

Dalton Transactions

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

A polymerized ionic liquid-supported B₁₂ catalyst with a ruthenium trisbipyridine photosensitizer for photocatalytic dechlorination in ionic liquids[†]

Wei Zhang,^{a,b} Hisashi Shimakoshi,^{*a} Noriyuki Houfuku,^a Ximing Song^b and Yoshio Hisaeda^{*a}⁵ Received (in XXX, XXX) Xth XXXXXXXXX 2014, Accepted Xth XXXXXXXXX 2014

DOI: 10.1039/b000000x

A visible light-driven photocatalyst by immobilizing a B₁₂ complex and a Ru(II) trisbipyridine photosensitizer in a polymerized ionic liquid (PIL) was developed. The synthesized copolymer was characterized by GPC, DLS, and its UV-vis absorption spectra and luminescence spectra. The Ru(II) trisbipyridine photosensitizer in the copolymer showed an enhanced emission compared to that of the monomer in the ionic liquid, 1-butyl-4-methylimidazolium bis(trifluoromethanesulfonyl)amide ([C₄mim][NTf₂]). Formation of the Co(I) species of the B₁₂ complex in the copolymer was confirmed by the UV-vis spectral change in [C₄mim][NTf₂] containing a sacrificial reductant (triethanolamine) during irradiation with visible light. The copolymer showed a high photocatalytic activity in various ionic liquids for the 1,1-bis(4-chlorophenyl)-2,2,2-trichloroethane (DDT) dechlorination with ~99% conversion after a 2 h visible light irradiation. Furthermore, both the B₁₂ catalyst and the photosensitizer in the polymer were easily recycled for use with the ionic liquid solvent without any loss of catalytic activity.

1. Introduction

Because of the recent environmental concerns, dehalogenation reactions are presently of great interest for their potential use in the treatment of halogenated solvent wastes as well as in remedial approaches to removing such chemicals from contaminated soils.¹ Vitamin B₁₂ derivatives have been used as excellent catalysts in the dehalogenation reaction since the Co(I) species of vitamin B₁₂ derivatives are supernucleophiles and can react with an alkyl halide to form an alkylated complex with dehalogenation.² The ability of vitamin B₁₂ derivatives to achieve reductive dehalogenations prompted us to investigate the catalysis of a vitamin B₁₂ derivative not only for the degradation of various halogenated organic compounds but also for establishing a more efficient and eco-friendly catalytic system.³ In 2004, we reported the dechlorination of the pollutant, 1,1-bis(4-chlorophenyl)-2,2,2-trichloroethane (DDT), in the presence of a catalytic amount of a vitamin B₁₂ derivative (heptamethyl cobyrinate perchlorate, Figure S1, ESI[†]) and a photosensitizer ([Ru(bpy)₃]Cl₂) under visible light irradiation.⁴ In this reaction, the supernucleophilic Co(I) species of the B₁₂ complex generated by electron transfer from the photosensitizer catalyzed the DDT dechlorination. Note that combined use of photosensitizer and cobalamin derivative as the binuclear Ru^{II}-Co^{II} complex for photoredox catalytic system was first reported by L. Walder *et al.*⁵ This system is superior to a chemical reductant system from the viewpoint of green chemistry, and is a simpler and more facile technique than the conventional electrochemical system.^{3d} However, the catalyst and the photosensitizer can not be recycled and organic solvents

were also used.

In recent years, ionic liquids have been the subject of considerable interest as promising media for chemical reactions because of their unique characteristics such as low melting point, negligible vapor pressure, non-flammability, high conductivity and the good solubility of many organic and inorganic compounds as well as biomaterials.⁶ Besides these merits, the recyclability of a catalyst, such as a transition metal complex dissolved in an ionic liquid, is an attractive feature of ionic liquids since the products can be separated from the ionic liquid by extraction, while the catalyst remains in the ionic liquid and can be reused. Based on this strategy, we demonstrated the recycled catalysis of a heptamethyl cobyrinate perchlorate in an ionic liquid with [Ru(bpy)₃]Cl₂ for the dechlorination of DDT under visible light irradiation.⁷ Although the vitamin B₁₂ derivative showed a high catalytic efficiency during the reaction, an excess amount of the photosensitizer was required for the reaction. Furthermore, only the vitamin B₁₂ derivative could be reused with the ionic liquids, but the photosensitizer could not. To alleviate these problems, we prepared a hybrid polymer containing both the photosensitizing unit and the vitamin B₁₂ derivative unit in the same polystyrene backbone.⁸ This hybrid polymer showed a high catalytic activity for the debromination of 2-phenethyl bromide due to the efficient electron transfer from the Ru(bpy)₃ moiety to the B₁₂ complex and eventually avoided the use of an excess amount of the Ru photosensitizer. However, this hybrid polymer with a polystyrene backbone was difficult to dissolve in the ionic liquids[†] and could not be recycled.

