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Visible Light Photoredox Catalyzed Biaryl Synthesis Using Nitrogen Heterocycles as Promoter

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KEYWORDS: Visible light photoredox; Biaryl synthesis; Catalysis; Phenanthroline radical anion; Single-electron-transfer

ABSTRACT: Although transition-metal-catalyzed direct arylation of aromatic C-H bonds is one of the most efficient ways to the construction of biaryl targets, it is also expected for other alternative methods that can use inexpensive catalysts and abundant solar energy to drive chemical reactions. Herein, we describe a new activation mode for biaryl synthesis by using photosensitive complex of potassium *tert*-butoxide (KO*t*-Bu) and nitrogenous heterocyclic ligands via visible light excitation. Under low-energy visible light irradiation, the single electron transfer from electron-donor KO*t*-Bu to electron-deficient nitrogenous heterocycle occurred in the inner of the complex by using potassium as a bridge atom. The ligand accepted the as-photoexcited single electron and transformed into stable radical anions which played a dominant role in the coupling reactions of benzene with aryl halides at ambient temperature. This reaction

paradigm features the use of inexpensive catalyst, abundant visible light energy and more accessible bromobenzene for the construction of biaryl compounds under rather mild conditions.

1. INTRODUCTION

The pursuit of new protocols to construct biaryl compounds is a key issue in modern organic synthesis since these substances are fundamental framework and starting stuff in a wide variety of fine chemical reactions. It is unarguable that transition-metal-catalyzed direct arylation of aromatic C-H bonds is one of the most efficient ways to the synthesis of biaryl targets.[1-6] However, these processes also suffered significant problems such as high economic cost and the presence of transition-metal impurities in the final products. Therefore, the transition-metal-free process has been emerged as an alternative strategy to perform C-C cross-coupling between unactivated arenes and aryl halides with the promotion of metal *tert*-butoxide as a base.[7-12] It is worthwhile to note that some classes of ligands containing nitrogen heterocycle were usually employed in these base-promoted systems, such as quinoline-1-amino-2-carboxylic acid,[8] an amino-linked nitrogen heterocyclic carbene (amino-NHC),[9] N,N'-dimethylethylenediamine (DMEDA),[10] 1,10-phenanthroline,[11] and its derivatives.[12] The results of previous studies showed that the nitrogenous bidentate chelating centers have the capability of coordinating with a metal ion to form five-membered ring structures,[8,12,13] and thus prompt the single-electron-transfer (SET) from metal *tert*-butoxides to ligands under conventional heating. There has been growing interest into the utilization of abundant and renewable sunlight in synthetic applications. Recently, Rossi group[14] reported the application of powerful light (two HPI-T 400W lamps) for direct arylation of benzene using potassium tert-butoxide (KO*t*-Bu) and dimethyl sulfoxide (DMSO) since DMSO solvates the KO*t*-Bu and affords the solvent-separated ion pair to act as an electron donor. Li group[15] employed visible light for direct arylation by introducing $Ir(ppy)_3$ (an effective photoredox catalyst) into a reaction system similar to Rossi group's. However, the arylation of benzene and more accessible aryl bromide required the combined use of visible light and heat (70 °C).

Encouraged by these results, we envisaged that it might be possible to drive the SET process in base-promoted systems using nitrogen heterocycle under visible-light irradiation since the proposed configuration of K ion to nitrogen heterocycle is analogous to that of polypyridyl complexes of ruthenium, a well-known visible light photoredox catalyst which undergoes a metal to ligand charge transfer (MLCT) under irradiation and generates photoexcited species to initiate reactions.[16] Herein, we established a new activation mode where the photosensitive complex of potassium tert-butoxide (KO*t*-Bu) and nitrogenous bidentate chelating ligands can be excited by visible light ($\lambda \geq 420$ nm) that are abundant in the solar spectrum and then initiate coupling reactions via SET process. This reaction paradigm features the use of inexpensive catalyst and abundant visible light energy for the construction of biaryl compounds under rather mild conditions.

2. RESULTS AND DISCUSSION

Generally, the observed color of a substance is said to be the complementary to the color of the absorbed visible light. When KO*t*-Bu and 1,10-phenanthroline in benzene was mixed with a stoichiometric ratio, a yellow solution was observed although either of them in benzene are colorless (Photograph, Figure 1). This indicates that a complex between KO*t*-Bu and 1,10-phenanthroline may be formed via coordination and can absorb light in the visible region. When the above mixed solution was analyzed by electron paramagnetic resonance (EPR) spectroscopy under visible light irradiation (420 nm $< \lambda <$ 780 nm), a strong EPR signal with a sharp splitting

