Journal of Materials Chemistry C

PAPER

View Article Online
View Journal | View Issue

Cite this: J. Mater. Chem. C, 2018, 6, 1731

Effective modulation of the photoluminescence properties of 2,1,3-benzothiadiazoles and 2,1,3-benzoselenadiazoles by Pd-catalyzed C–H bond arylations†

Imane Idris,[ab] Thibault Tannoux,[a] Fazia Derridj,[b] Vincent Dorcet,[a] Julien Boixel,* [a] Veronique Guerchais,* [a] Jean-François Soulé* [a] and Henri Doucet* [a]

Received 24th November 2017,
Accepted 5th January 2018

DOI: 10.1039/c7tc05395a

rsc.li/materials-c

A one step procedure towards the synthesis of 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 synthesized *via* two successive C–H bond arylations at C4 and C7 positions of the 2,1,3-benzothiadiazole unit. One of the major achievements of this methodology arises from the fine modulation of the fluorescence wavelength with emission colors covering blue to red regions 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 increasing number 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 inexpensive replacements 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 an example, in 2005, Ho *et al.* developed a new class of organics dyes (compound **I**) based on benzothiadiazole and benzoselenadiazole chromophores, which displayed a good power conversion efficiency (Fig. 1, left).[5] Benzothiadiazoles are also used as acceptor units in donor acceptor (D–A) conjugated polymers, such as the polymer solar cell **II** (Fig. 1, middle).[6]

Despite these widespread applications of 4-aryl-substituted 2,1,3-benzoselenadiazoles and 2,1,3-benzoselenadiazoles, their syntheses remain challenging and often require multiple steps. Protocols involving bromination, followed by palladium catalyzed (Suzuki,[7] Stille,[8] or Hiyama[7a,9]) cross-coupling reactions are the most commonly employed methods (Fig. 2a). Negishi reactions

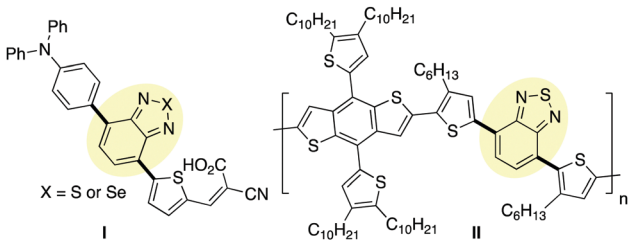


Fig. 1 Examples of useful molecules containing 4-aryl-benzothiadiazole or 4-aryl-benzoselenadiazole units.

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 (Fig. 2b).[10] Since the discovery of the Pd-catalyzed C–H bond arylation of heteroarenes using aryl halides by Nakamura *et al.*[11] and Otha *et al.*,[12] this methodology has emerged as one of the most reliable procedures for the eco-friendly formation of C–C bonds, for the access to a wide variety of arylated heterocycles.[13] In 2013, Marder *et al.* reported the first example of C–H bond activation of 5,6-difluoro-2,1,3-benzothiadiazole using 10 mol% $Pd(OAc)_2$ associated with 20 mol% di-*tert*-butyl(methyl)phosphonium tetrafluoroborate (Fig. 2c).[14] However, 2,1,3-benzothiadiazole was not reactive under these reaction conditions, demonstrating the huge impact of the fluorine atom in Pd-catalyzed C–H arylations *via* the 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

[a] Univ Rennes, CNRS UMR6226, F-3500 Rennes, France. E-mail: Julien.boixel@univ-rennes1.fr, jean-francois.soule@univ-rennes1.fr
[b] Laboratoire de physique et chimie des Matériaux (LPCM), UMMTO University, BP 17 RP, 15000 Tizi-Ouzou, Algeria

† Electronic supplementary information (ESI) available. CCDC 1564784, 1577123, 1564844 and 1576377. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7tc05395a

