



Visible-light-promoted aerobic oxidative hydroxylation of arylboronic acids in water by hydrophilic organic semiconductor

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ABSTRACT

A green and sustainable catalytic system was developed based on perylene diimide (PDI) organic semiconductor for the aerobic oxidative hydroxylation of arylboronic acids in aqueous solution with visible light. By using PDI-SN, a hydrophilic organic semiconductor, which can activate oxygen to produce superoxide radicals in aqueous solution, this reaction proceeds under ambient conditions: water as the solvent and air as the oxidant, giving various phenols as products with high yields. In contrast to methods using organic solvents, this novel process has the potential of green industrial application.

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Introduction

Phenols, as a common structural unit, widely exist in nature products and pharmaceuticals, are used for the synthesis of fine chemicals as useful intermediates [1]. For its important value, the approaches to their preparation has been widely concerned [2]. Among the methods as reported [3], the oxidative hydroxylation of arylboronic acids is considered to be a very effective way to prepare phenols. Various oxidants (mCPBA, Oxone, TBHP, PhI(OAc)₂, H₂O₂, etc.) are used for the synthesis of phenols [4–11]. In comparison with these stoichiometric oxidants, molecular oxygen (O₂ and air) attracts more attention due to its cheap and readily availability [12]. Consequently, the aerobic methods for the oxidative hydroxylation of arylboronic acids using molecular oxygen have also been developed [13–15]. Despite their achievements, more green protocols for this transformation are still highly desirable, and it would be valuable to develop a new catalytic system to avoid the use of transition-metals and violent organic solvents.

The development of green and sustainable approaches to the synthesis of fine chemicals is a primary aim nowadays. Recently, visible-light catalysis is considered as promising to achieve this objective [16]. Some photocatalytic systems based on transition metal complexes [17], solid materials containing transition metals [18–23], porous-organic frameworks [24], fullerenes [25], cova-

lent-organic frameworks [26], and organic photocatalysts [27] have been applied for the visible-light-promoted aerobic oxidative hydroxylation of arylboronic acids. Despite the high level of efficiency, these protocols usually require the use of non-reusable organic photosensitizers, transition metals or volatile organic solvents. From the perspective of sustainable and green chemistry, a reusable metal-free catalytic system using water as reaction medium is desirable for synthetic chemists. Therefore, the application of this system for the oxidative hydroxylation of arylboronic acids is highly expected.

In recent years, organic semiconductor photocatalysts have been extensively applied in splitting water into H₂ and O₂ [28], the degradation of pollutants [29] and CO₂ reduction [30] due to its high catalytic stability. These heterogeneous catalytic systems were favored by synthesis chemists as well because the catalysts can be reused and the products can be easily separated [31]. Recently, Xu and Chen's group reported a reusable photocatalytic system based on organic semiconductor C₃N₄ to realize the aerobic oxidative hydroxylation of arylboronic acids using EtOH as the solvent [32]. However, the performance for this transformation was poor when water as the reaction medium. Based on their studies and others [17–27], superoxide radicals (O₂^{•-}) is considered to be a critical oxidative specie for this transformation. According to the recent research by our group [33], the efficient production of O₂^{•-} in the water medium based on perylene diimide (PDI) organic semiconductor driven by visible light is certainly feasible. Following our continuing study of green synthesis [34], we envisioned that the photocatalytic oxidative hydroxylation of arylboronic

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acids in water could be achieved by PDI semiconductor catalytic system. In this regard, a green and sustainable method was developed for this transformation. This protocol has the following advantages: (1) A green catalytic system with metal-free, air as the oxidant and water as the solvent. (2) Good photo-oxidative selectivity and high functional-group tolerance; (3) Operationally simple and reusable catalyst. In contrast to methods using volatile organic solvents, this novel process has the potential of green industrial application.

