Photonic contacting of gas–liquid phases in a falling film microreactor for continuous-flow photochemical catalysis with visible light†

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A microstructured falling film reactor was applied to the dye-sensitized photochemical conversion of 1,5-dihydroxynaphthalene to juglone. This continuous-flow microreactor enables the efficient contacting of a gas and a liquid phase in combination with external irradiation by high-power LED arrays offering various wavelengths. Two sensitizers were used for the photochemical in situ generation of singlet oxygen as key step in the synthesis of the natural product juglone. The photochemical process was investigated according LED wavelength, LED power, oxygen partial pressure, reactor architecture, substrate concentration and flow rate, and optimized to a conversion of $X = 97\%$ with 99% selectivity. Based on the experimental results process parameters like quantum efficiency, productivity and space time yield were calculated and used for the evaluation of the photochemically catalyzed synthesis of juglone in continuous-flow mode.

Introduction

Photochemically catalysed reactions have become of fundamental interest in the recent years. Especially with the advent of photocatalytically active compounds and materials, which are able to absorb light in the visible region of the electromagnetic spectrum, many new synthetic methods have been developed for the preparation of valuable fine chemicals under mild reaction conditions. A broad variety of transformations can be performed with organometallic compounds like Ru- or Ir-based polypyridyl complexes. In conjunction with organocatalysts as chiral inducers stereoselective synthesis has been made possible as well. More recently the application of precious metal-free catalysts has amplified the development of cost-efficient synthetic protocols for photochemical reactions. Meanwhile it has been generally accepted that light, i.e. photons with defined wavelength, is a highly potent, selective and, in terms of Green Chemistry, a traceless reagent for synthetic organic chemistry.

The dye-sensitized activation of molecular oxygen offers an important strategy to incorporate oxygen into molecules under mild reaction conditions. A first industrial application of photochemical oxygen activation has made its way into production. The Sanofi process for the production of artemisinin is one important example for the in situ formation of singlet oxygen using tetraphenylporphyrine as visible light-absorbing sensitizer. Starting in 2013 the final production scale of 60 tons per year has already been reached in 2014. Two important prerequisites must be fulfilled in this case for a successful realization of dye-sensitized singlet oxygen formation: efficient oxygen gas contacting with the liquid phase and thorough irradiation of the reaction composition. In general, photochemical batch equipment, e.g. glass flasks and immersion-well setups with pressurized mercury lamps, often lack of efficient gas–liquid contacting and uniform irradiation of the reaction solution, possibly leading to prolonged irradiation and pronounced by-product formation. Pressurized mercury lamps are often used as light sources, although the emission of these high power lamps contains a considerable amount of UV light. Expensive filter equipment is necessary for the selection of defined emission bands as well as an efficient heat management for avoiding thermal reaction pathways.

Those limitations can be overcome by the application of continuously running microreactors and modern light emitting diodes (LEDs) making this combination a versatile tool for photochemical applications. Microstructured equipment is able to contact reagents in gas and/or liquid streams more efficiently due to a strongly increased surface to volume ratio. The reaction volume inside a microreactor is very small and suited for an excellent process control. Hot spot
formation becomes manageable by exact temperature control leading often to improved conversion and selectivity in the reaction.\textsuperscript{40} Especially the irradiation of the reaction solution becomes easier. Thin film formation in microchannels or capillaries with a small inner diameter allows the full irradiation of the complete reaction volume inside the microchannels.\textsuperscript{41} The irradiation time can be exactly controlled by the flow rate of the reaction composition being pumped through the microstructures. These advantages offer many possibilities for improving in parallel the economic and the environmental sustainability of a chemical process.\textsuperscript{42} LEDs fundamentally enhanced the application range of photoreactor design in 2005 using a FEP capillary wrapped around an immersion well with a UV light source inside a photoreactor.\textsuperscript{48,49} The tube-like capillaries with a small inner diameter allows the full irradiation of the liquid phase. Originally, the falling film microreactor (FFMR) was designed and successfully used as solvent evaporator and for highly exothermic reactions like hydrogenation of nitro groups.\textsuperscript{61–64} But its design (vide infra) also allows the selective irradiation of the reaction solution in its microstructure. Up to now the FFMRF has been applied to three continuous-flow photochemical reactions: a) photochlorination of aromatic isocyanates,\textsuperscript{65} b) cycloaddition of singlet oxygen into cyclopentadien,\textsuperscript{66} and c) cycloaddition of singlet oxygen into 1,5-dihydroxynaphthalene for the synthesis of juglone.\textsuperscript{67}

All reactions performed up to now lack of a detailed investigation of the process parameters of a continuous-flow photochemical reaction performed in the FFMRF. To close this gap, we investigated the juglone synthesis as benchmark reaction performed in the FFMRF with two sensitizers having different absorption wavelengths. The impact of the light source regarding the irradiation wavelength and the LED power are evaluated as well as the oxygen partial pressure and substrate concentration. Finally the architectural impact of the reactor will be evaluated as well. The quantum efficiency $q$, the productivity $L_0$ and the space time yield STY are calculated for comparing the FFMRF with other reactor types.