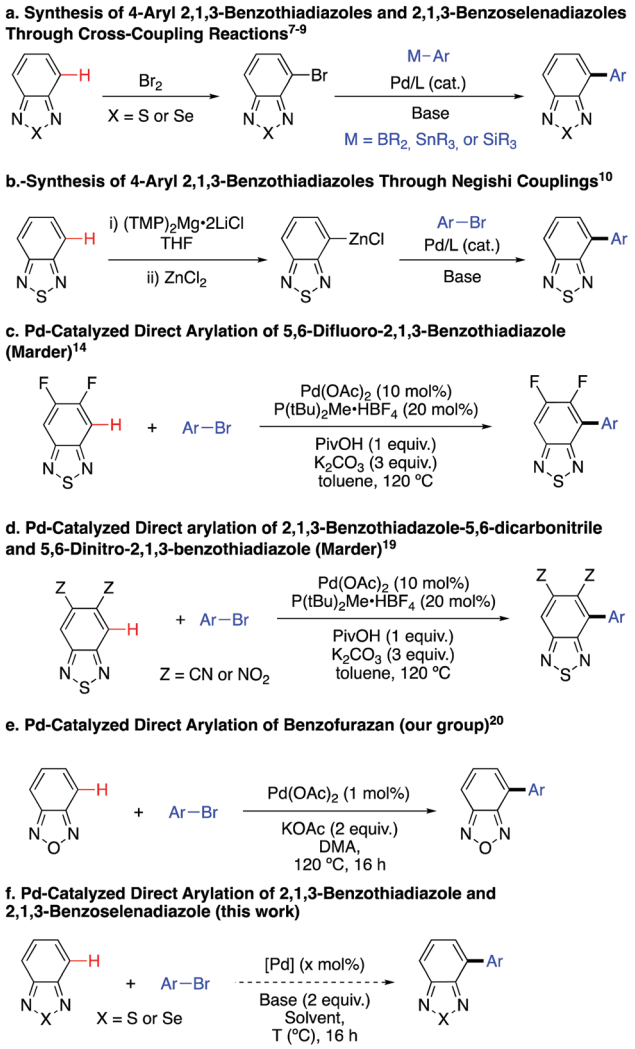


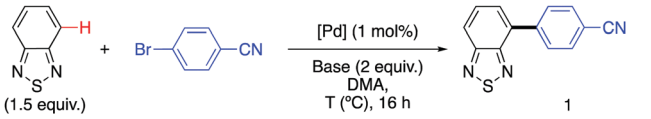
Fig. 2 Previously reported strategies to synthesize 4-aryl 2,1,3-benzothiadiazoles and 2,1,3-benzoselenadiazoles.

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] Later, Marder *et al.* extended the substrate scope to other electron deficient 2,1,3-benzoselenadiazoles such as 5,6-dicyano- and 5,6-dinitro-substituted ones (Fig. 2d).[19] To the best of 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 (Fig. 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 to gain the straightforward access to 4-arylated 2,1,3-benzothiadiazoles and 2,1,3-benzoselenadiazoles (Fig. 2e).

Results and discussion

Based on our recent results on palladium-catalyzed direct arylation of benzofurazan using aryl bromides as the aryl source,[20] we

Table 1 Optimization of the reaction conditions

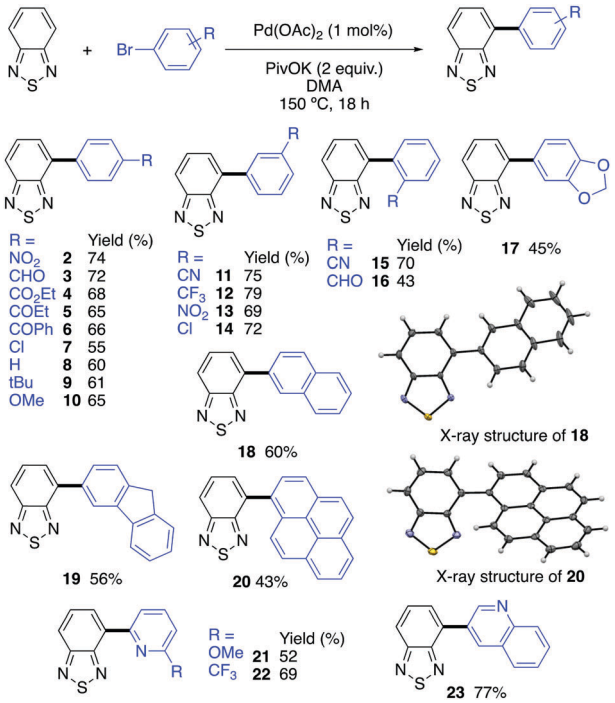


Entry	[Pd]	Base	T (°C)	Yield in **1**[a] (%)
1	$Pd(OAc)_2$	KOAc	120	0
2	$Pd(OAc)_2$	KOAc	150	52
3	$Pd(OAc)_2$	K_2CO_3	150	0
4	$Pd(OAc)_2$	PivOK	150	84
5	$Pd(OAc)_2$	$AdCO_2K$	150	65
6	$PdCl_2$	PivOK	150	82
7	$[Pd(C_3H_5)Cl]_2$	PivOK	150	77
8	$PdCl(C_3H_5)$(dppb)	PivOK	150	76

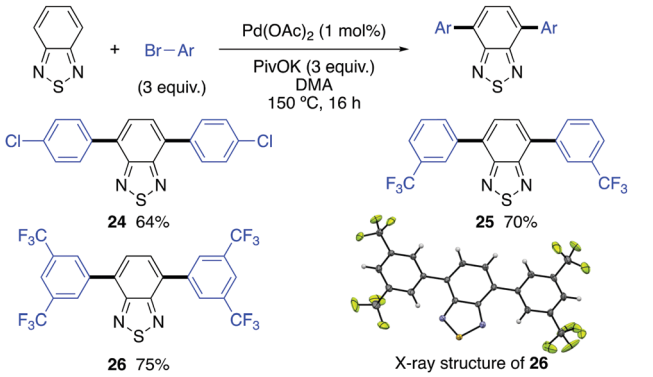
[a] Isolated yield.

