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# Synthesis, Crystal Structure and Luminescent Properties of 2D Zinc Coordination Polymers Based on Bis(1,2,4-triazol-1-yl)methane and 1,3-Bis(1,2,4-triazol-1-yl)propane

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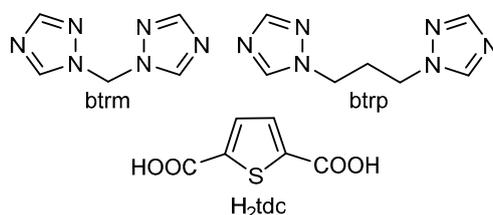
**Abstract:** Two new two-dimensional zinc(II) coordination polymers containing 2,5-thiophenedicarboxylate and bitopic ligands bis(1,2,4-triazol-1-yl)methane (btrm) or 1,3-bis(1,2,4-triazol-1-yl)propane (btrp) were synthesized. Synthesized compounds were characterized by IR spectroscopy, elemental analysis, powder X-ray diffraction, and thermal analysis. Crystal structures of coordination polymers were determined and their structural peculiarities are discussed. The differences in structural features, thermal behavior, and luminescent properties are discussed.

**Keywords:** zinc; coordination polymer; bitopic ligand; crystal structure; thermal analysis; luminescence; 2,5-thiophenedicarboxylic acid; bis(1,2,4-triazol-1-yl)methane; 1,3-bis(1,2,4-triazol-1-yl)propane

## 1. Introduction

Coordination polymers and metal-organic frameworks attract the unceasing attention of researchers due to their wide range of potential applications [1–6]. One of the universal approaches to the construction of metal-organic frameworks uses a combination of metal ions with aromatic di- or polycarboxylate donors and rigid or flexible N-donor bitopic ligands [7,8]. Among dicarboxylic acids, 2,5-thiophenedicarboxylic acid (H<sub>2</sub>tdc, Figure 1) was used to enhance the gas sorption properties of MOFs [9–11], fine-tune the topology of the constructed coordination polymers [12–14], prepare coordination polymers with luminescent properties [9,10,15] including those suitable for LED [16] applications, and sense metal ions and small molecules [17,18]. Metal-organic frameworks based on tdc<sup>2-</sup> donors demonstrating potential photocatalytic [19,20] and magnetic [21] applications were also reported. Bitopic heterocyclic ligands based on semi-rigid di(1,2,4-triazol-1-yl) derivatives [22] or flexible bis(imidazol-1-yl)alkanes [19,23–28] are usually used in combination with tdc<sup>2-</sup> and metal ions to build coordination networks. Despite a very large number of reported bis(imidazol-1-yl)alkane-linked frameworks based on H<sub>2</sub>tdc, no examples of coordination polymers with structurally similar bis(1,2,4-triazol-1-yl)alkanes have been prepared so far. There are a number of publications reporting the study of zinc coordination polymers based on 1,3-bis(1,2,4-triazol-1-yl)propane (btrp, Figure 1) and aromatic di-, tri-, and tetracarboxylates [29–43], and several examples of 1D coordination polymers [44,45] and discrete complexes [44,46,47] have

also been reported. Zinc coordination chemistry with bis(1,2,4-triazol-1-yl)methane (btrm, Figure 1) is much less studied, and only two examples of 1D coordination polymers have been reported so far [48,49].



**Figure 1.** Bis(1,2,4-triazol-1-yl)methane, 1,3-bis(1,2,4-triazol-1-yl)propane and 2,5-thiophenedicarboxylic acid ligands used in this work for the preparation of coordination polymers.

In order to explore the possibility of the preparation of new coordination polymers based on bis(1,2,4-triazol-1-yl) and H<sub>2</sub>tdc ligands with enhanced functional properties, we have studied the reaction between zinc nitrate, H<sub>2</sub>tdc, and btrm or btrp linkers. As a result, the first examples of bis(1,2,4-triazol-1-yl)methane and 1,3-bis(1,2,4-triazol-1-yl)propane-linked zinc-2,5-thiophenedicarboxylate coordination polymers were prepared, and their crystal structures, thermal behavior, and luminescent properties were investigated.

