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SUPPORTING INFORMATION FOR:

Photocatalytic function of polymer-supported B_{12} complex with ruthenium trisbipyridine photosensitizer

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Measurements.

Elemental analyses were obtained from the Service Center of Elemental Analysis of Organic Compounds at Kyushu University. The NMR spectra were recorded by a Bruker Avance 500 spectrometer at the Center of Advanced Instrumental Analysis at Kyushu University, and the chemical shifts (in ppm) were referenced relative to the residual protic solvent peak. 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 μm). The UV-vis absorption spectra were measured by a Hitachi U-3300 spectrophotometer at room temperature. The IR spectra were recorded by a JASCO FT-IR 460 plus KH spectrophotometer using KBr discs. The MALDI-TOF mass spectra were obtained by a Bruker autoflex II using 6-aza-2-thiothymine as the matrix. The ESR spectra were obtained on a Bruker EMX 8/2.7 spectrometer. The TEM image was acquired using a Hitachi H-8000 (acceleration voltage 200 kV) and the THF solution of polymer was cast on a carbon grid for the TEM measurement. Gel permeation chromatography (GPC) was carried out using a Hitachi ELITE LaChrom apparatus combined with diode array L-2455 and FL L-2485 attachments using three connected columns, Shodex GPC KD-805, KD-804 and KD-802, and DMF containing 5 mM LiBr as eluent.

Dynamic Light Scattering (DLS).

DLS was measured with a Zetasizer NanoZS (MALVERN) instrument at 25 °C using an incident He-Ne laser (633 nm). The correlation time of scattered light intensity $G(\tau)$ was measured several times and their averaged data were fitted to the equation 1, where B is the baseline, A is amplitude, q is scattering vector, τ is delay time, and D is the diffusion coefficient.

$$G(\tau) = B + A \exp(-2q^2 D\tau) \qquad (1)$$

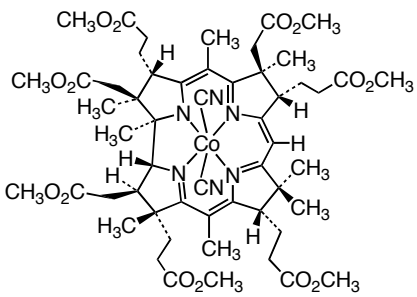
The hydrodynamic radius (R_H) of the scattering particles was calculated by the Stokes-Einstein equation (eq. 2), where η is solvent viscosity, k_B is Boltzmann's constant and T denotes the absolute temperature.

$$R_H = k_B T / 6\pi \eta D \qquad (2)$$

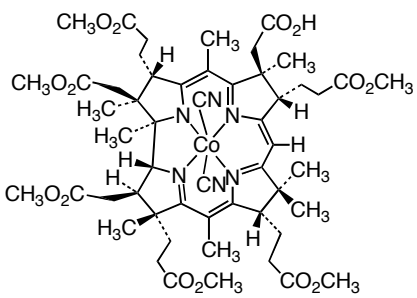
The polymer was dissolved in THF and the solution was passed through a 0.45-μm filter (HLC-disk, Kanto Chemical Co., Inc.).

Chemicals.

All solvents and chemicals used in the syntheses were of reagent grade and were used without further purification. DMF was of spectroscopic grade (WAKO, Japan) for UV-vis and PL measurements. 4-Amino-methylstyrene and 4'-methyl-2,2'-bipyridine-4-carboxylic acid were synthesized by reported procedures.[S1,S2] Dicyano heptamethyl cobyrinate (Chart 1) was synthesized by a previously reported method.[S3,S4] Synthesis of c-acid [Coα,Coβ-(di(cyano-κC)cob(III)yrinic acid-a,b,d,e,f,g-hexamethyl ester) (Chart 1) was previously reported by Keese[S5] and our groups.[S6]



Dicyano heptamethyl cobyrinate



c-Acid [Coα,Coβ-(di(cyano-κC)cob(III)yrinic acid-a,b,d,e,f,g-hexamethyl ester

Chart 1.

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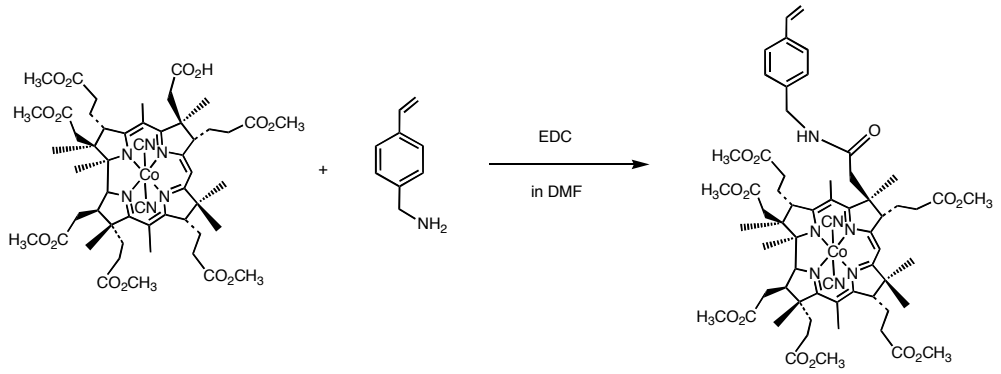
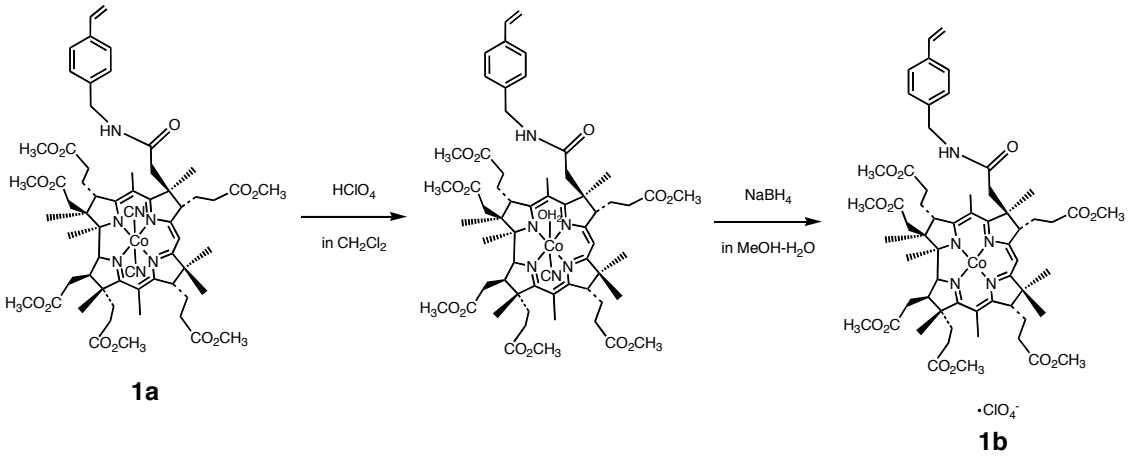
Synthesis of B_{12} derivative 1a.



