

SUPPORTING INFORMATION FOR:

**Green molecular transformation by B₁₂-TiO₂ hybrid catalyst as an
alternative to tributyltin hydride**

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Measurements.

Elemental analyses were obtained from the Service Center of Elemental Analysis of Organic Compounds at Kyushu University. The NMR spectra were recorded by a Bruker Avance 500 spectrometer at the Center of Advanced Instrumental Analysis of Kyushu University, and the chemical shifts (in ppm) were referenced relative to the residual protic solvent peak. The GC-MS were obtained using a Shimadzu GC-QP5050A equipped with a J&W Scientific DB-1 column (length 30 m; ID 0.25 mm, film 0.25 μm). The UV-vis absorption spectra were measured by a Hitachi U-3300 spectrophotometer at room temperature. The diffusion UV-vis reflectance spectra were measured by a Hitachi U-3300 spectrophotometer equipped with a Φ 60 integrating sphere at room temperature under nitrogen. The IR spectra were recorded by a JASCO FT-IR 460 plus KH spectrophotometer using KBr discs. The MALDI-TOF mass spectra were obtained by a Bruker autoflex II using 6-aza-2-thiothymine as the matrix. The ESR spectra were obtained using a JEOL JES-FE1G X-band spectrometer equipped with an Advantest TR-5213 microwave counter and an Echo Electronics EFM-200 NMR field meter at room temperature.

Chemicals.

All solvents and chemicals used in the syntheses were of reagent grade, and were used without further purification. The deuterium-labeled ethanols, $\text{C}_2\text{D}_5\text{OD}$ (99.5 % atom D), $\text{C}_2\text{D}_5\text{OH}$ (99.5 % atom D) and $\text{C}_2\text{H}_5\text{OD}$ (99.5 % atom D) were purchased from Aldrich.

Synthesis of cobyrinic acid: $[(\text{CN})(\text{H}_2\text{O})\text{Cob}(\text{III})_7\text{COOH}]\text{Cl}$

To a solution of heptamethyl dicyanocobyrinate, $[(\text{CN})_2\text{Cob}(\text{III})_7\text{C}_1\text{ester}]$ (1.0 g, 9.2×10^{-4} mol) in 300 mL of methanol was added 50 mL of aqueous NaOH solution (0.26 M) and stirred under room temperature. After 12 h, 1.5 mL of HCl aqueous solution (11 M) was added and the product was extracted with phenol (50 mL \times 3). 300 mL of diethyl ether was added to the phenol layer and the product was extracted with

H₂O (50 mLx3). The aqueous solution was concentrated under reduced pressure to afford a red solid. Yield 95 %; IR, ν/cm^{-1} : 3200 (O-H, str.), 2140 (CN, str.), 1720 (C=O, str.). TOF MS (MALDI, m/z): [M-CN-H₂O], 938. UV-VIS (in H₂O, nm), 352, 405, 492, 519.

