75 (dd, 1H, *J*=3.9 and 1.2 Hz, 3´´-H), 6.91-6.94 (m, 1H, 4´´-H), 7.00-7.04 (m, 3H, 3´´´-H + 5´´´-H + 4´-H), 7.11-7.14 (m, 2H, 5-H + 6-H), 7.29 (dd, 1H, *J*=5.1 and 0.9 Hz, 5´´-H), 7.33 (dd, 2H, *J*=7.2 and 2.1 Hz, 2´´´-H + 6´´´-H), 7.39-7.43 (m, 2H, 4-H + 7-H). ^{13}C NMR (acetone-d_6) δ 55.76 (O*C*H$_3$), 110.45 (C3´), 110.59 (C5´), 113.19 (C4´), 114.77

(C3´´´+ C5´´´), 115.50 (C4 + C7), 122.60 (C5 + C6), 125.74 (C3´´), 125.76 (C5´´), 127.76 (C4´´), 131.59 (C2´´´+ C6´´´), 132.25 (C1´´´), 133.36 (C2´), 135.25 (C2´´), 139.82 (C7a), 140.00 (C3a), 146.19 (C2), 160.89 (C4´´´). MS (FAB) *m/z* (%): 372 ($[M+H]^+$, 100), 371 (M^+, 64), 370 (9), 154 (6). HRMS: (EI) *m/z* (%) for $C_{22}H_{18}N_3OS$; calcd 372.1171; found 372.1169.

4.2.3. (1´´-(4´´´-Methoxyphenyl)-2´´-(2´-thienyl)pyrrolyl)-1,3-benzimidazole (5a). Brown solid (40%). Mp: 190.1-194.0 ºC. UV (dioxane): λ_{max} nm (log ε) 361.0 (4.04), 291.5 (3.41), 241.0 (3.95). IR (liquid film) *v* 3402 (NH), 2045, 1876, 1727, 1513, 1400, 1298, 1250, 1166, 1039, 938, 834, 745 cm^{-1}. ^1H NMR (acetone-d_6) δ 3.90 (s, 3H, OC*H*$_3$), 6.32-6.34 (m, 1H, 4´´-H), 6.62-6.64 (m, 1H, 3´´-H), 6.71 (d, 1H, *J*=3.9 Hz, 3´-H), 6.97-6.99 (m, 1H, 5´´-H), 7.07 (dd, 2H, *J*=9.0 and 2.1 Hz, 3´´´-H + 5´´´-H), 7.23-7.26 (m, 2H, 5-H + 6-H), 7.32 (dd, 2H, *J*=9.0 and 2.4 Hz, 2´´´-H + 6´´´-H), 7.55-7.58 (m, 2H, 4-H + 7-H), 7.74 (d, 1H, *J*=3.9 Hz, 4´-H). ^{13}C NMR (acetone-d_6) δ 55.86 (O*C*H$_3$), 110.07 (C4´´), 111.80 (C3´´), 115.25 (C3´´´+ C5´´´), 115.42 (C4 + C7), 123.52 (C5 + C6), 125.47 (C3´), 126.78 (C5´´), 128.20 (C4´), 129.00 (C2´´´+ C6´´´), 129.60 (C2´´), 131.33 (C2´ or C5´), 133.53 (C1´´´), 139.20 (C2´ or C5´), 139.50 (C7a + C3a), 147.45 (C2), 160.40 (C4´´´). MS (FAB) *m/z* (%): 372 ($[M+H]^+$, 100), 371 (M^+, 53), 322 (17), 154 (13). HRMS: (FAB) *m/z* (%) for $C_{22}H_{18}N_3OS$; calcd 372.1171; found 372.1172.