Polymerized ionic liquids (PILs), which carry an ionic liquid species in each of the repeating units, have attracted great interest

in the fields of polymer chemistry and materials science because of their combined unique properties of the ionic liquid and macromolecule.⁹ In spite of the many new properties and functions of PILs as an ion-conductive material, CO₂ absorbent and microwave absorbing materials,¹⁰ their application in catalytic chemistry is limited.^{9a} In order to develop the B₁₂ complex immobilizing polymer system in ionic liquid chemistry, we synthesized a new B₁₂ complex-Ru(II) photosensitizer hybrid polymer having a PIL backbone that could dissolve in the ionic liquids. Using this hybrid PIL, the photocatalytic dechlorination of DDT was achieved in various ionic liquids. Among the chlorinated organic compounds, DDT is characterized by a pronounced insecticidal property and has been used worldwide for the last several decades despite its known hazardous effects on human health and wildlife. Therefore, there is a pressing need for efficient methods for the degradation of such chlorinated compounds accumulated in the environments.¹¹ The methodology we reported here could be applicable to dechlorinate other chlorinated organic compounds such as perchloroethylene or tetrachloromethane.¹² The synthesis, photophysical property and catalysis for the DDT dechlorination of this unique hybrid polymer in ionic liquids are now reported.

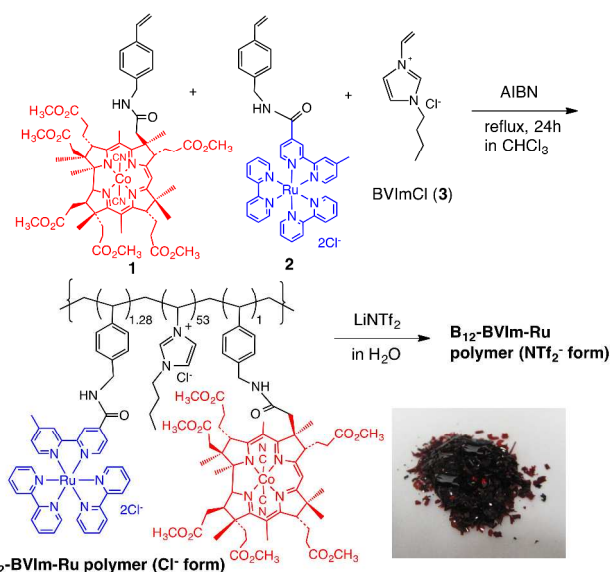


Figure 1. Synthesis of a PIL-supported B₁₂ catalyst with a trisbipyridine Ru(II) photosensitizer.

2. Experimental

2.1 Materials

All solvents and chemicals used in the syntheses were of reagent grade and used without further purification. The ionic liquids (Figure 2) were purchased from Kanto Chemical Co., Inc., and were dried under reduced pressure for 1 day before use. Dicyano heptamethyl cobyrinate (Figure S1, ESI[†]) was synthesized by a previously reported method.¹³ Syntheses of the B₁₂ monomer (1) and Ru monomer (2) (Figure 1) were previously reported by our group.⁸ Monomer BVImCl (3) (Figure 1) was prepared according to the literature.¹⁴

2.2 Characterization

The NMR spectra were recorded by a Bruker Avance 500 spectrometer at the Center of Advanced Instrumental Analysis of Kyushu University. The UV-vis absorption spectra were measured by a Hitachi U-3300 spectrophotometer at room temperature. The luminescence spectra were measured by a Hitachi F-4500 spectrophotometer in DMF and [C₄mim][NTf₂] at room temperature. The emission quantum yield (Φ_p) values were measured using an absolute photoluminescence quantum efficiency measurement system (Hamamatsu C9920-02) incorporating an integrating sphere. To measure the Φ_p , degassed solutions in DMF and [C₄mim][NTf₂] were prepared and the concentration was adjusted so that the absorbance of the solution at 455 nm would be less than 0.1. The excitation was performed at 455 nm. The MALDI-TOF mass spectra were obtained by a Bruker autoflex II using 6-aza-2-thiothymine as the matrix. Gel permeation chromatography (GPC) was carried out using a TOSOH HLC-8320GPC EcoSEC apparatus combined with RI and UV attachments using two connected columns, TSK-GEL G6000PWXL-CP and G3000PWXL-CP, and a 20 mM NaNO₃ aqueous solution as the eluent. The GC-mass spectra were obtained using a Shimadzu GC-QP5050A equipped with a J&W Scientific DB-1 column (length 30 m; ID 0.25 mm, film 0.25 μ m). The dynamic light scattering (DLS) was measured by a Zetasizer NanoZS (MALVERN) instrument at 25 °C using an incident He-Ne laser (633 nm).

2.3 Preparation of the hybrid polymer

The B₁₂ monomer (1) (71 mg, 0.06 mmol), Ru monomer (2) (49 mg, 0.06 mmol), BVImCl monomer (3) (536 mg, 2.88 mmol) and azobisisobutyronitrile (AIBN, 16 mg, 0.1 mmol) were dissolved in 8 mL of CHCl₃ and the solution was degassed with nitrogen for 30 minutes. The solution was refluxed for 24 h, then cooled to room temperature. The solution was next dropwise added to 50 mL of diethyl ether and the precipitate was collected by filtration, then washed with diethyl ether to remove any unreacted B₁₂ monomer. The solid was dissolved in a small amount of water and further purified by dialysis in water for 3 days in order to remove the unreacted Ru monomer and BVImCl monomer, then a B₁₂-BVIm-Ru (Cl⁻ form) aqueous solution was obtained. The UV-vis (in CH₃OH, nm) exhibited 288, 368, 456, 545, 583 (Figure 3). The contents of the B₁₂ and the Ru(bpy)₃ complexes in the polymer were determined by UV-vis spectroscopy using the standard data for dicyano heptamethyl cobyrinate, $\lambda(\epsilon) = 583$ (9.02×10^3), 456 (1.62×10^3) and Ru(bpy)₃ monomer, $\lambda(\epsilon) = 456$ (1.36×10^4) in methanol and were 6.80×10^{-5} mol/g and 8.68×10^{-5} mol/g of the polymer, respectively.

