

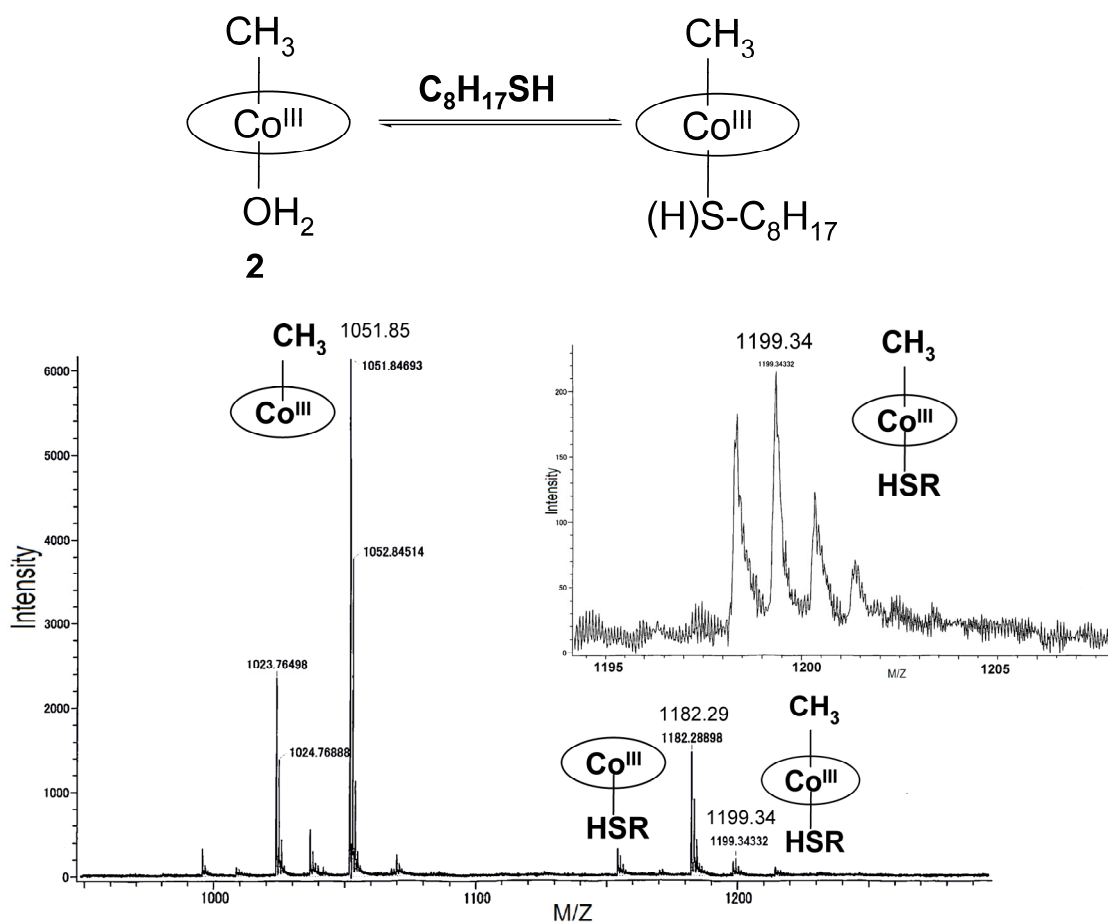
**Supplementary Information (ESI) for:**

**Vitamin B<sub>12</sub> model complex catalyzed methyl transfer reaction  
to alkylthiol under electrochemical conditions with sacrificial  
electrode**