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 °C, no reaction occurred between 2,1,3-benzothiadiazole and 4-bromobenzonitrile (Table 1, entry 1). Using a higher reaction temperature (*i.e.* 150 °C), arylated 2,1,3-benzothiadiazole **1**, resulting from C–H bond activation at the C4 position, was obtained with 52% yield (Table 1, entry 2). When the reaction was performed in the presence of K_2CO_3 as the base, no reaction occurred, while the use of potassium pivalate (PivOK) and potassium adamantane-1-carboxylate ($AdCO_2K$) allowed the formation of **1** with 84% and 65% yields, respectively. Other palladium sources were also evaluated (Table 1, entries 6–8). $PdCl_2$ displayed the reactivity similar to that of $Pd(OAc)_2$ 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 of **1**, which was 72% (Table 1, entry 7). Diphosphine palladium catalysts, such as $PdCl(C_3H_5)$(dppb), did not increase the yield compared to the phosphine-free procedure (Table 1, entry 8).

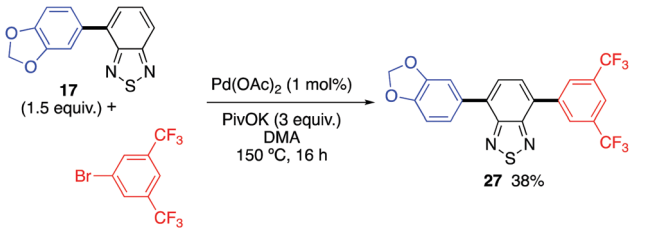
With the best conditions in hand, namely, 1 mol% phosphine-free $Pd(OAc)_2$ associated with PivOK as the base in DMA at 150 °C, we paid close attention to the scope of the reaction (Scheme 1). First, we examined the reactivity of *para*-substituted aryl bromides. Electron-deficient 4-bromonitrobenzene, 4-bromobenzaldehyde, ethyl 4-bromobenzoate, 4-bromopropiophenone and 4-bromobenzophenone reacted efficiently to deliver the 4-arylated 2,1,3-benzothiadiazoles **2–6** in 65–74% yields. However, 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 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 in this phosphine-free palladium coupling to afford **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 the *ortho*-substituted aryl bromides such as 2-bromo-



Scheme 1 Scope of aryl bromides in palladium-catalyzed direct C4 arylation of 2,1,3-benzothiadiazole.



Scheme 2 Scope of aryl bromides in palladium-catalyzed C4, C7 diarylation of 2,1,3-benzothiadiazole.



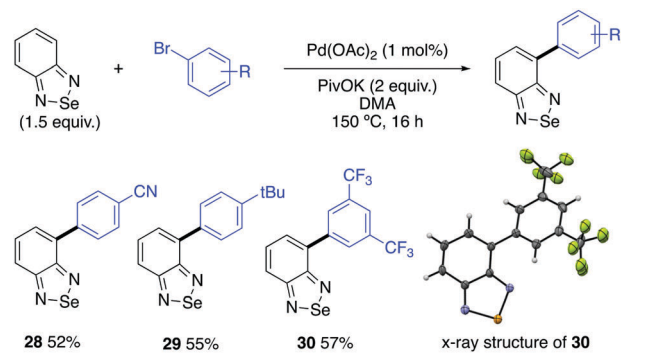
Scheme 3 An example of synthesis of a "push–pull" 4,7-unsymmetrical diaryl 2,1,3-benzothiadiazole by iterative palladium-catalyzed C–H bond arylations.

benzonitrile and 2-bromobenzaldehyde afforded the desired products **15** and **16**, respectively, in good yields. Furthermore, 1,3-benzodioxol motif was introduced on the 2,1,3-benzothiadiazole **17**, which was isolated with a 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 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.

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 with 3 equivalents of PivOK in DMA at 150 °C, 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, 4,7-bis(aryl)-2,1,3-benzothiadiazoles **25** and **26** were synthesized in good yields. The regioselectivity of the diarylation was confirmed by X-ray diffraction analysis of **26**.[21]

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–pull properties.

