

Short Note

4,7-Di(9*H*-carbazol-9-yl)-[1,2,5]oxadiazolo[3,4-*d*]pyridazine

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Abstract: Donor–acceptor–donor (D–A–D)-type molecules are considered as a promising class of NIR fluorescence materials. In this communication, 4,7-di(9*H*-carbazol-9-yl)-[1,2,5]oxadiazolo[3,4-*d*]pyridazine was obtained by dehydrogenation of 4,7-bis(1,2,3,4,4a,9a-hexahydro-9*H*-carbazol-9-yl)-[1,2,5]oxadiazolo[3,4-*d*]pyridazine with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in toluene. The structure of the synthesized compound was established by elemental analysis; high-resolution mass spectrometry; ¹H, ¹³C NMR, IR, and UV spectroscopy; and mass spectrometry. The photo-physical properties of the title compound were studied and compared with spectral data of the [1,2,5]thiadiazolo[3,4-*d*]pyridazine analogue.

Keywords: donor-acceptor-donor molecules; [1,2,5]oxadiazolo[3,4-*d*]pyridazines; carbazoles; dehydrogenation; luminescent properties



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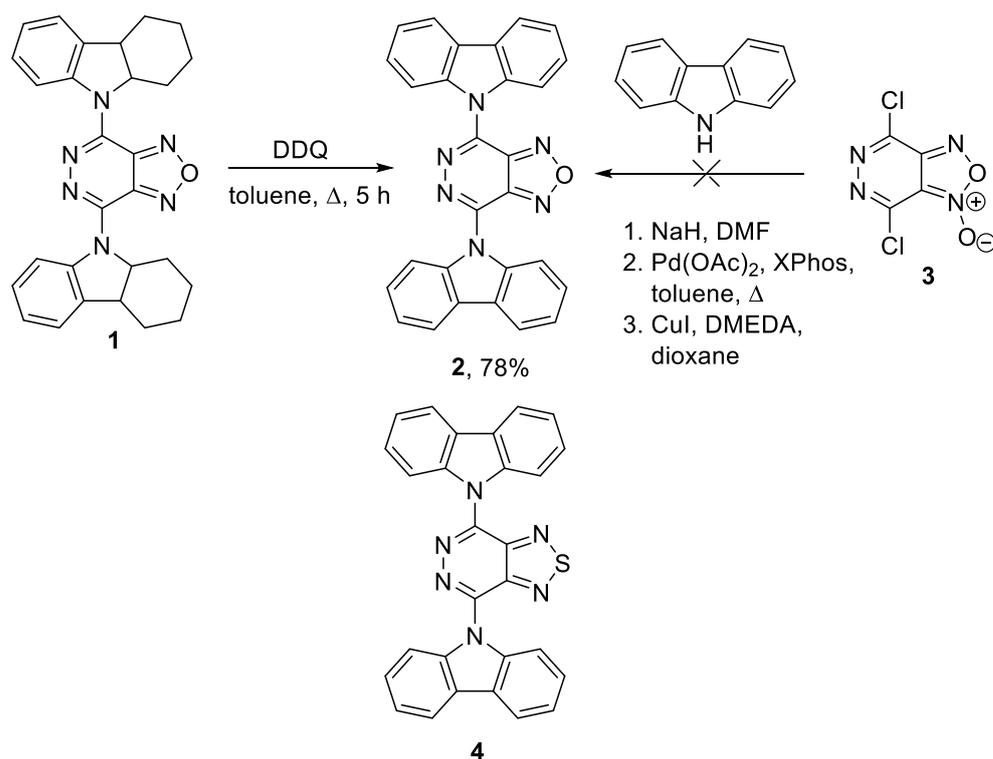
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1. Introduction

