

How the sun protection factor (SPF) of sunscreen films change during solar irradiation

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Supplementary Information

Figure S1. Erythema action spectrum (upper plot) and spectral irradiance of terrestrial sunlight $S(\lambda)$ corresponding to midday midsummer sunlight for latitude 40°N , solar zenith angle 20° and ozone layer thickness equal to 0.305 cm (lower plot). Data are from ref. 1.

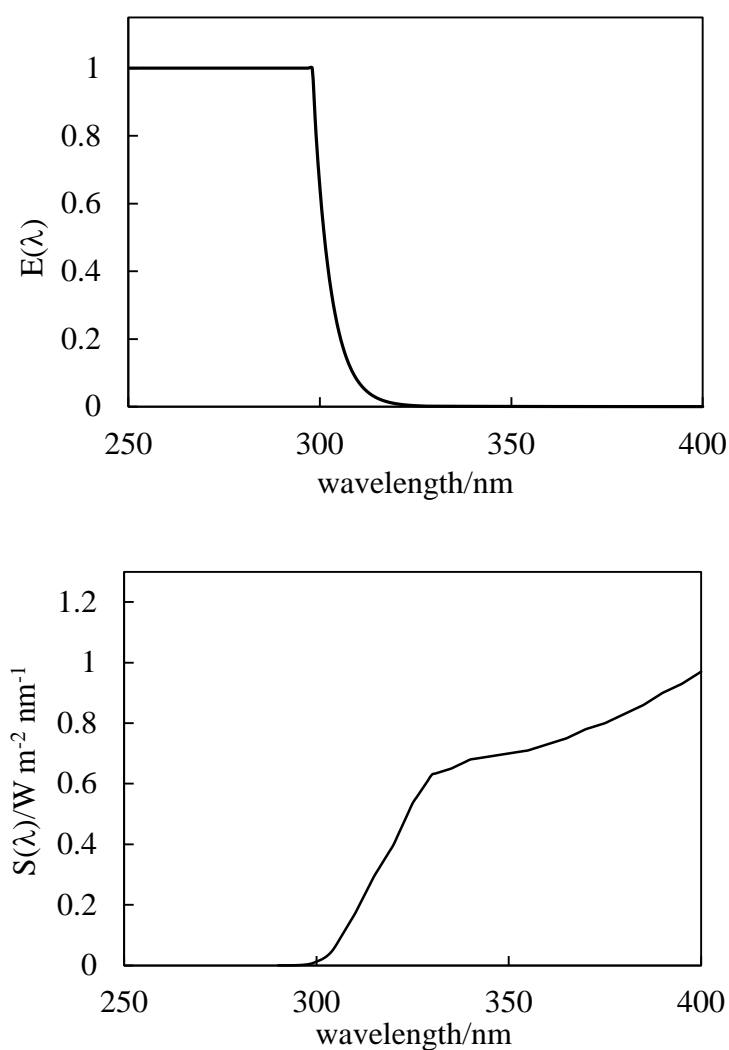


Figure S2. Extinction coefficient spectra of BEMT, DHHB, MC and AVB in squalane (upper plot) and PG (lower plot). No measurements were made for BEMT in PG owing to its low solubility in this solvent.

