

Supporting Information

Photooxidation of Aniline Derivatives Can Be Activated by Freezing Their Aqueous Solutions

Pablo Corrochano,[†] Dana Nachtigallová^{*,§} and Petr Klán^{*,†,‡}

[†] RECETOX, Faculty of Science, Masaryk University, Kamenice 5, 625 00 Brno, Czech Republic; [‡] Department of Chemistry, Faculty of Science, Masaryk University, Kamenice 5, 625 00 Brno, Czech Republic; [§] Institute of Organic Chemistry and Biochemistry, Flemingovo nám. 2, 166 10 Prague, Czech Republic.

* dana.nachtigallova@marge.uochb.cas.cz; klan@sci.muni.cz

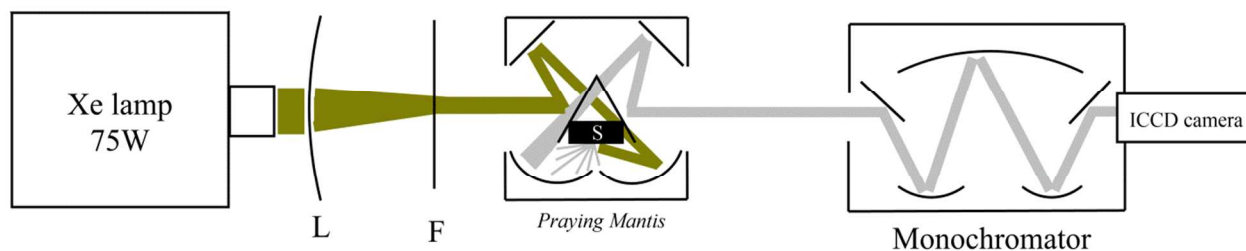
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Experimental Section

Materials and Methods. Aniline ($\geq 99.5\%$), *N,N*-dimethylaniline ($\geq 99.5\%$), and *N,N*-diethylaniline ($\geq 99.5\%$) were used without further purification. Milli Q water was obtained from a Millipore Simplicity 185 (conductivity = 18.2 M Ω cm).

Instrumentation. Absorption and diffuse reflectance spectra were recorded on a Cary 5000i spectrophotometer (Agilent). For liquid samples, standard 1-cm or 1-mm quartz cuvettes were employed. For ice samples, a Praying Mantis (Harrick Scientific) apparatus was used to acquire the diffuse reflectance spectra. This accessory consists of two 6X, 90° off-axis ellipsoid mirrors, arranged to discriminate against the collection of specular reflected radiation; a low-temperature reaction chamber (CHC, Harrick Scientific) was used to control precisely the sample temperature. The sample temperature was always equilibrated; the residence time of the samples in the cryostat was at least 5 min. No apparent change in the reflectance spectra was observed when the samples were kept at the given temperature for more than 20 min. At least three independent spectroscopic measurements were performed in each case, and the results were subsequently averaged.



Scheme S1. A homemade setup used to monitor the course of the reaction during irradiation of the frozen samples. The different colors used in the beams symbolize the radiation received by the sample (green) and diffuse light reflected from the sample (gray), used for monitoring the reaction. L = collimating lens, S = sample, F = cutoff filter.

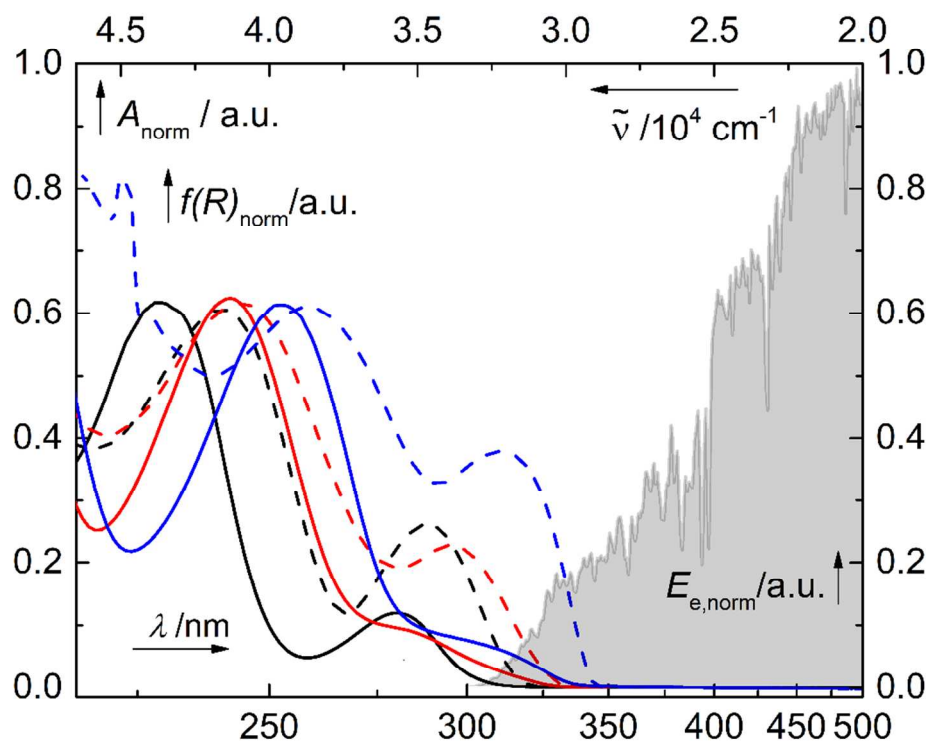


Figure S1. Comparison of the normalized absorption spectra and normalized remission function (Kubelka-Munk; $f(R)_{\text{norm}}$) of (a) ANI (black lines), DMA (red lines), and DEA (blue lines) in aqueous solutions at 298 K (solid lines, $c = 1 \text{ mM}$) and in frozen aqueous samples at 243 K (dashed lines, $c = 1.09 \times 10^{-3} \text{ mol kg}^{-1}$) vs. the normalized solar spectral irradiance at the Earth's surface (shaded region. Reproduced with permission from reference 1. Copyright 1985 Elsevier.).

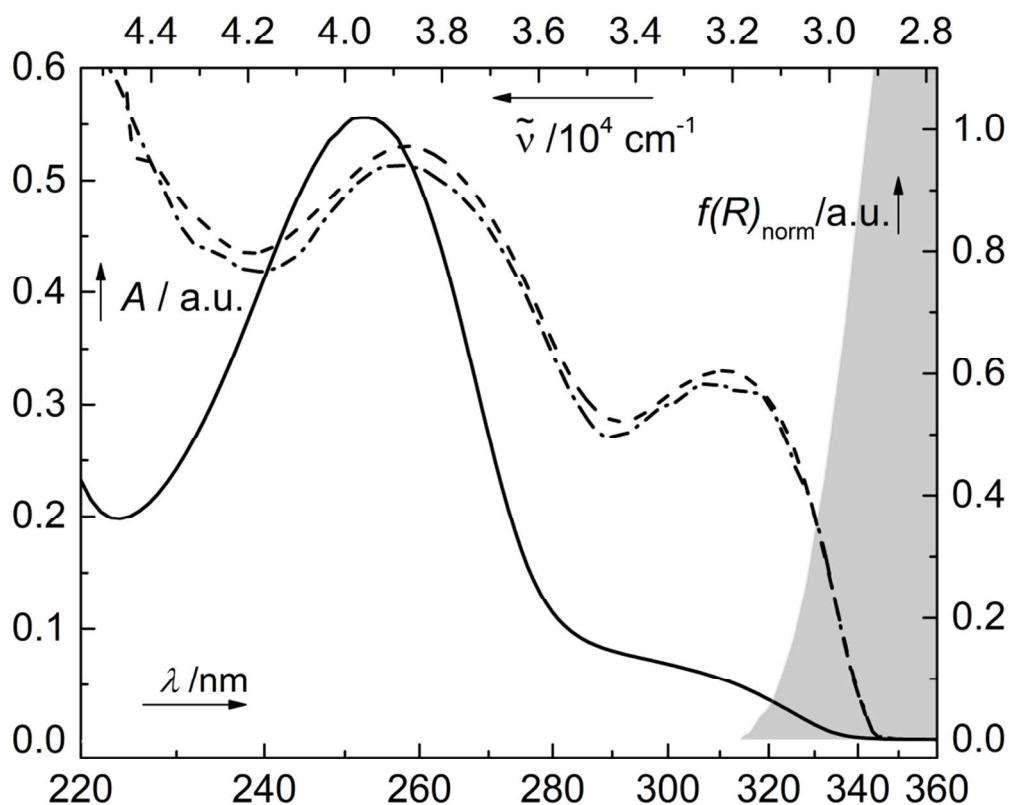


Figure S2. Absorption spectra and normalized remission function (Kubelka-Munk; $f(R)_{\text{norm}}$) of DEA ($c = 1 \text{ mM}$) in aqueous solution at 298 K (solid lines) and in frozen aqueous samples at 243 K: slow freezing (SLF) at 195 K (dashed line), shock freezing (SHF) at 77 K (dashed-dotted line), and vapor deposition (VD) on ice grains at 77 K (dotted line). The shaded region represents the cutoff filters used in the irradiation experiments (340 nm).

