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# Ligand-to-metal charge transfer of a pyridine surface complex on TiO<sub>2</sub> for selective dehydrogenative cross-coupling with benzene†

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Dehydrogenative cross-coupling (DCC) between pyridine and benzene proceeded selectively using a  $TiO_2$  photocatalyst under visible light irradiation at optimized concentrations of the substrates. Visible light induces ligand-to-metal charge transfer (LMCT) between pyridine and a  $TiO_2$  surface to give a pyridine radical cation, which produces a pyridyl radical by its deprotonation or oxidation of another pyridine molecule. The pyridyl radical attacks a benzene ring to form an  $sp^2C-sp^2C$  bond and a hydrogen atom is subsequently removed to complete DCC. Selective excitation of the pyridine LMCT complex in the presence of an excess amount of benzene would be the key for higher selectivity.

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# 1. Introduction

Photocatalytic organic transformation is a promising reaction system which can achieve unique and highly difficult reactions such as dehydrogenative cross-coupling (DCC) under ambient conditions. DCC is one of the most environmental-friendly and thus important reactions in organic synthesis.<sup>1,2</sup> Many DCC systems have been reported both in homogeneous and heterogeneous catalyses, usually utilizing heat or light as a driving force.<sup>3-7</sup> The reaction often proceeds in an oxidative manner by using an external oxidant such as molecular oxygen, in which the byproduct is water.<sup>8</sup> In semiconductor photocatalysis, however, DCC can be achieved in a dehydrogenative manner under ambient pressure and temperature,<sup>9-12</sup> where the byproduct is hydrogen gas, which is a promising energy carrier.<sup>13</sup> Therefore, photocatalytic DCC by semiconductor material has great potential and should be explored.

Photocatalytic DCC typically proceeds through a reaction between radical species generated by hole oxidation of organic molecules. Especially over  $\text{TiO}_2$ , one of the most practical photocatalysts with enough oxidation power to oxidize various molecules,<sup>14–18</sup> the reaction often proceeds through a radicalradical coupling mechanism,<sup>11,12,19</sup> which also allows undesired reactions such as homo-coupling. In order to oxidation of the substrate should be avoided. One of the ways to suppress unselective oxidation in TiO<sub>2</sub> photocatalysis is to utilize ligand-to-metal charge transfer (LMCT) between the TiO<sub>2</sub> surface and adsorbed molecules.<sup>20,21</sup> In this system, a photoformed hole is generated and present on the adsorbed molecule. Since the oxidative potential of this hole is less positive than that of an excited TiO<sub>2</sub> photocatalyst, undesired oxidation tends to be limited, allowing selective oxidation of the substrate. Although few studies were available on the utilization of the LMCT system to DCC, we have recently reported selective DCC between benzene or pyridine and cyclohexane through LMCT between TiO<sub>2</sub> and the aromatics.<sup>22,23</sup> In our systems, an aromatic radical cation generated by the LMCT of the aromatic-TiO<sub>2</sub> surface complex oxidizes cyclohexane to a cyclohexyl radical. The radical attacks an aromatic molecule to complete DCC between sp<sup>2</sup>C and sp<sup>3</sup>C through a radical addition and elimination mechanism. Formation of such surface complexes on the TiO<sub>2</sub> surface has been reported with various molecules such as alcohols,24,25 amines,<sup>26,27</sup> sulfides,<sup>28</sup> and aromatics.<sup>22,23,29,30</sup> Therefore, in order to extend the application of the LMCT-based system, we need to investigate how the system performs and whether the selectivity can be improved even in the presence of multiple adsorbates for surface complexation. Moreover, the scope of previous systems was limited to cross-coupling between  $sp^2C$  and  $sp^3C$ . Cross-coupling between  $sp^2C$  and  $sp^2C$  such as the formation of an arene-arene linkage is also important in organic synthesis because of a large number of important compounds containing the linkage in pharmaceutical, agrochemical, and natural product chemistry.<sup>31</sup> In the present study, we report a new LMCT-based DCC between sp<sup>2</sup>C and sp<sup>2</sup>C in the presence of two adsorbates for

improve the selectivity of DCC by TiO<sub>2</sub> photocatalysis, unselective

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surface complexation: pyridine and benzene. We found that selective DCC between these molecules can be achieved through LMCT excitation of the pyridine surface complex at optimized concentrations of the substrates in which an excess amount of benzene exists.

