The Influence of the Relative Position of the Thiophene and Pyrrole Rings in Donor-Acceptor Thienylpyrrolyl-Benzothiazole Derivatives. A Photophysical and Theoretical investigation

João Pina,∗a J. Sérgio Seixas de Melo,a Rosa M. F. Batista,b Susana P. G. Costa b and M. Manuela M. Raposo∗b

Received (in XXX, XXX) Xth XXXXXXXXX 200X, Accepted Xth XXXXXXXXX 200X
First published on the web Xth XXXXXXXXX 200X
DOI: 10.1039/b000000x

Abstract

A detailed spectroscopic and photophysical study has been carried out on a series of heterocyclic compounds -known to display nonlinear optical properties- consisting on one electron donating thienylpyrrolyl π-conjugated system functionalized with an electron acceptor benzothiazole moiety. The absorption, emission and triplet-triplet absorption together with all relevant quantum yields (fluorescence, intersystem crossing and internal conversion), excited state lifetimes and the overall set of deactivation rate constants (∗, IC and ISC) were obtained in solution at room (293
15
K) and low (77
15
K) temperature. The optimized ground-state molecular geometries for the compounds together with the prediction of the lowest vertical one-electron excitation energy and the relevant molecular orbital contours for the compounds were also determined using the density functional theory (DFT) at the B3LYP/3-21G* level. The experimental results showed that the photophysical properties are influenced by the relative position of the pyrrole and thiophene relative to the benzothiazole groups.

a Departamento de Química da Universidade de Coimbra, Rua Larga, 3004-535 Coimbra, Portugal

b Centro de Química, Universidade do Minho, Campus de Gualtar, 4710-057 Braga, Portugal
Introduction
The research for nonlinear optical (NLO) materials has been the focus of intense research in due part to their potential in applications including optical data transmission and information processing.1-5 High NLO responses are obtained when the materials possess large molecular hyperpolarizabilities and low optical loss.6, 7 A general approach to obtain materials with non-linear optical properties consists in the synthesis of chromophores involving electron-donor and electron-acceptor groups linked through a π-conjugated spacer. The use of organic π-conjugated systems is particularly relevant in the development of NLO materials since, amongst other properties, they can show large nonlinearities, and display ultra-fast responses, because the electronic polarization is nearly instantaneous.1 For these systems, optimization of the electron donor and electron acceptor characteristics of the substituents is needed to obtain maximum nonlinearity at a molecular level. For the π-conjugating bridge systems, several linear polyenes to various aromatic (heterocyclic) substituents have been used.8-11 Included in these, easily delocalized five-membered rings (such as furan and thiophene based π-conjugated spacers) have proved to increase the hyperpolarizabilities of NLO chromophores.1, 6, 7, 12, 13 This is in part due to the high chemical and thermal stability together with the displayed good optical properties which allow efficient π-electron delocalization.12-15 Although less investigated, pyrrole containing chromophores as the conjugated bridge, were found to display enhanced NLO properties in comparison with their analogues with furan or thiophene.16 This was attributed to the higher electron density in the pyrrole moiety compared to thiophene and furan which led to enhanced NLO effects.17, 18 This higher electron density (in the pyrrole ring) can be explained by the different electric dipole moment of pyrrole compared to thiophene and furan, with its direction from the heteroatom to the five-membered ring, thus enhancing the contribution of the n electrons of the nitrogen atom to the π-system. However, although the results showed that pyrrole moieties are promising building blocks for chromophores with enhanced NLO properties it was concluded that the increase or decrease of the molecular nonlinear activity on heteroaromatic systems depends on the nature of the aromatic rings as well as on the location of these heteroaromatic rings in the system.19, 20,21

An additional advantage of the use of π-excessive heteroaromatic groups in the conjugated bridge is that they also act as donor groups.

Having in mind our recent work, concerning the synthesis and photophysical properties of benzothiazole derivatives in conjunction with five membered heterocycles (thiophene and pyrrole),22, 23 we decided to investigate the effect of the presence and position of electron-rich and electron-deficient heterocycles on the photophysics of these compounds. The present work follows a previous report of the synthesis, the second-order hyperpolarizability (β) and thermal stability of 1-(alkyl)ary1-2-(2'-thienyl)pyrroles (acting as π-electron donors) end-terminated with a benzothiazole group (electron-withdrawing group).24 We have previously found that the position of the electron-deficient benzothiazole on the thienylpyrrolyl system had a marked influence on the nonlinear optical properties. With the present paper, we extend this study to the detailed spectroscopic (singlet and triplet state) and the photophysical properties in solution (at room and low temperature), together with the theoretical investigation (DFT) of the ground- and singlet excited state optimized geometries of these compounds.

