Radiometric Measurement Techniques for in-Depth Characterization of Photoreactors - Part 1: 2 Dimensional Radiometry

Supporting Information

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S1 Setup of the Device

S1.1 Radiometric Scanning Device

A description of the full 3D radiometric scanning device, including detailed drawings and bills of materials is published in the ESI of part 2. DOI: 10.1039/d0re00457j .[1] It is also published on GitHub `https://github.com/photonZfeed/multiDradiometry` and as a stable version in the Zenodo repository `https://doi.org/10.5281/zenodo.4898138` .

S1.2 Investigated Reactor Setup

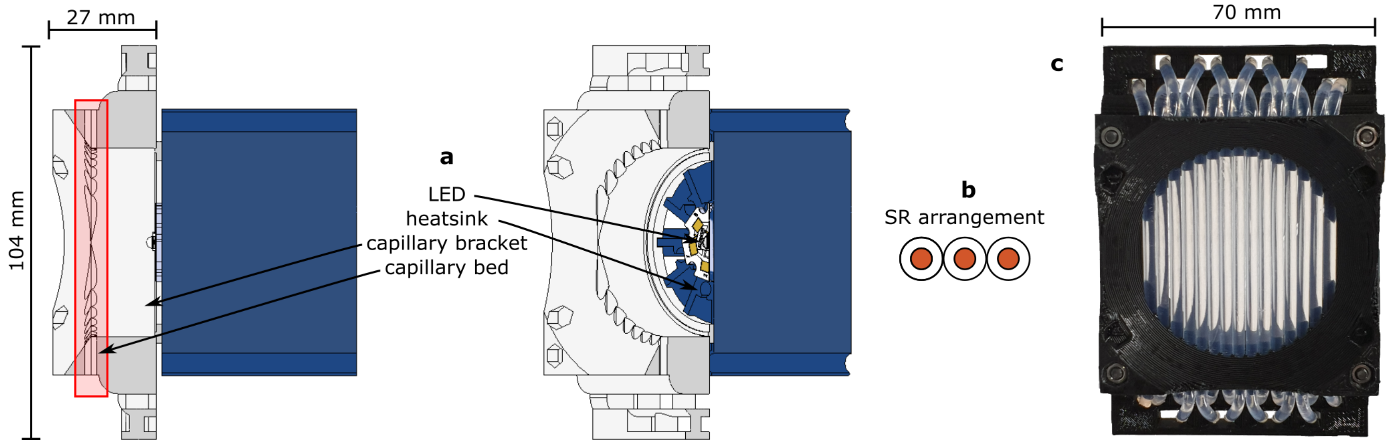

Figure S1 a: Two (cut) CAD views of the reactor for hosting single row (SR) capillaries. The capillary bed is highlighted with red. b: The single row (SR) capillary arrangement. c: photography of the 3D printed SR capillary scaffold with inserted capillaries.

S1.3 Approximated Area with Absorption less than 99 %

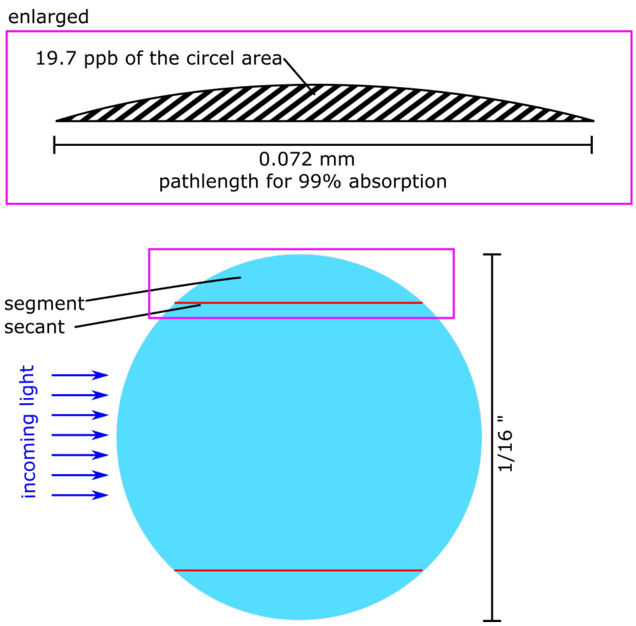

Figure S2 Illustration of the area in a 1/16 " capillary where the secants are shorter than 0.072 mm. This is the path length where a 7.4 mM MeOr solution absorbs 99 % of radiation at 465 nm.

S2 Results and Discussion

S2.1 Trigonometric Calculation

Knowing the distance from the LED to the detector, the approximated distance between the two gaps and the distance of the lines on the scanned canvas, it is possible to calculate the distance between the LED and the capillaries by the rule of three:

$$\frac{S_1}{F_1} = \frac{S_2}{F_2} \tag{1}$$

$$S_1 = \frac{S_2 \cdot F_1}{F_2} = \frac{145\,\text{mm} \cdot 3.175\,\text{mm}}{31.2\,\text{mm}} = 14.8\,\text{mm} \tag{2}$$

where S_1 is the distance between the LED and the capillaries, F_1 is the gap between the capillaries, S_2 is the distance between the LED and the virtual canvas and F_2 is the distance between the two visible lines on the canvas. The geometrical setup is shown in Fig. 6.

