

Proceeding Paper

# *N,N*-Dimethyl-4-amino-2,1,3-benzothiadiazole: Synthesis and Luminescent Solvatochromism †

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† Presented at the 25th International Electronic Conference on Synthetic Organic Chemistry, 15–30 November 2021; Available online: <https://ecsoc-25.sciforum.net/>.

**Abstract:** *N,N*-Dimethyl-4-amino-2,1,3-benzothiadiazole (BTD<sup>NMe2</sup>) was synthesized from the commercially available 2,1,3-benzothiadiazole (BTD) by nitration in a sulfonitric mixture, followed by a reduction of the nitro group and subsequent methylation with iodomethane. BTD<sup>NMe2</sup> was fully characterized by means of nuclear magnetic resonance (NMR) and infrared spectroscopy. The solutions of BTD<sup>NMe2</sup> in common organic solvents revealed to be appreciably luminescent in the visible range. The electronic transitions related to the absorption and emission properties were associated with the HOMO–LUMO energy gap by means of electrochemical measurements and DFT calculations. Finally, BTD<sup>NMe2</sup> was successfully used to prepare luminescent-doped poly(methyl methacrylate) samples.

**Keywords:** *N,N*-dimethyl-4-amino-2,1,3-benzothiadiazole; fluorescence; solvatochromism; 2,1,3-benzothiadiazole



**Citation:** Ferraro, V.; Giroto, M.; Bortoluzzi, M. *N,N*-Dimethyl-4-amino-2,1,3-benzothiadiazole: Synthesis and Luminescent Solvatochromism. *Chem. Proc.* **2022**, *8*, 87. <https://doi.org/10.3390/ecsoc-25-11658>

Academic Editor: Julio A. Seijas

Published: 13 November 2021

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## 1. Introduction

2,1,3-Benzothiadiazole (BTD) is a  $\pi$ -extended heteroarene used for a wide range of applications such as herbicide, fungicide, and antibacterial agents [1]. However, it is also applied for the preparation of luminescent materials owing to the strong withdrawing ability and behaviour as a fluorophore [2]. Intermolecular interactions such as heteroatom contacts and  $\pi$ – $\pi$  stacking determine well-ordered structures [3]. Over the last decades, polymers [4] and liquid crystals [5] containing BTD fragments were successfully exploited for advanced applications [6], such as organic light-emitting diodes (OLEDs) [7,8], dyes [9–14], and solar and photovoltaic cells [15–18]. 2,1,3-Benzothiadiazole-based compounds were also exploited as fluorescent probes for bioimaging in live cells [19–21] or as fluorescent polymeric thermometers for the determination of intercellular temperature [22,23]. Moreover, poly(benzothiadiazoles) were used as heterogeneous photocatalysts to promote various organic photoredox reactions under visible-light irradiation [24,25].

Despite the fact that 4-amino-2,1,3-benzothiadiazole was deeply investigated both as a free compound [26] and a possible ligand [27–33] for the preparation of transition metal complexes, *N,N*-dimethyl-4-amino-2,1,3-benzothiadiazole (BTD<sup>NMe2</sup>) is much less studied. The only preparation reported in literature dates back to 1976 [34], but the compound was only poorly characterized. Herein, we report an alternative synthesis and the characterization of BTD<sup>NMe2</sup>, with a particular interest in the photophysical properties of the compound. The possible application of BTD<sup>NMe2</sup> as a dopant for polymeric materials was also explored.

## 2. Materials and Methods

Commercial solvents (Merck) were purified following standard methods [35]. 2,1,3-Benzothiadiazole and the other reagents were Aldrich products, which were used as

received. Poly(methyl methacrylate) (PMMA,  $M_w = 86,000 \text{ g mol}^{-1}$ ) was a TCI Chemicals product. 4-Nitro-2,1,3-benzothiadiazole (BTD<sup>NO2</sup>) was synthesized by modifying a reported procedure [36]. An amount of 24 mL of H<sub>2</sub>SO<sub>4</sub> 98% and 8 mL of HNO<sub>3</sub> 70% were mixed in a flask and frozen with a nitrogen bath. 2,1,3-Benzothiadiazole (2.000 g, 14.7 mmol) was added, then the reaction was allowed to warm up at room temperature and stirred for three hours. The reaction mixture was then cooled with an ice bath, and water (15 mL) was slowly added. Subsequently, a solution containing about 18.0 g of NaOH in 40 mL of water was added within an hour. After removal from the ice bath, NaHCO<sub>3</sub> was added in small amounts until a neutral pH was reached. The product was extracted with 2 × 40 mL of dichloromethane, and the organic fraction was washed with water (2 × 20 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, and evaporated under reduced pressure to yield a reddish solid (yield: 95%).

