Supplementary Information

Synergy between Plant Phenols and Carotenoids in Stabilizing Lipid-bilayer Membranes of Giant Unilamellar Vesicles Against Oxidative Destruction

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S1. Photosensitized morphological changes of GUVs

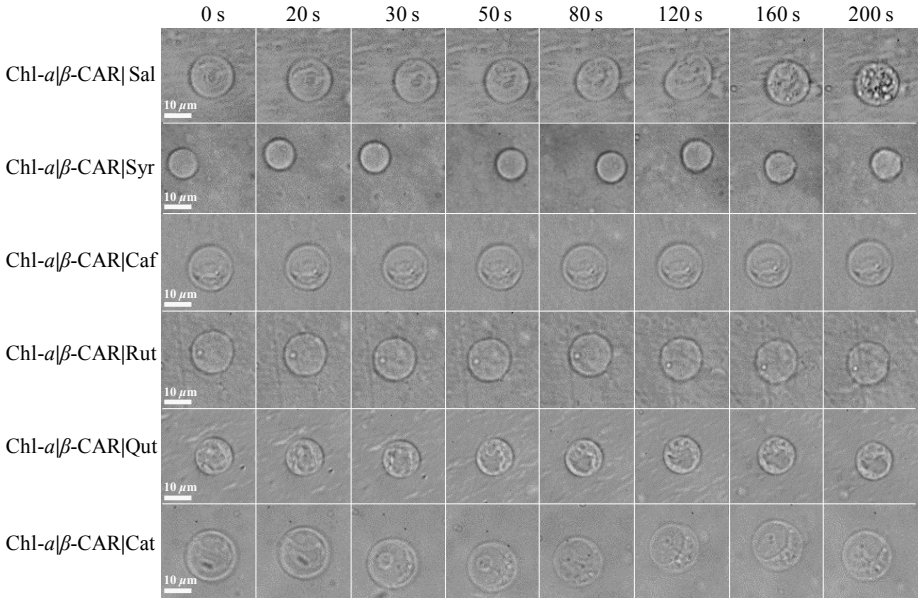

Figure S1. Optical microscopic images of GUVs recorded during the process of photosensitized oxidation. The GUVs incorporated with Chl-*a* (8.82×10^{-7} M) and *β*-CAR (4.41×10^{-7} M) were added with the indicated plant phenols (4.41×10^{-7} M; For molecular structures, see Scheme 1 of the main text).

