



Supramolecular Chemistry

ISSN: 1061-0278 (Print) 1029-0478 (Online) Journal homepage: http://www.tandfonline.com/loi/gsch20

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To cite this article: Keishiro Tahara, Kumiko Mikuriya, Takahiro Masuko, Jun-ichi Kikuchi & Yoshio Hisaeda (2015): Supramolecular system composed of B₁₂ model complex and organic photosensitizer: impact of the corrin framework of B₁₂ on the visible-lightdriven dechlorination without the use of noble metals, Supramolecular Chemistry, DOI: 10.1080/10610278.2015.1103373

To link to this article: http://dx.doi.org/10.1080/10610278.2015.1103373

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Supramolecular system composed of B_{12} model complex and organic photosensitizer: impact of the corrin framework of B_{12} on the visible-light-driven dechlorination without the use of noble metals

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(Received 24 August 2015; accepted 29 September 2015)

The visible-light-driven dechlorination system without the use of a noble metal has been developed. We screened the combination of cobalt catalysts having square-planar monoanionic ligands (hydrophobic B_{12} model complex 1/imine-oxime type complex 2) and typical red dyes (Rose Bengal 3/Rhodamine B 4/Nile Red 5) for the construction of a dehalogenation system via a noble-metal-free and visible-light-driven process. The combination of the hydrophobic B_{12} model complex 1 and Rose Bengal 3 exhibited the highest catalytic activity to 1,1-bis(4-chlorophenyl)-2,2,2-trichlor-oethane (DDT) to form the monodechlorinated compound, 1,1-bis(4-chlorophenyl)-2,2-dichloroethane, as the major product. The prolonged photocatalysis of DDT by the B_{12} -Rose Bengal system afforded the tri-dechlorinated compound, trans-4,4'-dichlorostilbene, as the major product. Furthermore, we investigated the mechanism of the dehalogenation cycle using various methods such as UV–vis spectroscopy and laser flash photolysis. Finally, we clarified the advantage of using the hydrophobic B_{12} model complex 1 as an electron acceptor as well as a cobalt catalyst in the organic dye-involved photocatalysis.

Keywords: vitamin B₁₂; dechlorination; DDT; visible-light-driven; organic dye; Rose Bengal

Introduction

Reducing the amounts of noble metals used in a reaction is a challenging issue that must be addressed for green and sustainable molecular transformations. In the research field of visible-light-driven reactions (1), noble metal-based sensitisers, such as Ru(II) and Ir(III) polypyridyl complexes, are widely used as photoredox catalysts (2). Recently, noticeable efforts have been made for replacing such noble metal-based sensitisers with inexpensive and readily available organic dyes (2e). These efforts can be classified into two groups: (i) monometallic to metal-free and (ii) bimetallic to monometallic systems. In the first group, $Ru(bpy)_{3}^{2+}$ (bpy = 2,2'-bipyridyl) was successfully replaced with organic dyes, such as Rose Bengal, in several visible-light-driven reactions (3). These reactions involve polymerisation (4), as well as functionalisation of C-H bonds adjunct to a nitrogen atom (5) and the asymmetric alkylation of aldehydes in combination with organocatalysts (6). Although these completely metal-free systems are ideal, organic dyes are not able to cover the entire range of reported redox catalysis at this time. In the second group, thus, minimum amounts of transition metal complex catalysts are used in combination with organic dye sensitisers. In several conventional bimetallic systems, one metal-based reagent (noble metal complex) was used as a redox photosensitiser and the other a redox catalyst (2j). The Ru(bpy)₃²⁺ sensitiser was successfully replaced with some organic dyes in several visible-light-driven systems such as H₂ evolution and CO₂ reduction (2k, 7).