The characterization data agree with those reported for the same product obtained with different synthetic routes [37]. The reduction of 4-nitro-2,1,3-benzothiadiazole (BTD<sup>NO2</sup>) to afford the corresponding 4-amino-2,1,3-benzothiadiazole (BTD<sup>NH2</sup>) was carried out following a reported procedure [38], with slight modifications. To a solution containing 2.000 g of BTD<sup>NO2</sup> (11.4 mmol) in 50 mL of ethanol, 9.208 g of FeSO<sub>4</sub>·7H<sub>2</sub>O (34.2 mmol), 4.878 g of ammonium chloride (91.2 mmol), 9 mL of water and 2.243 g of zinc dust (34.2 mmol) were added under vigorous stirring. The mixture was heated at 50 °C for three hours and, after cooling at room temperature, it was cleared by filtration on celite. The solid was washed with 3 × 10 mL of ethanol. The solution thus obtained was evaporated under reduced pressure. The crude product was dissolved in 40 mL of ethyl acetate, and 30 mL of a 25% aqueous solution of NH<sub>4</sub>Cl was added. The organic layer was extracted and washed with water (2 × 20 mL) and with 30 mL of a saturated aqueous solution of NaHCO<sub>3</sub>. The organic fraction was then dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The product was precipitated with isohexane and dried in vacuo (yield: 45%). The characterization data were in agreement with the data reported for the same product prepared with different synthetic routes [28].

Elemental analyses (C, H, N, S) were carried out using an Elementar Unicube microanalyzer. Infrared (IR) spectra were registered using a Perkin-Elmer SpectrumOne spectrophotometer between 4000 and 400 cm<sup>-1</sup> using KBr disks. Mono- and bidimensional nuclear magnetic resonance (NMR) spectra were collected employing Bruker Avance 300 and Avance 400 instruments operating respectively at 300.13 MHz and 400.13 MHz of <sup>1</sup>H resonance. The <sup>1</sup>H and <sup>13</sup>C NMR spectra referred to the partially non-deuterated fraction of the solvent, itself referred to as tetramethylsilane.

The absorption spectra were collected in the range 235–700 nm employing a Perkin-Elmer Lambda 40 spectrophotometer. Photoluminescence emission (PL) spectra were registered at room temperature using a Horiba Jobin Yvon Fluorolog-3 spectrofluorometer. A continuous wave xenon arc lamp was used as the source, and the excitation wavelength was selected using a double Czerny–Turner monochromator. Suitable long pass filters were placed in front of the acquisition systems. The detector was composed of a single monochromator iHR320 and a photomultiplier tube Hamamatsu R928. Fluorescence quantum yields  $\Phi_f$  of 5 × 10<sup>-5</sup> M solutions were calculated using 5 × 10<sup>-5</sup> M anthracene in ethanol as standard based on Equation (1) [39], where  $\Phi_{f, \text{std}}$  is the quantum yield of anthracene in ethanol (0.27),  $F$  and  $F_{\text{std}}$  are, respectively, the areas under the fluorescence emission bands of the sample and the standard,  $A$  and  $A_{\text{std}}$  are respectively the absorbance values of sample and standard at the excitation wavelength,  $n$  is the refractive index of the solvent used for the sample and  $n_{\text{std}}$  is the refractive index of ethanol.

$$\Phi_f = \Phi_{f, \text{std}} \cdot (F \cdot A_{\text{std}} \cdot n^2) / (F_{\text{std}} \cdot A \cdot n_{\text{std}}^2)^{-1} \quad (1)$$

Electrochemical measurements were carried out on dry acetonitrile solutions of BTD<sup>NMe2</sup> containing LiClO<sub>4</sub> as a supporting electrolyte and ferrocene (Fc) as an internal reference. The instrument used was an eDAQ ET014-199 potentiostat, connected to eDAQ 1 mm glassy carbon disk working electrode, eDAQ 1.6 mm diameter Pt/Ti counter-

electrode, and a Pt wire as a reference. Fc/Fc<sup>+</sup> couple was used as the internal standard, and all of the measurements were carried out at room temperature under an argon atmosphere.

