

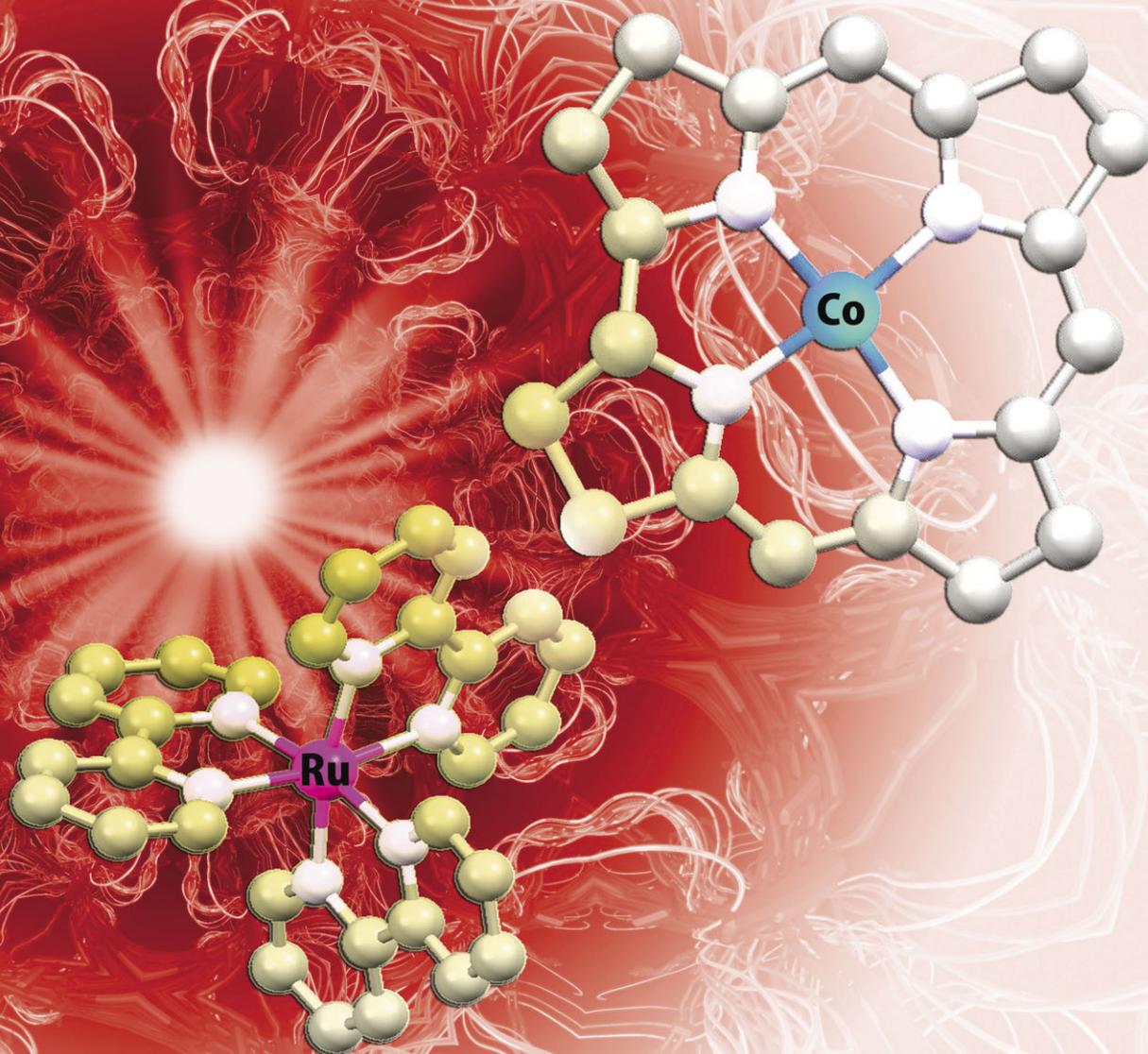
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COMMUNICATION

Photocatalytic function of a polymer-supported B₁₂ complex with a ruthenium trisbipyridine photosensitizer†Hisashi Shimakoshi,^a Masashi Nishi,^a Akihiro Tanaka,^{ab} Katsumi Chikama^b and Yoshio Hisaeda*^a

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The hybrid polymer was synthesized by a radical polymerization of a B₁₂ derivative and a Ru complex having styrene moieties in each peripheral position, and the hybrid polymer showed photocatalytic activity for molecular transformation with visible light irradiation.

