Graphical abstract

4a,c  5a,c  6a-d  R = alkyl or aryl
Synthesis and characterization of new thienylpyrrolyl-benzothiazoles as efficient and thermally stable nonlinear optical chromophores

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Abstract: The synthesis and full characterization of new chromophores with second-order nonlinearities containing thienylpyrrolyl and benzothiazolyl moieties are reported. The solvatochromic behavior of the compounds was investigated. The hyperpolarizabilities $\beta$ of derivatives 4-6 were measured using hyper-Rayleigh scattering and thermogravimetric analysis (TGA) was used to evaluate their thermal stability. The experimental results indicate that good nonlinearity–thermal stability is well balanced specially for chromophores 6b-c, making them good candidates for NLO applications.

Keywords: Thiophene; Pyrrole; Benzothiazole; Solvatochromism; hyper-Rayleigh (HRS) scattering; Thermal stability; Nonlinear optical (NLO) material.

1. Introduction

Materials with large nonlinear optical (NLO) response are of fundamental importance in modern communications technology, e.g. ultrafast image-processing, optical data processing, transmission and storage.1 Conjugated organic push-pull substituted chromophores are promising candidates for systems with high molecular hyperpolarizabilities $\beta$. In a search for improved response a wide range of structural
modifications to the donor, acceptor and $\pi$-conjugated moieties have been carried out.\textsuperscript{2} Experimental\textsuperscript{3} and theoretical\textsuperscript{4} studies have demonstrated that replacing the benzene ring of a chromophore bridge with easily delocalizable five-member heteroaromatic rings, such as thiophene, pyrrole and thiazole, results in an enhanced molecular hyperpolarizability of donor-acceptor compounds. 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.\textsuperscript{4,5} Several thiazole, imidazole, oxazole and phenyl analogues have been prepared and characterized for comparison of the nonlinear optical properties. These studies showed that the strength of the nonlinear response varies according to the following relationship thiazoles $>$ oxazoles $>$ imidazoles. However, 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 benzothiazole derivatives,\textsuperscript{4a-c,6} as well as conjugated thiophene and pyrrole heterocycles acting as donors, substituted with appropriate acceptor groups.\textsuperscript{7} Recent reports on the synthesis and characterization of chromophores in which the donor moiety is represented by a $\pi$-excessive five-membered heterocycle (pyrrole or thiophene) and the acceptor group is a deficient heterocyclic azine ring (pyridine, pyrazine, pyrimidine, pyridazine), which exhibit solvatochromic, electrochromic, photochromic, fluorescent and nonlinear optical properties.\textsuperscript{8,3g-i}

Our research on new organic and organometallic materials includes an interest in new molecules with application in optical and electronic devices.\textsuperscript{9-12} In particular, thienylpyrrole\textsuperscript{11} and benzothiazole\textsuperscript{12} derivatives which typically exhibit favorable fluorescence, solvatochromic, electrochemical, photochromic and NLO properties could be used in the manufacture of organic light-emitting diodes (OLEDs), semiconductor materials, in optical data storage devices and second-harmonic generators. We were therefore motivated to explore the potential of conjugated 1-(alkyl)aryl-2-(2'-thienyl)pyrroles as strong $\pi$-electron donor moieties functionalized with the benzothiazole group on the thiophene or on the pyrrole ring. Due to the deficiency of electron density on the ring C atoms, the benzothiazole heterocycle acts as electron-withdrawing group and also as an auxiliary acceptor. Moreover, the results obtained concerning the electron-withdrawing power of a series of 2-benzylazoles (thiazole, oxazole and imidazole) and their corresponding benzo-fused analogues in terms of
charge demand $c_x$, a quantity representing the fraction of $\pi$ negative charge withdrawn (delocalized) by the ring, indicate that $c_{\text{thiaz}} > c_{\text{oxaz}} > c_{\text{imidaz}}$. Furthermore, the large electronegativity and lone electron pairs of S and N atoms in benzothiazole and the extension of the conjugation length of the $\pi$-electron bridge lead also to an increase in molecular hyperpolarizability, showing that they are a good choice for NLO applications.\(^{4a,4d,6a}\)

As far as we know this is the first time that the synthesis and the characterization of UV–vis, solvatochromic, thermal and second-order NLO properties of thienylpyrrolyl-benzothiazoles are reported in the literature.

## 2. Results and Discussion

### 2.1. Synthesis

Recently we have developed a method for the synthesis of formylthienylpyrroles 1-3.\(^{11d}\) Compounds 1-3 with the formyl group at 5´-position or 3- and 5-position of the thiophene or pyrrole ring, respectively, were used as precursors of benzothiazoles 4-6 in order to evaluate the effect of the position of benzothiazole group on the optical properties of these chromophores. Benzothiazoles 4-6 with either alkyl or aryl donors on the thienylpyrrolyl system were obtained by reaction of $o$-aminobenzenethiol with formyl derivatives 1-3, in DMSO at 120 °C\(^{13}\) for 2–3 h (Scheme 1).

