Dyes and Pigments 95 (2012) 600–605

Contents lists available at SciVerse ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

2,1,3-Benzoxadiazole and 2,1,3-benzothiadiazole-based fluorescent compounds: Synthesis, characterization and photophysical/electrochemical properties

Behramand Behramand, Fernando Molin, Hugo Gallardo*

Departamento de Química, INCT Catalise, Universidade Federal de Santa Catarina, Florianópolis-SC 88040-900, Brazil

ARTICLE INFO

Article history:
Received 4 May 2012
Received in revised form
30 May 2012
Accepted 5 June 2012
Available online 4 July 2012

Keywords:
Benzoxadiazole
Benzothiadiazole
Sonogashira coupling
Fluorescence
Cyclic voltammetry
Band gap

ABSTRACT

Six new fluorescent compounds derived from 2,1,3-benzoxadiazole and 2,1,3-benzothiadiazole heterocycles with varying numbers of alkoxy chains were successfully synthesized. Sonogashira cross-coupling was used as the key synthetic step to link the central and terminal aromatic units through an acetylenic linker unit which ensures molecular planarity and extension of the conjugation. All of the synthesized compounds showed UV–vis absorption in the 426–437 nm range with reasonably high molar extinction coefficients. All six compounds emit in the green region of the visible spectrum with reasonably large Stokes shifts (95–107 nm) and medium emission efficiencies ($\Phi_f = 0.27–0.32$). Electrochemical studies showed that the compounds have closely spaced HOMO and LUMO energy levels and that they may present good electron transporting properties.

1. Introduction

Due to their environmentally-friendly, facile and economical processing and easy modification to provide desirable properties [1], organic fluorescent compounds have important applications in diverse fields including fluorescent organic nanoparticles (FONs) [2], organic light-emitting diodes (OLEDs) for electroluminescent devices and flat panel display technology [3], as solid state light sources for sign boards and light appliances, fluorescent probes in medical science for locating tumor cells [4], photoconductors for solar cells [5] and chemical sensors [6].

In relation to the search for organic fluorescent compounds with potential applications in diverse fields, we decided to exploit the fluorophoric nature of the heterocycles 2,1,3 benzoxadiazole, more specifically known as benzofurazan [7] and its sulfur containing analogue 2,1,3-benzothiadiazole. Both of these heterocycles possess planar molecular structures and their derivatives with extended conjugation usually present intense fluorescence [8]. Due to the presence of oxygen, the benzofurazan is more electronegative than 2,1,3-benzothiadiazole and its derivatives have mainly been used as fluorescent pre-column labeling reagents for amino acids and peptides analysis [9], as derivatization reagents for indirect HPLC enantioseparation [10] and for heavy metal detection [11].

Depending on the type of substituents, the derivatives of 2,1,3-benzothiadiazole have been shown to emit a variety of colors including red [12], blue [13] and green [14], the three fundamental colors for full color display. Due to its rigid planar structure, ability to form well-ordered crystals and efficient fluorophoric nature, we have used this system as the central core for luminescent liquid crystalline compounds [15]. More importantly, due to its electron-deficient nature, it has especially been used as an accepter unit in many donor-acceptor conjugated copolymers with small HOMO-LUMO band gap [16] for potential application in field effect transistors [17], light emitting diodes [18] and solar cells.

In this paper, we report the synthesis and characterization of six new light-emitting compounds **(1-6)** with a variable number of flexible alkoxy chains using 5,6-alkoxy 2,1,3-benzoxadiazole and 2,1,3-benzothiadiazole fluorophores as the central cores (Fig. 1). With the presence of pendent flexible alkoxy chains there was an improvement in the solubility of compounds.

2. Experimental

2.1. Materials and characterizations

4-Bromophenol 97%, 1-bromododecane 98%, methyl iodide and thionyl chloride 97% were purchased from Sigma–Aldrich; catechol

* Corresponding author. Fax: +55 48 37216850.
E-mail address: hugo.gallardo@ufsc.br (H. Gallardo).

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http://dx.doi.org/10.1016/j.dyepig.2012.06.001

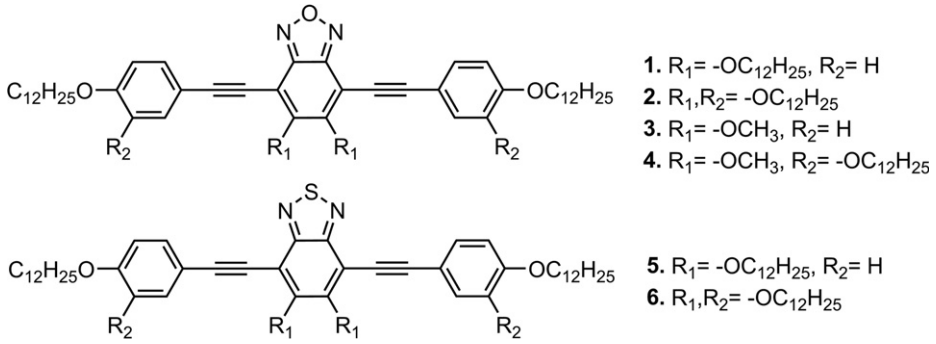


Fig. 1. Molecular structures of the newly synthesized compounds.

