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Photophysical and electrochemical properties of π-extended molecular 2,1,3-benzothiadiazoles

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Abstract—The reaction of 4,7-dibromo-2,1,3-benzothiadiazole with arylboronic acids (phenyl, 1-naphthyl, 4-methoxyphenyl, 4-chlorophenyl and 4-trifluoromethylphenyl) in the presence of catalytic amounts of a NCP-pincer palladacycle affords photoluminescent π-extended 4,7-diaryl-2,1,3-benzothiadiazoles **4a–e** in high yields. These 4,7-diaryl-2,1,3-benzothiadiazoles exhibit high fluorescent quantum yields, high electron affinities and adequate band gap values for testing as OLEDs. The 4,7-bis-naphthyl-2,1,3-benzothiadiazole **4b** presents two different lifetimes (bi-exponential decay) due to the presence of two atropisomers. The Sonogashira coupling reaction of 4,7-diethynyl-2,1,3-benzothiadiazole **6** with the corresponding halo-aryl compounds (iodobenzene, 1-bromonaphthalene, 4-iodoanisole, 4-bromo-*N*,*N*-dimethylaniline and 2-bromopyridine) afforded the photoluminescent π-extended 4,7-bis-alkynylaryl-2,1,3-benzothiadiazoles **7a–e**, also in high yields. These 4,7-diethynyl-2,1,3-benzothiadiazoles also present high fluorescent quantum yields, high electron affinities and adequate band gap values for testing as OLEDs. The 4,7-disubstituted-2,1,3-benzothiadiazoles **4a–e** and **7a–e** exhibit different electrochemical behavior. The presence of two ethynyl spacers in 2,1,3-benzothiadiazoles **7a–e** shifts the reduction potentials to less cathodic values and also results in two well-defined and distinct reduction processes.

1. Introduction

Fluorescent compounds have found widespread use in scientific and technological areas, especially as organic light-emitting diodes (OLEDs).[1] Due to their potential as constituents of OLEDs, much attention has been focused on π-conjugated molecules, their luminescent properties and their electronic and optoelectronic functions.[2] Only a few types of molecular building blocks have been exploited in the organic electronic area,[3a] such as quinoxalines,[3b] benzimidazoles[3c] and certain polymers.[3d] Among these building blocks, benzothiadiazoles are one of the most important classes due to their relatively high reduction potential and electron affinity, necessary for utilization in light-emitting diode (LED) technology. Indeed, the HOMO/LUMO levels of π-extended conjugated molecules are defined by their electron affinity (EA) and ionization potential (IP), which are correlated with electrochemical reduction and oxidation potentials. 2,1,3-Benzothiadiazole derivatives have several desirable characteristics: (a) benzothiadiazole-containing compounds can afford well-ordered crystal structures; and (b) benzothiadiazole derivatives normally are efficient fluorophores.[4] Highly fluorescent π-conjugated molecules are also of interest in other applications such as electroluminescent (EL) devices.[5] Surprisingly, the synthesis of benzothiadiazole derivatives and investigations of their photoluminescent properties are relatively limited. In fact, most of these studies have been centered on the preparation of 4,7-diphenyl-2,1,3-benzothiadiazole, 4,7-bis(4-methoxy-phenyl)-2,1,3-benzothiadiazole and 4,7-bis[(2-pyridyl)-ethynyl]-2,1,3-benzothiadiazole derivatives, which were obtained in moderate yields.[6] Moreover, only a few photophysical and electrochemical properties have been reported so far. In view of the very promising photoluminescent properties of these π-conjugated molecules, it is of a great interest to have a simple synthetic methodology for their preparation.

We report here that palladium promoted C–C coupling reactions of the Suzuki and Sonogashira type are effective methods for the construction of a new class of more highly luminescent π-extended 4,7-disubstituted-2,1,3-benzothiadiazoles. We also present the electrochemical and photoluminescent properties of ten such compounds, which indicate that they are indeed potential candidates for OLED devices.

Keywords: Sonogashira coupling; Spectrometry; OLED; Photoluminecent; Benzothiadiazoles.
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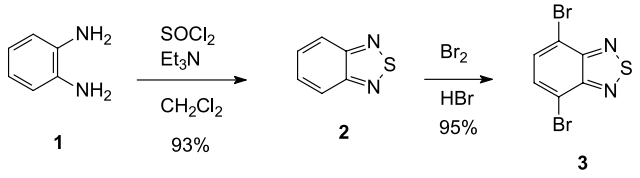
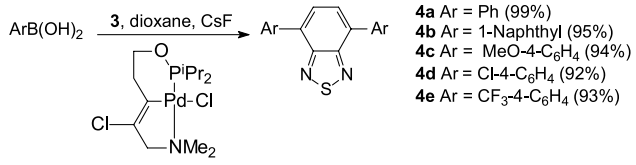
2. Results and discussion

Commercially available *o*-phenylenediamine, **1**, was treated with freshly distilled thionyl chloride in the presence of triethylamine in CH_2Cl_2 as solvent, affording 2,1,3-benzothiadiazole, **2**, in 93% yield after steam distillation.[7] Upon reaction with molecular bromine (added drop-wise very slowly) in hydrobromic acid, compound **2** gives exclusively the 4,7-disubstituted regioisomer **3** in 95% yield (Scheme 1).[8]