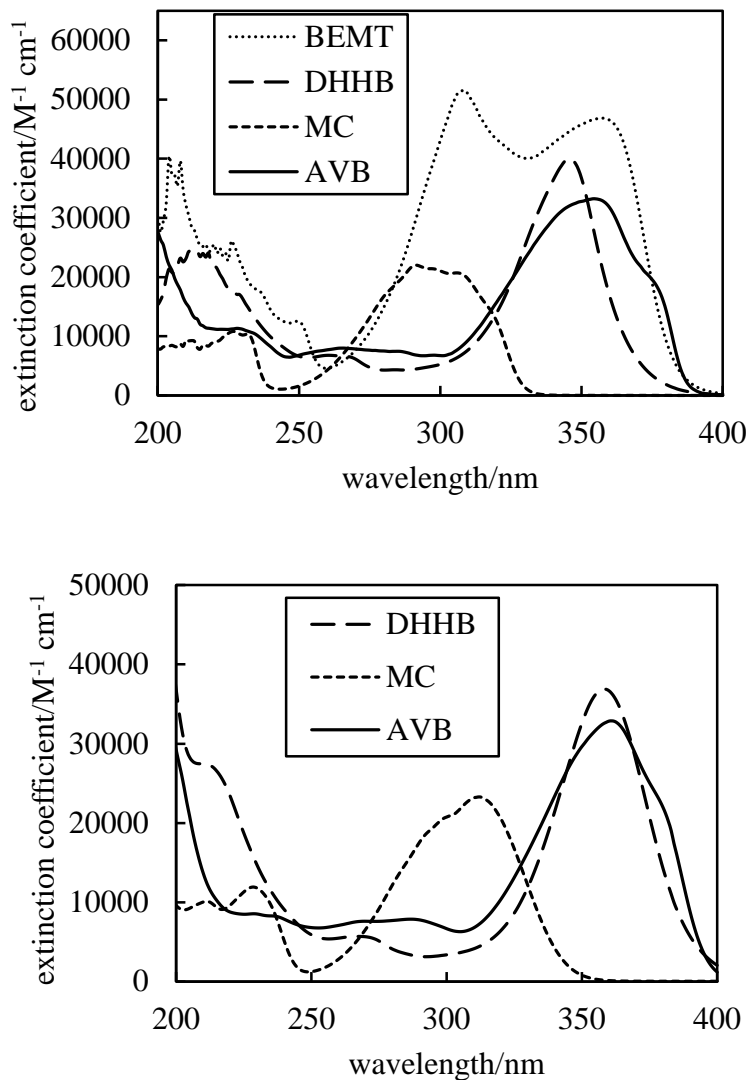
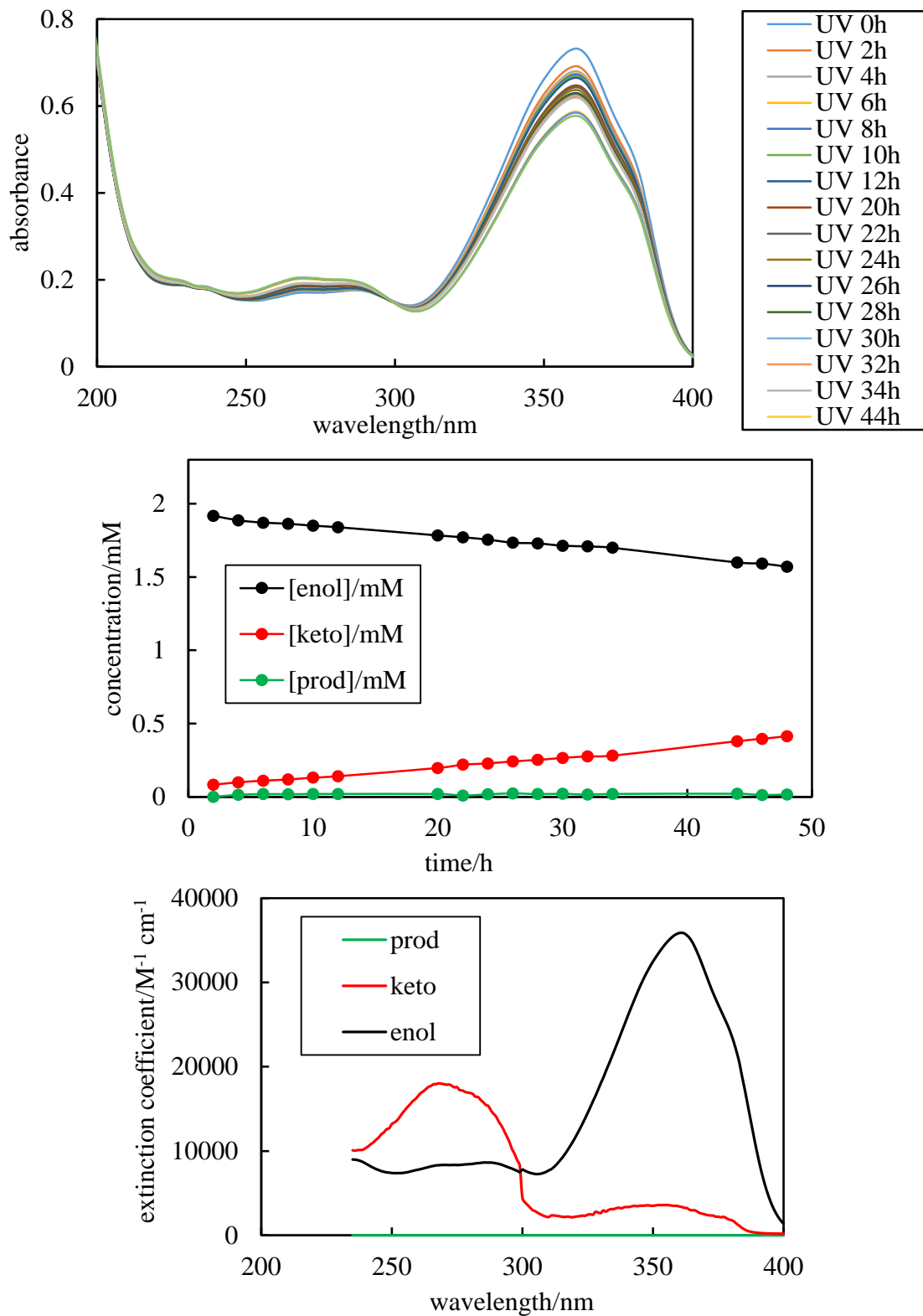


