Sustainable Synthesis

Ligand-Free Suzuki–Miyaura Cross-Coupling Reactions in Deep Eutectic Solvents: Synthesis of Benzodithiophene Derivatives and Study of their Optical and Electrochemical Performance

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Dedicated to Professor Franco Cozzi on the occasion of his 70th birthday.

Abstract: We report that dihalogeno-substituted benzodithiophenes (**BDTs**) undergo a smooth ligand-free Suzuki–Miyaura cross-coupling reaction, under air and moderate heating (60 °C), with aryl-, alkenyl- and alkynyltrifluoroborate salts in a biodegradable choline chloride-based eutectic mixture, thereby granting access to valuable π-conjugated **BDT** compounds (up to 79 % yield), which are gaining great interest in the field of material sciences. The optical and electrochemical properties of these systems have been thoroughly investigated by means of absorption and cyclic voltammetry measurements. The first electrooligomerization study of a representative **BDT** derivative has also been undertaken.

Introduction

Thiophene-fused polyaromatic compounds are a valuable class of organic π-conjugated materials in organic electronics.[1–4] Among them, tricyclic β-fused benzodithiophenes have received notable attention due to their rigid and planar molecular structure, extensive π-conjugation, and high charge-carrier mobility in the solid-state, mostly owing to the thienyl S/S interactions.[5] The proper adjustment of two sulfur atoms in the benzodithiophene core provides five diverse structural isomers, which are characterized by different degrees of curvature and electronic properties.

Over the years, some of us have been interested in the synthesis and functionalization of one of these isomers, namely the benzo[1,2-*b*:4,3-*b'*]dithiophene (**BDT**) and its derivatives,[6,7] which are useful building blocks to design functional materials in electronic devices. Indeed, **BDTs** have been successfully used as π-spacers[8–10] in metal-free organic dyes for solar cells, while 1,2-diarylethylene derivatives containing **BDT** units have been found to be stable fluorescent materials,[11] and thus widely employed for the fabrication of organic light-emitting diodes (OLEDs)[12] and as π-type semiconductors for organic thin-film transistors (OFETs).[13] On the other hand, **BDT**-based polymers have been reported as good donor units in donor–acceptor (D–A) copolymers for polymer solar cells (PSCs),[14] and their charge-carrier mobility and electrochromic switching ability have been extensively studied for potential applications in OFETs.[15–18] Furthermore, cyclic conjugated oligomers containing **BDT** units have also been synthesized in nanoscale dimensions[19,20] and represent promising functionalized supramolecular nanochannels for advanced chemical applications.

All the **BDT**-based polymers and cyclic oligomers reported in the aforementioned studies have been obtained through chemical or electrochemical polymerization of 2,7-dithienyl-substituted **BDT** monomers, which, in turn, have been synthesized by classical palladium-catalyzed Stille and Suzuki reactions starting from the corresponding 2,7-dibromo-substituted derivatives with 2-trimethylstannylthiophenes[16] and 2-thienylboronic acid,[17,20,21] respectively, in the presence of Pd(PPh$_3$)$_4$ or Pd(dppf)Cl$_2$ as catalyst and volatile organic compounds (VOCs) like DMF or toluene.

Despite the great potential of 2,7-disubstituted **BDTs** as advantageous building blocks for **BDT**-based polymers in elec-

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tronic devices, eco-friendly metal-catalyzed procedures to introduce aryl, alkenyl, or alkynyl pendants onto the **BDT** scaffold have still to be reported. In this context, the so-called Deep Eutectic Solvents (DESs) hold great promise as novel and emerging classes of environmentally responsible solvents, since they exhibit negligible vapor pressures, high thermal stability, essential nontoxicity, nonflammability, and easy recyclability.[22–24]

DESs are formed by two or more cheap and safe compounds, which include at least one hydrogen-bond donor [e.g., glycerol (Gly), urea, natural carboxylic acids, carbohydrates] and one hydrogen-bond acceptor (HBA) [e.g., choline chloride (ChCl), phosphonium salts], that when mixed at a determined molar ratio form a mixture with a melting temperature much lower than those of either individual components and that of an ideal liquid mixture because of an extended hydrogen-bond network between the components. Among HBAs, ChCl, also known as vitamin B4, is a biodegradable ammonium salt produced on the scale of a million metric tonnes per year as an additive in chicken food to accelerate growth. Because of a low ecological footprint and unusual physicochemical properties, DESs are progressively replacing toxic, petroleum-derived VOCs in several fields of science. New emerging applications are related to organometallics,[25–27] metal-,[28–34] bio-,[35–39] and organocatalysis,[40–42] electrochemistry,[43] photosynthesis,[44] and solar technology.[45–47]

Building upon our recent findings on metal-catalyzed cross-coupling reactions run in DESs in the absence of additional ligands,[30–32] herein we report a systematic study aimed at performing Suzuki–Miyaura (SM) coupling reactions between dibromo or diiodo **BDT** derivatives and (hetero)aryl-, alkenyl- and alkynyl boronic species in DESs, under ligandless and mild conditions. The newly 2,7-disubstituted **BDT** derivatives obtained in this study have been fully characterized, and their optical and electronic features thoroughly studied by means of UV/Vis absorption and cyclic voltammetry measurements. The fluorescence emission properties of three representative compounds have been also examined at room temperature in diluted solution. Finally, as a proof of concept, the electrochemical oligomerization of 2,7-dithienyl **BDT** monomers and the electrochromic switching ability of their corresponding oligomers have been preliminarily investigated.

Results and Discussion

Synthesis

We elected to study the Pd-catalyzed SM reaction between benzodithiophene dibromide **1a**[16] and the commercially available potassium phenyltrifluoroborate **2a** for the preparation of 2,7-diphenyl-substituted benzodithiophene **3a** in DESs. Capriati and co-workers recently reported that the environmentally friendly eutectic mixture ChCl/Gly (1:2 mol mol⁻¹) was an effective reaction medium for the synthesis of biaryl and terphenyl derivatives in the absence of additional ligands and under air, using as little as 1 mol-% Pd(OAc)₂ as catalyst and Na₂CO₃ as a base.[30] Under the best conditions set up in this study, a further

optimization of the reaction parameters led to the following results: (a) a temperature as high as 60 °C and a reaction time up to 72 h proved to be the best compromise for the synthesis of **3a** (79 % yield) (entry 1, Table 1) as either a higher temperature or the use of MW irradiation were detrimental to the yield of this adduct because of the formation of several unidentified by-products and the dehalogenated substrate **4** (entries 2–4, Table 1); (b) upon replacing **1a** with benzodithiophene diiodide **1b**[48] or **2a** with the corresponding phenylboronic acid **2b** or the phenylboronic acid pinacol ester **2c**, product **3a** was isolated in similar or lower yield (54–75 %) (entries 5–7, Table 1).