## Results and discussion

### Photomicroreactor and light sources

The FFMRF is composed of a back plate carrying the heat exchanging unit and the inlet and outlet for the reaction solution (details can be found in Fig. S1 and S2 in the ESI\textsuperscript{1†}). It is followed by the reaction plate as the first key element of the reactor. On the front side of the reaction plate microchannels with different geometries for each plate have been incorporated by wet chemical etching (Table 1).

The reaction solution is fed through the top slit and pulled into the microchannels by gravity and capillary forces. Depending on the flow rate and viscosity of the solution thin films can be generated far below 100 $\mu$m. The reaction plate
is fixed with a mask and sealing gasket followed by the top plate of the reactor housing. This last part contains the second key element of the reactor, an inspection window made of borosilicate glass (visible to irradiation: length $l_{irr} = 54$ mm, width $w_{irr} = 29$ mm, thickness: 12 mm). Due to the high transparency of borosilicate glass for visible light (90% for wavelengths of $370 \text{ nm} \leq \lambda \leq 2000 \text{ nm}$) it is most suitable for irradiating the thin film on the reaction plate with external light sources. Beside the inspection window the top plate carries the inlet and outlet devices of the gas phase, which is typically fed from bottom to top of the reactor. This arrangement allows a counter current flow of the gas stream against the liquid flow resulting in an excellent gas liquid contacting and mass transfer.

LEDs were installed as energy efficient sources for irradiation. Violet, royal blue, green and cold-white LEDs (GeTian Opto-Electronics CO., LTD.) were used in order to allow the selective irradiation of different photocatalysts (Table 2, Fig. 4).

An aluminium body was designed as heat sink carrying two LEDs (Fig. 1). These LED arrays can be fixed magnetically in front of the inspection window of the FFMR allowing a quick exchange of the array maintaining the same light path properties for all LEDs used in this work. Due to the LED’s wide angle of radiation of $120^\circ$ the complete reaction plate inside the reactor was irradiated. Special attention was drawn on a light-proof design of the LED array due to two reasons. First, the use of high-power irradiation, especially close to the UV region, requires safety precautions for protecting the eyesight of the experimenter. Second, light-tightness is the prerequisite for the full availability of all photons produced by the LED array inside the reactor to be used for the photochemical reaction.

Lab plant design

The lab plant was equipped with standard components for the complete set of experiments (Fig. 2). A water-filled thermostat (Julabo F10 and HC E07) was used to maintain the temperature of the FFMR at 20 °C. Synthetic air or pure oxygen (Linde AG) was released from a pressurized steel cylinder and broad to 1 bar application pressure with an appropriate pressure regulator (Linde AG, FMD 300-18). The fine regulation of current and voltage for the LED arrays were done with a standard power supply (Basetech BT-305). Two piston pumps (Chemyx Inc., Nexus 5000) were used to feed and withdraw the liquid phase from the FFMR. The gas flow rate was regulated by a mechanical rotameter (Baley, Fisher & Porter, G10A6142DA131X100). A flow chart can be found in Scheme S1 in the ESI.

For sample taking a device was implemented between the reactor outlet and the withdrawing pump using two needles inside a HPLC vial. The feeding needle was placed at the bottom of the vial, whereas the withdrawing needle was placed 12 mm above the vial’s bottom. This arrangement allows the continuous filling of the HPLC vial during the process with a defined volume of reaction solution. For each HPLC sample a

Table 1 Geometrical data of FFMR reaction plate microchannels

| Abbreviation | Channel number $N$ | Width $w_{ch}/\mu\text{m}$ | Depth $d_{ch}/\mu\text{m}$ | Length $L_{ch}/\text{mm}$ | Irradiated length $l_{irr, ch}/\text{mm}$ |
|--------------|-----------------|-----------------|------------------|-----------------|------------------|
| FFMR_600     | 32              | 600             | 200              | 78              | 54               |
| FFMR_1200    | 16              | 1200            | 400              | 78              | 54               |

Table 2 Spectral parameters of LED

| LED                | Emission maximum $\lambda_{\text{max}}/\text{nm}$ | FWHM$^a$/nm |
|--------------------|-----------------------------------------------|-------------|
| Violet             | 410                                           | 22          |
| Royal blue         | 455                                           | 24          |
| Green              | 520                                           | 37          |
| Cold-white (blue part) | 442 (sharp)                              | 22          |
| Cold-white (red part) | 550 (broad)                              | 123         |

$^a$ Full width at half maximum of the spectral band.
new vial was plugged onto the stationary mounted needles (see Fig. S3 in the ESI†). Details on the analytical HPLC method can be found on page S5 of the ESI†

Benchmark reaction and sensitizers

The photooxygenation of DHN has been performed in several types of flow reactors so far. Beside classical immersion well reactors equipped with mercury pressure lamps also sunlight collecting and concentrating reactors were used for the continuous-flow synthesis of juglone,69–71 whereas microscale reactors like capillary reactors overcome insufficient irradiation.57,72