Results and discussions

In our previous studies, efficient aerobic oxidation of cycloamines was realized using a hydrophilic photocatalyst PDI-SN [34], which consists of SiO₂ nanoparticles containing amino groups and PDI molecules. The high photo-oxidative activity was observed due to the minute aggregates of PDI molecules on the surface of SiO₂ nanospheres forming organic semiconductor and O₂^{•-} was detectable as the key reactive oxygen species. Therefore, our studies started with the aerobic oxidative hydroxylation of benzenboronic acid (**1a**) using PDI-SN as the photocatalyst. To our delight, the desired product phenol (**2a**) was obtained in a yield of 92% with triethylamine (TEA) as the electron donors and H₂O as the solvent under irradiation with 20 W 400 nm LED for 42 h (Table 1, entry 1). Inspired by the result, some control experiments including catalysts, electron donors, air and light irradiation were performed. These results clearly demonstrated that all factors are essential (Table 1, entries 2–5). Subsequently, the wavelengths of visible light sources were studied, with 400 nm leading to the highest catalytic activity (see Table S1 in the Supporting Information). It is worth mentioning that methanol (MeOH) as a solvent gave the best result and the substrate can be completely transformed to the corresponding phenol within 7 h in 93% yield (see Table S2. in the Supporting Information). It may be that MeOH acted as a role of electron donors.

In order to improve the reaction efficiency in water, other electron donors such as diisopropylethylamine (DIPEA) and triethanolamine (TEOA) were also investigated. To our delight, we found that TEOA was more efficient as electron donor, because the complete transformation took the shortest time with a comparable yield (Table 2, entry 3). This may be attributed to TEOA being water-soluble, which is consistent with the hydrophilic catalyst. Encouraged by this results, control experiments involving in the catalyst components were carried out. The hydrophilic nano-

spheres SN-NH₂ containing amino groups, as the precursors of PDI-SN, showed no catalytic activity (Table 2, entry 4). Poor performance was found when a self-assembly semiconductor PDINH as catalyst (Table 2, entry 5). This observation suggested the catalytic activity of PDI-SN in water is enhanced with the assistance of hydrophilic carrier SiO₂. Comparatively, the bulky g-C₃N₄, which was frequently used in semiconductor photocatalysis, was studied under the standard reaction conditions, but poor performance was observed (Table 2, entry 6).

With the optimal condition in hand, this green and sustainable catalytic protocol was then applied to the aerobic hydroxylation of diverse arylboronic acids. As shown in Table 3, various substituted arylboronic acids were compatible. The benzenboronic acids bearing a methyl, as substituted at 2-, 3-, and 4-positions were well tolerated, and the 2-position substitution afforded slightly lower yields, which is possibly attributed to the greater steric hindrance at the 2-position than that at the other positions (Table 3, 2b–2d). Consequently, sterically hindered 2,4,6-trimethyl substituted benzenboronic acid generated the desired product in lower yields of 66% (Table 3, 2e). In addition to alkyl substitution, the substrate containing other electron-donating group like 4-methoxyl substituted benzenboronic acid worked in this system as well in a more moderate yield (Table 3, 2f). On the other hand, the substrates containing the electron-withdrawing groups such as 4-F, 4-Cl, 4-Br and 4-I were converted into the corresponding phenols in good yields (Table 3, 2g–2j). Moreover, the substrates carrying stronger electron-withdrawing groups like 4-cyano-, 4-trifluoromethyl-, 4-methoxycarbonyl- and 4-acyl phenylboronic acids were transformed into the desired products in excellent yields (Table 3, 2k–2n). Particularly, such oxidative sensitive substrates as aldehydes, benzyl alcohols and anilines were also compatible with this procedure, affording the desired phenols in 78–86% yields (Table 3, 2o–2q). Additionally, the fused ring arylboronic acid like 1-naphthalenylboronic acid was subjected to this reaction system, and the desired product 1-naphthalenol was obtained in 90% yield (Table 3, 2r). Furthermore, the heterocyclic arylboronic acids such as 6-quinolinylboronic acid, (1H-indol-5-yl) boronic acid and 4-pyridinylboronic acid were also applicable in this protocol, generating the desired products in 76–92% yields (Table 3, 2s–2u).

