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

Open-Source 3D Printed Reactors for Reproducible Batch and Continuous-Flow Photon-Induced Chemistry: Design and Characterization

Supporting information

Tom M. Masson, Stefan D. A. Zondag, Jasper H. A. Schuurmans, Timothy Noël*

Flow Chemistry Group, van't Hoff Institute for Molecular Sciences (HIMS), Universiteit van Amsterdam (UvA), 1098 XH Amsterdam, The Netherlands.

* Corresponding Author: t.noel@uva.nl (Timothy Noël)

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Equipment

3D printing

The 3D printers employed, the Ultimaker S3 and S5, were used for all printings. Autodesk Inventor was used to design all assemblies and for slicing Ultimaker Cura was used. All parts were printed with polylactic acid (PLA). The files of all parts are available as .stl and .ipt and can be modified, if desired.

Filament and settings

A polylactic acid filament was used for the printing of all reactor parts (reference: https://www.123-3d.nl/PLA/PLA-p7334.html, 2.85 mm, manufactured by 123-3D, used in various colors). The method used in the printer was the "fast" method from Ultimaker Cura (70 mm/s speed). A layer height of 0.2 mm was used together with an outside brim of 7 mm for build plate adhesion and 15% triangle infill.

Reactor construction

The non-3D printed parts that were used in the construction of the reactors are listed in Table 1. Together with the 3D printed parts (Table 2 to 4) and standard construction tools (glue and reflective tape) the three distinct reactor types can be made. Figure S1to S3 show a step-by-step guide to build the reactor, with further explanation detailed in this section.

Table 1 Commercially available parts required to build the different reactors.

Part	Comments	Reference
Cooling fan	24V axial ventilator 50×50×15 mm	https://www.conrad.nl/nl/p/sunon-mf50152v1-1000u-a99-axiaalventilator-24-v-dc-28-9-m-h-l-x-b-x-h-50-x-50-x-15-mm-2147543.html?searchType=SearchRedirect
Power supply	24V power supply for the ventilators	https://www.conrad.nl/nl/p/hn-power-hnp12-240l6-stekkernetvoeding-vaste-spanning-24-v-dc-500-ma-12-w-512692.html
Threaded insert	Threaded insert M3×5×5 mm	Draadinzetstukken M3 x 5.0 x 5.0 (20 stuks) 123-3D 123-3d.nl
Magnets	Neodymium magnets 10×3 mm	https://www.conrad.nl/nl/p/maul-neodymium-magneet-o-x-h-10-mm-x-3-mm-schijf-zilver-10-stuk-s-6166396-1796544.html?insert=83&searchType=SearchRedirect
Reflective tape	Aluminum tape 50 m × 50 mm	https://www.conrad.nl/nl/p/tru-components-aft-5050-1564032-aluminium-tape-aft-5050-zilver-l-x-b-50-m-x-50-mm-1-stuk-s-1564032.html

UFO reactor

Table 2 3D-printed parts required to build the Uflow reactor

Part name	Comments	File name
Reactor box (128×128×90mm^3)	Can be printed with no supports preferably in dark colors.	Box.stl
Top cover (173×173×128mm^3)	Printed with support, different versions are available with different number of positions for 4, 8 and 12 vials. Current diameter of the tubes is 13.4 mm	Top cover 4/8/12 tubes.stl
Reflector (80×80×25mm^3)	Print with support	Reflector.stl

Stirring plate adaptor ($142{\times}142{\times}37mm^3$)	Can be printed with or without support. Two versions are available to fit stirring plates from IKA or Heidolf.	Bottom part IKA/Heidolf adaptator.stl

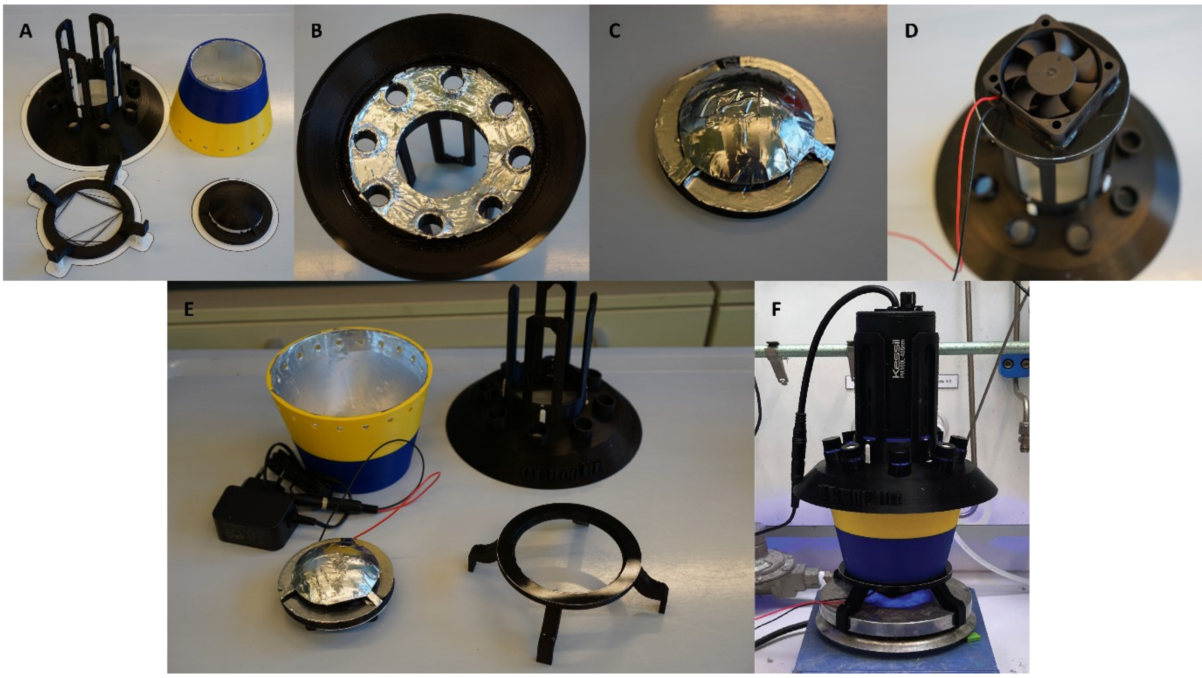

Figure S1 Step-by-step buildup of the batch UFO reactor.

