

Short Note

# 4,7-Bis(5-(9-hexyl-9H-carbazol-3-yl)thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-*d*]pyridazine

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**Abstract:** Donor molecules of the D- $\pi$ -A- $\pi$ -D type structure are often used for applications in organic photovoltaics. In this communication, bromination of 4,7-di(thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-*d*]pyridazine followed by Suzuki cross-coupling with carbazoleboronic acid gave 4,7-bis(5-(9-hexyl-9H-carbazol-3-yl)thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-*d*]pyridazine. The structure of the newly synthesized compounds was established by high resolution mass-spectrometry, <sup>1</sup>H, <sup>13</sup>C NMR, IR, and UV spectroscopy and mass-spectrometry. A study of the luminescent properties of the dye showed that it exhibits fluorescence in the near infrared region of the spectrum, which makes it a promising compound for use as an active emitting layer in NIR OLED as well as for other possible applications as an IR luminophore.

**Keywords:** [1,2,5]thiadiazolo[3,4-*d*]pyridazine; Suzuki cross-coupling; thiophene; carbazole; luminescence



**Citation:** Chmovzh, T.N.; Korshunov, V.M.; Taydakov, I.V.; Rakitin, O.A. 4,7-Bis(5-(9-hexyl-9H-carbazol-3-yl)thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-*d*]pyridazine. *Molbank* **2022**, *2022*, M1332. <https://doi.org/10.3390/M1332>

Academic Editor: Fawaz Aldabbagh

Received: 24 January 2022

Accepted: 4 February 2022

Published: 8 February 2022

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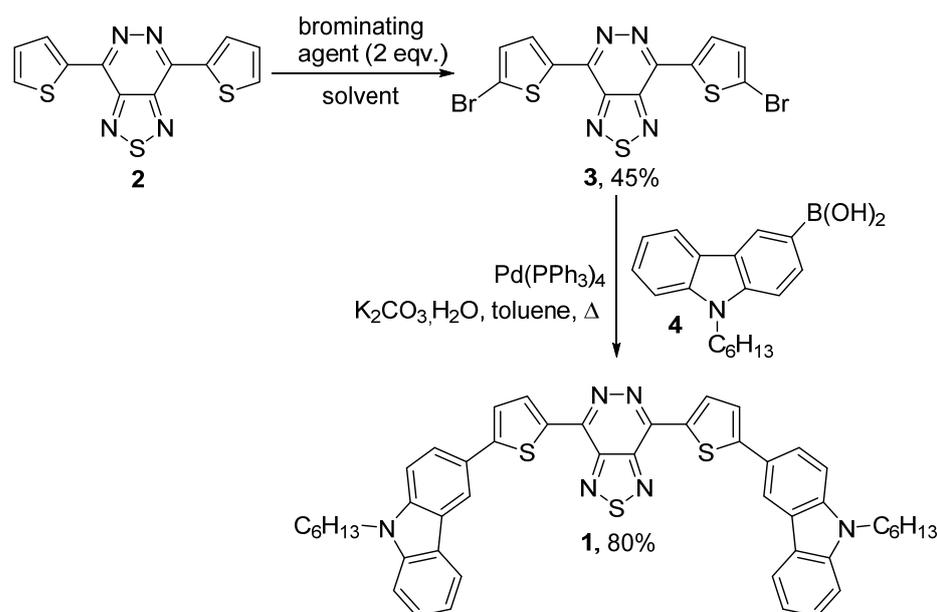
## 1. Introduction

