

Synthesis and photo-electro-thermal characterization of non-symmetrical 4,7-dibromobenzo[*c*][1,2,5]thiadiazole derivatives

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## 1

|    | Journal Pre-proof   |  |  |  |  |  |  |  |
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| 1  | Synthesis and photo-electro-thermal characterization of non-symmetrical   |  |  |  |  |  |  |  |
| 2  | 4,7-dibromobenzo[c][1,2,5]thiadiazole derivatives   |  |  |  |  |  |  |  |
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| 20 |   |  |  |  |  |  |  |  |
| 21 | Abstract  |  |  |  |  |  |  |  |
| 22 | This work describes the synthesis of new fluorophores based on non-symmetric                                      |  |  |  |  |  |  |  |
| 23 | 4,7-dibromobenzo[c][1,2,5]thiadiazole derivatives with benzene ethynyl  |  |  |  |  |  |  |  |
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25 were obtained using the Sonogashira cross-coupling reaction and produced

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tetrazole and propargyl carbazole as terminal groups. The new compounds

good yields. The benzothiadiazole derivatives presented absorption in the 26 27 ultraviolet-visible region (391-400 nm) ascribed to spin and symmetry allowed electronic transitions  ${}^{1}\pi\pi^{*}$ . The main fluorescence emission located at 460-500 28 29 nm was observed with solvatochromism up to 40 nm, indicating higher electronic delocalization in the excited state. Electrochemically, the compounds 30 are electroactive in both the anodic and cathodic potential range. The 31 32 magnitude of oxidation potentials ranged from 1.54 to 1.61 V vs. NHE and reduction potentials ranged from -2.00 to -2.05 V vs. NHE. The HOMO and 33 34 LUMO energies were calculated using cyclic voltammetry data. HOMO energies ranged from -6.16 to -6.23 eV and EA energies ranged from -2.57 to -2.62 eV, 35 and thus, the electrochemical band gap of compounds ranged from 3.56 to 3.66 36 37 eV. Thermogravimetric analysis showed that the compounds presented good thermal stability up to 200 °C. The DFT and TD-DFT calculations were 38 performed at the B3LYP/6-31G level of theory. The results show that the dipole 39 moment of the molecules varies tremendously from the electronic ground to 40 excited state, ensuring a charge transfer character. 41

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43 Keywords: 2,1,3-benzothiadiazole, carbazole, fluorescence, solvatochromism,
44 intramolecular charge transfer

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## 46 **1. Introduction**

Photoactive compounds based on the D- $\pi$ -A- $\pi$ -D system derived from the 4,7-dibromobenzo[*c*][1,2,5]thiadiazole (BTD) motif have been extensively studied in recent years due to their photophysical and optoelectronic properties [1,2], which can be tailored according to the electronic properties of the donor

and acceptor substituents present in positions 4 and 7 of the BTD moiety [3,4]. 51 In this sense, different synthetic methodologies can be found in the literature for 52 structural modification and consequent tuning of the BTD nucleus, leading to 53 changes in its organoelectronic properties. These methodologies involve 54 Sonogashira and Suzuki cross-coupling reactions, aromatic formulation, 55 amination reactions, click reactions, and others [1]. Thus, a wide range of 56 synthetic methodologies have been presented to date regarding the different 57 applications available for these compounds, such as in organic photovoltaic 58 cells (OPVs) [5-11], organic light-emitting diodes (OLEDs) [12-14], organic field-59 effect transistors (OFETs) [15], and organic thin-film transistors (OTFTs) 60 61 [16,17].

On the other hand, there is a class of non-symmetrical BTDs that can 62 63 end the possibility of C2 symmetry [18-20]. These derivatives have been cited to be involved in very interesting applications, such as sensors for metal 64 65 detection [21], solar cells sensitized by organic dyes (DSSCs) [22], enhanced two-photon absorption cross sections [23], as well as to present a large Stokes 66 shift and high fluorescent emission [21]. In general, non-symmetrical BTD 67 68 derivatives are structurally characterized by the chemical architecture D- $\pi$ -A, allowing energy levels for the LUMO orbital above the conduction band of 69 70 semiconductors such as TiO<sub>2</sub> (~4.0 eV vs vacuum). The latter provides a driving force for these compounds to inject electrons into their conduction band [24]. 71 Despite the almost absent in the literature, studies regarding the synthesis of 72 73 non-symmetric derivatives of BTD are of great importance, since new important 74 effects in their photophysical, thermal, and electrochemical properties can be obtained by inserting new substituents into their structure. 75

Therefore, this study reports the rational synthesis of non-symmetric 76 compounds based on the 4,7-dibromobenzo[c][1,2,5]thiadiazole unit containing 77 benzene ethynyl tetrazole and propargyl carbazole as terminal groups in the D-78  $\pi$ -A- $\pi$ -D system. The carbazole unit is an important substituent in organic 79 electronics, acting as a hole-transporting moiety bonded to the electron 80 acceptor moiety BTD. The non-symmetrical structure was proposed due to the 81 82 probable increase on its polarity allowed by the intramolecular charge transfer character in this electronic system. In addition, their photophysical, thermal, and 83 84 electrochemical characterization were also evaluated and discussed.

