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Environmental-friendly Catalysts Learned from Vitamin B12-Dependent Enzymes

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INTRODUCTION

It is widely known that vitamin B_{12} derivatives are unique coenzymes that possess cobalt–carbon (Co–C) bonds *in vivo* and are involved in a variety of catalytic functions in combination with various apoproteins.[1] Vitamin B_{12} is a metal complex in which cobalt ions are coordinated to 4 ring nitrogen atoms in a corrin ring (**Figure 1**). It was originally developed as a magic bullet for the treatment of pernicious anemia, and its unique structure was elucidated by Hodgkin *et al*. by X-ray crystallography.[2]

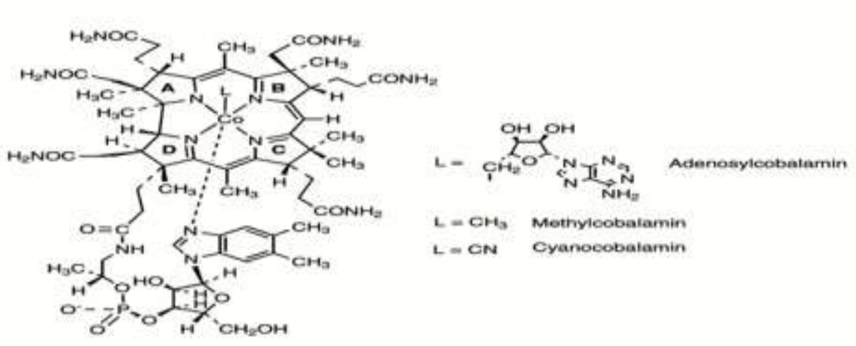
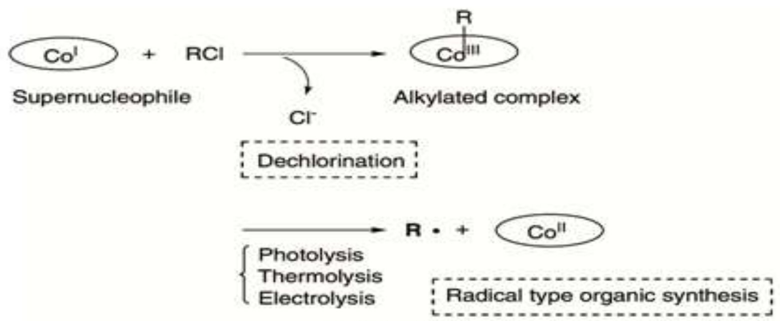
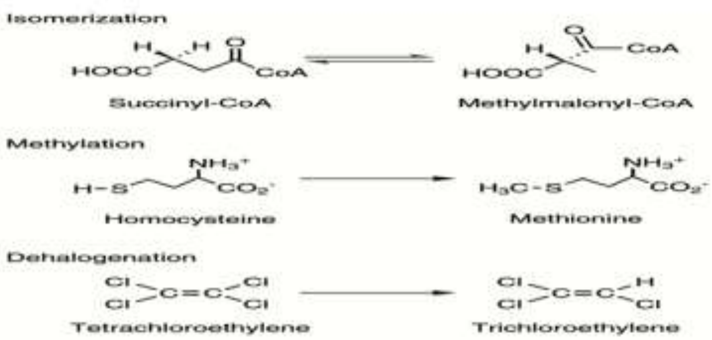


Figure 1. Structure of vitamin B_{12} derivatives.



Scheme 2.



Scheme 1.

