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ARTICLE

Effective Modulation of 2,1,3-Benzothiadiazoles and 2,1,3-Benzoselenadiazoles Photoluminescence Properties by Pd-Catalyzed C–H Bond Arylations

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A one step procedure towards 4-aryl-2,1,3-benzothiadiazoles, 4,7-diaryl-2,1,3-benzothiadiazoles and 4-aryl-2,1,3-benzoselenadiazoles using palladium-catalyzed regioselective C–H bond arylations of 2,1,3-benzothiadiazole and 2,1,3-benzoselenadiazole was developed. A donor–acceptor compound was also synthetized via two successive C–H bond arylations at C4 and C7 positions of the 2,1,3-benzothiadiazole unit. One of the major achivement of this methodoly refer from the fine modulation of the fluorescence wavelength with emission colors covering the blue to the red part of the visible spectrum by the simple introduction of the suitable aryl group on the 2,1,3-benzothiadiazole unit.

Introduction

Organic functional materials are finding more and more applications. Among them π-systems of polycyclic aromatic or heteroaromatic compounds such as 2,1,3-benzothiadiazole and 2,1,3-benzoselenadiazole are being actively investigated as cheap replacement of traditional inorganic semiconductors for the development of organic light-emitting diodes (OLED),[1] organic photovoltaics (OPV)[2] and bioprobes for bioimaging analyses.[3] These strong electron acceptor heterocycles represent a pivotal framework for the construction of organic donor–acceptor (D–A) dyes.[4] As example, in 2005, Ho and co-workers developed a new class of organics dyes (compound **I**) based on benzothiadiazole and benzoselenadiazole chromophores, which display a good power conversion efficiency (Figure 1, left).[5] Benzothiadiazoles are also used as acceptor units in donor acceptor (D–A) conjugated polymers, such as the polymer solar cell **II** (Figure 1, middle).[6]

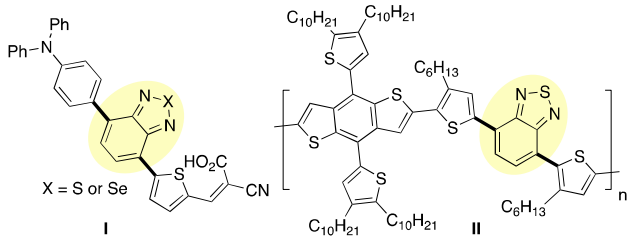

Figure 1. Examples of Useful Molecules Containing 4-Aryl-Benzothiadiazole or 4-Aryl-Benzoselenadiazole Units.

Despite these wide applications of 4-aryl-substituted 2,1,3-benzoselenadiazoles and 2,1,3-benzoselenadiazoles, their synthesis remains challenging and often requires multi-steps synthesis. Protocols involving bromination followed by palladium catalyzed Suzuki,[7] Stille,[8] or Hiyama[7a, 9] cross-coupling reactions are the most commonly employed (Figure 2a). Negishi reactions using an organozinc reagent prepared from benzofurazan through a magnesiation with bis(2,2,6,6-tetramethylpiperidin-1-yl)magnesium–lithium chloride complex ($TMP_2Mg{\cdot}2LiCl$) followed by transmetalation with zinc chloride, have also been reported (Figure 2b).[10] Since the discovery by Nakamura[11] and Otha[12] of the Pd-catalyzed C–H bond arylation of heteroarenes using aryl halides, this methodology has emerged as one of the most reliable for the eco-friendly formation of C–C bonds for the access to a wide variety of arylated heterocycles.[13] In 2013, Marder and co-workers reported the first example of C–H bond activation of 5,6-difluoro-2,1,3-benzothiadiazole using 10 mol% $Pd(OAc)_2$ associated to 20 mol% di-*tert*-butyl(methyl)phosphonium tetrafluoroborate (Figure 2c).[14] However, 2,1,3-benzothiadiazole was not reactive under these reactions conditions, demonstrating the huge impact of fluorine atom in