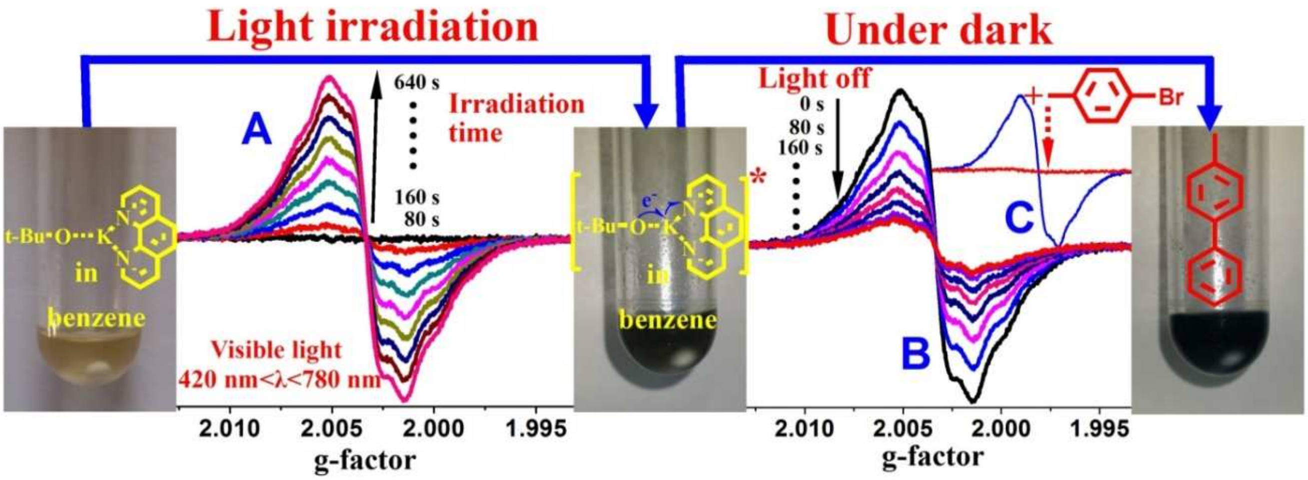
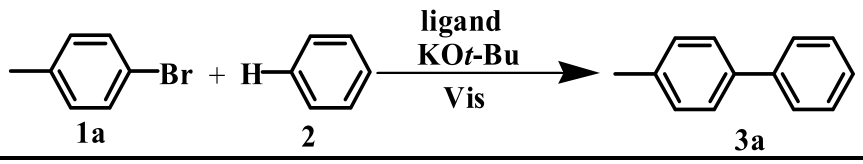
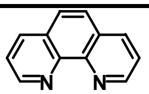
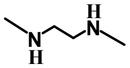
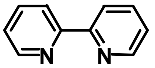
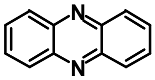
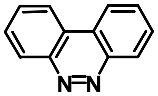
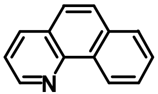
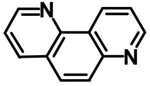
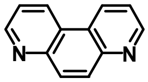
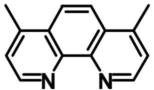
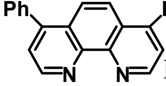


Figure 1. EPR spectra arising from the benzene solution of 1,10-phenanthroline and KO*t*-Bu under visible light excitation and their following decay after turning off the light (The photographs showing that the color changes of the mixed solution before and after light irradiation and the structure of the as-formed complex).

at g=2.0036 appeared, and its intensity increased with a prolonged irradiation time (A, Figure 1). Similar resonance characteristics for KO*t*-Bu and 1,10-phenanthroline have also been reported in studying the generation of radical intermediates in thermocatalysis.[10-13,17] On the contrary, no signal was obtained when the solution was kept in the dark or in the absence of KO*t*-Bu or 1,10-phenanthroline. Although the EPR spectrum shows little resolution and broad bands, the isotropic g factor of about 2.0036 and the hyperfine coupling constant of about 2.9 G (Figure 2a) was still determined for the equivalent nitrogen atoms' splitting in a phenanthroline radical anion which has a singly occupied b1(φ) orbital. This assignment is consistent with the previous reports for phenanthroline radical anion with a coordinating counterion such as K^+ in tetrahydrofuran.[18-20] The above results were also supported by theoretical calculations (Figures S2-4 and Tables S1-2). The natural bond orbital (NBO) and molecular orbital analyses based on the optimized structures of the formed complex in neutral and triplet states further show that the preferential pathway for electron transfer is from the KO*t*-Bu part to the 1,10-phenanthroline part

Table 1. Direct arylation of benzene with 4-bromotoluene.[a]



