Photoprotection or Photodamage: a Direct Observation of 
Nonradiative Dynamics from 2-Ethylhexyl 4-
Dimethylaminobenzoate Sunscreen Agent

Supporting Information

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Equation of log-normal line shape function

Figure S1 Steady state UV-Visible absorption and normalized fluorescence spectra of MDMABA in CH$_3$OH, CH$_3$OD, CD$_3$OD and CH$_3$CN

Figure S2 Steady state UV-Visible absorption and normalized fluorescence spectra of EDMABA in CH$_3$OH, CH$_3$CN and 70%H$_2$O/30%CH$_3$CN

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Figure S7 Experimental and fitted kinetic intensity decays of fs-TRF for MDMABA in CH$_3$OH and EDMABA in 70%H$_2$O/30%CH$_3$CN and comparison of the fs-TRF decay for MDMABA in CH$_3$OH, CH$_3$OD, CD$_3$OD and CH$_3$CN and EDMABA in CH$_3$OH, CH$_3$CN and 70%H$_2$O/30%CH$_3$CN

Figure S8 Fs-TRF spectra of MDMABA in CH$_3$OD

Figure S9 Broadband fs-TA of MDMABA in CH$_3$CN and in CH$_3$OH

Figure S10 Broadband fs-TA of EDMABA in CH$_3$CN and in CH$_3$OH

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Equation of log-normal line shape function

Log-normal line shape function used to simulate the experimentally measured fs-TRF spectra in CH$_3$OH and CH$_3$OD is as following:

\[
F(\nu) = \begin{cases} 
\exp\left[-\ln(2)\frac{\ln(1+\alpha)}{\gamma^2}\right] & \alpha > -1 \\
0 & \alpha \leq -1 
\end{cases}
\]

\[\alpha = 2\gamma(\nu - \nu_p)/\Delta\]

The four parameters, the peak height \(h\), the peak frequency \(\nu_p\), the asymmetry parameter \(\gamma\) and the width parameter \(\Delta\) are adjusted in a nonlinear least-square fitting to simulate the spectral profile of the steady state and fs-TRF spectra. Prior to the spectral simulation, the spectra have to convert from the unit of wavelength (\(\lambda\) in nm) to wavenumber (\(\nu\) in cm$^{-1}$) by using a relation \(F(\nu) = \lambda^2F(\lambda)\).

The log-normal simulation can also produce the integrated intensity (I) of the spectra as expressed in the following equation:

\[
I = \left(\frac{\pi}{4\ln(2)}\right)^{1/2} h\Delta \exp\left(\frac{\gamma^2}{4\ln(2)}\right)
\]

Figure S1 Steady state UV-Visible absorption and normalized fluorescence spectra of MDMABA in CH$_3$OH, CH$_3$OD, CD$_3$OD and CH$_3$CN.
Figure S2 Steady state UV-Visible absorption and normalized fluorescence spectra of EDMABA in CH₃OH, CH₃CN and 70%H₂O/30%CH₃CN.

Figure S3 Temporal evolution of fs-TRF spectra of MDMABA recorded at (a) 0-5 ps (0, 0.3, 0.5, 0.7, 1, 1.25, 1.75, 2, 2.5, 5 ps) and (b) 5-500 ps (5, 7, 10, 17.5, 35, 85, 200, 500 ps) in CH₃OH after photo-excitation. The scale of the “Relative Intensity” is enlarged ~25 times in (b) relative to (a). The inset in (a) shows the magnified view of the spectral evolution. The arrows represent the temporal evolution of the spectra.
Figure S4 Temporal evolution of fs-TRF spectra of EDMABA recorded at (a) 0-5 ps (0, 0.4, 0.6, 0.85, 1.25, 1.75, 2.5, 5 ps) and (b) 5-6000 ps (4, 200, 700, 1250, 2000, 3000, 4000, 6000 ps) in CH$_3$CN; (c) 0-5 ps (0, 0.4, 0.6, 0.85, 1.25, 1.75, 2.5, 5 ps) and (d) 5-1000 ps (5, 6, 8.5, 12.5, 20, 40, 85, 175, 300, 1000 ps) in CH$_3$OH; (e) 0-5 ps (0, 0.4, 0.6, 0.85, 1.25, 1.75, 2.5, 5 ps) and (f) 5-300 ps (5, 10, 17.5, 30, 50, 85, 300 ps) in 70%H$_2$O/30%CH$_3$CN after photo-excitation. The scale of the “Relative Intensity” is enlarged ~25 times in both (b) relative to (a), (d) relative to (c) and (f) relative to (e). The inset in (e) displays the enlarged view of the fs-TRF spectra at ~2.5 to 5 ps in 70%H$_2$O/30%CH$_3$CN after photo-excitation. The arrows represent the temporal evolution of the spectra.