## 2. Results and Discussion

### 2.1. Synthesis of Coordination Polymers

The coordination polymers **1** and **2** were characterized by thermal analysis, single crystal and powder X-ray diffraction methods, CHNS analysis, and IR spectroscopy. In addition, their photoluminescence properties were investigated.

Syntheses of coordination polymers by the reaction of zinc nitrate, btrp or btrm ligands, and 2,5-thiophenedicarboxylic acid (H<sub>2</sub>tdc) were carried out under solvothermal conditions at 95 °C in dimethylformamide (DMF). Zn-ligand-H<sub>2</sub>tdc ratios remained constant and equimolar in all experiments. The duration of heating was varied from 12 to 36 h in order to optimize the yield and purity of the crystalline product.

The reaction of equimolar amounts of zinc nitrate, btrm, and H<sub>2</sub>tdc in the DMF solution (Zn<sup>2+</sup> concentration 1.0 M) at 95 °C for 24 h gave prismatic crystals of coordination polymer [Zn(btrm)(tdc)]·nDMF **1**. The powder XRD analysis has shown that carrying out the reaction for a longer period of time (e.g., for 36 h) results in the formation of the additional unidentified product as an impurity. This impurity can be removed by washing the precipitate with warm DMF. The XRD patterns for compound **1** and the additional by-product are shown in Figure S1.

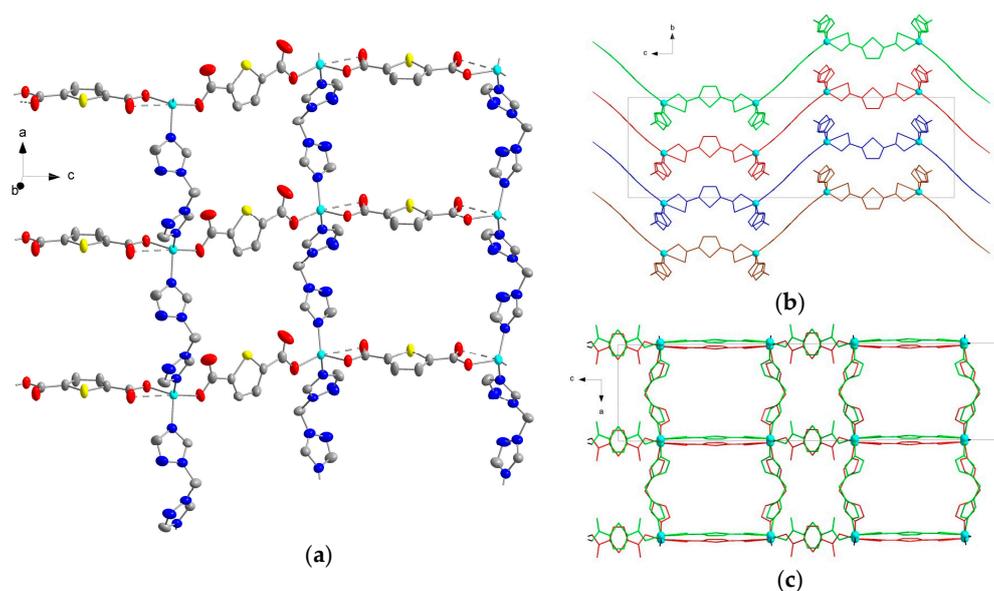
When equimolar amounts of zinc nitrate, btrp and H<sub>2</sub>tdc were heated in DMF solution (Zn<sup>2+</sup> concentration 1.0 M) at 95 °C for 12 h, and coordination polymer [Zn(btrp)(tdc)]·nDMF **2** as prismatic crystals suitable for X-ray structure determination was obtained. The powder XRD analyses of the polycrystalline sample in comparison with those simulated from single crystal data patterns are shown in Figure S2. The IR spectra of both compounds contain characteristic bands associated with vibrations of bis(triazol-1-yl) ligands and coordinated 2,5-thiophenedicarboxylate anions (Figure S3).