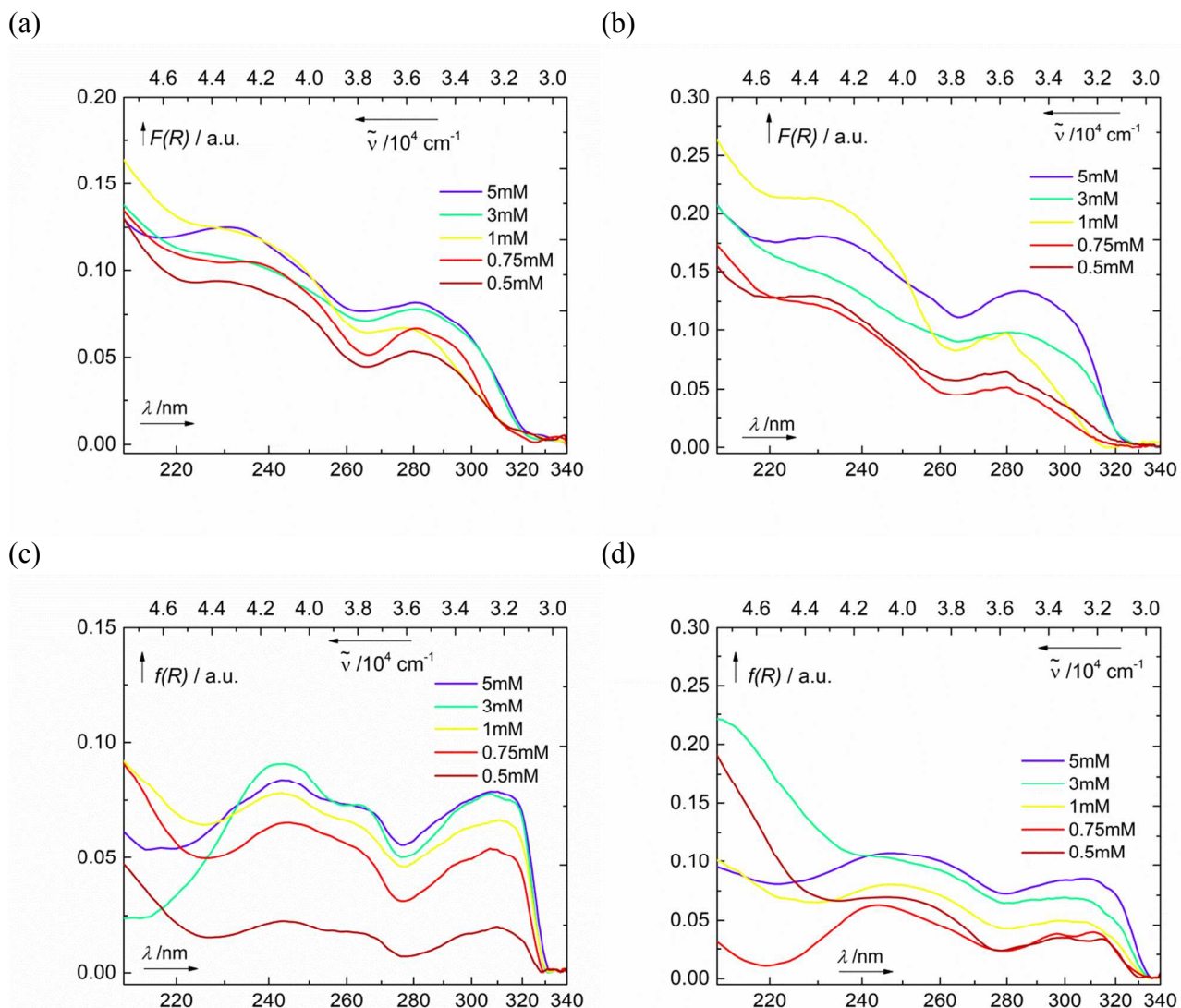
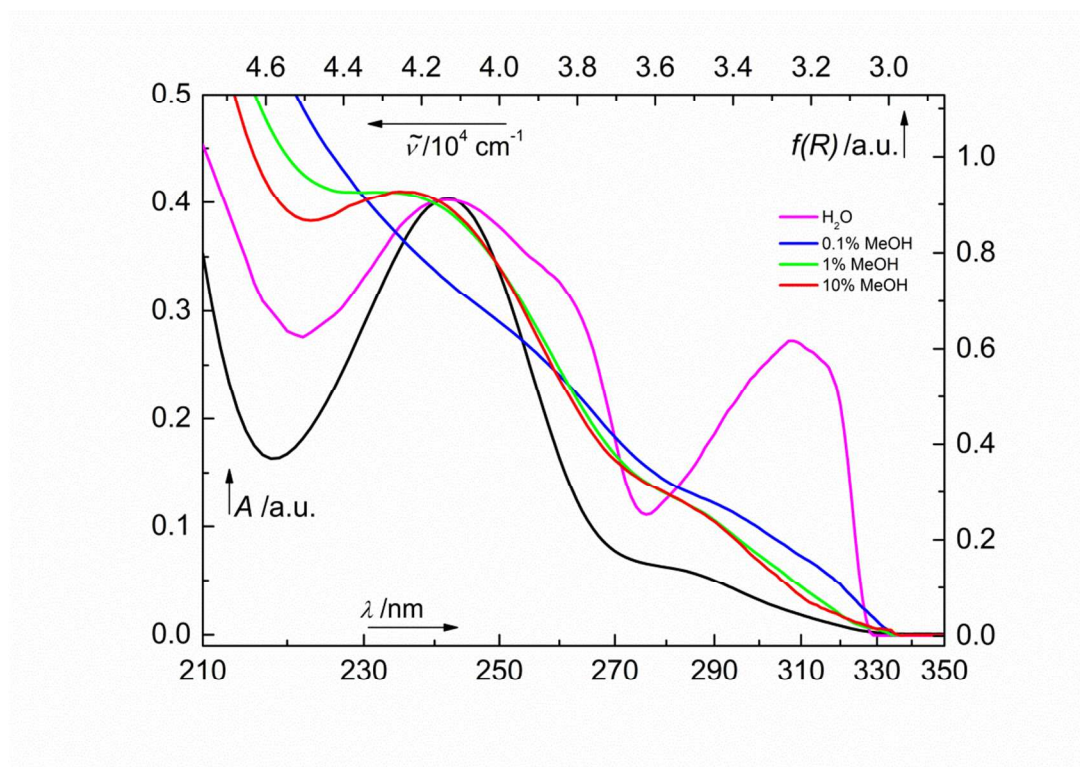
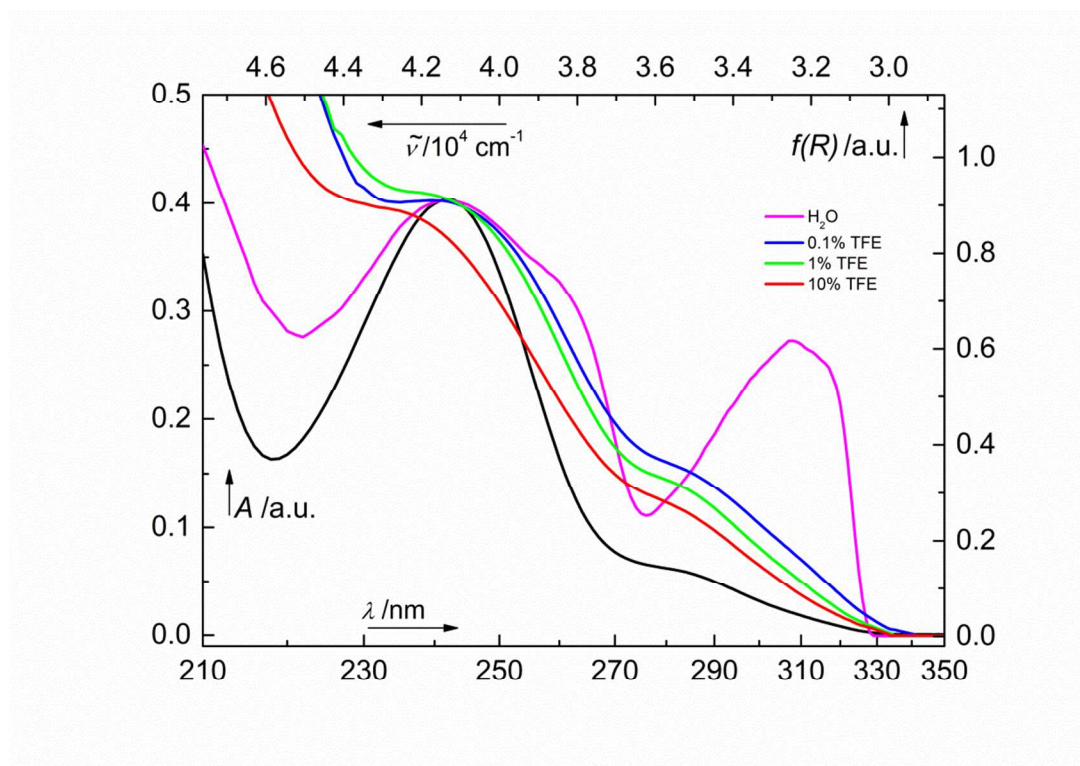


Figure S3. Remission function (Kubelka-Munk; $f(R)$) of SLF samples of ANI (a, b) and DMA (c, d) measured at different temperatures and concentrations. The samples were prepared at 183 K and measured at 183 K (left column) and 258 K (right column).

(a)



(b)



(c)

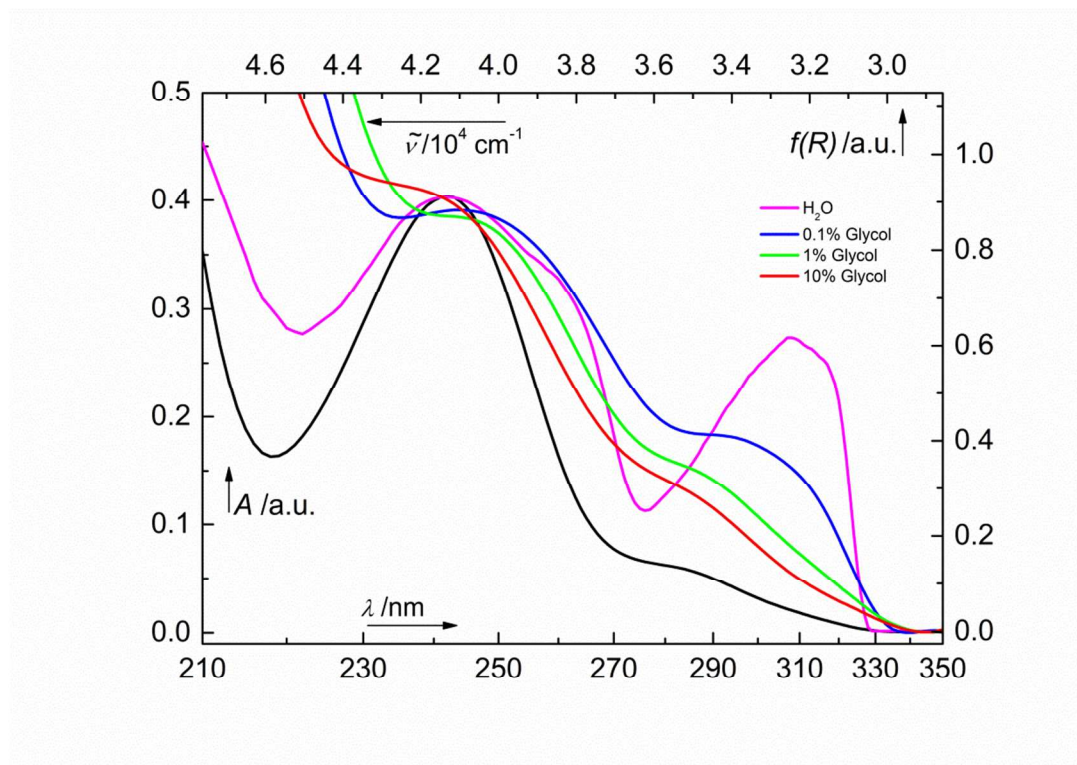


Figure S4. Remission function (Kubelka-Munk; $f(R)$) of SLF samples of DMA mixed with different amounts of (a) MeOH, (b) TFE and (c) ethylene glycol, prepared at 183 K and measured at 253 K.