Syntheses of selenium containing compounds and the further utilization of these compounds in organic synthesis for the preparation of organic materials have attracted less attention.[22] Although a wide variety of thiadiazole containing compounds are known, only 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 used for the direct arylation of 2,1,3-benzothiadaziole, namely, 1 mol% $Pd(OAc)_2$ associated with PivOK



Scheme 4 Scope of aryl bromides in palladium-catalyzed direct C4 arylation of 2,1,3-benzoselenadiazole.

as the base in DMA at 150 °C. Using 4-bromobenzonitrile, 1-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 were more sluggish than the reactions with 2,1,3-benzothiadiazole, resulting in some unidentified decomposition products, which might explain the reason for obtaining arylated products in lower yields.

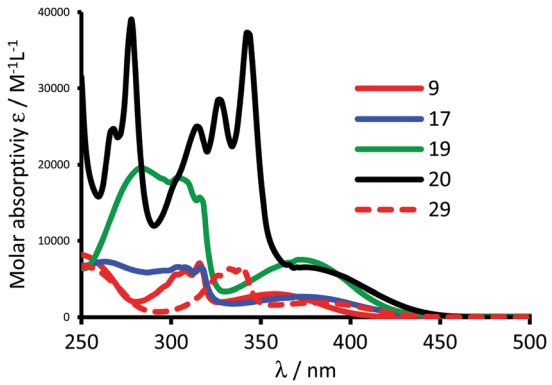


Fig. 3 Absorption spectra in CH_2Cl_2 at 298 K ($C \approx 10^{-5}$ M) of the mono-substituted compounds **9** (red line), **17** (blue line), **19** (green line), **20** (black line) and **29** (red dotted line).

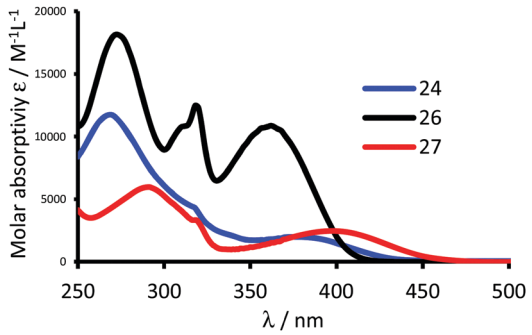


Fig. 4 Absorption spectra in CH_2Cl_2 at 298 K ($C \approx 10^{-5}$ M) of the di-substituted compounds **24** (blue line), **26** (black line) and **27** (red line).

Finally, in order to determine the scope of these new compounds as chromophores, preliminary photophysical studies were conducted. UV-visible absorption spectra of the mono-substituted **9**, **17**, **19**, and **20** and the di-substituted **24**, **26**, and **27** 2,1,3-benzothiadiazoles, and the benzoselenadiazole derivative **29** were recorded in a dichloromethane solution at room temperature (see Fig. 3 and 4); the corresponding data are summarized in Table 2. As a common feature for all the investigated compounds, their electronic absorption spectra exhibited a 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 was considered as a reference compound for the studied series.[24] The absorption spectrum of **9** shows a broad band centered at 250 nm and well-resolved bands from 280 to 325 nm in the UV region, while at lower energy a weaker and broad band which tails up to 420 nm is observed (Fig. 3). According to previous studies, the UV absorption bands of **9** arise from $^1(\pi-\pi^*)$ 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 by 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 entire spectrum due to additional $^1(\pi-\pi^*)$ 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**) leads to very intense absorption bands in the UV region; the absorption profile of the benzothiadiazole core are overlapped by the intense and well-resolved absorption bands of the pyrene moiety. The pyrene moiety in **20** induces a small red-shift of the CT band ($\Delta\lambda$ = 15 nm) as compared to 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

Table 2 Photophysical data of the investigated compounds

	Absorption	Emission at 298 K[a]	
	λ_{abs}[a]/nm (ε 10^3/M^{-1} cm^{-1})	λ_{em}[a]/nm	ϕ[a,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[c]	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 a CH_2Cl_2 solution at 298 K ($C \approx 10^{-5}$ 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.

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**) destabilizes 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 bearing two *p*-chlorophenyl groups (**24**) or two 3,5-bis(trifluoromethyl)aryl groups (**26**) exhibit similar absorption profiles, but with a blue-shift of the charge-transfer band in **24** as compared to **26**; this is attributed to the strong electron-withdrawing CF_3 groups (Fig. 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 $(CF_3)_2Ar$ and benzothiadiazole groups, which give rise to strong charge-transfer transitions.

