

Supporting information for

Excited state electron transfer after visible light absorption by the Co(I) state of Vitamin B₁₂

Darren Achey, Erinn Brigham, Brian N. DiMarco, and Gerald J. Meyer

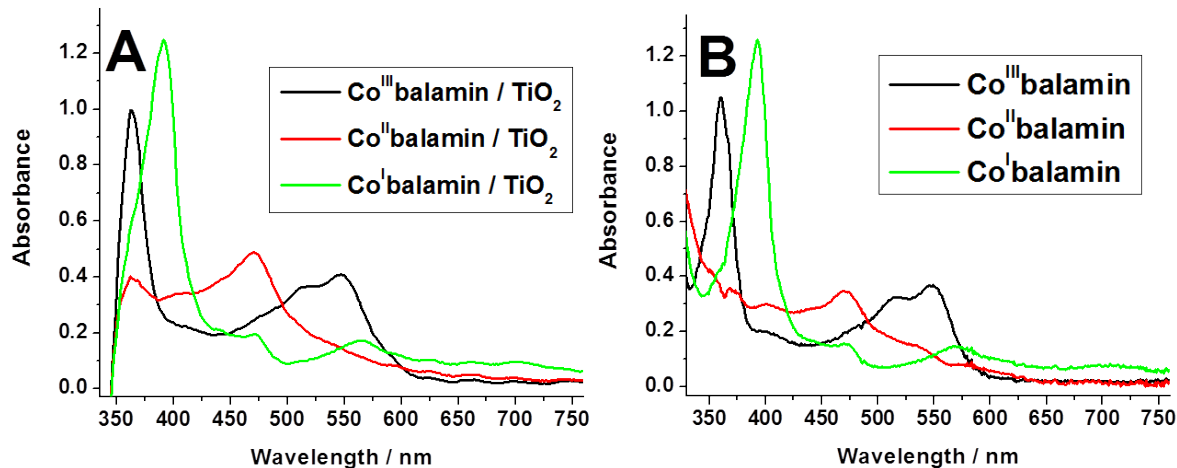


Figure S1. A) The absorbance of TiO₂|Cyanocob(III)alamin (black) and the electrochemically reduced TiO₂|Cob(II)alamin and TiO₂|Cob(I)alamin (red and green, respectively) in 100 mM TBAClO₄ CH₃CN. The contributions of the TiO₂ and TiO₂(e⁻) present at the required applied potential have been subtracted. B) The absorbance of cyanocob(III)alamin (black) in DMSO solution and the photochemically reduced cob(II)alamin (red) and cob(I)alamin (green) in DMSO solution. The photoreduction was accomplished in DMSO using a xenon lamp, Re(4,4'-diethylester-2,2'-bipyridine)(CO)₃(4-ethylpyridine)(OTf) as a photoreductant, and triethylamine as a sacrificial reductant.

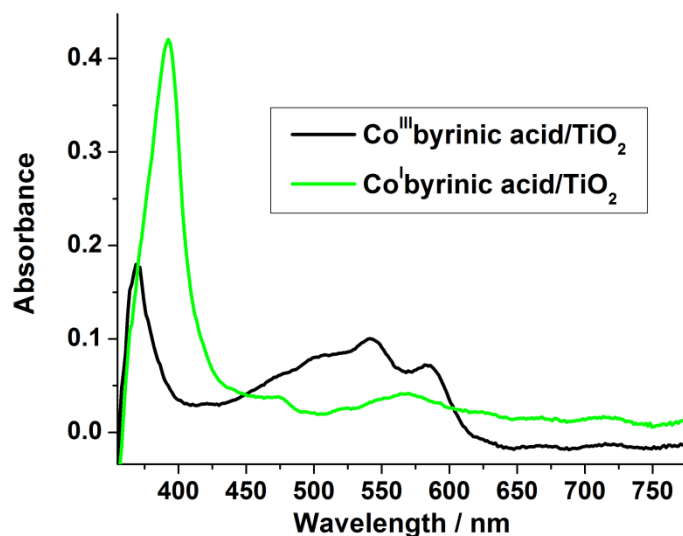


Figure S2. The absorbance of TiO_2 |Dicyanocobyrinate (black) and the electrochemically reduced TiO_2 |Cob(I)yrinate (green) in 100 mM TBAClO_4 CH_3CN . The contributions of the TiO_2 and $\text{TiO}_2(e^-)$ present at the required applied potential have been subtracted.

