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New photoactive D-π-A-π-D benzothiadiazole derivative: Synthesis, thermal and photophysical properties

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ABSTRACT

A new fluorophore containing a 2,1,3-benzothiadiazole unit containing alkylated tetrazoles terminal groups as electron donors connected through a π-conjugated system of type D-π-A-π-D was synthesized and electronically and electrochemically characterized. The compound in solution has an absorption maximum in the visible region (~417 nm) due to electronic transitions of type $^1\pi\pi^*$ ($\varepsilon \sim 10^4$ M^{-1} cm^{-1}) and intense fluorescence emission ($\Phi_F \sim 0.65$) located in the blue-green region depending on the solvent used with a Stokes' shift of ca. 75 nm. Evidences of intramolecular charge transfer character in the excited state was observed from the Lippert–Mataga correlation. The AFM images of the spin-coating depositions of compound **9** using chloroform as solvent on silicon substrate showed the formation of films with clusters. AFM images of the deposition of the acrylic thermoplastic resin doped with 0.05% of **9** showed the formation of a uniform, low-roughness film. Fluorescence emission was shown to be dependent on the method used for the formation of the films.

1. Introduction

In recent years, organic compounds have been described and studied with regard to their potential applications in optoelectronic devices [1] due to the prospect of developing smaller, flexible and lower-cost devices. The market for these compounds has been growing quickly due to their incorporation in organic photovoltaic cells (OPVs) [1–8], organic light-emitting diodes (OLEDs) [1,9–12], organic field-effect transistors (OFETs) [3], organic thin film transistors (OTFTs) [1,13–17], among others [1,3,18].

Polymers, small molecules, oligomers and hybrid compounds are typically used for these applications [19]. In this context, molecular or polymeric compounds using the electron acceptor 2,1,3-benzothiadiazole as the central unit connected to electron donors have exhibited intense luminescence and low band gap values with good thermal stability [20–27]. Additionally, highly conjugated compounds are of significant interest for the construction of organic solar cells due to the potential manufacturing of doped, flexible polymeric films [28], which could be processed on a large scale. Another advantage of using π-conjugated compounds is an increase in intramolecular charge transfer and a subsequent reduction of the band gap [3,18,29], which is important for applications in electronic devices [30].

The majority of π-conjugated organic compounds applied to opto-electronic devices exhibit a structure that is characterized by Donor-(π-conjugated system)-Acceptor-(π-conjugated system)-Donor (D-π-A-π-D) due to the effective intramolecular charge transfer produced by this structure [31,32]. Various molecular groups can be used as electron-acceptor units in the construction of molecules and polymers for potential applications in opto-electronic devices. The primary acceptor groups described in the literature are benzothiadiazole [30,33–38], thiophene [39–42], benzotriazole [43–45], and quinoxaline [46]. Heterocyclic tetrazoles, conversely, are rich in electrons, are easily excited with energy in the UV–Vis region and can act as electron donors. These electrons in resonance with the π-conjugated system are attracted to the electron-acceptor moiety. The π-conjugated system between the acceptor and donor provides

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the planarity required by the system for intramolecular charge transitions.

Within this context, we synthesized and characterized a compound containing alkylated tetrazole rings as the electron-donor groups connected by a π-conjugate system to the 2,1,3-benzothiadiazole group as an electron-acceptor unit based on their electron acceptor properties and their outstanding photophysical properties, beyond their high stability on both ground and excited states.