### 2.2. Crystal Structures

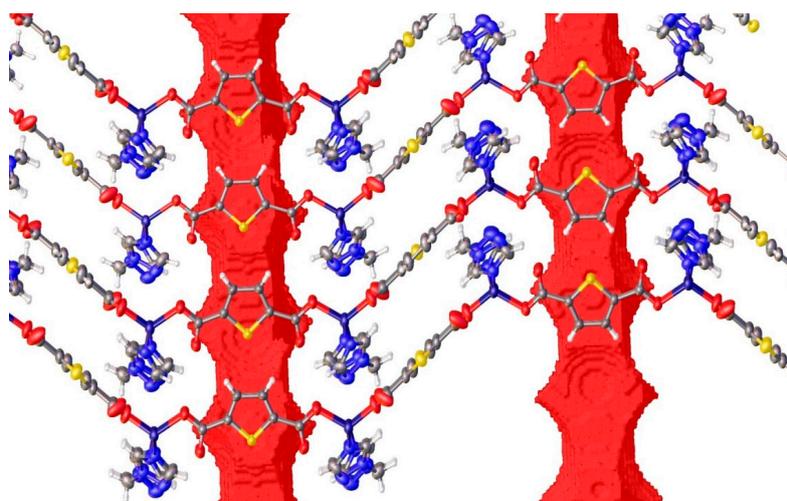
#### 2.2.1. Crystal Structure of Polymer [Zn(tdc)(btrm)]·nDMF (**1**)

The complex [Zn(tdc)(btrm)]·nDMF (**1**) is a 2D coordination polymer. The Zn atom coordinates two crystallographically independent (tdc)<sup>2-</sup> ligands (halves) to form chains (Figure 2a). Analysis of

bond lengths reveals the shortest distances for Zn1–O11 of 1.94 and Zn1–O21 of 1.99 Å typical for this type of coordination compound. Both (tdc)<sup>2−</sup> anions act as (μ-O)<sub>2</sub>-coordinating ligands. Zn1⋯O12 (2.99 Å) and Zn1⋯O22 (2.65 Å) distances are much longer, although the latter can be considered as a long range interaction in agreement with the analysis of normalized contact distances ( $d_{\text{norm}}$ ) on a Hirshfeld surface [50,51] (Figure S4a). In contrast to atom O22, atom O12 reveals contact with the H of the neighboring triazole unit, with a corresponding distance of 2.25 Å (Figure S4b). {Zn(tdc)} chains are linked by (μ-N)<sub>2</sub>-coordinating btrm ligands to form corrugated layers arranged along the *ac* plane (Figure 2b). Within the layer, Zn atoms deviate from their mean plane significantly by 3.54 Å (Figure S6). These layers are stacked one above the other (Figure 2c) leaving channel voids of *ca.* 35% filled by highly disordered DMF solvent molecules (Figure 3).