In 2 mL of dry CH_2Cl_2, 200 mg (0.186 mmol) of c-acid [Coα,Coβ-(di(cyano-κC)cob(III)yrinic acid-a,b,d,e,f,g-hexamethyl ester), 117 mg (0.959 mmol) of dimethyl aminopyridine, and 176 mg (0.919 mmol) of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC•HCl) were dissolved and the solution was stirred at 0 °C using an ice-bath under nitrogen atmosphere. To the solution was then added 133 mg (1.0 mmol) of 4-amino-methylstyrene, and the mixture was further stirred for 6 hr at 0 °C, then for12 hr at room temperature. To the resulting purple solution was added 50 mL of water followed by extract with CCl_4 (50 mL x 3). The organic layer was washed with 100 mL of 3% HCl aqueous solution, 100 mL of 5% KCN aqueous solution, and finally water (100 mL x 2). After drying over anhydrous Na_2SO_4, the CCl_4 extract was concentrated to dryness. The product was reprecipitated from CH_2Cl_2 upon addition of hexane to afford a purple powder. Yield 60 %; IR, ν/cm^{-1}: 1735 (ester C=O, str.), 1663 (amido C=O, str.), 1552 (amido N-H, str.). TOF MS (MALDI, *m/z*): $[M\text{-}CN]^+$, 1163, $[M\text{-}2CN]^+$, 1137. UV-vis (in CH_2Cl_2, nm), 315, 371, 504, 548, 587.

Synthesis of B_{12} derivative 1b.



A solution of **1a** (50 mg, 0.042 mmol) in CH_2Cl_2 (200 mL) was washed with 100 mL of 30% $HClO_4$ aqueous solution. The resulting red CH_2Cl_2 solution was further washed with water (100 mL x 3) and dried over anhydrous Na_2SO_4. The filtrate was then concentrated to dryness. The product was reprecipitated from benzene upon addition of hexane to afford a red powder. The obtained powder was dissolved in 200 mL of MeOH-H_2O (3:1, v/v) and $NaBH_4$ (0.5 g, 1.32 mmol) was added under bubbling nitrogen. The color of the solution immediately changed to dark green, then 1 mL of 30 % $HClO_4$ aqueous solution was added. The product was extracted with 200 mL of CH_2Cl_2, and the CH_2Cl_2 extract was washed with H_2O (100 mL x 3) and dried over anhydrous Na_2SO_4. The filtrate was then concentrated to dryness. The product was reprecipitated from benzene upon addition of hexane to afford a red powder. Yield 78 %; IR, ν/cm^{-1}: 1735 (ester C=O, str.), 1663 (amide C=O, str.), 1552 (amide N-H, str.), 1120 (ClO_4^-, str.). TOF MS (MALDI, *m*/*z*): $[M-ClO_4]^+$, 1137. UV-vis (in CH_2Cl_2, nm), 315, 353, 406, 468.

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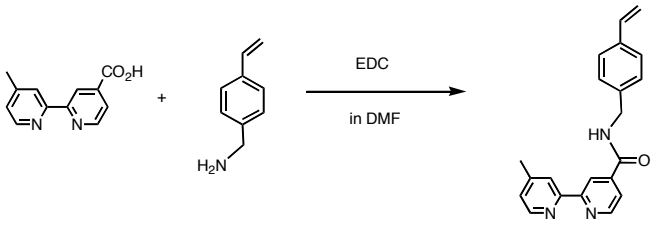
Synthesis of bipyridine derivative (L1).