The key step in the photooxygenation of 1,5-dihydroxynaphthalene (DHN) to juglone is the in situ formation of singlet oxygen that pursues a [4 + 2] cycloaddition with DHN.73–75 The resulting endoperoxide is unstable and is instantaneously transformed to juglone and water (Fig. 3). Singlet oxygen can be produced under harsh chemical conditions76 (being often not compatible with the stability of substrate molecules) or via a mild photocatalytic process.77 The latter case needs a sensitizer like rose bengal (RB) or mesotetraphenylporphyrine (TPP) exhibiting a triplet state energy greater than 95 kJ mol⁻¹.78 After irradiation with light of appropriate wavelength the sensitizer is excited first to its singlet state which undergoes intersystem crossing (ISC) to the triplet state.79 With a triplet oxygen molecule in close vicinity to the sensitizer energy transfer is possible yielding the highly reactive singlet oxygen species.79 Although RB achieves a high quantum yield for singlet oxygen formation, it is known that this naturally occurring dye decomposes quite rapidly by photobleaching.80 In the case of TPP the triplet quantum yield is slightly lower, but the photostability of the dye is considerably higher.81

To ensure comparability between the experiments both sensitizers are used under the same reaction conditions. RB is a salt which dissolves very good in aqueous solutions, but neither DHN nor TPP are soluble in water. In consequence, 2-propanol was chosen as environmental friendly solvent for all experiments.82 It has a cut-off wavelength of 240 nm ensuring that no interactions take place between the incident visible light and the reaction medium. The nonpolar TPP was substituted by its derivative mesotetracarboxyphenylporphyrine (TcPP) containing four free carboxylic acids in para-position of the phenyl residues.83 Despite a small bathochromic shift of the Soret band, these functional groups do not disturb the UV/vis absorption properties of the monomeric porphyrine core in polar solutions, but enhance the solubility of the sensitizer for its use in the chosen solvent.84 Details on the Synthesis of TcPP can be found in the ESI† on page S6.

Definitions and control experiments

For a clear comparison of all experiments throughout this work a set of physical and chemical reaction parameters were defined (Table 3). Variations of these parameters due to a detailed investigation of their impact on the photocatalytic process are mentioned accordingly.

The main parameters varied in this work are the type of sensitizer (rose bengal or TcPP) and the light source (green, royal blue, violet, and cold-white). For an easier description of the reaction conditions the following sensitizer-light source combinations are abbreviated as defined in Table 4.

A control experiment has been performed in order to assess the necessity of a sensitizer for a successful realization

![Photocatalytic cycle of TcPP for singlet oxygen formation as key step in juglone synthesis.](image)

**Fig. 3** Photocatalytic cycle of TcPP for singlet oxygen formation as key step in juglone synthesis.

### Table 3 Defined standard solution and standard reaction conditions for the continuous-flow synthesis of juglone in a FFMR

| Parameter                      | Value       |
|--------------------------------|-------------|
| Substrate concentration $c_{\text{DHN}}$ | $10 \times 10^{-3}$ mol L⁻¹ |
| Sensitizer concentration $c_{\text{sens}}$ | $0.5 \times 10^{-3}$ mol L⁻¹ |
| Solvent                        | 2-Propanol  |
| Liquid flow rate $f_1$         | 0.16 mL min⁻¹ |
| Gas flow rate $f_g$            | 100 mL min⁻¹ |
| Reactor temperature $T_{\text{FFMR}}$ | 20 °C |
| Reactor pressure $p_{\text{FFMR}}$ | Atmospheric pressure |
| LED array amperage $I_{\text{LED}}$ | 350 mA |

### Table 4 Abbreviations of sensitizer-light source combinations used in this work

| Sensitizer                         | Light source | Abbreviation |
|------------------------------------|--------------|--------------|
| Rose bengal                         | Cold-white   | RB-cw        |
| Violet                             | RB-v         |              |
| Royal blue                         | RB-b         |              |
| Green                              | RB-g         |              |
| meso-Tetracarboxy-phenylporphyrine | Cold-white   | TcPP-cw      |
| Violet                             | TcPP-v       |              |
| Royal blue                         | TcPP-b       |              |
| Green                              | TcPP-g       |              |
of the juglone synthesis. A standard solution without sensitizer was used under standard conditions with a cold-white LED providing the broadest emission range. As expected no conversion to juglone was observed due to the absence of singlet oxygen solely produced by an appropriate sensitizer. Besides this prove any photochemical decomposition pathways of the starting material could be ruled out as seen by the HPLC analysis. Further control experiments were performed in order to assess the photochemical decomposition of juglone during the irradiation. Compared to DHN juglone absorbs light in the visible spectrum which might lead to consecutive reactions (for the UV/vis absorption spectra, see Fig. S6 in the ESI†). Commercially available juglone was used as starting material in the standard solution instead of DHN. Four experiments were performed with RB-cw, RB-g, TcPP-cw and TcPP-v under standard conditions. HPLC analysis confirmed that no decomposition of juglone or any follow-up reactions occurred in these experiments.

Influence of light source on sensitizer excitation

As first parameter the emission wavelength was evaluated for both sensitzers with pure oxygen on a FFMR_1200 plate under standard conditions. RB and TcPP have a specific UV/vis absorption pattern which result in unique emission-absorption overlaps for each LED array (Fig. 4). Each overlap is representative for the excitation of the sensitizers and in consequence for the singlet oxygen formation.

