

Enhancing mass transport to improve the efficiency of self-shadowing photoreactions and enable scale-up

Florian Gaulhofer,[†] Markus Metzger,[†] Alexander Peschl,[‡] and Dirk Ziegenbalg^{*,†}

[†]*Institute of Chemical Engineering, Ulm University, Albert-Einstein-Allee 11, 89081 Ulm, Germany.*

[‡]*Peschl Ultraviolet GmbH, Weberstraße 19, 55130 Mainz, Germany.*

E-mail: dirk.ziegenbalg@uni-ulm.de

Supporting Information

1 Geometrical data and mesh

Fig. S1 shows the CAD model of a LED immersion lamp (TLED100) used in the simulation of the radiative transport inside the mini-plant photoreactor (MISCOP). Fig. S2 visualizes

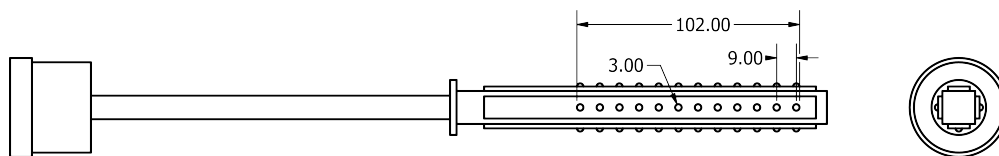


Figure S1 CAD model of the LED immersion lamp used in the OpenFOAM simulation. Units in mm.

the mesh of the MISCOP system equipped with the TLED immersion lamp (48 LEDs) and a SMX10 static mixer used in the OpenFOAM simulation. The colour coding is chosen according to the multi-region case. Two slices on the x-z and the x-y plane with an additional zoom to showcase the accuracy to map the geometry are shown. The refinement of the cells is achieved by the following adjustments: i) the initial discretization of the blockMesh

($n_x = 60$, $n_y = 48$, $n_z = 184$) ii) the refinement detail of each region (refinementSurfaces Level (2 2)) and iii) the amount of levels between regions (nCellsBetweenLevels 3).

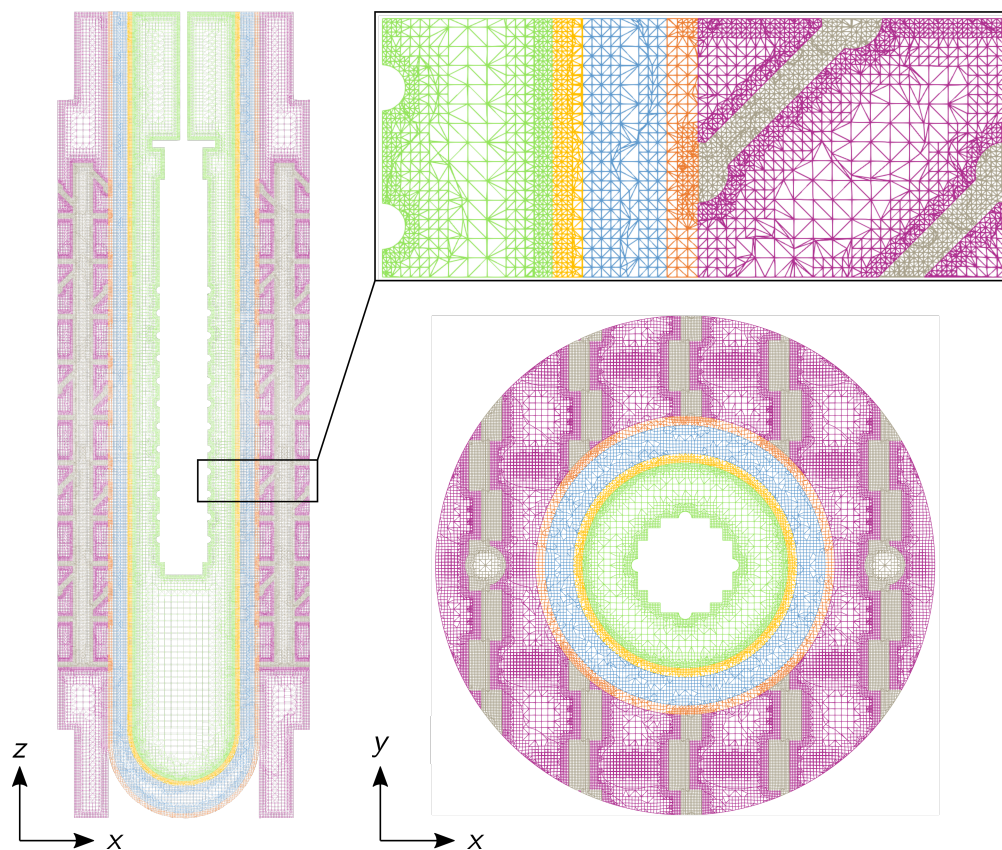


Figure S2 Multi-Region mesh used to calculate the radiation field with OpenFOAM.