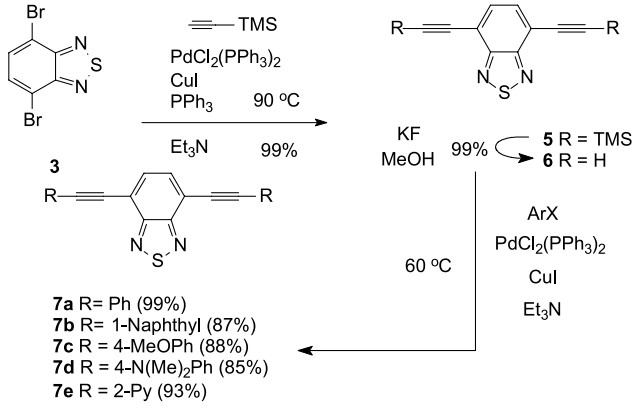
Scheme 1. Synthesis of benzothiadiazole **3**.

The Suzuki coupling reaction of compound **3** with phenyl or 1-naphthyl boronic acid, catalyzed by the NCP pincer palladacycle,[9] produced the desired bis-coupled π-extended 4,7-diarylsubstituted 2,1,3-benzothiadiazoles **4a–e** in excellent yields after column chromatographic purification (Scheme 2). Although compounds **4a** and **4c** have previously been prepared by using the classical Suzuki Pd coupling catalyst,[10] the yields were only 48%. With our methodology, these compounds are obtained in much higher yields (94–99% yield).



Scheme 2. Synthesis of π-extend benzothiadiazoles **4a–e**.

The Sonogashira cross-coupling reaction of **3** with trimethylsilylacetylene in the presence of $PdCl_2(PPh_3)_2$, CuI, and PPh_3 in NEt_3 at 90 °C produced the bis-coupling product **5**.[11] The de-protection of **5** with KF afforded **6** in quantitative yield after column chromatographic purification. A second Sonogashira cross-coupling reaction was conducted in the presence of $PdCl_2(PPh_3)_2$ and CuI, in NEt_3 at 60 °C with iodobenzene, 1-bromonaphthalene, 4-bromoanisole, 4-bromo-*N*,*N*-dimethylaniline or 2-bromopyridine, affording the desired products **7a–e**, respectively, in excellent yields after column purification (Scheme 3).[12] Although **7e** is a known compound,[6] the reported synthesis via a single Sonogashira coupling step had only a 47% yield and the electrochemical properties of the compound were not reported. Our methodology improves the yield to 93% in the final Sonogashira coupling, with a global yield of 87% for the synthesis.



Scheme 3. Synthesis of π-extend benzothiadiazoles **7a–e**.

All new compounds were fully characterized by FTIR, ^1H NMR and ^{13}C NMR, and high-resolution mass spectrometry (HRMS) and the data are in full accord with the proposed structures. Differential scanning calorimetry (DSC) was used to determine the thermal properties of compounds **4a–e** and **7a–e** (melting or decomposition temperatures). Table 1 summarizes the results of UV–vis (recorded in acetonitrile solution), fluorescence and electrochemical analyses (by cyclic voltammetry)[13] of the synthesized photoluminescent compounds **4a–e** and **7a–e** and some other known compounds (Scheme 4).

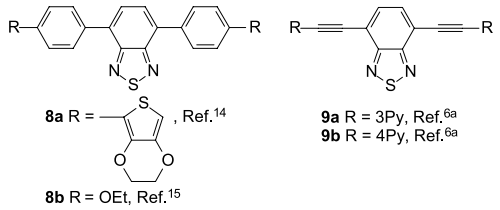
For all compounds, for which both the optical (E_{gap}^{op}) and electrochemical (E_{gap}^{el}) band gaps could be calculated,[17] there is excellent agreement between the two values. Moreover, the values are in the appropriate range (between 1.5 and 5.5 eV) for application in OLED devices.[18] For example, copolymers with the benzothiadiazole unit has a band gap values in the range of 2.03–8.61 eV[2c] and zinc complex with the 2,1,3-benzothiadiazole moiety has a band gap of 1.88 eV.[19] Many other examples with values in this range can be found in the literature.[20] The electron affinity (EA) and ionization potential (IP) have been determined using a known method ($EA = E_{red}^{onset} + 4.4$ eV and $IP = E_{oxi}^{onset} + 4.4$ eV).[3a] Molecules **4a–c** and **7a–e** also have high values of EA (2.72–3.72 eV). This is fundamental in order to allow electron injection from stable metal cathodes.[21] Comparison of **4a** and **7a** and of **4b** and **7b** indicates that the insertion of a triple bond does not significantly affect the band gap energies in molecules without electron donor or electron withdrawing groups, although the EA and IP diminish by about 0.5 eV upon extending the conjugation. A similar behavior is observed when a MeO group is inserted into molecules **4c** and **7c**. The insertion of a $N(Me)_2$ group in molecule **7d** indicates that the presence of an electron donating group does not significantly affect the electrochemical behavior of the compounds. With an electron withdrawing group, as in molecule **7e** (2-pyridyl, in this case), the reduction process begins at less cathodic values (−0.68 V) compared to molecules **7c** and **7d** (OMe and $N(Me)_2$ groups), which begin at −0.95 and −1.37 V, respectively. This fact indicates that electron withdrawing groups facilitate the reduction process. The presence of the triple bonds (compare compounds **4** and **7**) affects the electrochemical charge transfer processes by shifting the electrochemical window to more cathodic values.