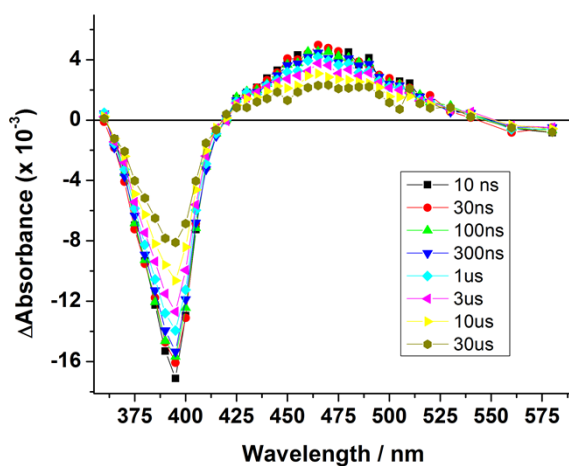


Figure S3. The change in absorbance of TiO_2 |Cob(I)yrinate after 532 nm pulsed laser excitation as a function of wavelength, at the indicated delay times.

The kinetics of interfacial charge recombination were modeled by the Kohlrausch Williams-Watts stretched exponential function¹⁻³ (Equation S1), which is commonly used for dispersive kinetics, using the least-squares error minimization with the Levenberg Marquardt iteration method in Origin 8.5:

$$\Delta Abs = A_0 e^{-\left(\frac{t}{\tau_0}\right)^\beta} \quad (S1)$$

ΔAbs is the change in absorbance, A_0 is the initial amplitude, t is time and τ_0 is a time constant, and $0 < \beta \leq 1$. The parameter β reflects the underlying distribution of rate constants; the larger β is the closer the kinetics come to being single exponential, while a small β indicates a broad distribution of lifetimes. The first moment of this function was taken as the ‘average’ lifetime, τ .⁴ The rate constant was obtained using the relation $1/k = \tau$.

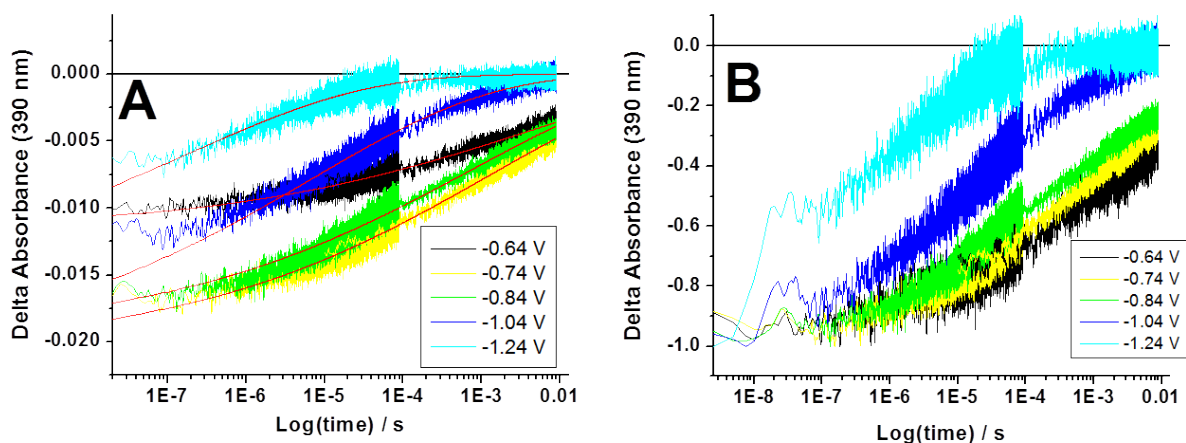


Figure S4. A) The change in absorbance of $\text{TiO}_2|\text{Cob(I)yrinate}$ at 390 nm after 532 nm pulsed laser excitation as a function of time. Fits to equation S1 with $\beta = 0.19$ are overlaid in red. B) The data in part A of this figure normalized to the initial absorbance change.

