

Supporting information

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

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


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## 1. Bond dissociation energy (BDE)

Some C–H Bond dissociation energies (BDEs) of pyridine and benzene reported in literature are summarized in Table S1.

**Table S1** C–H Bond dissociation energies of pyridine and benzene<sup>a</sup>

Compound	Site		BDE / kJ mol <sup>-1</sup>
Pyridine	2		439.3 ± 0.8
	3		468.6 ± 8.4
	4		468.6 ± 8.4
Benzene	-		472.2 ± 2.2

<sup>a</sup> The values were cited from Y. R. Ruo, *Comprehensive Handbook of Chemical Bond Energies*, CRC Press, 2007.

## 2. Blank test

Table S2 shows results of blank tests. The reaction did not proceed in dark or in the absence of the photocatalyst (Table S2, entries 1 and 2), which confirmed the reaction proceeds photocatalytically. Concomitant hydrogen production also confirmed the reaction took place dehydrogenatively (Table S2, entries 3). The amount of hydrogen is larger than expected from those of the detected organic products, as indicated by the large value of the H<sub>2</sub> balance. This could be due to undetected strongly adsorbed products on the catalyst surface or the progress of side reactions such as successive reactions of the products to form larger oligomers.

**Table S2** Results of blank tests<sup>a</sup>

Entry	Catalyst	Light	Products <sup>b</sup> / μmol			
			PhPs	BPs	BPh	H <sub>2</sub> (balance) <sup>c</sup>
1	Yes	No	n.d. <sup>d</sup>	n.d. <sup>d</sup>	n.d. <sup>d</sup>	n.d. <sup>d</sup> (-)
2	No	Yes	n.d. <sup>d</sup>	n.d. <sup>d</sup>	n.d. <sup>d</sup>	n.d. <sup>d</sup> (-)
3	Yes	Yes	1.6	0.14	0.12	3.4 (1.8)

<sup>a</sup> Reaction conditions: pyridine (0.1 mL, 1.2 mmol) and benzene (1.9 mL, 21 mmol) with a pristine TiO<sub>2</sub> photocatalyst (JRC-TiO-14, 0.1 g) were used, the reaction time was 2 h, and the irradiation wavelength was λ > 400 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> The H<sub>2</sub> balance was calculated as [actual amount of H<sub>2</sub> (μmol)]/[expected amount of H<sub>2</sub> from the total amount of the coupled products, PhPs, BPs, and BPh (μmol)]. <sup>d</sup> Not detected.

### 3. Optimization of titanium dioxide

The reaction tests were carried out with various pristine TiO<sub>2</sub> samples for the dehydrogenative cross-coupling (DCC) reaction under visible light irradiation ( $\lambda > 400$  nm). The results are shown in Table S3. The yield of PhPs increased with increasing the surface area of TiO<sub>2</sub> (Table S3, entries 1–6) and JRC-TIO-14 (Table S3, entry 6), which has the largest surface area, gave the largest amount of PhPs. A rutile sample showed comparable activity to JRC-TIO-14 (Table S3, entry 7). We employed JRC-TIO-14 as the TiO<sub>2</sub> photocatalyst in the following experiments. The larger specific surface area would be favorable to the surface complex formation.

**Table S3** Results of the reaction tests under photoirradiation with various pristine TiO<sub>2</sub> photocatalysts<sup>a</sup>

Entry	TiO <sub>2</sub>	Crystal phase	Specific surface area / m <sup>2</sup> g <sup>-1</sup>	Products / $\mu$ mol <sup>b</sup>			Selectivity to PhPs (%) <sup>d</sup>	
				PhPs	BPs	BPh	S <sub>Py</sub>	S <sub>Be</sub>
1	JRC-TIO-2	Anatase	18	n.d. <sup>c</sup>	n.d. <sup>c</sup>	n.d. <sup>c</sup>	-	-
2	JRC-TIO-13	Anatase	59	0.25	n.d. <sup>c</sup>	0.09	>99	59
3	JRC-TIO-7	Anatase	279	0.48	0.05	0.04	83	86
4	JRC-TIO-12	Anatase	290	0.58	0.03	0.08	88	78
5	JRC-TIO-9	Anatase	290–310	0.56	0.03	0.05	92	85
6	JRC-TIO-14	Anatase	338	1.6	0.14	0.12	85	88
7	JRC-TIO-6	Rutile	100	1.4	0.14	0.11	83	86

<sup>a</sup> Reaction conditions: pyridine (0.10 mL, 1.2 mmol) and benzene (1.9 mL, 21 mmol) were used with a pristine TiO<sub>2</sub> photocatalyst (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  $\pm$  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> Not detected. <sup>d</sup> Selectivity of DCC. The selectivity based on pyridine was calculated as  $S_{Py} = [100 \times \text{PhPs (mmol)}] / [(\text{PhPs} + 2 \times \text{BPs}) \text{ (mmol)}]$ ; the selectivity based on benzene was calculated as  $S_{Be} = [100 \times \text{PhPs (mmol)}] / [(\text{PhPs} + 2 \times \text{BPh}) \text{ (mmol)}]$ .