Compounds **4a**, **4b**, **4c**, and **7a** exhibit oxidation and reduction peaks (Fig. 1), which suggests the possibility of both hole and electron transport, leading to a single-layer electroluminescent device.[22] This fact is very important since it would not be necessary to employ different

Table 1. UV–vis, fluorescence and some electrochemical data for compounds **4a–e**, **7a–e**, **8a–b**, and **9a–b**[a]

Compound	E_{red}^{onset} (V)[b]	EA[c] (eV)	E_{oxi}^{onset} (V)[d]	IP[e] (eV)	E_{gap}^{el} (eV)[f]	Log ε	λ_{abs}^{max} (nm)	λ_{em}^{max} (nm)	Stoke's shift (nm)	Φ_f[g]	τ_f (Singlet) (ns)[h]	τ_T (Triplet) (μs)[i]	E_{gap}^{op} (eV)[j]
4a	−1.05	3.35	1.65	6.05	2.70	4.04	402, (380)[k], (379)[l]	487, (490)[k], (490)[l]	85	0.80, (0.80)[k], (0.74)[l]	12.2	—	2.73
4b	−1.18	3.22	1.44	5.84	2.62	4.08	360	517	157	0.17	4.96 and 2.38[m]	14.4	2.68
4c	−1.23	3.17	1.32	5.72	2.55	3.52	362	547	185	0.51	12.70	—	2.54
4d[k]	—	—	—	—	—	5.30	368	479	111	0.50	10.40	4.18	2.75
4e[k]	—	—	—	—	—	3.86	355	453	98	0.22	6.31	6.04	2.74
7a	−1.57	2.83	1.02	5.42	2.59	4.99	403	497	94	0.37	5.53	21.6	2.57
7b	−1.68	2.72	1.23	5.63	2.91	3.56	363	434	71	0.36	8.37	6.05	2.99
7c[n]	−0.95	3.45	1.47	5.87	2.42	4.40	393	542	149	0.29	6.42	20.01	2.37
7d	−1.37	3.03	1.61	6.01	2.98	4.11	407	438	31	0.15	8.18	23.02	2.93
7e	−0.68	3.72	1.93	6.33	2.61	4.40 (4.48)[o]	394 (393)[o]	469 (473)[o]	75	0.86 (0.87)[p]	4.52	29.50	2.60
8a[l]	na	na	na	na	na	na	481	630	149	0.75	na	na	na
8b[p]	na	na	na	na	na	4.07	410	546	136	0.75	na	na	na
9a[o]	na	na	na	na	na	4.45	396	479	83	0.80	na	na	na
9b[o]	na	na	na	na	na	4.43	388	464	76	0.87	na	na	na

[a] Electrochemical experiments in MeCN–CH_2Cl_2 (3/7 v/v) and potentials against ferrocene (Ref. 3a). Platinum was used as working electrode and as a counter electrode. All potentials were recorded versus Ag/AgCl (saturated) as a reference electrode.
[b] Onset cathode potential.
[c] Electron affinity.
[d] Onset anode potential.
[e] Ionization potential.
[f] Energy of the band gap (electrochemical).
[g] Quantum yield of fluorescence (quinine sulfate (Riedel) in 1 M H_2SO_4, Φ_f=0.55, as standard).
[h] Singlet lifetime, by single photon counting.
[i] Triplet lifetime, by nanosecond laser flash photolysis.
[j] Energy of the band gap (optical).
[k] The molecule did not form a film to be analyzed by thin film CV (only in solution).
[l] Ref. 14.
[m] Biexponential decay (two lifetimes).
[n] The monomer properties have not been described (Ref. 16). na, not available.
[o] Ref. 6a.
[p] Ref. 15.



Scheme 4. Other known benzothiadiazole systems.

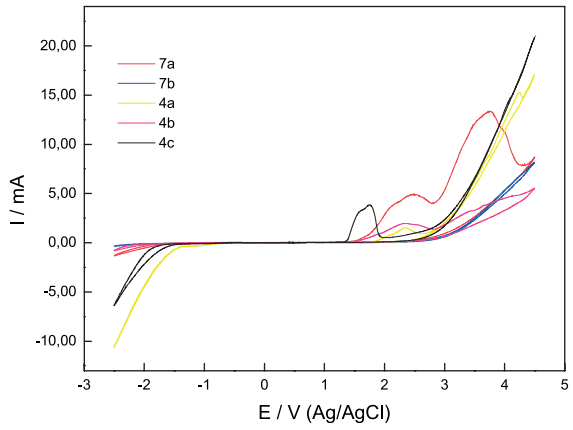


Figure 1. CV (thin film coated onto a Pt wire electrode) of compounds **4a–c** and **7a–b** recorded at scan rate = 40 mV/s in MeCN–CH_2Cl_2 (3/7 v/v).

molecules in the electron-transporting and hole-transporting layers of organic light emitting devices. Compound **7b** did not show current peaks associated with oxidation/reduction processes. In contrast, molecules **7c–d** (voltammograms not shown) do not show well-defined oxidation peaks. Compounds **4a–b** and **7a** exhibit two oxidation peaks involving multiple deelectronation processes. All molecules, however, show well-defined reduction peaks and, in some cases, two well-defined peaks (**4a** and **7b**). Due to the impossibility of forming films of molecules **4d** and **4e**, they could not be analyzed as a thin film coated onto a Pt wire electrode, only in solution.

