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Palladium-catalyzed C-H Bond Functionalization of Benzo[1,2-*b*:4,5-*b'*]dithiophene-4,8-dione: A One Step Access to 2-Arylbenzo[1,2-*b*:4,5-*b'*]dithiophene-4,8-diones

Manisha Durai,^[a] Linhao Liu,^[a] Pierre Frère,^{*,[b]} Thierry Roisnel,^[a] Véronique Guerchais,^{*,[a]} and Henri Doucet^{*,[a]}

[a] Mrs M. Durai, Dr. L. Liu, Dr. V. Guerchais, Dr. H. Doucet
Univ Rennes, CNRS, ISCR-UMR 6226
F-35000 Rennes
France
E-mail: henri.doucet@univ-rennes1.fr

[b] Pr. P. Frère
Univ Angers, MOLTECH-Anjou, UMR CNRS 6200
F-49045 Angers
France

Abstract: The reactivity of benzo[1,2-*b*:4,5-*b'*]dithiophene-4,8-dione in Pd-catalyzed C-H arylation was investigated. Using aryl bromides as aryl source in the presence of carbonate bases in 1,4-dioxane the mono-C2-arylated benzo[1,2-*b*:4,5-*b'*]dithiophene-4,8-diones were regioselectively obtained. This procedure allowed to introduce both electron-rich and electron-poor aryl substituents on the benzo[1,2-*b*:4,5-*b'*]dithiophene-4,8-dione unit. These conditions were also effective for the coupling with 1-bromonaphthalene, 9-bromophenanthrene as well as aryl bromides bearing synthetically useful nitrile, chloro and methoxy substituents. The photophysical properties of representative arylated compounds have been performed by joint experimental and theoretical studies.

Introduction

The field of optoelectronics incorporates the design and the synthesis of new photo-active components and the study of the photon-matter relationships, as well as the exploitation of the light interactions in the fabrication of electronic devices.^[1,2] Many strategies around the structure of the organic systems have been developed for controlling their electronic properties in the field of molecular electronics. As one of the most important rigid fused-ring structure, benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT) was extensively explored as π -electron donor in organic electronics. (Figure 1).^[3,4] By contrast, the chemistry of the related derivative benzo[1,2-*b*:4,5-*b'*]dithiophene-4,8-dione (BDT-DiO) is less explored. Replacing the central phenyl ring of BDT by an electron-accepting core might affect the optoelectronic properties of the resulting systems and pave the way for new applications such as TADF.^[5] Consequently, developing direct synthetic routes to access to functionalized BDT-DiO is highly desirable. Most of the synthesis starting from BDT-DiO involve the ketone functions to lead in fine to the development of BDT units.^[6] Reactions on thienyl units to extend the conjugation of the system while keeping the electron acceptor character remain quite rare.^[7]

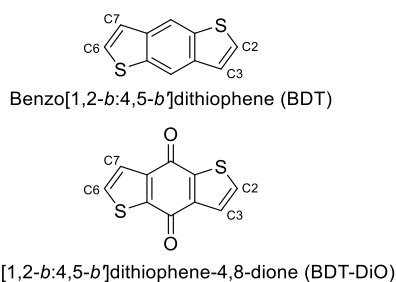
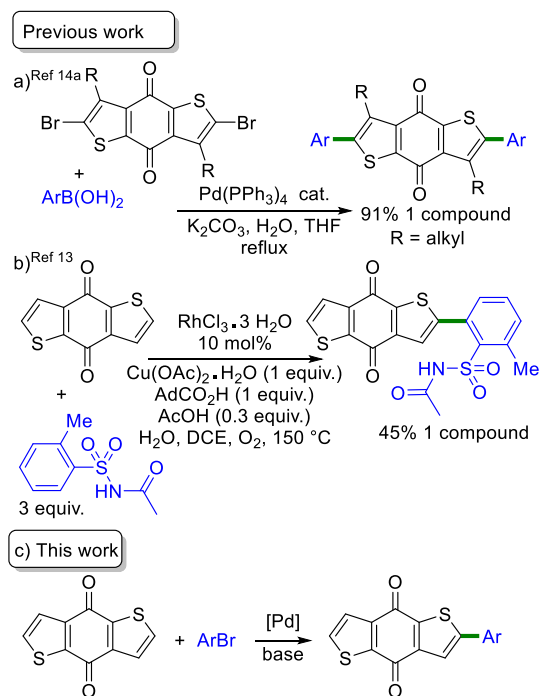


