

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

Rosa M. F. Batista,<sup>a</sup> Susana P. G. Costa,<sup>a</sup> M. Belsley<sup>b</sup> and M. Manuela M. Raposo<sup>a,\*</sup>

<sup>a</sup>Centro de Química, Universidade do Minho, Campus de Gualtar, 4710-057 Braga, Portugal

<sup>b</sup>Departamento de Física, Universidade do Minho, Campus de Gualtar, 4710-057 Braga, Portugal

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**Abstract**—A new series of thermally stable benzimidazole-based nonlinear optical (NLO) chromophores **4** and **5** have been developed. These chromophores possess a thienylpyrrolyl  $\pi$ -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. © 2007 Elsevier Ltd. All rights reserved.

## 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.<sup>1</sup> One commonly used strategy to design  $\pi$ -electron chromophores for second-order NLO applications is to end-cap a suitably 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  $\pi$ -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  $\beta$  values.<sup>2</sup> 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.<sup>3</sup> It has also been demonstrated that the electron density of the  $\pi$ -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  $\beta$  values.<sup>4</sup>

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  $\pi$ -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.<sup>5</sup> 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,<sup>6</sup> as well as conjugated thiophene and pyrrole heterocycles acting as auxiliary donors, substituted with appropriate acceptor groups,<sup>7,8</sup> whereas the benzimidazole heterocycle acts as an electron-withdrawing group and also as an auxiliary acceptor. Moreover, it extends the conjugation length of the  $\pi$ -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).<sup>6a,d,9</sup> 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.<sup>6a–g</sup>

**Keywords:** Thiophene; Pyrrole; Benzimidazole; Auxiliary donors and auxiliary acceptors; Solvatochromic probes; Hyper-Rayleigh scattering (HRS); Thermal stability; Nonlinear optics (NLO).

\* Corresponding author. E-mail: [mfox@quimica.uminho.pt](mailto:mfox@quimica.uminho.pt)

Particularly, the synthesis and characterization of new NLO chromophores, containing a  $\pi$ -excessive thienylpyrrolyl moiety and a 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*-azole rings in enhancing nonlinear response.<sup>8,10–11</sup> Especially, in the case of benzothiazole derivatives, we have studied the effect of the  $\pi$ -conjugated bridge on the fluorescence, solvatochromic, and nonlinear optical properties of bithienyl-,<sup>11a</sup> arylthienyl-,<sup>11b</sup> and thienylpyrrolyl-benzothiazoles.<sup>11d</sup> 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 better understand 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.<sup>12</sup> These methods usually use strong acid or alternatively harsh dehydration 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 et al.<sup>13</sup> reported the synthesis of 2-substituted benzimidazoles by a one-step reaction through the  $\text{Na}_2\text{S}_2\text{O}_4$  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** and **5** using formyl-thienylpyrroles **1** and **2** as precursors. The synthesis of compounds **1** and **2** was recently reported by us through formylation of 1-(alkyl)aryl-2-(2'-thienyl)pyrroles<sup>14</sup> using two distinct synthetic methods.<sup>15</sup> Formyl 1-(alkyl)aryl-2-(2'-thienyl)pyrroles **1** and **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** and **5** in order to evaluate the effect of the position of benzimidazole group on the optical properties of these chromophores. Therefore, compounds **4** and **5** with either alkyl or aryl donor on the thienylpyrrolyl system and H, OMe, CN or  $\text{NO}_2$  groups on the benzimidazole moiety, were prepared by a one-step reaction through the  $\text{Na}_2\text{S}_2\text{O}_4$  reduction of several *o*-nitroanilines **3** in the presence of formyl-thienylpyrroles **1** and **2** in DMSO at 120 °C for 15 h (Scheme 1). Under these conditions, compounds **4** and **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.

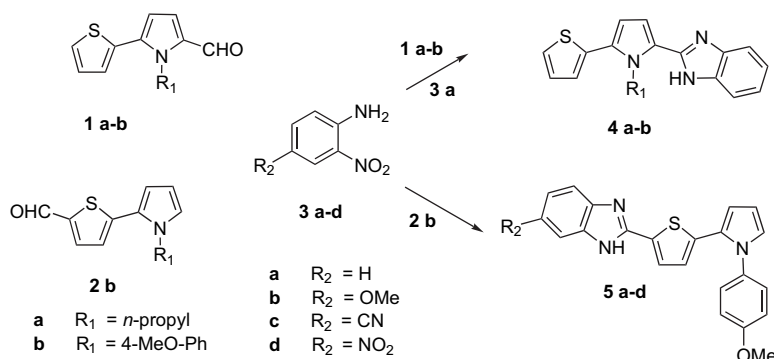
In the <sup>1</sup>H NMR spectra of benzimidazole derivatives signals at about 11.63 and 12.45–12.47 ppm for compounds **4a** and **5c** and **5d** were detected. All signals appeared as broad singlets and were attributed to the N–H in the benzimidazole moiety. A broad correlation could be observed between 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** and **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 <sup>1</sup>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  $\text{cm}^{-1}$ .