The real distance between the LED and the capillaries is 15 mm.

S2.2 Photon Flux

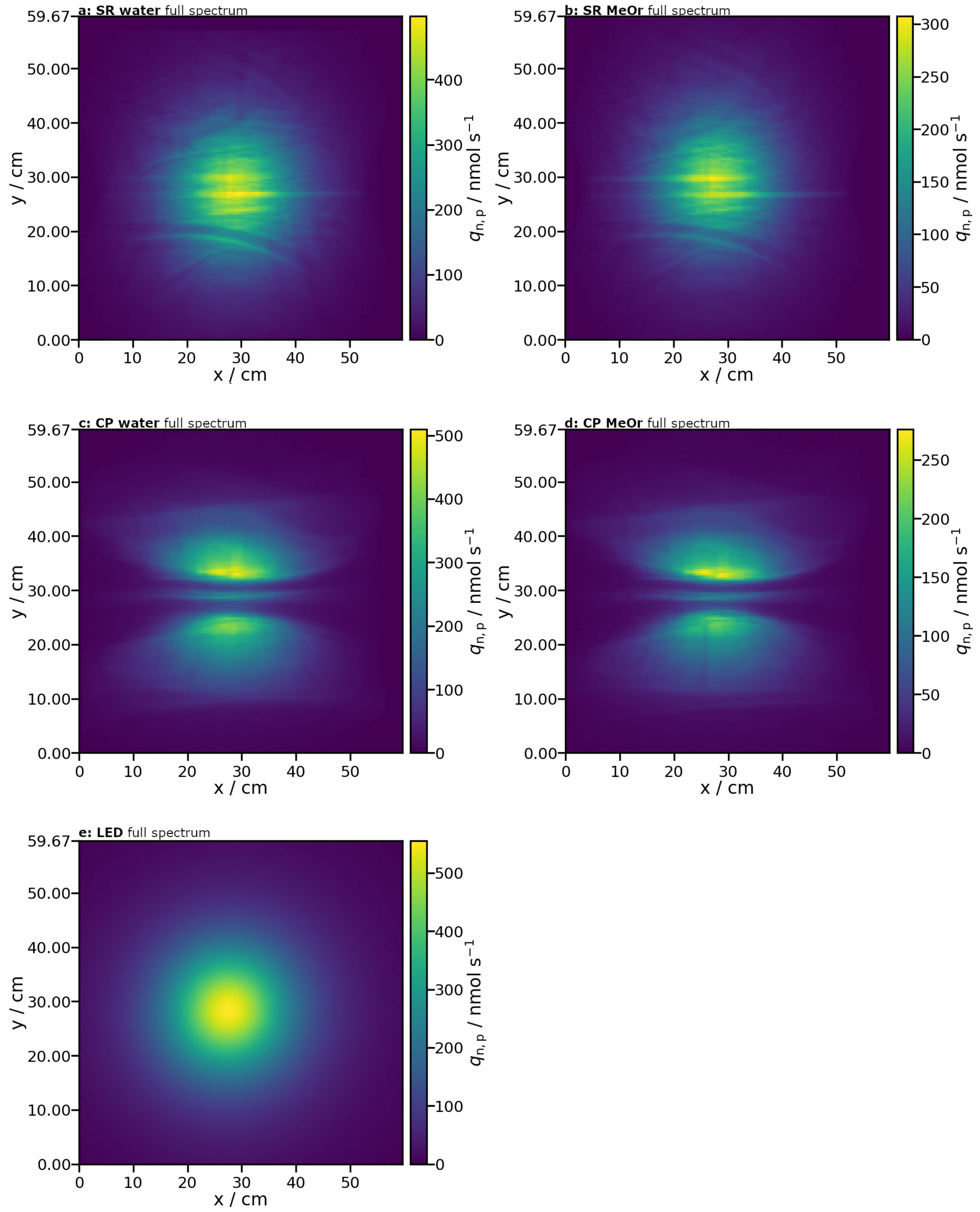

Figure S3 Photon-flux-heatmaps of the LED as well as the single row (SR) and closest-packed reactor (CP), each filled with either water or MeOr solution, calculated from the full measured spectrum.

