

Short Note

4,4'-([1,2,5]Thiadiazolo[3,4-*d*]pyridazine-4,7-diyl)bis(*N,N*-bis(4-methoxyphenyl)aniline)

Timofey N. Chmovzh ^{1,2} , Timofey A. Kudryashev ^{1,3} and Oleg A. Rakitin ^{1,*} ¹ N. D. Zelinsky Institute of Organic Chemistry Russian Academy of Sciences, 119991 Moscow, Russia² Nanotechnology Education and Research Center, South Ural State University, 454080 Chelyabinsk, Russia³ Department of Chemistry, Moscow State University, 119899 Moscow, Russia

* Correspondence: orakitin@ioc.ac.ru; Tel.: +7-4991-355-327

Abstract: Donor-acceptor-dyes with extended conjugation, such as D- π -A- π -D type, are being intensively investigated as components of near-infrared (NIR) organic light-emitting diodes (OLEDs). In this communication, novel D- π -A- π -D dye, 4,4'-([1,2,5]thiadiazolo[3,4-*d*]pyridazine-4,7-diyl)bis(*N,N*-bis(4-methoxyphenyl)aniline), was synthesized by Stille cross-coupling reaction of 4,7-dibromo-[1,2,5]thiadiazolo[3,4-*d*]pyridazine. The structure of newly synthesized compounds was established by elemental analysis, high-resolution mass-spectrometry, ¹H, ¹³C NMR, IR, and UV spectroscopy. The photophysical properties of the title compound were studied.

Keywords: donor-acceptor molecules; [1,2,5]thiadiazolo[3,4-*d*]pyridazines; Stille cross-coupling reaction; luminescent properties



Citation: Chmovzh, T.N.; Kudryashev, T.A.; Rakitin, O.A. 4,4'-([1,2,5]Thiadiazolo[3,4-*d*]pyridazine-4,7-diyl)bis(*N,N*-bis(4-methoxyphenyl)aniline). *Molbank* **2022**, *2022*, M1479. <https://doi.org/10.3390/M1479>