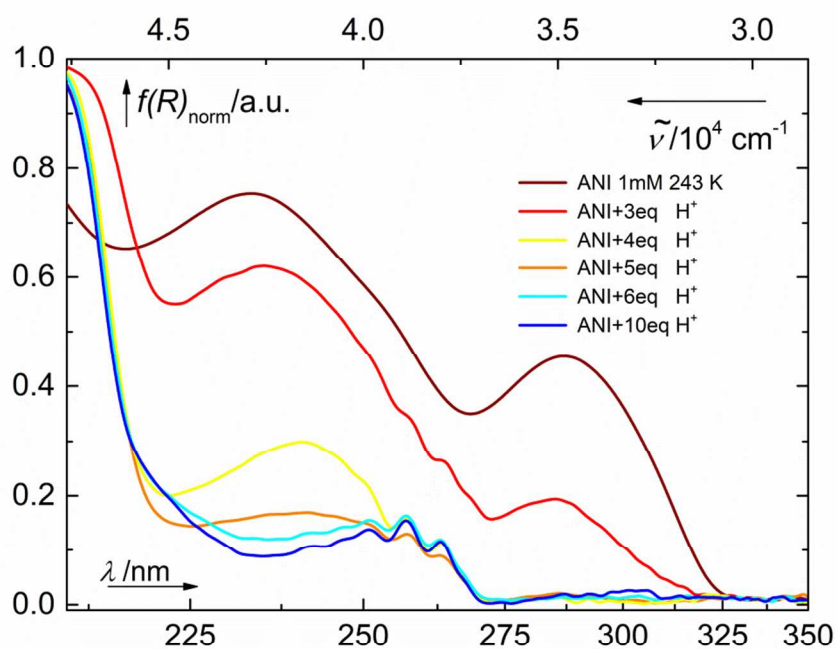
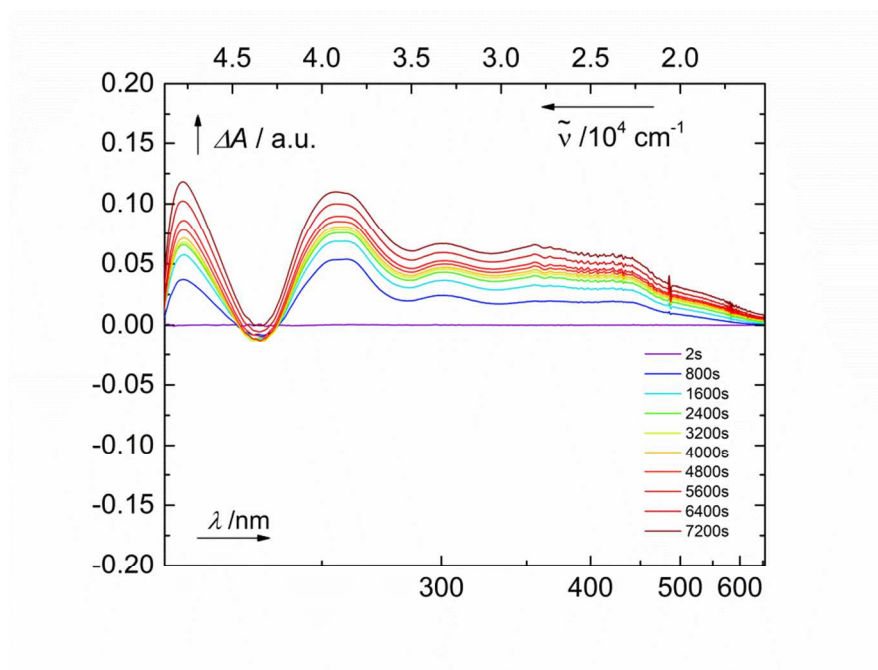


Figure S5. Remission function (Kubelka-Munk; $f(R)$) of SLF samples of ANI mixed with different amounts of HCl; prepared and measured at 183 K. The gradual disappearance of the ${}^1A \rightarrow {}^1L_b$ transition at higher acid concentrations was observed due to the protonation of the amino group.

(a)



(b)

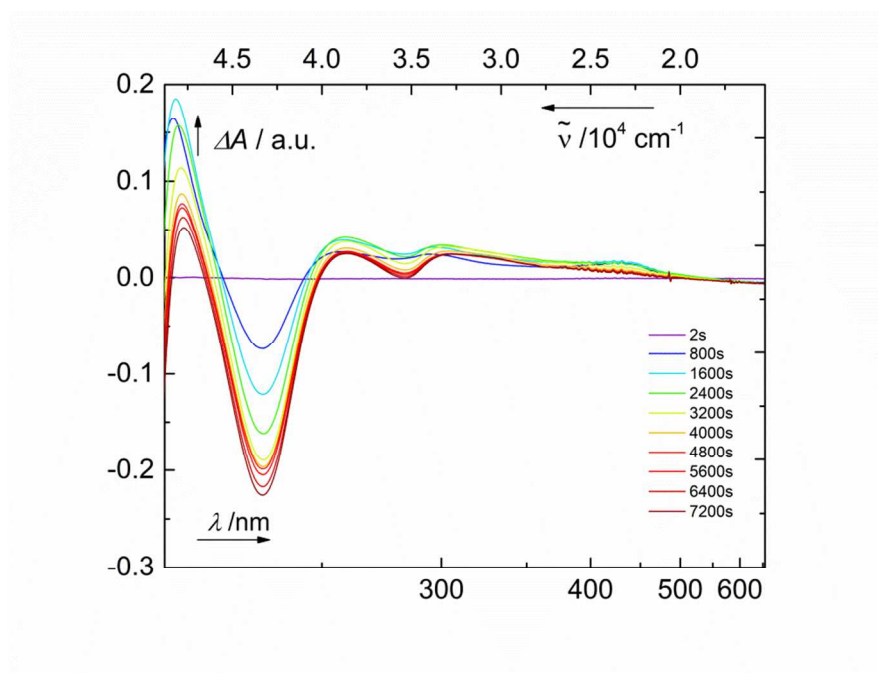
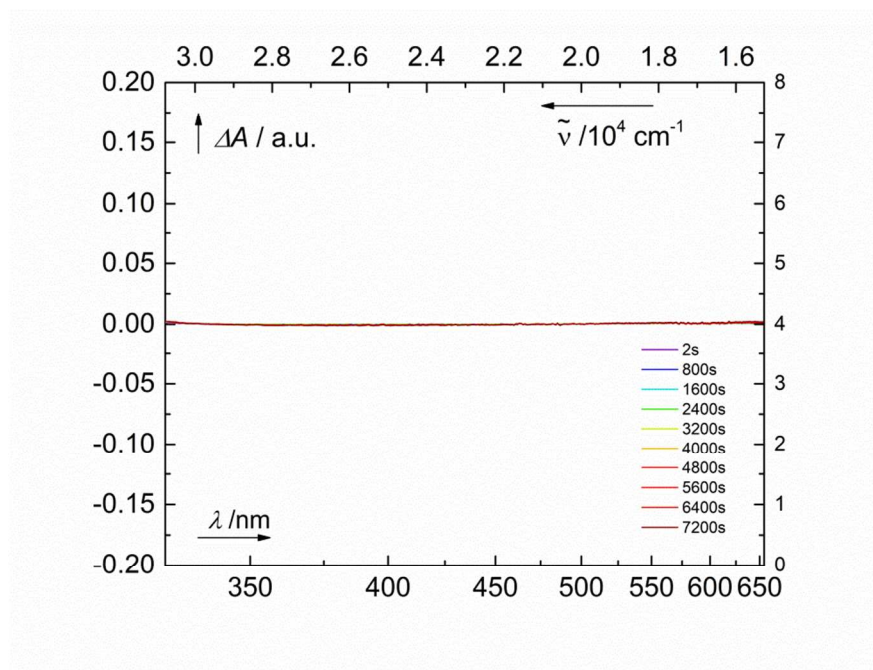


Figure S6. Difference absorption spectra of liquid samples containing ANI ($c = 5 \times 10^{-4}$ M) and hydrogen peroxide of (a) $c = 5 \times 10^{-4}$ M and (b) $c = 5 \times 10^{-2}$ M concentrations measured during irradiation without any cutoff filter ($T = 298$ K).

(a)



(b)

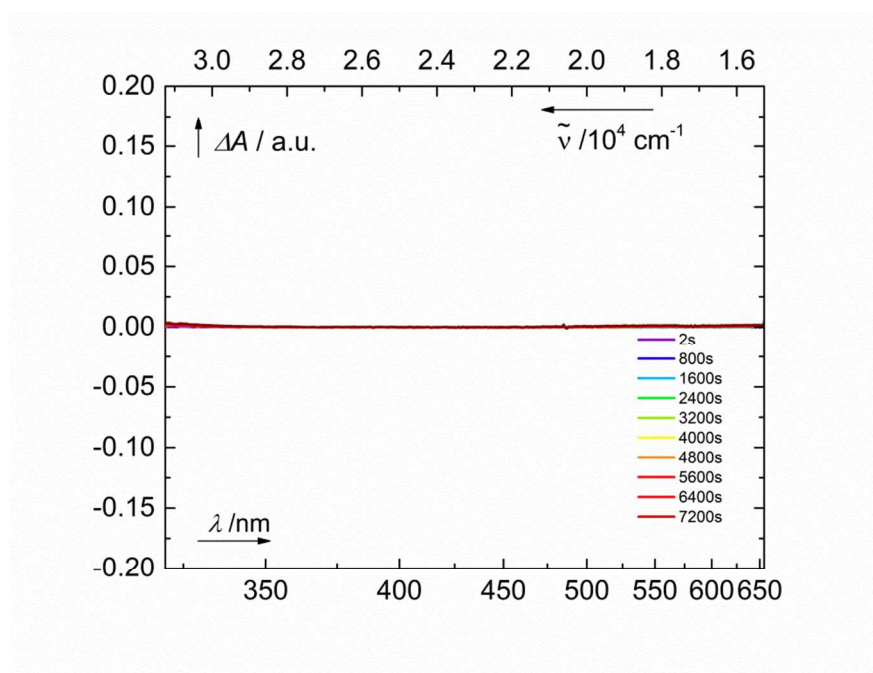
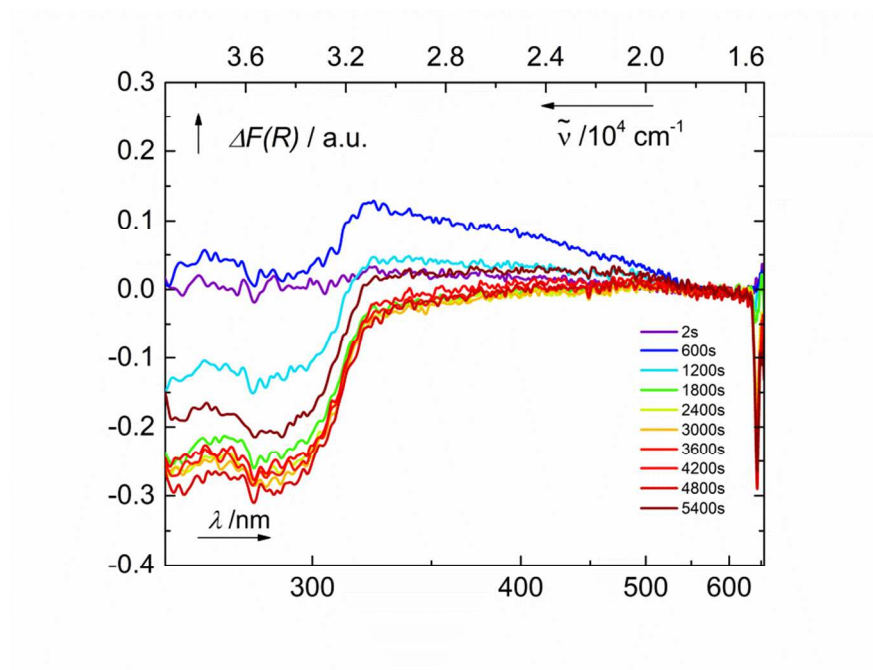