Figure 1. Structures of benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT) and benzo[1,2-*b*:4,5-*b'*]dithiophene-4,8-dione (BDT-DiO).

Over the past two decades, Pd-catalyzed C-H bond functionalization of several heteroarenes led to a revolution in the synthesis of arylated heteroarenes.^[8] Since Ohta and co-workers seminal results reported in 1992,^[9] several procedures allowing to prepare arylated thiophene derivatives have been reported.^[10] Very regioselective arylations at the C2- and/or C5-positions of thiophenes can be obtained in the presence of carboxylate bases, such as KOAc.^[11] By contrast, to the best of our knowledge, very few examples of arylations of benzo[1,2-*b*:4,5-*b'*]dithiophene-4,8-diones proceeding *via* a C-H bond functionalization have been reported.^[12,13] A single example of Rh-catalyzed oxidative coupling has been described (Scheme 1, b).^[13] For this reaction which afforded regioselectively the mono-C2-arylated BDT-DiO in 45% yield, the presence of a sulfonylacetamide substituent on the aryl coupling partner was needed to direct the C-H bond cleavage. Currently, the preparation of arylated BDT-DiO relies mostly on Suzuki coupling and gives the 2,6-diarylated compounds.^[14] For example, Chen, Yamashita et al. reported the Suzuki coupling of a 2,6-dibromobenzo[1,2-*b*:4,5-

b)]dithiophene-4,8-dione with an arylboronic acid (Scheme 1, a).^[14a] Organic reactions using *N,N*-dialkylthiophene-3-carboxamides and *n*BuLi or bromination of BDT-DiO also allowed to obtain a few BDT-DiO bearing substituents at 2,6-positions.^[15] To the best of our knowledge, the regioselective Pd-catalyzed C-H C2-arylation of BDT-DiO has not been described (Scheme 1, c). Therefore, the discovery of a simple procedure allowing to regioselectively introduce functionalized aryl groups at C2-position of BDT-DiO is still needed. Herein, we report *i*) conditions for the C2-arylation of BDT-DiO; *ii*) on the functional group tolerance on the aryl bromide; *iii*) photophysical properties of representative aryl substituted compounds alongside theoretical insights.

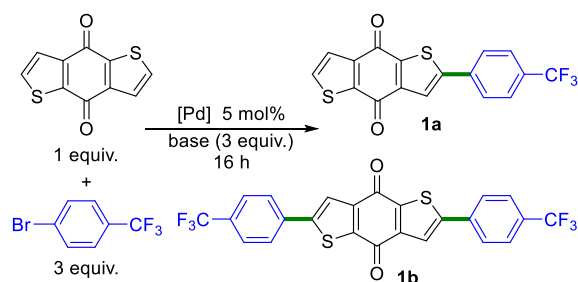


Scheme 1. Methods for the synthesis of 2-aryl- or 2,6-diaryl-benzo[1,2-*b*:4,5-*b'*]dithiophene-4,8-diones.