S2. Comparison of the $\Delta\Psi$-dependence of LP, $k_{\Delta E}$ and ΔE_{end}

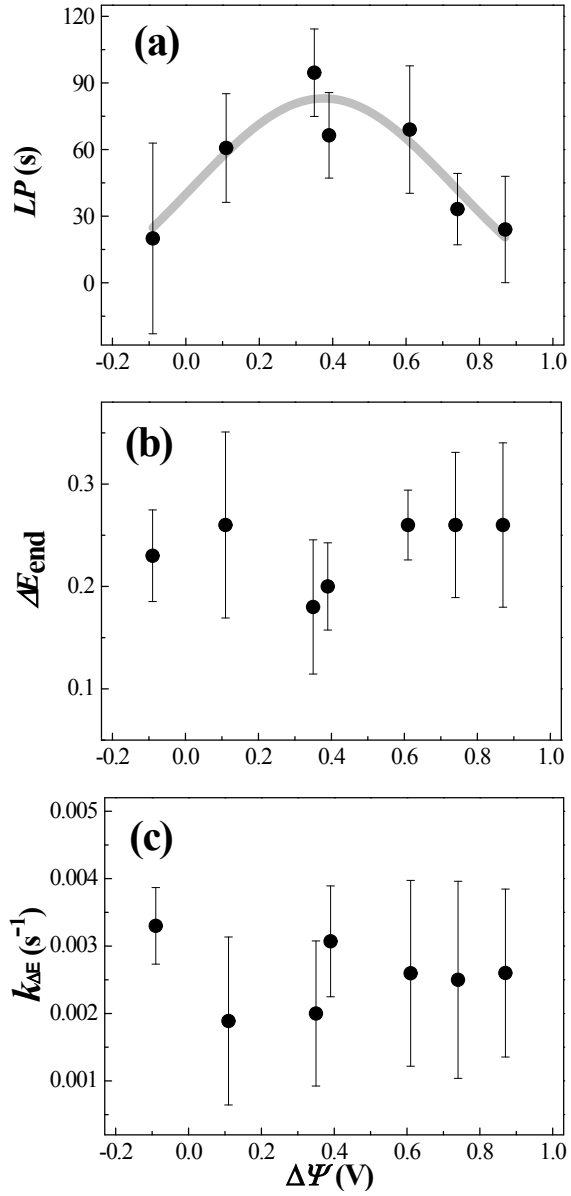

Figure S2. Plots of the parameters LP, $k_{\Delta E}$ and ΔE_{end} derived from GUV morphological changes against the potential difference between carotenoid radical cation and phenoxyl radical, $\Delta\Psi = \Psi(\beta\text{-CAR}^{\bullet+}) - \Psi(\varphi\text{-O}^{\bullet})$. The values of $\Psi(\varphi\text{-O}^{\bullet})$ and $\Psi(\beta\text{-CAR}^{\bullet+})$ are based on Ref. S1 and Ref. S2, respectively (cf. Table 1 of the main text).

S3. Quantification of relative contents of *β*-CAR in membranes by Raman spectroscopy