Small organic molecules containing donor (D) and acceptor (A) fragments have been intensively investigated in recent years in the design of various electronic devices, such as organic solar cells (OSCs) [1,2], n-type organic field effect transistors (OFETs) [3,4], and luminescent materials emitting in the visible and infrared regions [5,6]. Benzo[*c*][1,2,5]thiadiazole ring system is often used in these molecules as an electron-accepting building block [7,8]. Recently, the utilization of [1,2,5]thiadiazolo[3,4-*d*]pyridazine as an electron acceptor with ultrahigh electron deficiency for the preparation of dye-sensitized solar cells (DSSCs), D–A–D luminophores, and low-bandgap conjugated polymers has been reported [9–11]. Their oxygen analogues [1,2,5]oxadiazolo[3,4-*d*]pyridazines are less known but are considered promising precursors for these applications [12,13] and as energetic materials [14,15]. We have previously synthesized 4,7-bis(1,2,3,4,4a,9a-hexahydro-9*H*-carbazol-9-yl)-[1,2,5]oxadiazolo[3,4-*d*]pyridazine **1** [16]. Herein, we report the preparation of 4,7-di(9*H*-carbazol-9-yl)-[1,2,5]oxadiazolo[3,4-*d*]pyridazine **2** by dehydrogenation of [1,2,5]oxadiazolo[3,4-*d*]pyridazine **1** and investigation of its luminescent properties.

2. Results and Discussion

4,7-Di(9*H*-carbazol-9-yl)-[1,2,5]oxadiazolo[3,4-*d*]pyridazine **2** can be considered a promising candidate for a highly efficient red thermally activated delayed fluorescence emitter (TADF) and a high-efficiency organic light-emitting diode (OLED). It was found that compound **2** could not be obtained from dichloro derivative **3** because it did not react with carbazole either under aromatic nucleophilic substitution conditions or under Buchwald–Hartwig or Ullmann conditions (Scheme 1). Oxadiazolopyridazine **2** was successfully synthesized by the reaction of 4,7-bis(1,2,3,4,4a,9a-hexahydro-9*H*-carbazol-9-yl)-[1,2,5]oxadiazolo[3,4-*d*]pyridazine **1** at reflux in toluene for 5 h according to the known procedure described for its thiadiazole analogue **4** [17].



Scheme 1. Synthesis of 4,7-di(9*H*-carbazol-9-yl)-[1,2,5]oxadiazolo[3,4-*d*]pyridazine **2**.

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

The optical absorption spectra of compound **2** were measured in solvents with different polarities and compared with similar spectra of pyridazinethiadiazole **4** [10]. The spectra consisted of several spectral bands in the UV range of wavelengths attributed to π - π^* electron transition and one broad band in the visible region of the spectrum to intramolecular charge transfer process (ICT). The UV spectra for compounds **2** and **4** are qualitatively similar and have an absorption maximum at wavelengths of 321 and 350 nm, respectively. For compound **2**, the maxima of the ICT band are located in the longer wavelength spectral region 499–530 nm, depending on the polarity of the solvent, compared to pyridazinethiadiazole **4** [10]. The investigated compounds **2** and **4** exhibited fluorescence predominantly in the visible region of the spectrum ($\lambda_{\text{max}} = 656$ –706 nm). Compound **2** did not have fluorescence in solvents such as DMSO and acetonitrile due to the occurrence of nonradiative relaxation. The large Stokes shifts of 4700 and 4790 cm^{-1} may lead to a decrease in the fluorescence quenching of compound **2** in the solid state [18]. The luminescence intensity of the thiadiazole derivative **4** was significantly higher than that of the oxadiazole derivative **2**, probably due to the internal conversion in addition to the intersystem crossing of compound **2** [19]. The main photophysical parameters for compound **2**, such as absorption maximum wavelength λ_{abs} , maximum molar extinction ϵ_{max} , emission maximum wavelength λ_{em} , and Stokes shift value $\Delta\nu$, are given in Table 1. Thus, it was shown that 4,7-di(9*H*-carbazol-9-yl)-[1,2,5]oxadiazolo[3,4-*d*]pyridazine **2** exhibited fluorescence in the near-infrared region of the spectrum, which makes them a promising compound for use as possible applications as an NIR luminophore.

