

## Synthesis and structure-physicochemical properties relationship of thiophene-substituted *bis*(5,4-*d*)thiazoles

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 UV-Vis

### Abstract

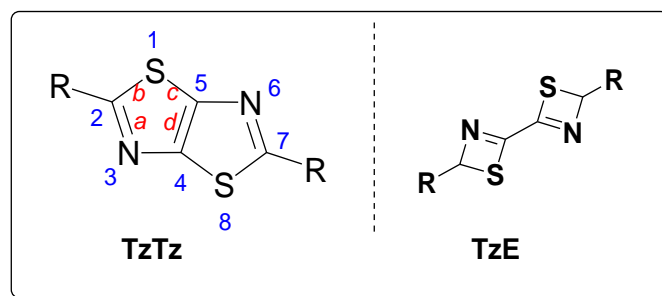
Substituted thiophene-2-carbaldehydes **1a–d** were utilized in the synthesis of symmetrically substituted thiazolo[5,4-*d*]thiazoles **3a–d**. *Bis*(5,4-*d*)thiazoles with thiophene core at the termini are the most employed in the chemistry of materials but exhibit insufficient solubility in majority of organic solvents with notable impact on the low yields of products. Accordingly, the synthetic approach towards 2,5-*di*-thiophen-2-yl-thiazolo[5,4-*d*]thiazole (**3a**) and its substituted derivatives **3b–d** is discussed under the various reaction conditions. Appropriate structural characterisations are included with emphasis on relationship between structure and physicochemical properties highlighting the UV-Vis and fluorescence.

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## Introduction

Thiazolo[5,4-*d*]thiazoles are an important class of bicyclic aromatic systems constructed from two [3.3.0]-fused thiazole rings acting as the electron-deficient moiety due to the presence of imine backbone (C=N, **TzTz**, Fig. 1) (Smirnova *et al.* 2006). The parent compound of this class was misstated as 2,2'-diaryl-4,4'-bisthiazethine (**TzE**, Fig. 1). Later, the 2,5-diaryl-thiazolo[5,4-*d*]thiazoles were established as thermodynamically favoured over bithiazetines (Johnson *et al.* 1970). Since the thiazoles are generally known as key structural units in a wide variety of natural products (i.e. abafungin, tiazofurin) (Arshadi *et al.* 2017) the fused *bis*(5,4-*d*)thiazoles have been initially screened as inhibitors of central nervous system and antibacterial agents. The high toxicity (LD<sub>50</sub> ≥ 0.5 g/Kg) associated with most of pattern TzTz derivatives when tested as CNS depressants, and insufficient antibacterial activity against

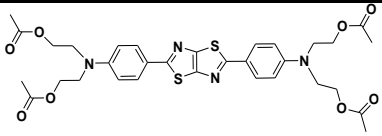
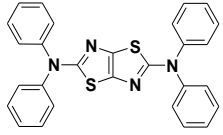
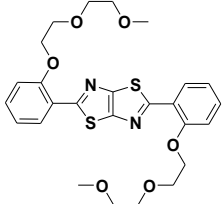
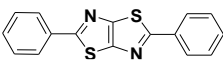
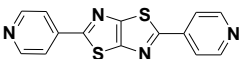
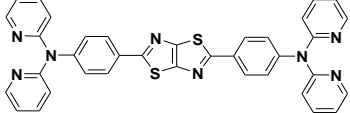
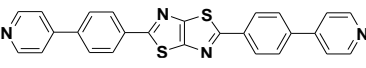
various strains of bacteria have excluded thiazolo[5,4-*d*]thiazoles suitable for further biological applications (Ketcham and Mah 1971). Re-interest in potential biological applications of these compounds was highlighted quite recently. Owing the rigid planar structure in the ground state and upon coordination (Millan *et al.* 2018) accompanied with the colorimetric change and often also with the fluorescent quenching thiazolo[5,4-*d*]thiazoles can effectively sense



**Fig. 1.** Structure of thiazolo [5,4-*d*]thiazole (**TzTz**) with atoms and bonds numbering and the structure of mis-stated 2,2'-diaryl-4,4'-bisthiazethine (**TzE**).