The Co(I) species of the cobalamin derivative (B₁₂) is widely known as a supernucleophile that forms an alkylated complex by reaction with an alkyl halide.^{1,2} Because the alkylated complex is a useful reagent for forming radical species as the cobalt–carbon bond is readily cleaved homolytically by thermolysis, photolysis and electrolysis, research interest is focused on the application of this compound to various molecular transformations.^{3,4} Recently, we reported the dechlorination of 1,1-bis(4-chlorophenyl)-2,2,2-trichloroethane (DDT) catalyzed by the B₁₂ derivative, heptamethyl cobyrinate perchlorate with a [Ru(II)(bpy)₃]Cl₂ photosensitizer by irradiation with visible light.⁵ Although the B₁₂ complex showed high catalytic efficiency in the reaction, an excess of the photosensitizer was required for the reaction. To alleviate this problem, we synthesized a new B₁₂ catalyst as shown in Fig. 1. In this compound, the photosensitizing unit and the B₁₂ catalytic unit are incorporated in the same polymer, which may allow efficient electron transfer from the Ru(bpy)₃ moiety to the cobalt center in the B₁₂ complex. In this study, the synthesis and catalysis of this hybrid polymer composed of the B₁₂ complex and a Ru(bpy)₃ photosensitizer are reported.

This copolymer was synthesized from the corresponding monomers (B₁₂ and Ru(bpy)₃ derivative (**1a**, **2**), and styrene monomers) by radical polymerization using azobisisobutyronitrile (AIBN) (ESI†). Each of the monomers has a styrene moiety with an amide linkage to the B₁₂ and ruthenium tris-bipyridine complexes. After polymerization, unreacted monomers were easily removed by the Soxhlet extraction method using methanol as the solvent. Molecular weight and

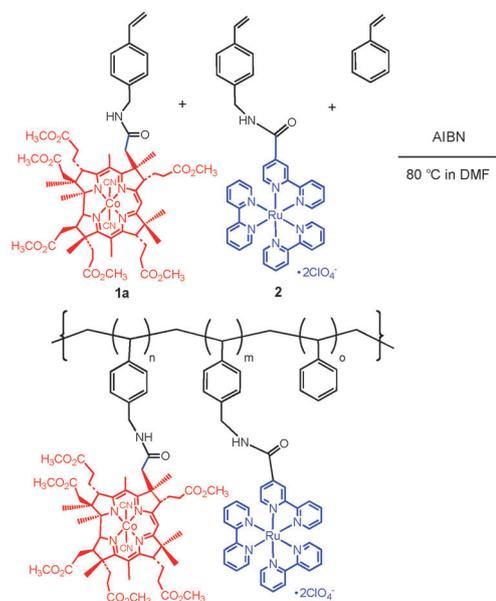


Fig. 1 Synthesis of polymer-supported B₁₂ catalyst and photosensitizer.

polydispersity of the polymer were determined by gel permeation chromatography (GPC) ($M_w = 39\,000$, $M_n = 27\,000$, $M_w/M_n = 1.4$) (Fig. S1, ESI†). The morphology and size of the polymer were analyzed by transmission electron microscopy (TEM) and dynamic light scattering (DLS). From the TEM image, a warped shape of the polymer was observed as shown in Fig. S2 (ESI†) and the size of the polymer was estimated to be about 7 nm. The size was also supported by DLS (Fig. S3, ESI†).

