Electronic Supplementary Material (ESI) for Reaction Chemistry & Engineering.

Radiometric Measurement Techniques for in-Depth Characterization of Photoreactors - Part 2: 3 Dimensional and Integral Radiometry

Supporting Information

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S2 Materials and Methods

S2.1 Mechanical Developments

Fig. S1 shows how a third moving axis is added to the scanning device. A z-carriage unit (right) is added to each z-axis aluminium rail. The carriages are each driven by a lead screw and always move synchronized. The carriages can be connected with aluminium rails on which the reactor or the light source is installed and then moved along the z-axis.

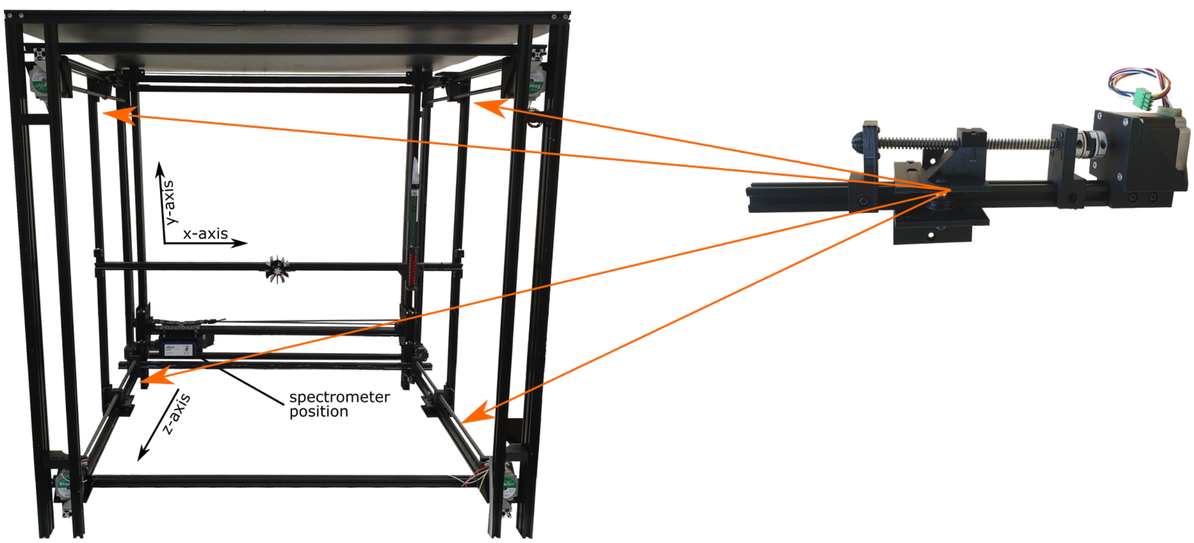

Figure S1 Pictures of the mechanical setup of the scanning device. Four z-carriages are installed along the z-axis rails. The carriage unit shown on the right is shortened to demonstrate the working principle.

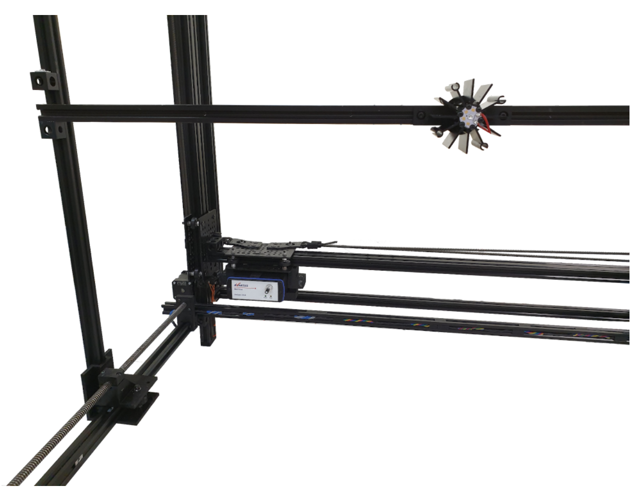

Figure S2 Picture of a part of the scanning device, illustrating how objects are mounted on the z-carriage.

S2.2 Mechanical Drawings and List of Parts

The mechanical setup of the scanning device was built to move the spectrometer in *x*- and *y*-direction and the light source in *z*-direction. The scaffold hosting all other mechanical parts is set up with OpenBuilds[1] linear aluminium beams with a length of 1 m. The main scaffold is built up from 12 main beams, namely 4 for every axis. In Fig. S5 ff. these beams are labelled as main x-beam, main y-beam and main z-beam. Further on, the setup can be subdivided in 4 module types, each presenting one or more corners of the cubic device. To give a general overview, these modules are shown in Fig. S3 as CAD-drawing as they are assembled in the actual device. Assigned colours do not always correspond to real colours but were chosen as visual aid. In addition, parts of the aluminium beam between the modules are cut out. The mechanical structure is self designed, the following parts or assemblies are customly designed, 3D-printed and displayed in dark grey in CAD-figures:

- 1 x spectrometer clamp
- 2 x belt connector
- 2 x pulley stabilizers
- 2 x 2 x *z*-lead screw support + cap
- 8 x side cover hook
- 4 x 2 x cover gantry spacer
- 2 x 2 x *z*-slides
- 4 x *z*-motor mounts
- 1 x endstop mount

These models are available on GitHub `https://github.com/photonZfeed/multiDradiometry` and as a stable version in the Zenodo repository `https://doi.org/10.5281/zenodo.4898138`. The Python code for controlling the scanning device and data evaluation are also publicly available in these repositories. The modules are named after their position in the coordinate system being scanned by the device. Following this rule, the module which is closest to the origin of the coordinate system is called 000-module. The individual modules are described in more detail and figure exerts below. Figure S4 **a** shows a picture of the assembled scanning device with the respective module coordinates.