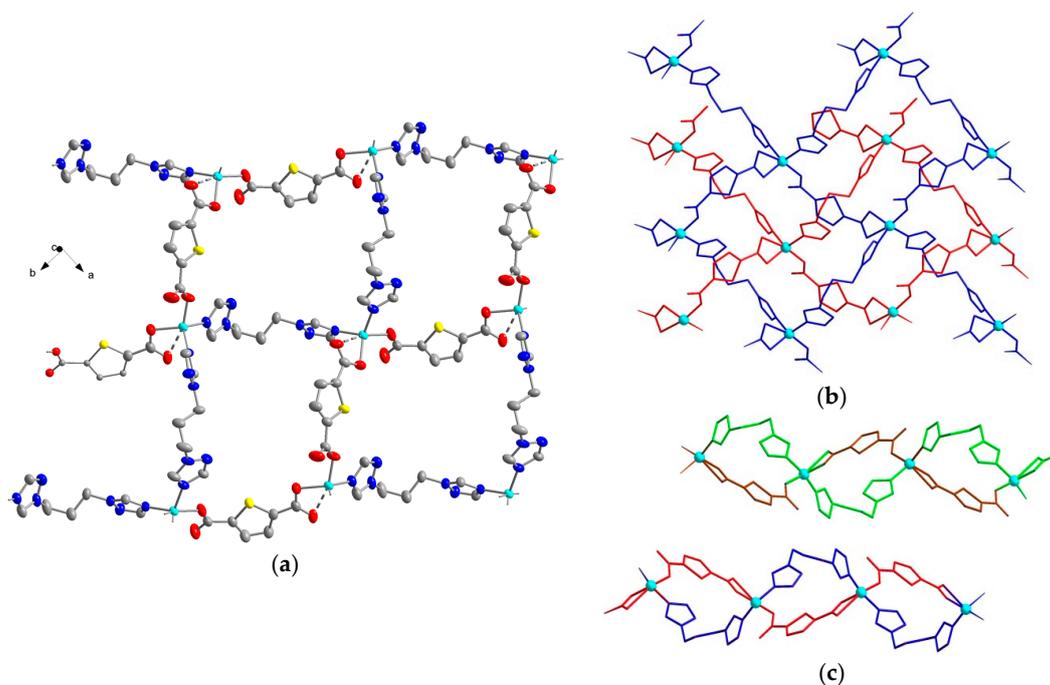
**Figure 2.** (a) Displacement ellipsoid plot of complex [Zn(tdc)(btrm)]·nDMF (1) showing 50% probability ellipsoids. H atoms are not shown for clarity. Dashed lines indicate long-range Zn⋯O interactions; (b,c) Relative arrangement of the layers of 1 colored green, red, blue, and brown.



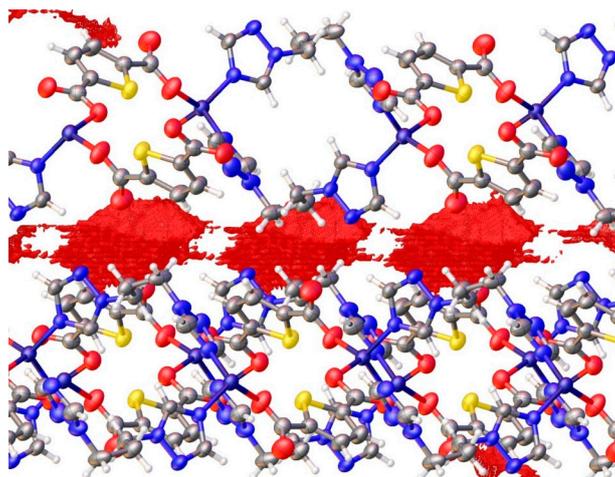
**Figure 3.** Representation of channel voids in the structure of the complex [Zn(tdc)(btrm)]·nDMF (1).

### 2.2.2. Crystal Structure of Polymer [Zn(tdc)(btrp)]·nDMF (2)

The complex [Zn(tdc)(btrp)]·nDMF (2) also has a 2D structure (Figure 4a). Similar to 1, a four-connected net of Zn atoms is observed, but (tdc)<sup>2-</sup> and btrp ligands alternate along the chains. The whole layer is arranged along the *ab* plane and it is less corrugated compared to layers of polymer 1. Within the layer, Zn atoms deviate from their mean plane by 0.55 Å (Figure S7). Similar to compound 1, the dicarboxylate ligand in complex 2 adopts a ( $\mu$ -O)<sub>2</sub>-coordination mode, revealing pairs of short (1.93, 1.98 Å) and long (2.61, 3.29 Å) Zn···O distances. According to the analysis of the  $d_{\text{norm}}$  map on the Hirshfeld surface, the O14 atom shows weak interaction with the Zn, as well as with the H<sub>1</sub> atom of the triazole unit with corresponding Zn···O and H···O distances of 2.61 and 2.53 Å (Figure S5). On the contrary, the O12 atom reveals no close contacts with Zn and H atoms. Crystal packing differences are observed for compounds 1 and 2. Coordination polymer 2 shows a double interpenetration of the layers with each Zn node of one array lying above or below the approximate center of the space of another layer (Figure 4b,c). Due to interpenetration, only separate voids filled by DMF molecules are revealed (Figure 5), with the solvent accessible volume (of *ca.* 22%) being lower than in 1. Each void contains one DMF molecule, which is disordered by two positions due to its proximity to an inversion center.