2 UV/vis analysis of reaction solution

Five samples with the same concentration ($c_{1,0} = 0.37 \text{ molL}^{-1}$) were analysed by UV/vis measurements in the cuvette reactor: i) a freshly prepared solution of species **1** as reference, ii) a freshly prepared solution containing species **1** and **2**, iii) the reaction solution after long-term irradiation (switched back to contain only species **1**), iv) the reaction solution after long-term irradiation containing species **1** and **2**, and possible side products, and v) a sample of the static mixer material (synthetic resin) dissolved in EtOH (tech). Sample i) and iii) were irradiated with $\lambda = 540 \text{ nm}$ light to remove species **1**. Samples ii) and iv) were irradiated with $\lambda = 365 \text{ nm}$ light to mimic normal reaction conditions and

form species **2**. The results are shown in Fig. S3.

The absorbance of the reference sample i) of species **1** shows a maximum at 257 nm with a second weaker band at 339 nm. Upon UV-irradiation of sample i), species **2** forms and a new band evolves at 535 nm (sample ii)). A slight bathochromic shift of the band around 339 nm towards 350 nm can be observed. The reference sample of synthetic resin (grey) shows a very strong absorption at $\lambda = 257$ nm.

The reaction solution shows a larger absorbance at $\lambda = 241$ nm than the reference solution after short-term irradiation (sample iii)). This is contrary to the measurements of a non-contaminated (fresh) solution (c. Fig. 7 in the main manuscript). The increase of the absorbances at $\lambda = 241$ nm is assigned to absorption by the synthetic resin, extracted from the static mixer material.

Comparison of the absorbances of the reaction solution after short- and long-term irradiation at $\lambda = 540$ nm shows a decrease of A for long-term irradiation, indicating a lower concentration of species **2**. The change in the absorption spectrum is also reflected in a colour shift of the solution from pink/purple toward orange/brown (see insert of Fig. S3).

3 $^1\text{H-NMR}$ analysis of reaction solution

$^1\text{H-NMR}$ spectroscopy was performed with an Avance Neo (400 MHz, Bruker Co., USA). The reference sample of species **1** was prepared by dissolving $5.58\ \mu\text{mol}$ in deuterated chloroform. The sample of the reaction solution ($c_{1,0} = 0.37\ \text{mol L}^{-1}$, $V = 15\ \text{mL}$) was evaporated, and the residue was dissolved in deuterated chloroform. The reference spectrum of 1,3,3-Trimethylindolino-6'-nitrobenzopyrylospirane is shown in Fig. S4.

The solvent signal (undeuterated chloroform) is found at $f = 7.26$ ppm. The spectrum resembles the characteristic structural parts of species **1**: 1) the N-bond methyl group at 2.74 ppm (carbon 21), b) methyl groups at carbons 19 and 20 (1.19 ppm and 1.30 ppm), c) aromatic protons at carbons 16 and 18 (8.01 ppm), d) proton at carbon 14 (5.85 ppm) and e) further protons of the ring structures (carbons 1 - 3, 6, 13, 15) in the range of 6.56 to

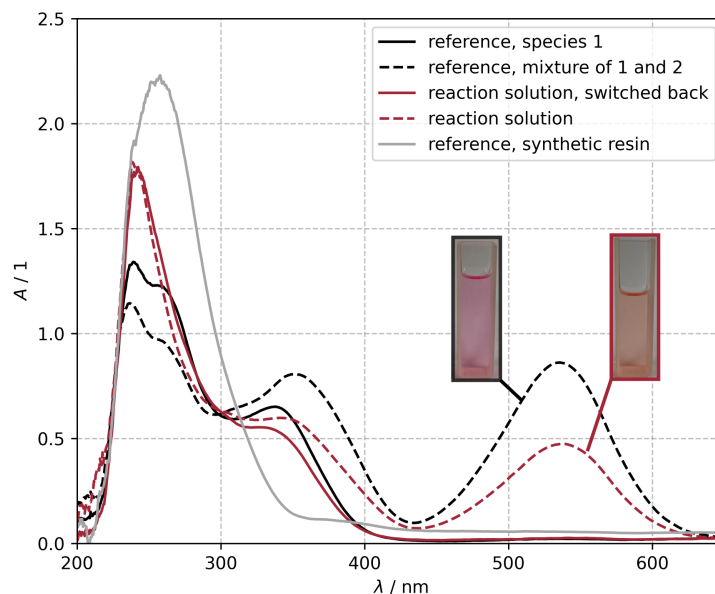


Figure S3 1) UV/vis spectra of the following samples: 1) reference solution only containing species 1 (black, —, $\lambda_{irr} = 540\text{nm}$), 2) reference reaction solution containing species 1 and 2 (black, --, $\lambda_{irr} = 365\text{nm}$), 3) reaction solution after short-term irradiation switched back to only contain species 1 (red, —, $\lambda_{irr} = 540\text{nm}$), 4) long-term irradiated reaction solution (red, --, $\lambda_{irr} = 365\text{nm}$), and 5) synthetic resin dissolved in EtOH (tech) (grey).