Reductive dehalogenation is of significant importance from the viewpoint of remediation technology and organic synthesis (8). While organic dyes are widely applied to the oxidative degradation of pollutants often by singlet oxidation evolution (9), their use in the reductive dehalogenation of alkyl halide pollutants has not yet been reported to the best our knowledge. Recently, $Ru(bpy)_3^{2+}$ has been demonstrated to be useful for the reductive cleavages of carbon-halogen bonds, generating halide anions and synthetically useful free radicals (10). However, the substrate scope is limited to benzyl halides or the alkyl halides activated by electron withdrawing groups. Radical sources for the application to C-C bond formations are also limited to such halide reagents. These limitations of both organic and inorganic photocatalysts for the reductive dehalogenation result from the fact that they do not have a sufficient nucleophilic activity. Therefore, to minimise the amounts of noble metal reagents used, as well as to effectively drive the reductive dehalogenation by visible light, the combination of organic dyes and transition metal catalysts is a practical method.

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Figure 1. Structures of cobalt complexes and organic photosensitisers.

Vitamin B₁₂ (cyanocobalamin) and its derivatives are efficient homogeneous catalysts for the reductive dehalogenation of alkyl halides and several radical-involved organic syntheses (11). They are cobalt complexes with a tetradentate corrin macrocycle at the equatorial positions and can acquire the cobalt oxidation states of Co(III), Co (II) and Co(I) (12). The Co(I) species of B_{12} is highly nucleophilic to organic halides to induce the oxidative addition of the alkylating agents to the metal centre with dehalogenation. The resulting Co-C bond is homolytically cleaved upon thermal or photochemical excitation to form the Co(II) species and synthetically useful alkyl radicals. Inspired by the reductive dehalogenases involving a B_{12} derivative as the active centre (13), the Co(I) species of B₁₂ was demonstrated to dehalogenate several halogenated pollutants in vitro often with an excess of chemical reductants (14). Driving the B₁₂-catalyzed reactions by visible light is a useful method for constructing an eco-friendly molecular transformation system. We have been dealing with a hydrophobic B_{12} model complex, heptamethyl cobyrinate perchlorate [Cob(II) 7C₁ester]ClO₄ 1 (15) as shown in Figure 1, and combined the B₁₂ model complex with $Ru(bpy)_3^{2+}$ to develop visible-light-driven dehalogenation systems (16). Unfortunately, the absorption band of $Ru(bpy)^{2+}$ overlaps that of 1 in the visible region and $Ru(bpy)^{2+}$ was not efficiently excited in the presence of 1 (see Table S1). Thus, we attempted to replace $Ru(bpy)_{2}^{2+}$ with well-known red dyes, Rose Bengal (17) and Rhodamine B (18), in our previous studies. However, the potential of the monometallic catalytic system composed of 1 and dyes has still not yet been fully clarified, because there is limited information on the photoinduced electron transfer between organic dyes and B_{12} derivatives, which is only from our previous reports. The choice of the appropriate reaction conditions would additionally allow for an efficient dehalogenation. In this study, we intend to screen the combination of typical red dyes and cobalt catalysts having a square-planar monoanionic ligand (corrin or imine-oxime type framework) (Figure 1). Moreover, we constructed the B_{12} model complex-photosensitiser supramolecular system for the visible-light-driven dechlorination of 1,1-bis(4chlorophenyl)-2,2,2-trichloroethane (DDT) and 1,1-bis(4chlorophenyl)-2,2-dichloroethane (DDD), well-known problematic persistent organic pollutants, without the use of noble metal sensitisers. Furthermore, we investigated the mechanism of the dehalogenation cycle using various methods such as UV-vis spectroscopy and laser flash photolysis. Finally, we clarified the advantage of using 1 as an electron acceptor as well as a cobalt catalyst in the organic dye-involved photocatalysis.

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_6 (C₂D₅OD) was purchased from ISOTEC. Heptamethyl cobyrinate perchlorate, [Cob (II)7C₁ester] ClO₄ **1** (*15*a) and diaqua(11-hydroxyimino-4,10-dipropyl-5,9-diazatrideca-4,9-dien-3-one oximato)cobalt(II) tetraphenylborate, [Co(II){(C₂C₃)(DO)(DOH) pn}]B(C₆H₅)₄ **2** (*19*) were synthesised by previously reported methods.