**Table 1.** Yields, <sup>1</sup>H NMR, IR, and UV–vis data of thienylpyrrolyl-benzimidazoles **4** and **5**

Entry	Formyl pyrrole	Product	Yield (%)	$\delta_{\text{H}}^{\text{a}}$ (ppm)	IR $\nu$ ( $\text{cm}^{-1}$ )	UV–vis $\lambda_{\text{max}}^{\text{b}}$ (nm) (log $\epsilon$ )
1	<b>1a</b>	<b>4a</b>	95	9.40–9.45	3430 (NH)	327 (4.45)
2	<b>1b</b>	<b>4b</b>	74	—	3435 (NH)	328 (4.36)
3	<b>2b</b>	<b>5a</b>	40	—	3380 (NH)	369 (3.88)
4	<b>2b</b>	<b>5b</b>	76	—	3389 (NH)	367 (4.37)
5	<b>2b</b>	<b>5c</b>	85	12.47	3412 (NH), 2213 (CN)	375 (4.35)
6	<b>2b</b>	<b>5d</b>	64	12.45	3362 (NH)	391 (4.29)

<sup>a</sup> For the NH proton of the imidazole ring of thienylpyrrolyl-benzimidazoles **4** and **5** (300 MHz, acetone-*d*<sub>6</sub>).

<sup>b</sup> All the UV–vis spectra were run in ethanol.



**Scheme 1.** Synthesis of thienylpyrrolyl-benzimidazoles **4** and **5** by reductive cyclization of *o*-nitroanilines with  $\text{Na}_2\text{S}_2\text{O}_4$  in the presence of formyl-thienylpyrroles **1** and **2**.

## 2.2. UV–vis study of benzimidazoles 4 and 5

The electronic spectra of benzimidazoles **4** and **5** were recorded in ethanol (Table 1). Communication between the electron donating and acceptor termini can be evaluated by comparing the  $\lambda_{\max}$  values. The influence of the position of the benzimidazole group on the pyrrole or on the thiophene ring on  $\lambda_{\max}$  of absorption for chromophores **4** and **5** is noteworthy. The difference in  $\lambda_{\max}$  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  $\lambda_{\max}$  of absorption for **5b** due to more extensive electron delocalization (Fig. 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.

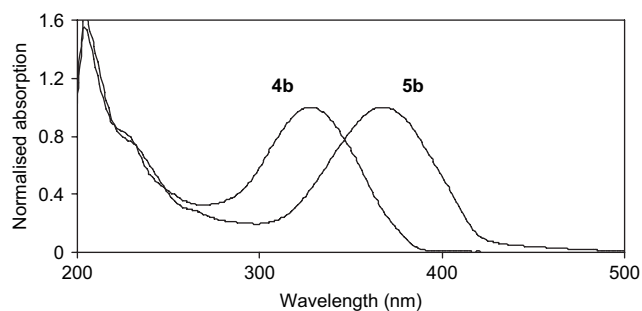


Figure 1. UV–vis spectra of compounds **4b** and **5b** recorded in ethanol.

The influence of the strength of the acceptor group is demonstrated by comparison of the absorption maxima of compounds **5a**, **5c**, and **5d** (Fig. 2) as the longest wavelength transition is shifted from 369 nm in benzimidazole **5a** ( $R_2=H$ , Table 1, entry 3) to 391 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.<sup>10c</sup>

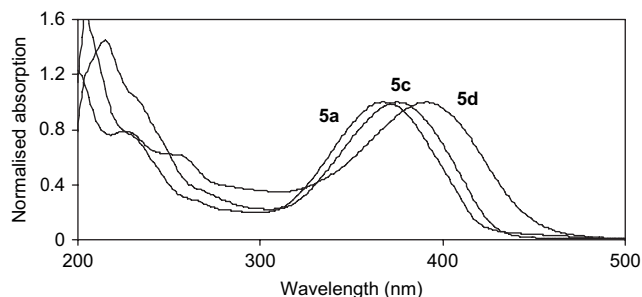


Figure 2. UV–vis spectra of compounds **5a**, **5c**, and **5d** recorded in ethanol.