L1

In 5 mL of dry DMF, 302 mg (1.4 mmol) of 4'-methyl-2,2'-bipyridine-4-carboxylic acid,[2] 394 mg (3.2 mmol) of dimethyl aminopyridine, and 622 mg (3.2 mmol) of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC•HCl) was dissolved and the solution was stirred at 0 °C using an ice-bath under nitrogen atmosphere. Then, to the solution was added 226 mg (1.7 mmol) of 4-amino-methylstyrene[1] and further stirred for 4 hr at 0 °C, then 24 hr at room temperature. After the resulting solution was pored into aqueous sodium carbonate solution, (>pH10), obtained white precipitate was collected by filtration. The product was recrystalized from methanol to afford a purple powder. Yield 45 %; TOF MS (MALDI, *m/z*): $[M+H]^+$, 330. ^{1}H NMR ($CDCl_3$, 500 MHz): δ=2.45 (s, 3H, -CH_3), 4.65 (d, 2H, -CH_2-), 5.26 (d, 1H, =CH_2), 5.75 (d, 1H, =CH_2), 6.68-6.74 (m, 1H, -CH=CH_2), 6.81 (s, 1H, NH), 7.16 (d, 1H, Ph), 7.32-7.41 (m, 4H, Ph), 7.81 (d, 1H, Ph), 8.28 (s, 1H, Ph), 8.50 (d, 1H, Ph), 8.61 (s, 1H, Ph), 8.79 (s, 1H, Ph).

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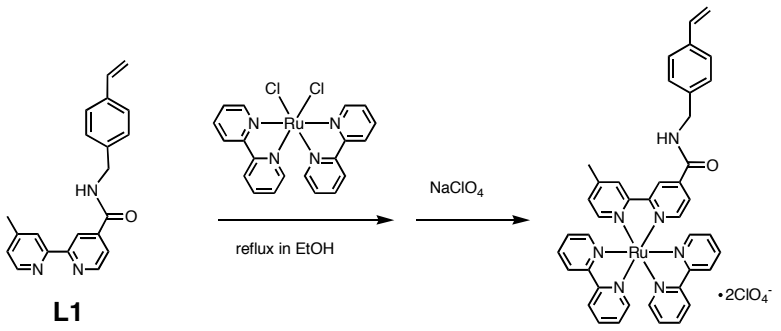
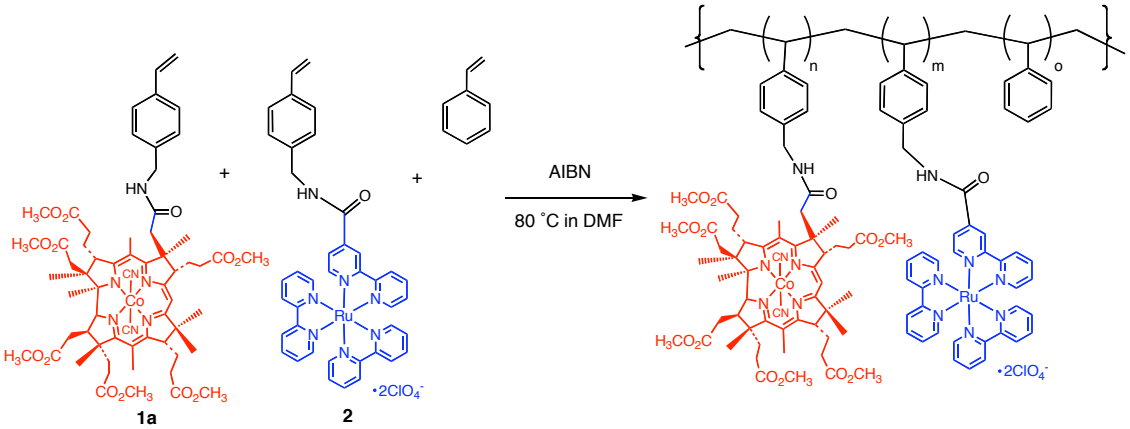
Synthesis of ruthenium trisbipyridine derivative (2).



The bipyridine derivative **L1** (60.5 mg, 0.18 mmol) and $Ru(bpy)_2Cl_2$ (158 mg, 0.36 mmol) were dissolved in ethanol (4 mL)-water (0.1 mL) under nitrogen, and the solution was refluxed for 24 hr. Then the solution was cooled to room temperature and resulting precipitate was removed by filtration. The resulting solution was evaporated under reduced pressure and residue was chromatographed on Sephadex LH-20 using CH_2Cl_2 as the eluent. The CH_2Cl_2 solution washed with saturated aqueous $NaClO_4$ solution, H_2O (100 mL x 3) and dried over anhydrous Na_2SO_4. The filtrate was then concentrated to dryness. The product was reprecipitated from CH_2Cl_2 upon addition of hexane to afford a red powder. Yield: 89 %; IR, ν/cm^{-1}: 1660 (amide C=O, str.), 1543 (amide N-H, str.), 1090, 1120, 1143 (ClO_4^-, str.). TOF MS (MALDI, *m/z*): $[M-ClO_4^-]^+$, 842. ^{1}H NMR ($CDCl_3$, 500 MHz): δ=2.60 (s, 3H, -CH_3), 4.62 (s, 2H, -CH_2-), 5.21 (d, 1H, =CH_2), 5.76 (d, 1H, =CH_2), 6.75-6.69 (m, 1H, -CH=CH_2), 7.35-7.42 (m, 5H, Ph), 7.47-7.51 (m, 4H, Ph), 7.64 (d, 1H, Ph), 7.81-7.85 (m, 4H, Ph), 7.97 (d, 1H, Ph), 8.12-8.15 (m, 4H, Ph), 8.69-8.72 (m, 5H, Ph), 9.10 (s, 1H, Ph). UV-vis (in CH_2Cl_2, nm), 288, 426, 456.

Preparation of B_{12}-Ru complex-styrene hybrid polymer (Figure 1).