Computational calculations were carried out using the range-separated hybrid DFT functional  $\omega$ B97X in combination with Alhrichs' and Weigend's def2-TZVP basis set [40–43]. The C-PCM conductor-like polarizable continuum model was added, considering acetonitrile as a continuous medium [44,45]. The TD-DFT approach was used to simulate the electronic transitions [46]. Gaussian 16 was employed as calculation software [47].

**Synthesis of *N,N*-dimethyl-4-amino-2,1,3-benzothiadiazole, BTD<sup>NMe2</sup>:** The *N*-methylation of 4-amino-2,1,3-benzothiadiazole (BTD<sup>NH2</sup>) was carried out by modifying a reported procedure [48]. An amount of 0.350 g of BTD<sup>NH2</sup> (2.3 mmol) were dissolved in 15 mL of *N,N*-dimethylformamide (DMF), then 3.179 g of K<sub>2</sub>CO<sub>3</sub> (23.0 mmol) and 1.4 mL of CH<sub>3</sub>I (23.0 mmol) were added under stirring. The mixture was heated at 75 °C for twelve hours. After cooling at room temperature, 50 mL of water were added, and the product was extracted with 2 × 80 mL of ethyl acetate. The organic fraction was washed with 100 mL of cold water, dried over Na<sub>2</sub>SO<sub>4</sub>, and evaporated under reduced pressure. The product was dissolved in 30 mL of pentane, the solution was purified by filtration, and the solvent was removed under nitrogen flow to afford a red oil (yield: 50%).

*Characterization of Di N,N-Dimethyl-4-amino-2,1,3-benzothiadiazole.*

Anal. calcd for C<sub>8</sub>H<sub>9</sub>N<sub>3</sub>S (179.24 g mol<sup>-1</sup>, %): C, 53.61; H, 5.06; N, 23.44; S, 17.89. Found (%): C, 53.40; H, 5.08; N, 23.35; S, 17.82. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 298 K)  $\delta$  7.49–7.40 (m, 2H, BTD), 6.57 (t, 1H, <sup>3</sup>J<sub>HH</sub> = 5.9 Hz, BTD), 3.29 (s, 6H, Me). <sup>13</sup>C {<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 298 K)  $\delta$  156.90 BTD-C<sub>ipso</sub>, 149.29 BTD-C<sub>ipso</sub>, 144.43 BTD-C<sub>ipso</sub>, 130.73 BTD-CH, 111.13 BTD-CH, 108.85 BTD-CH, 42.59 Me. IR (KBr disk, cm<sup>-1</sup>): 1587 m, 1545 s, 1494 m (aromatic  $\nu_{C-N}$  and  $\nu_{C-C}$ ).

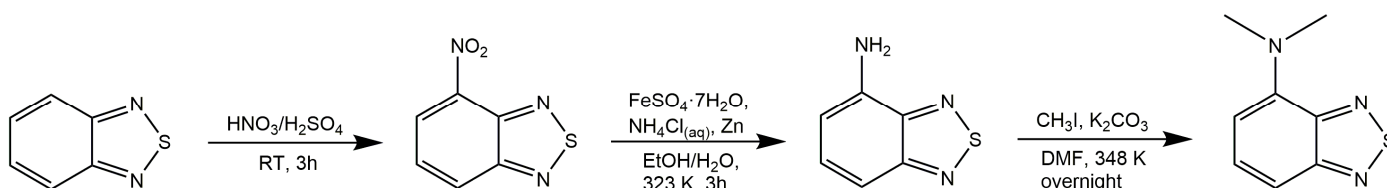
**Synthesis of BTD<sup>NMe2</sup>@PMMA:** An amount of 0.250 g of PMMA was dissolved in 6 mL of dichloromethane under slow stirring, then a solution containing 0.010 g of BTD<sup>NMe2</sup> in 4 mL of dichloromethane was added. The solution was transferred in a cylindrical polyethylene holder (1 cm diameter) and allowed to evaporate at room temperature. The polymeric film thus obtained was finally kept overnight under 10<sup>-2</sup> torr vacuum to remove traces of solvent.