Figure S7. Difference absorption spectra of liquid samples containing ANI ($c = 5 \times 10^{-4}$ M) and hydrogen peroxide of (a) $c = 5 \times 10^{-4}$ M and (b) $c = 5 \times 10^{-2}$ M concentrations measured during irradiation using a 320 nm cutoff filter ($T = 298$ K).

(a)



(b)

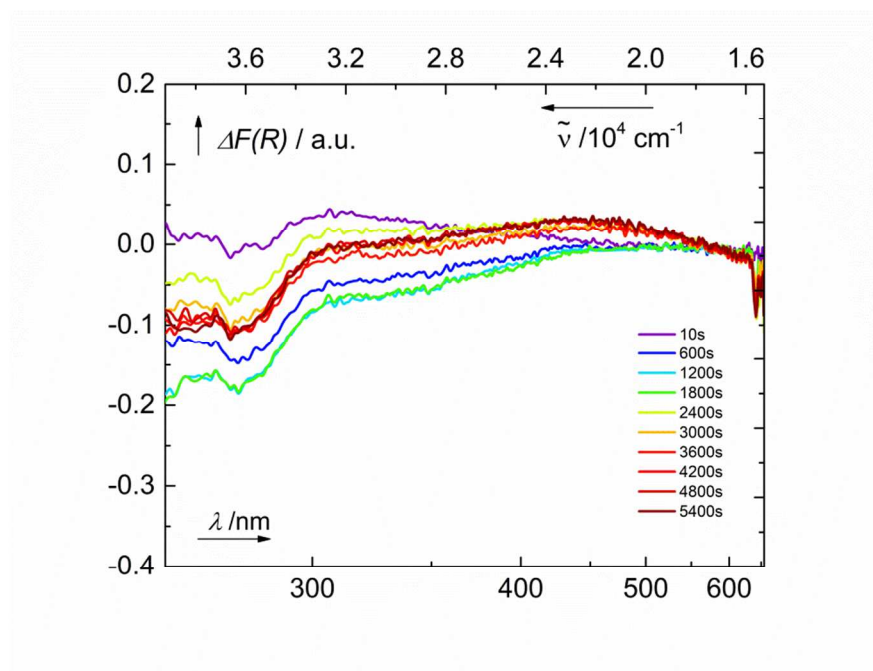
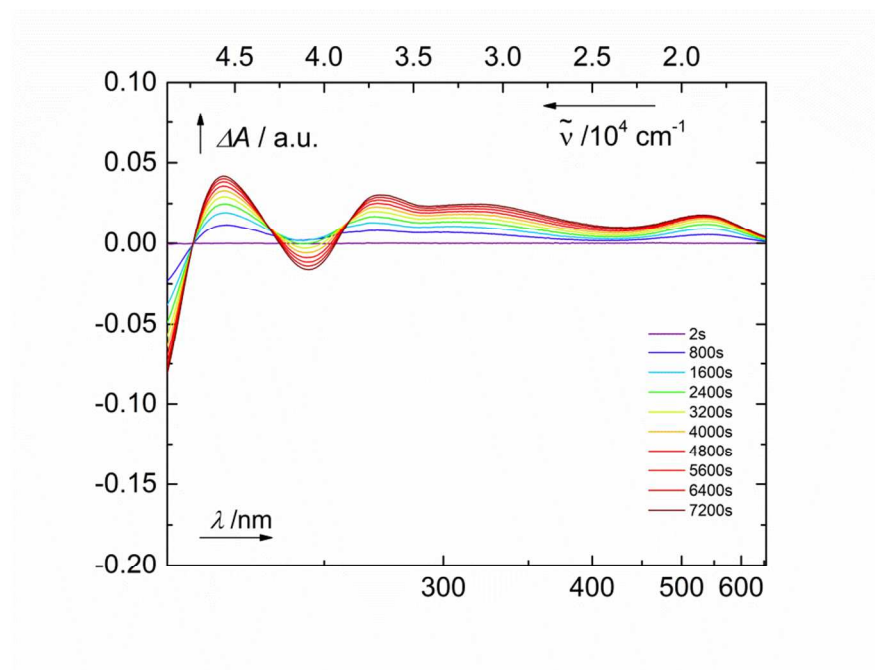


Figure S8. Difference absorption spectra of SLF samples containing ANI ($c = 5.45 \times 10^{-4}$ mol kg $^{-1}$) and hydrogen peroxide of (a) $c = 5.45 \times 10^{-4}$ mol kg $^{-1}$ or (b) $c = 5.45 \times 10^{-2}$ mol kg $^{-1}$ concentrations measured during irradiation without any cutoff filter ($T = 253$ K).

(a)



(b)

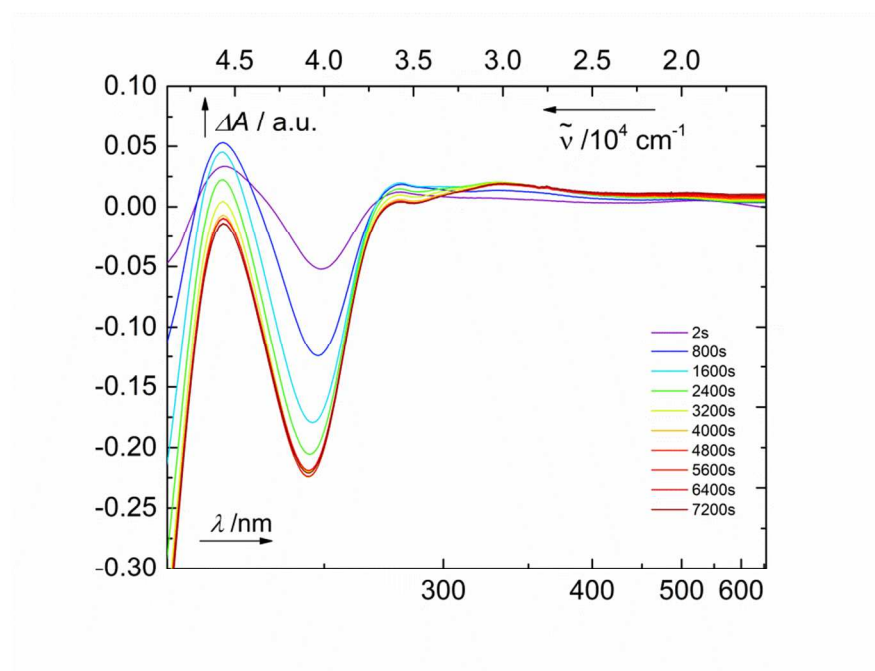
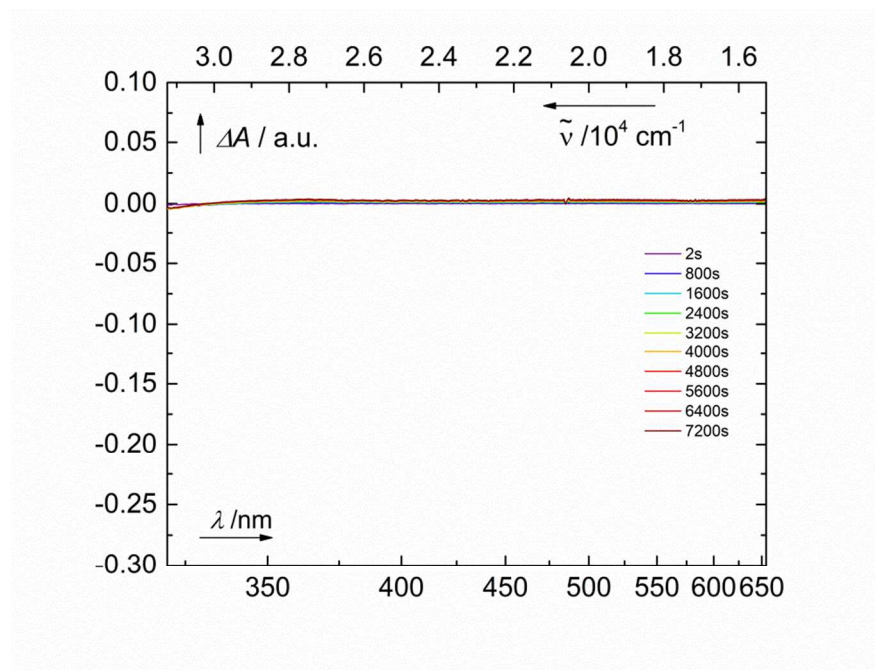


Figure S9. Absorption spectra of liquid samples containing DMA ($c = 5 \times 10^{-4}$ M) and hydrogen peroxide of (a) $c = 5 \times 10^{-4}$ M and (b) $c = 5 \times 10^{-2}$ M concentrations measured during irradiation without any cutoff filter ($T = 298$ K).