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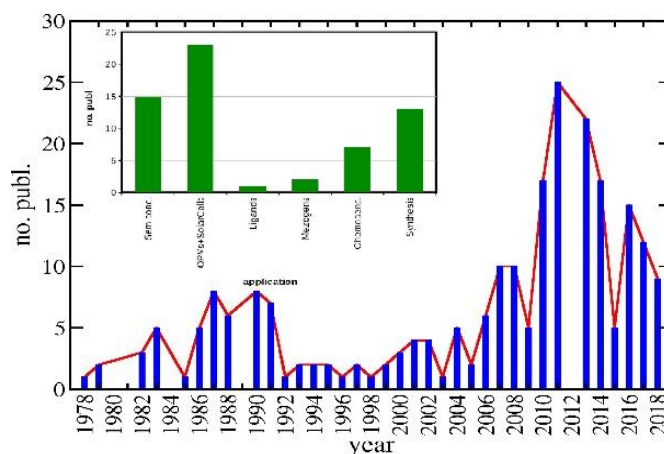
**Table 1.** Coordination of TzTz-based frameworks with variety of cations and their applications as chemosensors and other coordination compounds with miscellaneous utilizations.

TzTz-type compound	Cation/s	Colorimetric change and/or Fluorescent quenching / type	Reference
	Cu <sup>2+</sup>	color change from yellow to dark green (red shift: 400 nm ligand → 700 nm complex) selective fluorescent quenching	Jung <i>et al.</i> (2012)
	Cu <sup>2+</sup>	color change from yellow to blue (red shift: 400 nm ligand → 600 nm complex) selective fluorescent quenching	Zhang <i>et al.</i> (2014)
	Al <sup>3+</sup> Cr <sup>3+</sup>	fluorescent „on-off“ change upon coordination with cation	Jung <i>et al.</i> (2012)
	Ag <sup>+</sup> H <sup>+</sup>	UV-Vis change upon coordination protonization based on Pearson's principle of soft-soft acid-base/colorimetric change	Olgun and Güflen (2013)
	Zn <sup>2+</sup>	– /solvothormal charact./	Millan <i>et al.</i> (2018)
	Ru <sup>2+</sup>	fluorescence as the function of the redox state of complex with ruthenium	Hua <i>et al.</i> (2017)
	Zn <sup>2+</sup>	mixed-valence state characterised by IVCT <sup>#</sup> band in NIR (6,576 and 8,202 cm <sup>-1</sup> ) in MOFs*	Hua <i>et al.</i> (2018)