The oxidation state of the central cobalt ions range from +1 to +3; Co(I) imparts a gray-green color, Co(II) impart a yellow-to-orange color, and Co(III), which is the most common form, imparts a red color to the B12 derivatives, and is known as the "red vitamin." Methylcobalamin and adenosylcobalamin as the coenzyme forms are parts of *in vivo* enzymes that catalyze the biosynthesis of methionine and the isomerizations with carbon-skeleton rearrangements, respectively.3 Recent studies revealed that the complex of such corrin ring structures acts on the active center of the dechlorination reaction in anaerobic bacteria; this suggests a new function for the B12- dependent enzymes (**Scheme 1**).[4]**2. Modeling of vitamin B_{12}**Vitamin B_{12} is obtained on a large scale from cyanocobalamin-producing organisms for use as dietary supplements or livestock feed. Thus far, no problems have occurred with regards to the safety or economics of using natural vitamin B_{12} as a catalyst resource. However, natural vitamin B_{12} supplied from bacteria contains many vitamin B_{12}-related substances, suggesting that it may have a poor chemical stability. This is not because of the instability of the corrin ring structure, but because of the deterioration of the side-chain substituents. As will be described later, the corrin ring structure has a high stability. To use the vitamin B12 derivative as a catalyst, the following conditions should be satisfied: (1) the corrin ring structure should be retained, (2) the central cobalt atoms should be intact, and (3) the modifiable side-chains should be maintained. In light of these 3 conditions, we temporarily removed the physiologically essential side substituents from cyanocobalamin for synthesizing the hydrophobic vitamin B_{12} (heptametyl cobyrinate) by chemical modification of all the peripheral side-chains into ester groups (**Figure 2, Type A**).[6] About 80% of the hydrophobic vitamin B_{12} can be obtained using a single synthesis process by heating cyanocobalamin in alcohol in the presence of an acid catalyst, even when cyanocobalamin is used as the raw material, which is abundantly produced by microorganisms as mentioned above. Using the hydrophobic vitamin B_{12} as a starting material, it is possible to synthesize various B_{12} catalysts that can have wide applications (**Figure 2, Type B-D**). The corrin rings present in natural B_{12} are retained in the above-mentioned complexes, and hence, the redox potential and electronic property of the central cobalt ion of the synthetic B_{12} derivative are similar to those of natural B_{12}, suggesting that the synthetic B_{12} derivative will show a high reactivity during molecular transformations like original enzymes.[6]

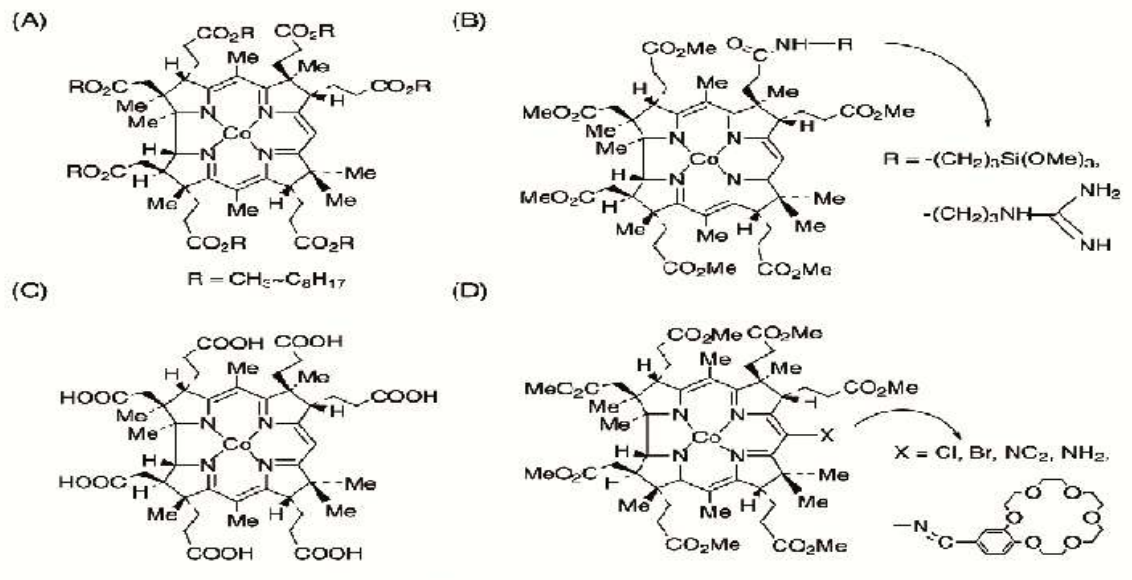


Figure 2. Modification of vitamin B_{12} derivatives.