S2.3 Peak Ratios

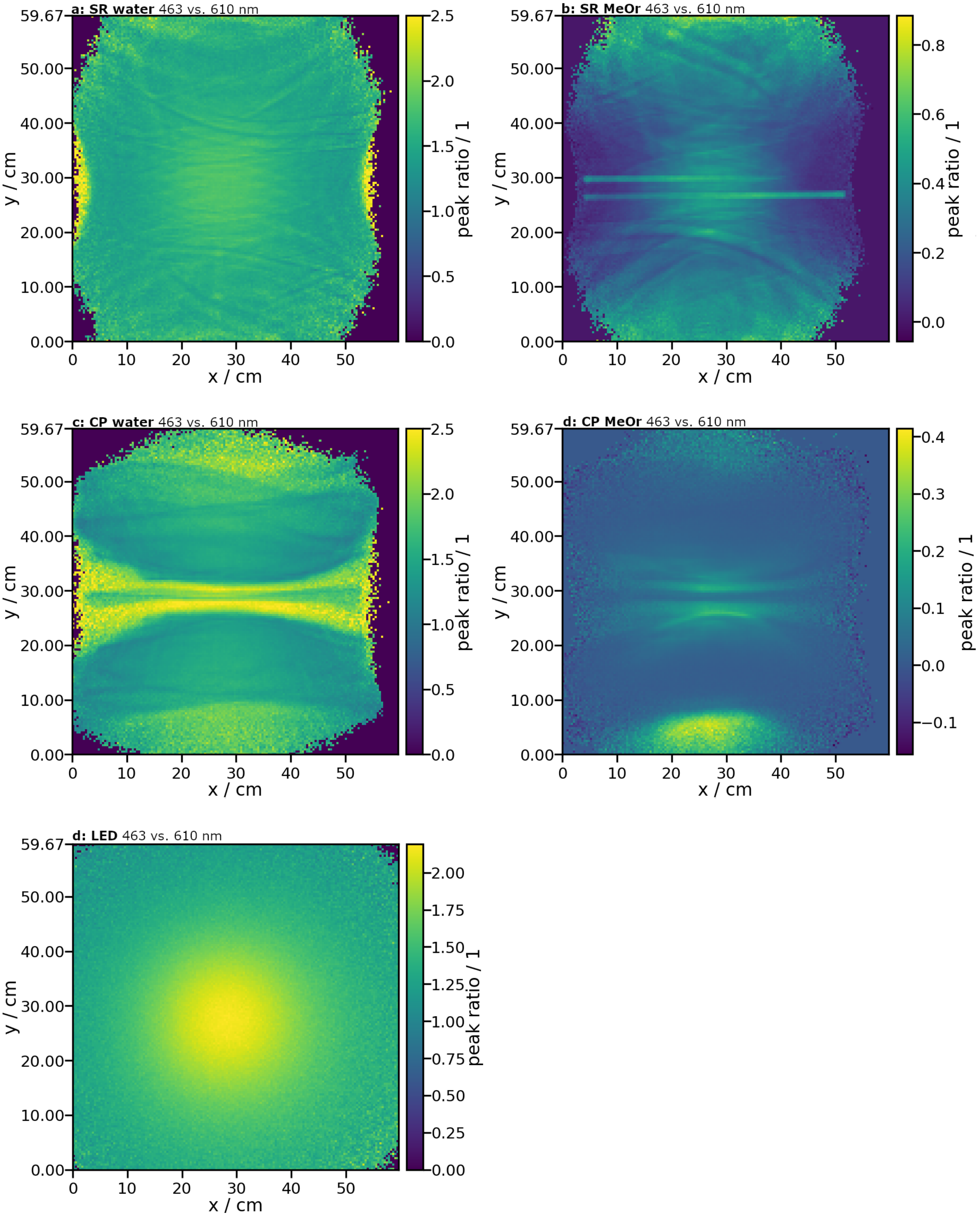

Figure S4 Peak ratio heatmaps of the LED as well as the single row (SR) and closest-packed reactor (CP), each filled with either water or MeOr solution . Displaying the ratio between the peak intensity at 465 nm and 609 nm. The heatmaps are scaled to the respective maximum.