Entry	Ligand	Condition	Yield (%)
1	 **L1**	Vis, 18 °C	**73**[g]
2[b]	L1	Heat, 100°C	**71**
3	-	Vis, 18 °C	**3**
4[c]	L1	Vis, 18 °C	**0**
5	L1	Dark, 18 °C	**0**
6[d]	L1	Vis, 6 °C	**70**
7[e]	L1	UV, 18 °C	**78**
8[f]	L1	Vis, 18 °C	**70**
9	 **L2**	Vis, 18 °C	**6**
10	 **L3**	Vis, 18 °C	**0**
11	 **L4**	Vis, 18 °C	**6**
12	 **L5**	Vis, 18 °C	**16**
13	 **L6**	Vis, 18 °C	**4**
14	 **L7**	Vis, 18 °C	**4**
15	 **L8**	Vis, 18 °C	**5**
16	 **L9**	Vis, 18 °C	**<1**
17	 **L10**	Vis, 18 °C	**81**[g]

[a] General reaction conditions: substrate (0.1 mmol), benzene (1 mL), base (4 equiv), ligand (50 mol%), temperature (18 °C, cycle water cooling), N_2 atmosphere, visible light irradiation (420 nm$<\lambda<$780 nm, 400 mW cm^{-2}, 24 h). [b] With a heating condition at 100 °C in the dark. [c] In the absence of base. [d] With a reaction temperature of 6 °C. [e] With an UV irradiation (320 nm$<\lambda<$

780 nm) for 6 h. [f] 4-bromotoluene(0.5 mmol) and benzene (5 mL) were used. [g] Trace amounts of the homo-coupling products biphenyl and 4,4'-dimethylbiphenyl of the substrates were identified only from mass spectrum.

by using potassium as a bridge atom. Therefore, we supposed that the unpaired electron residing on the ligand resulted in the formation of phenanthroline radical anion. As shown in Fig. 1B, the EPR signal for the as-obtained radical anions decayed gradually and lasted more than ten minutes after turning off the light. This suggests that the radical anion intermediates are stable and have a long lifetime to engage in the subsequent electron transfer process. When the electron-deficient 4-bromotoluene was rapidly injected to this excited system in the dark, a coupling product 4-methylbiphenyl was obtained surprisingly and the signal at g=2.0036 disappeared accordingly, demonstrating that the radical anion intermediate was responsible for the generation of biaryl product (C, Figure 1).

In view of the above findings, a series of arylation experiments were launched under continuous light excitation. The arylation of benzene with 4-bromotoluene proceeded under visible light irradiation using 50 mol% 1,10-phenanthroline in the presence of 4 equiv KO*t*-Bu as a base at 18 ^{o}C. The desired cross-coupling product 3a was obtained in 73% yield for 24 h (entry 1 of Table 1), slightly higher than that obtained under thermocatalytic condition at 100 ^{o}C (entry 2). Only 3% yield was obtained in the absence of 1,10-phenanthroline (entry 3) and no coupling product was obtained in the absence of KO*t*-Bu or light irradiation (entries 4 and 5), which indicates that the presence of KO*t*-Bu, 1,10-phenanthroline and light were essential to the reaction. Even at 6 ^{o}C, the yield of 3a was almost not affected (entry 6), which suggests that thermal process was not involved in the coupling reaction. Upon irradiation with high-intensity visible light, the increased EPR signals were observed, and the peak areas of EPR signals have a linear dependence with the corresponding yields of the biaryl product, which suggests that the