Experimental
The thienylpyrrolyl-benzothiazoles 1a and 2a-c were synthesized as elsewhere described.24 The solvents were all of spectroscopic or equivalent grade and used without further treatment. Absorption spectra and fluorescence were recorded on a Shimadzu UV-2100 and Horiba-Jobin-Ivon Fluorog 3-22 spectrometers respectively. Phosphorescence measurements were made in methylcyclohexane (MCH) glasses at 77 K and used the Horiba-Jobin-Ivon Fluorog 3-22 spectrometer equipped with a 1934D phosphorimeter unit and a 150 W pulsed xenon lamp. All the fluorescence and phosphorescence spectra were corrected for the wavelength response of the system.

The fluorescence quantum yields were measured using as standards terthiophene (ϕF=0.057) and quaterthiophene (ϕF=0.18) in MCH.25 The fluorescence quantum yields at 77 K were obtained by comparison with the spectrum at 293 K run under identical experimental conditions and the ϕF value was obtained by assuming that V77K/V93K=0.8.26 Phosphorescence quantum yields were obtained using benzophenone in ethanol solution (ϕF=0.84) as standard.26

The molar extinction coefficients (ε) were obtained from the slope of the plot of the absorption with six solutions of different concentrations vs the concentration (correlation values ≥0.999).

Fluorescence decays were measured using a home-built picosecond time correlated single photon counting (TCSPC) apparatus described elsewhere.27 Fluorescence decays and the instrumental response function (IRF) where collected using 4096 channels, until 5x10⁰ counts at maximum were reached. The full width at half maximum (FWHM) of the IRF was about 22 ps and was highly reproducible with identical system parameters. Deconvolution of the fluorescence decays curves was performed using the modulating functions of George Striker.28

The experimental setup used to obtain triplet spectra and triplet yields has been described elsewhere.29, 30 First-order kinetics was observed for the decay of the lowest triplet state. Special care was taken in determining triplet yields, namely to have optically matched dilute solutions (abs=0.2 in a 10 mm square cell) and low laser energy (≤ 2 mJ) to avoid multiphoton and T-T annihilation effects.

The triplet molar absorption coefficients were obtained by the energy transfer method.31 The triplet state molar absorption coefficients were determined using naphthalene, ε77=24500 M⁻¹ cm⁻¹ (415 nm) as triplet energy donor.26 The concentrations for the thienylpyrrolyl-benzothiazoles were 10⁻⁵ M and they were dissolved in 1mM methylcyclohexane solution of
naphthalene. Before experiments, all solutions were degassed with nitrogen for 30 minutes and sealed.

The \( \phi_Y \) values were obtained by comparing the \( \Delta O.D. \) at 525 nm of a benzene solution of benzophenone (bzph, the standard) and of the compound (cep, optically matched at the laser wavelength) using the equation: \(^{32}\)

\[
\phi_Y^{\text{cep}} = \frac{\epsilon_{TT}^{\text{cep}}}{\epsilon_{TT}^{\text{ref}}} \frac{\Delta O.D._{\text{cep}}^{\max}}{\Delta O.D._{\text{ref}}^{\max}} \cdot \phi_Y^{\text{cep}}
\]

(1)

Room-temperature singlet oxygen phosphorescence was detected in a Horiba-Jobin-Yvon SPEX Fluorog 3-22 equipped with a Hamamatsu R5509-42 photomultiplier cooled to 193 K in a liquid nitrogen chamber (Products for Research model PC176TSCF-005) The use of a Schott RG1000 filter was essential to eliminate from the infrared signal all of the first harmonic contribution of the sensitizer emission in the region below 850 nm. The sensitized phosphorescence emission spectra of singlet oxygen from optically matched solutions of the samples and that of reference were obtained in identical experimental conditions. The singlet oxygen formation quantum yield was then determined by comparing the integrated area under the sensitized emission spectra of singlet oxygen of the samples solutions (\( \int I(\lambda)\phi_Y^{\text{cep}} d\lambda \)) and that of the reference solution (\( \int I(\lambda)\phi_Y^{\text{ref}} d\lambda \)) and applying equation 2.