To gain insight into the heterogeneous nature of PDI-SN, photostability and reusability tests were performed (see the Supporting Information for details of the tests). The catalyst and filtrate were separated by filtration after photo-oxidation. The colorless filtrate suggested that the catalyst is stable because PDI molecules as a

Table 1
Control experiments.^{a,b}

| Entry | Catalyst | Light | Electron donor | Air | Yield (%) |
|-------|----------|-------|----------------|-----|-----------|
| 1 | + | + | + | + | 92 |
| 2 | – | + | + | + | 5 |
| 3 | + | – | + | + | n.r. |
| 4 | + | + | – | + | 8 |
| 5 | + | + | + | – | 16 |

c1ccc(cc1)B(O)O **1a** $\xrightarrow[\text{H}_2\text{O, r. t., air, 400 nm LED}]{\text{PDI-SN, TEA (2.0 equiv.)}}$ c1ccc(cc1)O **2a**

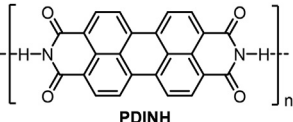
PDI-SN

^a Reaction conditions: benzenboronic acid (**1a**, 0.3 mmol), PDI-SN (10 mg), TEA (0.6 mmol), H₂O (1 mL), ambient air atmosphere under 20 W 400 nm LED irradiation for 42 h.

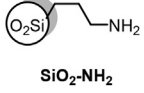
^b Yield determined by GC analysis with an internal standard (dodecane). n.r. = no reaction.

Table 2
Optimization of the reaction conditions.^{a,b}

| Entry | Catalyst | Electron donor | Time | Yield (%) |
|-------|-----------------------------------|----------------|------|-----------|
| 1 | PDI-SN | TEA | 42 | 92 |
| 2 | PDI-SN | DIPEA | 42 | 87 |
| 3 | PDI-SN | TEOA | 18 | 90 |
| 4 | SiO ₂ -NH ₂ | TEOA | 18 | <5 |
| 5 | PDINH | TEOA | 18 | 52 |
| 6 | g-C ₃ N ₄ | TEOA | 18 | 57 |



PDI-SN

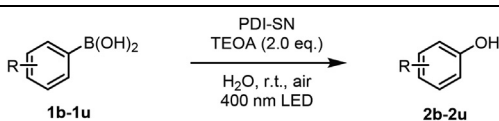
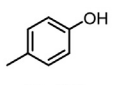
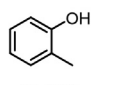
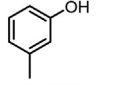
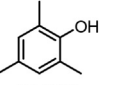
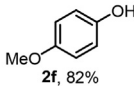
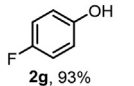
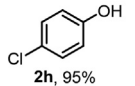
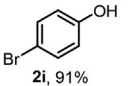
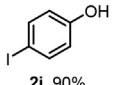
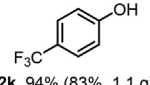
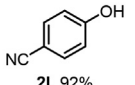
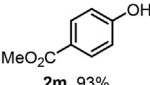
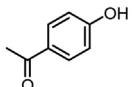
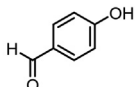
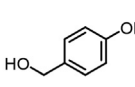
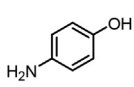
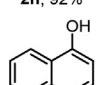
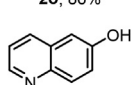
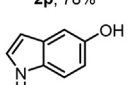
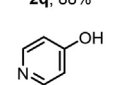


SiO₂-NH₂

^a Reaction conditions: benzenboronic acid (**1a**, 0.3 mmol), catalyst (10 mg), electron donor (0.6 mmol), H₂O (1 mL), ambient air atmosphere under 20 W 400 nm LED irradiation.

^b Yield determined by GC analysis with an internal standard (dodecane).