Compounds **7a–e** exhibit different electrochemical behavior from that of compounds **4a–e**, by comparing both series dissolved in solution. The former exhibit two well-defined sets of reduction peaks (from −1.0 to −1.3 V and from −1.7 to −1.9 V). This suggests the occurrence of two different processes when the species are reduced. Most

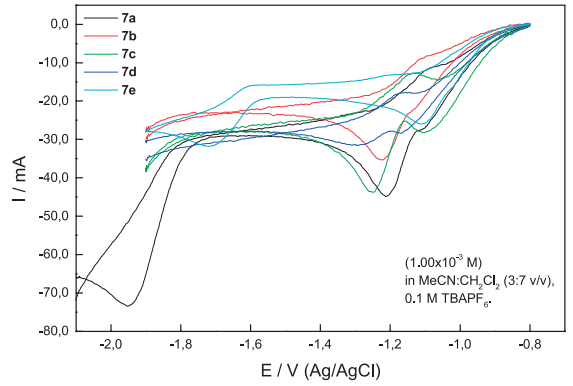


Figure 2. CV of compounds **7a–e** (1.00 mmol L^{-1}) dissolved in MeCN–CH_2Cl_2 (3/7 v/v) recorded at scan rate = 200 mV/s.

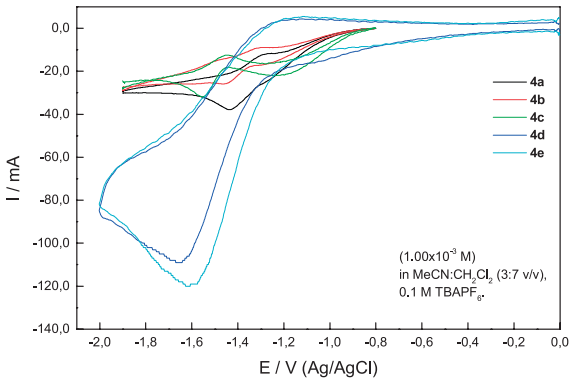


Figure 3. CV of compounds **4a–e** (1.00 mmol L^{-1}) dissolved in MeCN–CH_2Cl_2 (3/7 v/v) recorded at scan rate = 200 mV/s.

probably the first charge transfer process involves a quasi-reversible reduction of the benzothiadiazole ring (observed in both series), while the second is associated with reduction of the triple bond (Figs. 2 and 3). Apparently, the second charge transfer is an irreversible electrochemical process. As noted, both series exhibit the first process. This is indicated by the fact that the current versus potential curves have the same shape for all compounds (**4a–e** and **7a–e**, Table 2—see all individual CV curves in the Supporting information). Since compounds **4a–e** have no triple bond, the well-defined reduction process can only be attributed to reduction of the benzothiadiazole ring. A plausible mechanism for this process has been presented by Hirao et al.[23] An exception occurs in benzothiadiazole **4e**, which shows one defined irreversible reduction peaks, but in the same potential range.

Compounds **7a** and **7e** show two well-defined and very distinct reduction processes. The first one is similar to compounds **4a–e**, indicating that the benzothiadiazole ring is reduced in preference to the triple bond in those systems. The second process is the reduction of the triple bond, a process that cannot occur in molecules **4a–e**. Comparison of the reduction behavior of compounds **7a** and **7e** indicates that the second reduction process for **7a** occurs at much more cathodic values than that of **7e**. The origin of this difference is still not clear.

All compounds have rather good fluorescence quantum yields, especially **4a** ($\Phi_f = 0.80$) and **7e** ($\Phi_f = 0.86$), and show large Stoke's shifts (31–185 nm). The fluorescence quantum yield of benzothiadiazole **3** (without π-extended conjugation), which has not been reported before, is very low ($\Phi_f = 0.006$). The lowest energy absorption bands (in acetonitrile) are assigned to π–π* transitions by virtue of their large molar extinction coefficients (log ε values in the range of 3.52–5.30). The absorption (λ_{abs}^{max}) and emission (λ_{em}^{max}) maxima lie between 355–407 nm and 434–547 nm, respectively (Figs. 4 and 5). Molecules **4c** and **7c** (with a MeO group) have large Stoke's shifts, 185 and 149 nm, respectively. This indicates a very efficient intramolecular charge transfer (ICT) in the excited state between the terminal methoxy group and the benzothiadiazole nucleus.

Compound **4b** not only exhibits a large Stoke's shift (157 nm), but it is also the only compound whose

Table 2. Reduction and oxidation data of compounds **4a–e**, **7a–e**, **8a–b**, and **9a–b**

Compound	E^{o}_{red} (V) First process	E^{o}_{red} (V) Second process	E^{o}_{oxi} (V) First process	E^{o}_{oxi} (V) Second process	Reference
4a	−1.43 (−1.36)[a]	—[b]	1.48 (1.82)[a]	4.25 (−)[a]	This work and 14
4b	−1.45	—[b]	1.91	4.77	This work
4c	−1.55	—[b]	1.74	—	This work
4d	−1.66	—[b]	—[c]	—[c]	This work
4e	−1.62	—[b]	—[c]	—[c]	This work
7a	−1.21	−1.98	2.50	3.77	This work
7b	−1.13	—[b]	—[d]	—[d]	This work
7c	−1.10	—[b]	—[d]	—[d]	This work
7d	−1.16	—[b]	—[d]	—[d]	This work
7e	−1.11 (−1.18)[e]	−1.72 (−)[e]	3.54 (−)[e]	4.12 (−)[e]	This work and 6a
8a	−1.40	na	0.92	na	14
8b	na	na	na	na	15
9a	−1.08	na	na	na	6a
9b	−1.00	na	na	na	6a

[a] Ref. 14.
[b] The molecule has just one process.
[c] The molecule did not form a film to be analyzed by thin film CV (only in solution).
[d] The molecule did not show an oxidation peak, only E_{onset}.
[e] Ref. 6a. na, not available.