\[
\phi_Y^{\text{cep}} = \frac{\int I(\lambda)^{\text{cep}} d\lambda}{\int I(\lambda)^{\text{ref}} d\lambda} \phi_Y^{\text{ref}}
\]

(2)

with \( \phi_Y^{\text{ref}} \) the singlet oxygen formation quantum yield of the reference compound. 1H-Phenalen-1-one in toluene (\( \phi_Y = 0.93 \)) was used as standard. \(^{33}\)

The ground state molecular geometry was optimized using the density functional theory (DFT) by means of the Gaussian 03 program \(^{34} \), under B3LYP/3-21G* level \(^{35} \). \(^{36} \). Optimal geometries were determined on isolated entities in a vacuum and no conformation restrictions were imposed. For the resulting optimized geometries time dependent DFT calculations (using the same functional and basis set as those in the previously calculations) were performed to predict the vertical electronic excitation energies. The excited-state geometry for was optimized using the Hartree-Fock based single-excitation restricted configuration interaction (RCIS) \(^{37} \) method with the 3-21G* basis set. Molecular orbital contours were plotted using Molekel 5.3. \(^{38} \)

Results

Important features that will be considered in this study are the changes in the spectroscopic and photophysical properties induced by (i) the position of the benzothiazole moiety (linked to position 2- of the pyrrole or the thiophene ring) and (ii) the substitution on the nitrogen atom of the pyrrole ring (see Scheme 1). The structures of the investigated compounds are depicted in Scheme 1.
**Table 1** - Spectroscopic properties for the thienylpyrrolyl-benzothiazoles in toluene and methylcyclohexane at 293 K and 77 K.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \lambda_{\text{max}}^{S_1 \rightarrow S_0} ) (nm)</th>
<th>( \lambda_{\text{max}}^{S_1 \rightarrow S_0} ) (nm)</th>
<th>( \lambda_{\text{max}}^{S_1 \rightarrow S_0} ) (nm)</th>
<th>( \lambda_{\text{max}}^{S_1 \rightarrow S_0} ) (nm)</th>
<th>( \lambda_{\text{max}}^{S_1 \rightarrow S_0} ) (nm)</th>
<th>( \lambda_{\text{max}}^{S_1 \rightarrow S_0} ) (nm)</th>
<th>( \varepsilon^{S_0} ) (M(^{-1})cm(^{-1}))</th>
<th>( \varepsilon^{T_1} ) (M(^{-1})cm(^{-1}))</th>
<th>( \Delta \varepsilon^{S_0} ) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a (MCH)</td>
<td>355 (353)</td>
<td>341 (362)</td>
<td>410 (402, 425, 450)</td>
<td>397, 419, 442</td>
<td>560</td>
<td>28600</td>
<td>9600 (3453)</td>
<td>5174</td>
<td>3779</td>
</tr>
<tr>
<td>2a (MCH)</td>
<td>380 (375)</td>
<td>381 (385)</td>
<td>455 (432, 458)</td>
<td>430, 455</td>
<td>480</td>
<td>18100</td>
<td>6500 (4833)</td>
<td>4630</td>
<td></td>
</tr>
<tr>
<td>2b (MCH)</td>
<td>386 (380)</td>
<td>385 (390)</td>
<td>450 (429, 455)</td>
<td>427, 456, 485</td>
<td>475</td>
<td>12100</td>
<td>8850 (4338)</td>
<td>4369</td>
<td></td>
</tr>
<tr>
<td>2c (MCH)</td>
<td>392 (387)</td>
<td>388 (397)</td>
<td>452 (435, 460)</td>
<td>(442, 465)</td>
<td>480</td>
<td>23700</td>
<td>(8200) (4101)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) singlet (\(\varepsilon^{S_0}\)) and triplet (\(\varepsilon^{T_1}\)) molar extinction coefficients

\(^b\) Stokes-shift

---

**Figure 1** - Normalized absorption and fluorescence emission spectra for the thienylpyrrolyl-benzothiazoles 1-2 in methylcyclohexane solution at 293 K and 77 K.

