

## Supporting Information

# Visible-light-induced Photocatalytic Benzene/Cyclohexane Cross-coupling Utilizing a Ligand-to-metal Charge Transfer Benzene Complex Adsorbed on Titanium Oxides

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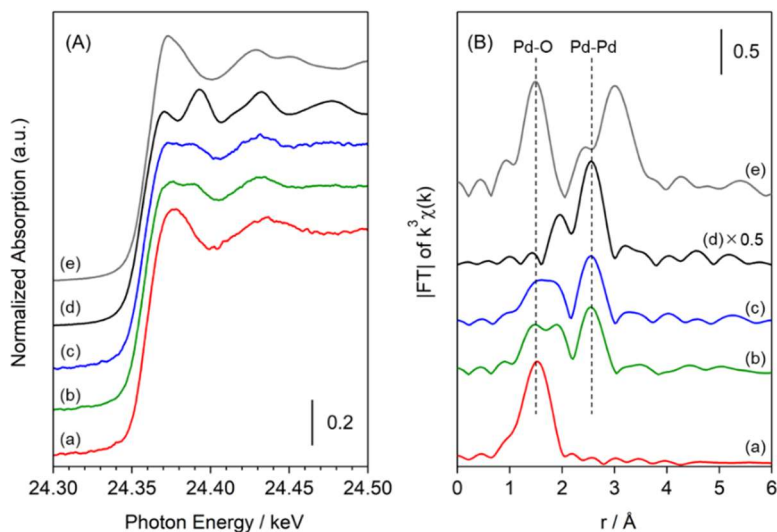
**Material and Synthesis.** An anatase TiO<sub>2</sub> powder (JRC-TIO-8, 338 m<sup>2</sup>g<sup>-1</sup>) was donated from the Catalysis Society of Japan. PdCl<sub>2</sub> (Kishida, 99%), H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O (Wako, 99.9%), RhCl<sub>3</sub>·3H<sub>2</sub>O (Kishida, 99%), HAuCl<sub>4</sub>·4H<sub>2</sub>O (Kishida, 99.9%), Ag(NO<sub>3</sub>) (Kishida, 99%), Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Wako, 98%) or Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Nacalai tesque, 98%) were used as a metal precursor of co-catalysts, and co-catalyst was loaded on the TiO<sub>2</sub> powder by a photodeposition method. The TiO<sub>2</sub> powder was dispersed in a methanol/water solution (25% v/v, 400 mL) containing the metal precursor (0.1 wt%), and irradiated using a xenon lamp (Perkin Elmer PE300BUV) with stirring for 30 min. The light intensity was 50 mW cm<sup>-2</sup> when measured at 365 ± 20 nm wavelength using a UV radiometer (Topcon, UVR-2, UD-36). After the filtration, the sample was washed with ion-exchanged water, and then was dried at 323 K. The catalyst is referred to as M/TiO<sub>2</sub> (M = Rh, Pt, Au, Pd, Ag, Ni, and Co). Pd/Al<sub>2</sub>O<sub>3</sub> sample was prepared using a conventional impregnation method using the PdCl<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> (JRC-ALO-7, 180 m<sup>2</sup> g<sup>-1</sup>, Catalysis Society of Japan) powder.

**Photocatalytic activity test.** Photocatalytic activity test was carried out using a closed reactor. The sample powder was added into a Pyrex test tube (20 mL), and was irradiated in air for 30 min to decompose impurities on the surface before the reaction. After the pretreatment, it was purged with Ar gas for 10 minutes followed by the addition of reactants (benzene and cyclohexane). Photo-irradiation was carried out using the 300W xenon lamp with a long pass filter (Asahi Spectra Co., Ltd. LU350, λ>350 nm or LU400, λ>400 nm) under stirring in an Ar atmosphere. The products in the liquid phase and the gas phase were analysed using GC-MS (Shimadzu, QP-5050A), and TCD-GC (Shimadzu, GC-8A), respectively. The cross-coupling selectivity based on cyclohexane (*S<sub>c</sub>*) and benzene (*S<sub>b</sub>*) was calculated using following equations.  $S_c (\%) = n_{PCH} \times 100 / (n_{PCH} + n_{BCH} \times 2)$ ,  $S_b (\%) = n_{PCH} \times 100 / (n_{PCH} + n_{BP} \times 2)$ , where *n* is amount of phenylcyclohexane (PCH), bicyclohexyl (BC), and biphenyl (BP).

**Action spectrum.** The action spectrum was measured with the same set-up with the photocatalytic activity tests. Another 300W Xe lamp (Asahi Spectra Co., Ltd. MAX-302) was used as a light source combined with band-pass filters of MX0360 (λ=360±10 nm), MX0380 (λ=380±10 nm), MX0400 (λ=400±10 nm), MX0420 (λ=420±10 nm), MX0440 (λ=440±10 nm), and MX0500 (λ=440±10 nm) (Asahi Spectra Co., Ltd.). The light intensity was measured using miniature fiber optic spectrometer (Ocean Optics, USB2000).

