Supplementary Information

Characterization of a Liquid-Core Waveguide cell for studying the chemistry of light-induced degradation

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A. Schematic drawing coupling pieces

Figure A.1: Cross section drawing of the coupling pieces of the LID (obtained from Dijkstra et al.\cite{dijkstra}). FT: fingertight; TH: termination head; QW: quartz window.
B. Variation due to filling procedure

![Graph showing intensity vs. flowrate for Type I and Type II LCW](image)

Figure B.1: Average transmitted light intensities (N=3) measured during the filling of a type I and type II LCW at different flow rates (50, 100, 150, 200, and 250 µL/min). The fluctuations in intensity in the type I LCW may be caused by the porous wall since these fluctuations are not present in the non-porous type II LCW.
C. Photon flux by actinometry

![Absorbance spectra of DAE](image)

*Figure C.1: The change in absorbance of DAE upon exposure of Vis or UV light (obtained from Roibu et al. [2]).*

For the purpose of turning DAE-c into DAE-o, the lamp was turned off and the UV shortpass filter was replaced by the 578 nm bandpass filter. To start the ring-opening reaction, the lamp was turned on again and the absorption spectra of this process were recorded in real-time.

The speed at which DAE-c turns into DAE-o was used to calculate the photon flux. To do so, the molar absorption coefficient ($\varepsilon$) at 578 nm was calculated first. Using UV light, a solution of DAE was turned into DAE-c until the signal became stable, indicating maximum conversion from open to closed, which is estimated to be about 79%, according to Irie et al. [3]. Then, to calculate the concentration of DAE-c at maximum conversion, the $\varepsilon$ at 562 nm was obtained from Sumi et al. [4]. With an $\varepsilon$ of 10900 M$^{-1}$cm$^{-1}$ at 562 nm, we determined the concentration of DAE-c to be 7.8*10$^{-6}$ M. Using this concentration, the $\varepsilon_{578\text{nm}}$ was also determined from the absorption spectrum at maximum conversion, which was 9954 M$^{-1}$cm$^{-1}$. 
Another important note has to be made regarding the solvent. We observed that if the Teflon material of the LCW was exposed to hexane for too long, the LCW started to deform. As the hexane is partially absorbed by the Teflon, the material swells over time. This does not have to cause a direct problem, except when the LCW starts to touch the outer tubing. A bright spot was observed at the location where this happened, indicating light loss. Therefore, the LID cell had to be filled with water for storage and in between experiments that were not performed consequently, which also made the tubing regain its original form.

Calculations:

The UV-induced conversion from the open to the closed form has a high quantum yield (0.45 at $\lambda = 268$ nm according to Sumi et al. 4), whereas the conversion back to the open form has a very low quantum yield which is wavelength dependent. Sumi et al. report the following dependence for the opening reaction 4:

$$ \log \Phi_{CO} = -2.67 + \frac{526}{\lambda}, \ 480 \ nm \leq \lambda \leq 620 \ nm $$

(Eq. C.1)

in which $\Phi_{CO}$ is the quantum yield for the opening reaction and $\lambda$ is the wavelength of irradiation (nm).

The calculation of the photon flux based on actinometric experiments is, traditionally, done as described in this section 2,5–7. Consider a photo-induced reaction of compound X to compound Y, this can schematically be written as:

$$ X \xrightarrow{\text{light}} Y $$

In such reactions, the absorption of an incoming photon is linked to the conversion ($R$) of X into Y. This can be visualized by, for example, the appearance of a new peak in the absorbance spectrum that is characteristic for the product formed. Actinometry experiments are set-up to track this change in concentration using absorption measurements. In the case of
the commonly used ferrioxalate actinometer, the conversion \( R \) is determined by means of a calibration curve.

The quantum yield, \( \Phi_\lambda \), represents the efficiency of a photo-induced reaction. It provides information about the number of the absorbed photons accompanied for such a reaction. Therefore, the change in concentration, \( c \), of the compound X can be calculated by:

\[
\frac{dc}{dt} = -\Phi_\lambda q_\lambda I_{abs} V_r
\]

in which \( I_{abs} \) is the absorbed photon flux in Einstein s\(^{-1}\) and \( V_r \) is the reaction volume (L).