In order to get more insight on the electronic properties of the compounds the ground state geometry of these was optimized at the DFT/B3LYP/3-21G* level (Figure 2). In addition for 2a, the singlet excited state geometry was optimized using the RCIS/3-21G* method and basis set (Figure 3).

**Figure 2** - B3LYP/3-21G* DFT optimized ground-state molecular structures for the thienylpyrrolyl-benzothiazoles 1-2 together with the relevant molecular orbital contours around the band gap.

**Figure 3** - DFT//B3LYP/3-21G* optimized lowest lying singlet (\(S_0\)) and the HF//RCIS/3-21G* singlet excited state (\(S_1\)) geometries for compound 2a.

Fluorescence decays (collected at the emission wavelength maximum) were measured in solution at room temperature and were all seen to fit to monoexponential decay laws (see Figure 4).
The triplet states of the oligomers were characterized from the transient triplet-triplet absorption spectra in toluene solution at 293 K (Figure 5). In addition to ground state depletion at shorter wavelengths, the spectra show a broad and intense triplet absorption in the 410-700 nm region (see Figure 5A).

For the thienylpyrrolyl-benzothiazoles phosphorescence was also investigated in methylcyclohexane glasses at 77 K and with our available current experimental setup we were only able to detect phosphorescence for compound 1a. In this case a structured emission band with a shoulder at 575 nm and maxima at 610 nm was observed (see Figure 5B). Compound 1a presents a low phosphorescence quantum yield ($\Phi_{ph}=0.005$) in agreement to what was previously found for short thiophene oligomers, 25, 29, 40, 41 thienyl-pyrrolyl oligomers 42 and oligothienyl-imidazole 43 derivatives. The phosphorescence lifetime ($\tau_{ph}$) for this compound was found to be 15 ms, see inset in Figure 5B.

Singlet oxygen quantum yields were also obtained by comparing the sensitized emission spectra from singlet oxygen, obtained in optically matched solutions of the samples and that of the reference 1H-phenalen-1-one, Table 2 (for more details see experimental section).

**Discussion**

**Spectroscopic behaviour**

The absorption spectra of the thienylpyrrolyl benzothiazoles are broad and devoid of vibrational structure. This behavior is consistent with the fact that the degree of rotational freedom around the thiophene-pyrrolyl, thiophene-benzothiazole and pyrrol-benzothiazol allows the existence of an ensemble of conformers in the ground-state leading to a broad (overlap of these multiple conformers) absorption. The placement of the benzothiazole moiety on the thiophene heterocycle on the thienylpyrrolyl system (2a), when compared to the derivative bearing the benzothiazole unit at the pyrrole ring (1a), leads to a red-shift in the absorption maxima in solution at 293 K by $\approx$25 nm (Table 1). This behaviour can be explained by a more extensive electron delocalization (increased intramolecular electron-transfer from the donor to the electron-acceptor group) with 2a 44 which in turn leads to an increase in hyperpolarizability when going from 1a (64x10^{-30} esu) to 2a (790 x10^{-30} esu). This is a well-known property of materials.
showing NLO properties and was previously reported for benzoimidazoles, benzothiazoles, and dicyanovinyl substituted thienylpyrroles derivatives where it was observed that the increase in the hyperpolarizability values is accompanied by an increase in the absorption wavelength maxima. This observation is in agreement with previous studies where it was concluded that the increase (or decrease) of the molecular NLO activity on heteroaromatic systems is related with the nature of the aromatic rings and on the location of these heteroaromatic chromophores in the systems.

In our particular case the decrease in hyperpolarizability, when the benzothiazole unit is connected to the pyrrole (1a), indicates that the pyrrole unit is not as good π-conjugated bridge as thiophene. This is due to the fact, that the pyrrole unit is the most electron-rich five-membered heteroaromatic ring (thus displaying higher aromaticity than the thiophene chromophore) and can counteracts the electron-withdrawing effect of the benzothiazole unit, hindering the electron delocalization.

For compounds 2a-c replacement from alkyl to aryl substituents in the pyrro moiety induces a slight red-shift (∼12 nm) in the absorption wavelength maxima. Contrary to the absorption band, the fluorescence emission spectra display vibrational structure thus showing that different geometries are adopted in the ground- and singlet excited-state. In agreement with this behavior are the large Stokes-shift values (ΔSS, Table 1) found for the compounds under study. More detail from the ground and excited states can be obtained from the analysis of the DFT calculations.