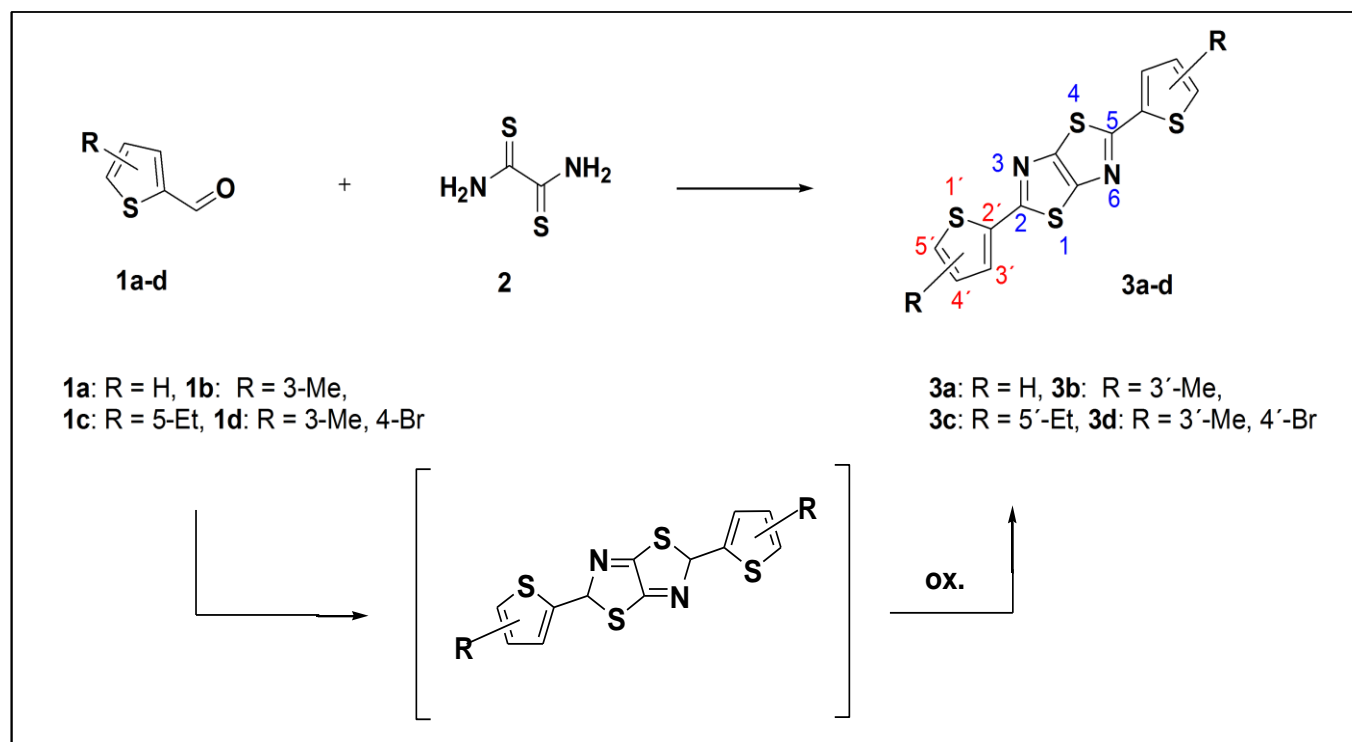
\*MOFs = metal organic frameworks with paddle-wheeled unit constructed of two monodentate fashion coordinated Zn(II).

<sup>#</sup>IVCT band = through-space intervalence charge transfer.

variety of cations (Jung *et al.* 2012; Sivaraman *et al.* 2018). In some of these compounds the bivalent sulphur atom makes close contact with electron-donating nitrogen/oxygen (Table 1), which is isosteric to the hydrogen-bonding interactions as important features of bioactivity in pharmaceuticals and natural drugs (Beno *et al.* 2015) what re-opens the possibility of research on the design of bis(5,4-d)thiazoles as bioactive compounds. However, these applications have lagged behind the use of TzTz units as monomeric building blocks in photovoltaics (Song *et al.* 2017) or co-polymers in semiconductors such as organic field emitting transistors (OFETs) (Ando *et al.* 2005) (Fig. 2).



**Fig. 2.** Number of publications on TzTz in the period 1978 – 2018 (Bevk *et al.* 2013) and our search update (June 2018).



**Scheme 1.** Synthesis of thiophene-based thiazolo[5,4-*d*]thiazoles **3a–d** according to Ketcham's method (Johnson and Ketcham 1960). The structure of intermediate formed during the reaction process is presented in brackets. The carbonyl substrate acting as the oxidizing agent of appropriate intermediate. Reaction conditions used in our approach are following: *Method A:* DMF (153 °C); *Method B:* *o*-dichlorobenzene (180 °C); *Method C:* nitrobenzene (211 °C).

Despite the significant interest in applications of *bis*(5,4-*d*)thiazoles the synthetic chemistry has only been explored to a minor extent (Dessi *et al.* 2014; Dessi *et al.* 2015; Papernaya *et al.* 2016). The most of procedures towards (hetero)aryl substituted thiazolo[5,4-*d*]thiazoles are still based on the condensation of dithioamide (2) with an excess of aldehyde (Johnson and Ketcham 1960). The reactions are most often performed in high boiling point solvents, such as dimethylformamide (DMF, 153 °C); *N,N*-dimethylacetamide (DMAc, 165 °C) or under solvent free conditions ( $\leq 200$  °C).