## 2.3. Solvatochromic study of benzimidazoles 4 and 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 in molecular hyperpolarizability, according 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.<sup>8a,b,d,10,11,16</sup>

Donor–acceptor substituted thienylpyrroles,<sup>8a,b,d</sup> bithienyl-, arylthienyl-, and thienylpyrrolyl-benz-X-azoles<sup>11</sup> 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** and **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**, **5b**, and **5d** showed the largest energy shifts in the absorption band ( $\Delta\nu=+607\text{ cm}^{-1}$  for **5a**,  $\Delta\nu=+731\text{ cm}^{-1}$  for **5b** and  $\Delta\nu=+1142\text{ cm}^{-1}$  for **5d**), so a full solvatochromic study involving 13 solvents was carried out. The maxima of the wavenumbers  $\nu_{\max}$  for chromophores **5a**, **5b**, and **5d** as well as the corresponding wavelength  $\lambda_{\max}$  are listed in Table 2 and compared to the solvent  $\pi^*$  values determined by Kamlet and Taft.<sup>17</sup> Noteworthy is the behavior of **5a**, **5b**, and **5d** in chlorinated solvents such as chloroform, which slightly deviates from linearity.<sup>8a,10b</sup> In view of the pronounced solvatochromism and the good correlation with  $\pi^*$  values for the 13 solvents investigated, compounds **5a** ( $\Delta\nu=+685\text{ cm}^{-1}$ ), **5b** ( $\Delta\nu=+807\text{ cm}^{-1}$ ), and **5d** ( $\Delta\nu=+1277\text{ cm}^{-1}$ ) seem to be very appropriate solvent polarity indicating dyes (Table 2).

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

We have used the hyper-Rayleigh scattering (HRS) method<sup>19,20</sup> to measure the first hyperpolarizability  $\beta$  of benzimidazoles **4** and **5**. *p*-Nitroaniline (*p*NA) was used as standard<sup>21,22</sup> in order to obtain quantitative values, while care was taken to properly account for possible fluorescence of the dyes (see Section 4 for more details). The static hyperpolarizability  $\beta$  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  $\beta$  values for benzimidazoles **4a** and **4b** 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.

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  $\beta$  values for benzimidazoles **5a**, **5c**, and **5d**. The  $\beta$  values for compounds **4a** and **4b** and **5a** having the unsubstituted benzimidazole group on the pyrrole or on the thiophene ring are 2–3 times greater than *p*NA, whereas the

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

Solvent <sup>a</sup>	$\pi^*$ <sup>b,17</sup>	Compound					
		<b>5a</b>		<b>5b</b>		<b>5d</b>	
		$\lambda_{\max}$	$\nu_{\max}$	$\lambda_{\max}$	$\nu_{\max}$	$\lambda_{\max}$	$\nu_{\max}$
<i>n</i> -Hexane	-0.08	358	27,933	364	27,473	385	25,974
Diethyl ether	0.27	359	27,855	365	27,397	387	25,839
Ethanol	0.54	362	27,624	368	27,174	391	25,575
1,4-Dioxane	0.55	361	27,701	367	27,248	390	25,641
Ethyl acetate	0.55	360	27,778	365	27,397	387	25,840
THF	0.58	360	27,778	365	27,397	389	25,707
Methanol	0.60	361	27,701	368	27,174	390	25,641
Acetone	0.71	361	27,701	368	27,174	394	25,381
Acetonitrile	0.75	361	27,701	368	27,174	398	25,126
Chloroform	0.76 <sup>18</sup>	365	27,397	375	26,666	395	25,316
DCM	0.82	365	27,397	371	26,954	394	25,381
DMF	0.88	365	27,397	371	26,954	397	25,189
DMSO	1.00	367	27,248	375	26,666	405	24,697

<sup>a</sup> Solvent used as received.

<sup>b</sup> The correlation coefficient  $r$  obtained for the linear solvation energy relationship with  $\pi^*$  values by Kamlet and Taft without chloroform was  $r=0.8489$  for **5a**, 0.8295 for **5b**, and 0.8479 for **5d**.

$\beta$  values for compounds having the cyano and nitro groups on the benzimidazole heterocycle substituted on the thiophene ring (**5c** and **5d**) are 7 times greater than  $pNA$ . Electron deficient heterocycles act as auxiliary acceptors, withdrawing electron density from acceptor substituents and hence increase 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,<sup>3h,5a,b,6e,26</sup> and also with our recent work<sup>8b,d,11d</sup> where it was concluded that the increase or decrease in the molecular nonlinear activity of heteroaromatic systems depends substantially on the electronic nature of the (hetero)aromatic rings.