In the case of RB the gradual increase in conversion correlates with the increasing overlap of light emission and dye absorption. The best yields were obtained for the cold-white and the green LED (Fig. 5). The broad emission of the cold-white LED covers the whole absorption band of RB in the visible region between 470 nm and 600 nm. Its peak emission is in perfect overlap with the maximum absorption of RB at 550 nm. The green LED emission spectrum overlaps only in part with the RB absorption, particularly in the low absorbing region between 470 nm and 550 nm. The small overlap in RB-v and RB-b is clearly confirmed by the low conversion of 9% and 15%, respectively. Concerning the product selectivity, RB-g achieved the highest selectivity of \( S = 93\% \), whereas RB-cw reached a slightly lower selectivity of \( S = 87\% \). Although RB-cw results in higher conversion compared to RB-g it was decided to the favour the higher selectivity with RB-g for further experiments.

The same experiments were performed with TcPP (Fig. 6), which exhibits a split visible light absorption pattern with the \( \text{Soret} \) band (\( \varepsilon_{\text{max}} = 416 \text{ nm} \)) and the \( Q \) bands (\( \varepsilon_{\text{max}} = 511, 547, 589, 646 \text{ nm} \)). As it was the case for RB-g and RB-cw the best spectral overlap gives the highest conversion. TcPP-v achieves a conversion of \( X = 76\% \). The excellent overlap of the violet emission band with the strongly absorbing \( \text{Soret} \) band of the porphyrin core strongly contributes to high conversions for TcPP-v. Due to a shift to lower wavelengths and in consequence due to a less good spectral overlap TcPP-b only achieves a conversion of \( X = 18\% \). In the case of TcPP-g the green light emission shows a very good overlap with the \( Q \) bands of the porphyrin core resulting in a conversion of \( X = 19\% \). The emission of the cold-white LED allows a small overlap with the strongly absorbing \( \text{Soret} \) band and a very
good overlap with the Q bands of the porphyrin core. This combination results for TcPP-cw in a conversion of X = 26%. Interestingly TcPP allows achieving higher selectivity than RB reaching nearly 100% for TcPP-v and TcPP-cw, 88% for TcPP-g and 78% for TcPP-b.

**Influence of LED power**

In close conjunction to the first parameter the impact of the light power was evaluated in a second set of experiments. The amperage $I_{LED}$ of the LED arrays was varied from 175 mA over 350 mA (standard value) to 530 mA. These values correspond to a power $P_d$ of 1.1 W, 2.38 W and 3.6 W respectively for the green LED array used in the tests. RB was applied on a FFMR_1200 plate under standard conditions with oxygen gas (Fig. 7).

The variation of the power has an impact on both the conversion and the selectivity. The increase in conversion can be attributed to the larger number of photons available with increasing power for singlet oxygen formation. Selectivity changed less strongly with increasing LED power, but with the same trend to higher values. In the case of switching the electrical power from 1.1 W to 2.38 W a relative increase in conversion of 48% and selectivity of 6% is given. The increase of electrical power from 2.38 W to 3.6 W (approx. 51%) results in a relative increase of only 9% and 2% for conversion and selectivity. These rather small differences are an important result for the optimisation of the photochemical process regarding its energy consumption. The low increase in conversion points to the fact that the larger number of available photons at 3.6 W are not used for the photochemical process.

**Influence of oxygen partial pressure**

The availability of dissolved oxygen is an important key factor for the singlet oxygen formation during the juglone synthesis. The solubility of oxygen in 2-propanol is given as its molar

\[
\text{Solubility of oxygen in 2-propanol: } 10^{-4} \text{ mol mol}^{-1}
\]

fraction with a value of $7.88 \times 10^{-4}$ mol mol$^{-1}$ at 20 °C and 1.013 bar. Applying Henry’s law results under these conditions in an oxygen concentration $O_2 c_oxygen = 10 \times 10^{-3}$ mol L$^{-1}$ (see Fig. S7 in the ESI†). The impact of the dissolved oxygen concentration was examined by the application of either pure oxygen ($O_2 p_oxygen = 1.013$ bar) or synthetic air with a fivefold lower oxygen content ($air c_oxygen = 2 \times 10^{-3}$ mol L$^{-1}$; $air p_oxygen = 0.202$ bar). RB was used as sensitizer on a FFMR_1200 plate under standard conditions. As can be seen in Fig. 8 the use of synthetic air has only a small negative impact on the conversion rate compared to pure oxygen. The slightly decreased conversion for RB-g by 2% and for RB-cw by 7% can be attributed to a lower oxygen concentration in the liquid phase due to the decreased oxygen partial pressure in the synthetic air gas phase. But in general the photochemical process does not seem to be mass transfer limited by the oxygen gas phase.

