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# Pyridin-2-ylthiazolothiazoles – Synthesis and photophysical properties

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ABSTRACT

Thiazolo[5,4-*d*]thiazoles are valuable materials for a range of technical and biological applications. They are used as chemosensors, electroluminescent materials, organic light-emitting diodes (OLEDs), in solar cells, in live-cell imaging, *etc.*, and for those applications π-extended thiazolo[5,4-*d*]thiazole derivatives are particularly attractive. A convenient synthetic route to non-symmetrical thiazolo[5,4-*d*]thiazoles bearing styrylpyridyl or hetarylvinylpyridyl groups, and their absorption and emission properties, is reported.

## Introduction

Thiazolo[5,4-*d*]thiazoles are a class of valuable heterocyclic compounds that have been used in a multiplicity of applications, namely in live-cell imaging [1], photocatalysis [2], chemoselective molecular sieving [3,4], and reversible photochromism [5]. They have also been used in organic aqueous redox flow batteries [6], as chemosensors [7–10], semiconductors for organic electronics [11–13], electroluminescent materials [14], temperature and humidity dual-responsive luminescent materials [15], voltage-sensitive dyes [16], organic light-emitting diodes (OLEDs) [17], organic field-effect transistors (OFETs) [18,19] and in solar cells [20–22]. The diversity of potential applications reveals the importance of these compounds.

The thiazolo[5,4-*d*]thiazole (TzTz) system exhibits a rigid and coplanar structure, an extended π-conjugated system, charge transfer capabilities, and high environmental stability. These properties are particularly relevant in the context of optoelectronic applications. [11,23,24] During the last decade, the number of publications based on TzTz-type materials has increased almost exponentially. Most of those publications are related with the synthesis of small TzTz molecules [21,25,26] or low bandgap TzTz-based polymers [27–30] and their use in bulk-heterojunction solar cells. TzTz derivatives have also been successfully used in dye-sensitized solar cells [31,32] and in perovskite solar cells [33].

Considering the properties and applications of TzTz, the development of new synthetic routes to this useful class of compounds is an important subject. In this paper, we report the synthesis of a TzTz bearing 6-methylpyridin-2-yl groups and its conversion into TzTz derivatives with extended π-conjugated systems. The synthetic route involved the bromination of the new TzTz, the formation of the corresponding phosphorus ylide and its reaction with aromatic aldehydes.

## Results and discussion

Thiazolo[5,4-*d*]thiazole (TzTz) derivatives are conveniently prepared from the reaction of aromatic aldehydes and dithiooxamide under conventional heating [34,35] or microwave irradiation [36]. We used the conventional heating method [35] to synthesize the 2,5-bis(6-methylpyridin-2-yl)thiazolo[5,4-*d*]thiazole (**1**), that was prepared in 75% yield from the reaction of 6-methylpyridine-2-carbaldehyde with dithiooxamide in nitrobenzene (Scheme 1) (see SI). A TzTz structurally related to **1** (with pyridin-2-yl groups instead of methyl groups) has been synthesized by this method [37]. The structure of the new compound was confirmed by $^{1}$H NMR, $^{13}$C NMR and MS spectra (see ESI). The $^{1}$H NMR spectrum of TzTz **1** shows the expected profile: a distinctive singlet at $\delta$ 2.64 ppm due to the resonance of the two methyl groups, and two doublets at 7.21 ppm and 8.03 ppm and a triplet at 7.71 ppm due to the resonances of the pyridyl protons ($H_5$, $H_3$ and $H_4$ respectively). In the $^{13}$C NMR spectrum, the presence of the characteristic signals of the TzTz unit at $\delta$ 158.9 and 171.1 ppm and of the methyl groups at $\delta$ 24.4 ppm is also consistent with the proposed structure. In the mass spectrum, the base peak at $m/z = 325$ corresponds to the protonated molecular ion $[M + H]^+$ of the proposed structure.

