Biophysical Journal, Volume 96

Supporting Material

Femtosecond Carotenoid to Retinal Energy Transfer in Xanthorhodopsin

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Supporting Information

Salinixanthin is carotenoid with complicated structure and contains a conjugated carbonyl group (Fig. S1) that is known to alter significantly excited-state properties in polar solvents (1-3). To test if salinixanthin excited-state properties are affected by solvent polarity, both steady-state and transient absorption spectra were measured for purified salinixanthin dissolved in n-hexane and methanol. Absorption spectra of salinixanthin in both solvents are shown in Fig. S2. No significant changes were observed upon changing solvent polarity, though resolution of the vibrational bands is slightly less in methanol than in n-hexane. Yet, the magnitude of this effect, which is one of the typical markers of the polarity-dependent behavior (1-3), is significantly less than for other carbonyl carotenoids. Transient absorption spectra at 1 ps after 485-nm excitation (Fig. S3) further demonstrate negligible polarity-dependent changes. The transient absorption spectrum in methanol is broader than that in n-hexane. This effect was observed also for other carbonyl carotenoids with long (N>10) conjugated chain, and it is attributed to a broader distribution of ground-state conformers in polar solvent (4). No polarity-dependent transient absorption bands characteristic of the intramolecular charge transfer (ICT) state have been observed for salinixanthin. The minor polarity effect is further underlined by identical lifetimes of the S_1 state as shown in Fig. S4. Kinetics were recorded at 600 nm (the maximum of the S_1-S_n band) and both kinetics can be fitted by the same time components. The rise of the S_1-S_n signal has a time constant of 115 fs that corresponds to the S_2 lifetime, major (90%) decay component is 2.6 ps, and minor component of 6 ps is necessary to take into account the lifetime of the S* state.

Comparison of excited-state dynamics of xanthorhodopsin and bacteriorhodopsin is shown in Fig. S5. After excitation of retinal at 580 nm, decays of stimulated emission of xanthorhodopsin and bacteriorhodopsin differ significantly. For both samples, a biexponential fit is necessary to get a satisfying fit. For bacteriorhodopsin, time components of 0.4 ps (76%) and 1 ps (23%) were found, in agreement with previous observations (5,6). Slower components of 0.7 ps (68%) and 3.3 ps (32%) were found for xanthorhodopsin. The same time constants, 0.7 and 3.3 ps, were obtained for xanthorhodopsin excited at 490 nm (Fig. S5).

References

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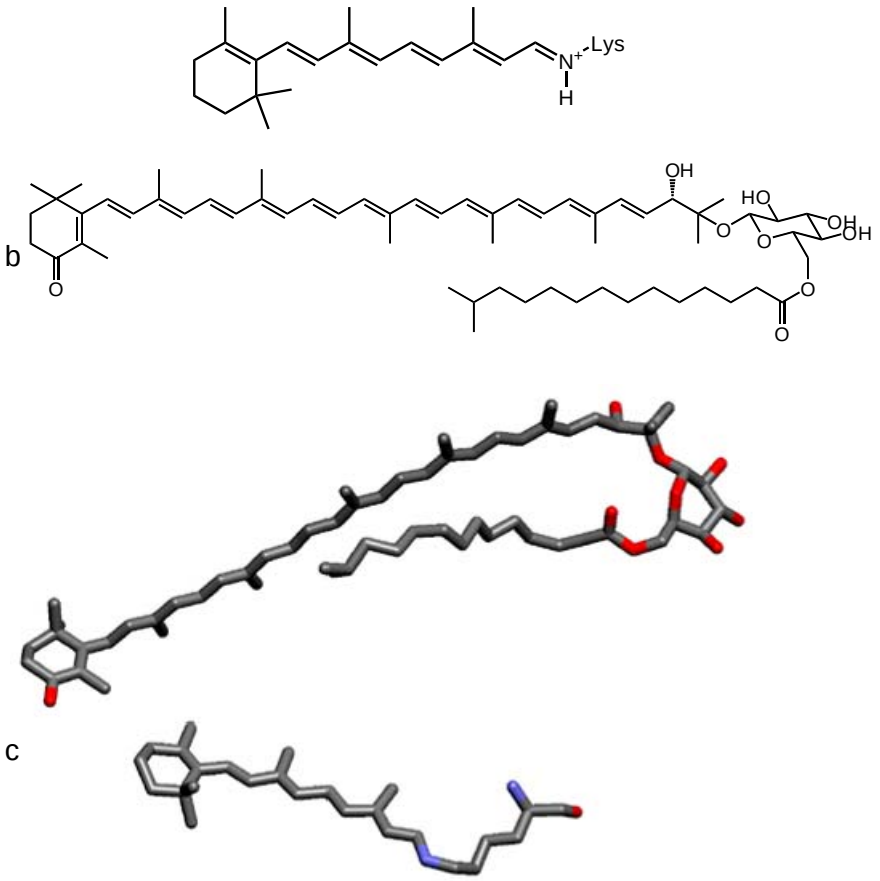