In general, the solubility of thiophene-substituted TzTz derivatives is the most suppressed affecting the tedious work-up and low yields. Accordingly, in our research the synthesis of a series of thiophene-substituted thiazolo[5,4-*d*]thiazoles **3a–d** is discussed under various reaction conditions (Scheme 1). Compounds **3a–d** are important intermediates for design of low molecular mass type chemosensors and building blocks for (opto)electronic materials. In this context, the physicochemical data (UV-Vis and fluorescence) are analyzed.

## Experimental

### General

All commercially available chemicals were used as received without further purification. Solvents were purified by standard methods and dried if necessary. Reactions were monitored by thin layer chromatography (TLC) on plates percoated with silica gel (SiGel 60 F<sub>254</sub>). Melting points were recorded on a Kofler hot plate apparatus and are uncorrected. The infrared spectra were taken on Agilent Cary 630 FTIR spectrometer with diamond ATR. Elemental analyses were obtained using a Flash EA 2000 CHNS/O-OEA analyser. <sup>1</sup>H NMR spectra (400 MHz) were measured as solutions in deuterated dimethylsulfoxide (DMSO-*d*<sub>6</sub>) on a Bruker Biospin type instrument, products were reported relative to tetramethylsilane (TMS, 0.0 ppm). Absorption spectra (UV-Vis) of solutions ( $c = 1.10^{-5}$  mol.L<sup>-1</sup>) in dimethylformamide were recorded on a UV 1650PC spectrometer (Schimadzu, Jpn) and the fluorescence on a RF 5301 PC type instrument (Shimadzu, Jpn).

## Synthesis

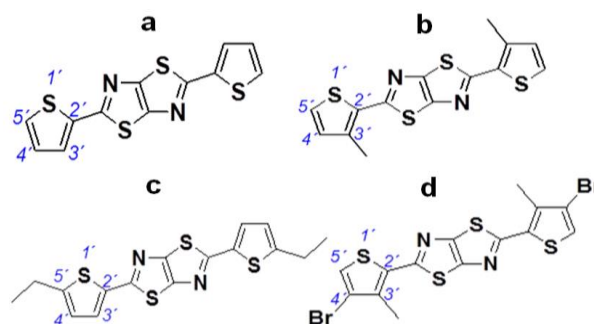
**Method A.** To the mixture of dithioxamide (**2**, 10.0 mmol; 1.10 g) in *N,N*-dimethylformamide (25 mL) solution of appropriate thiophene-2-carbaldehyde **1a–d** (40.0 mmol) in DMF (15 mL) was added at room temperature. The reaction mixture was stirred at the boiling point of DMF (153 °C) for 6 hours. The colour of the reaction changed to dark after the substrates became completely dissolved. After the reaction was stated as completed (TLC control), the reaction mixture was cooled to room temperature and diluted with water (15 mL). Crude mixture was extracted with chloroform (3 x 25 mL). Combined organic layers were dried with MgSO<sub>4</sub>, filtered and the solvent was evaporated. The dark crude product was analyzed (<sup>1</sup>H NMR) and then purified by flash column chromatography with chloroform as eluent. *Note.* In the crude residue the traces of the appropriate product were identified according to <sup>1</sup>H NMR. Only the substrates were retrieved in majority.

**Method B.** To the mixture of dithioxamide (**2**, 10.0 mmol; 1.10 g) in *o*-dichlorobenzene (25 mL) the solution of appropriate thiophene-2-carbaldehyde **1a–d** (40.0 mmol) in *o*-dichlorobenzene (15 mL) was added at room temperature. The reaction mixture was stirred at the boiling point of *o*-dichlorobenzene (180 °C) for 12 hours. The colour of the reaction changed to dark after the substrates became completely dissolved. After the reaction was stated as completed (TLC control), the mixture was cooled to room temperature and washed with water (25 mL) afterwards the slow precipitation of crude product occurred. The immiscible mixture was left to cool down to 0 °C overnight and the precipitate was filtered. The crude product was crystalized from methanol.

