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Received 5th May 2020, Accepted 15th June 2020 Dual aminoquinolate diarylboron and nickel catalysed metallaphotoredox platform for carbon-oxygen bond construction[†]

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Herein, aminoquinolate diarylboron complexes are utilized as photocatalysts in dual Ni/photoredox catalyzed carbon-oxygen construction reactions. Via this unified metallaphotoredox platform, diverse (hetero)aryl halides can be conveniently coupled with acids, alcohols and water. This method features operational simplicity, broad substrate scope and good compatibility with functional groups.

Visible light photoredox catalysis has emerged as a powerful tool in organic synthesis and enabled a myriad of previously challenging chemical transformations.¹ The feasibility of such photoredox processes relies heavily on the modularity and efficiency of the photocatalysts used. In this regard, octahedral Ru(II) or Ir(III)-polypyridyl complexes are ubiquitously employed as photoredox catalysts due to their readily modified photochemical properties, by introducing diverse substituents to the surrounding polypyridyl ligands.² Although their employment has got remarkable achievements, the development of organic photocatalysts containing no precious metals³ is still desirable in terms of cost, sustainability and residual metal concerns.

Four-coordinated organoboron compounds comprise a variety of molecules with diverse light-absorbing and emitting properties.⁴ Therefore, they have been widely applied in optoelectronics, organic field-effect transistors, sensory and imaging materials. However, their application as photoredox catalysts is rather limited, and the existing examples all take advantage of BODIPY-type dyes,⁵ to the best of our knowledge. Accordingly, we questioned whether we could develop another class of organoboron photosensitizers with adjustable supporting ligands and customized photocatalytic activities.

On the other hand, the classical transition metal-catalysed cross-coupling reaction⁶ has ushered in unprecedented opportunities for innovation, along with the renaissance of photoredox catalysis. Last decade has witnessed the successful merger of these two catalytic modes as metallaphotoredox catalysis.⁷ The dual metal/photoredox catalysed reactions have been exploited to forge diverse C-heteroatom bonds,8 where Ir or Ru-based complexes still play a predominant role as photocatalysts.

For example, in C-O coupling reactions, the seminal work from MacMillan group demonstrated the synthesis of aryl ethers⁹ and esters¹⁰ using $Ir[dF(CF_3)ppy]_2(dtbpy)PF_6$ (Ir-a) and $Ir(ppy)_3$ (Ir-b) as photocatalysts, respectively.¹¹ It was also pointed out the benzophenone was a moderately efficient photocatalyst for the esterification of aryl bromides.¹⁰ From these reports other organic photocatalysts have seen success in dual catalysed C-O formation, such as, 1,2-dicyano-3,4,5,6-tetrakis(diphenylamino)-benzene (4DPAPN),¹² thioxanthen-9-one (TXO),¹³ boron-dipyrromethene (BODIPY)¹⁴ and 1,3-dicyano-2,4,5,6-tetrakis(diphenylamino)benzene (4DPAIPN)¹⁵ (Scheme 1). However, the organic photocatalysts are often reported efficient for one specific type of C-O construction reaction.¹⁶ Therefore, there is still a need to develop other more flexible, readily modified and multipurpose organic photocatalysts.¹⁷ This opportunity spurred our following exploration, to develop and apply organoboron photocatalysts into a unified metallaphotoredox C-heteroatom coupling platform.

Initially, we envisioned acylated 8-aminoquinoline (AQ) to act as the chelating ligand and provide a modular π -conjugated framework to form boronyl adducts. From this core, the electronic properties can be modulated to tune the photoredox properties. A further benefit of this core would be its stability and availability. To obtain the target aminoquinolate diarylboron (AQDAB) complexes, a new synthetical protocol was identified, which treated acylated AQ to stable potassium aryltrifluoroborate (ArBF₃K) in the presence of Mn and *p*-tosyl chloride (Fig. 1). This approach bypassed the use of sensitive organometallic reagents and afforded aim-product PC1 in 95% yield, whose X-ray structure confirmed the diphenylboron moiety was chelated by two nitrogen atoms via one N-B



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Scheme 1 Construction of C–O bonds *via* nickel metallaphotocatalysis pathways.



Fig. 1 (a) The synthesis of aminoquinolate diarylboron complexes. (b) X-ray structure of **PC1**. (c) Fluorescence emission spectra of **PC1**, **PC6**, **PC7** in DMSO (5×10^{-4} M). (d) Cyclic voltammograms (CV) of **PC1** recorded in MeCN.

covalent bond and one N \rightarrow B dative bond. Notably, **PC1** is a bright yellow solid and can be stored in fume hood for months without decomposition. Then, different **AQDAB**-type complexes were obtained in good to excellent yields (for details, see supporting information), with variations on either AQ or diarylboron moiety. The spectral data confirmed that the electronics of AQ framework was critical to modify the absorption and emission band of these potential photocatalysts (Table S1, in ESI†).