Table 1. Optimization of the SM coupling in ChCl/Gly between BDT dihalides **1** and various boronic acid derivatives **2a–c**.[a]
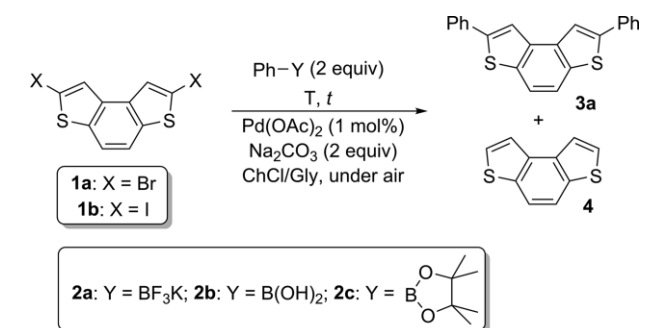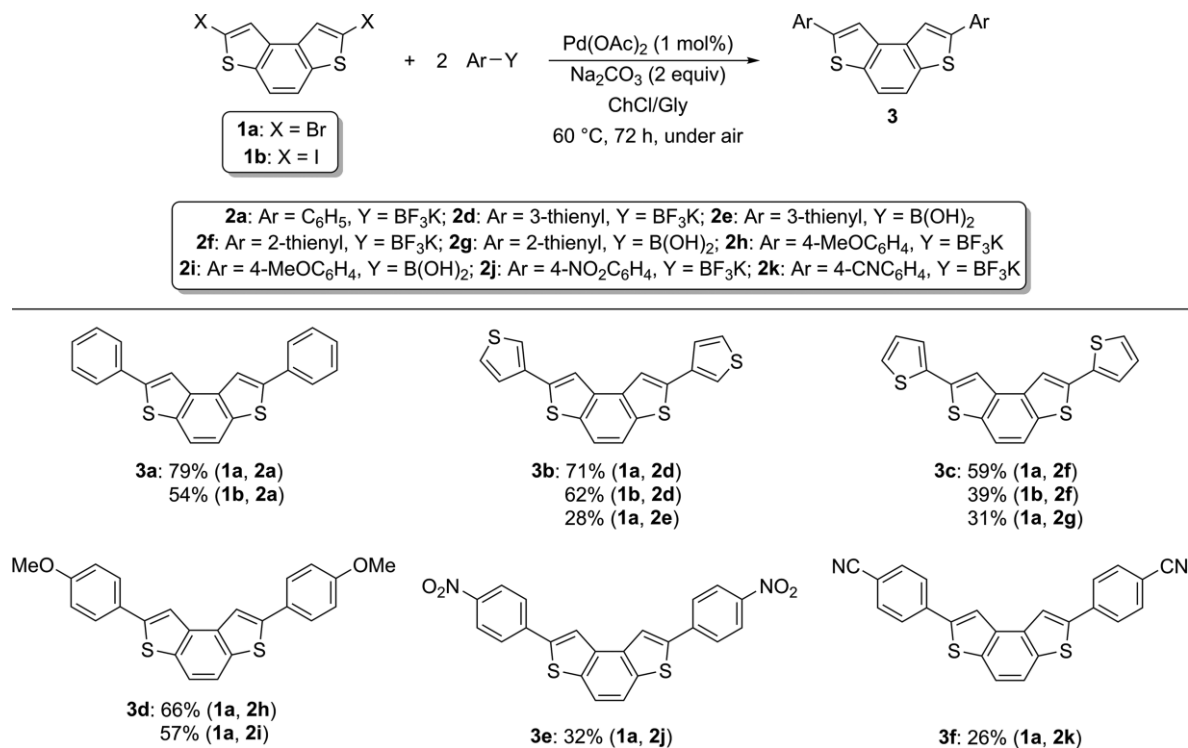

Entry	**1**	**2**	T [°C]/t [h]	**1/3a/4** ratio[b]	**3a** yield [%][c]
1	**1a**	**2a**	60/72	0:100:0	79
2	**1a**	**2a**	75/15	0:100:0	58
3[d]	**1a**	**2a**	60/0.5	56:20:24	–
4[d]	**1a**	**2a**	60/2	38:16:46	–
5	**1b**	**2a**	60/72	0:100:0	54
6	**1a**	**2b**	60/72	0:100:0	70
7	**1b**	**2c**	60/72	0:100:0	75

[a] Reaction conditions: 0.1 mmol **1**, 0.2 mmol **2**, 0.2 mmol Na₂CO₃, 1 mol-% Pd(OAc)₂, ChCl/Gly (1:2 mol mol⁻¹) (1.0 g), under air. [b] The normalized ratio was calculated by RP-HPLC (eluent: CH₃CN) on the crude reaction mixture. [c] Yield of isolated product. [d] Reactions were run under MW irradiation (60 °C, 60 W).

Of note, when dibromide **1a** was treated with phenylboronic acid **2b** in a mixture of toluene and MeOH (70 °C, 9 h) in the presence of Pd(dppf)Cl₂ (2.5 mol-%) and KF (3 equiv), in accordance to a procedure previously reported for the SM reaction of 2,7-dibromobenzodithiophenes with aryl boronic acids,[14] **3a** was isolated in 53 % yield only (see ESI).

With these optimized conditions in place, we sought to capitalize on this process by exploring the scope and limitations of the reaction with benzodithiophene dihalides **1a,b,** and a variety of commercially available (hetero)arylboronic species **2d–k** as nucleophilic partners. As reported in Scheme 1, benzodithiophene dibromide **1a** participated more effectively than the corresponding diiodide **1b** in the coupling process with both unsubstituted and electron-donating-substituted (hetero)aryltrifluoroborates, thereby delivering the expected adducts **3b–d** in 59–71 % yield.