*Note.* The mixture of products **3a–d** and the substrate **1a–d** was achieved with the ratio ¼ (aldehyde in majority).

**Method C.** To the mixture of dithioxamide (**2**, 10.0 mmol; 1.10 g) in nitrobenzene (25 mL) the solution of appropriate thiophene-2-carbaldehyde **1a–d** (40.0 mmol) in nitrobenzene (15 mL) was

added at room temperature. The reaction mixture was stirred at the boiling point of nitrobenzene (211 °C) for 5 hours. The colour of the reaction changed to dark after the substrates became completely dissolved. After the reaction was stated as completed (TLC control), the mixture was cooled to room temperature and diethylether was added to precipitate the product (15 mL). The precipitate was filtered, washed with diethylether (2x25 mL) to get rid of unreacted dithioxamide. The crude residue was crystallized from methanol with 15 – 25 % addition of *N,N*-dimethylformamide to increase the solubility. *Note.* Finally, pure products **3a–d** (Fig. 3) were isolated from the crude mixture after crystallization (methanol/DMF).



**Fig. 3.** Products isolated from mixture after crystallization (methanol/DMF) with atom numbering at thiophene core (corresponding with <sup>1</sup>H NMR signals, Table 2).

#### 2,5-Di-thiophen-2-yl-thiazolo[5,4-d]thiazole (**3a**)

Dark brown solid after the crystallization from methanol/DMF (ratio: 4/1). Yield 30 % (3.7 g, *Method C*) starting from thiophene-2-carbaldehyde **1a** (40.0 mmol, 4.5 g). Mp 228 – 235 °C. Anal. Calc. For. C<sub>12</sub>H<sub>6</sub>N<sub>2</sub>S<sub>4</sub> (306.45 g.mol<sup>-1</sup>): C 47.03, H 1.97, N 9.14, S 41.85 %. Found: C 47.29, H 2.09, N 9.70, S 41.25.

#### 2,5-Bis-(3-methylthiophene-2-yl)-thiazolo[5,4-d]thiazole (**3b**)

Brown-yellow solid after the crystallization from methanol/DMF (ratio: 6/1). Yield 31 % (4.1 g, *Method C*) starting from 3-methylthiophene-2-carbaldehyde **1b** For. C<sub>14</sub>H<sub>10</sub>N<sub>2</sub>S<sub>4</sub> (333.97 g.mol<sup>-1</sup>): C 50.27, H 3.01, N 9.14, S 37.58 %. Found: C 49.95, H 3.14, N 8.10, S 38.50.

*2,5-Bis-(5-ethylthiophene-2-yl)-thiazolo[5,4-d]thiazole (3c)*

Brown solid after the crystallization from methanol/DMF (ratio: 6/1). Yield 33 % (4.8 g, *Method C*) starting from 5-ethylthiophene-2-carbaldehyde **1c** (40.0 mmol, 5.6 g). Mp 200 – 205 °C. Anal. Calc. For. C<sub>16</sub>H<sub>14</sub>N<sub>2</sub>S<sub>4</sub> (362.00 g.mol<sup>-1</sup>): C 53.00, H 3.89, N 7.73, S 35.38 %. Found: C 53.24, H 3.87, N 7.89, S 35.50.

*2,5-Bis-(4-bromo-3-methylthiophene-2-yl)-thiazolo[5,4-d]thiazole (3d)*

Black solid after the crystallization from methanol/DMF (ratio: 3/1). Yield 22 % (4.3 g, *Method C*) starting from 4-bromo-3-methylthiophene-2-carbaldehyde **1d** (40.0 mmol, 8.2 g). Mp 296 – 300 °C. Anal. Calc. For. C<sub>14</sub>H<sub>8</sub>Br<sub>2</sub>N<sub>2</sub>S<sub>4</sub> (489.79 g.mol<sup>-1</sup>): C 34.16, H 1.64, N 5.69, S 26.05 %. Found: C 34.52, H 1.96, N 5.18, S 26.42.