The counter anions of B₁₂-BVIm-Ru (Cl⁻ form) were replaced by adding LiNTf₂ to the aqueous solution. The resulting precipitate was filtered and washed with H₂O, then dried to obtain the B₁₂-BVIm-Ru polymer (NTf₂⁻ form). The size of the polymer was estimated by DLS to be ca. 12.7 nm in [C₄mim][NTf₂] (Figure S2, ESI[†]).

2.4 General catalytic procedure

A 4 mL ionic liquid (their structure were shown in Figure 2) solution of the polymer ([B₁₂ unit] = 1×10^{-5} M; [Ru unit] = 1.28×10^{-5} M), DDT (3×10^{-3} M), and triethanolamine (0.5 M) was degassed for 4 h by a rotary pump, then the solution was stirred at room temperature during 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 2 h, the solution was first extracted with water to remove the triethanolamine, then the products and a small amount of unreacted substrate were obtained by further extraction with hexane/diethyl ether (3:1, v/v). After removing the solvent, a white solid was obtained and analyzed by ^1H NMR using 1,4-dioxane as the internal standard and GC-MS comparison with the purchased authentic sample or literature data.^{3,15,16} The ionic liquid phase including the polymer was dried under vacuum, then reused after adding fresh triethanolamine and the substrate.

3. Results and discussion

The copolymer (B_{12} -BVIm-Ru polymer) was synthesized from the corresponding monomers B_{12} (**1**), $\text{Ru}(\text{bpy})_3$ derivative (**2**) and the ionic liquid monomer [BVIm]Cl (**3**) by radical polymerization using AIBN as the initiator (Figure 1). The first two monomers have a styrene moiety with an amide linkage to the B_{12} and ruthenium trisbipyridine complexes. After polymerization, the unreacted B_{12} monomers were easily removed by washing with diethyl ether, and the other two kinds of monomers were removed by dialysis in water.

The molecular weight and polydispersity of the B_{12} -BVIm-Ru polymer (Cl^- form) were determined by gel permeation chromatography (GPC) ($M_w = 670,000$, $M_n = 350,000$, $M_w/M_n = 1.9$) (Figure S3, ESI[†]). Compared to our previous B_{12} -Ru photosensitizer hybrid polymer with a polystyrene backbone ($M_w = 39,000$),⁸ the molecular weight of this new polymer was dramatically increased when a polymerized ionic liquid was used as the backbone. The solubilities of the polymer in different kinds of solvents were studied and the results are listed in Table 1. The solubility of the polymer in water is significantly influenced by the counter ions of the polymer. When the counter ions are Cl^- , the polymer was well dissolved in water. When the counter ions were changed to NTf_2^- , the polymer becomes hydrophobic. The copolymers showed an excellent solubility in MeOH, DMF and ionic liquids, such as [C₄mim][NTf₂], *N*-methyl-*N*-propylpyrrolidinium bis(trifluoromethane-sulfonyl)amide ([P13][NTf₂]),^{17a} *N,N,N*-trimethyl-*N*-propyl-ammonium bis(trifluoro-methylsulfonyl)amide ([N₃₁₁₁][NTf₂])^{17a} and 1-butyl-4-methylimidazolium hexafluorophosphate ([C₄mim][PF₆]) (Figure 2) regardless of the counter ions.

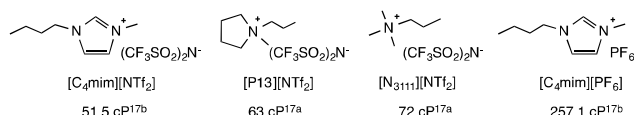


Figure 2. The structures and viscosities (at 298 K)¹⁷ of ionic liquids [C₄mim][NTf₂], [P13][NTf₂], [N₃₁₁₁][NTf₂] and [C₄mim][PF₆].

Table 1. Solubility of B_{12} -BVIm-Ru polymer.^a

	H ₂ O	MeOH	DMF	Et ₃ O	hexane	[C ₄ mim][NTf ₂]	[P13][NTf ₂]	[N ₃₁₁₁][NTf ₂]	[C ₄ mim][PF ₆]
Cl^- form	+	+	+	-	-	+	+	+	+
NTf_2^- form	-	+	+	-	-	+	+	+	+

^a +, soluble; ^b -, insoluble at room temperature. Concentration: 2 mg/1 mL solvent.