Results and Discussion

We employed BDT-DiO (1 equiv.) and 1-bromo-4-(trifluoromethyl)benzene (3 equiv.) as model substrates for our study (Table 1). We first investigated the reaction outcome with KOAc using 5 mol% PdCl(C₃H₅)(dppb) catalyst^[16] in DMA. This base associated to Pd-catalysts with this solvent were very effective in many cases for the direct arylation of 5-membered ring heteroarenes.^[8] However, these reaction conditions were completely ineffective at 80, 100 or 120 °C, as the target product **1a** was not detected although the BDT-DiO was completely consumed (Table 1, entries 1-3). In the absence of palladium catalyst with KOAc in DMA at 120 °C, no decomposition of BDT-DiO was observed indicating that the presence of both KOAc and palladium in the reaction mixture is required to promote this substrate decomposition. The use of CPME or 1,4-dioxane as the solvents was also ineffective with again a complete decomposition of BDT-DiO (Table 1, entries 4 and 5). By contrast, the use of Cs₂CO₃ with 5 mol% PdCl(C₃H₅)(dppb) catalyst at 120 °C in DMA afforded the desired product **1a** in quite good selectivity but in low yield (Table 1, entry 6). Under these conditions, a large amount of BDT-DiO remained unreacted, indicating that this substrate is more stable in the presence of Cs₂CO₃ base than with KOAc. A slightly better yield in **1a** was obtained using K₂CO₃ base, with again a partial conversion of BDT-DiO (Table 1, entry 7). A higher reaction temperature (150 °C) allowed to improve the yield in **1a** to 40% (Table 1, entry 9). The use of CPME, diethyl carbonate or xylene as the solvents was ineffective, whereas both DMF and NMP led to **1a** in low to moderate yields (Table 1, entries 10-15). In the course of these reactions, no formation of the diarylated product **1b** was detected. The best yield in **1a** (65%) was obtained using PdCl(C₃H₅)(dppb) catalyst associated to K₂CO₃, 1,4-dioxane as the solvent at 150 °C (Table 1, entry 16). It should be mentioned that in this solvent the formation of a diarylated BDT-DiO was detected in 17% selectivity by GC/MS of the crude mixture. The use of Pd(OAc)₂ associated to mono or diphosphine ligands or without phosphine ligand gave **1a** in lower yields (Table 1, entries 17-20). PdCl₂(PPh₃)₂ catalyst was also less effective than PdCl(C₃H₅)(dppb) (Table 1, entry 21). The use of Li₂CO₃ base instead of K₂CO₃ was completely ineffective (Table 1, entry 22). Finally, the influence of the amount of 1-bromo-4-(trifluoromethyl)benzene was determined. Using 1.5 or 2 equiv. of this aryl bromide, lower yields in **1a** were obtained (Table 1, entries 23 and 24), and the use of a very large amount (5 equiv.) of 1-bromo-4-(trifluoromethyl)benzene did not allow to significantly increase the amount of diarylation product (Table 1, entry 25). The high selectivity in mono-arylation product **1a** observed with all the reaction conditions indicates that the first arylation at C2-position deactivates the C6-position, probably due to electronic factors of this conjugated system.

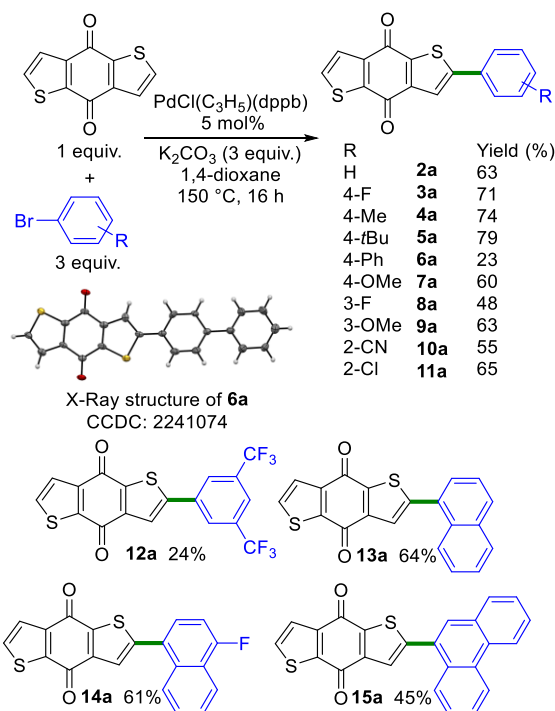
Table 1. Influence of the reaction conditions on the Pd-catalyzed reaction of benzo[1,2-*b*:4,5-*b'*]dithiophene-4,8-dione with 1-bromo-4-(trifluoromethyl)benzene.^[a]



