

Electronic Supplementary Information (ESI)

for

Photonic Contacting of Gas-Liquid Phases in a Falling Film Microreactor for Continuous-Flow Photochemical Catalysis with Visible Light

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1. Microstructured falling film reactor



Fig. S1 Fully disassembled FFMR (© Fraunhofer ICT-IMM).

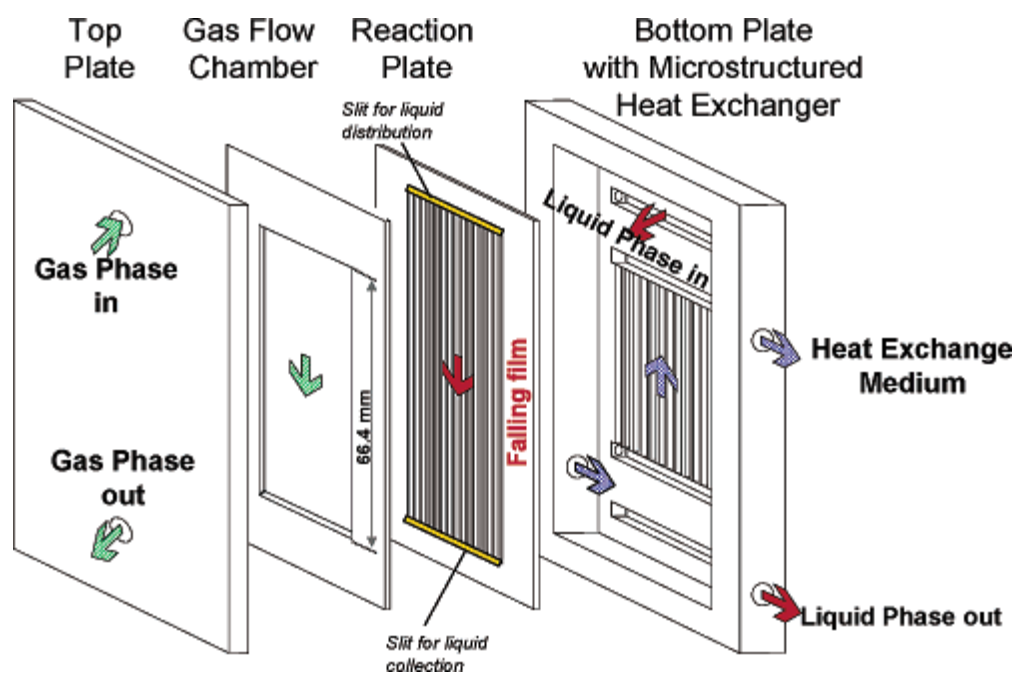
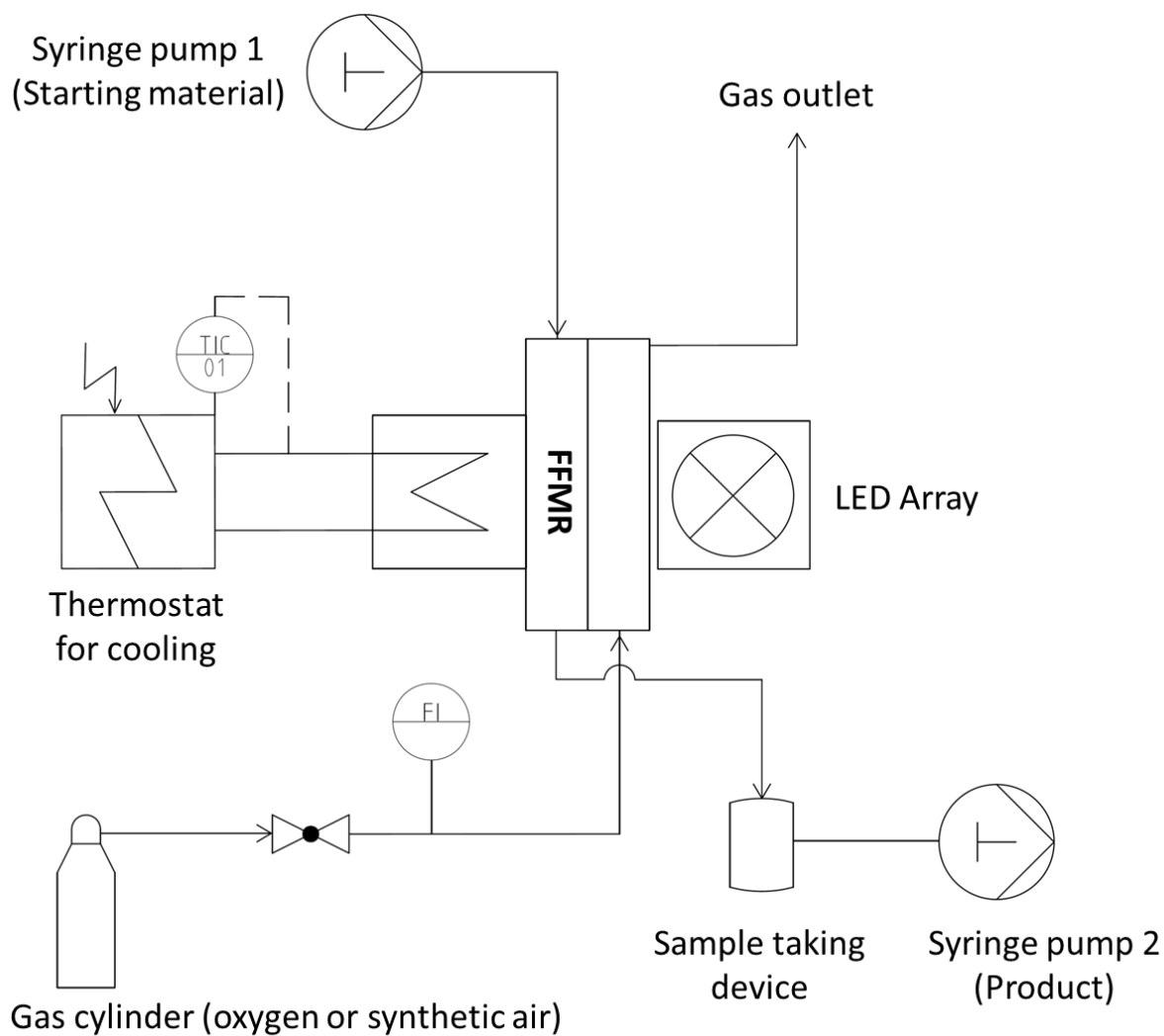