3. Electroorganic reaction using B_{12} complex

As described above, nucleophilic Co(I) species of the B_{12} derivative reacts with organic halides, which results in dehalogenation followed by the simultaneous production of an alkylated complex. Therefore, it may be important to develop a method to produce reactive Co(I) species to form the alkylated complex, which is a key intermediate of the B_{12}-dependent enzyme reaction. The synthesized B_{12} complex can be reduced by chemical reductants, such as sodium borohydride, metallic zinc, and sodium amalgam, thus the mass use of these chemical reagents is not desirable in terms of synthetic as well as recent green chemistry. Consequently, an electrochemical technique was used for generating Co(I) species of the B_{12} complex, in which the B_{12} complex works as a mediator for the electroorganic reaction (**Figure 3**).[7] We developed various molecular transformations by controlled-potential electrolyses at the potentials of –1.4 or –1.5 V *vs.* Ag/AgCl using the hydrophobic vitamin B12 as a mediator (**Scheme 3**). For example, when bromoalkyl acrylate was used as a substrate, large-membered ring lactones were synthesized by intramolecular cyclization of organic radical species generated by the homolytic cleavage of the alkylated complex (**Scheme 3**, **eq. 1**).[8] The formation of the alkylated complex as the intermediate was directly observed by monitoring the electrolysis solution using electrospray ionization mass spectrometry (ESI-MS) and UV-vis spectra. The hydrophobic vitamin B_{12} can also effectively act as a dechlorination catalyst of environmental pollutants, such as dichlorodiphenyltrichloroethane (DDT) (**Scheme 3**, **eq. 2**).9 It is noteworthy that the B12 catalytic system does not generate toxic secondary pollutants such as chlorine gas and phosgene, because the chlorine atoms are dechlorinated to harmless chloride ions during the reaction (**Scheme 2**). Furthermore, the B_{12} catalyst was not degraded after the reactions. Its high durability was confirmed by

UV-vis and mass spectrum analyses after the reaction. When other cobalt complexes, such as the porphyrin complex, were used under the same conditions, the complexes were severely degraded during the electrolysis.

