Photosensitizing catalysis of the B_<12> complex without an additional photosensitizer

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Photosensitizing catalysis of B_{12} complex without additional photosensitizer†

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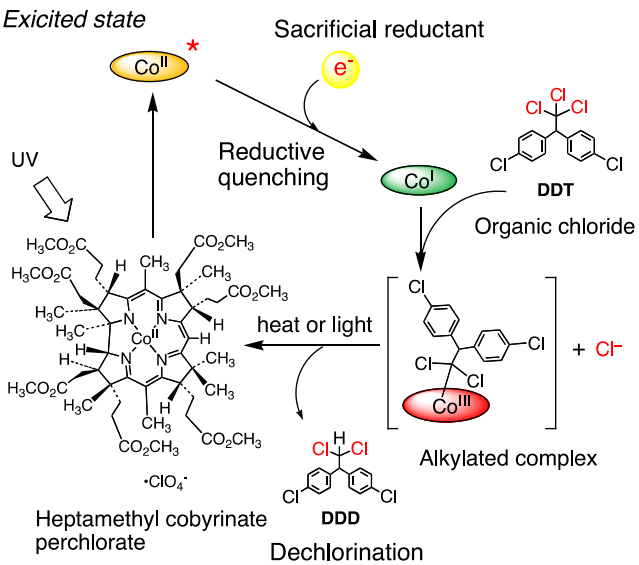
A cobalamin derivative, heptamethyl cobrinate perchlorate, was activated by UV light irradiation to form a Co(I) species in the presence of triethanolamine and used for a dechlorination reaction, and this photochemical reaction was accelerated in an ionic liquid.

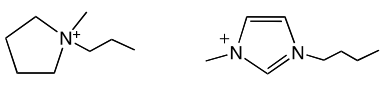
The cobalamin derivative (B_{12}) is a cobalt complex with a tetrapyrrole ring system (corrin ring) that has emerged in a variety of enzymes such as methylmalonyl CoA mutase, methionine synthase and reductive dehalogenase.[1] Inspired by the unique functions of these enzymes, various catalytic reactions have already been reported using B_{12} model complex such as the 1,2-migration of a functional group, dechlorination of organic chlorides, methylation of heavy metals and thiols, etc.[2] Among the B_{12} model complexes, the corrinoid compound was mostly developed in the B_{12} mimic reaction due to its structure and physicochemical properties similar to natural cobalamin.

Most of the catalytic reactions by the corrinoid compound were achieved using the supernucleophilicity of the reduced form of the Co(I) species.[3] Therefore, all of the catalytic reaction were coupled with a reducing system such as a chemical reductant ($NaBH_4$, Zn, Na amalgam and so on), electrochemical reduction and combined use with a photosensitizer.[2] Recently, we reported the dechlorination of 1,1-bis(4-chlorophenyl)-2,2,2-trichloroethane (DDT) catalyzed by the B_{12} derivative, heptamethyl cobyrinate perchlorate (Co(II) form), with a $[Ru(II)(bpy)_3]Cl_2$ photosensitizer by irradiation with visible light.[4] The B_{12} complex was reduced to form the reactive Co(I) species by electron transfer from the ruthenium photosensitizer in the presence of a sacrificial reductant. Although the B_{12} complex showed a high catalytic efficiency in the reaction, a photosensitizer was required for the reaction. If the B_{12} complex itself shows dual properties, photosensitization and catalysis, the catalytic reaction was achieved without any additional photosensitizer. To alleviate this problem, we started to explore the photosensitizing property of the cobalamin derivative and determined the unique photosensitizing property of the B_{12} complex, especially in an ionic liquid. The ionic liquid is a unique ion pair solvent having various properties such as high polarity, good conductivity and negligible vapor pressure.[5] In this paper, the unique photosensitizing property of the B_{12} complex in the ionic liquid and its application for DDT degradation without any photosensitizer are reported (Figure 1).

Fig. 1 Catalytic cycle of B_{12} complex by UV light irradiation.



The heptamethyl cobyrinate perchlorate was first synthesized by Eschenmoser's group[6] and used by many groups.[7] It shows a high solubility toward not only a variety of organic solvents, but also ionic liquids such as *N*-methyl-*N*-propylpyrrolidinium bis(trifluoromethanesulfonyl)amide ([P13][TFSA]) and 1-butyl-3-methyl imidazolium bis(trifluoromethanesulfonyl)amide ([bmim][TFSA]) (Chart 1).