Fig. S2 Working principle of the FFMR class. Reprinted (adapted) with permission from *Ind. Eng. Chem. Res.* 2005, 44, 1742-1751. Copyright (2005) American Chemical Society.

2. Lab plant flow chart



Scheme S1 Simplified flow chart of FFMR lab plant used for photochemically catalyzed synthesis of Juglone.

3. Sample taking device

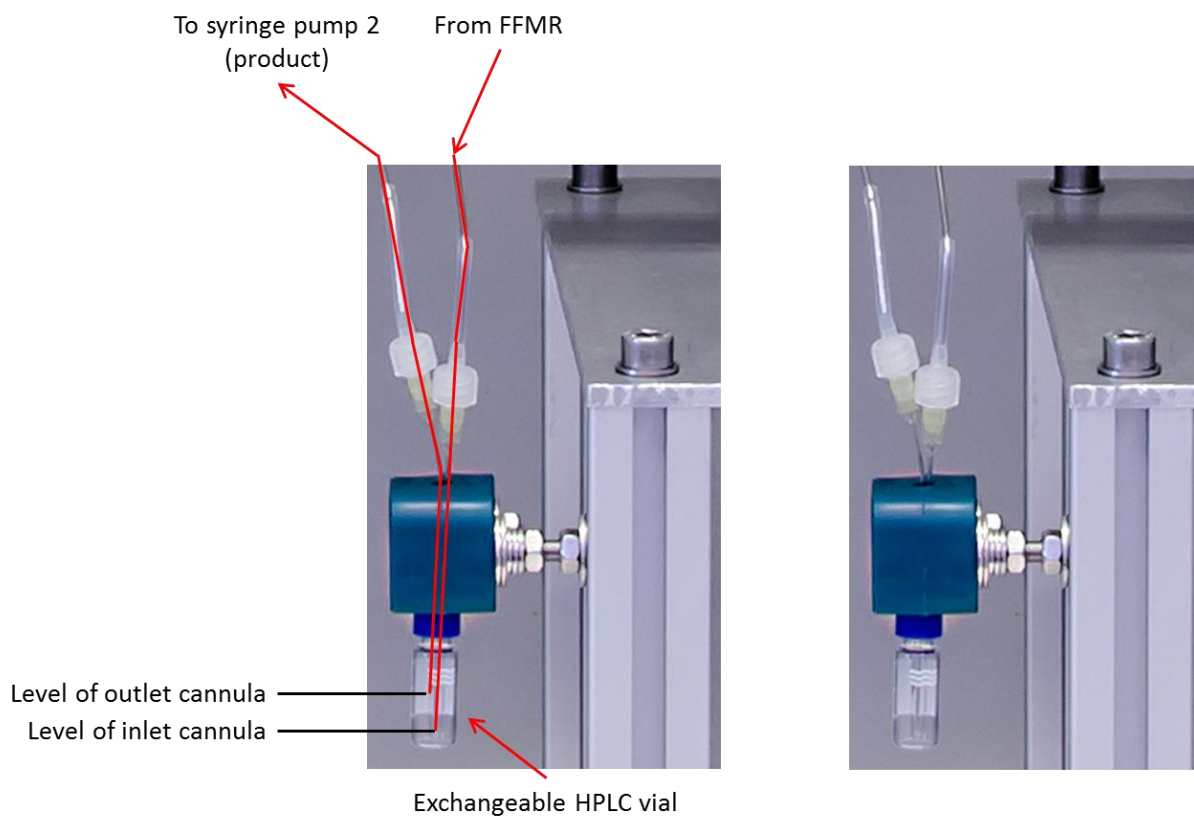


Fig. S3 Sample taking device with self-filling, exchangeable HPLC vial.

4. HPLC analysis and calibration

Table S1 Details of the HPLC method used for the analysis of the reaction solution.

Machine	Shimadzu HPLC 20A
Autosampler	Shimadzu SIC-20A HT
Column	Phenomenex Luna® 100A C18-2 length: 150 mm; ID: 4.6 mm; particles diameter: 3 µm
Eluent	0.1 M acetic acid in water / MeOH, 35/65 (v/v)
Flow rate	0.8 mL min ⁻¹
Temperature column oven	40 °C
UV detection	280 nm (DHN) 420 nm (Juglone)
HPLC sample preparation	500 µL sample solution diluted with 500 µL eluent
Injection volume	5 µL
t_r / min:	2.71 (DHN, 280 nm) 5.04 (Juglone, 420 nm)
Method runtime	10 min

Three samples for each concentration point (1 mM, 2.5 mM and 5 mM) were prepared for DHN and Juglone from appropriate mother solutions (10 mM in 2-propanol). In summary, 9 samples were analyzed for each compound. Since no data point had a variance superior to 10%, a linear fit was applied and a curve was established linking the peak area throughout a concentration range between 0 and 5 mM.

Table S2 Calibration data for the HPLC analysis.