Interestingly, the seleno-derivative **29** displays an absorption profile similar to its sulfur analogue **9** with absorption bands corresponding to $^1(\pi–\pi^*)$ transitions on the *tert*-butylphenyl substituent of the benzoselenodiazole core and at lower-energy, a moderately intense band arising from the charge-transfer transition (Fig. 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 moderate bathochromic effect of the CT transitions, which is a feature in agreement with previous reports on related benzoselenodiazole compounds.[23b,25]

The emission spectra of **9**, **17**, **19**, **20**, **24**, **26**, **27** and **29** are shown in Fig. 5 and the emission data are compiled in Table 2. Except compound **20**, all the 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**) irrespective of the nature of the substituent (Fig. 6). Interestingly, the emission color changes from blue (λ_{em} = 449 nm for **26**) to red (λ_{em} = 555 nm for **27**) in the visible spectrum, strongly depending on the nature of the incorporated aryl group on the benzothiadiazole core. The emission wavelength was 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 quantum yield (ϕ = 19%), which is 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, display an orange-red emission. The benzoselenodiazole **29** displays luminescence with a maximum at 503 nm, which is red-shifted by about 35 nm with respect to the analogue **9**; this feature is comparable to that reported for related benzoselenodiazole compounds (Fig. 5).[23b,25]

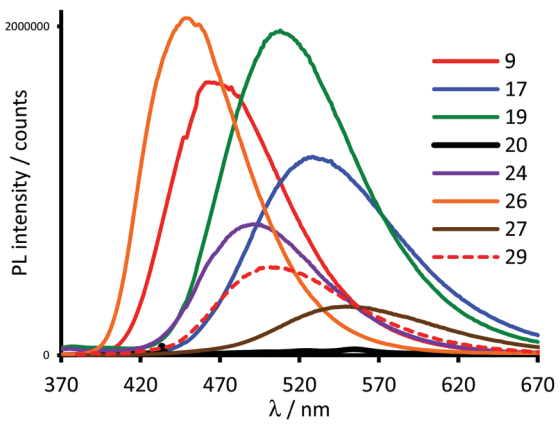


Fig. 5 Emission Spectra in CH_2Cl_2 at 298 K ($C \approx 10^{-5}$ M) of **9** (red line), **17** (orange line), **19** (pink line), **20** (black line), **24** (green line), **26** (blue line), **27** (brown line) and **29** (red dotted line), with λ_{ex} = 350 nm.

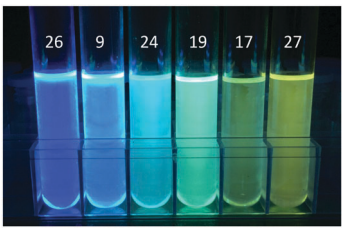


Fig. 6 Photograph of 2,1,3-benzothiadiazole derivatives in CH_2Cl_2 solution under 350 nm irradiation.

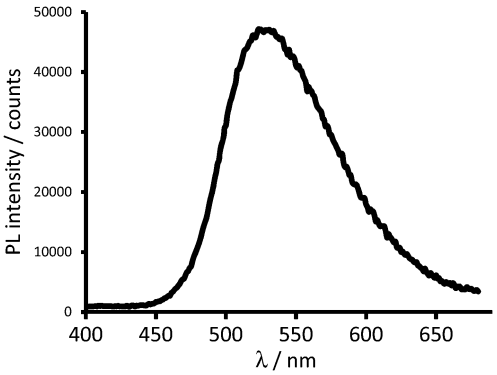


Fig. 7 Emission spectrum of **20** in a drop cast film from CH_2Cl_2 solution, with λ_{ex} = 350 nm.

It should be noted 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 subjected 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, which probably originated from the excimer state (Fig. 7).[26]

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 and KOAc as the base in DMA were found to be the best

reaction conditions. A wide range of functional groups such as methoxy, chloro, formyl, propionyl, benzoyl, ester, nitrile, trifluoromethyl or nitro on the aryl bromide were tolerated. Some sterically hindered, π-extended and heteroaromatic aryl bromides were also successfully employed, 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 blue to red regions of the visible spectrum. The combination of these photophysical effects makes such materials particularly interesting for photovoltaic and OLED applications.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We thank the Algerian ''Ministry of Higher Education and Scientific Research'' for a fellowship to I. I. We thank CNRS and ''Rennes Metropole'' for providing financial support.

