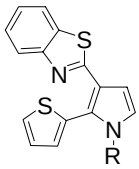
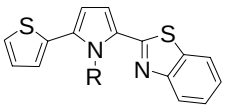
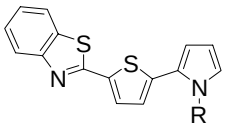
Graphical abstract



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 β 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 β. In a search for improved response a wide range of structural

modifications to the donor, acceptor and π-conjugated moieties have been carried out.[2] Experimental[3] and theorectical[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.[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,[4a-c,6] as well as conjugated thiophene and pyrrole heterocycles acting as donors, substituted with appropriate acceptor groups.[7]
Recent reports on the synthesis and characterization of chromophores in which the donor moiety is represented by a π-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.[8,3g-i]

Our research on new organic and organometallic materials includes an interest in new molecules with application in optical and electronic devices.[9-12] In particular, thienylpyrrole[11] and benzothiazole[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 π-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 π negative charge withdrawn (delocalized) by the ring, indicate that $c_{thiaz} > c_{oxaz} > c_{imidaz}$. Furthermore, the large electronegativity and lone electron pairs of S and N atoms in benzothiazole and the extension of the conjugation length of the π-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).

<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.

<table 1>

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 (λ_{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 λ_{max} compared to derivatives **4a**,**c** due to more extensive electron delocalization. Therefore, the difference in λ_{max} values between compounds **4** and **5** is in the range of 35-47 nm.

<figure 1>

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 cm^{-1}) and **6d** ($\Delta\nu$ = +581 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.

<table 2>

Compounds **6a** ($\Delta\nu$ = +1121 cm^{-1}) and **6d** ($\Delta\nu$ = +924 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.[9d] Noteworthy is the behavior of **6a** and **6d** in chlorinated solvents such as chloroform and dichloromethane, which sligthly deviates from linearity.[9b,11b] In view of the pronounced solvatochromism, the good correlation with π* 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[21-22] to measure the first hyperpolarizability β 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 β_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 β 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 β values for compounds having the benzothiazole group on the thiophene ring are 20-33 times greater than pNA, whereas the respective β_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 β values for pyrroles **6b-d**.

Comparison of the β values for **6c** (450×10^{-30} esu) and **5c** (85×10^{-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 electro-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 β. These findings are in accordance with theoretical[4a,6i] and experimental[6a] 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 ºC), measured at a heating rate of 20 ºC 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 β values from 330 × 10^{-30} to 550 × 10^{-30} esu and higher decomposition temperatures (T_d= 330-375 ºC).

3. Conclusions

In summary, we have synthesized new thienylpyrrolyl-benzothiazoles **4-6** from formyl-thienylpyrroles **1-3** in moderate to excelent 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, β, the data showing that β 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 ºC).

Experimental results for compounds **6b-d**, indicate that good nonlinearity-thermal stability is well balanced for these chromophores which possess β values from 330 ×

10^{-30} to 550 × 10^{-30} esu and the higher decomposition temperatures (T_d= 330–375 ºC), 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 (δ 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 ºC. 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 ºC 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 × 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'-Propyl-2'-(thien-2''-yl)pyrrol-3'-yl)-1,3-benzothiazole (4a). Orange oil (34%). UV (dioxane): λ_{max} nm (log ε) 318.0 (4.09), 303.0 (4.05); 289.0 (4.01), 240.5 (4.16). IR (liquid film) ν 3063, 2964, 2930, 2873, 1664, 1572, 1524, 1439, 1345, 1244, 1219, 1084, 965, 908, 848, 758, 728 cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.89 (t, 3H, *J*=7.5 Hz, C*H*$_3$), 1.75 (m, 2H, $CH_2CH_2CH_3$*),* 3.76 (t, 2H, *J*=7.5 Hz, $CH_2CH_2CH_3$), 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 $C_{18}H_{17}N_2S_2$; calcd 325.0833; found 325.0838.

4.2.2. 2-(1'-(4'''-Methoxyphenyl)-2'-(thien-2''-yl)pyrrol-3'-yl)-1,3-benzothiazole (4c). Yellow solid (48%). Mp: 165.4-166.6 ºC. UV (dioxane): λ_{max} nm (log ε) 319.0 (4.37), 305.5 (4.34), 292.0 (4.31), 244.5 (4.39). IR (KBr) ν 3103, 2960, 2852, 1607, 1514, 1443, 1322, 1235, 1111, 1032, 927, 907, 837, 754, 713 cm^{-1}. ^1H NMR ($CDCl_3$) δ 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). ^{13}C NMR ($CDCl_3$) δ 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 $C_{22}H_{17}N_2OS_2$; calcd 389.0782; found 389.0785.