It is worth noting that both dihalides **1a,b** hardly dissolve in the selected ChCl/Gly eutectic mixture, the bromide **1a** being even less soluble than diiodide **1b**. This would justify the different reactivity observed between the two substrates towards the

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Scheme 1. Synthesis of bis(hetero)aryl-substituted benzodithiophenes **3** via SM coupling between benzodithiophene dihalides **1** and (hetero)arylboronic acids **2e**, **2g** and **2i** or potassium (hetero)aryltrifluoroborates **2a**, **2d**, **2f**, **2h**, **2j** and **2k** in ChCl/Gly. Reaction conditions: 0.1 mmol **1**, 0.2 mmol **2**, 1 mol-% Pd(OAc)$_2$, 0.2 mmol Na$_2$CO$_3$, 1.0 g ChCl/Gly (1:2 mol mol^{-1}), under air. Yield of isolated product. After 72 h, no starting halide **1** was found in the reaction mixture.

SM reaction and, overall, the slower kinetics and the longer reaction times required when using such a eutectic mixture in place of a "classic" VOC (see Supporting Information). A time-conversion plot for the model reaction between bromide **1a** and phenyltrifluoroborate **2a** under the optimized reaction conditions has been included in the Supporting Information.

On the other hand, the presence of electron-withdrawing groups like -NO$_2$ and -CN in the nucleophilic partners **2j** and **2k** dramatically hindered the coupling process as the expected products **3e** and **3f** formed in 26–32 % yield only. Overall, the performance of (hetero)aryltrifluoroborates proved to be superior to that of the corresponding (hetero)arylboronic acids, as similarly ascertained in previous studies.[30]

To further expand the scope of this protocol, we also explored the coupling reaction between benzodithiophene dihalides **1** and alkenyltrifluoroborate **5** in order to synthesize the conjugated **BDT** derivative **6**. To this end, a brief screening of the experimental conditions was carried out (Table 2).

In this case, diiodide **1b** revealed to be a better electrophilic partner than the dibromide **1a** as it afforded the bis(styryl) derivative **6** in up to 74 % yield with complete consumption of the starting material after 24 h (entries 1 and 2, Table 2).

Of note, when using dibromide **1a**, the mono-substituted adduct **7** was also isolated from the reaction mixture in 27 % yield after 24 h reaction time (entry 2, Table 2).

As this derivative represents a useful intermediate for the synthesis of nonsymmetrical **BDT** derivatives, efforts were made to improve its yield. Using a strict 1:1 stoichiometry between **5** and **1a**, compound **7** was isolated in 46 % yield after 72 h (entry 3, Table 2). Finally, by reacting **7** with **2a** (1 equiv), under the

Table 2. Screening of the SM coupling in ChCl/Gly between benzodithiophene dihalides **1** and alkenyltrifluoroborate **5**.
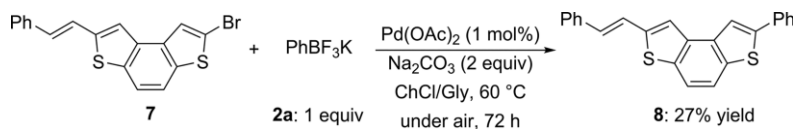

Entry[a]	**1**	**5** [equiv]	t [h]	**6** yield [%][b]	**7** yield [%][b]
1	**1b**	2	24	74	–
2	**1a**	2	24	62	27
3	**1a**	1	72	8	46[c]

[a] Reaction conditions: 0.1 mmol **1**, 0.2 or 0.1 mmol **5**, 1 mol-% Pd(OAc)$_2$, 0.2 mmol Na$_2$CO$_3$, 1.0 g ChCl/Gly (1:2 mol mol^{-1}), under air. Unless otherwise stated, conversion of **1** was quantitative after the reported period of time. [b] Yield of isolated product. [c] Bromide **1a** was recovered in 36 % yield.
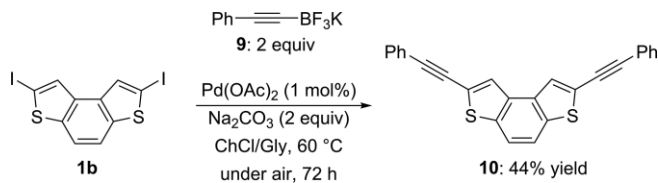
aforementioned optimized conditions, disubstituted product **8** was isolated in up to 27 % yield after 72 h, the starting bromide **7** being also recovered in 40 % yield (Scheme 2).

The utility of this protocol was also explored for performing Pd-catalyzed C(sp^2)–C(sp) SM cross-couplings. As shown in Scheme 3, the reaction between diiodide **1b** and alkynyl borate **9** (2 equiv) proceeded uneventfully, thereby leading to the conjugated bis(phenylalkynyl) adduct **10** in 44 % isolated yield.

Under these conditions, the coupling between bromide **1a** and **9** was ineffective. The newly synthesized benzodithiophene derivatives **3a**–**f**, **6**–**8,** and **10** were fully characterized by standard analytical and spectroscopic techniques (ESI), and small

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Scheme 2. Synthesis of nonsymmetrical benzodithiophene **8**.

Scheme 3. Synthesis of **10** via SM coupling between diiodide **1b** and alkynyl borate **9**.

yellow crystals of **3c** were also obtained from layered CH$_2$Cl$_2$ (DCM) and hexane. The unit cell was found with parameters a = 16.572(4), b = 5.7037(1), c = 32.1171(7) Å, $\alpha = \beta = \gamma = 90°$, V = 3036.9 Å^3, orthorhombic crystal system, Space Group 29 Pca2$_1$. The poor quality of the crystals, however, did not allow them to obtain a good refinement of the structure. Nevertheless, the connectivity of the atoms was established and is reported in Figure 1 using a ball and stick representation. Interestingly, preliminary data of the overall molecule disclosed an approximately planar geometry with the sulfur atoms of the σ-bonded thiophene substituents in a *trans*-conformation with the sulfur atoms of the three aromatic condensed rings.
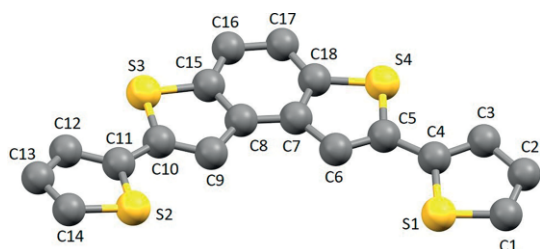

Figure 1. Ball and stick representation of molecule **3c**.