4.2.4. 6-Methoxy-2-(1´´-(4´´´-methoxyphenyl)-2´´-(2´-thienyl)pyrrolyl)-1,3-benzimidazole (5b). Yellow solid (76%). Mp: 72.2-74.4 ºC. UV (dioxane): λ_{max} nm (log ε) 364.0 (4.28), 244.5 (4.22). IR (KBr) *v* 3389 (NH), 3095, 2833, 1629, 1513, 1460, 1248, 1198, 1158, 1028, 834, 807, 716 cm^{-1}. ^1H NMR (acetone-d_6) δ 3.83 (s, 3H, OC*H*$_3$), 3.89 (s, 3H, OC*H*$_3$ Ar), 6.31-6.33 (m, 1H, 4´´-H), 6.59-6.60 (m, 1H, 3´´-H), 6.67 (d, 1H, *J*=4.2 Hz, 3´-H), 6.84 (dd, 1H, *J*=8.7 and 2.4 Hz, 5-H), 6.95-6.96 (m, 1H, 5´´-H), 7.05 (m, 3H, 3´´´-H + 5´´´-H + 7-H), 7.30 (dd, 2H, *J*=7.8 and 2.1 Hz, 2´´´-H + 6´´´-H), 7.42 (d, 1H, *J*=8.7 Hz, 4-H), 7.53 (d, 1H, *J*=3.9 Hz, 4´-H). ^{13}C NMR (acetone-d_6) δ 55.83 (O*C*H$_3$), 55.85 (O*C*H$_3$), 97.90 (C7), 109.97 (C4´´), 111.49 (C3´´), 112.57 (C5), 115.18 (C3´´´+ C5´´´), 116.60 (C4), 125.37 (C3´), 126.49 (C5´´), 126.56 (C4´), 128.13 (C2´´), 128.95 (C2´´´+ C6´´´), 132.82 (C2´ or C5´), 133.61 (C1´´´), 135.61 (C3a), 138.02 (C2´ or C5´), 140.26 (C7a), 147.42 (C2), 157.46 (C6), 160.32 (C4´´´). MS (FAB) *m/z* (%): 402 ($[M+H]^+$, 100), 401 (M^+, 87), 307 (28), 289 (14), 154 (79). HRMS: (FAB) *m/z* (%) for $C_{23}H_{20}N_3O_2S$; calcd 402.1276; found 402.1278.

4.2.5. 6-Cyano-2-(1´´-(4´´´-methoxyphenyl)-2´´-(2´-thienyl)pyrrolyl)-1,3-benzimidazole (5c). Pale green solid (85%). Mp: 176.8-178.2 ºC. UV (dioxane): λ_{max} nm (log ε) 363.0 (4.34), 284.5 (4.14), 211.5 (4.33). IR (KBr) *v* 3412 (NH), 3095, 2836, 2213 (CN), 1622, 1513, 1420, 1299, 1249, 1158, 1033, 952, 835, 733 cm^{-1}. ^1H NMR (acetone-d_6) δ 3.91 (s, 3H, OC*H*$_3$), 6.33-6.35 (m, 1H, 4´´-H), 6.65-6.67 (m, 1H, 3´´-H), 6.75 (d, 1H, *J*=3.9 Hz, 3´-H), 6.98-6.99 (m, 1H, 5´´-H), 7.06-7.11 (m, 2H, 3´´´-H + 5´´´-H), 7.31-7.36 (m, 2H, 2´´´-H + 6´´´-H), 7.54 (dd, 1H, *J*=8.4 and 1.5 Hz, 5-H), 7.66-7.71 (m, 2H, 7-H + 4´-H), 8.01 (broad s, 1H, 4-H), 12.47 (broad s, 1H, N*H*). ^{13}C NMR (acetone-d6) δ 55.87 (O*C*H$_3$), 110.11 (C4´´), 111.90 (C3´´), 115.27 (C3´´´+ C5´´´), 116.10 (*C*N), 120.41 (C7), 123.99 (C4), 125.51 (C3´), 126.93 (C5´´ + C5), 127.94 (C2´´), 128.58 (C4´), 129.05 (C6´´´+ C2´´´), 131.12 (C2´ or C5´), 133.48 (C1´´´), 138.67 (C3a), 139.86 (C2´ or C5´), 141.00 (C7a), 147.43 (C2), 148.16 (C6), 160.44 (C4´´´). MS (FAB) *m/z* (%): 397 ($[M+H]^+$, 67), 396 (M^+, 58), 307 (36), 289 (18), 155 (31), 154 (100). HRMS: (FAB) *m/z* (%) for $C_{23}H_{17}N_4OS$; calcd 397.1123; found 397.1116.