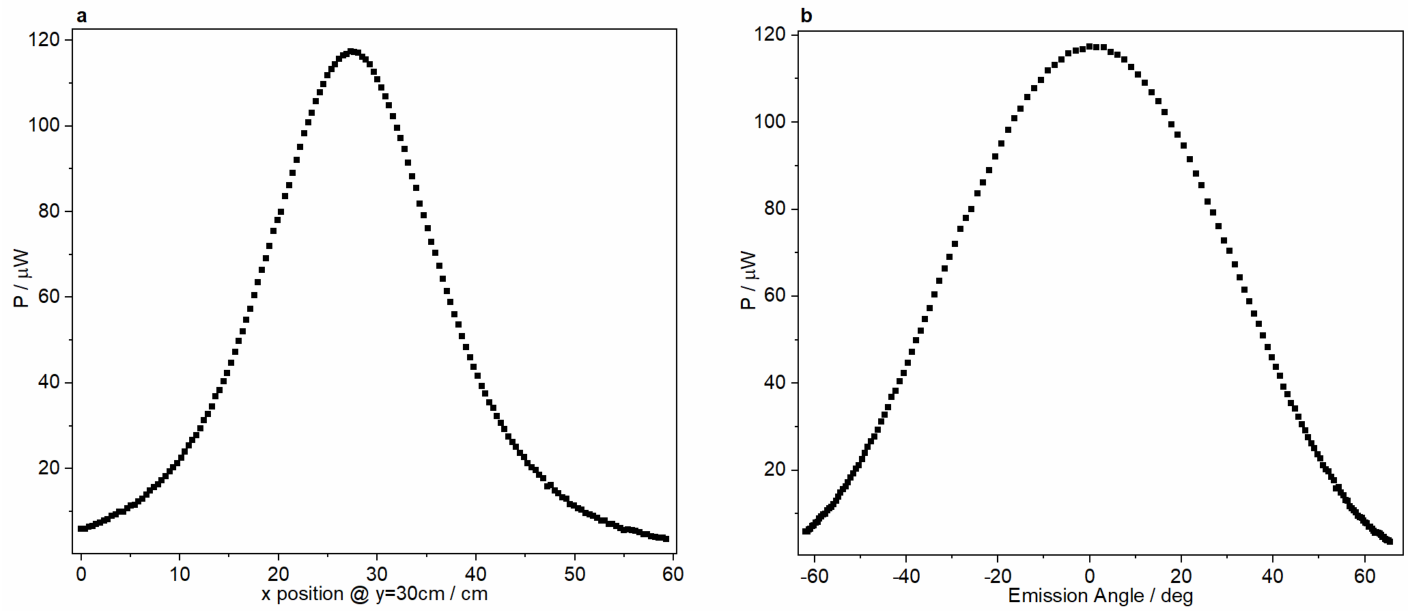

Figure S5 a: Received power per pixel over the x-position at y=30 cm. b: Received power per pixel over the emission angle, where x=27.3 cm is set to 0°. Extracted from ESI Fig. S3 **e**.

S2.4 Efficiencies

S2.4.1 Calculations used for Fig. S6

Reflected or unknown (rou) at first layer (L1):
The percentage of photons which do not pass the first capillary layer (filled with water) is calculated as the quotient of the absorbable photon flux after the SR setup filled with water and the measured photon flux of the LED.

$$\begin{aligned}\eta_{\mathrm{a,L1,rou}} &= \left(1-\frac{q_{\mathrm{a,SR,H_2O}}}{q_{\mathrm{a,LED}}}\right)\cdot 100\,\% \\ &= \left(1-\frac{0.874\,\mu\mathrm{mol\,s^{-1}}}{1.247\,\mu\mathrm{mol\,s^{-1}}}\right)\cdot 100\,\% \\ &= 30\,\%\end{aligned} \tag{3}$$

Absorption (abs) in first layer (L1):
The percentage of absorbed light in the first capillary layer was calculated as quotient of the absorbed photon flux in the first layer $(q_{\mathrm{a,SR,H_2O}} - q_{\mathrm{a,SR,MeOr}})$ and the measured photon flux of the LED.

$$\begin{aligned}\eta_{\mathrm{a,L1,abs}} &= \frac{\left(q_{\mathrm{a,SR,H_2O}} - q_{\mathrm{a,SR,MeOr}}\right)}{q_{\mathrm{a,LED}}}\cdot 100\,\% \\ &= \frac{\left(0.874\,\mu\mathrm{mol\,s^{-1}} - 0.224\,\mu\mathrm{mol\,s^{-1}}\right)}{1.247\,\mu\mathrm{mol\,s^{-1}}}\cdot 100\,\% \\ &= 52\,\%\end{aligned} \tag{4}$$

Reflected or unknown (rou) at second layer (L2):
The percentage of photons which do not pass the second capillary layer (filled with water) The absorptivity of the second layer is determined from the ratio of the systems filled with water. This share is then removed from the photon flux after the SR-reactor filled with MeOr solution.

$$\begin{aligned}\eta_{\mathrm{a,L2,rou}} &= \frac{\left(1-\frac{q_{\mathrm{a,CP,H_2O}}}{q_{\mathrm{a,SR,H_2O}}}\right)\cdot q_{\mathrm{a,SR,MeOr}}}{q_{\mathrm{a,LED}}}\cdot 100\,\% \\ &= \frac{\left(1-\frac{0.734\,\mu\mathrm{mol\,s^{-1}}}{0.874\,\mu\mathrm{mol\,s^{-1}}}\right)\cdot 0.224\,\mu\mathrm{mol\,s^{-1}}}{1.247\,\mu\mathrm{mol\,s^{-1}}}\cdot 100\,\% \\ &= 3\,\%\end{aligned} \tag{5}$$

Absorption (abs) in second layer (L2):
The percentage of absorbed light in the second capillary layer was calculated as quotient of the not absorbed photon flux in the first layer minus the not absorbed photon flux after the second layer and the measured photon flux of the LED.

$$\begin{aligned}\eta_{\mathrm{a,L2,abs}} &= \frac{\left(\frac{q_{\mathrm{a,CP,H_2O}}}{q_{\mathrm{a,SR,H_2O}}} \cdot q_{\mathrm{a,SR,MeOr}} - q_{\mathrm{a,CP,MeOr}}\right)}{q_{\mathrm{a,LED}}} \cdot 100\,\% \\ &= \frac{\left(\frac{0.734\,\mu\mathrm{mol\,s^{-1}}}{0.874\,\mu\mathrm{mol\,s^{-1}}} \cdot 0.224\,\mu\mathrm{mol\,s^{-1}} - 0.075\,\mu\mathrm{mol\,s^{-1}}\right)}{1.247\,\mu\mathrm{mol\,s^{-1}}} \cdot 100\,\% \\ &= 9\,\%\end{aligned} \tag{6}$$