The initial strategy to obtain π-extended thiazolothiazole derivatives from compound **1** included: the bromination of both methyl groups, conversion of the expected bis(bromomethyl)TzTz into the corresponding bis(phosphonium bromide) and, finally, its Wittig reaction with selected aromatic aldehydes. With this route it was expected to

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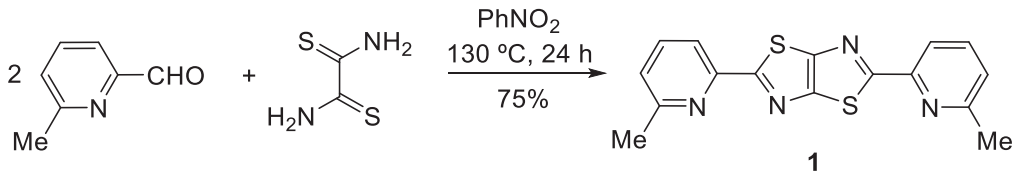
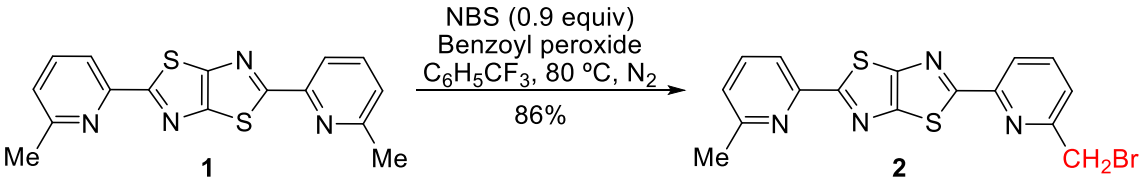
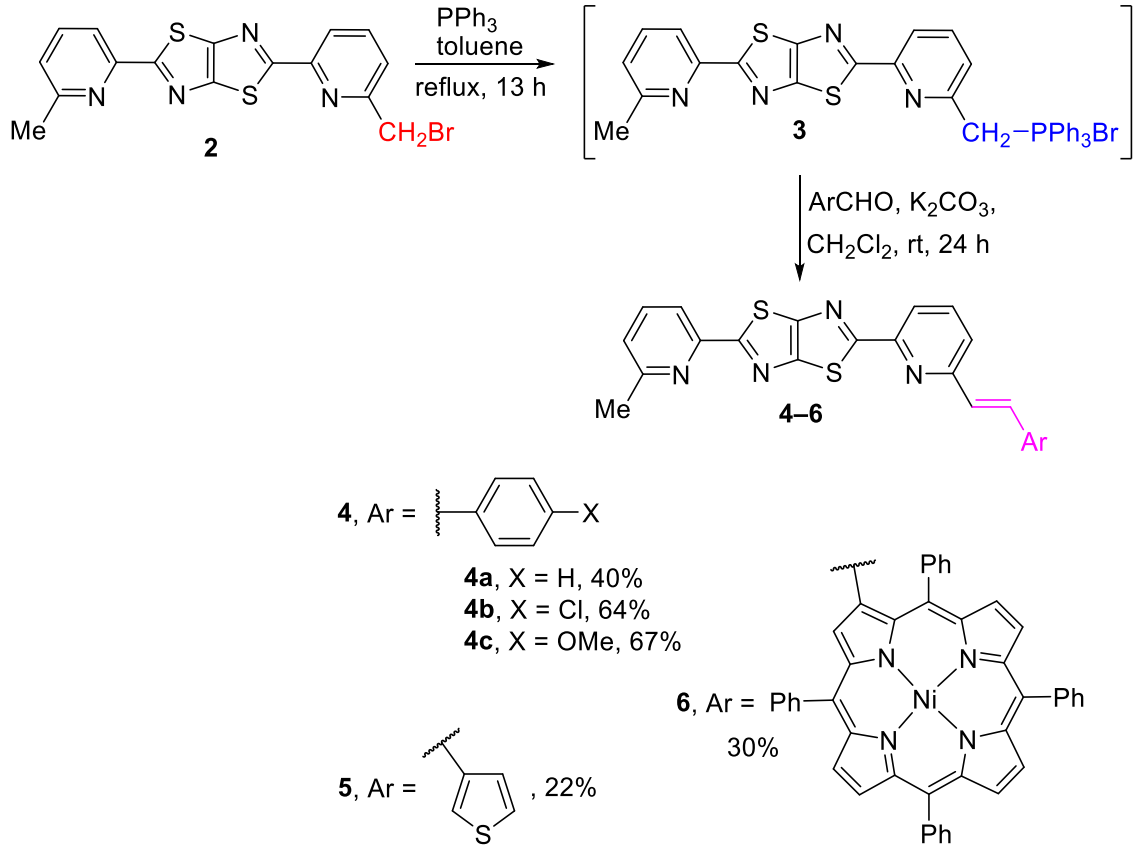