A. The different parts are 3D printed following the instructions given.

B-C. Reflective tape is applied on the visible surfaces of the top part, the reflector and the inside of the box.

D. A fan (50x50cm, 24V) is centered and glued at the bottom of the reflector. The use of screws is also possible, when adaptations to the original design are made this case. However, this was deemed to be not necessary for this assembly. The fan should be placed in the position where it is blowing inwards.

E-F. All the parts are assembled and put on top of a stirring plate, here IKA but the STL file for Heidolf stirring plates is also available.

Uflow reactors

Table 3 3D-printed parts required to build the Uflow reactor.

Part name	Comments	File name
Reactor box ($91{\times}91{\times}95mm^3$)	Can be printed with no supports, preferably in dark colors.	Box.stl
Coil holder ($78{\times}78{\times}66mm^3$) ($78{\times}78{\times}70mm^3$)	The coil holder is made out of two different parts that should clip together (some sanding/drilling might be necessary). Top holder magnet is designed to be printed with magnets inside the print. To do so, a pause in the G-code has to be created at the right layer (typically layer number 26 with 0.15 mm layer height). Can also be printed with no magnets, in that case the file Holder no magnet.stl can be printed twice. (magnets are present to facilitate the utilization of the reactor but are not mandatory)	Holder no magnet.stl Top holder magnet.stl
Top cover ($134{\times}134{\times}121mm^3$)	Print with support, preferably in dark colors.	Top cover.stl
Reflector ($107{\times}107{\times}103mm^3$)	Print with support.	Reflector+feet.stl

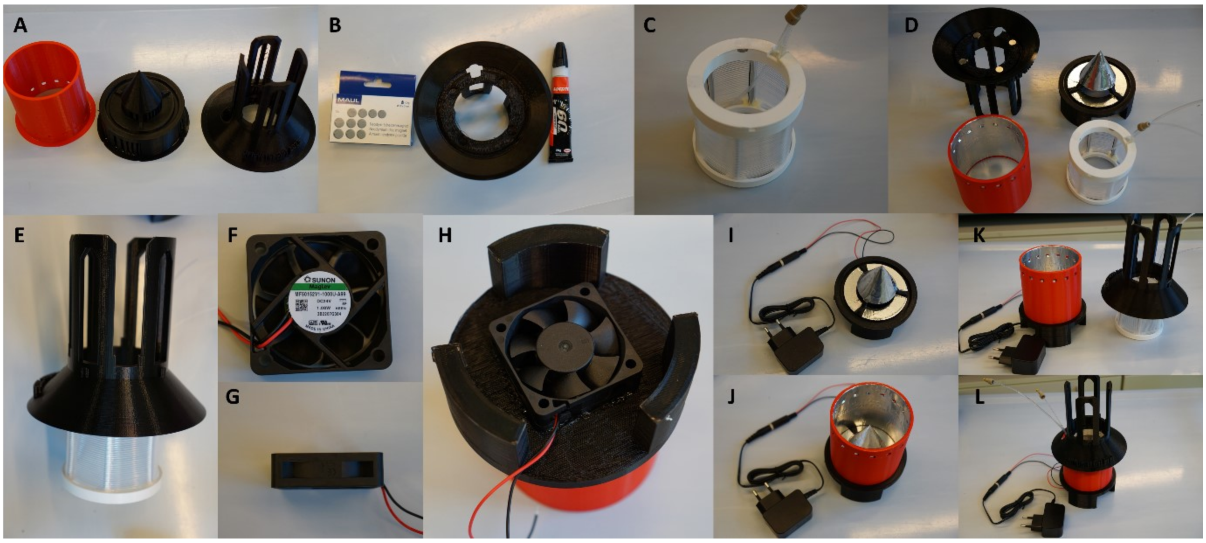

Figure S2 Step-by-step buildup of the Uflow reactor

A. The 3D printed parts are prepared, the supports and additional brims are removed

B. In the "Top cover" part, magnets are inserted in the 4 positions with strong glue. <u>Be sure to match the polarities to the ones in the coil holder.</u>

C. Cover the pillars of the coil holder with reflective tape (this will prevent degradation of the PLA). Coil the desired flow tubing around the pillars. The inlet and outlet of the coil have to go through the hole on top of the holder.

D. All the inside parts of the reactor are covered with reflective tape to shield the PLA from UV exposure and to reflect the photons towards the reaction mixture.

E. If the polarities of the magnets were respected the "Top cover" and the "coil holder" should click in place and the tubing should go through the side hole intended for.

F-G-H. A fan (50x50cm, 24V) is centered and glued at the bottom of the reflector. The use of screws is also possible, when adaptations to the original design are made this case. However, this was deemed to be not necessary for this assembly. The fan should be placed in the position where it is blowing inwards.