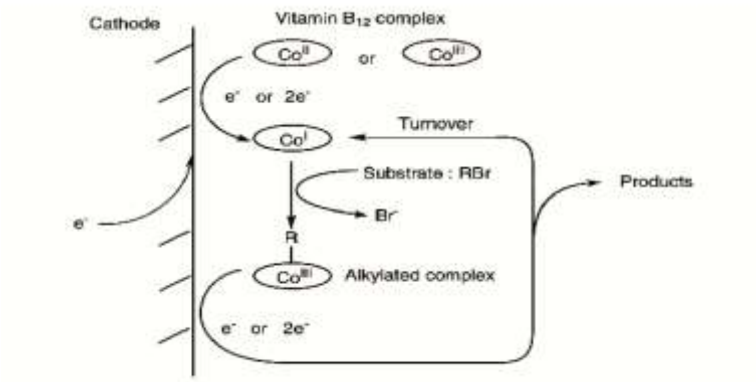
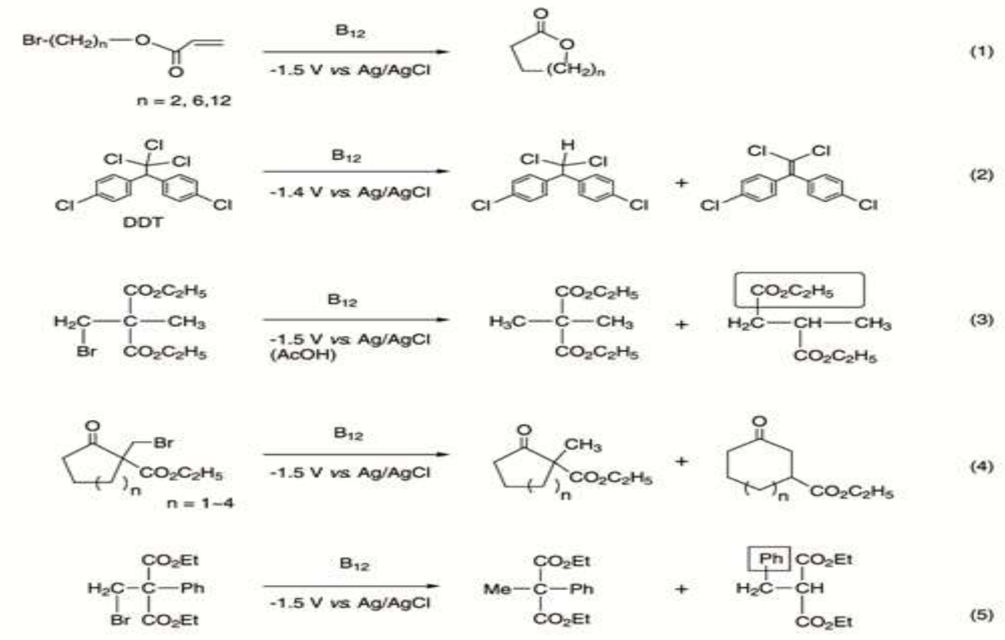


Figure 3. Electroorganic reactions mediated by vitamin B_{12} model complex.

To utilize repeatedly such a robust B_{12} catalyst, the B_{12} complex was immobilized on the electrodes or dissolved in an ionic liquid for recovering or recycling after the reaction. In the former case, the B_{12} complex could be immobilized on the platinum electrode surface at a coverage rate of approximately 1.6 × 10–10 mol/cm^2 by introducing a trimethoxysilyl group into the side-chain (**Figure 2, Type B**). The reactivity was evaluated using phenethyl bromide as the model substrate, which demonstrated a high catalytic activity with 6,000 turnover number per hour (**Figure 4**).[10] After the reaction, the product and the B_{12} catalyst could be easily separated as the B_{12} catalyst was immobilized on the electrode. Other examples of the B_{12}-modified electrodes were also reported, such as a polymer-covered electrode, interface-polymerized electrode, and sol-gel film doped electrode.11-13 On the other hand, when an ionic liquid was used as the reaction solvent, the B_{12} complex was supported in an ionic liquid and showed the following various benefits. In general, an electroorganic reaction was carried out in a polar organic solvent containing supporting electrolytes. However, such a reaction using organic solvents containing many of the supporting electrolytes may not be desirable with regard to the recent regulated use of chemical reagents, even though this procedure is used to degrade chlorinated organic compounds. Recently, electroorganic reactions in an ionic liquid have been increasingly studied in order to address such issues. The ionic liquid is a room temperature liquid salt under ordinary pressure, which is characterized by its nonvolatility, fire retardance, and excellent electrical conductivity and is a superior solvent for the electroorganic reactions.[14]



Scheme 3.

When the electrolysis of DDT was carried out in an ionic liquid by using the B_{12} complex as a catalyst, the reaction proceeded effectively in the same manner as the dechlorination reaction in the polar organic solvent containing supporting electrolytes. Furthermore, during the extraction process after the reaction, the product and B_{12} complex could be separated in the organic solvent layer and the ionic liquid layer, respectively. The B_{12} complex dissolved in an ionic liquid can be recycled for the reaction (**Figure 5**).15 More interestingly, the reactivity of the B_{12} complex improved in the ionic liquid; i.e., the conversion efficiency of the substrate increased approximately 4-times that of the reaction performed in dimethylformamide (DMF). This enhanced reactivity in the ionic liquid over that in DMF could be explained by the application of the Hughes–Ingold predictions16 of solvent polarity effects on reaction rates.