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## 86 2. Experimental

## 87 2.1 Materials and methods

4,7-Dibromobenzo[c]-1,2,5-thiadiazole, 1-bromooctane, 1-bromodecane, 88 1-bromododecane, triphenylphosphine, copper iodide, 4-bromobenzonitrile, 2-89 90 methyl-3-butyn-2-ol, bis(triphenylphosphine)palladium(II)dichloride, and 9Hcarbazole-9-ethanol were purchased from Sigma-Aldrich. Sodium azide (NaN<sub>3</sub>) 91 was acquired from Synth. The solvents and reagents were used as received or 92 purified using standard procedures [25]. Silica Gel 60 F254 was used for thin 93 layer chromatography, and silica Gel 60 Å (70-230 mesh) was used for column 94 95 chromatography. Proton and carbon nuclear magnetic resonance (<sup>1</sup>H and <sup>13</sup>C NMR) were recorded in CDCl<sub>3</sub> at 400 and 100 MHz, respectively. The chemical 96 shifts ( $\delta$ ) are reported in parts per million (ppm) relative to TMS (0.00 ppm), and 97 98 the coupling constants J are reported in Hertz (Hz). The compounds were also characterized using Fourier transform infrared (FTIR) spectra (600-4000 cm<sup>-1</sup>) 99 recorded by a Shimadzu IR Prestige-21 spectrophotometer with a resolution of 100

4 cm<sup>-1</sup> using KBr pellets. High resolution mass spectra (HRMS) were recorded 101 on a Micromass Q-Tof spectrometer, using electrospray ionization (ESI). UV-102 103 spectra were obtained using a vis absorption Shimadzu UV-2450 spectrophotometer. Steady-state fluorescence spectra were obtained using a 104 105 Shimadzu RF-5301PC spectrofluorometer. In addition, 5.0 nm slits were used for excitation and emission. For emission spectra, the absorption maximum 106 wavelength as excitation radiation was used. The guantum yield of fluorescence 107 108 was measured at 25 °C using coumarin 153 in ethanol as the guantum yield 109 standard [26]. Excited state dynamics were performed by the acquisition of the 110 fluorescence spectra using an ISS single photon counting spectrofluorometer 111 (model PC1) in solution with  $\lambda_{exc}$ =290 nm. Fluorescence decays were acquired 112 using the time-correlated single-photon counting (TCSPC) technique and an 113 Edinburgh Analytical Instruments FL 900 spectrofluorometer with an MCP-PMT 114 Hamamatsu R3809U-50 with a pulsed light emitting diode operating at  $\lambda_{exc}$ =290 nm (model EPLED-290, pulse width 875.7 ps). The instrument response 115 function was recorded using a Ludox<sup>®</sup> sample. The emission decays were fitted 116 as exponential functions using the software FAST, as expressed in Eq. (1): 117

118

119 
$$I(t) = \sum_{i=1}^{n} A_i e^{-\frac{t}{\tau_i}}$$
, Eq. (1)

120

121 Where I(t) is the signal intensity sum of the electronic excited species weighted 122 by  $A_i$  (pre-exponential factor) and with a lifetime constant  $\tau_i$ . For all fluorescence 123 decays, 10,000 counts were accumulated in the peak channel to determine the 124 lifetime. The value of  $\chi^2$  and a visual inspection of the residuals and the

autocorrelation function were used to determine the quality of the fit. Theresiduals of all curves are presented as supplementary data.

electrochemical measurements 127 The were performed using а PalmSens3 potentiostat/galvanostat (Palm Instruments BV). Cyclic voltammetry 128 (CV) experiments were performed at a scan rate of 50 mV s<sup>-1</sup> in solutions of 129 0.01 mol·L<sup>-1</sup> tetra-*n*-butylammonium hexafluorophosphate (TBAPF<sub>6</sub>) using 130  $CH_2CI_2$  as the supporting electrolyte and the ferrocene/ferricenium (Fc/Fc<sup>+</sup>) 131 132 redox couple as an internal reference. A three-electrode cell was used, 133 comprising a glassy carbon electrode (GCE) as the working electrode, a platinum wire as the counter electrode, and an Ag/Ag<sup>+</sup> electrode (0.01 M AgNO<sub>3</sub> 134 in acetonitrile) as the reference. Before each measurement, the cell was 135 deoxygenated by purging with argon. The thermal stability of compounds was 136 137 investigated using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Thermogravimetric measurements were performed using a 138 TG 50 Shimadzu thermal analyzer with a heating rate of 10 °C min<sup>-1</sup> from 25 to 139 140 900 °C under a nitrogen gas atmosphere. DSC analysis were performed using a Netzsch 3500 Sirius with a heating rate of 10 °C·min<sup>-1</sup> from 25 to 200 °C under 141 a nitrogen gas atmosphere. 142

143 Calculations of the electronic ground and excited state geometries, 144 frontier molecular orbitals (HOMO/LUMO), and vertical transitions were 145 performed using density functional theory and its time-dependent counterpart 146 (DFT/TDDFT) methods using B3LYP and 6-31G basis sets in ORCA 4.0 [27,28] 147 and Avogadro 1.2 software [29]. The ground state structure was further 148 optimized using B3LYP with D3BJ correction, from which the frontier molecular

orbitals (HOMO/LUMO) were extracted, along with the employment of CAM-B3LYP-D3BJ for obtention of the vertical transitions.

151

152 2.2 Synthesis

153 2.2.1 Synthesis of 9-(prop-2-yn-1-yl)-9H-carbazole 1

Carbazole derivative 1 was prepared as previously described in the 154 literature [30]. Initially, in a round-bottom flask, a mixture of carbazole (1.0 g, 6.0 155 mmol) and potassium hydroxide (0.67 g, 12.0 mmol) in DMF (15 mL) was 156 prepared under stirring in an ice bath. After 5 min, propargyl bromide (1.42 g, 157 12.0 mmol) was slowly added; the final mixture was stirred for 24 h at 25 °C. 158 After this period, the solvent was concentrated under vacuum and the crude 159 mixture was adsorbed on silica gel and purified by column chromatography 160 161 using 2% ethyl acetate in hexane (v/v) as an eluent.

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163 *9-(Prop-2-yn-1-yl)-9H-carbazole* **1**, white solid, yield 95%, mp 123-124 °C. FTIR 164 (NaCl) cm<sup>-1</sup>: 3263, 3040, 2928, 2848, 2117, 1454. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) 165 ppm: 8.15 (2H, d, J = 8.0 Hz), 7.73 (4H, m), 7.32 (2H, m), 5.06 (2H, d, J = 4.0166 Hz), 2.29 (1H, t, J = 4.0 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) ppm: 139.9, 125.9, 167 123.3, 120.4, 119.6, 108.9, 77.2, 72.2, 32.3. HRMS (ESI) found: [M+H]<sup>+</sup> 168 206.0983; molecular formula C<sub>15</sub>H<sub>12</sub>N requires [M+H]<sup>+</sup> 206.0970.