Figure S3. Upper plot: Spectra as a function of irradiation time (UV lamp at 7.2 cm) for 2 mM AVB in PG with path length 0.01 cm. Middle plot: Species concentrations obtained by fitting the measured spectra shown above. Lower plot: Derived extinction coefficient spectra of the enol, keto and product species.



Procedure used to calculate the spectra of AVB in solution films as a function of irradiation time.

1. For time zero, the initial absorbances due to each species are calculated using the relevant extinction coefficient spectra. Using guessed initial values of the two quantum yields (assumed to be wavelength independent) and the known spectral irradiance spectra of the light source, the rates of the enol to keto and keto to product processes are calculated (using equations 4-8) for each wavelength and summed over the emission wavelength range of the lamp to obtain the overall rates.
2. The irradiation time is incremented by a suitable time step and the overall photo-reaction rates from the previous time step are used to calculate the new concentrations of the enol, keto and prod species. Absorbances due to the individual species and total absorbance are calculated and used to derive the new values of the rates. In addition to obtaining the absorbance spectra at each time step, the SPF is also derived according to equation 2.
3. Step 2 is repeated over sufficient time steps until calculated spectra and SPF values are obtained which cover the same irradiation times as the measured spectra and the derived SPF values. For time steps at which measured and calculated spectra are available, the absolute differences between the measured and calculated spectra are summed. Using Solver, the two quantum yields are floated to minimise the residual sum between measured and calculated spectra as a function of irradiation time for the entire data set.

Figure S4. Comparison of measured (upper plot) and calculated (middle plot) spectra and SPF values (lower plot) for 8 mM AVB in PG with 0.01 cm path length as a function of irradiation time with the solar simulator. The legends indicate the irradiation times in hours.