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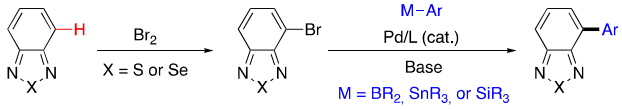
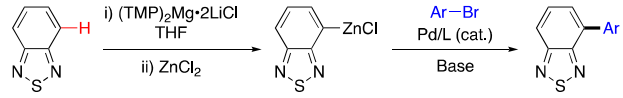
Pd-catalyzed C–H arylations via concerted-metalation deprotonation pathway.[15] This C–H bond protocol was then applied in polymerization using dibromobenzene derivatives,[16] and for the synthesis of organic dyes containing electron-rich (donor) and electron-poor (acceptor) sections.[17] An example of direct arylation at C4 position of 5-fluoro-2,1,3-benzothiadiazole has also been reported.[18] Latter, Marder and co-workers extended the substrate scope to other electron deficient 2,1,3-benzoselenadiazoles such as 5,6-dicyano- and 5,6-dinitro-substituted ones (Figure 2d).[19] To our knowledge there is no report on direct arylation, *via* a metal-catalyzed C–H bond activation, of unsubstituted 2,1,3-benzothiadiazole and 2,1,3-benzoselenadiazoles. Recently, we disclosed that phosphine-free palladium acetate catalyzes the C–H bond arylation of benzofurazan (Figure 2e).[20] Therefore, we decided to investigate the reactivity of unsubstituted 2,1,3-benzothiadiazole and 2,1,3-benzoselenadiazole in palladium-catalyzed C–H bond arylation for the straightforward access to 4-arylated 2,1,3-benzothiadiazoles and 2,1,3-benzoselenadiazoles (Figure 2e).

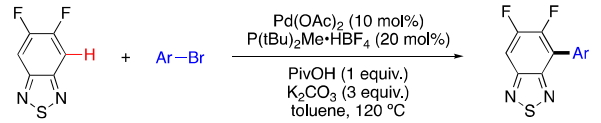
a. Synthesis of 4-Aryl 2,1,3-Benzothiadiazoles and 2,1,3-Benzoselenadiazoles Through Cross-Coupling Reactions[7-9]



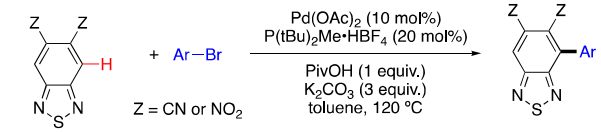
b.-Synthesis of 4-Aryl 2,1,3-Benzothiadiazoles Through Negishi Couplings[10]



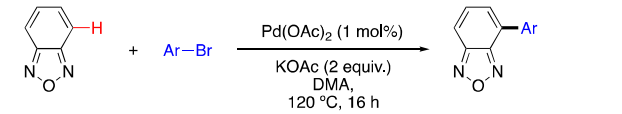
c. Pd-Catalyzed Direct Arylation of 5,6-Difluoro-2,1,3-Benzothiadiazole (Marder)[14]



d. Pd-Catalyzed Direct arylation of 2,1,3-Benzothiadazole-5,6-dicarbonitrile and 5,6-Dinitro-2,1,3-benzothiadiazole (Marder)[19]



e. Pd-Catalyzed Direct Arylation of Benzofurazan (our group)[20]



f. Pd-Catalyzed Direct Arylation of 2,1,3-Benzothiadiazole and 2,1,3-Benzoselenadiazole (this work)

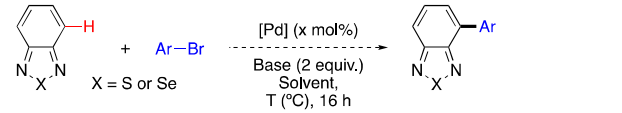
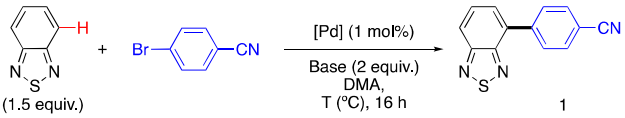