In the case of selectivity the use of synthetic air has a far more negative impact. Especially with RB-g the selectivity drops by 26%. In all other cases the selectivity decreases by a value of approx. 13%. One reason for this moderate selectivity might be a competing reaction that involves the sensitized conversion of the endoperoxide intermediate. Bicyclic endoperoxides are known to be cleaved by appropriate irradiation resulting in oxygen radicals. These radicals can react intermolecularly with a double bond yielding epoxides. The existence of a sensitizer can promote this reaction, if the sensitizer is not quenched upfront by another reaction pathway like the singlet oxygen formation (see Scheme S2 in the ESI†). Due to the absence of excess oxygen in synthetic air RB might promote this competing reaction which is less pronounced in an oxygen-rich solution.

**Influence of reaction plate architecture**

The FFMR design comprises different reaction plate architectures (Table 1). As known from literature each channel

\[
\begin{align*}
X & = 23, 88, 93, 95 \\
S & = 20, 34, 32, 37 \\
Y & = 35
\end{align*}
\]

**Fig. 7** Impact of light power on conversion and selectivity in juglone synthesis with RB and oxygen on a FFMR_1200 plate (■ conversion $X$; □ selectivity $S$; ■ yield $Y$).

\[
\begin{align*}
X & = 9, 51, 37, 21 \\
S & = 5, 12, 71, 87 \\
Y & = 9, 34, 32, 33
\end{align*}
\]

**Fig. 8** Impact of oxygen partial pressure on conversion and selectivity in juglone synthesis with RB on a FFMR_1200 plate (■ conversion $X$; □ selectivity $S$; ■ yield $Y$).
geometry can result in different thin film geometry. Variations in thin film thickness have an impact on the gas-liquid phase contacting behaviour and in consequence on the conversion and selectivity of the examined reaction. The thin film formation can be investigated with a confocal laser microscope. With this method the experimental comparison of uncoated FFMR_600 with FFMR_1200 plates gave at the same flow rate a greater film thickness for the FFMR_600 than for the FFMR_1200 plate. A greater film thickness results in a longer residence time at the same flow rate applied for both plates offering the same channel area ($A_{\text{channels}} = 1497.6 \text{ mm}^2$). This point is reflected by the results obtained in this experiment. For TcPP-v and RB-g a relative increase in conversion of 15% and 25%, respectively, is obtained using the plate with the smaller channel architecture (FFMR_600) providing a greater film thickness and a longer residence time (Fig. 9). Selectivity increases as well, but not as consistent as for the conversion. These results indicate that a longer residence time is beneficial for the photochemical conversion.

**Influence of substrate inlet concentration**

Three DHN inlet concentrations were evaluated ($5, 10, 20 \times 10^{-3} \text{ mol L}^{-1}$) keeping the amount of sensitizer constant at $5 \times 10^{-4} \text{ mol L}^{-1}$. All experiments were performed with synthetic air as oxygen source. For both RB-g and TcPP-v the conversion decreases with increasing DHN concentration (Fig. 10). This trend can be attributed to the higher relative amount of sensitizer and oxygen at lower substrate concentration.

With increasing DHN concentration the values for the selectivity seem to run into a plateau with approx. $S = 70\%$ for RB-g and $S = 88\%$ for TcPP-v. The higher selectivity for the lowest DHN concentration may result also from the competing reaction pathways between singlet oxygen formation and sensitized endoperoxide conversion. The more sensitizer and oxygen are available for singlet oxygen formation the less pronounced is the endoperoxide side reaction.

**Optimization of reaction parameters**

With the experimental results obtained so far the best combination was used for optimization. This was the case for TcPP-v with oxygen gas on a FFMR_600 plate under standard conditions ($X = 94\%, S = 99\%$). This arrangement was used for applying different LED power (Fig. 11A) and liquid flow rates (Fig. 11B). In the first case a lower LED power resulted in a significant relative loss in conversion of 25\%, whereas with a higher LED power the selectivity decreased by 6% close to full conversion. Hence, the tests with varying flow rates were performed with the medium LED power corresponding to $P_{\text{el}} = 2.45 \text{ W}$. As expected, with the lowest flow rate of $f_l = 0.12 \text{ mL min}^{-1}$ the highest conversion was achieved yielding $X = 97\%$ with $S = 99\%$. With increasing flow rate the conversion decreased steadily to $X = 65\%$ at $f_l = 0.44 \text{ mL min}^{-1}$ maintaining an excellent selectivity of $S = 99\%$.

**Theoretical part**

In this section the correlation between the hydrodynamic behaviour of the reactor and the irradiation by the external LED arrays is presented and discussed for the experimental results with TcPP-v and RB-g. This section is split into two parts. In the first part the hydrodynamic and general parameters of the FFMR and the LED arrays are mathematically described and presented. The thickness of the liquid thin film

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Fig. 9 Impact of plate architecture on conversion and selectivity in juglone synthesis with TcPP-v and RB-g with air ($X$: conversion; $S$: selectivity).

Fig. 10 Impact of DHN inlet concentration on conversion and selectivity in juglone synthesis with (A) RB-g and (B) TcPP-v on a FFMR_600 plate with air ($X$: conversion; $S$: selectivity).

