Time-resolved spectroscopic studies of B_{12} coenzymes: A comparison of the primary photolysis mechanism in methyl-, ethyl-, n-propyl- and 5'-deoxyadenosylcobalamin.

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Supporting Information

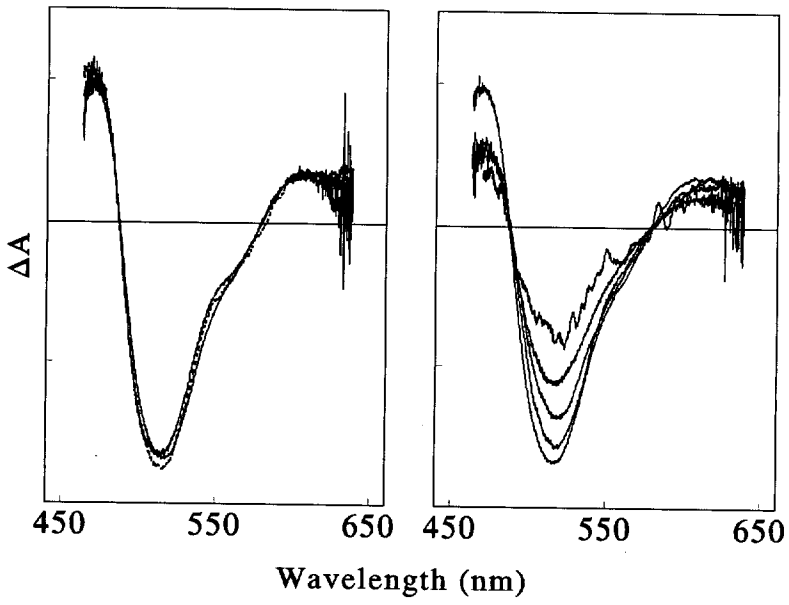

Figure S1. *Left hand panel*: Transient difference spectra obtained 15 ps (solid line), 50 ps (dashed lines) and 100 ps (solid line) after the photolysis of n-propylcobalamin at 400 nm. A modest evolution in the spectrum is observed around 550 nm over the first 50 ps. *Right hand panel*: Transient difference spectra obtained 100 ps, 200 ps, 400 ps, 800 ps and 5 ns following excitation of n-propylcobalamin at 400 nm. The spectral shape does not change on this time scale. The overall decay of the spectrum is attributed to geminate recombination of the initial radical pair.

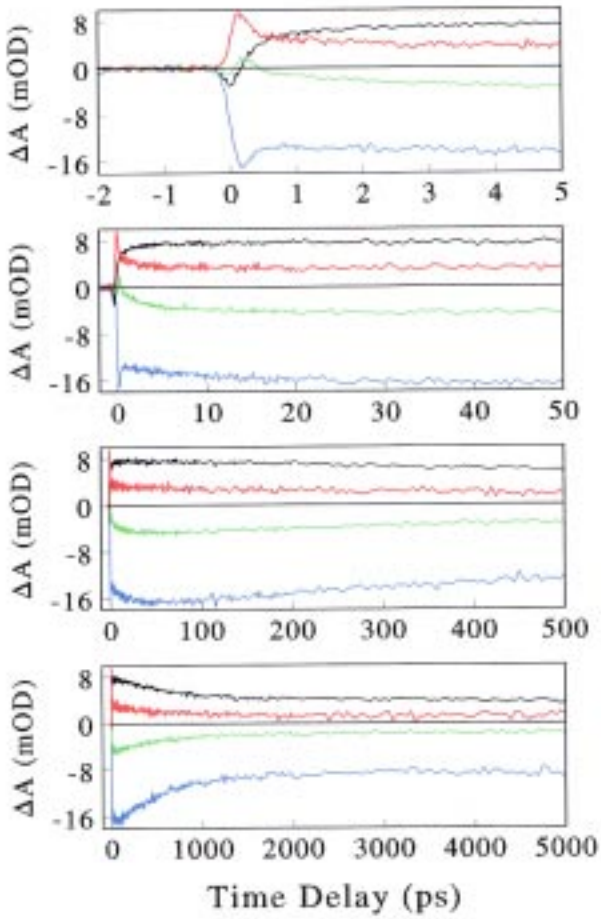

Figure S2. Transient kinetic measurements following excitation of n-propylcobalamin at 400 nm. Probe wavelengths are identified by color: 600 nm–red; 560 nm–green; 520 nm–blue; 470 nm–black.

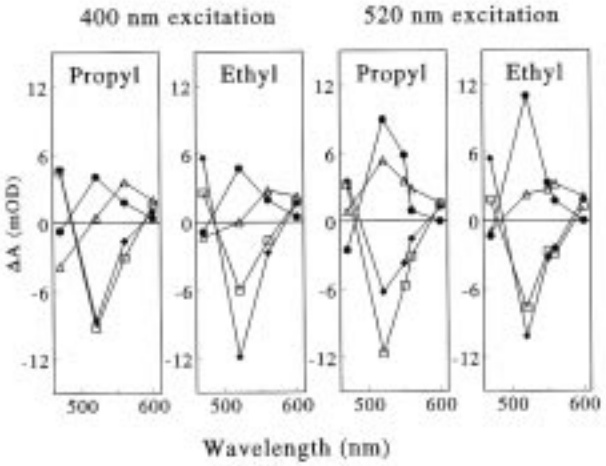

Figure S3. Decay associated difference spectra for ethyl- and n-propylcobalamin following excitation at 400 nm and 520 nm. The symbols represent:
-△- k_2, -●- k_3, -□- k_4, -◆- ∞.