The UV-vis spectrum of the hybrid polymer showed the typical shape for the B₁₂ and Ru(bpy)₃ complexes with absorption maxima at 587 nm and 456 nm, respectively (Fig. S4, ESI†). The contents of the B₁₂ and the Ru(bpy)₃ complex in the polymer were determined by UV-vis,† and the mole ratio of each unit was estimated to be B₁₂:Ru:Styrene = 1:1:98. These values were quite similar to the initial ratio of the starting monomers.§ From these data (molecular weight, size of polymer, and contents of B₁₂ and Ru complexes in the polymer), we can estimate the number of B₁₂ and Ru complexes in one polymer unit as both three molecules. In this polymer, the neighboring ruthenium photosensitizer is

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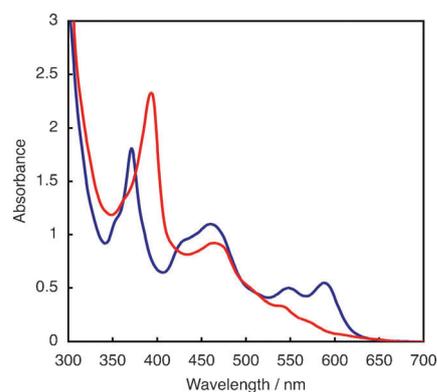


Fig. 2 UV-vis spectral change in the polymer (B_{12} unit, 5×10^{-4} M) in the presence of triethanolamine (1 M) by visible light irradiation ($\lambda \geq 420$ nm) under N_2 in DMF. (a) Before irradiation (blue line), (b) after 5 minute irradiation (red line).

expected to be an electron donor for B_{12} activation to form reactive Co(I) species.

Formation of the Co(I) species of the B_{12} complex in the polymer was monitored by UV-vis spectral change under irradiation with visible light ($\lambda \geq 420$ nm). The UV-vis spectrum of the starting polymer having a Co(III) form of B_{12} was changed to a new spectrum after visible light irradiation with absorption maxima at 390 nm in DMF containing a sacrificial reductant (triethanolamine) as shown in Fig. 2, which is typical for the Co(I) state of B_{12} .⁶

The photoreduction of B_{12} in the polymer was also investigated by ESR spectroscopy. When the Co(III) state of the B_{12} -Ru hybrid polymer was dissolved in DMF, the diamagnetic starting polymer showed no ESR signal (see Fig. S5(a), ESI[†]). After irradiation by visible light in the presence of triethanolamine, the typical Co(II) low-spin signal appeared ($g_1 = 2.39$, $g_2 = 2.29$, $g_3 = 2.00$, $A_2^{Co} = 48$ G, $A_3^{Co} = 136$ G).⁷ Upon subsequent irradiation by visible light, this signal disappeared to form the diamagnetic Co(I) species. According to these ESR spectral changes, stepwise one-electron reduction of cobalt center occurred by electron transfer from the ruthenium photosensitizer in the polymer to form the Co(I) state of B_{12} . Thus, we carried out a catalytic reaction using this hybrid polymer.

The catalytic reaction was carried out using phenethyl bromide as a substrate.[¶] The results are shown in Table 1. After 24 h with visible light irradiation, most of the phenethyl bromide was converted to ethylbenzene and styrene in 82 and 8% yields, respectively. The reaction did not proceed under dark conditions (entry 2 in Table 1).

In contrast, the conversion of phenethyl bromide was decreased to 66% when we used a 1:1 mixture of the Ru complex ($[Ru(bpy)_3]Cl_2$) and B_{12} catalyst (dicyano heptamethyl cobyrinate) (entry 3 in Table 1). Intramolecular electron transfer from the Ru complex to B_{12} should be accelerated in the polymer. Of course, the reaction did not proceed when we used the Ru complex or B_{12} catalyst alone (entries 4 and 5 in Table 1). To emphasize this polymer-supported effect, a catalytic reaction was carried out at a more dilute concentration as shown in Table 2. Under this condition, the effect of the polymer was clearly observed compared to the previous condition (Table 1), and the reaction