Optical and Electrochemical Studies

The optical properties of the novel **BDT** derivatives prepared were investigated by UV/Vis absorption spectroscopy in diluted DCM solution at room temperature and compared with those of the parent compound **4**. The molar absorptivity spectra are

depicted in Figure 2, and the optical features are summarised in Table 3. Three different sets of **BDT** derivatives have been compared and discussed: i) compounds **3a**, **3d** and **3f** bearing phenyl pendants with electron-rich or electron-withdrawing substituents (Figure 2a); ii) compounds **3b** and **3c** with thienyl pendants (Figure 2b); iii) compounds **3a**, **6** and **10** having phenyl, alkenyl, and alkynyl pendants, respectively (Figure 2c).

As a general trend, the introduction of a π-conjugated group, i.e. aryl, alkenyl or alkynyl moiety, on the two α-positions of the terminal thienyl rings of the benzodithiophene led to a consistent redshift (55–105 nm, Table 3) with respect to **4** in all examined cases. This is a well-established effect due to the enhanced conjugation of the **BDT**-framework induced by the α-substituents. Moreover, while **4** is characterized by a vibronically resolved structure, which is typical of rigid π-conjugated frameworks, a remarkable change of the absorption shape of the peaks was observed for derivatives **3a–d**, **3f**, **6**, **10**, being significantly less resolved than that of **4** (Figure 2). As shown in Figure 2a, diaryl-substituted systems **3a**, **3d,** and **3f** display very similar shapes, but they differ for the absorption maxima. While the absorption spectra of **3d**, bearing the electron-rich methoxy substituent, is very similar to that of **3a**, spectra of **3f**, having the electron-withdrawing cyano group, is significantly red-shifted (21 nm) as a consequence of a better conjugation through the **BDT** scaffold. As for derivatives disubstituted with thienyl rings, compound **3c**, bearing two thienyl rings connected to the **BDT** scaffold through the C$_\alpha$-C$_\alpha$ bond, showed a remarkable red-shift (23 nm) compared with **3b**, which holds two thienyl rings linked to the BDT core through the C$_\beta$-C$_\alpha$ bond (Figure 2b). Finally, by comparing the set of compounds **3a**, **6,** and **10**, a better conjugation, related to different pendants, was observed in the order alkenyl > alkynyl > aryl substituents (Figure 2c).

The electrochemical properties of **3a–f**, **6–8,** and **10** were investigated by cyclic voltammetry (CV) and are now discussed comparing their CV features with those of the parent compound **4** (Table 3). In particular, HOMO and LUMO levels as well as the energy gap values of these molecules were calculated
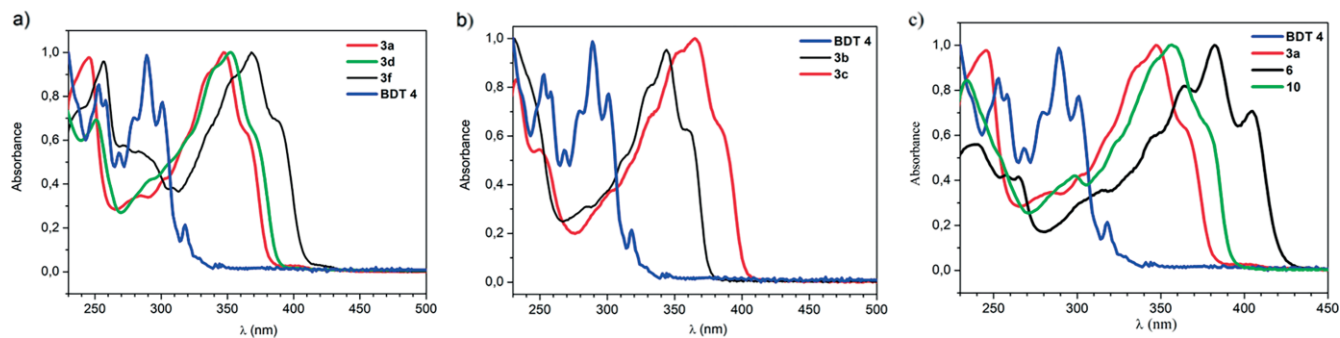

Figure 2. UV/Vis absorption spectra of **3a**, **3d** and **3f** (a), **3b** and **3c** (b), and **3a**, **6** and **10** (c), compared with the parent compound **BDT 4** (blue line).

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Table 3. Spectroscopic and cyclovoltammetric features[a] of **3a–f**, **6–8**, **10** and **4** as comparison, with the corresponding HOMO/LUMO energy levels and gaps.

Compound	λ_{max}[nm]/ log ε[b]	$E_{p,\,Ia}$ [V]	$E_{p,\,Ic}$ [V]	E_{HOMO} (max) [eV][c]	E_{LUMO} (max) [eV][d]	E_g (max) [eV]
4[e]	289/ 4.32	1.10	−2.99	−5.90	−1.81	4.09
3a	347/4.56	0.94	−2.60	−5.74	−2.20	3.54
3b	344/4.59	1.26	−2.18	−6.06	−2.62	3.54
3c	367/4.58	1.18	−2.11	−5.98	−2.69	3.29
3d	352/4.34	0.64	−2.87	−5.44	−1.93	3.51
3e	394/4.42	1.34	−1.49	−6.14	−3.31	2.83
3f	368/4.59	1.02	−2.16	−5.82	−2.64	3.18
6	382/4.71	0.58	−2.19	−5.38	−2.61	−2.77
7	382/4.54	0.80	−2.24	−5.60	−2.56	3.04
8	369/4.69	0.75	−2.46	−5.55	−2.34	3.21
10	357/4.57	1.06	−2.36	−5.86	−2.44	3.42

[a] CVs were recorder on GC electrode at 0.2 V s^{-1} potential scan rate in CH$_3$CN +TBAPF$_6$ 0.1 M. Potential values were referred to the intersolvental redox couple Fc$^+$|Fc|. [b] Molar absorptivities in diluted DCM solution (10^{-4} M). [c] E_{HOMO} (eV) = −1e x [($E_{p,Ia}$/V (Fc$^+$|Fc) + 4.8 V (Fc$^+$|Fc vs. zero)] (*maxima criterion*). [d] E_{LUMO} (eV) = −1e x [($E_{p,Ic}$/V (Fc$^+$|Fc|) + 4.8 V (Fc$^+$|Fc| vs. zero)] (*maxima criterion*). [e] Ref. 9.

according to the equations listed in Table 3. Unlike some BDT derivatives previously reported,[17] compounds **3a–f**, **6–8** and **10** were found to be soluble in acetonitrile at 0.001 M concentration, thus allowing us to perform the CV experiments in this solvent and tetrabutylammonium hexafluorophosphate (TBAPF$_6$) as the supporting electrolyte (for the CV patterns, see ESI). Acetonitrile, which does have a wider potential window, affords better observation of the reduction pattern of BDT derivatives since DCM potential window is significantly narrower on that side on account of the solvent bulk reduction at a rather early potential.