Entry	Catalyst	Solvent	Base	Temp. (°C)	Yield in 1a (%)
1	PdCl(C ₃ H ₅)(dppb)	DMA	KOAc	120	0
2	PdCl(C ₃ H ₅)(dppb)	DMA	KOAc	100	0
3	PdCl(C ₃ H ₅)(dppb)	DMA	KOAc	80	0
4	PdCl(C ₃ H ₅)(dppb)	CPME	KOAc	120	0
5	PdCl(C ₃ H ₅)(dppb)	1,4-dioxane	KOAc	120	0
6	PdCl(C ₃ H ₅)(dppb)	DMA	Cs ₂ CO ₃	120	21
7	PdCl(C ₃ H ₅)(dppb)	DMA	K ₂ CO ₃	120	26
8	PdCl(C ₃ H ₅)(dppb)	DMA	K ₂ CO ₃	100	16
9	PdCl(C ₃ H ₅)(dppb)	DMA	K ₂ CO ₃	150	40
10	PdCl(C ₃ H ₅)(dppb)	CPME	K ₂ CO ₃	120	12
11	PdCl(C ₃ H ₅)(dppb)	Diethyl carbonate	K ₂ CO ₃	150	9
12	PdCl(C ₃ H ₅)(dppb)	xylene	K ₂ CO ₃	150	<10
13	PdCl(C ₃ H ₅)(dppb)	NMP	K ₂ CO ₃	150	27
14	PdCl(C ₃ H ₅)(dppb)	DMF	K ₂ CO ₃	150	42
15	Pd(OAc) ₂	DMF	K ₂ CO ₃	150	14
16	PdCl(C ₃ H ₅)(dppb)	1,4-dioxane	K ₂ CO ₃	150	65% ^[b]
17	Pd(OAc) ₂	1,4-dioxane	K ₂ CO ₃	150	16
18	Pd(OAc) ₂ / dppe	1,4-dioxane	K ₂ CO ₃	150	17
19	Pd(OAc) ₂ / dppf	1,4-dioxane	K ₂ CO ₃	150	45
20	Pd(OAc) ₂ / 2 PPh ₃	1,4-dioxane	K ₂ CO ₃	150	28
21	PdCl ₂ (PPh ₃) ₂	1,4-dioxane	K ₂ CO ₃	150	42
22	PdCl(C ₃ H ₅)(dppb)	1,4-dioxane	Li ₂ CO ₃	150	0
23	PdCl(C ₃ H ₅)(dppb)	1,4-dioxane	K ₂ CO ₃	150	39 ^[c]
24	PdCl(C ₃ H ₅)(dppb)	1,4-dioxane	K ₂ CO ₃	150	49 ^[d]
25	PdCl(C ₃ H ₅)(dppb)	1,4-dioxane	K ₂ CO ₃	150	63 ^[e]

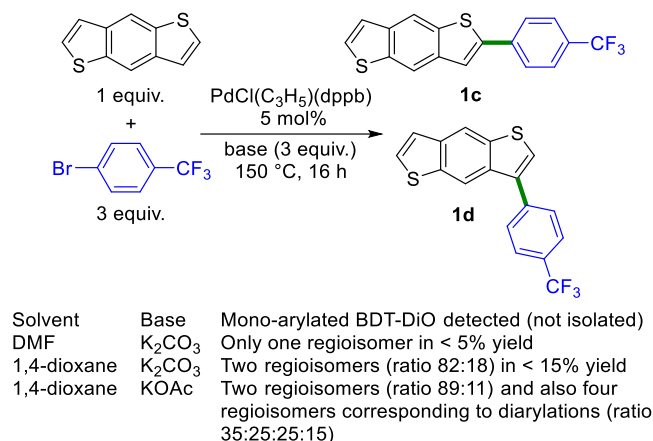
[a] [Pd] (0.05 equiv.), benzo[1,2-*b*:4,5-*b'*]dithiophene-4,8-dione (1 equiv.), 1-bromo-4-(trifluoromethyl)benzene (3 equiv.), base (3 equiv.), 16 h, isolated yields. [b] Ratio **1a**:diarylation 83:17 determined by GC/MS. [c] 1-Bromo-4-(trifluoromethyl)benzene (1.5 equiv.). [d] 1-Bromo-4-(trifluoromethyl)benzene (2 equiv.). [e] 1-Bromo-4-(trifluoromethyl)benzene (5 equiv.), ratio **1a**:diarylation 81:19 determined by GC/MS. The diarylated product could not be isolated.

