Supporting Information

Visible Light-catalytic Dehydrogenation of Benzylic Alcohols to Carbonyl Compounds by Using Eosin Y and Nickel-Thiolate Complex Dual Catalyst System

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1. Materials

Eosin Y, Ni(OAc)$_2$, 3-mercaptopropionic acid, benzyl alcohol, 4-methylbenzyl alcohol, 4-methoxybenzyl alcohol, 4-isopropylbenzyl alcohol, 4-chlorobenzyl alcohol, 4-bromobenzyl alcohol, 4-hydroxybenzyl alcohol, 1-(4-methoxyphenyl)ethanol, 1-phenyl-1-propanol, benzydryl, 4-phenyl-2-butanol, 3-phenyl-1-propanol, 1-phenyl-1,3-butanedione were purchased from Acros, TCI or Sigma-Aldrich. Other chemicals are of analytical grade without further purification unless otherwise noted. The ultrapure water with 18.2 MΩ cm (Mettler Toledo, FE20, China) was used throughout the experiment.

2. General procedure for photocatalytic dehydrogenation of benzylic alcohols reaction

A 10 mL Pyrex tube equipped with a rubber septum and magnetic stir bar was charged with 5 mL aqueous solution of 0.2 mmol substrate, Ni-MPA catalyst (0.015 mmol Ni(OAc)$_2$ and 0.15 mmol 3-mercaptopropionic acid) and eosin Y(0.002 mmol), then adjusted the pH to 8.50. The Pyrex tube was sealed and the mixture was bubbled with argon gas for 20 min. Then, 500 μL CH$_4$ was injected to the Pyrex tube as the internal standard. The mixture was then irradiated with a green LED light (λ = 525 nm) for 24 h at room temperature. After irradiation, gas composition is analyzed by gas chromatography (14B, Shimadzu) using thermal conductivity detector (TCD) with a 5 Å molecular sieve column and argon as the carrier gas. The solution was extracted with EtOAc (50 mL×3), washed with brine (50 mL×3), dried over Na$_2$SO$_4$. The products obtained after concentrated in vacuo were identified by $^1$H NMR.
3. Detection of hydrogen

![Fig. S1 GC/TCD chromatograph of H₂ production over time. Condition: LED (green light, 525 nm); room temperature; benzyl alcohol (0.2 mmol); Ni-MPA (7.5 mol%); eosin Y (1 mol%); H₂O (5 mL).](image)

4. Mechanism study

![Fig. S2 Kinetic trace at 560 nm when adding benzyl alcohol (BA, 1×10⁻³ M) to eosin Y (1×10⁻⁵ M) with 532 nm light in de-aerated H₂O-CH₃CN (3:2).](image)
**Fig. S3** GC/TCD chromatograph of H$_2$ production over time monitored by GC-TCD using He as carrier gas. Condition: LED (green light, 525 nm); room temperature; benzyl alcohol (0.2 mmol); Ni-MPA (7.5 mol%); EY (1 mol%); 5 mL H$_2$O or D$_2$O.

### 5. Large scale reaction of benzylic alcohol

Benzylic alcohol (2 mmol) was first dissolved in 1 mL CH$_3$CN solvent in a 100 mL reactor, followed by adding 40 mL aqueous solution of Ni-MPA catalyst (0.15 mmol Ni(OAc)$_2$ and 1.5 mmol 3-mercaptopropionic acid) and eosin Y (0.02 mmol), then adjusted the pH to 8.50. The reactor was sealed and the mixture was bubbled with argon gas for 20 min. The reactor was then irradiated with a 300 W xenon equipped with a filter (λ> 400 nm) for 27 h. The solution was extracted with EtOAc (50 mL×3), washed with brine (50 mL×3), and then dried over Na$_2$SO$_4$. Solvent was removed by rotary evaporation. The product was purified by flash chromatography with petroleum/EtOAc (10:1) and the isolated yield is 72%.