169

170 2.2.2 Synthesis of 4-(3-(9H-carbazol-9-yl)prop-1-yn-1-yl)-7-

171 bromobenzo[c][1,2,5]thiadiazole 3

Dichloromethane (20 mL) and triethylamine (5 mL) previously degassed with argon for 15 min were added to a round-bottom flask. Then, compound **2** 

174 (0.250 g, 0.85 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.03 g, 0.042 mmol), and Cul (3.8 mg, 0.02 mmol) were added and stirred at 60 °C for 15 min. Next, compound 1 (0.087 g, 175 176 0.42 mmol) was added to the mixture, and the reaction was maintained under an argon atmosphere for 3 h at 60 °C. After this period, the reaction mixture 177 178 was treated with 50 mL of an NH<sub>4</sub>Cl saturated solution and extracted with dichloromethane (3 x 50 mL), and the combined organic layers were dried 179 (MgSO<sub>4</sub>) and concentrated under vacuum. The crude was purified by column 180 181 chromatography on silica gel using hexane/dichloromethane 95:5 as an eluent.

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4-(3-(9H-Carbazol-9-yl)prop-1-yn-1-yl)-7-bromobenzo[c][1,2,5]thiadiazole 183 3, yellow solid, yield 51%, mp 197-198 °C. FTIR (NaCl) cm<sup>-1</sup>: 3012, 2954, 2814, 184 185 1620, 1486. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) ppm: 8.14 (2H, d, J = 8.0 Hz), 7.73 (1H, 186 d, J = 8.0 Hz), 7.64 (2H, d, J = 8.0 Hz), 7.54 (2H, m), 7.45 (1H, d, J = 8.0 Hz), 7.31 (2H, m), 5.44 (2H, s). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) ppm: 154.1, 152.9, 187 188 139.9, 133.6, 131.7, 126.0, 123.3, 120.5, 119.6, 115.5, 115.2, 108.9, 90.8, 79.2, 189 33.5. HRMS (ESI) found:  $[M+H]^+$  418.0001; molecular formula C<sub>21</sub>H<sub>1</sub>3BrN<sub>3</sub>S 190 requires [M+H]<sup>+</sup> 418.0014.

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## 192 2.2.3 General procedure for the synthesis of non-symmetrical BTDs **5a-c**

Dichloromethane (30 mL) and triethylamine (5 mL) previously degassed with argon for 15 min were added to a round-bottom flask. Then, compound **3** (0.1 g, 0.23 mmol),  $Pd(PPh_3)_2Cl_2$  (0.016 g, 0.023 mmol), and Cul (0.002 g, 0.023 mmol) were added and stirred at 60 °C for 15 min. Next, compound **4a** (0.065 g, 0.23 mol) was added to the mixture, and the reaction was maintained under an argon atmosphere for 2 h at 60 °C. After this period, the reaction

mixture was treated with 50 mL of an NH<sub>4</sub>Cl saturated solution and extracted with dichloromethane (3 x 50 mL), and the combined organic layers were dried (MgSO<sub>4</sub>) and concentrated under vacuum. The crude was purified by column chromatography on silica gel using hexane/dichloromethane 1:1 (v/v), as an eluent. The same procedure was used for the synthesis of compounds **5b-c**.

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4-(3-(9H-Carbazol-9-yl)prop-1-yn-1-yl)-7-(1-octanetetrazole-4-ethynylbenzene)-205 206 2,1,3-benzothiadiazole 5a, yellow solid, yield 47%, mp 147-151 °C. FTIR (NaCl) cm<sup>-1</sup>: 3020, 2919, 2840, 2201, 1442. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) ppm: 8.20 (2H, 207 d, J = 8.0 Hz), 8.15 (2H, d, J = 8.0 Hz), 7.78 (2H, d, J = 8.0 Hz), 7.70 (1H, d, J = 208 8.0 Hz), 7.65 (2H, d, J = 8.0 Hz), 7.55 (3H, m), 7.31 (2H, m), 5.48 (2H, s), 4.67 209 (2H, t, J = 8.0 Hz), 2.08 (2H, m), 1.28 (10H, m), 0.90 (3H, t, J = 8.0 Hz).210 211 NMR (CDCl<sub>3</sub>, 100 MHz) ppm: 164.3, 154.3, 154.1, 139.9, 133.2, 132.5, 128.0, 126.7, 126.0, 124.2, 123.3, 120.4, 119.6, 117.3, 116.3, 108.9, 97.0, 91.5, 86.6, 212 213 79.8, 53.3, 33.5, 31.7, 29.7, 29.4, 29.0, 28.8, 26.3, 22.6, 14.0. HRMS (ESI) 214 found: [M+H]<sup>+</sup> 620.2584; molecular formula C<sub>38</sub>H<sub>34</sub>N<sub>7</sub>S requires [M+H]<sup>+</sup> 215 620.2596.