The UV-vis spectrum of the B_{12} -BVIm-Ru polymer (Cl^- form) in MeOH showed the typical shape for the B_{12} and the $\text{Ru}(\text{bpy})_3$ complex with absorption maxima at 583 nm and 456 nm, respectively (Figure 3). The contents of the B_{12} and the $\text{Ru}(\text{bpy})_3$ complexes in the polymer were determined by UV-vis spectroscopy, and the molar ratio of each unit was estimated to be $\text{B}_{12} : \text{Ru} : \text{BVIm} = 1:1.28:53$. These values were similar to the initial ratio of the starting monomers (1:1:48). Based on the molecular weight and contents of the B_{12} and Ru complexes in the polymer, we estimated the number of B_{12} and Ru complexes in one polymer unit to be 56 and 72 molecules, respectively. In this polymer, the neighboring Ru photosensitizer is expected to be an electron donor for the B_{12} activation to form the reactive Co(I) species.⁸

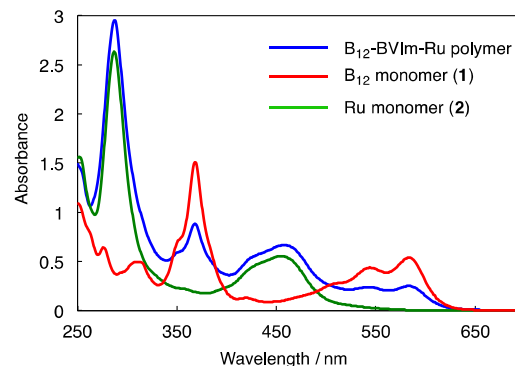


Figure 3. UV-vis spectra of B_{12} -BVIm-Ru polymer (Cl^- form), B_{12} monomer (**1**) and Ru monomer (**2**) in MeOH.

The photophysical property of the B_{12} -BVIm-Ru polymer (NTf_2^- form) was investigated by luminescence spectroscopy (Figure 4), and its luminescence quantum yield (Φ_p) was determined using an integrating sphere in an N_2 saturated solution at room temperature. In the ionic liquid [C₄min][NTf₂], luminescence of the polymer from the Ru complex moiety was observed at 644 nm with $\Phi_p = 11.9\%$, while Φ_p for $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ with the dicyano heptamethyl cobyrinate was 7.3% (Figure 4). Enhancement of the luminescence of the B_{12} -BVIm-Ru polymer in an ionic liquid was probably due to the rigidochromic effect of the polymer and the viscous ionic liquid media.¹⁸ The Ru complexes in the polymer may be removed from the bulk solvent, hence the rate of non-radiative decay may decrease.⁸ This is an advantage for the photosensitization reaction of the polymer in an ionic liquid. Furthermore, it is also deduced from the emission data that the triplet state of the Ru complex is not quenched by the B_{12} complex in the polymer. The so-called reductive quenching mechanism could be expected for the photo-induced catalytic reaction in the polymer system.^{4,8,19}

50

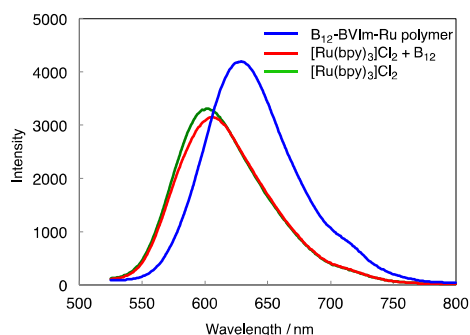


Figure 4. Emission spectra of B_{12} -BVIm-Ru polymer (NTf_2^- form) (blue line), $[Ru(bpy)_3]Cl_2 + B_{12}$ complex (dicyano heptamethyl cobyrinate) (red line) and $[Ru(bpy)_3]Cl_2$ alone (green line) in $[C_4mim][NTf_2]$ at room temperature; $\lambda_{ex}=455$ nm, $[B_{12} \text{ complex}]=1 \times 10^{-5}$ M; $[Ru \text{ complex}]=1.28 \times 10^{-5}$ M.

Formation of the Co(I) species of the B_{12} complex of the B_{12} -BVIm-Ru polymer (NTf_2^- form) was monitored by the UV-vis spectral change in $[C_4mim][NTf_2]$ containing a sacrificial reductant (triethanolamine) during visible light irradiation ($\lambda > 420$ nm) as shown in Figure 5a. Before irradiation, the B_{12} -BVIm-Ru polymer produced three characteristic peaks of the Co(III) species of the B_{12} complex at 368 nm, 543 nm and 583 nm. After being irradiated for 20 minutes, the peaks of the Co(III) species disappeared and one new peak at 390 nm was clearly observed, which is typical for the Co(I) state of the B_{12} complex.^{8,20} In contrast, a very slow Co(I) formation was observed when the corresponding vitamin B_{12} derivative (dicyano heptamethyl cobyrinate) and $[Ru(bpy)_3]Cl_2$ with the same concentration of polymer system were mixed in $[C_4mim][NTf_2]$ (Figure 5b). Thus the UV-vis spectroscopic change suggests a promising application of the hybrid polymer for a catalytic reaction utilizing Co(I) reactivity in an ionic liquid.