The B_{12} monomer **1a** (50.3 mg, 4.23 x 10^{-5} mol), Ru monomer **2** (39.5 mg, 4.20x10^{-5} mol), styrene monomer (426.3 mg, 4.10 x 10^{-3} mol), and azobisisobutyronitrile (AIBN, 19.4 mg, 1.18 x 10^{-4} mol) were dissolved in 0.5 mL DMF, and the solution was degassed by a freeze-pump-thaw cycle. The solution was stirred for 35 hrs at 70~80 °C and then cooled to room temperature. The product was precipitated with added methanol and the obtained powder was collected by filtration and was washed with hot methanol using a Soxhlet extractor. The product was reprecipitated from CH_2Cl_2 upon addition of hexane to afford a dark brown powder 256.8 mg. The weight average molecular weight, M_w, and the degree of dispersion, M_w/M_n, of the polymer were measured by gel permeation chromatography (with a polystyrene standard) and found to be 39,000 and 1.44 respectively. IR, ν/cm^{-1}: 1661 (amide C=O, str.), 1544 (amide N-H, str.), 1090, 1119, 1142 (ClO_4^-, str.). UV-vis (in CH_2Cl_2, nm), 288, 370, 428, 456, 549, 586. The contents of B_{12} and Ru complexes in polymer were calculated by UV-vis absorptions at 456 and 586 nm, and were 8.40x10^{-5} mol/g and 7.88 x 10^{-5} mol/g of polymer, respectively. The mole ratio n:m:o was 0.97 : 1.03 : 98.

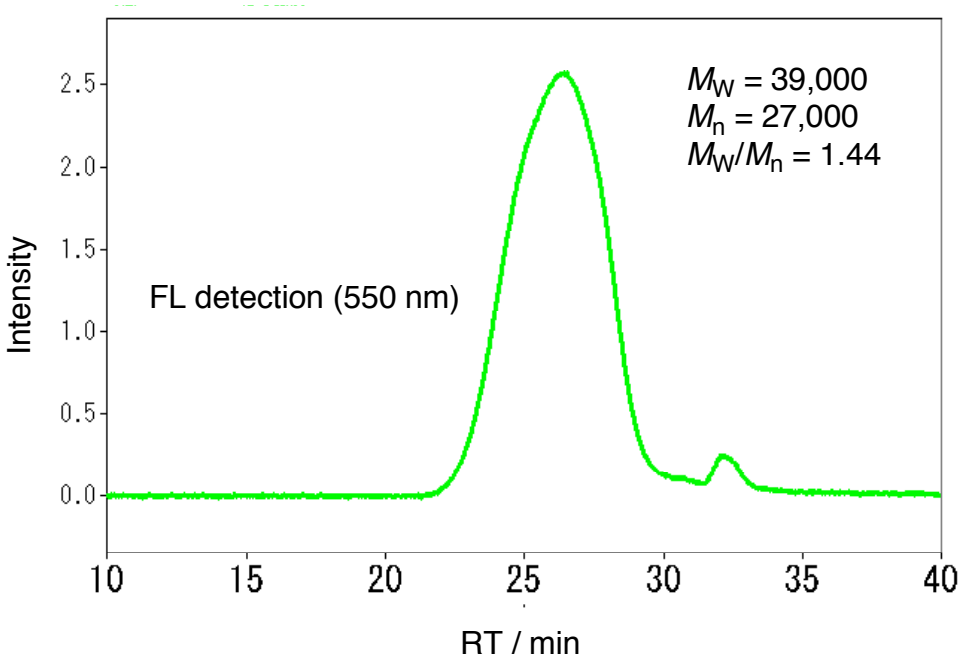


Figure S1 GPC of B_{12}-Ru complex-styrene hybrid polymer.

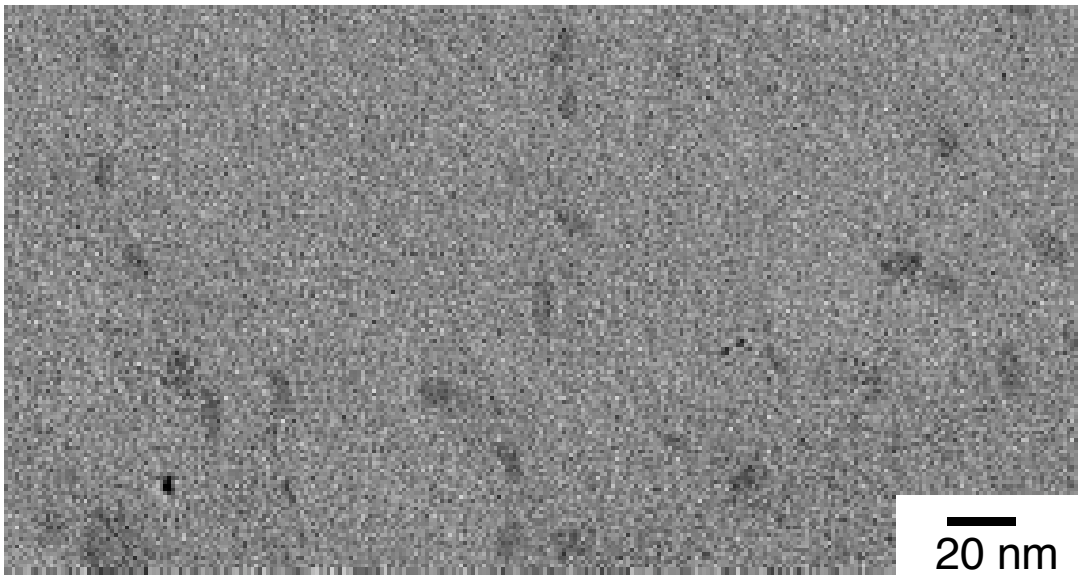


Figure S2 TEM image of B_{12}-Ru complex-styrene hybrid polymer.