The reaction is initiated by the formation of the corresponding imine that cyclises spontaneously, yielding the benzothiazoline, which is oxidised to the benzothiazole, aided by the oxidizing character of DMSO. Purification of the crude products by column chromatography gave pure benzothiazoles 4-6 in fair to excellent yields (34-93%). The structures of thienylpyrrolyl-substituted benzothiazoles 4-6 were unambiguously confirmed by their analytical and spectral data.

### 2.2. UV-vis study of benzothiazoles 4-6

The electronic spectra of thienylpyrrolyl-benzothiazole derivatives 4-6 in dioxane were recorded (Table 1). The position of the absorption bands is influenced by the structure
of the compounds, for example by the substituent on the nitrogen atom of the pyrrole ring and by the position of substitution of the benzothiazole moiety on the pyrrole or thiophene ring. The influence of the substituent on the nitrogen atom of the pyrrole ring is demonstrated by comparison of the absorption maxima of compounds 6a and 6d as the longest wavelength transition is shifted from 377.5 nm for 6a to 390.0 nm for 6d. The variation of the absorption peak ($\lambda_{\text{max}}$) with the position of the electro-deficient benzothiazole on the pyrrole or on the thiophene ring for derivatives 4-6 is noteworthy (Figure 1). Chromophores 6a,c which have the benzothiazole nucleus at the 5'-position of the thiophene ring, show marked bathochromic shifts ($ca$ 20-25 nm) in their CT bands compared with chromophores 5a,c which have the benzothiazole group in the 5-position of the pyrrole ring. Substitution of a bulky benzothiazolyl group at the 3-position of the pyrrole ring decreases the overlap between the orbitals of consecutive rings and hence shortens the effective conjugation length. Compounds 5a,c show bathochromic shifts in the absorption $\lambda_{\text{max}}$ compared to derivatives 4a,c due to more extensive electron delocalization. Therefore, the difference in $\lambda_{\text{max}}$ values between compounds 4 and 5 is in the range of 35-47 nm.

2.3. Solvatochromic study of benzothiazoles 4-6
Donor-acceptor substituted thienylpyrroles$^{11b-c,f}$ and benzothiazoles$^{12b-d}$ have been known to demonstrate strong solvatochromic behavior. In order to investigate if compounds 4-6 could act as suitable probes for the determination of solvent polarity, we carried out a preliminary study of the absorption spectra for compounds 4-6 in solvents with different polarities (diethyl ether, ethanol, chloroform and DMSO). We found that compounds 6a ($\Delta \nu = +832 \text{ cm}^{-1}$) and 6d ($\Delta \nu = +581 \text{ cm}^{-1}$) showed the largest energy shifts in the peak absorption band so a full solvatochromic study involving 13 solvents was carried out. The results are summarized in Table 2.

Compounds 6a ($\Delta \nu = +1121 \text{ cm}^{-1}$) and 6d ($\Delta \nu = +924 \text{ cm}^{-1}$) exhibit positive solvatochromism with respect to their CT absorption band, that is, the position of the
absorption maximum shifts to longer wavelengths as the polarity of the solvent increases due to a greater stabilization of the excited state relative to the ground state with increasing polarity of the solvent.\textsuperscript{9d} Noteworthy is the behavior of 6a and 6d in chlorinated solvents such as chloroform and dichloromethane, which slightly deviates from linearity.\textsuperscript{9b,11b} In view of the pronounced solvatochromism, the good correlation with $\pi^*$ values for the 13 solvents investigated, compounds 6a and 6d appear to be very appropriate solvent polarity indicating dyes.

2.4. Study of nonlinear optical properties and thermal stability of benzothiazoles 4-6

We have used the hyper-Rayleigh scattering (HRS) method\textsuperscript{21-22} to measure the first hyperpolarizability $\beta$ of benzothiazoles 4-6. p-Nitroaniline (pNA) was used as standard in order to obtain quantitative values, while care was taken to properly account for possible fluorescence of the dyes (see the experimental section for more details). The static hyperpolarisability $\beta_0$ values are calculated using a very simple two-level model neglecting damping. They are therefore only indicative and should be treated with caution. The measured $\beta$ value for compound 6a is abnormally large; this may be due to a two-photon resonance effect although no evidence of fluorescence at 532 nm was observed, and/or due to steric effects. The $\beta$ values for compounds having the benzothiazole group on the thiophene ring are 20-33 times greater than pNA, whereas the respective $\beta_0$ are 18-26 times greater. From Table 1 it is obvious that the increase of the donor strength of the group that substitutes the nitrogen atom on the pyrrole ring along the series Ph < 4-OMePh < 2,4-diOMePh, results both in red-shifted absorption maxima and enhanced $\beta$ values for pyrroles 6b-d.