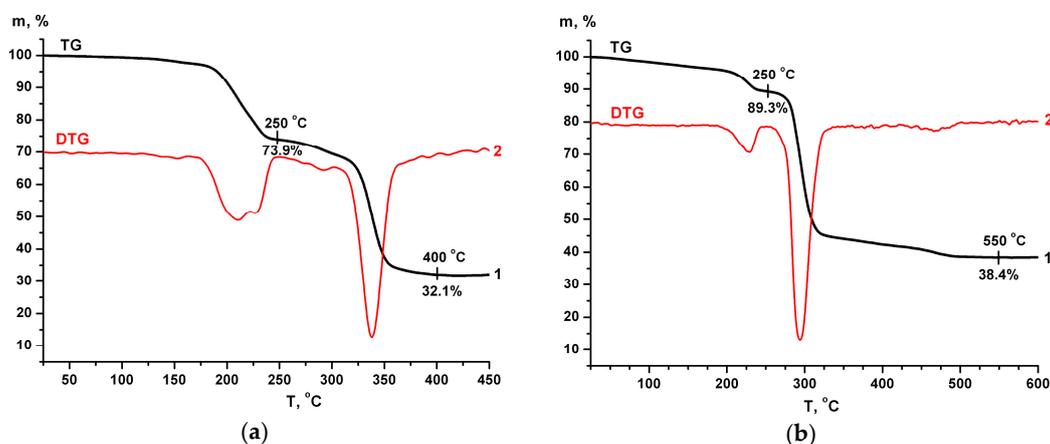
**Figure 4.** (a) Displacement ellipsoid plot of complex [Zn(tdc)(btrp)]·nDMF (2) showing 50% probability ellipsoids. H atoms are not shown for clarity. Dashed lines indicate long-range Zn···O interactions; (b,c). Relative arrangement of the layers of 1 colored green, red, blue, and brown.



**Figure 5.** Representation of the voids in the structure of the complex  $[\text{Zn}(\text{tdc})(\text{btrp})] \cdot n\text{DMF}$  (**2**).

### 2.3. Thermal Analysis

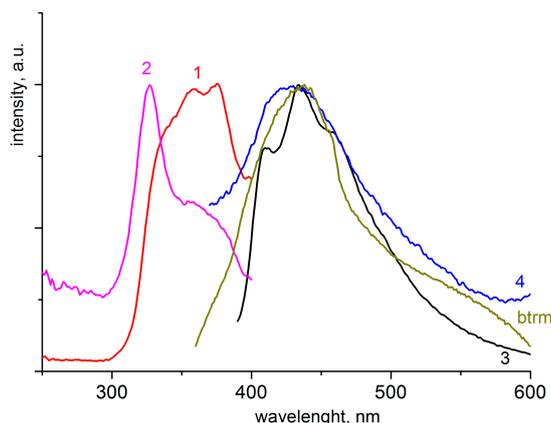
The analysis of the thermal properties of synthesized compounds revealed that the processes of removing guest molecules from coordination polymers **1** and **2** have some significant differences (Figure 6a,b). The process of desolvation for compound **1** starts at about 120 °C, while the desolvation process for **2** starts almost at room temperature. The number of guest molecules for **2** is variable and decreases under storage in air revealed by the results of CHNS analysis of the samples stored in air for a few weeks. The second step for both compounds starts at about 250 °C and lasts up to about 400 °C for **1** and up to 500 °C for **2**.