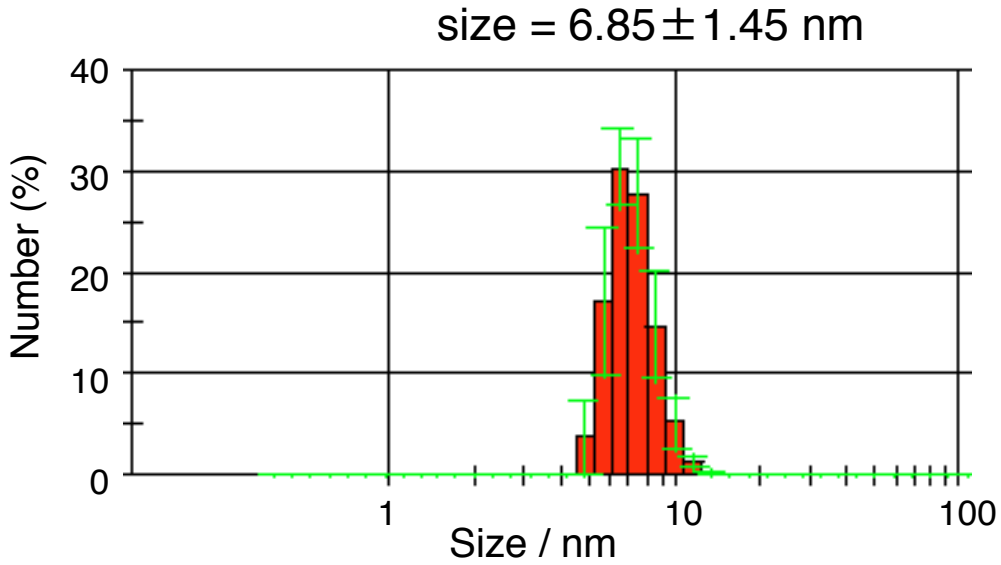


Figure S3 DLS data for B_{12}-Ru complex-styrene hybrid polymer.

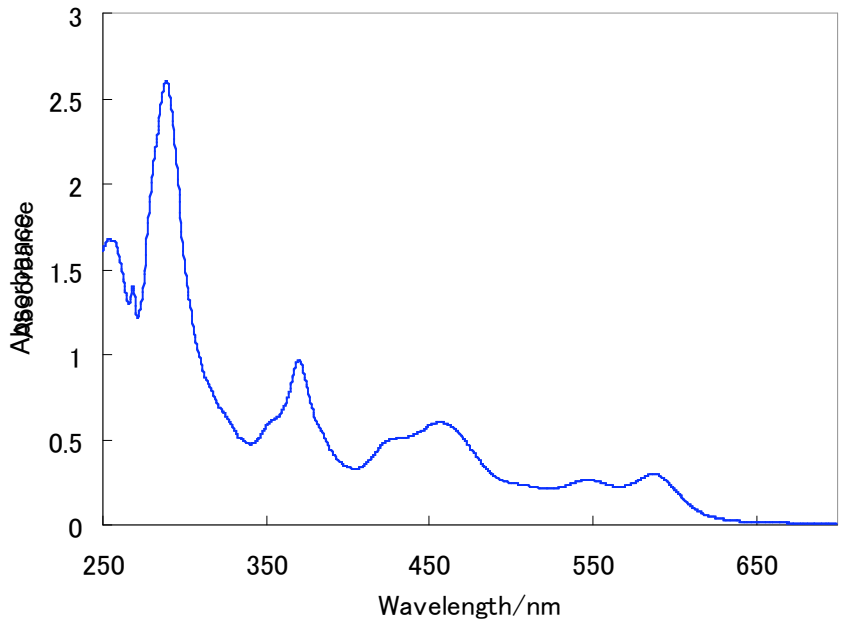


Figure S4 UV-vis spectrum of B_{12}-Ru complex-styrene hybrid polymer in CH_2Cl_2.

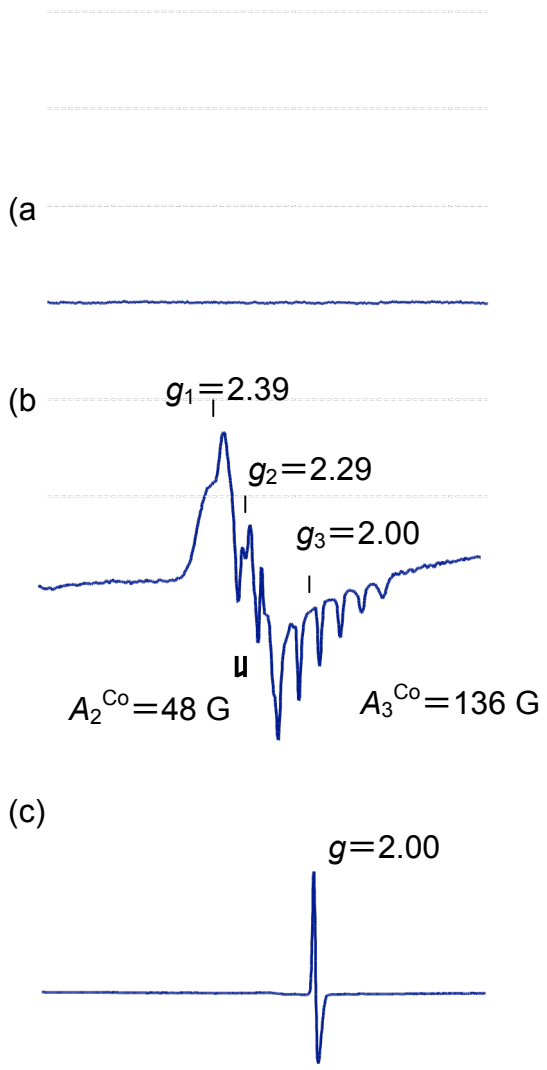
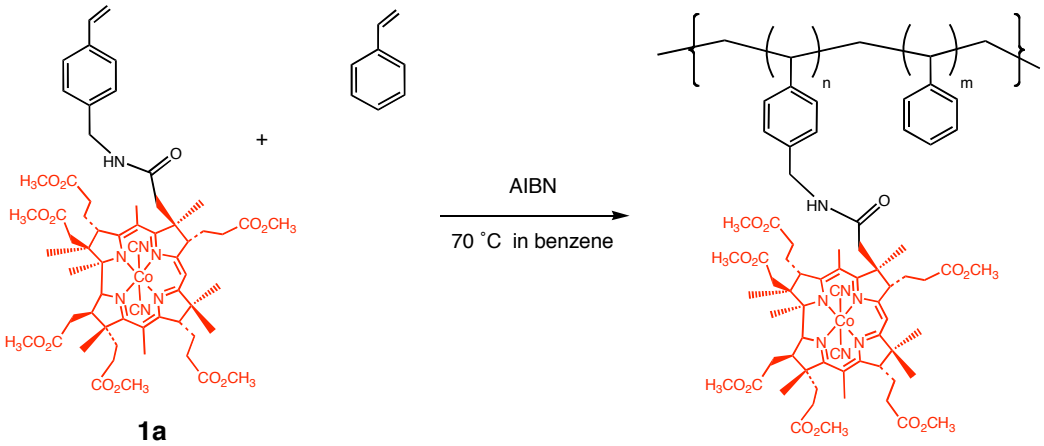