The reaction of electrochemically generated Co(I) with DDT is a ‘‘Menschutkin type of reaction’’ in which two neutral reactants, Co(I) and DDT, react to form charged products via a charge-separated activated complex in the polar ionic liquid, which ultimately decreases the activation energy, resulting in an increase in the reaction rate. A similar accelerating effect of the reaction in an ionic liquid has been closely examined by the reaction of methyl *p*-nitrobenzenesulfonate with tri-*n*-butylamine.[17] Actually, the *E*T N value[18] of the ionic liquid has been determined as a polarity index. For example, the value of 1-*n*-butyl-3- methylimidazolium tetrafluoroborate is 0.673, indicating it is highly polar compared to a polar organic solvent, such as DMF (*E*T N = 0.386).[19]

4. Photosensitized reaction of B12 complex

We attempted to design a light-driven catalysing system that could be used for the development of a clean molecular transformation using the B_{12} complex. Light is one of the abundant and cleanest energies on the earth and has been used in organic syntheses for a long time.

Thus, we focused on a ruthenium(II) tris bipyridine complex ([RuII(bpy)$_3$]Cl$_2$), which has been widely used as a photosensitizer, and constructed the catalyzing system using a photo-induced electron transfer reaction for producing Co(I) species.[20] The [RuII(bpy)$_3$]Cl$_2$ complex was excited under visible light irradiation and the [Ru(bpy)3]+ complex with high reduction potential (–1.35 V *vs.* Ag/AgCl) was produced due to reductive quenching by a sacrificial electron donor such as triethanolamine.[21] Therefore, it is possible to generate the catalytically active B12 complex (E1/2(CoII/CoI) = – 0.6 V *vs.* Ag/AgCl) by electron transfer from the ruthenium photosensitizer.

Based on this strategy as shown in **Figure 6**, the dechlororination of DDT was carried out using the B_{12} complex in the presence of the ruthenium photosensitizer and sacrificial electron donor. Consequently, most of the DDT was converted to DDD, a mono-dechlorination product, within 3 hours. The reaction was hardly facilitated in the absence of the B_{12} complex or in the dark.

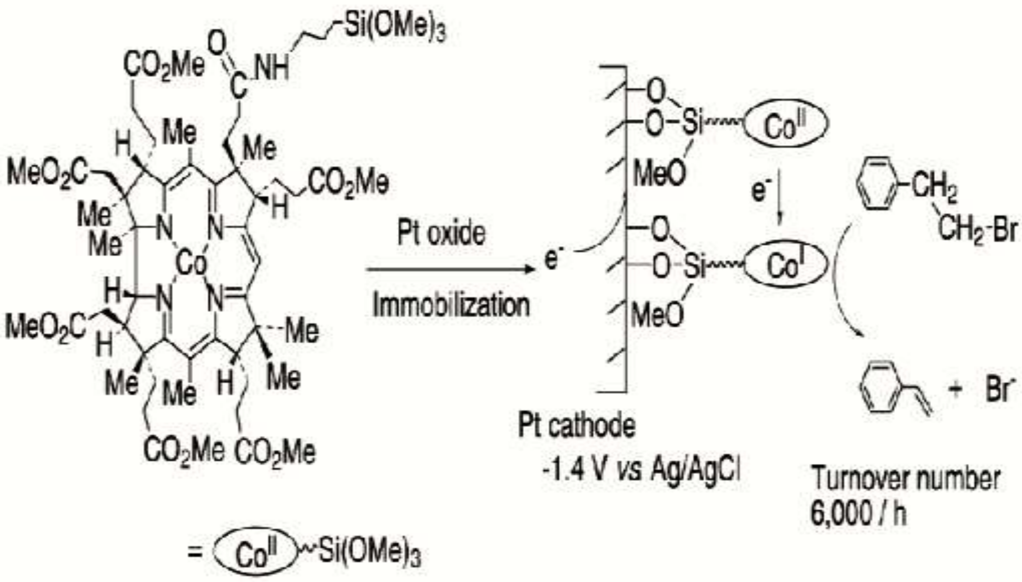


Figure 4. B_{12} modified electrode for electroorganic reaction.