# 2. Experimental section

#### 2.1. Catalyst preparation

Various TiO<sub>2</sub> powder samples were employed, which were donated by the Catalysis Society of Japan and denoted as JRC-TIO-2 (anatase phase,  $18 \text{ m}^2 \text{ g}^{-1}$ ), JRC-TIO-6 (rutile phase, 100 m<sup>2</sup> g<sup>-1</sup>), JRC-TIO-7 (anatase phase, 279 m<sup>2</sup> g<sup>-1</sup>), JRC-TIO-9 (anatase phase, 290-310 m<sup>2</sup> g<sup>-1</sup>), JRC-TIO-12 (anatase phase, 290 m<sup>2</sup> g<sup>-1</sup>), JRC-TIO-13 (anatase phase, 59 m<sup>2</sup> g<sup>-1</sup>), and JRC-TIO-14 (anatase phase, 338 m<sup>2</sup> g<sup>-1</sup>). All metal-loaded TiO<sub>2</sub> catalysts were prepared by a photodeposition method using TiO<sub>2</sub> powder and an aqueous methanolic solution of an appropriate metal precursor such as PdCl<sub>2</sub> (Kishida, 99%) or H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O (Wako, 99.9%) as follows. TiO<sub>2</sub> powder (4.0 g) was dispersed in ion-exchanged water (300 mL) and irradiated using a ceramic xenon lamp (PE300BUV) for 30 min. Then, methanol (100 mL) and the desired amount of the metal precursor solution were added to the suspension, and the contents were magnetically stirred for 15 min without irradiation, followed by stirring under the light for 1 h. The amount of the metal precursor solution was determined so as to fix the metal loading amount to 0.1 wt%. The product was then filtered by suction, washed with ionexchanged water, and dried at 323 K for 12 h to obtain metalloaded TiO<sub>2</sub> photocatalysts. The catalysts were referred to as M/TiO<sub>2</sub>, where M represents Pd or Pt.

#### 2.2. Reaction test

All of the chemicals were of analytical grade and were used without further purification. Before a photocatalytic reaction test, the M/TiO<sub>2</sub> sample (0.1 g) in a Pyrex glass tube (20 mL) was subjected to pre-treatment for 30 min under the xenon lamp light so as to clean its surface. Then, the reactants were added into the test tube, followed by 10 minutes of Ar bubbling, and stirring under light for the desired reaction time at room temperature. The light intensity was 160 mW  $\rm cm^{-2}$ measured at 415  $\pm$  55 nm in wavelength. After irradiation, 0.5 mL of the gaseous phase was collected by an air-tight syringe and was analyzed by a GC-TCD (Shimadzu, GC-8A). The reaction mixture was sampled by a syringe with a PTFE filter to separate the M/TiO<sub>2</sub> sample and then analyzed by a GC-MS (Shimadzu, GCMS-QP5050A). The amounts of products were determined from the GC-MS calibration curve of the authentic samples procured from the industries.

#### 2.3. Diffuse reflectance UV-vis spectroscopy

The UV-vis spectra of the powder samples were recorded in a diffuse-reflectance (DR) mode. A Pd/TiO<sub>2</sub> sample (JRC-TIO-14) was diluted with BaSO<sub>4</sub> by a factor of 100. For samples with an adsorbate, 50 mL of pyridine or benzene was added to 0.15 g of the diluted sample, followed by stirring for 30 min. Then, the desired amount of the sample (typically 0.13 g) was placed in a cell to fix the amount of the Pd/TiO<sub>2</sub> in the sample, and the spectrum was recorded using a UV-vis spectrophotometer (Jasco V-570) equipped with an integrating sphere, where BaSO<sub>4</sub> was used as a reference.

Table 1 Results of reaction tests performed under photoirradiation with the light of various limited wavelength ranges<sup>a</sup> M/TiO<sub>2</sub> hv 2-PhP 3-PhP 4-PhP + H<sub>2</sub> 2.2'-BP 2.3'-BP 2.4'-BP BPh Selectivity to PhPs<sup>d</sup> Products<sup>b</sup>/µmol Yield of PhPs<sup>c</sup> (%) (%) PhPs BPs BPh  $S_{\rm Py}$ Entry λ/nm Time/h Metal  $Y_{\rm Pv}$  $S_{\text{Be}}$ Pd 0.99 1.2 1 >350 0.2 1.7 0.14 44 42 2 > 400Pd 0.32 0.13 0.5 1.6 0.17 84 73 3 >4226 Pd 1.7Trace 0.09 0.14 >99 90 4 > 4002 Pd 5.2 0.49 0.96 0.43 84 73 5 >4002 Pt 6.1 1.1 1.1 0.5173 73 6 > 4002 1.6 0.14 0.12 0.13 85 87

