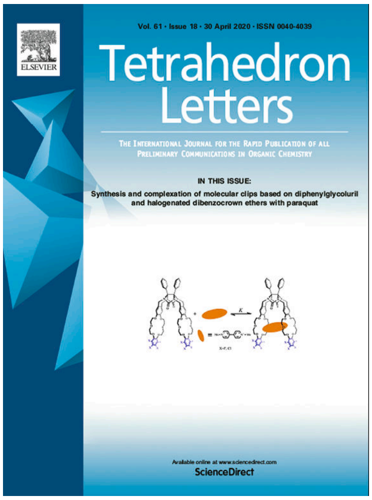

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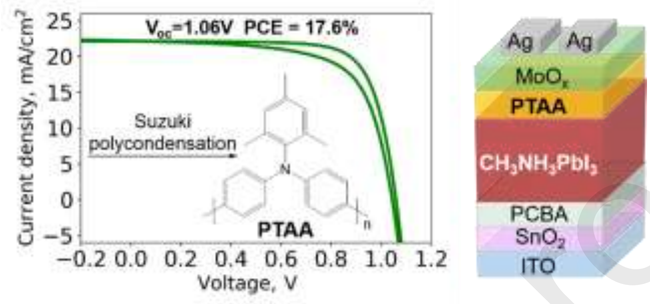

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Suzuki polycondensation for the synthesis of polytriarylamines: a method to improve hole-transport material performance in perovskite solar cells

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ABSTRACT

Polytriarylamines have attracted significant interest as hole transport materials for organic electronics. Herein we report the synthesis of a polytriarylamine (PTAA) using the Suzuki polycondensation reaction. The Pd-based catalytic system was optimized to obtain a polymer with a high molecular weight and low polydispersity. The synthesized PTAA polymer was evaluated as a hole transport material in perovskite solar cells with n-i-p configuration. The devices showed an improved power conversion efficiency of 17.6% and an open-circuit voltage of 1.06 V, whereas the referenced cells based on commercial PTAA delivered a lower efficiency of 16.7% and an open-circuit voltage of 1.02 V. Thus, the proposed synthetic approach yields high-quality PTAA with improved electrical properties.

Introduction

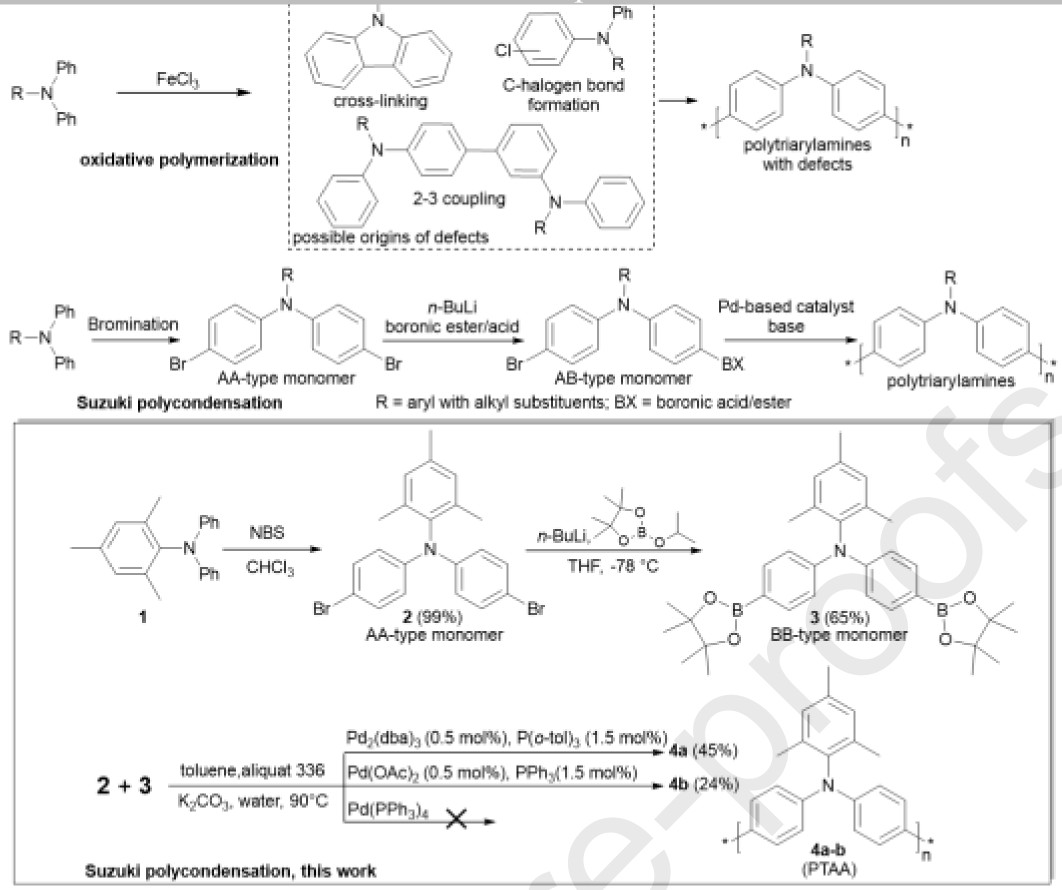
Perovskite solar cells have demonstrated remarkable progress with efficiency rising from 3.8% in the first report[1] to the current record of 25.2%[2] within less than a decade. One of the important components of perovskite solar cells is a hole transport layer (HTL), which selectively extracts and transports holes from the photoactive layer to a hole-collecting electrode. The most popular family of polymeric HTLs is represented by polytriarylamines with poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA) providing the highest efficiencies of up to 22.1% using appropriate doping.[3, 4]