Therefore, it is suggested that Co(I), which is produced by a photo-induced electron transfer reaction, might act as an active species to initiate the reaction. The ESR spectral change confirmed that the electron transfer reaction of the ruthenium photosensitizer reduces the B_{12} complex to Co(I) species. Characteristic ESR signals were detected for the paramagnetic Co(II) of B_{12}, while the corresponding ESR signals for diamagnetic Co(I) were absent in the photoreaction (**Figure 7**).

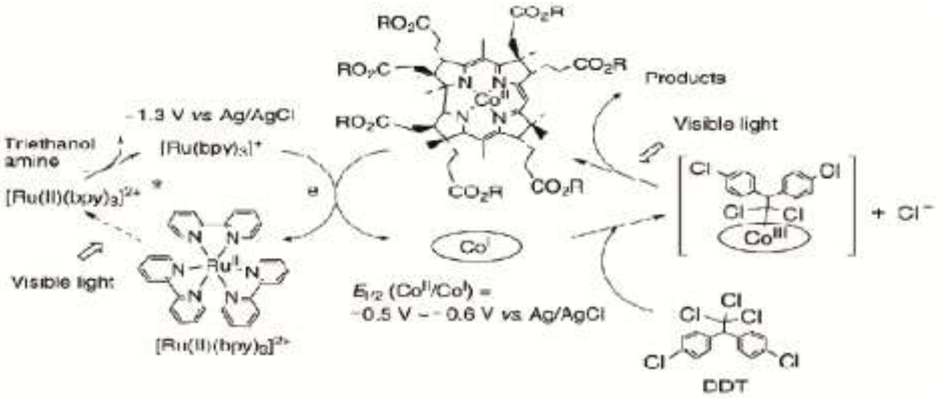


Figure 6. Sterategy for photosensitized system for B_{12} catalysis.

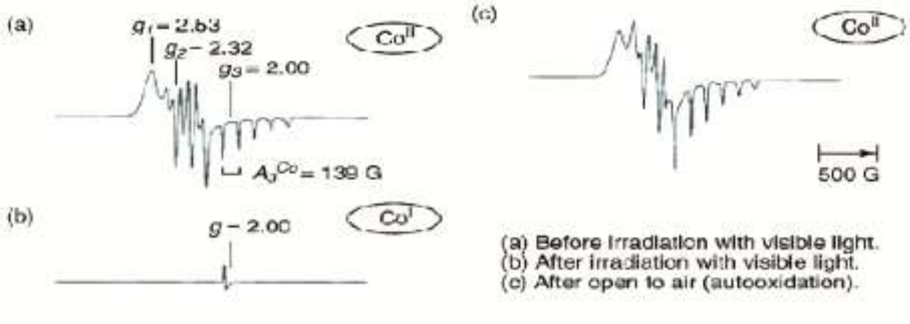


Figure 7. ESR sepectral change of vitamin B_{12} derivative in the presence of $[Ru(bpy)_3]Cl_2$ and triethanolamine.