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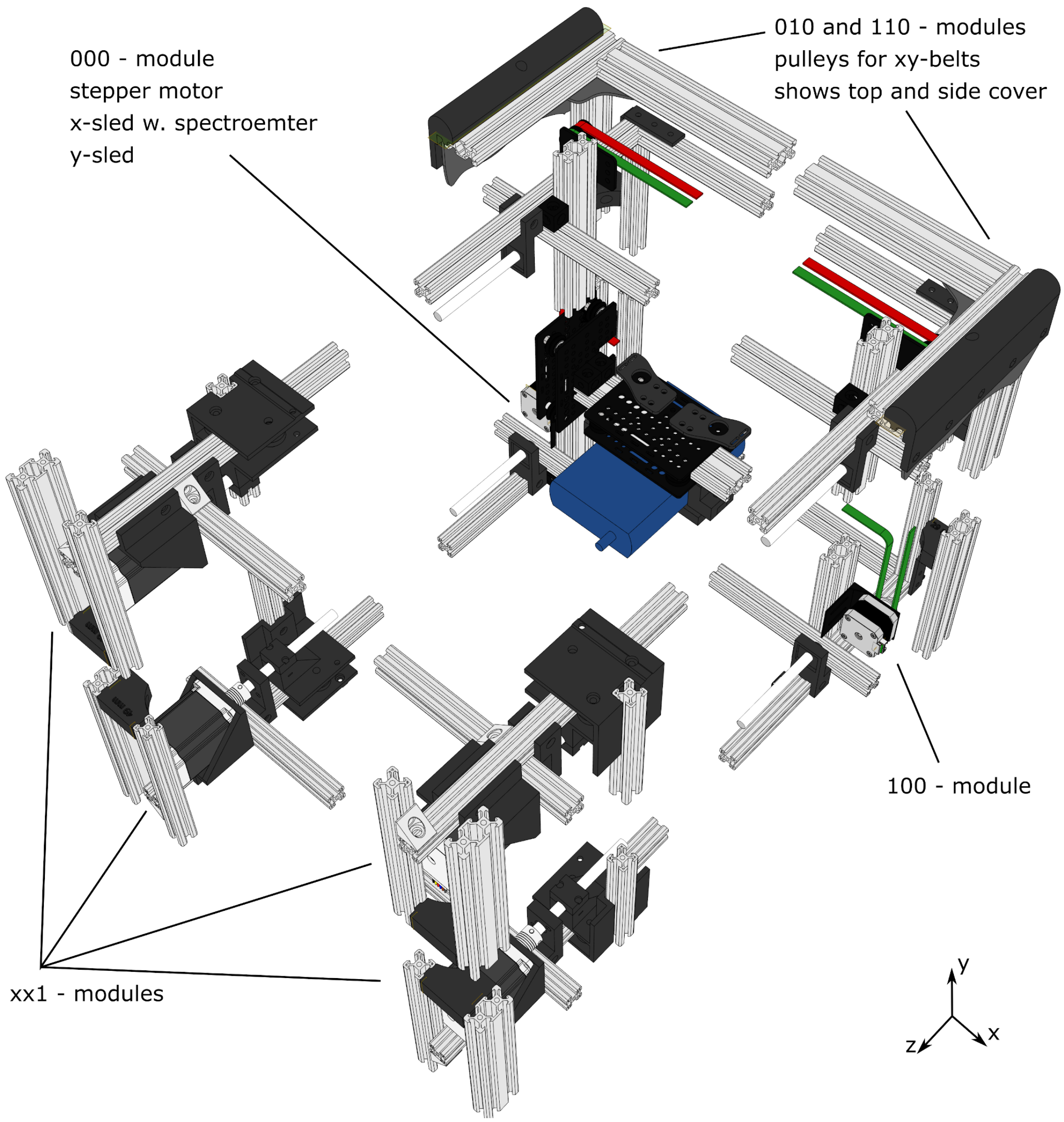


Figure S3 General overview with all building block corners of the scanning device.

S2.2.1 List of used Parts

OpenBulids V-Slot Rails
- 12 x 100x20x20 V-slot rails
- 4 x 860x20x20 V-slot rails (x,y-plane stabilization)
- 2 x 913x20x20 V-slot rails (moving z-connection)
- 1 x 975x20x20 V-slot rails (moving z-connection)
- 6 x 100x40x20 V-slot rails
- 2 x 960x40x20 V-slot rails (top cover plate)
- 1 x 810.4x40x20 V-slot rails (x-sled-rail)

000-module
- 1 x three way cube
- 2 x straight bracket
- 1 x cover gantry spacer
- 1 x leadscrew end holder + 2 x M3x10 + nuts
- 1 x 19x10x5 ball bearing (end holder)
- 1 x NEMA 17 stepper motor 4 x M3x8
- 1 x NEMA 17 90deg mount plate
- 1 x 13 m HTD 3M 9mm belt
- 1 x 16 teeth HTD 3M 9mm belt pulley
- 25 x M5x8 ISO 7380 + tee nuts + washers
- 2 x limit switch + limit switch mount + 4 x M3 + nuts

x,y-slides
- 6 x three way cube
- 2 x gantry Plate - Universal
- 4 x gantry Plate - Universal (cut to fit belts)
- 12 x V-slot wheels
- 12 x 6 mm spacer
- 12 x asymmetric spacer
- 12 x M5x35 ISO 7380 and nuts (wheels)
- 4 x smooth idler pulley 2 x M5x35 + nut + spacers
- 2 x pulley support 4 x M3x10 + nuts
- 1 x spectrometer clamp 4 x M5x15 + nuts 2 x M5x20 + nuts
- 2 x belt attachment 8 x M5x5 + nuts

100-module

- 1 x three way cube
- 1 x NEMA 17 stepper motor 4 x M3x8
- 1 x NEMA 17 90deg mount plate
- 1 x 16 teeth HTD 3M 9 mm belt pulley
- 1 x limit switch + z-endstop holder
- 1 x cover gantry spacer
- 2 x straight bracket
- 1 x leadscrew end holder
- 1 x 19x10x5 ball bearing (end holder)
- 18 x M5x8 ISO 7380 + tee nuts + spacers

010-module (and 110)

- 1 x leadscrew end holder + 2 x M3x10 + nuts
- 1 x 19x10x5 ball bearing (end holder)
- 2 x smooth idler pulley 1 x M5x30 + nut + spacers
- 1 x idler pulley plate
- 1 x cover gantry spacer
- 2 x straight bracket
- 1 x three way cube
- 15 x M5x8 ISO 7380 + tee nuts + washers

covers

- 1 x V-slot rails mentioned above
- 8 x M5x60 ISO 4762 (connect top rails)
- 8 x side cover hook
- 40 x M5x8 ISO 10642 + nuts
- 25 x M5x8 ISO 10642 + tee nuts (PP on top cover)
- 5 x 3x1000x1000 black PP

101-module (and 001,011,111)

- 1 x NEMA 23 motor + 4 x M4x10 + nuts
- 1 x z-motor mount
- 1 x leadscrew Tr.10x3x1000
- 1 x 6mm/10mm coupling
- 1 x tr.10 x 3 hex nut length:15mm width:17mm
- 1 x leadscrew support + 2 x M3x10 + nuts
- 1 x 19x10x5 ball bearing (end holder)
- 1 x z-slide
- 3 x V-slot wheels
- 1 x asymmetric spacer
- 3 x M5x40 ISO 7380 and nuts (wheels)
- 2 x M3x25 + square nut
- 1 x cover gantry spacer
- 2 x three way cube or corner bracket
- 14 x M5x8 ISO 7380 + tee nuts + washers

Table S1 List of all parts.