[P13][TFSA] [bmim][TFSA]

Chart 1

When heptamethyl cobrinate perchlorate was dissolved in an ionic liquid ([P13][TFSA]) or methanol containing 0.1 M triethanolamine (TEOA) and subsequently irradiated by UV light (λ_{max} = 365 nm)‡ under anaerobic conditions, the color of the solution changed from brown to dark green. This photoreaction was well monitored by UV-vis spectroscopy. The UV-vis spectrum of the starting Co(II) form of the B_{12} complex having absorption maxima at 314 nm and 468 nm was changed to a new

spectrum with absorption maxima at 390 and 560 nm which is typical for the Co(I) state of the B_{12} complex[8] by UV light irradiation as shown in Figures 2a (in [P13][TFSA]) and 2b (in MeOH).[§]

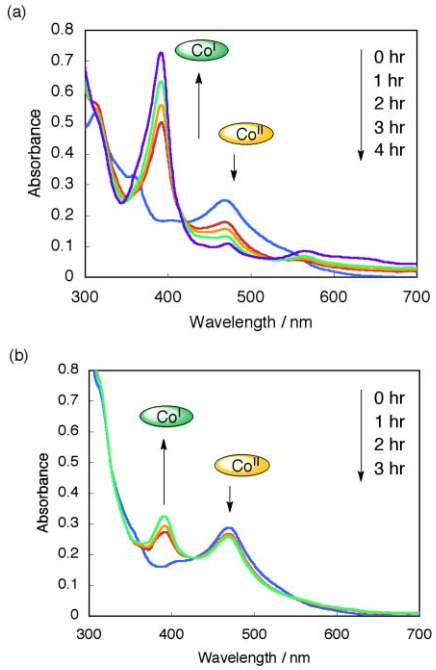


Fig. 2 UV-vis spectral change of B_{12} complex (2.9×10^{-5} M) in the presence of TEOA (0.1 M) by UV light irradiation (λ_{max} = 365 nm) under anaerobic condition; (a) in [P13][TFSA], (b) in MeOH.

From these UV-vis spectral changes, the rate constant for the Co(I) formation was determined to be $k = 2 \times 10^{-4}$ s^{-1} and 3×10^{-5} s^{-1} in [P13][TFSA] and MeOH, respectively (ESI†).[¶] This photochemical reaction was ca. 7 times enhanced in the ionic liquid. In [bmim][TFSA], the B_{12} complex showed a poor UV-vis change (Figure S1). Because the imidazolium-type ionic liquid has a relatively acidic C-H bond at the imidazole ring,[9] it should quench the Co(I) species of the B_{12} complex.[10]

The photoreduction of the B_{12} complex was also investigated by ESR spectroscopy. T he heptamethyl cobrinate perchlorate showed the typical Co(II) low-spin signal (g_1=2.51, g_2=2.25, g_3=2.00, A_2^{Co}=63 G, A_3^{Co}=134 G) in [P13][TFSA] containing 0.1 M TEOA as shown in Figure 3a.[11] After UV light irradiation, this signal almost disappeared to form the diamagnetic Co(I) species (Figure 3b). This ESR spectral change also indicated that the B_{12} complex was reduced to the Co(I) form by the UV light irradiation.

Two plausible mechanisms are shown in Figure 4. Once the Co(II) form of the B_{12} complex is excited, a ligand (corrin ring) to the metal charge transfer state may be formed. W hile the oxidation state of B_{12} was Co(III), an ultrafast electronic relaxation of the excited state vitamin B_{12} (cyanocobalamin) in the gas phase was reported by Shafizadeh et al.[12] The decay is interpreted as resulting from a ring to metal charge transfer. A similar excited state is predicted in the present case, and such a charge-separated (CS) state (Co(I) cation radical) could be stabilized in an ion-pair solvent, ionic liquid having a high polarity, and subsequent electron transfer from TEOA to form the reduced form of the B_{12}, Co(I) state (Figure 4a). Another possibility is forming an encounter complex between the excited B_{12} complex and TEOA. In this model, electron transfer from TEOA to the B_{12} complex in the encounter complex should form the CS state (Co(I)-$TEOA^{+\cdot}$). This charge-separated state could be stabilized in a polar ionic liquid to prevent a back-electron transfer process (Figure 4b). T o further understand the photosensitizing property of the B_{12} complex, ultrafast transition spectroscopy for the Co(II) state of corrinoid compound is needed.

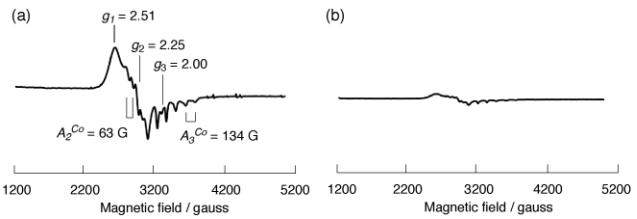


Fig. 3 ESR spectra of B_{12} complex (5.0×10^{-4} M) in the presence of 0.1 M TEOA in [P13][TFSA] at 100 K under anaerobic condition. (a) Before UV light irradiation, (b) after 2hr UV light irradiation.

