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COMMUNICATION

Visible-light-Enhanced Suzuki-Miyaura Coupling Reaction by Cooperative Photocatalysis with Ru-Pd Bimetallic Complex

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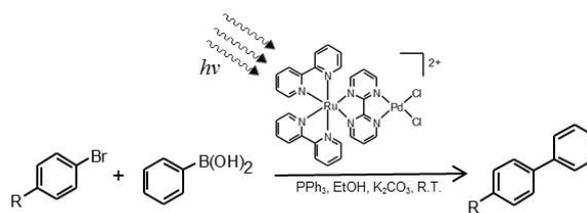
A photo-assisted Suzuki-Miyaura coupling reaction has been realized by molecule Pd(II) complex containing a Ru(II)-polypyridyl derivative as a visible light photosensitizing unit, where an electron transfer from excited Ru species to Pd forms an active electron rich Pd(0) and facilitates oxidative addition step with aryl halides.

The search for efficient solar energy conversion has attracted considerable attention owing to increasing energy and environmental concerns.¹ Photocatalysis enabling selective molecular transformations under visible sunlight irradiation is a permanent challenge as a potential alternative to conventional thermal catalysis. Photochemical excitation can be performed under mild conditions and circumvents the use of toxic reagents, which minimizes undesirable side reactions and contributes to energy saving. However, current application has predominantly focused on the photo reduction of H⁺ and CO₂ or oxidation reactions;²⁻⁷ practical photocatalysis being applied to the synthesis of specialty organic chemicals via carbon-carbon bond-formations are limited.⁸⁻¹⁰

Palladium-mediated cross-coupling reactions between aryl halides and nucleophiles, exemplified by Suzuki-Miyaura coupling reaction, have received wide interest due to its enormous synthetic potential to form new carbon-carbon bonds.¹¹ New classes of Pd complexes having Pd-carbon σ bonds, e.g. palladacycle complexes,¹² PCP pincer-type complexes,¹³ and N-heterocyclic carbenes (NHCs),¹⁴ have led to significant breakthroughs in this area. The first step of the catalytic cycle is an addition of the aryl halide to the Pd(0)L_n (L = ligand) to afford a σ -arylpalladium(II) complex, *trans*-ArPd(II)XL_n, which undergoes the reaction with base followed by transmetalation with organoborane, and the final product is generated by reductive elimination.¹⁵ In most cases, the oxidative addition is the rate determining step of the catalytic cycle, thus the primary importance to improve the catalytic activities and lower the reaction temperatures lies in the designing electron-rich Pd(0) complexes based on electron-donating and sterically hindered special ligands.^{13, 16}

In this paper, we proposed a new photo-assisted Suzuki-Miyaura

coupling reaction by bimetallic [(bpy)₂Ru(bpm)PdCl₂](PF₆)₂ (abbreviated as Ru-Pd complex, bpy: bipyridine, bpm: bipyrimidine) for the first time (Scheme 1). It is well known that the Ru(bpy)₃²⁺ and its derivatives absorb visible light as photosensitizer and lead to an excited singlet metal-to-ligand charge transfer (¹MLCT), which is then transferred with unit efficiency to a triplet MLCT (³MLCT) by intersystem crossing.¹⁷ The excited ³MLCT exhibits a phosphorescence emission,^{18, 19} while electron transfer reactions to the adjacent acceptors occur.⁸ We envisioned and herein verified that the excited Ru(II)-polypyridyl moiety could boost the formation of active electron rich Pd(0) and facilitates the rate-limiting oxidative addition step, which ultimately enhances the photocatalytic activity in Suzuki-Miyaura coupling reaction.



Scheme 1. Photo-assisted Suzuki-Miyaura coupling reaction mediated by Ru-Pd complex.