	Rails
12	1000x20x20 V-slot rail
4	860x20x20 V-slot rail
2	913x20x20 V-slot rail
1	975x20x20 V-slot rail
6	1000x40x20 V-slot rail
2	960x40x20 V-slot rail
1	810.4x40x20 V-slot rail
	OpenBulids Parts
2	idler pulley plate
2	NEMA 17 90deg mount plate
8	straight bracket
18	Three way cube
12	6 mm spacer
16	asymmetric spacer
2	gantry Plate - universal
4	gantry Plate - universal (cut to fit belts)
8	smooth idler pulley assembly
24	V-slot wheel assembly
	Screws and nuts
32	M3 nut
16	M3 square nut
32	M3x10 ISO 7380
8	M3x25 ISO 7380
12	M3x8 ISO 7380
16	M4 nut
16	M4x10
4	M5 1mm spacer
82	M5 nut
154	M5 tee nut
165	M5 washers
6	M5x20 ISO 7380
16	M5x35 ISO 7380
12	M5x40 ISO 7380
8	M5x60 ISO 4762
65	M5x8 ISO 10642
137	M5x8 ISO 7380
	Moving and other
2	16 teeth HTD 3M 9mm belt pulley
8	19x10x5 ball bearing
4	6mm/10mm coupling
4	leadscrew Tr.10x3x1000
4	tr.10 x 3 hex nut l:15mm w:17mm
5	3x1000x1000 black PP
13 m	HTD 3M 9mm belt
	Printed parts
8	cover gantry spacer
4	leadscrew end holder
4	leadscrew support
1	Spectrometer clamp
4	z-motor mount
4	z-slide
2	belt attachment
3	limit switch mount
2	pulley support
8	side cover kook
	Electronic parts
2	NEMA 17 stepper motor
4	NEMA 23 motor
1	24V power supply
6 m	end switch cable
1	Ind. IO-4 bricklet
1	IO-16 brikclet
3	limit switch
1	master brick
1	micro usb cable
1	mosfet driver module
3	stepper brick
15 m	stepper motor cable
2	tinker forge cable

S2.2.2 Detailed Drawings

Fig. S4 **b** shows a schematic setup of the used tinkerforge bricks to control the device.[tink] The master brick is connected to the PC running the controlling software. All bricks are stacked on top of each other, all bricklets are connected via cables. Each stepper brick is controlling one stepper motor for the x- and y-movement. Another stepper brick is controlling all stepper motors for the z-movement. One IO-16-bricklet is used to watch the end-stop triggers. A 24 V wall plug power supply is powering the stepper bricks as well as the cooling fan of the tinkerforge assembly. The used spectrometer and the power supply are connected directly to the PC via USB.

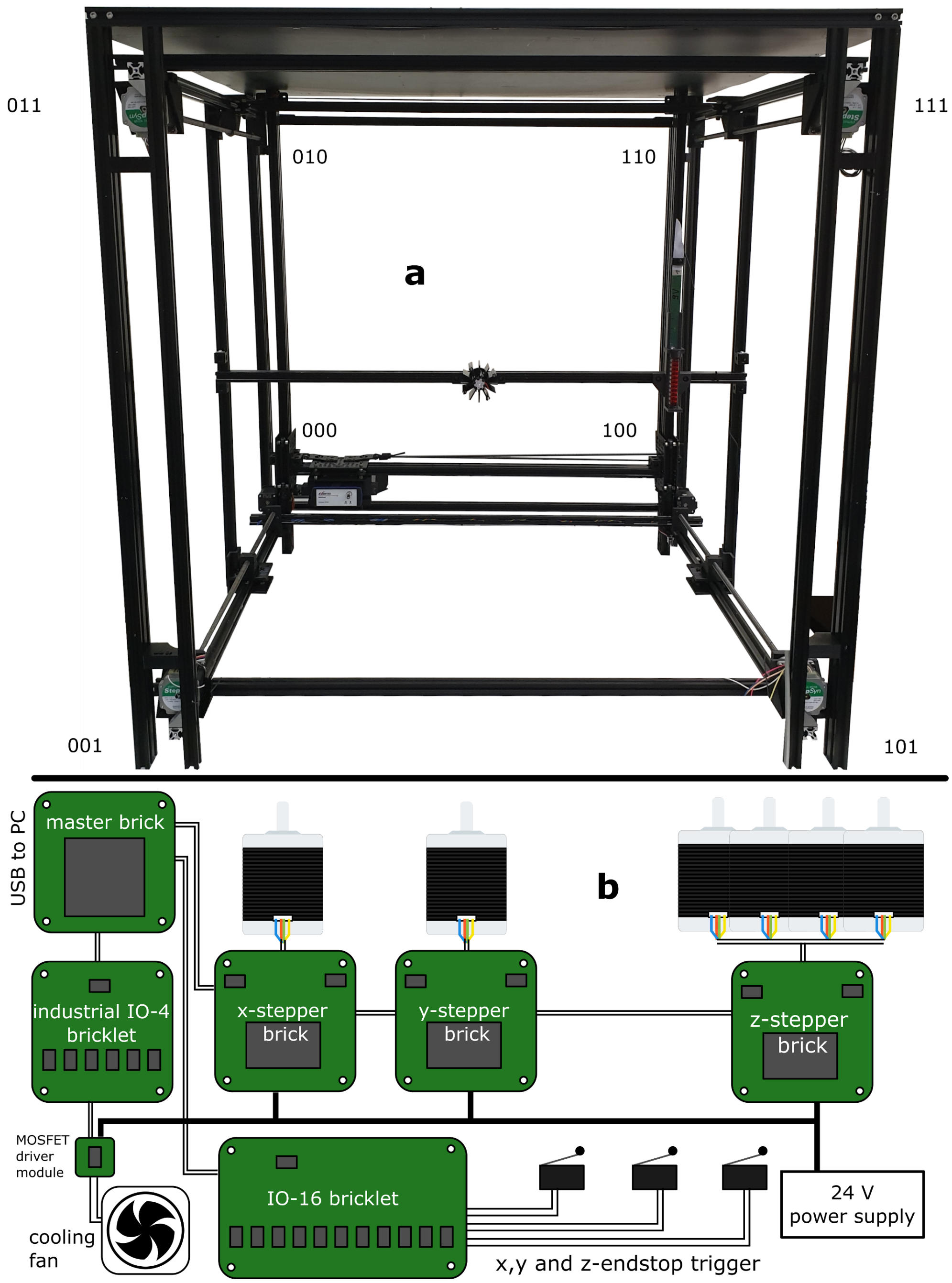


Figure S4 a: Picture of the scanning device with the respective module coordinates. **b**: Schematic of the tinkerforge setup.