## Results and Discussion

### Synthesis

Thiophene-substituted thiazolo[5,4-*d*]thiazoles are among all TzTz-based the most utilized in the optoelectronic materials, but in the same time are one of the most difficult for synthesis. Designed compounds **3a–d** were synthesized by initial one-step condensation reaction of appropriate thiophene-based substrate **1a–d** with dithioxamide (**2**, *Scheme 1*). The carbonyl substrate/dithioxamide ratio 4/1 was used as the optimal for successful reaction proceeding. The aldehyde primarily undergo the condensation reaction (–HC=O → –C=NH) followed by subsequent cyclization but, in the same is essential for final aromatization as

oxidizing agent (*Scheme 1*). Our initial approaches using DMF (*Method A*, 153 °C, 6 hours) and *o*-dichlorobenzene (*Method B*, 180 °C, 12 hours) have failed in products formation. Nitrobenzene was found to be optimal (*Method C*, 211 °C, 5 hours) and the target thiophene-substituted thiazolo[5,4-*d*]thiazoles **3a–d** were isolated in moderate yields (22 – 33 %) and satisfactory purity upon crystallization. In practice, nitrobenzene aside allows the better maintenance of the reaction temperature has few limitations. As the solvent is highly toxic and the products are usually not easily precipitable from the reaction mixture. This can be avoided by the use of *n*-butanol or performance of the reaction under microwave irradiation (MWO). Still, the solubility of carbonyl substrates in *n*-butanol could be insufficient and not all of the substrates are liquids as is required for MWO assisted reactions.

### Structure characterisation

Previously published 2,5-*di*-thiophen-2-yl- (**3a**) (*Jung et al. 2010*; *Dessi et al. 2013*) was selected as the representative compound for the structure characterisation. Full conversion of carbonyl substrates **1a–d** towards corresponding thiazolo[5,4-*d*]thiazoles **3a–d** was assigned by the disappearance of carbonyl proton (–HC=O) characteristic at  $\delta \approx 9.5$  ppm and further corroborated by the FTIR spectra where the stretching vibrations of carbonyl group (1,680 – 1,750 cm<sup>-1</sup>) vanished and the characteristic stretch vibration at  $\nu \approx 1,250$  cm<sup>-1</sup> was observed for C=N (*Table 2*). The chemical shifts of heteroaromatic protons H-3', H-4', H-5' revealed doublets for **3a–c** and singlet for **3d** in the range of 7.39 – 6.04 ppm.

The most intense downfield shift (paramagnetic) because of methyl's deshielding effect to 7.39

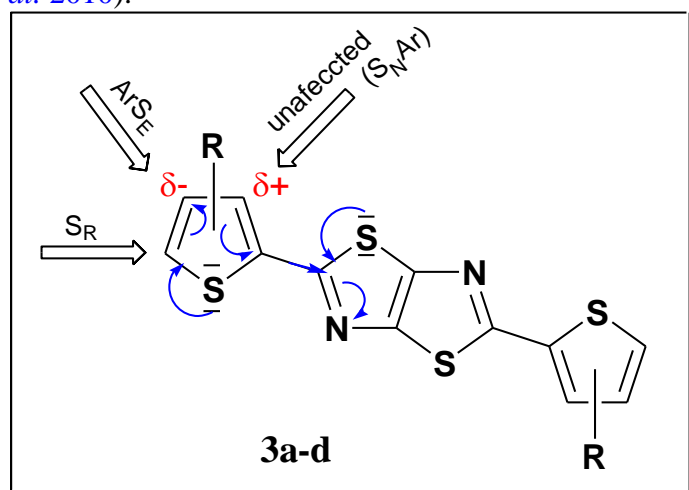
**Table 2.** Structure and product yields together with the specific chemical shifts ( $\delta$ /ppm) in <sup>1</sup>H NMR and vibrations ( $\nu$ /cm<sup>-1</sup>) in IR spectra for target thiophene-substituted thiazolo[5,4-*d*]thiazoles **3a–d**.