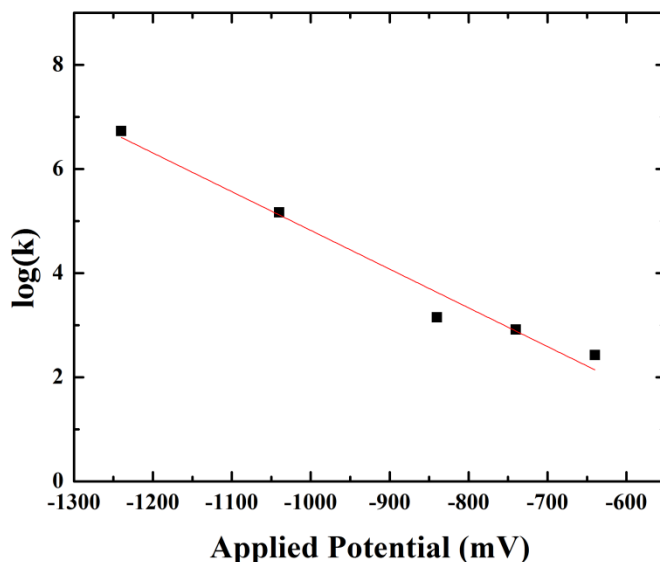


Figure S5. The logarithm of the rate constant k abstracted from the data in figure S3 using the KWW function (Equation S1) and the reciprocal relationship between lifetime and rate constant

($1/k = \tau$) plotted as a function of the applied potential vs. NHE. The relationship is similar to that seen for interfacial recombination in other TiO_2 |chromophore assemblies⁵⁻⁸

Table S1. Applied Bias and Average Lifetimes (τ).

Applied bias vs. NHE (V)	τ (κ_{WW}) (s^{-1})
-0.64	3.75×10^{-3}
-0.74	1.21×10^{-3}
-0.84	7.08×10^{-4}
-1.04	6.76×10^{-6}
-1.24	1.86×10^{-7}

Experimental

Materials. The following reagents were used as received from the indicated commercial suppliers: acetonitrile (Burdick and Jackson, spectrophotometric grade); dimethylsulfoxide (DMSO; Fisher Scientific, 99.9%); deionized water; tetra-*n*-butylammonium perchlorate (TBAClO₄; Fluka, >99.9%); tetra-*n*-butylammonium hydroxide (TBAOH; Fluka 1 M aqueous); vitamin B₁₂ (cyanocobalamin, Sigma-Aldrich, >98.5%); dicyanocobyrinic acid heptamethyl ester (Sigma-Aldrich, >95%); argon gas (Airgas, >99.998%); titanium(IV)isopropoxide (Sigma-Aldrich, 97%); fluorine-doped SnO₂-coated glass (FTO; Hartford Glass Co., Inc., 2.3 mm thick, 15 Ω/\square).

Preparations. *Sensitized Metal-Oxide Thin Film Electrode.* Transparent TiO₂ nanocrystallites (anatase, ~15 nm diameter) were prepared by hydrolysis of Ti(*i*-OPr)₄ using a sol-gel technique previously described in the literature.⁹ The sols were cast as mesoporous thin films (~5 μm thick), using Scotch tape as a spacer, by doctor blading onto transparent FTO conductive substrates. The thin films were annealed at 420^o C for 30 min under an atmosphere of O₂ flow.

The films were pretreated with aqueous base (TBAOH, pH ~ 11) for 10 min, followed by an acetonitrile wash, and were then immersed in acetonitrile solution containing cyanocobalamin (sparingly soluble) or dicyanocobyrinic acid heptamethyl ester (soluble). Over the course of 3 or more days, the films became colored (cyanocobalamin/pink, dicyanocobyrinic acid heptamethyl ester/purple) and were washed thoroughly with 100 mM TBAClO₄/acetonitrile and placed diagonally in a standard 1 cm² quartz cuvette containing the electrolyte solution. The electrolyte solution was purged with Ar(g) for at least 30 min prior to experimentation. The surface coverage, Γ , in mol / cm², was quantified from the measured absorption with the modified Beer-Lambert formula given in Equation S2,

$$Abs = 1000 \cdot \Gamma \cdot \varepsilon \quad (\text{S2})$$

where ϵ is the molar decadic extinction (absorption) coefficient, $\text{M}^{-1} \text{cm}^{-1}$, that was assumed to be unchanged whether in solution or on the surface. The complexes were typically anchored to the films in coverages of $\Gamma = 2 - 5 \times 10^{-9} \text{ mol/cm}^2$.