Academic Editor: Luke R. Odell

Received: 21 October 2022

Accepted: 1 November 2022

Published: 4 November 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

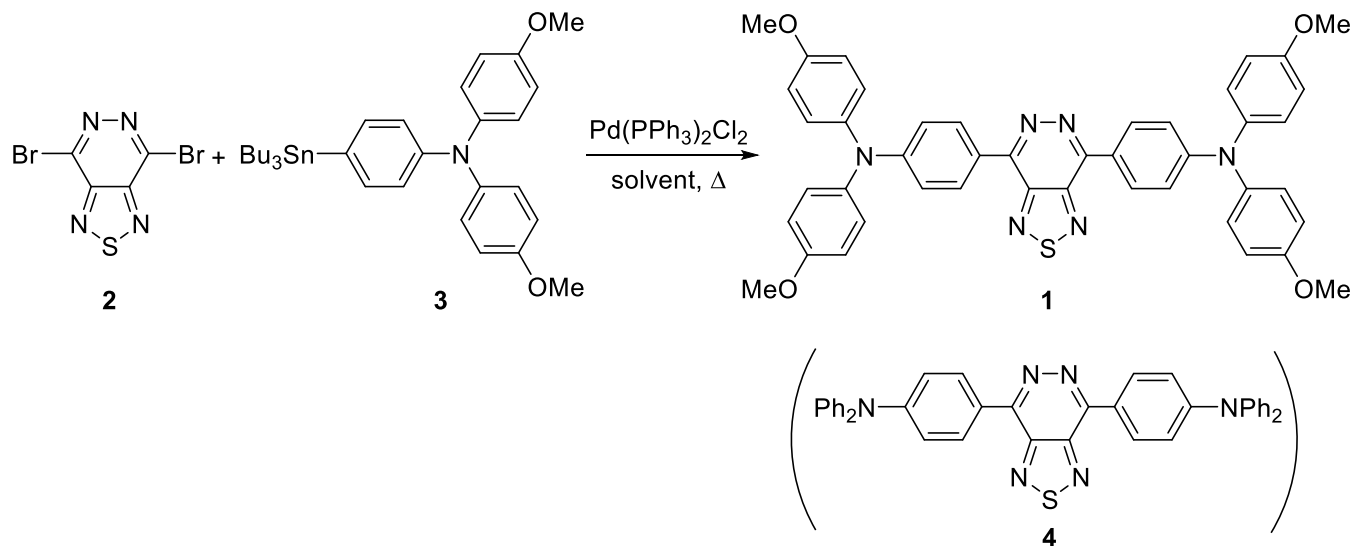
1. Introduction

In recent years, interest in organic light-emitting diodes (OLEDs) has increased due to their wide applications in various fields of modern technologies. An exceptional position among OLEDs is occupied by luminophores emitting in the near-infrared region, which are used in optical communication [1], night vision devices and sensors [2,3], (bio-)analytical sensors and bio-imaging applications [4,5], and in Li-Fi technologies [6]. When developing these materials, it is necessary to pay attention to the fact that they must have a narrow energy gap. Various combinations of small organic molecules containing donor (D) and acceptor (A) fragments can be employed in the structures of organic dyes to achieve these requirements. Since the degree of conjugation in simple D-A molecules is not sufficient for the emission maximum in the NIR region, π -spacers should be introduced in various positions. Recently our attention has been focused on a new ultrahigh electron deficient building block, [1,2,5]thiadiazolo[3,4-*d*]pyridazine, which has shown to be an important part of dye-sensitized solar cells (DSSCs), D-A-D luminophores and low-bandgap conjugated polymers [7–9]. In continuation of this work, we report the synthesis of 4,4'-([1,2,5]thiadiazolo[3,4-*d*]pyridazine-4,7-diyl)bis(*N,N*-bis(4-methoxyphenyl)aniline) **1** from 4,7-dibromo-[1,2,5]thiadiazolo[3,4-*d*]pyridazine **2** and investigation of its photophysical properties.

2. Results and Discussion

We have studied the Stille cross-coupling reaction of 4,7-dibromo-[1,2,5]thiadiazolo[3,4-*d*]pyridazine **2** with 4-methoxy-*N*-(4-methoxyphenyl)-*N*-(4-(tributylstannyl)phenyl)aniline **3** in the presence of dichlorobis(triphenylphosphine)palladium (Scheme 1, Table 1). The search for optimal conditions for the selective introduction of donor substituents was carried out by varying the nature of solvents, temperature, and time of chemical transformation. It was shown that when carrying out the reaction in boiling THF for 15 h, the yield of the bis-coupling product **1** did not exceed 15% (Table 1, entry 1). The replacement of THF with the higher boiling dioxane resulted in the replacement of both bromine

atoms with triphenylamine moieties within 24 h to give the bis-coupling product **1** in 35% yield (Entry 2). The best yield of the target product **1** (55%) was achieved by refluxing in toluene for 24 h. (Entry 3), similarly to how it was found by synthesis of its analog, 4,4'-([1,2,5]thiadiazolo[3,4-*d*]pyridazine-4,7-diyl)bis(*N,N*-diphenylaniline) **4** [10].



Scheme 1. Synthesis of 4,4'-([1,2,5]thiadiazolo[3,4-*d*]pyridazine-4,7-diyl)bis(*N,N*-bis(4-methoxyphenyl)aniline) **1**.

Table 1. Reaction of 4,7-dibromo-[1,2,5]thiadiazolo[3,4-*d*]pyridazine **1** with 4-methoxy-*N*-(4-methoxyphenyl)-*N*-(4-(tributylstannyl)phenyl)aniline **2**.