The scope of the C2-arylation of BDT-DiO with various aryl bromides was investigated using 5 mol% PdCl(C₃H₅)(dppb) catalyst with K₂CO₃ base in 1,4-dioxane (Scheme 2). Moderate yields of 63% and 71% in the desired products **2a** and **3a** were obtained by coupling with bromobenzene and 4-fluorobromobenzene. The use of methyl, *tert*-butyl, phenyl and methoxy *para*-substituted aryl bromides afforded the target products **4a-7a** in 23-79% yields. The regioselectivity of the arylations of **6a** was unambiguously assigned by X-ray analysis.^[17] A lower yield in **8a** was obtained from 3-fluorobromobenzene; whereas 3-bromoanisole gave the product **9a** with a similar yield that with 4-bromoanisole. The reactivity of the two more sterically hindered aryl bromides 2-bromobenzonitrile and 2-bromochlorobenzene was also examined and afforded again the expected products **10a** and **11a** in 55% and 65% yield, respectively. The presence of two electron-withdrawing CF₃ substituents on the aryl bromide was found to have a deleterious effect on the reaction. Using 3,5-bis(trifluoromethyl)bromobenzene the coupling product **12a** was obtained in only 24% yield. Conversely, bromo-substituted polycyclic aromatic hydrocarbons were well tolerated. From 1-bromonaphthalenes and 9-bromophenanthrene the products **13a-15a** were isolated in 45-64% yields.



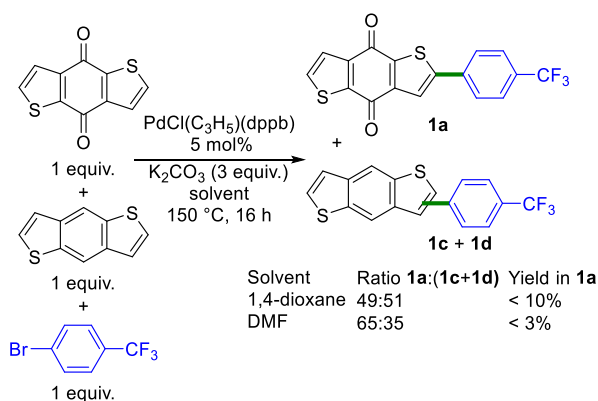
Scheme 2. Scope of the Pd-catalyzed direct C2-arylation of BDT-DiO using a set of aryl bromides.

To the best of our knowledge, the Pd-catalyzed direct arylation of unsubstituted BDT has not been reported, whereas, a few examples of reactions with 4,8-substituted benzo[1,2-*b*:4,5-*b'*]dithiophenes have been described.^[18-20] Therefore, we also applied our direct arylation conditions to BDT. However, this substrate was found to be almost completely unreactive in DMF (Scheme 3). The desired C2-arylated product **1c** could not be isolated, although a mono-arylation product was detected as traces in GC/MS analysis of the crude mixture. A slightly different result was obtained using 1,4-dioxane as the solvent with the formation of two mono-arylation products (ratio 82:18), but again no clean coupling product could be isolated. The use of KOAc base instead of K₂CO₃ led to an even more complex mixture of products as two mono-arylated and four di-arylated BDT derivatives were detected by GC/MS analysis of the crude mixture.