99%, 2-methyl-3-butyn-2-ol 98% and tin (II) chloride dihydrate were purchased from Acros Organics and used as received. N-bromosuccinimide was recrystallized from water (10 mL H_2O per 1 g of NBS) prior to its use. Toluene and dimethylformamide were dried over activated molecular sieves. Triethylamine was dried by heating under reflux in the presence of KOH and subsequent distillation. The intermediates were purified either by recrystallization in commercial grade solvents or via column chromatography on silica-gel 60-200 (mesh 60A). The final compounds were purified by column chromatography using flash silica gel. Preliminary purity tests were performed by developing thin layer chromatographs using silica-gel Si 60-F254 TLC plates purchased from Merck. Melting points were determined with an Olympus BX50 microscope equipped with a Mettler Toledo FP-82 hot stage. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury Plus spectrometer operating at 400 and 100.6 MHz, respectively. The data are reported as: chemical shift, multiplicity [s, singlet; d, doublet; t, triplet; q, quartet; qui, quintet; sep, septet; m, multiplet; br, broad; o, overlapping or as a combination of these e.g. dd, dt], coupling constant (J) and integration. Elemental analysis was carried out using a Carlo Erba model E-1110 instrument. IR and Mass spectra were obtained using Varian 3100 FT-IR Spectrometer and Bruker APCI/MS/MS Ion Trap mass spectrometer instrument respectively. Cyclic voltammetry was carried out on an Autolab PGSTAT128N potentiostat, connected to data processing software (GPES, version 4.9.007, Eco Chemie), at a scan rate of 50 mV/s.

2.2. General procedure for Sonogashira cross-couplings

In a flame dried Schlenk flask under argon, a mixture of the heterocycle **7-9** (0.4–0.5 mmol), $Pd(PPh_3)_2Cl_2$, PPh_3 and CuI (7 mol % each) in Et_3N (20–25 mL) was stirred at 50 °C for 20 min. A solution of the terminal aryl acetylene **10** or **11** (2.2 equivalent) in triethylamine (10 mL) was added drop-wise. After complete addition, the reaction mixture was stirred at 80–85 °C for 12–14 h. The reaction mixture was cooled to room temperature, filtered through a celite pad and washed with tetrahydrofuran. After vacuum evaporation of the solvent, the crude product was purified by column chromatography on flash silica gel (eluent 1–2% ethyl acetate: hexane) to furnish the respective final compound.

2.2.1. 4,7-Bis((4-(dodecyloxy)phenyl)ethynyl)-5,6-bis(dodecyloxy)-2,1,3-benzoxadiazole ***(1)***

Greenish-yellow solid; yield: 47%, m.p. = 40.0–41.6 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.5 (d, 4H, J = 8.8 Hz), 6.9 (d, 4H, J = 9.0 Hz), 4.4 (t, 4H, J = 6.4 Hz), 4.0 (t, 4H, J = 6.4 Hz), 1.9 (qui), 1.8 (qui), 1.3 (br), 0.9 (t, 12H). ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ: 160.0, 157.6, 152.2, 133.5, 115.1, 114.7, 108.5, 101.4, 81.2, 75.2, 68.2, 32.2, 29.7, 26.5, 23.0, 14.3. FT-IR (KBr, cm^{-1}): 2923, 2852, 2205, 1604, 1508, 1464, 1291, 1247. CI-MS $[M + H]^+$ calculated for $C_{70}H_{108}N_2O_5$ *m/z*: 1056.8; Found: 1058.0. CHN: Expected: C 79.49, H 10.29, N 2.65. Found: C 79.47, H 10.28, N 2.63.

2.2.2. 4,7-Bis((3,4-bis(dodecyloxy)phenyl)ethynyl)-5,6-bis(dodecyloxy)-2,1,3-benzoxadiazole ***(2)***

Bright orange colored solid; yield: 30%, m.p. = 60.0–61.5 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.2 (dd, 2H, J = 8.4 Hz, J^4 = 2.0 Hz), 7.1 (d, 2H, J^4 = 2.0 Hz), 6.8 (d, 2H, J = 8.4 Hz), 4.4 (t, 4H), 4.0 (ot, 8H), 1.8 (br), 1.3 (b), 0.9 (ot). ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ: 158.3, 150.5, 148.8, 147.8, 125.3, 116.6, 114.5, 113.1, 105.0, 102.2, 101.1, 79.4, 75.0, 69.3, 69.1, 31.9, 30.4, 29.7, 29.7, 29.4, 26.1, 26.0, 22.7, 14.1. FT-IR (KBr, cm^{-1}): 2918, 2860, 2204, 1597, 1514, 1467, 1301, 1265.CI-MS $[M + H]^+$ calculated for $C_{94}H_{156}N_2O_7$ *m/z*: 1426.2; Found: 1427.3. CHN: Expected: C 79.16, H 11.02, N 1.96. Found: C 79.13, H 10.98, N 1.99.