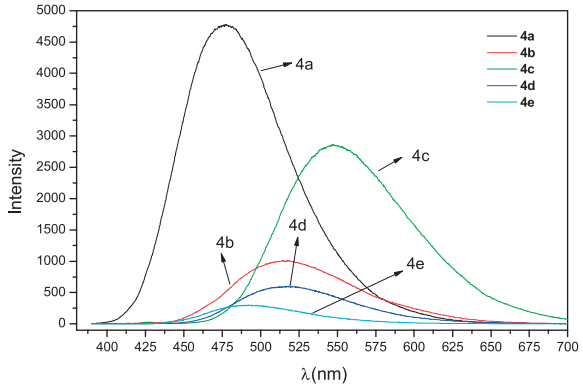


Figure 4. Fluorescence spectra of compounds **4a–e** in acetonitrile.

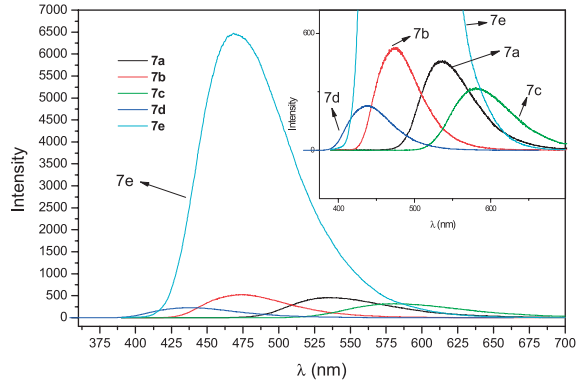


Figure 5. Fluorescence spectra of compounds **7a–e** in acetonitrile.

fluorescence decay exhibits two lifetimes (4.96 and 2.38 ns). Likewise, the ^{1}H and ^{13}C-{1*H*} NMR spectra of **4b** in DMSO-d_6 at room temperature (see Supporting information, also for fluorescence decay) show two sets of signals, indicating the presence of two isomers. The fact that these two sets of signals coalesce at 90–100 °C points to the existence at room temperature of two atropisomers in which the α-naphthyl groups are in *syn* or *anti* geometries (Fig. 6).

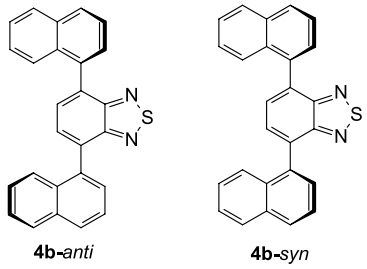


Figure 6. Compound **4b** atropisomers.

Although the presence of the triple bonds in compounds **7a–e** extends the π-conjugation compared to **4a–e**, this has only a secondary effect on the photophysical properties of the compounds, indicating that this structural change is not fundamental for the fluorescence process itself.

All compounds exhibit strong fluorescence and, with the exception of **4b**, a single fluorescence lifetime. Radiative decay rate constants ($=\Phi_f/\tau_f$) are in the range of 5×10^{7} s^{-1}, consistent with the observed range of log ε values for absorption, and are insensitive to the presence of the triple bond spacers. With the exception of molecules **4a** and **4c**, the remaining molecules show strong triplet–triplet absorption by laser flash photolysis (355 nm excitation, Nd-YAG laser) in the absence of oxygen, with triplet lifetimes in the range of 4–30 μs, indicating efficient intersystem crossing in these eight compounds. The strong triplet–triplet absorption and lack of noticeable laser-induced decomposition indicate high chemical stability also in the excited state. The only limitation would be the necessity of the absence oxygen, since the triplet states of all of the compounds are efficiently quenched by molecular oxygen (presumably via energy transfer to form singlet oxygen). The motives for the failure to observe triplet–triplet absorption with **4a** and **4c** are unclear and would require more detailed photophysical studies for clarification.

All of the compounds also present fluorescence in the solid state (Table 3).

Table 3. Excitation and emission maxima and Stoke's shifts for 2,1,3-benzothiadiazoles **4a–e** and **7a–e** in the solid state

Compound	λ_{abs}^{max} (nm)	λ_{em}^{max} (nm)	Stoke's shift (nm)
4a	426	493	67
4b	427	495	68
4c	418	526	108
4d	495	544	49
4e	430	501	71
7a	424	543	119
7b	422	500	78
7c	522	590	68
7d	442	514	72
7e	452	543	91

The absorption maxima are red-shifted in all cases and, with the exception of compounds **4b** and **4c**, so are the fluorescence emission maxima. The resultant Stoke's shifts in the solid state are smaller for compounds **4a–e** and **7c**, but larger for compounds **7a**,**b**,**d**,**e**.