Figure 2. Previous Strategies to Synthetize 4-Aryl 2,1,3-Benzothiadiazoles and 2,1,3-Benzoselenadiazoles

Results and Discussion

Based on our recent results on palladium-catalyzed direct arylation of benzofurazan using aryl bromides as aryl source,[20] we examined the reactivity of 2,1,3-benzothiadiazole (Table 1). Using our previously reported reaction conditions, namely 1 mol% $Pd(OAc)_2$ in the presence of KOAc in DMA at 120 ºC, no reaction occurred between 2,1,3-benzothiadiazole and 4-bromobenzonitrile (Table 1, entry 1). Using a higher reaction temperature (i.e. 150 ºC), arylated 2,1,3-benzothiadiazole **1**, resulting from C–H bond activation at the C4 position, was obtained in 52% yield (Table 1, entry 2). When the reaction was performed in the presence of K_2CO_3 as base, no reaction occurred; while the used of potassium pivalate (PivOK) and potassium adamantane-1-carboxylate ($AdCO_2K$) allowed the formation of **1** in 84% and 65% yields, respectively. Other palladium sources were evaluated (Table 1, entries 6-8). $PdCl_2$ displayed a similar reactivity than $Pd(OAc)_2$, as the arylated product **1** was isolated in 82% yield (Table 1, entry 6). Palladium dimer complex $[Pd(C_3H_5)Cl]_2$ gave a slightly lower yield in **1** of 72% (Table 1, entry 7). A diphosphine palladium catalysts such as $PdCl(C_3H_5)$(dppb) did not allow to increase the yield compared to phosphine-free procedure (Table 1, entry 8).

Table 1. Optimization of the Reaction Conditions



Entry	[Pd]	Base	T (ºC)	Yield in **1** (%)[a]
1	$Pd(OAc)_2$	KOAc	120	0
2	$Pd(OAc)_2$	KOAc	150	52
3	$Pd(OAc)_2$	K_2CO_3	150	0
4	$Pd(OAc)_2$	PivOK	150	84
5	$Pd(OAc)_2$	$AdCO_2K$	150	65
6	$PdCl_2$	PivOK	150	82
7	$[Pd(C_3H_5)Cl]_2$	PivOK	150	77
8	$PdCl(C_3H_5)$(dppb)	PivOK	150	76

[a] isolated yield

With the best conditions in hands, namely 1 mol% phosphine-free $Pd(OAc)_2$ associated to PivOK as base in DMA at 150 ºC, we payed close attention to the scope of the reaction (Scheme 1). First, we examined the reactivity of *para*-substituted aryl bromides. Electron-deficient 4-bromonitrobenzene, 4-bromobenzaldehyde, ethyl 4-bromobenzoate, 4-bromopropiophenone and 4-bromobenzophenone reacted nicely to deliver the 4-arylated 2,1,3-benzothiadiazoles **2**–**6** in 65–74% yields. 1-Bromo-4-chlorobenzene displayed a lower reactivity, as the desired product **7** was isolated in only 55% yield, due to the formation of a side product arising from the