The measured  $\beta$  value for compound **5b** is abnormally large ( $290 \times 10^{-30}$  esu), when compared to compounds **5a**, **5c**, and **5d**; 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** and **7** (Fig. 3),<sup>11d</sup> having the benzothiazole acceptor group attached to the thiophene or on the pyrrole heterocycles. In the case of benzimidazoles **4** and **5** and contrarily to the results obtained for benzothiazoles

**6** and **7**, no effect was observed on the  $\beta$  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 and 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 et al.<sup>27</sup> concerning the electron-acceptor properties of  $\pi$ -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  $\pi$  negative charge withdrawn, is particularly small for imidazole and benzimidazole heterocycles  $c_{\text{imidaz}}$  (0.382 for *N*-methylbenzimidazol-2-yl) compared to  $c_{\text{thiaz}}$  (0.457–0.471 for benzothiazol-2-yl). Several theoretical and experimental studies<sup>3h-k,5a,b,27</sup> could also explain the smaller nonlinearities of thienylpyrrolyl-benzimidazoles **4** and **5** compared to thienylpyrrolyl-benzothiazoles **6** and **7** with similar structures (Fig. 3).<sup>11d</sup>

Thermal stability of chromophores **4** and **5** was estimated by thermogravimetric analysis (TGA), measured at a heating rate of  $20 \text{ }^\circ\text{C min}^{-1}$  under a nitrogen atmosphere. The results obtained revealed the good thermal stability for all compounds, which could be heated up to  $T_d=326\text{--}401 \text{ }^\circ\text{C}$ .

**Table 3.** UV–vis absorptions,  $\beta$  and  $\beta_0$  values for compounds **4–6**,<sup>a</sup> and **7**<sup>11d</sup> and  $T_d$  data for compounds **4** and **5**

Compd	$\lambda_{\max}$ (nm) (log $\epsilon$ )	$\beta^b$ ( $10^{-30}$ esu)	$\beta_0^c$ ( $10^{-30}$ esu)	$T_d^c$ ( $^\circ\text{C}$ )	Compd	$\lambda_{\max}$ (nm)	$\beta^b$ ( $10^{-30}$ esu)	$\beta_0^c$ ( $10^{-30}$ esu)
<b>4a</b>	332.5 (4.53)	42	23	326	<b>6a</b>	353.0	64	32
<b>4b</b>	336.0 (4.45)	58	31	363	<b>6b</b>	366.0	85	39
<b>5a</b>	361.0 (4.04)	60	29	380	<b>7b</b>	386.5	450	180
<b>5b</b>	364.0 (4.28)	— <sup>d</sup>	— <sup>d</sup>	401	—	—	—	—
<b>5c</b>	366.5 (4.34)	114	53	390	—	—	—	—
<b>5d</b>	363.0 (4.29)	121	57	365	—	—	—	—
<i>pNA</i>	352.0	16.9 <sup>21,22</sup>	8.5	—	—	—	—	—

<sup>a</sup> Experimental hyperpolarizabilities and spectroscopic data measured in dioxane solutions.

<sup>b</sup> All the compounds are transparent at the 1064 nm fundamental wavelength.

<sup>c</sup> 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.<sup>23–25</sup>

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

<sup>e</sup> Decomposition temperature ( $T_d$ ) measured at a heating rate of  $20 \text{ }^\circ\text{C min}^{-1}$  under a nitrogen atmosphere, obtained by TGA.



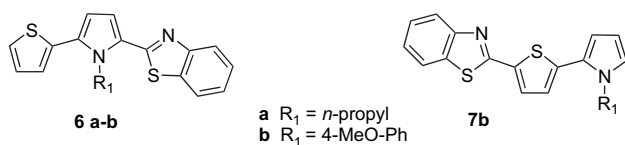


Figure 3. Structure of thienylpyrrolyl-benzothiazoles **6** and **7**.

Although alternative methods to prepare composite matrices do not require high temperatures, e.g. the use of high pressures and great thermal stability is much desirable for device applications.<sup>28</sup>

Our hyper-Rayleigh and thermal stability studies indicate that good nonlinear–thermal stability trade-off is achieved for chromophores **5c** and **5d**, which possess  $\beta$  values from  $114 \times 10^{-30}$  to  $121 \times 10^{-30}$  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 (**5c,5d**) provides a very efficient method to optimize both the molecular nonlinearities and thermal stabilities for these type of NLO chromophores.

### 3. Conclusions

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

- (i) compounds **4** and **5** were synthesized in moderate to excellent yields from easily available formyl-thienylpyrroles **1** and **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.

### 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  $^1\text{H}$  NMR and 75.4 MHz for  $^{13}\text{C}$  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 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 Espectrometría de Masas’ at the University of Vigo, Spain.

Light petroleum refers to solvent boiling in the range 40–60 °C. The synthesis of formyl-thienylpyrroles **1** and **2** was described elsewhere.<sup>15</sup>

**4.1.1. General procedure for the synthesis of thienylpyrrolyl-1,3-benzimidazoles 4 and 5.** A solution of *o*-nitroaniline (1 equiv) and formyl-thienylpyrrole (1 equiv) in DMSO (1 mL) was treated with  $\text{Na}_2\text{S}_2\text{O}_4$  (3 equiv), dissolved in a small volume of water, and heated at 120 °C with stirring for 15 h. The mixture was poured into water (20 mL) and extracted with ethyl acetate ( $3 \times 50$  mL). The organic layer was dried with magnesium sulfate and evaporated under reduced pressure to give the crude thienylpyrrolyl-benzimidazoles **4** and **5**, which were purified by chromatography on silica with increasing amounts of diethyl ether in light petroleum as eluent.