Notes and references

1 N. J. Findlay, B. Breig, C. Forbes, A. R. Inigo, A. L. Kanibolotsky and P. J. Skabara, *J. Mater. Chem. C*, 2016, **4**, 3774–3780.
2 Y. Wu and W. Zhu, *Chem. Soc. Rev.*, 2013, **42**, 2039–2058.
3 B. A. D. Neto, P. H. P. R. Carvalho and J. R. Correa, *Acc. Chem. Res.*, 2015, **48**, 1560–1569.
4 (*a*) J. E. Barnsley, G. E. Shillito, C. B. Larsen, H. van der Salm, L. E. Wang, N. T. Lucas and K. C. Gordon, *J. Phys. Chem. A*, 2016, **120**, 1853–1866; (*b*) L. Chen, X. Li, W. Ying, X. Zhang, F. Guo, J. Li and J. Hua, *Eur. J. Org. Chem.*, 2013, 1770–1780.
5 M. Velusamy, K. R. Justin Thomas, J. T. Lin, Y.-C. Hsu and K.-C. Ho, *Org. Lett.*, 2005, **7**, 1899–1902.
6 M. Wang, X. Hu, P. Liu, W. Li, X. Gong, F. Huang and Y. Cao, *J. Am. Chem. Soc.*, 2011, **133**, 9638–9641.
7 (*a*) Y. Geng, A. C. A. Chen, J. J. Ou, S. H. Chen, K. Klubek, K. M. Vaeth and C. W. Tang, *Chem. Mater.*, 2003, **15**, 4352–4360; (*b*) S.-i. Kato, T. Matsumoto, T. Ishi-i, T. Thiemann, M. Shigeiwa, H. Gorohmaru, S. Maeda, Y. Yamashita and S. Mataka, *Chem. Commun.*, 2004, 2342–2343; (*c*) X. Zhang, H. Gorohmaru, M. Kadowaki, T. Kobayashi, T. Ishi-i, T. Thiemann and S. Mataka, *J. Mater. Chem.*, 2004, **14**, 1901–1904; (*d*) D. Aldakov, M. A. Palacios and P. Anzenbacher, Jr., *Chem. Mater.*, 2005, **17**, 5238–5241; (*e*) M. Velusamy, K. R. J. Thomas, J. T. Lin and Y. S. Wen, *Tetrahedron Lett.*, 2005, **46**, 7647–7651; (*f*) M. Velusamy, K. R. J. Thomas, J. T. Lin, Y.-C. Hsu and K.-C. Ho, *Org. Lett.*, 2005, **7**, 1899–1902; (*g*) M. Haussler, Y. P. Lok, M. Chen, J. Jasieniak, R. Adhikari, S. P. King, S. A. Hague, C. M. Forsyth, K. Winzenberg, S. E. Watkins, E. Rizzardo and G. J. Wilson, *Macromolecules*, 2010, **43**, 7101–7110; (*h*) H. Zhang, X. Wan, X. Xue, Y. Li, A. Yu and Y. Chen, *Eur. J. Org. Chem.*, 2010, 1681–1687; (*i*) L. Han, X. Zu, Y. Cui, H. Wu, Q. Ye and J. Gao, *Org. Electron.*, 2014, **15**, 1536–1544; (*j*) X. Yang, J. Zhao, L. Wang, J. Tian and L. Sun, *RSC Adv.*, 2014, **4**, 24377–24383; (*k*) J. E. Donaghey, A. Armin, P. L. Burn and P. Meredith, *Chem. Commun.*, 2015, **51**, 14115–14118; (*l*) J. Geng, Y. Dai, X.-X. Wang, M.-Y. Hu, T. Tao and W. Huang, *Tetrahedron*, 2015, **71**, 654–662; (*m*) K. Zhu, C. A. O'Keefe, V. N. Vukotic, R. W. Schurko and S. J. Loeb, *Nat. Chem.*, 2015, **7**, 514–519; (*n*) D. L. Crossley, I. Vitorica-Yrezabal, M. J. Humphries, M. L. Turner and M. J. Ingleson, *Chem. – Eur. J.*, 2016, **22**, 12439–12448; (*o*) L. Wang, W. Huang, R. Li, D. Gehrig, P. W. M. Blom, K. Landfester and K. A. I. Zhang, *Angew. Chem., Int. Ed.*, 2016, **55**, 9783–9787; (*p*) R. Li, Z. J. Wang, L. Wang, B. C. Ma, S. Ghasimi, H. Lu, K. Landfester and K. A. I. Zhang, *ACS Catal.*, 2016, **6**, 1113–1121; (*q*) C. Song, Y. Ling, L. Jin, M. Zhang, D.-L. Chen and Y. He, *Dalton Trans.*, 2016, **45**, 190–197.
8 (*a*) K. R. J. Thomas, J. T. Lin, M. Velusamy, Y.-T. Tao and C.-H. Chuen, *Adv. Funct. Mater.*, 2004, **14**, 83–90; (*b*) G. Qian, Z. Zhong, M. Luo, D. Yu, Z. Zhang, D. Ma and Z. Y. Wang, *J. Phys. Chem. C*, 2009, **113**, 1589–1595; (*c*) G. Qian, Z. Zhong, M. Luo, D. Yu, Z. Zhang, Z. Y. Wang and D. Ma, *Adv. Mater.*, 2009, **21**, 111–116; (*d*) Y.-H. Chen, L.-Y. Lin, C.-W. Lu, F. Lin, Z.-Y. Huang, H.-W. Lin, P.-H. Wang, Y.-H. Liu, K.-T. Wong, J. Wen, D. J. Miller and S. B. Darling, *J. Am. Chem. Soc.*, 2012, **134**, 13616–13623; (*e*) C. Tong, J. Chang, J. M. Tan, G. Dai, K.-W. Huang, H. S. O. Chan and C. Chi, *Org. Biomol. Chem.*, 2013, **11**, 5683–5691; (*f*) S.-i. Kato, T. Furuya, M. Nitani, N. Hasebe, Y. Ie, Y. Aso, T. Yoshihara, S. Tobita and Y. Nakamura, *Chem. – Eur. J.*, 2015, **21**, 3115–3128; (*g*) S.-J. Woo, S. Park, J.-E. Jeong, Y. Hong, M. Ku, B. Y. Kim, I. H. Jang, S. C. Heo, T. Wang, K. H. Kim, J. Yang, J. H. Kim and H. Y. Woo, *ACS Appl. Mater. Interfaces*, 2016, **8**, 15937–15947.
9 K. Shimizu, Y. Minami, Y. Nakao, K.-i. Ohya, H. Ikehira and T. Hiyama, *Chem. Lett.*, 2013, **42**, 45–47.
10 (*a*) H. Langhals, P. Knochel, A. Walter and S. Zimdars, *Synthesis*, 2012, 3465–3477; (*b*) S. Zimdars, H. Langhals and P. Knochel, *Synthesis*, 2011, 1302–1308.
11 N. Nakamura, Y. Tajima and K. Sakai, *Heterocycles*, 1982, **17**, 235–245.
12 (*a*) A. Ohta, Y. Akita, T. Ohkuwa, M. Chiba, R. Fukunaga, A. Miyafuji, T. Nakata, N. Tani and Y. Aoyagi, *Heterocycles*, 1990, **31**, 1951–1958; (*b*) Y. Aoyagi, A. Inoue, I. Koizumi, R. Hashimoto, K. Tokunaga, K. Gohma, J. Komatsu, K. Sekine, A. Miyafuji and J. Kunoh, *Heterocycles*, 1992, **33**, 257–272.
13 (*a*) F. Kakiuchi and T. Kochi, *Synthesis*, 2008, 3013–3039; (*b*) L. Ackermann, R. Vicente and A. R. Kapdi, *Angew. Chem., Int. Ed.*, 2009, **48**, 9792–9826; (*c*) F. Bellina and R. Rossi, *Tetrahedron*, 2009, **65**, 10269–10310; (*d*) X. Chen, K. M. Engle, D.-H. Wang and J.-Q. Yu, *Angew. Chem., Int. Ed.*, 2009, **48**, 5094–5115; (*e*) T. W. Lyons and M. S. Sanford, *Chem. Rev.*, 2010, **110**, 1147–1169; (*f*) E. M. Beck and M. J. Gaunt, *Top. Curr. Chem.*, 2010, **292**, 85–121; (*g*) T. Satoh and M. Miura, *Synthesis*, 2010, 3395–3409; (*h*) C.-L. Sun, B.-J. Li and Z.-J. Shi, *Chem. Commun.*, 2010, **46**, 677–685; (*i*) S. H. Cho, J. Y. Kim, J. Kwak and S. Chang, *Chem. Soc. Rev.*, 2011, **40**, 5068–5083;