Transmitted (trans) after second layer (L2):
The percentage of transmitted light after both capillary layers was calculated as quotient of the photon flux after the CP-reactor filled with MeOr solution and the measured photon flux of the LED.

$$\begin{aligned}\eta_{\mathrm{a,L2,trans}} &= \frac{q_{\mathrm{a,CP,MeOr}}}{q_{\mathrm{a,LED}}} \cdot 100\,\% \\ &= \frac{0.075\,\mu\mathrm{mol\,s^{-1}}}{1.247\,\mu\mathrm{mol\,s^{-1}}} \cdot 100\,\% \\ &= 6\,\%\end{aligned} \tag{7}$$

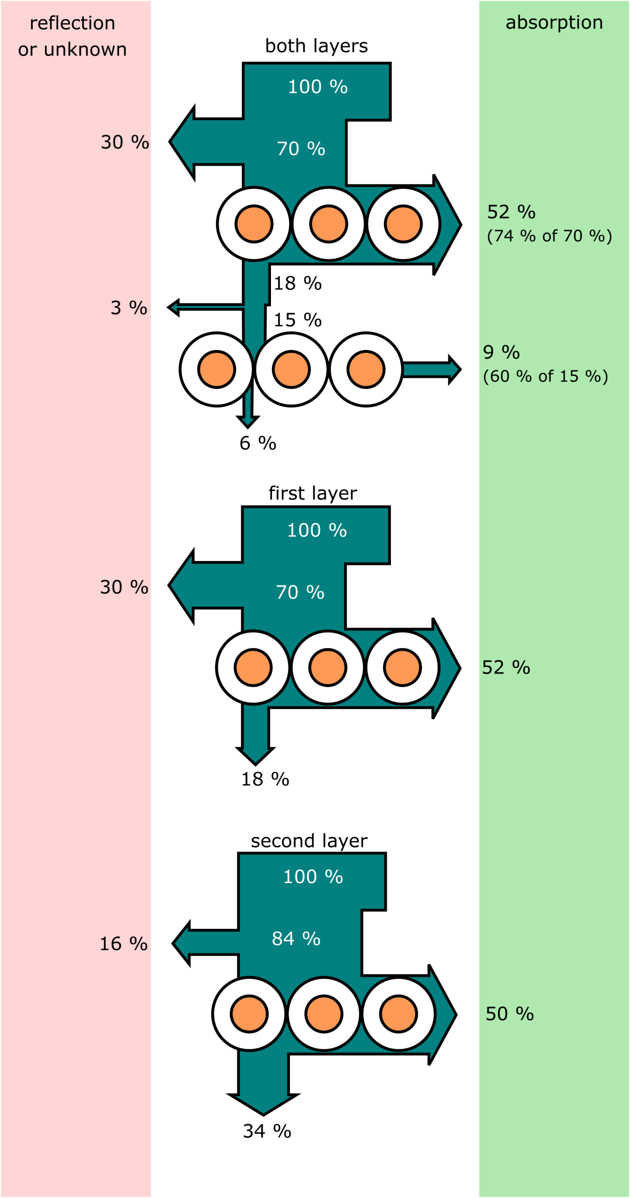

Figure S6 Sankey diagrams of the calculated efficiencies, for both layers and for each layer individually.

S2.5 Ray Tracing

For ray tracing with Optical Ray Tracer, following options were used:

beam count	1000	beam width	1
dispersion beams	0	diverging source	true
inter lens epsilon	1e-06	max intersections	64
surface epsilon	5e-04	IOR water	1.333
IOR PFA	1.344		

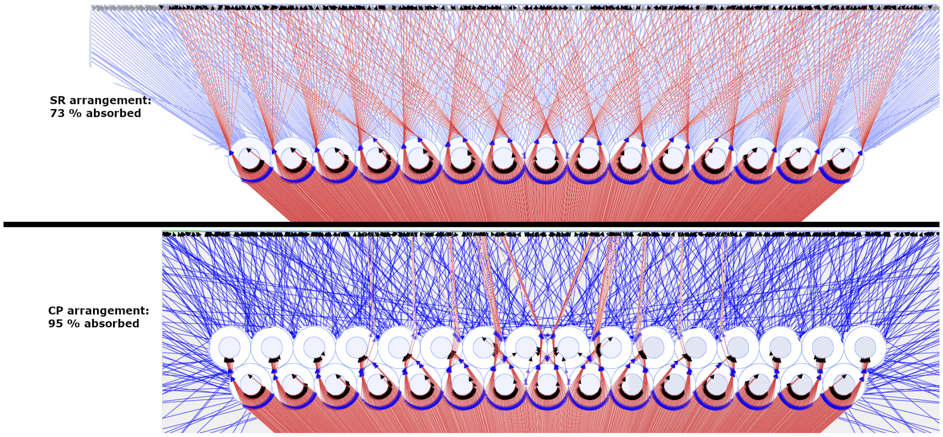

Figure S7 Illustration of the 2D ray tracing for the SR and the CP arrangement. Red rays: from simulation with absorber inside capillaries. Blue rays: from simulation with no absorber inside capillaries.