From the ground-state optimized geometries (DFT calculations) it was seen that for compound 1a a planar conformation is adopted by the pyrrobenzothiazole moieties and the terminal thiienyl unit present a dihedral angle of ∼50° with respect to the planar backbone (Figure 2). For compounds 2a-c a similar planar structure was found for the thienylbenzothiazoles cromophores and again the end-terminal unit (pyrrolyl) is slightly twisted, displaying a dihedral angle of ∼35°, 2a, and ∼25° for compounds 2c and 2d (Figure 2). The shorter conjugation length found for 5a can be explained by the more twisted (higher dihedral angle) end terminal thiienyl group that acts as a conjugation barrier when compared to compounds 2a-c.

From the TDDFT calculations on the previously optimized ground-state geometries it was possible to predict the lowest vertical one-electron excitation energy (Table 1). The predicted values 341 nm, 1a, 381 nm, 2a, 385 nm, 2b, and 388 nm, 2c, are in good agreement with the experimental values in solution (Table 1) which gives support for the calculated molecular geometries. Also worth noting is the fact that the calculated wavelength maxima, and consequently the decrease in the HOMO-LUMO energy difference, upon going from 1a to 2a accounts for the spectral red-shift observed in the absorption wavelength maxima (see Figures 1 and 2).

The excited-state geometry was optimized for 2a and it was seen that a total planarization of the compound backbone was achieved (Figure 3). This, together with the analysis of the relevant molecular orbital contours (Figure 2), where it was seen that going from the HOMO to the LUMO of the compounds a marked increase in the electron density cloud around the C-C bonds connecting the thiienyl, pyrrolyl and benzothiazole moieties is observed, shows that a quinoidal-type structure should be adopted in the excited state. TDDFT calculation were performed on the previously optimized excited-state geometry allowing the determination of the vertical radiative transition between the excited- (S1) and ground-state (S0). The theoretical value (423 nm) found is in good agreement with the experimental fluorescence wavelength maxima found for this compound (see Table 1) thus giving, once again, support for the calculated geometry.

Upon going to low temperature a slight increase in vibrational resolution was seen in the absorption and emission spectra. Contrary to what is observed in absorption where a ∼10 nm red-shift was observed when going from 293 K to 77 K for the emission band no significant changes were found (see Table 1 and Figure 1) thus indicating that similar geometries are adopted (quinoidal-like) in the excited state at 293 K and 77 K. Similar behavior was reported previously for mixed furan-pyrrole-thiophene containing oligomers and was attributed to a decrease of the relative population of more twisted conformers in the ground-state when going from 293 K to 77 K. In this situation the ground- and excited-state potential energy curves become more vertically aligned such that the vertical transition is more probable to a lower vibrational level, thus resulting in the observed red-shift of the absorption wavelength maxima at 77 K.

**Photophysical behaviour**

The photophysical parameters obtained in solution at 293 K and 77 K are shown in Table 2. From the overall data it can be seen that for all the compounds with exception of 1a the radiative decay channel is the main excited-state deactivation channel. For compound 1a, where the benzothiazole moiety is linked to the pyrrolyl unit, a decrease in the fluorescence quantum yield (ΦF) at 293 K when compared to compounds 2a-c, was observed. In this case, the radiationless processes are dominant and from these, the intersystem crossing (which can be seen from the ΦF, and kISC parameters in Table 2) is the preferred pathway for the excited-state decay. It is interesting to note that both the photophysical and spectroscopic properties of compound 1a are similar to the analogue thienyl-pyrrolyl-thiienyl (SNS) oligomer. A potential explanation for the observed behavior is that the less efficient delocalization of π-electrons seen for 1a (influenced by the position of the pyrro ring) induces a similar conjugation segment to that of SNS, and as consequence, 1a retains the characteristic photophysical properties of SNS. On the contrary, for 2a-c because of the higher charge-transfer character in the compounds there is more involvement of the benzothiazole unit, thus enhancing the fluorescence excited-state deactivation channel. The comparison with the bithienylbenzothiazole (BzT2a) and 2a shows that the substitution of a thiophene with a pyrrolyl ring increases the radiative channel. Indeed for BzT2a the quantum yields are ΦF=0.31, ΦF=0.52 and ΦF=0.17, whereas with 2a (Table 2) 0.7, 0.18 and 0.12 respectively, thus showing that, going from BzT2a to 2a the increase in fluorescence occurs with the concomitant
decrease of the intersystem crossing process. For 1a the low phosphorescence quantum yield and the high intersystem-crossing value indicate that the radiationless channel is the main route for the triplet state decay. In this case, from the onset of the phosphorescence emission band it was possible to estimate the triplet energy of 1a (2.30 eV). From this and the singlet energy (3.18 eV, taken from the intersection between the normalized absorption and emission spectra) it was obtained the singlet-triplet energy splitting, $\Delta E_{S1,T1}$ = 0.88 eV.