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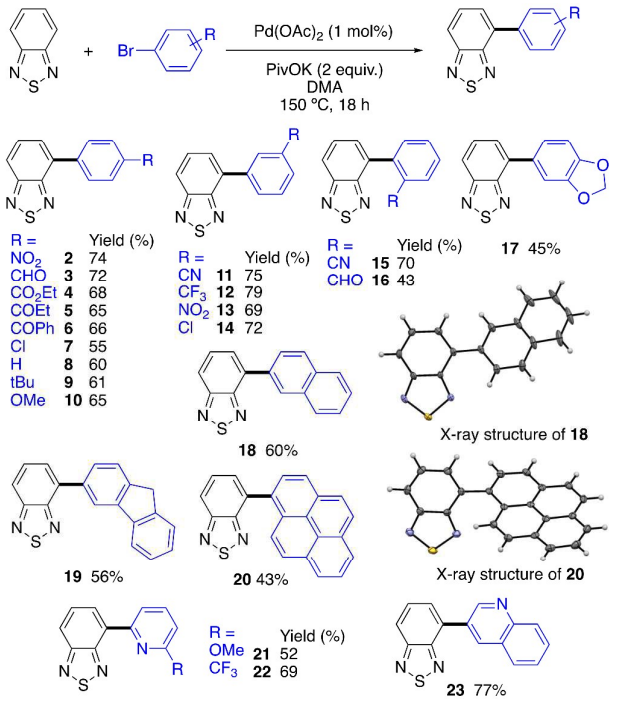
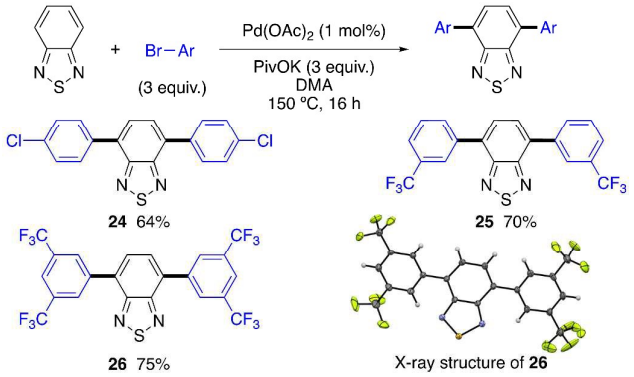
homocoupling of this aryl bromide. It should be noted that under these reaction conditions, the C–Cl bond did not react. Bromobenzene, 1-bromo-4-(*tert*-butyl)benzene and 4-bromoanisole have been successfully employed using this phosphine-free palladium coupling to give **8**–**10** in 60%–65% yields. A *meta*-substituent on the aryl bromide had almost no effect, as the desired arylated products **11**–**14** were obtained in good yields from 3-bromobenzonitrile, 1-bromo-3-(trifluoromethyl)benzene, 3-bromonitrobenzene, and 1-bromo-3-chlorobenzene. The reaction was almost not sensitive to the steric hindrance, as *ortho*-substituted aryl bromides such as 2-bromobenzonitrile, and 2-bromobenzaldehyde afforded the desired products **15** and **16** in good yields. 1,3-Benzodioxol motif has been introduced on the 2,1,3-benzothiadiazole **17**, which was isolated in 45% yield from 2,1,3-benzothiadiazole and 5-bromo-1,3-benzodioxole. Then, in order to show the potential of this method for the preparation of organic materials, we employed some π-extended aryl bromides as coupling partners. 2-Bromonaphthalene was efficiently coupled with 2,1,3-benzothiadiazole affording **18** in 60% yield. Its X-ray diffraction analysis confirmed the structure.[21] 3-Bromofluorene and 1-bromopyrene smoothly reacted allowing the formation of the 4-arylated 2,1,3-benzothiadiazoles **19** and **20** in 56% and 43% yields, respectively. *N*-containing heteroaryl bromides (e.g., 2-bromo-6-methoxypyridine, 2-bromo-6-(trifluoromethyl)pyridine, or 3-bromoquinoline) also nicely reacted to afford the desired products **21**–**23** in good yields.



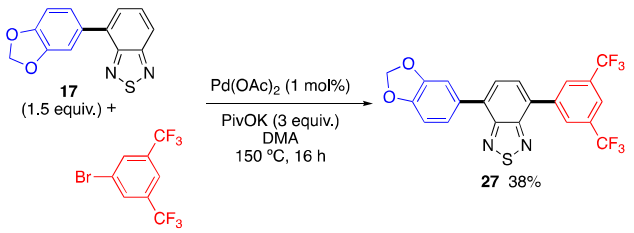
Scheme 1. Scope of Aryl Bromides in Palladium-Catalyzed Direct C4 Arylation of 2,1,3-Benzothiadiazole