Fig. S5 shows the 000-module including the xy-slid system moving the spectrometer. The Core-XY technique is used to move this slide system. One of two motors needed for this system is visible, connected to the red belt. The spectrometer is mounted on the slide moving in x-direction on an aluminium beam rail. This rail is held by the two slides moving in y-direction on two main y-beams as rails. The general equations describing the movement of the spectrometer in x- and y-direction are:

$$\Delta x = \frac{1}{2}\left(\Delta motor_{000} + \Delta motor_{100}\right) \tag{1}$$

and

$$\Delta y = \frac{1}{2}\left(\Delta motor_{000} - \Delta motor_{100}\right) \tag{2}$$

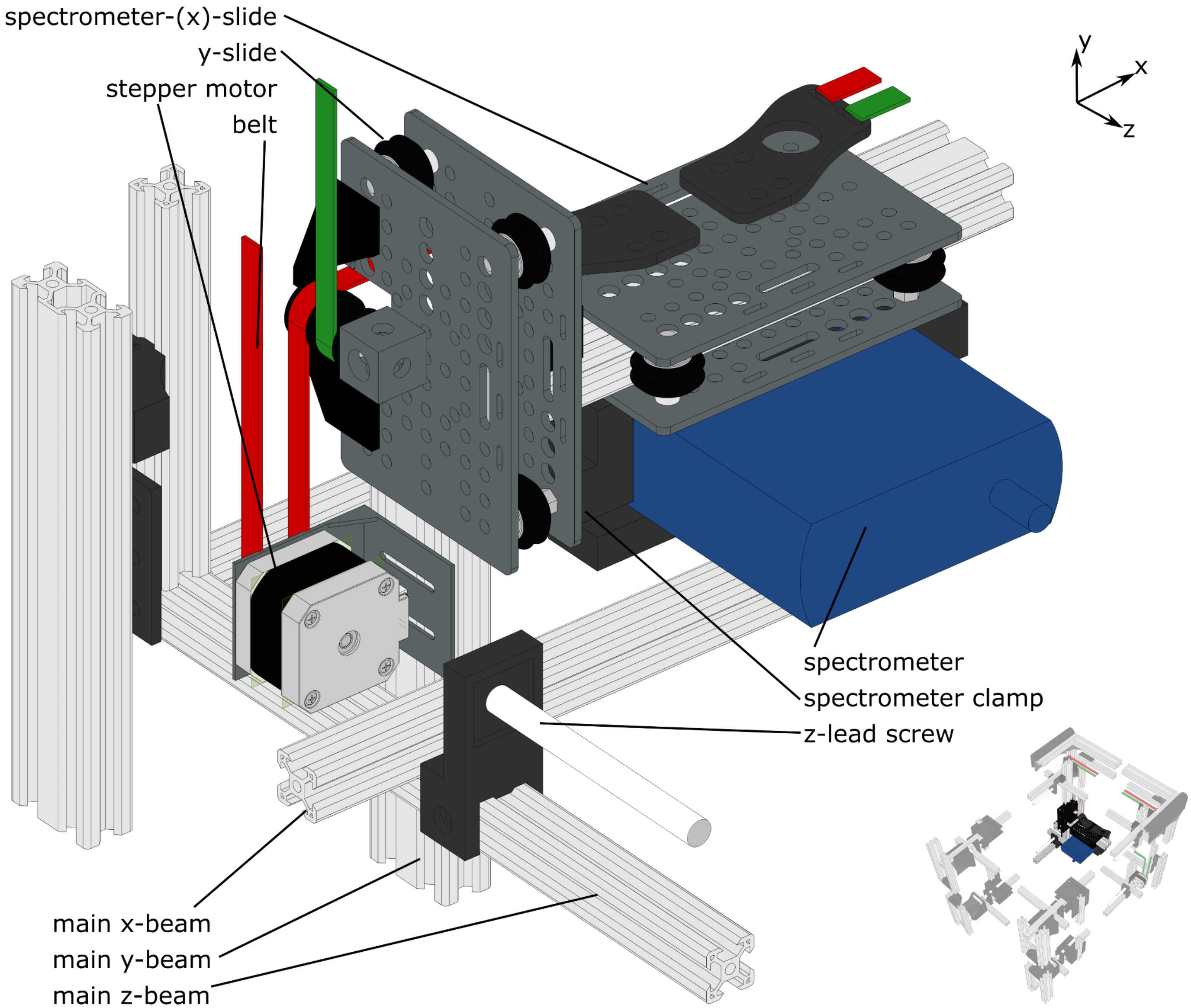


Figure S5 Drawing of the 000-module of the scanning device.

The second motor moving the spectrometer is visible in Fig. S6, connected to the green belt. Here the y-slide is omitted for a better display of the main x, y and z-beam. The latter also hosts the z-lead screw, which is driving the z-slide. The belts for the xy-slits are deflected by pulleys at the 010 and 110 position. The module at the 010 position is shown in Fig. S7 a.