<sup>*a*</sup> Reaction conditions: pyridine (0.10 mL, 1.2 mmol) and benzene (1.9 mL, 21 mmol) were used with a M/TiO<sub>2</sub> photocatalyst (JRC-TIO-14, 0.1 g), and the light intensity was 160 mW cm<sup>-2</sup> measured at a wavelength of 415 ± 55 nm. <sup>*b*</sup> PhPs: total amount of 2-PhP, 3-PhP, and 4-PhP. BPs: total amount of 2,2'-BP, 2,3'-BP, and 2,4'-BP. <sup>*c*</sup> Yield of PhPs based on the introduced pyridine. <sup>*d*</sup> Selectivity of DCC. The selectivity based on pyridine was calculated as  $S_{Py} = [100 \times PhPs (mmol)]/[(PhPs + 2 \times BPs) (mmol)]$ ; the selectivity based on benzene was calculated as  $S_{Be} = [100 \times PhPs (mmol)]/[(PhPs + 2 \times BPs) (mmol)]$ ; the selectivity based on benzene was calculated as  $S_{Be} = [100 \times PhPs (mmol)]/[(PhPs + 2 \times BPs) (mmol)]$ ; the selectivity based on benzene was calculated as  $S_{Be} = [100 \times PhPs (mmol)]/[(PhPs + 2 \times BPs) (mmol)]$ ; the selectivity based on benzene was calculated as  $S_{Be} = [100 \times PhPs (mmol)]/[(PhPs + 2 \times BPs) (mmol)]$ .

### 3. Results and discussion

#### 3.1. Photocatalytic reaction tests

A Pd/TiO<sub>2</sub> sample was examined for the reaction tests under photoirradiation with the light of various limited wavelength ranges (Table 1, entries 1-3). Several products were obtained such as 2-phenylpyridine (2-PhP), 3-phenylpyridine (3-PhP), and 4-phenylpyridine (4-PhP) as the DCC products (PhPs) as well as homo-coupled products formed from pyridine (bipyridyls (BPs): 2,2'-BP, 2,3'-BP, and 2,4'-BP) and benzene (biphenyl: BPh). The regioselectivity for the three PhPs was almost identical in most cases regardless of the irradiation wavelength, i.e., about 90% of 2-PhP, 4% of 3-PhP, and 6% of 4-PhP were formed. This is consistent with the C-H bond dissociation energy (BDE) of pyridine (Table S1, 439.3 kJ mol<sup>-1</sup> for site 2 and 468.6 kJ mol<sup>-1</sup> for sites 3 and 4, ESI<sup>+</sup>). Trimers from two pyridine molecules and one benzene molecule or one pyridine and two benzene molecules were not observed. The formation of BPh indicates that benzene was also activated during the reaction. Thus, a certain number of polymers could be formed although they cannot be detected by GC. The reaction did not proceed in the dark or in the absence of the photocatalyst (Table S2 entries 1 and 2, ESI,<sup>†</sup>), which confirmed that the reaction proceeds photocatalytically. Concomitant hydrogen production also confirmed that the reaction took place dehydrogenatively (Table S2, entry 3, ESI<sup>†</sup>).

Under photoirradiation of both UV and visible light ( $\lambda > 350$  nm, Table 1, entry 1), PhPs, BPs and BPh were obtained unselectively, where the selectivities to PhPs were calculated as 44% and 42% based on the products formed from pyridine ( $S_{Py}$ ) and benzene ( $S_{Be}$ ), respectively. The unselective product formation suggests that both pyridyl ( ${}^{\bullet}C_{5}H_{4}N$ ) and phenyl ( ${}^{\bullet}C_{6}H_{5}$ ) radicals were formed by the photocatalytic oxidation of the reactants by holes generated on the UV-light-activated TiO<sub>2</sub> photocatalyst, followed by successive radical-radical coupling.

Under visible light ( $\lambda > 400$  nm, Table 1, entry 2), in contrast, PhPs as cross-coupling products were successfully obtained as main products, which led to a higher selectivity ( $S_{Py} = 84\%$  and  $S_{Be} = 73\%$ ) than that under irradiation including UV light, although the production rates were lower due to the limited photon number for the limitation of wavelength range. The selectivity was further improved under more-limitedwavelength light ( $\lambda > 422$  nm, Table 1, entry 3) such as >99% for  $S_{Py}$  and 90% for  $S_{Be}$ . This result indicates a different reaction mechanism under visible light from that in the presence of UV light.

The effect of metal co-catalysts was also investigated (Table 1, entries 4 and 5). Generally, it is considered that metal co-catalyst on photocatalysts can suppress the recombination of photogenerated electrons and holes to enhance the photocatalytic activity.<sup>32–34</sup> Both Pd and Pt loaded samples showed higher activity than a pristine TiO<sub>2</sub> sample (Table 1, entry 6), which suggests that these metals actually work as a charge separator. At the same time, metal deposition decreased the selectivity. The Pd/TiO<sub>2</sub> sample showed higher *S*<sub>py</sub> (Table 1, entry 4) than the Pt metal loaded sample (Table 1, entry 5).

We have previously reported that a Pd cocatalyst on  $TiO_2$  can act as a catalyst which promotes the radical addition to benzene in some cross-coupling reactions.<sup>9,10,12,22</sup> Thus, the higher selectivity of the Pd-loaded sample in the present system would also be contributed from the presence of Pd metal catalysis. After optimization of the  $TiO_2$  photocatalyst (Table S3, ESI†), JRC-TIO-14, which has a large specific surface area, was chosen for the following experiments.