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 peak. 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 µm), respectively. The transient spectra of Rose Bengal in MeOH $(5 \times 10^{-5} \text{ M})$ were measured by a laser flash photolysis system (Unisoku TSP-1000 M). 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 obtained from nitrogensaturated solutions with at least five different concentrations of 1 or triethanolamine (TEOA). The first-order rate constants (k_{1st}^{obs}) were determined from the decay time profiles at 605 nm. The quenching rate constants (k_{α}) values were calculated from the pseudo-first-order plots $((k_{1st}^{obs})$ vs. [1] or [TEOA]) using a similarly reported procedure (20). The quenching experiments of the singlet excited state of 4 were performed using a Hitachi F-4501 spectrofluorometer at 25 °C. The fluorescence quenching of 4 by TEOA was analysed using a Stern-Volmer plot (21).

Photocatalysis

As a typical experiment of the photochemical reduction of **1**, the EtOH solution containing **1** (2.5×10^{-5} M), **3** (2.5×10^{-6} M), and TEOA (2.5×10^{-2} M) was bubble degassed for 15 min then irradiated by a 200 W tungsten lamp with a cut-off filter ($\lambda > 440$ nm). After irradiation, the photochemical reaction was followed by UV–vis spectroscopy. Reference experiments in the absence of TEOA, **3** or the visible light irradiation were performed in the same manner.

As a typical experiment of the photocatalytic dechlorination, the EtOH solution containing 1 (5.0×10^{-4} M), 3 (5.0×10^{-5} M), TEOA (5.0×10^{-1} M) and DDT (5.0×10^{-2} M) was bubble degassed for 15 min. The solution was stirred and irradiated by a 200 W tungsten lamp with a cut-off filter ($\lambda > 440$ nm) at ambient temperature for 1 h. After irradiation, water was added to the reaction solution and the products were extracted with diethylether and hexane. The products were identified by ¹H-NMR comparisons with the corresponding authentic samples (16, 22, 23). The authentic samples of trans-4,4'-dichlorostilbene (DCS) (14c), DDMS (22b) and TTDB (E/Z) (22a) were synthesised according to previously reported methods. The product yields were quantified by ¹H-NMR comparisons with 1,4-dioxane as the internal standard in the same manner as previous reports. The photocatalytic dechlorination was carried out in EtOH- d_6 ; the deuterium incorporation ratio in the dechlorinated product was determined by ¹H-NMR and GC-MS. The photocatalysis of DDD was performed in a similar manner.

Results and discussion

Photochemical reduction of B_{12} model complex

We first examined the reactivity of the organic dyes (Figure 1) for the photochemical reduction of the B_{12} model complex 1 to the supernucleophilic Co(I) species. We chose TEOA as an electron donor for the present B₁₂ model complex-organic photosensitiser supramolecular systems. This is because TEOA has been widely used as a sacrificial reducing agent for photocatalytic systems (2e). Indeed, it was demonstrated that Rose Bengal 3 (24) and Rhodamine B 4 (25) were quenched by tertiary amines. The UV-vis absorption spectrum of an EtOH solution of 1 containing Rose Bengal 3 (0.1 equiv. vs. 1) and TEOA is shown in Figure 2(a) (broken line). This is simply the sum of 1 and 3, indicating no interaction between both compounds in the ground state. Upon visible light irradiation ($\lambda > 440$ nm) for 5 min, the characteristic strong absorption at 391 nm indicative of the Co(I) species of 1 was observed under a N_2 atmosphere as shown in Figure 2(a) (solid line). Such a spectral change was not observed in the absence of 3(Figure 2(d)), TEOA or in the dark. This spectral change strongly suggests that compound 3 sensitises the reduction of 1 with TEOA as an electron donor in the B_{12} -Rose Bengal system (1 + 3). In the B₁₂-Rhodamine B system (1 + 4), the Co(I) species of 1 was also observed upon visible light irradiation as shown in Figure 2(b), although the efficiency of the formation of the Co(I) species of 1 was lower than that of the B_{12} -Rose Bengal system. In the B_{12} -Nile Red system (1 + 5), the Co(I) species of 1 was not observed even upon visible light irradiation for 60 min as shown in Figure 2(c). Thus, the order of the systems according to an increase in the efficiency of the photochemical reduction of 1 was determined; B_{12} -Nile Red $(1 + 5) < B_{12}$ -Rhodamine B (1 + 4) $< B_{12}$ -Rose Bengal (1 + 3).