Concentration c / mM	DHN area (280 nm)	Juglone area (420 nm)
1	1,738,835	877,779
	1,719,245	890,228
	1,740,326	895,592
2.5	4,323,431	2,486,002
	4,326,323	2,505,479
	4,338,919	2,529,595
5	8,498,687	5,262,240
	8,415,752	5,432,737
	8,351,760	5,400,518

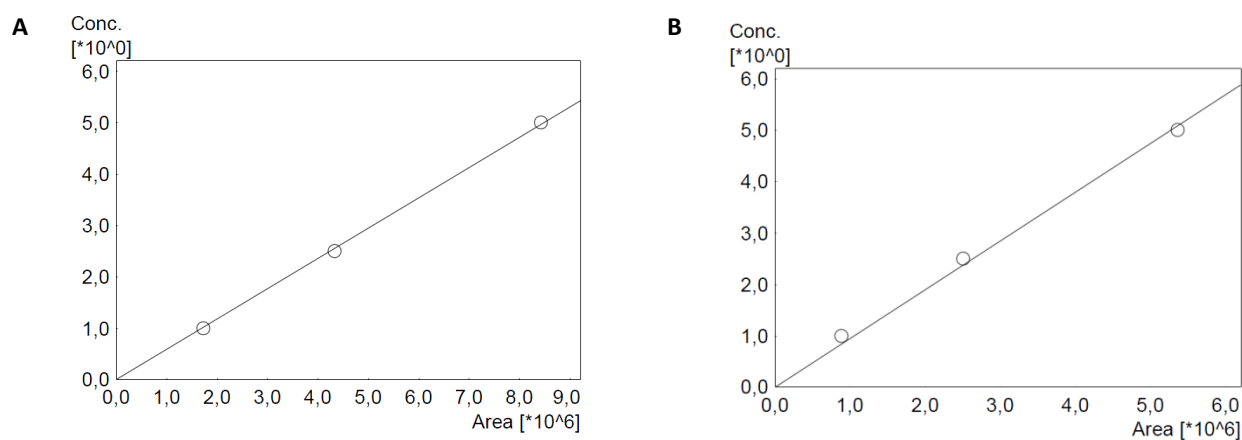


Fig. S4 Calibration curves of DHN (A) and Juglone (B).

5. TcPP Synthesis¹

Synthesis:

Equimolar amounts of 4-formylbenzoic acid (3.91 g, 26 mmol) and pyrrole (1.74 g, 26 mmol) were suspended in propionic acid (300 mL). The mixture was stirred at 120 °C for 4 hours. After this time the flask was slowly cooled down before methanol (400 mL) was added. The flask with the reaction mixture was placed in an ice bath for 60 min for precipitating the crude dye. The solution was filtrated with a Büchner funnel and washed with cold methanol (100 mL) and hot water (200 mL). Finally, the solid filter cake was stored overnight under air atmosphere.

Recrystallization:

The obtained powder was suspended in 200 mL ethyl acetate and heat a to 90 °C. Ethanol was then cautiously added until the crude material was fully solubilised (approx. 35 mL EtOH). At this moment, heating and stirring were stopped and the solution was slowly cooled down for the crystallisation of TcPP. The recrystallized product was filtrated over a Büchner funnel, washed with cold methanol and dried for 48 h at 80 °C in order to remove traces of solvent and water. The dye obtained had a strong violet colour (0.68 g, 0.85 mmol, yield: 14%).

¹H NMR (400 MHz, DMSO-d₆): δ = 13.31 (4H, br.s, COOH), 8.86 (8H, br.s, pyrrol-CH), 8.39 (8H, d, ³J = 8 Hz, Ar-CH), 8.35 (8H, d, ³J = 8 Hz, Ar-CH), -2.94 (2H, s, pyrrol-NH).