Table 1. Photophysical parameters obtained for 4,7-di(9*H*-carbazol-9-yl)-[1,2,5]oxadiazolo[3,4-*d*]pyridazine **2**: absorption maximum wavelength λ_{abs} , maximum molar extinction coefficient ϵ , wavelength of emission maximum λ_{em} , Stokes shift $\Delta\nu$.

Solvent	λ_{abs} (LE) nm	λ_{abs} (ICT) nm	ϵ_{max} $\text{mol} \times 10^{-1} \times \text{cm}^{-1}$	λ_{em} nm (cm^{-1})	Stokes Shift $\Delta\nu$ cm^{-1}
CHCl ₃	321	530	9710	706 (14,164)	4700
THF	321	501	9190	659 (15,174)	4790
DMSO	323	499	8850	-	-
MeCN	321	503	9580	-	-

3. Materials and Methods

4,7-Bis(1,2,3,4,4a,9a-hexahydro-9*H*-carbazol-9-yl)-[1,2,5]oxadiazolo[3,4-*d*]pyridazine **1** was prepared according to the published method [16]. 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). The melting point was determined on a Kofler hot-stage apparatus and is 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. The MS spectrum (EI, 70 eV) was obtained with a Finnigan MAT INCOS 50 instrument (Hazlet, NJ, USA). The IR spectrum was measured with a Bruker “Alpha-T” instrument in KBr pellet. The 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). Luminescence spectra were recorded using an Agilent Cary Eclipse (USA). The sample was placed in a 1 cm quartz cell at room temperature with 5×10^{-5} mol/mL concentration.

Synthesis of 4,7-bis(1,2,3,4,4a,9a-hexahydro-9*H*-carbazol-9-yl)-[1,2,5]oxadiazolo[3,4-*d*]pyridazine **2** (Supplementary Materials, Figures S1–S7) 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (74 mg, 0.32 mmol) was added to a solution of amine **1** (60 mg, 0.13 mmol) in toluene (12 mL). The mixture was refluxed for 5 h; diluted with EtOAc (30 mL); washed with aq. NaHSO₃, Na₂CO₃, water, and brine; dried over MgSO₄; and concentrated under reduced pressure. The crude product was purified by column chromatography (CH₂Cl₂/hexane, 2:1, *v/v*) to afford 45 mg (78%) of target compound **2** as a dark red solid, *R*_f = 0.3 (hexane–CH₂Cl₂, 2:1, *v/v*). m.p. = 182–184 °C. IR spectrum, ν , cm^{-1} : 1493, 1467, 1453, 1334, 1267, 1221, 1122, 744, 718, 675, 609. ¹H NMR (ppm): δ 8.16 (d, *J* = 7.3, 4H), 8.07 (d, *J* = 8.1, 4H), 7.53 (td, *J* = 8.1, 1.7, 4H), 7.47 (t, *J* = 7.3, 4H). ¹³C NMR (ppm): δ 143.1, 142.6, 139.0, 126.8, 125.9, 123.4, 120.3, 113.2. HRMS (ESI-TOF), *m/z*: calcd for C₂₈H₁₇N₆O [M + H]⁺, 453.1458, found, 453.1445. MS (EI, 70 eV), *m/z* (*I*, %): 455 ([M + 3]⁺, 10), 454 ([M + 2]⁺, 15), 453 ([M + 1]⁺, 99), 452 ([M]⁺, 100), 435 (98), 422 (50), 394 (98), 166 (40), 140 (12). Anal. calcd. For C₂₈H₁₆N₆O (452.1458): C, 74.33; H, 3.56; N, 18.57. Found: C, 74.30; H, 3.52; N, 18.50%.

Supplementary Materials: The following are available online: copies of ¹H, ¹³C NMR, IR, UV-Vis, luminescence and mass spectra for the compound **2**.

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