Figure 2. UV-vis spectra of EtOH solution containing a photosensitiser $(2.5 \times 10^{-6} \text{ M})$, 1 $(2.5 \times 10^{-5} \text{ M})$, and TEOA $(2.5 \times 10^{-2} \text{ M})$ before and after visible light irradiation ($\lambda > 440 \text{ nm}$); in the presence of (a) Rose Bengal 3, (b) Rhodamine B 4, (c) Nile Red 5 and (d) in the absence of a photosensitiser.

Catalytic dehalogenation of DDT and DDD

We examined the dechlorination of DDT, a well-known trihalomethane insecticide (26). In the B_{12} -Rose Bengal system (1+3), DDT was successfully dechlorinated upon visible light irradiation for 1 h using 1 (5 mol%), 3 (0.5 mol%) and TEOA (10 equiv.) in EtOH to form DDD as the major product as shown in Entry 4 in Table 1. This dechlorination did not efficiently proceed in the absence of either TEOA, 3 or in the dark as shown in Entries 5-7 in Table 1. Accordingly, it is obvious that compound 3 sensitises the B₁₂-mediated dechlorination with TEOA as an electron donor upon visible light irradiation. Combined with the former spectroscopic study, these results suggest that the generated Co(I) species of **1** is the active form of the dechlorination. In the presence of a spin-trapping reagent, α -phenyl-N-(t-butyl) nitrone (PBN), the yields of the dechlorinated products significantly decreased as shown in Entry 8 in Table 1. This result suggests the involvement of a radical intermediate in the dechlorination of DDT. When the dechlorination was carried out in C₂D₅OD, the deuterium incorporation in DDD was not observed, which was confirmed by ¹H-NMR and GC-MS. These results indirectly suggest that the TEOA is likely the major hydrogen atom source of the catalytic hydrodehalogenation.

The conversions of the B_{12} -Rhodamine (1 + 4) and B_{12} -Nile Red (1 + 5) systems significantly decreased to 25 and 11%, respectively (Entries 2 and 3 in Table 1). These low catalytic activities correspond to the inefficient formation of the Co(I) species for 1 in the B_{12} -Rhodamine and B12-Nile Red systems as observed in the former spectroscopic study. Thus, the efficient formation of the Co(I) species for 1 is critical for the construction of an efficient dechlorination system of DDT. Among the three red dyes, the excitation efficiency of the B₁₂-Nile Red system (1 + 5) is the lowest because Nile Red has the weakest absorption which overlaps the absorption of 1 as shown in Table S1 and Figure 2(c). This results in the lowest formation efficiency of the Co(I) species for 1 and the lowest conversion. The difference between the B_{12} -Rose Bengal (1 + 3) and B_{12} -Rhodamine (1 + 4) systems in the catalytic activity of DDT is discussed in the next section.

We were able to replace **1** in the B_{12} model complex-Rose Bengal system with an imime/oxime type cobalt complex, $[Co(II)\{(C_2C_3)(DO)(DOH)pn\}(H_2O)_2]B$ $(C_6H_5)_4$ **2** (19) as shown in Entry 9 in Table 1. However, this cobalt complex system (**2** + **3**) showed a 34% lower catalytic activity than the B_{12} model complex system (**1** + **3**). This is probably because the redox potential of



					Product yields (%) ^c				
Entry	Catalyst	Photosensitiser	Time (h)	Conversion ^b	DDD	TTDB (E/Z)	DCS	DDMS	Turnover numbers ^d
1	1	None	1	2	0	0	0	0	0
2	1	Rhodamine B 4	1	25	14	0	0	0	140
3	1	Nile Red 5	1	11	9	0	0	0	90
4	1	Rose Bengal 3	1	100	64	23/2	0	0	890
$5^{\rm e}$	1	Rose Bengal 3	1	2	0	0	0	0	0
$6^{\rm f}$	1	Rose Bengal 3	1	9	0	0	0	0	0
7	None	Rose Bengal 3	1	22	16	0	0	0	160
8^{g}	1	Rose Bengal 3	1	94	22	2/0	0	0	240
9 ^h	2	Rose Bengal 3	1	64	46	5/1	0	0	520
10	1	Rose Bengal 3	24	100	51	21/2	12	4	1060
11 ⁱ	1	Rose Bengal 3	24	100	2	40/4	44	1	1340
12 ^j	1	$[\operatorname{Ru}(\operatorname{bpy})_3]^{2+}$	1	21	14	0	0	0	140