7.21 ppm

δ_H (400 MHz, CDCl_3) 8.01 (2 H, d, J 8.4), 7.21 (1 H, td, J 7.7, 1.3), 7.09 (1 H, dd, J 7.3, 1.2), 6.95 - 6.86 (2 H, m), 6.77 (1 H, dd, J 8.4, 0.8), 6.56 (1 H, d, J 7.7), 5.87 (0 H, s), 5.85 (0 H, s), 2.74 (3 H, s), 1.30 (3 H, s), 1.19 (3 H, s).

Fig. S5 shows four $^1\text{H-NMR}$ spectra for: a) reference species 1, b) a sample of the irradiated reaction solution without the installed static mixers, c) a reference sample of synthetic resin, d) and the irradiated reaction solution with static mixers.

In the sample of the long-term irradiated reaction solution (s. Fig. S5 b) additional peaks are visible at $\delta = 9.9\text{ ppm}$, assigned to an aldehyde group and $\delta = 11.5\text{ ppm}$ assigned to a carboxylic acid group, likely being formed during the photodegradation.

To test for components dissolved from the mixer structures made from synthetic resin, parts of the mixer were immersed in ethanol, irradiated simultaneously for a few days and subsequently analysed by NMR (s. Fig. S5 c). A broad range of signals is visible which can

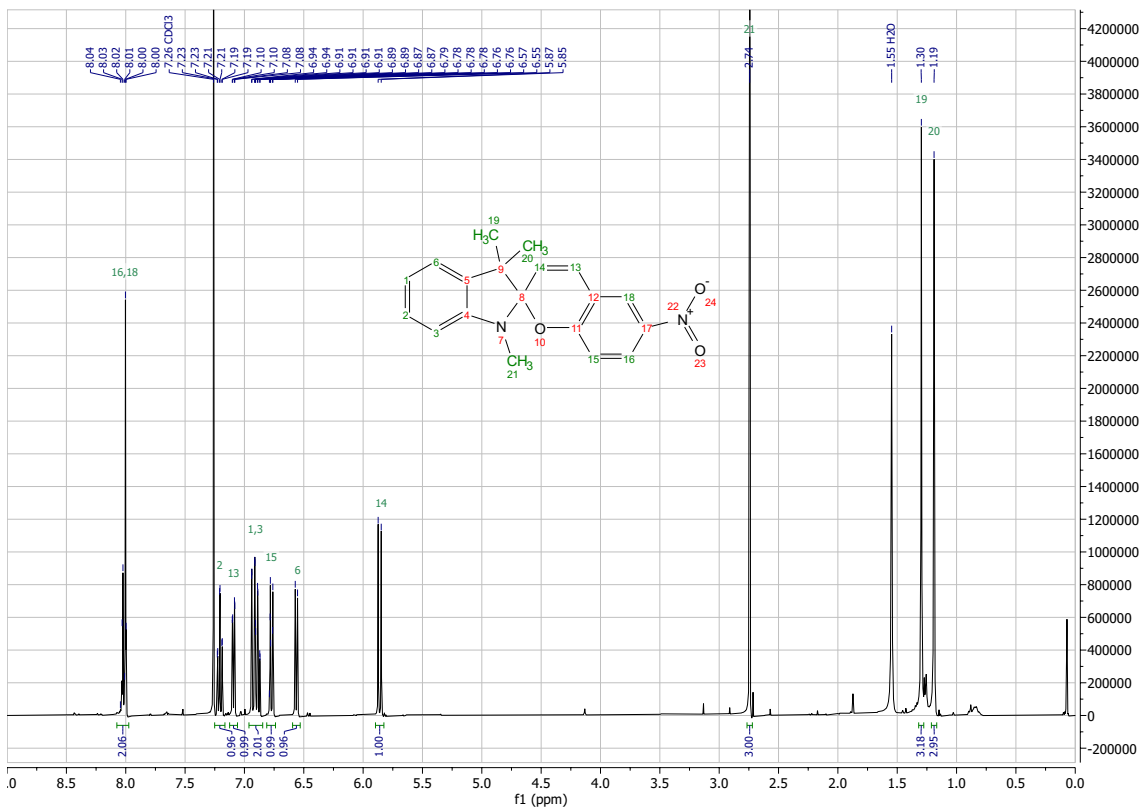


Figure S4 ¹H-NMR spectra of 1,3,3-Trimethylindolino-6'-nitrobenzopyrrolospirane (CAS:1498-88-0) in CDCl₃.

be assigned to a broad range of aliphatic peaks. Furthermore, various signals are found at chemical shifts larger than 11.5 ppm.