Comparison of the $\beta$ values for 6c (450 $\times$ 10\textsuperscript{-30} esu) and 5c (85 $\times$ 10\textsuperscript{-30} esu) shows that the substitution using the benzothiazole group at the 5'-position on the thiophene ring (6c) leads to a larger nonlinearity than the same electron-deficient heterocycle at 5'-position on the pyrrole ring (5c).

The results obtained showed that the location of the electron-deficient benzothiazole on the pyrrole or on the thiophene ring alone can either dramatically alter the overall molecular nonlinearity of the system. One must therefore view the thienylpyrrole and the benzothiazole moieties not simply as the conjugated segments but also as the structural units, which affects the overall electron transfer properties of the system. Pyrrole, being the most electron-rich five-member heteroaromatic ring, counteracts the
electron withdrawing effect of the benzothiazole heterocycle (in 5c), resulting in a decrease in $\beta$. These findings are in accordance with theoretical$^{4a,6i}$ and experimental$^{5a}$ studies reported before for related compounds, and also with our recent work$^{11f}$ where it was concluded that the increase or decrease of the molecular nonlinear activity on heteroaromatic systems depends on the nature and location of the aromatic rings in the system.

Thermal stability of chromophores 4-6 was estimated by thermogravimetric analysis. All samples had very high decomposition temperatures ($T_d= 302–375 \, ^\circ\text{C}$), measured at a heating rate of 20 °C min$^{-1}$ under a nitrogen atmosphere. Experimental results for compounds 6b-d, indicate that good nonlinearity–thermal stability is well balanced for these chromophores, which possess $\beta$ values from $330 \times 10^{-30}$ to $550 \times 10^{-30}$ esu and higher decomposition temperatures ($T_d= 330-375 \, ^\circ\text{C}$).

3. Conclusions

In summary, we have synthesized new thienylpyrrolyl-benzothiazoles 4-6 from formyl-thienylpyrroles 1-3 in moderate to excellent yields.

The solvatochromic behavior of compounds 4-6 was determined by regression analyses of absorption maxima in 13 solvents. Due to their pronounced solvatochromic properties benzothiazoles 4-6 and specially compounds 6a and 6d are suitable to investigate the solvent polarity by means of their absorption wavenumbers. Hyper-Rayleigh scattering was used to determine the first hyperpolarisability, $\beta$, the data showing that $\beta$ is dependent on the substituent on the pyrrole ring (alkyl or aryl) and on the position of substitution (3 or 5) of the benzothiazole group on the pyrrole or on the thiophene ring. It also show that the benzothiazoles have high molecular nonlinearities specially derivatives 6b-d, in which the benzothiazole group is substituted on the thiophene ring, as their values are 20–33 times higher that the well known pNA molecule.

Thermal stability of chromophores 4-6 was estimated by thermogravimetric analysis. All samples had very high decomposition temperatures ($T_d= 302–375 \, ^\circ\text{C}$).

Experimental results for compounds 6b-d, indicate that good nonlinearity–thermal stability is well balanced for these chromophores which possess $\beta$ values from $330 \times$
10\(^{-30}\) to 550 \(\times\) 10\(^{-30}\) esu and the higher decomposition temperatures (\(T_d= 330–375 \degree \text{C}\)), making them good candidates for NLO applications.

4. Experimental

4.1. Synthesis 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 (\(\delta\) relative to TMS and given in ppm). Peak assignments were carried out by the DEPT 135, HMQC (Heteronuclear Multiple Quantum Coherence) and HMBC (Heteronuclear Multiple Bond Coherence) 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 of the University of Vigo, Spain.

Light petroleum refers to solvent boiling in the range 40-60 \degree\text{C}. The synthesis of formyl-thienylpyrroles 1-3 was described elsewhere.\(^{11d}\)