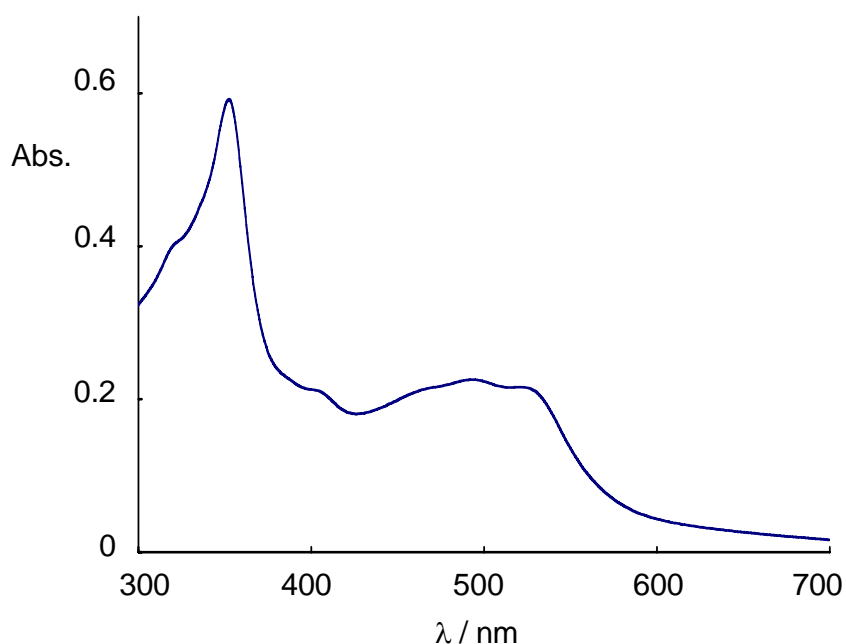


Fig. S1 UV-vis spectrum of [(CN)(H₂O)Cob(III)7COOH]Cl in EtOH.

Synthesis of diethyl 2-bromomethyl-2-phenylmalonate (1).

A solution of diethyl phenylmalonate (10.14 g, 43 mmol) in dry THF (40 mL) was dropwise added to a suspension of sodium hydride (2.68 g, 56 mmol) in dry THF (40 mL) with vigorous stirring at room temperature under a nitrogen atmosphere. Forty mL of dibromomethane (0.574 mol) was then added to reaction mixture. After the reaction mixture was refluxed for 4 hr, saturated aqueous ammonium chloride (100 mL) was added to it. The resulting product was extracted with diethyl ether (100 mL x 2), and the extract was washed with distilled water and dried over sodium sulfate. The filtrate was then concentrated to dryness, and the resulting product was purified by silica gel (Silica Gel 60N, spherical, neutral) column chromatography eluting with

benzene. Yield: 65 % as a colorless oil (**1**); GC-MS (EI, m/z): $[M]^+$, 328; IR (neat) 1730 (C=O); ^1H NMR (CDCl_3 , 500 MHz): δ =1.25 (t, 6H, $-\text{CH}_2\text{CH}_3$), 4.11 (s, 2H, $-\text{CH}_2-$), 4.20-4.30 (m, 4H, $-\text{CH}_2\text{CH}_3$), 7.32-7.49 (m, 5H, Ph); ^{13}C NMR (CDCl_3 , 125 MHz): δ =13.92, 34.68, 62.27, 63.45, 127.40, 128.09, 128.28, 134.67, 168.25; Anal. Calcd for $\text{C}_{14}\text{H}_{17}\text{Br}_1\text{O}_4$: C, 51.08; H, 5.21. Found; C, 51.31; H, 5.16.

Synthesis of diethyl 2-methyl-2-phenylmalonate (**3**).

This compound was obtained from the reaction of diethyl phenylmalonate with methyl iodide in a manner similar to that of **1**. Yield: 56 % as a colorless oil (**3**); GC-MS (EI, m/z): $[M]^+$, 150; IR (neat) 1730 (C=O); ^1H NMR (CDCl_3 , 500 MHz): δ =1.25 (t, 6H, $-\text{CH}_2\text{CH}_3$), 1.85 (s, 3H, $-\text{CH}_3$), 4.19-4.24 (m, 4H, $-\text{CH}_2\text{CH}_3$), 7.27-7.37 (m, 5H, Ph); ^{13}C NMR (CDCl_3 , 125 MHz): δ =13.92, 22.33, 58.80, 61.27, 127.45, 127.60, 128.20, 138.33, 171.66; Anal. Calcd for $\text{C}_{14}\text{H}_{18}\text{O}_4$: C, 67.18; H, 7.25. Found; C, 67.25; H, 7.14.

Synthesis of diethyl 2-benzyl-2-bromomalonate.

Five hundred μL of bromine (9.8 mmol) was added to a solution of diethyl benzylmalonate (2.5 g, 10 mmol) in diethylether (10 mL). The mixture was stirred for 4 hr at room temperature. A saturated aqueous solution of sodium thiosulfate was added to the reaction mixture and the organic layer was washed three times with water. The resulting solution was dried over anhydrous MgSO_4 , evaporated under reduced pressure and then chromatographed on silica gel (Silica Gel 60N, spherical, neutral) using dichloromethane/*n*-hexane (1:1) as the eluent. Yield: 79 % as a colorless oil; GC-MS (EI, m/z): $[M]^+$, 328; IR (neat) 1730 (C=O); ^1H NMR (CDCl_3 , 500 MHz): δ =1.28 (t, 6H, $-\text{CH}_2\text{CH}_3$), 3.60 (s, 2H, $-\text{CH}_2-$), 4.26 (m, 4H, $-\text{CH}_2\text{CH}_3$), 7.32-7.40 (m, 5H, Ph).