I. The fan is connected to an appropriate power supply.

J-K-L. The reactor is built up, connected and ready to use.

Fidget reactor

Table 4 3D-printed parts required to build the Fidget reactor.

Part name	Comments	File name
Lamp holder ($74×74×103 mm^3$)	To be printed 3 times with the same parameters without support. Magnets have to be inserted within the print. Typically a pause in the G-code has to be created at layer 26 with 0.15mm layer size. The magnets should be glued inside the print to attachment to the print head. (As an alternative to magnets, the lamp holders can be directly glued to the reactor box)	Kessil holder.stl × 3
Reactor box ($113×101×85 mm^3$)	To be printed with supports, preferably in dark colors.	
Coil holder ($96×84×7 mm^3$)	To be printed twice with no supports. It is combined with 3 brass rods (50 mm long, 10 mm diameter) and 12 transparent PMMA rods (50 mm long, 5 mm diameter). The rods are glued on one side, the PFA tubing is coiled around the rods and the top part was added to close the holder.	Coil holder.stl × 2
Top cover ($144×131×17 mm^3$)	Print without support, preferably in dark colors.	Lid small.stl
Reactor feet ($18×18×35 mm^3$)	Print without support, 3 times. After the print, inserts can be added to the part to include a screw thread.	Fidget foot.stl × 3

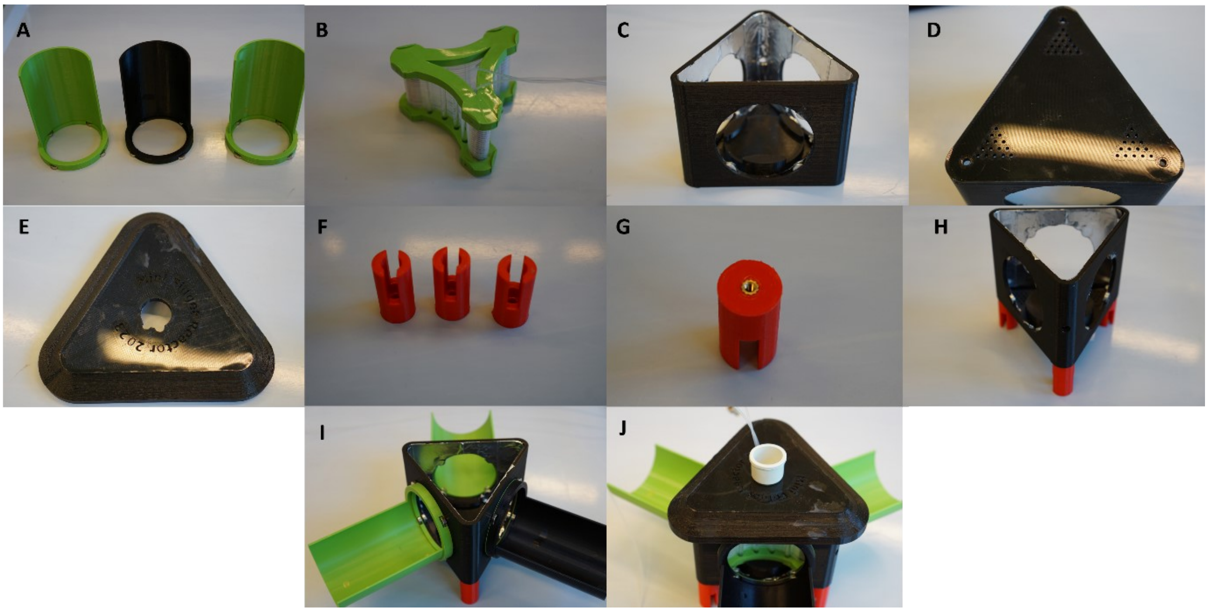

Figure S3 Step-by-step buildup of the Fidget reactor.

A. The lamp holders are printed with four magnets inserted during the print.

B. The reactor coil is built around the two 3D-printed coil holders, the brass pillars and the PMMA pillars.

C. The main reactor box is printed and magnets are inserted with glue in the side holes, they do not need to be added during the print. When the magnets are at the right positions (mind the polarities), reflective tape is used to cover the inside walls of the reactor. A hole has to be cut out for the compressed air tube to cool the reactor.

D. 3 screws are inserted in the 3 holes in the corners of the reactor. They'll be used to attach the feet. The small holes are designed to let the airflow out of the reactor.

E. After printing, the inside of the top cover of the reactor is covered with reflective tape.

F-G. Threaded inserts are added vertically in the 3D printed feet with an soldering iron

H. The screws inserted in the reactor are matched to the feet and the threaded inserts. The height of the reactor is here to allow the air to escape.

I–J. The lamp holders are connected, the coil is added in the middle of the reactor box and the reactor tubing is passed through the middle hole of the top cover of the reactor.

Experimental

General information

All reagents and solvents were used as received without further purification, unless stated otherwise. Reagents and solvents were bought from Sigma Aldrich, TCI, Fluorochem and Fisher Scientific and, if applicable, kept under argon atmosphere. Technical solvents were bought from VWR International and Biosolve, and were used as received.