4.2. General procedure for the synthesis of thienylpyrrolyl-1,3-benzothiazoles 4-6

The corresponding formyl-thienylpyrroles 1-3 (1 equiv) and \(o\)-aminobenzenethiol (1 equiv) were heated in DMSO (1 mL/ mmol) at 120 \degree\text{C} with stirring for 2-3h. The reaction was followed by TLC using diethyl ether/light petroleum 1:1 as eluent. When the reaction was complete, the reaction mixture was allowed to cool and poured into water and extracted with ethyl acetate (3 \(\times\) 50 mL/mmol). The organic layer was dried with magnesium sulphate and evaporated under reduced pressure. The crude residue was submitted to silica gel column chromatography using mixtures of diethyl ether and light petroleum of increasing polarity. The fractions containing the purified product were collected and evaporated under vacuum.
4.2.1. \(2-(1'\text{-Propyl-2'}\text{-thien-2''-yl}pyrrol-3'-yl)-1,3\text{-benzothiazole (4a)}\). Orange oil (34%). UV (dioxane): \(\lambda_{\text{max}} \text{nm (log } \varepsilon \text{)} 318.0 (4.09), 303.0 (4.05); 289.0 (4.01), 240.5 (4.16).\) IR (liquid film) \(v\) 3063, 2964, 2930, 2873, 1664, 1572, 1524, 1439, 1345, 1244, 1219, 1084, 965, 908, 848, 758, 728 cm\(^{-1}\). \(^1\)H NMR (CDCl\(_3\)) \(\delta \) 0.89 (t, 3H, \(J=7.5\) Hz, \(CH_3\)), 1.75 (m, 2H, \(CH_2CH_2CH_3\)), 3.76 (t, 2H, \(CH_2CH_2CH_3\)), 6.86 (d, 1H, \(J=3.0\) Hz, \(5'\)-H), 7.02 (d, 1H, \(J=3.0\) Hz, \(4'\)-H), 7.20-7.26 (m, 3H, \(6'\)-H + \(4''\)-H + \(3''\)-H), 7.38 (dt, 1H, \(J=8.1\) and 1.2 Hz, \(5\)-H), 7.64-7.68 (m, 2H, \(7\)-H + \(5''\)-H), 7.95 (dd, 1H, \(J=8.1\) and 1.2 Hz, 4-H). MS (FAB) \(m/z\) (%): 325 ([M+H]\(^+\), 100), 324 (M\(^+\), 25), 323 (23), 281 (11), 163 (9). HRMS: (FAB) \(m/z\) (%) for C\(_{18}\)H\(_{17}\)N\(_2\)S\(_2\); calcd 325.0833; found 325.0838.

4.2.2. \(2-(1'-(4'''\text{-Methoxyphenyl)-2'}\text{-thien-2''-yl}pyrrol-3'-yl)-1,3\text{-benzothiazole (4c)}\). Yellow solid (48%). Mp: 165.4-166.6 °C. UV (dioxane): \(\lambda_{\text{max}} \text{nm (log } \varepsilon \text{)} 319.0 (4.37), 305.5 (4.34), 292.0 (4.31), 244.5 (4.39).\) IR (KBr) \(v\) 3103, 2960, 2852, 1607, 1514, 1443, 1322, 1235, 1111, 1032, 927, 907, 837, 754, 713 cm\(^{-1}\). \(^1\)H NMR (CDCl\(_3\)) \(\delta \) 3.80 (s, 3H, OC\(_H_3\)), 6.83 (dd, 2H, \(J=9.3\) and 2.4 Hz, \(3''''\)-H + \(5''''\)-H), 7.00 (d, 1H, \(J=3.0\) Hz, \(5'\)-H), 7.07-7.10 (m, 1H, \(4''\)-H), 7.15-7.18 (m, 4H, \(3''\)-H + \(4'\)-H + \(2''\)-H + \(6''\)-H), 7.28 (dt, 1H, \(J=6.6\) and 1.5 Hz, 6-H), 7.42 (dt, 1H, \(J=8.4\) and 1.2 Hz, 5-H), 7.49 (dd, 1H, \(J=5.1\) and 1.2 Hz, \(5''\)-H) 7.70 (broad d, 1H, \(J=8.7\) Hz, 7-H), 8.05 (broad d, 1H, \(J=8.7\) Hz, 4-H). \(^1\)C NMR (CDCl\(_3\)) \(\delta \) 55.41 (OCH\(_3\)), 109.28 (C4'), 113.98 (C3'''' + C5'''''), 120.62 (C2'), 121.15 (C7), 121.94 (C4), 124.36 (C6), 124.79 (C5'), 125.92 (C5), 126.80 (C3'), 127.24 (C4'' + C2'''' + C6'''''), 129.32 (C5'''), 130.62 (C2'''), 132.11 (C3'''' + C1'''''), 134.35 (C7a), 152.22 (C3a), 158.86 (C4'''''), 161.35 (C2). MS (FAB) \(m/z\) (%): 389 ([M+H]\(^+\), 100), 388 (M\(^+\), 41), 387 (20), 154 (9). HRMS: (EI) \(m/z\) (%) for C\(_{22}\)H\(_{17}\)N\(_2\)S\(_2\); calcd 389.0782; found 389.0785.