(a)



(b)

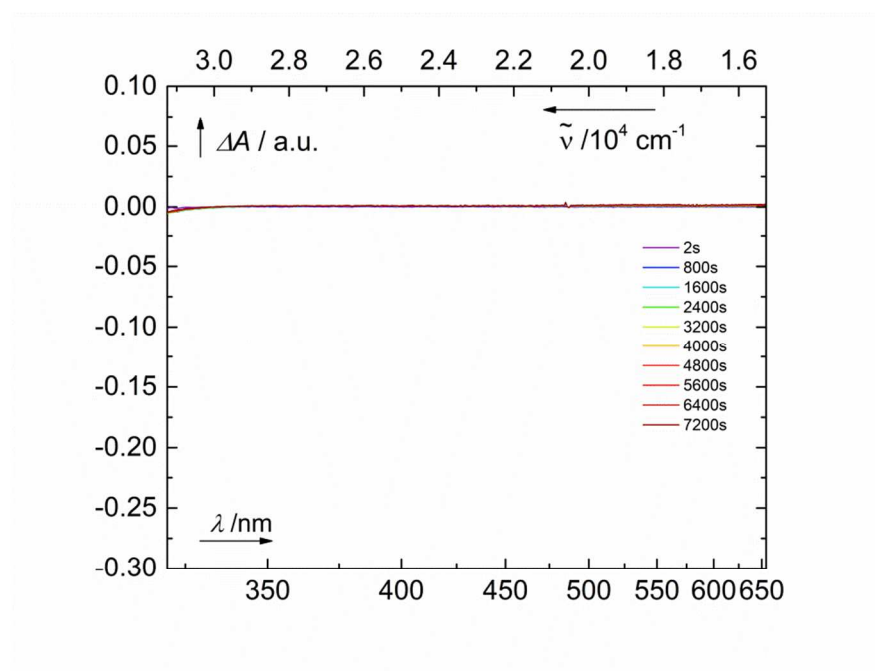
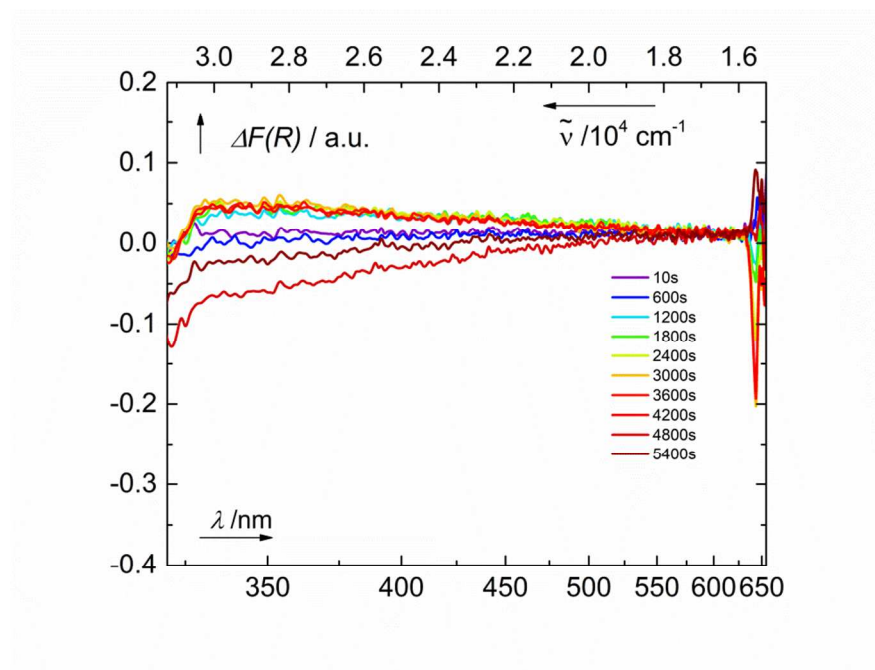


Figure S10. Absorption spectra of liquid samples containing DMA ($c = 5 \times 10^{-4}$ M) and hydrogen peroxide of (a) $c = 5 \times 10^{-4}$ M and (b) $c = 5 \times 10^{-2}$ M concentrations measured during irradiation using a 320 nm cutoff filter ($T = 298$ K).

(a)



(b)

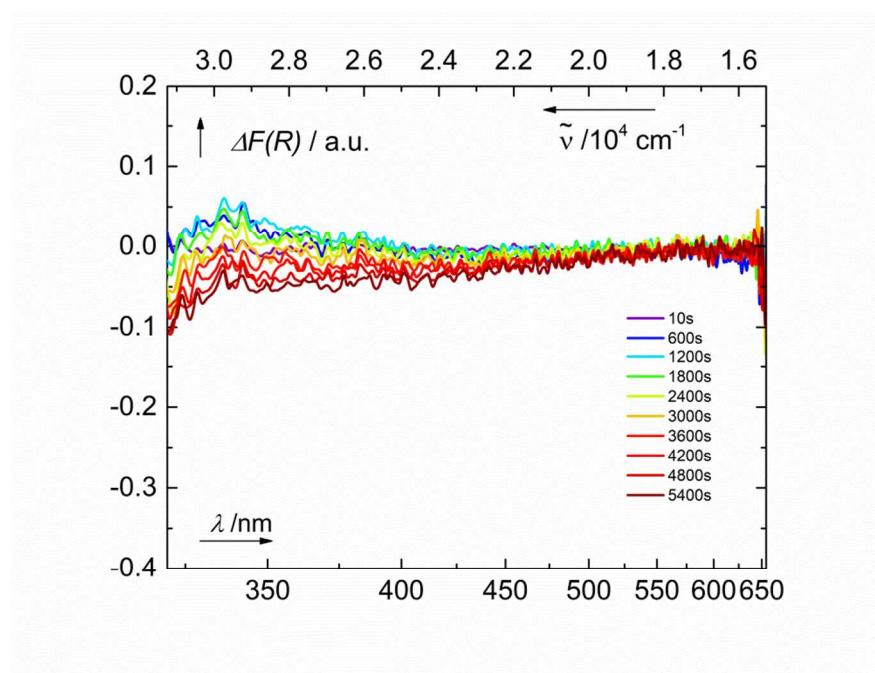
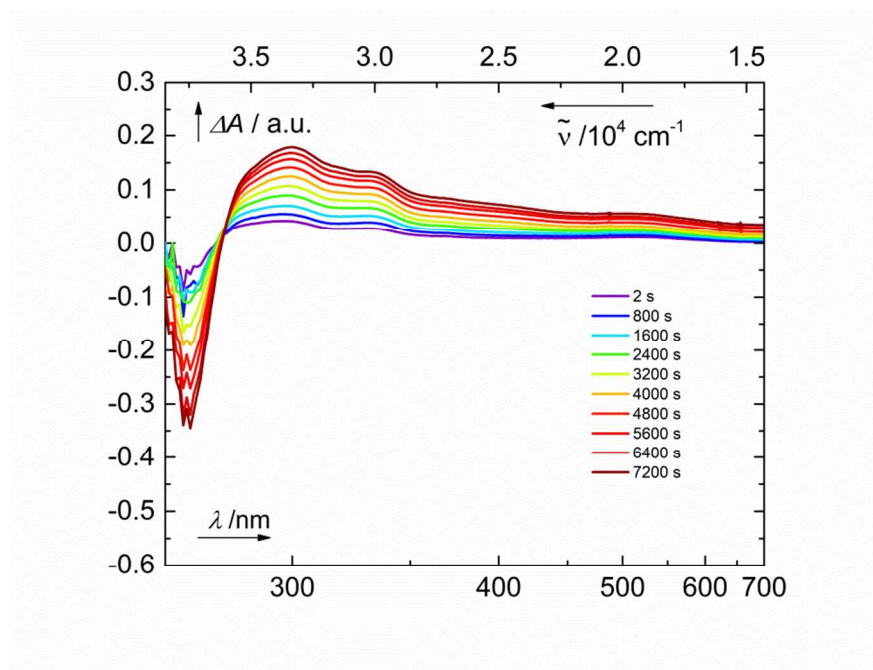


Figure S11. Absorption spectra of SLF samples containing DMA ($c = 5.45 \times 10^{-4} \text{ mol kg}^{-1}$) and hydrogen peroxide of (a) $c = 5.45 \times 10^{-4} \text{ mol kg}^{-1}$ and (b) $c = 5.45 \times 10^{-4} \text{ mol kg}^{-1}$ concentrations measured during irradiation using a 320 nm cutoff filter ($T = 253 \text{ K}$).

(a)



(b)

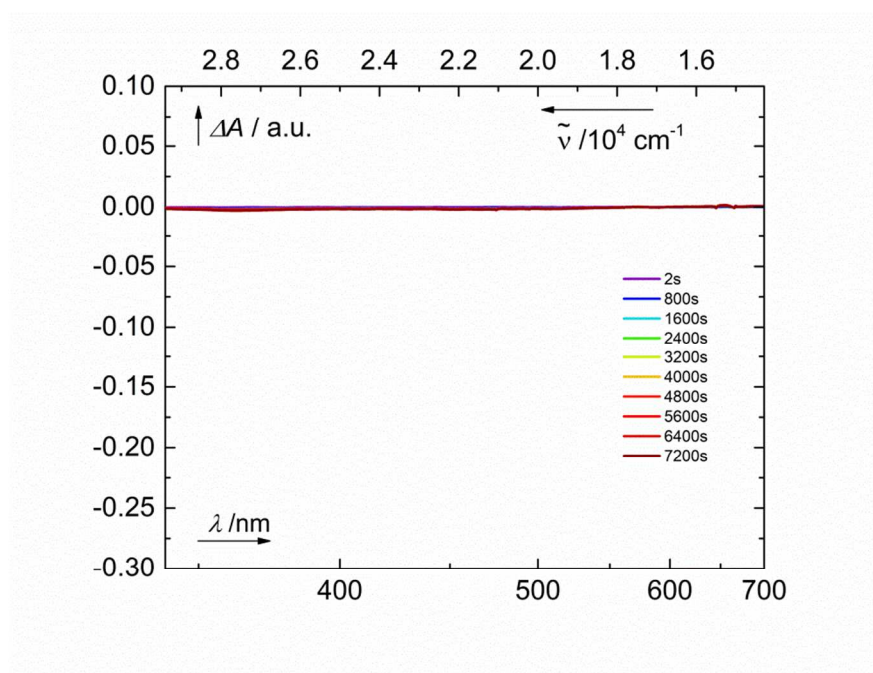


Figure S12. Absorption spectra of liquid samples containing DEA ($c = 5 \times 10^{-4}$ M) and hydrogen peroxide of $c = 5 \times 10^{-4}$ M concentration measured during irradiation (a) without an optical filter and (b) using a 320 nm cutoff filter ($T = 298$ K).