Scheme 3. Reactivity of BDT in Pd-catalyzed direct arylation.

In order to better understand the very low reactivity of BDT compared to BDT-DiO, we performed a competition reaction (Scheme 4). From an equimolar mixture of these two substrates (1 equiv.) in the presence of 1-bromo-4-(trifluoromethyl)benzene (1 equiv.) with 5 mol% PdCl₂(C₃H₅)₂(dppb) catalyst and K₂CO₃ base in 1,4-dioxane, the formation of products **1a** and **1c + 1d** in 49:51 ratio was observed with the formation of **1a** in <10% yield. In DMF, the selectivity was quite similar and the yield in **1a** was < 3%.



Scheme 4. Competition reaction using an equimolar mixture of BDT and BDT-DiO.

For representative molecules **1a** (4-CF₃), **2a** (4-H), **3a** (4-F), **4a** (4-Me), **6a** (4-Ph) and **7a** (4-OMe), theoretical calculations were performed at the ab initio density functional level with the Gaussian09 package by considering all derivatives in cyclohexane. Becke's three parameters gradient corrected functional (B3LYP) with a polarized 6-31G (d,p) was used for the geometrical optimization and for the determination of the HOMO and LUMO levels. The optimized topologies of the molecules are presented in figure S1 (see Supporting Information). All the molecules are slightly twisted, with a dihedral angle between the BDT-DiO moiety and the aryl group of about 27-30°. The frontier molecular orbitals, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are presented in Figure S2 and the corresponding energy levels are listed in Table 2. In all cases, including compounds **1a** and **3a** with aryl groups substituted with electron-withdrawing groups, the HOMO frontier orbitals are mainly localized on the aryl group and the thiophene units, while the LUMO are essentially localized on the BDT-DiO moiety. The trend of the energy levels of HOMO is in agreement with the electron donating properties of the compounds, going from -6.78 eV for **1a** (4-CF₃) to -6.18 eV for **7a** (4-OMe). Similarly, stabilization of the LUMO are also observed from going to **1a** (most electron-deficient substituent) to **7a** (most electron-rich substituent). Finally, TD-DFT calculations were performed to evaluate the singlet - triplet gap for compounds **1a** and **4a** (see Figure S3) which present net difference in terms of electronic structures and emission properties (*vide infra*). Compound **4a**, which displays a strong donor-acceptor (D-A) character, exhibits a smaller energy difference between T1 and S1 levels ($\Delta E_{ST} = 0.57$ eV) compared to that calculated for compound **1a** ($\Delta E_{ST} = 0.62$ eV).

However, ΔE_{ST} is somewhat higher than the optimal range for achieving an efficient thermally activated delayed fluorescence (TADF) phenomenon.^[21]

The absorption and emission studies have been performed in dilute cyclohexane solution (10^{-5} M) for compounds **1a**, **2a**, **3a**, **4a**, **6a** and **7a**.^[22] All the optical data are summarized in Table 2 and their UV-vis absorption spectra are shown in Figure 2. The spectra of the compounds are similar to one another and are characterized by three absorption bands, the highest energy bands around 290 nm and 350 nm can be attributed to ligand-centered $\pi-\pi^*$ (1LC) transitions of the BDT-DiO unit and the aryl groups. The lowest energy bands from 429 nm for **1a** to 484 nm for **7a** nm can be ascribed to $\pi-\pi^*$ transitions of the aryl group to the BDT-DiO core, which mainly correspond to the HOMO \rightarrow LUMO transition. The electronic absorption data clearly show the influence of the added substituent onto the aryl group, a bathochromic shift of 55 nm is observed when the 4- CF_3 substituent is replaced by a 4-OMe group. For compound **7a**, this band extends up to 550 nm, as a result of a strong intramolecular charge transfer (ICT), in agreement with TD-DFT calculations.