2.2.3. 4,7-Bis((4-(dodecyloxy)phenyl)ethynyl)-5,6-dimethoxy-2,1,3-benzoxadiazole ***(3)***

Yellow colored solid; yield: 52%, m.p. = 55.5–58.0 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.6 (d, 4H, J = 8.6 Hz), 6.9 (d, 4H, J = 8.6 Hz), 4.3 (s, 6H), 4.0 (t, 4H), 1.8 (qui), 1.3 (br), 0.9 (t). ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ: 160.0, 158.2, 147.8, 133.3, 114.7, 114.2, 105.0, 102.4, 100.3, 79.3, 68.2, 61.6, 31.9, 29.7, 29.6, 29.6, 29.3, 29.1, 26.0, 22.7, 14.1. FT-IR (KBr, cm^{-1}): 2923, 2849, 2207, 1730, 1604, 1508, 1466, 1306, 1251. CI-MS $[M + H]^+$ calculated for $C_{48}H_{64}N_2O_5$ *m/z*: 748.5; Found: 749.5. CHN: Expected: C 76.97, H 8.61, N 3.74. Found: C 76.98, H 8.59, N 3.75.

2.2.4. 4,7-Bis((3,4-bis(dodecyloxy)phenyl)ethynyl)-5,6-dimethoxy-2,1,3-benzoxadiazole ***(4)***

Bright orange colored solid; yield: 35%, m.p. = 61.0–63.0 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.2 (dd, 2H, J = 8.2 Hz, J^4 = 2.0 Hz), 7.1 (d, 2H, J^4 = 2.0 Hz), 6.9 (d, 2H, J = 8.2 Hz), 4.3 (s, 6H), 4.0 (ot 8H), 1.8 (quint), 1.3 (br), 0.9 (t). ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ: 158.3, 150.6, 148.8, 147.8, 125.4, 116.5, 114.3, 113.0, 105.0, 102.7, 100.3, 79.0, 69.4, 69.1, 61.7, 31.9, 29.4, 26.0, 22.7, 14.1. FT-IR (KBr, cm^{-1}): 2919, 2848, 2209, 1730, 1515, 1467, 1313, 1270. CI-MS $[M + H]^+$ calculated for $C_{72}H_{112}N_2O_7$ *m/z*: 1116.8; Found: 1117.9. CHN: Expected: C 77.37, H 10.10, N 2.51. Found: C 77.30, H 10.11, N 2.51.

2.2.5. 4,7-Bis((4-(dodecyloxy)phenyl)ethynyl)-5,6-bis(dodecyloxy)-2,1,3-benzothiadiazole ***(5)***

Yellow-green solid; yield: 48%, m.p. = 98.5–100.3 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.6 (d, 4H, J = 8.8 Hz), 6.9 (d, 4H, J = 8.8 Hz), 4.4 (t, 4H, J = 6.4 Hz), 4.0 (t, 4H, J = 6.6 Hz), 1.9 (qui), 1.8 (qui), 1.3 (br), 0.9 (t). ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ: 160.0, 157.6, 152.2, 135.5, 115.1, 114.7, 108.5, 101.4, 81.2, 75.2, 68.2, 32.2, 29.7, 26.5, 26.3, 23.0, 14.3. FT-IR (KBr, cm^{-1}): 2924, 2854, 2201, 1605, 1513, 1467, 1289,

1247. CI-MS $[M + H]^+$ calculated for $C_{70}H_{108}N_2O_4S$ *m/z*: 1072.8; Found: 1073.9. CHN: Expected: C 78.31, H 10.14, N 2.61. Found: C 78.26, H 10.14, N 2.57.

2.2.6. 4,7-Bis((3,4-bis(dodecyloxy)phenyl)ethynyl)-5,6-bis(dodecyloxy)-2,1,3-benzothiadiazole ***(6)***

Lime colored solid; yield: 51%, m.p. = 80.0–81.7 °C.^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.2 (dd, 2H, J = 8.2 Hz, J^4 = 2.0 Hz), 7.2 (d, 2H, J^4 = 2.0 Hz), 6.9 (d, 2H, J = 8.4 Hz), 4.4 (t, 4H, J = 6.6 Hz), 4.0 (ot, 8H), 1.9 (qui), 1.8 (qui), 1.3 (br), 0.9 (t). ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ: 157.7, 152.1, 150.5, 149.0, 125.6, 116.8, 115.1, 113.2, 108.5, 101.6, 80.8, 75.3, 69.5, 69.3, 32.2, 30.0, 29.9, 29.6, 29.4, 26.3, 23.0, 14.1. FT-IR (KBr, cm^{-1}): 2922, 2852, 2205, 1605, 1505, 1468, 1290, 1246. CHN: Expected: C 78.28, H 10.90, N 1.94. Found: C 78.29, H 10.80, N 1.90.

2.2.7. 4,7-Dibromo-5,6-bis(dodecyloxy)-2,1,3-benzoxadiazole ***(7)***

Off-white solid; yield: 90%, m.p. = 55.0–56.1 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.2 (t, 4H, J = 6.6 Hz), 1.9 (m, 4H), 1.5 (m, 4H), 1.3 (br), 0.9 (t, 6H, J = 0.7 Hz). FT-IR (KBr, cm^{-1}): 2954, 2919, 2851, 2331, 1734, 1612, 1473, 1380, 1296, 1187, 1072, 1014, 996, 948, 883, 723. CHN: Expected $C_{30}H_{50}Br_2N_2O_3$: C 55.73, H 7.79, N 4.33. Found: C 55.72, H 7.80, N 4.30.