Next, we investigated the effect of the concentration of the reactants on the reaction under visible light irradiation (Table 2). We carried out reaction tests with a fixed volume of the reaction solution (2.0 mL) but with a different ratio of pyridine and benzene. Compared to the ratio used above (Table 2, entry 1), an increase of the ratio of pyridine to benzene decreased  $S_{Pv}$  but increased  $S_{Be}$  (Table 2, entries 2-5), and a decrease of the ratio increased  $S_{Pv}$  but decreased  $S_{Be}$  (Table 2, entries 6 and 7). These results were plotted in Fig. 1. A low concentration of pyridine is necessary to achieve the selective cross-coupling with high  $S_{Pv}$  under visible light. The ratio of 0.05 with 1.2 mmol of pyridine and 21 mmol of benzene provided moderately high values in both selectivities,  $S_{Pv}$  and  $S_{\rm Be}$ , which was thus employed as standard conditions in the present study. This means that selective DCC can be achieved even in the presence of two adsorbates for surface complexation by optimizing their concentration. When a long-time reaction test was carried out under the optimized conditions, higher selectivities were maintained after 12 h and the yield reached 1.0% (Fig. 2). Any successive reaction products such as trimers were still not observed. We also calculated the apparent quantum efficiency (AQE) based on the following equation: AQE (%) =  $100 \times (\text{amount of PhPs})/(\text{number of incident photons})$ irradiated to the reactor). The AQE at 400 nm was 0.22%.

The bare TiO<sub>2</sub> promoted the DCC reaction (Table 1, entry 6), and TiO<sub>2</sub> photocatalyst and these molecules, pyridine and benzene, do not absorb visible light when they have no interactions. These facts propose that other visible-light responsive species must be generated in this system. According to our previous reports, both pyridine<sup>23</sup> and benzene<sup>22</sup> can form a surface complex with TiO<sub>2</sub> and absorb visible light ( $\lambda > 400$  nm)

 Table 2
 Results of the reaction tests with various concentrations of pyridine and benzene under visible light<sup>a</sup>

	Substrate/mmol		Ratio of	Products <sup>b</sup> /µmol			$\frac{\text{Selectivity}^{b}}{(\%)}$	
Entry	Pyridine	Benzene	benzene	PhPs	BPs	BPh	$S_{\rm Py}$	S <sub>Be</sub>
1 <sup><i>c</i></sup>	1.2	21	0.050	5.2	0.49	0.96	84	73
2	6.0	18	0.25	4.5	2.8	0.35	45	87
3	12	12	0.50	3.1	5.7	0.11	22	93
4	18	6.0	0.75	1.5	8.9	Trace	10	>99
5	24	0.50	0.98	0.10	9.7	Trace	0.50	>99
6	0.48	24	0.020	3.4	0.23	0.98	88	63
7	0.24	24	0.010	1.9	Trace	0.99	>99	49

<sup>*a*</sup> Reaction conditions: pyridine and benzene were used with a Pd/TiO<sub>2</sub> photocatalyst (JRC-TIO-14, 0.1 g), the reaction time was 2 h, the irradiation wavelength was  $\lambda > 400$  nm, and the light intensity was 160 mW cm<sup>-2</sup> measured at a wavelength of 415 ± 55 nm. <sup>*b*</sup> See the caption of Table 1. <sup>*c*</sup> These data were the same as those in Table 1 entry 4.



Fig. 1 Selectivities based on pyridine  $(S_{py})$  or benzene  $(S_{Be})$  in the reaction tests with various ratios of pyridine to benzene in visible light. Data were from Table 2.



**Fig. 2** Time course of the cross-coupling reaction between pyridine and benzene. Pyridine (0.1 mL, 1.2 mmol) and cyclohexane (1.9 mL, 21 mmol) with the Pd/TiO<sub>2</sub> photocatalyst (0.1 g) were used. The irradiation wavelength was  $\lambda > 400$  nm. See the caption of Table 1 for the definitions of the selectivity of DCC,  $S_{Py}$  and  $S_{Be}$ .

to be excited; the former forms through an acid–base interaction and the latter does through a  $\pi$  interaction with the surface. Thus, many reaction routes are possibly speculated. Since both homo-coupling products (BPs and BPh) were produced, both pyridine and benzene should be activated in the present conditions. Furthermore, in order to confirm which is the major active surface complex to produce PhPs under visible light conditions, we carried out the following experiments.