3. Conclusion

In summary, the Suzuki and Sonogashira couplings of 4,7-dibromo-2,1,3-benzothiazole with arylboronic acids and alkynes represent simple and effective methods for π-extension to obtain 4,7-disubstituted-2,1,3-benzothiadiazoles. The 4,7-diaryl-2,1,3-benzothiadiazoles **4a–e** possess moderate to high fluorescence quantum yields (0.17–0.80) and high electron affinities (3.17–3.35 eV). The fluorescence of 4,7-binaphthyl-2,1,3-benzothiadiazole, **4b**, exhibits bi-exponential decay, attributed to the presence of two atropisomers. The band gap values of 4,7-biaryl-2,1,3-benzothiadiazoles **4a–e** are in the adequate range (2.54–2.75 eV) for testing as OLEDs. The presence of ethynyl spacers in the 2,1,3-benzothiadiazoles **7a–e** does not have a negative impact on the photo-electronic properties of those compounds and their fluorescent quantum yields are likewise high (0.15–0.86). These alkynyl benzothiazoles do, however, possess different electrochemical behavior due to the presence of the reducible triple bond. The electron affinities of 4,7-bis-ethynylaryl-2,1,3-benzothiadiazoles **7a–e** are also high (2.72–3.72 eV) and their band gap values in the appropriate range for testing as OLEDs (2.37–2.99 eV).

4. Experimental

4.1. General

All catalytic reactions were carried out under an argon or nitrogen atmosphere in oven-dried resealable Schlenk tubes. All substrates were purchased from Acros and used without further purification. The PCN palladacycle catalyst precursor was prepared according to the reported method.[9] All new compounds were fully characterized after purification. NMR spectra were recorded on a Varian Inova 300 MHz or Varian Gemini 200 MHz spectrometers. Infrared spectra were registered on a Bomem B-102 spectrometer. Melting points were measured on a 12000 PL-DSC apparatus at a heating rate of 5 °C/min or in a Electrothermal IA9000 Melting Point apparatus. The purity of compounds **4a–e** and **7a–e** was checked by CG analysis on a HP-5890A chromatograph fitted with a DB17 capillary column (25 m) with temperature programming from 100 °C up to 250 °C at a heating rate of 15 °C/min. The pressure at the column head was 10 psi. Cyclic voltammograms (CV) were recorded on an Autolab PGSTAT 30 Potentiostat. A thin layer of molecules **4** and **7** was coated from its solution in CH_2Cl_2, using similar procedure employed for diphenylanthrazolines.[3a] UV–vis absorption spectra were taken on a Cary 50 Varian spectrophotometer or a Shimadzu Model UV-1601PC. For fluorescence quantum yields (quinine sulfate (Riedel) in 1 M H_2SO_4, $\Phi_f=0.55$, as standard), a Shimadzu UV-1601PC spectrophotometer and a Hitachi Model F-4500 spectrofluorometer were employed. Fluorescence decays were collected by the time-correlated single photon counting technique with an Edinburgh Analytical Instruments FL900 lifetime Spectrometer (H_2 lamp excitation source). Lifetimes were determined from the decays by using the FL900 convolution and fitting routines for mono- and bi-exponential decay. Nanosecond laser flash photolysis experiments were performed at 20 °C on air-equilibrated solutions (MeCN) and on solutions deoxygenated by exhaustive purging with solvent-vapor-saturated argon in cuvettes capped with a rubber septum. The Edinburgh Analytical Instruments LP900 laser flash photolysis system is equipped with a 450W Xe high pressure monitoring lamp and excitation was carried out with the third harmonic (355 nm) of a Surelite II-10 Nd-YAG laser. Solutions (MeCN) were stirred between each laser shot and 10 laser shots averaged to obtain the transient absorption decays. Solutions were monitored for laser-induced decomposition by conventional UV–vis absorption spectroscopy (Hewlett-Packard 8452A diode array spectrometer) and replaced by fresh solution at the first signs of decomposition. The standard exponential decay routines of the LP900 system software were used to analyze the decays of the transient and obtain the lifetimes of the excited species.

4.1.1. General procedure for the synthesis of benzothiadiazole 2. To a 1000 mL flask were added commercial *o*-phenylenediamine **1** (10.00 g, 92.47 mmol), 300 mL of CH_2Cl_2 and triethylamine (37.44 g, 369.98 mmol). The solution was stirred until total dissolution of the diamine **1**. Thionyl chloride was added dropwise very slowly and the mixture refluxed for 4 h. The solvent was removed in a rotatory evaporator and 700 mL of water added. Concentrated HCl was added to a final pH of 2. The desired compound was purified by direct steam distillation following addition of water to the mixture. The steam distilled mixture was extracted three times with 200 mL of CH_2Cl_2, dried over $MgSO_4$ and filtered. The solvent was removed, affording pure compound **2** in 93% yield (11.71 g, 85.99 mmol).

^{1}H NMR ($CDCl_3$): δ ppm 7.99 (dd, 2H, $J=3.3$, 4.6 Hz); 7.57 (dd, 2H, $J=3.1$, 6.8 Hz). ^{13}C NMR ($CDCl_3$): δ ppm 154.6; 129.1; 122.4. FTIR (KBr, cm^{-1}): 1659, 1433, 1264, 1104, 747. Mp 43.6–44.4. Lit.[7a,b] 44 °C.

