Electronic supplementary information

Color tuning of chlorophyll \( a \) and \( b \) pigments revealed from gas-phase spectroscopy

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Power dependence measurements

Chl\( \alpha \)-HCOO\(-\)

Figure 1. Photoinduced signal versus laser pulse energy of Chl\( \alpha \)-HCOO\(-\) in the Soret band (excitation wavelength: 430 nm). The photon number \((n)\) obtained from the fitted curve (red) is indicated in the figure. Due to saturation, the data points above 1.9 mJ are not included in the fit in case of prompt action (top).
**Figure 2.** Photoinduced signal versus laser pulse energy of Chlα-HCOO⁻ in the Q band (excitation wavelength: 660 nm). The photon number \( n \) obtained from the fitted curve (red) is indicated in the figure. In case of delayed action (bottom), a linear curve fits the data and thus \( n = 1 \).
**Figure 3.** Photoinduced signal versus laser pulse energy of Chlb-HCOO\(^{-}\) in the Soret band (excitation wavelength: 430 nm). The photon number (n) obtained from the fitted curve (red) is indicated in the figure. Due to saturation, the data points above 2.0 mJ are not included in the fit in case of prompt action (top).
Figure 4. Photoinduced signal versus laser pulse energy of Chlb-HCOO• in the Q band (excitation wavelength: 640 nm). The photon number \( n \) obtained from the fitted curve (red) is indicated in the figure.
Figure 5. Photoinduced signal versus laser pulse energy of (Chl)a$_2$-TMA$^+$ in the Soret band (excitation wavelength: 420 nm). The photon number (n) obtained from the fitted curve (red) is indicated in the figure. Due to saturation, the data points above 3.3 mJ are not included in the fit in case of prompt action (top), and not above 2.5 mJ in case of delayed action. In the latter, a linear curve fits the data and thus $n = 1$. 

prompt
Fit: $a^*x^n$, $n=2.1$

normalized photofragment yield (a.u.)

delayed
Fit: $a^*x$, 

Laser pulse energy (mJ)
Figure 6. Photoinduced signal versus laser pulse energy of (Chl)₂·TMA⁺ in the Q band (excitation wavelength: 650 nm). The photon number \( n \) obtained from the fitted curve (red) is indicated in the figure.
Figure 7. Photoinduced signal versus laser pulse energy of (Chl)$_2$·HCOO$^-$ in the Soret band (excitation wavelength: 430 nm). The photon number ($n$) obtained from the fitted curve (red) is indicated in the figure. In case of delayed action, a linear curve fits the data and thus $n = 1$. 
Figure 8. Photoinduced signal versus laser pulse energy of (Chl$b)_2$HCOO$^-$ in the Soret band (excitation wavelength: 450 nm). The photon number ($n$) obtained from the fitted curve (red) is indicated in the figure. In case of delayed action, a linear curve fits the data and thus $n = 1$. Due to saturation, data points above 2.8 mJ are not included in the fits.
Action spectra of Chl\textsubscript{a/b}-HCOO\textsuperscript{-} shown for different n

Figure 9. Dissociation action spectra of Chl\textsubscript{a}-HCOO\textsuperscript{-} are shown in blue (a, b); those Chl\textsubscript{b}-HCOO\textsuperscript{-} of in red (c, d). Action spectra based on prompt fragmentation are shown in panels a and c, and those based on delayed fragmentation in b and d. In a and c, Q bands (>500 nm) have been multiplied by a factor of three to better see spectral features. Vertical bars indicate the band maxima. n indicates the used photon number and the spectra are shown for both n=1.5 and n=2.0 to show that the band maxima are independent of n, and only the relative height of the Soret and Q band is affected by n.