Table 3
Visible-light-promoted aerobic oxidative hydroxylation of arylboronic acids.^{a,b}

|  | |
|--|--|
| 1b-1u | 2b-2u |
|  2b , 87% |  2c , 72% |
|  2d , 89% |  2e , 66% |
|  2f , 82% |  2g , 93% |
|  2h , 95% |  2i , 91% |
|  2j , 90% |  2k , 94% (83%, 1.1 g) ^c |
|  2l , 92% |  2m , 93% |
|  2n , 92% |  2o , 86% |
|  2p , 78% |  2q , 88% |
|  2r , 90% |  2s , 92% |
|  2t , 84% |  2u , 76% |

^aReaction conditions: Benzenboronic acid (**1a**, 0.3 mmol), PDI-SN (10 mg), TEOA (0.6 mmol), H₂O (1 mL), ambient air atmosphere under 20 W 400 nm LED irradiation for 18 h. ^b Isolated yield. ^c4-Trifluoromethyl phenoboric acid (**1k**, 8 mmol), PDI-SN (150 mg), TEOA (16 mmol), H₂O (15 mL), Combination of the light source of 2 X 20 W 400 nm LED irradiation for 52 h.

red dye have a high molar absorption coefficient. After being washed with acetone and dried in the air, the catalyst was reused in the aerobic oxidative hydroxylation of benzenboronic acid once again, and no significant loss of activity was observed even after 6 cycles (Figure 1). In addition, after comparing with the U-Vis and IR absorption spectra before and after the reaction, there was no significant change (see Fig. S3 in the Supporting Information). These results indicated the organic semiconductor PDI-SN can be applied as a robust heterogeneous photocatalyst.

In order to determine the source of oxygen atom in the product phenol, isotope labeling experiments were carried out

(Scheme 1a). When the air was replaced by isotope-labeled molecule oxygen (¹⁸O₂) balloon, the ¹⁸O-**2a** phenol as product was obtained, suggesting that the oxygen atom of the product comes from the air. A series of quenching experiments were conducted with the focus placed on the involved reactive oxygen species (ROS) [35]. When isopropyl alcohol (IPA), a common hydroxyl radical (HO·) quencher [36], was added in this reaction system, the yield of phenol was the same as without quencher, which implied that no involvement of HO· (Scheme 1b). Likewise, the yield of phenol was slightly lower than that without quencher when singlet oxygen (¹O₂) quencher 1,4-diazabicyclo[2.2.2]octane (DBACO)

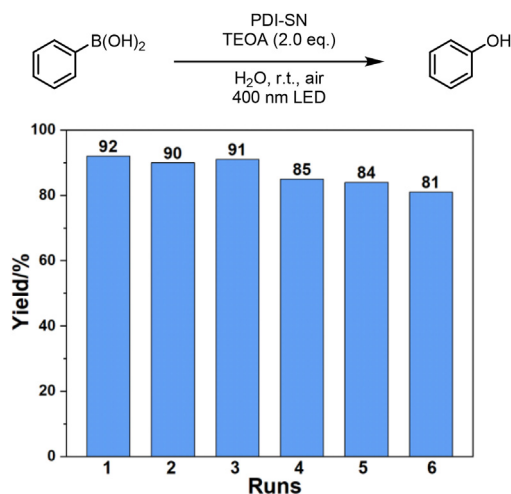
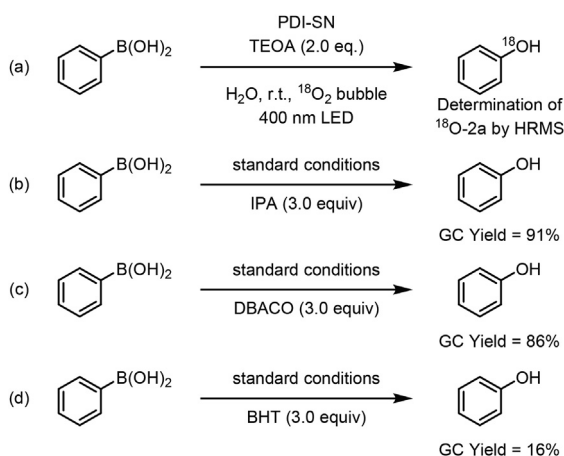