4.2.6. 6-Nitro-(1´´-(4´´´-methoxyphenyl)-2´´-(2´-thienyl)pyrrolyl)-1,3-benzimidazole (5d). Orange solid (64%). Mp: 113.1-115.8 ºC. UV (dioxane): λ_{max} nm (log ε) 363.0 (4.34), 284.5 (4.14), 241.5 (4.33). IR (KBr) *v* 3362 (NH), 3095, 2931, 1625, 1572, 1514, 1461, 1337, 1249, 1167, 1067, 1040, 835, 738, 720 cm^{-1}. ^1H NMR (Acetone-d_6) δ 3.92 (s, 3H, OC*H*$_3$), 6.35 (m, 1H, *J*=2.7 and 0.9 Hz, 4´´-H), 6.67 (m, 1H, 3´´-H), 6.78 (d, 1H, *J*=4.2 Hz, 3´-H), 7.00 (m, 1H, 5´´-H), 7.11 (dd, 2H, *J*=8.9 and 2.4 Hz, 3´´´-H and 5´´´-H), 7.34 (dd, 2H, *J*=9.0 and 2.4 Hz, 2´´´-H and 6´´´-H), 7.72 (m, 2H, 4´-H and 4-H), 8.17 (dd, 1H, *J*=9.0 and 2.1 Hz, 5-H), 8.44 (broad s, 1H, 7-H), 12.45 (broad s, 1H, N*H*). ^{13}C NMR (DMSO-d_6) δ 55.46 (O*C*H$_3$), 109.26 (C4´´), 111.17 (C3´´), 114.56 (C3´´´ + C5´´´), 117.54 (C7), 118.06 (C5), 123.15 (C4), 124.96 (C3´), 126.57 (C5´´), 128.33 (C2´´´ + C6´´´), 128.60 (C4´ + C2´´), 129.65 (C2´ or C5´), 131.91 (C1´´´), 134.54 (C3a), 139.49 (C2´ or C5´), 142.62 (C7a), 147.25 (C6), 151.20 (C2), 159.03 (C4´´´). MS (FAB) *m/z* (%): 417 ($[M+H]^+$, 34), 416 (M^+, 30), 307 (36), 289 (17), 155 (31), 154 (100). HRMS: (FAB) *m/z* (%) for $C_{22}H_{17}N_4O_3S$; calcd 417.1021; found 417.1023.

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

Hyper-Rayleigh scattering (HRS) was used to measure the first hyperpolarizability *β* of response of the molecules studied. The experimental set-up for hyper-Rayleigh measurements

is similar to the one presented by Clays et al.[19] 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 β values were calibrated using a reference solution of *p*-nitroaniline (*p*NA)[20] also dissolved in dioxane at a concentration of 1×10^{-2} mol dm^{-3} (external reference method). The hyperpolarizability of pNA dissolved in dioxane is known from EFISH measurements carried out at the same fundamental wavelength.[21-22] The concentrations of the solutions under study were chosen so that the corresponding hyper-Rayleigh signals fall 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. The error associated with the HRS measured β values is estimated to be less than 25% of the quoted values.

We took particular care to avoid reporting artificially high hyperpolarizibilites 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. The relevant equations are:

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

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

Here $S_{NB}^{2\omega}$ is the hyper Rayleigh scattering contribution to the signal, i.e. the signal that would have been measured using the "narrow" band filter if there were no fluorescence present. The fluorescence contribution to the signal measured using the narrow band interference filter is S_{NB}^{F}. The signals S_{NB} and S_{WB} are the actual signals measured (after correction for the solvent contribution) using the "narrow" (CVI model F1.5-532-4) and "wide" (CVI model F03-532-4) band interference 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%), A_{NB} and A_{WB} represent the area under the respective filter´s transmission curve. These values were carefully measured 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.

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_{NB}^{F} / S_{NB}
4a	0.36
4b	0.11
5a	0.55
5b	0.50
5c	0.64
5d	0.51

We estimate that the error associated with the above values is less than 20% of the value quoted.

4.4. Thermogravimetric analysis of compounds 4-5

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 700 ºC.

Acknowledgments

The authors thank the Fundação para a Ciência e Tecnologia (Portugal) for financial support to the Centro de Química and Centro de Física (Universidade do Minho). The authors are also grateful to Drª Paula Peixoto of the Departamento de Engenharia de Polímeros (Universidade do Minho) for the thermogravimetric analyses.

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Captions

Scheme 1. Synthesis of thienylpyrrolyl-benzimidazoles **4-5** by reductive cyclisation of *o*-nitroanilines with $Na_2S_2O_4$ in presence of formyl-thienylpyrroles **1-2**.

Table 1. Yields, ^{1}H NMR, IR and UV-vis data of thienylpyrrolyl-benzimidazoles **4-5**.

[a] For the N*H* proton of the imidazole ring of thienylpyrrolyl-benzimidazoles **4-5** (300 MHz, Acetone-d_6).

[b] All the UV/vis spectra were run in ethanol.