We first measured DR UV-vis spectra of pyridine or benzene adsorbed on a Pd/TiO<sub>2</sub> (JRC-TIO-14) sample (Fig. 3). The Pd/ TiO<sub>2</sub> sample was diluted with BaSO<sub>4</sub> for accurate measurement. The Pd/TiO<sub>2</sub> sample without adsorption of the reactants showed no photoabsorption beyond 400 nm in wavelength (Fig. 3A(a) and B(a)). The sample of pyridine adsorbed on the Pd/TiO<sub>2</sub> exhibited a large absorption band in the UV region (Fig. 3A(b)), and the additional absorption band of low intensity appeared beyond 400 nm (Fig. 3B(b)). The band which centers around 260 nm is attributed to pyridine molecules adsorbed physically or in the liquid phase and that centers around 300 nm and extends beyond 400 nm is LMCT excitation of the surface complex of adsorbed pyridine and the TiO<sub>2</sub> surface.<sup>23</sup> On the other hand, the sample adsorbing benzene (Fig. 3A(c)) showed a slightly larger absorption band compared with the  $Pd/TiO_2$  (Fig. 3A(a)) but much lower than the sample adsorbing pyridine (Fig. 3A(b)).

Next, we carried out adsorption tests to compare the abilities of pyridine and benzene to form a surface complex with TiO<sub>2</sub> (Table 3). Hexane was used as a solvent. When 24 µmol of pyridine was introduced, more than half of the introduced pyridine adsorbed on TiO<sub>2</sub> (Table 3, entry 1). When 27 µmol of benzene was introduced, only 2.0 µmol of benzene adsorbed (Table 3, entry 2). These results confirmed that pyridine is adsorbed on TiO<sub>2</sub> more preferentially than benzene, which could be due to the stronger interaction of pyridine with the surface. We also carried out reaction tests with neat substrates under photoirradiation (Table 4). In the light including UV light, both reaction tests gave homo-coupling products, and the ratio of BPs to BPh was 2.2 (Table 4, entries 1 and 2), meaning that photoexcited TiO<sub>2</sub> photocatalysts promote the homocoupling reaction of pyridine with two times higher rate. In visible light, the amount of the homo-coupling products was much larger with pyridine (Table 4, entry 1) than with benzene (Table 4, entry 2) and the ratio of BPs to BPh was 11 (Table 4, entries 3 and 4). When we consider that the photoinduced DCC proceeds through adsorption, photoexcitation, and the reaction of the radical species with other radicals or molecules, the large difference in the ratio of BPs to BPh in the homo-coupling reaction tests under the two photoirradiation conditions would be determined by the difference of the photoexcitation process



Fig. 3 (A) DR UV-vis spectra of (a) the Pd/TiO<sub>2</sub> sample diluted with  $BaSO_4$ , (b) pyridine adsorbed on the diluted Pd/TiO<sub>2</sub> sample, and (c) benzene adsorbed on the diluted Pd/TiO<sub>2</sub> sample. (B) Enlarged view of (A).

#### Table 3 Results of adsorption tests<sup>a</sup>

	Initial amount in the solution/µmol		Amount in at the adso equilibriur	the solution orption n/μmol	Adsorbed amount <sup>b</sup> /µmol		
Entry	Pyridine	Benzene	Pyridine	Benzene	Pyridine	Benzene	
1 2	24 0	0 27	11 0	0 25	13	2.0	

<sup>*a*</sup> Conditions: hexane was used as a solvent. The solution (2.0 mL, 12  $\mu$ M pyridine or 14  $\mu$ M benzene) was mixed with a TiO<sub>2</sub> photocatalyst (JRC-TIO-14, 50 mg), and then stirred for 1 h without photoirradiation. <sup>*b*</sup> Adsorbed amount was calculated as: (Initial amount in the solution ( $\mu$ mol)) – (Amount in the solution at the adsorption equilibrium ( $\mu$ mol)).

Table 4Results of the photocatalytic reaction tests with neat pyridine orbenzene under different wavelength light<sup>a</sup>

			Products <sup>b</sup> /µmol		
Entry	λ/nm	Substrate	BPs	BPh	Ratio of BPs to BPh
1 2 3 4	>350 >400	Pyridine Benzene Pyridine Benzene	57 n.d. 19 n.d.	n.d. 26 n.d. 1.7	2.2 11

 $^a$  Reaction conditions: pyridine or benzene (24 mmol) was used with a Pd/TiO<sub>2</sub> photocatalyst (0.1 g), the reaction time was 2 h, and the light intensity was 160 mW cm<sup>-2</sup> measured at a wavelength of 415  $\pm$  55 nm.  $^b$  See the caption in Table 1.

under these light conditions since adsorption and the reaction would be in common. These results suggest that pyridine can form the surface complex more easily and produce the homocoupling product under visible-light irradiation in the presence of TiO<sub>2</sub> than benzene. Therefore, it is suggested that the major visible-light-excited species in the mixture of pyridine and benzene would be the pyridine–TiO<sub>2</sub> surface complex. As discussed previously,<sup>23</sup> pyridine adsorbs on the TiO<sub>2</sub> surface through an acidbase interaction between the N atom in the pyridine ring and Ti cation on the surface. At the LMCT, an electron of the lone pair on the N atom would be excited to a localized 3d orbital on the Ti cation, and the excited state should be a pyridine radical cation ( $C_5H_5N^{\bullet+}$ ) adsorbed on the surface. The visible-light-induced reaction will start with the generation of this surface radical cation species.