Fig. 11 Impact of (A) LED power and (B) flow rate on conversion and selectivity in juglone synthesis with TcPP-v on a FFMR_600 plate and oxygen ($X$: conversion; $S$: selectivity; $Y$: yield).
inside the microchannels of the reaction plate is calculated as the main hydrodynamic parameter. The literature-known Nusselt eqn (1) allows a good approximation of the thin film thickness $\delta$ in the microchannels:\(^{52-94}\)

$$\delta = \sqrt{\frac{3f_l \mu_l}{N \rho_l \omega_{ch} g}} \quad [\mu m] \quad (1)$$

with $f_l$ as the liquid flow rate (0.16 mL min$^{-1}$), $\mu_l$ as the dynamic viscosity of 2-propanol at 20 °C (2.3 $\times$ 10$^{-3}$ kg m$^{-1}$ s$^{-1}$), $\rho_l$ as the density of 2-propanol at 20 °C (0.786 g mL$^{-1}$) and $g$ as the gravitational constant (0.981 m s$^{-1}$). The parameters $N$ and $\omega_{ch}$ describe the number of microchannels and their width.\(^95\) With eqn (2) the liquid phase volume $V_{irr}$ inside the irradiated part of the microchannels can be calculated, the appropriate residence time $t$ with eqn (3):

$$V_{irr} = \delta \times l_{irr, ch} \times w_{ch} \times N \quad [mL] \quad (2)$$

$$t = \frac{V_{irr}}{f_l} \quad [s] \quad (3)$$

Under standard reaction conditions the thickness of the liquid film is approx. 50 $\mu$m with a mean residence time of 19.4 s inside the irradiated microchannels. Based on the dimension of the inspection window of the FFMR the irradiated surface on the reaction plate inside the reactor can be calculated with eqn (4), whereas the irradiated surface of the microchannels can be calculated with eqn (5):\(^95\)

$$A_{irr} = l_{irr} \times w_{irr} \quad [m^2] \quad (4)$$

$$A_{irr, ch} = N \times l_{irr, ch} \times w \quad [m^2] \quad (5)$$

The irradiated microchannel area is with 1037 mm$^2$ approx. 65% of the entire irradiated area since the embossments between the microchannels are not wetted with the liquid phase. Table 5 summarizes the results of the calculation for the hydrodynamic parameters for the FFMR including the general parameters for the irradiated surfaces inside the microreactor.

In the case of the LED arrays the radiant power $P_{LED}$ of the array is either given in the technical data sheet or can be calculated with this data.\(^96,97\) The luminescent efficiency $\eta_{lum}$ of the LEDs can be calculated with eqn (6):

$$\eta_{lum} = \frac{P_{LED}}{P_{el}} \quad (6)$$

with $P_{el}$ as the electrical power of the LED array at a current $I_{LED}$ of 350 mA. With a transmission $T = 0.9$ for the borosilicate glass of the inspection window the radiant power available inside the FFMR can be calculated as well (eqn (7)):\(^68\)

$$P_{av, LED} = 0.9 \times P_{LED} \quad [W] \quad (7)$$

Table 6 summarizes the results of the calculation for the general parameters for the LED arrays used with the FFMR.

In the second part the photophysical parameters of the incident light and its interaction with the photocatalyst are mathematically described and presented (details and numbers of the calculation can be found on pages S10 and S11 of the ESI†).\(^31,98\) It has to be noted that the following equations and calculations reflect an idealized process in which the incident light trespasses the thin film just once. Any scattering effects or reflections from the reactor chamber walls resulting in multiple light transits through the solution are not considered.\(^99\) The relative radiant power $P_{rel, \lambda}$ of the LED arrays was extracted for each wavelength from the technical data sheet of the LED manufacturer. The decadic molar extinction coefficient was obtained from the UV/vis absorption spectra of both dyes. The density function of the light source $g_\lambda$ given by eqn (8) is defined as normalization factor for the calculation of the entire radiant power $\varphi_\lambda$ per wavelength in eqn (9):

$$g_\lambda = \frac{P_{av, LED}}{\sum_{\lambda, min} P_{rel, \lambda}} \quad [W] \quad (8)$$

$$\varphi_\lambda = P_{rel, \lambda} \times g_\lambda \quad [W \ nm^{-1}] \quad (9)$$

The available radiant power per wavelength in the microchannels $\varphi_{ch}$ is defined by the ratio of the entirely irradiated surface to the irradiated surface of the microchannels (eqn (10)):

$$\varphi_{ch} = \frac{\varphi_\lambda \times A_{irr, ch}}{A_{irr}} \quad [W \ nm^{-1}] \quad (10)$$