S2.6 Actinometry conditions and results

For the actinometric measurements, a Nichia NVSU233A-D1 SMD-LED (405 nm) was operated at 700 mA. According to the data sheet, the radiant flux for this condition is 0.98 W or, in photonic quantities, 3.362 μmol s^{-1}. The mean incident photon flux $q_{\mathrm{n,p}}$ was computed from the actinometer conversion in each layer. The $q_{\mathrm{n,p}}$ split up for different irradiation times t_{irr} is presented in table S1.

Table S1 Incident photon fluxes at different irradiation times in the three consecutive capillary layers.

t_{irr} / s	layer 1 / μmol s^{-1}	layer 2 / μmol s^{-1}	layer 3 / μmol s^{-1}
18	1.822	0.336	0.073
21	1.812	0.351	0.088
24	1.841	0.356	0.109
27	1.814	0.354	0.095
30	1.834	0.339	0.076
mean	1.824	0.348	0.090

S3 Data Processing

S3.1 Dark Correction

The measured counts over the wavelength (scope, S) are corrected with a dark measurement (D_λ), representing the counts over the wavelength measured by the spectrometer with no light.

$$S_{\lambda,-\mathrm{D}} = S_\lambda - D_\lambda \quad ; \quad [S_{\lambda,-\mathrm{D}}] = \mathrm{counts/nm} \tag{8}$$

S3.2 Noise Detection

Before further processing, the spectra are checked for a sufficient noise to signal ratio NTSR. Processing noisy spectra can lead to runaways in the processed data points, especially when integrating over the pixels, and consequently complicates interpretation. The noise to signal ratio is calculated by the ratio between the standard deviations s_1 and s_2 over the wavelength of two ranges of the measured spectra:

$$NTSR = \frac{s_1}{s_2} \tag{9}$$

The standard deviation s_i is calculated as:

$$s_i = \sqrt{\frac{\sum_{j=\lambda_{i,1}}^{\lambda_i,z} \left(S_{-\mathrm{D},j} - \bar{S}_{-\mathrm{D},\lambda_1,\lambda_2}\right)^2}{N-1}} \tag{10}$$

λ_1 and λ_2 are the borders of the respective wavelength ranges and N is the number of data points within this range. One range represents the noise of the measurement without detected light ("dark" regions), the other one the signal quantity of the measurement. For the used setup, the wavelength ranges from 300 nm to 389 nm and 389 nm to 800 nm were used as s_1 and s_2, respectively. The wavelengths of the first range are smaller than the emission wavelengths of the used LED, whereas the wavelengths of the second range match the emission wavelengths of the used LED. In case of a noise to signal ratio smaller than 0.55, the methods described in the following assign 0 or the colour black to the respective measurement point.

S3.3 Radiant Flux

The dark corrected scope data for each measurement point is multiplied with the calibration curve of the spectrometer, yielding the spectral irradiance E_λ:

$$E_\lambda = S_{-\mathrm{D}} \cdot \text{calibration curve} \quad ; \; [E_\lambda] = \mu\mathrm{W\,cm^{-2}\,nm^{-1}} \tag{11}$$

Predefined by the spectrometer's manufacturer, this conversion results in the received power of 1 cm^2, since, each spectrum is then scaled to the area of a pixel (3.9 mm x 3.9 mm), yielding the received spectral power of a pixel $P_{\lambda,\mathrm{px}}$:

$$P_{\lambda,\mathrm{px}} = E_\lambda \cdot 0.1521\,\mathrm{cm}^2 \quad ; \; [P_{\lambda,\mathrm{px}}] = \mu\mathrm{W\,nm^{-1}} \tag{12}$$

Integration over the wavelength λ yields the power of a pixel:

$$P_{\mathrm{px}} = \int_{\lambda_1}^{\lambda_2} P_{\lambda,\mathrm{x,y}} d\lambda \quad ; \; [P_{\mathrm{px}}] = \mu\mathrm{W} \tag{13}$$

Summation over the whole scanning surface gives the total received radiant flux P:

$$P = \sum_{i=x,y}^{x_{\max},y_{\max}} P_{\mathrm{px},i} \quad ; \; [P] = \mu\mathrm{W} \tag{14}$$

S3.4 Photon Flux

With the Planck-Einstein relation, the irradiance spectra can be converted to photon flux spectra. Each spectrum is then integrated over the wavelength and scaled to the area of a pixel (3.9 mm x 3.9 mm) to yield the photon flux per pixel:

$$q_{\mathrm{n,p,px}} = \int_{\lambda_1}^{\lambda_2} \frac{E_\lambda \cdot \lambda}{h \cdot c \cdot N_\mathrm{A}} d\lambda \cdot 0.1521\,\mathrm{cm}^2 \quad ; \; [q_{\mathrm{n,p,px}}] = \mu\mathrm{mol\,s^{-1}} \tag{15}$$