The triplet energy value obtained is similar to the value found for the SNS oligomer (2.25 eV). Upon cooling to 77 K a decrease in the $\phi_T$ values was seen (again the exception was 1a). A similar decrease in $\phi_T$ when going from 293 K to 77 K was previously reported for the thienyl-benzothiazoles derivatives but contrast with the behavior of thiophene and mixed furan-pyrrole-thiophene oligomers where an increase or constancy of this value is generally observed. An explanation to the observed behavior resides, as previously discussed, in the fact that at 77 K the emission results from an excited-state with the same geometry and energy that at 293 K but to a more planar ground-state (with higher energy at 77 K compared to 293 K). The better overlap between the $S_0$ and $S_1$ potential energy curves and the decrease in energy between the two states should promotes a better coupling between the radiationless modes of the excited- and ground-state thus enhancing the non-radiative decay channel with the concomitant decrease in $\phi_T$ at 77 K. Fluorescence lifetimes ($\tau_F$) collected in solution at 293 K did not reveal the presence of additional fast decay components that could be attributed to fast relaxation processes in the excited state (conformational relaxation or energy migration) thus in agreement with the existence of a rigid quinoidal-like structure in the excited state.

From the overall photophysical parameters (quantum yields and lifetimes) the rate constants for all the decay processes can be obtained. The radiative rate constants ($k_R$), for all the compounds (including 1a) present a approximately constant value (0.315-0.363 ns$^{-1}$) thus showing that the decrease in $\phi_T$ for compound 1a is not due to a decrease of this parameter but to an effective increase in the intersystem-crossing rate constant, $k_{ISC}$ (1.17 ns$^{-1}$ for 1a versus 0.055-0.089 ns$^{-1}$ for 2a-e). Singlet oxygen was detected by its characteristic phosphorescence following triplet energy transfer from the compounds. The quantum yields for singlet oxygen formation are very close to the quantum yields for triplet formation thus providing support for the calculated latter values and showing that the sensitization of molecular singlet oxygen is very efficient ($S_A = \phi_A/\phi_T \approx 1$).

It is also worth noting that the different alkyl chain at position 1 of the pyrrole ring has no significant influence in the spectral and photophysical properties of the compounds (2a, 2b and 2c), see Tables 1 and 2.

Conclusions

We have investigated the spectroscopic and photophysical properties of thienylpyrrolyl-benzothiazole derivatives in solution at 293 K and 77 K. It is shown that the position of the benzothiazole heterocycle on the thienylpyrrolyl system affects the extent of charge-transfer between the donor- and electron-acceptor groups and also induces profound changes in the photophysical properties. At room temperature, in general, placement of the benzothiazole group on the thienyl ring, when compared to the pyrrole ring, significantly enhances the radiative excited-state deactivation channel. This shows that the high fluorescence of the benzothiazole unit in conjugated organic oligomers and polymers can be tuned by the direct linking to the additional chromophoric unit, which in the present case was pyrrole vs. thiophene. In addition it was found that different alkyl chains at the nitrogen atom of the pyrrole ring have no effect on the spectral and photophysical properties of these compounds.

Acknowledgments

Thanks are due to the Foundation for Science and Technology (FCT-Portugal) for financial support through the Centro de Química-Universidade do Minho (Project PTDC/QUI/66251/2006). FCT is acknowledged for a post-doctoral grant to J. Pina (SFRH/BDP/65507/2009) and a PhD grant to R. Batista (SFRH/BD/36396/2007). We also thank J. P. B. Santos and N. Gonçalves for some of the preliminary spectral measurements.

References