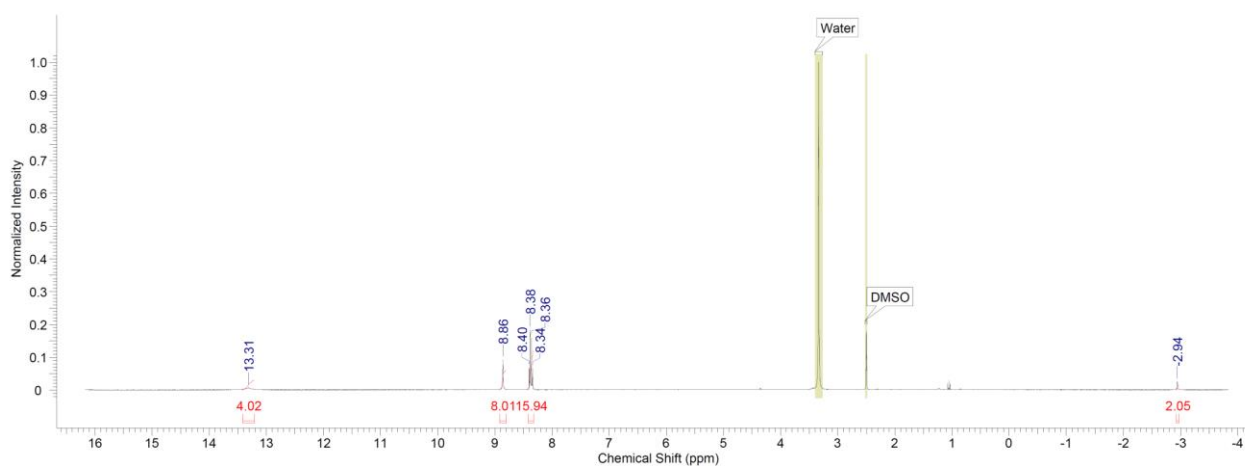


Fig. S5 ¹H NMR spectrum of TcPP.

6. UV/Vis absorption spectra of the DHN and Juglone

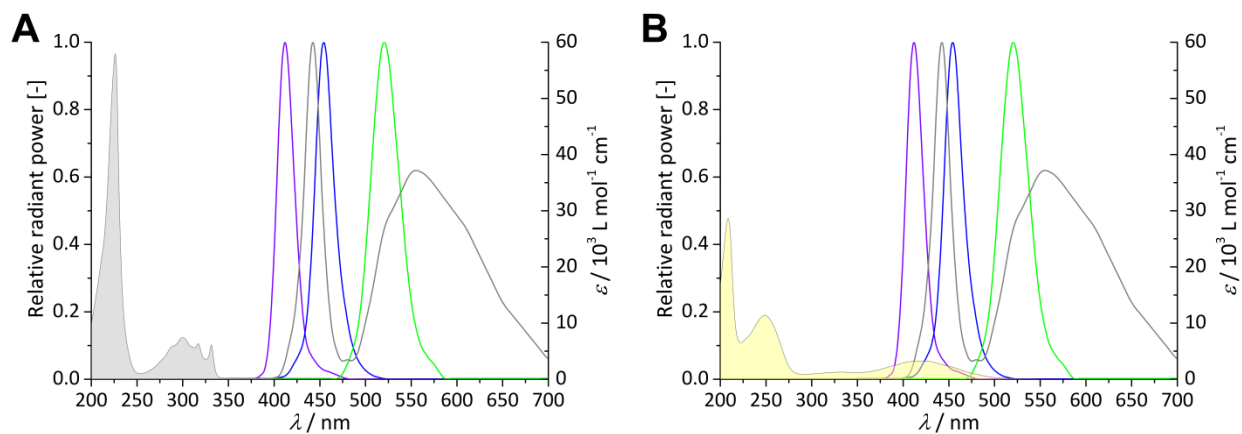


Fig. S6 UV/Vis absorption spectra of $0.5 \times 10^{-3} \text{ mol L}^{-1}$ DHN (A, grey area) and $1 \times 10^{-3} \text{ mol L}^{-1}$ Juglone (B, yellow area) in 2-propanol (right Y-axis = molar extinction coefficient). Coloured lines indicate the spectral emission bands of the violet, royal blue, green and cold-white LEDs (left Y-axis = relative radiant power).