Batch reactions

A stock solution of 50 mL is prepared to be sure that all reaction vials are charged with same reaction mixture. In a 100 mL flask, equipped with a stirring bar, tetra-n-butylammonium decatungstate (25 µmol, 0.5 mol%) was dissolved in 50 mL of acetonitrile. Cyclohexane (50 mmol, 10 eq.) and dimethyl maleate (5 mmol, 1 eq.) were added to the reaction mixture. 1-chloro, 4-fluorobenzene (5 mmol, 1 eq.) was added as an internal standard. This solution is sonicated to obtain an homogeneous mixture. After sparging with nitrogen, 4 mL of this stock solution was dispatched in 7 mL reaction vials and inserted into the UFO reactor system equipped with a 390 nm Kessil lamp at 25% light intensity. The vials are irradiated for 30 minutes and then analyzed by ^{1}H-NMR to measure the conversion of the starting material.

Flow reactions

This procedure is the same for the Uflow system, the Eagle Signify, the Vapourtec and the Fidget reactor. All the reactors are prepared to have 4 mL of irradiated volume with a 0.75 mm ID PFA tubing. Chemyx syringe pumps and IDEX connections were used for the flow system.

A stock solution of 50 mL is prepared to be sure that all reaction vials are charged with same reaction mixture. In a 100 mL flask, equipped with a stirring bar, tetra-n-butylammonium decatungstate (25 µmol, 0.5 mol%) was dissolved in 50 mL of acetonitrile. Cyclohexane (50 mmol, 10 eq.) and dimethyl maleate (5 mmol, 1 eq.) were added to the reaction mixture. 1-chloro, 4-fluorobenzene (5 mmol, 1 eq.) was added as an internal standard. This solution is sonicated to obtain an homogeneous mixture. After sparging with nitrogen the solution is loaded in a 25 mL syringe.

The flow reactor is first loaded with the reaction mixture with the light off. When the system is full, the syringe pump is set at the desired flow rate and the lamp is switched on. The reaction mixture is then collected in 2 mL vials, diluted with $CDCl_3$ and analyzed via ^{1}H-NMR. Every sample is collected over 30 seconds to measure the average conversion for every time point.

Additional experiments

Continuous-flow reactors

The initial reaction rates for the Uflow, Fidget, Signify Eagle (Figure S5) reactor and Vapourtec (Figure S6) reactor systems were determined at different optical powers. Data points exceeding 30% of conversion with regard to dimethyl maleate were discarded from the calculation, where linear regression was used to find the number for the initial reaction rate. Kinetic experiments conducted in the different configurations can be found in Figure S4.