Figure S5 ESR spectral change in B_{12}-Ru complex-styrene hybrid polymer in DMF. (a) Before irradiation, (b) after 1-minute irradiation with visible light, (c) after 5-minutes irradiation with visible light.

Preparation of B_{12} complex-styrene copolymer.



The B_{12} monomer **1a** (50.3 mg, 4.23×10^{-5} mol), styrene monomer (234.3 mg, 2.25×10^{-3} mol), and azobisisobutyronitrile (AIBN, 3.7 mg, 2.3×10^{-5} mol) were dissolved in 2 mL benzene, and the solution was degassed by a freeze-pump-thaw cycle. The solution was stirred for 24 hr at 70 ˚C and then cooled to room temperature. The product was precipitated with added methanol, and the obtained powder was collected by filtration and was washed with methanol to afford a dark brown powder, 81.3 mg. The weight average molecular weight, M_w, and the degree of dispersion, M_w/M_n, of the polymer were measured by gel permeation chromatography (with a polystyrene standard) and found to be 36,000 and 1.34, respectively. IR, ν/cm^{-1}: 1660 (amide C=O, str.), 1544 (amide N-H, str.). UV-vis (in CH_2Cl_2, nm), 314, 371, 503, 545, 587. The ontent of B_{12} complex in the polymer was calculated by UV-vis absorption at 587 nm and was 1.29×10^{-4} mol/g of polymer. The mole ratio n:m was 1.7 : 98.3. The UV-vis spectrum and GPC data of the B_{12} complex-styrene copolymer were shown in Figures S6 and S7, respectively.

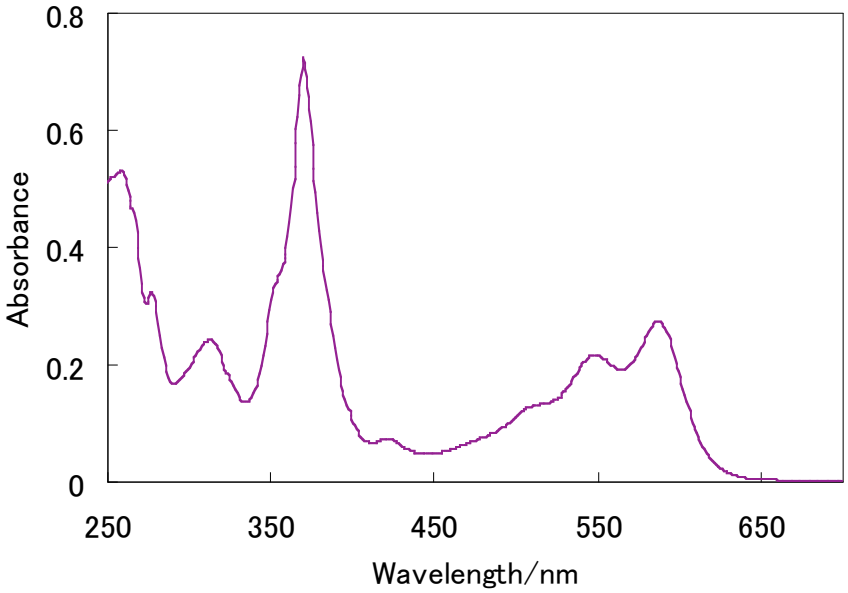


Figure S6 UV-vis spectrum of B_{12} complex-styrene copolymer in CH_2Cl_2.

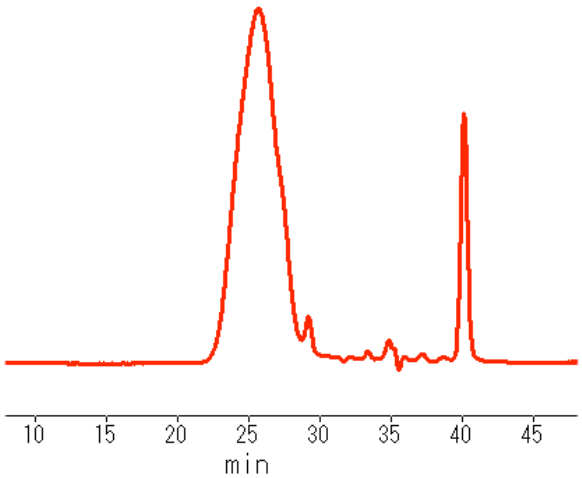


Figure S7 GPC of B_{12} complex-styrene copolymer (UV detector, 372 nm).