7. Oxygen gas-liquid mass transfer

The solubility of oxygen in 2-propanol is given in its molar fraction $x_{\text{oxygen}} = 0.000788 \text{ mol mol}^{-1}$ at $20 \text{ }^\circ\text{C}$ and 1.013 bar .² This corresponds to a concentration of 0.010 mol L^{-1} , using Eq. S1 with the density of 2-propanol $\rho_{\text{propanol}} = 0.78 \text{ g mL}^{-1}$ and the molecular weight of 2-propanol $M_{\text{propanol}} = 60.1 \text{ g mol}^{-1}$. Applying Henry's Law from Eq. S2 gives a Henry's constant $K_H = 9.824 \times 10^{-3} \text{ bar L mol}^{-1}$.³

$$c_{\text{oxygen}} = x_{\text{oxygen}} \times \frac{\rho_{\text{propanol}}}{M_{\text{propanol}}} \quad [\text{mol L}^{-1}] \quad (\text{Eq. S1})$$

$$K_H = \frac{p_{\text{oxygen}}}{c_{\text{oxygen}}} \quad [\text{bar L mol}^{-1}] \quad (\text{Eq. S2})$$

The oxygen saturation in 2-propanol at 1.013 bar is then $1 \times 10^{-2} \text{ mol L}^{-1}$ for pure oxygen and of $2 \times 10^{-3} \text{ mol L}^{-1}$ for air. The literature gives also the solubility of oxygen in 2-propanol for different temperatures between 0 and $50 \text{ }^\circ\text{C}$ as shown in Fig. S7A.² Little changes are observed and the lower the temperature, the higher the solubility of oxygen in 2-propanol. Fig. S7B shows the evolution of the solubility as function of the oxygen partial pressure p_{oxygen} using Henry's law given in Eq. S2. It is valid, since the oxygen concentration in 2-propanol is very low. An ideal solution can then be considered.