**4.1.1.1. 2-(1'-Propyl-2'-(2''-thienyl)pyrrolyl)-1,3-benzimidazole (4a).** Pale yellow solid (95%). Mp: 157.6–158.9 °C. UV (dioxane):  $\lambda_{\text{max}}$  nm (log  $\epsilon$ ) 332.5 (4.53), 242.5 (4.08), 225.5 (4.00). IR (KBr)  $\nu$  3087 (CH), 2951 (CH), 1571, 1433, 1402, 1387, 1339, 1200, 1117, 905, 989, 721, 699  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (acetone- $d_6$ )  $\delta$  0.88 (t, 3H,  $J=7.5$  Hz,  $\text{CH}_3$ ), 1.80–1.84 (m, 2H,  $\text{CH}_2\text{CH}_2\text{CH}_3$ ), 4.86 (t, 2H,  $J=7.5$  Hz,  $\text{CH}_2\text{CH}_2\text{CH}_3$ ), 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 (br s, 1H, NH).  $^{13}\text{C}$  NMR (acetone- $d_6$ )  $\delta$  11.03 ( $\text{CH}_3$ ), 25.33 ( $\text{CH}_2\text{CH}_2\text{CH}_3$ ), 47.89 ( $\text{CH}_2\text{CH}_2\text{CH}_3$ ), 111.66 ( $\text{C}3'$ ), 112.00 ( $\text{C}4'$ ), 116.88 ( $\text{C}7+\text{C}4$ ), 122.71 ( $\text{C}5+\text{C}6$ ), 125.53 ( $\text{C}2'$  or  $\text{C}5'$ ), 126.71 ( $\text{C}5''$ ), 127.27 ( $\text{C}3''$ ), 128.44 ( $\text{C}4''$ ), 131.47 ( $\text{C}2'$  or  $\text{C}5'$ ), 134.93 ( $\text{C}2''$ ), 139.18 ( $\text{C}7\text{a}$ ), 139.37 ( $\text{C}3\text{a}$ ), 147.18 ( $\text{C}2$ ). MS (FAB)  $m/z$  (%): 308 ( $[\text{M}+\text{H}]^+$ , 100), 307 ( $\text{M}^+$ , 83), 306 (10), 265 (16), 154 (29). HRMS: (FAB)  $m/z$  (%) for  $\text{C}_{18}\text{H}_{18}\text{N}_3\text{S}$ ; calcd 308.1221; found 308.1226.

**4.1.1.2. 2-(1'-(4'''-Methoxyphenyl)-2'-(2''-thienyl)pyrrolyl)-1,3-benzimidazole (4b).** Dark yellow solid (74%). Mp: 232.7–235.9 °C. UV (dioxane):  $\lambda_{\text{max}}$  nm (log  $\epsilon$ ) 336.0 (4.45), 283.5 (3.94), 274.5 (3.94), 241.5 (4.16). IR (KBr)  $\nu$  3435 (NH), 1639, 1624, 1511, 1431, 1299, 1249, 1107, 1007, 833, 744, 709  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (acetone- $d_6$ )  $\delta$  3.89 (s, 3H,  $\text{OCH}_3$ ), 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).  $^{13}\text{C}$  NMR (acetone- $d_6$ )  $\delta$  55.76 ( $\text{OCH}_3$ ), 110.45 ( $\text{C}3'$ ), 110.59 ( $\text{C}5'$ ), 113.19 ( $\text{C}4'$ ), 114.77 ( $\text{C}3''' + \text{C}5'''$ ), 115.50 ( $\text{C}4+\text{C}7$ ), 122.60 ( $\text{C}5+\text{C}6$ ), 125.74 ( $\text{C}3''$ ), 125.76 ( $\text{C}5''$ ), 127.76 ( $\text{C}4''$ ), 131.59 ( $\text{C}2''' + \text{C}6'''$ ), 132.25 ( $\text{C}1'''$ ), 133.36 ( $\text{C}2'$ ), 135.25 ( $\text{C}2''$ ), 139.82 ( $\text{C}7\text{a}$ ), 140.00 ( $\text{C}3\text{a}$ ), 146.19 ( $\text{C}2$ ), 160.89 ( $\text{C}4'''$ ). MS (FAB)  $m/z$  (%): 372 ( $[\text{M}+\text{H}]^+$ , 100), 371 ( $\text{M}^+$ , 64), 370 (9), 154 (6). HRMS: (EI)  $m/z$  (%) for  $\text{C}_{22}\text{H}_{18}\text{N}_3\text{O}\text{S}$ ; calcd 372.1171; found 372.1169.