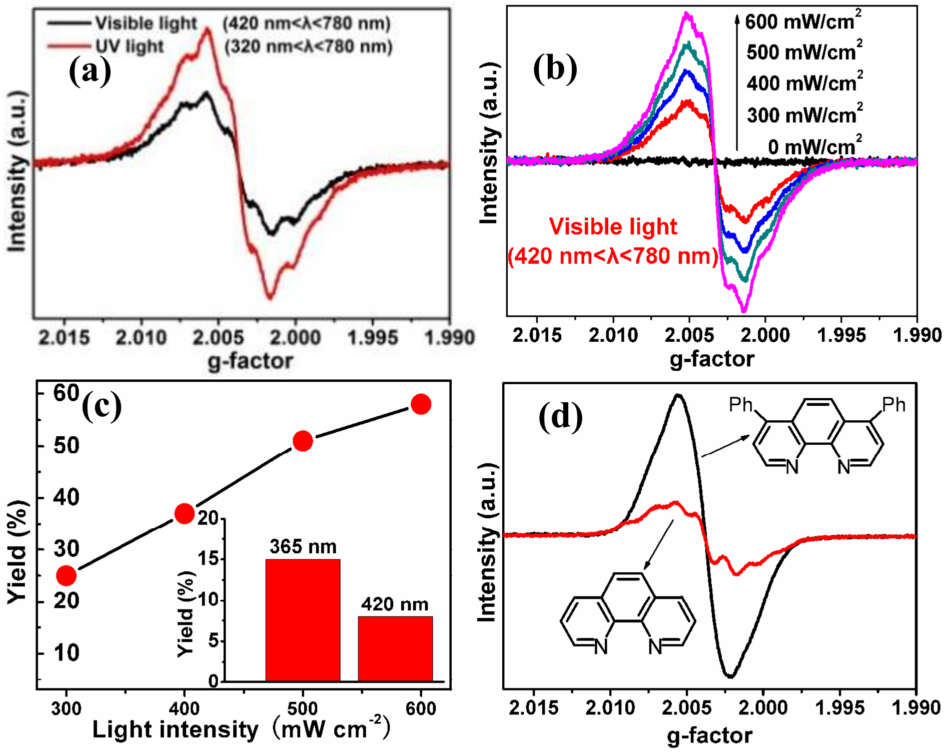


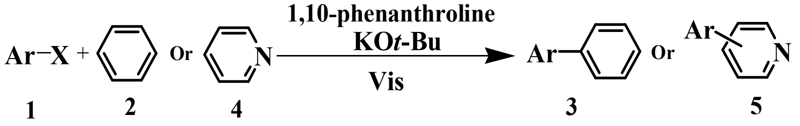
Figure 2. (a) EPR spectra recorded at different wavelengths of incident light. (b) EPR spectra recorded at different irradiation intensities. (c) The influence of irradiation intensity (12 h) and wavelength (5 h) of incident light on the yield of biaryl product. (d) EPR spectra for different nitrogen heterocycles.

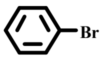
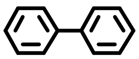
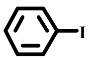
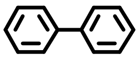
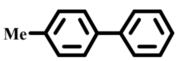
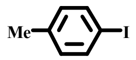
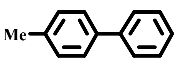
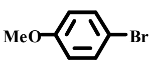
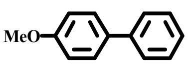
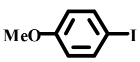
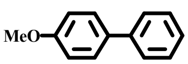
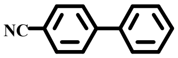
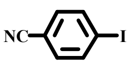
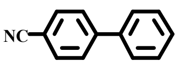
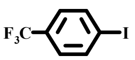
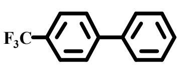
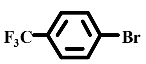
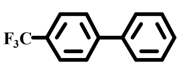
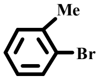
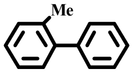
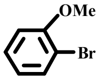
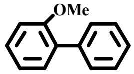
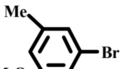
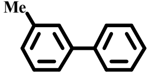
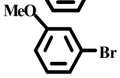
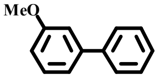
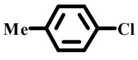
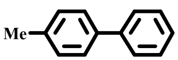
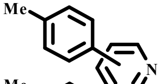
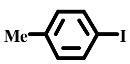
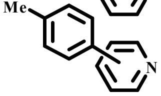
amount of radical anion intermediate notably influenced the yield of the cross-coupling product (Figure 2a-c and Figure S6). This also indicates that the coupling process over the as-formed complex is a typical photoredox catalytic reaction. When the reaction was scaled up by a factor of 5, the coupling product 3a was still obtained in a satisfying yield under the same photon flux per unit area (entry 8). Even under irradiation of household CFL lamp (16 W) for 60 h, the arylation of benzene with 4-iodotoluene or bromobenzene still gave the biaryl products in 79% and 67% yield, respectively (Table S7). This further confirms the availability and effectiveness of the as-established complex for biaryl synthesis.

The configuration stability of the radical anions would significantly influence the ability to supply electron for initiating subsequent coupling reactions. Therefore, the various ligands containing nitrogen heterocycles were tested. When 1,10-phenanthroline was replaced by other ligands (L2-L6, Table 1), much lower efficiency or no efficiency was observed for the coupling of benzene with 4-bromotoluene (entries 9-13). Phenanthrolines with nitrogen atoms at the 1,7- or 4,7-positions gave only 4% and 5% yields of 3a, respectively (entries 14, 15). These results indicated that the nitrogen atom position of the ligands significantly influenced electron transferring process due to ineffective coordination with KO*t*-Bu. The introduction of electron-donating methyl groups at the 4- and 7-positions of 1,10-phenanthroline resulted in little coupling product (entry 16), whereas the substitution of 1,10-phenanthroline with two phenyl groups at the 4- and 7-positions greatly increased the yield of 3a up to 81% (entry 17). This might arise from the differences of the electronic effect of methyl groups and the conjugative effect of phenyl groups, consistent with the previous report using phenanthroline derivates under elevated temperature.[12] The conjugated groups is more favorable for the ligand to accept single electron from KO*t*-Bu in the inner of the complex, which resulted in the formation of more stable radical anion intermediates for transferring electron in a further step onto 4-bromotoluene. This could be further confirmed by the evidence that the EPR signal intensity of 4,7-diphenyl-1,10-phenanthroline was rather higher than that of 1,10-phenanthroline under the same conditions (Figure 2d).