2.2.8. 4,7-Dibromo-5,6-dimethoxy-2,1,3-benzoxadiazole ***(8)***

Recrystallized from methanol. Off-white crystalline solid; yield: 49%, m.p. = 128.5–131.0 °C.^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.0 (s). FT-IR (KBr, cm^{-1}): 3010, 2952, 2847, 2363, 2136, 1608, 1530, 1477, 1382, 1310, 1075, 1010, 973, 879, 844, 732. CHN: Expected $C_8H_6Br_2N_2O_3$: C 28.43, H 1.79, N 8.29. Found: C 28.41, H 1.80, N 8.29.

2.2.9. 4,7-Dibromo-5,6-bis(dodecyloxy)-2,1,3-benzothiadiazole ***(9)*** *[19]*

Off-white fluffy crystalline solid; yield: 73%, m.p. = 60.4–61.0 °C (lit. 64–65 °C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.2 (t, 4H, J = 6.6 Hz), 1.9 (m, 4H), 1.3 (br), 0.9 (t, 6H, J = 7.0 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 154.5, 150.3, 106.2, 75.1, 31.9, 29.68, 29.65, 29.62, 29.60, 29.4, 29.3 25.9, 22.6, 14.1. FT-IR (KBr, cm^{-1}): 2958, 2903, 2845, 1471, 1384, 1292, 985, 946.

2.2.10. 1-Dodecyloxy-4-ethynylbenzene ***(10)*** *[20–22]*

Prepared according to our reported procedure. Oily liquid at room temperature; yield: 84%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.4 (d, 2H, J = 9.0 Hz), 6.8 (d, 2H, J = 9.0 Hz), 4.0 (t, 2H, J = 6.6 Hz), 3.0 (s, 1H), 1.8 (m), 1.3 (m), 0.9 (t, 6H, J = 7.0 Hz). ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 160.1, 134.0, 115.0, 114.7, 84.3, 76.2, 68.5, 32.6, 30.3, 30.0, 29.8, 26.6, 23.3, 14.6. FT-IR (KBr, cm^{-1}): 3318, 2923, 2854, 2109, 1887, 1607, 1506, 1469, 1289, 1249, 1170, 1108, 1026, 831.

2.2.11. 1,2-Bis(dodecyloxy)-4-ethynylbenzene ***(11)***

Greenish off-white crystalline solid; yield: 94%, m.p. = 37.0–39.2 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.1 (dd, 1H, J = 8.2 Hz, J^4 = 2.0 Hz), 7.0 (d, 1H, J^4 = 2.0 Hz), 6.8 (d, 1H, J = 8.4 Hz), 4.0 (m, 4H), 3.0 (s, 1H), 1.8 (m, 4H), 1.3 (br), 0.9 (t, 6H, J = 7.0). ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ: 150.3, 148.8, 125.7, 117.3, 114.3, 113.3, 84.2, 75.6, 69.5, 69.3, 32.17, 29.9, 29.6, 26.2, 22.9, 14.4. FT-IR (KBr, cm^{-1}): 3315, 2925, 2854, 2108, 1599, 1511, 1469, 1416, 1262, 1135, 1022, 853, 805.

2.2.12. 1,2-Bis(dodecyloxy)benzene ***(13a)***

The reaction mixture was heated under reflux at 90 °C overnight. *Work up:* The reaction mixture was first filtered under vacuum to remove K_2CO_3. Water (300 mL) was added to the filtrate to remove DMF and the product extracted with CH_2Cl_2 (3 × 100 mL), dried over $MgSO_4$, concentrated under reduced pressure and the resulting crude product was recrystallized in ethanol furnishing the pure alkylated product **13a** as needle-like white crystals. Yield: 86%, m.p. = 45.2–46.3 °C (lit. 45.0–48.0 °C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.9 (s, 4H), 4.0 (t, 4H, J = 6.6 Hz), 1.8 (m, 4H), 1.3 (br), 0.9 (t, 6H, J = 7.0 Hz). ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ: 149.4, 121.2, 114.3, 69.5, 32.2, 29.9, 29.6, 26.3, 22.9, 14.4. FT-IR (KBr, cm^{-1}): 2925, 2853, 1594, 1510, 1465, 1258, 1217, 1128, 747, 723.

2.2.13. 1,2-Dimethoxybenzene/Veratrol ***(13b)***

A mixture of catechol (11.95 g, 108.57 mmol) and K_2CO_3 (37.45 g, 271.4 mmol) in acetone was stirred under argon for 10 min at room temperature. Iodomethane (14.2 mL, 228 mmol) was added, stirred for 1.5 h at room temperature and then heated under reflux overnight at 60 °C. The reaction mixture was cooled to room temperature, vacuum filtered to remove K_2CO_3 and the filtrate concentrated under reduced pressure to furnish the oily product (14.6 g, 98%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.8 (m, 4H), 3.7 (s, 6H). FT-IR (KBr, cm^{-1}): 3103, 3055, 3000, 2853, 1610, 1494, 1476, 1322, 1253, 1152, 1120, 1004, 753.