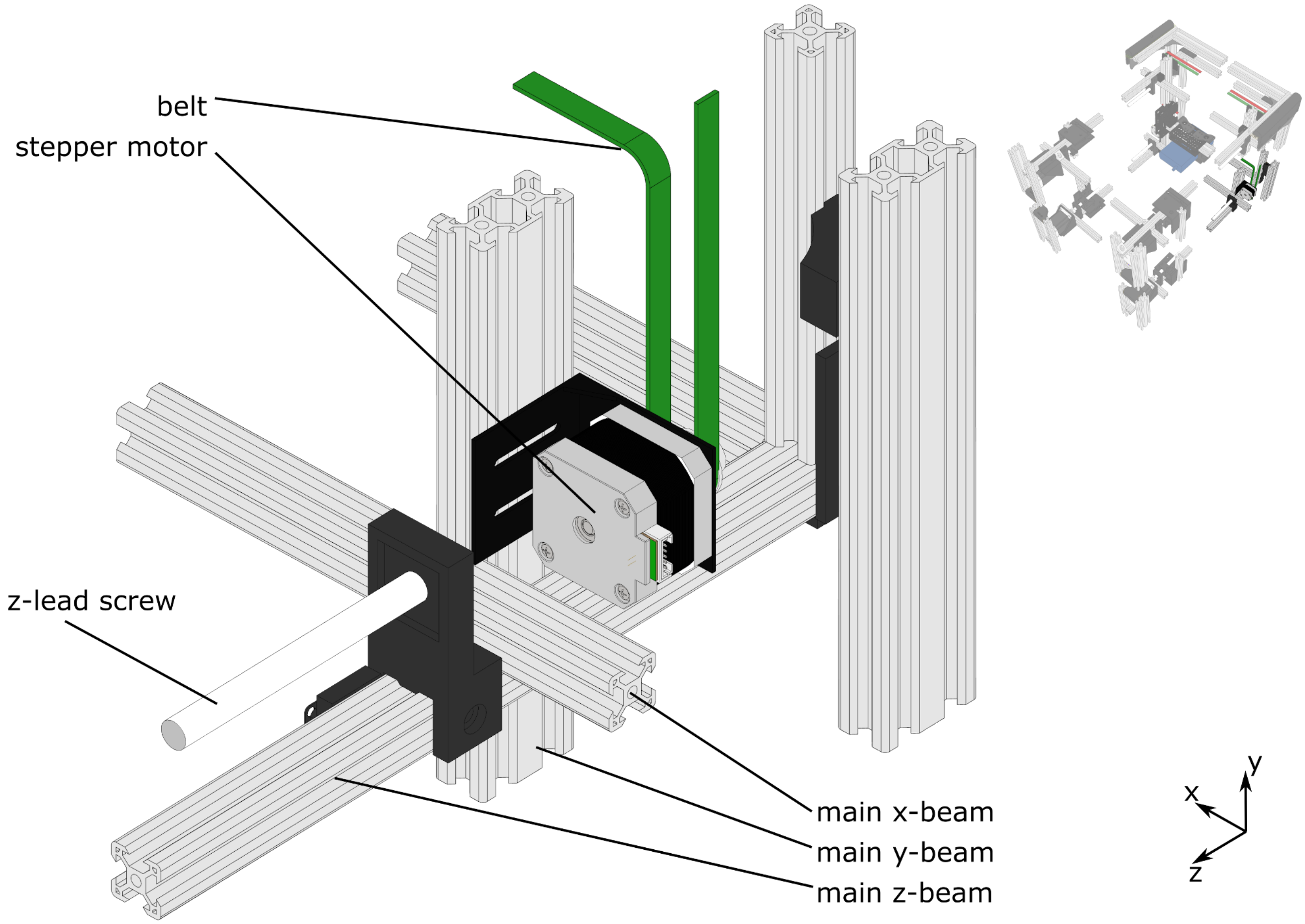


Figure S6 Drawing of the 100-module of the scanning device.

To protect the scanning device from interfering light, the device can be covered with black polypropylene panels. The panel on the top side is mounted on a frame of aluminium beams and is screwed to the main scaffold. On this top cover frame, the side cover panels can be mounted by hanging them on the aluminium beams of the top cover. This is also shown in Fig. S7 a. The hanging panels are then fixed at the cover gantry, which consists of aluminium rails connected with spacers to the main scaffold. The scaffold and spacers are shown in all CAD-figures, however, they are best visible in Fig. S7 b. This figure also shows one of 4 modules driving the z-slide assembly. This assembly consists out of four slides running in all main$z$-beams as rails. The slides are all driven by a lead-screw and a stepper motor, moving only at the same time. The z-slides can be connected by aluminium beams to establish a moving scaffold for hosting the light source.