Compound	R	Yield [%]	<sup>1</sup> H NMR [ $\delta$ /ppm]			IR [ $\nu$ /cm <sup>-1</sup> ] C=N
			H-3'	H-4'	H-5'	
<b>3a</b>	H	30	6.99	6.97	6.40	1,250
<b>3b</b>	3'-CH <sub>3</sub>	31	-	7.01	7.39	1,260
<b>3c</b>	5'-CH <sub>2</sub> CH <sub>3</sub>	33	6.70	6.70	-	1,250
<b>3d</b>	4'-Br-3'-CH <sub>3</sub>	22	-	-	7.35	1,250

and 7.35 ppm for H-5' is associated with 2,5-*bis*-(3-methylthiophene-2-yl)-thiazolo[5,4-*d*]thiazole (**3b**) and its C4'-bromo-substituted analogue **3d**. On the other hand, the protons of TzTz bearing the unsubstituted thiophene ring for compound **3a** and with ethyl group in C5' for compound **3c**, respectively, appear in the range of 6.99 – 6.40 ppm in accordance with the similar thiophene-substituted derivatives.

The complete structural characterisations are part of our subsequent research and herein are presented as the complementary statement supported by the elemental analysis (with deviation max. 0.4 %). Compounds **3a–d** were prepared as useful tools for the design of (opto)electronic materials when taking in account the further possibilities of the substitution and functionalization arising from the electronic effects in the structure of parent compounds (Fig. 4). Accordingly, the uncommon nucleophilic substitutions ( $S_NAr$ , Tokárová *et al.* 2017) are expected to the C4' of thiophene core, but with certainty this position will stay unaffected and 3-substituted thiophene-2-carbaldehyde have to be used when C3'-substituted TzTz products are required (Papernaya *et al.* 2016).

The electrophilic substitutions ( $ArSE$ ) are predicted to occur at the adjacent  $\beta$ -position (C4') (Dessi *et al.* 2013). On the C- $\alpha$  (= C5') the radical substitutions ( $S_R$ ) are quite common offering the possibility of subsequent alkylation *via* the cross-coupling manner (Jung *et al.* 2010).



**Fig. 4.** General structure of thiophene-substituted thiazolo[5,4-*d*]thiazoles **3a–d** presented herein, showing the electronic effects in the structure with prediction of possible substitution patterns.

## UV-Vis and fluorescence

The absorption (Fig. 5A) and fluorescence spectra (Fig. 6) of **3a–d** were examined in DMF solutions ( $1 \cdot 10^{-5}$  mol.dm<sup>-3</sup>). The absorption maximum of representative, the 2,5-*bis*-(3-methylthiophene-2-yl)-thiazolo[5,4-*d*]thiazole (**3a**), observed at 390 nm is assigned to the  $n \rightarrow \pi^*$  of *bis*(5,4-*d*)thiazole C=N group, while the less intense maximum at 275 nm to the  $n \rightarrow \sigma^*$  (C–N). The slight red-shift to 401 nm ( $n \rightarrow \pi^*$ ) is observed for 2,5-*bis*-(3-methylthiophene-2-yl)-thiazolo[5,4-*d*]thiazole (**3b**) as a result of electron-donating character of methyl group at C3' involved in the extension of the  $\pi$ -conjugation length. The 2,5-*bis*-(5-ethylthiophene-2-yl)-thiazolo[5,4-*d*]thiazole (**3c**) showed similar absorption bands as **3a** at 390 nm ( $n \rightarrow \pi^*$  / C=N) and 270 nm ( $n \rightarrow \sigma^*$  / C–N) as the consequence of almost no influence of ethyl group at C5' to  $\pi$ -conjugation of the whole system. The blue shift to 311 nm ( $n \rightarrow \pi^*$ ) for 2,5-*bis*-(4-bromo-3-methylthiophene-2-yl)-thiazolo[5,4-*d*]thiazole (**3d**) agrees with the fact, that the electron-donating halo-substituent at C4' has the strong influence on decrease of the  $\pi$ -conjugation (Andicsová-Eckstein *et al.* 2017). The solutions of the *bis*(5,4-*d*)thiazoles **3a–c** in DMF showed fluorescent (FL) emissions in the range of 450-470 nm when excited at the absorption maximum wavelengths and the colors were observed as yellow under a UV-lamp. For **3d**, with Br at C4', the fluorescence is strongly quenched as typical behaviour of similar, halogen-substituted thiophene-based compounds (Romiszewski *et al.* 2014).