The scope of this cross-coupling reaction was extended to a variety of aryl halides (Table 2). In most cases, the introduction of both electron-donating (entries 3-6) and electron-withdrawing groups (entries 7-9) into *p*-substituted aryl halides were beneficial for this cross-coupling reaction and afforded good yields for the desired products. However, carbon trifluoride group

Table 2. Direct arylation of benzene or pyridine with different aryl halides.[a]



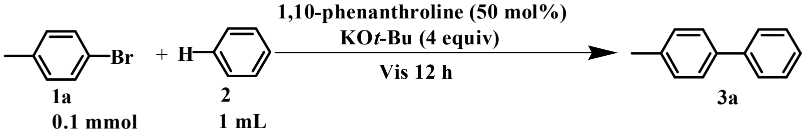
Entry	Ar-X	Products	Yield (%)
1	 1e	 3c	70
2	 1f	 3c	72
3	 1a	 3a	73
4	 1b	 3a	74
5	 1c	 3b	89
6	 1d	 3b	90
7[b]	 1k	 3h	77
8[b]	 1l	 3h	91
9	 1m	 3i	87
10	 1n	 3i	39
11	 1g	 3d	15
12	 1h	 3e	52
13	 1i	 3f	67
14	 1j	 3g	76
15	 1o	 3a	20
16[c]	 1a	 5a	95
17[c,d]	 1b	 5a	100

[a] General reaction conditions: substrate (0.1 mmol), benzene (1 mL), KO*t*-Bu (4 equiv), 1,10-phenanthroline (50 mol%), temperature (18 °C, cycle water cooling), N_2 atmosphere, visible light irradiation (420 nm$<\lambda<$780 nm, 400 mW cm^{-2}, 24 h). [b] Irradiation time of 1 h. [c] Substrate (0.5 mmol) and pyridine (5 mL) were used. GC yield based on 1a for 48 h and isomer ratio: *o*/*m*/*p*=1.0/1.2/3.9 determined by NMR. [d] GC yield based on 1b for 8 h and isomer ratio: *o*/*m*/*p*= 1.0/1.3/3.8 determined by NMR.

substituted bromobenzene (1n) gave the biphenyl product only in 39% yield, much lower than that using bromobenzene (entry 10). Surprisingly, the *p*-substituted aryl halides with electron-withdrawing –CN group (1k, entry 7, 1l, entry 8) exhibited extremely high reactivity. The coupling yields of 77% and 91% were obtained for 1 h respectively, comparable to those of other aryl halides for 24 h. This is obviously different from the thermocatalytic process with a poor reactivity for *p*-halogenated benzonitrile.[11] The transformation was sensitive to steric effects, and the yield of the coupling products for *o*-, *m*- and *p*-substituted aryl halides increased progressively (entries 3, 5, 11-14). The reactivity of aryl halides decreased in the order of iodides, bromides and chlorides (entries 3, 4, 15). In addition, this reaction can be extended to the coupling of electron-deficient pyridine and aryl halides, giving high yields of the coupling products (entries 16,17). Other arenes with different substituted groups were also tested to demonstrate the applicability of the reaction (Table S9). The arylation of 4-bromoanisole with substituted arenes afforded the corresponding products as a mixture of regioisomers, and the *ortho*-arylated product predominated. This result indicated that the substitution of benzenes will accelerate the coupling to the *ortho*-position with good regioselectivity, and the reaction went through a radical pathway.

To further verify SET mechanism, the coupling reaction was completely terminated by the addition of a typical electron scavenger (1,4-benzoquinone, BQ) as a result of the consumption of single electron by BQ, which was confirmed by the formation of benzo-semiquinone anion radical (Table 3 and Figure S11). A dominant pathway involving radicals in the cross coupling reaction was supported by the addition of 2,2,6,6-tetramethylpiperidine N-oxyl (TEMPO), a typical radical scavenger, to the reaction system. The yield of the coupling product decreased as the amount of TEMPO was increased, and when TEMPO was added at a concentration of 12