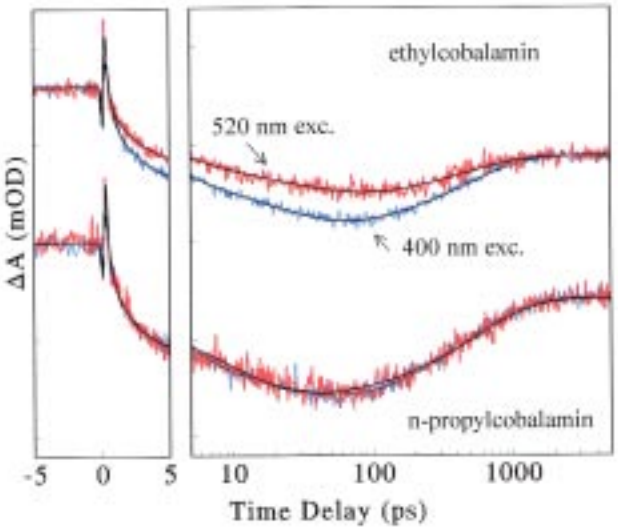

Figure S4. Comparison of transient kinetic measurements for ethylcobalamin and n-propylcobalamin following excitation at 400 nm and 520 nm, probed at 560 nm on the red edge of the bleach.

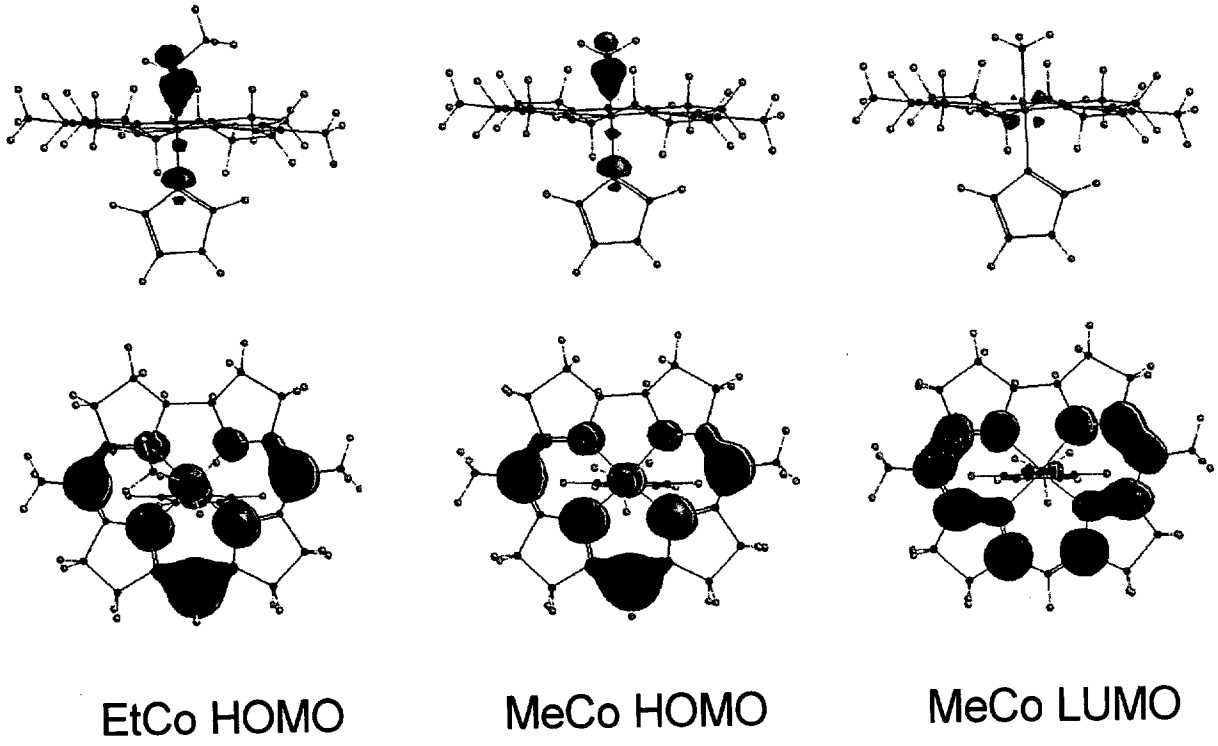

Figure S5. Two views of the HOMOs for ethyl- and methylcobalamin, and the LUMO for methylcobalamin. The top view is perpendicular to the imidazole-cobalt axis. In this view the corrin ring π orbitals have been removed to provide a better view of the axial orbitals. The lower view is along the imidazole-cobalt axis. In this view the corrin ring π orbitals have been retained.