Reduction of diethyl 2-benzyl-2-bromomalonate by TiO_2 (Scheme 1).

A mixture of diethyl 2-benzyl-2-bromomalonate (10 mg, 3.0×10^{-5} mol) and TiO_2 (P-25, 7 mg) was stirred in $\text{C}_2\text{H}_5\text{OD}$ under nitrogen gas atmosphere. After the solution was stirred for 12 hr under irradiation with 365 nm UV light, the TiO_2 was removed by filtration. The product was analyzed by GC-MS. The starting diethyl 2-benzyl-2-bromomalonate was almost converted to diethyl benzylmalonate (**2**), and the deuterium atom was incorporated into **2** with an 88 % content.

UV-vis spectral change for $\text{B}_{12}\text{-TiO}_2$ Under irradiation with UV light.

A five mg sample of $\text{B}_{12}\text{-TiO}_2$ was suspended in 3 mL of $\text{C}_2\text{H}_5\text{OH}$ and degassed by bubbling nitrogen. The solution was irradiated with UV light (365 nm) for 5 min. The spectral change was monitored by diffusion reflectance UV-vis spectroscopy. The solution showed the typical UV-vis spectrum for the Co(I) state of the cobalamin derivative with a reflectance maxima at 390 nm after irradiation with UV light as shown in Fig. S2.

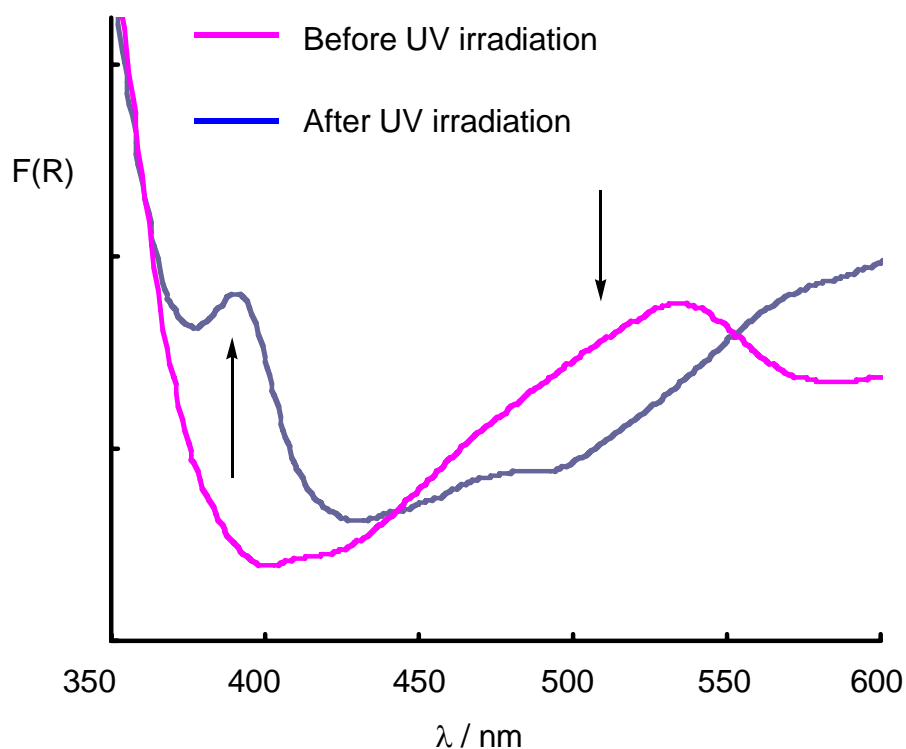


Fig. S2 Diffusion reflectance UV-vis spectra of $\text{B}_{12}\text{-TiO}_2$ in EtOH.