However, no complete absorption is achieved, so, Lambert-Beer is needed:

\[
A = -\log \frac{I_{transmitted}}{q_\lambda} = \epsilon cl
\]

in which \( A \) is the absorbance, \( I_{trans} \) is the transmitted light, \( q_\lambda \) is the initial (overall) photon flux (both einstein s\(^{-1}\)); \( \epsilon \) is the absorption coefficient (M\(^{-1}\)cm\(^{-1}\)); and \( l \) is the optical pathlength (cm). Thereby, making:

\[
I_{abs} = q_\lambda (1 - 10^{-\epsilon cl})
\]

Substitution of equation C.4 into equation C.2 results in \(^2\):

\[
\frac{dc}{dt} = -\frac{\Phi_\lambda q_\lambda}{V_r} (1 - 10^{-\epsilon cl})
\]

Integration of the formula gives a formula that relates the conversion to the photon flux:

\[
\left( \frac{\Phi_\lambda q_\lambda}{V_r} \right) t = c(0)R + \frac{1}{\epsilon l} \ln \left( \frac{1 - 10^{-\epsilon c(0)l}}{1 - 10^{-\epsilon c(t)l}} \right)
\]

in which \( t \) is the time of irradiation (s), \( R \) is the conversion of compound X to Y, \( c(0) \) is the initial concentration (M), \( c(t) \) is the concentration at time \( t \).
However, in our system, online and direct detection is required, since the exact number of photons inside the LCW must be determined. Lehóczki et al. proposed an alternative way of actinometry with online spectrophotometric detection \(^8\). They avoided the need of a calibration of the light source by continuously monitoring the absorption over time. A specific wavelength was chosen of which the change in absorbance was directly used to calculate the photon flux. They proposed the following formula, which was used in our calculations of the photon flux:

\[
q_\lambda = \left(\frac{dA_\lambda}{dt}\right) \times \frac{V_r}{\Phi_\lambda \epsilon_\lambda l}
\]

(Eq. C.7)

in which \(q_\lambda\) is the overall photon flux (einstein s\(^{-1}\)); \(V_r\) the reaction volume (L); \(\Phi_\lambda\) the quantum yield at wavelength \(\lambda\); \(\epsilon_\lambda\) is the absorption coefficient (M\(^{-1}\)cm\(^{-1}\)) and \(l\) is the optical pathlength (= length of the LCW, cm).
D. CV and EY degradation

Figure D.1: Molecular structure of eosin Y.

Figure D.2: Molecular structure of crystal violet.

Figure D.3: LC-PDA chromatogram obtained of analysis of an EY solution after 3-hr exposure, extracted at 254 nm.
Figure D.4: Proposed reaction mechanism for photodegradation of crystal violet. Both demethylation (1 → 7) takes place, as well as cleavage of the central carbon-atom, resulting in Michler’s ketone (4) and dimethylaminophenol (6). Figure obtained from Confortin and Kuramoto.9,10
Figure D.5: Normalized and smoothed absorption spectra of CV (peak 1) and degradation products (peaks 2-7 and 13) obtained from LC-PDA analysis of the 5-hr exposed CV sample.

Figure D.6: Normalized and smoothed absorption spectra of peaks 8 – 10 obtained during LC-PDA analysis of the 5-hr exposed CV sample.
Table D.1: LC-PDA peak table of the 5-hr exposed CV sample with tentative assignments.

<table>
<thead>
<tr>
<th>Peak number</th>
<th>RT (min)</th>
<th>abs max (nm)</th>
<th>Tentative assignment</th>
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<tr>
<td>1</td>
<td>18.99</td>
<td>590</td>
<td>CV</td>
</tr>
<tr>
<td>2</td>
<td>18.67</td>
<td>582</td>
<td>mono-demethylated CV</td>
</tr>
<tr>
<td>3</td>
<td>18.30</td>
<td>574</td>
<td>bis-demethylated CV</td>
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<td>4</td>
<td>17.89</td>
<td>568</td>
<td>tri-demethylated CV</td>
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<td>5</td>
<td>17.79</td>
<td>580</td>
<td>isomer of peak 4</td>
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<td>6</td>
<td>17.43</td>
<td>571</td>
<td>tetra-demethylated CV</td>
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<tr>
<td>7</td>
<td>17.01</td>
<td>560</td>
<td>penta-demethylated CV</td>
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<td>13.56</td>
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References