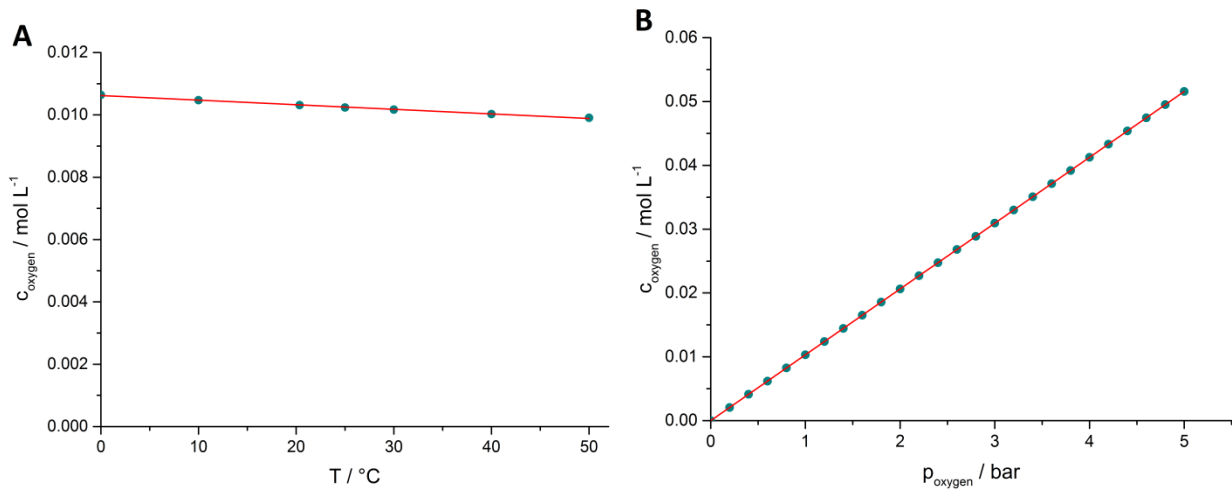
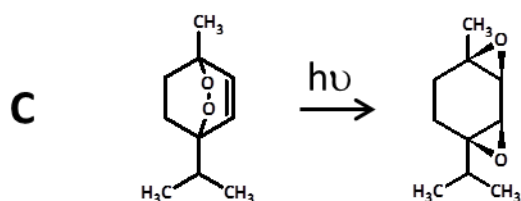
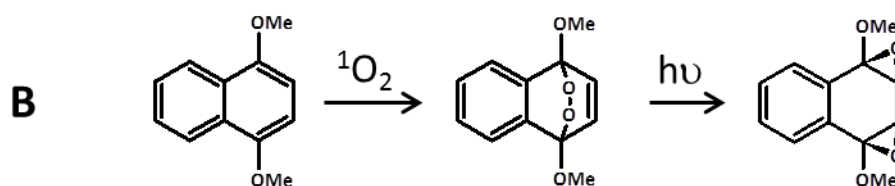
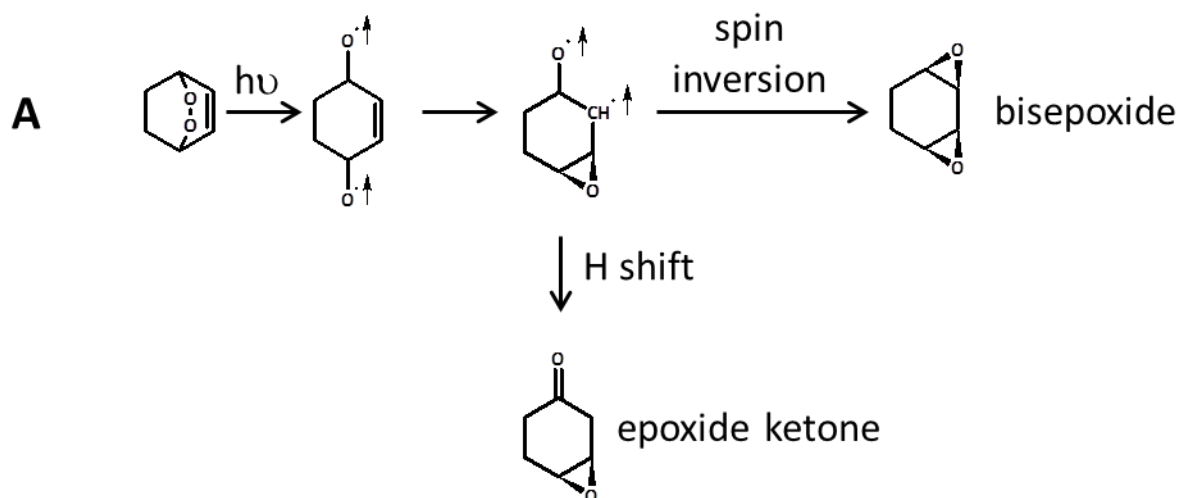


Fig. S7 Evolution of oxygen solubility in 2-propanol (A) with increasing temperature T at 1.013 bar and (B) with increasing oxygen partial pressure p_{oxygen} at $20 \text{ }^\circ\text{C}$.

8. Sensitized endoperoxide side-reaction⁴



Scheme S2 General scheme for the photolysis of endoperoxides to bisepoxides via spin inversion or to epoxide ketones via hydrogen shift (A); endoperoxide formation of 1,4-dimethoxynaphthalene with subsequent photolysis to the bisepoxide (B); photolysis of ascaridole to the appropriate bisepoxide (C).

11. Literature

- ¹ The synthesis of TcPP was adapted to the following literature: A. Alder, *J. Am. Chem. Soc.* 1966, **32**, 476.
- ² R. Battino, T. Rettich, T. Tominaga, *J. Phys. Chem. Ref. Data* 1983, **12**, 163.
- ³ R. Viadero, Henry's Law, in: *Water Encyclopedia*, John Wiley & Sons Inc., 2005.
- ⁴ M. Balci, *Chem. Rev.* 1981, **81**, 91.