Based on the experimentally obtained decadic molar extinction coefficient $e_\lambda$, the Napierian extinction coefficient $\mu_\lambda$ can be calculated for each wavelength (eqn (11)):

$$\mu_\lambda = e_\lambda \times c_{con} \times \ln(10) \quad [m^{-1}] \quad (11)$$

| Table 5 | Hydrodynamic and general parameters for the FFMR |
|---------|--------------------------------------------------|
| Thin film thickness $\delta$ | 50 $\mu$m |
| Irradiated volume $V_{irr}$ | 0.052 mL |
| Residence time $t$ | 19.4 s |
| Irradiated area in FFMR $A_{irr}$ | 1599 mm$^2$ |
| Irradiated area in microchannels $A_{irr, ch}$ | 1037 mm$^2$ |

| Table 6 | Available radiant power and luminescent efficiency of each LED array |
|---------|--------------------------------------------------|
| Voltage $U_{LED}$ at 350 mA | Violet LED | Green LED |
| 7 V | 6.8 V |
| Electrical power $P_{el}$ | 2.45 W | 2.38 W |
| Radiant power $P_{LED}$ | 0.84 W | 0.37 W |
| Luminescent efficiency $\eta_{lum}$ | 34.3% | 15.6% |
| Available radiant power $P_{av, LED}$ | 0.76 W | 0.34 W |
Eqn (10) and (11) can be used on base of the Lambert–Beer law for the calculation of the radiant power per wavelength absorbed by the sensitizer in the liquid thin film $\phi_{\text{abs}}$ (eqn 12):

$$\phi_{\text{abs} \lambda} = \phi_{\text{ch} \lambda} \times \left(1 - e^{(-1/\varepsilon_{\lambda} N_A)}\right) \left[\text{W nm}^{-1}\right] \quad (12)$$

With eqn (13) the photon absorption efficiency per wavelength $\eta_{\text{photon abs} \lambda}$ can be expressed by the ratio between the absorbed radiant power and the available radiant power per wavelength on the structured surface:

$$\eta_{\text{photon abs} \lambda} = \frac{\phi_{\text{abs} \lambda}}{\phi_{\text{ch} \lambda}} \quad (13)$$

The results from eqn (10) and (12) can now be converted into the molar amount of available photons (eqn (14)) and molar amount of absorbed photons absorbed by the sensitizer per wavelength during residence time $\tau$ (eqn (15)):

$$n_{\text{photons ch} \lambda} = \frac{\phi_{\text{ch} \lambda} \times \lambda \times \tau}{h \times c \times N_A} \left[\text{mol nm}^{-1}\right] \quad (14)$$

$$n_{\text{abs photons} \lambda} = \frac{\phi_{\text{abs} \lambda} \times \lambda \times \tau}{h \times c \times N_A} \left[\text{mol nm}^{-1}\right] \quad (15)$$

with $\lambda$ as the specific wavelength, $h$ as the Planck constant, $c$ for the speed of light and $N_A$ as the Avogadro constant. The results of eqn (10), (12), (14) and (15) represent the available and absorbed power and the molar amount of available and absorbed photons, respectively, for each wavelength. With eqn (16)–(19) these values are summarized in order to address the whole spectral emission and absorption range of the appropriate light source and sensitizer combination:

$$\phi_{\text{ch} \lambda} = \sum_{\lambda_{\text{min}}}^{\lambda_{\text{max}}} \phi_{\text{ch} \lambda} \left[W\right] \quad (16)$$

$$\phi_{\text{abs} \lambda} = \sum_{\lambda_{\text{min}}}^{\lambda_{\text{max}}} \phi_{\text{abs} \lambda} \left[W\right] \quad (17)$$

$$n_{\text{photons ch} \lambda} = \sum_{\lambda_{\text{min}}}^{\lambda_{\text{max}}} n_{\text{photons ch} \lambda} \left[\text{mol}\right] \quad (18)$$

$$n_{\text{abs photons} \lambda} = \sum_{\lambda_{\text{min}}}^{\lambda_{\text{max}}} n_{\text{abs photons} \lambda} \left[\text{mol}\right] \quad (19)$$

The energy efficiency $\eta_E$ can be described as the ratio between the absorbed power $\phi_{\text{abs}}$ against the electrical power $P_e$ (eqn (20)):

$$\eta_E = \frac{\phi_{\text{abs}}}{P_e} \quad (20)$$

Averaging the photon absorption efficiency over all wavelengths gives the mean photon absorption efficiency for the whole process (eqn (21)):

$$\bar{\eta}_{\text{photon abs}} = \frac{\lambda_{\text{max}} - \lambda_{\text{min}}}{\lambda_{\text{max}} - \lambda_{\text{min}}} \sum_{\lambda_{\text{min}}}^{\lambda_{\text{max}}} \eta_{\text{photon abs} \lambda} \quad (21)$$

The calculated result shows that TcPP-v is more efficient in the energy conversion as well as in the photon absorption with $\eta_E = 0.13$ and $\bar{\eta}_{\text{photon abs}} = 0.29$ compared to $\eta_E = 0.014$ and $\bar{\eta}_{\text{photon abs}} = 0.19$ for RB-g. The stronger efficiency of TcPP-v can be attributed to the better overlap of the main emission band of the LED array and the absorption band of the porphyrine sensitizer. One has also to keep in mind that both sensitizers have been used with the same molar concentration of $5 \times 10^{-4}$ mol L$^{-1}$ whereas the sensitizers differ in their extinction coefficients at their particular maximum absorption wavelength by a factor of approx. $4.7\left( \epsilon_{\text{TcPP}} = 476 \text{ mol}^{-1} \text{cm}^{-1} \text{L} \text{mol}^{-1} \text{cm}^{-1} \text{vs.} \epsilon_{\text{RB}} = 109 \text{ mol}^{-1} \text{cm}^{-1} \text{L} \text{mol}^{-1} \text{cm}^{-1} \right)$. Table 7