2. Experimental

2.1. Materials and methods

All reagents and solvents were purchased from commercial suppliers and used without further purification. The solvents were dried and distilled based on procedures detailed in the literature before use. The reactions were monitored by TLC using Silica Gel 60 F254, and visualization was achieved under UV light. Detection was achieved by exposure to iodine vapors or using an sulfuric acid solution with waterproof charring. Polymeric films were prepared using the styrenic thermoplastic acrylic resin WT014 (Resicolor Indústria de Produtos Químicos Ltda). FTIR spectra were described by KBr pellets with a resolution of 4 cm^{-1} between 400 and 4000 cm^{-1} in an IR Prestige 21 device (Shimadzu). The ^1H and ^{13}C NMR spectra were recorded in DMSO-d_6, MEOD or $CDCl_3$ at 400 and 100 MHz, respectively; the chemical shifts (δ) are reported in parts per million (ppm) relative to TMS (0.00 ppm), and the coupling constants J are reported in hertz (Hz). Spectroscopic grade solvents were used in fluorescence-emission and UV–Vis absorption spectroscopy measurements. UV–Vis absorption spectra were determined using a Shimadzu UV-2450 spectrophotometer, and steady-state fluorescence spectra were measured using a Shimadzu spectrofluorometer model RF-5301PC. The quantum yield of the fluorescence (Φ_{FL}) was performed with spectroscopic grade solvents using the dilute optical methodology. Quinine sulfate (Riedel) in H_2SO_4 1 M ($\Phi_{FL} = 0.55$) was used as a quantum yield standard [47,48]. The fluorescence lifetime was determined using an EasyLife V spectrophotometer, and the decay curves were analyzed using EasyLife V software from OBB. A nonlinear least squares method was used to determine the fit of the decay rate to a sum of exponentials; the value of χ^2, and a visual inspection of the residuals and the autocorrelation function were used to determine the quality of the fit. All measurements were performed at room temperature (25 °C). Low-resolution mass spectra were recorded on a Bruker Daltonics Autoflex apparatus for MALDI and on a Waters Micromass ZQ spectrometer for ESI/ApCI-ITD (Esquire 3000 + Bruker Daltonics).

Electrochemical measurements were performed with a Biologic potentiostat (model SP200). To investigate the photodecomposition of the materials, an 8W low-pressure mercury lamp from G-LIGHT (LT5 8W GER G13) and a UV camera were used. Studies of the thermal properties of the intermediate and final products were determined using a Shimadzu thermogravimetric analyzer (model TGA50) in an inert atmosphere (N_2) with a flow of 10 mL min^{-1} and a heating rate of 10 °C min^{-1}. The films were prepared by spin coating under vacuum using a Glove Box MBRAUN, model MB 200B with silicon plates as substrates. To study the morphologies of the materials, a Shimadzu atomic force microscope (model SPM-9700) was used.

2.2. Synthesis

2.2.1. 5-(4-bromophenyl)tetrazole **(2)**

A total of 5.05 g (27.74 mmol) of 4-bromobenzonitrile **(1)**, 28 mL of *N,N*-dimethylformamide, 9.05 g (169.2 mmol) of ammonium chloride and 11.3 g (173.8 mmol) of sodium azide were added to a 250 mL, two-neck, round-bottom flask. The reaction mixture was kept in a 12 h reflux and accompanied by TLC using a mixture of ethyl acetate and toluene (5:1 v/v) as an eluent. After this period, the temperature was lowered to 25 °C, and the mixture was poured into water and ice to allow precipitation to occur. The obtained solid was separated by filtration and purified by recrystallization in ethanol/water (1:1); yellow-colored crystals (68%) were then obtained. Melting point: 259–260 °C [49,50]. FTIR (KBr) ν_{max}/cm^{-1}: 3444, 3086, 3061, 3000, 1900, 1602. ESI Anal. Calcd. for $C_7H_5BrN_4$: *m/z* 226.9; found *m/z* 246.9 $[M+Na]^+$.