**Scheme 1.** Synthesis of the starting TzTz **1**.




**Scheme 2.** Monobromination of TzTz **1**.




**Scheme 3.** Synthesis of styryl- and hetarylvinyl-TzTz derivatives **4**–**6**.

obtain symmetrical bis(styrylpyridin-2-yl)thiazolothiazoles. However, when the bromination of TzTz **1** was carried out with two molar equivalents of *N*-bromosuccinimide (NBS) in the presence of a catalytic amount of the radical initiator benzoyl peroxide in trifluoromethylbenzene at 80 °C [38], a tribrominated TzTz was formed. The TLC of the reaction mixture revealed the formation of a major product which mass spectrum displayed a protonated molecular ion cluster at $m/z$ = 559/561/563/565 showing the isotopic pattern characteristic of three bromine atoms. This result, together with the $^1$H NMR spectrum of the isolated compound, suggested the substitution of three hydrogen atoms in TzTz **1** by bromine atoms producing the (bromomethyl)(dibromomethyl) TzTz derivative.

To our delight, the more useful monobrominated TzTz **2** could be obtained in 86% yield by bromination of TzTz **1** using 0.9 equivalents of NBS (Scheme 2). The structure of **2** was confirmed by its $^1$H NMR spectrum that showed two diagnostic singlets at $\delta$ = 2.64 and 4.62 ppm corresponding, respectively, to the methyl and bromomethyl groups. The mass spectrum showed the expected $[M + H]^+$ peaks at $m/z$ = 403 and 405 (for $^{79}$Br and $^{81}$Br, respectively).

The reaction of TzTz **2** with triphenylphosphine in refluxing toluene afforded the triphenylphosphonium bromide **3** (Scheme 3). The formation of this salt was confirmed by TLC and the reaction mixture was used directly in the reaction with benzaldehyde, 4-chlorobenzaldehyde, 4-methoxybenzaldehyde, thiophene-3-carbaldehyde and the 5,10,15,20-tetraphenylporphyrin-2-carbaldehyde Ni(II) complex. These reactions were carried out in the presence of $K_2CO_3$ at room temperature during

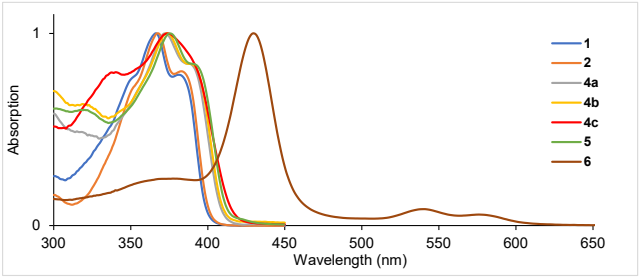



**Fig. 1.** Normalized absorption spectra for TzTz **1**, **2** and **4–6** in $CHCl_3$.

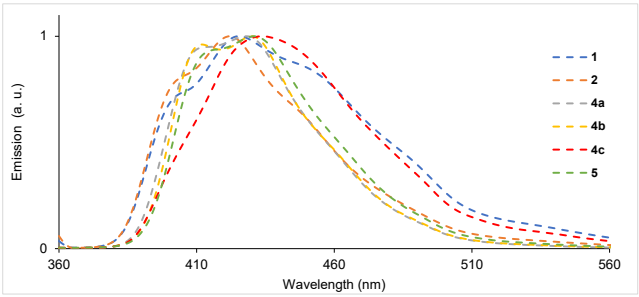



**Fig. 2.** Normalized emission spectra for TzTz **1**, **2**, **4** and **5** in $CHCl_3$.

**Table 1**
Absorption and emission data of **1**, **2** and **4–6** in chloroform.

| Dyes | $\lambda_{abs}$ (nm)[a] | log ε ($M^{-1}cm^{-1}$) | $\lambda_{em}$ (nm)[a] | Stokes shift ($cm^{-1}$)[b] | $\Phi_F$ (%)[c] |
|---|---|---|---|---|---|
| **1** | 352 sh | 4.65 | 404 | 3858 | 26 |
| | **366** | 4.75 | **426** | | |
| | 381 | 4.65 | 457 sh | | |
| | | | 485 sh | | |
| **2** | 353 | 4.93 | 406 | 3551 | 19 |
| | **367** | 5.06 | **422** | | |
| | 382 | 4.96 | 450 sh | | |
| **4a** | 323 sh | 4.23 | 414 | 3445 | 16 |
| | **373** | 4.45 | **428** | | |
| | 387 | 4.38 | 460 sh | | |
| **4b** | 323 | 4.34 | 412 | 3482 | 18 |
| | **374** | 4.53 | **430** | | |
| | 388 | 4.46 | 460 sh | | |
| **4c** | 340 | 4.66 | 402 sh | 3696 | 19 |
| | **374** | 4.71 | **434** | | |
| | 388 sh | 4.67 | 485 sh | | |
| **5** | 319 | 4.21 | 416 | 3465 | 18 |
| | **375** | 4.43 | **431** | | |
| | 390 | 4.35 | 460 sh | | |
| **6** | 371 | 4.47 | – | – | – |
| | **430** | 5.1 | | | |
| | 539 | 4.01 | | | |
| | 576 | 3.83 | | | |