*Characterization of BTD<sup>NMe2</sup>@PMMA.*

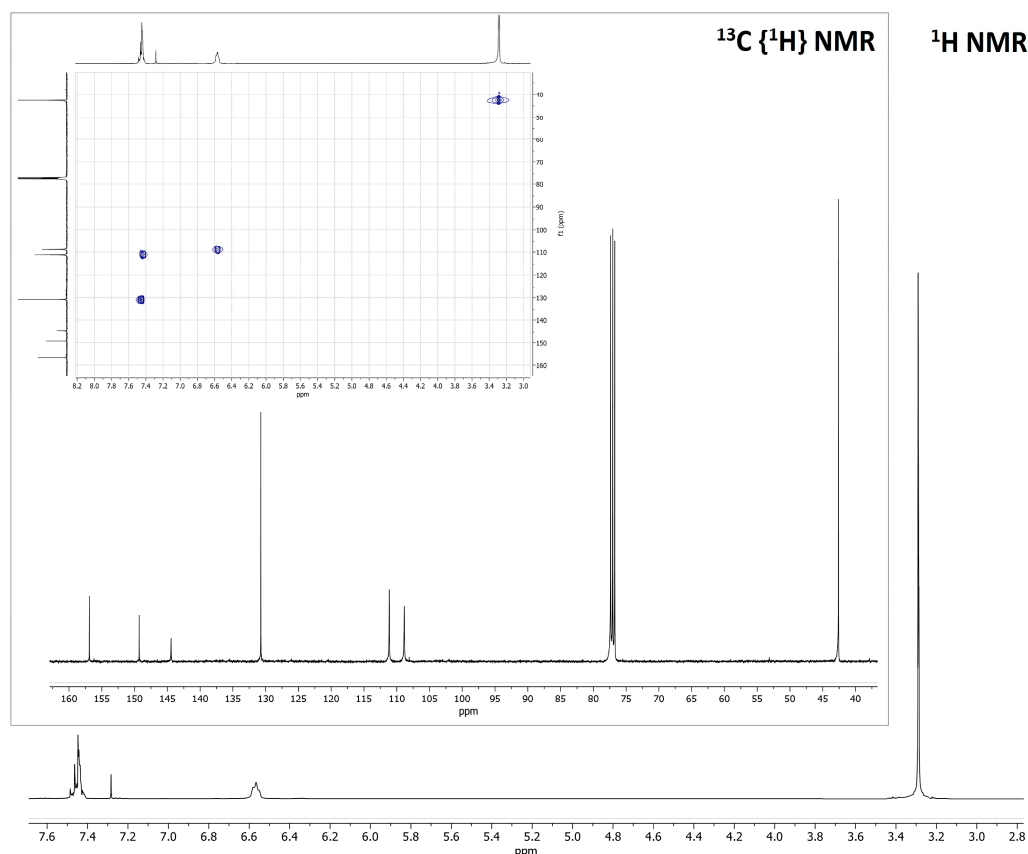
PL (solid sample,  $\lambda_{excitation}$  = 400 nm, nm): 606. PLE (solid sample,  $\lambda_{emission}$  = 605 nm, nm): <560.

### 3. Results and Discussion

The synthetic route here proposed for BTD<sup>NMe2</sup> starts with the nitration of the 2,1,3-benzothiadiazole heterocycle, followed by reduction of the nitro group and subsequent methylation with methyl iodide, as depicted in Scheme 1. As observable from the <sup>1</sup>H, <sup>13</sup>C {<sup>1</sup>H} and <sup>1</sup>H-<sup>13</sup>C HSQC NMR reported in Figure 1, the methyl groups are associated with a singlet at 3.29 ppm (<sup>13</sup>C resonance at 42.59 ppm), while the aromatic protons of the heterocycle resonate in the 7.50–6.50 range (<sup>13</sup>C resonances at 130.73, 111.13 and 108.85 ppm). The signals attributable to the three ipso-carbons can be detected, respectively, at 144.43, 149.28 and 156.90 ppm.