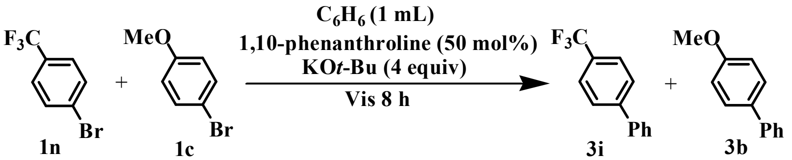
Table 3. Radical/electron trapping experiments.[a]



Entry	Additive	Yield (%)
1	none	37
2	BQ (2 equiv)	0
3	TEMPO (6 mol%)	7
4	TEMPO (12 mol%)	0
5	TBA$^+$PF$_6^-$ (2 equiv)	2

[a] General reaction conditions: substrate (0.1 mmol), benzene (1 mL), KO*t*-Bu (0.4 mmol, 4 equiv), 1,10-phenanthroline (0.05 mmol, 50 mol%), temperature (18 °C, cycle water cooling), N_2 atmosphere, visible light irradiation (420 nm<λ<780 nm, 400 mW cm^{-2}, 12 h). TBA$^+$PF$_6^-$ = tetra-n-butylammonium hexafluorophosphate.

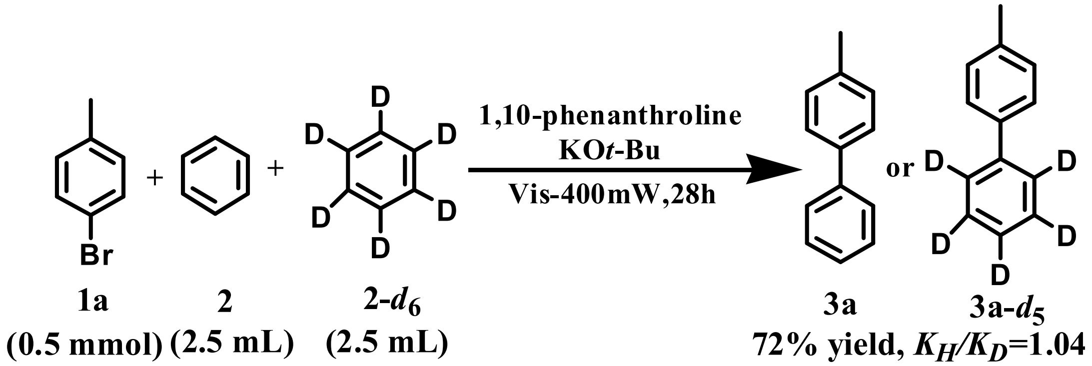
Table 4. Competition reaction between two aryl bromides.[a]



Entry	1n (mmol)	1c (mmol)	3i (%)	3b (%)
1	0.05	0.05	28	1
2	0.1	0	8	0
3	0	0.1	0	52

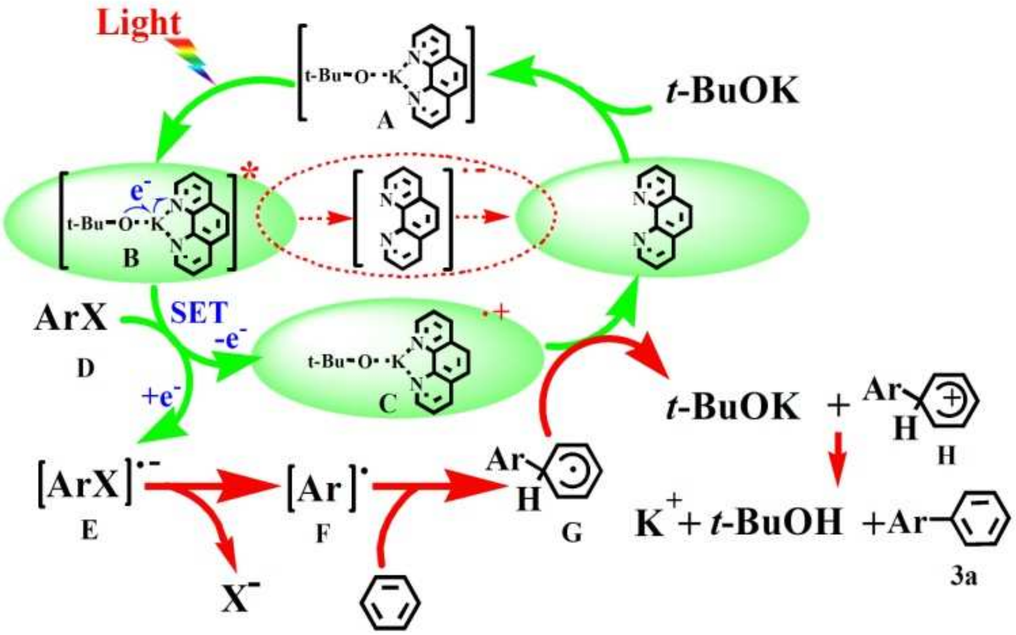
[a] General reaction conditions: substrate (0.1 mmol), benzene (1 mL), KO*t*-Bu (0.4 mmol, 4 equiv), 1,10-phenanthroline (0.05 mmol, 50 mol%), temperature (18 °C, cycle water cooling), N_2 atmosphere, visible light irradiation (420 nm<λ<780 nm, 400 mW cm^{-2}, 8 h).