#### 3.2. Isotope experiments

To get an insight into the reaction mechanism under each wavelength light, we carried out isotope experiments (Table 5). In the presence of UV light, the yields of PhPs in the reaction with pyridine– $d_5$  (Table 5, entry 2) were smaller than those in the reaction with normal reagents (Table 5, entry 1). The  $k_{\rm H}/k_{\rm D}$  value was greater than unity such as 1.9, which is recognized as the kinetic isotope effect (KIE). This means that the rate-determining step (RDS) in the formation of PhPs is the C–H bond cleavage in pyridine under irradiation with the light including UV light. This indicates that the C–H bond cleavage by the photogenerated hole takes place mainly in pyridine for

 Table 5
 Results of isotope experiments<sup>a</sup>

		Doutorotod	Product/ $\mu$ mol, $(k_{\rm H}/k_{\rm D})^b$			
Entry	λ/nm	compound	PhPs	BPs	BPh	
1 2 3 4 5	>350 >400	 C <sub>6</sub> D <sub>5</sub> N C <sub>6</sub> D <sub>6</sub>  C <sub>6</sub> D <sub>5</sub> N	$17 \\ 8.8 (1.9) \\ 15 (1.1) \\ 5.2 \\ 2.7 (1.9)$	$\begin{array}{c} 4.3 \\ 1.5 (2.9) \\ 6.3 (0.70) \\ 0.45 \\ 0.27 (1.7) \end{array}$	$3.0 \\ 4.1 (0.74) \\ 0.76 (4.0) \\ 0.80 \\ 1.1 (0.71)$	
6		$C_6D_6$	4.3 (1.2)	0.47 (0.96)	0.12 (7.0)	



the formation of PhPs, which gives a pyridyl radical ( ${}^{\bullet}C_{5}H_{4}N$ ). A step of radical formation of benzene should not be included in the major reaction of the pyridine radical since the C–H bond cleavage is more difficult in benzene than in pyridine in terms of their C–H BDEs (Table S1, ESI†). Thus, the pyridyl radical ( ${}^{\bullet}C_{5}H_{4}N$ ) attacks a molecular benzene ring to form an sp<sup>3</sup>-like transition state (eqn (1)), which would release a hydrogen atom to give PhPs (eqn (2)). The small KIE observed in the reaction with benzene- $d_{6}$  (Table 5, entry 3,  $k_{H}/k_{D}$  value was 1.1) indicates the presence of another route to form PhPs which involves the C–H bond cleavage in benzene. KIEs for BPs in the reaction with pyridine– $d_{5}$  and for BPh in that with benzene- $d_{6}$  (Table 5, entries 2 and 3) also evidenced that RDSs in the formation of BPs and BPh are the C–H bond cleavage in pyridine and benzene, respectively.

On the other hand, the  $k_{\rm H}/k_{\rm D}$  value was less than unity for the homo-coupling of non-deuterated compounds (Table 5, BPh in entry 2 and BPs in entry 3), that is, inverse KIEs were observed. This can be interpreted by the competitive oxidation of pyridine and benzene. During the reaction, the two molecules are supposed to competitively consume the limited number of photogenerated holes in TiO2. Since the C-D bond is stronger than the C-H bond, the use of a deuterated compound instead of the normal compound would slow down the oxidation of the corresponding compound. This would increase the availability of the hole for the counter compound and accelerate its oxidation, resulting in a higher yield of the homo-coupling products of the non-deuterated compound. Thus, together with the discussion for the result of PhPs, it is suggested that at least two processes take place for the cross-coupling in the presence of UV light; radical addition and elimination between the pyridyl radical and benzene molecule (eqn (1) and (2)), and minor radical-radical coupling between a pyridyl radical and phenyl radical (eqn (3)). Another possible process is radical addition and elimination between pyridine and a phenyl radical (eqn (4) and (5)). The lower selectivity in the presence of UV light (Table 1, entry 1) than that under visible light (Table 1, entries 2 and 3) suggests that large numbers of pyridyl and phenyl radical species give these products through many reaction routes.

$${}^{\bullet}C_{5}H_{4}N + C_{6}H_{6} \rightarrow [C_{5}H_{4}N - C_{6}H_{6}]^{\bullet}$$
(1)

$$[C_5H_4N - C_6H_6]^{\bullet} \rightarrow C_{11}H_9N (PhPs) + H^{\bullet}$$
 (2)