**Scheme 1.** Synthesis of *N,N*-dimethyl-4-amino-2,1,3-benzothiadiazole, BTD<sup>NMe2</sup>.



**Figure 1.**  $^1\text{H}$  NMR spectrum of  $\text{BTD}^{\text{NMe}_2}$ . Inset:  $^{13}\text{C}\{^1\text{H}\}$  NMR and  $^1\text{H}$ - $^{13}\text{C}$  HSQC in  $\text{CDCl}_3$  at 298 K.  $\text{CDCl}_3$ , 298 K.

The compound was isolated as a dark red oil that exhibited intriguing luminescent properties once dissolved in common organic solvents (see Figure 2). The pure oil itself did not display appreciable emissions probably because of concentration quenching. The evident solvatochromism was investigated considering four solvents characterized by different dielectric constants  $\epsilon$  (*n*-hexane, dichloromethane, acetone, and acetonitrile). The absorption and emission spectra are shown in Figure 2. The selected properties of the solvents, including the orientation polarizability  $\Delta f$  (see Equation (2)), are summarized in Table 1. The table also reports the absorption and emission maxima of  $\text{BTD}^{\text{NMe}_2}$ , Stokes shifts  $\tilde{\nu}_A - \tilde{\nu}_F$  and  $\Phi_f$  values, calculated accordingly to Equation (1).

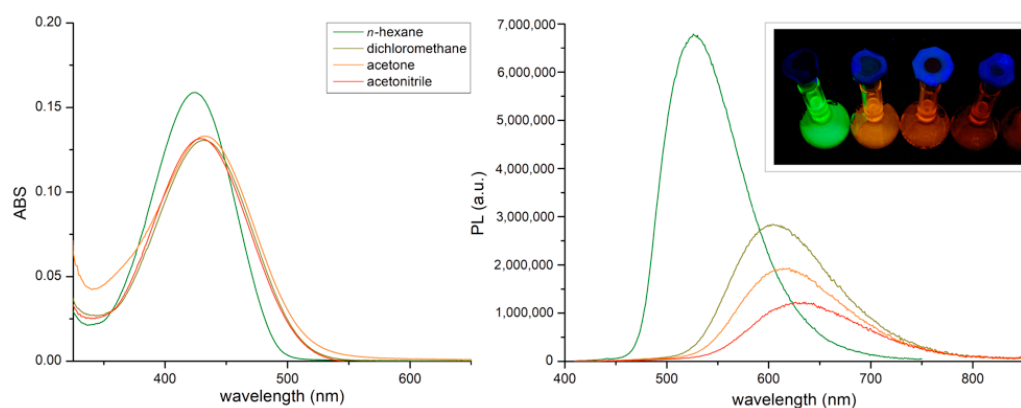
$$\Delta f = (\epsilon - 1)(2\epsilon + 1)^{-1} - (n^2 - 1)(2n^2 + 1)^{-1} \quad (2)$$

