## **Supporting Information**

## Carotenoid radical formation after multi-photon excitation of 8'-apo-βcarotenal

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**Fig. S1** Comparison of the steady-state absorption spectra of the  $\beta$ -apo-8'-carotenal in (a) *n*-hexane and (b) methanol before and after the 1300 nm multi-photon excitation experiments. Both samples were excited by the 15 mW pump.



Fig. S2 The steady-state absorption spectrum of the solvents in the NIR spectral region.



Fig. S3 Comparison of TA spectra after 280 and 480 nm excitation in (a) *n*-hexane and (b) methanol.



**Fig. S4** EADS obtained from global fitting of transient absorption data of  $\beta$ -apo-8'-carotenal in *n*-hexane (a), and methanol (b) after 280 nm excitation.