From here we started the photocatalytic investigations by studying the C–O coupling reactions between benzoic acid and 4-bromobenzonitrile, under the dual catalysis of nickel and the obtained **AQDAB** complexes. After systematic evaluation of the reaction parameters, the optimal conditions were identified and the aim-product **3aa** was obtained in 83% isolated yield (Table 1). With the aim of a general and robust procedure, these optimizations were performed under air. The absence of the photocatalyst, nickel catalyst or blue LEDs saw no product (Table S8, ESI†), indicating a dual photoredox/nickel-catalyzed process. Also, the tested variations of photocatalyst, nickel source, ligand, base, solvent and photosource from the optimal conditions were detrimental to the yield (Tables S2–S7, ESI†).



 a Isolated yields. dtbpy, 4,4'-di-tert-butyl-2,2'-dipyridyl. b Kessil lights used. c 80 °C.

Next, the generality of this dual catalytic system was investigated (Table 1). First, a wide range of benzoic acid derivatives with electron-withdrawing or electron-donating groups located at either ortho, meta or para position were effectively coupled with aryl bromides or more reactive aryl iodides. The corresponding products were obtained in generally medium to excellent yields, demonstrating the robustness of this protocol towards the electronic and steric variations on the acid counterparts (3aa-3ak). Also, naphthoic acids, polysubstituted benzoic acids, trans-cinnamic acids, and heterocyclic aromatic acids could efficiently participate in the coupling reactions (3al-3at). The application of the drug molecule Probenecid (Probalan) afforded target compound 3au in moderate yields. As for the substrate scope of aryl halides, those containing electronwithdrawing groups generally provided better yields (3fa-3ia, 3ka, 3ma). For the relatively electronic richer or more sterically encumbered substrates (3la), heating the reaction mixture to 80 °C could afford the coupling products in moderate to good yields (3ba-3ea, 3ja, 3la). The reaction between 4-bromo-2-(trifluoromethyl)pyridine and benzoic acid could give 3na in 55% yield.

Encouraged by these results, we were curious if this dual catalytic system could be applied to forge C-O linkages in phenols or aryl ethers. Gratifyingly, further modifications to the optimal conditions of aromatic acids afforded both phenols and anisole (Table 2). In both cases, H₂O or alcohols were used as excessive coupling counterparts, and the use of N,Ndiisopropylethylamine (DIPEA) was essential. The indispensability of nickel, PC1, and blue LEDs for the reactions illustrated the underlying dual metallaphotoredox pathways (Tables S9 and S10, ESI[†]). As shown in Table 2, the substrate scope of these transformations was then explored. Different aryl halides, including chlorides, bearing nitriles (4a, 4j, 5a, 5f), esters (4b, 4c, 4g, 5b, 5g), ketones (4d, 5c, 5d) could all be wellaccommodated. Also, in these cases, the reactivity of the relatively electronic richer aryl halides could be enhanced by raising the reaction temperature (4e, 4f). Heterocyclic aromatic bromides could also couple H₂O or MeOH to afford target products (4h, 5h, 5i). Notably, when 3,5-dibromobenzonitrile was treated with H₂O, 3-hydroxybenzonitrile 4j was obtained in 50% yield, indicating the existence of the debromoprotonation process. Using H218O instead of H2O, 18O-labeled 4k was obtained in 90% yield, which turned out that the hydroxyl group in these products originated from H_2O , instead of O_2 in the atmosphere.

Regarding the mechanism, putative oxidative addition species **Ni-A** was obtained from Ni(COD)₂, methyl 4-bromobenzoate, and dtbpy. This complex was found to be catalytically active, affording **3ha** in 27% NMR yield and demonstrating the involvement of Ni(π)-aryl species in the catalytic cycle (Scheme 2). In the reported literature, ^{9–16} C–heteroatom construction reactions were envisioned to involve different reaction pathways (ET, ¹⁸ SET, or radical mechanism), based on the nucleophiles and reaction conditions used. At this stage, we attribute the reactivity observed for all transformation to be mediated *via* an ET pathway, since the cyclic voltammetry (Fig. 1d) shows irreversible oxidation and reduction of **PC1**. Irreversibility suggests that no electron transfer processes





are occurring as **PC1** could not be regenerated and helps delineate these pathways. However, further mechanistic studies are currently ongoing to elucidate the mechanistic similarity and difference of these reactions in more detail.

In conclusion, we have developed a mild and practical synthetic strategy to access a series of four-coordinated aminoquinolate diarylboron compounds. Such compounds can be implemented as photosensitizer in visible-light-mediated metallaphotoredox catalysed C–O cross-coupling reactions. A wide array of O-based nucleophiles, including carboxylic acids, water, alcohols, were effectively coupled with (hetero)aryl halides under this operationally simple dual catalytic system, affording the corresponding product in moderate to excellent yields. We anticipate this organoboron photocatalyst to be an inexpensive, sustainable complement to the existing photocatalysts in metallaphotoredox reactions. Further applications of these compounds are ongoing in our laboratory.

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Conflicts of interest

There are no conflicts to declare.

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