^aConditions: $[1] = 5.0 \times 10^{-4}$ M, [Photosensitiser] = 5.0×10^{-5} M, [DDT] = 5.0×10^{-2} M, [TEOA] = 5.0×10^{-1} M, N₂ atmosphere with irradiation by a 200 W tungsten lamp ($\lambda > 440$ nm) in EtOH.

^bConversion of DDT was estimated by the recovery of DDT.

^cProducts were analysed by NMR.

^dTotal turnover numbers based on the initial concentration of photosensitiser.

^eThe reaction was carried out in the dark.

^fIn the absence of TEOA.

^gIn the presence of PBN (0.25 M)

 ${}^{h}_{h}[\mathbf{2}] = 5.0 \times 10^{-4} \text{ M}.$

ⁱIn MeOH.

 ${}^{j}[[Ru(bpy)_{3}]^{2+}] = 5 \times 10^{-5} M.$

the Co(II)/Co(I) (i.e. the accessibility to the catalytically active Co(I) species) of 2 is -0.13 V lower than that of 1 (Table S1). In addition, the solution of the cobalt complex was decolorised during the course of the photochemical reaction, indicating the low stability of 2. Utilising the good stability of 1 under the photochemical conditions, the B_{12} -Rose Bengal system (1 + 3) can be used for the prolonged photocatalysis of DDT. Upon prolonged visible light irradiation for 24 h in methanol, DCS and DDMS were obtained as the dechlorinated products as shown in Entry 11 in Table 1. In this case, the yield of DDD significantly decreased, suggesting that the DDD formed from DDT was converted into DCS and/or DDMS. It should be noted that the present B₁₂ model complex-Rose Bengal system can dechlorinate DDT to form the tri-dechlorinated compound (DCS) as the major product.

The B_{12} model complex–Rose Bengal system was further utilised for the dechlorination of the relatively less reactive DDD. DDD was successfully dechlorinated upon visible light irradiation for 24 h to form DCS and DDMS as the dechlorinated products as shown in Table 2. These dechlorinated products were also obtained from DDD in the previous catalytic systems of 1 (22b, 23a). The dechlorination of DDD in MeOH gave the highest catalytic activity. This is because the reaction of the Co(I) species of 1 and DDD (two neutral reactants) favourably proceeds in polar solvents to form the alkylated Co(III) complex of 1 (a charged product) via a charge-separated activated complex (27). The product distributions of DCS and DDMS in Entry 2 in Table 2 are similar to those in Entry 11 in Table 1. These results confirm the above-mentioned suggestion that DDT was dechlorinated to DDD, which was further dechlorinated to the di- and/or tri-dechlorinated products as shown in Entry 11 in Table 1.

Mechanistic aspects

To gain a mechanistic insight into the B_{12} -Rose Bengal system (1 + 3), quenching experiments of both the singlet and triplet excited states of 3 (*¹RB²⁻ and *³RB²⁻) in MeOH were performed. No fluorescent quenching of 3 was observed upon the addition of either TEOA or 1.





^aConditions: $[1] = 5.0 \times 10^{-4}$ M, [Rose Bengal] = 5.0×10^{-5} M, [DDD] = 5.0×10^{-2} M, [TEOA] = 5.0×10^{-1} M, solvent: EtOH, N₂ atmosphere with irradiation by a 200 W tungsten lamp ($\lambda > 440$ nm) for 24 h.

^bConversion of DDD was estimated by the recovery of DDD.

^cProducts were analysed by NMR.

^dTotal turnover numbers based on the initial concentration of Rose Bengal.