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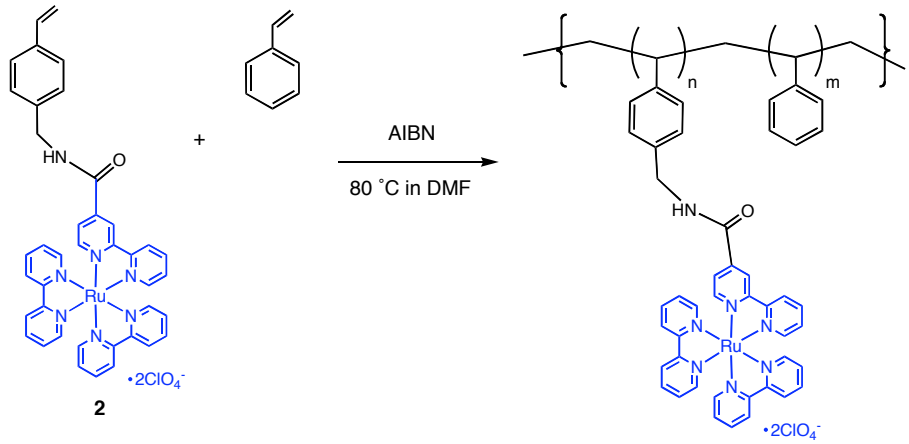
Preparation of Ru complex-styrene copolymer.



The Ru monomer **2** (19.8 mg, 2.11 x 10^{-5} mol), styrene monomer (281.4 mg, 2.70 x 10^{-3} mol), and azobisisobutyronitrile (AIBN, 4.4 mg, 2.67 x 10^{-5} mol) were dissolved in 0.2 mL DMF, and the solution was degassed by a freeze-pump-thaw cycle. The solution was stirred for 12 hr at 70~80 °C and then cooled to room temperature. The product was purified by a Sephadex LH-20 column using THF as an eluent. The product was reprecipitated with added methanol to the CH_2Cl_2 solution, and the obtained powder was collected by filtration to afford a red-purple powder, 157.8 mg. The weight average molecular weight, M_w, and the degree of dispersion, M_w/M_n, of the polymer were measured by gel permeation chromatography (with polystyrene standard) and found to be 40,000 and 1.74 respectively. IR, ν/cm^{-1}: 1660 (amide C=O, str.), 1543 (amide N-H, str.), 1089, 1119, 1142 (ClO_4^-, str.). UV-vis (in CH_2Cl_2, nm), 288, 428, 456. The content of Ru complex in the polymer was calculated by UV-vis absorption at 456 nm and was 6.33 x10^{-5} mol/g of polymer. The mole ratio n:m was 0.7:99.3. UV-vis spectrum and GPC data of the Ru complex-styrene copolymer were shown in Figures S8 and S9, respectively.

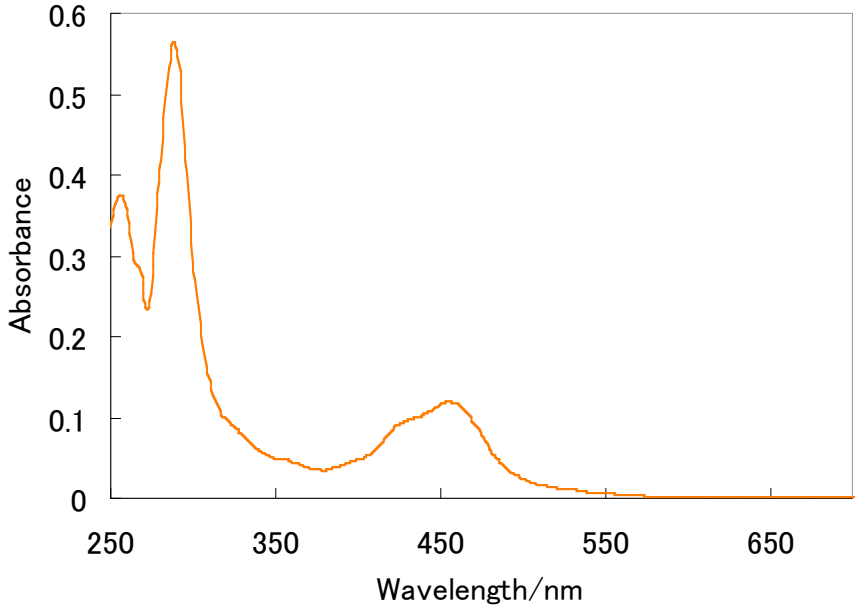


Figure S8 UV-vis spectrum of Ru complex-styrene copolymer in CH_2Cl_2.