All derivatives show energy gap values lower than that of parent **BDT 4**, according to their optical behavior. Indeed, the better conjugation (lower energy gap) induced by the alkenyl > alkynyl > aryl substituents in **6**, **10**, and **3a**, respectively, were also observed from the energy gaps trend, in accordance with spectroscopic results. Moreover, the electron-withdrawing or -donating character of substituents at the *para*-position of the phenyl groups should tune the HOMO energy levels.

In particular, a linear relationship E_{HOMO} vs. σ_{para} Hammett constants for compounds **3a** (selected as reference), **3d**, **3e,** and **3f** was found (see ESI). Compound **3e** displayed a completely different reactivity according to the fact that the ingress of the electrons is on the nitro group. The reduction of these molecules became easier as soon as the electron-withdrawing character of the substituent increased. Conversely, oxidation resulted more difficult, with related potential values following the sequence: OMe <Ph <CN < NO$_2$. In the case of nonsymmetrical **BDT** derivatives **6–8**, the oxidation was less favored by varying only one substituent on the **BDT** fragment, according to the trend CH=CHPh < Ph < Br.

Finally, the emission properties of derivatives disubstituted with thienyl rings, **3b**, and **3c**, were examined and compared with those of diphenyl-substituted system **3a** (Figure 3). All the compounds showed a fluorescence emission at room temperature in diluted DCM solutions due to the lowest excited state as demonstrated by the excitation spectrum. The excited state is very little distorted as observed for the small red Stokes shift registered, and the excited state emission lifetimes are monoexponential for all the analyzed compounds and in the order of one ns (1.1–1.8 ns).
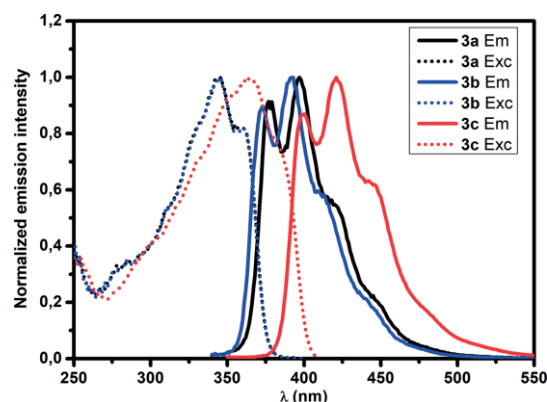

Figure 3. Normalised emission (solid lines, λ_{exc} = 310 nm) and excitation spectra (dotted lines) of **3a** (λ_{em} = 420 nm) **3b** (λ_{em} = 420 nm) and **3c** (λ_{em} = 433 nm) in DCM solution (10^{-5} M) at room temperature.

It is worth mentioning that the photoluminescent quantum yields (PLQY) in solution of **3a**, **3b**, and **3c** are 80, 49, and 71 %, respectively, that are remarkably high.

Preliminary Electrooligomerization Study of 3b and 3c

The electrooxidation ability of monomers **3b** and **3c** was preliminarily investigated by potentiodynamic electrodepositions, cycling around the first oxidation peak on glassy carbon electrode in CH$_3$CN + TBAPF$_6$ 0.1 M, in a three-electrode minicell. Compound **3b** showed a practically null formation of electroactive product on the electrode surface. This behavior could be ascribed to the β–α connection between the thienyl ring and the **BDT** unit, which could induce a more three-dimensional and rigidity character to the starting monomer **3b**. On the contrary, virtually unlimited electrodeposition could be obtained employing derivative **3c** (Figure 4a). The related electroactive films appeared stable upon repeated "stability cycles", which were performed cycling around the first oxidation peak in a monomer-free solution (Figure 4b).

The oligomeric pattern is similar to the ones obtained for the oligo/polymerization of common conjugated polythiophenes.[49] In fact, the oligomerization for compound **3c** occurs
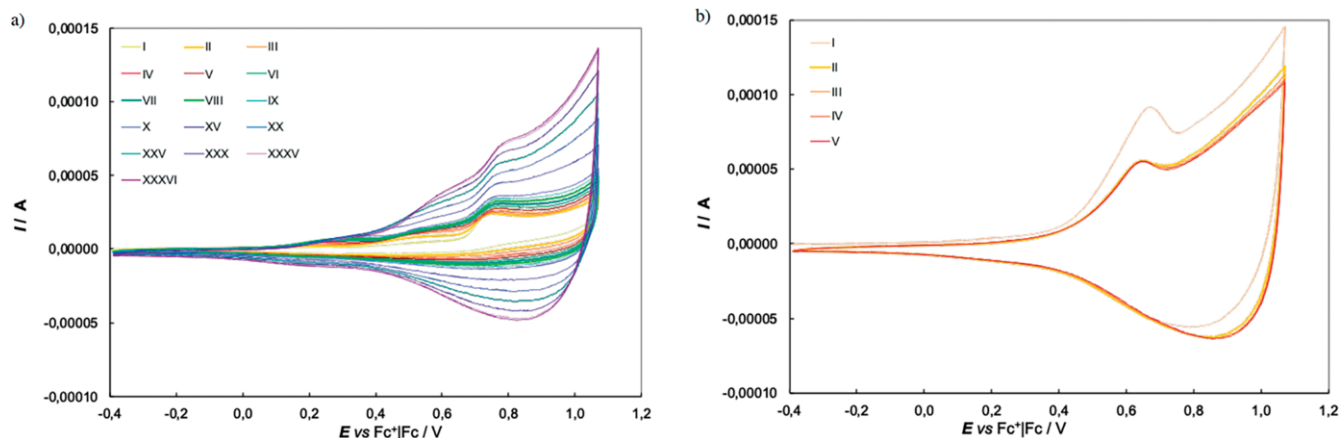
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Figure 4. a) Electrodeposition of **3c** monomer (1 mM) on glassy carbon electrode, at 0.2 V s^{-1} potential scan rate in 0.1 M TBAPF$_6$ as supporting electrolyte performing 36 deposition cycles; b) stability cycles of the film obtained from **3c** molecule in a monomer free solution at 0.2 V s^{-1} potential scan rate.

on the two α-homotopic positions on the two thienyl rings linked to the **BDT** unit. Films deposited by electrodeposition of monomer **3c** were analyzed by MALDI-TOF analyses and clearly displayed the presence of a mixture containing dimeric, trimeric, tetrameric and pentameric species (see ESI).