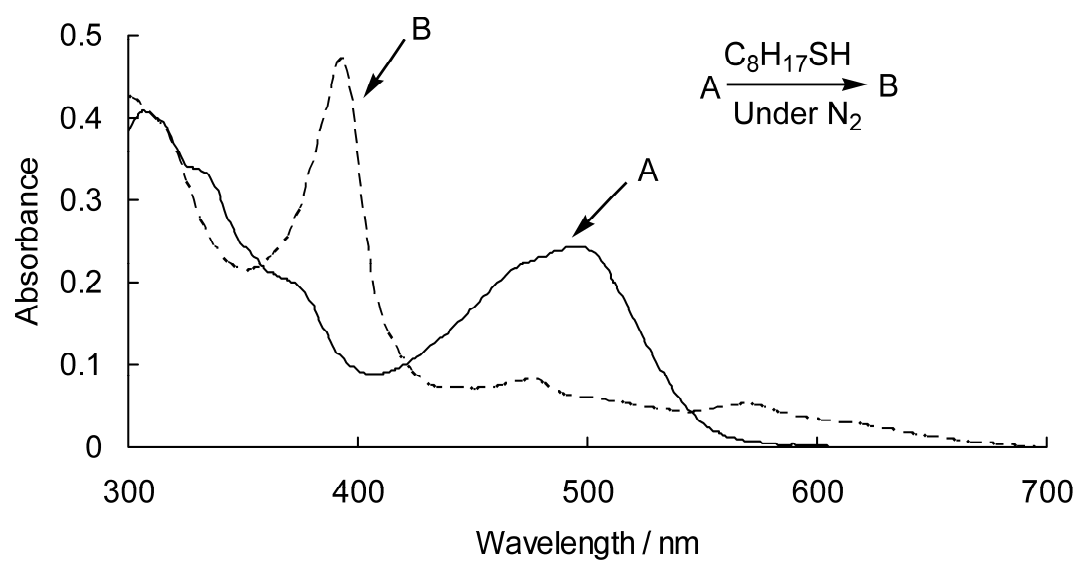
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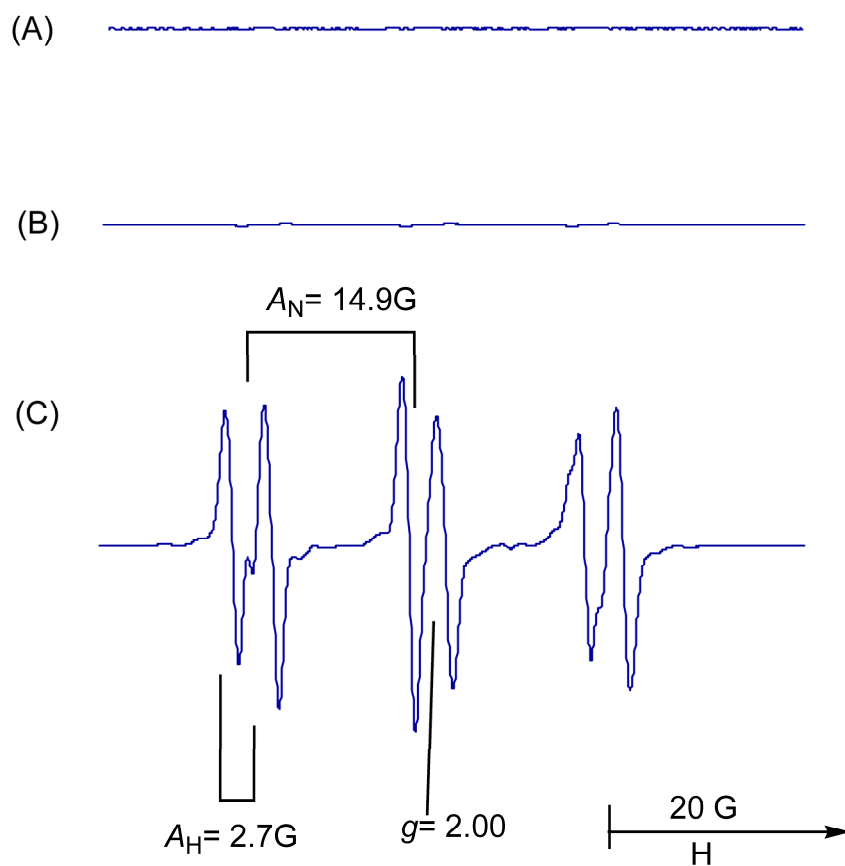
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**Fig. S1** Interaction of  $[(\text{CH}_3)(\text{H}_2\text{O})\text{Co}(\text{III})7\text{C}_1\text{ester}]\text{ClO}_4$  **2** and 1-octanethiol observed from ESI MS spectra in DMF with a 1:100 mol-equiv. for the complex **2** and 1-octanethiol.



**Fig. S2** Interaction of  $[(\text{CH}_3)(\text{H}_2\text{O})\text{Cob}(\text{III})7\text{C}_1\text{ester}]\text{ClO}_4$  **2** and 1-octanethiol observed from electronic spectra in DMF under anerobic conditions. (A): complex **2** ( $15.0 \times 10^{-5}$  M) in DMF; (B): after 1-octanethiol ( $8.7 \times 10^{-3}$  M) was immediately added.



**Fig. S3** ESR spectrum of (A): the DMF solution of  $[(\text{CH}_3)(\text{H}_2\text{O})\text{Cob}(\text{III})7\text{C}_1\text{ester}]\text{ClO}_4 \mathbf{2}$  ( $2.4 \times 10^{-3}$  M) containing  $2.3 \times 10^{-1}$  M of PBN in the dark; (B): after 1-octanethiol ( $1.1 \times 10^{-1}$  M) was added; (C): the solution of (A) was irradiated with visible light for 1 min. 1 G=0.1 mT