2.2.14. 1,2-Bis(dodecyloxy)-4,5-dinitrobenzene ***(14a)*** *[23]*

Prepared as reported for an analogous conversion. Bright yellow solid; yield: 88%, m.p. = 79.0–80.0 °C (lit. 81.0–82.0 °C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.3 (s, 2H), 4.1 (t, 4H, J = 6.4 Hz), 1.9 (m, 4H), 1.5 (m), 1.3 (br), 0.9 (t, 6H, J = 7.0 Hz). ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ: 152, 136.7, 108, 70.4, 32.16, 29.9, 29.5, 28.9, 22.9, 14.4. FT-IR (KBr, cm^{-1}): 2123, 3070, 2917, 2850, 1727, 1586, 1529, 1465, 1372, 1334, 1289, 1225, 1070, 1041, 987, 949, 909, 872, 823.

2.2.15. 1,2-Dimethoxy-4,5-dinitrobenzene ***(14b)*** *[24]*

Prepared according to previously reported procedure. Bright yellow colored fine crystals; yield: 72%, m.p. = 128.2–129.5 °C (lit. 129.0–131.0 °C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.3 (s, 2H), 4.0 (s, 6H). FT-IR (KBr, cm^{-1}): 3067, 2986, 1585, 1522, 1370, 1325, 1287, 1234, 1045, 875, 789.

2.2.16. 5,6-Bis(dodecyloxy)-2,1,3-benzothiadiazole ***(16)*** *[19]*

Recrystallized from ethanol. Off-white crystalline solid; yield: 73%, m.p. = 95.0–96.7 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.1 (s, 2H), 4.1 (t, 4H, J = 6.6 Hz), 1.9 (m, 4H), 1.5 (m, 4H), 1.3 (br), 0.9 (t, 6H, J = 7.0). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 154.0, 151.3, 98.3, 69.1, 31.9, 29.68, 29.65, 29.3, 28.7, 25.9, 22.6, 14.1. FT-IR (KBr, cm^{-1}): 2910, 2850, 1497, 1467, 1321, 1197, 855.

2.2.17. 5,6-Bis(dodecyloxy)-2,1,3-benzoxadiazole ***(17a)***

Recrystallized from ethanol to furnish **17a** as off-white solid; yield: 77%, m.p. = 107.3–108.8 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.8 (s, 2H), 4.1 (t, 4H, J = 6.6 Hz), 1.9 (m, 4H), 1.3 (br), 0.9 (t, 6H, J = 7.0 Hz). FT-IR (KBr, cm^{-1}): 2913, 2847, 1502, 1471, 1318, 1202, 848. CHN: Expected $C_{30}H_{52}N_2O_3$: C 73.72, H 10.72, N 5.73. Found: C 73.72, H 10.69, N 5.70.

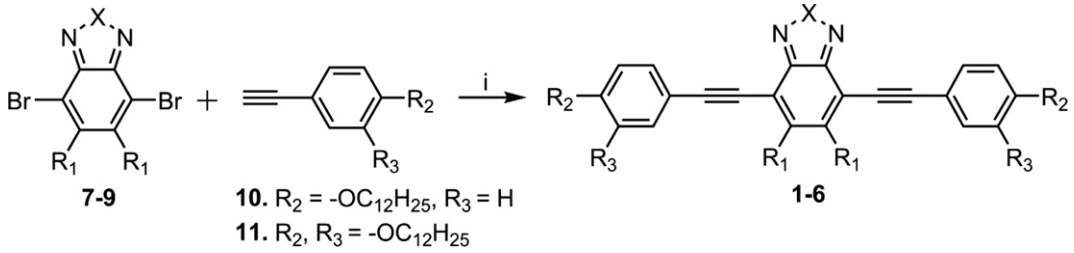
2.2.18. 5,6-Dimethoxy-2,1,3-benzoxadiazole ***(17b)***

Recrystallized from methanol. Yellow needle-like crystals; yield: 81%, m.p. = 195.0–197.0 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.9 (s, 2H), 4.0 (s, 6H). ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ: 155.4, 146.7, 90.7, 56.6. FT-IR (KBr, cm^{-1}): 3146, 3082, 3069, 2995, 2943, 2847, 2442, 1635, 1544, 1521, 1447, 1368, 1244, 1224, 1178, 1001, 854. CHN: Expected $C_8H_8N_2O_3$: C 53.33, H 4.48, N 15.55. Found: C 53.30, H 4.50, N 15.56.

3. Results and discussions

3.1. Synthesis and characterization

The synthetic strategy to obtain the target compounds **(1-6)** utilized Sonogashira cross-coupling [25] of the separately prepared



Scheme 1. Key step in obtaining the target compounds **1-6**, i) $Pd(PPh_3)_2Cl_2$, PPh_3, CuI, Et_3N, 80–58 °C, 12–14 h.

terminal aryl acetylenic **(10,11)** and central heterocyclic intermediates **(7-9),** using the $Pd(PPh_3)_2Cl_2$ catalyst, as the key step (Scheme 1).