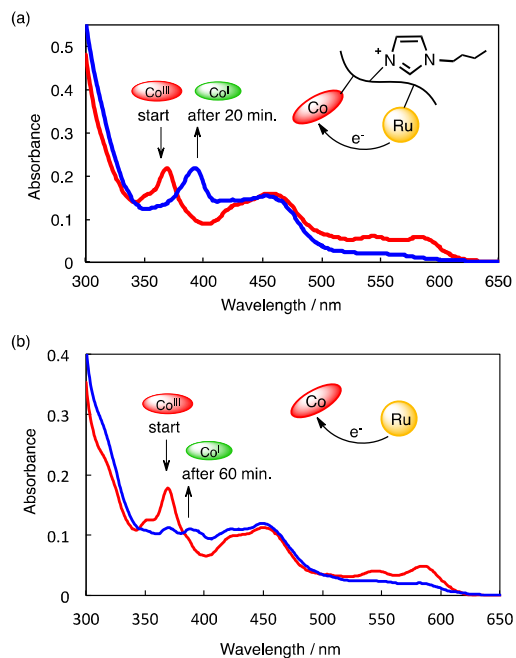
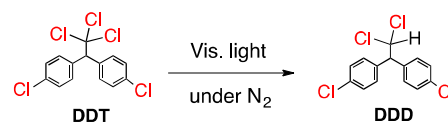


Figure 5. UV-vis spectral change in the polymer (NTf_2^- form) (a) and monomer mixtures (b) (B_{12} unit, 5×10^{-6} M) in the presence of triethanolamine (1 M) by visible light irradiation ($\lambda > 420$ nm) under degassed conditions in $[C_4mim][NTf_2]$.

The catalytic reaction was carried out using DDT as a substrate in various ionic liquids (their structure were shown in Figure 2) and DMF. The results are summarized in Table 2. For the B_{12} -BVIm-Ru polymer, DDT was almost completely converted to the monodechlorinated product, 1,1-bis(4-chlorophenyl)-2,2-dichloroethane (DDD) after 2 h by visible light irradiation in $[C_4mim][NTf_2]$, $[P13][NTf_2]$ and $[N_{3111}][NTf_2]$ (entries 1-3 in Table 2). The reaction did not proceed under dark conditions (entry 4 in Table 2). When we used the B_{12} catalyst or the Ru complex alone, the yields of DDD were much lower, which are 9% and 19%, respectively (entries 5 and 6 in Table 2). In contrast to the results in the polymer system, the yield of DDD decreased to 27% when we used a 1:1.3 mixture of the B_{12} complex (dicyano heptamethyl cobyrinate) and $[Ru(bpy)_3]Cl_2$ in $[C_4mim][NTf_2]$ (entry 7 in Table 2). The yield of DDD depended on the viscosity of the ionic liquid. The yield decreased to 32% in the more viscous ionic liquid, $[C_4mim][PF_6]$ ($c_p=257.1$ at 298 K) (entry 8 in Table 2) but still higher than 13% in monomer system (entry 9 in Table 2). In this way, the polymer system possessed a much higher catalytic activity than the non-polymer system even in a highly viscous ionic liquid. The results shown here indicated that the reaction efficiency of the polymer system was significantly enhanced compared to that of the non-polymer system, which should be attributed to the enhanced luminescence of the Ru complex and the fast intramolecular electron transfer from the Ru complex to B_{12} complex in the polymer.²¹

Table 2. Photocatalytic dechlorination of DDT catalyzed by the B_{12} complex^a



Entry	Catalyst	Solvent	Conversion (%) ^b	Yield (%) ^b	TON ^c
1	B_{12} -BVIm-Ru polymer	$[C_4mim][NTf_2]$	99	99	300
2	B_{12} -BVIm-Ru polymer	$[P13][NTf_2]$	99	95	285
3	B_{12} -BVIm-Ru polymer	$[N_{3111}][NTf_2]$	96	91	273
4	B_{12} -BVIm-Ru polymer ^d	$[C_4mim][NTf_2]$	0	0	-
5	B_{12} ^e	$[C_4mim][NTf_2]$	12	9	27
6	$[Ru(bpy)_3]Cl_2$ ^f	$[C_4mim][NTf_2]$	23	19	-
7	$B_{12} + [Ru(bpy)_3]Cl_2$ ^{e,f}	$[C_4mim][NTf_2]$	32	27	81
8	B_{12} -BVIm-Ru polymer	$[C_4mim][PF_6]$	38	32	96
9	$B_{12} + [Ru(bpy)_3]Cl_2$ ^{e,f}	$[C_4mim][PF_6]$	15	13	39
10	B_{12} -BVIm-Ru polymer ^g	DMF	100	67	203
11	$B_{12} + [Ru(bpy)_3]Cl_2$ ^{e,f,h}	DMF	100	81	245

^a Conditions: $[B_{12} \text{ complex}] = [Ru \text{ complex}] = 1 \times 10^{-5}$ M in the polymer, $[DDT] = 3 \times 10^{-3}$ M, $[triethanolamine] = 0.5$ M. $\lambda \geq 420$ nm under nitrogen at room temperature. Reaction time, 2 h.

^b Conversion and yield were based on initial concentration of the substrate.

^c Turnover numbers (TON) were based on $[B_{12} \text{ complex}]$. ^d In the dark.

^e Dicyano heptamethyl cobyrinate was used; $[B_{12} \text{ complex}] = 1 \times 10^{-5}$ M. ^f $[Ru \text{ complex}] = 1.28 \times 10^{-5}$ M. ^g DDMS (8%), DDMU (2%) and TTDB (E/Z) (2%) were formed. ^h DDMS (2%), DDMU (1%) and TTDB (E/Z) (1%) were formed.