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217 4-(3-(9H-Carbazol-9-yl)prop-1-yn-1-yl)-7-(1-decanetetrazole-4-ethynylbenzene)-218 2,1,3-benzothiadiazole **5b**, yellow solid, yield 40%, mp 144-149 °C. FTIR (NaCl) 219 cm<sup>-1</sup>: 3010, 2916, 2842, 2209, 1455. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) ppm: 8.20 (2H, 220 d, *J* = 8.0 Hz), 8.15 (2H, d, *J* = 8.0 Hz), 7.78 (2H, d, *J* = 8.0 Hz), 7.71 (1H, d, *J* = 221 8.0 Hz), 7.67 (1H, d, *J* = 8.0 Hz), 7.57 (3H, m), 7.32 (3H, m), 5.48 (2H, s), 4.67 222 (2H, t, *J* = 6.0 Hz), 2.08 (2H, m), 1.28 (14H, m), 0.90 (3H, t, *J* = 8.0 Hz). <sup>13</sup>C 223 NMR (CDCl<sub>3</sub>, 100 MHz) ppm: 164.3, 154.3, 154.1, 139.9, 133.2, 132.5, 132.4,

| 224 | 128.0, 126.7, 126.0, 124.2, 123.3, 120.5, 119.6, 117.3, 116.3, 108.9, 97.0, 91.5,   |
|-----|---|
| 225 | 86.6, 79.8, 53.3, 33.5, 31.8, 29.7, 29.4, 29.3, 29.2, 28.9, 26.3, 22.6, 14.1.       |
| 226 | HRMS (ESI) found: $[M+H]^+$ 648.2900; molecular formula $C_{40}H_{38}N_7S$ requires |
| 227 | [M+H] <sup>+</sup> 648.2909.  |

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229 4-(3-(9H-Carbazol-9-yl)prop-1-yn-1-yl)-7-(1-dodecanetetrazole-4-

ethynylbenzene)-2,1,3-benzothiadiazole 5c, yellow solid, yield 41%, mp 142-230 231 146 °C. FTIR (NaCl) cm<sup>-1</sup>: 3015, 2918, 2849, 2209, 1459, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 232 MHz) ppm: 8.20 (2H, d, J = 8.0 Hz), 8.15 (2H, d, J = 8.0 Hz), 7.78 (2H, d, J = 8.0 Hz), 7.71 (1H, d, J = 8.0 Hz), 7.66 (2H, d, J = 8.0 Hz), 7.55 (3H, m), 7.32 233 (2H, m), 5.48 (2H, s), 4.67 (2H, t, *J* = 6.0 Hz), 2.08 (2H, m), 1.28 (18H, m), 0.90 234 (3H, t, J = 8.0 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) ppm: 164.3, 154.3, 154.1, 139.9, 235 236 133.2, 132.5, 132.4, 128.0, 126.7, 126.0, 124.2, 123.3, 120.5, 119.6, 117.3, 116.3, 108.9, 97.0, 91.5, 86.6, 79.8, 53.3, 33.5, 31.9, 29.7, 29.6, 29.5, 29.4, 237 238 29.3, 28.9, 22.7, 14.1. HRMS (ESI) found: [M+H]<sup>+</sup> 676.3251; molecular formula 239  $C_{42}H_{42}N_7S$  requires  $[M+H]^+$  676.3222.

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- 241 3. Results and discussion
- 242 3.1 Synthesis

243 In order to obtain the desired non-symmetrical compounds **5a-c**, the side groups carbazole 1 [30] and the tetrazoles 4a-c [31,32] were prepared as 244 245 previously described in the literature. In general, compound 1 was synthesized 246 through the nucleophilic substitution reaction between carbazole and propargyl 247 bromide. Potassium hydroxide was used as the base and DMF as the solvent 248 without tetrazoles 1-alkanetetrazole-4the need for heating. The

ethynylbenzenes 4a-c were obtained by the formation of the tetrazole ring from 249 the reaction of 4-bromobenzonitrile with sodium azide and ammonium chloride 250 251 in the DMF solution to form the 5-(4-bromophenyl)tetrazole. The latter was alkylated with the respective 1-bromoalkane in the presence of potassium 252 253 acetone. forming the derivative 5-(4-bromophenyl)-2carbonate in alkanetetrazole, which reacted with the 2-methyl-3-butyne-2-ol using the 254 Sonogashira coupling reaction under an inert argon atmosphere to produce an 255 alcohol intermediate. The latter was unprotected when using sodium hydroxide 256 in toluene to form the terminal alkynes **4a-c**. 257

258 Compound 3 was obtained by mono-coupling between the benzothiadiazole (2) with carbazole 1 in the molar ratio 1:2 (carbazole 1: 259 benzothiadiazole 2). This step was performed according to the Sonogashira 260 261 reaction conditions using copper iodide, bis(triphenylphosphine)palladium chloride, and a dichloromethane/triethylamine mixture as the refluxing solvent 262 263 (Scheme 1). Compound 3 was purified using column chromatography and 264 obtained in moderate yields (46%). Sequentially, the non-symmetric compounds **5a-c** were synthesized by reacting equimolar amounts of compound **3** with the 265 terminal alkynes 4a-c also according to the Sonogashira reaction conditions. 266 267 The desired compounds were purified using column chromatography and 268 obtained in moderate yields (54%). Spectroscopic characterizations were performed for all intermediates and final compounds, and the results are 269 270 presented in the supplementary material.

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274 **Scheme 1**. Synthesis of non-symmetrical BTD based compounds **5a-c**, where

275 (i) and (ii) are  $CH_2CI_2$ ,  $PdCI_2(PPh_3)_2$ ,  $Cul, Et_3N$ .

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## 277 3.2 Photophysical characterization

278 The UV-vis absorption and steady-state fluorescence emission spectra were used to investigate the photophysical properties of the obtained non-279 280 symmetrical BTDs. The compounds were investigated in solutions of different organic solvents (10<sup>-6</sup> M). The relevant data are summarized in Table 1. From 281 the UV–Vis spectra of compounds **5a-c** shown in Figure 1, absorption maxima 282 located between 391-400 nm can be observed. Although changes in the solvent 283 polarity allowed a solvatochromic effect of ~8 nm, no clear tendency was 284 observed. The latter indicates that these compounds present an almost absent 285 charge transfer in the ground state. 286



288

Figure 1. UV–Vis absorption spectra in solution of non-symmetrical BTDs 5a-c
in different organic solvents [ca. 10<sup>-6</sup> M].