Figure S5 fs-TRF anisotropy spectra of EHDMABA in 70%H$_2$O/30%CH$_3$CN recorded at 0.5 and 5 ps after photo-excitation.
Figure S6 Temporal evolution of fs-TRF spectra of EHDMABA recorded at (a) 0-4 ps (0, 0.4, 0.6, 0.85, 1.25, 1.75, 2.5, 4 ps) and (b) 4-2000 ps (4, 5, 8.5, 15, 30, 50, 100, 200, 400, 2000 ps) in CH$_3$OD; (c) 0-4 ps (0, 0.4, 0.6, 0.85, 1.25, 1.75, 2.5, 4 ps) and (d) 4-1000 ps (4, 8.5, 20, 50, 85, 125, 200, 1000 ps) in 70%D$_2$O/30%CH$_3$CN after photo-excitation. The scale of the “Relative Intensity” is enlarged ~8 times in both (b) relative to (a) and (d) relative to (c). The arrows represent the temporal evolution of the spectra.

Figure S7 Experimental and fitted kinetic intensity decays of fs-TRF at early time delay for (a) MDMABA in CH$_3$OH and (b) EDMABA in 70%H$_2$O/30%CH$_3$CN up to ~20 ps; and comparison of ~560 nm fs-TRF decay for (c) MDMABA in CH$_3$OH (○), CH$_3$OD (■), CD$_3$OD (●) and CH$_3$CN (Δ); and (d) EDMABA in CH$_3$OH (○), CH$_3$CN (Δ) and 70%H$_2$O/30%CH$_3$CN ( dấu hỏi ) at late time delay up to ~1 ns.
Figure S8 Temporal evolution of fs-TRF spectra of MDMABA recorded at (a) 0-5 ps (0, 0.5, 0.7, 1, 1.5, 2, 3, 5 ps) and (b) 5-700 ps (5, 7, 10, 15, 30, 100, 250, 700 ps) in CH$_3$OD after photo-excitation. The scale of the “Relative Intensity” is enlarged ~25 times in (b) relative to (a). The insets in (a) shows the magnified view of the spectral evolution. The arrows represent the temporal evolution of the spectra.

Figure S9 Temporal evolution of broadband fs-TA of MDMABA recorded at (a) 0-100 ps (0, 0.25, 0.5, 0.85, 1.25, 3, 12.5, 100 ps), (b) 100-6000 ps (100, 500, 1500, 2000, 3500, 6000 ps) in CH$_3$CN, and recorded at (c) 0-20 ps (0, 0.25, 0.5, 0.85, 1.5, 3, 20 ps), (d) 20-6000 ps (20, 60, 100, 175, 250, 400, 6000 ps) in CH$_3$OH after photo-excitation. The arrows indicate temporal evolution of the spectra.
Figure S10 Temporal evolution of broadband fs-TA of EDMABA recorded at (a) 0-100 ps (0, 0.25, 0.5, 0.85, 1.25, 3, 12.5, 100 ps), (b) 100-6000 ps (100, 500, 1500, 2000, 3500, 6000 ps) in CH$_3$CN, and recorded at (c) 0-20 ps (0, 0.25, 0.5, 0.85, 1.5, 3, 20 ps), (d) 20-6000 ps (20, 60, 100, 150, 200, 300, 6000 ps) in CH$_3$OH after photo-excitation. The arrows indicate temporal evolution of the spectra.

Figure S11 Experimental (circle, triangle) and fitted (line) kinetic trace of the fs-TA of EHDMABA at early (a, c, e) and late (b, d, f) times after the excitation in CH$_3$CN (a, b), CH$_3$OH (c, d) and 70%H$_2$O/30%CH$_3$CN (e, f).