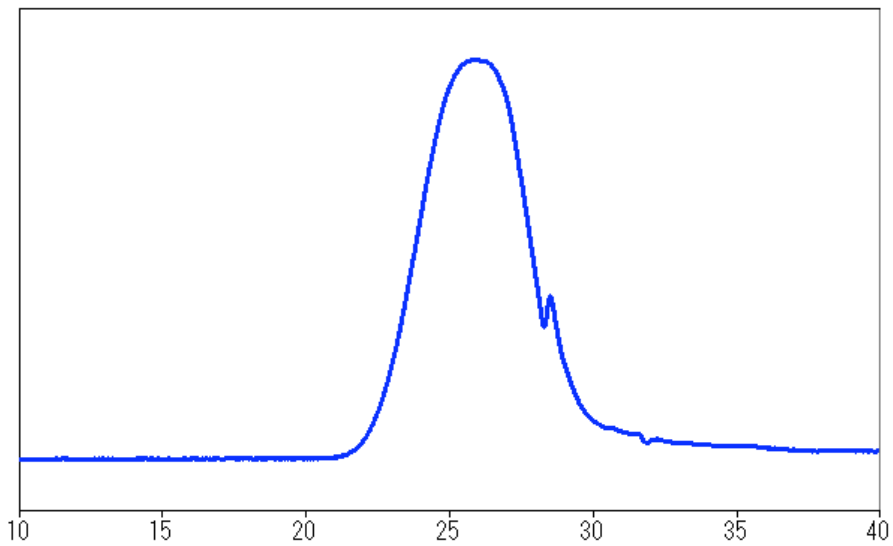


Figure S9 GPC of Ru complex-styrene copolymer (UV detector, 280 nm).

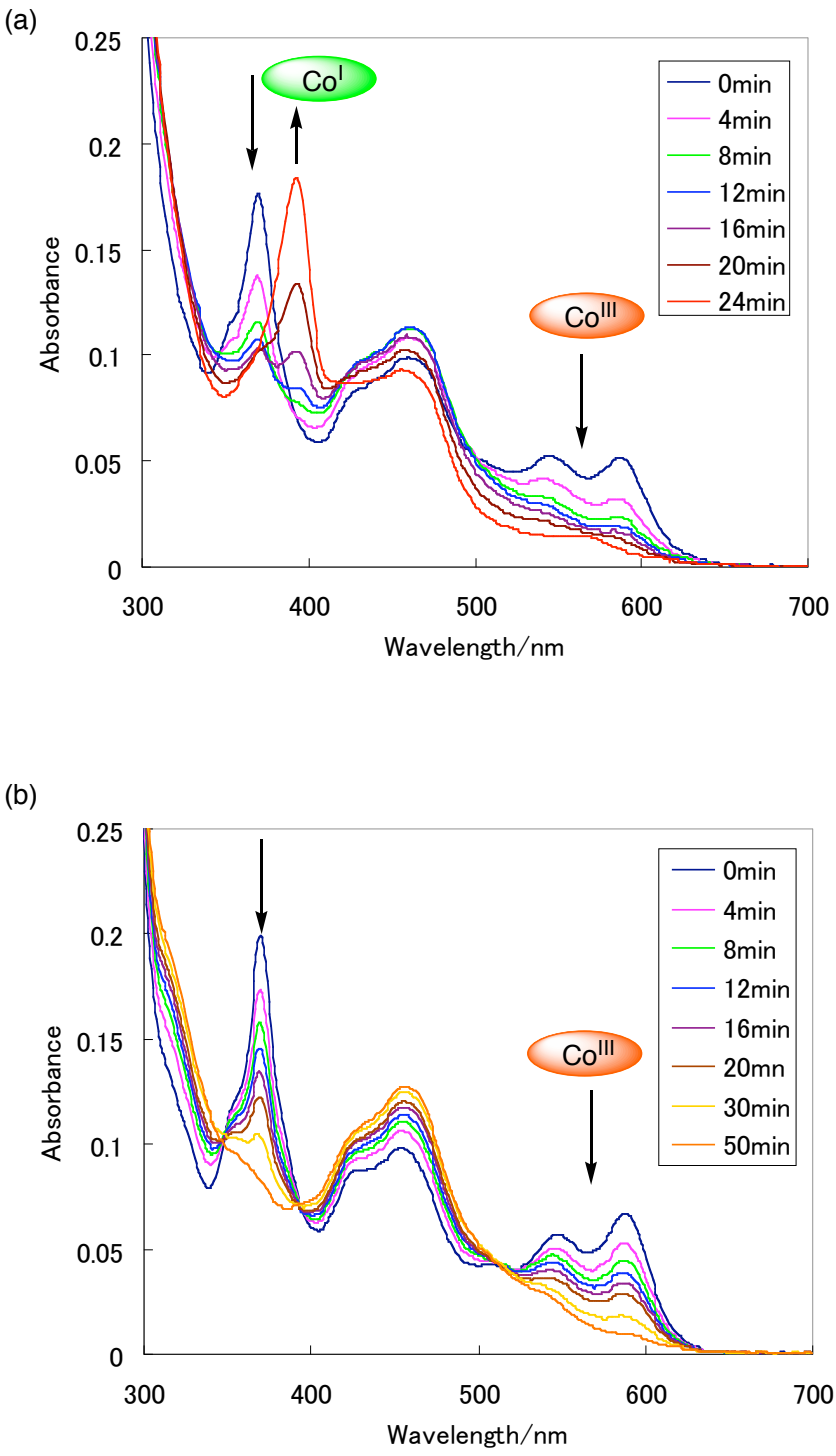


Figure S10 UV-vis spectral changes in B_{12} complex in the presence of triethanolamine (1 M) by visible light irradiation ($\lambda \geq 420$ nm) under N_2 in DMF. (a) Polymer system, [B_{12} unit] = [Ru unit] = 6 x 10^{-6} M, (b) dicyano heptamethyl cobyrinate and $[Ru(bpy)_3]Cl_2$ were used as B_{12} and Ru complexes, respectively. [B_{12}] = 6 x 10^{-6} M, [Ru complex] = 6 x 10^{-6} M.

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