4.2.3. \(2-(1'\text{-Propyl-5'}\text{-thien-2''-yl}pyrrol-2'-yl)-1,3\text{-benzothiazole (5a)}\). Dark green oil (75%). UV (dioxane): \(\lambda_{\text{max}} \text{nm (log } \varepsilon \text{)} 353.0 (4.49), 256.5 (4.40), 241.0 (4.13).\) IR (liquid film) \(v\) 3103, 3067, 2963, 2871, 1595, 1541, 1482, 1434, 1392, 1312, 1248, 1195, 1046, 933, 899, 756 cm\(^{-1}\). \(^1\)H NMR (CDCl\(_3\)) \(\delta \) 0.93 (t, 3H, \(J=7.5\) Hz, \(CH_3\)), 1.79-1.87 (m, 2H, \(CH_2CH_2CH_3\)), 4.69 (t, 2H, \(J=7.5\) Hz, \(CH_2CH_2CH_3\)), 6.39 (d, 1H, \(J=3.9\) Hz, \(4'\)-H), 6.88 (d, 1H, \(J=4.2\) Hz \(3'\)-H), 7.12-7.18 (m, 2H, \(4''\)-H + \(3''\)-H), 7.34 (dt, 1H, \(J=7.2\) and 1.2 Hz, \(5''\)-H), 7.45 (dt, 1H, \(J=7.2\) and
1.2 Hz, 5-H), 7.84 (dd, 1H, J=8.7 and 1.2 Hz, 7-H), 7.95 (dd, 1H, J=8.1 and 1.2 Hz, 4-H).  
$^{13}$C NMR (CDCl$_3$) δ 10.88 (CH$_3$), 24.72 (CH$_2$CH$_2$CH$_3$), 42.72 (CH$_2$CH$_2$CH$_3$), 111.59 (C4’), 115.13 (C3’), 121.04 (C7), 122.54 (C4), 124.51 (C6), 125.91 (C5), 126.02 (C5’”), 126.70 (C3’”), 127.42 (C4’”), 127.47 (C5’”), 132.24 (C2’), 133.87 (C7a), 133.90 (C2’”), 154.38 (C3a), 160.18 (C2). MS (FAB) m/z (%): 325 ([M+H]$$^+$$, 81), 324 (M$$^+$$, 100), 307 (25), 289 (13), 155 (22), 154 (71). HRMS: (FAB) m/z (%) for C$_{18}$H$_{17}$N$_2$S$_2$; calcd 325.0833; found 325.0837.

4.2.4. 2-(1’-(4’’-Methoxyphenyl)-5’-(thien-2’’-yl)pyrrol-2’-yl)-1,3-benzothiazole (5c). Brown solid (35%). Mp: 154.9-156.3 ºC. UV (dioxane): $\lambda_{\text{max}}$ nm (log $\varepsilon$) 366.0 (4.51), 257.5 (4.12), 244.0 (4.20). IR (KBr) ν 3060, 2931, 2852, 1513, 1480, 1434, 1299, 1251, 1043, 758, 693 cm$^{-1}$. $^1$H NMR (CDCl$_3$) δ 3.95 (s, 3H, OCH$_3$), 6.67 (d, 1H, J=3.9 Hz, 3’-H), 6.73 (broad d, 1H, J=3.9 Hz, 3’’-H), 6.86-6.89 (m, 1H, 4’’-H), 7.03-7.06 (dd, m, H, J=3.9 Hz, 5’’-H), 7.11 (dd, m, H, J=5.5 and 1.2 Hz, 5’’-H), 7.24 (broad t, m, H, J=8.4 Hz, 6-H), 7.35-7.41 (m, 4H, 2’’-H + 6’’-H + 5-H + 4’-H), 7.65 (broad d, m, H, J=8.7 Hz, 7-H), 7.94 (broad d, m, H, J=8.7 Hz, 4-H).  
$^{13}$C NMR (CDCl$_3$) δ 55.60 (OCH$_3$), 110.46 (C3’), 114.78 (C3’’ + C5’’’), 120.97 (C7), 121.90 (C4), 124.35 (C6), 125.08 (C5’’), 125.15 (C3’’’), 126.25 (C5), 127.04 (C4’’’), 129.65 (C5’ + C1’’’), 131.68 (C2’’’ + C6’’’), 133.75 (C2’ + C2’’), 133.97 (C7a), 152.02 (C3a), 158.70 (C2), 161.04 (C4’’’). MS (FAB) m/z (%): 389 ([M+H]$^+$, 100), 388 (M$$^+$$, 76), 387 (10), 219 (7). HRMS: (FAB) m/z (%) for C$_{22}$H$_{17}$N$_2$OS$_2$; calcd 389.0782; found 389.0778.