(*j*) N. Kuhl, M. N. Hopkinson, J. Wencel-Delord and F. Glorius, *Angew. Chem., Int. Ed.*, 2012, **51**, 10236–10254; (*k*) B.-J. Li and Z.-J. Shi, *Chem. Soc. Rev.*, 2012, **41**, 5588–5598; (*l*) M. C. White, *Synlett*, 2012, 2746–2748; (*m*) J. Yamaguchi, A. D. Yamaguchi and K. Itami, *Angew. Chem., Int. Ed.*, 2012, **51**, 8960–9009; (*n*) S. I. Kozhushkov and L. Ackermann, *Chem. Sci.*, 2013, **4**, 886–896; (*o*) R. Rossi, F. Bellina, M. Lessi and C. Manzini, *Adv. Synth. Catal.*, 2014, **356**, 17–117; (*p*) M. Zhang, Y. Zhang, X. Jie, H. Zhao, G. Li and W. Su, *Org. Chem. Front.*, 2014, **1**, 843–895; (*q*) M. R. Yadav, R. K. Rit, M. Shankar and A. K. Sahoo, *Asian J. Org. Chem.*, 2015, **4**, 846–864; (*r*) K. Hirano and M. Miura, *Chem. Lett.*, 2015, **44**, 868–873; (*s*) K. Yuan, J.-F. Soulé and H. Doucet, *ACS Catal.*, 2015, **5**, 978–991; (*t*) C. B. Bheeter, L. Chen, J.-F. Soulé and H. Doucet, *Catal. Sci. Technol.*, 2016, **6**, 2005–2049.