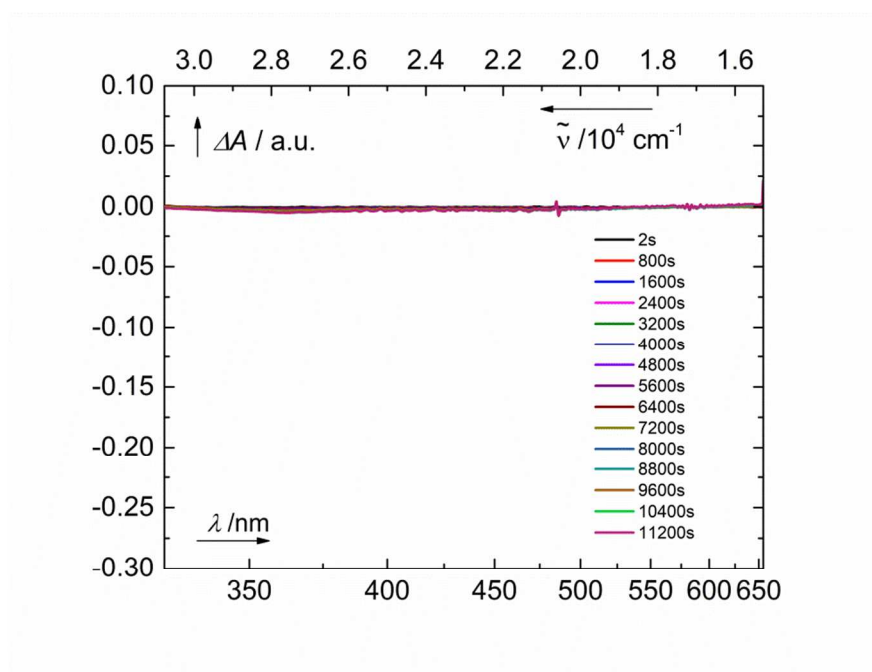


Figure S13. Difference spectra of DMA ($c = 5 \times 10^{-4}$ M) in a liquid aq. sample containing hydrogen peroxide ($c = 5 \times 10^{-2}$ M) when irradiated over 8 h using a 320 nm cutoff filter.

Upon irradiation, liquid samples exhibited pronounced decline of the $^1A \rightarrow ^1L_a$ transition band of an aniline derivative as well as simultaneous appearance of the new absorption bands centered at 255, 305, 360, and 450 nm for ANI (Figure S6), 270, 330, and 530 nm for DMA (Figures S9), and 300, 335, and 525 nm for DEA (Figure S12). Similar bands appeared for the SLF samples containing ANI (Figure S8) and DMA (Figure S11), although the restricted mobility of the photoproducts generated in the frozen matrix do not allow molecular diffusion allowing oligomer growth.^{2, 3}

Reaction Conversions

The estimated reaction conversions for SLF samples of DMA and DEA ($c = 0.5$ mM, $c_{\text{H}_2\text{O}_2} = 0.05$ M) was calculated by measuring the disappearance of the initial product using spectrophotometric methods, corroborated by the preparation and analyses of similar samples ($c = 5$ mM, $c_{\text{H}_2\text{O}_2} = 0.5$ M) in D_2O for NMR measurements. Due to concentration difference in concentration used in NMR experiments, the conversions presented in this article are estimates.

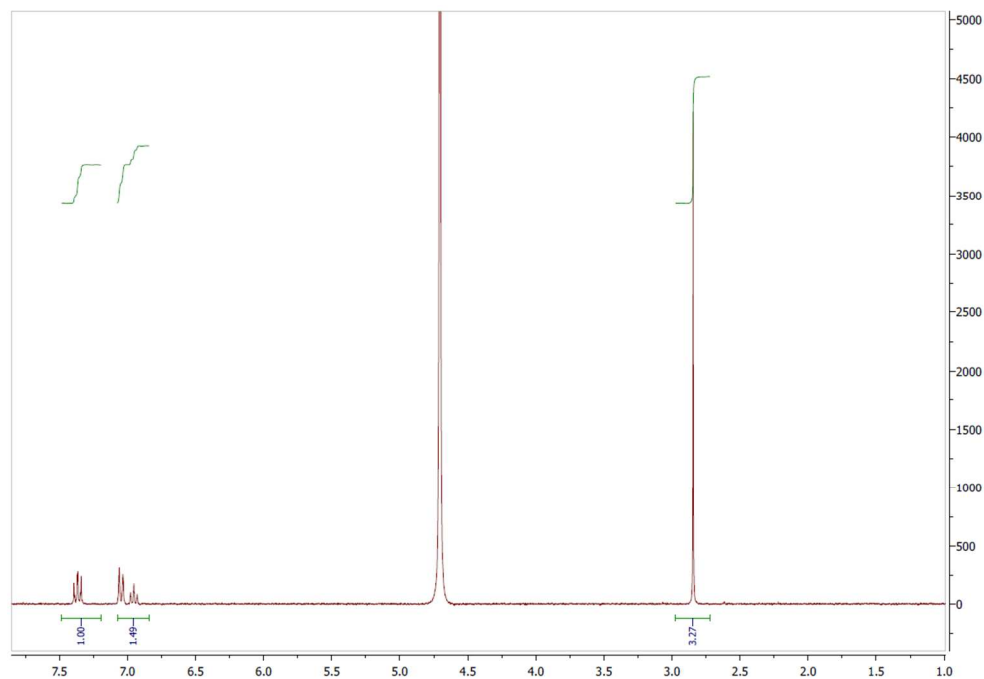


Figure S14. ^1H -NMR (D_2O) spectrum of a DMA SLF sample before irradiation.

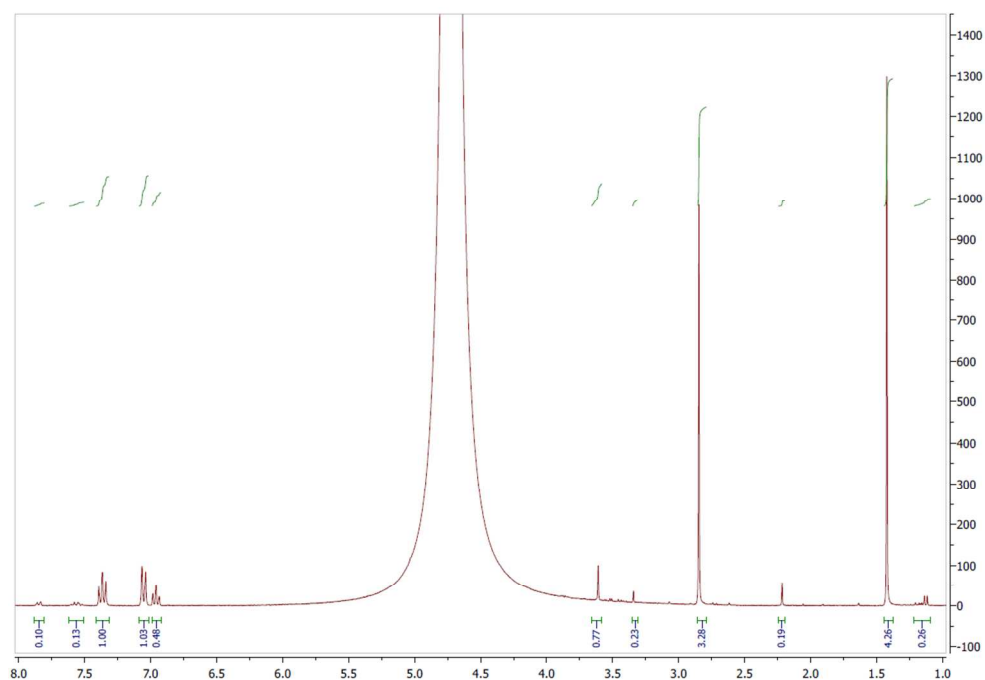


Figure S15. ^1H -NMR (D_2O) spectrum of a melted DMA SLF sample after 7200 s of irradiation through a cutoff filter. The estimated reaction conversion is $\sim 10\%$.

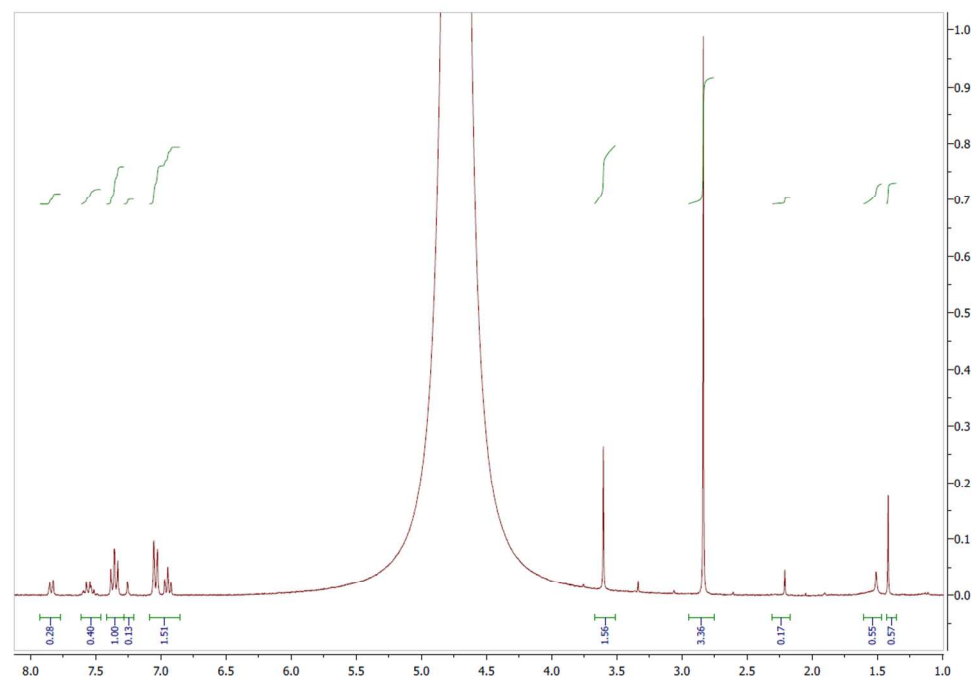
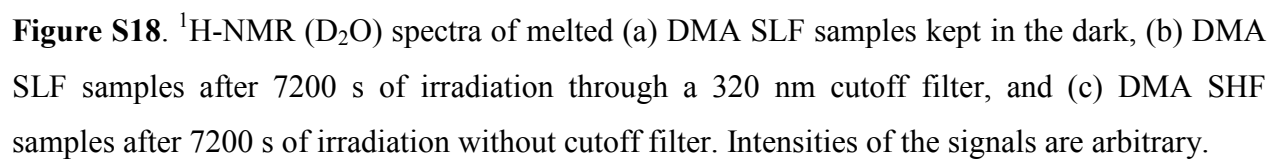
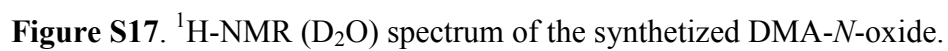


Figure S16. ^1H -NMR (D_2O) spectrum of a melted DMA SHF sample after 7200 s of irradiation through a cutoff filter. The estimated reaction conversion is $\sim 35\%$.