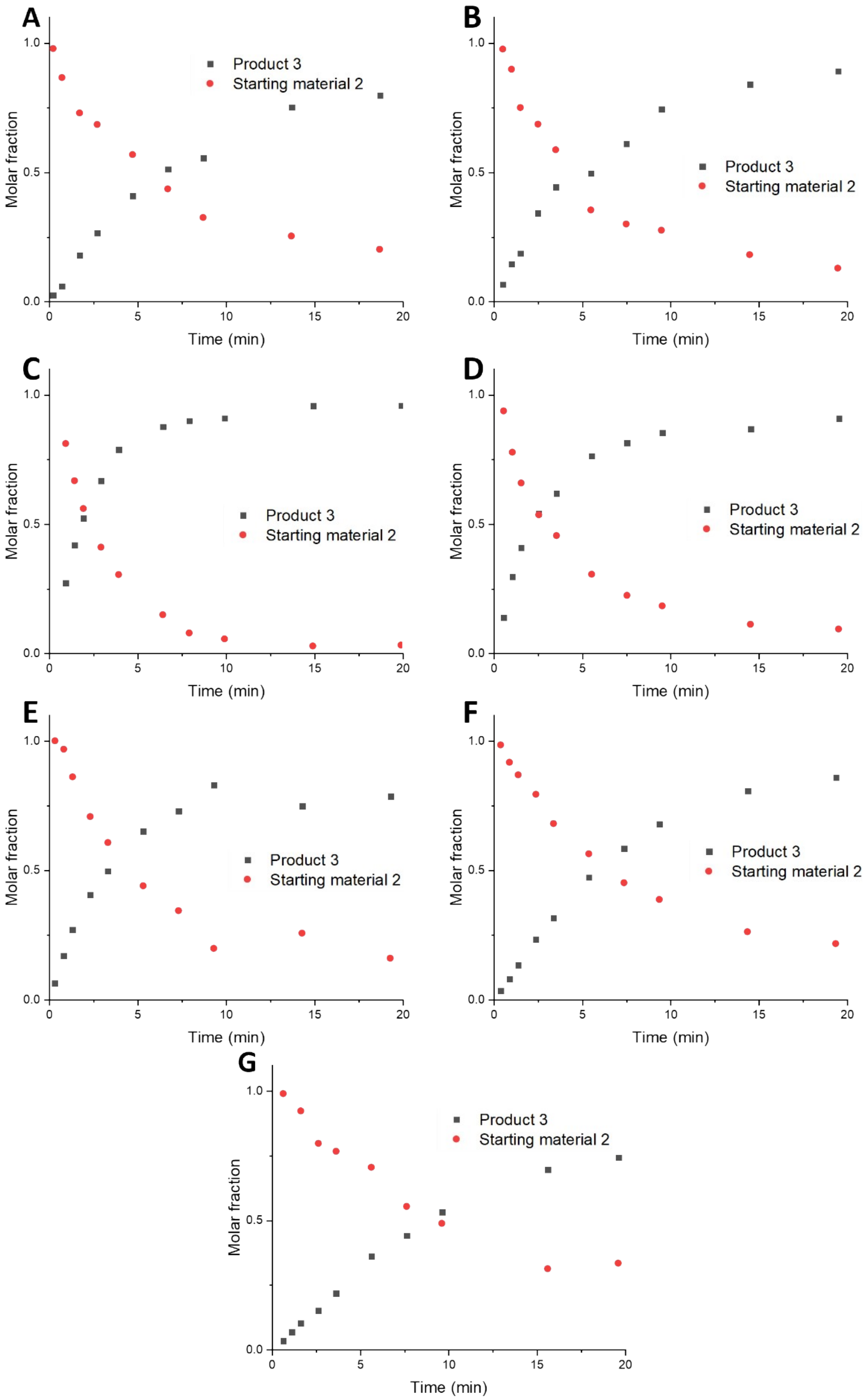

Figure S4 The reaction composition (molar fraction based on dimethyl maleate and reaction product) against the time for different reactor configurations. A) Vapourtec reactor at 60W input power. B) Vapourtec reactor at 120W input power. C) Signify Eagle reactor at max power. D) Signify Eagle reactor at 20% light intensity. E) Signify Eagle reactor at 10% light intensity. F) Fidget reactor at 9.25W optical power. G) Uflow reactor at 50% light intensity.

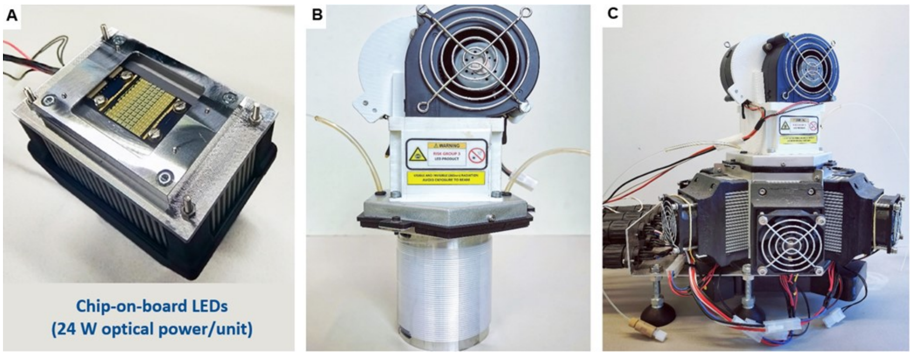

Figure S5 Signify Eagle reactor system with A) 6 chip-on-boards LEDs. B) The reactor coil. C) The whole reactor system assembled.

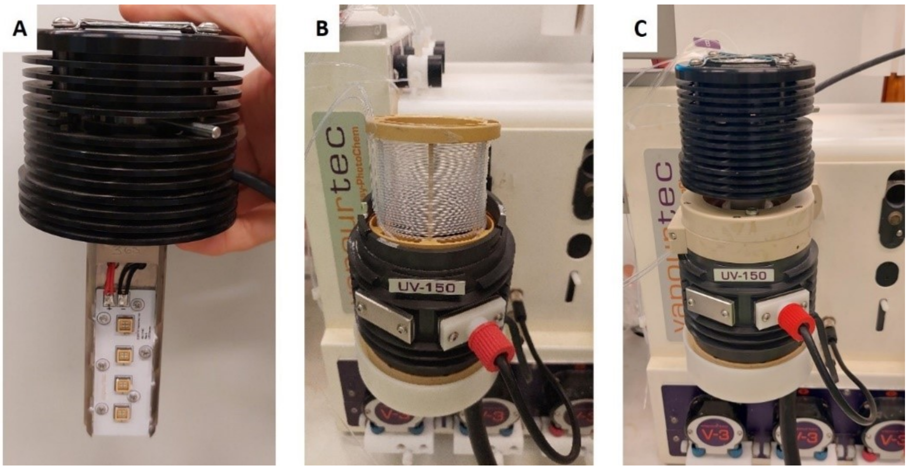

Figure S6 Vapourtec reactor system A) LED light source. B) The reactor coil. C) The whole reactor system assembled.

Temperature evolution

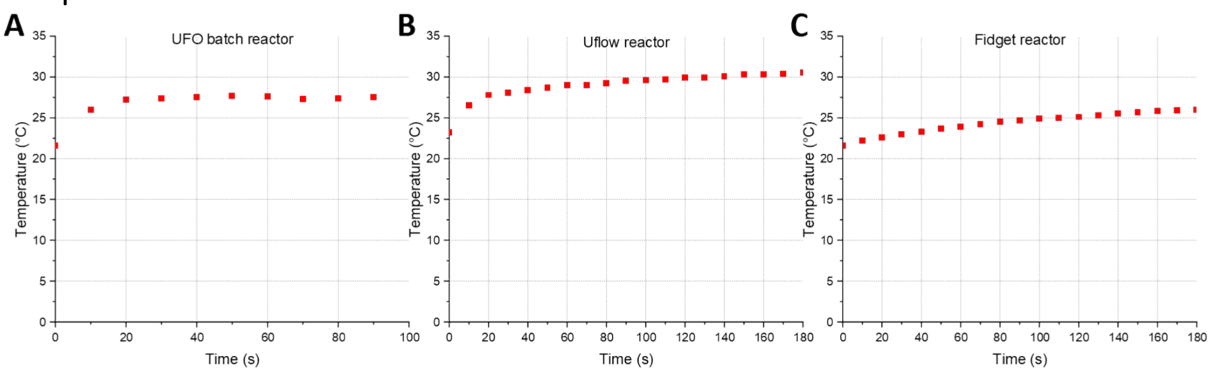

Figure S7 Temperature evolution inside the different reactors. A) In the UFO batch reactor, B) In the Uflow reactor, C) In the fidget reactor.