**Table 1.** Fluorescence data of  $\text{BTD}^{\text{NMe}_2}$  in different solvents.

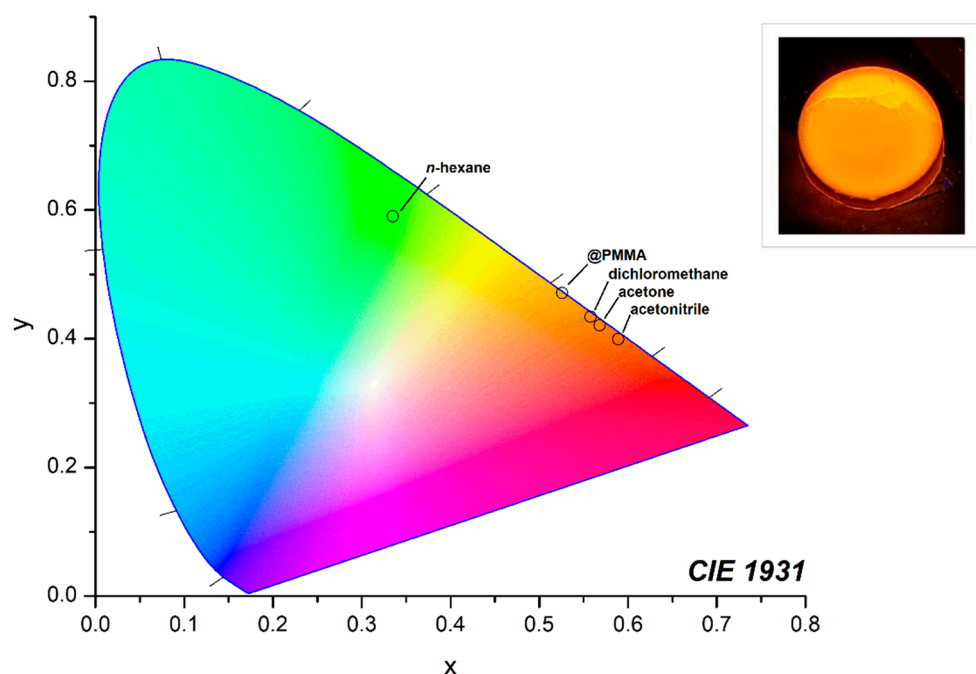
Solvent	$\epsilon$	$n$	ABS Max (nm) <sup>a</sup>	PL Max (nm) <sup>b</sup>	$\tilde{\nu}_A - \tilde{\nu}_F$ ( $\text{cm}^{-1}$ )	$\Phi_f$ (%) <sup>c</sup>	$\Delta f$
<i>n</i> -hexane	1.9	1.375	424	526	4559	52	0.001
Dichloromethane	8.9	1.424	432	604	6613	41	0.217
Acetone	20.7	1.359	433	616	6872	23	0.284
Acetonitrile	37.5	1.479	430	630	7448	16	0.305

<sup>a</sup> 298 K. <sup>b</sup>  $\lambda_{\text{excitation}} = 390$  nm, 298 K. <sup>c</sup> Data obtained using a solution of anthracene in ethanol as standard ( $\Phi_f = 27\%$ ) [49].

As presented in Figure 2 and Table 1, the solvents characterized by higher  $\epsilon$  values determine a bathochromic shift of the emission maxima in solution together with an increase in the Stokes shift, which varies from  $4559\text{ cm}^{-1}$  in hexane to  $7448\text{ cm}^{-1}$  in acetonitrile (see Table 1). The greatest variations occur on changing the solvent from hexane to dichloromethane, with a shift of the emission maximum from 526 to 604 nm and a consequent increase of the Stokes shift from  $4559\text{ cm}^{-1}$  to  $6613\text{ cm}^{-1}$ . The CIE 1931 chromaticity coordinates are reported in the diagram in Figure 3, where the change of emission is observable from yellowish-green to reddish-orange on increasing the  $\epsilon$  value. The colour purity of the emission of  $\text{BTD}^{\text{NMe}_2}$  in hexane is 0.79, while it is almost unitary for the other solvents.



**Figure 2.** Absorption (left) and emission (right) spectra of  $5 \times 10^{-5}\text{ M}$  solutions of  $\text{BTD}^{\text{NMe}_2}$  in different solvents recorded at room temperature. Inset: picture of the solutions under UV light ( $\lambda_{\text{excitation}} = 365\text{ nm}$ ).