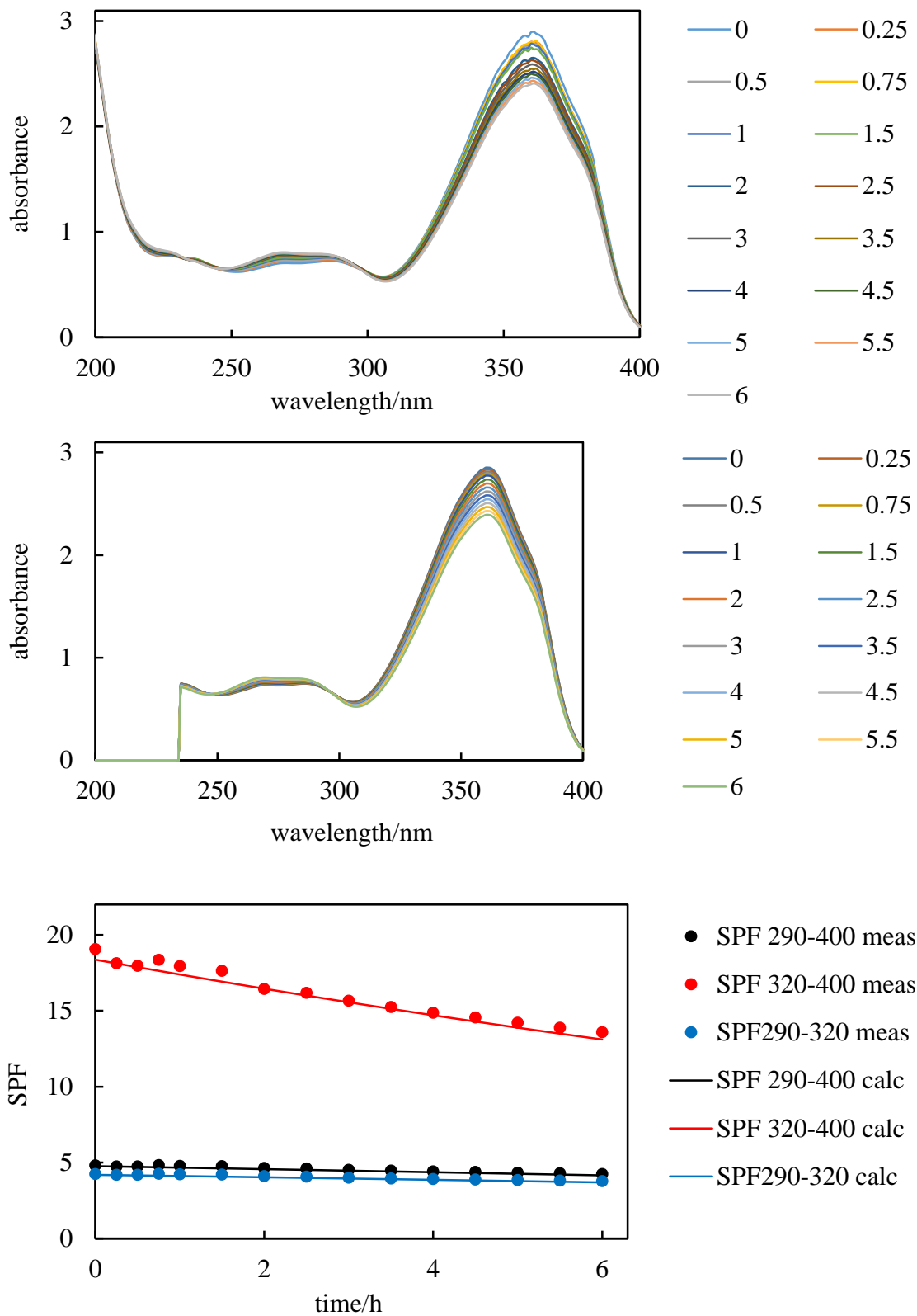
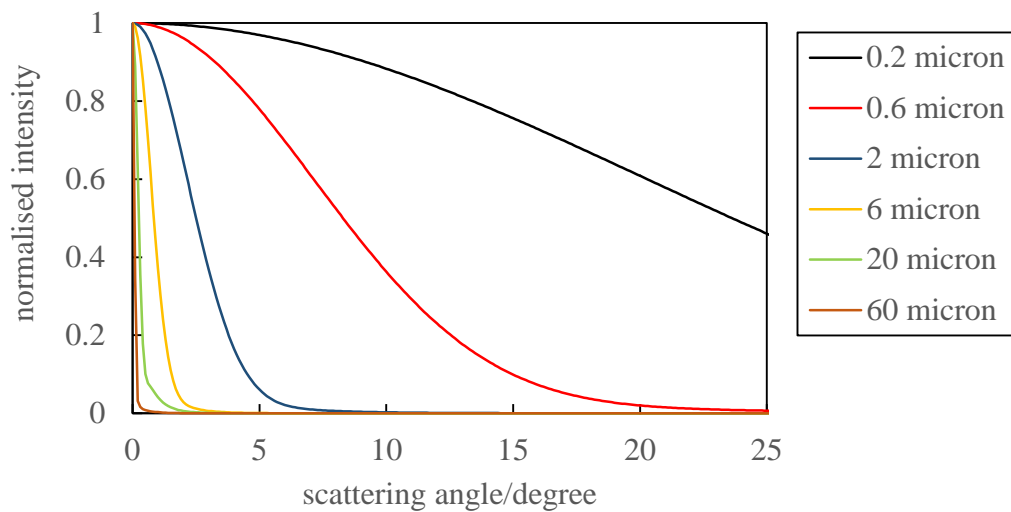