Next, we investigated the formation of symmetrical 4,7-diaryl-2,1,3-benzothiadiazoles (Scheme 2). Using 3 equivalents of 1-bromo-4-chlorobenzene and 1 equivalent of 2,1,3-benzothiadiazole in the presence of 1 mol% $Pd(OAc)_2$ associated to 3 equivalents of PivOK in DMA at 150 ºC, we were pleased to isolate 4,7-bis(4-chlorophenyl)-2,1,3-benzothiadiazole (**24**) as the major product in 64% yield. From 1-bromo-3-(trifluoromethyl)benzene and 1-bromo-3,5-bis(trifluoromethyl)benzene, the 4,7-bis(aryl)-2,1,3-benzothiadiazoles **25** and **26** were synthetized in good yields. The regioselectivity of the diarylation was confirmed by X-ray diffraction analysis of **26**.[21]



Scheme 2. Scope of Aryl Bromides in Palladium-Catalyzed C4,C7 Diarylation of 2,1,3-Benzothiadiazole.

Using this methodology, we also carried out the straightforward synthesis of an unsymmetrical 4,7-diaryl-2,1,3-benzothiadiazole *via* two successive Pd-catalyzed C–H bond arylations (Scheme 3). Starting from **17**, a second arylation using 1-bromo-3,5-bis(trifluoromethyl)benzene afforded the 4,7-unsymmetrical diaryl 2,1,3-benzothiadiazole **28** in 38% yield, which should display push-pool properties.



Scheme 3. Example of Synthesis of a "Push-Pull" 4,7-Unsymmetrical Diaryl 2,1,3-benzothiadiazole by Iterative Palladium-Catalyzed C–H Bond Arylations

Syntheses of selenium containing compounds and the further utilization of these compounds in organic synthesis for the preparation of organic materials attracted less attention.[22] While a wide variety of thiadiazole containing compounds are known, on the contrary, a limited number of selenadiazoles containing compounds have been prepared.[23] Therefore, we turned our attention to the reactivity of 2,1,3-benzoselenadiazole in Pd-catalyzed C–H bond arylation (Scheme 4). For these reactions, we employed the same reaction conditions than for direct arylation of 2,1,3-benzothiadaziole, namely, 1 mol% $Pd(OAc)_2$ associated with PivOK as base in DMA at 150 ºC. Using 4-bromobenzonitrile, 1-

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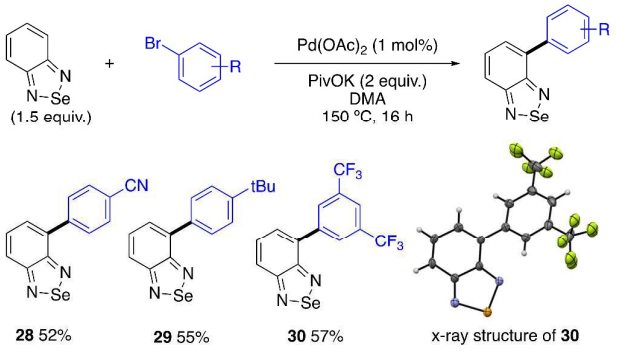
bromo-4-(*tert*-butyl)benzene and 1-bromo-3,5-bis(trifluoromethyl)benzene, we successfully prepared the 4-aryl-2,1,3-benzoselenadiazoles **28–30** in 52-57% yields. The regioselectivity of the arylation of 2,1,3-benzoselenadiazole was confirmed by X-ray diffraction analysis of **30**.[21] It should be noted that the reactions with 2,1,3-benzoselenadiazole are more sluggish than the reactions with 2,1,3-benzothiadiazole giving some unidentified decomposition products, which might explain that arylated products are obtained in lower yields.