Interestingly, more dechlorinated products, 1,1-bis(4-chlorophenyl)-2-chloroethane (DDMS), 1,1-bis(4-chlorophenyl)-2-chloroethylene (DDMU) and 1,1,4,4-tetrakis(4-chloro-phenyl)-2,3-dichloro-2-butene (TTDB(*E/Z*)), were obtained in low viscous DMF (entries 10 and 11 in Table 2) although almost same conversions of DDT after 2h reaction. The sum of the yields of these products were higher using the B₁₂-BVIm-Ru polymer system than that of the B₁₂ + [Ru(bpy)₃]Cl₂ system. This unique catalysis may be caused by the PILs backbone in the B₁₂-BVIm-Ru polymer. Further study is needed to elucidate the effect of the PILs during the catalysis.

Furthermore, due to its excellent solubility in ionic liquids, the B₁₂-BVIm-Ru polymer can quantitatively remain in the ionic liquid phase after the extraction procedure, hence the B₁₂-BVIm-Ru polymer could be successfully reused for the catalytic reaction together with the ionic liquid as shown in Figure 6. The product can be well separated from the ionic liquid by extraction with hexane/diethyl ether (3/1, v/v), while the B₁₂-BVIm-Ru polymer quantitatively remained in the ionic liquid after the extraction procedure. Therefore, the B₁₂-BVIm-Ru polymer was recycled for the next run with the ionic liquid solvent. Indeed, the DDT dechlorination proceeded with almost the same efficiency in the second and third runs (conversions of DDT, 2_{nd} 98% and 3_{rd} 94%) in [C₄mim][NTf₂] as shown in Table 3. It should also be noted that both the B₁₂ and the Ru complexes could be recycled at the same time in the polymer system, while only the B₁₂ complex can be recycled in our previously reported system.⁷

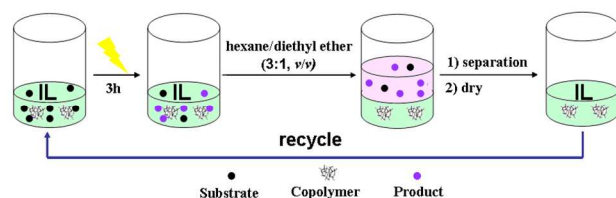


Figure 6. Schematic diagram for recycling of the polymer with ionic liquids.

Table 3. Recycled catalysis of the Ru-BVIm-B₁₂ polymer with ionic liquid, [C₄mim][NTf₂] for the dechlorination of DDT.^a

Cycle	Conversion (%)	DDD yield (%)
1	>99	99
2	98	98
3	94	93

^a Conditions: [B₁₂ complex] = 1 × 10⁻⁵ M; [Ru complex] = 1.28 × 10⁻⁵ M; [DDT] = 3 × 10⁻³ M, [triethanolamine] = 0.5 M, λ ≥ 420 nm under nitrogen at room temperature. Reaction time, 2 h. Conversion of DDT and the yield of product were based on initial concentration of the substrate.

4. Conclusion

In summary, a PILs-supported B₁₂ catalyst with a Ru(II) trisbipyridine photosensitizer as a visible light-driven photocatalyst was successfully synthesized. The hybrid polymer showed an enhanced emission and a relatively higher quantum

yield compared to the monomer mixture in the ionic liquid due to the rigidchromic effect of the polymer, and a visible light-driven catalytic reaction efficiently proceeded in the ionic liquids using the hybrid polymer. This catalytic system is environmental friendly since the catalyst and the solvent can be easily reused without any loss of catalytic efficiency. Therefore, this study will provide a potential application of PILs to catalytic chemistry and contribute to the development of an eco-friendly catalyst. Application of this PILs-supported B₁₂ catalyst for various molecular transformations is in progress in our laboratory.

This study was partially supported by a Grant-in-Aid for Scientific Research on Priority Areas (No. 20031021) and Innovative Areas (No. 25105744) and the Global COE Program “Science for Future Molecular Systems” from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan, and a Grant-in-Aid for Scientific Research (C) (No. 23550125) and (A) (No. 21245016) from the Japan Society for the Promotion of Science (JSPS), General Sekiyu Foundation, the Kyushu University P&P Program and Natural Science Foundation of Liaoning Province (Science and Technology Department) of China (201102084).

Notes and references

^aDepartment of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Motoooka, Fukuoka 819-0395, Japan. E-mail: shimakoshi@mail.cstm.kyushu-u.ac.jp,

yhisatcm@mail.cstm.kyushu-u.ac.jp; Fax: +81-92-802-2827; Tel: +81-92-802-2826

^bLiaoning Provincial Key Laboratory for Green Synthesis and Preparative Chemistry of Advanced Materials, College of Chemistry, Liaoning University, Shenyang 110036, P.R.China

[†] Electronic Supplementary Information (ESI) available: [Figure S1-S4]. See DOI: 10.1039/b000000x/

[‡] No colour ascribed to B₁₂ or Ru(bpy)₃ units in the hybrid polymer is appeared in the ionic liquid solutions such as [C₄mim][NTf₂] or [P13][NTf₂].

[§] This behaviour is typical for ionic liquid media. In DMF, the Φ_p value of the polymer was 8.1% (Figure S4).

[¶] Due to its trichloromethylated structure, DDT could be reductively dechlorinated to DDD by [Ru(bpy)₃]Cl₂ photosensitizer with simple electron transfer.

1 (a) M. M. Häggblom, I. D. Bossert, eds., *Dehalogenation Microbial Processes and Environmental Applications*, Kluwer Academic Publishers, Boston, 2003; (b) F. Alonso, I. P. Beletskaya and M. Yus, *Chem. Rev.*, 2002, **102**, 4009.