Figure S5. Calculated scattering intensity (normalised with respect to the scattering intensity at zero scattering angle) versus scattering angle for PG-in-SQ emulsion drops with 30% polydispersity and the mean diameters shown in the key. The incident light wavelength for these calculations is 300 nm.



Procedure used to calculate the spectra of AVB in emulsion films as a function of irradiation time.

1. For time zero, the six initial concentrations are entered and the absorbances due to each species are calculated using the relevant extinction coefficient spectra. Using the values of the four quantum yields (assumed to be wavelength independent) listed in Table 1, the spectral irradiance spectra of the light source, guessed values of P_{enol} and P_{keto} , the rates of the enol to keto and keto to product processes in each solvent are calculated for each wavelength and summed over wavelength to obtain the overall rates. These calculations are not sensitive to the value of P_{prod} because its absorbance is low and similar in both solvents. For this reasons, P_{prod} was set to 0.
2. The time is incremented by a suitable time step, the overall rates from the previous time step and the relationships between the different concentrations are used to calculate the new concentrations of the enol, keto and prod species in both solvents. The individual species' absorbance values and the total absorbances (with and without addition of the specular absorbance due to the emulsion scattering) are calculated and used to derive the new values of the rates. In addition to obtaining the overall specular absorbance spectra at each time step, the SPF (derived from the total absorbance without the emulsion scattering contribution) is calculated according to equation 2.
3. Step 2 is repeated over sufficient time steps until calculated specular spectra and SPF values are obtained which cover the same irradiation times as the measured spectra. For time steps for which both measured and calculated spectra are available, the absolute differences between the measured and calculated spectra are summed. Using Solver, the two unknown partition coefficients are floated to minimise the residual sum between measured and calculated spectra as a function of irradiation time.

Figure S6. Comparison of measured (upper plot) and calculated (lower plot) spectra for 5 mM AVB in a PG-in-SQ emulsion with 50 vol% PG, stabilised with 1 wt% of 23 %SiOH silica particles and 0.01 cm path length as a function of irradiation time with the UV lamp at 7.2 cm. The legend indicates the irradiation time in hours. The dashed line shows the measured specular absorbance spectrum of the emulsion alone.