Finally, a preliminary investigation of the electrochromic ability of these oligomeric films was carried out taking into account that only one study on the electrochromic ability of BDT polymers has been reported so far.[17] To this end, the oligomer obtained from **3c** was electrodeposited in a three-electrode minicell but on ITO as a working electrode. When the film was in its neutral state, an orange-yellow color was observed. When the applied potential was gradually increased to 0.5 V vs. Fc$^+$|Fc (onset value of the oligomer), both the oxidation state of film and changes in its internal electronic structure occurred. When the film was fully oxidized to 1.0 V vs. Fc$^+$|Fc, the oligomer color definitely switched to blue, in agreement with that previously observed for similar BDT co-monomers.[17]

Conclusion

In summary, we have developed a general procedure for the synthesis of 2,7-diaryl-substituted **BDTs 3** (up to 79 % yield) by exploiting a palladium-catalyzed ligand-free Suzuki–Miyaura reaction between dibromide **1a** or diiodide **1b** and aryltrifluoroborate salts **2** using ChCl/Gly as an environmentally benign and biodegradable unconventional solvent, under air and mild conditions. Further, we have applied this methodology to synthesize in ChCl/Gly the symmetric alkenyl- and alkynyl-substituted π-conjugated systems **6** and **10** (44–74 % yield) starting from trifluoroborate salts **5** and **9** as nucleophilic partners. Most of the molecules prepared within this work represent a useful platform to access more complex structures by downstream modification of the functional groups (e.g., -CN, -NO$_2$, -OMe) present in compounds **3d–f** or through oligomerization processes as in the case of the thienyl-substituted derivative **3c**. Thus, this study represents an important step forward for the successful use of DESs in SM cross-coupling reactions for the synthesis of π-conjugated heteroaryl systems of relevance in

the field of material sciences. Finally, the optical and electrochemical characterization of these systems were also carried out by absorption measurements and cyclic voltammetry experiments, respectively, and the results found were in agreement with those previously reported for similar functionalized **BDTs**. Of note, some derivatives display photoluminescent quantum yields (PLQY) in solution significantly high (up to 80 %). A preliminary investigation on the electrooligomerization properties of **3c** was also undertaken. This study confirmed that *ad hoc* functionalized **BDT** scaffolds are suitable co-monomers *en route* to oligomers displaying electrochromic properties.

Experimental Section

General Information: Commercial reagents and solvents were purchased from Sigma-Aldrich and used without further purification. 2,7-Dibromo-benzo[1,2-*b*:4,3-*b'*]dithiophene (**1a**)[16] and 2,7-diiodo-benzo[1,2-*b*:4,3-*b'*]dithiophene (**1b**)[48] were synthesized as previously reported. Deep Eutectic Solvent choline chloride (ChCl)/glycerol (Gly) (1:2 mol mol^{-1}) was prepared by heating whilst stirring at 60 °C for 10 min the corresponding individual components until a clear solution was obtained.[23] Thin-layer chromatography (TLC) was performed with Aldrich silica gel 60 F254 precoated plates, and plates were visualized with short-wave UV light (254 nm). Column chromatography was carried out with Aldrich silica gel (70–230 mesh). Melting points were determined with a Büchi Melting Point B-540 apparatus and are uncorrected. UV/Vis spectra were recorded with a 500 Evolution Thermo Electron Corporation spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded at 25 °C using a Bruker AC-300 or a Bruker AC-600 MHz spectrometer. Chemical shifts were reported relative to the residual protonated solvent resonances (^{1}H: δ = 7.26 ppm for CDCl$_3$ and δ = 5.32 ppm for CD$_2$Cl$_2$, ^{13}C: δ = 77.16 for CDCl$_3$). Chemical shifts are given in ppm and coupling constants in Hz. High Resolution Mass Spectra (Electron Ionization) HRMS (EI) were recorded on a FISONS - Vg Autospec- M246 spectrometer. The purity of final compounds **3a–f**, **6–8** and **10** was determined by reverse-phase RP-HPLC analysis performed on an Agilent 1100 series system, equipped with DAD 300 analyzer, using the analytical column Zorbax Eclipse XDB-C18 (150 mm × 4.6 mm 5 μm) at a flow rate of 1 mL/min. Solvent A (water) and solvent B (acetonitrile) were used in 10:90 ratio under isocratic conditions with UV detection at 254 nm.

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General procedure for the synthesis of compounds 3a–f, 6–8, and 10. To a mixture of a boron species **2** (0.2 mmol or 0.1 mmol) in ChCl/Gly (1.0 g), dibromo-benzodithiophene **1a** or diiodo-benzo-dithiophene **1b** (0.1 mmol), Pd(OAc)$_2$ (0.3 mg, 0.001 mmol, 1 mol-%) and Na$_2$CO$_3$ (22 mg, 0.2 mmol) were sequentially added. The resulting suspension was stirred at 60 °C under air for the period of time reported in Table 1, Table 2 and Scheme 1, Scheme 2, and Scheme 3. The outcome of the reaction was monitored by HPLC and TLC analysis of a sample of the reaction mixture diluted with CH$_2$Cl$_2$. After being cooled to room temperature, the reaction mixture was poured into water (10 mL) and the aqueous layer was extracted with CH$_2$Cl$_2$ (3 × 10 mL). The combined organic phases were dried with Na$_2$SO$_4$ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to provide the desired products **3a–f**, **6–8**, and **10**. RP-HPLC analyses showed that these compounds had chemical purity ranging from 95 to 99 %.