Spectroscopy. Steady-state UV-visible absorption spectra were obtained on either a Varian Cary 50 spectrophotometer or a Hewlett Packard 8453 Photodiode Array spectrophotometer at room temperature. Nanosecond transient absorption were obtained on an apparatus similar to that which has been previously described. Samples were irradiated with 532 nm light from a frequency doubled Q-switched, pulsed Nd:YAG laser (Quantel USA (BigSky) Brilliant B; 5-6 ns full width at half-maximum, 1 Hz, ~ 10 mm in diameter) directed 45° to the FTO side of a TiO_2 film. The excitation fluence was measured by a thermopile power meter (Moletron) and was typically $< 2 \text{ mJ/cm}^2$. A 150 W xenon arc lamp served as the probe beam (Applied Photophysics) that was aligned orthogonally to the laser excitation and directed to a monochromator (Spex 1702/04) optically coupled to an R928 photomultiplier tube (Hamamatsu). Transient data were acquired on a computer-interfaced 350 MHz digital oscilloscope (LeCroy 9450). In typical experiments, 30 laser pulses were averaged at each monitoring wavelength.

Electrochemistry. Electrochemical measurements utilized a potentiostat (BAS model CV-50W or Epsilon electrochemical analyzer) in a standard three electrode arrangement with a glassy carbon disk (solution) or sensitized TiO_2 thin film deposited on FTO glass (surface) working electrode, a Pt gauze or Pt disk (Bioanalytical Scientific Instruments, Inc.) counter electrode, and aqueous Ag/AgCl (KCl saturated) reference electrode. All potentials are reported *vs.* NHE unless otherwise noted. The ferrocenium/ferrocene ($\text{Fe}(\text{Cp})_2^{+/0}$) half-wave potential was measured both before and after experiment in a 100 mM TBAClO_4 /acetonitrile electrolyte and was used as a standard to calibrate the reference electrode. Conversion to *vs.* NHE was achieved by correcting for the expected ferrocenium/ferrocene $E_{1/2}$ of + 310 mV *vs.* the KCl-saturated aqueous calomel electrode (SCE), where SCE is +241 mV *vs.* NHE.

The general procedure for spectroelectrochemical measurements was similar to that which has been previously reported.¹⁰ Spectroelectrochemistry was executed through simultaneous application of an applied potential bias while monitoring the UV-Vis absorption of the $\text{TiO}_2|\text{Cob}$ thin film electrode which was oriented diagonally in a square quartz cuvette. The electrolyte was 100 mM tetrabutylammonium perchlorate in CH_3CN . At each potential step, a spectrum that was invariant with time was recorded. Single-wavelength absorption features plotted as a function of potential bias were proportional to the cumulative formation/loss of states. The spectra of Co(II) and Co(I) species were recorded after the associated peaks no longer grew in intensity with incrementally more negative applied bias, but before the associated peaks began to decrease in intensity with increasingly negative applied bias.

1. R. Kohlrausch, *Ann. Phys. Chem. Leipz.*, 1854, **91**, 56–82.
2. G. Williams and D. C. Watts, *Trans. Faraday Soc.*, 1970, **66**, 80–85.
3. H. Scher and E. W. Montroll, *Phys. Rev. B*, 1975, **12**, 2455–2477.
4. V. V. Pavlishchuk and A. W. Addison, *Inorganica Chim. Acta*, 2000, **298**, 97–102.
5. E. C. Brigham and G. J. Meyer, *J. Phys. Chem. C*, 2014, **118**, 7886–7893.
6. D. Achey, S. Ardo, H.-L. Xia, M. A. Siegler, and G. J. Meyer, *J. Phys. Chem. Lett.*, 2011, **2**, 305–308.
7. S. A. Haque, Y. Tachibana, D. R. Klug, and J. R. Durrant, *J. Phys. Chem. B*, 1998, **102**, 1745–1749.
8. J. Nelson, S. A. Haque, D. R. Klug, and J. R. Durrant, *Phys. Rev. B*, 2001, **63**, 205321.
9. T. A. Heimer, S. T. D’Arcangelis, F. Farzad, J. M. Stipkala, and G. J. Meyer, *Inorg. Chem.*, 1996, **35**, 5319–5324.
10. S. Ardo, D. Achey, A. J. Morris, M. Abrahamsson, and G. J. Meyer, *J Am Chem Soc*, 2011, **133**, 16572–16580.