Organic  $\pi$ -conjugated molecules have attracted significant attention for the construction of various organic optoelectronic devices (OPVs), such as organic light emitting diodes (OLEDs), organic field effect transistors (OFETs), organic solar cells (OSCs), and others [1–3]. Of the numerous combinations of donor, acceptor, and  $\pi$ -spacer building blocks, molecules with the D- $\pi$ -A- $\pi$ -D configuration are being intensively studied as donors for OPVs due to their low-lying HOMOs and small band gap [4–6]. Most of these molecules use benzo[*c*][1,2,5]thiadiazole as the electron-deficient building block [7–9]. D- $\pi$ -A- $\pi$ -D type molecular donor dyes containing benzo[*c*][1,2,5]thiadiazole as an internal acceptor (A), carbazole as a donor (D), and thiophene as a spacer ( $\pi$ ) have been successfully employed for the creation of photovoltaic materials [10–12]. Recently, the synthesis of a new strong electron-withdrawing building block [1,2,5]thiadiazolo[3,4-*d*]pyridazine [13] and the selective conditions for its conversion to 4,7-hetaryl[1,2,5]thiadiazolo[3,4-*d*]pyridazines in palladium-catalyzed cross-coupling reactions were published [14]. Herein, we report the synthesis of 4,7-bis(5-(9-hexyl-9H-carbazol-3-yl)thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-*d*]pyridazine **1** by bromination of 4,7-di(thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-*d*]pyridazine **2** followed by Suzuki cross-coupling with carbazole boronic acid.

## 2. Results and Discussion

The bromination of 4,7-di(thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-*d*]pyridazine **2** with several brominating agents was studied (Scheme 1, Table 1). A search for the optimal conditions for the selective introduction of two bromine atoms was carried out by varying the nature of the solvent, temperature, and the reaction time. It was shown that when using *N*-bromosuccinimide (NBS) in CHCl<sub>3</sub> at room temperature, the yield of the bis-bromo

adduct **3** did not exceed 10% (Table 1, Entry 1). Raising the reaction temperature (60 °C) led to the formation of polybrominated adducts while lowering the yield of dibromo derivative **3** (Table 1, Entry 2). The replacement of CHCl<sub>3</sub> by DMF resulted in an insignificant increase in the yield of compound **3** up to 25% (Table 1, Entry 3). The best yield **2** (45%) was achieved when dioxane dibromide (2 equiv) in CHCl<sub>3</sub> was used as a brominating agent (Table 1, Entry 4). The structure of 4,7-bis(5-bromothiophen-2-yl)-[1,2,5]thiadiazolo[3,4-*d*]pyridazine **3** was proven by high-resolution mass spectrometry, <sup>1</sup>H, <sup>13</sup>C NMR, IR, and UV spectroscopy.



**Scheme 1.** Synthesis of 4,7-bis(5-(9-hexyl-9H-carbazol-3-yl)thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-*d*]pyridazine **1**.

**Table 1.** Reaction of 4,7-di(thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-*d*]pyridazine **2** with brominating agents.

Entry	Brominating Agent	Solvent	Temperature, °C	Time, h	Yield of <b>3</b> , %
1	NBS	CHCl <sub>3</sub>	25	15	10
2	NBS	CHCl <sub>3</sub>	60	6	8
3	NBS	DMF	25	48	25
4	Br <sub>2</sub> -dioxane	CHCl <sub>3</sub>	25	48	45

The synthesized compound **3** was investigated using the Suzuki cross-coupling reaction with carbazole boronic acid **4** in order to obtain the target D- $\pi$ -A- $\pi$ -D dye. It was shown that the complete conversion of dibromo derivative **3** occurred within 24 h in refluxing toluene in the presence of a Pd(PPh<sub>3</sub>)<sub>4</sub> catalyst with the formation of a high yield of bis-coupling product **1** (Scheme 1).

The electronic absorption and fluorescence spectra of compound **1** were recorded. In the UV spectra (see Figure S9 in Supplementary Materials), a wide spectral band (120 nm FWHM) was observed in the green-red region of the spectrum as well as several less broad bands in the UV range. The wavelength of the absorption maximum showed a blue-shift from 585 nm for slightly polar CHCl<sub>3</sub> to 567 nm for polar mediums such as THF and DMSO. On the contrary, the wavelengths of the maxima in the UV part of the spectrum coincided in the spectra for all solvents. These spectral features show the nature of  $\pi$ - $\pi^*$  transitions. In the photoluminescence spectra, two spectral components were found to be well resolved with maxima at wavelengths of 760–790 nm and at 840 nm, respectively (see Figure S10 in Supplementary Materials). The wavelength of the maximum of the first band increased