mol%, the transformation was completely inhibited (Table 3, entries 3, 4). The introduction of TBA$^+$PF$_6^-$ also decreased the yield of the biaryl product greatly (entry 5), demonstrating the presence of ion radicals in the reaction.[21,22] A further competitive experiment with equimolar amounts of 1c and 1n in the presence of benzene was also carried out (Table 4). Although the presence of 1c or 1n alone gave 52% or 8% of the corresponding coupling product, respectively, a more electron-deficient 1n with benzene have higher reactivity than 1c in the coexistence of two components, consistent with the SET mechanism.[12,23] The kinetic isotopic effect of benzene showed a low K_H/K_D value of 1.04 for the coupling reaction, indicating that the cleavage of C-H bonds in benzene is not the rate-determining step (Scheme 1). Therefore, we concluded that the production of radicals via SET process was the dominant step. Additionally, the controlled reaction using bromobenzene as the sole starting material under the same condition also gave the coupling products of bromobiphenyl and biphenyl (Table S10 and Scheme S2), which well supports that the aryl radicals from the reduction of aryl halide are key intermediates for initiating subsequent reactions with benzene.



Scheme 1. KIE experiment of the model reaction.

On the basis of the above experimental evidence and previous reports, a plausible radical involving mechanism initiated by a light responsive SET process is proposed in Scheme 2.[10-13,17] When KO*t*-Bu and 1,10-phenanthroline in benzene was mixed stoichiometrically, a complex with visible light absorption formed via a five-membered ring structure between K ion and phenanthroline. Under visible light irradiation, the SET from electron-donor KO*t*-Bu to



Scheme 2. Proposed plausible mechanism.

electron-deficient phenanthroline occurred in the inner of the complex by using potassium as a bridge atom. Thus, phenanthroline accepted an electron and transformed into radical anion corresponding to the EPR signal at g=2.0036. Then the electron can be captured by aryl halide to give an $[ArX]^{\cdot -}$ radical anion and complex radical cation intermediate C, resulting in the disappearance of the EPR signal at g=2.0036. The $[ArX]^{\cdot -}$ radical anion subsequently dissociated into aryl radical which can combine with benzene to give cyclohexadienyl radical G. DFT calculations (Table S2) suggest that the radical cation C is unstable and more apt to oxidize G, which was also reported in previous literatures.[9,12] The oxidation of G by radical cation C gave cation H, which was deprotonated to give biaryl 3a and *t*-BuOH. The regenerated phenanthroline continued to combine with fresh KO*t*-Bu for initiating a new reaction cycle. In view of this, the phenanthroline can be supposed as the crucial promoter or catalyst of this cross-coupling reaction. The coordinated complex of phenanthroline with KO*t*-Bu can be excited by visible light, and the corroborative evidence for the formation of phenanthroline radical anion that plays a dominant role in the aromatic cross-coupling reactions were uncovered for the first time. Moreover, we obtained a good yield of biaryl only under visible-light irradiation (λ≥420 nm) for more accessible bromobenzene, comparable to that obtained under thermocatalytic condition at 100 °C.

3. CONCLUSIONS

We have developed a visible light photoredox catalyzed coupling reaction of aryl halides with benzene through using nitrogen heterocycles as promoter. The conclusive evidence in the EPR spectra supported that the formed phenanthroline radical anion via SET process played a dominant role in the formation of biaryl products. This system can also be applied to other aryl halides and analogous nitrogen heterocycles, and offers a green and sustainable route to the construction of the biaryl products.