Entry	Solvent	Temperature, °C	Time, h	Yield, of 1%
1	THF	78	15	15
2	Dioxane	81	24	35
3	Toluene	110	24	55

The structure of 4,4'-([1,2,5]thiadiazolo[3,4-*d*]pyridazine-4,7-diyl)bis(*N,N*-bis(4-methoxyphenyl)aniline) **1** was confirmed by elemental analysis, high-resolution mass-spectrometry, ¹H, ¹³C NMR, IR, and UV spectroscopy.

We measured the optical absorption spectra for compound **1** in CH₂Cl₂. The spectra consisted of several spectral bands in the UV wavelength range and one wide band in the visible spectral region, which is explained by the intramolecular charge transfer process (ICT). The position of the short-wavelength maximum at 293 and 343 nm indicates that this band is associated with the π-π* electronic transition, while the maximum of the ICT bands is located in the spectral region of 560 nm. Compound **1** exhibited fluorescence predominantly in the visible region of the spectrum (λ_{max} = 650 nm), however, with extremely low fluorescence intensity, probably due to the presence of non-radiative relaxation in compound **1**. It should be noted that analog **1**, 4,4'-([1,2,5]thiadiazolo[3,4-*d*]pyridazine-4,7-diyl)bis(*N,N*-diphenylaniline) **4**, which we obtained earlier [10], exhibited absorption in chloroform at 548 nm, while the emission maximum was 755 nm; however, luminescence quenching was not observed in this case. The main photophysical parameters for compounds **1** and **4**, such as absorption maximum wavelength λ_{abs}, maximum molar extinction ε_{max}, emission maximum wavelength λ_{em}, and Stokes shift value Δν, are given in Table 2.

Table 2. Photophysical parameters obtained for 4,4'-([1,2,5]thiadiazolo[3,4-*d*]pyridazine-4,7-diyl)bis(*N,N*-bis(4-methoxyphenyl)aniline) **1** and 4,4'-([1,2,5]thiadiazolo[3,4-*d*]pyridazine-4,7-diyl)bis(*N,N*-diphenylaniline) **4**: absorption maximum wavelength λ_{abs} , maximum molar extinction coefficient ϵ , the wavelength of emission maximum λ_{em} , Stokes shift $\Delta\nu$.

Compound	Solvent	λ_{abs} nm	λ_{abs} (ICT) nm	ϵ_{max} $\text{mol} \times \text{L}^{-1} \times \text{cm}^{-1}$	λ_{em} nm (cm^{-1})	Stokes Shift $\Delta\nu$ cm^{-1}
1	CH ₂ Cl ₂	293, 343	560	22,666	650 (15,384)	3092
4	CHCl ₃	350	548	3800	755 (17,869)	5003

In conclusion, 4,4'-([1,2,5]thiadiazolo[3,4-*d*]pyridazine-4,7-diyl)bis(*N,N*-bis(4-methoxyphenyl)aniline) **1** was successfully synthesized from 4,7-dibromo-[1,2,5]thiadiazolo[3,4-*d*]pyridazine **1** by the Stille cross-coupling reaction. The luminescent properties of compound **1** were investigated.

3. Materials and Methods

4,7-Dibromo-[1,2,5]thiadiazolo[3,4-*d*]pyridazine **2** [11] and 4-methoxy-*N*-(4-methoxyphenyl)-*N*-(4-(tributylstannyl)phenyl)aniline **3** [12] were prepared according to the published methods. The solvents and reagents were purchased from commercial sources and used as received. Elemental analysis was performed on a 2400 Elemental Analyzer (Perkin Elmer Inc., Waltham, MA, USA). Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. ¹H and ¹³C 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 CDCl₃ solution, with TMS as the standard. J values are given in Hz. IR spectrum was measured with a Bruker "Alpha-T" instrument in a KBr pellet. High-resolution MS spectrum was measured on a Bruker micrOTOF II instrument (Bruker Daltonik GmbH, Bremen, Germany) using electrospray ionization (ESI). Solution UV-visible absorption spectra were recorded using an Agilent Cary 60 spectrophotometer (USA). The sample was placed in a 1 cm quartz cell at room temperature with a 5×10^{-5} mol/mL concentration. Luminescence spectra were recorded using an Agilent Cary Eclipse (USA). The sample was placed in a 1 cm quartz cell at room temperature with a 5×10^{-6} mol/mL concentration.

