

SUPPORTING INFORMATION FOR:

**Photosensitizing catalysis of B₁₂ complex without additional
photosensitizer**

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Measurements.

Elemental analyses were completed at the Service Center of Elemental Analysis of Organic Compounds of Kyushu University. The NMR spectra were recorded by a Bruker Avance 500 spectrometer at the Center of Advanced Instrumental Analysis of 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 μ m). 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 by a Bruker EMX 8/2.7 spectrometer.

Chemicals.

All solvents and chemicals used in the syntheses were of reagent grade and used without further purification. Heptamethyl cobyrinate perchlorate (Figure 1) was synthesized by a previously reported method.^{7a} The ionic liquids, *N*-methyl-*N*-propylpyrrolidinium bis(trifluoromethanesulfonyl)amide ([P13][TFSA]) and 1-butyl-3-methyl imidazolium bis(trifluoromethanesulfonyl)amide ([bmim][TFSA]) (Chart 1) were purchased from Tokyo Chemical Industry Co., Ltd. and Kanto Chemical Co., Inc., respectively, and were dried under reduced pressure for 1 day before use.

Photoreaction of B₁₂ complex, heptamethyl cobyrinate perchlorate in [bmim][TFSA].

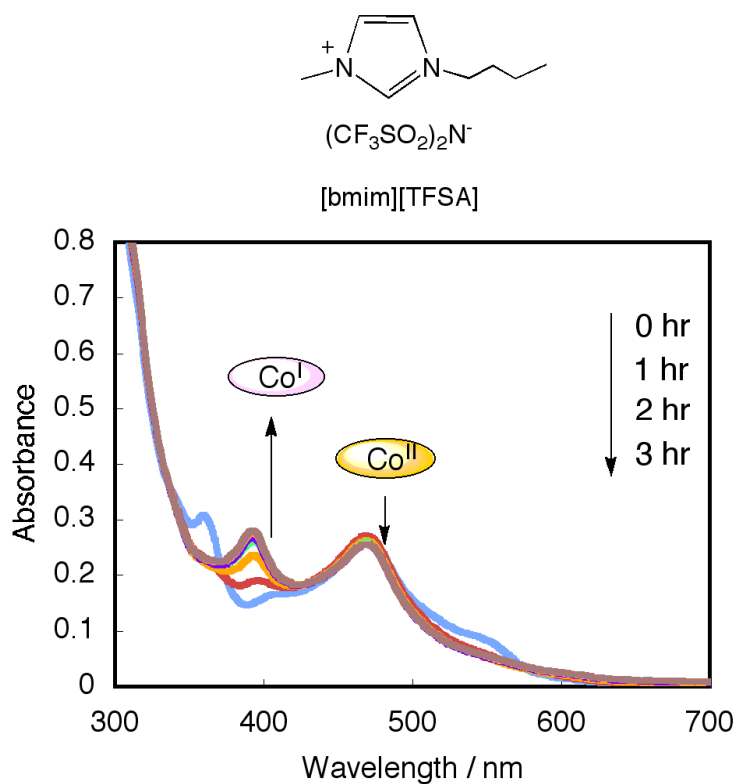


Figure S1 UV-vis spectral change of B₁₂ complex (2.9×10^{-5} M) in the presence of TEOA (0.1 M) by UV light irradiation ($\lambda_{\text{max}} = 365$ nm) under degassed condition in [bmim][TFSA].

Determination of rate constant for Co(I) formation of B₁₂ complex by UV light irradiation.

Using the change in absorption at 468 nm in Figures 2a and 2b, the rate constant (k) for the Co(I) formation was determined using the following equation at 25 ± 1 °C, where k is the rate constant, A_{468} is the absorption at 468 nm, A_{∞} is the final absorption at 468 nm, t is the irradiation time and C is a constant. The temperature was directly determined using a thermometer on the surface of the reaction cuvette during the UV light irradiation.

$$\ln(A_{468}-A_{\infty}) = -kt + C$$

Recovery of B₁₂ complex after photocatalytic reaction.

After the photocatalytic dechlorination of DDT by the B₁₂ complex, the B₁₂ complex remained in ionic liquid. The red-brown colored ionic liquid layer was dried under reduced pressure for 24 hr. The recovery of the B₁₂ complex was evaluated by UV-vis spectroscopy as shown in Figure S2.

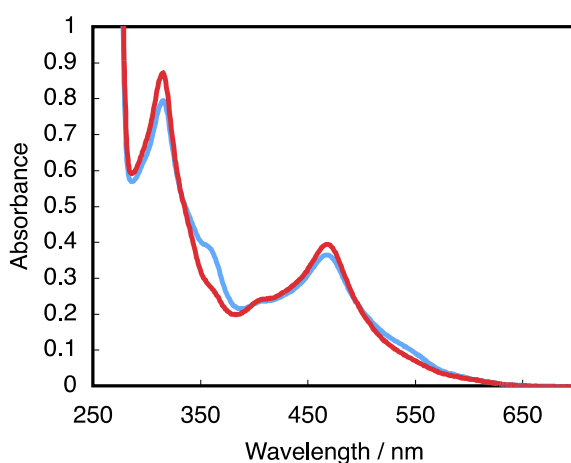


Figure S2 UV-vis spectra of B₁₂ complex in [P13][TFSA]. (a) Before photo-reaction, blue line, (b) after recovery procedure, red line.