4.1.2. General procedure for the synthesis of 4,7-dibromobenzothiadiazole 3. To a 500 mL two-necked round bottom flask were added benzothiadiazole **2** (10.00 g,

73.44 mmol) and 150 mL of HBr (47%). A solution containing Br_2 (35.21 g, 220.32 mmol) in 100 mL of HBr was added dropwise very slowly (slow addition is essential!). If necessary, an additional 100 mL of HBr can be added to the solution. After total addition of the Br_2, the solution was refluxed for 6 h. Precipitation of an orange solid was noted. The mixture was allowed to cool to room temperature and sufficient saturated solution of $NaHSO_3$ added to consume completely any excess Br_2. The mixture was filtered under vacuum and washed exhaustively with water. The solid was then washed once with cold Et_2O and dried under vacuum for ca. 20 h, affording the desired dibrominated product **3** in 95% yield (20.51 g, 69.77 mmol).

^{1}H NMR ($CDCl_3$/DMSO-d_6—two drops): δ ppm 7.73 (s, 2H). ^{13}C NMR ($CDCl_3$/DMSO-d_6—two drops): δ ppm 152.6; 132.1; 113.6. Mp 187–188 °C. Lit.[8] 188–189 °C.

4.2. General procedure for the Suzuki coupling reactions

An oven-dried resealable Schlenk tube was evacuated and back-filled with Ar and charged with CsF (568 mg, 3.74 mmol), arylboronic acid (3.74 mmol) and the NCP pincer palladacycle (1 mol%).[9] Compound **3** (500 mg, 1.70 mmol) was added in 1,4-dioxane (5 mL). The reaction mixture was stirred at 130 °C for 18 h. The solution was then allowed to cool to room temperature and the solvent evaporated under reduced pressure. The crude material was chromatographed directly on silica gel with Et_2O.

4.2.1. Benzothiadiazole 4a. ^{1}H NMR ($CDCl_3$): δ ppm 8.23 (d, 2H, J=6.4 Hz), 7.97–7.24 (m, 10H). ^{13}C NMR ($CDCl_3$): δ ppm 137.3, 136.5, 133.9, 133.2, 113.8, 113.0. FTIR (KBr, cm^{-1}): 1586, 1463, 1424, 1333. Mp 84 °C HRMS calcd for $C_{18}H_{12}N_2S$ 288.07212, found 288.07212.

4.2.2. Benzothiadiazole 4b. ^{1}H NMR ($CDCl_3$): δ ppm 8.02–7.25 (m, 16H). ^{1}H NMR (DMSO-d_6, 20 °C): δ ppm 8.42–8.33 (m, 2H), 8.22–8.02 (m, 2H), 7.94–7.81 (m, 4H), 7.77–7.58 (m, 3H), 7.52–7.41 (m, 5H). ^{1}H NMR (DMSO-d_6, 100 °C): δ ppm 8.21–8.10 (m, 2H), 7.98–7.86 (m, 2H), 7.63–7.42 (m, 5H), 7.40–7.28 (m, 4H). ^{13}C NMR (DMSO-d_6): δ ppm 153.8, 152.7, 135.5, 134.5, 133.2, 132.9, 132.3, 131.9, 130.9, 130.6, 129.1, 128.7, 128.3, 128.2, 128.1, 127.9, 127.7, 127.4, 126.4, 126.0, 125.9, 125.7, 125.5, 125.4, 125.3, 124.9. FTIR (KBr, cm^{-1}): 3037, 1589, 1506, 1483, 1396, 1325, 1265. Mp 184 °C. HRMS calcd for $C_{26}H_{16}N_2S$ 388.10342, found 388.10445.

4.2.3. Benzothiadiazole 4c. ^{1}H NMR ($CDCl_3$): δ ppm 3.89 (s, 6H), 7.08 (d, 4H, J=8.4 Hz), 7.70 (s, 2H), 7.32 (d, 4H, J=8.2 Hz). ^{13}C NMR ($CDCl_3$): δ ppm 159.6, 154.1, 132.2, 130.3, 129.9, 127.4, 114.0, 55.4. FTIR (KBr, cm^{-1}): 3029, 2954, 1604, 1519, 1284. Mp 207 °C. HRMS calcd for $C_{20}H_{16}N_2O_2S$ 348.09325, found 348.09323.

4.2.4. Benzothiadiazole 4d. ^{1}H NMR (DMSO-d_6): δ ppm 8.20–7.70 (m, 6H) 7.69–47 (m, 4H). ^{13}C NMR (DMSO-d_6): δ ppm 153.1, 152.3, 133.5, 132.6, 130.9, 128.7, 112.8. FTIR (KBr, cm^{-1}): 3045, 1529, 1469, 1094. Mp 170 °C. HRMS calcd for $C_{18}H_{10}Cl_2N_2S$ 355.994176, found 355.99416.

4.2.5. Benzothiadiazole 4e. ^{1}H NMR ($CDCl_3$): δ ppm 8.14–7.58 (m, 10H). ^{13}C NMR ($CDCl_3$): δ ppm 153.8, 153.7, 152.9, 152.8, 129.5, 129.4, 128.7, 128.4, 125.6, 125.59, 113.8. FTIR (KBr, cm^{-1}): 2924, 1669, 1334, 1169. Mp 103 °C. HRMS calcd for $C_{20}H_{10}F_6N_2S$ 424.046890, found 424.04688.