4.2.5. 2-(1’’-Propyl-2’’-(thien-2’’-yl)pyrrolyl)-1,3-benzothiazole (6a). Dark green solid (36%). Mp: 65.3-67.0 ºC. UV (dioxane): $\lambda_{\text{max}}$ nm (log $\varepsilon$) 377.5 (4.47), 256.0 (4.23), 244.0 (4.23). IR (KBr) ν 3102, 2966, 2930, 1526, 1477, 1301, 1256, 1230, 1081, 1027, 906, 833, 804, 751, 726 cm$^{-1}$. $^1$H NMR (CDCl$_3$) δ 0.93 (t, 3H, J=7.5 Hz, CH$_3$), 1.80 (m, 2H, CH$_2$CH$_2$CH$_3$), 4.08 (t, 2H, J=7.5 Hz, CH$_2$CH$_2$CH$_3$). 6.21-6.23 (m, 1H, 4’’-H), 6.45-6.47 (m, 1H, 3’’-H), 6.81-6.83 (m, 1H, 5’’-H), 7.04 (d, 1H, J=3.9 Hz, 4’-H), 7.38 (dt, 1H, J=7.5 and 1.5 Hz, 6-H), 7.48 (dt, 1H, J=7.5 and 1.5 Hz, 5-H), 7.60 (d, 1H, J=3.9 Hz, 3’-H), 7.86 (dd, 1H, J=7.5 and 1.5 Hz, 7-H), 8.02 (dd, 1H, J=7.5 and 1.5 Hz, 4-H).  
$^{13}$C NMR (CDCl$_3$) δ 11.17 (CH$_3$), 24.67 (CH$_2$CH$_2$CH$_3$), 49.45 (CH$_2$CH$_2$CH$_3$), 108.34 (C4’’), 111.29 (C3’’), 121.37 (C7), 122.75 (C4), 124.20 (C5’’), 125.06 (C4’’),
125.08 (C6), 125.88 (C2''), 126.39 (C5), 129.02 (C3'), 134.51 (C7a), 135.18 (C2' or C5'), 139.31 (C2' or C5'), 153.69 (C3a), 161.27 (C2). MS (EI) m/z (%): 325 (M++1, 23), 324 (M+, 100), 282 (21), 281 (15). HRMS: (EI) m/z (%) for C_{18}H_{16}N_{2}S_{2}; calcd 324.0755; found 324.0760.

4.2.6. 2-(1''-Phenyl-2''-(thien-2'-yl)pyrrolyl)-1,3-benzothiazole (6b). Dark green solid (48%). Mp: 73.1-74.9 °C. UV (dioxane): λ_{max} nm (log ε) 374.5 (4.23), 256.0 (3.98), 241.5 (4.12). IR (KBr) ν 2924, 1725, 1595, 1528, 1496, 1434, 1256, 1232, 1071, 805, 760, 724, 696 cm⁻¹. ¹H NMR (CDCl₃) δ 6.36-6.38 (m, 1H, 4''-H), 6.44 (d, 1H, J=3.9 Hz, 4'-H), 6.63-6.65 (m, 1H, 3''-H), 6.94-6.95 (m, 1H, 5''-H), 7.32-7.35 (m, 4H, 6-H + 3 × Ph-H), 7.37 (d, 1H, J=3.9 Hz, 3'-H), 7.41-7.48 (m, 3H, 5-H + 2 × Ph-H), 7.82 (broad d, 1H, J=7.2 Hz, 7-H), 7.99 (broad d, 1H, J=8.1 Hz, 4-H). ¹³C NMR (CDCl₃) δ 109.69 (C4''), 112.06 (C3''), 121.33 (C7), 122.72 (C4), 124.86 (C6), 124.99 (C4''), 125.77 (C5''), 126.35 (C5), 126.61 (2 × Ph-C), 126.77 (C2''), 127.90 (1 × Ph-C), 128.91 (C3'), 129.26 (2 × Ph-C), 134.51 (C7a), 134.62 (C2' or C5'), 139.17 (C2' or C5'), 139.76 (C1'''), 153.71 (C3a), 161.25 (C2). MS (EI) m/z (%): 359 (M⁺+1, 25), 358 (M⁺, 100), 254 (6), 149 (15). HRMS: (EI) m/z (%) for C_{21}H_{14}N_{2}S_{2}; calcd 358.0598; found 358.0594.