Under photoexcitation at 290 nm, compounds **1a**, **2a**, **3a**, **4a**, **6a** and **7a** are weakly emissive in fluid cyclohexane solution (Figure S4). The wavelengths of the maxima for the emission band gradually increase by increasing the electron-donating character of the aryl substituent, from 531 nm (**1a**) to 565 nm (**7a**). The incorporation of a *p*-methoxy group results in an emission red-shift of 35 nm with respect to that of the *p*- CF_3 -substituted derivative. The photoluminescence quantum yield of all compounds are in the range 5-12%, except for the derivatives **1a** and **3a** featuring an electron accepting substituent (QY < 1%).

Table 2. Calculated energy levels,^[a] UV-Vis absorption in cyclohexane solution^[b] and emission in cyclohexane solution^[c] of representative compounds.

Entry	Compound	Theoretical HOMO (eV) LUMO (eV) ΔE (eV)	UV-Vis absorption		Fluorescence	
			λ_{max} (nm)	ϵ M ⁻¹ cm ⁻¹	λ_{em} (nm)	$\Phi_{sol}^{[d]}$ (%)
1	1a - CF_3	-3.51	290	26800	531	< 1
		-6.78	357	8180		
		3.27	429	1700		
2	2a - H	-3.39	285	30800	534	11
		-6.45	360	9500		
		3.06	452	2260		
3	3a - F	-3.41	285	29530	530	<1
		-6.52	361	9463		
		3.11	443	2100		
4	4a - Me	-3.34	289	34772	541	14
		-6.35	363	10234		
		3.01	470	3190		
5	6a - Ph	-3.37	296	32970	550	8
		-6.23	365	8791		
		2.86	472	3192		
6	7a - OMe	-3.31	291	29270	565	5
		-6.18	364	8179		
		2.87	484	3190		

[a] B3LYP (6.31G (d,p)). [b] 10^{-5} M. [c] $\lambda_{exc} = 290$ nm. [d] Absolute quantum yield measured with an integrated sphere.

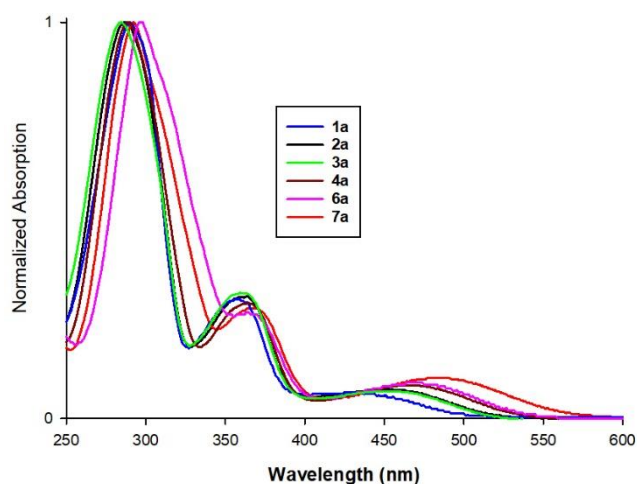


Figure 2. UV-Vis spectra of compounds **1a**, **2a**, **3a**, **4a**, **6a** and **7a** in cyclohexane (10^{-5} M).

It is noteworthy that the more emissive compound **4a**, having a strong ICT character, displays solvatochromic properties. This is illustrated by a red shift of 60 nm of the emission spectra in cyclohexane and CHCl_3 , leading to a change of the emission color from yellow to orange as shown in Figure 3.