Fig. S1. Chemical structures of the retinal chromophore (a), salinixanthin (b), and mutual orientation of the chromophores in xanthorhodopsin (c).

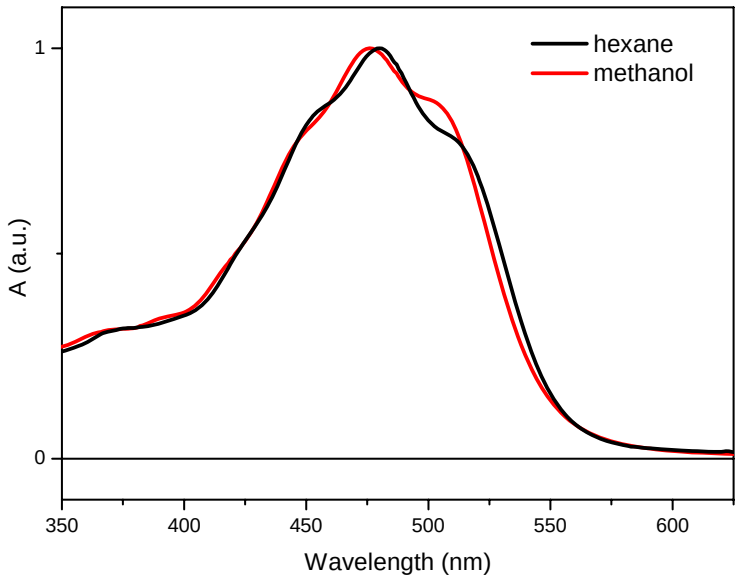

Fig. S2. Absorption spectra of salinixanthin in *n*-hexane (black) and methanol (red).

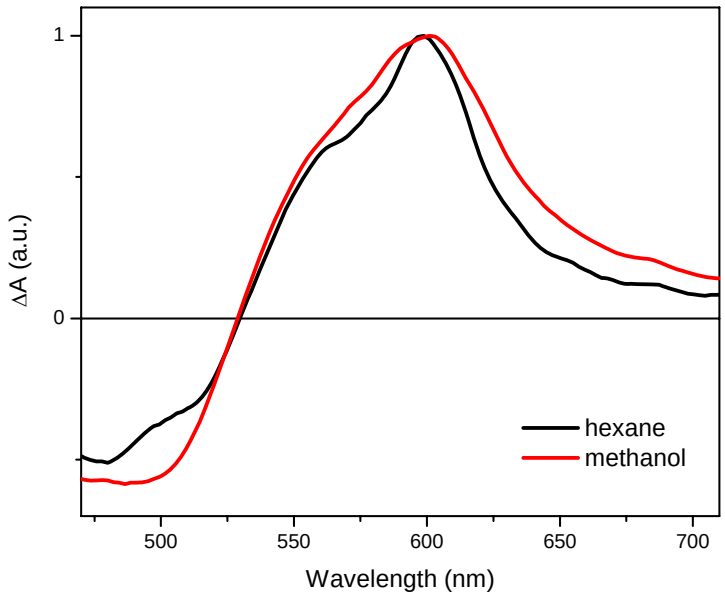

Fig. S3. Transient absorption spectra of salinixanthin in *n*-hexane (black) and methanol (red) recorded 1 ps after excitation at 485 nm. Spectra are normalized to maximum.