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The molar absorptivity coefficients were obtained using the Beer-Lambert law, and they are presented in Table 1. The Strickler–Berg relations were used to calculate the oscillator strength ( $f_e$ ) presented in Eq. (2) and the theoretical rate constant for emission ( $k_e^0$ ) presented in Eq. (3) [33]. In addition,  $k_e^0$  was used to calculate the pure radiative lifetime  $\tau^0$ , defined as  $1/k_e^0$  [34], and its values are also shown in Table 1.

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299 
$$f_e \approx 4.3 x 10^{-9} \int \varepsilon d\bar{v} \, \text{Eq.} (2)$$

301 
$$k_e^0 \approx 2.88 x 10^{-9} \bar{v}_0^2 \int \varepsilon d\bar{v} \text{ Eq. (3)}$$

The oscillator strength values at approximately 0.71-0.95 indicated highly 303 304 probable electronic transitions. In addition, the molar absorptivity coefficient values of  $\sim 10^4$  M<sup>-1</sup>·cm<sup>-1</sup>, as well as calculated radiative rate constants of  $\sim 10^8$  s<sup>-1</sup> 305 <sup>1</sup>, indicated spin- and symmetry-allowed electronic transitions, which could be 306 related to  ${}^{1}\pi\pi^{*}$  transitions. The comparable constant radiative lifetime ~10<sup>-9</sup> s 307 also indicated that absorptions populated the same excited state. The structural 308 variation of the compounds, with aliphatic chains from  $C_8$  to  $C_{12}$  in the tetrazolic 309 310 ring, was observed to not significantly influence the behavior in the ground state. In order to obtain the fluorescence emission spectra, the absorption 311 maxima wavelengths were used as excitation radiation. The obtained data are 312 313 summarized in Table 1. The respective fluorescence spectra of the non-314 symmetrical BTDs **5a-c** in different organic solvents are shown in Figure 2.

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### 316

Figure 2. Normalized steady-state fluorescence emission spectra in solution of
 non-symmetrical BTDs 5a-c in different organic solvents [ca. 10<sup>-6</sup> M].

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320 The studied compounds showed the main fluorescence emission located between 460 and 500 nm, with a relatively large Stokes shift (3836-5707 cm<sup>-1</sup>). 321 322 Changes in the solvent polarity indicated a solvatochromic effect of 21 nm (5a), 323 40 nm (5b), and 11 nm (5c). The values of the Stokes shift combined with the 324 solvatochromic effect show a relationship between the emission band and the 325 solvent polarity, indicating a small charge transfer characteristic in the excited state. The compounds showed fluorescence quantum yields below 10%, as 326 327 previously observed in similar compounds [31]. Excitation spectra were acquired in different organic solvents using the fluorescence emission maxima 328 329 as the observation wavelength (Figure 3). These data are also summarized in

Table 1. The excitation spectrum indicates the wavelengths that will induce the emission of light by the molecule from the lowest excited state in a monitored wavelength and shows the  $S_0$ - $S_1$  band. The compounds showed similar excited spectra and presented the lowest energy absorption features around 410 nm. Regarding the excited state, the profile in the excitation and emission spectra also were similar. On the other hand, the fluorescence quantum yield was higher in the compound with the shorter carbonic chain.

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339 Figure 3. Excitation spectra in solution of non-symmetrical BTDs 5a-c in

340 different organic solvents [ca. 10<sup>-6</sup> M].

**Table 1**. Photophysical data of compounds **5a-c** where  $\lambda_{abs}$  is the absorption maxima (nm),  $\varepsilon$  is the molar extinction coefficient (10<sup>4</sup> M<sup>-1</sup>·cm<sup>-1</sup>), *f* is the calculated oscillator strength,  $k_e^0$  is the calculated radiative rate constant (10<sup>8</sup> s<sup>-1</sup>),  $\tau^0$  is the calculated pure radiative lifetime (ns),  $\lambda_{em}$  and  $\lambda_{exc}$  are the emission and excitation maxima (nm),  $\Delta\lambda_{ST}$  is the Stokes shift (nm/cm<sup>-1</sup>), and QY is the fluorescence quantum yield (%).

| Compound | Solvent           | $\lambda_{abs}$ | 3    | f    | ke⁰  | τ <sup>0</sup> | $\lambda_{\text{ex}}$ | $\lambda_{em}$ | $\Delta\lambda_{ST}$ | QY   |
|----------|-------------------|-----------------|------|------|------|----------------|-----------------------|----------------|----------------------|------|
|          | 1,4-Dioxane       | 394             | 7.94 | 1.36 | 8.77 | 1.14           | 415                   | 479            | 85/4504              | 2.07 |
|          | Dichloromethane   | 400             | 5.82 | 1.04 | 6.53 | 1.53           | 417                   | 482            | 82/4253              | 3.03 |
| 5a       | Methanol          | 393             | 6.73 | 1.20 | 7.75 | 1.29           | 410                   | 491            | 98/5079              | 2.01 |
|          | Acetonitrile      | 392             | 8.95 | 1.62 | 10.5 | 0.94           | 411                   | 480            | 88/4677              | 3.00 |
|          | Dimethylsulfoxide | 395             | 7.75 | 1.45 | 9.30 | 1.08           | 412                   | 470            | 75/4040              | 2.69 |
|          | 1,4-Dioxane       | 392             | 4.35 | 0.82 | 5.32 | 1.88           | 422                   | 476            | 84/4502              | 5.44 |
|          | Dichloromethane   | 398             | 4.48 | 0.28 | 1.74 | 5.74           | 426                   | 490            | 92/4717              | 2.05 |
| 5b       | Methanol          | 389             | 4.58 | 0.85 | 5.63 | 1.78           | 420                   | 500            | 111/5707             | 1.56 |
|          | Acetonitrile      | 396             | 5.75 | 1.10 | 7.03 | 1.42           | 431                   | 493            | 97/4969              | 2.83 |
|          | Dimethylsulfoxide | 391             | 7.00 | 0.28 | 1.81 | 5.54           | 421                   | 460            | 69/3836              | 2.12 |
|          | 1,4-Dioxane       | 394             | 7.91 | 0.94 | 6.04 | 1.66           | 416                   | 478            | 84/4460              | 3.90 |
|          | Dichloromethane   | 398             | 3.74 | 0.71 | 4.49 | 2.23           | 415                   | 484            | 86/4464              | 1.91 |
| 5c       | Methanol          | 394             | 4.40 | 0.75 | 4.83 | 2.07           | 413                   | 489            | 95/4931              | 1.47 |
|          | Acetonitrile      | 395             | 7.43 | 0.95 | 6.06 | 1.65           | 429                   | 484            | 89/4655              | 1.36 |
|          | Dimethylsulfoxide | 391             | 5.42 | 0.88 | 5.73 | 1.75           | 414                   | 487            | 96/5042              | 1.58 |