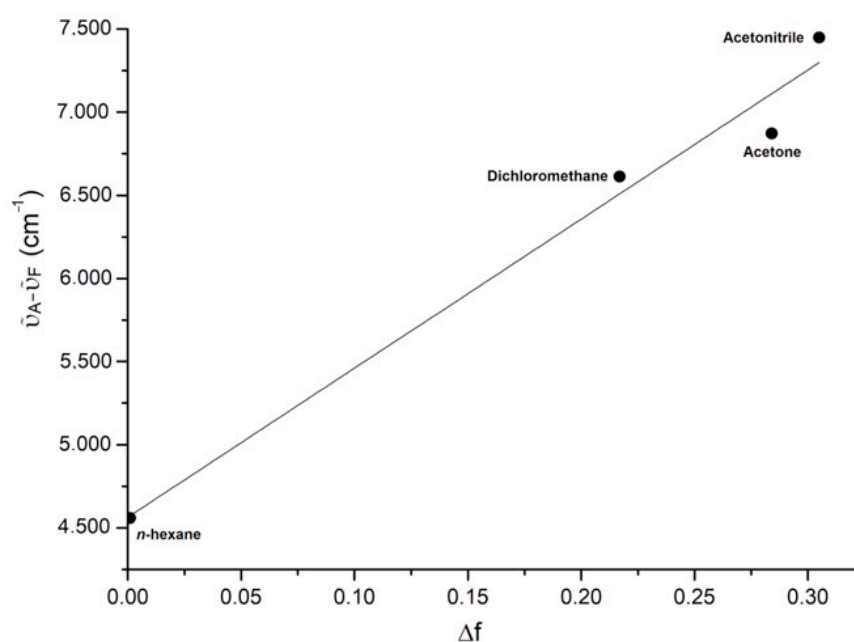


**Figure 3.** CIE 1931 chromaticity diagram of  $\text{BTD}^{\text{NMe}_2}$  in different solvents and in PMMA (*n*-hexane:  $x = 0.335$ ,  $y = 0.590$ ; dichloromethane:  $x = 0.558$ ,  $y = 0.434$ ; acetone:  $x = 0.561$ ,  $y = 0.421$ ; acetonitrile:  $x = 0.589$ ,  $y = 0.399$ ; @PMMA:  $x = 0.526$ ,  $y = 0.471$ ). Inset:  $\text{BTD}^{\text{NMe}_2}$ @PMMA excited at 365 nm.

The increase of the dielectric constant also causes a decrease in the fluorescence quantum yield, from 52% (hexane) to 16% (acetonitrile), probably attributable to the relative increase of non-radiative decay because of the red-shift of the emission.

As observable in Figure 4, the Stokes shift  $\tilde{\nu}_A - \tilde{\nu}_F$  increases roughly linearly with the orientation polarizability  $\Delta f$  (Pearson's coefficient  $R = 0.99$ ), accordingly to the Lippert–Mataga equation (Equation (3)) [50,51].  $h$  is Planck's constant,  $c$  is the speed of light in a vacuum,  $a_s$  is the radius of the cavity in which the molecule resides, and  $\mu_e$  and  $\mu_g$  are the dipole moments of the excited and ground state, respectively. The plot in Figure 4 confirms that the solvatochromic effect is related to specific solute–solvent interactions that involve the polarization [52].

$$\tilde{\nu}_A - \tilde{\nu}_F = 2 \cdot h^{-1} c^{-1} \cdot (\mu_e - \mu_g)^2 \cdot a_s^{-3} \cdot \Delta f + \text{constant} \quad (3)$$