Synthesis of 4,4'-([1,2,5]thiadiazolo[3,4-*d*]pyridazine-4,7-diyl)bis(*N,N*-bis(4-methoxyphenyl)aniline) **1** (Supplementary Materials).

PdCl₂(PPh₃)₂ (51 mg, 15 %mol) and stannane **3** (534 mg, 0.9 mmol) were added to a solution of 4,7-dibromo-[1,2,5]thiadiazolo[3,4-*d*]pyridazine **2** (100 mg, 0.3 mmol) in anhydrous toluene (4 mL). The resulting mixture was degassed with argon in a sealed vial and then stirred at 110 °C for 24 h. On completion (TLC monitoring the disappearance of starting materials), water (30 mL) was added to the reaction mixture, which was then extracted with CH₂Cl₂ (3 × 35 mL). The combined organic extracts were washed with brine, dried over MgSO₄, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (Silica gel Merck 60, eluent hexane–CH₂Cl₂, 2:1, *v/v*). Yield 122 mg (55%), violet solid, R_f = 0.3 (hexane–CH₂Cl₂, 2:1, *v/v*). Mp = 137–139 °C. IR spectrum, ν , cm⁻¹: 2927, 2834, 1597, 1505, 1402, 1235, 1287, 1242, 1191, 1135, 1033, 829, 780, 575, 526. ¹H NMR (ppm): δ 8.62 (d, *J* = 8.0, 4H), 7.16 (d, *J* = 7.7, 8H), 7.08–6.99 (m, 4H), 6.90 (d, *J* = 8.1, 8H), 3.83 (s, 12H). ¹³C NMR (ppm): δ 156.9, 151.7, 150.9, 150.1, 139.5, 131.2, 127.8, 118.4, 115.0, 55.6. HRMS (ESI-TOF), *m/z*: calcd for C₄₄H₃₇N₆O₄S [M + H]⁺, 745.2592, found, 745.2577. UV-Vis spectra (in CH₂Cl₂), λ_{max} : 293 nm (ϵ = 38,313 M⁻¹ cm⁻¹), 343 nm (ϵ = 35,924 M⁻¹ cm⁻¹), 560 nm (ϵ = 22,666 M⁻¹ cm⁻¹). Luminescence spectra (in CH₂Cl₂), λ_{max} : 650 nm. Anal. calcd for C₄₄H₃₆N₆O₄S (744.8607): C, 70.95; H, 4.87; N, 11.28. Found: C, 70.48; H, 4.60; N, 11.20%.

Supplementary Materials: The following are available online: copies of ¹H, ¹³C NMR, IR, UV-Vis, luminescence, and HRMS-spectra for compound **1**.

Author Contributions: Conceptualization, T.N.C.; methodology, O.A.R.; software, T.N.C.; validation, O.A.R.; formal analysis, investigation, T.N.C. and T.A.K.; resources, O.A.R.; data curation, O.A.R.; writing—original draft preparation, T.N.C.; writing—review and editing, T.N.C.; 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 received no external funding.

Data Availability Statement: Not applicable.