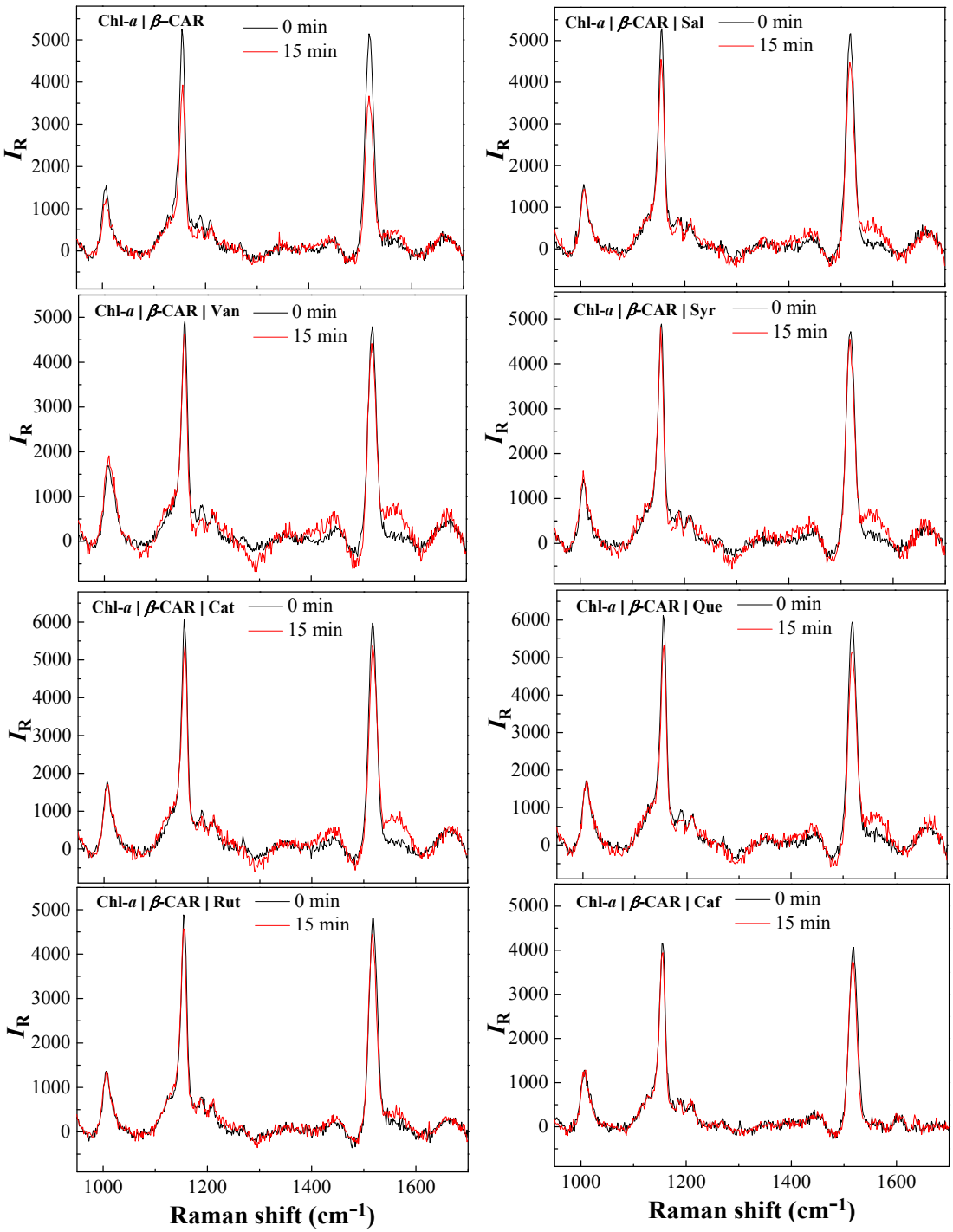

Figure S3. Raman spectra of *β*-CAR in SUV membranes doped with Chl-*a* (8.82 × 10^{-6} M) and *β*-CAR (4.41×10^{-6} M) at the presence of different plant phenols (4.41×10^{-6} M). Each panel compares the spectra recorded prior to blue-light illumination (405 nm, 30 mW) and 15 min after. The pair of key Raman lines at ~1520 cm^{-1} and ~1154 cm^{-1}, respectively, are originated from the symmetric C=C stretching (ν_1 mode) and the symmetric C-C stretching coupled with C-H bending (ν_2 mode).[S3]

S4. UV-visible absorption spectra of the SUVs preparations for laser flash photolysis

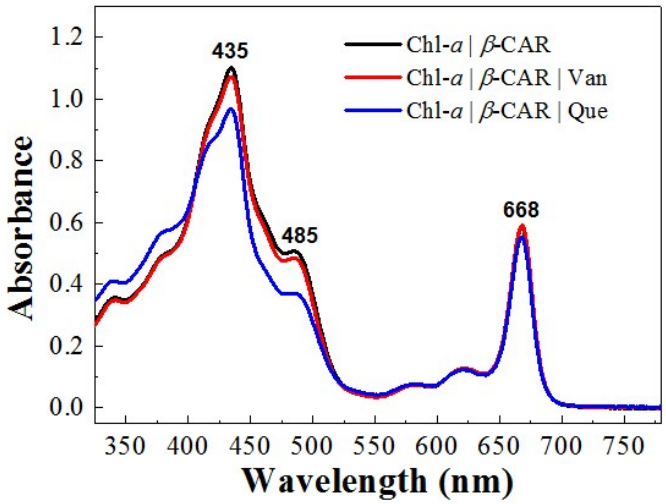

Figure S4. UV-visible absorption spectra of the SUV preparations for submicrosecond time-resolved absorption spectroscopic measurements. The SUVs were doped with Chl-*a* (7.0×10^{-6} M) and *β*-CAR (3.5×10^{-6} M) and incubated with Que or Van (3.5×10^{-6} M).

S5. Determination of the $\log_{10}$ partition coefficients and the dissociation constants of the polyphenols

TABLE S1. *n*-Octanol/water partition coefficients (log*P*) at pH 7.4 determined following the protocols as described in Ref. S4. Dissociation constants (pK_a),[a] percentages of deprotonated forms (7-O^-) and protonated neutral forms (PNF) of the plant phenols at pH 6.8.

Phenols / ***Properties***	**salicylic acid**	**vanillic acid**	**syringic acid**	**caffeic acid**	**rutin**	**quercetin**	**(+)-catechin**
log*P*	-1.05	-0.64	-1.18	-0.57	-0.22	2.07	0.08
pK_{a1}	2.79 (1-COOH)	4.16 (1-COOH)	3.93 (1-COOH)	3.45 (1-COOH)	6.37 (7-OH)	6.38 (7-OH)	9.01 (3′-OH)
pK_{a2}	13.23 (2-OH)	10.14 (4-OH)	9.55 (4-OH)	9.28 (5-OH)	7.96 (5-OH)	7.85 (5-OH)	9.62 (5-OH)
pK_{a3}					8.56 (4′-OH)	8.63 (4′-OH)	10.8 (4′-OH)
pK_{a4}					11.91 (5′-OH)	10.29 (3-OH)	12.65 (3-OH)
7-O^- (%)					69.2	57.6	
PNF (%)					25.9	25.8	99.4

[a] Calculated with Marvin Calculator Plugins. Marvin 18.24.0 2018, ChemAxon (http://www.chemaxon.com).

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