2,7-Diphenylbenzo[1,2-*b*:4,3-*b*′]dithiophene (3a). The crude reaction product obtained from the Pd-catalyzed SM reaction of **1a** with **2a** (Table 1, entry 1) was purified by column chromatography on silica gel with a mixture of hexane and CH$_2$Cl$_2$ (9:1) as the eluent to afford **3a** as a yellow solid. Yield: 27 mg; 79 %; m.p. (pentane) 164–165 °C; ^{1}H NMR (600 MHz, CDCl$_3$): δ = 7.95 (s, 2H), 7.79 (d, J = 7.6 Hz, 4H), 7.75 (s, 2H), 7.46 (t, J = 7.4 Hz, 4H), 7.37 (t, J = 7.4 Hz, 2H); ^{13}C NMR (150 MHz, CDCl$_3$): δ = 144.7, 136.3, 135.5, 134.3, 129.0, 128.3, 126.5, 118.6, 117.5; UV/Vis (CH$_2$Cl$_2$): λ_{max} (log ε) = 347 nm (4.56). HRMS (EI): m/z calcd. for C$_{22}$H$_{14}$S$_2$: 342.0537, found 342.0520.

2,7-Bis(thien-3-yl)-benzo[1,2-*b*:4,3-*b*′]dithiophene (3b). The crude reaction product obtained from the Pd-catalyzed SM reaction of **1a** with **2d** (Scheme 1) was purified by column chromatography on silica gel with a mixture of hexane and CH$_2$Cl$_2$ (9:1) as the eluent to afford **3b** as a yellow solid. Yield: 25 mg; 71 %; m.p. (hexane/CH$_2$Cl$_2$) 209–210 °C; ^{1}H NMR (600 MHz, CDCl$_3$): δ = 7.79 (s, 2H), 7.71 (s, 2H), 7.58–7.55 (m, 2H), 7.50–7.48 (m, 2H), 7.43–7.42 (m, 2H); ^{13}C NMR (75 MHz, CDCl$_3$): δ = 139.4, 135.8, 135.7, 135.2, 126.7, 126.1, 121.2, 118.4, 117.5; UV/Vis (CH$_2$Cl$_2$): λ_{max} (log ε) = 344 nm (4.59). HRMS (EI): m/z calcd. for C$_{18}$H$_{10}$S$_4$: 353.9665, found 353.9651.

2,7-Bis(thien-2-yl)-benzo[1,2-*b*:4,3-*b*′]dithiophene (3c). The crude reaction product obtained from the Pd-catalyzed SM reaction of **1a** with **2f** (Scheme 1) was purified by column chromatography on silica gel with a mixture of hexane and CH$_2$Cl$_2$ as the eluent to afford **3c** as a yellow solid. Yield: 19 mg; 59 %; m.p. (hexane/CH$_2$Cl$_2$) 185–187 °C. ^{1}H NMR (600 MHz, CDCl$_3$): δ = 7.75 (s, 2H), 7.68 (s, 2H), 7.34–7.32 (m, 4H), 7.10–7.08 (m, 2H); ^{13}C NMR (150 MHz, CDCl$_3$): δ = 137.8, 137.4, 136.0, 135.1, 128.0, 125.5, 125.0, 118.5, 117.9; UV/Vis (CH$_2$Cl$_2$): λ_{max} (log ε) = 367 nm (4.58); HRMS (EI): m/z calcd. for C$_{18}$H$_{10}$S$_4$: 353.9665, found 353.9656.

2,7-Bis(4-methoxyphenyl)-benzo[1,2-*b*:4,3-*b*′]dithiophene (3d). The crude reaction product obtained from the Pd-catalyzed SM reaction of **1a** with **2h** (Scheme 1) was purified by column chromatography on silica gel with a mixture of hexane and CH$_2$Cl$_2$ (9:1) as the eluent to afford **3d** as a yellow solid. Yield: 26 mg; 66 %; m.p. (hexane) 238–240 °C; ^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.81 (s, 2H), 7.73–7.70 (m, 6H), 7.00–6.97 (m, 4H), 3.88 (s, 6H); ^{13}C NMR (75 MHz, CDCl$_3$): δ = 159.8, 144.5, 135.9, 135.5, 127.7, 127.2, 118.2, 116.4, 114.4, 55.4; UV/Vis (CH$_2$Cl$_2$): λ_{max} (log ε) = 352 nm (4.34); HRMS (EI): m/z calcd. for C$_{24}$H$_{18}$O$_2$S$_2$: 402.0748, found 402.0762.

2,7-Bis(4-nitrophenyl)-benzo[1,2-*b*:4,3-*b*′]dithiophene (3e). The crude reaction product obtained from the Pd-catalyzed SM reaction of **1a** with **2j** (Scheme 1) was purified by column chromatography on silica gel with CH$_2$Cl$_2$ as the eluent to afford **3e** as an orange solid. Yield: 14 mg; 32 %; m.p. (hexane/CH$_2$Cl$_2$) 301 °C (dec.); ^{1}H NMR (300 MHz, CDCl$_3$): δ = 8.34 (d, J = 8.9 Hz, 4H), 8.13 (s, 2H), 7.94 (d, J = 8.9 Hz, 4H), 7.85 (s, 2H); UV/Vis (CH$_2$Cl$_2$): λ_{max} (log ε) = 394 nm (4.42); HRMS (EI): m/z calcd. for C$_{22}$H$_{12}$N$_2$O$_4$S$_2$: 432.0238, found 432.0260. The ^{13}C NMR spectrum was not recorded for **3e** because of its low solubility in the common deuterated solvents.

4,4′-(Benzo[1,2-*b*:4,3-*b*′]dithiophene-2,7-diyl)dibenzonitrile (3f). The crude reaction product obtained from the Pd-catalyzed SM reaction of **1a** with **2k** (Scheme 1) was purified by column chromatography on silica gel with a mixture of hexane and CH$_2$Cl$_2$ (6:4) as the eluent to afford **3f** as an orange solid. Yield: 10 mg; 26 %; m.p. (hexane/CH$_2$Cl$_2$) 291–293 °C; ^{1}H NMR (300 MHz, CDCl$_3$): δ = 8.06 (s, 2H), 7.89–7.86 (m, 4H), 7.83 (s, 2H), 7.76–7.73 (m, 4H); ^{13}C NMR (75 MHz, CDCl$_3$): δ = 142.7, 138.4, 137.4, 135.5, 132.9, 126.8, 119.6, 119.5, 118.6, 111.6; UV/Vis (CH$_2$Cl$_2$): λ_{max} (log ε) = 368 nm (4.59); HRMS (EI): m/z calcd. for C$_{24}$H$_{12}$N$_2$S$_2$: 392.0442, found 392.0442.