Maintaining a stable operation temperature is key for the reproducibility of photochemical reactions. To monitor the temperature evolution in our 3D printed reactors, a thermocouple is inserted inside the reactors. After switching on the lamp(s) and the cooling system, the temperature is recorded every 10 seconds. In Figure S7A the temperature inside the batch system rises quickly and stabilizes around 27 °C. Similarly, the single-lamp flow system stabilizes around 30 °C (Figure S7B), after approximately 3 minutes. These results indicate that the air flow, provided by the fan, is sufficient to maintain the temperature inside the reactor below 30 °C. However, fan-cooling was found to be insufficient for the Fidget reactor, employing 3 Kessil lamps, leading to the design of a different cooling system. Here, compressed air is used to keep the temperature constant at approximately 27 °C, as can be seen in Figure S7C.

Actinometry experiments

The procedure to chemically determine the photon flux was derived from potassium ferrioxalate actinometry.[1–3] A 6 mM solution of potassium ferrioxalate (Alfa Aesar) in 50 mM sulfuric acid (Sigma Aldrich) solution was made. This solution was loaded in a glass vial (Pyrex, filled with 4 mL of the reaction mixture) with a magnetic stirrer, four of these vials were placed in the UFO reactor with the light source placed in the center (Kessil PR160L 370nm Gen1). The light source was turned on for a set time, under continuous stirring of the reaction mixture. After the irradiation time, the vials were taken out of the reactor and a sample of 0.1 mL was taken from each vial. These samples were diluted with water (1.4 mL) and 0.6 mL of this diluted sample solution was added to a buffer solution (2 mL). The buffer consisted of 1,10-phenanthroline (6 mM, Sigma Aldrich), sodium acetate (0.6 M, Sigma Aldrich) and sulfuric acid (0.18 M), in water. The samples were subsequently measured using a UV-VIS Spectrophotometer (UV-2700, Shimadzu) in a quartz cuvette at the absorption peak of the formed complex found at 510 nm (molar absorption coefficient of 11.114 $mM^{-1}cm^{-1}$)[1].

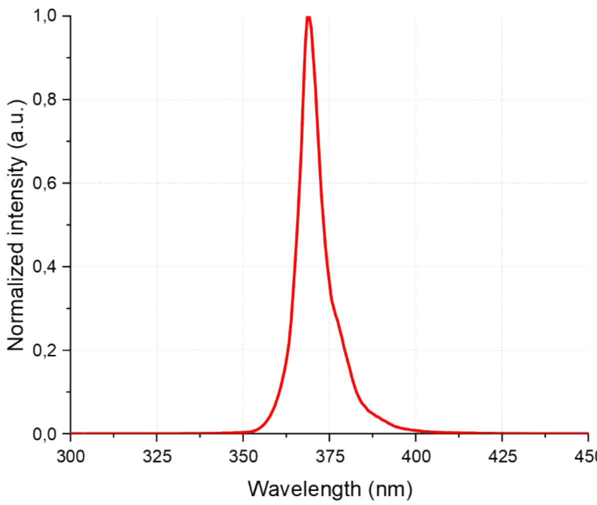

Figure S8 The spectral intensity distribution of the 370nm PR160L light source.

The effective photon flux for each of the vials can be determined by setting up a molar balance over the system. Wavelength dependency of the parameters can be included by accounting for the photon-based spectral distribution of the used light source (Equation (1, Figure S8). The total photon flux is given by a summation over all the individual wavelengths (Equation (2). It is assumed that the quantum yield is wavelength independent[4] and that the optical pathlength is equal to the geometric average ($\frac{\pi R}{2}$), resulting in a situation in which the majority of the photons incident on the vial are absorbed at the starting conditions of the experiment. The differential equation (Equation (3)) was solved with variable-step, variable-order (VSVO) solver for stiff differential equations and the photon flux could be fitted using a non-linear least squares method. Further details on absorbance characteristics, and setting up and solving the balance can be found in ref[1]. Results of the actinometric experiments and the fit made are shown in Figure S9.

$$g_{p,\lambda} = \frac{G_{n,p,\lambda}\Delta\lambda}{G_{n,p}} \tag{1}$$

$$q_{n,p} = \Sigma q_{n,p,\lambda} = q_{n,p}\Sigma g_{p,\lambda} \tag{2}$$

$$\frac{dN_A}{dt} = -q_{n,p}\varphi \sum_{\lambda_1}^{\lambda_{end}} g_{p,\lambda}(1 - exp(-\kappa_{A,\lambda}C_A l)) \tag{3}$$

Symbol list:

C_A	Concentration of potassium ferrioxalate	mol m^{-3}
$g_{p,\lambda}$	Spectral distribution function	-
$G_{n,p,\lambda}$	Spectral photon flux	mol s^{-1} nm^{-1}
l	Optical path length	m
N_A	Amount of moles of potassium ferrioxalate	mol
$q_{n,p}$	Received photon flux	mol s^{-1} or Einstein s^{-1}
t	Time	s

Greek symbols

κ_A	Napierian absorption coefficient of potassium ferrioxalate	m^2 mol^{-1}
λ	Wavelength	m
φ	Quantum yield	-