Table 1 Photocatalytic reaction of B_{12} complex^a

Entry	Catalyst	Conversion ^b (%)	Yield ^b (%)		
			EB	ST	TON ^c
1	B_{12} -Ru polymer	98	82	8	270
2	B_{12} -Ru polymer ^d	0	0	0	0
3	B_{12} , $[Ru(bpy)_3]Cl_2$	66	59	4	189
4	$[Ru(bpy)_3]Cl_2$ ^e	0	0	0	—
5	B_{12} ^f	0	0	0	0

^a Conditions: $[B_{12}] = [Ru \text{ complex}] = 1 \times 10^{-4}$ M in polymer, $[substrate] = 3 \times 10^{-2}$ M, $[triethanolamine] = 1$ M. Solvent, DMF, $\lambda \geq 420$ nm under N_2 at room temperature. Reaction time, 24 h.

^b Conversion was estimated by the recovery of the substrate. Yields were based on initial concentration of the substrate. ^c Turnover numbers (TON) were based on $[B_{12}]$. ^d In the dark. ^e $[Ru \text{ complex}] = 1 \times 10^{-4}$ M. ^f Dicyano heptamethyl cobyrinate was used; $[B_{12}] = 1 \times 10^{-4}$ M.

Table 2 Photocatalytic reaction of the B_{12} complex under diluted conditions^a

Entry	Catalyst	Conversion ^b (%)	Yield ^b (%)		
			EB	ST	TON ^c
1	B_{12} -Ru polymer	27	22	1	690
2	B_{12} , $[Ru(bpy)_3]Cl_2$	3	1	1	60

^a Conditions: $[B_{12}] = [Ru \text{ complex}] = 1 \times 10^{-5}$ M in polymer, $[substrate] = 3 \times 10^{-2}$ M, $[triethanolamine] = 1$ M. Solvent, DMF, $\lambda \geq 420$ nm under N_2 at room temperature. Reaction time, 24 h. ^b Conversion was estimated by the recovery of the substrate. Yields were based on initial concentration of the substrate. ^c Turnover numbers (TON) were based on $[B_{12}]$.

efficiency of the polymer system was dramatically enhanced compared to that of the non-polymer system.

Indeed, a UV-vis spectral change for the formation of the Co(I) species by visible light irradiation was still observed under highly diluted conditions ($< 1 \times 10^{-5}$ M) in the polymer system (Fig. S10a, ESI[†]), while such a spectral change was not observed in the non-polymer system (Fig. S10b, ESI[†]). At a high concentration (1×10^{-4} M), the distance between the ruthenium photosensitizer and the B_{12} catalyst is very small (but not so close at least over 10 \AA since no concentration quenching was observed in ruthenium unit, data not shown) in both the polymer and non-polymer systems. In contrast, at a low concentration (1×10^{-5} M), the Ru photosensitizer and B_{12} catalyst were separated in the non-polymer system, whereas both units are close in the polymer system as shown in Fig. 3. Therefore, efficient electron transfer from the Ru complex to the B_{12} catalyst should occur in the hybrid polymer. In other words, fixation of the Ru and B_{12} catalyst in the same polymer unit retains photo-catalytic efficiency under a diluted condition and allows effective utilization of a small amount of the catalyst.

Furthermore, it is noteworthy that because $[Ru(bpy)_3]Cl_2$ is used as an excellent photo-redox catalyst due to its reducing ability ($Ru(bpy)_3^+$, -1.33 V vs. SCE in CH_3CN)⁸ and was developed in the field of green organic chemistry,⁹ substrates

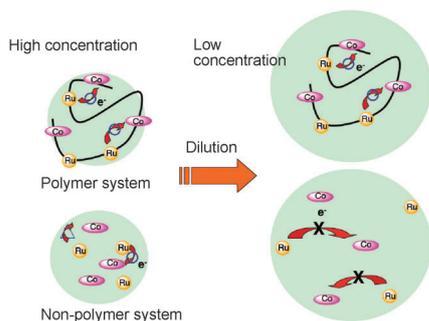


Fig. 3 Schematic representation of concentration dependency for electron transfer behaviours of catalysts.