**Figure 6.** Curves of thermal analysis for compound **1** (a) and for compound **2** (b).

### 2.4. Luminescent Properties

The luminescence and excitation spectra of compounds **1** and **2** are shown in Figure 7. Upon excitation at 375 nm (for **1**) and at 330 nm (for **2**), the photoluminescence spectra demonstrate wide bands with maxima at 430 and 440 nm, respectively. The band of **1** is vibrationally resolved with two shoulders having bathochromic and hypsochromic shifts. The excitation spectrum of **1** also has a vibrational resolution. The ligands btrm and btrp (for images of btrp spectra, see ref. [43]) reveal broad emission bands with the maxima at 410 and 440 nm, respectively. The excitation bands of coordination polymers are relatively narrow, while for the ligands, these bands are wide. It is interesting to note that the quantum yield (QY) for **1** is several times higher than the QY of the btrm ligand. On the contrary, the QY for **2** decreases by a few orders compared to the btrp ligand (Table 1).



**Figure 7.** Normalized emission ( $\lambda_{\text{ex}} = 330$  nm and 375 nm) and excitation spectra: 1, 3—compound **1**; 2, 4—compound **2**. Normalized emission ( $\lambda_{\text{ex}} = 330$  nm) spectrum of btrm.

**Table 1.** Photoluminescence data for coordination polymers **1**, **2** and ligands btrm, btrp.

	<b>1</b>	<b>2</b>	<b>Btrm</b>	<b>Btrp</b>
Ex, nm	330	375	330	260 br
Em, nm	410 (sh), 430, 460 (sh)	440	440	410
QY	0.1	<0.005 <sup>1</sup>	0.03	0.04

<sup>1</sup> QY is too low to be measured.

### 3. Experimental Section

#### 3.1. Materials and Methods

The starting reagents used for the synthesis of coordination compounds— $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (chemical grade) and dimethyl formamide (analytical grade)—were used as received. Btrm and btrp ligands were prepared as reported previously [43]. Elemental analysis was carried out on a Eurovector EuroEA 3000 analyzer (Eurovector SPA, Redavalle, Italy). Infrared (IR) spectra of solid samples as KBr pellets were recorded on a FT-801 spectrometer ( $550\text{--}4000\text{ cm}^{-1}$ , Kailas OU, Tallin, Estonia). Polycrystalline samples were studied in  $2\theta$  range  $5^\circ\text{--}60^\circ$  on a DRON RM4 powder diffractometer (Burevestnik, Saint Petersburg, Russia) equipped with a  $\text{CuK}\alpha$  source ( $\lambda = 1.5418\text{ \AA}$ ) and graphite monochromator for the diffracted beam. Indexing of the diffraction patterns was done using data for compounds reported in the JCPDS-ICDD database [52].

The thermal stability of coordination polymers was studied in inert (He) atmosphere. Thermogravimetric measurements were carried out on a NETZSCH thermobalance TG 209 F1 Iris (Erich NETZSCH GmbH & Co. Holding KG, Selb, Germany). Open  $\text{Al}_2\text{O}_3$  crucibles were used (loads 5–10 mg, heating rate  $10\text{ K}\cdot\text{min}^{-1}$ ).

Room temperature excitation and emission spectra were recorded with a Horiba Jobin Yvon Fluorolog 3 photoluminescence spectrometer (Horiba Jobin Yvon, Edison, NJ, USA) equipped with a 450 W ozone-free Xe-lamp, cooled PC177CE-010 photon detection module with a PMT R2658, and double grating excitation and emission monochromators. Powdered samples for measurements were placed between two non-fluorescent quartz plates. Quantum yields were determined using a Quanta- $\phi$  integrating sphere. Excitation and emission spectra were corrected for source intensity (lamp and grating) and emission spectral response (detector and grating) by standard correction curves.

#### 3.2. X-ray Structure Determination

Single-crystal XRD data for the complexes **1** and **2** were collected on a Bruker Apex DUO diffractometer (Bruker Corporation, Billerica, MA, USA) equipped with a 4K CCD area detector

at 298(2) K using graphite-monochromated MoK $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) (Table 2). The  $\varphi$ - and  $\omega$ -scan techniques were employed to measure intensities. Absorption corrections were applied with the use of the SADABS program [53]. The crystal structures were solved by direct methods and refined by full-matrix least squares techniques with the use of the SHELXTL package [54]. Atomic thermal displacement parameters for non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were calculated corresponding to their geometrical conditions and refined using the riding model. DFIX, DANG restraints, and EADP constrains were applied to atoms of the disordered DMF molecules of **2**. In compound **1**, solvent molecules displayed unresolvable disorder. Therefore, the structure was treated *via* the PLATON/SQUEEZE [55] procedure to remove the contribution of the electron density in the solvent regions from the intensity data. The total potential solvent accessible void volume was estimated to be *ca.* 1300  $\text{\AA}^3$  and the electron count per unit cell was 380, which were assigned to eight DMF molecules per unit cell and one molecule per formula unit.