14 J. Zhang, W. Chen, A. J. Rojas, E. V. Jucov, T. V. Timofeeva, T. C. Parker, S. Barlow and S. R. Marder, *J. Am. Chem. Soc.*, 2013, **135**, 16376–16379.

15 (*a*) M. Lafrance, C. N. Rowley, T. K. Woo and K. Fagnou, *J. Am. Chem. Soc.*, 2006, **128**, 8754–8756; (*b*) M. Lafrance, D. Shore and K. Fagnou, *Org. Lett.*, 2006, **8**, 5097–5100; (*c*) T. Yan, L. Zhao, M. He, J.-F. Soulé, C. Bruneau and H. Doucet, *Adv. Synth. Catal.*, 2014, **356**, 1586–1596; (*d*) M. He, J.-F. Soulé and H. Doucet, *ChemCatChem*, 2014, **6**, 1824–1859; (*e*) M. He, J.-F. Soulé and H. Doucet, *ChemCatChem*, 2015, **7**, 2130–2140.

16 X. Zhang, Y. Gao, S. Li, X. Shi, Y. Geng and F. Wang, *J. Polym. Sci., Part A: Polym. Chem.*, 2014, **52**, 2367–2374.

17 X. Kang, J. Zhang, D. O'Neil, A. J. Rojas, W. Chen, P. Szymanski, S. R. Marder and M. A. El-Sayed, *Chem. Mater.*, 2014, **26**, 4486–4493.

18 C.-Y. He, C.-Z. Wu, F.-L. Qing and X. Zhang, *J. Org. Chem.*, 2014, **79**, 1712–1718.

19 J. Zhang, T. C. Parker, W. Chen, L. Williams, V. N. Khrustalev, E. V. Jucov, S. Barlow, T. V. Timofeeva and S. R. Marder, *J. Org. Chem.*, 2016, **81**, 360–370.

20 I. Idris, F. Derridj, J.-F. Soulé and H. Doucet, *Adv. Synth. Catal.*, 2017, **359**, 2448–2456.

21 CCDC 1564784 (**18**), 1577123 (**20**), 1564844 (**26**) and 1576377 (**30**)†.

22 (*a*) A. Skhiri, R. Ben Salem, J.-F. Soulé and H. Doucet, *ChemCatChem*, 2017, **9**, 2895–2913; (*b*) A. Skhiri, R. B. Salem, J.-F. Soulé and H. Doucet, *Chem. – Eur. J.*, 2017, **23**, 2788–2791.

23 (*a*) W.-Q. Zhang, Q.-Y. Li, Q. Zhang, Y. Lu, H. Lu, W. Wang, X. Zhao and X.-J. Wang, *Inorg. Chem.*, 2016, **55**, 1005–1007; (*b*) M. Velusamy, K. R. J. Thomas, J. T. Lin and Y. S. Wen, *Tetrahedron Lett.*, 2005, **46**, 7647–7651.

24 (*a*) B. A. D. Neto, A. S. A. Lopes, G. Ebeling, R. S. Gonçalves, V. E. Costa, F. H. Quina and J. Dupont, *Tetrahedron*, 2005, **61**, 10975–10982; (*b*) P. Wei, L. Duan, D. Zhang, J. Qiao, L. Wang, R. Wang, G. Dong and Y. Qiu, *J. Mater. Chem.*, 2008, **18**, 806–818; (*c*) R. Misra, P. Gautam, T. Jadhav and S. M. Mobin, *J. Org. Chem.*, 2013, **78**, 4940–4948; (*d*) T. Jadhav, B. Dhokale, Y. Patil, S. M. Mobin and R. Misra, *J. Phys. Chem. C*, 2016, **120**, 24030–24040; (*e*) T. O. Lopes, D. A. Silva Filho, A. A. Lapis, H. C. Oliveira and B. A. Neto, *J. Phys. Org. Chem.*, 2014, **27**, 303–309.

25 S. Mondal, M. Konda, B. Kauffmann, M. K. Manna and A. K. Das, *Cryst. Growth Des.*, 2015, **15**, 5548–5554.

26 F. M. Winnik, *Chem. Rev.*, 1993, **93**, 587–614.