with increasing polarity, so this component can be attributed to the radiation of the state with charge transfer. On the contrary, the emission maximum in the second band remained unchanged in different solvents, which indicates that the nature of the long-wavelength component is not related to charge transfer. We measured a photoluminescence quantum yield of 10% in  $\text{CHCl}_3$  with the absolute method. This value is typical for the most organic dyes with emissions in the NIR region of the spectrum [15]. Thus, it was shown that D- $\pi$ -A- $\pi$ -D dye **1** based on 1,2,5-thiadiazolo[3,4-*d*]pyridazine core, containing carbazole as a donor and thiophene as a  $\pi$ -spacer, exhibits fluorescence in the near infrared region of the spectrum, which makes it a promising material for use as an active emitting layer in NIR-OLEDs as well as for other possible applications as an IR luminophore.

The structure of 4,7-bis(5-(9-hexyl-9*H*-carbazol-3-yl)thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-*d*]pyridazine **1** was confirmed by elemental analysis, high-resolution mass spectrometry,  $^1\text{H}$ ,  $^{13}\text{C}$  NMR, IR, and UV spectroscopy.

### 3. Materials and Methods

4,7-Di(thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-*d*]pyridazine **2** [13] and (9-hexyl-9*H*-carbazol-3-yl)boronic acid **4** [16] were prepared according to published methods. The solvents and reagents were purchased from commercial sources and used as received. The elemental analysis was performed on a 2400 Elemental Analyzer (Perkin Elmer Inc., Waltham, MA, USA). The melting point was determined on a Kofler hot-stage apparatus and was uncorrected.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were taken with a Bruker AM-300 machine (Bruker AXS Handheld Inc., Kennewick, WA, USA) (at frequencies of 300 and 75 MHz) in  $\text{CDCl}_3$  solution with TMS as the standard. *J* values are given in Hz. The IR spectrum was measured with a Bruker "Alpha-T" instrument (Santa Barbara, CA, USA) in a KBr pellet. The high-resolution MS spectrum was measured on a Bruker microTOF II instrument (Bruker Daltonik GmbH, Bremen, Germany) using electrospray ionization (ESI). Optical absorption spectra were obtained at ambient temperature using a JASCO V-770 spectrophotometer in the range of 180–2500 nm. The experiments were carried out for the compound in the solutions poured into 1-cm-pathlength quartz optical cells. The sample was dissolved in different solvents, such as chloroform ( $\text{CHCl}_3$ ), tetrahydrofuran (THF), and dimethyl sulfoxide (DMSO) (HPLC-grade super gradient, Panreac, Spain), with concentrations of about  $10^{-5}$  mol/L. Photoluminescence spectra were recorded at room temperature with a Horiba-Jobin-Yvon Fluorolog-QM spectrofluorimeter equipped with a 75 W CW ArcTune xenon lamp and a Hamamatsu R-FL-QM-R13456 photomultiplier that was sensitive in the 200–980 nm emission range. For the QY measurements, a K-covered integrating sphere (GMP SA, Zürich, Switzerland) was mounted inside the spectrofluorimeter. The sample was placed into the sphere in a quartz vial. All QY measurements were repeated at least three times to achieve an experimental error below 15%.

Synthesis of 4,7-bis(5-bromothiophen-2-yl)-[1,2,5]thiadiazolo[3,4-*d*]pyridazine **3**. (Supplementary Materials).

Dioxane dibromide (163 mg, 0.66 mmol) was added to a solution of 4,7-di(thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-*d*]pyridazine **2** (100 mg, 0.33 mmol) in  $\text{CHCl}_3$  (4 mL). The resulting mixture was degassed by argon in a sealed vial and then stirred at 25 °C for 48 h. On completion, water (20 mL) was added to the reaction mixture and the organic layer was extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 20$  mL), dried with  $\text{MgSO}_4$ , and then concentrated in vacuo. The residue was purified by column chromatography on silica gel (Silica gel Merck 60, eluent  $\text{CH}_2\text{Cl}_2$ –hexane, 1:1, *v/v*). Yield 68 mg (45%), red solid,  $R_f = 0.6$  ( $\text{CH}_2\text{Cl}_2$ ). Mp > 250 °C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 2961, 2925 and 2854 (all C-H), 1628 (C=N), 1533, 1434, 1262, 1091, 1025, 855, 799.  $^1\text{H}$  NMR (ppm):  $\delta$  8.44 (d, *J* = 4.3, 2H), 7.26 (d, *J* = 4.3, 2H).  $^{13}\text{C}$  NMR (ppm):  $\delta$  146.6, 146.5, 138.4, 132.2, 130.8, 119.4. HRMS (ESI-TOF), *m/z*: calcd for  $\text{C}_{12}\text{H}_5^{79}\text{Br}_2\text{N}_4\text{S}_3$  [*M* + *H*]<sup>+</sup>, 458.8038, found, 458.8028.