5. B_{12}-TiO_2 hybrid catalyst

Recently, hybrid catalysts composed of a metal complex and various semiconductors with photosensitizing ability have been reported.[22,23] According to this technique, it is possible to develop a hybrid catalyst with concerted effects of metal complexes and semiconductors. Thus, we focused on titanium oxide,[24] which is an n-type semiconductor, to develop a light energy driven B_{12}-TiO_2 hybrid catalyst. The reduction power of the excited electrons in the titanium oxide (TiO_2)-conduction band (–0.5 V *vs.* normal hydrogen electrode (NHE))[25]

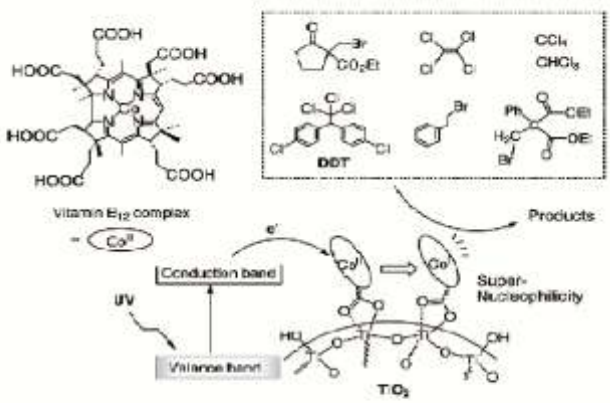


Figure 8. Molecular transformations catalyzed by B_{12}-TiO_2 hybrid catalyst.

Enabled the reduction of the B_{12} complex to the catalytically active Co(I) species, and this indicated that a light energy-driven hybrid catalyst can be developed by immobilizing the B_{12} complex on TiO_2. In this case, TiO_2 not only played a role as a scaffold for the B_{12} complex, but also served as an electron source for the reduction of the B_{12} complex (**Figure 8**). Here, the B_{12} complex was immobilized on TiO_2 by multiple interactions of the carboxyl groups of B_{12} (**Figure 2, Type C**) and surface hydroxyl groups of TiO_2. Approximately 3–4 × 10–5 mol (40–50 mg) of the B_{12} complex (cobyrinic acid) was found to immobilize on 1 g of TiO2 and 70–80% of the TiO_2 surface was covered with

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the B_{12} complex. The resulting B_{12} complex was firmly immobilized on the TiO_2 surface, and the immobilization remained stable for more than 1 year even after being dispersed in various organic solvents, such as an alcohol, and was not separated by ultrasonic treatment. When a degradation reaction of a chlorinated organic compound, such as DDT, is performed using this hybrid catalyst, only a few milligrams of the catalyst can dechlorinate 100 times that of DDT in approximately 1 day.[26] The hybrid catalyst was activated by light energy so that neither chemical reagents nor expensive reactors are required. Ultraviolet irradiation provided by black light (365 nm) is sufficient for the photoexcitation of TiO_2. Furthermore, both the B_{12} complex and TiO_2 are non-toxic, thus the B_{12}-TiO_2 hybrid catalyst may be an environmental/human friendly catalyst. In addition, we investigated the use of the hybrid catalyst in radical reactions for organic synthesis. This result indicated that this hybrid catalyst could be applied to various molecular transformations, including the above-mentioned ring expansion reactions (**Scheme 3, eq. 4**) and 1,2-migration of the functional group (**Scheme 3, eq. 5**). Thus, the hybrid catalyst can be used as an alternative for the conventional radical organic synthetic reagent that uses a tin compound (Bu_3SnH/AIBN system). TiO_2 can also be immobilized on carriers, such as glass substrates and beads, when it is converted to slurry sol solutions. Thin films of TiO_2 (with a thickness of a few hundred nanometers), which are prepared on glass substrates by dip-coating, can be hybridized with the B_{12} complex by only dipping into the B_{12} complex solution containing carboxyl groups. Thus the prepared B_{12}-TiO_2 hybrid catalyst on a glass plate also catalyzed the abovementioned reactions (**Figure 9**). The immobilization of the $B_{12}TiO_2$ hybrid catalyst on a glass plate can simplify the reaction process, and furthermore, facilitate the separation procedure of the product from the reaction mixture.