This stands in contrast to effective triplet quenching of 3 upon the addition of TEOA or 1. The transient spectra of Rose Bengal $(5.0 \times 10^{-5} \text{ M})$ were measured in the presence of 1 equivalent of [Cob(II)7C1ester]ClO4 as shown in Figure S1(a). The absorbance of $*^{3}RB^{2-}$ at 605 nm was decayed within a few tens of microseconds as shown in Figure S1(b). The pseudo-first-order plots vs. [1] or [TEOA] gave k_q values of 1.0×10^6 and $7.2 \times 10^9 \text{ M}^{-1} \text{s}^{-1}$, respectively. Based on these results, two possible mechanisms are proposed as shown in Scheme 1(a). Not the singlet, but a triplet excited state of 3 ($^{*3}RB^{2-}$) participates in the electron transfer. This is consistent with previous reports about the quenching reactions of 3 that Rose Bengal 3, a heavy atom substituted xanthene dye, is notable for its high quantum yield of the *³RB²⁻ formation (ca. 1) and fairly long lifetime of $*^{3}RB^{2-}$ ($t_{1/2} = 0.1-0.3$ ms) (28). The oxidative quenching is thermodynamically possible to afford the one-electron-reduced species (RB \cdot^{3-}) and the Co(I) species of 1 (E^0 (RB^{·-/*3}RB²⁻) = -0.94 V, E^0 (Co(II)/Co (I)) = -0.64 V vs. SCE) (15, 29). The reductive quenching is also thermodynamically possible to afford the one-electron-reduced species (RB³⁻) and the oneelectron-oxidised species of TEOA following the electron transfer from RB^{3-} to 1 (E^0 (RB^{2-}/RB^{3-}) = -1.03 V vs. SCE) (29). At the same concentrations of TEOA (5.0×10^{-1} M) and 1 (5.0×10^{-4} M) as those of the photocatalysis conditions, the reductive and oxidative quenching rates were calculated using the k_q values and determined to be $5.0 \times 10^5 \text{ s}^{-1}$ and $3.6 \times 10^6 \text{ s}^{-1}$, respectively. Thus, the oxidative quenching favourably proceeds over the reductive quenching during photocatalysis because the former rate is a factor of 7.2 greater than the latter rate. While Rose Bengal is often used for photooxidative organic molecular transformations utilising starting organic substrates as electron donors, few are

reported for its application to photoreductive transformations (4, 5). Given that the reduction power of $*^{3}RB^{2-}$ or RB^{.3-} is relatively lower than that of ${}^{3*}Ru(bpy)_{3}^{2+}$ or Ru(bpy)₃⁺, it should be noted that the good accessibility of **1** to the Co(I) species is beneficial for the construction of the reductive dehalogenation system. The relatively high redox potential for the Co(II)/Co(I) couple of **1** results from its monoanionic corrin framework.

A previously reported study has shown that 3 is reductively photobleached in the presence of TEOA (24b), and the present photocatalysis is also accompanied with the bleaching of 3 as indicated in Figure 1(a). This bleaching is due to the hydrogen atom abstraction of RB^{.3-} to form the hydrated species (RBH³⁻) as shown in Scheme 2 (24b, ¹). RB^{.3-} is more easily formed as the concentration of the Co(II) species of the B₁₂ model complex decreases and that of the Co(I) species increases in the absence of the halogenated substrates. Actually, this photobleaching was well suppressed upon the addition of 1, and efficiently upon the addition of 1 and DDT within 1 h under the photocatalysis conditions, followed by UV-vis spectroscopy. The UV-vis spectral change revealed that 80% of 3 were unchanged with no evidence of photobleaching after the photocatalytic reaction of DDT. This result confirms the good stability of the photosensitiser in the present system.