 ${}^{\bullet}C_{5}H_{4}N + {}^{\bullet}C_{6}H_{5} \rightarrow C_{5}H_{5}N - C_{6}H_{5}$  (3)

$$C_5H_5N + {}^{\bullet}C_6H_5 \rightarrow [C_5H_5N - C_6H_5]^{\bullet}$$
(4)

$$\left[C_{5}H_{5}N-C_{6}H_{5}\right]^{\bullet} \rightarrow C_{11}H_{9}N\left(PhPs\right) + H^{\bullet}$$
(5)

Under visible light, the  $k_{\rm H}/k_{\rm D}$  values for PhPs and BPs in the reaction with pyridine- $d_5$  were 1.9 and 1.7, respectively (Table 5, entry 5), and the  $k_{\rm H}/k_{\rm D}$  value for BPh in that with benzene- $d_6$  was 7.0 (Table 5, entry 6). These KIEs confirmed that RDSs in their formations under visible light are the same as discussed above in the UV light case: RDS in the formation of PhPs and BPs is C-H bond cleavage in pyridine, while RDS in the formation of BPh is that in benzene. Simultaneously, it was suggested that the C-H bond dissociation by the hole takes place only in pyridine during the formation of PhPs by considering their C-H BDEs. On the other hand, the yield of BPs was not changed in the reaction with benzene- $d_6$  (Table 5, entry 6, the  $k_{\rm H}/k_{\rm D}$  value was 0.96) while inverse KIE was still observed for BPh in the reaction with pyridine- $d_5$  (Table 5, entry 5, the  $k_{\rm H}/k_{\rm D}$  value was 0.71). This different result from the UV light case suggests that the competitive oxidation of pyridine and benzene is not the case in this condition. Reaction under visible light would be initiated by the LMCT excitation of the pyridine-TiO<sub>2</sub> surface complex as suggested from the larger adsorption amount and higher visible-light activity of pyridine than benzene (Tables 3 and 4). The surface radical cation produces a pyridyl radical by its deprotonation or oxidation of another pyridine molecule, and the radical attacks the benzene ring. The cross-coupling proceeds through a radical addition and elimination mechanism. The use of an excess amount of benzene to pyridine would allow selective addition of the pyridyl radical to benzene due to the high collision frequency

between the radical and benzene. Due to the low concentration of pyridine, homo-coupling of pyridyl radicals to form BPs would also be suppressed for the same reason. The low rate for BPh formation suggests the lower reactivity of the surface pyridine cation to benzene for phenyl radical formation. The inverse KIE for BPh in the reaction with pyridine– $d_5$  could be due to the faster formation of the phenyl radical through the oxidation of benzene by the pyridine radical cation.

#### 3.3. Proposed reaction mechanism

Based on all of the results, a tentative reaction mechanism for the photocatalytic DCC between pyridine and benzene is proposed as follows, where the Pd/TiO<sub>2</sub> photocatalyst is shown as a representative. Since the different light conditions gave different results, it is obvious that the UV light and the visible light give different reaction mechanisms.

In the light including both UV and visible light, the contribution by the UV light excitation is considered to be very predominant (Fig. 4A). The UV light excites the TiO<sub>2</sub> photocatalyst to give photogenerated electrons and holes in the conduction band and valence band, respectively. The electrons are transferred to the Pd nanoparticles, while the holes are trapped on the  $TiO_2$  surface (step (i)). Pyridine and benzene are competitively oxidized by the holes to the corresponding radical species (steps (ii) and (iii)). Then, the radical-radical coupling of these radicals affords the DCC products (PhPs, step (iv)) as well as the homo-coupling products (BPs and BPh, steps (v) and (vi)). Protons are reduced by electrons on the Pd cocatalyst to give molecular hydrogen (step (vii)). This is a two-photon process (Fig. 4A). Another possible route to form the crosscoupling product is radical addition-elimination: the addition of the pyridyl radical to a benzene molecule to form an sp<sup>3</sup>centered transition state, and the elimination of a hydrogen



Fig. 4 Schematic image of tentative reaction mechanism for photocatalytic DCC between pyridine and benzene under UV and visible light (A), and visible light (B). 2-PhP and 2,2'-BP were chosen as representative products among PhPs and BPs, respectively.

radical from this transition state (steps (viii) and (ix)). In this case, the proton is reduced by the electron on the Pd nanoparticles, followed by a reaction with the hydrogen radical to give molecular hydrogen (step (x)). The step (ix) itself would be thermodynamically favorable since the molecule can regain its aromaticity by releasing a H radical. Therefore, acceleration of a H radical elimination by other species or proton elimination by further photoexcitation of the transition state would not be necessary. This reaction between the pyridyl radical and benzene molecule can be catalyzed by the Pd nanoparticles.<sup>9,10,12,22</sup>

