



# Highly selective Palladium-catalyzed Suzuki coupling reaction toward chlorine-containing electroluminescence polymers



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## ABSTRACT

High selectivity and yield from aryl–aryl coupling reactions between chlorine-containing aromatic bromides and organoboron reagents are reported. The variable reaction selectivity between the bromine and chlorine mainly depends on the electronic effects of the aromatic substrates. The reactivity of the chlorine can be completely restrained by employing the optimized Palladium catalysts, which can be used for the preparation of the chlorine-bearing molecules. Then, a series of high molecular weight conjugated copolymers with chlorine on the backbones are straight forward synthesized for the first time under Suzuki condensation reaction. The polymers show large Stokes shifts and low self-absorption. Efficient and high brightness red emission centre at about 636 nm can be obtained when doping the resulting polymer into F8BT.

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## 1. Introduction

The chlorine-containing organic conjugated molecules are drawing more and more attention recently because of the potential as strong competitors for optoelectronic materials [1]. To the best of our knowledge, there are still few reported chlorine-bearing aryl materials, because of the synthetic difficulties. To acquire chlorine-functionalized organic materials, a post-chlorine-functionalization method has been reported [2]. However, controlling the chlorine ratio and chlorine position during the post chlorine processing is extremely difficult and almost impossible. As such, the development of more efficient approaches for the preparation of chlorine-bearing molecules is highly desirable for the field of material chemistry. Science seminal work by Suzuki and co-workers in 1979 [3], transition-metal-catalyzed coupling reactions of aromatic halides with organoboron compounds have been recognized as one of the most powerful tools to prepare organic conjugated molecules [4]. For the leaving halogen groups in such a reaction, it has been well established that the order of the reactivity in the coupling partner decreased as  $I > Br > Cl > F$  [5]. Among the halides, fluoride

is much more stable and is not involved in the reaction, which is a significant advantage and has already been used for the construction of fluorine-containing aryl–aryl bonds [6]. However, it is a challenge to prepare chlorine-bearing aryl compounds by the Suzuki coupling reaction because the aromatic chloride tends to participate in the reaction [7], resulting in poor selectivity with aromatic bromide or iodide, low yield for the target compound and cross-linking reactions for polymerization. In this context, the complete restraint for the reactivity of chlorine is the key process for the synthesis of chlorine-bearing molecules by Suzuki coupling reaction, especially for the polymers.

Herein, four chlorine-containing aromatic bromides with different electronic effects are chosen as the model substrates to investigate the influence of the different substrates properties on the coupling selectivity between bromine and chlorine. Then, four Pd complexes are used as the catalysts to optimize the coupling reaction conditions so as to completely suppress the coupling reactivity of chlorine. The benzothiadiazole (BTH) unit is a well-known electron-deficient system that has found use as the acceptor to construct the donor-acceptor (D–A) conjugated polymers, especially for the light emitting polymers [8]. Therefore, finally, the chlorine-bearing D–A alternating BTH-based copolymers are obtained by standard Suzuki condensation reaction for the first time using the optimized coupling reaction conditions, as well

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characterized by dopant/host blended device to study the EL performance of PLEDs.

## 2. Results and discussion

### 2.1. Optimization for the coupling reaction conditions

The optimized processes are shown in Scheme 1. 2-Bromo-5-chlorothiophene (A1), 1-bromo-4-chlorobenzene (A2), 5,8-dibromo-6,7-dichloro-2,3-bis(3-(octyloxy)phenyl)-quinoxaline (A3) [9], and 4,7-dibromo-5,6-dichlorobenzo[c][1,2,5]thiadiazole (A4) [10] were chosen as the model reagents, which had a strong electron-donating ability, a weak electron-donating ability, a medium electron-withdrawing ability and a strong electron-withdrawing ability, respectively. Four widely used Pd complexes, Pd(pph<sub>3</sub>)<sub>4</sub>, (P-1) [11] Pd(pph<sub>3</sub>)<sub>4</sub>/CuBr, (P-2) [12] Pd<sub>2</sub>(dba)<sub>3</sub>/P(o-tol)<sub>3</sub> (P-3) [13] and Pd(dppf)Cl<sub>2</sub> (P-4) [14] were investigated to prepare the target compounds B1, B2, B3 and B4. The ratios of the byproducts with one substitution of the chlorine atom, B1–Cl, B2–Cl, B3–Cl and B4–Cl were simultaneously monitored.