[a] $10^{-5}$ mol.$L^{-1}$ in $CHCl_3$; $\lambda_{max}$ in bold.
[b] Stokes shift calculated as the difference (in wavenumbers) between the first maximum of the first absorption band and the first maximum of the fluorescence band [41].
[c] Excitation at 350 nm; calculated using as fluorescence standard 2,5-diphenylthiazolo[5,4-*d*]thiazole ($\Phi_F$ = 16% in $CHCl_3$) [40].

24 h and the expected compounds **4–6** were isolated in 22–67% yields (see experimental details in SI). The structures of compounds **4–6** were unambiguously established from their NMR (1D and 2D) and mass spectra (see SI). Their $^1H$ NMR spectra showed, in addition to the signals of the pyridyl protons, two doublets in the 7.0–8.0 ppm region corresponding to the two vinylic protons; the large proton–proton coupling constant ($J$ = 16.0 Hz) indicated a *trans* configuration for the double bond. The mass spectra of compounds **4–6** showed, in all cases, the peaks corresponding to the $[M + H]^+$ ion: $m/z$ = 413 for **4a**, 447 and 449 for **4b**, 443 for **4c**, 419 for **5**, and 1005 for **6.**

The absorption and emission spectra of TzTz **1**, **2** and **4–6** are shown in Figs. 1 and 2 and their main features are summarized in Table 1. All compounds displayed maximum absorption wavelength between 340 and 400 nm with two absorption bands, with the exception of thiazolothiazole–porphyrin conjugate **6** which absorption spectrum is dominated by the intense Soret band together with the Q bands of the porphyrin unit [39]. The UV–Vis spectra of the condensation products **4** and **5** showed a red shift of *ca.* 8 nm relatively to the spectra of TzTz **1** and **2**, as a result of the increased π-conjugated system due to the presence of the styryl and hetarylvinyl groups. This red shift is not evident in the absorption spectrum of **6** as the band of the TzTz moiety, centered at 375 nm, partially overlaps with the porphyrin's Soret band at 431 nm. All compounds show fluorescence with maximum emission wavelengths between 400 and 430 nm, except compound **6** that is not emissive. The emission spectra have the expected mirror symmetry relationship with the corresponding lowest energy absorption band, defining Stokes shifts in the range 3465–3858 $cm^{-1}$, in accordance to the parent compound 2,5-diphenylthiazolo[5,4-*d*]thiazole (3739 $cm^{-1}$ in $CHCl_3$) [40]. Compound **6** is non-emissive due to the presence of the Ni (II) complex of the porphyrin moiety that deactivates the singlet state via low lying charge-transfer states [39].

## Conclusions

The selective monobromination of TzTz **1** followed by the one-pot reaction of the bromomethyl derivative with triphenylphosphine and aromatic aldehydes allowed the access to non-symmetrical π-extended TzTz derivatives that display strong fluorescence emission (except the porphyrin derivative **6**, as expected for a Ni(II) complex). This is a versatile synthetic approach that may be extended to the synthesis of TzTz derivatives bearing other functional units just by selecting the adequate aldehydes. Due to their emission properties, the new compounds may be useful as fluorescent probes in various applications, mainly in chemical sensing. Studies concerning the application of these compounds as chemosensors are currently under investigation in our laboratories.

### *CRediT authorship contribution statement*

**Ana F.R. Cerqueira:** Investigation, Writing – original draft. **Maria G.P.M.S. Neves:** Supervision, Writing – review & editing. **A. Jorge Parola:** Supervision, Writing – review & editing. **Augusto C. Tomé:** Conceptualization, Methodology, Supervision, Funding acquisition, Writing – original draft.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.

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