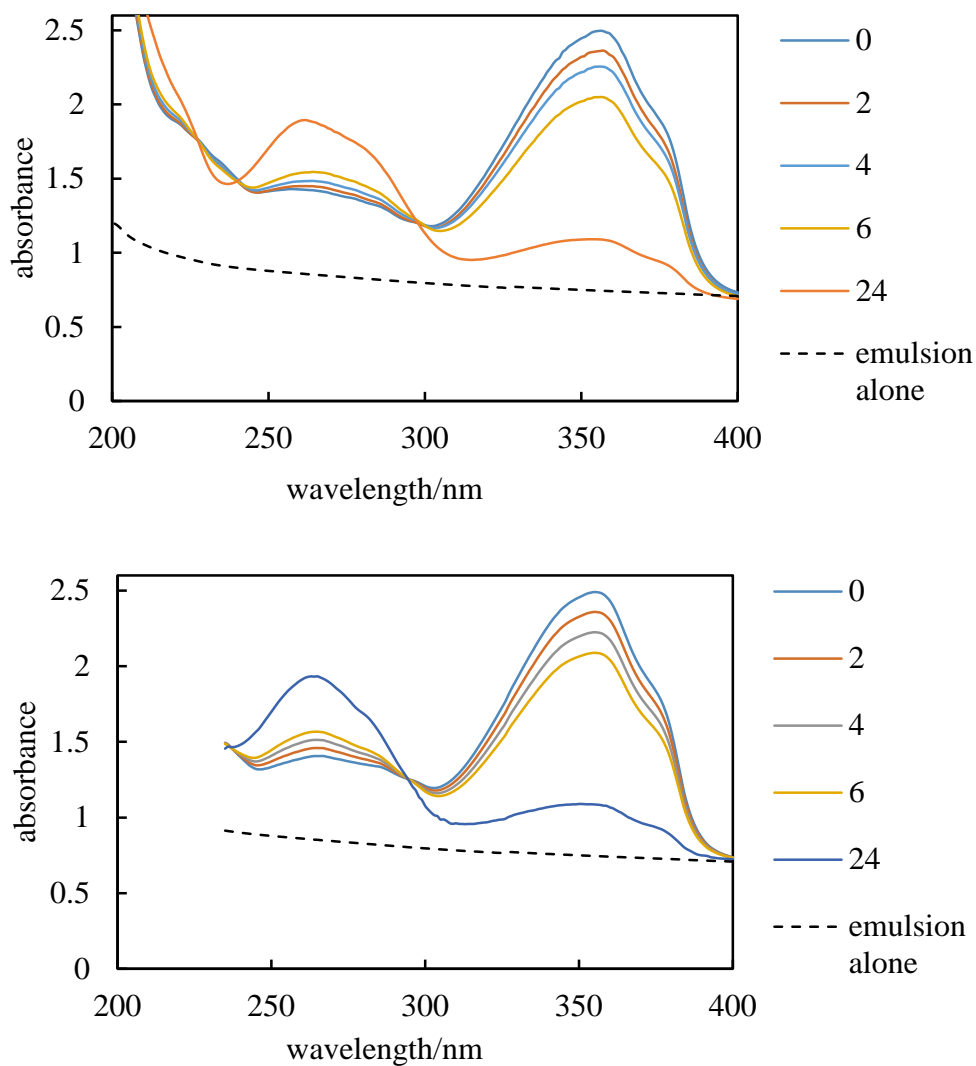


Figure S7. Comparison of measured (upper plot) and calculated (lower plot) spectra for 8.38 mM MC in a PG-in-SQ emulsion with 50 vol% PG, stabilised with 1 wt% of 23 %SiOH silica particles and 0.01 cm path length as a function of irradiation time with the UV lamp at 7.2 cm. The legend indicates the irradiation time in minutes. The dashed line shows the measured specular absorbance spectrum of the emulsion alone.

