Supporting Information

for

A method to determine the correct photocatalyst concentration for photooxidation reactions conducted in continuous flow reactors

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Descriptions of material and methods, flow setup, and LED characterization
Materials and methods

UV–vis spectra were recorded on an Agilent Cray 60 UV–vis spectrometer, using a Hellma High Precision Cell (light path 0.5 mm). All samples were collected in graduated flasks using a valve time-controlled by an Arduino microprocessor in order to validate the liquid flow rate. The conversion of alpha-terpinene was determined by NMR spectroscopy. The $^{13}$C-decoupled $^1$H NMR spectra were recorded with a Magritek Spinsolve 43 Carbon Ultra. The NMR samples were measured as collected. Citronellol samples were quenched with 2 equiv of a 0.25 N solution of PPh$_3$ in dichloromethane, and the conversion was determined by GC using tetradecane as an internal standard. The emission spectra of the LEDs were measured using a HERA Admesy spectroradiometer.

All solvents used were HPLC grade. The compounds were purchased and used as received from Sigma Aldrich (phenothiazine 98%, methylene blue, eosin Y 99%, erythrosin B 90%, fluorescein, citronelol 95%) and TCI (rose bengal, 9,10-dicyanoanthracene 98%, 9,10-dimethylanthracene 98%, tetraphenylporphyrin 98%, tris(2,2'-bipyridyl)ruthenium(II) chloride hexahydrate 98%, alpha-terpinene 90%).

Experimental procedure

As a flow reactor system, the commercially available Corning® Advanced-Flow™ Lab Photo Reactor was used (Figure S1). The solution containing the compound to be oxidized and the photosensitizer were pumped at a given flow rate (e.g., 1 N alpha-terpinene in toluene, flow rate 1 mL/min). The gas flow was started with the corresponding flow rate (here 44.8 mL/min at 1 bar), and the light source was switched on. The back pressure regulator was controlled using compressed nitrogen, and the pressure was increased until 8 bar, as measured at the entrance of the photoreactor. Samples were collected after a
liquid volume corresponding to at least 3 times the reactor volume had passed (here $3 \times 2.7 \text{ mL at } 1 \text{ mL/min} = 8.1 \text{ min}$). Samples were collected into a graduated flask using a valve controlled with an Arduino [1]. The waste was collected in a bottle permanently purged with nitrogen gas.

![Figure S1: Corning® Advanced-Flow™ Lab Photo Reactor setup (the front protection was removed for the picture. Note: do not run a photochemical experiment with an open photoreactor).](image)

**Characterization of the light source**

The distance of the light source to the fluidic module (3.4 cm) was fixed. This was optimized earlier using Zemax (www.zemax.com) in order to guarantee a homogenous illumination (Figure S2).
Figure S2: Calculated illumination at a 3.4 cm distance (LED-to-module).

Two LED panels containing 6 different wavelengths were used. The wavelength 344 nm was not used. The light power was measured using a spectroradiometer (HERA Admesy), and the measured spectra are shown in Figure S3.

Figure S3: Emission spectra of the LEDs.

Analyses

$^1$H NMR analysis was preferred as the much faster method (1 min for one NMR measurement vs 40 min for GC (triple injection)) [2]. Figure S4 shows three
representative $^1$H NMR spectra of alpha-terpinene (1 N) in toluene. The top shows a starting solution while the middle and bottom show an incomplete reaction (3 mL/min flow rate). The top and middle spectra are $^{13}$C-decoupled, and the bottom spectrum is a standard $^1$H NMR spectrum. The integration of the double bond region of the terpene and using the signals of the aromatic system of toluene as references indicated 75% conversion vs 77% found by via GC.

**Figure S4:** $^{13}$C-decoupled $^1$H NMR spectra of the starting solution (top), the incomplete reaction (middle), and a regular $^1$H NMR spectrum of the incomplete reaction (bottom).
References

1. Details on the sampler: Material list, STL files for the printed parts and application for android phones can be requested from the author