Electronic Supplementary Information for

Eco-friendly Molecular Transformations Catalyzed by Vitamin B₁₂ Derivative with Visible-Light-Driven System

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Experimental

Materials

All chemicals were of reagent grade and used as received. Ethanol (EtOH) and methanol (MeOH) were distilled over magnesium treated with iodine in a nitrogen atmosphere. Ethanol- d_1 (C₂H₅OD) and ethanol- d_6 (C₂D₅OD) were purchased from ISOTEC and deuterium oxide (D₂O) was from Merck. Heptamethyl cobyrinate perchlorate, **1** was synthesized by a previously reported method.^{S1}

General analyses and measurements

The UV-vis absorption spectra were measured using a Hitachi U-3300 spectrometer at room temperature. The ¹H and ¹³C NMR spectra were recorded by a Bruker Avance 500 spectrometer installed at the Center of Advanced Instrumental Analysis in Kyushu University, and the chemical shifts (in ppm) were referenced relative to the residual protic solvent peek. The elemental analysis was obtained from the Service Center of Elementary Analysis of Organic Compounds at Kyushu University. The GC and GC-MS data were obtained using a Shimadzu GC-2010 and GC-QP5050A equipped with a J&W Scientific DB-1 column (length 30 m; ID 0.25 mm, film 0.25 μ m), respectively. The transient spectra of Rose Bengal in MeOH (5 x 10⁻⁵ M) were measured by a laser flash photolysis system (Unisoku TSP-1000M). A Xe arc lamp was employed as the source of the probe light to follow the spectral changes, and samples were excited by 532 nm light from a Nd:YAG laser (5 ns fwhm) with 7-10 mJ power. The subsequent triplet quenching measurements were made on nitrogen-saturated solutions of at least five different concentrations of 1 or TEOA, as shown in Fig. S3. The first-order rate constants (k_{1st}^{obs}) were determined from the decay time profiles at 605 nm. The values of k_q were calculated from the pseudo-first-order plots (k_{1st}^{obs} versus [1] or [TEOA]) using a similarly reported procedure.⁸²

Steady-state photolysis

The EtOH solution containing 1 (2.5 x 10^{-5} M), 2 (2.5 x 10^{-6} M) and TEOA (2.5 x 10^{-2} M) was

bubble degassed for 15 min then irradiated with a 200 W tungsten lamp with a cutoff filter ($\lambda >$ 440nm). After irradiation, the photochemical reaction was followed by UV-vis spectroscopy. Reference experiments in the absence of TEOA, **2** or the visible light irradiation was performed in the same manner. The D₂O solution containing cyanocobalamin (2.5 x 10⁻⁵ M), **2** (2.5 x 10⁻⁶ M) and TEOA (2.5 x 10⁻² M) was also performed in the same manner.

Photocatalysis

As a typical experiment, the EtOH solution containing 1 (5.0 x 10^{-4} M), 2 (5.0 x 10^{-5} M), TEOA (5.0 x 10^{-1} M) and DDT (5.0 x 10^{-2} M) was bubble degassed for 15 min. The solution was stirred and irradiated with a 200 W tungsten lamp with a cutoff filter ($\lambda > 440$ nm) at ambient temperature for 1h. After irradiation, water was added to the reaction solution and the products were extracted with diethylether and hexane. Photocatalysis of other halogenated substrates were performed in a similar manner with the irradiation time described in Table 1. The products of entries 1, 2, 3 and 8 were identified by GC, GC-MS and/or NMR comparisons with the corresponding authentic samples which were synthesized according to the previously reported methods.^{S2-S5} The product of entry 4 (Deschloroalachlor) was isolated from the present photocatalysis system by silica gel chromatography eluted with chloroform and identified by GC, GC-MS and NMR analyses and an elemental analysis, which is consistent with previously reported studies as follows.^{S6} The products of entries 5, 6 and 7 were identified by GC, GC-MS and/or NMR comparisons with the comparisons with chloroform and identified by GC, GC-MS and NMR analyses and an elemental analysis, which is consistent with previously reported studies as follows.^{S6} The products of entries 5, 6 and 7 were identified by GC, GC-MS and/or NMR comparisons with the corresponding authentic samples commercially available.

Deschloroalachlor: isolated yield: 84%. ¹H-NMR (CDCl₃): δ 1.26 (t, 6H, -Ph(CH₂CH₃)₂), 1.77 (s, 3H, -C(O)CH₃), 2.60 (m, 4H, -Ph(CH₂CH₃)₂), 3.48 (s, 3H, -OCH₃), 4.93 (s, 2H, -OCH₂N-), 7.22 (d, 2H, *H*(Ph)), 7.33 (t, 1H, *H*(Ph)), ¹³C-NMR (CDCl₃): δ 14.8 (-Ph(CH₂CH₃)₂), 22.5 (-C(O)CH₃), 24.1 (-Ph(CH₂CH₃)₂), 58.0 (-OCH₃),80.2 (-NCH₂O-), 127.1, 129.0 (-C(Ph)H), 139.9 (-C(Ph)N-), 142.1 (-C(Ph)CH₂-), 173.0 (-C(O)). GC-MS *m/z*: 235 [M]⁺, 203 [M-OCH₃-H]⁺, 178 [M-COCH₃, CH₃H]⁺, 161 [M-COCH₃, OCH₃]⁺. Found: C, 71.22; H, 8.98; N, 5.77. Calc. for C₁₄H₂₁NO₂: C, 71.46; H, 8.99; N, 5.95.