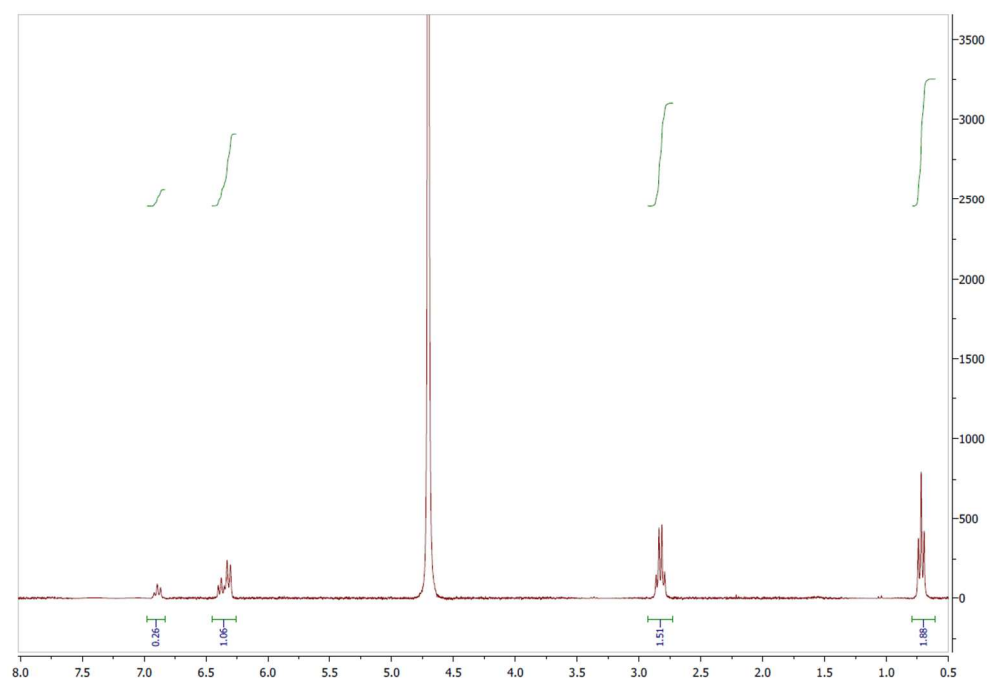


Figure S19. ^1H -NMR (D_2O) spectrum of a SLF DEA sample before irradiation.

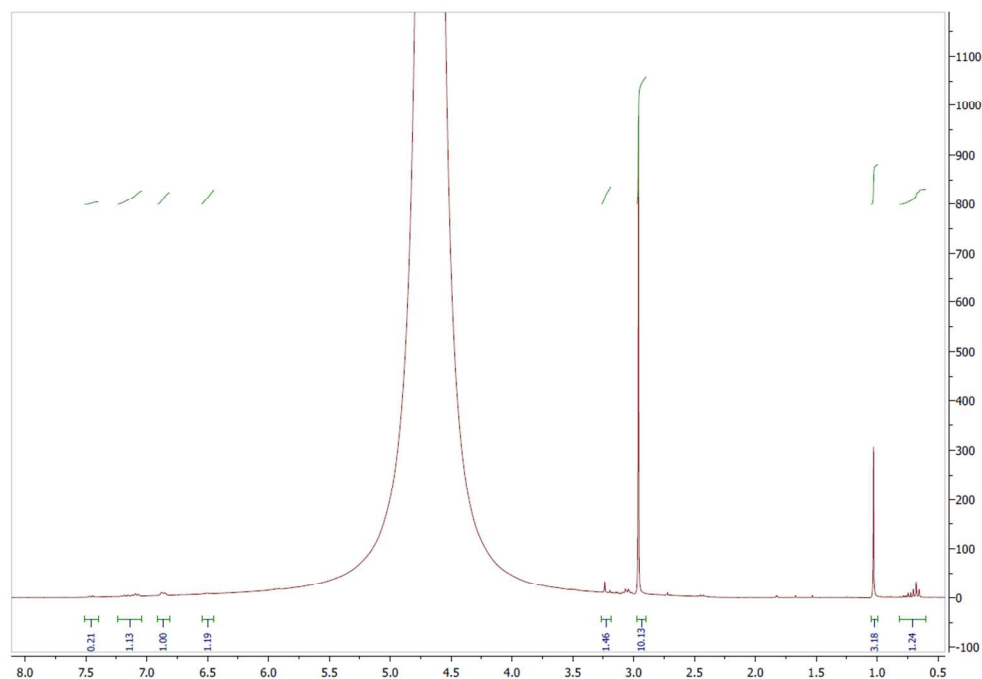


Figure S20. ^1H -NMR (D_2O) spectra of melted DEA SLF samples after 7200s of irradiation through a 320 nm cutoff filter. The estimated reaction conversion is $\sim 40\%$. The appearance of signals in the aliphatic region suggests the formation of lower-MW products, typical from mineralization process.

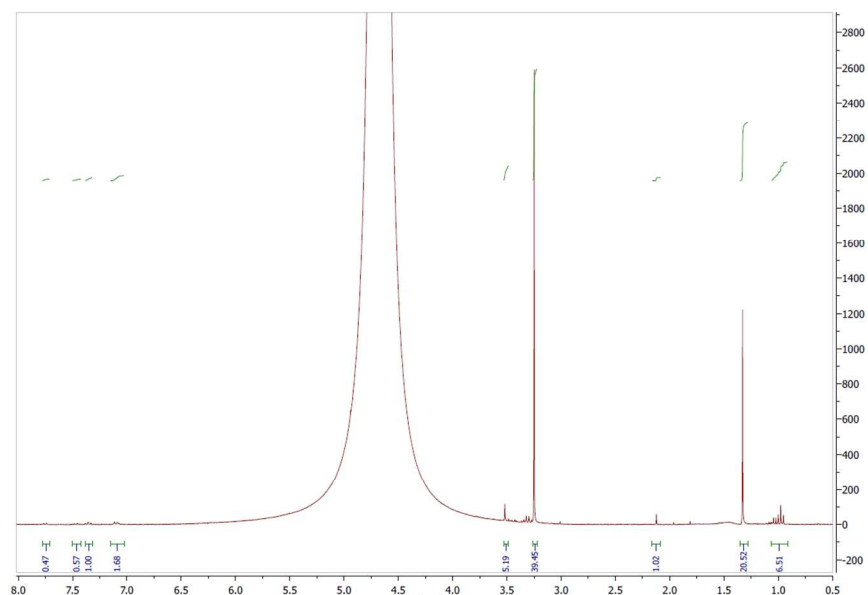


Figure S21. ^1H -NMR (D_2O) spectra of melted DMA SHF samples after 7200 s of irradiation through a 320 nm cutoff filter. The estimated reaction conversion is $\sim 100\%$. The appearance of signals in the aliphatic region suggests the formation of lower-MW products, typical from mineralization process.

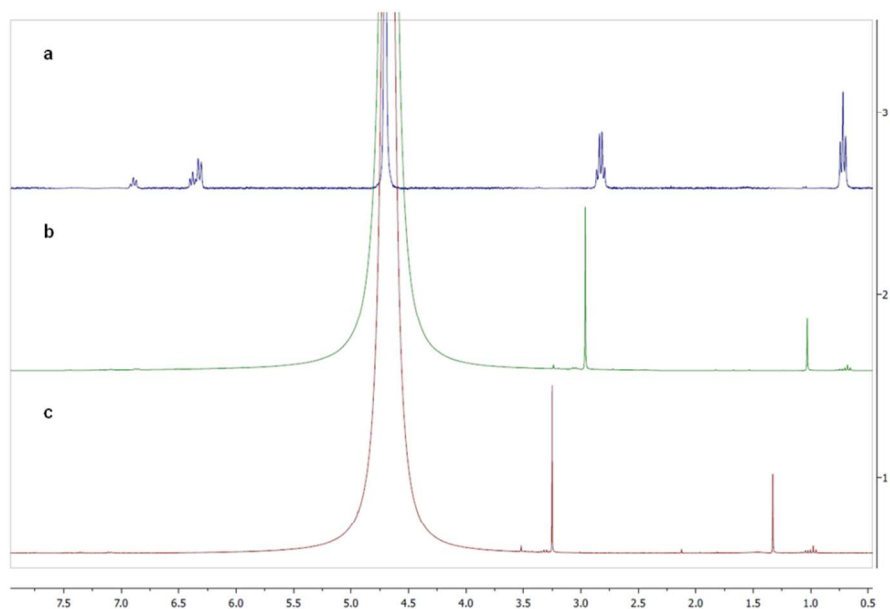


Figure S22. ^1H -NMR (D_2O) spectra of melted (a) DEA SLF samples kept in the dark, (b) DEA SLF samples after 7200 s of irradiation through a 320 nm cutoff filter, and (c) DEA SHF samples after 7200 s of irradiation without through a cutoff filter. Intensities of the signals are arbitrary.

