

Synthesis and Characterization of Ligand Modified Vitamin B₁₂ and Evaluation of the Catalytic Activities

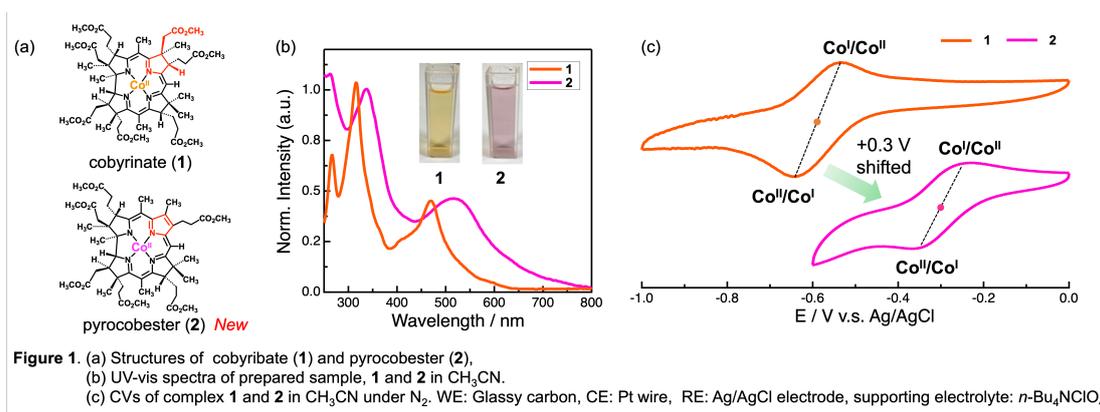
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Vitamin B₁₂ is a unique metal complex which has the cobalt ion and the corrin as a centered metal and a ligand, respectively. The Co(I) state of the vitamin B₁₂ reacts alkyl halide to form alkylated complex by the S_N2 type reaction and proceed the several catalytic reactions via alkyl radicals formed by homolysis of the cobalt-carbon bond.¹ Based on these characters of the vitamin B₁₂, many B₁₂-inspired reactions have been developed.² In general, many researchers have used the cobyrinate complex (**1**) as the B₁₂ derivatives. In this work, we succeeded the synthesis and characterization of the Co(II) state of pyrocobester (**2**) with π -expanded structure. Moreover, we clarified the catalytic reactivities of the complex.

The pyrocobester was synthesized by the pyrolysis of the cobyrinate.³ The absorption of the pyrocobester showed efficiently red-shift compared to the cobyrinate because of the conjugated corrin ligand (**Figure 1. (b)**). Furthermore, Co(II)/Co(I) redox potentials were +0.3 V shifted (**Figure 1. (c)**). In addition, the spectrum was changed after adding the CH₃I as the substrate. It is suggested that Co(I) state of pyrocobester reacted with CH₃I and alkylated complex (CH₃-Co(III)) was formed.

We constructed the eco-friendly photocatalytic system composed of the pyrocobester as the active center and tungsten oxide (WO₃) as visible light responsive photocatalyst. In this system, Co(I) species was formed under visible light irradiation by using water (or methanol) as electron source. In this presentation, we will report experimental detail of pyrocobester chemistry.



1) D. Gryko et al., *Chem. Soc. Rev.*, **2015**, *44*, 3391. 2) H. Shimakoshi, Y. Hisaeda, *Chem. Rec.*, **2021**, *21*, 2080. 3) B. Kräutler et al., *Helv. Chim. Acta.*, **1983**, *66*, 1493.