Scheme 4. Scope of Aryl Bromides in Palladium-Catalyzed Direct C4 Arylation of 2,1,3-Benzoselenadiazole

Finally, in order to determine the interest of these new compounds as chromophores, preliminary photophysical studies have been conducted. UV-visible absorption spectra of the mono-substituted **9**, **17**, **19**, **20** and the di-substituted **24**, **26**, **27** 2,1,3-benzothiadiazoles, and the benzoselenadiazole derivative **29** were recorded in dichloromethane solution at room temperature, (see Figures 3 and 4) and the corresponding data are summarized in Table 2. As common feature for all the investigated compounds, their electronic absorption spectra exhibit characteristic set of absorption bands for benzothiadiazole and benzoselenadiazole derivatives, with intense and well-resolved absorption bands in the UV region, from 250 to 350 nm, together with a moderately intense and broad absorption band tailing up in the visible region of the spectrum. The mono-substituted 2,1,3-benzothiadiazole **9**, bearing a *tert*-butyl group on the aryl substituent is considered as a reference compound for the studied series.[24] The absorption spectrum of **9** shows, in the UV region, a broad band centered at 250 nm and well-resolved bands from 280 to 325 nm, while at lower energy a weaker and broad band which tails up to 420 nm is observed (Figure 3). According to previous studies, the UV absorption bands of **9** arises from $^1(\pi\text{-}\pi^*)$ transitions of the *p*-*tert*-butylphenyl substituent and the benzothiadiazole core, respectively.[24c] At lower energy, from 325 to 420 nm, the broad absorption band is assigned to charge transfer transition (CT) from the electron-donating aryl substituent to the π* accepting benzothiadiazole moiety.[24c] Replacing the *p*-*tert*-butylaryl substituent by the benzodioxole in **17**, red-shifts the CT transition of 50 nm, as a result of larger electron-donating properties of the dioxole group. In comparison with **9**, the fluorene-based 2,1,3-benzothiadiazole **19** exhibits higher absorptivity within the whole spectrum, due to additional $^1(\pi\text{-}\pi^*)$ transitions of this π-extended system but with no significant shift of the absorption bands. Similarly, replacing the fluorenyl (**19**) by a pyrenyl group (**20**), gives rise to very intense absorption bands in the UV region, the absorption profile of the benzothiadiazole core being overlapped by the intense and well-resolved absorption bands of the pyrene moiety. The pyrene moiety in **20** induces a small red-shifted of the CT band ($\Delta\lambda$ = 15 nm), compared with the fluorene substituent in **19**. Based on previous experimental and theoretical studies of benzothiadiazole derivatives, the observed spectral changes by incorporation of various aromatic substituents can be interpreted as a modification of the highest-occupied molecular orbital (HOMO) while the lowest-unoccupied molecular orbital (LUMO), centered on the core, stays almost unchanged.[24c] In other words, increasing the electron-richness (**17**) and/or extension of the π-system (**19**, **20**) destabilize the HOMO energy level resulting in a decrease of the HOMO-LUMO gap with respect to **9**. As far as the di-substituted 2,1,3-benzothiadiazoles are concerned, compounds **24** bearing two *p*-chlorophenyl and **26** having with two 3,5-bis(trifluoromethyl)aryl groups, exhibit similar absorption profiles with a blue-shift of the charge-transfer band in **24**, compare to **26**, attributed to the strong electron-withdrawing CF_3 groups (Figure 4). As expected, the compound **27** shows the lowest-energy CT band centered at 400 nm, due to the presence of both electron-donating dioxole substituent and electron-accepting $(CF_3)_2$-Ar) and benzothiadiazole groups, which give rise to strong charge-transfer transitions.

Table 2. Photophysical Data of the Investigated Compounds.

	Absorption λ_{abs}[a]/nm (ε 10^3/$M^{-1}cm^{-1}$)	Emission at 298 K[a] λ_{em}[a]/nm	φa,b
9	306 (5.8), 316 (7.0), 358 (3.0)	468	0.88
17	266 (7.2), 308 (6.1), 318 (5.7),376 (2.3)	530	0.79
19	284 (19.4), 306 (18.2), 316 (15.7),376 (7.5)	510	0.90
20	268 (24.7), 378 (39.0), 316 (24.8), 326 (28.4), 344 (36.9), 382 (6.3)	530 [d]	nd
24	270 (11.7), 320 (3.3), 384 (1.9)	492	0.53
26	272 (18.1), 312 (10.8), 320 (9.8), 362 (10.8)	449	0.89
27	291 (5.9), 318 (3.4), 400 (3.4)	555	0.19
29	250 (6.6), 333 (6.3), 383 (1.9)	503	0.42

[a] Measured in CH_2Cl_2 solution at 298 K (C ≈ 10^{-5} M), with 350 nm excitation. [b] ref : $Ru(bpy)_3Cl_2$. [c] Measured in a drop casted film, from CH_2Cl_2 solution, λ_{ex} = 350 nm.