2.2.2. 5-(4-bromophenyl)-2-dodecanetetrazole **(3)**

A total of 2.50 g (11.11 mmol) of 5-(4-bromophenyl)tetrazole **(2)**, 30 mL of acetone, 1.68 g (12.16 mmol) of potassium carbonate and 3.11 g (12.48 mmol) of 1-bromododecane were added to a 100 mL, two-neck, round-bottom flask. The mixture was subjected to magnetic stirring in reflux for 44 h and accompanied by TLC using a mixture of toluene and ethyl acetate (9:1 v/v) as an eluent. Then, the mixture was filtered and evaporated under reduced pressure. The obtained solid was purified via recrystallization in ethanol; a white solid (79%) was obtained. Melting point of 54–55 °C. FTIR (KBr) ν_{max}/cm^{-1}: 2954, 2918, 2848, 1602. ^1H NMR ($CDCl_3$, δ ppm): 8.02 (d, 2H, $J = 8.60$ Hz); 7.62 (d, 2H, $J = 8.21$ Hz); 4.62 (t, 2H, $J = 7.03$ Hz); 2.10–1.95 (m, 2H); 1.45–1.30 (m, 2H); 1.30–1.15 (m, 16H); 0.87 (t, 3H, $J = 6.25$, 7.03 Hz). ^{13}C NMR ($CDCl_3$, δ ppm): 156.8, 124.8, 120.9, 119.2, 117.2, 46.0, 24.6, 22.3, 22.0, 21.5, 19.0, 15.3, 6.8.

2.2.3. 5-[4-(2-methyl-3-butyne-2-ol-phenyl)]-2-dodecanetetrazole **(4)**

A total of 2.00 g (5.08 mmol) of **3**, 60 mL of dry Et_3N/THF (1:1), 0.183 g (0.26 mmol) of bis(triphenylphosphine)palladium(II) dichloride and 0.069 g (0.26 mmol) of triphenylphosphine were added to a 100 mL, three-neck, round-bottom flask protected by a calcium-chloride drying tube. Under an inert atmosphere of argon, the mixture was heated to 55 °C, at which 0.025 g (0.13 mmol) of copper iodide (CuI) was added, and 0.850 mL (8.72 mmol) of 2-methyl-3-butyne-2-ol dissolved in 10 mL of dry Et_3N/THF (1:1) was added dropwise over a 30-min period to the reaction mixture. The mixture was kept under reflux for 6 h and was accompanied by TLC using a mixture of hexane and ethyl ether (7:3 v/v) as an eluent. Then, the mixture was removed from heat, was filtered at room temperature through Celite® and was concentrated in a rotary evaporator under reduced pressure. The resulting solid was purified by a silica-gel chromatography column, and ethyl hexane/ether (9:1) was used as eluent. After purification, 1.94 g (96%) was obtained. Melting point: 64–65 °C. FTIR (KBr) ν_{max}/cm^{-1}: 3313, 3055, 2958, 2920, 2850. ^1H NMR ($CDCl_3$, δ ppm): 8.09 (d, 2H, $J = 8.20$ Hz); 7.52 (d, 2H, $J = 8.20$ Hz); 4.64 (t, 2H, $J = 7.03$ and 7.32 Hz), 2.55 (s, 1H); 2.06 (q, 2H, $J = 7.03$ Hz); 1.65 (s, 6H); 1.45–1.32 (m, 2H); 1.32–1.22 (m, 16H); 0.89 (t, 3H, $J = 6.44$ and 6.74 Hz). ^{13}C NMR ($CDCl_3$, δ ppm): 164.9, 164.4, 132.1, 127.1, 126.6, 124.6, 95.5, 81.6, 65.5, 53.3, 31.9, 31.4, 29.5, 29.3, 28.8, 26.3, 22.6, 14.1.

2.2.4. 1-dodecanetetrazole-4-ethinylbenzene **(5)**

A total of 1.94 g (4.89 mmol) of 5-[4-(2-methyl-3-butyne-2-ol-phenyl)]-2-dodecanetetrazole **(4)**, 54 mL of toluene and 0.250 g (6.25 mmol) of sodium hydroxide were added to a 100 mL round-bottom flask. A micro distillation apparatus was used to slowly heat the mixture; also, a mixture of 5 mL acetone/toluene was distilled over 4 h. The reaction was accompanied by TLC using a mixture of hexane and ethyl ether (6:4 v/v) as an eluent. The solution was filtered at room temperature on Celite® and concentrated on a rotary evaporator under reduced pressure. The resulting solid was purified by a silica-gel chromatography column and ethyl