The Hirshfeld promolecular surface mapped over  $d_{\text{norm}}$  plots of the complexes **1** and **2** was built using the Crystal Explorer (version 17.5) program [56].

**Table 2.** Crystallographic data for compounds **1** and **2**.

Parameter	Compound 1	Compound 2
Empirical formula	C <sub>11</sub> H <sub>8</sub> N <sub>6</sub> O <sub>4</sub> SZn	(C <sub>13</sub> H <sub>12</sub> N <sub>6</sub> O <sub>4</sub> SZn)·0.5(C <sub>3</sub> H <sub>7</sub> NO)
Formula weight	385.66	450.26
Crystal system	orthorhombic	monoclinic
Space group	<i>Pbcm</i>	<i>P2<sub>1</sub>/c</i>
Unit cell dimensions <i>a</i> , $\text{\AA}$	9.3189(3)	6.4235(2)
<i>b</i> , $\text{\AA}$	11.5387(3)	15.4396(5)
<i>c</i> , $\text{\AA}$	37.2569(11)	19.2190(7)
$\beta$ , $^\circ$		90.7550(10)
Volume, $\text{\AA}^3$	4006.2(2)	1905.90(11)
<i>Z</i>	8	4
Density (calcd.), g·cm <sup>−3</sup>	1.279	1.569
<i>F</i> (000)	1552	920
Abs. coefficient, mm <sup>−1</sup>	1.352	1.436
Crystal size, mm <sup>3</sup>	0.18 × 0.17 × 0.08	0.40 × 0.30 × 0.10
2 $\theta_{\text{max}}$ , $^\circ$	51.60	51.60
Index range	−11 ≤ <i>h</i> ≤ 7 −14 ≤ <i>k</i> ≤ 14 −45 ≤ <i>l</i> ≤ 45	−7 ≤ <i>h</i> ≤ 7 −18 ≤ <i>k</i> ≤ 18 −23 ≤ <i>l</i> ≤ 23
Reflections collected	42,882	29,130
Independent reflections	3900 [ <i>R</i> (int) = 0.0416]	3405 [ <i>R</i> (int) = 0.0381]
Completeness to 2 $\theta$ = 50.5, %	99.8	99.4
Reflections, <i>I</i> ≥ 2 $\sigma$ ( <i>I</i> )	3201	3405
Parameters	210	244
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> 1 = 0.0356 <i>wR</i> 2 = 0.0836	<i>R</i> 1 = 0.0356 <i>wR</i> 2 = 0.1064
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0470 <i>wR</i> 2 = 0.0871	<i>R</i> 1 = 0.0378 <i>wR</i> 2 = 0.1084
GoF	1.048	1.060
Residual electron density (min/max, e/ $\text{\AA}^3$ )	−0.282/0.310	−0.613/0.952

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 1584008 for compound **1** and 1584007 for compound **2**. Copies of the data can be obtained free of charge from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

