

Supplementary information for

Organically modified titania having a metal catalyst:

**A new type of liquid-phase hydrogen-transfer photocatalyst working under visible
light irradiation and H₂-free conditions**

Experimental

Chemicals

All reagents were purchased from Wako Pure Chemical Industries, Ltd. and used without further purification.

Preparation of 2,3-dihydroxynaphthalene-modified TiO₂ (TiO₂-DHN)

Methanol solution (3 cm³) of 2,3-dihydroxynaphthalene (5 mg, corresponding to 1 wt%) was added to TiO₂ (495 mg) in an evaporating dish, and methanol was evaporated over a water bath at 313 K until dried powder was obtained.

Preparation of Pa-loaded TiO₂-DHN (Pd/TiO₂-DHN)

Photodeposition was used for preparation of Pd/TiO₂-DHN, i.e., for loading of a Pd catalyst (0.1 wt%) on TiO₂-DHN. In an aqueous methanol solution (10 vol%, 10 cm³) containing palladium(II) chloride, TiO₂-DHN particles were suspended, and the suspension was photoirradiated for 60 min with a 400 W high-pressure mercury arc ($\lambda > 300$ nm, Eiko-sha, Osaka) with magnetic stirring under argon (Ar) at 298 K. Analysis of the liquid phase after photoirradiation revealed that Pd has been almost completely deposited on the TiO₂-DHN particles. After photoirradiation, the Pd/TiO₂-DHN was recovered, washed repeatedly with water by vigorous mixing, centrifuged (20 min at 3500 rpm) three times, and then dried at 293 K *in vacuo* for 60 min.

Photocatalytic reaction

Thus-prepared Pd/TiO₂-DHN (50 mg) was suspended in acetonitrile (5 cm³) containing alkene (50 μ mol) and a hole scavenger (triethanolamine, 80 μ mol) in a test tube. The tube was sealed with a rubber septum and then irradiated with visible light of

two sets of a blue LED (420-530 nm, 137 ± 4 mW/cm², Hayashi Watch Works, Tokyo) from two directions under Ar with magnetic stirring at 298 K. The emission spectrum of light from a blue LED is shown in Figure 1(a). After the reaction, the gas phase was analyzed by a gas chromatograph (Shimadzu, GC-8A equipped with an MS-5A column). After the suspension had been filtered to remove the particles, the amounts of products and starting compounds remaining were determined by a gas chromatograph (Shimadzu GC-2025 equipped with a DB-1 column).