4. EXPERIMENTAL DETAILS

General procedure for the direct arylation of benzene or pyridine with aryl halides. All reagents were commercially available and used without further treatment. Benzene was anhydrous, and all glassware used in the reactions was completely dried to exclude the introduction of water. Prior to the reaction, all manipulations were performed using Schlenk tubes and in a nitrogen-filled glovebox at room temperature. Typically, a 10 mL Schlenk tube was charged with 1,10-phenanthroline (9 mg, 0.05 mmol) and KO*t*-Bu (45 mg, 0.4 mmol). Benzene or pyridine (1 mL) and aryl halides (0.1 mmol) were then added. After that, the tube was removed from the glovebox, and the resulting mixture was stirred upon visible light irradiation with a xenon lamp (PLS-SXE300C, Beijing Perfect Light Co) equipped with an IR-cutoff filter (λ<780 nm) for providing the visible light (λ>420 nm) or UV light (λ>320 nm) through the combination of different filters. The tube reactor was immersed in a transparent vessel with jacket connected to a circulating cooling water source controlled by a thermostatic apparatus. Some different UV sources were also provided by 4-W UV lamps with certain wavelengths centered at 254 nm or 365 nm (Philips, TUV 4W/G4 T5 or TL 4W/05). The irradiance spectrum and energy of the light incident on the suspension were measured with a spectroradiometer (International Light Technologies Model ILT950), about 400mW cm^{-2} (420~780 nm wavelength range) for visible light case, 300 mW cm^{-2} (320~780 nm wavelength range) for UV case and 60 mW cm^{-2} (certain wavelengths centered at 254 nm or 365 nm), respectively. The illuminated area was estimated to be about 1 cm^{2} corresponding to the cross section of the columned tube. After reaction, *n*-octane (0.05 mmol) was added into the reaction mixture and then the mixture was centrifugalized. The as-obtained supernatant liquid was injected into the GC equipped with FID detector (Agilent Technologies, GC6890N) for analysis. A HP-5 5% phenyl methyl siloxane column (30 m × 0.32 mm × 0.5 μm) was used. The chemical structures of the products were confirmed by comparison with standard chemicals and GC-MS (Agilent Technologies, GC6890N, MS 5975). The yield of the cross-coupling product was described as the ratio of the moles of the generated biaryl compound in the reaction to the initial moles of the corresponding aryl halide.

Procedure of cross-coupling reaction under thermal condition. A 10 mL Schlenk tube was charged with 1,10-phenanthroline (9 mg, 0.05 mmol), KO*t*-Bu (45 mg, 0.4 mmol), benzene (1 mL) and 4-bromotoluene (0.1 mmol) in the glovebox. The sealed tube was then removed from the glovebox and the containing mixture was stirred at 100°C under dark for 24 h. The final products were allowed to cool to room temperature and *n*-octane (0.05 mmol) was added into the mixture. After centrifugalizing, the as-obtained supernatant liquid was injected into the GC and GC-MS (a solvent delay time of about 5 min was set before the acquisition) for further analysis.

Procedure of cross-coupling reaction for separating products. A 25 mL Schlenk tube was charged with 1,10-phenanthroline (45 mg, 0.25 mmol), KOt-Bu (225 mg, 2.0 mmol), benzene or pyridine (5 mL) and aryl halides (0.5 mmol) in glovebox. Then the tube was removed from the glovebox and the resulting mixture was stirred upon visible light irradiation (providing 400 mW cm^{-2} visible light) for 24 h. The reaction was quenched with water in excess and the residue was extracted with copious ethyl acetate. The combined organic phase was concentrated under vacuum. The crude product was purified by semipreparative HPLC (60% MeCN, 0.1% TFA) to give desired product. Semipreparative HPLC was performed using an ODS column (ODS-A, 10×250 mm, 5 μm) at 5 mL/min. ^{1}H NMR and ^{13}C NMR were recorded on a BRUKER BIOSPIN AVANCE III spectrometer using TMS as the internal standard.

Procedure of KIE experiment (scheme 1). A 25 mL Schlenk tube was charged with 1,10-phenanthroline (45 mg, 0.25 mmol), KO*t*-Bu (225 mg, 2.0 mmol), benzene (2.5 mL), benzene-d_6 (2.5 mL) and 4-bromotoluene (0.5 mmol) in glovebox. Then the tube was removed from the glovebox and the resulting mixture was stirred upon visible light irradiation (providing 400 mW cm^{-2} visible light) for 24 h. The reaction was quenched with water in excess and the residue was extracted with copious ethyl acetate. The combined organic phase was concentrated under vacuum. The crude product was purified by semipreparative HPLC (60% MeCN, 0.1% TFA) to give the desired product.

Detection of radical anion. The electron paramagnetic resonance (EPR) measurements were conducted according to the following procedures. A solution containing KO*t*-Bu (0.2 mmol), nitrogen heterocyclic compound (0.025 mmol) and benzene (0.2 mL) was placed into a quartz cell, and then the quartz cell was sealed. All these procedures were operated in glovebox under N_2 atmosphere. The quartz cell was then irradiated with different light sources of xenon lamp at the range of 320 nm~780 nm, and the spectra were recorded in situ with a Bruker A300 instrument operating in the X-band at room temperature.

ASSOCIATED CONTENT

Supporting Information.

Experimental section, computational details, extra cross-coupling reactions, the copies of NMR spectra and mass spectra for all the cross-coupling products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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