Reductive Bleaching Behavior of Rose Bengal

Three different MeOH solutions of **2** (5.0 x 10⁻⁵ M) containing (a) TEOA (5.0 x 10⁻¹ M), (b) TEOA (5.0 x 10⁻¹ M) + **1** (5.0 x 10⁻⁴ M), and (c) TEOA (5.0 x 10⁻¹ M) + **1** (5.0 x 10⁻⁴ M) + DDT (5.0 x 10⁻² M) were prepared, and each solution was bubble degassed for 15 min. The solutions were stirred during the irradiation by with a 200 W tungsten lamp with a cutoff filter ($\lambda > 440$ nm) at ambient temperature in the same manner as the photocatalysis conditions. In each reaction solution, the reductive bleaching behavior of **2** was followed by UV-vis spectroscopy. The reaction solution was diluted 25 fold before the measurement.

CI		 CI			
Entry	Compound	Conversion	DDD Product viel	$\frac{\Pi D}{ds(\%)^c}$	B(EIZ)
Bhuy	Compound	of DDT $(\%)^{b}$	DDD	TTDB(E/Z)	
1	B ₁₂ , Rose Bengal	100	64	23/2	1000
2	B ₁₂ , Rose Bengal ^{<i>e</i>}	2	-	-	20
3	B_{12} , Rose Bengal ^f	9	-	-	90
4	B ₁₂	2	-	-	20
5	B ₁₂ , Rose Bengal ^g	94	22	2/-	940
6	B_{12} , $Ru(bpy)_3^{2+h}$	21	14	-	210 ^{<i>i</i>}

Table S1 Catalytic dehalogenation of DDT mediated by B₁₂-Rose Bengal system.^a

^{*a*} Conditions: [1] = 5.0 x 10⁻⁴ M, [2] = 5.0 x 10⁻⁵ M, [DDT] = 5.0 x 10⁻² M, [TEOA] = 5.0 x 10⁻¹ M, solvent: EtOH, N₂ atmosphere with irradiation by a 200 W tungsten lamp ($\lambda > 440$ nm) for 1 h. ^{*b*} Conversion was estimated by the recovery of DDT. ^{*c*} Products were analyzed by NMR. ^{*d*} Total turnover numbers based on the initial concentration of **2**. ^{*e*} The reaction was carried out in the dark. ^{*f*} In the absence of TEOA. ^{*g*} In the presence of PBN (1.25 M). ^{*h*} [Ru(bpy)₃²⁺] = 5.0 x 10⁻⁵ M. ^{*i*} Total turnover numbers based on the initial concentration of Ru(bpy)₃²⁺.

Table S2Deuterium atom incorporation ratio of DDD- d_1 .^a

Solvent	D-atom incorporation ratio of DDD- d_1 (%) ^b			
Ethanol- d_6 (C ₂ D ₅ OD)	<1			
Ethanol- d_1 (C ₂ H ₅ OD)	<1			
^{<i>a</i>} Conditions: $[1] = 5.0 \times 10^{-4} \text{ M}, [2] = 5.0 \times 10^{-5} \text{ M}, [DDT] = 5.0 \times 10^{-2} \text{ M}, [TEOA] = 5.0 \times 10^{-1} \text{ M},$				
N ₂ atmosphere with irradiation by a 200 W tungsten lamp ($\lambda > 440$ nm) for 1 h. ^b Determined by				
¹ H-NMR and GC-MS.				

References

- S1. Y. Murakami, Y. Hisaeda and A. Kajihara, Bull. Chem. Soc. Jpn., 1983, 56, 3642.
- S2. S. D. Islam and O. Ito, J. Photochem. Photobiol. A Chem., 1999, 123, 53.
- H. Shimakoshi, M. Tokunaga and Y. Hisaeda, *Dalton Trans.*, 2004, 878; H. Shimakoshi, M. Tokunaga, T. Baba and Y. Hisaeda, *Chem. Commun.*, 2004, 1806; H. Shimakoshi, E. Sakumori, K. Kaneko and Y. Hisaeda, *Chem. Lett.*, 2009, **38**, 468; Shimakoshi, M. Abiru, S. Izumi and Y. Hisaeda, *Chem. Commun.*, 2009, 6427.
- S4. D. Zanette and F. Nome, J. Org. Chem., 1979, 44, 2308.
- S5. P. Dowd and S. -C. Choi, J. Am. Chem. Soc., 1987, 109, 3493; P. Dowd and S. -C. Choi, Tetrahedron, 1989, 45, 77.
- S6. G. R. Eykholt and D. T. Davenport, *Environ. Sci. Technol.*, 1998, **32**, 1482; M. L. Hladik, J. J. Hsiao and A. L. Roberts, *Environ. Sci. Technol.*, 2005, **39**, 6561.



Fig. S1 UV-vis spectra of EtOH solution of a vitamin B_{12} derivative 1 (2.5 x 10⁻⁵ M), Rose Bengal 2 (2.5 x 10⁻⁶ M) containing TEOA (2.5 x 10⁻² M).



Fig. S2 UV-vis spectra of aqueous solution containing cyanocabalamin (2.5 x 10^{-5} M), Rose Bengal **2** (2.5 x 10^{-6} M) and TEOA (2.5 x 10^{-2} M) before and after the irradiation of visible light ($\lambda > 440$ nm).



Fig. S3 UV-vis spectral changes in EtOH solutions of 2 containing (a) TEOA, (b) TEOA + 1, and (c) TEOA + 1 + DDT upon irradiation of visible light ($\lambda > 440$ nm).



Fig. S4 First-order decay rate constants (k_{1st}^{obs}) of Rose Bengal as a function of the concentration of (a) TEOA and (b) 1.