There are various approaches to the synthesis of polytriarylamines. One of them is based on the oxidative polymerization of monomeric triarylamines with reagents such as $FeCl_3$.[5-7] On one hand, this reaction is rapid and the oxidizing reagents are inexpensive. On the other hand, due to the abundance of various side reactions, oxidative polycondensation produces low-quality polymers suffering from poor regioregularity, low molecular weights and multiple types of defects (e.g. crosslinking, carbon-halogen bond formation, Scheme 1a).[8-12] Therefore, such materials are not optimal for electronic applications, in particular in photovoltaic devices.

On the contrary, metal-catalyzed polycondensation reactions afford high-quality polymers at the cost of additional synthetic steps required to obtain auxiliary monomers and the need for expensive metal-based catalysts. Among the different metal-catalyzed cross-coupling reactions, Buchwald-Hartwig C-N coupling represents the most prevalent pathway for polytriarylamine synthesis.[13-16] Ullman polycondensation,[8, 17] and Yamomoto polycondensation[18] were also used for the synthesis of polytriarylamines such as PTAA.

Another type of metal-catalyzed reaction is the Suzuki-Miyaura polycondensation, which requires halogen-substituted and boron-substituted derivatives. The initial monomers might include both functional groups and in this case, they are referred to as AB-type monomers, where A and B represent halogen and boron functional groups, respectively. The Suzuki polycondensation using AB-type monomers was previously applied for the synthesis of PTAA as shown in Scheme 1b.[19] Typically, the AB-type monomer is prepared from an AA-type monomer by lithiation with a stoichiometric amount of *n*-butyllithium and quenching of the intermediate with the appropriate boronic ester.[19, 20] The AB-type monomer, in this case, should be extensively purified from the unreacted AA-type reagent, BB-type byproduct, and also dehalogenated products with only one functional boronic ester group, which can play the role of end cappers in polycondensation reactions. The high purity of AB-type monomer can be achieved with column chromatography, which in turn can damage the boronic ester functional groups.

Herein, we report the synthesis of PTAA *via* the Suzuki polycondensation reaction starting from AA-type and BB-type monomers. We demonstrate that purification of the BB-type monomer can be performed with simple recrystallization and precipitation, which is faster, easier, and more reliable for boronic esters as compared to column chromatography. Moreover, the yield of the BB-type monomer (65%) is superior compared to the yield of the AB-type monomer after column chromatography purification (49%).[19]



Scheme 1. Synthetic routes to polytriarylamines: oxidative polymerization (a); Suzuki polycondensation using AB-type monomers (b); Suzuki polycondensation using AA-type and BB-type monomers presented in this work (c).

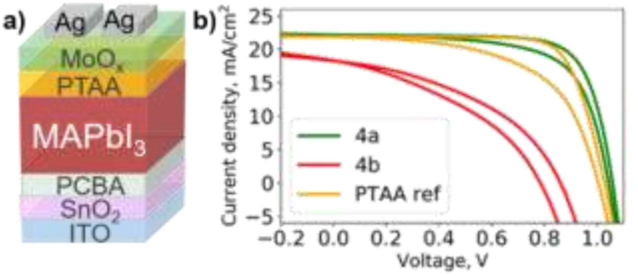
Results and Discussion

The synthetic route used for the preparation of PTAA applied in our work is depicted in Scheme 1c. Compound **1** was synthesized *via* Buchwald-Hartwig coupling between commercially available 2,4,6-trimethylaniline and bromobenzene. The subsequent bromination of **1** produced the AA-type monomer **2** with a quantitative yield.[19] Monomer **2** was additionally sublimated under reduced pressure leading to 99% purity according to high-performance liquid chromatography (HPLC). The BB-type monomer **3** was obtained by the lithiation of **2** with 4 equivalents of *n*-butyllithium followed by the addition of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.[21] The high purity of the monomer **3** (97% by HPLC) was achieved simply by precipitation from isopropanol and further recrystallization from chloroform upon the addition of methanol.