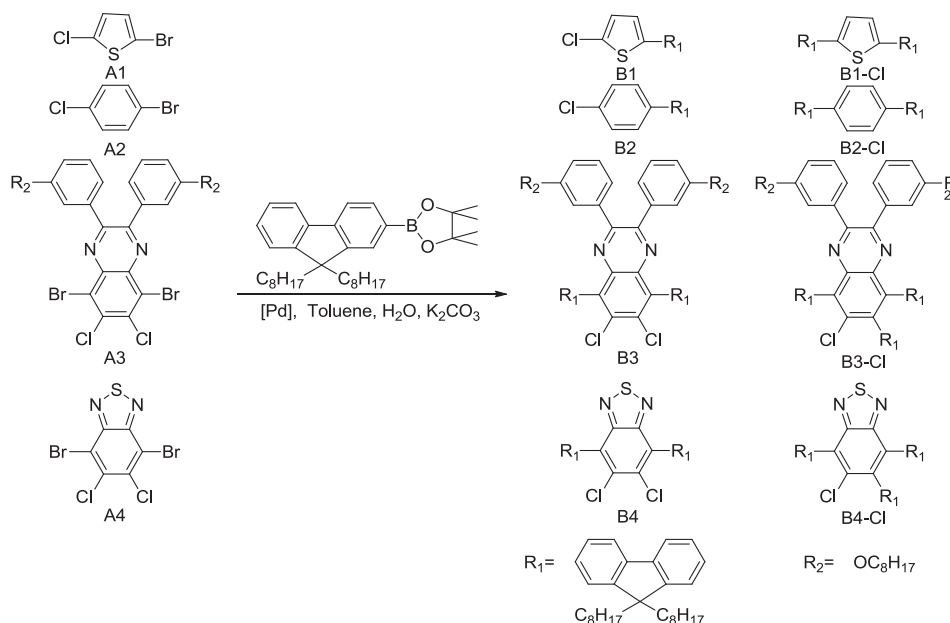
For the strong electron-donating compound A1, the Suzuki coupling reaction occurred chemoselectively at the aryl-bromine without the B1 byproduct, and a perfect yield (greater than 96%) was earned for all four catalysts (Table 1, entries 1–4). When the aromatic unit was a phenyl, which is a relatively weaker electron-donating group than thiophene, A2 provided a similar result to that of A1 (entries 5–8). The above two Suzuki couplings could smoothly work for the aromatic bromides on electron-releasing parent structures to afford the chlorine-containing biaryls in high yields.

When the coupling reaction occurred on the electron-deficient aromatic quinoxaline, the optimized yields of the target molecule B3 and the byproduct B3–Cl were 40% and 27%, respectively, when Pd<sub>2</sub>(dba)<sub>3</sub>/P(o-tol)<sub>3</sub> was utilized as the catalyst, as shown in Table 2. The Pd<sub>2</sub>(dba)<sub>3</sub>/P(o-tol)<sub>3</sub> catalyst showed poor reactivity for both bromide and chloride, as well as very low selectivity between these two halides. When Pd(dppf)Cl<sub>2</sub> was used as the catalyst, the yield of B3 increased to 86% with 12% of the byproduct B3–Cl, meaning that Pd(dppf)Cl<sub>2</sub> could enhance the reactivity of the bromide and partly

suppress the reactivity of the chloride. However, the selectivity was still poor. The Pd(pph<sub>3</sub>)<sub>4</sub>/CuBr catalyst, provided different yields of the product and the byproduct (91% and 5%, respectively), indicating a much better selectivity compared with the above two catalysts, while the resulting yield of the product was still not enough, especially for polymerization because the existence of B3–Cl will lead to cross-linking reactions. The Pd(pph<sub>3</sub>)<sub>4</sub> catalyst exhibited the best performance with a yield of over 96%, and there was no B3–Cl found, which showed that the catalyst could completely suppress the reactivity of chlorine.

For the strong electron-acceptor A4, in which the aromatic group is benzo[c][1,2,5]thiadiazole, the reactivity of bromine atoms was very low when used Pd(pph<sub>3</sub>)<sub>4</sub>/CuBr, Pd<sub>2</sub>(dba)<sub>3</sub>/P(o-tol)<sub>3</sub> and Pd(dppf)Cl<sub>2</sub> as catalysts, the yields of B4 respectively were 20%, 28% and 26% (Table 2, entries 6–8). All the yields of B4–Cl were below 15%, indicating a weak reactivity for chlorine atoms, and a low selectivity between chlorine and bromine. Most importantly, Pd(pph<sub>3</sub>)<sub>4</sub> was employed in the reaction as the catalyst, affording the product in high yield (greater than 96%, entry 5) without couplings of chlorides, which showed that the Pd(pph<sub>3</sub>)<sub>4</sub> could totally restrain the reactivity of the chlorine atoms. The corresponding polymers were synthesized using this reaction condition (Scheme 2).

Density functional theory (DFT) calculations and cyclic voltammetry (CV) measurements of the four starting materials were performed to understand the influence of the electronic effects of the aromatic substrates on the Suzuki coupling reaction selectivity between aryl-chlorine and aryl-bromine. Four reference compounds without chlorine were also characterized. The electronic densities of the HOMOs and LUMOs were distributed on the entire molecules except for A3 and A3-Cl, in which the LUMOs were distributed on the quinoxaline unit and the HOMOs were distributed on the phenoxy unit (Fig. S1, Supporting Information). According to the CV results (Fig. S2, Supporting Information), the E<sub>LUMO</sub> and E<sub>HOMO</sub> of A1 were below that of A1-Cl, indicating that the chlorine atom had an electron-withdrawing ability [15]. The same results were found for A2 and A3. However, a contrary result was found for A4, in which the chlorine atoms possessed an electron-donating ability [16], leading to a higher E<sub>LUMO</sub> and E<sub>HOMO</sub> than



Scheme 1. Optimization for the coupling reactions.

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