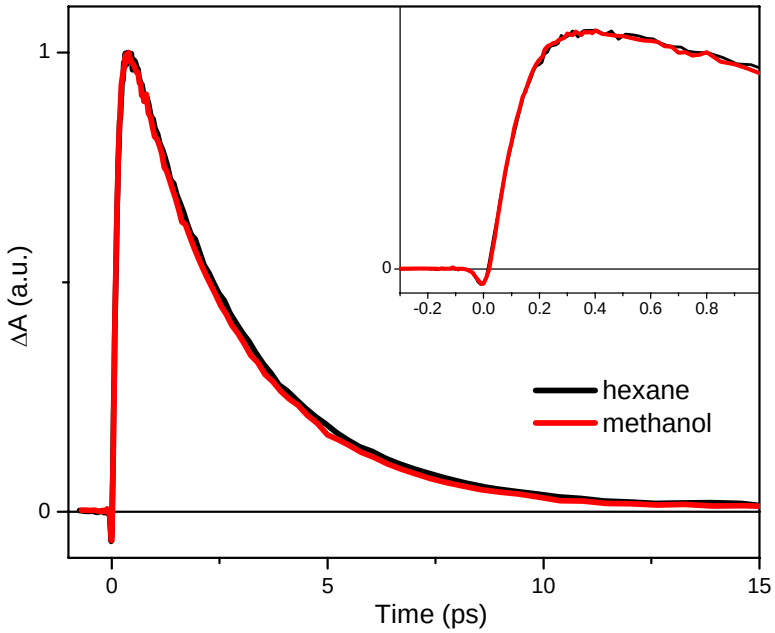

Fig. S4. Kinetics measured at the peak of the S_1-S_n transition (600 nm) for salinixanthin in *n*-hexane (black) and methanol (red). Inset shows the rise of the S_1-S_n signal.

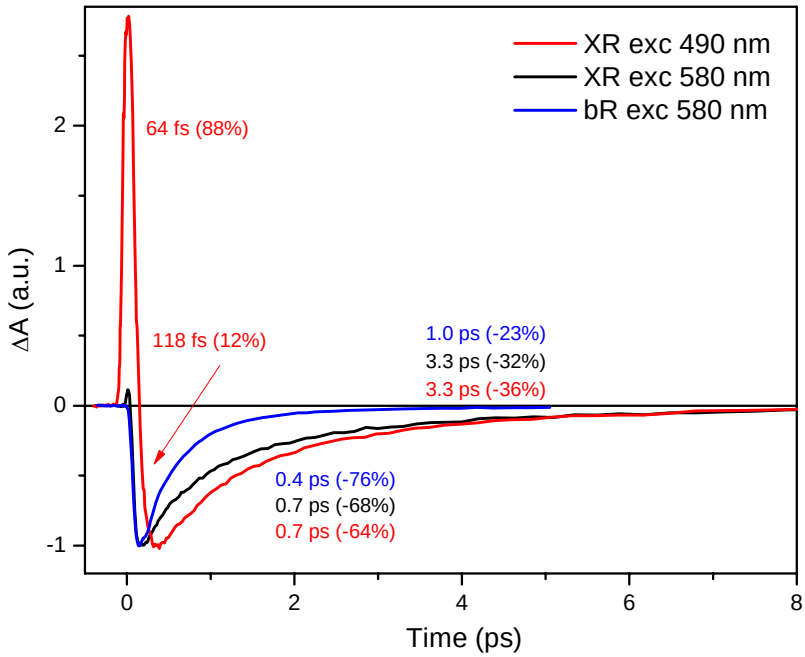

Fig. S5. Kinetics probed at 900 nm after excitation of xanthorhodopsin at 490 nm (red) and 580 nm (black), and of bacteriorhodopsin excited at 580 nm (blue). Time components and their relative amplitudes obtained from fitting have the same color code.