**X-ray absorption near edge structure (XAFS) spectra.** Pd K-edge XAFS spectra were recorded at room temperature at the NW10A beamline of KEK-PF using a Si(311) double crystal monochromator. The XAFS measurements of Pd/TiO<sub>2</sub> samples were performed in fluorescence mode using a Lytle detector, and a Pd foil and PdO pellet were measured in transmission mode. The Pd/TiO<sub>2</sub> samples were sealed in a polyethylene bag immediately after the reactions under UV-visible or visible light for 1 hour to minimize the air oxidation of the Pd species. XAFS data analysis was performed with the Athnea software. The  $k^3$ -weighted EXAFS spectra were Fourier transformed in the  $k$  range of 2.8–10.2 Å<sup>-1</sup>.

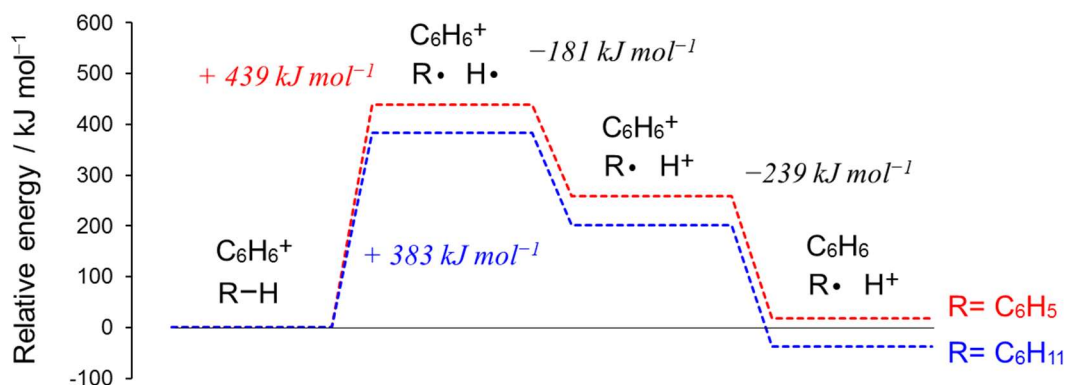
Figure S1(A) shows the XANES spectra of the Pd/TiO<sub>2</sub> samples before and after reactions. The spectrum shape of the sample before reaction (a) was similar to that of PdO reference pellet (e), and in the EXAFS spectrum, a band derived from Pd-O scattering was clearly observed as shown Fig. S1(B), which strongly indicated that the Pd oxide species were formed before reaction. After reactions using UV-visible or visible lights, the shape of XANES and EXAFS spectra were changed (b and c). A band of Pd-Pd scattering appeared in the EXAFS spectra, indicating that the Pd oxide species were reduced to Pd metal particles during the reactions. In the XANES and EXAFS spectra, no difference of the Pd state was observed depending on the wavelength of the light, indicating that the state of Pd is similar during the reactions under UV-visible and visible lights.



**Fig. S1** Pd-K edge XANES (A) and Fourier-transformed EXAFS (B) spectra. (a): a Pd/TiO<sub>2</sub> sample before reaction, (b) a Pd/TiO<sub>2</sub> sample after reaction under UV-visible light ( $\lambda > 350$  nm), (c) a Pd/TiO<sub>2</sub> sample after reaction under visible light ( $\lambda > 400$  nm), (d): Pd foil, and (e) PdO pellet.

**Diffuse reflectance UV-Vis adsorption spectra.** To investigate the absorber of visible light, we measured UV-Vis DRS of the powder samples (100 mg) with and without adsorbates of benzene or cyclohexane (40 uL).

**Free energy calculation.** Change of Gibbs energy ( $\Delta G^\circ$ ) of the reaction between benzene radical cation and R-H (R=C<sub>6</sub>H<sub>5</sub>, C<sub>6</sub>H<sub>11</sub>) was estimated using the C–H bond dissociation energies (BDEs) and one electron oxidation potential of benzene ( $E_{\text{ox}} = 2.48$  V vs SCE).<sup>1</sup> The Gibbs energy of the C–H bond dissociation of benzene and cyclohexane were calculated to be 439 and 383 kJ mol<sup>-1</sup>, respectively, where the values were given by the BDEs in benzene and cyclohexane (472.2 and 416.3 kJ mol<sup>-1</sup>, respectively)<sup>2</sup> minus the entropy factor ( $T\Delta S$ , taken in all the cases as 33 kJ mol<sup>-1</sup> at 298 K)<sup>3</sup>. The oxidation potential of H<sup>•</sup> to H<sup>+</sup> was  $-1.87$  V (vs SCE) in acetonitrile.<sup>3</sup> The energy diagram was shown in Fig. S2, and the  $\Delta G^\circ$  values of the reaction between benzene radical cation and benzene and cyclohexane (eq. 11 and 12 in the main text) were calculated to be 19 and  $-37$  kJ mol<sup>-1</sup>, respectively.



**Fig. S2** Energy diagram used for the calculation of the Gibbs energy change.

## Reference

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