Subscript

λ	At wavelength λ

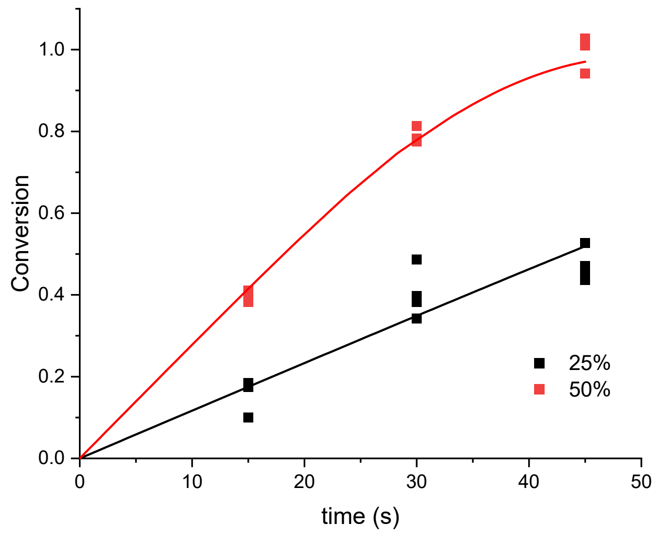

Figure S9: Data obtained from potassium ferrioxalate actinometric experiment done at two power settings 25% and 50% with a Kessil lamp 370nm. Solid lines represent the fit made to determine the photon flux. Squares represent the data points measured on the four different positions of the UFO reactor.

Ray-tracing simulations

The ray-tracing simulations were performed for all three introduced reactors using COMSOL Multiphysics 5.4's Geometric Optics module. A time-dependent solver was set up, where time-stepping was calculated with the generalized alpha algorithm, and the linear system of equations was solved iteratively with the GMRES method. Using the previously validated Kessil lamp model, as reported by our group,[1] the reactor geometries were loaded into COMSOL as STEP files. For the UFO reactor, all outer surfaces of the reaction mixture were defined as absorbing surfaces. For the flow reactors, the irradiated reaction mixture was approximated as a projected area of the coiled/wound capillary. These irradiated surfaces were then defined as accumulators, where the incident rays are frozen upon intersection, depositing the ray's power onto the surface.

Any surface that was covered with reflective tape in the 3D-printed reactors was modelled as a perfect specular reflector, with the associated 7.5% energy loss per interaction, per ray. For the simulations without reflective tape this energy loss was set to 100% to terminate the otherwise reflected rays. Any other surfaces of non-transparent materials were set as perfect absorbers, also terminating the ray from the simulation. Transparent materials were modelled using material discontinuities, obeying the Fresnel equations using the material's respective refractive indices to determine reflected/refracted fractions of incident rays, hereby propagating the refracted ray, and generating a new reflected ray, attributing them both their associated energy.

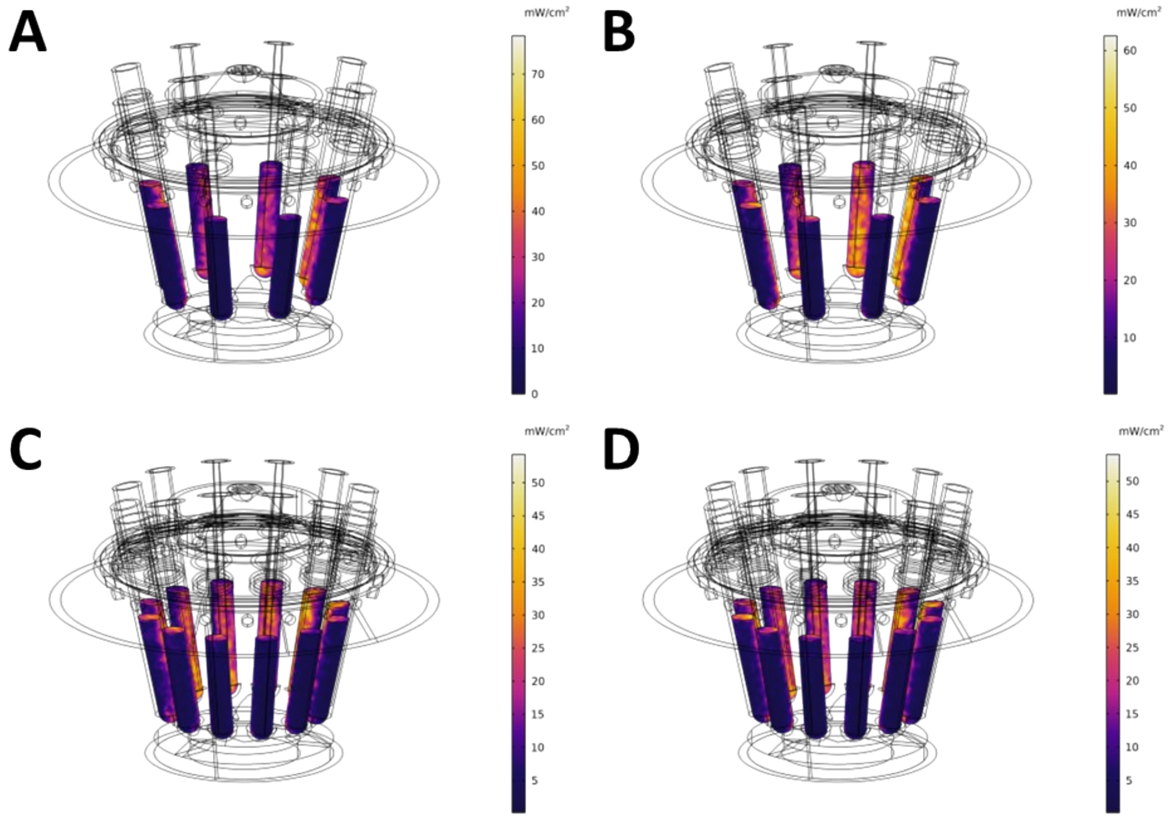

Figure S10. Irradiation profiles of the other UFO reactor configurations using a Kessil PR160L-370nm at 100% intensity setting. A) 8-vial UFO-I. B) 8-vial UFO-II. C) 12-vial UFO-I. D) 12-vial UFO-II.