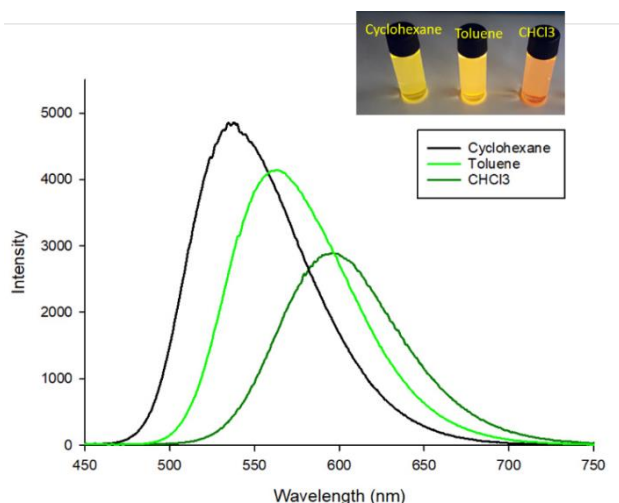


Figure 3. Emission spectra of **4a** ($\lambda_{\text{exc}} = 290$ nm) in solution (10^{-5} M) in various solvents.

Conclusion

In summary, we report herein the first general method for the synthesis of C2-aryl-substituted BDT-DiO. Using appropriate reaction conditions, the Pd-catalyzed C-H functionalization at C2-position of BDT-DiO by aryl bromides proceeds in good to high yield. The nature of the base as well as the solvent was found to be crucial to obtain the desired products. This procedure tolerates several useful substituents on the aryl bromide such as methoxy, fluoro, chloro, nitrile or trifluoromethyl. However, better yields were generally obtained using electron-deficient aryl bromides. In addition, our procedure uses easily available substrates and an air-stable catalyst associated to K_2CO_3 as inexpensive base. This inedited synthetic scheme which employs very simple reaction conditions should be attractive to chemists looking for easy routes to functionalized BDT-DiO. The influence of the added aryl group on the BDT-DiO on the photophysical properties has been evaluated on representative derivatives diversely substituted. The easy tuning of the electronic properties of arylated BDT-DiO, thanks to this new synthetic access, opens up new perspectives for potential optoelectronic applications.^[5]

Experimental Section

Benzo[1,2-*b*:4,5-*b'*]dithiophene-4,8-dione (BDT-DiO) (98%) and benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT) (98%) were purchased from TCI. [Pd(C₆H₅)Cl]₂ (98%) and 1,4-bis(diphenylphosphino)butane (dppb) (98%) were purchased from Merck. 1,4-Dioxane (99%) and K₂CO₃ (99%) were purchased from Fisher scientific. These compounds were not purified before use. All reagents were weighed and handled in air. All reactions were carried out under an inert atmosphere with standard Schlenk techniques. ¹H, ¹⁹F and ¹³C NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer. High-resolution mass spectra were measured on a Bruker MaXis 4G spectrometer. Most of the products **1a-15a** exhibit a low solubility in CDCl₃. Melting points were determined with a Kofler hot bench system.

General procedure for palladium-catalyzed synthesis of 2-(aryl)benzo[1,2-*b*:4,5-*b'*]dithiophene-4,8-diones:

The reaction of the aryl bromide (3 mmol), benzo[1,2-*b*:4,5-*b'*]dithiophene-4,8-dione (0.220 g, 1 mmol) and K₂CO₃ (0.414 g, 3 mmol) in the presence of PdCl(C₆H₅)(dppb) (30.5 mg, 0.05 mmol) at 150 °C during 16 h in 1,4-dioxane (4 mL) under argon affords the coupling products **1a-15a** after evaporation of the solvent and purification on silica gel. Eluent heptane/CH₂Cl₂: 30/70 for all compounds.

UV-Vis and Fluorescent Spectroscopy. Absorption spectra were recorded on a Shimadzu UV-1800 spectrophotometer. Fluorescent emission spectra were obtained on a FP-8500 spectrofluorometer. The fluorescence quantum yields both in solution and in the solid state were measured using an ILF-835 | 100 mm Integrating Sphere.

DFT calculation. The geometrical optimization was carried out at the B3LYP/6-31g(d,p) level of theory implemented on the Gaussian 09 package.

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Keywords: Benzo[1,2-*b*:4,5-*b'*]dithiophene-4,8-dione • C-H bond functionalization • DFT calculations • Homogeneous catalysis • Photophysical properties

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