4.3. General procedure for the Sonogashira coupling reactions

A mixture of **3** (1.593 g, 5.42 mmol), trimethylsilylacetylene (1.410 g, 14.35 mmol), $Pd(PPh_3)_2Cl_2$ (20 mg), cuprous iodide (20 mg), and triphenylphosphine (70 mg) was suspended in triethylamine (20 mL), and the resulting suspension was stirred and heated at 90 °C for 4 h. The solvent was evaporated and the crude product chromatographed directly with diethyl ether, affording a yellow solid. The isolated product **5** (air unstable) was dissolved in methanol (25 mL), treated with potassium fluoride (1.260 g, 21.68 mmol) and stirred at room temperature overnight. The solvent was evaporated and the crude product chromatographed directly with ether, affording a yellow solid. Compound **6** (very unstable) was immediately submitted to a second Sonogashira reaction. A mixture of **6** (0.998 g, 5.42 mmol), the corresponding halogenated compound (11.38 mmol), $Pd(PPh_3)_2Cl_2$ (20 mg), and cuprous iodide (20 mg) was suspended in triethylamine (20 mL), and the resulting suspension was stirred and heated at 60 °C for 18 h. The solvent was then evaporated and the crude product chromatographed directly with ether–*n*-hexane (20/80), affording the desired products **7a–e**.

4.3.1. Benzothiadiazole 5. Compound **5** is unstable and becomes a dark brown solid in a few minutes. ^{1}H NMR ($CDCl_3$): δ ppm 7.37 (s, 2H), 0.10 (s, 18H). ^{13}C NMR ($CDCl_3$): δ ppm 154.15, 133.08, 117.21, 103.58, 99.96, 0.11. FTIR (KBr, cm^{-1}): 2152, 1536, 1248, 842.

4.3.2. Benzothiadiazole 6. Compound **6** is unstable and becomes a dark brown solid in a few minutes. ^{1}H NMR ($CDCl_3$): δ ppm 7.76 (s, 2H), 3.69 (s,2H). ^{13}C NMR ($CDCl_3$): δ ppm 154.23, 133.14, 116.65, 85.33, 78.87. FTIR (KBr, cm^{-1}): 3052, 2988, 2294, 1545, 1426.

4.3.3. Benzothiadiazole 7a. ^{1}H NMR ($CDCl_3$): δ ppm 8.69 (d, 2H, J=4.6 Hz), 7.89 (s, 2H), 7.79–7.68 (m, 4H), 7.35–7.27 (m, 2H). ^{13}C NMR ($CDCl_3$): δ ppm 154.26, 132.37, 131.92, 129.02, 128.37, 122.39, 117.08, 97.41, 85.23. FTIR (KBr, cm^{-1}): 3037, 1537, 840, 750, 688. Mp 159 °C. HRMS calcd for $C_{22}H_{12}N_2S$ 336.07212, found 336.07217.

4.3.4. Benzothiadiazole 7b. ^{1}H NMR ($CDCl_3$): δ ppm 8.21 (d, 2H, J=8.2 Hz), 7.80–7.23 (m, 14H). ^{13}C NMR ($CDCl_3$): δ 154.14, 134.47, 133.08, 131.84, 129.78, 128.19, 127.81, 127.21, 126.96, 126.58, 126.07, 122.71, 116.56, 78.85. FTIR (KBr, cm^{-1}): 2935, 2860,1585, 1265, 844, 742, 615. Mp 116 °C. HRMS calcd for $C_{30}H_{16}N_2S$ 436.10342, found 436.10340.

4.3.5. Benzothiadiazole 7c. ^{1}H NMR ($CDCl_3$): δ ppm 7.74 (s, 2H), 7.61 (d, 4H, J=8.8 Hz), 6.92 (d, 4H, J=8.8 Hz), 3.85 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 160.14, 154.30, 133.51, 132.08, 117.02, 114.53, 114.04, 97.60, 84.31, 55.33. FTIR

(KBr, cm^{-1}): 3044, 1599, 1509, 1289. Mp 201 °C. HRMS calcd for $C_{24}H_{16}N_2O_2S$ 396.093250, found 396.09407.

4.3.6. Benzothiadiazole 7d. ^1H NMR ($CDCl_3$): δ ppm 7.76 (d, 2H, $J=1.0$ Hz), 7.29 (d, 4H, $J=9.0$ Hz), 6.58 (d, 4H, $J=8.8$ Hz) 2.92 (s, 3H) 2.91 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 154.31, 149.45, 133.22, 131.63, 116.71, 114.04, 108.44, 85.33, 78.89. FTIR (KBr, cm^{-1}): 3089, 2924, 1574, 1489, 1444, 1239. Mp 178 °C. HRMS calcd for $C_{26}H_{22}N_4S$ 422.156519, found 422.15663.

4.3.7. Benzothiadiazole 7e. ^1H NMR ($CDCl_3$): δ ppm 8.69 (d, 2H, $J=4.6$ Hz) 7.89 (s, 2H), 7.79–7.68 (m, 4H), 7.35–7.27 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 154.27, 150.29, 142.70, 136.19, 133.06, 127.96, 123.41, 116.97, 96.39, 84.45. FTIR (KBr, cm^{-1}): 3049, 2924, 1574, 1489, 1444, 1239. Mp 233 °C. Lit.[6a]=232–234. Anal. Calcd For $C_{20}H_{10}N_4S$ C, 70.99; H, 2.98; N, 16.56; S, 9.48. Found: C, 70.51; H, 2.94; N, 16.55.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2005.08.093. The complete set of the UV–vis, ^1H and ^{13}C NMR and Fluorescence spectra, and cyclic voltammograms and HRMS of the new compounds are available.

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