The sample of the reaction solution (s. Fig. S5 d) shows the characteristic aromatic peaks of reference species **1** and additionally broad aliphatic peaks. It is concluded that the synthetic resin dissolved in ethanol during the reaction. Peaks of degradation product of the spiropyran at 9.9 and 11.5 ppm are present as well. The low intensities are reasoned by a shorter irradiation time (hours instead of days).

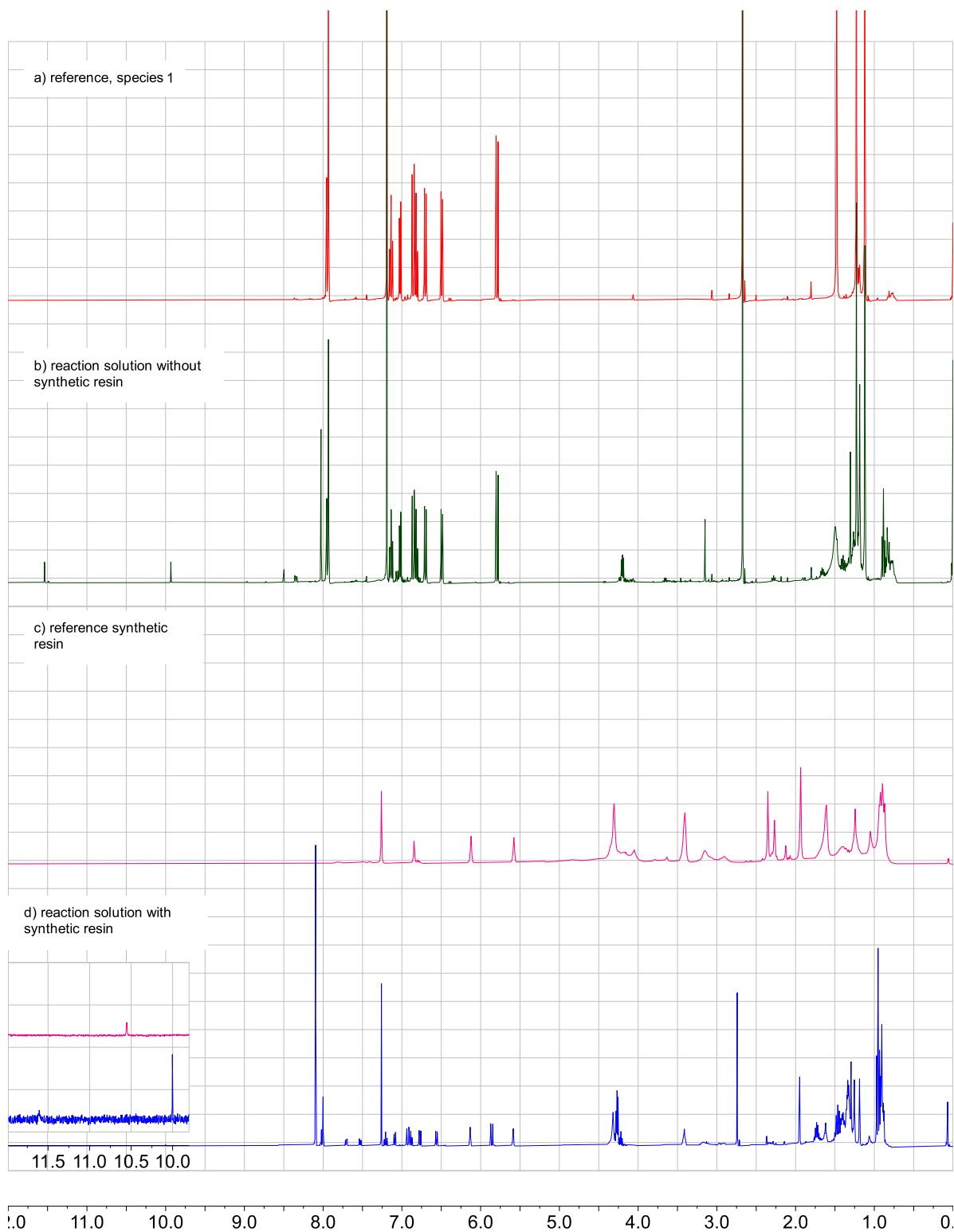


Figure S5 $^1\text{H-NMR}$ spectra of a) reference species 1, b) reaction solution after long-term irradiation without static mixer, c) reference synthetic resin, and d) reaction solution after long-term irradiation with installed static mixers.