**4.1.1.3. (1''-(4'''-Methoxyphenyl)-2''-(2'-thienyl)pyrrolyl)-1,3-benzimidazole (5a).** Brown solid (40%). Mp:

190.1–194.0 °C. UV (dioxane):  $\lambda_{\max}$  nm (log  $\epsilon$ ) 361.0 (4.04), 291.5 (3.41), 241.0 (3.95). IR (liquid film)  $\nu$  3402 (NH), 2045, 1876, 1727, 1513, 1400, 1298, 1250, 1166, 1039, 938, 834, 745  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (acetone- $d_6$ )  $\delta$  3.90 (s, 3H,  $\text{OCH}_3$ ), 6.32–6.34 (m, 1H,  $4''\text{-H}$ ), 6.62–6.64 (m, 1H,  $3''\text{-H}$ ), 6.71 (d, 1H,  $J=3.9$  Hz,  $3'\text{-H}$ ), 6.97–6.99 (m, 1H,  $5''\text{-H}$ ), 7.07 (dd, 2H,  $J=9.0$  and 2.1 Hz,  $3'''\text{-H}+5'''\text{-H}$ ), 7.23–7.26 (m, 2H, 5-H+6-H), 7.32 (dd, 2H,  $J=9.0$  and 2.4 Hz,  $2'''\text{-H}+6'''\text{-H}$ ), 7.55–7.58 (m, 2H, 4-H+7-H), 7.74 (d, 1H,  $J=3.9$  Hz,  $4'\text{-H}$ ).  $^{13}\text{C}$  NMR (acetone- $d_6$ )  $\delta$  55.86 ( $\text{OCH}_3$ ), 110.07 ( $\text{C}4''$ ), 111.80 ( $\text{C}3''$ ), 115.25 ( $\text{C}3'''+\text{C}5'''$ ), 115.42 ( $\text{C}4+\text{C}7$ ), 123.52 ( $\text{C}5+\text{C}6$ ), 125.47 ( $\text{C}3'$ ), 126.78 ( $\text{C}5''$ ), 128.20 ( $\text{C}4'$ ), 129.00 ( $\text{C}2'''+\text{C}6'''$ ), 129.60 ( $\text{C}2''$ ), 131.33 ( $\text{C}2'$  or  $\text{C}5'$ ), 133.53 ( $\text{C}1'''$ ), 139.20 ( $\text{C}2'$  or  $\text{C}5'$ ), 139.50 ( $\text{C}7\text{a}+\text{C}3\text{a}$ ), 147.45 ( $\text{C}2$ ), 160.40 ( $\text{C}4''$ ). MS (FAB)  $m/z$  (%): 372 ( $[\text{M}+\text{H}]^+$ , 100), 371 ( $\text{M}^+$ , 53), 322 (17), 154 (13). HRMS: (FAB)  $m/z$  (%) for  $\text{C}_{22}\text{H}_{18}\text{N}_3\text{O}_5$ ; calcd 372.1171; found 372.1172.

**4.1.1.4. 6-Methoxy-2-(1''-(4'''-methoxyphenyl)-2''-(2'-thienyl)pyrrolyl)-1,3-benzimidazole (5b).** Yellow solid (76%). Mp: 72.2–74.4 °C. UV (dioxane):  $\lambda_{\max}$  nm (log  $\epsilon$ ) 364.0 (4.28), 244.5 (4.22). IR (KBr)  $\nu$  3389 (NH), 3095, 2833, 1629, 1513, 1460, 1248, 1198, 1158, 1028, 834, 807, 716  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (acetone- $d_6$ )  $\delta$  3.83 (s, 3H,  $\text{OCH}_3$ ), 3.89 (s, 3H,  $\text{OCH}_3$  Ar), 6.31–6.33 (m, 1H,  $4''\text{-H}$ ), 6.59–6.60 (m, 1H,  $3''\text{-H}$ ), 6.67 (d, 1H,  $J=4.2$  Hz,  $3'\text{-H}$ ), 6.84 (dd, 1H,  $J=8.7$  and 2.4 Hz, 5-H), 6.95–6.96 (m, 1H,  $5''\text{-H}$ ), 7.05 (m, 3H,  $3'''\text{-H}+5'''\text{-H}+7\text{-H}$ ), 7.30 (dd, 2H,  $J=7.8$  and 2.1 Hz,  $2'''\text{-H}+6'''\text{-H}$ ), 7.42 (d, 1H,  $J=8.7$  Hz, 4-H), 7.53 (d, 1H,  $J=3.9$  Hz,  $4'\text{-H}$ ).  $^{13}\text{C}$  NMR (acetone- $d_6$ )  $\delta$  55.83 ( $\text{OCH}_3$ ), 55.85 ( $\text{OCH}_3$ ), 97.90 (C7), 109.97 ( $\text{C}4''$ ), 111.49 ( $\text{C}3''$ ), 112.57 (C5), 115.18 ( $\text{C}3'''+\text{C}5'''$ ), 116.60 (C4), 125.37 ( $\text{C}3'$ ), 126.49 ( $\text{C}5''$ ), 126.56 ( $\text{C}4'$ ), 128.13 ( $\text{C}2''$ ), 128.95 ( $\text{C}2'''+\text{C}6'''$ ), 132.82 ( $\text{C}2'$  or  $\text{C}5'$ ), 133.61 ( $\text{C}1'''$ ), 135.61 (C3a), 138.02 ( $\text{C}2'$  or  $\text{C}5'$ ), 140.26 (C7a), 147.42 (C2), 157.46 (C6), 160.32 ( $\text{C}4''$ ). MS (FAB)  $m/z$  (%): 402 ( $[\text{M}+\text{H}]^+$ , 100), 401 ( $\text{M}^+$ , 87), 307 (28), 289 (14), 154 (79). HRMS: (FAB)  $m/z$  (%) for  $\text{C}_{23}\text{H}_{20}\text{N}_3\text{O}_5$ ; calcd 402.1276; found 402.1278.