These simulations provided the expected maximum optical power received by the reaction mixture's outer surfaces, by integrating the simulated irradiation profiles. These profiles for the UFO reactor configurations not shown in the manuscript are presented in Figure 9. The configurations of the UFO reactor with vial positions and light source orientation are visualized in Figure 10.

The ray-tracing simulations have provided data for all vial positions of all UFO reactor configurations and both continuous-flow reactors. These simulations were carried out both with and without the reflective tape for a generic normalized Kessil light source model. This allows us to approximate the simulated received radiant power of any of the vials or reactor coils through a simple calculation. In Table 5 multiplication factors are given for all power settings of the three Kessil lamps validated through radiometry. Multiplying these factors with the normalized values in Table 6 for the UFO reactor or Table 7 for the continuous-flow reactors yields the expected received radiant power in [W], which can be transformed into a photon flux. For the chemical actinometry performed in the 4-vial UFO reactor, with reflective tape, this would constitute an average of 8.2% per vial, with 25% and 50% intensity settings for the Kessil PR160L-370nm lamp, constituting 0.81 and 1.69 W, respectively. This yields 66 and 139 mW, respectively, with the values determined through actinometry being 72 and 172 mW, respectively (see Figure S9).

Table 5. Multiplication factors for the three validated lamp designs at varying intensity settings. These numbers apply to the Kessil PR160L series.

Intensity setting [%]	370nm [W]	370nm Gen2 [W]	390nm [W]
25	0.81	2.28	2.69
50	1.69	4.96	5.51
75	2.58	6.60	8.28
100	3.45	9.32	11.37

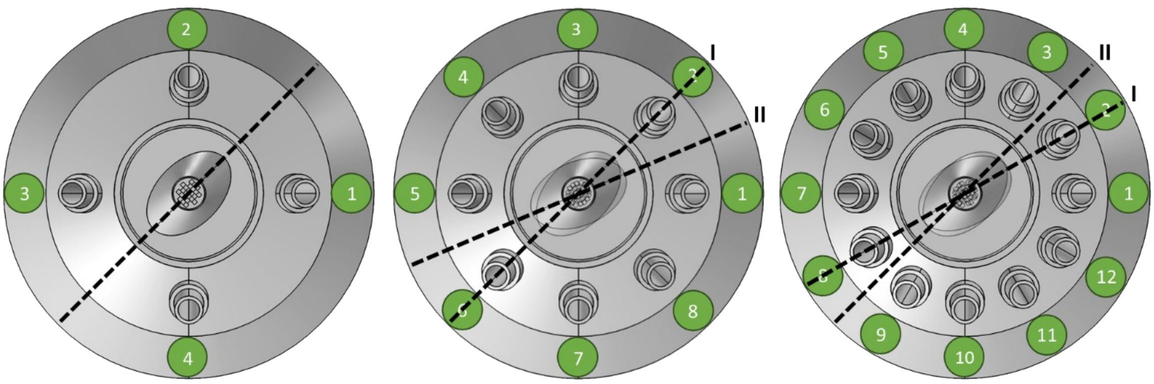

Figure S11. The three UFO lid designs with 4, 8, and 12 vials respectively. The tube positions as used for Table 6 have been labelled appropriately. For the 8- and 12-vial design, the relevant lamp orientations (I and II) are shown by the dashed line through the major axis of the linear reflector.

Table 6. Percentage values for all vial positions for the three different UFO reactor lid designs. The UFO reactor configurations from Figure 10 are used for the I and II labels. Tape signifies either Y(es), with a reflectance of 0.925, or N(o), with a reflectance of 0. The first row indicates the vial number, and all further numbers are received radiant power given as percentages [%].

Reactor	Tape	Average	1	2	3	4	5	6	7	8	9	10	11	12
4-vial UFO	Y	8.2	8.1	8.3	8.0	8.3	-	-	-	-	-	-	-	-
	N	2.8	2.8	2.9	2.6	2.9	-	-	-	-	-	-	-	-
8-vial UFO - I	Y	7.3	7.1	8.8	7.4	5.9	7.1	8.9	7.4	6.0	-	-	-	-
	N	3.0	2.9	3.9	3.0	2.2	2.7	4.0	3.0	2.4	-	-	-	-
8-vial UFO - II	Y	7.4	8.4	8.3	6.4	6.5	8.4	8.3	6.5	6.4	-	-	-	-
	N	3.0	3.5	3.4	2.6	2.6	3.4	3.4	2.7	2.7	-	-	-	-
12-vial UFO - I	Y	6.2	6.9	7.5	6.7	5.6	5.1	5.5	6.7	7.6	6.8	5.5	5.1	5.5
	N	3.2	3.3	4.0	3.2	2.7	2.4	2.5	3.2	4.1	3.3	2.7	2.4	2.6
12-vial UFO - II	Y	6.3	6.1	7.5	7.3	6.3	5.2	5.4	6.0	7.5	7.3	6.3	5.3	5.4
	N	3.1	3.0	3.9	3.7	3.0	2.6	2.7	2.8	3.7	3.6	3.1	2.7	2.7

Table 7. Percentage values for the two flow reactors. Tape signifies either Y(es), with a reflectance of 0.925, or N(o), with a reflectance of 0.

Reactor	Tape	Received radiant power [%]
Uflow	Y	38.9
	N	32.3
Fidget	Y	77.3
	N	76.2

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