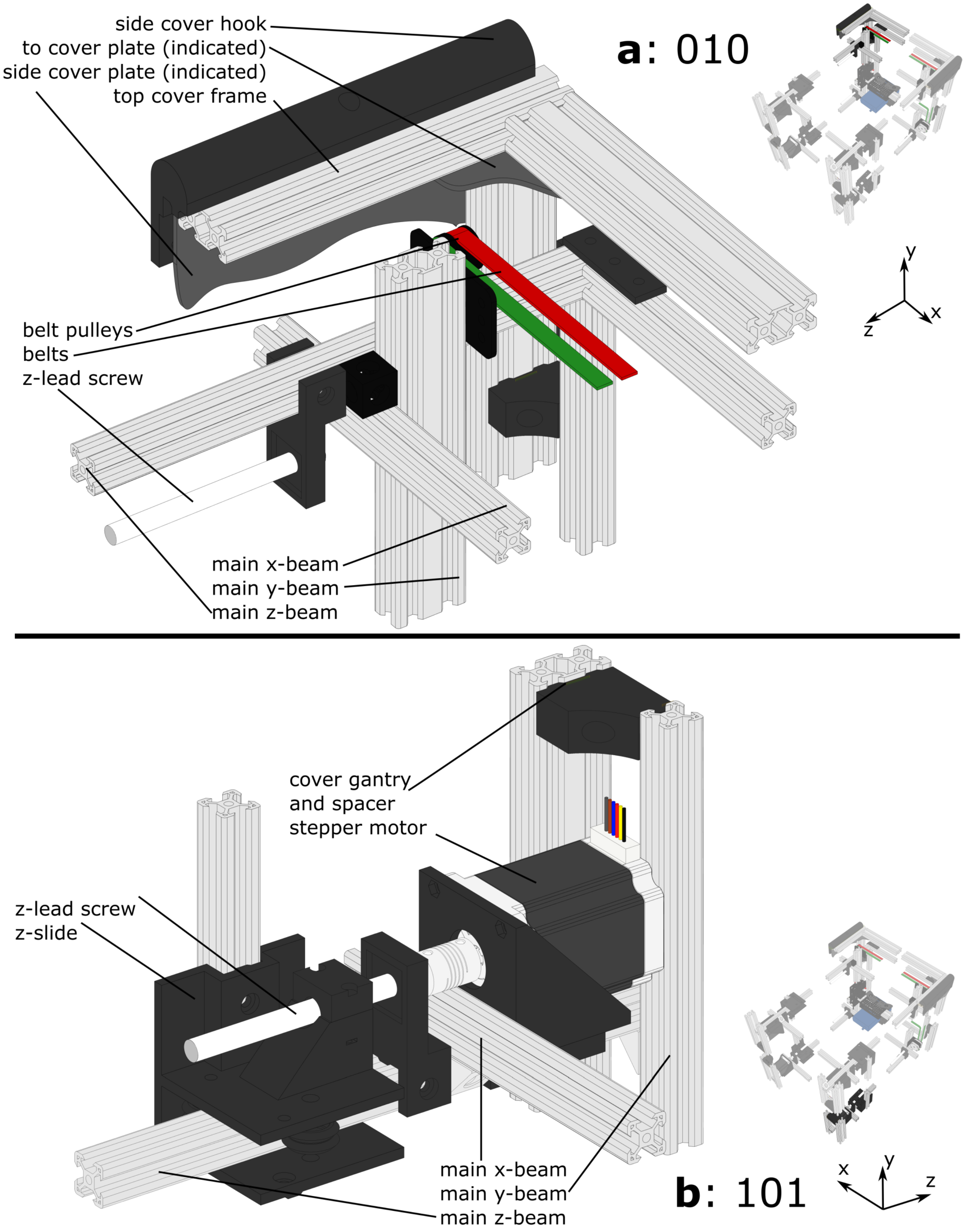


Figure S7 Drawing of the 010- and 101-module of the scanning device.

S2.3 Investigated Reactor Setups

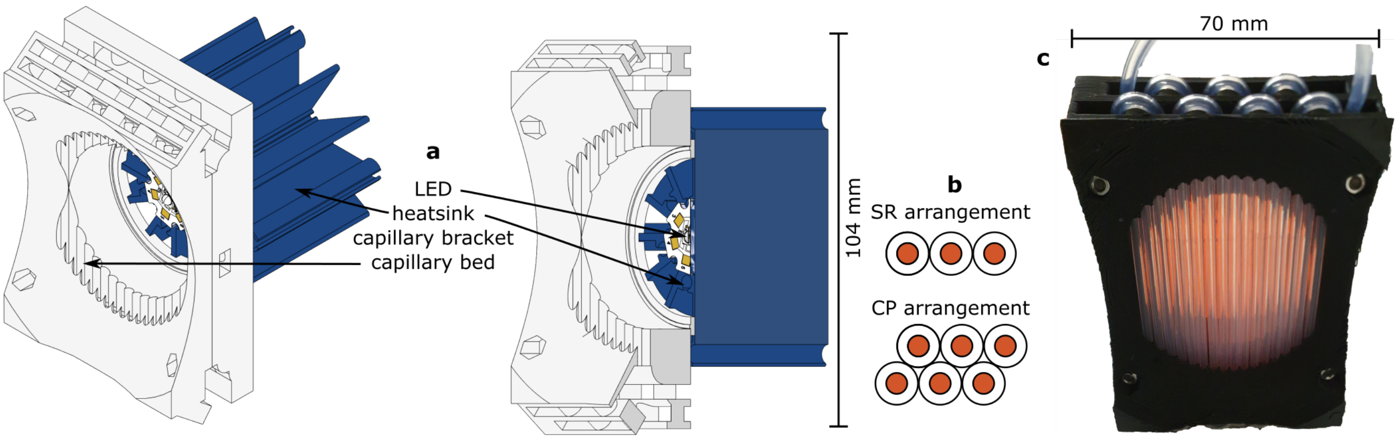


Figure S8 a: Two (cut) CAD views of the reactor for hosting closest packed (CP) capillaries. **b**: The single row (SR) and closest packed (CP) capillary arrangements. **c**: photography of the 3D printed capillary scaffold with inserted capillaries.[2]

S2.4 Integrating Sphere Measurements

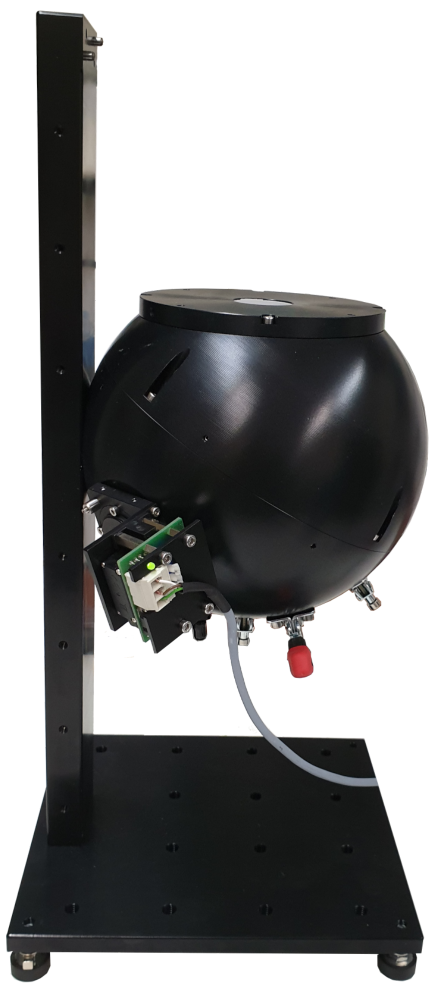


Figure S9 Picture of the integrating sphere. The opening of the sample port is visible.

S2.4.1 Heatmaps Along Hyperplanes

Videos provided as ESI are named according to the figure numbering in the article. For instance, the animation corresponding to the $q-y,z$-heatmap of the vial filled with water in Fig. 6 is named `Fig6_a.mp4`.

The 3D animation of the q_a-surface-plot for the SR setup and a PR-surface-plot of the CP setup are called `animated_SR_qna.mp4` and `animated_CP_ratios.mp4`.