2 (a) Y. Hisaeda and H. Shimakoshi, in *Handbook of Porphyrin Science* (Eds.: K. M. Kadish, K. M. Smith and R. Guilard), World Scientific, 2010, **10**, 313-370; (b) B. Kräutler, *Vitamin B₁₂ and B₁₂-Proteins*, ed. B. Kräutler, D. Arigoni and B. T. Golding, Wiley-VCH, Weinheim, 1998; (c) G. N. Schrauzer, E. Deutsch, *J. Am. Chem. Soc.*, 1969, **91**, 3341; (d) G. N. Schrauzer, E. Deutsch and R. J. Windgassen, *J. Am. Chem. Soc.*, 1968, **90**, 2441; (e) Y. Hisaeda, K. Tahara, H. Shimakoshi and T. Masuko, *Pure Appl. Chem.*, 2013, **85**, 1415.

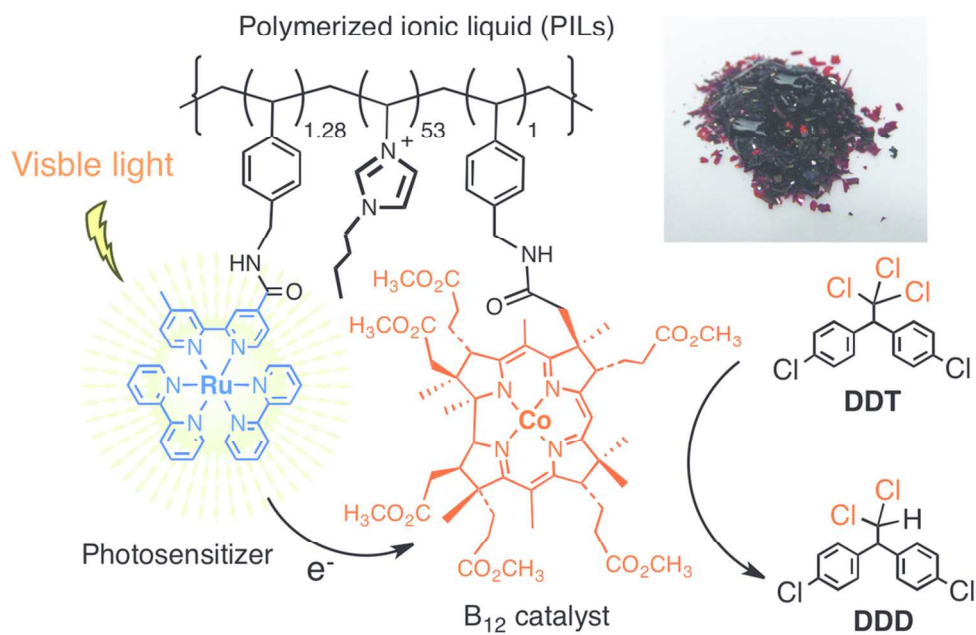
3 (a) H. Shimakoshi, M. Nishi, A. Tanaka, K. Chikama and Y. Hisaeda, *Chem. Lett.*, 2010, **39**, 22; (b) H. Shimakoshi, E. Sakumori, K. Kaneko and Y. Hisaeda, *Chem. Lett.*, 2009, **38**, 468; (c) Md. A. Jabbar, H. Shimakoshi and Y. Hisaeda, *Chem. Commun.*, 2007, 1653 (d) H. Shimakoshi, M. Tokunaga and Y. Hisaeda, *Dalton Trans.*, 2004, 878; (e) H. Shimakoshi, M. Tokunaga, K. Kuroiwa, N. Kimizuka and Y. Hisaeda, *Chem. Commun.*, 2004, 50.