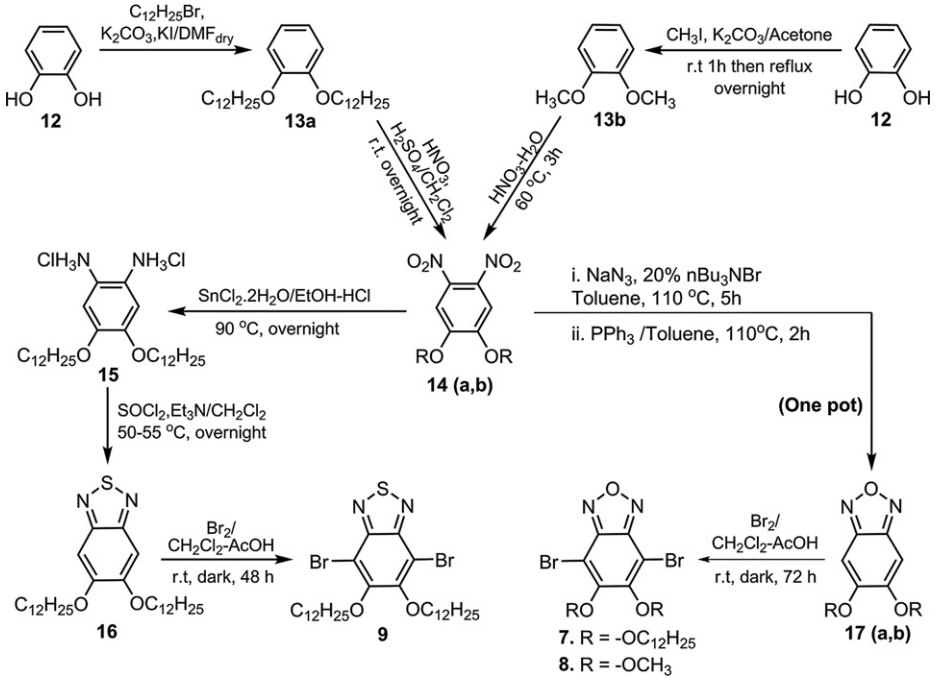
The terminal acetylenic intermediates 1-(dodecyloxy)-4-ethynylbenzene **(10)** and 1,2-bis(dodecyloxy)-4-ethynylbenzene **(11)** were prepared from their respective aryl bromide via a palladium-copper-catalyzed cross-coupling reaction (Sonogashira coupling) according to the literature [20–22,26]. The acetylenic moiety was introduced using 2-methyl-3-butyn-2-ol which is much cheaper than trimethylsilyl-acetylene, although relatively harsh conditions are required for the release of the protecting group [27–29].

The central fluorogenic heterocycles (**7-9**) were synthesized from commercial catechol **12** as shown in Scheme 2. Catechol **12** was alkylated to 1,2-bis(dodecyloxy)benzene **13a** as described in the literature [30] with an improved yield achieved through experimental and work-up modification. The compound **13a** was nitrated to **14a** using HNO_3–H_2SO_4 as the nitrating mixture as reported for an analogous transformation [23].

Attempt to transform veratrol **13b** to 4,5-dinitroveratrol **14b** using HNO_3–H_2SO_4 as the nitrating mixture proved to be harsh and 3,4,5-trinitroveratrol was obtained. The desired transformation was achieved using 70% aqueous nitric acid [24]. Treating the intermediates **14a** and **14b** with NaN_3 and tetra-n-butylammonium bromide as phase transfer catalyst (PTC) followed by PPh_3 furnished, respectively, the intermediates **17a** and **17b** in a *one-pot* reaction [31]. The reduction of **14a** to the diamine salt **15** and subsequent cyclization with thionyl chloride led to **16.** Attempts to cyclize the intermediate **14b** to 5,6-dimehoxy-2,1,3-benzothiadiazole using either the $SnCl_2$ reduction-$SOCl_2$ cyclization or through the hydrogenation-$SOCl_2$ cyclization route led to a solid product that was insoluble in all common organic solvents as well as in water and was not identified. Finally, the heterocyclic intermediates **16, 17a** and **17b** were functionalized for the final cross-coupling step by brominating them in the dark using bromine in acetic acid/CH_2Cl_2. Both benzoxadiazole and benzothiadiazole have electron-accepting five-membered hetero-aromatic units containing two imine (–C=N–) groups. Because of the electron withdrawing ability of the imine group, the ^{13}C NMR data of target compounds show chemical shifts for C atoms of the imine group around 157–160 ppm.

3.2. Photophysical properties

As envisioned, all of the final compounds showed intense fluorescence, emitting in the green region of spectrum under a UV lamp. Their absorption and fluorescence parameters were measured in dilute chloroform solutions and are shown in Table 1. Due to their structural similarities, all of the compounds present very similar absorption (Fig. 2) and emission patterns (Fig. 3). All compounds show



Scheme 2. Synthetic route of the functionalized central heterocycles **7-9**.

Table 1
Photophysical parameters of the final compounds.