Whereas N_A is the Avogadro constant ($6.022\,140\,76 \cdot 10^{23}\,\mathrm{mol}^{-1}$). Summation over the whole scanning surface gives the total received photon flux of the complete measuring canvas.

$$q_{\mathrm{n,p}} = \sum_{i=x,y}^{x_{\max},y_{\max}} q_{\mathrm{n,p,px,i}} \quad ; \; [q_{\mathrm{n,p,px}}] = \mu\mathrm{mol\,s^{-1}} \tag{16}$$

S3.5 Calculation of the absorbable light fraction

The efficiency of the investigated reactor system was calculated as the ratio between the detected photon flux of the measurements with and without MeOr solution in the capillaries. Since the fraction of incident light, which is not absorbable by the MeOr solution, must be considered, this fraction was calculated with the Lambert-Beer law and the absorbance of a MeOr solution. Because of aggregation effects, the spectral absorbance of a MeOr solution changes for concentrations larger than 1 mM and does not follow the Lambert-Beer law any more.[2] Due to the high absorbance, the measured absorbance was very noisy for $\lambda < 550\,\mathrm{nm}$ and would have complicated calculations. Hence, a fit function was used to model the absorbance curve A_art (Fig. S9). For this a skewed Gaussian function is used:

$$A_\mathrm{art} = f(x;A;\mu;\sigma;\gamma) = 10^{\left(7 \cdot \frac{A}{\sigma\sqrt{2\pi}} \exp\left(\frac{-(x-\mu)^2}{2\sigma^2}\right)\left(1+erf\left(\frac{\gamma(x-\mu)}{\sigma\sqrt{2}}\right)\right)\right)} \tag{17}$$

With $A = 16386626.6$, $\mu = 567.358141$, $\sigma = 37193531.6$, and $\gamma = -2830490.97$. The not absorbable part of the measured LED spectrum then can be calculated according to

$$P_{\lambda,\mathrm{na}} = \frac{P_\lambda}{A_\mathrm{art}} \tag{18}$$

The not absorbable fraction, exemplarily shown in ESI Fig. S9 as solid line, was subtracted from the measured irradiance to receive the absorbable power $P_{\lambda,\mathrm{a}}$, exemplarily shown in ESI Fig. S9 as dots and dash line.

$$P_{\lambda,\mathrm{a}} = P_\lambda - P_{\lambda,\mathrm{na}} \tag{19}$$

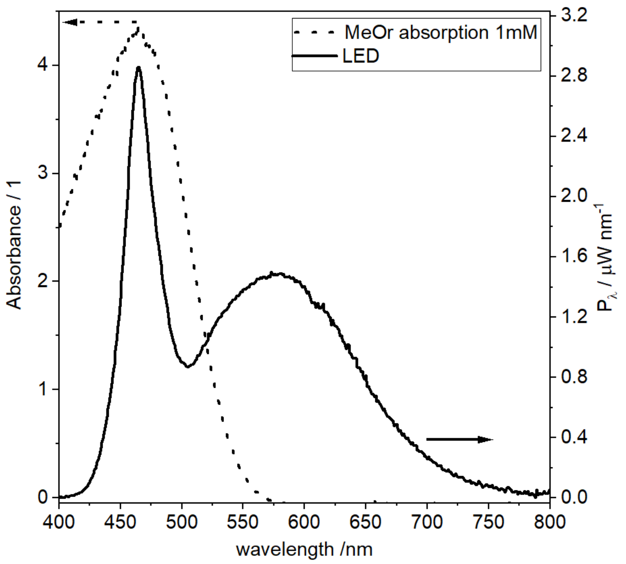

Figure S8 Dotted: Calculated absorbance for a 1 mM MeOr solution and a path length of 1/16". Solid: LED spectrum.

The not absorbable photon flux $q_{\mathrm{n,p,na}}$ and the absorbable photon flux $q_{\mathrm{n,p,a}}$ can be calculated according Equations 15 and 16.

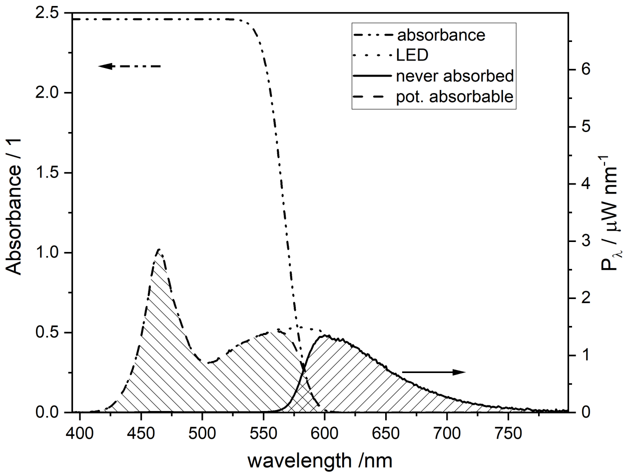

Figure S9 The LED spectrum, divided in an absorbable part and a not absorbable part by the use of the absorbance curve.