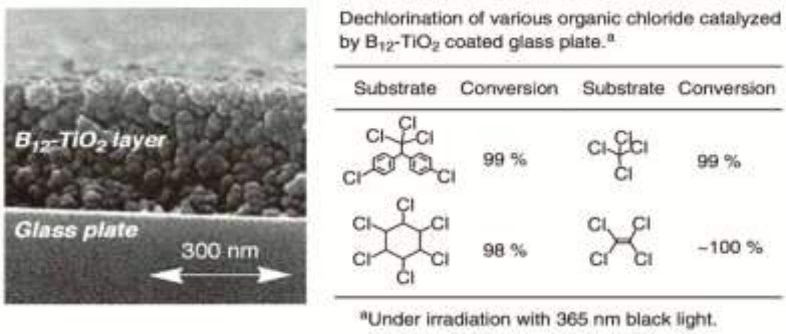
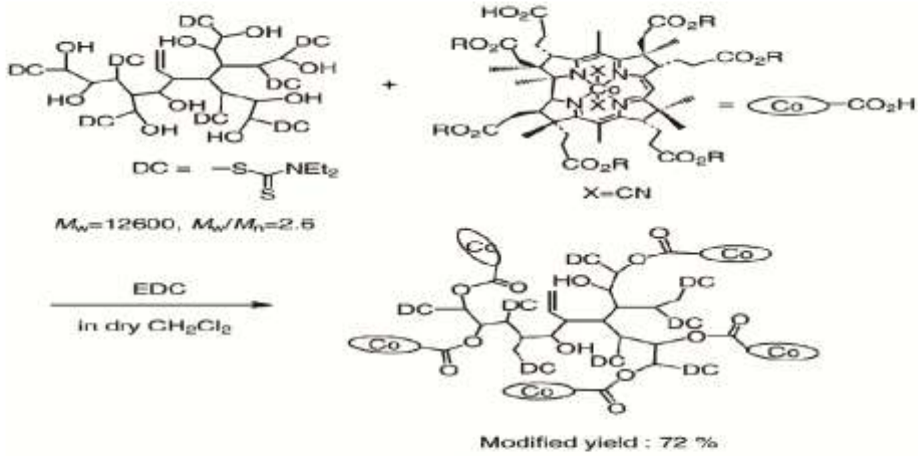


Figure 9. Immobilization of B_{12}-TiO_2 hybrid catalyst onto glass plate.

6. Vitamin B_{12}-hyperbranched polymer hybrid catalyst

A hyperbranched polymer is one of the dendric polymers that are synthesized via a one-step polymerization reaction in an inexpensive and easy way, and it has various advantages when compared to dendrimers, which are synthesized via multiple-step polymerizations.[27] Furthermore, as the polymer has a higher solubility and lower solution viscosity compared to linear polymers, it is expected to be used in a homogeneous solution.[28] In fact, the hyperbranched polymers that have many terminal functional groups due to their highly branched structure are appropriate for carrying functionalized molecules.[29] Considering the nanospace provided by the hyperbranched polymers as a new catalyst reaction field, the B_{12}-hyperbranched polymer hybrid catalyst was synthesized (**Scheme 4**).[30] The amount of B_{12} complex used can be adjusted to somewhere between a few % and 70% per terminal functional groups of the hyperbranched polymers, and the density of the B_{12} complex can be readily controlled. When the B_{12} complex is densely immobilized, a cooperative effect of the adjacent complex facilitates the dimerization reaction of phenethyl bromide.[31] It is expected that the variable size and main chain polymer of the hyperbranched polymer will be able to produce various reaction characteristics.



Scheme 4.

CONCLUSIONS

We have outlined the development of molecular transformations learned from the B_{12}-dependent enzymes. The hybrid catalyst composed of synthesizing metal complexes, which are similar to the active center of the B_{12} enzyme, enabled various molecular transformations including environmatally-friendly organic synthesis reactions and degradation reactions of organic halides pollutants by an electroorganic reaction or a photochemical reaction. Combining the benefits of natural enzymes and engineering methods will allow the development of a new catalyst system that will exceed biological reactions. The development of this bio-inspired chemistry introduced by us will play an important role in the next generation's science and technology.

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