**4.1.1.5. 6-Cyano-2-(1''-(4'''-methoxyphenyl)-2''-(2'-thienyl)pyrrolyl)-1,3-benzimidazole (5c).** Pale green solid (85%). Mp: 176.8–178.2 °C. UV (dioxane):  $\lambda_{\max}$  nm (log  $\epsilon$ ) 363.0 (4.34), 284.5 (4.14), 211.5 (4.33). IR (KBr)  $\nu$  3412 (NH), 3095, 2836, 2213 (CN), 1622, 1513, 1420, 1299, 1249, 1158, 1033, 952, 835, 733  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (acetone- $d_6$ )  $\delta$  3.91 (s, 3H,  $\text{OCH}_3$ ), 6.33–6.35 (m, 1H,  $4''\text{-H}$ ), 6.65–6.67 (m, 1H,  $3''\text{-H}$ ), 6.75 (d, 1H,  $J=3.9$  Hz,  $3'\text{-H}$ ), 6.98–6.99 (m, 1H,  $5''\text{-H}$ ), 7.06–7.11 (m, 2H,  $3'''\text{-H}+5'''\text{-H}$ ), 7.31–7.36 (m, 2H,  $2'''\text{-H}+6'''\text{-H}$ ), 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 (br s, 1H, 4-H), 12.47 (br s, 1H, NH).  $^{13}\text{C}$  NMR (acetone- $d_6$ )  $\delta$  55.87 ( $\text{OCH}_3$ ), 110.11 ( $\text{C}4''$ ), 111.90 ( $\text{C}3''$ ), 115.27 ( $\text{C}3'''+\text{C}5'''$ ), 116.10 (CN), 120.41 (C7), 123.99 (C4), 125.51 ( $\text{C}3'$ ), 126.93 ( $\text{C}5''+\text{C}5$ ), 127.94 ( $\text{C}2''$ ), 128.58 ( $\text{C}4'$ ), 129.05 ( $\text{C}6'''+\text{C}2'''$ ), 131.12 ( $\text{C}2'$  or  $\text{C}5'$ ), 133.48 ( $\text{C}1'''$ ), 138.67 (C3a), 139.86 ( $\text{C}2'$  or  $\text{C}5'$ ), 141.00 (C7a), 147.43 (C2), 148.16 (C6), 160.44 ( $\text{C}4''$ ). MS (FAB)  $m/z$  (%): 397 ( $[\text{M}+\text{H}]^+$ , 67), 396 ( $\text{M}^+$ , 58), 307 (36), 289 (18), 155 (31), 154 (100). HRMS: (FAB)  $m/z$  (%) for  $\text{C}_{23}\text{H}_{17}\text{N}_4\text{O}_5$ ; calcd 397.1123; found 397.1116.