S3.6 Colour

By calculating the theoretical colour perceived by the human eye, interpretation of changes to the spectrum is simplified. The respective colour for each measurement position was calculated according to Hunt and Pointer with code from Christian Hill, using the CIE 1931 standard colorimetric observer, yielding a sRGB value.[3, 4] The respective colour is plotted in a heatmap.

Figure S10 shows the CIE 1931 standard colour matching functions $\bar{x}_\lambda$, $\bar{y}_\lambda$ and $\bar{y}_\lambda$. The integral of the product of P_λ with the respective colour matching function yields the CIE tristimulus values X, Y and Z:

$$X = \int P_\lambda \bar{x}_\lambda d\lambda, \tag{20}$$

$$Y = \int P_\lambda \bar{y}_\lambda d\lambda, \tag{21}$$

$$Z = \int P_\lambda \bar{z}_\lambda d\lambda \tag{22}$$

These values are normalized over their sum:

$$x = \frac{X}{X+Y+Z}, \quad y = \frac{Y}{X+Y+Z}, \quad z = \frac{Z}{X+Y+Z} = 1 - x - y \tag{23}$$

The RGB values were then calculated using the matrix of the NTSC primary colour chromaticities, which indicate a triangle region in the CIE standard chromaticity diagram:

$$\begin{pmatrix} x_\mathrm{r} & x_\mathrm{g} & x_\mathrm{b} \\ y_\mathrm{r} & y_\mathrm{g} & y_\mathrm{b} \\ z_\mathrm{r} & z_\mathrm{g} & z_\mathrm{b} \end{pmatrix} = \begin{pmatrix} 0.67 & 0.21 & 0.14 \\ 0.33 & 1.71 & 0.08 \\ 1-x_\mathrm{r}-y_\mathrm{r} & 1-x_\mathrm{g}-y_\mathrm{g} & 1-x_\mathrm{b}-y_\mathrm{b} \end{pmatrix} \tag{24}$$

With the relation

$$\begin{pmatrix} x_\mathrm{r} & x_\mathrm{g} & x_\mathrm{b} \\ y_\mathrm{r} & y_\mathrm{g} & y_\mathrm{b} \\ z_\mathrm{r} & z_\mathrm{g} & z_\mathrm{b} \end{pmatrix} \begin{pmatrix} r \\ g \\ b \end{pmatrix} = \begin{pmatrix} x \\ y \\ z \end{pmatrix} \tag{25}$$

the RGB values were calculated by multiplication of the inverse matrix of the primary colour chromaticities with the (x,y,z) vector. If the values of (x,y,z) point outside the triangle defined by the primary colour chromaticities, negative r, g or b occur. These RGB sets are scaled to positive values by adding the absolute value of the negative value to all components of the RGB set.

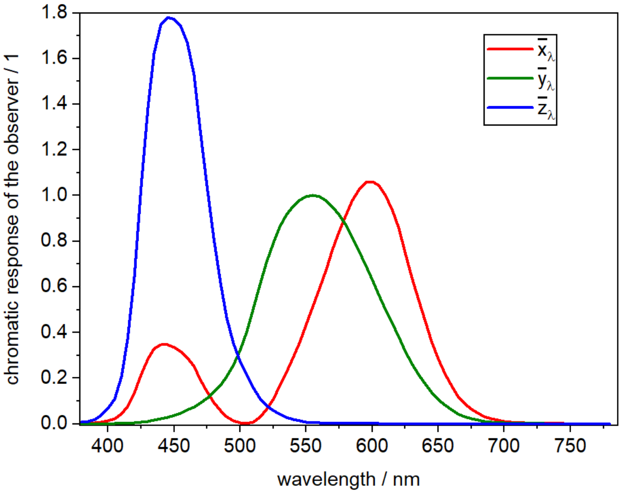

Figure S10 The CIE XYZ standard observer colour matching functions.[4]

S3.7 Peak Ratio

The peak ratio PR was calculated by dividing the mean spectral power in the range of 462 nm to 464 nm by the mean irradiance in the range of 609 nm to 611 nm.

$$\mathrm{PR}_{\frac{463}{610}} = \frac{\frac{\sum_{i=462\,\mathrm{nm}}^{464\,\mathrm{nm}} P_i}{N_\mathrm{detector\ pixels}}}{\frac{\sum_{i=609\,\mathrm{nm}}^{611\,\mathrm{nm}} P_i}{N_\mathrm{detector\ pixels}}} \tag{26}$$

The number of detector pixels $N_\mathrm{detector\ pixels}$ for both wavelength ranges was 4 for the used spectrometer.

References

1 M. Sender and D. Ziegenbalg, *Reaction Chemistry & Engineering*, 2021, DOI: `10.1039/D0RE00457J`.

2 K. L. Kendrick and W. R. Gilkerson, *Journal of Solution Chemistry*, 1987, **16**, 257–267.

3 R. W. G. Hunt and M. Pointer, *Measuring colour*, Wiley, Chichester West Sussex U.K., 4th ed., 2011.

4 Christian Hill, *Converting a spectrum to a colour*, https://scipython.com/blog/converting-a-spectrum-to-a-colour/, (accessed April 2020).