Finally, the Suzuki polycondensation reaction was performed with various catalytic systems. The first catalyst tetrakis(triphenylphosphine)palladium was used previously for the synthesis of low molecular weight triarylamine-based compounds.[22] However, this catalytic system failed to initiate the polycondensation of PTAA in our experiments. An alternative catalyst based on the combination of palladium acetate and triphenylphosphine led to low molecular weight polymer **4b**. The third catalytic system comprised of tris(dibenzylideneacetone)dipalladium and tri(*o*-tolyl)phosphine led to polymer **4a.** Polymers **4a** and **4b** were extensively purified with sequential Soxhlet extractions using methanol, acetone, and chloroform.

The relative molecular weight characteristics and polydispersity indexes of the chloroform fractions of **4a** and **4b** and commercial PTAA (**PTAA ref**), most probably synthesized by Suzuki polycondensation from the AB-type monomer,[15] were obtained using gel permeation chromatography (GPC). These characteristics are summarized in Figure 1 and the GPC traces are presented in Figure S4 (ESI). According to the GPC analysis, polymer **4a** had a lower average molecular weight (M_n) and narrower molecular weight distribution (M_w/M_n) as compared to **PTAA ref**, whereas polymer **4b** had twice lower M_n compared to **4a**.

All three batches of PTAA were evaluated as hole transport layer (HTL) materials in perovskite solar cells with n-i-p configuration (Fig. 1a). The optimized perovskite solar cell architecture was comprised of ITO (indium tin oxide) covered with an electron transport layer of SnO_2 passivated with a fullerene derivative phenyl-C_{61}-butyric acid (PCBA).[23, 24] The film of conventional lead halide perovskite material $CH_3NH_3PbI_3$ was deposited atop SnO_2/PCBA. A polymeric HTL based on one of **4a**, **4b,** or **PTAA Ref** polymers was spin-coated from the



PTAA	M_n	M_w/M_n	V_{OC}, V	J_{SC}, mA/cm^2	FF, %	PCE, %
4a	20.8	1.4	1.06	22.1	75	17.6
4b	10.7	1.4	0.97	19.8	43	8.2
PTAA ref	25.2	2.2	1.02	21.8	75	16.7

Figure 1. Configuration of the perovskite solar cell (a); J-V characteristics of perovskite solar cells with PTAA **4a**, **4b** and **PTAA ref** applied as the hole transport material (b).

chlo

Optimal film deposition conditions for each PTAA batch were evaluated in the preliminary experiments.

Finally, the hole-collecting electrode consisting of MoO_x(10 nm) and Ag (100 nm) was deposited by thermal evaporation under vacuum thus completing the configuration of the perovskite solar cell $ITO/SnO_2/PCBA/CH_3NH_3PbI_3/HTL/MoO_x/Ag$ as illustrated in Figure 1a.

The *J-V* characteristics of the best devices fabricated with all three polymer batches are presented in Figure 1b. The cells incorporating polymer **4b** demonstrated low power conversion efficiencies (PCE) of 8.2% with a modest fill factor (FF) of 43%. These results confirmed the poor electronic quality and, consequently, the suboptimal charge transport properties of low molecular weight polymer **4b**. On the contrary, the devices with HTL based on **PTAA Ref** and **4a** delivered much higher efficiencies of 16.7% and 17.6%, respectively. To the best of our knowledge, these are among the highest efficiency values demonstrated for perovskite solar cells with an undoped PTAA layer. The fill factors (FF) and current densities (J_{SC}) were comparable for devices with both polymer batches. The current density values were additionally reconfirmed with external quantum efficiency measurements (Fig. S6). Importantly, the open-circuit voltage (V_{OC}) of the devices with **4a** approached 1.06 V, which was notably higher compared to the cells with **PTAA Ref** yielding a V_{OC} of 1.02 V. The higher V_{OC} reached for devices with **4a** indicates a decrease in the density of the defects at the perovskite/HTL interface suppressing trap-assisted recombination of charge carriers.[25]

Conclusion

To conclude, the proposed approach for PTAA synthesis from AA- and BB-type monomers using the Suzuki polycondensation reaction led to a high-quality polymer with narrow molecular weight distribution. The obtained polymer was applied as a hole-transport material in dopant-free perovskite solar cells, which demonstrated improved performance with the efficiency reaching 17.6% due to the reduced defect density at the perovskite/PTAA interface. Our results emphasize the importance of the synthetic route choice for designing high electronic quality materials for photovoltaic applications.

Acknowledgements

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Supplementary Material

Experimental procedures, material characterization, device fabrication data, and external quantum efficiency spectra can be found in the Electronic Supplementary Information.

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PTAA is synthesised from AA-type and BB-type monomers *via* Suzuki polycondensation

The Pd-based catalytic system for PTAA synthesis is optimized

Perovskite solar cells with PTAA hole-transport material show 17.6% efficiency

Superior performance of the synthesized PTAA is attributed to its improved quality