Synthesis of 4,7-bis(5-(9-hexyl-9*H*-carbazol-3-yl)thiophen-2-yl)-[1,2,5]thiadiazolo[3,4-*d*]pyridazine **1**. (Supplementary Materials).

In a 50 mL round-bottom flask, 4,7-bis(5-bromothiophen-2-yl)-[1,2,5]thiadiazolo[3,4-*d*]pyridazine **3** (60 mg, 0.13 mmol) and carbazole boronic acid **4** (88 mg, 0.3 mmol) were dissolved in toluene (15 mL), and a 2M solution of K<sub>2</sub>CO<sub>3</sub> (2 mL) was added. The mixture was degassed for 20 min with a stream of argon, and then Pd(PPh<sub>3</sub>)<sub>4</sub> (28 mg, 20 mmol %) was added. After refluxing for 24 h, the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>; organic solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (Silica gel Merck 60, eluent CH<sub>2</sub>Cl<sub>2</sub>–hexane, 1:2, *v/v*). Yield 83 mg (80%), violet solid, R<sub>f</sub> = 0.3 (CH<sub>2</sub>Cl<sub>2</sub>). Mp > 250 °C. IR spectrum,  $\nu$ , cm<sup>-1</sup>: 2923 and 2852 (all C-H), 1622 (C=N), 1597, 1538, 1444, 1154, 798. <sup>1</sup>H NMR (ppm):  $\delta$  8.16 (s, 2H), 8.06 (s, 2H), 7.91 (d, *J* = 7.4, 2H), 7.54 (d, *J* = 7.8, 2H), 7.31 (t, *J* = 7.5, 2H), 7.18–7.08 (m, 8H), 4.02 (t, *J* = 7.4, 4H), 1.71–1.68 (m, 4H), 1.25–1.19 (m, 12H), 0.77–0.75 (m, 6H). <sup>13</sup>C NMR (ppm):  $\delta$  151.3, 147.3, 146.9, 140.7, 140.3, 135.5, 133.7, 126.0, 124.7, 124.0, 123.1, 123.0, 122.6, 120.6, 119.2, 117.6, 109.0, 108.9, 43.1, 31.5, 29.7, 27.0, 22.6, 14.0. HRMS (ESI-TOF), *m/z*: calcd for C<sub>48</sub>H<sub>45</sub>N<sub>6</sub>S<sub>3</sub> [M + H]<sup>+</sup>, 801.2862, found, 801.2867. Anal. calcd. for C<sub>48</sub>H<sub>44</sub>N<sub>6</sub>S<sub>3</sub> (800.2862): C, 71.97; H, 5.54; N, 10.49. Found: C, 71.48; H, 5.45; N, 10.30%.

**Supplementary Materials:** The following are available online: copies of <sup>1</sup>H, <sup>13</sup>C NMR, IR, HMRS, UV-Vis, and mass-spectra for compounds **3** and **1**.

**Author Contributions:** Conceptualization, O.A.R. and I.V.T.; methodology, O.A.R.; software, T.N.C.; validation, O.A.R.; formal analysis, investigation, T.N.C. and V.M.K.; resources, O.A.R.; data curation, O.A.R. and I.V.T.; writing—original draft preparation, O.A.R.; writing—review and editing, O.A.R. and I.V.T.; visualization, O.A.R.; supervision, O.A.R.; project administration, O.A.R.; funding acquisition, O.A.R. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by the Russian Science Foundation under grant number 20-73-00220.

**Data Availability Statement:** Not applicable.

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

**Sample Availability:** Samples of the compounds **1–3** are available from the authors.

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