In our previous study, the fluorescence quenching rate constant (k_q) of **4** with TEOA was determined to be $4.7 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ (18). This result is consistent with a previous report that the singlet excited state of **4** (*¹Rho) is reductively quenched by tertiary amines such as triethylamine (25). At the same concentration of TEOA (5.0×10^{-1} M) as that of the photocatalysis condition, the reductive quenching rate was calculated using the k_q value and determined to be $2.35 \times 10^8 \text{ s}^{-1}$. On the other hand, fluorescent quenching of **4** was not observed upon

Entry

1

2

3



► ¹*Rho

Oxidative Quenching

RB³-

(b) Rho -

F

³ *RB ^{2–}	+	Coll	 RB∓	+	Col
RB-	+	TEOA	 RB ^{2–}	+	TEOA:

hυ **Reductive Quenching**

^I *Rho	+ TEOA>	Rho∓ +	TEOA:
Rho∓	+ (Coll)	Rho +	Co

Scheme 1. Photochemical steps leading to the Co(I) species of 1 using 3 and 4.

the addition of 1. Based on these results, a possible mechanism is proposed as shown in Scheme 1(b). *¹Rho is reductively quenched by TEOA to form the one-electron-reduced species of 2 (Rho⁻). The electron transfer from Rho⁻ to 1 affords the formation of the Co(I) species of the B₁₂ model complex because the combination of 1 and 2 is thermodynamically favourable $(E^0 (Rho/$ Rho^{•–}) = -0.8 V vs. SCE) (30). However, the disadvantage of using 4 is that the reductive quenching of $*^{1}$ Rho competes with the radiative and nonradiative processes deactivation from *¹Rho $(k_r = 2.0 \times 10^8 \text{ s}^{-1})$ of $k_{\rm nr} = 3.0 \times 10^8 \text{ s}^{-1}$) (31). Actually, the B₁₂-Rhodamine B system did not more efficiently generate the photoreduced 1 than that of the B12-Rose Bengal system as shown in Figure 2(b). Thus, the use of an organic dye, which initiates the electron transfer from the triplet excited state rather than the singlet, is an important point for constructing the efficient B12-involved photocatalytic system.

Based on the present and previous studies (22, 23, 32), a plausible dechlorination mechanism in the B_{12} -Rose Bengal system (1+3) is proposed as shown in Scheme 3. Initially, the triplet excited state of 3 is oxidatively quenched by 1 to form the RB^{-} and the Co(I) species of 1. The RB^{-} is oxidised by TEOA to form 3 and the nitrogen-centred radical cation (TEOA $^{+}$). It was proposed that the deprotonation of TEOA.⁺ by TEOA vields a carbon-centred radical and that the hydrogen atom abstraction at TEOA by TEOA.⁺ yields another carbon-centred radical (33) as shown in Figure S2 The supernucleophilic Co(I) species of the B₁₂ model complex dechlorinates DDT to form a Cl-eliminated radical species and 1. The radical species abstracts hydrogen mainly from TEOA to form DDD as indirectly implied by the reaction in C₂D₅OD. A further one-electron reduction of the Cl-eliminated radical species affords a carboanion, which is transferred by a further Cl⁻ elimination to a carbene resulting in dimerisation to form TTDB in the presence of an excess of TEOA as an electron donor. The turnover numbers based on 1 and 3 were 89 and 890, respectively. The DDD formed from DDT is further dechlorinated by the Co(I) species of the B₁₂ model complex to form an alkylated complex (Figure S3). According to a previous mechanistic study on the reaction of vitamin B_{12} with DDD (14c, 34), the alkylated complex reacts via a cobalt chloride a-elimination to yield DCS. This is analogous to the reaction of an organic gem-dihalide with copper (35). The α -elimination generates a carbenoid-type intermediate which will readily rearrange into the product. DDMS is formed by the hydrogen abstraction of the radical species resulting from the homolysis of the alkylated complex. The turnover numbers based on 1 and 3 reached 134 and 1340, respectively.

Our previously reported B_{12} -Ru(bpy)²⁺ system showed 140 turnovers for the photocatalysis of DDT relative to Ru(bpy)²⁺ as shown in Entry 12 in Table 1 (16). It should be noted that the turnover numbers of the present B_{12} -Rose Bengal system (1 + 3) is a factor of 6.4 greater turnovers than those of the B_{12} -Ru(bpy)²⁺



Scheme 2. Reductive bleaching of 3.