4.2.3. 2-(1'-Propyl-5'-(thien-2''-yl)pyrrol-2'-yl)-1,3-benzothiazole (5a). Dark green oil (75%). UV (dioxane): λ_{max} nm (log ε) 353.0 (4.49), 256.5 (4.40), 241.0 (4.13). IR (liquid film) ν 3103, 3067, 2963, 2871, 1595, 1541, 1482, 1434, 1392, 1312, 1248, 1195, 1046, 933, 899, 756 cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.93 (t, 3H, *J*=7.5 Hz, C*H*$_3$), 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, 6-H), 7.39 (dd, 1H, *J*=4.5 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 (*C*H_3), 24.72 (CH_2*C*H_2CH_3), 42.72 (*C*$H_2CH_2CH_3$), 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 $C_{18}H_{17}N_2S_2$; 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): λ_{max} nm (log ε) 366.0 (4.51), 257.5 (4.12), 244.0 (4.20). IR (KBr) ν 3060, 2931, 2852, 1513, 1480, 1434, 1299, 1251, 1043, 844, 758, 693 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 3.95 (s, 3H, OC*H*$_3$), 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, 2H, *J*=8.7 and 2.1 Hz, 3'''-H and 5'''-H), 7.11 (dd, 1H, *J*=5.5 and 1.2 Hz, 5''-H), 7.24 (broad t, 1H, *J*=8.4 Hz, 6-H), 7.35-7.41 (m, 4H, 2'''-H + 6'''-H + 5-H + 4'-H), 7.65 (broad d, 1H, *J*=8.7 Hz, 7-H), 7.94 (broad d, 1H, *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 $C_{22}H_{17}N_2OS_2$; 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): λ_{max} nm (log ε) 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, C*H*$_3$), 1.80 (m, 2H, CH_2C*H*$_2$$CH_3$*),* 4.08 (t, 2H, *J*=7.5 Hz, C*H*$_2$$CH_2CH_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$) δ 11.17 (*C*H_3), 24.67 (CH_2*C*H_2CH_3), 49.45 (*C*$H_2CH_2CH_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 $C_{18}H_{16}N_2S_2$; 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 ºC. 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 ($CDCl_3$) 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). ^{13}C NMR ($CDCl_3$) 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 $C_{21}H_{14}N_2S_2$; 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 ºC. 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 ($CDCl_3$) δ 3.88 (s, 3H, OCH_3), 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). ^{13}C NMR ($CDCl_3$) δ 55.46 (OCH_3), 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 $C_{22}H_{16}N_2S_2O$; 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 ºC. UV (dioxane): λ_{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}. ^1H 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 (O*C*H_3), 55.73 (O*C*H_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 $C_{23}H_{18}N_2S_2O_2$; 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 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.[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 β values were calibrated using a reference solution of *p*-nitroaniline (pNA)[22] 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.[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

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

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 approximately 15%.

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). 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:

Compound	S_{NB}^{F} / S_{NB}
4a	0.49
4c	0.53
5a	0.59
5c	0.25
6a	---
6b	0.30
6c	0.14
6d	---

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 ºC min^{-1} heating rate and were characterized between 25 and 700 ºC.

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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, β and β_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 $\beta_0 = \beta\,[1-(\lambda_{max}/1064)^2][1-(\lambda_{max}/532)^2]$; 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 ºC min^{-1} under a nitrogen atmosphere, obtained by TGA.

Table 2. Solvatochromic data [λ_{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 **π*** values by Kamlet and Taft without chlorinated solvents was $r = 0.9451$ for **6a** and 0.8987 for **6d**.

Tables

Table 1

Compd	Yield (%)	λ_{max} (nm)	β[b] (10^{-30} esu)	β_0[c] (10^{-30} esu)	T_d (ºC)[e]
4a	34	318.0	75	44	—
4c	48	319.0	73	43	369
5a	75	353.0	64	32	—
5c	35	366.0	85	39	336
6a	36	377.5	890[d]	380	302
6b	48	374.5	330	150	330
6c	93	386.5	450	180	357
6d	67	390.0	550	220	375
pNA	—	352.0	16.9[17-18]	8.5	—

Table 2

Solvent[a]	π^*[19]	6a		6d	
		λ_{max} (nm)	ν_{max} (cm^{-1})	λ_{max} (nm)	ν_{max} (cm^{-1})
n-hexane	-0.08	370.0	27027	384.0	26049
diethyl ether	0.27	374.0	26738	389.0	25706
ethanol	0.54	379.0	26385	391.0	25575
toluene	0.54	380.0	26316	393.0	25445
dioxane	0.55	379.0	26385	390.0	25641
ethyl acetate	0.55	377.0	26525	389.0	25707
THF	0.58	379.0	26385	392.0	25510
methanol	0.60	378.0	26455	391.0	25575
acetonitrile	0.75	378.0	26455	390.0	25641
chloroform	0.76[20]	373.0	26809	388.0	25773
DCM	0.82	377.0	26525	389.0	25707
DMF	0.88	384.0	26041	395.0	25316
DMSO	1.00	386.0	25906	398.0	25125

Scheme 1

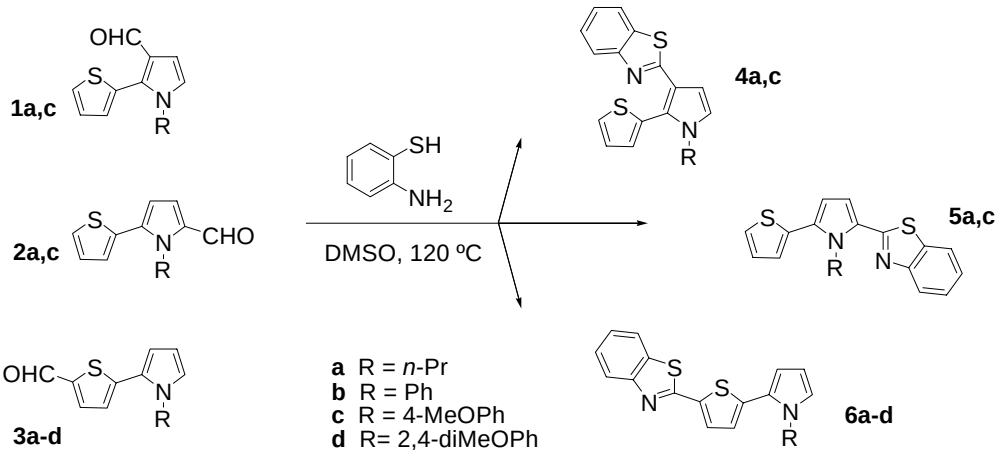

Figure 1