| Entry | TcPP-v | RB-g |
|-------|--------|------|
| 1     | 0.0095 | 0.008 |
| 2     | 0.0414 | —    |
| 3     | 0.06 mmol h$^{-1}$ | 0.03 mmol h$^{-1}$ |
| 4     | 0.09 mmol h$^{-1}$ | —    |
| 5     | 0.22 mol s$^{-1}$ m$^{-3}$ | 0.14 mol s$^{-1}$ m$^{-3}$ |
| 6     | 0.48 mol s$^{-1}$ m$^{-3}$ | —    |
summarizes the results of the theoretical evaluation for TcPP-v and RB-g.

The quantum efficiency $q$, the productivity $L_p$ and the space time yield STY represent three important parameters for comparing a (photochemical-) process, which has been performed in different reactor types. The quantum efficiency $q$ can be calculated with eqn (22) via the ratio of the molar amount of juglone produced during the residence time against the molar amount of photons absorbed by the sensitizer:

$$ q = \frac{f \times c_{\text{in}}}{{n_{\text{DPS}}} \times t} $$

The productivity $L_p$ represents the molar quantity of juglone produced per unit of time (eqn (23)):

$$ L_p = f \times c_{\text{in}} \times Y \ [\text{mmol h}^{-1}] $$

The space time yield STY normalizes the productivity of the process to the liquid volume in the reactor (eqn (24)):

$$ \text{STY} = \frac{L_p}{V_{\text{eff}}} \ [\text{mmol h}^{-1} \text{m}^{-3}] $$

All three parameters have been calculated for TcPP-v and RB-g used under standard reaction conditions with air on a FFMR_600 reaction plate and for TcPP-v also with oxygen gas (Table 8). In corollary to the efficiency results discussed above TcPP-v shows higher quantum efficiency than RB-g (Table 8, entry 1). Especially with oxygen gas TcPP-v shows an approx. 1.8 times higher quantum efficiency than RB-g. The same trend can be seen for the productivity $L_p$ and the STY: RB-g/air < TcPP-v/air < TcPP-v/oxygen (Table 8, entry 3–6).

These results can be compared with literature data from Oelgemöller et al. for the FFMR$^{67}$ and from de Oliveira et al. for a capillary reactor$^{57}$ using eqn (23) and (24) (Table 9). For better comparability only results were used which were obtained with white light sources. In the case of the FFMR processes it can be clearly seen that $L_p$ and STY have been increased by a factor of up to 21 solely due to an improved light source architecture in our system (Table 9, entry 1–4). Furthermore, the capillary reactor can be seen as scale-up approach to the FFMR. A 37-fold increase in productivity (Table 9, entry 5) shows the strong impact of the different reactor architecture with larger reactor volume (25 mL) and higher liquid flow rate (0.75 mL min$^{-1}$).$^{100}$ In reverse, the STY of the FFMR is approx. 7 times higher than for the capillary reactor. Comparing the productivity of the capillary reactor with our optimized process in the FFMR using TcPP-v (Table 8, entry 4) instead of TcPP-cw (Table 9, entry 5) diminishes the factor of 37 to 8 for the productivity increase. This clearly indicates that an even higher productivity would be possible for the capillary reactor, if its light source would be optimized to the sensitizer, i.e. by using violet light for covering the Soret band of the porphyrin.

### Conclusions

With the results of this work we present a detailed investigation of the utilization of a microstructured falling film reactor for a photochemical application with visible light. The excellent capability of the FFMR to contact gas and liquid phases is combined with high-power LED arrays for the photonic contacting of the liquid phase that contains the metal-free sensitizers. With this setup singlet oxygen is produced in situ for the photochemically catalysed oxygenation of 1,5-dihydroxynaphthalene to juglone. Detailed investigations were performed according the light source, radiant power, oxygen partial pressure, reaction plate architecture, and substrate concentration. After optimization of the reaction conditions a conversion rate as high as 97% at 99% selectivity was achieved for the porphyrine sensitizer irradiated with violet light under pure oxygen gas atmosphere. The photochemical process in the FFMR was also theoretically investigated. It could be shown that the quantum efficiency can be improved by chemical reaction optimization, e.g. switch to pure oxygen gas, and physicochemical optimization, with e.g. a good spectral overlap of the emission and absorption bands of the chosen photocatalyst and LED array. Productivity and space time yield were compared with literature data showing that both parameters can be increased dramatically with
specific adaptation of the light source to the reactor. Based on these results ongoing research activities investigate the variance in selectivity depending on the sensitizer-light source combination. Scale-up approaches and a more detailed observation of the irradiation characteristics inside the reactor chamber will be performed for a deeper understanding of the impact of scattering and reflection effects on the photochemical process in continuous-flow. This might allow on these results ongoing research activities investigate the absorption wavelength of the sensitizer used.

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