Due to the presence of a carbazole moiety in the BTD structures, the excited state photophysics of the studied compounds was thoroughly investigated, where their emission spectra were also acquired by exciting them at  $\lambda_{exc}$ =290 nm. By doing so, an emission band around  $\lambda_{em}$ =350 nm was also observed, indicating that the systems are not completely conjugated (Figure 4).



**Figure 4.** (a-c) Steady-state fluorescence emission spectra in solution of nonsymmetrical BTDs **5a-c**, respectively, in different organic solvents [ca. 10<sup>-6</sup> M] under an excitation of 290 nm. (d) PL spectrum of 9*H*-carbazole-9-ethanol (Aldrich) is also presented at an optical density ~0.1 to simulate the carbazole motif photophysics.

Hence, to further understand the deactivation dynamics in these compounds, the fluorescence decays were determined using the TCSPC technique by exciting the molecules at  $\lambda_{exc}$ =290 nm with a pulsed excitation source. Figure 5 presents the fluorescence decay curves of the non-symmetrical BTD **5b**. The additional compounds showed similar behavior and are presented as supplementary data. The relevant data is summarized in Table 2.



**Figure 5.** Fluorescence decays and respective exponential fit for the nonsymmetrical BTD **5b** at the (a) short and (b) long emission wavelengths.

In general, three different lifetime constants were obtained for the three compounds in all studied solvents. The decays obtained at the emission band from the carbazole unit were adjusted as mono and biexponential functions, with the longest component belonging to the carbazole unit. This assignment was performed after comparing the decays with the fluorescence lifetime of 9*H*-

carbazole-9-ethanol in 1,4-dioxane ( $\tau_2$ =10.00 ns) (data not shown, see supplementary material). The curves acquired at the red-shifted bands were only adjusted by biexponential decays, and the shortest components were always similar to the ones found for the decays acquired at  $\lambda_{em}$ =350 nm, indicating spectral overlap between the two emission bands. Finally, the other two lifetime constants were assigned based on the results from theoretical predictions. The shortest component found on both sets of decays were attributed to the benzothiadiazole moiety ( $\tau_1$ ), because it also emits in the blue region of the electromagnetic spectrum [2,35], and the longest one observed in the decays of the red-shifted bands were attributed to the conjugated system benzothiadiazole-tetrazole ( $\tau_3$ ). The latter is due to the intramolecular charge transfer process, as demonstrated by theoretical predictions. The obtention of bipolar host materials presenting intramolecular charge transfer is an interesting strategy for improvement of OLED devices [36], allowing these compounds to be envisaged for such technological application.

**Table 2**. Time-resolved photophysical data of compounds **5a-c** and 9*H*-carbazole-9-ethanol, so-called carbazole, where  $\lambda_{em}$  is the emission maxima (nm) at the excitation wavelength of 290 nm,  $\tau$  is the experimental fluorescence lifetime (ns), A is the respective pre-exponential factor, and  $\chi^2$  indicates the quality of the fit.

| Compound  | Solvent           | $\lambda_{em}$ | ${\tau_1}^a$ | <b>A</b> <sub>1</sub> | $\tau_2^{b}$ | <b>A</b> <sub>2</sub> | $\tau_3^{c}$ | <b>A</b> <sub>3</sub> | χ²    |
|-----------|-------------------|----------------|--------------|-----------------------|--------------|-----------------------|--------------|-----------------------|-------|
|           | 1 4 Dievono       | 350            | 1.36         | 18                    | 9.46         | 82                    | -            | -                     | 1.089 |
|           | 1,4-Di0xane       | 479            | 1.88         | 77                    | -            | -                     | 4.06         | 23                    | 1.014 |
|           | Methanol          | 350            | -            | -                     | 10.2         | 100                   | -            | -                     | 1.098 |
| 50        |                   | 476            | 4.15         | 50                    | -            | -                     | 6.67         | 50                    | 1.053 |
| Ja        | Acetonitrile      | 350            | 3.05         | 12                    | 7.17         | 88                    | -            | -                     | 1.151 |
|           |                   | 456            | 2.99         | 41                    |              | -                     | 4.87         | 59                    | 1.188 |
|           | Dimethylsulfoxide | 350            | -            | -                     | 11.1         | 100                   | -            | -                     | 1.113 |
|           | Dimetryisuitoxide | 476            | 2.03         | 68                    | -            | -                     | 7.29         | 32                    | 1.168 |
|           | 1 1-Dioxane       | 350            |              | -                     | 9.17         | 100                   | -            | -                     | 1.316 |
|           | 1,4-Dioxane       | 462            | 5.50         | 64                    | -            | -                     | 5.88         | 36                    | 1.149 |
|           | Methanol          | 350            | -            | -                     | 11.4         | 100                   | -            | -                     | 1.194 |
| 5h        |                   | 450            | 2.87         | 24                    | -            | -                     | 4.86         | 76                    | 1.168 |
| 50        | Acetonitrile      | 350            | 2.22         | 18                    | 9.18         | 82                    | -            | -                     | 1.470 |
|           |                   | 480            | 2.63         | 32                    | -            | -                     | 5.32         | 68                    | 1.114 |
|           | Dimothylsulfoxido | 350            | -            | -                     | 10.9         | 100                   | -            | -                     | 1.117 |
|           | Dimetryisulloxide | 481            | 2.12         | 70                    |              |                       | 8.17         | 30                    | 1.307 |
|           | 1 1-Dioxane       | 350            | -            | -                     | 11.6         | 100                   | -            | -                     | 1.240 |
|           |                   | 462            | 4.00         | 67                    | -            | -                     | 9.11         | 33                    | 1.057 |
|           | Methanol          | 350            | -            | -                     | 12.00        | 100                   | -            | -                     | 1.109 |
| 50        | Methanol          | 481            | 2.39         | 16                    | -            | -                     | 5.75         | 84                    | 1.146 |
| 50        | Acetonitrile      | 350            | -            | -                     | 8.12         | 100                   | -            | -                     | 1.196 |
|           | Acctomatic        | 451            | 3.57         | 90                    | -            | -                     | 7.20         | 10                    | 0.984 |
|           | Dimethylsulfoxide | 350            |              | -                     | 10.4         | 100                   | -            | -                     | 1.175 |
|           |                   | 481            | 1.98         | 77                    | -            | -                     | 6.95         | 23                    | 1.154 |
| Carbazole | 1,4-Dioxane       | 357            | -            | -                     | 10.0         | 100                   | -            | -                     | 1.180 |