[(bpy)₂Ru(bpm)](PF₆)₂ was prepared according to a literature procedure.²⁰ A mixture of [(bpy)₂Ru(bpm)](PF₆)₂ and Pd(CH₃CN)₂Cl₂ was reflux in acetone solution for 2h, giving a [(bpy)₂Ru(bpm)PdCl₂](PF₆)₂, which was characterized by NMR spectroscopy.²¹ The UV-vis spectra of the complexes are illustrated in Fig. 1. A mononuclear Ru complex without Pd center exhibits intense UV absorption ($\lambda_{\text{max}} = 250\text{-}300$ nm) attributed to a ligand centered $\pi \rightarrow \pi^*$ transition and a visible absorption ($\lambda_{\text{max}} = 400\text{-}500$ nm) due to a MLCT. The low energy absorption bands in the visible region were slightly broader than that of the Ru(bpy)₃²⁺ complex because of the overlapping with the MLCT transition of d(Ru) $\rightarrow \pi^*$

(bpy) and $d(\text{Ru}) \rightarrow \pi^*(\text{bpm})$.²² A dinuclear Ru-Pd complex also shows the similar absorption spectrum owing the incorporation of Ru(II)-polypyridyl moiety, and a low energy absorption band due to MLCT is slightly shifted to longer wavelength.

The emission spectra were measured in degassed ethanol solution at room temperature ($\lambda_{\text{ex}} = 420 \text{ nm}$). As shown in **Fig. 2**, the emission of the mononuclear Ru complex can be observed at 656 nm, which is ascribed to the lowest lying $^3\text{MLCT} [(d\pi(\text{Ru}) \rightarrow \pi^*(\text{bpy}))$ or $[(d\pi(\text{Ru}) \rightarrow \pi^*(\text{bpm}))$ owing to the dominant LUMO character. It is known that its intensity is slightly lower than that of the $\text{Ru}(\text{bpy})_3^{2+}$ complex because of the presence of a quenching pathway by the lone-pair electrons of the bpm ligand.²³ The emission of the Ru(II)-polypyridyl moiety substantially quenched upon introduction of the Pd center, implying that an intramolecular electron transfer process is enhanced. The red shift of the maximum wavelength is attributed to the lowering of the π^* -energy level of bpm, which resulted in decrease $[(d\pi(\text{Ru}) \rightarrow \pi^*(\text{bpy}))$ $^3\text{MLCT}$ emission energy.²¹ A mixture of the mononuclear Ru complex and the $(\text{bpy})\text{PdCl}_2$ complex exhibited an essentially same intensity as that of only mononuclear Ru complex, suggesting that covalent linkage of the two metal units is essential for attaining effective electron transfer from Ru to Pd moiety, presumably because of the short lifetime of $^3\text{MLCT}$ excited state of $[\text{Ru}(\text{bpy})_2(\text{bpm})]^{2+}$ (90 ns).²⁴

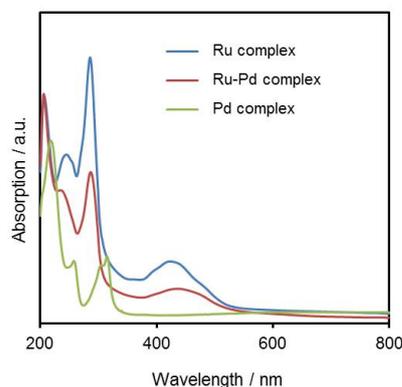


Figure 1. UV-vis spectra of $[(\text{bpy})_2\text{Ru}(\text{bpm})](\text{PF}_6)_2$, $[(\text{bpy})_2\text{Ru}(\text{bpm})\text{PdCl}_2](\text{PF}_6)_2$ and $(\text{bpy})\text{PdCl}_2$ complexes in EtOH solution.