Table 2. Solvatochromic data [β_{max} (nm) and $\bar{\upsilon}_{max}$ (cm^{-1}) of the charge-transfer band] for thienylpyrrolyl-benzimidazoles **5a-b** and **5d** in selected solvents with π* values by Kamlet and Taft.[17]

[a] Solvent used as received.

[b] The correlation coefficient *r* obtained for the linear solvatation energy relationship with π* values by Kamlet and Taft without chloroform was *r* = 0.8489 for **5a**, 0.8295 for **5b** and 0.8479 for **5d**.

Table 3. UV-vis absorptions, β and β_0 values for compounds **4-5**[a] and **6-7**[11d] and T_d data for compounds **4-5**.

[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.[23-25]

[d] The hyperpolarizability for compound **5b** proved to be abnormally large, possibly due to a two photon resonance enhancement effect, so no value is given.

[e] Decomposition temperature (T_d) measured at a heating rate of 20 ºC min^{-1} under a nitrogen atmosphere, obtained by TGA.

Figure 1. UV-visible spectra of compounds **4b** and **5b** recorded in ethanol.

Figure 2. UV-visible spectra of compounds **5a** and **5c-d** recorded in ethanol.

Figure 3. Structure of thienylpyrrolyl-benzothiazoles **6**-**7**.

~~**Figure 4.** TGA thermogram of compound **5b**.~~

Tables

Table 1

Entry	Formyl pyrrole	Product	Yield (%)	δ_H (ppm)[a]	IV ν (cm^{-1})	UV-vis λ_{max} (nm)[b] (log ε)
1	**1a**	**4a**	95	9.40-9.45	3430 (NH)	327 (4.45)
2	**1b**	**4b**	74	---	3435 (NH)	328 (4.36)
3	**2b**	**5a**	40	---	3380 (NH)	369 (3.88)
4	**2b**	**5b**	76	---	3389 (NH)	367 (4.37)
5	**2b**	**5c**	85	12.47	3412 (NH) 2213 (CN)	375 (4.35)
6	**2b**	**5d**	64	12.45	3362 (NH)	391 (4.29)

Table 2

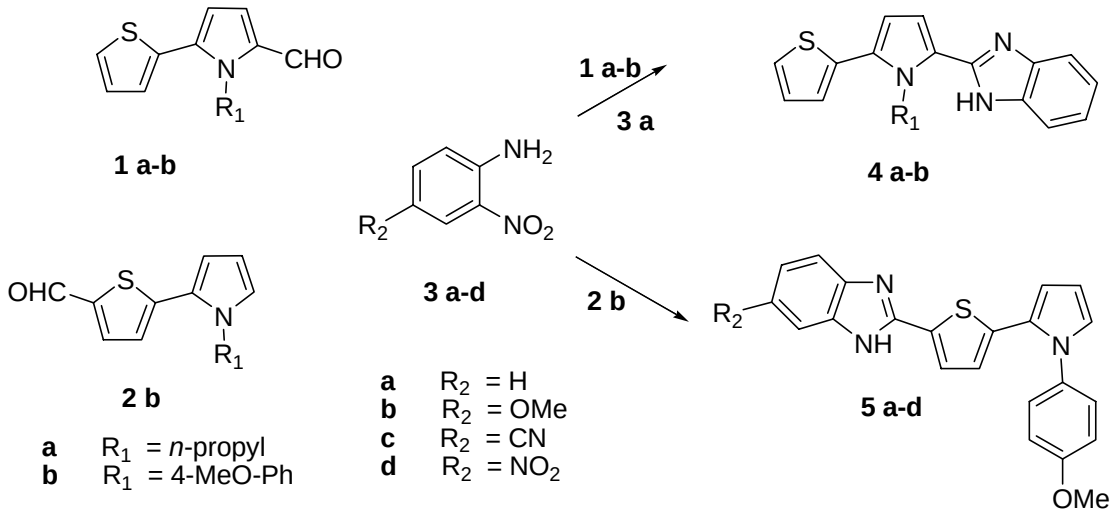
Solvent	π^*[17]	Compound					
		5a		**5b**		**5d**	
		λ_{max}	ν_{max}	λ_{max}	ν_{max}	λ_{max}	ν_{max}
n-hexane	-0.08	358	27933	364	27473	385	25974
diethyl ether	0.27	359	27855	365	27397	387	25839
ethanol	0.54	362	27624	368	27174	391	25575
1,4-dioxane	0.55	361	27701	367	27248	390	25641
ethyl acetate	0.55	360	27778	365	27397	387	25840
THF	0.58	360	27778	365	27397	389	25707
methanol	0.60	361	27701	368	27174	390	25641
acetone	0.71	361	27701	368	27174	394	25381
acetonitrile	0.75	361	27701	368	27174	398	25126
chloroform	0.76[18]	365	27397	375	26666	395	25316
DCM	0.82	365	27397	371	26954	394	25381
DMF	0.88	365	27397	371	26954	397	25189
DMSO	1.00	367	27248	375	26666	405	24697