are limited to electron-deficient compounds to undergo efficient one-electron reduction, whereas our catalyst utilizing the supernucleophilicity of the Co(I) species overcomes this problem (compare entries 1 and 4 in Table 1).¹⁰

As for the mechanism, intrapolymer and interpolymer electron transfer are possible in the hybrid polymer. Based on this question, we carried out the following experiment. We synthesized a B₁₂ polymer and a Ru complex polymer (ESI[†]), and a catalytic reaction was carried out using a 1 : 1 mixture of these homo-polymers (reaction conditions were the same as in Table 2). Catalytic efficiency was decreased to 9% conversion of the substrate when we used a mixture of these homo-polymers. Therefore, the predominant electron transfer from the Ru complex to B₁₂ should occur in the same polymer unit.¹¹

Finally, we investigated the photosensitizing mechanism of the Ru complex in the polymer. The Ru complex is activated by visible light irradiation, and in general, reductive and oxidative quenching mechanisms exist in the ruthenium trisbipyridine complex.⁸ To elucidate the quenching mechanism, the steady-state emission from the triplet state of the Ru complex in the polymer and its lifetime were measured. After exciting the metal to ligand charge transfer (MLCT) transition band of the Ru complex at 456 nm, a strong emission at 638 nm was observed with a fluorescence quantum yield, $\Phi_f = 5.3\%$ in DMF. Because these values were similar to those of [Ru(bpy)₃]Cl₂ ($\Phi_f = 6.8\%$ in DMF),¹² the triplet state of the Ru complex in the polymer is not quenched by B₁₂. Therefore, electron transfer to B₁₂ mainly occurs by a reductive quenching mechanism of the Ru complex. After visible light irradiation, the triplet state of the Ru complex is quenched by a sacrificial reductant to form one-electron reduced species, and that reduces the B₁₂ to form the Co(I) species. The thus-formed Co(I) species attacked phenethyl bromide to form ethylbenzene and styrene.⁶

In summary, a light-driven catalytic reaction efficiently proceeded with the hybrid polymer composed of the B₁₂ catalyst and a Ru photosensitizer under irradiation with visible light. The present system is economical in reducing the amount of catalyst, and, therefore, would be readily applicable to the design of an eco-friendly catalyst.

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Notes and references

† The contents of B₁₂ and Ru(bpy)₃ complexes in the polymer were determined by UV-vis spectroscopy using the standard data for dicyano heptamethyl cobyrinate, $\lambda(\epsilon) = 587 (1.14 \times 10^4)$, 456 (2.47×10^3) and Ru(bpy)₃ monomer, $\lambda(\epsilon) = 456 (1.60 \times 10^4)$ in CH₂Cl₂.

§ It was noted that the copolymerization of the Co(II) state of the B₁₂ monomer (**1b**) (ESI[†]), Ru monomer and styrene (starting with a 1 : 1 : 98 mole ratio) failed to incorporate the B₁₂ unit in the polymer (obtained 0.16 : 0.21 : 99.63 mole ratio). Due to the high radical affinity of the Co(II) complex, the radical polymerization by AIBN was presumably inhibited.

¶ General procedure: a 2 mL DMF solution of polymer (B₁₂ and Ru complexes contents, both 1.0×10^{-4} M), phenethyl bromide (3×10^{-2} M), triethanolamine (1 M) and diphenyl (5 mg) as internal standard was degassed by nitrogen bubbling for 30 minutes; then the solution was stirred at room temperature under irradiation by a 200 W tungsten lamp with a 420 nm cut-off filter (Sigma Koki, 42 L) and a heat cut-off filter (Sigma Koki, 30 H). After 24 h, the solution was passed through a silica gel column (CH₂Cl₂ eluent) to remove the polymer and triethanolamine, and the products were analyzed by GC-MS.

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