4 H. Shimakoshi, M. Tokunaga, T. Baba and Y. Hisaeda, *Chem. Commun.*, 2004, 1806.

5 B. Steiger, E. Eichenberger, L. Walder, *Chimia*, 1991, **45**, 32.

- 6 (a) Y. Hamada, K. Yoshida, R. Asai, S. Hayase, T. Nokami, S. Izumi, T. Itoh, *Green Chem.*, 2013, **15**, 1863; (b) K. Ohira, Y. Abe, K. Suzuki, M. Mizuno, Y. Amano, T. Itoh, *ChemSusChem.*, 2012, **5**, 388; (c) J. P. Hallett, T. Welton, *Chem. Rev.*, 2011, **111**, 3508; (d) Y. Abe, K. Yoshiyama, Y. Yagi, S. Hayase, M. Kawatsura, T. Itoh, *Green Chem.*, 2010, **12**, 1976; (e) N. V. Plechkova, K. R. Seddon, *Chem. Soc. Rev.*, 2008, **37**, 123; (f) V. I. Parvulescu, C. Hardacre, *Chem. Rev.*, 2007, **107**, 2615; (g) M. Smiglak, A. Metlen and R. D. Rogers, *Acc. Chem. Res.*, 2007, **40**, 1182; (h) T. Itoh, S. Han, Y. Matsushita, S. Hayase, *Green Chem.*, 2004, **6**, 437; (i) T. Itoh, N. Ouchi, Y. Nishimura, H. S. Hui, N. Katada, M. Niwa, M. Onaka, *Green Chem.*, 2003, **5**, 494; (j) J. Dupont, R. F. de Souza and P. A. Z. Suarez, *Chem. Rev.*, 2002, **102**, 3667.
- 7 H. Shimakoshi, S. Kudo and Y. Hisaeda, *Chem. Lett.*, 2005, **34**, 1096.
- 8 H. Shimakoshi, M. Nishi, A. Tanaka, K. Chikama and Y. Hisaeda, *Chem. Commun.*, 2011, **47**, 6548.
- 9 (a) J. Yuan, D. Mecerreyes and M. Antonietti, *Prog. Polym. Sci.*, 2013, **38**, 1009; (b) Y. Kohno, Y. Deguchi and H. Ohno, *Chem. Commun.*, 2012, **48**, 11883; (c) J. Yuan, S. Soll, M. Drechsler, A. H. E. Müller and M. Antonietti, *J. Am. Chem. Soc.*, 2011, **133**, 17556; (d) J. Yuan, M. Antonietti, *Polymer*, 2011, **52**, 1469; (e) K. Nakashima, N. Kamiya, D. Koda, T. Maruyama and M. Goto, *Org. Biomol. Chem.*, 2009, **7**, 2353; (f) O. Green, S. Grubjesic, S. Lee and M. A. Firestone, *J. Macromol. Sci., Part C: Polym. Rev.*, 2009, **49**, 339; (g) M. D. Green and T. E. Long, *J. Macromol. Sci., Part C: Polym. Rev.*, 2009, **49**, 291; (h) H. Ohno, K. Ito, *Chem. Lett.*, 1998, 751.
- 10 (a) J. Y. Yuan, M. Antonietti, *Polymer*, 2011, **52**, 1469; (b) M. Yoshizawa, W. Ogihura and H. Ohno, *Polym. Adv. Technol.*, 2002, **13**, 589; (c) M. Yoshizawa, H. Ohno, *Electrochim Acta*, 2001, **46**, 1723.
- 11 (a) C. Holliger, S. Gaspard, G. Glod, C. Heijman, W. Schumacher, R. P. Schwarzenbach and F. Vazquez, *FEMS Microbiol. Rev.*, 1997, **20**, 517; (b) M. L. Hitchman, R. A. Spackman, N. C. Ross and C. Agra, *Chem. Soc. Rev.*, 1995, 423.
- 12 (a) H. Shimakoshi, M. Abiru, K. Kuroiwa, N. Kimizuka, M. Watanabe, Y. Hisaeda, *Bull. Chem. Soc. Jpn.*, 2010, **83**, 170; (b) H. Shimakoshi, Y. Maeyama, T. Kaieda, T. Matsuo, E. Matsui, Y. Naruta and Y. Hisaeda, *Bull. Chem. Soc. Jpn.*, 2005, **78**, 859.
- 13 (a) L. Werthemann, R. Keese and A. Eschenmoser, unpublished results; see: L. Werthemann, Dissertation, ETH Zürich (No. 4097), Juris Druck and Verlag, Zürich, 1968; (b) Y. Murakami, Y. Hisaeda and A. Kajihara, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 3642.
- 14 (a) K. Qiao, F. Ono, Q. Bao, D. Tomida and C. Yokoyama, *J. Mol. Catal. A: Chem.*, 2009, **303**, 30; (b) R. Marcilla, J. A. Blazquez, J. Rodriguez, J. A. Pomposo and D. Mecerreyes, *J. Polym. Sci.: Part A: Poly. Chem.*, 2004, **42**, 208.
- 15 D. Zanette and F. Nome, *J. Org. Chem.*, 1979, **44**, 2308.
- 16 L. L. Miller, R. S. Narang and R. D. Goodin, *J. Org. Chem.*, 1973, **38**, 340.
- 17 (a) H. Sakaabe and H. Matsumoto, *Electrochem. Commun.*, 2003, **5**, 594; (b) A. J. McLean, M. J. Muldoon, C. M. Gordon and I. R. Dunkin, *Chem. Commun.*, 2002, 1880.
- 18 W. R. Glomm, S. Volden, J. Sjöblom and M. Lindgren, *Chem. Mater.*, 2005, **17**, 5512; T. G. Kotch, A. J. Lees, S. J. Fuerniss, K. I. Papatomas and R. W. Snyder, *Inorg. Chem.*, 1993, **32**, 2570; M. Wrighton and D. L. Morse, *J. Am. Chem. Soc.*, 1974, **96**, 998.
- 19 (a) V. Balzani, G. Bergamini, F. Marchioni and P. Ceroni, *Coord. Chem. Rev.*, 2006, **250**, 1254; (b) A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser and A. V. Zelewsky, *Coord. Chem. Rev.*, 1988, **84**, 85.
- 20 H. Shimakoshi, L. Li, M. Nishi and Y. Hisaeda, *Chem. Commun.*, 2011, **47**, 10921.
- 21 Leading paper for the antenna property of a Ru trisbipyridine complex-supported polymer, see: M. Sykora, K. A. Maxwell, J. M. DeSimone and T. J. Meyer, *Proc. Natl. Acad. Sci. U. S. A.*, 2000, **97**, 7687.

A visible light-driven catalytic reaction efficiently proceeded in ionic liquids using a PILs-supported B₁₂ catalyst with a Ru(II) trisbipyridine photosensitizer.



101x82mm (300 x 300 DPI)