S2.4.2 Efficiency Calculations for the Vial Setup

Efficiency of the vial setup scanned with 51 μM MeOr solution:
The fraction of photons which were absorbed in the vial, filled with a 51 μM MeOr solution, is calculated as the quotient of the absorbed photons by the vial filled with the 51 μM MeOr solution ($q_{a,H_2O} - q_{a,MeOr,51\,\mu M}$) and the measured photon flux of the LEDs.

$$\begin{aligned}\eta_{real} &= \left(\frac{q_{a,H_2O} - q_{a,MeOr,51\,\mu M}}{q_{a,LEDs}}\right)\cdot 100\,\% \\ &= \left(\frac{1373\,\mu mol\,s^{-1} - 403\,\mu mol\,s^{-1}}{1936\,\mu mol\,s^{-1}}\right)\cdot 100\,\% \\ &= 50\,\%\end{aligned} \tag{3}$$

Efficiency of the vial setup with full absorption:
The fraction of photons which were absorbed in the vial, filled with a MeOr solution absorbing every incident photon, is calculated as the quotient of the theoretically absorbed photons by the vial filled with a fully absorbing MeOr solution ($q_{a,H_2O} - q_{a,95\%}$) and the measured photon flux of the LEDs.

$$\begin{aligned}\eta_{fullabs} &= \left(\frac{q_{a,H_2O} - q_{a,95\%}}{q_{a,LEDs}}\right)\cdot 100\,\% \\ &= \left(\frac{1373\,\mu mol\,s^{-1} - 67\,\mu mol\,s^{-1}}{1936\,\mu mol\,s^{-1}}\right)\cdot 100\,\% \\ &= 68\,\%\end{aligned} \tag{4}$$

$q_{a,95\%}$ was calculated by setting all data points with a transmission lower than 0.95 to zero, only photons that do not interact with the inside of the vial are left.

Efficiency of the vial setup with full absorption and 80 % LEDs:
By multiplication of $q_{a,LEDs}$ with 0.8, it is assumed, that the LEDs which are directed into the inside of the vial, are not existent.

$$\begin{aligned}\eta_{real} &= \left(\frac{q_{a,H_2O} - q_{a,95\%}}{q_{a,LEDs}\cdot 0.8}\right)\cdot 100\,\% \\ &= \left(\frac{1373\,\mu mol\,s^{-1} - 67\,\mu mol\,s^{-1}}{1936\,\mu mol\,s^{-1}\cdot 0.8}\right)\cdot 100\,\% \\ &= 84\,\%\end{aligned} \tag{5}$$

Efficiency of the vial setup as scanned with 51 μM MeOr solution and 80 % LEDs:

$$\begin{aligned}\eta_{real} &= \left(\frac{q_{a,H_2O} - q_{a,MeOr,51\,\mu M}}{q_{a,LEDs}\cdot 0.8}\right)\cdot 100\,\% \\ &= \left(\frac{1373\,\mu mol\,s^{-1} - 403\,\mu mol\,s^{-1}}{1936\,\mu mol\,s^{-1}\cdot 0.8}\right)\cdot 100\,\% \\ &= 60\,\%\end{aligned} \tag{6}$$

S3 Results and Discussion

S3.1 Correction of the Error Introduced Using a Cosine Corrector

The correction method is assuming that the ratio $X(\theta)$ between the measured radiation $P_{dir}(\theta)$ and the value $P_{dir}(0°)\cdot\cos(\theta)$) is 1.[3,4] The measured intensity can be corrected by

$$P_{dir}(0°) = \frac{P_{dir}(\theta)}{X(\theta)\cdot\cos(\theta)}. \tag{7}$$

For correcting a 2D heatmap dataset of a light source using equation 7, the incident angle must be calculated for every pixel of the x,y-heatmap from the known position of the light source relatively to the virtual canvas. The angle θ of light from a point light source (e.g. LED) hitting the cosine corrector is calculated with

$$\theta_{px,z} = \arctan\left(\frac{\|\overline{a_{px}}\|_F}{d_z}\right) \tag{8}$$

whereas d_z is the distance between the cosine corrector and the light source measured parallel to the z-axis. $\|\overline{a_{px}}\|_F$ is the distance between the light source's centre to the cosine corrector on the x,y-hyperplane and calculated as Frobenius norm of the respective vector between the coordinate of the light source (L) and the measuring position (M_{px}):

$$\|\overline{a_{px}}\|_F = \left(\sum_{i=1}^{n} abs(\overline{(LM_{px})_i})^2\right)^{1/2} \tag{9}$$

The individual correction values $C_{px,z}$ are multiplied with the raw measurements, e.g. for the received energy:

$$C_{px,z} = \frac{1}{\cos\left(\theta_{px,z}\right)} \tag{10}$$

$$P_{\lambda,px,z,\mathrm{corr}} = P_{\lambda,px,z} \cdot C_{px,z} \tag{11}$$

S3.2 AVRPA calculations

The AVRPA of two vial setup configurations are calculated. $L_{\mathrm{p,V,50\,\%}}$: As measured in reality. $L_{\mathrm{p,V,68\,\%}}$: assuming that all light in the MeOr solution is absorbed:

$$L^{\mathrm{a}}_{\mathrm{p,V,50\,\%}} = \frac{q}{V} = \frac{2\cdot 10^{-6}\,\mathrm{mol\,s^{-1}}\cdot 50\,\%}{8\cdot 10^{-6}\,\mathrm{m^3}} = 0.125\,\mathrm{mol\,s^{-1}\,m^{-3}} \tag{12}$$

$$L^{\mathrm{a}}_{\mathrm{p,V,68\,\%}} = \frac{q}{V} = \frac{2\cdot 10^{-6}\,\mathrm{mol\,s^{-1}}\cdot 68\,\%}{8\cdot 10^{-6}\,\mathrm{m^3}} = 0.17\,\mathrm{mol\,s^{-1}\,m^{-3}} \tag{13}$$

S3.3 Integrating Sphere Measurements

For calculating the integral transmission from two heatmaps, the mean received power (P) of a square with the size of 11 × 11 pixels, centred on the intensity maximum of the LED-heatmap, is calculated with:

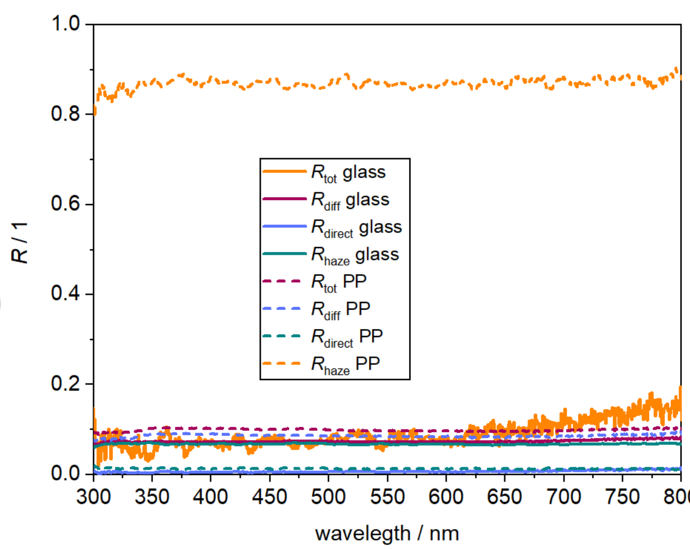
$$P_{\lambda,\mathrm{cut}} = \frac{\sum_{x,y=25.4\,\mathrm{cm},26.5\,\mathrm{cm}}^{29.6\,\mathrm{cm},30.8\,\mathrm{cm}} \cdot P_{\lambda,px}}{11^2} \tag{14}$$