## Conclusions

The synthesis and optical properties of a series of thiazolo[5,4-*d*]thiazoles bearing the substituted thiophene ring at the termini have been investigated. Thiophene core in the target *bis*(5,4-*d*)thiazoles **3a–d** offers the possibility of subsequent functionalization according to suggested substitution pattern (Fig. 2) as one of the key requisites in materials design. Exchange of hydrogen to bromo- or other halo-substituent seems to play an important role in blue-shifted UV-Vis and hindered fluorescence. On the other hand, the alkyl-substitution along with position on which

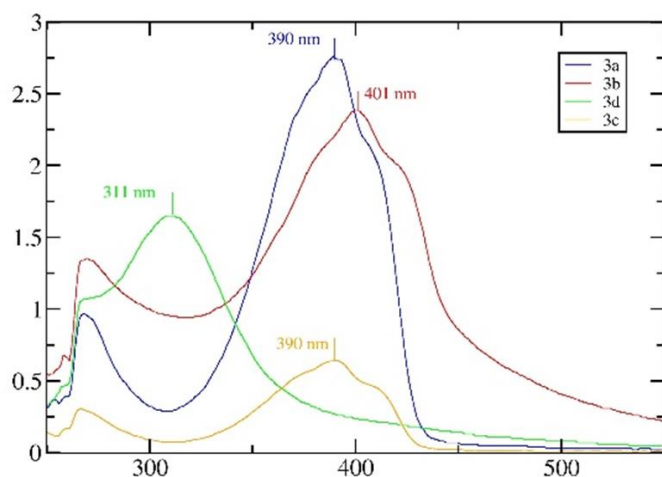


Fig. 5. UV-Vis spectra of **3a–d**.

position of the thiophene core is attached significantly influences the optical properties – i.e. red-shifted UV-Vis with alkyl at C3' no change in UV-Vis with alkyl at C5'. Accordingly, the substitution of the thiophene moiety in thiophene-containing thiazolo[5,4-*d*]thiazole could be

## Acknowledgments

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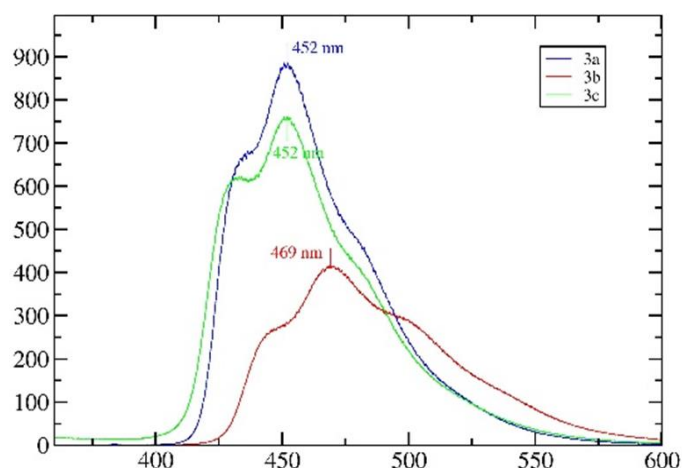


Fig. 6. FL emission of **3a–c**.

recognized and further managed according to requirements on these compounds as building blocks for (opto)electronic materials (i.e. as monomers for copolymers of different n- or p- type semiconductors,  $\pi$ -spacers or electron-withdrawing moieties for dye sensitized solar cells, ligands).

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