Compound	λ_{max} (nm)[a]	ε ($Lmol^{-1}cm^{-1}$)	λ_{ex} (nm)	λ_{em} (nm)	Stokes shifts (nm)[b]	Φ_f[c]
1	429	26,400	436	535	99	0.31
2	437	25,200	449	552	103	0.28
3	426	18600	435	536	101	0.31
4	435	26,000	448	555	107	0.27
5	429	19,400	442	543	101	0.32
6	428	30,200	440	535	95	0.32

[a] Solutions in 5×10^{-6} mol L^{-1} in $CHCl_3$.
[b] Stokes shifts = $\lambda_{em} - \lambda_{ex}$.
[c] Measured in $CHCl_3$, using 4,7-bis(phenylethynyl)-2,1,3-benzothiadiazole ($\Phi_f = 0.37$) as the standard [8].

Table 2
Electrochemical data and molecular orbital energies for final compounds.

Compounds	E_{ox}[a] (vs. Fc/Fc^+)	E_{red}[a] (vs. Fc/Fc^+)	E_{HOMO}[b] (eV vs. vacuum)	E_{LUMO}[b] (eV vs. vacuum)	E_{gap}[c] (eV)	E_g^{opt}
1	0.70	−1.24	−5.50	−3.56	1.94	2.56
2	0.80	−1.27	−5.60	−3.53	2.07	2.50
3	0.76	−1.22	−5.56	−3.58	1.98	2.55
4	0.64	−1.27	−5.44	−3.53	1.91	2.50
5	0.85	−1.72	−5.65	−3.08	2.57	2.54
6	0.93	−1.21	−5.73	−3.59	2.14	2.55

[a] E_{ox} (vs. Fc/Fc^+) = E_{ox} (vs. Ag+) − 0.43, E_{red} (vs. Fc/Fc^+) = E_{red} (vs. Ag+) − 0.43.
[b] $E_{HOMO} = (-4.8 - E_{ox})$, $E_{LUMO} = (-4.8 - E_{red})$.
[c] $E_{gap} = E_{ox} - E_{red}$ or $E_{gap} = E_{HOMO} - E_{LUMO}$.

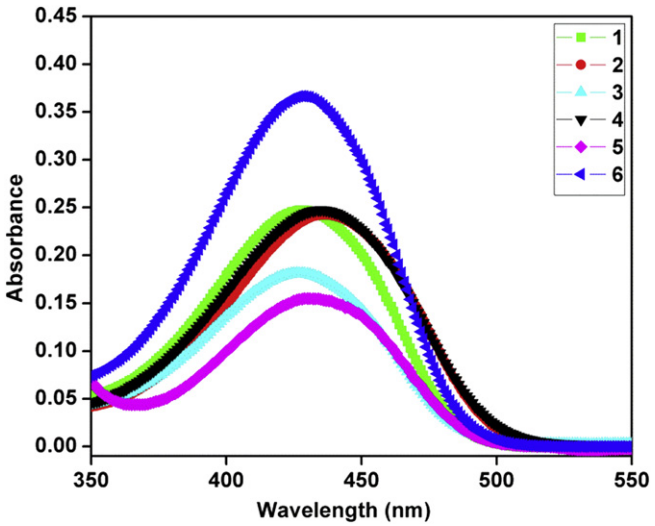


Fig. 2. UV–vis absorption spectra of the final compounds in $CHCl_3$.

maximum absorption within a narrow range of 426–437 nm (Fig. 2) with reasonably high absorption coefficients (Table 1). Shrinking the dodecyloxy groups on the heterocyclic centers in **1** and **2** to methoxy groups resulted in slight blue shifts in the absorptions maxima of **3** and **4**. Moreover, the presence of an additional terminal dodecyloxy chain in **2** and **4**, compared to **1** and **3**, caused a reasonable red shift in the absorption maxima. In the case of 2,1,3-benzothiadiazoles, an additional chain results in a slight blue shift. Compared to the benzoxadiazoles **1** and **2**, their sulfur-containing analogues **5** and **6** absorb at slightly shorter wavelengths. This blue shift in the absorption may be attributed to a slightly diminished delocalization of the lone pair on sulfur towards nitrogen due to the difference in the sizes of the participant orbitals and more polarizable nature of the sulfur.

The fluorescence spectra of the compounds show emission maxima λ_{em} between 535 and 555 nm. The Stokes shifts presented are in the range of 95–107 nm, which indicates only a small region of coincidence between the absorption and emission (Fig. 3). This finding indicates that re-absorption of the emitted light is almost negligible, which is very important in order to avoid undesired loses in the LED performance. The relative fluorescence efficiencies were determined in $CHCl_3$ solutions using 4,7-bis(phenylethynyl)-2,1,3-benzothiadiazole ($\Phi_f = 0.37$) as the standard [8]. All compounds showed moderate quantum yields ($\Phi_f = 0.27$–0.32) with the sulfur-based compounds (**5, 6**) being slightly more efficient.