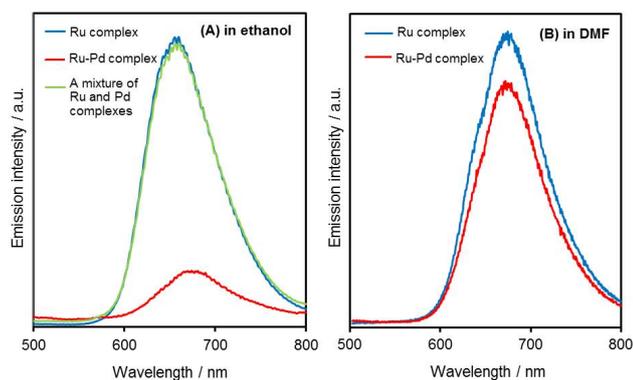


Figure 2. Emission spectra of $[(\text{bpy})_2\text{Ru}(\text{bpm})](\text{PF}_6)_2$, $[(\text{bpy})_2\text{Ru}(\text{bpm})\text{PdCl}_2](\text{PF}_6)_2$ and a physical mixture of $[(\text{bpy})_2\text{Ru}(\text{bpm})](\text{PF}_6)_2$ and $(\text{bpy})\text{PdCl}_2$ in EtOH solution (A) and in DMF solution (B) ($\lambda_{\text{ex}} = 420 \text{ nm}$).

As shown in **Fig. 3**, Suzuki-Miyaura coupling reaction of bromobenzene and phenylboronic acid were carried out in the presence of PPh_3 (2.0 mol%) and K_2CO_3 (100 mol%) in ethanol solvent at room temperature. As expected, the visible light irradiation ($\lambda > 420 \text{ nm}$) significantly enhanced the catalytic activity compared to that under dark conditions by a factor of 2 using Ru-Pd complex (1.0 mol%), giving the corresponding coupling product. No significant reaction was observed either in the presence of the mononuclear Ru complex or in the blank experiment under visible light irradiation. The enhancement of catalytic activity cannot be observed using a mixture of mononuclear Ru complex and analogous $(\text{bpy})\text{PdCl}_2$ complex. This result is well collaborated with the results of phosphorescence measurement and suggests that the electron transfer from Ru to Pd moiety is crucial for attaining enhanced photocatalytic activity. The use of only $(\text{bpy})\text{PdCl}_2$ complex also did not show enhancement effect. The catalytic activity in the absence of PPh_3 was extremely low whose TON corresponds to ca.1, indicating that PPh_3 acts as a reductant of Pd(II) and stabilizer of in situ generated Pd(0).²⁵ Electronic variation of the *p*-substituted aryl bromides did not significantly affect the reaction rates and the corresponding coupling products were obtained. Unfortunately, the present photocatalytic system did not allow the reaction of chloroarenes.

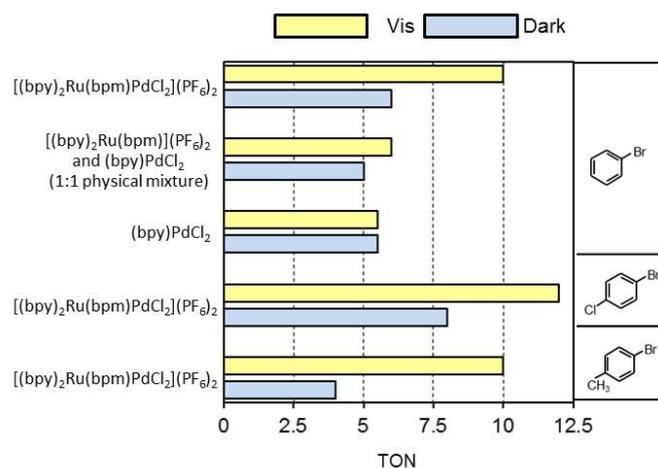


Fig. 3. Suzuki-Miyaura coupling reactions of bromobenzenes under several sets of conditions. Reaction conditions: bromobenzene ($5 \times 10^{-2} \text{ mmol}$), phenylboronic acid ($5 \times 10^{-2} \text{ mmol}$), catalyst ($5 \times 10^{-4} \text{ mmol}$), PPh_3 ($1 \times 10^{-3} \text{ mmol}$) and K_2CO_3 ($5 \times 10^{-2} \text{ mmol}$), EtOH (10 mL), Ar atmosphere, 6 h. Irradiation was performed from the side using a 500 W Xe lamp through the glass filter ($\lambda > 420 \text{ nm}$).