**4.1.1.6. 6-Nitro-(1''-(4'''-methoxyphenyl)-2''-(2'-thienyl)pyrrolyl)-1,3-benzimidazole (5d).** Orange solid (64%). Mp: 113.1–115.8 °C. UV (dioxane):  $\lambda_{\max}$  nm (log  $\epsilon$ ) 363.0 (4.34), 284.5 (4.14), 241.5 (4.33). IR (KBr)  $\nu$  3362 (NH), 3095, 2931, 1625, 1572, 1514, 1461, 1337, 1249, 1167, 1067, 1040, 835, 738, 720  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (acetone- $d_6$ )  $\delta$  3.92 (s, 3H,  $\text{OCH}_3$ ), 6.35 (m, 1H,  $J=2.7$  and 0.9 Hz,  $4''\text{-H}$ ), 6.67 (m, 1H,  $3''\text{-H}$ ), 6.78 (d, 1H,  $J=4.2$  Hz,  $3'\text{-H}$ ), 7.00 (m, 1H,  $5''\text{-H}$ ), 7.11 (dd, 2H,  $J=8.9$  and 2.4 Hz,  $3'''\text{-H}$  and  $5'''\text{-H}$ ), 7.34 (dd, 2H,  $J=9.0$  and 2.4 Hz,  $2'''\text{-H}$  and  $6'''\text{-H}$ ), 7.72 (m, 2H,  $4'\text{-H}$  and 4-H), 8.17 (dd, 1H,  $J=9.0$  and 2.1 Hz, 5-H), 8.44 (br s, 1H, 7-H), 12.45 (br s, 1H, NH).  $^{13}\text{C}$  NMR (DMSO- $d_6$ )  $\delta$  55.46 ( $\text{OCH}_3$ ), 109.26 ( $\text{C}4''$ ), 111.17 ( $\text{C}3''$ ), 114.56 ( $\text{C}3'''+\text{C}5'''$ ), 117.54 (C7), 118.06 (C5), 123.15 (C4), 124.96 ( $\text{C}3'$ ), 126.57 ( $\text{C}5''$ ), 128.33 ( $\text{C}2'''+\text{C}6'''$ ), 128.60 ( $\text{C}4'+\text{C}2''$ ), 129.65 ( $\text{C}2'$  or  $\text{C}5'$ ), 131.91 ( $\text{C}1'''$ ), 134.54 (C3a), 139.49 ( $\text{C}2'$  or  $\text{C}5'$ ), 142.62 (C7a), 147.25 (C6), 151.20 (C2), 159.03 ( $\text{C}4''$ ). MS (FAB)  $m/z$  (%): 417 ( $[\text{M}+\text{H}]^+$ , 34), 416 ( $\text{M}^+$ , 30), 307 (36), 289 (17), 155 (31), 154 (100). HRMS: (FAB)  $m/z$  (%) for  $\text{C}_{22}\text{H}_{17}\text{N}_4\text{O}_5\text{S}$ ; calcd 417.1021; found 417.1023.

**4.1.2. Nonlinear optical measurements for compounds 4 and 5 using the hyper-Rayleigh scattering (HRS) method.**<sup>19</sup> Hyper-Rayleigh scattering (HRS) was used to measure the first hyperpolarizability  $\beta$  response of the molecules studied. The experimental set-up for hyper-Rayleigh measurements is similar to the one presented by Clays and Persoons.<sup>19</sup> 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  $\sim 0.5$  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 centered 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 centered on the temporal position of the incident laser pulse. The hyper-Rayleigh signal was normalized at each pulse using the second harmonic signal from a 1-mm quartz plate to compensate for fluctuations in the temporal profile of the laser pulses due to longitudinal mode beating.

Dioxane was used as a solvent, and the  $\beta$  values were calibrated using a reference solution of *p*-nitroaniline (*p*NA)<sup>20</sup> also dissolved in dioxane at a concentration of  $1 \times 10^{-2}$  mol  $\text{dm}^{-3}$  (external reference method). The hyperpolarizability of *p*NA dissolved in dioxane is known from EFISH measurements carried out at the same fundamental wavelength.<sup>21,22</sup> 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  $\mu\text{m}$  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:

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

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 less than 25% of the quoted values.

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 centered 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

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

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

here  $S_{\text{NB}}^{2\omega}$  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  $S_{\text{NB}}^{\text{F}}$ . The signals  $S_{\text{NB}}$  and  $S_{\text{WB}}$  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  $T_{\text{NB}}$  and  $T_{\text{WB}}$  are, respectively, the transmission of the ‘narrow’ and ‘wide’ band interference filters at the second harmonic wavelength (47.6 and 63.5%),  $A_{\text{NB}}$  and  $A_{\text{WB}}$  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 and 2.18 nm for  $A_{\text{NB}}$  and  $A_{\text{WB}}$ , 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	$S_{\text{NB}}^{\text{F}}/S_{\text{NB}}$
<b>4a</b>	0.36
<b>4b</b>	0.11
<b>5a</b>	0.55
<b>5b</b>	0.50
<b>5c</b>	0.64
<b>5d</b>	0.51

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

#### 4.1.3. Thermogravimetric analysis of compounds 4 and 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<sup>-1</sup> flow rate. All samples were subjected to a 20 °C min<sup>-1</sup> heating rate and were characterized between 25 and 700 °C.

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