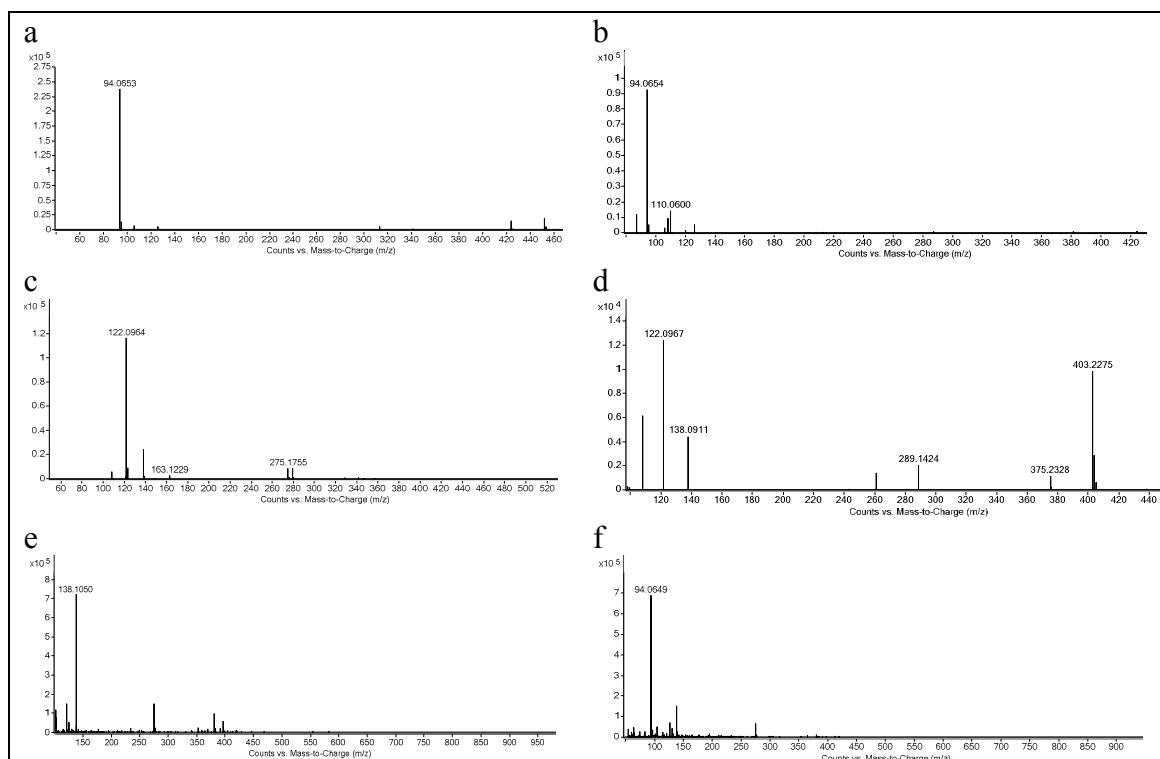


Figure S23. HRMS analyses of irradiated (a) liquid (298 K), (c) SLF (253 K; through a 320 nm cutoff filter) and (e) SHF (253 K, through a 320 nm cutoff filter) ANI/H₂O₂ samples, as well as (b) liquid (298 K) (d) SLF (253 K, through a 320 nm cutoff filter), and (f) SHF (253 K, through a 320 nm cutoff filter) DMA/H₂O₂ samples. The analyses were carried out under nitrogen flow (5 L min⁻¹).

Table S1. The redox potentials and E_{00} and ΔG^0 values.

$$\Delta G^0 = E(D^+/D) - E(A/A^-) - E_{00} \quad (1)$$

donor	$E_{1/2}(D^+/D)/V^a$	acceptor	$E_{1/2}(A/A^-)/V$	E_{00}/eV^d singlet	E_{00}/eV^d triplet	$\Delta G^0/eV$ singlet	$\Delta G^0/eV$ triplet
ANI	0.98	O ₂	-0.57^a $(-0.40^b)^5$	3.94	3.43	-2.39	-1.88
DMA	0.81		-0.57	3.81	3.34	-2.43	-1.96
DEA	0.76		-0.57	3.70	3.25	-2.37	-1.92
ANI	0.98	H ₂ O ₂	0.09 ^{c6}	3.94	3.43	-3.05	-2.54
DMA	0.81		0.09	3.81	3.34	-3.09	-2.62
DEA	0.76		0.09	3.70	3.25	-3.03	-2.58

^a 1 atm O₂ vs. NHE, converted to SCE. ^b 1 M of O₂ vs. NHE, converted to SCE. ^c NHE converted to SCE. ^d Our experimental values.

Computational Methods

The initial structures of Ani and DMA monomer and dimer associates on the ice surface were obtained from the molecular dynamics simulations on the benzene monomer and dimers. In these simulations, the force field parameters for benzene were adopted from the GROMOS 53a6 all-atom force field⁷ and the TIP5P-Ew model for the water molecules.⁸

Several snapshots of monomers and dimer associates with respect to the ice surface were further optimized at the DFT level, employing the B97D functional⁹ and TZVP basis set.¹⁰ The reliability of the B97D functional to model aromatic dimers was shown on the calculations of naphthalene dimer complexes by comparing the results with those of the more accurate DFT/CC scheme.¹¹

The cluster calculations included all water molecules within the distance of 0.9 nm from the center of mass from each adsorbent molecule. The water molecules found within 0.6 nm were optimized, whereas the remaining ones were fixed. To simulate a water environment in liquid aqueous aniline and dimethylaniline solutions, the cluster incorporating the surrounding molecules located up to 0.6 nm from the center of mass of an aniline were considered. The approach described here was already used in our previous studies on the spectroscopic properties of aromatic hydrocarbons at the ice-air interface.^{8, 12-14}

Calculations of the monomer and dimer absorption spectra in water and on the ice surface were performed at the ground-state optimized geometries with the second-order algebraic diagrammatic construction ADC(2),^{15, 16} using a spin-component scaled approach¹⁷ with the resolution-of-identity method and the def2-TZVP basis set.

Table S2. The absorption energies of aniline monomer and dimers calculated at the SCS-ADC(2) level using def2-TZVP basis set. The oscillator strengths of the transitions are given in parentheses.

Monomer				
	$S_0 \rightarrow S_1$		$S_0 \rightarrow S_2$	
	ΔE (eV)	λ (nm)	ΔE (eV)	λ (nm)
Liquid	4.589	270	5.337	232
	(0.027)		(0.117)	
Frozen	4.555	272	5.410	229
	(0.044)		(0.244)	

Dimer								
	$S_0 \rightarrow S_1$		$S_0 \rightarrow S_2$		$S_0 \rightarrow S_3$		$S_0 \rightarrow S_4$	
	ΔE (eV)	λ (nm)	ΔE (eV)	λ (nm)	ΔE (eV)	λ (nm)	ΔE (eV)	λ (nm)
ANI_D1	4.515	275	4.783	259	5.447	228	5.709	217
ANI_D2	3.830	324	4.827	257	5.120	242	5.246	236

Table S3. The absorption energies of dimethylaniline monomer and dimers calculated at the SCS-ADC(2) level using def2-TZVP basis set.

Dimer ^a				Monomer ^b		
		ΔE (eV)	λ (nm)		ΔE (eV)	λ (nm)
DMA_D1	$S_0 \rightarrow S_1$	4.385 ^a (4.189)	283 (296)	$S_0 \rightarrow S_1$	4.409	281
	$S_0 \rightarrow S_2$	4.399 (4.405)	282 (281)		4.414	281
	$S_0 \rightarrow S_3$	5.249 (5.033)	236 (246)	$S_0 \rightarrow S_2$	5.302	234
	$S_0 \rightarrow S_4$	5.305 (5.180)	234 (239)		5.308	234
DMA_D2	$S_0 \rightarrow S_1$	4.349 (4.271)	285 (290)	$S_0 \rightarrow S_1$	4.454	278
	$S_0 \rightarrow S_2$	4.396 (4.496)	282 (276)		4.502	275
	$S_0 \rightarrow S_3$	5.075 (5.022)	244 (247)	$S_0 \rightarrow S_2$	5.240	237
	$S_0 \rightarrow S_4$	5.193 (5.165)	239 (240)		5.306	237
DMA_D3	$S_0 \rightarrow S_1$	4.271	290	$S_0 \rightarrow S_1$	4.447	279
	$S_0 \rightarrow S_2$	4.342	286		4.452	278
	$S_0 \rightarrow S_3$	5.038	246	$S_0 \rightarrow S_2$	5.312	233
	$S_0 \rightarrow S_4$	5.224	237		5.316	233

^a calculated in the gas phase, energies obtained from calculations with water molecules are given in parentheses

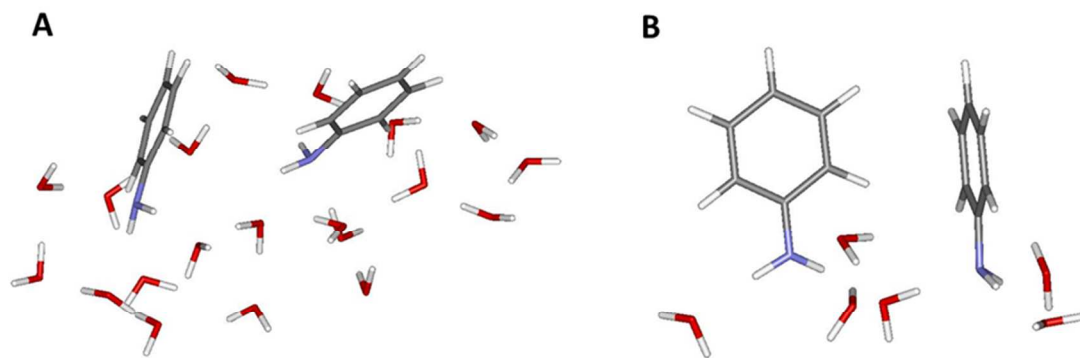


Figure S24. Structures of aniline dimer associates ANI_D1 (A) and ANI_D2 (B).

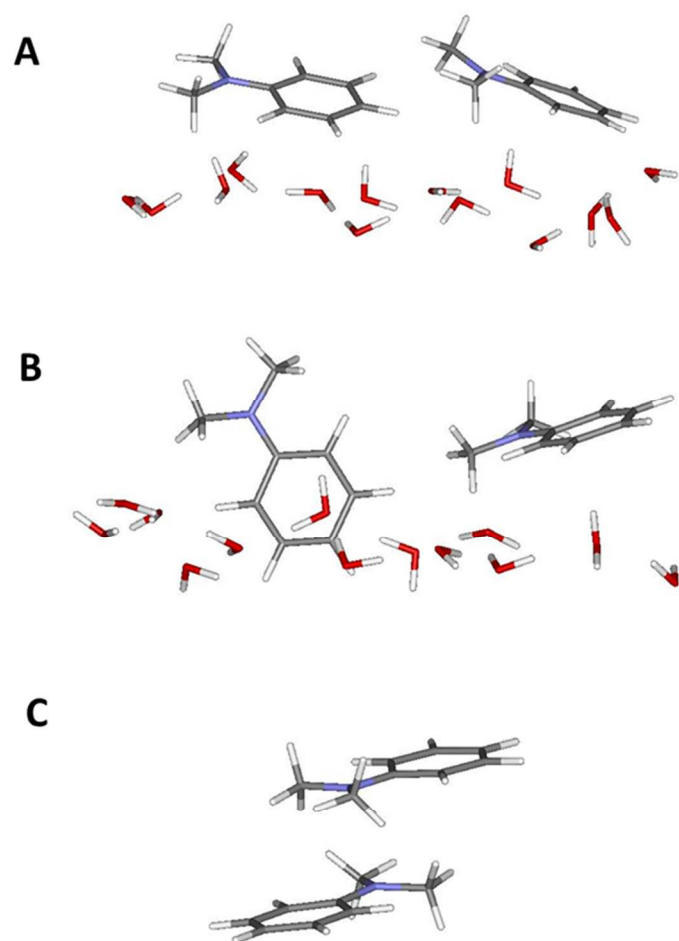


Figure S25. Structures of dimethylaniline dimer associates: DMA_D1 (A), DMA_D2 (B), and DMA_D3 (C).

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