With respect to the bases, K_2CO_3 gave the best result, while the reaction using NEt_3 or CsCO_3 as a base were sluggish gave lower TONs. The low activity using NEt_3 is in contrast to that with the visible-light promoted Sonogashira coupling reaction using $\text{PdCl}_2(\text{CH}_3\text{CN})_2$, $\text{P}(t\text{-Bu})_3$ and $\text{Ru}(\text{bpy})_3^{2+}$, in which NEt_3 acts as a favorable base to afford the coupling products.¹³ Among the solvents examined, ethanol was excellent solvent, while acetonitrile and DMF gave poor results. This behaviour may be explained by the suppression of electron transfer from Ru to Pd moiety in such polar aprotic solvents with high coordination ability; the decrease of emission intensity of the dinuclear Ru-Pd complex relative to mononuclear Ru complex in DMF is not remarkable compared with

that in ethanol (**Fig. 2B**). Thus the use of ethanol solvent is more advantageous in enhancing the catalytic activity. The detail study to understand this phenomenon further is under investigation.

The present dinuclear Ru-Pd complex allows the oxidative addition of alkyl halide and its product has been previously established by MS and NMR spectroscopy.²² In the Ru-Pd complex system, the competitive Suzuki-Miyaura coupling reactions in an equimolar mixture of *p*-substituted bromobenzenes using **2** under visible-light irradiation gave a Hammett ρ value of 0.52, which is substantially smaller than 2.96 obtained under the conventional thermal conditions. This low ρ value indicates the acceleration of the oxidative addition, which is considered the rate-determining step in the Suzuki-Miyaura coupling reaction, by the formation of active electron rich Pd(0) species via electron transfer from excited Ru species to Pd(0). The XAFS measurement suggests that the Pd species keeps its original monomeric structure even after the reaction without the formation of Pd agglomeration (**Fig. S1 Table S1**). Moreover, Pd K-edge XANES spectrum after the reaction showed a slight shift of edge position toward lower energy compared to that before reaction, indicating that the Pd species changed to Pd⁰ after the reaction.

In conclusion, we demonstrated the harvesting light energy for attaining organic transformation by the bimetallic molecule complex consists of Ru(II)-polypyridyl derivatives as a visible light absorption unit and catalytically active Pd site enabling Suzuki-Miyaura coupling reactions. Catalytic activity under visible-light irradiation was enhanced compared to that under conventional thermal reactions. Our strategy would be a potential tool for the direct utilization of sunlight for attaining industrially crucial catalytic reactions.

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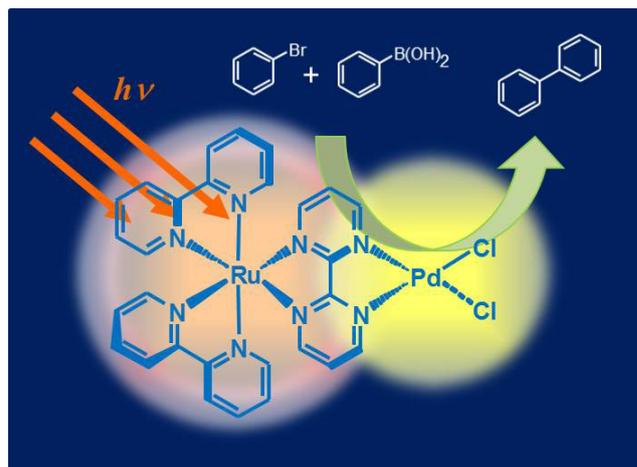
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† Electronic Supplementary Information (ESI) available: [Experimental procedures and XAFS]. See DOI: 10.1039/b000000x/

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Graphic Abstract



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