Interestingly, the seleno-derivative **29** displays similar absorption profile than its sulfur analogue **9**, with absorption bands corresponding to $^1(\pi\text{-}\pi^*)$ transitions on the *tert*-butylphenyl substituent of the benzoselenodiazole core and at

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lower-energy, a moderately intense band arising from the charge-transfer transition (Figure 3). Notably, compared with **9** the seleno-derivative **29** exhibits a large red-shift of the absorption bands belonging to the benzoselenodiazole core and a moderately bathochromic effect of the CT transitions, a feature in agreement with previous reports on related benzoselenodiazole compounds.[23b, 25]

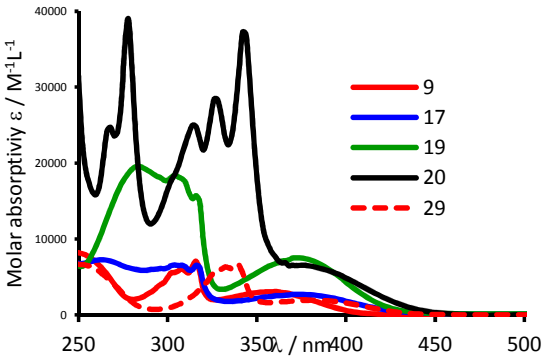


Figure 3. Absorption Spectra in CH_2Cl_2 at 298 K (C ≈ 10^{-5} M) of the Mono-Substituted Compounds **9** (red line), **17** (blue line), **19** (green line), **20** (black line) and **29** (red dotted line).

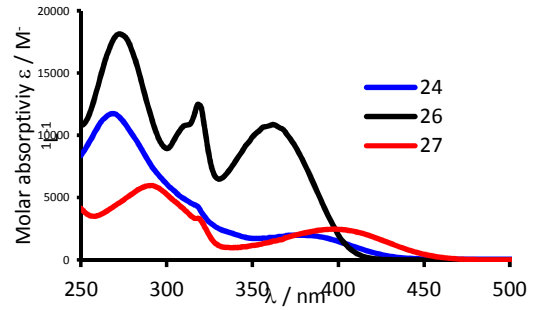
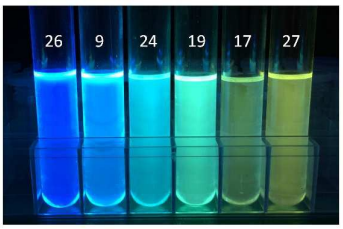


Figure 4. Absorption Spectra in CH_2Cl_2 at 298 K (C ≈ 10^{-5} M) of the Di-Substituted Compounds **24** (blue line), **26** (black line) and **27** (red line).

quantum yield (Φ = 19 %), in agreement with the energy gap law. Compounds **9** and **26** display a blue emission, while **17** and **19** bearing an electron donating aryl or a fluorenyl group, respectively, emit in the orange-red region of the spectrum. The benzoselenodiazole **29** displays luminescence with a maximum at 503 nm, red-shifted by about 35 nm with respect to the analogue **9**, a feature comparable to that reported for related benzoselenodiazole compounds.[23b, 25]



Photograph of 2,1,3-Benzothiadiazole Derivatives in CH_2Cl_2 Solution under 350 nm Irradiation