3.3. Electrochemical properties

Cyclic voltammetry (CV) experiments were performed in solutions of 0.1 M tetra-n-butylammonium hexafluorophosphate ($TBAPF_6$) in CH_2Cl_2 as the supporting electrolyte and the ferrocene/ferricenium (Fc/Fc^+) redox couple as an internal reference. A three-electrode cell was used, comprised of a glassy carbon electrode (GCE) as the working electrode, a platinum wire as the counter electrode and an Ag+/AgCl electrode as the reference. Prior to each measurement, the cell was deoxygenated by purging with nitrogen.

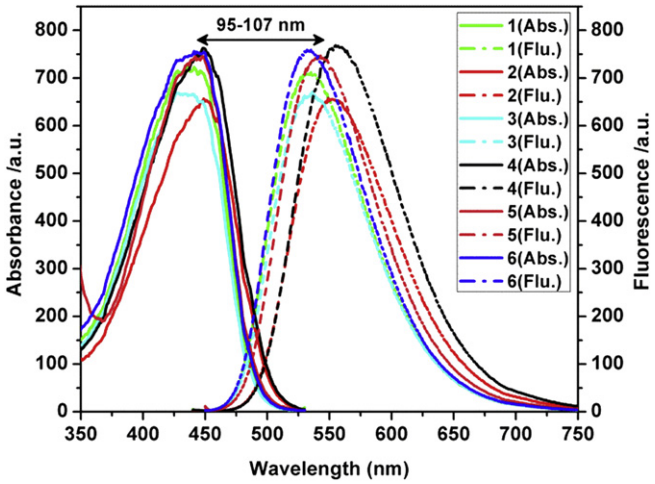


Fig. 3. The emission spectra of target compounds in $CHCl_3$.

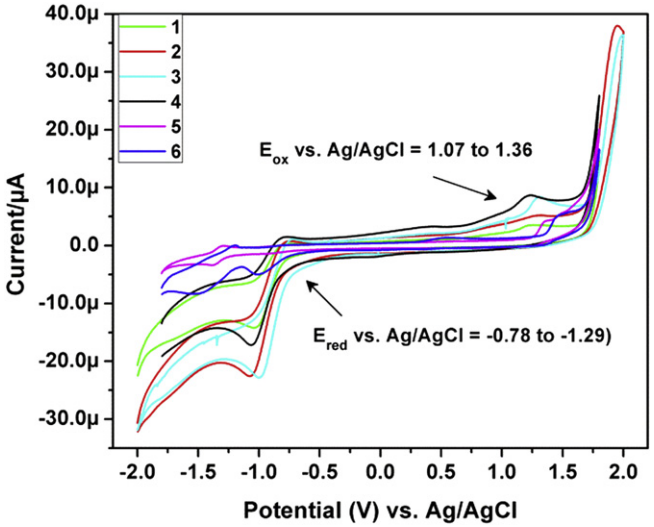


Fig. 4. Cyclic voltammograms of the target compounds vs. Ag/AgCl.

The CV results were used to investigate the redox behavior of the final compounds and to assess the HOMO and LUMO energy levels. The data are summarized in Table 2.

As can be seen in Fig. 4, all of the final compounds show single irreversible oxidation peaks between 1.07 and 1.36V vs. Ag/AgCl (0.64–0.93 vs. Fc/Fc^+ couple) and reduction peaks between −0.78 and −1.29 V vs. Ag/AgCl (−1.21 to −1.72 vs. Fc/Fc^+ couple). The potential values obtained with respect to the Fc/Fc^+ redox couple were converted to the vacuum scale using the standard approximation that the Fc/Fc^+ HOMO level is −4.8 eV [17,32]. The HOMO and LUMO energy levels of the final compounds were calculated as −5.44 to −5.73 eV and −3.08 to −3.59 eV, respectively. The electrochemical and optical band gaps were calculated as 1.91–2.57 eV and from 2.50 to 2.56 eV, respectively.

4. Conclusions

In summary, six new highly conjugated compounds bearing either the 2,1,3-benzoxadiazole or 2,1,3-benothiadiazole fluorophores as the central cores, with varying numbers of terminal alkoxy chains and alkoxy chains of different lengths on the central rings, were synthesized using Sonogashira cross-coupling as the key synthetic step. All compounds emitted in the green region of the visible spectrum and their photophysical parameters were measured. The type of central heterocycle and the alkoxy chains attached to it showed a slight influence on the absorption and emission characteristics. However, the number of terminal alkoxy chains showed a moderate effect on the absorption characteristics. These compounds possess medium fluorescence-emitting abilities with Φ_f values of 0.27–0.32 and reasonable Stokes shifts (95–107 nm). Electrochemical measurements revealed that the target compounds possess small band gaps between 1.91 and 2.57 eV.

Acknowledgments

We thank the following institutions for financial support: CAPES/PNPD, CNPq/PRONEX/FAPESC, INCT-Catálise and TWAS, the Academy of Sciences for the Developing World. The authors thank Dr. Haidi Fiedler from Universidade Federal de Santa Catarina (UFSC) for providing free access to the photophysical equipments and to Jorge A. Pedro for assistance in photophysical characterizations and prof. Dr. Hernán Terenzi for free access to Ion Trap mass spectrometer instrument at CEBIME-UFSC.

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