

## Supporting Information

Ultrafast excited-state dynamics and photolysis in base-off B<sub>12</sub> coenzymes and analogs: Absence of the trans-nitrogenous ligand opens a channel for rapid nonradiative decay.

Jian Peng, Kuo-Chun Tang, Kaitlin McLoughlin, Yang Yang, Danika Forgach, and Roseanne J. Sension\*

1. Comparison of species associated difference spectra for propylcobalamin as a function of the time constant for the long decay component.

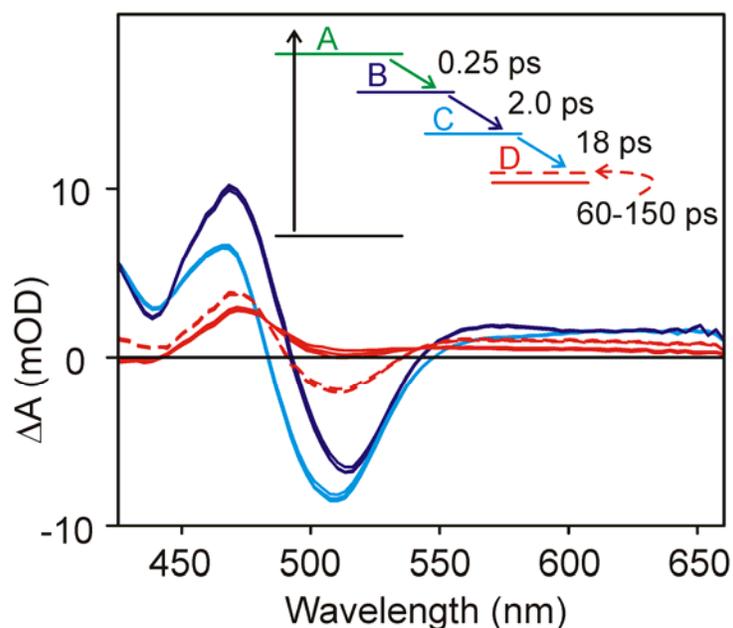


Figure S1. Species associated difference spectra calculated for PrCbl with  $\tau_4 = 60$  ps, 100 ps, and 150 ps. The precise value of this time constant has little influence on the calculated spectra of these species.

2. Calculation of estimated excitation percentages for propylcobalamin and methylcobalamin.

For PrCbl the concentration was  $1.3 \times 10^{-3}$  M and the extinction coefficient at 405 nm is  $6.5 \times 10^3$  M<sup>-1</sup> cm<sup>-1</sup>, thus the absorbance of the sample was 0.97 and 89% of the available photons were absorbed. The estimated pulse energy at the sample was 0.45 μJ. At  $4.9 \times 10^{-19}$  J/photon, absorption of 89% of incident photons will yield  $8.2 \times 10^{11}$  excited molecules. The spot size was 0.2 mm diameter and the number of molecules in the focal area was  $2.8 \times 10^{13}$ . Thus the fraction excited is estimated at  $0.82/28 = 0.03$ . This fraction is used in the reconstruction in Figure 6.

The MeCbl transient absorption was obtained with 410 nm excitation in a 0.5 mm sample cell. The concentration was  $2.1 \times 10^{-3}$  M and the extinction coefficient at 410 nm is  $5.4 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ , thus the absorbance of the sample was 0.57 and 73% of the available photons were absorbed. The estimated pulse energy at the sample was 1  $\mu\text{J}$ . At  $4.84 \times 10^{-19}$  J/photon, absorption of 73% of incident photons will yield  $1.5 \times 10^{12}$  excited molecules. The number of molecules in the focal area is estimated at  $2.0 \times 10^{13}$ . Thus the fraction excited is estimated at  $1.5/20 = 0.075$ . This fraction is used in the reconstruction in Figure 7.

### 3. Comparison of the estimated species associated spectra for AdoCbl and PrCbl.

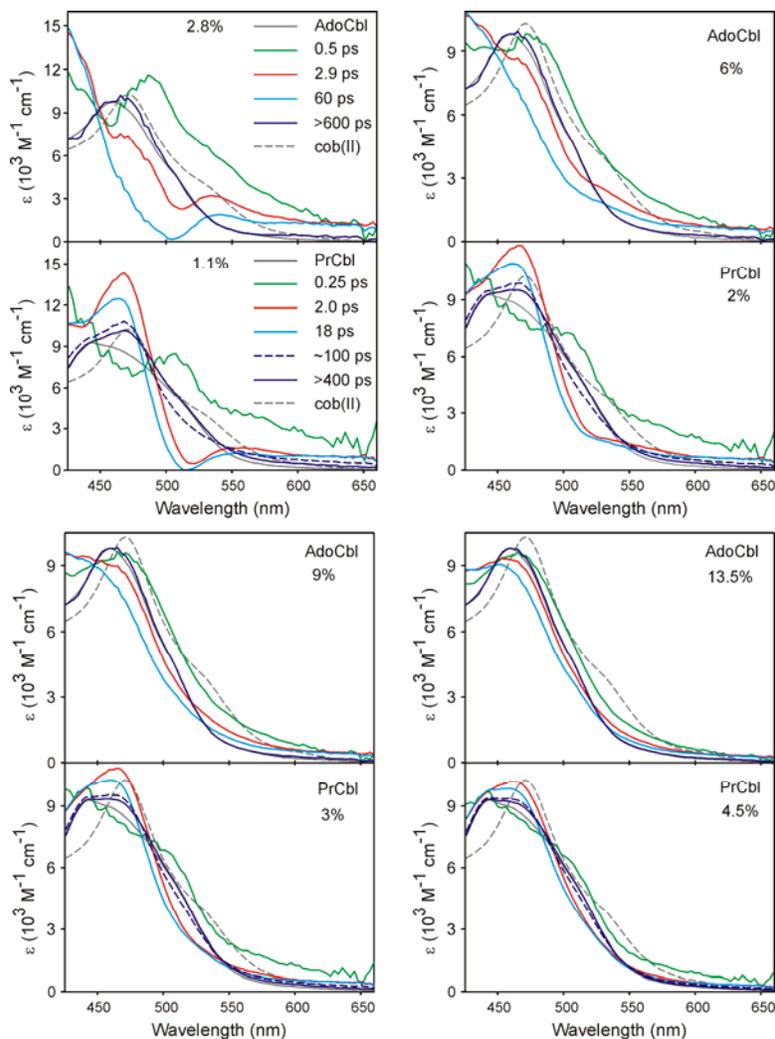


Figure S2. Calculated species associated spectra for the minimum reasonable excitation percentage retaining a positive absorbance at all wavelengths (2.8% and 1.1%), a percentage half way between the minimum and the best estimate (6% and 2%), the best estimate (9% and 3%), and a percentage 50% greater than the best estimate (13.5% and 4.5%). There are quantitative differences, but the results are qualitatively similar across this range except at the lowest excitation percentages.