<sup>a</sup>BTD fluorophore; <sup>b</sup>Carbazole fluorophore; <sup>c</sup>BTD-tetrazole fluorophore

## 3.3 Theoretical calculations

The structure of the chromophore was optimized by DFT under vacuum using a methyl group as the substituent on the alkyl chains, because it will not affect the main molecular electronic structure (Figure 6). The ground state geometry presents a dihedral angle of 179.6° formed on the saturated carbon between carbazole and the alkyne unit and a dipole moment of  $\mu_g = 4.19$  Debye.



**Figure 6**. (a) Top and (b) lateral view of the optimized geometry at the ground state of a non-symmetrical BTD used as a model of the synthesized compounds **5a-c**.

Despite the presence of this saturated carbon, predictions of frontier molecular orbitals indicated a charge transfer character from the carbazole unit toward the benzothiadiazole (HOMO  $\rightarrow$  LUMO transition). Specifically, the conjugated framework evolving from the tetrazolic moiety and benzothiadiazole moieties became clear after the analysis of other sets of molecular orbitals (Figure 7). The charge transfer character was finally concluded from

optimization of the excited state structure (TD-DFT), which possess a dipole moment of  $\mu_e = 25.0$  Debye ( $\Delta \mu = 20.81$  Debye). Considering the predicted electronic transitions, vertical excitations of  $\lambda_{abs} = 392$  nm and 280 nm with biggest oscillator strengths (*f*=0.86 and 0.68, respectively) were identified, matching with experimental values of carbazole and benzothiazole-tetrazole moieties.



**Figure 7**. HOMO (left) and LUMO (right) orbitals of a non-symmetrical BTD used as a model of the synthesized compounds **5a-c**.

## 3.4 Electrochemical characterization

Figure 8 revealed that compounds **5a-c** are electrochemically active in the studied potential range. At more negative potential values, the compounds exhibit a well-defined reduction process with an onset potential of -2.00 to -2.05 V *vs.* Ag/Ag<sup>+</sup>, which may be related to the formation of anionic radicals [31]. The scans performed at more positive potential values showed an irreversible oxidation process with an onset potential of 1.54 to 1.61 V *vs.* Ag/Ag<sup>+</sup> due to the

electrochemical formation of the cation radical. The HOMO and LUMO energy levels of these compounds were determined by the ionization potential (IP) and electron affinity (EA), respectively, which could be correlated with electrochemical processes accessed by CV, where the potentials were standardized with a Fc/Fc<sup>+</sup> couple. The IP and EA values were calculated using the empirical Eqs. (4) and (5) [37]:

$$IP = -(E_{oxi}^{onset} + 4.44) \text{ eV, Eq. (4)}$$
$$EA = -(E_{red}^{onset} + 4.44) \text{ eV, Eq. (5)}$$

where  $E_{oxi}^{onset} \overline{E}_{oxi}^{onset}$  and  $E_{red}^{onset}$  represent the oxidation onset potential and reduction onset potential, respectively. The electrochemical data obtained from these calculations are summarized and compared in Table 3.



**Figure 8**. Cyclic voltammogram of a glassy carbon electrode in 0.1  $TBAPF_6/CH_2Cl_2$  at 50 mV·s<sup>-1</sup> of non-symmetrical BTDs **5a-c**.

**Table 3.** Electrochemical properties of non-symmetrical BTDs **5a-c**, where  $E_{oxi}^{onset} E_{oxi}^{onset}$  is the onset potential of oxidation,  $E_{red}^{onset} E_{red}^{onset}$  is the onset potential of reduction, IP (HOMO) is the ionization potential, EA (LUMO) is the electron affinity, and  $E_{gap}^{ele}$  is the electrochemical band gap.

| Baramatora                          | Non-symmetrical BTDs |       |       |  |  |  |  |  |
|-------------------------------------|----------------------|-------|-------|--|--|--|--|--|
| Farameters                          | 5a                   | 5b    | 5c    |  |  |  |  |  |
| E <sup>onset</sup> (V) <sup>a</sup> | 1.79                 | 1.72  | 1.77  |  |  |  |  |  |
| E <sup>onset</sup> (V) <sup>a</sup> | -1.87                | -1.84 | -1.82 |  |  |  |  |  |
| IP (HOMO) (eV) <sup>b</sup>         | -6.23                | -6.16 | -6.21 |  |  |  |  |  |
| EA (LUMO) (eV) <sup>c</sup>         | -2.57                | -2.60 | -2.62 |  |  |  |  |  |
| $E_{gep}^{sis}(eV)$                 | 3.66                 | 3.56  | 3.59  |  |  |  |  |  |

<sup>a</sup>versus NHE; <sup>b</sup>calculated using Eq. (3); <sup>c</sup>calculated using Eq. (4).