The transmission is then calculated as quotient of the measured and extracted mean received power of the light source with and without installed reactor:

$$T_{\lambda,\mathrm{reactor}} = \frac{P_{\lambda,\mathrm{cut,reactor}}}{P_{\lambda,\mathrm{cut,LED}}} \tag{15}$$

S3.3.1 PP and Glass Plates

(a)



(b)

Figure S10 a: Picture of the investigated FFF printed PP plate. **b:** Reflection measurements of 3 mm borosilicate glass and 1 mm 3D-printed polypropylene (PP) plate.

S3.3.2 PFA Capillaries

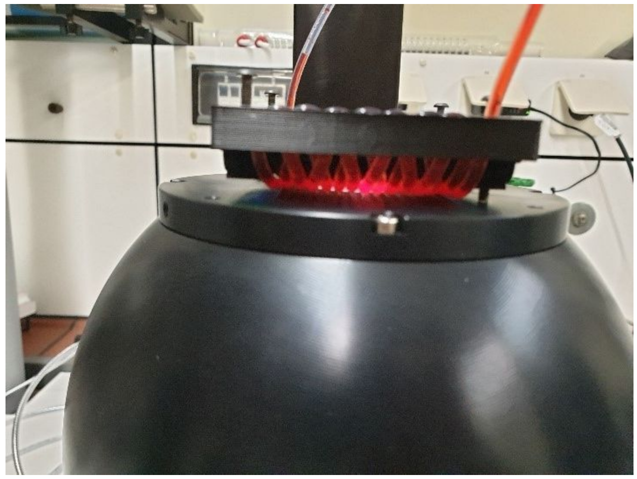


Figure S11 Picture of the SR reactor, positioned over the sample port of the integrating sphere. The top part of the reactor, holding the capillaries in place was removed to allow positioning of the capillaries directly on the sample port.

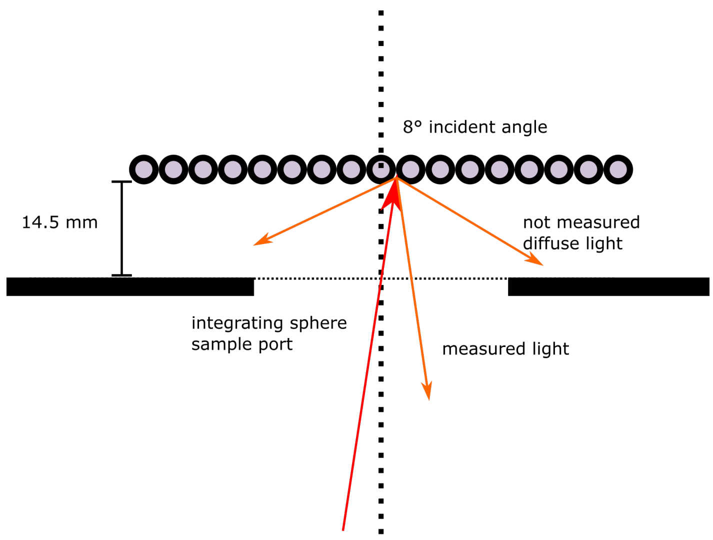


Figure S12 Sketch of the effect of capillaries with distance to the integrating spheres sample port.

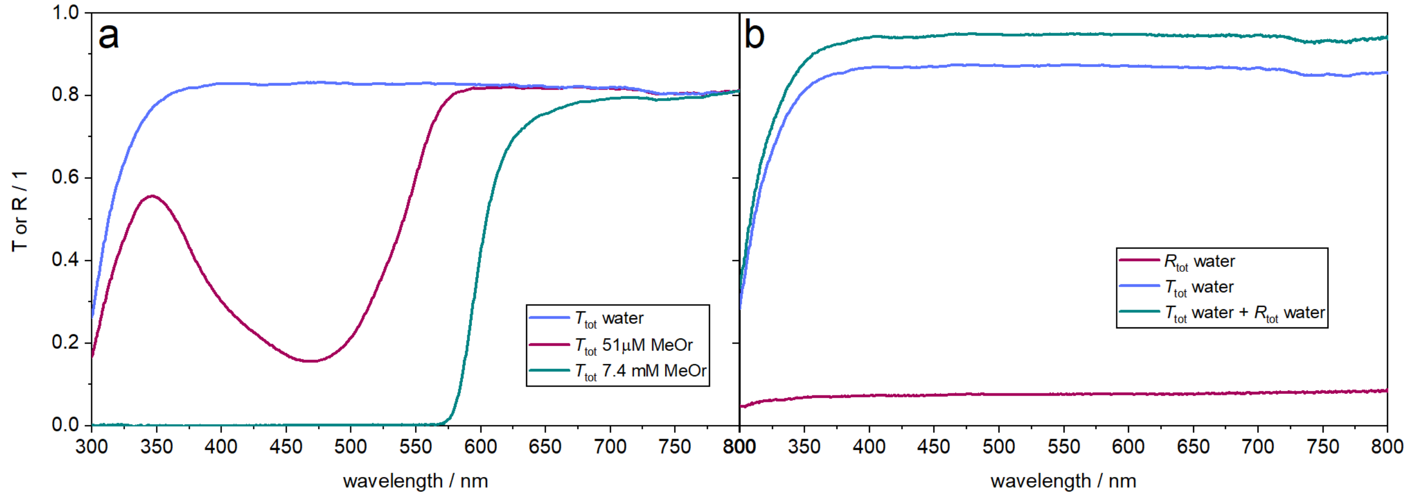


Figure S13 a:T_{tot} of the batch vial, either filled with water, a 51 µM or 7.4 mM solution of MeOr. b: R_{tot} and T_{tot} of the batch vial filled with water.

References

1 *Open Builds Projektwebsite*, https://openbuilds.com/, (accessed April 2020).

2 M. Sender, B. Wriedt and D. Ziegenbalg, *Reaction Chemistry & Engineering*, 2021, DOI: `10.1039/D0RE00456A`.

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