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

References

1. Le, S.T.; Kanesan, T.; Bausi, F.; Haigh, P.A.; Rajbhandari, S.; Ghassemlooy, Z.; Papakonstantinou, I.; Popoola, W.O.; Burton, A.; Le Minh, H.; et al. 10 Mb/s visible light transmission system using a polymer light-emitting diode with orthogonal frequency division multiplexing. *Opt. Lett.* **2014**, *39*, 3876. [[CrossRef](#)] [[PubMed](#)]
2. Tessler, N.; Medvedev, V.; Kazes, M.; Kan, S.; Banin, U. Efficient Near-Infrared Polymer Nanocrystal Light-Emitting Diodes. *Science* **2002**, *295*, 1506–1508. [[CrossRef](#)] [[PubMed](#)]
3. Schanze, K.S.; Reynolds, J.R.; Boncella, J.M.; Harrison, B.S.; Foley, T.J.; Bouguettaya, M.; Kang, T.-S. Near-infrared organic light emitting diodes. *Synth. Met.* **2003**, *137*, 1013–1014. [[CrossRef](#)]
4. Eliseeva, S.V.; Bünzli, J.-C.G. Lanthanide luminescence for functional materials and bio-sciences. *Chem. Soc. Rev.* **2010**, *39*, 189–227. [[CrossRef](#)] [[PubMed](#)]
5. Zampetti, A.; Minotto, A.; Cacialli, F. Near-Infrared (NIR) Organic Light-Emitting Diodes (OLEDs): Challenges and Opportunities. *Adv. Funct. Mater.* **2019**, *29*, 1807623. [[CrossRef](#)]
6. Haigh, P.A.; Bausi, F.; Ghassemlooy, Z.; Papakonstantinou, I.; Le Minh, H.; Fléchon, C.; Cacialli, F. Visible light communications: Real time 10 Mb/s link with a low bandwidth polymer light-emitting diode. *Opt. Express* **2014**, *22*, 2830. [[CrossRef](#)] [[PubMed](#)]
7. Chmovzh, T.N.; Knyazeva, E.A.; Tanaka, E.; Popov, V.V.; Mikhailchenko, L.V.; Robertson, N.; Rakitin, O.A. [1,2,5]Thiadiazolo[3,4-d]Pyridazine as an Internal Acceptor in the D-A- π -A Organic Sensitizers for Dye-Sensitized Solar Cells. *Molecules* **2019**, *24*, 1588. [[CrossRef](#)] [[PubMed](#)]
8. Korshunov, V.M.; Chmovzh, T.N.; Chkhetiani, G.R.; Taydakov, I.V.; Rakitin, O.A. New D–A–D luminophores of the [1,2,5]thiadiazolo[3,4-d]pyridazine series. *Mendeleev Commun.* **2022**, *32*, 371–373. [[CrossRef](#)]
9. Leventis, A.; Chmovzh, T.N.; Knyazeva, E.A.; Han, Y.; Heeney, M.; Rakitin, O.A.; Bronstein, H. A novel low-bandgap pyridazine thiadiazole-based conjugated polymer with deep molecular orbital levels. *Polym. Chem.* **2020**, *11*, 581–585. [[CrossRef](#)]
10. Korshunov, V.M.; Chmovzh, T.N.; Freidzon, A.Y.; Minyaev, M.E.; Barkanov, A.D.; Golovanov, I.S.; Mikhailchenko, L.V.; Avetisov, I.C.; Taydakov, I.V.; Rakitin, O.A. Small D- π -A- π -D organic dyes for near-infrared emitting OLEDs with excellent external quantum efficiency. *Dye. Pigment.* **2022**, *208*, 110860. [[CrossRef](#)]
11. Chmovzh, T.; Knyazeva, E.; Lyssenko, K.; Popov, V.; Rakitin, O. Safe Synthesis of 4,7-Dibromo[1,2,5]thiadiazolo[3,4-d]pyridazine and Its SNAr Reactions. *Molecules* **2018**, *23*, 2576. [[CrossRef](#)] [[PubMed](#)]
12. Siddiqui, A.; Thawarkar, S.; Singh, S.P. A novel perylenediimide molecule: Synthesis, structural property relationship and nanoarchitectonics. *J. Solid State Chem.* **2022**, *306*, 122687. [[CrossRef](#)]