4.2.7. 2-(1''-(4'''-Methoxyphenyl)-2''-(thien-2'-yl)pyrrolyl)-1,3-benzothiazole (6c). Dark green solid (93%). Mp: 141.8-143.5 °C. UV (dioxane): λ_{max} nm (log ε) 386.5 (4.25), 257.0 (4.13), 242.0 (4.09). IR (KBr) ν 2922, 1515, 1484, 1247, 1043, 901, 842, 755, 717 cm⁻¹. ¹H NMR (CDCl₃) δ 3.88 (s, 3H, OC₃H₃), 6.33-6.35 (m, 1H, 4''-H), 6.47 (d, 1H, J=3.9 Hz, 4'-H), 6.61-6.63 (m, 1H, 3''-H), 6.88-6.90 (m, 1H, 5''-H), 6.96 (d, 2H, J=9 Hz, 3''''-H + 5''''-H), 7.26 (d, 2H, J=9 Hz, 2''''-H + 6''''-H), 7.34 (dt, 1H, J=6.6 and 1.2 Hz, 6-H), 7.38 (d, 1H, J=4.2 Hz, 3'-H), 7.46 (dt, 1H, J=6.9 and 1.2 Hz, 5-H), 7.82 (dd, 1H, J=8.1 and 0.9 Hz, 7-H) 7.98 (dd, 1H, J=7.5 and 0.6 Hz, 4-H). ¹³C NMR (CDCl₃) δ 55.46 (OCH₃), 109.33 (C4'''), 111.35 (C3'''), 114.33 (C3''' + C5'''''), 121.28 (C7), 122.64 (C4), 124.47 (C4''), 124.92 (C6), 125.97 (C5'''), 126.30 (C5), 127.13 (C2''), 127.96 (C2''' + C6''''), 128.93 (C3'''), 132.64 (C1'''''), 134.35 (C2' or C5''), 134.46 (C7a), 139.32 (C2' or C5'), 153.68 (C3a), 159.19 (C4'''''), 161.26 (C2). MS (EI) m/z (%): 389 (M⁺+1, 27), 338 (M⁺, 100), 373 (29), 194 (8). HRMS: (EI) m/z (%) for C_{22}H_{16}N_{3}S_{2}O; calcd 388.0704; found 388.0706.
4.2.8. 2-(1''-(2''',4'''-Dimethoxyphenyl)-2'''-(thien-2'-yl)pyrrolyl)-1,3-benzothiazole (6d). Dark green solid (67%). Mp: 141.2-142.8 °C. UV (dioxane): $\lambda_{\text{max}}$ nm (log ε) 390.0 (4.42), 260.0 (4.08), 243.0 (4.17). IR (KBr) ν 2926, 1727, 1610, 1590, 1516, 1444, 1308, 1207, 1161, 1131, 1118 cm$^{-1}$. $^1$H NMR (CDCl$_3$) δ 3.68 (s, 3H, OCH$_3$), 3.89 (s, 3H, OCH$_3$), 6.35-6.37 (m, 1H, 4''-H), 6.52 (d, 1H, $J$=3.9 Hz, 4'-H), 6.54-6.57 (m, 2H, 3''''-H + 5''''-H), 6.64-6.66 (m, 1H, 3'''-H), 6.79-6.81 (m, 1H, 5''-H), 7.24 (d, 1H, $J$=9 Hz, 6''''-H), 7.33 (dt, 1H, $J$=6.9 and 1.2 Hz, 6-H), 7.38 (d, 1H, $J$=3.9 Hz, 3'-H), 7.44 (dt, 1H, $J$=6.9 and 1.2 Hz, 5-H), 7.81 (dd, 1H, $J$=6.9 and 1.2 Hz, 7-H), 7.97 (dd, 1H, $J$=6.9 and 1.2 Hz, 4-H). $^{13}$C NMR (CDCl$_3$) δ 55.55 (OCH$_3$), 55.73 (OCH$_3$), 99.75 (C3''' or C5'''), 104.33 (C3''' or C5'''), 109.19 (C4''), 110.22 (C3'''), 121.26 (C7), 121.79 (C1'''), 122.58 (C4), 123.19 (C4'), 124.84 (C6), 126.14 (C5'''), 126.25 (C5), 128.06 (C2'''), 128.96 (C3'), 129.67 (C6'''), 133.75 (C2' or C5'), 134.44 (C7a), 139.84 (C2' or C5'), 153.72 (C3a), 156.29 (C2''''), 161.00 (C4'''), 161.42 (C2). MS (EI) m/z (%): 419 (M$^+$+1, 27), 418 (M$^+$, 100), 403 (22), 360 (6), 209 (8). HRMS: (EI) m/z (%) for C$_{23}$H$_{18}$N$_2$S$_2$O$_2$; calcd 418.0810; found 418.0807.

4.3. Nonlinear optical measurements for compounds 4-6 using the hyper-Rayleigh scattering (HRS) method$^{21}$

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 the one presented by Clays et al.$^{21}$ The incident laser beam came from a Q-switched Nd:YAG laser operating at a 10 Hz repetition rate with approximately 20 mJ of energy per pulse and a pulse duration (FWHM) of 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 profiles 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 (pNA)$^{22}$ also dissolved in dioxane at a concentration of $1 \times 10^{-2}$ 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.$^{17-18}$ The concentrations of the solutions under study ($10^{-4}$ M) 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

$$I_{2\omega} = G \left[ N_{\text{solvent}} \left\langle \beta_{\text{solvent}}^2 \right\rangle + N_{\text{solute}} \left\langle \beta_{\text{solute}}^2 \right\rangle \right] I_{\omega}^2$$

where the factor G is an instrumental factor that takes into account the detection
efficiency (including geometrical factors and linear absorption or scattering of the
second harmonic light on its way to the detector) and local field corrections. The
brackets indicate an average over the spatial orientations of the molecules. The error
associated with the HRS measured $\beta$ values is estimated to be approximately 15%.