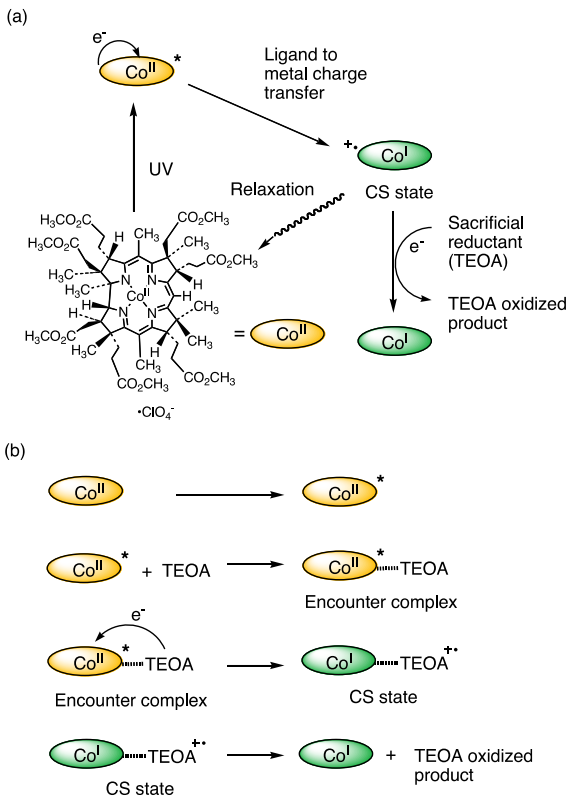
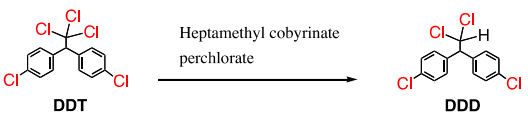


Fig. 4 Proposed photosensitizing mechanisms of B_{12} complex by UV light irradiation in the presence of TEOA.

The catalytic reaction was carried out using DDT as a substrate.[#] The results are shown in Table 1. After a 2 hr UV light irradiation, DDT was converted to a monodechlorinated compound, 1,1-bis(4-chlorophenyl)-2,2-dichloroethane (DDD) in 72 % yield (Entry 1 in Table 1). The reaction did not proceed in

the dark (Entry 2 in Table 1). In MeOH, the yield of DDD was only 9 % which reflects the Co(I) formation efficiency. As for the mechanism, nucleophilic attack of the Co(I) species on DDT could form an alkylated complex as an intermediate as shown in Figure 1.[4,13] This alkylated complex homolysis by UV light irradiation or thermolysis forms a substrate radical. Hydrogen abstraction from the bulk formed DDD as a dechlorinated product. After the photoreaction with workup,[#] most of the B_{12} catalyst remained in the ionic liquid and was quantitatively recovered as confirmed by UV-vis spectra (Figure S2). Therefore, the B_{12} complex could be reused for the successive reaction. In fact, the DDT dechlorination reaction proceeded with almost the same efficiency in the second and third runs (yields of DDD, 2nd 70 % and 3rd 68 %).

Table 1 Photocatalytic dechlorination of DDT catalyzed by B_{12} complex.[a]



Entry	Solvent	Irradiation	Yields (%)[b]	TON[c]
1	[P13][TFSA]	UV	72	35
2	[P13][TFSA]	dark	0	0
3	MeOH	UV	9	4

[a] Condition: $[B_{12}] = 4.4 \times 10^{-5}$ M, $[DDT] = 2.2 \times 10^{-3}$ M, [triethanolamine] = 0.1 M. λ_{max} = 365 nm under degassed condition at room temperature. Reaction time, 2 hr.
[b] Yields were based on initial concentration of the substrate.
[c] Turnover numbers (TON) were based on $[B_{12}]$.

In summary, the photosensitizing property of the B_{12} complex under anaerobic conditions was investigated. The reductive quenching of the excited state of the B_{12} complex by a sacrificial reductant provided the reduced form of the B_{12} complex, Co(I) species. This photosensitizing property of the B_{12} complex was used for dechlorination of the pollutant, DDT. Therefore, the results reported here will open a door to the new use of the corrinoid compound in photocatalytic chemistry.

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Notes and references

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† Electronic supplementary information (ESI) available: Details of experimental procedures. See: DOI: ##########

‡ Black light (UVP, XX-15BLB) was used for the UV light irradiation (1.76 mW cm^2 at 12-cm distance).

§ The photochemical reaction did not proceeded under visible irradiation using a 200-W tungsten lamp with a 420-nm cut-off filter (Sigma Koki, 42L) and a heat cut-off filter (Sigma Koki, 30H).

¶ In MeOH, the photochemical reaction slowly proceeded without TEOA. Therefore, MeOH also acts as a weak sacrificial reductant.

General procedure: A 4 mL [P13][TFSA] solution of the B_{12} complex (4.4×10^{-5} M), DDT (2.2×10^{-3} M) and triethanolamine (0.1 M) was degassed by freeze-pump-thaw cycles. The solution was then stirred at room temperature under irradiation by 365 nm UV light.‡ After 2 hr, the product was extracted with ether-hexane (1:3 v/v). The product, DDD, was identified by NMR and GC-MS comparison with the purchased authentic sample. The B_{12} complex remaining in the ionic liquid was recycled after being dried under reduced pressure for 24 hr.

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