Table 3

Cpd.	λ_{max} (nm) (log ε)	β[b] (10^{-30}esu)	β_0[c] (10^{-30}esu)	T_d (ºC)[e]	Cpd.	λ_{max} (nm)	β[b] (10^{-30} esu)	β_0[c] (10^{-30}esu)
4a	332.5 (4.53)	42	23	326	**6a**	353.0	64	32
4b	336.0 (4.45)	58	31	363	**6b**	366.0	85	39
5a	361.0 (4.04)	60	29	380	**7b**	386.5	450	180
5b	364.0 (4.28)	---[d]	---[d]	401	---	---	---	---
5c	366.5 (4.34)	114	53	390	---	---	---	---
5d	363.0 (4.29)	121	57	365	---	---	---	---
***p*NA**	352.0	16.9[21-22]	8.5	---	---	---	---	---

Schemes

Scheme 1



Figures

Figure 1

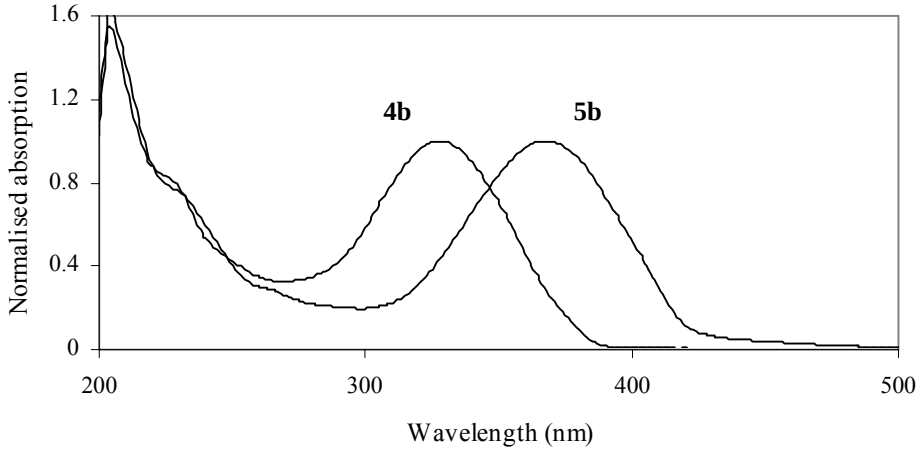


Figure 2

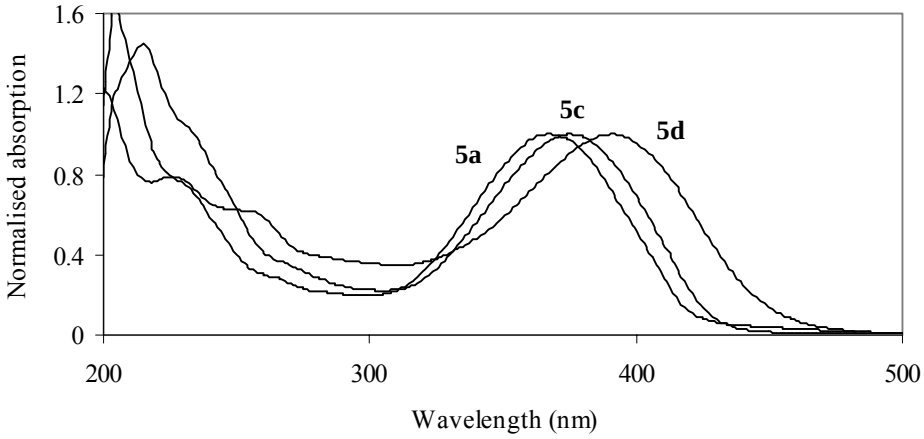
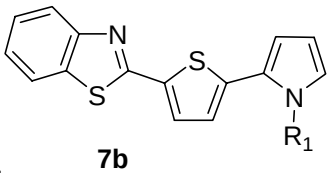


Figure 3

6 a-b

a R_1 = *n*-propyl
b R_1 = 4-MeO-Ph



7b

~~**Figure 4**~~