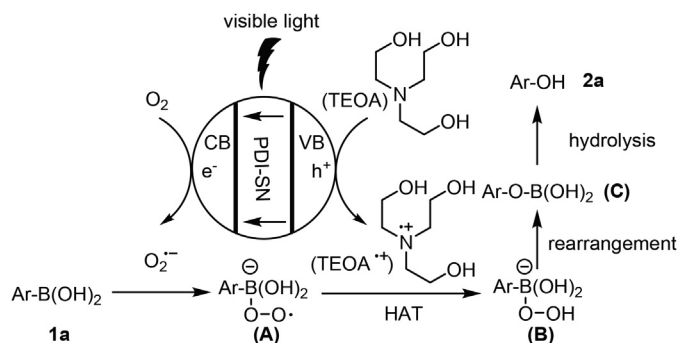
Fig. 1. Recycling test of the PDI-SN catalyst. Reaction conditions: benzeneboronic acid (**1a**, 0.3 mmol), TEOA (0.6 mmol), PDI-SN (30 mg), and H₂O (1 mL), ambient air atmosphere under 20 W 400 nm LED irradiation for 18 h.



Scheme 1. Reactive oxygen species quenching experiments. Reaction conditions: benzeneboronic acid (**1a**, 0.3 mmol), TEOA (0.6 mmol), PDI-SN (30 mg), quencher (0.9 mmol) and H₂O (1 mL), ambient air atmosphere under 20 W 400 nm LED irradiation for 18 h.

was added [37], suggesting that ¹O₂ was not the reactive oxygen species (Scheme 1c). In the presence of superoxide radical (O₂^{•-}) quencher butylated hydroxytoluene (BHT) [38], the results of severe inhibition indicated that the reaction may involve O₂^{•-} (Scheme 1d) and it was supported by EPR studies. The DMPO-O₂^{•-} signal could be detected when the PDI-SN were irradiated for 2 min and no signals were observed without light irradiation (see Fig. S4 in the Supporting Information). The aforementioned results demonstrated that O₂^{•-} may be the ROS in this reaction system.

Based on the above-mentioned experimental observations and the previous literatures [32], a plausible mechanism of the aerobic oxidative hydroxylation of arylboronic acids is proposed (Scheme 2). At first, the organic semiconductor PDI-SN is excited under visible-light irradiation to generate electron-hole pairs. Then, O₂ in the air quenches the photo-generated electrons, thus generating O₂^{•-} as the reactive oxygen species. Meanwhile, the electron donor TEOA are oxidized by photo-generated holes through a single electron transfer (SET) process, thus forming radical cation TEOA^{•+}. Next, the substrate **1a** reacts with O₂^{•-} to generate the radical anion intermediate A, which then reacts with



Scheme 2. Proposed mechanism for the aerobic hydroxylation of aryl boronic acids.

TEOA^{•+} through a well-established HAT mechanism [39] to form intermediate B. Finally, the product **2a** phenol is obtained by rearrangement of intermediate B into intermediate C with subsequent hydrolysis. In this way, both O₂^{•-} as the intermediates of hole-oxidation and TEOA^{•+} as the intermediates of electron-reduction are applied to the path of aerobic oxidative hydroxylation of arylboronic acids.

In conclusion, a green and sustainable photocatalytic system based on a hydrophilic organic semiconductor PDI-SN was developed for the aerobic oxidation hydroxylation of arylboronic acids in aqueous solution. In this reaction, various phenols were obtained with high yields under metal-free and ambient conditions using air as green oxidant and water as green solvent. The photostability and reusability tests indicated that the PDI-SN is a robust heterogeneous photocatalyst. More green and sustainable synthetic strategies using water as reaction medium are going on in our laboratory.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.tetlet.2020.152010>.

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