2,7-Bis((*E*)-styryl)benzo[1,2-*b*:4,3-*b*′]dithiophene (6). The crude reaction product obtained from the Pd-catalyzed SM reaction of **1b** with **5** (Table 2, entry 1) was purified by chromatography on silica gel with a mixture of hexane and CH$_2$Cl$_2$ (90:10) as the eluent to afford **6** as an orange solid. Yield: 25 mg; 74 %; m.p. (hexane/CH$_2$Cl$_2$) 253–254 °C; ^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.69 (s, 2H), 7.59 (s, 2H), 7.54 (d, J = 7.5 Hz, 4H), 7.40–7.37 (m, 6H), 7.29 (d, J = 7.2 Hz, 2H), 7.06 (d, J = 16.0 Hz, 2H); ^{13}C NMR (75 MHz, CDCl$_3$): δ = 143.5, 136.6, 135.8, 134.9, 130.8, 128.8, 128.1, 126.6, 122.2, 121.2, 118.9; UV/Vis (CH$_2$Cl$_2$): λ_{max} (log ε) = 382 nm (4.71); HRMS (EI): m/z calcd. for C$_{26}$H$_{18}$S$_2$: 394.0850, found 394.0835.

(*E*)-2-Bromo-7-styrylbenzo[1,2-*b*:4,3-*b*′]dithiophene (7). The crude reaction product obtained from the Pd-catalyzed SM reaction of **1a** with **5** (Table 2, entry 3) was purified by chromatography on silica gel with a mixture of hexane and CH$_2$Cl$_2$ (90:10) as the eluent to afford **7** as a colorless solid. Yield: 17 mg; 46 %; m.p. (hexane/CH$_2$Cl$_2$) 177–179 °C; ^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.69 (d, J = 8.5 Hz, 1H), 7.65 (s, 1H), 7.62 (d, J = 8.5 Hz, 1H), 7.54–7.52 (m, 3H), 7.40–7.35 (m, 3H), 7.37 (t, J = 7.3 Hz, 1H), 7.05 (d, J = 16.0 Hz, 1H); ^{13}C NMR (75 MHz, CDCl$_3$): δ = 137.3, 132.8, 131.1, 129.2, 128.8, 128.6, 128.1, 127.5, 126.6, 126.4, 124.8, 122.0, 120.8, 118.8, 118.0; UV/Vis (CH$_2$Cl$_2$): λ_{max} (log ε) = 382 nm (4.54); HRMS (EI): m/z calcd. for C$_{18}$H$_{11}$BrS$_2$: 369.9486, found 369.9484.

(*E*)-2-Phenyl-7-styrylbenzo[1,2-*b*:4,3-*b*′]dithiophene (8). The crude reaction product obtained from the Pd-catalyzed SM reaction of **7** with **2a** (Scheme 2) was purified by column chromatography on silica gel with a mixture of hexane and CH$_2$Cl$_2$ (95:5) as the eluent to afford **8** as a yellow solid. Yield: 10 mg; 27 %; m.p. (hexane/CH$_2$Cl$_2$) 192–194 °C; ^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.88 (s, 1H), 7.79–7.68 (m, 4H), 7.66 (s, 1H), 7.54 (d, J = 7.4 Hz, 2H), 7.48–7.29 (m, 7H), 7.06 (d, J = 16.0 Hz, 1H); ^{13}C NMR (75 MHz, CDCl$_3$): δ = 144.9, 143.4, 136.6, 136.4, 135.8, 135.4, 135.1, 134.3, 130.7, 129.0, 128.8, 128.3, 128.1, 126.6, 126.5, 122.2, 121.2, 119.0, 118.5, 117.5; UV/Vis (CH$_2$Cl$_2$): λ_{max} (log ε) = 369 nm (4.69); HRMS (EI): m/z calcd. for C$_{24}$H$_{16}$S$_2$: 368.0693, found 368.0692.

2,7-Bis(phenylethynyl)benzo[1,2-*b*:4,3-*b*′]dithiophene (10). The crude reaction product obtained from the Pd-catalyzed SM reaction of **1b** with **9** (Scheme 3) was purified by column chromatography on silica gel with a mixture of hexane and CH$_2$Cl$_2$ (95:5) as the eluent to afford **10** as a yellow solid. Yield: 17 mg; 44 %; m.p. (hexane/CH$_2$Cl$_2$) 178–179 °C; ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ = 7.89 (s, 2H), 7.79 (s, 2H), 7.62–7.56 (m, 4H), 7.43–7.38 (m, 6H); ^{13}C NMR (75 MHz, CDCl$_3$): δ = 137.5, 134.0, 131.6, 128.8, 128.5, 126.5, 124.0, 122.5, 119.3, 95.4, 82.9; UV/Vis (CH$_2$Cl$_2$): λ_{max} (log ε) = 357 nm (4.57); HRMS (EI): m/z calcd. for C$_{26}$H$_{14}$S$_2$: 390.0537, found 390.0534.

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V. Pelliccioli, G. Dilauro, S. Grecchi, S. Arnaboldi, C. Graiff, F. M. Perna, P. Vitale, E. Licandro, A. Aliprandi, S. Cauteruccio,* V. Capriati* 1–9

Ligand-Free Suzuki–Miyaura Cross-Coupling Reactions in Deep Eutectic Solvents: Synthesis of Benzodithiophene Derivatives and Study of their Optical and Electrochemical Performance
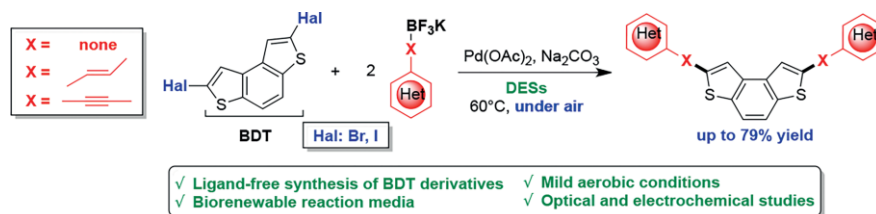
Valuable π-conjugated benzodithiophene derivatives have been prepared through a ligand-free Suzuki–Miyaura cross-coupling reaction, under mild aerobic conditions, in deep eutectic solvents (DESs) as environmentally responsible reaction media, and their optical and electrochemical properties were investigated.

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