We took particular care to avoid reporting artificially high hyperpolarizabilities 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:
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). From our measurements we conclude that compounds 6a and 6d emit negligible fluorescence at 532 nm. When using the “narrow” band filter the estimated fraction of the total detected signal due to fluorescence is listed in the following table:

<table>
<thead>
<tr>
<th>Compound</th>
<th>$S_{NB}^F / S_{NB}$</th>
</tr>
</thead>
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<tr>
<td>4a</td>
<td>0.49</td>
</tr>
<tr>
<td>4c</td>
<td>0.53</td>
</tr>
<tr>
<td>5a</td>
<td>0.59</td>
</tr>
<tr>
<td>5c</td>
<td>0.25</td>
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<tr>
<td>6a</td>
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<tr>
<td>6b</td>
<td>0.30</td>
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<tr>
<td>6c</td>
<td>0.14</td>
</tr>
<tr>
<td>6d</td>
<td>---</td>
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</table>
We estimate that the error associated with the above values varies between 5% and 15% of the value quoted.

4.4. Thermogravimetric analysis of compounds 4-6

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 °C min\(^{-1}\) heating rate and were characterized between 25 and 700 °C.

Acknowledgments

Thanks are due to Foundation for Science and Technology (Portugal) for financial support through 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.

References


FIGURE CAPTIONS

Figure 1. UV/Vis absorption spectra of compounds 4a-6a in dioxane.

SCHEME TITLES

Scheme 1. Synthesis of benzothiazoles 4-6 from formyl-thienylpyrroles 1-3.

TABLES CAPTIONS

Table 1. Yields, UV-vis absorptions, $\beta$ and $\beta_0$ values and $T_d$ data for compounds 4-6.\(^a\)

\(^a\) 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 $\beta_0 = \beta [1-(\lambda_{\text{max}}/1064)^2][1-(\lambda_{\text{max}}/532)^2]$; damping factors were not included.\(^{14-16}\)
\(^d\) The hyperpolarizability for compound 6a proved to be extraordinarily large, possibly due to a two photon resonance enhancement effect.
\(^e\) Decomposition temperature ($T_d$) measured at a heating rate of 20 °C min\(^{-1}\) under a nitrogen atmosphere, obtained by TGA.

Table 2. Solvatochromic data [$\lambda_{\text{max}}$ (nm) of the Charge-Transfer band] for compounds 6a and 6d in selected solvents.

\(^a\) Solvents used as received. The correlation coefficient $r$ obtained for the linear solvatation energy relationship with $\pi^*$ values by Kamlet and Taft without chlorinated solvents was $r = 0.9451$ for 6a and 0.8987 for 6d.
## Tables

### Table 1

<table>
<thead>
<tr>
<th>Compd</th>
<th>Yield (%)</th>
<th>( \lambda_{\text{max}} ) (nm)</th>
<th>( \beta^b ) (10(^{-30}) esu)</th>
<th>( \beta_0^c ) (10(^{-30}) esu)</th>
<th>( T_d ) (°C)(^e)</th>
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<tr>
<td>4a</td>
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<td>890(^d)</td>
<td>380</td>
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<td>352.0</td>
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<td>8.5</td>
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Table 2

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<th>Solvent(^a)</th>
<th>(\pi^{19})</th>
<th>6a</th>
<th>(\lambda_{\text{max}}) (nm)</th>
<th>(\nu_{\text{max}}) (cm(^{-1}))</th>
<th>6d</th>
<th>(\lambda_{\text{max}}) (nm)</th>
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</table>
Scheme 1

\[ \text{Scheme 1} \]

\[ \begin{align*}
1a,c & \quad \begin{array}{c}
\text{OHC} \\
\text{S} \\
\text{N}
\end{array} \\
2a,c & \quad \begin{array}{c}
\text{SH} \\
\text{S} \\
\text{N}
\end{array} \\
3a-d & \quad \begin{array}{c}
\text{SH} \\
\text{S} \\
\text{N}
\end{array}
\end{align*} \]

\[ \text{DMSO, 120 °C} \]

\[ \begin{align*}
a & \quad R = \text{n-Pr} \\
b & \quad R = \text{Ph} \\
c & \quad R = \text{4-MeOPh} \\
d & \quad R = 2,4-diMeOPh
\end{align*} \]

Figure 1

\[ \begin{align*}
\text{Wavelength (nm)} & \quad 250 \quad 300 \quad 350 \quad 400 \quad 450 \quad 500 \\
\text{Abs} & \quad 0 \quad 0.5 \quad 1 \quad 1.5 \quad 2 \quad 2.5 \quad 3 \quad 3.5
\end{align*} \]