Scheme 3. Proposed mechanism of the dechlorination of DDT mediated by the B12-Rose Bengal system.

system. This enhanced catalytic activity results from the fact that the red dye **3** has a strong absorption in the visible region and the triplet excited state of **3** is efficiently quenched by the oxidative quenching of **1**. In comparison to Rose Bengal, $\text{Ru}(\text{bpy})^{2+}$ has a weaker absorption in the visible region and is less efficiently excited due to the overlap of the absorption with **1**. We have successfully replaced $\text{Ru}(\text{bpy})^{2+}$ with Rose Bengal and increased the catalytic activity to DDT.

Conclusions

In this paper, we screened the combination of typical red dyes and cobalt catalysts having a square-planar monoanionic ligand for the construction of a visiblelight-driven dehalogenation system without the use of noble metal-based sensitisers. When we used a hydrophobic B_{12} model complex 1, the order of the systems according to an increase in the efficiency of the dehalogenation of DDT was determined as follows: B12-Nile Red $(1 + 5) < B_{12}$ -Rhodamine B $(1 + 4) < B_{12}$ -Rose Bengal (1 + 3). This order is the same as the order of systems according to an increase in the efficiency of the reduction of **1**. Thus, the efficiency of the formation of the Co(I) species of 1 is critical for the construction of an efficient dechlorination system of DDT. Among the three red dyes, the excitation efficiency of the B₁₂-Nile Red system is the lowest because Nile Red has the weakest absorption which overlays with the absorption of 1, affording the lowest conversion of DDT. The B_{12} -Rhodamine B system exhibited a 75% lower conversion of DDT than the B12-Rose Bengal system because the reductive quenching of *1Rho competes with the other deactivation processes from *1Rho. Rose Bengal, a heavy atom-substituted xanthene dye and having a high quantum yield of the *³RB²⁻ formation and a fairly long lifetime of *3RB²⁻, efficiently catalyses the photochemical reduction of 1 mainly via the oxidative quenching of $*^{3}RB^{2-}$. When we used Rose Bengal, the B_{12} -Rose Bengal system (1 + 3) exhibited a factor of 1.7 greater turnover numbers for the dechlorination of DDT than the cobalt imine-oxime complex-Rose Bengal system (2+3). The higher dechlorination activity of 1 than that of 2 is due to its higher accessibility to the Co(I) species and stability under the photochemical conditions. These advantages result from the monoanionic corrin framework of 1, which was obtained by the chemical modification of the naturally occurring vitamin B₁₂. The prolonged photocatalysis of DDT by the B12-Rose Bengal system (1+3) afforded the tri-dechlorinated compound (DCS) as a major product. By replacing Ru $(bpy)^{2+}$ with Rose Bengal, the present B₁₂-Rose Bengal system (1 + 3) exhibited a factor of 6.4 greater catalytic activity to DDT than that of our previously reported B₁₂- $Ru(bpy)^{2+}$ system. We concluded that the combination of the cobalt corrin complex derived from the naturally occurring vitamin B_{12} (1) and the heavy atom substituted xanthene dye, which can initiate the electron transfer from the fairly long lived triplet excited state (3), achieved the dechlorination of DDT and DDD via a visible-light-driven and noble-metal-free process. This study provides new insight into not only the substitution of the noble metal-based sensitisers, but also the expansion of the range of the conventional photocatalysis from the viewpoint of green molecular transformation.

Funding

This work was supported by the Grant-in-Aid for Scientific Research on Innovative Areas 'Stimuli-responsive Chemical Species for the Creation of Functional Molecules' [grant number 15H00952]; the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan and a Grant-in-Aid for Challenging Exploratory Research [grant number 26620156]; from the Japan Society for the Promotion of Science (JSPS).

Disclosure statement

No potential conflict of interest was reported by the authors.

Supplemental material

Supplemental data for this article can be accessed here: http://dx.doi.org/10.1080/10610278.2015.1103373.

Note

1. RBH^{3-} would be the active species for the background dehalogenation of DDT in the absence of **1** (Entry 7 in Table 1). The RBH^{3-} species did not contribute to the dechlorination result of DDT by the B₁₂-Rose Bengal system (Entry 4 in Table 1) because the oxidative quenching favorably proceeds over the reductive quenching during the photocatalysis.

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Supramolecular system composed of B12 model complex and organic photosensitizer: impact of the corrin framework of B12 on the visible-light-driven dechlorination without the use of noble metals

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