Under visible-light irradiation (Fig. 4B), the surface complex consisting of adsorbed pyridine and a Ti cation, in which an acid-base N-Ti coordinate bond is formed using the lone pair on the nitrogen atom (step (xi)), is photoexcited to generate an excited electron from the lone pair. The electron is injected into the conduction band of TiO<sub>2</sub> via the surface Ti cation, followed by transfer to the deposited Pd nanoparticles, while a hole remains as a pyridine radical cation (step (xii)). The radical cation is deprotonated (step (xiii)) or oxidizes another pyridine molecule (step (xiv)) to produce a pyridyl radical and a proton, and the DCC reaction proceeds through the radical additionelimination process between the pyridyl radical and a benzene molecule (step (xv) and (xvi)). The adsorbed pyridine molecules would not be static on the surface but rather dynamic in an adsorption-desorption equilibrium, that is, they act not only as a visible-light-harvesting group but also as a substrate. Apart from the LMCT sites, the proton is reduced by the electron on the Pd nanoparticles, followed by a reaction with the hydrogen radical to give molecular hydrogen (step (xvii)). The reaction under visible light should be a one-photon process (Fig. 4B). In this mechanism, pyridine radical cation forms selectively instead of the photogenerated holes, suppressing the formation of phenyl radical. Therefore, the homo-coupling of benzene is suppressed. In addition, the attack of pyridine radical to the benzene molecule is dominant due to an excess amount of benzene, suppressing the homo-coupling of pyridine.

Under UV light

$$Pd/TiO_2 + h\nu \rightarrow e_{Pd}^- + h_{TiO_2}^+$$
(i)

$$C_5H_5N + h_{TiO_2}^{+} \rightarrow {}^{\bullet}C_5H_4N + H^{+}$$
(ii)

$$C_6H_6 + h^+_{TiO_2} \rightarrow {}^{\bullet}C_6H_5 + H^+$$
(iii)

$$^{\bullet}C_{5}H_{4}N + ^{\bullet}C_{6}H_{5} \rightarrow C_{11}H_{9}N (PhPs) (iv)$$

$${}^{\bullet}C_{5}H_{4}N + {}^{\bullet}C_{5}H_{4}N \rightarrow C_{10}H_{8}N_{2} (BPs)$$
 (v)

$${}^{\bullet}C_{6}H_{6} + {}^{\bullet}C_{6}H_{6} \rightarrow C_{12}H_{12} (BPh)$$
 (vi)

$$2H^+ + 2e^-_{Pd} \rightarrow H_2 \qquad (vii)$$

$$^{\bullet}C_{5}H_{4}N + C_{6}H_{6} \rightarrow [C_{5}H_{5}N - C_{6}H_{6}]^{\bullet}$$
 (viii)

$$[C_5H_5N-C_6H_6]^{\bullet} \rightarrow C_{11}H_9N (PhPs) + H^{\bullet}$$
(ix)

$$\mathbf{H}^{+} + \mathbf{H}^{\bullet} + \mathbf{e}^{-}_{\mathbf{Pd}} \to \mathbf{H}_{2} \tag{X}$$

Under visible light

$$C_5H_5N + Ti_{TiO_2} \rightarrow C_5H_5N - Ti_{TiO_2}$$
 (surface complex) (xi)

$$C_5H_5N-Ti_{TiO_2} (surface \ complex) \rightarrow C_5H_5N^{\bullet^+} + Ti_{TiO_2} + e^-_{Pd}$$
(xii)

$$C_5H_5N^{\bullet^+} \rightarrow {}^{\bullet}C_5H_4N + H^+$$
 (xiii)

$$C_5H_5N^{\bullet^+} + C_5H_5N \rightarrow C_5H_5N + {}^{\bullet}C_5H_4N + H^+$$
 (xiv)

$$^{\bullet}C_{5}H_{4}N + C_{6}H_{6} \rightarrow [C_{5}H_{5}N - C_{6}H_{6}]^{\bullet}$$
 (xv)

$$\left[C_{5}H_{5}N-C_{6}H_{6}\right]^{\bullet} \rightarrow C_{11}H_{9}N (PhPs) + H^{\bullet} \qquad (xvi)$$

$$H^{+} + H^{\bullet} + e^{-}_{Pd} \rightarrow H_2 \qquad (xvii)$$

# 4. Conclusions

LMCT excitation of the pyridine– $TiO_2$  surface complex by visible light was utilized to promote DCC between pyridine and benzene. The presence of an excess amount of benzene is important to obtain high selectivity. The selective formation of radical species due to the unique mechanism was successfully demonstrated. Although the efficiency of the reaction and product yield are not satisfactory, this study expanded the possible use of aromatic-semiconductor surface complex systems for DCC reactions, in which the selectivity can be improved merely by changing the irradiation wavelength without any additives or modifications of the photocatalyst.

## Conflicts of interest

There are no conflicts to declare.

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