### 3.3. Synthesis of Compounds

#### 3.3.1. Synthesis of [Zn(btrm)(tdc)]·nDMF (**1**)

Solution of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (1.0 M, 0.64 mL, 0.64 mmol) in DMF was added to the mixture of btrm ligand (96 mg, 0.64 mmol) and 1.6 mL of 0.4 M H<sub>2</sub>tdc (0.64 mmol) solution in DMF in a glass vial. The mixture was stirred for several minutes at room temperature until the complete dissolution of all reagents. The vial was placed in an oven at 95 °C for 24 h. Then, the vial was removed from the oven and cooled to room temperature. Colorless prismatic crystals were formed on the bottom. The crystals were washed twice with 2 mL of DMF and then stored in the glass vial under DMF. The yield was about 120 mg (*ca.* 40%). IR bands, cm<sup>-1</sup>: 3124, 2930, 1671, 1610, 1529, 1469, 1374, 1289, 1210, 1120, 1032, 990, 909, 859, 819, 780, 745, 673, 638. Elemental analysis: found, %: C 36.1, H 3.4, N 21.2, S 7.2; calculated ([Zn(btrm)(tdc)]·nDMF, n = 1), %: C 36.7, H 3.3, N 21.4, S 7.0.

#### 3.3.2. Synthesis of [Zn(btrp)(tdc)]·nDMF (**2**)

Solution of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (1.0 M, 0.5 mL, 0.5 mmol) in DMF was added to the mixture of btrm ligand (89.1 mg, 0.5 mmol) and 1.25 mL of 0.4 M H<sub>2</sub>tdc (0.5 mmol) solution in DMF in a glass vial. The mixture was stirred for several minutes at room temperature until the complete dissolution of all reagents. The vial was placed in an oven at 95 °C for 12 h. Then, the vial was removed from the oven and cooled to room temperature. Colorless prismatic crystals formed on the bottom. The crystals were washed twice with 2 mL of DMF and then stored in the glass vial under DMF. The yield was about 100 mg (*ca.* 40%). IR bands, cm<sup>-1</sup>: 3125, 2934, 1668, 1630, 1590, 1531, 1461, 1353, 1280, 1209, 1173, 1128, 995, 899, 812, 769, 677, 651, 587. Elemental analysis: found, %: C 39.1, H 3.5, N 20.0, S 6.6; calculated ([Zn(btrp)(tdc)]·nDMF, n = 1), %: C 39.5, H 3.9, N 20.1, S 6.6.

## 4. Conclusions

In summary, this study presents the two first examples of zinc coordination polymers with 2,5-thiophenedicarboxylic acid, in which bis(1,2,4-triazol-yl)methane or 1,3-bis(1,2,4-triazol-yl)propane play the role of auxiliary ligands. Both compounds are two-dimensional coordination polymers. In the case of a shorter btrm linker, the layers are stacked above each other forming channels (*ca.* 35 % of cell volume) filled with DMF molecules. The use of longer and more flexible btrp linkers results in the formation of doubly-interpenetrated layers with closed voids (*ca.* 22 % of cell volume). Thermal analysis of coordination polymers has shown that the solvate molecules are easier to remove in the case of the btrm linker. The quantum yield of **1** was found to be several times higher than that of the btrm ligand. On the contrary, the quantum yield of **2** decreases by a few orders relative to the btrp ligand.

**Supplementary Materials:** The following are available online at [www.mdpi.com/2073-4352/7/12/354/s1](http://www.mdpi.com/2073-4352/7/12/354/s1), Figure S1: XRD patterns of compound **1**, Figure S2: XRD patterns of compound **2**, Figure S3: IR spectra of coordination polymers **1** and **2**, Figure S4: (a,b) The  $d_{\text{norm}}$  Hirshfeld surface of (tdc)<sup>2-</sup> ligands of the complex [Zn(tdc)(btrm)]·0.5DMF (**1**), Figure S5: The  $d_{\text{norm}}$  Hirshfeld surface of (tdc)<sup>2-</sup> ligand of the complex [Zn(tdc)(btrp)]·0.5DMF (**2**) in different projections, Figure S6: Fragment of the layer of the complex **1**, Figure S7: Fragment of the layer of the complex **2**.

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**Author Contributions:** Evgeny Semitut and Andrei Potapov conceived and designed the experiments; Evgeny Semitut and Taisiya Sukhikh carried out the synthesis; Taisiya Sukhikh performed X-ray structure determination and analyzed the results; Evgeny Filatov performed X-Ray powder diffraction analysis; and Alexey Ryadun investigated luminescent properties. All authors took part in writing and discussion processes.

**Conflicts of Interest:** The authors declare no conflict of interest.

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