A comparison of the data presented in Table 1 with the electrochemical properties of non-symmetrical BTDs **5a-c** indicates that modifying the alkyl tetrazole moiety affects the band gap energies of these molecules. The different electrochemical behaviors resulting from modifying fluorophores derivatives consequently cause changes in the HOMO and LUMO values, as well as the band gaps values of the molecules, showing that the electrochemical properties have changed due to the structural variation of the compounds, with aliphatic chain C<sub>8</sub>, C<sub>10</sub>, and C<sub>12</sub> in the tetrazolic ring.

## 3.5 Thermal characterization

The DSC analyses of the of non-symmetrical BTDs **5a-c** are presented in Figures 9a-c, respectively. It can be observed that the melting temperature  $(T_m)$  during the first heating cycle was found for compound **5a** at ~145 °C ( $\Delta H_m$ = -

45.26 J·g<sup>-1</sup>) and for compound **5b** at ~65 °C ( $\Delta H_m$ = -2.21 J·g<sup>-1</sup>), which is probably related the removal of the residual solvent to (hexane/dichloromethane) at ~122 °C ( $\Delta H_m$ = -15.22 J·g<sup>-1</sup>) and ~143 °C ( $\Delta H_m$ = -42.71 J·g<sup>-1</sup>), respectively, indicating a possible polymorphism of the structure due to the presence of the solvent. For compound 5c the melting temperature during the first heating cycle was at ~128 °C ( $\Delta H_m$ = -64.66 J·g<sup>-1</sup>) [38]. During the second heating cycle, the studied compounds presented different curves with cold crystallization  $(T_{cc})$  of the amorphous materials and melting temperature (T<sub>m</sub>). T<sub>cc</sub> and T<sub>m</sub> values for compound **5a** were found at ~92 °C ( $\Delta$ H<sub>cc</sub>= 11.97  $J \cdot g^{-1}$ ) and ~113 °C ( $\Delta H_m$ = -5.23  $J \cdot g^{-1}$ ), for compound **5b** at ~76 °C ( $\Delta H_{cc}$ = 5.89  $J \cdot g^{-1}$ ) and ~112 °C ( $\Delta H_m = -4.78 J \cdot g^{-1}$ ), and for compound **5c** at ~73 °C ( $\Delta H_{cc} =$ 7.83  $J \cdot g^{-1}$ ) and ~103 °C ( $\Delta H_m$ = -3.17  $J \cdot g^{-1}$ ), respectively. Compound **5b** was the only one that presented a crystallization temperature (T<sub>cr</sub>) during cooling at ~76 °C ( $\Delta H_{cr}$ = 2.594 J·g<sup>-1</sup>), probably due to crystallization of the first crystalline phase formed (polymorphism). The changes in the values of  $T_m$  and  $\Delta H_m$  during the second heating could be related to morphological changes after recrystallization [39].



**Figure 9.** DSC curves (exo up) of non-symmetrical BTDs (a) **5a**, (b) **5b**, and (c) **5c** at a heating rate of 10 °C·min<sup>-1</sup> from 25 to 200 °C under a nitrogen gas atmosphere and (d) TGA curves with a heating rate of 10 °C·min<sup>-1</sup> from 25-900 °C under a nitrogen gas atmosphere.

The thermogravimetric curves (TGA) of the studied non-symmetrical BTDs presented three main steps of weight loss, as depicted in Figure 9d. The DTG curves are presented as supplementary material. The first step between 100 and 160 °C corresponds to the removal of water molecules. After that, the compounds start to decompose at ~200 °C. The maximum degradation temperature (T<sub>d</sub>) in the second step is located at ~280 °C and the third step at ~450 °C. These results indicate a relatively high thermal stability of the compounds [40].

## 4. Conclusions

New non-symmetric compounds composed of the 4,7-dibromobenzo [c][1,2,5]thiadiazole unit were synthesized using a multiple methodology involving the cross-coupling reaction. with moderate vields. The benzothiadiazole derivatives presented an intense band at 391-400 nm related to the electronic transitions from  $S_0 \rightarrow S_1$  and showed a  ${}^1\pi\pi^*$  character involving the HOMO and LUMO orbitals. The obtained Strickler-Berg parameters corroborate these observations. These benzothiadiazole derivatives presented single fluorescence emission band at approximately 460-500 nm. а Electrochemical studies of benzothiadiazole derivatives show that the magnitude of oxidation (1.54 to 1.61 V vs. NHE) and reduction potentials (-2.00 to -2.05 V vs. NHE) can be applied to determine HOMO and LUMO levels, respectively. The HOMO energies (-6.16 to -6.23 eV), LUMO energies (-2.57 to -2.62 eV), and band gap (3.56 to 3.66 eV) values show that these compounds have promising potential for applications in organic electroluminescent materials. The compounds presented good thermal stability up to 200 °C when investigated using TGA, and they are important for applications in DSSCs.

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## **Highlights**

- Non-symmetrical 4,7-dibromobenzo[*c*][1,2,5]thiadiazole derivatives obtained through cross-coupling reactions

- Absorption in the ultraviolet-visible region ascribed to spin and symmetry allowed  ${}^{1}\pi\pi^{*}$  electronic transitions.

- Solvatochromic effect in the excited state up to 40 nm indicating significative electronic delocalization.

- Theoretical calculations indicate remarkable variation of the dipole moment from electronic ground to excited state related to charge transfer character.

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#### **Declaration of interests**

■ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

□The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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