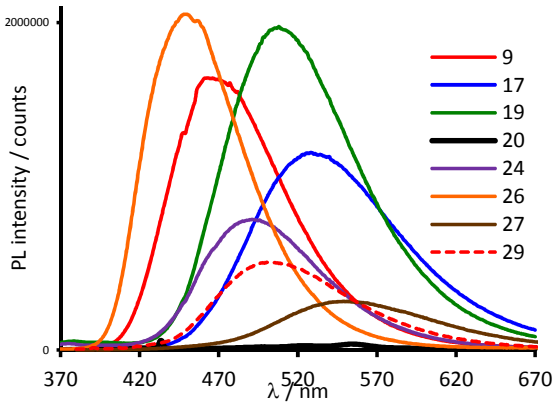


Figure 5. Emission Spectra in CH_2Cl_2 at 298 K (C ≈ 10^{-5} M) of **9** (red line), **17** (orange line), **19** (pink line), **20** (black line), **24** (green line), **26** (blue line), **27** (brown line) and **29** (red dotted line), with λ_{ex} = 350 nm.

The emission spectra of **9**, **17**, **19**, **20**, **24**, **26**, **27** and **29** are shown in Figure 5 and the emission data are compiled in Table 2. Except compound **20**, all investigated compounds are strongly emissive in dichloromethane solution at room temperature. Remarkably, they exhibit good to excellent photoluminescence quantum yield (Φ) in solution as high as 90 % (**19**), whatever the nature of the substituent. Interestingly, the emission color goes from the blue (λ_{em} = 449 nm for **26**) to the red (λ_{em} = 555 nm for **27**) part of the spectrum, strongly depending on the nature of the incorporated aryl group on the benzothiadiazole core. The emission wavelength is fine-tuned by changing the electronic richness of the system and/or by introducing an extended π-system (fluorene, pyrene), as well as by replacing the sulfur atom by Se (**9** vs. **29**). The emission can be controlled by the CT transitions. For instance, the multi-polar derivative **27** displays the more red-shifted emission, consistently with CT absorption bands at lower-energy. However, this red-shifted fluorescence is accompanied with a decrease of the photoluminescence

Note that compound **20** is non-emissive in fluid solution. This behavior can be explained by the presence of the pyrenyl group since pyrenes are known to be subject to self-quenching through the formation of aggregates or excimers in solution. Interestingly, the luminescence of **20** can be turned-on in the solid state. The solid-state fluorescence, measured on a drop casted film at 298 K (from dichloromethane solution), is characterized by a broad emission band centered at 530 nm, likely originated from the excimer state (Figure 6).[26]

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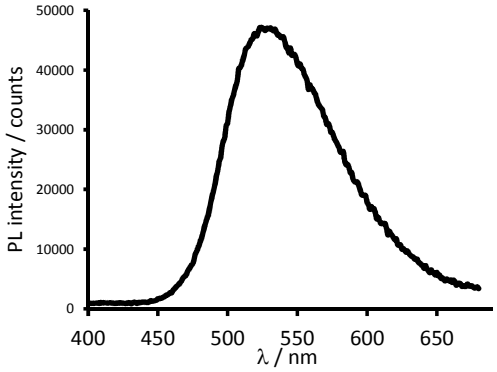

Figure 6. Emission Spectrum of **20** in a Drop Cast Film from CH_2Cl_2 solution, with λ_{ex} = 350 nm.

Conclusions

In summary, 2,1,3-benzothiadiazole and 2,1,3-benzoselenadiazole can be efficiently arylated at C4/C7 positions *via* palladium catalyzed C–H bond activation. Simple phosphine-free palladium acetate associated to KOAc as base in DMA was found to be the best reaction conditions. A wide range of functions such as methoxy, chloro, formyl, propionyl, benzoyl, ester, nitrile, trifluoromethyl or nitro on the aryl bromide is tolerated. Some sterically hindered, π-extended and heteroaromatic aryl bromides have also been employed successfully, demonstrating the potential of this methodology for the preparation of organic materials. Interestingly, this method allows the introduction of aryl substituents with different electronic properties in one step resulting in a fine modulation of the fluorescence wavelength with emission colors covering the blue to the red part of the visible spectrum. The combination of these photophysical effects make such materials especially interesting for photovoltaic and OLED applications.

Conflicts of interest

There are no conflicts to declare.

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