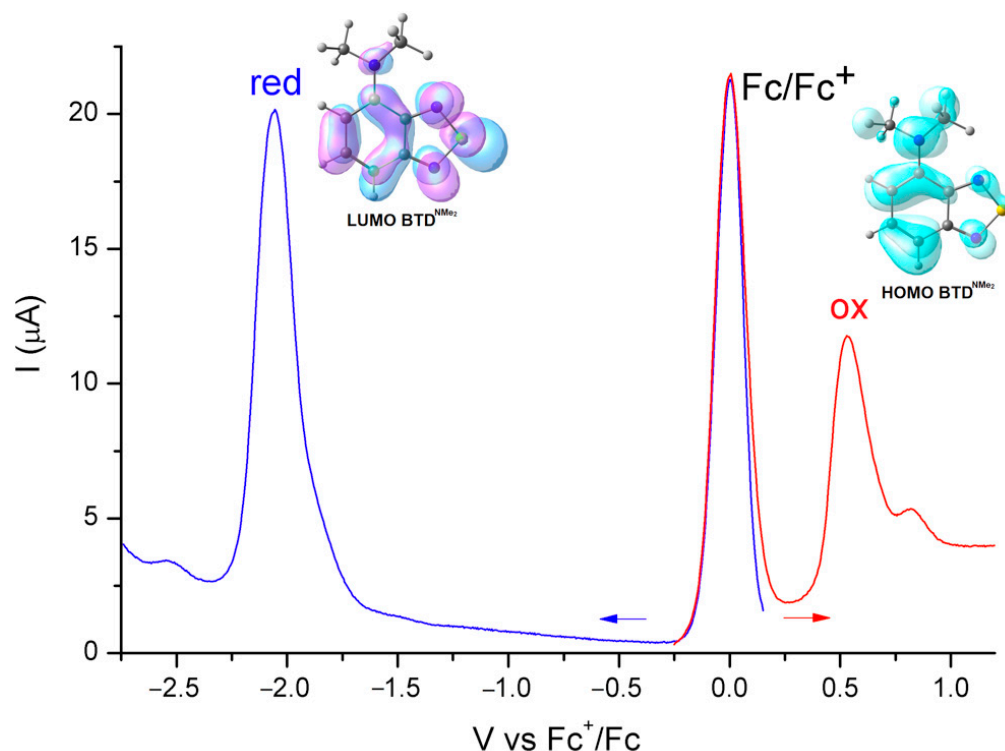
**Figure 4.** Lippert–Mataga plot.

The radius obtained from the C-PCM/DFT optimization of the structure of  $\text{BTD}^{\text{NMe}_2}$  is 3.92 Å. Based on Equation (3), the increase of dipole moment from the ground to the excited state is about 7 D.

The luminescent properties of  $\text{BTD}^{\text{NMe}_2}$  were maintained after encapsulation in the PMMA matrix. The emission falls in the orange region of the CIE diagram with unitary colour purity, as observable in the CIE 1931 chromaticity diagram and the picture reported as an inset in Figure 3.

The photoluminescent properties were justified by means of electrochemical measurements and DFT calculations. As observable from the square wave voltammetry reported in Figure 5, the HOMO–LUMO gap can be estimated at around 2.5 eV, considering the irreversible oxidation and reduction processes. Such an outcome is in agreement with the onset of the absorption spectrum using acetonitrile as solvent. The TD-DFT calculations confirm that the lowest energy transition occurs between HOMO and LUMO, which are the  $\pi$  and  $\pi^*$  frontier molecular orbitals mostly localized on the benzothiadiazole skeleton, with a contribution from both the molecular orbitals of the *N,N*-dimethylamino moiety (Figure 5).





**Figure 5.** Square wave voltammetry of  $\text{BTD}^{\text{NMe}_2}$  ( $\text{CH}_3\text{CN}/\text{LiClO}_4$ , ferrocene as internal reference, blue line: reduction, red line: oxidation) and frontier molecular orbitals (surface isovalue = 0.03 a.u.).

#### 4. Conclusions

*N,N*-Dimethyl-4-amino-2,1,3-benzothiadiazole ( $\text{BTD}^{\text{NMe}_2}$ ) was prepared from 2,1,3-benzothiadiazole in a three-step synthetic path that involved nitration, subsequent reduction and methylation. The compound was fully characterized by means of nuclear magnetic resonance (NMR) and infrared spectroscopy. The compound was revealed to be highly fluorescent and characterized by a noticeable solvatochromism. The emission features rationalized based on electrochemical measurements and DFT calculations were maintained once embedded in the poly(methyl methacrylate). The photoluminescence properties exhibited by the  $\text{BTD}^{\text{NMe}_2}$  make it a suitable candidate for advanced technology applications, and further functionalizations are currently under investigation.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/ecsoc-25-11658/s1>.

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

**Funding:** This research was funded by Università Ca' Foscari Venezia, Bando Spin 2018, D. R. 1065/2018 prot. 67416.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** Data is contained within the article.

**Acknowledgments:** Università Ca' Foscari Venezia is gratefully acknowledged for financial support (Bando Spin 2018, D. R. 1065/2018 prot. 67416). We acknowledge CINECA (COLUMN and COLUMN21 projects) for the availability of high-performance computing resources.

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

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